

## ABSTRACT

Title of Document: **REDOX AND SOIL MANIPULATION  
EFFECTS ON DITCH SOIL PHOSPHORUS  
PROCESSING**

**David E. Ruppert, PhD, 2012**

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Ditches increase the connectivity of landscapes to open water systems, potentially facilitating the degradation of downstream waterways. A treatment and an observational experiment were conducted to identify processes behind phosphorus (P) cycling in ditch soils. If the ditch had not undergone recent dredging soils were observed in the treatment experiment to release P to surface water whether the soil system was iron (Fe)-oxidizing or Fe-reducing. Also in the treatment experiment, Fe was released to surface water in appreciable amounts only if the soil system was Fe-reducing. From the observational experiment P release due to mineralization was inferred due to a positive trend with temperature. Also in the observational experiment Fe-reducing conditions were weakly correlated with diminished P concentrations in the ditch water. It was inferred that emergent Fe(II) released from within the soil through reductive dissolution captures P from ditch surface water upon oxidation. In the treatment experiment dredging and saturated conditions resulted in similar effluent P concentrations as drained soils that

were undredged. This may explain a lack of dredging effect that was observed in the field.

REDOX AND SOIL MANIPULATION EFFECTS ON DITCH SOIL  
PHOSPHORUS PROCESSING

By

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## Dedication

This dissertation is dedicated to my parents, David and Barbara Ruppert.

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# **Chapter 1: Introduction**

## **Eutrophication**

A large and growing share of the world's meat supply is produced in an industrial context, such that the place of cultivation of grain feeds, the location of animal husbandry, the returning of animal wastes to the landscape, and the consumption of product are displaced from one another (Naylor et al., 2005). This decoupling discourages the internalization of social and environmental costs with the economic costs associated with meat production, and the prices paid for meat by consumers (Naylor et al., 2005).

Such externalized costs include eutrophication, the over-enrichment of surface waters such that algal primary productivity is heightened, resulting in algal blooms and, upon algal decay, zones of reduced oxygen content. These algal boom and bust cycles are now a worldwide phenomenon (Tilman et al., 2001; Doney et al., 2010; Diaz, 2001), occurring in estuaries such as the Chesapeake Bay (Simon et al., 2005), shallow marine areas such as the Continental Shelf of the Gulf of Mexico (Rabalais et al., 2001), the South China Sea (Naylor et al., 2005), and freshwater lakes (Conley et al., 2009). In the next forty years, zones of eutrophication are projected to spread nearly three-fold from levels in 2000 (Tilman et al., 2001). The result will be at best losses in fish biomass (Doney et al., 2010) despite already low historic levels of larger consumer fish species (Jackson et al., 2001).

Such effects are already evident in the Chesapeake Bay, where anoxic (0-0.2 mg dissolved oxygen (DO) L<sup>-1</sup>) conditions occur between April and October and take up more than one km<sup>3</sup> of Chesapeake Bay mainstem when peaking in July and August (Chesapeake Eco-check, 2011). This is a considerable volume in a body of water with an average depth of 6.4 m (Chesapeake Bay Program, 2001a). The volume of Chesapeake Bay mainstem experiencing oxygen stress (2-5mg DO L<sup>-1</sup>), when bacteria begin to use NO<sub>3</sub> as an electron receptor instead of oxygen (Doney et al., 2010), occupies between six and ten km<sup>3</sup> (Chesapeake Eco-check, 2011). One of many factors damaging to the Chesapeake Bay ecosystem, eutrophication and anoxic zones are partially responsible (Chesapeake Bay Program, 2011b) for challenges associated with submerged aquatic vegetation, oysters, crabs, menhaden and rockfish (Chesapeake Bay Program, 2011c).

Eutrophication leads to ecosystem degradation through pathways other than anoxia. Eutrophic environments favor plants that can respond to increased nutrient levels by taller growth. The result is less diverse plant communities competing for light and not nutrients. Such communities displace more diverse, though lesser-biomass communities that were previously limited by nutrients.

Nitrogen (N) and phosphorus (P) are considered largely responsible for the development of anoxic conditions, since one or the other is usually the limiting nutrient from the perspective of algal growth and in many cases these elements need to be managed together (Conley et al., 2009). Nitrogen and P are both considered major pollutants of the Chesapeake Bay with agricultural manure considered responsible for 26% of P loadings to the Bay, with another 19% supplied by inorganic agricultural

fertilizers (Chesapeake Bay Program, 2011d), but N and P throughputs are of sufficient size to be of worldwide concern (Röckstrom et al., 2009).

Excess P application in the form of manure occurs because a high percentage of manure is water and is expensive to ship (Naylor et al., 2005). This results in repeated application to the same land (Sharpley and Moyer, 2000) often to meet the nitrogen needs of crops (Maguire et al., 2005). This generally results in over-application for P, no matter the manure type (Maguire et al., 2005).

On the Delmarva Peninsula, which is responsible for only a share of the nutrient loadings received by the Chesapeake Bay, 760 million broiler chickens were produced in 2009 (Delmarva Poultry Industry, 2010), and likely more than  $10^8$  kg P in the form of manure (Hill and Cade-Menun, 2009). Delmarva soils are, in many places, chronically over-fertilized with P. Without technical innovation with respect to P concentrations in manure or novel uses for poultry manure, current eutrophication problems of the receiving waters of the Delmarva Peninsula are a problem in their own right, and prefigure those of landscapes where industrial-scale animal husbandry is beginning or has yet to start.

### **The landscape of the Lower Delmarva and the need for drainage**

Industrial-scale animal husbandry in the Delmarva is concentrated in the south, in the Delaware counties of Kent and Sussex (the county of greatest poultry production in the USA in 2009), the Maryland counties of Dorchester, Caroline, Wicomico, Worcester and Somerset and the Virginia county of Accomack (Delmarva Poultry Industry, 2010). These counties are of low relief and elevation, and contain large areas where the drainage

class of natural (pre-drainage) soil is “poorly drained” or “very poorly drained” (Soil Survey Staff, 2011). In the Maryland portion of the Lower Eastern Shore 183,000 acres is drained artificially in a network created for the purposes of agriculture (Maryland Department of Agriculture). Drainage facilitates the use of fields by heavy equipment in the Spring, when water tables would typically be high and soil disruption and compaction would otherwise occur due to decreased shear strength when the water content of soils are above the plastic limit.

### **Types of drainage**

Drainage is typically accomplished through the use of either buried ‘tile’ (tubing), or ‘field’ or ‘primary’ ditches. The former allows for cropping directly over the point of drainage whereas the latter splits the landscape into fields, with field ditches constituting the lengthwise boundaries. In soils with limited saturated hydraulic conductivity, drainage through field ditches would require a small width between ditches and therefore excessively narrow fields. For this reason drainage in the glaciated and finely textured Midwest, USA and much of Ontario, Canada is accomplished by tiles. The soils of the Mid Atlantic Coastal Plain (MACP), which are formed primarily from marine sediments, are sufficiently coarse-textured for fields of adequate width with open drainage. Field ditches and tiles have the same function: to intercept rising groundwater and deliver it to a drainage network.

## **Types of ditches and the definition of ditch**

Since field ditches intercept a rising water table they are the most elevated landscape features to channel surface water. They are the first order streams of ditch networks in which ever larger ‘secondary’ or ‘collection’ ditches bring drainage to receiving waters. Ditch depth and restricting layers decide the frequency of contact between ditches and the water table, and ditch longitudinal relief and channel roughness decide ditch flow velocity. Despite a simple definition for ‘ditch’ – a channel sculpted to speed the removal of water from a landscape – ditch hydrology depends on many factors and not all ditches are the same.

Many Midwestern ditches are channelized streams; they are many kilometers in length and drain areas of many square kilometers (Smith, 2009, Smith and Huang, 2010; Powell et al., 2007a; Powell et al., 2007b). Such ditches likely feature year-round flows of sufficient velocity to preclude soil development; their channel materials are sediment. Primary ditches are rarely over ½ km in length, drain landscapes of only a few hectares, and are sufficiently shallow to lie above the water table many times throughout the year. This fluctuating hydrology gives primary ditches a biogeochemistry similar to that of wetlands and creates materials which have undergone sufficient transformations and translocations to be identified as soils (Vaughan et al., 2008). Hence, while the term ‘ditch’ may be universally applied, the term refers to different landscape features that should not be confused.

## **Ditches are more than conduits of water**

Though the original purpose of drainage was agricultural, ditches have become of increased interest for their effects on habitat and biodiversity (Blann et al., 2009; Herzon and Helenius, 2008), role in handling storm water in urbanizing landscapes (Maryland Department of Agriculture), provision of connectivity between chronically over-fertilized landscapes and eutrophic downstream waters (Kleinman et al., 2007; Dukes and Evans, 2006), and potential for nutrient removal (Needelman et al., 2007a; Moore and Kroger, 2011). Nutrient processing, which concerns much of this dissertation, is a function of biogeochemical processes.

## **Biogeochemistry of primary ditches**

The form and oxidation state of elements in soils is determined by many factors, including interactions between the chemical species and the organisms present. All organisms derive energy from redox reactions which necessarily involve the displacement of electrons. Electron-donating and -receiving species (redox couples) can be placed – assuming some standard conditions – on a relative scale regarding potential energy. Differences between oxidizing and reducing species on this scale indicate the energy benefit to the organism using that redox couple. While most bacteria use the same redox couple as higher animals, namely the removal of electrons from reduced organic carbon and placing those electrons onto oxygen gas, many different types of bacteria are capable of using other redox couples that do not involve oxygen as the electron acceptor or organic matter as the electron donor. In systems where organic matter is not abundant, or in systems where oxygen is depleted, bacteria capable of oxidizing and reducing other

species have a competitive advantage. In environmental systems (such as saturated ditches) where oxygen is depleted but not organic matter, bacteria play an active role in the reduction of nitrogen, manganese, Fe, sulfur and even carbon. Upon aeration these reduced species may be quickly re-oxidized either through abiotic or bacterially catalyzed processes. Redox processes in soils are extremely complicated because any redox process is possible and probably occurring as long as it is energetically favorable and is not poisoned by environmental conditions, and because even relatively simple redox changes such as the oxidation of Fe(II) to Fe(III) include many intermediate steps (Burns et al., 2011).

Another factor governing the chemistry of natural systems is the formation or dissolution of minerals depending on the activities of chemical species. Similar to redox reactions, the direction of formation/dissolution reactions is governed by potential energy, though the kinetics of formation/dissolution and redox reactions are not related to potential energy in the same way for all minerals.

It is important to keep in mind that only a portion of the mass of an environmental system plays a chemical role. In the following sections the most basic redox and mineralogical material is discussed as is relevant for ditch P, but these remarks apply to compounds at the surfaces of soil particles, since it is only at the interface between materials that chemical reactions take place. Weathering processes are responsible for the slow breakdown and release of constituents to the environmental system where they can react and transform based on interactions with other environmental constituents, but weathering processes are not the only processes that might introduce P-reactive minerals to ditches.

## Iron: Fe(II), Fe(III) and ferrihydrite

The 'reduced' form of Fe is Fe(II), the stable form of iron under reducing conditions. Reduced Fe predominates in primary minerals, is soluble as the colorless  $\text{Fe}^{2+}$  ion, and forms secondary minerals, including oxides, in reducing environments. Soils with Fe in the reduced state often appear gray in color because of the lack of Fe(III) as a pigment, or because Fe may have been lost altogether as a result of the movement of pore water flushing soluble  $\text{Fe}^{2+}$  from the system. However, Fe(II) containing minerals may appear black (FeS) or green.

When the activities of ions in solution exceed the equilibrium constants (related to potential energy) of minerals, those minerals will begin to form (Lindsay, 1979). Since the equilibrium constants of Fe(II) minerals are relatively high, higher concentrations of  $\text{Fe}^{2+}$  and other ions are needed for Fe(II) minerals to form.

The 'oxidized' form of Fe is Fe(III), which predominates in secondary minerals of oxidizing environments. Fe(III) minerals tend to have lower equilibrium constants and therefore form at lower concentrations; as a result  $\text{Fe}^{3+}$  is far less soluble than  $\text{Fe}^{2+}$ , though  $\text{Fe}^{3+}$  solubility is increased (Lindsay, 1979), and therefore  $\text{Fe}^{3+}$  movement is possible, at very low pH. Fe(III) oxides, and chelates, tend to be yellow, orange, or red, or brown. Because of its relatively high tolerance to dissolution at moderately acidic pHs, Fe(III) oxides tend to persist relative to other minerals in acidic environmental systems.

Under environmental conditions, the formation of Fe(III) oxyhydroxides from  $\text{Fe}^{2+}$  or Fe(II) oxyhydroxides exposed to oxidizing conditions takes on the order of minutes (pH~7.5) to hours (pH<6.5) (Davidson and Seed, 1983). The mineral formed, 'ferrihydrite', is not crystalline, but rather 'paracrystalline', or of 'short-range order', and



contains water in its structure. Ferrihydrite has a higher surface area than crystalline Fe(III) oxyhydroxides [(reported as  $\text{m}^2 \text{g}^{-1}$ ) hematite 9 (Huang et al., 2004) and 22 (Parfitt et al., 1975), goethite 80 (Parfitt and Atkinson, 1976) , and lepidocrocite 108 (Parfitt et al., 1975), whereas ferrihydrite is reported by Wilson et al. (2004) to have  $250 \text{ m}^2 \text{ g}^{-1}$ , and ‘Fe hydroxide gel’  $257 \text{ m}^2 \text{ g}^{-1}$  by Parfitt et al. (1975)]. Formulas for ferrihydrite range from  $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$  (Sparks, 2003) to  $\text{FeOOH} \cdot n\text{H}_2\text{O}$  (Seehra et al., 2010) as may be fitting for a mineral without long-range structure. Lindsay (1979) does not use the term ‘ferrihydrite’ at all, but rather discusses ‘amorphous’ Fe and ‘soil’ Fe. Ferrihydrite is generally considered the most soluble of Fe(III) oxides (Schwertmann, 1991), and the form of oxidized, mineral Fe most available to plants (Schwertmann, 1991).

Under laboratory conditions pure ferrihydrite slowly transforms to crystalline goethite or other minerals (Schwertmann et al., 2000; Liu, 2010; Das, 2011), but in natural environments the occurrence of ligands such as organic acids, phosphate ( $\text{PO}_4$ ) and silicate ( $\text{SiO}_4$ ) which are incorporated into the ferrihydrite upon formation are found to further disrupt structure (Eusterhues, 2011; Cismasu, 2011) and impede this transformation (Schwertmann, 1991; Cornell and Schwertmann, 1979) or cease it altogether (Rhoton and Bigham, 2005).

Primary drainage ditches experience frequent cycles of inundation and reducing conditions alternating with drying and oxidation. Ferrous  $\text{Fe}^{2+}$  liberated from primary minerals or amorphous  $\text{Fe}^{2+}$  or Fe(II) oxides formed from the reduction of Fe(III) (Patrick and Khalid, 1974) may be expected, as above, to oxidize to ferrihydrite. Redox cycling, high organic matter (OM) contents, and high levels of other anions in ditches encourage the formation of and retard the transformation away from ditch soil Fe(III) as ferrihydrite,

thus ferrihydrite may be expected to be the predominant form of Fe(III) in ditches. In a ditch in Germany (Schwertmann, 1966) and in two ditches in the MACP (Needelman et al., 2007b) ferrihydrite was interpreted as being the only, or close to only, form of iron present.

Complexes of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  and organic matter readily form and have been inspected in the contexts of marine (Petrovic and Kastalan-Macan, 1996), coal (Janos et al., 2011; Guardado 2007; Guardado, 2008), peat (Sharma et al., 2010; Garcia-Mina 2006), and compost (Garcia-Mina, 2006). Due to the high amount of OM and Fe in ditch O and A horizons, Fe-OM complexes may be a significant ditch Fe pool. Since natural ferrihydrite is known to incorporate organic matter, there is a continuum of morphology from OM complexed with individual Fe ions, ferrihydrite complexed with OM, and OM-containing ferrihydrite. A system of ‘metal-humic complexes’ with mass ratios of Fe to humic or fulvic acids between 0-10 is described by Garcia-Mina et al. (2006).

A commonly used method of quantifying complexed Fe, amorphous Fe (hydr)oxides and associated constituents is extraction with acid ammonium oxalate, or Tamm’s reagent. The metal extraction works based on chelation by oxalate (Fernandez R. et al., 2008) followed by dissolution of the complex, which for amorphous and humus-complexed Fe occurs with relatively fast kinetics (Vodyanitskii, 2001). However the dissolution of Fe species is not restricted only to amorphous and OM-complexed Fe (Loeppert and Inskeep, 1996); the presence of various mineral species (Vodyanitskii, 2001) including Fe(II) species (Sulzberger et al., 1989) and even light (Loeppert and Inskeep, 1996) have been found to catalyze the oxalate-based dissolution of some crystalline Fe. Tamm’s reagent likely also dissolves some nano-scale crystalline Fe

compounds (Thompson et al., 2006). In the end the proper functioning of Tamm's reagent to selectively target paracrystalline and organically complexed species is due to the relatively fast kinetics of these species over more crystalline forms (Vodyanitskii, 2001). The extraction is typically performed at pH=3, by lowering the pH of 0.175 M or 0.2 M ammonium oxalate with similarly dilute oxalic acid or concentrated HCl (Loeppert and Inskeep, 1996). The extraction is performed for a short time (2-4 hours) to allow for the dissolution of primarily target species (Vodyanitskii, 2001). Because the oxalate-Fe(II) complex is less soluble than the Fe(III) complex (Vodyanitskii et al., 2007), Tamm's reagent may be best suited as an extractant of Fe(III). The oxalate extraction was used by McGahan et al. (2003) to extract short-range order Fe and Al from soils in different stages of acidification.

Numerous wetland researchers have used the oxalate extraction. Ditches are places where  $\text{Fe}_{\text{ox}}$  accumulates relative to field soils (Lookman et al., 1996). The oxalate extraction has also been used (SurrIDGE et al., 2007) and recommended (Richardson, 1985) as an extractant of Al in the context of wetlands.

Ditch systems will gain in Fe through three mechanisms: 1) sedimentation due to bank failures or field runoff and 2) influx of  $\text{Fe}^{2+}$  and colloidal Fe from groundwater and 3) weathering and oxidation of in-ditch mineral material.

## **Aluminum**

Aluminum has only one oxidation state under environmental conditions, Al(III), and is not directly subjected to redox related changes in speciation and mineralogy as is Fe. Like  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , is poorly soluble and first forms amorphous oxyhydroxides when

precipitating (Navratil, 2009; Kopacek, 2005). These amorphous materials develop more crystalline structure over time (Lindsay, 1979).  $\text{Al}^{3+}$  is a smaller ion than  $\text{Fe}^{3+}$ , allowing Al to substitute for Fe(III) (Jentzsch and Penn, 2006; Chadwick et al., 1986; Schwertmann, 1991) in oxyhydroxides. Al may be released to solution if reductive dissolution of Fe oxyhydroxides occurs in which Al is entrained. The lack of a soluble redox state, however, limits the ability of Al to move relative to Fe. Similar to Fe, Al (hydr)oxides tend to be relatively resistant to dissolution at moderately low pHs and therefore are associated with acidic environmental systems. However, Al hydroxides are sufficiently susceptible to dissolution at pHs below 5.5 so as to reach levels toxic for plants. Since Fe is soluble only at much lower pHs (Lindsay, 1979) in this respect Al can be more mobile than Fe, and has been observed to mobilize in watersheds which were artificially acidified (SanClements et al., 2010). Similar to Fe, Al also readily forms OM complexes (Guardado, 2008; Petrovic and Kastelan-Macan, 1996), and may do so more readily than Fe (Lookman et al., 1996). Al and OM are highly correlated in Virginia Piedmont and Coastal Plain wetlands (Axt and Walbridge, 1999). Also similar to Fe, Al will enter ditches through erosion of field surfaces and ditch banks, colloidal and dissolved forms through groundwater, and the weathering of phyllosilicates (SanClements et al., 2010). However Aluminum lacks a highly soluble state similar to that of reduced Fe.

## **Sulfur**

Sulfur (S) is capable of many oxidation states (Lindsay, 1979). Reduced S(-II) and S(-I) form insoluble metal sulfides with the exception of calcium and magnesium

sulfides (Lindsay, 1979). Sulfur reduction occurs in soil systems when sulfate ( $\text{SO}_4$ ) becomes the electron receptor for bacterial metabolism, forming  $\text{H}_2\text{S}$  (Pfeiffer, 1994).  $\text{H}_2\text{S}$  functions not only as a supply of reduced S for the formation of  $\text{FeS}$ , but as a reducing agent, such that it can create  $\text{Fe}^{2+}$  by reducing  $\text{Fe(III)oxyhydroxides}$  (Pfeiffer, 1994).

Iron monosulfides are black in color. When encountered near the soil surface of aquatic habitats they are easily suspended and often contain a component of organic matter. Such suspensions have been termed ‘monosulfidic black ooze’ (MBO) in the Australian literature (Ward et al., 2010; Bush et al., 2004) and are of interest for their chemistry and reactivity. Though containing mostly S(-II) minerals, MBOs may contain elemental sulfur (Ward et al., 2010) or pyrite ( $\text{FeS}_2$ ) (Bush et al., 2004).  $\text{FeS}$  is expected to change through time to  $\text{FeS}_2$  through a redox reaction with elemental sulfur, which itself is created through the partial oxidation of  $\text{H}_2\text{S}$  (Pfeiffer, 1994). As a result (young) reduced soil S is predominantly  $\text{FeS}$ ; and (old) geologic deposits of reduced sulfur tend to be  $\text{FeS}_2$ .

The presence of reduced sulfur is a potential danger for aquatic habitats. The oxidation of reduced sulfur releases sulfuric acid (Fanning and Fanning 1989) which can radically lower pH and releases metals previously made insoluble in their sulfide form. This oxidation is abiotic, may occur within minutes, and can completely consume dissolved oxygen (Bush et al., 2004). Monosulfidic black oozes have been observed in primary ditches in Maryland (Vaughan et al., 2008; Needelman et al., 2007b).

## **Phosphorus**

In most environmental situations, P is not redox sensitive so its speciation is controlled by pH. In most cases, whether dissolved, chelated, adsorbed, or organic, P is found as  $H_xPO_4^{(3-x)-}$ , where the distribution of 'x' diminishes with increasing pH (Lindsay, 1979). For example in the moderately acidic range between pH 4 and 6, the heightened presence of hydrogen (H) induces virtually all dissolved P to be of the form  $H_2PO_4^-$ ; for pH below 4 an increasing amount is found in the even more protonated form  $H_3PO_4$  (Lindsay, 1979).

P is a necessary component of all life forms, and is found in all cells in the form of ATP and DNA. As such P is present in living plant and animal biomass. Upon death of the organism the P will be released and will either be taken up by a consuming predator, detritivore or plant, retained by soil mineral/organic material, may precipitate in place with other soil solution constituents, may be lost from the soil environment through leaching to groundwater or layers of regolith inaccessible to organisms of the solum, or lost to other portions of the landscape in runoff. Mineral-bound P is often displaced through runoff-associated erosion.

### **Phosphorus exports from a MACP ditched landscape**

A study was performed by Kleinman et al. (2007) including two ditches from a farm in the MACP. They found that annual dissolved reactive P (DRP) (roughly analogous to dissolved inorganic P) export from the two ditches averaged between 0.1 and 8.4 kg DRP  $ha^{-1} yr^{-1}$ , with lower values corresponding to years with reduced overall ditch flow. These values corresponded to average ditch effluent of 0.07 and 1.23 mg DRP

$L^{-1}$ , respectively. Since the commonly cited eutrophication threshold of  $0.03 \text{ mg P } L^{-1}$  (Dodds et al., 1997; Dodds et al., 1998) is 2 to 40 times below these yearly averages it is clear that these ditches – the least P-exporting ditches in the study – are contributing to poor water quality downstream.

In a companion study by Vadas et al. (2007) groundwater at the same farm averaged  $0.53 \text{ mg DRP } L^{-1}$  at a depth roughly equal to the depth of these ditches. Therefore the ditches studied by Kleinman et al., (2007) may at different times mitigate or exacerbate the short-term export of P from the landscape studied. although ditches can only be a long-term P sink since they begin with no P).

### **Mechanisms of P retention**

Soils have many mechanisms by which P may be retained (Nichols, 1983). These processes are, in no particular order, physical adsorption onto mineral species, chemical adsorption onto mineral species, chemical adsorption onto OM-metal complexes, occlusion by mineral species, precipitation by mineral species, settling of P-laden mineral and organic particles, microbial uptake, plant uptake, entrainment onto living plant biomass and sequestration through the lack of mineralization of a portion of senesced plant biomass. The following sections describe these processes in greater detail.

#### **P fixation by minerals – chemical adsorption through the formation of inner sphere complexes by ligand exchange**

Ligand exchange is the competitive displacement of one or more anions by a different anion or groups of anions. Ligand exchange is a major mechanism of P retention

in natural and artificial substrates. The formation of  $\text{CaHPO}_4$  from  $\text{CaCO}_3$  (Molle et al., 2003) implies the ligand exchange of  $\text{HPO}_4$  and  $\text{CO}_3$ ; the formation of ‘monodentate’ metal-O- $\text{PO}_2\text{OH}$  or ‘bidentate bridging’ metal- $\text{PO}_2\text{OH}$ -O-metal structures from metal (hydr)oxides implies the ligand exchange of  $\text{HPO}_4$  and OH (Parfitt, 1975; Parfitt, 1979; Parfitt, 1989; Borggaard et al., 2005). These formations are clearly inner-sphere complexes since they involve the direct chemical attachment between metals and a  $\text{PO}_4$ -O. Given the number of bonds between the  $\text{PO}_4$  and sorbing surface, monodentate complexes are believed to be more readily exchangeable than binuclear bridges. Resolving inner sphere complexes in the wet laboratory is accomplished using specialized extractants designed to alter the chemistry of the extracted soil, such as (chelating) oxalate, or (reducing/dissolving and chelating) dithionite-citrate (see Loeppert and Inskeep, 1996). With these extractants competitive (oxalate) or thermodynamic stability altering (dithionite) mechanisms are used to break apart chemically bonded species.

For ligand exchange to be a major mechanism of P sorption, P must be an excellent competitor, and in many contexts it is (Jara et al., 2006; Zhu et al., 2011). This may be due to its high basal charge (-3) and the relatively weak electronegativity of P (equal to H, but less than N, C or S) which renders the P-O bond more polar (Chang, 1991) with the fractional electron charge separation skewed towards the O atom, rendering the O atom more charge dense and therefore reactive. Organic matter (Lyons et al., 1998; McDowell and Condron, 2001; de Mesquita Filho and Torrent, 1993), citric acid (Hutchison and Hesterberg, 2004), organic phosphorus (Leytem, 2002), sulfate (Smolders et al., 2010), oxides of arsenic (Fritzsche et al., 2011; Zhu et al., 2011) and



other anions (Parfitt et al., 1975; Parfitt, 1989; Sah and Mikkelsen, 1986a) have been demonstrated to compete with  $\text{PO}_4$  for sorption sites on ferrihydrite and other Fe and Al oxides.

In a comparison of the ability of different ligands to displace adsorbed arsenite and arsenate,  $\text{PO}_4$  was found by Zhu et al. (2011) to be superior to  $\text{SeO}_4$ ,  $\text{SeO}_3$ ,  $\text{SO}_4$ , oxalate, malate tartrate and citrate. Sodium pyrophosphate,  $\text{Na}_2\text{P}_2\text{O}_7$ , a compound made up of a simple polymer of  $\text{PO}_4$ , is deliberately used to outcompete organic matter for the complexation of metals (Loeppert and Inskeep, 1996). Sulfate was found to make much weaker complexes than P with Fe(III) in a study by El Samrani et al. (2006). Nevertheless the competitive interaction between  $\text{PO}_4$  and  $\text{SO}_4$  is emphasized by some authors (Smolders, 2010).

Competition is significantly impacted by the order of addition of the competing anions, with the relative advantage going to the anion in place before the addition of the competing ion (Violante and Gianfreda, 1993; Zhu et al., 2011). Such effects can also interact with pH (Liu et al., 1999).

The binding sites appropriate for the ligand exchange of P are often limited. The formation of monodentate or bidentate bridges of  $\text{PO}_4$  onto metal (hydr)oxides appears to be restricted to exchange with singly coordinated (e.g. 'aluminol' Al-OH) metal-OH or metal- $\text{OH}_2$  groups, which make up only a fraction of the mineral surface (Parfitt, 1975). Such groups are present upon the surfaces of Al and Fe (hydr)oxides (Parfitt, 1975) and on the edges of phyllosilicates though the relative contribution of this latter population is often small relative to that of Fe and Al.

Ligand exchange is facilitated by association of  $H^+$  with the above-mentioned singly coordinated hydroxyl groups. The resulting metal- $OH_2$  complex is unstable and can be displaced by an anion. As pH drops, the equilibrium concentration of these  $H^+$  associated hydroxyl groups increases and the potential for ligand exchange increases. Sorption of P onto goethite increases from pH 12 through pH 3 (Hingston et al., 1972); sorption of P onto an aluminohydroxide shows a maximum near pH=4 (Tanada et al., 2003).

Among Fe and Al(hydr)oxides P sorption varies greatly. While singly coordinated OH/ $OH_2$  groups are of about the same density on Al and Fe(hydr)oxide surfaces, different minerals have different surface area and therefore different amounts of OH/ $OH_2$  groups of single coordination. Minerals with the largest surface area and therefore P sorption capacity are not crystalline in structure, but paracrystalline materials such as Fe-based ferrihydrite or amorphous Al-based allophane. Hence, minerals such as ferrihydrite and allophane tend to have higher P-sorption capacity than more crystalline minerals.

### **P fixation by minerals – physical adsorption through the formation of outer sphere complexes**

Outer sphere complexes are not direct chemical attachments between sorber and sorbent. Rather, they are electrostatic associations mediated through the soil solution between positive charges on the sorbent and the anion. In an outer sphere complex the anion remains surrounded by a shell of water molecules and is therefore not directly bonded to the mineral surface. As such, this source of P sorption is the weakest of all, and much of the water extractable P of soil material is made up of outer sphere complexes.

Such weak sorption means that it only begins to be effective when other, stronger sorption sites are filled. Nichols (1983) reports that physical adsorption is partly a function of concentration, and begins at about  $0.1 \text{ mg P L}^{-1}$ , but only predominates over chemical adsorption at concentrations ten times higher. Physically adsorbed P is typically measured in the wet lab with dilute salt extractions (meant to be weak competitors; targeting weakly mineral-attracted P), or anion exchange resins (which remove P from the soil solution, encouraging physically adsorbed P to enter the soil solution itself, etc.) (see Kuo, 1996). These techniques do not chemically alter the soil being studied.

Coulombic attraction between anions and mineral sorbents is a function of pH. pH controls the equilibrium association of H and  $\text{PO}_4$  (see above) and heavily influences the abundance of OH vs.  $\text{OH}_2$  on mineral surfaces. The point of zero charge for most Fe and Al (hydr)oxides occurs between pH equal to 7.5 and 9, which is much higher than that of most secondary aluminosilicates. The result is that between pH 2 and 7 secondary Al and Fe minerals have an overall positive surface charge, whereas P is an anion. Apparent positive surface charge can also be created by cation bridges between a negatively charged mineral location and P, hence solution cations can effect P sorption (Rupa et al., 2001). Coulombic attraction is essential for the functioning of outer-sphere complexes. Therefore, as with inner-sphere complexes, acidic pH favors outer-sphere P sorption onto Fe and Al (hydr)oxides.

### **P fixation by minerals – occlusion and precipitation of P**

Early researchers ascribed metal-P precipitates the primary role in P retention by mineral materials (Mortimer, 1940), and the distinction between chemically adsorbed and

precipitated P may be a question of semantics (Nichols, 1983). However, contemporary researchers ascribe most P retention phenomena to adsorption (Harvey and Rhue, 2008), and only occasionally on mineral-P precipitation. Operationally, occluded or precipitated P would be observed using techniques similar to those used for chemically adsorbed species, and in addition acid-based extractions (Loeppert and Inskeep, 1996, Bertsch and Bloom, 1996) designed to dissolve more than soil mineral coatings.

Metal phosphates as a whole are relatively insoluble (Lindsay, 1979), and have been found by some researchers to be responsible for P retention. Biosolids amended with hydrates of  $AlSO_4$  and  $FeSO_4$  to achieve  $Al/P=1$  and  $Fe/P$  near .5 were found to result in the formation of Al-P and Fe-P precipitates (Huang et al. 2007).  $CaCO_3$  exposed to a  $PO_4$  solution was found to precipitate  $CaHPO_4$  (Molle et al., 2003). The importance of soluble metal for the formation of precipitates may be very important. Whereas calcium (Ca) has been found to form precipitates of P, Ca is relatively soluble and therefore abundant in soil solution; Al and Fe are relatively insoluble and therefore less abundant in soil solution, and this may account for the frequency with which P-retention is ascribed to adsorption onto Al- and Fe-(hydr)oxides and not to formation of Al and Fe phosphates. P precipitation into a particular metal phosphate will occur when cations and P are of sufficient activity relative to the equilibrium constant for the mineral in question (Lindsay, 1979), and will constitute an appreciable sink for P only when the ratio of metal atoms to P is great enough.

Precipitation experiments involving separate solutions of P and Al and P and Fe were performed by Hsu (1976). Ratios of metal:P = 5 resulted in virtually total metal and P removal from solution at pH between 6 and 8 for aluminum and 5.5 and 7 for Fe. When

1:4 < Al:P < 1:6, and 1:2 < Fe:P < 1:6 in solution, 1:1 metal:P precipitates were formed at pH ranging from 4 to 5.6 for Al and 2.5-4.5 for Fe (Hsu 1976). Instead of competing with P, hydroxide and sulfate facilitated precipitation by helping to balance charge (Hsu 1976). Complete removal of P was achieved by Fytianos et al. (1998) when Fe:P = 2.55. A suite of pH, Fe and P input concentrations in laboratory batch samples were used.

Ecosystem-based research has also identified critical ratios of Fe:P. In a study of peat mesocosms Zak et al. (2004) identified the formation of Fe(hydr)oxide surfaces within the peat at the boundary between oxidizing and reducing conditions. If Fe:P>3:1 in the reduced pore water below these Fe surfaces then virtually no P could be measured in the waters above the Fe surface. Zak et al. (2004) speculated that these Fe(hydr)oxide layers prevented the diffusion of P from reducing to oxidize zones. Relative abundance of Fe:P in reduced pore water has been used by Surridge et al. (2007) and Young and Ross (2001) in interpretation of their results. Zak et al. (2010) developed the work of Zak et al. (2004), identifying Fe:P =10 in soil materials as critical for the formation of Fe-adsorbing barriers. Pore water ratios of Fe:P=3.5 and soil content ratios of Fe:P=10 have been identified by Geurtz et al. (2008) not only for similar effects with respect to P contents of oxidized and reduced pore water, but also for a correlation with endangered species. Above pore water ratios of Fe:P=1 Geurtz et al. (2008) found endangered macrophyte wetland species numbers to increase, with additional effects occurring at higher pore water Fe:P ratios.

Adsorbed P changes the point of zero charge of the mineral onto which it adsorbed, rendering it more negative. As a result, cations may become attracted to the adsorbed P, resulting in the buildup of metal-P layers, 'occluding' P in the layers below

the surficial layer. Precipitation of P-based minerals can form an indefinitely large pool of P sorption, as long as ion concentrations are sufficiently high to support mineral precipitation.

### **P fixation by minerals – additional notes**

Natural minerals are seldom (hydr)oxides of single metals species (Harvey and Rhue, 2008), and the sorption behavior of these mixtures depends on composition. In a study of amorphous materials made up of various percentages of Al and Fe, Harvey and Rhue (2008) found that crystallinity depended on Al/Fe content, and that P sorption and rate of sorption was a function of Al/Fe and crystallinity, with sorption rates increasing with Al content and decreasing with crystallinity.

Due to their limited crystallinity, paracrystalline materials are not at their lowest energy state. As a result, though their P binding capacity -- due to surface area -- is heightened relative to more crystalline species, the strength of their binding of P is diminished. In a study of hydrous Fe gel, created upon the reduction of more crystalline soil material, Patrick and Khalid (1974) observed diminished P sorption capacity at low solution P concentrations and heightened P sorption capacity at high solution P concentrations, relative to the original material. They attributed the relatively poor sorption behavior at low solution P to a relative lack of very low energy binding sites, and the enhanced P sorption at high solution P to the relative abundance of higher energy binding sites, which, at lower solution P values were not effective P sorbers. These phenomenon were attributed by Patrick and Khalid (1974) to the amorphous nature of the Fe(hydr)oxide gel.

The many mechanisms whereby P may be retained in solid form, and the strength of this retention when P concentrations are low has given rise to the practice of protecting against erosion and sedimentation as a means of protecting water quality against excessive P loadings. However, different P retention processes have different stability; and the equilibrium sorption and release of P is partly a function of soil solution P concentration, since some P retention mechanisms become favorable only when others are exhausted. This is a well known phenomenon and is manifested in ‘batch’ studies in which differential removal or release of P is recorded depending on the amount of P added (Poethig, 2010).

#### **P fixation by minerals – reaction rates**

The different mechanisms available for P retention in soils are also manifested by complex rates of P removal from solution. Typically observed are fast – minutes (Tanada et al., 2003) or hours (Parfitt, 1989) – phases of sorption attributed to ligand exchange and physical adsorption (Nichols, 1983; Harvey and Rhue, 2008), with physical adsorption occurring at the fastest rate. For simplified, highly crystalline sorbents such as laboratory produced goethite, the ‘fast’ mechanism is the only means of P sorption (Parfitt, 1989). In naturally occurring minerals, and especially amorphous materials, pore spaces and disruptions and edges are more frequent, and P can attach to these or penetrate through them slowly diffusing into the material. Further disruption of materials can occur by the displacement of  $\text{SiO}_4$  by P, which can create even more possible sites for P binding (Parfitt, 1978). As time passes following fertilizer application P loses solubility (Parfitt, 1978). In contrast, therefore, to the quicker reaction of ligand exchange a ‘slow’

reaction is observed in natural minerals in which P becomes more intimately associated with the sorbing material.

### **P fixation by organics – OM-metal-P complexes**

While OC is often well correlated with P in the environment, much of this association is attributed to metals functioning as bridges between OM and P, either as individual metal atoms or colloidal metal oxides complexed with OM (Gerke, 2010; Dolfing et al., 1999; Bloom, 1981). These complexes have been found to be effective sorbers of P (Janos et al. 2011), though in an agricultural context they are preferred over the formation metal-P precipitates (Delgado et al., 2002) because of OM-metal-P complexes can be less soluble (Gerke, 2010). In a ditch context the ability of such complexes to retain P is clearly related to the stability of the OM-metal-P bonding and solubility. In a study of Fe(II)-OM complexes with no metal-adsorbed P, Garcia-Mina (2006) found that an Fe-humic acid complex with the humic acid isolated from an acidic peat increasingly precipitated as pH descended from 9 to 4 and that precipitation further increased as the mass ratio of Fe(II) to humic acid increased from 0 to 10. Similar Fe(II)-fulvic acid complexes showed little response to pH between pH 9 and 4, but as with the Fe(II)-humic acid complex, increased precipitation occurred with increased Fe(II) relative to fulvic acid (Garcia-Mina, 2006). Hence, the solubility of Fe(II)-OM complexes was minimized by lower pH and high amounts of Fe relative to the weight of the acid. Complexes of dissolved OM-Fe(III)-arsenic(III) were found to form out of solution in a matter of hours and had stability constants between 4.4 and 5.6 (Liu et al., 2011b). The nature of chelation and therefore partial obstruction of the metal atom may reduce



sorption rates. Humic acids derived from coal were found by Janos et al. (2011) to take several days to reach equilibrium with solution P. Petrovich and Kastalan-Macan (1996) found pH dependency in the stability of Me-OM-P chelates. Operationally, one means of measuring organic-associated metals involves the use of a pyrophosphate [ $P_2O_7^{4-}$ ] solution (Loeppert and Inskeep, 1996), which is designed to outcompete organic-Fe chelators for Fe, however the use of such a solution to measure OM-Fe-P is problematic due to the obvious P interference it would create if colorimetric techniques could not distinguish between phosphate and pyrophosphate.

### **P fixation by organics – direct sequestration of P in detritus**

Retention of P by direct sequestration in detritus is slow. Nichols (1983) cites 10-100 g dry matter accumulation  $m^{-2} yr^{-1}$  in climates such as Canada, Ireland and Finland, and 300-400 g dry matter  $m^{-2} yr^{-1}$  in warmer climates. Accumulation in the Everglades is consistent with these latter figures. Craft and Richardson (1993) cite Peat accumulation in an undisturbed portion of the Everglades to be 2 mm  $yr^{-1}$ , which is 400 g  $m^{-2} yr^{-1}$  assuming that 200 g dry mass  $m^{-2}$  is equivalent to 1mm of accumulation. Similarly, Mitsch and Gosselink (2007) estimate peat accumulation to be up to 2 mm  $yr^{-1}$  in northern inland bogs. Since this P part of the biomass of originally fibric material

Storage of P as a proportion of dry matter has been estimated to be between 0.05 and 0.12% (Nichols, 1983). If the most optimistic biomass accumulation figures are used the P content of accumulating peat would be  $0.0012 g P g^{-1} dry matter^{-1} * 400 g dry matter m^{-2} yr^{-1} = 0.48 g P m^{-2} yr^{-1}$ . These estimates assume ('oligotrophic') marsh undisturbed by eutrophication. In marshes disturbed by eutrophication biomass would be increased.

Enriched areas of the Everglades store OM at  $5.9 \text{ mm yr}^{-1}$  ( $1180 \text{ g m}^{-2} \text{ yr}^{-1}$ ), nearly three times the level measured for an unenriched portion (Craft and Richardson, 1993). Some plants, such as cattail (*typha lattifolia*) store more P (up 0.3% of dry mass) in high P environments (Kadlec, 2005). Using these revised figures for P storage, appropriate to eutrophic systems of high productivity, plant based sequestration of P may be estimated to be  $0.003 \text{ g P g}^{-1} \text{ dry matter}^{-1} * 1200 \text{ g dry matter m}^{-2} \text{ yr}^{-1} = 3.6 \text{ g P m}^{-2} \text{ yr}^{-1}$ . This amount, and the one above for oligotrophic wetlands, fall within the  $0.1\text{-}4 \text{ g P m}^{-2} \text{ yr}^{-1}$  which Kadlec (2005) estimates for detrital P sequestration potential. Such limited P sequestration, says Kadlec (2005) ‘is of great importance for lightly loaded wetlands, but of no importance for heavily [P] loaded systems.’

These estimates are for total P storage associated with peat. In the everglades P stored as ‘recalcitrant’ (Craft and Richardson, 1995) organic P is estimated to be 65% of total P in enriched areas and 52% in unenriched areas (0-5 cm) (Qualls and Richardson, 1995). Koch and Reddy (1992) (0-40 cm) estimated 70% organic P storage in enriched and 78% in unenriched areas of the everglades. Other peat associated fractions measured by Qualls and Richardson (1995) were Ca-P (12% of peat associated P) and Al/Fe-P (7% of peat associated P). Hence, not all P retention reported for peat accumulation is related only to sequestration of plant biomass P (Reddy et al. 1993), and the P sequestration rates suggested by Kadlec (2005) ought to be revised downward if only residue-based sequestration is to be estimated.

## **Microbial biomass and P storage and release**

In ditches microbes play an important role in P uptake. In a fluvium Shigaki et al. (2008) found a trend of additional P release from sediments that had been irradiated in order to lyse microbes. Sharpley et al. (2007) found in sediments from an agricultural ditch that 42% of P uptake could be attributed to microbes; in sediment from ditches in forest and mixed-use watersheds microbial assimilation was attributed to a smaller share of P uptake (Sharpley et al., 2007). In the context of edge-of-field runoff, microbial uptake has accounted for more than 30% of sediment P entrainment (McDowell and Sharpley, 2003). Operationally this P can be measured using a technique to lyse bacteria (chloroform fumigation (Needelman et al., 2001); microwave irradiation (Islam and Weil, 1998)) and then measure the difference in P content between treated and untreated soil using a water or dilute salt extraction.

Upon drying and rapid rewetting microbial biomass can be lost relative to constantly moist controls (Blackwell et al., 2009; Mondini et al. 2002) because of the lysing of cells (Salema et al., 1982). Dried and rewetted soils have been found to release soluble OP in proportion to microbial biomass P (Turner and Haygarth, 2001). Therefore while microbes can be significant sinks of P, microbial P can be released upon changes in soil water content. In general the drying of soils has been found to affect their functioning (Bartlett and James, 1980).

## **Mechanisms of P release**

Similar to the previous section on mechanisms of P retention, mechanisms of P release include not only cell lysis upon drying or rewetting as discussed above, but also

mineralization of senesced organic matter, weathering of mineral material, reductive dissolution of Fe-based substrates to which P is attached, competitive interactions between  $\text{PO}_4$  and other anions, and pH-based solubility changes. These mechanisms are discussed below.

### **Mechanisms of P release – complexation of P-associated metals and competitive interactions**

The exudation of low molecular weight organic acids by plants and fungi allows for Fe (Schwertmann 1991) and P (Gerke, 2010; Long et al., 2008; Richardson et al., 2009) to be more plant available. This can also occur through organic acids released as plant residue breakdown products (Pavinato and Rosolem, 2008).

The strength of such chelation is primarily related to the density of carboxyl groups (Ryan et al., 2001). These organic acids have a heightened ability to solubilize P since not only can they compete with surface-sorbed P through ligand exchange, but chelate Fe and Al, creating a soluble complex which precludes P precipitation. At pH=3 oxalate is used to selectively dissolve amorphous and OM-complexed Al and Fe, and is the recommended extraction for ferrihydrite (Loeppert and Inskeep, 1996) and Al-associated P in wetlands (Richardson, 1985).

Other competitive anions can displace P. Additions of  $\text{SO}_4$  were found by Geelhoed et al. (1997) to increase P availability to maize. Sulfate generated from the oxidation of FeS by  $\text{NO}_3$  has been implicated by Smolders et al. (2010) in the eutrophication of many wetlands through competitive interactions with  $\text{PO}_4$  in which the

PO<sub>4</sub> is desorbed. This phenomenon is the mechanism behind the use of salt solutions to measure physically adsorbed P.

### **Mechanisms of P release – increased solubility at lower pH**

Amorphous materials have relatively high equilibrium constants, indicating that higher solution pH and metal concentrations are needed for them to persist relative to crystalline species (Lindsay, 1979). Drops in pH have been shown to mobilize Al and Al-sorbed P in an acidified watershed relative to a control (SanClements et al. 2010). This phenomenon is the mechanism behind the use of acids (Loeppert and Inskeep, 1996; Bertsch and Bloom, 1996) to shift the thermodynamic stability of solid minerals to dissolved species that can then be measured.

### **Mechanisms of P release – reductive dissolution of P-sorbing Fe**

Drops in redox potential have been shown to reduce P-sorbing Fe(III) (hydr)oxides to more soluble Fe(II). This is the mechanism behind the use of dithionite (Loeppert and Inskeep, 1996) as a reducing agent for the purposes of extracting Fe-based mineral coatings from soils. While Fe(II)(hydr)oxides are amorphous and may persist, the energy of P-binding becomes weaker, so that binding capacity is expanded only at very high solution P concentrations, and under lower P concentrations P is released (Patrick and Khalid, 1974). Alternatively, the hydroxide may also dissolve to Fe<sup>2+</sup> ('reductive dissolution') with the simultaneous release of Fe<sup>2+</sup> and P to solution (SurrIDGE et al., 2007; Heiberg et al., 2010; Banach et al., 2009; Berryman et al., 2009). In either case there is danger of large amounts of P release upon the development of reducing

conditions in soils (Zak et al., 2004; Oxmann et al., 2010; Pant et al. 2002). This process was first documented in lake sediments by Einsele (1936) and Mortimer (1940, 1941). While Mortimer (1940) attributed this release to the dissolution of  $\text{FePO}_4$ , more modern researchers (Shenker et al., 2005; Heiberg et al., 2010) cite the dissolution of P-bound Fe(III)oxides. Ditch soil material gathered from 17 Delaware ditches and then incubated anaerobically for 21 days released P that was well correlated ( $r=0.66$ ) with soil material Fe content (Sallade and Sims, 1997b). Release of P is of major concern from rewetted fens once used for agriculture and being considered once again as wetlands (Zak et al., 2004; Zak et al., 2010; Surridge et al., 2007; Meissner et al. 2010).

These same concerns have led to warnings (Sharpley et al., 2007; Gilliam and Skaggs, 1986) that the use of controlled drainage in ditches presents a danger of P release. However, meta analyses (Evans et al., 1995; Skaggs et al., 1994) indicate that the use of controlled drainage does not release more P than conventional drainage, despite sometimes elevated P levels in ditches under controlled drainage (Amatya et al., 1998). The cited mechanism is decreased ditch outflow (Evans et al., 1995).

P release through the reductive dissolution of Fe may be buffered by the presence of non-redox sensitive elements. Buffering of Fe-released P by calcium (Shenker et al., 2005; Berryman et al., 2009); and by Al (Murray and Hesterberg, 2006; Kopacek et al., 2005) has been documented. Eutrophic lakes were found to have internal P cycling controlled by Fe whereas meso- and oligotrophic lakes had internal control of P dominated by Al (Amirbahman et al., 2003). In some circumstances the adsorption of P onto Fe and Al (hydr)oxides appears to restrict (hydr)oxide susceptibility to reductive dissolution (Fernandez et al., 2008).

Therefore, while the release of P under anaerobic conditions is commonly observed and has been documented in ditch soil materials (Sallade and Sims, 1997b), other outcomes may occur depending on specifics of soil properties and experimental conditions (Zhang et al., 2010). The reoxidation of reduced Fe and the restoration of P-sorption capacity has been observed under some circumstances (Heiberg et al., 2010; Zak et al., 2004). The influence of oxidation/reduction cycles on ditch soil P release deserves study.

### **Mechanisms of P release – saturation of P sorption capacity**

While the accumulation of P-based minerals or metal (hydr)oxides allows for the indefinite removal of P from soil solution (see above), any non-accreting material has finite P sorption capacity, and as discussed above regarding ‘batch’ studies, P retention or release results from an interaction of the soil material with the soil solution. In practice, many researchers have found that with respect to initially P-free water, P desorption functions as a two stage process, with soil P contents below a threshold releasing P minimally, but above that threshold P release occurring at an increased rate (Maguire and Sims, 2002; Sims et al., 2002).

One means of identifying such a threshold is the ‘degree of phosphorus saturation’ (DPS) which is simply the molar ratio of oxalate extractable P ( $P_{ox}$ ) to oxalate extractable Al ( $Al_{ox}$ ) and Fe ( $Fe_{ox}$ ). Some researchers include a parameter ‘ $\alpha$ ’ (less than or equal to 1) in the denominator (Butler and Coale, 2005, Kleinman et al., 2000) which may be used to adjust for the fact that not all metal atoms in amorphous Fe and Al

coatings are available for P sorption. Beck et al. (2004) describe this factor as the value of DPS for a particular soil or soil type at P saturation.

Confusion arises regarding 'DPS' because the term is used in many different contexts. Sallade and Sims (1997b) use DPS to describe the ratio of NaOH-extractable P to a quantity that is not a direct measurement of the sorbent as in the ratios above.

Maguire and Sims (2002) use the similar ratio of Mehlich-3 extractable components ( $P_{M3} (Al_{M3} + Fe_{M3})^{-1}$ ). See Beck et al. (2004) for a discussion of the origin and practical difficulties with the DPS concept.

For field soil material, and when  $\alpha=1$ ,  $DPS = P_{ox} (Al_{ox} + Fe_{ox})^{-1}$  values lower than 20-25% are correlated with relatively low water extractable (WEP) values; for greater DPS values, increasing DPS correlates with rapidly increasing WEP (Maguire and Sims 2002). Lower values of DPS change points (12% to 18%, adjusting for  $\alpha=1$ ) have been recorded by Butler and Coale (2005) and Kleinman et al. (2000). Such 'change points' in the behavior of WEP relative to DPS occur because of the saturation of potential P binding sites, resulting in remaining P being held more loosely (Pierzynski et al., 2005). High enough DPS values can lead to leaching. In sandy soils significant P leaching has been observed with DPS (adjusting for  $\alpha=1$ )  $> 45\%$  (Nelson et al., 2005) and  $> 32\%$  (Siemens et al., 2008).

The identification of DPS-based change points of WEP or leachable P means that ratios of P to Fe and Al could be used to predict the potential for phosphorus release. Since change points in WEP slope vs. DPS occur in field soil material at as little as DPS = 12% and 18%, then field soils may require at least 5-10 Fe or Al atoms to reliably retain a single P atom.



In studies of mesocosms from peat fens, Zak et al. (2004), and Zak et al. (2010) report that pore water ratios of  $\text{Fe}/\text{P} > 3$  protected surface waters from high concentrations of P. The mechanism of this protection was the formation of a thin horizontal Fe concentration that formed at the boundary of Fe-oxidizing and –reducing conditions (Zak et al., 2004). The net upward movement of Fe from anaerobic to aerobic zones is referred to as ‘Fe pumping’ (Sah et al., 1989) and results in concentrations of poorly crystalline Fe (Maynard, 2009). Iron concentrations and diminished P concentrations above versus below the Fe were also observed by Young and Ross (2002) in an experiment involving mesocosms of field soil material. Such protection of surficial waters from subsurface waters in peat mesocosms with pore water  $\text{Fe}/\text{P} = 2.2$  was not observed by Surridge et al. (2007). Zak et al. (2010) report that peat  $\text{Fe}/\text{P} > 10$  are needed to produce pore water  $\text{Fe}/\text{P} > 3$ .

The studies of Zak et al. (2004), Zak et al. (2010), Surridge et al. (2007) and Young and Ross (2001) involved sampling floodwater and pore water in mesocosms where hydrology was static and therefore only diffusion and not mass flow was responsible for the movement of solutes. Hence a P-sorbing Fe lens could easily form due to the static nature of the experiments.

Concentrations of P-sorbing Fe have been observed in the field. Lenses similar to those observed by Zak (2004) and Young and Ross (2001) have been observed in the field in wetlands and have substantial P sorption capacity (Maynard et al., 2009). Concentrations of P-sorbing Fe(III) were found to occur in oxidizing macropores in a soil that featured micro-pore water that was reducing (Sade et al., 2010). These researchers observed that P in the ditch draining this soil was relatively low ( $< 0.08 \text{ mg P L}^{-1}$ ), These

researchers hypothesized that Fe and P, solubilized due to reductive dissolution in soil meso and micro pores, were retained by the formation of  $\text{Fe}(\text{OH})_3$  and subsequent P sorption in oxidizing soil macropores. Hence, systems more dynamic than mesocosms of stagnant-hydrology can form P barriers at the interface of Fe-oxidizing and –reducing conditions.

### **Mechanisms of P release – heterotrophy**

Organic matter stimulates heterotrophic microbial activity which is maximized under aerated conditions (Dyer, 2003). Under anaerobic conditions a less powerful electron sink must be utilized, resulting in diminished activity. As a result, saturated conditions often lead to the accumulation of organic materials that can be subjected to high rates of mineralization if aerated conditions re-establish. Hence the degradation of organic materials ('mineralization') in wetlands upon artificial drainage and the release of high amounts of nutrients, including soluble P, when wetland hydrology is restored (Zak et al., 2010). Longer periods of aeration between flooded conditions lead to increased release of soluble P upon flooding (Olila et al., 1997). Eutrophic conditions may also increase the rate of peat mineralization (Constanje et al., 2006).

Temperature increases microbial activity above a biological zero (Boulêtreau et al., 2012; Vaughan et al., 2009; Rabenhorst, 2005,), but higher temperatures (>45 °C) reduce microbial activity (Liu et al., 2011a). Hence temperature may also positively affect mineralization at typical environmental temperatures.

## **Morphology of primary ditches**

Soils may be identified through the formation of pedogenic horizons or through the ability to support plants (Soil Survey Staff, 2010). In the MACP, soils have been observed in field ditches that had been undredged for at least seven years (Vaughan et al., 2008). These soils were described as Sulfidic, Aeric, Humaqueptic, and Typic Endoaquents, Humaqueptic and Typic Psammaquents and Haplic Sulfaquents (Vaughan et al., 2008). As such they contained A and C horizons and frequently experienced saturation due to freely draining groundwater rise.

Field ditch A horizons are formed from the autochthonous accumulation of organic matter often mixed with mineral colluvial and alluvial mineral particles (Vaughan et al., 2008). In North Carolina sediment deposition occurs most reliably during the growing season, when plants enhance hydraulic roughness (Lecce et al., 2006). Under vegetation ditch banks are stable and do not contribute large amounts of sediment, but gullies, connecting ditches to fields, are significant sediment sources (Lecce et al., 2006). As zones of mixing of OC and mineral material, A horizons are zones of heightened OC content and more strongly develop structure when not constantly inundated (Vaughan et al., 2008). Field ditch soils have also been observed to be high in oxalate- (Vaughan et al., 2007a) and dithionite-citrate-extractable (Sallade and Sims, 1997a) Fe and Al, with higher Fe content than adjacent field soils (Vaughan et al., 2007b). This Fe accumulation relative to field soils suggests groundwater input of Fe to ditches (Vaughan et al., 2007a).

As observed by Vaughan et al. (2007b), ditch O horizons are also highest in Fe, with average values of Fe and P dropping precipitously from O to A horizons and below

(Vaughan et al., 2007b). Such a distribution could result from the retention of Fe(III) and Fe-sorbed P at the ditch surface. Ditch O and A horizons were found by Vaughan et al. (2007b) to have DPS values roughly similar to change points in the solubility of sorbed P identified by other researchers (Butler and Coale, 2005). These DPS values were also elevated above those of ditch C horizons.

### **Water quality of ditch effluent**

Water quality in undredged ditches in the MACP has been documented by Kleinman et al. (2007), who documented 5 years of annualized concentrations, loads and losses of P from the same two ditches at the UMES farm which were the subject of study in chapter four of this dissertation. Over the five year monitoring span these ditches averaged between 0.07 and 1.23 mg DRP (analogous to dissolved inorganic P) L<sup>-1</sup>. These concentrations appear roughly correlated to ditch flow (Kleinman et al., 2007). For one year of the study concentrations from several more ditches at the UMES farm were reported with concentrations ranging from 0.25 to 4.05 mg DRP L<sup>-1</sup>. Since the threshold for eutrophication in freshwater is commonly cited as 0.02 or 0.03 mg dissolved inorganic P L<sup>-1</sup> (Dodds et al., 1997; Dodds et al., 1998), these ditches on average would be contributing to eutrophication downstream if these concentrations were exported. While for years of little flow average ditch exports may be as small as 0.2 kg DRP, years of high flow featured DRP > 18.9 kg. Therefore, while years of low flow can feature very little export, concentrations in the ditch water itself are eutrophic. The ditches of the study of Kleinman et al. (2007), were undredged and unmodified. Eutrophic conditions in

these ditches and the potential for large P exports from these ditches beg the question of how ditch management options might affect P retention and transport.

## **Management interventions for primary ditches**

### **Dredging and mowing**

Dredging and mowing are performed to restore hydraulic conductivity to ditches. Mowing controls woody vegetation that in time might divert ditch flow and undermine ditch banks. Dredging lowers the overall surface of the ditch, allowing the ditch to intercept the water table at lower depths. On the Eastern Shore of Maryland mowing is performed annually whereas dredging are performed decadal; in North Carolina dredging may be performed biennially (Lecce et al., 2006). A dredging operation is alternatively known as a 'cleanout'.

Dredging of primary ditches remove ditch O and A horizons and often portions of the C horizon. As a result dredging removes the portion of ditch soil highest in P, and P-sorbing Fe and Al. In fluvaria these pre-dredge materials remove more P from high-P water, and release more P to low-P water than materials remaining after dredging (Shigaki et al., 2008). Fluvarium studies of materials from secondary 'collection' ditches of the Midwest offer different results; in these studies (Smith et al. 2006, Smith et al. 2007) pre-dredge sediments sorb more P (from high P water) but release less (to low P water), in contrast to Shigaki et al. (2008). Perhaps accounting for this discrepancy is DPS; dredging lowered DPS for Shigaki et al. (2008), but raised DPS for the materials studied by Smith et al. (2006) and Smith et al. (2007). Another explanation may be the higher OM content of the pre-cleanout Coastal Plain soils; abundant OM-metal

complexes in Coastal Plain soils, with lower binding energies for P, may represent large pools for P sorption, but only when P is highly abundant. Alternatively, higher OM contents may also lead to the partial reduction of ferrihydrite and the creation of high-capacity but low binding energy Fe gels similar to those of Patrick and Khalid (1974).

Dredging appears to have long-term benefits with respect to P transport.

Monitoring of Midwestern collection ditches before and after dredging was performed by Smith and Huang (2010). They found that nutrient exports from reaches dredged in the previous twelve months were diminished relative to undredged reaches. These authors attributed this difference to oxidation of newly exposed sediments, heightened sedimentation rates and processes related to colonizing biota. These results are extremely promising from the perspective of lowering ditch P throughput, but as discussed above this study applies to ditches quite different from MACP field ditches

Most dredging studies have employed disrupted soil material in non-redox controlled fluvial systems (Shigaki et al., 2008; Smith et al., 2007; Smith et al. 2006) and most have concerned Midwestern collection ditches (Smith and Huang, 2010; Smith et al., 2007; Smith et al. 2006) which are substantially different, as discussed above, from field ditches. Since much of the work regarding dredging has occurred in a system different from field ditches of the MACP, and since the one dredging study in the MACP employed disrupted soil material in a fluvial system, a field study of the effects of dredging in the MACP fills a major gap in our ability to understand the behavior of MACP field ditches upon dredging.

## **Controlled drainage**

Controlled drainage (also known as ‘water control’) has been discussed above. While causing greater P concentrations in soil pore water (Amatya et al., 1998) and therefore the specter of heightened P release from ditches (Sharpley et al., 2007), controlled drainage generally reduces P loads from ditches (Ramoska et al., 2011; Wesstrom et al., 2001; Wesstrom and Messing, 2007; Wahba et al., 2001) through the action of reduced outflow volume (Evans et al., 1995). In a context of free drainage resident groundwater at the UMES site was found to have P levels drop to negligible levels within 15 days after rainfall (Vadas et al., 2007). Hence another mechanism, perhaps operational in controlled drainage, would be increased residency time of groundwater in soils and the slow P sorption by soils that may accompany it.

Because under controlled drainage ditches are saturated more constantly than when freely draining, controlled drainage is likely to manipulate the redox state of ditch soils. Because redox features, and therefore loci of redox phenomena, are structure dependent it makes sense to study soil with its structure undisrupted. Hence, in contrast to the many studies of the effect of redox on disrupted soil materials (Sah et al., 1989; Sah and Mikkelsen, 1986a; Sah and Mikkelsen, 1986b) a study of the impact of redox on intact soils may shed more realistic results regarding P sorption/desorption behavior and the response of P-sorbing Fe, which is redox sensitive, and highly present in ditch soils in the MACP (Vaughan et al., 2007a; Vaughan et al., 2007b).

## **Dissertation justification and objectives**

### **The limitations of previous studies**

In the MACP previous studies have mapped the properties of the surficial layers of a drainage ditch network (Vaughan et al., 2007a), have described the vertical arrangement of P in the soils of that network (Vaughan et al., 2007b), and have described the morphology and USDA Soil Taxonomy classification of ditch soils (Vaughan et al., 2008). Therefore, while MACP ditch pedology has been inspected, the water quality implications of MACP ditch pedology have not. Other studies have inspected the P transport functioning of ditch materials in soil slurries (Sallade and Sims, 1997a; Sallade and Sims, 1997b; Sah et al., 1989; Sah and Mikkelsen, 1986a; Sah and Mikkelsen, 1986b).

In both the Midwest and Coastal Plain (Shigaki et al., 2008; Sharpely et al., 2007) fluvaria have been used to inspect the P sorption and release of pre- and post-dredged soil materials. In these studies these soil materials have been disrupted, and therefore lack their original structure and arrangement of horizons as would be the case with ditches in the Coastal Plain (Vaughan et al., 2008). Therefore there is the need to study the effects of dredging on P transport from the perspective of intact ditch soil since soil architecture puts the chemical processes studied in soil material in context. This is especially important in light of the redox fluctuations that ditch soils undergo upon drainage or saturation (Needelman et al. 2007b), because redox phenomena in soils interact with structure. The impact of reducing conditions on P cycling has been studied, but many of these studies utilize disrupted materials (Sallade and Sims, 1997b; Sah et al., 1989; Sah



and Mikkelsen, 1986a; Sah and Mikkelsen, 1986b). Studies of the effects of reducing conditions on P mobility using intact soil have not been performed on soils from ditches, but rather on soils from wetlands (Zak et al., 2010; Surridge et al., 2007; Zak et al., 2004; Young and Ross, 2001). These studies feature statically imposed hydrologies, or hydrologies that do not allow inference to ditch systems, because the evacuation of groundwater out of ditch soils is not included in these studies. Therefore there is the need to 1) study the effects of reducing conditions on P transport in undisrupted ditch soils, 2) to do so in the context of the MACP, and 3) to do so using a hydrology that mimics that of ditches. The study of reducing conditions in ditches or simulated ditch systems is likely to shed insight into the behavior of ditches under controlled drainage.

While field studies of P transport of ditches have been performed they have inspected the effect of dredging on Midwest collection ditches (Smith and Huang, 2010), or quantified annual trends in P transport from the MACP (Kleinman et al., 2007). But these studies have not offered insight into the environmental variables that control processes (e.g. mineralization, reductive dissolution of P-sorbed Fe) that may give rise to changes in P exports. In addition no field study on the effects of dredging has been reported for the MACP.

## **Justification**

To sum up the specifically ditch-related material from the MACP in this introductory chapter: 1) ditch materials have been described as soils (Vaughan et al., 2008), 2) ditch soils experience a sharp downward gradient in Fe and P content from surficial layers to layers below (Vaughan et al. 2007b), 3) materials from dredged and

undredged ditches respond differently to solutions of different P concentration, with materials from undredged ditches tending to sorb more P from high-P water and release more P to low-P water than materials from dredged ditches (Shigaki et al., 2008). 4) Ditch soils become Fe-reducing when saturated (Needelman et al., 2007). 5) Iron-reducing environments induce P solubility in ditch soil material (Sallade and Sims, 1997b), and 6) ditches are exporting large loads of P at concentrations high enough to induce eutrophication (Kleinman et al., 2007).

By the beginning of my dissertation research, there was not a study that put these different phenomena together into a cohesive whole. With the exception of variable P concentrations in test solutions, my dissertation, involving a controlled experiment and a (largely) observational study seeks to integrate these different phenomena into an interpretable unit.

In this dissertation I describe two studies which further develop our understanding of the role of ditch soils, ditch management, and environmental conditions in P export and retention from ditches. Noting that previous studies of P release or retention (Shigaki et al., 2007; Sallade and Sims 1997b) have used ditch soil material but not intact ditch soils in experimental units, in this dissertation measurements will be taken in the lab or in the field from experimental units in which the structure of ditch soil horizons has been unaltered. The study of ditch soils will add realism unavailable in studies of ditch soil materials; whereas the latter are studies of chemical processes, the use of intact soils allows for studies of chemical processes in the context of soil structure. Redox phenomena interact with structure, and redox phenomena are a key factor in ditch P retention/release.

In addition a field study of in-ditch process related to P had not been performed in the MACP.

### **Dissertation objectives**

My objectives in this dissertation were: 1) to gain a soil-profile based understanding of the interactions of P with ditches, 2) to understand the effects of and dredging on ditch morphology and P-transport functioning, 3) to measure the effects of saturation on ditch morphology and P-transport functioning, and create hypotheses regarding the effects of controlled drainage on P-transport functioning, 4) to see if ditch P sorption capacity could be enhanced through manipulation of autochthonous ditch materials (soil and water), and 5) to explore the importance of temperature and reducing conditions on ditch P concentrations.

### **Experimental strategy**

To achieve these objectives two research projects were undertaken. The first was an experiment involving mesocosms. Mesocosms were selected as experimental units instead of fluvial or structureless sediment sample batch studies because unlike these other methods mesocosms allow an intact soil body to be brought to a controlled setting. I did not wish to pack mesocosms with material, even if trying to reproduce native-soil bulk density and use material from different horizons packed as such. To use disrupted material would be to exchange the geometry of soil macropores from a pedogenically derived state to one which did not reflect actual pore architecture in the field. Studying undisrupted soil keeps the P-reactive soil coatings of pore linings and ped surfaces as surficial features, and allows experimental units to better reflect field processes. While

use of intact soils was done at the cost of added variability, it reflected variability found in the field and offered an expanded scope of inference beyond packed columns.

Mesocosms are well suited to soil and hydrologic interventions, including the use of a dynamic vertical hydrology as (roughly speaking) occurs in the field. Mesocosms allowed the pursuit a profile-based understanding of P transport (my first objective). Mesocosms were taken from a ditch before and after dredging (Objective 2). Further soil and hydrology manipulations were then imposed on the mesocosms. The purpose of the additional hydrology manipulations was to observe the outcomes of different hydrologies on ditch mesocosm effluent P and ditch soil P as well as the impact on P-sorbing soil Al and Fe. These manipulations were not intended to simulate ditch hydrology with its sudden rises and gradual falls, but rather created end-member regimes to highlight the effects of processes related to hydrology and aeration. The hydrologic treatments were: saturation, lack of saturation, and a hybrid hydrology with alternating periods of saturation and lack of saturation. These hydrology regimes were then punctuated with periods of simulated groundwater rise in order to inspect the effect of saturation or lack thereof on vertical P transport through the profile (Objective 3). The purpose of the additional pedology manipulations was to observe the effects of different surficial states of ditch soil on mesocosms effluent P in which materials endemic to ditches (O horizons and mucky-mineral materials) were manipulated (Objective 4). Through the manipulation of autochthonous materials (soil and hydrology) the study was intended to shed insight into the ability of such manipulations to control P cycling. Results of this experiment are shared in chapters two and three.

The second study was observational in nature. The purpose of this study was to relate ditch environmental variables to variations in ditch P effluent (Objective 5). In this study logged data (ditch surface temperature, soil Eh and groundwater depth) was logged and related to ditch effluent P concentrations. Because the monitoring of such variables is an intensive processes I chose to study a limited number (n=2) of ditches. By measuring environmental variables leading up to a rain and ditch flow event, this study was intended to shed light into possible mechanisms of ditch P release in the field. Results of this experiment are shared in chapter 4.

## **Chapter 2: The effect of soil and hydrologic manipulation on phosphorus storage and release in field ditch mesocosms**

### **Introduction**

Low relief landscapes often require artificial drainage to support agriculture. In agricultural landscapes where field soils are coarse textured and have sufficient hydraulic conductivity, field-scale drainage is often supplied by open ditches. These landscapes are common in Coastal Plain regions worldwide. Field ditches are of interest for their role in P transport and storage (Needelman et al., 2007a), because eutrophication is a problem in many regions (e.g., Boesch et al., 2001; Rabalais et al., 2001). Specific emphasis has been placed on understanding how common ditch management practices such as dredging and controlled drainage affect the fate of P in ditches (Sharpley et al., 2007; Smith and Pappas 2007; Shigaki et al., 2008).

A common ditch management practice is dredging, which removes accumulated materials so that rising groundwater may be intercepted at a lower depth. In MACP ditches the uppermost of these materials are O and A horizons (Vaughan et al., 2008) in which paracrystalline iron (Fe) and aluminum (Al) has accumulated in steep gradients at the surface (Vaughan et al., 2007b; Table 3.2). Paracrystalline Fe is favored in zones of frequent redox changes and organic matter accumulation (Schwertmann, 1991) such as ditches (Schwertmann 1966; Needelman et al. 2007b). Because these paracrystalline

oxides have large surface areas (Rhoton and Bingham, 2005; Richardson, 1985), but diminished binding energies relative to more crystalline materials, uppermost ditch surface horizons possess a substantial capacity to remove P from, or release P to oxidized fluvarium waters (Sharpley et al., 2007; Shigaki et al., 2008) depending on initial aqueous P concentrations. Dredging removes horizons concentrated in paracrystalline oxides and the material remaining in ditches after dredging has been found to release and sorb less P (Shigaki et al., 2008). In a field study of Midwestern collection ditches Smith and Huang (2010) found that lower P loads persisted in dredged reaches than in those of undredged reaches for the first year after dredging.

A second common ditch management practice is controlled drainage in which drainage is restricted by outlet dams (Gilliam and Skaggs 1986) or staggered weirs (Kroger et al., 2008) to retain sediments, promote denitrification, and decrease export of dissolved constituents by mechanically limiting flow (Evans et al., 1995). Needelman et al. (2007b) and Sharpley et al. (2007) suggested that the reduced flow of controlled drainage may prompt the reductive dissolution of Fe and release of Fe-bound P.

Ditch soils contain thin (<5cm) surficial horizons that are highly concentrated in OM, P, Al and Fe relative to horizons below (Vaughan et al., 2007b). While these horizons have been described (Vaughan et al., 2008), their role in ditch P cycling relative to other soil horizons has not been explored.

Across-factorial laboratory mesocosm experiment was conducted in which soil and hydrologic states of intact ditch mesocosms were manipulated. Mesocosms were selected as experimental units because they allowed for intact soils, to be easily pedologically and hydrologically manipulated in a controlled setting, and because the

vertical geometry of them was well suited to study the vertical rise of groundwater. The objectives of these manipulations were to inspect the 1) effect of dredging on P retention in and P release from intact ditch soil profiles, 2) influence of hydrology on P retention in and P release from intact ditch profiles, 3) influence of hydrology on ditch P mineralogy, and 4) importance of ditch surficial materials to P cycling.

Mesocosms were collected from a drainage ditch before and after dredging (Objective 1). Additional soil manipulations were performed on mesocosms taken before dredging to inspect the functioning of added or removed surficial material (Objective 4). Mesocosms were subjected to three hydrologies (saturation, moist but drained, and a hydrology which alternated between the two states which were end members in a continuum of possible hydrologies). The purpose of these treatments was to observe the effect of hydrology on soil Fe and Al (Objective 3), and on soil and pore water P (Objective 2). These hydrologies were not intended to mimic specific ditch types or management options, but rather to explore the behavior of ditch soils under hydrologic extremes. A salt solution mimicking the contents of groundwater at the UMES site was periodically input through the mesocosms to facilitate examination of the P contents of the effluent pore water (Objective 2). Upon the end of the experiment mesocosms were opened, horizons identified and acid ammonium oxalate extractions performed in order to measure the paracrystalline and OM-associated P, Fe and Al present (Objective 3). My experiment was designed to investigate general mechanisms operating in ditch soils, we therefore gathered the mesocosms from a single section within one ditch in order to minimize inter-mesocosm variability rather than collecting mesocosms from multiple ditches in order to have a broad inference space.



We hypothesized that: 1) (similar to Shigaki et al., 2008) mesocosms gathered after dredging would sorb and release less P than undredged mesocosms, 2) saturated, static conditions in mesocosms would result in Fe-reducing conditions (Needelman et al., 2007b) and the release of Fe-associated P (Sallade and Sims, 1997b), 3) alternating periods of Fe-oxidizing and -reducing conditions in mesocosms would increase  $Fe_{ox}$  relative to control (due to the tendency of alternating cycles of oxidizing and reducing conditions to transform more crystalline Fe species to paracrystalline Fe), and 4) ditch surficial materials would play a role disproportionate to their volume or mass in the retention or release of P, since ditch surficial materials were found by Vaughan et al. (2007b) to be high in P. My experiment was intended to shed light on the efficacy of manipulating hydrology and native ditch materials for the purposes of encouraging P retention in ditch soils.

## **Materials and Methods**

### **Study site**

Intact cylindrical mesocosms of ditch soil (Vaughan et al., 2008) were obtained from the University of Maryland Eastern Shore (UMES) Research Farm (38°12'22"N, 75°40'35"W). The specific ditch had been the subject of previous investigations, alternatively referred to as 'Ditch 1' (Kleinman et al., 2007; Shigaki et al., 2008; Church et al., 2010), and 'Dx1' (Vaughan et al., 2008, 2007a, 2007b). Prior to field work in 2006, the ditch had been undredged for at least ten years. Further knowledge regarding upkeep dredging and original dredging of the ditch is unknown (Vaughan et al., 2008). Since the most recent cleanout the ditch had accumulated between 10 and 40 cm of loam- and silt-

loam-textured materials. These horizons were described by Vaughan et al. (2008) as mucky A, non-mucky-modified A, Ag, and O horizons. The corresponding ditch soils were classified as Aerlic and Humaqueptic Endoaquents (Vaughan et al., 2008). Soils of fields surrounding the ditches, and forming the watershed of the ditches, are mapped as predominantly Quindocqua (Fine-loamy, mixed, active, mesic Typic Endoaquults), Othello (Fine-silty, mixed, active, mesic Typic Endoaquults) and similar soils distinguished by deltaic and marine sediments overlain by 20<sup>+</sup>cm of eolian materials (Soil Survey Staff, 2011). The underlying marine sediments contain many layers of different textures roughly parallel to the surface; this likely creates many parallel, vertically stacked aquitards.

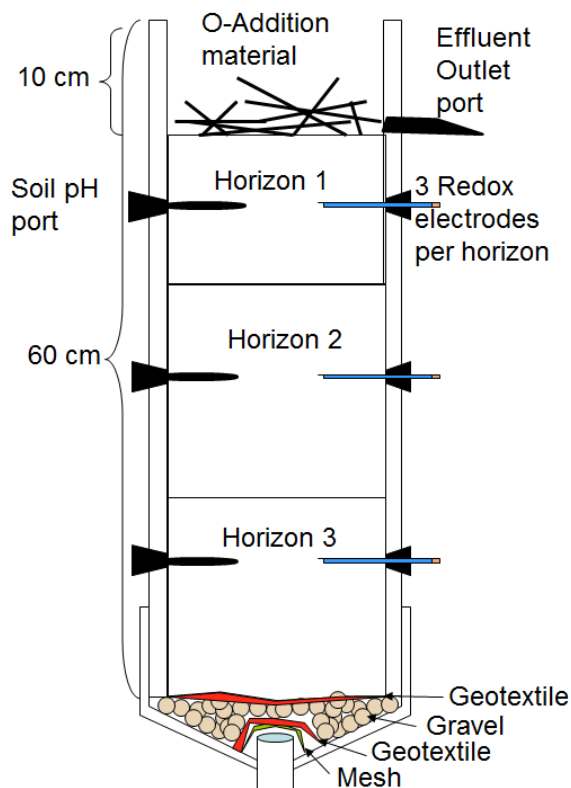
Previously, the farm had been a place of intensive broiler production for 20 years. Mehlich-3 P levels of field soils of 300 mg kg<sup>-1</sup> minimum (Kleinman et al., 2007), and averages above 500 mg kg<sup>-1</sup> have been observed at the UMES farm site (Vaughan et al., 2007a). These values are roughly one order of magnitude above values recommended for crop production in the region (Pennsylvania State University, 2011).

### **Soil mesocosm collection**

In June of 2006, mesocosms (15-cm wide x 40-cm deep) were collected from a 40-m reach near the ditch outlet. Mesocosms were taken from the same ditch and as close as possible to one another in order to minimize variability between the eventual experimental units, since I was interested in resolving responses to ditch soil processes without the heterogeneity that sampling from many ditches would have afforded. The 40-m reach used for mesocosm gathering was believed at the time to be free of a restricting

layer that had been observed elsewhere in auger borings and a nearby field soil pit. Fifteen-cm internal diameter PVC tubes (sharpened at the bottom) were vertically driven into the soil to a depth of 40 cm and removed laterally. Prior to dredging, 83 'Undredged' mesocosms were extracted. During the extraction of Undredged mesocosms, some surface soil compaction was observed (ratio of mesocosm soil length to original soil depth  $\sim 0.95$ ), with most of that compaction likely occurring in upper horizons.

At the University of Maryland Research Greenhouse Complex the mesocosms extracted before ditch dredging were air dried (27-33 C) in order to shrink the soil such that paraffin could be applied as deep as possible between the soil and PVC tube to preclude bypass flow. Although this drying could be expected to change some of the chemistry of the mesocosms (Bartlett and James, 1980), particularly by making P more labile in the short term (Xu et al., 2011), the need to curtail bypass flow was considered essential in order to be able to reliably gather mesocosm pore water. Despite the attempt to scout a ditch reach without a restricting layer, a restricting layer was found in the C horizons of many mesocosms, and therefore C horizons were removed from all Undredged mesocosms. The shortened mesocosms, containing only O and A materials and extending between 18 and 40 cm in depth, were fitted with geotextile fabric, acid-washed gravel (to remove P-sorbing Fe and Al coatings) and a plastic drain screen such that the soil material received adequate support upon cementing of the PVC end cap (Figure 2.1). To allow simulated ground water rise and drainage, a hole was drilled through each PVC end cap and a threaded port was added to which 0.95-cm diameter tubing could be either attached (as a source of input water from 1-L Mariotte bottles), or detached (to permit free drainage).



**Figure 2.1. Mesocosm construction.** A subset (see Table 2.2) of mesocosms was instrumented with redox electrodes and pore water samplers. Mesocosms were not packed but contained the horization of the micro site from which they were gathered. Typical horization of ditch soils is roughly provided by Table 3.2.

Three weeks after the initial mesocosms were gathered, the ditch was dredged.

Two weeks after dredging, six additional ‘Dredged’ mesocosms were extracted.

Unlike mesocosms gathered before dredging, which originally contained O, A, and C materials, Dredged mesocosms nearly exclusively contained ditch C material (Table 3.2). To avoid the restricting layer found in the C material of Undredged mesocosms, Dredged mesocosms were gathered 160 m upstream within the same ditch. Handling of Dredged mesocosms after extraction was identical to Undredged mesocosms except that Dredged mesocosms contained no restricting layer and therefore were not shortened. Fewer Dredged mesocosms were gathered since differences between them and

Undredged mesocosms were expected to be large, and smaller replication was considered adequate for sufficient statistical power.

### **Simulated groundwater**

Periodically mesocosms were flooded from below with simulated groundwater such that effluent, emerging from the top of the mesocosm, could be collected and analyzed for P. The rising trajectory of input water in my mesocosms reflected the rise of groundwater which occurs in ditches (Vadas et al., 2007), but my simulated groundwater additions were not intended to mimic the ditch hydrograph. Simulated groundwater was created from a combination of inorganic salts (Table 2.1).

Constituents of the simulated groundwater were determined by averaging values from shallow wells deployed by Vadas et al. (2007) in proximity to the ditch. The P concentration resulting from this analysis was more than an order of magnitude above concentrations ( $0.03 \text{ mg P L}^{-1}$ ) commonly cited as eutrophication thresholds (Dodds et al., 1997; Dodds et al., 1998).

**Table 2.1. Constituents of simulated groundwater used as input water during upwellings.**

<b>Constituent</b>	<b>mg L<sup>-1</sup></b>	<b>mmol L<sup>-1</sup></b>
<b>SO<sub>4</sub>-S</b>	<b>261.5</b>	<b>2.72</b>
<b>Cl</b>	<b>19.1</b>	<b>0.53</b>
<b>NO<sub>3</sub>-N</b>	<b>16.4</b>	<b>0.26</b>
<b>PO<sub>4</sub>-P</b>	<b>0.48</b>	<b>0.005</b>
<b>Na</b>	<b>35.7</b>	<b>1.55</b>
<b>Mg</b>	<b>34.5</b>	<b>1.42</b>
<b>Ca</b>	<b>34.8</b>	<b>0.87</b>
<b>K</b>	<b>4.8</b>	<b>0.12</b>

Simulated groundwater was delivered to the bottom of each mesocosm using tubing connected to 1-L Mariotte bottles. Each bottle was positioned so that a hydraulic head of 40 cm existed relative to the top of the mesocosm soil, where a drainage hole had been installed (Figure 2.1). This hydraulic head was found to provide conductivities between 0.25 and 0.02 L min<sup>-1</sup>. I speculate that my mesocosms were not of sufficient cross section to integrate all of the variability of hydraulic conductivity present in the ditch reach where mesocosms were gathered.

## **Mesocosm experiments**

### **Experimental design**

The mesocosm study assessed the effects of soil manipulations and hydraulic conditions on P cycling within ditch soils. The effect of dredging (Objective 1) was evaluated using mesocosms gathered from a ditch before ('Undredged') and after ('Dredged') a dredging event. The importance of ditch surficial horizons (Objective 4) was inspected through the addition ('O-Addition') or removal ('Surficial Removal') of ditch surficial material from some Undredged mesocosms. Several Undredged mesocosms did not have surficial materials manipulated ('Control'). Under the Surficial Removal treatment the upper 2-cm of surface soil was removed. Under the O-Addition treatment 100-g (air dry) material was added to the existing mesocosm soil surface. O-Addition material was sourced from the ditch from which the mesocosms were extracted and was a mucky peat with 10% clay and 14.9% organic carbon. Oxalate-extractable Fe, Al and P were 370, 29 and 25 mmol kg<sup>-1</sup>, respectively in the O-Addition material. For the Surficial Removal treatment the upper 2 cm of materials was removed because this was

approximately the average depth of surface horizons (usually O and mucky A horizons) observed in the field up on mesocosm extraction. Upon opening of mesocosms at the end of the experiment surficial mesocosm horizons were found to be slightly deeper (Table 3.2).

The four soil treatments were placed in a crossed factorial design (Table 2.2) with three hydraulic treatments. ‘Saturated’ mesocosms experienced constant saturation throughout the experiment.. ‘Drained’ mesocosms were allowed to freely drain throughout the experiment except during periods of simulated groundwater rise. ‘Alternating’ hydrology mesocosms experienced both drained and saturated conditions (Table 2.2).

**Table 2.2. Treatment structure of experiment and replication of mesocosms (and Eh and pore water samplers used for pore water pH).**

Soil Treatments†		Hydraulic Treatments‡		
		Drained	Saturated	Alternating
		----- n -----		
Un- Dredged	Surf. Removal	6(2)§	6(2)	6(2)
	Control	6(2)	6(2)	6(2)
	O-Addition	6(2)	6(2)	6(2)
	Dredged	2(1)	2(1)	2(1)

† ‘Pre-dredge’ ditch mesocosms were gathered before dredging; ‘O-Addition’ 100 g Organic materials were surficially added to mesocosms; ‘Surf. Removal’ 2-cm of surficial materials was surficially removed from mesocosms; ‘Dredged’ ditch mesocosms were gathered from the same ditch after dredging.

‡ ‘Saturated’ mesocosms were saturated between upwellings of simulated groundwater; ‘Drained’ mesocosms were drained between upwellings of simulated groundwater;

‘Alternating’ mesocosms were drained after odd numbered simulated groundwater rise events.

§ Number not in parentheses gives number of experimental units allocated to the indicated treatment.

Numbers in parentheses give the number of replicates of that treatment instrumented with platinum-tipped electrodes and pore water samplers. Pore water samplers were used to find pH of mesocosm pore water.

These hydrologic treatments were designed to span the diversity of hydrologies that ditches experience in the field. As such they were expected to shed insight into the

effects of hydrology on mineralogy (Objective 3) and soil effluent P (Objective 2).

Mesocosms were randomly assigned to treatments and bench locations shaded from the sun in a climate-controlled greenhouse space at the University of Maryland Research Greenhouse Complex. Greenhouse temperatures ranged from 10 °C during winter to 32 °C in summer.

### **Simulated groundwater manipulations**

Prior to the start ('Pre-experiment'; Table 2.3) of the experiment all mesocosms were in a freely draining but moistened state. The experiment started with the input of water to each mesocosm from the bottom ('Upwelling/effluent collection #1'; Table 2.3). Effluent was collected upon its emergence from the mesocosm top . While there were three overall experimental treatments for hydrology (Saturated, Drained, Alternating; Table 2.2, Table 2.3), there were at any time only two temporary hydrology states (saturated, drained; Table 2.3) to which a mesocosm could be subjected.

At the end of the first upwelling period, 'Drained' and 'Alternating' treatments were drained, though to these units, throughout 'Equilibration period 1', additional distilled water was added so that the upper horizon of the mesocosms did not become air dry. Units assigned to 'Saturated' hydrology treatments were not drained, but distilled water (to avoid confounding average ionic strength with hydraulic treatment) was added to the tops of mesocosms to maintain 10 cm of floodwater at the top of the mesocosm.



**Table 2.3. Experimental timeline of static hydrologic periods and ‘upwellings’ of simulated groundwater rise in which mesocosm effluent was gathered for analysis**

Overall Hydraulic Treatment†	Pre-experiment‡	Upwelling/effluent collection #1§	Interim period¶	Upwelling/effluent collection #2	Interim period	Upwelling/effluent collection #3	Interim period	Upwelling/effluent collection #4	Interim period	Upwelling/effluent collection #5
	Temporary state#		73 days		264 days		20 days		27 days	
			Temp. State		Temp. state		Temp. state		Temp. state	
<b>Drained</b>	<b>drain.</b>		<b>drain.</b>		<b>drain.</b>		<b>drain.</b>		<b>drain.</b>	
<b>Saturated</b>	<b>drain.</b>		<b>sat.</b>		<b>sat.</b>		<b>sat.</b>		<b>sat.</b>	
<b>Alternating</b>	<b>drain.</b>		<b>drain.</b>		<b>sat.</b>		<b>drain.</b>		<b>sat.</b>	

†‘Drained’ mesocosms were drained following each ‘upwelling event’; ‘Saturated’ mesocosms were held saturated throughout the experiment; ‘Alternating’ mesocosm were drained or remained saturated after an upwelling in a cyclic fashion.

‡Before the first upwelling all mesocosms were at field capacity, but unsaturated.

§Experiment consisted of five upwellings in which simulated groundwater (Table 2.1) were added to the bottom of each mesocosm (1 L mesocosm<sup>-1</sup> day<sup>-1</sup>) and effluent was collected from the top for analysis. This upward movement of input water was meant to simulate groundwater rise through the ditch soil.

¶Between upwellings, interim periods occurred in which a mesocosm was held either in a drained or saturated ‘temporary state’.

#‘Temporary state’ gives the hydrology that mesocosms experience at any particular time. ‘D’ indicates a drained state (held near field capacity); ‘S’ indicates a saturated state in which mesocosms were inundated with water such that 10 cm of free water persisted above the soil surface.

The end of the first equilibration was followed by a second period of simulated groundwater rise (Table 2.3). At the end of this second upwelling, Drained units were drained, but Saturated and Alternating hydrology treatment mesocosms were not. Further application of hydrology is described in Table 2.3. While simulated groundwater rise was originally intended to occur regularly, complications regarding effluent water analysis resulted in irregular periods between upwelling events (Table 2.3). This irregularity meant that the effects of environmental variables within the greenhouse space (e.g. temperature, which ranged from 10-32 °C) and interim period length could not be separated.

## **Measurement of pore water redox and pH**

A subset of mesocosms was outfitted per horizon with platinum electrodes (3 per horizon) and a single pore water sampler (macrorhizon, Soil Moisture Corp.) to measure soil oxidation reduction potential (ORP) and pH, respectively (Table 2.1). A subset of mesocosms was chosen in order to limit handling time associated with Eh and pH measurements, since so many experimental units (60) existed. Horizon locations within mesocosms were estimated based on observation of the mesocosm in the ditch profile prior to its lateral excavation. Measurements of ORP were made using calomel reference electrodes (Corning and Fisher brands), multimeters, and additional units (Rabenhorst, 2009) which provided increased internal resistance to make reliable, drift free, measurements. Due to the calomel reference, 244 mV was added to each ORP reading to account for the difference between the calomel and the standard hydrogen electrode ( $E_h$ ) (Stumm and Morgan, 1996).

## **Effluent collection and measurement**

Effluent water was collected in 1-L bottles. Time needed to gather 1-L of effluent water from each mesocosm ranged from 5 minutes to more than an hour. While effluent was dripping from mesocosm effluent ports into effluent bottles, effluent bottles were open to the air, and after the bottle had received 1 L of effluent a 30 mL volume of air-filled headspace remained between the surface of the effluent and the bottle closure. On the same day in which effluent was collected effluent bottle content was homogenized by shaking. After shaking, subsamples were collected with minimal headspace and refrigerated at 4° C. The first time mesocosms experienced saturation prior to an

upwelling was during upwelling #2 (Saturated mesocosms, Table 2.3). Effluent from these mesocosms was found to transform from clear to orange within an hour 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 upon re-entry to the oxidizing environment outside of the mesocosms. To keep effluent constituents soluble, for the final three upwellings a small amount of HCl (similar to Zak et al., 2009) was added to effluent collection bottles for all mesocosms such that the final effluent pH was approximately 2 (dilution was minimal). Acidification of samples was found not to interfere with colorimeter absorbance.

Effluent was measured for reactive P. Unfiltered samples were checked individually to ensure that no Tyndall effect indicating colloids was observed before colorimetry. If a Tyndall effect was observed, the sample was allowed to settle for several hours and the supernatant was processed; the sample was filtered with a 0.45- $\mu$ m filter when after several hours of settling time a Tyndall effect was still observed in the upper part of the settling vial. Such filtering occurred in approximately 5% of cases. The molybdenum blue method used was based on the autoanalyzer method of Kryskalla et al. (2003), modified to meet the purposes of a manually operated colorimeter ('Genesis 10', Thermo Fisher Scientific Corp., Waltham, MA).

This method of Kryskalla et al. (2003) features the following stocks and reagents: 1) sixty g of sodium lauryl sulfate (SLS) [ $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ , FW=288.38] dissolved in 240 mL of distilled water to form SLS stock; SLS reagent was formed by diluting SLS stock 1:10. 2). Three g of potassium antimony tartrate (PAT) [ $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ , FW=333.93] was dissolved in distilled water to form 1 L of PAT stock. 3) 4.5 g of

ascorbic acid ( $C_6H_8O_6$ , FW=176.1) was dissolved in distilled water to form 250 mL of ascorbic acid stock; this stock was diluted 1:6 to form ascorbic acid solution. 4) Acid molybdate-antimony reagent formed from 72 mL concentrated sulfuric acid, 7.7 g of ammonium molybdate [ $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ , FW=1235.86] and 50 mL of PAT stock diluted together to 1L of solution. To mix the acid molybdate-antimony reagent the sulfuric acid was first diluted to make a solution of approximately 700 mL before the ammonium molybdate and PAT stock were added before the final dilution.

In the modified method used in the work presented here: 1) 5 mL of sample was homogenized with 3 mL of SLS reagent, 2) equal parts acid-molybdate antimony and ascorbic acid reagents were homogenized together to form colorant, 3) 3 mL of colorant were homogenized with the 8 mL of sample/SLS solution, 4) between 15 min and 1 hr after mixing of the colorant and sample-containing solutions, the resulting solution was measured for absorbance at 880 nm. In the autoanalyzer method of Kryskalla et al. (2003) acid ammonium molybdate reagent is added to the sample-containing solution previous to the addition of ascorbic acid.

### **Mesocosm Soil Collection and Measurement**

Upon the end of the experiment, mesocosms were stored in a cold room (4° C) for an average time of one week (stay in cold room ranged from 2 days to 14 days) before opening with a table saw. Horizons were identified according to hand texturing and visual and material clues such as Munsell color, structure, and redox feature type and abundance and degree of humification of OM. Because mesocosm soils were to be assayed for total C and mineralogical, not biological or short-term volatile or moisture sensitive quantifies

such as N species, soils were air dried prior to further analysis. Horizon descriptions may be found in chapter 3.

Oxalate extractions (0.5-g soil:20-mL 0.2 M ammonium oxalate acidified with oxalic acid to pH=3; similar to Sah and Mikkelsen, 1986b) were performed in the dark on material from individual horizons using an end-over-end shaker operating at 20 rpm. Shaking time was two hours. After shaking samples were centrifuged 10 min at 10,000 rpm. Supernatants were analyzed for 1) oxalate-extractable P ( $P_{ox}$ ) using the molybdenum blue method of Kryskalla et al. (2003) modified for a manual colorimeter (see above) and for 2) oxalate-extractable Fe and Al ( $Fe_{ox}$  and  $Al_{ox}$ , respectively) on an atomic absorption flame spectrophotometer (AAAnalyst 200, Perkin-Elmer Corp., Waltham, Massachusetts). Organic carbon was measured (LECO CHN-2000 analyzer, LECO Corp., St. Joseph, Michigan) after grinding with an agate pestle such that ground material passed through a 0.6-mm sieve.

Horizons were distinguished by matrix color, redox feature color and abundance, consistence of organic matter, texture and organic carbon content. C horizons were distinguished from A and O horizons due to a lack of organic matter pigment. A and Ag and mucky A horizons were distinguished from O horizons using the formula: *Organic C (%) = 12 + clay\*0.1*, where 'clay' = the percent clay present (Soil Survey Staff, 2010). Soils lying above this line were designated as 'O' horizons (Soil Survey Staff, 2010). Mucky A horizons were distinguished as lying below the above line and above the following line: *Organic C (%) = 5 + clay\*0.1*. Soils lying below this latter line, with value 4 or more and chroma 2 or less according to the Munsell system, were designated as 'gleyed' A or C horizons ('Ag' and 'Cg' respectively) since their lack of brightness, or

gleying, was considered 'strong' (Schoeneberger et al., 2002) under these conditions, and was assumed to be due to Fe-reducing conditions predominating from time to time in ditch soil environments. Soils that were not C horizons or in any of the other above categories were designated as A horizons.

### **Data processing and analysis – Eh and pH**

To see if hydrology or soil treatments affect the redox state of experimental units Eh and pH values were averaged over time and over horizons so that a single response for Eh and pH was obtained per mesocosm. Lowermost horizons were dropped from the averaging because Drained and temporary drained state mesocosms often had perched water resident in their lowest horizons which produced low Eh values for these horizons. The lowermost horizons of mesocosms were generally the largest in volume and mass, and including them in the weighted averages was believed to artificially lower whole mesocosm Eh since it was not believed that lowermost horizons of mesocosms were reducing throughout. The effect of hydrology on Eh and pH between Dredged mesocosms could not be evaluated since replication=1 of Eh and pH measurements per treatment applied to Dredged mesocosms (Table 2.2). Eh and pH comparisons could be made between Dredged and Undredged treatments because three Dredged mesocosms were instrumented with Eh and pore water probes (Table 2.2). For statistical analyses the SAS (SAS 9.2, SAS Institute, Cary, NC) MIXED procedure was used. Hydraulic and soil treatments were considered fixed factors.

### **Data processing and analysis – mesocosm effluent P**

Effluent P data from the first five days of each upwelling were averaged over day of upwelling, so that units of analysis were not effluent P on individual days, but effluent P per upwelling period. My experimental interest lay with the experimental objectives: the effects of hydrology and soil manipulations and their interaction (if significant). My upwelling methodology was a means of implementing an upwelling, and did not model the rising and falling limbs of the hydrograph. By averaging over upwelling days for each individual upwelling event, the analysis remained focused on experimental objectives.

Effluent P exhibited a trend of increasing variance with increasing average response (data not shown), and therefore these data were log transformed prior to statistical analysis. Statistical analysis of these repeated measures data was performed with the SAS MIXED procedure. Inclusion of Alternating mesocosms in the model resulted in an over counting of experimental units ('pseudoreplication'; Hurlbert, 1984). As a result Alternating mesocosms were not included in analysis of effluent P. Tukey-adjusted multiple means comparison tests were performed if the overall F-test was significant.

### **Data processing and analysis – mesocosm horizons**

To estimate P sorption saturation, the Degree of Phosphorus Saturation (DPS) (= the molar ratio of  $P_{ox} [\alpha(Fe_{ox}+Al_{ox})]^{-1}$ ) was calculated for each soil horizon. I used  $\alpha$  ('saturation factor') = 1 as suggested by Beck et al. (2004). These researchers found that the use of a non unitary saturation factor lead to complexities in interpretation of P saturation of Fe and Al-based sorption capacity. The SAS REG procedure was used to

perform a stepwise regression of  $P_{ox}$  against  $Fe_{ox}$  and  $Al_{ox}$  in order to determine relative importance of Fe and Al to P sorption in soil horizons. In scatter plots of  $P_{ox}$  vs.  $Fe_{ox}$ ,  $Al_{ox}$  vs.  $Fe_{ox}$ , and  $P_{ox}$  vs.  $Al_{ox}$  changes in slope were observed. To test the validity of modeling with change points, simple linear models were compared with change point models. Change point models were developed according to the 'linear spline' model of Fitzmaurice et al. (2004) using the SAS MIXED procedure. Minimization of Aikake's 2<sup>nd</sup> order Information Criterion (AICC) (Burnham and Anderson, 2002) was used to determine optimal change points. AICC is a standard output of SAS PROC MIXED. When optimal change points were determined the AICC output of SAS PROC MIXED was used to compare linear spline to simple linear models. The regression model used for scatterplots of  $P_{ox}$ ,  $Fe_{ox}$  and  $Al_{ox}$  was the model that had a lower AICC. Differences in AICC greater than 15-20 are discussed by Anderson (2005) as indicating that the model with the higher AICC is highly implausible.

### **Data processing and analysis – soil response to treatment**

The SAS MIXED procedure was used to analyze soil data on the basis of whole mesocosms, since they were the experimental units. Whole mesocosm response was calculated from individual horizons by weighted averaging according to mass of horizon. Differing mesocosm mass, which resulted from the different depths of A horizons in each mesocosm, was controlled for in the analysis by using mesocosm mass as a covariate.



## **Data processing and analysis – estimating selected ditch and mesocosm P contents**

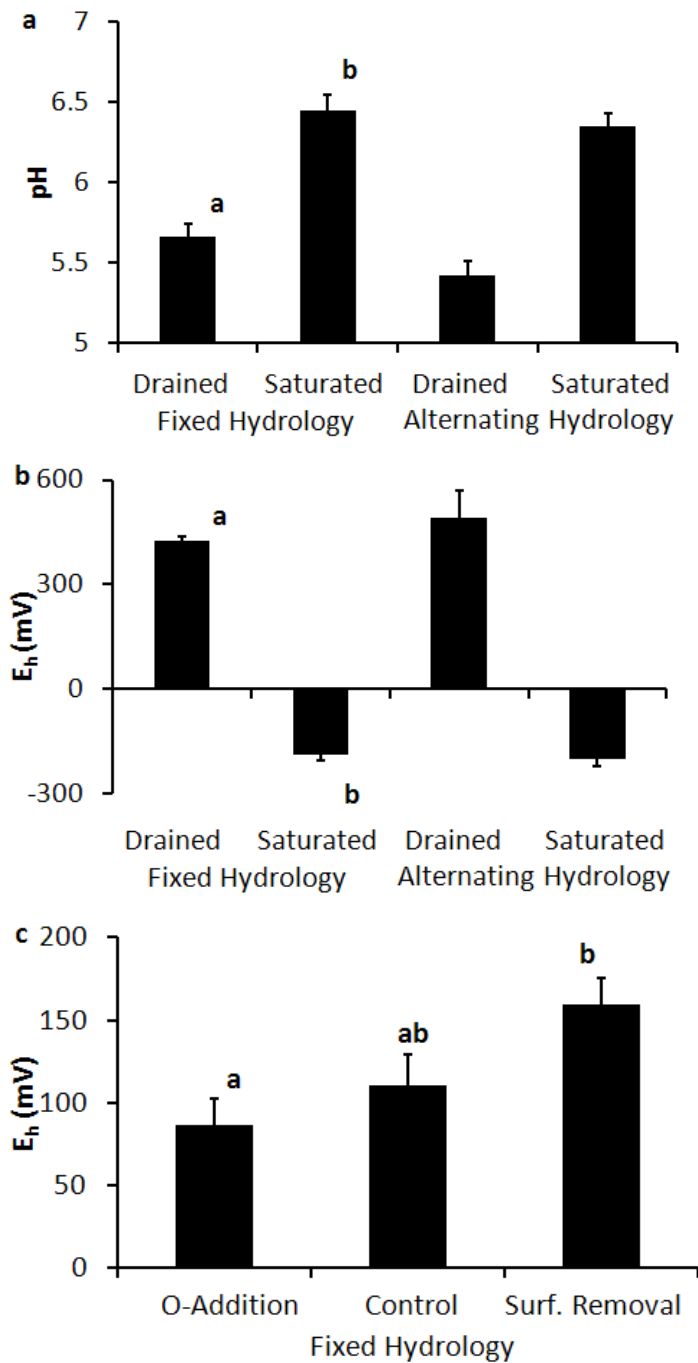
The total amount of  $P_{ox}$  contained in ditch O and A horizons was estimated from Control mesocosms. Ditch dimensions of length (300 m) and width (0.5 m) (Needelman et al. 2007b) were multiplied by average mesocosm depth (0.19 m) to determine ditch volume. Average mesocosm volume (3.46 L) and dry mass (3.62 kg) and  $P_{ox}$  content (18.74 mmol P kg<sup>-1</sup>) were then used to determine ditch  $P_{ox}$  content. Also estimated was the share of mesocosm profile depth and  $P_{ox}$  content represented by the uppermost original horizon before pedologic manipulation.

## **Results**

### **Eh and pH**

Dredged and Undredged mesocosms were not statistically different in their mean Eh ( $p>0.9$ ) and pH ( $p>0.5$ ) values. Among Undredged mesocosms, interactions between hydrology and soil treatments were not significant for Eh ( $p>0.5$ ) and pH ( $p>0.9$ ), but main effect differences did occur—Drained Undredged mesocosms had lower pH ( $p<0.001$ ) and higher Eh ( $p<0.0001$ ) than Saturated Undredged mesocosms (Fig. 2.2ab).

Among Undredged mesocosms, soil manipulations did not affect pH ( $p>0.6$ ), but Eh was affected ( $p<0.06$ )—Surficial Removal of soil material resulted in higher Eh ( $p<0.05$ ) than that of the O-Addition treatment (Fig. 2.2c).



**Figure 2.2. Undredged mesocosm response (a) pH and (b) redox potential (relative to the standard hydrogen electrode (E<sub>h</sub>)) response of Undredged mesocosms to hydrology and (c) E<sub>h</sub> response of Undredged mesocosms to soil treatments. Bars indicate standard error.**

## **Effluent P**

The hydrology X soil X time treatment interaction was not significant ( $p>0.09$ ) for effluent P, but the three two-way interactions among these factors were. These three two-way interactions are reported below. Raw and averaged raw data are available for view in the appendix (Fig. A.1; Fig. A.2).

### **Hydrology across upwelling events (time)**

At the start of the experiment, when all mesocosms were in a drained state prior to the first upwelling (Table 2.2), effluent P was approximately equal to input P (Fig. 2.3a). The behavior of Drained and Saturated mesocosms began to differ after the first upwelling, with Saturated mesocosms releasing larger amounts of P (Fig. 2.3a). Alternating hydrology mesocosms functioned similarly to either Drained or Saturated mesocosms (Fig. 2.3a), depending on their temporary hydraulic state prior to the upwelling (Table 2.2). Despite differences in time between upwelling events (Table 2.3; Fig. A.3a), response to hydrology state remained relatively uniform (Fig 2.3a; Fig A.3a).

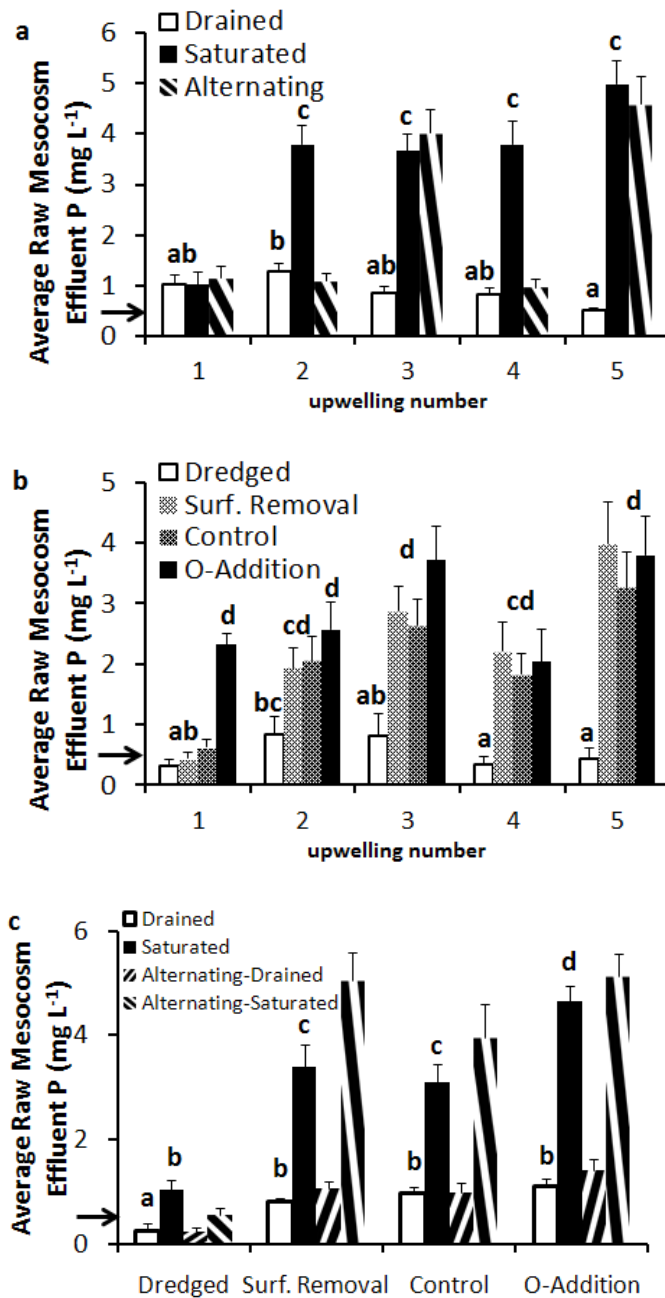
### **Soil treatment across upwelling events (time)**

The O-Addition treatment released more P than other soil treatments during the first upwelling (Table 2.2); all other treatments produced effluent of approximately the same P content as simulated input groundwater during the first upwelling (Fig. 2.3b). Following the first upwelling, effluent P from all Undredged mesocosms was similar and significantly higher than that of Dredged mesocosms, which produced effluent P closer to input P (Fig. 2.3b).

### **Hydrology across soil treatment**

On average, Drained or Dredged mesocosms released less P than Saturated or Undredged mesocosms (Fig. 2.3c). Mean effluent P was greatest in Saturated mesocosms with O-material addition (Fig. 2.3c) although this effect was a function of temporarily heightened P release during the first upwelling (see Fig. 2.3b).

All the Undredged treatments, no matter the hydrology, produced greater effluent P than was contained in input water (Table 2.3). This difference was much greater when Undredged mesocosms were Saturated and not Drained. Dredged mesocosm effluent P could not be distinguished from input water P (Table 2.3), though the statistical power of the test was low (Tables 2.2, 2.3). Dredged, Saturated mesocosms produced the same amount of effluent P as Undredged, Drained mesocosms (Fig 2.3c).



**Figure 2.3. (a) Effluent phosphorus (P) concentration of hydrology treatments vs. upwelling event. (b) Effluent P concentration of soil treatment versus upwelling event. (c) Effluent P concentration of hydrology treatments versus soil treatments.** Significant differences ( $p < 0.05$ ) between means are specified by nonsimilar letters. Arrow represents concentration of P in input water. Statistical evaluation of differences between treatment means and input water are made in Table 2.4. Alternating hydrology treatments were not tested statistically so as to avoid pseudoreplication.

**Table 2.4. Significance of difference between mesocosm effluent and P content (0.48 mg P L<sup>-1</sup>) of input water used in simulated groundwater input.**

Mesocosm soil treatment†	Mesocosm hydrology treatment means and significance relative to input‡								
	----- Drained -----					----- Saturated -----			
	n	mg P§L <sup>-1</sup>	SE¶	ΔP(%)#	t††	mg PL <sup>-1</sup>	SE	ΔP(%)	t
Dredged	2	0.24	0.33	-50	NS‡‡	1.03	0.45	+115	NS
Un-dredged Surf. Removal	6	0.81	0.19	+68	*	3.41	0.98	+610	**
Control	6	0.98	0.24	+104	*	3.10	0.81	+546	**
O-Addition	6	1.11	0.30	+131	**	4.64	0.69	+867	**

†‘Dredged’ mesocosms gathered after dredging; ‘Pre-dredge’ mesocosms gathered before dredging; ‘Surf. Removal’ 2-cm of surficial materials removed; ‘O-Addition’ 100 g Organic materials surficially added.

‡‘Drained’ mesocosms drained between upwellings of simulated groundwater; ‘Saturated’, mesocosms saturated between upwellings of simulated groundwater.

§‘P’ Phosphorus. Means and standard errors are from raw data.

¶‘SE’ Standard Error.

#‘ΔP(%)’ Percent change relative to input (0.48 mg P L<sup>-1</sup>).

††‘t’ Student’s *t* statistic. Statistical tests were performed on log-transformed data to compare mg P L<sup>-1</sup> of treatment means with input water (0.48 mg P L<sup>-1</sup>).

‡‡‘NS’ not significant.

\* Significant at the 0.05 level.

\*\* Significant at the 0.01 level.

## Effluent and surface water Fe

As stated in the Materials and Methods section, an orange precipitate that formed on the insides of collection bottles was interpreted as a Fe precipitate and therefore of evidence of Fe in mesocosm effluent. This orange precipitate was more abundant in mesocosms that had been saturated prior to the start of upwellings. Hence it was interpreted that mesocosms saturated prior to the start of upwellings released more Fe to effluent water. A similar precipitate formed on the mesocosm soil surface and the interior walls of the mesocosm surrounding the stagnant surface water in saturated-state mesocosms. (Images of these precipitates may be viewed in illustrations 3.5 and 3.6.) In

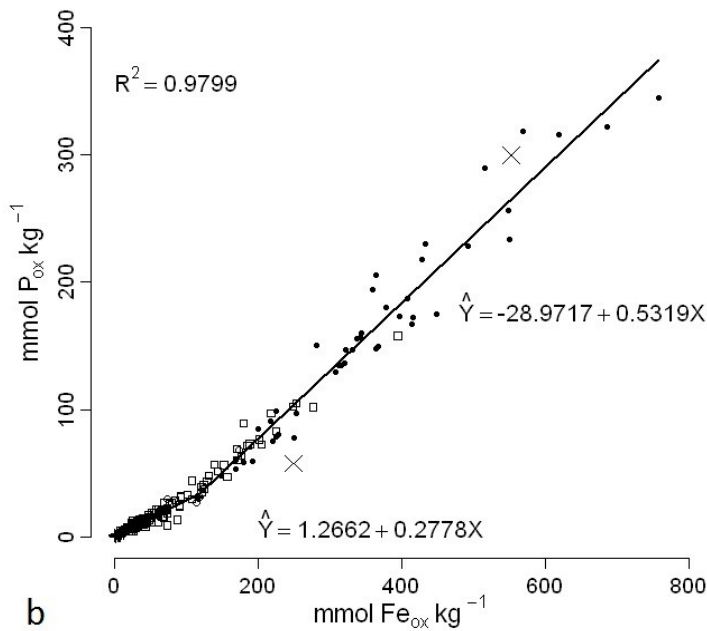
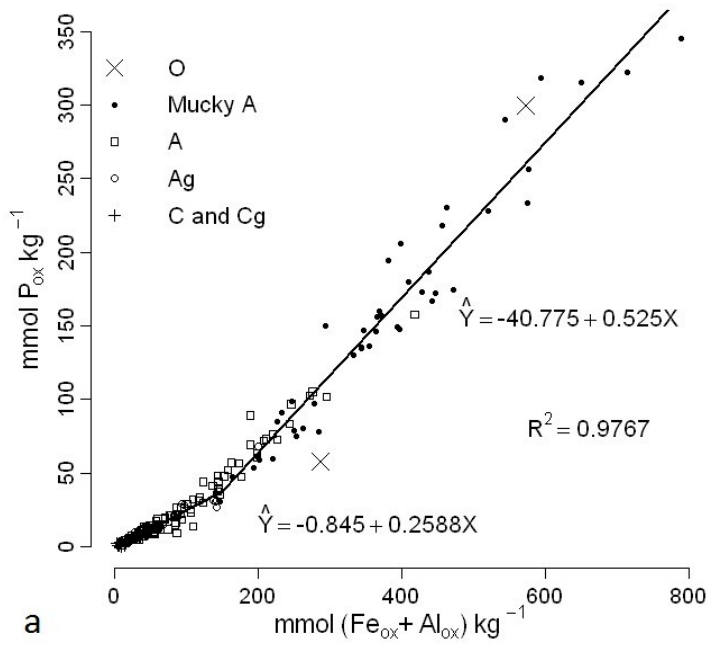
the lab Fe oxides can be synthesized from  $\text{Fe}^{2+}$  containing solutions under aerated conditions (Karaagac and Kockar, 2012).

## **Soil material**

### **Individual horizons**

Stepwise simple linear regression indicated a significant relationship between  $P_{\text{ox}}$ ,  $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$  (e.g.  $p < 0.01$ ). Oxalate-extractable Fe accounted for 97% ( $R^2 = 0.97$ ) of the variation in  $P_{\text{ox}}$ ; adding  $\text{Al}_{\text{ox}}$  to the model accounted for less than an additional 1% of variation of  $P_{\text{ox}}$ . However inspection of the  $P_{\text{ox}}$  vs.  $(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})$  scatterplot indicated the possibility of a change point in slope between 100 and 200 mmol  $(\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})$   $\text{kg}^{-1}$ . Use of a change point in slope of 150 mmol  $(\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})$   $\text{kg}^{-1}$  (Fig. 2.4a) was found to provide a minimal AICC (1681), substantially lower than the AICC of the simple linear model (1787) (Fig. 2.4a).

The three relationships between the three unique combinations of  $P_{\text{ox}}$ ,  $\text{Al}_{\text{ox}}$  and  $\text{Fe}_{\text{ox}}$  each exhibited significant (e.g.  $p < 0.01$ ) simple linear relationships. However, change point fits were superior to simple linear models according to the AICC criterion, with a difference in AICC of  $> 20$  when simple linear models were compared to linear splines (Fig. 2.4bcd). Oxalate-extractable P vs.  $\text{Fe}_{\text{ox}}$  had an AICC-minimizing change point at 119 mmol Fe  $\text{kg}^{-1}$  (Fig. 2.4b),  $\text{Al}_{\text{ox}}$  vs.  $\text{Fe}_{\text{ox}}$  had an AICC-minimizing change point at 114 mmol Fe  $\text{kg}^{-1}$  (Fig. 2.4c),  $P_{\text{ox}}$  vs.  $\text{Al}_{\text{ox}}$  had an AICC-minimizing change point at 15 mmol Al  $\text{kg}^{-1}$  (Fig. 2.4d).



**Figure 2.4. Scatterplots of oxalate-extractable phosphorus ( $P_{ox}$ ), iron ( $Fe_{ox}$ ) and aluminum ( $Al_{ox}$ ) of ditch soil mesocosms denoted according to horizon type. (a)  $P_{ox}$  vs.  $Fe_{ox}$  and  $Al_{ox}$ ; (b)  $P_{ox}$  vs.  $Fe_{ox}$ .**



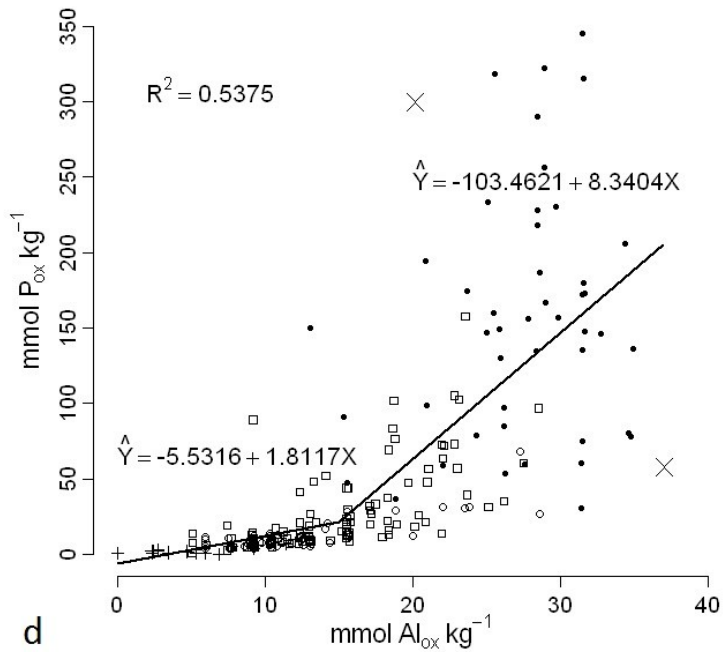
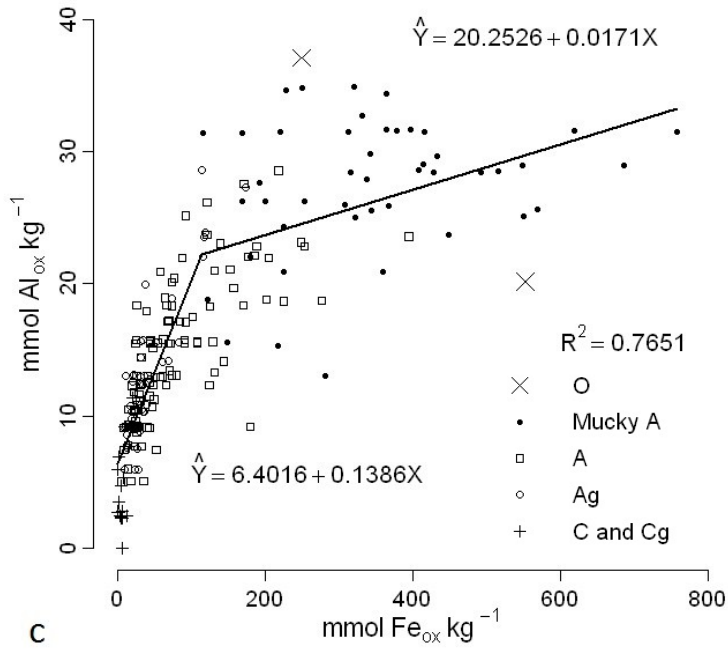
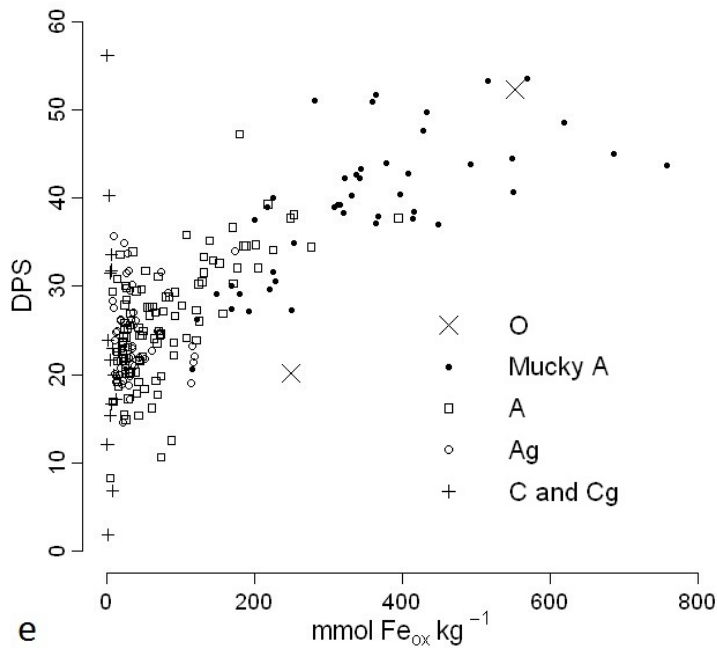


Fig. 2.4 (continued) (c)  $\text{Al}_{\text{ox}}$  vs.  $\text{Fe}_{\text{ox}}$ , (d)  $\text{P}_{\text{ox}}$  vs.  $\text{Al}_{\text{ox}}$ .



**Figure 2.4 (continued) (e) Degree of Phosphorus Saturation ( $DPS = P_{ox} (Al_{ox} + Fe_{ox})^{-1}$  on a molar basis) versus  $Fe_{ox}$ .**

Note that  $DPS$  vs.  $Fe_{ox}$  (Fig. 2.4e) appears to have a change in variance or slope at approximately the same level of  $Fe_{ox}$  as determined for other scatterplots. This was not tested, nor was the fit of a simple linear model, since  $DPS$  and  $Fe_{ox}$  are not independent. The P sorption capacity of mesocosm soils was dominated by Fe. When expressed in terms of moles of atoms the maximum observed concentration of  $Fe_{ox}$  in these soil horizons was approximately 20 times greater than that of  $Al_{ox}$  (Fig. 2.4).

The highest concentrations of  $P_{ox}$ ,  $Fe_{ox}$  and  $Al_{ox}$  were found in mucky A horizons which were the dominant surface horizon of mesocosms (Table 3.2). The uppermost horizons of (undredged) Control mesocosms were found to be  $2.78 \pm 1.3$  cm in thickness, containing  $19.6 \pm 10.9$  mmol  $P_{ox}$ , and accounting for 31% of whole mesocosm  $P_{ox}$  content.

Change points in the behavior of  $P_{ox}$ ,  $Al_{ox}$  and  $Fe_{ox}$  with respect to one another occur approximately at the lowest concentrations of these analytes in mucky horizons.

### Whole mesocosms

Undredged mesocosms contained more  $Fe_{ox}$ ,  $Al_{ox}$ , and  $P_{ox}$  than Dredged mesocosms ( $p < 0.01$ ) (Table 2.5); however, no difference in DPS was detected ( $p > 0.4$ ). Among Undredged mesocosms, Saturated mesocosms contained less  $Fe_{ox}$  ( $p < 0.01$ ),  $Al_{ox}$  ( $p < 0.03$ ), and  $P_{ox}$  ( $p < 0.01$ ) than the other two hydrologic treatments (Table 2.5). The Surficial Removal treatment resulted in less  $Fe_{ox}$  ( $p < 0.01$ ) and  $Al_{ox}$  ( $p < 0.01$ ) relative to the soil Control (Table 2.6), but did not affect  $P_{ox}$  ( $p > 0.08$ ).

**Table 2.5. Oxalate-extractable iron ( $Fe_{ox}$ ), aluminum ( $Al_{ox}$ ) and phosphorus ( $P_{ox}$ ) of soil mesocosms taken from a ditch before and after dredging.**

	Undredged†	Dredged
	-----mmol kg <sup>-1</sup> -----	
$Fe_{ox}$	52.2±2.4a‡	6.4±1.3b
$Al_{ox}$	13.2±0.4a	4.9±0.9b
$P_{ox}$	18.4±0.9a	2.3±0.3b

† 'Dredged' mesocosms gathered after dredging; 'Undredged' mesocosms gathered before dredging.

‡ Within rows, means followed by different letters are significantly different according to Tukey-adjusted means comparison tests. Uncertainties are standard error.

Oxalate-extractable P content of ditch O and A horizons in a 300-m ditch of width 0.5 m was determined to be 18.0 kg P. Mesocosms of the Control treatment were found to contain 63.6±21.6 mmol  $P_{ox}$ .

**Table 2.6. Mean whole mesocosm response to hydraulic and soil treatment.**

	<b>Mesocosm hydraulic treatment†</b>		
	<b>Drained</b>	<b>Saturated</b>	<b>Alternating</b>
	<b>mmol kg<sup>-1</sup></b>		
<b>Fe<sub>ox</sub>‡</b>	<b>57.0±3.1a§</b>	<b>41.1±3.1b</b>	<b>58.0±3.1a</b>
<b>Al<sub>ox</sub>¶</b>	<b>13.3±0.5ab</b>	<b>12.2±0.5a</b>	<b>14.0±0.5b</b>
<b>P<sub>ox</sub>#</b>	<b>20.3±1.2a</b>	<b>14.6±1.2b</b>	<b>20.3±1.2a</b>
	<b>Mesocosm soil treatment††</b>		
	<b>Surf. Removal</b>	<b>Control</b>	<b>O-Addition</b>
	<b>mmol kg<sup>-1</sup></b>		
<b>Fe<sub>ox</sub></b>	<b>44.4±3.1a</b>	<b>59.0±3.0b</b>	<b>52.7±3.1ab</b>
<b>Al<sub>ox</sub></b>	<b>11.9±0.5a</b>	<b>14.0±0.5b</b>	<b>13.5±0.5ab</b>
	-----%-----		
<b>DPS‡‡</b>	<b>27.6±0.9a</b>	<b>22.5±0.8b</b>	<b>25.4±0.6ab</b>

†‘Drained’ mesocosms were drained following each ‘upwelling event’; ‘Saturated’ mesocosms were held saturated throughout the experiment; ‘Alternating’ mesocosm were drained or remained saturated after an upwelling in a cyclic fashion.

‡‘Fe<sub>ox</sub>’, oxalate-extractable iron.

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

¶‘Al<sub>ox</sub>’, oxalate-extractable aluminum.

#‘P<sub>ox</sub>’, oxalate-extractable phosphorus.

††‘Surf. Removal’ mesocosms had 2 cm of surficial materials removed; ‘O-Addition’ mesocosms had 100 g Organic materials surficially added.

‡‡‘DPS’, degree of phosphorus saturation ( $=P_{ox} / (Fe_{ox} + Al_{ox})^{-1}$ ).

## Discussion

### The effects of saturated conditions in mesocosms and speculation regarding controlled drainage in ditches

My results indicated that reducing conditions predominated under saturated, zero-flow conditions (Fig. 2.2ab). My results also indicated that under these conditions concentrations of P above input water levels existed in pore water that was evacuated through simulated groundwater rise (Fig. 2.3), and that this response remained uniform (Fig 2.3a) even with variation in the time between upwellings (Table 2.3; Fig. A3). Conditions of saturation and very low flow likely predominate in ditch soils under

controlled drainage. If this is the case, and if convected to the ditch surface then large amounts of P could be released (Fig. 2.3).

However, under controlled drainage pore water may not be convected from ditch soil in large amounts. Our experiment employed a hydrology involving upwellings of more than a soil pore volume in which pore water was conducted by mass flow to the mesocosm surface. While such a hydrology likely characterizes free flowing ditches, especially when rain events are large, it may overemphasize convection relative to diffusion-dominated P transport, which is likely of greater importance under controlled drainage. Under controlled drainage the potential difference between ditch and groundwater is minimal due to restricted drainage. In some peat mesocosm systems of inundated but stagnant hydrology substantial P release to surface waters has not been observed due to the formation of P-sorbing Fe oxides at the boundary between oxidized and reduced zones (Zak et al., 2004). In our experiment, Fe precipitates formed near the soil surface and on mesocosm walls in saturated-state mesocosms (Ill. 3.5; Ill. 3.6). These precipitates are evidence of the diffusion of reduced Fe out of pore water and into oxidized zones similar to Zak et al. (2004), and could perform the same P-sorbing function observed by those researchers. However, such an effect has not yet been observed in ditches. Amatya et al. (1998) recorded heightened ditch P concentrations resulting from controlled drainage, but generally controlled drainage has been found to export less P than free drainage because of restricted flow (Evans et al., 1995).

## **Dredging**

Dredging was found to lower effluent P values (Fig. 2.3) such that they could not be distinguished from input P levels (though our statistical power was low) (Table 2.3). Our effluent P results are consistent with those of Shigaki et al. (2008) who observed in fluvialia decreased P release from materials from a dredged versus an undredged ditch. The source of materials of Shigaki et al. (2008) is the same as that of the mesocosms of the present study. In a field study of Midwestern collection ditches Smith and Huang (2010) observed decreased P loads in dredged ditch reaches versus undredged reaches for up to a year after dredging. The results of our study and the studies cited above are in contrast to those of Smith (2006) and Smith and Pappas (2007) who observed in fluvialia increased P release from Midwest collection ditch sediments collected post dredging relative to sediments collected before dredging. The results of Smith (2006) and Smith and Pappas (2007) are considered to apply only in the short term by Smith and Huang (2010) who cite the oxidation of reduced sediments, introduced sediments 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. In addition, the work of Smith and Huang (2010), Smith and Pappas (2007), and Smith (2006) occurred within collection ditches in the Midwest, such that their findings may not apply in our context in the MACP.

While dredging lowered effluent P in mesocosms (Fig. 2.3a), dredging and hydrology interacted: Dredged, Saturated mesocosms released the same amount of P as Undredged, Drained mesocosms (Fig. 2.3c). Because saturation can be expected to increase in frequency in the upper part of dredged ditch soils due to the lowering of the

ditch surface under dredging, the above result does not lead to clear interpretation with respect to field ditch soils. When hydrology is held constant dredging lowers effluent P; when hydrology goes from drained to saturating dredging has no effect.

### **No treatment increased soil Fe<sub>ox</sub> or Al<sub>ox</sub>**

Alternating cycles of Fe reduction and oxidation can support the development of oxalate-extractable Fe relative to more crystalline Fe forms (Schwertmann, 1991), but we did not observe an increase in overall soil Al<sub>ox</sub> or Fe<sub>ox</sub> with the Alternating hydraulic treatment (Table 2.5). We interpret this result to indicate that the mesocosm soil coatings consisted nearly exclusively of oxalate extractable materials, namely paracrystalline and OM-metal complexes prior to the initiation of the experiment.

As observed in effluent collection bottles, mesocosm pore water contained Fe that began to precipitate soon after emergence. Typically, newly and rapidly precipitated Fe is amorphous or paracrystalline (Schwertmann 1991) and is often ferrihydrite (Schwertmann 1993). Reduced Fe delivered to ditches through groundwater could be expected to precipitate as oxalate-extractable Fe(III)(hydr)oxides. These amorphous or paracrystalline forms would be maintained in field ditches due to cycling between Fe-reducing and -oxidizing conditions (Schwertmann 1991). Field ditches also accumulate OM, which impedes the formation of crystalline oxides (Schwertmann 1991) and provides for the formation of metal-OM chelates (Gerke, 2010; Petrovic and Kastelan-Macan, 1996). Noncrystalline oxides and some metal-OM chelates are oxalate susceptible (Loeppert and Inskeep, 1996). The UMES ditches receive high concentrations of P in groundwater (Vadas et al., 2007) and surface runoff (Kleinman et al., 2007).

Phosphate and other anions impede the formation of crystalline Fe oxides (Schwertmann, 1991). These same factors, taken together, would diminish the crystallinity of Fe(hydr)oxides that entered ditches as colluvium (Schwertmann 1991). Ditches appear to be well suited for the establishment and maintenance of amorphous, paracrystalline, and OM-complexed Fe. If the transformation to ferrihydrite and Fe-OM complexes was virtually complete even as mesocosms were first collected, then Fe<sub>ox</sub> could not be further developed. Our data are consistent with the interpretations made by Needelman et al. (2007b) and Schwertmann (1966) of essentially 100% non- or para-crystalline Fe in ditches and drainage tile soils. This ratio is much higher than those commonly observed in non-ditch soils. For example, in cultivated and forest plots from a study in South Carolina ratios of oxalate- to dithionite-citrate-extractable Fe were observed between 0.25 and 0.04 in soil from the upper 7.5 cm (Li, 2009). The average ratio of oxalate- to dithionite-citrate-extractable Fe in shales of the Maryland Triassic basin is 0.05 (Elless and Rabenhorst, 1994).

### **Surficial ditch horizons**

Our data indicate that P lost from our mesocosms came from the mesocosm interior. Except for initial release of large amounts of P from O-Addition mesocosms, which may have been due to mineralization between collection of the peat and the start of the experiment, or may have been due to an initial disequilibrium between our added peat and the mesocosms onto which it was placed, the addition of O horizon material to, or removal of the upper 2 cm soil from Undredged ditch mesocosms did not affect long-term performance regarding effluent P (Figure 2.3, Table 2.3). This is despite the fact that



a high percentage (31%) of mesocosm  $P_{ox}$  was contained just within the upper 2.8 cm of Control mesocosms. In other words, while 25% of total ditch  $P_{ox}$  content was removed by the Surficial Removal treatment (Table 2.5), effluent P was not affected (Figure 2.3b).

If mesocosm surfaces did not release P it is also unlikely that they could have substantially captured it given the nature of our experiment. Because effluent water was immediately collected after emergence from the mesocosm top, emergent waters did not flow across the soil surface as with ditches in the field. As a result, processes requiring surficial lateral flow were not taken into account in this study. As indicated by the precipitation of Fe oxides in collection bottles of saturated-state mesocosms, substantial Fe was released by mesocosms with Fe-reducing interiors. This effluent Fe could represent a significant P sorption capacity that in our setting had little opportunity to settle on the top of the soil surface.

The hypothesis of surficial Fe-oxidation and capture of P goes far in explaining 1) the extreme vertical gradient in  $P_{ox}$  and  $Fe_{ox}$  observed by Vaughan et al. (2007b) (and in table 3.2) as well as 2) the close correlation of  $Fe_{ox}$  and  $P_{ox}$  in soil mesocosms (Fig. 2.4) and the increased capture of  $P_{ox}$  by  $Fe_{ox}$  which occurs among (surficial) mucky-A horizons (Fig. 2.4b) (and the differing relationships between  $P_{ox}$ ,  $Fe_{ox}$  and  $Al_{ox}$  for different soil horizons as found in soil cores in chapter 4). If, as in this experiment, the interior of ditch soils is out of equilibrium with respect to P in ground water, then the interior of ditch soils could be expected to release P to the ditch surface where it could be precipitated by newly forming Fe oxides from Fe that has been introduced from groundwater and solubilized from reduced zones. As the surface of the ditch ascends and prior surfaces become buried, they too would become Fe and P donors as the zone of Fe

oxidation and P capture moves upwards, so that subsurface Fe and P is not evidence of current ditch soil P capture, but the legacy of P sorbed to surface-precipitated Fe that was then subsequently buried. While the above explanation of the distribution of Fe and P in ditches is only a hypothesis, note among Undredged mesocosms a clear downward trend in whole mesocosm Eh according to the amount of material accumulated at the top of mesocosms (Fig. 2.2c). My Undredged soil treatments can be thought of as a simulation of pedogenic cumulation (Surficial Removal, Control, O-Addition). That this pedologic gradient had a real effect on whole mesocosm Eh demonstrates that the accumulation of surficial material could have an effect on the mobility of within-soil Fe and P. Note as well that the range of DPS among predominantly subsurface horizons (C, Cg, Ag and A) has very little linear character when plotted against  $Fe_{ox}$ , but for predominantly surficial horizons (mucky A and O), appears to take on a much more linear character (Fig. 2.4e). This is to say that the P-sorption capacity of mesocosm soils exhibits little evidence of dependence on Fe among predominantly subsurface horizons, but more evidence of a degree of dependence on Fe among predominantly surficial horizons.

### **The limitation of ditch geometry**

The preferential surficial accumulation of Fe and P in ditches exposes a key weakness in their efficacy as sorbers of P. The narrow geometry of ditches is poorly suited for maximum P retention. Narrow ditches may flush newly emerging Fe from the ditch before the Fe has the opportunity to form P-sorbing (hydr)oxides. Narrow cross sections also accelerate the accumulation process, minimizing the time that the ditch surface remains exposed before burial. Alternative ditch designs which increase ditch

surface area throughout the hydrograph (Evans et al., 2007) or only during peak flow (Powell et al. 2007a; Powell et al., 2007b) are being implemented. Artificial P-sorbing materials (Ippolito et al., 2003) may also be used to increase P retention in ditches (Penn et al., 2007). The use of such materials effectively expands the surface area of ditches even when these materials occupy compact volumes in engineered structures.

### **An alternative means of evaluating the P-sorbing potential of ditches**

The concepts of convective versus diffusional flow suggest an alternative means of evaluating ditch P-sorption capacity than typical extraction techniques. For ditches with relatively little colluvial contributions, P, Fe, and Al would be delivered to ditches through groundwater flow. This is likely the case at the UMES farm. Whereas Vaughan et al. (2007a) reported mean values of 37 mmol Fe<sub>ox</sub> kg<sup>-1</sup> and 41 mmol Al<sub>ox</sub> kg<sup>-1</sup> for 0-5 cm materials for UMES farm ditches (*n*=405), Church, in unpublished data relating to a published study (Church et al., 2010), recorded aqua regia Fe and Al for transects of field soils parallel to UMES farm ditches of 18 and 81 mmol kg<sup>-1</sup>, respectively (*n*=245). The heightened presence and importance relative to Al of Fe in ditch soils (Figure 2.4) point to Fe accumulation through a groundwater and not colluvial pathway. In a study of the ditch from which mesocosms were taken, and a companion ditch, Kleinman et al. (2007) observed more than 96% of total P in ditch effluent having arrived in ditches through subsurface flow.

Because Fe accumulates in UMES ditches through a groundwater and not colluvial pathway, Fe and P enter these ditches simultaneously. If the majority of P sorption in ditches occurs during the oxidation of Fe(II) to Fe(III) and the formation of

oxalate-extractable Fe compounds, then the P sorption capacity of a ditch may be best determined through the ratio of P to Fe in near-ditch groundwater instead of through the inspection of ditch soil material. This is because tests for P-sorption capacity like DPS assume that P is being added to a system where the amount of P-sorbing materials (Fe and Al) is static. While this may be true of field soils, it is not true of ditch soils in which the groundwater pathway adds not only P to the ditch soil system, but Fe and Al as well. The mechanism of P retention by groundwater Fe oxidizing upon emergence was not measured in this experiment since emerging water was gathered immediately upon emergence and Fe was not part of the input water used in this experiment (Table 2.1).

## **Conclusions**

Mesocosms taken from a ditch before dredging released additional P to simulated groundwater; mesocosms taken from the same ditch after dredging had effluent P statistically indistinguishable from input values. While for any particular hydrology dredging lowered effluent P, dredging and hydrology interacted: Dredged, Saturated mesocosms release similar effluent P to Undredged, Drained mesocosms. Manipulations of in-ditch materials and hydrology failed to diminish ditch mesocosm P throughput or to enhance P-sorption capacity of ditch soils. Undredged ditch soils in my study did not sorb P within the soil profile, but mesocosm effluent was inferred to contain large amounts of precipitable Fe that could capture P upon oxidation at the ditch surface. Degree of P saturation and other techniques for determining effective P storage capacity may be of limited application in ditches since the amount of P-sorbing materials in ditch soils may be expected to be more dynamic than in field soils.

# **Chapter 3: Drainage ditch soil morphology as expressed in intact soil mesocosms subjected to hydrologic and soil treatments**

## **Introduction**

Field ditches (Ill. 3.1) are often the primary means of drainage in wet landscapes of low relief. Some ditch materials are sufficiently stable to undergo soil formation processes (Vaughan et al., 2008). Ditch soils are periodically saturated by a rising water table, and with sufficient time after dredging they tend to accumulate high amounts of organic matter (OM) (Vaughan et al., 2008). As a result, iron (Fe)-reducing conditions occur (Needelman et al., 2007b). The relative solubility of reduced Fe (Lindsay, 1979) means that redox gradients in time and space may be expected to encourage the formation of redox concentrations and depletions in ditch soils. The development of redox features has been studied in initially featureless intact upland soil mesocosms exposed to different organic matter types and wetland hydrology (Gray, 2010), in experimental units of homogenized soil material (Vepraskas and Bouma, 1976) in created wetlands (Vepraskas et al., 2006; Stolt et al., 2000), and in comparison studies across many wetlands (Ming et al., 2011; Morgan and Stolt, 2006; Fiedler and Sommer, 2004). The loss or retention of Fe has nutrient management implications as Fe, particularly ferrihydrite, is a strong sorber of phosphorus (P) and is abundant in ditches (Vaughan et al. 2007ab).



**Illustration 3.1. Typical field ditch in Somerset County, Maryland.**

In this paper I describe changes in matrix color and other aspects of soil morphology that occurred in ditch soil mesocosms subjected to hydrologic and soil-related manipulations relating to common means of ditch management, for example dredging practices or the saturated conditions of controlled drainage. We hypothesized that these manipulations would create changes in Fe-mineralogy and abundance. Since ditches function as the headwater streams of drainage networks and Fe plays a crucial role in P retention, knowledge of the effects on ditch management on Fe are important to understanding the management of ditches for the sake of water quality

## **Materials and Methods**

Cylindrical mesocosms (15 cm inner diameter; 40 cm depth) were gathered from a drainage ditch at the UMD Research Farm at Princess Anne, MD (38°12'22"N, 75°40'35"W). Ditch soils at this location are classified as Aeric and Humaqueptic Endoaquents (Vaughan et al., 2008). Surrounding field soils are mapped as predominantly Quindocqua series (Fine-loamy, mixed, active, mesic Typic Endoaquents), Othello series (Fine-silty, mixed, active, mesic Typic Endoaquents) and similar soils distinguished by fluvio-deltaic and marine sediments overlain by approximately 20 cm of loessal materials (Soil Survey Staff, 2011). Among the many parallel marine sediments among which are likely frequent aquitards there are pyrite-rich layers (Ill. 3.2) which are thought to contribute large amounts of iron and sulfur to ditch materials (Vaughan et al., 2008) and groundwater (Chapter 2). Mesocosms were arranged in a completely randomized cross factorial design consisting of soil and hydrology manipulations.



**Illustration 3.2. Near-surface (gray) sulfidic materials at the same field site (University of Maryland Eastern Shore Research Farm, Princess Anne, MD) from which mesocosms in my study were taken.** Such near-surface sulfides were not present in ditches studied in this dissertation, but this picture illustrates the redox biogeochemistry of ditches and the likely origin of the large amount of sulfate (Table 2.1) present in groundwater at the UMES site. Repeated, horizontal aquitards are likely present with significant lateral flow resulting.

“Control” treatments preserved the ditch soil mesocosms without alteration. “O-Addition” mesocosms had 100 g of dry ditch peat, taken from elsewhere in the ditch, added to the soil surface in the mesocosms. “Removal” mesocosms had 2 cm of surficial materials removed. Mesocosms used for these “Undredged” soil treatments were collected one month prior to dredging (Ill. 3.3).





**Illustration 3.3. Ditch dredging in Somerset County, Maryland.** Spoil is typically spread near the ditch. (Courtesy Brian A. Needelman)

“Reference” mesocosms were similar to Control mesocosms, except that Reference mesocosms were set aside at the start of the experiment and were not subjected to any hydrology treatments as with experimental Control, O-Addition, or Removal mesocosms. About two weeks after dredging additional “Dredged” mesocosms were collected from the same ditch (Ill. 3.4) and received no further manipulation of soil materials.



**Illustration 3.4. Erosion of ditch banks several weeks after dredging.** Note the slumped ditch sides, structureless materials occupying the channel, inclusions of former A horizon material with plants occasionally in the channel, and lack of vegetative growth on ditch banks.

The hydrology treatments applied were termed “Saturated”, “Drained” or “Alternating.” In “Saturated” mesocosms, soils were maintained under 10 cm of stagnant headwater while “Drained” mesocosms were allowed to freely drain, and the “Alternating” mesocosms were alternately maintained between drained and saturated states between hydrological upwelling events. Periodic upwellings of simulated groundwater occurred in all mesocosms as a means of further simulating ditch hydrology.

The timing of hydraulic manipulations is provided in Table 3.1. The experiment consisted of five upwellings in which simulated groundwater was added to the bottom of

each mesocosm and effluent was collected from the top. This upward movement of input water was meant to simulate groundwater rise through the ditch soil. Before the first upwelling all mesocosms were at field capacity, but unsaturated. After the first upwelling ‘Saturated’ mesocosms remained saturated, ‘Drained’ mesocosms were drained at the end of each upwelling and maintained at field capacity in their upper parts between upwellings, and ‘Alternating’ mesocosm were drained or remained saturated after an upwelling in a cyclic fashion. Between upwellings, periods of static hydrology occurred (Table 3.1).

**Table 3.1. Experimental timeline of static hydraulic states and ‘upwelling’ periods of simulated groundwater rise in mesocosms.**

Overall Hydraulic Treatment†	Pre-experiment‡	Upwelling/effluent collection #1§	Interim period¶	Upwelling/effluent collection #2	Interim period	Upwelling/effluent collection #3	Interim period	Upwelling/effluent collection #4	Interim period	Upwelling/effluent collection #5
			73 days		264 days		20 days		27 days	
Temporary state#			Temp. State		Temp. state		Temp. state		Temp. state	
Drained	drain.		drain.		drain.		drain.		drain.	
Saturated	drain.		sat.		sat.		sat.		sat.	
Alternating	drain.		drain.		sat.		drain.		sat.	

† ‘Drained’ mesocosms were drained following each ‘upwelling event’; ‘Saturated’ mesocosms were held saturated throughout the experiment; ‘Alternating’ mesocosm were drained or remained saturated after an upwelling in a cyclic fashion.

‡ Before the first upwelling all mesocosms were at field capacity, but unsaturated.

§ Experiment consisted of five upwellings in which simulated groundwater (Table 2.1) was added to the bottom of each mesocosm (1 L mesocosm<sup>-1</sup> day<sup>-1</sup>) and effluent was collected from the top for analysis. This upward movement of input water was meant to simulate groundwater rise through the ditch soil.

¶ Between upwellings, interim periods occurred in which a mesocosm was held either in a drained or saturated ‘temporary state’.

# ‘Temporary state’ gives the hydrology that mesocosms experience at any particular time. ‘D’ indicates a drained state (held near field capacity); ‘S’ indicates a saturated state in which mesocosms were inundated with water such that 10 cm of free water persisted above the soil surface.

At end of the experiment mesocosms were opened with a table saw and individual horizons were identified using soil structure, resistance to penetration by a knife, texture,

soil matrix color and redox feature color and abundance. Horizon properties were characterized using hand texturing, comparisons with Munsell color charts, bulk density by recording horizon volume in the mesocosm and water content from an oven dried (105°C) subsample, pH using a glass electrode (1:1 distilled water), and organic carbon content by dry combustion (Leco CNH-2000, St. Joseph, MI). Paracrystalline iron oxides ( $\text{Fe}_{\text{ox}}$ ) were extracted using acid ammonium oxalate (Sah and Mikkelsen, 1986b). In the observation of Munsell hue, value, and chroma interpolation was sometimes used (to the tenths place) when the soil color occurred between different chips. All color comparisons were performed by the author under uniform fluorescent lighting in the same room. Soil horizon types (O, mucky A, A, Ag, C and Cg) were distinguished according to presence of organic carbon, soil texture, and Munsell value and chroma as described in chapter 2.

Statistical analyses were performed to compare soil morphological features (hue, value, chroma of soil matrix and redox features, and abundance of redox features) between horizon types (to gain a conceptual picture of differences between horizons; Table 3.2), and as a function of hydrology and soil treatments (to see if redoxymorphic features were affected by treatments; Table 3.3). Munsell hue, value and chroma data were not normally distributed, and no normalizing distributions could be identified. Analyses were performed on untransformed data. Properties of individual horizon types were compared using weighted averages (by mass) per horizon type per mesocosm. Weighted averages per mesocosm (by horizon mass) of matrix and redox feature color and abundance were used to evaluate the effect of experimental treatments. Only soil horizons that were in place in mesocosms prior to the experiment were included (e.g. the added O horizons were not included).

To provide a continuous scale for comparing Munsell hue, a unitless scale was created where 5YR=15, 10YR=20, and 5Y = 25, like that used by Rabenhorst and Parikh (2000). Analysis was performed using the MIXED procedure of SAS (SAS 9.3, Cary, NC) on raw data. For the comparison of horizon properties, if a trend in variance with predicted value was observed for treatment residuals data were cubed-root transformed to remove the trend. Variables that were transformed are labeled as such. Tukey-adjusted multiple means comparisons were performed if overall F tests were significant. Similar testing was performed to compare matrix and redox feature color across hydrology and soil treatments of Undredged mesocosms, and across hydrology treatments of Dredged mesocosms. The ESTIMATE statement in the SAS MIXED procedure was used to compare Undredged mesocosms to Reference (Ill. 3.5) mesocosms.

## **Results**

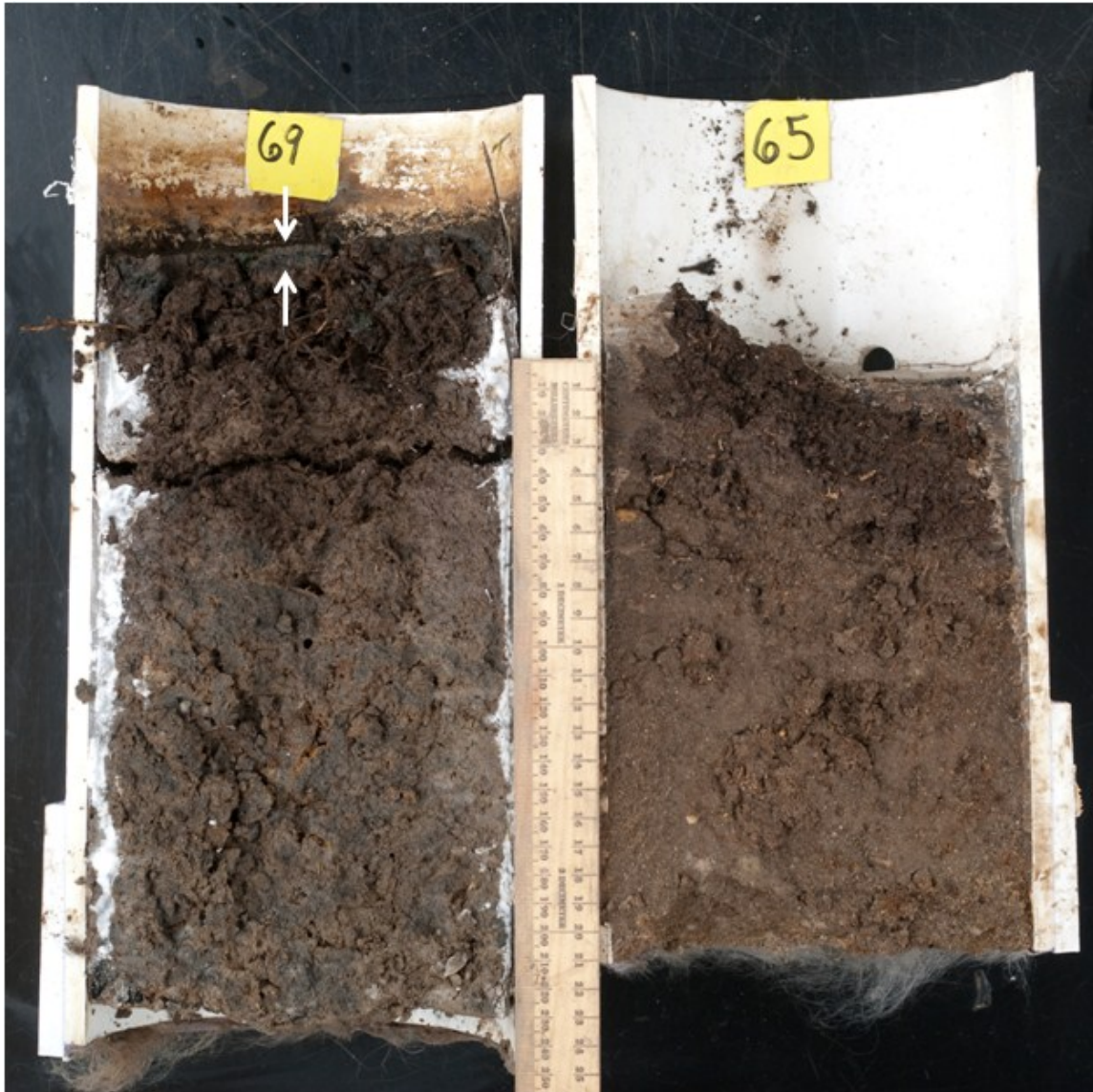
### **Mesocosm horizons**

Undredged mesocosms (Ill. 3.5; Ill. 3.6) contained O, mucky A, A and Ag horizons, while Dredged mesocosms (Ill. 3.7) contained C and Cg horizons. Ditch soil horizons decreased in organic carbon with depth ( $p<0.001$ ) while also becoming lighter in color (matrix value,  $p<0.001$ ) and denser ( $p<0.001$ ) (Table 3.2). Ditch soils also decreased in Fe<sub>ox</sub> content with depth ( $p<0.001$ ). Mucky A horizons were redder than A, Ag and Cg horizons (matrix hue,  $p<0.001$ , Table 3.2). C horizons were brighter than other horizons (matrix chroma,  $p<0.001$ , Table 3.2). The mesocosms had a clay maximum in the A and Ag horizons. The most common textures observed for each horizon type became coarser with depth (Table 3.2). The order given in table 3.2 (left to

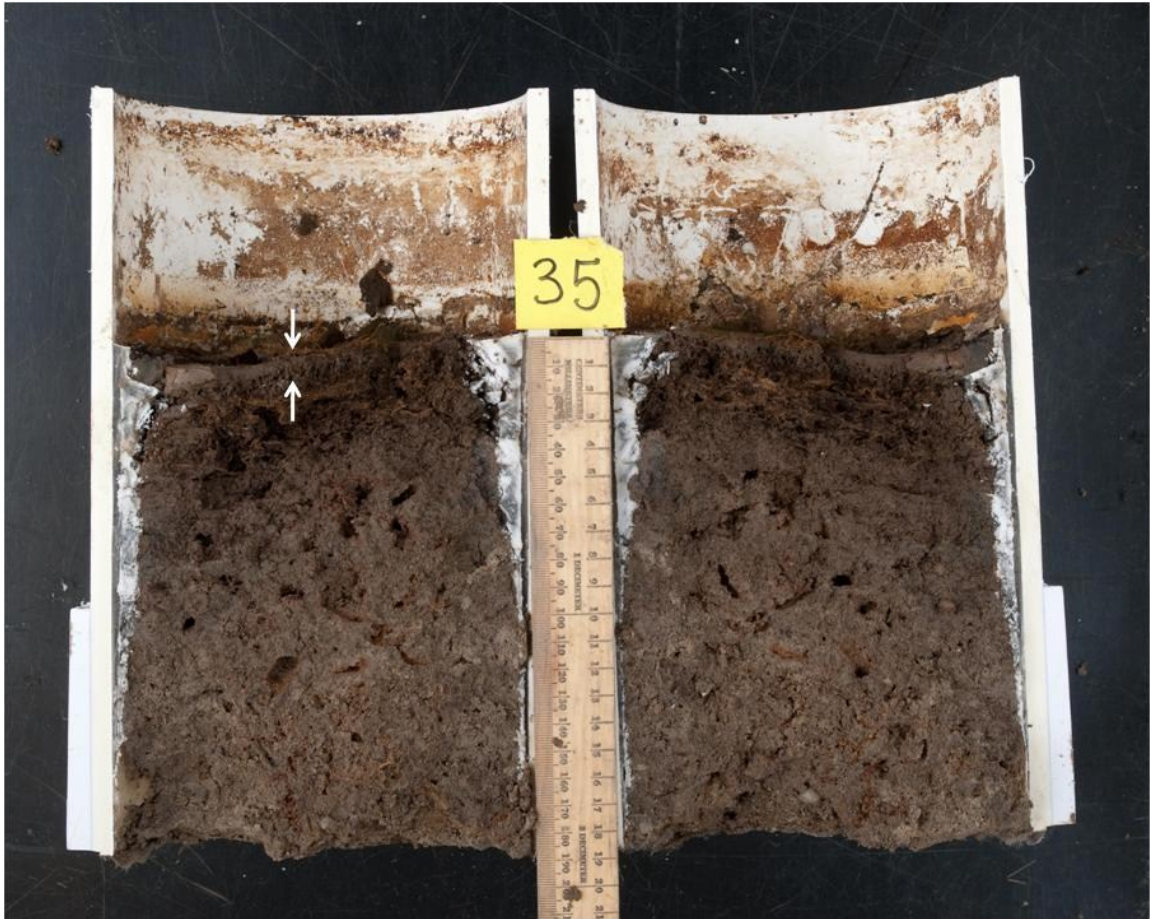
right) for soil horizons from Undredged mesocosms tended to predominate vertically in the mesocosms themselves, with O horizons, where present, occurring on the surface, and Ag horizons, where present, at the lowest depths in mesocosms.

A feature observed in Alternating and Saturated mesocosms was the newly formed surficial silty horizon which we called “silt caps” (Ill. 3.5; Ill. 3.6). No Drained or Dredged mesocosms had silt caps. Silt caps varied in thickness between 0.5 cm and 3 cm and were structureless and massive. These horizons were not present when the experiment began and were therefore not included in the analysis of mesocosm soil characteristics.

Horizons from Dredged mesocosms sometimes had inclusions of A-horizon material (Ill. 3.7). Their surficial horizons tended to be structureless with lower horizons tending to be platy (Ill. 3.7). Average depth (and standard deviation) to platy materials was 11.6 (4.6) cm.



**Illustration 3.5. Side by side comparison of (left) a ‘Saturated O-Addition’ mesocosm exposed to saturation throughout the experiment and to the addition of organic materials to the surface, and (right) a ‘Reference’ mesocosm that experienced no experimental treatments.** Note, in the Saturated mesocosm the presence of the silt cap, given by arrows, added organic materials (lying above the ruler), Fe monosulfides (which had already begun to fade by the time the picture was taken after mesocosm opening), and the Fe released from the mesocosm which has stained the upper part of the mesocosm wall. Note as well the redder matrix hue of the Reference mesocosm relative to that of the Saturated mesocosm. (Courtesy Edwin Remsberg)



**Illustration 3.6. Soil mesocosm** taken from a ditch before dredging and then exposed to the ‘Surficial Removal’ soil treatment in which 2 cm of surficial materials were removed, and then subjected to the ‘Alternating’ hydrology, in which mesocosm hydrology switched between drained and saturated states. Note the silt cap (white arrows) above the mucky A horizon (to 3.5 cm), overlying an A1 (to 10cm) and A2 horizon (to bottom). Note the redox depletions surrounding redox concentrations in some pores. (Courtesy Edwin Remsberg)





**Illustration 3.7. Mesocosm taken 14 days after dredging of ditch and then subjected to experimental treatments.** Note platy structure of materials left in place despite dredging. Note the lack of structure and inclusion of A material from colluvium/alluvium which collected at the surface between dredging and mesocosm harvest.

**Table 3.2. Properties of Mesocosm Horizons.**

Horizon properties	Mesocosm† / Horizon type					
	Undredged				Dredged	
	O	Mucky A	A	Ag	C	Cg
<b>n</b>	2	35	51	34	2	6
<b>width (cm)</b>	1	3.3	12.8	9.7	10.8	16.4
<b>OC‡ (%)</b>	15.4±3.1a§	8.7±0.2a	2.0±0.2b	1.4±0.1b	0.12±0.12c	0.14±0.04c
<b>Fe<sub>ox</sub>¶ (mmol kg<sup>-1</sup>)</b>	382±98a	330±19a	57±5b	31±4c	7±7d	4±3d
<b>P<sub>ox</sub>(mmol kg<sup>-1</sup>)</b>	300±42a	156±11a	27±3b	13±2c	1.4±0.5d	2.4±0.3d
<b>matrix hue# (Munsell)</b>	(10.0±0. 7)YRa	(9.3±0.2)YRa	(9.7±0.1)YRb	(9.9±0.2)YRb	(10.0±0. 7)YRa	(10.0±0.4)YRb
<b>matrix value (Munsell)</b>	2.0±0.4a	2.8±0.1a	3.2±0.1b	4.2±0.1c	5.0±0.4cd	5.0±0.2d
<b>matrix chroma (Munsell)</b>	2.0±0.3a	1.8±0.1a	1.8±0.1a	1.6±0.1a	4.6±0.3b	1.7±0.2a
<b>pH</b>	4.4±0.1a	4.9±0.1b	5.2±0.1cd	5.3±0.1c	4.7±0.2ab	4.8±0.1ab
<b>bulk density (g cm<sup>-3</sup>)</b>	0.16±0.09a	0.29±0.02a	0.98±0.04b	1.15±0.05b	1.38±0.21bc	1.63±0.15c
<b>clay (%)</b>	5.0±2.9abc	10.5±0.5b	12.9±0.4c	12.8±0.5c	5.7±4.2bc	3.6±1.2a
<b>texture(s)</b>	Oe	L, SiL, Si	LS, SL, L, SiL	SL, L, SiL	S, LS, L	S, LS
<b>dominant texture</b>	Oe	SiL	L	L	LS	LS

† ‘Dredged,’ mesocosms gathered after dredging; ‘Undredged,’ mesocosms gathered before dredging.

‡ OC, organic carbon. Analysis was performed after a cubed-root transform to correct an upward trend in the range of residual values against treatment means.

§ Within rows, means followed by the same letter are not significantly different at the 0.05 level according to Tukey-adjusted means comparison tests.

Uncertainties are standard error.

¶ Fe<sub>ox</sub>, oxalate-extractable iron. Statistical analysis was performed after a cubed-root transform to correct an upward trend in the range of residual values against treatment means.

# 10.00YR=0.00Y.

## **Analysis of redox features on the mesocosm scale**

### **Soil color as a function of hydrologic and soil treatments**

Interactions between hydrologic and soil treatments had no significant effect ( $p>0.05$ ) on soil color variables. Significant main effects included hydrology, which yellowed redox concentrations with increasing saturation ( $p<0.001$ , concentration hue, Table 3.3). Continuously saturated mesocosms had redox depletions with yellower hues than those in Alternating mesocosms ( $p<0.01$ , depletion hue, Table 3.3). Continuous saturation of mesocosms rendered depletions darker than mesocosms held at field capacity ( $p<0.01$ , depletion value, Table 3.3). The removal of high-OM surficial materials resulted in redox concentrations with higher values than those in other mesocosms ( $p<0.02$ , concentration value, Table 3.3). Soil colors in mesocosms from the ditch after dredging showed no response to treatments ( $p>0.05$ ). Experimental treatments did not affect abundance of concentrations or depletions ( $p>0.05$ ). Average Munsell color properties of whole mesocosms are given in Table 3.4.

**Table 3.3. Response of Undredged mesocosm Munsell color components to hydrology and soil treatments. Comparison between treatments and against Reference† mesocosms.**

-----Effect of hydrology‡-----				
Morphological feature	Munsell variable§	Drained	Alternating	Saturated
matrix concentration	Hue	(0.0±0.4¶)Y#	(0.1±0.4)Y	(0.5±0.4)Y*††
depletion	Hue	(7.1±0.3)YRa‡‡	(8.5±0.3)YRb	(9.8±0.4)YRc***§§
depletion	Value	(9.2±1.23)YRab	(0.1±0.7)Ya	(2.5±0.6)Yb
		4.3±0.3a	3.7±0.1a	3.0±0.1b
-----Effect of soil treatments¶¶-----				
Morphological feature	Munsell variable	Surf. Removal	Soil Control	O-Addition
concentration	Value	3.8±0.1a	3.3±0.1b	3.3±0.1b

† ‘Reference’ mesocosms did not undergo experimental treatments but were otherwise identical to mesocosms used during the experiment. Mean Reference mesocosm matrix and concentration hues were (9.8±0.3)YR and (7.8±0.4)YR, respectively.

‡ ‘Drained’ mesocosms were drained following each ‘upwelling event’; ‘Saturated’ mesocosms were held saturated throughout the experiment; ‘Alternating’ mesocosms were drained or remained saturated after an upwelling in a cyclic fashion.

§ Only statistically significant differences are displayed. Munsell hue, value and chroma of individual horizon types are displayed in table 3.2, and overall averages across mesocosms may be found in table 3.4

¶ Uncertainties are standard error.

# 10.00YR=0.00Y.

†† ‘\*’ indicates significant difference relative to Reference mesocosms at the 0.05 level.

‡‡ Within rows, means followed by the same lower-case letter are not significantly different according to Tukey-adjusted means comparison tests at the 0.05 level.

\*\*\* indicates significant difference relative to Reference mesocosms at the 0.001 level.

¶¶ ‘Surf. Removal’ mesocosms had 2 cm of surficial materials removed; ‘O-Addition’ mesocosms had 100-g organic materials surficially added. ‘Soil Control’ mesocosms were not altered pedologically, but underwent the various experimental hydrologies.

**Table 3.4 Average Munsell color properties of Undredged mesocosms**

	Hue	Value	Chroma	Abundance (%)
Matrix	(0.2Y)±1.0†	3.5±0.4	1.8±0.4	NA
Concentrations	(8.4YR)±1.8	3.5±0.5	4.2±0.9	8.2±6.5
Depletions	(1.3Y)±2.4	3.4±0.6	1.7±1.1	18.1±15.6

† Uncertainties are standard deviation.

### Undredged mesocosms relative to Reference mesocosms

Relative to Reference mesocosms, soil matrix hues were yellower in the Saturated

O-Addition and Control treatments (Table 3. 5, Ill. 3.5). Regardless of soil treatment,

saturation resulted in yellower soil concentration colors, and in the Drained Control treatment concentrations had redder hues relative to Reference mesocosms (Table 3.5). Comparison of Undredged to Reference mesocosms found that matrix and concentration hues of Saturated treatments were yellower than those of Reference mesocosms (Table 3.3). Elless et al. (1996) observed the yellowing of soil matrices in B and C horizons of soils in toeslope positions relative to soils in higher landscape positions in red Triassic soils in Central Maryland.

**Table 3.5. Interaction between hydrology and soil treatments and comparisons of Undredged mesocosm treatments to Reference† mesocosms.**

Hydrology‡	Soil treatments§	Matrix	Concentrations
		----- Munsell hue¶ -----	-----
Drained	Surf. removal	(0.5±0.4)Y	(7.0±0.6)YR
	Soil Control	(9.7±0.4)YR	(6.1±0.6)YR*#
	O-Addition	(9.9±0.4)YR	(8.3±0.6)YR
Alternating	Surf. removal	(10.0±0.4)YR	(8.6±0.6)YR
	Soil Control	(0.3±0.4)Y	(8.7±0.5)YR
	O-Addition	(0.1±0.4)Y	(8.1±0.6)YR
Saturated	Surf. removal	(9.6±0.4)YR	(9.7±0.6)YR*
	Soil Control	(1.1±0.4)Y**††	(9.3±0.6)YR*
	O-Addition	(0.9±0.4)Y*	(10.3±0.6)YR**

†‘Reference’ mesocosms did not undergo experimental treatments but were otherwise identical to mesocosms used during the experiment. Mean reference mesocosm matrix and concentration hues were (9.8±0.3)YR and (7.8±0.4)YR, respectively.

‡‘Drained’ mesocosms were drained following each ‘upwelling event’; ‘Saturated’ mesocosms were held saturated throughout the experiment; ‘Alternating’ mesocosm were drained or remained saturated after an upwelling in cyclic fashion.

§‘Surf. Removal’ mesocosms had 2 cm of surficial materials removed; ‘O-Addition’ mesocosms had 100-g organic materials surficially added. ‘Soil Control’ mesocosms were not altered pedologically, but underwent the various experimental hydrologies.

¶10.00YR = 0.00Y. Only hue is specified as value and chroma did not exhibit significant interactions between hydrology and soil treatments. Value and chroma of mesocosm soil horizons may be found in Table 3.2. Overall value and chroma of mesocosms may be found in Table 3.4.

# ‘\*’ indicates significant difference relative to Reference mesocosms at the 0.05 level.

†† ‘\*\*’ indicates significant difference relative to Reference mesocosms at the 0.01 level.

## Discussion

### Arrangement of soil horizons

In Undredged mesocosms soil horizons tended to be arranged in the following vertical order: O, mucky A, A, Ag as in table 3.2. Correlating with this tendency for vertical arrangement was a corresponding drop in OC, P<sub>ox</sub> and Fe<sub>ox</sub> (Table 3.2). These trends corresponded to the expected conditions in ditches of decreased OM input with depth, and increased frequency of Fe-reducing conditions with depth since lower

horizons were expected to be in contact with groundwater more frequently. Fe-reducing conditions tend to make Fe more mobile and hence less ubiquitous as a pigmenting agent, leading to soil gleying or the formation of redox features.

### **Redox feature abundance**

Treatments did not affect the abundance of redox features observed. Dredged ditch mesocosms were relatively low in Fe (Table 3.2) and may not have had enough Fe for observable concentrations or depletions to develop. Undredged ditch mesocosms contained soils with abundant OM and Fe. Increased duration of saturated/reducing conditions in these soils might be expected to increase redox feature expression (Morgan and Stolt, 2006; Fiedler and Sommer, 2004), at least to a point (Vepraskas et al., 2006). The failure to observe changes in abundance of redox features in this experiment is likely due to several factors. The majority of the volume of drained mesocosms never experienced reducing conditions such that soil Fe could be mobilized (Chapter 2), and all mesocosms experienced periodic upwellings each of more than a soil pore volume. Any reduced Fe that had migrated toward a macrospore could have been removed by upwelling water. Iron removal from mesocosms was observed in the precipitation of Fe oxides in mesocosm effluent (Chapter 2; Ill. 3.5; Ill. 3.6). Iron removal was also observed in Saturated mesocosms, which contained less Fe than Drained or Alternating mesocosms (Table 2.6). In Alternating mesocosms, simulated-groundwater upwellings occurred following the saturated periods, which likely moved reduced and soluble Fe that might otherwise have precipitated in pore linings upon oxidation when the mesocosm was drained.

## **Yellowing of colors with saturation**

The Saturated treatment resulted in yellower concentrations and depletions than other hydrology treatments, though this yellowing was sometimes less than a Munsell hue unit different from the hues of the other hydrology treatments (Table 3.3) and might therefore be very hard to perceive by the eye. Saturation also resulted in yellower hues (in the matrix and in concentrations) relative to those in Reference mesocosms (Table 3.5). Goethite hues typically span 10YR – 2.5Y with yellower hues favored by smaller crystal size (Schwertmann, 1993). Small crystal size is favored by high phosphate, silicon, or OM contents (Schwertmann, 1993). Since phosphorus and OM (Table 3.2) are abundant in these ditch mesocosms, relatively small crystal size goethite may be expected. Ferrihydrite is a paracrystalline Fe oxide characteristic of high OM environments where Fe(II) oxidation occurs relatively suddenly (Schwertmann, 1993). As such it is characteristic of drainage ditches (Schwertmann, 1993) and has been observed in them (Needelman et al., 2007b; Schwertmann, 1966) or in drainage pipes (Schwertmann and Fischer, 1973). Ferrihydrite is a redder pigment than goethite, typically having hues between 5 YR and 7.5 YR (Schwertmann, 1993). It is also generally more soluble than more crystalline Fe oxyhydroxide minerals (Schwertmann, 1991). The yellower hues associated with constant saturation in my mesocosms may be due to the preferential dissolution of ferrihydrite over the small-crystal-size goethite. Yellowing in a Brazilian orison has been attributed to the transformation of hematite to goethite (Fritsch et al., 2005).

My mesocosms were extracted from ditch soils which receive significant amounts of Fe carried in discharging water to the ditch soil from pyrite-bearing marine sediments



in the surrounding landscape (Vaughan et al., 2008; Ill. 3.2). In this experiment there was no addition of Fe to the system, and Fe emerging with simulated groundwater was flushed from mesocosms (Chapter 2). During interupwelling periods saturated-state mesocosm soil would seek equilibrium with soil pore water Fe. Since no Fe was included in the water added to mesocosms all of the Fe present in soil pore water would have to come from the mesocosm soil. The omission of Fe in simulated groundwater therefore likely induced heightened loss of Fe from soil mesocosms relative to ditch soils in the field. The difference in Fe lost between soils in my laboratory mesocosms and soils in the field would depend on groundwater concentrations of Fe, which have not been described.

### **Silt caps**

Thin (0.5 – 3 mm) silt caps were observed as the uppermost layer in Alternating and Saturated mesocosms but not in Drained mesocosms. Silt caps may represent a translocation associated with upwelling events in mesocosms that were saturated prior to the upwelling, but no suspended sediment was observed in effluent water during upwellings. Rather, periodic replenishment of mesocosm headwater, performed so that introduced water was deflected so as not to hit the soil surface directly, may have disturbed high *n* value materials induced by saturation (Vaughan et al., 2008), with silt settling last, forming caps. The introduced water was distilled so that ionic strength would not build over time in the mesocosms, but the low ionic strength of the water may have further contributed to dispersion of surface material. A water reservoir used by Gray (2010) provides a means of manipulating mesocosm water level with no direct disturbance of the soil surface.

## **Evidence for substantial post-dredging colluviation and alluviation**

Previous research of ditch morphology describes the upper surface of ditch C horizons as reflecting the depth of the most recent dredging event (Vaughan, 2005). This is likely not the case as there appears to be substantial colluvium/alluvium present as structureless material in the upper parts of Dredged-ditch mesocosms (Ill. 3.7). Structureless materials would likely have formed when colluvium from exposed ditch banks became dispersed by surficial ditch water (Ill. 3.4). Note the 'islands' of A horizon material (Ill. 3.4) that fell into the ditch. The platy structure of materials in the lower parts of Dredged-ditch mesocosms (Ill. 3.7) may reflect the structure of subsurface marine sediments, or it may be induced by the scraping action of the dredging bucket, as in plow pans. In these soil mesocosms we believe the subsurface materials of platy structure reflect the actual depth of dredging. The thick ( $11.6 \pm 4.6$  cm) layer of colluvium/alluvial material present in my dredged-ditch mesocosms indicates a loss of drainage capacity just two weeks post dredging.

## **Conclusions and Implications**

My study examined the morphological effects of hydrologic and addition/removal treatments applied to soils from a drainage ditch sampled before and after dredging. No change was observed in the abundance of redoximorphic features as a result of my manipulations. My experimental methods did not favor development of redox concentrations since periods of reduction and saturation ended with upwellings of water that flushed Fe from the system.

Instead, relative to other treatments, constant saturation developed yellower hues both in the soil matrix and in iron concentrations. This yellowing is interpreted as a loss of paracrystalline ferrihydrite, and an exposure of small-crystal-size goethite. The loss of ferrihydrite, a mineral noted for its P-sorption properties, may indicate diminished P-sorption potential of drainage ditch soils. With further quantification, ditch matrix or redox feature color might be a means of quickly scouting zones of retained P or high P retention capabilities in drainage ditch networks.

Mesocosms taken from the study ditch post-dredging showed a large volume of colluvial/alluvial materials. These materials represent not only a loss of drainage capacity but demonstrate that over extended periods sediment may be exported from newly dredged ditches. To protect water quality, measures may need to be taken to protect stream systems from the short to medium term sediment loads created by dredging.

# **Chapter 4: The influence of temperature, soil redox state and dredging management on phosphorus levels in ditch surface**

## **Water**

### **Introduction**

Field ditches function as intermittent headwater streams in artificial open drainage networks and intercept the water table as it rises following precipitation. Ditches are under scrutiny for the role they play in the conductance of nutrients and agricultural chemicals. The exportation of phosphorus (P) to downstream waterbodies is of concern on the local (Boesch et al., 2005) and global (Rockström et al., 2009) level, and a growing body of studies has inspected management options in ditches in order to minimize P exports (Needelman et al. 2007a).

Unlike nitrogen, P is not redox sensitive under environmental conditions, but it sorbs readily to iron (Fe) minerals which experience large changes in stability as a function of redox potential (Eh) and pH (Lindsay, 1979). Heightened concentrations of P in pore water are routinely recorded in systems that transition from Fe oxidizing to reducing conditions (SurrIDGE et al., 2007; Zak et al., 2004). Redox transitions in ditches are caused by the inundation of ditch soils by rising groundwater, and the consumption of oxygen by the microbial community such that other elements including Fe become electron acceptors of microbial metabolism (Needelman et al., 2007b).

The development of reducing conditions is dependent on temperature and organic matter (OM). Below 8-10 °C in the Mid-Atlantic Piedmont the onset of reducing

conditions is delayed (Vaughan et al., 2009), whereas between 8 and 20°C substantial Fe reduction can be recorded in as little as a week (Rabenhorst and Castensen, 2005).

Sufficient OM is also necessary for reducing conditions (Needelman et al., 2007b) since organic carbon is used by many microbial guilds as an electron and carbon source (Dyer, 2003).

Undredged field ditches contain large amounts of organic matter, much of it concentrated in surficial O and A horizons (Table 3.2; Vaughan et al., 2007). Associated with this organic matter are also large stores of Fe and P (Table 3.2; Vaughan et al., 2007b). Upon dredging these horizons generally are removed (Table 3.2; Needelman et al., 2007b).

There are many environmental and management factors that affect potential release of P directly (by removal or transformation of P), or indirectly (by influencing Eh). While descriptive field studies of ditch soils have been performed (Vaughan et al., 2008; Vaughan et al. 2007a; Vaughan et al., 2007b), few studies have measured ditch processes in the field (Smith and Huang, 2010; Smith, 2009; Kleinman et al., 2007), but many studies have examined ditch materials in controlled settings through the study of mesocosms (Chapter 2; Chapter 3) or fluvaria (Shigaki et al., 2008; Smith and Pappas, 2007; Sharpley et al., 2007; Smith et al., 2006) or batch studies (Sallade and Sims, 1997a). In the mesocosm experiments of chapter 2 and chapter 3, simulated groundwater was inputted into intact ditch mesocosms from below and effluent was collected from the mesocosm top. The Dredged treatment did not alter the P content of mesocosm effluent relative to input, but the Undredged treatment with its high OM, P and Fe contents released greater P in effluent relative to values in input water. The effect of Undredged

mesocosms was amplified if reducing conditions preceded the rise of simulated groundwater.

In uptake experiments in fluvaria in which initial dissolved P concentrations are high (2.5 mg P-L; Shigaki et al., 2008) (16 mg P L<sup>-1</sup>; Smith and Pappas, 2007) materials taken from a ditch before dredging sorbed more P than materials taken from a ditch after dredging. However when these same materials were subsequently exposed to zero-P water for a desorption phase Shigaki et al. (2008) observed less P release from dredged-ditch materials, but Smith and Pappas (2007) and Smith et al. (2006) observed more P release from dredged-ditch materials. The results of Smith and Pappas (2007) and Smith et al. (2006) stand in contrast to those of Smith and Huang (2010) who observed in-the-field decreases in soluble P in ditch reaches which had been dredged in the previous twelve months. While Shigaki et al. (2008) were studying field ditches in the U.S. MACP, Smith and Huang (2010), Smith and Pappas (2007) and Smith (2006) were studying collection ditches in the U.S. Midwest. These ditch systems differ in depth and hydrology and may not fall within the same scope of inference.

There has been no published field study regarding the impact of environmental variables or ditch cleanouts on the P concentrations of MACP ditches. In this paper I present soil and water chemistry data taken from two field ditches. My objectives were to describe variation in ditch effluent P, and some possible sources (temperature, redox state, dredging) of that variation. Also described in this chapter are the results of a field soil study that examined P<sub>ox</sub>, Fe<sub>ox</sub> and Al<sub>ox</sub> over time in the soil surface (0-5 cm) and at depth in cores. This study was intended shed insight into the relationships between the measured variables according to horizon type and position within the ditch.

## Materials and Methods

### Study site

The studied ditches (38°12'22"N, 75°40'35"W) were located at the Research Farm of the University of Maryland, Eastern Shore (UMES), Princess Anne, Maryland. The two ditches were parallel to one another at opposite edges of the same field and drained to the same collection ditch. At their upper reaches these ditches were 0.2 m deep; at their outlets about 0.8 m deep (before dredging). Images of these and similar ditches can be found in chapter 3 and Needelman et al. (2007b). The study ditches were listed as ditches 'Dx1' and 'Dx2' in Vaughan et al. (2007ab and 2008) who characterized the soils in these ditches as Sulfidic, Aeris, Humaqueptic or Typic Endoaquents, or as Typic Psammaquents. In a study of yearly loads and losses of P and N from ditches at the UMES research farm by Kleinman et al., (2007) these ditches are 'Ditch 1' and 'Ditch2'. These ditches are also the subject of Needelman et al. (2007b). Upon the start of field work in Spring/Summer 2005 both ditches had been undredged for at least seven years (Vaughan et al. 2008), and had well developed O and A horizons containing large amounts of OC (Table 3.2; Vaughan et al., 2008). Ditch 1 was dredged in late July, 2006, which increased its depth by approximately 0.25 m. Ditch 2 remained undredged. Rainfall at the site averaged 1110 mm year<sup>-1</sup>; the landscape contained little relief and height above mean sea level was 7 m (Vaughan et al., 2008). Field soils at the site consisted of deltaic and marine sediments overlain by over 20 cm of loessal materials and were mapped as Quindocqua (Fine-loamy, mixed, active, mesic Typic Endoaquilt), Othello (Fine-silty, mixed, active, mesic Typic Endoaquilt) and similar soils (Soil Survey

Staff, 2011). There are many thin parallel layers within the underlying marine sediments with contrasting texture, the fine textured layers are likely aquitards. Some of the fine-textured layers are pyrite-bearing; they are believed to be the source of considerable Fe and sulfur (S) to the ditch system (Vaughan et al., 2008).

## **Datalogging**

Electronic monitoring of ditch water oxygen, pH and temperature and ditch soil redox was begun in May 2005. Both ditches were instrumented with Campbell Scientific (Logan, UT) dataloggers (CR10x) and multiplexers (AM16/32A). Ditch 1 had datalogger stations near its outlet and at its middle; ditch 2 had a datalogger station only at its outlet. Data was recorded every five minutes. Ditch soil redox per horizon was characterized with five hand built Pt electrodes (Owens et al., 2005), a calomel reference (Corning and Fisher brands), and a hand built salt bridge. A correction of +244 mV was added to redox output in order to adjust for the calomel reference against the standard hydrogen electrode. Probes resold by Campbell Scientific (Logan, UT) were used to measure ditch water pH (CSIM11), temperature (107-L) and dissolved oxygen content (CS512). To avoid freezing conditions, probes were typically removed in November and redeployed in April. For protection probes were placed in a rectangular PVC housing with holes drilled in the side to allow ditch water to enter on the upstream side of the housing and exit on the downstream side. Within the housing platinum electrodes were inserted into soil horizons identified from a small hole excavated 1 foot in front of the housing. Housing locations had to be changed several times over the course of the experiment. Therefore for each datalogging station platinum electrodes were not inserted into the same location



and depths throughout the monitoring. However, while depths of horizons changed, the same general horizons were typically found. In undredged ditches: A1 and A2 horizons generally to 5 and 10 cm respectively, and Ag1 and Ag2 horizons generally to 25 and 40 cm, respectively. After dredging of ditch 1 horizons present were C horizons to approximately 4 cm, 18 cm and 30 cm. The pH probe and temperature probe were inserted together into a stilling well which penetrated below the floor of the protective housing. The DO probe rested on the channel bottom of the ditch, within the protective housing. Electronic monitoring of ditches ended in May 2009. Periodically pore water samples or slurries (1:1, DI) were made in order to characterize pH of soil at the same depth that electrodes were buried. Statistical analysis was performed using SAS PROC MIXED to inspect the correlation of pH, DO, and temperature.

### **Ditch effluent P**

Ditch effluent passed through a 0.8-m H-flume from which an automatic sampler (Sigma 900max, Hach Corporation, Loveland, CO) would aspirate flow-proportionate samples. After aspiration, samples were stored at 4°C until analyzed for dissolved reactive P (DRP) using Lachat QuickChem Method 10-115-01-1-A (Diamond 1995) and total P (TP) using a persulfate digestion (Patton and Kryskalla, 2003) of unfiltered samples. Analysis of TP was performed colorimetrically ( $\lambda=712$  nm) using a modification of Murphy and Riley (1962). Sampling and analysis are described in further detail in Kleinman et al. (2007).

Different flow events were considered to be statistically independent, and were binned according to Fe-redox status. Iron redox status was determined using the

Technical Standard for anaerobic conditions ( $Eh < 595 - 60 * pH$ ), an empirical equation developed by the National Technical Committee for Hydric Soils (NTCHS, 2006). At the field site, average pH of soil pore water during saturated conditions was determined to be 5.3, so that  $Eh < 275 = (595 - 60 * 5.3)$  was considered the threshold for Fe-reducing conditions. Flow events for which Fe-reducing soil conditions ( $Eh < 275$  mV) persisted continuously among the uppermost population of redox electrodes for seven days prior to the upwelling were considered 'reducing'; other flow events were considered 'oxidizing'. The period of seven days was chosen to allow reductive dissolution of Fe to reach appreciable levels in newly Fe-reducing soils when temperatures were above 8°C (Vaughan et al. 2009, Rabenhorst and Castenson, 2005).

### **Surficial soil samples**

Surficial soil samples were taken to a depth of 5 cm at four times (August 2005, January 2006, May 2006, and previous to dredging in July 2006). Samples were collected every 20 m at both the ditch channel 'bottom' and at a 'bench' position 10-20 cm away on either side, where the ditch channel began to transition to the ditch bank.

Samples were retrieved using a thin sharpened steel ring of 15.24 cm inner-diameter and height of 5 cm. This device allowed a specific soil volume (912 cm<sup>3</sup>) to be collected. Before sampling, a drywall knife was used to cut into the soil around the outside perimeter of the ring, in order to cut roots and fibrous materials. The ring was then impressed into the soil until the upper surface was flush with the soil. The ring and its undisturbed contents were then removed using a round-point shovel to lift the ring and enclosed sample out of the ditch. The drywall knife was then used to shave the lower

surface of the soil so that it was flush with the sharpened bottom of the ring. The resulting 5-cm-thick disk of soil was then split into distinguishable horizons, which were bagged separately. Samples were stored on ice until brought to the lab on the same day on which sampling took place, and the moist weight of each was measured. Subsamples were taken to measure pH (1:1, DI) and moisture content (loss of mass after 24 hrs in a drying oven at 105 °C). Bulk density was calculated. Samples were then air dried and ground to pass a 2 mm sieve.

### **Soil core samples**

Soil core sampling occurred at four times (August 2005, February 2006, May 2006, and previous to dredging in July 2006). The first two samplings utilized a 5.08 cm coring device which failed after sampling of ditch 1 in February, 2006. A 3.66 cm inner-diameter coring device was used for the latter two samplings. The second and narrower sampler represented an improvement not only in reliability, but in its ability to recover samples from greater depths. After sampling the samples were then frozen at -16°C to preserve sample mineralogy until the cores were opened with a table saw and individual horizons were air dried (because biological information and volatile elements such as nitrogen were not of interest) and ground to pass a 2-mm sieve prior to analysis. Similar to surface samples individual soil core horizons were analyzed for pH and bulk density.

### **Soil phosphorus, iron and aluminum characterization surface and core samples**

Acid ammonium oxalate extractions (20 mL, 0.2-M ammonium oxalate solution acidified to pH=3 with 0.2 M oxalic acid; similar to Sah and Mikkelsen, 1986b) were

performed on 0.5-g subsamples from air-dried and ground surface and core horizons. The extraction occurred in the dark using an end-over-end shaker rotating at 0.33 Hz for 2 hours. Centrifugation at 10,000 rpm for 10 minutes was used to create a solution free of colloidal materials. The supernatant was diluted with distilled water such that oxalate-extractable Fe ( $Fe_{ox}$ ) and Al ( $Al_{ox}$ ) could be measured on an Atomic Absorption spectrophotometer (AAAnalyst 200, Perkin-Elmer, Waltham, MA); oxalate-extractable P ( $P_{ox}$ ) was measured using an ascorbic acid method (Kryskalla, 2003) modified for use on a manually operated colorimeter (Genesis 10, ThermoFisher, Waltham, MA). The ratio of  $P_{ox} (Al_{ox} + Fe_{ox})^{-1}$ , commonly called the degree of phosphorus saturation (DPS), was calculated.

### **Soil carbon and nitrogen from soil mesocosms**

From ditch 1 soil mesocosms were gathered, treated and sampled as reported in chapters 2 and 3. After sampling total organic C and total N were measured using a CHN device (LECO CHN-2000 analyzer, LECO Corp., St. Joseph, Michigan) after grinding with an agate pestle such that ground material passed through a 0.6-mm sieve.

### **Statistical analysis**

#### **Logged data and ditch effluent P**

The SAS (version 9.3, Cary, NC) MIXED procedure was used to inspect the influence of temperature, dredging and soil redox status on effluent P content. The temperature used in the analysis was the average temperature registered by the ditch-deployed temperature probe for the five days previous to the flow event which tripped the

ditch water autosampler. The five day period was chosen arbitrarily before the analysis as a means of coupling the overall P concentration of the flow event with prevailing environmental conditions. Because individual flow events were considered to be independent, multiple units of analysis existed per ditch. This represents a pseudoreplication (Hurlbert 1984) with respect to the true experimental units which were ditches. Therefore the scope of inference for the analysis of logged data is not all ditches similar to my studied ditches, but only the two ditches of this study.

### **Surface samples and soil cores**

Summary tables of surface and soil core data were created from SAS PROC MIXED (version 9.3, Cary, NC) analysis of individual horizons. Regression analyses of surface sample and soil core data were performed with the SAS MIXED and REG procedures. For surface sample regressions the same method described in chapter 2 was used to determine if a linear spline was a better model than a simple linear fit. For soil core data a separate stepwise regression was performed for each horizon type to determine the relative strength of correlation of  $Fe_{ox}$  and  $Al_{ox}$  to  $P_{ox}$  on a horizon basis.

Surface samples were also analyzed for the effect of time of sampling, longitudinal trends (along the length of the ditch) and the effect of cross sectional position in the ditch (bench vs. bottom) sampling locations using the SAS MIXED procedure. To do this data were averaged so that a single value existed per ditch, per sampling time, per longitudinal and cross sectional sampling location. By having a unique value per ditch, sampling time, and sampling location, pseudoreplication (the use of correlated samples as independent samples) was avoided (Hurlbert, 1984). When an

interaction involving sampling time was significant, the SAS MIXED or REG procedures were used to determine which sampling times had significant relationships with the other factor. By examining samples taken from within the same ditch, scope of inference in this analysis is only the two ditches of the study. Data from soil cores were averaged per ditch, per sampling event, and per horizon type to see if changes occurred among horizon types as a function of time of sampling.

## **Results**

### **Logged data**

Ditch 1 contained surface water during 37% and 68% of the study period, before and after dredging, respectively. Ditch 2 was never dredged and contained surface water during 41% of the period of study.

Average pH of ditch surface water at each location was found to be between 5.5 and 6 (Table 4.1). The mean DO content of this surface water was hypoxic ( $<2\text{-}3\text{mg DO L}^{-1}$ ; Rabalais et al., 1999; Ecological Society of America), but Fe-oxidizing ( $>348\text{ mV}$ ,  $\text{pH}=5.5$ ; Stumm and Morgan 1996) and aerobic relative to the technical standard for anaerobic conditions ( $Eh=595\text{-}60\text{*pH}$ ; NTCSH, 2007) (Table 4.4). Measured values of DO may be underestimates as water flow past the DO membrane in my housing was likely below the recommended velocity ( $5.1\text{ cm s}^{-1}$ ; Sensory, Garden Grove, CA) when ditch flow was not at peak. In ditch water samples no correlation was detected between pH and DO ( $P>0.99$ ), pH and temperature ( $P>0.94$ ), or DO and temperature ( $P>0.88$ ).

**Table 4.1. Surface water chemical variables in two ditches measured during rain-induced ditch flows**

Location†	pH-----		DO‡-----		Eh§-----		DRP¶-----		TP#-----	
	n		N	mg L <sup>-1</sup> ‡	n	mV	n	mg L <sup>-1</sup>	n	mg L <sup>-1</sup>
D1O	28	5.9±0.7††	27	0.42±0.31	27	830±55	16	1.4±1.1	16	2.0±1.2
D1M	16	5.6±0.6	15	0.25±0.09	15	859±32	NA	NA	NA	NA
D2O	64	5.7±0.8	62	0.32±0.15	62	843±55	15	1.4±1.1	15	2.3±1.2

† D1O: outlet of ditch 1; D1M: midpoint of ditch 1; D2O: outlet of ditch 2

‡ DO: Dissolved oxygen

§ Eh: Redox potential relative to the standard hydrogen electrode. Calculated from DO using

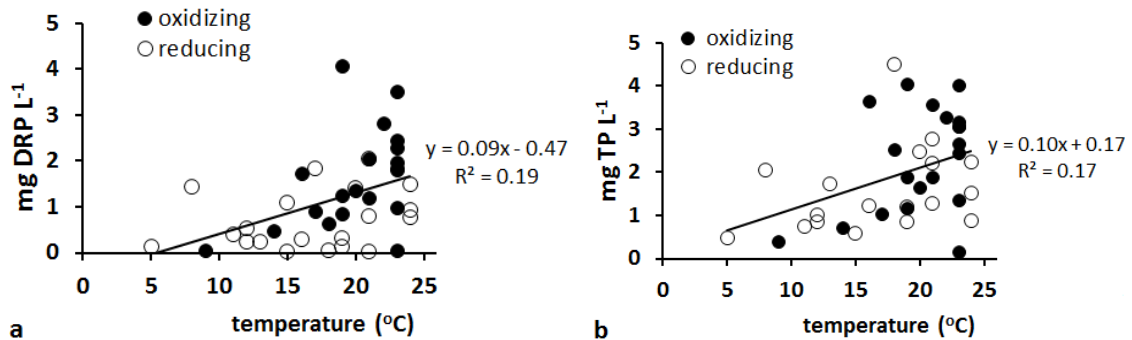
¶ DRP: Dissolved reactive phosphorus

# TP: Total phosphorus

††Uncertainties are standard deviation

### Ditch effluent P and soil redox state

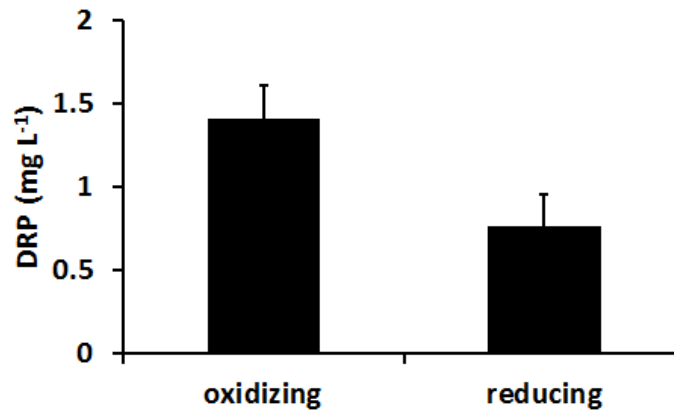
Using the full model (dredging, redox, temperature) no factor or interaction was significant for DRP (i.e.  $p>0.05$ ). However any term involving dredging was highly insignificant (i.e.  $p>0.83$ ). By removing dredging from the model the effect of temperature attained significance for both DRP ( $p<0.02$ ) and TP ( $p<0.03$ ) with increasing temperatures giving rise to greater P concentrations at the ditch outlet (Figure 4.1ab).



**Figure 4.1. P concentration at outlets of two ditches in the Mid-Atlantic Coastal Plain. (a) DRP: dissolved reactive phosphorus; (b) TP: total phosphorus.** Lines result from regression against all data points. ‘[O]xidizing’: within seven days prior to flow-producing rain event redox conditions in the upper-most monitored soil horizon were Fe-oxidizing. ‘[R]educing: within seven days prior to flow-producing rain redox conditions in upper most monitored soil horizon were continuously reducing.

The percent composition of the ditch outlet P was different under different redox conditions ( $p < 0.01$ ). Under oxidizing conditions DRP constituted  $66 \pm 5\%$  of total ditch outlet P; under reducing conditions this percentage fell to  $41 \pm 6\%$ .

The effect of redox status on DRP was not statistically significant ( $p < 0.14$ ), but represented a strong trend with events for which the pre-rainfall redox state was continuously reducing having lower ditch outlet DRP concentrations (Fig. 4.2).



**Figure 4.2. Phosphorus concentration at the outlet of two ditches as a function of the redox state previous to waterflow event.** Oxidizing: uppermost soil horizon monitored was not continuously reducing for seven days previous to the ditchflow event. Reducing: uppermost soil horizon monitored was continuously reducing for seven days previous to the ditchflow event. DRP: dissolved reactive phosphorus. Error bars are standard error. Significance of this difference is  $> 0.05$ .

### Surface samples

Sampling to 5-cm depth at bench and bottom locations of ditch channels revealed only O and A horizons (Table 4.2). These horizons were higher in  $\text{Fe}_{\text{ox}}$  than  $\text{Al}_{\text{ox}}$ , with channel bottoms containing higher  $\text{Fe}_{\text{ox}}$ ,  $\text{Al}_{\text{ox}}$ , and  $\text{P}_{\text{ox}}$  than bench locations and O horizons containing higher concentrations of oxalate-extractable analytes than A horizons



(Table 4.1). Degree of P saturation was the highest in O horizons taken from the channel bottom (Table 4.2).

**Table 4.2. Summary of surface samples (0-5 cm) taken from two ditches at the UMES farm.**

Sampling location† and master horizon type	N	Fe <sub>ox</sub> ‡	Al <sub>ox</sub>	P <sub>ox</sub>	DPS§	ρ <sub>b</sub> ¶	pH
		mmol kg <sup>-1</sup>			%	g cm <sup>-3</sup>	
Bench	A	115 84.5±6.4a#	28.8±2.0a	33.5±2.9a	28±2a	0.61±0.02c	5.2±0.1a
	O	88 144.6±9.5b	42.5±3.5a	56.2±4.0b	28±2a	0.32±0.01a	5.1±0.1a
Bottom	A	114 111.6±8.9ab	37.9±2.3a	43.5±4.0ab	27±2a	0.54±0.01b	5.0±0.1a
	O	104 192.4±12.4c	57.6±6.6b	89.8±6.5c	39±2b	0.30±0.01a	5.0±0.1a

† Bottom: sampling occurred at the lowest point in the ditch channel; Bench: sampling occurred in a slightly elevated position 10-20 cm lateral to channel bottom.

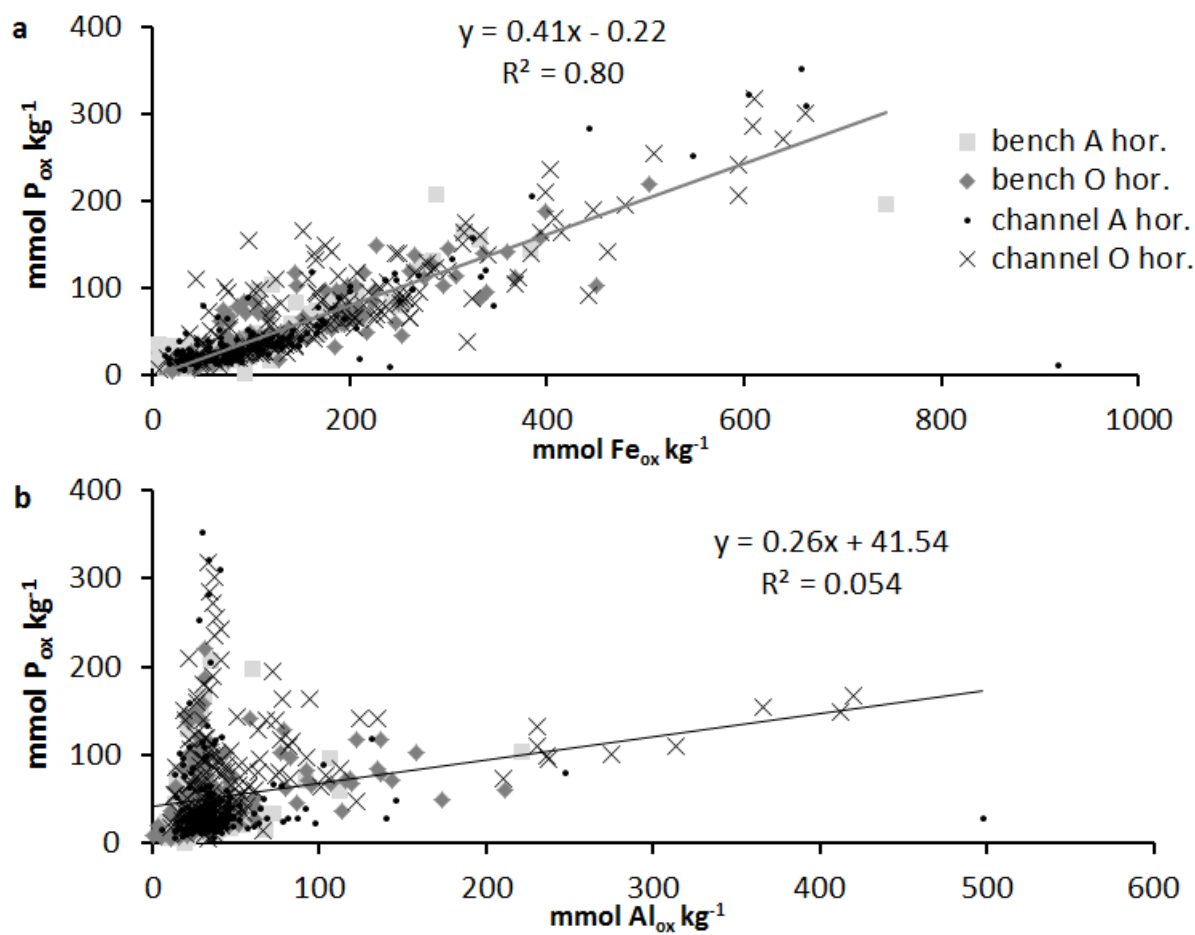
‡ Fe<sub>ox</sub>: oxalate extractable iron.

§ DPS: Degree of phosphorus saturation ( $P_{ox} (Al_{ox} + Fe_{ox})^{-1}$  on a molar basis).

¶ ρ<sub>b</sub>: bulk density.

# Numbers in the same row which do not share the same letter are statistically different at the 0.05 level after Tukey-adjusted means comparisons. Uncertainties are standard error.

Significant relationships in surface samples were found between P<sub>ox</sub> and Fe<sub>ox</sub> ( $p < 0.01$ ; Fig. 4.3a) and between P<sub>ox</sub> and Al<sub>ox</sub> ( $p < 0.01$ ; Fig. 4.3b). However P<sub>ox</sub> was much more correlated to Fe<sub>ox</sub> than to Al<sub>ox</sub> (Fig. 4.3ab). Oxalate-extractable Al was not significantly related to Fe<sub>ox</sub> ( $p > 0.95$ ; Fig. 4.3c). DPS was not tested for a relationship with Fe<sub>ox</sub> (because the two are not independent). The sum of Fe<sub>ox</sub> and Al<sub>ox</sub> was related to P<sub>ox</sub> better through a linear spline (AICC=5881; change point=122 mmolFe<sub>ox</sub> kg<sup>-1</sup>) than through a simple linear regression (AICC=5901) (Fig. 4.3e).



**Figure 4.3. Scatterplots of oxalate-extractable phosphorus ( $P_{ox}$ ), iron ( $Fe_{ox}$ ) and aluminum ( $Al_{ox}$ ) for surficial surface samples (0-5cm) at two ditches at the Research Farm at the University of Maryland Eastern Shore according to horizon type and sampling location. Single outlier at  $> 800$  mmol  $Fe_{ox}$  or  $> 900$  ( $Fe_{ox}+Al_{ox}$ )  $kg^{-1}$  was ignored when regressions were tested. (a)  $P_{ox}$  vs.  $Fe_{ox}$ , (b)  $P_{ox}$  vs.  $Al_{ox}$ .**

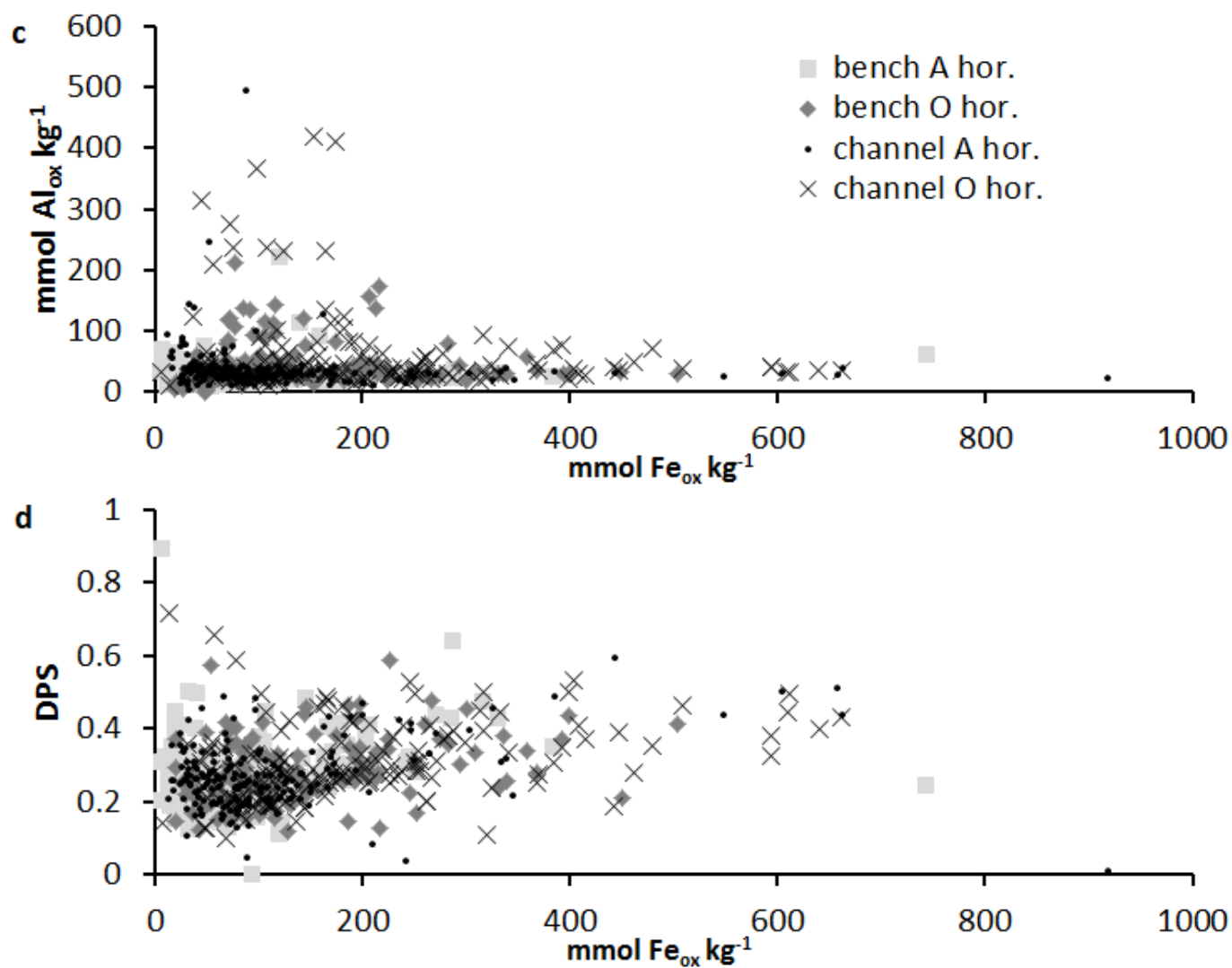


Figure 4.3 (continued) (c)  $\text{Al}_{\text{ox}}$  vs.  $\text{Fe}_{\text{ox}}$ , (d) DPS ( $=P_{\text{ox}} (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})^{-1}$ ) on a molar basis) vs.  $\text{Fe}_{\text{ox}}$ .

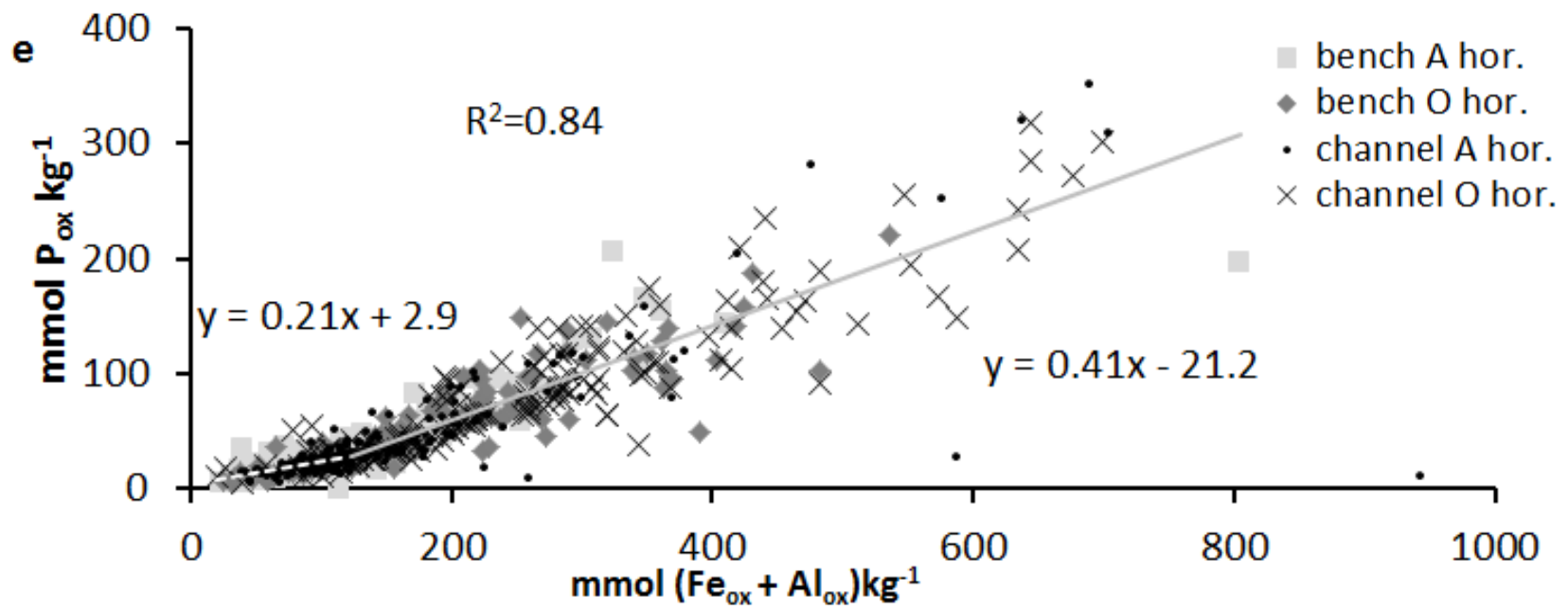


Figure 4.3. (continued) (e)  $P_{ox}$  vs.  $Fe_{ox} + Al_{ox}$ .

When subsamples were averaged to avoid pseudoreplication (Hurlbert, 1984) so that unique values existed per ditch, per sampling time, per longitudinal ditch sampling location and per cross sectional sampling location, results of full-model analyses appeared as in Table 4.3.

**Table 4.3. P values of full model analyses of measured ditch properties**

Effect†	$\log_{10}(\text{Fe}_{\text{ox}})\ddagger$	$\log_{10}(\text{P}_{\text{ox}})$	$\log_{10}(\text{Al}_{\text{ox}})$	pH	DPS§
Xsection	<b>0.0028</b>	<b>0.0007</b>	<b>0.3040</b>	<b>0.9580</b>	<b>0.0761</b>
time	<b>0.3653</b>	<b>0.2830</b>	<b>0.7300</b>	<b>&lt;0.0001</b>	<b>0.4356</b>
Xsection x time	<b>0.0707</b>	<b>0.4983</b>	<b>0.9244</b>	<b>0.1447</b>	<b>0.9356</b>
regression	<b>&lt;0.0001</b>	<b>&lt;0.0001</b>	<b>&lt;0.0001</b>	<b>0.3901</b>	<b>0.0472</b>
regression x Xsection	<b>0.6950</b>	<b>0.4196</b>	<b>0.1950</b>	<b>0.2332</b>	<b>0.0659</b>
regression x time	<b>0.0322</b>	<b>0.0252</b>	<b>0.5984</b>	<b>0.0003</b>	<b>0.8504</b>
Regression x time x Xsection	<b>0.2886</b>	<b>0.4458</b>	<b>0.9938</b>	<b>0.3879</b>	<b>0.9728</b>

† Xsection: cross sectional sampling location (bench or channel); time: time of sampling (Aug '05, Jan '06, May '06, July '06); regression: regression of variable against longitudinal sampling location (0-300 m).  
 ‡ oxalate extracted analytes were  $\log_{10}$  transformed due to non-normality of untransformed populations.  
 § □DPS: Degree of phosphorus saturation ( $P_{\text{ox}} (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})^{-1}$  on a molar basis).

The  $\text{Fe}_{\text{ox}}$  and  $\text{P}_{\text{ox}}$  contents of surficial samples were found to vary according to cross sectional location (Table 4.4). These variables were more concentrated in bottom locations than at bench locations (Table 4.4).

**Table 4.4. Differences in oxalate-extractable Fe and P between bench and bottom locations in surface samples (0-5 cm) taken from two ditches at the UMES farm.**

Sampling location	$\text{Fe}_{\text{ox}}$	$\text{P}_{\text{ox}}$
	-----mmol $\text{kg}^{-1}$ -----	
<b>Bench</b>	<b>73.4±3.7a†</b>	<b>29.0±1.6a</b>
<b>Bottom</b>	<b>105.4±5.2b</b>	<b>43.6±2.4b</b>

† In the same column means and standard errors followed by different letters are statistically different at the 0.05 level.

Regressions of  $\text{Fe}_{\text{ox}}$ ,  $\text{P}_{\text{ox}}$ ,  $\text{Al}_{\text{ox}}$  and pH against longitudinal (ditch length) sampling location were found to show dependence on time of sampling (Fig. 4.4). For  $\text{Fe}_{\text{ox}}$  (Fig. 4.4a) and  $\text{P}_{\text{ox}}$  (Fig. 4.4b) May '06 sampling did not exhibit a linear trend with ditch length ( $p>0.18$ ,  $0.59$ , respectively), but other sampling times did (e.g.  $p<0.05$ ), with higher values of  $\text{Fe}_{\text{ox}}$  and  $\text{P}_{\text{ox}}$  predominating near the ditch outlet. The slopes and intercepts of these statistically significant regressions were not statistically distinguishable from one another for both  $\text{Fe}_{\text{ox}}$  ( $p>0.25$ , slope;  $p>0.16$ , intercept; Fig. 4.4a) and  $\text{P}_{\text{ox}}$  ( $p>0.12$ , slope;  $p>0.40$ , intercept; Fig. 4.4b). The high values for  $\text{Fe}_{\text{ox}}$  and  $\text{P}_{\text{ox}}$  observed at the far end of the ditch system in May '06 (Fig. 4.4ab) eliminated significant regressions over ditch length. Samples taken in May '06 and July '06 exhibited significant linear relationships between  $\text{Al}_{\text{ox}}$  and ditch length ( $p<0.01$ ,  $0.03$ , respectively) (Fig. 4.4c). These linear relationships were not differentiable in terms of slope ( $p>0.12$ ) and intercept ( $p>0.40$ ). The samplings previous to these did not result in significant linear regressions of  $\text{Al}_{\text{ox}}$  against ditch length (Aug '05,  $p>0.99$ ; Jan '06,  $p>0.14$ ); this occurred because of outlying data points at the extremes of ditch length. When these were removed the slope of  $\text{Al}_{\text{ox}}$  vs. length cannot be distinguished between the four sampling times ( $p>0.91$ ) (Fig. 4.4c). In contrast to  $\text{P}_{\text{ox}}$  and  $\text{Fe}_{\text{ox}}$ ,  $\text{Al}_{\text{ox}}$  exhibited increasing concentrations away from the ditch outlet (Fig. 4.4c).

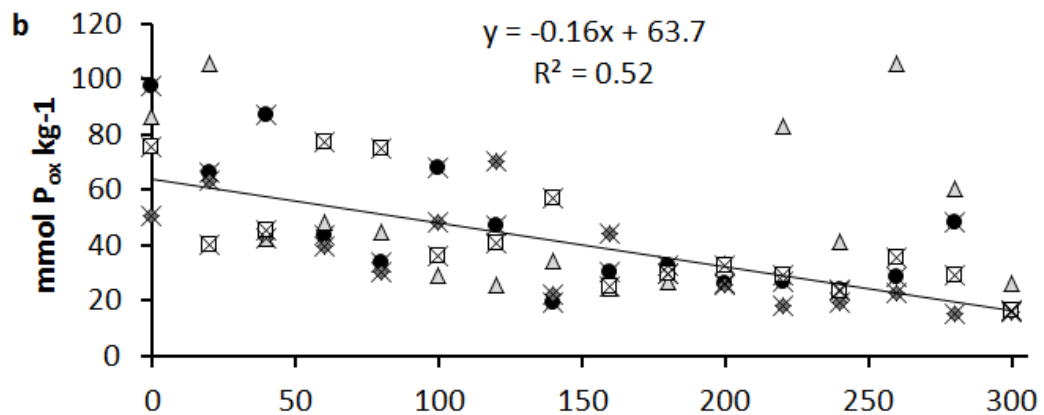
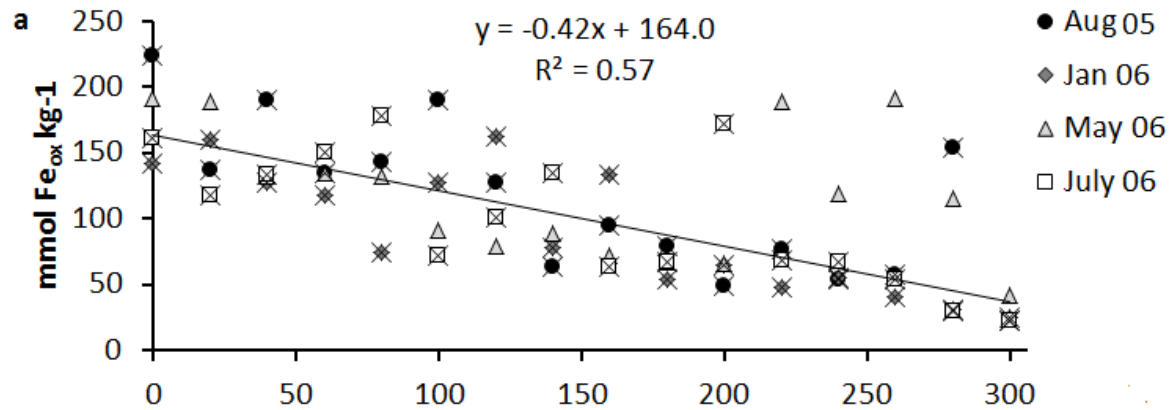


Figure 4.4. Oxalate-extractable iron (Fe<sub>ox</sub>), phosphorus (P<sub>ox</sub>), and aluminum (Al<sub>ox</sub>) versus longitudinal ditch length as a function of time of sampling. Sampling times for which a significant ( $p < 0.05$ ) slope was determined between the measured variable and ditch length in a simple linear regression analysis are denoted with 'X's. Regression lines and equations apply only to sample times with significant relationships. (a) Fe<sub>ox</sub> and (b) P<sub>ox</sub>.

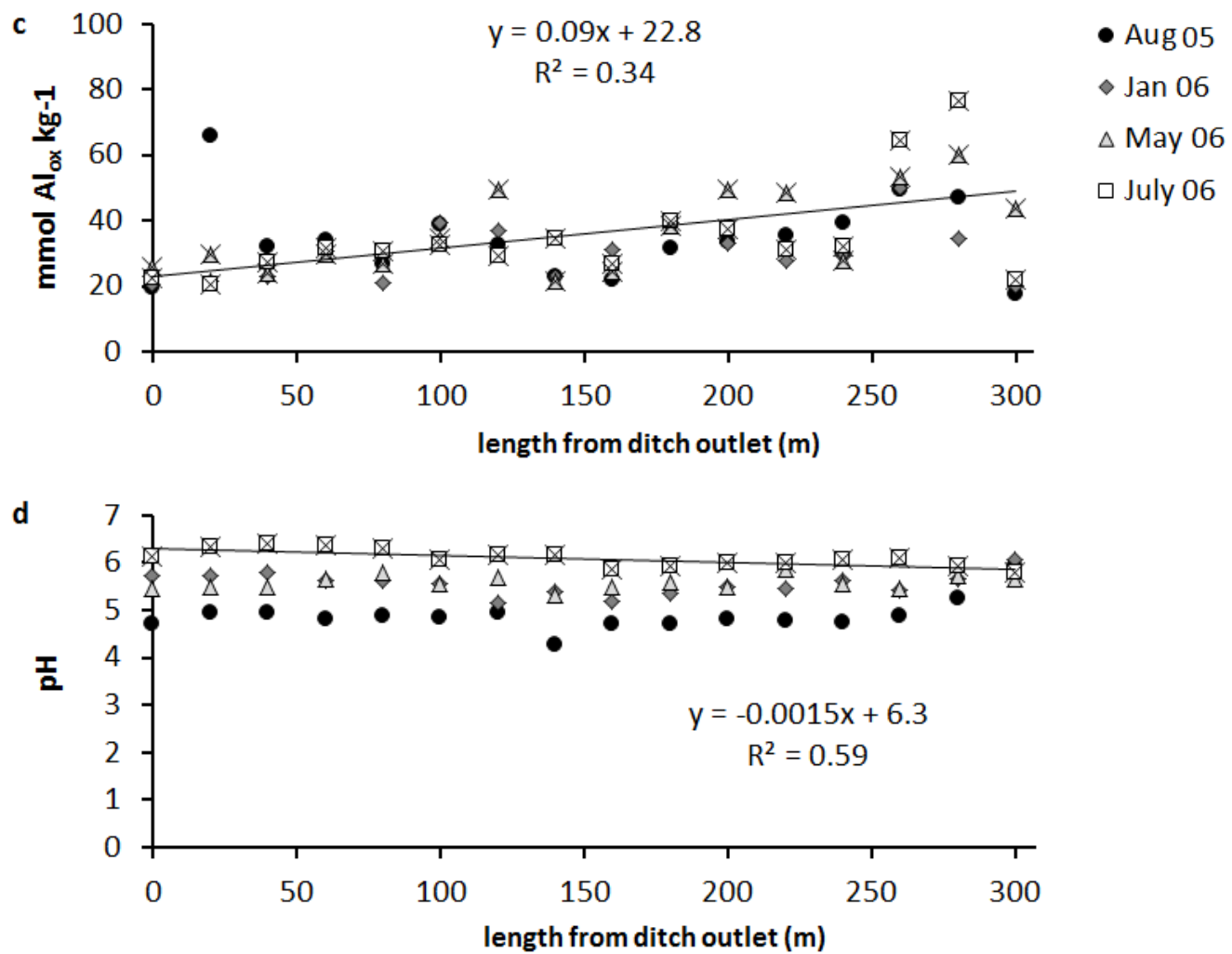


Figure 4.4. (continued) (c)  $\text{Al}_{\text{ox}}$  and (d) pH.



July '06 sampling indicated a slight trend of increasing pH toward the ditch outlet (Fig. 4.4d) in contrast to other sampling times in which no trend with ditch length was detected (e.g.  $p > 0.11$ ). Note the stratification of pH observable in Fig. 4.4d; differences between averages across sampling times were quite significant (see 'time',  $p < 0.0001$ , Table 4.3). July '06 sampling occurred when ditch conditions were inundated after several rain events, whereas August '05 sampling occurred when soils were quite dry (and aerated). This likely explains the higher pHs of July '06 samples vs. the lower pHs of those of August '05.

### **Soil cores**

Soil core horizon  $Fe_{ox}$ ,  $P_{ox}$  and  $Al_{ox}$  dropped off steeply with depth and contained more  $Fe_{ox}$  than  $Al_{ox}$  (Table 4.5). DPS however remained uniform among A horizons and O horizons. Overall,  $P_{ox}$  was related in a simple linear fashion to both  $Fe_{ox}$  and  $Al_{ox}$  (i.e.  $p < 0.01$ ), but correlation was greater between  $P_{ox}$  and  $Fe_{ox}$  ( $R^2 = 0.77$ ) than between  $P_{ox}$  and  $Al_{ox}$  ( $R^2 = 0.48$ ).

However, when broken down by horizon type (Table 4.6) the importance of  $Fe_{ox}$  to  $P_{ox}$  was greatest only in the uppermost horizons (O horizons) of soil cores. In O horizons  $Fe_{ox}$  content provided a better fit of  $P_{ox}$  than  $Al_{ox}$  in a stepwise linear regression. However, in (lower) A, Ag and AC horizons,  $Al_{ox}$  provided better fits. For the deepest horizons sampled (C and Cg) neither  $Al_{ox}$  or  $Fe_{ox}$  had a significant simple linear relationship (e.g.  $p > 0.35$ ) with  $P_{ox}$  (Table 4.6).

**Table 4.5. Summary of selected properties of horizons observed in ditch cores.**

Horizon type†	N	length‡ cm	Fe <sub>ox</sub> § mmol kg <sup>-3</sup>	Al <sub>ox</sub> mmol kg <sup>-3</sup>	P <sub>ox</sub> mmol kg <sup>-3</sup>	Fe <sub>ox</sub> :P <sub>ox</sub>	DPS¶ %	pH	ρ <sub>b</sub> # g cm <sup>-3</sup>
O	29	3	175±12a††	62±5a	69±5a	2.7±4.9ab	29±4a	5.1±0.1ab	0.33±0.10a
A	43	15	39±9b	26±4b	16±4b	2.6±3.8a	26±3a	5.1±0.1ab	0.87±0.08b
Ag	16	13	39±15b	19±6bc	14±6b	4.3±6.2ab	24±6ab	5.2±0.1ab	1.09±0.13bc
AC	24	17	16±12b	7±5c	5±5b	6.4±5.0ab	28±5a	5.2±0.1a	1.46±0.10cd
C	52	33	12±9b	5±4c	1±3c	19.6±3.6b	9±3b	4.8±0.1b	1.61±0.07d
Cg	51	40	9±9b	5±4c	2±3c	13.1±3.6ab	15±3ab	4.9±0.1b	1.48±0.07cd

† Displayed in order of increasing predominant depth found in soil cores with the exception of C and Cg horizons which were found throughout the lower parts of ditch cores in either order and sometimes in alternating order. O, A, Ag and some AC horizons were removed from ditch 1 by dredging part way through my field study.

‡ length: average length of this horizon type across all soil cores.

§ Fe<sub>ox</sub>: oxalate-extractable iron.

¶ DPS: Degree of phosphorus saturation ( $=P_{ox} (Fe_{ox} + Al_{ox})^{-1}$  on a molar basis).

# ρ<sub>b</sub>: bulk density.

†† Within the same column, means and standard errors not ending in the same letter are statistically different at the 0.05 level according to Tukey-adjusted means comparisons. Uncertainties are standard error.

**Table 4.6. Results of stepwise linear regression of soil core data for oxalate-extractable P (P<sub>ox</sub>) vs. Fe<sub>ox</sub> and Al<sub>ox</sub>.**

Horizon type	Best one variable model (primary)	R <sup>2</sup> using only primary	P-value of primary in full model	Other variable (secondary)	R <sup>2</sup> of full model	P-value of secondary in full model
O	Fe <sub>ox</sub>	0.76	<0.0001	Al <sub>ox</sub>	0.83	0.0104
A	Al <sub>ox</sub>	0.26	0.0012	Fe <sub>ox</sub>	0.34	0.454
Ag	Al <sub>ox</sub>	0.94	<0.0001	Fe <sub>ox</sub>	0.94	0.4337
AC	Al <sub>ox</sub>	0.6	0.0001	Fe <sub>ox</sub>	0.61	0.543
C	Al <sub>ox</sub>	0.0074	0.5801	Fe <sub>ox</sub>	0.0091	0.7875
Cg	Fe <sub>ox</sub>	0.0213	0.3552	Al <sub>ox</sub>	0.0239	0.7475

Over the course of the sampling period properties of some horizons were observed to change (Table 4.7). CA horizons exhibited a higher DPS in May '06 than at other sampling times, Fe<sub>ox</sub> was significantly higher in Cg horizons in July '06 than at other sampling times, and P<sub>ox</sub> was significantly higher in O horizons in Aug '05 than at other sampling times (Table 4.7).

**Table 4.7. Soil horizon types with significantly different properties upon repeated sampling over a year.**

Horizon type	Aug '05	Jan '06	May '06	July '06
-----DPS† (%)-----				
CA	0.22±0.03a‡	NA	0.41±0.03b	0.18±0.03a
-----Fe <sub>ox</sub> (mmol kg <sup>-1</sup> )-----				
Cg	6.5±1.6ab	7.7±1.7ab	4.5±1.6a	16.9±1.6b
-----P <sub>ox</sub> (mmol kg <sup>-1</sup> )-----				
O	91.1±4.3a	45.5±6.1b	68.9±4.3ab	46.9±4.4b

† DPS =  $P_{ox} (Al_{ox} + Fe_{ox})^{-1}$  on a molar basis. Where the 'ox' subscript indicates the oxalate-extractable fraction of the element found within the soil horizon.

‡ Within the same row means and standard deviations followed by different letters are statistically different at the 0.05 level.

### Soil mesocosms

Soil horizons were found to have C:N near 15:1 (Table 4.8). Variability in C:N increased in subsurface horizons.

**Table 4.8. C:N ratio of ditch soil horizons**

Horizon	N	C:N
O	18	14±1†
A	188	13±3
Ag	50	16±7
C		NA
Cg	10	17±49

†Uncertainties are standard error.

## **Discussion**

### **Factors affecting ditch effluent P**

#### **Temperature**

The large influence of temperature in positively influencing ditch P was likely due to a microbial mechanism since abiotic desorption phenomena are weakly and negatively temperature dependent (Kadlec and Reddy, 2001). Mineralization, reductive dissolution of P-binding Fe, or extreme soil drying and the release of P upon rewetting (Xu et al., 2011; Turner and Haygarth, 2001) were likely responsible for the positive trend of ditch P with temperature. Microbial activity is generally expected to increase with temperature (Campbell and Reece, 2002), with an approximate doubling of activity with every 10°C increase (Ladd et al., 1985) beyond a 'biological zero' threshold (Rabenhorst, 2005). Reduction of Fe(III) to Fe(II) was found by Rabenhorst and Castenson (2005) to decrease below 2°C even when conditions were anaerobic. These same researchers found that between 2 and 8 °C Fe reduction could be induced, with temperatures above 8 °C supporting substantial Fe reduction within seven days. Between 3 and 13.5°C increasing temperature decreased time needed for saturated Fe-oxidizing soils to become Fe-reducing (Vaughan et al., 2009). Under aerobic conditions gains in microbial activity are thought to continue to 30 or 40°C. Mineralization of P under anaerobic conditions is also positively dependent on temperature (Kadlec and Reddy, 2001). In my data, higher temperatures did not always result in heightened ditch P, but the upper range of ditch P effluent climbed upward (Fig. 4.1a). Carbon to nitrogen ratios similar to finished compost (Brady and Weil, 2008) in all horizon types (Table 4.8) is evidence of mineralization.

Aerobic versus anaerobic mineralization may also be used to explain the share of TP that was DRP. Under oxidizing conditions a greater share of TP was DRP (66%) whereas under reducing conditions only 41% of TP was DRP. Ditch soil C:N, ditch water DRP:TP, and ditch water P content as a function of temperature indicated that aerobic and anaerobic mineralization played an important part in the release of P from my study ditches.

### **Reducing conditions and ditch outlet P**

I observed a trend in which ditches released less P when their soils were Fe-reducing prior to rainfall. I speculate that when soils are reducing, not only does soluble P emerge with groundwater to the ditch surface but that soluble Fe(II) does as well, and that under the Fe-oxidizing conditions (Table 4.1) of freely flowing ditch surface water this soluble Fe is oxidized and precipitated in the presence of emergent P which then has a ready and non-occluded sorption site. Under Fe-oxidizing conditions a relative scarcity of Fe emerges with P so that less P can be retained by mechanisms autochthonous to groundwater. Instead, P emerging under Fe-oxidizing conditions can only be retained by existing surficial oxides and complexes that have DPS values (Table 4.2; Table 4.5) indicating already high saturation of P sorption capacity (Butler and Coale, 2005). In such a case, depending on the equilibrium P concentration of these surface materials relative to surface water P content, even more P may be released. In any event under Fe-oxidizing soil conditions emergent P has no strong retention mechanism as with emergence under Fe-reducing soil conditions.

A P-retaining Fe-reoxidation mechanism has been documented by the same researchers who have observed heightened P concentrations in porewaters of saturated ditch and peat mesocosms. A subsurface layer of P-sorbing Fe oxides was found by Zak et al. (2004) in their studies of saturated peat mesocosms. Their hydrology was static and the Fe-oxides formed were hypothesized by these researchers to have formed at the boundary of Fe-oxidizing and reduced zones which occurred below the surface of the peat. Zak et al. (2004) measured pore water P above and below the Fe layer and found higher P concentrations below than above, hypothesizing that the Fe layer restricted P diffusion into the Fe-oxidizing zone. These researchers assert that when  $\text{Fe:P} > 3$  in Fe-reducing pore water, enough Fe exists to lower pore water P to  $< 1 \mu\text{molL}^{-1}$  ( $0.031 \text{ mgL}^{-1}$ ) under oxidizing conditions. Phosphorus capture by precipitating Fe undergoing oxidation has been used by other researchers to explain pore or surface water P levels within oxic and anoxic zones (Guertz et al., 2010, Heiberg et al., 2010; Surridge et al., 2007).

Unlike Zak et al. (2004), the mesocosm experiment (Chapter 2; Chapter 3) employed a dynamic hydrology in which ditch mesocosm pore water was forced from the mesocosm by simulated groundwater rise. I observed the formation of Fe oxides *outside* of the soil mesocosms, in effluent collection bottles which needed to be acidified to keep the Fe oxides soluble. This demonstrated the occurrence of post-emergent Fe-oxidation of ditch soil pore water, albeit in the context of a laboratory experiment. Nonetheless Fe-oxidation upon emergence into Fe-oxidizing conditions (Chapter 2; Ill. 3.5; Ill. 3.6) and its potential for P sorption (Zak et al., 2004) have been demonstrated.

Surficial reoxidation of within-soil reduced-Fe explains the heightened DPS of channel bottom surface samples (Table 4.2) and the extreme gradient in Fe and P that occurs for soil surficial horizons (Table 4.5). In this study ditch channel bottom O horizons were observed to have heightened DPS relative to other surficial horizons in ditch channel bottoms or bench locations (Table 4.2). Because of their surficial position and often fibric character ditch O horizons feature a large amount of surface area exposed to Fe-oxidizing (Table 4.1) ditch surface water. In the channel bottom location these horizons are exposed most frequently to ditch surface water. Due to their location and structure they are a ready substrate for Fe(hydr)oxide neoformation and therefore for the formation of relatively non-occluded Fe. Event partial reduction may free Fe(III)(hydr)oxides of sorbates (Heiberg et al., 2010). Neoformation of fresh FeIII(hydr)oxides may explain the heightened DPS of these horizons relative to channel A horizons (Table 4.2) which are reducing in their interiors when saturated.

The subsurface reductive dissolution of Fe that I have supposed and its (supposed) export to ditch surfaces where oxidation and precipitation occurs would also explain the steep upward gradient in Fe and P that occurs near the ditch surface (Table 4.5; Vaughan et al., 2007). If correct, then ditch subsurface Fe may largely be the legacy of surficial Fe deposition onto older slowly buried surfaces. This buried Fe and associated P is stored temporarily until it is flushed back up to the new surface.

Even if surficial oxidative Fe-precipitation may be operative in my ditch, it has limited power to curtail ditch P exports in my study. Ratios of soil Fe:P >10 have been found by wetland researchers to be necessary in order to limit P exports below eutrophication thresholds in wetlands (Zak et al., 2010; Guertz et al., 2010) assuming no

additional P sources. In my study  $Fe_{ox}:P_{ox}$  was less than 10 in O and A horizons (Table 4.2; Table 4.4; Table 4.5). Iron's was near 10 for C and Cg horizons, but the absolute amounts of Fe and P in the C and Cg horizons is minimal (Table 4.5). Hence my study ditches have only a limited capacity to control their own P exports let alone the presence of additional P arriving in upwelling groundwater. These ditches would appear to be good candidates for the use of exogenous P-sorbing materials to bolster the presence of P-sorbing elements.

If P retention in my study ditches is a function of surface area, then the narrow geometry of ditches likely constrains their ability to retain P since surface area is limited and burial by colluvium, alluvium, or plant detritus is accelerated. This suggests that more P can be retained using alternative ditch designs in which floodplains (Powell et al., 2007a; Powell et al. 2007b, Katakana and Ward, 2007) or wetlands (Evans et al., 2007) are engineered into ditched landscapes, thereby increasing surface area. Floodplain surface area has been found to correlate positively with increase P retention (Noël and Hop, 2009). Artificial P-sorbing materials can be seen as a means of effectively increasing the surface area of ditches.

### **Dredging**

We did not find that dredging decreased ditch effluent P. High-P materials are removed by dredging (Table 2.5; Table 3.2). Fluvarium water equilibrating with surficial material gathered from ditch 1 before and after dredging found higher P contents in waters exposed to pre-dredging surficial materials (Shigaki et al., 2008). In a Midwest collection ditch dredging reduced P (Smith and Huang, 2010). However, there is



literature that has also demonstrated a lack of P mitigation by dredging (Smith et al., 2006).

A lack of drainage effect in the field experiment may be explained by the fact that: 1) dredging results in soils that are more frequently saturated in their upper parts due to the lowering of the ditch surface and 2) in the mesocosm experiment that Saturated Dredged mesocosms released the same amount of P as Drained Undredged mesocosms (Fig. 2.3c). If dredging removes the ability of a ditch to deliver Fe or other P-sorbing constituents to surface waters (as observed in undredged mesocosms in chapter 2) then surface water P cannot be diminished through sorption to them, and resulting P concentrations at the outlet reflect equilibrium-seeking process between ditch surface water and sediments.

Other mechanisms may be responsible as well for a lack of dredging effect in the field. The Dredged mesocosms of chapters 2 and 3 were gathered soon after dredging, which was before substantial colluvium from surrounding field soils entered the dredged ditch (Ill. 3.4). Field soils at the UMES site are more concentrated in P than are ditch soils, likely because the flushing effect of ditch water desorbs P from relatively high DPS ditch materials. If field soil colluvium entered the dredged ditch as a result of bank instability (Ill. 3.4) then the lack of decreased P effluent with dredging may have been the results of the substantial P introduced into ditch 1 after dredging. Alternatively dredged ditch materials may function neutrally relative to groundwater P as in table 2.4, but groundwater levels may have become subsequently elevated. A third possibility regarding a lack of difference due to dredging regards the likely lateral flow which may often occur at the UMES site due to flat Coastal Plain sediments with many parallel

aquitards (Ill. 3.2). Under such situations, much of the groundwater entering ditches may not rise up through the full bulk of accumulated ditch materials in undredged ditches, or may bypass it altogether and fall into the ditch from an episaturated zone, rendering the difference made by dredging less important. For this hypothesis to be true surface water in equilibrium with undredged materials would have to have similar concentrations as surface water in contact with dredged materials. The experiment by Shigaki et al. (2008), in which dredged and undredged materials were found to have different P-adsorption/desorption behavior would seem to deny on this hypothesis. The limited replication of dredging in this experiment (n=1) merits a subsequent study in which the effects of dredging in many field ditches is measured.

### **Soil data**

Surficial soil samples in the ditches studied show a clear correlation between  $P_{ox}$  and  $Fe_{ox}$  (Fig. 4.3) and a trend during three of four sampling periods of increasing  $P_{ox}$  and  $Fe_{ox}$  with proximity to the ditch outlet (Fig. 4.4). Core samples demonstrate a dominant importance of  $Fe_{ox}$  to  $P_{ox}$  for O horizons (Table 4.6), but also show that  $Fe_{ox}$  becomes of secondary importance for horizons below, with  $Al_{ox}$  being dominant. Interestingly, neither  $Fe_{ox}$  nor  $Al_{ox}$  were well correlated with  $P_{ox}$  in C and Cg horizons. In chapter 2 Dredged mesocosms (Made up mostly of C and Cg horizons) were found to be Fe-reducing under saturation. In this chapter C and Cg horizons were found to be of significantly lower pH relative to other horizons, and of sufficiently low pH for Al to be mobile. I speculate that the ditch C and Cg horizons studied were temporally sufficiently anoxic, and sufficiently acidic to mobilize both Fe and Al. These data were consistent

with the hypothesis that Fe is flushed from subsurface horizons during periods of reduction and upon emergence to the ditch surface the Fe captures P upon oxidation.

Some changes were observed as a result of seasonal sampling in both surficial (Fig. 4.4) and soil core samples (Table 4.7). Among surficial samples a limited number of outlying data points appear to skew the regression analysis away from otherwise consistent trends across different sampling times. Among soil cores the different sampling times resulted in three horizon types with statistically significant differences. These differences show no indication of being interrelated.

## **Conclusions**

In my intensive, though low n study of two ditches in the MACP, dredging did not result in a change in ditch effluent P. However effluent P was correlated with increasing temperature. Periods of constantly Fe-reducing conditions for at least seven days previous to rainfall resulted in a nonsignificant trend in which ditch effluent was lower in P than when conditions were oxidizing for at least some time seven days previous to rainfall. I speculate that mineralization or the heightened release of P from dried and rewetted soils may be responsible for the positive correlation of effluent P with temperature. I also speculate that under reducing conditions Fe is transferred from ditch soils to the ditch surface with groundwater, and that upon emergence this Fe oxidizes and forms a P-sorbing substrate. Observational soil data from the study ditches is consistent with this hypothesis, but this mechanism was not directly measured in this study.

## **Chapter 5: Summary and Conclusions**

### **Summary**

I conducted a mesocosm and field study designed to 1) to gain a soil-profile based understanding of the interactions of P with ditches, 2) to understand the effects of dredging on ditch morphology and P-transport functioning, 3) to measure the effects of saturation on ditch morphology and P-transport functioning, and create hypotheses regarding the effects of controlled drainage on P-transport functioning, 4) to see if ditch P sorption capacity could be enhanced through manipulation of autochthonous ditch materials (soil and water), and 5) to determine the importance of temperature and reducing conditions on ditch P concentrations.

Soil mesocosms were placed in an unbalanced cross factorial design with soil (dredged, undredged with surface removal, undredged control, undredged with surficial organic matter added) and hydrology (drained, saturated, alternating) as factors. Bottom to top input of simulated groundwater was used to evaluate pore water P concentrations, and destructive sampling of mesocosms after the experiment was used to inspect impacts upon soil. In the field study, logged soil (redox and temperature) data was used to understand conditions antecedent to ditch flow, and was compared with P concentrations obtained from automated samplers. To facilitate intensive monitoring only two ditches were studied, one of which was dredged during the monitoring period. Before dredging the two ditches were repeatedly sampled surficially and with coring devices. A list of the specific results of the mesocosm experiment and the field study is available in the appendix.

## **Conclusions and implications**

**During upwellings ditch soils interiors tend to lose Fe and P, but these elements can be captured upon emergence.**

I observed multiple lines of evidence that ditch soil P sorption is primarily a surficial process and that ditch soil interiors are primarily locations of P release during periods of upwelling groundwater. The conclusion of a lack of P sorption by ditch soil interiors was supported by the mesocosm experiment, in which effluent P was never distinguishably lower than input P in any mesocosm treatments. This was true especially of Undredged mesocosms, which always contributed to the P content of effluent water, even when Fe-oxidizing prior to upwellings. The P concentration of our input water was deliberately chosen based on groundwater data from the field and it was very high: 15-20 times the eutrophication threshold for fresh water. Since exchange substrates are more likely to become sinks for aqueous species at higher concentrations of those species, the ditch soils of the mesocosm experiment would require extremely high aqueous P concentrations before they would become P-sorbing.

The mechanism of surficial P sorption in ditch soils supported by my results is that during periods of Fe-reducing conditions in ditch soils coupled with an upwelling hydrology, Fe and P are simultaneously mobilized from the ditch soil interior to ditch surface water where the oxidation and precipitation of the recently mobilized Fe serves as a substrate for P sorption onto ditch soil surfaces. The mobilized Fe comes from the ditch soils themselves or from deeper groundwater. My results supporting this mechanism from the mesocosm experiment were:

- 1) Saturated mesocosms released P and, in the form of an orange precipitate, Fe. Such a precipitate was not observed in mesocosms that were drained prior to upwellings of simulated groundwater.
- 2) Saturated mesocosms lost soil Fe<sub>ox</sub> and P<sub>ox</sub> relative to mesocosms held in a drained state.
- 3) Saturated mesocosms developed yellow matrix and concentration hues relative to drained mesocosms and reference (not subjected to any treatment) mesocosms. This yellowing was interpreted as a loss of ferrihydrite, which typically imparts redder colors to soils (Schwertmann, 1993)..

Together these findings indicated an upward export of Fe and P from mesocosm soils, and the formation, in the form of an Fe precipitate, of a possible substrate for P sorption.

My field study provided further supporting information for this mechanism:

- 1) Ditch soils exhibited a high downward gradient in Fe and P concentrations from surficial horizons to subsurface horizons.
- 2) Ditch soil horizons typical of the surface were highly correlated in Fe and P; this correlation was weaker for soil horizons deeper in the profile.
- 3) Surficial Fe and P became more concentrated down slope in ditches (consistent with a sedimentation process).

4) Monitoring of ditch effluent P concentrations and ditch soil variables indicated a downward trend in ditch P effluent concentrations when ditch soils had been reducing for seven days.

The hypothesis of surficial P capture by soil-interior-sourced-Fe has the following implication(s):

1) Fe delivery to ditches must be proportionate to phosphorus delivery if ditches are to have a meaningful impact on ditch water P concentrations. Identical implications exist for other P sorbing elements (Al, Ca, Mn). Therefore in the context of ditches the ratio of P (Fe+Al)<sup>-1</sup> (or similar) is better conceptualized not as a soil-derived quantity (like DPS), but as a groundwater-derived 'delivery ratio'.

2) Where Fe is the dominant element behind P capture, the active zone of P sorption in ditches may be constrained by the effective surface area of the ditch, because burial in ditch sediments will turn Fe-captured P into soluble P upon the reductive dissolution of Fe that accompanies burial. Surficial oxidation and reductive dissolution accompanying burial is a form of vertical element cycling that helps to explain the gradient in Fe and P with depth in ditch soils.

3) Accumulation of P in surface water under controlled drainage may not be a concern if near-soil surface waters are oxidizing and sufficient Fe is present in pore water. In unrestricted ditches delivery of Fe and P occurs through convection, but under controlled drainage diffusion likely plays a much expanded role. If pore water constituents diffuse towards a low activity Fe and P zone because of the precipitation of P-sorbing Fe then P

concentrations in surface waters would be diminished relative to concentrations in the absence of such a P-sorbing process. This process – of diffusion and towards an oxidation front – has been called ‘Fe-pumping’ by Sah et al. (1989) and has been observed by other researchers (Zak et al., 2004).

**Ditch effluent P was positively correlated with ditch water temperature.**

Temperature likely is a factor controlling mechanisms more directly responsible for P release, since the correlation between temperature and ditch effluent P was not strong. These mechanisms include aerobic or anaerobic mineralization, or the P release that accompanies the rewetting of soils after a period of drying, since drying rates and temperature are related.

**In the MACP dredging may interact with dredging-related hydrologic changes to curtail otherwise beneficial impacts.**

Dredging resulted in the loss of O and A horizons from the ditch mesocosms and the loss of accumulated OM, Fe, Al and P. In the mesocosm experiment this resulted in diminished P exports relative to Undredged mesocosms, but Dredged Saturated mesocosms were found to deliver the same amount of effluent P as Undredged mesocosms that were in a drained state prior to upwellings.

In the field experiment dredging did not lower ditch effluent P concentrations relative to P concentrations before dredging. Dredging studies show variable impact, with some studies showing diminished P uptake and heightened release of P from dredged-ditch materials (Smith and Pappas, 2007; Smith et al., 2006), others showing the opposite



(Shigaki et al., 2008) and some studies demonstrating improved water quality in the field as a result of dredging (Smith and Huang, 2010).

The lack of dredging effect observed in the field may be explained by the mechanism(s) behind the equivalent P output of Dredged, Saturated mesocosms and Undredged, Drained mesocosms. Dredging lowered the ditch surface putting a greater percentage of the soil profile in contact with groundwater than before dredging. But dredging did not reduce the ability of the ditch soil to become Fe-reducing when saturated, despite the removal of large amounts of carbon. Hence Dredged mesocosms are more likely to be in a saturated and reducing state before an upwelling than Dredged ditches are, and these two states: Saturated, Dredged; Drained, Undredged were equivalent in terms of effluent P in the mesocosm study. Furthermore, if upwelling pore water from dredged soils contains little Fe or other P-sorbing constituents then this pore water would not be able to reduce soluble P upon emergence, and the impact of dredging, despite the removal of much P from the profile, would be smaller than expected.

The performance of ditch impact upon the P cycle depends on many factors, including: the redox state of the soil through which the groundwater is upwelling, the concentrations of P-sorbing constituents in soil materials and groundwater, soil/water temperature, antecedent soil material moisture content, and the presence of competing ions for sorption capacity.

In this dissertation, the impact of dredging on some of these factors was to: 1) lower the ditch surface, saturating a greater portion of ditch soil materials more frequently, 2) remove organic matter, a soil constituent which a) tends to directly

compete with P for sorption onto anion exchange surfaces, but b) indirectly supports P sorption through forming a chelating substrate for colloidal and otherwise dissolved sequihydroxides that retain some P sorption capacity; c) forms a necessary substrate for reducing conditions to develop, and 3) remove P and Fe and other accumulated P-sorbing materials. I did not find that dredging diminished the tendency of ditch soils to become Fe-reducing upon saturation.

By removal of accumulated materials the process of equilibrium-seeking between water and surficial materials is greatly transformed, with much lower P-sorption capacity in place when ditch water P is highly concentrated (because of a lack of P-sorbing elements at the ditch surface), and much lower P desorption potential when ditch water P concentrations are low (because of removed P). Ditch P cycling involves the interplay between loss of P from ditch soils to rising groundwater, versus the ability of the resulting surficial ditch water (through the mechanism proposed above) and surficial materials to capture this emerged P.

**My dissertation does not demonstrate a clear potential for the manipulation of autochthonous materials in ditches at the UMES Research Farm to result in non-eutrophic waters at ditch outlets.**

No treatment in the mesocosm experiment was capable of lowering effluent P relative to input P . This may be because of the suitable mineralogy that ditches naturally develop through redox cycling is difficult to improve.

The Alternating hydrology was intended to decrease the crystallinity of Fe oxides in ditch mesocosms making a larger amount of Fe oxides susceptible to the oxalate extraction, and therefore of a class with especially high P-sorption capacity, but this did not occur (Table 2.6). Such a result is consistent with Needelman et al. (2007b) and other studies in which ditches (Schwertmann, 1966) or drainage tiles (Fisher and Schwertmann, 1973) have been found to contain Fe near-exclusively in oxalate-extractable form. The paracrystalline nature of ditch Fe is consistent with the mechanism of Fe(III) formation in which Fe(II) is oxidized quickly upon emergence into aerated waters as would occur upon groundwater emergence into ditch surface water. At the UMES site a relatively small amount of water found in ditches is delivered through overland flow and therefore the majority of water entering a ditch does so through a groundwater pathway (Kleinman et al., 2007).

The high surface area of paracrystalline Fe renders it well suited to P sorption under oxidizing conditions. If ditch Fe is nearly exclusively in this form then there is little in-ditch manipulation that can be done to increase Fe-based P sorption capacity of autochthonous Fe.

Manipulations of soil surficial materials did not change ditch mesocosm effluent P (Fig. 2.3b). This corroborates the hypothesis of the active site of ditch P capture as a surficial process and not a soil-interior process, or a process requiring certain soil characteristics, save the presence of reducible Fe in the soil profile to serve as a reservoir of surface-oxidizable and P-capturing Fe.

From the mesocosm study there appears to be little opportunity for the manipulation of autochthonous ditch materials (soil) or processes (water) in order to maximize ditch P retention, save perhaps the alteration of ditch geometry towards greater surface area (Evans et al., 2007; Powell et al., 2007a; Powell et al., 2007b). The ditches at the UMES farm export large amounts of P (Kleinman et al. 2007). This calls into question the ability of ditches to act as effective mitigators of chronically over fertilized fields, because notwithstanding the high sulfate presence in groundwaters of the UMES farm, the Fe-rich geologic setting should be relatively advantageous for this purpose. At my field site, to reduce ditch effluent P below concentrations which cause eutrophication exogenous materials such as various P sorbing materials (Ippolito et al., 2011; Penn et al., 2007) or additional management options appear to be necessary. Perhaps the biggest lesson learned from this study is the inadequacy of ditch-based environmental services to reduce effluent P concentrations when industrial scale loads are placed within their landscapes.

## **Additional thoughts and suggestions for further work**

**1) The effect of dredging on field ditch effluent P needs to be quantified using a replicated study.** In the field study reported here only one ditch experienced a dredging treatment. Since dredging is a common practice and has been found by other researchers to offer promise of higher water quality (Smith and Huang, 2010; Shigaki et al., 2007) it deserves further treatment in the MACP.

**2) Field work in MACP ditches needs to be replicated beyond one field site.** Much of the recent work on ditches in the MACP, including this dissertation, has occurred at the UMES Research Farm. Inferences across the whole MACP should not be based on data from one location.

**3) Additional research is needed on alternative ditch designs and P-sorbing materials.** Ditch effluent water almost always had an (overall) average (per event) P concentration exceeding the eutrophication threshold of  $0.02 \text{ mg P L}^{-1}$ . My study manipulating ditch-autochthonous materials failed to diminish input P, and in many cases added to input P that was more than an order of magnitude above levels that promote eutrophication.

**4) Quantification of delivery of P, Al, Fe and other potential P-sorbing quantities is needed in groundwater entering ditch soils, in newly emerging pore water, and in ditch water at various stages in the drainage network.** Such work would give insight to the potential for P capture from a site, and would help serve as a test of the hypothesis that surficial P capture occurs because of surficial Fe oxidation from emerging reduced

groundwater. The work of Zak et al. (2004) and Guertz et al. (2010) would be instructive for those designing such studies.

**5) In the mesocosm experiment the means of inputting water to ditches was unrealistic in that it was discrete and did not simulate the rise and fall of a ditch hydrograph.** The slow descent of groundwater through the soil profile represents a descending oxidation front that could be a source of P capture within the ditch profile. Since this mechanism is diffusion and not convectively controlled it likely represents a small share of potential in-ditch P storage potential. Nevertheless it points to an in-soil P storage process. Vadas et al. (2007) observed a diminishment of well water P over the course of days following rain events. They hypothesized that P was being sorbed by soil mechanisms. If field soils are capable of sorbing P before that P makes it to surface water systems, then the movement of that P should be curtailed. This suggests that ditch depths may want to be more tightly engineered to provide enough rooting depth for plants, but not excessive drainage.

**6) The effects of structure and redox heterogeneity on P sorption and release in ditch soils has not been inspected.** While this study employed intact soils, it did not examine where P is sorbing or desorbing within a ditch soil horizon. By elucidating the locations and relative pool sizes of P sorption and release, it may make it possible to engineer ditch soils more effective at P retention, at least in contexts where P loads are relatively small. While ditch soils in this study exported P during upwellings, the downward movement of subsiding groundwater was not inspected, and as described earlier in the dissertation may be a period when P capture occurs within ditch soils,

though the scale of this P capture is likely small relative to exports during times of upwelling.

**7) Practitioners should re-examine the use of the term ‘undredged’ for future publications.** ‘[U]ndredged’ only has a meaning relative to dredging. Farm managers may not know how to interpret the term or be able to tell if their particular ditch soil is more dredged or undredged in character. Preferable terms to ‘dredged’ might be ‘accumulated’ or ‘accumulating’ since they: 1) describe processes that continue to unfold the moment after dredging ceases, 2) can be qualified (e.g. ‘lightly accumulated’, ‘heavily accumulated’, ‘sediment accumulated’; ‘organic accumulated’), 3) are intuitive, and 4) are close to what might be the best term from a pedology perspective: ‘cumulized’ or ‘cumulizing’.

**8) What does ditch soil P equilibrium look like?** While soils are never in equilibrium, especially ditch soils, they presumably go from a state of low P concentrations to high P concentrations in the period following dredging. During this time the ditch is on average accumulating P. Once the ditch P level becomes more stable (assuming it does) the ditch becomes at times a P exporter or P capturer depending on environmental and management conditions. To understand the role of ditches in agroecological P cycles, quantifying the variables controlling the period of average P accumulation would be an important contribution. This would allow managers to more optimally schedule dredging operations, assuming that erosion of ditch banks can be controlled in more dredging-intensive management regimes.

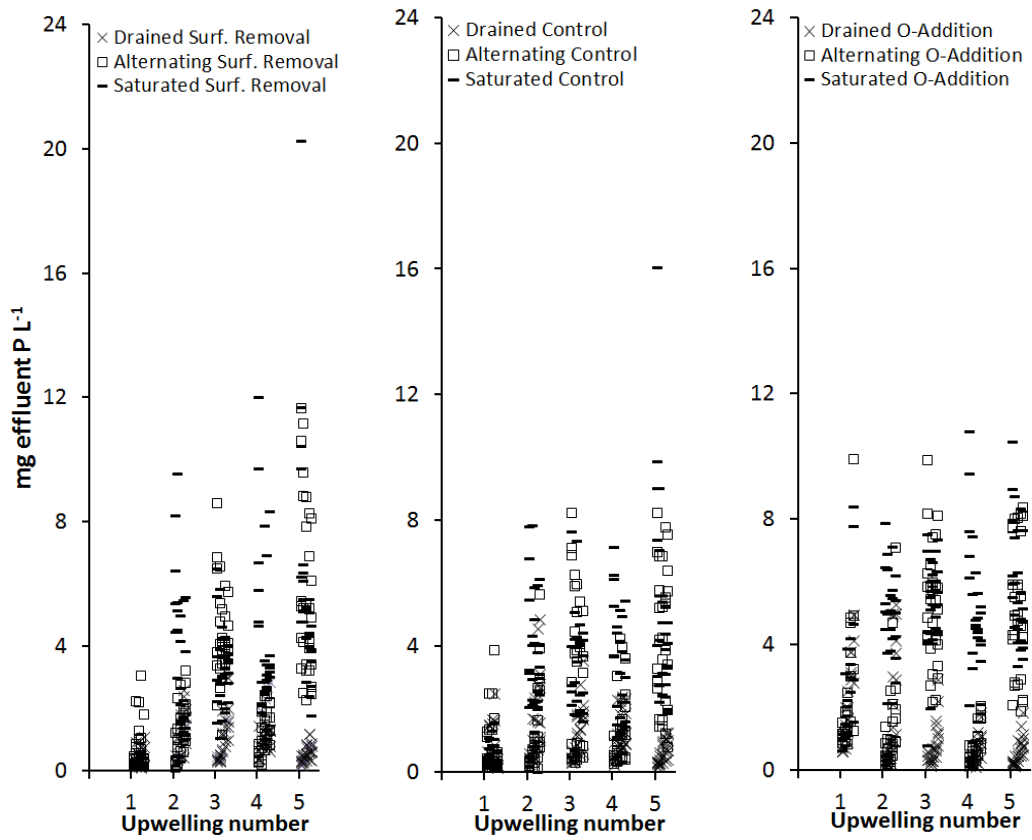
**9) Ditches should not be seen as a silver bullet regarding the limiting of P exports.**

While they are the primary streams of ditched landscapes, ditches are also the last line of

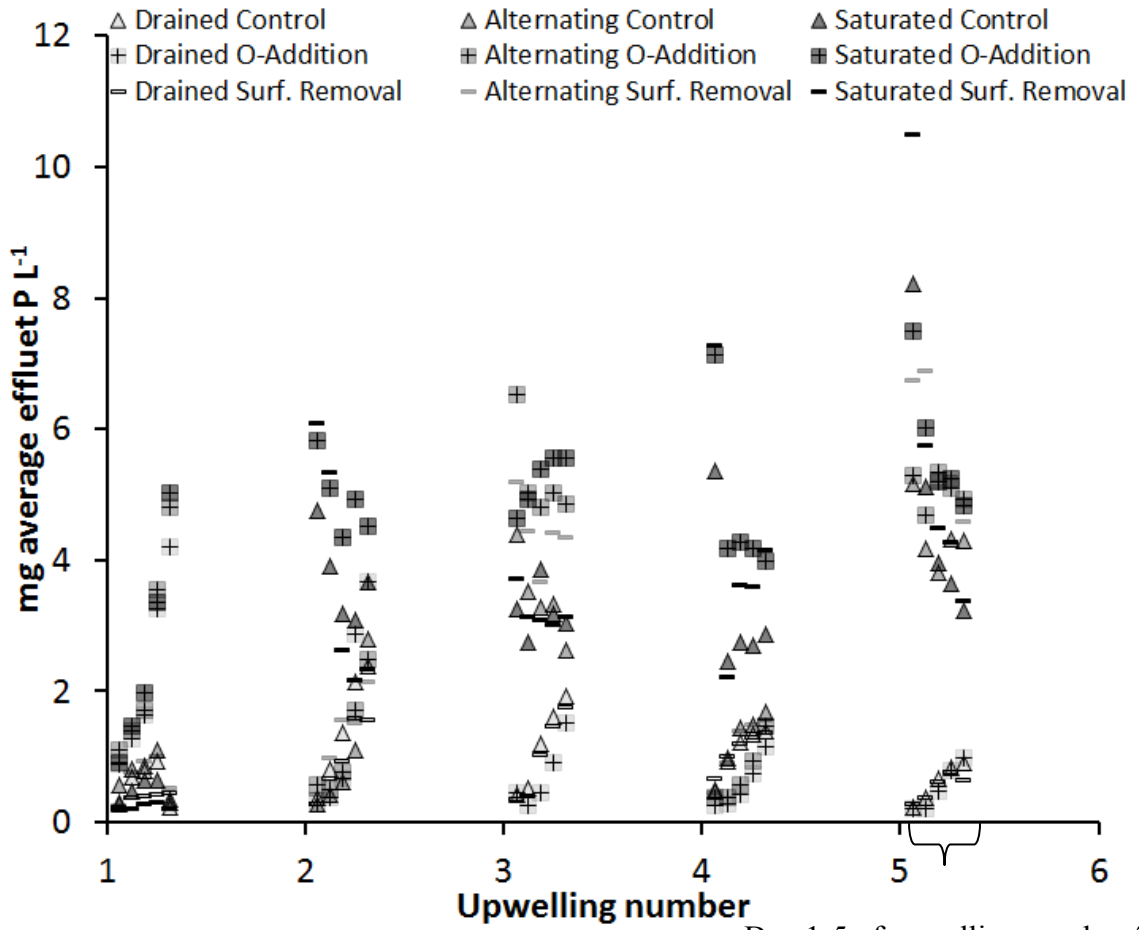
defense at the field scale for excessive nutrient transport. From an ecosystem perspective P exports from field ditches should be below eutrophication thresholds, or even more ideally groundwater P should be below eutrophication thresholds before it makes it to field ditches. From this dissertation and Kleinman et al. (2007) we know that ditches at the UMES farm do not provide non-eutrophying waters to points downstream. While P-sorbing materials or other techniques may be used to address this, the source of the problem ultimately is manure P content and management. The consuming public can only have the opportunity to make informed choices, a suite of choices will only exist, and farm managers can only have the money to handle manure in ways that preclude excessive P movement if the cost of non-eutrophication-inducing manure management is included in commodity pricing. The environmental costs of production should be included in the product's retail price.



## Appendix



**Figure A.1. Raw mesocosm effluent P from the first five days of each of five upwellings of simulated groundwater through mesocosms.**



**Figure A.2. Average mesocosm effluent P from the first five days of each of five upwellings of simulated groundwater through mesocosms.**

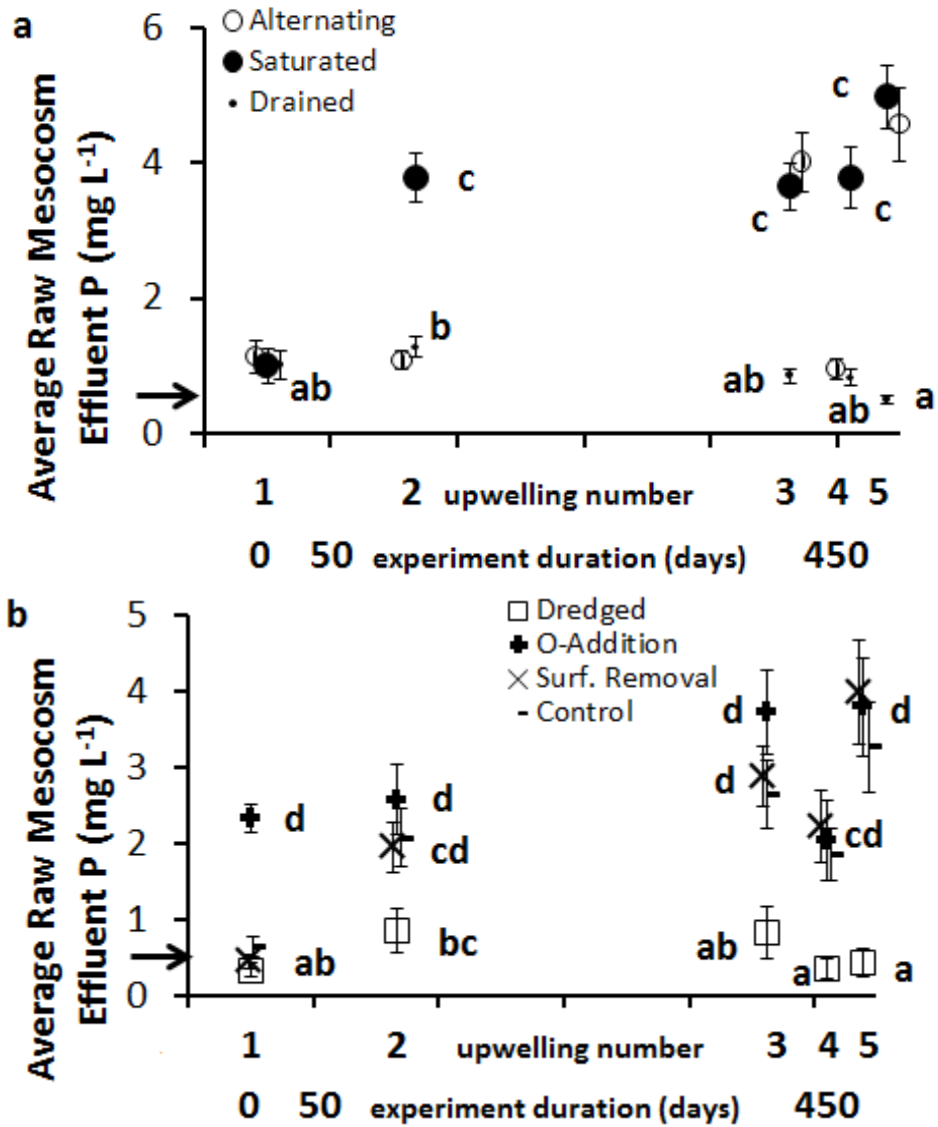


Figure A.3. Mesocosm effluent data displayed according to day of experiment upon which upwellings occurred (a) according to hydrology treatment, (b) according to soil treatment.

**Particular findings of the mesocosm and field study are listed in this portion of the appendix.**

In the mesocosm experiment I found that : 1) Dredged mesocosms contained C horizons of diminished OM, Fe<sub>ox</sub>, Al<sub>ox</sub> and P<sub>ox</sub> content relative to the A horizons of Undredged mesocosms, 2) Dredged mesocosm treatments produced effluent that could not be statistically distinguished from input water, though the power of these tests was small (n=2), 3) Undredged mesocosms produced effluent that was higher in P than input water and Dredged mesocosms, 4) among Undredged mesocosms soil treatments did not have an impact on effluent P, 5) saturation vs. drained states resulted in Fe-oxidizing vs. Fe-reducing conditions regardless of soil treatment, though under saturation Undredged mesocosms could be distinguished according to Eh with greater accumulation of materials resulting in lower Eh, 6) saturation previous to simulated ground water rise produced higher effluent P than when mesocosms were in a drained state prior to the upwellings of simulated groundwater, 7) pre-upwelling saturation produced effluent that created an orange precipitate within an hour after escape from the mesocosm; this precipitate was judged to be Fe-containing, 8) soils of Saturated mesocosms were found to have lost Fe<sub>ox</sub> and P<sub>ox</sub> relative to Drained and Alternating mesocosms, 9) Saturated mesocosms were found to have yellowed matrix and redox feature colors relative to other hydrology treatments, 10) Alternating hydrology mesocosms were not found to have increased Fe<sub>ox</sub> in a statistically significant way, 11) regressions between mesocosm soil P<sub>ox</sub> Fe<sub>ox</sub> and Al<sub>ox</sub> were found to be better fit through a (2-stage) linear spline than through a simple linear model, and that the change point in slope in these models occurred around 115 mmol Fe<sub>ox</sub> kg<sup>-1</sup>, 15 mmol Al<sub>ox</sub> kg<sup>-1</sup> and , 38 mmol P<sub>ox</sub> kg<sup>-1</sup>; these values roughly

correspond to the presence of the least  $P_{ox}$ ,  $Al_{ox}$  and  $Fe_{ox}$ -containing mucky A horizons present in mesocosms, and 12) among mesocosm soils  $P_{ox}$  and  $Fe_{ox}$  were (overall) better correlated than  $P_{ox}$  and  $Al_{ox}$ .

In the field study I found that: 1) ditch effluent concentrations were eutrophic, 2) ditch effluent P was correlated with temperature, 3) ditch effluent P tended toward lower values when the uppermost monitored horizons in ditch soils were saturated continuously for at least seven days before the rain event that caused increased ditch flow (this effect was not significant but was a strong trend; the power of this test was low on account of low replication ( $n=2$ ) in this intensive study), 4) undredged ditch surface samples had high correlation between  $Fe_{ox}$  and  $P_{ox}$ , and poorer correlation between  $Fe_{ox}$  and  $Al_{ox}$ , 5) surface samples from undredged ditches featured correlations between  $Fe_{ox}$ ,  $P_{ox}$  and  $Al_{ox}$  with ditch length, with  $Fe_{ox}$  and  $P_{ox}$  increasing in concentration toward the ditch outlet and  $Al_{ox}$  having increasing concentrations away from the ditch outlet, 6) ditch channel bottoms were higher in  $Fe_{ox}$  and  $P_{ox}$  than ditch channel benches, 7) soil cores taken along the ditch length showed surficial horizons with higher  $Fe_{ox}$ ,  $Al_{ox}$  and  $P_{ox}$  contents than horizons lower in the profile, and 8) the O horizons of soil cores were found to have  $Fe_{ox}$  and  $P_{ox}$  well correlated, but in A horizons  $P_{ox}$  was more correlated with  $Al_{ox}$ ; in C horizons  $P_{ox}$  was not correlated either with  $Al_{ox}$  or  $Fe_{ox}$ .

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