

Phosphorus biogeochemistry of wetlands in agricultural watersheds

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Abstract

Within agricultural watersheds, wetlands are located at the interface between terrestrial uplands and truly aquatic systems. Therefore, the processes occurring within wetland systems affect down stream water quality as water and associated nutrients such as phosphorus (P) are typically transported from upland areas to aquatic systems. This review will describe some of the common forms of P found in wetland soils/sediments and the processes responsible for P transformation and translocation. Phosphorus can enter a wetland as organic and inorganic fractions. Calcium (Ca) compounds determine the availability of inorganic P in alkaline soils while, in acidic soils iron (Fe) and aluminium (Al) controls P solubility. Inorganic P has four main fractions of decreasing bioavailability. Phosphorus sorption is one of the main processes involved in inorganic P biogeochemistry in wetland soils/sediments. Sorption is controlled by the concentration of phosphate in soil porewater and solid phases. Maximum sorption capacity of a soil can be determined using empirical models. Typically, soils only sorb P when added P in solution has a higher concentration than soil porewater. Phosphorus precipitation involves the reaction of phosphate ions with metallic cations forming solid precipitate. Inorganic P forms dominate the bioavailable fractions, whereas organic P fractions typically dominate the total P content of wetland soils/sediments. Organic P compounds can also be fractionated in decreasing order of bioavailability. At the wetland ecosystem-scale processes involved in long term P retention include: sorption on wetland substrates and the accumulation and subsequent accretion of new soil/sediment material.

Keywords: wetlands, phosphorus, adsorption, precipitation, retention, accretion.

Introduction

At the landscape-scale, streams and wetlands form a critical interface between uplands and truly aquatic systems such as lakes and rivers, as all of these systems are hydrologically linked by surface and/or subsurface flows (Mitsch and Gosselink, 1993). Since the Green Revolution of the 1960s this hydrological continuum between uplands, wetlands, and aquatic systems has become disconnected; often times, there are direct hydrological linkages between uplands and aquatic systems or hydrological inputs to wetland areas from uplands, which are extreme, in comparison to natural flows, due to changes in land drainage. Ultimately, changes in land use, for example the conversion of uplands and wetland areas to agricultural land alter natural landscape drainage patterns. In addition, modern agricultural practices typically require nutrient inputs. Phosphorus inputs can include animal feed, artificial fertilizers, animal manures and

biosolids. Historically, animal manures and fertilizers were land applied to agronomic crops and grassland areas based on nitrogen (N) availability in manures and fertilizers, and plant uptake rates of receiving crops (Whalen and Chang, 2001). However, this can lead to excess applications of P with the continued application of manures and fertilizers in some areas resulting in the build up of soil P concentrations above that required for plant growth (McDowell and Sharpley, 2001). Excess applications reported for areas in the US have ranged from 1 to 9 kg P ha⁻¹ (Slaton *et al.*, 2004); whereas annual P surpluses of about 20 kg P ha⁻¹ yr⁻¹ is reported for European farms (Edwards and Withers, 1998). Presently, many nations are adopting a more integrated approach to nutrient management whereby N and P application rates are based on crop uptake, available spread land areas, along with management practices beginning to consider nutrient fate and transport beyond the field, in an effort to become more sustainable (O'Connor *et al.*, 2005).

Both the hydrological alteration of watersheds by agriculture and the imbalance between nutrient inputs and outputs, which ultimately degrades water quality can be somewhat offset or mitigated by the use of both natural and constructed wetland ecosystems (Reddy *et al.*, 1995; Axt and Walbridge, 2003; Bruland, 2003; Koskiahio, 2003). Thus, it is important to understand the biogeochemical processes regulating P transformation and translocation within wetland ecosystems, as P is the main nutrient responsible for the eutrophication of freshwater systems.

The purpose of this paper is to provide an overview of P biogeochemistry in wetland ecosystems. It will outline (i) the forms of P in wetland ecosystems, (ii) characteristics of wetland soils and sediments (ii) inorganic P retention mechanisms, (iii) main forms of organic P in wetlands, and (iv) the processes involved in P retention by wetland systems.

Phosphorus forms in wetland ecosystems

Phosphorus retention within wetlands (either constructed or natural) can be defined as the capacity of that system to remove water column P through physical, chemical, and biological processes, and retain it in a form that is not easily released under normal environmental conditions (Reddy *et al.*, 1999; Reddy and Delaune, In press). When P enters a wetland, it is often present in both organic and inorganic forms, and the relative proportion of each depend upon soil, vegetation, geology, topography and land use characteristics of the surrounding watershed. Phosphorus forms that enter a wetland are typically grouped into: (i) dissolved inorganic P (DIP), (ii) dissolved organic P (DOP), (iii) particulate inorganic P (PIP), and (iv) particulate organic P (POP) (Figure 1).

The particulate and soluble organic P fractions may be further separated into labile and refractory components. Dissolved inorganic P is bioavailable, whereas organic and particulate forms must undergo transformation to inorganic forms before being bioavailable (Reddy *et al.*, 1995 and 1999). Both biotic (biological) and abiotic (non-biological) processes regulate P transformation and translocation. Biotic processes can include assimilation by vegetation, plankton, periphyton and microorganisms; whereas abiotic processes can include sedimentation, adsorption by soils, precipitation, and exchange processes between soil and the overlying water column.

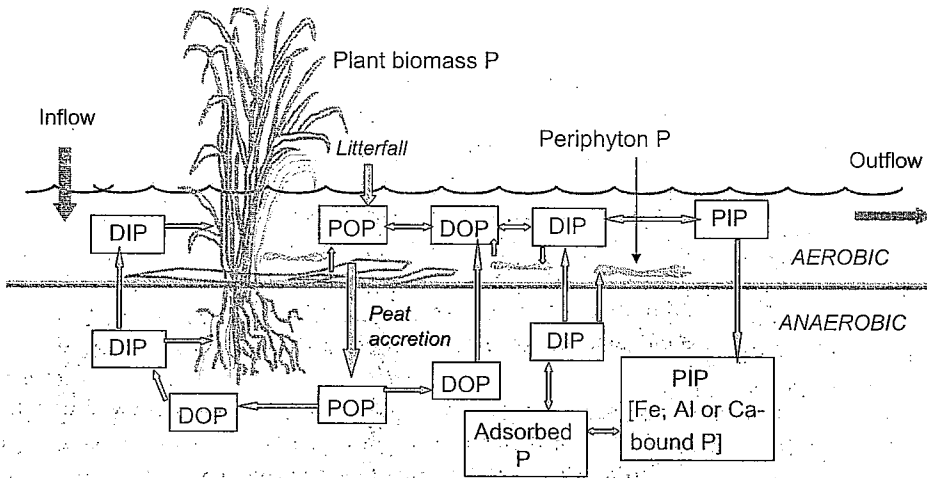


Figure 1. Schematic of phosphorus cycle in wetlands. Phosphorus fractions include dissolved inorganic P (DIP), dissolved organic P, particulate organic P, particulate inorganic P (PIP), soil adsorbed P, iron (Fe), aluminium (Al) and/or calcium (Ca) bound to PIP. (Source: Reddy and DeLaune, In press).

Both organic and inorganic soluble P forms are transported within the water column, but they are transported through soil porewater. Phosphorus present in the water column is subject to changes in physicochemical characteristics of the water itself, as it flows through different reaches of the wetland and associated aquatic systems. The transport processes involved in mobilisation of P between sediment and/or soil porewater and overlying water column are advection, dispersion, diffusion, seepage, resuspension, sedimentation, and bioturbation.

Characteristics of wetland soils/sediments and overlying water columns

Oxygen diffusion in wetland soils is much slower than diffusion in a well aerated terrestrial soil such as an upland grassland soil. Slow O_2 diffusion rate in wetland water columns and high O_2 demand by soil biological communities, results in consumption of O_2 at wetland soil surfaces. This can result in the formation of a predominantly anaerobic soil that has a thin oxidised or aerobic soil layer at the soil/water interface (Mitsch and Gosselink, 1993; D'Angelo Reddy, 1994; Kadlec and Knight, 1996). Thus, two distinct soil layers are often present. They are an aerobic soil layer at the soil surface, where aerobic microbes are involved in biogeochemical reactions that use O_2 as their terminal electron acceptor, and an underlying soil layer that is predominantly anaerobic, where anaerobic microorganisms metabolise using alternative terminal electron acceptors to O_2 such as NO_3^- , Mn^{2+} , Fe^{2+} , SO_4^{2-} and CH_4^+ .

In wetlands that are eutrophic such as wetlands that are used to treat runoff from agricultural areas that have high N and P levels, O_2 concentrations of the water column typically reach low levels or can become anoxic. In such instances, there is not a strong diurnal cycle of oxygen in wetland surface waters (typically during day time, high O_2 levels can occur in water column,

as a result of photosynthesis by algae, while during nighttime microbial respiration leads to a decrease of O_2 in water columns) in comparison to a natural non-impacted wetland.

Inorganic phosphorus

The availability of P in alkaline mineral wetland soils is controlled by the solubility of calcium (Ca) compounds. In mineral wetland soils that are acidic, Fe and Al minerals control the solubility of inorganic P. When soluble P is added at high concentrations to soils, insoluble mineral phosphates can form with Fe, Al and/or Ca. This process results in significant decreases in bioavailable forms of P in soils. Phosphorus loading, pH, and redox potential (a measure of electron pressure that indicates whether soils are aerobic or anaerobic) govern the stability of these phosphate minerals within soils and overlying waters.

Typically, inorganic P forms in soils are characterised based on their differential solubility in chemical extractants. Early fractionation schemes (Chang and Jackson, 1957; Petersen and Corey, 1966; Williams *et al.*, 1971) grouped soil P fractions into: (i) P present as orthophosphate ions sorbed onto surfaces (non-occluded P); (ii) P present within the matrices of P-retaining components (occluded P); and (iii) P present in discrete phosphate minerals. These schemes were modified and adapted to lake and estuarine sediments, which are typically mineral soils and later to wetland soils, which typically have high amounts of organic matter. The inorganic P fractionation schemes adopted identified the following pools: (i) exchangeable P, (ii) Fe and Al bound P, (iii) Ca and Mg bound P, and (iv) residual P (Hietjens and Lijklema, 1980; van Eck, 1982; Psenner and Pucsko., 1988; Cooke *et al.*, 1992; Ruttenberg, 1992; Olila *et al.*, 1995; Reddy *et al.*, 1998).

Two examples in figure 2 show these different P pools that range from relatively labile fractions to more residual P fractions in selected stream sediments and wetland soils of a South Florida agricultural watershed. In this example, the inorganic P extracted with potassium chloride (KCl) represents loosely absorbed P. This fraction is considered bioavailable, therefore it can either be taken up by vegetation and/or microbes. The sodium hydroxide (NaOH) extracted P represents inorganic fractions associated with Fe and Al, and represents P that is not readily available to the overlying water column. However, under anaerobic conditions the P associated with Fe may be released from soil to water (Wildung *et al.*, 1977; Furumai and Ohgaki, 1982; Hosomi *et al.*, 1981), whereas P bound to Al is not affected by changes in redox conditions (Moore and Reddy, 1994). The P flux from soil to water is dependent on the concentration gradient between underlying material and the overlying water column. The hydrogen chloride (HCl) fraction represents P associated with Ca and Mg and is relatively stable and not readily bioavailable. Calcium bound P such as apatite is typically found to be unavailable (Pettersson, 1986; Gunatilaka, 1988). Alkali extractable organic P includes both readily available organic P (microbial biomass P) and slowly available organic P (P associated with fulvic and humic acids). Residual P represents highly resistant organic P or unavailable mineral bound P not extracted either with a strong alkali or an acid.

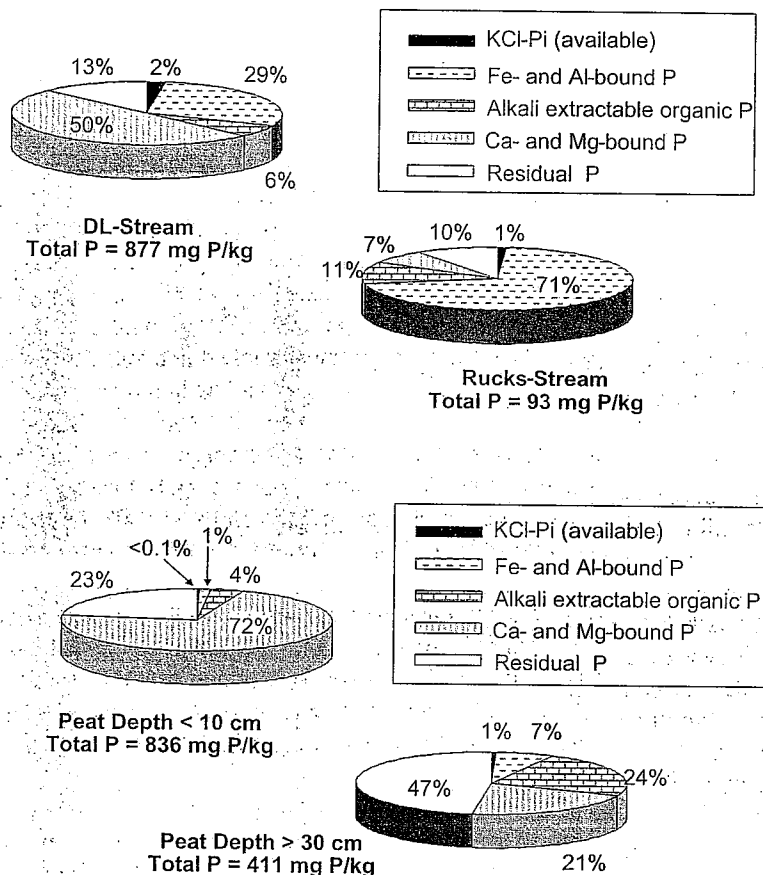


Figure 2. Phosphorus fractions in stream sediments (above) and wetland soils (below) in south Florida (Source: Reddy et al., 1995).

Soil P levels in wetlands

Total P (TP) in soils of wetlands is typically determined by either a wet ashing method or by perchloric acid digestion. Total P content of wetland soils can vary due to physicochemical characteristics, historical nutrient and hydrological loading. Values can range from 30 to 500 mg P kg⁻¹ in wetlands that are not impacted by anthropogenic P loading, whereas wetlands receiving high P inputs for example from confined animal operations, can be up to 10,000 mg P kg⁻¹.

Adsorption-desorption in wetland soils and sediments

Adsorption refers to movement of soluble inorganic P from soil porewater to soil mineral surfaces, where it accumulates without penetrating the soil structure. Phosphorus adsorption capacity of a soil generally increases with clay content or mineral components of that soil (Rhue and Harris, 1999). Absorption is where soluble inorganic P penetrates into the solid

phase and desorption refers to the release of adsorbed inorganic P from mineral surfaces into soil porewater. The balance between P adsorption and desorption maintains the equilibrium between solid phase and P in soil porewater. This phenomenon is defined as phosphate buffering capacity, which is analogous to pH buffering capacity of a soil (Barrow, 1983; Froelich, 1988; Rhue and Harris, 1999).

The sorption of P by soil is controlled by the concentration of phosphate in soil porewater and the ability of the solid phase to replenish phosphate into soil porewater. When soil particles become saturated with P, and soil porewater has low concentrations of P, there is a net movement of P from soil to soil porewater until there is equilibrium between soil and soil porewater P concentrations. Sorption is generally described as a two-step process:

1. Phosphate rapidly exchanges between soil porewater and soil particles or mineral surfaces (adsorption)
2. Phosphate slowly penetrates into solid phases (absorption). Similarly, desorption of P can also occur in a two-step process.

Phosphorus sorption isotherms

The phosphorus sorption capacity of a soil is typically measured using a sorption isotherm in the laboratory by mixing a known amount of soil or sediment with a solution containing a known range of P concentrations. The mixtures are equilibrated for a fixed period (usually 24 hours) at a constant temperature under continuous shaking (Nair *et al.*, 1984). Phosphorus not recovered in solution is assumed adsorbed onto solid phases. The term sorption used in the literature generally refers to both adsorption on the surface of the solid phase (or retaining component) and absorption by the solid phase (diffusion into the retaining component). Typically, P adsorption by soil increases with increasing soil porewater P concentration, until all sorption sites are occupied. At that point, adsorption theoretically reaches its maximum sorption capacity (S_{\max}) as shown in figure 3. Maximum sorption capacity of a soil can be determined using a Langmuir model. Other models commonly used include in soil chemistry include Freundlich and Tempkin models (Reddy *et al.*, 1999; Rhue and Harris, 1999).

A sorption equilibrium between soil and soil porewater P concentrations can be achieved when the concentration of P in soil porewater does not change; therefore the rates of adsorption and desorption are similar, as there is no net movement of P from soil to water or vice versa. This is known as the equilibrium phosphorus concentration (EPC_0). At this point, soils exhibit their maximum buffering capacity for changes in soil porewater P concentrations (Bridgman *et al.*, 2001). At low P concentrations, the relationship between adsorption and soil porewater P concentration is linear. The intercept on the y-axis, as indicated by S_0 (Figure 3) is the P adsorbed or desorbed under ambient conditions. If P is added to soil at concentrations lower than the soil porewater EPC_0 , then that soil will tend to release P, until a new equilibrium is reached and vice-versa. It should be remembered that soils adsorb P only when added P concentration in solutions are higher than soil porewater EPC_0 . Similarly, at the wetland-scale, if the water entering a wetland has P concentrations below EPC_0 , then that soil (in theory) should tend to release P to overlying water. If the water entering a wetland has a P concentration greater than the EPC_0 determined, then that soil should tend to retain P, as the P concentration gradient is from overlying water to underlying soil/sediment.

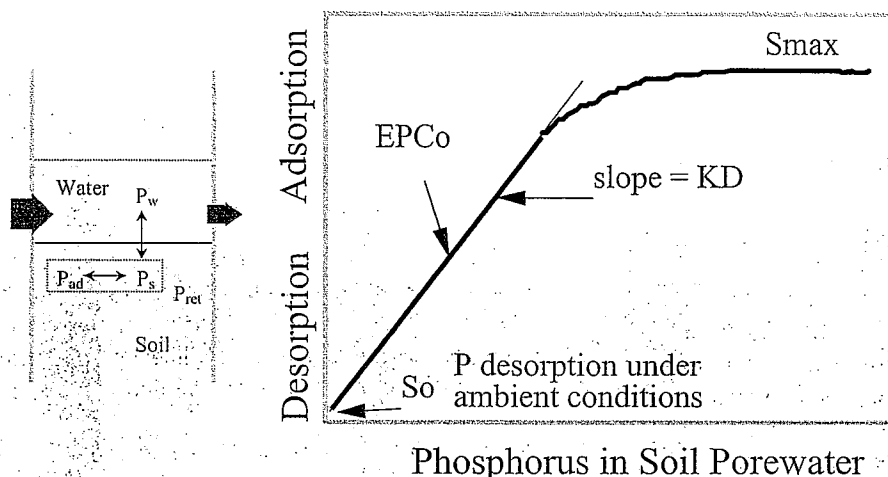


Figure 3. Schematic of phosphorus sorption isotherm. The maximum sorption is known as the S_{max} and is estimated using the Langmuir sorption model. The equilibrium phosphorus concentration (EPC_0) is the solution concentration, where adsorption is equal to desorption; therefore there is no net movement of P. Phosphorus adsorbed or desorbed under ambient conditions is commonly referred to as native adsorbed P (S_0) (Adopted from Reddy and DeLaune, *In press*).

Chemical precipitation reactions in wetland soils and sediments

Precipitation can refer to the reaction of phosphate ions with metallic cations such as Fe, Al, Ca, or Mg, forming amorphous or poorly crystalline precipitate solids. These reactions typically occur at high concentrations of either phosphate or the metallic cations (Rhue and Harris, 1999). An example of some precipitation reactions under alkaline and acid soil conditions are shown in equations 1 and 2.



In calcium dominated wetlands such as areas in the Florida Everglades, the presence of high Ca^{2+} content in water columns can result in the formation of phosphate precipitates such as: calcium phosphate (Equation 1) and hydroxyapatite. Long-term P accumulation in portions of the Florida Everglades was linearly correlated with Ca accumulation, suggesting the possibility of P and $CaCO_3$ interactions (Reddy *et al.*, 1993). Dissolution and solubilisation of solid precipitates can also take place. Dissolution occurs when the concentration of any one reactant decreases below the solubility product of that compound. Of some 200 phosphate minerals identified, only a few are of significance in wetlands. Strengite ($FePO_4$), variscite ($AlPO_4$), and vivianite ($Fe_3(PO_4)_2$), that can occur in wetlands dominated by acidic soils, whereas beta tricalcium phosphate ($B-Ca_3(PO_4)_2$) and hydroxyapatite ($Ca_5(PO_4)_3OH$) can occur in soils dominated by Ca.

Phosphorus retention and release in wetland soils and sediments

Abiotic P retention by wetland soils is regulated by various physicochemical properties present within wetland environments and they can include: pH, redox potential, Fe, Al, and Ca content of soils, organic matter content, P loading, hydraulic loading, and ambient P content of soils. Several researchers report significant correlations between amorphous and poorly crystalline forms of Fe and Al, which are typically extracted with an ammonium oxalate extraction, with P retention (sorption) by mineral soils (Berkheiser *et al.*, 1980; Khalid *et al.*, 1977; Richardson, 1985; Walbridge and Struthers, 1993; Gale *et al.*, 1994; Reddy *et al.*, 1998). It is important to note that in terrestrial soils such as those in grassland pastures, Fe and Al are typically found in crystalline forms, whereas in wetland soils, these ions typically occur in amorphous forms, which have greater surface areas for P sorption reactions to occur. Also, the presence of organic matter in wetland soils and sediments is important in P retention processes (Gale, 1994; Reddy *et al.*, 1998). Iron and Al that complex with organic matter may be responsible for such a relationship, suggesting an indirect positive effect of organic matter complexes on P retention (Syers *et al.*, 1973; Zhou *et al.*, 1997; Rhue and Harris 1999). In contrast, organic matter in terrestrial soils typically occludes P retention mechanisms with negative correlations between P sorption and organic matter reported (Dubius and Becquer, 2001).

In addition to the physicochemical characteristics of soils and sediments, the soil/sediment water interface in wetlands is important in regulating P dynamics. Processes affecting P exchange at the soil/sediment water interface include: (i) diffusion and advection due to wind-driven currents in overlying waters, (ii) diffusion and advection due to flow and bioturbation, (iii) processes within the water column itself (mineralization, sorption by particulate matter, and biotic uptake and release), (iv) diagenetic processes (mineralization, sorption and precipitation dissolution) in bottom sediments, (v) the presence of oxygen at the soil/sediment-water interface, and (vi) P flux from water column to soil mediated by evapotranspiration by vegetation.

Within overlying wetland waters and within soil porewater, the solubility of P is influenced by pH and redox potential (Eh). In a pH range of 5-8, P solubility is low at an Eh of about 300 millivolts (mV), which can result in low P concentration in soil solutions (Patrick, 1968; Patrick *et al.*, 1973). However, as the Eh decreases from 300 mV to -250 mV, P solubility increases at all pH levels, resulting in high P concentration in soil porewater (Ann *et al.*, 2000). Phosphorus solubility is highest under low pH and low Eh conditions. Under acidic conditions, an increase in P solubility is primarily due to reduction of ferric phosphate (Equation 3).



In soils dominated by Fe minerals, reduction of the soluble ferrous oxyhydroxide compounds results in amorphous "gel-like" reduced ferrous compounds with larger surface area than crystalline oxidised forms, as previously mentioned. A reduced soil (that has low or no availability of oxygen; therefore low redox potential) has many more sorption sites, as a result of the reduction of insoluble ferric oxyhydroxide compounds to more soluble ferrous oxyhydroxide compounds (Patrick and Khalid, 1974). Even though reduction increases sorption sites, these sites have lower P bonding energies for phosphate than do the smaller number of

sites available in aerobic soils such as terrestrial grassland soils. Thus, a reduced soil will adsorb a large amount of P with a low bonding energy, thus desorption potential is high, while an oxidised soil will adsorb less P, but hold it more tightly (Patrick and Khalid, 1974). The proximity of aerobic and anaerobic interfaces in wetland soils can promote oxidation-reduction of Fe and its regulation of P solubility to the water column (Figure 4).

In sulphate dominated wetlands, production of hydrogen sulphide (H_2S) (through biological reduction of sulphate (SO_4^{2-}) and formation of ferrous sulphides may preclude P retention by ferrous iron (Caraco *et al.*, 1991). In Fe and Ca dominated systems, Moore and Reddy (1994) observed that Fe oxides likely control the behaviour of inorganic P under aerobic conditions, while Ca-phosphate mineral precipitation governs the solubility under anaerobic conditions.

During an annual timescale both constructed and natural wetland soils and sediments can undergo periods of water flooding, saturation and dry down. Studies undertaking periods of drying anaerobic soils report that phosphate buffering capacity of soils and sediments decreases upon drying (Twinn, 1987; Qui and McComb, 1994; Baldwin, 1996), while others show an increase in the degree of phosphate adsorption upon drying (Barrow and Shaw, 1980). In mineral wetland soils, drying potentially decreases the degree of hydration of iron-hydroxide gels, hence increasing surface area, resulting in increased P sorption. However, McLaughlin *et al.* (1981) observed that drying synthetic iron and aluminium oxyhydroxide increased crystallinity and decreased P sorption capacity. Under flooded and drained conditions, Sah *et al.* (1989a, b, and c) showed an increase in amorphous iron suggesting that a greater surface area was present for P sorption.

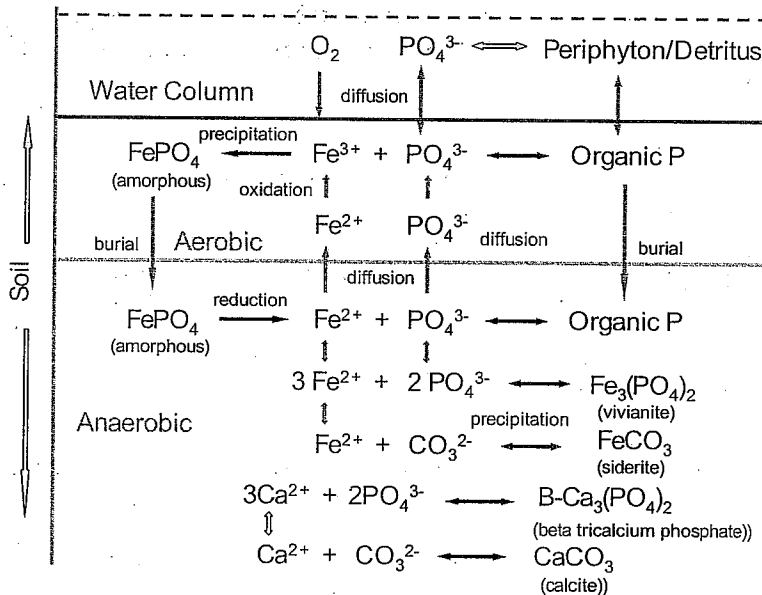


Figure 4. Phosphorus retention and release processes in water column, aerobic soil layer and anaerobic soil layer of a wetland ecosystem (Source: Moore and Reddy, 1994).

Organic phosphorus

Wetland soils are often characterised by the accumulations of organic matter (Mitsch and Gosselink, 1993; Kadlec and Knight, 1996). Due to low mineral matter content and high organic matter content, a large proportion of P in wetlands is stored in organic forms (Reddy *et al.*, 1998; Newman and Robinson, 1999). Sources of organic P in wetlands include the organic P associated with detrital organic matter from macrophytes, algae/periphyton/microbes and organic matter in incoming wetland waters. In terms of a wetland within an agricultural watershed, other organic P compounds can include organic P forms associated with herbicides, pesticides, fungicides and incoming agricultural drainage waters.

Forms of organic phosphorus

Organic P forms can be generally grouped into: (1) easily decomposable organic P (nucleic acids, phospholipids and sugar phosphates), and (2) slowly decomposable organic P (inositol phosphates or phytin). Similar to inorganic P fractions, the fractions of organic P can be conventionally distinguished by sequential and nonsequential alkali and acid extraction and fractionation procedures. They can be classed in decreasing order of bioavailability from; microbial biomass P, labile organic P, fulvic acid bound P, humic acid bound P, and residual organic P. Although these separations allow some evaluation of properties, the organic P fractions can be obscure and variable. Other methods such as bioassays with microbes (bacteria and algae) can yield insights into the bioavailability of organic P fractions. In general, large quantities of organic P can be immobilised in wetland soils, and only a small portion of the total organic P content is bioavailable. A major portion of organic P is stabilised in relatively recalcitrant organic P compounds.

Plant derived organic phosphorus

Phosphorus is a major constituent of macromolecules, particularly in nucleic acids (DNA and RNA), in phospholipids of biological membranes, and as monoesters of a variety of compounds such as those involved in biochemical pathways. In growing microorganisms, more than half of the organic P is in nucleic acids. In plants, inositol hexaphosphate can form a major storage compound for P, particularly in plant seeds. Higher aquatic wetland plants assimilate most of their P by the root-rhizome system from the wetland soil/sediment (Wetzel, 2001). Rates of P uptake and excretion by roots and leaves of submersed macrophytes, (macrophytes are plants that grow in or on the margins of water) are dependent on the P concentrations of soil porewater. Algae, bacteria, and other organisms attached to foliage can assimilate a large proportion of P that is directly removed from the water column (Moeller *et al.*, 1988). During the growing season, about 25 to 75% of the above ground P present in wetland macrophytes is translocated to rooting tissues (Granéli and Solander, 1988; Wetzel, 2001). With vegetation senescence, nutrients and residual fractions of P can leach from plant tissue. The release of P from this material is often rapid and can release from 20 to 50% of total P content in a few hours and 65 to 85% during longer periods (days). Rates of leaching are often greater from roots than from leaves. The residual detrital material is deposited on wetland soil surfaces, and becomes an integral part of the soil, thus providing long-term storage.

Organic phosphorus sorption and precipitation reactions

Organic P is readily sorbed onto clays and soil organic matter. Inositol phosphates are sorbed to clays to a greater extent than simple sugar phosphates, nucleic acids, and phospholipids. The extent and the rate of sorption depend on soil physicochemical properties and the molecular size of organic P. In acid soils, inositol phosphate is regulated by the amount of Fe and Al oxides, while under neutral and alkaline soils inositol phosphate is regulated by organic matter, clays, and Ca minerals. Phyllosilicates such as the clay mineral montmorillonite has greater affinity to sorb organic P than the other minerals such as illite, and kaolinite.

Organic P compounds can form complexes with metallic cations. The ability to form complexes depends on the number of phosphate groups in organic P compounds. For example, inositol phosphates have a greater ability to form complexes than nucleic acids and phospholipids. Similar to humic and fulvic acid complexes with metals, organic P compounds can form stable complexes with Cu^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+} and Ca^{2+} . These complexes are stable at neutral pH. Although, stability of these complexes in wetland soils is not known, soil anaerobic conditions typically increases dissolved organic matter and associated organic P, thus increasing complexation with metallic cations. In minerals soils, reduction of ferric iron to ferrous iron can decrease potential complexation of organic P, whereas oxidation of ferrous iron to amorphous ferric oxyhydroxide can increase organic P complexation.

Phosphorus retention in wetland systems

The mechanisms that remove P in emergent vegetated wetlands both natural and constructed include: sorption on antecedent substrates, storage in biomass, and the formation and accretion of new sediments and soils (Kadlec, 1997). Thus, when evaluating a wetland ecosystem to retain P, all these components should be quantified. The first two processes are saturable, meaning they have a finite capacity and therefore cannot contribute to long-term, sustainable P removal. It is the saturation of these two pools that lead to the advance of a P front such as evident in Water Conservation 2A of the Florida Everglades. New P additions of incoming waters typically create elevated P concentrations in wetland inflow areas. A P gradient exists between inflow points and the downstream unaffected area, both in wetland surface waters and in soils (DeBusk *et al.*, 1994 and 2001). This phenomenon has been observed in both constructed and natural marsh ecosystems, for large and small additional P loadings. Phosphorus gradients are observed to lengthen, and consequently become less steep. For stable annual additions, the position of the gradient achieves a stable position.

The third and main process responsible for long term sustainable P retention is the accretion of new soils and sediments (Richardson *et al.*, 1999). This process has been verified to operative over a wide range of climatic and geographical conditions and accretion rates reported can vary from $0.4 - 4 \text{ g P m}^{-2} \text{ yr}^{-1}$ in natural wetlands (Mitsch, 1992; Faulkner and Richardson, 1989; Craft and Richardson, 1993) depending on degree of impaction. Within the USA, a long-term data base on a northern peat wetland used for wastewater treatment demonstrates that during a 30 year study period the wetland removed over 90% of the added P; peat accreted at a rate of $2\text{-}3 \text{ mm yr}^{-1}$ during operation (Kadlec, 1993).

Conclusions

Within agricultural watersheds wetlands can be located between terrestrial uplands such as grassland and tillage areas and truly aquatic systems such rivers, streams, lakes and estuarine areas. Contaminant and nutrient loss such as phosphorus (P) from agriculture is typically transported from upland areas to aquatic systems. Therefore, due to the landscape position of wetlands, the processes occurring within wetlands, will affect down stream water quality and should be considered in watershed water quality management.

Phosphorus biogeochemistry in wetlands involves a complex of physical, chemical and biological processes occurring in wetland water columns, soils/sediments and biomass. Phosphorus that enters a wetland is in either inorganic and/or inorganic forms. Inorganic forms include exchangeable P, P bound to Ca/Mg, P bound to Fe and Al and remaining fractions of P that are residual. Phosphorus sorption and precipitation are two of the main processes in P retention by mineral wetland soils and sediments. Some of the controlling factors of sorption (which refers to both ad- and absorption) are the concentration of phosphate in soil porewater and the ability of the solid phase to replenish phosphate into porewater. Typically, soils sorb P only when added P concentration in solutions is higher than soil porewater concentrations. Precipitation involves the reaction of phosphate ions with metallic cations (both of which have to be present in high concentrations) forming precipitate solids. In general, abiotic P retention by wetland soils is regulated by various physicochemical properties such as pH, redox potential, Fe, Al, and Ca content of soils, organic matter content, P loading, and ambient P content of soils.

Organic P fractions can be the major portion of the total P content in wetland soils/sediments and usually comprises more than half of the soil total P content. Organic P fractions are also classed in decreasing order of bioavailability. Some organic P fractions can be hydrolysed to bioavailable forms such as fulvic acid bound P, whereas residual organic P is highly resistant.

The mechanisms that remove P at the emergent vegetated wetland-scale, which may be a constructed or a natural system within an agricultural watershed include: sorption on antecedent substrates, storage in biomass, and the formation and accretion of new sediments and soils. The first two processes have a finite capacity to retain P, while the third, accretion of soils and sediments is a sustainable long-term process and the rate of which, depends on nutrient impaction of the receiving wetland.

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