Phosphorus Retention in Streams and Wetlands: A Review

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ABSTRACT: Wetlands and streams buffer the interactions among uplands and adjacent aquatic systems. Phosphorus (P) is often the key nutrient found to be limiting in both estuarine and freshwater ecosystems. As such, the ability of wetlands and streams to retain P is key to determining downstream water quality. This article reviews the processes and factors regulating P retention in streams and wetlands and evaluates selected methodologies used to estimate P retention in these systems. Phosphorus retention mechanisms reviewed include uptake and release by vegetation, periphyton and microorganisms; sorption and exchange reactions with soils and sediments; chemical precipitation in the water column; and sedimentation and entrainment. These mechanisms exemplify the combined biological, physical, and chemical nature of P retention in wetlands and streams. Methodologies used to estimate P retention include empirical input-output analysis and mass balances, and process kinetics applied at various scales, including micro- and mesocosms to full-scale systems. Although complex numerical models are available to estimate P retention and transport, a simple understanding of P retention at the process level is important, but the overall picture provided by mass balance and kinetic evaluations are often more useful in estimating long-term P retention.

I. INTRODUCTION

Phosphorus (P) is one of the major nutrient-limiting in many freshwater ecosystems. During the last 5 decades, many studies have been conducted to determine the fate of P in freshwater systems, including streams and wetlands (Johnston, 1991; Boers et al., 1993; Reddy and Flaig, 1995). At the landscape level, streams and wetlands form a critical interface between uplands and adjacent water bodies, as all of these ecosystems are hydrologically linked. Water and associated contaminants (such as P) are transported from uplands either by subsurface or surface flow. In the context of adverse environmental and ecological impact, nutrients are considered as contaminants. Surface flow can include first-, second-, and third-order streams as well as the associated riparian floodplains, marshes, and swamps. In low-gradient systems, streams are largely composed of interconnected marshes and swamps. To improve drainage in agricultural areas, ditches are often cut to connect isolated wetlands. The resulting flow of water in the drainage basin

follows a complex path through wetlands, ditches, and streams. Thus, P loading to the receiving aquatic system depends on the retention capacity of these components of the basin.

Retention is defined as the capacity of streams and wetlands to remove water column P through physical, chemical, and biological processes and retain it in a form not readily released under normal conditions. Retention of nutrients at wetland and stream interfaces decreases the load to downstream aquatic systems (such as lakes, rivers, fjords, and the sea) (Johnston, 1991). Streams and wetlands not only store nutrients but also transform nutrients from biologically available forms into non-available forms and vice versa. Thus, it is important to include the contribution of streams and wetlands in retaining nutrients when developing best management practices for a drainage basin. Land use practices in uplands, along with processes occurring in the streams and wetlands, should all be considered in nutrient management options for a water body. This landscape approach to evaluating the effects of cumulative impacts of wetlands on water quality has been suggested by Whigham et al. (1988).

Best management practices (BMPs) implemented in upland basins may not be adequate to meet discharge water quality requirements. Consequently, to achieve required load reductions, it may be necessary to consider the nutrient retention capacity of wetland and stream systems. The purpose of this article is to: (1) present a critical review of the processes and factors regulating P retention in streams and wetlands, (2) identify and evaluate laboratory and field methods used to estimate P retention, and (3) identify simple models to estimate P assimilation in streams and wetlands.

II. PHOSPHORUS RETENTION MECHANISMS

Phosphorus entering a wetland or stream is typically present in both organic and inorganic forms. The relative proportion of each form depends on soil, vegetation, and land use characteristics of the drainage basin. To trace the transport and transformations of P, it is convenient to classify forms of P entering into these systems as: (1) dissolved inorganic P (DIP), (2) dissolved organic P (DOP), (3) particulate inorganic P (PIP), and (4) particulate organic P (POP) (Figure 1). The particulate and soluble organic fractions may be further separated into labile and refractory components. Dissolved inorganic P is considered bioavailable, whereas organic and particulate P forms generally must undergo transformations to inorganic forms before being considered bioavailable. Other researchers have proposed three size fractions of P: dissolved (DP, < 0.45 μm), fine particulate (FPP, 0.45 μm to 1 mm), and course particulate (CPP > 1 mm) (D'Angelo and Webster, 1991) to help define sedimentation, transportability, and reactivity. However, these size fractions of P are not necessarily indicative of P bioavailability or chemistry. Both biotic and abiotic mechanisms regulate relative pool sizes and
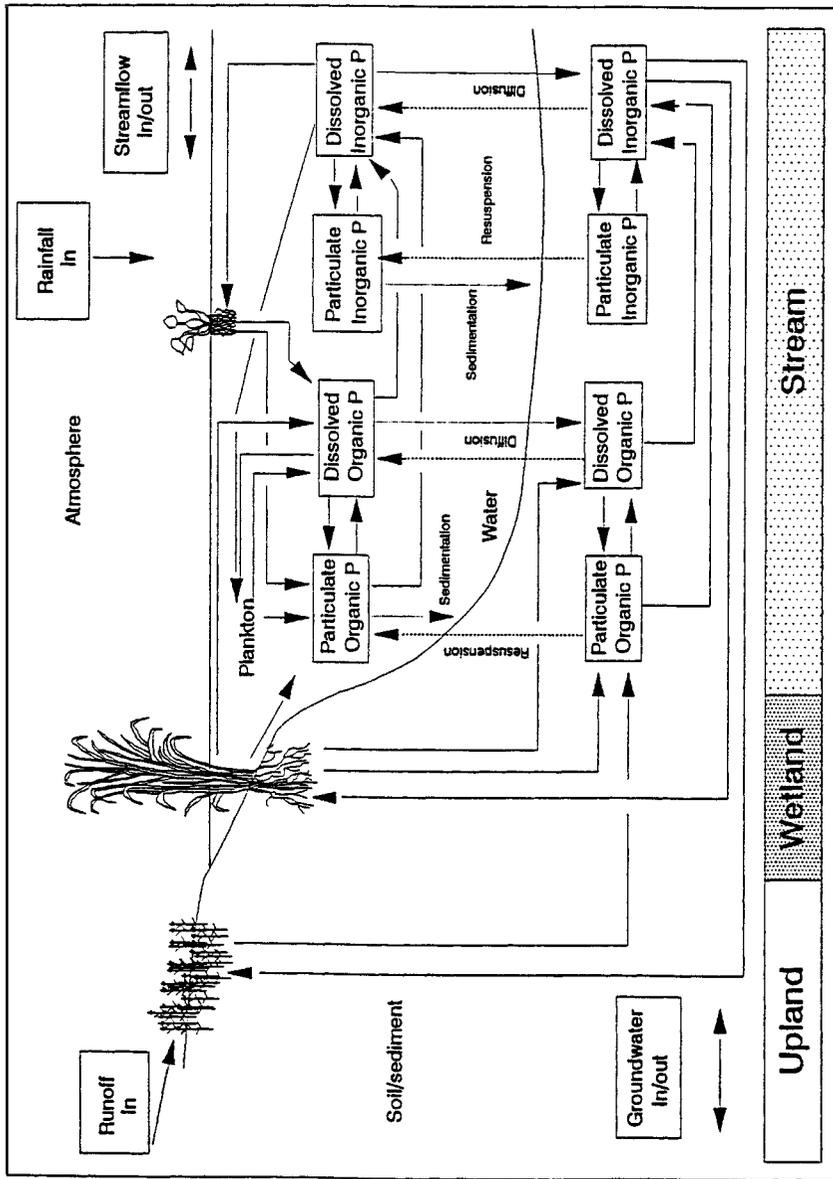
FIGURE 1. Forms and interactions of P in upland, wetland, and stream systems. (From Scinto, 1990.)

transformations of P compounds within the water column and sediment/soil. Alterations in these fractions can occur during flow in streams and wetlands that depend on the physical, chemical, and biological characteristics of the systems (Meyer and Likens, 1979). Thus, when evaluating P retention capacities of wetlands and streams, both biotic and abiotic processes must be considered. Biotic processes include assimilation by vegetation, plankton, periphyton, and microorganisms. Abiotic processes include sedimentation, adsorption by sediments/soils, precipitation, and exchange processes between soil/sediment and the overlying water column.

A. Assimilation and Release by Vegetation

Phosphorus assimilation and storage in plants depends on vegetative type and growth characteristics. Floating and emergent macrophytes are usually present near shorelines of streams, and the P transported in the stream may not be in direct contact with the plant roots. Submerged vegetation has limited potential for P storage, but can alter the physicochemical environment of water, resulting in chemical precipitation (Reddy et al., 1987). Thus, uptake of P by vegetation is typically minimal in stream systems.

In wetlands, however, vegetation often plays a significant role in P assimilation and storage (Figure 2). Floating macrophytes usually are present in areas with deep water and absorb P directly from the water column. Because of rapid turnover, P storage is short-term, and much of the P is released back into water after upon vegetative decomposition (Reddy and DeBusk, 1987; 1991; Mitsch et al., 1995). Emergent macrophytes have an extensive network of roots and rhizomes and have great potential to store P. They have more supportive tissue than floating macrophytes and have a high ratio of below-ground biomass (roots and rhizomes) to above-ground biomass (stem and leaves), providing ideal anatomical structures for P storage.

Although emergent macrophytes effectively store P, very little of the water column P is directly assimilated by these plants (Richardson and Marshall, 1986). Such plants are rooted in soil, and the majority of their P requirements is usually met from soil porewater P. For example, Correll et al. (1975) found surface roots of *Typha* to be responsible for removal of added ^{32}P, but there was no evidence of direct absorption from the water column. Similarly, Davis (1982) detected only 2 to 4% of added ^{32}P in the living tissue of *Cladium* and *Typha*. Although water column P is not assimilated directly by these plants, active uptake of soil porewater P can potentially establish gradients between the water column and soil/sediment, thus improving overall P retention.

Phosphorus uptake by macrophytes is maximum during the peak growing season, followed by decrease or even cessation in the fall/winter (Wilkins, 1984). Other researchers (Boyd, 1969, 1970, 1971; Garver et al., 1988; Smith et al., 1988) observed that uptake rates of essential nutrients by many aquatic macrophytes are
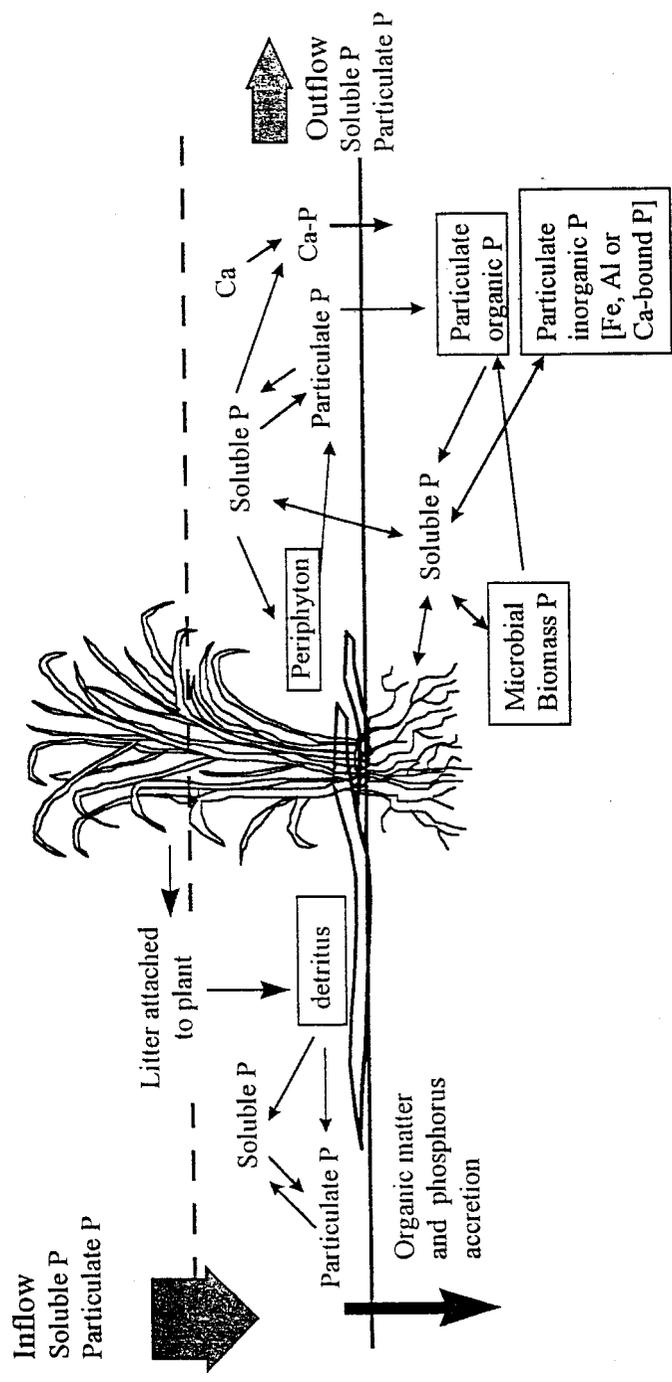
FIGURE 2. Schematic of P cycling as influenced by vegetation components of streams and wetlands.

highest during early spring growth, before maximum growth rate is attained. This early uptake and storage of nutrients provide a competitive edge for growth-limiting nutrients during the periods of maximum demand (Boyd and Vickers, 1971).

Another important response to seasons is the translocation of nutrients within the plant. Prior to fall senescence, the majority of important ions is translocated from shoot portions to the roots and rhizomes. These stored nutrients are used during early spring growth (Dykyjova and Kvet, 1978; Garver et al., 1988; Smith et al., 1988). Phosphorus storage in vegetation can range from short to long term, depending on type of vegetation, litter decomposition rates, leaching of P from detrital tissue, and translocation of P from above-ground to below-ground biomass. Phosphorus storage in the above-ground biomass of emergent macrophytes is usually short term, with a large amount of P being released during decomposition of detrital tissue. The above-ground parts of most macrophytes grow and die on a cycle ranging from the annual growing season in northern climates to faster cycles in southern climates. Shoot turnover times in subtropical zones are as short as 2 to 3 months (Davis, 1994). Root turnover times are largely unstudied, but are estimated at 1.5 to 3 years (Prentki et al., 1978). In addition, many macrophytes possess the ability to translocate nutrients from above-ground parts to their roots, and to use these stored materials to foster growth during the early part of the growing season. Approximately 45% of the P lost from living *Typha* sp. shoots was translocated to roots and rhizomes (Davis and van der Valk, 1983). Below-ground storage of P is often underestimated, and its fate and stability are not clearly understood.

Unlike emergent vegetation, trees in forested wetlands provide long-term storage. Reported P uptake rates in forested wetlands are 1 to 15 kg ha^{-1} yr^{-1} (Reddy and DeBusk, 1987). Mitsch et al. (1979) reported that net annual uptake of P in a cypress swamp represented 10% of the gross retention by the wetland. Net assimilation of P in wood is small, when compared with leaves, thus a substantial portion of P is recycled in litter fall.

Above-ground vegetation produces detrital material as a result of senescence and frost damage. Most of this detrital material is either attached to the primary plant or detached and deposited on the soil surface. In forested wetlands, detrital production occurs primarily through litter fall. A number of studies have been reported on the breakdown of detrital tissue in lakes, streams, and wetlands (Brinson et al., 1981; Carpenter et al., 1983; Godshalk and Wetzel, 1978; Polunin, 1984; Reddy and DeBusk, 1991; Reddy and Sacco, 1981; Wetzel, 1990). Many studies employed litter bag techniques and measured rapid turnover rates, based on loss in dry weight of detrital tissue. However, this technique may only provide information on the breakdown of large organic compounds into low-molecular-weight organic compounds. These low-molecular-weight organic compounds may readily leach out of the litter bags, thus overestimating the decomposition (mineralization) rate. The detrital tissue deposited on the soil surface is subject to aerobic and anaerobic decomposition, depending on hydrology and availability of alternate electron acceptors (D'Angelo and Reddy, 1994a,b).

Above-ground plant parts return leached P to the water after death and decomposition and deposit refractory residuals on the soil/sediment surface. However, dead roots decompose underground, therefore adding refractory compounds to subsurface soils and leachates to the porewater in the root zone. Thus, the above-ground portion of the macrophyte cycle returns P to the water, while the below ground biomass returns P to the soil. Nutrient loading to wetlands produces a larger standing crop and stimulates the entire biocycle. Incremental storage of P in biomass occurs due to the stimulation of growth, producing larger quantities of leaves, roots, and litter. Relative rates of biological processes regulating P cycle are speeded up in a system receiving sustained addition of nutrients.

The net effect of vegetation on P retention depends on type of vegetation, root-shoot ratio, turnover rates of detrital tissues, C/P ratio of the detrital tissue, type of metabolic pathways, and physicochemical properties of the water column. Phosphorus is cycled in soil-water-plant components as follows: herbaceous vegetation rooted in soil obtains most of its P needs from the soil porewater and translocates it to above-ground vegetation to support active vegetative growth. After maturity and senescence, a substantial portion of P present in above-ground vegetation is translocated into below-ground biomass (roots and rhizomes). In nutrient-rich systems, up to 80% of the P stored in some aquatic macrophytes detrital tissue is released into the water column either by initial leaching or as a result of decomposition (Reddy et al., 1995a). The residual detrital material is deposited on the soil surface and becomes an integral part of the soil, thus providing long-term storage. However, over the short term, rapid turnover rates and cycling can contribute bioavailable P to the water column and influence water quality.

B. Assimilation and Release of Phosphorus by Periphyton and Microorganisms

Periphyton can be present as floating mats attached to macrophytes or as benthic layer at soil/sediment and floodwater interface. Benthic periphyton utilizes P from both soil/sediment and from the water column (Hansson, 1989). Epiphytic periphyton receive P largely from water column and P released from senescent macrophyte tissue (Riber et al., 1983). A small amount of P is also derived by epiphytic periphyton from living tissue of macrophytes (Carignan and Kalff, 1982). The floating periphyton derives P essentially from the water column. Chemical composition of periphyton varies depending on water column P, water flow, and type of macrophytes (Hansson, 1989). Phosphorus content of periphyton was shown in the range of 0.1 to 4.5 mg g^1 (dry wt), but the P content of 1.1 to 2.2 mg g^{-1} is necessary for normal growth (Muller, 1983; Riber et al., 1993; Swift and Nicholas, 1987; Grimshaw et al., 1993). High P concentrations reported were the result of 'luxury uptake', which is commonly observed in P-enriched water (Muller, 1983; Riber et al., 1983; Cotner and Wetzel, 1992; Adey et al., 1993).

Adey et al. (1993) observed P saturation at water column P concentration of 0.025 mg L^{-1}, suggesting that mass loading is more important than water column P concentrations.

Periphyton can play a major role in regulating P concentrations of the water column (Figure 2). Periphyton can assimilate both organic and inorganic forms of P (Bentzen et al., 1992) and can induce marked changes in pH and dissolved oxygen concentration of the water column and the soil-floodwater interface (Carlton and Wetzel, 1988). These changes can potentially influence the solubility of P, especially in streams and wetlands. Periphyton is known to mediate the precipitation of CaCO$_3$ (Gleason, 1972) and to co-precipitate P (Otsuki and Wetzel, 1972). However, in a recent chemical analysis of periphyton obtained from the Florida Everglades, it was found that < 20% of the total P in periphyton was present as P associated with Ca and Mg, whereas the remaining P was in organic forms (Scinto and Reddy, 1995). These results suggest active biological uptake by periphyton.

In wetlands and streams with abundant periphyton activity, much of the P in the water column is intensively recycled within the periphyton component of the system (Wetzel, 1990). Under these conditions, very little of the water column P is assimilated by macrophytes. Additionally, flux of P from the soil to the overlying water column is influenced by periphyton at the soil-floodwater interface, which incorporates much of the P into periphyton mats. During macrophyte senescence, dormancy and decomposition of detrital tissue released P is actively utilized by periphyton communities (Carlton and Wetzel, 1988). In systems dominated by high Ca^{+2} activity, periphyton-induced pH changes can co-precipitate P with CaCO$_3$ within periphyton mats. The periphyton and Ca-P complex is eventually incorporated into soil mass, as evidenced by a linear relationship between long-term Ca and P accumulation in the Everglades ecosystem (Reddy et al., 1993).

The role of microorganisms in the transformation of organic P to inorganic P in soils and sediments has long been recognized. The catabolic activities catalyze the mineralization of organic P, while during growth microorganisms assimilate and transiently store P in their biomass. Bacterial biomass C/P ratio of < 20 indicates P is not limiting in the systems. The biomass C/P ratios were found to be influenced by the redox condition and the presence of selected electron acceptors. For example, C/P ratios of 56, 43, 9, and 6 were observed in a wetland soil maintained under aerobic-, nitrate-, and sulfate-reducing conditions, and methanogenic conditions, respectively (McLatchy and Reddy, 1996). In lake sediments, bacterial biomass P was positively correlated to primary production or organic matter-settling rate (Gachter and Meyer, 1993).

Microorganisms also can play a major role in retaining P in streams with organic matter inputs, such as those receiving leaf litter material from shoreline littoral zone or organic loading from waste effluent (Cooke, 1992; Gachter and Meyer, 1993). Although bacteria are generally considered decomposers that simply mineralize organic P, they have also been shown to regulate the P flux across the sediment-water interface (Kleeberg and Schlungbaum, 1993) and contribute to terminal

P burial through production of refractory organic compounds (Gachter and Meyer, 1993). Microorganisms incorporate dissolved P into cellular constituents, that then become integral parts of the particulate matter. Through the formation of polyphosphate compounds, microorganisms are able to survive in alternating oxidation-reduction environments (Davelaar, 1993). This luxury consumption of P (polyphosphate formation) can significantly influence the concentration of P in the water column by removing P at high water column concentrations and contributing P when the water column concentrations are low. In a woodland stream, about 80 to 91% of total P retention was attributed to microbial uptake, with the remainder attributed to abiotic processes (Elwood et al., 1981; Newbold et al., 1983). Similarly, about 60% P retention was attributed to microorganisms in wetland treatment systems (Lee et al., 1975; Sloey et al., 1978).

C. Forms of Soil and Sediment Phosphorus

Phosphorus in wetlands and stream and lake sediments is found in organic and inorganic forms. The relative proportion of each form depends on the nature and origin of these materials. Inorganic P compounds are associated with amorphous and crystalline forms of Fe, Al, Ca, and other elements. Organic P forms are generally associated with living organisms and consist of easily decomposable P compounds (nucleic acids, phospholipids, and sugar phosphates) and slowly decomposable organic P compounds (inositol phosphates—phytin).

Inorganic P forms in soils and sediments are characterized based on their differential solubilities in various chemical extractants. The early fractionation schemes (Chang and Jackson, 1957; Petersen and Corey, 1966; Williams et al., 1971) grouped soil P into: (1) P present as orthophosphate ions sorbed onto the surface of P-retaining components (nonoccluded P), (2) P present within the matrices of P-retaining components (occluded P), and (3) P present in discrete phosphate minerals such as apatite.

The sequential extraction procedure by Chang and Jackson (1957) involved a series of solvents as follows: 0.5 N NH_4F (Al-P), 0.1 N NaOH (Fe-P), 0.5 N H_2SO_4 (Ca-Mg-P), $Na_2S_2O_4$- citrate (reductant-soluble Fe-P), 0.5 N NH_4F (occluded Al-P), and 0.1 N NaOH (occluded Fe-Al-P). In more recent fractionation schemes developed for sediments, the redox-sensitive P forms such as occluded and reductant-soluble P are no longer distinguished from the other forms of inorganic P (Hieltjes and Lijklema, 1980; van Eck, 1982). Other methods have recognized the shortcomings of the Chang and Jackson (1957) method such as poor reproducibility of the reductant-soluble P fraction (Frink, 1969) and precipitation of CaF_2 during NH_4F addition in calcareous systems (Williams et al., 1971). The newly formed CaF_2 is capable of resorbing inorganic P released in the succeeding extractions and hence could result in underestimation of one fraction and overestimation of the others (Syers et al., 1973). In addition, the use of dithionite-citrate reagent was

found to be ineffective in separating Ca-Mg-P from Fe-P because citrate is a strong complexing agent for Ca (Hieltjes and Lijklema, 1980). The 1 M NH$_4$Cl (pH 7.0) extractant has been reported to remove the carbonates and the loosely bound P and Ca, thus preventing P adsorption by carbonates in the succeeding alkaline treatment (Hieltjes and Lijklema, 1980).

A more detailed P fractionation scheme was proposed by van Eck (1982) that categorized P into six pools: (1) exchangeable P, (2) labile organic P, (3) carbonate-bound P, (4) Fe-Al-P, (5) Ca-P, and (6) resistant organic P. This scheme defined exchangeable P as 0.5 M NaCl-extractable, carbonate-bound and labile organic P as 1 M NH$_4$Cl-extractable, Fe-Al-P as 0.1 M NaOH-extractable, and Ca-Mg-P as 0.5 M HCl-extractable. Carbonate-bound P is defined as P that is sorbed or associated with free Ca or Mg carbonates. The labile organic P was proposed as an intermediate pool between readily available and unavailable P and represents those P compounds affected by mobilization and immobilization processes (van Eck, 1982). The organic P extracted by 0.1 M NaOH is usually calculated from the difference of P concentrations in digested and undigested extracts. The P remaining in the final residue is the highly resistant organic P, usually calculated by difference using total P (determined separately by digestion methods) and the sum of all extractable inorganic P fractions (Mehta et al., 1959; Williams et al., 1976a).

The terminology used for P fractions is mostly operational (Psenner et al., 1988). Recent workers suggest the use of technical terms such as "reactive P" and "nonreactive P" for sediments in place of "inorganic P" and "organic P" (Pettersson and Istvanovics, 1988; Psenner and Pucsko, 1988). Some studies have introduced a conventional naming based on the extractant, that is, NH$_4$Cl-P, NaOH-P, or NaOH-RP, and NaOH-NRP, if "reactive (R)" and "nonreactive (NR)" forms are to be specified (Pettersson, 1986; Psenner and Pucsko, 1988). "Reactive P" is defined as P that responds to colorimetric tests (Murphy and Riley, 1962) without preliminary hydrolysis or oxidative digestion of the sample.

The P removed by the first one or two extracting solutions in a sequential fractionation method is usually considered bioavailable (Gunatilaka, 1988; Psenner et al., 1988). Depending on the strength of the extracting solution and the fractionation method, bioavailable P has been estimated from such extracts as: 1 M NH$_4$Cl (Hieltjes and Lijklema, 1980; van Eck, 1982), 1 M KCl (Reddy et al., 1995a), 0.1 M NaOH (Wildung et al., 1977; Hieltjes and Lijklema, 1980; Ostrofsky, 1987), citrate-bicarbonate-dithionite (Williams et al., 1971), and nitrolotriacetic acid (NTA) (Golterman et al., 1969; Gunatilaka et al., 1988). The Ca-bound P (HCl-RP) such as apatite was found to be unavailable (Pettersson, 1986; Gunatilaka, 1988), while the redox-sensitive Fe-bound P may become available under anaerobic conditions (Wildung et al., 1977; Furumai and Ohgaki, 1982; Hosomi et al., 1981).

In a recent study, Olila et al. (1995) determined P reactivity and bioavailability in lake sediments as determined by the different P fractions and their distribution. Reactive and nonreactive P fractions in Lake Apopka and Lake Okeechobee sediments were determined using sequential extractions with NH$_4$Cl-NaOH-HCl. The
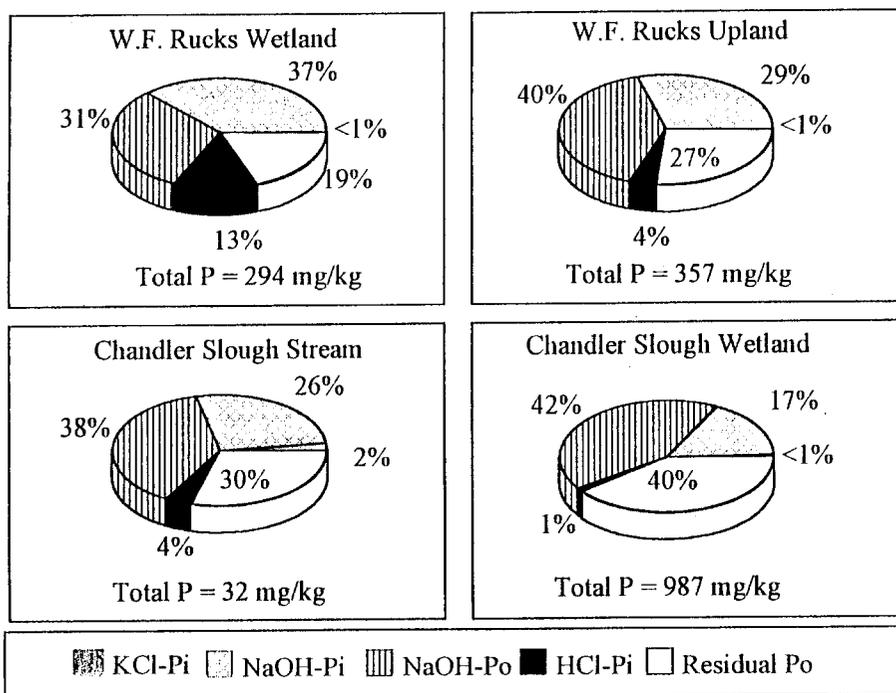
FIGURE 3. An example of forms of phosphorus in wetland soils and stream sediments in selected sites of Lake Okeechobee Basin. $KCl-P_i$ = adsorbed P potentially bioavailable; $NaOH-P_i$-Fe/Al bound inorganic P; $NaOH-P_0$ = organic P associated with humic and fulvic acids; $HCl-P_i$-Ca/Mg bound inorganic P; Residual P = resistant organic P and mineral bound inorganic P. (From Reddy, K. R., unpublished results.)

unconsolidated flocculent (UCF) layer (surface 0 to 30 cm) of Lake Apopka sediments had high NH_4Cl-P concentrations (5 to 13% of TP), with the carbonate-associated P and labile organic P constituting about 36 and 42% of NH_4Cl-P, respectively. The high porewater-P (1 to 6% of TP) and NH_4Cl-P concentrations in the UCF layer constitute a large reservoir that serves as a source of P to the overlying water column. The marl layer of Lake Apopka sediments had NH_4Cl-P concentration of < 1% of TP, with HCl-P (35% of TP) and residual P (64% of TP) as the dominant P fractions. Results indicate that 1 M NH_4Cl (pH 7.0) and 0.5 M HCl may not be extracting distinct pools of P. The mud sediments of Lake Okeechobee were dominated by HCl-P (65% of TP) followed by residual P (28% of TP), with low NH_4Cl-P (2% of TP) and NaOH-P (5% of TP) concentrations. The peat and littoral sediments of Lake Okeechobee, however, had high NH_4Cl-P (9 to 10% of TP) and NaOH-P (6 to 18% of TP) concentrations that were comparable to those of Lake Apopka UCF sediments. The NaOH-P fractions in mud and littoral sediments of Lake Okeechobee decreased with depth and were associated with oxalate-

and CDB-extractable Fe ($p < 0.01$). One example in Figure 3 shows labile and non-labile pools of P in selected stream sediments and wetland soils of Lake Okeechobee Basins. In this example, soils and sediments were sequentially extracted with selected chemicals using the modified soil P fractionation scheme (Olila et al., 1995). The inorganic P extracted with neutral salt such as KCl represents loosely absorbed P, which usually accounts for less than 2% of the total P. This pool of P is considered bioavailable, as it is sufficiently labile to enter soil/sediment porewater for uptake of plants or potential flux into overlying water column. The NaOH-P_i represents inorganic P associated with Fe and Al (included occluded P) and represents P not readily available. The HCl-P_i represents P associated Ca/Mg, is relatively stable and not readily available. 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 alkali or acid.

Wetland soils and some stream sediments are often characterized with high organic matter content, thus the characteristics and the factors regulating the breakdown of organic matter determine the long-term storage of nutrients in organic pool. In many wetlands, because of low mineral matter and high organic matter, P is stored in organic pools. Most of the studies in wetlands have focused on inorganic P forms and considered bioavailability of organic P sources less important because of a relatively slow rate of decomposition under anaerobic conditions. However, in most soils, a major portion of total P is present in organic forms (Stevenson, 1982), with about 87% of total P in swamp sediments (Hesse, 1962), 40 to 90% in Everglades Histosols (D'Angelo and Reddy, 1991), and 10 to 70% in lake sediments (Sommers et al., 1972). Due to predominance of organic P in soils, and its existence in different forms of varying degrees of availability, mineralization of organic P can play an important role in contributing to the bioavailable pool (Hedley and Stewart, 1982; Condron et al., 1985).

The range of organic P forms found in soils include phospholipids, nucleic acids, inositol phosphates, glucose-6-phosphates, glycerophosphate, phosphoproteins, and polymeric organic P of high-molecular-weight compounds (Stewart and Tiessen, 1987). 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). A linear relationship has been shown between microbial biomass C and P of soils (Anderson and Malcolm, 1974; Bowman and Cole, 1978; Brooks et al., 1982; Bowman, 1989; Ivanoff and Reddy, 1996). Appropriate chemical extraction methods are used traditionally to characterize these forms, based on their ease of extraction with selected chemicals. These fractions include: (1) a labile pool, extracted with 0.5 M NaHCO$_3$, (2) a moderately labile pool, consisting of acid soluble organic P and alkali soluble inorganic P, (3) a moderately resistant fraction (fulvic acid P) and (4) a highly resistant fraction (humic acid P and humin P). Although these methods are rapid and

simple, they only provide indirect evidence of different forms based on the ease of extraction with specific chemical reagents.

The fact that certain organic P compounds mineralize more rapidly than others has led to the concept of labile organic P that potentially consists of organic P pools that undergo rapid microbial breakdown. Traditionally, this pool of P is extracted with $NaHCO_3$, and the P extracted represented plant available P (Bowman and Cole, 1978). Alternatively, enzyme assays have been used to determine the organic P mineralization potential of soils and sediments (Rojo et al., 1991; Newman and Reddy, 1993).

The proportion (% of total P) and nature of organic P in wetlands depends on soil type, type of organic loading from external sources, and deposition of dead algal cells and detrital tissue from aquatic vegetation. Soils with high organic C generally have a greater proportion of total P in organic forms. Consequently, peat-dominated wetlands have a higher proportion of organic P compared with soils with high mineral matter. Although a large proportion of total P is in organic form, only a small portion of this pool may be biologically active. In upland soils, this fraction was shown to be rapidly turned over and made available to plants (Chater and Mattingly, 1980; Sharpley, 1985; Stewart and Tiessen, 1987). Thus, to describe P behavior in wetlands, it is critical to understand the interaction of microbes, fauna, and vegetation and their role in P cycling (Cosgrove, 1977; Coleman et al., 1983; Tate, 1984). Organic P associated with humic and fulvic acid represents >40% of total P (Swift and Posner, 1972; Brannon and Sommers, 1985). The fulvic acid P, which constitutes a large fraction of the organic P in most soils and is likely that this pool is derived from plant litter and recently deposited organic matter (Stewart and Tiessen, 1987).

The rate of organic P mineralization is regulated by the relative proportion of labile and non-labile pools. The balance between mineralization (breakdown of organic P to inorganic P) and immobilization (assimilation of inorganic P into microbial biomass) depends on the C/P ratio of the organic matter and type of electron acceptors involved in the decomposition (aerobic vs. anaerobic). The mineralization of organic compounds is affected by the extracellular enzymes, such as phosphatase, and measurement of enzyme activity may provide an indication of potential organic P mineralization (Golterman, 1984). Significant correlations were observed between microbial respiration rates and phosphatase activity, suggesting microbes as a major source of phosphatase activity (Gould et al., 1979). Conflicting correlations between phosphatase and organic P have been reported by several researchers (summarized by Harrison, 1983). However, correlations were highly significant between labile pools of organic P and phosphatase activity.

The processes and rate at which organic P compounds are hydrolyzed into bio-available pool (labile pool) is controlled by various physical, chemical, and biological factors coupled with environmental influences in the soil-water column of a wetland. In wetlands, nutrient cycling is governed by microbial metabolic activities functioning in the soil profile, which includes aerobic, facultative anaerobic

and obligate anaerobic. The rate of microbial breakdown of organic P not only depends on substrate characteristics but also on availability of electron acceptors such as O_2 (aerobic), NO, Fe^{3+}, Mn^{4+} (facultative anaerobic) and SO^{2-}_4, CO_2 (obligate anaerobic) (Fenchel and Jorgensen, 1977). In a recent study, McLatchy and Reddy (1996) have shown the effect of alternate electron acceptors and the associated redox conditions on P mineralization. For example, organic P mineralization rates were approximately 3-fold higher in an organic soil incubated under aerobic conditions, when compared with nitrate, sulfate, and bicarbonate reducing conditions. A similar response was also observed for microbial biomass (Reddy and McLatchy, 1996).

D. Retention and Release of Phosphorus by Soils and Sediments

Research on lakes and streams has repeatedly attributed the major loss of P from water column to settling of particles onto the sediments (Caraco et al., 1991). Thus, the extent to which sediments interact with overlying water column is one factor that regulates the productivity of an aquatic system. The ability of stream sediments and wetlands to retain P depends on the physico-chemical characteristics of the sediment or wetland soil. Inorganic P added at concentrations considerably greater than those present in the porewater of sediments or wetland soils is retained by oxides and hydroxyoxides of iron and aluminum and by calcium carbonate. At low P loadings, wetland, soil or stream sediments release rather than retain P (Khalid et al., 1977; Logan, 1982; Sonzogni et al., 1982; Richardson, 1985).

The adsorption isotherms of soils and sediments are usually measured by mixing a known amount of soil or sediment with a solution containing known P concentrations. The mixtures are equilibrated for a fixed period (usually 24 h) at a constant temperature and under continuous shaking (Nair et al., 1984). Phosphorus not recovered in solution is assumed to be adsorbed on solid phase. The plot showing P adsorbed (on y-axis) and P in solution (on x-axis) is called adsorption isotherm or buffer isotherms (Figure 4a). 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). In many cases P sorbed on solid phase is usually not desorbed with a neutral salt such as NaCl or KCl and do not follow adsorption isotherm, an effect called hysteresis. This effect is a function of solid phase physicochemical characteristics, P loading rate, and residence time. This hysteresis effect is due to P diffusion into solid phase and is observed in soils and sediments having active reaction surfaces. For example, ligand exchange of P for surface aquo and hydroxyl groups bonded to Al and Fe is shown to result in monodentate: bidentate or binuclear forms of adsorbed P (Bohn et al., 1985). The formation of binuclear and bidentate bonds and precipitation are less reversible than monodentate bonds. This irreversible pool represents long-term storage in soils. Once the sites are saturated (e.g., in soils and
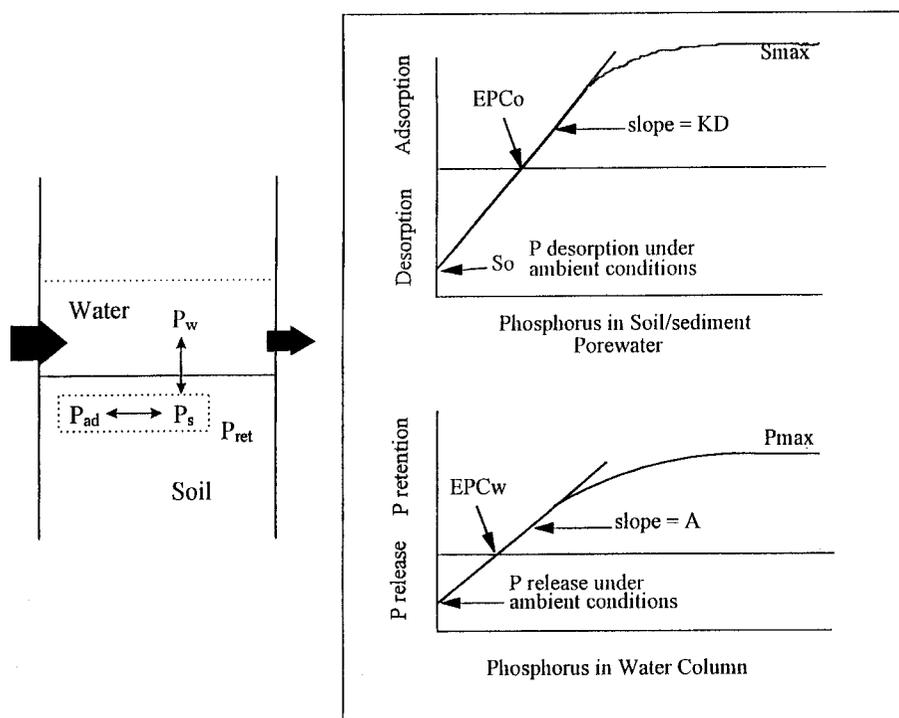
FIGURE 4. (a) Schematic of P sorption isotherms for wetland soils and sediments. K = partition coefficient related to P buffering capacity; EPC_o = equilibrium P concentration, where adsorption equals desorption; So = native P present in sorbed phase under ambient conditions. (b) Schematic of phosphorus retention isotherm for soil/sediment water column. A = phosphorus assimilation coefficient; P_{max} = phosphorus retention maximum; P_0 = maximum P release potential of native soils or sediments; EPC_w = equilibrium P concentration in the water column at which point P retention equals release. (From Reddy et al., 1995.)

sediments with historical P loading or those low in clay mineral surfaces), the desorption potential increases. Sorption is envisioned as a two-step process in which a rapid phase corresponds to initial retention on a surface and a slower phase corresponding to diffusion into a solid phase involved in sorption (Barrow, 1983 a,b; Portielje and Lijklema, 1993). Several reviews have discussed the mechanisms of P sorption in acid soils by Al and Fe and in alkaline soils by Ca and Mg compounds (Syers et al., 1973; Berkheiser et al., 1980; Bostrom et al., 1982; Logan, 1982; Sonzogni et al. 1982; Froelich, 1988; Sanyal and DeDatta, 1991). The above reviews indicate that several phosphate minerals regulate the solubility of dissolved P in the interstitial waters, soils, and sediments. Some examples of these minerals include apatite, hydroxyapatite, fluorapatite, octocalcium phosphate strengite, vivianite, variscite, and wavellite. Because of the complexity involved in mineral formation and solubility of minerals, it is difficult to attribute P retention

to any one single mineral. The general conclusions made, based on previous research are (1) in acid soils, P is fixed as A1 and ferric phosphates, if the activities of these cations are high, (2) in alkaline soils, P fixation is governed by the activities of Ca and Mg, and (3) P availability is greatest in soils and sediments in slightly acidic to neutral pH.

Mobility of P is governed by P retention capacity and P buffer intensity of wetland soils and stream sediments. Phosphorus retention capacity refers to the maximum available sites, which is determined physicochemical properties and P already present on solid phase. This is also referred to as buffer capacity of the soil analogous to pH buffering (Froelich, 1988). Soils and sediments having large capacity for P sorption with small increments in solution P concentration are considered to be highly buffered and sorption in these soils or sediments is irreversible. Buffer intensity refers to strength of adsorption. High buffer intensity reflects in low-solution P concentration. Maximum P retention capacity of soil/sediment is generally reached following saturation of all sorption sites. Several researchers have reported significant correlations between amorphous and poorly crystalline forms of Fe and Al, with P retention maximum of soils (Berkheiser et al., 1980; Khalid et al., 1977; Richardson, 1985; Walbridge and Struthers, 1993; Gale et al., 1994). This suggests that P sorption in soils/sediments is associated with amorphous and poorly crystalline forms of Fe and Al. Statistical ($p < 0.01$) correlation of S_{max} (sorption maxima) with TOC (total organic C) suggests that organic matter can also play a major role in P sorption (Reddy et al., 1995a). Iron and Al complexed with organic matter may be responsible for P sorption, suggesting an indirect effect of organic matter that may explain the correlation of S_{max} with TOC (Syers et al., 1973). In sediments/soils dominated by Fe minerals, reduction of the soluble ferrous oxyhydroxide compounds results in more sorption sites. This reduction is the result of facultative organisms using ferric iron as an electron acceptor during their metabolic process in the absence oxygen. Although reduction may create larger surface area for sorption of P, the binding energy associated with P sorption is low and desorption potential is high (Patrick and Khalid, 1974). Although the P sorption capacity may be low under oxidized conditions, P sorbed is held more tightly than under reduced conditions. These effects result in high EPC (equilibrium P concentration of soils or sediments where adsorption equals desorption) values under reduced conditions than under oxidized conditions. An increase in P solubility in mineral wetland soils and sediments has been attributed to the reduction of ferric phosphate compounds to move soluble ferrous forms and to the hydrolysis of P compounds. In sulfate-dominated anaerobic sediments, production of H_2S (through biological reduction of SO_4^{2-}) and formation of ferrous sulfides may preclude P retention by ferrous iron; hence, P is released (Caraco et al., 1991).

The sorption capacities of soils/sediments measured in studies reported were based on soil/sediments mixed continuously with P-enriched water. Phosphorus retention by soils and sediments can only occur when inorganic P is in direct

contact with the adsorbent. In stream and wetlands, water column P must diffuse into underlying soils or sediments before it can be retained. This happens only when water column P concentration is higher than the soil/sediment porewater concentration. Thus, areal P retention by stream sediments and wetlands under field conditions depends on P diffusion from the water column to the underlying soil or sediment, and P concentration of the porewater and physicochemical characteristics at the sediment-water interface. The sediment/soil sorption data alone are not readily useful in predicting the P retention capacity in a dynamic wetland-stream system, unless consideration is given to the P concentration of the overlying water, water depth, total organic carbon, and associated transport processes (Lijklema, 1993; Reddy et al., 1995).

E. Chemical Precipitation of Phosphorus in the Water Column

Photosynthesis and respiration can initiate significant changes in water column pH on a diurnal basis. These processes can increase pH to as high as 10, depending on the buffering capacity of the water column, precipitate a significant portion of water column P as calcium phosphate where dissolved Ca is available. However, Diaz et al. (1994) noted that about 75 to 90% of the P precipitated was solubilized when pH levels decreased to below 8 as a result of an increase in CO_2 levels. Retention of P by precipitation will be significant in waters with high Ca^{+2} and alkalinity but insignificant in poorly buffered water columns. In high Ca^{+2} and mildly alkaline waters, House (1990) attributed only 6% of the overall P removal to co-precipitation, while the remainder was due to biological uptake. However, Salinger et al. (1993) found metastable calcium phosphate species to be a predominant form of P transported in the River Jordan. In the water column of wetlands and streams, chemical reactions associated with P solubility are regulated by dissolved Fe and Ca.

The precipitation of P as calcium phosphate has been studied extensively by soil scientists in evaluating applied fertilizer reactions. Initial adsorption of P onto calcite was followed by precipitation as calcium phosphate (Cole et al., 1953; Griffin and Jurinak, 1973; Freeman and Rowell, 1981). Similar reactions can occur at the soil-floodwater interface of calcareous wetlands and streams. For example, long-term P accumulation in the Everglades marsh is linearly correlated with Ca accumulation, suggesting the possibility of P and $CaCO_3$ interactions (Reddy et al., 1993).

III. PHOSPHORUS TRANSPORT

Transport processes affect the availability of P for assimilation by biota and retention by soils and sediments. Phosphorus is transported through streams in soluble and particulate forms. Although these fractions do not describe the functional

chemical or biological behavior, they are useful in quantifying physical behavior during transport. Both organic and inorganic soluble P forms are transported with the water and are subject to changes in the physicochemical characteristics of the water as it flows through different reaches of a stream system. The transport processes involved in mobilization of P between sediment or soil and overlying water column are advection, dispersion, diffusion, seepage, resuspension, sedimentation, and bioturbation (Lijklema, 1993).

A. Advective Transport in Surface Water

The primary transport process in streams and wetlands is the advective flow of water downstream. Streams and wetlands are open systems where dissolved and suspended materials are transported through the system, interacting with sediments and vegetation along the flow path. Advective transport occurs primarily in defined channels with dispersive and diffusive flow horizontally through wetlands, floodplains, and vegetative islands (Kadlec, 1987), and vertically through transient stream storage zones and bed sediments.

The magnitude and distribution of advective flow affects the overall distribution of sediment and solutes in the stream system. At low flow and shallow depth interactions occur primarily with main channels, whereas at high flow and high depth riparian floodplains and seasonal wetlands are inundated. Under these conditions, water moves along a tortuous path, having considerable interaction with the wetland. At high flow and high depth, vegetation is matted by the shear forces and water flows quickly through the channels. Also, additional areas of the wetland are inundated, increasing the overall residence time during stormflow. There is a seasonal variability in advective flow that affects the distribution of solutes and sediments. Usually, there is an increase in flow rates in the fall or spring that provides greater transport capacity for solutes and sediments. This increase may result in a greater delivery of materials to the stream system or a greater removal from the system. To a lesser extent, storm runoff can redistribute materials during the growing season.

Dispersive flow is controlled by the velocity of the flowing water and the roughness of the flow path. Rocks, islands, organic debris, and vegetation protruding into the flow path increase dispersion. In an inundated stream reach spatial distribution of stagnant pools, armored channels, debris, and vegetative islands influence the effective residence time within the wetland. Residence time in the wetland is decreased and particulate P is diverted away from vegetated areas where settling and entrapment occurs (Fennessy et al., 1994). At the individual plant level, dispersive processes affect the movement of water through islands of vegetation and interactions with macrophytes and epiphytes. At the microscopic level, dispersive forces affect the development of the boundary layer along sediment and vegetative surfaces. At high flow the thickness of the boundary layer is reduced,

improving the diffusion of solutes to the surfaces. High flow also replenishes the water column solute content and maintains diffusion gradients of solutes. The variable roughness of the surfaces induce turbulence that reduces the boundary layer thickness.

B. Sedimentation and Entrainment

Sedimentation and entrainment exist as a balance between erosive and resistant forces. Sediment transport is controlled by velocity that provides the shear force for erosion and the capacity for particle entrainment. During low flow, many systems behave as sediment traps and function filters for suspended materials, but are erosive during high flow (Hill, 1982; Svendsen and Kronvang, 1993). Mitsch et al. (1979) reported that sediments in a riparian floodplain retained 10 times more P from floodwater than was released the remainder of the year. The floodplain retained 3.6 g P m^{-2} yr^{-1} or 4.5% of inflow P. Dorioz et al. (1989) reported accumulations of P at flow rates < 0.7 m^3 s^{-1}. Within stream systems, there is a mosaic of reaches that are either erosive or sedimentary. In high gradient systems, these are pools and ripples (Kim et al., 1990), and in low gradient systems, channels and islands (Hammer and Kadlec, 1986).

Sedimentation describes a number of processes that affect P assimilation, including settling of inorganic suspended particles, settling and adhesion of organic particles, and accumulation of heterotrophic and autotrophic organic materials. Often, soluble P is converted by phytoplankton into particulate P and is trapped within the littoral zone vegetation (Simmons and Cheng, 1985). The sediments deposited on the soil surface can be organic or mineral depending on the watershed and the hydrologic conditions. In wetlands, incoming water velocity is reduced by tortuous flow paths and the presence of vegetation, resulting in settling of particulate matter and associated nutrients. Sediment accumulation can provide a long-term sink (storage) for P and other nutrients. Therefore, internally generated sediments are deposited and remain trapped, except for local stirring effects, such as bioturbation, wind-driven mixing, and gas ebullition phenomena.

Wetlands generate particulate matter via several processes. Decomposition and fragmentation of macrophytic detrital tissue produce particulate matter. Microflora and microfauna die and leave microdetritus, such as exoskeletons and algal debris. The magnitude of this production is often much larger than that associated with incoming and departing flows. For example, a 2.3-ha cattail marsh in Illinois, constructed to retain river-borne sediments, trapped 143 gm^{-2} of total suspended solids (TSS) during the 1991 growing season, based on inflow-outflow (I/O) measurements (Hey et al., 1994). However, sedimentation traps operated over the same period, which were designed to prevent resuspension, trapped 1200 gm^{-2} (Fennessy et al., 1994). During the growing season, the I/O TP removal was 0.2 gm^{-2}; the sediment trap accumulation was 7.5 gm^{-2} of P. Thus, gross P accretion can far outweigh

net P trapping. The gross accreted P is largely returned either to surface waters (via above-ground leaching and decomposition), or to porewater (from older materials that subsequently become buried by newer sediments).

Riparian buffer zones adjacent to streams are effective traps for sediments and nutrients discharged from adjacent farming and urban activities. About 50% of total P discharged from agricultural areas (Cooper and Gilliam, 1987) was deposited with the sediment in an Atlantic Coastal Plain watershed during a 25-year period. Similarly, Lowrance et al. (1984) measured a total P retention of 30% in riparian areas of a watershed in Georgia. In both watersheds, P retention was associated with sediment deposition.

Resuspension and transport of settled sediments is unlikely in wetlands, except under high flow velocity, which may occur during an extreme weather event. However, mixing due to bioturbation can contribute both soluble P from porewater and available particulate P to the water column (Lijklema, 1993). In systems with high macrobenthos activity, physical mixing can greatly increase the oxidized layer at the sediment-water interface and increase P retention.

Entrainment results when there is sufficient capacity of the flowing water to remove soluble and particulate P. Soluble P may be entrained by leaching of dissolved organic and inorganic P from detrital macrophyte and periphyton or release from surface sediments. Where the flowing water has low soluble P concentration, rapid replacement of the water column creates a large gradient and increases diffusive flux of P from sediments. Periphyton mats have been shown to be more conservative in retention of P through biological processes. Particulate P may be entrained by the direct shearing force of flowing water or by scouring from sediment entrained in flowing water (Svendsen and Kronvang, 1993). Entrainment is limited by the capacity of the flowing water and the potentially available material. Because entrainment is a direct function of stream velocity, stream beds and unvegetated sediments are more susceptible to this mechanism of P removal than wetlands.

C. Phosphorus Exchange between Soil/Sediment and the Overlying Water Column

Transport of dissolved P across the soil/sediment-water interface, as well as movement within the sediment profile, is an important mechanism affecting the chemical characteristics of the water and productivity of wetlands and streams. These transport mechanisms include: (1) sedimentation of particulate matter and accretion on soil surfaces, (2) dissolved P and pore water flow, caused by a hydrostatic pressure gradient of ground water, (3) molecular diffusive flux, and (4) mixing of sediment and water at the interface as a result of bioturbation and water turbulence (Lijklema, 1993). Depending on physicochemical characteristics of the water column and the sediment/soil-floodwater interface, wetland soils and stream sediments act as either sources or sinks for P. Transfer of P from or to the soil/sediment occurs primarily through deposition or resuspension of particulate matter. Because

deposition usually exceeds resuspension and release of dissolved P, net transfer is to soil or sediments. Deposition of particulates is more likely to occur in wetlands than streams due to the much slower movement of water. Transport of P in streams is mainly as soluble P (Pionke and Kunishi, 1992). Therefore, the fraction being retained is most likely associated with particulate components. However, sorption of soluble P by suspended material can be a significant means of P transport in agriculturally impacted areas (Sharpley et al., 1981). Because the porewater P concentration generally exceeds the P concentration of the overlying water column, a simple diffusive flux model can be used to calculate the potential P release across the soil/sediment-water interface. Selected examples for Florida's wetlands and streams are shown in Figure 5. These profiles represent typical porewater concentration of soils and sediments in impacted and unimpacted systems.

The boundary layer separating the sediment-soil complex from the surface waters of a wetland is often poorly defined. Flocculent sediments, litter, and microtopography combine to create a complex interface. However, the diffusion boundary layer is relatively thin, usually occupying a small fraction of the height of the water column in a surface flow wetland. Various mixing processes serve to equalize local concentrations throughout the bulk of the surface water including wind-driven mixing, rain-driven mixing, velocity profile mixing, and bioturbation. Under these circumstances, the transfer of dissolved species to or from the upper layer of porewater to the bulk surface water is most often described by a mass transfer equation that combines the diffusion coefficient and the boundary layer thickness into a single transport coefficient:

$$J = \frac{D}{\delta}(C_i - C) = k(C_i - C) \tag{1}$$

where C = surface water P concentration, gm^{-3}; C_i = interfacial P concentration, gm^{-3}, D = diffusion coefficient, $m^2\,d^{-1}$; k = mass transfer coefficient, $m\,d^{-1}$; J = vertical mass transfer flux, soil to surface water, $g\,m^{-2}\,d^{-1}$; δ = boundary layer thickness, m.

Estimates of mass transfer coefficients are in the range of k = 0.01 to 0.1 m d^{-1}. The diffusion coefficient for phosphorus is on the order of $7.6 \times 10^{-5}\,m^2\,d^{-1}$. Therefore, the diffusion boundary layer thickness is in the range of d = 0.00076 to 0.0076 m (0.76 to 7.6 mm). These values are indicative of P fluxes that can move significant amounts of P to and from the wetland soils. As a consequence, rates of transfer are controlled by flow, uptake and diffusion processes within the soil column and not by the relatively fast transfers within the surface water.

Phosphorus regeneration (mineralization) in soils and sediments is greatest in the surface layers and decreases with depth. Likewise, total P is usually greater in the surface layers and decreases with depth. However, dissolved P usually shows steep gradients in the surface depths, with lowest concentrations at the soil/sediment interface. The dissolved P concentration at this interface is regulated by the
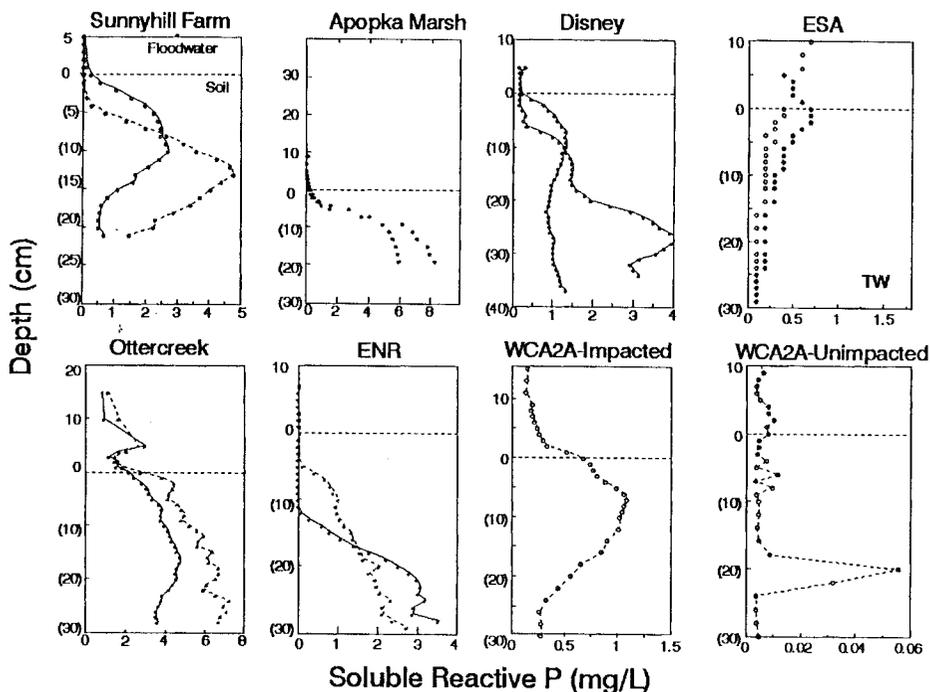
FIGURE 5. Distribution of dissolved P in soil/sediment-water column at selected sites in Florida. Sunnyhill Farm = A formerly agricultural land converted to wetland (Oklawaha River Basin, Central Florida) about 8 years ago; Apopka marsh = a formerly agricultural land converted to wetland (Lake Apopka, Central Florida) about 3 years ago; Disney = a natural wetland (Orlando, Florida) used to dispose secondarily treated sewage effluent; ESA = A natural wetland (Orange County, Florida) used for disposal of secondarily treated sewage effluent; Otter Creek = a stream impacted by dairy farms in the Okeechobee Basin, Florida; ENR = Everglades nutrient removal project sites—a formerly agricultural land converted to wetland (South Florida) about 3 years ago; WCA-2A Impacted = Water Conservation Area 2A of the Everglades impacted by agricultural drainage water; WCA-2A—unimpacted = Water Conservation Area 2A unimpacted—site located in the interior marsh.

physicochemical properties of this boundary layer. For example, the oxidized layer at this interface can be regulated by (1) oxygen demanding species or oxygen consumption rate and (2) oxygen production and consumption by periphyton mats. The oxygen fluctuation coupled with the presence of ferric iron can regulate soluble P exchange between soil/sediment and overlying water column. The oxidized layer functions as a potential sink for P diffusing upward from underlying reduced layers and for P diffusing downward from the water column (Sundby et al., 1992; Moore and Reddy, 1994; Scinto and Reddy, 1995).

Dissolved P exchange plays a significant role in overall P assimilation by streams and wetlands. On a longer time scale, the soil/sediment-water interface is

TABLE 1
Calculated Soluble Phosphorus-Diffusive Flux from Selected
Wetland and Streams of Florida

Site	Diffusive flux mg P m^{-2} day^{-1}	Ref.
Lake Apopka Marsh	0.1 to 3.2	D'Angelo and Reddy (1994a)
Lake Apopka Marsh[a]	2.4 to 5.5	D'Angelo and Reddy (1994a)
Disney World	0.3 to 1.1	Reddy (unpublished results)
Orange County	0.02 to 0.16	Reddy (unpublished results)
WCA-2A—Everglades	0.02 to 0.7	Koch and Reddy (1992)
ENR—wetland	0.3 to 1.6	Reddy (unpublished results)
ENR—wetland[a]	9.2	Reddy (unpublished results)
Otter Creek	−0.8 to 3.3	Reddy et al. (1995)

[a] Fertilized agricultural lands recently converted to wetlands.

constantly changing, as a result of accretion of new organic matter derived from vegetation or external loads. With time, this mechanism results in assimilation of P. However, on a shorter time scale, mixing by bioturbation or by resuspension during high water flow velocity, can move some of the P-enriched anaerobic sediments into oxygenated water column. The dissolved P is precipitated rapidly with Fe, or assimilated by microorganisms, and redeposited on the soil surface.

A number of studies have calculated P flux using simple diffusion models and pore water P concentration profiles (D'Angelo and Reddy, 1994a; Klump and Martens, 1981; Sundby et al., 1992). Soluble P flux from soil to overlying water column is variable, with values in the range of 0.02 to 3.2 mg P m^{-2} day^{-1} (Table 1). Although these studies predicted potential P flux based on porewater concentration profiles, no increase in water column P was observed, suggesting dynamic changes at the soil/sediment water interface.

In the absence of infiltrating surface waters, diffusion and mass flow are the only mechanisms for downward movement of P into the soil and into the zone root. The presence of the soil matrix prevents convection currents; thus, the diffusive process is further restricted to molecular diffusion. The model for this process is the diffusion equation:

$$J_D = -D\frac{dC}{dz} \tag{2}$$

where C = P concentration, g m^{-3}; D = diffusion coefficient, m^2 d^{-1}; J_D = vertical diffusion flux, g m^{-2} d^{-1}; z = vertical distance, m.

The value of the diffusion coefficient in pure water is of the order of 7.6×10^{-5} m^{-2} d^{-1} at 25°C, for $H_2PO_4^-$, which is the dominant inorganic form of phosphate at low to circumneutral pH (CRC, 1992). Values in the soil porewater are likely to be lower because of a tortuosity effect. In general, concentration gradients are variable in both magnitude and direction.

Some idea of the importance of the diffusive process may be gained by examining the situation of mildly eutrophic surface waters overlying a fully P saturated peatland. Reddy et al. (1991) report SRP porewater gradients as large as 3.0 gm^{-4} in the top 20 cm of an Everglades cattail-dominated peatland. Under these circumstances, the diffusion flux predicted by Eq. 2 is:

$$J_D = -\left(7.6 \times 10^{-3}\right)(3)(365) = 0.083 \ \ g \ \ m^{-2} \ \ yr^{-1} \qquad (3)$$

The porewater in the top 20 cm contained approximately 0.08 g P m^{-2}, and the sorbed, bicarbonate extractable P was also approximately 0.08 g P m^{-2}. As a consequence, the estimated turnover time of the labile phosphorus pool in the upper soil horizon would be about 2 years if the only operative mechanism was diffusion.

Uptake rates in that Everglades environment were independently measured and found to be an order of magnitude higher than the predicted diffusive flux (Reddy et al., 1991; Richardson et al., 1992).

Plant uptake is a significant factor in comparison to diffusional transport. In a mildly eutrophic marsh, annual biomass production of 500 g m^{-2} at 0.2% P requires 1.0 g m^{-2} yr^{-1} supplied to the root zone. Diffusional gradients apparently cannot supply this amount of P; consequently, its source must be internal to the root zone. That source is the decomposition of the detritus from preceding years' litter, some of which may be associated with root turnover.

D. Interaction with Groundwater

Another mode of advective transport includes interaction with groundwater or the hyporheic zone (Harvey and Bencala, 1993). The hyporheic zone is the region of interaction between the stream and the groundwater that returns water to the stream (Bencala, 1993). Depending on the piezometric surface, groundwater may seep into the stream or streamwater may infiltrate into the groundwater (Rigler, 1979). In the case of transient groundwater movement, the direction of water flow depends on the water stage in stream or wetland. The direction and velocity of groundwater flow affect the transport of P as well as other solutes. Groundwater inflow may provide substantial nutrient loads to the channel (Stanford and Ward, 1988). During infiltration, advective and dispersive processes enhance downward movement of dissolved oxygen and cations as well as P. This movement may increase P retention capacity of the sediments. Downward advection increases the thickness of the aerobic zone and assimilation within the sediment. Phosphorus

also can be transported to groundwater. Where seepage dominates, Eh, pH, and solute content of interstitial water are dominated by the groundwater.

Vertical flows of water in the upper soil horizon are driven by gravity and by plant uptake to support transpiration. In an aquatic system, without emergent transpiring plant parts, vertical downflow will be driven solely by gravity. Water infiltration flow is then computed from the water pressure (hydraulic head) gradient between the saturated soil surface and the receiving aquifer, multiplied by the hydraulic conductivity of the soil. This flow moves the phosphorus in the overlying water downward into the root zone.

If the hydraulic conductivity of the soil layers beneath the root zone is very low, then percolation to groundwater is effectively blocked. In aquatic and wetland systems with fully saturated soils or free surface water, the meteorological energy budget requires the vaporization of an amount of water sufficient to balance solar radiation and convective losses. Some of this vaporization is from the water surface (evaporation); some is from the emergent plants (transpiration). Emergent plants "pump" water from the root zone to the leaves, from which water evaporates through stomata, which constitutes the transpiration loss. In a densely vegetated wetland, transpiration dominates the combined process (evapotranspiration = ET) (Kadlec et al., 1987). Water for transpiration must move through the soil to the roots. That movement is vertically downward from overlying waters in most wetland situations. In temperate climates, ET ranges from 60 to 200 cm yr^{-1}, but is maximized in that part of the year with greatest solar radiation.

Thus, transpiration has the potential to move on the order of 1 m per year of water vertically downward to the root zone. That water carries with it the phosphorus concentration associated with the bottom layer of overlying water. In the case of the Everglades peatland cited above, that concentration is of the order of 1.0 mg L^{-1} (Reddy et al., 1991). The vertical flux of phosphorus due to transpiration supply therefore is 1.0 m $yr^{-1} \times 1.0$ g $m^{-3} = 1.0$ g P m^{-2} yr^{-1}.

In the case of a downward water flow in soils without plant uptake, a chromatographic "front" of increased P concentrations move downward in response to a sustained increase in the P concentration in overlying waters. For most soils, this will be a sharp front, as predicted from typical sorption isotherms and mass balance (Gerritse, 1993). Phosphorus arriving at the front is stored in porewater and on sorption sites; water leaving the front in the downward direction will have the equilibrium concentration for the soils ahead of the front. The equilibrium storage potential of the soil is:

$$C_T = \theta C + \rho_b C_s = \left(\theta + \rho_b \frac{C_s}{C} C = fC \right) \tag{4}$$

where C = porewater P concentration, g m^{-3}; C_s = P concentration on soil, mg kg^{-1}; C_T = total P concentration in soil plus porewater, g m^{-3}; f = soil storage factor, dimensionless; P_b = soil bulk density, kg m^{-3}; c = soil water content, fraction of volume.

The ratio C_s/C is determined from the sorption isotherm. Wetland water content is often in the range 0.3 to 0.9, and bulk densities range from 0.05 for flocculent sediments to over 1.5 for mineral soils. Values of f typically range from near unity to over 100. The velocity of the P front is related to the storage potential of the soil. The frontal velocity is given by (Gerritse, 1993):

$$u_f = \frac{u}{f} \tag{5}$$

where u = water velocity, m d^{-1}; u_f = P front velocity, m d^{-1}.

IV. METHODOLOGIES TO ESTIMATE PHOSPHORUS RETENTION

Several methodologies exist to estimate P retention by wetlands and streams. These include (1) mass balance based on input-output analysis (Kadlec, 1978), (2) sediment or organic matter accumulation rates (Johnston, 1991; Craft and Richardson, 1993; Reddy et al., 1993), and (3) measuring changes in the P concentration of the soil/sediment porewater column (Mayer and Gloss, 1980; Patrick and Khalid, 1974; Reddy et al., 1996). These approaches are used both in the laboratory and under field conditions.

A. Laboratory Methods—Batch Incubation Studies

Batch incubation studies are generally used to estimate P sorption capacities of sediments and soils. The capacity of sediment/soil to retain added P often is described by simple adsorption isotherms, which relate P concentration in solution to the amount of P retained by the sediment or soil. In these studies, a known amount of soil or sediment is added to solutions of different P concentrations, and the suspensions are equilibrated for a known period (usually 24 to 72 h) at a constant temperature. Phosphorus lost from solution is assumed to be adsorbed on solids. This methodology to measure P sorption has been widely used by several researchers over the last 2 decades (Berkheiser et al., 1980; Hammer and Kadlec, 1980; Khalid et al., 1977; McCallister and Logan, 1978; Richardson, 1985). The most popular mathematical models used to describe P sorption are the Langmuir and Freundlich equations:

Langmuir:

$$S = \left[\left(S_{max} kC \right) / \left(1 + kC \right) \right] - S_o \tag{6}$$

Freundlich:

$$S = KC^N - S_o \tag{7}$$

where S_{max} = P retention capacity, mg kg^{-1}; S = P retained (sorbed) by the solid phase; mg kg^{-1}; k = a constant related to bonding energy, L mg P^{-1}; C = P in solution after equilibration, mg L^{-1}; S_o = P retained under ambient conditions, mg kg^{-1}; K = phosphate adsorption coefficient, L kg^{-1}; N = empirical constant (N < 1). At solution P concentrations of < 5 mg L^{-1}, a simple linear adsorption isotherm can be used, at low concentration N = 1. Eq. 2 reduces to:

$$S = KC - S_o \tag{8}$$

To obtain parameters for the above equations, P sorption should be measured at a number of concentrations. This method cannot be used rapidly on a wide range of soils. A single-point isotherm was used by Bache and Williams (1971) to determine P sorption capacity of a wide range of soils. The approach involves measuring P sorption at one fixed concentration after fixed equilibration period (18 h). The P sorption index (Bache-Williams index) is calculated as follows:

$$PSI = S/\log C_t \tag{9}$$

where PSI = sorption index; C_t = concentration of P in solution after an 18-h equilibration period. This index is measured at P concentration at the upper-end scale of an isotherm. This method was later applied for wetland soils by Walbridge and Struthers (1993). Single point isotherms cannot provide parameters such as K, EPC, and S_0, which are critical in describing P retention characteristics of soils and sediments.

The Langmuir equation is useful in estimating the maximum capacity of soils and sediments to sorb P. The Freundlich equation is used to calculate P buffer intensity. High K values suggest strong affinity for P and thus low P concentration in the porewater. Many of the sorption parameters were highly correlated with soil physicochemical characteristics.

The following empirical relationship was derived for a number of wetland soils and stream sediments in the Lake Okeechobee Basin, Florida (Reddy, 1991).

$$S_{max} = 0.24 \quad oxalate[Fe + Al]r^2 = 0.872 \quad n = 60 \tag{10}$$

where S_{max} is same as in Eq. 1; [Fe + Al] = oxalate extractable Fe and Al expressed in mmoles kg^{-1}. Eq. 5 is applicable for S_{max} values in the range of 0 to 30 mmol kg^{-1} and for oxalate extractable [Fe + Al] in the range of 0 to 100 mmol kg^{-1}. The slope

0.24 in Eq. 5 represents the fraction of oxalate Fe + Al that can potentially retain P. Other researchers have reported values of this slope to be in the range of 0.4 to 0.6 (van der Zee and van Riemsdijk, 1988; Lookman et al., 1995). Similar empirical relationships have correlated P sorption to extractable Fe, Al, Ca, and to TOC concentrations of soils/sediments (Aulenbach and Meisheng, 1988; Cooke, 1992; Froelich, 1988; Gale et al., 1994). Similarly, the PSI values (Eq. 9) were highly correlated with oxalate extractable Fe and Al of several wetland soils (Walbridge and Struthers, 1993).

Carman and Wulff (1989) measured the P sorption capacities of different sediments from the Baltic sea and showed that the shallow oxidized sediments function as major sinks for P from the water column. Several studies have radiolabeled used ^{32}P to estimate P adsorption capacities of sediments (Furumai et al., 1989; Istvanovics et al., 1989). Furumai and Ohgaki (1989) used ^{32}P to estimate P adsorption capacities and exchange characteristics of sediments from Lake Kasumigaura, Japan. They reported that anaerobic conditions induced a large release of P and an increase in exchangeable P, especially below pH 8. Values for exchangeable P under these conditions ranged from 27 to 49% of total P in the sediments. Sediment P fractionation data for these sediments showed that Fe and Al were the dominant cations influencing P retention capacity.

B. Laboratory Methods—Sediment/Soil Column Studies

Intact sediment/soil column experiments provide a straightforward estimate of assimilation capacity of stream/wetland systems (Aulenbach and Meisheng, 1988; Diaz and Reddy, 1995; Holdren and Armstrong, 1980; Masscheleyn et al., 1992; Reddy and Reddy, 1993). The advantage of this technique is that it includes the effects of diffusion and influences of complex processes at of the soil-floodwater interface on P retention or release by soil. Reddy et al. (1995a,b) used intact sediment/soil cores to estimate P retention capacities of selected stream/wetland systems from the Lake Okeechobee Basin and calculated assimilation capacities of the sediments/soils as follows:

$$P_r = AC - P^1 \tag{11}$$

where P_r = phosphorus retention by sediments, mg P m^{-2}; A = phosphorus retention coefficient, L m^{-2}; C = water column P concentration, mg L^{-1}; P^1 = phosphorus release potential under ambient conditions, mg m^{-2}. The above equation is similar to Eq. 8, except in Eq. 11, P retention includes the effects of diffusion of P from water column to the soil or sediment. The "A" in the above equation is analogous to the K in Eq. 8. The following relationships described P retention by all stream sediments and wetland soils sampled in the Lake Okeechobee Basin (Reddy et al., 1995a).

$$\text{Stream sediments} \qquad P_r = 128C - 12; \; r_2 = 0.96 \qquad (12)$$

$$\text{Wetland soils} \qquad P_r = 118C - 54; \; r_2 = 0.71 \qquad (13)$$

Eq. 11 yields an indication of threshold concentrations (equilibrium P concentrations) in the water column, where P retention equals P release, i.e., $P_r = 0$

$$P^1 = AC \qquad (14)$$

$$EPC_w = P^1 / A \qquad (15)$$

where EPC_w = threshold concentration, mg L^{-1}. Water column P concentrations $> EPC_w$ suggests net P retention by soils and sediments, while water column P concentration $< EPC_w$ suggest net P release by soils and sediments. For the relationships shown in Eq. 12 and 13, calculated EPC_w values were 0.10 mg P L^{-1} for stream sediments and 0.46 mg P L^{-1} for wetland soils in the Lake Okeechobee basin (Reddy et al., 1995a).

C. Field Methods: Wetlands

The laboratory studies described estimate above measured process-level P assimilation in the various components of the stream sediment/wetland soil systems. A mass balance approach based on input-output budgets and analysis of various components of wetlands and streams provides a broader view of P assimilation. Phosphorus inputs measured in these systems usually include surface water, groundwater, precipitation, and overland flow. Measured P outputs include surface runoff and drainage. Based on input-output analysis for a large number of constructed and natural wetlands in North America, Kadlec and Knight (1995) reported the following empirical equation:

$$C_o = 0.34 C_i^{0.96} \quad R^2 = 0.73 \quad n = 373 \qquad (16)$$

$$\text{Standard Error in } \ln C_o = 1.09$$

where C_o is the P concentration in outflow ($0.009 < C_o < 20$ mg P L^{-1}); C_i is the P concentration in inflow ($0.02 < C_i < 20$ mg P L^{-1}). The difference between C_i and C_0 is the loss of P from the water column, or that assimilated by plants, microorganisms, and soil. The above equation indicates that 73% of the variability in projected P retention was explained by P input load for wetlands. The database covers total P loads ranging from 0.2 to 1000 g P m^{-2} yr^{-1}. Eq. 10 is empirical and yields only a preliminary

estimation of P removal rates by wetlands. Actual assimilation capacities vary with site-specific physical, biological, and chemical conditions and with P loading rates.

A steady-state, time-averaged mass balance model was reported by Kadlec (1993, 1994). This model is based on the internal mass balance for water and includes an empirical first-order rule for P uptake. In one-dimensional, plug flow form:

$$QL\frac{dC}{dx} = -kAC \qquad (17)$$

where A = wetland area, = LW, m^2; C = P concentration, g m^{-3}; k = first-order areal rate; constant, m d^{-1}; Q = water flow rate, m^{3}d^{-1}; L = exit travel distance, m; W = wetland width, m; $\times$ = travel distance, m. This first-order model is analogous to lake phosphorus models in use (Vollenweider, 1975; Canfield and Bachman, 1981). The model in this form assumes no atmospheric or groundwater losses or gains of P or water. However, it is easily extended to hydrologic conditions involving water losses or gains, and to situations involving other P inputs and outputs (Kadlec and Knight, 1995).

Integration of Eq. 17 from the wetland inlet to an arbitrary interior point in the wetland outlet yields the following:

$$\frac{C}{C_i} = \exp\left(-\frac{kW}{Q}x\right) \qquad (18)$$

where C = P concentration at location x, g m^{-3}; C$_i$ = inlet P concentration, g m^{-3}.

This exponentially decreasing P concentration along the distance of travel has been observed repeatedly in wetlands. At x = L, Eq. 18 reduces to, e.g.,

$$\frac{C_o}{C_i} = \exp\left(\frac{kW}{Q}L\right) = \exp\left(-\frac{k}{q}\right) \qquad (19)$$

where C$_o$ = outlet P concentration, g m^{-3}; q = hydraulic loading rate, m d^{-1}.

The plug flow assumption is not justified in many cases because flow through wetlands exhibits both macro- and meso-scaled dispersion. When tracer-tested, wetlands display flow characteristics intermediate between plug flow and complete mixing. These intermediate conditions may be modeled by a series compartmentalization of the flow path into a number (N) of well-mixed units (Kadlec, 1994), yielding a different relationship between C$_i$ and C$_o$:

$$\frac{C_o}{C_i} = \left(1 + \frac{k}{Nq}\right)^{-N} \qquad (20)$$

where N = number of compartments As N increases, Eq. 20 converges to Eq. 19. Many tracer tested wetlands appear to function in the range $2 < N < 4$.

Note that detention time, although not explicit in Eqs. 17 to 19, may be used as an alternate to hydraulic loading rate. The required relations are

$$\tau = \frac{\varepsilon \bar{h}}{q} \quad \text{and} \quad k_v = \frac{k}{\bar{h}} \tag{21}$$

where k_V = first-order volumetric uptake rate constant, d^{-1}; $\tilde{h}$ = mean wetland depth, m; ε = water volume fraction, ca. 0.95 to 0.98; t = nominal detention time in the wetland, d.

Uptake is assumed to be proportional to wetland surface area, and this assumption is supported by data checks. Thus, for surface flow wetlands, k is constant and k_V is inversely proportional to depth. This model successfully describes the long-term average P removal in herbaceous wetlands, but is insufficiently detailed to describe short-term fluctuations. Fast phenomena are inherently stochastic and therefore not amenable to deterministic modeling.

Longer-term transients, such as adaptation to new flows of water and phosphorus, may be described by the model, but rate constants during the transient are not necessarily those that will prevail in a more stationary state. This may be readily visualized for the common case of a new source of water and phosphorus introduced into a wetland. Unless the wetland is already completely eutrophic, the added nutrients will stimulate more plant growth, including algae and macrophytes. This new biomass contains phosphorus and hence requires a proportionate uptake from the water. However, after a new and larger standing crop has developed, there is no further net uptake by plants, and the rate constant is lower.

Values of the rate constant (k in Eq. 19) are known for numerous marshes. In the absence of flow data that defines the flow pattern, data analysis utilized the plug flow assumption, because that assumption returns the smallest (most conservative) value of the rate constant. Based on the data from 83 wetland cells, the calculated rate constant was $k = 12 \pm 6$ m yr^{-1} (Table 2). However, forested wetlands appear to operate at a lower uptake rate, with $k = 3.1 \pm 5.0$ m yr^{-1} for wetlands in the North American Database for treatment wetlands (Kadlec and Knight, 1995; Knight et al., 1993). The rate constant is insensitive to temperature, including those typical of northern winters.

Implicit in the first-order areal formulation is the rate of P accretion within a particular region of the wetland. The P removed from the water is envisioned to accumulate in the wetland biota and sediments, as the gaseous loss of P is usually discounted. There are some reports of phosphine gas emission from wetlands (Dévai et al., 1988; Gassman and Glindemann, 1993), but these have not been widely accepted. If the biomass and water storages are in a relatively stationary state—neither increasing nor decreasing over an averaging period—then the

TABLE 2
First-Order Phosphorus Rate Constant for Emergent Marshes

Site	No. of wetlands	Years of operation	Data years	HLR cm day⁻¹	TP In mg L⁻¹	TP Out mg L⁻¹	K m yr⁻¹
Des Plaines, IL	4	6	6	4.77	0.10	0.02	23.7
Jackson Bottoms, OR	17	3	2	6.34	7.51	4.14	14.2
Lakeland, FL	6	7	7	7.43	6.54	5.69	3.4
Pembroke, KY	2	6	2	0.77	3.01	0.11	9.3
Great Meadows, MA	1	ca. 70	1	0.95	2.00	0.51	5.7
Fontanges, QUE	1	2	2	5.60	4.15	2.40	11.2
Houghton Lake, MI	1	16	16	0.44	2.98	0.10	11.0
Cobalt, ONT	1	2	2	7.71	1.68	0.77	20.9
Brookhaven, NY	1	3	3	1.50	11.08	2.33	8.9
Leaf River, MS	3	5	5	11.68	5.17	3.96	11.2
Clermont, FL	1	3	3	1.37	9.14	0.15	23.4
Sea Pines, SC	1	9	8	20.20	3.94	3.36	11.7
Benton, KY	2	6	2	4.72	4.54	4.10	2.4
Listowel, ONT	5	4	4	2.41	1.91	0.72	8.2
Humboldt, SAS	5	3	3	3.04	10.16	3.24	12.8
Warrant County, TN	9	1	1	9.44	0.29	0.16	20.1
Iron Bridge, FL	16	7	7	2.69	0.43	0.10	13.5
Boney Marsh, FL	1	11	11	2.21	0.05	0.02	14.2
WCA2A, FL	1	30	14	0.93	0.12	0.02	10.2
OCESA, FL	4	6	6	0.83	0.27	0.16	6.4
Kis-Balaton, HUN	1	10	5	3.30	0.54	0.23	8.6
Average				4.7	3.6	15	12.0
St. Dev.				4.7	3.5	18	6.0

From Kadlec and Knight, 1995.

P removed from the water should be found in the wetland sediments and soils. After such possible adaptation trends are over, the accretion is

$$J = kC \tag{22}$$

where J = P accretion rate, g m⁻² d⁻¹.

As discussed above, the water phase concentration often shows an exponential decrease; therefore, the P accretion rate also should show an exponential decrease (Figure 7) and should account for all P removed from the surface water:

$$J = kC_i \exp\left(-\frac{kW}{Q}x\right) \tag{23}$$

This mass balance, and the exponential trend, has been thoroughly confirmed for WCA-2a in the Everglades (Reddy et al., 1993; Craft and Richardson, 1993; Walker, 1995). As a corollary, it is seen that a wetland will generally not possess a single P accretion rate; rather there is a strong spatial distribution of accretion rates. If the decreasing exponential accretion rate is averaged over the whole wetland, a single mean accretion number is generated; however, it then depends on hydraulic loading rate and inlet P concentration:

$$J = qC_i \left[1 - \exp\left(-\frac{k}{q} \right) \right] \tag{24}$$

where J = average P accretion rate over the wetland, g m^{-2} d^{-1}.

Phosphorus lost from the water column is retained in below-ground biomass, soil, and litter components of wetlands and streams. Storage in below-ground biomass occurs by translocation of P from above-ground biomass; the amount stored in this component is usually underestimated and the stability of this pool is unknown. The litter undergoes decomposition, and the soluble P is either released into the water column or retained by soil and microorganisms. These processes result in a net accumulation of organic matter and, as such, net P retention (Nichols, 1983; Howard-Williams, 1985; Richardson and Marshall, 1986). In addition, sedimentation of particulate matter loaded into these systems can increase soil mass and long-term P retention.

Sediment and nutrient accumulation rates have been estimated for many wetlands using ^{137}Cs as a marker (Craft and Richardson, 1993; DeLaune et al., 1978; Kadlec and Robbins, 1984; Patrick and Delaune, 1990; Reddy et al., 1993). In all these studies, peat accretion rates were measured using the maximum peak of ^{137}Cs corresponding to the period of maximum deposition from above-ground thermonuclear testing. Peat and sediment accumulation above this peak correspond with accumulation since 1964.

D. Field Methods: Streams

Phosphorus assimilation by streams is also estimable using a simple first-order rate equation, as shown previously (Newbold et al., 1981; 1983). The assimilation rate constant (k) measured as a function of time is related to the length of stream or wetland and flow velocity (Newbold et al., 1981)

$$k_t = v / S_w \tag{25}$$

where v = velocity of water flow and S_w = phosphorus uptake length. The concentration of P at any distance (x) from the source is given by:

TABLE 3
Phosphorus Assimilation Coefficients for Stream and Wetlands
Expressed as a Function of Distance from the Point Source

System	Phosphorus Assimilation Coefficient (A) m^{-1}	Ref.
South Platte River (Colorado)	1.76×10^{-5}	Keup (1968)
Pigeon River (North Carolina)	3.2×10^{-5}	Keup (1968)
Woodland Stream (Tennessee)	0.22×10^{-2} to 3.4×10^{-2}	Mulholland et al. (1990)
Hugh White Creek (North Carolina)	0.03	Munn and Meyer (1990)
Watershed 2 (North Carolina)	0.0015	Munn and Meyer (1990)
Coastal Plain Stream (Tennessee)	0.006	Newbold et al. (1981)
Otter Creek (Lake Okeechobee, FL)	0.6×10^{-4} to 2.9×10^{-4}	Reddy et al. (1994)
Everglades Marsh (WCA-2a)	2.7×10^{-4} to 5.7×10^{-4}	Reddy et al. (1993)

$$C_t = C_o \exp\left(-kt(x/v)\right) \tag{26}$$

Eq. 20 can also be expressed as:

$$C_t = C_o \exp-\left(A'x\right) \tag{27}$$

where $A' = kt/v$ and has units of m^{-1}. Phosphorus assimilation coefficients calculated using this equation ranged from 0.00018 to 0.04 m^{-1} (Table 3). Data on stream flows are not available to convert these constants into similar units as those shown in Table 2.

Phosphorus assimilation as a function of time was described by the sum of two exponentials (Rigler, 1979) as shown below:

$$C_t = \left[aC_o \exp\left(-k_i t\right)\right] + \left[(1-a)C_o \exp\left(k_2 t\right)\right] \tag{28}$$

The above equation was modified by Simmons and Cheng (1985) to account for the variation due to dilution and phosphorus load (concentration and flow) as described by:

$$C_t Q_t = \left[a C_o Q_o \exp(-k_i t) \right] + \left[(1-a) C_o Q_o \exp(k_2 t) \right] \qquad (29)$$

where Q = stream flow.

This first-order relationship was used to calculate P assimilation in streams as a function of distance from the source (Fisher, 1977; Keup, 1968; Mulholland et al., 1990; Simmons and Cheng, 1985). The limitations of Eq. 26 are that it assumes steady state conditions (effective steady flow), constant input from a point source, and no dilution from other sources in the stream. These shortcomings have been partially compensated for by the modifications described in Eqs. 28 and 29.

Intuitively, P assimilation by streams should follow the plug flow approximation rather than the single well-mixed unit concept because of the long and linear nature of the water body. Although the mixing intensity in slow-moving streams and in shallow ponds is about the same as it is in wetlands (Kadlec, 1994), the long linear nature of streams makes this effect small compared with advective flow. Therefore, the first-order formulation has been used, expressed in terms of stream length (Newbold et al., 1981, 1983):

$$\frac{C}{C_i} = \exp\left(-\frac{kW}{q} x \right) = \exp\left(-\frac{x}{L_p} \right) \qquad (30)$$

where L_p = constant, P assimilation length, m

The constant "L_P" is equal to the stream flow per unit width, L = Q/W, divided by the first-order areal rate constant k. It represents the distance over which 63% of the incoming P is assimilated. Table 3 gives sample values of k and L_P for streams of different sizes and P loadings.

Most of the literature treats the case of point source discharges into unidirectional overland flows. Steady state (or the equivalent, long-term averaging) is presumed. If there are no significant additions of water or phosphorus from other sources, the simple first-order equations shown here have proven useful (Keup, 1968; Simmons and Cheng, 1985; Fisher, 1977; Mulholland, et al., 1990). Extensions may be easily made to account for other inputs, but not for high-frequency dynamics.

IV. MODELING OF PHOSPHORUS RETENTION

An important step in water-quality management in a watershed is forecasting P retention in streams and wetlands (McCutchean, 1989). The model should be sufficiently general to be used throughout a drainage basin and be sensitive to changes in the important characteristics of various streams, canals, and sloughs

within the wetland system, to the degree that the rates of P assimilation are significantly different (HydroQual, 1995; Bicknell et al., 1993). Such a model would describe long-term retention of P and predict long-term effects of changing land use and water management (Lijklema, 1993).

Many models have been developed to simulate P assimilation in wetlands (McCutcheon, 1989, Donigian and Huber, 1990; Mitsch and Jorgensen, 1990; Barnes et al., 1994). These models vary in complexity and range of applicability. Barnes et al. (1994) has placed the models in one of several groups: basic box models that are used to explore specific relationships, water-quality models that stress physical transport and geochemical transformations, eutrophication models that describe explicit biological detail associated with algal blooms, and complex ecosystem models that focus on community structure such as food web models. These may be one-compartment box models with simple or complex P transformations (Finn, 1990; Kadlec and Knight, 1996), simple multicompartment models useful to describe and design wetland treatment systems or ecosystem analysis (Ondok, 1990; StraOkraba, 1994), or describe P behavior and transport in large-scale systems (Ditoro and Fitzpatrick, 1993; HydroQual, 1995). In addition to these groups, there are sediment flux models that describe the interaction of P with aerobic and anaerobic sediment (Kamp-Nielsen, 1983; Di Toro and Fitzpatrick, 1993).

Models describing wetlands and water quality are reviewed and categorized in the literature (Mitsch et al., 1988). Several models describe and evaluate P assimilation in wetland systems (Hammer, 1989; Kadlec, 1987; Moshiri, 1993), provide detailed models of physical, chemical, and biological processes in single stream reaches (Kim et al., 1990; Triska et al., 1989). McCutcheon (1989) reviewed several stream water-quality models ranging from steady-state flow with simple kinetics, to unsteady hydrodynamics with dynamic water quality. Models simulating P fate and transport in streams and wetlands are coupled models of water transport and solute transformations. Streams and wetlands are partitioned into segments based on their physical and biological characteristics. Biogeochemical processes are applied within each segment, while transport among the segments is simulated using a model that calculates flow rates. Transport models may describe water flow as steady flow or dynamic in one, two, or three dimensions (Lung, 1993). For wetland systems, one- and sometimes, two-dimensional flow is adequate to describe the flow field (McCutcheon, 1989; HydroQual, 1995).

A. Correlations

The simplest wetland P-models are empirical correlations between inflow and outflow (I/O) data that apply no known principles, such as mass conservation and are usually presented in the form of a graph or regression equation. Eq. 16 represents one form of this simplistic data representation. In Figure 6, input loading of P describes the average P concentration in the wetland outflow, based on the data
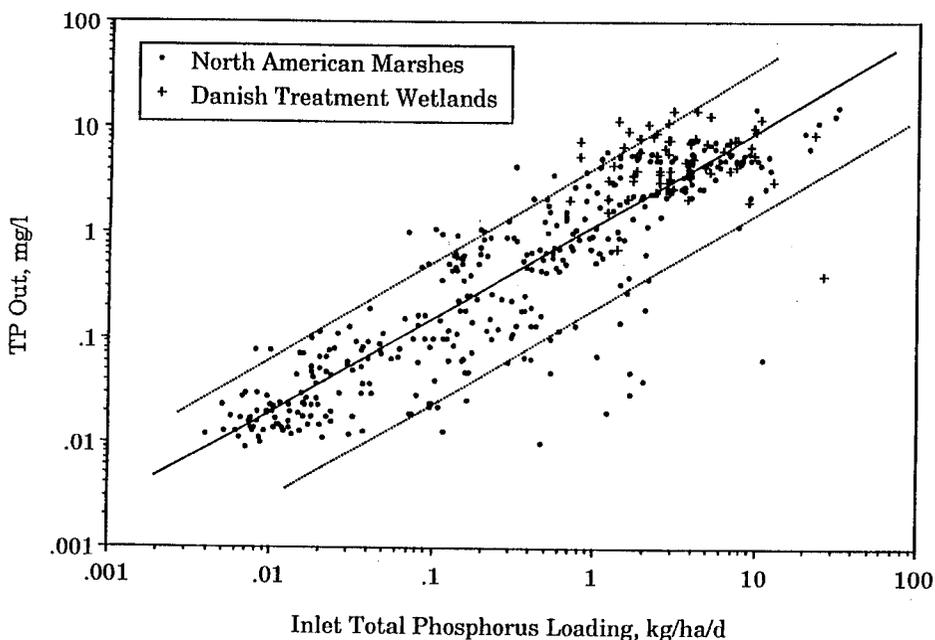
FIGURE 6. Output phosphorus concentration versus input P-loading to wetlands. The solid line shows the central tendency. The dashed lines represents the 5th and 95th percentiles. (From Kadlec and Knight, 1995; Schierup et al., 1990.)

from over 100 wetlands, taken primarily from the North American Database (Knight et al., 1993) and from the Danish Database (Schierup, et al., 1990). Because of the large variety of wetlands represented, scatter is large. Management or design decisions can be roughly assessed by their position relative to the performance of this large group of wetlands. Proposed projects located on the upper line are expected to produce P concentrations in ≥95% of the wetlands represented.

There are several multiple regression models that describe specific relationships of P loading or uptake with sediment, habitat, or wetland type (Ball and Trudgill, 1995). These relationships have limited use outside the domain of the data from which they were developed (Lijklema, 1993). One type of correlation model is the unit area response function for estimating P loading (Heaney et al., 1977; Donigian and Huber, 1990; Novotry, 1992). These loading functions often include the effect of P assimilation in wetlands and ephemeral streams.

B. Internal Mass Balance Models

Part of the scatter in regressions of I/O data is due to variation in hydrologic factors, including water inflow rate, rainfall, evapotranspiration (ET), and infiltration.

These can easily have predictable results, such as evaporative concentration of incoming P due to ET. The combination of the internal P mass balance, the internal water mass balance, and the removal rate equation comprises the model.

The P removal rate equation could contain any of several factors pertinent to the removal rate. For instance, Eq. 22 implements a simple mass action rule: P removal is proportional to P concentration in the water. For the case of steady flow, and no external sources, the water balance reduces to a condition of constant water flow. Importantly, this class of models now contains information on internal P concentrations and can be validated from transect data. When the assimilation equation is simple, the resulting equation for concentrations is simple, for example, such as Eq. 18.

There can be computational difficulties when multiple wetlands, ponds, and streams combine to form a geographical unit. Further, simple uptake rules often fail to describe the sequence of events that may take place over time. Calibration of the model must cover a time period sufficient to include a typical suite of meteorological and ecological events. Even then its predictive power is restricted to future sequences that include only those events.

C. Compartmental Mass Balance Models

The internal mass balance uptake models focus on the wetland water body and ignore apportionment of nutrients to the various parts of the ecosystem (including soils, live biomass, standing dead biomass, and litter). Detailed mechanistic models have been developed for specific systems such as a salt marsh (Pomeroy and Wiegert, 1981), freshwater wetland nutrient budget (Hopkinson and Day, 1980; Huff and Young, 1980; Kadlec and Hammer, 1988; Christensen et al., 1994), and lakes (Janse et al., 1992). For example, Janse et al. (1992) developed a single compartment model with a high degree of complexity. The model simulated detailed P exchange between biological components that included three functional groups of phytoplankton, zooplantkton, detritus, macrobenthos, and fish. The model was highly responsive to management alternatives, measured on an annual basis. However, the model did not reproduce various aspects of system behavior. It was limited by a lack of available data. Christensen et al. (1994) used a simple box model with two sediment layers to simulate soluble and particulate P transport and interaction with sediment and plants. Kadlec and Hammer (1988) included two soil layers, litter, standing dead, and live woody and nonwoody biomass as compartments in a wetland model that required over 20 parameters. The less ambitious Christensen et al. (1994) model considered soil, macrophytes, and plankton in addition to water, but still needed over a dozen adjustable parameters to describe the transfers between compartments. The necessary calibration data were available in both studies because of extremely costly accompanying research.

When a landscape element containing multiple wetland, stream, and pond ecosystems is considered, the implementation of a compartment model requires a fairly sophisticated set of computer programs, and a powerful computer for executing them.

D. Ecosystem Models

This category includes models that describe changes in habitat resulting from changes in environmental conditions (Costanza and Sklar, 1989; Mitsch, 1983, Ondok, 1990). The description does not imply a predetermined progression of species, but, rather, the change of species composition in response to factors related to human intervention. In the water treatment wetland context, this means the responses to changes in hydroperiod.

There are a large number of models that have been developed to simulate the changes in plant community structure resulting from changes in the biogeochemical environment (Mitsch and Jorgensen, 1990; Ondok, 1990; StraÓkraba, 1994). These models have detailed descriptions of plant communities that respond to changes in nutrient loading. Although not designed to simulate P assimilation, they simulate algal community dynamics and macrophyte P uptake (Ondok, 1990), which may be critical components of the wetland.

E. Transport Models

Water transport is a basic component for most solute transport/retention models. Hydrodynamic models have been developed to describe water movement in two- or three-dimensions (McCutcheon, 1989). With simplifying assumptions, hydraulic routing can estimate water flow, but this requires detailed information about flow geometry, which is highly site-specific. This may be necessary to simulate P behavior and transport in critical systems such as Chesapeake Bay and the Florida Everglades. However, to simplify data collection and model development, hydrologic models are developed based on a mass balance of water flow. These models are often adequate to describe the time-varying behavior of water and solute transport. A mass-balance approach is useful when the relationships between physical and chemical mechanisms are dynamic and variable on a larger scale (Berndtsson, 1990). In effect, these models average the transient behavior in order to describe monthly or seasonal flows in a given region. Hydrologic models can be used to develop regional models where detailed wetland and stream morphology are unavailable.

Simulation of P assimilation in wetlands combines P biogeochemistry with two-dimensional transport. Hammer and Kadlec (1986) modeled overland flow through a marsh. The model was based on the hydrodynamics of the marsh using

site topography, longitudinal porosities of the natural channels, and water mass balance to predict velocities. A one-dimensional longitudinal model was sufficiently complex to describe water flow and water levels. Some parameters for the model were estimated based on calibration, others came from independent studies. The model reproduced a monthly period of record based on daily water flow data and detailed topography.

Several models have been developed for solute transport in streams (Triska et al., 1989; Kim et al., 1990). These models describe transient nutrient assimilation, storage in streams, and nutrient uptake lengths (McKnight and Bencala, 1990; Kim, 1994). Solute transport is based on the advective-dispersive flow, with diffusion and convective exchange with the hyporheic zone. At this scale, a single stream reach, solute exchange with nonflowing water is an important process, but transient soluble storage does not affect steady-state estimation of storage. Jackman et al. (1984) treated transient storage in creeks as dead zones and sorption as a diffusion process. The hydrodynamic components of this model (estimates of stream velocity and dispersion) were calculated from field measurements of tracer transport. Unfortunately, application of these models is limited to the streams where they are developed (Bencala, 1984; Kadlec, 1987).

These transport models can be used to simulate phosphorus spiraling. Phosphorus spiraling describes the uptake of P from flowing water by the benthic periphyton community and movement and transformation within the community before release to the flowing water. The transport models may include the processes controlling spiraling explicitly or represent those processes as a single, integral length coefficient. Most of the processes occur at a spatial and temporal scale too fine for explicit modeling. Although simulation of spiraling is important for analyzing the effect of nutrient uptake on ecosystems, it does not describe long-term assimilation of P in wetlands.

F. Sediment Flux Models

The interaction of P with sediment is complex and has resulted in the development of models specifically designed to describe nutrient flux from sediments (Ariathurai and Krone, 1977; Kamp-Nielsen, 1983; Di Toro and Fitzpatrick, 1993). These models range from descriptions of P exchange with detritus and sediment (Reimold, 1974) to detailed description of P interactions in sediment and water column (Lijklema, 1993). Empirical sediment exchange models require site-specific data (Lung, 1993), such as a settling rate coefficient (Kamp-Nielsen, 1983). Models that simulate long-term system behavior require modeling of the sediment mass balance for P in sediment, and the fast processes such as microbial uptake are incorporated into equilibrium coefficients (Lijklema, 1993). These models are driven by the slow processes of mineralization and diffusion.

Van der Molen (1991) developed a sediment P exchange model that adequately reproduced P retention in a lake. However, the model was limited by lack of data,

spatial variability of the sediment, and uncertainty about settling rates. Di Toro and Fitzpatrick (1993) developed a sediment flux model that includes particulate and soluble P in water phase, and sediment partitioning, digenesis, and burial. An empirical relationship described oxygen flux and redox potential at the sediment/water interface. Mineralization rates of three organic matter reactivity classes (rapid, slow, and nonreactive) modeled changes in the sediment matrix with time, and predicted release of organic P. The model simulated the seasonal P flux reasonably well, but did not predict point-wise distribution of fluxes due to limited spatial data on sediment characteristics. It may be necessary to use time-series analysis to describe input-output behavior (Lijklema, 1993; Ball and Trudgill, 1995). Bath and Marais (1993) modeled sedimentation, mobilization, and transport of bed load sediment. Phosphorus assimilation was described primarily by sediment exchange. However, none of the available sediment-P interaction models handles periphyton communities well (DiToro and Fitzpatrick 1995).

Some detailed models predict P behavior at the sediment/water interface, including one that tracks the biogeochemistry of detritus, dissolved oxygen, N, P, and Si in multiple sediment layers (Smits and van der Molen, 1993). The model contains numerous parameters estimated (and calibrated) from field data and the literature. The model simulates the thickness of the oxidized layer, concentration of nutrients in porewater, and mass flux. However, the model underestimates deep P removal, which prompted the authors to recommend more analysis on P behavior in active sediments. The accuracy of the results were limited by spatial variability of the lake sediments.

G. Watershed Models

Watershed models developed to simulate basin hydrology also simulate the transport of P (Metcalf and Eddy, 1971; McCutcheon, 1989; Caussade and Prat, 1990; Donigian and Huber, 1990). Most of the models have limited application due to the spatial variability within the watershed (Caussade and Prat, 1990) and the complexity of the interactions of P with the environment (Donigian and Huber, 1990), and these models often are difficult to calibrate, verify, and apply (Engel et al., 1993). These models that focus on downstream impacts are often insensitive to high-frequency events or nutrient loading source area analysis (Donigian and Huber, 1990). Although there are many runoff models that estimate P loads from agricultural land, models are not sufficiently developed to evaluate the movement of P from animal waste through wetlands (Culley et al., 1990).

Many detailed models have been developed to simulate the effect of acid rain on solute transport through catchments (Ball and Trudgill, 1995). These models are primarily concerned with solute transport through soil, although some models, such as SHETRAN (Ewen, 1995), include stream and river transport functions. These models are focused on cations and rarely describe P biogeochemistry in detail.

There are watershed models for both urban and non-urban nonpoint source pollution. Three of the more advanced models, that have some features for simulating P assimilation are the SWAP, HSPF, and SWMM models. Arnold et al. (1994) developed the SWAT model to assess nonpoint source pollution from agricultural land management. The SWAT model estimates off-site P loads. Further downstream interacts are limited to P interaction with sediment as the sediment is deposited. The HSPF model is the most detailed, comprehensive watershed modal available for simulating nonpoint source P loading (Donigian and Huber, 1990). The model simulates P loads from permeable land surfaces, including the loads from agricultural land (Donigian et al., 1995). Unlike other runoff models, HSPF simulates P interactions with sediment and the biological community in downstream receiving water (Bicknell et al., 1993). The SWMM model was developed to simulate discharge from urban stormwater systems (Metcalf and Eddy, 1971; Hopkinson and Day, 1980; Huber and Dickinson, 1988). Heidtke and Auer (1993). Urban non-point source models are aimed at runoff and do not include routing or wetland chemistry (Donigian and Huber, 1990).

H. Advanced Models

Several advanced water-quality models have been developed to simulate P transport and transformations in streams and wetlands. These models include HSPF (Bicknell et al., 1995), DUFLOW (van Duin et al., 1995), CE-QUAL-RIV1 (Environmental Lab, 1990), QUAL-2E (Brown and Barnwell, 1985), MIKE12 (Bach and Jensen, 1994), RCA (HydroQual, 1995), and WASP4 (Ambrose et al., 1988). These models simulate P transformations in the water column and sediment for systems that are primarily one-dimensional, downstream transport.

The HSPF model simulates P interaction with sediments as well as zooplankton and benthic algae in the river reach and reservoir component (Bicknell et al., 1993). In the WASP4 model, mineralization and settling of organic-P, dissolved inorganic-P, and phytoplankton-P uptake are all considered. Phosphorus settling and interaction with benthic layers are modeled as an empirical function of the inorganic fraction of P and oxygen dynamics of the sediment. QUAL-2E simulates P transformations for steady-state one-dimensional flow in streams and lakes. Phosphorus transformations include organic-P transformations in addition to inorganic-P transformations. However, the model has a weak sediment-P interaction component (Donigian and Huber, 1990).

The models, WASP4, CE-QUAL-RIV1, and RCA, simulate P transport for dynamic flow when coupled to an appropriate hydrodynamic model. Cerco and Cole (1992) developed a complex model for evaluating eutrophication in the Chesapeake Bay involving a three-part modeling effort: hydrodynamics, water quality, and sediment P flux. The water-quality component included a eutrophication module with three algal groups with production and predation, hydrolysis of POP,

mineralization of DOP, particle settling, and solute exchange. The model also considered the transformations of labile POP and refractory POP. Both CE-QUAL-RIV1 and RCA have detailed sediment P transformation components in addition to the eutrophication component (HydroQual, 1995). RCA, however, is a proprietary model based on the Chesapeake Bay eutrophication model (HydroQual, 1995). The CE-QUAL-RIV1 model contains a eutrophication component and a sediment exchange component (Environmental Lab, 1990). The presumed P sinks are sediment and plant uptake. The sediment component has both aerobic and anaerobic layers. MIKE12 accounts for water-quality transformations in the water column, including zooplankton, phytoplankton, macrophytes, and sediment interactions. The model was developed for simulating eutrophication in bays, rivers, and estuaries. DUFLOW, a routing model. It contains a eutrophication component that is similar to QUAL2E and WASP4 (van Duin et al., 1995). It includes algae-P interactions, dissolved inorganic-P, dissolved organic-P, and particulate organic-P transformations and a simple sediment exchange algorithm.

Frequently, models are not functional, too complex, and contain unnecessary detail (Kadlec and Knight, 1996; Lijklema, 1993). These models suggest a level of accuracy not justified by analytical or experimental resolution of system characteristics. Parameter estimation and error propagation are often significant problems in models with (multiple) estimated or calibrated parameters. They cannot be verified, however, as they are incomplete descriptions and require empirical data that are not completely known (Orekes et al., 1994). Nevertheless, a model can perform well against observational data, even if it cannot be verified because it can be used to describe a certain behavior within the available data. In most situations with limited field data, long-term P assimilation can be estimated by simple transfer functions (Kadlec and Knight, 1996).

Mechanistic models are generally complex and difficult to use (McCutcheon, 1989). Frequently, models are not functional, too complex, and require several coefficients. This level of complexity may not be needed to describe long-term behavior of P retention by wetlands. Complex models, with detailed descriptions of wetland processes, are good for modeling of specific wetland systems for treatment design or for investigating specific relationships (Mitsch and Jorgensen, 1990). These models require a good description of the physical transport and wetland morphology (Barnes et al., 1994), and, unless carefully calibrated, can produce large errors (Engel et al., 1993).

There is a trade-off of complexity for accuracy (Costanza and Sklar, 1989). Often, simple models reproduce general characteristics of system, where the system is controlled by a few critical physical and biological characteristics (Barnes et al., 1994). A model should be selected for the scale appropriate to the processes being evaluated (Lijklema, 1993). Detailed spatial modelling may not be necessary when simulating a single end point (Ball and Trudgill, 1995). Model selection should be based on ease of use, flexibility, suitability for project objective, support, and track record (McCutcheon, 1989).

VI. CASE STUDIES

A. Wetlands

The retention of P in wetlands decreases P loading to downstream aquatic systems such as rivers and lakes. The delay in transport caused by storage in wetlands can be on the order of days to many years, depending on the stability of the stored P. Although wetlands store P in the system, they do have a finite capacity, and P loading beyond their capacity to assimilate P can be detrimental to both the wetland ecosystem and downstream water quality.

Phosphorus retention in wetlands is regulated by vegetation, periphyton and plankton, plant litter and detrital accumulation, soil physicochemical properties water flow velocity, water depth, hydraulic retention time, length-to-width ratio of the wetland, P loading, and hydrologic fluctuations. In evaluating wetlands for P assimilation, it is necessary to consider (1) short-term storage mediated by assimilation into vegetation, periphyton, and incorporation into detrital tissue, and (2) long-term storage mediated by assimilation by soil and accretion of organic matter. Short-term storage and associated P dynamics significantly impact on long-term storage and discharge water quality.

Numerous laboratory and field studies have been conducted to determine the P assimilation capacity of wetlands. These studies included both constructed and natural wetlands materials for P removal. However, many of these studies evaluated only short-term processes and failed to adequately assess long-term storage capacity and reliability of wetlands for nutrient removal.

Statements appear in the literature to the effect that "wetlands may be either sinks or sources of P, depending upon site specific factors." This statement carries the ominous connotation that there are major doubts on the reliability of P assimilation in wetlands. In fact, there is overwhelming evidence that emergent flow-through marshes with long hydroperiods reliably provide long-term storage of P. The data in Table 2 indicate that, on an average, 83 wetlands currently in operation in diverse settings function as net P sinks.

Input/output P data from several wetlands (Figure 6) represent the frequencies ranging from daily to monthly (averaged over three months) comprising each of the four seasons of the year. Over 97% of these data quarters show that the wetlands are operating as a P concentration reducer, irrespective of season. The same is not necessarily true for other types of wetlands. For example, only 67% of the data pairs for forested wetlands in the NADB exhibit reduced P concentration. A mechanistic explanation of this observation is unavailable.

If the hydroperiod of an emergent marsh is short, meaning that it lacks surface water over a significant portion of the year, then P storage becomes less likely. Newly formed organic sediments become exposed to air, oxidize, and release P in available forms. After rewetting, that P is free to move out of the wetland with flowing waters. The same phenomenon may be associated with the

restoration or construction of a wetland on previously drained or dry sites. Antecedent land uses can provide mobile P forms during a period of adaptation to the new hydroperiod.

Some of the confusion in the literature concerning the source/sink question arises from the character of the data and the methods of analysis. Some potential difficulties are: (1) *Failure to identify and measure all inputs and outputs of P and water*. Some studies, such as that for Brillion Marsh in Wisconsin, have documented P concentrations in only one input stream and one output stream, despite the fact that other flows entered the marsh (Fetter et al., 1978). Further, the only measured flow was the wastewater addition, which was estimated to be about 7% of the total stream inflow. Mass balances therefore were poorly estimated. (2) *Use of only one form of P*. The various forms of P include particulate, organic and inorganic, and dissolved organic and inorganic P. Interconversions can be rapid. Therefore, a wetland may be a "source" of one form and "sink" for other forms, simultaneously. For example, Gehrels and Mulamoottil (1990) reported that an Ontario marsh reduced total P by 50%, but increased dissolved P by 22%. In contrast to the Brillion Marsh study, all components of the water and P mass balances were independently measured (Fetter et al., 1978). (3) *Comparison of synchronous flows and grab samples*. Detention times in wetlands are often on the order of 1 or more weeks. Consequently, P concentrations in the outflow may reflect, to some extent, the incoming P from 1 to several weeks in the past. Whenever there are significant changes in inlet flows and concentrations as a function of time, synchronous grab samples may give erroneously high or low estimates of removal. The Brillion marsh study provides a good example of this problem. Fetter et al. (1978) estimated that detention times in the marsh ranged from 12 to 145 days, with an average of 48 days. Clearly, it is dangerous to draw conclusions about seasonal behavior from contemporaneous monthly grab samples from inlets and outlets in this system. If the marsh exhibited plug flow, water arriving in late spring would not exit until early fall. More than 2 years data would be required to properly establish seasonal patterns, yet this article is often cited as demonstrating a "spring flush" of phosphorus. Composite, flow-weighted sampling over many detention times is required to alleviate this difficulty. (4) *Grab sampling of a strongly variable flow or concentration. Natural stream flows often display a high coefficient of variation for flow rate and concentration*. A single grab sample may represent either end of the range of values. Fetter et al. (1978) sampled inflows every 4 h in an intensive study, and found $C - = 1.6 \pm 1.2$ mg L^{-1}. A grab sample at 8:00 AM on the first day gave 3.8 mg L^{-1}; a grab at 8:00 AM on the second day gave 0.4 mg L^{-1}. Composite, flow-weighted sampling is required to alleviate this difficulty.

Studies of natural wetland P processing are numerous and reported in many formats. Wetland ecologists tend to report short-term, process-oriented results from natural wetlands, as typified by van der Valk and Davis (1978), Mitsch and Reeder (1991), and Perry et al. (1981). However, the use of both natural and constructed wetlands for water-quality improvement has generated many more data

sets. These cover two principal types of systems: stormwater treatment and domestic wastewater polishing.

Urban stormwater systems are described and summarized by Strecker et al. (1992). The 15 constructed wetlands in that survey were all net sinks for P, but 5 of the 11 natural wetlands were sources. Design guidelines for the configuration of these wetlands for effective nutrient, sediment, and metal trapping are available (Schueler, 1992).

Wetland systems are also used to treat agricultural field runoff. The Soil Conservation Service of USDA developed guidelines for implementing such systems (DuPoldt et al., 1992). Successful P trapping (virtually 100%) was demonstrated for these systems (Higgins et al., 1993), which now number 10 in the state of Maine and lesser numbers in other states (Wengrzynek, personal communication). The Water Conservation Areas (WCA-1, WCA-2a, WCA-3) of the Everglades in Florida have been studied intensively for many years and consistently have provided P removal from agricultural runoff (SFWMD, 1992). In addition, constructed agricultural runoff wetland systems in Illinois, Texas and central Florida have returned data over periods up to eleven years. These studies all have well-defined hydrologic information, because the wetlands are confined by dikes and berms, and surface flows are measurable at structures. As a result, these wetlands all have well-defined P mass balances, and they all act as P sinks. Data acquisition on most of these wetlands has included extensive information on soils and biota, as well as hydrology and water quality.

Wetlands are also used to remove P from treated domestic wastewater. These polishing wetlands receive secondary- or tertiary-treated water and further reduce nutrient content. Constructed, polishing wetlands also have the advantage of well-defined hydrology. Extensive compliance data acquisition is required by discharge permits, and additional research is frequently mandated. Flows and concentrations are measured at the greatest frequency for inputs and outputs; internal concentrations are monitored less frequently. Daily and weekly measurements are not uncommon. The large amounts of data so generated are contained in project reports that do not often get wide distribution. The North American Database (NADB) (Knight et al., 1993) is an (incomplete) effort to make that information available to the public. Phosphorus data are included for about 100 wetlands, including marshes, forested wetlands, and subsurface flow wetlands. Table 2 gives sample marsh performance data compiled from the NADB.

Polishing wetlands all reduce P in surface waters. Indeed, only 4 of 67 constructed wetlands receiving primary wastewater (TP = 9 mg L^{-1}) in Denmark report higher outlet than inlet concentrations. Interestingly, phenomena that have been reported for natural wetlands do not necessarily occur in treatment wetlands of similar character. For instance, the "spring flush" of phosphorus, described by Lee et al. (1975) for a central Wisconsin cattail marsh, did not occur in any of five cattail marshes in any of 4 years in southern Ontario (Hershkowitz, 1986).

Wetlands provide multiple microenvironments that provide the necessary conditions for interconversions of various forms of phosphorus. For instance, marshes typically have decreasing vertical redox profiles, and soils in the root zone are usually anaerobic. Some of the sorbed phosphorus that reaches this zone may be solubilized. If the soils or sediments are not vegetated, this released P can diffuse back to the surface waters. However, vegetative uptake, or readsorption at the sediment-water interface, apparently prevents net movement out of the sediments in wetlands (Cooke, 1992).

Much of the literature deals with the disposal and treatment of municipal wastewaters, and many of these systems are not being continuously monitored. The efficiency of P removal by these systems is evaluated as 'black boxes' by monitoring the inflow and outflow concentrations and mass loads. Few studies provide comprehensive mass balances for wetlands receiving P inputs. Based on the results reported in the literature, it can be concluded that wetlands usually are effective in trapping nutrients, at least at certain times of the year (van der Valk et al., 1979).

A long-term data base on a northern peat wetland used for wastewater treatment indicates the reliability of wetlands in removing 97% of added P consistently over a 15-year study period (Kadlec, 1993). Phosphorus removal in this wetland followed first-order kinetics with a rate constant of 11 m yr^{-1}. In this wetland, peat accreted at 2 to 3 mm yr^{-1} during the 15 years of operation (Kadlec, 1993). Sedimentation (mineral and organic sediments derived from external sources) and peat accretion (recalcitrant organic matter derived from aquatic biota) result in long-term P storage in wetlands. Johnston (1991) summarized the annual P accumulation rates in selected wetlands with mineral and organic soils. Wetlands with mineral soils accumulated 0.1 to 8.2 g P m^{-2} yr^{-1} (average = 1.46 g m^{-2} yr^{-1}), when compared with 0.04 to 1.1 g P m^{-2} yr^{-1} (average = 0.26 g P m^{-2} yr^{-1}) in wetlands with organic soils (Johnston, 1991). In a recent study, Craft and Richardson (1993) and Reddy et al. (1993) measured P accumulation rates in the range of 0.04 to 1.12 g P m^{-2} yr^{-1} in the Everglades Water Conservation Area 2A (Figure 7).

When wetland inflow exceeded outflow, a net retention of total P was observed in a wetland adjacent to a lake (Clausen and Johnson, 1990). The percentage of mass retained by the wetland was independent of areal loading rate. Other wetlands have shown nutrient release during spring and fall but retention during summer (Lee et al., 1975; van der Valk et al., 1979). However, not all wetlands function as net sinks for added P. Although wetlands transform some of the nonlabile pools of P into labile pools over the short term, they typically function as net sinks for total P. In a wetland receiving sewage effluent for 10-year period, Cooke et al. (1992) observed P deposition as a primary removal process, and most of the settled P was associated with oxalate-extractable Fe. This form of P is potentially unstable under anaerobic conditions and could become a source with a change in the oxidation-reduction status of the soil. However, release of P to the overlying water may be minimal due to readsorption at the oxidized soil-floodwater interface.
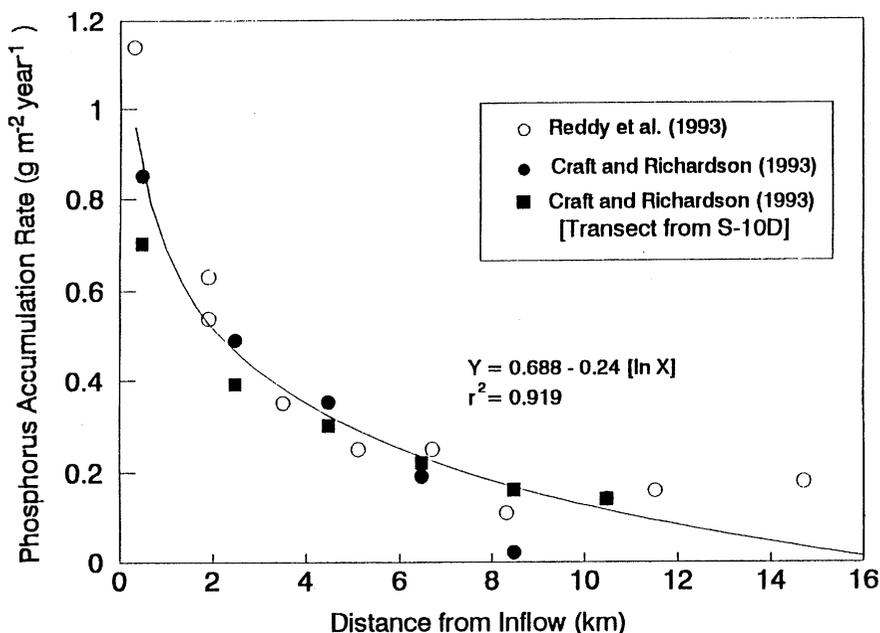
FIGURE 7. Phosphorus accretion rates in the Everglades Water Conservation Area 2A. (From Craft and Richardson, 1993; Reddy et al., 1993.)

B. Streams

Phosphorus retention within a stream system or its transformation into biologically unavailable forms can significantly impact productivity of downstream water bodies. The rate at which P is removed in these systems varies with flow velocity, discharge, biological, and chemical characteristics of the water column and the underlying sediments. Although many comprehensive studies have been conducted on P cycling and budgets in lakes, few studies have been reported on the fate of P in streams.

Phosphorus uptake negatively correlated with stream velocity (Meyer, 1979; Newbold et al., 1983). Phosphorus uptake was high during low summer flows, with about 92 and 44% of P input retained by Duffin Creek and the Nottawasaga River in southern Ontario, Canada, respectively (Hill, 1982). Similar trends were also observed by streams draining pine and hardwood catchments in the southern Appalachian mountains (D'Angelo and Webster, 1991). Streams in these catchments more effectively retained P in autumn when discharge was low than during large storms in the spring. Catchment location (slope) also significantly influenced P uptake, probably because higher velocities obviated organic matter accumulation in the stream beds. This relationship between slope and P retention indicates that geomorphology is an important factors influencing P retention.

Radiotracer studies demonstrated aquatic biota P assimilation in flowing streams (Davis and Foster, 1958; Ball and Hooper, 1961; Elwood and Nelson, 1972), including periphytic algae and aquatic macrophytes (Aiba and Ohtake, 1977). These studies support the premise that bioavailable P forms are the most important to quantify. Ball and Hooper (1961) showed that the distance a P tracer traveled 500 to 12,500 m in flowing water. Other researchers suggested that P cycles in streams be considered spirals, because of continuous downstream displacement of P as it cycles in the system (Webster, 1975; Webster and Patton, 1979). Newbold et al. (1981) developed an index of spiraling, which provides a measure of P utilization relative to the available supply from upstream. Using this approach, Newbold et al. (1981) estimated a spiral length of 193 m for P in a small woodland stream in Oak Ridge, Tennessee. Phosphorus uptake lengths of 32 to 40 m were measured with two headwater streams, one in the Appalachian mountains of North Carolina, and the other in the Cascade range of Oregon (Munn and Meyer, 1990). The P uptake rates in either stream were related to a combination of sediment infiltration rates and the quality of organic material rather than sediment size fraction. Similarly, Newbold et al. (1983) positively related P retention and particulate organic matter in the stream. Phosphorus uptake in Nepean River, New South Wales, Australia, was attributed primarily to assimilation in the littoral zone, while soluble P loss by inert particle uptake and chemical precipitation did not appear to be significant (Simmons and Cheng, 1985).

Sediment resuspension during stream flow can regulate the P concentration of the water column. Over shorter time scales (minutes), sorption/desorption processes played a minimal role in regulating dissolved P concentration of the water column (Prairie and Kalff, 1988). However, these researchers recognize that sorption/desorption processes could significantly influence stream water dissolved P over longer time scales.

Svendsen and Kronvang (1993) intensively sampled four 80-m reaches of a Danish lowland river to estimate the amounts of total P retained in the system. Reaches dominated by submerged macrophytes stored 20 to 30 g P m^{-2}, compared with 10 g P m^{-2} for sandy and gravely reaches. In-stream retention effectively reduced nutrient export to downstream systems in low flow periods, especially in areas with macrophytes. However, P retained by sediments can be mobilized during storm flows and vegetative clearing operations (Svendsen and Kronvang, 1993).

Phosphorus retention in stream systems is regulated by both biotic and abiotic factors. The role of sediments in regulating P concentrations of the porewater and the overlying water column is well known (Johnson et al., 1976; McCallister and Logan, 1978; Hill, 1982; Reddy et al., 1994). Meyer (1979) reported abiotic sorption by stream sediments as primary regulators of P concentration in Bear Brook, New Hampshire. However, other studies indicated strong biotic control of P uptake (Gregory, 1978; Ball and Hooper, 1961; Vincent and Downes, 1980; Elwood et al., 1981). Phosphorus retained by sediments can be mobilized rapidly during storm events. Mulholland et al. (1985) reported that 75% of the particulate

organic matter transport occurred during 17% of the storm flows in an average year. The capacity of stream systems to retain P can be evaluated by determining the stability of retained P. Minshall et al. (1983) found small headwater streams were more effective in retaining nutrients than mid-sized and larger streams. Ecosystems with a large pool of organic matter are more stable than systems with low organic matter (Golley, 1974; O'Neill and Reichle, 1980).

VII. POLICY IMPLICATIONS

Phosphorus assimilation in wetlands and streams is important in watersheds with significant non-point source contributions from agriculture. It may be necessary to forecast the expected P assimilation for a section of wetland or stream to determine the impact on a downstream water body. This is important where wetlands are used to clean or polish river water (Des Plaines River; Mitsch et al., 1995), or reduce P loads before entering a lake (Reddy and Flaig, 1995), or determine the size of constructed wetlands along a flowpath (Walker, 1995)

Reasonable forecasts of long-term P assimilation are based on the sediment accumulation rates and sediment P sorption capacity. These are a function of the sediment and soil type, inflow volume and mass loading, and retention time. A method that estimates the P settling rate processes would be sufficient to estimate assimilation. Processes that include vegetation and periphyton behavior as well as chemical precipitation are part of the overall settling rate. In many systems the P sorption capacity of the soil and sediment is finite. In other systems, the P sorption capacity appears to be extended due to the addition of metal ions through animal manure.

The three primary mechanisms for long-term assimilation are the deposition of incoming particles and their associated P load; formation of chemical precipitates containing P; and the accumulation of organic matter, as a byproduct of the carbon cycle, and its associated P content. In the event of a new water addition to a previously impacted wetland, sorption processes may provide for short-term assimilation, or may operate in reverse to release P to the surface water, depending on how much available P is in the antecedent soils. Therefore, an important consideration in forecasting adsorptive P assimilation is identification of the equilibrium background water concentration (EPC_w), which corresponds to the existing amount of mobile P in the soils and sediments. If surface water is at higher concentrations, there is still capacity for further P accumulation; however, if water concentrations are lower than this threshold concentration, P may be released from the sediments. Threshold concentration in South Florida has been found to be in the range of 9 to 400 µg/L. The release of stored P may be managed via hydrologic control, by allowing incorporation of the released P into the carbon cycle under no-flow conditions. If the antecedent soils are highly loaded with P, and there is not time for such management, then P releases will occur over a transition period during which the carbon cycle catches up with the new hydraulic and P loading.

The effect of changing wetland characteristics, or restoration of wetlands, can increase the P assimilation in a wetland/stream system. Mitigation or restoration of on site ponds and wetlands will enhance the estimated assimilation. On site wetlands will be the most effective in P assimilation, because the P concentration is greatest when undiluted by runoff from undisturbed sites. The assimilation capacity may be changed by modification of the biological community, which may occur due to changes in hydroperiod or nutrient loading. Changes in hydroperiod may result from changes in upstream land use or structural changes in the wetlands and streams channels. Changes in the biological community will result from changes in hydroperiod and nutrient load, but also can be changed by direct planting and changes in stream back structure. Creation of off-channel flowways, enhanced riparian floodplains, and retention lakes have been used successfully to improve nutrient retention. The utility of these methods depends to a large degree on the morphology of the wetland/stream system.

CONCLUSIONS

The reduction of phosphorus loading from uplands into receiving aquatic systems depends on the assimilation capacity of wetlands and streams. The latter involves physical, biological, and chemical processes that ultimately retain P in biologically unavailable forms. Phosphorus uptake by vegetation is mostly balanced by release during decomposition of detrital tissue. In systems with a net accretion of organic sediments, vegetation contributes to assimilation capacity.

Periphyton and microorganisms influence the P assimilation capacity of wetlands in several ways. They can act as transformers of P between biologically available and unavailable forms. More importantly, both groups alter the chemistry of their surroundings, thus influencing the P chemistry of the system. Periphyton-induced pH changes in the water column can cause coprecipitation of P with $CaCO_3$. The activity of sediment microorganisms alters the oxidation-reduction status of the system, causing changes in the availability of sorption sites on amorphous Fe and Al compounds.

Transport phenomena such as sedimentation, molecular diffusion, and mixing affect the availability and reactivity of phosphorus. Physicochemical characteristics of the soil/sediment and water column such as pH, dissolved O_2, clay content, reactive Fe, Al, Ca, and Mg contribute to the P assimilation capacity of the system. Although the biological and chemical factors are interrelated, biological uptake and release provides the greatest influence on water column P concentrations.

Methodologies for estimating P assimilation in wetlands and streams include mass balances, and process kinetics applied to microcosms, mesocosms, pilot, and full-scale systems. Batch soil microcosms can estimate P sorption capacity and relate retention to physicochemical properties of the substrate. Because this technique excludes diffusion constraints and biological contributions, its usefulness as

a gauge for P assimilation by real world wetland-stream system is questionable. Kinetic studies using sediment-water columns are probably better gauges of true abiotic assimilation, because they consider process dynamics.

The mass balance approach provides an ecosystem level view of P assimilation and is extremely useful for evaluating the overall functioning of wetland/stream systems. However, our inability to measure all inputs and outputs into a system often limits the usefulness of this technique. Assumptions such as steady state conditions, constant inputs, and no dilution are often required when using this technique in complex natural assemblages of ecosystems. These assumptions limit the reliability of this approach. Sedimentation and peat accretion rates have estimated nutrient accumulation rates in a few wetlands. This technique is useful in providing long-term estimates of P retention.

Phosphorus retention in wetlands is regulated by a variety of biological, physical, and chemical factors. When evaluating wetlands P assimilation, one must consider both short-term storage (assimilation into vegetation, microorganisms, periphyton, and detritus) and long-term storage (assimilation by soil and accretion of organic matter). Wetlands typically function as net sinks for total P.

Phosphorus retention by stream systems is dominated by physical processes such as flow velocity, discharge, and water depth. However, the same biological and chemical processes that regulate P retention in wetlands regulate P in streams. Abiotic processes controlling P retention in streams are dominated by sediment sorption reactions. However, biological uptake can account for the majority of dissolved P transformations in streams. Long-term storage of P in stream sediments is inhibited by rapid mobilization and transport that occurs during storm events.

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