PHOSPHORUS RETENTION AND SORPTION BY CONSTRUCTED WETLAND SOILS

END OF PROJECT REPORT

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INTRODUCTION

Phosphorus (P) is an essential macronutrient in all biological organisms (Fox, 1993; Sharpley and Rekolainen, 1997). However, excess P can play a major role in the eutrophication of freshwater systems (Tanner et al., 1995). In Ireland, nutrient losses such as nitrogen (N) and P from agricultural practices continue to contribute to eutrophication of surface waters (Stapleton et al., 2000; Cleneghan, 2003). Eutrophication occurs when surface waters become over-enriched with nutrients such as N and P. This stimulates plant and algal growth, which subsequently dies and decomposes; thereby reducing, dissolved oxygen concentrations in water columns, which is detrimental to aquatic life (Jeffrey, 1998). Since the onset of eutrophication worldwide, much research has focused on understanding the processes regulating P within truly aquatic freshwater systems such as lakes and rivers (Li et al., 1972; Schindler 1977; Holdren and Armstrong, 1980; Fox, 1993; Goltermann, 2001). Subsequently, many technologies in association with management systems have been devised both to prevent and mitigate the loss of P, which can cause eutrophication of surface waters.

One approach, which is a land-based ecologically engineered method, is the use of wetlands to help mitigate P loss from agricultural practices. Wetlands ecosystems are not truly aquatic freshwater systems; rather they are transition zones between terrestrial and truly aquatic systems (Mitsch and Gosselink, 1993; Kadlec and Knight, 1996). Wetland ecosystems both constructed and natural are becoming important mitigating measures in water resource management around the world, as they have the ability to cycle and retain nutrients such as P (Gale et al., 1994; Mitsch et al., 1995; Reddy et al., 1999; Uusi-Kämppä et al., 2000; Braskerud, 2002).

Retention of P by wetland ecosystems can be defined as the ability to remove water column P through physical, chemical and biological processes (Gale et al., 1994; Reddy et al., 1999). Phosphorus sorption and precipitation are some of these processes that are important, as they regulate inorganic P dynamics within soils and sediments (Bache, 1964; Reddy et al., 1980; Yuan, 1980; Sanyal and De Datta, 1991; Reddy, et al., 1998; Rhue and Harris, 1999). Phosphorus sorption capacities of soils are often related to the amount of poorly crystalline and amorphous forms of aluminium (Al) and iron (Fe) (Ponnamperuma, 1972; Khalid et al., 1977; Van der Zee et al., 1988; Reddy et al., 1995; Reddy et al., 1998; Axt and Walbridge, 1999). Sorption is typically greater under aerobic soil/sediment conditions than anaerobic conditions (Li et al., 1972; Moore and

Reddy, 1994; Nürnberg, 1988; Ann, Reddy and Delfino, 2000). However, fluctuating aerobic and anaerobic conditions of soils and sediments can also cause transformation of crystalline Al and Fe compounds to more amorphous forms under anaerobic conditions, which have greater surface areas for P sorption reactions to occur (Patrick and Khalid, 1974; Kuo and Mikkelsen, 1979; Sah and Mikkelsen, 1986; Sah and Mikkelsen, 1986a).

Processes involved in long-term P retention, as apposed to short term P retention by wetland soils and sediments, includes accretion and decomposition of detrital material, and its associated P content (Richardson and Marshall, 1986; Kadlec, 1989; Richardson and Craft, 1993; Mitsch and Gosselink, 2000). Inorganic P can also react with Al and Fe that is associated with wetland soil and sediment detrital matter (Axt and Walbridge, 1999; Rhue and Harris, 1999) as organic matter has a high cation exchange capacity (Mitsch and Gosselink, 1993). More extensive reviews of inorganic and organic wetland P biogeochemistry can be found elsewhere (Mitsch and Gosselink, 1993; Kadlec and Knight, 1996; Newman and Robinson, 1999; Reddy et al., 1999; Wetzel, 1999).

PHOSPHORUS SORPTION AND PRECIPITATION

The ability of soils and sediments to retain P can depend on processes of P sorption and precipitation with different forms of Fe, Al and Ca. (Reddy et al., 1980; Yuan, 1980; Holtan et al., 1988; Sanyal and De Datta, 1991; Rhue and Harris, 1999). Sorption refers to both adsorption on solid surfaces and absorption into solid phases of Al and Fe oxides and other mineral surfaces (Bache, 1964; Rhue and Harris, 1999). Phosphorus adsorbs to mineral surfaces and once all surface sites are filled, P begins to diffuse into the particle via absorption (Reddy et al., 1999; Sanyal and De Datta, 1991). Sorption processes are temporally dependent, pH controlled and process rates decrease with time (Barrow, 1984; Bolan et al., 1985).

It is generally understood that Al and Fe oxides can occur as amorphous (predominantly found in anaerobic flooded soils) and/or as crystalline structures (predominantly found in aerobic terrestrial soils) in soils (Sah et al., 1989; Sanyal and De Datta, 1991; Fresse et al., 1992). Amorphous oxides of Al and Fe often exhibit greater reactive surface areas than crystalline forms for P sorption and can be determined using ammonium oxalate extraction procedures (McKeague and Day, 1966; Rhue and Harris, 1999). Khalid et al.

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(1977) initially suggested that there is a relationship between ammonium oxalate-extractable Fe content of soils and P adsorbed under flooded conditions. In wetland soils and stream sediments impacted by dairy effluent in Florida, USA, ammonium oxalate-extractable Fe and Al accounted for 87% of P sorption (Reddy et al., 1998). In other similar studies, Reddy et al. (1995) indicated that ammonium oxalate-extractable Fe and Al accounted for 71% of total P (TP) bound in stream sediments and about 43% of TP bound in wetland soils. The P stored in stream sediments was primarily in inorganic portions, while in wetland soils, P was stored in inorganic and organic forms (humic and fulvic acid bound P). Van der Zee et al. (1986) indicated that for sandy terrestrial soils in the Netherlands, P sorption was linearly related to the sum of ammonium oxalate-extractable Fe and Al. In increasing magnitude, sandy calcareous soils, acid sandy soils, neutral clays and clays with high Fe concentrations had an ability to retain P (Ponnamperuma, 1972).

Precipitation processes involve the removal of P from solution by the combination with Al [Equation 1], Fe and Ca cations to form new solid precipitates (Bache, 1964; Sanyal and De Datta, 1991; Rhue and Harris, 1999).

$$Al^{3+} + PO_4^{3-} = AlPO_4 \qquad\qquad [1]$$

Reactions with calcite surfaces involve initial adsorption of small amounts of P, which can be followed by precipitation of Ca bound P (Cole et al., 1953). Cations such as Na, K, and Mg can also affect P adsorption, as they can displace Ca, thereby freeing up Ca to sorb P (Roborage and Corey, 1979). Precipitation of P as insoluble Ca bound P [Equation 2] is a dominant transformation in wetland soils and sediments at pH values greater than 7 (Faulkner and Richardson, 1989).

$$Ca^{2+} + HPO_4^{2-} = CaPO_4 \qquad\qquad [2]$$

Calcium bound P was found to be a dominant fraction of TP within lake sediments in Florida, USA (Moore, Reddy, and Graetz, 1991). Precipitation of Ca ions with P can govern P solubility under reduced conditions (Reddy and Graetz, 1981; Moore and Reddy, 1994).

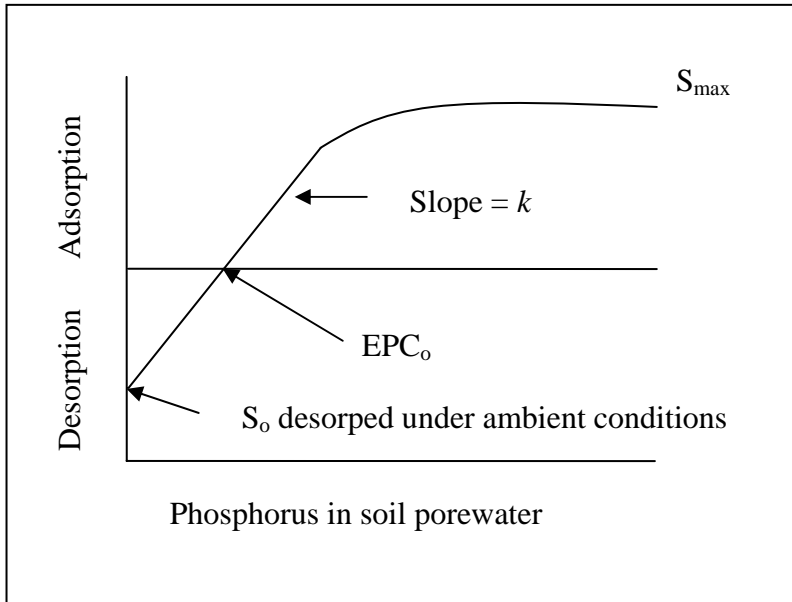## PHOSPHORUS ADSORPTION ISOTHERMS

Phosphorus adsorption isotherms are useful to quantify P sorption processes by soils and sediments. They are usually measured by mixing a known amount of soil or sediment with a solution containing a range of known P concentrations. Soil solutions are equilibrated (by shaking) for 24 hours at a constant temperature (Nair et al., 1984). The difference in amounts of P

adsorbed and recovered in solution at each concentration after equilibration are considered P adsorbed by soil or sediment (Pant and Reddy, 2001a; Reddy et al., 1999) (Figure 1).   Three P adsorption isotherms often used include Langmuir, Freundlich and Tempkin models (Barrow, 1978; Sanyal and De Datta, 1991; Rhue and Harris, 1999; Graetz and Nair, 2000), the most common of which are Langmuir and Freundlich models (Reddy et al., 1999; Rhue and Harris, 1999).   The Langmuir model has advantages in comparison to Freundlich's, as it provides more information on P sorption parameters (Graetz and Nair, 2000). It assumes that adsorption occurs at specific sites and that once these sites are occupied no further adsorption occurs. Phosphorus adsorption maximum (S_{max}) values and bonding energy (k) values can be determined using Equation [3] (Reddy et al., 1998; Rhue and Harris, 1999; Graetz and Nair, 2000).

$$C/S = 1/kS_{max} + C/S_{max} \qquad\qquad [3]$$

where C is solution P concentration (mg l^{-1}), S is the amount of P sorbed (mg kg^{-1}), S_{max} is the adsorption maximum (mg kg^{-1}), and k is a constant related to bonding energy (l mg^{-1}).

Adsorption

Desorption

Phosphorus in soil porewater

S_{max}

Slope = k

EPC_o

S_o desorped under ambient conditions

Figure 1: Sketch of phosphorus (P) sorption isotherms for soils. S_{max} = maximum P sorption capacity; EPC_o = equilibrium P concentration, where adsorption equals desorption; k = bonding energy; and S_o = initial P present in the adsorbed phase. (Source: Adopted from Reddy et al., 1999).

The Freundlich model is often described in linear form [Equation 4] (Graetz and Nair, 2000).

$$\log S = \log K + n \log C \qquad\qquad [4]$$

where S is the amount of P sorbed mg kg^{-1}, K is the adsorption constant (mg kg^{-1}), n is a constant (l kg^{-1}), and C is solution P concentration (mg l^{-1}).

Multipoint adsorption isotherms like those described above are time consuming (Reddy et al., 1999). To overcome this, several researchers adopted single point adsorption indices (Bache and Williams, 1971; Simard et al., 1994; Reddy et al., 1998). A single point P sorption index involves measuring P sorption at a known P concentration (instead of a range of known P concentrations) after an equilibrating period.

Bolan et al. (1985) considers that simple kinetic equations like those described above often fail to take into account the effect of time, P sorption parameters must be also regarded as unknown functions of pH and ionic strength. Also, P adsorption isotherms are limited in their ability to describe P sorption (Rhue and Harris, 1999) and thus should be viewed as functional models.

EQUILIBRIUM PHOSPHORUS CONCENTRATIONS

Equilibrium phosphorus concentration (EPC_0), which is a P adsorption isotherm parameter, can be defined as the P concentration in solution when P is neither adsorbed nor desorbed by soil (Taylor and Kunishi, 1971; Reddy et al., 1980; Pierzynski et al., 1994). Equilibrium P concentrations can be determined from P isotherm data, where soluble reactive P (SRP) sorbed is plotted against P concentration in solution at low concentrations (Figure 1). These values are useful in P sorption studies between soils and overlying waters, as they can give an indication of previous P loading onto soils. Increases in EPC_0 values can reflect increases in P loading (Reddy, et al., 1996). Soil solution concentrations greater than an EPC_o value determined for a particular soil suggests that the soil will sorb P, whereas soil solutions lower than an EPC_0 determined suggest that soil will desorb P. In practice, application of agricultural wastes to soils can increase EPC values and P desorption, while also decreasing P adsorption capacities of soils (Reddy et al., 1980).

An analogous term to EPC_0, and one that maybe more applicable to surface water quality within wetland systems and determining whether a wetland is a sink or a source of P at any given time, is equilibrium P concentration of

overlying wetland floodwaters (EPC_w). These concentrations can be determined from soil/sediment column experiments (as opposed to batch incubations using 50 ml centrifuge tubes), where P retained or released by soil is plotted against P concentration in overlying floodwaters (Reddy et al., 1999). Reddy et al. (1995) in their study of wetland soils and stream sediments within an agricultural watershed in Florida, USA defined EPC_w, as "P concentration of overlying floodwater, where no net P is either retained or released." Values averaged 0.13 mg l^{-1} of SRP for stream sediments in Lower Kissimmee River Basin, Florida, whereas nutrient impacted wetland soils in Fisheating Creek and Istokpoga Basins had higher concentrations in overlying waters of about 1.95 and 3.9 mg l^{-1}, respectively. When overlying wetland floodwater concentrations are above EPC_w, underlying soils and sediments can theoretically act retain P. Alternatively, soils release P, if concentrations are lower than EPC_w values (Reddy et al., 1995; Newman and Pietro, 2001; Pant and Reddy, 2001a).

EFFECT OF AEROBIC/ANAEROBIC CONDITIONS ON SOILS AND SEDIMENTS

Phosphorus biogeochemistry in flooded soils and sediments differs from oxidized upland and other terrestrial soils, as P adsorption is affected by hydrological regimes (Kuo and Mikkelsen, 1979). Under reduced, anaerobic conditions, Fe plays a major role in P dynamics. Reduction of Fe and its re-precipitation to form ferrous (Fe^{2+}) minerals are dominant processes under anaerobic conditions (Rhue and Harris, 1999). Einsele (1936) and Mortimer (1941) first proposed that there was a reduction of ferric iron (Fe^{3+}) to more soluble ferrous (Fe^{2+}) forms in anaerobic lake sediments [Equation 5].
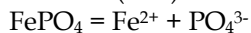
$$FePO_4 = Fe^{2+} + PO_4^{3-} \qquad\qquad [5]$$

This indicated a redox-controlled process with the net result being the release of previously bound P. It is presently well-recognised that P fluxes can occur from sediment/soil to overlying waters in flooded environments (Li et al., 1972; Nürnberg, 1988; Ann, Reddy and Delfino, 2000). Redox potential below 250 milli volts can cause reduction of Fe^{3+} to Fe^{2+} (Mitsch and Gosselink, 2000). Flooded soils and sediments can also have upper oxidised surface soil/sediment layers, where diffusing Fe^{2+} from anaerobic zones is oxidised to Fe^{3+} (Moore and Reddy, 1994).

Aluminium is not involved in oxidation-reduction reactions (Reddy et al., 1998), but is affected by changes in pH. Flooding can also cause transformation of crystalline Al and Fe compounds to more poorly crystalline

or amorphous forms (Patrick and Khalid, 1974; Kuo and Mikkelsen, 1979; Sah and Mikkelsen, 1986; Sah and Mikkelsen, 1986a). Amorphous forms have greater surface areas and thus have an increased ability to sorb P (Kuo and Mikkelsen, 1979). Sah and Mikkelsen (1989) found that in over 50% of soils investigated in their study, flooding alone increased P sorption from 10 to 70%. When soils undergo alternate wetting and drying cycles, soil aggregates can also disintegrate exposing new soil surfaces for P sorption (Olsen and Court, 1982).

Gale et al. (1994) suggested that P adsorption maximums in wetlands soils impacted by wastewaters were higher, when soils were incubated under aerobic conditions (S_{max} values ranged from 196 to 1821 mg kg^{-1}) in comparison to soils incubated under anaerobic conditions (values ranged from 32 to 1415 mg kg^{-1}). In a similar study, Reddy et al. (1998) found that anaerobic incubated natural wetland soils that were previously impacted by dairy effluent sorbed 39% less P than soils aerobically incubated. These studies suggest that the net effect of anaerobic conditions is decreased P sorption, which is probably due to factors that include reduction of ferric compounds, increased ionic strength and pH, and displacement of Fe and Al phosphates by organic anions (Reddy et al., 1999).

LONG-TERM PHOSPHORUS RETENTION BY WETLANDS

Long term P retention can be defined as the capacity to remove water column P and retain it in a form that is not readily released under normal environmental conditions (Reddy et al., 1999). Lack of understanding of these processes limited effective long-term P retention by wetland systems (both natural and constructed) used to improve water quality (Richardson, 1985); however, the last 20 years of research has provided information resulting in improved treatment wetland effectiveness for P retention at the operational level (DeBusk et al., 2001). It is often suggested that to retain P on a long-term basis using wetland systems, mass P input rates should be limited to long-term storage capacities (Richardson and Craft, 1993; Richardson, 1999).

Mechanisms, processes and interactions controlling long-term P retention can include deposition of incoming particles and their associated P load; hydraulic residence time; formation of chemical P precipitates; accretion and partial decomposition of organic and detrital material (Bloom, 1981; Richardson and Marshall, 1986; Kadlec, 1989; Craft and Richardson, 1993; Mitsch and Gosselink, 2000; Pant and Reddy, 2001); P gradient between overlying water

and underlying soil/sediment; and physicochemical characteristics at oxidized sediment-water interfaces (Reddy et al., 1995, 1996, and 1999; Pant and Reddy, 2001a). Phosphorus can also react with Al and Fe that is associated with soil organic matter (Axt and Walbridge, 1999; Rhue and Harris, 1999). Mortimer (1942) first indicated that an organic component such as humified material forms part of an adsorbing complex. Nichols (1983) emphasised that organic matter itself has almost no capacity to fix P, rather the presence of combined Fe and Al in humic and fulvic acid molecules is a prerequisite to stable complex organo-metallic P compounds (Sinha, 1971). Such compounds can be highly resistant to decomposition (Sinha, 1971a). Other studies have observed positive relationships between P sorption and total organic carbon (Gale et al., 1994; Reddy et al., 1998).

CASE STUDIES

To compare P retention between case studies it is important to consider relative trends in data rather than absolute values because wetland ecosystems are spatially and temporally dynamic systems with few studies being directly comparable. In low nutrient impacted natural wetland ecosystems such as the Everglades in Florida, USA, total P can accumulate at a rate of about 70 to 230 mg m^{-2} yr^{-1}, whereas sites within the Everglades that are more severely nutrient impacted, TP can accumulate at a rate of about 460 mg m^{-2} yr^{-1} (Richardson, 1985). Richardson and Qian (1999) suggested using modelling that once long-term TP loading to Water Conservation Area 2A of the Florida Everglades remained at 1 g of P m^{-2} yr^{-1}, wetland surface outflow concentrations should also remain relatively constant. As P loading increases to 10 g m^{-2} yr^{-1}, TP output concentrations can also exponentially increase (Richardson, 1999). In other natural wetland systems in the USA, Mitsch et al. (1995) showed that riparian freshwater marshes retained between 0.5 to 3 g of TP m^{-2} yr^{-1}, which resulted in wetland surface outflow concentrations ranging between 10 and 60 µg l^{-1}.

Gale et al. (1994) observed that a constructed wetland, used for treated wastewater disposal retained about 0.8 g of P m^{-2} yr^{-1}, whereas a wetland receiving secondarily treated municipal wastewater at a loading rate of 1.5 g P m^{-2} yr^{-1} had TP removal efficiencies of about 68% (Nichols, 1973).

At a landscape level and with a particular reference to P loss from agriculture, Uusi-Kämppä et al. (2000) and Braskerud (2002) determined that constructed wetlands located within Nordic agricultural watersheds retained up to 44% of incoming TP from non-point source pollution. Braskerud's (2002) findings

were equivocal to about 26-71 g of P m^{-2} yr^{-1}, most of which was composed of particulate P. In an agricultural watershed in Florida, natural wetlands and streams retained 18% of P imported to the watershed (Reddy et al., 1996).

OBJECTIVES OF EXPERIMENT

The objectives of this experiment were to determine the ability of two constructed wetland soils (that were previously used to treat farmyard dirty water) to retain P from overlying surface waters using intact soil/water columns extracted from two constructed wetland sites. First order rate constants were determined to investigate theoretical hydraulic residence times for P retention within the soil/water columns. The P sorption capacity of the soils was also measured using P adsorption isotherms. Phosphorus sorption parameters were quantified on a depth-specific basis (0-2 cm, 2-5 cm and 5-10 cm). Soil properties regulating P sorption in these two constructed wetland soils were also investigated.

MATERIALS AND METHODS

Site Descriptions

Constructed wetland soils were collected from two dairy farms during January 2002, each site represented a different P loading. Site one was at the Teagasc Research Centre, Johnstown Castle, Co. Wexford (Irish national grid reference E: 301524; N: 121744) (Figure 2; Plate 1). Soils were classified as a complex of imperfectly drained gleys and well to moderate draining brown earths. Site two was at a private farm at Dunhill, Co. Waterford (Irish national grid reference E: 250309; N: 100578) (Figure 2; Plate 2) where soils were classified as regosols that were poorly drained alluvial soils.

Both constructed wetlands were used to treat farmyard dirty water. Farmyard dirty waters can be composed of milking parlour washings, silage/manure effluents, rainfall on open yard areas and general yard washings (Cumby et al., 1999). Selected characteristics of farmyard dirty water entering the constructed wetland systems at the different sites are shown in Table 1.
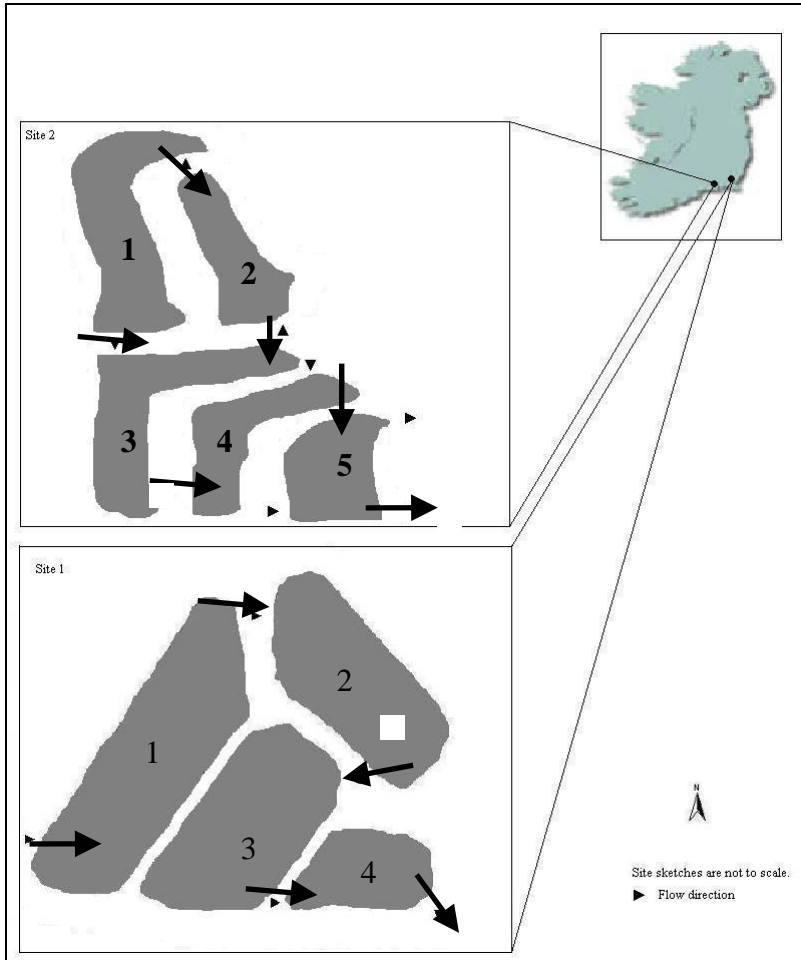
Figure 2: Sketch of constructed wetland site layout at (1) Johnstown Castle, Co. Wexford and (2) Dunhill, Co. Waterford.

Plate 1. Integrated constructed wetland at Teagasc Research Centre, Wexford.

Plate 2. Integrated constructed wetland at Dunhill, Co. Waterford.

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Table 1. Water quality characteristics of farmyard dirty water ± one standard error entering the two constructed wetland sites between December 2001 and January 2002								
				Parameter†				
Site	**SRP**		**NH$_4^+$**		**BOD$_5$**		**TSS**	
					mg l^{-1}			
Johnstown Castle	12.5	± 3.9	32.1	± 10.0	2565	± 474	972	± 275
Dunhill	25.5	± 5.5	51.5	± 13.5	715	± 275	194	± 34

† SRP, soluble reactive phosphorus; NH$_4^+$, ammonium; BOD$_5$, five day biological oxygen demand; TSS, total suspended solids.

Sample Collection

Three surface soil samples (0-10 cm) were taken at random within the first treatment cell of each site using a hand trowel. Samples were placed in plastic zipblock bags and transported in a cooler on ice to the laboratory for soil characterisation analyses.

For the soil/water column experiment, 18 intact soil/water columns were randomly taken from treatment cell one of each site. Wavin pipes (60 cm length x 10 cm internal diameter) were sharpened at one end and hammered down to a soil depth of 30 cm. Soil/water columns were dug out with a spade, plugged with wavin stoppers and sealed water tight with silicon. Overlying site floodwaters were siphoned off, but the soils were left saturated. The columns were placed in holders and transported to the laboratory for experimental study.

For P adsorption isotherm studies, three depth-specific (0-2 cm, 2-5 cm and 5-10 cm) soil samples were taken randomly from each treatment wetland cell within each site, using a simple coring device that consisted of a narrow diameter polyethylene pipe (50cm length x 2 cm internal diameter). The pipe was pushed down to a soil depth of 15 cm and pulled up with the adhered extracted soil sample in the pipe. Soil samples were extruded from the pipe

using a narrow extruder; soils were sectioned at the specific depth, placed in sample bags and transported in cooler on ice, to laboratory for isotherm studies and analyses.

Soil Characterisation

The surface soil samples were analysed for pH, particle size distribution (percentage of sand, silt and clay fractions), TP, total nitrogen (TN) and oxalate-extractable P, Al and Fe. Soil pH was measured in a 1:2 (soil/water mixture) using a pH meter with glass and calomel electrodes. All soil samples were then air-dried at 40°C, sieved, machine ground to 2 mm and stored for analyses at room temperature. Particle size distribution of soils was determined by the pipette method (Gee and Bauder, 1965). Soil TP content was determined by combusting one gram of soil at $550°C$ in a muffle furnace for four hours. Ash was then dissolved in 6 M HCl (Andersen, 1976) and the digestate analysed for TP using a modified ascorbic acid method (John, 1970). To determine TN, one gram of soil was digested on a Kjeldahl block digester with one kjeltab, 15 ml of concentrated H_2SO_4, and 3 ml of 100 volumes hydrogen peroxide. Digestion times were one hour at $150°C$ and one half hour at $39°C$. Digestate was analysed colorimetrically at 650 nm using an auto analyser following Berthelot reduction using the salicylate method (Houba et al., 1987). To quantify amorphous Fe, Al, and P, soils were extracted with 0.175 M ammonium oxalate and 0.1 M oxalic acid at a soil to solution ratio of 1:50 for 4 hours (Khalid et al., 1977). Extracts were centrifuged at 3,000 rpm and filtered to 0.45 µm using membrane filters. Solutions were analysed for Fe, Al and P using atomic adsorption spectrophotometry (AAS) (Gale et al., 1994).

Column Study

A soil/water column experiment was conducted using the intact soil/water columns from each site to determine P release and retention by soils. Phosphorus release and retention rates for the purposes of this study were defined as the P flux to or from soil on a mass per unit area rate basis (mg m^{-2} d^{-1}). Distilled water was spiked at 0, 1, 5, and 15 mg l^{-1} as KH_2PO_4. Spiked waters (1.2 l in volume) were placed into columns to an overlying water depth of 15 cm and remained in the cores for a 30-day hydraulic residence time (HRT). Each experimental unit was replicated three times. Intact soil/water columns were attached to holding racks and placed out of doors (Plate 3).
Overlying floodwater samples (20 ml) were taken on days 0, 2, 5, 8, 11, 15, 18, 21, 27, and 30. Samples were filtered (0.45 µm) and analysed for SRP using a modified ascorbic acid method (John, 1970).

This column study was conducted between January 8th and February 7th, 2002. Mean daily temperature and rainfall for that period were 8.3 ± 0.3°C and 6 ± 1 mm, respectively. Temperature data was recorded daily by a nearby automatic weather station. On site daily rainfall data was recorded manually using a rain gauge. Average rainfall SRP concentrations were determined from three samples taken during the column experiment. The hydraulic loading and subsequently P mass loading rate of rainfall, P mass load in overlying water column and total mass load in column were determined for each sampling period [Equation 6]. This was done to determine soil/water column effect in releasing or retaining P, rather than soil column and rainfall effect.

$$(C_c * V_c) + (C_r * V_r) = C_t * V_t \qquad [6]$$

where

C_c = soluble reactive P concentration in water column, (mg l^{-1})

V_c = volume of overlying water in column, (l). Initial core volume (1.2 l) minus the overlying floodwater sample volumes for each sampling period. This volume did not take into account rainfall

C_r = soluble reactive P concentration in rainfall, (mg l^{-1}), which was a sampling period average

V_r = volume of rainfall onto core, (l). Determined in volume, as the daily rainfall (mm) on column multiplied by the column surface area (m^2)

C_t = soluble reactive P concentration actually measured in overlying water of column, (mg l^{-1})

V_t = total volume of overlying water in column, (l). This was the total volume taking into account initial volume of overlying water in column, rainfall and floodwater sampling.

Plate 3. One replicate of intact soil/water columns mounted on holding rack.

Phosphorus release from soil to water or P retention by soil was determined as outlined by Pant and Reddy (2003):

$$(C_t - C_{t+1}) * V/A \qquad = \qquad P_r \qquad [7]$$

where

C_t = P concentration in water column of core at time t, mg l^{-1}
V = volume of surface water in core, l
A = surface area of soil water column, m^2
C_{t+1} = P concentration at next sampling day, mg l^{-1}
P_r = soluble reactive phosphorus release/retention, mg m^{-2}.

To determine release and retention on a daily rate basis (mg m^{-2} d^{-1}) release and retention data were divided by number of sampling days per sampling period.

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Phosphorus Adsorption Isotherms

Phosphorus adsorption isotherms were conducted on the depth-specific soil samples (0-2 cm, 2-5 cm, and 5-10 cm) to determine P sorption parameters of the two constructed wetland soils. One gram of dry, finely ground soil was placed into 50 ml centrifuge tubes. Soils were incubated with 20 ml of 0.01 M KCl containing 0, 0.1, 0.5, 1, 5, 10, 50 and 100 mg l^{-1}, as KH$_2$PO$_4$ (modified from Reddy et al., 1998). Tubes were shaken for 24 hours, centrifuged at 3000 rpm for 10 minutes and filtered to 0.45 µm using membrane filters. Filtrates were analyzed for SRP using a modified ascorbic acid method (John, 1970). Phosphorus adsorbed or desorbed by soil was calculated as shown in Equation [8]. Phosphorus not recovered in solution was assumed retained by soil (Reddy et al., 1998):

$$[(C_o * V)-(C_t * V)]/M \qquad = \qquad S^{'} \qquad [8]$$

where

C_o = concentration of P initially added to extracting solution, mg l^{-1}

V = volume of extracting solution, l

C_t = concentration of P in filtered extracted solution after 24 hours of equilibration, mg l^{-1}

M = mass of dry soil used, kg

S' = phosphorus sorbed by soil, mg kg^{-1}.

Equation 8 does not take into account the amount of native P adsorbed (S_0). Thus, ammonium oxalate-extractable P, which can be a large portion of soil TP, was determined and assumed to account for native P (van der Zee and Riemsdijk, 1988; Freese et al., 1992). The sum of native P and P sorbed by solid phase (S_0 + S') represents the actual amount of P adsorbed (S) by soil (Gale et al., 1994; Graetz and Nair, 1995; Reddy et al., 1998).

Values of P adsorbed (S) by soil were fitted to the linear version of the Langmuir model using Equation [3]. Equilibrium P concentration (EPC$_0$) values were determined as they can give a theoretical indication as to whether P is either adsorbed or desorbed by soil (Taylor and Kunishi, 1971; Reddy et al., 1980; Pierzynski et al., 1994). This can be calculated from the intercept of the y-axis using the linear relationship between S' and solution SRP concentration at low concentrations (< 10 mg l^{-1}) where R^2 is greater than 95% (Reddy et al., 1998; Graetz and Nair, 2000) (Figure 1).

Data Analyses

Experimental treatment significant differences (P < 0.05) were determined using student t-tests and analysis of variance (ANOVA). Linear correlations

were determined using the Pearson product-moment correlation. Non-normal data was log transformed and transformed data was tested for normality. Within ANOVA, all pairs were compared using Tukey-Kramer's honest significant difference (HSD). Linear regression analyses of transformed data were by the standard least squares method. All statistical analyses were performed using JMP software programme (SAS Institute Inc., Cary, North Carolina). First order exponential decay curves were fitted to non transformed data using SigmaPlot 2000 Version 6 (SPSS Inc., Chicago, Illinois).

## RESULTS AND DISCUSSION

Initial Soil Characterisation

Constructed wetland soils had relatively low pH values. Johnstown Castle site soils had higher pH values than those at Dunhill (Table 2). Higher TP and TN in Dunhill soils may suggest a greater historical nutrient loading effect (Reddy et al., 1998). Percentages of silt and clay were also higher in Dunhill soils relative to Johnstown Castle site soils (Table 2), which implies that Dunhill soils may have the potential to sorb greater amounts of P relative to Johnstown Castle soils, as Al and Fe oxides are predominantly associated with clay fractions (Fresse et al., 1992; Loeppert and Inskeep, 1996; Rhue and Harris, 1999; Pant and Reddy, 2001a).

Column Study

The purpose of the column study was to investigate SRP release and retention rates (mg m^{-2} d^{-1}) by soil in the soil/water columns from each of the constructed wetland sites during a 30 day HRT. In columns flooded with distilled water (0 mg l^{-1}), there was a net increase of overlying floodwater P concentration during the first two days of the experiment (Figure 3). This indicates that concentrations of P in soil porewater were higher than those in overlying floodwaters. The P disequilibrium between underlying soil and overlying water resulted in a net diffusion of P from soil to overlying floodwater (Reddy et al., 1999; Pant and Reddy et al., 2003). Pant and Reddy (2001) investigated water draw down effects on wetland detrital material and found that P release from detrital material to overlying water occurred within three days of flooding. This illustrates that independent of material type (soil or detrital material) if there is a P concentration gradient between overlying waters and underlying soils/sediments (with underlying material having higher concentrations than overlying waters) P release will occur (Reddy et al., 1995).

Table 2: Selected physicochemical characteristics of constructed wetland soils ± one standard error (n = 3).

| Site	Sand		Silt		Clay		pH		TN		TP		Organic matter	
	%								mg kg^{-1}				%	
Johnstown Castle	55	± 1.1	33	± 0.2	12	± 0.9	6.7	± 0.03	1100	± 29	450	± 29	5	± 0.1
Dunhill	12	± 0.3	55	± 2.0	33	± 1.7	5.5	± 0.03	3917	± 183	867	± 33	13	± 0.6
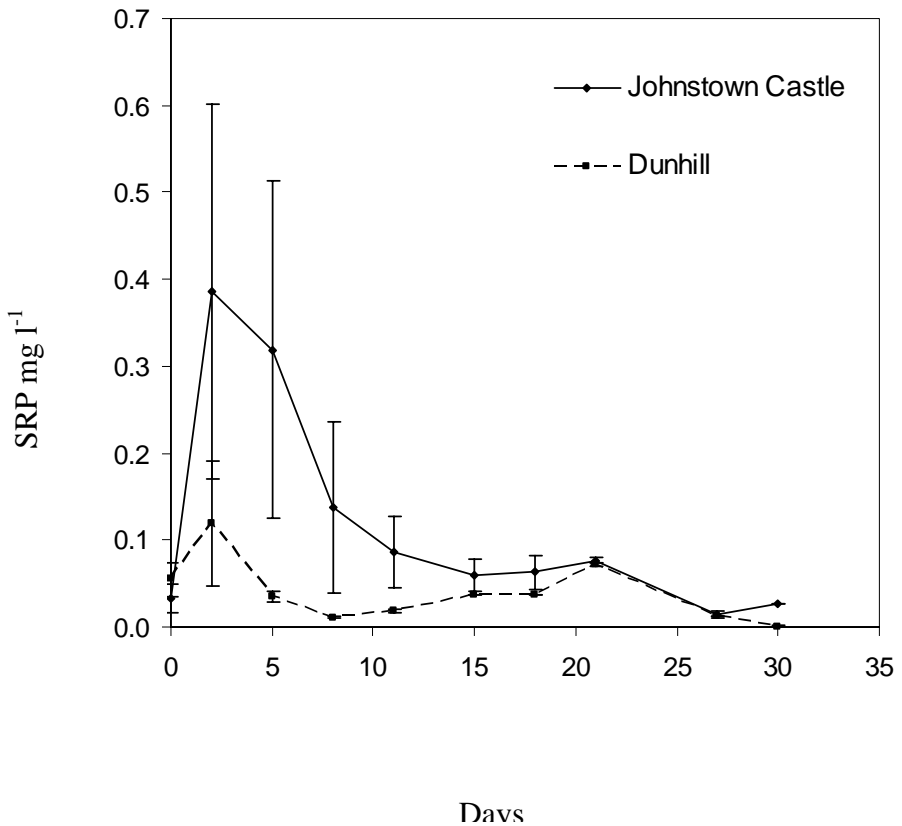
Figure 3: Soluble reactive phosphorus (SRP) concentration increase and reduction (± one standard error) in overlying distilled floodwaters of Johnstown Castle and Dunhill soil/water columns during the 30 day hydraulic residence time.

There was some difference, although not significant in P release rates from Johnstown Castle and Dunhill soils during the first two days of the experiment, suggesting that soil porewater P concentrations were sufficiently large that release rates during these two days, were independent of site soil effects. After the first two days of the column experiment, there was a general decrease in overlying water P concentrations through day 30, suggesting that soils, which had distilled water as their overlying floodwaters generally retained P (Table 3). Phosphorus concentrations in overlying floodwaters that were initially spiked at 1, 5, and 15 mg SRP l^{-1} also showed a decrease in concentrations indicating retention, until day 30 of the experiment (Table 3; Figure 4). During the 30 days of the column experiment, soils with overlying floodwaters initially at 0 mg and 1 mg SRP l^{-1} had similar P retention rates (Table 3). Soils with overlying floodwaters initially spiked at 5 and 15 mg SRP l^{-1} had significantly higher P retention rates than all other soils ($P < 0.05$) with no significant differences between site soils. Thus, as P loading increases, P retention also increases (Gale et al., 1994; Reddy et al., 1995). Phosphorus added to overlying waters at concentrations greater than those present in soil porewater, typically results in P retention by wetland soils (Reddy et al., 1995; Reddy et al., 1999). Areal P retention can depend on P diffusion from the water column to underlying soil, P concentration of porewater, and physiochemical characteristics of the sediment-water interface (Reddy et al., 1999). Some landscape and soil/water column studies have reported that constructed and natural wetland soils can retain between 7 and 45 mg m^{-2} d^{-1} (Reddy et al., 1996; Pant and Reddy, 2003). Thus, in theory Johnstown Castle and Dunhill constructed wetland soils have a relatively high capacity to retain P; however this is dependent on overlying P load.

At the end of the column experiment on day 30, Dunhill soils that had floodwaters spiked at 1 mg l^{-1} had lower P concentrations in overlying floodwaters than the same site soils with overlying floodwaters spiked at 5 mg l^{-1}, and both site soils with overlying waters spiked at 15 mg l^{-1} ($P < 0.05$). This may reflect the higher buffering capacity of Dunhill soils to changes in floodwater P concentrations, relative to Johnstown Castle soils as Dunhill surface soils (0-2 cm) had higher P adsorption bonding energy values (determined from P adsorption isotherms, which will be discussed later) than Johnstown Castle surface soils (Table 4). The only significant difference in P concentrations of overlying floodwaters of Johnstown Castle soils were between those that were initially spiked at 1 and 15 mg SRP l^{-1} ($P < 0.05$)
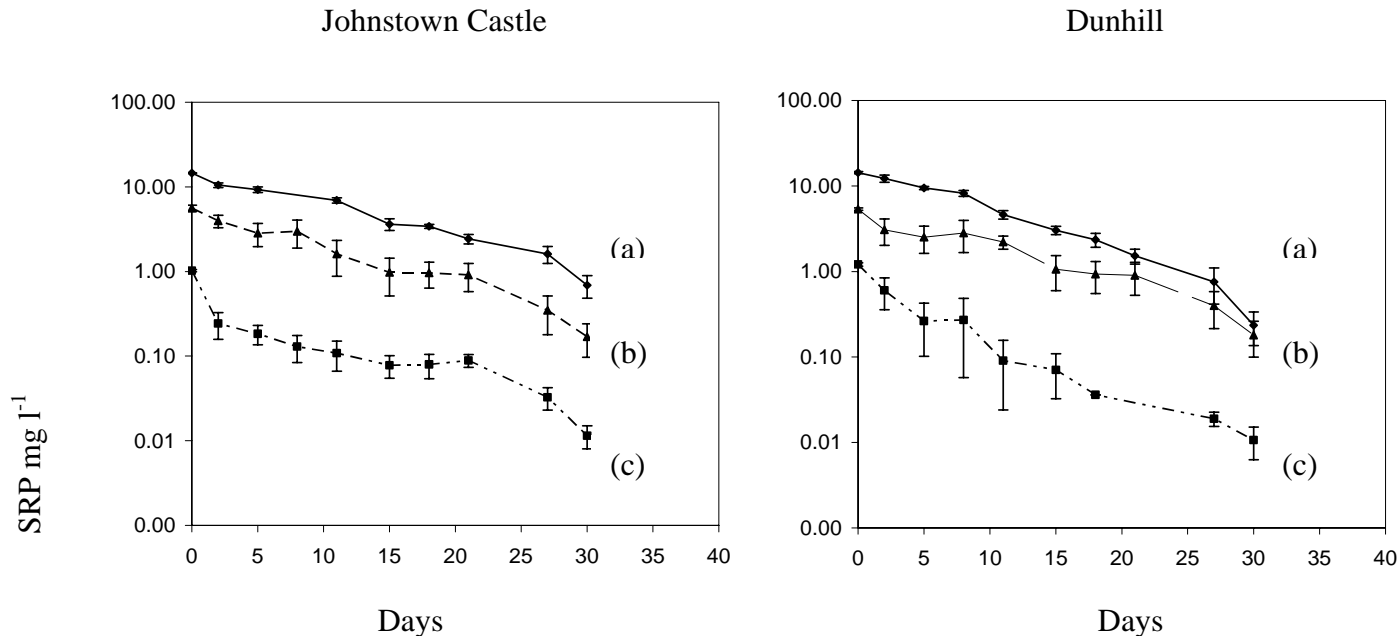
Figure 4: Changes in overlying floodwater soluble reactive phosphorus (SRP) concentrations of soil/water columns of Johnstown Castle and Dunhill during the 30 day HRT. Error bars represent ± one standard error. Overlying floodwaters were spiked at (a) 15, (b) 5, and (c) 1 mg SRP l^{-1}.

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Site	Initial SRP concentration in overlying water	Retention	
	mg l^{-1}	—mg m^{-2} d^{-1}—	
Johnstown Castle	0	1.7	± 1.1
Dunhill	0	0.3	± 0.2
Johnstown Castle	1	1.0	± 0.3
Dunhill	1	2.0	± 0.9
Johnstown Castle	5	18.8	± 4.4
Dunhill	5	16.0	± 5.0
Johnstown Castle	15	50.9	± 4.5
Dunhill	15	60.9	± 4.2

Table 3. Average soluble reactive phosphorus (SRP) retention by constructed wetland soils ± one standard error during the 30 day soil/water column experiment ($n = 3$).

During the 30 day HRT, SRP concentrations of floodwaters in both site columns decreased exponentially with time (Figure 5). First order removal rate constants, which are one of the constants (b) in exponential decay curves (Equation 5) were determined for non-transformed overlying floodwater P concentration data during the 30 HRT.
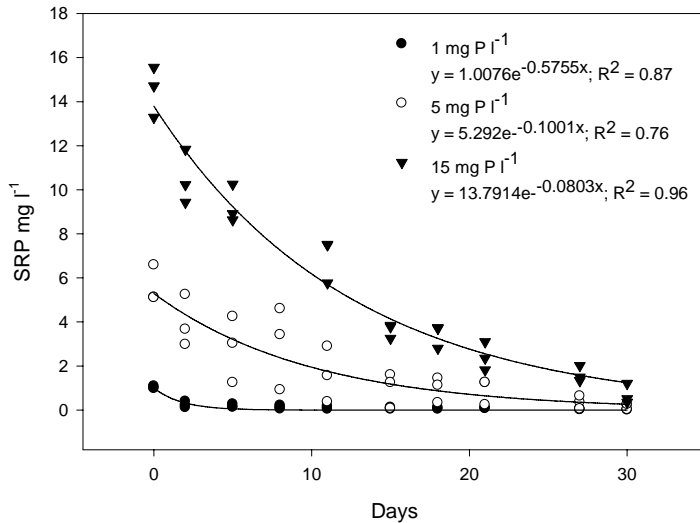
$$Y = ce^{bx} \qquad [5]$$

where c and b are constants, and e is the base of the natural logarithm.
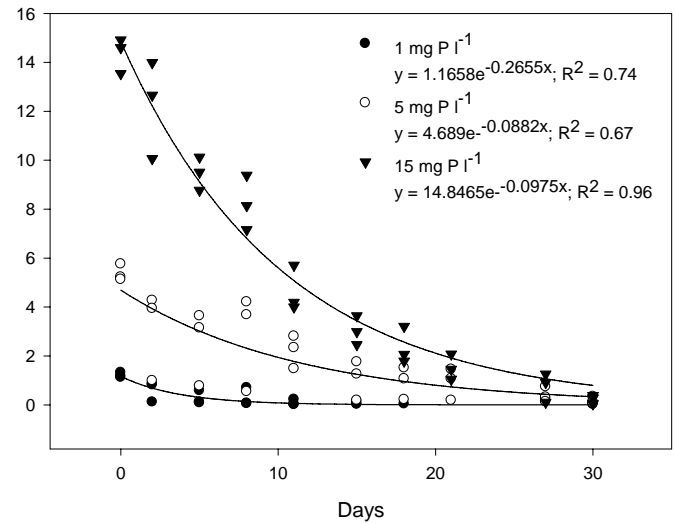
| | | Langmuir model | | | | Ammonium oxalate extractable | | | |
| | | | | | | | | | |

Table 4. Mean phosphorus (P) sorption parameters and ammonium oxalate extractable metals in soils by depth ± one standard error (n = 3).

Soil	Depth	Equilibrium P concentration EPC_o		Native adsorbed P S_o		Maximum P sorption S_{max}		Bonding energy k		Al		Fe	
	cm	—mg l^{-1}—		————mg kg^{-1}————				—l kg^{-1}—		————mg kg^{-1}————			
Johnstown Castle	0-2	0.008	± 0.002	222	± 47	674	± 62	0.88	± 0.096	1172	± 106	4470	± 445
Johnstown Castle	2-5	0.008	± 0.002	134	± 10	641	± 62	0.43	± 0.033	844	± 61	3758	± 456
Johnstown Castle	5-10	0.004	± 0.002	111	± 29	538	± 42	2.33	± 1.330	814	± 123	2752	± 774
Dunhill	0-2	0.019	± 0.008	1070	± 42	1601	± 32	5.33	± 1.670	2198	± 83	8204	± 443
Dunhill	2-5	0.019	± 0.005	1066	± 285	1707	± 326	2.00	± 0.577	2266	± 342	8834	± 472
Dunhill	5-10	0.014	± 0.003	668	± 133	1083	± 114	1.33	± 2.848	1772	± 158	7000	± 109

Johnstown Castle

Dunhill

- 1 mg P l^{-1}
  $y = 1.0076e^{-0.5755x}$; $R^2 = 0.87$
- 5 mg P l^{-1}
  $y = 5.292e^{-0.1001x}$; $R^2 = 0.76$
- 15 mg P l^{-1}
  $y = 13.7914e^{-0.0803x}$; $R^2 = 0.96$

- 1 mg P l^{-1}
  $y = 1.1658e^{-0.2655x}$; $R^2 = 0.74$
- 5 mg P l^{-1}
  $y = 4.689e^{-0.0882x}$; $R^2 = 0.67$
- 15 mg P l^{-1}
  $y = 14.8465e^{-0.0975x}$; $R^2 = 0.96$

Figure 5: First order removal rate constants for Johnstown Castle and Dunhill constructed wetland soils with overlying floodwaters spiked at 1, 5 and 15 mg SRP l^{-1}. Relationships at all concentrations were significant at the *P* < 0.001 level.

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First order removal rate constants can be used to determine half-lives, which in this context can be considered the time required to reduce floodwater P concentration by 50% (Gale et al., 1994). They can also be used to estimate how long it takes natural attenuation processes to achieve a specific remediation goal concentration as shown in Equation [6] (Newell et al., 2002).

$$t \quad = \quad -Ln[C_{goal}/C_{start}]/k$$
[6]

where t is the time taken to reach remediation goal (units of time), C_{goal} is the goal concentration (mg l^{-1}), C_{start} is the start concentration (mg l^{-1}), and k is the first order removal rate constant.

Rate constants were highest in columns spiked at 1 mg SRP l^{-1} ($P < 0.001$). Johnstown Castle columns spiked at 1 mg SRP l^{-1} had higher values than Dunhill columns spiked at 1 mg SRP l^{-1} (Figure 5; $P < 0.05$). High rate constants can indicate high potential rates of nutrient removal (Gale et al., 1994). When columns were spiked at 5 mg SRP l^{-1} or higher, there was no treatment difference between rate constant values. First order rate constants determined for this study ranged from 0.083 to 0.5755 d^{-1}, which was higher than those previously reported (0.035 to 0.069 d^{-1}) by Gale et al. (1994) that investigated constructed wetland soils that were previously used to treat municipal wastewater.

The "Phosphorus Regulations" which were transposed into Irish law in 1998 set water quality target concentrations dependent on river biological quality and lake trophic status. An average TP concentration of 20 µg l^{-1} was set for lakes (depending on trophic status) and a total molybdate reactive phosphate median concentration of 30 µg l^{-1} was set for rivers (depending on biological quality) (Brogan et al., 2001; Cleneghan, 2003).

To estimate (theoretically) how long it would take to remove sufficient P from overlying floodwaters to reach a goal concentration of 30 µg SRP l^{-1}, Equation [6] was used. Johnstown Castle soils that had overlying floodwaters spiked at 1 mg SRP l^{-1} could achieve it within 6 days, whereas it took Dunhill soils 13 days. Floodwaters at 5 mg l^{-1}, took 51 and 58 days for Johnstown Castle and Dunhill soils, respectively. However, when soils had floodwaters initially spiked at 15 mg l^{-1} the relationship was reversed. Dunhill soils achieved 30 µg SRP l^{-1} within 64 days, whereas it took Johnstown Castle soils 77 days. These relationships were not further investigated.

It is important to remember that column studies such as those undertaken are small-scale experiments that are powerful tools, as they allow for experimental replication, treatment manipulation and experimental control (Southwood,

1987; Hilborn and Ludwig, 1993; Petersen et al., 1997; Fraser, 1999; Odum and Odum, 2003). However, they also have limitations (Southwood, 1987; Ahn and Mitsch, 2002) and should not be used to extrapolate to large wetland ecosystem-scales. Small-scale experiments are subject to "experimental artefacts" and the relevance of such small-scale studies must be tested at larger ecosystem-scales (Carpenter, 1996; Drenner and Mazumdar, 1999). Other factors that need considering at wetland ecosystem-scale are biological, chemical and physical processes and their interactions (Reddy et al., 1995, Kadlec and Knight, 1996; Reddy et al., 1999) at these larger scales.

Oxalate Extractions and Phosphorus Adsorption Isotherms

Native adsorbed P (S_0) was greater in Dunhill soils at all depths than in Johnstown Castle soils (Table 4) with no significant difference in S_0 between soil depths. Maximum P sorption (S_{max}) values of Dunhill soils were generally greater than Johnstown Castle soils. Dunhill soils had highest S_{max} values at soil depths 0-2 cm and 2-5 cm ($P < 0.05$), whereas there was no difference in S_{max} values with depth in Johnstown Castle soils. High S_{max} values may reflect high amounts of ammonium oxalate Al and Fe content of soils (Table 4). Results indicate that S_{max} values of the two soils ranged between 538 to 1,707 mg kg^{-1}, which is within the range of other similar studies (10-3,100 mg kg^{-1}) (Gale et al., 1994; Litaor, et al., 2003; Reddy et al., 1998; White et al., 2000; Zhou and Li, 2001). There was some variability in P bonding energy (k) between and within site soils; however, the only significant difference was the high bonding energy in surface soils (0-2 cm) of Dunhill ($P < 0.05$). Soluble P diffuses slowly from soils with high k values (Reddy and Rao, 1983), which may reflect the relatively high buffering capacity of Dunhill soils observed in the previous column experiment.

Equilibrium P concentrations were similar between and within site soils (Table 4). Soils typically sorb P at solution concentrations greater than EPC_0 values (Khalid et al., 1977; Richardson, 1985, Rhue and Harris, 1999; Reddy et al., 1999; Graetz and Nair. 2000; Bridgham et al., 2001). As both soils have low EPC_0 values, this indicates that soils have a good ability to sorp P. Soils typically display their maximum buffering capacity for solution P at their EPC_0 (Bridgham et al., 2001).

Generally, Dunhill soils contained about twice as much Fe and Al as Johnstown Castle soils (Table 4). Correlation coefficients were determined for P sorption parameters and ammonium oxalate extracts of Fe and Al (Table 5). Equilibrium P concentration and S_{max} values correlated significantly with

Table 5. Correlation matrix for P sorption parameters (equilibrium P concentration, EPC_0; maximum P sorption capacity, S_{max}; and bonding energy, k) and ammonium oxalate extractable metals (Al_{ox} and Fe_{ox}) of constructed wetland soils (n = 18).

|	EPC_o		S_{max}		k		Al_{ox}		Fe_{ox}
EPC_o	1								
S_{max}	0.508	*	1						
k	0.294	NS	0.619	**	1				
Al_{ox}	0.683	**	0.905	***	0.706	**	1		
Fe_{ox}	0.670	**	0.846	***	0.638	**	0.899	***	1

oxalate extractable Fe and Al. Regression analysis between S_{max} and oxalate extractable Al suggests that by knowing the Al content of soils, S_{max} values could be predicted (Figure 6). Similar significant relationships were observed between P sorption parameters as determined using the Langmuir model and oxalate extractable Al and Fe (Table 5). It is well established that P sorption in wetland soils is controlled and regulated by both Al and Fe (Reddy and Rao, 1983; Faulkner and Richardson, 1989, Johnston, 1991; Gale et al., 1994; Kadlec and Knight, 1996; Reddy et al., 1998; Bridgham et al., 2001). Generally, Al oxides have higher adsorption capacities for P than Fe oxides; however Fe oxides have higher bonding energies for P relative to Al oxides (Bolan and Barrow, 1984).

CONCLUSIONS

Phosphorus plays a major role in the eutrophication of freshwater systems. Wetland systems either natural or constructed have an inherent ability to cycle and retain P. Physical, chemical and biological processes regulate P retention in wetland soils and sediments. Of those processes, sorption and precipitation are important in retaining P. Sorption is typically greater under aerobic soil/sediment conditions than anaerobic conditions.   Under anaerobic conditions, Fe plays a major role in P dynamics, whereas Al is not affected by changes in redox. Precipitation of P as insoluble Ca bound P is a dominant transformation at high pH. Long-term P retention by wetland systems includes accretion and decomposition of organic and detrital material, and its associated P content. Case studies reviewed illustrated that P retention in natural and constructed wetland systems can vary by several orders of

magnitude depending on site-specific factors. The literature reviewed also indicates that using wetlands to retain P from agricultural practices is significant and variable.
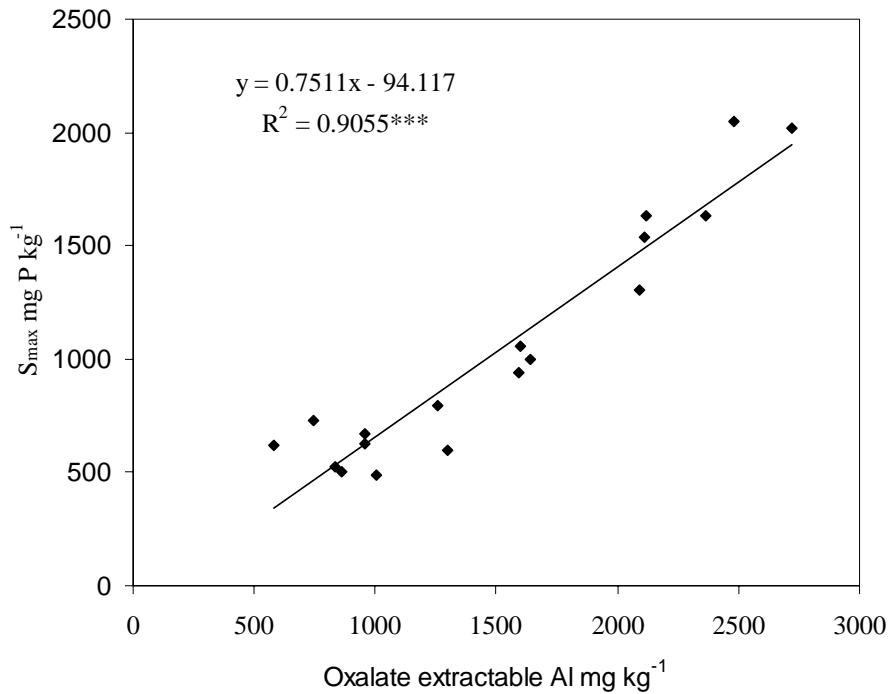
Figure 6: Relationship between P sorption maximum (S_{max}) values and oxalate extractable Al for the two constructed wetland soils (n = 18).

Findings of the 30-day column experiment indicate that both constructed wetland soils retained P. However, when P concentrations of overlying floodwaters were low (distilled water), soils tended to release P during the first two days of the experiment. This suggests that although soils typically retained P during the experiment, short term fluxes of P to overlying waters can occur. This highlights the important of dynamics and sink-source relationships. Soils with overlying waters initially spiked at 5 and 15 mg l-1 had highest P retention rates indicating that as P loading increased, P retention by soils also increased. It is important to remember that P release and/or retention in "wetland ecosystems" (as opposed to soil/water column studies) is a net result of physical, chemical, and biological processes in overlying waters, underlying soils and biological components such as vegetation and microbial assemblages. Therefore it is not appropriate to extrapolate from such small-scale studies to the large ecosystem-scale, but rather use these studies as templates for further investigation at higher scales.

In theory, if constructed wetland output SRP concentrations are to achieve a 30 µg l-1, long hydraulic residence times may be required. Theoretical HRT determined for soil/water columns ranged from 6 to 77 days depending on initial P concentrations of overlying waters in soil/water columns. However, to test this at the operational wetland-scale a dye tracing study would be required to determine actual hydraulic residence times required at the constructed wetland scale.

Phosphorus adsorption isotherms, which are independent of P load, illustrate that constructed wetland soils at Dunhill had higher S_{max} than soils at Johnstown Castle. Surface soils at Dunhill also had highest P bonding energies. This may reflect the relatively high buffering capacity of Dunhill soils in comparison to Johnstown Castle soils, as observed on the final day of the soil/water column experiment. Equilibrium P concentrations were similar between and within site soils. Phosphorus sorption parameters correlated well with site soil characteristics such as oxalate extractable Fe and Al, whereas differences in P release and retention in the column study were largely governed by P concentrations in overlying waters.

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