Phosphorus sorption by sediments in a subtropical constructed wetland receiving stormwater runoff

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ABSTRACT

This study investigated the potential of using a mixture of fishpond bund material, completely decomposed granite and river sand as substrate in a constructed wetland for phosphorus removal. Core samples were collected from the newly constructed Hong Kong Wetland Park (HKWP) receiving influent stormwater from a nearby new town, and batch incubation experiments were conducted to determine the P sorption characteristics of sediments. The HKWP sediments adsorbed the majority of available P in the initial 20 min of incubation, with a first-order rate constant of $1.01–2.11\,h^{-1}$. Sediments in the reedbeds and freshwater marshes possessed a great capacity for P adsorption with the high Langmuir sorption maxima ($478–858\,mg\,kg^{-1}$) and Freundlich adsorption constants ($417–672\,L\,kg^{-1}$) obtained, attributable to the high amorphous iron and aluminium concentrations compared to other constructed wetlands. Moreover, sediment equilibrium P concentrations were generally low ($4.6–23.6\,\mu g\,L^{-1}$), facilitating a net P adsorption by sediments under moderate P loadings. Yet, the amount of P adsorbed by the HKWP sediments was limited by the low ambient porewater P concentrations and there was even a risk of P desorption when sediments in the freshwater marshes were resuspended into the water column. While substrates in the HKWP demonstrated a great potential for P adsorption, consideration should also be given to P loadings in influent water to fully utilize the P sorption capacity of sediments and enhance the P removal efficiency of constructed wetlands.

1. Introduction

Phosphorus (P) is regarded as a common limiting nutrient in aquatic ecosystems (Wetzel, 2001) and hence its concentration in water bodies should be appropriately controlled to safeguard water quality. Wetlands, being "kidneys of the landscape", receive water and waste from a variety of natural and anthropogenic sources and cleanse them before discharging downstream (Mitsch and Gosselink, 2000). With an ability to retain and transform P, wetlands are increasingly constructed worldwide as a low-cost and environmentally friendly means to improve the quality of municipal and industrial wastewater (White et al., 2000), agricultural runoff (Koskiaho et al., 2003) and urban stormwater (Somes et al., 2000). However, the performance of constructed wetlands is not always satisfactory, with considerable variations in P removal efficiency being reported that range from a 70% net retention to a 48% net release of soluble P (Greenway and Woolley, 1999; Heyvaert et al., 2006). In order to optimize the design of constructed wetlands for P retention, there is a need to study thoroughly the

various biogeochemical processes occurring inside the black-box of the wetland ecosystem.

Various wetland components play a role in the retention of water-borne P. While uptake by plants, periphyton and microbes can give rise to an initial rapid removal of P, the soil compartment represents a major P sink in wetlands in the long run (Sakadevan and Bavor, 1998). Adsorption by sediments is considered as one of the dominant long-term P storage mechanisms in wetlands (Richardson, 1999). Yet, the magnitude of P sorption is finite and limited (Richardson and Craft, 1993), as sediment sorption sites could become saturated when subject to prolonged nutrient loading (Meuleman et al., 2003). Determination of maximum P sorption capacity (S_{max}) is thus essential for predicting the long-term sustainability of sediments in assimilating additional P. Depending on the filter medium and experimental conditions used, P sorption capacity can vary by three orders of magnitude from 46 to 44,200 mg kg^{-1} among substrates (Johansson Westholm, 2006). Sediment S_{max} is found to be positively correlated with the proportion of fine particles and concentrations of amorphous Fe, Al and total organic carbon (Reddy et al., 1999; McGechan and Lewis, 2002). Moreover, the amount of P adsorbed by sediments is potentially affected by the sorption rate, as equilibrium conditions may not be attained under a short duration of contact between the water column and sediments (Lopez et al., 1996). Compared to the large number of P sorption kinetic studies conducted on sediments in natural waterbodies (e.g. Lopez et al., 1996; Zhou et al., 2005), only a few have been reported on constructed wetland substrates (e.g. Arias et al., 2003; Cui et al., 2008). The kinetic process of sediment P adsorption in constructed wetlands warrants further investigation to enhance P removal and provide parameter input data for modelling sediment P dynamics.

Meanwhile, a higher maximum P sorption capacity exhibited by sediments does not necessarily assure a lower P concentration in the solution (Pant and Reddy, 2001); because a net adsorption of P onto the sediment surfaces must first occur in order to take advantage of the availability of sorption sites. Wetland sediments function as a phosphate buffer by either adsorbing P from or desorbing P into the porewater, depending on the physico-chemical properties of sediments and water. In general, there is a net adsorption of P when inorganic P is added at a concentration significantly greater than that in porewater, while a net desorption of P by sediments occurs at low P loadings (Reddy et al., 1999). As such, it is necessary to determine also the conditions under which adsorption or desorption of P by wetland sediments takes place.

The Hong Kong Wetland Park (HKWP), being the largest constructed wetland established in the territory, serves as an ecological mitigation site compensating for the loss of natural wetlands owing to the Tin Shui Wai new town development. In addition, it is hoped that the construction of HKWP can provide other ancillary benefits, including the promotion of ecotourism and purification of part of the stormwater collected in nearby urban areas (Cha, 2004). Numerous studies have demonstrated the potential use of natural materials like sand and oyster shell (Arias et al., 2001; Park and Polprasert, 2008), as well as industrial by-products like furnace slag and fly ash (Mann, 1997; Cui et al., 2008) as substrates in constructed wetlands for the removal of P. However, it is not known whether sediments in the reedbeds and freshwater marshes of the HKWP, with a mixture of fishpond bund material, decomposed granite and river sand, could effectively sorb P from the stormwater influent. In view of the paucity of information on P sorption characteristics of sediments in subtropical Asian constructed wetlands, this study was conducted to: (i) investigate the P sorption kinetics of the HKWP sediments; (ii) determine the P sorption parameters of the HKWP sediments; and (iii) examine the conditions under which the HKWP sediments adsorb and desorb P.

2. Materials and methods

2.1. Study site description

The Hong Kong Wetland Park is a 600,000 m^2 constructed wetland complex situated in the northwestern New Territories, Hong Kong (22° 28′N, 114° 00′E) (Fig. 1). Comprising a mosaic of various wetland types, including reedbeds, freshwater marshes and inter-tidal mudflats, the HKWP has served as a buffer zone between the ecologically sensitive Mai Po Ramsar Site and Tin Shui Wai new town since the completion of its construction in late 2003. This study focuses on the reedbeds and freshwater marshes only because they have the same type of topsoil that comprises 55% pond bund material, 30% completely decomposed granite, and 15% clean river sand. The bund material is obtained from nearby aquaculture ponds, while river sand is commercially available as construction materials. Highly decomposed granite is abundant in the hot and humid Hong Kong with intense geological weathering processes.

The surface flow reedbeds and freshwater marshes in the HKWP are hydrologically interconnected. The 16,000 m^2 reedbeds receive input of stormwater from the Eastern Temporary Channel draining the Tin Shui Wai urban catchment as well as treated water recycled from the storage pond of the HKWP. After passing through the reedbed filters, influent water enters the smaller Freshwater Marsh 2 (17,700 m^2) and then the larger Freshwater Marsh 1 (53,000 m^2) (Fig. 1). Water residence time in the whole system is approximately 28 days. Sluice gates are used to manipulate water levels in different wetland compartments, which range from 0.2 m in the reedbeds to a maximum of some 2 m in the freshwater marshes. The reedbeds are planted with common reeds (Phragmites australis), while the freshwater marshes are dominated by sedges and submerged aquatic macrophytes.

2.2. Sample collection and treatment

A total of eight sampling points were chosen along the hydrologic path in the HKWP, with two points selected in the Phragmites reedbeds (RB1–2), two in Freshwater Marsh 2 (FM1–2) and four in Freshwater Marsh 1 (FM3–6) (Fig. 1). The eight selected sites were spaced about 100 m apart. Five replicate sediment cores were retrieved randomly at each point by a hand corer in January 2005. Upon return to the laboratory, the top 5 cm surface sediments were extruded, homogenized and stored at 4 °C until further analysis. Porewater was promptly extracted in the laboratory by centrifuging field-moist sedi-
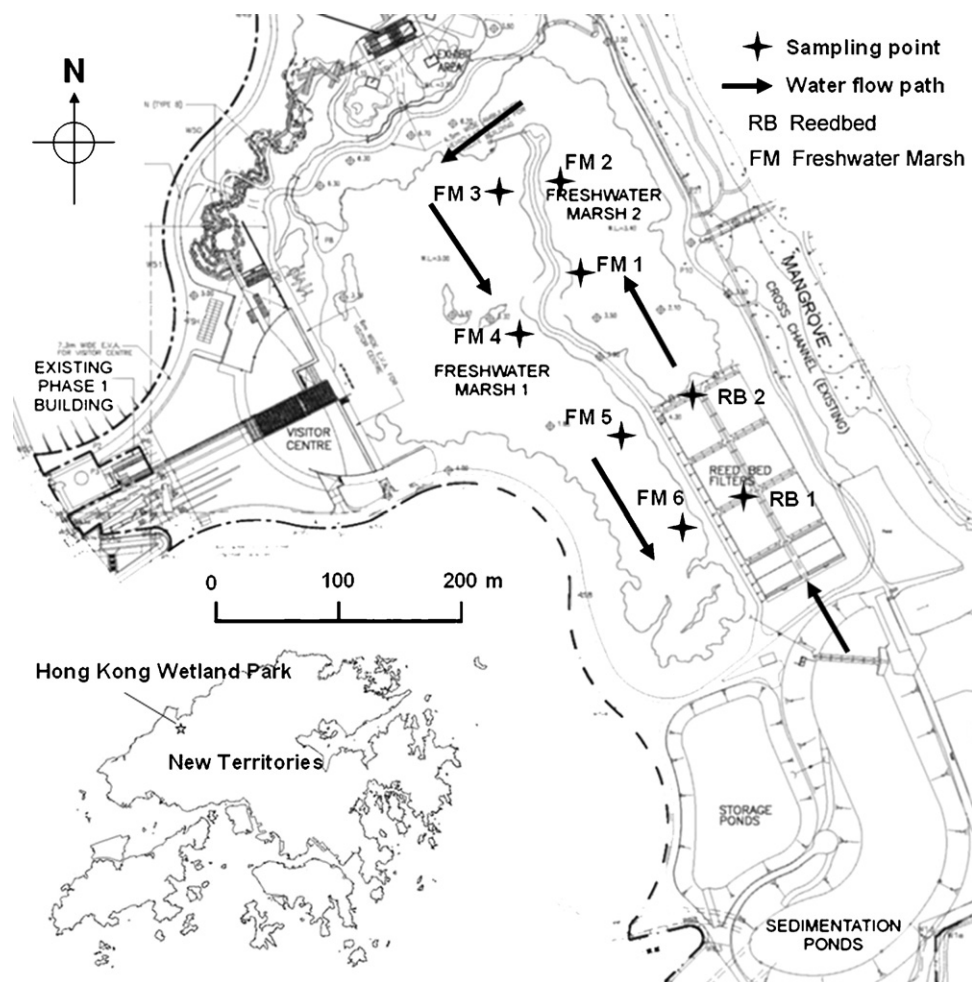
Fig. 1 – Map of the Hong Kong Wetland Park indicating the sampling locations and water flow path.

ments at 5000 rpm for 10 min in a refrigerated centrifuge and an aliquot of the supernatant was analyzed for P. Also, triplicate surface water samples were collected at the eight sites in January and September 2005, immediately filtered in the laboratory by Whatman GF/C filters and the filtrates analyzed for P.

2.3. Sorption kinetics

Sorption kinetics of the HKWP sediments were studied using samples collected at RB1 and FM4. Approximately 5 g (d.w.) of fresh sediments was added to a series of 250 mL conical flasks containing 150 mL of 0.01 M KCl solution spiked at two different P levels (viz. 20 and 50 mg P L^{-1}). Following the addition of 2 drops of chloroform to inhibit microbial activity, the flasks were immediately covered with parafilm and constantly shaken on a ping-pong shaker at 200 rpm at room temperature. At 11 different time intervals (0.17, 0.5, 1, 2, 4, 6, 9, 12, 24, 48 and 72 h), 5 mL of sediment slurry was sampled from each flask, centrifuged at 5000 rpm for 10 min and the supernatant immediately analyzed for P. The experiments were conducted in duplicate and the sediment to solution ratio was assumed to be constant throughout the incubation period.

2.4. Batch incubation experiments

Phosphorus sorption characteristics of HKWP sediments were investigated using batch incubation experiments. One gram (d.w.) of fresh sediments was added to a series of 50 mL centrifuge tubes containing 30 mL of 0.01 M KCl solution spiked at ten different initial P concentrations (0, 0.03, 0.1, 0.2, 0.5, 1, 5, 10, 50 and 100 mg P L^{-1} as KH$_2$PO$_4$). Sediments were neither dried nor sieved, since drying and sieving could lead to oxidation of sediments and thus alteration in P sorption capacity (Cyr and Nurnberg, 2005). After adding two drops of chloroform, the tubes were shaken in a water bath shaker at 200 rpm at 25 $\pm$ 1 °C for a 24-h equilibration period. The suspensions were then centrifuged at 5000 rpm for 10 min and an aliquot of the supernatant was immediately analyzed for P. The experiments were conducted in triplicate and the amount of P adsorbed by wetland sediments was calculated as the difference in mass of P initially added and P recovered in solution after the 24-h equilibration. Following the completion of adsorption incubation experiments, desorption experiments were immediately conducted on the sediment residues. The residues were shaken with 30 mL of P-free 0.01 M KCl solution for 24 h at 25 $\pm$ 1 °C. The suspensions were then

centrifuged and supernatants analyzed for P. The mass of P recovered in solution represented the amount of P desorbed by sediments.

2.5. Estimation of sorption parameters

Sorption data obtained from batch incubation experiments were fitted non-linearly to two commonly used adsorption models, namely the Langmuir and Freundlich models, using Microcal Origin 7.0. Phosphorus sorption capacity of sediments in the HKWP was estimated by the Langmuir adsorption isotherm: $S_1 + S_0 = S_{max}kC/(1 + kC)$, where S_1 is the amount of P sorbed during sorption experiment ($mg\,P\,kg^{-1}$), S_0 is the amount of native sorbed P ($mg\,P\,kg^{-1}$), S_{max} is P sorption maximum ($mg\,P\,kg^{-1}$), k is the bonding energy constant ($L\,mg\,P^{-1}$), and C is equilibrium P concentration after 24-h equilibration ($mg\,P\,L^{-1}$). Oxalate-extractable P was assumed to represent the native sorbed P in sediments prior to batch incubation (Freese et al., 1992). On the other hand, the Freundlich adsorption constant of HKWP sediments was determined by fitting sorption data to the Freundlich adsorption isotherm: $S_1 + S_0 = KC^b$, where K is the Freundlich adsorption constant ($L\,kg^{-1}$), and b is an empirical constant ($b < 1$). Zero equilibrium phosphorus concentration (EPC_0) was determined graphically as the x-intercept of the plot of the amount of P sorbed against the initial P concentrations at near ambient levels.

2.6. Sample analysis

Phosphate concentrations in the supernatant and overlying water samples were determined by the molybdenum blue method (Murphy and Riley, 1962). Sediment pH was determined using a 1:2.5 sediment to deionized water ratio. Particle size distribution of sediment was determined by the hydrometer method (Bouyoucos, 1951). Native sorbed P, amorphous iron (Fe) and aluminium (Al) in sediments were extracted in the dark by acid ammonium oxalate (Loeppert and Inskeep, 1996), and the concentrations determined by ICP-OES (PerkinElmer, Optima 5300 DV). Sediment organic matter was quantified gravimetrically by loss-on-ignition (LOI) at 550 °C for 4 h. Total Fe, Al and P in sediments were determined by digestion with a 2:10:1 mixture of 60% perchloric acid, concentrated nitric acid and concentrated sulphuric acid at 200 °C.

3. Results and discussion

3.1. Sediment properties

Table 1 summarizes the physico-chemical properties of sediments at the eight sampling sites. The HKWP sediments generally had a sandy clay loam texture with sand content exceeding 50%, since a considerable portion of substrate was derived from coarse-textured decomposed granite and river sand, and there was less accretion of unconsolidated fine particles in newly constructed wetlands (Campbell et al., 2002). Sediments in the HKWP were slightly alkaline, with pH values ranging from 7.2 to 7.6. Near neutral pH is typically found in flooded anaerobic soils, owing to reduction of $FeCO_3$ in acid

Table 1 – Physico-chemical properties of sediments in the Hong Kong Wetland Park.

Site	Sand (%)	Silt (%)	Clay (%)	pH	Oxalate-extractable			Total			LOI (%)
					P ($mg\,kg^{-1}$)	Fe ($mg\,kg^{-1}$)	Al ($mg\,kg^{-1}$)	P ($mg\,kg^{-1}$)	Fe ($mg\,kg^{-1}$)	Al ($mg\,kg^{-1}$)	
RB1	51	16	34	7.60	339	13,638	2180	354	16,793	16,465	4.97
RB2	25	25	50	7.63	273	11,270	2162	333	21,994	26,123	4.96
FM1	69	10	21	7.42	333	9,648	1508	422	15,744	16,846	2.93
FM2	70	7	24	7.20	353	11,330	1655	426	12,602	11,458	3.84
FM3	57	15	29	7.38	308	10,056	1529	394	11,538	12,606	2.30
FM4	63	10	27	7.35	321	9,889	1656	354	17,130	21,990	3.33
FM5	70	12	18	7.52	279	9,503	1521	355	14,832	17,341	3.35
FM6	52	14	34	7.60	332	11,928	1836	357	10,733	11,467	2.56

soils and production of CO_2 in alkaline soils (Vepraskas and Faulkner, 2001).

Sediments in the HKWP had similar total P concentrations across the eight sites (333–426 mg kg^{-1}), which were at moderate levels compared to 32–49 and 485–1419 mg kg^{-1} reported in the Florida and Australian constructed wetlands, respectively (Gale et al., 1994; Sakadevan and Bavor, 1998). Average sediment organic matter content was higher in the reedbeds (5.0%) than in the freshwater marshes of the HKWP (3.1%), but overall was significantly lower than 10.4% found in nearby natural marshes (Lai and Lam, 2008), which could possibly be attributed to lower primary productivity and insufficient time for accretion of organic materials in the constructed wetland.

Ammonium oxalate in an acidic medium selectively extracts non-crystalline forms of Fe and Al in sediments (Pant et al., 2002). Oxalate-extractable Fe and Al concentrations in the HKWP averaged 10.9 and 1.8 g kg^{-1}, respectively, which were higher than those obtained in constructed wetlands in Australia (Fe: 8.2 g kg^{-1}) (Sakadevan and Bavor, 1998), Ireland (Fe: 6.3 g kg^{-1}, Al: 1.6 g kg^{-1}) (Dunne et al., 2005), and Florida in the US (Fe and Al: <0.1 g kg^{-1}) (Gale et al., 1994). Such high concentrations could be explained by the use of decomposed granite in the substrate, which contains abundant sesquioxides arising from strong weathering of primary minerals and leaching of silicate in a humid subtropical climate (Brady and Weil, 2008). Moreover, amorphous Fe was the dominant Fe form in the HKWP sediments, constituting about 72% of total Fe.

3.2. Phosphorus sorption kinetics

Phosphorus sorption by sediments is considered a time-dependent process (Appan and Wang, 2000). Fig. 2 shows that the adsorption kinetic curves of HKWP sediments rose sharply during the first hour of incubation, with a steeper slope obtained with the use of higher initial P concentration of 50 mg P L^{-1} than 20 mg P L^{-1}. A positive relationship between initial sorption rate and initial P concentration was also reported for sediments in the East Anglian eutrophic
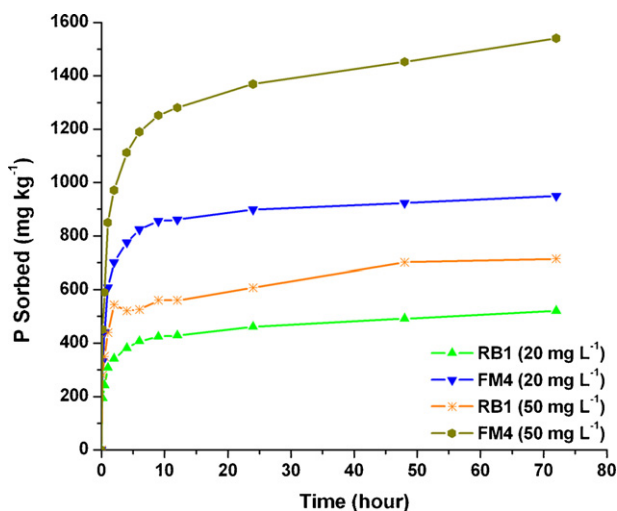
Fig. 2 – Kinetic curves of phosphorus adsorption by the Hong Kong Wetland Park sediments.
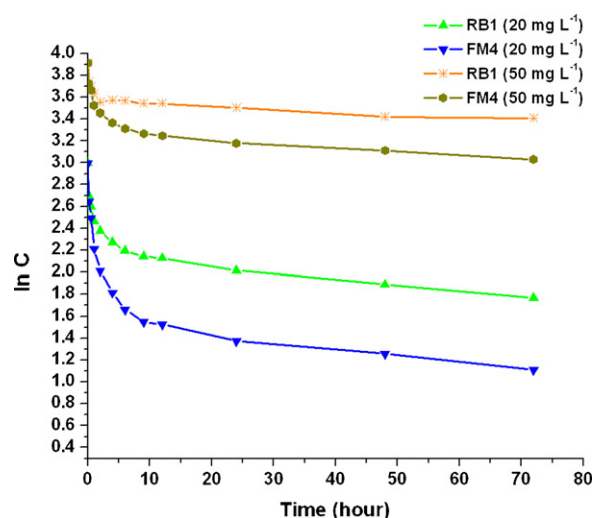
Fig. 3 – Plot of logarithm of solution phosphorus concentration against time for the Hong Kong Wetland Park sediments.

reservoirs (Redshaw et al., 1990) and the Chinese lake Taihu (Zhou et al., 2005). Following an initial increase in slope, the kinetic curves flattened off after 12–24 h with no further significant change in the amount of P sorbed. This suggests that a dynamic pseudo-equilibrium between the solid and solution phases in sediments may be attained after 24 h (Fox et al., 1989) and justifies the use of a 24-h incubation period in the batch incubation experiments for determining sorption maxima of the HKWP sediments. True equilibrium between sediments and interstitial water, as Froelich (1988) suggested, can seldom be attained on laboratory time scales, unless solution P concentrations used are near that of the ambient levels.

To better characterize changes in P sorption rate of sediments, the logarithm of solution P concentration was plotted against incubation time. As shown in Fig. 3, the curves could be broadly divided into three major sections, each of which had a distinct slope representing a specific sorption stage. The slope of straight line best fitted to each section of the curve gave the first-order adsorption rate constant and the duration of each sorption stage was determined by solving pairs of linear equations of the fitted lines (Appan and Wang, 2000). Table 2 summarizes the results of sorption duration and first-order rate constant of P sorption of the HKWP sediments.

Phosphorus adsorption by sediments has been regarded as a multiple kinetic process involving at least an initial fast adsorption step followed by a slower adsorption stage (Lopez et al., 1996). The first stage of P sorption was completed within 20 min for both RB1 and FM4 sediments (Table 2), which was in agreement with values of 10–30 min reported in other similar studies conducted on aquatic sediments (Fox et al., 1989; Wang et al., 2005) and much shorter than the water residence time in the HKWP. The highest first-order adsorption rate constants (1.01–2.11 h^{-1}) were obtained at this stage, with the majority of P adsorption being completed during this short period of time. Ion exchange and ligand exchange were likely the two most dominant mechanisms contributing to the high sorption rate determined (Rhue and Harris, 1999).

Table 2 – Kinetic parameters of phosphorus sorption by Hong Kong Wetland Park sediments.

Site	Initial P added ($mg\,L^{-1}$)	Sorption duration		First-order rate constant		
		Stage 1 (min)	Stage 2 (h)	Stage 1 (h^{-1})	Stage 2 (h^{-1})	Stage 3 (h^{-1})
RB1	20	15.0	5.98	1.80	0.07	0.006
FM4	20	18.0	6.05	2.11	0.14	0.007
RB1	50	11.4	1.63	1.01	0.09	0.003
FM4	50	16.8	6.03	1.12	0.06	0.004

Table 3 – Phosphorus sorption parameters of sediments in Hong Kong Wetland Park.

Site	Langmuir isotherm: $S_1 + S_0 = S_{max}kC/(1+kC)$			Freundlich isotherm: $S_1 + S_0 = KC^b$			P_r (% P_{ad})
	S_{max} ($mg\,kg^{-1}$)	k ($L\,mg^{-1}$)	r^2	K ($L\,kg^{-1}$)	b	r^2	
RB1	584	93.8	0.48	489	0.10	0.89–0.94	75
RB2	585	71.0	0.41–0.62	465	0.11	0.88–0.98	84
FM1	478	86.1	0.48–0.62	417	0.07	0.90–0.96	47
FM2	788	29.4	0.64–0.72	577	0.13	0.99	83
FM3	547	58.0	0.50–0.69	525	0.11	0.96–0.99	71
FM4	841	31.7	0.66–0.73	592	0.14	0.93–0.99	88
FM5	785	18.2	0.73–0.76	515	0.15	0.94–0.98	88
FM6	858	89.1	0.41–0.51	672	0.14	0.94–1.00	88

Data were means of triplicate values, except for r^2 values which were presented as the range obtained from triplicate measurements. S_{max}: Langmuir sorption maximum. k: Bonding energy constant. K: Freundlich adsorption constant. b: Empirical constant related to bonding intensity. P_r: Phosphorus retained in a relatively stable form. P_{ad}: Phosphorus adsorbed.

The second stage of P sorption took a considerably longer time than the preceding step, lasting for 1.6–6.1 h (Table 2). First-order rate constants at this stage ranged from 0.06 to 0.14 h^{-1}, which were approximately an order of magnitude lower than those of the initial step. Lower adsorption rate in this phase could be attributed to the slow diffusion and penetration of P into defect sites and pores in sediments (Slomp and Van Raaphorst, 1993). The third adsorption stage commenced after 1.8–6.4 h of incubation, depending on the sediment and initial P concentration used (Table 2). First-order rate constants of P adsorption at this stage varied from 0.003 to 0.007 h^{-1}, implying that sorption rates were very low with no appreciable changes in the amount of P sorbed over time. This slow sorption phase could last for weeks or even months and often involves numerous processes including diffusion, precipitation, adsorption and desorption (Rhue and Harris, 1999; Appan and Wang, 2000).

3.3. Phosphorus sorption parameters

Sorption isotherms are useful in summarizing large amounts of sorption data and illustrating the relationship between aqueous concentration of adsorbate and the amount of adsorption by the solid phase sorbent at constant temperature (Stumm and Morgan, 1996). The Langmuir adsorption isotherm assumes the occurrence of monolayer adsorption with uniform binding energy (Rhue and Harris, 1999), while the Freundlich adsorption isotherm assumes the presence of chemosorption processes in addition to surface adsorption (Sundareshwar and Morris, 1999). Table 3 shows that sorption data of the HKWP sediments were described only fairly by the Langmuir isotherm, with r^2 values ranging from 0.41 to 0.76. In contrast, sorption data were well fitted to the empir-

ical Freundlich isotherm with r^2 values over 0.9, suggesting more complex mechanisms other than surface adsorption were involved in sediment P sorption. Moreover, phosphorus adsorption isotherms of the HKWP sediments were generally L-shaped (Fig. 4), indicating that P adsorption increased with a greater magnitude at low equilibrium P concentrations than at high P loadings where P sorption sites were mostly saturated.

The Langmuir adsorption isotherm provides a good estimate of theoretical adsorption maxima and hence the capacity of sediment–water systems in removing P. Langmuir adsorption maxima (S_{max}) of the HKWP sediments ranged between 478 and 858 $mg\,kg^{-1}$ (Table 3), which were higher than 150–260 and 196–281 $mg\,kg^{-1}$ reported for constructed wet-
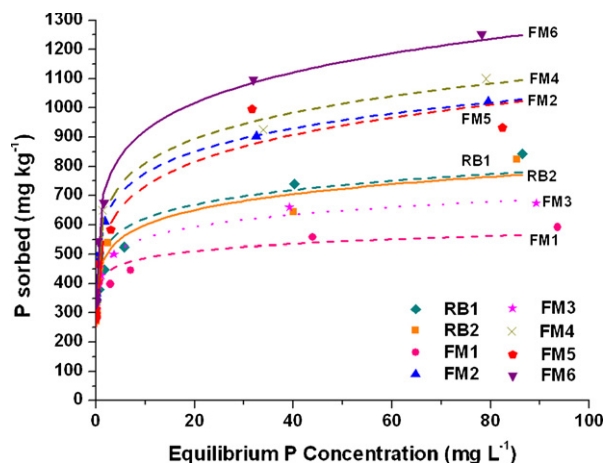

Fig. 4 – Phosphorus adsorption isotherms of sediments in the Hong Kong Wetland Park. Lines are Freundlich isotherms fitted to the data.

Table 4 – Zero equilibrium phosphorus concentrations (EPC$_0$) and phosphorus concentrations in porewater and overlying water of the Hong Kong Wetland Park.

Site	EPC$_0$ (μg L^{-1})	Porewater P (μg L^{-1})	Overlying water P	
			Wet season (μg L^{-1})	Dry season (μg L^{-1})
RB1	14.8 ± 3.17	21.6 ± 1.54	13.4 ± 1.73	10.3 ± 1.94
RB2	4.6 ± 1.40	19.5 ± 0.75	39.6 ± 3.38	7.5 ± 0.15
FM1	19.6 ± 2.06	28.1 ± 0.57	4.0 ± 0.35	6.7 ± 0.03
FM2	23.6 ± 2.31	29.4 ± 0.78	3.3 ± 0.80	7.1 ± 0.07
FM3	19.5 ± 4.49	26.5 ± 1.12	1.1 ± 0.27	7.1 ± 0.13
FM4	15.4 ± 2.57	21.4 ± 1.03	4.7 ± 3.46	6.9 ± 0.20
FM5	21.0 ± 3.27	22.7 ± 0.72	1.3 ± 0.15	9.8 ± 0.10
FM6	18.7 ± 8.00	18.3 ± 0.45	1.2 ± 0.07	7.5 ± 0.15

land sediments in Florida (Gale et al., 1994) and Korea (Yoo et al., 2006) respectively. Moreover, lower S_{max} were obtained for the use of gravels (26–48 mg kg^{-1}, Mann, 1997) and sand as wetland substrates (303–500 mg kg^{-1}, Pant et al., 2001). Although industrial by-products such as oil shale ash and coal, steel and blast furnace slag are shown to have much higher S_{max} (1430–65,000 mg kg^{-1}) for effective P removal in constructed treatment wetlands (Sakadevan and Bavor, 1998; Cui et al., 2008; Kaasik et al., 2008), the ecological impacts of applying these materials in mitigation wetlands like the HKWP should first be thoroughly assessed where supporting a diversity of flora and fauna is also an important goal. In addition to the high maximum sorption capacity at high solution P concentrations, the HKWP sediments also exhibited considerable relative sorption capacity at a low equilibrium P concentration of 1 mg L^{-1} with the high Freundlich adsorption constants obtained (417–672 L kg^{-1}, Table 3). This could be attributed to the high concentrations of amorphous Fe and Al in the HKWP sediments in providing abundant specific surface area for P adsorption to take place (Paludan and Jensen, 1995). Thus, increasing the proportion of completely decomposed granite in the substrate mix is expected to enhance the P sorption capacity considerably, since it contributes the majority of sediment non-crystalline Fe and Al. It is also worth noting that influent water in the HKWP first flow through an oyster shell bed before reaching the reedbeds and freshwater marshes. The use of oyster shell has been shown to effectively increase the adsorption capacity of filter medium and thus longevity of constructed wetland in removing P (Seo et al., 2005; Park and Polprasert, 2008).

Adsorption of P onto metal oxide surfaces of sediments is potentially reversible depending on the type of reactions involved and time of incubation (Barrow, 1979; Rhue and Harris, 1999). The difference between the amount of P sorbed during adsorption experiments (P_{ad}) and that released in desorption experiments indicated the amount of P retained in a relatively stable form (P_r). The mean percentage retention of adsorbed P was then determined as the slope of the linear fit line that was forced through the origin in the plot of P_r against P_{ad} (Pant and Reddy, 2001). Except at FM1, the HKWP sediments retained 71–88% of the adsorbed P after 24-h equilibration of the sediment residues with 0.01 M P-free KCl solution (Table 3), thus demonstrating a high irreversibility of sorption reactions. There was only a small proportion of previously sorbed P being released back into

the solution during desorption experiments. Such hysteretic phenomenon, with desorption of P not following the pattern of adsorption isotherms, was likely caused by the formation of less reversible bidentate and binuclear bonds following the diffusion of P into the solid phase (Reddy et al., 1999). Meanwhile, the observed hysteresis might also be due to differences in P adsorption and desorption rates within the time scale of this experiment (i.e. 24 h). Given adequate time and sufficiently low P concentration, most adsorbed P could possibly be desorbed in a reversible fashion (Rhue and Harris, 1999).

3.4. Adsorption–desorption equilibrium

A net adsorption of P must first take place before the phosphorus sorption capacity of sediments could be utilized. Depending on the dynamic equilibrium between solution and solid phases, phosphorus can either be adsorbed by or desorbed from sediments. Determination of sediment EPC$_0$ value, the concentration at which no net adsorption or desorption of P occurs, can shed light on the direction of sorption processes. If solution P concentration is greater than sediment EPC$_0$, a net adsorption of P by sediments occurs, and vice versa. The HKWP sediments had very low EPC$_0$ values in the range of μg (4.6–23.6 μg L^{-1}, Table 4), suggesting that soluble P would be readily adsorbed under moderate to high P loadings. Indeed, given the greater ambient porewater P concentrations than the corresponding EPC$_0$ values (Table 4), the HKWP sediments were expected to adsorb P from solutions. However, the amount of P sorbed would not be very significant owing to the small difference between EPC$_0$ values and porewater P levels in the HKWP sediments. In wetland systems that have relatively low P loadings as in the HKWP, P uptake by macrophytes and periphyton mats might play a more important role in P removal when P adsorption by sediments becomes less effective (Gaiser et al., 2005).

Induced by strong wind and water currents especially during episodic storm events, resuspension of unconsolidated surface sediments is very effective in shallow water systems (Reddy et al., 1996). Upon sediment resuspension, the contact between sediments and overlying water in wetlands is increased and resuspended sediments can either act as a P sink by sorbing water column P, or as a P source by mixing P-enriched sediment porewater with and desorbing sediment bound phosphate into the overlying water (Brezonik

and Pollman, 1999; Sondergaard et al., 2003). Since resuspended sediments exchange P directly with the water column, comparisons were made between sediment EPC_0 values and overlying water P concentrations to examine the influence of sediment resuspension on P sorption. In the HKWP that received influents from urban stormwater, overlying water P concentrations were found to be lower than sediment EPC_0 values in the freshwater marshes in both the wet and dry seasons (Table 4), thus suggesting a potential risk of P desorption when sediments were resuspended into the water column. It should be noted that overlying water P concentrations were only determined at a few sampling occasions in this study. Given the expected seasonal and episodic variations in water quality associated with rainfall events, the direction of P sorption might actually change several times at different times of year depending on water column P concentrations.

While sorption parameters like S_{max} and EPC_0 provide useful information regarding the ability of sediments in sorbing P, they should only be viewed as experimental values. Langmuir adsorption maxima determined in batch incubation experiments were based on mixing soil continuously with P-laden water (Reddy et al., 1998). Yet, in actual field conditions, water movements through soil pores are often slow and dissolve P is only in contact with a small proportion of the sediment matrix (Richardson and Vaithiyanathan, 1995), resulting in a possibly lower S_{max} value than that estimated in the laboratory. As P has to diffuse from the overlying water to the sediment before it can be retained, the actual P retention by constructed wetlands under field conditions should also consider factors including water residence time, infiltration capacity of sediments, diffusive flux across the sediment–water interface, P concentration in the porewater and physico-chemical properties of sediments (Sakadevan and Bavor, 1998; Reddy et al., 1999).

4.   Conclusion

This study demonstrated the potential use of a mixture of pond bund materials, completely decomposed granite and river sand as substrate for P removal in constructed wetlands. Results of kinetic experiments showed that the HKWP sediments adsorbed the majority of P within the first 20 min of incubation, with a pseudo-equilibrium between the solution and solid phases being attained in 24 h. Moreover, the HKWP sediments had great maximum and relative P sorption capacities as indicated by the high Langmuir sorption maxima and Freundlich adsorption constants, owing to the high concentrations of amorphous Fe and Al. Furthermore, sediment EPC_0 values were in the low range of μg, implying a net adsorption of P readily under moderate P loadings. Yet, low P concentrations of influent stormwater in the HKWP limited the amount of P that could be adsorbed, and led to a potential release of previously sorbed P from sediments into the water column upon scouring and resuspension of bottom sediments by wind and water currents. To fully capitalize on the high sorption capacity of the HKWP sediments, consideration should be given to introduce influent water with higher P loading such as those in the nearby eutrophic Deep Bay area.

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