

# Dissolved Phosphorus Retention of Light-Weight Expanded Shale and Masonry Sand Used in Subsurface Flow Treatment Wetlands

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Using surface flow constructed wetlands for long-term phosphorus (P) retention presents a challenge due to the fact that P is stored primarily in the sediments. Subsurface flow wetlands have the potential to greatly increase P retention; however, the substrate needs to have both high hydraulic conductivity and high P sorption capacity. The objective of our study was to assess the P retention capacity of two substrates, masonry sand and light weight expanded shale. We used sorption/desorption isotherms, flow-through column experiments, and pilot-scale wetlands to quantify P retained from treated municipal wastewater. Langmuir sorption isotherms predicted that the expanded shale has a maximum sorption capacity of 971 mg/kg and the masonry sand 58.8 mg/kg. In column desorption and column flow-through experiments, the masonry sand desorbed P when exposed to dilute P solutions. The expanded shale, however, had very little desorption and phosphorus did not break through the columns during our experiment. In pilot cells, masonry sand retained (mean  $\pm$  standard deviation)  $45 \pm 62$  g P/m<sup>2</sup>/yr and expanded shale retained  $164 \pm 110$  g P/m<sup>2</sup>/yr. We conclude that only the expanded shale would be a suitable substrate for retaining P in a subsurface flow wetland.

## Introduction

Constructed wetlands were initially believed to provide efficient, long-term retention of phosphorus (P) from polluted waters until it was realized that newly constructed wetlands

quickly become saturated with respect to P (1, 2). It is now understood that long-term P retention in wetlands is a challenge, especially when the dominant form of P is dissolved. Many municipal, agricultural, and stormwater discharges have large proportions of total P in the dissolved form. The greatest capacity for long-term storage of P in surface water wetlands is in the substrate through either peat building, which is the dominant process in wetlands without mineral soils, or adsorption to mineral sediments (3). Richardson and Craft (2) estimated a global average of P burial through peat accretion at 0.5 g P/m<sup>2</sup>/yr. At this rate, 683 acres (276 ha) would be required to treat 1 million gallons per day (3785 m<sup>3</sup>/d) of wastewater with an initial P concentration of 2 mg/L to a final effluent concentration of 1.0 mg/L. There is a need, therefore, to improve the areal efficiency of P retention in constructed wetlands. Our study estimates areal P retention utilizing substrates with high sorption capacity and high hydraulic conductivity.

Phosphorus sorption in freshwater wetland soils is usually controlled by iron (Fe) and aluminum (Al) in acidic soils and calcium (Ca) and magnesium (Mg) in alkaline soils (3–5). Phosphorus may be removed from solution by nonspecific physical adsorption (ion exchange), specific chemical adsorption/precipitation and complexation (4). The first mechanism, ion exchange, is driven by the surface charge and surface area of particles. Physically adsorbed phosphate is not held as tightly by the soil as it can be desorbed with water. The second mechanism, chemical adsorption, involves ligand exchange. This occurs when the oxygen atoms in the phosphate ions displace the surface hydroxyl groups and water molecules coordinated with Fe and Al (6).

Adsorption of phosphate by silicate clay minerals appears to occur in a similar manner, with phosphate bonding to the Al atoms exposed at the edges of the clay particles and the substitution of phosphates for silicate in the clay matrix comprising the primary mechanisms of phosphorus–clay interaction (7).

Both physical and chemical sorption processes can be rapid, occurring within minutes of mixing. Slower reactions continue to remove phosphate from solution for periods of from several days to several months. Continued removal of phosphate from solution has been attributed to physically adsorbed P forms shifting to chemically adsorbed forms, the diffusion of phosphate adsorbed on the surface of structurally porous oxides of Fe and Al to positions inside the matrix, and the precipitation of crystalline Fe, Al, and Ca phosphates (6).

Wetlands with highly sorptive soils, however, may retain low quantities of P due to inadequate sediment–water contact. This applies to surface water wetlands with high water depth and systems with substrates of low hydraulic conductivity. For example, the chemistry and high surface area of many mineral clays contributes to their high P sorption capacity, but their low hydraulic conductivities limit sediment–water contact and thus their opportunity to retain P is severely reduced.

The use of various substrates in subsurface flow wetlands for P sorption capacity has been investigated in both laboratory experiments and small-scale constructed wetlands (8–12). Several studies have assessed the 24-h P sorption capacity of various light-weight aggregates, slags, and sands. Zhu et al. (13) found that two iron-rich sands from Montana had an average P sorption capacity of 441 mg/kg, whereas P sorption capacity of various aggregate materials ranged from 37 to 3460 mg/kg. Few studies, however, have examined P retention of media under both batch loading (sorption

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isotherms) and continuous loading (pilot cells). The purpose of this research was to assess P retention by two media, masonry sand and expanded shale (manufactured by Texas Industries, Streetman, Texas) in a subsurface flow constructed wetland and compare it to P retention in an adjacent surface flow wetland with native soil. We also compare the sorption capacity of these two materials as determined by isotherm experiments to their performance in both flow-through column experiments and pilot-scale constructed wetlands.

## Methods and Materials

**Site Description.** The project is located at the Pecan Creek Water Reclamation Facility (PCWRF) in Denton, Texas. Effluent from PCWRF, treated by activated sludge, was diverted to the project area. During the study period, mean ( $\pm$ standard deviation) total suspended solids and total P of the effluent were 1.81 ( $\pm$ 1.35) and 1.85 ( $\pm$ 0.95) mg/L, respectively.

**Physical Characteristics.** Expanded light-weight shale utilized in this study is manufactured from shallow shale deposits mined from a location near Streetman, Texas. The shale is sorted by size and then fired for 30–40 min in a rotary kiln to temperatures of approximately 2000 °F (1093 °C). The result is a stable, porous material with little organic material. The manufacturer reported the following chemical composition for their expanded shale: Al<sub>2</sub>O<sub>3</sub> 15.86%, Fe<sub>2</sub>O<sub>3</sub> 5.80%, CaO 1.44%, and MgO 1.68%; thus, Al and Fe are major components of this material. Masonry sand is a readily available, fine-grained sand commonly used as an ingredient in mortar and plaster and as fill during various construction activities. It has been washed to remove clay, silt, and organics. Particle size distribution and soil porosity of masonry sand and expanded shale were determined by standard procedures (14). The hydraulic conductivity of masonry sand and expanded shale was determined in the laboratory using a Soiltest K-605 constant head permeameter. Hydraulic conductivity (*K*) was calculated using Darcy's law (14).

**Sorption Isotherms.** Sorption isotherms express the variation of specific adsorption with equilibrium concentrations of adsorbate in bulk solutions at constant temperature (15). There are several relationships used to describe the experimental isotherm. The Langmuir model (eq 1) describes deposition of a single layer of solute molecules on the surface of the solid and thus may be used to predict the maximum sorptive capacity of the sorbent for the given sorbate at the experimental temperature,

$$C_e/(x/m) = (1/ab) + (C_e/b) \quad (1)$$

where *x/m* is the mass of solute adsorbed per gram of sorbent at concentration *C<sub>e</sub>* (g/kg), *a* is the adsorption constant related to the binding energy, *b* is the mass of solute adsorbed in forming a complete monolayer on the sorbent surface (L/g), and *C<sub>e</sub>* is the concentration in solution at equilibrium (mg of P/L).

Barrow (16) examined phosphate sorption over much longer periods of time and modified the empirical Freundlich equation to describe the process (eq 2),

$$X = kC^a t^b \quad (2)$$

where *X* is the mass of solute adsorbed per gram of sorbent at concentration *C<sub>e</sub>* (mg/g), *C* is the concentration in solution at equilibrium (mg of P/L), *t* is the time, and *k*, *a*, and *b* are constants.

The effects of time (*t*) and initial phosphate concentration (*C<sub>0</sub>*) on sorption for both media were modeled using the linear form of eq 2.

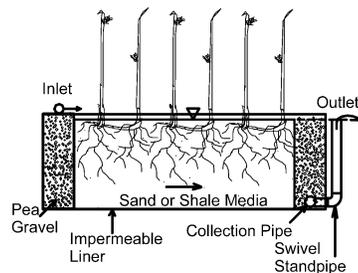


FIGURE 1. Cross-sectional view of one pilot cell. Cells are 3 ft (0.9 m) high, 4 ft (1.2 m) wide, and 8 ft (2.4 m) long. Separate inlet and outlet compartments approximately 1 ft (30.5 cm) in length were filled with pea gravel to promote even distribution of wastewater.

Sorption isotherms in this study were constructed according to methods described in OECD (17). Solutions were analyzed for soluble reactive phosphate (SRP) using the ascorbic acid method. Two types of isotherm experiments were conducted. The first used low initial concentrations of P (0, 0.5, 1.0, 2.0, and 3.0 mg of SRP) to assess sorption at the low levels typically observed in wastewater effluents. These low-level experiments were repeated at 3, 10, 30, 100, and 300 h to estimate the rate of sorption. The second experiment used high P concentrations in the range 0, 20, 40, 80, 160, and 320 mg of SRP so that comparisons to other materials could be made. These high P experiments were also used to assess P desorption in the two medias. Desorption was measured by immediately adding fresh, dilute solution to the media, shaking for 24 h, and analyzing the filtrate. Three desorptions were performed, the first two with solutions of fresh wastewater effluent (0.4 mg of SRP) and the third with deionized water.

The effect of pH on sorption to expanded shale was examined by constructing isotherms with pH-buffered phosphate solutions. Three pH levels, 4–5, 6–7, and 8–9, were examined using initial SRP concentrations of 0, 3, 10, 30, and 100 mg/L. Two pH levels, 4–6 and 8.5–9.5, were examined using initial SRP concentrations of 0, 0.5, 1.0, 2.0, and 4.0 mg/L.

**Column Flow-Through Experiments.** Phosphorus breakthrough curves were used to quantify P sorption under continuous loading. Four columns were constructed of 4-in.-diameter polyvinyl chloride (pvc) pipe and packed with masonry sand or expanded shale. Secondary treated effluent entered the bottom of the columns under constant pressure and exited near the top. Sampling of flow-through experiments was conducted by taking grab samples of inflow and outflow solutions over a period of several days. The flow rate (*Q*) of each column was measured manually. Samples were analyzed for pH, conductivity, temperature, and SRP; the ratio of outflow concentration (*C<sub>e</sub>*) to inflow concentration (*C<sub>0</sub>*) was plotted against the cumulative volume of wastewater flowing through the column(s). Mass of P retained was determined by integration of these plots.

**Pilot Cells.** Although flow-through columns have the advantage of examining P sorption under nearly ideal hydraulics and continuous loading, they do not simulate the conditions of a full-scale treatment wetland. Pilot cell studies were designed to include the effects of P cycling between biotic and abiotic compartments and provide a more realistic prediction of long-term P retention. Subsurface flow pilot cells were built from two plywood structures divided into three cells by adding internal walls. The cells were 3 ft (0.9 m) high, 4 ft (1.2 m) wide, and 8 ft (2.4 m) long and lined with 0.045-mm-thick rubber pond liner (PondGard, Swanton, Ohio) (Figure 1).

Each cell was planted with 30 plugs of *Schoenoplectus californicus* (C.A. Mey). Each cell had an inlet meter that recorded cumulative inflow; however, these meters failed

**TABLE 1. Physical Characteristics of Masonry Sand and Expanded Shale**

characteristic	masonry sand	expanded shale
effective size ( $D_{10}$ ) ( $\mu\text{m}$ )	110	720
uniformity coefficient	1.4	2.3
density ( $\text{kg}/\text{m}^3$ )	1670	728
porosity ( $n$ )	0.304	0.594
hydraulic conductivity ( $K$ ) (m/d)	17.3	92.2
pH of 10 g of material in 50 mL of water	8.28	9.38

during the study after which manual measurements were substituted. Cells A, B, and C contained masonry sand and cells X, Y, and Z contained expanded shale. Approximately twice monthly, grab samples were collected from one of the cell inlets ( $P_{in}$ ) and all six pilot cell outlets ( $P_{out}$ ). Samples were analyzed for SRP, pH, temperature, and conductivity. Every fifth sample was duplicated. We estimated P retained by the sand or shale by multiplying the difference between  $P_{in}$  and  $P_{out}$  by the volume of water treated.

**Surface Flow Wetland.** To compare our subsurface flow pilot cells to a surface flow wetland, we also monitored an adjacent, 2-acre treatment wetland. Beginning in November of 2000, we collected grab samples approximately halfway through the wetland's flow path ( $Wet_{Mid}$ ) and at the outfall ( $Wet_{out}$ ). This small wetland, which was originally constructed to address toxicity issues, receives the same treated effluent as the flow-through columns and pilot cells. Hemming (18) estimated the wetland's nominal hydraulic retention time to be approximately 4.3 d. The wetland had water depths of approximately 30 cm and was heavily vegetated, primarily with *Typha* sp. (cattails), *Lemna* sp. (duckweed), *Pontedaria cordata* (pickerelweed), *Ludwigia* sp. (water primrose), and *Schoenoplectus* sp. (bulrush).

## Results and Discussion

**Physical Characteristics.** Expanded shale had a larger effective size, a higher hydraulic conductivity, and greater porosity than masonry sand (Table 1). The higher porosity in the expanded shale probably stems from internal micropores within individual particles as well as greater voids between neighboring particles due to their rectangular shape. Micropores in the shale probably contribute to a larger surface area than that of masonry sand, despite sand's smaller particle size.

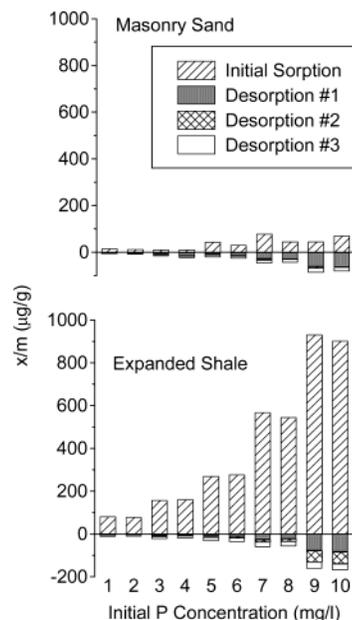
**Sorption Isotherms.** The expanded shale had a sorption capacity, as estimated by the Langmuir model, of 971 mg/kg, compared to 58.8 mg/kg for masonry sand. Furthermore, in desorption experiments the expanded shale was found to release relatively little of the sorbed phosphate, while the sand released most or all of the sorbate (Figure 2). Masonry sand desorbed between 65 and 120% of P originally sorbed in the high-concentration experiment, compared to expanded shale which desorbed between 10 and 19% of previously sorbed P.

We observed additional P sorption in both materials with extended shaking time. Expanded shale, for example, reduced P levels from 3 to 0.49 mg/L in 3 h and to 0.016 mg/L in 300 h (Figure 3). Multiple regression on the log-transformed data yielded the following models:

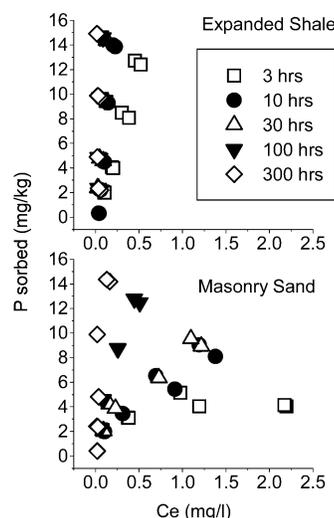
$$\text{masonry sand } x/m = 0.01C^{0.796}t^{0.137} \quad (p < 0.0001; R^2 = 0.923)$$

$$\text{expanded shale } x/m = 0.005C^{0.990}t^{0.014} \quad (p < 0.0001; R^2 = 0.978)$$

Others have observed that the amount of phosphorus removed by soils receiving long-term wastewater applications



**FIGURE 2. Initial sorption with concentrations of phosphorus (P) ranging from 20 to 320 mg/L, followed by two desorptions with wastewater (#1 and #2) and one desorption with deionized water (#3).**



**FIGURE 3. Sorption isotherms for masonry sand and expanded shale conducted for increasing equilibrium times of 3, 10, 30, 100, and 300 h. The initial phosphate-P concentrations for each isotherm were 0.5, 1.0, 2.0, and 3.0 mg/L.**

was many times greater than the amount predicted using 24-h sorption experiments (19, 6). Short-term, or rapid sorption, may involve interactions with easily accessible surface minerals such as precipitation, anion exchange, and the replacement of  $-\text{OH}_2$  or  $-\text{OH}$  groups with phosphate ions (20, 21). In expanded shale, additional sorption may result from transport of phosphate ions into less accessible sorption sites located within micropores. Longer term P retention in many soils may be enhanced by the increasing insolubility, over time, of compounds formed during rapid sorption (20). In addition, longer term sorption rates are influenced by diffusion of phosphorus through the metal phosphate precipitate to the unreacted metal oxide surface, which is a function of the phosphorus concentration gradient between the bulk solution and the interface between the metal oxide and the metal phosphate (22). In sorption isotherm experiments conducted by Barrow (16), solution P concentrations continued to decrease for at least 1000 days.

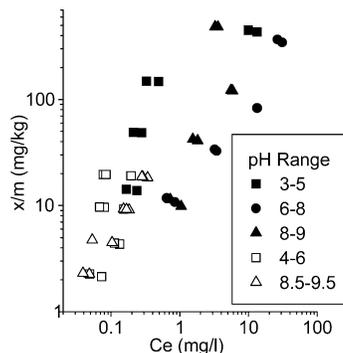


FIGURE 4. Sorption isotherms for expanded shale conducted at pH values ranging from 3 to 5 to 8.5–9.5. Initial SRP concentrations were high (solid symbols, 3, 10, 30, and 100 mg/L) and low (open symbols, 0.5, 1, 2, and 4 mg/L).

Barrow (16, p 735) concluded that “the initial reaction with the surface of a soil particle induces a diffusion gradient toward the interior of the particle and begins a solid-state diffusion process.”

Masonry sand also continued to remove P with increasing shaking time, but did not remove as much P as expanded shale. Masonry sand reduced P from 3 to 2.19 mg/L in 3 h, and after 300 h, P was reduced to 0.145 mg/L (Figure 3).

Application of these results to wastewater treatment operation suggest that an expanded shale system receiving wastewater with 3.0 mg/L and an effluent target of 0.5 mg/L would be most efficient with a hydraulic retention time as short as 3 h. On the other hand, a system using the masonry sand would require 100 h to achieve an effluent with 0.5 mg/L. Further increases in retention time would not substantially improve sorption in either material and could result in desorption in masonry sand. These results led us to design our pilot cells with the shortest possible hydraulic retention time.

In unbuffered isotherm experiments, expanded shale typically raised the pH to 8 and above in a 24-h period. This was most likely due to the presence of soluble hydroxides on the surface of the shale. During pH-controlled experiments sorption was highest at pH 3–4 for solutions with an initial [SRP] of 30 mg/L or less (Figure 4), suggesting P association with soluble  $Al^{3+}$ . At pH 8–9, formation of various calcium phosphate compounds is favored, depending on [SRP], ionic activity, temperature, and other factors (21). Sorption was highest at high pH in solutions with initial [SRP] of 0.5, 1.0, and 100 mg/L. Enhanced P retention at high pH and high [SRP] may be a result of the formation of dicalcium phosphate ( $CaHPO_4 \cdot 2H_2O$ ), which is predicted at pH 8–9 with [SRP] = 100 mg/L, but not at [SRP] = 30 mg/L (21). This precipitate may be redissolved if pH decreases, but in time (i.e., 3–6 months) it is typically replaced by more stable and less soluble calcium phosphates minerals such as octacalcium phosphate [ $Ca_8H(PO_4)_3$ ] and hydroxyapatite [ $Ca_5(PO_4)_3(OH)$ ] (23). At lower [SRP] representative of municipal and agricultural wastewaters (0.5–4.0 mg/L), all of the pH solutions reduced [SRP] to below 0.5 mg/L.

The lowest P retention occurred at pH 6–8, the pH most likely to be encountered in natural and wastewater environments. This is a result of increased solubility of Fe, Al, and Ca phosphate compounds at this pH range. At moderate pH ranges, however, interactions between phosphate and silicate compounds occur (20). Silica is a primary component of both masonry sand and expanded shale.

**Flow-Through Column Experiments.** In flow-through columns experiments, P retention was also higher in columns containing expanded shale. In the four sand columns, breakthrough occurred at approximately 250 L (Figure 5), followed by desorption of previously sorbed P between 750

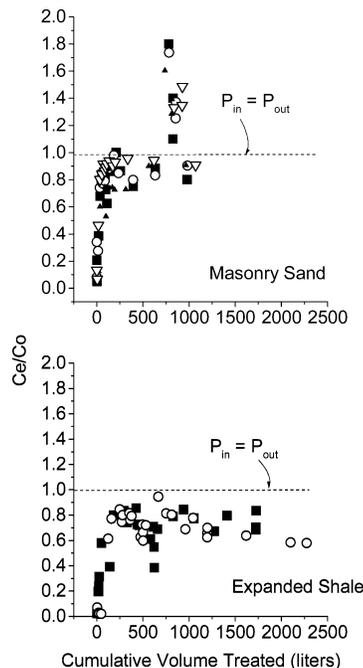


FIGURE 5. Phosphorus breakthrough in columns with masonry sand or expanded shale receiving continuous flow of treated effluent. The broken line ( $C_e/C_0 = 1$ ) represents the breakthrough point.

and 1000 L. Additional sorption occurred after 1000 L. Net sorption by masonry sand was essentially zero because the sand desorbed all of the P that was initially sorbed. The desorption is based on three samples after incoming P concentrations dropped from 2.62 to 1.54 mg/L and remained below this level. When  $C_0$  increased again, sand in the column sorbed added P. The observed desorption was consistent with desorption in high-concentration isotherm experiments; that is, masonry sand easily desorbs previously sorbed P when exposed to more dilute P solution. It appears that P is only loosely sorbed to the sand surface, probably through ion exchange, which is easily reversed. The pH of sand columns ranged from 7.5 to 8.4 during the experiments, compared to pH 6.7–7.8 of the inflow.

Initially, expanded shale columns followed a P retention pattern similar to the masonry sand (Figure 5), that is, an initial period of high P retention and a rapid approach toward saturation. Easily accessible sorption sites on the exterior of the particles are probably being utilized during this phase. Unlike masonry sand, however, breakthrough did not occur in either shale unit; instead, the rate of P removal from solution decreased but then remained more or less stable for the remainder of the experiment. This longer term phase may reflect molecular diffusion of P to less accessible sorption sites located within micropores. Expanded shale columns had pH values ranging from 9.6 to 7.6, compared to pH 7.0–8.0 of the inflow. Expanded shale increased the pH of the incoming wastewater more than 2 units during the first half of the experiment, but this increase fell to approximately 1 pH unit increase by the end of the experiment. The decreasing pH during the second half of the experiment may have contributed to sustained P retention as association with hydrous oxides of Al and Fe, and silicates, would be favored.

The two expanded shale units retained 45% and 40% of incoming wastewater SRP. However, total mass of SRP retained by Columns 1–2 (407 mg/kg) was much higher than that retained by Columns 3–4 (135 mg/kg) due to greater volume of wastewater treated (despite our efforts to maintain similar flow rates). Of interest is the fact that substantially higher flow rates through Columns 1–2 did not diminish the percentage of P retained.

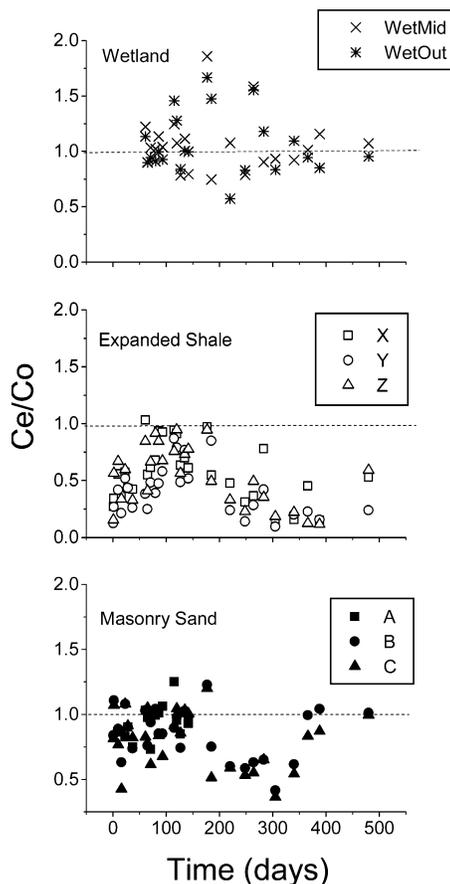
**TABLE 2. Characteristics of Three Pilot Cells (A, B, and C) Contained Masonry Sand and Three (X, Y, and Z) Contained Expanded Shale. All 6 Pilot Cells Had Approximately 90% Coverage with *Schoenoplectus californicus***

	masonry sand (A,B,C)	expanded shale (X,Y,Z)
substrate volume (L) per unit	1930	1930
mass substrate (kg) per unit	3220	1400
pore volume (L) per unit	587	1146
approximate head (cm)	15	15
days operated	392	416
estimated quantity wastewater treated (m <sup>3</sup> )	430	490
estimate hydraulic loading rate (cm/d)	46	55

**Subsurface Flow Pilot Cells.** Pilot cells were operated and monitored from September 2000 to January 2002; however, Cell A developed a leak early in the study and was taken off-line. Selected physical and operational parameters of pilot cell units are provided in Table 2. Meters used to measure flow rates into the cells failed after several months and manual flow measurements were taken for the remainder of the study. The values of incoming [SRP] ( $P_{in}$ ) during the study ranged from 0.364 to 2.25 mg/L (Table 3) with the lowest concentrations occurring after periods of heavy rain. Expanded shale had the highest percent SRP retention (51%); masonry sand averaged only 14%. Expanded shale also retained SRP regardless of season, whereas masonry sand exported SRP occasionally, primarily during the rainy season when incoming [SRP] was very dilute (Figure 6). This is consistent with observed desorption by masonry sand in isotherm and column experiments.

Effluent from the three shale cells had the lowest mean SRP concentrations ( $P_{out}$ ), whereas the highest were from the two surface wetland locations (Figure 7). Mean  $P_{out}$  from the pilot cells X, Y, and Z were not significantly different from each other but were significantly less than mean  $P_{out}$  of masonry sand, both surface water wetlands, and  $P_{in}$  (Tukey's multiple range test,  $\alpha = 0.05$ ,  $P_{in} = Wet_{Out} = Wet_{Mid} = A = B = C > Z = Y = X$ ).

Expanded shale sorption capacity showed no distinct trend toward saturation or desorption, which was also consistent with isotherm and column studies. By contrast, the surface water wetland appeared to export P randomly (Runs test,  $\alpha = 0.05$ ), suggesting that the surface water wetland is saturated with respect to P.



**FIGURE 6. Ratio of effluent soluble reactive phosphate (SRP) to incoming SRP ( $C_e/C_0$ ) for the pilot cells and adjacent surface water wetland. The dashed line is where  $C_e/C_0 = 1$ ; data above this line represent an export of SRP. Sampling of the surface water wetland did not begin until day 60. Cell A (masonry sand) developed a leak early in the study and was taken off-line.**

We used the volume of wastewater treated (Table 2) and the mean delta P for each material (Table 3) to calculate the annual amount of P retained per unit area. By this calculation, masonry sand retained (mean  $\pm$  standard deviation)  $45 \pm 62$  g of P/m<sup>2</sup>/yr. Expanded shale retained over 3 times more P than masonry sand at  $164 \pm 110$  g of P/m<sup>2</sup>/yr. Estimates of P retention for both materials are much higher than P

**TABLE 3. Means, Standard Deviation, and Range of SRP Concentrations, delta P ( $P_{in} - P_{out}$ ), and  $C_e/C_0$  for Pilot Cells, Inflow, and Wetland Stations**

	inflow $P_{in}$	pilot cells						adjacent wetland	
		A	B	C	X	Y	Z	Wet <sub>mid</sub>	Wet <sub>out</sub>
Soluble Reactive Phosphorus (SRP) (mg/L)									
mean (mg/L)	1.54	1.40	1.29	1.215	0.82	0.58	0.76	1.57	1.51
standard deviation	0.455	0.309	0.435	0.429	0.397	0.244	0.392	0.536	0.391
grand mean, S.D. and n	N/a	1.28 + 0.411 (n = 73)			0.703 $\pm$ 0.366 (n = 86)			1.54 + 0.465 (n = 44)	
minimum	0.36	1.00	0.45	0.31	0.22	0.21	0.23	0.45	0.61
maximum	2.35	1.86	2.05	1.92	1.86	1.19	1.67	2.30	2.26
n	29	15	29	29	29	29	28	22	22
$P_{in} - P_{out}$ (delta P) (mg/L)									
mean (mg/L)	N/a	0.09	0.25	0.3272	0.72	0.96	0.79	0.00	-0.06
standard deviation	N/a	0.186	0.344	0.383	0.539	0.631	0.587	0.344	0.280
grand mean, S.D.	N/a	0.25 + 0.343			0.84 + 0.563			-0.029 $\pm$ 0.312	
minimum	N/a	-0.272	-0.162	-0.105	-0.059	-0.826	0.021	-0.805	-0.851
maximum	N/a	0.437	1.259	1.374	1.857	2.063	1.991	0.847	0.464
n	29	15	29	29	29	29	28	22	22
$C_e/C_0$									
grand mean and S.D.	N/a	0.855 $\pm$ 0.199			0.492 $\pm$ 0.26			1.062 $\pm$ 0.273	

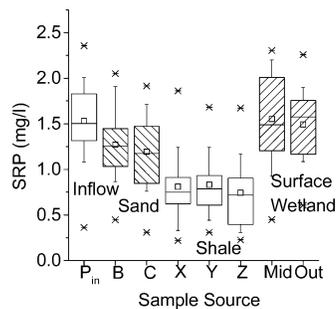


FIGURE 7. Box plots of incoming wastewater ( $P_{in}$ ), effluent from two sand pilot cells (B and C), three shale pilot cells (X, Y, and Z) and two locations within the surface flow wetland (Middle and Out). Sand pilot cell A was taken off-line due to a leak early in the study. Horizontal lines denote the 25th, 50th, and 75th percentile values. The error bars denote the 5th and 95th percentile values. The two symbols below the 5th percentile error bar denote the 0th and 1st percentile values. The two symbols above the 95th percentile error bar denote the 99th and 100th percentiles. The square symbol in the box denotes the mean of the column of data.

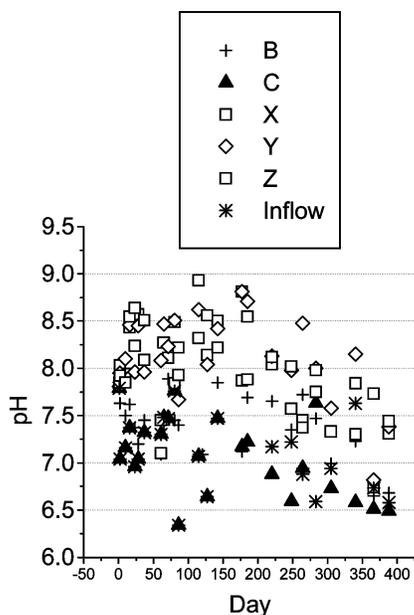


FIGURE 8. Pilot cell and inflow pH over the course of the study. Cells B and C contain masonry sand and Cells X, Y, and Z contain expanded shale.

retention via peat accretion in surface flow wetlands, which is generally regarded to be only  $0.5 \text{ g of P/m}^2/\text{yr}$  (2). They are also substantially higher than P retention estimates for surface flow wetlands treating river water with high particulate P loads. For example, we calculated P retention of  $4.4 \text{ g/m}^2/\text{yr}$  for a constructed flood plain wetland receiving Trinity River water (24). Mitsch et al. (25) reported  $0.5\text{--}3.0 \text{ g/m}^2/\text{yr}$  P retention in constructed wetlands along the Des Plaines River. Incoming concentrations of suspended solids were high in both studies; thus, the primary mechanism of P removal was attributed to sedimentation.

In 24-h isotherm experiments, column flow-through studies, and longer-term pilot cell operations, our expanded shale demonstrated retention of dissolved P. Initial sorption, which usually occurred at high pH, is rapid, probably due to ion exchange (physical sorption) and ligand exchange (chemical sorption) with surface hydroxides. Slower, prolonged P retention by expanded shale may be associated with chemical and physical sorption to less accessible sites located within micropores of this porous material. Longer term sorption may also be a function of diffusion of P into

the interior of the particle. As pH decreased in column and pilot cell studies, reactions with hydrous oxides of Al + Fe would be favored, and formation of Al-P, as well as Fe-P compounds, may contribute to the long-term P retention in expanded shale columns and pilot cells. Releases of previously sorbed P from expanded shale were minimal in desorption experiments and were not observed during the field studies. Subsequent sequential fractionation of material taken from the pilot cells indicates that Fe + Al bound P (extracted with NaOH) was the most important storage compartment for retained P (26). Given the high Al + Fe content of the material, these results are consistent with our expectations that expanded shale would provide high sorption capacity that would not be easily reversed. Other researchers (27, 28) have found that sorption capacity of materials such as zeolite and light expanded clay aggregates (LECA) were closely correlated to both oxalate extractable Fe + Al.

Despite some reported successes with sand in subsurface flow treatment wetlands, our study found that masonry sand is a poor candidate for dissolved P retention. Its P sorption capacity as estimated by the Langmuir sorption model was only  $58.8 \text{ mg/kg}$ , compared to  $971 \text{ mg/kg}$  for the expanded shale. Masonry sand also readily desorbed P when exposed to more dilute solution in both isotherm desorption and column experiments. Some of the low P retention by masonry sand may have been due to its poor hydraulics. Although sand's hydraulic conductivity ( $K$ ) in the lab seemed adequate, when scaled up to the columns and pilot cells, flow rates were much lower and short-circuiting occurred. The aerial retention rate of expanded shale was 40 times greater than P retention reported for sedimentation and over 100 times greater than global estimates of peat accretion. We attribute this in part to the excellent hydraulics provided by expanded shale as well its high surface area and sorption affinity. By contrast, the adjacent, aged, surface flow wetland randomly exported P, probably due to P saturation of sediments at the sediment-water interface. Given the high rates of soluble P retained by expanded shale in our subsurface flow pilot cells, these systems warrant further and longer term study.

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