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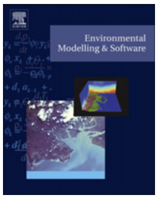

Evaluation of the Langmuir model in the Soil and Water Assessment Tool for a high soil phosphorus condition

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ABSTRACT

Phosphorus adsorption by a water treatment residual was tested through Langmuir and linear sorption isotherms and applied in the Soil and Water Assessment Tool (SWAT). This study uses laboratory and greenhouse experimental Phosphorus data to evaluate the performance of a modified version of SWAT for high P concentration simulation development. A combination of vegetative filter strips (VFS) and water treatment residuals (WTR) were used to reduce soluble P runoff concentration. To effectively simulate the concentration measured in the experiments, a Langmuir model was incorporated into SWAT. The effective depth of surface runoff and soil interaction over a small subwatershed (0.07 km^2) was based on an experimentally determined WTR rate of 64 Mg ha^{-1}. A continuous flow method for rapid measurement of soil hydraulic properties was used to determine soil water contents and hydraulic conductivities. A parameter sensitivity analysis to model output indicated that the Soil Conservation Service runoff curve number for moisture soil condition II was the most responsive to change for this subwatershed. The SWAT model yielded significantly different soluble P and P leached amounts once the Langmuir model was included as an option to the linear P sorption model. With this new adaptation, SWAT was able to simulate higher P concentrations as validated by laboratory and greenhouse experimental data. The laboratory and greenhouse assessment of the WTR provided insight into the data required to evaluate the incorporation of the Langmuir model into a watershed scale tool. The choice of P model simulation (between the Freundlich option already in SWAT and the Langmuir method) was included in a sensitivity analysis performed to define the model sensitivity to selected parameters. This study provides one case of higher P conditions that SWAT was able to more adequately simulate with the Langmuir model incorporated.

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1. Introduction

A Langmuir sorption equation is commonly used by soil scientists to monitor phosphorus (P) sorption and availability (Hussain et al., 2003), This study uses laboratory and greenhouse experimental P data to evaluate the performance of a modified version of the Soil and Water Assessment Tool (SWAT) with the Langmuir P isotherm for simulating high runoff P concentrations.

The soil through which P moves plays a vital role in its retention and availability to nearby waterways. Whether P remains in a soluble form and becomes adsorbed through purposeful conservation measures has been the focus of several scientific studies (Holford, 1979; Gale et al., 1994; Akhtar et al., 2003). Because of its contribution to algal blooms which can result in anoxia and fish kills, P mobility, especially in the agricultural sector, continues to be of primary environmental concern (Reddy et al., 1998; Dunne et al., 2005; Zhang et al., 2008).

Surface applications of manure and other amendments to agricultural land can impact P availability in the surface environment (Sims et al., 1998) and groundwater (McDowell et al., 2001). Agricultural fields can transfer P via overland flow when it is present in excess of crop requirements (Langlois and Mehuys, 2003). Since application rates of organic amendments (i.e. manures, litters, biosolids) were traditionally based on crop N requirements, P was often applied in excess contributing to environmental pollution. Soil moisture conditions and soil texture in addition to intensity, duration and timing of rainfall events after an organic amendment application affects P movement as well. Nutrient management programs continue to develop to identify the

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optimum P application rates for a variety of scenarios and soil combinations. Phosphorus can be leached, transported with sediment and organic matter, and desorbed or precipitated depending on the environmental pH conditions; however, it typically remains in the top 15 cm of soil in sandy clay loam soils. Plants can absorb soluble P that can be released later when plants or organic amendments (i.e. manure) decompose.

Water treatment residuals continue to predominantly be disposed in landfills and lagoons. Finding an economically viable and environmentally beneficial alternative would protect water quality and reduce municipal costs. The application of a high-Al bearing amendment to adsorb P in addition to a physical barrier can protect groundwater in addition to surface water (McDowell et al., 2001). Surface application of water treatment residual (WTR) to reduce P runoff has been successfully employed as a best management practice for poultry litter-treated land (Basta and Storm, 1997; Daniel et al., 1999; Basta, 2000). Due to changing USEPA regulations (2001) for confined animal feeding operations, it is imperative that the regulations are based on data that relate to regions with similar climates, since these best management practices are site specific. Other studies have incorporated WTR at various depths into the soil profile to reduce soluble P runoff (DeWolfe, 1990; Eaton and Sims, 2001) or to determine its impact on soil test P (STP) (Jacobs and Teppen, 2001). Water treatment residual composition depends on the drinking water treatment facility from which it was collected. Chemical treatments vary widely affecting the WTR compositions and P sorption ability. Gallimore et al. (1999) demonstrated the effectiveness of surface applied WTR in addition to vegetative filter strips (VFS) to reduce soluble P. Few references that provide VFS data for minimally irrigated conditions in semi-arid and arid environments (less than 30–35 cm precipitation; Fasching and Bauder, 2001).

The application of the SWAT hydrologic model is well documented at many spatial and temporal scales throughout the world (Gassman et al., 2007); however, improvements to the P algorithms are needed to address conditions that are not adequately represented by the linear P sorption equation. Environmental examples that potentially require usage of the Langmuir model to capture high P concentrations in the soil and water are reduced tropical soils that can release bound P, soils that received successive amendment (manure) loadings that are near P saturation capacity as sources of P, and when a linear isotherm cannot be assumed at a low concentration range. This study evaluated a modified SWAT's capacity to capture saturated P conditions in a WTR that had been measured with greenhouse and laboratory experiments. Greenhouse plot studies have been used in favor of larger scale experiments due to costs and inherent uncertainties and variabilities within natural systems (Owusu-Bennoah and Acquaye, 1996; Smith et al., 2009). The present study uses a combination of vegetative filter strips and water treatment residuals (WTR) to reduce total P (TP) and molybdate reactive P (DRP) in runoff and determine if an optimum rate of WTR application can be identified to reduce P. The SWAT watershed model was used to assess whether a modified P algorithm with a Langmuir model can capture high soluble P runoff concentrations for a soil amendment at saturated P capacity. Olsen and Watanabe (1957) and Villapando and Graetz (2001) utilized the Langmuir model from the equation that Langmuir (1918) developed for gaseous adsorption on solids because of its ability to estimate P sorption maxima ($S_{\max}$) and a constant related to soil's binding energy (K_d). These authors applied the Langmuir model to describe the strength of the bonding energy of P within acidic soils compared to calcareous soils and to describe dairy manure impacted soils with high P conditions, respectively. The Langmuir model continues to be used readily in P sorption studies due the validity of heterogeneous soil systems behaving as a mixture of homogeneous surfaces with each P compound in its respective particle being independently equilibrated with the P in solution (Pant and Reddy, 2001). The Agricultural Policy EXtender model (APEX; Williams and Izaurralde, 2005) that simulates small watersheds uses a modified approach to the linear form of the Langmuir model to capture high phosphorus concentrations. A modified approach to the Langmuir model does not allow for isotherm linearity in low concentrations (Zhou et al., 2005). The addition of this algorithm to the current version of SWAT expands the model's ability to simulate higher P concentrations including high P saturated soils and soil amendments that were previously not addressed by the linear sorption model.

2. SWAT model background

The Soil and Water Assessment Tool (SWAT) model is a physically-based quasi-distributed parameter model that performs all calculations on a daily time step to quantify effects of watershed management and climate conditions of flow, sediment, nutrient, and pesticide response. SWAT simulates hydrology as a two component system – land hydrology and channel hydrology. SWAT contains several hydrologic components (surface runoff, ET, recharge, and stream flow) that have been developed and validated at smaller scales within the EPIC (Williams et al., 1989), GLEAMS (Knisel, 1980), and SWRRB models (Arnold and Williams, 1987). Water can be transferred from any reach to another reach within the basin. The model simulates a basin by dividing it into subwatersheds that account for differences in soils and land use. Interactions between surface flow and subsurface flow in SWAT are based on a linked surface-subsurface flow model developed by Arnold et al. (1993). The surface runoff hydrologic component uses Manning's formula to determine the watershed time of concentration and considers both overland and channel flow. Lateral subsurface flow can occur in the soil profile from 0 to 2 m as noted below (Arnold et al., 1993). The SWAT model is continually being enhanced to improve its accuracy in simulating environmental processes affected by best management practices (Green et al., 2006; Gassman et al., 2007).

Components of P modeled by SWAT include soil P-water–plant interactions and management activities, such as: mineralization, decomposition, and immobilization, P sorption, leaching, and organic and inorganic fertilizer P application. The transfer of soil P to runoff water is a process in SWAT that occurs within the 1–10 mm depth (Neitsch et al., 2002) and is controlled by physical and chemical processes such as diffusion, desorption, and dissolution (Hansen et al., 2002). Soil inorganic P is divided into solution, active and stable pools where the solution pool is in rapid equilibrium with the active pool (Neitsch et al., 2002). Sorbed P is considered relatively unavailable in the model and is reflected in the SWAT parameter Phoskd, which is referred to as K_d throughout this study. The K_d parameter (L kg^{-1}) is a constant related to the binding energy of P to a substance. The SWAT model default value for K_d is 175 indicating that it has an affinity for soil that is 175 times stronger than to water. Solution P can also be lost directly via preferential flow or runoff which can add significantly to the amount of P lost from the watershed. According to Hansen et al. (2002), the potential for P loss is greatest when a runoff event occurs shortly after surface application of manure or fertilizer.

3. Water treatment residual and alum

Alum [aluminum sulfate: $Al_2(SO_4)_3 \cdot 14H_2O$] is the precursor to the WTR byproduct. Alum is a coagulant that municipalities use in the water treatment process to remove turbidity, color, taste, and odor from raw water while augmenting sedimentation rates. Water treatment residuals generally consist of sand, silt, clay, organic substances, and coagulated aluminum compounds. The potential benefits of applying WTR to the soil include increased soil moisture retention and aeration (Bugbee and Frink, 1985) and greater soil aggregation and soil water holding capacity (Rengasamy et al., 1980). Therefore, P removal from solution may also occur due to adsorption and precipitation reactions induced by Ca^{2+} ions in solution. Pote et al. (1996) confirmed a linear relationship exists between soil test P and runoff P. Therefore, to minimize P loading either the source of the P must be lessened or the sorption capacity of the material through which the P moves must be increased.

The effective depth of interaction between the surface material and runoff will limit the amount of WTR that needs to be applied as long as the soil surface is completely covered (Green, 2004). Any topographical variation such as an accumulation of vegetative residue on the surface or mass of WTR (due to its alum coagulation properties) not evenly distributed on the surface will impact runoff flow paths thereby impacting the ability of the WTR to retain P. The flow velocity and VFS box slope will also affect runoff dynamics and the WTR's P retention ability.

4. Greenhouse and laboratory experiments

4.1. Overland flow manifold

An overland flow design (Green, 2004) was designed for this study because northern Colorado is considered a semi-arid area, less than 40 cm of rain annually so rainfall simulation would not produce adequate runoff for continual P evaluation. Also, in an effort to remediate lagoon water effectively and cost-efficiently, a manifold system dispersed water that contained sediment versus a sprinkler system. With longer contact-time between the sediment and vegetation, more P could be removed from the water.

The overland flow manifold system allowed sheet flow to be introduced at the upper end of the VFS. The manifold system had 11 holes that were 0.28 cm in diameter drilled into 3.8 cm schedule 40 PVC pipe with capped ends. A port for the pump-hose connection to the manifold was located in the middle of the manifold so that water flowed equally to either side. An adjustable hose clamp controlled the water flow rate into the manifold. A runoff event flow rate of 0.1 L s^{-1} was selected because water reached the end of the box with this rate.

4.2. Greenhouse vegetative filter strip (soil) box

Greenhouse VFS boxes measuring 2 m × 1 m × 15 cm (Fig. 1) were constructed. Two weeks were allowed as a settling time for the soil before the four runoff events commenced. Each box was then halved lengthwise to allow for duplicate plots leaving the water transport path as long as possible while minimizing the amount of soil required per box. The box was then filled with an unnamed Aridic Argiustoll that was collected from the top 15 cm adjacent to a feedlot in northern Colorado. It is important to note that the structural integrity of the soil was disrupted since the soil was moved from the field and repacked into the boxes. WTR collected from a local water treatment facility was surface applied at multiple rates five different rates in duplicate in the greenhouse boxes distributed a priori.

The dimensions of the experimental greenhouse plot data that the model will attempt to accurately simulate are 2 m × 0.0 m × 15 cm. Plot design (Fig. 2) is described in Green (2004) which illustrates interior metal borders within the wooden box frame to minimize preferential flow and water loss where the soil separates from the wood. A flow rate of 0.03 L s^{-1} was determined based on achieving runoff at the base of the plot.

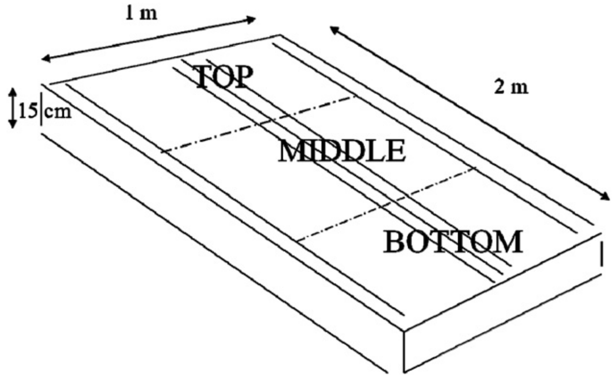

Fig. 1. Vegetative filter strip box dimensions.

The chemical and physical properties of the soil and WTR are in Table 1.

Crested wheatgrass (*Agropyron cristatum* Ephraim), western wheatgrass (*Pascopyrum smithii* Rosanna), and streambank wheatgrass (*Elymus lanceolatus* ssp. *psammophilus* Sodar) were planted in each box. These species were selected because they are cool season, long-lived, drought tolerant, perennial grasses. The crested wheatgrass is a bunch grass while the streambank and western wheatgrasses are strongly rhizomatous sod-formers. A typical wheatgrass fertilizer blend of 21–18–18 ($N-P_2O_5-K_2O$) was applied during watering treatments for the first two weeks to establish the grasses. The vegetation was established to a height that would exist in the field (at least an average measured height of 15 cm above the soil surface) before runoff events occurred.

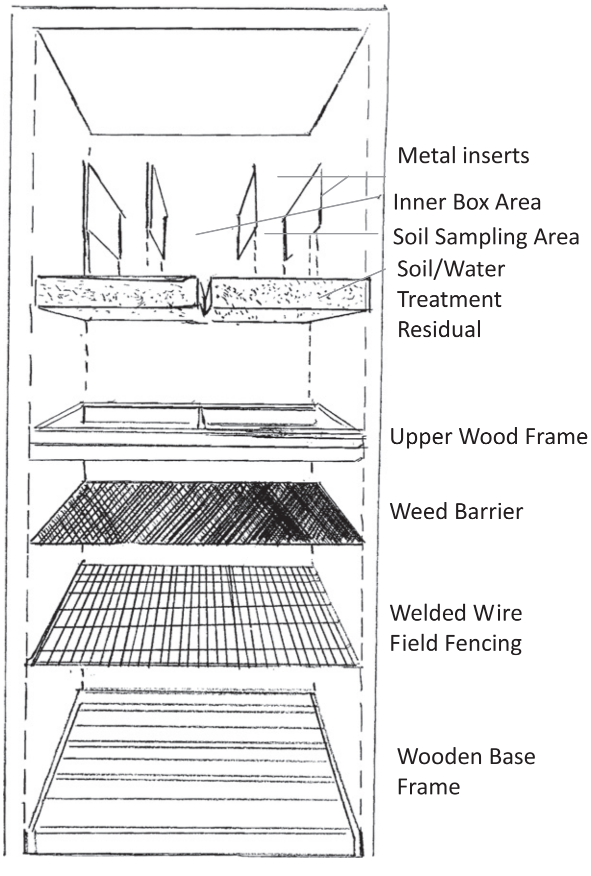

Fig. 2. Vegetative filter strip box construction.

Table 1
Soil and water treatment residual physical and chemical properties.

Soil properties	pH	Texture (Sand/silt/clay)	Bulk density (g cm^{-3})	EC (dS m^{-1})	CEC (cmol$_c$ kg^{-1})	CCE (g kg^{-1})	Total Al, Ca, Fe, P (mg kg^{-1})
Soil	7.5	53/14/33	1.4	1.1	60	85	1100, 1200, 2000, 60
Water Treatment Residual	7.3	50/16/34	1.6	1.5	45.9	90	23 500, 1000, 23 900, 370
Method	Schofield and Taylor (1955)	Gee and Bauder (1986)	Black (1965)	Rhoades (1996)	Rhoades (1982)	Jackson (1968)	Fassel and Kniseley (1974); Dahlquist and Knoll (1978)

4.3. Sampling protocol

Runoff samples were collected at 30-s increments for the first 5 min after runoff occurred, at 2-min intervals for the next 30 min, and finally every 5 min until steady state was achieved (the rate of runoff became constant at the end of the plot). Plots were allowed to dry for 48 h before beginning the next runoff event. All runoff water samples were analyzed for DRP (Murphy and Riley, 1962; Sims, 1997). After establishment of the vegetation to 15 cm above the soil surface, the runoff events began at intervals of one week to allow for the soil to become less saturated. A total of four runoff events took place. Each runoff event occurred until steady state was achieved.

Initial soil moisture samples were collected using a soil sampling device prior to each run to ensure that the runoff events were occurring on soil with matric potentials between field capacity and wilting point. These samples were taken from outside of the inner box at the upper, middle, and lower sections of the box so that soil within the inner box was minimally disturbed (Fig. 1). The soil moisture samples were collected randomly in duplicate and were divided into 0–5-, 5–10-, and 10–15-cm depth increments. Initial soil P samples were taken at the top, middle, and lower portions of the box from within the inner area before the first runoff event. Final soil P samples were taken after each runoff event, and these values served as the initial soil P value for the following runoff event. Soil samples were measured for STP. The soil moisture sample was placed into a soil moisture can and dried in a 105 °C oven for 24 h. After soil samples were taken, new soil was placed in the holes and, if WTR was required, then a small amount was placed on the surface. The holes were filled so that soil water flow within the boxes was not impacted.

4.4. Phosphorus methodology

Total P is considered to be the total amount of P in dissolved and particulate phases. The soil digestion methods of Fassel and Kniseley (1974) and Dahlquist and Knoll (1978) were used on unfiltered samples and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to determine TP, Al, Fe, and Ca. Soil (1 g) and water (1 mL) samples were digested with perchloric and nitric acids in a 200 °C heating block until 2.0–3.0 mL was left in the digestion tube. The samples were then placed in a 100 °C heating block for 2 h after which they were left to cool and then brought to volume. The samples then were shaken and left to settle for 12 h. A portion of the sample was poured off into smaller tubes after which they were ready for analysis (Table 1).

The dissolved inorganic P was determined by the molybdate reactive P methodology of Murphy and Riley (1962). Soil test P is also referred to as Olsen-P or sodium bicarbonate-P. This method is used in the western U.S. because it is the best method suited for calcareous soils. The soil samples were air-dried and the water samples were stored at 4 °C until ICP-AES or spectrophotometric analysis. The DRP samples were analyzed within 24 h of sampling due to potential P transformations, i.e. cellular turnover. The depth of soil sampling for this research was set at 15 cm because most soil P remains within this zone because of sorption or plant absorption occurring.

4.5. Sorption, experimental

Batch P isotherms were conducted for the unnamed Aridic Argiustoll and the WTR using 1.0 g (<2 mm fraction) of material, respectively, per 25 mL (Sims, 1997) of soluble P solution (10 and 20 mg L^{-1} for the soil; 250 and 500 mg P L^{-1} for the WTR). Five sets of material samples with each solution replicated in triplicate (totaling 60 samples), were shaken for 24 h in 50-mL polypropylene centrifuge tubes. The samples were centrifuged for 20 min at 10 000 rpm at 23 °C. Each subsequent day after centrifugation, 5.0 mL of the filtrate was withdrawn and was replaced by 5.0 mL of DI water. The samples were re shaken; the procedure continued until no P was detectable as determined by the Molybdate Blue method.

Sorption and desorption experiments were performed using a modified method of Sims (1997). Sorption isotherms helped determine the retention of P by the soil and the WTR. A KH_2PO_4 (in deionized (DI) water) solution was used as a P source to determine P sorption and desorption isotherms for the unnamed Aridic Argiustoll and the WTR to produce a soil or WTR:solution ratio of 1:25 in tubes with at approximately 50% head space. For the soil and WTR sorption isotherms (Figs. 3 and 4, respectively), six samples at five solution concentrations were selected. One gram of material was placed in 25 mL of the appropriate solution into a 50-mL polypropylene centrifuge tube and was shaken for 16 h. The samples were then centrifuged at 10,000 rpm for 20 min at room temperature. Five mL of the filtrate were withdrawn until the DRP was completed. Sorption and desorption isotherms were created by plotting the final P concentration (final P concentration − control soluble P concentration) in the liquid phase (C_L; mg L^{-1}) versus the concentration in the solid phase (C_S; mg kg^{-1}; determined from Eq. (1)),

$$C_S = \frac{V_a(C_a - C_L)}{M} \tag{1}$$

where V_a is the volume added (L), C_a is the concentration added (mg L^{-1}), and M is the mass of soil material (kg).

The desorption isotherms (Table 2) use an extension of Eq. (1) to account for the volume withdrawn to measure P in solution Eq. (2),

$$C_S = \frac{1}{M}\left[V_a(C_a - C_j) - \sum_{j=1}^{n} C_{j-1}{}^{*}V_j^w\right] \tag{2}$$

where C_j is the final liquid concentration (mg L^{-1}), j is the lower bound of summation, n is the upper bound of summation, C_{j-1} is the final liquid concentration from the previous sample (mg L^{-1}), and V_j^w is the volume withdrawn for the sample's liquid concentration (L).

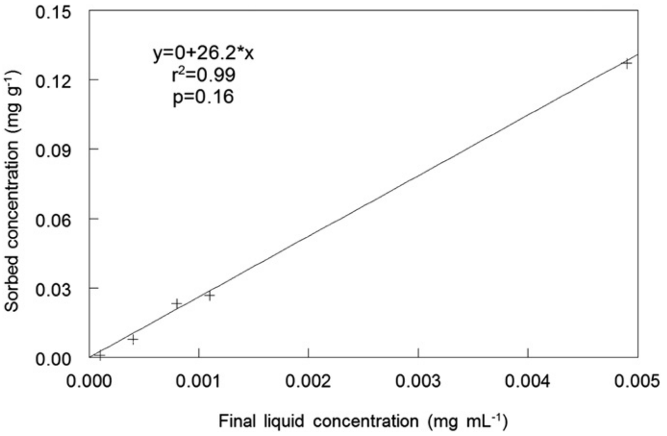

Fig. 3. Unnamed Aridic Argiustoll phosphorus sorption isotherm.

5. Model parameter estimation

5.1. Phosphorus sorption models

According to the Langmuir sorption model (Fig. 5; Eq. (3)), at equilibrium the total amount of P sorbed in the soil (C_S, mg kg^{-1}) for a uniform surface can be described as:

$$C_S = S_{\max} K_d C_I / (1 + K_d C_L) \tag{3}$$

where C_I (mg L^{-1}) is the initial equilibrium solution P concentration, ($S_{\max}$ (mg kg^{-1}) is the P sorption maxima, K_d (L kg^{-1}) is generally a constant related to the binding energy at equilibrium (adsorption constant) and in this study represents the soil phosphorus soil partitioning coefficient, and C_L (mg L^{-1}) is the final equilibrium concentration in the solution.

Table 2
Unnamed Aridic Argiustoll and water treatment residual phosphorus desorption isotherm correlation values.

Material	Solution	r^2	*p* value
Soil	10 mg P L^{-1}	0.95	<0.001
	20 mg P L^{-1}	0.57	<0.001
Water treatment residual	250 mg P L^{-1}	0.97	<0.001
	500 mg P L^{-1}	0.92	<0.001

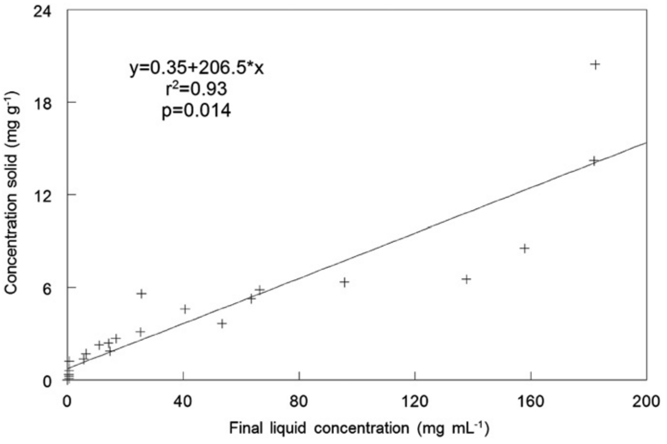

Fig. 4. Water treatment residual phosphorus sorption isotherm.

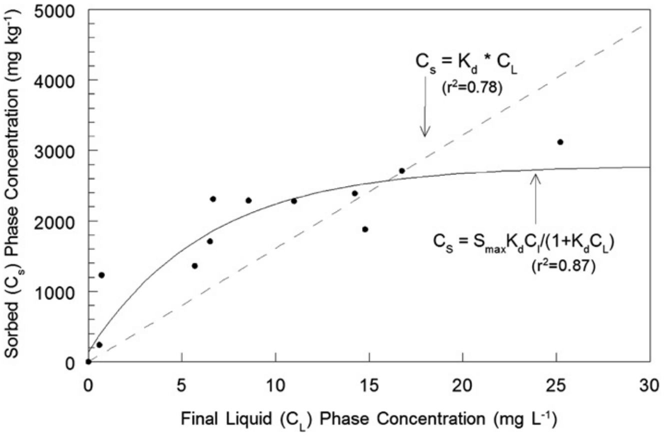

Fig. 5. Freundlich and Langmuir models based on phosphorus isotherm data.

The Freundlich model (Freundlich, 1926; Fig. 5; Eq. (4)) takes the form:

$$C_S = K_d C_L \tag{4}$$

Fourteen solutions ranging from zero to 110 mg P L^{-1} samples are presented in Fig. 5 and Table 3 to demonstrate the ionic affinity P has to remain sorbed to the soil containing WTR. A linear regression analysis was performed between C and C/S to derive the values for K_d and $S_{\max}$ as the slope and the intercept, respectively (Olsen and Watanabe, 1957; Atalay, 2001). Regression analysis was performed using PROC REG in SAS v. 8 to determine the $S_{\max}$ value. According to Harter (1984) a plot as shown in Fig. 5 will always provide a statistically significant correlation coefficient. The best fit test is the shape of the equation modeled for the adsorption isotherm. Fig. 5 shows that the Langmuir model addressed the data curvature and maxima more efficiently than the Freundlich model.

5.2. SWAT model parameters

The soil water content (θ) and hydraulic conductivity (K), which are needed for flow direction and rate prediction in unsaturated soil, were determined simultaneously by using a continuous flow method for rapid measurement of soil hydraulic properties (Butters and Duchateau, 2002) (Table 4). This method uses a combination of direct Darcian analysis and numerical inversion of Richards' equation in order to estimate hydraulic properties suggested by Ahuja

Table 3
Water treatment residual Langmuir model parameter values.

Solution P initial concentration[a] (C_I; mg L^{-1})	Sorbed phase concentration (C_S; mg g^{-1})	Final liquid phase concentration[b] (C_L; mg L^{-1})	$S_{\max}$ (mg kg^{-1})	K_d (L kg^{-1})
0.0	0.0	0.00	3150	200
0.5	0.0	0.00	3150	200
2.0	0.0	0.00	3150	200
5.0	0.0	0.0	3150	200
10	0.58	0.24	3150	200
15	0.70	1.23	3150	200
25	5.68	1.36	3150	200
50	6.49	1.71	3150	200
60	14.78	1.88	3150	200
75	10.98	2.28	3150	200
90	14.23	2.39	3150	200
100	16.75	2.71	3150	200
110	25.21	3.12	3150	200

[a] Based on soil phosphorus isotherm experiment methodology (Green, 2004).
[b] Final concentration corrects for initial P attached to soil.

Table 4
Determination of soil hydraulic parameters using the van Genuchten (vG) and Brooks–Corey (BC) models.

WTR rate (Mg ha^{-1})	Soil sampling depth (cm)	Model	θ_S	θ_r	α (cm^{-1})	m	l	K_S (cm min^{-1})
Rate 0; Rep 1	0–5	vG	0.48	0.21	0.37	2.17	0.37	0.04
		BC	0.48	0.21	0.12	0.41	0.23	0.04
	7–11	vG	0.49	0.20	0.032	2.62	5.1e-4	0.05
		BC	0.49	0.19	0.10	0.47	1.3e-3	0.05
Rate 0; Rep 2	0–5	vG	0.49	0.15	0.025	2.29	1.4	0.04
		BC	0.49	0.14	0.10	0.45	0.78	0.04
	7–11	vG	0.49	0.17	0.029	2.72	0.045	0.05
		BC	0.49	0.16	0.10	0.56	1.7e-3	0.05
Rate 64; Rep 1	0–5	vG	0.50	0.17	0.032	1.85	1.42	0.10
		BC	0.50	0.15	0.083	0.45	1.73	0.10
	7–11	vG	0.44	0.16	0.028	2.24	0.38	0.05
		BC	0.44	0.15	0.13	0.43	1.4e-4	0.05
Rate 64; Rep 2	0–5	vG	0.53	0.22	0.50	2.33	0.28	0.14
		BC	0.53	0.22	0.15	0.64	0.10	0.14
	7–11	vG	0.49	0.19	0.046	1.79	0.43	0.05
		BC	0.49	0.18	0.14	0.41	0.55	0.05

Note: In the Brooks–Corey form, $\alpha = |1/h_e|$ where h_e is the air-entry pressure.

and El-Swaify (1976). Richards' equation was assumed to govern water flow (Rassam and Cook, 2002). The K estimate using this analysis is sensitive to the soil sample length and the lower boundary rate of pressure change (Butters and Duchateau, 2002). The analysis allows for wetting and/or draining hydraulic conductivity ($K(h)$) and water conductivity $\theta(h)$ with their respective pressure (matric) potentials over the tensiometer range (0–1500 cm) while keeping the physical significance of the hydraulic parameter estimates. Flow cell measurements were required to obtain parameter estimates θ_S (saturated soil water content), θ_r (residual soil water content), K_s (saturated hydraulic conductivity), the soil water characteristic function (α; cm^{-1}); and the fitting parameters l and m (Eq. (5)),

$$m = 1 - l/n \tag{5}$$

where n is a fitting parameter related to the tortuosity and connectivity of the capillary tubes (Table 4). The WTR application rates (0 and 64 Mg ha^{-1}) that were the most informative regarding P reduction are discussed further. The van Genuchten (van Genuchten, 1980; vG) and Brooks-Corey (Brooks and Corey, 1966; BC) models were used to determine soil hydraulic properties for unsaturated steady flow in the soil with either 0 or 64 Mg WTR ha^{-1} (Table 4).

The default K_d value for SWAT is 175 L kg^{-1}, therefore whether the high or the low end of the SWAT model K_d range (100–200) is used provides minimal difference compared to when the Langmuir equation is used when considering P and WTR. This new addition still does not address the nonlinear desorption process nor the inherent variability of the different materials.

Using the Langmuir isotherm component, a K_d of 200 L mg^{-1} was determined with a S_{max} of 3120 mg kg^{-1} Heil and Barbarick (1989) found that WTR (pH 5.1 and $CaCO_3$ equivalent (CCE) of 170 g kg^{-1}) could sorb 740–3500 mg P kg^{-1} Ippolito et al. (1999) used a WTR (pH 6.9; CCE not reported) that could sorb 12 500 mg P kg^{-1} Castro and Torrent (1998) found that P retention increases with the ratio of clay to CCE. Since the WTR has more slightly more clay and silt (most likely increased by the presence of the alum polymer) and a little more CCE than the soil, the WTR probably would have a higher P retention capacity in addition to its high-Al content (23 000 mg kg^{-1} vs. 1100 mg kg^{-1} for the soil). Both the unnamed Aridic Argiustoll and the WTR had low initial total P contents (approximately 370 and 60 mg kg^{-1}, respectively), a soil clay content of 33% and WTR clay content of 34%, and CCE's of approximately 0.07%. A higher clay or CCE would have potentially increased the P sorption capacity of the soil.

The SWAT model used the soil and WTR physical and chemical properties determined from the laboratory and greenhouse experiments for parameter values. For this research, the Soil Conservation Service (SCS) approach (Smith and Williams, 1980) was used due to the high water draining capacity of the WTR and the sandy clay loam. The precipitation was set to reproduce a rainfall event that would create saturated soil conditions to induce runoff (51 mm per day per runoff event; equivalent to the rate used in the greenhouse VFS box to generate runoff). The amount of soluble P available as a fertilizer for the active mineral pool was increased to saturate the WTR to create desired high P conditions. A subwatershed was selected because of the previous success in SWAT with a subwatershed with a size of 0.07 km^2 (Green et al., 2007). Two simulations were conducted with the VFS plants already established in the month of June: with one surface applied WTR and one with soil only.

5.3. *Model evaluation procedure*

Bärlund et al. (2007) used the SWAT model in a Finnish catchment to assess its usefulness to evaluate management impacts, such as nutrient load reductions. While the model proved its worthiness, it also demonstrated the necessity to adequately parameterize, calibrate and validate the model. These authors identify the need to include a parameter sensitivity analysis to concentrate on the more influential parameters that impact calibration. Krysanova et al. (2007) and Rao et al. (2007) agreed with the previous authors that there is a demonstrated need for powerful calibration and validation techniques for hydrological models. In addition, there is a need to identify the criteria to achieve an adequate validation which is based on sensitivity and uncertainty analyses to determine the most influential parameters and evaluate the model's uncertainty in relation to input data. Miller et al. (2007) emphasizes the importance of the process used for parameter estimation; the higher the degree of spatial variability, the greater the complexity of correctly estimating parameter values.

A parameter sensitivity analysis allows the model to focus on the parameters that contribute the most to the output variance due to input variability (Holvoet et al., 2005). Whether the calibration is manual or automated, a complex hydrologic model contains several parameters of which, depending on the study, can have only a few or several sensitive parameters. A model parameter sensitivity analysis was performed to elucidate the model's sensitivity to selected parameters for runoff at the outlet of the subwatershed.

Table 5
Nonlinear exponential rise equation r^2 values of the dissolved molybdate reactive P ratio (DRP_{out}/DRP_{in}) versus time (min) from vegetative filter strip boxes with different water treatment residual application rates.

Runoff event	0 Mg ha^{-1}	16 Mg ha^{-1}	32 Mg ha^{-1}	64 Mg ha^{-1}	128 Mg ha^{-1}	256 Mg ha^{-1}
1	0.004	0.63	0.54	0.60	0.71	0.64
2	0.15	0.11	0.43	0.60	0.70	0.39
3	0.32	0.02	0.61	0.63	0.55	*no value
4	0.00	0.69	0.47	0.69	0.41	0.39

*No value due to a lack of convergence to a nonlinear exponential regression equation.

The Morris qualitative screening method (Morris, 1991) was used initially to determine model sensitivity to selected parameters among those suggested by the SWAT documentation (Neitsch et al., 2002) and previous analyses (van Griensven et al., 2006; Green and van Griensven, 2008). The K_d variable was added to the list of parameters in the sensitivity analysis, resulting in a total of 12 potentially relevant parameters screened by the Morris method. This method uses a random One-factor-At-a-Time (OAT) design in which only one input parameter (X_i) is modified between two successive runs of the model. The marginal change induced in the model outcome $Y = Y(X_1, X_2,\ldots, X_m)$ can be unambiguously attributed to such a modification by means of an elementary effect (e_i) defined by:

$$e_i = \frac{Y_{i+1} - Y_i}{\Delta X_i} \quad (6)$$

where Y_{i+1} is the new outcome, Y_i is the previous outcome, and ΔX_i is the variation in the parameter. Based on the sensitivity analysis results, a rank was assigned to order the parameters on the basis of model sensitivity from the highest to the lowest. The parameter with the highest rank was adjusted first, followed by the other relevant parameters.

The simulated surface flow was increased through calibrating the following parameters: runoff curve number for soil moisture condition II (CN2), soil evaporation compensation factor (ESCO), surface runoff lag coefficient (SURLAG), and available soil water capacity (SOL_AWC). The CN2 parameter was set to a value recommended by the USDA-SCS National Engineering Handbook (USDA, 1972). The P-related calibrated parameters adjusted were the P percolation coefficient (PPERCO) and K_d. All other parameters were kept at the SWAT default values.

6. Results and discussion

6.1. Vegetative filter strip greenhouse study

The dissolved molybdate reactive P (DRP) concentrations observed in runoff (DRP_{out}) were used in a ratio with the DRP concentration that was measured from the manifold (DRP_{in}) during its related runoff event (Tables 5 and 6). The 64 Mg WTR ha^{-1} rate consistently had r^2 values that generally increased with consecutive runoff events; however, this finding did not identify what WTR rate was optimal for P retention since it is only a measure of goodness of fit to an equation. Since no statistically significant ($p < 0.10$) difference occurred above 64 Mg WTR ha^{-1} DRP_{out}/DRP_{in} average concentration for the average of the four runoff events, this rate was used in SWAT model simulations. Using regression analysis, the control was significantly different ($p < 0.10$) from the plots that contained WTR with regards to DRP runoff concentrations.

Fig. 6 illustrates the extent of variability between runoff events for a given WTR rate. The period less than 10 min demonstrates that less runoff occurred due to the soil and/or WTR properties. An expanded exponential rise equation fit the data best (Eq. (7)):

$$y = (a + b) - b^{-ct} \quad (7)$$

where y is the normalized (DRP_{out}/DRP_{in}) P concentration, where DRP_{out} is the runoff DRP concentration (mg L^{-1}) and DRP_{in} is the concentration (mg L^{-1}) of the water added to the VFS box, a is the normalized initial P concentration, b is the normalized plateau increment above the initial P concentration, c is a rate constant, and t is time.

Soil test P concentrations were analyzed to elucidate if an optimal WTR rate for P retention could be identified. The 0–5 cm depth had significantly ($p < 0.05$) more STP than the 5–10 and 10–15 cm increments. It was expected that the WTR rate with the lowest runoff P concentrations would have the highest STP concentrations. Sediment P was not measured because little or no particulate matter greater than 2 μm was in the collected runoff.

6.2. SWAT model results

The sensitivity analysis results obtained from this study are very similar to others (Lenhart et al., 2002; Wang et al., 2006; Green and van Griensven, 2008; Licciardello et al., 2011). Each of these studies found CN2, Sol_AWC, and/or ESCO to rank as one of the most sensitive parameters. Precipitation-related parameters should be more sensitive than water quality parameters since precipitation is the most variable of all the constituents. Using SWAT's parameter sensitivity analysis procedure resulted in CN2 being the most responsive parameter. Increased values of CN2 imply an increase in the surface runoff. van Griensven et al. (2006) determined that the CN2 value has great importance in water quality simulation. The CN2 and ESCO parameters were found to be more sensitive to input variability than the SURLAG and P-related calibration parameters PPERCO and K_d. Table 7 lists the sensitivity analysis procedure ranking results.

Table 6
Vegetative filter strip molybdate reactive P ratio (MRP_{out}/MRP_{in}) runoff concentrations with replicate average value for the entire duration of a runoff event per runoff event at different water treatment residual application rates.

Runoff event	0 Mg ha^{-1}	16 Mg ha^{-1}	32 Mg ha^{-1}	64 Mg ha^{-1}	128 Mg ha^{-1}	256 Mg ha^{-1}
1	0.96	0.94	0.84	0.80	0.80	0.78
2	0.94	0.92	0.85	0.78	0.77	0.78
3	0.93	0.95	0.88	0.78	0.76	0.76
4	0.96	0.95	0.86	0.78	0.77	0.77
Average	0.948	0.940	0.858	0.785	0.775	0.773

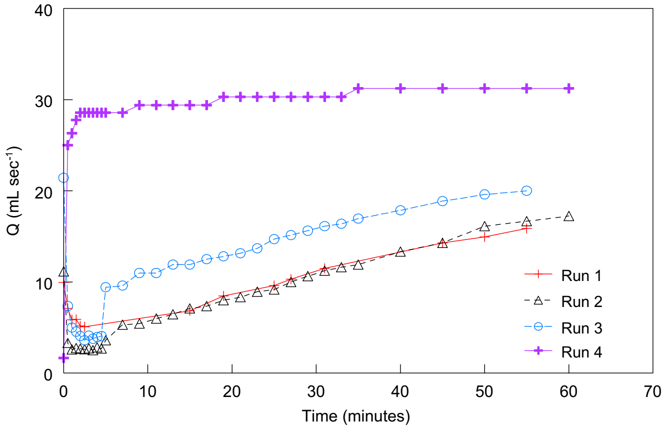

Fig. 6. Hydrograph of the water treatment residual rate 64 Mg ha^{-1} event for four runoff events in the vegetative filter strip plot.

The aging of the VFS and the saturation of sorptive sites on the WTR particles was indirectly addressed in SWAT. These components would greatly impact the accuracy of the simulation. Even though a runoff event should ideally be a good test of the model, the model is only as good as the data provided to the model. By no means will the results from a 1 m × 0.5 m × 15 cm plot be able to identically simulate the processes at a field or watershed scale; however, they may provide an indication as to the P pollution potential within an area.

In addition to the control plots, the highest rate of WTR applied that makes a statistically significant impact on P sorption is simulated by SWAT. Broadcast application of 0 and 64 Mg ha^{-1} rates of WTR were applied in duplicate in manufactured greenhouse boxes (Green, 2004). The effective depth of soil:water interaction (the depth that the surface soil (and/or WTR) interacts with runoff) over a small subwatershed (0.07 km^2) was based on an experimentally determined WTR rate of 64 Mg ha^{-1}. The thickness of the WTR was set to 10 mm, representing the 64 Mg WTR ha^{-1} rate. Modeling simulations identified that a continuous WTR was necessary in order to have meaningful results otherwise P reduction was insignificant.

The precipitation was set to reproduce a rainfall event that would create saturated soil conditions to induce runoff. The Langmuir model parameter associated with Eq. (3) was embedded into SWAT (Table 8) in order to simulate soluble P runoff concentration measured experimentally from a greenhouse experiment containing WTR (Table 9). Using laboratory isotherm data as well as additional soil and WTR physical and chemical properties from additional experiments stated above, a Langmuir coefficient of 0.63 L kg^{-1} was determined for the Langmuir model explained in Eq. (3). Implementing the Langmuir model into the SWAT code with a new parameter, aptly named the Langmuir coefficient (L kg^{-1}), resulted in significantly different soluble P in runoff at the measured outlet and P leached through the soil profile values (5.7 and 0.6 kg P ha^{-1}, respectively) from the values predicted by the traditional linear P method (0.5–0.9 and 1.3 kg P ha^{-1}, respectively) as presented in Table 8.

Table 7
Model results of sensitivity analysis procedure.

Name	Min.	Max.	Definition	Process[b]	Rank
CN2	35	98	SCS runoff curve number for soil moisture condition II	SR	1
ESCO	0	1	Soil evaporation compensation factor	E	2
Sol_AWC	0	1	Available water capacity of the soil layer (mm mm^{-1})	S	2
Surlag	0	10	Surface runoff lag coefficient	SR	4
PPERCO	10	17.5	Phosphorus percolation coefficient	N	6
K_d[a]	100	200	Phosphorus soil partitioning coefficient	N	6

[a] K_d = represents the P sorption constant for the Freundlich and Langmuir methods (K_d = SWAT parameter Phoskd).
[b] SR = surface runoff; E = erosion; S = soil; N = nutrient cycling.

Table 8
SWAT model P output values with and without Langmuir equation addition.

Physical matrix	Soil	WTR	WTR	WTR
Equation	Freundlich	Freundlich	Freundlich	Langmuir
K_d (L kg^{-1})	175	100	200	na
Langmuir coefficient (L kg^{-1})	na	na	na	0.63
Soluble P loss via surface runoff at simulated outlet (kg ha^{-1})	0.5	0.9	0.5	5.7
P leached through top soil layer (kg ha^{-1})	1.3	1.3	1.3	0.6

Accounting for the runoff generated in the greenhouse and the subwatershed (approximately 51 mm), SWAT predicted 11.1 mg L^{-1} of soluble P loss via surface runoff at the simulated outlet while a mean of 10.6 mg L^{-1} of soluble P was measured in the surface runoff at the designated outlet from the greenhouse experiment.

The soil and WTR sorption isotherms provided the P partitioning coefficients required by the SWAT model to more adequately simulate P processes. Desorption isotherms demonstrated that the sorption process is not readily reversible under the conditions of experiments conducted for this study.

Water treatment residual additions can decrease P runoff concentration compared to soil as evidenced by DRP experimental data. Greenhouse VFS runoff DRP concentration data indicated that WTR depth is more important than WTR rate to significantly reduce runoff P (considering that there is continuous soil coverage). A likely explanation for this result is the depth of mixing for surface water and soil water interaction. The effectiveness of WTR is only as pervasive as the depth at which the surface water and soil water can interact, therefore, allowing P sorption to occur.

SWAT may not have been able to previously model high P concentrations because it only had the option of a linear adsorption isotherm. The Langmuir model adaptation made to SWAT may assist P concentration simulations for soils/amendments that are at or near P saturation capacity such as those that are inundated with manure/fertilizer treatments; tropical soils with lower P sorption capacities (1:1 soil mineralogy dominant); reduced conditions, then the procedure adopted by SWAT is preferred because it is not assumed that the isotherm is linear at a low concentration range. If only $S_{\max}$ is needed because of the user's objective and the range of the P data then both the Freundlich and the Langmuir model approaches are acceptable, however if the lower or upper isotherm range is needed then the Langmuir model may be the better approach.

SWAT currently assumes that the P in manure is added directly to the P pools in the upper soil layer (1 cm). Phosphorus may remain soluble in a “manure layer” longer than a soil layer and thus

Table 9
Mean dissolved molybdate reactive P (mg L^{-1}) concentrations in runoff from vegetative filter strip boxes for two water treatment residual rates.

Runoff event	Water treatment residual rate	
	0 Mg ha^{-1}	64 Mg ha^{-1}
1	0.004	10.60
2	0.15	10.60
3	0.32	10.63
4	0.00	10.69

SWAT may underestimate P movement shortly after a manure application. The improvement to the SWAT P routine can potentially address reduced tropical soils that can release bound P, soils that received successive amendment (manure) loadings that are near P saturation capacity as sources of P, and when a linear isotherm cannot be assumed at a low concentration range.

7. Conclusion

Phosphorus transport knowledge continues to play an important role in contaminant modeling. Phosphate will mostly be retained by soils as long as there is sufficient contact with the soil/amendment particle. Each soil and/or amendment has to be adequately parameterized to be accurately simulated in environmental models especially regarding pollutant transport. As policy questions increase in complexity, scientists have to anticipate the problems and the solutions. Establishing databases for model simulations to be able to answer policy questions more rapidly would be a great benefit. This study is one step closer to addressing P model development by modifying SWAT with the Langmuir model to account for high soluble P concentrations. This study's results demonstrate how experimental data can impact environmental model development. The greenhouse and lab experimental data can be extended to other semi-arid soils with similar texture. Based on how well the model performed at small scales, with additional testing at a range of spatial scales, it should be able to address other high P conditions (i.e. high rates of manure).

GOVT EEO statement

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