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Phosphorus Sorption Capacity of Six Iowa Soils before and after Five Years of Use as Vegetative Treatment Areas

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Abstract

Accumulation of phosphorus in soil is a major factor limiting the operational life (period of time where the soil can serve as an effective phosphorus sink) of land application waste disposal systems. Better evaluation of phosphorus operational life requires improved understanding of how manure application to soil can affect its phosphorus sorption characteristics. In this study, laboratory experiments were conducted to investigate the impact of feedlot runoff effluent application on phosphorus sorption capacities, equilibrium phosphorus concentrations, and phosphorus buffering capacities of six Iowa soils. Soil samples were collected from vegetative treatment areas that had received feedlot runoff application for the previous five years and from a paired grassed area that did not. Subsamples of each soil were incubated with a series of 12 phosphorus solutions ranging in concentration from 0 to 200 mg P/L to determine the sorption characteristics and results fitted to the Langmuir model to determine the phosphorus equilibrium concentration, phosphorus buffering capacity, and maximum phosphorus sorption capacity. Results indicated that vegetative treatment areas generally had elevated phosphorus equilibrium concentrations, indicating an elevated risk of loss of dissolved phosphorus. In most cases, the ability of the soil to sorb phosphorus was significantly increased, as was the remaining phosphorus sorption capacity of the soil. These results indicate that vegetative treatment area life could be greatly extended due to soil property modifications that occur as a result of system operation.

Keywords

Equilibrium phosphorus concentration, Feedlot runoff, Langmuir sorption model, Phosphorus, Phosphorus sorption, Vegetative treatment system

Disciplines

Agriculture | Bioresource and Agricultural Engineering | Environmental Indicators and Impact Assessment

Comments

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PHOSPHORUS SORPTION CAPACITY OF SIX IOWA SOILS BEFORE AND AFTER FIVE YEARS OF USE AS VEGETATIVE TREATMENT AREAS

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ABSTRACT. *Accumulation of phosphorus in soil is a major factor limiting the operational life (period of time where the soil can serve as an effective phosphorus sink) of land application waste disposal systems. Better evaluation of phosphorus operational life requires improved understanding of how manure application to soil can affect its phosphorus sorption characteristics. In this study, laboratory experiments were conducted to investigate the impact of feedlot runoff effluent application on phosphorus sorption capacities, equilibrium phosphorus concentrations, and phosphorus buffering capacities of six Iowa soils. Soil samples were collected from vegetative treatment areas that had received feedlot runoff application for the previous five years and from a paired grassed area that did not. Subsamples of each soil were incubated with a series of 12 phosphorus solutions ranging in concentration from 0 to 200 mg P/L to determine the sorption characteristics and results fitted to the Langmuir model to determine the phosphorus equilibrium concentration, phosphorus buffering capacity, and maximum phosphorus sorption capacity. Results indicated that vegetative treatment areas generally had elevated phosphorus equilibrium concentrations, indicating an elevated risk of loss of dissolved phosphorus. In most cases, the ability of the soil to sorb phosphorus was significantly increased, as was the remaining phosphorus sorption capacity of the soil. These results indicate that vegetative treatment area life could be greatly extended due to soil property modifications that occur as a result of system operation.*

Keywords. *Equilibrium phosphorus concentration, Feedlot runoff, Langmuir sorption model, Phosphorus, Phosphorus sorption, Vegetative treatment system.*

The fate of phosphorus is one of the most critical factors for determining the sustainability, life expectancy, and effectiveness of land application waste treatment systems (Shober and Sims, 2003). In most land application systems the amount of waste applied is constrained by either hydraulic or nitrogen loading considerations; this typically results in phosphorus application in excess of agronomic demand and can cause accumulation of phosphorus in the soil profile (Sui et al., 1999). This is potentially of environmental concern if the increased phosphorus levels result in greater mobility and transport to surface waters (Tunney et al., 1997; Sharpley, 2000). In crop production systems, this concern is typically related to the possibility of erosion and transport of phosphorus enriched soil particles (Sharpley et al., 2003). As a result, many states have proposed application limits based on phosphorus indexes, which switch application constraints to phosphorus loading when soil phosphorus levels build to a critical threshold set by site-specific erosion conditions and distances to surface waters (Mallarino et al., 2005). Similar issues exist on municipal wastewater treatment system land application areas; however, since these systems typically utilize perennial vegetation, concern over erosion and transport of particulate-bound phosphorus is minimized. In this case, phosphorus application typically isn't limited by soil P test levels, but is instead limited by the ability of the soil to react with the phosphorus and prevent its transport. Since most soils have high phosphorus fixing capacities, the amount of phosphorus that can be applied is quite substantial. However, research has indicated that continual application of excess phosphorus, i.e., above the agronomic requirement, can change soil phosphorus chemistry and increase solubility, potentially leading to leaching or enhanced transport of dissolved phosphorus in surface runoff (Sharpley et al., 2004), and failure of the waste treatment system.

Although this disposal approach to waste treatment has generally been limited to municipalities, the increasing concentration of the animal feeding industry and the decoupling of grain and animal production systems have prompted renewed interest in advanced treatment techniques for disposal of byproducts associated with animal production, specifically manures and process wastewaters. Although many treatment options have been

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suggested, most still rely on land application for final disposal due to the difficulty in meeting the stringent water quality limitations required for discharge. This has created a demand for agricultural waste management systems where the main goal is no longer to utilize nutrients for agronomic production, but instead is to minimize the costs of treating and handling the production byproducts while minimizing any pollution associated with their management and disposal. One example of this type of system is the use of vegetative treatment systems (VTSs) for feedlot runoff control. These systems provide a lower cost alternative to the traditional storage-land application system for managing feedlot runoff (Bond et al., 2011), but are designed based on a waste disposal paradigm.

A VTS is a combination of treatment components, at least one of which utilizes vegetation, to manage runoff from open lots (Koelsch et al., 2006). A VTS typically consists of a solid settling basin followed by either a vegetative treatment area (VTA) or a VTA in combination with a vegetative infiltration basin (VIB), although other configurations are possible. Briefly, a sloped VTA is an area level in one dimension with a slight slope along the other, to facilitate sheet flow, planted and managed to maintain a dense stand of vegetation (Moody et al., 2006). Operation of a sloped VTA consists of applying solid settling basin effluent uniformly across the top of the vegetated treatment area and allowing the effluent to sheet-flow down the slope. Ikenberry and Mankin (2000) identified several possible methods in which effluent was treated by VTAs, including settling solids, infiltration, and filtering of the effluent as it flowed through the vegetated area. A VIB is a flat area, surrounded by berms, planted to perennial vegetation. A VIB uses a flood effect to distribute effluent over the surface. These areas have drainage tiles located 1 to 1.2 m (3.4 to 4 ft) below the soil surface to encourage infiltration. The tile lines collect effluent that percolates through the soil profile and transport it to a sump, where it receives additional treatment, often through use of a VTA. Nutrient and pathogen removal in the VIB relies on effluent filtration as it percolates through the soil, plant uptake and harvest, degradation of the nutrients and pathogens by soil fauna, and sorption of contaminants to soil particles and organic matter.

Vegetative treatment systems are capable of converting applied carbon and nitrogen to gaseous forms (either aerobic or anaerobic decomposition for carbon and ammonia volatilization or denitrification for nitrogen), and thus remove them from the internal nutrient cycling of the treatment system; this doesn't occur for phosphorus. Thus the only environmentally acceptable method for removing phosphorus from the treatment area is via vegetative uptake and harvest; this implies that vegetative treatment systems rely heavily on the soil system to filter and retain phosphorus applications, especially when nutrients are supplied in excess of crop need. In practice, phosphorus transport is controlled in large part by the sorption behavior of the soil, which can be investigated by equilibrating soil with solutions of differing phosphorus concentrations and then evaluating how the applied phosphorus partitions between the soil and liquid phase. This approach is based on observations that when material containing phosphorus is applied to soil, the soluble forms of phosphorus decrease with time (Holford et al., 1997), preventing losses of soluble phosphorus in runoff and leaching to groundwater but also reducing plant availability (Sui and Thompson, 2000).

Although phosphorus sorption experiments have been widely employed for estimating phosphorus mobility in soils, relatively little work evaluating how a soil's phosphorus sorption capacity and sorption strength are modified by previous phosphorus application is available. Work that has been done has been inconclusive, indicating that in some cases (soil × manure application combinations) the ability of soil to sorb new additions of phosphorus has been significantly decreased, while in other cases the soil's ability to retain new phosphorus is increased (Singh and Jones, 1976; Field et al., 1985; Sharpley et al., 1993). The issue of repeated application is discussed only briefly in the review of Barrow (2008), but in it he suggests that when a nutrient, such as phosphorus, is added to a previously fertilized soil; the sorption curve followed will not be the same as it would have been if all the nutrient addition had occurred at once. Further, he (Barrow, 2008) suggests understanding how the pathways of sorption are altered and the overall impact on sorption parameters are in need of greater evaluation.

The issue of phosphorus retention in soils is especially relevant to waste management systems where repeated application of phosphorus containing products is common. Thus, the objective of this work was to evaluate and compare phosphorus sorption patterns from paired soils that either received or didn't receive continuous application of feedlot runoff over the previous five years. The analysis was performed for six sites, at each site soil from the vegetative treatment area and from a paired grass area, was collected and the phosphorus sorption experiment performed. Comparing the patterns from the two soils allows an evaluation of the impact use of the vegetative treatment system had on soil phosphorus sorption properties and provides insight into how the life expectancy and performance of these waste management systems had changed.

METHODS AND MATERIALS

SITE DESCRIPTIONS

Six vegetative treatment systems were located on concentrated animal feeding operation (CAFO) sized open lot beef feeding operations throughout the state of Iowa and intensively monitored over a four-year period by Iowa State University. The sites were described in detail in Andersen et al. (2013) and are only briefly discussed here. Data summarizing the characteristics of the Iowa State University (ISU) monitored portions of the feedlots and VTSs are provided in table 1. Information shown includes the maximum cattle capacity of the feedlot, the VTS configuration, the size of the drainage area (feedlot and additional contributing area), the volume of the settling basin, the area of the VIB (where applicable), and the area of the VTA. Conditions at each site are summarized in the following section.

Central Iowa 1 (CN IA 1) was a 3.09 ha feedlot permitted for 1,000 head of cattle. Runoff effluent drained into a solid settling basin (SSB) designed to hold 4,290 m^3 of effluent. The VTA consisted of two channels operated in parallel; each channel was 24 m wide and averaged 311 m long, had an average slope of 2%, and was surrounded by 0.4 m high berms to keep outside runoff out. Central IA 1 VTA soil consisted of Clarion loam, Cylinder loam, and Wadena loam (Soil Survey Staff, 2010). The VTS at Central Iowa 2 consisted of a SSB, VIB, and VTA. Runoff from the 1.07 ha feedlot drained into a concrete SSB which released effluent into a 0.32 ha VIB. Effluent captured in VIB tiles was pumped onto a VTA with a slope of 0.5%. Soils in the VIB consisted of Nicollet loam and Webster clay loam and the VTA was Harps loam (Soil Survey Staff, 2010). Northwest Iowa 1 (NW IA 1) consisted of a 2.91 ha feedlot permitted to hold 1,400 head of cattle. Feedlot runoff was collected in a SSB with a volume of 3,700 m^3. The SSB outlet pipe discharged onto VTA (0.3% slope) consisting of Galva silty clay and Radford silt loam soils (Soil Survey Staff, 2010). Northwest Iowa 2 (NW IA 2) had an SSB-VIB-VTA system designed to control runoff from a 2.96 ha concrete feedlot. A settling basin collected the feedlot runoff and released it to a 1.01 ha VIB drained by 15 cm diameter perforated tiles installed 1.2 m deep and spaced 4.6 m apart. Flow from the tile lines was collected in a sump and pumped onto the VTA divided into two 27 m wide channels. Each channel had a slope of 3% and was surrounded by 0.2 m high berms to keep outside runoff from entering the treatment channel. The channel receiving effluent was switched manually by the producer. Northwest Iowa 2 soils consisted of Moody silty clay loam (Soil Survey Staff, 2010). Southwest Iowa 1 (SW IA 1) was a 7.49 ha feedlot with an 11,550 m^3 solid settling basin that released effluent to a 4.05 ha VTA was divided into ten channels. Tile lines, installed to control water table depth below the system and enhance infiltration of effluent into the soil, surrounded each of the VTA channels (3% slope). Soils in the VTA consisted of mostly Judson silty clay loam and smaller areas of Colo-Ely complex (Soil Survey Staff, 2010). Southwest Iowa 2 (SW IA 2) was a 3.72 ha feedlot. Runoff drained into a solid settling basin and was released to a 3.44 ha VTA (1% slope) constructed with earthen berm level spreaders along the length. The spreaders slowed the flow of effluent through the system, increasing the time for infiltration and promoting sedimentation of particulates suspended in the flow. Southwest Iowa 2 VTA soil consisted of Kennebec silt loam (Soil Survey Staff, 2010). At each site grass areas of the same soil series were found and sampled to evaluate soil phosphorus sorption properties of soil not receiving the effluent application; these properties are thought to represent the original site conditions prior to use of the vegetative treatment system, and thus provide an opportunity to evaluate the impact of five years of runoff effluent application. At SW IA 2 this soil was collected from a pasture facility located near the VTA. At the other sites the paired grass area was located between the feedlot site and nearby streams or road (shoulder of the ditch). These sites were mostly unmanaged grass areas of buffer strips. They were not fertilized or harvested for forage, though the grass was typically cut once or twice per year.

SOIL SAMPLING AND ANALYSIS

At each of the six sites, five soil samples were collected from the vegetative treatment area and five more from the paired grass area that did not receive the feedlot runoff effluent application. These samples were collected in July of the fifth year of system operation. Each soil sample was collected by compositing soil from five randomly selected locations within the vegetative treatment area or paired grass area; at each sampling location, a push-probe was used to collect soil to a depth of 15.2 cm (6 in.) from 20 spots within a 1.5 m radius of the selected location. This sampling methodology was used to minimize the within treatment component variability due to differences in greater phosphorus loading near settling basin inlets, possible flow channelization altering nutrient distribution within treatment area, and to minimize the impact of variability in soil properties over the relatively large sampling areas. Collected soil was placed in a plastic bag, placed on ice, and brought back to the Agricultural Waste Management Lab at Iowa State University. Once back the soil samples mass was determined and they were spread out on trays to air dry. Aggregates were crushed and sieved to pass a screen with 2 mm openings. Rocks and visible vegetation were removed during the sieving process. The mass of soil passing and retained on the 2 mm screen was determined to estimate the amount of course fraction present in each soil. A subsample of the soil passing the 2 mm screen was dried in an oven at 105°C for 24 h to determine the air-dried moisture content of the soil. The remaining soil was placed in screw-cap plastic bottles and stored until use in the phosphorus sorption curve incubations.

In addition to these properties, the soil texture, organic matter content, particle density, and pH were also measured. Soil texture was measured on soil that received

Table 1. Summary of the system configuration and vegetative treatment system components at each site.

Site	No. of Cattle	VTS Components[a]	Drainage Area (ha)	SSB (m^3)	VIB (ha)	VTA (ha)
Central Iowa 1	1,000	1 SSB - 2 VTA	3.09	4,290	--	1.49
Central Iowa 2	650	1 SSB - 1 VIB - 1 VTA	1.07	560	0.32	0.22
Northwest Iowa 1	1,400	1 SSB - 1 VTA	2.91	3,710	--	1.68
Northwest Iowa 2	4,000	1 SSB - 1 VIB - 1 VTA	2.96	1,120	1.01	0.60
Southwest Iowa 1	2,300	1 SSB - 10 VTA	7.49	11,550	--	4.05
Southwest Iowa 2	1,200	1 SSB - 1 VTA	3.72	6,275	--	3.44

[a] SSB – Solid Settling Basin; VIB – Vegetative Infiltration Basin; VTA – Vegetative treatment area.

no pretreatment to remove organic matter. The sand fraction was measured by placing a 10 g sample in a sieve with mesh openings of 53 μm and then washing the particles until no more passed the sieve. The sand fraction was washed into a pre-weighted tin, dried in an oven at 105°C for 24 h and the mass of sand determined. The mass of clay was determined by diluting the volume of silt/clay solution to 1 L, vigorously agitating the sample for 5 min to homogenize the solution and then allowing it to settle. After 3 h and 54 min a 10 mL sample was pipetted from 5 cm below the water surface. This sample was placed in a pre-weighed tin, the mass of solution determined, and then placed in the 105°C oven, dried, and the mass determined again, allowing calculation of the solids content of the sample. This sample was assumed to represent the clay particle fraction. The total mass of clay particles was calculated by multiplying the determined solids concentration in this sample times the 1 L volume of solution. The percent of sand and clay was determined by dividing the mass of each by the total mass of soil used. The percent silt was calculated based on the difference. The soils organic matter content was determined by first drying a 10 g soil sample at 105°C for 24 h in a pre-weighed crucible. After oven drying, the sample was cooled in a desiccator and weighed again. The sample was then placed in a muffle furnace and heated to 450°C for 4 h; then again allowed to cool in a desiccator and weighed. The organic matter content was considered to be the loss of mass upon ignition. Particle density was determined by placing approximately 10 g of soil in a 100 mL flask with a capillary stopper to ensure filling to a consistent volume. The mass of the flask was determined empty, filled with just water, filled with just the 10 g soil sample, and filled with a soil sample and water solution. This allowed calculation of the mass of water displaced to determine the volume the soil particles occupied. Particle density was determined based on the mass of soil used and the volume of water displaced. Finally, the pH of the soil was determined using both a 1:1 dilution in deionized water and a 1:2 soil:solution ration in 0.01 M CaCl2 solution. In brief, 10 g of air-dried soil was diluted in the specified amount of solution (10 mL distilled water for the 1:1 solution and 20 mL of 0.01 M $CaCl_2$ solution for the 2:1 dilution), the solution was then stirred vigorously and allowed to settle for 10 minutes, then vigorously stirred again and allowed to settle for 20 min. The pH of the supernatant was then read from a glass pH electrode with digital readout that had been calibrated using a 3-point calibration (pH standard solutions of 4.00, 7.00, and 10.00). These soil properties are summarized in table 2. In all cases the soil textures determined in the VTA and the paired grassland soil sample were similar as was the determined particle density. At some locations we did find increased organic matter in the paired grassland soil. Typically, most sites did have significant differences between the pH of the VTA soil and the soil from the paired grass area, with VTA soil typically having a more basic reaction; however, this wasn't universally true as SW IA 2 had no difference while the VTA soil was more acidic reaction at SW IA 1.

PHOSPHORUS SORPTION EXPERIMENT

Phosphorus sorption curves were developed using the method of Graetz and Nair (2009). One gram of air-dried soil was placed into each of ten, 50 mL centrifuge tubes with screw-on caps and mixed with 25 mL of 0.01 M calcium chloride ($CaCl_2$) solution containing phosphorus concentrations of 0, 1, 2, 5, 10, 25, 50, 100, 150, and 200 mg KH_2PO_4-P/L. Two additional centrifuge tubes received 0.25 and 0.50 g of soil, respectively, which were mixed with 25 mL of 0.01 M calcium chloride solution with 0 mg KH_2PO_4-P/L. These higher dilution ratio samples were added to better evaluate the response of the soil at the low phosphorus concentration range. This was done as we were particularly interested in if the soil's equilibrium phosphorus concentration had been altered. Samples were placed horizontally on an orbital shaker and shaken end-to-end for 24 h at 22±2°C. Samples were then placed upright and allowed to settle for 1 h. The supernatant was filtered through a 0.45 μm filter. Dissolved reactive phosphorus (DRP) concentrations were analyzed

Table 2. Soil characteristics for Central Iowa 1 (CN IA 1), Central Iowa 2 (CN IA 2), Northwest Iowa 1 (NW IA 1), Northwest Iowa 2 (NW IA 2), Southwest Iowa 1 (SW IA 1), and Southwest Iowa 2 (SW IA 2).[a]

Site	TRT	Sand (%)	Silt (%)	Clay (%)	Soil Texture	Particle Density (g/cm^3)	Organic Matter (mg/kg)	pH in Water (1:1)	pH in $CaCl_2$ (1:2)
	VTA	54 (5)	31 (5)	15 (4)	Sandy Loam	2.32 (0.11)	37,262 (3,706)	**7.60 (0.11)**	**7.12 (0.14)**
CN IA 1	Paired	54 (2)	34 (2)	11 (2)	Sandy Loam	2.30 (0.12)	37,317 (5,979)	**7.40 (0.09)**	**6.92 (0.10)**
	p-value					0.68	0.99	**0.01**	**0.04**
	VTA	46 (2)	33 (6)	21 (6)	Loam	2.37 (0.08)	**24,748 (3,345)**	**8.08 (0.11)**	**7.73 (0.12)**
CN IA 2	Paired	42 (6)	40 (3)	18 (7)	Loam	2.27 (0.12)	**43,193 (2,284)**	**7.48 (0.04)**	**7.16 (0.05)**
	p-value					0.14	**0.00**	**0.00**	**0.00**
	VTA	22 (7)	69 (6)	9 (4)	Silty Loam	2.28 (0.10)	**42,277 (3,516)**	7.16 (0.07)	**6.83 (0.04)**
NW IA 1	Paired	18 (3)	70 (2)	12 (5)	Silty Loam	2.25 (0.10)	**35,988 (926)**	7.12 (0.15)	**6.63 (0.09)**
	p-value					0.69	**0.00**	0.44	**0.00**
	VTA	20 (2)	69 (4)	11 (2)	Silty Loam	2.30 (0.11)	35,525 (4,443)	**7.32 (0.26)**	**6.97 (0.23)**
NW IA 2	Paired	17 (3)	69 (2)	14 (5)	Silty Loam	2.17 (0.07)	40,614 (4,033)	**7.01 (0.15)**	**6.62 (0.11)**
	p-value					0.07	0.09	**0.05**	**0.02**
	VTA	15 (4)	75 (5)	10 (3)	Silty Loam	2.31 (0.11)	30,344 (2,830)	**7.39 (0.06)**	**6.93 (0.10)**
SW IA 1	Paired	12 (2)	76 (5)	12 (5)	Silty Loam	2.34 (0.11)	26,923 (2,211)	**7.91 (0.03)**	**7.41 (0.06)**
	p-value					0.72	0.07	**0.00**	**0.00**
	VTA	21 (10)	66 (13)	13 (7)	Silty Loam	2.24 (0.08)	**30,400 (4,639)**	7.61 (0.05)	7.17 (0.05)
SW IA 2	Paired	16 (4)	74 (3)	10 (2)	Silty Loam	2.32 (0.10)	**38,543 (5,354)**	7.62 (0.10)	7.26 (0.11)
	p-value					0.19	**0.03**	0.76	0.14

[a] Items bolded were significantly different at $\alpha < 0.05$. Values in parenthesis represent the standard deviation of the replicate soil samples.

spectrophotometrically at a wavelength of 880 nm using a Genesys 6 (Thermo Electron Corporation, Madison, Wis.) photospectrometer following the ascorbic acid method procedure (AWWA, 1998). The amount of phosphorus sorbed by the soil was calculated as the difference between the amount of phosphorus added in the equilibrating solution and the amount remaining in the equilibrated solution after 24 h of contact with the soil.

PHOSPHORUS SORPTION CURVE FITTING

Sorption data were fitted with a modified Langmuir sorption curve (eq. 1) as presented by Zhou et al. (2005). In this equation S' represents the amount of phosphorus sorbed by the soil from the applied solution (mg P/kg soil), S_{max} represents the maximum amount of phosphorus the soil can sorb (mg P/kg soil), k is a constant related to the binding energy of phosphorus to the soil (L/kg), C is the concentration of phosphorus remaining in solution after equilibration with the soil (mg P/L), C_0 is the concentration of phosphorus in solution after equilibration when the initial solution contained no phosphorus (mg P/L), V is the volume of solution used in the equilibration (mL), and M is the mass of soil used in the incubation (g). As used here, there were three fitting parameters in this equation: k, S_{max}, and C_0. In this case, C_0 was used as a fitting parameter since three, rather than just one, soil samples were equilibrated with the 0 mg P/L solution. This equation was compared against the data generated using equation 2, and measured values of initial and equilibrated solution phosphorus concentration, to determine phosphorus sorption. In this equation, C_i represents the initial concentration of the phosphorus solution and all remaining terms are as defined previously.

$$S' = \frac{S_{\max} kC}{1+kC} - \left(\frac{S_{\max} kC_0}{1+kC_0} + \frac{C_0 V}{M} \right) \tag{1}$$

$$S' = \frac{(C_i - C)V}{M} \tag{2}$$

This modified version of the Langmuir sorption curve was selected because in some instances the equilibrated soil was calculated to have negative sorption, i.e., phosphorus on the soil desorbed into solution. This is typical of soils with high initial phosphorus concentrations and occurs because the true value of sorbed phosphorus (S) consists of both phosphorus sorbed during the incubation (S') and initially sorbed phosphorus that is exchangeable (S_0), as shown in equation 3. The modified Langmuir equation accounts for this desorption of legacy phosphorus and recognizes that it is a function of the dilution ratio used in the experiment.

$$S = S_0 + S' \tag{3}$$

Equation 1 was fit to each data set using nonlinear regression. S_{max}, k, and C_0 were iteratively adjusted to minimize the sum of the squared differences between S' calculated using equations 1 and 2. This nonlinear regression was performed using the Solver function of Microsoft Excel and was performed for each of the 60 soil samples; all parameters were allowed to vary freely except for C_0, which was required to have a value greater than or equal to zero. Based on the values of the fitted parameters, five additional terms were calculated, these were: the equilibrium phosphorus concentration (EPC_0) in mg P/L, the amount of native sorbed phosphorus (S_0) in mg P/kg soil, the soil's phosphorus buffering capacity (BC) in ([mg P/kg soil] / [mg P/L]), the remaining sorption capacity of the soil (mg P/kg soil), and the percent phosphorus saturation of the soil (%). These were calculated using equations 3, 4, 5, 6, and 7, respectively. Their meanings are discussed below.

$$EPC_0 = \frac{S_0}{k(S_{\max} - S_0)} \tag{4}$$

$$S_0 = \frac{S_{\max} kC_0}{1+kC_0} + \frac{C_0 V}{M} \tag{5}$$

$$BC = \frac{S_{\max} k}{(1+kC)^2} \tag{6}$$

$$SC = S_{\max} - S_0 \tag{7}$$

$$\%Sat = 100 \frac{S_0}{S_{\max}} \tag{8}$$

The EPC_0 is the solution phosphorus concentrations that causes an equal amount of sorption and desorption of phosphorus and is often interpreted as an indicator of the soluble phosphorus loss potential of the soil. Higher values indicate potential for phosphorus to be lost to runoff or drainage water (Zhou et al., 2005; Zhang et al., 2009), while low values indicate reduced loss potential. It should be recognized that the value calculated is a function of the conditions used in the study and does not directly provide *in situ* values of soil solution phosphorus concentration, although work by Zhang et al. (2009) did suggest the two were correlated. S_0 indicates the amount of phosphorus sorbed to the soil under field conditions and provides an index to assess if use of a soil as a vegetative treatment area has increased the amount native phosphorus sorbed to the soil. The BC provides an index of the ability of a soil to resist further increases in soil solution phosphorus concentration as it provides information on how much phosphorus can be sorbed before the soil solution concentration increases by 1 mg P/L; this term is calculated based on the first derivative of equation 1. The SC provides information about how much more phosphorus could potential be sorbed by the soil and the percent phosphorus saturation indicates how much of the phosphorus sorption capacity is currently filled by native phosphorus.

STATISTICAL ANALYSIS METHODS

An analysis of variance was conducted using SAS version 9.2 software (SAS Institute Inc., Cary, N.C.) to evaluate statistical differences in EPC_0, S_0, BC, SC,% Sat, S_{max}, and k. The statistical model used consisted of Site, Application History (VTA or Grass), a Site*Application

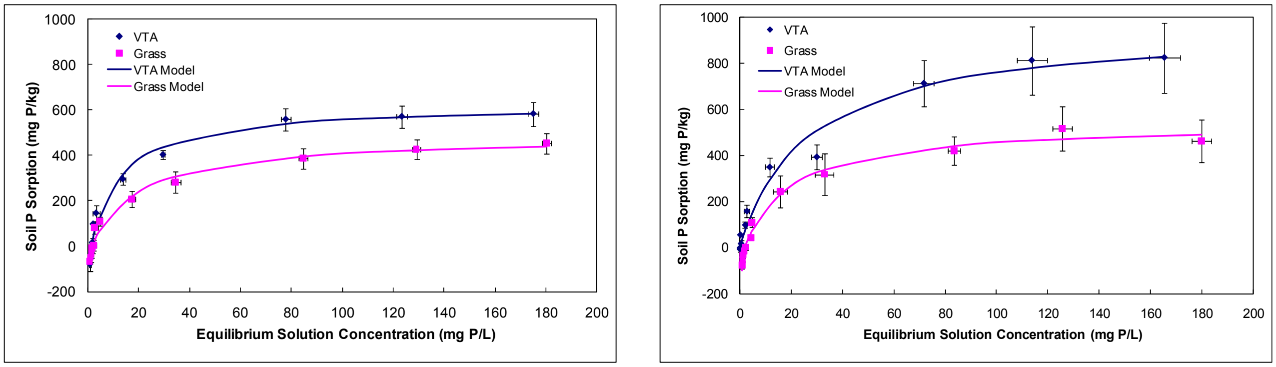
History interaction, and replication nested within the Site*Application History interaction. Contrast statements were used to determine if within site differences in soil sorption parameters existed between the VTA and Grassland use history at each site.

RESULTS AND DISCUSSION

ANALYSIS OF PHOSPHORUS SORPTION CURVES

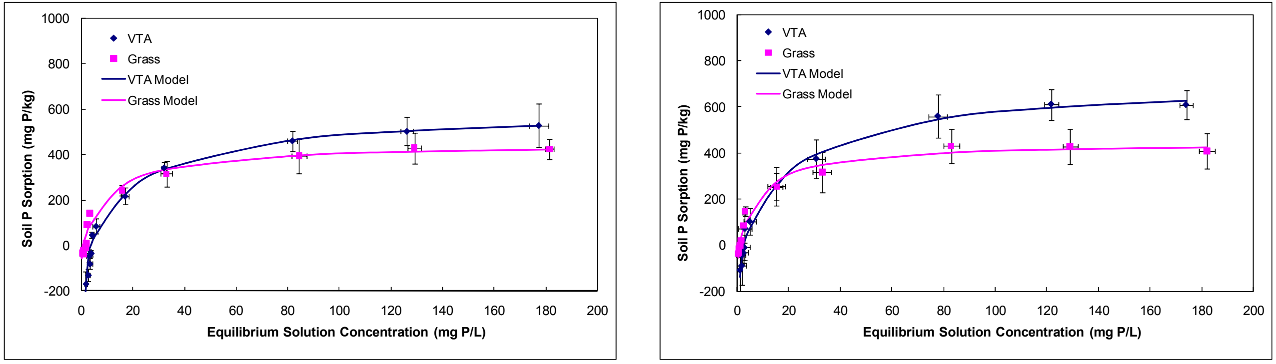
Figure 1 a-f shows the complete phosphorus sorption curves for the VTA and Grassland soils at each of the six sites. Each point on a figure represents the average value of five replicate soil samples from within the VTA or the paired grass area. Also displayed in the figures is the fitted Langmuir sorption curve for each of the Site*Application combinations. All data was well fit by the Langmuir equation with R^2 values greater than 0.98. All samples also exhibited a plateau to the amount of phosphorus that could be sorbed with this generally occurring at soil solution equilibrium concentration of around 80 mg P/L, providing visual support that a Langmuir type model was appropriate for analysis and interpretation of the results.

Five of the six sites showed the same general trend, greater amounts of phosphorus sorption by the VTA soil samples than the grass-area soil samples at high solution phosphorus concentrations. The only site not following this trend was SW IA 1, where the grass soil had slightly higher phosphorus sorption capacities than the vegetative treatment area soil. At low equilibrium solution phosphorus concentration most sites had greater phosphorus sorption by the grass soil samples than the VTA soils samples. This reduction of phosphors sorption at low solution concentra-



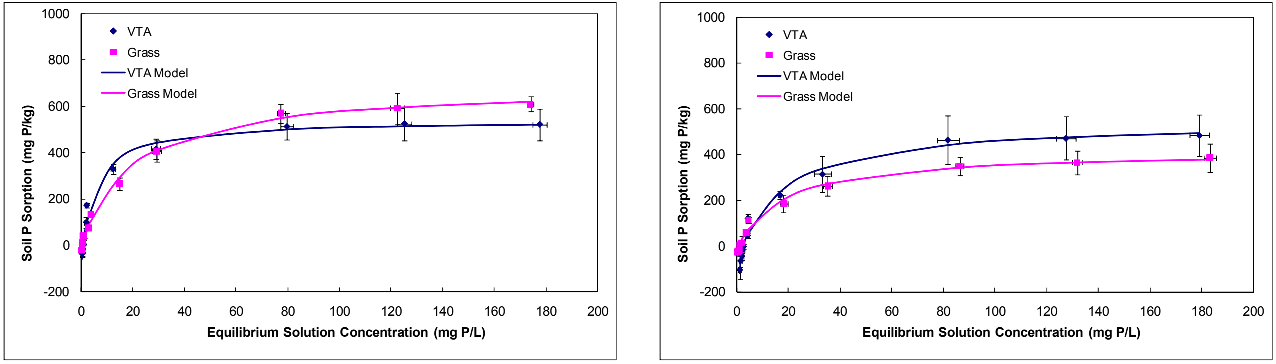
(a) Central Iowa 1

(b) Central Iowa 2



(c) Northwest Iowa 1

(d) Northwest Iowa 2



(e) Southwest Iowa 1

(f) Southwest Iowa 2

Figure 1. Phosphorus sorption curves for vegetative treatment area and grassed area soils. Each point in the figures represents the average of five soil samples. Solid lines represent model fits of the modified Langmuir equation to monitored data.

†Error bars in the x direction represent the standard deviation of the measured equilibrium concentration for each initial phosphorus concentration. Error bars in the y-direction represent a standard deviation of the calculated soil sorption.

tions was expected as the five years of use as a vegetative treatment area had drastically increased soil test phosphorus concentrations by 100 to 400 mg Melich-3 P/kg soil at most sites (Baker et al., 2013). Central Iowa 2 was unique in that its vegetative treatment area soil exhibited higher sorption at low concentrations than the soil samples from the grass area. The VTA soil at this site had exhibited steady to lower Melich-3 phosphorus concentrations over the previous three years and had a neutral phosphorus balance over this time, i.e., phosphorus additions to the VTA were approximately equal to phosphorus losses in VTA runoff and removal with harvested vegetation (Baker et al., 2013). This may have altered its legacy phosphorus levels and made the soil more amenable to future phosphorus sorption. This soil was unique in that the VTA soil exhibited a substantial decline in soil organic matter as compared to the paired grass area as well as change to substantially more basic soil reaction. It is possible that this decline in soil organic matter resulted in less competition between soil organic matter and phosphate for binding sites on the surface of soil particles. This mechanism was strongly supported by the work of Fu et al. (2013) who showed that humic compounds competed with phosphate for binding sites on goethite particles. Alternatively, the more basic soil reaction may be altering the sorption mechanisms from a state where iron and aluminums complexes dominate to a reaction where calcium complexes become more important Reddy and DeLaune (2008).

CALCULATED PHOSPHORUS SORPTION PARAMETERS

Average results of phosphorus sorption properties, calculated based on the fitted Langmuir equation, are shown in table 3. Parameters shown include the equilibrium phosphorus concentration (EPC_0), the amount of native sorbed phosphorus (S_0), the phosphorus buffering capacity (BC), the phosphorus binding energy (k), the maximum phosphorus sorption capacity of the soil (S_{max}), the remaining soil phosphorus sorption capacity (SC), and the percent phosphorus saturation (% P Saturation). Data was analyzed in two ways, the first was to perform a site-by-site comparison between the vegetative treatment area and grassed area soil samples to evaluate if statistical differences existed. In addition to this analysis, a second where data was blocked by site was performed to evaluate if results could be generalized across the sites used in this study. These results are discussed below for each parameter.

The first parameter investigated was the equilibrium phosphorus concentration. This value represents the solution phosphorus concentration where sorption and desorption are equal. Values determined at these sites ranged from a low of 0.00 mg P/L for the CN IA 2 VTA soil (below detection limit) to a high of 3.82 mg P/L for the NW IA 1 VTA soil. These values are similar to those reported by Sui and Thompson (2000) for biosolids amended soils in Iowa, but are generally lower than those found by Zhang et al. (2009) for surface soil horizons in vegetative treatment areas on New York farms that had received runoff effluent application for a comparable amount of time. Four of the sites equilibrium phosphorus concentrations were significantly different in the VTA soil than grassed area soil samples. These were CN IA 2, NW IA 1, NW IA 2, and SW IA 2. At all these sites, except CN IA 2, the equilibrium phosphorus concentration was significantly greater in the vegetative treatment area soil

Table 3. Average results of phosphorus sorption properties, calculated based on the fitted Langmuir equation.

Site	Land Use	(EPC_0)[a] (mg P/L)	S_0[b] (mg P/kg)	BC[c] (L/kg)	k[d] (L/mg)	S_{max}[e] (mg P/kg)	SC[f] (mg P/kg)	% P Saturation[g]
CN IA 1[h]	VTA	1.25	73	**52**[i]	0.092	**732**	**659**	10.1
	Grass	1.44	40	**26**	0.055	**556**	**516**	7.3
	p-value	0.631	0.077	**0.005**	0.140	**0.010**	**0.022**	0.268
CN IA 2	VTA	**0.00**	**0**	39	0.040	**997**	**997**	**0.0**
	Grass	**1.70**	**66**	34	0.071	**595**	**529**	**10.8**
	p-value	**<0.001**	**<0.001**	0.554	0.220	**<0.001**	**<0.001**	**<0.001**
NW IA 1	VTA	**3.82**	**127**	**28**	**0.053**	**761**	**634**	**16.7**
	Grass	**0.79**	**40**	**47**	**0.114**	**525**	**485**	**7.7**
	p-value	**<0.001**	**<0.001**	**0.036**	**0.017**	**<.0001**	**0.017**	**<0.001**
NW IA 2	VTA	**2.93**	74	**37**	**0.053**	**847**	**772**	8.6
	Grass	**0.71**	47	**56**	**0.135**	**517**	**470**	8.7
	p-value	**0.006**	0.153	**0.040**	**0.002**	**<0.0001**	**<0.001**	0.944
SW IA 1	VTA	0.61	**60**	**90**	**0.183**	632	**571**	**9.7**
	Grass	0.35	**13**	**36**	**0.052**	735	**722**	**1.8**
	p-value	0.510	**0.014**	**<0.001**	**<0.001**	0.121	**0.016**	**0.003**
SW IA 2	VTA	**2.15**	**75**	30	0.059	**658**	**583**	**11.0**
	Grass	**0.72**	**16**	24	0.057	**470**	**453**	**3.5**
	p-value	**<0.001**	**0.003**	0.518	0.935	**0.006**	**0.036**	**0.004**
SEM		0.27	13	6	0.017	33	43	1.8

[a] Equilibrium phosphorus concentration (EPC_0),

[b] Native sorbed phosphorus (S_0),

[c] Phosphorus buffering capacity (BC),

[d] Phosphorus binding energy (k),

[e] Maximum phosphorus sorption capacity (S_{max}),

[f] Remaining soil phosphorus sorption capacity (SC), and

[g] Percent phosphorus saturation (% P Saturation) of vegetative treatment area and grassed area soil samples.

[h] Central Iowa 1 (CN IA 1), Central Iowa 2 (CN IA 2), Northwest Iowa 1 (NW IA 1), Northwest Iowa 2 (NW IA 2), Southwest Iowa 1 (SW IA 1), and Southwest Iowa 2 (SW IA 2). SEM = standard error of the mean.

[i] Bolded values indicate that the value for the VTA and grass soils samples were statistically different ($p < 0.05$) at that site.

than in the grassed area soil, indicating increased risk of soluble phosphorus losses in drainage water and the possibility of soluble phosphorus transfer to runoff water. Overall, the results indicated that using vegetative treatment areas will on average increase soil equilibrium phosphorus concentrations (p-value = 0.0301). This result was as expected as most of the VTA soils exhibited substantial increases in soil P concentrations (Baker et al., 2013). Similarly, the native sorbed phosphorus was also significantly higher in VTA soil than in the grassed area soil (p-value = 0.0036). All sites except Central Iowa 2 showed this trend with three of the sites having significantly higher native sorbed phosphorus levels than the grassed area at that site. These results were expected as all the VTAs, except Central Iowa 2, had received and retained large amounts of phosphorus over the previous five years based on Melich-3 phosphorus test results (Baker et al., 2013). Central Iowa 2 was unique in that phosphorus inputs to its treatment area were low due to the effective removal in the vegetative infiltration basin.

The phosphorus buffering capacity indicates the soils ability to retain new phosphorus while minimizing change in soil solution concentration. No consistent trend across the sites was seen for this parameter ($p = 0.1184$); however, on average the VTA soils had a higher buffering capacity than soil samples from the grassed area. This was unexpected as we anticipated that incorporating large amounts of phosphorus into the soil would have reduced the soil's ability to buffer solution phosphorus concentrations from change with future phosphorus additions. The site-by-site trend also show this inconsistency with two of the sites, Central Iowa 1 and Southwest Iowa 1, having significantly increased buffering capacities, and two, Northwest Iowa 1 and Northwest Iowa 2, having significantly decreased buffering capacities. In all cases, the buffering capacities reported here are similar to those reported by Sui and Thompson (2000) for an Iowa Mollisol receiving applications of biosolids. This would seem to indicate that these soils had a history of high levels of phosphorus application which is supported by the relatively high Melich-3 soil test P levels (90 – 300 mg Melich-3 P/kg soil) present prior to use as vegetative treatment areas (Baker et al., 2013).

No general effect on phosphorus sorption strength, i.e., binding energy, was seen ($p = 0.9747$). This was surprising as Iyamuremye et al. (1996), Holford et al. (1997), and Sui and Thompson (2000) had all reported significant decreases in phosphorus binding strength with manure application. In our study, two of the sites, Northwest Iowa 1 and Northwest Iowa 2, exhibited this pattern of significant decreases in binding energy; however, Southwest Iowa 1 exhibited a significant increase in binding energy. The other three sites showed no significant change in binding energy. The inconclusive results, i.e., both increases and decreases in the soil's phosphorus binding energy, are similar to those reported by Laboski and Lamb (2004), whom found that manure application could either increase or decrease binding energy.

In general, the results showed a strong trend of increasing maximum phosphorus sorption capacity with use as a vegetative treatment area ($p < 0.0001$). Results from individual sites also indicated this trend of increasing maximum phosphorus sorption capacity with all sites except Southwest Iowa 1, which had no statistical difference in maximum sorption capacity, having significantly higher sorption capacities in the VTA soil than in the grassed area soil. Similarly, Laboski and Lamb (2004) reported increases in the phosphorus sorption capacity of a Nicollet soil treated with manure and found that greater increases in phosphorus sorption capacity occurred at higher manure application rates.

In most cases, the increase in maximum phosphorus sorption capacity were of greater magnitude than increases in native sorbed phosphorus, so statistical results for remaining sorption capacity were similar to those of the maximum sorption capacity. In general, the VTA soils had significantly greater ($p < 0.001$) sorption capacity than the soil samples from the grassed area. These results were unexpected as we had hypothesized that the high phosphorus loading rates these systems received would fill up the soil's existing sorption capacity. This result has important implications for projecting the phosphorus saturation life expectancy of these vegetative treatment systems, indicating that they may be able to fix phosphorus for greater lengths of time than originally anticipated (Baker et al., 2013); however, without knowing the mechanism of this rejuvenation in phosphorus sorption capacity, further projections of phosphorus saturation life expectancy are also uncertain. Although these results of increasing phosphorus saturation life expectancy were unexpected, they aren't unprecedented. Similar increases in phosphorus sorption life were seen for the Muskegon wastewater treatment system (Hu et al., 2006) in Michigan.

Results indicated that use as vegetative treatment areas significantly ($p = 0.0497$) increased the percent phosphorus saturation of the soil samples. This result held true at three sites, which individually exhibited significant increases in percent phosphorus saturation, these were NW IA 1, SW IA 1, and SW IA 2. An increase in percent phosphorus saturation was also seen at Central Iowa 1; however, at this site the change wasn't significant. Central Iowa 2 showed a significant decrease in phosphorus saturation in the VTA as compared to the grass while NW IA 2 soil remained unchanged. At NW IA 2 this was caused by a large increase in the soil's phosphorus sorption capacity while at CN IA 2 this was caused by losses of easily desorbed phosphorus from the soil.

Future work should seek to evaluate how this phosphorus is partitioning in the soil, i.e., what pools are accumulating this phosphorus and the mechanisms responsible for its retention in the soil without increasing native sorbed phosphorus. Additionally, investigations into the mechanisms increasing the soil's phosphorus sorption capacity could be beneficial for siting similar waste treatment systems.

CONCLUSION

Phosphorus retention in vegetative treatment areas is very dependent on the phosphorus sorption and desorption properties of the soil. Our laboratory studies indicate that use of soil as a vegetative treatment area is likely to increase the phosphorus concentration of the amended soil and of phosphorus in the soil solution (as evidenced by the increase in equilibrium phosphorus concentration). However, our results also suggested that continued application of feedlot runoff has the potential to significantly increase the soils phosphorus sorption capacity (S_{max}), with most sites experiencing increases of between of 175 and 400 mg P/kg soil in sorption capacity when compared to the grassed area soil samples. Despite these increases in phosphorus sorption capacity most soils also showed significant increases in their percent saturation with phosphorus. This could be significant as authors have indicated that losses of phosphorus can increase rapidly when percent phosphorus saturation reaches a change point where losses of soluble phosphorus increase rapidly.

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