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Kinetics of Phosphorus Sorption in Vegetative Treatment Area Soils

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Abstract
Vegetative treatment systems have been proposed and are being utilized to treat runoff from animal feeding operations. These systems use soil and vegetation to remove contaminants (solids, phosphorus, and nitrogen) from the feedlot runoff water and limit potential impacts runoff could have on water quality. Research has shown that these systems soils play a key role in retaining the phosphorus. Thus, the purpose of this experiment was to determine the rate of phosphorus sorption by the soil and in so doing evaluate the impact the runoff contact time with the soil has on phosphorus removal from the solution and retention in the soil. In this experiment, a phosphorous solution of 100 mg P/L, taken to approximate concentrations in the feedlot runoff, was added to soil samples obtained from three different locations in Iowa. After adding the phosphorous solution to each soil sample, the sample was continuously mixed and a sample of solution collected at 0, 1, 2, 4, 7, 14, 21 and 28 days to measure the amount of phosphorus remaining in solution. The results indicated that in most cases phosphorus was quickly sorbed as equilibrium was reached within approximately 24-hours. This indicates that relatively short contact times are required to phosphorus removal; however, in several cases phosphorus removal occurred more slowly and might place a limit on appropriate application rates. The results indicated that phosphorus sorption generally occurred more quickly in VTA soils than in the grass soil samples. Based on the measured sorption parameters, VTA areas ranging from 0.5 â€“ 2.25 hectares are required per hectare of feedlot area.

Keywords
Feedlot runoff, phosphorus, soil sampling, vegetative treatment system, equilibrium phosphorus concentration

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Abstract. *Vegetative treatment systems have been proposed and are being utilized to treat runoff from animal feeding operations. These systems use soil and vegetation to remove contaminants (solids, phosphorus, and nitrogen) from the feedlot runoff water and limit potential impacts runoff could have on water quality. Research has shown that these systems soils play a key role in retaining the phosphorus. Thus, the purpose of this experiment was to determine the rate of phosphorus sorption by the soil and in so doing evaluate the impact the runoff contact time with the soil has on phosphorus removal from the solution and retention in the soil. In this experiment, a phosphorous solution of 100 mg P/L, taken to approximate concentrations in the feedlot runoff, was added to soil samples obtained from three different locations in Iowa. After adding the phosphorous solution to each soil sample, the sample was continuously mixed and a sample of solution collected at 0, 1, 2, 4, 7, 14, 21 and 28 days to measure the amount of phosphorus remaining in solution. The results indicated that in most cases phosphorus was quickly sorbed as equilibrium was reached within approximately 24-hours. This indicates that relatively short contact times are required to phosphorus removal; however, in several cases phosphorus removal occurred more slowly and might place a limit on appropriate application rates. The results indicated that phosphorus sorption generally occurred more quickly in VTA soils than in the grass soil samples. Based on the measured sorption parameters, VTA areas ranging from 0.5 – 2.25 hectares are required per hectare of feedlot area.*

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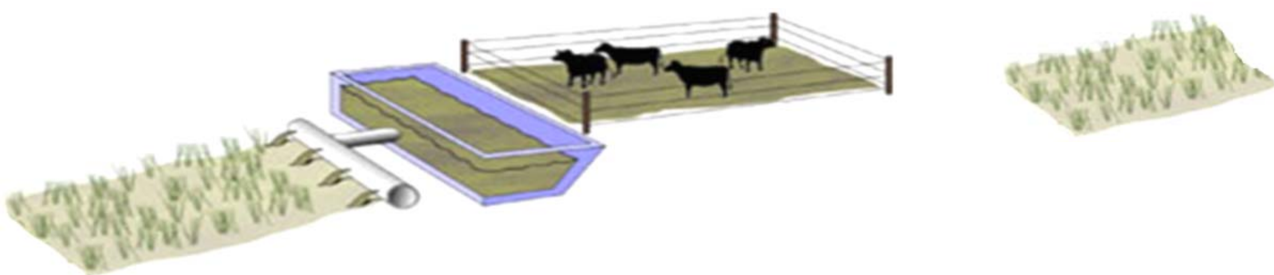
Introduction

Phosphorus is an important nutrient for crop production, however excessive application can cause harm to aquatic ecosystems through the process of eutrophication. Even when properly managed some phosphorus may be lost, which can be critical to water quality due to the sensitivity of aquatic organisms to even low concentrations of phosphorus (Stutter et al., 2009; Huang et al., 2011). The US Environmental Protection Agency (EPA) has set a goal to reduce total phosphorus loads in the Mississippi River by 45%, with a 29% reduction in phosphorus from nonpoint sources (USEPA, 2013). Agriculture, and in particular animal agriculture, is one of the main sources of phosphorus, thus properly managing nutrients from animal manure has become increasingly important to reduce the potential contamination of waterways (Dorioz et al., 2006).

Manure management at open feedlots typically consists of two components; solids handling system that includes manure scraping from the feedlot pens and a liquid handling system that deals with rainfall runoff from the feedlot. The traditional system for liquid manure management from large scale cattle feedlots is storage in basins followed by land application. However, with increased cattle feedlot capacities, hauling distances to properly utilize the manure have increased. This results in increased cost of hauling manure. This could lead to more dilute manures, such as feedlot runoff, being treated as a waste. Thus it has become necessary to find a more economical way to manage the large amounts of manure that the animals produce. One solution for managing nutrients from the runoff produced at these farms is the implementation of a vegetative treatment system (VTS). VTSs are an economical solution because they are less costly to construct than the traditional containment basin system while still meeting EPA regulations for nutrient management (Baker et al., 2013). As shown in Figure 1, a typical VTS collects feedlot runoff in the Solid Settling Basin (SSB) and then releases it on to the Vegetative Treatment Area (VTA). The SSB removes the solids, while the VTA, which is an area of permanent vegetation, is responsible for treating dissolved nutrients and potential contaminants, such as nitrogen and phosphorus, in the runoff.

Research has shown that soil and vegetation can be effective at treating phosphorus (Roberts et al., 2011). In the VTA, phosphorus is removed from the feedlot runoff through the natural processes of phosphorus sorption to soils and vegetative uptake. Sorption refers to phosphorus that has either been sorbed by soil particles or precipitated into compounds such as calcium phosphates. Phosphorus that does not sorb to the soil leaves the VTA as dissolved reactive phosphorus (DRP), which can cause increased growth of algae when it reaches natural waterways, leading to eutrophication (Shober et al., 2009; Stoner et al., 2012).



(a) (b)

Figure 1: (a) Diagram of a typical VTS. Components from left to right are VTA, SSB, and feedlot area. "VTA" soil samples were collected within the VTA area. (b) Grass area near feedlot that did not receive runoff, in which "grass" soil samples were collected.

Currently VTAs are typically sized either based on nitrogen and hydraulic loading, however it is possible that VTAs may receive phosphorus from the effluent at a rate that is faster than it can be sorbed to the soil. If this occurs some of the phosphorus has the potential to be leached below the rooting zone and potentially transported to natural waters. Research in Iowa has suggested that on average phosphorus concentrations in the effluent of VTAs were reduced by 40-70% (Andersen et al., 2013) and mass reductions were 90-100% (Andersen et al., 2011d) of that applied. Andersen et al. (2011a) and Baker et al. (2013) showed that phosphorus was being applied in excess of the amount that could be removed via vegetation harvest on these VTAs, and as a result was rapidly accumulating in the soil. These results indicate that longer contact times between the applied runoff water and VTA soil may be required to encourage greater concentrations reductions. Therefore, evaluation of phosphorus sorption kinetics is necessary to determine necessary retention times should a release occur. Moreover, as the data of Andersen et al. (2012) indicated significant increase in phosphorus concentration in various forms within the vegetative treatment area soil and changes to the soil phosphorus sorption capacity (Andersen et al., 2011b) it is important to evaluate how sorption kinetics might have changed over time. From this data, recommendations on the daily phosphorus loading rate can be developed and ultimately improved VTA sizing and management recommendations improved.

Materials and Methods

Site Descriptions

VTAs located on commercial open lot beef feeding operations at three locations in Iowa (figure 2) were intensively monitored over a four year period by Iowa State University (ISU). The sites were described in Andersen et al. (2013) and only briefly detailed here. Data summarizing the characteristics of the ISU monitored portions of the feedlots and VTSs are provided in Table 1. Information shown includes the maximum cattle capacity of the feedlot, the soil type of the VTA, the size of the drainage area (feedlot and additional contributing area), the storage volume of the SSB, the area of the VTA, and the drainage area to VTA ratio. Conditions at each site are summarized in the following section.

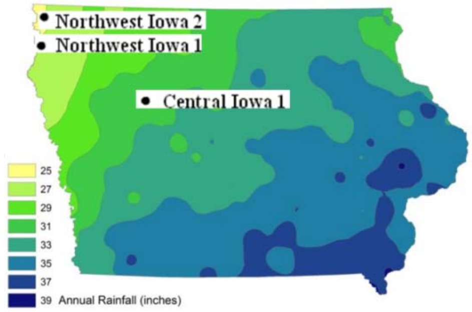


Figure 2: Locations of VTA sites in relation to average annual precipitation in the state of Iowa.

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 designed to hold 4,290 m^3 of effluent. CN IA 1 VTA soil consisted of Clarion loam, Cylinder loam, and Wadena loam (Soil Survey Staff, NRCS USDA, 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 consisting of Galva silty clay and Radford silt loam soils (Soil Survey Staff, NRCS USDA, 2010). Northwest Iowa 2 (NW IA 2) had a 2.96 ha concrete feedlot. A SSB with a volume of 1,120 m^3 collected the feedlot runoff and released it to a 1.61 ha VTA. NW IA 2 soils consisted of Moody silty clay loam (Soil Survey Staff, NRCS USDA, 2010).

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

Site	No. of Cattle	Soil Type	SSB (m^3)	Drainage Area (ha)	VTA (ha)	Drainage Area to VTA Ratio
CN IA 1	1,000	Clarion loam, Cylinder loam, Wadena loam	4,290	3.09	1.49	2.07
NW IA 1	1,400	Galva silty clay, Radford silt loam	3,710	2.91	1.68	1.73
NW IA 2	4,000	Moody silt clay loam	1,120	2.96	1.61	1.84

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 feedlot runoff effluent application on phosphorus sorption kinetics.

Soil Sampling and Analysis

At each of the three sites, three soil samples were collected from the VTA that had received runoff for at least five years (Figure 1a) and three more from the paired grass area that did not receive the feedlot runoff effluent application (Figure 1b). 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 inches) from twenty 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 ISU Agricultural Waste Management Lab. In the lab, mass of the soil samples 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 coarse 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 hours 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 experiment.

Phosphorus Sorption Experiment

From each group of grass and VTA soils from each site, one gram of air-dried soil was placed into each of eight 50 mL centrifuge tubes with screw-on caps and mixed with 25 mL of a solution containing a concentration of phosphorus of 100 mg P/L made from monopotassium phosphate (KH_2PO_4) and 0.01 M calcium chloride ($CaCl_2$). $CaCl_2$ was used because research has indicated that it can be used to approximate the salt content of feedlot runoff (Bhadha et al., 2011; Penn et al., 2007).The concentration of 100 mg P/L was chosen because it is the typical concentration of phosphorus in feedlot runoff. An initial sample was taken directly from the 100 mg P/L solution to serve as the initial 0 day sample. Samples were placed horizontally on an orbital shaker and shaken end-to-end at 25±2°C at a speed of 200 rpm for the following times: 1, 2, 4, 7, 14, 21 and 28 days. At the end of each time interval the supernatant was filtered through a 0.45 μm filter. Samples were placed in the freezer from the time they were filtered to the time they were analyzed. Three samples were taken from each initial concentration and averaged. DRP concentrations were analyzed spectrophotometrically at a wavelength of 880 nm using a Genesys 6 (Thermo Electron Corporation, Madison, WI) photo spectrometer following the 4500-P E. Ascorbic Acid Method for measuring soluble phosphorus (APHA, 1998). Samples were compared to calibration curve with R^2 value of 0.995 or greater to determine the phosphorus concentration.

Determination of Soil Phosphorus Sorption

The amount of phosphorus sorbed by the soil was calculated as the difference between the amount of phosphorus initially added to the soil and the amount remaining in the solution after the time interval as shown in Equation 1:

$$q_e = \frac{(c_o - c)V}{m} \tag{1}$$

where q_e is the amount of phosphorus sorbed in mg/g, c_o is the initial phosphorus concentration and c is the measured phosphorus concentration at the specified time, with both concentrations being in mg/L, V is the volume of phosphorus solution in L and m is the mass of soil used in kg.

Phosphorus Sorption Kinetic Modeling

A pseudo first-order model was used to model the kinetics of phosphorus sorption using the following equation (Eljamal et al., 2013):

$$\frac{dq}{dt} = k_1(q_e - q) \tag{2}$$

where k_1 is the rate constant of pseudo first-order sorption (d^{-1}), q is the amount of phosphorus sorbed at time t in mg/g, q_e is the amount of sorption at equilibrium in mg/g, and t is the contact time in days. After integration of Equation 2 for the boundary conditions $q = 0$ at $t = 0$ and $q = q$ at $t = t$, Equation 2 becomes:

$$q = q_e(1 - e^{-k_1 t}) \tag{3}$$

Equation 3 was fit to the average sorption data using a minimization of least square fitting procedure. The minimization was performed using the solver function of Microsoft Excel and varying the q_e and k_1 parameters. An analysis of variance was conducted using JMP Pro 10 as a split-plot design to evaluate if significant differences in sorption between the VTA and Grass soils had occurred at any of the times at the three differing locations.

Results and Discussion

Effect of Time on Equilibrium Concentration

The equilibrium phosphorus concentration is the point at which the rate of phosphorus sorption is equal to the rate of desorption, and it will appear that the soil is unable to sorb more phosphorus. This value provides the maximum extent to which the soil can accumulate phosphorus at a certain solution concentration. Figure 3 (a, b, c) shows the amount of phosphorus sorbed by grass and VTA soils at each of the three sites over a 28 day period and the fitted kinetic equation. Statistical analysis was performed to determine if either the extent of phosphorus sorption or the amount of sorption at any the measured times were statistically different than the VTA or grass soils. The results indicated that the extent of phosphorus sorption did not differ between the VTA and Grass soils at any of the three locations, but that the rate at which sorption occurred did differ for two of the three sites.

Table 2 shows the rate constants and amount of sorption at equilibrium for each treatment at the three sites. The graphs show that samples rapidly sorbed phosphorus during the first 24 hours of the contact time for NW IA 1 and NW IA 2 as the time constant for the northwest Iowa sites was generally less than 1/3 day and therefore over 95% of the maximum sorption potential would be reached within 1 day. At CN IA 1, the rate of sorption was slower than for NW IA 1 and 2 because the graphs indicate that equilibrium was reached within about five days for the VTA samples and ten days for the grass samples. It can be seen that at both Central Iowa 1 and Northwest Iowa 2 the soil exhibited a more expedient sorption of phosphorus than the soil samples from the grass area. This corresponds to the work of Andersen et al. (2011b) whom found higher phosphorus sorption capacities of VTA soils when using a 24-hour incubation time to approximate equilibrium. However, the results here would seem to indicate that the actual capacity of the soil to sorb phosphorus hasn't changed, only the speed at which sorption occurs.

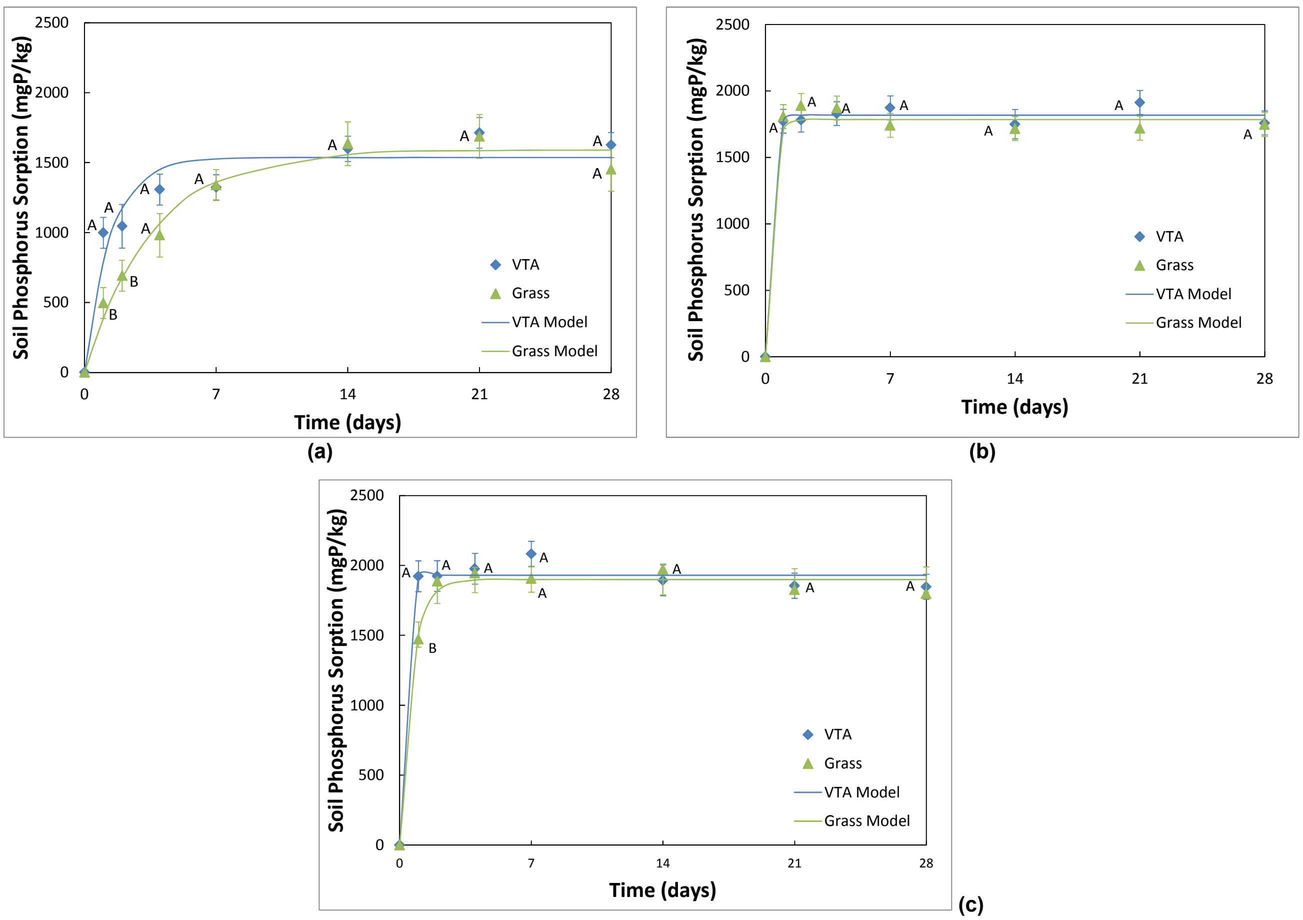


Figure 3: Phosphorus sorption over time for VTA and Grass samples when incubated with a solution with an initial phosphorus concentration of 100 mg P/L solutions over 28 day time period at (a) Central Iowa 1, (b) Northwest Iowa 1, and (c) Northwest Iowa 2. Error bars indicate the standard error of the mean of the measured phosphorus sorption. Differing letters within a sampling day represent significant differences in phosphorus sorption at α = 0.05.

Table 2: Variables used in modeling phosphorus sorption kinetics with a 1st order model. Parameters include the rate constant and sorption capacity.

Site	Type	Rate Constant (k_1) (d^{-1})	Amount of Sorption at Equilibrium (q_e) (mg P/kg soil)
CN IA 1	VTA	0.720	1536
	Grass	0.276	1590
NW IA 1	VTA	3.64	1818
	Grass	3.05	1785
NW IA 2	VTA	5.58	1929
	Grass	1.57	1899

VTA Design and Management Implications

The time for soil to reach phosphorus sorption equilibrium is important for sizing and managing VTAs to allow the appropriate retention times to treat phosphorus and ensure that it is retained in the soil. To illustrate this, the phosphorus sorption parameters determined here are used to evaluate what this would mean in terms of phosphorus loading capacity.

Runoff control systems on open lot beef feeding operations are required to contain all direct precipitation and runoff resulting from any storm of equal or smaller magnitude the 25-year, 24-hour event (USDA, 2011). This is approximately 13 cm (5.1 inches) throughout most of Iowa. Assuming the feedlot would have a curve number of around 91 (Wulf and Lorimor, 2005) than approximately 11.9 cm (4.68 inches) or runoff would be generated. This runoff needs to be emptied from a settling basin within 72 hours of the rainfall event if the basin is non-lined (Iowa DNR, 2007). This is also necessary to maintain sufficient capacity for future rainfall events. This means that for every hectare of feedlot area we need to dispose of 400 m^3 of settled effluent per day after the design storm.

Assuming we would like to retain most of the phosphorus in the top 15 cm (6 inches) we'd desire at least three time constants worth of contact time between the applied runoff and the soil (this would remove 95% of the phosphorus that could be removed). This means that at these sites contact times of one to eleven days would be required. Assuming the soil porosity is near 50% then for every cm of water applied the water would move through 2 cm of soil; this implies that to keep the applied effluent in the top 15 cm of soil only 7.5 cm of effluent could be applied within calculated contact period. Based on these requirements VTA to feedlot area ratios of around 2.2 to 0.5 would be required to limit leaching of phosphorus through the top 15 cm of the soil profile. Results are summarized in table 3.

Table 3: Measured time constant, required soil-effluent contact time, maximum application rate based on phosphorus sorption kinetics, and the resulting VTA to feedlot area ratio.

Site	k_1 (d^{-1})	Time Constant (d)	Contact Time (d)	Maximum Application Rate (cm/d)	VTA :Feedlot Area Ratio
CN IA 1	0.72	1.39	4.17	1.8	2.22
NW IA 1	3.64	0.275	0.824	9.1	0.440
NW IA 2	1.57	0.637	1.91	3.9	1.02

Conclusions

The purpose of this experiment was to determine the rate of phosphorus sorption by the soil and in so doing evaluate the impact the runoff contact time with the soil has on phosphorus removal from the solution. In this experiment, a phosphorous solution of 100 mg P/L, taken to approximate concentrations in the feedlot runoff, was added to soil samples obtained from three different locations in Iowa. At each location, soil was collected from a paired grass area (to approximate a newly constructed vegetative treatment area) and from a vegetative treatment area that had been used for feedlot runoff treatment for five years. After adding the phosphorous solution to each soil sample, the sample was continuously mixed and a sample of solution collected at 0, 1, 2, 4, 7, 14, 21 and 28 days to measure the amount of phosphorus remaining in solution. The results indicated that in most cases phosphorus was quickly sorbed and equilibrium was reached within approximately 24 to 48 hours. This indicates that relatively short contact times are required to phosphorus removal; however, in several cases phosphorus removal occurred more slowly and might place a limit on appropriate application rates. Based on the measured sorption parameters, VTA areas ranging from 0.5 – 2.25 hectares are required per hectare of feedlot area at these sites.

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