

Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials

C.J. Penn, R.B. Bryant, P.J.A. Kleinman, and A.L. Allen

Abstract: The loss of nutrients, particularly phosphorus (P), in agricultural drainage waters is a priority conservation concern. Open drainage ditches concentrate runoff and therefore offer opportunities for capturing P in runoff from large areas of land. This paper provides an overview of the potential to use P sorbing materials in drainage ditches to sequester dissolved P from ditch water. We describe factors affecting the selection of P sorbing materials for use in treating ditch water and review several approaches to their application in ditches. In addition, experiential insight is provided with regard to developing and installing a P removal structure within a ditch that has high concentrations of dissolved P in flow. Preliminary data indicate that such structures have great promise in treating not only dissolved P in ditch flow, but also trace metals (arsenic, copper, nickel, zinc).

Key words: drainage ditches—phosphorus removal structure—phosphorus sorbing materials—water quality

Concern over accelerated eutrophication in many agricultural watersheds has focused attention on novel management practices to reduce phosphorus (P) transfers from agricultural fields to downstream surface waters (Sims et al. 1998; He et al. 2006). Although the existing management practices can successfully reduce particulate P losses to surface waters, relatively few management practices have been developed to curtail dissolved P transfers (Sharpley 1992). Increasingly, investigators are turning to the use of phosphorus sorbing materials (PSMs) to decrease the potential for soils and manures to release dissolved P to runoff water (Stout et al. 1998; Ippolito et al. 2003; Moore and Miller 1994; Elliott et al. 2002).

Phosphorus “sorption” refers to the combined processes of adsorption and precipitation of P from dissolved to solid forms. Phosphorus sorbing materials typically contain appreciable concentrations of aluminum (Al), iron (Fe), calcium (Ca), or magnesium (Mg), with solubility depending on chemical forms and other properties such as pH. Phosphorus sorbing materials include products such as alum (aluminum sulfate),

gypsum (calcium sulfate), natural or synthetic Al and Fe oxides, and a wide range of industrial byproducts.

A reduction in dissolved P losses in runoff is expected when PSMs are applied to high P soils because PSMs have been shown to decrease water solubility of soil P (Rhoton and Bigam 2005; Peters and Basta 1996; Callahan et al. 2002; Elliott et al. 2002). Research has clearly established that the treatment of poultry manure with alum reduces the potential for P loss in runoff when the manure is land applied in comparison with untreated poultry manure (DeLaune et al. 2004; Warren et al. 2006). Penn and Bryant (2006) broadcast several PSMs to cattle loafing areas where soil Mehlich-3 P levels were from 400 to 800 mg kg⁻¹ (0.79 to 1.59 lb ton⁻¹) and found that dissolved P concentrations in runoff one week after application were lower from soils amended with PSMs than from unamended soils. However, these runoff P reductions were only temporary, disappearing within several weeks. Consequently, Penn and Bryant (2006) concluded that, for high P soils, it might be more efficient to treat runoff water than the soils themselves.

Amending surface waters with PSMs is a common practice throughout the US (Minneapolis Park and Recreation Board 2001; Lind 2002; California Regional Water Quality Control Board 2001). Application of PSMs, typically alum, will reduce dissolved P concentrations in solution, thereby decreasing the potential for P to contribute to algal blooms (Lind 2002). For example, following alum addition to two sandpit lakes in the Platte River basin (Fremont, NE), total P was reduced from >100 mg L⁻¹ to <50 mg L⁻¹ (>13.2 to < 6.6 oz gal⁻¹; Holz and Hoagland 1999). Liquid alum additions have also been shown to reduce soluble P in irrigation return flows (Leytem and Bjorneberg 2005).

To date, little work has been conducted on the use of PSMs in drainage ditches. Because ditches represent areas of concentrated, often times convergent, flow in agricultural landscapes, drainage networks provide opportunities for targeted application of remedial practices that would otherwise be too costly to apply across a landscape. For instance, the removal of P from drainage ditch flow has a higher likelihood of improving downstream water quality than does the treatment of riparian buffers because the P in drainage ditch flow is more likely to be exported to downstream water bodies. Furthermore, treating drainage ditches at one point, or along one reach, has the potential to capture P from an entire catchment, making it a spatially efficient means of mitigating nonpoint source P pollution. Installation of a structure with contained PSMs into surface waters would not only remove P at a single point but also allow for the ultimate removal of P from the watershed after the P saturated materials are taken out of the structure.

This study explores factors affecting the use of PSMs in treating ditch flow. In particular, we review properties of PSMs that affect their use in ditches and describe methods for

Chad J. Penn is an assistant professor of soil and environmental chemistry in the Department of Plant and Soil Science, Oklahoma State University, Stillwater, Oklahoma. **Ray B. Bryant** is a research unit leader and **Peter J.A. Kleinman** is a soil scientist at the Pasture Systems and Watershed Research Management Unit, USDA Agricultural Research Service, University Park, Pennsylvania. **Arthur L. Allen** is an associate professor in the Department of Agriculture at the University of Maryland Eastern Shore, Princess Anne, Maryland.

treating ditch water with PSMs. To illustrate the importance of these factors, a case study is provided in which PSMs are being used to treat flow from a ditch at the University of Maryland Eastern Shore research farm on the Delmarva Peninsula with annual P export in excess of 25 kg ha⁻¹.

Phosphorus Sorbing Materials

A variety of materials exist that have the potential for use in sorbing P from ditch flow (table 1). These materials range widely in their availability, quantity, cost, and transport characteristics, as well as in their effectiveness in sorbing P. Note that there is some overlap between the traditional agricultural amendments and water and wastewater treatment chemicals. For example, quick lime, hydrated lime, and alum are used in both settings (table 1).

Among agricultural amendments, quick lime is considered extremely reactive, caustic, and must be handled carefully. Limestone and hydrated lime are also commonly used for increasing pH, with limestone being the least reactive. Although gypsum has very little effect on pH, it is much more soluble than limestone. The Ca in these products promotes the formation of insoluble Ca phosphates; however, P sorption by these products is directly proportional to their solubility. Most of the agricultural amendments and water and wastewater treatment chemicals are non-hazardous, but care should be taken to avoid ingestion or inhalation. In addition, many of these materials can be corrosive if stored under moist conditions. The water and wastewater treatment chemicals listed in table 1 are considered highly soluble and reactive sources of Al, Fe, and Ca, and are therefore excellent PSMs.

Industrial by-products tend to be heterogeneous in nature, with some notable exceptions (byproduct gypsum), but have the greatest potential for being both inexpensive (even free) and locally available (minimal transportation costs). Indeed, there may be considerable incentive by a byproduct generating industry to support alternative uses of byproducts as the most common fate of these materials is disposal in landfills. Most of these materials are less reactive than chemicals used in water and wastewater treatment; the reactivity of these waste products is dependent on the chemical form of the P sorbing element. For example, some municipalities use alum as a drinking water treatment chemical, and

Table 1
Potential phosphorus sorbing materials and main phosphorus sorbing elements.

Material	P sorbing element
Traditional agricultural amendments	
Ground limestone (calcium carbonate)	Ca
Quick lime (calcium oxide)	Ca
Hydrated lime (calcium hydroxide)	Ca
Gypsum (calcium sulfate)	Ca
Water and waste water treatment chemicals	
Calcium chloride	Ca
Aluminum chloride	Al
Alum (aluminum sulfate)	Al
Ferric sulfate	Fe
Ferric chloride	Fe
Byproducts	
Calcium silicate slag	Ca
Cement kiln dust	Ca
Wood ash	Ca
Paper mill lime	Ca
Fly-ash (coal fired)	Ca, Fe, Al: varies
Drinking water treatment residuals	Al > Fe, Ca
Paper mill sludge	Al, Ca
Acid mine drainage residuals	Fe > Al, Ca: varies
Bauxite mining waste	Al, Fe > Ca
Foundry sand	Fe, Al > Ca
Waste gypsum	Ca

the remaining residuals are often sent to a land fill, even though they typically possess a high P sorption potential due to the presence of amorphous Al and Fe minerals. Certain industries may produce by-products rich in gypsum from mining or production of dry-wall. Other potential by-products include "slag" from the steel industry, "sludge" from the paper industry, foundry sand from metal casting, and waste products from bauxite processing.

Phosphorus Sorption Material Characteristics

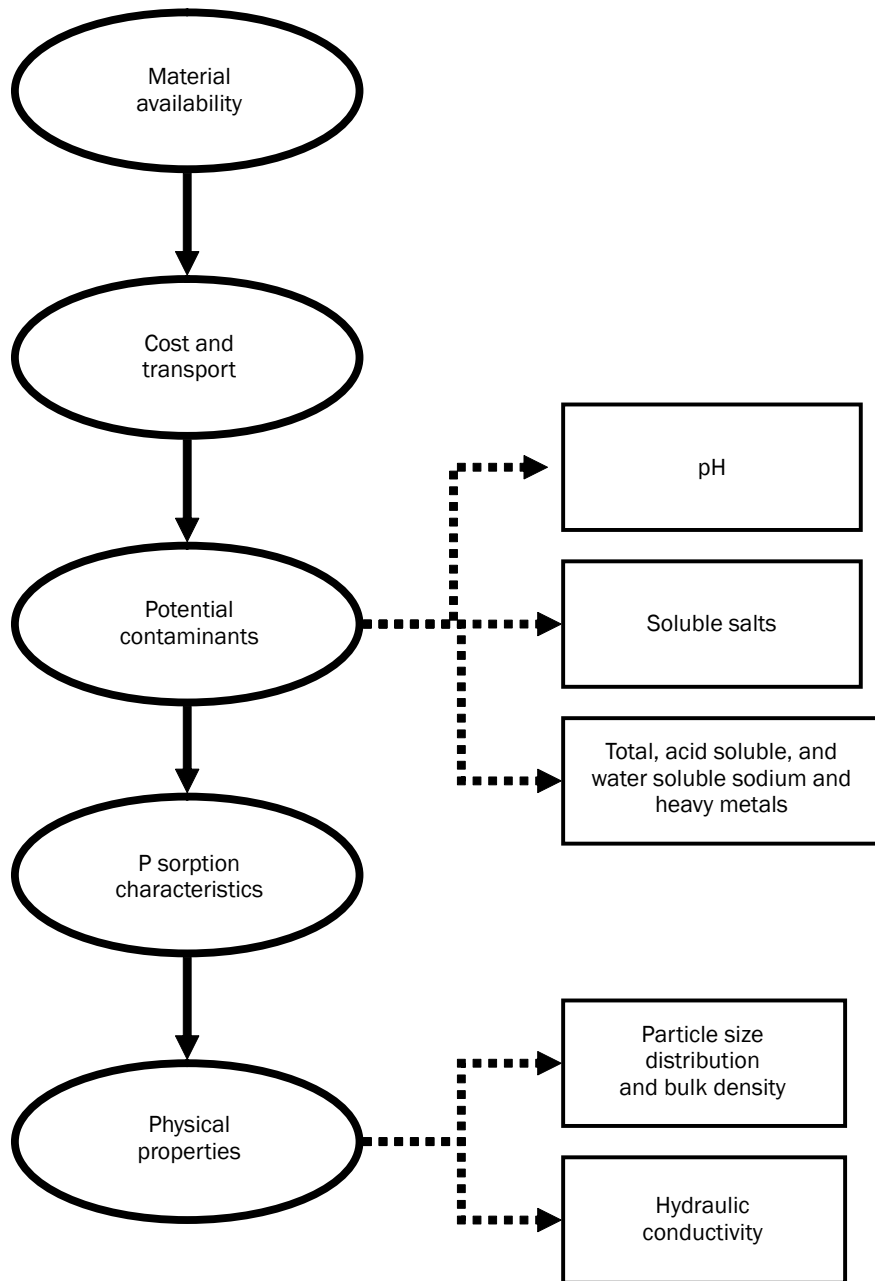
As depicted in figure 1, the key factors in selecting a PSM are material cost/availability, potential contaminants, P sorption characteristics, and physical properties. Details of important P sorption characteristics are provided in figure 2. Depending on how the PSMs will be applied or used, physical properties, such as particle size and hydraulic conductivity of the material, may be important. From a practical standpoint, acquisition and disposition factors, such as availability of the material, potential utilization or

disposal of spent material, and costs, should be considered.

Phosphorus Sorption Mechanisms. In addition to simple estimation of P sorption capacity, knowledge of the forms of the main P sorbing elements (Ca, Mg, Fe, and Al) may suggest the mechanism(s) in which P is removed from solution. This becomes important in choosing a material that is most suited to a particular end use as it affects sorption capacity, retention, kinetics, and the form of sorbed P in the spent material (Penn and Bryant 2006). Although total Ca, Mg, Fe, and Al content is useful for understanding P sorption, total elemental content provides little information on chemical forms, which are important to understand the reactivity and nature of the association with P (Dayton and Basta 2005). As opposed to total elemental content, amorphous Al and Fe, as determined by ammonium oxalate extraction (Dayton and Basta 2005; McKeague and Day 1966), is a better indication of the P sorbing potential of these elements. Among Fe and Al forms, the amorphous pool represents the most reactive portion able to remove soluble

Figure 1

Overall process for screening materials for potential use as phosphorus sorbing materials in phosphorus removal structures.



P from solution. Similarly, extraction with dithionite–citrate–bicarbonate extracts mostly free amorphous and crystalline Fe and Al; i.e. Fe and Al not associated with layer silicates (Loeppert and Inskeep 1996). Although various studies have shown that amorphous Al + Fe alone is a good indicator of P sorption capacity (Elliott et al. 2002), materials utilized in our past experiments exhibited a weak relationship because other P sorbing

elements (i.e. Ca and Mg) are present either in the sorption material or in the matrix of the sorption environment.

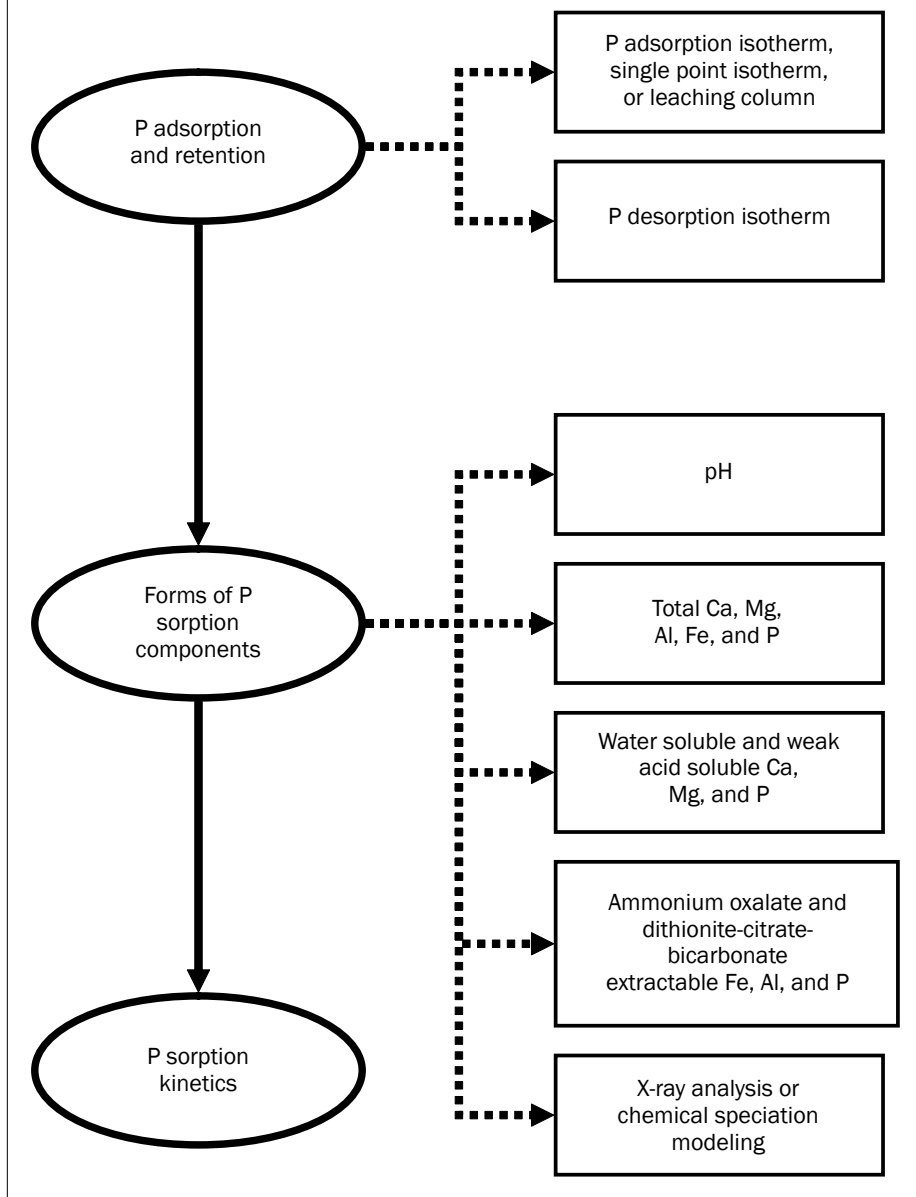
For Ca and Mg rich materials, total content is important but can also be potentially misleading without an indicator of chemical forms. Because P mostly reacts with Ca and Mg to precipitate (as opposed to adsorb) Ca and Mg phosphates, these two elements must be dissolved in solution for effective P

removal. Therefore, the amount of Ca and Mg extracted from a material by water or a mildly acid solution can be a good indicator of a materials' ability to remove P from solution by precipitating Ca/Mg phosphates (Moore and Miller 1994; Dou et al. 2003). For example, among several Ca dominated materials that we characterized, the one with the median total Ca concentration was still able to remove more P from solution compared to the material with the highest total concentration of Ca. The explanation was that the material with the lower total Ca content had 3 to 19 times more water soluble Ca compared to the material with the highest total Ca content, making it more effective at precipitating calcium phosphate. In addition, the higher portion of total Ca in a water soluble form for this material could be explained by the pH and crystalline form of Ca present. The less effective P removing material consisted of Ca in the form of calcite at a pH of 8.2, while the more effective material contained Ca in the form of gypsum (calcium sulfate). Note that gypsum solubility is higher than calcite and is not affected by pH. The different Ca minerals in the materials were identified by x-ray diffraction, but could also be predicted by use of a chemical speciation model.

Phosphorus Sorption Capacity and Retention Characteristics. The pH of the sorption material and its environment is a major determinant of effective P sorption capacity and retention. In general, for Al and Fe to be effective at removing dissolved P from solution, the pH should be less than 7.5, otherwise the mineral surfaces will have significantly fewer positive charged sites (Rhoton and Bigham 2005). In fact, Al and Fe are most effective at P adsorption at acidic pH (McBride 1994); however, one must also consider the optimal pH of the aquatic system since a pH < 5.5 may be detrimental to aquatic life (Novotny 2003). Likewise, Ca and Mg tend to be more effective at precipitating P at a pH between 6 and 7.5 due to the fact that the solubility of Ca and Mg phosphates tend to increase with decreasing pH below 6, but solubility also increases with increasing pH above 7.5 (Lindsay 1979; Dou et al. 2003).

The most direct method of determining P sorption capacity is the adsorption isotherm and the single point P isotherm, in which known concentrations of P solution are equilibrated with the materials before P

Figure 2
Screening process for quantifying the phosphorus sorption characteristics of potential phosphorus sorbing materials.



analysis of the equilibrated solution. More difficult but also more useful is an estimation of P sorption via leaching column; i.e. a known P solution is leached through a column of the material at a constant flow rate and the effluent is analyzed for dissolved P. By simulating multiple events on an Al/Fe material over a period of several days, we have observed significant increases in sorption capacity during intervals between leaching events that were attributed to sorbed P being converted to more strongly bound forms—a process that resulted in more sorption sites becoming available prior to the next leach-

ing event (Hsieh et al. forthcoming).

The ability of a PSM to retain previously sorbed P is important for determining its total effectiveness. The percentage of P retained after 5 sequential desorptions with deionized water or a dilute salt solution such as CaCl_2 , or KCl is one indicator of a PSM's ability to retain sorbed P.

Assessing P sorption kinetics: P sorption kinetics can be estimated by batch or flow-through techniques (Sparks et al. 1996). Although more difficult, a flow-through kinetics method is obviously more appropriate when a structure is designed such that

ditch water flows through the PSM. Due to different mechanisms of soluble P reduction between Ca + Mg versus Fe + Al materials, the Fe and Al based materials are better suited for conditions in which the contact time between the water and PSM is relatively short. Peak et al. (2002) investigated the mechanism of P solubility reduction in alum (aluminum sulfate) amended poultry litter using an x-ray absorption spectroscopy technique to identify P forms and found that P was mostly chemisorbed onto the surface of amorphous Al hydroxides, rather than precipitated as Al phosphate species. Chemisorption/ligand exchange of soluble P on the surface of Al and Fe minerals is rapid in comparison with the reaction of dissolved P with Ca and Mg that results mostly in Ca and Mg phosphate precipitation. In general, under ideal conditions, P removal by Fe and Al materials is more efficient compared to Ca and Mg rich materials in terms of sorption capacity, retention, and kinetics (Moore and Miller 1994; Dou et al. 2003; Dao et al. 2005).

In regard to an active “flow-through” structure, our results from previously conducted P sorption kinetics experiments suggest the use of a Fe/Al dominated PSM if the structure retention/contact time is less than 20 minutes, due to the fact that Fe and Al can remove P from solution much faster compared to Ca and Mg. However, for situations in which the retention/contact time is high and the P concentration of the water is less than 2 mg P L^{-1} , (0.26 oz gal^{-1}) a Ca/Mg based material would be suitable.

Potential contaminants: One must be cautious whenever foreign materials are to be placed within an aquatic system. Obviously, the PSMs themselves should not contribute to water quality degradation, such as by causing water pH to drop below 5.5 or increase above 7.5, nor should they significantly increase the soluble salts content of aquatic systems because they can cause problems for aquatic life (Novotny 2003). Materials that contain heavy metals such as Cu, Zn, Cd, Co, As, and Ni should be treated with caution. If these elements are present in amounts that exceed background levels in soils and sediments, then they should only be used in contained systems where the risk of particulate material being introduced into the aquatic system is minimal.

The form in which these elements are present should be thoroughly characterized

to determine their solubility. Obviously, materials containing readily soluble forms of these elements should not be used for P sorption, but determining that such elements are present in insoluble forms does not necessarily indicate they are safe for use (Basta et al. 2005). The chemical environment of the contained system can affect the solubility of these elements through changes in pH or redox potential. In general, these elements become more soluble under low pH and if sorbed to Fe minerals, may dissolve under reducing conditions. The design of a contained system should ensure that the chemical environment does not allow pH and redox potential to fluctuate in ranges that promote the solubility of these elements (Chuan et al. 1996; Koski-Vahala and Hartikainen 2001). This may place severe restrictions on the use of Fe oxide rich materials that contain heavy metals; when used in contained systems, they must not be allowed to become anaerobic.

Physical Properties and Acquisition/Disposition Factors. Physical properties of a potential PSM may dictate its suitability for a specific use, especially among flow-through structures in which the materials are contained. Some materials, such as synthetic gypsum, which is a byproduct resulting from flue gas desulfurization carried out by electric generation or industrial plants that burn coal as a fuel, have relatively uniform physical properties. Other materials, such as water treatment residuals (WTRs), which are a byproduct of purification of drinking water, can vary greatly in both physical and chemical properties (Dayton and Basta 2005). Due to variable water content in WTR, these materials exist as slurries and gels that can harden to rock-like particles upon air drying. Since transportation of PSMs represents a major cost, reduced water content is usually desirable. Physical characteristics of the ideal PSM for a specific use usually hinges on the balance between maximum surface area and a particle size distribution that meets other design requirements, such as handling or, in the case of a flow-through system, hydraulic conductivity. Due to potential heterogeneity of the material, direct measurement of hydraulic conductivity by measuring flow under a constant head is the best approach for determining this design parameter.

Acquisition and disposition factors should be assessed early in the design process. Unless cost share measures are in place, the use of PSMs represents an added cost of produc-

tion that can easily erase the profitability of most agricultural land uses. Although many industrial byproducts having desirable P sorbing characteristics and are available at little or no cost because agricultural use is an alternative to land filling, local availability of a specific PSM in sufficient quantities is an important factor affecting transportation costs. The disposition of spent material, that which has reached a sorption maximum that effectively reduces its effectiveness below a desired level, may represent an even greater cost. Common alternatives for disposing of the spent material include land filling, land applying, or recharging for reuse. The cost of land filling is usually prohibitive; land application may be a feasible alternative if it results in P removal or net permanent sequestration of P relative to the water body of concern. One advantage of a Ca/Mg based material is that the resulting P saturated material may have value as a P fertilizer source when amended to acid soils. That value may help offset transportation and any installation and maintenance costs. On-site recharging of spent material becomes a trade off between maintenance costs that offset transportation costs.

Addressing the practical aspects of a P sorption system can be far more challenging than designing a system that functions effectively to reduce soluble P in ditch drainage water. But unless the practical aspects, including overall costs are addressed, wide-spread adoption of the system will not occur.

Methods to Treat Ditch Flow with Phosphorus Sorbing Materials

Broadcasting. The most basic approach to influencing ditch water quality with PSMs is to broadcast them directly into the ditch. Although this method may be effective for reducing the solubility of P at the interface of the water column and ditch soils/sediments, it does not ensure that the materials will come in significant contact with ditch flow. In fact, under high flow conditions contact between the broadcast materials and the flow may be minimal, resulting in low potential for sorption processes to occur. Furthermore, materials that are broadcast to ditches are difficult to collect once they become saturated with respect to P. Therefore, any P that is sorbed by broadcast material will remain within the ditch system. There is a risk that the P sorbed by broadcast materials will some day be released to ditch flow, either by

erosional processes or by desorption of the P. Thus, despite the low cost of broadcasting materials to ditches, the anticipated effectiveness of this method of substantially affecting P in ditch flow is low.

Flow Dosing. One approach to reducing dissolved P that has been demonstrated in a variety of ditch systems involves the regulated addition, or “dosing” of a PSM (typically liquid alum) into flowing ditch water. This concept has been applied to reducing P concentrations in city storm water drainage (Johnson Engineering 2005; Lind 2002), dairy manure effluent (Jopson 2004; Lind 2002), and irrigation return flow (Leytem and Bjorneberg 2005). Although this practice has been shown to significantly reduce dissolved P concentrations, the cost of an automated dosing/injection system can be high. Another concern with dosing is that the sorbed P is not removed from the ditch system. Therefore, dosing techniques can be improved by adding a “trap” for the newly sorbed P, so that it is concentrated at one point where it can eventually be collected (e.g., a sand filter or settling basin downstream of the dosing point). Liquid alum is ideally suited to trapping sorbed P from dosing systems as the alum forms flocs that readily settle from the water column.

Flow-Through Structures. In comparison with broadcasting PSMs, a variety of structures can be used to improve contact between PSMs and ditch flow. Such structures involve greater initial investment to install, but, over the long-term, have the potential to sustain water quality improvements resulting from the use of the PSMs. An effective P removal structure must be able to conduct water through it at a rate sufficient to capture the majority of flow during average precipitation events and sorb P quickly relative to the flow rate. The rate in which a PSM can remove P from a solution is key to determining its suitability for a certain P removal structure or situation.

Typically, contact between ditch water and PSMs in P removal structures declines as flow increases as the flow bypasses the materials due to their fixed hydraulic conductivity. Basic designs for P removal structures simply involve placing PSMs within a material (e.g., landscaping fabric) that is in turn located within in a ditch where it comes into contact with flow. For instance, a “sock” of fabric may be filled with PSM and layed across the bottom of a ditch. With such designs,

the proportion of flow coming into contact with the PSM is primarily a function of the hydraulic conductivity of the material and the profile of the material in the ditch.

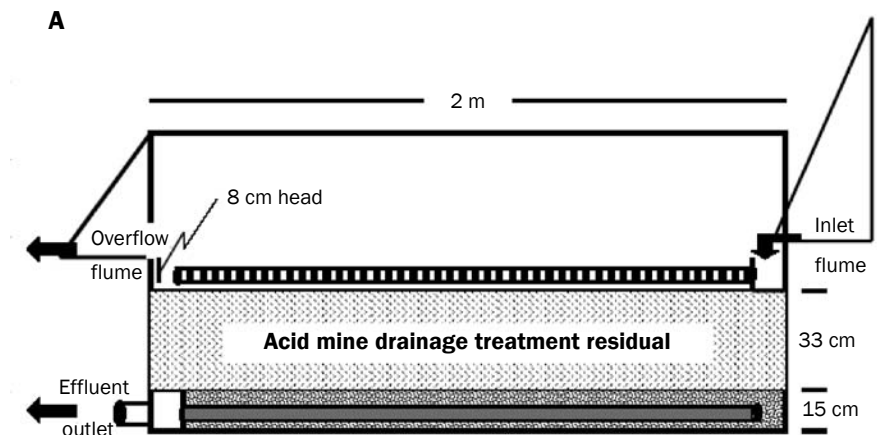
More involved designs for P removal structures concentrate ditch flow to improve contact with PSMs. Examples include flume-type structures that channel flow through a screen of PSMs and retention ponds with sub-surface drainage in which a dam diverts flow through a bed of PSMs. With such systems, ditch water is forced through the PSMs and the materials are not lost in ditch flow, allowing them to be eventually removed from the structure when they become saturated with P. It is important to note that these types of designs may be difficult to implement in some settings. For instance, there may be insufficient gradient within a ditch to allow flow to use retention-type designs that require sub-surface drainage.

Developing a Flow-Through Structure for Phosphorus Removal in a Small Ditch Draining Point and Nonpoint Sources

The concept of removing P from ditch flow using PSMs was tested at the University of Maryland Eastern Shore research farm located on the Delmarva Peninsula. The research farm was formerly a broiler chicken operation with over 25 years of intensive litter application to farm fields and an average Mehlich-3 P concentration of field soils exceeding 400 mg kg^{-1} ($0.00638 \text{ oz lb}^{-1}$). Losses from ditches draining the farm are considerably higher than those previously reported for the area, and are described in detail by Kleinman et al. (Forthcoming). One ditch, which drained less than one ha of land, was the site of several barns and a litter stacking area. That ditch yielded approximately 13 kg (28.6 lb) soluble P from June, 2005 to May, 2006. With the exception of one extreme flow event associated with tropical storm Cindy that occurred on July 7, 2005, ditch flow monitoring data from January 2005 to May 2006 showed that flow exceeded 5.71 L s^{-1} ($0.2 \text{ cubic feet per second [cfs]}$) only 20% of the time, but that flow did account for 40% of the flow in the ditch. Due to the size of the ditch, excessive dissolved P concentrations, and typical flow rates, a P removal structure was developed for that ditch to remove dissolved P and other possible contaminants from ditch flow water using an industrial byproduct. Our goal was to design a structure to reduce

Figure 3

(A) Cross sectional diagram of the phosphorus removal structure that is partially buried to accommodate the inlet flume installed at the ditch bottom. (B) Phosphorus removal structure.



Note: The effluent pipe discharges at a point down stream that allows for a 1% slope from the effluent outlet.

soluble P losses through this ditch by 50% and serve for a period of one year before replacement of the PSM would be required.

Phosphorus Removal Structure Design. Several PSMs were characterized for potential use in the structure (figures 1 and 2), including fly-ash, drinking WTRs, bauxite processing waste, waste gypsum, and three different acid mine drainage residuals. Based on the screening results, an acid mine drainage

residual was chosen for the following reasons: low risk of causing potential contamination (low heavy metals concentrations, low soluble Na, near neutral pH), highest P sorption capacity compared to the other materials, fast P sorption kinetics due to high Al/Fe contents, and high hydraulic conductivity. This material is well suited for a flow-through structure at this site since its high hydraulic conductivity will allow large volumes of

water to pass through, and its relatively fast P sorption kinetics will allow for efficient P removal of the passing water.

The P removal structure was designed to allow sampling and measurement of incoming ditch flow through a flume, distribute it over the surface of a PSM, collect and sample the effluent through a tile drain that empties further down the ditch, and measure overflow during events that exceed the structure maximum flow rate (figure 3). Since the PSM used in the field experiment was mainly Fe based, the structure was designed to allow free drainage during dry periods without ditch flow so that the material would not become reduced, which would result in the dissolution of Fe and any P associated with it (Koski-Vahala and Hartikainen 2001).

The acid mine drainage residual that was selected for use has a P sorption capacity of 48 mg P g⁻¹ (7.66 oz lb⁻¹) material as measured by the single point P isotherm method. To meet the goal of sorbing >7 kg (15.4 lb) of P, a total mass of approximately 200 kg (440 lb) of acid mine drainage residual was needed. Based on the hydraulic conductivity of the acid mine drainage material as determined by measuring flow under a constant head, a structure with a horizontal surface area of 1 m × 2 m (3.28 ft × 6.56 ft) resulted in a flow rate of 5.71 L s⁻¹ (0.2 cfs) for the designed structure.

Since one objective of our P removal structure was to sequester P from passing water while preventing losses of the PSM from the structure to the water body, a sand filter layer was placed directly underneath the PSM. We also incorporated a “trash screen” into the structure in order to allow for easy removal of materials that collect on top of the PSM. Because one of the purposes of a P removal structure is to permit P saturated materials to be removed from the system, the box design with removable trash screen allows for easy access, removal, and replacement of PSMs.

Phosphorus Removal Structure Performance. The first runoff producing event that occurred after installation was an extreme event associated with tropical storm Ernesto that passed over the region (approximately 30 cm [12 in] of precipitation in 24 hours). The P removal structure was able to capture approximately 43,000 L (1,135 gal) of ditch flow. During peak flow, dissolved P concentrations were ~16 mg L⁻¹ (2.12 oz gal⁻¹) while

low flow conditions resulted in P concentrations between 6 and 7 mg L⁻¹ (0.79 and 0.92 oz gal⁻¹). Seventy-five to 95% of total P in ditch flow was in the dissolved form. This high proportion of dissolved P in ditch flow justifies the use of a P removal structure, since particulate P could be reduced by simply reducing erosion or capturing sediment. A total of 99% of dissolved P was removed from ditch water that flowed through the structure, equivalent to 0.54 kg (1.3 lb) of P. In addition to P, the structure was also successful at sequestering metals from ditch flow. Aluminum and Fe concentrations were reduced by the structure, suggesting that Al and Fe minerals that made up the PSM were not soluble.

Among heavy metals dissolved in ditch water, the P removal structure reduced As concentrations to near zero, removing 63% of As from ditch flow that passed through the structure. Copper and Zn loads of captured ditch flow were also reduced by 99% and 94%, respectively. Similar reductions were also observed for Mo and Ni. Sequestration of heavy metals by the acid mine drainage residual material in the P removal structure is expected since Fe and Al oxyhydroxides are known to strongly chemisorb heavy metals (Sparks 2003). Elevated As, Cu and Zn concentrations in ditch flow likely originated from adjacent agricultural fields, since industrial sources are not known to be present near this location. The 30-year history of poultry litter application to certain fields or prior use of certain pesticides are likely the sources of As, Cu, and Zn (Mitchell and Tu 2006; Jackson et al. 2003; Wood et al. 1996).

Phosphate Removal Structure Limitations. Although the P removal structure performed as expected during the first flow event after installation, the goal of removing 50% of the annual soluble P loss may not be realized due to the importance of extreme events. When flow from tropical storm Cindy that occurred on July 7, 2005, is included in the ditch flow monitoring data that were used for the design parameters, the flow exceeded 5.71 L s⁻¹ (0.2 cfs) approximately 25% of the time during flow events, but that flow accounted for 87% of the flow in the ditch. Whereas it seemed reasonable to exclude this event and base the design on average events, the very first event after installation illustrated the importance of extreme events. The P removal structure was only able to treat 9% of the flow during that event.

Additionally, the requirement that the structure be free draining during dry periods to prevent reduction of Fe oxides required a 50 cm (20 in) drop between the ditch bottom and the outflow tile at the base of the structure that drained the PSM. This requirement does pose a limitation to wide spread adoption of this specific design. At our site, the shallow field ditch was connecting with a much deeper public drainage ditch such that the required height difference between box inflow and outflow could be obtained.

Summary and Conclusions

Phosphorus removal structures provide several advantages over traditional use of using PSMs. Structures can sequester dissolved P from ditch flow (or other water bodies) without contaminating the system with PSMs, while also allowing for the eventual removal of P from the ditch. This aspect is particularly important since traditional applications of PSMs (such as alum) to water bodies only reduce the solubility of P, rather than removing P from the system. Most PSMs can be classified into two groups: Ca/Mg and Al/Fe based. The Ca/Mg based PSMs remove P by precipitation reactions that occur much slower compared to adsorption (chemisorption) reactions of P with Al/Fe oxides/hydroxides. Therefore, a good Ca/Mg based PSM for use in a P removal structure should have high Ca/Mg water solubility, which is typically dependent on pH and chemical form. Further, the pH of a proper PSM should fall between 5.5 and 7.5 for ideal P sorption and to prevent negative effects on aquatic systems. Potential PSM for use in a P removal structure should also not have elevated electrical conductivity, heavy metals, or Na concentrations. Rapid hydraulic conductivity and P sorption kinetics of PSM is essential to removing dissolved P from passing water in a confined “flow-through” P removal structure where space is limited. If possible, we recommend the use of a “flow-through” P removal structure design since water flowing through (rather than around) contained PSMs will have maximum contact.

In general, Ca/Mg based materials are less efficient and sorb P much slower compared to Al/Fe based materials; therefore Al/Fe based materials are necessary for systems with relatively high flow rates. In addition, we recommend that P removal structures be constructed with an overflow device, a filter

layer of sand below PSM layer to prevent loss of material to the aquatic system (ditch), trash screen to prevent large debris from entering structure, free drainage when Fe based materials are used, and easy access to materials for removal/replacement.

We described one example of the development of a P removal structure for use in a small ditch draining point and non-point sources of P. The P removal structure employed in this study contained acid mine drainage residuals as a PSM and sequestered 99% of dissolved P that flowed through the structure (0.54 kg [1.19 lb]) during a single 24-hour runoff event. From the standpoint of quantifying the water quality improvement benefits of a management practice, P removal structures offer an additional advantage in that the amount of dissolved or total P removed by a structure is easily quantified compared to estimation of potential P load reductions via riparian buffer strips or other nonpoint type practices.

References

- Basta, N.T., J.R. Ryan, and R.L. Chaney. 2005. Heavy metal and trace element chemistry in residual-treated soil: A review of impacts on metal bioavailability and sustainable land application. *Journal of Environmental Quality* 34:49-63.
- California Regional Water Quality Control Board. 2001. Status report on Lake Elsinore water quality restoration activities. www.swrcb.ca.gov/rwqcb8/pdf/06-01-01/item17.pdf.
- Callahan, M.P., P.J.A. Kleinman, A.N. Sharpley, and W.L. Stout. 2002. Assessing the efficacy of alternative phosphorus sorbing soil amendments. *Soil Science* 167:539-547.
- Chuan, M.C., G.Y. Shu, and J.C. Liu. 1996. Solubility of heavy metals in a contaminated soil: Effects of redox potential and pH. *Water, Air, and Soil Pollution* 90:543-556.
- Dao, T.H., E.E. Codling, and R.C. Schwartz. 2005. Time-dependent phosphorus extractability in calcium and iron treated high phosphorus soils. *Soil Science* 170:810-821.
- Dayton, E.A., and N.T. Basta. 2005. A method for determining the phosphorus sorption capacity and amorphous aluminum of aluminum-based drinking water treatment residuals. *Journal of Environmental Quality* 34:1112-1118.
- DeLaune, P.B., P.A. Moore, Jr., D.K. Carman, A.N. Sharpley, B.E. Haggard, and T.C. Daniel. 2004. Development of a phosphorus index for pastures fertilized with poultry litter—factors affecting phosphorus runoff. *Journal of Environmental Quality* 33:2183-2191.
- Dou, Z., G.Y. Zhang, W.L. Stout, J.D. Toth, and J.D. Ferguson. 2003. Efficacy of alum and coal combustion by-products in stabilizing manure phosphorus. *Journal of Environmental Quality* 32:1490-1497.
- Eghball, B., J.F. Shanahan, G.E. Varvel, and J.E. Gilley. 2003. Reduction of high soil test phosphorus by corn and soybean varieties. *Agronomy Journal* 95:1233-1239.
- Elliott, H.A., G.A. O'Connor, P. Lu, and S. Brinton. 2002. Influence of water treatment residuals on phosphorus solubility and leaching. *Journal of Environmental Quality* 31:1362-1369.
- Gallagher, R.N., C.O. Weldon, and F.C. Boswell. 1976. A semiautomated procedure for total nitrogen in plant and soil samples. *Soil Science Society of America Journal* 40:887-889.
- Hanks, R.J., and G.L. Ashcroft. 1980. *Applied Soil Physics*, 62-65. New York: Springer-Verlag.
- He, Z.L., M.K. Zhang, P.J. Stoffella, X.E. Yang, and D.J. Banks. 2006. Phosphorus concentrations and loads in runoff water under crop production. *Soil Science Society of America Journal* 70:1807-1816.
- Holz, J.C., and K.D. Hoagland. 1999. Effects of phosphorus reduction on water quality: Comparison of alum-treated and untreated portions of a hypereutrophic lake. *Journal of Lake and Resource Management* 15:70-82.
- Hsieh, C., A.P. Davis, and B.A. Needelman. Forthcoming. Bioretention column studies of phosphorus removal from urban stormwater runoff. *Water Environment Research*.
- Ippolito, J.A., K.A. Barbarick, D.M. Heil, J.P. Chandler, and E.F. Redente. 2003. Phosphorus retention mechanisms of a water treatment residual. *Journal of Environmental Quality* 32:1857-1864.
- Jackson, B.P., P.M. Bertsch, M.L. Cabrera, J.J. Camberato, J.C. Seaman, and C.W. Wood. 2003. Trace element speciation in poultry litter. *Journal of Environmental Quality* 32:535-540.
- Johnson Engineering. 2005. Literature review of stormwater treatment best management practices in Florida. Report prepared for Lee County Board of County Commissioners. Fort Myers, FL.
- Jopson, H.L. 2004. Nutrient and solids removal by lime and alum treatment of flushed dairy manure. M.S. thesis, University of Florida, Gainesville.
- Kleinman, P.J.A., A.L. Allen, B.A. Needelman, A.N. Sharpley, P.A. Vadas, L.S. Saporito, G.J. Folmar, and R.B. Bryant. 2007. Dynamics of phosphorus transfers from heavily manured Coastal Plain soils to drainage ditches. *Journal of Soil and Water Conservation* 62(4):225-235.
- Koski-Vahala, J. and H. Hartikainen. 2001. Phosphorus mobilization from various sediment pools in response to increased pH and silicate concentration. *Journal of Environmental Quality* 30: 546-552.
- Leytem, A.B., and D.L. Bjorneberg. 2005. Removing soluble phosphorus in irrigation return flows with alum additions. *Journal of Soil and Water Conservation* 60:200-208.
- Lind, C.B. 2002. Livestock waste management and lake rehabilitation. *Clearwaters* 32(1). <http://www.nywea.org/clearwaters/pre02fall/321030.html>.
- Lindsay, W.L. 1979. *Chemical Equilibrium in Soils*. New York: John Wiley and Sons.
- Loeppert, R.H., and W.P. Inskeep. 1996. Iron. *In Methods of Soil Analysis*, Part 3, ed. D.L. Sparks, 646-647. SSSA Book Ser. 5. Madison, WI: SSSA.
- McBride, M.B. 1994. *Environmental Chemistry of Soils*. New York: Oxford University Press.
- McKeague, J., and J.H. Day. 1966. Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science* 46:13-22.
- Minneapolis Park and Recreation Board. 2001. Good news for powderhorn lake (and its neighbors!). <http://www.minneapolisparke.org/default.asp?PageID=708>.
- Mitchell, C., and S. Tu. 2006. Nutrient accumulation and movement from poultry Litter. *Soil Science Society of America Journal* 70:2146-2153.
- Moore, P.A., Jr., and D.M. Miller. 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. *Journal of Environmental Quality* 23:325-330.
- Moore, P.A., Jr., T.C. Daniel, J.T. Gilmour, B.R. Shreve, D.R. Edwards, and B.H. Wood. 1998. Decreasing metal runoff from poultry litter with aluminum sulfate. *Journal of Environmental Quality* 27:92-99.
- Murphy, J., and J.R. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27:31-36.
- Novotny, V. 2003. *Water Quality*, Second Ed. New York: J. Wiley and Sons.
- Pautler, M.C., and J.T. Sims. 2000. Relationships between soil test phosphorus, soluble phosphorus, and phosphorus saturation in Delaware soils. *Soil Science Society of America Journal* 64:765-773.
- Peak, D., J.T. Sims, and D.L. Sparks. 2002. Solid-state speciation of natural and alum-amended poultry litter using XANES spectroscopy. *Environmental Science and Technology* 36:4253-4261.
- Penn, C.J., and R. Bryant. 2006. Application of phosphorus sorbing materials to streamside cattle loafing areas. *Journal of Soil and Water Conservation* 61:303-310.
- Peters, J.M., and N.T. Basta. 1996. Reduction of excessive bioavailable phosphorus in soils by using municipal and industrial wastes. *Journal of Environmental Quality* 25:1236-1241.
- Rhoton, F.E., and J.M. Bigham. 2005. Phosphate adsorption by ferrihydrite-amended Soils. *Journal of Environmental Quality* 2005 34:890-896.
- Sharpley, A.N., S.J. Smith, O.R. Jones, W.A. Berg, and G.A. Coleman. 1992. The transport of bioavailable phosphorus in agricultural runoff. *Journal of Environmental Quality* 21:30-35.
- Sims, J.T., R.R. Simard, and B.C. Joern. 1998. Phosphorus loss in agricultural drainage: Historical perspective and current research. *Journal of Environmental Quality* 27:227-293.
- Stout, W.L., A.N. Sharpley, and H.B. Pionke. 1998. Reducing soil phosphorus solubility with coal combustion by-products. *Journal of Environmental Quality* 27:111-118.
- Sparks, D.L., T.H. Carski, S.E. Fendorf, and C.V. Toner IV. 1996. Phosphorus. *In Methods of Soil Analysis*, Part 3, ed. D.L. Sparks, 1275-1308. SSSA Book Series No. 5. Madison, WI: SSSA.
- Sparks, D.L. 2003. *Environmental Soil Chemistry*. Academic Press, USA.
- Warren, J.G., S.B. Phillips, G.L. Mullins, D. Keahey, and C.J. Penn. 2006. Environmental and production consequences of using alum-amended poultry litter as a nutrient source for corn. *Journal of Environmental Quality* 35:172-182.
- Wood, B.H., C.W. Wood, K.H. Yoo, K.S. Yoon, and D.P. Delaney. 1996. Nutrient accumulation and nitrate leaching under broiler litter amended cornfields. *Communications in Soil Science and Plant Analysis* 27:2875-2894.