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# Impacts of Phosphorus Lost from Agricultural Fields on Water Quality and Gypsums Capacity to Reduce the Loss to Tile Drainage

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# Impacts of Phosphorus Lost from Agricultural Fields on Water Quality and Gypsums Capacity to Reduce the Loss to Tile Drainage

By

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**Acknowledgments**

To those who shaped, molded and motivated me throughout life.  Thank you.

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## A LITERATURE REVIEW

### Nutrients and Water Quality

Water quality impairment is a growing issue in the United States and many other countries. It is no surprise that humans play a large part in the creation of that problem. In the United States alone, more than 100,000 miles of rivers, close to 2.5 million acres of lakes, reservoirs and ponds, and more than 800 square miles of bays and estuaries are classified as having poor water quality due to excess sediment or nutrient levels (EPA, 2019). Human impacts on poor water quality come from a number of sources, with agricultural practices being one of the leading culprits for many water bodies. Agricultural impacts come primarily from excess loss of nitrogen (N) and phosphorus (P) from fields to streams that reach major surface water bodies (EPA, 2019). Natural soil levels of these two nutrients often limit crop growth, driving the need for their application in large amounts for profitable farming. This is why, along with potassium, they are known as macronutrients.

Some forms of N in drinking water, such as nitrate and nitrite, may directly cause health problems in humans. One needs to look no further than what has happened in the Des Moines, Iowa, area over the past couple of decades as an example of what needs to be avoided. Nitrate concentrations in surface waterways have increased about 50% since 1999 (Schapiro, 2018). Nitrate pollution alone increased five times between 2002 and 2016, much of which is coming from agriculture (Schapiro, 2018). The end result often is low-quality drinking water for local residents and those downstream. Residents who are exposed to this type of nutrient polluted water may face increasing risk of cancer and birth defects among other health concerns (Schapiro, 2018).

Most often, however, the harmful effects of both N and P occur indirectly by promoting excessive growth of algae and other microorganisms in surface water bodies. Excessive N and P application rates for crops or poor nutrient and soil management practices facilitate the loss of these nutrients from fields. During intense rain events, surface runoff and leaching through the soil profile carry N and P to surface or groundwater. Excessive N and P levels in surface water bodies lead to algae blooms, eutrophication, and hypoxic zones, all of which impair aquatic ecosystems (EPA, 2019). Eutrophication and hypoxic zones occur when an excessive supply of these nutrients encourages the growth of algae and microorganisms that breakdown organic matter. When the algae die, the oxygen in the water is depleted, effectively suffocating other organisms (EPA, 2019). Moreover, extreme eutrophication may stimulate the growth of bacteria that release toxins, which can lead to health problems for humans and other animals that come in contact with the polluted water (EPA, 2019). Although both N and P can promote algae growth and eutrophication of water bodies, P usually limits algae growth in freshwaters whereas N usually is the limiting nutrient oceans, bays, and gulfs.

## Phosphorus and Water Quality

The US Geological Survey points to nonpoint agricultural contributions as one of the largest contributors of P to surface water (Jiang et al., 2019). The loss of P to waterways does not typically bring about negative impacts without certain conditions to foster the issue. Severe algae blooms are most prominent in areas where currents are slow or where water is shallow and stagnant (EPA, 2019). These areas build up levels of nutrients in the water, promote algae growth, and retain both algae and organic matter produced with algae death. This type of scenario played out in northwestern Ohio, in 2014. In August of that year, citizens living in the city of Toledo woke up to the news that their tap water, derived from Lake Erie, was too dangerous to drink, cook, bathe, or otherwise use (Lee, 2014). An algal bloom was the cause, but contrary to popular belief, the toxin causing the issue, in this case, was not produced by algae. It was produced by a cyanobacterium known as Mycrocystis (Lee, 2014), whose excess growth often is a consequence of eutrophication. If ingested, the toxin can cause paralysis and seizures in humans and animals (Lee, 2014). This bacterium prefers warm (above 60 degrees Fahrenheit) and nutrient rich waters, which encourages algae growth (Wilson et. al, 2018). Lake Erie is the warmest, shallowest, southernmost, and most nutrient-rich of the Great Lakes as shown in Figure 1 (Wilson et al., 2018).

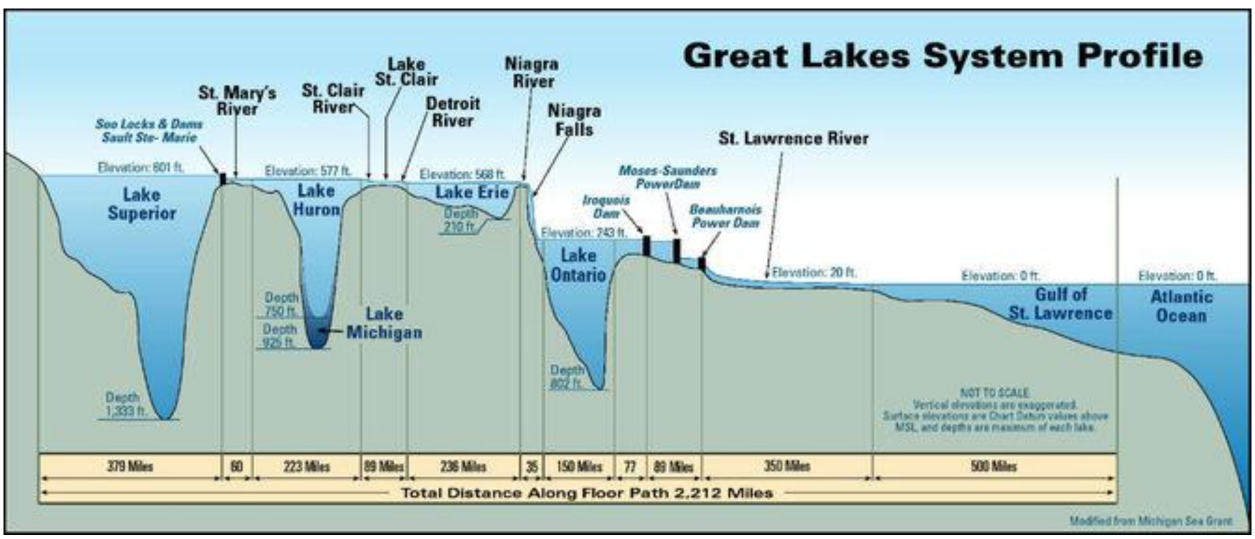


Figure 1: Great Lakes depth and water flow to the Atlantic Ocean (Butauski, 2019).

The amount of P delivered to surface water bodies is influenced by various elements, usually grouped into source and transport factors (Sharpley, 1985; Lemunyon and Gilbert, 1993; Sharpley et al., 1994, Mallarino et al., 2002). Source factors include soil physical and chemical properties, soil P level, the P source, rate and method of application among others. Midwestern soils can contain as much as 500-1000 ppm of total P in organic or inorganic forms, which can vary greatly with depth. Most of that nutrition is unavailable to plants (Schulte and Kelling, 1996). Fertilization and manure applications over decades increased these levels in many soils, mainly in the surface 15 to 20 cm. Most P fertilizers used today contain mostly water-soluble P and a small proportion that becomes soluble after application to moist soil. Animal manures, in contrast to the popular belief, have variable but usually high proportions of organic and inorganic P compounds that are soluble or quickly solubilize or hydrolyze in the soil and behave as P fertilizers (Barbazan et al. 2009; Kaiser et al, 2010; Sawyer and Mallarino, 2016). Soluble P applied to a soil is rapidly retained by soil constituents in most situations within hours or days. This is due to precipitation as new compounds, from rapid reaction with soil cations in the soil solution, adsorption by some minerals (such as calcium carbonates and both iron and aluminum oxides and hydroxides), and colloids with positively charged surfaces (Schulte and Kelling, 1996). The P retained by soils most often becomes part of the so-called "labile" soil P pool, which becomes available to plants as they start taking up P, and is the fraction of soil P that soil-test methods recommended for crop production attempt to measure. This is because this soil pool fraction relates better to crop P sufficiency and response to fertilization (Tisdale et al., 1993). In some soils, however, a variable proportion of retained P can evolve over a period of weeks or months to forms of low crop-availability. The loss of P availability over time generally happens in soils with extremely acid pH having exchangeable aluminum (such as in some southern US regions and forest-derived soils), alkaline due to presence of calcium carbonate (such as in the northwestern Corn Belt, northern Great Plains, and some western states), with high levels of Fe oxides and hydroxides (such as many volcanic soils and some tropical soils), and clay textured soils (Tisdale et al., 1993). In all soils, except very sandy soils, however, the reaction of applied soluble P with soils results in very low soluble P in the soil solution a few days or weeks after application.

The transport factors affecting P delivery from the soils to groundwater or surface water bodies in combination with P application timing and placement often are more important than the source, although there are significant interactions among these. The climate is an important factor because it is characterized by amounts of rainfall or snowfall as well as seasonal patterns and intensity. Landscape factors include field slope which affects soil and water loss; presence of subsurface drainage tiles that collect and deliver much water and P that would go to deep into the soil profile, underlying material, or groundwater; and proximity to a stream among others (Sharpley et al., 1994; Sims et al., 1998). The Iowa P Index (and others) is one example of assessment tools developed to estimate the relative contribution of various interacting factors to the risk of P loss from fields. The Iowa P index is one of the few that consider P loss with subsurface drainage (Mallarino et al., 2002; USDA-NRCS, 2002).

Phosphorus can be delivered to surface water bodies as particulate P in sediment (P bound to soil particles) or dissolved P in surface water runoff or subsurface flow mainly through seepage and tile drainage. Given P reactions in soils discussed above, surface runoff often contains much higher proportion of particulate P than dissolved, although the proportion of dissolved P can be high in some conditions, such as in fertilized or manured fields managed with no-till and forages for hay or pasture. However, most or all the P in subsurface drainage is dissolved P, although a few times tile drainage may contain significant concentrations of sediment and particulate P if runoff gets to unprotected inlets (by grass or other means to filter soil form runoff) connected to subsurface tiles. Dissolved P is considered the most critical P form contributing to accelerated algae growth in surface waters. In the long-term, however, a major portion of the particulate P can be utilized by algae (and be a major cause of eutrophication) after physical and chemical changes that facilitate changes to dissolved P. This occurs at variable speeds depending on water flow, water chemistry, sediment agitation at the bottom of streams or larger water bodies, and other factors (Correll, 1998). In many watersheds of the Corn Belt, depending on the size and region, both surface runoff and tile drainage contribute significant amounts of particulate and dissolved P.

The most commonly measured P fractions in runoff are dissolved reactive P (DRP) and total P (which included dissolved and particulate P). The DRP fraction is measured after filtering runoff and is primarily orthophosphate since it is measured colorimetrically with the Murphy and Riley method (Murphy and Riley, 1962). In tile drainage, the most common P fractions measured are DRP by first filtering and also total reactive P (TRP), which is also measured with the Murphy and Riley method but without filtering because often times, little sediment is delivered by this transport mechanism.

According to Daloglu et al., (2012), more frequent large rainfall events and several changes in cultural practices among farmers are playing a primary role in the observed rise in P pollution. The conclusions by these researchers are based on the results of using the Soil and Water Assessment Tool (SWAT) to model DRP loss to surface water, from 1970 to 2010, in fields throughout the Sandusky River Watershed. The scientists used specific precipitation patterns to simulate those that were actually being observed. The results were clear. The frequency of strong rainfall events, which increased in the spring over that timeframe, played a direct part in increased modeled DRP loads (Daloglu et al., 2012). To bring further verification, the model was also run with observed weather events randomized over time as well as with the same weather events played out in reverse order. In other words, the reverse order simulation put 2010 rain events in the year 1970, 2009 events in 1971 and so on. As shown in Figure 2, the randomized evaluation flattened the curve of DRP discharge but reversing the weather patterns and putting 2010 rain events in 1970 decreased DRP loads. The findings pointed to cultural practices associated within the earlier decades as playing a larger role in the retention. Specifically, these practices would have been more conventional tillage with a larger amount of fertilizer being applied in the spring (Daloglu et al., 2012).

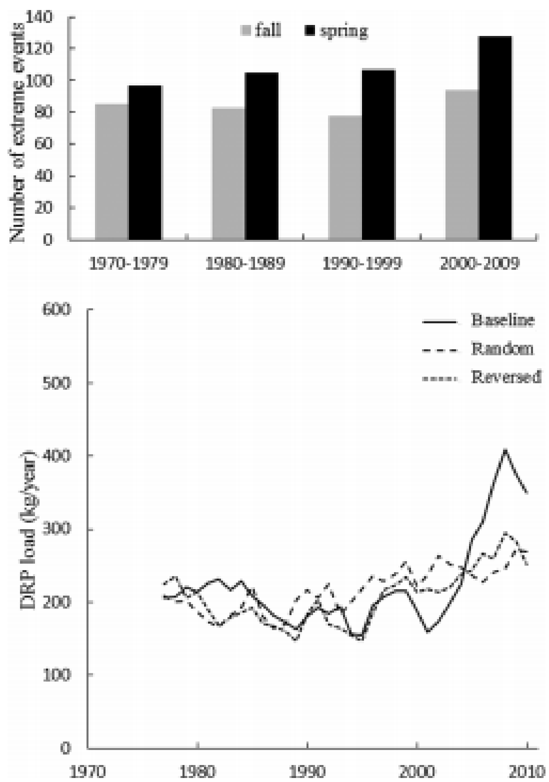


Figure 2: Number of extreme rainfall events and DRP loads for different modeled scenarios (from Daloglu et al., 2012).

## Subsurface Drainage and P Losses

In some areas of the United States, as in many other regions of the world, agriculture has shifted towards the use of tile drainage for more rapid excess water removal from soils. Artificial subsurface tile drainage systems and channels to deliver drainage to streams were installed many decades ago in the North Central Region of the USA (mainly during the 1920s and 1930s) to allow for crop production in large areas of native grasslands with poorly drained but potentially very productive soils. Tile drainage systems allow for crop production in areas that otherwise would be wetlands, and in surrounding field areas with moderate drainage, allows for more timely field operations. Tile drainage enables a grower to manage temporarily saturated soil conditions during periods of excessive rainfall or shallow water tables (University of Illinois Extension, 2017). The tiled area has increased rapidly in the North Central Region over the last decade probably due to more frequent excessive soil moisture in spring and increased farmer awareness of drainage benefits (University of Illinois Extension, 2017). In addition, the frequency of systemized tile with tighter spacing is increasing. Iowa, Illinois, Indiana, Ohio, and Minnesota have approximately 39 million hectares (about 40% of the total crop production area) with artificial subsurface drainage (USDA NASS, 2014).

Improving subsurface drainage typically reduces surface runoff, which often has higher concentrations of sediment and P than subsurface drainage (Gilliam et al., 1999; Baker et al., 2004). However, some argue that this yield-enhancing practice has a significant negative impact on surface waters of the surrounding areas. Tile drainage can increase the overall export of water, and perhaps P, from land due to increased connectivity of the landscape (Reid et. al., 2018). Studies conducted in Ohio on silt loam and clay loam soils showed that tile lines resulted in 41% of total water exports annually from the land in question (Reid et. al., 2018). This number likely changes based on spacing of tile lines and other field or watershed characteristics. Higher levels of water export with drainage have been found by other research, such as the 96% of total water export found over a 5-year period in a clay soil in Ontario (Reid et. al., 2018). In conditions with little slope and surface runoff, the P lost with tile drainage can be very large, higher than with runoff, and may mirror that with surface runoff in areas with moderate erosion and surface runoff.

There are two pathways water can take while flowing down the soil profile before reaching a tile buried in the soil. One is through the soil matrix and the other is through macropore flow. It is believed that macropore flow is the greatest contributor of P to water that flows through soil profiles to groundwater or to surface water bodies through tile lines, especially when water infiltrates soils shortly after P is applied, before is retained or absorbed by crops (Hooda et al., 1999; Reid et. al., 2018; Grant et al., 2019). This is because water that would enter tile lines directly from the soil matrix may carry less P as a result of more tortuous water flow through small diameter pores and a filtering process by the soil matrix even in high-testing soils given high P retention by most soils compared with nitrate, for example. The soil total porosity and the proportion of macropores is affected by numerous soil physical and chemical properties, and the proportion of macropores as well as the diameter and continuity also is affected by soil freezing and thawing, expansion and contraction due to moisture changes, root channels when roots die and decompose, and channels created by earthworms or other soil fauna. A study and discussion of soil macroporosity and the many factors affecting it is beyond the scope of this creative component, however.

Soil texture plays a very large role in the number of macropores, with fine textured soils containing more than coarse textured soils, whereas soil moisture before a rainfall event also plays a major role in controlling the amount and flow of infiltrating water through the soil profile. A study conducted on no till fields in Ontario by Grant el al., 2019 sought to quantify these effects through the use of blue stain in order to visualize vertical water movement in different soils having varying texture and antecedent moisture. They used four plots at each of two fields, each having topsoil with different textures. One with clay texture and the other with silt loam. A simulated rainfall event was applied to two plots at each site to prewet the soil and none to the other two plots before conducting the staining study. After one day, they sprayed a dye solution to all plots, and one day later excavated soil around the plots to quantify the degree of dying in eight profiles from each plot. Results summarized in Fig. 3 show significant preferential flow in both soils with both moisture treatments. However, they found that the finer-textured soil had deeper dye penetration but more dispersed concentration than the silt loam soil, which indicates less penetration but greater concentration. The depth of penetration was the greatest in the dry clay soil, with a penetration of 100 cm. This increase was presumed to be from more macroporosity and especially the presence of desiccation cracks in the clay soil under dry conditions. Soil moisture did not seem to play a role in the silt loam profiles as the penetration was similar. Silt loam soils do not typically contain desiccation cracks, which likely explains a major portion of the difference between the moisture treatments. Another important takeaway from the study was the results observed for soil matrix dye penetration. Regardless of texture or moisture, this study showed very little soil matrix dye penetration. The results ultimately point to clay soils having the highest contribution to preferential flow pathways through the soil profile, with dry conditions increasing that result even further. The authors did not measure P concentrations in the leachates, but concluded that large rainfall events following dry conditions in fine-textured soils are more likely to transport P rapidly to tile drains due to increased water preferential flow, whereas P loss in other soils would be less affected by antecedent moisture.

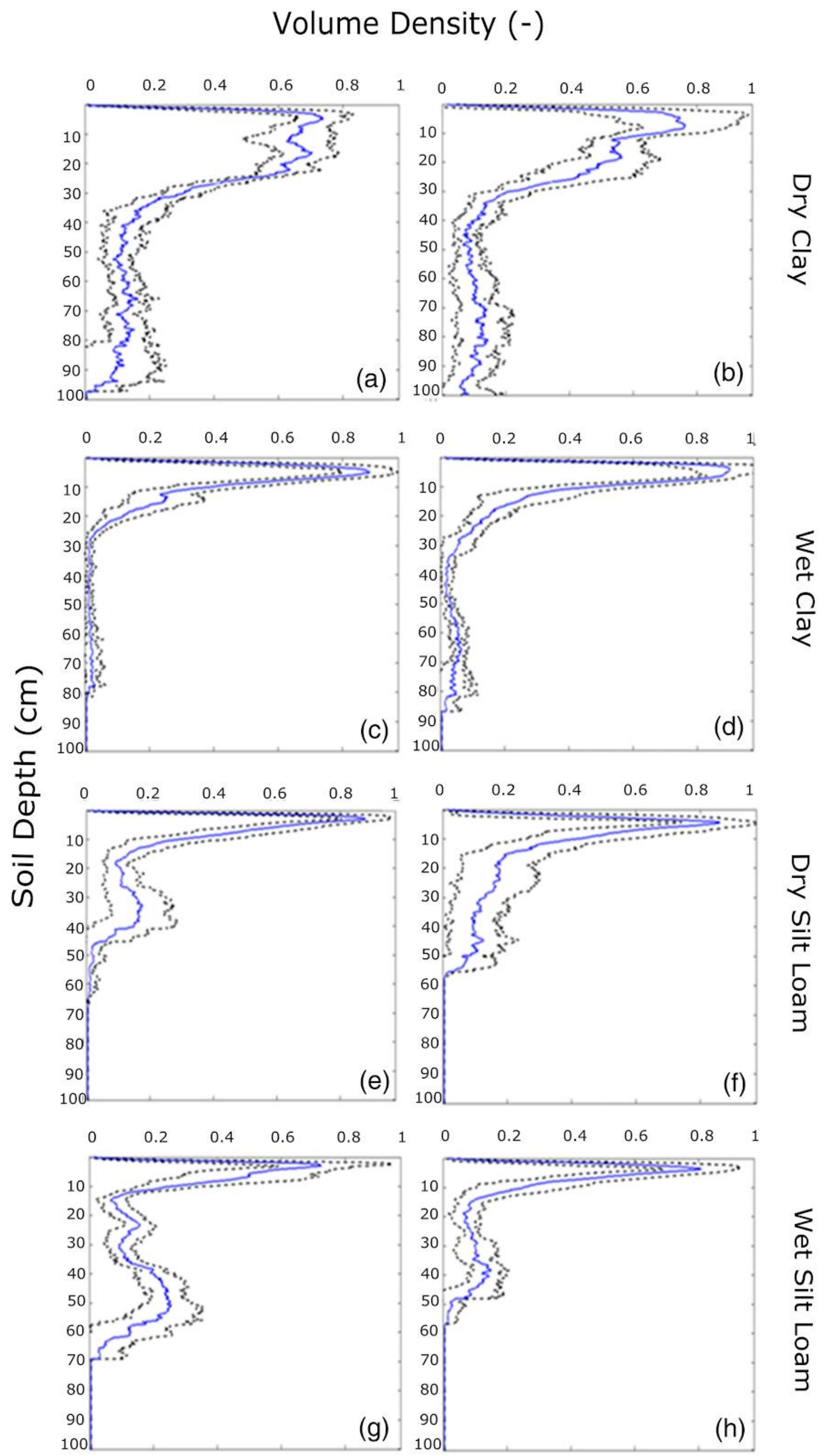

Figure 3: Mean volume density of soil stained at each depth (blue line) ± one standard deviation (dashed grey lines) across all eight profiles within a plot. The pair of horizontal graphs (a, b; c, d; e, f; and g, h) indicate results for the two plots at each field for each antecedent moisture treatments (from Grant et al., 2019).

Results of studies of vertical leaching through soil profiles should be interpreted with caution, however, because lateral water movement through subsoils is an important mechanism for delivering water and solutes to tile drains. This is because subsoil with few lateral macropores and low P levels can limit water and P transport to tiles. Research in Iowa subsoils, most of which have very low P concentration, show that subsoil can be very effective at filtering P moving laterally to tile drains (Allen et al., 2012).

The key to reduce P loss with tile drainage is to reduce water flow to tiles and/or reduce dissolved P concentration in water. Common management practices that are very effective at reducing P loss with surface runoff, such as no-till, cover crops, buffer strips, and subsurface P placement are not effective at reducing P loss through tile drainage. No-till, for example, can increase water and P flow through tile drainage by increasing water infiltration due to reduced surface runoff. No-till also can increase tile flow by increasing the number of continuous vertical soil macropores, which primarily are old root channels or worm holes (Grant et al. 2019). In addition, tile lines often bypass riparian zones as well as buffer strips along field edges where P in surface water is filtered. Edge of field bioreactors using wood chips or other carbonaceous crop materials that are effective at reducing nitrate concentration in tile drainage that leaves a field are not effective at reducing P loss (Pluer et al., 2016; Rambags et al., 2016), whereas use of biochar byproduct of diverse processes showed inconsistent results (Bock et al., 2914; Pluer et al., 2016). Ongoing research is studying what type of materials could be low cost and effective to be used as edge of field tools to reduce P concentration in tile drainage, but at the moment there are no specific recommendations or adoption in production agriculture (Antonio P. Mallarino, Iowa State University Extension, personal communication).

## Potential Value of Gypsum and Alum Soil Amendments to Reduce P Loss from Fields

Researchers and professionals are actively seeking ways to maintain or enhance the sustainability of crop production by improving soil chemical or physical properties and reduce dissolved P loss from agricultural fields. Many farmers are using soil and water conservation practices such as no-till, cover crops, extended rotations with forages or pastures, and others. One additional way farmers and researchers have begun to stem the tide is by exploring the use of soil amendments such as alum (aluminum sulfate) and gypsum (calcium sulfate). These products have been commonly used in agriculture for other purposes, and a brief review of their properties and common use is worthy.

### Gypsum and Alum as a Source of Sulfur and Soil Amendment

Gypsum is found naturally, with different degrees of crystallization and purity. It generally results from the evaporation of saline lake and sea water over geological time periods and is common in sedimentary deposits, although it also is formed in hot springs, from volcanic vapors, and sulfate solutions that crystallize in veins or caves. The white or gray-colored rocks are mined from open-pit or underground deposits, then crushed, screened, and used for a variety of purposes with or without further processing. Under geological conditions of high temperature and pressure or by artificial heating, gypsum is mostly anhydrite ($CaSO_4$ with no water), but agricultural gypsum generally is hydrated, is not treated with heat or chemicals, and consists of

$CaSO_4 \cdot 2H_2O$. Hydrated gypsum is sparingly soluble in pure water, but still is more soluble than limestone in soils with neutral or alkaline pH. When applied to soils, gypsum solubility is higher than in pure water and the dissolution rate depends on several factors including degree of crystallization, particle size, soil moisture, and other soil properties (Tisdale et al., 1993). Gypsum dissolves in water or in the soil solution to release $Ca^{2+}$ and $SO_4^{2-}$ ions. As with gypsum, alum is also found naturally. It is sometimes found in the almost pure aluminum sulfate form, which is not hydrated [$Al_2(SO_4)_3$] but often can be. Alum is also found as $XAl(SO_4)_2 \cdot H_2O$), where X is a monovalent cation such as potassium or ammonium. Alum with only Al or with ammonium ($NH_4^{1+}$) is used for several industrial processes, to remove excess P from industry wastewater or by water treatment plants. It is soluble in water and releases $Al^{3+}$ and $SO_4^{2-}$ ions.

Sulfur (S, a secondary nutrient) deficiency for crops is becoming common in humid areas of the Midwest due to reductions of atmospheric S deposition from pollution controls. Both alum and gypsum products have S that solubilizes when applied to soils and could be used to supply S for crops. Gypsum is commonly used for these purposes, but alum is not, however, because alum acidifies soils, and its continued use decreases soil pH, increases solubility and exchangeable soil Al to potentially toxic levels for plants. Its use would also require large and frequent applications of limestone to maintain pH at optimum levels (Tisdale et al., 1993). Gypsum is among the best low cost and most commonly used source of S for field crops and also supplies calcium (Ca), which is another secondary nutrient (Tisdale et al., 1993; Franzen et al., 2006; Sawyer et al., 2016). However, there are very few soils and commodity field crops in the Midwest for which Ca is likely to be deficient, because Ca deficiency is typically only found in very sandy or lixiviated soils of poor mineralogy. Gypsum even at very high rates does not change soil pH in the vast majority of soils (may decrease pH in highly alkaline sodium (na)-affected soils and increases pH in extremely acidic soils with high levels of exchangeable Al), so liming is recommended to increase soil pH in acidic soils (Tisdale et al., 1993; Franzen et al., 2006).

Gypsum, through the supplied Ca, may also improve soil structure and water infiltration through the soil profile because Ca helps stabilize organic matter in soils and acts as a glue to agglomerate mineral soil particles into aggregates (Tisdale et al., 1993; Sparks, 2002). Also, Ca application helps leach soil soluble or exchangeable cations that are undesirable in high concentrations mainly in fine-textured soils developed on parent materials very poor in Ca-bearing minerals, fine-textured and highly alkaline soils due to high Na levels, and fine-textured soils with low organic matter and unusually high exchangeable magnesium (Mg) compared with Ca (Ilyas et al., 1993; Tisdale et al., 1993; Ritchey et al., 1995; Sparks, 2002; Favaretto et. al, 2006; Franzen et al., 2006; King et al., 2016). The beneficial effect of Ca amendments, even with no soil pH change, in soils affected by high Na levels is explained by lower ionic potential of Na (due to lower negative ionic charge and higher radius) compared with Ca. It has been observed that soils with very high Mg levels also may develop unfavorable physical properties and can reduce infiltration rates as compared with soils high in Ca. The main reason for this is smaller hydration ionic radius of Ca as opposed to Mg ions (Sparks, 2002), and hydrated Mg ions at very high exchangeable soil Mg/Ca levels are known to disperse clay particles as well as increase ponding of water at the surface level (Keren, 1989; Curtin et al., 1994). Applied Ca can decrease Na or Mg levels in the soil by outcompeting them at exchange sites, and because Ca increases clay flocculation and improves both soil aggregation and water infiltration. Therefore, gypsum additions can improve soil physical properties, supply Ca for crops in the few soils where it is deficient and facilitate leaching of Na or Mg from the soil when there is sufficient water infiltration by irrigation or high rainfall. However, soils with Ca deficiency for crops or soils affected by high Na or Mg levels are rare in the North Central Region.

For decades, mined gypsum had been the only source of agricultural gypsum in the world and the USA, is still the most used in Iowa and many states, and it is sold granulated or finely ground forms. Currently, however, another source of gypsum is becoming common particularly in states with coal-based power plants. This gypsum is flue gas desulfurization (FGD) gypsum, which is a byproduct of coal fired electrical power plants (Dontsova et al., 2005). It is created as fly ash from the coal combustion process is filtered in a limestone slurry and is marketed in powder or granulated forms. Very scarce research has compared effects of mined or byproduct gypsum sources on soil chemical or physical properties. There are no reasons to expect differences, however, because gypsum mined for agricultural use is hydrated and more soluble that naturally dehydrated or heated gypsum which usually is used for industrial or construction purposes (Dontsova et al., 2005). A study conducted by Amezketa et al. (2005) found no differences in crusting prevention between mined gypsum and byproduct gypsum from coal-burning power plants in non-sodic and sodic soils.

Because of the potential additional benefits of gypsum beyond S supply for crops, improvement of soil physical properties and perhaps reducing dissolved P loss from fields, a National Resources Conservation Service (NRCS) national conservation practice standard relating to gypsum amendments was released in 2015 (USDA-NRCS, 2015). This publication has suggestions for high gypsum application rates to increase soil cation exchange capacity (CEC), Ca saturation, and reduce dissolved P loss from fields. However, researchers and technical NRCS personnel in Iowa and other states of the western Corn Belt are uncertain if gypsum applied to rich prairie soils would have benefits outside of supplying S for crops (which has been shown in very different soils of other states) due to lack of local research.

Recent research in Iowa, Kansas, and Wisconsin showed that soil physical properties improvement with high rates of gypsum is unlikely in most soils and management practices of the central and western Corn Belt, where high organic matter and exchangeable Ca/Mg and Ca/Na ratios are common. Research in Wisconsin studied effects of several surface-applied rates of FGD on soil penetration resistance, hydraulic conductivity, bulk density, and aggregate stability within a year of application, at ten fields in watersheds draining to the Great Lakes (Buckley and Wolkowski, 2014). This study showed no effect on penetration resistance or hydraulic conductivity at any site, a positive decrease in bulk density at only two of the ten sites, and no effect of the lower application rates on aggregate stability at any site. In fact, high rates actually showed a decrease in aggregation at each site. Work in Kansas evaluated effects of gypsum byproduct of coal-burning power plants on crop yield and several soil health metrics in two, three-year trials managed with no-tillage in two non-sodic soils (Presley et al., 2018). The study showed no gypsum effects on soil bulk density, aggregate stability, and water infiltration in any trial or year. Recent Iowa work evaluated effects of mined gypsum, for soybean-corn-soybean rotations managed with no-tillage in two soils by applying several combinations of single initial rates and annual rates (Mallarino et al., 2020). Gypsum increased soil aggregate stability at a northeast Iowa site (Kenyon soil series) where gypsum did not increase crop yield, but not in a central Iowa site (Clarion soil series) where gypsum increased yield one year. Contrary to expectations, the soil in which gypsum improved aggregate stability had the highest organic matter (4.1% versus 3.1%) and also the strongest aggregate stability of the untreated control (soil pH, texture, CEC, and Ca saturation were approximately similar).

**Alum and Gypsum Amendments Effects on Dissolved P loss with Surface Runoff**

It is commonly known in the science and agricultural world that increased water infiltration rates through soil conservation practices can reduce soil and nutrient losses from farmland by reducing erosion and surface runoff. Since both alum and gypsum amendments affect soil aggregation and stability, in some conditions, and when added to soils combine with P in the soil solution, these products also may play a role in the loss of P with surface runoff.

Many studies since the 1990s have shown that alum mixed with solid poultry manure can greatly reduce dissolved P in surface runoff including flood water (Moore and Miller, 1994; Shreve et al., 1995; Smith et al., 2001; Moore and Edwards, 2007; Mallarino and Haq, 2012; McDowell and Norris, 2014; Torbert and Watts, 2014; Huang et al., 2016; Watts and Torbert, 2016; Dharmakeerthi et al., 2018). This is a practical and cost-effective practice for manure from turkeys and confined broiler operations but is not so practical for egg layer hens grown in cages. As was noted above, one inconvenience of alum is that with continued use it acidifies soils and results in high potentially phytotoxic Al levels. This is not typical however, at least for a few years with poultry manure, because it has a high calcium carbonate concentration stemming from high Ca in the diet and, in the case of egg layers, disposed eggshells. Even alum-treated manure can increase soil pH (Moore and Edwards, 2005).

Calcium phosphate formed from gypsum applications, has higher solubility than aluminum phosphates in pure water. In soils, this varies greatly however, because soil pH, proportions and concentrations of other cations in the soil solution, and both chemical and mineralogical properties of the soil that mediate dissolution and precipitation reactions can alter solubility. In contrast to alum, gypsum is more benign to soil health, plants, and the environment in general and usually is less costly compared with alum. Fewer and more recent studies have been conducted to assess the effects of gypsum when mixed with manure. The majority of studies have been conducted with field or indoor rainfall simulations and have shown that indeed, gypsum amendments can reduce loss of dissolved P with surface runoff (Torbert et al., 2005; Favaretto et al., 2006; Mallarino and Haq, 2012, Uusi-Kämppä, 2012; Endale et al., 2014; Adeli et al., 2017). The efficacy of the gypsum amendment varied greatly among studies due to variation in soil properties, P sources, the way either gypsum or P sources were applied, the type of soil cover (i.e., bare soil, grain crop residues, or established forage stands), and the timing of application in relation to time to runoff among other factors. Scarce research has compared gypsum products with different particle sizes. Recent research conducted at two Iowa sites evaluated effects of several rates of granulated or powdered gypsum applied alone or at the same time P fertilizer was applied (Mallarino and Haq, 2020). Just one site found a small reduction of dissolved or particulate P loss with surface runoff, and the two sources did not differ.

Comparison of results from the most relevant studies considered above suggests that the effectiveness of gypsum has been more variable and slightly less efficient than of alum. This type of comparison is risky, however, because of the differences among procedures and conditions of the studies. Few studies have compared alum, gypsum and other amendments effects on P loss from fields. An early incubation study (Moore and Miller, 1994) measured water-extractable P after mixing poultry litter with alum, sodium aluminate, quick lime, slaked lime, both calcitic and dolomitic limestone, gypsum, ferric and ferrous chloride, or ferric and ferrous sulfate. Treatments with alum, quick lime, slaked lime, iron chloride and iron sulfate were the most effective at reducing water-extractable P from the manure and was reduced from more than 2000 mg P $kg^{-1}$ to less than 1 mg P $kg^{-1}$. The effectiveness of gypsum and sodium aluminate was much lower, reducing water-extractable P by only 50 to 60%, and the effectiveness of the limestones was even lower. Torbert at al. (2005) worked with large boxes filled with soil having a sod cover, composted dairy manure, and rainfall simulations, and reported that iron sulfate amendment reduced P loss with runoff more than did limestone and gypsum. Field rainfall simulations in an Iowa research study, compared alum and gypsum capacities to reduce dissolved, bioavailable, and particulate P loss with surface runoff in two sites when mixed with egg layer poultry manure (Mallarino and Haq, 2012). The results showed much smaller benefits on both dissolved and total P loss stemming from gypsum compared with alum. Uusi-Kämppä et al. (2012) compared dissolved and total P loss with surface runoff in an indoor rainfall simulation study with blocks of undisturbed grassland soil high in P after treatment with gypsum, calcium carbonate, iron-rich gypsum, and ferric sulfate. Treatments included a first rainfall simulation and a second after freezing and thawing the soils. They reported that rainfall after freezing and thawing increased dissolved P loss with all amendments. Compared with the higher loss for an untreated control, dissolved P in surface runoff decreased 57 to 80% in the case of the iron amendments but dissolved P in runoff at the gypsum and calcium carbonate sites did not differ from the untreated control.

**Gypsum Amendment Effects on Dissolved P Loss with Subsurface Drainage**

With much information showing the benefits of alum and often to a lesser extent of gypsum at reducing dissolved P loss with surface runoff, it is possible that both products also may reduce dissolved P lost to tile drainage. The use of alum with this purpose is not practical or desirable for reasons explained before, except perhaps when applying egg layer manure. Therefore, no study was found in the literature concerning the use of alum to reduce P loss with tile or other forms of subsurface drainage, although reviewed studies with poultry manure incubation studies with water-soluble P extraction Moore and Miller (1994), strongly suggested that amendments with alum (and also iron chloride or iron sulfate) would be more effective than gypsum or limestone at reducing P loss with subsurface drainage. Anderson et al. (2018) used intact soil columns brought indoor from fields testing very high in P as a result of having received poultry manure treated with alum or untreated at different rates for a long time to study the effect of alum on P leaching through the soil profile. They leached the soils with water at intervals over a period of one year and reported that alum reduced total dissolved P and total P concentrations in leachate by 83 and 80%, respectively, compared with untreated manure.

Few field studies have evaluated effects of gypsum on P loss with subsurface tile drainage. A reason for this may be that field level studies of tile drainage are costly, especially when it comes to replication. The trials that have been conducted at the laboratory using soil columns or at the field have shown inconsistent results, and the reason is not entirely clear.

Indoor leaching studies through soil that is removed from a field and placed in columns with or without amendments can provide useful comparisons of potential P movement through soil but should be interpreted with caution. Zhu and Alva (1994) worked with a Florida sandy soil (Pineda series) in columns and reported 35 and 54% reduction of dissolved P leaching with the addition of 4500 and 9000 kg $ha^{-1}$ of gypsum, respectively, when the materials were placed on the surface of the soil columns. Leached P was further decreased by 74% when materials were mixed with the surface 2 cm of soil. Coale et al. (1994) used an organic Florida soil (Pahokee muck series) with pH 7.6 to 7.8 in columns 22-cm tall, and treatments were commercial agricultural gypsum, residue from a municipal drinking water treatment plant (composed of calcium oxide, aluminum sulfate, and a starch-based polymer), and commercial agricultural dolomitic limestone mixed with the top 8-cm depth at rates equivalent to 0, 4000, 8000, and 12000 kg $ha^{-1}$ of dry material. Gypsum reduced total dissolved P in the leachates significantly by approximately 20 to 40% across successive leaching and rates compared with the control and exceeded the other two materials as well. Favaretto et al., (2012) worked with an Indiana silt loam soil (Miami series) in columns 15-cm tall, and treatments were a control, analytical grade gypsum at a rate equivalent to 5000 kg $ha^{-1}$ applied to the surface of the columns, a similar gypsum rate mixed into the 2.5-cm depth, and alteration of five target exchangeable Ca/ Mg ratios. Gypsum applied to the surface or mixed into the 2.5-cm depth significantly decreased DRP in the leachates (by 36 and 43%, respectively) and the Ca/Mg rations did not have statistically significant effects. These results from this study should be interpreted with much caution, however, because the vast majority of the total P leached (71 to 85% across all treatments) was particulate P, which seldom is the case with subsurface drainage.

Field evaluations with tile drainage were even scarcer. A paired field-scale study was conducted to evaluate effects of successive FGD gypsum applications in two tiled fields in Mercer County, Ohio, with somewhat poorly drained Blount silt loam soil (King et al., 2016). No gypsum was applied to one field (drained area 3.7 ha) and 2240 kg $ha^{-1}$ was applied to the other field (drained area 4.5 ha) in fall 2013 (soybean residue, incorporated by vertical tillage) for the 2014 crop year (corn) and again in January 2015 for that crop year (no-till corn). The control and treatment fields average Mehlich-3 soil-test P levels were extremely high, testing at 481 and 498 ppm, respectively, which results from heavy manure application in previous years. Figure 4 shows a key graph from the published paper. In the year between the first and second gypsum application, DRP and total P concentrations in tile drainage were reduced by 21 and 10%, respectively, but there was no reduction in DRP and total P loads because gypsum increased tile flow. The authors did not calculate separate results for the year after the second gypsum application, and instead presented the accumulated results for the two periods. The accumulated results showed that the gypsum applications reduced DRP and TP concentrations in drainage and also reduced DRP load by 35% and total P load by 15%. The authors pointed out that they also measured surface runoff flow and P losses for these fields, and that the combined runoff and tile drainage flow was not affected by the gypsum applications, although drained areas for runoff and tile drainage were similar for the control field (3.7 ha) but for the treated field the runoff area was larger than the area drained by tiles (5.4 and 4.5 ha, respectively). The authors concluded that multiple applications may be needed to attain the full potential benefits of gypsum, although recognized the study treatments and methods cannot fully support this conclusion.

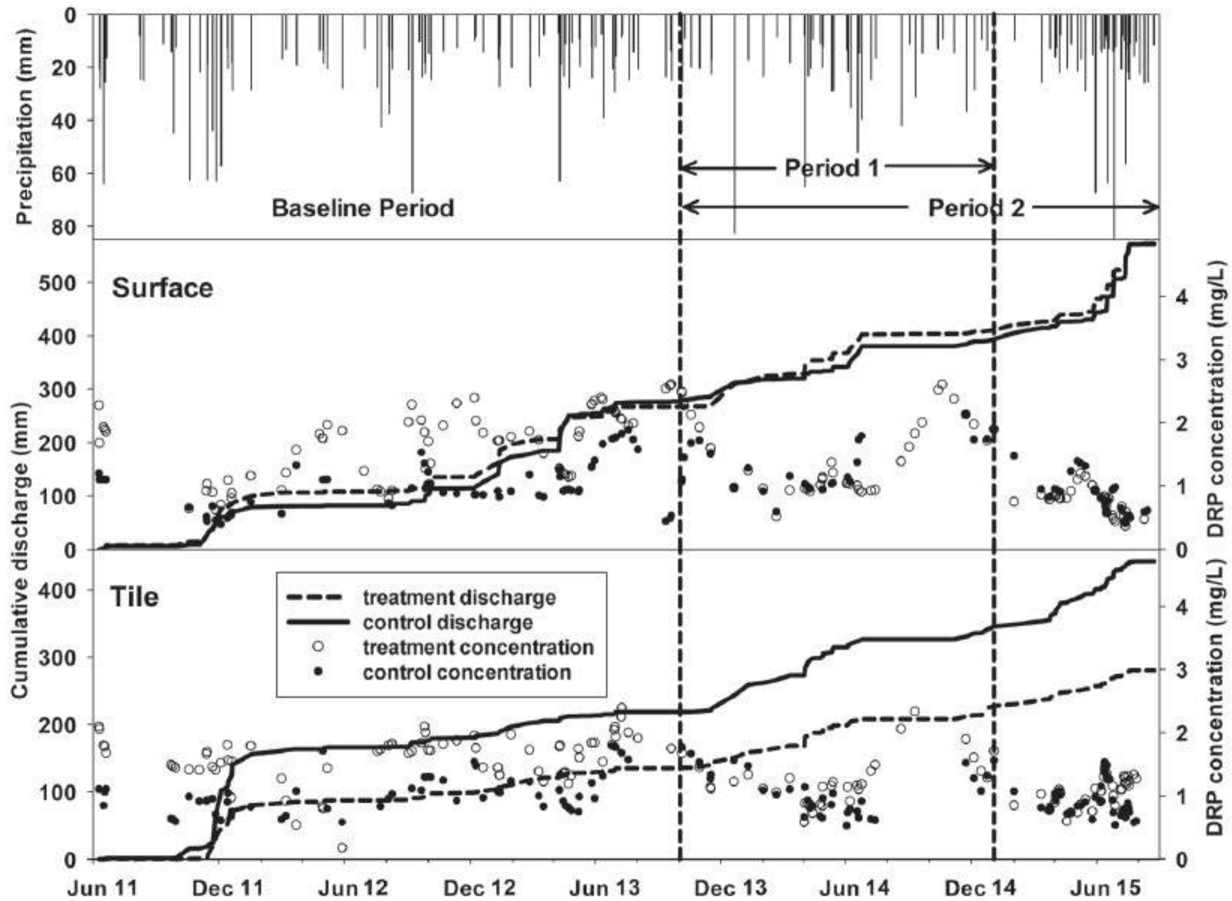


Figure 4. Effect of gypsum on dissolved reactive P (DRP) concentrations in tile drainage as evaluated by a paired watershed study in Ohio (from King et al., 2016).

A multiyear study conducted by researchers from Iowa State University evaluated the effect of gypsum on P loss with tile drainage at a site with Kenyon-Clyde loam soils. The site had six large 1-acre plots each draining separately. For many years these sites had similar management practices, namely continuous corn, tillage, and injected N-based liquid swine manure each year (without additional P fertilization). From 2016 until 2019 (four crop years) gypsum was applied to three plots and the previously mentioned management practices continued for the six plots. A gypsum rate of 2240 kg $ha^{-1}$ was applied twice, before tillage in fall 2015 and again before tillage in fall 2017. Soil-test P was statistically similar for plots of both treatments, although there was large variability commonly found in manured fields. The annual application of N-based manure during several years had increased the topsoil P level but not subsoil levels. On average across treatments and years, soil profile Bray-1 P was 129, 33, 5, 6, and 7 ppm for depths of 0-6, 6-12, 12-24, 24-36, and 36-48, respectively. These topsoil P values are common in fields where N-based animal manure has been applied for corn during many years, although these were much lower than those in the Ohio reviewed study by King et al., (2016). Drainage total reactive P (TRP) was measured on unfiltered samples by the Murphy and Riley (1962) method, but all drainage samples were clear without obvious sediment. The overall P loss was very low, and gypsum had no statistically significant effects on TPR concentrations or water flow in any year. On average across the four years, TPR was 40 ug/L with or without gypsum, although the annual average ranged from 7 to 106 ug/L. The authors explained very low drainage P concentrations by high but not extremely high topsoil P levels and very low subsoil P levels. Previous Iowa research (Allen et al., 2012) had shown that Iowa subsoils have properties that effectively filter lateral P flow from highly concentrated zones to tile drains.

## Summary and Conclusions

The purpose of this creative component was to provide insight as to what published literature can tell us about gypsum's capacity to retain P in the soil and in particular reduce P loss through subsurface tile drainage. Phosphorus is a nutrient of key importance to plant growth, and sufficient concentrations in soils are essential to profitable food and feed production. However, excessive P application and crop or soil management practices that result in increased dissolved or particulate P loss from fields result in water quality impairment. In addition, the improvement of poorly drained agricultural land through tiling to increase crop yield facilitates the flow of water and nutrients to surface water bodies such as streams, lakes, and even as far as the oceans. Therefore, water quality impairment can be minimized by avoiding excessive P applications to the land and use of management practices that minimize soil and water loss while maintaining profitable crop production.

However, many agricultural fields already have very high P levels, and in some conditions and for some loss pathways even improved soil and water conservation practices are not sufficient to significantly reduce P loss. This is the case of fields with little slope and poor natural drainage that are tiled to allow for grain crop production. Therefore, use of soil amendments that increase P retention in the soil while not reducing crop-available P would be desirable and very useful to maintain profitable crop production while reducing P loss from fields and water quality impairment.

Extensive research has shown that alum amendments are very efficient at reducing P loss with surface runoff, especially loss of dissolved P which is most active at encouraging algae growth and eutrophication of surface water bodies. Continued use of alum is not sustainable, however, because it acidifies soils and can easily increase exchangeable or soluble Al to levels that are phytotoxic and very frequent application of high lime rates would be needed to avoid problems. Scarcer research has shown lesser and more inconsistent effects of gypsum at reducing P loss with surface runoff, but it is more sustainable, and its use may also improve soil properties and increase crop yield.

Research to evaluate effects of soil amendments such as alum or gypsum on P loss with tile drainage has been much less than for surface runoff. One likely reason is that in most fields with some slope, particulate P loss through soil erosion and dissolved P loss through surface runoff are much higher than P loss through subsurface drainage. Another likely reason is that tile drainage research is much more complicated and can be much more expensive than for surface runoff.

No research has investigated the use of alum to reduce P loss with subsurface tile drainage, probably because of the reasons suggested above, and research with gypsum has been very scarce. A few indoor studies with soil columns suggested that gypsum has good potential to reduce P loss with subsurface drainage, but this type of research cannot directly be extrapolated to field conditions. Only two adequality replicated field studies were found in peer-reviewed scientific journals or published technical reports. These were conducted in very different conditions, and it is not surprising that the conclusions were also very different. A 2-year study in Ohio at a field with topsoil testing extremely high in P (about 20 times the optimum soil-test level for corn) but without P application for corn during the study, used a gypsum rate of 2240 kg $ha^{-1}$ applied twice, once for each year of the study. The results showed that gypsum reduced dissolved P loss with tile drainage by 35%, and that this can be an effective soil amendment. A 4-year study in Iowa at a site with topsoil testing high in P but much lower than for the Ohio soil (about five times the optimum soil-test level for corn) that received annual applications of N-based swine manure for corn, used a gypsum rate of 2240 kg $ha^{-1}$ twice over the 4-year study (before the first year and the third year). This study showed very low dissolved P loss through tile drainage, with or without gypsum application, and no gypsum effect at reducing P loss.

No strongly supported conclusions can be drawn from the few indoor studies conducted in soil columns whose results cannot be directly applied to tiled fields. Adding to this difficulty, the two field studies were conducted in very different conditions and produced very different conclusions. The results of do suggest, however, that gypsum is likely to be a useful amendment to reduce P loss with subsurface tile drainage in soils with very high topsoil P and with subsoil properties that cannot efficiently filter P flow to tile drains. Therefore, additional research at the field conducted in different soils conditions are required before expensive, high rates of gypsum, with the specific purpose of reducing P loss with tile drainage, can be recommended to producers with confidence.

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