Chad J. Penn James M. Bowen

Design and Construction of Phosphorus Removal Structures for Improving Water Quality



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This Springer imprint is published by Springer Nature The registered company is Springer International Publishing AG The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland For Father Ken Harder and my doctoral advisors, Greg L. Mullins and Lucian W. Zelazny.

"The rare, strange thing is to hit the mark; the gross, obvious thing is to miss it. We feel it is epical when man with one wild arrow strikes a distant bird. Is it not also epical when man with one wild engine strikes a distant station? Chaos is dull; because in chaos the train might indeed go anywhere, to Baker Street or to Bagdad. But man is a magician, and his whole magic is in this, that he does say Victoria, and lo! It is Victoria. No, take your books of mere poetry and prose; let me read a time table, with tears of pride. Take your Byron, who commemorates the defeats of man; give me Bradshaw, who commemorates his victories. Give me Bradshaw, I say!"

-Gabriel Syme in The Man Who Was Thursday, by G.K. Chesterton (1908)

Preface

Phosphorus (P) input to surface waters is considered the most limiting nutrient with regard to eutrophication. The result has been a negative impact on recreation, ecosystem diversity, drinking water treatment, and the associated economics of each. Depending on region, over 50% of P inputs to surface waters may be from non-point sources such as agriculture, horticulture, urban/suburban lawns, and golf courses. The problem of non-point P pollution is further aggravated by "legacy" P in soils that has accumulated over several decades. Such legacy P will require several decades of P "draw-down" from the soils with forage crops and improved nutrient management. In the meantime, high concentrations of dissolved P will continue to leak out of these systems into surface waters. Even when conventional best management practices (BMPs) are employed, they will do little to prevent losses of dissolved P since conventional BMPs are mostly intended for reducing erosion and therefore particulate forms of P.

While the long-term solutions of nutrient management, P draw-down, and manure transport programs are being implemented, the P removal structure can be implemented to prevent dissolved P losses in the short term. At the most basic level, a P removal structure is a landscape-scale filter that utilizes P sorption materials (PSMs), which have a strong affinity for dissolved P. Structures are designed such that PSM is able to be replaced after they are no longer effective at removing P.

The purpose of this book is to introduce the P removal structure as a new BMP for reducing dissolved P loading to surface waters from non-point source pollution, provide guidance on designing site-specific P removal structures, and provide instruction on use of the design software, "Phrog" (Phosphorus Removal Online Guidance). This book initially provides a review of the nature and sources of non-point source P pollution, examines short- and long-term solutions to the problem, and provides detailed theory on design and operation of the P removal structure. As with many areas of study, one of the best methods of communicating concepts is through illustrations and examples. This book is no exception; several years of experience in studying P sorption and constructing P removal structures at multiple scales and settings is utilized for providing real examples and applications. With an understanding of the P removal structure established, the reader is instructed on how

to obtain all of the necessary inputs for properly designing a site-specific P removal structure for meeting a desired lifetime and performance, or how to predict the performance and lifetime of a previously constructed P removal structure. For the readers who already possess the Phrog design software or are interested in obtaining it, Chap. <u>7</u> is dedicated to detailed use of the software as demonstrated with various examples of structure design and prediction. Last, we provide recommendations and guidance for safe and beneficial disposal of spent PSMs that are no longer effective at removing dissolved P.

While this book may serve as a traditional textbook on the topic, the intended audience is practitioners and policy makers in environmental quality, agriculture, and water quality with regard to reducing non-point source P pollution to surface waters. The purpose of this book is to promote and disseminate the construction of P removal structures throughout the world. This encompasses government agencies such as the USDA, NRCS, and EPA, state and local agencies such as Departments of Agriculture, Departments of Environmental Quality, and municipalities, non-profit organization dedicated to water quality and agriculture, the environmental engineering and consulting industry, and golf course superintendents.

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Terms and Abbreviations

Terms

DP	Dissolved P (mass per unit volume)
TP	Total P (mass per unit volume)
PP	Particulate P (mass per unit volume)
PPmass	Particulate P (mass per unit mass of sediment)
CP _{add}	Cumulative P added to the PSM (mass of P per unit mass PSM)
CP _{rem}	Cumulative P removed by the PSM (mass of P per unit mass PSM)
CP _{add} Max	Maximum CP_{add} where phosphorus is no longer removed (mass of P per unit mass PSM)
b	Coefficient in the design curve equation (unitless)
m	Coefficient in the design curve equation (unitless)
PL _{annual}	Annual dissolved P load (mass)
Goal	Target cumulative P removal goal (%)
DL	Design lifetime targeted for P removal structure (time)
DP _{avg}	Average dissolved P concentration in flow (mass of P per unit volume
-	of water)
CP _{add} RG	The value of $\ensuremath{\text{CP}_{\text{add}}}$ that corresponds to a specific targeted cumulative P
	removal goal (i.e. Goal) (mass of P per unit mass of PSM)
UL	Ultimate lifetime of PSM (time)
FV _{annual}	Average annual flow volume (volume)
PL _{area}	Annual dissolved P load (mass per unit area)
RC	Runoff coefficient (unitless)
CA	Contributing area (area)
Q _p	Peak flow rate (volume per unit time)
i	Design rainfall intensity (length per unit time)
D	Diameter (length)
S	Slope (unitless)
n	Mannings roughness coefficient (unitless)
A _{Mann}	Channel cross sectional area used for Manning's equation (area)
V	Flow velocity (length per unit time)

Hydraulic radius of channel used in Manning's equation (length)
Wetted perimeter of channel used in Manning's equation (length)
Flow rate (volume per unit time)
Saturated hydraulic conductivity (length per unit time)
Depth of PSM (length)
Change in water potential (length)
Area of PSM bed (area)
Bulk density (mass per unit volume)
Particle density (mass per unit volume)

Abbreviations

Р	Phosphorus
DP	Dissolved phosphorus
PP	Particulate phosphorus
PSM	Phosphorus sorption material
CAFO	Confined animal feeding operation
Ca	Calcium
Fe	Iron
Al	Aluminum
Mg	Magnesium
N	Nitrogen
S	Sulfur
STP	Soil test P
M3	Mehlich-3
B1	Bray-1
WSP	Water soluble phosphorus
WS	Water soluble
DI	Deionized
CaCO ₃	Calcium carbonate
AMDRs	Acid mine drainage residuals
WTRs	Drinking water treatment residuals
FGD	Flue gas desulfurization
Phrog	Phosphorus Removal Online Guidance
RT	Retention time
LSS	Local sorption saturation
EPA	Environmental Protection Agency
NRCS	Natural Resource Conservation Service
SPLP	Synthetic precipitation leaching procedure
TCLP	Toxic characteristics leaching procedure
EC	Electrical conductivity

Chapter 1 Introduction to Phosphorus and Water Quality

1.1 The Role of Phosphorus in Ecosystems

Phosphorus (P) is essential for all life on this planet. Energy within plants and animals is captured in phosphorus bonds allowing it to be stored for later use or transported to other areas of the organism. Phosphate groups are the backbone of both DNA and RNA, the very building blocks of our genetic code. Phospholipids within cell membranes enable separation of two liquid environments that can have very different pH values, as well as solute concentrations, without which the cell would be unable to function. In agriculture, crop production where grain and biomass is harvested is not possible without the addition of P (Fig. 1.1). Among all of the nutrients that are necessary for plant growth, P is needed in the second highest concentration. How can an element so vital to our survival be considered a pollutant?

1.1.1 Eutrophication

Phosphorus is vital for all plants to thrive, including aquatic plants. In a freshwater setting, such as a lake or stream, P tends to be the most limiting factor for plant growth, so small additions of P can have dramatic effects on an ecosystem.

The trophic level of water refers to how biologically productive the water is and can be determined using some combination of nutrient concentrations, water clarity, and number of phytoplankton present. Common trophic levels include oligotrophic, mesotrophic, and eutrophic with increased levels of production, respectively. Eutrophic waters, like those in Fig. 1.2, are easily identified by the rampant plant growth which can take many forms; including Duckweed that resembles small lily pads, an amorphous algae, and the possibility of dead fish. Eutrophication can occur naturally over the course of the life of a water body, but it can also be accelerated due to human activity; under this condition, it is often referred to as "cultural eutrophication".







Fig. 1.2 *Left photograph*: eutrophic pond covered with duckweed that collects runoff from a poultry farm. *Right photograph*: eutrophic pond that receives subsurface drainage from residential turfgrass. Photo Credit: James Bowen, University of Kentucky



Fig. 1.3 A sign posted on a beach indicating unsafe conditions due to a recent algal bloom. Photo courtesy of J.L. Graham, U.S. Geological Survey

Throughout the course of this book, whenever eutrophication is mentioned we will be referring to cultural eutrophication and not the natural process.

The water quality issues that stem from eutrophication are seen even after an algal bloom dissipates. The first obvious issues are due to the presence of the algae which can take over the entire water's surface. Aesthetically, the water body will be less appealing due to the thick layer of algae, so people are less likely to travel to the site for walking, hiking, or picnics. The aesthetics also reduces the value of the site for people who don't even visit, but gain some satisfaction from knowing that the lake is in good condition if they choose to make use of it.

When algal blooms are present, any contact with the water becomes problematic. Staying on the shore or boating in the water can still expose the user to water spray which can contain toxins produced by algal blooms. This threat worsens with primary body contact with contaminated water, so swimming or drinking the water is not advisable for humans or animals. Even if the algae present do not produce toxins, the inconvenience of cleaning the algae off of anything that came in contact with the water, such as your dog or boat, can dissuade someone from returning until the bloom is gone (Fig. 1.3).

Lack of recreation and limited cases of illness are important consequences of eutrophication, but algal blooms have far greater impacts. These blooms are capable of producing water soluble toxins which can cause illness and even death in live-stock and humans alike. This issue is more prevalent in livestock due to lower quality water sources, but has been observed in human drinking water supplies. In the summer of 2014, an algal bloom in Lake Erie (Fig. 1.4) resulted in excessive growth of a cyanobacteria that produced microcystins, which entered the drinking water treatment plant that provides for Toledo, Ohio. Microcystin is very resistant to degradation, so standard water purification techniques do little to reduce the concentration.



Fig. 1.4 Satellite image of Western and Central Lake Erie during an algal bloom in 2011. MODIS image processed by Space Science and Engineering Center, Univ. of Wisconsin and provided by Great Lakes CoastWatch

In ordinary conditions, it can take 10 weeks for half of this toxin to degrade. In that particular situation, the concentration exceeded 1 μ g L⁻¹, or one part microcystin per billion parts of water, which triggered a 3-day long ban on using tap water for drinking, cooking, or showering. Unlike other organic contaminants, microcystin can survive boiling, so approximately 500,000 people were forced to use bottled water. Eventually, the concentrations decreased below the detection limit and the ban was lifted, but the threat of additional outbreaks remain. Additional testing equipment was added in 2015 to monitor microcystin levels, which allows personnel more time to alter treatment to reduce toxin levels. This threat can be managed, but the costs of monitoring and additional treatment have to be recouped with increased utility costs being the most obvious source. Smaller water treatment plants most likely lack the means of removing the toxin even if they detect its presence.

After the algal bloom dies off, the algae sink into the water and are broken down by other organisms. While this abundant food source may seem to be a boon for them, the increased activity quickly uses up the dissolved oxygen present in the water. Gases diffuse rather slowly through water, so oxygen loss in deep water can take some time to be replaced. This problem is exacerbated in lakes during hot weather: fish move to deeper depths to escape warm water at the surface only to find water with very little oxygen available. This can lead to scenarios where the surface is littered with dead fish like the small pond shown in Fig. 1.2. If conditions remain unchanged, the entire ecosystem of the water is altered with a reduction in larger fish and an overall reduction in biodiversity. The P that caused the explosion in growth is able to cycle in the system as the biota decompose and release nutrients back into the water column.

1.1.2 Cultural and Political Response to Eutrophication Issues

Water quality is a function of intended water use, so the threshold for "pollution" varies with use. For example, drinking water sources are naturally held to a higher standard than a lake used for hydroelectric power. Public opinion and safety have been two major drivers of environmental reform. The Great Lakes region in the United States is a prime example of public outcry influencing environmental regulation. In June of 1969, the Cuyahoga River caught fire due to oil and other debris accumulating as it flowed through Cleveland. This fire was not an uncommon occurrence since the same river had caught fire at least 13 times since 1868 and rivers in other industrial cities had suffered similar fires. The fire was reported in the August issue of *Time* magazine which spurred national outrage at the condition of American rivers. This public outcry helped drive creation of the Great Lakes Water Quality Agreement of 1972 which aimed to restore water quality of the Great Lakes through a joint Canadian and United States effort. The dramatic changes made to the Federal Water Pollution Control Act of 1948, hereafter known as the Clean Water Act, was amended in 1972. The intention was to provide a regulation framework for pollution discharge, empowered the Environmental Protection Agency (EPA) to set standards, and help fund construction of wastewater treatment plants.

1.2 Sources of Phosphorus Transported to Surface Waters

Any source of excess P entering a water body has the potential to trigger eutrophication, but some sources are easier to control than others. Sources are generally classified as either point or non-point, based on whether there is one specific point emitting the nutrient, such as a pipe (point source), or if the release is diffuse, such as nutrient runoff from a field (non-point source). Point sources are easier to identify and monitor compared to non-point.

1.2.1 Point Sources (Wastewater Treatment Plants)

One of the largest P point sources are wastewater treatment plants (WWTP), which discharge varying amounts of P directly into water bodies (Fig. 1.5). The amount of P released by any given WWTP will be a function of the influent the plant has to treat and the efficiency of the treatment process. When discussing P release to the environment, concentrations can be deceiving, so the concept of the load can be useful to compare different sources. The load is simply the average concentration multiplied by the volume of water released that results in a mass of P which is much easier to use in comparing different sources (more detail on this is found in Chap. 3). Following World War II, laundry detergents moved from bar soaps with little to



Fig. 1.5 An example of a modern wastewater treatment plant (WWTP) located next to the river where treated effluent is released. Photo Credit: Google Earth image

no P to more sophisticated versions that relied on phosphates to counteract hardness in water that interfered with surfactants. These new detergents worked well in new machines, but introduced a new source of P into WWTPs which were ill equipped to handle. At the peak usage of these detergents, approximately half of the P in wastewater effluent was due to laundry detergents (Litke, 1999). As a response to that, laundry detergent chemistry was changed and the treatment within the WWTPs was improved, resulting in considerable reductions in P loads from plants.

1.2.1.1 Phosphorus in Soaps

The focus on laundry detergent's impact on eutrophication started in the late 1960s with the formation of the Joint Industry-Government Task Force on Eutrophication which tasked industry with replacing P in their detergents. The task force stalled due to health and safety issues with P replacements prompting Congress to call for a ban on phosphate in detergents within the next 2 years. Industry responded by restricting P to 8.7% of laundry detergents by weight in 1970. This voluntary restriction was followed by a series of bans that started with five Illinois cities in 1971 and ultimately resulted in 21 states with a complete ban on P in domestic laundry detergent. The increasing pressure from these bans led to industry removing P from domestic laundry detergent in 1994. A similar battle for removal of P from dishwasher detergents occurred recently. Seventeen states banned P use in dishwasher detergents in 2010. In 2014, Proctor & Gamble released a statement that they will

be removing P from their entire line of detergents. The reduction of P that reaches the WWTP helps reduce the treatment cost and amount of P released into our waters.

1.2.1.2 Wastewater Treatment Processes

Treatment methods for wastewater are similar, but not all methods may be needed at each WWTP. This results in each plant being unique to the time it was built or upgraded, and to the characteristics of the waste it was designed to treat. For simplicity, there are three basic methods employed at a WWTP: primary, secondary, and advanced or tertiary treatment. Primary treatment consists of allowing solids to settle from the water and then separating solid from liquid. The effluent produced from primary treatment will appear clearer than the untreated influent, but still contains organics and nutrients which cause serious issues when released. Nutrients can trigger eutrophication and the introduction of organics for microbes will reduce dissolved oxygen within the water body. Primary treatment was very common prior to passage of the Clean Water Act (CWA), which helped fund upgrades and construction of WWTPs.

The CWA also set standards for effluent which led to inclusion of secondary treatment at WWTPs. This secondary treatment aims to reduce organics present within the influent. Activated sludge, a common method, utilizes microorganisms to degrade organics within an aerated tank which is then pumped into a settling tank where the sludge is removed and water is released. This sludge is then returned to the aerated tank in order to be reused. From 1972 until 1996, the United States went from very little treatment to almost all WWTPs equipped with primary and secondary treatment. Tertiary or advanced treatment is a catch- all term for any process that is not primary or secondary, so the presence and type of treatment will vary with the needs of each plant. In the context of this book, tertiary treatments of interest include anything to further reduce nutrients prior to releasing effluent into a water body. This treatment can include chemical treatments to cause P to precipitate and remove solids from the water, filters that remove ions from solution, or filters that rely on chemical reactions to attract and bind nutrients. Any additional treatment will increase operating cost, increase land needed, and potentially reduce the volume of waste a plant can handle, so these tertiary treatments are only implemented when necessary to meet regulations. The reduction in P entering into these plants coupled with increasing technology driven by regulation has helped reduce P loads leaving WWTPs. Monitoring and further P reductions for WWTPs are straightforward since there is a single point where effluent is released and additional treatments can be added relatively easily.

1.2.2 Non-point Phosphorus Sources and Forms

On the other hand, non-point sources of P are difficult to monitor and treat due to their diffuse nature. When non-point sources are discussed, agriculture is often mentioned first, although any land that has high levels of P either due to natural processes or human activity is capable of being a source. In order to be a source, the land has to contain appreciable P concentrations or have P recently applied, and be hydrologically connected to a surface water body. Without this connection there is no means for the P to reach the surface water and trigger eutrophication. Hydrologic connections can become complicated because areas may only be connected during larger storm events, which makes identification of non-point sources even more difficult.

At the most basic level, P in water is transported in either the "particulate" or the "dissolved" form. Dissolved P is simply P that is dissolved in water. Dissolved P is often in the form of the phosphate polyatomic anion, or PO_4^{3-} for short. Particulate P is the P that is bound to a solid material, typically soil. The P bound onto soil particles includes P that is part of soil organic matter, P that is precipitated as various calcium (Ca), aluminum (Al), magnesium (Mg), and iron (Fe) phosphate minerals, and P that is bound to the surfaces of various soil minerals. The form of P being transported has a profound impact on the receiving water body, and it also dictates how to best manage that non-point P source. Although this will be discussed in more detail in Chap. 2, it can be summarized by stating that dissolved P is immediately 100% bioavailable upon reaching a surface water ecosystem, and that conservation practices that reduce particulate P transport are usually not effective for preventing dissolved P transport.

Non-point source P can be transported directly from P-rich amendments such as chemical fertilizer, manure, or compost (i.e. incidental P losses), and it can also occur from soils that have been built up to high soil P concentrations due to previous excessive applications of P-rich amendments. The P "build-up" within soils is said to be a legacy of the prior management, leading to the term "legacy" P. The formation of legacy P soils is discussed in greater detail in Chap. 2.

Phosphorus was traditionally described an "immobile" soil nutrient due to low soil solution solubility (Brady and Weil 2008), that is, most soil P is bound strongly to soil minerals. Thus, control of P losses was once synonymous with erosion control. In one sense, the notion of P immobility is accurate since the amount that dissolves in solution is generally negligible relative to total soil P; however, this is only true for soil P and not manure or fertilizer. Consider the contrast with nitrogen (N) in agricultural soils, for example, in that a much higher percentage of the total soil N is soluble and plant available.

While P does indeed bind tightly to soil minerals, as the soil P concentration increases so does the solubility of the P (see Chap. 2). The result is that for high P soils, tiny amounts of P dissolves when in contact with water. For example, a soil testing 500 mg P kg⁻¹ of soil, roughly 1000 lb in the top 6 in. of soil, could release approximately 1 mg P L⁻¹ of water into runoff water. While this loss of P is somewhat negligible in the context of agricultural and horticultural plants, it could be devastating to a receiving water body and the soil could continue to leak this P for years to come. With cessation of soil P applications combined with soil P drawdown through the use of plants or other P removal practices, eventually the soil will no longer be a source, but this process can take decades depending on the current level in the soil (see Chap. 2). Legacy P can be found in many different environments even though it is primarily associated with agriculture.

1.2.2.1 Urban Grassed Areas

Urban areas can be prime sources for P runoff due in part to fertilizer applications associated with residential lawns and golf courses, as well as leaves or lawn clippings. Phosphorus can also be found in winter deicers including some salts, sand, and food by-products like corn steep residue and beet juice. Residential lawns can become a source very easily when homeowners or landscaping companies do not perform soil tests prior to applying fertilizers. Maintaining a lawn with minimal removal of clippings will not require much P fertility, so annual applications of a P fertilizer will eventually transform the lawn into a non-point source. Unfortunately, most of the fertilizers that are readily available for purchase are "complete" which means they contain nitrogen, phosphorus, and potassium. Building up the levels of P within the soil are one issue in urban areas, but direct runoff of the fertilizer is another key issue. Since residential neighborhoods are designed with storm water management in mind, as soon as runoff water or fertilizer leaves the lawn it will soon make its way into a ditch or nearby creek. Coupled with steep slopes and the possibility of careless application, this can lead to substantial amounts of fertilizer entering our waterways.

A study conducted in the late 1990s examined water quality in several areas of Madison, Wisconsin by collection of runoff samples from various surfaces within different residential neighborhoods. Lawns in one neighborhood were found to produce runoff with 0.79 mg total P L⁻¹ and 0.37 mg dissolved P L⁻¹. Another nearby neighborhood produced lawn runoff at much higher values with 1.61 mg total P L^{-1} and 0.77 mg dissolved P L⁻¹. Both of these neighborhoods produced runoff with dissolved P that was approximately 50% of the runoff total P concentration, but these ratios will change depending on the source of the P and conditions. If a lawn had poor grass coverage then soil would erode transporting the P attached to it (i.e. particulate P) out of the neighborhood. Conversely, if all of the lawns had excellent grass coverage then erosion would be limited, so the amount of dissolved P would likely rival that of total P. In these two neighborhoods, lawns were found to account for 56–70% of the total P and 69–75% of the dissolved P in runoff. Streets were responsible for 20–33% of the total P and 15–21% of the dissolved P, with rooftops and parking lots providing the remainder (Waschbusch et al. 1993). These values provide some insight into P losses from a residential area, but the actual values will vary by neighborhood, season, and sampling methodology. Runoff sampling is not necessary for the typical homeowner. Simply arming oneself with some basic knowledge of nutrient management, conducting soil testing prior to applying fertilizer, and maintaining good grass coverage is enough to prevent P loss from residential areas. These same problems can be found in other urban grassed areas, but other problems may plague golf courses.

Golf courses are more intensively managed than a home lawn due to the nature of their business, providing a well-manicured grass area year round. Poorly managed courses may suffer from similar problems as home lawns, but there are other issues inherent to their design which may allow them to become non-point sources. The grass at a golf course must be presentable year round which entails regular applications of fertilizers, pesticides, and irrigation. Short grass coupled with clear, sloped paths and consistent irrigation results in appreciable volumes of runoff which deliver nutrients with it. Increased drainage water is lost from the greens due to installation of subsurface drainage which reduces the potential for dissolved P to bind to the soil and increases the potential for losing dissolved P. Turfgrass requires well-drained soils and adequate levels of water-relatively high in comparison to most crops. In order to meet these requirements, the subsurface of a golf course may be replaced with a layer of highly permeable sand. This sand allows for water to drain much quicker than normal soil, so nutrients that would normally have time to bind with soil or be used by plants are instead leached downwards. Depending on the topography of the site or if drains are set up underneath the greens, this water can be directed into drainage ditches or stored in ponds onsite. Monitoring at a Minnesota golf course showed that levels of both total and dissolved P were greater at the outflow of the course compared with the water entering the course. The P applications were made in late spring, but the peak concentrations in runoff were not seen until late summer during the drier part of the year. Irrigation to maintain the grass alters the hydrology of a site by maintaining the hydrologic connection year round and constantly leaking dissolved nutrients into surface waters. The maximum concentrations produced by this site were 0.34 mg dissolved P L⁻¹ and 1.11 mg total P L⁻¹ while the median values of 0.01 mg dissolved P L⁻¹ and 0.03 mg total P L⁻¹ were much lower (King and Balogh 2011). The amount of P lost at a golf course will vary with management, as well as the time of year and location of the sampling event. Over the course of 5 months, an urban Oklahoma watershed that consisted of mostly residential housing and only a small portion of a golf course, produced a maximum concentration of 1.61 mg dissolved P L⁻¹ with an average flow-weighted concentration of 0.59 mg dissolved P L⁻¹ (Penn et al. 2012). The nature of a golf course which alters a site's hydrology and moisture regime requires careful management to avoid becoming a source of P to waters.

1.2.2.2 Agricultural Areas

Agriculture is usually the first source mentioned when discussing eutrophication, especially for non-point sources. This reputation is not without reason since some of the biggest sources of P outside of WWTPs are concentrated animal feeding operations (CAFO). It is important to note that CAFOs are considered point sources and are subject to regulation through the Clean Water Act which requires a National Pollutant Discharge Elimination System (NPDES) permit. Over-application of manure to fields nearby to these CAFOs has built up the soil test P of some soils to concentrations which will require decades to reach safe levels, even after cessation of manure applications. The development of legacy P in these soils coupled with tightening regulations in some watersheds have resulted in agricultural producers being forced to transport manure off of their farm to prevent further soil P build-up. If managed properly, manure is an excellent source of nitrogen and phosphorus, as well as providing the added benefit of organic matter, unlike inorganic fertilizers.

Regardless of the nutrient amendment used to build up P levels in a soil, once values reach a certain soil concentration the site becomes a non-point source if it is hydrologically connected. Agricultural producers can take soil samples and consult information disseminated by local land grant universities for guidance on managing P to prevent build-up through a nutrient management plan (see Chap. 2). The problem with P that can make it a "legacy issue" is the lag time between management changes and results in the soil. If a farmer takes over a field with that has a large amount of legacy P then that field will continue to be a source even if that farmer utilizes traditional conservation practices and a nutrient management plan. For example, a long-term study conducted in Maryland built up soils to elevated levels of P and then evaluated the soil P reduction from crop uptake, or "draw-down". After 8 years of consistent crop growth and removal and no additional P applications, the soil test P levels for all treatments were still well in excess of the crop requirement for proper plant growth, and high enough to produce an appreciable concentration of P in the drainage water.

Runoff in a watershed with agricultural activity can vary spatially and temporally depending on the size of the storm or anthropogenic activity. Larger storms can produce runoff from land that is not normally hydrologically connected to surface waters. Spikes of P in runoff can be seen after fertilizer application to fields or after manure is cleaned out of barns which exposes the P source to the elements. On a poultry farm in Oklahoma, the dissolved P concentrations in runoff from directly around the poultry houses varied from 0.08 to 14.7 mg L⁻¹ depending on when the sample was taken. These values were sustained by soils that ranged from 65 to 420 mg P kg⁻¹ and any spilled poultry litter outside the house that occurred when houses were cleaned out or birds harvested. That particular poultry farm is managed in accordance with regulations, utilizes best management practices concerning storage of poultry litter, and does not apply litter to the field. The legacy P present in the field is still a long-term source even though the farm is managed properly.

With the advent of the Soil Conservation Service (now the Natural Resource Conservation Service; NRCS), many conservation practices were developed to decrease soil erosion. It was formerly understood that P losses were primarily associated with sediments (Brady and Weil 1999); thus erosion control practices limited P loss. However, this is not necessarily true for dissolved P. Since particulate P is attached to soil, anything that reduces soil loss will also reduce loss of particulate P. Widespread adoption of BMPs such as reduced tillage, contour farming, and stream buffer zones has greatly reduced particulate P loss, but does little for loss of dissolved P from legacy soils (see Chap. 2 for more details). The lack of concern about dissolved P losses occurred, not through ignorance of the knowledge of small amounts of dissolved losses, but because of the disconnection between agriculture and aquatic ecology, and the inherent difference in the scale of impacts of dissolved P on crops compared to aquatic ecosystems. For example, the critical P concentration in solution necessary for growing various crops ranges from 0.008 to 1.6 mg L⁻¹. However, depending on N concentration and microcystis strain, dissolved P concentrations as low as 0.11 mg L⁻¹ can cause a dramatic increase in microcystis growth. Microcystis are capable of producing the toxin, microcystin, harmful to humans.

1.3 Best Management Practices and Dissolved Phosphorus Losses

To illustrate the differences between dissolved and particulate P losses with management, consider the widespread implementation of several conservation practices such as reduced and no-tillage within the watersheds that feed ten tributaries of Western Lake Erie. With implementation, bioavailable particulate P loading decreased from 1991 to 2012, but the dissolved P loading dramatically increased during this period of re-eutrophication of Lake Erie (Baker et al. 2014). Much more will be discussed regarding various conservation practices and their ability to limit particulate and dissolved P loading in Chap. 2. In summary however, it is clear that conventional best management practices do not sufficiently prevent dissolved P losses from legacy P soils. Thus, the focus of this book is to provide technical information on a new best management practice that targets dissolved P losses: the P removal structure.

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Chapter 2 Reducing Phosphorus Transport: An Overview of Best Management Practices

2.1 Dealing with Eutrophication: Treat the Symptoms or the Cause?

The effects of eutrophication described in Chap. 1, mostly the impacts on recreation, ecology, aesthetics, and drinking water treatment, can be directly treated. These "symptoms" of eutrophication are directly remedied through killing excessive algae and plants by algaecides, physical removal of algae, aeration, updates and improvements to drinking water treatment facilities, and injection of chemicals such as aluminum sulfate into surface waters. However, each of these remedies tend to be very expensive. Also, many of them result in only temporary improvements of the symptoms since the cause of the eutrophication is left un-mitigated.

Use of algaecides will quickly kill the organism, but eventually the algae will begin to grow again since the nutrient rich conditions of the water has not changed. Direct harvest and removal of algae and aquatic plants is a slight improvement over the use of algaecides since removal of the biomass also removes the P held within it. Chemicals such as aluminum sulfate (alum), aluminum chloride, and certain calcium chemicals are sometimes injected into a eutrophic water body in order to reduce the solubility of P, preventing it from being bioavailable to aquatic organisms and thereby preventing further growth. While direct injection of chemicals can be successful for reducing algal growth, the positive result is temporary. Simply put, the chemicals only change the chemical form of the P to make it less bioavailable, but it does not remove it from the water body. Eventually with time and changing conditions, the chemically bound P will revert back into dissolved P. Aeration is also a direct shortterm fix that adds oxygen to the water, preventing the massive oxygen depletion that causes fish kills. Last, improvements and updates to existing drinking water treatment plants are extremely expensive, and in some cases unable to immediately remedy the problem. For example, during the mycrocystin toxin outbreak in Lake Erie in the summer of 2014, the Toledo drinking water treatment plant was unable to remove the toxin and boiling the water did nothing to improve the safety of drinking the water.

In general, these direct remedies are not only temporary, but expensive and inefficient. Instead, it is more efficient and economical to treat the cause of eutrophication i.e. point and non-point source N and P pollution, rather than the symptoms. Several cities, such as Des Moines and New York City, have already realized the efficacy and economy in treating the source, as opposed to treating the effects of eutrophication.

2.2 Incidental vs. Legacy Phosphorus Losses

In beginning a discussion on non-point source P pollution, it is helpful to differentiate between two main sources of non-point P: incidental and legacy P. Incidental P is the P that is transported directly from a non-soil P source, i.e. chemical fertilizer and organic P sources such as manure and compost. This incidental P is lost when the P source is highly concentrated and has not yet had sufficient time or opportunity to react with the soil. When the applied P reacts with the soil, it becomes part of the soil P pool. If the soil P pool is large, then it can become a non-point P source that is often labelled as "legacy P", introduced in Chap. 1.

Incidental P losses are common when manure or other organic P sources are improperly stored outdoors in areas where runoff can directly interact with the P source. Another common example is areas where manure is highly concentrated, as commonly observed around confined animal feeding operations (CAFOs). For this reason, clean water that flows onto CAFOs (i.e. "run-on") must be diverted and any runoff that originates from the CAFO area where manure is concentrated, must be collected and properly disposed. Many consider CAFOs to be potential point sources of nutrient pollution. Proper design of a CAFO and runoff collection systems are able to prevent incidental P losses from areas directly around the CAFO facilities. Non-manure sources of P can also become a source for incidental P losses; for example, silage storage bunkers are capable of releasing dissolved P concentrations similar to animal manure.

Incidental P losses also occur when P is land applied to soils as either chemical fertilizer or organic P. Applied fertilizer and manure P reacts relatively quickly with soil, reducing its solubility compared to the raw material alone. However, if a runoff event occurs before the applied P is able to react with the soil, then a high concentration of P will be lost in runoff. Simply put, increased physical contact and time of contact between soil and applied P will dramatically decrease P losses in runoff. For example, surface applied fertilizer and manure P that has little physical interaction with the soil, applied immediately prior to a runoff event will result in the highest possible P losses in runoff. For this reason, several states such as Ohio and Wisconsin provide online guidance for farmers with regard to risk of applied nutrient losses in runoff, based on meteorological predictions. The greater the rainfall/runoff event, the more P will be transported, both incidental and legacy P sources. Figure 2.1 illustrates the dissolved P losses from a poultry CAFO over a 2.5 year monitoring period. Over that time, over 50% of the dissolved P that was lost in runoff had occurred in only three rainfall/runoff events. These three rainfall events were among the largest rainfall events over the monitoring period.



Fig. 2.1. Aerial view of a poultry farm where runoff flow and dissolved P concentration was monitored over a 2.5 year period. The source of P in runoff was both incidental P loss from poultry manure spilled outside the barns and soil legacy P. Notice that over 50% of the dissolved P load lost in runoff had occurred in only three runoff events, which were the largest rainfall events over the time period

Increasing physical contact between applied P and soil for reducing incidental P losses can be accomplished by using liquid P sources and/or incorporating applied P with tillage implements. If runoff is the main pathway for nutrient loss, then placing the applied P below the surface where it is in less contact with runoff will also reduce P losses. This can be achieved through incorporation with tillage, subsurface banding of chemical fertilizer, or direct injection of organic P sources below the surface.

Incidental P losses also occur in urban and suburban areas. Bare soils with surface applied fertilizer, fertilizer applied directly onto sidewalks and streets, and fertilizer applied to areas with high runoff potential immediately before a large rainfall/ runoff event will each result in elevated incidental non-point P losses.

Incidental P losses can generally be prevented through:

- · Proper storage of materials with high P concentrations
- Minimizing runoff from around those P sources and capturing any runoff that does occur from them
- Limiting application rates
- Incorporation of the P source into soils to increase soil contact and reduce runoff
 contact



Fig. 2.2. As soils accumulate more P and become "legacy sources", they possess greater potential to release dissolved P in runoff and subsurface drainage water. Adapted from Penn et al. (2006), with permission from the author

 Timing P applications to avoid large rainfall/runoff events that occur immediately after application

Compared to legacy (soil P) losses, incidental P losses can be much more devastating with only a single event. Legacy P is essentially soil P that has been built up to high enough concentrations that the soil itself becomes a potential non-point P source. While the magnitude of P lost from legacy P sources is much less compared to incidental P lost on an event basis, incidental P losses occur less frequently.

2.3 Legacy Phosphorus

Applied P transforms into the soil P pool. Eventually, with enough P applications at rates beyond plant needs, soils can become a stable legacy P source that frequently releases small amounts of P into runoff and drainage water. Contrary to incidental P sources, legacy P is more difficult to manage. Changes to management can immediately and dramatically reduce incidental P losses. However, due to the highly stable nature of legacy P, changes in management are less effective at reducing dissolved P losses from legacy P sources. This problem with legacy P sources is threefold:

- Soil P concentrations are highly correlated with dissolved P concentrations lost in runoff and drainage water (Fig. 2.2)
- Legacy P soils tend to remain elevated in P for many years after efforts to reduce soil P levels have begun (Fig. 2.3)
- While many best management practices are able to keep particulate P contained, they do little for dissolved P losses or are temporary in nature



Fig. 2.3. Changes in soil test P concentrations with drawdown. *Upper bar graph* shows the expected change in Mehlich-3 soil P concentrations from six different crops on both a sandy and clayey soil, in a single growing season; these calculations assumed average yields. *Lower figure* illustrates the time required to reduce Mehlich-3 soil P concentrations in a corn grain-soybean rotation assuming average yields, for both sandy and clayey soils

As discussed in Chap. 1, the main issue with legacy P sources is dissolved P losses since particulate P can easily be contained through erosion control practices. Briefly, particulate P is P that is bound to soil and solid matter, while dissolved P is essentially the P that is free in solution. Therefore, dissolved P will move wherever the water flows. See Chap. 1 for a more detailed discussion about dissolved vs. particulate P losses.

Management of legacy P is best understood and examined from a systems perspective (Fig. 2.4). In general, we can consider the control of both dissolved and particulate P losses from legacy P soils in three phases: prevention of legacy P from occurring, and then if it does occur, containment of the P onsite and remediation to remove the P.



Fig. 2.4. A systems perspective for legacy P management. Control of dissolved and particulate P losses (ovals and boxes, respectively) from legacy soils is achieved through an array of best management practices in three stages: prevention of legacy P, containment of the P on-site, and remediation of the legacy P

2.3.1 Preventing Legacy P from Occurring

The most efficient and cost effective technique for dealing with legacy P is to prevent soils from becoming legacy P sources in the first place. Preventing legacy sources from occurring can be summarized in a single sentence: do not excessively and frequently apply P to soils beyond what will be removed by the harvested portion of the plant. This is achieved through basic nutrient management planning. Unlike nitrogen, P will build up in soils if it is applied beyond the need of plants. Eventually, if the soil P levels becomes high enough, it can become a potential nonpoint P source (Fig. 2.2). While existence of a legacy P soil alone is not enough to categorize a site as a non-point P source, it is one of the requirements for P transport to occur. In the philosophy of the NRCS "Phosphorus Site Index" tool, a site must not only possess a P source, but also a hydrologic connection to a surface water body in order to contribute P to that water body. In other words, it must possess both a P source and a means of transport. To what degree a soil P level must be elevated before it is considered a potential source is often debated, and it is important to keep in mind that agronomic soil tests and thresholds are not necessarily the same as environmental P thresholds.



Fig. 2.5. Traditional animal agriculture nutrient cycling for P. Livestock feed is produced on-farm and only a fraction of the P leaves the farm in the form of produce, while the rest remains as manure where it is used to grow more feed. The exported P is replaced with commercial fertilizer. Figure credit: Hailin Zhang, Oklahoma State University

2.3.1.1 Nutrient Management Planning

Proper nutrient management planning for P is essentially managing soil P levels at or near, optimum levels for crop or turf production. For production systems that do not involve CAFOs, nutrient management planning is very simple. Maintain soil P levels at concentrations suitable for production, and do not apply P beyond plant needs if the soil P concentration is already at or near adequate concentrations in order to prevent soil P build-up. In order to understand why nutrient management planning is more challenging for CAFOs, it is first necessary to discuss nutrient cycling in the traditional animal agriculture system (Fig. 2.5).

Traditionally, all of the feed used to support the livestock was produced through crop production located on-farm (Fig. 2.5). After being fed to livestock, 25–40% of the P contained in that animal feed was exported from the farm in the form of agriculture produce. Thus, 60–75% of the P contained in the animal feed passes through the animal in the form of manure, which is land applied back onto the soil that produces further crops/feed for the animals. In order to compensate for the P exported from the farm through produce, chemical fertilizer is amended to the soil. Through proper distribution and application of manure, and when necessary, fertilizer, this



Fig. 2.6. Contrary to traditional livestock farms, the nutrient cycling for confined animal feeding operations (CAFO) is fragmented, resulting in an appreciable soil P imbalance since most P stays on farm in the form of manure

traditional system prevents soils from P build-up and from becoming legacy P sources.

In CAFOs, the nutrient cycle is fragmented and no longer localized (Fig. 2.6). The livestock feed is only partially supplied from the local farm since it is not large enough to produce enough crops to satisfy all of the livestock production, and therefore is supplemented with feed made from crops that are typically grown in the Mid-Western U.S. In essence, this results in a geographic imbalance in soil P levels since the majority of nutrients imported into a CAFO in the form of livestock feed will remain on the CAFO, allowing P to accumulate in the soils through land application of the manure. Simply put, more P is imported onto the farm than the farm is capable of utilizing/exporting, and therefore the soils accumulate P quickly and become legacy P sources. This problem is often exacerbated since manure is typically applied at rates to satisfy the nitrogen demand of crops. The N:P ratio of animal manure is typically greater than the N:P ratio of crops, which means that more P is added than what is required by the plant.

Nutrient management planning principles can also be applied to turf production on golf courses and residential areas to prevent soils from becoming legacy P sources. Through use of soil testing and knowledge of turf demand for P, managers, landscapers, and homeowners can reduce the risk of adding P fertilizer beyond the need of the turf. Problems occur in urban/suburban areas when soils are not tested and P fertilizer is continuously applied without knowing if it is needed or not. This problem is further aggravated through use of mulching mowers that act to recycle the P in grass clippings back into the soil, which in combination with continued fertilizer P applications, can quickly cause soil P to accumulate. On the other hand, when turf grass is mowed and bagged, the P contained in the grass clipping is removed from the soil, and depending on the soil P levels, may need to be supplemented through P fertilizer. When the clippings are recycled back into the soil to be used as a source of P, the fertilizer applications should be reduced or eliminated, according to soil P tests. The P fertility regime for a turf system where the grass clippings are removed will require much more P than for a system where clippings are not removed.

2.3.1.2 Manipulation of Animal Diet

With the modern CAFO system, more P is imported onto the farm than the crops on that farm can utilize (Fig. 2.6). Part of this problem is due to the fact that livestock are somewhat inefficient at absorbing the P contained in animal feed. Thus, improvements in the livestock diet can reduce the P concentration in the manure and/or allow P to be better absorbed by the animal. Through this, P accumulation on the farm will be reduced since livestock P will be exported through produce (i.e. milk, meat, and eggs).

Several aspects of animal diet can be manipulated to reduce the total P concentration in manure. This includes minimizing the feed required per unit gain, minimizing feed wastage, and matching the dietary P levels with livestock requirements. Simply reducing the dietary P level can drastically reduce P concentrations in manure without decreasing livestock performance.

For non-ruminant livestock such as swine and poultry, the problem of poor P absorption by the animal is especially problematic, since they are unable to utilize the majority of the P contained in corn-soybean meal. This poor utilization by nonruminants is a result of their inability to digest phytate-P, which is the organic form of P contained in much of the livestock feed (corn and soybean). As a result, poultry and swine growers often supplement dietary P with inorganic P supplements. To improve P absorption of phytate-P, phytase enzyme can be added to the diet in order to make phytate-P more available to the animal. Also, varieties of corn and soybean that possess lower concentrations of phytate-P can be used to increase P absorption i.e. "high available P" corn and soybean. Through improvement of phytate-P utilization and use of high available P corn and soybean, managers can also reduce the amount of inorganic P supplements in the diet. Figure 2.7 illustrates how reduction of inorganic P supplements and addition of phytase enzyme in poultry diets can reduce both total and water soluble P in the resulting manure. The reduction in manure total P directly translates to less land area required for land application of the manure to meet crop P needs as dictated by the nutrient management plan. However, such P reductions may still not be enough to reduce the imbalance between P import and export on the CAFO. In that case, animal manure must be exported from the farm to prevent soil P build up.


Fig. 2.7. Poultry diets can be adjusted in order to reduce the total and water soluble P concentrations in the resulting manure. This is also true for other livestock diets, although only non-ruminants will respond to additions of phytase enzyme to their diet. Data adapted from Penn et al. (2004), with permission from the author

2.3.1.3 Manure Export

Another option for CAFOs or for any farm that imports more P through livestock feed than the crops can utilize, is to physically export the manure P from the farm to P deficient soils. Manure is clearly an excellent resource for soils and growing plants. Instead of supplying only N, P, and K, it has an advantage over chemical fertilizer in that it can additionally provide Ca, Mg, and S, micronutrients, organic matter, and calcium carbonate equivalent for maintaining or increasing pH. Overall, use of manure as a nutrient source can increase soil quality compared to chemical fertilizer. While CAFOs typically produce more P than required by crops on-farm, other non-CAFO farms often require additional P inputs (Fig. 2.8). However, transportation of manure is greatly limited due to the relatively low concentration of nutrients compared to commercial fertilizer. Animal manure can be purchased for a cost that is often much less than the value of the nutrients contained in the manure,



Fig. 2.8. Example of P supply in the form of broiler (poultry) litter and the soil-crop P demand throughout the state of Oklahoma. Adapted from Penn et al. (2011)

however, transportation is the biggest cost in obtaining it. For this reason, only relatively dry manure such as poultry litter can be transported appreciable distances. The economic return on using transported animal manure as a nutrient source compared to commercial fertilizer is a function of the crop being grown, rate of nutrient application, and especially the transportation distance (Fig. 2.9).

Since transportation cost is the biggest obstacle to manure transport, any practices that reduces manure moisture content or concentrates the nutrients will improve the economics of transport. For example, manure drying, dewatering, pelletizing, and composting, can all improve the potential for excess manure to be transported off a CAFO, in order to prevent their soils from becoming legacy P sources. However, such manure processing requires further costs that may or may not be viable under certain situations.



Fig. 2.9. Example economics for poultry litter transportation in Oklahoma for growing sweet sorghum as a biofuel crop. The probability of achieving a greater economic return from using poultry litter compared to commercial fertilizer as a nutrient source is a function of how far the litter is transported and the nutrient application rate. Application rates correspond to total N, P_2O_5 , and K_2O applied, which was 90, 78, and 77 kg ha⁻¹ for rate A, 135, 116, and 115 kg ha⁻¹ for rate B, and 180, 155, and 153 kg ha⁻¹ for rate C, respectively. Adapted from Penn et al. (2014) with permission from author

2.3.2 Containment of Legacy Phosphorus Losses

If proper nutrient management planning is not executed and prevention of soil P buildup fails to the point of becoming a legacy P source, then that P must be contained and remediated. In this section, we examine containment of legacy P, that is, to reduce the loss of P in runoff and drainage water that leaves a site possessing legacy soils. Containment of legacy P can be reduced to three categories of practices: tillage, soil and manure amendments, and soil and water transport reduction. Throughout this discussion of containment, it is important to keep in mind that these practices do not eliminate the legacy P source, it will only contain it. Therefore, containment practices must be used in conjunction with remediation of legacy P (Fig. 2.4).

2.3.2.1 Tillage Practices

Tillage practices can impact both dissolved and particulate P losses (Fig. 2.4), although sometimes a tillage practice will decrease loss of one form of P while increasing loss of the other form. In general, reduced and no-tillage systems can appreciably reduce loss of particulate P through reduction of erosion. However, if P



Fig. 2.10. Tillage of high P soils can reduce runoff dissolved P concentrations (*upper figure*) if soil P is concentrated near the surface, but tillage can also increase particulate P losses (*middle figure*) due to increased sediment losses in runoff (*bottom figure*). Figure adapted from Sharpley (2003), with permission from author

is applied to the surface and not incorporated over many growing seasons/applications, then soil P levels can build up in the upper inch of soil where it can interact with and release dissolved P in runoff even though particulate P loss is minimal.

One potential remedy to the situation of P stratification at the soil surface is to provide tillage in order to mix the high P surface soil layer with the low P soil located beneath that layer. Figure 2.10 shows how tillage of a stratified high P soil can decrease the loss of dissolved P compared to the un-tilled soil. It should be noted that this remedy will only reduce dissolved P losses if the underlying soil is lower in P concentra-



Fig. 2.11. Manure water soluble phosphorus (P) concentrations with application of various rates of P sorption materials (PSMs), for dairy, swine, and poultry (*Upper, middle* and *lower figure*, respectively), after 24 h. Initial water soluble P concentrations for non-amended manure was 3062, 6710, and 14,539 mg kg⁻¹ for dairy, swine, and poultry, respectively. *AMDR* acid mine drainage residual, *WTR* drinking water treatment residual

tion compared to the surface layer i.e. the soil P must be stratified. However, notice that this practice also resulted in a temporary increase in particulate P loss, which was due to greater sediment loss (erosion) resulting from the soil disturbance.

2.3.2.2 Soil and Manure Amendments

As previously discussed in Chap. 1 and shown in Fig. 2.10, if soil erosion is minimized, then particulate P losses are also minimized. However, if the soil P concentrations are elevated, the soil may still behave as a source of dissolved P to runoff and drainage water. One method of containing dissolved P on-site is to reduce the soil P solubility through application of P sorption materials (PSMs). P sorption

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Fig. 2.12. Direct application of P sorption materials (PSM) to soils can decrease soil water soluble P concentrations (*upper figure*) and therefore the concentration of dissolved P in runoff (*lower figure*). PSMs were applied at 20 g 100 g⁻¹ in the runoff experiment (*lower figure*), except for gypsum which was applied at 5 g 100 g⁻¹. The soil used in this experiment was an Othello sandy loam. *AMDR* acid mine drainage residual, *WTR* drinking water treatment residual. Control soil received no amendment

materials will be discussed extensively throughout this book, but briefly, PSMs are materials that have a high chemical affinity for P and therefore reduce P solubility. Amending animal manure with PSMs can greatly reduce the water solubility of manure P, as illustrated in Fig. 2.11. While most of the PSMs described in this book are industrial by-products, PSMs that are currently used as manure amendments are usually not by-products. For example, aluminum and iron sulfates and chlorides are more commonly used as manure amendments for reducing P solubility than industrial by-products. Use of aluminum sulfate (alum) on poultry litter is the most common example. Essentially, with PSM amendments the P is bound in a poorly soluble form in the manure, and after land application of the amended manure, less P will dissolve during runoff/drainage events thereby reducing dissolved P losses.

Phosphorus sorption materials can also be amended directly to legacy P soils to similarly reduce P solubility. Figure 2.12 shows how different PSMs reduced water soluble P concentrations in a high P soil, and the subsequent reduction in runoff dissolved P losses compared to a non-amended control soil. While amendment of PSMs to manure and high P soils are effective at reducing dissolved P concentrations in

runoff and drainage water, it is important to keep in mind that such reductions are only temporary. Eventually, most of the P bound to the PSM will revert back to the previous, more soluble chemical form. The amount of time required for this to occur will vary as a function of the soil properties, P levels, PSM used, and application rates. In previous research on cattle loafing areas, soils amended with PSMs reduced runoff dissolved P concentrations for <28 days (Penn and Bryant 2006). After 28 days, runoff dissolved P concentrations were not significantly different from non-amended soils. In other cases, dissolved P reductions may be maintained for years. Still, reducing dissolved P losses through PSM amendments is beneficial even if it is temporary.

2.3.2.3 Soil and Water Transport Reduction

While PSM amendments reduce dissolved P losses through reducing dissolved P concentrations in runoff and drainage water, BMPs targeted at flow reductions can contain legacy P by reducing the volume of water that is transported off-site. As previously mentioned, P is transported off-site through water movement. If that water is prevented from leaving the site, then both dissolved and particulate P losses are minimized. Practices such as reduced and no-tillage can appreciably contain P loads by reducing runoff through increasing the infiltration of water downward into the soil.

A common practice for reducing the volume of runoff water lost from a site is through the use of a vegetated filter strip (Fig. 2.13 upper left photograph), which serves to promote infiltration of runoff leaving a field before it reaches a ditch or stream. However, once a vegetated buffer strip becomes saturated with water, it will no longer reduce the volume of runoff water leaving a site. The vegetated filter strips also serve to physically filter sediment from runoff, and therefore reduce particulate P concentration. Another issue with vegetated filter strips is that they tend to accumulate P, sometimes to the point of becoming dissolved P sources themselves (Deng et al. 2011; Borin et al. 2005). Thus, while they are very effective at reducing particulate P losses, they are somewhat ineffective at reducing dissolved P transport in cases where runoff volumes are not minimized (Hoffmann et al. 2009).

Constructed wetlands are also similar to vegetated filter strips in that they act to reduce the total runoff water volume that leaves a site and captures sediment and particulate P. However, P still remains in the system and dissolved P can be released from the wetlands with large flow events unless the wetland is periodically dredged and plants harvested. A disadvantage of wetlands is that they are often designed to achieve a long retention time for the water, sometimes several days. For water to remain in the wetland for a long period, its area must be extremely large. Thus, treatment wetlands tend to be many acres in size.

For subsurface drainage pipes, which is common in the Mid-Western U.S., flow volumes can be reduced through flow-control structures that act as a small adjustable dam for subsurface water (Fig. 2.13). Through raising the height of the riser boards, subsurface water can be prevented from flowing off-site, and therefore

2.3 Legacy Phosphorus



Fig. 2.13. Examples of best management practices for reducing flow volumes and therefore P loads. *Upper left photograph* depicts a vegetated filter strip meant to increase infiltration of runoff water and decrease sediment loss from the surrounding row crops. *Upper right photograph* is a constructed wetland. *Lower diagram* is a flow-control structure for limiting flow from tile drains. *Upper left photograph*: Stan Livingston of the USDA-ARS. *Upper right photograph*: James Bowen of University of Kentucky. *Lower diagram*: NRCS

contain the P. Drainage water management has been shown to reduce dissolved P loads by 40–68% (Williams et al. 2015).

2.3.3 Remediation of Legacy Phosphorus

While containment of P losses from legacy P soils is necessary, it is important to keep in mind that 100% containment is not possible. Containment does not alleviate the root of the problem, it simply keeps the P isolated on the terrestrial landscape, temporarily. Containment of legacy P must also be practiced in conjunction with remediation of the legacy P (Fig. 2.4). Regarding remediation of non-point P losses from legacy soils, depending on the practice it can be either highly responsive or slowly responsive with respect to time. The less responsive technique of P drawdown will ultimately eliminate the legacy P source, given enough time, but does little to reduce dissolved P losses in the short term. Opposite to that, the more responsive technique of using P removal structures will immediately remove



Fig. 2.14. Example of a P removal structure that treated runoff from a poultry CAFO. High P water flowed into the structure on the upslope side, where it filtered through the contained PSM (treated steel slag) and drained out on the other side. This structure removed about 3 lb of dissolved P per year while it was monitored (2.5 years). Structures can be designed to achieve desired P removal targets and lifetimes

dissolved P in runoff, but does nothing to eliminate the source of the dissolved P since dissolved P losses are negligible compared to the soil P supply. Both techniques need to be used in combination in order to achieve the greatest possible dissolved P reductions.

2.3.3.1 Eliminating the Source: Phosphorus Drawdown (Phyto-remediation)

When the P source to runoff and drainage water are legacy P soils, the most obvious solution is to first cease all P applications and then reduce the amount of P contained in those soils. Soil P reduction is achieved through plant uptake of P, followed by harvesting the plant biomass and therefore the P contained within it. This is the long term solution to eliminating legacy P sources.

Different crops and turf grass vary in their ability to uptake soil P (Fig. 2.3). While P uptake through harvested plants can remove around 5–25 mg P kg⁻¹ soil per harvest, the P uptake does not correspond to an equal decrease in agronomic and environmental soil test P indicators because such tests only extract a fraction of the soil total P content. For example, even though a typical alfalfa harvest will remove around 8 mg P kg⁻¹ soil, this will only decrease the soil Mehlich-3 P concentration by 1–3 mg P kg⁻¹ soil. In other words, the total soil P pool acts to buffer

the soluble and "labile" P pools, and this buffering ability is a function of soil properties. For example, Fig. 2.3 illustrates how a more highly P-buffered soil (high clay) will decrease less in soil Mehlich-3 P concentrations compared to a less P-buffered soil (sandy), given the same amount of total P removed from the soil by the plants. The result is that sandy-textured soils will require less time to remediate the legacy P compared to heavy-textured soils. In a review of P drawdown on different soils and crops, Sharpley et al. (2013) showed that soil test P levels (Olsen, Mehlich-1, Mehlich-3, Morgan's, or Bray-1) decreased anywhere from 30 to 0.4 mg kg⁻¹ per year.

Regardless of soil type, the greater the soil P concentration, the more time it will require for P drawdown to decrease soil P to safe levels. While this attacks the source of dissolved P losses, it is an extremely slow process, often requiring decades. During this slow period of P drawdown, the soil is still behaving as a P source and releasing appreciable P concentrations to water.

2.3.3.2 Phosphorus Removal Structures: Immediately Responsive P Reductions

Soil legacy P drawdown is absolutely necessary for solving the problem of excessive dissolved P losses in drainage water, as it eliminates the source. However, as described in the previous section, this may require decades, and dissolved P losses will continue until the source is eliminated. The P removal structure, which is the topic of this book, is intended to trap and filter the dissolved P in runoff and drainage water until the P source is eliminated. Chapter 3 is dedicated to a more detailed explanation of the P removal structure and how it works. Briefly however, the P removal structure is a landscape-scale filter containing PSMs that have an affinity for dissolved P. Flowing water rich in dissolved P passes through a PSM, the P binds to the material, and low-P water is discharged. The P removal structure is strategically placed to filter water before it reaches a surface water body. Periodically, the filter media (i.e. the PSM) is replaced with fresh material or rejuvenated. The example P removal structure shown in Fig. 2.14 removed 3 lb dissolved P per year over the 2.5-year monitoring period. Chapter 3 illustrates many different styles of P removal structures.

This new BMP has the potential to reduce dissolved P losses while the necessary but slow P drawdown process is also taking place to eliminate the source. Figure 2.15 illustrates how the slow process of legacy P drawdown allows for release of high dissolved P concentrations in runoff for many years, but when used in combination with a P removal structure, the runoff P concentrations are greatly minimized early in the P drawdown process. The justification of the need for P removal structures is threefold: current BMPs are only slightly effective for reducing dissolved P losses from legacy P soils, dissolved P losses will be sustained for many years in the beginning of the drawdown process, and dissolved P is 100% bioavailable to aquatic ecosystems, unlike particulate P.



Fig. 2.15. *Upper diagram*: Calculated runoff dissolved P concentrations over time through implementation of soil P drawdown, P removal structure, soil P drawdown in combination with a P removal structure, and no remediation. *Bottom diagram* illustrates the relative contribution of each practice toward decreasing runoff dissolved P concentrations when both practices are simultaneously implemented. Assumptions: initial soil P level = 200 mg kg⁻¹ Mehlich-3 P; P drawdown = 4 mg kg⁻¹ Mehlich-3 P per year; P removal structure constructed and maintained to remove 40% of runoff dissolved P; Runoff dissolved P concentration calculated based on relationship between Mehlich-3 P concentration and dissolved P concentration (Vadas et al. 2005)

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Chapter 3 Phosphorus Removal Structures as a Short-Term Solution for the Problem of Dissolved Phosphorus Transport to Surface Waters

3.1 Purpose, Concept, and General Theory of Phosphorus Removal Structures

In this chapter the general theory of the purpose and operation of P removal structures for treating dissolved P is presented and explained along with the necessary components for any P removal structure. While P removal structures can take many different forms, these four components must be present for a P removal structure to be effective: (1) an effective P sorption material (PSM) in a sufficient quantity, (2) containment of the PSM, (3) the ability to replace the PSM when necessary, and (4) passive drainage via gravity at sufficient flow rates suitable for the site. Because the conceptual application is flexible and allows for a diversity of scenarios and structures, many different types of P removal structures are presented in this chapter. For example, runoff interception box filters, ditch drainage filters, subsurface tile drain filters, urban storm water inlets, agricultural surface and blind inlets, urban "bioretention cells", and treatment of domestic wastewater can all be designed to possess the four necessary components of a P removal structure.

3.1.1 How the Phosphorus Removal Structure Works for Removing the Target Pollutant: Dissolved Phosphorus

The target P form in which the P removal structures are designed to remove, is dissolved P. As briefly discussed in Chap. 2, the justification for targeting dissolved P and constructing P removal structures in certain situations is three-fold: the readily bioavailability of dissolved P, the poor ability of BMPs in reducing dissolved P losses from legacy soils, and the high P legacy soils as a continuous source of dissolved P to drainage water. Dissolved P is 100% biologically available upon deposition into an aquatic ecosystem. On the other hand, the bioavailability of particulate P will vary as a function of the (1) mineralogy of the sediment, (2) the concentration and forms of total P contained on the sediment, and (3) the dissolved P concentration of the receiving surface water. This makes dissolved P more potent and dangerous to aquatic ecosystems compared to particulate P since an explosion in plant and algal growth could occur immediately with deposition of dissolved P. While transport of particulate P can be immediately reduced by conventional BMPs that reduce erosion, these traditional BMPs typically do little to inhibit dissolved P losses.

Last, the high P soils, which are one of the major sources of the dissolved P in non-point source drainage water, are long-term sources of dissolved P for several decades i.e. "legacy P" (Chap. 2). In fact, such legacy soil P sources will continue to release dissolved P to drainage water for many years, even while long term solutions to legacy P (such as nutrient management and P drawdown) are being implemented. While these long term solutions are absolutely necessary to solve the problem of dissolved P transport and eutrophication, the use of P removal structures can be used to reduce dissolved P loading to surface waters in the short term. More pointedly, as the long-term solutions slowly decrease the source of P (i.e. legacy P; Fig. 2.3), the soil will continue to release dissolved P to drainage water every time there is a rainfall-runoff-drainage event until the soil P concentrations are reduced to acceptable levels (Fig. 2.15).

At its most basic level, a P removal structure is simply a landscape-scale filter containing a reactive substrate with a high affinity for dissolved P. The structure is placed in a suitable location (see Sect. 3.1.1.2) with a known excess P issue, and designed so that high P water is able to flow through the substrate, known as P sorption materials (PSMs). Then, the clean water is passively discharged through drainage pipes while the P is retained on the PSMs (Fig. 3.1).

The P removal structure is ideally designed to remove a desired amount of P, usually expressed as a percentage of the load of dissolved P leaving the site in captured drainage water and entering the structure, over a chosen time period. After the contained PSMs are no longer able to remove dissolved P, i.e. they are "spent", or after the they are no longer removing dissolved P at an acceptable rate, they are either removed from the structure and replaced with new PSMs, or chemically rejuvinated.

3.1.1.1 Essential Components of a Phosphorus Removal Structure

A P removal structure can appear in a variety of forms and settings, including urban, horticultural, and agricultural. Regardless of the appearance, form, and shape of the structure or the setting, all P removal structures have the same four basic components:

1. Contains a sufficient mass of an unconsolidated PSM (P sorption material). The material must have a strong capacity to adsorb P. PSMs are usually industrial by-products or manufactured (see Chap. 4). However, there are some PSMs that occur naturally.



Fig. 3.1 Diagram illustrating the basic premise of a P removal structure. Regardless of appearance, all P removal structures must possess four basic components: contain a sufficient mass of an unconsolidated P sorption material (PSM), the PSM is contained and placed in a hydrologically active area with high dissolved P concentrations, untreated water is able to flow through the contained PSM at a suitable rate, and the PSM is able to be removed and replaced after it is no longer effective at removing P or able to remove P at the minimum desired level.

- 2. The PSM is contained and placed in a hydrologically active area that receives and/or exhibits high dissolved P concentrations.
- 3. High dissolved P water is able to flow *through* the contained PSM at a suitable flow rate.
- 4. The PSM is able to be removed and replaced after it is no longer effective at removing P or able to remove P at the minimum desired rate.

A "sufficient mass" of PSM is the amount of a specific PSM necessary to meet the desired P removal goal and lifetime for the specific conditions of the site. Determining the necessary mass of a particular PSM is one of the fundamental outputs from conducting a proper design of a P removal structure. The sufficient mass of PSM required for a particular site is a function of many factors discussed in Chap. 6, and can easily





Fig. 3.2 Upper photos: while filter socks are effective at preventing transport of soil and particulate P, they are mostly ineffective at removing dissolved P due to poor contact between the dissolved P in water and the PSM contained in the sock, and also due to small amounts of PSM. Lower figure: demonstration of the impact of water flow through a PSM vs. flow over a PSM using a sieved steel slag. *Upper left photo* credit: USDA-ARS Image Gallery. *Upper right photograph* is courtesy of York County (PA) Conservation District. Data in *lower figure* courtesy of Isis Chagas, USDA-ARS National Soil Erosion Research Laboratory

be determined using the Phrog software. Briefly, the sufficient mass of PSM is a function of P removal goals, drainage water volumes and P concentrations at the site, retention time of the drainage water within the PSMs, and the chemical and physical characteristics of the PSMs to be used in the structure. Depending on the scenario, the PSMs can be contained by earthen berms, metal, wood, plastic, or concrete borders, inside a tank or box, within a ditch and retained with a small dam, etc.

The necessity of the untreated water to be able to flow through a PSM is especially important. While it is tempting to simply incorporate PSMs to the soil surface of constructed wetlands, apply PSMs to the surfaces at the edge of fields where contaminated runoff must pass over, or even wrapping a "sock" containing PSMs around a drainage outlet (Fig. 3.2), such efforts are generally non-effective or short lived (King and Balogh, 2013). For PSMs to effectively sorb dissolved P from runoff, they must have sufficient contact with the runoff or drainage water. Water that simply flows over the top of a PSM will have minimal contact with the PSM, such as PSM-amended buffer zones and constructed wetlands. Regarding the example shown in Fig. 3.2, while the filter sock is effective at preventing particulate matter and soil from flowing offsite, the water will flow under or over the sock, preventing sufficient contact between dissolved P and the PSM contained inside of the sock. Such filter socks also possess too little mass of PSM to be effective in most cases.

3.1.1.2 Site Requirements for a Phosphorus Removal Structure

P removal structures are only viable under certain conditions and will have to be custom designed for each location. There are several site requirements for a P removal structure:

- 1. Flow convergence to a single point where the water can be directed into a P removal structure, or the ability to manipulate the landscape to achieve this.
- 2. Appreciable dissolved P concentrations in flow. This typically occurs in areas where soil test P is high or P is often applied at the surface with no incorporation (usually chemical fertilizer or manure). A threshold dissolved P concentration of $0.2-0.3 \text{ mg } \text{L}^{-1}$ is a good rule of thumb. The higher the P concentration, the greater efficiency regarding load reduction.
- 3. Hydraulic head, which is required to "push" water through a PSM. In practical terms, the hydraulic head is a function of the slope of the site (i.e. change in elevation) or the depth of a ditch if a structure is to be built in a drainage ditch, or ultimately drain into a ditch. If there is no possibility of creating hydraulic head, then a pump must be used.
- 4. Sufficient space to accommodate the PSM.
- Hydrologic connectivity to surface waters. In other words, P contained in runoff or drainage water cannot cause problems in aquatic systems if the water is unlikely to reach surface waters.

A ditch is an example of a landscape feature that serves as a point where water converges, and therefore a good potential interaction point for placement of a P removal structure (Fig. 3.3). Another example of a point of concentrated flow that may already exist is a subsurface drainage pipe such as a tile drain or an urban storm water inlet (Fig. 3.4). The topography of the site plays a vital role in transport of water to the structure and the rate of flow through it, so properly positioning the structure and, if necessary, use of berms will help channel runoff into the structure (Fig. 3.5). For water to flow through the porous PSM, hydraulic head will be necessary. The maximum hydraulic head for a site is simply the amount of elevation change across a certain known distance (i.e. length). Flow rate of water through the PSM is determined in part by the hydraulic head. For structures built in drainage ditches or that will drain into a ditch, the depth of the ditch is a limiting factor for hydraulic head. This is discussed in more detail in Chap. 6.

Structures will only be successful in areas that produce a high concentration of dissolved P in drainage water. Thus, it is essential to obtain some estimate of both the typical dissolved P concentration in the drainage water and average annual load at the site of interest. As a rule of thumb, it is generally not efficient to treat water with a dissolved P concentration less than around 0.2 mg L^{-1} ; however, this value will vary as a function of the PSM. Soil test P concentrations can be used to help



Fig. 3.3 Drainage ditches in agricultural or urban environments can serve as an ideal intercession point for the construction of a P removal structure if the dissolved P concentrations are high. Photo credits—*upper*: Joshua Bradley, Oklahoma State University; *lower*: Gene Hahn, University of Kentucky

estimate dissolved P concentrations in runoff and subsurface drainage water if direct measurements cannot be obtained. Estimating dissolved P concentrations in runoff and drainage water as a function of soil test P values are presented in Chap. 6.

3.1.2 Choosing the Most Efficient Target Locations for a Phosphorus Removal Structure

Assuming that a location is suitable for construction of a P removal structure as outlined in the previous section, the most efficient location for P removal are those with the highest P concentrations and P loads. Such locations are known as "hot



Fig. 3.4 Storm water drop inlets in urban areas and subsurface drainage lines represent areas where water flow is concentrated and therefore a potential location for a P removal structure if the dissolved P concentrations are elevated. *Lower photo* is courtesy of Stan Livingston, USDA-ARS

spots", and are often considered to be responsible for the majority of P transported to surface waters by non-point sources. In assessing the most efficient locations for P removal structures, it is important to consider dissolved P concentrations in the drainage water and the load of P transported. The P load is the actual mass of P that is transported from the site to surface waters, and it is a function of both the concentration of P (mass per volume of water) and volume of water transported:

$P load = P concentration \times volume of water transported$ (3.1)

While it is easy to apply threshold aquatic ecosystem P concentrations to drainage water, it is not logical to use such values for setting limits or guidelines for drainage water/runoff concentrations for two reasons: in-stream/in-water body



Fig. 3.5 The earthen berms in the left photograph were constructed to channel water into the entrance of the P removal structure (*right photo*). View in the *right photo* is from the uphill side looking downward into the direction of water flow. Berms are highlighted between the *dashed lines*. Photo credit: Stuart Wilson, TLDR consulting.

processes and consideration of P loads. First, consider that the P concentrations within the water body of interest constitute the end of most importance. Although that concentration will vary with time, the critical factor controlling the P concentration in that water body is the total mass of P within it. The P concentration of drainage traveling to the water body and even after being deposited into the water body will be affected by several processes that will change its dissolved concentration. Essentially, dissolved P concentrations will fluctuate as a function of dilution, concentration, uptake by organisms, sorption to sediment, and desorption from sediment to solution. Even within a water body, the dissolved P concentration will decrease with further flow inputs from low P drainage water (i.e. dilution), and increase with evaporative losses. While the dissolved P concentrations will fluctuate, the dissolved concentration is mostly a function of the total P mass within that body of water. For this reason, the USEPA and other agencies have set guidelines and limits for P transport based on loads, not concentrations. For the same reason, one should consider P loads being transported from a potential site when considering construction of a P removal structure. In practice, the most efficient sites for targeting P reductions with P removal structures are those with the highest loads of dissolved P.

That being said, dissolved P concentration in the drainage/runoff water is also important in choosing the most efficient site for constructing a P removal structure. The most obvious reason for this is evident by the fact that P concentration is a component of quantifying the P load, shown in equation 3.1. i.e. the greater the P concentration, the greater the P load. The second reason why dissolved P concentration is critical in assessing which sites are the best candidates for construction of the

most efficient P removal structure is less obvious. The PSMs used to trap and remove dissolved P (i.e. sorb P) from water are more thermodynamically favored to sorb P when dissolved P concentrations are higher. The higher the dissolved P concentration, the more efficient it is to treat. This is true regardless of whether the P sorption mechanism is precipitation as a solid P mineral or adsorption onto the surface of a mineral by the ligand exchange mechanism (mechanisms of P sorption by PSMs will be discussed in detail in Chap. 4). Essentially, there is equilibrium between the dissolved P in solution and the sorbed, solid-phase P that becomes bound to the PSM:

dissolved
$$P + PSM \leftrightarrow PSM$$
 bound P (3.2)

Higher dissolved P concentrations provide greater chemical potential or chemical "pressure" to push the reaction towards sorption of P into the solid phase with the PSM, thereby taking the dissolved P out of solution and keeping it contained in the P removal structure. As a rule of thumb, it is always more efficient to target hot spots with higher P concentrations compared to lower concentrations. Considering an equivalent load basis, it will require less PSM mass to construct the P removal structure at the hot spot than at the more P-dilute location for removing the same load of P. An example of this concept is described in the next section.

3.1.2.1 Example of Choosing the Most Efficient Location for Constructing a Phosphorus Removal Structure

It is most efficient and effective to target "hot spot" locations where the dissolved P concentrations are high, and to trap the P prior to the water flowing into a larger water body or stream where it will become diluted. Consider a hypothetical example from the Florida Everglades region. Assume that the large drainage canal shown in Fig. 3.6 has a daily flow of 1 million gallons per day (3.8 million liters per day) and a flow-weighted dissolved P concentration of 0.01 mg L^{-1} . The load (equation 3.1) of P delivered in a single day would be 0.085 lbs. Next, consider the much smaller hypothetical drainage ditch in Fig. 3.6. This drainage ditch would be a P hot spot with a dissolved P concentration of 0.3 mg L⁻¹. For this example, assume that the drainage ditch contributed 10,000 gallons per day (38,000 L per day). The result would be a load of 0.025 lbs dissolved P per day, which is nearly 30% of the daily load of the large canal. Therefore, building a structure on the smaller, more concentrated drainage ditch could capture an amount of P equivalent to 30% of the P load of the large canal, with only having to treat a volume of water that represents only 1% of the large canal's flow volume. Further, let us consider the situation if the smaller drainage ditch was a tributary to the large canal. In that case, the combined flow would be 1.01 million gallons per day, 0.012 mg L^{-1} of dissolved P, and a P load of 0.11 lbs per day. In this case, 30% of the dissolved P load is found in the hot spot drainage ditch, which is also much more suitable for treatment than the large



Fig. 3.6 Example drainage canal (*left*) and on-farm drainage ditch (*right*) found in Florida. Low-flow drainage water with high P concentrations are more efficient locations for removing dissolved P with a P removal structure compared to high-flow drainage where dissolved P has already been mostly diluted. *Left photograph*: Wikamedia Commons, "Cross Fla Barge Canal SR19W-01.jpg. Right photograph is courtesy of Bill Frank, www.jaxshells.org

canal due to the lower flow rates, size, and higher P concentrations. It would be more expensive and less efficient to attempt to treat the water after it discharged into the larger canal. As a rule of thumb, it is always more efficient to treat the source possessing higher dissolved P concentrations with regard to efficiency of P load removal. Consider a hypothetical structure design for two different drainage ditches, each with the exact same physical layout and flow characteristics (4 million gallons per year). Assume that the first ditch possesses a dissolved P concentration of 0.5 mg L⁻¹ and second has 3 mg L⁻¹. Using a certain steel slag for structure design to meet a 40% cumulative P removal goal over 1 year, the first ditch would require 67 tons and the second, 320 tons. The associated P removal would be 6.6 and 40 lbs of P removed in 1 year. Thus, even though the ditch with lower P concentrations, the mass of P removed in 1 year is six times greater for the ditch with higher P concentrations. Also consider that in that single location, 40 lbs of P can be removed in 1 year, without having to build six different structures.

Another illustration of this concept is shown in Fig. 3.7. Many agricultural fields in the upper Midwestern U.S. contain subsurface drainage that ultimately outlets into ditches that eventually convey the water into streams and lakes. Such fields and ditches contain several subsurface drainage pipes, but should a P removal structure be built for each pipe? Again, in order to maximize efficiency, one should target the pipes that transport the highest dissolved P concentrations and loads. However, if the drainage water from each of the subsurface pipes is highly concentrated, then one should consider constructing a single ditch-filter where all of the ditch water will be treated after the subsurface pipes outlet into the ditch.



Fig. 3.7 Typical tile drain outlets into ditches for farms in the upper mid-western U.S. A single ditch on one farm can have many subsurface drainage outlets. In choosing a location for a P removal structure, one should choose to treat the subsurface drains that have the highest dissolved P concentrations. If all of the subsurface drainage is elevated in dissolved P, then the entire ditch can serve as a location for a ditch-filter. Photo credit: Stan Livingston, USDA-ARS.

3.2 Examples and Applications of Phosphorus Removal Structures

An effective P removal structure can appear in many different forms and locations, just as long as the requirements for an effective structure listed under Sect. 3.1.1.1, and site requirements listed under Sect. 3.1.1.2, are all met. In short, any concentrated flow containing elevated dissolved P concentrations can be treated with a P removal structure. Due to the flexibility of the P removal structure concept, structures can take on many forms, including open surface PSMs beds, subsurface PSM beds, ditches containing PSMs (i.e. ditch filters), large cartridges or modular boxes placed in ponds or in the subsurface, etc. Such structures can treat surface runoff or subsurface drainage from agriculture, residential, golf course, and horticultural operations, effluent from domestic wastewater systems, or effluent from municipal wastewater systems. Table 3.1 provides references to different types of P removal structures.

Style of structure	P sorption material	Setting	References
Confined bed	AMDR	Municipal wastewater	Dobbie et al. (2009)
Blind inlet	Limestone	Agricultural drainage	Feyereisen et al. (2015)
Confined bed	AMDR	Fish hatchery effluent	Sibrell and Kehler (2016)
Recirculating confined bed	EAF Slag	Recirculating domestic wastewater	Claveau-Mallet et al. (2015)
Cartridge filter	Blast furnace slag	Golf course drainage	Agrawal et al. (2011)
Confined bed	Sachtofer PR®	Agricultural runoff	Klimeski et al. (2015)
Confined bed/large cartridge filter	Ca-rich hydrated oil shale ash	Municipal wastewater	Koiv et al. (2010)
Blind inlet	Melter slag and basic slag	Agricultural drainage	McDowell et al. (2008)
Confined bed	Melter slag	Municipal wastewater	Shilton et al. (2006)
Blind inlet	Fe-coated sand (WTR)	Agricultural drainage	Groenenberg et al. (2013)
Bio-retention cell	WTR	Urban stormwater runoff	Liu and Davis (2014)
Pond filter	EAF slag and treated slag	Recirculating urban pond	Penn and McGrath (2011)
Confined bed	Treated slag	Agricultural runoff	Penn et al. (2014a)
Runoff interception trenches (confined bed)	EAF slag	Turfgrass runoff	Wang et al. (2014)
Confined bed	EAF slag	Golf course and residential runoff	Penn et al. (2012)
Confined bed	EAF slag	Golf course and residential runoff	Penn et al. (2014b)
Modular box	EAF slag	Agricultural runoff	Penn et al. (2016)
Ditch filter	EAF slag and FGD gypsum	Agricultural runoff	Penn et al. (2016)
Ditch filter	FGD gypsum	Agricultural runoff	Bryant et al. (2012)
Confined bed	Marl gravel	Swine farm wastewater	Szogi et al. (1997)
Runoff interception trenches (confined bed)	Burnt lime, spent lime by-product, mixed lime	Agricultural runoff	Kirkkala et al. (2012)
Confined bed	Shell sand	Domestic wastewater	Sovik and Klove (2005)
Confined bed	Filtralite-P [™]	Municipal wastewater	Adam et al. (2006)

 Table 3.1
 Summary of recent studies conducted on field scale or pilot scale phosphorus removal structures

(continued)

Style of structure	P sorption material	Setting	References
Confined bed	Calcite	Municipal	Arias et al. (2003)
		wastewater	
Confined bed	EAF slag	Dairy effluent	Weber et al. (2007)
Ditch filter/confined bed	AMDR	Agricultural runoff	Penn et al. (2007)
Bio-retention cell	Fly-ash	Urban runoff	Chavez et al. (2015)

Table 3.1	(continued)
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AMDR acid mine drainage residual, WTR drinking water treatment residual, EAF electric arc furnace



Fig. 3.8 Modular Box style P removal structure constructed on a poultry farm. *Upper photo* shows the poultry farms and the basin/pond in which all runoff flows into. The water in the pond can only exit by flowing through the perforated metal boxes shown in the *bottom left photo*. The perforated metal boxes are removable and inside consists of a perforated pipe and the PSM. *Upper right photo* shows the inside of the box before being completely filled with PSM. The perforated pipe is plumbed to a drain that carries the treated water to a nearby drainage ditch. Photo credit: Josh McGrath, University of Kentucky

3.2.1 Modular Box

Figure 3.8 shows a modular box style of P removal structure located on a poultry farm. The P-rich runoff flows into the catch-basin, and the water can only exit the basin by flowing through the P removal structure. The structure itself is a perforated metal box that contains about 1000 lbs of PSM, and a perforated pipe in the center.



Fig. 3.9 A "ditch-filter" style of P removal structure. The *upper* and *lower photos* show the ditch-filter during and after construction, respectively. A flow control structure is used to maintain hydraulic head on the PSMs in the ditch, and water is forced to drain through the bed of PSMs into a series of buried perforated pipe that transfers the treated water to another drainage ditch in the rear. For this type of structure, it is very important to consider the loss of ditch flow capacity by placing PSMs into the ditch. Photo credit: Josh McGrath, University of Kentucky

The perforated pipe transports the treated water to another pipe that carries it to a nearby ditch. The metal boxes can be detached from the plumbing and lifted with an excavator or a front-end loader when the PSM needs to be replaced.

3.2.2 Ditch-Filter

A common type of P removal structure in flat areas that require either surface or subsurface drainage is the ditch filter (Fig. 3.9). Ditches are an ideal intercession point to treat water with high dissolved P concentrations. The upper photo in Fig. 3.9 shows the flow control structure that is used to raise the depth of water in the ditch, and the series of perforated pipes that drain the ditch-filter, prior to burial of the pipe with the PSMs. A shallow dam can be used as an alternative to the flow-control structure in order to create the hydraulic head for pushing water through the PSMs. The lower photo in Fig. 3.9 shows the completed structure actively filtering water. The water drains through the bed of PSMs and into the buried pipe, which transfers the treated water into a ditch located behind the flow control structure. This ditch structure contains approximately 60 tons of PSM. The PSMs are typically removed with an excavator, but a fast and easy method for removing the PSM can be achieved with a vacuum/suction excavator, and eliminate possible damage to buried drainage pipes.

3.2.3 Surface Confined Bed

For locations that require high peak flow rates and non-restricted drainage, in swales for example, the confined bed style of P removal structure is often ideal. Figure 3.10 shows a confined bed structure located on a golf course, which treats both golf course and residential runoff from a 150 acre watershed. Runoff water from the culvert and the golf cart path flows into the inlet pipes that are connected to a manifold of perforated pipes in order to evenly distribute the water over the bed of PSMs. The water then infiltrates through the PSM bed (about 3 tons) and drains into a pipe which outlets into the ditch. The front of the structure can be un-bolted and removed to allow for a skid-steer or a front end loader to enter the structure and easily remove the PSMs after the inlet manifold pipes are removed.

3.2.4 Cartridges

Cartridge style P removal structures are very attractive due to the ease in which the PSMs can be replaced when necessary. However, one major disadvantage of the cartridge filter is that they are often unable to hold appreciable amounts of PSM and therefore would require constant replacement. This is illustrated in Fig. 3.11. Because of their limited size, cartridges are not suitable for treating large volumes and flow rates. Each cartridge in Fig. 3.11 holds less than 10 lbs of PSM, and would only be sufficient in scenarios with limited flow volumes; proper design and site characterization can prevent such problems, as discussed in Chap. 6. However, large cartridges can be constructed and utilized to treat significant flow volumes, as shown



Fig. 3.10 A "confined bed" style P removal structure located on a golf course. *Upper left photo* shows the 150 acre watershed that drains into the confined bed of PSMs (*green dot*). *Upper right photo* shows the manifold of perforated pipe that evenly distributes water over the bed of PSMs before draining into the outlet pipe. *Lower photos* show the completed structure. Photo credit: Chad Penn, USDA-ARS

in Fig. 3.12. The cartridge filter shown in Fig. 3.12 is easily removed with equipment when replacement of PSM is necessary; this type of structure is especially ideal for treating surface runoff in urban areas within the traditional surface inlet system shown in Fig. 3.4.

3.2.5 Pond Filter

A P removal structure can be constructed to passively treat pond water as it drains out of the pond as shown in Fig. 3.8, or one can be constructed to actively treat water within the pond as shown in Fig. 3.13. The pond filter in Fig. 3.13 utilizes a pump to lift the water from the pond into a bed of PSMs located inside the small building. The water then drains through the PSMs and flows back into the pond by gravity. Thus, the water in the pond is cycled through the PSMs much like a pool filter



Fig. 3.11 Examples of a cartridge style P removal structure. For the three upper photos, the principal is the same as the modular box shown in Fig. 3.8 The outer-ring is filled with PSM and water flows through the PSM into the center ring, which is connected to a pipe at the bottom for transferring the treated water. The photo on the *upper right* shows several cartridges installed in a drainage ditch with a flow-control structure for maintaining hydraulic head. *Lower photograph* shows a cartridge style P removal structure that treats a subsurface tile drain. While designed for easy cleanout/replacement, the small mass of PSM contained is a major disadvantage. *Upper photo* credits: Gene Hahn, University of Kentucky. Lower photo is courtesy of Barry Husk, Blue Leaf Inc.

operates. Due to the need for a pump, this type of filter may be more costly than the others that rely on gravity to move water into and out of the PSMs. We do not recommend directly treating ponds in this manner unless the dissolved P concentrations are very high. Occasionally, this is observed. A golf course in Oklahoma has reported dissolved P concentrations that exceeded 1 mg L⁻¹ in several of their ponds. However, most ponds typically possess a dissolved P concentration too low for efficient direct treatment (i.e. less than 0.2–0.3 mg L⁻¹ threshold). This illustrates the principal that it is always more efficient to treat the "hot spots" before they drain into a larger water body where the P becomes diluted. For example, while a pond may exhibit eutrophication, the concentration may not be high enough for a P removal structure to be efficient. However, locating and treating the hot spot that feeds into the pond before that high P water reaches the pond will be highly efficient. Otherwise, that high P water becomes diluted after flowing into the pond and then becomes much less efficient to treat and remove.



Fig. 3.12 Example of a large cartridge style P removal structure for treating surface drainage. This large PSM cartridge treats surface runoff that flows into it, and is easily removed and replaced with a front-end loader or excavator. This particular style of P removal structure is ideal for surface inlets in urban areas. Photo credit: upper photographs - Josh McGrath, University of Kentucky; lower photographs - Barry Husk, Blue Leaf

3.2.6 Blind/Surface Inlets

Surface, or "blind" inlets shown in Figs. 3.14 and 3.15 are being adopted for improving drainage in poorly drained soils, and to reduce nutrient transport. If a PSM is used to construct the surface inlet, then the inlet is essentially a variation of the confined bed style filter shown in Fig. 3.10. Surface inlets are constructed at lowlying areas within a field where runoff water often accumulates. A framework of perforated pipe is buried in a layer of aggregate, and the pipe is plumbed into a tile drain pipe to carry the water away into a ditch. Water must flow through the aggregate in order to drain from the field. Again, if a coarse textured PSM such as steel slag is used, then the surface inlet becomes a P removal structure. Sometimes the surface inlets are covered up with soil.

Blind inlets can be constructed so that water is treated as it flows through the PSM from the top-downward or from the bottom-upward. The difference between the two styles is shown in Fig. 3.14, where a and b refer to the top-downward flow and bottom-upward flow, respectively. The advantage of bottom-upward flow design is that it allows the depth of the PSM to be much greater than a top-downward flow design, which can be important in situations where there is little hydraulic head to push water through the PSM such as a flat landscape where a shallow ditch represents the point of ultimate drainage. The importance of hydraulic head for achieving proper drainage and meeting desired flow rates is discussed in detail in Sect. 6.2.3.

The lower photo in Fig. 3.14 illustrates a blind inlet where flow is treated from the bottom-up. Consider the flow movement in several steps:



Fig. 3.13 Pond filter style P removal structure. This type of P removal structure is more costly if a pump is needed. Water from the pond is pumped into the building (*upper photo*), which contains a bed of PSMs (*lower photo*). The water drains through the PSMs, allow dissolved P to sorb to them, and drains back via gravity to the pond. Treating ponds is generally not recommended unless the dissolved P concentrations are very high. Photo credit: Chad Penn, USDA-ARS

- 1. First, similar to the top-down flow design, the surface inflow water is collected at the surface where it infiltrates into a sediment trap (usually a gravel or sand layer).
- Unlike the top-down flow design, the water is collected in a perforated collection manifold before it reaches the PSM bed. An impermeable layer/liner located between the inflow collection manifold and the PSM bed is necessary in this design.
- 3. This upper collection manifold transports the untreated water into a single pipe that flows directly to the bottom of the PSM where the water is then evenly distributed throughout the PSMs.



Fig. 3.14 Three-dimensional cutaway of two different types of surface/blind inlets that can serve as a P removal structure if constructed using a PSM. The *upper figure* illustrates a structure where treated water flows through the PSM from the top-downward. *Bottom figure* illustrates design for flow through PSM from the bottom-upward, which is made possible through use of an impermeable layer/liner and plumbing that forces collected water into the bottom of the structure. This style of design is useful for sites that are limited based on hydraulic head. *Diagrams* created by Stan Livingston, USDA-ARS

- 4. The hydraulic head, which in this case is equal to the distance between the elevation of the inlet at the surface and the bottom elevation of the PSM bed, provides the energy to push the water upward through the PSM bed.
- 5. Treated water is then collected in another manifold of perforated pipes where it is able to flow out of the structure.

For blind inlets in which the water is treated by flowing from the bottom-upward, it is important to maintain a liner or impermeable layer between the surface water collection manifold and the treated water collection manifold. Otherwise, the untreated water can by-pass the PSM bed and flow directly to the outlet, untreated. If a bottom-up flow design is used in soils where there is potential for significant water to flow out of the PSM bed and into the surrounding soils, such as sandy soils, then the bottom and sides of the PSM bed must also be lined with an impermeable liner. Bottom-up flow design is restricted to certain PSMs since they may become anaerobic, so Fe and S rich materials should not be used in this case. This is discussed in more detail in Chap. 6.



Fig. 3.15 Surface inlets for tile drainage can serve as P removal structures if constructed using a PSM. The surface inlet is constructed in a low spot where the surface runoff collects within a field. The frame of subsurface drainage pipe, which is ultimately plumbed into a tile drain pipe, is backfilled with an aggregate. Photo credit: Stan Livingston, USDA-ARS

3.2.7 Bio-Retention Cell

Another BMP that is similar to agricultural surface inlets, except that it is typically constructed in urban areas, is the bio-retention cell (Fig. 3.16). If a bio-retention cell is constructed using a PSM, then it effectively serves as a P removal structure. The principal is the same: the cell is constructed to collect surface runoff from within a small sub-watershed, and within the cell a bed of PSMs is placed on top of a subsurface drainage network. Bio-retention cells also serve as storm water retention basins to help buffer the peak flow rates in urbanized areas. Some bio-retention cells have been constructed with a fly-ash plus sand mixture as a PSM. Researchers at Oklahoma State University have found that a 95:5 mixture of sand:fly-ash served well to reduce dissolved P losses from water draining from bio-retention cells.



Fig. 3.16 Bio-retention cells, sometimes known as "rain gardens", can also serve as a P removal structure if a PSM is used to construct the sub-layers. These units can help to buffer storm water release and also reduce nutrient transport in urban areas. Functionally, bio-retention cells operate in the same manner as the surface inlets shown in Fig. 3.14. Diagram is courtesy of Dr. Glenn Brown and Katy Hallgren, Oklahoma State University

3.2.8 Subsurface Tile Drain Filter

Many regions of the world require artificial drainage in order to make agricultural production possible or improve production on soils that are naturally poorly drained. While subsurface drainage (e.g. tile drainage) is very effective at improving agricultural production, it can permit water to potentially "short-circuit" the system by allowing nutrient rich water to directly drain to surface waters instead of slowly leaching deeper into the soil where P is tightly sorbed. When tile drainage exists in soils that are elevated in P levels, appreciable dissolved P loads and concentrations can be lost in the drainage water as it flows directly into drainage ditches that eventually flow into streams, rivers, and lakes. However, the concomitant reduction in



Fig. 3.17 Diagram of a subsurface tile drain P removal structure. A tile drain is plumbed directly into a PSM bed that is buried below the surface, which allows the water to flow through the PSM bed and outlet into a buried pipe or drainage ditch. The structure can be designed have water flow from the top-downward (a) or the bottom-upward (b). Design b is useful for sites that are limited based on hydraulic head due to a shallow drainage ditch, flat landscape, or a current tile outlet drain located near the bottom of a drainage ditch. Diagram created by Stan Livingston, USDA-ARS

surface runoff due to implementation of tile drains may result in a net reduction in P transport compared to no tile drains.

Tile drains represent another potential intercession point where dissolved P can be treated by a P removal structure. A subsurface tile drain filter is simply a buried PSM bed where the tile drain is directly plumbed into the structure and treats the water before it reaches a drainage ditch (Figs. 3.17 and 3.18). Similar to the blind inlets, the subsurface tile drain filters can be designed to treat water with topdownward or bottom-upward flow (Fig. 3.17). The reasons for choosing a bottomupward flow design is the same as the blind inlet: to minimize the footprint of the structure by allowing the PSM bed thickness to be greater while still achieving proper drainage. Depending on the amount of PSM necessary for achieving the P removal goals, a buried tank could be used to contain the PSMs, such as a septic tank shown in Fig. 3.18. In addition, a subsurface tile drain filter using a bottomupward flow design could be combined with a blind inlet, where the structure is able to treat both surface water that flows into a depression and the tile drain that is directly plumbed into it (Fig. 3.19).



Fig. 3.18 Example of a subsurface tile drain filter during construction. The tile drain is plumbed into a tank containing PSMs where the water is evenly distributed throughout. The treated water is then able to continue to drain out to a ditch. Any flow that exceeds the capacity of the filter is able to by-pass. This particular unit was designed and constructed by Stone Environmental

3.2.9 Waste-Water Treatment Structures

The potential styles and application of P removal structures are endless. Consider that P removal structures can also be used to treat effluent from domestic wastewater and municipal wastewater. Several researchers in the U.S., Europe, New Zealand, and Canada have utilized steel slag and acid mine drainage treatment residuals as a PSM for removing dissolved P from wastewater. Domestic wastewater systems (Fig. 3.20) lend themselves to easy adaptation of a P removal structure, due to the high dissolved P concentrations in effluent (> 5 mg L⁻¹) and the nature of contained and concentrated flow. As P-rich effluent flows out of a septic tank, it can be made to flow into a contained unit of PSMs such as a sub-surface cartridge filter (Fig. 3.12), subsurface bed (Figs. 3.17 and 3.18), or pumped into a surface bed of PSMs (Fig. 3.13) prior to being discharged to a traditional septic absorption-percolation field. Another possibility is to construct the septic absorption-percolation field (i.e. leach-bed) with a PSM itself.

Small (less than 1 million gallons per day; MGD) wastewater treatment plants are also well suited to construction of P removal structures for similar reasons. Depending on the current setup of the waste-water treatment plant and the cost of


Fig. 3.19 Combination blind inlet with tile drain filter from Figs. 3.14b and 3.17b. *Top photo* shows the drainage outlet side and bottom shows the tile drain inlet side. Water is treated by flowing through the PSM bed from the bottom-upward

locally available PSMs, it may be more economical to remove dissolved P with a P removal structure than traditional tertiary treatment using chemicals such as aluminum and iron chlorides, and calcium hydroxide. An example of two wastewater treatment facilities in New Zealand that utilized steel slag in a P removal structure is shown in Fig. 3.21.

3.2.10 Treatment at Confined Animal Feeding Operations

Confined animal feeding operations (CAFOs) are a strong candidate for P removal structures. Many CAFOs contain wastewater lagoons for managing their nutrients. This is especially common for swine and dairy facilities, although some egg layer operations will have manure lagoons. Also, runoff from around beef cattle feedlots are often required by law to collect all water in a lagoon in order to prevent a point discharge of nutrients from the property (Fig. 3.22). The lagoon water and nutrients are typically managed by utilization as irrigation onto nearby agricultural fields. However, these facilities often no not possess enough land area to dispose of all of the P contained in the effluent, and the soil P values have drastically increased due to application beyond the P needs of crops. Regulating agencies in many states do not permit effluent application onto soils that have already reached a specified soil P level threshold. Thus, such CAFOs are faced with the choice of finding an



Fig. 3.20 Phosphorus removal structures could be easily incorporated into traditional domestic waste water treatment systems and for small municipal waste water treatment plants (lower photo). Upper diagram courtesy of William Kiely, W&M Kiely Ltd., www.wmkiely.ie

alternative application site/disposal for their lagoon effluent, or remove the P from the effluent in order to continue to apply it onto their current fields. A P removal structure in such a situation would remove the P to acceptable levels and allow continued application.



Fig. 3.21 Phosphorus removal structures used to treat municipal wastewater at wastewater treatment plants located in New Zealand. Both P removal structures utilize steel slag. Photo credit: Harsco Metals and Minerals



Fig. 3.22 Manure lagoons (*left photo*) and runoff from beef cattle feedlots (*right photo*) are typically very high in dissolved P concentrations. Photo credit: USDA Image Gallery

3.2.11 Treatment at Silage Bunkers

In addition to manure lagoons and runoff from feedlots, many dairy CAFOs possess silage bunkers for storage and use of silage throughout the year (Fig. 3.23). The raw effluent from silage is extremely high in terms of dissolved P concentrations, which can reach the magnitude of hundreds of ppm. Although the raw effluent is diluted when it is transported in runoff, the resulting concentration of P is extremely high (between 5 and 100 mg L⁻¹) and can result in a high load of P loss. Some dairy farms capture the runoff water from around silage storage areas and remove the particulate matter with various sized screens to reduce transport of particulate P (Fig. 3.23). At that point, the water is often discharged to a vegetated



Fig. 3.23 Silage storage bunkers (*upper photo*) are capable of releasing a large load of dissolved P into the environment. In some silage storage bunkers, runoff is channeled through a series of screens to remove solid particle to prevent particulate P transport (*lower photo*), and then the water is typically discharged to a vegetated treatment area to promote infiltration of the water. A P removal structure could be configured to this system to remove dissolved P after the particulate P has been removed. Photos courtesy of Erie County, NY NRCS

filter strip consisting of established grass, designed to promote infiltration of the high P water into the soil. Runoff from silage storage areas are ideal applications for P removal structures, and adaptation would be especially simple if the runoff is already being collected at a single point for subsequent discharge to a vegetated treatment area.

3.3 Summary of P Removal Structure Styles

Regardless of the style of the P removal structure, they all work the same way if properly designed with incorporation of the necessary components (Sect. 3.1.1.1). The previous section illustrated how each of these components can be met for a variety of situations, and so the appearance and application of a P removal structure can be quite diverse. Keep in mind that other styles in addition to what was presented may also be effective. The diversity of P removal structures is ultimately a result of the diversity among site conditions, available PSMs, economics, and to some degree, personal preference and aesthetics. Often times, based on the site conditions, the P removal structure style can be narrowed down to only a couple of options. For example, for a region with tile drainage, the choice of structures will be mostly limited to blind inlets, subsurface tile drain structures, and ditch structures. Chapter 4 focuses on PSMs, how they work, and how to choose a PSM. After narrowing down several (or one) PSMs, the first step should be to determine how much of that PSM is required for the site of interest (Chap. 6). Knowing the mass of PSM required, certain structures may be eliminated due to constraints such as area. For example, if a site requires 40 tons of a certain PSM, it is likely not feasible to utilize modular-box (Sect. 3.2.2) or cartridge style (Sect. 3.2.4) structures. Other styles of structures may be limited due to the maximum hydraulic head at site. Chapter 6 is dedicated to the step-by-step process of determining the required inputs for a design and conducting the structure design. In addition to great diversity among the style of P removal structures, there is also a great deal of potential sites for application of the P removal structure. Regardless of whether the sites are agricultural, urban, horticultural, industrial, or waste-water treatment, a P removal structure can be applied as long as the site requirements listed in Sect. 3.1.1.2 are met.

Many different types of P removal structures have been constructed using various different styles, P sources, and locations. Table 3.1 provides a summary of recent studies that employed a field scale or pilot scale P removal structure.

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Chapter 4 Phosphorus Sorption Materials (PSMs): The Heart of the Phosphorus Removal Structure

4.1 What Are PSMs?

"Phosphorus sorption materials", or PSMs, are unconsolidated solids that have a strong affinity for dissolved P. A PSM has the ability to remove dissolved P from solution by binding P to it. In general, PSMs are rich in aluminum (Al), iron (Fe), or calcium (Ca), as these elements are mostly responsible for binding P. Magnesium (Mg) can also bind P to some extent, but not as effectively as Al, Fe, and Ca. PSMs are the "heart" of the P removal structure because they constitute the filter medium by which dissolved P is removed from the polluted water and contained within the structure. Because PSMs are unconsolidated, they contain pore space in which water can pass through the material, allowing direct contact between the solids and liquid phase that contains the dissolved P. This chapter describes some common PSMs, how different PSMs are able to remove P from water, and the physical and chemical attributes most important to characterizing them. Chapter 5 presents detailed methods for how to characterize PSMs for their ability to remove dissolved P under representative conditions, and characterize PSMs for those relevant physical and chemical attributes and safety.

4.1.1 Examples of PSMs

Many PSMs are by-products from the waste stream of several industries. Thus, secondary use of these by-products as PSMs represents a beneficial re-use of materials that would normally be considered a waste product. Regardless of the source, a PSM must be rich in Al, Fe, Ca, or Mg. Table 4.1 lists examples of several PSMs

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Table 4.1 Several potential by-product PSMs, the dominant P sorption elements contained withinthem, and examples of several studies that illustrate the potential for each PSM to remove P fromsolution

	Main P sorbing	
By-product PSM	elements	Studies illustrating P sorption
Fly-ash	Ca, Mg, Al, and Fe; varies	10, 13, 14, 26, 34, 44, 49, 50, 51
Blast furnace slag	Ca, Mg, Al, and Fe; varies	1,5, 8, 9, 14, 15, 18, 19, 21, 25, 27, 33
Electric arc furnace slag	Ca, Mg, Al, and Fe; varies	4, 20, 23, 30, 48, 49
Melter slag	Ca, Mg, Al, and Fe; varies	2, 12, 17, 21, 22
Bauxite waste (red and brown mud)	Ca, Mg, Al, and Fe; varies	10, 25, 34, 50
Drinking water treatment residuals (WTRs)	Ca, Mg, Al, and Fe; varies	24, 39, 46, 47, 49, 50, 51
Titanium oxide manufacturing by-product	Fe and Al	
Foundry sand	Mg, Fe, and Al	
Fe-coated sand	Fe	31, 36, 45
Flue gas desulfurization (FGD) gypsum	Са	48, 49, 50, 51
Mg fertilizer by-product	Mg	
Crushed concrete	Са	8
Sandblast grit	Fe and Al	
Acid mine drainage residuals (AMDRs)	Ca, Al, and Fe; varies	3, 9, 11, 16, 25, 32, 48, 49, 50
Metal fabrication shavings and iron filings	Fe and Al	35
Wollastonite	Ca	1, 33, 40, 41, 42
Crushed sea shells/marl	Ca	5, 28, 43
Light weight expanded clay aggregates (LECA)	Ca, Al, and Fe; varies	6, 10, 28, 29, 38
Oil shale ash	Са	7, 10
Serpentine	Mg	23, 28
Biotite	Al and Fe	37

¹Gustafsson et al. (2008), ²Bourke et al. (2005), ³Sibrell et al. (2009), ⁴Claveau-Mallet et al. (2011), ⁵Hedstrom (2006), ⁶Karczmarczyk et al. (2014), ⁷Koiv et al. (2010), ⁸Dunets et al. (2015), ⁹Klimeski et al. (2014), ¹⁰Drizo et al. (1999), ¹¹Dobbie et al. (2009), ¹²Pratt et al. (2007a), ¹³Ugurlu and Salman (1998), ¹⁴Johansson (1999), ¹⁵Oguz (2004), ¹⁶Wei et al. (2008), ¹⁷Pratt et al. (2007b), ¹⁸Bowden et al. (2009), ¹⁹Kostura et al. (2005), ²⁰Drizo et al. (2002), ²¹McDowell et al. (2008), ²²Shilton et al. (2006), ²³Drizo et al. (2006), ²⁴Makris and Harris (2006), ²⁵Baker et al. (1998), ²⁶Zhang et al. (2008), ²⁷Sakadevan and Bavor (1998), ²⁸Karczmarczyk and Bus (2014), ²⁹Forbes et al. (2005), ³⁰Claveau-Mallet et al. (2013), ³¹Groenenberg et al. (2012), ³²Sibrell and Tucker (2012), ³³Eveborn et al. (2009), ³⁴Li et al. (2006), ³⁵Erickson et al. (2012), ³⁶Boujelben et al. (2008), ³⁷Hartikainen and Hartikainen (2008), ³⁸Yaghi and Hartikainen (2013), ³⁹Makris et al. (2005), ⁴⁰Brooks et al. (2000), ⁴¹Geohring et al. (1999), ⁴⁷Hill et al. (2000), ⁴³Roseth (2000), ⁴⁴Agyei et al. (2002), ⁴⁵Chardon et al. (2012), ⁴⁶Gallimore et al. (1999), ⁴⁷Liu and Davis (2014), ⁴⁸Penn et al. (2016), ⁴⁹Stoner et al. (2012), ⁵⁰Penn et al. (2011), ⁵¹Penn and Bryant (2006)



Fig. 4.1 Examples of several potential PSMs: (a) acid mine drainage residuals (AMDRs), (b) steel slag, (c) drinking water treatment residuals (WTRs), (d) manufactured PSM known as "Blue Leaf", (e) fly-ash, and (f) metal shavings. Photo credit: James Bowen and Joshua Bradley

that are by-products, the main P sorption elements that are typically contained in them, and several studies that indicated their ability to sorb P from solution. Photographs of several PSMs are shown in Fig. 4.1 as a reference. Many by-product PSMs are produced at the magnitude of several hundred million tons per year (Table 4.2). Some by-products are partially disposed of through beneficial re-use such as application to agricultural soils, and millions of tons of potential by-product PSMs are sent to landfills. Clearly, beneficial re-use as PSMs represents a solution that would conserve landfill space and also save industry money. While many byproducts may serve as excellent PSMs, not all by-products are necessarily safe to use as a PSM. This will be discussed in more detail later.

Material	Annual production (million tons)
Fly-ash ^a	50–75
Bottom-ash	15–20
Flue gas desulfurization (FGD) gypsum	11–28
Iron and steel slag ^b	15–22
Drinking water treatment residuals (WTRs) ^c	1–7
Foundry sand waste ^d	10–15
Acid mine drainage residuals (AMDRs) ^e	1–5

 Table 4.2 Estimated U.S. annual production for several potential by-product PSMs.

^aFly-ash, bottom-ash, and FGD gypsum data from the American Coal Ash Association ^bUSGS Mineral Commodities Summary, 2015

^cPersonal communication. Hershel A. Elliott, Department of Agricultural and Biological Engineering, Penn State University. Value is an approximation based on the volume of drinking water treated annually in the U.S.

^dFoundry sand: Collins and Ciesielski (1994)

^ePersonal communication. Robert Nairn, School of Engineering and Environmental Science, University of Oklahoma. Value is an approximation

Steel production throughout the world results in millions of tons of a by-product known as steel slag that is rich in Fe, Al, Ca, and Si (Fig. 4.2). Steel slag is often gravelly in texture and can be sieved to achieve different particle size distributions. The most common use for slag is in construction, especially road construction. Different types of steel production results in different slag materials; the main methods are blast oxygen furnace (BOF), electric arc furnace (EAF), and melter slag. Of these, BOF and EAF are the most common. The BOF and EAF materials tend to be very rich in Ca and are somewhat alkaline. In fact, the fine particles from BOF and EAF are often used as agricultural liming agents and also as Si fertilizer since they are dominated with Ca oxide and Ca silicate minerals compared to the larger size fractions.

In the case of acid mine drainage residuals (AMDRs), one pollution source can be cleaned up and actually used to help solve the problem of eutrophication. Acid mine drainage typically occurs during mining operations where soil and rock located deep below the Earth's surface are exposed to oxygen. If the geologic material exposed contains minerals rich sulfides such as pyrite, oxidation will result in production of enormous amounts of acid. This acid dissolves Fe and Al minerals and typically has a pH less than 3. One of the most common sources of acid mine drainage is from coal mines. After the sulfide minerals associated with a mine have been exposed to oxygen they can continue to produce acid mine drainage for decades. The resulting drainage water is acid in pH and has high concentrations of dissolved Fe, Al, and occasionally trace metals. To remedy this problem, various engineering techniques have been developed to neutralize the acidity in the acid mine drainage in order to prevent further aquatic ecosystem damage. Neutralization



Fig. 4.2 *Upper photo*: view of a slag handling facility at a steel mill located in Wilmington, DE (photo courtesy of Gene Hahn). *Lower*: diagram of the blast oxygen furnace and electric arc furnace methods for making steel (figure courtesy of the National Slag Association)

of the acid mine drainage results in the precipitation of Fe and Al oxide and hydroxide minerals that settle out of the water as solids; these minerals are known as AMDRs and tend to have a strong affinity for P. In addition, since Ca oxides, hydroxides, and carbonates are often used to neutralize the acidity of acid mine drainage, the resulting AMDRs can be rich in Ca as well which can also potentially



Fig. 4.3 *Left*: aerial view of an acid mine drainage treatment facility for treating drainage from Tar Creek, located near Miami, Oklahoma. *Right*: close up photograph of a passive acid mine drainage treatment pond. Photographs courtesy of Dr. Bob Nairn, University of Oklahoma

remove P from solution. Figure 4.3 shows an acid mine drainage treatment facility that treats Tar Creek, which suffers from lead and zinc mining that occurred nearly a century ago, located near Miami, Oklahoma. The AMDRs that form from this process must be cleaned out routinely and disposed of; this represents a very large potential source of PSMs.

The coal-fired power industry produces several materials that can serve as potential PSMs: flue gas desulfurization (FGD) gypsum, fly-ash, and bottom ash, depending on the stage of the process (Fig. 4.4). The combined production of these by-products from the power industry probably represents the largest source of potential PSMs in the U.S. (Table 4.2). Coal-fired power plants are located throughout the U.S. The materials tend to be rich in Ca, and thus have potential to remove P by precipitation as a Ca phosphate. However, a major disadvantage of these materials is that they are often composed of very small particle sizes and thus will possess a poor ability to convey water through them. Fly-ash also has the additional problem of hydrating and then hardening like concrete, so it must always be mixed with sand or pelletized. In fact, one of the most common secondary uses of fly-ash is as an ingredient to concrete.

Many drinking water supplies in the U.S. ultimately come from surface bodies of water. These surface waters often contain suspended sediment that must be removed prior to disinfection and subsequent distribution. Chemicals such as Ca hydroxide, and Al/Fe chlorides and sulfates are typically used to flocculate the suspended sediment as part of the drinking water treatment process. The resulting sediment, known as "water treatment residuals" (WTRs) is a waste product that is rich in silt and clay-sized particles, plus some unreacted flocculent. Both the clay minerals and unreacted flocculent contained in WTRs typically have a strong affinity for P, and therefore can serve as an effective PSM. On a weight basis, WTRS are highly sorptive compared to some other PSMs, but they also tend to suffer from a poor ability to conduct water through them. Because surface water reservoirs for drinking water are found throughout the U.S., so it is with geographic distribution of WTRs. These



Fig. 4.4 *Upper*: schematic of the steam generating process for coal-fired power plants and the resulting waste products of bottom ash, fly ash, and flue gas desulfurization (FGD) gypsum. *Lower*: photograph of several tons of FGD gypsum to be placed into a ditch-style P removal structure on the Eastern Shore of Maryland. Photograph courtesy of Gene Hahn

materials are often piled up outside of drinking water treatment facilities until they are disposed of through land application or taken to a landfill.

Other industries produce by-products capable of sorbing P in varying degrees. Certain types of metal casting involve the use of sand as a mold for the molten metal. This sand is known as "foundry sand" or "green sand", and after continuous use, can become rich in Al and Fe from the molten metal. At some point, the sand can no longer be used for casting and must be disposed of. Because of its sandy texture, foundry sand usually has a strong ability to conduct water through it, but its ability to sorb P will vary tremendously between samples. Caution should be exercised in that some foundry sands may be elevated in trace metals and also certain organic compounds that were used as binders during the casting process. The

materials listed in Table 4.1 are not meant to be an exhaustive list of all potential by-product PSMs. However, one can see that many different types of industries can produce potential PSMs such as mining (e.g. red mud from bauxite/Al mining), fertilizer production, metal fabrication and even the food production industry.

In addition to by-product PSMs, there are several manufactured PSMs available for purchase with more coming on the market every year. The composition of manufactured PSMs is essentially the same as by-product PSMs in that the materials are rich in Al and Fe oxides/hydroxides, or highly soluble Ca minerals. However, manufactured PSMs are often created with ideal particle size distributions to attain good flow rates through them, which is something that can be an issue for several byproduct PSMs. One major disadvantage of manufactured PSMs compared to byproduct PSMs is the high cost. Although often very effective, the cost of manufactured PSMs will range from 8 to 40 dollars per lb. This is usually cost prohibitive for most P removal structures. However, if the manufactured PSM is required in much smaller amounts compared to the locally available by-product PSM, then it could be cost efficient to use a manufactured PSM. Use of the PhrogTM software (presented in Chap. 7) can be used to quickly compare efficacy and efficiency of PSMs for a particular site and P removal structure. Several examples of manufactured PSMs that are currently on the market:

- "SorptiveMEDIA" from Imbrium
- "NutriLoxx®" from Filtrexx
- "Filtralite-P®" from Filtralite
- "Phosphorus Sponge" from Meta Materia
- "Bio-Max" from ABS Materials Inc.
- "Ultra-Phos Filter[®]" from UltraTech
- Materials made by Blue Leaf Inc.
- Materials from Iron Oxide Recovery Inc.
- "Smart Sponge" from AbTech Industries
- "Absol®" from Svesten AB
- "Polonite[®]" from Ecofiltration
- "PhosRedeem®" from U.S. Iron
- "Bayoxide®" from Bayer

4.1.2 Choosing a PSM

Several factors are important to choice of PSM. Many potential by-product PSMs may be available to you, but which one is ideal for your particular site and application? Figure 4.5 provides a guide for what to consider when choosing a PSM. The most obvious consideration is material availability. Because PSMs are necessary in relatively large quantities for most applications (in the magnitude of tons), it is important that the PSM be somewhat locally available. The closer the PSM source is to the location of the P removal structure to be constructed, the lower cost of transportation. Regarding the cost of the material itself, many by-product PSMs can



Fig. 4.5 Considerations in choosing a PSM for a P removal structure

be obtained for zero or low cost. For example, many steel mills will sell slag for 2–10 dollars per ton, and some may even provide custom sieving/screening. Thus, the biggest cost associated with by-product PSMs is the transportation required to move the material to the location where the P removal structure is to be constructed. The greater PSM mass required and the further the distance, the greater cost. Other factors must be considered in comparing the economics of using different PSMs, but mass required and distance is the most formidable.

Next, it is extremely important that a PSM be safe and its use not result in a new pollution problem. In other words, choice of PSMs must also consider any potential contaminants that might be contained in the PSM. This is not much of an issue for manufactured PSMs, but by-product PSMs must be examined carefully prior to use in a P removal structure. Some PSMs can release elevated concentrations of trace metals and sodium to solution. For example, while many red mud samples (bauxite mining waste) are excellent at sorbing P, some samples release excessive concentrations of trace metals and sodium to solution that could be dangerous to aquatic ecosystems if used in large amounts. Suggestions on PSM safety testing methodology and thresholds for different contaminants are discussed in greater detail later in this chapter.

Clearly, an effective PSM must have the capacity to sorb P to it, thereby allowing it to remove P from a passing solution. Not only must the PSM be able to sorb P, but it must be able to sorb P under relatively low solution P conditions (~0.2–0.3 mg L^{-1}), possess a capacity to sorb an appreciable amount of P, and sorb P in a timely fashion. One of the big advantages of a P removal structure is that they can be constructed in a relatively small footprint since only a small retention time is required. A small retention time is only possible when the PSMs employed within them are able to sorb P very quickly. If a PSM is unable to sorb P quickly from a passing solution, then it will not serve well in a P removal structure. Materials with a strong ability to remove a large amount of P from solution quickly will reduce the overall cost of the structure compared to PSMs with a lesser P sorption capacity since a lower total mass of the PSM and a smaller footprint will be required.

Physical properties are also important to choosing a PSM for a P removal structure. This will be discussed in greater detail later in the chapter. Briefly, the physical properties most important to choosing a PSM are particle size distribution, bulk density, porosity, and hydraulic conductivity. All of these parameters are required inputs to PhrogTM in order to make a proper design of a P removal structure. The importance of these properties can be summarized in that they directly impact the mass of PSM required and the flow rate of water through the P removal structure. Recall from Chap. 3 that one of the requirements for a P removal structure is that it should conduct water through the PSM at an acceptable flow rate. Simply put, if a PSM has a low potential to conduct water through it quickly (i.e. small hydraulic conductivity), then that PSM must be placed at a smaller depth, therefore a larger area/footprint, in order to meet the desired flow rate for the P removal structure. Obviously a larger footprint takes up valuable space, and it also increases the cost of construction of the P removal structure. PSMs with higher bulk density, P sorption ability, and hydraulic conductivity translate to a smaller P removal structure and therefore lower cost of construction. Again, the PhrogTM software allows the user to quickly explore different PSMs in order to help estimate cost of construction and make an informed decision.

4.2 What Makes a Material an Effective PSM?

As described in the previous section, there are three main groups of characteristics that must be considered when assessing a potential PSM. The material must be able to sorb P at an acceptable level in a timely fashion, conduct water through it at an acceptable flow rate, and it must be safe to use in the environment. This section will examine each of those three necessary PSM characteristics in detail.

4.2.1 P Sorption Capacity and Kinetics of P Removal

For a material to be considered a viable PSM, it must be able to sorb P at a sufficient amount and also sorb P relatively quickly. The maximum amount of P that a PSM can sorb under a given set of conditions is known as the P sorption "capacity" of PSM. The most important conditions that impact the P sorption capacity of a PSM are the concentration of P in the inflow that is entering into the PSM and the amount of time that the PSM is in contact with that water (i.e. retention time). The P sorption capacity for PSMs will vary as a function of the inflow P concentration, and for some PSMs, the retention time.

Regarding P sorption capacity, higher inflow P concentrations almost always increases the total amount of P removed (i.e. sorbed) from solution compared to lower inflow P concentrations (Fig. 4.6). This is especially true for certain Ca-based PSMs such as gypsum, in which P removal dramatically increases with inflow P concentration. This is one of the reasons why it is always more efficient to target P removal structures at the sites with the highest P concentrations. As discussed in Chap. 3, solution P concentration is essentially the chemical potential or "pressure" to promote sorption onto a solid PSM (see equation 3.2). In this case, sorption mechanisms are generally ligand exchange or precipitation as a solid; this will be discussed in more detail in the next section. Some PSMs are simply not as capable of removing P from solutions with low P concentrations ($\sim 0.2-0.3 \text{ mg L}^{-1}$) compared to other PSMs. For example, FGD gypsum has only a fraction of the P sorption capacity than AMDRs at both low and high P concentrations (Fig. 4.6). Clearly, for use in a P removal structure, a PSM with a higher P sorption capacity is desired as this will reduce the mass of PSM required and the overall footprint of the structure.

Broadly speaking, there are two main methods for assessing the P sorption capacity of a PSM: predict the P sorption capacity by measuring certain chemical characteristics of the PSM, or by direct measurement of P sorption. Concerning direct measurement of P sorption, there are two general approaches: batch and flow-through techniques. Flow-through techniques are far superior to a batch technique, but flow-through is more difficult, time-consuming, and costly than batch. These techniques, including chemical characterization for prediction of P sorption capacity, will be presented in detail in Chap. 5.

Not only does a PSM need to be able to sorb an acceptable amount of P onto it, it must also sorb P in a timely fashion. The ability of PSMs to sorb P with respect to time is known as the "kinetics of P sorption". Again, since ideal P removal structures are designed to have a relatively short contact time between the water and the PSM, the PSM must be able to sorb a sufficient amount of P during that time. This is in contrast to biological P removal such as treatment wetlands, which can require a retention time of many hours to days, and also explains why such treatment requires several acres of land. In general, PSMs that require a longer period of time to sorb P (i.e. require a longer retention time) are said to have slow P sorption kinetics. On the other hand, PSMs that can sorb P very quickly under conditions of a short retention time are said to possess fast P sorption kinetics. Figure 4.6 illustrates how the P sorption capacity is affected by an increasing retention time. Notice that some of PSMs shown in Fig. 4.6 are not strongly affected by retention time; such PSMs have fast P sorption kinetics. Other PSMs such as AMDR1 and FGD gypsum show increasing P sorption with increased retention time. There are some PSMs that have such tremendous P sorption kinetics that they are able to sorb P faster than we can force water through them. An example of this is Excel minerals shown in Fig. 4.6; the P sorption capacity actually increased with decreasing retention time. In other words, the lower rate of P addition to the material, which is a function of the retention time, was limiting P sorption more than the speed of the chemical reaction. Both the amount and speed in which P is sorbed are a function of the P sorption



Inflow P concentration (mg L⁻¹)

Fig. 4.6 Maximum P removal by PSMs under flow-through conditions (i.e. P removal when inflow = outflow concentration) at a retention time of 0.5, 3, 6, 8, and 10 min, and inflow P concentrations of 0.5, 1, 5, 10, and 15 mg L⁻¹. (a) AMDR1, (b) AMDR2, (c) AMDR3, (d) AMDR4, (e) slag fines, (f) fly-ash1, (g) fly-ash2, (h) FGD gypsum, (i) Ca-WTR, (j) Al-WTR1, (k) Al-WTR2, and (l) Excel Minerals



Fig. 4.7 Illustration of the general P sorption mechanisms by Fe/Al-rich and Ca-rich PSMs *Upper portion* shows ligand exchange of P onto Fe and Al oxides/hydroxides. *Lower portion* shows how Ca-rich PSM can precipitate P as Ca phosphates. Ligand exchange is typically a very fast reaction (seconds to minutes) while Ca phosphate precipitation ranges from seconds to days, depending on pH and pH buffer capacity

mechanisms. Ultimately, it is the chemical character of the PSM that dictates the P sorption mechanisms, which is mostly ligand exchange and precipitation (Fig. 4.7). These mechanisms are discussed in detail in the following section.

4.2.1.1 P Sorption Mechanisms and Sensitivity to Retention Time

In general, effective P sorption mechanisms by PSMs can be categorized in one of two groups: ligand exchange or precipitation (Fig. 4.7). Anion exchange is excluded as an "effective" mechanism of P sorption in the context of PSMs because anion exchange is 100% reversible. Under relatively constant conditions, ligand exchange and precipitation are much less reversible than anion exchange.

Ligand exchange is a mechanism that only occurs onto variable charged minerals. A variable charged mineral is one in which the surface charge changes mostly as a function of pH: as the pH increases, the surfaces of variable charged minerals become more negative due to the de-protonation of valence un-satisfied terminal functional groups:

$$---MOH_{2}^{+0.5} \longleftrightarrow ---MOH^{-0.5} + H^{+}$$

$$(4.1)$$

Where the line indicates that the functional group is connected to a PSM and "M" represents Al or Fe (usually). Going forward from reactants (left side) to products (right side) is a de-protonation reaction. However, the reaction can proceed backwards as indicated by the double arrow if the H⁺ concentration becomes high (i.e. low pH conditions). When reaction 4.1 proceeds backwards, the surface functional group of the mineral is protonating and becoming more positive. Thus, as pH decreases, the surface terminal functional groups become more positively charged. The following is an example of a protonation reaction of a surface functional group that results in a more positively charged surface:

$$---MOH^{0} + H^{+} \longleftrightarrow ---MOH_{2}^{+}$$

$$(4.2)$$

These protonation and de-protonation reactions are dictated by thermodynamics and therefore each reaction possesses a unique "equilibrium constant" (i.e. K value). In other words, the reactants and the products are in equilibrium with each other, which is why pH determines the degree in which the terminal hydroxide functional groups are protonated or de-protonated, thus determining the charge.

In general, the variable charged minerals most often found in PSMs are rich in Al and Fe oxides/hydroxides and 1:1 minerals such as kaolinite. The Al and Fe oxides and hydroxides may be crystalline and exist in the form of bayerite, boehmite, corundum, diaspore, and gibbsite for Al minerals, and goethite, hematite, ferrihydrite, and lepidocrocite, for Fe minerals. However, Al and Fe oxides/hydroxides also tend to be in an amorphous (e.g. non-crystalline) form in PSMs. The functional groups found on those minerals that are capable of variable charge also serve as the site for ligand exchange of P.

Ligand exchange of P onto variable charged minerals has the potential to occur onto positive, negative, and neutral functional groups, although it will occur most readily onto positively charged functional groups. This is a major distinction from anion exchange, as anion exchange can only occur on a positively charged surface. An example of a ligand exchange reaction for P onto a variable charged functional group is shown in the following reaction (from Essington, 2004):

$$---MOH_{2}^{+0.5} + H_{2}PO_{4}^{-} \to MOPO_{3}H_{2}^{-0.5} + H_{2}O$$
(4.3)

where M is Al or Fe contained in an oxy/hydroxide. Figure 4.8 illustrates three different types of bonds that can result from ligand exchange of phosphate onto a variable charged surface: monodentate-mononuclear, bidentate-mononuclear, and bidentate-binuclear. Notice that for each of these bonds, there is no water molecule located between the phosphate and the surface of the mineral; this is known as an "inner sphere" bond, which is covalent and somewhat irreversible by nature (under normal circumstances). While all of these are very strong covalent bonds between phosphate and the mineral, bidentate-binuclear is the least reversible followed by



Fig. 4.8 Illustration of P sorption to metal oxides/hydroxides minerals by the ligand exchange mechanism as (a) monodentate-mononuclear, (b) bidendate-mononuclear, and (c) bidendate-binuclear. "M" indicates aluminum or iron

bidentate-mononuclear, then monodentate-mononuclear. The reason for this is because phosphate held by monodentate-mononuclear has one bond with a single functional group, whereas for bidentate-mononuclear a single phosphate has two bonds with the mineral. A bidentate-binuclear bond is even stronger because a single phosphate has two bonds with functional groups that are coordinated with functional groups from two different metal ions. It is believed that when a variable charged mineral is initially free of phosphate, the initial P added to it will be sorbed by ligand exchange as a bidentate-binuclear bond, then monodentate-bicnuclear, and finally monodentate-mononuclear. This is partly the reason why P that is initially applied to a "clean" mineral is held the strongest, and any P added after that is held with less strength.

Regarding reaction kinetics and therefore impacts of retention time on P sorption by ligand exchange, the ligand exchange reactions are generally very fast, meaning that a long retention time is not required for P sorption by this mechanism. Ligand exchange usually occurs within seconds or less. On the other hand, the kinetics of precipitation of P can be much slower, depending on the conditions. A simplified generic precipitation reaction is shown below:

$$a\mathbf{M}^{m_{+}} + b\mathbf{L}^{n_{-}} \longleftrightarrow \mathbf{M}_{a}\mathbf{L}_{b}$$
 (solid) (4.4)

where M is a metal such as Ca, Al, or Fe, and L is a ligand (e.g. phosphate PO_4^{3-}). Superscripts m+ and n- is the charge of the metal and ligand, respectively, and coefficients *a* and *b* are the number of moles of the metal and ligand, respectively. Note that precipitation reactions must be both charge and mass balanced. The "solid" indicates the formation of a solid precipitant. Phosphate readily forms precipitants with Al³⁺, Fe³⁺, and Ca²⁺ that is in solution. The reaction 4.4 clearly shows how precipitation can be an effective mechanism for P removal in a P removal structure: the dissolved P in solution (i.e. phosphate) comes into contact with a dissolve metal cation, and the two precipitate to form a new solid that effectively takes dissolved P out of the solution phase. Because precipitation reactions are equilibrium-based, increased concentrations of both the metal cation and dissolved P will increase the degree of precipitation by providing chemical potential to form the reaction products (i.e. solid precipitant). Thus, precipitation reactions are most effective when P concentrations are very high. This is essentially how tertiary P treatment is often performed at wastewater treatment plants: highly soluble Al, Fe, or Ca salts are added to the wastewater to provide strong chemical potential for reaction 4.4 in order to remove P from solution. Precipitation reactions tend to be much more responsive to increasing dissolved P concentration compared to ligand exchange reactions. Regarding kinetics, precipitation reactions are generally slower than ligand exchange reactions, but precipitation can become very fast as chemical potential is increased, such as increasing the concentration of the reactants (i.e. high phosphate and metal concentrations in solution). This will be discussed in more detail below.

Calcium-Based PSMs

The dominant mechanism for P removal by Ca-based PSMs is precipitation as Ca phosphates (reaction 4.4). Several potential Ca-based PSMs are listed in Table 4.1. Generally, by-products from coal-fired power production are Ca-based, as well as blast furnace and electric arc furnace steel slag, and certain WTRs. Characterization data for specific PSM samples are shown in Table 4.3. Based on the characterization shown in Table 4.3, slag, fly-ash, FGD gypsum, marble tailings, Wollastonite, Ca-WTR, and sieved limestone will all remove P by precipitation with Ca. The treated slag will not remove P by Ca phosphates due to the treatment process changing it from a Ca- to Al/Fe-based material. Also, some AMDRs such as AMDR2 and 4 in Table 4.3 will remove P with both Ca and Al/Fe.

In order for a Ca-based PSM to be effective at removing P from solution by precipitation, the PSM must be capable of two things:

- Readily dissolve sufficient Ca²⁺ into solution
- Maintain and buffer the pH to a high enough level to promote precipitation for the given level of dissolved Ca²⁺ and phosphate.

Equation 4.5 below illustrates a typical Ca phosphate precipitation reaction:

$$\operatorname{Ca}^{2+} + \operatorname{H}_2\operatorname{PO}_4^{-} + 2\operatorname{H}_2\operatorname{O} \leftrightarrow \operatorname{CaHPO}_4 \cdot 2\operatorname{H}_2\operatorname{O}_{(\operatorname{solid})} + \operatorname{H}^+.$$
(4.5)

Precipitation-dissolution reactions are quantified by a K value (equilibrium constant); K values for several different Ca phosphate minerals are listed in Table 4.4. As reaction 4.5 proceeds from left to right, a solid Ca phosphate mineral is formed. If the reaction proceeds from right to left, then the solid mineral dissolves to produce Ca and P into solution. Because of meta-stability that is often displayed with Ca phosphate minerals, the most soluble Ca phosphate mineral will precipitate first, and with time it will slowly crystallize into the least soluble Ca phosphate mineral. Note that precipitation of amorphous Ca phosphate minerals can also occur. As described in the previous section, the concentration of the P (i.e. ligand) and the

	Total	Total	Total	Oxalate	Oxalate			
	Ca, g	Al, g	Fe, g	Al, g	Fe, g	BIª, Eq		Crystalline
Material	kg ⁻¹	pН	minerals					
AMDR1	0.2	2.0	455	0.1	26	0	3.2	Goethite
AMDR2	23	98	189	47	30	0.016	7.1	Hematite,
								gypsum
AMDR3	8.3	9.3	338	0.4	40	0.001	6.4	Goethite
AMDR4	204	17	118	5.4	33	0.136	8.2	Calcite
Slag fines	272	37	155	0.9	4.4	0.051	11.3	Portlandite
Fly-ash1	151	87	42	27	8.6	0.048	11.4	Quartz
Fly-ash2	153	65	37	29	10	0.071	11.4	Quartz
FGD gypsum	209	0.8	1.8	0.06	0.6	0.002	8.1	Gypsum
Limestone (0.05–0.25 mm)	163	1.4	24	ND	ND	0.015	9.4	ND
Ca-WTR	286	14	7.2	5.2	1.0	0.070	8.9	Calcite
Slag (4–6 mm)	164	27	280	23	2.4	0.008	10.9	ND
Treated slag (6–14 mm)	288	28	112	1.1	2.3	0	5.7	Calcite, gypsum
Slag (6–14 mm)	256	33	191	0.32	1.9	0.001	10.9	Portlandite, calcite
Al-WTR1	3.3	157	17	58	2.5	0.002	7.3	Quartz
Al-WTR2	19	81	15	37	2.1	0.005	7.3	Quartz
Al-WTR3	2.3	57	14	3.9	28	0.001	6.8	ND
Marble	177	3.1	5.6	ND	ND	0.011	9.3	ND
tailings								
Wollastonite	147	5.1	33	ND	ND	0.007	9.6	ND

Table 4.3 Chemical properties of some example by-product PSMs used in P removal structures

AMDR acid mine drainage residual, FGD flue gas desulfurization, WTR water treatment residual, ND not determined

 $^a\text{Buffer}$ index; equivalents of acid kg^{-1} required to decrease solution pH to 6.0. See Chap. 5 on methods of characterization

 Table 4.4 Examples of several calcium phosphate minerals that can potentially precipitate in Ca-rich PSMs when used in a P removal structure

Calcium phosphate mineral	Formula	Log K of dissolution
Monocalcium phosphate	$Ca(H_2PO_4)_2 \bullet H_2O$	-1.15
Brushite	CaHPO ₄ •H ₂ O	0.63
Monetite	CaHPO ₄	0.30
Octacalcium phosphate	$Ca_4H(PO_4)_3 \bullet 2.5H_2O$	11.76
β-tricalcium phosphate	β -Ca ₃ (PO ₄) ₂ (c)	10.18
Hydroxyapatite	Ca ₅ (PO ₄) ₅ OH	14.46

Data from Lindsay (1979)

metal ion (i.e. Ca^{2+}) partly control the extent of the formation of the solid Ca phosphate mineral. Increasing P and Ca concentrations provide the chemical potential to force the reaction to occur and move from the left side to produce the products i.e. precipitated solid, on the right side of the reaction. Thus, the more a PSM is able to dissolve and provide Ca^{2+} to solution, the more P can be removed from that solution.

Close observation of a Ca phosphate precipitation reaction (equation 4.5) also reveals that pH has an impact on the removal of P from solution by Ca. Notice the presence of H⁺ (acid) on the products side of the reaction. Thus, higher amounts of H⁺ will push the reaction backwards and prevent the solid Ca phosphate from precipitating. In other words, low pH conditions will not favor removal of P by Ca-based PSMs. On the other hand, low concentrations of H⁺ (i.e. high pH) will favor the precipitation of P with Ca by allowing the reaction to proceed from reactants to products. Because of this, it is very important that a Ca-based PSM also be able to maintain a pH level in solution greater than 6.

Dissolution reactions for three common Ca bearing minerals found in several PSMs include the following:

$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + CO_{2(g)}$$
 (4.6)

$$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-} \tag{4.7}$$

$$CaO + 2H^+ \leftrightarrow Ca^{2+} + H_2O$$
 (4.8)

As these minerals dissolve (i.e. reaction proceeds from left to right), the Ca²⁺ produced from dissolution can then precipitate with solution P that is flowing into the PSM, as described in reaction 4.5. In other words, reactions 4.6-4.8 have the ability to "feed" Ca²⁺ to dissolved P in solution (reaction 4.5) and subsequently precipitate the P as a solid. Ca minerals vary in their ability to provide Ca^{2+} to solution, i.e. some minerals are more soluble than others. These Ca minerals shown in reactions 4.6–4.8 differ from each other in regard to solubility, pH buffering capacity, and the impact of pH on their solubility. CaCO₃ minerals are generally less soluble than gypsum at pH 7 and above, while CaSO₄ minerals on the other hand have minimal impact on increasing pH compared to CaCO₃. CaO and Ca(OH)₂ minerals are highly soluble at pH levels of 9 and below, which not only release Ca²⁺ to the solution for precipitation of Ca phosphates, but it also maintains an elevated pH that is suitable for Ca phosphate precipitation. The notion of increased solution Ca concentrations and pH on precipitation of Ca phosphate minerals is shown visually in Fig. 4.9. Simply put, PSMs that produce lower Ca²⁺ concentrations in solution will require a higher pH to appreciably reduce solution P concentrations, and PSMs such as gypsum that maintain a lower solution pH level must dissolve greater amounts of Ca²⁺ in order to be able to remove appreciable amounts of solution P. Limestone (CaCO₃) often makes a poor PSM because of its relatively low solubility in water when pH > 7. However, some limestone samples are occasionally



Fig. 4.9 Solubility/precipitation lines for the Ca phosphate mineral, brushite, shown as a function of solution pH and Ca^{2+} concentration. This illustrates the importance of a PSMs ability in maintaining both an elevated pH and Ca^{2+} concentration for the purpose of precipitating P as a Ca phosphate to remove P

acceptable PSMs when they possess an appreciable amount of fine particles, which increases solubility and therefore the ability to provide Ca to solution.

Not only does the ability of the PSM to dissolve Ca2+ and maintain an elevated pH in solution have an impact on the amount of P that can be removed from water, it also has an impact on the P sorption kinetics. Briefly, the higher the pH of the solution, the faster the solution P can be precipitated with Ca²⁺. If the PSM is not able to maintain an elevated solution pH as indicated by its pH buffer capacity, then Ca phosphate will precipitate more slowly and therefore such a PSM would require a greater retention time with the inflowing water. Ca-based PSMs that are unable to maintain an elevated solution pH or Ca²⁺ concentration are said to be "retention time-sensitive". When constructing a P removal structure using a retention timesensitive PSM, a higher retention time will be required in the design in order to remove adequate P. Figure 4.10 illustrates the impact of retention time and inflow P concentration on a retention time-sensitive material, Filtralite-P[®], which is a manufactured PSM. The LSS and K values in Fig. 4.10 are the maximum P sorption capacity and the affinity of P for the material, respectively. For each size fraction, notice that as the inflow P concentration increases, so does the LSS and K values that indicate P removal. Next, for each inflow P concentration, an increase in the retention time from 30 s to 9 min also increases the P removal, which indicates that the PSM is sensitive to retention time.

Sensitivity of a Ca-based PSM to retention time is often explained by pH buffer capacity. For example, Fig. 4.11 shows the change in pH, P sorption, and thermodynamics of P sorption with step titration of P into two different size fraction of



Fig. 4.10 Example of impact of retention time and inflow concentration on P sorption by a Ca-based PSM. Sorption parameters under flow-through conditions are shown for Filtralite-P[®]: local sorption saturation (LSS) (\mathbf{a} , \mathbf{b} , and \mathbf{c}) and K values (\mathbf{d} , \mathbf{e} , and \mathbf{f}) estimated for five different retention times and four inlet P concentrations. 4–2 mm (\mathbf{a} , \mathbf{d}), 2–1 mm (\mathbf{b} , \mathbf{e}), and 1–0.5 mm (\mathbf{c} , \mathbf{f}) sized fractions. Error bars represent standard error of estimate. Increasing values of LSS and K indicate a greater degree of P sorption by the PSM. Figure courtesy of Gry Lyngsie, Lund University

Filtralite-P[®]. Figure 4.11a indicates that the smaller size fraction (1–0.5 mm) of Filtralite-P[®] is able to remove more P from solution than the larger size fraction (2–1 mm). The heat of reaction shown in Fig. 4.11c, d also indicate the greater amount of P sorption in the smaller size fraction. However, Fig. 4.11b indicates why this occurred; notice that while both materials had an initial pH > 10, the smaller sized fraction was better able to buffer the pH and prevent it from dropping as rapidly as the larger sized fraction. Again, the ability of a PSM to maintain an elevated pH and also supply Ca²⁺ to solution will result in greater and faster P removal. PhrogTM software is able to determine if a specific PSM is retention time-sensitive or not, based on the chemical characterization of the PSM input by the user.



Fig. 4.11 Example of the impact of pH on P removal by Ca-based PSMs. Phosphorus sorption, pH, and heat of reaction resulting from step titration of P into two particle size fractions of a Ca-based PSM (Filtralite-P[®]). *Solid* and *open squares* indicate the 2–1 and 1–0.5 mm size fractions, respectively. (a) The amount of sorbed P as a function of injection number for direct comparison with the multi-point P thermogram; (b) pH resulting from the P additions shown in (a), (c) thermogram (heat rate output) for multi-point titration of Filtralite-P with 0.01 M NaH₂PO₄ as measured with a calorimeter (*upward* and *downward peaks* indicate exotherms and endotherms, respectively), (d) corresponding integration of the thermograms. Error bars are standard deviations. Figure courtesy of Gry Lyngsie, Lund University

Iron and Aluminum-Based PSMs

Some PSMs listed in Table 4.1 such as AMDRs, bauxite waste, foundry sand, and metal filings, are often Al/Fe-based. Certain materials such as WTRs may be Al/Fe-based or Ca-based, depending on the manner in which they were produced. While melter slag can be Al/Fe-based, blast furnace and electric arc furnace slag are usually Ca-based, even though they contain appreciable amounts of Fe and Al within them. It is important to understand that just because a material is rich in Al and Fe, it may not be able to sorb P by that mechanism unless the Al and Fe are in the proper form and "active". Through a routine chemical characterization, the PhrogTM software is able to estimate if and how much of the total Al and Fe contained in a PSM will be active in removing P from solution.

As previously discussed, Al and Fe-based PSMs mostly remove P from water by the process of ligand exchange. While such PSMs are also capable of removing P by anion exchange reactions, we exclude that from this discussion since P bound by anion exchange mechanisms are reversible and therefore not stable. Similar to Ca-based PSMs, the Al and Fe-based PSMs can also remove P by precipitation as Al and Fe phosphates. However, for this to occur it would require that Al³⁺ and Fe³⁺ be in solution in sufficient quantities (equation 4.4); the problem is that Al and Fe minerals found in PSMs will not dissolve appreciable Al³⁺ and Fe³⁺ unless the pH is less than 4.5. Such a low pH is uncommon for most PSMs. For this reason, precipitation of Al and Fe phosphates will also be excluded from this discussion.

A major distinction of the ligand exchange mechanism typical to Al/Fe-based PSMs from the precipitation reactions of the Ca-based PSMs is that ligand exchange is very fast. Ligand exchange often occurs on the scale of seconds or less, and therefore it is a common observation that increased retention time does not appreciably increase P removal for Al/Fe-based PSMs. However, after a PSM becomes saturated with P, it will tend to become more retention time-sensitive. Another major distinction of the ligand exchange mechanism for the Al/Fe-based PSMs is that increased P concentrations generally have less impact on P removal compared to Ca-based PSMs.

Similar to the precipitation reactions discussed for the Ca-based PSMs, pH is a major factor that can impact the efficiency of P removal by Al/Fe-based PSMs. As a result, P sorption by ligand exchange onto variable charge Al and Fe minerals decreases as the pH increases. There are two reasons for this: first, increasing pH makes the surface charge on the mineral more negative, which reduces the attraction of the negatively charge phosphate ions $(H_2PO_4^-, HPO_4^{2-}, PO_4^{3-})$ for the surface. The second and most important reason is that hydroxide is a strong competitor with phosphate for surface sites, and hydroxide concentration increases with pH. Both PO_4^{3-} and OH^- are ligands that compete for the same sites on variable charge minerals. However, OH^- is a more effective competitor than PO_4^{3-} as it is considered a potential determining ion (PDI). Hydroxide becomes an extremely competitive ion for surfaces at elevated pH. As a rule of thumb, Al/Fe-based materials with pH greater than 8.5 should not be considered a PSM, unless the pH is adjusted downward.

In addition to the fast kinetics of P removal, another advantage of Al/Fe-based PSMs is that they can potentially be recharged after they are no longer effective at removing P. Since the P is bound by ligand exchange to a functional group on a variable charged mineral, the P can be replaced with an OH⁻, thereby displacing P back into solution where it can be flushed out:

$$M--OPO_{3}^{2-}+OH^{-} \longleftrightarrow M--OH^{-}+PO_{4}^{3-}$$
(4.9)

This process not only removes P but also effectively prepares (i.e. recharges) the active functional groups for further P sorption, allowing it to serve a PSM again. The process is illustrated in Fig. 4.12. In practice, recharging the variable charged minerals in Al/Fe-based PSMs is accomplished by treating the spent PSM with a solution containing a low concentration of NaOH or KOH, such as 0.01 M, collecting the leachate, and either properly disposing of the P rich solution or removing the P from that solution. The P from that waste solution can be removed by adding $CaCl_2$ to it, which will precipitate the P as a solid Ca phosphate mineral that can be



Fig. 4.12 Illustration of the general process for potentially recharging Fe and Al-based PSMs for continued P removal by the PSM. After the PSM is saturated with P, the bound P can be removed with a hydroxide solution and allow for continued P removal. The stripped P solution is collected and can be reclaimed as a P fertilizer if precipitated with Ca

used as a P fertilizer. Sibrell et al. (2009) was able to successfully strip P from an AMDR using nearly 60 bed volumes of 0.01 M NaOH, and then subsequently precipitated P from that waste solution by adding between 1.6 and 2 moles of Ca per mole of P. This process of recharging Al/Fe-based PSMs could potentially save countless dollars that would otherwise be required for replacing and disposing of spent PSMs. Also, if a P removal structure is designed with this in mind, then the PSM could be recharged in-situ, eliminating the need to remove the PSM from the structure.

4.2.2 Physical Properties Important to PSMs

There are four main physical properties that are important to use of a PSM in a P removal structure: particle size distribution, hydraulic conductivity, porosity, and bulk density. Particle size distribution is important for two reasons. First, smaller

PSM	Saturated hydraulic conductivity: K (cm s ⁻¹)	Porosity (%)	Bulk density (g cm ⁻¹)	Mean particle size (mm)
WTR	0.000036-0.0003	50-60	0.6–1	0.19–1.8
AMDR	0.001-0.1	45-60	0.3–0.8	0.35–3.6
Sieved steel slag (6–25 mm)	>1	35–45	1.5–1.8	14–18
5:95 fly-ash:sand mixture	0.0006-0.03	30-70	1.1–1.6	1.2–2.3
FGD gypsum	0.005-0.01	50-60	1.1–1.3	0.01-0.06
Wollastonite	0.6–1	35-50	1-1.2	1–1.3
Sieved limestone tailings (excluded <0.5 mm)	0.6–1	35–50	1.5–1.7	1.6–1.9

 Table 4.5
 Physical properties of several PSMs that are relevant to the design of P removal structures

WTR water treatment residual, AMDR acid mine drainage residual, FGD flue gas desulfurization

sized particles have greater surface area which generally improves P removal. More important however is the impact of particle size distribution on bulk density, porosity, and hydraulic conductivity. Bulk density is defined as the mass per unit volume of the bulk material, which includes pore space. For example, the bulk density of soil generally varies from 1 to 1.5 g cm^{-3} . The bulk density of PSMs can highly vary as shown in Table 4.5. The bulk density will partly dictate the total volume, and therefore the footprint of the structure. Porosity is defined as the total volume of pore space per unit volume of bulk material; this is usually expressed as a percentage. For example, soils often have a porosity of around 50%; the porosity of PSMs varies from about 35 to 70%. Porosity represents the amount of water that can be held by a PSM. Keep in mind that it is the ability of water to pass through the unconsolidated PSM that allows P to be removed by allowing the P-rich water to come into contact with the solid minerals. Porosity of the PSM will also have a direct impact on the retention time of the P removal structure.

Hydraulic conductivity is the most important physical parameter of a PSM in design of a P removal structure. Simply put, water must be able to flow through the PSM in order for P to be removed, and it must flow through the PSM at an acceptable rate for the P removal structure to be practical. Saturated hydraulic conductivity is a physical property of a PSM that partly dictates how fast water can move through it. For example, clayey soils have a low hydraulic conductivity in the magnitude of 0.0001 cm s⁻¹, while well sorted sand is much more permeable at around 0.1 cm s⁻¹. Gravel-sized material will have a hydraulic conductivity of 1 cm s⁻¹ or greater.

The Darcy equation is used in measurement of the saturated hydraulic conductivity (Chap. 5) and also in designing the P removal structures (Chap. 6). Ultimately, the hydraulic conductivity has a tremendous influence on the maximum flow rate, retention time, and required depth and area of the P removal structure. For a given mass, PSMs with a low value of hydraulic conductivity, such as some WTRs and fly-ash:sand mixtures (Table 4.5) translates to a more shallow depth of the PSM, and therefore a larger footprint for the P removal structure. On an equal mass basis, materials with high values of saturated hydraulic conductivity such as sieved slag and AMDRs (Table 4.5) will result in a P removal structure with a smaller footprint. With regard to retention time, PSMs with smaller values of hydraulic conductivity will be able to achieve longer retention times more easily than more conductive materials; this can become very important for PSMs that are retention time-sensitive.

4.2.3 Safety Considerations of PSMs

Although many by-product PSMs from industrial sources are excellent at removing P from solution, not every sample is safe for use in a P removal structure. While many PSMs are indeed safe for use, one should always be cautious of excessive heavy metals, sodium, titratable acidity, and alkalinity. Of these, the biggest risk is heavy metals, which are toxic to humans if consumed at high enough concentrations.

4.2.3.1 Heavy Metals

Unfortunately there are no direct regulations to guide us in regard to determining if a PSM is unacceptable or not. However, there are regulations pertaining to water, soil, and waste that can be applied to PSMs used in P removal structures. For example, metals threshold concentrations for land application of biosolids (e.g. treated sewage sludge), soil concentration action levels for EPA Superfund program, typical soil concentrations, and threshold water concentrations for the purpose of human consumption and ecosystem function. From these guides, we can take a very safe and conservative approach by applying them to PSMs that could potentially be used in P removal structures. Using these guides, we must consider the potential pathways for the metals to be consumed by humans and accumulate in the environment.

To assess exposure pathways, we must consider both the total concentration of the metal found in the PSM, and the solubility of it. Sometimes a PSM may contain a high concentration of a heavy metal, but if that metal is not soluble then it is not very dangerous. Simply put, heavy metals can only do harm when they are bioavailable, and if that metal is released into solution, then it is highly available for consumption by organisms and for transport via water flow. If a metal in a PSM is not soluble, then the only way it can do harm is if it is directly ingested. One should also consider that it is also possible for a material to contain low total concentrations of heavy metals, making it appear benign, but it may still possess a high solubility. Total metals concentrations are typically determined by heated acid digestion methods (discussed in Chap. 5) that release nearly 100% of the metal from the solid material, followed by an analysis of the resulting acid extract for metals. The

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Table 4.6	EPA drinking water and freshwater limits for trace metal concentrations, range of trace
metal conc	centrations found in benchmark soils of Oklahoma, and EPA thresholds for trace metals
in "excepti	ional quality biosolids"

	EPA drinking water maximum contaminant	EPA freshwater criterion maximum ^b .	Typical concentrations in	EPA ceiling concentrations for exceptional quality
Element	level ^a , mg L ⁻¹	mg L ⁻¹	soils ^c , mg kg ⁻¹	biosolids ^d , mg kg ⁻¹
As	0.01	0.36	1–34	75
Ва	2	NA	NA	NA
Cd	0.005	0.0037	0.13-0.80	85
Cr (total)	0.1	NA	4–70	3000
Cr (III)	NA	0.55	NA	NA
Cr (VI)	NA	0.015	NA	NA
Cu	1.3	0.017	2–33	4300
Pb	0.015	0.065	3–32	840
Hg	0.002	0.0021	NA	17
Ni	NA	1.4	2–57	420
Se	0.05	0.02	NA	36
Ag	NA	0.0034	NA	NA
Zn	NA	0.11	0.13-0.18	7500

NA not available ^aUSEPA (2016) ^bUS Code of Federal Regulations (2016) ^cRichards et al. (2012) ^dUSEPA (1994)

resulting total metals concentrations in the solid PSM can be examined in light of the values listed in Table 4.6, i.e. typical metals concentrations in soils and the EPA ceiling concentrations for exceptional quality biosolids. The former will allow you to simply compare the metals concentration in the PSM to that of typical soils; while there is no absolute threshold value for rejecting a PSM using this table, it is helpful in that it provides a frame of reference. The biosolids metals threshold is from the EPA 503 rule regarding land application of "exception quality" biosolids. An exceptional quality biosolids is one that does not require a permit for land application, and can generally be sold in retail stores such as farm supply and gardening stores.

More important than the total metals concentration in PSMs is the solubility of such metals. Assessing metal solubility in the PSM involves extracting/equilibrating it with a water solution of some type, and measuring how much of the metals dissolve into the solution. The concept is that this will provide an indication of how much of the metal will be released into water as the P-rich inflow water flows through the PSM and is eventually discharged. This can be done by a variety of techniques using pure water or a low pH-buffered water to simulate a worst case scenario. Testing the PSM with low pH water is a safe and conservative approach because the solubility of heavy metals increases with decreasing pH, except for

molybdenum. One such technique that is described in Chap. 5 is the "synthetic precipitation leaching procedure", or SPLP. The SPLP was originally designed to simulate conditions where materials stored on the surface are in contact with acid rain or leachate from acid soils. Regardless, the use of a low pH solution as the extracting solution will provide a worst case scenario for metals solubility. The SPLP test should not be confused with the "toxic characteristics leaching procedure" (TCLP) for metals, which is inappropriate for PSMs. The purpose of the TCLP is to determine if a solid material is suitable for disposal into a regular landfill, or if it must be disposed of into a special hazardous waste landfill. In other words, the TCLP test is for landfill disposal, and just because a material may pass a TCLP test does not warrant its safety for land application or use in a P removal structure.

Another consideration in addition to the type of extracting solution used, is the nature of the extraction itself. First, extractions for soluble metals in PSMs should be conducted under shaking-reciprocating batch conditions; this increases the extraction of the metals relative to what would be expected in a P removal structure, therefore providing the worst case scenario concentration. All of the methods described for soluble metals extraction in Chap. 5 involve shaking the PSM in a tube with the extracting solution for a given amount of time. Second, one may choose to conduct a single extraction or a sequential extraction where the same PSM is repeatedly exposed to a fresh extracting solution after the previous extract is removed from the batch. At the end of the sequential extractions, each extract is analyzed for metals concentration. Interpretation of the soluble extraction metals concentrations can be compared to EPA threshold concentrations for metals in drinking water and for freshwater ecosystems (Table 4.6). Even though P removal structures will rarely discharge directly to a drinking water source, and are unlikely to ever treat the majority of all the water that constitutes a drinking water source, it is wise to be extra cautious and employ the EPA threshold listed in Table 4.6 as a guide.

For example, for the poultry farm P removal structure described in Penn et al. (2014), a subset of 18 pairs (inflow-outflow) of samples were tested for a variety of elements. The concentration of the outflow was compared to the inflow for each pair; any decrease in the outflow relative to the inflow was considered a sorption event and any increase was considered a release event. The results shown in Table 4.7 are the five elements that had one or more release events. The number of sorption and release events are shown for each element, with the majority of the release events from Ca and S, which was not surprising given the high Ca and S content in the treated slag that was utilized as the PSM. While there is no standard for Ca in drinking water, the EPA has a secondary standard for sulfate of 250 mg SO₄ L⁻¹ (~83 mg S L^{-1}), due to taste and odor (USEPA 2009). Given that SO₄ is the most common form of inorganic S found in oxidized soils, it is a safe assumption that most of the S present was SO₄. Solution Mo was released in ten of the sample sets, but the maximum difference between the inflow and outflow was relatively low at $0.06 \text{ mg } \text{L}^{-1}$ and there is no current EPA standard for Mo. There was an even split of sorption and release events for Ba for the 18 sample pairs, but the maximum release event only increased the Ba concentration by 0.02 mg L⁻¹. The EPA drinking water standard for Ba is $2 \text{ mg } \text{L}^{-1}$, so the increase due to the structure is not a safety

	No. of release events	No. of sorption events	Minimum release (mg L ⁻¹)	Maximum release (mg L ⁻¹)	EPA standard (mg L ⁻¹)
Ca	18	0	6.20	226	None
S	15	3	-56.7	606	250 (SO ₄)
Mo	10	2	-0.03	0.06	None
Ba	9	9	-0.01	0.02	2.0
Cr	2	1	-0.01	0.01	0.1

 Table 4.7 Influent and effluent water analysis from a subset of 18 random outflow and inflow sample pairs from the poultry farm P removal structure (Fig. 3.5), conducted for safety assessment

Release concentration is outflow concentration minus inflow concentration. "Release Event" is a filtration event where outflow concentration > inflow concentration and "Sorption is where outflow concentration". EPA primary and secondary drinking water standards are shown for comparison to maximum release concentrations. Elements with less than two release events are not shown

issue. Chromium, in excess of 0.1 mg L⁻¹ can cause allergic dermatitis (USEPA 2009), a painful skin condition, but the highest amount released was 0.01 mg L⁻¹. There were only three sample pairs with measurable Cr, with two of them releasing 0.01 mg L⁻¹ and one of them removing 0.01 mg L⁻¹ that was present in the influent. While the release of any Cr is not ideal, the concentration released by the structure is not high enough to warrant concern. The elements released are compared to drinking water standards (Table 4.6) in order to gauge potential risk, although the effluent was an appreciable distance from a drinking water source. While safety must be addressed before an industrial by-product can be used in a P removal structure (Penn et al. 2011), this data set along with two previous studies which tested treated water for heavy metals and boron from non-treated slag P removal structures over the course of 8 months, showed that treated and non-treated steel slag can potentially be used safely (Wang et al. 2014; Penn et al. 2012).

4.2.3.2 pH and Alkalinity

Effluent pH is an important consideration with regard to discharge to surface waters. Excessive pH that is too acid or basic could cause problems in aquatic ecosystems. Many PSMs cause the pH of passing water to be in the "near neutral" range of 6–8, while other PSMs can result in a water pH that is more basic in nature (>8; Table 4.3). However, consider that the pH of naturally occurring runoff and groundwater in many regions will range from 8 to 9. Still, it is very important to not disregard a Ca-based PSM simply because of a high pH that exceeds 9. Keep in mind that pH is simply a measurement of the concentration of the protons in solution, and in no way is indicative of the ability of that PSM to *maintain* a high pH upon mixing with other water or after coming into contact with soils and sediments. The ability of a solution to maintain a high pH is more important than the pH itself, and is known as the alkalinity of a solution. On the flip side, for acid solutions, their ability to maintain

or buffer a low pH is known as titratable acidity. The same principle applies: just because something has a low pH does not necessarily make it dangerous unless it also has the ability to maintain that pH and force the pH of the entire system to also change to an excessive pH level. Consider an analogy, soda pop will have a pH between 2.5 and 4.75, yet when a person consumes a soda it does not damage their throat with acid burns. This is because although the pH is low, it has does not have a high amount of titratable acidity and is not able to strongly influence the pH of the human body and other systems that are buffered. Obviously the dose or volume of solution has a major impact as well. For example, acid mine drainage is a tremendous ecological problem because the pH of the water is not only low, but contains a large amount of total acidity. If acid mine drainage also constitutes a large percentage of stream flow, then the problem is magnified.

Regarding alkalinity, the following illustrates the importance of alkalinity rather than sole reliance on effluent pH. The pH and alkalinity of outflow of treated water from a P removal structure containing a sieved steel slag with average particle size of 14 mm and pH of 9.4 was monitored. Although the pH of the treated water increased from 7.7 to 9.2, the alkalinity only increased from a level of 77 to 81 mg $CaCO_3 L^{-1}$ for the inflow and outflow, respectively. Keep in mind that addition of alkalinity to aquatic ecosystems is typically a very positive aspect as minimum alkalinity of 20 mg CaCO₃ L⁻¹ is required for aquatic ecosystems and an alkalinity up to 400 mg L⁻¹ has no impact on human health (USEPA 1986). A second example: the pond filter shown in Fig. 3.13 was partially a closed system due to no outlet, therefore filtration of the water in the pond provided a worst-case scenario for how filtration with a PSM could affect the pH of the pond water. Pond water was continuously re-circulated from the pond to the filter, which would drain through the alkaline filter media back into the pond. After several months of testing alkaline media in which the entire volume of pond water was filtered through the media many times, the pH of the pond water never decreased, even though the pH of the drainage water from the filter ranged from 9 to 11. While the pH of the drainage water from the filter was elevated, it was not alkaline enough to change the pH of the pond water, even though the drainage water was not being diluted with other water.

4.3 The Paradox of Many PSMs

One of the greatest challenges in designing a P removal structure is choosing a PSM that has sufficient P sorption capability and hydraulic conductivity, allowing for an ideal and efficient design for the specific site. While almost any PSM can be used in design of a P removal structure, some materials will simply allow for a much more economical and efficient structure. Figure 4.13 illustrates the "paradox" that is commonly observed for many PSMs, in that PSMs that possess the highest capacity to sorb P from solution also tend to have the lowest hydraulic conductivity. The practical consequence of such a PSM, is that while a relatively small mass of PSM will be required to meet the user's P removal goals for the site, either a large hydraulic head


Fig. 4.13 Illustration of the paradox between physical and chemical properties often observed for many PSMs. PSMs that are able to conduct water at a high rate tend to sorb less P compared to PSMs that have a low hydraulic conductivity. However, there are some PSMs that tend to be somewhat "balanced" with regard to the ability to conduct water and sorb P. P sorption maximum (S_{max}) determined by a Langmuir isotherm is useful for comparing the P sorption ability between PSMs, but should never be used to design a P removal structure. Note that the values indicated for drinking water treatment residuals (WTRs), sieved slag, and acid mine drainage residuals (AMDRs) are from real samples, and are not meant to represent all samples of each respective PSM

(i.e. depth of water on top of the PSM) will be required, or the PSM depth must be kept to a minimum in order to meet the user's minimum flow rate goal. If the desired minimum flow rate for the structure is not very high, then this is not a problem. However, if the desired minimum flow rate is appreciable, then meeting this flow rate ultimately translates to expanding the area of the P removal structure by minimizing PSM depth. The required area may not be available at the site, or the larger required area of the structure may be cost prohibitive.

On the other side of the paradox is the notion that PSMs that possess the highest hydraulic conductivity tend to sorb P less efficiently. The practical consequence of this is that a greater relative mass of the PSM will be required to meet the desired P removal goals, although high flow rates through the structure will be easily achieved with a smaller footprint. The potential drawback of this consequence is that it could cost significantly more for obtaining a larger mass of that particular PSM. The design process illustrated in Chap. 6 demonstrates and takes into account physical properties such as hydraulic conductivity, determines the necessary mass of PSMs, and considers the area restraints for a particular site in estimating the most suitable



Fig. 4.14 Three techniques for dealing with the problem of PSMs with insufficient hydraulic conductivity (Ksat) for meeting site specific flow rate requirements. While each technique may be a viable solution to the problem, there are potential drawbacks that could occur

design. This entire process is greatly simplified through use of the Phrog software, demonstrated in Chap. 7.

Figure 4.13 lists WTRs as a material that often falls into the category of high P sorption ability, but low hydraulic conductivity, while sieved steel slag, which is a gravel-like material, has the opposite problem. While PSMs on either side of the paradox can still be suitable for many situations, there are some PSMs that tend to be more "balanced" with regard to P sorption and hydraulic conductivity. Many samples of AMDRs tend to be ideal in this regard. Manufactured PSMs also tend to be very well balanced because they are designed and made with both of those material properties in mind.

4.3.1 Potential Solutions for PSMs with Insufficient Hydraulic Conductivity

In general, there are three main techniques for dealing with PSMs that possess insufficient hydraulic conductivity for a specific site and user goal (Fig. 4.14). One of the most common solutions is to dilute the PSM with sand. For example,

for many fly-ash samples, it is impossible to use pure fly-ash in any P removal structure unless it is mixed with sand at a 95:5 ratio of sand to fly-ash. Other PSMs with low hydraulic conductivity may not necessarily require dilution to allow water to flow through them, but dilution could appreciably improve it. However, dilution with course material should be performed with caution, and the final PSM-sand mixture should always be tested for physical properties prior to use in a P removal structure. While this will often work well to solve the problem in many situations, there are three potential pitfalls. First, some sand materials that are obtained from sand quarries will contain a relatively high percentage of clay and silt particles, thereby providing a dilution material that has a poor hydraulic conductivity itself. Second, one needs to consider the increase in the size of the P removal structure by using a diluted material with greater hydraulic conductivity, and the associated cost; it might be more cost efficient to use the pure un-diluted PSM and simply utilize a greater area (i.e. smaller depth of PSM). Phrog software is extremely useful in allowing the user to compare these different possible scenarios. Third, for some PSM-sand or PSM-gravel mixtures, the finer PSM particles may act to fill in the pore space between the larger sand and gravel particles. Effectively, that could result in a mixture that has a similar hydraulic conductivity as the pure un-diluted PSM, gaining nothing for the user. For this reason, it is critical that all PSMs diluted with other materials be tested for hydraulic conductivity and other physical properties, prior to deployment in a P removal structure.

A second potential solution is to pelletize the PSM and form larger granules that are stable in water (Fig. 4.14). This has been accomplished for AMDR samples and also for some Ca-based PSMs. Because this requires specialized equipment and chemical binders, one drawback is the increased cost. Another potential drawback of pelletization is that P sorption of the PSM is likely to decrease due to the decrease in surface area. However, this decrease in P sorption may be worth it for the gain in hydraulic conductivity and achieving a more "balanced" PSM.

The third potential solution is to construct two P removal structures in series with each other (Fig. 4.14). One of the PSM beds is composed of a high P sorption material with low hydraulic conductivity, which will handle the flow from "normal" flow events, and the other PSM bed is composed of a low P sorption material with large hydraulic conductivity to handle the high flow events. The two beds are connected to each other through an overflow pipe; when the inflow rate exceeds the max drainage rate of the PSM with high P sorption capacity, the excess water flows into the secondary bed of more permeable material. The obvious drawback of this solution is that two different PSMs are required to construct the structure. Another potential drawback is that the cleanout schedule for the two different PSM beds will likely not overlap since the two different PSM beds will be exposed to different P loads and because the materials will have different P sorption capacities.



Fig. 4.15 Cutaway of a clogged PSM bed that consisted of un-sieved electric arc furnace steel slag. The brown-orange precipitant at the surface and in the pore space are precipitated Ca carbonate, sulfate, and silicate minerals that formed and ultimately restricted all flow after about 100 h of flow through the PSM bed. The inset photograph shows a solid piece of the precipitant that formed in the drainage pipe of the P removal structure. For this reason, steel slag should always be screened to remove the fine particles prior to use in a P removal structure

4.3.2 A Note on the Use of Steel Slag and Chemical Treatment

Steel slag is a relatively abundant PSM that is found throughout the U.S. and the world (Table 4.2). However, blast furnace and electric arc furnace steel slag are quite prone to clogging when used in a P removal structure. The fines contained in steel slag are highly soluble Ca minerals such as portlandite. These minerals are positive with regard to P removal because they dissolve quickly and maintain a high Ca concentration and pH for precipitating Ca phosphate from inflow water. The problem is that much of this newly dissolved Ca will also re-precipitate into less soluble silicate and carbonate minerals. When this occurs to an excessive degree, the newly formed minerals can clog the pore space of the slag and greatly impede drainage through it. The photograph in Fig. 4.15 shows the result; the brown-orange colored materials located on the top of the PSM bed and in the pore space is the newly precipitated Ca minerals that resulted in 100% flow restriction after this P removal structure (pond filter) had received about 100 h of flow through it. The subset in Fig. 4.15 shows a large piece of the precipitant that clogged the drainage

pipe for the structure. Analysis of the precipitant showed it to consist of mostly Ca, silica, sulfate, and carbonate. Another problem that can occur with the use of steel slag is that as the newly dissolved Ca from the slag begins to precipitate with P and also as a Ca carbonate mineral as it drains through the profile, these flocs often escape capture and drain out. These flocs often contain a high amount of P on them due to the P sorption that is occurring in the PSM bed. The logical solution is to prevent the loss of these P-rich flocs, however, they are extremely small in size, and attempts to filter out the flocs have resulted in 100% restricted drainage.

As a solution, steel slag must be sieved to remove the smallest particles that cause the problem. The disadvantage to this is that P sorption capacity is decreased. However, without sieving out the fine particles, most slag PSM beds will clog. Laboratory experiments with different size fractions and hydraulic conductivity measurements have shown that slag hydraulic conductivity will remain high after many hours of flow if the particles less than 0.5 mm are removed from the slag. Typically, this is accomplished by screening the slag with a 6.35 mm (1/4 in.) sieve, and using only the material that is retained on the screen. A smaller mesh can be used, but it is important that all particles less than 0.5 mm in size are removed. On the other hand, one should not retain slag with an excessively large mesh because there is an inverse relationship between slag particle size and P sorption capacity. Thus, we recommend a maximum sieve size of 18 mm in order to maintain decent P sorption capacity. In summary, steel slag material should be sieved (keeping what is retained) with a screen size of at least 0.5 mm, and a maximum of 18 mm in order to prevent clogging, yet maintain a good P sorption capacity. Screening slag on a large scale is often offered as a service by slag suppliers such as Phoenix, Edwin Levy Co., and TMS International. Also, gravel, sand, and lime quarries may be willing to sieve steel slag on a large scale upon request.

Because of this compromise between decreasing P sorption and preventing clogging as achieved through sieving out the fine particles, a solution was developed to minimize the loss in P sorption capacity. The sieved slag can be chemically treated in order to increase the P sorption capacity of this highly conductive material in order to achieve a more "balanced" PSM with regard to P sorption capacity and hydraulic conductivity (Fig. 4.13). Consider that the hydraulic conductivity of a sieved slag sample is typically at least 1 cm s^{-1} (Table 4.5). Chemical treatment of the sieved slag enables this PSM to sorb much more P than non-treated slag (Fig. 4.16). This chemical treatment can be conducted either *in-situ* or *ex-situ* of P removal structures, and in some cases has been used to recharge the PSM after the slag had become no longer effective at removing P. Treated slag has been used successfully in several P removal structures; on average, chemical treatment increases P sorption by 3-4 times, thereby decreasing the tonnage of PSM required for the structure, and the overall size. Chemical treatment of slag for increasing P sorption is a proprietary process owned by Oklahoma State University and licenses are available through its Technology Development Center, which will provide technical information to licensees.



Fig. 4.16 Cumulative P removal by treated and non-treated slag under flow-through conditions (30 s retention time and 1 ppm inflow P concentration), tested before and after chemical treatment of the slag. *Lower photograph* shows treated vs. non-treated slag

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Chapter 5 Characterization of PSMs

5.1 Measuring and Estimating P Removal: Flow-Through vs. Batch Tests

Clearly, the heart of a P removal structure is use of a PSM that has the ability to remove P from solution. This ability must be quantified for two purposes. First, quantification of P removal is necessary for simply comparing one PSM to another in choosing between several PSMs. Second, quantification is required for designing the structure and determining what mass of the PSM will be required to meet the user defined goals for the conditions and site of interest. There are two types of methods for comparing PSMs to each other with regard to P sorption ability: flow-through P sorption tests and batch sorption tests. With regard to quantifying P sorption by a PSM for use in design of a P removal structure, the only suitable data is from flow-through experiments conducted to determine the "design curve" described below; batch P sorption data is not acceptable. However, the design curve can also be estimated using a chemical characterization combined with the Phrog software.

A summary of a general method for testing P sorption in a batch test is shown in Fig. 5.1. Again, this method is only suitable as an index for comparing the P sorption capacity of various PSMs, and the values cannot be used in design of a P removal structure. A flow-through P sorption technique (Fig. 5.2) is superior to a batch technique for quantification of P removal for design purposes, for several reasons described below. Simply put, a flow-through technique is representative of the processes occurring in a P removal structure, whereas the batch technique is not.

Flow-through techniques allow for use of low inflow P concentrations that are representative of drainage and wastewater dissolved P concentrations. Continuous input of low P concentrations to the PSM allows for realistic P loading (i.e. cumulative mass of P added per mass PSM) to the PSM. While low input P concentrations



Fig. 5.1 General procedure for conducting a batch P sorption isotherm for comparing P sorption abilities between PSMs. This method only serves as an index for comparing PSMs, and the results are not suitable for use in design of a P removal structure

can be used in a batch P sorption test (Fig. 5.1), the added solution P in a tube or bottle will not approach a realistic P loading to the PSM.

- Flow-through techniques allow for a constant input P concentration. For the batch method, the added solution P concentration will not be maintained if the PSM sorbs much of the P. In contrast, for a flow-through method, the inflow solution P concentration is always maintained by continuous replenishment. It is critical that input solution P concentrations be maintained as a constant because this directly impacts the degree of P removal, as discussed in Chap. 4.
- Flow-through techniques take into account the impact of retention time on P removal. Within a P removal structure, P-rich water comes into contact with a given mass of PSM for a finite amount of time. This retention time can have a big impact on P removal for some PSMs (Chap. 4).
- Flow-through techniques involve the continuous removal of P sorption reaction products. Without removal of reaction products such as carbonate, protons, hydroxide, and sulfate, the P sorption reaction becomes inhibited. A P removal structure naturally removes P sorption reaction products, and a batch sorption test will not capture this characteristic.

5.2 The P Removal Design Curve

The first step to designing a P removal structure is to estimate how much P a particular PSM will be able to remove from the water. While batch isotherms are easier and less expensive to complete than conducting a flow-through sorption experiment, it does not accurately simulate the real world conditions of a filter which will be subject to continuous additions of P rich water during runoff events, the removal of



Fig. 5.2 Schematic of the general procedure for conducting a flow-through P sorption test on PSMs. This procedure results in direct measurement of the "design curve" necessary for designing a P removal structure. The design curve can also be predicted using PSM properties input into the Phrog model. Note that tubes inside of Mariotte bottle are glass. Flow-through cells can be constructed using filtration assemblies sold by Savillex

reaction products, and limited contact time. A design curve must be determined either directly through a flow-through experiment or estimated through a model. A design curve is simply a mathematical relationship that quantifies the change in P sorption onto a PSM with cumulative P loading of the material, under specific conditions of contact time (retention time) and inflow dissolved P concentration (Fig. 5.3). Simply put, the design curve is an essential tool for properly designing a P removal structure for specific conditions. Details on exactly how the design curve is used to design a P removal structure presented in detail in Chap. 6.



5.2.1 Method for Direct Measurement of the Design Curve: Flow-Through Experiment

Figures 5.2 and 5.4 illustrate the general layout for conducting a small-scale flowthrough P sorption experiment for directly obtaining a design curve. Note that the resulting design curve produced from this method is only valid for the inflow P concentration and retention time utilized in the test.

- 1. Materials: Mariotte bottle (at least 3 L) with rubber stopper and glass tubes, low flow peristaltic pump, plastic tubing, flow through cells and racks, 0.45 μ m filter, pure silica sand, Erlenmeyer flasks, glass sample vials, timer, scale, and sodium (or potassium) phosphate monobasic (NaH₂PO₄·H₂O).
- 2. The PSMs being tested should be air-dried and mixed well to ensure a representative sample is taken, and weighed out into small plastic cups. If the sample mass is less than 5 g then lab grade sand (pure silica sand, 14808-60-7; Acros organics, Morris Plains, New Jersey) should be added to bring the total mass to 5 g. Record the sample mass.
 - (a) Important: The sample should not be crushed for this test. The sample should be tested in the same form it will be used in the field.
- 3. Note: sand is used to bring the total mass to 5 g to achieve a pore volume of 1.28 cm³ (5 g of sand; 40% porosity). This constant pore volume allows the user to adjust the retention time of the experiment by using different flow rates.

Fig. 5.4 Photograph of the general layout for conducting a flow-through experiment: Materials shown include Mariotte bottle for supplying inflow P solution, flow through cell with filter and PSM contained within it, special rack for holding flow-through cell, peristaltic pump, timer, collection containers, and sample vials



Retention time (RT) is the amount of time that the material is in contact with the solution and is calculated as:

$$Retention time = \frac{sample \ total \ pore \ volume}{flow \ rate}$$
(5.1)

- Where sample total pore volume is in units of mL and flow rate is in units of mL min⁻¹. The sample total pore volume is calculated based on the porosity and bulk density of the PSM and the silica sand. Using this approach, one can vary the amount of sand added to the PSM (to change total pore volume) or the flow rate used in the experiment in order to achieve the desired retention time.
 - (a) Typical flow rates used to meet retention times between 0.5 and 10 min range from 2.6 to 0.13 mL min⁻¹.
 - 4. The mass of PSM used will depend on the sorption capacity of the PSM. The goal is to choose a suitable amount of PSM that will not result in 100% or 0% P removal for the duration of the entire experiment. Sometimes determining the suitable mass for the experiment is determined by trial and error. If there is little to no P removal over the entire duration of the experiment, then increase the mass used. On the other hand, if the P removal does not decrease to approximately 15–20% over the duration of the experiment, then decrease the mass.

- 5. P inflow solutions should be made using sodium (or potassium) phosphate monobasic (NaH₂PO₄·H₂O). Begin by making a concentrated stock solution and then dilute it to reach the desired concentration. A few drops of chloroform can be added to the solution to inhibit algae growth.
- 6. Each flow-through cell should be used with a single peristaltic pump. Using a tubing chart that is typically provided by manufacturers of peristaltic pumps, it is possible to determine the range in flow rate for a given tubing size and the speed of the pump. The "variable flow mini pumps" sold by Fisher and VWR (either low flow or ultra-low flow) and shown in Fig. 5.4, work very well for conducting these small-scale flow-through experiments
 - (a) Note: Calibrating the pumps can be one of the most time consuming and labor intensive portion of the flow-through setup and one of the most important since the flow rate is a key component of all calculations. If the power to the pump is turned off then the flow rate will change. Once the pump is calibrated make sure the pump is left running.
- 7. Note: The "in" tubing should connect to the bottom of the flow-through cell and the "out" tubing should flow into the collection container. The pump is pulling the solution from the bottom of the flow-through cell.
- 8. Important: The tubing should not be left on the pump overnight. It is under tension which will reduce the lifespan of the tubing.
- 9. The flow-through cell shown in Figs. 5.2 and 5.4 should be screwed together and placed in a rack specially built for fitting the flow-through cell and allowing it to keep the bottom of it elevated enough to place a rubber stopper (or some type of fitting) and tubing into the bottom. Gently place the rubber stopper or fitting that houses the tubing into the bottom of the flow-through cell. Fill the cell with DI water and turn the pump on for calibration of flow rate.
 - (a) Important: Wait until there is no air present in the tubing before continuing.
- 10. Tare a scale using an empty sample vial (20 mL vial). Place the "out" tubing into the vial and start a 3 min timer. At the end of the 3 min, remove the vial, weigh it (units of grams), and divide by 3. The result is the flow rate in mL min⁻¹. The measured flow rate needs to be close enough to the target that it round to it, e.g. 0.754 or 0.746 to meet a target of 0.75, but not 0.755 or 0.744.
 - (a) Important: Do not shut off the pump or remove the tubing once the pump is calibrated. It will change the flow rate. Pumps can be calibrated and shut off the day before running a flow-through experiment. While they will still need to be calibrated the day of the experiment, this can reduce the time it takes to do so.
 - (b) The pumps need to be calibrated the morning of the experiment and the actual flow rate has to be recorded for each cell during the experiment for every sample interval. This is described in detail below.
- 11. Fill the Mariotte bottles with the P solution. Each flow-through cell should be used with a single Mariotte bottle. For each bottle, take a subsample and fill a

20 mL sample vial and place it in the sample collection tray. Record this sample as the time 0 for that cell. It will be used to calculate the P load entering that flow-through cell and the P removal of that material.

- 12. Place the rubber stopper with two glass tubes into the Mariotte bottle firmly (Figs. 5.2 and 5.4). The glass tube with the hose attached must be at a lower elevation (only a few mm) in the bottle than the other glass tube; this is critical for proper function of the Mariotte bottle.
- 13. Unscrew the flow-through cell, place a 0.45-µm filter inside the cell, and reassemble the cell carefully.
- 14. Pour the PSM sample uniformly into the flow-through cell. Make sure the entire sample makes it into the cell.
- 15. Record the weight of two 200-mL Erlenmeyer flasks (or beakers) assigned for each flow-through pump/cell. Mark the bottles to associate them with their respective pump and mark the flasks as "A" and "B", for example. It is very important to keep both flasks associated with their respective pumps. Switching the bottles for a different pump will cause the precise flow rate calculations to be incorrect.
- 16. After all of the samples are in the cells, use a syringe to inject air into the open glass tube at the top of the Mariotte bottle. Important: The Mariotte tubing has to be occasionally monitored throughout the experiment. It cannot be allowed to go dry. If the entire cell goes dry then the data for that cell is not usable. If the tubing goes dry, use the syringe to inject air into the bottle to restart the flow.
- 17. After all of the cells have started flowing (water is dripping out of the outflow tubing), then start the timer for 30 min. Tubing should be set to direct solution into flask A. After 30 min, switch tubing from flask A to B. Weigh flask A for each pump and record the bottle + solution weight; subtract the empty flask weight to determine the volume of the sample assuming that 1 mL = 1 g. Divide the weight by 30 to obtain flow rate in mL min⁻¹. Record this flow rate for each 30 min time period. The flow rate may slightly vary with time.
 - Note: It is often beneficial to take the two sample at 15 min intervals, with the remaining samples at 30 min intervals. Regardless, be sure to record the sampling interval and account for it in calculating the net flow rate for each interval.
- 18. Swirl the water sample in the flask to mix it, and then pour a sub-sample into a vial to store it until analysis. Label the vial. Discard the remaining water in the flask. The flask should be ready for the next switch in 30 min.
- 19. After the cells have flowed for 5 h through the PSMs, it is time to take the final outflow samples and turn off the pumps. Make sure to remove the tubing from the pumps and rinse with DI water. Excess P solution can be saved for other experiments.
- 20. Analyze all P solutions by a colorimetric technique or by ICP-AES, including the background inflow P sampled from the Mariotte bottle. If concentrations are expected to be less than 1 ppm, then use a colorimetric technique for greater

accuracy. For each sampling time period (usually 30 min), calculate the amount of P added to the PSM (mg P kg⁻¹ PSM):

$$P added = \frac{flow rate(mL \min^{-1}) \times 30 \min \times inflow P conc(mg L^{-1})}{mass PSM(g)}$$
(5.2)

- 21. Knowing the amount of P added at each time interval, sequentially sum the values of P added to calculate cumulative P added at each time interval.
- 22. Calculated discrete P removal for each time interval:

Discrete P removal (%) =
$$\frac{Outflow P concentration(mg L^{-1})}{Inflow P concentration(mg L^{-1})}$$
(5.3)

23. As shown in Fig. 5.3, plot discrete P removal (y-axis) vs. cumulative P added (x-axis) for each sampling interval. Fit an exponential equation to this relationship. The resulting equation is the design curve that is specific to that PSM tested at the inflow P concentration and retention time:

$$Discrete P removal(\%) = be^{m \times CP_{add}}$$
(5.4)

Where CP_{add} is cumulative P added to the PSM (mg P kg⁻¹ PSM); Coefficients *b* and *m* are coefficients of the exponential equation that predicts discrete P removal. Use of the design curve for designing P removal structures is described in detail in Chap. 6.

5.2.2 Indirect Estimation of the P Design Curve Through Characterization of PSMs

Since conducting a flow-through experiment for each PSM at every P inflow concentration and RT of interest is cumbersome and expensive, we developed a model for predicting the equation for the design curve. This model is incorporated into the Phrog software and essentially it predicts the equation for the design curve as a function of PSM properties, inflow P concentration, and retention time. To achieve this, the m and b values for the design curve equation (5.4) are predicted as a function of retention time (RT in minutes) and inflow P concentration (P as mg L⁻¹ in the equations below).

$$\log(-m) = (\alpha RT) + (\beta P) + \chi \tag{5.5}$$

$$\log(b) = (\delta RT) + (\varepsilon P) + \mu$$
(5.6)

After log transformation, coefficients *b* and *m* from equations 5.5 and 5.6 become the y-intercept and slope, respectively, for the relationship between discrete P removal and CP_{add} that are used in equation 5.4. The coefficients, α , β , χ , δ , ε , and μ are specific to each individual PSM, and are predicted by the Phrog software as a function of total Ca, Fe, and Al, amorphous Al and Fe, pH, pH buffer index, and mean particle size. The advantage of predicting the design curve by this method is that it eliminates the need to conduct flow-through experiments on each PSM at every P inflow concentration and RT combinations of interest. A validation of this model was presented in Penn et al. (2016). Methods for measuring each of these necessary parameters are described below.

5.2.2.1 pH Measurement

The pH of the PSM is a "master variable" that dictates the effectiveness of Ca contained in a Ca-based PSM or Al/Fe contained in an Al/Fe-based PSM, with regard to sorption of P from solution.

- 1. Weigh 3 g of the PSM into a snap vial and then add 15 mL of de-ionized (DI) water. The mass can be adjusted as long as the 1:5 solid to DI ratio is maintained. Note: A check soil sample should be included in each set of samples, as well as a duplicate.
 - (a) Do not crush or grind samples.
- 2. Shake snap vials for 1 min.
- 3. Wait 20 min.
- 4. Shake snap vials a second time for 1 min.
- 5. Wait 20 min for a second time.
- 6. Test pH and electrical conductivity (EC) using the appropriate calibrated meters.

Notice that EC can also be measured on this same sample. Although EC is not necessary in prediction of the design curve, it is recommended that each sample be tested for EC in order to ensure that the material is not unsafe due to excessive salinity.

5.2.2.2 Measurement of Total Ca, Al, and Fe by Total Digestion

Total digestion is necessary for determining the total concentrations of P sorbing elements, and also heavy metals with regard to safety. Essentially, the PSM is digested using strong acids and heat, with the resulting digestate solution analyzed for the elements of interest by ICP-AES or atomic absorption (AA) techniques.

 Reagents and materials: concentrated HCl, concentrated HNO₃, 1:1 mixture of HNO₃ and DI water, 30% hydrogen peroxide, and deionized water. Hot plate, Whatman #42 filter paper, funnels and funnel stand, 125 mL Erlenmeyer flasks, and thermometer. Reagent needed per sample: 5 mL concentrated HCl, 13 mL hydrogen peroxide, 10 mL concentrated HNO₃, 10 mL 1:1 HNO₃:DI water.

- 2. Weigh 0.50 ± 0.01 g of dry sample into a 125 mL Erlenmeyer flask. Note: Particles larger than 2 mm should be ground prior to digestion. A fine, relatively uniform sample will digest easier and provide more accurate values, so grinding is preferable for most samples. Note: Use wide mouth flasks since they allow for faster evaporation during Step 7.
- 3. For each set of samples digested, a method blank should be produced that is carried through all of the same steps as the samples (i.e. receives all the reagents that the samples do). A reference sample (check soil) and a duplicate of one of the samples should also be produced.
- 4. Cautiously add 10 mL of the 1:1 HNO₃ reagent to the flasks and mix the slurry carefully to avoid getting particles on the sides of the flasks. Use the hot plate to heat the samples to 95 °C for 10–15 min. Do not allow samples to boil. Note: Samples may need to be rotated on the hot plate to ensure even heating. Important: The samples cannot be allowed to boil anytime during this process. Any particles or liquids on the sides of the flasks will result in incomplete digestion. Use a water bottle with DI water to gently remove particles from the side of the flask if this does occur.
- 5. Allow samples to cool to about 80 $^{\circ}$ C and then add 5 mL of concentrated HNO₃ and then heat back up to 95 $^{\circ}$ C for 30 min. Note: The additional acid added can be used to clean any particles or liquid off of the sides of the flasks.
- 6. Repeat Step 5 to ensure complete digestion.
- 7. Allow the solution to evaporate to 5 mL without boiling and without the flask drying completely. Note: A 125 mL Erlenmeyer flask with 5 mL of water in it can be useful as a visual aid to help in this step. Important: The flasks cannot be allowed to dry out in this step. There has to be liquid covering the bottom of the flask.
- 8. Let the sample cool, then cautiously add 2 mL of deionized water and 3 mL of hydrogen peroxide. Return the flasks to the hot plate for warming. Take care that liquids do not leave the flasks due to excessively vigorous effervescence. Heat until effervescence subsides, then cool the flasks.
- 9. While warming the flasks, add hydrogen peroxide in 1 mL aliquots until effervescence is minimal or until the general appearance of the sample is unchanged. Do not exceed 10 mL of hydrogen peroxide per sample in this step. Note: Most samples will require all ten additions of hydrogen peroxide.
- 10. Cautiously add 10 mL of deionized water and 5 mL of concentrated HCl and then return flasks to the hot plate. Cover flasks with watch glasses and heat for an additional 15 min without boiling.
- 11. Allow the flasks to cool, and then filter through Whatman #42 filters into 50 mL volumetric flasks. After filtration is complete, bring the samples to volume using deionized water.
- 12. Analyze the resulting solutions using ICP-AES or another appropriate method for quantification of the concentrations of P sorbing elements (Ca, Fe, Al) and

any heavy metals of interest. The Ca, Fe, and Al values are input into the Phrog software after conversion into units of mg kg^{-1} PSM.

13. Reference: USEPA (1996)

5.2.2.3 Measurement of Amorphous Al and Fe

As discussed in Chap. 4, one of the most important groups of minerals for sorption of P are Fe and Al oxides and hydroxides, especially amorphous forms of these minerals. The purpose of this extraction is to selectively dissolve (and therefore quantify) the amount of amorphous Al and Fe oxides and hydroxides contained in a PSM.

- Materials: ammonium oxalate [(NH₄)₂C₂O₄·H₂O, formula weight 142.11], Oxalic acid (H₂C₂O₄·2H₂O, formula weight 126.06), sample shaker, Whatman #42 filter paper, filter funnel and filter stand, pH meter. Reagent needed per sample: 40 mL of the extracting solution.
- 2. Making 1 L of the extracting solution: Dissolve 28.42 g of ammonium oxalate into a 1 L volumetric flask and bring to volume with deionized water. Dissolve 25.21 g of oxalic acid into a second 1 L volumetric flask and bring to volume with deionized water. In a large beaker mix approximately 700 mL of the oxalate solution with approximately 535 mL of the oxalic acid solution. Check the pH of the mixture and adjust to a pH of 3.0 ± 0.05 using the oxalic acid solution to lower the pH and the ammonium oxalate solution to increase it. Excess oxalic acid and oxalate solutions can be stored in the refrigerator, but the final, mixed solution should be made the day of extraction and not stored.
- 3. Weigh 1.00 g of PSM into a 50 mL centrifuge tube. If a representative sample cannot be obtained with only one g of PSM, then increase the mass and use a larger container, but be sure to maintain the 1:40 solid:solution ratio. Important: For each set of samples extracted a method blank should be produced that is carried through all of the same steps as the samples (i.e. receives all the reagents the samples do). A reference sample (check soil) and a duplicate of one of the samples should also be produced.
 - (a) Do not crush or grind samples used in extraction
- 4. Add 40 mL of the extracting solution to each centrifuge tube and cap tightly. Each tube should be wrapped in aluminum foil, so that only the cap is visible and the sample inside is not exposed to light.
- 5. Place samples on a shaker table and shake at low speed for 2 h. Cover the shaker with a large cardboard box to ensure the reaction occurs in the absence of light.
- 6. Centrifuge at 2000 rpm for 15 min.
- 7. Filter through Whatman #42 filter paper into glass vials.
- 8. Analyze the samples on ICP-AES using ammonium oxalate standards which include Fe, Al, Mg, and P in the matrix solution. The Fe and Al values, after converted to units of mg kg⁻¹ PSM, are inputs into the Phrog model.
- 9. References: Iyengar et al. (1981), McKeague and Day (1966)

5.2.2.4 Measurement of pH Buffer Index

As discussed in detail in Chap. 4, the ability of a Ca-based PSM to maintain a solution pH above 6 is critical to precipitation of Ca phosphate. The pH buffer index method was developed in order to serve this purpose in the context of PSMs and P removal structures.

This method is ideally conducted with an automatic and programmable pH titrator. However, traditional hand titration with a burette is also possible. After extracting the PSM, the resulting solution is titrated with a solution of HCl to an endpoint of pH 6. It is important that the pH of 6 be met for 5 s in order for the endpoint to be truly reached. The titrant (HCl) concentration used will vary depending on the buffering capacity of the sample. For poorly buffered samples, a lower HCl concentration must be used, and vice versa. To ensure that a final titration curve is adequate, one may need to test several titrant concentrations. A rule of thumb is addition of 5 or more mL of titrant to achieve the endpoint will ensure a quality curve, although occasionally this is not possible for some extremely poorly buffered samples.

- 1. Materials: automatic pH titrator, (or alternatively a pH meter with a 50 mL burette, stir plate, stir bar, and stop watch), 250 mL centrifuge bottle, sample shaker, centrifuge, 40-mL pipette, beaker, and concentrated HCl.
- 2. From concentrated acid, make a solution of 0.5 N HCl. Dilute this solution to achieve desired titrant concentration. For most samples, a titrant concentration of 0.001 or 0.005 is sufficient for achieving the endpoint with a total volume of 5 mL or more.
- 3. Sample Preparation:
 - (a) Add 2 g of PSM and 200 mL of DI water into centrifuge bottle. Repeat for all samples, keeping in mind that PSM samples should not be allowed to sit in water for any longer than necessary.
 - Do not crush or grind samples used in extraction.
 - (b) Place bottle on shaker and shake on "Low" for 5 min.
 - (c) Immediately place bottles into centrifuge.
 - (d) Spin the samples at 5000 RPM for 10 min.
 - (e) Remove samples from centrifuge and immediately remove a 40 mL subsample of solution from the top of the centrifuge bottle and place into >75 mL volume container.
 - (f) This is the sample that will be titrated.
- 4. Complete electrode calibration and then place stir bar and electrode in sample.
- 5. Begin the titration. If conducting the titration by hand, record the volume added and pH after each addition of titrant.
- 6. When the solution pH decreases below the endpoint of pH 6 for at least 5 s, the titration endpoint is completed.

- 7. The total volume of titrant required to reach the endpoint should not be less than 5 mL or greater than 25 mL. If it is less than 5 mL, decrease titrant strength. If greater than 25 mL, increase titrant strength. However, for some PSMs that are extremely poorly buffered, it will be impossible to achieve the endpoint with more than 5 mL.
- 8. Calculate the buffer index using the total volume of titrant added, concentration of acid used, and mass of PSM:

$$Buffer index = \frac{titrant \ concentration \times titrant \ volume \times 5}{PSM \ mass}$$
(5.7)

9. Where buffer index is in units of eq kg⁻¹ PSM, titrant concentration is the strength of the acid in eq L⁻¹, and PSM mass is 2 g. The multiplier value of 5 is due to the fact that only 40 mL of the 200 mL extracted was titrated. This value of buffer index is input into Phrog.

5.2.2.5 Measurement of Mean Particle Size

While mean particle size is obviously a physical parameter, it also has major implications to the chemical behavior of PSMs and other solid materials. Particle size is inversely related to surface area, and surface area provides the reaction sites where P sorption-related reactions occur. For Ca-based PSMs, smaller particle sizes translate to higher solubility of Ca into the solution for precipitating Ca phosphate, as well as provide a surface for the precipitation reaction to occur on. For Al and Fe-based PSMs, a smaller particle size results in a greater density of terminal hydroxide sites in which ligand exchange of P onto the mineral can occur.

This method is based on ASTM D422 which is used to determine the particle distribution curve for soils. If the material being measured is relatively coarse, a sieved slag for example, then the hydrometer portion can be omitted. The particle distribution curve is constructed by plotting the particle size (diameter in mm) versus the percent finer (the percent of the sample by mass that is finer than that diameter particle). After the curve is plotted, perform a polynomial regression on the data points that will be used to calculate any relevant D_X values where D is the diameter in mm and X is the percent finer than that diameter in mm. For the Phrog software, the mean particle size (D_{50}) is required, but other D_X values can be used to estimate the saturated hydraulic conductivity of the material in cases where saturated hydraulic conductivity is not directly measured.

 Materials: Sieves #4, 10, 20, 30, 40, 50, 60, 70, 100, 120, 140, 200, collection pan, sieve shaker, 250 mL container, sodium hexa-meta-phosphate (SHMP), 1-L graduated cylinder, hydrometer used for soil particle size analysis (ASTM 152H), thermometer, scale, metal or plastic plunger for mixing slurry in the graduated cylinder, and drying oven.

- 2. Weigh out initial sample mass. Sieve sample through a #10 sieve and record the mass retained and the mass passing. Choose a mass so that approximately 115 g for sandy samples and 65 g for finer textured samples, will pass through the #10 sieve.
- 3. Carefully collect the sample retained on the #10 sieve, as it will be sieved using a set of coarser sieves (i.e. #4 through #8). If there is no material retained on the #10 sieve (i.e. material is very fine textured), then step 3 can be skipped.
 - (a) The size and number of sieves required for this will vary with material. Choose the largest sieve size such that all of the material will pass through it. The sieve with the smallest openings to be used should be #4.
 - (b) Stack the sieves on top of each other, place PSM on the top sieve, and place them on a sieve shaker for 10 min.
 - (c) Record the mass retained on each sieve.
- 4. Weigh out approximately 15 g of the portion that passed #10 sieve, place in the oven at 110 °C for 24 h, and then weigh again in order to determine moisture content. The moisture content calculated from this sample is used to correct for hygroscopic moisture in the sample mass used in the hydrometer method.
- 5. From the portion that passed through the #10 sieve, weigh out a sample for hydrometer analysis (~100 g for sandy samples or ~50 g for finer ones).
- 6. Make sufficient SHMP solution for all samples and blank: 125 mL per sample. Make SHMP solution by dissolving 50 g of SHMP per L of DI water.
- 7. Place the hydrometer PSM sample in a 250 mL container, pour in 125 mL of the SHMP solution, and place on the shaker table overnight. A blank, one container with just 125 mL of SHMP, should be placed on the shaker with the samples. There can be temperature differences between the samples and blank if the blank is not shaken overnight.
- 8. Transfer the sample-water slurry from the container into a 1 L graduated cylinder. Ensure the container is empty using deionized water (DI). Bring the cylinder to 1 L volume using DI water. Note: this same process should be completed for all samples, including the blank (and check if used).
- 9. Stir the first cylinder using the plunger for 1 min. After stirring, remove the plunger and take hydrometer readings at the necessary intervals.
 - (a) Readings should be taken 2, 5, 15, 30, 60, 250, and 1140 min after mixing.
 - (b) When taking a hydrometer reading, insert the hydrometer about 20–25 s before the reading. After taking the reading, remove the hydrometer and place it with a spinning motion into a graduate cylinder filled with DI water to clean it.
 - (c) After each reading, take the temperature of the suspension.
 - (d) Important: Prior to starting the experiment, the spacing between readings has to be calculated (sample 1 reading at 2, 5 min, etc., sample 2 reading at 3, 6 min, etc., sample 3 reading at 4, 7 min, etc.). There cannot be overlap,

i.e. readings for two samples at the same time. There has to be at least 1 min between initial readings to account for stirring, but this can be increased to prevent overlapping.

- 10. After the final hydrometer reading, place a #200 sieve into a sink and pour the graduated cylinder into it. Wash the cylinder out onto the sieve using tap water. Wash the material retained on the sieve using tap water until the water is clear.
- 11. Transfer the sample retained on the #200 sieve into a 250 mL beaker and place into a 110 °C oven until dry. Tap water can be used to rinse the sample into the beaker.
 - (a) Note: In order to speed the drying process, some of the water can be removed prior to placing the beaker in the oven. Let the particles settle to the bottom and then carefully pipette clear water from the top of the container. Take care not to disturb or remove any of the particles.
- 12. After the sample is dry (usually 24 h at 110 °C), transfer the sample to a weigh boat, weigh, and record this mass. Sieve the samples for 10 min using a stack of sieves: #10, #20, #30, #40, #50, #60, #70, #100, #120, #140, and #200. Record the mass retained on each sieve.
- 13. Record and make the appropriate calculations for estimating the mean particle size (D50). All calculations below assume use of hydrometer ASTM 152H. The first set of calculations are for the hydrometer data:

$$D = K \times \sqrt{L/T} \tag{5.8}$$

Where D is the particle diameter in mm, K is a constant determined from Table 5.1 based on the measured temperature, T is the elapsed time in which the hydrometer reading was taken, and L is the effective depth (cm) calculated by the following equation:

$$L = 16.3 - 0.164 \times R \tag{5.9}$$

Where R is the reading that was recorded on the hydrometer at time T. The corrected hydrometer reading (R_c) that considers the blank SHMP solution with no sample and the impact of temperature is calculated as:

$$R_c = R - R_o + C_T \tag{5.10}$$

Where R_0 is the hydrometer reading taken from the blank SHMP solution with no sample in it, and C_T is the temperature correction for the hydrometer reading, obtained from Table 5.1.

The equation for calculation of percent finer ($\%_F$), which is conducted for every hydrometer reading and therefore every particle size diameter (D) associated with that reading, is as follows:

-	1	-	-	,	2			-		
	Specific grav	ity of soil parti	cles							
Temperature (°C)	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85	C_{T}
16	0.01530	0.01506	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356	-0.9
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338	-0.7
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321	-0.5
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.01323	0.01305	-0.3
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289	0
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273	0.2
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258	0.4
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243	0.7
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229	
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215	1.3
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201	1.65
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188	2
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175	2.5
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162	3.05
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149	3.8

Table 5.1 Values of K and temperature correction (C_T) for use in computing particle size diameter from hydrometer analysis. K is determined as a function of both temperature and soil particle specific gravity (i.e. particle size density in units of g cm⁻³) and C₋ is a function of temperature only

5.2 The P Removal Design Curve

$$\mathscr{W}_F = \frac{R_C \times a}{M_S} \times 100 \tag{5.11}$$

 M_s is the oven dry mass of soil placed in the 1-L graduated cylinder for the hydrometer test. The correction factor, a, is required when the particle size density (P_s) is not equal to 2.65 g cm⁻³, and is determined by the following equation:

$$a = \frac{1.65 \times P_s}{2.65 \times (P_s - 1)} \tag{5.12}$$

If the particle size density is 2.65, then the value for a in equation 5.11 is equal to 1. After the percent finer ($\%_F$) value is calculated for each hydrometer reading, the $\%_F$ value is then adjusted based on the amount of sample that was retained on the #200 sieve after pouring the contents of the 1-L graduated cylinder into it:

$$\mathscr{H}_{FA} = \mathscr{H}_{F} \times \left(\frac{dry\,mass\,retained\,on\,\#\,200\,sieve}{dry\,mass\,of\,sample\,used\,in\,hydrometer\,test}\right)$$
(5.13)

As a result of the hydrometer calculations, you should have a particle size diameter (D) and an adjusted percent finer ($\%_{FA}$) for every hydrometer reading that was taken.

14. Next, for the portion of the sample that was sieved in steps 3 and 10–12, the $%_{\rm F}$ values for the coarse particles in the sample are determined. The first step is to calculate the percent retained on each sieve ($%_{\rm R}$):

$$\mathscr{H}_{R} = \left(\frac{\text{mass retained on sieve}}{\text{mass of sample placed on the first sieve in stack}}\right) \times 100$$
(5.14)

Keep in mind that if the sample was very course, then sieves were used in two different stages: during step 3 for sieving the coarse materials that were initially retained on the #10 sieve, and also during steps 10–12 for the finer portion where the material in the graduated cylinder was poured onto a #200 sieve. The $%_R$ and $%_F$ values need to be calculated separately for the materials sieved in step 3 and 10–12 because the denominator of equation 5.14 might be different.

After the value of \mathscr{H}_R is obtained for each sieve (i.e. for each corresponding particle size diameter) using equation 5.14, the \mathscr{H}_F is calculated first for the largest sieve diameter (i.e. the smallest sieve #) that was used in a stack of sieves. This specific \mathscr{H}_F value will be referred to as the \mathscr{H}_1 value, with the "1" indicating use of the largest sieve opening used in that stack:

$$\mathscr{W}_{F1} = 100 - \mathscr{W}_{R1} \tag{5.15}$$



Fig. 5.5 A sample particle size distribution curve for a PSM. The best fit polynomial curve equation can be used to find D_x values (i.e. y-axis variable) that represent the particle size in mm where X% of all particles are finer (i.e. x-axis variable, $\%_F$). The D_{50} value which represents the particle size in which 50% of all the particles are smaller than (i.e. D value corresponding to a $\%_F$ value of 50), is used as an input into Phrog. Also, in the absence of a saturated hydraulic conductivity test, values determined from the particle sized distribution curve can be used to estimate saturated hydraulic conductivity

For particle diameters for all remaining sieves in a stack, the \mathscr{W}_F calculation utilizes the \mathscr{W}_F value determined from the previous larger sieve size utilized. This specific \mathscr{W}_F value will be referred to as the \mathscr{W}_{FX} value, with x referring to the next largest sieve size opening. For example, \mathscr{W}_{F2} is the second largest sieve opening used, \mathscr{W}_{F3} is the third largest, etc.

$$\mathscr{W}_{F_{X}} = \mathscr{W}_{F_{X-1}} - \mathscr{W}_{R_{X}} \tag{5.16}$$

15. Tabulate $%F_A$ (x-axis) and corresponding D values (y-axis) determined from the hydrometer method (equation 5.13) into separate columns. Then include the particle size diameter of the sieves in the D column, and list the corresponding $%_{FX}$ values determined in step 14 (from equations 5.15 and 5.16). Plot the two variables in a single figure with D values on the y-axis, and perform a polynomial regression to obtain a well-fit regression line that adequately fits the data. Using the equation for this line, insert a value of 50 for the x-variable (i.e. percent finer), and solve for the y-variable (i.e. particle size diameter, D). This value is input into Phrog when estimating the design curve based on PSM properties. An example of a particle size distribution curve and its respective equation is shown in Fig. 5.5.

5.3 Methods of Physical Characterization of PSMs Necessary for Designing a P Removal Structure

While the P removal design curve for the PSM will ultimately determine the mass of the PSM required for the site characteristics and P removal goals, the physical properties of the PSM will partly dictate the footprint, retention time, and overall layout of the PSMs in the P removal structure. These physical properties include bulk density, porosity, particle size density, and saturated hydraulic conductivity. These values are required inputs for the Phrog software.

5.3.1 Measurement of Bulk Density

Bulk density is the mass of PSM per unit volume of solids plus pore space. For input into Phrog, it is reported on a dry-weight basis:

$$BD = \frac{Mass \, of \, dry \, PSM}{Volume \, of \, solids \, and \, pore \, spaces} \tag{5.17}$$

Where the mass of dry PSM is in units of g, and volume is in units of cm³. Unlike particle size density, the bulk density takes into account the pore space in the PSM.

- 1. Materials: scale, container of known volume, and glass stir rod.
 - (a) If the volume of a container is unknown, weigh it before and after filling it up to the top with water. The mass of the water is equal to the container volume in units of cm³.
- 2. Determine the weight of the dry container
- 3. Using the dry container, pour the PSM into it to completely fill the container. Allow the container to be "heaping" with the PSM.
- 4. Tap on the container five times with a glass stir rod. Repeat on the opposite side of the container. This helps to allow the particles to settle.
- 5. Scrape off the heaping soil with the stir rod.
- 6. Weight container with PSM in it. Subtract mass of empty container to determine the mass of PSM alone.
- 7. Insert container volume into the denominator of equation 5.17 and the PSM mass into the numerator to calculate bulk density.

5.3.2 Measurement of Porosity and Particle Density

Porosity is the ratio of the volume of PSM pores to the total PSM volume. In general, finer textured PSMs tend to have greater porosity than PSMs with larger particle size. Particle density (P_s) is the mass of solid particles per unit volume of solid particles (i.e. excluding pore volume):

$$P_{s} = \frac{mass \, of \, dry \, PSM}{volume \, of \, solids \, only} \tag{5.18}$$

The units for mass and volume for equation 5.18 are g and cm³, respectively. The average particle density of soil is 2.65 g cm⁻³, but this value may not be appropriate for PSMs since many of them are different from soils. Particle density is used to relate bulk density to porosity.

- 1. Materials: 50 mL graduated cylinder and funnel.
- 2. Add exactly 25 mL of DI water to graduated cylinder.
- 3. Gently pour in 20 g of PSM. Use a funnel if necessary.
- 4. After all settling has occurred and air bubbles have been removed, record the new volume, X2.
- 5. Particle density is calculated as:

$$P_s = \frac{20}{X2 - 25} \tag{5.19}$$

Where the final units will be in g cm⁻³. Using both particle density and bulk density, porosity can then be calculated by:

$$Porosity = 1 - \frac{BD}{P_s}$$
(5.20)

5.3.3 Measurement of Saturated Hydraulic Conductivity

Unfortunately, the hydraulic conductivity of a material is more difficult to measure directly unless one can gain access to a permeameter. For this purpose, ASTM method D2434-68 (Standard test method for permeability of granular soils) is utilized. Many private civil engineering testing laboratories offer testing for hydraulic conductivity. However, if the user has the particle size distribution curve for the PSM as described in Sect. 5.2.2.5, then the hydraulic conductivity can be estimated using one of two models depending on whether it is predominated by smaller particle sizes like a soil or larger sizes like a gravel (Canga et al. 2013; Salarashayeri and Siosemarde 2012). Incidentally, private civil engineering testing laboratories

also provide analysis for particle size distribution curves. The curve equation (e.g. Fig. 5.5) can be used to find d_x values that represent the particle size in mm in which X% of all particles are smaller than; these values can be used to estimate hydraulic conductivity. Using the polynomial regression for that particle size distribution, the user can input any given X value (%) to calculate d_x . For example 10% can be input into X for the given regression equation in order to find d_{10} , which is the particle size diameter in which 10% of all particles are smaller than. The values for d_{10} , d_{50} , and d_{60} can then be inserted into equation 5.21 to estimate saturated hydraulic conductivity:

Saturated Hydraulic Conductivity
$$\left(\frac{m}{day}\right) = 10.06 + 118.54(d_{10})$$

-12.50 $(d_{50}) - 7.32(d_{60})$ (5.21)

Equation 5.21 was developed on soils, so it is better used for materials that contain smaller particles, such as acid mine drainage residuals and other soil-like materials (Salarashayeri and Siosemarde 2012). For input into Phrog, saturated hydraulic conductivity must be in units of cm s⁻¹, thus the result from equation 5.21 must be divided by 864 to convert units.

Equation 5.22 below was developed using larger sized porous materials that may be found in a variety of P removal structures, and therefore is better suited for coarser materials, such as sieved steel slag (Canga et al. 2013). For this estimate, the user must determine d_{20} and d_{50} from the particle size distribution curve.

$$\log\left(Saturated Hydraulic Conductivity\left(\frac{cm}{day}\right)\right)$$

= 4.66 + 0.63 × log(d₂₀) + 0.94 × log(d₅₀) (5.22)

An inverse log function must first be applied to the resulting value from equation 5.22, and then divided by 86,400 to convert into units of cm s⁻¹ for Phrog input. If direct measurement of the hydraulic conductivity or estimation using the two previous equations is not possible, then average values for a material can be used (Table 4.5), but it is not advisable.

References: Canga et al. (2013), Salarashayeri and Siosemarde (2012)

5.4 Methods of Safety Characterization of PSMs

As discussed in Chap. 4, there is a need to verify the safety of PSMs before placing them into a P removal structure. For the most part, if there is a risk from a PSM, the most probable potential risk will be heavy metals. Regarding metals, both the total

amount and the solubility of the metals needs to be considered, with greater emphasis on solubility. The most difficult aspect is interpretation of the results. To aid in this effort, review Sect. 4.2.3.1 and use Table 4.6 as a guide.

5.4.1 Total Metal Concentration by Digestion

The method for determining total metal concentrations in PSM is the same total digestion method described for Ca, Fe, and Al, in Sect. 5.2.2.2. The only difference is that the final extracted solution must be additionally tested for As, Ba, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, and Zn using ICP-AES or AA instruments. The results can be examined in light of Table 4.6, particularly the typical concentrations in soils and also the threshold concentrations for exceptional quality biosolids.

5.4.2 Method for Water Soluble Metals

Regarding solubility of metals, the most basic test is a simple water extraction. While the results are not perfectly transferable to the context of concentrations in a water body, they do provide a worst case scenario for resulting metals concentrations if every drop of water entering a surface water body was filtered through the PSM. Thus, application of the results of the water soluble concentrations (per volume of water) to Table 4.6 (thresholds for drinking water and aquatic life) is extremely cautious.

- 1. Materials: 50 mL centrifuge tubes, shaker, vacuum filter apparatus and 0.45 μ m filter, and glass vials or tubes to store extract prior to analysis.
- 2. Weigh 2 g of the PSM into a centrifuge tube and then add 20 mL of DI water. The mass can be adjusted as long as the 1:10 solid to DI ratio is maintained.
 - (a) Note: A check soil sample should be included in each set of samples, as well as a duplicate.
- 3. Place the samples on the shaker and shake on low speed for 1 h.
- 4. Remove the samples from the shaker and place in a centrifuge. Spin the centrifuge at 5000 RPM for 10 min.
- 5. Vacuum filter the samples through a $0.45 \mu m$ filter into glass tubes or vials.
 - (a) Note: Take care when decanting the samples since it is easy to clog the filter if excess amounts of solids are poured in the filter.
- 6. Analyze the extracts using ICP-AES or AA with salinity and trace metal standards.

Additional/Alternative sequential extraction method: after the extraction process has been completed, one can choose to do a sequential extraction on the same PSM. Typically, this is done up to five times, but there is no limit. To do this, simply take extra care to not lose any of the solid PSM when pouring off the supernatant, and then refill the centrifuge tube with 20 mL of water and repeat steps 3 to 6. Again, this can be performed any number of times. The advantage is that it somewhat simulates the long term release of metals to solution.

5.4.3 Synthetic Precipitation Leaching Procedure (SPLP)

The purpose of this method, which is discussed in detail in Chap. 4, is to estimate the concentration of metals that would leach out of the PSM in an acidic environment, specifically with acid rain falling upon the PSM. Because it is unlikely that PSMs will be exposed to an acidic environment in a P removal structure, the SPLP test represents a worst-case scenario. The results of this test should be examined in the same way as the water soluble metals.

- 1. Materials: concentrated nitric (HNO₃)and sulfuric acid (H_2SO_4), 50 mL centrifuge tubes, centrifuge, vacuum filtration system, 0.45 µm filter, and glass tubes or vials to collect filtered extract.
 - (a) Stock Solution: A 60:40 H_2SO_4 to HNO_3 solution is diluted and used to lower pH of deionized water to 4.2 (±) 0.05.
 - Mix 6 g of standard stock H_2SO_4 and 4 g of standard stock HNO_3 in a small beaker. Then add 1 mL of this 60:40 mixture to 500 mL deionized water to create the solution to be used in the extraction.
- Using a pH meter, bring 1000 mL of DI water to a pH of 4.2 (±) 0.05 by adding one drop of the stock solution at a time. This will be called the extraction solution. (For most DI water with an initial pH of 5.65, approximately 20–30 drops are used to lower pH to 4.2)
- 3. Weigh out 1 g of PSM and place in a 50 mL centrifuge tube.
- 4. Add 20 mL of the extraction solution (20:1).
- 5. Shake for 18 h.
- 6. Centrifuge at 5,000 RPMs for 10 min.
- Filter using a vacuum filtration system and 0.45 μm glass fiber filters, and collect extract in glass tubes or vials prior to analysis.
- 8. Analyze the extracts for trace metals by ICP-AES or AA.
- 9. Similar to the water soluble extraction described in Sect. 5.3.2, this method can also be conducted sequentially.

Reference: Hageman et al. (2000)

References

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Chapter 6 Designing a Phosphorus Removal Structure

6.1 Designing Structures to Achieve Target P Load Removal and Lifetime

At the most basic level, designing a P removal structure to achieve a target P removal over a target lifetime is a function of estimating the necessary mass of PSM needed. The P removal design curve, discussed in Chap. 5, is a critical tool in the design process.

6.1.1 Use of the Design Curve and Governing Equations for Designing Structures

The design curve, i.e. mathematical relationship between percent P removed (discrete) and cumulative P added to the PSM, for a given retention time (RT) and inflow P concentration (Fig. 5.3 and Eq. 5.4) is integrated to estimate cumulative P removal for a given P load to the PSM:

$$CP_{rem}\left(\%\right) = \frac{\int_{0}^{CP_{add}} \left(be^{m \times CP_{add}}\right) dCP_{add}}{CP_{add}}$$
(6.1)

Where CP_{rem} is cumulative P removed, CP_{add} is the cumulative P added per mass of PSM (mg kg⁻¹), and *m* and *b* are the coefficients from the exponential equation that describes discrete P removal (i.e. design curve). An example of a P removal design curve and subsequent cumulative P removal curve resulting from integration is illustrated in Fig. 6.1. Essentially, this equation allows you to calculate how much P will be removed, or retained by the PSM, after a given amount of dissolved P has



Fig. 6.1 *Top*: Example of a P design curve (i.e. discrete P removal) with the associated equation that describes discrete P removal as a function of cumulative P added to the PSM (CP_{add}). *Bottom*: Example integration of the design curve, which produces the cumulative P removal (CP_{rem}) curve. For this example, the PSM was a treated and sieved steel slag sample from Tube City IMS, tested under the conditions of a 30 s RT and 1 ppm inflow P concentration

flowed into the structure. Dividing the integrated design curve by 100 instead of CP_{add} results in CP_{rem} in units of mg P kg⁻¹ PSM:

$$CP_{rem}\left(mg\,kg^{-1}\right) = \frac{\int_{0}^{CP_{add}}\left(be^{m\times CP_{add}}\right)dCP_{add}}{100}$$
(6.2)

The final loading point at which the PSM's discrete P removal (%) is approximately zero, i.e. when the PSM is spent and inflow P equals outflow P concentration, can be determined by using the coefficients from the design curve:

$$CP_{add} \max\left(mg \, kg^{-1}\right) = \frac{\ln\left(b\right)}{-m} \tag{6.3}$$

This value of maximum P added represents the P loading to the PSM in which it is no longer effective at removing any additional P. Input of $CP_{add}Max$ into either Eq. 6.1 or 6.2 for CP_{add} will result in the maximum CP_{rem} in percent or mg kg⁻¹, respectively. This allows one to estimate what the total P removal will be over the lifetime of a given PSM, under the RT and inflow P conditions of the design curve.

As an example, consider the design curve shown in Fig. 6.1. By inserting values of 83.8 and -0.004 from Fig. 6.1 into coefficients *b* and *m* of Eq. 6.3, it is found that the CP_{add}Max that can be added to this particular PSM under the conditions of the design curve is about 1100 mg P kg⁻¹. Any additional P added to the PSM beyond that point will result in zero P removal. Essentially, this is the point where the discrete P removal line in Fig. 6.1 intersects with the x-axis. Further, if that value of CP_{add}Max is inserted into Eqs. 6.1 and 6.2 for CP_{add} along with values for *b* and *m*, then it is determined that the maximum cumulative P removal for this PSM under the given conditions is 207 mg P kg⁻¹, or 18.7% of the cumulative P that was added to the PSM.

6.1.2 Determining the Required Mass of PSM for a P Removal Structure

It is through the use of the equations for the design curve, whether directly measured or estimated based on PSM characterization (see Chap. 5), combined with Eqs. 6.1–6.5, that are used to determine the required mass of PSM to achieve the target P removal for a specific site. Along with P removal goals, site-specific inputs must also be known. Specifically, in order to determine the required mass of a specific PSM for a P removal structure, the user must either determine or assume values for:

- Annual dissolved P load at the site (PL_{annual})
- Target cumulative P removal goal (goal; %)
- Target design lifetime for the P removal goal (DL; years)
- Typical dissolved P concentrations in flow (DP_{avg}; in mg L⁻¹ or ppm)

Methods for estimating the annual P loads for a site will be discussed in detail later in this chapter. In order to provide an example of determining PSM mass in a hypothetical situation, we will assume an annual P load of 30 lbs (13.6 kg). The target cumulative P removal goal and DL is the choice of the designer. For this example we will design a structure to remove 40% of the cumulative P load that occurs over 3 years, using the PSM shown in Fig. 6.1. Using the same *m* and *b* values from the design curve shown in Fig. 6.1, we first need to determine the CP_{add} value that corresponds to the target P removal goal of 40%. In other words, insert the goal value (40%) into Eq. 6.1 for CP_{rem} and solve for the corresponding
CP_{add} value. This particular CP_{add} value is known as the $CP_{add}RG$, and is calculated with Eq. 6.4:

$$CP_{add}RG = \frac{-b - goal \times ProductLog\left(-\frac{b}{e^{(b/goal)} \times goal}\right)}{m \times goal}$$
(6.4)

Where $CP_{add}RG$ is in units of mg P kg⁻¹ PSM, and "goal" is the target cumulative P removal goal in %. Input of these values into Eq. 6.4 produces a $CP_{add}RG$ value of 430 mg kg⁻¹. This means that the PSM in Fig. 6.1 will receive a cumulative P loading of 430 mg P kg⁻¹ at the point where the cumulative P removal goal of 40% is met. Note that this calculation rests on the assumptions in the design curve from Fig. 6.1: specifically that the typical dissolved P concentration at the hypothetical site is 1 ppm and the structure to be constructed will be designed for a 30 s retention time. The 40% removal from a cumulative P input load to the PSMs of 430 mg kg⁻¹ PSM translates to a cumulative P removal of 172 mg kg⁻¹ PSM.

Next, knowing the CP_{add} RG value for the site in question for a specific PSM to be employed, the required PSM mass (in metric tons) to meet the P removal goal and design lifetime (DL; years) for that P removal goal can be determined. This calculation also requires an estimate of the annual P loading at the site (PL_{annual}, in grams):

$$PSM mass = \frac{PL_{annual} \times DL}{CP_{add} RG}$$
(6.5)

Continuing with the same example, insertion of 430 mg kg⁻¹ for CP_{add} RG, a 3 year DL value, and 13,600 g (30 lbs) for PL_{annual}, results in a required mass of 95 metric tons. With 95 metric tons of PSM achieving 40% CP_{rem} after 3 years, through input of 430 mg P kg⁻¹ PSM (CP_{add}), the total mass of P removed is 37 lbs (16.8 kg). Note that the structure will continue to remove P beyond 3 years with 95 metric tons of PSM, but CP_{rem} will decrease below 40% after that time. However, the ultimate lifetime (UL) in which the P removal structure will no longer be effective at removing dissolved P (i.e. when discrete P removal =0%) can be calculated as:

$$UL = \frac{CP_{add} \max \times PSM \max}{PL_{annual}}$$
(6.6)

Recall that $CP_{add}Max$ previously calculated for this hypothetical scenario was 1100 mg kg⁻¹ (Eq. 6.3). Input of all the variables into Eq. 6.6 results in an UL of about 8 years. Also recall that the CP_{rem} at the point of $CP_{add}Max$ was 206 mg kg⁻¹. Thus, after about 8 years, this P removal structure containing 95 metric tons of the PSM from Fig. 6.1 will no longer be effective after removal of about 45 lbs. of dissolved P (20 kg). Notice that this is only an increase in cumulative P removal of about 8 lbs., or 17% after the additional 5 years. The decrease in P removal efficiency

with further P loading is evident in Fig. 6.1; P removal efficiency decreases rapidly with initial CP_{add} , until reaching a certain point. Thus, it is important to choose a PSM-replacement schedule that is efficient and economical for the designed structure. Using the present hypothetical scenario, perhaps rather than waiting 8 years until the PSMs are spent, it might be justifiable to replace the PSMs at 3–4 years, which is before the P removal efficiency drastically decreases.

Again, consider that these calculations are partly a function of the coefficients from the design curve. Thus, if we changed the inflow P concentration to something other than 1 ppm, or if the PSM was sensitive to retention time and the retention time was changed, then the results would also change as the design curve itself would then be different. Clearly, the design curve would change if a different PSM was utilized. Chapters 4 and 5 discuss how PSM design curve coefficients (b and m) vary as a function of inflow P concentration and retention time.

While making the calculations for determining the required mass for a desired P removal structure (with specified goals) is simple once the equation for the appropriate design curve is obtained, it is important to keep in mind that PSM mass is only one design aspect of a P removal structure. One must also consider the necessity of meeting minimum desired flow rates, achieving the desired retention time (if applicable), not exceeding area constraints, and not excessively inhibiting flow rate in a drainage ditch. Thus, the greatest challenge of designing a P removal structure is balancing and meeting each of the criteria/constraints.

6.2 Site Characterization Inputs Required for Conducting a Design

From the previous example, several assumptions were made with regard to site characteristics and inputs, for example, annual P loads and the feasibility to construct a structure possessing nearly 100 tons of a PSM. Much of this chapter is dedicated to providing guidance in determining the values for the required inputs. For point sources such as a waste water treatment plant, obtaining the necessary inputs for conducting a design is relatively easy, as all such facilities have detailed records with regard to flow rates, flow volumes, and dissolved P concentrations. However, for non-point flow sources, these inputs are more difficult to obtain, as described in the following sections.

6.2.1 Average Annual Dissolved P Load

The average annual P load (PL_{annual} ; in grams) is critical to conducting a design, as this value will directly affect the mass of required PSMs, which will then have an effect on the size of the P removal structure. Average annual P load is calculated by

multiplying the average dissolved P concentration (DP_{avg} ; in mg L⁻¹ or ppm) by the average annual flow volume (FV_{annual}; in L) produced at the site:

$$PL_{annual} = \left(FV_{annual} \times DP_{avg}\right) / 1000 \tag{6.7}$$

Occasionally there are estimates available for annual P loading in local areas, expressed as a function of area (PL_{area}). For example, a common value assigned to PL_{area} for subsurface drains in the Western Basin of the Lake Erie Watershed is 0.2 to 0.5 lbs acre⁻¹ year⁻¹ (0.1 to 0.23 kg ha⁻¹ year⁻¹). If PL_{area} is known, then PL_{annual} can be calculated if the contributing area (CA) for the site is also known:

$$PL_{annual} = PL_{area} \times CA \times 1000 \tag{6.8}$$

where PL_{annual} , PL_{area} , and CA are in units of grams, kg ha⁻¹ year⁻¹, and ha, respectively.

6.2.1.1 Average Annual Flow Volume

When PL_{annual} or PL_{area} are not available, accurate estimation of FV_{annual} and DP_{avg} is critical since these will dictate the load of P that enters that structure. Similar to estimating peak runoff flow rates, FV_{annual} can be obtained for surface runoff by techniques such as the Rational Runoff Coefficient method, which is simply based on cover, soil drainage, contributing area (CA), and average annual rainfall depth. Some common values for the runoff coefficient (RC) used in Eq. 6.9 are shown in Tables 6.1 and 6.2 for various soil, vegetation, and topography, but values for other

Table	6.1	Runof	f coeffi	cients	(RC)	for a	variety	of so	oil types,	vegetation	, and	topogr	aphies
(Jarret	t 199	7), for	use in	estima	ating a	averag	ge annua	l flow	volumes	and peak	runof	f rates	by the
rationa	ıl me	thod (E	Eqs. <mark>6.9</mark>	and <mark>6</mark> .	11)								

Vegetation	Topography	Open sandy loam ^a	Clay and silt loam ^b	Tight clay ^c
Woodland	Flat	0.1	0.30	0.40
	Rolling	0.25	0.35	0.50
	Hilly	0.30	0.50	0.60
Pasture	Flat	0.10	0.30	0.4
	Rolling	0.16	0.36	0.55
	Hilly	0.22	0.42	0.6
Cultivated	Flat	0.30	0.50	0.6
	Rolling	0.40	0.60	0.7
	Hilly	0.52	0.72	0.8

^aSoil types assumed to be equivalent to Hydrologic Group A

^bSoil types assumed to be equivalent to Hydrologic Group B and C

°Soil types assumed to be equivalent to Hydrologic Group D

Table 6.2 Runoff	Type of drainage area
Coefficients (RC) for urban	Lawns
average annual flow volumes	Sandy soil, flat, 2%
and peak runoff rates by the	Sandy soil, average, 2–7%
rational method (Eqs. 6.9 and	Sandy soil, steep, 7%
6.11). Values from Jarrett	Heavy soil, flat, 2%
997).	Heavy soil, average, 2-7%
	Heavy soil, steep, 7%
	Commercial
	Downtown areas
	Neighborhood areas
	Residential
	Single-family areas
	Multi units
	Detached Multi units
	Attached Suburban
	Apartment dwelling areas
	Industrial
	Light areas
	Heavy areas
	Parks, cemeteries
	Playgrounds
	Railroad yard areas
	Unimproved areas
	Streets
	Asphaltic
	Concrete
	Brick
	Drives and walks
	Roofs

conditions can also be found in other sources. If a site contains several land uses listed in Tables 6.1 and 6.2, then an overall weighted runoff coefficient must be calculated for the site.

$$FV_{annual} = RC \times Average Total Annual Rainfall \times CA \times 100,000$$
(6.9)

Where FV_{annual}, annual rainfall, and CA are in units of L, cm, and ha. Annual rainfall data can be obtained from the Natural Resources Conservation Service (NRCS) National water and climate center, and from the National Oceanic and Atmospheric Administration (NOAA).

0.05-0.10

0.10-0.15

0.15-0.20

0.13-0.17

0.18-0.22 0.25-0.35

0.70-0.95 0.50-0.70

0.30-0.50 0.40 - 0.600.60-0.75 0.25-0.40 0.50 - 0.70

0.50-0.80 0.60-0.90 0.10-0.25 0.20-0.35 0.20-0.40 0.10-0.30

0.70-0.95 0.80-0.95 0.70 - 0.850.75-0.85 0.75-0.95 Phrog software requires input of FV_{annual} and DP_{avg} , and then utilizes Eq. 6.7 to calculate PL_{annual} . However, some users may have knowledge of DP_{avg} and PL_{annual} , but not FV_{annual} . In that case, FV_{annual} can be simply calculated by:

$$FV_{annual} = \frac{PL_{annual}}{DP_{avg}} \times 1000 \tag{6.10}$$

Where Pl_{annual}, DP_{avg}, and FV_{annual} are in units of g, mg L⁻¹, and L, respectively.

Less information is available for estimating FV_{annual} for subsurface drains. However, a general rule of thumb is that subsurface drainage will remove between 20 to 40% of annual rainfall depth. In that case, the runoff coefficient in Eq. 6.9 can be replaced with a value between 0.2 and 0.4, in estimation of FV_{annual} for subsurface drainage systems.

6.2.1.2 Average Dissolved P Concentration

Average dissolved P concentration is critical for not only determining if a site is a suitable candidate for a P removal structure (Chap. 3), but also for proper design of a structure. Obtaining a good estimate for DP_{avg} can be challenging. Broadly speaking, there are two general approaches for estimating DP_{avg} : through direct measurements of dissolved P in runoff and drainage water, or by predicting the value through knowledge of soil test P concentrations.

At the most basic level, one may obtain a crude estimate of dissolved P concentrations in the drainage water by obtaining "grab" samples and having them tested for dissolved P, which involves filtering the sample with a 0.45 μ m filter prior to analysis. However, since grab samples usually consist of one sample collected per flow event, it is extremely important that effort be made to obtain a representative sample, both spatially and temporally. For example, do not take a sample from stagnant water, or only from a single season of the year. In the realm of grab samples, it is best if samples from multiple sized flow events are obtained, not just samples from only the large flow events, or only the small flow events. Although not ideal, the dissolved P concentrations from such samples can at least provide an estimate for what to expect from that particular drainage source. Be careful not to rely only on the dissolved P concentrations from the low flow events, and keep in mind that the majority of dissolved P delivered in runoff and drainage occurs from around 10% of the biggest annual flow events, which are typically the biggest flow events.

Occasionally, if a site was monitored with automated equipment, one may possess both flow rate and P concentration data. Such data sets are usually large since automated sampling regimes are programmed to take multiple samples during a single flow event. In this case, it is important that the "flow-weighted" average P concentration be determined. Doing this will prevent small flow events that deliver a lesser load of P, from biasing the average dissolved P concentration.

For the second general approach, estimation of dissolved P through knowledge of soil test P concentrations is often reasonable because the main non-point source

Table 6.3 Relationships for predicting dissolved P concentrations in runoff, leachate, and subsurface drainage from soil Mehlich-3 P (M3P), water extractable P (WEP), and M3 saturation ratio $(M3_{sR}: P/[Al + Fe])$

Drainage scenario	Equation
Runoff dissolved P	0.002 × M3P or B1P + 0.0435
Runoff dissolved P	0.0112 × WEP + 0.0669
Leachate dissolved P ^a	0.0023 × M3P - 0.062
Leachate dissolved P ^b	0.0147 × M3P – 3.06
Leachate dissolved P ^c	$0.0098 \times M3_{SR} + 0.108$
Leachate dissolved P ^d	$28.44 \times M3_{sr} - 5.71$
Tile drain and runoff dissolved P	$0.0031 \times M3P - 0.0446$

Units for drainage water P concentrations are in mg L⁻¹ and soil P concentrations are in mg kg⁻¹. $M3_{SR}$ is calculated on a molar basis and the resulting value is unitless. Equations are from Vadas et al. (2005); Sims et al. (2002); Duncan et al., (2017)

^aFor soils with M3P values less than 140 mg kg⁻¹

^bFor soils with M3P values greater than 140 mg kg⁻¹

 $^{\circ}$ For soils with M3_{SR} values less than 0.2

^dFor soils with M3_{SR} values greater than 0.2

of dissolved P loads to surface waters is usually from soils that have accumulated "legacy P" (Chap. 2). There are several sources in the literature that describe the relationships between soil test P concentrations and dissolved P concentrations in runoff, but one of the most useful is that of Vadas et al. (2005), where the authors compiled data from several studies, which encompassed different conditions and soil types. From this, the authors provided a relationship for estimating *runoff* dissolved P concentrations from soil Mehlich-3, Bray-1, and water extractable P concentrations (M3P, B1P, and WEP, respectively). Also, Sims et al. (2002) provided several relationships for calculating dissolved P concentrations in leachate from soil M3P and M3 saturation ratio (M3_{SR}). These relationships are summarized in Table 6.3. Again, consider that these relationships are only valid for soils that have not been immediately amended with manure or chemical fertilizer. Much less information is available regarding the prediction of dissolved P concentrations in subsurface drainage, although a relationship between soil M3P and dissolved P in both runoff and tile drainage was provided by Duncan et al. (2017), which is included in Table 6.3.

Although not exactly the same as subsurface drainage, the leachate relationships presented in Table 6.2 could be used to estimate P concentrations in subsurface drainage, but consider that subsurface drainage is likely to have slightly higher P concentrations than those predictions due to greater macropore flow.

Determining appropriate values for DP_{avg} is extremely important for two reasons. First, DP_{avg} must be known in order to estimate or determine (measure) the corresponding design curve, which is function of the PSM, inflow P concentration and retention time. Second, this value is used to directly estimate PL_{annual} for the site. Both will impact the ultimate size of the P removal structure by affecting the mass of the PSM.

6.2.1.3 Example Calculations of Annual P Load

Example 1: Runoff Originating from Around CAFO Units

Assume a 7 acre (2.83 ha) area around a confined animal feeding operation (CAFO), which includes where the animals are housed, animal feed is delivered and stored, and manure is stored before being loaded for eventual land application outside of that 7 acres. Assume that this area drains to a single location through surface runoff, where a P removal structure can potentially be constructed. The farm is located in upstate NY, and receives an average of 45 in. (114 cm) of precipitation/year. Assume that the 7-acre contributing area (CA) consists of the following:

- 20% roof area
- 5% dirt driveway
- 40% light industrial (equipment, movement of feed, animals, manure, etc). Dirt, not paved. Mehlich-3 STP is 2000 mg kg⁻¹.
- 35% pasture (hilly topography, soils with hydrologic group B). Mehlich-3 P is 50 mg kg⁻¹.

Using Tables 6.1 and 6.2, the weighted runoff coefficient is 0.62, calculated by the sum of CA × RC e.g. $(0.2 \times 0.85) + (0.05 \times 0.80) + (0.40 \times 0.65) + (0.35 \times 0.42)$. Plugging this value in along with the average annual rainfall and 7-acre (2.83-ha) contributing area into Eq. 6.9 yields an average annual runoff volume of 19.8 million L (5 million gallons). Next, the average dissolved P concentration can be estimated from the soil Mehlich-3 P values through use of the appropriate equations in Table 6.3. The equation in Table 6.3 estimates that the dissolved P concentration from directly around the barn (light industrial area) and bordering pasture would be 4 and 0.14 mg L^{-1} , respectively. However, consider that the area around the barn contributes only 2.8 acres of runoff with a runoff coefficient of 0.65. Thus, this area would contribute about 8.39 million L (2.18 million gallons) per year (Eq. 6.9). Considering the total annual runoff volume from the site, this volume from the "light industrial area" would constitute about 42% off all the runoff. This illustrates how the contribution of runoff is not necessarily equal to percent contributing area. In this example, 42% of all the runoff is coming from 40% of the total area. Similarly, the fraction of annual flow from the pasture area is about 23% (RC = 0.4), which constitutes 35% of the site area.

These fractions of flow contribution must be considered in estimating the weighted dissolved P concentration for the entire site. For this example, we will assume negligible dissolved P loss from the road and roofs. Weighted P concentration for the site can then be estimated by multiplying the percent runoff contribution by the average dissolved P concentration for each land use, and then summing the values e.g. $(0.52 \times 4 \text{ mg L}^{-1}) + (0.24 \times 0.14 \text{ mg L}^{-1}) + (0.24 \times 0 \text{ mg L}^{-1}) = 2.11 \text{ mg L}^{-1}$. Knowing the annual flow volume and the average weighted dissolved P concentration, Eq. 6.7 is used to estimate the annual P load to be 40,778 g (92 lbs).

Example 2: Runoff Originating from Several Suburban Housing Developments

For this example, assume a 30 acre (12.1 ha) sub-watershed that consists of several housing developments located in central Michigan with annual precipitation of 34 in. (86 cm) per year:

- 15% housing (single family residential)
- 60% lawn (sandy soil with average slope of 5%). Mehlich-3 P is 300 mg kg⁻¹.
- 25% asphalt roads

Similar to the previous example, use Table 6.2 to calculate the weighted runoff coefficient along with Eq. 6.9 for estimation of the average annual flow volume. Runoff coefficient = $(0.15 \times 0.4) + (0.60 \times 0.125) + (0.25 \times 0.875) = 0.3537$. Thus annual runoff flow volume = 36.8 million L (9.59 million gallons). Similar to the last example, only the lawn will be considered a P source, with 7.8 million L of runoff occurring from this area, or 21.2% of the total annual volume from the entire site. Using Table 6.3 and the appropriate equation, the average dissolved P concentration from the lawns is estimated to be 0.64. Thus, after weighing for percent runoff contribution, the overall weighted averaged dissolved P concentration for the site is 0.1356 mg L⁻¹. Using Eq. 6.7 and the total flow volume for the site, the annual P load is 4990 g (11 lbs).

Example 3: Tile Drainage from an Agricultural Field

In this case, we are examining a 60 acre (24.3 ha), tile-drained row crop field in Eastern Iowa with 30 in. (76 cm) of annual rainfall. Through periodic testing of the tile drainage water throughout the year, it was estimated that the average dissolved P concentration is 0.3 mg L^{-1} .

Since this field is tile drained, we can use the estimate for average conversion of precipitation depth to runoff depth, of 0.2–0.4. Thus, we will assume that 30% of the annual precipitation will be lost in tile drainage, and this value will take the place of the runoff coefficient in Eq. 6.9. Considering this 30% value along with the average annual precipitation and size of the field, Eq. 6.9 produces an estimate of 55 million L (14 million gallons) of drainage water per year. With the average dissolved P concentration of 0.3 mg L⁻¹, Eq. 6.9 results in an annual P load of 16,600 g (36 lbs).

6.2.2 Peak Flow Rates

Knowledge of peak runoff rates (Q_p) for various sized storm events is critical since each structure must be designed to handle a flow rate equal to or greater than the peak flow rate. Simply put, water must be able to flow through the P removal structure in order for the structure to remove P; therefore, it is important that the structure is designed to be able to handle flow rates produced from appreciable sized storms since large storm events tend to deliver the greatest P loads to surface waters. One of the required design inputs that is a direct result of peak flow rate estimates, is the target minimum flow rate for the structure. Clearly, it is in the best interest of the designer to choose a target minimum flow rate that corresponds to the peak flow rates for large-sized storm events.

6.2.2.1 Surface Runoff

Estimation of Q_p for different size storms (i.e. storm return period) can be completed using techniques such as the Curve Number Method developed by the NRCS, the Rational Method (Water Pollution Control Federation), or a computer model which utilizes these methods such as the Soil and Water Assessment Tool (SWAT) (Arnold et al., 1998; NRCS, 2004). For the Curve Number method of determining peak flow rates (Q_p) for runoff, certain information about the site is required for calculation:

- · Hydrologic group of the soils present in the contributing area
- Contributing area (CA)
- · Percent area of the different land uses/ground cover within that area
- Hydraulic length, which is the distance from the furthest point in the contributing area to the outlet
- Average slope of the watershed
- Depth of precipitation for storm events of interest

The depth of precipitation for various sized storm events can be obtained from the National Oceanic and Atmospheric Administration. Specifically, Technical Paper No. 40: "Rainfall Frequency Atlas of the United States for Durations from 30 minutes to 24 Hours and Return Periods from 1 to 100 Years" (http://www.nws. noaa.gov/oh/hdsc/PF_documents/TechnicalPaper_No40.pdf). These precipitation values are specific to region and are typically obtained by viewing maps for storms of a specified return period. Choosing an appropriate storm size is important because storm size is proportional to runoff flow rates and volumes, therefore the required structure size will be larger for storms with a less frequent return period (i.e. larger storms). For example, a user may be interested in designing a structure that can treat flow from a 2 year-24 h storm, which means that this size storm and its associated depth of rainfall is likely to only occur once every 2 years. This depth of rainfall is used with the other listed required information for estimating the peak runoff flow rate at the site.

In addition to the Curve Number Method, Q_p value can also be determined using the Rational Method, which is a function of:

- Design rainfall intensity, (i)
- Runoff coefficient (RC)
- Contributing area (CA)

The Rational Method for calculating Q_p (gallons min⁻¹) is as follows:

$$Q_p = RC \times i \times CA \times 440 \tag{6.11}$$

Where RC is dimensionless, i is in cm h^{-1} , and CA is ha. Local i values as a function of time and storm size (i.e. return period) can be obtained from the NOAA's National Weather Service Hydrometeorological Design Studies Center (Precipitation Frequency Data Server; PFDS). The precipitation frequency data server can be accessed at: http://hdsc.nws.noaa.gov/hdsc/pfds/. For example, if the 10-min precipitation depth value for a 2 year storm is reported to be 0.9 cm, this is equivalent to an i value of 5.4 cm h^{-1} .

Consider an example for calculating the peak runoff flow rate for a 50 acre (20 ha) field located in southern Missouri for the peak 24 h rainfall intensity in a 2 year storm interval. Note that this model storm was chosen randomly; other storm intervals and durations could be chosen as well. The field is a pasture on a "rolling" topography with soils classified as hydrologic drainage group C. First, the RC is estimated using Table 6.1 to be 0.36. Next, the peak rainfall intensity for southern Missouri for a 60 min storm having an interval of 2 years is 0.149 in. h^{-1} (0.38 cm h^{-1}). Using Eq. 6.11, the peak runoff rate for this site would be 1200 gpm.

Regardless of the method used to determine Q_p , it will require that some variables be obtained directly from visiting the site, such as predominant cover. Other information required for estimating Q_p , either by the Rational Method or the Curve Number Method, can be obtained using aerial maps, soil survey available at the NRCS Web Soil Survey (https://websoilsurvey.sc.egov.usda.gov/App/HomePage. htm), and computer programs such as the Water Erosion Prediction Project (WEPP) available online at http://milford.nserl.purdue.edu (Flanagan et al. 2001). Regarding Curve Number Method, the NRCS provides this service of determining Q_p as one component of the process for designing various best management practices such as grassed waterways. Also, many environmental consulting agencies are equipped to estimate curve number or estimate peak flow rates by other methods.

6.2.2.2 Subsurface Drain Pipes

If water from a subsurface drain is the target for a P removal structure such as a tile drain filter, the approach for estimating Q_p is simplified if the assumption is made that the pipe is flowing at full capacity. Clearly, this assumption may ultimately result in slightly over-designing the P removal structure. However, it is better to build the structure with the extra capacity to handle unusually large flow events rather than undersize.

$$Q_{p} = \frac{\left[0.463D^{\frac{8}{3}} \times S^{\frac{1}{2}}\right]}{n} \times 448.8$$
(6.12)

Pipe material	Manning's n value
Asbestos-cement	0.009
Cast iron	0.012
Clay, drainage tile	0.012
Concrete	0.015
Corrugated plastic	0.015
Metal, corrugated	0.025
Steel, riveted, spiral	0.016
Vitrified sewer pipe	0.013
Polyvinyl chloride (PVC)	0.009-0.011
Polyethylene (PE): corrugated with smooth inner walls	0.009-0.015
Polyethylene (PE): corrugated with corrugated inner walls	0.018-0.025

 Table 6.4
 Manning's roughness coefficient (n) values for various pipe materials

Where Q_p is in gallons min⁻¹ (gpm), D is diameter of drain pipe in ft, S is slope of the pipe in decimal form (elevation drop in pipe/distance run), and n is Manning's roughness coefficient.

As an example, calculate the peak flow rate from a tile drained field that ultimately drains into a single trunk line that is 8 in. in diameter, made of clay, with a slope of 0.1%. Inserting the n value of 0.012 from Table 6.4, diameter of 0.66 ft, and slope of 0.001 into Eq. 6.12, the resulting peak flow rate is about 186 gpm.

6.2.2.3 Drainage Ditches and Channels

As discussed in Chap. 3, drainage ditches are an ideal location for constructing a P removal structure. After conducting a survey of the drainage ditch at a site, it is relatively easy to obtain estimates of flow rates within a ditch through use of the Manning's equation. However, unlike estimating peak flow rates for surface runoff, this method does not involve use of specific storm size. Essentially, after the dimensions of the ditch are measured, the estimated flow rates are determined as a function of the depth of water in the ditch. Thus, the designer must choose what depth of water in the ditch will represent the target minimum flow rate for the P removal structure. Clearly, the assumption with the least risk would be to design the structure to achieve a flow rate equal to when the ditch is 100% full of water (i.e. water depth = ditch depth). However, this might not be economically feasible, may excessively decrease the flow capacity of the ditch, and depending on the site, such a condition may be extremely rare.

The Manning's equation is:

$$Q_p = (A_{Mann} \times V) \times 448.8 \tag{6.13}$$

Table 6.5 Roughness	Type of channel and lining	n value				
coefficients (n) of channels	Rigid lined channels					
and ditches for estimating	Asphalt	0.015				
Manning's equation	Concrete	0.017				
(Eq. 6.13–6.15)	Concrete, rubble	0.024				
	Gabions	0.027				
	Metal, corrugated	0.027				
	Plastic, lined	0.013				
	Reno mattress	0.025				
	Shotcrete	0.016				
	Vegetation	Vegetation				
	Long (12–24 in.)	0.08				
	Short (2–6 in.)	0.04				
	Earth channels					
	Firm soil, sand or silt	0.02				
	Stiff clay, alluvial silts	0.025				
	Shales and hardpan	0.025				
	Graded silt and loam	0.03				
	Dredged earth channels	0.028				
	Earth, straight and uniform	0.023				
	Earth bottom, rubble sides	0.030				
	Large ditch, no vegetation	0.035				
	Small ditch, no vegetation	0.040				
	Rock cuts, smooth and uniform	0.030				
	Rock cuts, jagged and irregular	0.040				
	Cobbles and shingles	0.035				
	Stony bed, weeds on bank	0.035				
	Straight, uniform	0.0225				
	Winding, sluggish	0.025				

Where Q_p is in gpm, A_{Mann} is the cross sectional area of the flow in ft² and V is the average flow velocity perpendicular to the cross sectional area in ft s⁻¹. The value of V is determined by:

$$V = \frac{1.486}{n} R_h^{\frac{2}{3}} \times S^{\frac{1}{2}}$$
(6.14)

Where n is Manning's roughness coefficient for open channels (Table 6.5), S is the slope of the ditch in the direction of flow (unitless decimal: elevation drop per length of run), and Rh is the hydraulic radius in ft. Hydraulic radius is calculated as:

$$R_h = \frac{A_{Mann}}{W_p} \tag{6.15}$$



Fig. 6.2 Channel cross-section formulas used for estimating ditch flow-parameters (Eqs. 6.15–6.17) with the Manning's equation. Cross-sections *1*, *2*, *3*, and *4* are for *trapezoidal*, *triangular*, *parabolic*, and *rectangular shaped ditches*, respectively

Where W_p is the wetted perimeter in ft, i.e. the sum of the length of the surfaces in direct contact with the water. Values for A_{Mann} and W_p are calculated as a function of the shape of the ditch, using equations shown in Fig. 6.2.

In practice, determining the target minimum Q_p value for a ditch-style P removal structure would involve

- Site survey to determine:
 - ditch shape and dimensions necessary for the equations in Fig. 6.2
 - ditch slope (S)
 - type of lining on the ditch for choosing the proper n value in Table 6.5
- Choose the water depth (d) that will represent the target minimum flow rate for the ditch filter
- Insert all values into the appropriate equations in Fig. 6.2 for calculation of A_{Mann} and Wp
- Insert A_{Mann} and Wp into Eq. 6.15
- Insert R_h into Eq. 6.14
- Insert V into Eq. 6.13

Note that the top width (t) shown in the equations for each channel shape (Fig. 6.2) will need to be measured or calculated at the target water depth (d) of interest.

Example Calculation of Peak Flow Rate for a Ditch

For this example we will estimate the peak flow rate for a 5 ft deep trapezoidalshaped drainage ditch, when the water is 3 ft deep. Assume that a site survey was conducted to determine:

- Trapezoidal channel with a top width of 12 ft, bottom width of 4 ft. The top width at the water depth of interest is 10 ft.
- Grass cover in the channel at approximately 16 in. tall
- Ditch slope of 0.1%

For this problem, it is critical to consider that we are not trying to determine the peak flow rate capacity of the ditch, only the peak flow rate when the ditch has 3 ft of water in it. In reference to the trapezoidal channel in Fig. 6.2, we can deduce that the e value is 6 ft (i.e. 10 ft width measured at the depth of interest minus 4 ft bottom width). Thus, the z value for our depth of interest is 2. Using the appropriate equations in Fig. 6.2, A_{Mann} is calculated to be 30 ft² and W_p is 17.4 ft, knowing that d, b, and t are 3, 4, and 10 ft, respectively. Inserting the values for A_{Mann} and W_p into Eq. 6.15 yields 1.7 ft for the value of R_h . Next, Table 6.4 is used to determine that the slope and R_h value previously calculated. From this, a velocity of 0.84 ft s⁻¹ is calculated, which is finally inserted into Eq. 6.13 along with the value for A_{Mann} in order to estimate flow rate. Thus, when the water depth in this ditch is 3 ft deep, the flow rate is approximately 11,300 gpm.

6.2.3 Hydraulic Head and Maximum Area for Structure

Hydraulic head, or "hydraulic gradient" is the force that allows water to flow through saturated porous media (such as soil or PSMs), and is extremely important to the design of a P removal structure. Obviously, water must flow through the PSM in order for the P removal structure to operate (Chap. 3). Ultimately, the flow rate through the PSMs contained in the structure is a function of hydraulic head, hydraulic conductivity, and the depth of the PSM. Hydraulic conductivity is a function of the physical nature of the PSM (discussed in Chaps. 4 and 5). Hydraulic head, on the other hand, is a function of the site.

The maximum hydraulic head for a site must be known in order to conduct a proper design, since this will partly control flow rate through the structure and dictate the necessary area of the structure. Or in the case of a ditch-style structure, the hydraulic head will partly dictate the length of the structure. A greater hydraulic head will permit for a deeper PSM depth (if necessary), which translates to a smaller potential footprint for a P removal structure. Put another way, assuming 100% gravitation flow (i.e. no pumps), the hydraulic head for a site represents the maximum possible depth of the PSM bed, since water cannot flow uphill. Occasionally, the required area for meeting the target minimum flow rate for a P removal structure will be greater than the maximum area that is available for constructing the structure. Thus, it is important that the constraint for maximum potential area (or length for a ditch-style filter) to be sacrificed for a structure be determined at the beginning of the design process since hydraulic head, target minimum flow rate, and hydraulic conductivity of PSM, will directly impact the required area for the PSM bed.

6.2.3.1 Hydraulic Head for Un-sealed Structures with Flow from Top-Downward

Ultimately, the hydraulic head for a site is the elevation difference between the proposed inlet and the proposed point in which drainage occurs. Estimating the maximum hydraulic head for a site is dependent on the type of structure that is to be constructed. For a P removal structure constructed at the surface for intercepting and treating surface runoff, such as the structures shown in Figs. 3.1, 3.5, and 3.10, the hydraulic head is essentially a function of the slope. The higher the slope, the more hydraulic head is available for pushing water through the PSM bed (Fig. 6.3) The maximum hydraulic head can be determined by measuring slope and



Fig. 6.3 An illustration of the concept of hydraulic head for P removal structures to be designed for intercepting surface runoff. *Upper picture* shows a proposed site for P removal structure outlined with the maximum allowable area chosen by the designer. *Lower cutaway diagram* illustrates the elevation difference from proposed inlet to outlet, which is the maximum hydraulic head for that potential structure



Fig. 6.4 Maximum hydraulic head If the proposed P removal structure is an un-sealed buried bed with normal flow through the PSMs from the top-downward, such as the tile drain filter shown in Fig. 3.17a or the surface/blind inlet shown in Fig. 3.14a. In that case, the maximum hydraulic head for that structure is the elevation difference between the outlet of the tile drain to be treated and the bottom of the drainage ditch in which the tile currently drains into. If the buried bed is sealed at the top, bottom, and sides, and flow is directed through the PSMs from the bottom-upward (Figs. 3.14b and 3.17b), then the drainage ditch depth is inconsequential and the hydraulic head is simply equal to the chosen depth of the buried PSM bed

calculation of the elevation change after assuming the maximum length of the structure over that slope. Also, hydraulic head can be estimated by using simple line levels.

For ditch-style P removal structures (e.g. Fig. 3.9) that are constructed in urban or agricultural drainage ditches (e.g. Fig. 3.3), the potential maximum hydraulic head is essentially the depth of the drainage ditch. For surface P-filter beds such as bioretention cells and blind inlets (Figs. 3.14 and 3.15), the hydraulic head is the elevation difference between the point of the highest water ponding level (or overflow) and the point of ultimate drainage, which is often near the bottom of a drainage ditch. In some cases it may be desirable to construct a subsurface P removal structure such as the unit shown in Fig. 3.17 for treating tile drainage before reaching a drainage ditch. In that case, the hydraulic head for the buried bed that is plumbed into a tile drain pipe is ultimately the elevation difference between the current tile drain outlet and the bottom of the ditch in which the tile pipe currently drains into (Fig. 6.4), if the structure being designed to flow from the top-downward.

6.2.3.2 Hydraulic Head for Sealed Structures with Flow from Bottom-Upward

For some sites that simply lack hydraulic head due to shallow slope or because the drainage ditch that drains a structure is excessively shallow, there is an alternative. For example, consider a site that is very flat and the nearby drainage ditch is relatively shallow at two feet deep. In that case, construction of a P removal structure such as a surface/blind inlet, bio-retention cell, or subsurface tile drain filter with normal flow occurring from the top-downward Figs. 3.14a, 3.16, and 3.17a would be limited since the PSM bed would be restricted to a shallow depth in order to ensure proper drainage. Recall that a shallow depth of PSM translates to a large footprint for a P removal structure and therefore could be problematic for a site. A solution is to contain the PSMs in the structure within a unit that is sealed at the top, sides, and bottom, and to pipe the inflow water directly into the bottom of the structure which will force the inflow water to move through the PSM bed from the bottom-upward. Such a design is shown in Figs. 3.14b and 3.17b. For this type of design, the water is treated by flowing from the bottom-upward instead of the topdownward and is discharged at the same elevation in which it initially entered the structure. For the blind inlets that flow from the bottom-upward shown in Figs. 3.14b and 3.19, the unit is sealed near the top in order to prevent inflow water moving through the PSMs from the top-downward, which would cause most of the inflow water to bypass the PSM as it moves directly to the drain located near the top. Without the sealed top in this upward flow design for a blind inlet, inflow water would initially fill the PSM bed like a bath-tub, and then the remaining water that entered would simply flow directly into the outlet, untreated. For this scenario of a sealed bed with flow occurring from the bottom-upward, the hydraulic head is simply equal to the difference in elevation between the inlet and the bottom of the PSM bed. If the outlet elevation is the same as the inlet i.e. the PSM bed thickness is equal to the hydraulic head, then the hydraulic gradient is equal to one. If the outlet elevation is less than the inlet, i.e. the PSM bed thickness is less than the hydraulic head, then the hydraulic gradient will be greater than one and provide greater potential to "push" water through the PSMs at a faster flow rate. See Sect. 6.3.1 for a more detailed discussion.

Depending on the required mass and volume for the PSMs, the materials could be contained as a "sealed bed" within a tank made out of metal, plastic, or concrete (such as a septic tank). For larger volumes, the PSM bed could be sealed by simply using a liner on the top, sides and bottom, although in some cases the soils that constitute the sides and bottom may be relatively impermeable and not require a liner. *This solution is only viable for PSMs that remove P through Al and Ca, not for Fe-rich PSMs*. Because of the flow design from the bottom-upward, the PSM bed will remain saturated with water after the flow event ceases. Under saturated conditions, the PSM bed will become anaerobic and Fe-minerals will dissolve. If any of the Fe-minerals possess phosphate on them, then dissolution will re-release the P back into the solution. This could also be a problem for sulfur-rich PSMs.

6.3 Drainage of the P Removal Structure: Balancing Flow Rate with Retention Time

As discussed in Chap. 3, a critical characteristic of a P removal structure is that it be able to handle an appreciable flow rate of water through the PSMs, relative to the site. *Again, the water must flow through the PSM, not flow over top of them.* Choosing a reasonable target flow rate for a structure can only be determined after characterizing the site for peak flow rates. After determining the necessary mass of PSM required to meet the P removal goals, a designer must determine how to achieve the target flow rate through that specific mass of PSM within the constraints of maximum hydraulic head at the site, PSM physical properties, and maximum area or length that can be sacrificed for the structure. To further complicate the task, one additional constraint that may exist depending on the PSM is the necessary retention time for the structure.

6.3.1 Water Flow Through the P Removal Structure

The flow rate through a P removal structure can be summarized using the Darcy equation:

$$Q = \left(AK_{sat} \times \frac{\Delta \psi}{D_{PSM}}\right) \times 14.7 \tag{6.16}$$

Where Q is the flow rate through the PSMs (gpm), A is the surface area of the PSM bed in which water infiltrates into (ft²), K_{sat} is the saturated hydraulic conductivity of the PSM (cm s⁻¹), $\Delta \Psi$ is the change in water potential and D_{PSM} is the depth of the PSM. Depth and $\Delta \Psi$ can be in any units of length, as long as they are both the same units (i.e. the units cancel out). Figure 6.5 illustrates the physical nature of A, D_{PSM} , and $\Delta \Psi$ for any PSM bed. Essentially, $\Delta \Psi$ is the hydraulic head value discussed in Sect. 6.2. The principle of Darcy flow of water through media is the same regardless of whether or not the flow is occurring from the top-downward or the bottom-upward. Figure 6.6 illustrates how hydraulic head is measured in situations where a P removal structure is designed to flow from the bottom-upward. Equation 6.16 shows how the flow rate through any P removal structure is essentially a function of the hydraulic head ($\Delta \Psi$), depth of the PSM bed (D_{PSM}), surface area of the bed (A), and hydraulic conductivity (K_{sat}). While hydraulic conductivity and hydraulic head are inherent to the PSM and site location, respectively, and cannot be changed, one can manipulate the PSM bed surface area and depth in order to achieve the target minimum flow rate. Inserting the target flow rate for Q and known values



Fig. 6.5 Illustration of the parameters used in the Darcy equation (Eq. 6.18) for flow through a saturated PSM bed

for K_{sat} and $\Delta \Psi$ into Equation 6.16, it can be solved for various combinations of A and D_{PSM} (or insert a constraining value for either A or D_{PSM}) until a suitable outcome is achieved.

6.3.1.1 Uniform Inflow Distribution

Regarding the methods described in Sect. 6.3 for designing structure to meet the minimum retention time and flow rate, and also regarding algorithms within the Phrog software, the underlying assumption is that the maximum distance in which water will flow through the PSM bed, is equal to the depth (D_{PSM} value) of the PSM bed. This means that the inflow water to the structure must be evenly distributed on the surface (A) of the structure, and drainage out of the structure occurs immediately after the water has flowed through the PSM bed. If water is able to pond on the surface where infiltration through the PSM occurs, then by default, the water is evenly distributed. For example, the ditch-style filter, bio-retention cells, and blind inlets described in Chap. 3 often operate in this fashion. If a ponded condition does



Fig. 6.6 Illustration of the parameters used in the Darcy equation (Eq. 6.18) for flow through a saturated PSM bed from the bottom-upward. The Darcy principle is the same for bottom-upward and top-downward flow. In this case the hydraulic head is the difference in elevation between the inlet to the P removal structure and the bottom of the PSM bed. Although the hydraulic head is the same in both **a** and **b**, the PSM depth is equal to the hydraulic head for **a**, which results in a hydraulic gradient equal to one. But in scenario **b**, PSM depth, or more importantly, the distance between the bottom of the PSM bed and the outlet, is less than the hydraulic head. While both scenarios will allow water to flow through the PSM to the outlet, scenario **b** will have a greater flow rate due to a hydraulic gradient greater than one

not occur, then it is necessary to create a system, usually with perforated pipe near the surface, to evenly distribute the inflow water. One of the assumptions for all Phrog software design output is that the structure will be constructed such that the inflow will be even distributed on top of the PSMs, and that drainage pipe will be used to remove the water after it has moved through the PSM bed (Sect. 6.3.3).

6.3.2 Retention Time

As discussed in Chaps. 3 and 4, some PSMs are sensitive to retention time, which is essentially the average time it takes for a molecule of water to pass through the PSM bed. For PSMs that are sensitive to retention time, an increased retention time will

increase P removal. This is why it is important that the retention time of the design curve used for determining the required mass of PSM, correspond with the target retention time of the actual structure to be constructed. If the PSM is not sensitive to retention time, then this is not an issue. Flow rate (Q) through the structure is related to the structure retention time through the following equation:

$$Retention time = \frac{total \ pore \ volume \ of \ PSM \ bed}{Q} \tag{6.17}$$

Where Q and total pore volume must be in the same units of volume; the resulting units for retention time will be in the unit of time that was employed for Q. For example, if total pore volume and Q are in units of gallons and gpm, respectively, then the resulting units for retention time will be minutes. Total pore volume can be estimated knowing the porosity of the PSM and the total volume of the PSM bed, or from the total mass of the PSM bed if the bulk density is known in addition to the porosity. Chapter 5 describes bulk density and porosity, and how to measure them.

$$Total \ pore \ volume = length \times width \times depth \times porosity$$
(6.18)

Where length, width, and depth of the PSM bed must all be in the same units, and porosity is the measured value of the PSM (in decimal form, unitless). Total pore volume will be in the units of length chosen, cubed. If the mass of the PSM is known:

$$Total \ pore \ volume = \left(\frac{PSM \ mass \times 236}{BD}\right) \times \ porosity \tag{6.19}$$

Where total pore volume is in units of gallons, PSM mass is in tons, bulk density (BD) is in g cm^{-3} or kg L^{-1} , and porosity is in decimal form.

One can see from Eqs. 6.17 to 6.19 that retention time of the structure is directly a function of the total mass of PSM and the flow rate of water through the PSMs. Next, recall that the flow through the structure is a function of the physical layout of the PSM bed (i.e. area and depth of PSMs; Eq. 6.16). Therefore, the biggest challenge of a design is determining a physical layout that meets both the minimum retention time and flow rate, using the necessary PSM mass, without exceeding the physical constraints of the site or those set by the user.

If a structure is to be constructed to meet a specified retention time under the targeted peak flow rate, then Eq. 6.17 creates another constraint for design: maximum flow rate with regard to meeting a specific retention time. This maximum flow rate for meeting retention time may conflict with the minimum targeted flow rate through the structure. For example, assume that for a hypothetical structure, the design target flow rate is that the structure must handle a peak flow of at least 500 gpm. However, if a minimum retention time is also targeted in design of the

structure, say, 5 min, then there now exists a constraint for the maximum flow rate that corresponds with that retention time. To continue with the example, after determining the required PSM mass to meet the removal goal, if the resulting total pore volume of the PSM bed was 2000 gallons and the minimum target retention time was 5 min, then the corresponding maximum allowable flow rate through that structure without violating the minimum retention time would only be 400 gpm. The problem in that case is that it becomes impossible to meet both the target retention time and the target peak flow rate for that particular PSM bed. If the minimum target peak flow rate is met, then the retention time will be too short, but if the minimum retention time is met then the minimum target peak flow rate will not be met. This "balance", based on a given mass of PSM required to meet the P removal goal and lifetime, can be very difficult to achieve. This is another reason why the use of the Phrog software is advantageous as such calculations can be determined instantly. In some cases, the use of the subsurface drainage pipe layer can be manipulated to help solve this unbalance if it occurs.

6.3.3 Drainage of the P Removal Structure

During a flow event, the final step in P removal is discharge of the treated water from the structure. Clearly, if the treated water is not discharged, then new "dirty" high-P water will not be able to enter the P removal structure and be treated. Sections 6.3.1 and 6.3.2 discussed how to design a structure to push water through the PSMs at the desired flow rates and retention time, but after the water drains through the PSM, the water must be able to exit the structure. This is achieved through a subsurface drainage layer consisting of drain pipe.

Thus, a subsurface drainage layer such as the one shown in Fig. 6.7 is required for most structures. Without the drainage layer, the flow through a P removal structure would be severely limited since it would rely solely on lateral Darcy flow through the PSM layer. Due to its proven utility in research and demonstration filters, as well as its availability at local hardware stores, perforated PVC pipe and corrugated plastic pipe is recommended for use in the subsurface drainage layer. The factors affecting flow rate of water in the pipe are the slope of the pipe, which affects the velocity and the friction that water is subjected to by the roughness and diameter of the pipe. As evident in Eq. 6.12, the relationship between flow rate and pipe diameter is not linear, so a doubling pipe diameter on flow becomes important in designing a structure since the cost and ease of installation can vary with different sizes of pipe.

Using Eq. 6.12 and Table 6.4, one can determine the perforated pipe material, diameter, number of pipes, and slope of the pipe within the structure that will meet



Fig. 6.7 The subsurface drainage layer of a P removal structure was exposed prior to the addition of the PSM. The drainage layer consisted of 4 in. (10.16 cm) diameter perforated PVC pipes

the necessary flow rate for moving the treated water out of the structure. For example, if the design flow rate through the PSM is 500 gpm and the chosen pipe is 4-in. diameter perforated PVC pipe set to a 1% slope in the structure, Eq. 6.12 estimates that the max flow per pipe is about 111 gpm, and therefore five pipes are necessary to meet the design flow rate. The designer also needs to consider the constraint of pipe size as a function of PSM bed depth. For example, using an 8 in. diameter pipe in a PSM bed that is only 5 in. deep is not logical. In choosing number and size of drainage pipe for a structure, the goal is for total pipe drainage flow to be equal to or exceed the Darcy flow through the PSM bed (Eq. 6.16).

This aspect of the design must be conducted while considering the retention time. Specifically, if the PSM is sensitive to retention time and thus the structure is to be constructed to meet a certain minimum retention time, as discussed in Sect. 6.3.2, then this translates to a new constraint of maximum flow rate of water through the structure (Eq. 6.17) for meeting retention time. In addition to the necessity of subsurface drainage in the structures, the drainage design can additionally be conducted to restrict flow rate through the structure in order to meet the retention time. Again, as discussed in Sect. 6.3.2, this restriction is only a viable option when the maximum flow rate required to meet retention time is equal to or greater than the targeted peak flow rate for the structure. If the maximum flow rate for meeting the required retention time is less than the targeted peak flow rate through the structure, then the mass of the PSM bed (and therefore the total pore volume) must be changed in order to achieve the balance between the two different flow rate constraints.

General Procedure for Conducting a Structure Design 6.4 and Information Obtained

6.4.1 General Design Procedure

- 1. Characterize and survey the site of interest
 - (a) Determine peak flow rates (Sect. 6.2.2)
 - (b) Determine average annual flow volume (Sect. 6.2.1.1)
 - (c) Estimate typical dissolved P concentrations (Sect. 6.2.1.2)
 - (d) Estimate the maximum potential hydraulic head at the location where the structure may be built, along with maximum area that can be utilized (Sect. 6.2.3)
- 2. Calculate average annual P load (Eqs. 6.7 and 6.8)
- 3. Determine design curve for potential PSMs to be used in the structure by one of the two methods:
 - (a) Estimate design curve from chemical and physical characterization (Chap. 5) under the conditions of the typical dissolved P concentrations for the site and using target retention time values (Phrog software), or
 - (b) Directly measure the design curve from flow-through analysis under the conditions of the typical dissolved P concentrations for the site and using target retention time values (Chap. 5)
- 4. Characterize the potential PSMs for physical characteristics (Chap. 5)
- 5. Choose the target cumulative P removal goal (%) and the corresponding lifetime
- 6. Calculate the cumulative P added to the PSM that corresponds to the removal goal, using the design curve previously estimated/measured (Eqs. 6.1, 6.2, and **6.4**)
- 7. Calculate the required PSM mass to meet the P removal goal (Eq. 6.5)
- 8. Calculate the ultimate lifetime of the structure (Eq. 6.6)
- 9. Choose the target peak flow rate that you want the structure to handle
- 10. Insert target peak flow rate and maximum site hydraulic head into Eq. 6.16, insert a value for either PSM depth or bed area, and then solve for the remaining variable i.e. either area or PSM depth).
 - (a) Note: if inserting a value for PSM depth, it must be less than or equal to hydraulic head
 - (b) For a ditch-style structure, the associated channel cross-section equations (Fig. 6.2) must be additionally utilized in order to determine length or PSM depth.
 - (c) For a ditch-style structure, the hydraulic gradient $\left(\frac{\Delta\Psi}{D_{PSM}}\right)$ must be set to 1.

Otherwise, excessive damming to the ditch may occur.

- 11. If PSM is not sensitive to retention time, then proceed to estimate drainage pipe requirement step 13).
- 12. If PSM is sensitive to retention time, then insert minimum target retention time from the condition of design curve, and also the total bed pore volume (Eq. 6.18 or 6.19) into Eq. 6.17 and determine the maximum flow rate that corresponds with the target minimum retention time
 - (a) If this corresponding flow rate is greater than the target peak flow rate for the structure (step 9), then proceed to determine drainage pipe requirement (step 13). If it is less than the target peak flow rate, then either:
 - i. increase total volume (therefore mass) of PSM bed to increase the maximum flow rate corresponding with the minimum retention time, and calculate the resulting increase in PSM mass
 - ii. or decrease the target peak flow rate to a level equal to the maximum flow rate for meeting retention time
 - (b) If the PSM mass was increased in order to satisfy both the target peak flow rate and the maximum flow rate required for the minimum retention time, (step 12.a.i) then determine the new area (or length) of the PSM bed using Eqs. 6.18 and 6.19 (or additionally for ditches, use cross-section equations in Fig. 6.2).
 - i. If the maximum area or length constraint is not exceeded, then the solution is viable.
 - 1. Since the PSM mass was increased, estimate the new P removal and lifetime of the structure using Eqs. 6.1–6.6
 - ii. If the maximum area or length constraint is exceeded, then decrease the P removal goal and return to step 5.
- 13. Determine subsurface drainage pipe requirement
 - (a) Choose desired pipe diameter and the slope of the pipe within the PSM bed. Pipe diameter cannot exceed the PSM depth.
 - (b) Calculate maximum pipe flow rate using Eq. 6.12
 - (c) Estimate the number of pipes required to meet the final target peak flow rate, and determine if they will fit along the length or width of the structure.
- 14. If the P removal structure is a ditch structure, determine the flow capacity reduction of the ditch resulting from construction of the structure
 - (a) Determine the new peak flow rate *through the ditch (not the PSMs)* using the Manning's equation since the effective depth of the ditch has been reduced by placing a PSM in it (Sect. 6.2.2.3)
 - (b) Then sum the peak flow rate *through the PSMs* with the new ditch peak flow rate determined in the previous step (i.e. ditch flow that occurs on top of the PSMs, not through them). This sum is the total ditch flow capacity

- (c) Calculate the % reduction in total ditch flow capacity relative to the condition where no P removal structure is built. Determine if this flow reduction is acceptable for the site and conditions.
- i. If the % reduction in ditch flow capacity is not acceptable, decrease PSM depth and calculate the resulting increase in the length of the ditch structure.

6.4.2 General Results from Conducting a Proper Design

- 1. Required mass of the specific PSM for meeting the specified user goals (% cumulative removal and lifetime) for that site, under the P inflow concentrations and retention time for the design curve utilized.
- 2. Orientation of the PSM materials and structure in order to meet the target peak flow rate and minimum retention time (if applicable)
 - (a) Depth of PSMs
 - (b) Area of PSMs
 - (c) For ditch-style structure: length of PSMs
 - (d) Depth of structure i.e. additional hydraulic head for pushing water through PSMs
- 3. Required number of drainage pipe of the user-specified diameter
- 4. For ditch-style structures: % reduction in total ditch flow capacity

6.5 Optional: Total and Particulate P Removal with Sediment Reduction

Although the purpose of the P removal structure is to remove dissolved P from flow, which is obviously the target for the design process, the structures can also remove particulate phosphorus by trapping sediment. Sediment can be a problem for some PSMs because it could cause clogging. Thus, for some PSMs that consist of fine textures, it may be advantageous to treat inflow water for sediment removal prior to entering the P removal structures with various methods that range in sophistication from sedimentation basins to grass buffers.

However, for other PSMs that are less sensitive to clogging in a structure, trapping the sediment can be a desirable option. Thus, after a designer has obtained a satisfactory design for meeting dissolved P reduction goals, it is relatively easy to estimate how much particulate, and therefore total P, will also be reduced through that design. As discussed in the first two chapters, particulate P is accomplished through sediment reduction.

6.5.1 Estimating Sediment Load Reduction

The sediment removal efficiency of any P removal structure can be calculated through the single collector removal efficiency (Ryan and Elimelech 1996):

$$\eta = \frac{I}{UC_{o}A} \tag{6.20}$$

Where C_o is the sediment inflow concentration (g m⁻³), U is the fluid approach (superficial) velocity (m min⁻¹), I is the sediment deposition rate that flows onto the structure (g min⁻¹), and A is the area of the PSM bed (m²). The U value is determined by:

$$U = \frac{Q}{A \times porosity} \tag{6.21}$$

Where Q is flow rate in units of $m^3 \min^{-1}$, and porosity of the PSM is in decimal form. In practice, after the value for single collector removal efficiency is determined, that value for η is inserted into Eq. 6.22 to calculate the sediment reduction value for the desired time period:

sediment reduction =
$$1 - \left(e^{-\frac{3(1-porosity)\eta D}{r}}\right)$$
 (6.22)

Where D is the depth of the PSM bed (m) and r is the average radius of the PSM particles (m). Most of the parameters used in Eqs. 6.20-6.22 are already known through the process of designing the P removal structure; area of PSM bed, PSM porosity, and inflow flow rate. For inflow flow rate, use the target peak flow rate in which the structure was designed for, as it will result in the estimation of a worst case scenario regarding sediment trapping. Clearly, there is a need for an estimate of average sediment concentration in the water to be treated. Estimating sediment concentration may be difficult through grab sample collection due to the inherent variability in sediment transport. Even more difficult is estimation of the sediment deposition/inflow rate onto the PSM bed (I), as this requires knowledge of the mass of sediment that is transported per unit time during flow events. Tools such as the Water Erosion Prediction Project (WEPP) have the ability to predict the mass of sediment lost and the duration of flow for estimating the I value. A less sophisticated approach would be to use the Revised Universal Soil Loss Equation (RUSLE), which will provide a value of soil loss in units of mass per area per unit time. That value could then be combined with some estimate of the amount of time that water would be flowing into the P removal structure (i.e. flow duration).

The following is an example for a P removal structure constructed on a CAFO in Eastern Oklahoma:

- target peak flow rate of 400 gpm (0.025 m³ min⁻¹)
- inflow sediment concentration of 100 g m³ (0.1 g L⁻¹)
- sediment deposition rate onto structure of 0.64 g min⁻¹
- PSM bed area and depth of 39.8 m² and 0.5 m, respectively
- PSM characteristics of 0.38 porosity and average particle radius of 0.004 m

The resulting η and U value are 0.0974 (unitless) and 0.00165 m min⁻¹, which is then input into Eq. 6.22. Sediment reduction is calculated to be nearly 1 (i.e. 100%) for the given conditions.

6.5.2 Estimating Total P and Particulate P Reductions from Sediment Removal Within the Structure

Total P (TP) and particulate P (PP) reductions can be estimated after the reduction in sediment has been calculated. This relies on the simple mass balance:

$$TP = PP + DP \tag{6.23}$$

Where TP, PP, and DP are all in units of mg L^{-1} . Since PP is defined as the P that is bound onto sediment, then knowledge of the sediment concentration can be used to estimate the concentration of P on the sediment i.e. PP expressed per mass of sediment (PP_{mass}):

$$PP_{mass} = \frac{TP - DP}{sediment}$$
(6.24)

Where PP_{mass} is in units of mg P mg⁻¹ sediment, and sediment is in units of mg L⁻¹. Assuming that the value for PP_{mass} is constant, then the new TP value can be calculated after sediment concentration reduction has been calculated (described in Sect. 6.5.1):

$$TP = (PP_{mass} \times sediment) + DP \tag{6.25}$$

For example, consider a site with 10, 1, and 100 mg L⁻¹ inflow concentrations of TP, DP, and sediment, respectively, therefore an inflow PP concentration of 9 mg L⁻¹. Assume that this P removal structure is able to achieve sediment reduction of 50%, and DP reduction of 30%. The PP_{mass} from Eq. 6.24 results in a value of 0.09 mg P mg⁻¹ sediment. Next, the sediment and DP trapping of the structure will reduce those concentrations to 50 and 0.7 mg L⁻¹, respectively. Inserting the new DP and sediment values into Eq. 6.25, along with the previously calculated value for

 PP_{mass} will result in the new outflow TP concentration of 5.2 mg L⁻¹. Inserting that new outflow TP value into Eq. 6.23 along with the outflow DP concentration results in an outflow PP concentration of 4.5 mg L⁻¹. Thus, the PP reduction in this case would be 50% and TP reduction equals 45%.

The Phrog software will calculate TP and PP reductions if the user includes the additional inputs required beyond that which is necessary for designing a P removal structure i.e. inflow sediment and TP concentration, and sediment deposition rate (I). Again, the purpose of the software is to estimate a design to meet target DP reductions under the given conditions and user defined goals, but it can additionally provide TP, PP, and sediment reductions that result as a function of the final design.

6.6 Further Considerations in Design and Construction

6.6.1 Free Drainage

Although mentioned several times throughout this book, it is worth dedicating a small section to the importance of designing and building structures that drain freely in between flow events when Fe-rich PSMs are used. Free drainage is only necessary for Fe-rich and certain sulfur-rich PSMs.

All of the structures and designs that allow water to flow through the PSMs from the top-downward and drain at the bottom of the PSM bed are free-draining. That is, they will not maintain saturated conditions after the flow event has ceased. On the other hand, structures in which the flow occurs from the bottom-upward and the water flows out at the top of the PSM bed, will remain saturated with water. In this scenario, it is possible for the Fe contained in Fe-rich PSMs to become electrically reduced and change from Fe³⁺ to Fe²⁺, which dissolves much of the mineral. With dissolution of the Fe mineral, much of the P held onto it will also be re-dissolved into solution. This process of the PSM bed becoming anaerobic can also produce an unpleasant odor as the Fe-oxide and Fe-hydroxide minerals that are usually red, orange, or yellow begin to produce a black color. Such anaerobic conditions can also produce hydrogen sulfide gas if the PSM contains appreciable sulfate concentrations.

6.6.2 Using a "Cap Layer" for Fine-Textured PSMs

The "paradox" of using fine-textured PSMs was discussed in Chap. 4. While these PSMs are often superior to coarse PSMs in P removal capabilities due to their chemistry, their physical properties can present challenges. One consideration that should be made in conducting a design when using fine-textured PSMs is the physical stability of the PSM. In other words, will the PSM wash away and erode, thereby leaving the structure? While this is not an issue in certain applications such as subsurface tile drain filters, modular boxes, blind inlets, bio-retention cells, and bed filters such as pond filters and wastewater treatment, it is a risk for ditch filters and confined beds that treat surface runoff where the water is moving with greater energy (Figs. 3.9 and 3.10).

In scenarios where there is risk of erosion and direct loss of the PSM, one should consider placing a capping layer of course material on top of the PSM to keep it in place. An alternative would be to apply a membrane that physically retains the material, but allows the inflowing water to infiltrate into it.

6.6.3 Use of Flow Control Structures

Flow control structures are devices attached to drainage pipes that essentially dam up the water to desired elevations. The most popular flow control structure is known as the "Agri-drainTM". While they are mainly used to control water table height for management of soil moisture content and nutrient retention, they can be used in conjunction with a P removal structure for increasing hydraulic head and controlling flow rates. This has been done for both subsurface tile drain filters and ditch filters. The ditch filter shown in Fig. 3.10 illustrates the use of a flow-control structure at a culvert pipe for maintaining a head of water on top of the PSM bed within the ditch.

6.6.4 Overflow

While P removal structures are designed to handle a specified target peak flow rate, the structure must allow for extreme flow events beyond the designed peak flow rate to by-pass or overtop the structure. For surface structures such as confined boxes, ditch filters, blind inlets, and bio-retention cells, this is not an issue since excessive water will simply over-top the structure, although a surface by-pass might avoid some erosion damage around the unit. However, for subsurface structures that treat tile drains (Fig. 3.17), a flow by-pass is essential, particularly if a PSM bed ever became clogged or developed flow restrictions. If flow was restricted in a subsurface tile drain filter, the result would be flooding within the contributing area. For a top-downward flow design, this by-pass could easily be installed by simply adding a second outlet on top of the PSM bed that would only carry water when the untreated water becomes ponded to a certain depth on top of the PSM bed. This could also be accomplished for a subsurface unit with bottom-upward flow design by placing a "T" at the inlet (Fig. 3.17b) with a check valve that has some slight resistance to opening.

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Chapter 7 Using the Phrog Software

The purpose of this chapter is to provide guidance to the users of the Phrog software with regard to (1) designing P removal structures and for (2) predicting the performance of existing or potential structures. Second, this chapter provides several examples of real scenarios for using the software. The Phrog software allows the user to quickly design a site specific and PSM specific P removal structure for meeting specified P removal goals. Normally, this process is extremely cumbersome, but the software allows for this task to be completed in minutes, and permits for exploration of adjustments in variables to examine the impact on the final design. For example, changing from one PSM to another, increasing or decreasing P removal goal or lifetime, inflow P concentration, annual flow volume, hydraulic head, preferred drainage pipe diameter, etc. Not only will the Phrog software provide a design for each scenario, but it will also provide the user with an annual table of P removal.

In addition, one of the biggest advantages of using the Phrog software is that it eliminates the need for the user to directly measure the design curve for their PSM of interest, at the P concentration and retention time of interest. Through use of several proprietary algorithms, a routine characterization of the PSM input into Phrog will allow it to predict the design curve for any P concentration and retention time. The routine characterization was described in detail in Chap. 5. This model used to predict the design curve as a function of PSM properties, input P characterization, and retention time, was validated through application to several field, pilot, and laboratory P removal reactors (Penn et al., 2016).

7.1 Designing a P Removal Structure vs. Predicting Performance of an Existing Structure

The Phrog software provides two different tabs that allow a user to either design a P removal structure, i.e. the "Design Structure" tab, or predict performance of a previously constructed or hypothetical structure i.e. the "Existing Structure" tab

Design a new structu	re	Quantify existing structure			
Design Structure Existing Stucture		Design Structure Existing Stucture			
Desired Retention Time (min)	0	Average Phosphorus Concentration (mg/L)	0		
Average Dissolved P Concentration (mg/L)	0	Annual Flow Volume (gallons)	0		
Annual Flow Volume (gallons)	0	Subsurface Drainage (Backward Pequires	0		
Desired Removal Goal (%)	0	Drainage (backward Required	0		
Desired Lifetime (years)	0	Drainage Pipe Slope (decimal)	0		
Drainage Pipe Diameter (inches)	0	Number of Subsurface Drainage Pipes	0		
Drainage Pipe Slope (decimal)	0				

Fig. 7.1 The "Design Structure" tab and "Existing Structure" tab from the Phrog software. Only one of these two will be visible at a time, but both are shown here to highlight the different inputs

(Fig. 7.1). For example, perhaps a user is not as interested in designing a custom built structure, but rather implementing the use of "cookie-cutter" or "black-box" P removal structure. In order to know how these structures will perform and how long they will last, the "Existing Structure" tab should be utilized. For custom built structures, use the "Design Structure" Tab.

7.2 Two Broad Styles for P Removal Structures: Bed vs. Ditch Structure

Regardless of whether the user is designing a structure or predicting the performance of an existing structure, the Phrog software allow the user to specify between a bed of PSMs installed on the surface or subsurface, and a P removal structure constructed within a ditch. This is found by clicking on the tabs labeled with the terms, "Bed" or "Ditch". However, the "Design Structure" tab must also be selected to correspond with the "Design Bed Size" or "Design Ditch Size" tabs in order to design those structures. Likewise, the "Existing Structure" tab must be selected to correspond with either the "Existing Bed Size" or "Existing Ditch Size" tabs, when the intention is to quantify the performance of a ditch or bed P removal structure that already exists (Fig. 7.2). All of the structures shown in Chap. 3 are examples of bed structures, except for the ditch-style P removal structure. As previously discussed, drainage ditches present a simple and readily accessible point for construction of a P removal structure. The inputs for bed and ditch structures are mostly the same, although there are some major differences that are highlighted below.



Fig. 7.2 A screenshot of the Phrog software is shown with the corresponding tabs for designing or quantifying a bed or ditch structure. The tabs on the left must correspond with the tabs on the right in order to operate the program correctly

7.3 Specific Inputs Required for Design of a P Removal Structure

The design and prediction of P removal structures are based on site inputs and on the ability of the PSM to sorb P. Site inputs (Chap. 6) are mostly average values, so the structure lifetime and P removal are only as accurate as the inputs. All design recommendations are based on an average annual P load. In reality, if rainfall is significantly less than average (most of the flow inputs are based on this condition), then the cumulative amount of P removed will be less than expected over the time period of interest. The lifetime will then increase, since less runoff is produced and thus less P loading to the structure than expected over that time period. The upside of this situation is that the PSM will last longer than expected. Again, it is critical to obtain reasonable inputs for both the PSM and site characteristics; the design and predictions are only as accurate as the inputs.

7.3.1 Chemical and Physical Characteristics of PSM to Be Used

Regardless of whether a ditch or bed structure is to be constructed, or if the purpose is to predict performance of an existing structure or design a new structure, the heart of either process is the quantification of the ability of the PSMs to remove P from solution under various conditions. In other words, a representative P removal design curve is necessary. As discussed in Chaps. 5 and 6, there are two main methods for



Fig. 7.3 Two options for the PSM design curve utilized in the structure design or prediction: estimate the design curve coefficients based on chemical characterization of PSM, or input the design curve coefficients from a previously conducted flow-through analysis (see Chap. 5)



Fig. 7.4 Using the Reset/Preset button, the user can explore structure design and predictions with various PSMs that were previously chemically characterized. Selecting one of the preset PSMs will populate the chemical characteristics shown in Fig. 7.3, under "Estimate Design Curve". CAUTION: these pre-sets should only be used for exploring potential scenarios. Do not design or predict structure performance using these pre-sets; chemical characteristics and design curve coefficients of the actual PSMs to be used must be input for accurate design and prediction

quantifying the P removal design curve for a PSM, and Phrog will allow for either approach: direct input of design curve coefficients from a measured flow-through analysis, or estimation of the coefficients as a function of PSM chemical characterization. Figure 7.3 shows the choice of tabs in Phrog for either approach. *To aid in exploring potential structure designs, Phrog has a set of PSM pre-sets (Fig. 7.4) that*



Fig. 7.5 Required input for PSM physical characteristics. These properties are extremely important in calculating the required mass of PSM and proper orientation for achieving the minimum target peak flow rate and retention time

populate the chemical characterization (Fig. 7.3). However, this should only be used to explore potential options, and never be used to design or predict performance of a real structure. Values for characterization of the actual PSM to be utilized in the structure should always be used.

The advantage of chemically characterizing the PSM and allowing Phrog to estimate the design curve coefficients, is that this allows for the design/prediction of a structure for any inflow P concentration and retention time. The user only needs to conduct a chemical characterization on the PSM of interest and input the results. On the other hand, if the user inputs design curve coefficients that were directly measured in a PSM flow-through analysis, then use of those coefficients are restricted for the inflow P concentration and retention time conditions that were utilized for that specific flow-through test i.e. it is much less flexible. Thus, the use of Phrog combined with simple chemical characterization of PSMs will save countless hours and dollars consumed in determining design curve coefficients for every possible combination of inflow P concentration and retention time for that PSM. The characterization required for estimating the design curve is shown in Fig. 7.3. The methods for analysis required for the characterization of PSMs was described in detail in Chap. 5. The required input physical characteristics window is shown in Fig. 7.5. The impact of these properties on structure design and performance was discussed in Chap. 4, and the detailed methods for analysis in Chap. 5. Briefly, the hydraulic conductivity of the PSM will have a large impact on the design of the structure since it partly dictates flow rate through a material. For materials with a very low hydraulic conductivity, the depth of material will need to be somewhat shallow, forcing the structure to be larger in area to achieve higher target peak flow rates. Materials with large hydraulic conductivity can be stacked deeper and still achieve high flow rates. However, as discussed in Chaps. 4 and 6, excessive flow rates can make it difficult to achieve a long retention time. This paradox of meeting desired flow rates and retention times described in Chap. 6 is one of the most difficult aspects of conduct-
ing a design, but as demonstrated later in this chapter, Phrog is able to complete this task quickly and accurately. The bulk density of the PSM will partly dictate the mass and volume of PSMs required, and the porosity will additionally have an impact on the retention time of the structure.

Clearly, it is critical that the user input the actual values for the material of interest that will potentially be utilized in the structure instead of relying on previously measured values for the same type of PSM collected at a different time or location. Tremendous variability may occur among the same types of PSMs, even if they are collected from the same location.

7.3.2 Site Characteristics, Constraints, and Target P Removal Goals

Every site has different drainage water flow rates, P concentrations, P loads, hydraulic head, etc., and therefore every structure will need to be designed differently, even if the exact same PSM is utilized. Thus, similar to the PSM characterization, the design or performance prediction is only as good as the site inputs. Phrog requires input for most of the site characteristics described in Chap. 6, and Chap. 6 serves as a guide for how to estimate those required inputs. Clearly, estimation of some of the input characteristics will require a site visit/survey. See Chap. 6 for details on how to obtain, measure, and estimate those inputs. Figures 7.1 and 7.2 shows the input boxes and tabs for site characteristics, constraints, and target P removal goals.

7.3.2.1 Desired Retention Time (Minutes)

The user must input the retention time they desire for the structure, but depending on the material used, the retention time may not be a constraint. This is due to the fact that for some materials, retention time has little impact on the P sorption. The Phrog software is able to determine if a material is sensitive to retention time based on the PSM chemical characterization. If the user has chosen to directly input design curve coefficients determined from a flow-through analysis instead of PSM chemical characterization (Fig. 7.3), then that same retention time used in that flowthrough analysis must be input into Phrog under "Desired Retention Time" (Fig. 7.1), in which it will become a constraint.

If a user chooses to allow Phrog to estimate the design curve coefficients based on input of the chemical characterization, and if Phrog then deems that PSM to be retention time-sensitive, then any value input for retention time will automatically change from whatever the user inputs, to 10 min. This default value of 10 min was chosen based on experimentation with several different retention times using retention time-sensitive PSMs; this high retention time for such materials will maximize P removal per unit mass, thereby decreasing the required mass of the PSM to achieve the desired performance goals. See Chap. 4 for a discussion on the impact of retention time.

For retention time-sensitive materials, the software will meet the 10 min retention time even if it has to sacrifice the minimum target peak flow rate through the filter. The relationship between retention time, flow rate, and PSM porosity is described in detail in Chap. 6. For a given retention time, the pore volume and flow rate are proportional, so to achieve a higher flow rate and keep retention time the same, the pore volume must be increased. The software makes use of this relationship in a feature demonstrated later in a case study example.

7.3.2.2 Dissolved P Concentration (mg L⁻¹)

Ideally, flow-weighted dissolved P concentrations should be input by the user. Otherwise, the user should input typical dissolved P concentrations determined by grab samples or by estimates based on soil test P values as previously discussed in Chap. 6. This value directly impacts the P load entering the structure, and therefore is a major factor controlling the mass of the PSM required to meet the desired removal goal.

7.3.2.3 Annual Flow Volume (Gallons)

The annual flow volume is also necessary for the software to estimate the dissolved P load entering the structure. The larger the annual flow volume, the larger the dissolved P load, and thus a greater requirement for PSM mass. Methods for estimating annual flow volume were provided in Chap. 6.

7.3.2.4 Desired Removal Goal (%) and Lifetime (Years)

The desired removal goal is the target cumulative percentage of dissolved P removal over a chosen time period, i.e. the desired lifetime. The desired lifetime is the number of years that is desired for the structure to last until the desired removal goal (specified by user) is met. For example, a 50% removal goal and 3 year lifetime means that the design goal is for a structure that will remove 50% of all the dissolved P that flows into the structure over a 3 year period. The greater the desired removal goal, the greater the required mass of PSM and size of structure. Realistic values must be chosen since some materials are not capable of removing extremely large percentages of dissolved P with appreciable P loading. If the user chooses a desired removal goal that is beyond the capacity of that particular PSM, then Phrog automatically reduces the desired removal goal to the maximum for that PSM, as estimated by the chemical characterization. For example, some materials that are rich in Fe and Al oxides/hydroxides are able to remove high percentages of dissolved P with appreciable P loading, other materials such as gypsum are unable to do so. The desired lifetime is used in conjunction with the desired removal goal, and therefore partly dictates how much PSM is required and how large the structure will need to be.

7.3.2.5 Drainage Pipe Diameter (Inches) and Slope (Decimal Form)

In order for both the software and the P removal structure to function, there must be subsurface drainage pipes used in the structure (Chap. 6). The program allows the user to input a specific pipe diameter. The output of the software will include the number of pipes that that the structure will require, for that specific pipe diameter; this makes it easy to compare various pipe sizes. A larger sized pipe will decrease the number needed, which could possibly reduce transportation and construction costs. When Phrog calculates the required size of the P removal structure, it takes into account the volume of the drainage pipes since this volume will not be filled with PSMs. The slope of the drainage pipe within the structure has a direct impact on the flow rate of water through the pipes. Flow rate from the pipes increase with increasing slope of the pipes. Therefore, choosing pipe slope has similar implications and flexibility as choosing drainage pipe diameter.

7.3.2.6 Minimum Peak Flow Rate Through Structure (gpm)

The "minimum flow rate" through the structure is essentially the minimum target peak flow rate that the user desires for the structure to be able to handle. Simply put, the structure must be able to handle the high flow rates produced at the site in order to be able to remove appreciable dissolved P in water; the structures cannot remove P if water does not flow through them (see Chap. 4). Methods for estimating this value on a site-specific basis was provided in Chap. 6. This value has a tremendous impact on the orientation of the structure, specifically the depth of the PSM and the area or length of the structure.

7.3.2.7 Maximum Decrease in Ditch Flow Capacity (for Ditch Structures Only: %)

First, the hydraulic head for a ditch P removal structure is ultimately a function of the depth of the ditch (Chap. 6), and Phrog takes this into account with the required inputs for a ditch P removal structure. While deep ditches are able to provide ample hydraulic head for pushing water through a thick layer of PSMs at a sufficient rate, there is a trade-off in the fact that the depth of PSM placed in a ditch is directly proportional to the loss of ditch flow capacity. Specifically, the ultimate purpose of a ditch is to quickly convey water off of the landscape; filling a ditch with a PSM will therefore decrease its ability to perform that function. For this reason, the Phrog software allows the user to specify the maximum amount of ditch flow capacity that they are willing to sacrifice in construction of the P removal structure. Thus, Phrog will limit the depth of the PSM, partly based on meeting the constraint of not exceeding this specified maximum decrease in ditch flow capacity.

7.3.2.8 Maximum Length and Width (ft)

For a bed-style structure, this is the area constraint for a site, or it could ultimately be a cost restraint. Compared to a bed structure, a ditch P removal structure is already partly fixed in area, since the ditch itself limits the area for the PSM to be placed, although ditch shape can occasionally be manipulated from trapezoidal to rectangular. For ditch structures, the maximum length is the length of the ditch that ultimately dictates the maximum size of the P removal structure. Thus, for design of a ditch P removal structure, the user must specify the maximum length of the ditch that may be utilized for the structure.

7.3.2.9 Hydraulic Head (Inches)

As previously illustrated and discussed in Chap. 6 (Figs. 6.3–6.6), the hydraulic head is essentially the maximum change in elevation from the inlet of the structure to its potential drainage point. For a buried PSM bed that treats a subsurface tile drain with water flowing from the top-downward (Chap. 3), hydraulic head is the elevation difference between the point where the tile drain enters the P removal structure, and the bottom of the ditch where the tile ultimately drains into. Usually, the elevation of the point where the tile drain enters the P removal structure is very close to the elevation of the tile drain outlet in the ditch to which it drains to. If the buried subsurface tile drain treatment structure is to be constructed for water flow from the bottom-upward (Fig. 3.17b), then the hydraulic head is the difference in elevation between the inlet to the P removal structure and the maximum depth that one is willing to allow for the PSM bed (Fig. 6.6).

7.3.2.10 Ditch Characteristics: Size and Lining (for Ditch Structures Only)

The top and bottom width of the ditch (ft), and the depth (ft) are all required inputs for ditch-style structures. The depth of a drainage ditch is essentially equal to the maximum amount of hydraulic head for a ditch P removal structure. The slope of the ditch affects the flow rate of water through that it. This is important when Phrog calculates the maximum decrease in ditch flow capacity due to placing a PSM in the ditch.

The value for Manning's roughness coefficient for the ditch lining partly describes the friction of water flowing through a ditch, as a function of the surface condition of the ditch. For example, grass, stone, or soil each result in different amounts of friction with flowing water, and therefore have a unique impact on the flow rate of water through the ditch. Surfaces and their corresponding Manning's roughness coefficients are shown in Table 6.5.

7.3.3 Additional Inputs for Predicting Performance of an Existing Structure

Most of the same variables that were described for designing a P removal structure are also used for predicting the performance of an already existing P removal structure. However, there are some additional inputs for this process. Obviously there is no need to input target P removal goals or desired flow rates and retention time. Instead, information on the size of the constructed structure is critical. Moreover, an accurate site and PSM characterization is still required.

7.3.3.1 Number of Drainage Pipes

In addition to input of pipe diameter, Phrog users must input the actual number of drainage pipes that were used in the constructed P removal structure. This is important for estimating the maximum flow rate through the structure.

7.3.3.2 Length and Width of Structure (ft)

Phrog users must input the actual dimensions of a constructed (or hypothetical) bed structure, regardless of whether it is a surface or subsurface structure. For a ditch P removal structure, only the length of the structure is required since ditch dimensions will also be input.

7.3.3.3 Mass (Tons) and Depth (Inches) of PSM

Input for PSM mass and depth is simply the actual mass and depth of the PSMs used in a previously constructed or hypothetical structure. If the mass of PSM is not known, it can be estimated using the volume and the PSM bulk density. Volume can be calculated based on the area and depth of the PSMs.

7.3.4 Optional Inputs for Estimating Total and Particulate P Removal

If total or particulate P loss from a site is a major concern, then other BMPs are better suited to reduce erosion, thereby reducing total and particulate P transport from the site. However, the Phrog software has the ability to estimate the amount of total P and particulate P removed by the P removal structure if the user provides a few additional inputs (Fig. 7.6). This will not alter the design of the structure since the purpose is to create or adapt a design for achieving a desired dissolved P removal. Total and particulate P removal is simply a calculation conducted by Phrog after the



Fig. 7.6. Optional input window for prediction of total and particulate P removal. Use of this window will not alter the design of the structure as the target for design is always dissolved P removal. However, Phrog will additionally predict total and particulate P removal after completion of the design process for achieving the desired dissolved P removal, or after input of current/hypothetical structure characteristics

design process has been completed, or after input of current or hypothetical structure characteristics. For this optional prediction, only three new variables need to be input: total P concentration, sediment concentration, and sediment deposition rate. Although this procedure requires the mean particle size diameter of the PSM, that specific parameter is already required for estimation of the PSM design curve coefficients. However, if a user inputs design curve coefficients from a flow through experiment, then it will be necessary to input the mean particle size diameter shown in Fig. 7.6 in order to predict total and particulate P reduction.

7.3.4.1 Total P and Sediment Concentration (mg L⁻¹)

Similar to dissolved P concentrations, the best input for total P and sediment concentrations is a flow-weighted mean. But again, if that is not possible, a user may obtain some typical values for total P concentrations by capturing grab samples from the site during a variety of different sized storms (Chap. 6). Also, values may be predicted from relationships developed between soil properties and losses in runoff/drainage. Programs such as SWAT are also able to predict total P and sediment concentrations in runoff (Chap. 6).

7.3.4.2 Sediment Deposition Rate (g min⁻¹)

Of all the required inputs for predicting total and particulate P reduction, sediment deposition rate is the most difficult to estimate. Deposition rate is the grams of sediment that is delivered to the structure per minute of flow. Since the flow rate and

sediment concentration entering the structure will vary, measuring the deposition rate without constant monitoring will be difficult, but it can be estimated using certain assumptions. For the demonstration of the total P removal option described below, we assumed that all of the annual flow volume would be delivered at the highest flow rate, so the minutes of flow could be calculated by dividing the annual flow volume by the peak flow rate; this resulting value (time) can then be divided into an estimate for annual sediment load (mass). As discussed in Chap. 6, use of the WEPP model can provide an estimate of both total flow duration and total sediment loss for a site, which can be used to easily calculate sediment deposition rate.

7.4 General Output from Phrog Software When Conducting a Design

The Phrog output from designing a P removal structure will include the necessary physical specifications for the construction of the structure. In addition, Phrog will also provide guidance for the user if the constraints make it impossible for obtaining a design that meets the input targets. Last, the software will also provide predictions on the actual performance of the structure with regard to flow rates, retention time, and annual P removal. Examples of these outputs will be shown in detail in the case study examples shown later in this chapter.

7.4.1 Output: Physical Construction Specifications

- *Mass of PSM required (tons)*: Simply put, this is the required mass of the PSM for meeting the P removal goals for the site conditions specified in the input, as well as the desired retention time (if retention time-sensitive). This required mass of PSM is specific to the PSM chemical characteristics input by the user, or alternatively, the design curve coefficients. Again, if design curve coefficients determined from a previously conducted flow-through analysis are input, then the user should have also input the dissolved P concentration and retention time that corresponded with that same analysis.
- *Depth of PSM (inches)*: This is the required depth in which the PSM should be placed in the structure in order to treat the water at the desired retention time (if retention time-sensitive), and additionally meet the target minimum peak flow rate.
- Depth of structure (for bed structures only: inches): The total depth of the PSMs plus hydraulic head. Occasionally, the software will estimate a depth of structure that is greater than the depth of the material in order to allow some depth of water to be "stacked up" on top of the PSM. This usually occurs for PSMs with very low hydraulic conductivity, in order to increase the hydraulic gradient and

therefore meet the required flow rate. In this situation, the structure would need to be constructed so that the excess water does not flow over the PSMs and escape untreated. In some cases this would require building the structure with sides that are higher than the elevation of the top of the PSM bed. This parameter is not calculated for ditch P removal structures because Phrog assumes that the hydraulic gradient in ditch structures is equal to 1, i.e. the ditch water is dammed up to a depth equal to the PSM depth, and no higher.

- *Length and width, or length alone for ditch structures (ft)*: The required length and width for the PSM bed. For ditch-style structures, this specification refers to the required length of the ditch that must be consumed with PSMs.
- *Number of pipes needed in structure*: Phrog will choose the proper number of drainage pipes, of the specified diameter, in order to achieve proper flow through the structure, either to limit it in order to meet a certain retention time or to meet or exceed the minimum flow requirement (see Chap. 6). Note that Phrog has a minimum PSM depth that is equal to the specified pipe diameter. This is done in order to ensure that the pipes are completely buried in the PSM. Phrog also considers the total volume of pipe in the structure when making length and width calculations.

7.4.2 Output: Predicted Structure Performance and Guidance in Obtaining a Suitable Design

- Actual retention time (minutes): This is the estimated retention time (minimum) for the structure if it is built to the physical specifications provided in the output. If the PSM is not sensitive to retention time, then the output will additionally state, "Material not sensitive to RT changes". If the PSM is sensitive to the retention time, then the software will produce a design that has a retention time equal to or greater than the desired retention time.
- Actual maximum flow rate through PSM (gpm): The software attempts to produce a design that meets or exceeds the desired minimum target peak flow rate. If the desired flow rate is not met, Phrog produces the message, "Flow rate not met". If this occurs, then Phrog will additionally provide a suggestion for increasing the lifetime of the structure in order to meet the flow rate requirement (see below).
- Actual decrease in ditch flow capacity (ditch structures only: %): This is the calculated value for the decrease in ditch flow capacity if the structure is built to the physical specifications described in the output. As previously described, construction of a ditch structure, assuming no modification to ditch dimensions, will always decrease the total ditch flow capacity since construction of a structure involves addition of solid material to the ditch.
- *Estimated lifetime to meet both the minimum target peak flow rate and retention time (years)*: This is for retention time-sensitive PSMs only. If the minimum

target peak flow rate is not met, then Phrog will calculate a suggestion for increasing the lifetime of the structure in order to meet both the flow rate and retention time. Increasing the lifetime will increase the mass of the PSM which will increase the area, and therefore the flow rate through the structure.

• Annual P removal table: This is a year by year output of cumulative P removal presented as a percentage of the total mass of P that flowed into the structure up to that time. Cumulative P removal is also presented as a load (lb). If the user chose to utilize the additional option of estimating total P and particulate P removal, then the table will additionally provide cumulative removal for those constituents as well. The final time listed in the annual P removal table is the ultimate lifetime of the P removal structure (Chap. 6). Essentially, this is the point at which the P removal structure will no longer be able to remove any dissolved P, i.e. the inflow dissolved P concentration will equal the treated water dissolved P concentration.

7.5 Case Studies Using Phrog to Design or Predict

In order to instruct and also highlight some of the various applications of P removal structures, several structures will be designed or quantified in the following sections using the Phrog software. The purpose is to illustrate how different factors affect design, and also highlight the flexibility of the software. These scenarios were chosen to help reinforce how performance goals, site hydrology, and the PSM characteristics interact to produce a viable structure and how to manipulate them to meet the user's goals. Sites and PSM characteristics are real values whenever possible, so that these examples are very representative of a real design. All screenshots shown in the following sections are taken from the current version of Phrog, which can be obtained through Oklahoma State University Technology Transfer Office.

7.5.1 Design a Ditch Structure: Details of Phrog Use and Example of How to Simultaneously Meet the Target Flow Rate and Retention Time

7.5.1.1 Inputs

The eastern shore of Maryland is drained by a series of large ditches that help prevent water from ponding on the relatively flat farmland. The agricultural land produces runoff and subsurface flow that can be elevated in dissolved P, which has caused problems with eutrophication in the Chesapeake Bay. In order to combat P loss, P removal structures have been built in these ditches to intercept and treat runoff water before it reaches the Chesapeake Bay. The ditches are an ideal interception point to treat runoff since the runoff naturally converges to them, in addition to the



Fig. 7.7 Illustration of the required ditch measurements for conducting a proper design of a ditchstyle P removal structure, or prediction of the performance of a real or hypothetical structure



Fig. 7.8 Two of the input tabs of the Phrog software are shown with values that correspond to the Maryland ditch structure example. The site flow and ditch characteristics, specifically P loading and dimensions, are highlighted%

hydraulic head for pushing water through the PSMs, which is a function of the depth of the ditch. An illustration of the inputs for designing a ditch-style P removal structure is shown in Fig. 7.7.

This particular ditch drains approximately 25 acres with an annual flow volume of 1 million gallons and an average dissolved P concentration of 1 mg L^{-1} ; this was input into the "Design Structure" tab shown in Fig. 7.8. The ditch is 12 ft wide at the top, 8 ft wide at the bottom, and 5 ft deep with a trapezoidal shape, which is com-

Design Structure Existing Stucture		Design Bed Size Existing Bed Size Desi	gn Ditch Size	Existing Ditch Size
Desired Retention Time (min)	10	Minimum Flow Rate Through Filter (gpm)	400	Л
Average Dissolved P Concentration (mg/L)	1	Maximum Decrease in Ditch Flow (%)	35]
Annual Flow Volume (gallons)	1000000	Maximum Allowable Length (feet)	500	1
Desired Removal Goal (%)	35	Ditch Top Width (feet)	12]
Desired Lifetime (years)	1	Ditch Bottom Width (feet)	8]
		Ditch Depth (feet)	5]
Drainage Pipe Diameter (inches)	4	Ditch Slope (decimal)	0.001]
Drainage Pipe Slope (decimal)	0.01	Manning's Roughness Coefficient	0.07	1

Input removal goals

Input site constraints and flow goal

Fig. 7.9. Two of the input tabs of the Phrog software are shown with values that correspond to the Maryland ditch structure example. The removal goals and flow constraints, i.e. the minimum target peak flow rate, are highlighted%

mon for drainage ditches in this region. The input ditch dimensions, ditch slope, and the Manning's Roughness Coefficient for the Design Ditch Size tab is shown in Fig. 7.8. The Manning's Roughness Coefficient was chosen to represent grass that was >6 in. Notice that the slope of this ditch is extremely flat at only 0.1%.

The minimum target peak flow rate through the filter and the maximum allowable decrease in ditch flow capacity must be chosen by the user (Fig. 7.9); these will vary from site to site. The minimum flow rate should be chosen with care since most of the P will be lost with larger events. As previously discussed, the software also allows for input of a constraint on the maximum allowable decrease in flow capacity for the ditch after installation of the filter. Given that the purpose of ditches is to convey flow from runoff or tile drainage, it is important that the ditch can still meet the purpose for which it was designed after installation of the filter. For this example we chose a minimum flow rate of 400 gpm and a maximum decrease in flow of 35% of the original; this was input into the Design Ditch Structure tab shown in Fig. 7.9. Also shown in this example, the user can input the maximum length of ditch that is able to be sacrificed for use as a P removal structure; in this case the maximum length is specified as 500 ft.

The desired removal goal and the desired lifetime must be chosen by the user; these two values will greatly impact the size of the P removal structure. Specifically, (1) the desired lifetime, (2) desired P removal goal, and (3) the affinity of the PSM for P (as quantified by the design curve) will be the biggest factors affecting the mass of PSM required, which directly impacts the total size of the structure.

For this first example, we chose to remove 35% of the annual load for 1 year (Fig. 7.9). Also for this example, we chose to use a 4 in. diameter pipe with a slope of 0.01 (i.e. 1%) as shown as input in Fig. 7.10.

The next step is to choose a PSM to be used in this structure and then input the characteristics specific to that PSM. For this example, we will use a flue-gas desulfurization (FGD) gypsum which is an industrial by-product that is rich in Ca, but poorly buffered at high pH values. Figure 7.11 illustrates the input of the physical

Input drainage pipe diameter and slope of pipe to be used in structure



Fig. 7.10. One of the input tabs of the Phrog software with values that correspond to the Maryland ditch structure example, specifically for the user's choice of drainage pipe diameter and pipe slope to be used in the ditch structure



Fig. 7.11. A screenshot of the Phrog software is shown with the chemical and physical characteristics inputs highlighted for the Maryland ditch structure design using FGD gypsum. The values for chemical characteristics will be used to estimate the P removal design curve coefficients specific to that PSM, under the conditions of the input retention time goal and average dissolved P concentration for the site. The physical characteristics are critical to determining the proper orientation of the PSM bed for meeting both the desired retention time and minimum target peak flow rate and chemical characteristics. The bulk density is used to calculate the volume required for the structure, so the structure size reported in the output will be incorrect if the bulk density is not input accurately. The actual retention time is calculated using the porosity, thus an accurate value is especially critical for retention time sensitive materials. The gypsum used in this example has a medium hydraulic conductivity of 0.01 cm s⁻¹ compared to a sieved slag which can exceed 1 cm s⁻¹.

Finally, the user must input information about the P removal design curve for the PSM. For this example, we will predict the design curve coefficients instead of direct input. Thus, we will use the "Estimate Design Curve" tab. The software estimates the P removal design curve for the specified P inflow concentrations and desired retention time for that PSM. For this purpose, the user must input a variety of chemical characteristics shown in Fig. 7.11. These chemical characteristics were discussed in Chap. 4, with the detailed methods in Chap. 5. Values for this PSM were taken from a characterization completed on an actual FGD gypsum. Based on the characterization, Phrog would classify this as a Ca-based material that is sensitive to retention time. Because of that, Phrog will automatically set the desired retention time for 10 min in the case where a structure is being designed; that is not true when the software is predicting the performance of an existing structure. Input of the retention time is shown in Fig. 7.12. With all of the inputs completed, the design is executed by clicking the "Go" button shown in Fig. 7.13.



Fig. 7.12 Input of the desired retention time for the PSM to be used in the example design for the Maryland ditch structure example. If the P removal design curve is estimated using PSM characteristics instead of direct input of the design curve coefficients, and if Phrog determines that the PSM is sensitive to retention time, then the software will automatically set the desired retention time to 10 min, regardless of what is input by the user. This is not true when Phrog is predicting the performance of an existing structure

			Amr	monium Oxalate Alum	ninum (mg/kg)	56	.32
Total P Removal (optional))		A	Ammonium Oxalate In	on (mg/kg)	60	9.64
Mean Particle Size of Filter Media (mm)			Buffer Index (equiva	alents of acid per kg o	of material to reduc	e pH to 6) 0.	318
Average Total Phosphorus Concentration (mg/L)		0		Mean Particle Size	e (mm)	0.0	0.0412
Average Sediment Concentration (m	ng/L)	0		pH		8.	8.12
Deposition Rate (grams of sediment/minu	te of flow)	0		Total Aluminum (r	mg/kg)	78	1.85
				Total Calcium (m	ig/kg)	20 25	9000
				Total Iron (mg/	(kg)	17	91.28
Material Physical Characteris	tics						
Bulk Density (o/cm ³)	1.4						
source and (grann)							
Hydraulic Conductivity (cm/sec)	0.01						
Hydraulic Conductivity (cm/sec) Porosity (decimal)	0.01						
Hydraulic Conductivity (cm/sec) Porosity (decimal)	0.01						
Hydraulic Conductivity (cm/sec) Porosity (decimal)	0.01		Design Bed Siz	Existing Bed Size	Design Ditch Size	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Stucture	0.01		Design Bed Siz Minimum Flow	e Existing Bed Size Rate Through Filter (Design Ditch Size gpm) 400	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Stucture Desired Retention Time (min)	0.01		Design Bed Siz Minimum Flow Maximum De	e Existing Bed Size Rate Through Filter (ecrease in Ditch Flow	Design Ditch Size gpm) 400 (%) 35	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Stucture Desired Retention Time (min) Average Dissolved P Concentration (mg/l.)	0.01 0.45		Design Bed Siz Minimum Flow Maximum Je Maximum Je	Existing Bed Size Rate Through Filter (ecrease in Ditch Flow Allowable Length (fee	Design Ditch Size gpm) 400 (%) 35 t) 500	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Stucture Desired Retention Time (min) Average Dissolved P Concentration (mg/L) Annual Flow Volume (gallons)	0.01 0.45		Design Bed Siz Minimum Flow Maximum De Maximum J Ditch	Existing Bed Size Rate Through Filter (ecrease in Ditch Flow Allowable Length (fee Top Width (feet)	Design Ditch Size gpm) 400 (%) 35 t) 500 12	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Stucture Desired Retention Time (min) Average Dissolved P Concentration (mg/L) Annual Flow Volume (gallons) Desired Removal Goal (%)	0.01 0.45 10 1 1000 000 35		Design Bed Siz Minimum Flow Maximum J Maximum J Ditch Ditch B	Existing Bed Size Rate Through Filter (ecrease in Ditch Flow Allowable Length (fee Top Width (feet) Rottom Width (feet)	Design Ditch Size gpm) 400 (%) 35 t) 500 12 8	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Stucture Desired Retention Time (min) Average Dissolved P Concentration (mg/L) Annual Flow Volume (gallons) Desired Removal Goal (%) Desired Lifetime (years)	0.01 0.45 10 1 1000 000 35 1		Design Bed Siz Minimum Flow Maximum D Maximum J Ditch Ditch B Ditch B	Existing Bed Size r Rate Through Filter (cerease in Ditch Flow of Allowable Length (feet) hottom Width (feet) ch Depth (feet)	Design Ditch Size gpm) 400 (%) 35 t) 500 12 8 5	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Stucture Desired Retention Time (min) Average Dissolved P Concentration (mg/L) Annual Flow Volume (gallons) Desired Removal Goal (%) Desired Lifetime (years)	0.01 0.45 10 1000 000 35 1		Design Bed Siz Minimum Flow Maximum D Maximum / Ditch B Ditch B Ditch D	Existing Bed Size Rate Through Filter (ecrease in Ditch Flow ie Allowabie Length (feet Top Width (feet) ch Depth (feet) h Slope (decimal)	Design Ditch Size gpm) 400 (%) 35 (%) 500 12 8 5 0.001	Existing Ditch	Size
Hydraulic Conductivity (cm/sec) Porosity (decimal) Design Structure Existing Structure Desired Retention Time (min) Average Dissolved P Concentration (mg/L) Annual Flow Volume (gallons) Desired Removal Goal (%) Desired Lifetime (years) Drainage Pipe Diameter (inches)	0.01 0.45 10 1 1000000 35 1 4		Design Bed Siz Minimum Flow Maximum D Maximum / Ditch B Ditch B Ditch B Ditch Manning's	e Existing Bed Size (Rate Through Filter (ecrease in Ditch Flow Allowable Length (fee Top Width (feet) ototom Width (feet) n Slope (decimal) Roughness Coefficien	Design Ditch Size gpm) 400 (%) 35 (%) 500 12 8 5 0.001 nt 0.070000-	Existing Ditch	Size

Fig. 7.13 After all inputs are completed, execute the design or prediction by clicking the "Go" button

7.5.1.2 Outputs and Responding to Unmet User Goals

The output from Phrog contains all of the information required to build a P removal structure and includes information about removal performance and whether or not the user's goals were met. The output for the example ditch structure design is shown in Fig. 7.14 with the specific structure requirements highlighted. The first line is the required mass of PSM, which in this case is 45.37 tons of gypsum; this amount of gypsum could be delivered in two tractor trailer loads. The depth of material is only 6.3 in., which is not surprising given the low hydraulic conductivity of this material. Low conductivity materials must be spread thin over a large area to be able to handle appreciable flow rates and not exceed the maximum decrease in ditch flow capacity specified by the user. Phrog constrains the depth of material to be no less than the diameter of the subsurface drainage pipe, so that water has to flow through the material before entering the pipe. The output also specifies the length of the ditch structure to be 281.7 ft. Last, the number of subsurface drainage pipes required for this ditch structure is shown to be four pipes, of the diameter specified by the user (4 in.). If the software calls for more pipes than the user wishes to use, simply increase the pipe diameter or reduce the minimum flow rate through the filter at the input, and rerun the program.



Specifications on how to build structure with FGD gypsum: 35%-one year removal

Fig. 7.14 A Phrog screenshot of the output of physical requirements for the first attempt to design the Maryland ditch structure using FGD gypsum as the PSM, and a goal of 35% P removal over 1 year

The rest of the output shows how well the design met the user's constraints and goals, which is highlighted in Fig. 7.15. The software calculates and reports the actual retention time at the maximum flow rate for the structure, after the design is completed. If the PSM is not retention time sensitive then the output will state "non-retention time sensitive". In some rare cases, if the retention time is not met for a sensitive material a message will appear in red. For this current example, Fig. 7.15 shows that Phrog was able to produce a design in which the minimum retention time was met, but was not able to meet the minimum target peak flow rate through the structure. Phrog reports the actual flow rate that the structure can handle and highlights it in red if it is less than the user's specified goal. The actual decrease in ditch flow is also listed as a percentage of the original flow. In this example the material was shallow enough that there is no decrease in ditch flow with the addition of the P removal structure.

For design outputs that are unable to meet the flow requirements, there is an additional calculated output variable that estimates the lifetime required to meet both the retention time and minimum target peak flow rate goals. As the lifetime is increased, the required mass of PSM increases, which increases the pore volume and surface area. The increased surface area increases the flow rate through the material, but does not sacrifice retention time, because a proportional amount of pore space is also added with the increased mass. This in turn makes higher flow rates attainable without reducing the retention time, so both goals can be met. For some PSMs that are not sensitive to retention time and have very low hydraulic



Fig. 7.15 A Phrog output screenshot for the design of the Maryland ditch structure for the first attempt that highlights the goal report. In this example, the retention time goal of 10 min was achieved, but the minimum target peak flow rate was not, as evident by the corresponding message. In such a case, Phrog will provide a new suggested lifetime to input in order to meet both the flow rate and retention time goal. The PSM used in this example is FGD gypsum with a P removal goal of 35% over 1 year



Fig. 7.16 A Phrog output screenshot for the design of the Maryland ditch structure for the first attempt that highlights the P removal performance over the lifetime of the designed structure, based on the output specifications shown in Fig. 7.14. The PSM used for this example is FGD gypsum with a P removal goal of 35% over 1 year

conductivity, the increase in mass and therefore surface area can help increase flow of the water down into the subsurface drainage layer, allowing for greater flow rates through the filter. Regardless, the user simply needs to change the desired lifetime to the one suggested in red text and rerun the software.

The last portion of the output is a table that specifies P removal on an annual basis, expressed as both a percentage of the cumulative dissolved P removed and the cumulative mass (in lb) removed (Fig. 7.16). In this example, the design meets the user goal of 35% cumulative P removal in 1 year, but the table shows that the material will last 1.733 years (i.e. "ultimate lifetime"), removing 21.5% of the dissolved P that enters the structure during that time. The final listed time is essentially the



Fig. 7.17 Phrog output screenshot for the second attempt for the design of the Maryland ditch structure with FGD gypsum after increasing the input lifetime from 1 to 3 years. Notice that after re-running the program with an increase in the input lifetime goal of at least 1.3 years, as suggested after the first design attempt, that both the retention time and flow rate goals are now met

predicted total lifetime that the P removal structure will be able to remove any dissolved P at all. At that point, the concentration of dissolved P entering the structure is the same as the concentration of treated water exiting the structure, and therefore the material is "spent". The year by year breakdown provides the complete performance of the structure and allows the user to make an informed decision on when to replace the PSM.

Since the design did not meet our minimum flow goal, and thus it called for increasing the lifetime in order to meet the goal, we will rerun the program with an increased lifetime of 3 years instead of 1 year. All of the other inputs were left unchanged before clicking "Go" to obtain the new output shown in Fig. 7.17. The mass increased from 45.3 to 136 tons or three times as much, which makes sense given the increase in lifetime from 1 to 3 year. The depth of material increased from 6.3 to 14 in., which caused the length of the structure to only increase an additional 60 ft for a final length of 340 ft; this was well within the maximum of 500 ft we input for this example. The specified user goals were all achieved as shown in the output; flow rate of 444 gpm and retention time of almost 24 min. A dramatic change in the output compared to the previous output is found in the table of annual performance; this structure is predicted to last a bit over 5 years before it is spent, compared to the previous 1.7 years in the last example. If this larger structure exceeded the available length, then another PSM with a greater P affinity would be required, or the user could decrease the acceptable minimum flow rate.

7.5.1.3 Conducting a Second Ditch Structure Design for the Same Site with a Different PSM

One benefit of Phrog is the ability to test out a variety of scenarios for a site, such as different PSMs or performance goals, without having to do the cumbersome calculations by hand or spreadsheet. Using the same inputs for site characteristics and goals, the continuing example illustrates a change in the PSM from the FGD gypsum to a medium quality steel slag that has been sieved to particles >1/4 in. diameter. In this case, the pre-set input chemical characteristics for a medium quality, sieved EAF slag was used. The physical characteristics input into Phrog included bulk density, hydraulic conductivity, and porosity values of 1.7 g cm⁻³, 1 cm s⁻¹, and 0.38, respectively. The output from the same scenario with this steel slag is shown in Fig. 7.18. This PSM is also a retention time sensitive material, so the retention time of 10 min was met at the cost of the minimum flow rate that was specified (400 gpm). The structure is much smaller in length than the previous 1-year gypsum design due a greater depth of material: 18 in. versus 6.3 in. for the gypsum, which allows for a much shorter structure (only 46 ft long). Unfortunately, the minimum flow rate was not met, so we will increase the desired lifetime to 3 year based on the suggestion to increase to at least 2.66 years, and re-run the program. The output shown in Fig. 7.19 shows that all of the goals, including removal percentage, retention time, minimum flow rate, and decrease in ditch flow, were all met. This slag ditch structure uses less material and less space than the previous FGD gypsum design, so it may be a better option if slag is locally available.

The medium quality steel slag was an improvement over the gypsum with regard to space, but neither material was able to meet all of our goals with a desired lifetime of 1 year. However, there is a treatment process that can, on average, increase the P affinity of the slag by four times that of an untreated slag of the same particle size (see Chap. 4). For this next example, we will use all of the same inputs as the previous examples and only change the chemical characteristics of PSM to reflect this "treated" slag material. The design output using this treated slag in the ditch with a desired lifetime of 1 year is shown in Fig. 7.20. By using the treated slag we were able to meet all of the specified goals, including the minimum flow rate at a desired lifetime of 1 year. The other two materials required increasing the structure lifetime in order to meet all of the goals.

The most obvious difference between the treated slag, untreated slag, and FGD gypsum is their affinity for P which is evident by the mass required to meet the removal goal; 6.4, 31.8, and 45.4 tons, respectively. Both of the slag structure designs were much shorter in length than the gypsum structure due to their higher hydraulic conductivity which allowed for the material to be deeper, yet still maintain high flow rates. While the treated slag might seem like the obvious choice, there are other factors to consider: availability of PSM, size of the structure (i.e. length or area), ability to treat the slag, and the cost associated with all of these factors. Another advantage of the treated slag is the ability to chemically rejuvenate it several times prior to disposal (Chap. 4).



Fig. 7.18 Phrog output screenshot for the first attempt for the design of the Maryland ditch structure using a medium quality sieved EAF steel slag for a P removal goal of 35% over 1 year. Similar to the first design attempt with FGD gypsum, notice that the minimum target peak flow rate was not met, and thus Phrog provided a suggested revised input for lifetime in order to satisfy both flow rate and minimum retention time



Fig. 7.19 Phrog output screenshot for the second attempt for the design of the Maryland ditch structure using a medium quality sieved EAF steel slag for a P removal goal of 35% over 3 years. All constraints were met



Fig. 7.20 Phrog output screenshot for the design of the Maryland ditch structure using a treated and sieved EAF steel slag for a P removal goal of 35% over 1 year. All constraints were met. Notice the appreciably lower mass required compared to the FGD gypsum and non-treated slag design for the same scenarios in Figs. 4.14 and 4.18

7.5.2 Predict Performance of an Existing Ditch Structure

Not only does the Phrog software allow users to design a structure to meet certain goals, as shown in the previous examples, but it can also be used to quantify the performance of an existing structure. The site characteristics used in the previous example were taken from actual data collected at a Maryland ditch structure, so we will use the same inputs to estimate the performance of a real ditch structure that has been constructed. This particular structure contains FGD gypsum. Use of the software for predicting the performance of a structure also requires input of PSMs chemical and physical characteristics. The input tabs for "Existing Structure" shown in Fig. 7.21 require similar information as the "Design Structure" tabs. The site characteristics include the average dissolved P concentration and annual flow volume, as illustrated in the previous examples for the design process.

The size of the ditch and flow characteristics, such as the slope and Manning's roughness coefficient, are used to calculate the peak flow rate of the ditch, in order to estimate the decrease in flow rate due to the structure. The mass of PSM and its orientation, depth and length in this case are each input into the software in order to predict performance. Finally, the diameter and number of subsurface drainage pipes utilized are input by the user, allowing for calculate what the retention time will be for the structure, and if the PSM is sensitive to retention time then this will be reflected in the design curve used to predict P removal. After running the program,



Fig. 7.21 Input data for the case study example of estimating the performance of a previously constructed ditch-style P removal structure. Phrog input for prediction of performance requires site characteristics including ditch dimensions and also structure measurements-characteristics



Fig. 7.22 Phrog output for predicting the performance of an existing ditch-style P removal structure located in Maryland, containing FGD gypsum. The input site characteristics for flow and actual structure measurements for this example are shown in Fig. 7.21. The chemical and physical characteristics of the FGD gypsum used in this structure is the same used for the previous ditch design example, as shown in Fig. 7.11

the output quantifying the ditch structure will have three main parts as shown in Fig. 7.22. The first part reports the maximum flow through the structure (gpm) and the retention time (min). The next portion is the actual decrease in total ditch flow capacity due to the construction of the structure, which was 60.7% in this case. Since this is an existing structure, there is nothing that can be done to change this loss of flow capacity until the PSM is replaced. Considering that these drainage ditches were constructed to handle a certain amount of flow, a large loss in flow capacity such as this could lead to possible flooding. While it is useful to quantify an existing structure with Phrog, if this structure had instead been initially designed

using Phrog and then built accordingly, the large loss in ditch flow capacity could have been prevented by simply specifying a desired maximum. The last portion of the output is the year by year breakdown of the cumulative P removal both as a percentage and a load of dissolved P. The final entry in the table is when the PSM is no longer able to remove any dissolved P ("ultimate lifetime").

7.5.3 Design a Subsurface Bed Structure for Treating Tile Drainage

Tile drained fields are common in the Midwest due to high water tables that interfere with agricultural operations. Water is drained from underneath the surface using a series of pipes which feed into drainage ditches (Chap. 3). Unfortunately, the effluent from these drains can contain high concentrations of N and P. Phosphorus removal structures can be implemented with other best management practices (BMPs) to help reduce nutrient loss from the site. There are several locations within these watersheds where a P removal structure could be built, including in the drainage ditches, as a blind inlet, or as a buried bed between the tile drain and the drainage ditch. For this example, we will focus on designing a structure that is a subsurface bed (top-downward flow) located between the end of a tile drain and a drainage ditch (such as the structure shown in Fig. 3.17a). This particular field produces 4,755,000 gal of drainage annually, a peak flow rate of 71.3 gpm, and an average dissolved P concentration of 0.28 mg L⁻¹. As shown in Fig. 3.17a, the structure would be supplied by a trunk line and be located below the surface in order for water to freely flow through the structure. Ultimately, if the design is for flow from the top-downward, it is the elevation of the tile drain outlet in the ditch and the distance between that outlet and the bottom of the ditch that provides the hydraulic head for drainage. Thus, the buried bed of PSMs cannot be deeper than the elevation of the bottom of the ditch into which it drains. This is not true if the PSM bed is constructed to flow from the bottom-upward (Fig. 3.17b).

For this first example we are designing a subsurface bed that is constrained to 30 ft by 30 ft based on the site characteristics, with removal goals shown in Fig. 7.23. While there is a relatively large volume of annual runoff, almost 5 million gal, the P concentration of 0.28 mg L⁻¹ results in an annual P load that can be handled with a relatively small sized structure. We will set a goal to remove 45% of the load for 1 year. For this potential structure, there were several PSMs that were locally available and properly characterized. Thus, we will design this structure using two of those PSMs: a Ca-based drinking water treatment residual (WTR) and wollastonite, a calcium silicate mineral. We will start with the WTR which is a relatively fine material with a mean particle size of 1.8 mm, bulk density of 1.2 g cm⁻³, and a hydraulic conductivity of 0.005 cm s⁻¹. Shown in Fig. 7.24, the design output for the Ca-based WTR meets all of our goals with a little over 6 tons of PSM in a structure that is 30×14 ft. Notice that because of the low hydraulic conductivity of this PSM, the design requires 7.1 in. of head on top of the



Input site characteristics

Fig. 7.23 Input for example of the design of the subsurface tile drain structure (bed structure). For this example, the structure is to be designed to utilize a Ca-based drinking water treatment residual (WTR) as the PSM.



Fig. 7.24 Design output for the subsurface tile drain P removal structure using input shown in Fig. 7.23, a 45%-1 year removal goal, and a Ca-based WTR as the PSM

4.9 in. depth of the PSM (i.e. 12 in. total depth of structure). Thus, this structure must be constructed to allow for the tile drain water to "stack up" 7.1 in. on top of the PSM bed. The structure design will meet our 1 year goal of 45% and it will last over 2 years before it is completely spent.

What if we wanted to remove more P in 1 year than 45%? Using the same site characteristics and PSM, a designer could change the desired removal from 45% to 70% and observe how this changes the design. The 70% removal design shown in



Fig. 7.25 Design output for the subsurface tile drain P removal structure using input shown in Fig. 7.23, with an increased P removal goal of 70% over 1 year, using the same PSM that was used in Fig. 7.24 (Ca-based WTR). Notice the increase in size and longevity compared to the design in Fig. 7.24

Fig. 7.25 is only 1.5 times the area of the structure that removed 45%, but still fits within our constraints of a 30×30 ft bed. Notice that this was achieved because the PSM bed thickness increased from 4.9 to 7.8. This illustrates how Phrog will always minimize the area of the structure when attempting to meet all of the constraints. The predicted performance of this structure is much better than the previous scenario even though it is only slightly larger in area than the original design. Instead of being spent after about 2 years, this structure will last just over 6 years and it will remove over 14 lb of P compared to the 5.8 lb for the previous design. The Phrog software makes it easy to compare a variety of situations which allows the user an opportunity to choose a design that meets their needs at the greatest feasibility. The table output provided shows a breakdown of the annual cumulative P removal, allowing the user to choose the most feasible time to replace the PSM in the structure. For this example, the structure removed almost 8 lb in the first year, but that dropped off quickly with only an additional 3.63, 1.69, and 0.8 lb for years 2, 3, and 4, respectively.

7.5.3.1 Example of Exceeding Area Constraint

For the final example with this material, we will use the same inputs and change the removal goal to 70% for 5 years. The structure does not fit in our maximum allowable area (Fig. 7.26). The program will continue with a design by estimating the minimum size. It does meet our removal goal and will continue to remove P for just over 30 year. If the PSM is left until spent, this structure will remove 72.22 lb of



Fig. 7.26 Design output for the subsurface tile drain P removal structure using input shown in Fig. 7.23, with an increased P removal goal of 70% over 5 years, using the same PSM as used in Figs. 7.24 and 7.25 (Ca-based WTR). Notice that the area constraint for the structure was exceeded. However, Phrog will still continue with the design and prediction table. The size and degree of P removal is much greater compared to the structure designs in Figs. 7.24 and 7.25

dissolved P, but should it be replaced sooner? There is a tradeoff between the cost of replacing the PSM in the structure and the amount of P being removed by the structure that will dictate when it should be cleaned out. The cleanout schedule will depend on a variety of factors, including removal goals and availability of funds. It is important to remember that the software makes all calculations based on the user inputs, so the design is based on an average year. If the site is located in an area that is experiencing drought and does not produce runoff, then the structure will not remove the estimated amount of P and will last longer than predicted.

7.5.3.2 Example of Comparing Two Different Ca-Based PSMs in Structure Design

For the next example we will use the same inputs as the first scenario with one change: the PSM used will be wollastonite. Wollastonite is a Ca silicate mineral that contains some Fe, Al, and magnesium (Mg), so it will be in the Ca-based group of materials. Because it relies on Ca phosphate precipitation, the pH must be above neutral and the material must be able to maintain that elevated pH in order for the PSM to be effective at removing P. The design output for this structure for a 45%-1



Fig. 7.27 Comparison of design output for a 45%-1 year removal goal for a Wollastonite PSM vs. the Ca-based WTR in Fig. 7.24, for the subsurface tile drain P removal structure using input shown in Fig. 7.23. Notice the dramatic size increase (area and mass) compared to Fig. 7.23

year removal goal is shown in Fig. 7.27, which is in sharp contrast to the structure design for the Ca-based WTR shown in Fig. 7.24 under the same conditions. The mass of wollastonite required to meet the goals is about 64 tons and covers an area of 3681 ft² compared to just over 6 tons of WTR that fit in 420 ft². The two materials have one distinct chemical difference: their buffer index, which is ten times higher for the WTR. This buffering has a dramatic impact on the ability of a Ca-based material to sorb P, which is highlighted in the difference in the mass required for wollastonite and WTR in meeting the same P removal goals. If the user only has a small area available for the P removal structure, then the wollastonite would not be feasible with the current goals, so another PSM would have to be used or the removal goals would need to be reduced. The ability to easily work through these different scenarios with Phrog allows the user to find the appropriate design for their needs.

7.5.4 Predict the Performance of a Blind Inlet and Demonstration of Predicting Particulate and Total P Removal

In tile drained fields there are small depressions where water collects that were originally drained using tile risers. This riser would connect the surface to the tile drain below, but circumvent the soil allowing sediment and nutrients to reach the tile drain without coming into contact with the soil. In order to help reduce nutrient and sediment loss, some tile risers have been replaced with inlets that consist of a gravel or sand bed that connects to the tile drain. An example of these blind inlets are



Fig. 7.28 Physical and chemical characterization input for a sieved limestone used in the blind inlet example. Notice that the optional information for predicting total and particulate P removal was also input.

shown in Figs. 3.14 and 3.15. Water flows through the porous media before entering the tile drain which allows for sediment deposition and sorption of nutrients. The media used for these inlets is usually a gravel or sand which work well for physical filtration. If the gravel used is a limestone material then precipitation of Ca phosphates is possible depending on the pH and buffering capacity of the material. If the media is a PSM, then these inlets can be considered a P removal structure since it encompasses all of the characteristics of a structure (Chap. 3), and therefore can be designed or estimated using the Phrog software. For this example we will examine a blind inlet for an Indiana field that drains about 12 acres with an average dissolved P concentration of 0.25 mg L⁻¹, total P concentration of 0.75 mg L⁻¹, sediment concentration of 10 mg L⁻¹, and produces an annual flow volume of 2,830,000 gal.

We will use Phrog to estimate the removal performance of an existing blind inlet using the site characteristics previously listed. The blind inlet is $14 \times 14 \times 2$, and filled with 16 tons of limestone gravel. For predicting the performance of an existing or hypothetical structure, this information must be input along with the chemical and physical characterization of the PSM in the structure (Figs. 7.28 and 7.29). The software will use the dimensions of the filter and the number of drainage pipes in conjunction with the physical characteristics of the PSM to calculate flow through the filter and the retention time. This information is reported along with removal performance. Notice that for the current structure drainage input, we only input a single 4-in. drain pipe; even though the blind inlet contains several pipes, the flow rate is limited to the single drain pipe that all of the pipes are connected to. For this blind inlet, the material is a relatively large limestone gravel with a mean particle size of 8 mm and a relatively low buffer index as shown in Fig. 7.28. The chemical characteristics of limestone gravel can vary with the source, so it is important to characterize prospective PSMs in order to accurately estimate P removal. In addition, because we have knowledge of the total P and sediment concentration flowing into the blind inlet, we will also predict total and particulate P removal.



Fig. 7.29 Input of site characteristics and dimensions of a hypothetical blind inlet used in the example for predicting the performance of a previously constructed blind inlet.

Dradiated lineactors								
Predicted ilmestone		Quanti	fying an E	xisting	g Structure (Bed)			
blind inlet performance	Actual flow rate through the filter (gpm)					73.9861		
Existing Bed Structure	Actual	retention	time (min)			16.409		
	Years	DP (%)	DP(lbs)	PP (%)	PP(lbs)	TP (%)	TP(lbs)	
	0.9854	21.5	1.251	31.51	0.9688	28.18	2.219	
		Quant	ifying an	Existing	g Structu	re (Bed)		
Predicted slag blind	Detual	flow rat				72 9961		

Due distant also a blind		Quanti	liying an	Existing	g structur	e (Bed)	
Predicted slag blind	Actual	5					
inlet performance	throu	igh the fi	ilter (gpm)				
Existing Bed Structure	Actual :	retention	time (min)		12.1924	
Entrolling Dea orraceare							
	Years	DP (%)	DP(lbs)	PP (%)	PP(lbs)	TP (%)	TP(lbs)
	1	30.44	1.797	93.79	2.926	72.67	4.723
	1.465	21.5	1.859	93.79	4.286	69.69	6.145

Fig. 7.30 The predicted performance of the hypothetical blind inlet containing a either a sieved limestone material or sieved slag, with site and structure characteristics shown in Figs. 7.28 and 7.29. Note that the sieved slag has superior dissolved P and particulate P removal due to a greater pH buffer index and smaller particle size, respectively.

The Phrog output for quantifying an existing structure is different from the design output since the structure is already built, and therefore only the performance is reported as shown in Fig. 7.30. The first item reported is the actual maximum flow rate through the structure, and the corresponding retention time. The other portion of the output is the same removal performance table that is produced for the design of a structure. This blind inlet will remove about 1.25 and 2.2 lb of dissolved and total P, respectively, in about 1 year before it is no longer able to removed dissolved P.

For the next example, we investigate how the blind inlet would perform if we replaced the sieved limestone gravel with a sieved slag material. The results are also

		Quanti	fying an	Existing	g Structu	ce (Bed)	
	Actual throu	flow rate igh the fi	; ilter (gpm)			73.9861	
	Actual	retention	time (min	.)		11.5828	
	Years	DP (%)	DP(lbs)	PP (%)	PP(lbs)	TP(%)	TP(lbs)
	1	53.67	3.168	19.45	0.6068	30.86	3.775
	2	43.72	5.162	19.45	1.214	27.54	6.376
Existing Bed Structure	3	37.44	6.632	19.45	1.82	25.45	8.452
-	4	32.67	7.715	19.45	2.427	23.86	10.14
	5	28.84	8.514	19.45	3.034	22.58	11.55
Prodicted treated	6	25.7	9.103	19.45	3.641	21.53	12.74
Fieulcieu lieuleu	7	23.08	9.537	19.45	4.248	20.66	13.78
slag blind inlet	8	20.87	9.857	19.45	4.854	19.92	14.71
side sinta inter	9	19.	10.09	19.45	5.461	19.3	15.55
performance	10	17.39	10.27	19.45	6.068	18.76	16.33
	11	16.01	10.39	19.45	6.675	18.3	17.07
	12	14.81	10.49	19.45	7.282	17.9	17.77
	13	13.76	10.56	19.45	7.889	17.55	18.45
	13.03	13.73	10.56	19.45	7.907	17.54	18.47

Fig. 7.31 The predicted performance of the hypothetical blind inlet containing a sieved-treated slag material, using site and structure characteristics shown in Figs. 7.28 and 7.29. Notice the increase in dissolved P removal compared to non-treated slag in Fig. 7.30

shown in Fig. 7.30. The blind inlet with slag has a greater ultimate lifetime and P removal. While both structures have an appreciable retention time, the slag blind inlet has superior dissolved P removal compared to the limestone due to a greater pH buffer index. This further illustrates the importance of the ability of a Ca-based PSM to buffer the pH above 6.5 with regard to dissolved P removal (Chap. 4). The particulate P removal of the slag material was also higher in the slag blind inlet due to the smaller particle size; the mean particle size diameter of the limestone was 8 mm compared to 1.1 mm for the slag. Notice that the flow rate through the structure did not change; this is because both materials have a very high hydraulic conductivity, and therefore the flow rate was limited by the maximum flow capacity of the single 4 in. pipe that drained the blind inlet.

For the last comparison, we maintained the exact same conditions, but changed the PSM in the current blind inlet to a treated slag material (Chap. 4). The results in Fig. 7.31 illustrate the superior ability of treated slag to remove dissolved P compared to normal slag and limestone. Another advantage of the treated slag is that it can be chemically rejuvenated several times before it is no longer effective at removing dissolved P; depending on how the P removal structure is designed, this rejuvenation could be conducted in place.

This series of examples illustrated the influence of PSM quality on P removal, so it is vital that the PSMs used, or to be used, have been adequately characterized both chemically and physically. Using the PSM characterization and Phrog, a user can explore a variety of scenarios, including different PSMs and goals. While this series of examples was dedicated to predicting the performance of constructed blind inlets, it is important to keep in mind that one could easily use Phrog to actually design the blind inlets in order to achieve desired flow rate, dissolved P, particulate P, and sediment removal.

7.5.5 Bio-retention Cells

Runoff from urban areas is an issue due to large impervious areas, such as parking lots where water cannot infiltrate, resulting in a large volume of runoff produced in a short time period. Low impact development reduces the change in a site's hydrology due to urban development by utilizing green roofs, permeable pavement, bioretention cells, and other BMPs that increase infiltration or buffer runoff. The bio-retention cell, or "rain garden", is constructed by removal of native soil which is replaced by a media layer, like the one shown in Fig. 3.16. The surface of the bioretention cell is covered with a thin layer of soil or rocks which serve as growth media for plants, such as bushes or grass. The subsurface drainage and the porous media make an easy path for water to flow through after it passes through the initial soil or rock layer. The size of the bio-retention cell is a product of the runoff volume produced in a specific sized storm that the designer wishes the structure to handle. A completed bio-retention cell, such as the one shown in Fig. 3.16, can make an attractive addition to the landscape while also aiding in storm water retention and treatment of runoff water depending on the type of filter media used. Similar to blind inlets, if a PSM is used as the filter media and the area has elevated P, then the bio-retention cell meets all of the characteristics of a P removal structure (Chap. 3). Runoff enters the structure and flows through a PSM, and the PSM can be cleaned out after it is eventually spent. Since the bio-retention cell is a bed of material with a drainage layer, it is no different than any other PSM bed, and thus requires the same inputs.

7.5.5.1 Example Bio-retention Cell Design and Demonstration of Altering Subsurface Drainage Pipe Diameter

The inputs and desired removal goals for an example site are shown in Fig. 7.32, taken from a real urban site. For this example, a new media for use in bio-retention cells will be applied: a 95% fly ash-5% sand mixture as the PSM. The goal is to remove 50% of the cumulative P load over 25 years. The site produces almost 200,000 gal of runoff annually that has an average dissolved P concentration of 0.5 mg L⁻¹. The maximum size of the bio-retention cell is 35 ft wide, 35 ft long, and 2 ft deep, and it must be able to handle at least 40 gpm. This is a relatively small flow rate to handle and the resulting annual P load of 0.2 lb of P would normally not require a large structure, but the desired lifetime of 25 year will require a large structure.

For the initial design shown in Fig. 7.33, this structure will require four 2-in. diameter pipes to achieve 46.6 gpm of flow. All of our goals and constraints are achieved with 108.7 ton of PSM that is placed in a $35 \times 32 \times 2$ ft deep structure. The design meets our flow and dissolved P removal goals while fitting within the maximum area. This structure will remove 10.2 and 13.5 lb of dissolved and total P, respectively, over 25 years, with an ultimate lifetime of 72 years while removing 21.5% and 50.9% of the dissolved and total P load, respectively, before the material is spent.

		Estimate Design Curve	Manually Input D	esign Curve (y=be ^m	×)		
		Ammonium Oxalate Aluminum (mg/kg)					
Total P Removal (optional)	Am	34					
Mean Particle Size of Filter Media (mm)	2.27	Buffer Index (equivalents of acid per kg of material to reduce pH to 6)					
Average Total Phosphorus Concentration (mg/L)	0.8		2.27				
Average Sediment Concentration (mg/L)	1.5		8.479				
Deposition Rate (grams of sediment/minute of flow	v) 0.05		Total Aluminum (r	na/ka)		556	
			Total Aluminum (r	ng/kg)		00057	
			Total Calcium (m	g/kg)		9957	
			Total Iron (mg/	kg)		694	
Material Physical Characteristics							
Bulk Density (g/cm ³) 1.5	55						
Hydraulic Conductivity (cm/sec) 0.2	36						
Porosity (decimal) 0.3	31						
Design Structure Existing Stucture		Design Bed Size	Existing Bed Size	Design Ditch Size	Existing D	itch Size	
Desired Retention Time (min) 10		Maximum Width	of Structure (feet)	35			
Average Dissolved P Concentration (mg/L) 0.5		Maximum Length	of Structure (feet)	35			
Annual Flow Volume (gallons) 196258	3	Minimum Flo	ow Rate (gpm)	40			
Desired Removal Goal (%) 50		Hydraulic H	lead (inches)	24			
Desired Lifetime (years) 25		Note: Hydraulic H	lead is equal to the eleve	ation drop over			
		the maximum leng	gth or the elevation diffe	rence between			
Drainage Pipe Diameter (inches) 2		in	let and ultimate outlet.				
Drainage Pipe Slope (decimal) 0.01							

Fig. 7.32 Input for designing a bio-retention cell using a 95:5 ratio of sand:fly-ash as the PSM for a target cumulative P removal of 50% over 25 years. Inputs include site flow characteristics and hydraulic head, PSM chemical and physical characteristics, size constraints, minimum target peak flow rate, and P removal goals and lifetime. Input characteristics are courtesy of Dr. Glenn Brown, Oklahoma State University

The diameter and slope of the pipes used in the subsurface drainage layer have a dramatic effect on the maximum flow rate a structure can handle. The choice of pipe diameter can impact the cost of materials and installation, so we will look at a couple of alternatives to this design. We will use all of the same site characteristics, goals, constraints, and PSM, but use a different diameter pipe. In comparison to specifying a 2-in. diameter pipe for construction in the input, changing this value to 4-in. or 6-in. diameter pipe results in dramatic increases in the flow rate of the bioretention cell. While the specification of different pipe size does not impact the total mass of PSM required for meeting the P removal goal, the 2, 4, and 6-in. drain pipe resulted in maximum flow rates of 46.6, 73.9, and 218.1 gpm. The limiting factor in flow rate through the structure in this case is due to the subsurface drainage, so the increase in flow is due solely to the increased pipe diameter. This also changes the number of required pipes from four to one. While the required mass of PSM is not affected, the size of the structure may be affected: for example, increasing the specified pipe diameter increased the width of the structure by 0.05 ft. Phrog will automatically increase the size of the structure to compensate for the volume displaced by the subsurface drainage pipes. Phrog allows the user to try out a variety of pipe sizes and slopes for each design.

	Bed Output						
	Mass	Require	d (tons)	108.7			
tructure physical design	Depth o	of Materi	al (inches)				
ci accure priysical acsign	Depth o	f Structu	are (inches	1)	24		
necifications	Lengt?	of Stru	cture (ft)	35.			
pecifications	Width	of Struc	cture (ft)			32.1358	
	Numbe	r of Subs	urface			4	
	Dra	inage Pip	pes Needed				
	٨	ctual RT	(min)		Material to RT	is not se changes .	nsitive 111.771
Meets flow rate goal	Actual M Rate 1	(aximum F Through t	low he PSM (gps	n)	46.6083		
	Estimat to me	ed lifeti et both s	ime ninFR and R	т		144	
	Years	DP (%)	DP(1bs)	PP(%)	PP(lbs)	TP(%)	TP(lbs)
	1	96.88	0.7933	100.	0.1298	98.05	0.9231
	2	93.89	1.538	100.	0.2596	96.18	1.797
	3	91.02	2.236	100.	0.3894	94.39	2.625
	9	88.27	2.891	100.	0.5192	92.67	3.41
	5	85.63	3.506	100.	0.649	91.02	4.155
	0	83.1	9.083	100.	0.7788	59.99	9.801
		80.67	9.029	100.	0.9086	87.92	5.532
	0	70.34	5.132	100.	1.030	00.90	6 776
	10	73.94	6.055	100	1,298	83.72	7.353
	11	71.88	6.474	100.	1.428	82.42	7,902
	12	69.89	6.868	100.	1.558	81.18	8,425
Design Bed Structure	13	67.98	7.237	100.	1.687	79.99	8.924
	14	66.15	7.583	100.	1.817	78.84	9.4
	15	64.39	7.908	100.	1.947	77.74	9.855
	16	62.69	8.213	100.	2.077	76.68	10.29
	17	61.06	8.499	100.	2.207	75.66	10.71
	1.8	59.49	8.768	100.	2.336	74.68	11.1
							11.49
	19	57.97	9.019	100.	2.466	73.73	
	19 20	57.97 56.52	9.019 9.256	100.	2.466 2.596	73.73	11.85
	19 20 21	57.97 56.52 55.12	9.019 9.256 9.477	100.	2.466 2.596 2.726	73.73 72.82 71.95	11.85
	19 20 21 22	57.97 56.52 55.12 53.76	9.019 9.256 9.477 9.685	100.	2.466 2.596 2.726 2.856	73.73 72.82 71.95 71.1	11.85 12.2 12.54
	19 20 21 22 23	57.97 56.52 55.12 53.76 52.46	9.019 9.256 9.477 9.685 9.881	100. 100. 100. 100.	2.466 2.596 2.726 2.856 2.985	73.73 72.82 71.95 71.1 70.29	11.85 12.2 12.54 12.87
Masternaria	19 20 21 22 23 24	57.97 56.52 55.12 53.76 52.46 51.21	9.019 9.256 9.477 9.685 9.881 10.06	100. 100. 100. 100. 100.	2.466 2.596 2.726 2.856 2.985 3.115	73.73 72.82 71.95 71.1 70.29 69.51	11.85 12.2 12.54 12.87 13.18
Meets removal goal	19 20 21 22 23 24 25	57.97 56.52 55.12 53.76 52.46 51.21 50.	9.019 9.256 9.477 9.685 9.881 10.06 10.24	100. 100. 100. 100. 100.	2.466 2.596 2.726 2.856 2.985 3.115 3.245	73.73 72.82 71.95 71.1 70.29 69.51 68.75	11.85 12.2 12.54 12.87 13.18 13.48

Fig. 7.33 Phrog output for the design of a bio-retention cell intended to remove 50% of cumulative P over 25 years, using a 95:5 sand:fly-ash mixture. Site inputs, constraints, and PSM characteristics are shown in Fig. 7.32

7.5.5.2 Predict Performance of an Existing Bioretention Cell

For the final example using a bioretention cell, we will use Phrog to estimate the removal performance of an existing bioretention cell located in Oklahoma. This particular unit was filled with 293.3 tons of a 95:5 sand:fly-ash mixture that is less pH buffered than the mixture used in the previous design example. This was a relatively large structure at $70 \times 29 \times 3$ ft deep. The site produced an annual runoff volume of 472,743 gal with an average dissolved P concentration of 0.5 mg L⁻¹. The total P removal of the structure can also be estimated due to knowledge of total P concentration, sediment concentration, and the sediment deposition rate. All site characteristics, PSM physical and chemical characteristics, and the dimensions of the bioretention cell were input into Phrog as shown in Fig. 7.34. The structure performance output shown in Fig. 7.35 estimated the lifetime of the PSM at almost 50 years with a cumulative removal of 21.5% dissolved P and 47.7% of total P. The flow rate through the structure, 23.3 gpm, is limited by the subsurface drainage, so an increase in the diameter or number of pipes would increase this flow rate. For this structure, 20 lb of dissolved P is removed in 30 years, but over the next 20 years only another 1.12 lb is removed; this drastic decrease in dissolved P removal

		Estimate Design Curve	Manually Input (Design Curve (y=be ^{mx}	()	
		Ammonium Oxalate Aluminum (mg/kg)				47
Total P Removal (optional)		Amn	62			
Mean Particle Size of Filter Media (mm)	2.27	Buffer Index (equivalent	pH to 6)	0.076		
Average Total Phosphorus Concentration (mg/L)	0.75	sener meen (equineri		2 27		
Average Sediment Concentration (mg/L)	1.15			0.006		
Deposition Rate (grams of sediment/minute of flow)	0.05		рн			0.000
			Total Aluminum (r	ng/kg)		215
			Total Calcium (m	g/kg)		4938
			Total Iron (mg	kg)		336
Material Physical Characteristics						
Bulk Density (g/cm ³) 1.55						
Hydraulic Conductivity (cm/sec) 0.36						
Porosity (decimal) 0.31						
Design Structure Existing Stucture		Design Bed Size	Existing Bed Size	Design Ditch Size	Existing Dr	tch Size
Average Phosphorus Concentration (mg/L)	0.5	Length of Structure	e (feet) 70			
Annual Flow Volume (gallons)	472743	Width of Structure	e (feet) 29.3			
		Depth of Material	l (inch) 33			
Subsurface Drainage (Backward Require	ed)	Mass of Material	(tons) 293.	3		
Drainage Pipe Diameter (inches)	2	thidraulic blood (onchor) 26				
Drainage Pipe Slope (decimal)	0.01	rijardane ricaa (i	Jo So			
Number of Subsurface Drainage Pipes	2	Note: Hydraulic Head the maximum length o inlet a	is equal to the elevati or the elevation different and ultimate outlet.	on drop over nce between		

Fig. 7.34 Input for predicting the performance of an existing bio-retention cell located in Oklahoma, using a 95:5 ratio of sand:fly-ash as the PSM. Inputs include site flow characteristics and hydraulic head, PSM chemical and physical characteristics, subsurface drainage characteristics, and the dimensions of the bioretention cell. Input data courtesy of Glenn Brown, Oklahoma State University

efficiency should be considered when deciding on a cleanout schedule. The reporting of annual removal allows for informed decisions to be made concerning the maintenance of these structures that is based on removal performance.

7.5.6 Design a Confined Bed Located on a CAFO

This example will illustrate how much more efficient it is to focus on targeting nonpoint source P sources that are extremely high in dissolved P concentrations and loads, than dilute P concentrations and smaller loads. For this hypothetical scenario, we will design a confined bed P removal structure such as the units shown in Figs. 3.5 and 3.10 that could be located on a confined animal feeding operation (CAFO) such as a poultry, swine, or dairy farm, or a cattle feedlot. Due to the nature of CAFOs, runoff produced from these areas tend to have extremely high dissolved P concentrations, and therefore are capable of producing large losses of dissolved P loads. Figure 7.36 shows the inputs and constraints for this hypothetical structure and site, with a dissolved P concentration of 8 mg L⁻¹ and an annual flow volume of

Elow rate through	Quantifying an Existing Structure (Bed)							
riow rate through	Actual	flow rat	e	23.3042				
	thro	ugh the f	ilter (gpm)					
structure and	Actual	retention	n time (min	i)	603.14			
rotontion time	Years	DP (%)	DP(1bs)	PP(%)	PP(1bs)	TP(%)	TP(lbs)	
recention time	1	95.52	1.884	100.	0.2606	97.01	2.145	
	2	91.3	3.602	100.	0.5211	94.2	4.123	
	3	87.33	5.167	100.	0.7817	91.55	5.949	
	4	83.59	6.595	100.	1.042	89.06	7.637	
	5	80.07	7.896	100.	1.303	86.71	9.199	
	0	76.75	9.083	100.	1.563	89.5	10.65	
		70.67	11 15	100.	2.084	80.44	12.25	
	0	67.88	12.05	100	2.345	78.50	14.30	
	10	65.25	12.87	100.	2.606	76.83	15.48	
	11	62.76	13.62	100.	2.866	75.17	16.48	
	12	60.41	14.3	100.	3.127	73.61	17.42	
	13	58.18	14.92	100.	3.387	72.12	18.31	
	14	56.08	15.49	100.	3.648	70.72	19.13	
	15	54.08	16.	100.	3.908	69.39	19.91	
	16	52.2	16.47	100.	4.169	68.13	20.64	
	17	50.4	16.9	100.	4.429	66.94	21.33	
	18	48.71	17.29	100.	4.69	65.8	21.98	
	19	47.09	17.65	100.	4.951	69.73	22.6	
Existing Bed Structure	20	13.30	17.97	100.	5.211	63.71	23.19	
Exceeding bed berocoure	22	42 78	18 54	100.	5 792	61 82	24.27	
	23	41 41	18 79	100.	5 003	60.94	24.78	
	24	40.16	19.01	100.	6.253	60.11	25.26	
	25	38.97	19.22	100.	6.514	59.31	25.73	
	26	37.84	19.4	100.	6.774	58.56	26.18	
	27	36.75	19.57	100.	7.035	57.84	26.61	
	28	35.72	19.73	100.	7.296	57.15	27.02	
	29	34.74	19.87	100.	7.556	56.49	27.43	
	30	33.8	20.	100.	7.817	55.87	27.82	
	31	32.9	20.12	100.	8.077	55.27	28.19	
	32	32.04	20.22	100.	8.338	54.69	28.56	
	33	31.22	20.32	100.	8.598	59.15	28.92	
	39	20.44	20.41	100.	0.039	53.02	29.27	
	36	28.96	20.57	100.	9.38	52.64	29.95	
	37	28.27	20.63	100.	9.641	52.18	30.27	
	38	27.61	20.69	100.	9.901	51.74	30.6	
	39	26.98	20.75	100.	10.16	51.32	30.91	
litetara da lifadiara d	40	26.37	20.8	100.	10.42	50.91	31.22	
Ultimate lifetime of	41	25.78	20.85	100.	10.68	50.52	31.53	
	42	25.22	20.89	100.	10.94	50.15	31.83	
	43	24.68	20.93	100.	11.2	49.78	32.13	
DSM and cumulative	44	24.16	20.97	100.	11.46	49.44	32.43	
r Sivi allu cultulative	95	23.66	21.	100.	11.72	49.1	32.72	
	47	23.17	21.03	100.	12.99	10.78	33.01	
	48	22.26	21.08	100.	12.51	48.18	33.58	
P removal						10.10		
	49.8	21.5	21.12	100.	12.98	47.67	34.09	

Fig. 7.35 Predicted performance of an existing bio-retention cell with characteristics described in Fig. 7.34

7 million gallons. Since we will assume a site with limited space for a P removal structure (maximum area of 20×20 ft), a very potent PSM must be chosen, or a very modest P removal goal. Thus, for this example we will examine the use of an acid mine drainage treatment residual (Chap. 4). The P removal goal is 40% over 1 year, with a minimum target peak flow rate of 500 gpm.

The design output shown in Fig. 7.37 illustrates that a relatively small mass of the PSM is required to meet the goal, but must be spread out over an appreciable area in order to meet the flow rate goal of 500 gpm. Due to the fine physical nature of the PSM, it would be necessary to place a layer of gravel or sand on top of the PSM to prevent it from being washed away. Notice that this structure will remove an extremely large load of dissolved P in only 1 year (187 lb) with only 15 tons of the PSM. By the end of year 2, the cumulative dissolved P retained decreases to 30% with a cumulative removal of 283 lb. Compare this amount of P removal to the other examples in this chapter and notice how extraordinary this value is. As discussed in Chap. 3, this demonstrates how it is much more efficient to determine the location of P "hot spots" and focus efforts on those sources, compared to more dilute sources.

			Estimate Design Curve	Manually Input D	esign Curve (y=be ^{mx})		
			Ammo	nium Oxalate Alum	352]	
Total P Removal (option	nal)		Amr	monium Oxalate Iro	on (mg/kg)	124372	i
Mean Particle Size of Filter Medi	a (mm)	0.23	Buffer Index (equivalen	ts of acid per ka o	f material to reduce nH to 6)	0	í
Average Total Phosphorus Concentra	ation (mg/L)		builet maex (equivalen	to or actor per kg o	(material to reduce pri to o)	0.22	i
Average Sediment Concentration	n (mg/L)			Mean Particle Size	(mm)	0.25	4
Deposition Rate (grams of sediment/m	inute of flow			pH		б.]
Deposition rate (grans of scamenon	indie of non			Total Aluminum (n	ng/kg)	2340	
				Total Calcium (m	g/kg)	0	
				Total Iron (mg/	kg)	543 545]
Material Physical Character	ristics						
Bulk Density (g/cm ³)	0.8	8					
Hydraulic Conductivity (cm/s	ec) 0.1						
Provide Conducting (cross	0.5						
Porosity (decimal)	0.5						
Design Structure Existing Stucture			Design Bed Size	Existing Bed Size	Design Ditch Size Existing D	Ditch Size	
Desired Retention Time (min)	10		Maximum Width	of Structure (feet)	20		
Average Dissolved P Concentration (mg/L)	8	ī	Maximum Length	of Structure (feet)	20		
Annual Flow Volume (gallons)	7 000 000	ī	Minimum Flo	w Rate (gpm)	500		
Desired Removal Goal (%)	40	1	Hydraulic H	ead (inches)	24		
Desired Lifetime (years)	1]	Note: Hydraulic He	ad is equal to the eleve th or the elevation diff	ation drop over		
Drainage Pipe Diameter (inches)	4		inie	t and ultimate outlet.			
Drainage Pipe Slope (decimal)	0.01						

Fig. 7.36 Inputs for design of a confined bed P removal structure on a hypothetical CAFO with very high dissolved P concentrations and loads. Inputs include site flow characteristics and constraints, and physical and chemical characteristics of the acid mine drainage treatment residual to be used as the PSM. The P removal goal is 40% over 1 year with a minimum target peak flow rate of 500 gpm



Fig. 7.37 Design specifications for the confined bed P removal structure located on a hypothetical CAFO, with site characteristics and design goals shown in Fig. 7.36. This structure utilizes an acid mine drainage treatment residual as the PSM

7.5.7 Wastewater Treatment Plant Tertiary P Treatment and Example Use of Direct Input of Design Curve Coefficients

For some small wastewater treatment plants, it may be feasible to construct a P removal structure for tertiary treatment of effluent dissolved P. The P loads in effluent from treatment plants can be extremely large due to very high volumes of water and moderate dissolved P concentrations. As discussed in Chap. 3, there are some examples of wastewater treatment plants that have utilized a P removal structure for tertiary P treatment.

Due to the high dissolved P loads, it is best to utilize more efficient PSMs, such as those rich in Fe and Al oxides, in order to reduce the total mass of PSM and conserve space and cost. For example, acid mine drainage treatment residuals, certain drinking water treatment residuals, treated slag, and certain manufactured PSMs (Chap. 4). For this example, we will conduct a design for a small wastewater treatment plant located in southern Indiana that produces 1 million gallons of effluent per day, with a typical dissolved P concentration of 1.22 mg L⁻¹. The P removal goal is 50% over 1 year and a minimum target peak flow rate of 700 gpm, through use of a confined bed of PSMs. Unlike the previous examples, notice that the potential hydraulic head for this site is much greater at 12 ft (Fig. 7.38). Also, this example will utilize design curve coefficients that were directly measured by a flow-through experiment using the same inflow P concentration at the site and input into Phrog. If the flow-through experiment did not use an inflow P concentration of 1.22 mg L^{-1} , then the design curve coefficients would not be valid for conducting this design. The PSM for this particular design is a manufactured PSM that is rich in Fe oxides, and therefore is not sensitive to retention time. Thus, we do not need to be concerned with designing the structure to meet a certain retention time in this case.

The site and PSM characteristics, P removal goals, choice of subsurface drainage pipe to be used, and area constraints are shown as the inputs in Fig. 7.38. Notice the use of the "Manually Input Design Curve" tab, instead of "Estimate Design Curve". Figure 7.39 shows the results of the Phrog design based on the inputs shown in Fig. 7.38. Although a relatively large mass of the PSM is required to meet the P removal goals at 497 tons, notice that this structure will remove almost 2000 lb of dissolved P in a single year, and almost 3000 lb after 2 years. One issue is the cost of such manufactured PSMs. As an alternative, one could utilize acid mine drainage residuals, which are similar in chemical composition; these byproducts can often be obtained for no cost, except for transportation and preparation of materials (i.e. dewatering and drying). However, the cost of some Fe oxide-rich manufactured PSMs may be offset by the ability to strip the P off of the material and regenerate them as described in Chap. 4. This is also true for acid mine drainage treatment residuals.

As a comparison, consider what the size and cost of the structure would be if a treated slag was used instead of the manufactured PSM. To achieve the same removal goal, it would require nearly 8000 tons of treated slag (Fig. 7.40). If the slag was available for \$3 per ton, it would cost around \$23,000 for the slag, not including transportation or chemical treatment. On the other hand, at \$8 per pound
			Estimate Desig	gn Curve	Manually Input D	esign Curve (y=be ^m	^x)
			Slope (m)	-0.000	02		
Total P Removal (optional)			Intercept (b)	71			
Mean Particle Size of Filter Media (n	nm) 1	4.					
Average Total Phosphorus Concentration	n (mg/L) 0)					
Average Sediment Concentration (m	g/L) 0)					
Deposition Rate (grams of sediment/minut	te of flow))					
Material Physical Characterist	ics	_					
Bulk Density (g/cm ³)	0.5						
Hydraulic Conductivity (cm/sec)	0.1						
Porosity (decimal)	0.6						
Design Structure Existing Stucture			Design Be	ad Size	Existing Red Size	Design Ditch Size	Existing Ditch Size
Desired Retention Time (min)	10		Maujaura	a Miliata	of Structure (feet)	20	existing orten size
Average Dissolved P Concentration (mg/L)	1.22		Maximun	n width	of Structure (reet)	30	
Annual Flow Volume (gallons)	3650000-		Maximum	i Length	for structure (reet)	30	
	00		Minir	num Flo	w Rate (gpm)	700	
Desired Removal Goal (%)	50		Hyd	draulic H	lead (inches)	144	
Desired Lifetime (years)	1		Note: Hy	rdraulic H	ead is equal to the eleve	tion drop over	
			the max	indim deng	et and ultimate outlet.	rence between	
Drainage Pipe Diameter (inches)	4						
Drainage Pipe Slope (decimal)	0.01						

Fig. 7.38 Inputs for design of confined bed P removal structure for treatment of effluent from a small waste water treatment plant. The PSM to be used in this design is a manufactured PSM that is rich in Fe oxides. Notice the direct input of the design curve coefficients that are specific to the inflow P concentration of 1.22 mg L^{-1} . The P removal goal is 50% over 1 year



Fig. 7.39 Design specifications for the confined bed P removal structure to be constructed at a small waste water treatment plant, with site characteristics and design goals shown in Fig. 7.38. This structure utilizes a manufactured PSM rich in Fe oxides that could potentially be stripped of P and recharged as described in Chap. 4



Fig. 7.40 Design specifications for the confined bed P removal structure to be constructed at a small waste water treatment plant, with site characteristics and design goals shown in Fig. 7.38. This structure utilizes a treated slag material described in Chap. 4. Notice the much larger mass of PSM required compared to the manufactured PSM in Fig. 7.39; however, the cost of construction may still be less for the treated slag unit

of manufactured PSM, the cost of the PSM alone for this structure would be almost 8 million dollars. Even if the total cost of the slag, chemical treatment, and transportation was \$100,000, it would require 100% regeneration of the manufactured PSM for 80 years to offset the 8 million dollar cost in comparison to the treated slag structure. While the slag is required at a much greater mass, it may be more feasible than a manufactured PSM if the slag source is in close proximity to the waste-water treatment plant. If possible, the most cost effective choice in this scenario would be the use of an acid mine drainage treatment residual, since it can be obtained at a low cost and will remove P similarly to the manufactured PSMs rich in Fe oxides.

Reference

Penn, C.J., J. Bowen, J.M. McGrath, G. Fox, G. Brown, and R. Nairn. 2016. Evaluation of a universal flow-through model for predicting and designing phosphorus removal structures. *Chemosphere.* 151: 345–355.

Chapter 8 Disposal of Spent Phosphorus Sorption Materials

Eventually the PSMs will reach the end of their useful lifetime in a P removal structure, and then they must be disposed of. As discussed in Chap. 3, it is critical that the P removal structure be designed so that the PSMs can easily be physically removed and periodically replaced. What can be done with spent PSMs? At the very least, they could be sent to a landfill, which is the fate of many of the by-product materials that will never be used in P removals structures. However, landfill disposal of spent PSMs is costly and consumes valuable landfill space for materials that truly belong there. A more economical approach is for land application or other beneficial re-use of the PSMs. Considering that most PSMs are usually by-products from various industries, their use in a P removal structure is clearly a secondary beneficial re-use, and disposal of the spent PSMs can then represent a tertiary beneficial re-use, if properly done under the right circumstances.

A constant theme throughout this chapter is that disposal of spent PSMs must be conducted according to the characteristics of the material. The potential for the spent PSM to be beneficial or cause a problem is a function of both the material characteristics and the context and conditions of the disposal scenario. This is true for the handling of any waste material. For example, depending on manure properties and the disposal method and conditions, animal manure can either be a great resource or a source of pollution (Chap. 2).

8.1 Use of Spent PSMs as a P Fertilizer

The most obvious question for potential beneficial reuse is whether or not the spent PSMs can be used as a P fertilizer for agronomic or horticultural crops. The answer to this question is highly dependent on the type of PSM and the degree of P saturation on it. Or more directly, the concentration of P inflow that the PSM was treating. The more P-saturated the material, the better it will serve to release the P that is



Fig. 8.1 Diagram illustrating solution P dynamics. The solid P from a spent PSM or a soil amended with a spent PSM (quantity) supplies the solution P (intensity), where a plant is able to uptake the nutrient. The chemically bound P that constitutes the quantity is in equilibrium with the solution P. Thus, depending on the two pools, P may be desorbed, sorbed, dissolved, or precipitated

bound to it. The amount of P held onto the solid PSM is known as the "quantity", and the P that is in solution as supplied by the quantity is called the "intensity". Plants uptake P from the solution phase of the soil, not directly from the solid phase (Fig. 8.1). Depending on the quantity-intensity behavior, some PSMs hold onto P so tightly that even after they become relatively highly saturated with P due to high inflow concentrations, they will still not release much P back into solution after they are removed from the P removal structure.

After the spent PSMs are removed from the structure, they will presumably no longer be exposed to high dissolved P conditions. Consider that the P bound to a PSM will develop an equilibrium with the solution around it:

$$PSM \ bound \ P \leftrightarrow solution \ P \tag{8.1}$$

Therefore, the more P that is bound to the PSM (i.e. quantity), and also the lower the concentration of P in the solution around it, the more P will desorb and dissolve from the PSM into the solution (i.e. intensity). Again, this is illustrated in the balance between the quantity and intensity in Fig. 8.1. For PSMs that bind P extremely strong, particularly those that bind P by Fe and Al mechanisms (Chap. 4), the result

is a low solution P concentration at equilibrium. In fact, if there is appreciable P in the soil in which the spent PSM is placed into, it could possibly bind up soil P upon application. Phosphorus sorption materials that were utilized under high P environments such as treating wastewater, will always have greater potential to release P back to solution or serve as a plant fertilizer after they become spent compared to PSMs that become spent under lower P conditions, such as agricultural tile drainage water. For example, it has been shown that EAF slag that became spent from treating dairy effluent was able to serve as a slow-release fertilizer (Bird and Drizo 2009).

To illustrate the differences in P release from different PSMs, consider the degree of P release from several spent PSMs after placing them into P-free water, which is a best case scenario for P release and somewhat unrealistic under field conditions for when materials are land applied. In this example, the PSMs were previously treated with P under flowing conditions at concentrations ranging from 0.05 to 1 mg L⁻¹ before being exposed to the P-free water. A Fe-rich PSM known as "CFH" released about 10% of the previously sorbed P under flowing conditions, while the Ca-based PSM (FiltraliteTM) was able to release 35–90%. Clearly, the sorption and desorption data showed that the CFH material not only had a stronger capacity to remove P from solution compared to the manufactured and Ca-based FiltraliteTM, but it also better retained the P after it was spent. Researchers in the U.K. have shown that Fe-rich acid mine drainage residuals that become spent through treating waste water with a high P concentration (>10 mg L^{-1}), were able to serve as a suitable slow-release P fertilizer (Dobbie et al. 2005). This is possible for other types of PSMs, but only if they were produced from treatment of water with high P concentrations for an extended time period.

Clearly, if the spent PSM has a strong potential to release P back to solution, then it should be properly managed so that it can be used as a P fertilizer and treated as such with regard to environmental quality. On the other hand, if the spent PSM has little potential to release P to solution, and assuming that there are no safety considerations associated with the material, it will be less limited in disposal options. However, it may or may not produce agronomic or horticultural benefits.

8.1.1 Testing PSMs to Determine Potential for P Release to Plants or Runoff After Land Application to Soil

Determining the potential for surface applied PSMs to release P to runoff is relatively straightforward compared to estimating their value as a P fertilizer. While there are many possible methods for testing the ability of a PSM to release P for plant uptake, there is little to no guidance for interpreting the meaning of the results. Ultimately, the best test of plant availability is to conduct a greenhouse pot experiment in which the soils of interest are amended at various rates of the spent PSM, and the resulting plant growth is quantified and compared to a control. In addition to explaining the concepts of material testing, this section will attempt to provide some guidance on the use of simple tests for assessing spent PSMs as fertilizer sources. At the very least, these methods will serve to allow one to compare different spent PSMs to each other.

Not only can the spent PSM itself serve as a potential source or sink for P after land application, but if the original P removal structure also captured a significant amount of sediment, then that sediment may also release or sorb P. For example, after cleanout of a P removal structure in which a sieved slag material was used, it was found that 130 lb of sediment was retained by the three-ton structure. The fine particles transported in runoff are often enriched in P, and therefore this trapped sediment must also be considered in disposal.

8.1.1.1 Assessing the Potential for a Spent PSM to Release P to Runoff or Leachate

Regarding P release in runoff, a very simple test is to conduct a water extraction, identical to the method described in Chap. 5 that is conducted for the purpose of screening samples for safety. The premise is simple: use of P-free water will allow some of the PSM-bound P to dissolve and desorb in achieving equilibrium between the solid and the solution phase (equation 8.1). Again, use of the P-free water will result in a release of the maximum amount of P to the water. This water extraction test can additionally be conducted sequentially, as described in Chap. 5. The greater the resulting solution concentration, the greater potential for that PSM to serve as a fertilizer or release P to runoff.

As an example, the ability of spent slag to desorb P was tested in order to determine the best end use for this material that had already reached its useful lifetime as a P filter media. If the material is able to desorb an appreciable amount of P then its best disposal option would be as a type of landscape mulch where the soluble P could be utilized to by plants. However, the spent slag (>6.35 mm) from the P removal structure only desorbed a small amount of P resulting in a concentration of 0.03 mg P L⁻¹ when clean water was reacted with the material for several hours. Therefore, this material will not release enough P to runoff water to cause water quality problems.

Although the water extraction test is an easy starting point for assessing the potential for a PSM to release P to solution, it is important to keep in mind that the chemical conditions in which the spent PSM is placed will also impact P release. As previously discussed, a high P environment will prevent P release, but depending on the pH of the environment, use of a non-pH buffered solution as an extractant may underestimate potential P release to solution. This is mostly an issue for Ca-based spent PSMs, as the Ca phosphates found in them tend to be more soluble at acid pH levels (Chap. 4). This can be a benefit if the purpose of the spent PSM is to serve as a fertilizer. On the other hand, depending on the context, this characteristic of Ca phosphates could be a problem for water quality if not properly handled. One of the tests to gauge the potential for the PSM to release P under acid soil conditions is the SPLP extraction described in Chaps. 4 and 5.

Purpose	Method	Notes
Estimate potential P	Extraction with P-free water	
release to runoff and leachate water	Synthetic precipitation leaching procedure (SPLP)	
Estimate potential P solution intensity level	Extraction with 0.1 M Na acetate at pH 5–6.5	For materials applied to acid soils or exposed to rainfall with low pH, use
for a growing plant	Extraction with 0.1 M Na bicarbonate at pH 7–8.2	Na acetate. For application to basic soils, use Na bicarbonate. Adjust
	Extraction with P-free water	extractant pH appropriately.
Estimate potential P quantity for supplying a plant throughout an entire growing season	Directly extract P from the PSM using an agronomic soil test P extractant: Mehlich-3, Mehlich-1, Bray-1, Morgan, or Olsen	If amending a soil with the spent PSM, use the soil test extractant appropriate to that region. If directly growing plants in the spent PSM, use Olsen for Ca-based PSMs and
	Amend soil with spent PSM in laboratory, incubate, and then extract the soil with a soil test extractant	the other extractants for Fe and Al-based PSMs
Directly measure P availability to plants	Amend soil with spent PSM in a greenhouse with a plant established in the amended soil. Monitor plant growth	

Table 8.1 Methods and analyses for assessing the potential for spent PSMs to release phosphorus into runoff or serve as a fertilizer after land application

Note that all materials must also be screened for safety before land application, using similar techniques as those described for PSM safety pre-screening in Chap. 4

8.1.1.2 Assessing the Potential Use of Spent PSMs as Fertilizer

Assessing the potential for a spent PSM to serve as a fertilizer is less straightforward because the ability of a plant to obtain P from a solid material occurs on a different timescale and conditions compared to simple release of P to runoff or leachate water. While runoff and leachate water only interact with soil and PSMbound P for a relatively short time period, plant roots are in contact with the media for an entire growing season, making it difficult to predict how much P will become available to the plant. Plants are only able to take up P after the P has been released from the solid phase to the solution. The higher the P concentration in solution (i.e. intensity), and the greater the ability of that solid media to continue to replenish the solution throughout time (i.e. quantity), the better the material will serve as a fertilizer (Fig. 8.1). Thus, while a test such as the water extraction (Table 8.1) described for assessing potential release P to runoff is still helpful in this context, it does not capture the entire picture of P availability to the plant. Instead, the water extraction simply provides information on the solution intensity at a specific moment, and provides no information on the ability of that material to continue to supply the solution with that P concentration over a growing season.

Still, the water extraction test is useful. Consider the spent steel slag described in the previous section that produced 0.03 mg P L⁻¹ as determined by water extraction. A useful parameter for comparison is that most plants require a concentration of about 0.2 mg L⁻¹ in solution for optimum growth. Therefore, this material will likely not serve well as a P source to plants. As another example, consider a sand/fly-ash mixture used in four different Oklahoma bioretention cells and assessed after seven years of use. Depending on the bioretention cell and the P loading that it incurred over seven years, the equilibrium P concentration (intensity) assessed by water extraction ranged from 0.08 to 0.26 mg L⁻¹. In light of the general threshold of 0.2 mg L⁻¹, some of these solution P concentrations are high enough to be considered "adequate" for plants, although the water extraction test does not provide any information on the ability of that material to continue to supply the solution with P throughout an entire growing season.

Clearly, there is an additional need to assess the quantity of P, that is, the source of P that supplies the solution P (intensity) (Fig. 8.1). At the most basic level, the ultimate test for P quantity of a spent PSM is total P determined by an acid digestion. This is the same method described for assessing total Ca, Al, Fe, and trace metals in Chap. 5. The problem with this approach in this context is that not all of the PSM-bound P will ever be released to the solution, even under the best possible circumstances over a period of decades. For example, consider the previously mentioned sand/fly-ash mixture sampled from bioretention cells: the total P concentration ranged from 240 to 465 mg kg⁻¹, while the water extractable P was only 0.8-2.6 mg kg⁻¹. This illustrates how the solution intensity is often a very small percentage of the total quantity of P held onto the solid material.

Since not all of the P held onto the spent PSM will become plant available, another approach for estimating the quantity is to extract the material with a chemical extractant that will represent the amount of P that can potentially be released over a growing season; this is the general approach for assessing soil P availability. One of the reasons why this approach is effective is because while not all of the PSM-bound P will be released, a portion of it will be released as a function of the environment in which the material is placed in. For example, if a spent PSM, rich in Ca phosphates, is applied to an acid soil then the Ca phosphates are more likely to dissolve and supply the plant with P. If the spent PSMs are to be land applied to acid soils, then extraction with a dilute strong acid, or with a weak acid (e.g. acetic acid) may help to at least gauge the potential for the material to release P. If the spent PSMs are to be applied to soils with neutral to basic pH, then extraction with sodium bicarbonate would be more suitable (Table 8.1). If the spent PSMs are able to release any P at all, then it will most likely be a slow P release throughout the growing season. The degree of such a P release is difficult to gauge with a single extractant. Continuing with our example of the sand/fly-ash mixture sample taken from the bioretention cell, extraction with a dilute strong acid (Mehlich-3 extraction) estimated 7.6–21.8 mg P kg⁻¹ for the materials. In the context of a traditional soil test, which is the intended purpose of the Mehlich-3 test, this material would be considered "low" to "optimum" in plant available P. One of the most useful parameters in estimating the potential for a material to serve as a P fertilizer is to calculate the percentage of the intensity as the quantity. In other words, calculate what portion of the soil P quantity is able to release P into solution. This is similar to what is known as the Q/I ratio.

Testing spent PSMs to determine their potential fertilizer use is not straightforward because the environment in which the material is placed will impact the release to plants. Therefore, a more direct measure of the potential for a spent PSM to serve as a fertilizer would be to conduct a soil incubation for several weeks after directly amending the soil of interest with the material. The difference in the agronomic soil test P level before adding the amendment and after the incubation will provide an indication for its potential to release P to plants. A suitable agronomic soil test extractant should be used to accomplish that. Specifically, one should use the appropriate soil test extraction recommended by the Land Grant University for that region. This type of approach is more time consuming and expensive, yet more effective than extraction of the PSM alone. For example, after saturating an FGD gypsum material in the laboratory with P, we applied it to soils that had a pH <5. This represented a best case scenario for reuse of a spent gypsum material as a fertilizer. Gypsum forms Ca phosphates upon reaction with solution P in a P removal structure, which tend to be relatively soluble in acid soils. After amendment of the spent gypsum to a silt loam and a sandy loam and subsequent incubation for 183 days, it was found that the agronomic soil test P level (Mehlich-3 in this case) increased from a level of 40 mg kg⁻¹ for the un-amended control, to 50 mg kg⁻¹ for the silt loam, and from 61 to 84 mg kg⁻¹ for the sandy loam (Grubb et al. 2011, 2012).

If the intended use is to utilize the spent PSM as a growth media (i.e. directly grow plants in a pure spent PSM), as opposed to land application of them to soils, then the agronomic soil test used to estimate quantity must be chosen as a function of the characteristics of the spent PSM (Table 8.2). For Fe and Al-based PSMs, one can utilize an assortment of different agronomic extractions listed in Table 8.1, but for Ca-based PSMs, the Olsen extraction should be used. Again, interpretation of the results should be made according to the specific extractant.

The most direct method for assessing the ability of a PSM to serve as a fertilizer upon land application or as a plant growth media, is to simply grow the plant of interest in a greenhouse using the intended soil, at the application rates of interest. One can monitor the plant growth in comparison to a control soil that has no amendment. This method also helps to determine what the most suitable rates are for land application. However, this approach is more time and labor intensive compared to the previously described quick soil test extractions. Bird and Drizo (2009) land applied spent EAF slag from a dairy effluent filter, onto *Medicago sativa* (alfalfa) and found that it served as a slow release P fertilizer.

8.2 Extraction of P from Spent PSMs and Potential Recharge

As an alternative to the land application of spent PSMs to be used as a P fertilizer, a common desire is to be able to remove/extract the P from the spent PSM which can then be used as less diluted P fertilizer. While this has been previously achieved, it is only feasible under limited circumstances.

Potential benefit with land	
application	Material
Increased soil CEC or AEC	WTRs, AMDRs, fly-ash, metal shavings/filings, bauxite waste
Increased soil base saturation	Ca-based WTRs, AMDRs, fly-ash, FGD gypsum, crushed concrete, steel slag, limestone fines, marble tailings, wollastonite
Liming agent for increasing pH	Ca-based WTRs, AMDRs, fly-ash, crushed concrete, steel slag, limestone fines, marble tailings
Ca or Mg source	Ca-based WTRs, AMDRs, fly-ash, FGD gypsum crushed concrete, steel slag, limestone fines, marble tailings, wollastonite
S source	FGD gypsum, fly-ash, steel slag, AMDRs, WTRs
Micronutrient source	WTRs, foundry sand, metal shavings/filings, bauxite waste
K source	Foundry sand, WTRs, fly-ash, AMDRs, steel slag
Si source	Steel slag, fly-ash, wollastonite
Increased water holding capacity in sandy soils	WTRs, AMDRs, fly-ash, bauxite waste
Improved drainage and stability in heavy soils	Ca-based WTRs, AMDRs, fly-ash, steel slag, FGD gypsum, crushed concrete, foundry sand, limestone fines, marble tailings, wollastonite

 Table 8.2
 Potential soil and crop benefits with land application of various by-product spent PSMs

Note that all materials must be tested in order to estimate the potential benefits, hazards, and also to determine the proper land application rates

WTRs drinking water treatment residuals, AMDRs acid mine drainage residuals, FGD gypsum flue gas desulfurization gypsum

For Fe and Al-based PSMs, the P can be removed/stripped off of the spent PSM with a strong base solution such as calcium, potassium, or sodium hydroxide. Care must be taken to not use excessive concentrations and dissolve the Fe/Al oxyhydroxides; the purpose is to remove the phosphate held by ligand exchange and maintain the mineral. In this case, the Fe and Al-based PSM is recharged and can be used again in a P removal structure. This process was described in Chap. 4 (Fig. 4.12). The P found in the leachate solution can then be re-precipitated as a calcium phosphate through addition of calcium chloride to the solution. This process was successfully demonstrated by Sibrell et al. (2009) through use of AMDRs. For the treated steel slag materials described in Chap. 4, there is also a recharge process that is effective for them, although it will not release P into solution.

For Ca-based PSMs, the P can be dissolved through addition of acid. However, this will also dissolve much of the Ca that constitutes the PSM itself, and therefore will not recharge the PSM for future use. One possibility for stripping and recharge is to treat the Ca-based PSM with a highly buffered solution at a high pH. The effect is somewhat different compared to the Fe and Al-based PSMs because P is held by precipitation in Ca-based PSMs, not ligand exchange (Chap. 4). While Ca phosphates dissolve in acid conditions, they will also dissolve if the solution pH becomes excessively basic as well. Essentially, as the pH reaches 9 and above, hydroxide and carbonate become more thermodynamically favorable to react and precipitate with

the Ca. This would dissolve the Ca phosphate but allow the Ca to re-precipitate as Ca hydroxide minerals, which are very effective at P removal. High pH solutions that contain silica would also have the same effect in precipitation of Ca silicate minerals and liberation of the phosphate precipitated with Ca.

8.2.1 Stripping P from Spent PSMs: Is It Worth It?

The practicality and feasibility of stripping P from spent PSMs is generally only worthwhile for the purpose of recharging the PSM to be used again in the P removal structure, not for the value of P fertilizer. Often, this recharge process can be conducted in-situ. However, for the purpose of stripping P to obtain a P fertilizer is typically not worthwhile. The reason is due to the paradox between the great difference between P needs of plants and the relatively small amount of dissolved P that is lost in drainage water from the landscape to be treated by the P removal structure. Plants require a large amount of P while dissolved P losses are very small compared to plant need. Yet this relatively small loss of P that is somewhat inconsequential to crop production is large enough to be devastating to water quality. This can be illustrated with an example: consider the more extreme scenarios for dissolved P losses from the landscape. For instance, the dissolved P loss from CAFOs is often 0.5-1 lb P acre⁻¹ year⁻¹. On the other hand, the typical P application for agronomic crops and forages ranges from 10 to 70 lb P acre⁻¹. Consider that the current cost of P fertilizer is about \$1 lb^{-1} of P (i.e. \$0.43 lb^{-1} of P₂O₅). Thus, in order for the cost to be worthwhile from the perspective of recovering usable P fertilizer, the total cost of the process must be maintained at around \$1 lb⁻¹ of P recovered. This is not feasible considering that the P held onto the PSM is relatively dilute (30–5000 mg kg⁻¹), and therefore it would require handling many tons of PSM in order to extract a small amount of P. For example, consider a best case scenario where a 10-ton P removal structure possesses 3000 mg P kg⁻¹ at cleanout. In handling 10 tons of PSM, only 60 lb of P could be recovered at most, which is only about a \$60 value from the perspective of P fertilizer. Consider that this 60 lb of P would only be enough to fertilize around 1-6 acres for one year. The economics for stripping P for the purpose of recovering fertilizer improves as the value of P fertilizer increases.

Thus for current economics, it is generally not cost-effective to strip P off of spent PSMs recovered from non-point sources solely for the purpose of reusing the P as fertilizer. However, it could possibly be cost-effective for point sources of P containing high P concentrations and flow volumes such as a waste water treatment plant or manure lagoon. Each possibility should be examined on a case-by-case basis. This is not meant to imply that it is only worth \$1 lb⁻¹ to remove dissolved P from non-point sources. Again the value of P must be considered in context. On an equal mass basis, removing dissolved P from drainage water is worth much more than the value of P as a plant fertilizer because of the context of the impact of dissolved P on aquatic ecosystems (Chap. 1), and the general thermodynamic barrier inherent to capturing a dilute P concentration that is spread out over a very large area. In other

words, it requires a tremendous amount of energy to concentrate P when it is dilute and spread out over many acres, and therefore a greater amount of capital will be required to capture or concentrate this dissolved P. Perhaps a better way to normalize the value of P removal is to consider the cost required per lb of P removal for a waste water treatment plant. Even for a relatively predictable point P source with very high dissolved P concentrations, it still costs \$50–\$700 per lb P removed. Consider that it is much more difficult to remove dissolved P from the dilute non-point sources of P in the landscape. While this cost might seem excessive, it appears very reasonable from the context of economic losses due to surface water eutrophication that impacts everything from drinking water treatment to tourism.

While it is generally not cost-effective to strip P from spent PSMs from the perspective of P fertilizer value and P reuse, this may not be true for stripping P in order to reuse a PSM. Considering the costs associated with disposing of spent PSMs and obtaining fresh PSMs, it may be cost-effective in many situations to strip the P from the spent PSMs in order to recharge them.

8.3 Land Application of Spent PSMs to Soils for Benefits Other than P Fertilizer

Many PSMs possess properties that can make them useful for purposes other than P fertilization. Depending on the material being applied and the receiving soil, some PSMs can increase soil pH, base saturation, cation and anion exchange capacity, water holding capacity, potassium (K), secondary nutrients such as Ca, Mg, and S, and micronutrients such as B, Zn, and Cu. In general, most materials will contain little to no nitrogen and organic carbon.

Regarding plant Ca sources and possible liming materials, the most obvious example is Ca-based PSMs such as FGD gypsum, fly-ash, electric arc furnace and blast furnace slag, Ca-based drinking water treatment residuals (WTRs), and certain acid mine drainage residuals (AMDRs). These materials are often a source of plant available Ca due to their solubility in acid soils. In addition, some of those materials possess alkalinity and therefore have the potential to increase soil pH. Considering that acid soils will also typically suffer from low base cation saturation on the cation exchange complex i.e. excessive Al³⁺ and H⁺ on the cation exchange complex, the application of certain Ca-based PSMs will not only increase the pH, but also the base saturation. This is accomplished through neutralizing acidity, precipitation of plant toxic Al³⁺ into solid Al hydroxide minerals, and filling the cation exchange complex with Ca and Mg.

While most Ca-based PSMs will serve as a Ca and Mg source to plants in acid soils, fewer of these PSMs will be able to serve as a liming agent (i.e. increase soil pH). For PSMs to be able to significantly increase soil pH, they must contain some anions of neutralizing power that accompany the cations. As a result, we typically observe that the PSMs with the best "lime-power" contain Ca and Mg oxides, hydroxides, carbonates, or silicates. Just because a material contains Ca and Mg does not necessarily mean that it will have the potential to behave as a liming material. For example, some materials such as gypsum are rich in Ca but have no capacity to increase pH due to the lack of a neutralizing anion, as sulfate generally has little to no effect on soil pH. Still, gypsum is considered a highly valuable soil amendment as it has shown to improve Ca and S fertility, and soil chemical and physical properties. In order to determine the proper application rate of the spent PSMs to soils for increasing the pH to a desired level, it is necessary to first have the material tested for neutralizing power, i.e. alkalinity. This is accomplished by measuring the "Ca carbonate equivalent" (CCE) of the material by adding it to a known volume and concentration of strong acid, and then back-titrating the reacted mixture with a base to quantify how much of the PSM was neutralized by the acid. This test is often conducted by commercial soil and material testing laboratories. Knowing the CCE per unit mass of the PSM, a land applicator can then rely on the accepted soil test for the region for determining soil lime requirement, which will provide a recommendation for the mass of CCE to be applied per acre.

Some PSMs will possess valuable amounts of S and certain micronutrients. Flue gas desulfurization gypsum is the best example of a material that is an excellent source of S, a necessary plant nutrient that is needed in relatively large amounts. Steel slag is also a good source of plant available S as it often contains Ca sulfate. Fly-ash and other coal combustion by-products often contain appreciable amounts of S, Ca, Mg, K, and micronutrients such as Cu, Mo, and Zn. However, some of these materials can contain excessive heavy metals as well (see discussion below on safety and also Chap. 4). Adding K to soils is especially attractive since this is considered a macronutrient. Certain smelter wastes are often good sources of certain micronutrients, but must be examined for safety and be applied properly. Acid mine drainage residuals are rich in Fe, S, and sometimes micronutrients. Depending on how the material was produced it could also be a rich source of Ca and Mg as well as possessing some acid neutralization potential. Drinking WTRs are often enriched in nutrients because they are composed of fine particles that were lost in runoff to streams and reservoirs before being captured at a drinking water treatment plant. Thus, depending on the sample, WTRs can be an excellent source of plant nutrients if the sediment source was from agricultural soils. In addition, some WTRs are produced at the treatment plant through addition of Ca minerals to the water, which will result in a material with high Ca content and potential to serve as a liming agent. Although Si is only considered a micronutrient for certain crops such as rice and sugarcane, certain spent PSMs such as steel slag can serve as an excellent source of Si to this crops.

Some spent PSMs can have an impact on soil physical properties, either directly or indirectly. Indirectly, the addition of highly Ca soluble materials such as spent FGD gypsum or fly-ash can improve the flocculation status of a soil by shrinking the electrical double layer of soil particles. Essentially, because Ca has a high charge to radius ratio, it allows soil particles to approach each other closely and results in a better aggregated soil. This better flocculated and aggregated soil has less erosion, better water infiltration, drainage, and gas exchange, and is generally more stable. An example is how FGD gypsum has been used for years to indirectly improve soil

physical properties by filling much of the cation exchange complex with Ca. Spent PSMs can also directly improve soil physical properties in certain situations. Specifically, the application of fine textured materials such as drinking WTRs to sandy soils will improve water holding capacity, and likewise the application of a sieved steel slag material with sand and gravel-sized particles may improve the drainage of high clay soils.

Depending on the mineralogical make-up, spent PSMs can also improve soil quality by increasing the capacity of the soil to retain cations and anions, i.e. cation exchange capacity (CEC) and anion exchange capacity (AEC). Specifically, the Fe and Al-based PSMs are rich in variable charge minerals, which can increase the net negative (CEC) and net positive (AEC) charge of the soil. The ultimate benefit is that the soil will be able to retain more nutrients such as nitrate, ammonium, phosphate, trace minerals, and base cations such as Ca and Mg. The charge of these minerals is a function of the pH. As discussed in Chap. 4, increasing pH will increase the negative charge (CEC) and decreasing pH will increase positive charge (AEC).

Since spent PSMs are generally low in organic matter, they can be blended with other by-products (non PSMs) that are rich in organic matter and nitrogen to create excellent potting or planting mediums and synthetic soils. Non-PSM by-products such as yard clippings, distillers grains, biosolids, animal manure, compost, and food wastes have a low mineral component, opposite of spent PSMs. As a result, blending these organic materials with spent PSMs will complement each other synergistically in creation of an ideal plant medium for either land application, use in pots, or as a synthetic soil in remediation efforts. These materials have been successfully blended many times for creation of a new material that serves as a better plant medium than if each material had been utilized alone. In blending by-products, one must also consider physical properties, not just balancing nutrients and chemical parameters. For example, the texture, porosity, and bulk density of the final blend is extremely important to the ultimate use of growing plants. Some successful examples of blending materials includes a mixture of FGD gypsum, yard waste compost, and biosolids. Another example is wood ash, biosolids, and crushed concrete. Whatever the materials to be blended, each component must be analyzed for safety considerations.

8.3.1 Safety Considerations in Land Application of Spent PSMs

Just as all by-product PSMs must be screened prior to use in a P removal structure, the spent PSMs must also be tested in order to determine if there are any hazards with land application of the materials. Technically, if the PSM is safe enough to use in a P removal structure as determined by the initial screening discussed in Chaps. 4 and 5, then it will be safe for land application.

As discussed in Chap. 4, the materials must especially be examined for heavy metals content. While there are clear rules for land application of biosolids based on trace metal content, there is little to no such guidance for other by-products in most states. However, in North Carolina, the Department of Environment and Natural Resources offers excellent guidance for the land application of industrial by-products, including steel slag and fly-ash. The Industrial Resources Council (IRC: www.industrialresourcescouncil.org) is a very useful resource for obtaining information about beneficial reuse of industrial by-products and can provide guidance on where to find information on state regulations, if any.

We recommend that the land applicator seek to learn the local or state rules for land application of by-products that are not biosolids, and obtain permits if necessary. If there is no available guidance, then one should take a similar approach as to what was described in Chap. 4 for screening PSMs for use in a P removal structure. Again, this approach should consider not only the total concentration of the metals to be applied, but also the water solubility of the metals. Examples of total metals and nutrient concentrations in several by-products are shown in Table 8.3. In addition, Table 8.4 also provides examples of water-soluble concentrations. Note that the purpose of these tables is simply to provide an example, and those specific values should not be used to guide PSM screening for use in a P removal structure or land application; each material must be individually analyzed. Although it is not a perfect guide since the PSMs are obviously not biosolids, the EPA 503 rules for land application rates based on not exceeding annual and lifetime cumulative metals loading rates (Table 8.5).

8.4 Alternative to Land Application of Spent PSMs

Many industrial by-products that are used as PSMs can be beneficially used in ways other than land application. One of the best examples of this is sieved steel slag. Since sieved steel slag is a gravel-like material, it makes an excellent cover for farm roads and other dirt roads. Because it is gravel, it can essentially be used as construction material. In fact, the most common use for steel slag is in the construction industry, particularly in road construction. Many state Department of Transportation (DOT) facilities regularly utilized steel slag in road construction. These gravelly spent PSMs can also serve as a good mulch in certain areas.

Other alternatives to land application include use as a confined geotechnical fill such as building subbase, parking lot base and subgrade fill, road base, bridge abutment backfill, and utility trench backfill, encapsulated transportation facility embankment, capped transportation facility embankment, unconfined geotechnical fill, un-bonded and bonded surface course, decorative stone, cold weather road abrasive, and landfill daily cover. Some states provide guidance and regulations on such uses, for example, the Wisconsin Department of Natural Resources offers

Table o. E	valuptes o					ctars for			u tat uy-pround				
Material	Zn	Cu	Mn	As	Cr	Cd	Ni	В	Ca	Mg	K	S	Fe
FGD gypsum-1	4.4	9.4	4.9	11.9	0.9	0.4	0.2	3.9	147,052	466	121	111,939	1101
FGD gypsum-2	7.0	2.1	10.4	12.4	0.4	0.4	1.5	14.6	209,000	1501	316	156,991	1791
Foundry sand	67	09	185	12.5	28	2.5	573	34	9433	75,787	275	359	19,976
Fly-ash	106	109	BD	81.7	48	11	36	698	153,547	28,468	2173	6660	36,637
Al-based WTRs-1	33	72	2034	262	102	20	17	49	3276	1643	2016	5316	16,823
Al-based WTRs-2	42	109	12,147	205	19	10	28	59	18,235	1578	15,916	1994	3525
Ca-based WTRs	19	2.7	154	30	6.5	2.0	6.2	7.5	286,628	19,060	1757	8494	7177
Bauxite waste	BD	BD	BD	109	513	19	40	753	15,000	1663	565	848	213,217
AMDR-1	24	BD	457	267	17	17	37	1088	8342	1167	1670	6311	338,804
AMDR-2	444	2.8	10,004	40	6.8	7.1	334	291	204,779	34,852	463	17,082	118,258
AMDR-3	BD	BD	373	57	12	50	59	1628	BD	BD	174	9355	455,681
EAF steel	1174	387	15,011	65	2535	13	149	868	176,317	58,074	313	5583	235,602
slag													
Do not use th	uis table as	a guide	for land appl	lication o	of spent PS	SMs: co	nduct a	chemical	characterizatio	on on the actu	al material t	o be land appli	ied. All values
are in units of	f mg kg ⁻¹ .	Values d	letermined by	v using th	ie total dig	testion 1	nethod o	described	in Chap. 5				

Table 8.3 Examples of total concentrations of nutrients and metals found in some industrial hy-moduct PSMs

WTRs drinking water treatment residuals, AMDRs acid mine drainage residuals, FGD gypsum flue gas desulfurization gypsum, EAF electric arc furnace "BD" indicates measurement below detection limit

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Material	Zn	Cu	Mn	As	Cr	Cd	Ni Ni	Ca	Mg	K	Fe
FGD	0.0005	BD	0.005	0.004	0.0035	BD	0.006	667	0.239	0.87	0.01
gypsum-1									1		
FGD gvpsum-2	0.0005	0.0025	0.0155	0.0025	0.0035	0.0005	0.006	652	3.7	1.6	0.03
Foundry	0.15	0.172	0.06	0.006	0.015	0.001	0.074	13.3	0.061	3.9	12.6
sand											
Fly-ash	BD	0.006	BD	BD	0.102	BD	BD	104	0.093	5.4	0.03
Al-based	BD	0.023	5.3	0.004	0.003	BD	0.004	42	2.0	3.7	0.02
WTRs-1											
Al-based	BD	0.013	0.18	0.017	0.004	0.0005	0.004	218	2.6	6.5	0.02
WTRs-2											
Ca-based	0.022	0.009	0.02	0.01	0.0035	BD	0.005	75	218	30	0.02
WTRs											
Bauxite	0.021	0.019	0.008	0.04	0.022	0.0005	0.01	3.4	0.93	7.8	2.5
waste											
AMDR-1	0.0006	0.0014	0.36	0.004	0.003	0.0005	0.005	390	24	6.2	0.013
AMDR-2	0.02	0.007	0.006	0.007	0.004	BD	0.016	71	212	12	0.03
AMDR-3	0.12	0.002	7.3	0.008	0.004	0.003	1.4	105	3.2	3.3	0.09
EAF steel	BD	0.032	BD	0.003	0.04	BD	BD	34	0.10	8.5	0.03
slag											
Do not use this	table as a guid	de for land ap	plication of sp	ent PSMs: cond	luct a chemic	characteriz	ation on the	actual mat	erial to be la	and applied.	All values

Table 8.4 Examples of water-soluble concentrations of nutrients and metals found in some industrial by-product PSMs

are in units of mg L⁻¹. Values determined by using the water extraction method described in Chap. 5

WTRs drinking water treatment residuals, AMDRs acid mine drainage residuals, FGD gypsum flue gas desulfurization gypsum, EAF electric arc furnace "BD" indicates measurement below detection limit

			EPA annual	EPA cumulative
	EPA pollutant	EPA ceiling	pollutant	lifetime pollutant
	concentrations for	concentration	loading limits	loading limits
	exceptional quality	limits for all	for biosolids	for biosolids
Material	biosolids (mg kg ⁻¹)	biosolids (mg kg ⁻¹)	(kg ha ⁻¹ year ⁻¹)	(kg ha^{-1})
As	41	75	2.0	41
Cd	39	85	1.9	39
Cr	1200	3000	150	3000
Cu	1500	4300	75	1500
Pb	300	840	15	300
Hg	17	57	0.85	17
Мо	-	75	-	-
Ni	420	450	21	420
Se	36	100	5.0	100
Zn	2800	7500	140	2800

 Table 8.5
 EPA rules for land application of biosolids (EPA 503 Rule; USEPA 1994)

While not ideal for industrial by-products, it does provide some guidance in the absence of state rules specific to other industrial by-products. "Exception quality" biosolids are those that require no permit for land application. Loading limits are the maximum amount of the metal that can be applied in a single year and also over the lifetime of the site (i.e. cumulative)

excellent guidance within their office of Waste & Materials Management (Chapter NR 538, Wis. Adm. Code; PUB-WA1796).

Regardless of the method of beneficial reuse and disposal of spent PSMs, safety considerations must be taken into account in the context of the disposal method. For example, land application onto agricultural land presents a very different context than utilizing the spent PSMs as a fill material or surface course. Again, it is critical that local and state regulations are respected in such uses.

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Erratum to: Phosphorus Sorption Materials (PSMs): The Heart of the Phosphorus Removal Structure

Erratum to: Chapter 4 in: C. Penn, J.M. Bowen, *Design and Construction* of Phosphorus Removal Structures for Improving Water Quality, DOI 10.1007/978-3-319-58658-8_4

The original version of this chapter was inadvertently published with an incorrect reference (Slag 1; Table 4.2 and Fig. 4.1c) in the caption of Table 4.7. The correct reference is updated as "Fig. 3.5".

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