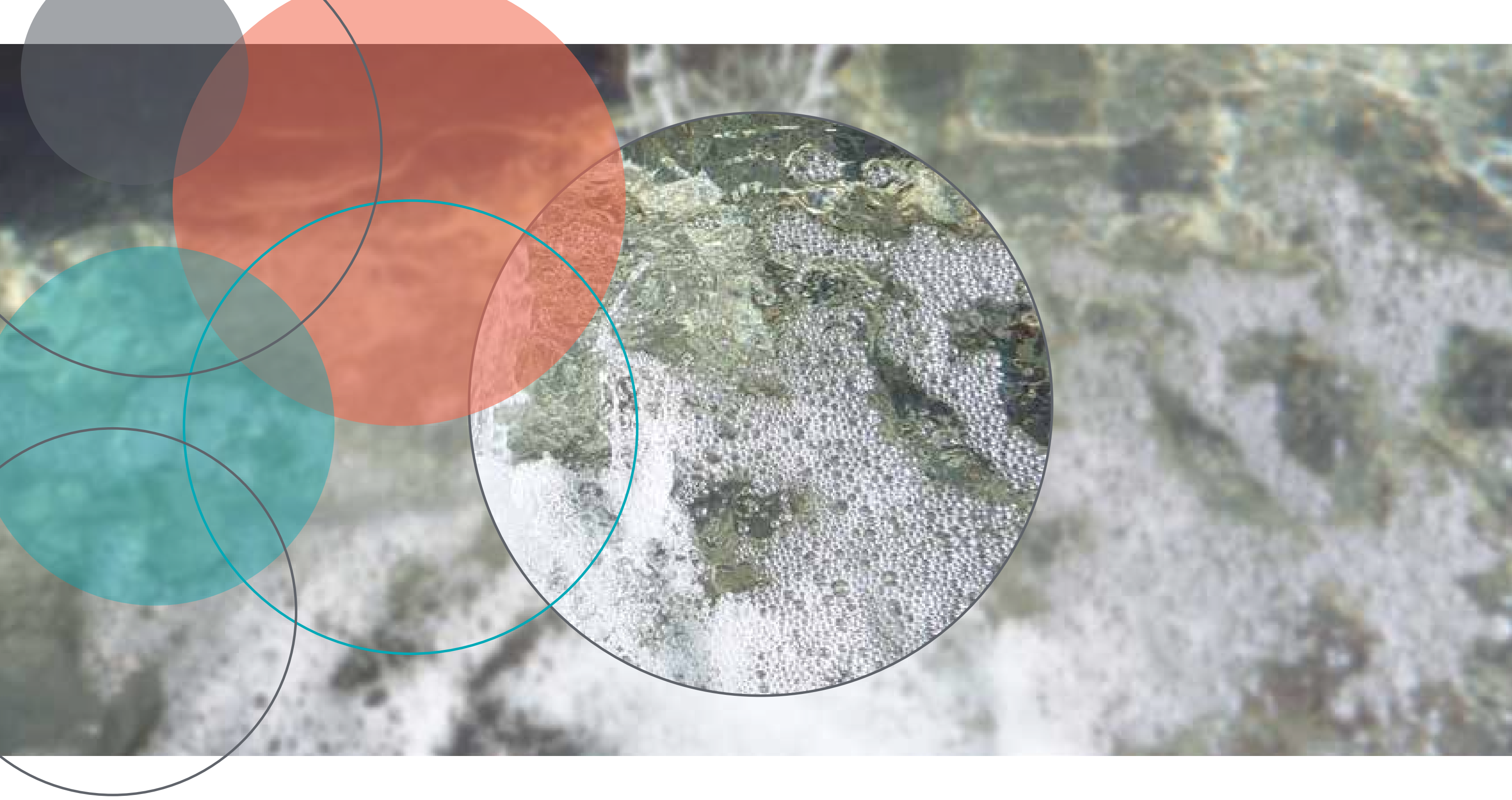

Tertiary Phosphorus Removal

MARCH 2019

The 2008 *Tertiary Phosphorus Removal Compendium* was written to identify knowledge gaps to be addressed by the Nutrient Removal Challenge. That document contains state-of-the-art knowledge to achieve reliable, cost-effective nutrient removal. The 2008 compendium included a number of questions and challenges to reduce nutrients in advanced treated wastewater. This 2019 compendium revision contains a summary of the findings presented in reports and documents generated by the researchers and contributors.

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●●●● PHOSPHORUS REMOVAL BACKGROUND

Chemical and biological phosphorus removal processes have been used to reliably reduce phosphorus to 1 mg/L and often to 0.5 mg/L with conventional chemical or biological phosphorus removal processes and secondary treatment (Neethling et al. 2005). Additional tertiary processes are required to polish secondary effluent phosphorus to achieve greater reliability and reduce phosphorus concentrations to meet lower limits. Filtration (conventional solids separation processes) can be used to remove suspended solids and thus particulate phosphorus and, when coupled with additional chemical phosphorus removal, can often reduce total phosphorus (TP) concentrations well below 0.5 mg/L. For example, two Clean Water Services facilities in Oregon have met a 0.07 mg/L or 70 ug/L monthly median TP discharge limit since the early 1990s using tertiary sedimentation and filtration processes with chemical addition. Treatment processes and performance statistics for other water resource recovery facilities (WRRFs) with low phosphorus limits have been studied as part of the Nutrient Removal Challenge (Bott and Parker 2011). This compendium on tertiary phosphorus removal focuses on factors that need to be considered to reduce phosphorus below 0.5 mg/L and, in particular, the requirements to reduce phosphorus to very low limits, to 0.1 mg/L (100 ug/L) or lower.

What Are Conventional Phosphorus Removal Processes?

Biological and chemical processes have been used for many years to remove phosphorus.

Enhanced Biological Phosphorus Removal (EBPR) is a modification of the activated sludge process that will increase phosphorus efficiency from a typical value of 20 percent to 75 percent or more. In the 1950s, Greenburg et al. (1955) proposed that activated sludge could take up phosphate at a level beyond its normal microbial growth requirements. Levin and Shapiro (1965) were the first to report EBPR in the District of Columbia activated-sludge plant, and by the 1970s, work in the United States and South Africa (Barnard 1974) clearly demonstrated that EBPR can occur. EBPR processes will reduce the effluent total phosphorus to 0.5-1.0 mg/L without filtration. EBPR processes include anaerobic zones to select for the growth of phosphorus-accumulating organisms (PAOs) that perform EBPR.

Chemical phosphorus removal is achieved by adding chemicals to the wastewater at a well-mixed location, followed by flocculation and solids removal. The commonly used chemicals are aluminum (Al(III)), ferric (Fe(III)) and calcium (Ca(II)). In wastewater treatment, the chemicals can be added before a primary clarifier or other solids separation device. The effluent phosphorus concentration is determined by the dose and other chemical reactions. An effluent of 0.5-1 mg/L can typically be achieved without constructing specific post-secondary treatment facilities.

What Effluent Phosphorus Concentration Can Be Achieved with Conventional Phosphorus Removal Processes?

Conventional Phosphorus Removal processes using chemical addition or EBPR can achieve 0.5-1.0 mg/L. Additional polishing with filtration or other tertiary processes is required to reduce phosphorus reliably below these limits.

What Are the Essential Elements of Tertiary Phosphorus Removal Processes?

Wastewater treatment processes that achieve low phosphorus concentrations (<50 ug/L) typically follow conventional phosphorus removal. Many tertiary processes, which are mostly physical and chemical processes, have been used to polish effluents. The chemical process first converts soluble reactive phosphorus to a solid particle followed by removal of particulate phosphorus by a physical process. These include some of the following elements:

- Chemical addition to react with the soluble phosphorus species and produce a solid precipitant.
- Chemical flocculants to capture small particulates for removal in solids separation processes.
- Chemical removal onto a reactive surface of preformed precipitants or other surfaces (such as iron oxide coated sand).
- Solids separation to remove particulate phosphate species.
- Adsorption through the contact of phosphorous in water phase to solid phase, such as the flocs retained by filters (Jenkins 2007).
- Treatment processes and performance statistics for WRRFs with low phosphorus limits were studied as part of the Nutrient Removal Challenge (Bott and Parker 2011). The reader is referred to this study and a related compendium (WRF 2019a) for additional details.

PHOSPHORUS SPECIES AND THEIR REMOVAL IN TERTIARY PROCESSES

What Are the Different Phosphorus Species in Wastewater and Treated Effluents?

A review of phosphorus species and measurement methods and issues was presented in a WRF compendium on low phosphorus concentration measurement (WRF 2019b) and best practices for phosphorus analytical methods by Smith (WRF 2015).

Phosphorus in raw domestic wastewater to WRRFs consists of ortho-phosphorus (PO_4-P), condensed polyphosphates, and organic phosphorus in soluble and particulate form. PO_4-P is readily available for uptake by bacteria, archaea, and algae. Organic phosphorus and condensed polyphosphates may be transformed to PO_4-P by hydrolysis and biotransformations.

Phosphorus species classification applicable to raw wastewaters, treated effluents, and surface waters is shown in Table 1 below. The species and concentrations are based on specific analytical methods, which are summarized in Standard Methods Section 4500-P A. (APHA 2005) along with a similar illustration of the phosphorus fraction. Similar to nitrogen, the total phosphorus concentration is equal to the sum of the soluble phosphorus (SP) and particulate phosphorus (pP) concentrations. For WRRFs design and operated to achieve low effluent permit limits for phosphorus, the effluent phosphorus is mainly in the soluble form.

Table 1 - Phosphorus Species in Wastewater Treatment

<table>
<tr><th colspan="6">Total P (TP)</th></tr>
<tr><th colspan="3">Soluble P (SP)</th><th colspan="3">Particulate P (pP)</th></tr>
<tr><td rowspan="2">Soluble Reactive P (SRP)</td><td colspan="2">Soluble Non-reactive P (SNRP)</td><td rowspan="2">Particulate Reactive P (pRP)</td><td colspan="2">Particulate Non-reactive P (pNRP)</td></tr>
<tr><td>Soluble Acid Hydrolyzable P (SAHP)</td><td>Soluble Organic P (SOP)</td><td>Particulate Acid Hydrolyzable P (pAHP)</td><td>Particulate Organic P (pOP)</td></tr>
</table>

For total phosphorus (TP) determination, a digestion procedure using persulfate, nitric acid, or perchloric acid (persulfate is the most preferred method) converts the phosphorus to PO_4-P, which is measured by a colorimetric procedure. For samples without preliminary hydrolysis or oxidative digestion, the phosphorus concentration measured is referred to as reactive phosphorus. The procedure may also detect a small amount of condensed polyphosphates in addition to PO_4-P. Thus, as shown in Table 1, the TP minus the reactive P (RP) is equal to the non-reactive P (NRP). The NRP is equal to the sum of the acid hydrolysable P (AHP) and the organic P (OP).

Of these two, the AHP is determined by direct measurement involving a boiling-water temperature and sulfuric acid addition. For soluble P and particulate P, the SOP is equal to the SNRP minus the SAHP and the pOP is equal to the pNRP minus the pAHP, respectively. Particulate P concentrations are normally determined by subtracting the measurements for a filtered sample from the measurements for an unfiltered sample.

What Are the Soluble Phosphorus Species in Wastewater?

Soluble phosphorus is defined as the phosphorus species passing through a 0.45 um filter by both EPA method 365.2 and Standard Methods 4500-P, including both colloidal and truly soluble species. Other filter sizes can be used, but 0.45 um is most commonly used in the wastewater industry. “Soluble” is often used interchangeably with “dissolved,” and “particulate” is often used in place of “insoluble” or “suspended.” Phosphorus compounds are not isolated and identified directly; rather, phosphorus compounds are grouped into fractions and defined by the analytical method used to measure them. While there are other methods of analysis, the Standard Methods and EPA method of colorimetric analyses following some level of digestion is most common. There are three analyses that are typically performed: direct colorimetry, sulfuric acid digestion/colorimetry, and persulfate digestion/colorimetry. The differences between these analyses define the three soluble phosphorus fractions.

Direct colorimetry measures mostly orthophosphate. While EPA Method 365.3 suggests this fraction is comprised entirely of orthophosphates, Standard Methods 4500-P recognizes that some small quantity of other phosphorus compounds respond to direct colorimetry, and, thus, more accurately identifies this fraction as being simply “reactive phosphorus” rather than “orthophosphate phosphorus.” The difference between sulfuric acid digestion/colorimetry and direct colorimetry analyses defines the “acid-hydrolyzable phosphorus” fraction, comprised mostly of condensed phosphates (polyphosphates (chain structure)) and metaphosphates (ring structure). The difference between the persulfate digestion/colorimetry and the sulfuric acid digestion/colorimetry analyses defines the “organic phosphorus” fraction, comprised mostly of the organically bound phosphorus in phospholipids, sugar phosphates, nucleotides, and phosphoamides.

See also discussion detailed discussion on best practices for measuring phosphorus species in Smith (WRF 2015) and *Low P Concentration Measurements Compendium* (WRF 2019b).

What Are the Particulate Phosphorus Species in Wastewater?

Particulate phosphorus species include the particles excluded by filtration. It is more technically accurate to define these as “non-filterable” phosphorus—representing particles retained by 0.45 um filtration. Particulate phosphorus represents organic and inorganic phosphorus, chemical precipitants, and biomass—all particles larger than the filter exclusion size. Some colloidal particulates will pass through the filter, be detected in the soluble fraction, and be missing from the particulate fraction – even though it is a small particle. See *Low P Concentration Measurements Compendium* (WRF 2019b).

How Are the Different Chemical Species Removed from Wastewater?

Phosphorus species must be converted to a solid form in order to be removed from water. All phosphorus entering a treatment plant therefore exits the treatment plant as a solid (residual) stream or leaves with the effluent (liquid stream).

Table 2 summarizes the processes used to convert/remove phosphorus species from wastewater. (Note that the species are not distinct.)

Table 2 - Conversion and Removal Processes for Various Phosphorus Species

Species	Common Conversion or Removal Process
Organic-P	Organic phosphorus can be converted to orthophosphate and polyphosphate, some organics degrade very slowly
Orthophosphate	Most abundant phosphorus species Reactive species in chemical reactions and consumed in biological growth
Polyphosphates	Condensed orthophosphates Possibly reacts with metal salts Can be used for biological growth
Chemical Phosphorus	Precipitated phosphates formed by reacting orthophosphate with metal salts, or precipitates as phosphate hydroxides
Biological Phosphorus	Phosphorus incorporated into the biomass for growth Excess phosphorus may accumulate under certain conditions

How Is Reactive Phosphorus Removed from Wastewater by Chemical Treatment?

Reactive phosphorus is defined in Standard Methods as, "Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample." Standard Methods continues, stating, "While reactive phosphorus is largely a measure of orthophosphate, a small fraction of any condensed phosphate present usually is hydrolyzed unavoidably in the procedure. Reactive phosphorus occurs in both soluble and suspended forms." Reactive phosphorus is therefore primarily orthophosphate, and defined based on the standard analytical technique used.

Chemical phosphorus removal utilizes reactions between phosphate in water and other chemical species or compounds, usually multivalent metal ions, to form precipitates of sparingly soluble metal phosphate salts that can subsequently be removed from the liquid using a solids separation process. The commonly used chemicals are aluminum (Al(III)), ferric (Fe(III)), and calcium (Ca(II)).

The chemical reaction of phosphorus with aluminum and ferric salts in a liquid environment is complex. The classic model of a metal reacting with a phosphate to produce a metal-phosphate precipitant ($AlPO_{4(s)}$ or $FePO_{4(s)}$) does not occur under the conditions in a wastewater treatment plant (Smith et al. 2007). The precipitant is a complex structure where metal hydroxides are formed and phosphate bonds with the metal hydroxide complex.

- The metal reacts with water to produce metal hydroxides. These metal hydroxides (typically shown as the basic chemical form of $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$) actually form hydrated forms and precipitate as an amorphous complex that will change structure and form with time.
- Phosphate forms bonds with the metal hydroxyl complex. These bonds are very strong and bind the phosphate to the structure. The amount of phosphate that binds to the metal hydroxide is still a topic of discussion. Current research suggest that the stoichiometric ratio of metal:phosphorus (Me:P) in the precipitant depends on many factors, including the phosphate concentration in the liquid, chemical dose, age of the hydroxyl complex, mixing, and many other factors (Szabo et al. 2008, de Haas et al. 2000, Yang et al. 2006).

The removal of the efficiency of phosphates depends on the chemical dose, pH, and temperature. To complicate matters, the metal hydroxyl precipitant and reactions also depend on mixing intensity, age of the precipitant, and other factors. The required dose must therefore often be determined from practical experience for a given application.

See Gu et al. (2014b) for additional information about removal of specific phosphorus species in WRRFs.

How Is Soluble Non-reactive Phosphorus (SNRP) Removed from Wastewater by Chemical Treatment?

Soluble non-reactive phosphorus is defined as the difference between the total soluble phosphorus and soluble reactive phosphorus. The chemical species making up the non-reactive phosphorus is unknown, but could include polyphosphates, condensed phosphates, soluble organic phosphorus species, and other phosphorus-containing species.

SNRP removal mechanisms are complex and not well understood, but depending on the chemical structure of the compound, can include adsorption, filtration, and coagulation. Depending on the structure, some portion of the soluble acid-hydrolyzable and/or soluble organic phosphorus fractions simply cannot be removed by tertiary processes and are considered recalcitrant or non-reactive. It is suspected that recalcitrant phosphorus is mostly, if not entirely, comprised of soluble organic phosphorus (Neethling et al. 2007).

In advanced tertiary phosphorus removal processes, effluent recalcitrant sNRP is expected to be approximately 10 ug/L as shown by Benisch et al. (2007) and other Nutrient Challenge work subsequently discussed. Transient effluent sNRP concentrations may be higher and affected by commercial and/or industrial wastewaters. Lancaster and Madden (2008) measured intermittent recalcitrant phosphorus concentrations up to 500 ug/L for a domestic wastewater with nearly 50 percent commercial and industrial components revealed (Lancaster and Madden, 2008).

See Gu et al. (2014b) for additional information about removal of specific phosphorus species in WRRFs.

How Is Acid Hydrolysable Phosphorus Removed from Wastewater by Chemical Treatment?

Acid hydrolysable phosphorus refers to phosphorus compounds that are converted to orthophosphate (reactive phosphorus) under mild acid/boiling conditions. The sample pH is adjusted to the phenolphthalein endpoint (<8.2) before boiling for 90 minutes. Standard Methods states that these compounds "include condensed phosphates such as pyro-, tripoly-, and higher-molecular-weight species such as hexametaphosphate. In addition, some natural waters contain organic phosphate compounds that are hydrolyzed to orthophosphate under the test conditions. Polyphosphates generally do not respond to reactive phosphorus tests but can be hydrolyzed to orthophosphate by boiling with acid."

Work under the Nutrient Removal Challenge, discussed subsequently, has shown that significant fractions of secondary effluent SAHP can be removed in tertiary phosphorus removal processes. The exact mechanisms of removal were not studied, but it is possible that the phosphate species in this group may react with metals salts (aluminum and iron) similar to orthophosphate and may be removed by a similar mechanism.

See Gu et al. (2014b) for additional information about removal of specific phosphorus species in WRRFs.

How Is Soluble Organic Phosphorus Removed from Wastewater by Chemical Treatment?

Organic phosphorus includes soluble and particulate forms of phosphorus contained in organic compounds. There is no simple analytical procedure to measure organic phosphorus, making it difficult to track its removal. The soluble organic phosphorus is the portion that is in solution (not particulate) and is measured as the fraction that passes a 0.45 um filter. Technically, it should be referred to as the "filterable" fraction.

Organic phosphorus compounds are calculated from total phosphorus measurements, which include a digestion step to oxidize all organic compounds. Standard Methods recognize three digestive methods using perchloric acid, nitric acid-sulfuric acid, or persulfate oxidation. Standard Methods states that these organic phosphorus compounds represent "phosphate fractions that are converted to orthophosphate only by oxidation destruction of the organic matter present are considered 'organic' or 'organically bound' phosphorus. The severity of the oxidation required for this conversion depends on the form—and to some extent on the amount—of the organic phosphorus present."

The above analytical definition of organic phosphorus is tied to the "severity of oxidation." The analytical challenge is to measure the inorganic phosphorus fraction independently, which requires the ability to differentiate between the polyphosphates, condensed phosphates, and organic phosphorus. The current methods rely on differing acid hydrolysis methods that cannot distinguish between these fractions.

Work under the Nutrient Removal Challenge, discussed subsequently, has shown that significant fractions of secondary effluent SOP can be removed in tertiary phosphorus removal processes. The exact mechanisms of removal were not studied, but it is possible that the phosphate species in this group may react with metals salts (aluminum and iron) similar to orthophosphate and may be removed by a similar mechanism.

See Gu et al. (2014b) for additional information about removal of specific phosphorus species in WRRFs.

What Are Soluble Phosphorus Species Concentrations in Tertiary Phosphorus Removal Effluents?

Concentrations of the various phosphorus species is a function of the treatment process and methods used to achieve very low effluent P concentrations. The Nutrient Removal Challenge report NUTR1R06l (Gu et al. 2014b) provides information on a comprehensive study of phosphorus species concentrations across secondary and tertiary treatment processes from 12 full-scale facilities. The tertiary phosphorus removal methods included granular media filtration, membrane filtration, single- and two-stage filtration, and tertiary clarification with filtration. A key general finding was that as the effluent TP concentration was lowered due to chemical treatment and filtration or membrane separation, the SRP decreased to very low concentrations and the SAHP and SOP fraction increased. The secondary processes used EBPR and/or chemical precipitation with metal salts. In chemical precipitation alum or ferric metal salts are commonly added to form metal hydroxides, which sorb the soluble P and remove it from the system in particulate form. Some of the SAHP and SOP was also sorbed.

Examples of tertiary treatment process influent and effluent phosphorus species concentrations from Gu et al. (2014b) are given in Table 3. This represents only a portion of the results in the report and the facilities selected for the table were those that had SP concentrations above 0.05 mg/L due to less upstream chemical treatment. Both SRP and SNRP including SOP and SAHP were removed by chemical treatment. With high chemical dose, the effluent SRP was below 10 ug/L and about 70 percent of the remaining effluent SP was SNRP, primarily in the form of SOP versus SAHP. The report also showed variations in SAHP and SOP concentrations and percentage of the total SP for different facilities.

Table 3 - Influent and Effluent Soluble Phosphorus Species for Tertiary Treatment Processes for Different Nutrient Removal Facilities

Tertiary Process	Influent Soluble P, ug/L					Effluent Soluble P, ug/L					% NRP
	SRP	SOP	SAHP	SNRP	Soluble TP	SRP	SOP	SAHP	SNRP	Soluble TP	
Sedimentation	54	113	83	196	250	1	8	1	9	10	90
Co Mag Sedimentation	2447	157	64	221	2668	1	4	2	6	7	86
Densa Sedimentation	1523	58	33	91	1614	1	1	2	3	4	75
Single-stage Filtration	599	21	20	41	640	100	5	1	6	106	6
Membrane	413	22	1	23	436	8	13	3	16	24	67
Multi-stage Filtration	498	30	12	42	540	5	9	1	10	15	67
Multi-stage Filtration	3178	28	264	292	3470	1	6	1	7	8	88

Source: Gu et al. 2014b

How Is Particulate Phosphorus Removed from Wastewater by Chemical Treatment?

Chemicals can be added to enhance particulate removal in unit processes. In this application, the chemical is added to flocculate and captures small phosphorus particles. Various polymers have been used to enhance the solids capture of fine particles to improve their removal in biological processes and with solids separation processes.

Once the phosphorus is converted to a solid form, it still needs to be captured and removed from the liquid. Note that chemically precipitated phosphorus particles will dissolve during the analysis and measure as reactive phosphorus. This will create the appearance of higher orthophosphate in the sample.

Research Needs

The structure and flocculation of small phosphorus particles have not been established. While the processes are expected to follow the normal solids separation fundamentals, the pH dependency of the phosphorus precipitant and surface chemistry of metal hydroxide/phosphorus complexes are not established. For example, is the optimum pH for phosphorus precipitation the same as for flocculation?

How Are Particulate Chemical Phosphorus Particles Removed from Wastewater?

Particulate phosphorus removal can be achieved with conventional and emerging solids removal equipment. Solids removal equipment must be designed to handle the increased solids loading associated with chemical addition for phosphorus removal.

The following processes are typical of solids separation processes and presented in more detail elsewhere:

- Conventional sedimentation/filtration facilities
- High-rate sedimentation/filtration using ballasted sedimentation, solids blanket clarifiers, tube settlers, contact clarification, or other processes
- Direct filtration (without sedimentation facilities) using a variety of filter styles
- Two-stage filtration using two filter units in series
- Microfiltration or nanofiltration
- Magnetic-based separation using a ballasted separation and magnetic polishing step

See solids separation discussion below.

What Is the Bioavailability of Phosphorus in Tertiary Phosphorus Removal Effluents?

Several studies were done under the Nutrient Removal Challenge using samples from full-scale nutrient removal facilities to evaluate the bioavailability of effluent soluble phosphorus. Brett and Li (2015) evaluated the bioavailability of phosphorus in secondary and tertiary effluents from 12 facilities, while Gu et al. (2014a) focused on the bioavailability of SOP with samples from five process technologies at three facilities. The last study by Li et al. (2015) evaluated the uptake rates of both effluent SON and SP by algae with samples from five facilities. Bioavailable phosphorus (BAP) in these studies was measured by a similar bioassay procedure using S*elanastrum capricornutum* inoculant that was grown in accordance with standard methods (APHA 2005).

The studies showed that SRP and SNRP from tertiary phosphorus removal processes include both bioavailable and non-bioavailable fractions. The BAP fraction of effluent TP and SP correlated to phosphorus concentration and tended to decrease as effluent P concentration decreased. For very low effluent TP concentrations below 30 ug/L, the percent BAP is quite low ranging from 10 to 20 percent of the TP.

Brett and Li (2015) measured the reactive P concentration and bioavailability of nine commonly occurring organic-P compounds in biological processes, different humic substances, and seven inorganic-P compounds. Their findings are summarized in Table 3 according to the chemical category, speciation category, and bioavailability. The results show that some substances measured as nonreactive P can be bioavailable. These are SOP compounds and include byproducts of biological organisms such as ATP, DNA, and RNA. Tripolyphosphates compounds were also compounds that would be measured as nonreactive compounds but could be bioavailable. Humic substances have been thought to contain both non-bioavailable nitrogen and phosphorus in other studies but were categorized as nonreactive and non-bioavailable in Table 4. Future work could consider analyses for these compounds in effluents from nutrient removal facilities.

Table 4 - Summary of Speciation Reactivity and Bioavailability Measurements for Inorganic and Organic Phosphorus

(Containing Compounds that May Be Present in Nutrient Removal Facilities)

Chemical Category	Speciation Category	Bioavailability	Example Compounds
Inorganic	Reactive	Bioavailable	Ca-P
Inorganic	Nonreactive	Nonbioavailable	Al-P, Pyro-P
Inorganic	Reactive	Nonbioavailable	Apatite, Ca-hydroxyapatite
Inorganic	Nonreactive	Mostly Bioavailable	Tripoly-P
Organic	Nonreactive	Bioavailable	ATP, DNA, RNA
Organic	Nonreactive	Nonbioavailable	Phytic Acid
Humic	Nonreactive	Nonbioavailable	Humic Complexes

Source: Brett and Li 2015

CHEMICAL REACTIONS

Overview of Phosphorus Removal Chemistry

Chemical phosphorus removal is achieved by adding chemicals to the wastewater at a well-mixed location, followed by flocculation and solids removal. The commonly used chemicals are aluminum (Al(III)), ferric (Fe(III)), ferrous (Fe(II)), and calcium (Ca(II)). In wastewater treatment, the chemicals can be added before a primary clarifier or other solids separation device. The effluent phosphorus concentration is determined by the dose and other chemical reactions. An effluent of 0.5-1 mg/L can typically be achieved without constructing specific tertiary treatment facilities.

The understanding of the metal salt-phosphorus chemistry has increased rapidly since early 2000, as the surface complexation model has emerged and the phosphorus/metal/hydroxyl complex becomes better understood. Prior precipitation-equilibrium relationships are challenged with new data showing that lower concentrations are possible. Other chemical processes, such as adsorption, co-precipitation, crystal changes, and aging, are being studied, improving our understanding of the complex chemistry involved.

This section presents the chemistry of using metal salts to remove phosphorus from wastewater, the reactions, and the factors affecting the process efficiency.

What Chemicals Are Used to Precipitate Phosphorus?

Aluminum and iron-based salts are typically used for chemical phosphorus removal. Aluminum is dosed in the form of alum, polyaluminum chloride, or other hydrated aluminum compounds such as aluminum chlorohydrate. Iron is added as ferric or ferrous iron salt (chloride), but in some cases "pickle liquor" (from industrial iron works) that contains primarily ferric chloride, can be used.

Which Aluminum-based Chemicals Are Typically Used?

Alum is the most commonly used trade chemical for aluminum (Al(III)). Alum is aluminum sulfate and contains 14 waters of crystallization. Other formulations with 18 or even 24 waters of crystallization can be produced, but alum with 14 waters of crystallization is commercially used because it increases the aluminum content of the chemical and is a stable when stored. "Dry Alum" is therefore aluminum sulfate as $Al_2(SO_4)_3 \cdot 14H_2O$ (preamble to ANSI/AWWA STANDARD B403-03). Note that alum specifications typically state the Al_2O_3 or Al content.

When added to precipitate phosphorus, the following equivalents exist for alum:

1 mol alum = 594 g alum = 54 g Al (2 mol aluminum ion)
100 g/L alum = 168 mM alum = 337 mM Al
100 mg/L alum = 9.1 mg/L Al = equivalent of 17.2 mg/L Al_2O_3
100% alum = 9.1% Al = 17.2% Al_2O_3

Polyaluminum chloride (PACl) is another aluminum based chemicals commonly used. Various different formulations of PACl are available from different chemical suppliers. PACl has the advantage that it is hydrated and does not suppress pH when added to water. It is therefore attractive for poorly buffered waters. When dosing PACl, the chemical dose must be converted to an equivalent Al or Al_2O_3 concentration. Dosage of chemical needs to be distinguished from dosage of the trade product in calculations.

Alum doses for scientific discussion or fundamental presentations are expressed in terms of the Al(III), and typically on a molar basis. Engineering and treatment plant applications, however, typically express doses in terms of "alum." One should therefore exercise care when reporting, interpreting, and expressing alum dose. The relationships in the equations on the previous page show the conversion. A molar ratio of 1:1 mol aluminum/mol P is, therefore, equivalent to ~0.87 g Al/g P; or ~9.6 g alum/g P.

Which Iron-based Chemicals Are Typically Used?

Ferric chloride (a.k.a. "ferric") is the most commonly used trade chemical for ferric iron (Fe(III)). Ferrous chloride and sulfate is used for adding ferrous iron (Fe(II)).

Liquid ferric chloride is an orange brown aqueous solution that is acidic and very corrosive. There is opportunity for confusion since the trade chemical is called "ferric" as is the iron (III) ion. The two are quite distinct, though. Commercial ferric is typically specified as "dry ferric chloride" (ANSI/AWWA STANDARD B407-05).

When added to precipitate phosphorus, the following equivalents exist for ferric:

1 mol ferric chloride = 162 g ferric chloride = 56 g Fe(III)
100 g/L ferric (chloride) = 617 mM ferric (chloride) = 617 mM Fe(III)
100 mg/L ferric (chloride) = 35 mg/L Fe
100% ferric = 35% Fe

Ferric doses for scientific discussion or fundamental presentations, are expressed in terms of the Fe(III), and typically on a molar basis. Engineering and treatment plant applications, however, typically express doses in terms of "ferric." One should therefore exercise care when reporting, interpreting, and expressing alum dose. The relationships in the equivalents above show the conversion. Dosage of chemical needs to be distinguished from dosage of trade product in calculations. A molar ratio of 1:1 mol Fe/mol P is therefore equivalent to ~1.8 g Fe/g P; or ~5.2 g ferric chloride/g P.

What Is a Surface Complexation Model?

A surface complexation model (SCM) attempts to examine the molecular level electrostatic and chemical bonding forces that determine the retention of cations and anions on mineral surfaces such as oxides. The SCM determines surface potential and the influence of sorbates, and the electrostatic behavior of water and ions for two or three layers. Integrating the influence of the mineral surface acidity constants, Ka1 and Ka2, the SCM is used to develop a model to understand ion adsorption on a mineral surface across a pH range. This allows determination of the zero point of charge (ZPC) when the negatively charged surface sites are balanced with an equivalent proton balance, thus providing a transition point for anionic or cationic adsorption. For example, the ZPC of hydrous ferric oxide (HFO), freshly formed in contact with air has been shown to be about 6.6, whereas the ZPC of Geothite (ἀ-FeOOH) exceeds 8. SCMs have been widely used to better understand contaminant transport phenomena in soils, radioactive waste, mining impacted areas and in engineered adsorption related processes, such as water treatment (Dzombak et al. 1990, James et al. 1977, Nowack et al. 1997).

How Do I Perform a Jar Test?

Despite its apparent simplicity, jar testing requires skill and careful planning. Many good texts and protocols are available to guide the analyst. Special jar-testing equipment with multiple beakers and speed control mixers are commercially available.

Jar tests are used to establish the relationship between chemical doses or combinations of chemicals, under various conditions (mixing, pH, temperature, etc.). It is a useful method to determine the impact of chemical addition under controlled conditions. The goals of the testing will determine the exact method followed in terms if mixing intensity, time, and sequencing of chemical addition.

The key to jar testing is to maintain the same physical test conditions. The mixing intensity, duration, method of adding chemicals, etc., should remain consistent from test to test. Also, the sample added to the individual jars should be well mixed, so that each jar has the same material. This goal is difficult to achieve for jar tests developed to study chemical addition to raw wastewater. Excellent mixing during chemical addition is used to disperse the chemical rapidly when studying the fundamental chemical reactions. However, when using jar testing to optimize chemical addition, flocculation and separation of a full-scale facility, the mixing and flocculation conditions are selected to match those of the full-scale facility. Similar, reaction and flocculation times will be selected to match the field conditions.

The most important key when conducting a jar test is to keep the experimental conditions consistent other than variables being studied. For example, maintain the same mixing intensity and contact times for different chemicals or pH conditions being investigated.

What Are the Principal Phosphorus Precipitants that Form?

Chemical precipitants form from reactions with various chemical compounds. These chemicals form a variety of precipitants, most complex precipitants that change depending on the chemistry, pH, composition, type of chemical, age, and other factors.

Phosphate is found as H_2PO_4- and HPO_4^{2-} species in solution at circumneutral pH, with H_2PO_4- being found in more acidic solution and HPO_4^{2-} being found in more basic solution. Phosphate can adsorb on reactive iron oxy-hyroxide surfaces by forming the complexes $\equiv FeH_2PO_4$, $\equiv FeHPO_4$-, and $\equiv FePO_4^{2-}$. For ferrihydrite there is direct X-ray spectroscopic evidence for removal of phosphate from solution by inner-sphere surface complexation. Surface complexation will result in a monolayer of phosphate ions on the metal oxide surface. With solution concentrations of ferric ions and phosphate that exceed Ksp there is a potential for precipitation from solution as $FePO_{4(s)}$ or as a surface precipitate at a reactive iron oxide surface site with the potential to form embedded layers of iron and phosphate (Willett et al. 1988, Arai et al. 2001, Khare et al. 2004). Research under the Nutrient Removal Challenge showed the role of adsorption and/or complexation in removal of reactive or unreactive phosphorus to the already-formed chemical precipitates or complexes from alum addition in a similar manner as for ferric-mediated phosphorus removal (Smith and Gray 2014).

How Do the Organics in Wastewater Affect Phosphorus Removal Chemical Reactions?

Wastewater treatment processes can produce soluble polyanionic humic and fulvic acid polymers that are degradation products of biopolymers naturally present in municipal wastewater streams. With their polyanionic electrolytic properties, humic substances are important in the dissolution, transport, and precipitation of positively charged inorganic ions. When iron and aluminum metal salts are used as coagulants, flocculants, or adsorptive media for phosphorus removal, excess humic substances can form insoluble complexes with metal ions and their mineral oxides, thereby blocking sites for reactive phosphorus removal. Alternatively, phosphate is known to form mixed complexes with fulvic acid and trace metal ions. This presents the potential for quantitative complexion of phosphate in water with humic substances, thus making removal using chemical processes more difficult (Stumm and Morgan 1962, Black and Christman 1963, Wilson 1959, Ramamoorthy and Manning 1974, Steelink 1977).

Research Needs

The reactions and impact of organic compounds on chemical phosphorus removal needs to be quantified to determine the types and degree of interference expected from organics normally present in the wastewater. Organic molecules themselves can also contain phosphorus and may not react with the iron or aluminum compounds in the water.

What Are the Chemical Reactions of Ferric and Phosphate?

Ferric ion released into solution at sufficient concentrations rapidly hydrolyzes and precipitates as a hydrous ferric oxide (HFO) with high surface area and reactive surface functional groups. Phosphate has a high adsorptive binding strength to ferric oxides and will compete with and displace AsO_4^{3-}, SO_3^{2-}, MoO_4^{2-}, CrO_4^{2-}, SO_4^{2-}, SeO_4^{2-}, Br^-, I^-, and Cl^- given sufficient time.

Chemical precipitation of $FePO4(s)$ based on solubility product calculations does not occur above pH 5 and at the relatively low concentrations typically found in most wastewater. It is now recognized that the mechanism of orthophosphate removal from wastewater using ferric iron treatment is adsorption on iron oxides (Ryden et al. 1977a, Ryden et al. 1977b, McBride 1994, Geelhoed et al. 1997, Newcombe et al. 2008).

What Is the Equilibrium Constant for Phosphorus and Ferric?

At the low concentrations of phosphate-P typically found in wastewaters, the dominant removal mechanism upon addition of Fe(III) salts will be the formation of hydrous ferric oxides (HFO) and the subsequent formation of stable surface complexes with anionic phosphate (Dzombak and Morel 1990, Gustafsson 2003).

The HFO surface reactions and intrinsic constants for trivalent phosphate anions are:

$$\equiv FeOH^0 + PO_4^{3-} + 3H^+ \leftrightarrow \equiv FeH_2PO_4 + H_2O \qquad \log K_1 = 32.08 \qquad (1)$$
$$\equiv FeOH^0 + PO_4^{3-} + 2H^+ \leftrightarrow \equiv FeHPO_4^- + H_2O \qquad \log K_2 = 26.39 \qquad (2)$$
$$\equiv FeOH^0 + PO_4^{3-} + H^+ \leftrightarrow \equiv FePO_4^{2-} + H_2O \qquad \log K_3 = 20.73 \qquad (3)$$

How Much Ferric Is Needed to Remove Phosphorus?

Traditionally the ferricphosphate precipitant $FePO_{4(s)}$ was thought to be the primary precipitant in wastewater treatment. However, recent research (Smith et al. 2008) showed a complex structure, with several fundamental reactions occurring simultaneously as iron reacts to form ferric hydroxides and phosphates.

The amount of phosphate that binds to the metal hydroxide is still a topic of discussion. Current research suggest that the stoichiometric ratio of metal:phosphorus (Me:P) in the precipitant depends on many factors, including the phosphate concentration in the liquid, chemical dose, age of the hydroxyl complex, mixing, and many other factors (Szabo et al. 2008, de Haas et al. 2000, Yang et al. 2006).

The ratio of Fe:P on a molar basis range from approximately 1:1 mol Fe/mol P to greater than 10:1 mol Fe/mol P. Hermanowicz (2006) showed full-scale and laboratory data relating the residual phosphorus to the Fe/P dose.

Does ORP Affect Phosphate-ferric Reactions?

Solution pH, followed by dissolved oxygen (DO) and redox potential (ORP), all affect P removal approaches that use iron salts. Reduction of ferric iron to ferrous iron can happen at low redox potentials and through the action of dissimilatory iron reducing bacteria (DIRB). Ferric hydroxide addition has been shown to have a favorable effect on phosphate elimination during anaerobic digestion of activated sludge. This has been shown to result from enhancement of DIRB activity and the concomitant reduction of ferric iron to ferrous iron in DIRB respiration. Ferrous iron can react to form $FeHPO_4$; however, high DO (e.g., 1.0–5.7 mgl–1), mid-range redox potential (e.g., 57–91 mV), and high pH (e.g., 7.5–8.0) available in some wastewaters can oxidize the majority of added ferrous iron (Stabnikov et al. 2004, Thistleton et al. 2001).

What Is the Optimal pH for Phosphorus Removal Using Ferric?

Recent work by Szabo et al (2008) showed that there is an optimum pH for phosphorus removal, but that the optimum is relatively wide—ranging from pH 5 to pH 7—with deterioration outside this pH range. At acidic pH, soluble phosphate complexes form and, at higher pH, some soluble iron-hydroxide complexes start to form with a resulting decrease in the phosphorus removal efficiency.

How Fast Does Ferric React to Form Ferric Hydroxides?

Ferric iron is a strong Lewis acid, and, when released into solution, it rapidly hydrolyzes forming a basic salt with a hydroxyl group and subsequently precipitates as an oxide. Depending on reaction conditions and time, hydrous ferric oxides (HFO) formed when ferric salts are added to water can consist of amorphous ferric hydroxide (am-$Fe(OH)_{3(s)}$), ferrihydrite ($Fe_pO_r(OH)_s \cdot nH_2O$), goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH), and hematite ($\alpha$-$Fe_2O_3$). Since ferric iron is a strong Lewis acid, low solution pH and alkalinity can limit hydrolysis and the subsequent production of oxy-hydroxide precipitants. Given sufficient alkalinity, the formation of ferric iron precipitants in most waters and wastewaters is very rapid; usually within milliseconds (Schwertman and Cornell 2000).

How Fast Does Phosphorus React with Ferric Hydroxides?

The rate of reactive removal of phosphate from solution using iron metal salt addition depends on many factors, including water chemistry (e.g., competitive reactions such as siderite formation), reactant concentrations, energy of mixing, and temperature. In typical wastewater applications with sufficient mixing and alkalinity, the removal reaction appears to have a fast stage that removes the majority of the soluble phosphate (~90 percent) in less than a minute, followed by a slow step that occurs at a significantly slower rate (McLaughlin et al. 1977, Parfitt 1989).

Does Pre-formed Ferric Hydroxide Remove Phosphorus?

Pre-formed iron oxy-hydroxide and iron oxide solids will remove phosphate from water; however, their activity will vary according to the surface area of the formed mineral, the reactive sites available in that mineral form, and interaction of solution pH and the point of charge (ZPC) of the specific mineral that has formed. Aging of the iron oxide mineral, in general, will decrease the removal and increase the ZPC, often above pH 8. In general, concomitant formation of iron oxy-hydroxide solids and surface complexation of the phosphate moiety will yield higher rates of removal. This will occur when phosphorus containing wastewater is treated with Fe(III) solutions. (Madrid and DeArambarri 1985, Denham 2007).

Does the Ferric Precipitant Change Over Time?

The structure of the iron oxide mineral change over time as shown by Szabo et al. (2008). The ferric hydride structure changes from an amorphous precipitant to a hard mineral structure over time (months).

The mineral structure appears to affect the phosphorus chemistry fundamentally: first, during the initial precipitation, phosphate is included in the structure of the surface complexation model structure. If present during the crystal growth phase, the phosphorus is included in the crystal. As the crystal ages and becomes harder, diffusion to bond with the metal is much more difficult and inefficient (from a metal dose/phosphorus removal perspective).

How Does Mixing Affect Phosphorus Precipitation with Ferric?

Energy of mixing will allow for non-diffusion limited formation of iron oxy-hydroxide precipitants with the potential for simultaneous surface complexation of available solution phosphate to reactive surface sites. Hence, rapid mixing is favorable for P removal. Mixing at very high energy can result in high shear forces that limit floc size and this can have a negative impact on settling and filterability.

Does Polymer Improve Phosphorus Removal?

Polymer does not react with phosphate to produce insoluble particulates but is used to enhance particulate phosphorus removal. Polymer is used to flocculate small particles and also to improve the capture efficiency of some solids separation devices.

Polymer is added as a flocculation aid to capture small colloidal solid phosphorus containing particles and enhance particle growth to form larger particles. The polymer acts to neutralize the particle charge and stabilize the colloidal particles that form when a metal salt is added to wastewater. In addition, the long chain organic molecule used as a building block for the polymer acts as a bridge to flocculate particles.

Polymers also enhance solids separation processes such as sand filters or ballasted sedimentation to attach the colloidal phosphorus containing particles to the sand and remove it.

What Are Similarities and Differences in Alum-mediated and Ferric-mediated Phosphorus Removal Mechanisms?

Prior to the start of the Nutrient Removal Challenge a new mechanism for phosphorus removal by chemical precipitation involving a surface complexation model was put forth by Smith et al. (2008) based on work with ferric chloride. Alum treatment was investigated under the Nutrient Removal Challenge to determine if a similar phosphorus removal mechanism and treatment behavior as that for ferric chloride was occurring with alum. This work is summarized in the Nutrient Removal Challenge White Paper NUTR1R06cc (WRF 2015). The results of this work and the practical significance of the implications of the surface complexation model by alum and ferric salts are discussed.

The iron surface complexation model involves precipitation of hydrous ferric oxide (HFO), with the simultaneous complexation of phosphate species. The HFO floc contains active sites for phosphorus removal by coprecipitation. The model also suggests that preformed flocs from ferric salt addition can also have phosphorus removal ability and aged flocs have less removal capacity. In the model, development with ferric addition phosphorus removal occurred by a fast first step in a matter of minutes, followed by more (but much slower) removal in a second step in about 24 hours.

In the study with alum (Smith et al. 2014) a similar surface complexation model was appropriate in describing phosphorus removal by alum but the kinetic rates were much faster for alum with only one step in a time scale of seconds. The study also found that the phosphorus removal efficiency by alum was optimal at a pH around 6.0 but good efficiency also occurred within a pH range of 5.0 to 8.0. Ferric was more efficient than alum for P removal only at acidic pH values below 6.0.

The studies investigating the phosphorus precipitation model with ferric and alum were done with only phosphorus, metal salt, and alkalinity solutions. Key conclusions from their work were as follows:

1. Above a pH of 5.0, essentially complete precipitation of the added metal salt occurs.
2. The final phosphorus concentration decreases with increasing molar doses of metal salts. At a molar dose of 6.0 mol/mol P or above, a minimal phosphorus residual exists that may be as low as 10 ug/L, depending on the wastewater characteristics.
3. Pre-polymerized metal salt is less efficient for P removal then alum and ferric salts.
4. Increasing concentrations of alkalinity, soluble and total COD, and total suspended solids (TSS), decrease the phosphorus removal efficiency at a given dose.
5. Increase mixing intensity where the metal salt is added to the phosphorus-containing flow improves the phosphorus removal efficiency.

What Are Other Practical Implications of the Capacity of Metal Hydroxides to Sorb Phosphorus?

The ability of metal hydroxides to remove phosphorus has great significance for phosphorus removal, control, and recovery. Maher et al. (2014) found that the alum sludge high adsorptive capacity and rapid kinetics can be used to stabilize phosphorus removal by recirculating chemical sludge to upstream processes and ahead of the chemical addition point to achieve lower effluent soluble P concentrations at lower molar doses of aluminum. The ability of metal hydroxides to sorb phosphorus has been observed in other chemical solids recycle streams from tertiary processes to the headworks of WRRFs. In addition, the chemical sludge will interfere with phosphorus recovery.

SOLIDS SEPARATION

Effective solids separation is essential to achieve phosphorus removal. Chemical reactions are used to convert soluble phosphorus species into particulates, which must be removed from the liquid in order to eliminate the phosphorus. The resulting total phosphorus concentration from solids separation processes is a function of solids removal efficiency, phosphorus content of the solids, and the amount of soluble phosphorus.

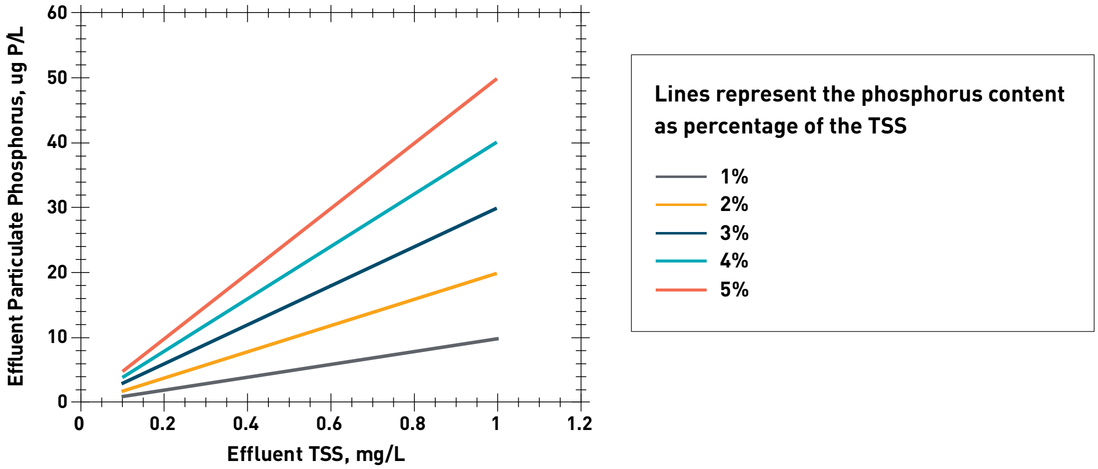
The phosphorus content of the solids plays an important role in achieving low phosphorus concentrations. The phosphorus content of the solids depends on the type of solids retained and the pretreatment, for instance:

- Activated Sludge MLSS, without EBPR: 1% – 3% P
- Activated Sludge MLSS, with EBPR: 2% – 8% P

The phosphorus content of tertiary solids is highly variable and is determined to a large extent by the Me/P (Metal/Phosphorus) dose ratio. Since almost all of the metal salt is precipitated as a metal hydroxide complex to produce particles, solids produced under a higher Me/P dose will have lower phosphorus concentration than the solids produced at a lower Me/P dose.

A lower phosphorus content in the solids is beneficial to achieve low effluent phosphorus concentrations. For example, if the solids contain 5 percent P, then the effluent TSS of 1 mg/L will contribute 50 ug P/L. The figure below shows the relationship between the effluent particulate phosphorus and effluent TSS as the phosphorus content of the solids change from 1 to 5 percent. This figure shows that in order to meet an effluent particulate phosphorus concentration of 10 ug/L, the effluent TSS must be reduced to 0.2 mg/L for a high (5 percent) phosphorus content. If the phosphorus content of the solids is low (1 percent), then the 10 ug/L limit can be met with as much as 1 mg/L.

Figure 1 - Relationship between Effluent Particulate Phosphorus and TSS Concentration



The discussion above illustrates the two key features of the solids removal process:

1. To meet very low phosphorus limits, the solids separation process must be very efficient and produce effluent TSS concentrations to non-detectable levels.
2. The solids separation process must be able to handle high chemical doses required for tertiary phosphorus removal to low concentrations.

What Processes Are Used to Separate Chemical Precipitants?

The following processes are typical of solids separation processes:

- **Sedimentation/Filtration Facilities.** Many different type of filters (dual media filters, trimedia filters, deep bed filters, others) have been used. Including sedimentation facilities (conventional or other solids removal facilities) provides a secondary barrier to improve performance. Examples of this approach are Clean Water Services in Portland, OR, where this type arrangement has consistently met a 70 ug/L effluent TP permit limit.
- **Direct Filtration.** Direct filtration (without sedimentation facilities) using different types of filters (dual media filters, trimedia filters, deep bed filters, others) have been used. This provides a single barrier for solids separation. An example of this approach is the City of Las Vegas, where this type arrangement has consistently met a 170 ug/L effluent TP permit limit.
- **Two-stage Filtration.** Two-stage filtration has been used to improve separation of phosphorus containing particles. By using two filters in series, an additional removal barrier is provided to improve reliability and performance. This type of technology has been able to reduce TP below 50 ug/L in New York City watershed at Stamford, Delhi, and Walton.
- **Membrane Filtration.** Membrane filtration with micro-, ultra-, or nanofiltration will theoretically remove all particulate phosphorus species larger than the nominal membrane pore size including smaller colloidal particles otherwise passing a 0.45-um filter. In practical application, though, defects in the membrane can allow colloidal and larger particles to escape to the product water. An example of this approach is the City of Coeur d'Alene, ID that has consistently produces effluent TP less than 10 ug/L.

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