Treatability and fate of various phosphorus fractions in different wastewater treatment processes

A. Z. Gu, L. Liu, J. B. Neethling, H. D. Stensel and S. Murthy

ABSTRACT

The increasingly more stringent phosphorus (P) discharge limits, which are below the concentrations reliably achievable with currently available technologies, demand for better understanding of phosphorus removal mechanisms. This study investigated the compositional fractions of phosphorus (P) in various effluents as well as the efficacy of different levels of treatment processes for removing different fractions of P in wastewater. The results showed that BNR can effectively remove most fractions of P, with relatively higher efficiencies (>93%) towards bioavailable forms of P including soluble reactive P (sRP), particulate reactive P (pRP) portion and particulate acid hydrolysable P (pAHP) and, it showed relatively lower efficiency (78%) towards organic P. Soluble acid hydrolysable P (sAHP) was not effectively removed (<40%). Chemical P removal process was more effective for elimination of sRP, sAHP and particulate organic P (pOP), but was not as effective for removing pAHP and, it exhibited nearly no removal of dissolved organic P (DOP). We found that chemical P removal process led to a significant increase in the concentration of pRP by up to 255%, indicating that these pRP (presumably as chemically bounded P) are likely formed through chemical precipitation/co-adsorption. Only 22% and 64% of the pRP was removed through tertiary clarifier and filtration, respectively. This implies that chemical addition converts sRP into particulate-associated P, mostly as pRP that was not easily removed by sedimentation and filtration, therefore, the efficacy of chemical P removal highly depends on the effectiveness of solid and liquid separation process. As more sRP and particulate P were removed through the series of treatment processes, the percentage contribution from organic P increases with the level of treatment due to its recalcitrant nature. Our results indicated that in order to achieve extremely low effluent P levels, technologies and processes that can enhance pRP and DOP removal will be required.

Key words | BNR, phosphorus fractionation, phosphorus removal, nutrient removal

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INTRODUCTION

Phosphorus (P) in wastewater discharge was regulated because P is often the limiting nutrient for the primary productivity of a body water and excessive P can lead to eutrophication. Recently, there has been increasing demand to achieve very low effluent total phosphorus (TP) due to more stringent discharge limits imposed on wastewater treatment plants in the U.S. To address water quality problems, state environmental agencies and the U.S. Environmental Protection Agency (EPA) are requiring dischargers to reduce and achieve total phosphorus effluent concentrations as low as 0.009 to 0.05 mg/l (Ragsdale 2007). These have motivated the publicly owned treatment works (POTWs) to investigate and evaluate treatment alternatives to achieve effluent TP that is approaching or below the limits of current achievable in practice.

Current phosphorus removal practice employs biological, chemical, or combined biological and chemical processes. Biological phosphorus removal relies on the function of a

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specific group of polyphosphate-accumulating microorganisms (PAOs) that are capable of taking up excessive phosphorus as intracellular storage, and the phosphorus is removed from the liquid by sludge wasting. Chemical phosphorus removal is achieved by the addition of salts of multivalent metal ions (e.g. alum, ferric iron) to form precipitates of sparingly soluble metal phosphate complexes. Both of these processes target at eliminating only soluble ortho-P or those forms in the influent that can convert into ortho-P during the treatment process, by transforming it into solids phase followed by subsequent solid and liquid separations. Since most permit limits are based on total phosphorus (TP), the effluent P level is affected by both the effectiveness of chemical and/or biological P treatment processes as well as the final solid and liquid separation efficiencies.

Phosphorus appears in wastewater in many forms and phosphorus fractions can be differentiated in terms of soluble (pass 0.45 μm filter) and particulate forms, as well as their reactivity under acid and heat, which was the basis for analytical methods applied to analyze different forms of phosphorus. For both particulate and soluble form of phosphorus, they can be fractionized into reactive phosphorus (normally assumed as ortho-P, which can be a free ion or chemically bound), acid hydrolysable phosphorus (e.g. polyphosphate and condensed P), and organic phosphorus (e.g. intracellular molecules that contain phosphorus, element and refractory (non-biodegradable) phosphorus associated with cell dacay debris) (Standard Methods 2005). As more advanced treatment processes are pushed to eliminate nearly all the ortho-P in order to meet the extremely low TP limits, other factions of P in the final effluent become relevant and important. Currently, little is known about the nature of various forms of P and their susceptibility to different P removal processes. A few recent studies showed that the fractional composition of phosphorus and their removal efficiency vary among wastewater effluents from different treatment processes (Benisch *et al.* 2007; Neethling *et al.* 2007; Lancaster & Madden 2008; Gu *et al.* 2009). Questions remain on: what is the lowest level of TP that can be achieved with available treatment technologies? What are the compositions of effluent TP from different treatment processes? What fractions can be further removed and via what mechanisms in order to meet more stringent limits?

The overall objective of this study is to investigate the efficacy of different available treatment technologies and processes for removing different fractionation of phosphorus in the wastewater. In this study, we analyzed various phosphorus fractions from various effluents at a full-scale wastewater treatment plant (WWTP) referred as plant N in the United States and they include influents and effluents from the secondary biological treatment, the followed chemical precipitation P removal process and the final tertiary dual/mono media filtration process. The results revealed the treatability and susceptibility of various forms of phosphorus to different phosphorus removal technologies and mechanisms, and provided insights and the directions for improvement and development of treatment technologies for achieving more advanced P removal beyond current limits.

MATERIALS AND METHODS

Sample location and collection

Phosphorus speciation analysis was performed with effluents from various processes at the WWTP N (U.S.) and the sampling locations were indicated as dots in Figure 1. Two sets of 24-hr composite water samples (on in winter and one in summer) were collected from wastewater treatment plant N site, filtered through 0.45 μm membrane filters immediately upon arrival and then stored at 4°C until analysis (within 24 hrs).

This facility currently treats an average influent flow of 45 mgd and the monthly and weekly average permit limit for total phosphorus is 0.18 mg/L and 0.27 mg/L, respectively. The WWTP N treatment processes consist of screening, primary clarification, step-feed biological nutrient removal (BNR) followed by secondary clarification, tertiary clarification with ferric chloride addition for chemical phosphorus removal and filtration through dual/mono media gravity bed filters. Tertiary sludge is routed to the primary clarifiers. Some of the primary clarifier sludge is routed to a gravity thickener acting as a fermenter to produce more biodegradable carbon source, which can help improve the reliability of P removal in the BNR. Sludge from tertiary clarifier was also returned to the primary clarifier. Removed solids from the primary and secondary clarifiers are dewatered by lime addition, filter presses and centrifuge, and then incinerated in multiple hearth incinerators.

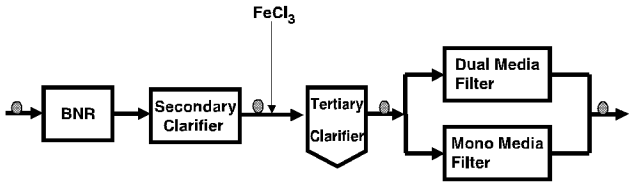

Figure 1 | Flow schematic of secondary and tertiary treatment processes at WWTP-N (Dot points indicate the sampling locations for phosphorus fractionation analysis).

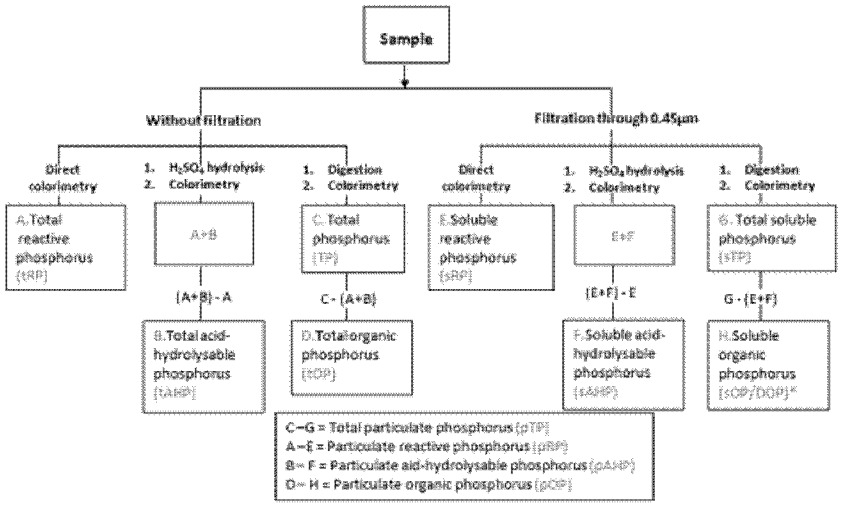

Figure 2 | Analytical methods for determination of various phosphorus fractions.*Both "soluble" and "dissolved" are defined as the species that can pass through 0.45 μm filter. Soluble organic phosphorus (sOP) is also referred as dissolved organic phosphorus (DOP).

Methods for P speciation determination

Figure 2 summarizes terms and definitions of various phosphorus fractions based on standard methods, which are referred in this study. The analysis was performed based on the average of duplicate samples for each fraction of different samples and the coefficient of variation (which is the standard deviation divided by the mean times 100%) was within 15% for each duplicate test.

Conventional P fractionation methods according to Standard Methods (4500-P) are applied to determine the various fractions of phosphorus in treated wastewater samples and the detection limit is 0.002 mg P/L. Based on standard methods, the portion that can pass through 0.45 μm filter is defined as soluble fractions. Particulate fractions are calculated as the difference between total P and soluble P. The procedure described here is based on the quantitative conversion of orthophosphates to a colored species, molybdenum blue, whose absorbance can be measured using UV/Vis Spectroscopy. Absorbance is directly proportional to concentration, as given by the Beer-Lambert Law: $A = \epsilon bc$, where ϵ is the molar absorptivity constant at a given wavelength, b is the path length and c is the concentration. The unknown phosphate concentration will be calculated using a calibration curve established with standards. A Shimadzu UVmini-1240/UVmini-1240 V spectrophotometer (Shimadzu, Tokyo, Japan) with light source (190–1100 nm) and 10 cm cuvette (Starna Cells Inc., Atascadero, CA) was applied.

RESULTS AND DISCUSSION

Wastewater influent phosphorus fractions and possible sources

The composition of total phosphorus (TP) in wastewater can vary highly depending on the industrial sources, water conservation, or whether a detergent ban is in place. Some phosphorus is present in all biological material, as it is an essential nutrient and part of a cell's energy cycle. Phosphorus is used in fertilizers, detergents, and cleaning agents and is present in human and animal waste. Phosphorus species in wastewater can be differentiated in terms of their reactivity under acid and heat according to the Standard Methods, which was applied to analyze different forms of phosphorus in this study. Phosphorus can be divided into three operational classes based on their response to analytical methods used: reactive, acid-hydrolysable and organic phosphorus. (A, B, D, respectively, as shown in Figure 1). Within each class, phosphorus can be further divided into two portions: soluble and particulate forms. Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion are defined as reactive phosphorus, which include various orthophosphates (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4) according to EPA method. Note that these so-called reactive orthophosphates include both soluble forms as well as those associated with some particulate matter via adsorption or complexation. In addition, some small quantity of phosphorus compounds other than orthophosphates (such as

PO_4-P that loosely attached or absorbed on to precipitates or/and enzyme-mediated hydrolysis of organic compounds) respond to direct colorimetry. The acid hydrolysable phosphorus reflects polyphosphates and condensed phosphates (Pyrophosphate, tripolyphosphate, Metaphosphate and intracellular polyphosphate granules) that could be transformed into reactive phosphorus with acid addition. Organic phosphorus includes intracellular molecules that contain phosphorus, element and refractory (non-biodegradable) phosphorus associated with cell dacay debris, or other unknown sources. It can also be divided into biodegradable and non biodegradable fractions. Particulate organic phosphorus is generally precipitated out and removed with the sludge. Soluble organic biodegradable phosphorus can be hydrolyzed into orthophosphate during the treatment process. Soluble non-biodegradable organic phosphorus will pass through a wastewater treatment plant and become the refractory portion in the final effluent (Benisch *et al.* 2007; Neethling *et al.* 2007; Lancaster & Madden 2008; Gu *et al.* 2009). For the P in particulate forms of each category, chemically bounded phosphorus plays an important role. Chemically bounded phosphorus can exist in original influent and can also be created by chemical P removal process due to chemical addition (e.g. alum or ferric). It might include both phosphorous-metal precipitates and P (reactive, hydrolysable and organic P) co-precipitated and adsorbed onto precipitants and metal hydroxides.

Removal of various P fractions by different treatment processes

Figure 3 shows the removal of each P fraction as the wastewater undergoes sequential treatment processes at the WWTP-N. The effluent from primary clarifiers, which is also the influent to BNR, mainly consisted of sRP (1.569 mg/L, 57%), pAHP (0.574 mg/L, 21%), pRP (0.466 mg/L, 17%) and a very small amount of pOP (2.3%) and DOP (0.5%). Note that the BNR influent sample was taken before the RAS return, therefore the pAHP mostly likely included condensed phosphates, which come from the original influent. The secondary step-feed BNR process removed nearly 95% of the sRP from 1.569 mg/L to 0.079 mg/L. It also removed about 95% and 94% of the pAHP and pRP, respectively, indicating that pAHP and pRP were hydrolyzed and/or became bioavailable during the biological treatment process. Chemical addition to tertiary clarifier further removed sRP by 96% to 0.003 mg/L, which remains as residual in the effluent from the tertiary filtration. Chemical P removal via ferric addition (ferric as $FeCl_3$, 7.4 mg/L during sampling period) removed not only the remaining soluble form of reactive P and acid hydrolysable P, but also most of the remaining pOP and pAHP. The removal of the later was presumably by co-precipitation with ferric-phosphate complexes. Interestingly, particulate reactive P increased noticeably (by 255%) after chemical additional and tertiary clarification, indicating that these are likely formed through chemical precipitation/co-adsorption and they are chemically-bounded P as previously mentioned. This portion chemically bounded reactive P was not able to settle in the tertiary clarifier and need to be effectively removed via filtration process as shown in Figure 3. Previous studies indicated that chemically bounded P chemistry is rather complex that it involves not just simple precipitation of ferric phosphate, but also adsorption and co-precipitation of phosphate as well as precipitation of mixed cation phosphates (e.g. calcium, magnesium, iron, or aluminum phosphates, or hydroxyphosphates). The direct precipitation of pure ferric phosphate does not appear to occur to any significant extent at pH values above 5 (Takacs *et al.* 2006; Smith *et al.* 2008; Szabo *et al.* 2008). This indicates that the components of pRP can be complex due to different operating conditions and other mechanisms, such as adsorption and co-precipitation of phosphate, can contribute more to the formation of pRP rather than precipitation of ferric phosphate. Therefore, the chemical composition of the particulate reactive P is not clear and it likely includes the ortho-P that was loosely attached to very fine chemical precipitated particles via adsorption/co-precipitation, and/or the P in precipitates that might dissolve during the reactive P analysis procedure (diluted sulfuric acid was added during colorimetric reactive P measurement).

Tertiary filtration process was able to provide additional removal of those particulate P fractions likely associated with fine particles that were not eliminated via secondary clarification. Note that soluble condensed/poly P (sAHP) was

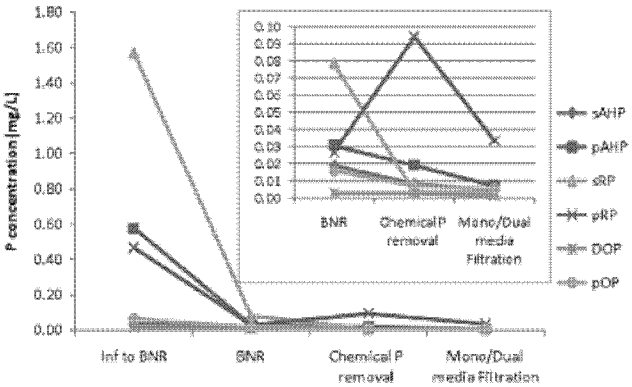

Figure 3 | Removal of various P fractions through different processes at WWTP N.

also further removed by the tertiary chemical P removal process, suggesting that sAHP was likely hydrolysed into ortho-P during this process or it is also possible that it was directly adsorbed on to coagulants and/or flocculants. After the final filtration, majority of the TP in the final effluent became pRP (62%, in Figure 5), implying that although chemical addition at sufficient dosage can convert soluble reactive P (sRP) into pRP, yet its final removal from the liquid stream depends greatly on the efficiency of solids and liquid separation process. Among all the P fractions, DOP remained consistent with 0.003 mg/L as residual in the effluents as it passed through BNR and tertiary chemical P removal processes. This clearly demonstrated that this fraction of DOP is refractory and it could not be effectively removed even by the enhanced tertiary processes. Other removal approaches and mechanisms need to be investigated to specifically target for removal of DOP. For this reason, from here on, we will refer the DOP as refractory dissolve organic P (rDOP) because of its recalcitrant nature as observed in our study.

Comparison of phosphorus speciation in effluents from various treatment processes

Figures 4 and 5 show the distribution and comparison of TP fractions from three different treatment processes at the WWTP N. The primary effluent (influent to BNR) consisted mostly of sRP (ortho-P, 57%), pAHP (21%) and pRP (17%). Note that the primary sludge fermenter effluent and ferric-laden tertiary clarifier sludge are returned to the primary clarifier, which may attribute to the AHP and pRP in the BNR influent. sRP (45%), pAHP (18%) and pRP(15%) dominate the effluent from BNR, which has the similar composition as the influent to BNR except for the slightly increased percentage of organic portion and sAHP. It implies that organic P and sAHP may be generated in the biological process. The chemical P removal followed by clarification can reduce TP concentration to as low as 0.135 mg/L and the process converted most sRP into pRP, resulting in the chemical P removal process effluent that had a dominant portion of particulate P (0.122 mg/L, 90%), in which nearly 72% was pRP. The remaining fraction of the tertiary clarifier effluent after chemical addition was DOP, (6%, 0.008 mg/L), sRP (2%, 0.003 mg/L) and sAHP (2%, 0.003 mg/L). The final effluent from the subsequent mono/dual media filtration ended up with 84% of particulate P, which included 62% of pRP, 13% of pAHP and 9% of pOP. As more sRP and pTP were removed through the series of treatment processes, the contribution of other two fractions of TP, namely acid hydrolysable P (AHP) and organic P (OP) become higher in the

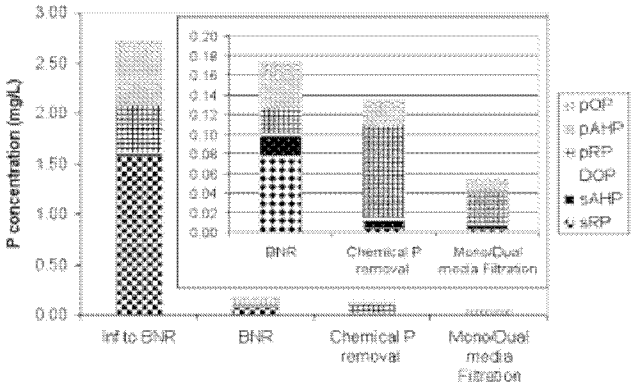

Figure 4 | TP fractions in various effluents at the WWTP-N.

final effluent, contributing to 21% and 11% of the total effluent P. The final effluent composition indicated that if further and the maximal TP removals are to be attained, more advanced solid and liquid separation process beyond the mono/dual media filters for more efficient removal of particulate P, especially for pRP and DOP, is needed.

Efficacy of different treatments for removing various fractions of P

Table 1 summarizes the effectiveness of different treatment for removing different fractions of P. BNR can effectively (>93%) remove most fractions of TP, with relatively higher efficiencies towards bioavailable forms of P including soluble reactive P, particulate reactive P portion and most (79%) organic P. It had rather low removal efficiency for sAHP, indicating that a portion of the original sAHP in the influent was not easily bioavailable for microorganism in the BNR process, or there is production of sAHP in the BNR process. Chemical P removal process poorly removed organic P (<45%). Chemical P removal process was more effective for elimination of sRP, sAHP and pOP, but was not as effective for removing pAHP

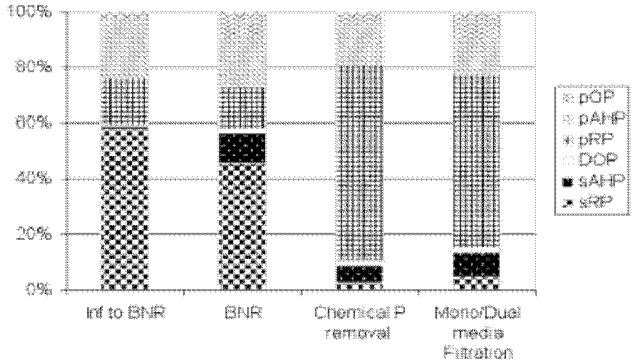

Figure 5 | Distribution of TP fractions in various influent and effluents at WWTP-N.

Table 1 | Efficacy (percentage removal) of different treatment for removing various fractions of P in the BNR influent

	TP	sTP	pTP	tAHP	sAHP	pAHP	tRP	sRP	pRP	tOP	DOP	pOP
BNR	94	94	94	92	40	95	95	95	94	79	83	75
Chemical P removal	24	86	−66	54	56	37	7	96	−255	44	0	56
Mono/Dual media Filtration	59	42	62	50	45	64	63	20	64	35	60	26
Total	98	99	96	98	86	99	98	100	93	92	93	92

and, it exhibited nearly no removal of DOP. The chemical composition and the mechanism of sAHP and pOP removal by chemical addition are not fully understood. One possible explanation could be that the pOP is most likely in colloidal form, which can co-precipitate with precipitant that cannot pass 0.45 μm filter. In regard to sAHP, either sAHP can be hydrolyzed into sRP to be further removed via chemical precipitation/adsorption or, sAHP itself can be adsorbed onto precipitants. In comparison, pAHP removal was much less than sAHP removal implying that pAHP is not as easy hydrolysed into ortho-P as sAHP. The DOP fraction seemed to be completely resistant to chemical P removal with clarification alone, yet could be eliminated rather effectively by the following filtration process, indicating that DOP was likely removed via adsorption mechanisms that may have kinetic and contact area limitations. This is consistent with our previous study on the adsorption of DOP via various adsorption media (Gu *et al.* 2007, 2009), which showed that DOP could be removed by a number of different adsorption media tested. pRP can be created through chemical addition process and its removal seems to rely on the following filtration process, suggesting that pRP is the form of very fine particulates that need effective filtration to be removed.

CONCLUSIONS

The combination of enhanced biological phosphorus removal, chemical phosphorus removal with chemical addition and tertiary filtration effectively reduces total phosphorus concentrations from 2.77 mg/L to 0.054 mg/L, which is well below the 0.18 mg/L permit limit at the WWTP N.

Although chemical addition at sufficient dosage can convert soluble reactive p (sRP) into particulate-associated P, mostly as pRP, yet its final removal from the liquid stream depends greatly on the efficiency of solids and liquid separation process. As TP was removed to as low as 0.054 mg/L after passing through mono/dual media filtration, the dominant fraction left in the filtration effluent became particulate reactive phosphorus. If maximal TP removals are to be attained to achieve extremely low level of TP, then more advanced solid and liquid separation process such as multi-stage multi-media filtration or enhanced ballasted sedimentation combined with filtration will likely be needed (Gu *et al.* 2009).

Total phosphorus consists of many fractions and its removal depends on the removal efficiency for each fraction. In order to achieve lower P level than current permit, it's necessary to evaluate the effectiveness of processes for removing each P fraction since the resistance of any fraction of phosphorus may affect the TP level in final effluent.

Different level of treatment processes can effectively remove certain fractions of phosphorus. In this study, sRP was the fraction that was removed most effectively through both BNR and chemical P removal processes. And as sRP is removed and TP concentration in the effluent is reduced, other fractions such as organic phosphorus and acid-hydrolysable phosphorus become relevant important to achieve lower P level. On the other hand, some of the refractory fraction remaining in final treated effluent might not be from original influent and they can be created by certain treatment process (e.g. pRP which is reacted by chemical P removal process, AHP can be produced by enhanced biological phosphorus removal process).

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