SNRP 101: Fond du Lac WWTP Lab Experiences

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ABSTRACT

The City of Fond du Lac, Wisconsin Regional Wastewater Treatment Plant (FDL WWTP) has a proposed phosphorus water quality based effluent limit (WQBEL) of 0.04 milligrams per liter (mg/L) effective January 1, 2022. Because of this stringent limit, the plant laboratory staff has explored a multitude of phosphorus species with a primary focus on soluble non-reactive phosphorus (sNRP). FDL currently experiences a sNRP average of 0.08 mg/L and has become increasingly interested in how this sNRP level may affect the ability to meet a future phosphorus limit of 0.04 mg/L.

KEYWORDS: *Phosphorus speciation, soluble non-reactive phosphorus (sNRP), phosphorus removal, low phosphorus concentration*

INTRODUCTION

The City of Fond du Lac, Wisconsin Regional Wastewater Treatment Facility (FDL WWTP) serves the population of not only the City of Fond du Lac which is approximately 43,000 people but also the population of an Outlying Sewer Group which includes an additional 30,000 people and has a design flow of 9.84 MGD. The facility utilizes the activated sludge process and anaerobic digestion and typically uses aluminum sulfate for phosphorus removal.

Like many other wastewater treatment facilities in the state of Wisconsin, the FDL WWTP is preparing to meet a much lower final effluent phosphorus limit. A predicated effluent limit of 0.04 mg/L has forced the facility to look in to multiple options and treatment methods to determine the best course of action to meet the future limit. The options and treatment methods piloted here include the following: CoMag™, full-scale biological phosphorus removal, full-scale chemical phosphorus removal using cerium chloride (SorbX $_{100}$), Ovivo® TriSep membrane filtration, ACTIFLO®, Aqua-Aerobics AquaDisk® followed by Aqua Ultrafiltration™, and even a nutrient harvesting process. Over the course of the past several years, each pilot study that has been conducted at the facility to determine if a 0.04 mg/L concentration is achievable has shown that it will be difficult and costly meet the future limit. It has become apparent there is something affecting the ability of most of these processes to achieve results below the 0.04 mg/L concentration.

For each pilot study, the on-site laboratory staff has played a significant role in analyzing and collecting data. In evaluation of phosphorus removal efficiencies of the pilots, sNRP presence

has been suspected to affect achievable levels of phosphorus removal. Due to this finding, the laboratory staff has devoted a significant amount of time investigating this phenomenon, including developing a standard operating procedure to analyze and properly measure sNRP and validate the accuracy of all data obtained.

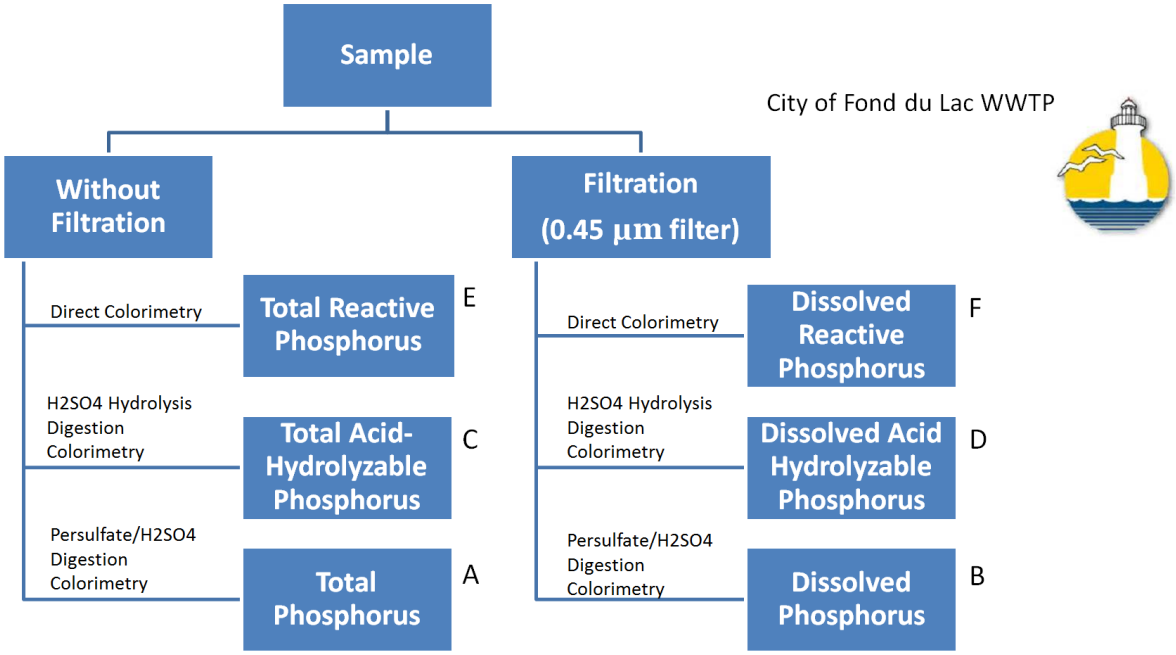
In addition to the pilot study findings and daily final effluent phosphorus speciation, it has been noticed that some treatment processes may influence the removal levels of sNRP. For this reason, the laboratory staff has also analyzed numerous samples that have been collected from high strength waste haulers, industries, Outside Sewer Group, and normal influent wastewater flows to determine levels of incoming sNRP. The reason much emphasis has been focused on sNRP levels at FDL is the average sNRP value is around 0.08 mg/L. This may pose a serious problem if the facility needs to meet a 0.04 mg/L limit.

Another reason sNRP may be an issue for the FDL WWTP is the fact that the facility will not only have a concentration limit of 0.04 mg/L but will also have a mass limit. The mass limit will be an important consideration because FDL is greatly impacted by inflow and infiltration and during a high flow rain event, the facility may have difficulties meeting the mass limit. Overall, it has been found that only certain processes seem to show good removal efficiencies and it may require a combination of treatment processes/methods to remove the sNRP below 0.04 mg/L at a significant cost to the rate-payers of the City. Ultimately, the level of sNRP in the FDL wastewater may determine what treatment methods are utilized in the future at the facility. This has given rise to the importance of knowing various sNRP data points and understanding contributors.

METHODOLOGY

Phosphorus can be broken down into two primary forms, organic and inorganic. With this distinction, further speciation can be conducted to determine the various phosphorus species such as insoluble, polymerized, and non-reactive. Particulate phosphorus refers to any form of phosphorus which is retained by a 0.45 µm pore size filter. Soluble/dissolved/filterable, which can all be used interchangeably, refer to any form of phosphorus which passes through a filter with a pore size of 0.45 µm. It should be noted that the filtrate that passes through a 0.45 µm filter may also contain fine particles and colloids (Neethling, et al. 2007). sNRP can be calculated by determining the difference between soluble total phosphorus (sTP) and soluble reactive phosphorus (sRP). A majority of sNRP is soluble organic (sOP) and the remainder is soluble polymerized (sPoly). Figure 1 shows a breakdown of how the various fractions were analyzed and calculated.

Figure 1 - Phosphorus speciation flow chart and calculations.



A	Total Phosphorus
B	Total Soluble Phosphorus
C	Total Acid Hydrolyzable Phosphorus
D	Total Soluble Acid Hydrolyzable Phosphorus
E	Total Reactive Phosphorus (Ortho)
F	Total Soluble Reactive Phosphorus (Ortho)

A-B	Total Insoluble
C-E	Total Polymerized
D-F	Soluble Polymerized (Soluble Poly P)
A-C	Total Organically Bound
B-D	Soluble Organically Bound
A-E	Total Non-Reactive
B-F	Soluble Non-Reactive (SNRP)

The FDL laboratory used *Standard Methods* analytical methods to distinguish various phosphorus fractions in their wastewater and other facility contributors. The FDL laboratory has fine-tuned their technique and has determined that the dirtier a sample is, the longer the sample takes to filter. Therefore, in some circumstances for analysis of sludge, industrial, hauler, or plant influent samples it was necessary to pre-filter samples with a glass fiber 1.5 µm filter prior to filtration with the 0.45 µm filter. Another helpful technique utilizes a benchtop centrifuge followed by filtration of the sample.

Instrumentation used for the analysis of samples was a Thermo Scientific GENESYS 10 Spectrophometer with a MDL of 0.01 mg/L and a Seal AQ2 Discrete Analyzer with a MDL of 0.005 mg/L.

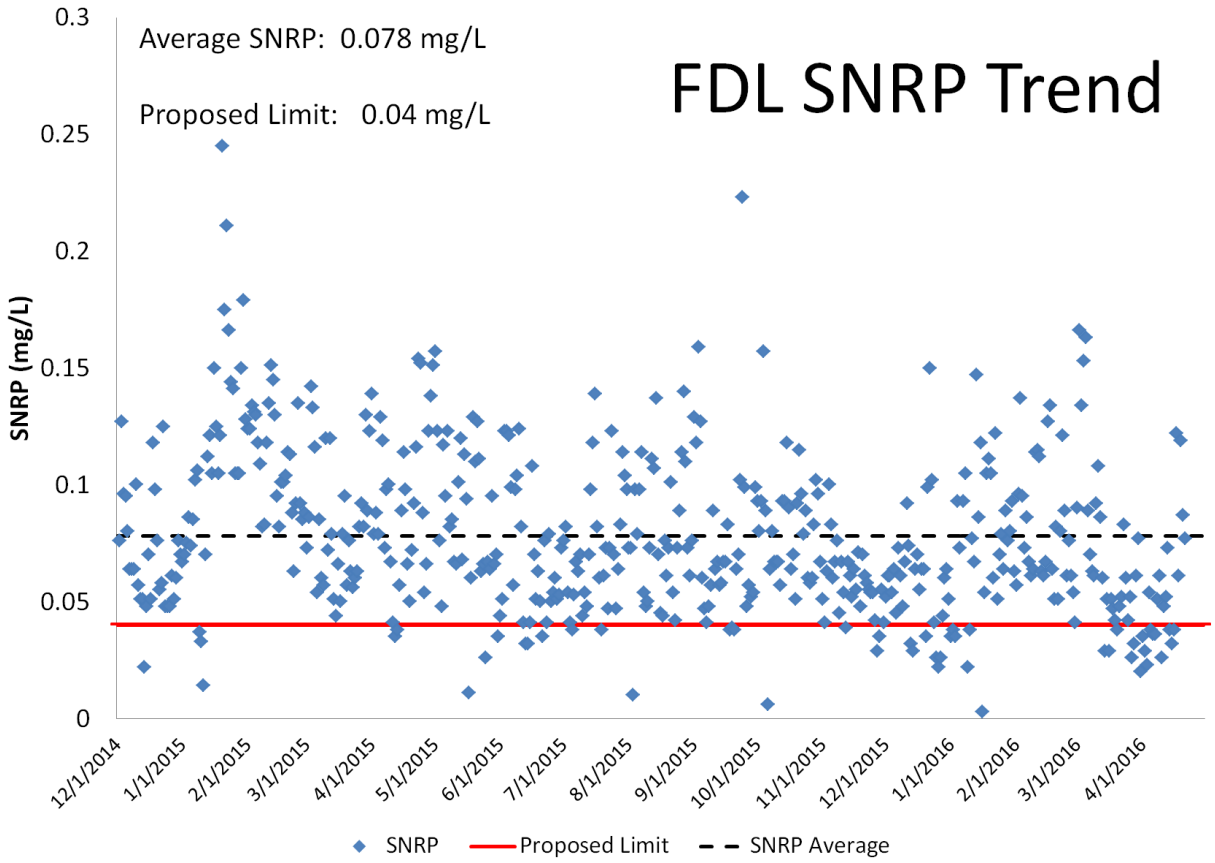
Careful consideration was given to contamination and the laboratory periodically analyzed filtered blanks to ensure no background could be attributed to filtration technique and equipment.

RESULTS/DISCUSSION

The FDL laboratory has been analyzing their sNRP in excess of a year and a half and has become well adept at sNRP analysis. The FDL WWTP currently experiences sNRP levels of

approximately 0.08 mg/L which is double the concentration of the 0.04 mg/L WQBEL. See Figure 2.

Figure 2 – FDL WWTP sNRP average versus proposed WQBEL.



Fond du Lac relied on Neethling (2007) to provide general direction on sNRP analysis and technique. However, because of the vast amount of data generated, it was important to the FDL WWTP to not only generate data for research but also ensure the data being collected was accurate. Therefore, the FDL laboratory conducted a comparison study with the Wisconsin State Lab of Hygiene (WSLH) to confirm its laboratory results.

Overall, the FDL laboratory results when compared to the WSLH had a relative percent difference (RPD) of less than 25%. The Wisconsin Department of Natural Resources (WiDNR) typically recommends comparison results be within 10% but in the case of lower concentration samples they allow for up to 25%. The FDL laboratory trended very closely with the WSLH for sTP analysis (See Figure 3) but experienced RPDs of up to15% for comparison sRP results (See Figure 4). It is speculated that the increased RPDs for sRP analyses was experienced due to the fact that the WSLH performed the filtration step for sRP samples analyzed at their facility and the FDL staff performed filtration for sRP samples analyzed in-house. The same phenomenon was not experienced with the analysis of sTP samples because FDL submitted a filtered sample to the WSLH for the sTP analysis. Differences in filtration equipment and analyst technique likely contributed to the discrepancies in sRP data.

Figure 3 – FDL laboratory versus WSLH sTP results.

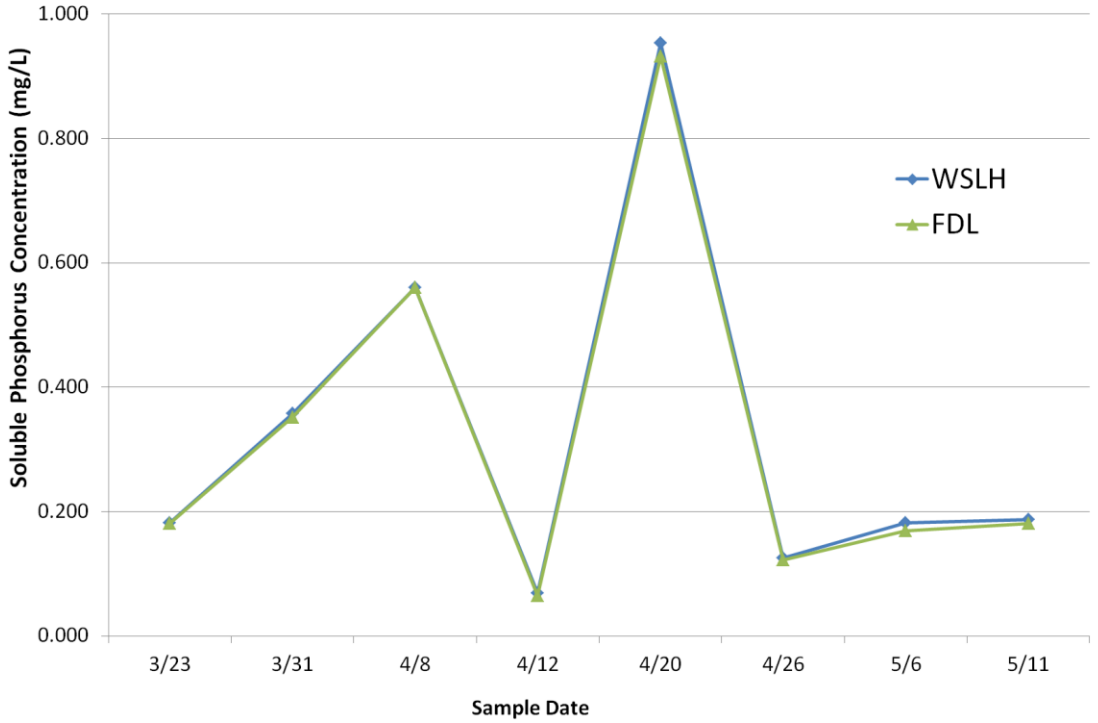
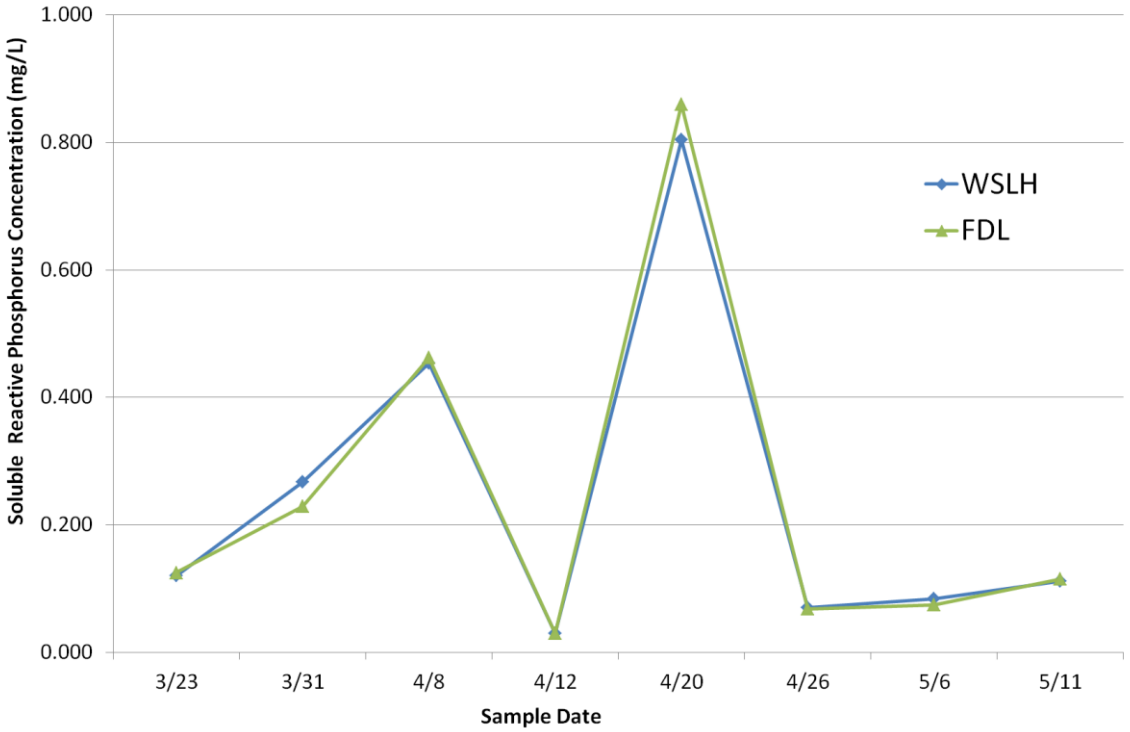


Figure 4 - FDL laboratory versus WSLH sRP results.



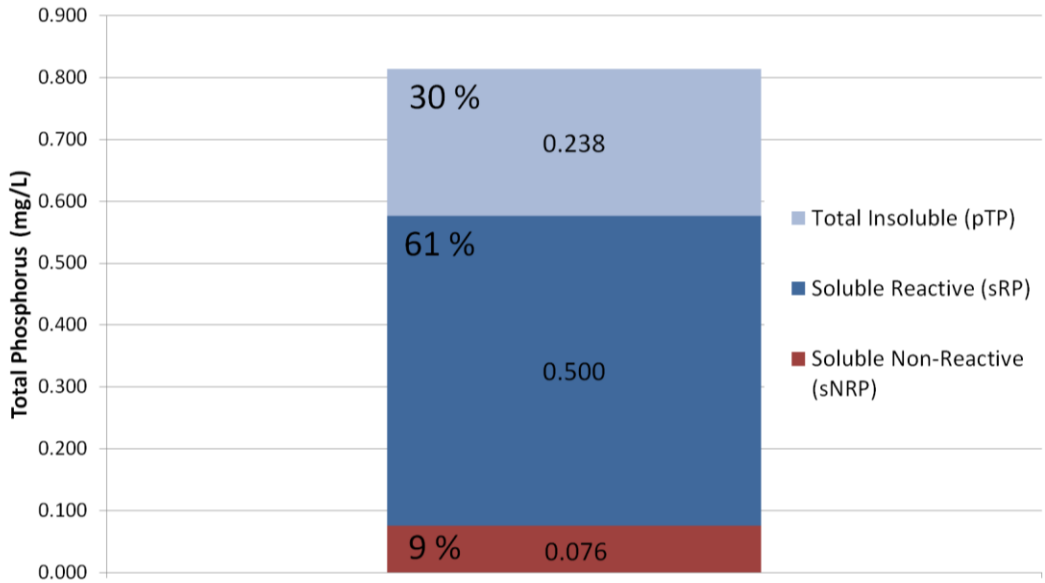
Further breakdown of phosphorus species can be conducted with the analysis of total phosphorus (TP), sTP, acid hydrolyzable (tAHP), soluble acid hydrolyzable (sAHP), reactive phosphorus (tRP), and sRP. With the analysis of these six phosphorus fractions, the FDL laboratory was able to determine the average phosphorus fractions that can be attributed to things such as organically bound and polymerized phosphorus in the plant influent versus the final effluent. The results can be found in table 1.

Table 1 – FDL average influent and effluent phosphorus species concentrations.

	Phosphorus Species	Influent	Effluent
A	Total Phosphorus (TP)	4.635	0.814
B	Total Soluble Phosphorus (sTP)	2.448	0.576
C	Total Acid Hydrolyzable Phosphorus (tAHP)	3.497	0.697
D	Total Soluble Acid Hydrolyzable Phosphorus (sAHP)	2.223	0.535
E	Total Reactive Phosphorus (tRP)	2.787	0.601
F	Total Soluble Reactive Phosphorus (sRP)	2.126	0.500
A-B	Total Insoluble (pTP)	2.187	0.238
C-E	Total Polymerized (tPoly)	0.710	0.095
D-F	Soluble Polymerized (sPoly)	0.096	0.035
A-C	Total Organically Bound (tOP)	1.138	0.117
B-D	Soluble Organically Bound (sOP)	0.225	0.041
A-E	Total Non-Reactive (tNRP)	1.849	0.212
B-F	Soluble Non-Reactive (sNRP)	0.321	0.076
E-F	Particulate Reactive P (pRP)	0.660	0.101

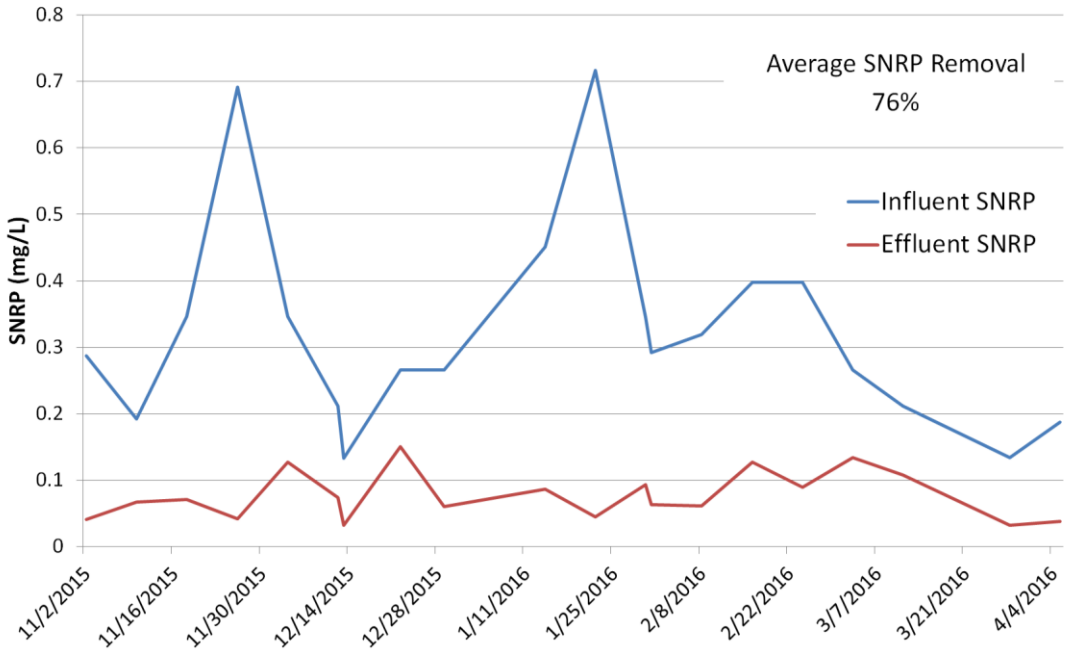
The FDL WWTP phosphorus was further evaluated for differences attributed to insoluble and soluble reactive fractions. A breakdown of these phosphorus species can be found in Figure 5 below. When evaluated under these conditions, the phosphorus most often experienced at the FDL WWTP is sRP with pTP and sNRP also present in varying degrees.

Figure 5 – FDL insoluble versus soluble speciation.



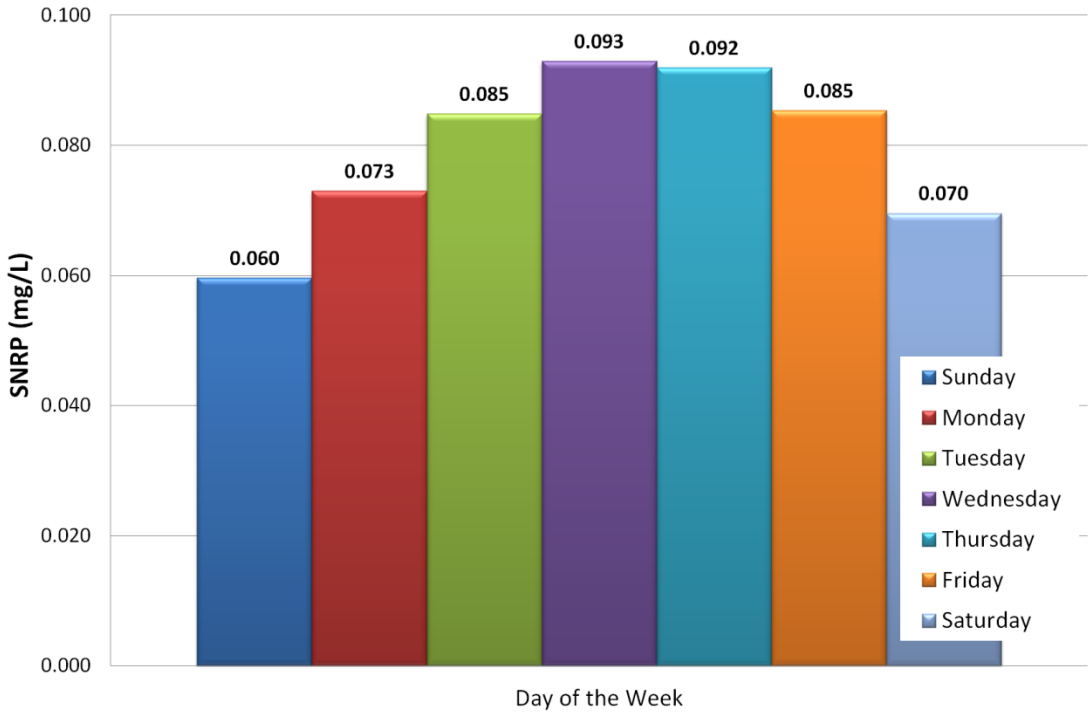
According to Neethling et al. (2007) phosphorus species vary from facility to facility depending on treatment characteristics such as type of phosphorus removal methods (chemical, biological, or filtration) as well as plant recycle flows and substrate acceptance policies. Therefore, FDL felt it was necessary that in addition to daily final effluent sNRP determinations, plant influent should also be analyzed for various fractions of phosphorus to determine facility removal efficiencies. Figure 6 shows the FDL WWTP sNRP removal efficiency.

Figure 6 – FDL WWTP influent versus final effluent sNRP.



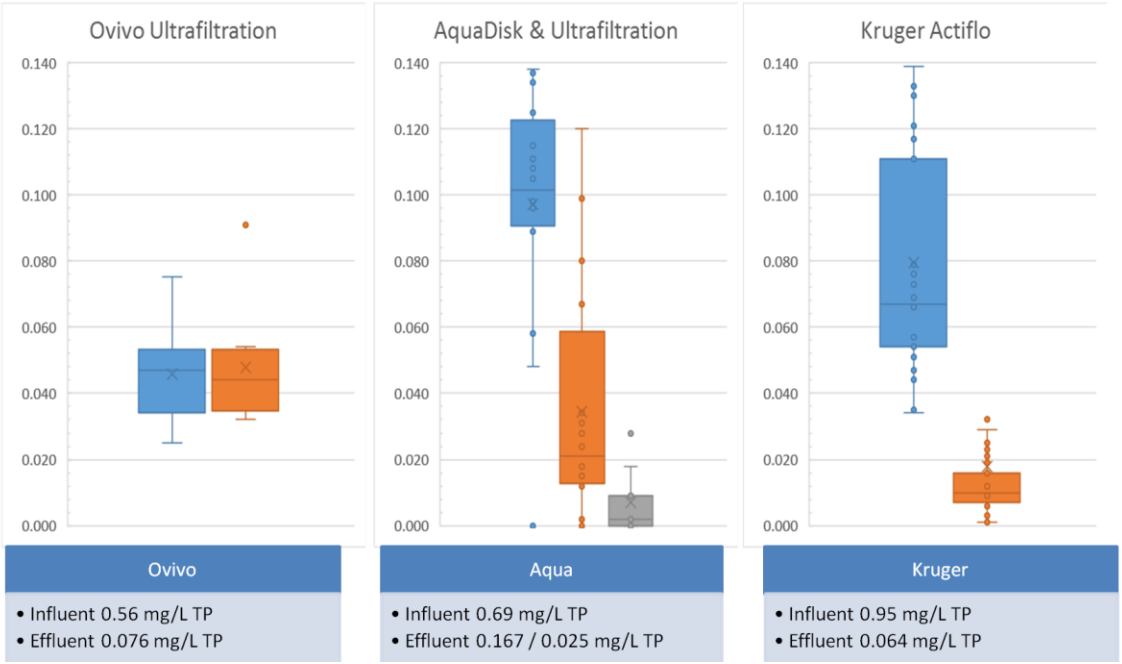
In addition to monitoring the facility effectiveness on removal of sNRP from the influent to the final effluent, the data was scrutinized to determine any trends that may arise. When looking at sNRP by day of the week, it became apparent that sNRP increased throughout the week with the facility experiencing the highest average sNRP values on Wednesday and Thursday as can be seen in Figure 7. The increase in sNRP throughout the week coincides with the operation of our dewatering centrifuges and our centrate recycle stream and demonstrates the impact the side stream has on our facility sNRP.

Figure 7 – FDL sNRP by day of the week.



As part of our facility study of feasible alternatives, the FDL WWTP has conducted a variety of tertiary treatment pilot studies including CoMag™ and Actiflo® (ballast settled floc processes), Ovivo® (ultrafiltration membrane), AquaAerobics® (cloth disk followed by membrane filtration), AirPrex™ (nutrient harvesting), and SorbX® (cerium chloride phosphorus removal chemical). The FDL laboratory performed extensive sNRP analysis during the Ovivo, Aqua Aerobics, and Actiflo pilot projects to determine removal capabilities. The graphs in Figure 7 show the removal efficiencies of sNRP in blue, orange, and gray experienced during these pilots with a table below indicating the pilot total phosphorus results.

Figure 7 – FDL pilot phosphorus removal results.



CONCLUSIONS

Analysis of the various fractions of phosphorus has provided the City of Fond du Lac valuable information towards their future compliance options. Specifically, evaluations of sNRP have been targeted to determine the feasibility of meeting future effluent requirements. Current effluent sNRP concentrations exceed future WQBELs, therefore phosphorus reductions of all fractions are necessary. Elevated sNRP was observed to increase with increased side stream loadings. sNRP is linked to the presence of colloidal particles. This link is further supported by the pilot testing data, which exhibits a trend of increased sNRP removal with increased colloidal removal (coagulation and flocculation) upstream of the technology.

Moving forward, Fond du Lac hopes to acquire recommendations and/or comments from the Wisconsin DNR in relation to sNRP and what it may mean for area TMDL studies and phosphorus WQBELs. Future direction for Fond du Lac will likely include assessing changes in sNRP under various treatment conditions such as centrate recycle changes and bio-P. Additionally, we will continue to assess local industries, high-strength waste, and septage/holding/portable waste. Fond du Lac would also like to conduct a bioavailability study using algae and assessing phosphorus uptake.

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REFERENCES

Neethling, J.B., Benisch M., Clark, D., Fisher, D., and Gu, A. (2007) Phosphorus speciation provides direction to produce 10 µg/L Proceeding of WEF/IWA Nutrient Removal Conference, Baltimore.

Standard Methods for the Examination of Water and Wastewater 21st Edition (2005). American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Association (WEF).