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Treatment of Reverse Osmosis Brine with Advanced Oxidative Processes for Enhanced Phosphorus Removal

MSc. Thesis

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a Master of Science in Chemistry

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Abstract:

Current regulations for sensitive receiving waters are approaching the limit of technology for phosphorus removal and improved methods are required. Existing methods target removal of the orthophosphate form of phosphorus, but to achieve low effluent limits other non-reactive (NRP) forms, such as condensed phosphate and organic phosphorus, must be removed as well. This could be accomplished by developing a quaternary step in wastewater treatment that utilizes reverse osmosis (RO) followed by advanced oxidation processes (AOP) on the produced brine (RO concentrate). The objective during advanced treatment is to convert NRP in the brine to reactive phosphorus for removal by traditional chemical addition methods; however, the various antiscalants utilized for RO membrane maintenance can contribute phosphorus to the brine. To test brine treatment as a viable alternative to achieve low effluent phosphorus, antiscalant-free brine, demonstration facility-produced brine, four commercially available antiscalants and various representative model phosphorus compounds were evaluated for treatment effectiveness. For antiscalant addition experiments the dosage of antiscalant was designed to match the necessary concentration for effective RO membrane maintenance. The advanced oxidation processes evaluated were 100 ppb peroxide for 30 minutes, 50 ppm bleach for 30 minutes, pH 2 for 30 minutes, and 100 ppb peroxide at pH 2 for 30 minutes. The use of chemical addition as a pretreatment was also evaluated. Treatment effectiveness was determined by measuring residual total phosphorus post AOP treatment after a subsequent 6 ppm alum treatment. The use of 30 ppm alum chemical addition as a pretreatment effectively improves the use of AOPs for P removal from 57% up to 73% for a 100 ppb peroxide at pH 2 treated antiscalant free brine. The most effective chemical AOP after a 30 ppm alum pretreatment was 100 ppb peroxide at pH 2 which achieved 73% TP removal for the antiscalant-free brine, 84% TP removal in the demonstration facility produced brine, 66-82% TP removal for the brine amended with the three commercially available antiscalants, and 3-92% TP removal for the various phosphorus standards. A comparison removal using a multiphase treatment which employs UV digestion with 3000 ppm peroxide at pH 2 and 80-90°C for 1 hour was also evaluated and achieved 81-94% TP removal in the two brines and four antiscalant-dosed brines, as well as 73-84% TP removal in the various phosphorus standards. The effectiveness of treatments at converting NRP seems to be bond type dependent, such that phosphate-esters, followed by phospho-esters are the most convertible, whereas phosphonate bonds seem to be resilient to conversion. Therefore RO shows potential for quaternary treatment to achieve low phosphorus levels. The RO brine can concentrate nutrients (whether naturally occurring or contributed by antiscalants), which can be removed by chemical addition as well as via AOP processes.

Keywords: Brine, Reverse Osmosis, Advanced Oxidative Processes, Non-reactive phosphorus, Antiscalants

Executive Summary

Over the last few decades the regulations regarding the contribution of phosphorus from industry, including municipal wastewater treatment facilities, have been continuously tightened in efforts to prevent the potential impacts associated with excess phosphorus, as a required nutrient, to the environment—namely eutrophication. Presently, wastewater treatment facilities are able to remove the majority of phosphorus in the reactive and easily removed orthophosphate form however, there are limitations present in current technologies, which primarily employ chemical addition using metal salts (ferric, alum or lime). Current technologies will be unable to achieve the progressively reduced allowable limits if the limits are reduced to values that would require the removal of the non-reactive phosphorus portion as well. As a result, advancements in wastewater treatment must target the minor and difficult to remove non-reactive phosphorus species in an effort to meet the continuously decreasing phosphorus requirements as are enforced by current legislation.

An example of such legislation specifically regards Lake Simcoe; located in Southern Ontario, this lake has been severely impacted by the effects of eutrophication due to contribution of excess phosphorus. Although the majority of phosphorus contributed to the lake system is a result of agricultural land in the surrounding watershed, efforts to reduce phosphorus from all sources entering the lake system have been directed according to the Lake Simcoe Phosphorus Reduction Strategy (LSPRS), adopted in 2010. Working within the constructs of the LSPRS, York Region, a large region within the watershed, seeks to reduce the annual load of phosphorus entering the lake, specifically by adopting innovative removal techniques in a new wastewater treatment facility with advanced treatment systems that would serve part of the population of the watershed presently and would be able to accommodate future growth.

The proposed method of innovation is to include a quaternary-step in the treatment of wastewater that would employ microfiltration and reverse osmosis (RO), which are used in wastewater reclamation. RO would be used to produce an ultra-pure permeate and a concentrated brine (high in dissolved salts,

organics, contaminants, including phosphorus). The brine could then be further treated using advanced oxidative processes (AOPs) in order to convert non-reactive phosphorus (NRP) to reactive phosphorus (RP) to be removed by chemical addition. AOPs have recently been evaluated as effective means for the oxidation of organic contaminants to less harmful forms, specifically in response to the increasing attention to the presence of pharmaceuticals in wastewater. The increased success of AOP treatment on dissolved organic carbon (DOC) after RO concentration has also been studied by Zhou *et al.* (2011). The extension of the oxidative effect of these processes to oxidize compounds containing phosphorus in order to release the NRP and oxidize it to the orthophosphate form for subsequent removal is a logical progression; in fact preliminary application of AOPs on oxidation of phosphorus compounds for removal has already been completed by Jiang *et al* (2009) evaluating ferrate and Petrucci *et al* (2003) who optimized Fenton's Reagent.

The initiative towards a quaternary-step was to take place in two Phases. Phase 1 involved an initial mass screening of AOPs, including a primary focus on disinfectants already used in industry, for time and dose dependency in mono- and di-applications on bench-top RO produced brine. Brine for Phase 1 was generated from secondary effluent that was collected from a treatment facility in Mount Albert, ON (site of the eventual continuously run demonstration facility). Phase 2 would involve optimization of the most successful treatments selected from Phase 1 on three types of brine, all of which had undergone a pretreatment of 30 ppm alum to help reduce compounds that interfere with AOP treatment, ie DOC and orthophosphate. Initially optimization would occur using bench-top RO produced brine generated from microfiltration permeate produced at the demonstration facility, without antiscalant present but after chloramination to determine the effects of chlormaination on AOP treatment (antiscalant-free brine). After optimization, the treatments would be evaluated on bench-top RO produced brine dosed with various commercially available antiscalants to determine the effect of antiscalant on phosphorus contribution and AOP treatment (antiscalant-dosed brine). Finally, the optimized AOP treatments would be evaluated on continuously produced RO brine from the RO unit at the demonstration facility containing antiscalant in order to mimic the application of the treatments in a fully operational facility (continuously produced brine).

Parallel investigation into the effect of AOP treatments on phosphorus speciation by bond type using representative phosphorus compounds was also completed using the optimized conditions from Phase 2. The compounds evaluated, after 30 ppm alum pretreatment, included sodium phenyl phosphate dibasic dihydrate (a C-O-P, or phospho-ester bond, ATP (a C-O-P, or phospho-ester bond and P-O-P, or phosphate ester) and diethyl (hydroxymethyl) phosphonate ((Hydroxymethyl) phosphonic acid diethyl ester) (a C-P, or phosphonate). The degree of AOP effectiveness by bond type would provide insight into the potential content by bond type of NRP compounds.

Treatment effectiveness would be evaluated by the lowest resultant residual total phosphorus concentrations after subsequent chemical addition (6 ppm alum) (RTP_{PT}) with comparison to the goal RTP_{PT} of 30 ppb P as suggested by the Provincial Water Quality Objectives as a level which would be protective of aquatic life. Although the LSPRS suggest reductions in overall annual loads, the goal of 30 ppb P provides a benchmark estimation of success. Treatment effectiveness was also evaluated with percent total phosphorus removals.

Phase 1 resulted in the selection of three individual treatments and one combination treatment with percent removals and RTP_{PT}s as follows: 10 ppm NaOCl at room temperature for 0.5hrs that resulted in %TP removals of 42% and an RTP_{PT} of 36 ± 1.0 µg P/L; 100 ppb H_2O_2 at room temperature for 1.5 hrs, which achieved %TP removals of 45% and an RTP_{PT} of 34 ± 14 µg P/L; acidification to pH 2 at room temperature for 1.5 hrs, which reached 61% TP removal and an RTP_{PT} of 24 ± 1 µg P/L, while the best combination treatment utilized 1 ppm H_2O_2 at pH 2, achieving 69% TP removal and an RTP_{PT} of 19 ± 3 µg P/L . However, the highest conversions and subsequent removals of phosphorus compounds occurred after treatment with a multi-combination treatment utilizing photolysis and 3000 ppm peroxide at pH 2 and 90°C for 1 hour, which achieved 85% TP removal and an RTP_{PT} of 9 ± 1 µg P/L. The successful application of these treatments exceeded others evaluated and provided evidence for the use of AOP treatments for oxidation of NRP compounds for the effective release and subsequent removal of orthophosphate after chemical addition.

Phase 2 yielded the following optimizations of each of the selected AOPs on 30 ppm alum pretreated brine: 100 ppb H_2O_2 for 30 minutes, 50 ppm NaOCl for 30 minutes, pH 2 for 30 minutes, and 100 ppb H_2O_2 + pH 2 for 30 minutes. Treatment effectiveness for the selected and optimized AOPs on antiscalant-free brine ranged from 62-73%, with the most effective AOP after a 30 ppm alum pretreatment being 100 ppb peroxide at pH 2 treatment which achieved 73% TP removal. The antiscalant dosed brines also were treated most effectively by the 100 ppb peroxide at pH 2 treatment achieving 66-82% TP removal for the four commercially available antiscalants. In the continuously produced brine from the demonstration facility %TP removals of 84% were observed in three of the four AOPs, while 83% TP removal was observed for NaOCl. Although the goal of 30 ppb P RTP was not achieved in any of the above described trials, RTP_{PT} values of below 35 ppb P were achieved for all treatments within standard deviation except NaOCl in the antiscalant-free brine. Similarly, SpectraGuard, one of the evaluated antiscalant dosed brines resulted in similar RTP_{PT}s for all AOP treatments, again with the exception of NaOCl. However, as was observed in Phase 1, the most successful AOP used a combination of photolysis and 3000 ppm peroxide at pH 2 and 90°C for 1 hour and resulted in 83% removal for the antiscalant-free brine, 94% for the continuously produced brine and 81-91% for the four antiscalant-dosed brines. These removals resulted in RTP_{PT}s of below 20 ppb P for the first two brines and below the goal of 30 ppb for each of the antiscalant-dosed brines, with the exception of Vitec 4000 which reached 31 ppb RTP_{PT}. Therefore the application of these AOPs as viable methods of phosphorus reduction and removal are possible and should be continued to be evaluated and optimized for other parameter variations.

Results for the representative phosphorus compounds varied in effectiveness by bond type with the combination of phospho-ester and phosphate-ester in ATP being the most susceptible to oxidation, achieving %TP removals of 92% for 100 ppb peroxide at pH 2, phenyl phosphate with a single phospho-ester bond achieved a maximum percent TP removal of 52% for 100 ppb peroxide, while the phosphonate species was virtually resistant to any treatment. After treatment with the combination of photolysis and 3000 ppm peroxide at pH 2 and 90°C for 1 hour, however, removals of 73-94% were achieved, with the least success observed in the phosphonate compound. Overall, the qualitative effect of the evaluated AOPs on various bond types can be determined and could be utilized for evaluating whether treatments would be effective based on speciation results from actual wastewater samples, identified from High Performance Liquid Chromatography (HPLC) or mass spectrometry.

Overall this project successfully evaluated the potential for AOPs to effectively convert NRP to RP in RO brine as part of a quaternary step in wastewater treatment. The resistance to AOP treatment by bond type also provides insight into the potential site-specific application of quaternary treatment.

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To my big brother, who influences me more than he knows, I'd like to say "I'm done now", "Yes, I have another graduation thing coming around" and "No, I'm not a doctor, yet". You and your loving wife and beautiful daughter provide a rock for me and something to look forward to when my learning days are done, that's if they ever finish—proving once again, as you always say, you got the looks and I got the brains.

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Lastly, I want to thank the two people who really started my love of science, Brian Lasenby and Jason Broderick— I never thought I would take it this far, what did you two get me into!

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Table 1.1: List of Acronyms

Acronym:	Definition:
TP	Total Reactive Phosphorus. All phosphorus in sample (persulfate digestion)
sTP	Soluble Reactive Phosphorus. All phosphorus in filtered sample (persulfate digestion). Samples filtered using a 0.2 micron hollow fiber polysulfone media filter.
tmAHP	Total Measured Acid Hydrolysable Phosphorus. Phosphorus measured in sample after acid hydrolysis (HNO_3-H_2SO_4 digestion)
smAHP	Soluble Measured Acid Hydrolysable Phosphorus. Phosphorus measured in filtered sample after acid hydrolysis (HNO_3-H_2SO_4 digestion). Samples filtered using a 0.2 micron hollow fiber polysulfone media filter.
tAHP	Total Acid Hydrolysed Phosphorus. Fraction of phosphorus in sample hydrolysed by strong acid. tAHP = tmAHP-tRP
sAHP	Soluble Acid Hydrolysed Phosphorus. Fraction of phosphorus in filtered sample hydrolysed by strong acid. Samples filtered using a 0.2 micron hollow fiber polysulfone media filter. sAHP = smAHP-sRP
tOP	Total Organic Phosphorus. Organic phosphorus in sample. tOP = TP-tmAHP
sOP	Soluble Organic Phosphorus. Organic phosphorus in filtered sample. Samples filtered using a 0.2 micron hollow fiber polysulfone media filter. sOP = sTP-smAHP
RTP_{CA}	Residual Total Phosphorus after Chemical Addition. Fraction of total phosphorus remaining after chemical addition ($AlSO_4$ or $FeCl_3$) and filtration using a 0.2 micron hollow fiber polysulfone media filter.
RTP_{PT}	Residual Total Phosphorus Post AOP Treatment. Fraction of total phosphorus remaining AOP treatment and subsequent chemical addition ($AlSO_4$ or $FeCl_3$) and filtration using a 0.2 micron hollow fiber polysulfone media filter.
LSPRP	Lake Simcoe Phosphorus Reduction Plan
LSPRS	Lake Simcoe Phosphorus Reduction Strategy
NRP	Non-Reactive Phosphorus
RP	Reactive Phosphorus
RO	Reverse Osmosis
BPR	Biological Phosphorus Removal

MF or UF	Microfiltration or Ultrafiltration
ROP	Reverse Osmosis Permeate
AOPs	Advanced Oxidation Processes
GAC or PAC	Granular Activated Carbon or Powdered Activated Carbon
DOC `	Dissolved Organic Carbon
PCO	Photocatalytic Oxidation
COD or BOD	Chemical Oxygen Demand or Biological Oxygen Demand
PAA	Peracetic Acid or Peroxyacetic Acid
inOP	Inorganic Phosphorus
ROC	Reverse Osmosis Concentrate or brine
MFP	Microfiltered Permeate
RWW	Raw waste water, actually secondary effluent from Mt Albert Facility
WPCP	Water Pollution Control Plant
HPLC	High Performance Liquid Chromatography
UYSS	Upper York Sewage Solutions
UYSS EA	Upper York Sewage Solutions Environmental Assessment

Chapter 1: **Background**

Phosphorus is a naturally occurring element that is required by all living organisms; however, excess phosphorus in the environment has the potential to cause eutrophication. Both naturally occurring and exacerbated by anthropogenic activity, the process of eutrophication is caused by the accumulation of dead organic matter from aquatic organisms that deplete dissolved oxygen levels, increase temperature and increase sedimentation. The increase in dead organic matter is the result of nutrient (ie. phosphate and nitrate) enrichment of lakes and slow moving rivers, which cause increased algal and plant populations that will eventually die (Art, 1993; Lawrence and Jackson, 1998). As a result of anthropogenic activities agricultural run-off and municipal wastewater effluent are potential sources of phosphorus to the environment. In response to environmental impacts governments have imposed increasingly strict regulations on effluent nutrient concentrations; therefore continued advancements in phosphorus removal from wastewater are a necessity. Current regulations for sensitive receiving waters are approaching the limit of technology for phosphorus removal and improved methods are required. One such initiative that seeks to reduce the phosphorus load present in its municipal effluents is the Lake Simcoe Phosphorus Reduction Plan (LSPRP), which is a part of multi-dimensional activities that strive to reduce phosphorus contributions from all sources.

Lake Simcoe is the largest inland lake in Ontario, other than the Great Lakes. It is surrounded by many urban sprawls (Figure 1.1b) and is as most lakes, an attractive living and tourist destination.The area is rich in history and natural beauty, which makes tourism and agricultural use the area’s economical focus. Forty-seven percent of Lake Simcoe’s watershed, outlined in the darkened region of the map (Figure 1.1a), is used for agriculture. However, because of the surrounding lands fertility, the lake system has become negatively affected by anthropogenic pollution. The average annual phosphorus load from 2002-2007 was 72 T, which is more than double the 32 T/yr calculated prior to the 1800’s influx of inhabitants, subsequent land clearing and agricultural usage. As a result the lake has its share of environmental issues including eutrophication and species decline, both due in part to the presence of excess phosphorus from the surrounding urban and rural communities. Due to eutrophication effects, lake temperatures have risen, O_2 levels have declined and plant growth has become choking to the aquatic inhabitants (World Resources Institute). These effects combined have seriously impacted the sensitive and specific breeding grounds of many of the lakes susceptible species. In addition to eutrophication and ecosystem impacts, excess nutrients cause algal blooms, which appear as green slime layers and affect the appearance of the lake and thus tourism within the area. Increased nutrient content also results in bacterial blooms, which can be dangerous to swimmers and water enthusiasts and often cause the closing of beaches. Improvements to these conditions began in the 1980's when efforts to restore the lake were initiated (LSPRS, 2010).

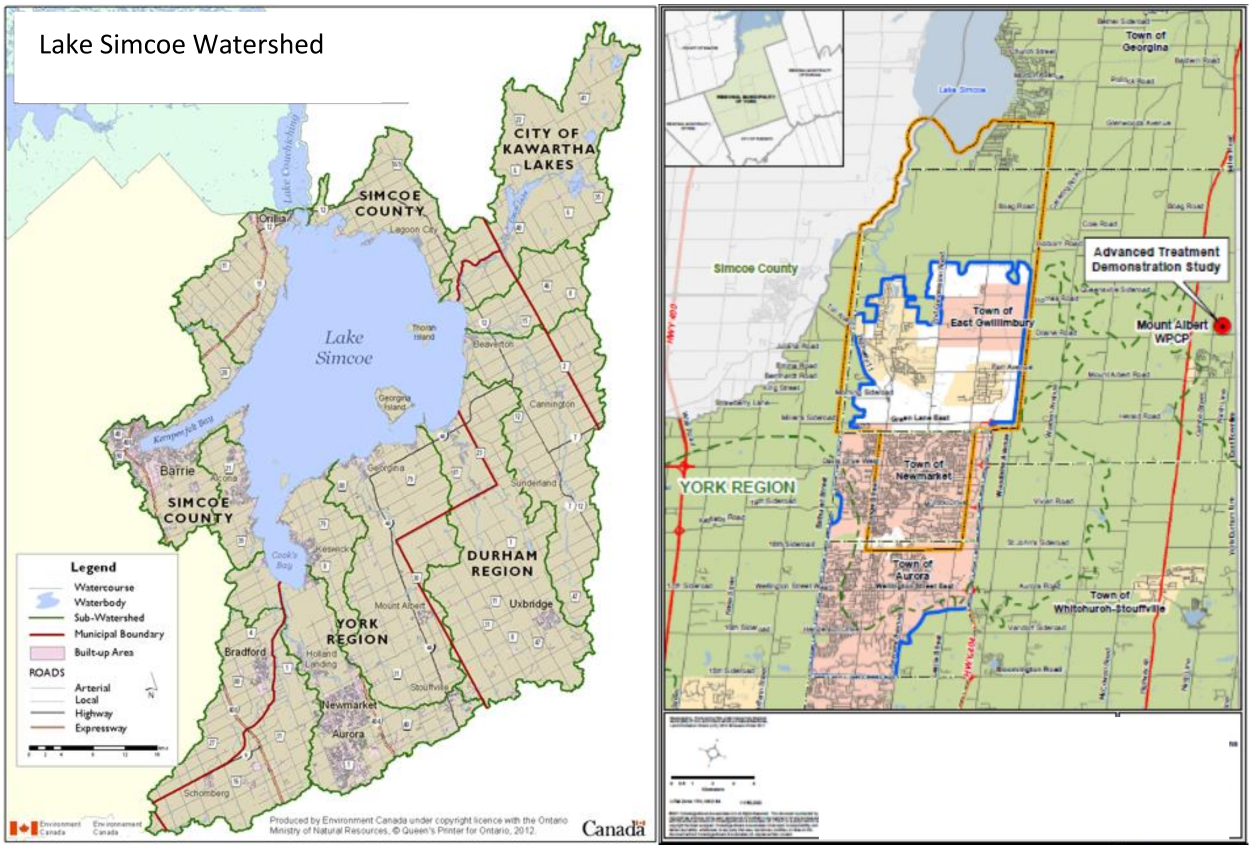


Figure 1.1a and b: The surrounding watershed that feeds Lake Simcoe is depicted in the shaded portion of Figure 1.1a. Agricultural use accounts for 47% of this area. Figure 1.1b depicts the urban centers that surround the lake and contribute to its contaminant load. The bench scale sampling facility and location of the demonstration facility is marked on Figure 1.1b at Mount Albert. Figures from LSPRS 2010 (a) and from the Upper York Sewage Solutions Environmental Assessment (b)

In 1981, The Lake Simcoe Environmental Management Strategy was enacted by a multi-agency partnership of provincial ministries, as well as the Federal Government, to help control and reduce the phosphorus inputs into the lake. This began a decades long attempt to take back the lake and protect the sensitive spawning environments and species that call the lake home. The Intergovernmental Action Plan in 2006 completed the Assimilative Capacity study to model the growing populations' impact on the watershed at present and in the future. These studies gave rise to the Lake Simcoe Protection Act in 2008, which set forth the Lake Simcoe Environmental Protection Plan in 2009. The following year the LSPRP and the Lake Simcoe Phosphorus Reduction Strategy were adopted in June, which identified a combined sustainable annual phosphorus load of 3.2 T/yr for all treatment facilities discharging into Lake Simcoe. This load allocation accounts for the current contribution of phosphorus from sewage treatment facilities (7%) and applies it to the goal of overall phosphorus loading of 44 T/yr. The LSPRP intends to reduce the total phosphorus load by 40%, down to a sustainable and acceptable 44 T/yr. The current baseline load allocation for the sewage treatment facilities is 7.2 T/yr and the reduction of this loading by over half is not practical, however, the overall goal load for the lake is 44 T/yr, which can be achieved by reductions from all phosphorus contributing sources. Reductions from other sources could provide phosphorus load offsets that could be used to help the sewage treatment facilities to meet their reduction goals, although this approach is not yet specifically defined as part of the LSPRP.

The Provincial Water Quality Objectives (July 1994) suggest less than 30 ppb phosphorus to be present in rivers or streams in order to be protective of aquatic life; the ideal range for lakesystems is a residual phosphorus concentration of 10-20 µg P/L. These criteria should be considered when discharging wastewater effluent. The region of Upper York, as one of the larger regions encompassed in the Lake Simcoe watershed depicted in Figure 1.1a, seeks to reduce the annual load of phosphorus entering the lake specifically by adopting innovative removal techniques in a new wastewater treatment facility that would serve part of the population of the watershed presently and would be able to accommodate future growth. The region uses the guidelines suggested by the PWQO as minimum goals for the effluent leaving this newly proposed facility. Upper York Region contains the existing full-scale wastewater treatment facility (Mount Albert Water Pollution Control Plant (WPCP)) where bench-scale sampling occurred for Phase 1 of this project (Figure 1.1b) and is home to the Demonstration Facility (Mount Albert, ON) for Phase 2 of the project..

1.1 Phosphorus Speciation

Phosphorus is present within the matrix in various reactive (orthophosphate) and non-reactive forms (condensed phosphates, mineral phosphates, organic and inorganic phosphates). Non-reactive phosphorus (NRP) species contain phosphorus in forms that prevent its direct removal with chemical addition; it is defined as the difference between total phosphorus (TP) and reactive phosphorus (orthophosphate), without clear indication to its exact speciation (WERF, 2008; Gu *et al.*, 2007). As outlined in Figure 1.2, the major divisions of phosphorus present in wastewater are dissolved and particulate phosphorus, which are based on size separation by filtration. Each division can be further broken down and characterized. Particulate phosphorus is characteristically insoluble and often be found adsorbed to other waterborne particles or in crystalline or amorphous particles. Although controlling total phosphorus concentrations in effluent is the primary goal in wastewater treatment, secondary and tertiary treatment, focuses on dissolved phosphorus, which includes orthophosphate, inorganic and organic condensed phosphorus, although particulate phosphorus is still removed during these processes. The majority of particulate phosphorus is removed during primary filtration or clarification (Hammer and Hammer, 2001). The majority of phosphorus in raw influent is orthophosphate (anywhere between 50-80%), whereas NRP species (inorganic and organic condensed) account for the remainder (WERF, 2008). Existing methods target removal of the orthophosphate form of phosphorus, usually by chemical removal via addition of a metal salt to precipitate the phosphate and filtration, but to achieve low effluent limits the NRP forms must be removed as well (Maher and Woo, 1998). Although chemically non-reactive, it is possible that the NRP species are biologically reactive and could still contribute to eutrophication

(Ekholm and Krogerus, 2003). In order to convert NRP to RP the covalent bonds binding the phosphorus up must be broken, such as the oxidation of organics that could be bond to phosphorus (phospho-ester, phosphate-ester or phosphonate). Once the NRP has been converted to a more reactive form of phosphorus, chemical removal can act to further reduce the total phosphorus, which would reduce the nutrient loading of natural systems, such as Lake Simcoe.

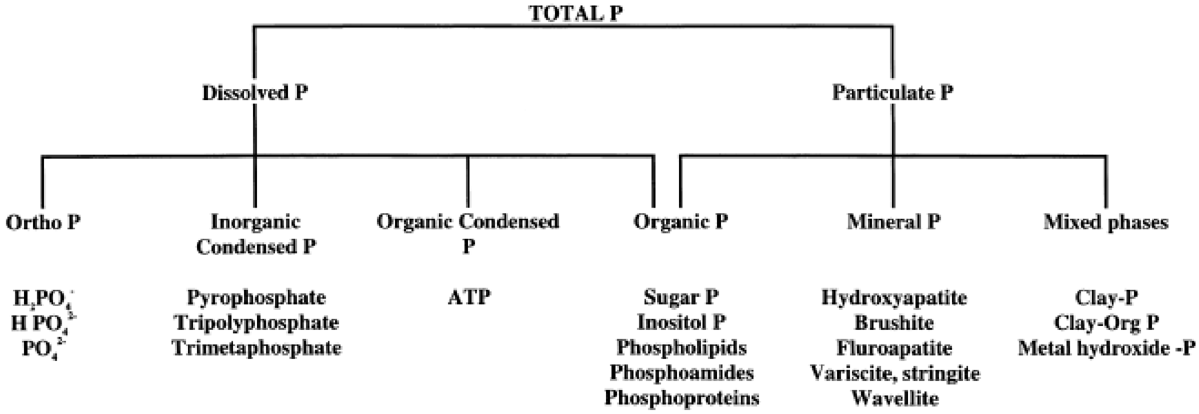


Figure 1.2: Phosphorus species present in wastewater. The classification of total phosphorus into subgroups and proposed examples of phosphorus species found in each subgroup (Maher and Woo, 1998).

1.2 Wastewater Treatment

A wide variety of treatment technologies are used in wastewater treatment and improvements to each step in the treatment process are ongoing. The basic schematic of a treatment facility is presented in Figure 1.3. Preliminary treatment removes solids, large grit and debris before the water enters the main treatment steps in order to minimize and prevent damage to the equipment throughout the processing facility. Primary treatment involves the removal of scum from the water's surface and primary sedimentation, where larger suspended particles and organic material are settled out forming sludge. Sedimentation can be enhanced by the addition of coagulants that promote flocculation; this process also promotes phosphorus removal. A biologically activated sludge is formed during secondary treatment via aeration. This process utilizes microbes to digest organic material, producing water and carbon dioxide as byproducts along with new microbes to maintain the population. The microbial uptake of phosphorus accounts for 10-30% of the reduction of total phosphorus, which can be enhanced 2.5-4 times using phosphorus accumulating organisms. Waste activated sludge is removed to prevent overpopulation of the microbes. The sludge removed during primary and secondary treatments is then digested for stabilization and removed to a landfill, with or without prior incineration, or, more commonly in Ontario, applied to agricultural lands as a beneficial re-use practice. Tertiary treatment, or advanced treatment is a blanket term for a variety of treatments (Hammer and Hammer, 2001) that can be used singly or in combination that allow for the removal of more specific contaminants, such as pharmaceuticals and phosphorus. Types of tertiary treatments include membrane filtration and separation, dechlorination, ion exchange, activated carbon adsorption and biological, physical or chemical removal (coagulation), as well as many others (Siemans AG, 2001; Gu *et al.*, 2007). Disinfection using UV or chlorination occurs before effluent leaves the facility. This project seeks to evaluate a fourth or quaternary treatment step in order to effectively reach effluent limits.

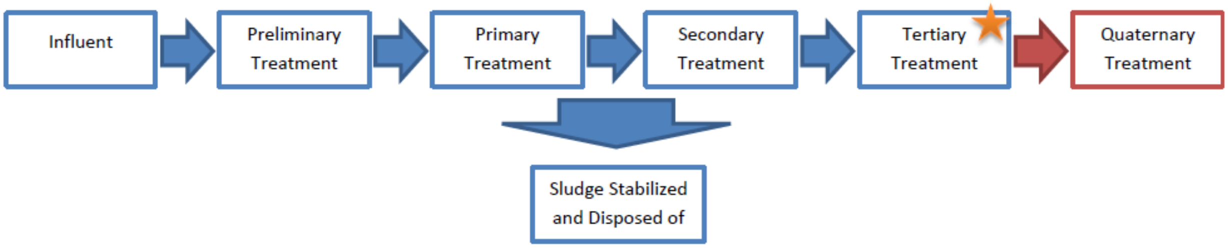


Figure 1.3: Basic flow chart schematic of wastewater treatment denoted in blue. The tertiary processes used in this project include chemical removal and microfiltration, highlighted by the star. The red denotes the addition this project seeks to test, including reverse osmosis and AOP treatment of the resulting brine

1.3 Phosphorus Removal Processes

In order to remove phosphate in its many forms, wastewater treatment facilities often use a combination of removal technologies that include chemical removal, usually by aluminum or iron salts, and enhanced biological phosphorus removal (BPR) using microbial activated sludge (deHass *et al.*, 2000). Chemical removal has been well studied using various metal salts to determine the optimal conditions for phosphate removal. Metal salt addition is essential in reaching low effluent phosphorus levels; however, both ferric and aluminum salts, are only capable of removing orthophosphate, while organic phosphates and polyphosphates remain (WERF, 2008). For this reason many converting technologies are required to improve the removal of phosphorus down to the required limits (Lancaster *et al.*, 2008). Phosphate is removed from wastewater by two mechanisms, a fast and immediate removal, termed instantaneous phosphorus removal, which occurs within the first minute after salt addition and a longer process, termed slow phosphorus removal, which can take several hours up to days to maximize removal (Szabo *et al.*, 2008). Co-precipitation of phosphate by the metal salt (ex. Fe(III)) is believed to be the principal mechanism of removal within the instantaneous phosphorus removal stage, while adsorption becomes the leading removal process during the slow phosphorus removal stage (Smith *et al*., 2008; WEF, 2010).

1.4 Mixing Intensity and Other Considerations Affecting Phosphorus Removal

Mixing intensity (G) is quantitatively measured using the velocity gradient multiplied by time in order to determine the particle-to-particle collisions per unit time per unit volume. It is a function of mixing zone volume and mixing velocity with units of inverse time (Field *et al*, 2005).

Mixing intensity within a wastewater treatment facility is usually low, with G values of 20 to 100 s^{-1}; however, experimentally Szabo *et al*. (2008) found that higher G values, 300-1000 s^{-1} provide more effective removal of phosphate due to the increased opportunity for contact between the continuously moving metal (Fe(III)) and phosphate ions (Takács *et al.*, 2006).

Other considerations that contribute to the effectiveness of chemical phosphorus removal are pH and water hardness. The effects of pH on speciation and thus chemical phosphate removal using ferric salts have been widely studied and were determined to occur optimally at a pH of 6.2-7 (Takács *et al*., 2006), while Smith *et al*. (2008) found that up to 99% of the influent orthophosphorus can be chemically removed with a pH as low as 4 with Fe(III). Removals using alum optimally occur with pH between 6 and 8.5. (Mohammed and Shanshool, 2009). The presences of both magnesium and calcium have been shown to increase the precipitation of phosphate by forming various complexes with the metal-phosphate species or with phosphate alone and thus improve the removal process (Gilmore, 2011; WEF, 1998).

The residual phosphorus after the fast co-precipitation stage of removal, at a particular Fe:P ratio of 1:1.8 and initial phosphate concentration of 4.1 mg P/L, can be related to mixing intensity according to the following equation experimentally determined by Szabo *et al*. (2008):

$$P = 0.805e^{-0.006G} \text{ (mg P/L)} \quad \textbf{(1)}$$

where P is residual orthophosphate.

The slow adsorption stage of phosphate removal was studied in depth by Gilmore (2011) who tested 4 factors that may affect phosphate removal, Fe dose, mixing intensity, pH, and water hardness. The mixing intensities used were 376 s^{-1} for fast mixing, and 23.5 for slow mixing, while water hardness was 170 mg $CaCO_3$/L, P:Fe dose was 1:5 and pH was 6. The rates of phosphate adsorption were determined and are summarized in Table 1.1 according to the previously stated parameters:

Table 1.1: First order kinetic rate constants for the adsorption (k_1) and de-adsorption (k_{-1}) of phosphate by iron reaching equilibrium.

	Forward Reaction (k_1) (µg P/L*h)	Reverse Reaction (k_{-1}) (µg P/L*h)
Fast Mixing	1380	109
Slow Mixing	213	40.4

Similar studies evaluating surface complexation still need to be performed on alum, although similar reactions are likely (WERF, 2008).

Enhanced biological phosphorus removal (BPR) has been intensively studied as a highly effect removal technology for phosphorus. The uptake of the polyphosphates occur naturally for the microorganism (ex. Acinetobacter, Aeromonas and Pseudomonas (Comeau *et al.,* 1986) and it can be stored as an energy source which effectively removes it from the wastewater (Smolders *et al.,* 1995). Uptake of phosphorus by microorganisms can occur in aerobic conditions and is reversed in anaerobic conditions; it is dependent upon several factors. Both require an initial anaerobic process that allows the microorganisms to consume acetate, storing it as poly-β-hydroxybutyrate (PHB), which will be metabolised later during the uptake of phosphate under aerobic conditions (Smolders *et al.,* 1995).

1.5 Multistep Tertiary Treatment- Available Options for Improved Phosphorus Removal

Due to the essential role played by chemical addition in reaching low residual phosphorus levels multistep tertiary treatment using filtration, coagulation and adsorption have also been studied and have been shown to be highly effective and efficient at removing phosphorus. Studies by Gu et al (2007) have shown that this combination of tertiary treatment has been able to achieve a residual phosphorus level of approximately 20 µg P/L. These studies also determined that the residual phosphorus was primarily organic phosphorus, although the exact chemical composition was not determined, and that this fraction needs to be treated in order to ensure these ultra-low levels of residual phosphorus are achievable. Lancaster et al (2008) confirmed this finding and extended it to include condensed as well as organic phosphorus as the major components present in residual effluent phosphorus.

The combination of tertiary treatments, including chemical addition and micro- or ultra-filtration, with a proposed implementation of a quaternary step that utilizes reverse osmosis (RO), as described in Figure 1.3, followed by treatment of the RO concentrate that is produced as a result of RO treatment could result in the further reduction of phosphorus in effluent. The benefit of RO treatment is that it allows for a cost-effective way to reclaim water from wastewater treatment; both the permeate and further treatment of the RO concentrate could offer a sustainable way to treat wastewater, while producing minimal by-products (Zhou *et al.*, 2011). In fact 75-85% of the feed wastewater is reclaimed during permeate and simultaneous RO concentrate production (Zhou *et al.*, 2011). As a comparison, Comerton *et al.* (2005) reports removal of nitrates from the permeate of greater than 90%; this evidence lends support to the potential application of this combination tertiary treatment to the removal of phosphorus. Therefore further study of treating the RO concentrate is required.

1.6 Filtration Techniques

Microfiltration (MF) or Ultrafiltration (UF) use low-pressure membrane filters with fibre diameter openings on the micron scale. These filtration units effectively remove various suspended and colloidal particles, even pathogens and therefore are a useful step in the removal of particulate phosphorus, as well as some larger colloidal phosphorus species present in the wastewater matrix (Dialynas *et al.*, 2008). The utilization of these filtration units in combination with reverse osmosis is a well-studied treatment and a pilot facility exploring the application in municipal wastewater reclamation have been built in Chania, located in Western Crete, an island belonging to Greece (Dialynas *et al.*, 2008; Zhao *et al*, 2012). At present the development of micro- or ultrafiltration followed by RO is being focused on as a major step in the removal of antibiotics and other pharmaceuticals. Dolar *et al.* (2012) studied various combinations of RO and nanofiltration membranes and determined that >90% of pharmaceuticals could be removed using this treatment combination. Due to the extreme effectiveness of this technology, as well as its continued advancement and recent reduced cost, Dolar *et al.* (2012) predicts the future wide scale application of these units in the wastewater industry. Therefore this filtration and RO combination can logically be extended to the successful concentration of phosphorus containing compounds for further treatment.

1.7 Reverse Osmosis- Concentrate and Permeate Production and Disposal

Reverse osmosis (RO) uses high pressure membrane filtration to remove particles down to the µm scale, including dissolved salts and nutrients. The RO treatment allows the dissolved particles to be concentrated into a brine solution (concentrate) and allows the permeate, which is very low in the dissolved materials to be released (after disinfection and re-introduction of necessary cations and anions) into the receiving waters. RO concentration occurs because specific solutes are impermeable to the membrane and are thus concentrated inside the membrane, termed ‘solute rejection’, while the permeate is released (Figure 1.5). Bellona *et al.* (2004) describe the mechanism(s) that lead to solute rejection, which allows these solutes to be concentrated. Solute rejection by filtration/RO membrane units is influenced by both solute and membrane characteristics, as well as the influent feed composition and the operating conditions. Rejection occurs by a singularly or combinatorial mechanism of three different mechanisms; these mechanism are size exclusion, charge exclusion or physico-chemical interactions between the solute, the solvent and the membranes (Bellona *et al.*, 2004).

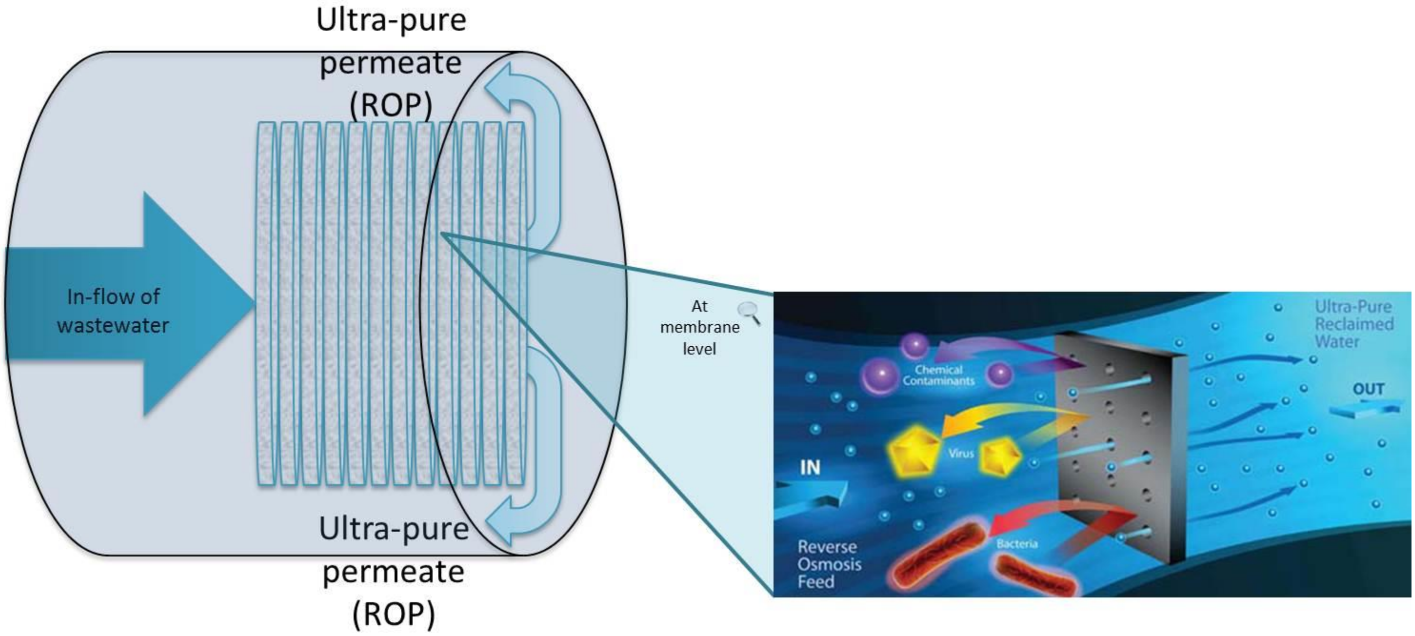


Figure 1.4: Simplified pictorial description of how RO mechanisms work and how the RO concentrate is formed. Some constituents that are retained in the concentrate are described with others discussed in the paragraph below. Figure Modified from UYSS figure.

Ozaki and Li (2002) determined that the major solutes present in RO concentrate are dissolved inorganics and soluble, low molecular weight refractory organics, including petrochemicals, pharmaceutical products, pesticides, endocrine disruptors, anti-scaling chemicals (used to prevent carbonate and other chemical accumulation on membrane surface), disinfection byproducts, personal care products, soluble microbial products, bacteria, pathogens, or cell debris, and that the concentrate is a valuable indicator for influent water quality (concentrate high in these compounds is a indicator of low water quality); water may require further treatment to be safe for discharge to the environment) (Zhao *et al*, 2012).

Although the permeate is easily disposed of into receiving waters once it has been disinfected and component salts reintroduced (required due to the toxicity to aquatic species of pure water (Levine and

Saltzman, 2001)); the brine is much harder to dispose of because of its high concentrations of salts and pollutants, which cannot be released into most natural systems due to the toxic nature of such high concentrations. Common brine disposal techniques include deep ground injection; discharging to other wastewater collection systems; and release into open oceans, where high salt and nutrient concentrations are not an issue (Howe). For the Lake Simcoe Area, deep ground injection and ocean disposal are not applicable; transport to the ocean would be too costly for the volume produced; and deep ground injection is limited by capacity and the potential effects to groundwater —thus not improving the pre-existing problem. Another alternative would be evaporation; however, the volume of brine produced at even a moderately sized facility would be far too costly to evaporate.

Although there are not current regulations for all of the organic constituents present in the brine, the RO concentrate or brine created by RO treatment processes can contain high contaminant concentrations (Zhou *et al.*, 2011), which could be treated further prior to discharge to the environment. Further treatment could include: further RO treatment, advanced oxidation processes (AOPs), coagulation/flocculation with metal salts or, more common adsorption using granular activated carbon (GAC) and powdered activated carbon (PAC). These treatments are used to remove the organic pollutants to meet regulatory requirements, where available, for release to the environment (Zhao *et al*, 2012; Zhou *et al.*, 2011). Adsorption using activated carbon has been demonstrated to be up to 90% effective at the removal of organics from the RO concentrate; however adsorption does not eliminate the pollutant and instead merely transfers it to the adsorbed phase where it would still need to be treated in order to prevent ecotoxicity (Zhou *et al.*, 2011). Therefore AOPs present an efficient way to effectively breakdown the pollutants, rendering them non-toxic; AOP treatments would benefit not only phosphorus removal but also water quality by removing potentially toxic substances. This further treatment of the brine using AOPs is considered a part of quaternary treatment and the extension of AOPs to improving phosphorus removal is the focus of this project.

1.8 Advanced Oxidation Processes—Applications in RO Concentrate and Wastewater Treatment

Advanced oxidation processes are the more costly route as compared to treatment solely using chemical addition and are only recently being further developed. An attractive AOP is any that produce hydroxyl radicals (•OH), which non-selectively and readily oxidize many of the organic constituents that are present in the RO concentrate. Due to the highly reactive nature of these radicals, utilization of these AOPs in 'concentrated flowstreams' or as pre-treatments can reduce the presence of DOC, or produce simpler, more biodegradable forms of organics (Zhou *et al.*, 2011). The efficacy of hydroxyl radicals is contributed in part due to the very short life-span of these radicals in natural and drinking waters, as well as wastewater, which is approximately 10 µs. This short life-span is attributed to the radical's oxidizing ability to initiate and propagate the chain reaction associated with the production of other free radicals from organic or inorganic compounds, which in turn can oxidize more compounds or terminate with another free radical (Caretti and Lubello, 2003). Current AOPs utilized to remove the organic pollutants include sonolysis, photocatalytic oxidation (PCO) (UV-TiO_2 or boron-doped diamond (BDD)), ozone oxidation (ozonation, O_3), peroxide oxidation (H_2O_2) and electrochemical oxidation (Zhou *et al.*, 2011; Zhao *et al*, 2012). Intensive research has been conducted in the application of these AOP treatments for the reduction of DOC, many having highly successful outcomes; however AOPs have not been studied in any depth for the oxidation of phosphorus compounds. Appendix A provides a detailed discussion of the application of various AOPs in regards to the effectiveness at oxidizing DOC and the reduction of COD and BOD from the literature.

In review of the literature and the ability of AOPs to oxidize DOC, it is possible to extend the application of these oxidizers and others to the potential oxidation of phosphorus from its many, and potentially complex organic forms. As well, it is reasonable to conclude that coagulation of organic phosphorus is possible and could be utilized as a pretreatment for RO concentrate followed by subsequent AOP oxidation as an effective means of phosphorus reduction from wastewater effluent.

Proposed mechanisms of hydroxyl radical formation using the various AOPs described above:

UV/H_2O_2: $H_2O_2 + \text{UV light} \rightarrow 2\ {\cdot}OH$ (1)
$H_2O_2 \rightarrow HOO^- + H^+$ (2)
${\cdot}OH + H_2O_2 \rightarrow {\cdot}OOH + H_2O$ (3)
${\cdot}OH + HOO^- \rightarrow {\cdot}OOH + OH^-$ (4)
$2\ {\cdot}OOH \rightarrow H_2O_2 + O_2$ (5)
$2\ {\cdot}OH \rightarrow H_2O_2$ (6)
${\cdot}OH + {\cdot}OOH \rightarrow H_2O + O_2$ (7)

(Venkatadri and Peters, 1993)

US/H_2O_2: $H_2O_2 + \text{sonation} \rightarrow 2\ {\cdot}OH$ (8)

UV/O_3: $O_3 + H_2O + \text{UV light} \rightarrow 2\ {\cdot}OH + O_2$ (9)

UV/H_2O_2/O_3: $O_3 + H_2O_2 + H_2O + \text{UV light} \rightarrow 4\ {\cdot}OH + O_2$ (10)

US/O_3: $O_3 + \text{sonation} \rightarrow O + O_2$ (11)
$O + H_2O \rightarrow 2\ {\cdot}OH$ (12)

US/ H_2O_2/O_3: $O_3 + H_2O_2 + H_2O + \text{sonation} \rightarrow 4\ {\cdot}OH + O_2$ (13)

UV/TiO_2/O_3: $TiO_2 + \text{UV light} \rightarrow e^- + H^+$ (14)
$e^- + O_3 \rightarrow {\cdot}\ O_3^-$ (15)
${\cdot}\ O_3^- + H^+ \rightarrow {\cdot}OH + O_2$ (16)

(Zhou *et al*., 2011)

Fe^{2+}/H_2O_2: $H_2O_2 + Fe^{+2} \rightarrow 2\ {\cdot}OH + Fe^{3+} + OH^-$ (17)

Catalytic decomposition of H_2O_2 with Fe^{+3} that results in hydroperoxyl radicals:

$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{—}OOH^{2+} + H^+$ (18)
$Fe\text{—}OOH^{2+} \rightarrow {\cdot}O_2H + Fe^{2+}$ (19)
${\cdot}O_2H + Fe^{2+} \rightarrow Fe^{3+} + HO_2^-$ (20)
${\cdot}O_2H + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2$ (21)
${\cdot}OH + H_2O_2 \rightarrow {\cdot}O_2H + H_2O$ (22)

(Chamarro *et al*., 2001)

PAA/UV: $CH_3CO_3H + \text{UV light} \rightarrow CH_3CO_2{\cdot} + {\cdot}OH$ (23)
$CH_3CO_2{\cdot} \rightarrow CH_3{\cdot} + CO_2$ (rapid) (24)
$CH_3CO_3H + {\cdot}OH \rightarrow CH_3CO_4H_2 \rightarrow CH_3CO_2H + {\cdot}OOH$ or
$CH_3CO_3H + {\cdot}OH \rightarrow CH_3CO_2{\cdot} + O_2 + H_2O$ (25)

*Note: the presence of H_2O_2 in the PAA solution causes the regeneration of PAA once it undergoes the initial radical formation (according to Le Chatelier's Prinicple) and the formation of extra hydroxyl radicals (Caretti and Lubello, 2003).

Proposed mechanisms of AOP oxidation that do not utilize hydroxyl radicals described above:

Redox Chemistry:

FeO_4^{2-}

$FeO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Fe^{3+} + 4H_2O$ $E^0 = +2.20$ V (acidic conditions) (26)

$FeO_4^{2-} + 4H_2O + 3e^- \leftrightarrow Fe(OH)_3 + 5OH^-$ $E^0 = +0.72$ V (neutral conditions) (27)

(Jiang *et al*, 2009)

$FeO_4^{2-} + R\dot{C}OH \rightarrow HFeO_4^{2-} + RCO$ (reaction with organic radicals) (28)

NaOCl:

$HClO + H^+ + 2e^- \leftrightarrow Cl^- + H_2O$ $E^0 = +1.482$ V (from perchloric acid) (29)

(Bielski, 1991)

Proposed generalized mechanism for oxidative degradation of organic pollutants using the hydroxyl radicals produced during AOP treatment:

$$AOP \rightarrow \cdot OH \xrightarrow{\text{+ organic pollutants}} CO_2 + H_2O + \text{inorganic ions} \qquad (30)$$

*can also be applied to the degradation of inorganic compounds

(Caretti and Lubello, 2003)

$$RH + \cdot OH \rightarrow H_2O + R\cdot \rightarrow \text{further oxidation} \qquad (31)$$

(Venkatadri and Peters, 1993)

1.9 Research Goals and Objectives

In order to help reduce the social and environmental impacts, Lake Simcoe has been placed under strict regulations concerning phosphorus load allocations. As part of the underlying constructs of the LSPRS, York Region has initiated investigations into the development of new and more effective wastewater treatment facilities to accommodate growth in the service area while respecting the spirit and intent of the LSPRS. This project sought to provide a realistic, cost-effective method recommendation for refractory phosphorus removal as a result of quaternary treatment (AOP) from RO concentrate for a potential full scale wastewater treatment facility that meets phosphorus load allocations assigned by the LSPRP. As part of the LSPRP and in conjunction with various partners this project intends to accomplish the following objectives:

1. Bench-scale assessment using bench-top produced RO concentrate (Phase 1):

   a. Evaluate several advanced oxidation processes (AOPs) independently and in bi-combinations for effectiveness at increasing total reactive phosphorus (tRP) in RO concentrate, while simultaneously evaluating the effective reduction of total phosphorus (TP) after metal salt addition (RTP).

   b. Optimize AOPs with respect to dosage, contact time, pH and temperature to ensure optimal effectiveness in the conversion of non-reactive phosphorus to reactive phosphorus (RP) and subsequent removal with coagulation.

2. Pilot-scale assessment using RO concentrate produced from a demonstration facility located in Mt Albert (Phase 2):

   a. Refine optimizations for the most successful AOPs with the optimal parameters identified during bench-scale assessment and evaluate the effectiveness with demonstration-scale produced brine in order to maximize phosphorus conversion and removal efficiency for demonstration-scale application.

Although not specifically evaluated within this project, this research will be part of a larger assessment that will evaluate the benefits and costs resulting from the use of quaternary treatment using RO and AOP treatment of the resulting brine for improved phosphorus removal in a new Water Reclamation Centre. This will be compared to the cost of construction of a pipeline from a collection system that would service the growing communities, through the Oak Ridges Morraine. This pipeline would connect to the existing York Durham Sewer System (YDSS) to convey raw wastewater to Duffin Creek WPCP prior to discharge to Lake Ontario, which is a larger, deeper lake as an alternative servicing solution. These are two of the alternatives identified in the Terms of Reference for the Environmental Assessment process by Upper York Sewage Solutions in order to meet the growth of the upper portion of York Region while respecting the protection of Lake Simcoe as well as other regulatory requirements. Overall the goal of this project was to explore the potential application for AOPs on RO concentrate (ROC) as a quaternary treatment for the effective reduction of phosphorus, specifically NRP, from bench-scale to demonstration-scale. Specifically the project, through the treatment of ROC, would allow water to remain in the Lake Simcoe watershed by achieving a phosphorus concentration that is within the LSPRS constructs. This project would allow the effects of anthropogenic activities that result from the continued input of phosphorus on sensitive ecosystems to be decreased. By developing phosphorus removal techniques from wastewater effluent which will aid in the protection of sensitive water systems, these environmental concerns can be reduced if not averted. Concurrently, this project will help advance the knowledge of combined coagulation and filtration as an effective means of tertiary treatment, while also promoting the use of quaternary treatment, such as reverse osmosis and AOP, in order to increase water reclamation from wastewater effluents—a goal that has long reaching effects with respect to fresh water usage and water shortages.

1.10 Analytical Techniques

1.10.1 Colorimetric Determination of Phosphorus Speciation

Orthophosphate concentration is quantified using colorimetry by measuring absorbance via UV/Vis spectroscopy according to Beer-Lambert Law. This law is described in the mathematical relationship presented in equation 1, which directly relates the concentration of a solute (c) to the absorbance of a coloured complex (A) modified by a extinction coefficient (ε, specific to the compound, in M^{-1} cm^{-1}) and the light path of the instrument (b, in cm) (Harris, 2003).

$$A = \varepsilon bc \quad (1)$$

Standard methods (4500-PE.) suggest three options for the colorimetric determination of phosphorous which are selected depending on the concentration of orthophosphorous in the test sample, they include the vanadomolybdophosphoric acid method—useful with phosphorus ranges from 1 to 20 mg P/L, the stannous chloride method—requires longer path lengths for low phosphorus concentrations and the ascorbic acid method. The ascorbic acid method is primarily suited for low range phosphorus determination, particularly in the range of 0.01 to 6 mg P/L. Phosphorus quantification occurs in two steps: (1) conversion of the various phosphorus forms to dissolved orthophosphate, and (2) colorimetric quantification using UV/Vis spectrometry.

The conversion or digestion step is dependent on the fraction of phosphorous of interest; total reactive phosphorous (tRP) does not require preliminary hydrolysis or oxidative digestion step, acid hydrolysable phosphorus (AHP) converts the dissolved and particulate condensed phosphates to orthophosphate using acid, water-boiling temperature and time, and lastly total phosphorus (TP) is digested using the persulfate oxidation digestion with water-boiling temperatures and time. These divisions can be further subdivided into total (includes dissolved and particulate) and soluble after 0.45 µm pore filtration (only dissolved). These divisions are summarized in Figure 1.6. Based on these fractions, a variety of other phosphorus species can be calculated, such as non-reactive phosphorus (NRP, difference between TP and RP) and organic phosphorus (OP, TP-AHP-RP or TP-(measured AHP=AHP+RP)) (Worsfold *et al*, 2005).

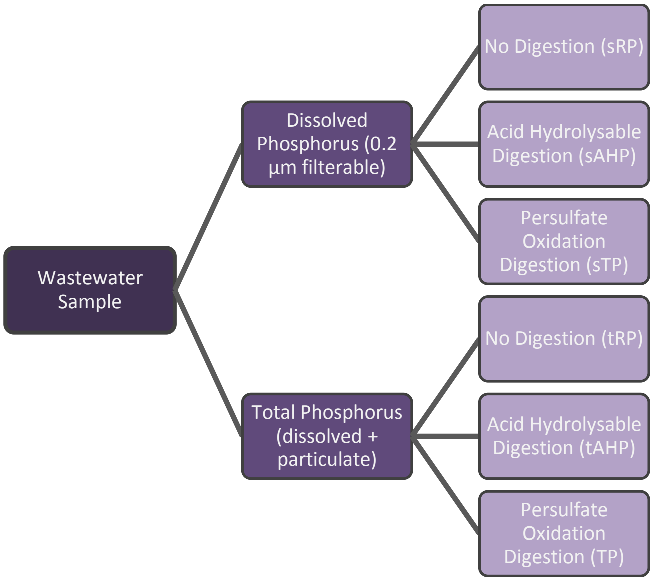


Figure 1.5: Digestion technique utilized by phosphorus fraction determination

Colorimetric determination using the ascorbic acid method occurs under the following conditions: potassium antimonyl tartrate and ammonium moylbdate are mixed in a heteropoly acid (i.e H_2SO_4) reacts with the orthophosphate present in the sample. This reaction produces phosphomolybdic acid that is then reduced by the ascorbic acid present in the mixed reagent in order to form the molybdenum blue coloured complex (Standard Methods (4500-PE.)), see reaction 32-33 below. This complex (Figure 1.7) is then quantified by UV/Vis absorbance spectrometry by measuring absorbance between 650 and 880 nm (Gilmore *et al*, 2008), with the absorbance maxima occurring at the latter end of the range.

$$\text{Ascorbic Acid} + H_2O \rightarrow \text{Dehydroascorbic Acid} + 2e^- + 2H^+ \tag{32}$$

$$\begin{aligned} &12\,(NH_4)_2Mo(VI)O_4 + H_3PO_4 \rightarrow (NH_4)_3PMo_{12}(VI)O_{40}\ \text{(clear)} + 12\,H_2O + 2e^- \\ &\qquad \rightarrow (NH_4)_3PMo_{12}(IV)O_{40} + 12\,H_2O\ \text{(blue)} \end{aligned} \tag{33}$$

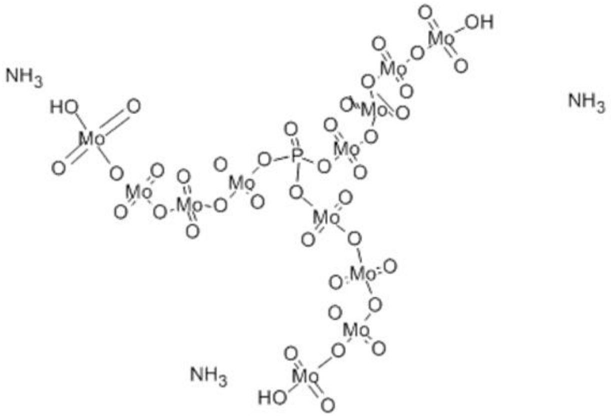


Figure 1.6: Phosphomolybdendum coloured complex, $H_3PMo_{12}O_{40}$. Image from chemicalbook.com.

As observable from the complex above, the concentration of phosphorus is directly proportional to the concentration of the coloured complex at a 1:1 ratio. The mixed reagent uses a ratio and development time developed for an extended path length of 10 cm by Gilmore *et al* (2008).

Worsfold *et al* (2005) describe the necessity of including quality assurance and quality control compounds in the persulfate digestion technique in order to ensure the breakdown of the complex bonds. The group describes the three classes of phosphorus containing compounds, those with C-O-P bonds, those with P-O-P bonds and, to a lesser extent, those with C-P bonds. Worsfold *et al* suggests that QA/QC standards should be performed on compounds that contain each type of bond in order to ensure the completeness of the oxidative digestion and a method of monitoring recovery for complex samples.

Chapter 2: Phase 1—Bench Scale Assessment

Abstract— Excess phosphorus in the environment has the potential to cause eutrophication. Municipal wastewater effluent is a potential source of phosphorus to the environment. Despite strict regulations, the need for continued advancements in phosphorus removal from wastewater is a necessity. Current regulations for sensitive receiving waters are approaching the limit of technology for phosphorus removal and improved methods are required. Existing methods target removal of the orthophosphate form of phosphorus, but to achieve low effluent limits other, less reactive forms, such as condensed phosphate and organic phosphorus, must be targeted for removal as well. Various bench-top oxidative technologies are compared based on effectiveness at converting the complex phosphorus compounds to the more easily removed orthophosphate. The oxidative technologies assessed, independently and in combination, include hydrogen peroxide, sodium hypochlorite, Fenton's Reagent, peracetic acid, TiO_2, ozone, ferrate, and photolysis using ultra-violet (UV) light, as well as hydrolysis with acid. Each technology will be assessed using reverse osmosis brine collected from secondary treated effluent. The most successful performing independent AOP was acidification to pH 2, which reached 61% TP removal, while the best combination treatment utilized 1 ppm H_2O_2 at pH 2, achieving 69% TP removal. However, the highest conversions and subsequent removals of phosphorus compounds occurred after treatment with a multi-combination treatment utilizing photolysis and 3000 ppm peroxide at pH 2 and 90°C for 1 hour, which achieved 85% TP removal. The application of AOP can therefore be employed to convert phosphorus compounds to a removable form allowing for significant reduction in total phosphorus in RO produced brine.

Keywords: Brine, Reverse Osmosis, Advanced Oxidative Processes, Non-reactive phosphorus

2.1 Introduction

In the last few decades much emphasis has been placed on improving effluent quality in all areas of industry including wastewater treatment. A primary focus of these improvements has been nutrient removal, namely phosphorus, in order to prevent potential environmental impacts, such as eutrophication.

The wastewater industry currently uses multi-step practices in order to remove phosphorus in its many environmentally complex forms; however, the majority of the available technologies can only effectively remove orthophosphate, which is the easily removed reactive form. Despite these advances, continued progress must be made as regulations concerning effluent nutrient contents are reaching the limits of the current technologies (Siemans AG, 2001; Gu *et al.,* 2007).

In order to continue the advancements in nutrient removal technologies the remaining, more complex fractions of dissolved phosphorus, such as condensed and organic phosphates, must be targeted for removal as well. A potential method of removal of these phosphorus forms involves conversion of the non-reactive (NRP), and thus converts non-removable phosphorus fractions into a more reactive form of phosphorus (RP), orthophosphate, which can then directly be precipitated by conventional chemical addition.

The proposed improvements to wastewater treatment would use microfiltration as a part of tertiary treatment, followed by a new quaternary step, which would include concentration of the wastewater using reverse osmosis in order to produce an ultra-pure permeate and a highly concentrated brine that could be then treated with advanced oxidative technologies (AOP) in order to oxidize the NRP forms to the more easily removed RP form. AOPs have been used conventionally as methods of clarification and disinfection within the wastewater industry, but have emerged as potential treatments for removing various pollutants, such as pharmaceuticals (Zhou *et al.,* 2011; Zhao *et al*, 2012).

The most promising oxidants are those that generate hydroxyl radicals (•OH), which non-selectively and readily oxidize many of the organic constituents that are present in the RO concentrate, and can convert NRP to RP (Zhou *et al.*, 2011). This occurs according to the following general mechanism:

Proposed generalized mechanism for oxidative degradation of organic pollutants using the hydroxyl radicals produced during AOP treatment:

$$\text{AOP} \rightarrow {\cdot}\text{OH} \xrightarrow{\text{+ organic pollutants}} CO_2 + H_2O + \text{inorganic ions} \quad (1)$$

*can also be applied to the degradation of inorganic compounds

(Caretti and Lubello, 2003)

$$\text{RH} + {\cdot}\text{OH} \rightarrow H_2O + \text{R}{\cdot} \rightarrow \text{further oxidation} \quad (2)$$

(Venkatadri and Peters, 1993)

Of the current AOPs that have been studied for removal of organic pollutants, photocatalytic oxidation (PCO) (UV-TiO_2), ozone oxidation (ozonation, O_3), peroxide oxidation (H_2O_2), Fenton's Reagent, photolysis (UV light), peracetic acid oxidation (PAA), as well as those that do not generate free radicals, including ferrate oxidation (FeO_4^{2-}), hypochlorite oxidation and acid catalyzed hydrolysis will be evaluated independently and in bi-combinations during the initial phase of screening. The effects of other parameters, including pH and heat will also be evaluated for the potential to optimize treatment at varying dose and contact times. Treatment effectiveness will be evaluated by the increase in RP and subsequent decrease in TP after chemical addition using bench-top produce brine from secondary effluent of a WPCP in Mount Albert.

The objective of this project is to select a few AOPs for further evaluation and optimization during pilot-scale assessment using demonstration facility produced brine.

2.2 Methodology

2.2.1 Sample Collection, Preparation and Storage

For the Phase I: Bench-scale testing, wastewater samples were collected from the Mount Albert WPCP as secondary effluent on July 26, 2011, August 23, 2011, October 13, 2011, January 4 and 5, 2012 (pooled), March 5, 2012. Mount Albert resides within the Lake Simcoe watershed and thus would have wastewater of similar composition to that of the proposed demonstration facility and potential full scale facility—providing a representative sample, which would allow for the most direct comparisons between bench-scale and full scale effectiveness. Multiple sampling events were required throughout Phase 1 due the potential for brine characteristics to change in the samples, which were only stable for approximately 1 month. Stability was determined by periodic speciation reassessment after the initial speciation of the brine; once speciation began to deviate a new sample was obtained. Each brine sampling was fully characterized before any AOP treatments were performed and periodically between sampling dates to monitor potential changes.

The grab samples were transported in new 5 gallon plastic buckets to the CRA facility in Waterloo for processing. The samples were then microfiltered using a 0.2 micron hollow fiber polysulfone media filter from Siemens UF Hollow Fiber Media Filter Cartridges. After filtration the samples were treated using bench-top reverse osmosis (ROCHEM Model RO RO DT01-H-SS unit) with 10 micron ROCHEM membranes (pre-assembled stack of 10 discs and 9 membranes) and the RWW was concentrated by 80-85% of the volume. 2 sets of grab samples of the secondary effluent, the MF permeate, the RO permeate and the ROC were also taken, one for the WLU lab and one for comparative analysis with Maxxam. The ROC was then deposited into new 5 gallon buckets and delivered to WLU. Upon arrival samples were stored at 4°C until testing. For testing, a 1 L aliquot was removed after the buckets were thoroughly mixed and were refrigerated at 4°C until treatment or analysis; similarly a 250 mL aliquot was filtered using a 25 mm syringe filter with a 0.2 μm polyethersulfone membrane (VWR International) and refrigerated for analysis.

2.2.2 Advanced Oxidation Treatments

Many advanced oxidative processes were evaluated with respect to dose, contact time and a variety of other parameters; these are presented in Table 2.1.

Table 2.1: Various AOPs evaluated, doses, contact times and other parameters varied for Phase 1: Bench-Scale Testing.

Sample Date	Oxidative Treatment	Dose	Contact Time (hrs)	Other Parameters Varied
July 26, 2011	Ferrate[1]	1.5, 3, 4, 6 ppm	N/A	None
October 13, 2011	Hydrogen Peroxide	0.1, 0.25, 0.5 ppm 1, 10, 50 ppm	0.5, 1, 1.5, 2, 2.5, 3 0.5, 1, 1.5, 2	pH (↓to 5.5), temperature (↑to 35°C), Quencher
October 13, 2011	UV Photolysis[2]	250, 500, 1000, 1500 mJ/cm^2	Until dose achieved	None
October 13, 2011	Ozone[3]	2, 5, 10, 20 ppm	Until dose achieved	None
October 13, 2011	Fenton's Reagent	Ratio Fe:H_2O_2 1:1→ 0.1:1.62 ppm 1:5 → 0.1:8.1 ppm 1:5 → 1:81 ppm	0.5, 1, 1.5, 2, 2.5, 3 0.5, 1, 1.5, 2, 2.5, 3 0.5, 1, 1.5, 2, 2.5, 3	pH (↓to 4.5)
January 4-5. 2012	PAA	0.1, 1 ppm 5, 10, 100 ppm	0.5, 1, 1.5, 2 0.16, 0.33, 0.5, 0.66	Quencher
January 4-5. 2012	Acid (H_2SO_4)	pH 1 pH 2 pH 3	1.5 0.5, 1, 1.5, 2, 2.5, 3 1.5	None
January 4-5. 2012	NaOCl	1, 3, 5, 10 ppm	0.5, 1, 1.5, 2	Quencher
January 4-5. 2012 March 5, 2012	Nano-TiO_2 Catalyzed UV Photolysis[4]	5.1, 10.2 kWh/m^3 5.1, 10.2, 20.4 kWh/m^3	0.108, 0.217 0.108, 0.217, 0.433	Adsorption prior to UV exposure, mixing, additive (ADX)
	Combination Treatments			
January 4-5. 2012	UV + H_2O_2[3]	1000 mJ/cm^2 + 0.05, 0.5, 5 ppm	Until dose achieved + 1.5	None
January 4-5. 2012	UV + Ozone[3]	1000 mJ/cm^2 + 8, 20 ppm	Until dose achieved	None
January 4-5. 2012	UV + Ferrate[3]	1000 mJ/cm^2 + 5 ppm	Until dose achieved + N/A	None
January 4-5. 2012	PAA + Ferrate[3]	0.05, 0.5, 1 ppm + 5 ppm	1.5 + N/A	None
January 4-5. 2012	H_2O_2 + Ferrate[3]	0.5, 1 ppm + 5 ppm	1.5 + N/A	None
January 4-5. 2012	Ozone + Ferrate[3]	5, 8, 20 ppm + 5 ppm	Until dose achieved + N/A	None
January 4-5. 2012	Ozone + PAA[3]	20 ppm + 0.05, 0.5, 1 ppm	Until dose achieved + 1.5	None
January 4-5. 2012	Ozone + H_2O_2[3]	20 ppm + 0.05, 0.5, 1 ppm	Until dose achieved + 1.5	None
January 4-5. 2012	Ozone + UV[3]	8, 20 ppm + 1000mJ/cm^2	Until dose achieved	None
January 4-5. 2012 March 5, 2012	Acid + Peroxide	pH 2 + 1 ppm pH 2 + 3000 ppm pH 3 + 3000 ppm pH 2 + 0.05, 0.5, 3000 ppm	0.5, 1, 1.5, 2 1 1 1.5	UV photolysis, heat 87°C and 82°C

Notes: [1] Treatment performed by Ferrate Treatment Technologies; analysis performed by Holly Gray
[2] Treatment performed by Trojan Technologies, 3020 Gore Rd London, ON; analysis performed by Petrease Patton
[3] Treatment performed by Kansas City; analysis performed by Petrease Patton
[4] Treatment performed by Purifics, 340 Sovereign Rd London, ON; analysis performed by Petrease Patton

All treatments performed solely at Wilfrid Laurier University (WLU) (PAA, hydrogen peroxide, NaOCl, Acid and Fenton's Reagent) were performed at room temperature, circumneutral pH (unless otherwise specified) and without mixing (apart from 30 seconds on medium speed to initially distribute AOP chemical). All doses were calculated to treat 100-200 mL of unfiltered ROC. All time dependency evaluated treatments were sub-sampled at half hour increments; 10 mL were removed in triplicate for tRP analysis, 5 mL were removed in triplicate for TP analysis and 15 mL were removed for sTP analysis following a chemical addition with 10 ppm $FeCl_3$ (Fluka, 98%) or 6 ppm alum ($Al_2(SO_4)_3 \cdot 18H_2O$, EMD, 99%) performed with moderate mixing and filtration through a 0.2 µm polyethersulfone membrane (VWR International) syringe filter. Temperature variation was performed using an oven (VWR); pH was adjusted using 5N H_2SO_4 (Sigm-Aldrich, 95-98%) and 5N NaOH (Sigma-Aldrich, 99%). For the acid and peroxide combination treatment was performed using the Metrohm 750 UV digester. For those performed at the various co-operating facilities, samples were shipped in a cooler at 4°C, treated and returned to WLU in a cooler at 4°C and were analyzed for phosphorus speciation, including tRP, TP and RTP after chemical addition within 24 hours of arrival.

Table 2.2: Chemicals used for these treatments listed in Table 2.1 with manufacture.

Product:	**Manufacturer:**	**Description:**
30-32% wt Hydrogen Peroxide	Sigma-Aldrich	Potassium Stannate stabilizer, 99.99%
32% wt Peracetic Acid	Sigma-Aldrich	6% Hydrogen peroxide, 40-45% acetic acid
10-15% wt Sodium Hypochlorite	Sigma-Aldrich	99%
Iron (II) Chloride	Fluka	≥98%
Sodium Metabisulfite	Sigma-Aldrich	≥99%
Sulfuric Acid	Sigma-Aldrich	95-98%
Sodium Hydroxide	Sigma-Aldrich	99%

2.2.3 Sample Analysis

It was determined early on that due to the very small pores size of the MF, only the soluble fractions of phosphorus remained in the ROC. Therefore, those values reported as totals, denoted with a t in front of the speciation name, are actually the soluble totals after MF filtration and any value reported as soluble, denoted with an s in front of the speciation name, has been filtered through a 0.2 micron filter.

Digestion for TP, sTP and AHP occurred in a HACH DBR 200 digester. Ammonium peroxydisulfate (Alfa Aesar, 98%) was added to 5 mL of sample (treated or untreated) for TP and sTP digestion, along with acid according to stand procedure. Following digestion TP, sTP and AHP samples were cooled to room temperature and neutralized using phenolphthalein indicator and 5N NaOH (Sigma-Aldrich, 99%). All samples were then diluted to 10 mL using a volumetric flask and Milli-Q water. Reactive phosphorus, using 10 mL samples in triplicate, did not undergo digestion but were brought to room temperature before addition of the mixed reagent.

All colorimetric analysis was performed following standard methods (4500-PE.) using freshly made (daily) 0.05 mg P/L and 0.1 mg P/L from a 1000 mg P/L stock solution of KH_2PO_4 (BDH, ≥99%); blanks and standards were measured in duplicate, while samples were measured in triplicate. The signal intensity was measured using a 10 cm quartz cylindrical cell (Starna Cell) at 835 nm, with an integration time of 45-60 and 60 scans to average and a fiber optic spectrometer (Ocean Optics) and the SpectraSuite program by Ocean Optics. The light-source was allowed to warm up for 30 minutes before measuring began.

The mixed reagent was prepared fresh and added to samples in 2-3 minutes intervals and incubated for 30 minutes before being measured. The mixed reagent contains 50% sulfuric acid (Sigma-Aldrich, 95-98%), 15% ammonium molybdate tetrahydrate (BDH, 81-83%), 5% antimonyl tartrate trihydrate (Sigma-Aldrich, ≥99%), and 30% ascorbic acid (Alfa Aesar, 98+%).

Samples were measured, starting with the blanks and standards by pipetting a small amount into the cell with a Pasteur pipette to rinse the cell, and then the cell was filled with the sample; this was repeated between each blank, standard and sample. The sample was then placed into the cell holder and the intensity monitored until the signal intensity was stable; four measures were then recorded over approximately 20 seconds. These were imported by hand into Excel, converted to absorbance by the following equation:

Absorbance= log(average blank intensity/ average sample intensity)

The blanks and standards were used to produce a standard curve and Beer's Law was used to calculate the concentration of orthophosphate in the sample in µg P/L.

2.3 Results and Discussion:

The major sampling events' speciation data is presented in Figure 2.1 with standard deviations; these are the relevant sampling events for Phase 1 because these samples were also treated with the various advanced oxidation processes. The other sampling event, August 23, 2011 was only produced in small quantities in order to monitor phosphorus fluctuations between major sampling events.

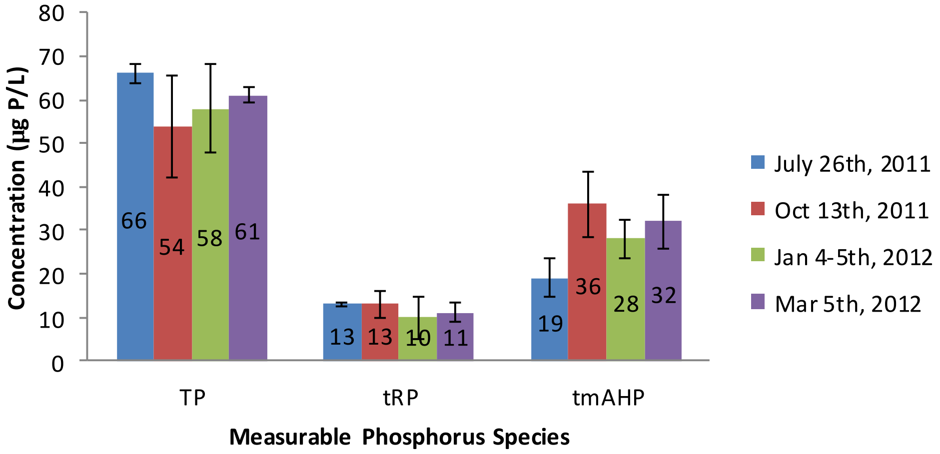


Figure 2.1: Speciation data across the four major sampling events with standard deviations based on triplicate sample analysis. Phosphorus fraction concentration reported in µg P/L. All are the measurable totals for the respective fraction with TP representing total phosphorus, tRP representing total reactive phosphorus, and tmAHP representing total measurable acid hydrolysable phosphorus (tAHP+tRP).

As visible in Figure 2.1 the TP and tRP do fluctuate some throughout the year, whereas the majority of the fluctuations occur within the acid hydrolysable fractions. The total phosphorus ranges between 54 and 66 µg P/L, with tRP ranging from 10 to 13 µg P/L; however when considering standard deviation the samples do not appear to be that different due to large deviations. The most distinct variation occurs in the total measurable acid hydrolysable fractions with a range of 19 to 36 µg P/L and even when considering the standard deviations large variation still occurs. Due to the irreproducibility of the mAHP measures and the rationale described in Appendix B, this fraction will not be evaluated or discussed during the assessment of the AOP techniques.

The fluctuations in speciation data for soluble and total phosphorus were graphed to observe any seasonal variations in phosphorus concentrations over the various fractions and included the August 23, 2011 sampling event for completeness (Figure 2.2 and 2.3).

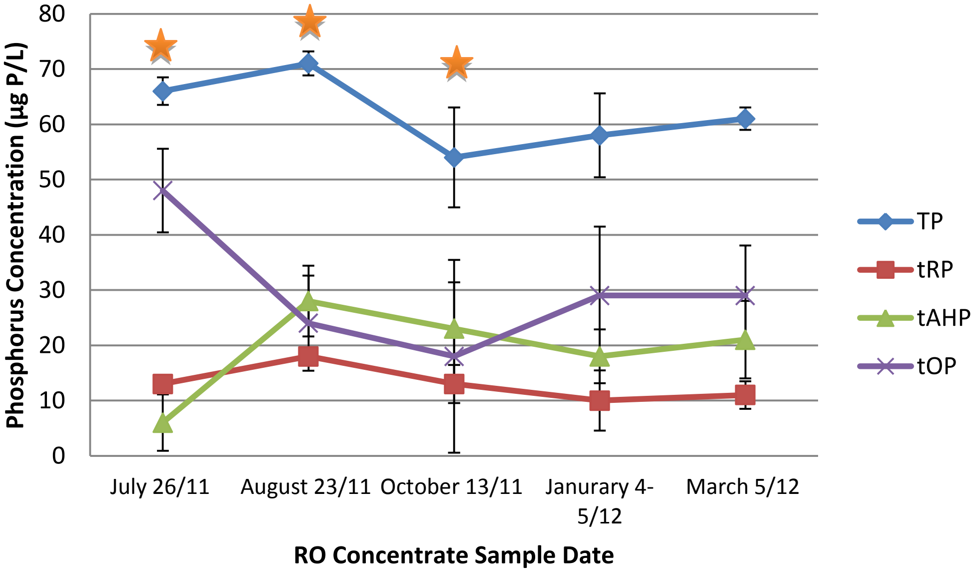


Figure 2.2: Seasonal variation of total phosphorus for four fractions TP, tRP, tAHP and tOP across the five sampling events associated with Phase 1. Phosphorus concentrations reported in µg P/L. Stars denote significant difference within 95% confidence interval with the previous data point.

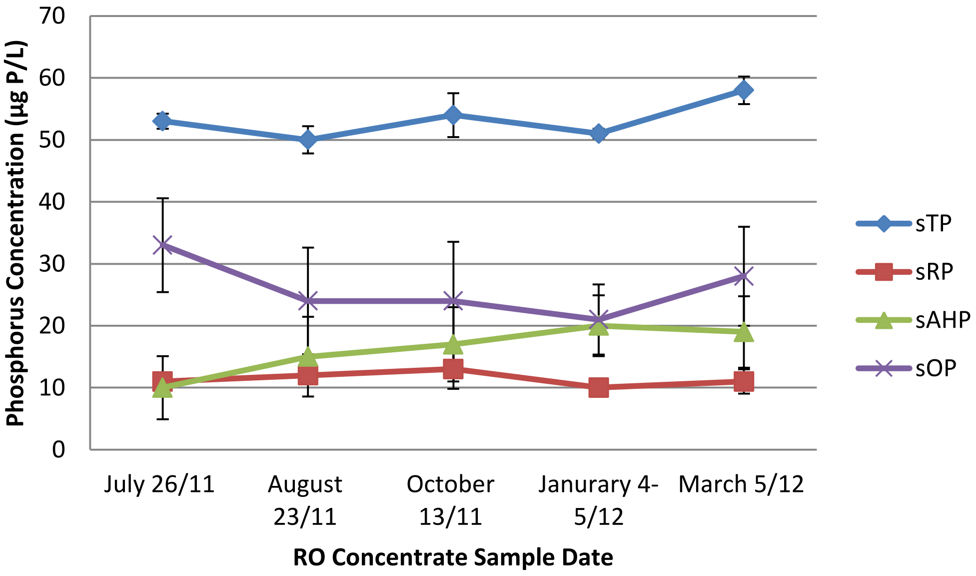


Figure 2.3: Seasonal variation of soluble phosphorus for four fractions sTP, sRP, sAHP and sOP across the five sampling events associated with Phase 1. Phosphorus concentrations reported in µg P/L.

As is observable from the trends above, the fluctuations within the total or soluble fractions of phosphorus occur within standard deviations and therefore ensure water and brine quality similarities, which allow comparability between AOP tests and conclusions for treatment effectiveness.

The main goal of Phase 1: Bench Scale testing was to evaluate each oxidative technology, independently or in combination, for its effectiveness at converting NRP to RP; however the RP that was generated as a result of treatment must be removable by metal salt addition. Therefore in order for the treatment to be considered effective the tRP must be removed to decrease TP to below the goal limit of 30 µg P/L. This goal could provide a suitable effluent concentration, after reblending with the permeate, to meet the load allocations required by the LSPRS. The 30 µg P/L is the concentration of phosphorus that can be present in streams and rivers that does not negatively impact aquatic life as stated by the Provincial Water Quality Objectives. The concentration of phosphorus after metal salt addition is referred to as Residual Total Phosphorus after Chemical Addition (RTP_{CA}) or as Residual Total Phosphorus Post AOP Treatment (RTP_{PT}). The relation between these terms is presented in equation 5 and holds true within standard deviation. Therefore any NRP converted to RP can be removed by metal salt addition.

$$TP = tRP \text{ (from oxidative treatment)} + RTP_{PT} \text{ (after treatment and metal salt addition*)} \tag{5}$$

*10 ppm $FeCl_3$ or 6 ppm alum

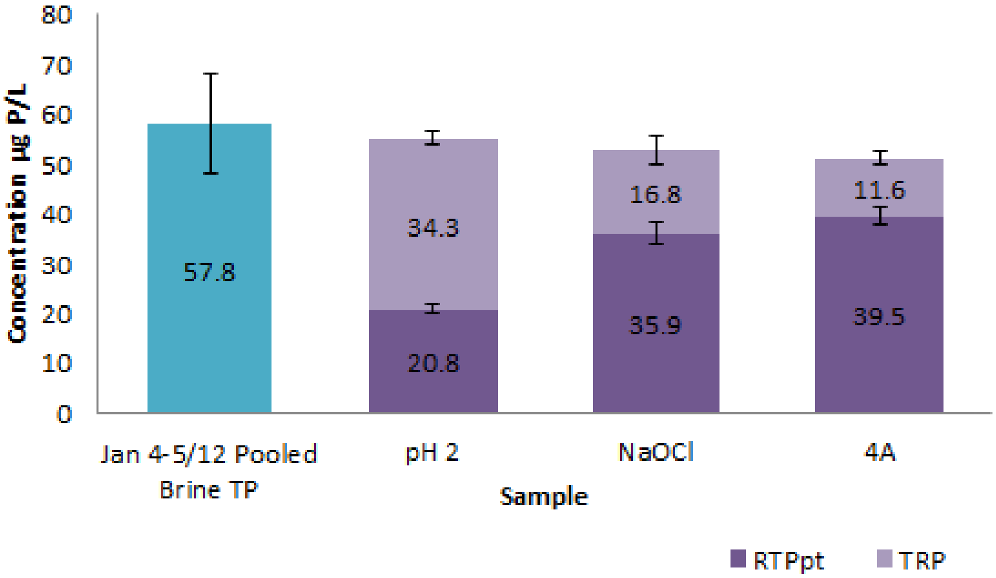


Figure 2.4: Mass balance **c**omparison data showing the conversion of NRP to RP and subsequent removal with metal salt addition for acid, NaOCl and TiO_2 treatment. 4A denotes sample treated by Purifics Inc, the sample was acidified to strip CO_2 from the sample and then reneutralized before treatment by photocatalysis. This sample was treated for 26 minutes, which accounts for a dose of 20.4 kWh/m^3. Treatments were performed on the January 4-5/12 pooled sample and are therefore compared to the TP for that sampling date. Results are reported in µg P/L and RTP_{PT} is the residual phosphorus concentration after 6 ppm alum addition and filtration with a 0.2 micron filter.

As Figure 2.4 displays, phosphorus is conserved through treatment and subsequent removal with metal salt addition such that the sum of the tRP produced as a result of the treatment and the RTP_{CA} remaining after metal salt addition is equal to the TP for that sample within standard deviation. Figure 2.4 uses two successful AO treatments performed at WLU and one performed at an outsourced company to describe and confirm this relationship. Therefore results described as increasing tRP or decreasing TP are comparable because of this relationship. This is especially relevant because some of the evaluated AOP treatments simultaneously oxidized and coagulate phosphorus, such as ferrate and Fenton’s Reagent. In these instances tRP was not measurable and instead only TP and RTP_{PT} could be quantified. Therefore when comparing these treatments it is possible to calculate the increase in tRP from TP and RTP_{PT} data (or the RTP_{PT} from tRP and TP data), which allows direct percent conversion or percent removal comparisons.

2.3.1 Best Performing AOP Treatments

2.3.1.1 Hydrogen Peroxide

AOP assessment began with hydrogen peroxide, which was found to interfer with the mixed reagent used for spectrometric analysis. For this reason a quencher had to be identified that could be added to the sample to quench the remaining peroxide and would not contribute to the absorbance of the molybdate complex. Some quenchers attempted were tannic acid, which was effective, but caused the sample to colour and was only effective at low doses, and HS^-, which was highly ineffective and produced an intense red colour, which would interfere with measurement at 835 nm. Ascorbic acid was then tested because of its pre-existing use as part of the mixed reagent as a reducer; from this it was thought that no interference would occur and the peroxide residual would be quenched. This was confirmed by performing an external calibration using blanks and standards (0.05 and 0.1 mg P/L) and adding the same amount of ascorbic acid used to quench the peroxide. This calibration was performed simultaneously with a normal calibration in order to compare any changes in absorbance; none were found. AOP testing to evaluate time and dose dependence for low and high peroxide doses were continued using ascorbic acid as a quencher. Three low doses of peroxide, 100, 250 and 500 ppb, and three high doses of peroxide, 1, 10 and 50 ppm, were evaluated for time dependence over 3 hours and 2 hours, respectively, at room temperature, neutral pH and without mixing; results are displayed in Figure 2.5 a and b.

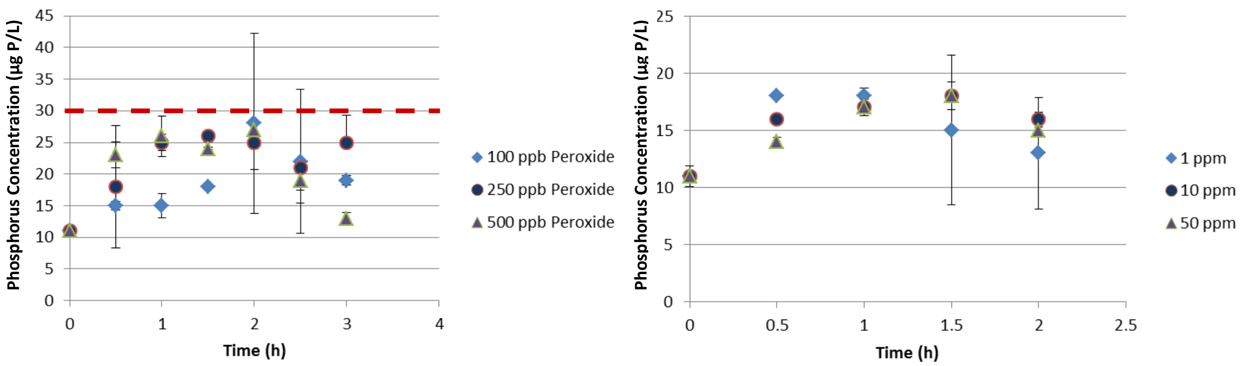


Figure 2.5 a and b: Low and peroxide dose time dependence performed on the unfiltered October 13, 2011 brine sample (TP concentration was 54 µg P/L. Subsamples were removed every 0.5 hours and quenched with a corresponding molar dose of ascorbic acid, tRP was measured. Results are presented in µg P/L. The red dotted line indicates the goal tRP concentration of 30 µg P/L, tRP above this line indicates success. Error bars are standard deviation on multiple samples.

The October unfiltered brine sample was used for this AOP and it has a tRP concentration of 13 µg P/L, which is marked at time zero. In order to reach the RTP_{PT} goal of 30 ppb, tRP must be increased to 30 µg P/L (calculated using the average TP for all samples of 62 ± 6.4 µg P/L and equation 5). The 100ppb dose saw the highest conversion in multiple replicates after 2 hours reaching a tRP of 28 ± 14 µg P/L, while the high peroxide doses did not even reach the conversion effectiveness of the low doses—note the scale in Figure 2.5 a and b—and resulted in very little conversion of NRP to RP. In all concentration trials, reversion from RP to NRP was observed and tRP decreased after 1.5-2 hours. This can be explained by the forming of non-reactive peroxy-phosphate compounds, which are unavailable for complex formation with the molybdenum blue mixed reagent. The higher dosages of peroxide were found to have conversion that was almost non-existent. It is thought that the high doses result in a high concentration of hydroxide radicals, which scavenge one another and result in 'self-quenching' of the peroxide or termination of the radicals (reaction 34), which makes the radicals unavailable to react with the NRP compounds.

$$2{\cdot}OH \rightarrow H_2O_2 \tag{34}$$

This phenomenon is discussed in by Petrucci *et al* (2003) when evaluating the conversion effectiveness and optimal parameters of Fenton's Reagent. The group observed bell-shaped curves when evaluating percent conversion against the increasing concentration of H_2O_2 for several concentrations of Fe(II). The group observed conversion increase until a maximum, and then a subsequent decrease as the peroxide dose was increased past this maximum.

The primary issue with the hydrogen peroxide results presented in Figure 2.5 a and b were the very large standard deviations, which caused the treatment effectiveness to be questioned. It was determined that with a more effective quencher these deviations might be reduced and therefore other quenchers were then analyzed. Dithionite, which has a greater electron transfer and is a more efficient reducer, was evaluated. External calibrations comparing the effectiveness of the quencher and potential interference were performed in the same manner as with ascorbic acid. Quenching was observed and no interference was seen. Metabilsulfite was also tested in the same manner; the results showed a decrease in standard deviations and therefore metabisulfite (provides $4e^-$) was selected as the ultimate quencher. The redox chemistry of the quenching of hydrogen peroxide is displayed below.

$$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O \tag{35}$$

Metabilsulfite ($S_2O_5^{2-}$) is a hybride anion of dithionite ($S_2O_4^{2-}$) and dithionate ($S_2O_6^{2-}$)

$$\text{Dithionite: } S_2O_4^{2-} + 4\,H_2O \rightarrow 2\,SO_4^{2-} + 8\,H^+ + 6\,e^- \tag{36}$$

$$\text{Dithionate: } S_2O_6^{2-} + 2\,H_2O \rightarrow 2\,SO_4^{2-} + 4\,H^+ + 2\,e^- \tag{37}$$

Average number of electrons transferred = (6+2)/2 = 4

2.3.1.2 pH Adjustment

The adjustment of pH was also evaluated because of the use of acid in the TP digestion process. Sulphuric acid was used to reduce the pH of the brine and the contact time was set for 1.5 hours, this is the time used for the acid hydrolozable digestion and it was thought to be a sufficient bench-mark for evaluation of pH adjustment. The pH of the brine was adjusted to pH 1, 2 and 3 for 1.5 hours at room temperature and without mixing. Neutralization was performed after 1.5 hours using sodium hydroxide and phenolphthalein indicator; an external calibration was performed with the addition of H_2SO_4 and subsequent neutralization following the same procedure to ensure no interference was caused by the extra acid, base and indicator—all of which are used in the TP digestion technique.

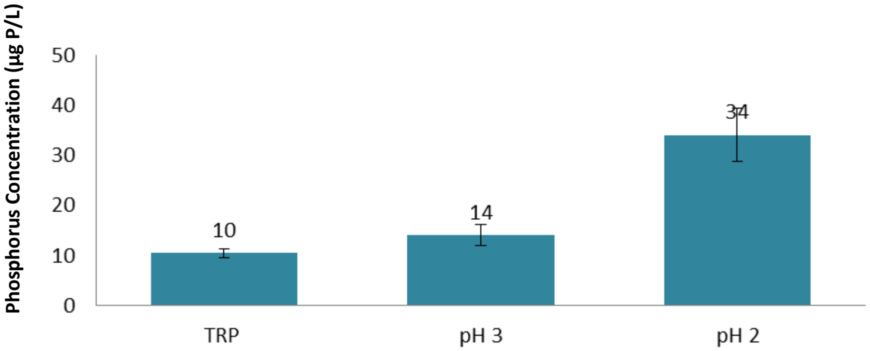


Figure 2.6: pH conversion effectiveness performed on January 4-5, 2012 pooled brine sample. pH was adjusted using H2SO4 and neutralization was performed with NaOH. Results are presented in µg P/L. tRP is the concentration of RP in the untreated brine sample. Error bars are standard deviation on multiple samples.

The results of sample acidification are presented in Figure 2.6; however, pH 1 is not included due to the inconsistency and the irreproducibility of the results. The January 4-5, 2012 pooled brine sample had an untreated and unfiltered tRP concentration of 10 µg P/L, which is represented as the first column. Acidification to pH 2 saw the highest conversion of NRP to RP with a maximum tRP of 34±5 µg P/L. Although only two pH values produced stable results, a pH dependency is observed. These results led to evaluation of time dependence of this treatment.

The acidification following the same procedure was performed on the March brine sampling event to ensure that the treatment was effective and not a result of the January brine’s matrix. Time dependency was evaluated over 2.5 hours; the results are displayed in Figure 2.7.

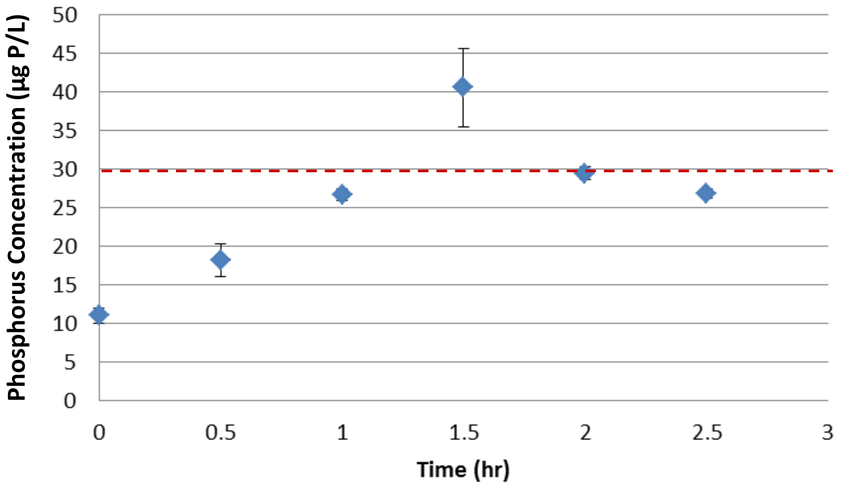


Figure 2.7: pH time dependence was performed on the unfiltered March 5, 2012 brine sample. Subsamples were removed every 0.5 hours and neutralized with NaOH. Results are presented in µg P/L. The red dotted line indicates the goal tRP concentration of 30 µg P/L.

The March unfiltered brine sample was used for this AOP and it has a tRP concentration of 11 µg P/L, which is marked at time zero. In order to reach the RTP_{PT} goal of 30 ppb, tRP must be increased to 30 µg P/L (calculated using the average TP for all samples of 62 ± 6.4 µg P/L and equation 5). A contact time of 1.5 hours was confirmed as the optimal contact time for the conversion of NRP to RP. The maximum conversion was consistent with the results from the January brine sample within standard deviation and achieved a tRP of 41±5 µg P/L, which is greater than the goal of 30 µg P/L. The decrease after 1.5 hours is unexpected, but could be a result of hydrolysed phosphate groups interacting with other functional groups present on DOC becoming non-reactive once again.

2.3.1.3 Hydrogen Peroxide, UV Photolysis and pH Adjustment

It is commonly known that Fenton’s Reagent, which uses hydrogen peroxide as its oxidizer, is more efficient at an acidic pH Petrucci *et al* (2003). This concept was extended to the use of peroxide at a lower pH to determine if this combination could improve the effectiveness of both AOPs. Several low and high peroxide doses, 0.05, 0.5, 1 and 3000 ppm, were evaluated at pH 2, room temperature and without mixing after a 1.5 hour contact time; the results are in Figure 2.8. It should be noted that the 3000 ppm dose was included because that is the dose recommended by manufacturer of the UV digester , which was also evaluated during combination AOP assessment.

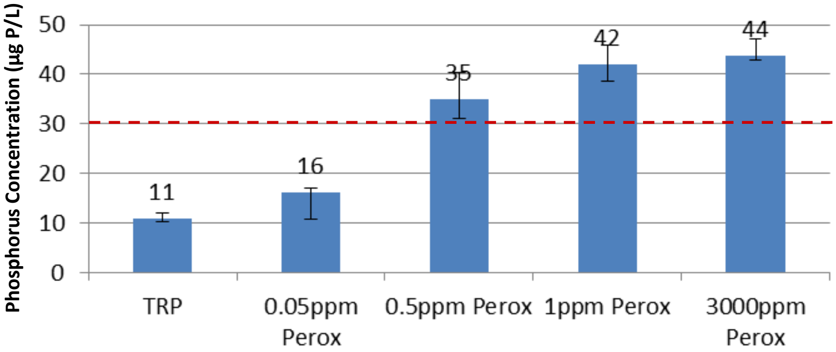


Figure 2.8: Peroxide and pH combined effects on NRP conversion to RP was evaluated on the March 5, 2012 unfiltered brine. After 1.5 hours the sample was neutralized with NaOH and quenched with sodium metabisulfite. TRP is the concentration of RP in the untreated brine sample. Results are presented in µg P/L. The red dotted line indicates the goal tRP concentration of 30 µg P/L. Error bars are standard deviation on multiple samples.

The March unfiltered brine sample, with an initial tRP concentration of 11 µg P/L, which is marked by the first bar in Figure 2.8, was used for the combination of peroxide and acidification. **In order to reach the RTP$_{PT}$ goal of 30 ppb, tRP must be increased to 30 µg P/L (calculated using the average TP for all samples of 62 ± 6.4 µg P/L and equation 5).** A peroxide dose dependence is observed for AOP treatment at pH 2 with a 1.5 hour contact time, such that as peroxide dose increases, so does conversion of NRP to RP. The negligible difference within standard deviation between the 0.5, 1 and 3000 ppm peroxide dose suggests that the conversion of NRP to RP does plateau with a tRP of 35±5, 42±3 and 44±3 µg P/L for the peroxide doses, respectively. The combination of the peroxide at pH 2 provides results that are better than either of the AOPs alone and surpasses the goal of 30 µg P/L for the conversion to RP.

The evaluation of the combination treatments of UV and peroxide, with and without pre-acidification to pH 2 and 3 were performed in order to maximize conversion. The UV digestion using the Metrohm 750 UV digester procedure uses a peroxide dose of 3000 ppm and the application of heat between 80 and 90°C for 1 hour. After treatment the samples were quenched with metabilsulite and neutralized (if at pH 2) with NaOH.

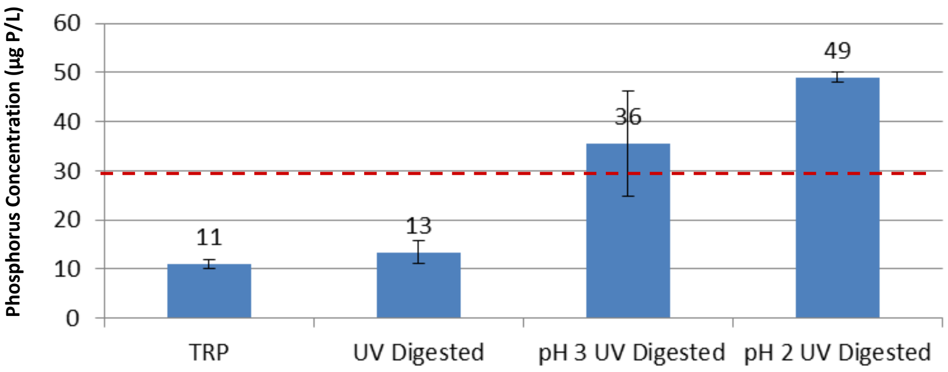


Figure 2.9: UV and peroxide, with and without pH adjustment combined effects on NRP conversion to RP was evaluated on the January 4-5, 2012 pooled unfiltered brine. After 1.5 hours the sample was neutralized with NaOH and quenched with sodium metabisulfite. TRP is the concentration of RP in the untreated brine sample. Results are presented in µg P/L. The red dotted line indicates the goal tRP concentration of 30 µg P/L. Error bars are standard deviation on multiple samples.

The results presented in Figure 2.9 show the combined treatments on the January 4-5/12 pooled brine sample, which has an untreated and unfiltered tRP concentration of 11 µg P/L. In order to reach the RTP_{PT} goal of 30 ppb, tRP must be increased to 30 µg P/L (calculated using the average TP for all samples of 62 ± 6.4 µg P/L and equation 5). The conversion of NRP to RP observed in the UV digested sample is low and this is likely due to the UV and heat oxidizing the peroxide and making it unavailable to react with the phosphorus species. There is a slight pH dependence observed between pH 2 and 3, however pH 2 yielded the most consistent results during multiple trials reaching a maximum conversion of NRP to RP of 49±1 µg P/L. This is the best conversion of all the individual and combined treatments evaluated during Phase 1 and accounts for a conversion of 85% (71- 100% within standard deviation) of the TP to RP; however due to the cost of heating the ROC to this temperature and exposing it to UV for the duration required, this is not likely a feasible option for full-scale wastewater treatment facilities. However, the effects of temperature and UV should be evaluated more to determine the effects of each and to assess if moderate temperatures would be just as effective.

2.3.1.4 Sodium Hypochlorite (Bleach)

The assessments of AOPs individually ended with sodium hypochlorite, which is commonly used in wastewater treatment as an oxidizer/disinfectant. Normal dosing and contact time for hypochlorite is 5 ppm for 0.5 hours (Spellman, 2009); however, the dose and time dependence needed to be evaluated on the ROC to determine the effectiveness for quaternary treatment. The major factoring affecting the effectiveness of hypochlorite is the chlorine demand of the system, which needs to be overcome in order to have residual hypochlorite available to react with the NRP species. The chlorine demand is directly linked to the presence of ammonia in the system, such that the addition of chlorine from the hypochlorite reacts with the ammonia to form mono-, bi- and trichloramines (Spellman, 2009). Once all the ammonia has been reacted the remaining hypochlorite is available to oxidize the phosphorus species. Several doses, 1, 3, 5 and 10 ppm, were evaluated for time dependence over 2.5 hours at room temperature, neutral pH and without mixing. Hypochlorite oxidation is very comparable to that observed in hydrogen peroxide and therefore a quencher was assumed to be required for analysis to prevent interference with the mixed reagent. Sodium metabisulfite, which was an established quencher used with hydrogen peroxide, was again employed to stop the reaction. The redox chemistry for this reaction is depicted in reaction 29, 36 and 37; results for NaOCl time and dose dependence are displayed in Figure 2.10.

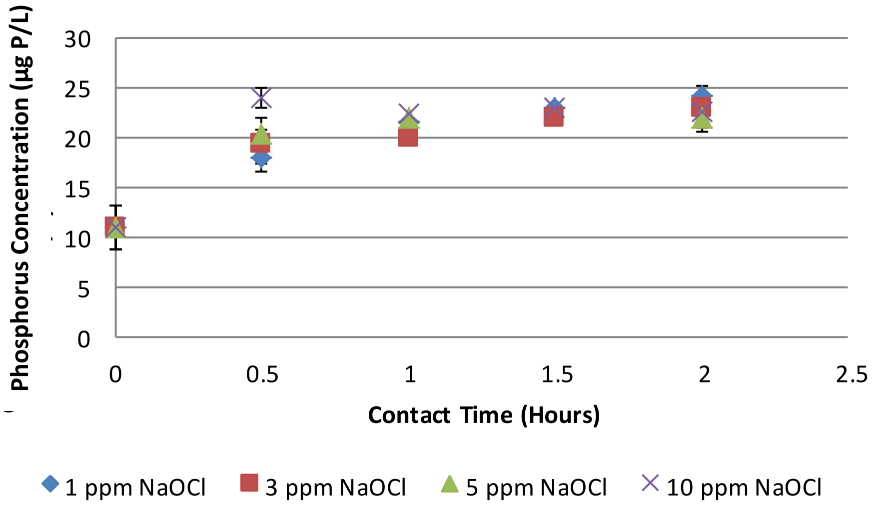


Figure 2.10: Time and dose dependence for NaOCl performed on the January 4-5, 2012 pooled unfiltered brine. Subsamples were removed every 0.5 hours and quenched with a corresponding molar dose of sodium metabisulfite. Results are presented in µg P/L. Error bars are standard deviation on multiple samples.

The January 4-5/12 pooled unfiltered brine sample was used for this AOP and it has a tRP concentration of 11 µg P/L, which is marked at time zero. Time and dose dependencies were observed with hypochlorite treatment, with the most significant increases in tRP occurring within the first 0.5

hours—as predicted by the literature description of hypochlorite usage—followed by a minimal further increase in tRP and a plateauing effect. The 10 ppm dose after 0.5 hours was the most effective at oxidizing NRP to RP and reached a maximum of 24±1 µg P/L with a minimum contact time. This AOP is one of the most cost-effective oxidative treatments evaluated; however, on its own, it does not reach the goal conversion of 30 µg P/L and therefore further evaluation of the chlorine demand of the ROC and potential improvements with pH adjustments need to be performed.

2.3.2 Summary of Evaluated Techniques

The above techniques were the best performing AOPs evaluated for time/dose dependencies individually and in combination. However, all other individual and combination AOPs were evaluated. A summary of the techniques under the optimal parameters are described in Figures 2.11 and 2.12.

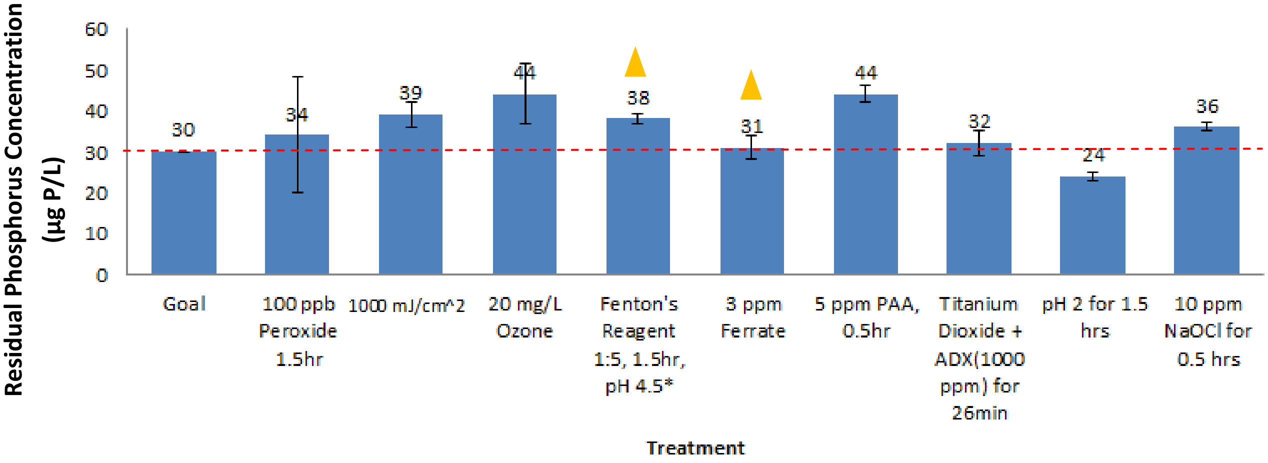


Figure 2.11: Summary comparing the various AOPs evaluated during Phase 1 individually. The values reported are the minimum RTP_{PT} achieved for the AOPs under the optimal conditions evaluated (calculated or measured). RTP_{PT} is the residual total phosphorus concentration post treatment and a subsequent 6 ppm alum addition. Values are reported as RTP_{PT} due to the differences in brine speciation and the use of Fenton's Reagent and ferrate, which are oxidizers/coagulants. Measured RTP_{PT} values are marked with a triangle; all others were calculated using the difference between the average TP of 62 µg P/L, which is the average of all 5 sampling events and the maximum tRP measured (according to equation 5). Removal reported in µg P/L. The goal bar and red line represent the maximum TP allowable for the ROC after treatment; values below this are deemed successful. Error bars are standard deviation on multiple samples.

The individual assessments of the AOPs, presented in Figure 2.11, provided a wide range of effectiveness at converting NRP to RP, with the most successful being treatment with pH adjustment to 2 for 1.5 hours with an sTP of 24±5 reached. Treatment with 10 ppm hypochlorite for 0.5 hours, photocatalyzed titanium dioxide, ferrate and peroxide were all very close at reaching the 30 µg P/L goal with RTP_{PT} of 36±1, 32±3, 31±3 and 34±14 µg P/L respectively reached. In actuality most treatments did reach the goal within standard deviation; however, pursuing the lowest cost alternatives as the first priority, as no other benefit can be defined at this time using the higher cost alternatives, was the direct reason the AOP options selected were hypochlorite and hydrogen peroxide, which are comparatively inexpensive, stable and do not require complicated engineering to incorporate into a potential plant. Fenton's Reagent should be further evaluated at increasingly acidic conditions to achieve the optimal pH range as described in literature, as well the reagent ratios of H_2O_2:Fe(II) should also be varied to determine any increase in effectiveness. Ozone and UV did not convert NRP to RP very effectively and were considered too expensive to undergo further evaluation. PAA presented an effective alternative to peroxide in theory, however, did not do well during bench-scale evaluation. Although not support by an example in literature, it is possible that similar hydroxyphosphate complexes as observed in peroxide treatment or other radical complexes were formed during PAA treatment. This might happen to a greater extent than that observed in peroxide and therefore make the converted NRP irremovable by chemical addition because of complex formation. As well, PAA is primarily used in disinfection of drinking water and therefore has not been thoroughly evaluated for its effect at chemical oxidation (Caretti and Lubello, 2003).

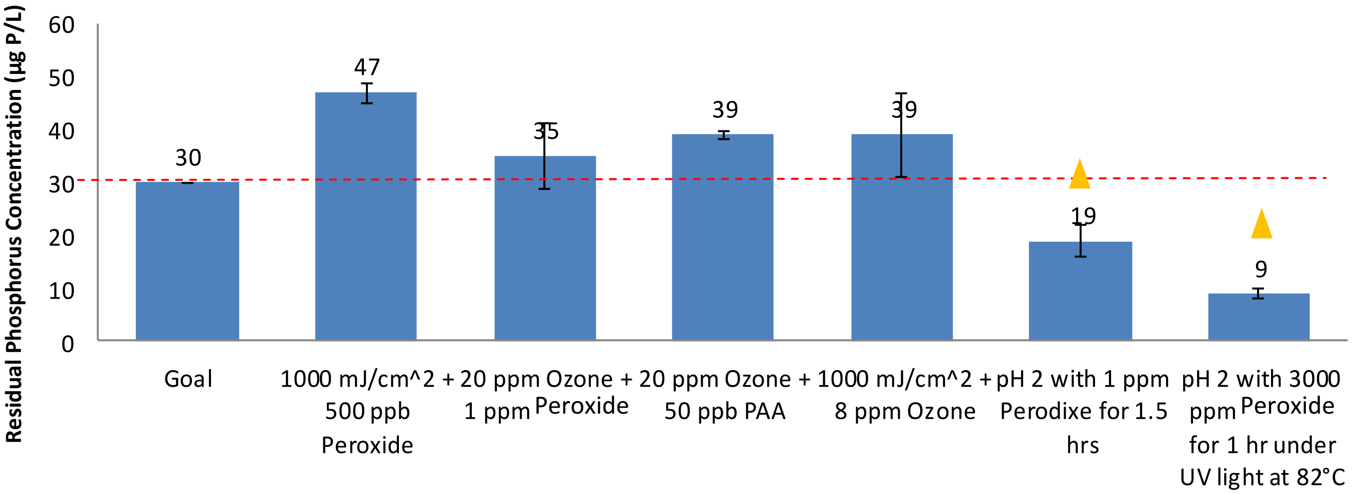


Figure 2.12: Summary comparing the various AOPs evaluated during Phase 1 in combination. The values reported are the minimum RTP_{PT} achieved for the AOPs under the optimal conditions evaluated. Values are reported as RTP_{PT} for easy comparison to individually evaluated treatments. Measured RTP_{PT} values are marked with a triangle; all others were calculated using the difference between the average TP of 62 µg P/L, which is the average of all 5 sampling events and the maximum tRP measured. Removal reported in µg P/L. The goal bar and red line represents the maximum TP allowable for the ROC after treatment; values below this are deemed successful. Error bars are standard deviation on multiple samples.

As presented in Figure 2.12, the most successful combination AOPs evaluated during Phase 1 were the acid and peroxide combinations, however, as previously noted, using the UV digestion with heat is a more expensive option for continuous operation due to the use of heat and light, which would require an expensive installation of the light and heating source. Therefore, referring to table 2.3, the most successful, and cost effective combination treatment in terms of not requiring specialized instruments to treat the brine was acidification to pH 2 combined with 1 ppm peroxide for 1.5 hours. Ozone and peroxide were also relatively effective at meeting the RTP_{PT} requirement of 30 µg P/L, reaching 35±6 µg P/L, which meets the goal within standard deviation. However, ozone generation would also require extra engineering and installation costs in order to run and meet the 30 ppm goal. For these reasons this technology was not further evaluated.

Table 2.3: Summary Table of % NRP Conversion and % TP Removal for all AOP Treatments, Doses and Contact Times

	AOP Treatment	Dose	Contact Time	Other Parameters	% NRP Conversion	% TP Removal
Individual AOP	Ferrate*	1.5 ppm	N/A	N/A	N/A	19-58%
		3 ppm	N/A	N/A	N/A	34-50%
		4 ppm	N/A	N/A	N/A	23-34%
		6 ppm	N/A	N/A	N/A	32-44%
	Hydrogen Peroxide	0.1 ppm	0.5 hr	Quencher: Ascorbic Acid	5-13%	NM
			1 hr	Quencher: Ascorbic Acid	9-19%	NM
			1.5 hr	Quencher: Ascorbic Acid	10-16%	27-37%
			2 hr	Quencher: Ascorbic Acid	8-52%	NM
			2.5 hr	Quencher: Ascorbic Acid	11-42%	NM
			3 hr	Quencher: Ascorbic Acid	18-30%	NM
		0.25 ppm	0.5 hr	Quencher: Ascorbic Acid	0-26%	NM
			1 hr	Quencher: Ascorbic Acid	13-33%	NM
			1.5 hr	Quencher: Ascorbic Acid	7-37%	NM
			2 hr	Quencher: Ascorbic Acid	1-36%	NM
			2.5 hr	Quencher: Ascorbic Acid	16-34%	NM
			3 hr	Quencher: Ascorbic Acid	20-35%	NM
		0.5 ppm	0.5 hr	Quencher: Ascorbic Acid	8-31%	NM
			1 hr	Quencher: Ascorbic Acid	10-36%	NM
			1.5 hr	Quencher: Ascorbic Acid	12-31%	NM
			2 hr	Quencher: Ascorbic Acid	13-38%	NM
			2.5 hr	Quencher: Ascorbic Acid	0-26%	NM
			3 hr	Quencher: Ascorbic Acid	3-16%	NM
		1 ppm	0.5 hr	Quencher: Ascorbic Acid	13-17%	NM
			1 hr	Quencher: Ascorbic Acid	13-17%	NM
			1.5 hr	Quencher: Ascorbic Acid	0-23%	NM
			2 hr	Quencher: Ascorbic Acid	0-17%	NM
		10 ppm	0.5 hr	Quencher: Ascorbic Acid	12%	NM
			1 hr	Quencher: Ascorbic Acid	11-14%	NM
			1.5 hr	Quencher: Ascorbic Acid	16%	NM
			2 hr	Quencher: Ascorbic Acid	12-16%	NM
		50 ppm	0.5 hr	Quencher: Ascorbic Acid	6-10%	NM
			1 hr	Quencher: Ascorbic Acid	14%	NM
			1.5 hr	Quencher: Ascorbic Acid	13-20%	NM
			2 hr	Quencher: Ascorbic Acid	9%	NM
	UV Photolysis	250 mJ/cm^2	Until Dose Achieved	N/A	0-9%	6-9%
		500 mJ/cm^2	Until Dose Achieved	N/A	10-23%	17-20%
		1000 mJ/cm^2	Until Dose Achieved	N/A	18-30%	0-64%
		1500 mJ/cm^2	Until Dose Achieved	N/A	1-27%	0-1%
	Ozone	2 ppm	Until Dose Achieved	N/A	2-7%	0-22%
		5 ppm	Until Dose Achieved	N/A	0%	23-38%
		10 ppm	Until Dose Achieved	N/A	13-17%	26-30%
		20 ppm	Until Dose Achieved	N/A	19%	24-27%
	Fenton’s Reagent*	Ratio Fe:H_2O_2 1:5 → 0.1:8.1 ppm	0.5 hr	N/A	NM	15-30%
			1 hr	N/A	NM	18-30%

		1.5 hr	N/A	NM	0-10%
		2 hr	N/A	NM	0%
		2.5 hr	N/A	NM	0%
	1:5 → 0.1:8.1 ppm	0.5 hr	pH 4.5	NM	22-23%
		1 hr	pH 4.5	NM	22-24%
		1.5 hr	pH 4.5	NM	18-24%
		2 hr	pH 4.5	NM	14-17%
		2.5 hr	pH 4.5	NM	6-8%
	1:5 → 1:81 ppm	0.5 hr	pH 4.5	NM	0%
		1 hr	pH 4.5	NM	0%
		1.5 hr	pH 4.5	NM	0-4%
		2 hr	pH 4.5	NM	9-21%
		2.5 hr	pH 4.5	NM	0%
PAA	0.1 ppm	0.5 hr	Quencher: Ascorbic Acid	0-1%	NM
		1 hr	Quencher: Ascorbic Acid	0%	NM
		1.5 hr	Quencher: Ascorbic Acid	6-21%	NM
		2 hr	Quencher: Ascorbic Acid	0%	NM
	1 ppm	0.5 hr	Quencher: Ascorbic Acid	6%	NM
		1 hr	Quencher: Ascorbic Acid	6%	NM
		1.5 hr	Quencher: Ascorbic Acid	4-19%	NM
		2 hr	Quencher: Ascorbic Acid	4%	NM
	5 ppm	0.08 hr	Quencher: Ascorbic Acid	13%	NM
		0.16 hr	Quencher: Ascorbic Acid	10-13%	NM
		0.33 hr	Quencher: Ascorbic Acid	0-15%	NM
		0.5 hr	Quencher: Ascorbic Acid	11%	NM
		0.66 hr	Quencher: Ascorbic Acid	17%	NM
	10 ppm	0.08 hr	Quencher: Ascorbic Acid	15%	NM
		0.16 hr	Quencher: Ascorbic Acid	12-18%	NM
		0.33 hr	Quencher: Ascorbic Acid	11-23%	NM
		0.5 hr	Quencher: Ascorbic Acid	4-21%	NM
		0.66 hr	Quencher: Ascorbic Acid	0-19%	NM
	100 ppm	0.08 hr	Quencher: Ascorbic Acid	2-5%	NM
		0.16 hr	Quencher: Ascorbic Acid	0-10%	NM
		0.33 hr	Quencher: Ascorbic Acid	0%	NM
		0.5 hr	Quencher: Ascorbic Acid	1-10%	NM
		0.66 hr	Quencher: Ascorbic Acid	6%	NM
Acid (H_2SO_4)	pH 2	0.5 hr	N/A	0-14%	NM
		1 hr	N/A	30-75%	NM
		1.5 hr	N/A	37-59%	64-67%
		2 hr	N/A	34-37%	NM
		2.5 hr	N/A	30-34%	NM
	pH 1	1.5 hr	N/A	28-100%	NM
	pH 2	1.5 hr	N/A	3-10%	NM
NaOCl	1 ppm	0.5 hr	Quencher: Metabisulfite	11-22%	NM
		1 hr	Quencher: Metabisulfite	19-29%	NM
		1.5 hr	Quencher: Metabisulfite	25-29%	NM
		2 hr	Quencher: Metabisulfite	29-31%	NM
	3 ppm	0.5 hr	Quencher: Metabisulfite	18-21%	NM
		1 hr	Quencher: Metabisulfite	19-23%	NM
		1.5 hr	Quencher: Metabisulfite	25%	NM
		2 hr	Quencher: Metabisulfite	27%	NM
	5 ppm	0.5 hr	Quencher: Metabisulfite	18-25%	NM
		1 hr	Quencher: Metabisulfite	25%	NM
		1.5 hr	Quencher: Metabisulfite	25%	NM

			2 hr	Quencher: Metabisulfite	25-28%	NM
		10 ppm	0.5 hr	Quencher: Metabisulfite	27-31%	38-44%
			1 hr	Quencher: Metabisulfite	24-27%	NM
			1.5 hr	Quencher: Metabisulfite	27%	NM
			2 hr	Quencher: Metabisulfite	23-30%	NM
	TiO_2 POC*	5.1 KWh/m^3	0.108 hr	N/A	NM	0%
		10.2 KWh/m^3	0.217 hr	N/A	NM	12-30%
		5.1 KWh/m^3	0.108 hr	Acidification and reneutralization before treatment	NM	20-22%
		10.2 KWh/m^3	0.217 hr	Acidification and reneutralization before treatment	NM	0-2%
		20.4 KWh/m^3	0.433 hr	Acidification and reneutralization before treatment	NM	15-20%
		0 KWh/m^3	0 hr	Acidification and reneutralization before treatment. Titanium dioxide and ADX added without light, with mixing titanium dioxide + ADX(500ppm)	NM	19-21%
		5.1 KWh/m^3	0.108 hr	Acidification and reneutralization before treatment. Titanium dioxide and ADX added with light, with mixing titanium dioxide + ADX(500ppm)	NM	28-30%
		10.2 KWh/m^3	0.217 hr	Acidification and reneutralization before treatment. Titanium dioxide and ADX added with light, with mixing titanium dioxide + ADX(500ppm)	NM	0-16%
		20.4 KWh/m^3	0.433 hr	Acidification and reneutralization before treatment. Titanium dioxide and ADX added with light, with mixing titanium dioxide + ADX(1000ppm)	NM	40-50%
Combination AOP	UV + H_2O_2	1000 mJ + 0.05 ppm H_2O_2	Until Dose Achieved	N/A	0-14%	NM
		1000 mJ + 0.5 ppm H_2O_2	Until Dose Achieved	N/A	7-15%	NM
		1000 mJ + 5 ppm H_2O_2	Until Dose Achieved	N/A	6-16%	NM
	UV + Ozone	1000 mJ+8 ppm Ozone	Until Dose Achieved	N/A	30-36%	NM
		1000 mJ+20 ppm Ozone	Until Dose Achieved	N/A	40-50%	NM
		8 ppm Ozone+1000 mJ	Until Dose Achieved	N/A	34-40%	NM
		20 ppm Ozone+1000 mJ	Until Dose Achieved	N/A	38-39%	NM
	UV + Ferrate*	Failed QA/QC- Not Repeated				
	PAA + Ferrate*	Failed QA/QC- Not Repeated				

	H_2O_2 + Ferrate*	Failed QA/QC- Not Repeated				
	Ozone + Ferrate*	Failed QA/QC- Not Repeated				
	Ozone + PAA	20 ppm Ozone + 0.05 ppm PAA	Until Dose Achieved	N/A	25-31%	NM
		20 ppm Ozone + 0.5 ppm PAA	Until Dose Achieved	N/A	9-11%	NM
		20 ppm Ozone + 1 ppm PAA	Until Dose Achieved	N/A	22-26%	40-42%
	Ozone + H_2O_2	20 ppm Ozone + 0.05 ppm H_2O_2	Until Dose Achieved	N/A	0-42%	NM
		20 ppm Ozone + 0.5 ppm H_2O_2	Until Dose Achieved	N/A	15-22%	NM
		20 ppm Ozone + 1 ppm H_2O_2	Until Dose Achieved	N/A	17-59%	42-56%
	Acid+ H_2O_2	pH 2 + 0.05 ppm H_2O_2	1.5 hr	Quencher: Metabisulfite	11%	NM
		pH 2 + 0.5 ppm H_2O_2	1.5 hr	Quencher: Metabisulfite	37-59%	NM
		pH 2 + 1 ppm H_2O_2	0.5 hr	Quencher: Metabisulfite	30-33%	NM
			1 hr	Quencher: Metabisulfite	44%	NM
			1.5 hr	Quencher: Metabisulfite	52-64%	83-90%
			2 hr	Quencher: Metabisulfite	33-39%	NM
		pH 2 + 3000 ppm H_2O_2	1.5 hr	Quencher: Metabisulfite	60-71%	NM
	Acid + H_2O_2 +UV + heat	pH 3 + 3000 ppm H_2O_2	1 hr	UV light, 87°C	23-82%	NM
		pH 2 + 3000 ppm H_2O_2	1 hr	UV light, 87°C	71-73%	NM
		pH 2 + 3000 ppm H_2O_2	1 hr	UV light, 82°C	86-89%	NM

Note: NM denotes that tRP was not measured for the % NRP conversion or that RTP_{PT} was not measured for % TP removed. A * denotes the AOP treatments that cause precipitation as part of the treatment and therefore only RTP_{PT} could be evaluated.

The following equations describe how the above calculations were performed, including a modification that allows for variation in RTP recoveries for pre-treated brine.

$$\%\ \text{NRP Conversion} = \left(\frac{\text{Increase in tRP} \pm \text{Std Dev}}{NRP}\right) 100\%, \text{ where NRP} = \text{TP} - \text{tRP} \tag{6}$$

$$\%\ \text{TP Removal} = \left(\frac{TP - RTP_{PT}}{TP}\right) 100\% \tag{7}$$

2.4 Conclusion

In summary of Phase 1, the application of AOP treatments on RO produced brine is possible and can result in significant reductions in total phosphorus. The reduction of total phosphorus is a direct result of NRP being converted to RP or to a more reactive form that can be removed by chemical addition.

The most effective converting techniques evaluated were 100 ppb peroxide, pH 2, 1 ppm peroxide at pH 2, each for 1.5 hours at room temperature, without mixing and 10 ppm hypochlorite for 0.5 hours at room temperature, without mixing. These independent and combination treatments resulted in percent TP removals of 45%, 61%, 69% and 42%, respectively.

However, the treatment that resulted in the highest percent TP removal employed a multi-treatment approach using photolysis and 3000 ppm peroxide at pH 2 and 80-90°C; this treatment had a resultant percent TP removal of 85%.

These techniques will be further evaluated and optimized using demonstration-scale produced brine in Phase 2 in order to determine their possible inclusion as a part of quaternary treatment for ROC.

Chapter 3: Phase 2—Demonstration Facility

Abstract— The potential application of reverse osmosis followed by AOP treatment of the produced brine as a quaternary step in wastewater treatment would continue the technological advancement for nutrient removal in effort to reach ever decreasing regulations for effluent limits for highly sensitive lake systems. RO would be applied in order to produce a further treatable concentrate, high in nutrients, such as phosphorus and other potentially interfering components, which can be blended with the sequentially produced ultra-pure permeate upon discharge, resulting in significant reductions in phosphorus loading into the environment. This would reduce the potential eutrophication effects that municipal wastewater contributes to aquatic ecosystems. The AOP treatments would target the difficult to remove NRP species and after subsequent chemical addition would result in greater TP removals then can be achieved by current treatment practices alone. Antiscalant-free brine, brine containing antiscalant produced at a demonstration facility, as well as several representative phosphorus containing compounds were treated with select AOPs and analyzed for reduction in TP. Pretreated wastewater was concentrated using a bench-top RO unit, brine was collected from the Demonstration Facility and representative compounds were prepared in milli-Q water. The advanced oxidation processes evaluated were 100 ppb H_2O_2 for 30 minutes, 50 ppm NaOCl for 30 minutes, pH 2 for 30 minutes, and 100 ppb H_2O_2 + pH 2 for 30 minutes. The use of chemical addition as a pretreatment was also evaluated. Treatment effectiveness was determined by measuring Residual Total Phosphorus Post AOP Treatment after a subsequent 6 ppm alum treatment (RTP_{PT}). The use of 30 ppm alum chemical addition as a pretreatment effectively improves the use of AOPs for P removal from 57% up to 73% for a 100 ppb peroxide + pH 2 treated antiscalant free brine. The most effective chemical AOP after a 30 ppm alum pretreatment was 100 ppb peroxide + pH 2 treatment which achieved 73% TP removal for the antiscalant-free brine and 84% in the Demonstration Facility continuously produced brine. AOP effectiveness was directly affected by the type of bond present in the representative P compounds. Therefore RO can be utilized to concentrate nutrients into brine, which can be further treated using AOPs for successful nutrient removal.

Keywords: Brine, Reverse Osmosis, Advanced Oxidative Processes, Chemical Pre-treatment

3.1 Introduction

The application of reverse osmosis (RO) in wastewater treatment is well documented at fully operational municipal wastewater treatment plants (WWTP); this technology provides a quaternary step in an already multistep treatment process, but with highly beneficial outcomes in regards to meeting strict effluent criteria. The utilization of RO allows for the production of ultra-pure water permeate, which has ultra-low concentrations of ions, organics or nutrients; the consequence of this permeate production is the simultaneous production of a concentrate, which is high in ionic content, as well as organics, contaminants and nutrients. The production and further treatment of the produced concentrate (brine) to reduce potentially hazardous constituent concentrations is possible and was studied by Zhou *et al.* (2011) to determine the effect of advanced oxidative processes (AOP) on organic contaminants present in the concentrate with favourable results.

It has been determined in Chapter 2 that AOP treatments can effectively be used to reduce the phosphorus concentration in bench-top RO produced brine. The best performing AOPs were 100 ppb H_2O_2 for 30 minutes, 50 ppm NaOCl for 30 minutes, pH 2 for 30 minutes, and 100 ppb H_2O_2 + pH 2 for 30 minutes. However the brine produced by full scale facilities also contain a variety of potentially interfering compounds, such as chloramination and the presence of antiscalant. Although not completed in this project, the effect of other specific wastewater characteristics, such as other organic pollutants, need to be evaluated to determine potential interferences with doses and contact times for AOPs used to oxidize non-reactive phosphorus (NRP) to reactive phosphorus (RP).

The primary differences between the bench-top produced brine and brine produced from the continuously running facility would be chloramination and the presence of antiscalants that are added in the demonstration facility produced brine. These factors should be evaluated independently for their effects on AOP treatment. Antiscaling chemicals can potentially be major sources of phosphorus, contributing both easily removed orthophosphate and also potentially contributing the more difficult to remove NRP, particularly in the form of phospho-organics or even inorganic condensed phosphates

(Dudley and Baker, PermaCare). The contribution of these phosphorus compounds, as well as the potential presence of other organic constituents, could reduce the effectiveness of the AOP treatments due to the increase in compounds that would be readily oxidized and thus could “out compete” the targeted NRP compounds and deplete the available oxidant. Chlorination is performed in order to reduce microbe populations to ensure any pathogenic organisms cannot occur in populations large enough to cause disease when effluent is discharged from the facilities (Spellman, 2009).In facilities using RO, chloramination is used for biofouling control on the membranes, instead of chlorination due to the production of chlorine radicals during chlorination that would damage the RO membranes. . Chloramination offers an effective means of biofouling control for RO membranes; however, the application of this treatment can modify the DOC present in the wastewater (Spellman, 2009), which, if phosphorus was associated with the modified DOC, could reduce the effectiveness of the AOP treatment at converting the NRP to RP compounds for removal.

The variety of potential phosphorus containing compounds present in the complex samples would also influence the efficacy of oxidation and subsequent removal. Major phosphorus species present in wastewater have been evaluated by Maher and Woo (1998), but the effect of AOP treatment on these complex phosphorus species is still unknown. Therefore determining the fractions of NRP being oxidized by the respective AOPs would be relevant in determining which treatment would be most effective. In order to determine the effects various bond types have on AOP treatments some representative phosphorus species were treated with the selected AOPs. The bonds types included a representative phospho-organic species containing a C-O-P bond, a representative biological, complex triphosphate species containing a C-O-P bond and 2 P-O-P bonds and a representative phosphonate species containing a C-P bond.

As part of the Upper Yor Sewage Solutions Environmental Assessment, reducing phosphorus in the RO concentrate would allow implementation of the long term RO concentrate management strategy such that the additional water quantity of the RO concentrate remains in the Lake Simcoe watershed. At the Mt Albert treatment plant near Newmarket, ON there is a continuously operating demonstration facility using RO as part of a quaternary wastewater treatment step. Samples from this facility are utilized here on the brine to test AOP treatments recommended in Chapter 2.

The objective of Phase 2 was to evaluate the potential effects of chloramination on AOP treatment of the RO brine. This objective was accomplished by generating brine post chloramination, which could be compared to the results of Phase 1. The presence of antiscalants would be evaluated separately, and are discussed in Chapter 3. As a second objective, AOP evaluation on representative phosphorus compounds would provide insight into the types of NRP species present in the wastewater matrix and their ability to undergo oxidation.

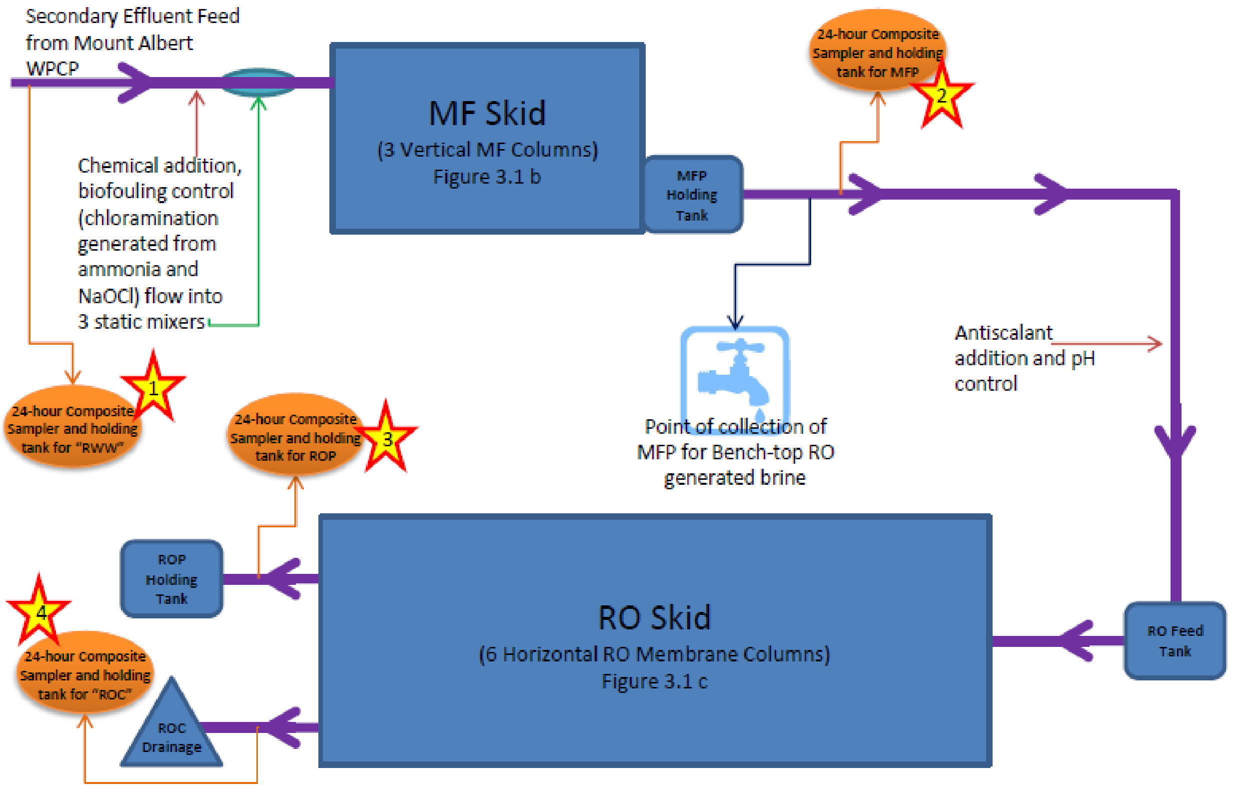
As a method of insuring brine quality and performance of the MF and RO units, weekly samples were also measured in order to determine total phosphorus (TP) for 4 points (idenitified in Figure 3.1a) within the demonstration facility treatment facility and total reactive phosphorus (tRP) for 3 points. QA/QC was also completed using sodium phenyl phosphate dibasic dihydrate as an analytical TP digestion standard and a 1 ppb orthophosphate standard as a detection limit control.

3.2 Methodology

3.2.1 Sample Collection, Preparation and Storage

For Phase 2: Demonstration-Scale Testing, 24-hour composite wastewater samples were collected from the demonstration facility built at the Mount Albert WPCP. This site was selected as it is within the watershed of Lake Simcoe and the wastewater produced here would be representative of wastewater that could be produced at the future full scale facility. The demonstration facility uses on-site skids containing pilot scale versions of the MF and RO technologies, pictured in Figure 3.1 b and c.

These samples were taken from different points within the treatment process in order to evaluate the mass balance of phosphorus throughout the plant and the tertiary treatment in order to determine MF, RO and eventual treatment effectiveness. The approximate locations of 24-hour composite sample collections are identified in Figure 3.1 below. Samples were collected and then shipped to WLU by mail in a cooler at approximately 4°C, where they were stored in a refrigerator at 4°C until testing.



(a)

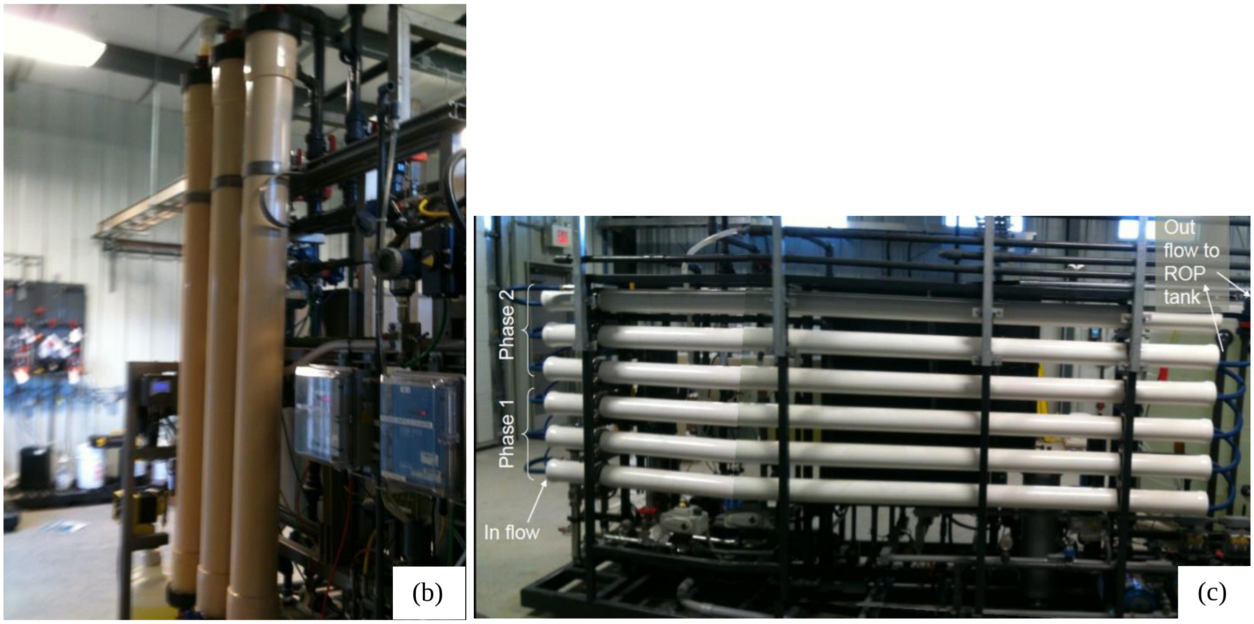


Figure 3.1a-c: (a) Schematic of the demonstration facility at Mount Albert WPCPStars indicate 24-hour composite -sampling locations; 1-RWW, 2-MFP, 3-ROP and 4-ROC **(b)** MF columns on the MF skid at the demonstration facility located at the Mount Albert Wastewater treatment plant. These columns are 10'long and contain filters with diameter openings of 0.2 microns. (c) RO membranes on the RO skid at the demonstration facility located at the Mount Albert Wastewater treatment plant. The membranes have pores with diameters of 0.001 µm, which allow for the production of an RO concentration that is high is dissolved solutes and a permeate (ROP) that is extremely low in dissolved solutes.

Mass balance was evaluated throughout the plant by performing TP analysis on reverse osmosis permeate (ROP), Microfiltration permeate (MFP), raw wastewater (RWW) (actually secondary effluent from Mount Albert WPCP, termed RWW for Demonstration facility) and reverse osmosis concentrate (ROC) and determination of tRP in MFP, RWW and ROC samples.

For antiscalant-free brine, wastewater was collected from the MF permeate produced in the demonstration facility after primary filtering and chloramination. To collect enough volume for bench-top RO processing, the sample was transported in new 5 gallon plastic buckets to the Conestoga-Rovers and Associates (CRA) facility in Waterloo. The samples were were treated using bench-top reverse osmosis (ROCHEM Model RO RO DT01-H-SS unit) with 10 micron ROCHEM membranes (pre-assembled stack of 10 discs and 9 membranes) and the ROC was concentrated by a factor of 6.7. This allows for 85% of the incoming MFP to be treated to produce ROP, which has ultra-low phosphorous levels. The remaining 15% is ROC which would be treated using advanced oxidation for phosphorus removal .A set of grab samples of the secondary effluent, the MF permeate, the RO permeate and the ROC were also taken. The ROC was then deposited into new 5 gallon buckets and delivered to WLU.

Upon arrival samples were stored at 4°C until testing. For testing, a 1 L aliquot was removed after the buckets were thoroughly mixed and were refrigerated at 4°C until treatment or analysis

There were three sampling dates involved in the described tests July 5/12, September 7/12 and February 15/13.

3.2.2 Advanced Oxidation Treatments

For the demonstration-scale study, four of the AOPs tested during Phase 1 were selected for the efficiency and cost-benefit analysis: 1 ppm hydrogen peroxide, 10 ppm NaOCl, pH 2 and 1 ppm hydrogen peroxide at pH 2. The parameters used to evaluate the AOPs before optimization are listed in table 3.1.

Table 3.1: AOPs selected from Phase 1. AOP conditions, including dose, contact time and use of quencher or neutralization.

	Dose	**Contact Time**	**Quenching or Neutralization**
Hydrogen Peroxide	1 ppm	1.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:2.8 ppm)
NaOCl	10 ppm	0.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:1.12 ppm)
pH 2	N/A	1.5 hrs	Neutralized to pH 7
Hydrogen Peroxide at pH 2	1 ppm	1.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:2.8 ppm)

*All treatments performed at room temperature without mixing

AOP treatments were applied to weekly mass balance samples and then optimized using antiscalant-free brine. Samples were pretreated with 30 ppm alum for 1 hour followed by filtration with a 0.2 µm filter before optimization occurred. The re-evaluation and optimization occurred using the July 5/12 sampling event by varying the time and dose parameters and treating 100 mL of unfiltered brine, quenching or neutralizing with sodium metabisulfite (Sigma-Aldrich, ≥99%) and NaOH (Sigma-Aldrich, 99%) the reaction then removing 5 mL aliquots in triplicates for TP analysis and treating the remaining volume with 6 ppm alum for 20 minutes at room temperature with moderate mixing. These samples were then filtered using a 25 mm Syringe filter with a 0.2 µm polyethersulfone membrane (VWR International); 5 mL aliquots were removed in triplicate for RTP_{PT} analysis.

After optimization using the antiscalant-free brine, the AOPs, under the new parameters, would then be evaluated on a second brine sampling event that had been pretreated with 30 ppm alum, September 7/12, in order to determine consistency between samples. The AOPs with the specific parameters were as follows in table 3.3.

Table 3.2: AOPs selected from Phase 1 and optimized in Phase 2. AOP conditions, including dose, contact time and use of quencher or neutralization .

	Dose	Contact Time	Quenching or Neutralization
Hydrogen Peroxide	100 ppb	0.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:2.8 ppm)
NaOCl	50 ppm	0.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:1.12 ppm)
pH 2	N/A	0.5 hrs	Neutralized to pH 7
Hydrogen Peroxide at pH 2	100 ppb	0.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:2.8 ppm)

*All treatments performed at room temperature without mixing

The chemicals used throughout Phase 2 are listed with manufacturer in Table 3.3.

Table 3.3: Chemicals used for these treatments listed in Table 3.1 and 3.2 with manufacture.

Product:	Manufacturer:	Description:
30-32% wt Hydrogen Peroxide	Sigma-Aldrich	Potassium Stannate stabilizer, 99.99%
10-15% wt Sodium Hypochlorite	Sigma-Aldrich	99%
Sodium Metabisulfite	Sigma-Aldrich	≥99%
Sulfuric Acid	Sigma-Aldrich	95-98%
Sodium Hydroxide	Sigma-Aldrich	99%

The AOP treatments listed in Table 3.2 were also applied to the Dec 5, 2012 weekly mass balance sample, as well as the three representative phosphorus containing compounds sodium phenyl phosphate dibasic dihydrate, ATP and diethyl (hydroxymethyl) phosphonate.

3.2.3 Sample Analysis

All colorimetric analysis was performed following standard methods (4500-PE.) using freshly made (daily) 0.05 mg P/L and 0.1 mg P/L from a 1000 mg P/L stock solution of KH_2PO_4 (BDH, ≥99%); blanks and standards were measured in duplicate, while samples were measured in triplicate. The mixed reagent for colourimetric phosphorus determination was prepared and added to duplicate blanks and standards and triplicate samples in 3 minutes intervals and incubated for 30 minutes before being measured. Samples were measured, starting with the blanks and standards by pipetting a small amount into the cell with a Pasteur pipette to rinse the cell, and then the cell was filled with the sample; this was repeated between each blank, standard and sample. The sample was then placed into the cell holder and absorbance was measured using a Cary 50 UV/Vis Spectrometer (dual beam instrument) and the associated Simple Reads Program with a 10 cm path length cell holder adapter and a 10 cm quartz cell (Starna Cells) at 835 nm with a 1.000 second total exposure. Each sample was evaluated for 1 minute, with absorbance readings being taken every 10 seconds to ensure the sample was stable and fully developed. The absorbance values were the imported into Excel, the blanks and standards were used to produce a standard curve and Beer's Law was used to calculate the concentration of orthophosphate in the sample in mg P/L.

3.2.4 Quality Control and Quality Assurance

Quality control and assurance was performed using sodium phenyl phosphate as a representative organic phosphate compound. This compound contains a COP bond and is commonly used in assurance tests for total phosphorus analysis and monitors the conversion efficiency of the persulfate digestion. The lowest acceptable conversion efficiency that was allowed was 95%, while the high end was 105%; outside this range the experimental for that particular analysis was not considered.

3.2.5 Representative Phosphorus Compounds

The representative phosphorus species utilized were sodium phenyl phosphate dibasic dihydrate (also used as QA/QC for TP digestion) as a representative phospho-organic species containing a C-O-P bond, adenosine 5′-triphosphate disodium salt hydrate as a representative biological, complex triphosphate species containing a C-O-P bond and 2 P-O-P bonds and diethyl (hydroxymethyl) phosphonate as a representative phospho-organic species containing a C-P bond. All AOP treatments would be performed in the same manner as on the brine samples, including the 30 ppm pretreatment.

3.3 Results and Discussion

The concentrate produced by the demonstration facility during Phase 2 was initially assumed to be similar to that produced during bench-scale due to the usage of the Mount Albert WPCP secondary effluent as the influent to the demonstration plant. The ROC produced from bench-scale, as discussed in Chapter 2, contained a TP of between 60 to 80 μg P/L, Figure 3.2 displays the TP content of the ROC for the demonstration facility for the first 9 weeks of operation.

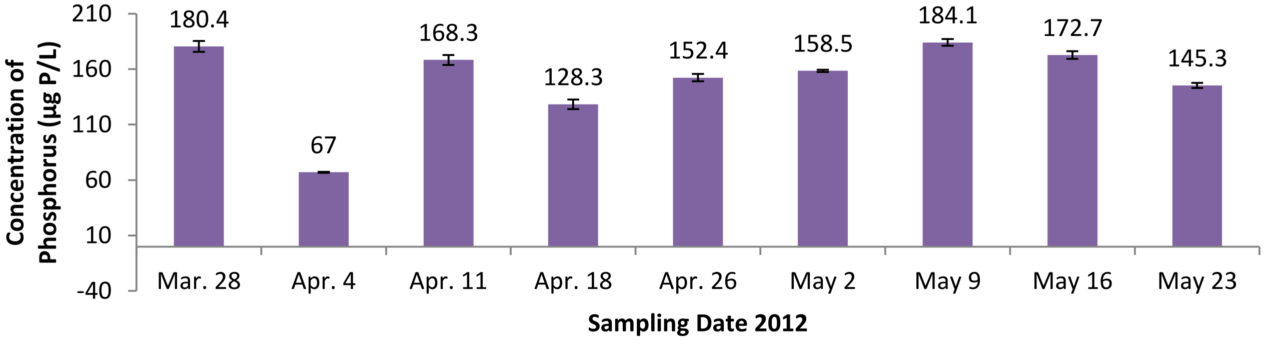


Figure 3.2: Variation in total phosphorus concentration in μg P/L for the demonstration plant over the weekly sampling dates. Error bars are standard deviation on multiple samples.

The March 28, 2012 sample contained 180 μg P/L, which is almost triple the concentration of phosphorus observed during bench-scale, while the RWW, MFP and ROP remained virtually unchanged from bench-scale to demonstration-scale. It was believed that the additional phosphorus must be contributed by one of the additives used in the treatment plant to prevent scaling (antiscalant, prevents $CaCO_3$ accumulation) or biofouling of the RO membrane. Phosphorus compounds are commonly used to prevent antiscaling, however, industrial chemicals are not required to report constituents that are below 1% in their products, therefore the phosphorus content of the selected antiscalant (Vitec 8200; Avista Technologies, San Marcos, CA, USA) was unknown. As visible in Figure 3.2, there is a marked drop in TP for the April 4, 2012 sample; it is thought that antiscalant was unintentionally not added during that sampling event and is likely a demonstration facility produced antiscalant-free brine. Without the antiscalant present TP returned to bench-scale levels. Antiscalant was reintroduced for the April 11, 2012 sampling and the increase was again observed. Although there is fluctuation within the TP for the samples, total phosphorus concentrations are generally between 130-190 µg P/L. This large variation is likely due to the antiscalant and the efficiency of the RO at the time of sampling. The goal range is to concentrate the MFP by a factor of 6-7, however, that does produce a large window for variation; as well the amount of antiscalant added is programmed to be 2 mg/L, although this dosage has never been analytically monitored. These factors contribute to the variation of TP observed in Figure 3.2.

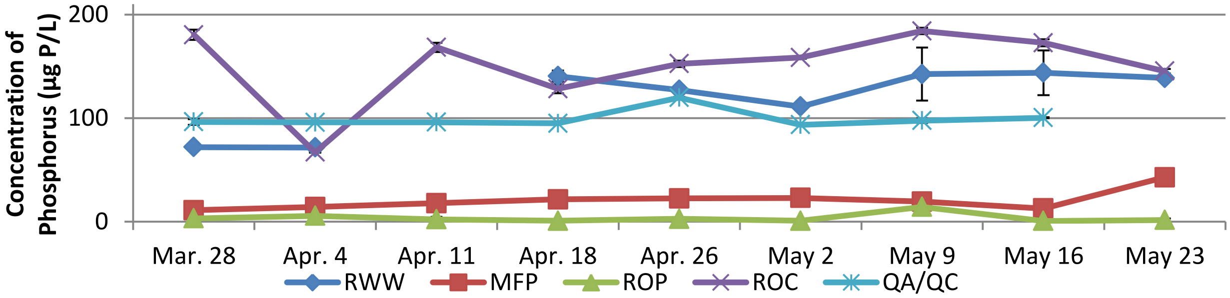
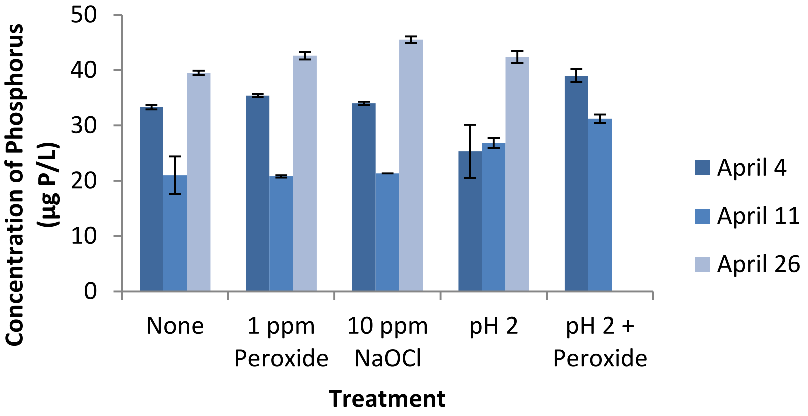


Figure 3.3: Fluctuations in the weekly sample total phosphorus in the RWW, MFP, ROC and ROP for the demonstration plant. QA/QC provides confirmation of digestion efficiency and validity of the analytical technique. A known concentration of phenyl phosphate (100 µg P/L) is digested and measured with every digestion series in order to determine recovery of phosphorous from an organic source. A recovery of 100% ± 5% is considered acceptable, while a recovery of 100% ± 10% is considered with caution. Phosphorus reported in µg P/L. Error bars are standard deviation on multiple samples.

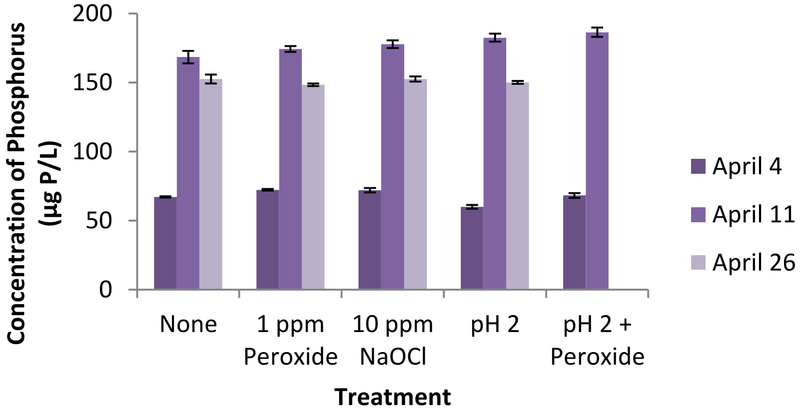
Figure 3.3 displays the normal ranges observed in the ROP, the MFP and RWW, as well as ROC for the new demonstration facility and 100 ppb P QA/QC analysis for the total phosphorus digestion procedure. The variation observed in ROP total phosphorus is very small with a normal range of 0.7-7 µg P/L, while MFP varies slightly greater than ROP, with a normal ranges 15-25 µg P/L and RWW hovers around an average of 134 µg P/L. The largest fluctuations in total phosphorus are observed in ROC for the reasons previously discussed. Quality assurance and quality control (QA/QC) were performed using phenyl phosphate ($C_6H_5PO_4Na_2 \cdot 2H_2O$) as a representative organic phosphorus constituent to ensure that complete digestion was occurring in the complex wastewater samples throughout Phase 2. Recovery or 100% ± 5% was considered reasonable within standard variation to be confident in the digestion procedure and the ability to recover phosphorus.

3.3.1 AOP Effectiveness on Demonstration-Scale Produced Brine Containing Antiscalant

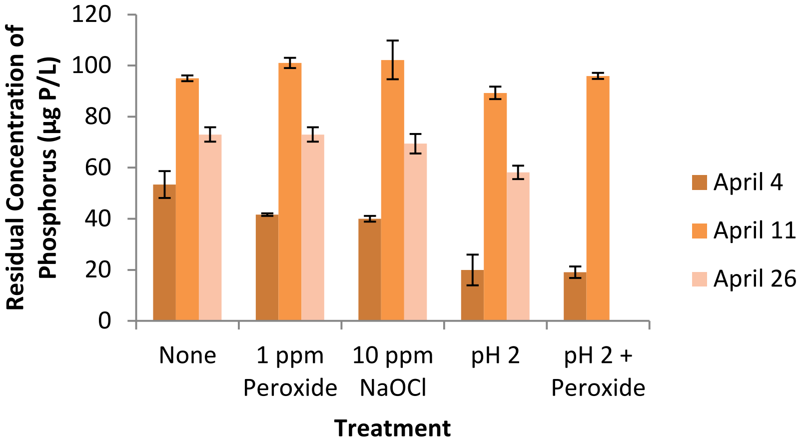
The four AOP treatments selected were applied to the brine containing the antiscalant to determine what effect the antiscalant would have on treatment effectiveness. The sample dates used to evaluate the AOPs were April 4, 2012, which was thought to not contain antiscalant but was produced at the demonstration plant, April 11 and April 26, 2012, which both had antiscalant added during production. The treatments were performed as described in Table 3.1; tRP, TP and RTP_{PT} after 6 ppm alum addition were measured for each treatment. April 26, 2012 was only used to evaluate treatment 1-3, the pH 2 + peroxide treatment was not evaluated for this sample date. These tests were performed without initial alum pretreatment. The results are displayed in Figure 3.4a-c.



(a) tRP



(b) TP (Recovery Samples)



(c) RTP$_{PT}$

Figure 3.4: AOP treatments of Demonstration-scale brine. (a) tRP, (b) TP and (c) RTP$_{PT}$ after 6 ppm alum addition and filtration. Phosphorus concentration reported in µg P/L. Error bars are standard deviation on multiple samples.

The treatments performed on the April 4, 2012 brine were as effective as was determined during Phase 1, although tRP data does not show the trend well and suggests a larger percentage of the total phosphorus is reactive than compared to Phase 1 brine. This observation is likely due to the decrease in chemical addition performed at the Mount Albert Facility that feeds the secondary effluent into the demonstration facility. This decrease was requested to ensure that the demonstration facility could accommodate a realistic amount of phosphorus entering the facility while maintaining an ROP that was still ultra-low (≤10 µg P/L) in phosphorus.

As displayed in figure c, after 6 ppm alum addition TP removals for the April 4 sampling of 20%, 42%, 44%, 77% and 72% for untreated, peroxide, hypochlorite, pH and pH and peroxide, respectively, were achieved. These percent TP removals were greater than either of the other two sample dates. Both acidification and pH 2 + peroxide achieved the goal RTP$_{PT}$ of 30 µg P/L, confirming the results observed during Phase 1, whereas the other dates did not, primarily because of the initial TP concentration and the presence of the antiscalant, which most likely contained more complex NRP compounds. TP removals for the AOP treatments on April 11, 2012 brine were 44%, 42%, 42%, 51% and 49%, respectively. A similar pattern was observed for the April 26, 2012 brine sample, which had a TP removals from the non-treated brine of 52% and across the three treatments the respective TP removals were very similar, achieving removals of 51%, 54% and 61%.

Therefore the AOPs were virtually ineffective in the brine containing antiscalant; even though TP removal was relatively high, around 40-60%, removal effectiveness did not increase significantly once the brine was treated if antiscalant was present. The effectiveness is determined by comparing the residual NRP in the brine treated only with 6 ppm alum (RTP_{CA}) and those treated with the AOPs and subsequent alum treatment (RTP_{PT}), as described by equation 7 and 8. However, during AOP testing on the brine containing antiscalant it was observed that TP removal was greater than NRP conversion, suggesting that antiscalant contributed NRP must be removable by alum addition.

The ability to use alum addition as a potential pretreatment was evaluated for improving AOP treatment. It was reasoned that this pretreatment step would not only improve the treatments by reducing the initial TP concentration, but, as it is well documented, alum can effectively remove organics, specifically those with negatively charged functional groups, such as carboxy groups, and would reduce the amount of organic material to be oxidized, thus allowing the oxidants better access at the NRP compounds.

3.3.2 Chemical Removal as a Pretreatment

The ability of metal salt addition to remove NRP contributed by the antiscalant was evaluated by measuring RTP_{CA} after increasing doses of alum 6, 12, 18 and 24 ppm alum, as well as 10 ppm $FeCl_3$. ROC samples were treated with alum for 20 minutes with moderate mixing at room temperature and neutral pH, followed by filtration using a 0.2 µm filter. The antiscalant containing brine samples used to evaluate NRP removal were April 11 and 18, 2012, which had TP values of 168.3 ± 4.5 and 128.3 ± 4.3 µg P/L. The removal trends are described in Figure 3.5.

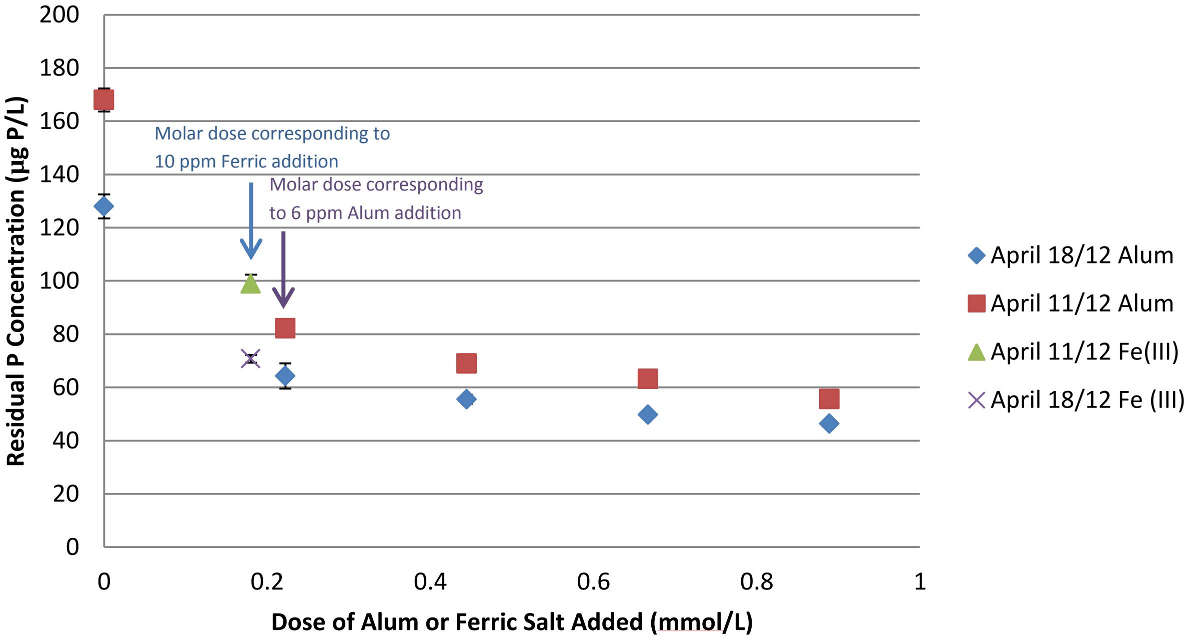


Figure 3.5: Alum dose dependencies for NRP removal from brine containing antiscalant for April 11 and April 18, 2012 sample dates. Comparison of 6 ppm alum (purple) with 10 ppm Fe(III) (blue) at same molar ratio. Metal salt dosing occurred at room temperature for 20 minutes at neutral pH with moderate mixing and was followed by filtration using a 0.2 µm filter. Phosphorus concentration reported in µg P/L. Error bars are standard deviation on multiple samples. Error bars are standard deviation on multiple samples.

Alum appears to have a dose dependent removal effect on NRP, such that as the dose of alum is increased, the removal of TP is increased and RTP_{CA} subsequently decreased. The decrease in RTP_{CA} is beyond what should be observed if only tRP was removed, such that the removal of tRP for April 11 and 18, 2012, which was 21.0 ± 3.4 and 22.9 ± 0.8 µg P/L, respectively, would result in a RTP_{CA} of 147.3 ± 7.9 and 105.4 ± 5.1 µg P/L, respectively. However, after just 6 ppm alum addition, RTP_{CA}s of 82.2 ±1.4

and 64.3 ± 4.7 µg P/L were achieved; 10 ppm ferric additions saw RTP_{CA}s of 99.1 ± 3.2 and 70.7 ± 1.4 µg P/L. This similar molar ratio between 6 ppm alum and 10 ppm ferric also suggests that alum is more effective at removal of NRP than ferric salts. The lowest RTP_{CA} achieved using 24 ppm of alum was 55.6 ± 1.8 µg P/L for the April 11 brine sample and 46.4 ± 0.6 µg P/L for the April 18 brine sample.

These removals are up to 67% and 64% of the total phosphorus, 3.5-5.5 times greater than expected if only tRP was removed. NRP removal by metal salt addition has not been thoroughly explored; therefore the mechanism of this removal is unknown. However, NRP removal could be the result of complexation between the organic functional groups, such as carboxylic acids, and the metal surfaces, a complex that has been well documented. Another possibility is that alum or other phosphorus binding metal is already present in the system as nanoparticles or colloids that are too small to be removed by filtration. Phosphorus bound to these alum nanoparticles or colloids are coagulated and flocculated once the large doses of alum are administered. The added alum also binds phosphorus adding to what already can be removed and the larger flocs are removed from suspension and filtered out. These hypotheses need further evaluation and the phosphorus containing components of the antiscalants need to be further characterized in order to determine the mechanistic effect of NRP removal by metal salts.

The RTP_{CA} values achieved by alum over dosage are consistent with the RTP_{CA}s for the naturally occurring phosphorus as observed in Phase 1 and in the April 4, 2012 antiscalant free brine. Therefore the additional phosphorus contributed by the antiscalant can be removed, which would allow for the AOP treatments to effectively be performed.

The effectiveness of an alum overdose pretreatment was evaluated using the April 26 brine containing antiscalant. A 30 ppm alum dose was administered at room temperature, neutral pH with moderate mixing for 30 minutes, followed by filtration using a 0.2 µm filter. After the pretreatment, the regular AOP treatments were performed as described previously. A comparison of the effectiveness of the AOPs with and without alum pretreatment is summarized is Figure 3.6.

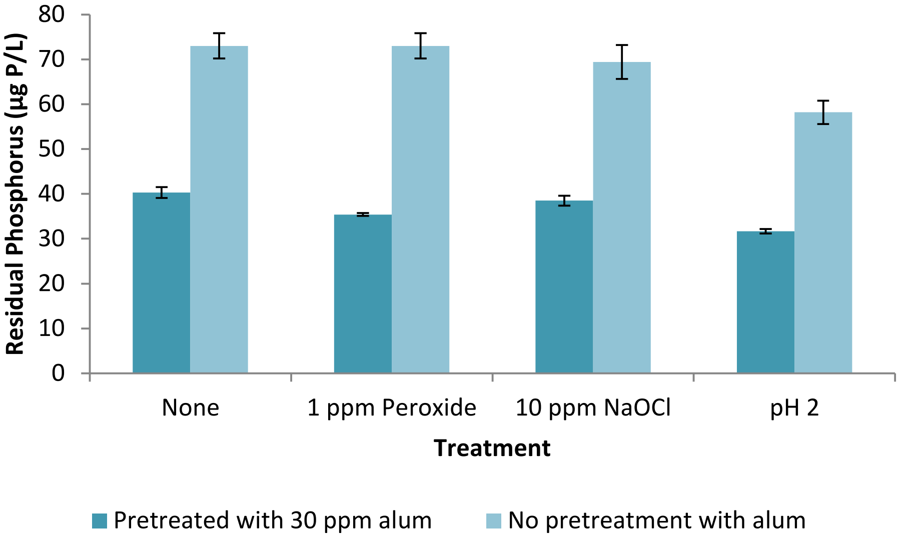


Figure 3.6: Comparison of AOP effectiveness using RTP_{PT} for the April 26 brine sample containing antiscalant with and without 30 ppm alum pretreatment. Phosphorus concentration in µg P/L. Error bars are standard deviation on multiple samples.

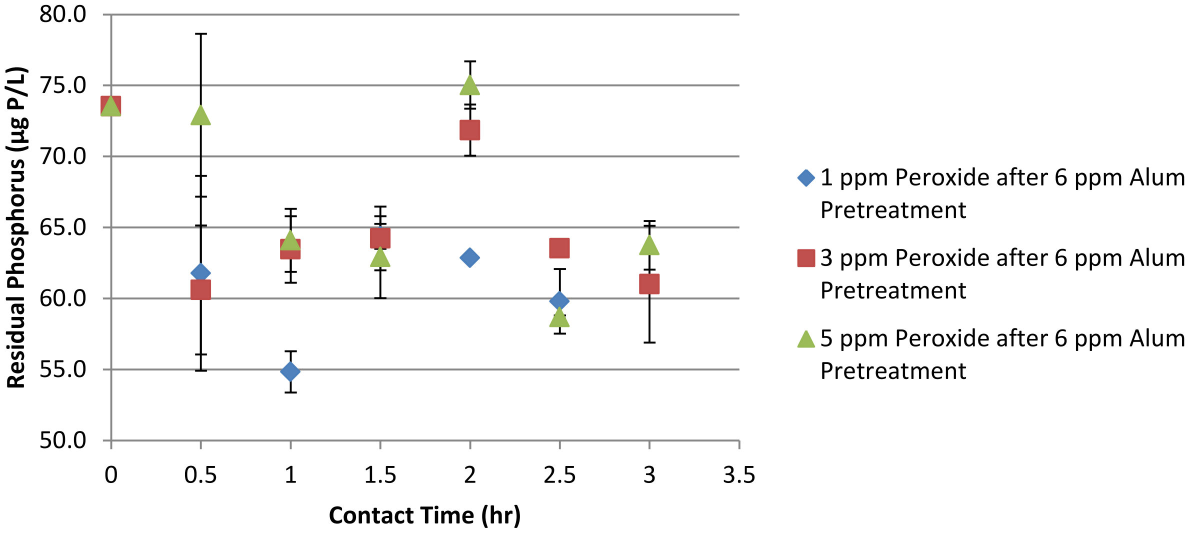
Pretreatment with alum increases TP removal drastically, untreated TP removal was increased to 74% from 52%. Acidification to pH 2 after pretreatment saw the lowest RTP_{PT} at 31.7 ± 0.5 µg P/L, which is twice as effective as without the pretreatment and is almost achieving the goal of lowering RTP_{PT} to 30 µg P/L. Therefore a pretreatment step would be possible to remove the antiscalant added to protect the RO membranes and would not interfer with the AOP treatments or their effectiveness at NRP conversion. However, it is notable that the RTP_{PT} for the AOP treated samples is not that different than the RTP_{CA} for the pretreated brine that did not undergo further AOP treatment. In all treatments conversions of less than 10 µg P/L were observed, which does not concur with the results observed from Phase 1 and supports the assumption that brine characteristic had changed, likely as a result of chloramination or the addition of antiscalant. Therefore optimizations to reduce the impacts of these changes need to be further evaluated.

3.3.3 Re-evaluation of the AOPs Selected from Phase 1: Optimizing with Antiscalant Free Demonstration Plant Brine

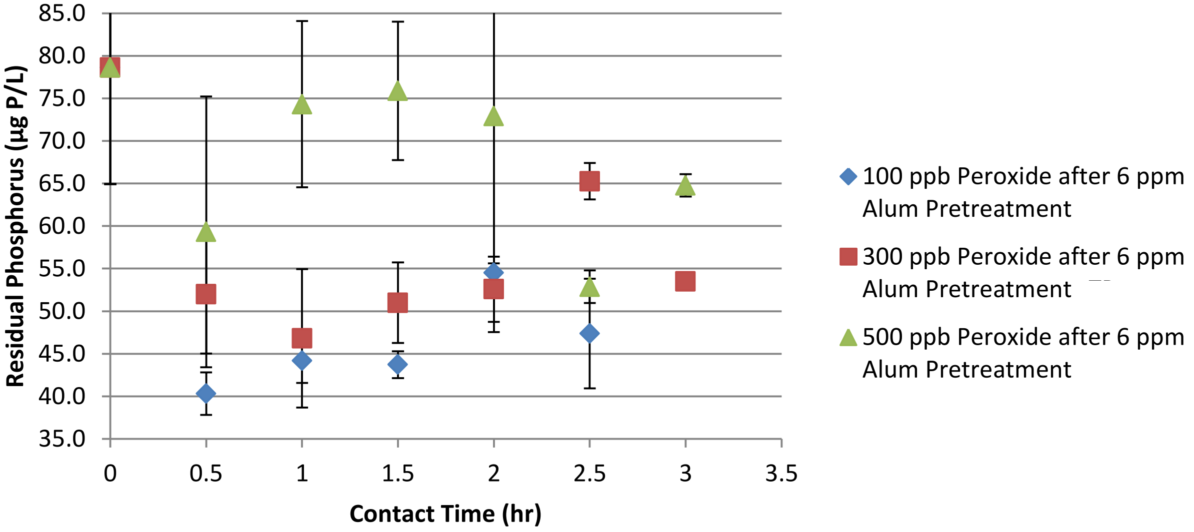
The ability of the AOP treatments to convert the NRP to RP for chemical removal in the antiscalant-free brine had to be evaluated in order to determine if the brine would react as it had during bench-scale assessment or if the brine varied in composition. As well, the effect of chemical addition using alum as a pretreatment had to be evaluated in order to determine if it changed dose or contact time for the selected AOPs. In order to do this antiscalant-free brine was produced. Re-evaluation of the four selected AOP treatments from Phase 1 was then performed to determine time and dose dependencies for the new brine and after the alum pretreatment. The re-evaluation is described by AOP.

3.3.3.1 Hydrogen Peroxide

Re-evaluation of hydrogen peroxide using antiscalant-free brine initially used a 6 ppm alum pretreatment instead of a 30 ppm alum pretreatment. The July 9/12 brine has a TP of 131.9 ± 5.3 µg P/L, after 6 ppm chemical addition the RTP_{CA} of 73.9 ± 4.5 µg P/L. Low doses of peroxide at 100, 300 and 500 ppb and high doses of 1, 3 and 5 ppm were evaluated every 30 minutes for 3 hours. Figure 3.7a and b show the dose and time dependencies for low and high doses of peroxide.



(a)



(b)

Figure 3.7: RTP_{PT} data for time and dose dependencies for hydrogen peroxide in 6 ppm alum pre-treated brine. Figure (a) are the high doses evaluated at 1, 3 and 5 ppm. Figure (b) are the low doses evaluated at 100, 300 and 500 ppb. Samples all quenched with metabisulfite. RTP_{PT} measured in µg P/L. Error bars are standard deviation on multiple samples.

The results achieved during the time-dependency evaluation confirm those observed during bench-scale testing such that lower hydrogen peroxide doses achieved lower RTP_{PT} than the higher doses, with the lowest RTP_{PT} of 40.3 ± 2.5 µg P/L occurring with the 100 ppb dose. Uniquely the conversion was achieved much faster than that observed during Phase 1 and was achieved in only 30 minutes. This could be due to the fact that the 6 ppm alum pretreatment removes the tRP from the brine and prevents any peroxyphosphate complexes from forming which prevent the oxidation process. Also it is likely that the pretreatment removes organics that could be oxidized by the peroxide and prevent the reaction from occurring with the NRP compounds.

Again the phenomenon of reversion of RP back to NRP is observed after the 1.5-2 hour time mark. This observation is consistent with that observed during Phase 1: bench-scale testing and is explained previously with literature citation. Within standard deviation the conversion of NRP to RP seems to be relative stable for the first 1.5 hours; this trend is especially noticeable in the 100 ppb dose but does occur in all three of the low doses.

Although the goal RTP_{PT} of 30 µg P/L was not met, overall with pretreatment with 6 ppm alum and subsequent treatment with 100 ppb hydrogen peroxide, a TP removal of 48% was achieved within 30 minutes, which is greater than the 27-37% observed in Phase 1, without pretreatment of alum.

After achieving such a low RTP_{PT} using a pretreatment with 6 ppm alum followed by AOP treatment, it was determined that using a 30 ppm alum pretreatment would reduce the initial RP more and would allow AOP treatment to better target the NRP. This alum overdose would also likely remove some of the NRP as was observed when the dose dependency of alum was evaluated and the results suggested that more phosphorus was being removed than what was contributed solely by the RP faction. The remaining three AOP treatments were evaluated after an initial pretreatment of 30 ppm alum to the July 9/12 brine. The RTP_{CA} for the 30 ppm alum pretreated brine was 56.4 ± 3.4 µg P/L, which is very similar to that observed in Phase 1 brine sampling.

3.3.3.2 Peroxide and Reduced pH

Hydrogen peroxide at a reduced pH (2, 3 and 4) was evaluated using the peroxide dose that achieved the lowest RTP_{PT}, which was the 100 ppb dose, every 30 minutes for 1.5 hours as that was the longest contact time achieved before reversion was observed in the peroxide tests in Phase 1. However, the pretreatment with alum was increased from 6 ppm to 30 ppm. Figure 3.8 displays the results.

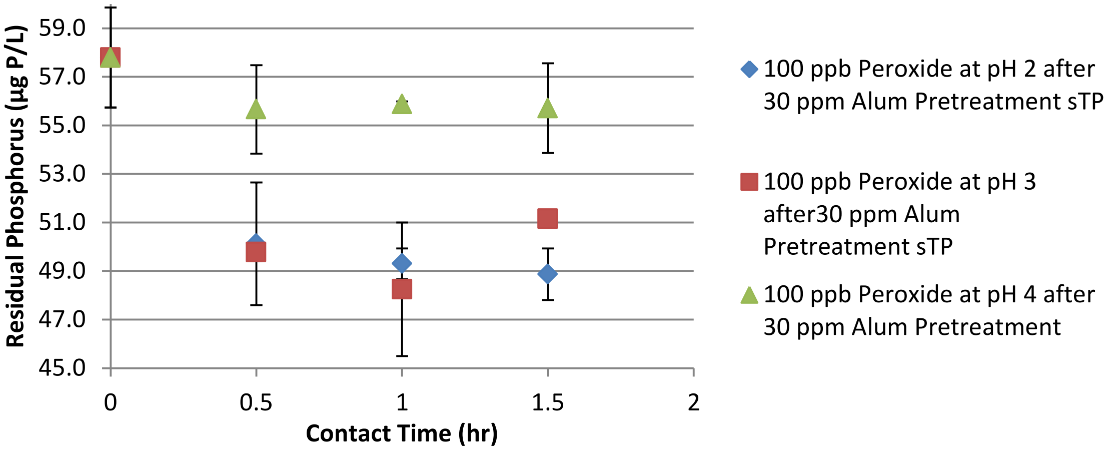


Figure 3.8: 100 ppb peroxide and pH time dependence for pH 2, 3 and 4 was performed on the July 9, 2012 brine sample that had been pretreated with 30 ppm alum. Subsamples were removed every 0.5 hours and neutralized with NaOH and quenched with metabisulfite. Results are RTP_{PT} presented in µg P/L. Error bars are standard deviation on multiple samples.

Peroxide treatment using 100 ppb hydrogen peroxide at a pH of 2 and 3 were very comparable achieving a RTP_{PT} after 1 hour at pH 3 of 48.2 ± 2.7 µg P/L and after 1.5 hours at pH 2 of 48.9 ± 1.1 µg P/L. The standard deviations for the pH 3 and peroxide treated samples were larger than those observed in the pH 2 and peroxide treated samples; however the results at the two pHs are quite similar. There was a slight reversion observed in the pH 3 and peroxide treated sample at the 1.5 hour sampling that is significantly different according to standard deviation that was not observed in pH 2 and peroxide.

Within standard deviation there was no effect of peroxide at pH 4 at converting NRP to RP. This trend needs to be evaluated at pH 7 after a 30 ppm alum pretreatment before further conclusions can be drawn about the increase in effectiveness of peroxide at reduced pH.

However, the best conversion and therefore the lowest RTP_{PT} occurs with pH 2 and 3 after as little as 0.5 hours, within standard deviation, but due to the reversion observed after 1.5 hours at peroxide and pH 3, it was determined that peroxide at pH 2 provides more stable results. This corresponds to an increase in TP removal of 11% from the 30 ppm pretreated RTP_{CA} and 32% TP removal from the 6 ppm RTP_{CA}, and is consistent with conversions observed in Phase 1, but still does not reach the goal RTP_{PT} of 30 µg P/L.

3.3.3.3 pH Adjustment

The reduction of pH alone was then evaluated for its effect on 30 ppm alum pretreated brine by subsampling every 30 minutes for 1.5 hours as that was the longest contact time achieved before reversion in the pH + peroxide tests was observed. The pH was adjusted to pH 2, 3 and 4 using a pH meter and the subsamples were then neutralized with sodium hydroxide to circumneutral. From the subsamples, triplicate samples for TP and tRP analysis were removed and the remainder was treated with 6 ppm alum for 20 minutes with moderate mixing, at room temperature and circumneutral pH. The sample was then filtered through a 0.2 µm filter and analyszed for RTP_{PT}.

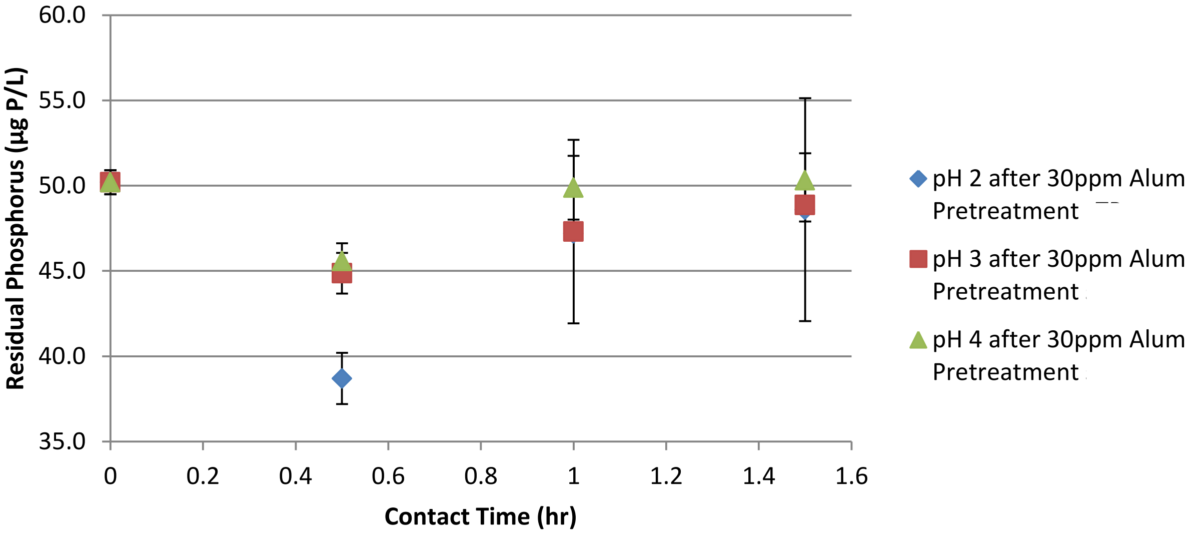


Figure 3.9: RTP_{PT} for pH 2, 3 and 4 time dependencies using the July 9/12 brine pretreated with 30 ppm alum. Subsamples were removed every 0.5 hours and neutralized with NaOH. Results are RTP_{PT} presented in µg P/L. Error bars are standard deviation on multiple samples.

The RTP_{PT} results, displayed in Figure 3.9, for the pH adjustment confirm those observed with pH and peroxide that 0.5 hours is sufficient contact time and that pH 2 has the lowest RTP_{PT}, achieving 38.7 ± 1.5 µg P/L, which is an increase in TP removal of 23% increase from that observed in the RTP_{CA} after 30 ppm alum pretreatment and an increase in TP removal of 48% from that observed in the RTP_{CA} after 6 ppm alum pretreatment. Based on bench-scale results it is unusual that pH 3 did so poorly and so comparably to pH 4 after 0.5 hours, but comparably to pH 2 and pH 4 at the hour and 1.5 hour contact times.

The phenomenon of reversion of RP to NRP is also observed after the 30 minutes mark, this is consistent with observations from Phase 1, but does occur sooner. This is likely due to the fact that there is less RP present at time zero and the newly converted RP is unstable. Therefore the results of the pH adjustment suggest that after 0.5 hours at pH 2 the best conversion can be observed. Acid treatment does not reach the goal of 30 µg P/L, however produces the highest removal of the three AOPs re-evaluated, which is consistent with the removal observed during Phase 1, although it is less effective overall as compared to bench-scale results.

3.3.3.4 Sodium Hypochlorite

As a result of the differences in water chemistry that would be observed in the demonstration and full-scale facility regarding ammonia content, which would result because of the limitations at the Demonstration Facility in maintaining the minimum excess ammonia to ensure no free chlorine, the chlorine demand of the brine needed to be determined before re-evaluation of NaOCl occured. The formation of mono-, di- and trichloroamines would prevent the added chlorine from the hypochlorite compound from acting on the NRP species. This was not considered during Phase 1 because the secondary effluent from the Mount Abert facility likely contained minimal ammonia as secondary treatment includes extended aeration to achieve very low ammonia concentrations. As well, the brine used was always older and thus would have lost the ammonia to volatilization. The chloramination process used at the Demonstration Facility in Phase 2, required ammonia to be added in excess and there were initial control limitations to the ammonia addition pump. Therefore this demand needed to be overcome and the dose required for AOP treatment determined. Fresh brine was prepared for this purpose, however, due to technical issues the brine was at room temperature for over 24 hours. This would cause all the ammonia to volatilize and thus remove any chlorine demand.

The demand was determined regardless and the results are presented in Figure 3.10.

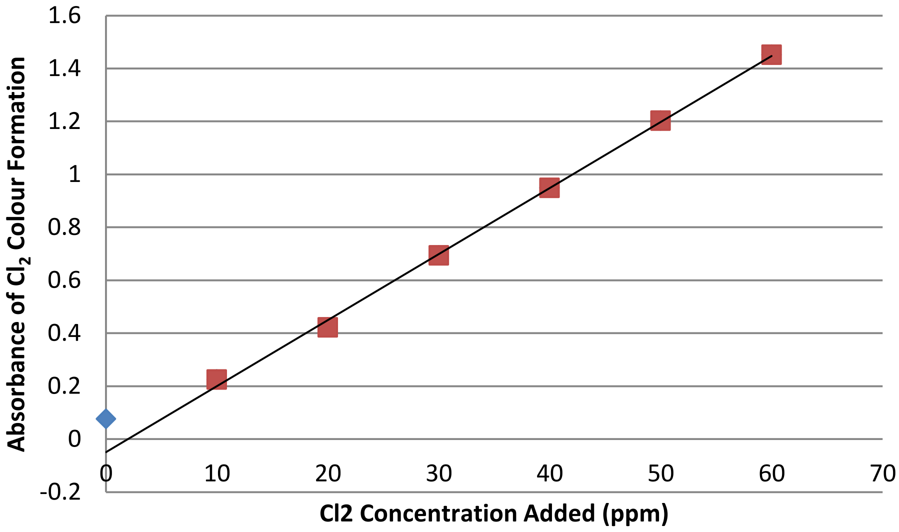


Figure 3.10: Chlorine Demand for Sept 7/12 Brine. Chlorine demand is 2 ppm. Response is linear, the equation of the line was y=0.0249x – 0.0496, with an R^2 value of 0.9986. Note that the test was performed at a 1:10 dilution of the sample, but the dilution has been corrected for in the figure. Error bars are standard deviation on multiple samples.

The chlorine demand was determined to be 2 ppm and the data suggests a linear response after about 5 ppm. Therefore a dose beyond the demand is necessary in order for the AOP treatment to have maximum effectiveness. Doses of 10, 50 and 100 were selected in order to determine the conversion of NRP to RP; 10 ppm is the dose selected from Phase 1, however, the actual chlorine demand needs to be determined from fresh brine and therefore the doses selected would ensure that the demand would be overcome.

A contact time of 1 hour was determined to be a sufficient maximum based on literature as it is twice the suggested minimum contact time of 30 minutes that is used for effluent disinfection (Spellman, 2009). Although this offers no specific insight into NRP conversion, it is a relevant starting point as an existing practical wastewater treatment process. The pH was monitored and adjusted to circumneutral after the dose of sodium hypochlorite was added to control that variable and prevent lower RTP_{PT} yields, which would occur as hypochlorite is more effective at increased pHs. Subsampling occurred at the 30 and 60 minute times and the samples were quenched with the corresponding molar dose of metabisulfite. September 7/12 brine had a similar $\mathrm{RTP}_{\mathrm{CA}}$ after 30 ppm alum treatment of 51.3 ± 3.7 µg P/L.

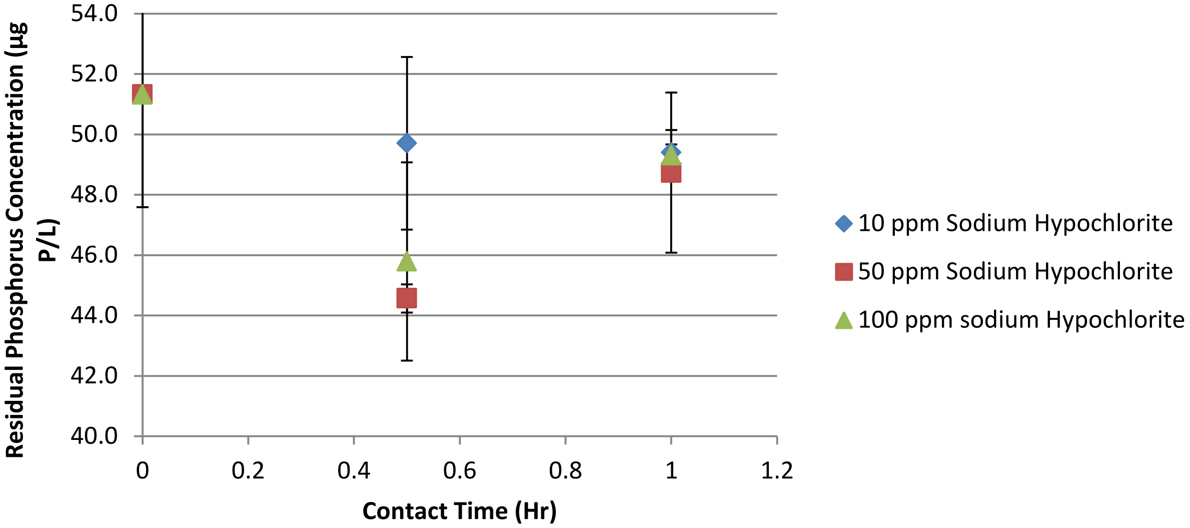


Figure 3.11: Time and dose dependence for NaOCl performed on the Sept 7/12 brine pretreated with 30 ppm alum. Subsamples were removed every 0.5 hours and quenched with a corresponding molar dose of sodium metabisulfite. Results are presented in µg P/L. Error bars are standard deviation on multiple samples.

Figure 3.11 displays the results of the time and dose dependencies for sodium hypochlorite. A dose of 50 ppm sodium hypochlorite resulted in the lowest $\mathrm{RTP}_{\mathrm{PT}}$ of 44.6 ± 0.6 µg P/L after 30 minutes. There is not a strong dose dependency because of the large standard deviations observed, however a variation in effectiveness is notable at 30 minutes, but this disappears at 1 hr. Unique to this round of testing of sodium hypochlorite a reversion and increase in $\mathrm{RTP}_{\mathrm{PT}}$ is observable for 50 and 100 ppm doses of hypochlorite. These results need to be further evaluated with more time points before 30 minutes in order to determine the full effect that sodium hypochlorite is having on the NRP. A comparable dose of sodium hypochlorite was not completed during Phase 1 and does not reach the goal $\mathrm{RTP}_{\mathrm{CA}}$ of 30 µg P/L , but the TP removal for the 50 ppm dose after 0.5 hours was a 19% increase to that observed in the $\mathrm{RTP}_{\mathrm{CA}}$ after 30 ppm alum pretreatment.

Overall the results of Phase 2 confirm what was observed during Phase 1, but do display some differences in regards to dose and contact time required. These are most likely the result of variation in the composition of the brine as well as the reduction in organic compounds attributed to the 30 ppm alum pretreatment.

3.3.4 Optimal Parameter Evaluation

After re-evaluation of the selected AOP treatments for optimal parameters using the brine produced by a bench-top reverse osmosis (ROCHEM Model RO RO DT01-H-SS unit) unit (as discussed earlier) followed by a 30 ppm alum pretreatment, the optimal parameters were evaluated according to Table 3.2 in Chapter section 3.2.2.

The results of the AOP treatments on the September 7/12 brine sample are displayed in Figure 3.12. The RTP_{CA} for each of the AOPs were performed after treatment, without subsequent chemical addition to ensure sample recovery and verify the decrease in RTP was a direct result of the AOP treatment. As is observed in the data the RTP_{CA} is relatively conserved, but there are variations in the recovery for each treatment and therefore these samples allow for the individual treatment effectiveness to be calculated using the RTP_{CA} for the respective treatment.

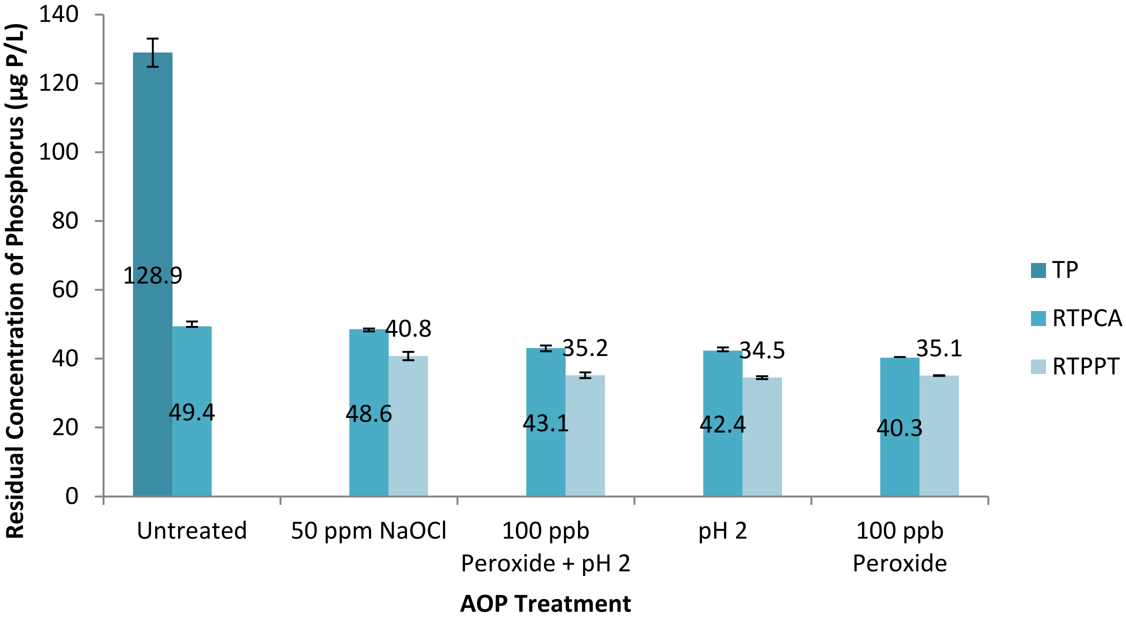


Figure 3.12: Selected AOP treatments under optimal parameters evaluated on September 7/12 produced brine. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples.

Using equation 7 the %TP removal can be calculated for pretreatment without subsequent AOP treatment, 50 ppm NaOCl, 100 ppb Peroxide, 100 ppb Peroxide + pH 2 and pH 2, respectively as 62%, 68%, 73%, 73% and 73%. Modifying equation 7 to account for the variation observed in the recovery RTP_{CA} samples and to demonstrate the effectiveness of AOP treatment after chemical addition alone, equation 8 demonstrates the following removals:

$$\%\ \text{RTP Removal} = \left(\frac{RTP_{CA} - RTP_{PT}}{RTP_{CA}}\right) 100\% \qquad (8)$$

Untreated with chemical addition alone is set as 0%, whereas 50 ppm NaOCl, 100 ppb Peroxide, 100 ppb Peroxide + pH 2 and pH 2, respectively achieve 16%, 13%, 18%, and 19%. These results are consistent throughout the study suggesting that pH 2 and peroxide at pH 2 are the most effective AOP treatments.

Comparing the treatment effectiveness between brine sampling events, we see that the treatment effectiveness is relatively conserved across samples, such that %TP removals for the optimal parameters on the July 9/12 brine were 66%, 62% and 71% for 50 ppm NaOCl, 100 ppb Peroxide + pH 2 and pH 2, respectively, with the only major deviation occurring in the 100 ppb peroxide and pH. It is important to note that the direct comparison with the 100 ppb peroxide was not made due to the use of only a 6 ppm alum pretreatment during re-evaluation of peroxide time-dose dependencies.

The treatments performed after 30 ppm alum pretreatment are capable of reaching very low RTP levels, however do not reach the goal of a RTP less than 30 ppb P. The resultant %TP removals are higher than those observed during bench scale assessment for all treatments except acid, but this is likely the result of differences in the brine, however the removals are comparable. Overall the selected AOP treatments have been optimized using a 30 ppm alum pretreatment and are capable of reaching low RTP levels. The inclusion of other parameter variations, such as the addition of heat, with a moderate increase to 35°C would likely improve the treatments and should be evaluated in future to determine the possible increase in AOP effectiveness. Although the goal of 30 ppb RTP is not reached, the effectiveness suggests that it is possible to reach those limits provided that the NRP present in the sample is capable of undergoing AOP oxidation. This capability was explored further when the representative phosphorus compounds were evaluated.

Initially the objective for Phase 2 was to evaluate and optimize the selected AOP treatments for brine produced continuously using the RO skid at the demonstration facility. Sample was to be collected using composite samplers and the treatments evaluated. However, the presence of antiscalant, as well as other changes in the brine’s composition made that difficult. These issues were effectively reduced if not removed by using a chemical addition of 30 ppm alum as a pretreatment to the AOPs, as determined during Phase 2. Therefore evaluation of the AOP treatments on brine produced continuously using the demonstration facility’s RO skid and collected using a composite sampler would give insight into the possible effectiveness of these treatments on such brine. The sample date chosen for this evaluation was one of the weekly samples used for mass balance tracking. The December 5/12 sample contained the Vitec 4000 as the antiscalant and was fully produced within the demonstration facility, which would allow for its composition to resemble brine produced at the potential full scale facility. The TP for December 5/12 was initially determined to be 357.1 ± 0.4 µg P/L and tRP was 71.6 ± 0.4 µg P/L, when re-measured directly before AOP treatment evaluation TP was 359.8 ± 2.1 µg P/L and tRP was 73.4 ± 2.3 µg P/L, which is essentially the same when standard deviation is considered. Therefore the brine composition in regards to phosphorus was not effected by storage and thus adequate for testing.

The December 5/12 brine was pretreated with 30 ppm alum for one hour and filtered in the same manner as the brine produced in Waterloo. This yielded a RTP_{CA} of 66.1 ± 1.0 µg P/L, which is an 82% removal of TP with chemical addition alone and far greater than what would be predicted with RP removal only, which agrees with the RTP_{CA}s previously observed for the weekly mass balance samples from April that all demonstrate this kind of removal. Again this removal is likely the result of organic phosphorus removal, as chemical addition is known to remove DOC compounds. Results are displayed in Figure 3.13.

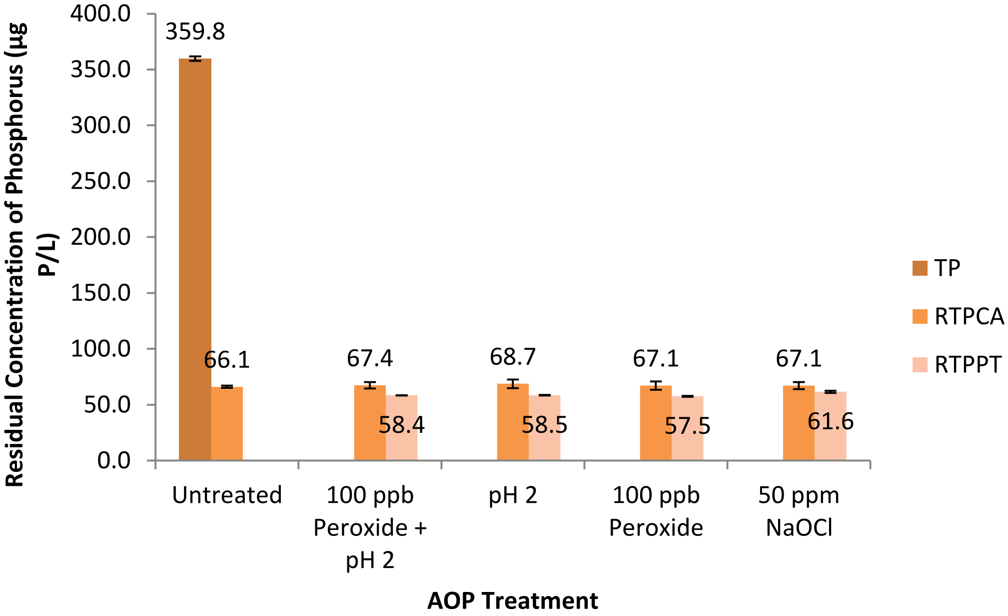


Figure 3.13: Selected AOP treatments under optimal parameters evaluated on September 7/12 produced brine. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples.

Sample recoveries (RTP_{CA}) were again performed on each AOP treated sample to ensure the decrease in RTP was a direct result of the AOP treatment. The RTP_{CA} concentration is conserved across treatments, including the untreated RTP_{CA}, which allows for %TP removal to be calculated using equation 7. The percent TP removal for each of the treatments, 100 ppb Peroxide + pH 2, pH 2, 100 ppb Peroxide and 50 ppm NaOCl, respectively are 84%, 84%, 84% and 83%. The percent removals observed in the December 5/12 brine are far greater than that observed in any of the other brine samples produced using the bench-top RO in Waterloo. This is likely do to the fact that the initial concentration of phosphorus is greater in the RO skid produced brine, by an approximate factor of 3. Even after 30 ppm alum pretreatment the RTP_{CA} present in the RO skid produced brine from December 5/12 is still 30% greater than that in the brine produced using the bench-top RO in Waterloo. It is likely that there is still residual NRP or RP present in the RO skid produced brine that can be removed by chemical addition, or that the NRP present in this sample is capable of undergoing oxidation, which allows for the further decrease in RTP that is observed.

Although the %TP removals are approximately 10% higher than those previously observed during AOP evaluation, the absolute RTP_{PT}s achieved remain twice as high as the goal of 30 ppb RTP. This observation is likely the result of the greater content of NRP associated with the presence of the antiscalant and as a result of the brine compositions itself. It is possible that the presence of the antiscalant might contribute NRP species, such as those containing a phosphonate bond or those with complex organic side chains that are impervious to oxidative treatment, as is suggested by the results of the AOP treatments on the representative phosphorus compounds. Therefore using particular antiscalants might inhibit the achievement of the 30 ppb RTP goal, which will be evaluated and discussed in Chapter 4.

3.3.5 Representative Phosphorus Containing Compounds

The complexity of wastewater samples has been characterized and the major components of both wastewater and brine have been identified (Zhao *et al*, 2012); the various phosphorus species present in wastewater can be part of these components, as forms of NRP or as orthophosphate. The easy removal of orthophosphate with simple chemical addition has been thoroughly studied and has been demonstrated within this study as well. However, the removal of NRP species or the ability to convert NRP species to RP species for chemical removal has not been thoroughly evaluated.

The use of sodium phenyl phosphate dibasic dihydrate initially as a QA/QC compound, as it is commonly used, demonstrated the reproducibility of the compound for a known concentration, as well as the recoverability of the sample through total phosphorus digestion. The compound, presented in Figure 3.14 is an organic compound containing a C-O-P bond (phospho-ester bond, C-O has bond energy of 360 kJ/mol, O-P has a bond energy of 335 kJ/mol), but does not contain any functional group, other than the phosphate group that could be bound by or interact with the alum salt.

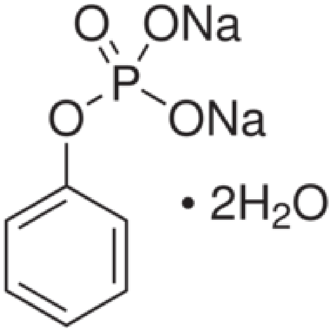


Figure 3.14: Structure of sodium phenyl phosphate dibasic dehydrate, used in QA/QC and as a representative C-O-P bond organic compound

Therefore any removal by chemical addition would be directly caused by the interaction of the metal salt and the phosphate group. The ability of alum to remove phenyl phosphate would confirm both the known capability of alum to remove DOC by interacting with negatively charged functional groups present on the DOC, as well as the observation that NRP can be removed by chemical addition. The phenyl group also offers an electron withdrawing environment that would make oxidation more difficult, thus providing a good NRP species that could mimic contaminants actually found in the environment, such as those contributed by industry or pharmaceuticals.

A second representative phospho-organic compound, suggested by Mahr and Woo as a constituent of wastewater, is adenosine 5′-triphosphate disodium salt hydrate (ATP), which is a biologically produced phosphorus species that would be present in wastewater due to the high microbial populations and would be released upon disinfection and clarification. Depicted in Figure 3.15, ATP contains a C-O-P bond (phospho-ester bond, C-O has bond energy of 360 kJ/mol, O-P has a bond energy of 335 kJ/mol) and 2 P-O-P bonds (phosphate ester bond, O-P has a bond energy of 335 kJ/mol), which makes the structure more complex due to the multiple phosphate groups that need to be hydrolyzed in order to be removed by chemical addition as well as oxidation of the C-O-P bond to release the last phosphate group.

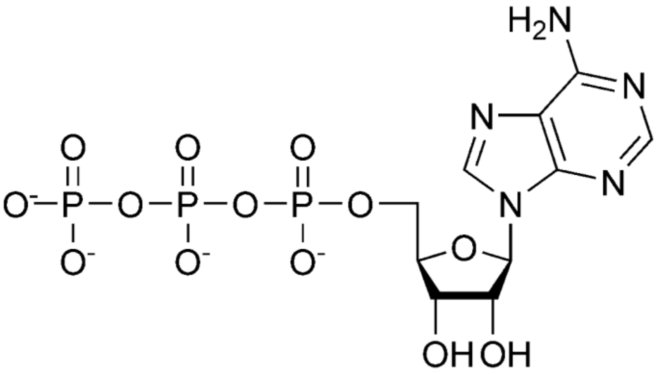


Figure 3.15: Structure of adenosine 5′-triphosphate disodium salt hydrate, used as a representative organic compound containing a C-O-P bond (phospho-ester bond) and 2 P-O-P bonds (phosphate ester bond)

The potential ability of this compound to undergo chemical removal before hydrolysis or oxidation is likely due to the four available negatively charged sites present on the phosphate groups, and the alcohol groups, which have a pKa of 6.6 (McElroy and Glass, 1951). This molecule also offers potential points of interference as other functional groups could undergo oxidation, and thus deplete the available oxidant. ATP is likely very receptive to acid catalyzed hydrolysis to the multiple phosphate ester bonds, as well as the phospho-ester bond.

The last representative phosphorus compound evaluated was diethyl (hydroxymethyl) phosphonate ((Hydroxymethyl) phosphonic acid diethyl ester). This compound, depicted in Figure 3.16, would represent the most difficult type of phosphorus containing bond, the C-P bond (bond energy 265 kJ/mol), or phosphonate bond. It is the least likely to undergo oxidation due to the (nonpolar) covalent nature of the bond (ΔElectronegativity≤0.5) and therefore the most difficult type of NRP to oxidize.

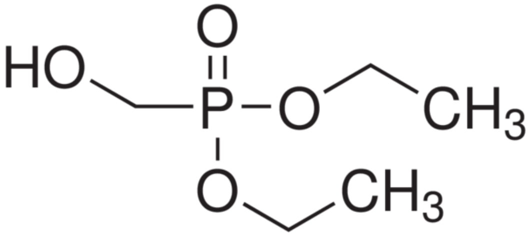
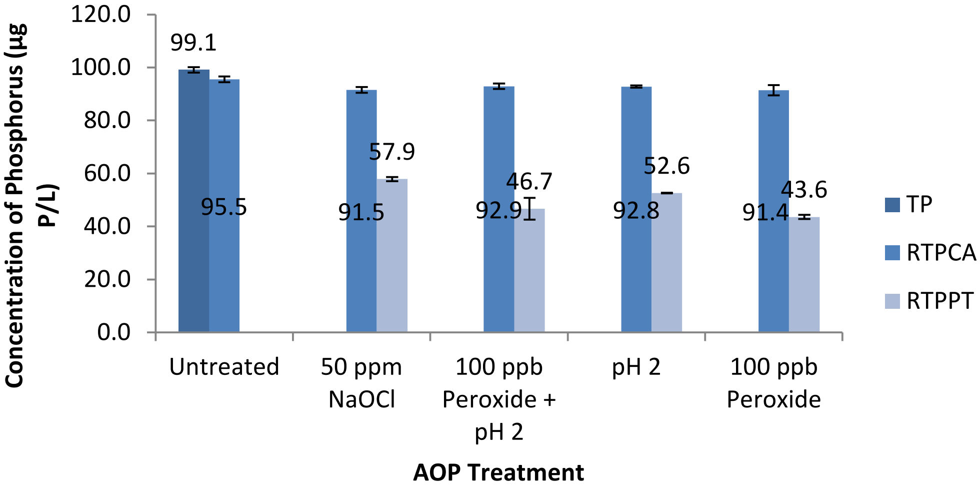


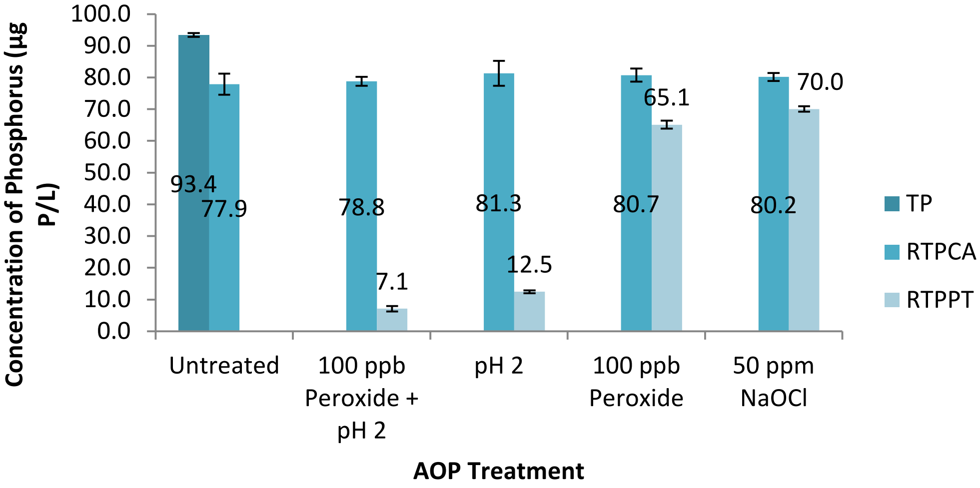
Figure 3.16: Structure of diethyl (hydroxymethyl) phosphonate, used as a representative phosphonate compound containing a C-P bond

The pKa of this acid would allow it to be protonated at neutral pH, as is predicted by the pKa of a similar acid (McElroy and Glass, 1951), and thus limits the availability of this functional group for interaction with the metal salt during chemical addition. The phosphonate compound also has competing sites of oxidation with the 2 C-O-P bonds present as esters, which could allow for further removal with chemical addition after treatment by exposing the negatively charged oxygens. Phosphonates are common chemical additives used in antiscalants to prevent fouling of the RO membranes (Dudley and Baker, PermaCare) and are likely to be present in potentially significant concentrations considering the effluent limit goal for this project. Therefore the inclusion of a phosphonate compound is logical due to the likely presence of a similar compound in RO brine as well as a representative NRP compound.

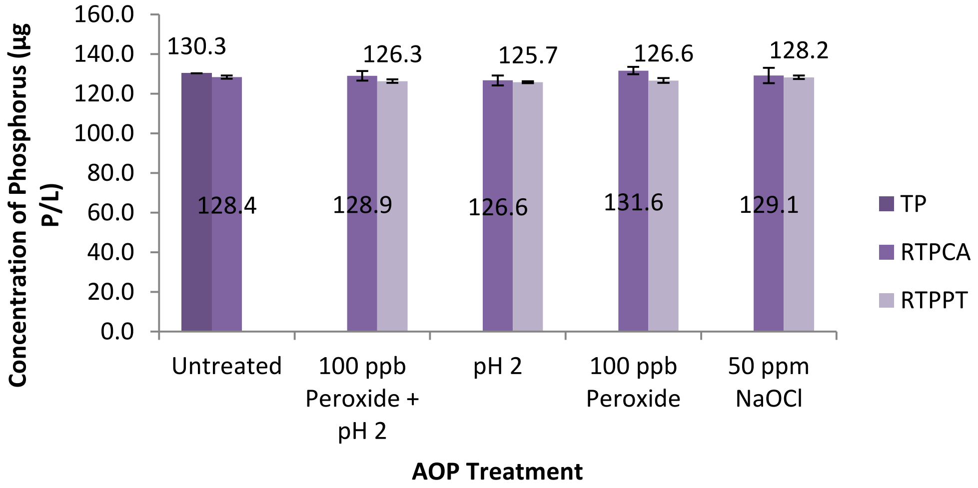
Each of the four AOP treatments evaluated during Phase 2, were evaluated in the same manner as the treatments were for the brine sample; each received a 30 ppm alum pretreatment before AOP treatments were applied. Each treatment was evaluated using both recovery RTP_{CA} as well as RTP_{PT} in order to ensure the conversion to RP and subsequent removal was from the AOP treatment alone. Figures 3.17 a-c summarize the results:



(a)



(b)



(c)

Figure 3.17a-c: Selected AOP treatments under optimal parameters performed on representative phosphorus compounds**.** a) Sodium phenylphosphate, b) ATP and c) Phosphonate compound. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples

Each of the standards were prepared to have an initial concentration of phosphorus of approximately 100 ppb; this value was arbitrarily selected, but does correspond to a phosphorus concentration that is between the concentrations observed in Phase 1 and Phase 2. After a pretreatment of 30 ppm alum for each standard a general trend for effectiveness was observed. Using equation 7, the percent TP removals was calculated to be 4%, 17% and 1% for phenyl phosphate, ATP and the phoshonate compound, respectively. The removal by chemical addition matches the predicted removal efficiencies discussed above in regards to the interaction of the alum salt with the various functional groups present on each of the compounds. ATP achieves the greatness removal by chemical addition alone due to the presence of multiple negative charges present on the phosphate groups; phenyl phosphate results in little removal as the interaction between alum and the phosphate group might be disrupted or precipitation limited due to the presence of the ring. As predicted the phosphonate compound achieves almost no removal via chemical addition alone as a result of the limited availability of a functional group to interact with.

The effectiveness of the AOP treatments on phenyl phosphate, Figure 3.17a, followed the same general trend as those observed in the brine samples, such that 100 ppb Peroxide at pH 2 saw the highest removal within standard deviation, whereas bleach saw the least removal. The recovery samples for each of the AOP treatments are not 100% conserved, as the standard deviation do not overlap, but are quite similar. Equation 7 and 8 will be used to describe the overall percent TP removal and the increase in removal beyond that caused by only chemical addition. As calculated using equation 7, %TP removal was 42%, 53%, 47% and 56% for 50 ppm NaOCl, 100 ppb Peroxide + pH 2, pH 2 and 100 ppb Peroxide, respectively; when using equation 8, and accounting for variation observed in the recovery samples, the percent removals beyond that caused by chemical addition only were 37%, 50%, 43% and 52%. The similar conversion effectiveness of peroxide with and without acid is similar to the results observed on the brine, whereas pH alone seems to be less effective at oxidizing phenyl phosphate. It is interesting to note that the overall %TP removals for each treatment on the brine are higher, however the percent removal after chemical addition, as calculated in equation 8, are actually three times higher in the standard than those observed in the brine. This suggests that the initial chemical addition is more effective in the brine, but on the individual compounds the oxidative treatments are responsible for the decrease in TP. This observation is likely a result of the oxidation of DOC that takes place in the brine concurrently as the C-O-P bond is also oxidized to release phopshate. In the representative standard solution, there was no competing DOC that could deplete the available oxidant. As well the greater reduction in overall TP is likely caused by the removal of phosphorus containing DOC compounds during the initial alum pretreatment.

The general effectiveness trend can easily be predicted for ATP, such that acid with and without peroxide would be the most effective against the bonds present in ATP. Acid catalyzed hydrolysis of phosphate ester bonds, of which ATP has three, as well as phospho-ester bonds (ATP has one) is well studied and common in the literature (Hutchings *et al.,* 1981). These bonds are easily broken by a relatively complex mechanism, which would produce orthophosphate that could be removed by chemical addition. As is observable in Figure 3.17b, the conversion of NRP to RP is drastic with %TP removals of 92% and 87% being achieved for 100 ppb Peroxide + pH 2 and pH 2, respectively, with removal efficiencies beyond that achieved by chemical addition alone of 91% and 84%. The recovery samples for each treatment on ATP are conserved within standard deviation and thus the untreated TP and RTP_{CA} values were used in the calculations. The effect of acid on this type of bond is extreme and can account for the majority of removal, insofar as the increased removal in the acid solution in the presence of peroxide is less than what is observed for oxidation by peroxide alone. Therefore in the combination treatment acid must hydrolyze bonds that could be oxidized by peroxide, essentially converting them before peroxide has the opportunity too. However, if the data is evaluated differently, it would appear that the presence of acid increases the effectiveness of peroxide, such that the increase in %TP removal from pH 2 to 100 ppb Peroxide + pH 2 (12.5 reduced to 7.1 µg P/L) is 43%, whereas the peroxide alone only achieves a 30% increase in %TP removal. This observation is logical due to the improvement of peroxide oxidation of organic compounds in the presence of acid as is supported and describe thoroughly in the literature and in Appendix A. Although, peroxide and hypochlorite treatment did not achieve such extreme removals as was observed with acid, they did accomplish significant removals that are comparable to, albeit less than, what is observed both in antiscalant free brine and in the phenyl phosphate standard with 100 ppb Peroxide achieving 30% TP removal, while 50 ppm NaOCl achieved 25% or 16% and 10% increases in removal beyond chemical addition alone. The reduction in oxidation efficiency is likely the result of the complexity of the compound as well as the presence of multiple bonds undergoing oxidation.

As was predicted the ability to oxidize and remove the phosphonate species is almost negligible; 30 ppm pretreatment as discussed earlier only resulted in a 1% TP removal, applying each of the selected AOP treatments increased removal to 2-3%, an increase of only 1-2% beyond that removed by chemical addition alone. Therefore it can be concluded that phosphonate species will unlikely successfully undergo oxidative treatment and thus are likely a constituent of residual phosphorus compounds present in the antiscalant free brine and continuously produced brine, existing as NRP.

Table 3.4: Summary of %TP removal for each treatment on each representative phsophorus compound.

		% TP Removals				
		AOP Treatments				
		Untreated (30 ppm alum Pretreatment only)	100 ppb Peroxide + pH 2	pH 2	100 ppb Peroxide	50 ppm NaOCl
Representative Phosphorus Compounds	Sodium Phenyl Phosphate	4%	53%	56%	47%	43%
	ATP	17%	92%	87%	30%	25%
	Phosphonate	1%	3.1%	3.5%	2.8%	1.6%

Results calculated using equation 7.

Table 3.4 provides a summary of the effectiveness of each AOP treatment of the representative phosphorus species and compares it with chemical addition alone. Based on the potential for oxidation and subsequent removal of each bond type, it can be hypothesized that with increasing content of phosphonate and phospho-ester bonds, the effectiveness of AOP treatment decreases. This trend can be used to qualitatively evaluate the potential effectiveness of AOP treatment on wastewater if the compositions of phosphorus species are known. Therefore the higher content of phosphonate containing NRP species the more resistant the wastewater is to AOP treatment.

3.3.6 An Alternative Option

During bench-scale assessment it was determined that the four selected AOPs offered the best NRP to RP conversion at the lowest cost estimated for each process; however, the treatment procedure that resulted in the lowest RTP utilized the Metrohm UV Digester with 3000 ppm peroxide at pH 2 and 80-90°C for 1 hour. This treatment offered a RTP 3 times lower than the residual phosphorus goal of 30 ppb, but would also be costly as it requires excess chemicals, heat and UV light. Although achieving similar percent conversions throughout Phase 1 and Phase 2 using the evaluated AOPs, the absolute goal of 30 ppb P was not achieved within standard deviation, with the lowest absolute RTP of 34.5 ± 0.4 ppb for pH 2; the failure to do so likely being a result of changes in the brine. The question was posed whether the goal of 30 ppb RTP could be reached for this new brine and attempting that goal using the Metrohm UV Digester with 3000 ppm peroxide at pH 2 and 80-90°C for 1 hour was evaluated for each of the 30 ppm alum pretreated February 15/13 and December 5/12 brines, as well as each of the representative phosphate compounds. Figure 3.18 presents the results of this combination treatment.

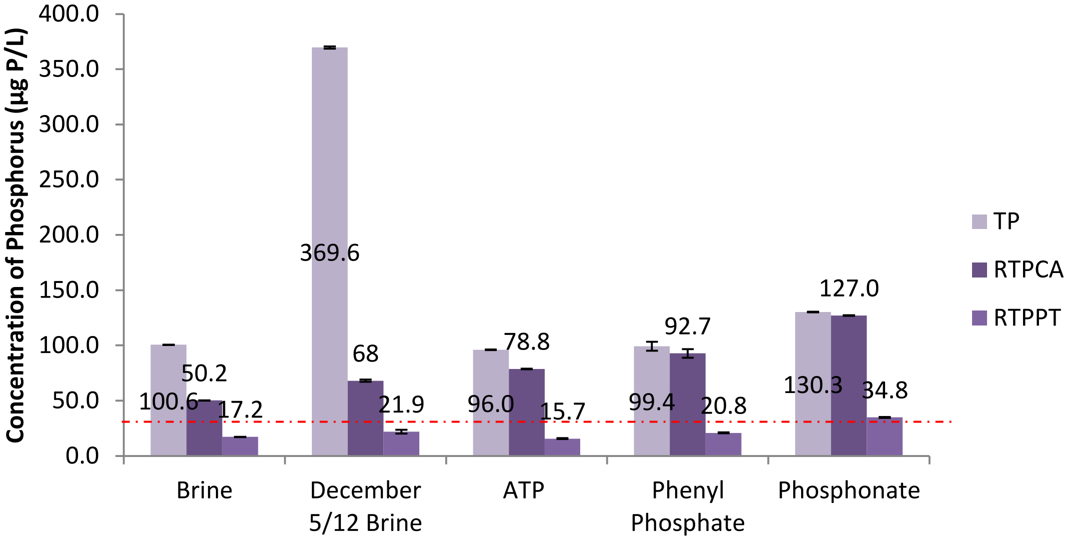


Figure 3.18: Effect of using the Metrohm UV Digester with 3000 ppm peroxide at pH 2 and 80-90°C for 1 hour on conversion of NRP to RP in antiscalant-free brine, continuously produced brine from Demonstration facility and the 3 representative phosphorus containing compounds. All samples are 30 ppm alum pretreated; RTP_{CA} and RTP_{PT} both measured. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples. Red line represents the goal of 30 ppb RTP as determined by the PWQG.

As is displayed on the figure, all brines and representative compounds, except the phosphonate species, achieved conversion of RP to NRP that surpassed the 30 ppb RTP guideline using this combination treatment. Percent TP removal were similar to those observed during bench-scale assessment, achieving removals of 83%, 94%, 84%, 79% and 73% for the antiscalant free brine, the December 5/12 brine, ATP, phenyl phosphate and the phosphonate compound, respectively.

Comparing the combination treatment on the representative phosphorus species, the general trend of effectiveness is maintained, such that ATP is most convertible and the phosphonate species is the least convertible. This also suggests that phosphonates or similar complex are present in the brine samples and therefore limits the conversion effectiveness. The most notable conversion decrease is observed in the December 5/12 sample, which reaches a 94% removal and surpasses the goal of 30 ppb; this suggests that treatment of continually produced brine is possible and can reach required limits, but takes a combination of treatments to achieve this goal.

The likely resulting improvement is the application of heat, which improves both the acid catalyzed hydrolysis, as well as peroxide oxidation—as described in literature, coupled with the UV light, which would act on the DOC and remove the potentially interfering compounds, as the digester is meant to oxidize DOC. The application of UV light and heat also likely prevents the formation of any peroxyphosphate compounds, which can reduce effectiveness of peroxide by making the compound non-reactive, as has been demonstrated in this study, as well as literature, by ensuring the complete breakdown of peroxide into water and oxygen gas.

3.4 Conclusion

The AOPs selected from bench-scale assessment have been re-optimized in order to account for the changes in the brine, including chloramination, which can modify existing phosphorus containing DOC and make it less responsive to treatment. The optimal parameters include a 30 ppm alum pretreatment, which significantly removes phosphorus as well as DOC, both of which improve AOP treatments by limiting interfering compounds that could deplete the oxidants in both the antiscalant free brine and the continuously produced brine, as well as the representative phosphorus compounds. Pretreatment alone achieves 50-60% removal of the phosphorus present in the brine sample; although it is not as effective in the representative compounds, achieving less than 20 percent in the most susceptible species (ATP) and less than 4% in the other two compounds (phenyl phosphate and phosphonate). AOP optimized treatments included 100 ppb Peroxide with and without acidification to pH 2, acidification to pH 2 alone and 50 ppm NaOCl treatment. All treatments were optimized for a contact time of 0.5 hours without mixing, at room temperature and circumneutral pH unless otherwise stated. AOP treatment of the antiscalant-free brine yielded %TP removals of 62-73% and 83-84% in the December 5/12 continuously produced brine. In the representative phosphorus compounds, effectiveness was the direct result of the type of bond present, such that phosphate esters were readily broken, followed by phospho-ester bonds, while phoshonate species were not receptive to oxidation or acid hydrolysis within any appreciable levels.

Conversion of NRP to RP was possible, but not within the goal limits described in the PWQG, unless intense combination treatment was performed using a combination of UV light, 3000 ppm peroxide, heat to 80-90°C and acidification to pH 2. This treatment surpassed the goal in all systems tested except for the phosphonate species, confirming its resistance to oxidation. However, the other systems did achieve 79-94% TP removals, the highest to occur within this project.

Overall, it is evident that AOP treatment can convert NRP to RP effectively and this effectiveness is improved by the application of combination treatments and heat. Further evaluation to determine the minimum heat required should be completed for cost-effectiveness.

Chapter 4: Antiscalants—Contribution of Phosphorus and Effect on AOP Treatment

Abstract—The application of reverse osmosis in wastewater treatment has been utilized to achieve extremely low nutrient levels. However, the various antiscalants available can contribute phosphorus to the RO brine. Excess phosphorus (P) in the environment has the potential to cause eutrophication. Current regulations for sensitive receiving waters are approaching the limit of technology for phosphorus removal and improved methods are required. Existing methods target removal of the orthophosphate form of phosphorus, but to achieve low effluent limits other forms, such as condensed phosphate and organic phosphorus, must be removed as well. Four commercially available antiscalants were evaluated for the contribution and potential interference with AOP treatment in brine. Wastewater was concentrated using a bench-top RO unit and an equivalent dose of each antiscalant was added to the brine. The advanced oxidation processes evaluated were 100 ppb H2O2 for 30 minutes, 50 ppm NaOCl for 30 minutes, pH 2 for 30 minutes, and 100 ppb H2O2 + pH 2 for 30 minutes. The use of chemical addition as a pretreatment was also evaluated. Treatment effectiveness was determined by measuring Residual Total Phosphorus Post AOP Treatment after a subsequent 6 ppm alum treatment (RTPPT). The most effective chemical AOP after a 30 ppm alum pretreatment was 100 ppb peroxide + pH 2 treatment which achieved 66-82% TP removal for the four commercially available antiscalants. Therefore RO can be utilized to concentrate nutrients (whether naturally occurring or contributed by antiscalants) into brine, which can be further treated for nutrient removal.

Keywords: Antiscalant, RO Produced Brine, Advanced Oxidative Processes Chemical Pretreatment

4.1 Introduction

Reverse osmosis uses specialized membranes that employ multiple characteristics, including size and charge rejection, in order to produce an ultra-pure permeate and highly concentrated concentrate or brine. However, in order to produce the concentrate, high concentrations of sparingly soluble salts from the feed water are forced to accumulate at the membrane surface while the ultra-pure water permeates through the pores. When the concentrations exceed the solubilites for the respective salts, precipitation occurs and this can lead to scale formation on the membrane (Ghafour, 2002). Table 4.1 below lists various common scalants and foulants (Ghafour, 2002; Plottu-Pecheux *et al.*, 2002). If left untreated the resultant scales can cause reduced effectiveness of the membrane, increased energy costs and result in lower pressure of the system, this can lead to reduced flow rates, reduced productivity, reduced concentration effectiveness and can result in permeates with higher dissolved ion concentrations and reduced water quality. Scale formation can result in more frequent cleanings, which result in shut downs and replacement of membranes, which are both expensive and inefficient (Ghafour, 2002; Dudley and Baker, PermaCare).

Table 4.1: Common scalants, including chemical formulas and foulants (Dudley and Baker, PermaCare).

Scalant/Foulant	Chemical Formula
Scalants:	
Calcium Carbonate	$CaCO_3$
Calcium Sulfate	$CaSO_4$
Barium Sulfate	$BaSO_4$
Strontium Sulfate	$SrSO_4$
Calcium Fluoride	CaF_2
Foulants:	
Colloidal Particles:	
Silica	SiO_2
Salts of Iron, Manganese and Aluminum	$Fe(OH)_3$, $FeSiO_3$, $Mn(OH)_2$ and $Al(OH)_3$
Organic Matter	
Humic Acid	N/A
Fulvic Acid	N/A
Biological Development	
Biofilms	N/A
Microorganisms	N/A

Scales develop in three key stages, as depicted in Figure 4.1. Stage 1 involves the dissolved ions concentrating at the boundary layer on the membrane-separating surface; as the concentration increases the ions begin clustering—forming proto-nuclei (≤1000 atoms), which with treatment could be easily dispersed. The second stage is marked by the ordering of ions within the ever-growing proto-nuclei, creating nuclei with regular, repeating shapes; again with treatment this stage can be reversed. Scale formation culminates in stage 3, which is markedly irreversible, such that the nuclei grow into crystals, with growth continuing as long as the particular salt is present at concentrations above the solubility (Dudley and Baker, PermaCare).

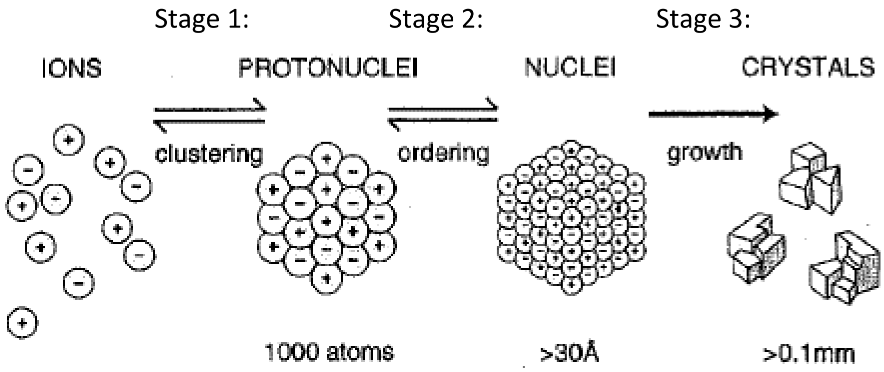


Figure 4.1: Mechanism of scalant formation at the membrane surface. From Figure 1 by Dudley and Baker, PermaCare

The types of scales that result are directly controlled by the quality and source of the feedwater, which can be assessed by chemically evaluating the bulk feedwater and by using the empirically measured Silt Density Index (a measure of water's fouling capacity of RO membranes) (Dudley and Baker, PermaCare). Although all scales form under the same mechanism, their formation is controlled by the specific solubility product, which is directly affected by bulk water chemistry. Bulk water chemistry also helps determine the most appropriate antiscalant to use because it can target the most prevalent scale in the particular system, for example pH control is used only to control calcium carbonate formation (Dudley and Baker, PermaCare), while sodium hexametaphosphate (SHMP) primarily inhibits calcium sulfate, and silica can be removed with increased chemical addition (Al-Shammiri *et al.,* 2000).

In order to prevent the potential issues surrounding the use of RO, antiscalants have been developed as a method to pretreat the feedwater and prevent scale formation (Al-Shammiri *et al.,* 2000). Antiscalants effectively prevent fouling of the membrane and do so by disrupting scale formation in one or more of three particular ways:

1. *Threshold Effect*: Inhibition of precipitation after solubility is exceeded. Prevents stage 1 of scale formation. Examples of antiscalants that employ this method of control are phosphonate-based.
2. *Crystal Distortion Effect*: Distortion of crystal growth, forming irregular crystals, which do not scale well. Prevents stage 2 scale formation. Examples of antiscalants that affect this stage are polyacrylic acids $[CH_2CHCOOH]_n$ (MW= 1,500–2,500).
3. *Dispersancy*: Place charge on crystal surface causing it to repel similar charges and crystal to disperse back into the feedwater. This inhibits the final stage of scale formation. Polymers, such as polyacrylic acid, display this type of affect at high molecular weight.

Common types of antiscalants include sodium hexametaphosphate (SHMP), proprietary and non-proprietary organic compounds, including polymers and phosphonates. Most employ a threshold effect, often coupled with one of the other two effects. Phosphonate-based antiscalants (or “super-threshold effectors”) are very common and effective as they also serve to prevent corrosion, fouling and sequester excess iron from solution, as well as being remarkable stable (Dudley and Baker, PermaCare).

As described, the selection of specific antiscalants should be based on the chemistry of the feedwater and what needs to be controlled; however, when the goal is to control the phosphorus release in the permeate and concentrate, then selection of the most appropriate antiscalant becomes even more important. Based on literature and industry, antiscalants containing phosphorus are common and prevalent, often directly using phosphorus-containing species as the active ingredient (Dudley and Baker, PermaCare). These antiscalants then remain in the brine after RO treatment, and when the objective is to oxidize the NRP to RP present in the brine for subsequent removal to reach ultra-low effluent criteria, the effect of the antiscalants on the contribution of phosphorus, as well as the oxidative process must be evaluated.

4.2 Methodology

Overall the results of Phase 2 confirmed what was observed during Phase 1, but the AOPs needed to be evaluated for the antiscalant-dosed brines. After concentration of the brine, each of the four prospective antiscalants was added in a dose representative of the antiscalant doses at the demonstration facility, approximately 2 mg/L.

4.2.1 Sample Collection, Preparation and Storage

For antiscalant-free brine, wastewater was collected from the influent from the demonstration facility, but after primary filtering and chloramination. The sample was transported in new 5 gallon plastic buckets to the CRA facility in Waterloo for processing. The samples were then microfiltered using a 0.2 micron hollow fiber polysulfone media filter from Siemens UF Hollow Fiber Media Filter Cartridges. After filtration the samples were treated using bench-top reverse osmosis (ROCHEM Model RO RO DT01-H-SS unit) with 10 micron ROCHEM membranes (pre-assembled stack of 10 discs and 9 membranes) and the ROC was concentrated by 80-85% of the volume. 2 sets of grab samples of the secondary effluent, the MF permeate, the RO permeate and the ROC were also taken, one for the WLU lab and one for comparative analysis with Maxxam. The ROC was then deposited into new 5 gallon buckets and delivered to WLU. Upon arrival samples were stored at 4°C until testing. For testing, a 1 L aliquot was removed after the buckets were thoroughly mixed and were refrigerated at 4°C until treatment or analysis

A dose of 10 μL/L of brine was calculated for the Vitec8200, which would approximately contribute the extra 100 ppb of phosphorus that was observed with the brine processed at the demonstration facility. The calculation is below.

Sample Calculation for Vitec 8200

Antiscalant specific gravity (SG): 1.31

TP in antiscalant (AS): 9,688 mg/L

Concentration factor of Brine (ROC): 6.7 (accoμnts for ~85% concentration)

Weight of P in AS: (TP conc. in AS)/ (SG * 1000*1000) = 7.4 μg TP/mg AS

TP concentration in 2 mg AS/L: (2 mg AS/L) * (7.4 μg TP/mg AS) = 15 μg TP/L

Concentration factor = 1/ (1-0.85) =6.7

TP in ROC: 15 *6.7 = 98 μg TP/L

Volume of Antiscalant to add: ((0.098 mg P/L * 1L)/9866 mg P/L)*(1x10^6) = 10 μL

This same 10 μL/L of brine dose was used for the SpectraGuard and the Protec RO so that the differences between the doses would only be the factor contributing phosphorus. These antiscalant-dosed brines will be prepared and allowed to incubate overnight to ensure any reaction or interaction that would take place between the antiscalant and the brine would have occurred. The various commercially available antiscalants evaluated are liseted in Table 4.2.

Table 4.2: Commercially available antiscalants and antifoulants evaluated during Phase 2, Manufacturer and acquirement.

Antiscalant/Antifoulant	Manufacturer	Company Location	Method of Aquirement
SpectraGuard	Professional Water Technologies Inc.	La Mirada Court, Vista, CA	Donated by Company
Protec Ro	Protec Arisawa	Internationally Based	Donated by Company
Vitec 8200	Avista Technologies,	San Marcos, CA, USA	Provided by Demonstration Facility
Vitec 4000	Avista Technologies,	San Marcos, CA, USA	Provided by Demonstration Facility

The antiscalant-dosed brines will then be treated with a 30 ppm pretreatment of alum before being treated with each of the four selected advanced oxidative processes (AOP) optimized in Chapter 3 and described in Table 4.3. The brines were treated after a 30 ppm pretreatment with alum followed by filtration through a 0.2 µm filter.

There were two sampling dates involved in the described tests September 7/12 and February 15/13.

4.2.2 Advanced Oxidation Treatments

For the evaluation of antiscalants effects on AOPs, the four AOPs tested are outline in Table 4.3.

Table 4.3: AOPs selected from Phase 1 and optimized in Phase 2. AOP conditions, including dose, contact time and use of quencher or neutralization

	Dose	Contact Time	Quenching or Neutralization
Hydrogen Peroxide	100 ppb	0.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:2.8 ppm)
NaOCl	50 ppm	0.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:1.12 ppm)
pH 2	N/A	0.5 hrs	Neutralized to pH 7
Hydrogen Peroxide at pH 2	100 ppb	0.5 hrs	Quenching with Metabisulfite (Ratio of peroxide to quencher 1 ppm:2.8 ppm)

*All treatments performed at room temperature without mixing

These four AOPs were applied to antiscalant-dosed brine produced by bench-top RO concentration of influent after chloramination from the demonstration facility. AOP evaluation occurred by treating 100 mL of unfiltered brine, quenching or neutralizing the reaction with sodium metabisulfite (Sigma-Aldrich, ≥99%) and NaOH (Sigma-Aldrich, 99%) then removing 5 mL aliquots in triplicates for TP analysis and treating the remaining volume with varying doses of alum for 20 minutes at room temperature with moderate mixing. These samples were then filtered using a 25 mm Syringe filter with a 0.2 µm polyethersulfone membrane (VWR International); 5 mL aliquots were removed in triplicate for RTP_{PT} analysis.

4.2.3 Sample Analysis

All colorimetric analysis was performed following standard methods (4500-PE.) using freshly made (daily) 0.05 mg P/L and 0.1 mg P/L from a 1000 mg P/L stock solution of KH_2PO_4 (BDH, ≥99%); blanks and standards were measured in duplicate, while samples were measured in triplicate. The mixed reagent for colourimetric phosphorus analysis was prepared and added to duplicate blanks and standards and triplicate samples in 3 minutes intervals and incubated for 30 minutes before being measured. Samples were measured, starting with the blanks and standards by pipetting a small amount into the cell with a Pasteur pipette to rinse the cell, and then the cell was filled with the sample; this was repeated between each blank, standard and sample. The sample was then placed into the cell holder and absorbance was measured using a Cary 50 UV/Vis Spectrometer (dual beam instrument) and the associated Simple Reads Program with a 10 cm path length cell holder adapter and a 10 cm quartz cell (Starna Cells) at 835 nm with a 1.000 second total exposure. Each sample was evaluated for 1 minute, with absorbance readings being taken every 10 seconds to ensure the sample was stable and fully developed. The absorbance values were the imported into Excel, the blanks and standards were used to produce a standard curve and Beer's Law was used to calculate the concentration of orthophosphate in the sample in mg P/L.

4.2.4 Quality Control and Quality Assurance

Quality control and assurance was performed using sodium phenyl phosphate as a representative organic phosphate compound. This compound contains a COP bond and is commonly used in assurance tests for total phosphorus analysis and monitors the conversion efficiency of the persulfate digestion. The lowest acceptable conversion efficiency that was allowed was 95%, while the high end was 105%; outside this range the experimental for that particular analysis was not considered.

4.3 Results and Discussion

4.3.1 Antiscalants and Cleaning Chemicals Contribution of Phosphorus

The observed increase in phosphorus concentration in the brine containing antiscalant from the demonstration facility, as demonstrated in Chapter 3, suggested the presence of phosphorus in both the antiscalant and cleaners, this in turn lead to direct testing to determine the exact phosphorus concentration. Various antiscalants and cleaners were tested to determine which had the lowest phosphorus content. The chemicals tested included Vitec 8200 and 4000 (both dispersants), SpectraGuard (a dispersant) (the antiscalants), and Protec RO (primarily an antifoulant) and the cleaners RO Clean L211 and L403; the results are presented in Figure 4.2. Concentrations of phosphorus are described in Table 4.4.

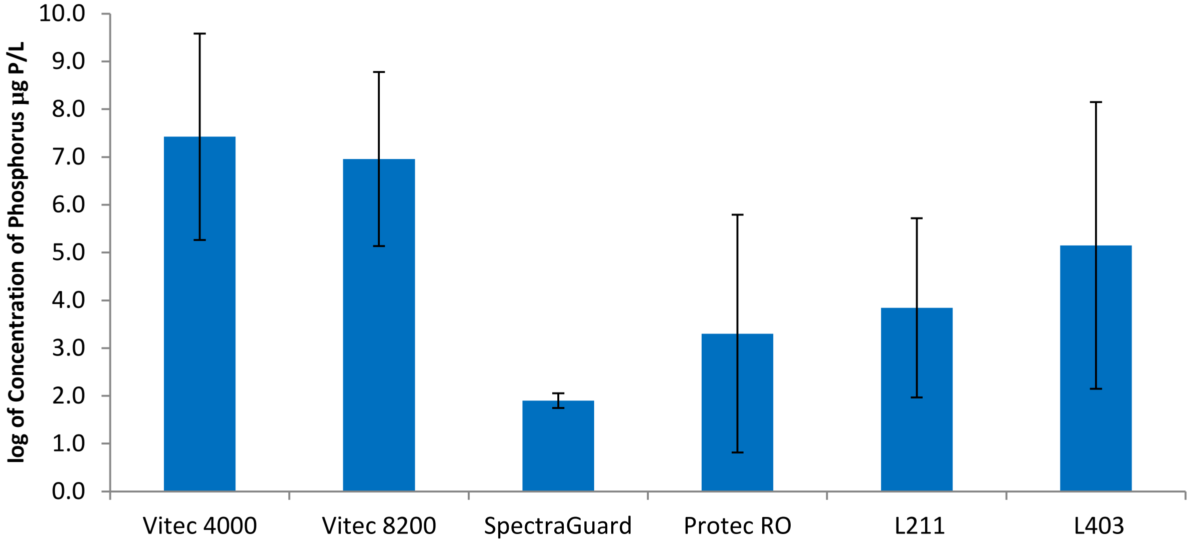


Figure 4.2: Concentration of total phosphorus in cleaners and antiscalants used at the demonstration facility. Log(concentration of phosphorus). L211 and L403 are cleaners produced by the providers of the Vitec8200 and V400 antiscalants. Phosphorus concentration reported in µg P/L. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples

Vitec8200 was used at the facility throughout the first 6 months of demonstration scale testing, although the data suggests that SpectraGuard has the lowest phosphorus. SpectraGuard was used during the fall 2012, but it was not as an effective antiscalant compared to Vitec8200; in December the antiscalant was changed to Vitec4000 for the remainder of the study. Protec RO was never applied in the demonstration facility.

Table 4.4: Concentration summary for the antiscalants without dilutions ± standard deviations

Antiscalant Evaluated	Concentration of P
Spectraguard	80 +/- 0.7 µg P/L
Vitec 8200	9688 +/- 7 mg P/L
Vitec 4000	28 350 +/- 40 mg P/L
Protec	2000 +/- 307 µg P/L

The contribution of antiscalants and cleaners in RO brine is inevitable for a continuously running facility, which means the additional phosphorus contributed by the antiscalants is also unavoidable; however, the selection of particular antiscalants can minimize this addition, as is observable in Table 4.4. SpectraGuard and Protec RO are marketed as phosphorus free, and based on the concentration of these two antiscalants, the additional phosphorus contributed would be minimal if not negligible. The two Vitec products, on the other hand, contribute a significant amount of phosphorus to the system, despite the marketed claim that Vitec8200 is phosphate and phosphonate free. Performing calculations for the first three antiscalants to determine the contribution of phosphorus made by each, considering chemical characteristics, concentration factors in brine production and recommended dosages for each product, Table 4.5 summarizes these values.

Table 4.5: Contribution of Phosphorus by each antiscalant considering dosages, constants and concentration factors

Antiscalant	Unit	Vitec 8200	SpectraGuard	Vitec 4000
TP content	mg/L	9,688	0.08	28,350
Specific Gravity of Antiscalant	-	1.31	1.04	1.10
Antiscalant Dose	(mg/L)	2	2.7	2
Concentration factor		6.7	6.7	6.7
Mass of TP in the Antiscalant	(µg/mg)	7.4	0.00008	26
TP concentration added to the RO feed by Antiscalant	(µg/L)	15	0.000208	51
TP in ROC added by Antiscalant	(µg/L)	98	0.0014	344

The Vitec products both increase phosphorus concentrations dramatically in brine, with Vitec 8200 causing a factor of 2 increase, and Vitec 4000 producing a factor of 3 increase, while the contribution made by SpectraGuard is negligible. The trends in additional phosphorus can be observed in the mass balance data for the weekly samples monitoring the demonstration facility's performance, which is presented in Appendix C.

During Phase 2 the removal efficiency of chemical addition was evaluated on continuously produced brine from the demonstration facility (Chapter 3.3.2). This demonstrated that the NRP contributed by the antiscalant could be removed by chemical addition to a certain degree; however the potential for interaction between the antiscalant contributed P and the organic compounds in the brine was not known. Therefore the ability to remove the antiscalant NRP in the absence and presence of DOC needed to be determined.

The removal of the excess NRP, however, is only relevant in the Vitec antiscalants because the other two antiscalants contribute insignificant amounts of NRP and therefore was performed using only Vitec 8200 and 4000. This removal was evaluated using prepared antiscalant in Milli-Q water that was salted-up to the salinity of brine using NaCl. The antiscalants were then dosed with alum at 6, 15, 30 and 50 ppm for 1 hour with mixing, followed by a 0.2 µm filtration, to observe the effects on removal. This was repeated in the presence of DOC that was added to a concentration of 10 mg C/L from a known DOC concentrate from South Hampton. The results are displayed in Figure 4.3 and 4.4.

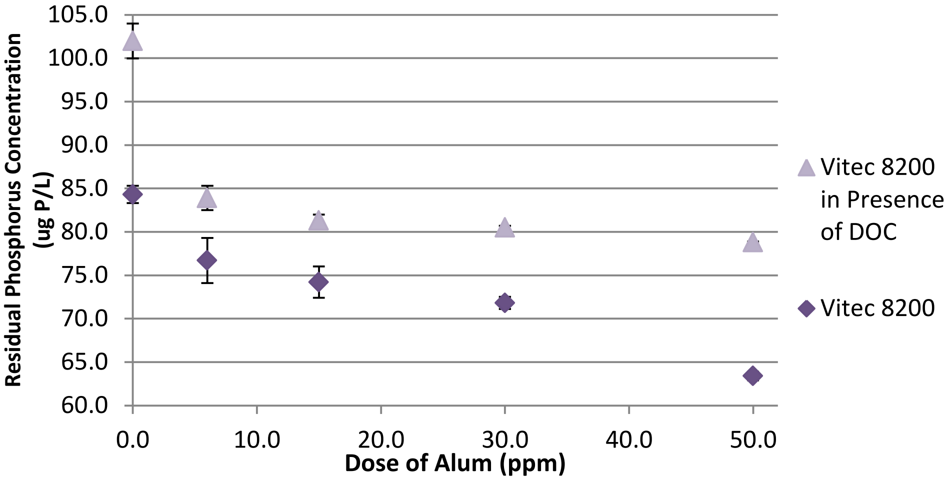


Figure 4.3: Dose dependence of NRP removal from Vitec 8200 in the presence and absence of DOC by chemical addition. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples

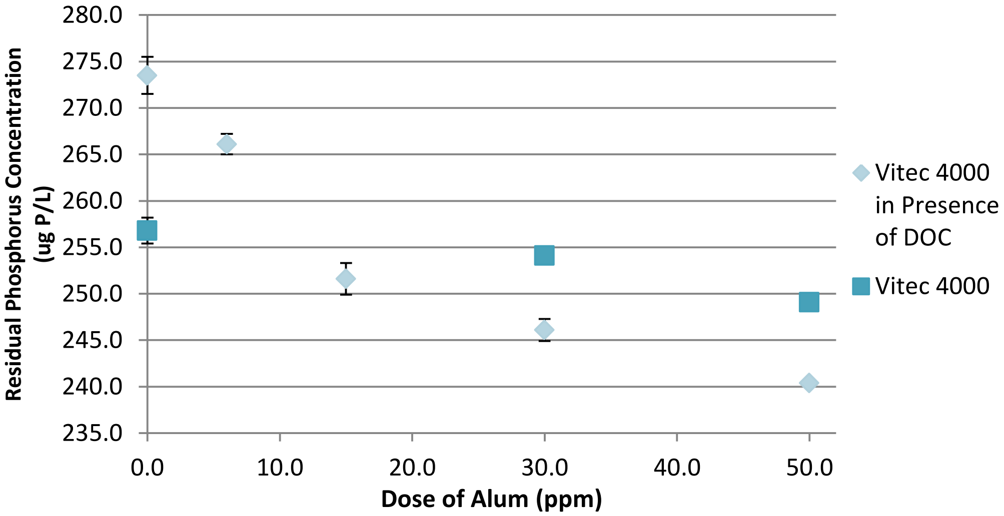


Figure 4.4: Dose dependence of NRP removal from Vitec 4000 in the presence and absence of DOC by chemical addition. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples

The results of the chemical addition tests suggest that in the presence of DOC both Vitec 8200 and 4000 demonstrate dose dependent removal, but not to the extent that is observed in the antiscalant-dosed brine. In the absence of DOC Vitec 8200 underwent a 21 ppb P removal for the 50 ppm alum treatment, which is a 25% TP removal, however, Vitec 4000 after 50 ppm alum treatment only decreased in percent TP by 3%, which is equivalent to a 8 ppb P removal. In the presence of DOC, %TP removals increase for Vitec 4000 to 12%, which is an increase in percent TP removal by a factor of 4. Vitec 8200, actually saw a decrease in TP removal by 2%, but it is important to acknowledge that the South Hampton DOC source did contribute phosphorus, approximately 20 ppb P, which most likely contributed NRP that couldn't be removed by chemical addition alone. The decrease in RTP observed between the untreated Vitec 8200/4000 without DOC and the 50 ppm alum treated with DOC was 5.5/16.6 ppb P, so removal due to the association with the DOC by the antiscalant contributed P is likely, but does not account for the percent TP removals observed in the antiscalant brine by alum addition—for 30 ppm alum resulted in 69% and 78% for Vitec 8200 and 4000, respectively. Therefore there is likely another contributing factor, such as potential interactions with other cations or conversion occurring within the brine during production that increases the ability for alum to remove the antiscalant contributed P and thus contributes to the high percent TP removals observed in the antiscalant brines.

4.3.2 Effect of Antiscalants on AOP Treatment

After determining that antiscalants can be significant contributing sources of phosphorus in brine and that P contributed by antiscalants can interact with DOC and other unknown components of the brine, the ability of the AOP treatments to convert the NRP of the antiscalants to RP for chemical removal had to be evaluated in order to determine which antiscalant would be best to proceed with. The other major issue that the antiscalants present is more DOC, which can be oxidized instead of the NRP, thus depleting the oxidant and reducing the effectiveness of the treatment.

The AOPs, under the new parameters as determined in Phase 2 and outline in Table 4.3, were evaluated on antiscalant-dosed brine, which was prepared in lab using the antiscalant concentrate and the September 7/12 antiscalant-free brine (produced in Waterloo) as described in the methodology.

Each of the antiscalant-dosed brines, SpectraGuard, Protec RO, Vitec 8200 and Vitec 4000 were evaluated in the same manner as the brine, including performing RTP_{CA} recoveries after each AOP treatment. The results of the four AOP tests on the four antiscalant-dosed brines are displayed in Figure 4.5a-d.

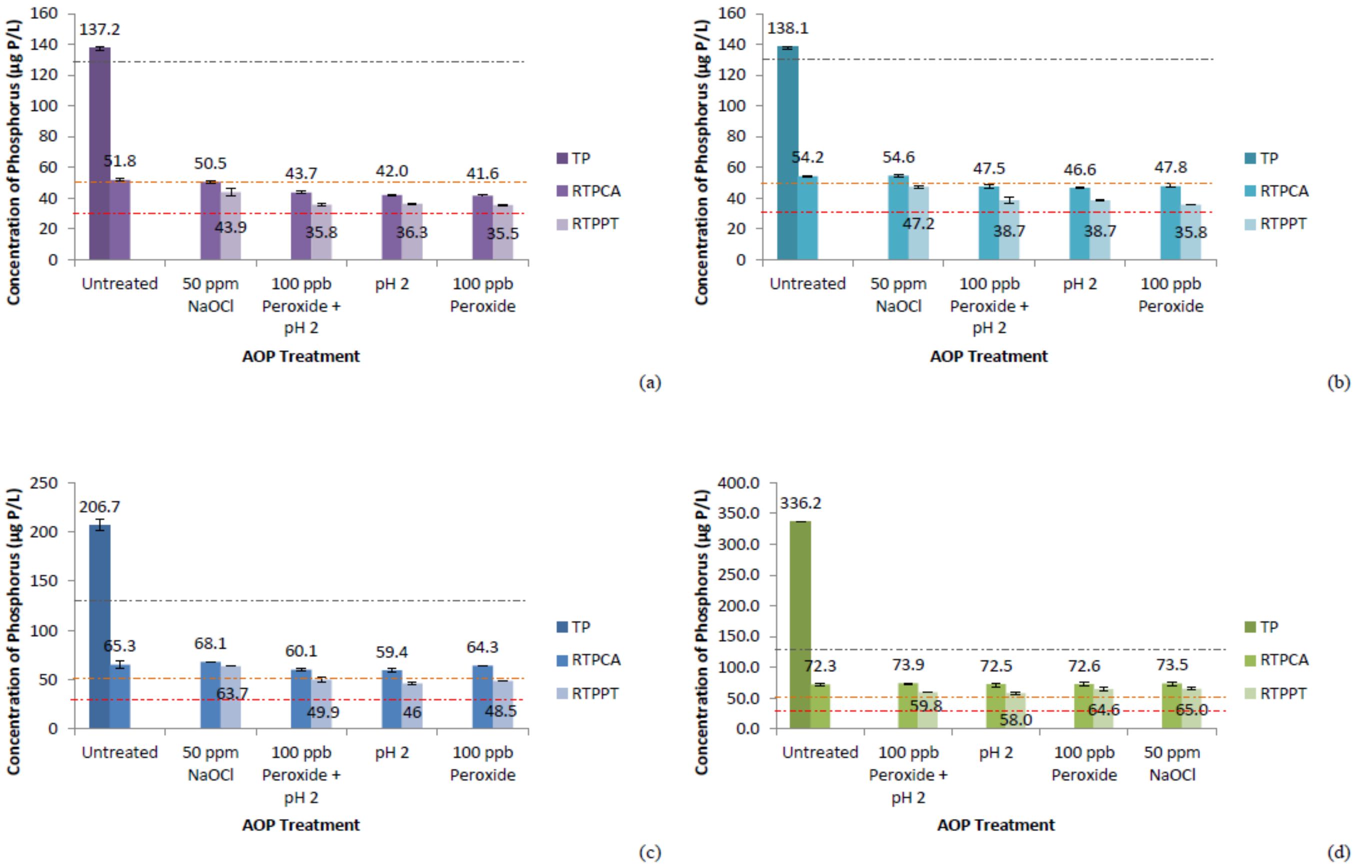


Figure 4.5a-d: (a) SpectraGuard, (b) Protec RO, (c) Vitec 8200 and (d) Vitec 4000. Selected AOP treatments under optimal parameters performed on antiscalant- dosed brines (2 mg AS/L). RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples. Grey dashed line represents the TP for antiscalant-free brine , Orange dashed line represents RTP_{CA} for the antiscalant-free brine and the Red dashed line represents the goal RTP limit of 30 ppb P as stated in the PWQG

The comparison of the four evaluated antiscalants is presented to include the TP of the antiscalant-free brine (130 ppb P), as the grey dashed line, and thus show the contribution of TP made by the antiscalant at the 2 mg AS/L dose. Similarly the orange dashed line represents the RTP_{CA} for the antiscalant-free brine (50 ppb P), and thus the antiscalant contribution of NRP that remains after 30 ppm alum chemical pretreatment. The red dashed line demonstrates the RTP goal according to the PWQG of 30 ppb P. As is observed from Figure a and b, the contribution of phosphorus by SpectraGuard and Protec RO is minimal, and the addition is easily removed using the 30 ppm alum pretreatment, as is observed by the negligible difference between the RTP_{CA} of the respective untreated antiscalants and the orange dashed line representing the RTP_{CA} of the antiscalant-free brine. The Vitec antiscalants, however, contribute significant amounts of phosphorus, with Vitec 8200 adding approximately 80 ppb P to TP and 15 ppb P to RTP_{CA}; likewise, Vitec 4000 contributes 200 ppb P to TP and 23 ppb P to RTP_{CA}. This corresponds to a 62% and 154% increase to TP and a 30% and 46% increase to RTP_{CA} for Vitec 8200 and 4000, respectively. The additional phosphorus contributed by the antiscalants is no doubt coupled with the addition of DOC, which will reduce the effectiveness of the AOP treatments because the organics will be competitively oxidized. As well, the likelihood of the proprietary compounds within the antiscalants containing a phosphonate is high, as phosphonates are commonly used antiscalants, as previously discussed.

Conversion of NRP to RP in SpectraGuard and Protec RO are very comparable to the conversions observed in the antiscalant-free brine, confirming the observation that these two antiscalants do not contribute a significant amount of phosphorus and in addition do not contribute a significant amount of DOC that competes for oxidation. For SpectraGuard, Protec RO and Vitec 8200, the RTP_{CA} recoveries performed after AOP treatment are comparably different than that observed in the untreated antiscalant brine and therefore will be compared using equation 7 to show percent TP removal, as well as equation 8 to show percent removal after pretreatment. Vitec 4000, however, achieved RTP_{CA} recoveries that are comparable to the RTP_{CA} for the untreated Vitec 4000, and therefore can be described using %TP removal only.

Alum pretreatment alone achieves significant removals in all of the antiscalant brines, with RTP_{CA}s achieving %TP removals of 62%, 61%, 68% and 78% for SpectraGuard, Protec RO and Vitec 8200 and 4000, respectively.

4.3.2.1 50 ppm Hypochlorite

As has been observed throughout Phase 1 and 2 of the project, oxidation using 50 ppm hypochlorite has been the least effective of the four selected AOPs, but it is the highest dosed chemical. For SpectraGuard and Protec RO, treatment with hypochlorite achieved %TP removals of 63% and 66%, while the two Vitec chemicals reached 67% and 81% for 8200 and 4000, respectively. Percent removal above RTP_{CA} for SpectraGuard, Protec RO and Vitec 8200 achieved 13%, 14% and 6%, respectively. These values demonstrate that hypochlorite is equally effective in SpectraGuard and Protec RO, but is almost ineffective in converting NRP to RP in Vitec 8200. In Vitec 4000, a 10% decrease in RTP_{CA} was observed between untreated and treated samples, which falls between the conversions observed in the other three antiscalants. This suggests that there is a chemical difference between the proprietary formulations of the Vitec compounds; this is confirmed by evaluating the product sheets that compare the antiscalant abilities for various scalants and foulants. The ineffectiveness of the hypochlorite treatment is likely due to the increased DOC, which is likely easier to oxidize by this AOP treatment, which supports the use of hypochlorite as a clarifying agent within treatment facilities.

As well, the chloramination of the brine possibly causes modifications to the DOC already present in the brine and if phosphorus is associated with the modified DOC, then removal would be increasing difficult. It is also possible that the antiscalants could contribute ammonia to the system and if this occurred than this would increase the free chlorine demand of the antiscalant brine and would competitively reduce the hypochlorite present as chloramines are formed.

If the absolute values are discussed and the conversions are compared to the red goal line, than hypochlorite as an AOP treatment is ineffective at achieving the goal regardless of which antiscalant is present, but achieves similar RTP_{PT} values as the antiscalant-free brine when SpectraGuard and Protec RO are used.

Overall, when comparing the %TP removals for the antiscalant brines as compared to the antiscalant-free brine, SpectraGuard and Protec RO achieve the same conversion of NRP to RP and therefore do not affect oxidation using hypochlorite. The two Vitec compounds do significantly reduce the effectiveness of conversion using hypochlorite in an absolute sense, likely due to the contribution of DOC and TP to the brine. Therefore, these two antiscalants reduce the effectiveness of AOP treatment of brine by resulting in higher RTP.

4.3.2.2 100 ppb Peroxide

Treatment of the antiscalant brines with 100 ppb peroxide yielded the third best results when comparing the increase in RTP removal using equation 8. Similarly as was observed in hypochlorite, SpectraGuard and Protec RO did not affect the AOP treatments, and the respective conversions were observed, %TP removals of 70% and 69%, and increase in RTP removals above RPT_{CA} of 15% and 25%. This confirms what has been observed throughout testing with AOPs, and achieves similar results as compared to the antiscalant-free brine (69% and 13%). This does suggest that Protec RO contributed phosphorus is slightly more susceptible to oxidation than that contributed by SpectraGuard, due to the AOP being the most effective in the Protec RO brine. The two Vitec compounds, on the other hand, react very differently to peroxide oxidation, such that Vitec 8200 achieves a %TP removal of 69% and an increase in RTP removal of 25%, similar to the conversion effectiveness observed in SpectraGuard and Protec RO, but Vitec 4000 only achieves a %TP removal of 81%, which corresponds to an increase in RTP removal of only 11%. Therefore the chemical differences between these two compounds are again observed.

If the absolute values are regarded it appears that peroxide achieves RTP_{PT} values that are very close to the red goal line of 30 ppb P, but does not reach it. However, when compared to the RTP recoveries it seems that peroxide treatment affects RTP recovery, which is also consistent throughout AOP evaluation on the various brines and compounds tested.

The ability of peroxide to oxidize DOC is also well studied and therefore the DOC already present in the brine, as well as that added by the antiscalant, likely are limiting factors to the effectiveness of peroxide treatment. It is also likely that some of the converted RP could interact with the peroxide to form peroxyphosphates, which was observed in Phase 1 and Phase 2. The radicals produced in the destruction of perioxide also could cause DOC to form radicals or expose other functional groups that could then bind the converted RP. All of these are likely reasons for the reduced effectiveness of peroxide in the two Vitec antiscalants.

Therefore, peroxide maintains its conversion effectiveness in the SpectraGuard and Protec RO antiscalant brines, achieving %TP removals that are comparable to those observed in the antiscalant-free brine and thus suggest that these antiscalants do not interfere with AOP treatment. The Vitec compounds do reduce conversion effectiveness, and even though they achieve similar %TP removals, they do not allow a significant increase in %TP removal after the initial chemical addition and result in higher measured RTP.

4.3.2.3 100 ppb Peroxide at pH 2

The use of 100 ppb peroxide at pH 2 has been equally as effective as pH 2 alone throughout Phase 2, but was slightly more effective during the initial Phase of study, although the results were comparable. The successfulness of this treatment is likely the result of acid catalyzed hydrolysis of phosphate-ester and phospho-ester bonds, which are present in the DOC. The ability to distinguish these types of bonds results from the work with representative phosphorus compounds in Chapter 3.

Treatment with peroxide and acid yielded conversions similar to that observed in antiscalant-free brine for SpectraGuard and Protec RO, achieving %TP removals of 68% and 66%, while attaining decreases in RTP beyond that caused by chemical addition alone of 18% and 19%, respectively. The effectiveness of the AOP treatments are conserved in the presence of the antiscalants, SpectraGuard and Protec RO, such that the absolute removals are also comparable to antiscalant free brine, with

SpectraGuard achieving 35.8 µg P/L and Protec RO reaching 38.7 µg P/L, which are close to, but do not exceed, even with standard deviations, the goal of 30 ppb P as suggested by the PWQG.

The Vitec compounds react similarly, reaching the highest %TP removals with acid with and without acidification. Vitec 8200 and 4000 achieve %TP removals of 71% and 82%, which is an increase of 17% and 19% above RTP_{CA} of the untreated antiscalant- dosed brine. The effects of these antiscalants do not appear to interfere with this AOP treatment, however, the absolute RTPs for these compounds are almost double that which is acceptable by the PWQG, and only account for an increase in 3% and 4%, respectively, when looking at %TP removals for the treated and untreated compounds. It is likely that these compounds do not contain the more easily hydrolyzed bonds, but could contain phosphonate bonds, making these compounds more resistant to oxidation.

Overall, peroxide in acidic conditions is as effective in the presence of SpectraGuard and Protec RO as it is in antiscalant-free brine, achieving similar absolute RTP_{PT}s, which are almost reaching the goal of 30 ppb P. The Vitec compounds, although most susceptible to this treatment as compared to the previously discussed AOPs, do not achieve comparable %TP increases with treatment and therefore inhibit the AOPs by contributing excess phosphorus containing species, which are potentially very resistant to hydrolysis or oxidation, or by contributing excess DOC, which prevents targeted hydrolysis or oxidation on the phosphorus containing species.

4.3.2.4 Acidification to pH 2

Acidification is comparable to peroxide at pH 2, often reaching similar conversions and absolute RTP_{PT}s in the antiscalant-free brine. This is likely a result of the ability to catalyze hydrolysis reactions, which as suggested by the representative phosphorus compounds, including ATP and phenyl phosphate, is possible when phospho-esters and phosphate esters occur in the compounds.

SpectraGuard and Protec RO antiscalants again prove to not affect AOP treatment at pH 2, achieving %TP removals comparable with those observed in antiscalant-free brine, reaching 69% and 66%. These %TP removals correspond to decreases in RTP of 14% and 17%, respectively, which are directly comparable to the 73% TP removal and 17% RTP decrease observed in the antiscalant-free brine. The absolute RTPs reached are 36.3 and 38.7 µg P/L, which, although does not reach the goal of 30 ppb P for the RTP, do reach RTPs that are reasonably close.

The Vitec compounds achieve results that are also comparable to those observed by peroxide and acid, with Vitec 8200 attaining a %TP removal of 71%, while Vitec 4000 achieves 83%. These improvements account for a RTP decrease in 23% and 20% for the two respective compounds, however, this only accounts for increases in %TP removal of 3% and 5% when compared to the RTP_{CA} in the untreated antiscalant-free brine. The ability to have a greater effect on %TP removal of Vitec 4000 for acid with and without peroxide suggest that Vitec 4000 might have a greater number of hydrolysable bonds than Vitec 8200, however the difference is not likely significant.

Therefore this final treatment confirms that none of the selected AOP treatments are affected by SpectraGuard or Protec RO, as the conversions observed are conserved between these antiscalants and the antiscalant-free brine. This however, is not the case for the Vitec compounds, which both obviously reduce the effectiveness of the AOP treatment, such that absolute RTP_{PT}s are twice as high in the antiscalant-free brine, and do not begin to reach the goal of 30 ppb P.

4.3.3 An Alternative Option

As was determined during both Phase 1 and Phase 2, using a multi-combination treatment permits an RTP_{PT} below the suggested goal of 30 ppb P from the PWQG for antiscalant-free brine, as well as a variety of representative phosphorus compounds, including the highly stable phosphonate bond. This treatment utilizes a Metrohm UV Digester with 3000 ppm peroxide at pH 2 and 80-90°C for 1 hour. Although, this treatment is extreme, its application in wastewater treatment is possible within engineering possibilities. The application of this treatment on antiscalant brine, after a 30 ppm alum pretreatment yielded the following removals, depicted in Figure 4.6.

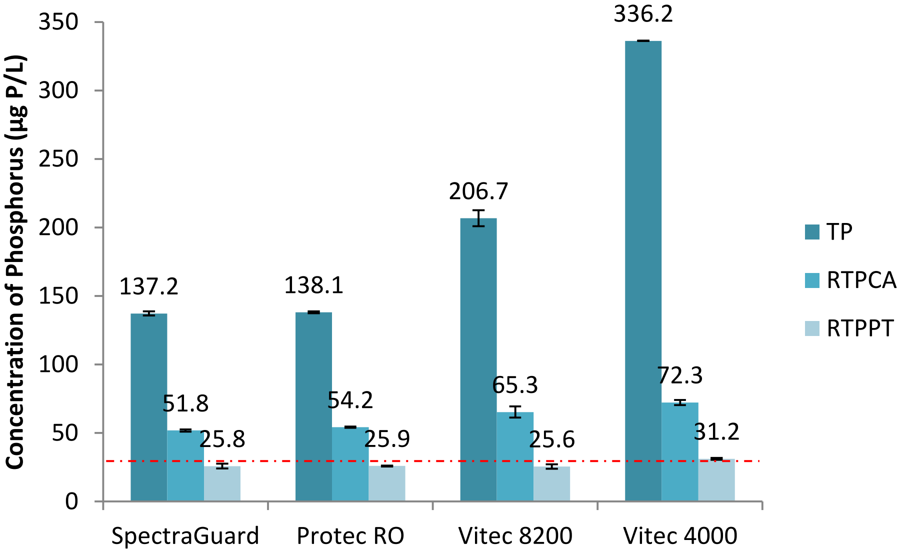


Figure 4.6: Effect of using the Metrohm UV Digester with 3000 ppm peroxide at pH 2 and 80-90°C for 1 hour on conversion of NRP to RP in the four evaluated antiscsalants. All samples are 30 ppm alum pretreated; RTP_{CA} and RTP_{PT} both measured. RTP presented in µg P/L. Error bars are standard deviations for the triplicate samples. Red line represents the goal of 30 ppb RTP as determined by the PWQG.

The use of this multi-combinational treatment successfully reaches the goal of 30 ppb P RTP within standard deviation, and surpasses for three of the four antiscalants. This is likely possible because of the application of heat on the brine, which would help increase the effectiveness of the treatment and allow conversion of the more difficult NRP species, as is observed in the application of this treatment on the stable phosphonate species. In fact the RTP_{PT} for the phosphonate species evaluated in Chapter 3 is very similar to that achieved in the Vitec 4000 antiscalant brine, suggesting that this proprietary compound might contain a phosphonate, which are common in antiscalants due to the inherent stability of the bond.

The percent TP removals observable for all antiscalants were 81%, 81%, 88% and 91% for SpectraGuard, Protec RO, Vitec 8200 and Vitec 4000, respectively. These %TP removal are comparable to those observed in the antiscalant free brine, as well as the Dec 5/12 continuously produced brine, which confirms that SpectraGuard and Protec RO do not contribute, nor effect AOP treatment; as well as the presence of Vitec 4000 in the Dec 5/12 brine. The most notable difference between the AOP evaulations previously performed on the antiscalant- dosed brines is the effect of the multi-combinational treatment on Vitec 8200, which reaches absolute RTP_{PT} values that are comparable to those achieved in the antiscalant-free, SpectraGuard and Protec RO brines. It is likely that this compound does not contain phosphonate species, and thus does not contribute those to the brine, which is probable as Vitec 8200 is marketed as phosphonate free.

Therefore using any of the studied antiscalants, as well as this aggressive AOP treatment using Metrohm UV Digester with 3000 ppm peroxide at pH 2 and 80-90°C for 1 hour reaching the PWQG is possible. This confirms the overall effectiveness of this combination treatment on any type of phosphorus containing species and the ability to effectively convert NRP to RP for subsequent removal. The application of this technology would allow for effluent limits to surpass current goals for highly sensitive systems and would be useful in future to ensure limits are maintained for impacted areas.

4.4 Conclusion

Overall, the contributions of phosphorus from selected antiscalants were evaluated, and confirmed comparing doses utilized in the demonstration facility. It was determined that antiscalants that are marketed as phosphorus free do contain phosphorus, but as in the case of SpectraGuard and Protec RO, the concentration contributed for the corresponding required dose of the antiscalant does not significantly contribute phosphorus to the ROC. Vitec 8200, which is marketed as phosphonate free, is likely free of this type of phosphorus containing species, but does contribute a significant amount of phosphorus to the system; however, the most phosphorus is contributed by Vitec 4000.

The optimized parameters determined on antiscalant-free brine were found to be still applicable in the presence of antiscalants. SpectraGuard and Protec RO did not significantly contribute phosphorus or DOC that interfered with the AOP treatments, which allowed for conversion effectiveness to be conserved in the presence of these antiscalants. SpectraGuard had %TP removals of 63-70%, while Protec RO achieved percent TP removals of 65-69%; both of which agree with that observed in antiscalant-free brine. Similar absolute RTP_{PT}s were also observed for the antiscalants, SpectraGuard and Protec RO brines, which also confirms the effectiveness; however, in neither instance was the goal of 30 ppb P RTP ever reached using the four selected AOPs that were optimized in Phase 2. Vitec 8200 and 4000, reduced the effectiveness of AOP treatment, and although %TP removals of 81-83% were observed, the increase beyond that which was removed by chemical addition alone was not substantial.

The use of the multi-combinational treatment, however, did result in achieving the goal of 30 ppb P for all antiscalants, within standard deviation, suggesting that this treatment could be used to oxidize even the most stable phosphorus bond in phosphonates and reach required levels. This treatment achieved the highest removals, reaching 81-91%, which agrees with those observed in the antiscalant-free brine and the continuously produced brine. If this AOP combination could be implemented within a treatment facility than reaching the effluent limits would be possible.

Chapter 5: Project Conclusions

The evaluation of the potential application of AOPs on RO concentrate as a quaternary treatment for the effective reduction of phosphorus from wastewater was successfully performed and can provide insight into the long term management strategy developed under the UYSS EA for treatment of ROC for phosphorus removal such that is could be blended with ROP for surface discharge.

The mass screening of the AOP treatments that occurred during Phase 1 of the project resulted in the selection of three independent AOPs and one combination AOP. These were selected as the most effective lowest cost alternative; the effectiveness would also be compared to an extreme multi-AOP treatment throughout the phases. The selected AOP treatments, %TP removal effectiveness and average residual total phosphorus after treatment and subsequent chemical addition (6 ppm alum) were as follows: 10 ppm NaOCl at room temperature for 0.5 hrs, which resulted in %TP removals of 38% and an RTP_{PT} of 36 ± 1.0 µg P/L; 100 ppb H_2O_2 at room temperature for 1.5 hrs, which achieved %TP removals of 37% and an RTP_{PT} of 34 ± 14 µg P/L; acidification to pH 2 at room temperature for 1.5 hrs, which reached 61% TP removal and an RTP_{PT} of 24 ± 1 µg P/L, while the best combination treatment utilized 1 ppm H_2O_2 at pH 2, achieving 69% TP removal and an RTP_{PT} of 19 ± 3 µg P/L . The multi-combination treatment utilizing photolysis and 3000 ppm peroxide at pH 2 and 90°C for 1 hour, yielded the highest conversions and subsequent removals of phosphorus such that an 85% TP removal and an RTP_{PT} of 9 ± 1 µg P/L were achieved.

Phase 2 optimized the most successful treatments selected from Phase 1 on 30 ppm alum pretreated bench-top RO produced brine generated from MFP from the demonstration facility, without antiscalant present, but after chloramination to determine the effects of chloramaination on AOP treatment. The optimization resulted in the following AOP treatments: 100 ppb H_2O_2 for 30 minutes, 50 ppm NaOCl for 30 minutes, pH 2 for 30 minutes, and 100 ppb H_2O_2 + pH 2 for 30 minutes. The optimized AOPs performed on antiscalant-free brine resulted in treatment effectiveness ranging from 62-

73%, with the most effective AOP after a 30 ppm alum pretreatment being 100 ppb peroxide + pH 2 treatment which achieved 73% TP removal.

Phase 2 also applied the optimized AOPs to bench-top RO produced brine dosed at industrially relevant calculated doses with one of the four evaluated antiscalants, SpectraGuard, Protec RO, Vitec 8200 and Vitec 4000. These antiscalant-dosed brines were evaluated to determine the effect of antiscalant on phosphorus contribution and AOP treatment after a pretreatment of 30 ppm alum. The antiscalant-dosed brines were treated most effectively by the 100 ppb peroxide + pH 2 treatment, achieving 66-82% TP removal for the four commercially available antiscalants. SpectraGuard and Protec RO did not significantly contribute phosphorus or DOC that interfered with the AOP treatments as compared to the antiscalant-free brine, which allowed for conversion effectiveness to be conserved in the presence of these antiscalants. Vitec 8200 and 4000, which both significantly contributed phosphorus, reduced the effectiveness of AOP treatment, and although %TP removals of 81-83% were observed, the increase in %TP removal beyond that which was removed by chemical addition alone was not substantial.

Lastly, Phase 2 applied the optimized AOP treatments on continuously produced RO brine from the RO unit at the demonstration facility containing antiscalant (Dec 5, 2012 ROC) in order to mimic the application of the treatments in a fully operational facility. In the continuously produced brine %TP removals of 84% were observed in three of the four AOPs, while 83% TP removal was observed for NaOCl.

As was observed in Phase 1, the multi-combination treatment utilizing photolysis and 3000 ppm peroxide at pH 2 and 90°C for 1 hour, achieved the highest conversions and subsequent removals of phosphorus throughout Phase 2. The application of this treatment to the antiscalant-free brine, to the four antiscalant-dosed brines and to the continuously produced brine resulted in 83%, 94% and 81-91% TP removals, respectively.

The removals that resulted from the multi-combination treatment resulted in RTP_{PT}s below 20 ppb P for the antiscalant-free and continuously produced brines and below the goal of 30 ppb for each of the antiscalant-dosed brines, with the exception of Vitec 4000 which reached 31 ppb RTP_{PT}. The goal of 30 ppb P RTP was not achieved in any of the individual or the combination AOPs; however, RTP_{PT} values of below 35 ppb P were achieved for all treatments within standard deviation except NaOCl in the antiscalant-free brine. With the exception of SpectraGuard, none of the evaluated antiscalant-dosed brines resulted in RTP_{PT}s below approximately 40 ppb P.

Evaluation of optimized AOP treatments from Phase 2 on conversion of NRP to RP by bond type were completed in parallel using representative phosphorus compounds. The compounds evaluated were sodium phenyl phosphate dibasic dihydrate (a C-O-P, or phospho-ester bond, ATP (a C-O-P, or phospho-ester bond and P-O-P, or phosphate ester) and diethyl (hydroxymethyl) phosphonate ((Hydroxymethyl) phosphonic acid diethyl ester) (a C-P, or phosphonate). ATP was most susceptible to oxidation with100 ppb peroxide at pH 2 achieving %TP removals of 92%; phenyl phosphate yielded a maximum percent TP removal of 52% for 100 ppb peroxide, while the phosphonate species was virtually resistant to any treatment. The multi-combination treatment utilizing photolysis and 3000 ppm peroxide at pH 2 and 90°C for 1 hour, however, achieved removals of 73-94% for the three representative compounds, with the most removal observed for ATP and least success observed in the phosphonate compound.

The performed evaluations during Phase 1 and 2, as well as the parallel investigation into AOP effectiveness by bond type provides insight into the potential development and instillation of quaternary treatment into wastewater treatment facilities that discharge to highly impacted watersheds, where other alternative treatments or brine disposals are not possible. Although, this extreme course of action would not be financially suitable or environmentally required by most facilities presently or in the future, the quaternary step demonstrates the ability to advance what today’s technologies can do for tomorrow’s concerns.

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Appendix A: Literature Review of AOP Application to DOC Reduction

The application of oxidizing chemicals in wastewater treatment has been extensively evaluated over many years, specifically regarding the application in disinfection. These applications focus on the ability of the oxidants to target organic material, especially as the targets are micro-organisms, viruses and pathogens. The extension of the oxidants to clarifying water by also targeting DOC, organic pollutants and other complex constituents is novel in its potential to oxidize non-reactive phosphorus, but has been extensively evaluated in regards to improving effluent quality by oxidizing residual pollutants, such as pharmaceuticals, ecotoxic refractory organics, and residual inorganic pollutants.

The combination of advanced oxidative processes (AOP), as these oxidizing chemicals have been termed, with RO treatment has been regarded as a potentially highly successful alternative to treating the bulk water, as it provides a targeted approach to a smaller subset water volume that is highly concentrated with the target compounds. This increase in concentration will increase the likelihood of contact between target and oxidizing molecules and thus increase the effectiveness of the treatments.

As well, the use of oxidizing chemicals in treatment of effluents of industries has also been widely studied. The novel application of AOP treatment at converting non-reactive phosphorus to the readily removed orthophosphate within these industrial effluents however is rare, and the potential to extend these AOP treatments to the wastewater industry is not implausible. The following literature review provides a discussion of the application of AOPs for oxidation of various pollutants in the above described situations. The mechanisms of action for the various described AOP treatments are described in Chapter 1.8.

A.1 Photocatalytic Oxidation

Studies by Westerhoff *et al.* (2009) and Chaplin *et al*. (2010) evaluating UV-TiO_2 and BDD, respectively, for DOC conversion effectiveness and energy consumption were performed. The multi-hour studies respectively found a DOC reduction of 30 mg/L (from 40 mg/L to 10 mg/L) consuming 9.6 kW h/m^3 and a DOC conversion of 75% after 8 hours with an energy consumption of 6.9 kW h/m^3. The use of UV-TiO_2 for heterogeneous photocatalysis using titanium dioxide as the catalyst is an attractive option due to the possible use of solar radiation as the energy source, while TiO_2 is a cost-effective, non-toxic and photochemically stable catalyst. Dialynas *et al.* (2008) evaluated the effectiveness of UV-TiO_2 under industrial relevant application conditions of 1 hour of TiO_2/RO concentrate slurry agitation in the dark (ensures saturation for catalyst adsorption), followed by a 1 hour exposure using a 9 W radium lamp (350-400nm) at a catalyst dose of 0.5-1 g/L and filtration using a 0.45 µm membrane filter. Conversion of DOC in the dark produced 30% conversion after the hour for both catalytic doses. When UV light was applied for 10 minutes DOC conversion was 41% and 49% for catalyst doses of 0.5 and 1 g/L. After 10 minutes they saw a plateau in DOC conversion. These studies provide evidence in the potential utilization of photocatalysis in advanced oxidation of organic phosphorus. The phosphorus is bound up in various complex compounds and has to be released in order to be removed be chemical addition. The best way to release the phosphorus is oxidation and then subsequent conversion to orthophosphate for removal.

Although there is plenty of positive research supporting the use of AOPs as DOC reducers in RO concentrate, it is known that only a small portion of the refractory organics are mineralized, and regardless of oxidant dose or contact time increases, these conversion values seem to have plateaued. Therefore using multiple oxidizers in combination or using AOPs as part of other pretreatments, such as coagulation, sµggests a way to overcome the limitations experienced by using individual AOPs (Zhou *et al.*, 2011). Although not well investigated, studies supporting this notion performed by Lee *et al.* (2009) found that using ozonation as brine pretreatment and following that with biological activated carbon treatment increased biodegradability of the organics and could produce a 90% removal, however, only 20-30% of the organics present were mineralized.

A.2 Independent and Combination Tests for Sonolysis, PCO, O_3 and H_2O_2

Zhou *et al.* (2011) also studied four AOP treatments (sonolysis (US), photocatalytic oxidation with UVA or UVC/TiO_2, ozone oxidation, and peroxide oxidation) individually, in various bi- and tri-combinations and in combinations with coagulation using $FeCl_3$ and AC adsorption using PAC and GAC for the effectiveness at DOC removal from RO concentrate. It was determined that after a 1 hour contact time the most effective individual, bi- and tri-combination treatments for DOC removal, respectively were ozonation with a 21.7% DOC removal, UVA/TiO_2/O_3 with a 52.2% DOC removal and US/H_2O_2/O_3 with 31.4% DOC removal. AOPs were determined to effectively breakdown the complex organics into small MW organics that can be biodegraded. Zhou *et al.* also determined that coagulation with $FeCl_3$ at a 1mM (5 min at 180rpm mixing, 10 min at 45 rpm mixing and 30 min sedimentation) dose produced 26% DOC removal; this finding confirmed studies by Shon *et al.* (2004) who demonstrated a 52% DOC removal and Dialynas *et al.* (2008) who observed a 69% DOC removal, but was significantly lower. Coagulation of DOC with $FeCl_3$ is responsible for removing high MW organics (MW>10^4 kDa) that are AOP resistant, while the soluble, low MW organics persist. Although the DOC removal was lower with coagulation alone as compared to the 88% and 95% DOC removal observed with 5 g/L doses of GAC and PAC, respectively; as a pre-treatment $FeCl_3$ was preferred over AC adsorption because of the improved biodegradability and decreased ecotoxicity of the refractory organics after AOP treatment observed with $FeCl_3$ pre-treatment. Zhou *et al.* also investigated the use of coagulation pre-treatment with individual, bi- and tri-combinations of the four AOPs. DOC removal was determined after a 1mM $FeCl_3$ dose with the same conditions as above and a 1 hour contact time for AOPs, the most effective treatments were UVC/TiO_2 with a total DOC removal (AOP removal + 26.4% removal for coagulation) of 54.4%; UVA/TiO_2/O_3 with a total DOC removal of 68.1%; and UVA/H_2O_2/O_3 with a total DOC removal of 64.2%. When the contact time of $FeCl_3$ pre-treated RO concentrate was extended to 6hrs photocatalysis using UVC/TiO_2 was able to achieve a 95% removal of DOC (Zhou *et al.*, 2011).

A.3 Ferrate

A more extensively studied oxidizer, Ferrate (VI) (FeO_4) is the strongest oxidant (under acidic conditions because of the increase in redox potential, but still very effective at neutral pH) of all those that are commonly used in wastewater treatment and disinfection; it also has the capability of performing simultaneous coagulation as the ferrate (VI) ion is reduced to Fe(III) or ferric hydroxide during the oxidation of other constituents. It has been previously shown to be effective at degrading organic pollutants, including endocrine disruptors and pharmaceuticals, as well as inorganic pollutants in both drinking and wastewater treatment (Jiang and Lloyd, 2002; Jiang *et al*, 2009). Although extremely effective as an oxidant, the instability of the compound in solution and the associated high production costs of the stable solid do not make it a likely candidate for wide-scale usage within the industry. However, these limitations could be removed if the ions were produced and applied on-site and *in situ*. This prospective idea was evaluated by Jiang *et al* (2009) at a pilot-scale facility in the UK (Hailsham North Wastewater Treatment Works of Southern Water Ltd) where the ferrate would be produced on site using electrochemical generation. The effectiveness was evaluated by measuring the reduction in suspended solids (SS), COD, BOD and phosphate (P). A non-linear dose dependence was observed for the reduction of each parameter, with increasing removal being observed for increasing concentrations of Fe^{+6}, with a plateau effect beginning to occur in each parameter after the highest dose (0.04 mg Fe^{+6}/L). Resulting percent removals for SS, COD, BOD and P at a Fe^{+6} dose of 0.03 mg/L at pH 8 were 79%, 50%, 30% and 56%, respectively. All parameters, except BOD, overlapped—within standard deviations—with the observed removals using ferric sulphate at a dose of 37 mg Fe/L; residual Fe concentrations were also 69 times lower with ferrate than with ferric sulphate. Jiang *et al* (2009) conclude that ferrate can be effectively produced on site and that it has potential and promising applications for reducing COD, BOD, removing suspended solids, as well as phosphate using low Fe^{+6} doses (0.005-0.04 mg/L), which are one hundred times less than the normally required Fe(III) dose.

A.4 Fenton's Reagent

Fenton's Reagent (Fe^{+2}/ H_2O_2) is another strong oxidant that also undergoes simultaneously coagulation with Fe(III) and has also been shown to effectively degrade organic pollutants, which allows removal or increases later biodegradability. Oxidation by Fenton's Reagent also occurs through a mechanism that utilizes free hydroxyl radical formation, which makes it a favourable AOP. Chamarro *et al*. (2001) found that Fenton's Reagent is highly effective at oxidative degradation of smaller organic compounds and increases the biodegradability of more complex organic pollutants. The group explored several different ratios for Fe/H_2O_2, organic content/H_2O_2, and Fe/organic content, and determined that these ratios were pH (acidic performed best, pH 2-4, 5) and organic pollutant characteristic dependent (Chamarro *et al*., 2001). Petrucci *et al* (2003) used Fenton's Reagent to oxidize phosphorus compounds in wastewater from a safety match company and found it highly effective against a simulated wastewater containing phosphate, phosphite and hypophosphite. The group determined that, pH, temperature and the ratio of Fe(II) to H_2O_2 and the initial phosphorus concentration all play a significant role in oxidation effectiveness. They determined that pH 3.5 and 20°C were the optimal conditions for Fenton's Reagent and the [P]:[H_2O_2]:[Fe(II)] ratio that performed best when the initial phosphorus was 250 ppm was a 1:1.73:0.39 when the reagents were added simultaneously. The group also evaluated adding peroxide and Fe(II) in 3 sequential steps and found that a similar conversion efficiency was achieved, but the sequential method used less reagent to reach the same conversion percentage (Petrucci *et al,* 2003). Therefore this treatment could be extended to phosphorus oxidation in ROC treated waste water.

A.5 UV, PAA and NaOCl

Other commonly used oxidizers and disinfectants in wastewater treatment that have been well studied are the application of ultraviolet light, peracetic acid (PAA) and sodium hypochlorite (NaOCl) individually or in combination. A study performed by Caretti and Lubello (2003) evaluated the disinfection effectiveness as a result of hydroxyl radical formation and subsequent membrane disruption of PAA, UV and the addition of PAA up- and downstream from UV treatment (PAA/UV and UV/PAA) in wastewater collected from three treatment facilities in Tuscany, Italy. Disinfection using oxidation was observed to occur in both PAA and UV treatments individually, as has been previously demonstrated. It is also important to note that PAA does not produce any harmful or toxic by-products during its degradation or reaction with organics and is therefore popular as a green chemical. The group concluded that the best method of disinfection was observed with addition of 2 ppm PAA upstream from UV exposure at 192 mJ/cm^2, which substantially surpassed the disinfection efficiency of the individual treatments and the UV/PAA treatment due to the vast increase in the hydroxyl radical formation associated with exposing PAA to UV light (determined via spectroscopic analysis (Caretti and Lubello, 2003). Hypochlorite is a historically used chemical for oxidation/disinfection that has wide application in the wastewater industry. In a study performed by Aslam *et al* (2004) which evaluated the oxidation and disinfection potential of hydrogen peroxide, sodium hypochlorite and calcium hypochlorite by evaluating the reduction in COD and BOD of wastewater from a textile plant found that both hypochlorite effectively reduced COD and BOD. Calcium hypochlorite reduced COD by 62% and BOD by 74%, while sodium hypochlorite reduced COD and BOD by 56% and 51%, respectively at 25°C with a 1440 min retention time. Under the same conditions hydrogen peroxide only achieved a 41% reduction in COD, but a 52% reduction in BOD. The group saw increase reductions in both parameters for all oxidants as the temperature increased from 25°C to 50°C and 100°C. Therefore the application of commonly used oxidants/disinfectants to the potential oxidation of phosphorus from its many organic and inorganic forms and subsequent removal should also be explored.

A.6 Conclusion

The application of these AOP treatments in the effective oxidation of DOC, as well as other various pollutants, including phosphite and hypophosphite has been shown to be possible an dapplicable in bench-scale studies. This application is possible in ROC and the bulk water and therefore is worth pursuing as potential treatments for converting non-reactive phosphorus to the readily removable orthophosphate form.

Appendix B: AHP Issues and Exclusion Rationale

The large variations and standard deviations observed in the tmAHP for the various brine sampling events is also observed when evaluating the speciations performed on various AOP treated samples. In theory the AOP conversion of NRP to RP should occur by converting either the AHP or the organic (OP) fractions of the brine, both fractions, however are calculated using the tmAHP as equation 3 and 4 describe.

$$tAHP = tmAHP-tRP \quad (3)$$

$$tOP = TP-tmAHP \quad (4)$$

When analyzing the data from the speciations of treated brine one should see an increase in tRP and no change in tmAHP or tOP because the AHP converted to RP would not change the total tmAHP as described by rearranging equation 4 (tmAHP =AHP + tRP). However, when looking at Figure B.1 it is easy to see the wide variation in tmAHP and that it tends to fluctuate regardless of the changes in tRP.

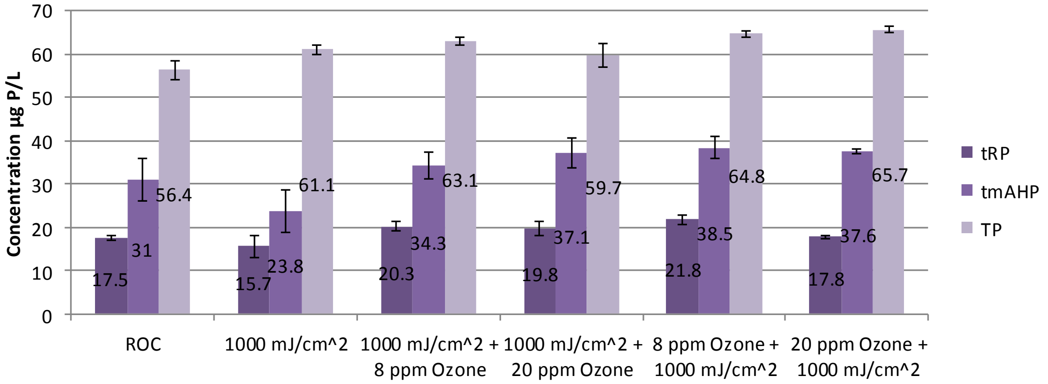


Figure B.1: Speciations performed on various AOP treated brine from January 4-5, 2012 pooled sampling. The concentration of phosphorus is reported in µg P/L.

The increases or decreases in tRP do not correspond proportionally to the changes in tmAHP for the same January 4-5, 2012 pooled brine sample. Also the standard deviations associated with the tmAHP are much larger than those associated with either TP or tRP, this is consistent with the difficulty in reproducibility that is associated with measuring tmAHP within the same sample. For these reasons tmAHP was not considered when discussing AOP effectiveness, was not measured for most of the AOP treatments and was completely disregarded as a measure during Phase 2 AOP evaluations or mass balance.

Appendix C: Mass Balance Data for the Weekly Sampling Events

Mass balance samples were collected almost every week from various points in the demonstration facility as depicted in Figure 3.1 throughout Phase 2 of the project. The samples were collected in the manner described in Chapter 3.2.1 and shipped to WLU as well as another analytical lab for comparative analysis.

C.1 100 ppb Sodium Phenyl Phosphate Dibasic Dihydrate as QA/QC for Mass Balance Monitoring

Early on in the mass balance monitoring it was decided to include a 100 ppb QA/QC compound to ensure TP digestion was completely digesting all samples, which would allow for the most accurate monitoring of the systems performance, including the influent to the facility, the MF skid, the RO skid and its products. The compound selected for this use was sodium phenyl phosphate dibasic dihydrate. This compound is commonly used for QA/QC as it contains only one phosphate group and allows for easy calculations for recovery, in fact the digester unit and purchased standard methods kits for phosphorus analysis suggest the use of this compound for recovery QA/QC.

The QA/QC standard was used to ensure digestion completeness. A recovery of 100 ppb ± 5 ppb P was considered acceptable. In Table C.1, which provides a summary of the mass balance data throughout Phase 2, the QA/QC recovery only deviates from the acceptable 100 ppb ± 5 ppb P five times out of the almost 50 sets of measurements, but if standard deviations are considered (Figure C.1) the number of recoveries that don't meet the 100 ppb ± 5 ppb P guidelines falls to two—marked with yellow stars on the figure. The dates upon which these deviations occurred were repeated to ensure accuracy (repeated measures not included in summary table), as well the data was statistically compared to data obtained from Maxxam throughout Phase 2. The comparisons are presented in the various figures below.

Table C.1: Mass balance data for multiple points within the demonstration facility at Mount Albert throughout Phase 2. Includes QA/QC recoveries of sodium phenyl phosphate dibasic dihydrate and an ultra-low level orthophosphate standard.

	tRP			**TP**				**QA/QC TP**	
	MFP	RWW	ROC	ROP	MFP	RWW	ROC	100 ppb P Phenyl Phosphate	1 ppb Orthophosphate
Sample Date:									
April 4/12	N/M	N/M	33	6	14	72	67	N/M	N/M
April 11/12	N/M	N/M	21	2	18	21	168	N/M	N/M
April 18/12	N/M	N/M	23	1	22	140	128	96	N/M
April 26/12	N/M	N/M	39	3	22	127	152	96	N/M
May 2/12	N/M	N/M	40	1	23	111	158	95	N/M
May 17/12	3	49	60	1	13	144	173	94	N/M
May 23/12	20	78	36	2	43	139	145	97	N/M
June 1/12	3	94	288	3	26	157	437	96	N/M
June 13/12	19	97	51	7	29	175	235	97	N/M
June 20/12	68	156	567	4	94	166	778	88	N/M
June 27/12	25	71	152	4	42	176	316	94	N/M
July 5/12	5	26	76	2	18	85	220	101	N/M
July 11/12	12	41	63	10	32	148	213	92	N/M
July 19/12	4	37	134	11	26	67	212	99	N/M
July 25/12	11	76	143	7	32	277	201	97	N/M
August 1/12	90	223	784	4	123	240	1260	99	N/M
August 8/12*	11	116	126	2	47	182	246	97	N/M
August 15/12*	15	70	121	2	66	101	177	93	N/M
August 22/12*	4	132	139	1	25	181	25	95	N/M
August 29/12	8	127	109	7	30	250	181	97	N/M
September 5/12	4	87	146	6	31	129	184	93	N/M
September 12/12	14	110	230	10	74	127	377	99	1
September 19/12*	4	98	163	4	42	148	216	99	1
September 26/12*	36	182	295	1	30	124	331	99	1
October 3/12**	15	179	228	1	29	278	249	97	1
October 10/12	26	76	200	4	48	211	245	96	1
October 17/12	12	55	86	2	28	140	204	96	1
October 24/12	13	28	79	2	22	85	104	97	1
November 1/12	44	153	270	2	21	79	359	99	1
November 7/12	27	144	60	2	31	183	86	99	1
November 14/12	27	84	136	5	34	135	159	98	1
November 21/12	10	39	49	3	22	107	234	99	1
December 5/12	12	178	72	5	27	238	357	99	1
December 12/12	5	164	55	3	29	255	412	100	1
December 19/12	8	167	63	6	31	260	414	100	1
January 9/13	12	230	89	3	40	339	414	100	1

January 16/13	5	125	45	4	23	209	329	100	1
January 23/13	6	155	36	2	19	201	383	100	1
February 6/13	10	99	60	2	23	168	448	99	1
February 13/13	13	3	63	2	26	113	464	99	1
February 21/13	18	89	94	3	31	159	508	99	1
February 28/13	21	88	120	5	30	130	605	99	1
March 6/13	14	81	78	4	36	123	439	98	1
March 13/13	N/A	82	214	N/A	N/A	121	637	98	1
March 20/13	5	52	38	3	25	107	406	97	1
March 27/13	5	55	22	2	20	104	382	97	1

*Denotes ROP TP samples remeasured utilizing the 1 minute incubation time for the mixed reagent after the protocol was tested and recovery of 1 ppb standard was achieved.

**Denotes the sample date that the 1 minute incubation time for ROP TP analysis was put into practice; all dates after this had ROP TP samples evaluated using the shortened incubation time of 1 minute. All other samples were measured using 30 minute incubation with mixed reagent. All dates before this used 30 minute incubation time for ROP TP analysis, with the exceptions of those denoted with *.

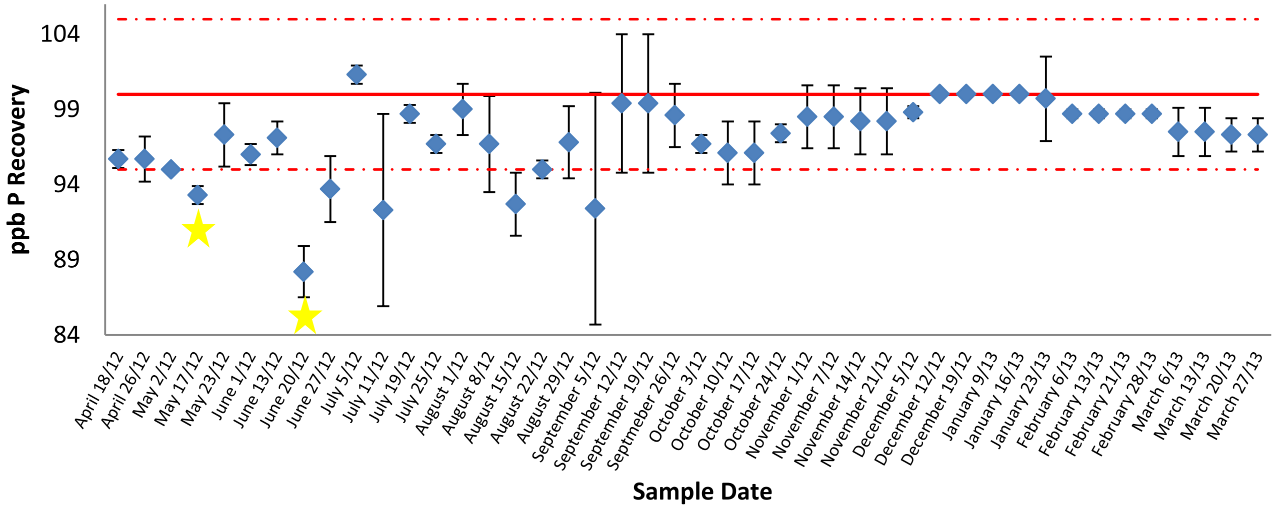
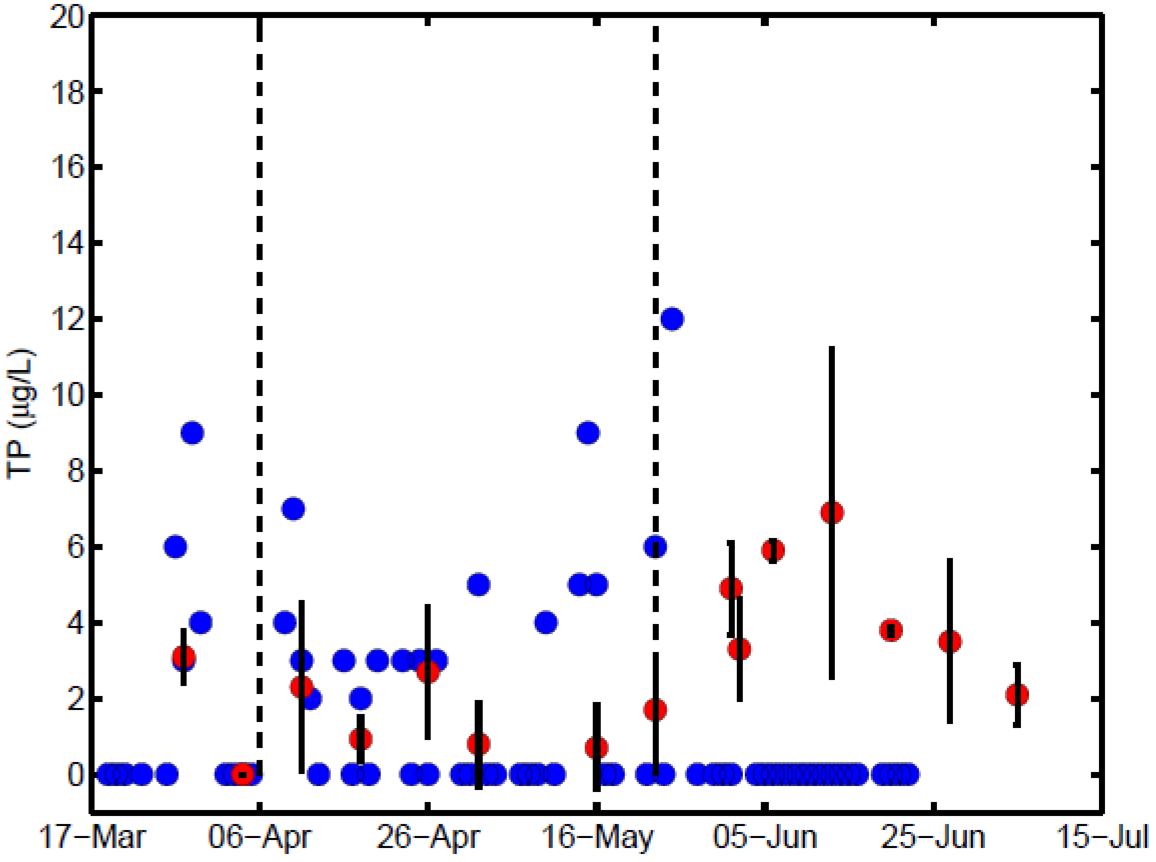


Figure C.1: QA/QC recoveries of sodium phenyl phosphate dibasic dihydrate, including standard deviations from triplicate analysis. Red dashed lines represent the ± 5 ppb acceptable limits; the solid line represents 100 ppb; yellow stars denote measurements that fall outside of the acceptable 100 ± 5 ppb range

C.2 Development of New Protocol Regarding Mixed Reagent Incubation Time for TP Determination in Solutions with Ultra-low Phosphorus Concentration—Inter-lab Comparison

An integral measurement that reflected the quality of water produced at the demonstration facility and thus represented the effectiveness of the RO treatment was the TP present in the ROP (RO permeate). The ROP was analyzed in the same manner as the three other samples using standard methods and an incubation time with the mixed reagent of 30 minutes, however, upon comparison to the data from Maxxam it was noted that the ROP TP data achieved by WLU was systematically higher than that observed by Maxxam (Figure C.2a and b). This observation led to an investigation into the analysis techniques applied by the analytical company.



(a)

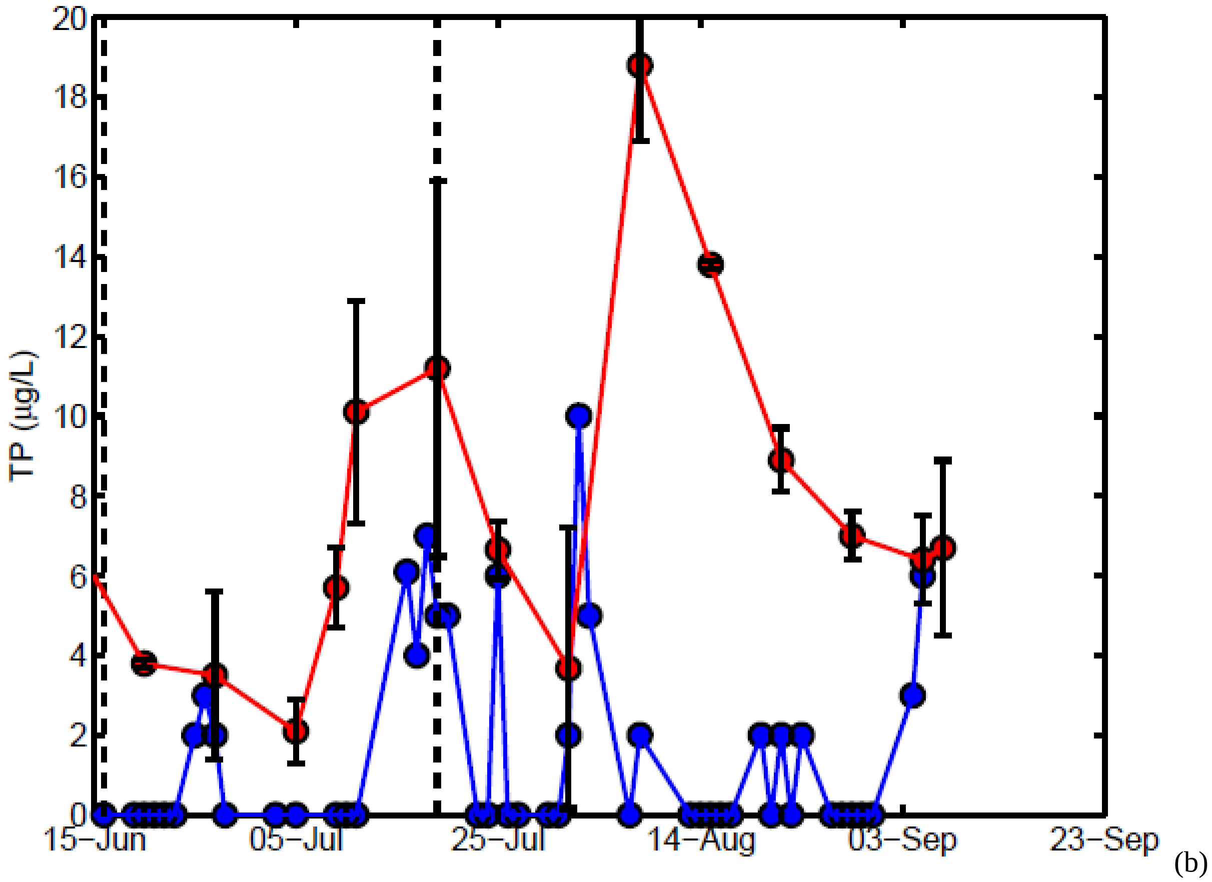


Figure C.2a and b: Total Phosphorus for ROP samples for the demonstration facility on various sampling dates, (a) From first quarter of operation at the demonstration facility and (b) from the second quarter of operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples

After communication with Maxxam it was determined that a much shorter contact time was applied for low level phosphorus recovery, such that a flow-through system that utilized incubation times (with the mixed reagent) of 40 seconds was standard practice for the company. At this time it was also communicated to WLU that the samples were heated to 37ºC during incubation and before analysis. This corresponds to deviations between the measured values for some of the samples, such as RWW—which if heated before tRP analysis could have interfered with the formation of the phosphomolybdate complex, resulting in a lower tRP for those samples. As well, the longer incubation time in the presence of the mixed reagent would also result in higher tRP measures due to the acid catalyzed hydrolysis of phosphates from particulate matter in the unfiltered RWW samples, which would easily occur in the acidic conditions used by the mixed reagent.

These changes were then optimized for analysis at WLU, such that an incubation time with the mixed reagent was set to 1 minute for the blanks, a newly instituted 1 ppb orthophopshtae standard and the ROP for TP analysis. These changes would minimize the potential competing side reactions of the molybdate complex with itself, which can occur in the acidic conditions that the analysis is performed under, especially in such ultra-low phosphorus concentrations over an incubation time of 30 minutes.

Before the analysis under the altered parameters, ROP concentrations of TP for the sample dates denoted with a * in Table 8.1were measured to be as follows in Table 8.2, while after the implementation of the shortened incubation time with the mixed reagent, the TP concentrations were also as follows in Table 8.2.

Table C.2: Evaluating the effects of incubation time with the mixed reagent on ultra-low phosphorus concentrations in ROP for various sample dates.

ROP TP		
	1 minute Incubation	30 minute Incubation
Sample Date		
August 8/12	2	19
August 15/12	2	14
August 22/12	1	8.9
Septmeber 19/12	4	17
Septmeber 26/12	1	20

As is easily notable in Table 8.2, using a much shorter reaction time provides significantly lower TP measures for ROP. However, this method needed to be evaluated against a standard of known concentration in order to ensure that all phosphates were being complexed and were thus represented in the TP data, and that no self-complexation with molybdate was occurring. This was accomplished by including a 1 ppb P orthophosphate standard with each mass balance and analysis sample set. This was also compared against a 30 minute incubation time for the 1 ppb standard for the first three sampling dates, before the new method was adopted. This comparison is visible in Figure C.3. The 30 minute incubation times with the mixed regent are denoted with a star.

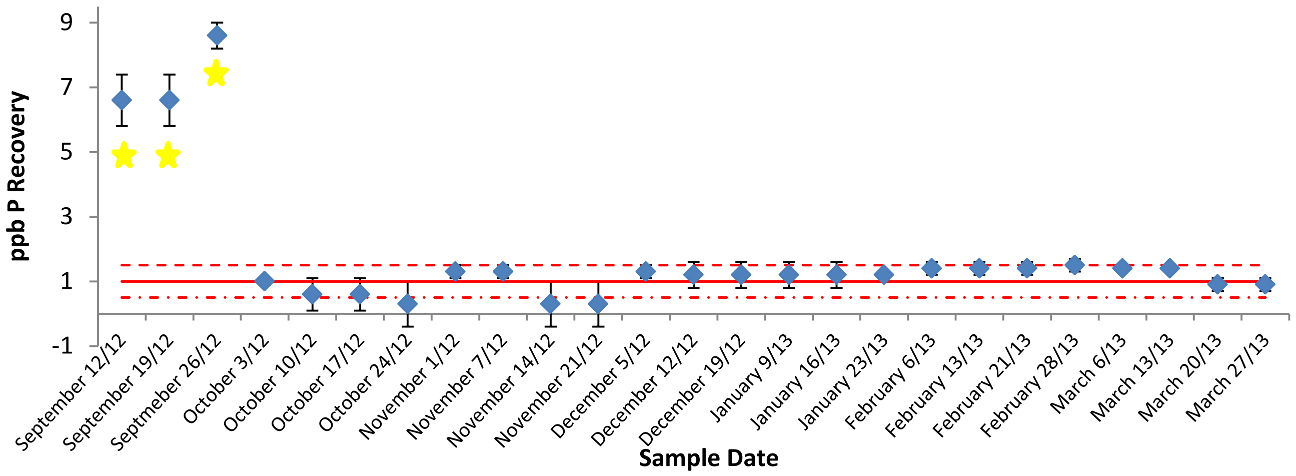


Figure C.3: QA/QC recoveries of a 1 ppb orthophosphate standard measured after 1 minute incubation with mixed reagent, including standard deviations from triplicate analysis. Red dashed lines represent the ± 0.5 ppb; the solid line represents 1.0 ppb; yellow stars denote measurements that fall outside of the 1.0 ± 0.5 ppb range, which were measured using a 30 minute incubation time with the mixed reagent

As is depicted in Figure C.3, using an incubation time of 30 minutes can cause up to an order of magnitude over-estimation for ultra-low level phosphorus concentrations, as was observed in the 1 ppb standards measured on sample dates September 12, 19 and 26/12. After this sample date, the shorter 1 minute incubation was used and yielded very reliable and reproducible recoveries for the 1 ppb standard and therefore justified this procedural modification for the blanks and the ROP TP analysis. This recovery was repeated with every sample date to ensure consistency.

After the adjustment to the shortened incubation time protocol, the ROP data between labs agreed far better than it had before. Figure C.4 demonstrates this agreement. It is important to note that once the incubation time was optimized, the detection limit for WLU using a 10 cm pathlength cell was approximately 1 ppb, whereas Maxxam considered any data point below 2 ppb to be considered non-detect, in Figure C.4 these non-detect data are plotted at 1 ppb.

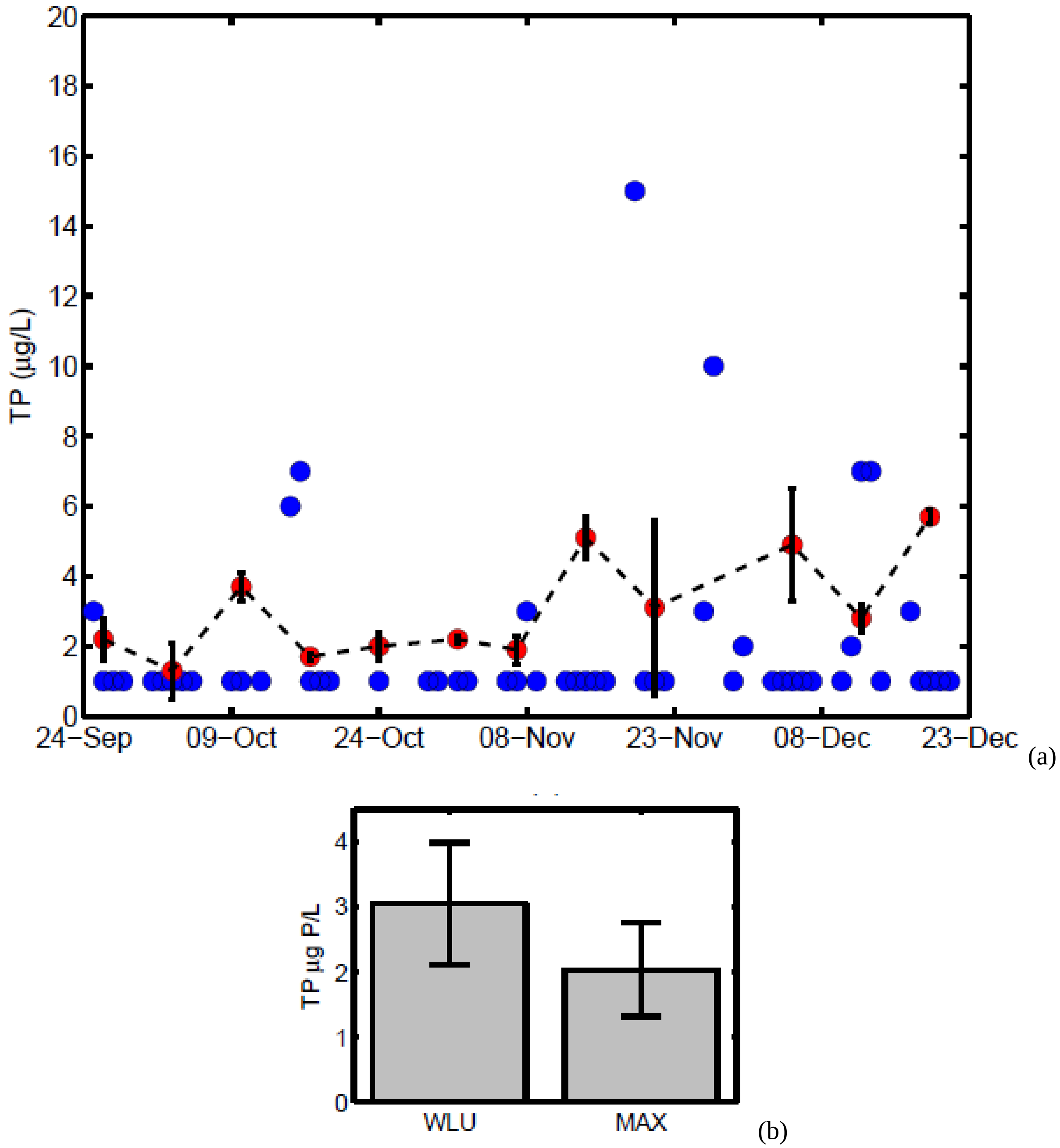


Figure C.4a and b: (a) Total Phosphorus for ROP samples for the demonstration facility during sampling dates for the third quarter operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples. (b) The mean of the data from both labs over the sampling times described in (a) and the error bars represent the 95% confidence intervals. Note: non-detects were considered to be 1 ppb when performing this analysis

Overall, the data from WLU, depicted in red, and that from Maxxam, depicted in blue, agree within standard deviation in Figure C.4a, as well as within 95% confidence intervals in Figure C.4b once the modified protocol is used for analysis of TP in ROP.

C.3 Standard Protocol Variations—Inter-lab Comparison and effects on tRP of RWW

Other deviations discovered during communication with Maxxam, included heating the samples to 37°C during incubation were also evaluated for effects on the measured data. Total reactive phosphorus (tRP) for the RWW sample was evaluated using a 40 second and a 30 minute incubation time with the mixed reagent after reaching 37°C, as well as a 30 minute incubation time at room temperature. The results are summarized in Table 8.3.

Table C.3: Evaluating the effects of time and heating to 37°C on tRP measurements for RWW from August 22/12 sampling date.

	30 minute Incubation, room temperature	40 second Incubation, 37°C	30 minute Incubation, 37°C
tRP Concentration (µg P/L)	131.7 ± 10.1	38.8 ± 5.2	92.0 ± 21.4

Table 8.3 displays the effects of heating on tRP measures, achieving a tRP concentration 30% lower than that measured according to the unmodified standard methods, while the shortened incubation time yielded a concentration 71% lower than that achieved under standard methods. These extreme variations in data display the effects of changing small parameters in standard methods, which does not instruct to heat the sample and suggests measuring within 30 minutes of beginning incubation with the mixed reagent, without stating an exact incubation time.

Figure C.5 demonstrates these effects in the RWW samples collected from the demonstration facility during the second and third quarters of operation, which were analyzed for tRP. In both Figures 8.5 a and b, a systematic difference between the Maxxam and WLU data is observed, such that Maxxam data is consistently lower than that measured at WLU. This observation is consistent with that observed during the evaluation of the effects of heat and shortened incubation time with the mixed reagent described above. It is important to note that this systematic difference is only observed in the unfiltered tRP for RWW and does not exist in any other sample for either tRP or TP.

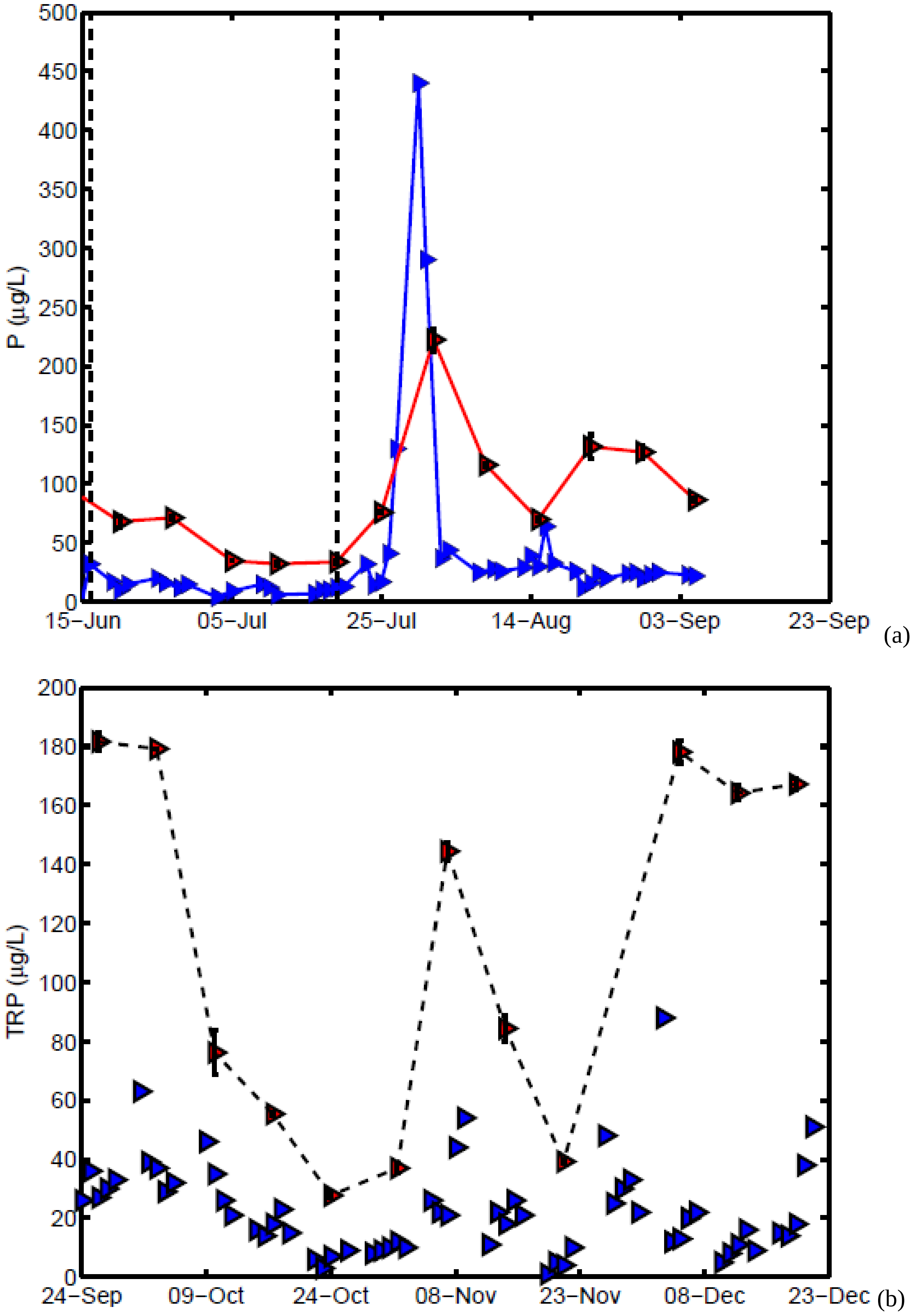


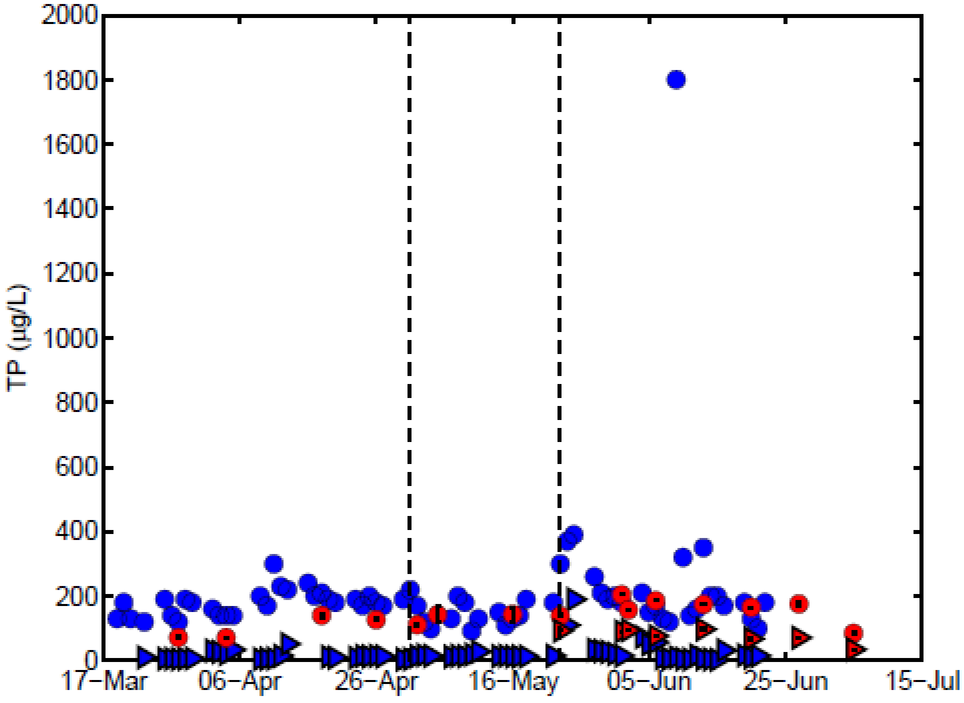
Figure C.5a and b: Total Reactive Phosphorus for RWW samples for the demonstration facility during sampling dates for the second (a) and third (b) quarter operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples

The differences between the data from the two labs is significant, such that for the data presented in Figure C.5b the mean ± the 95% CI for WLU is 111.22 ± 63.12 µg P/L, while Maxxam is 22.95 ± 16.06 µg P/L, which causes a 79% difference between the two labs around the mean. These differences are most likely due to the reasons discussed above, and cause great disparities in data analysis as a result of open interpretation of standard methods.

C.2 Inter-lab Comparison of Total Phosphorus in MFP, RWW and ROC

Comparing data for the TP measurements on these samples for the first three quarters of operation at the demonstration facility provide consistent results within 95% confidence intervals, regardless of the variations in analysis technique. This is likely the result of relatively high concentrations of phosphorus and complete conversion to orthophosphate during TP digestion, both of which prevent variation due to particulate matter (binding phosphorus) or ultra-low phosphorus concentrations. The comparison results are displayed below.

C.2.1 Total Phosphorus—RWW



(a)

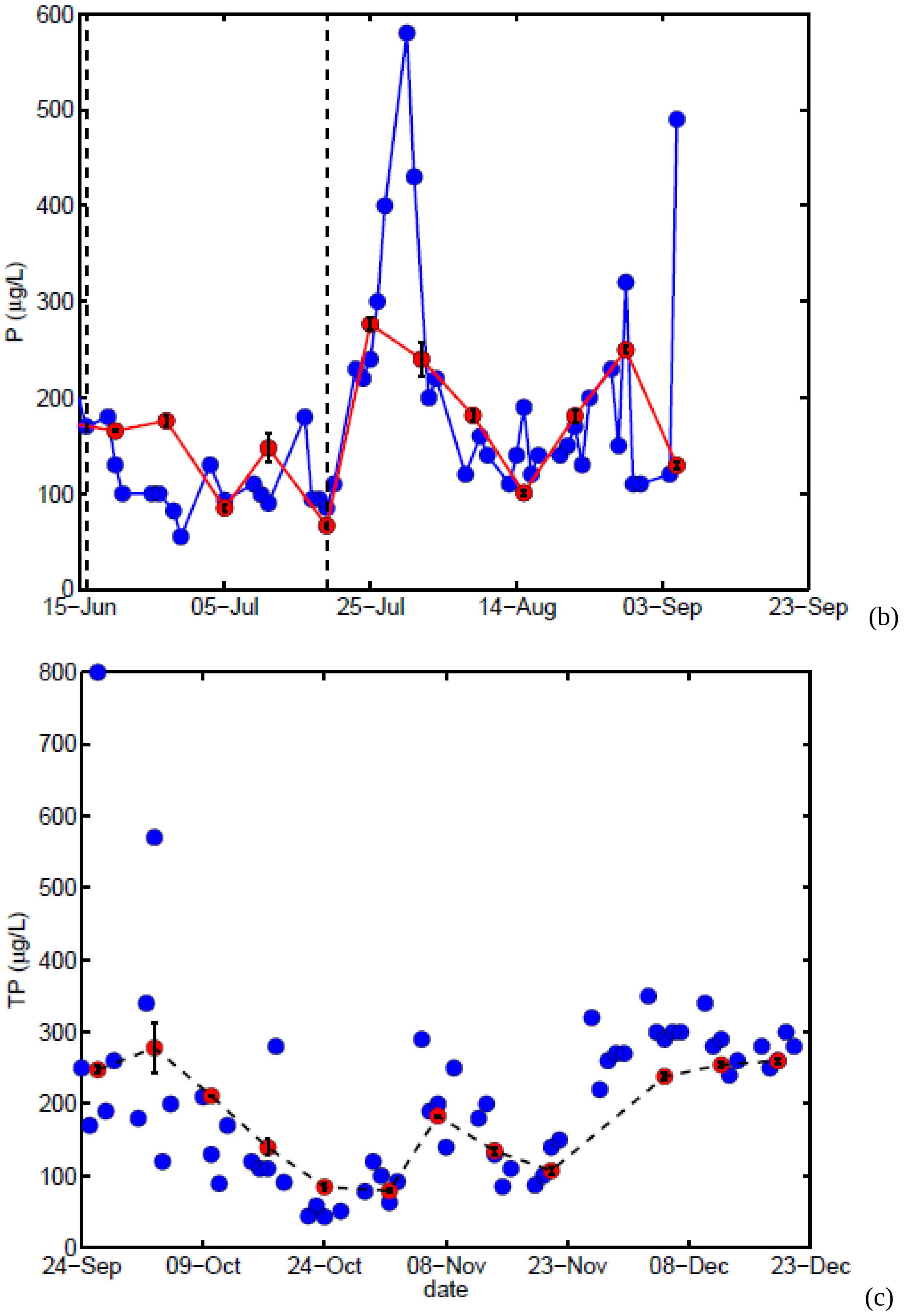
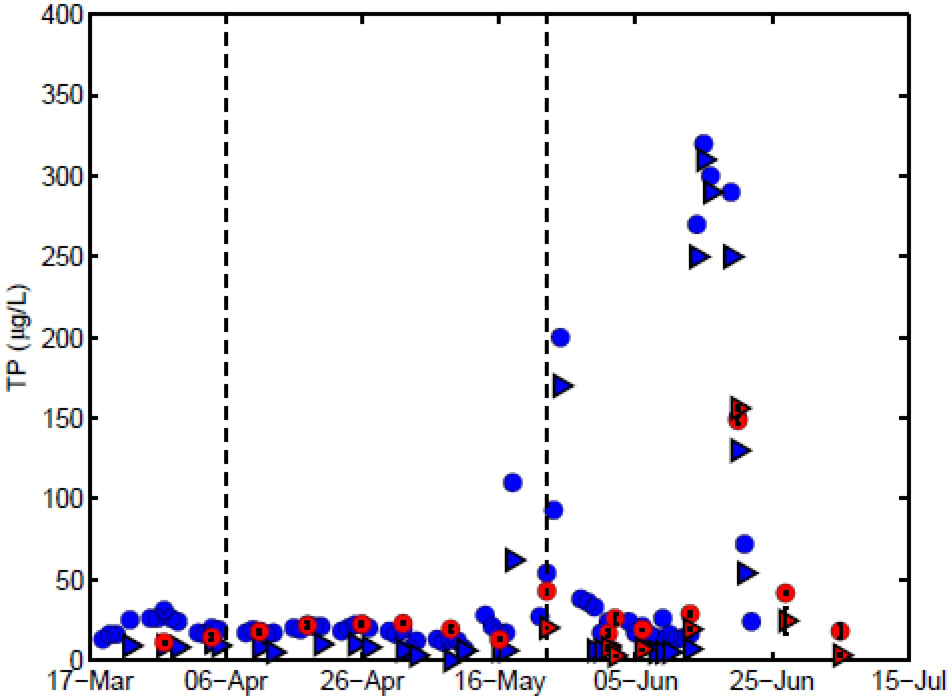
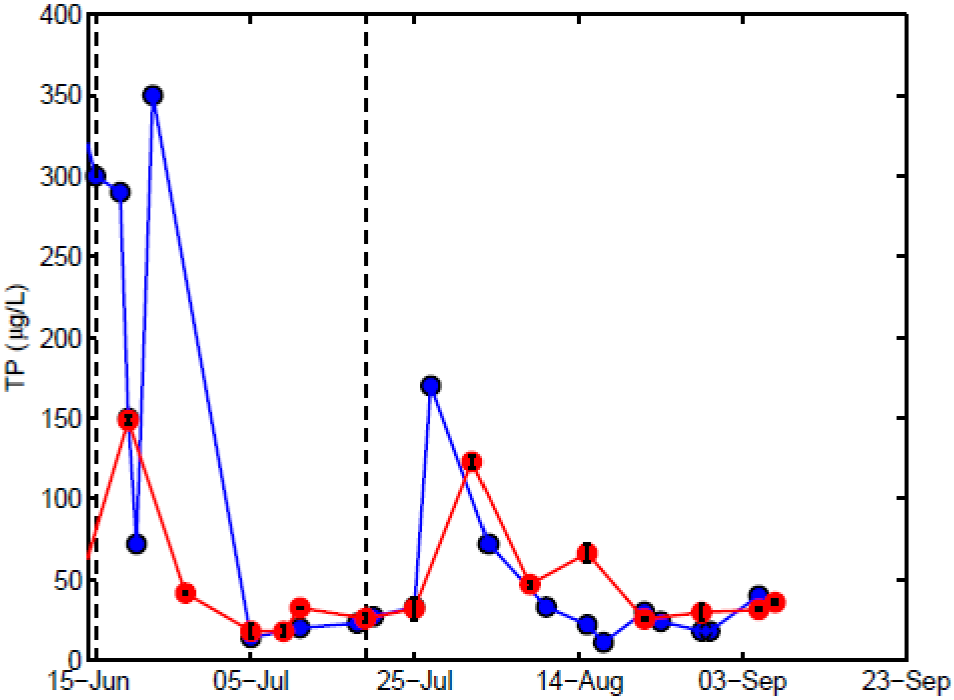


Figure C.6a-c: Total Phosphorus for RWW samples for the demonstration facility during sampling dates for the first (a), second (b) and third (c) quarter operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples

C.2.2 Total Phosphorus—MFP



(a)



(b)

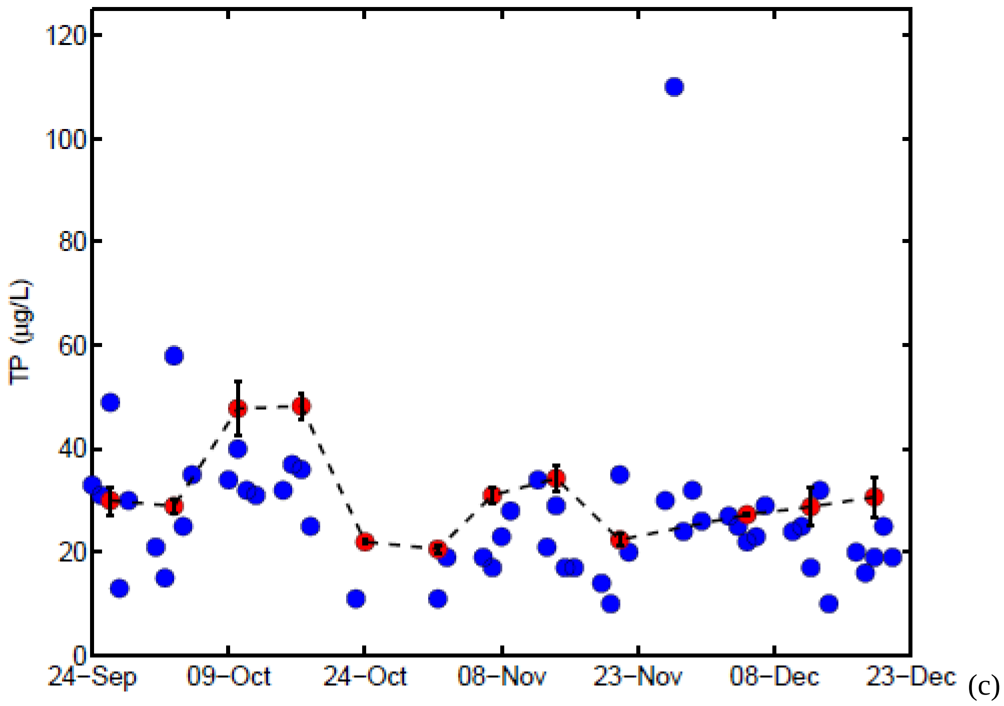
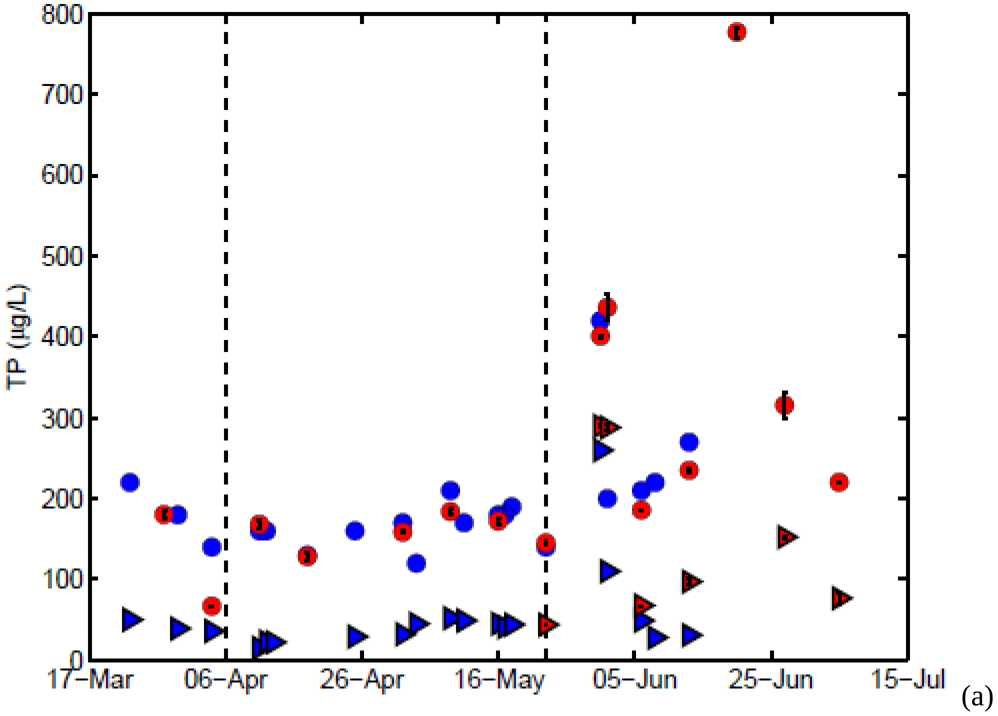


Figure C.7a-c: Total Phosphorus for MFP samples for the demonstration facility during sampling dates for the first (a), second (b) and third (c) quarter operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples

C.2.3 Total Phosphorus—ROC



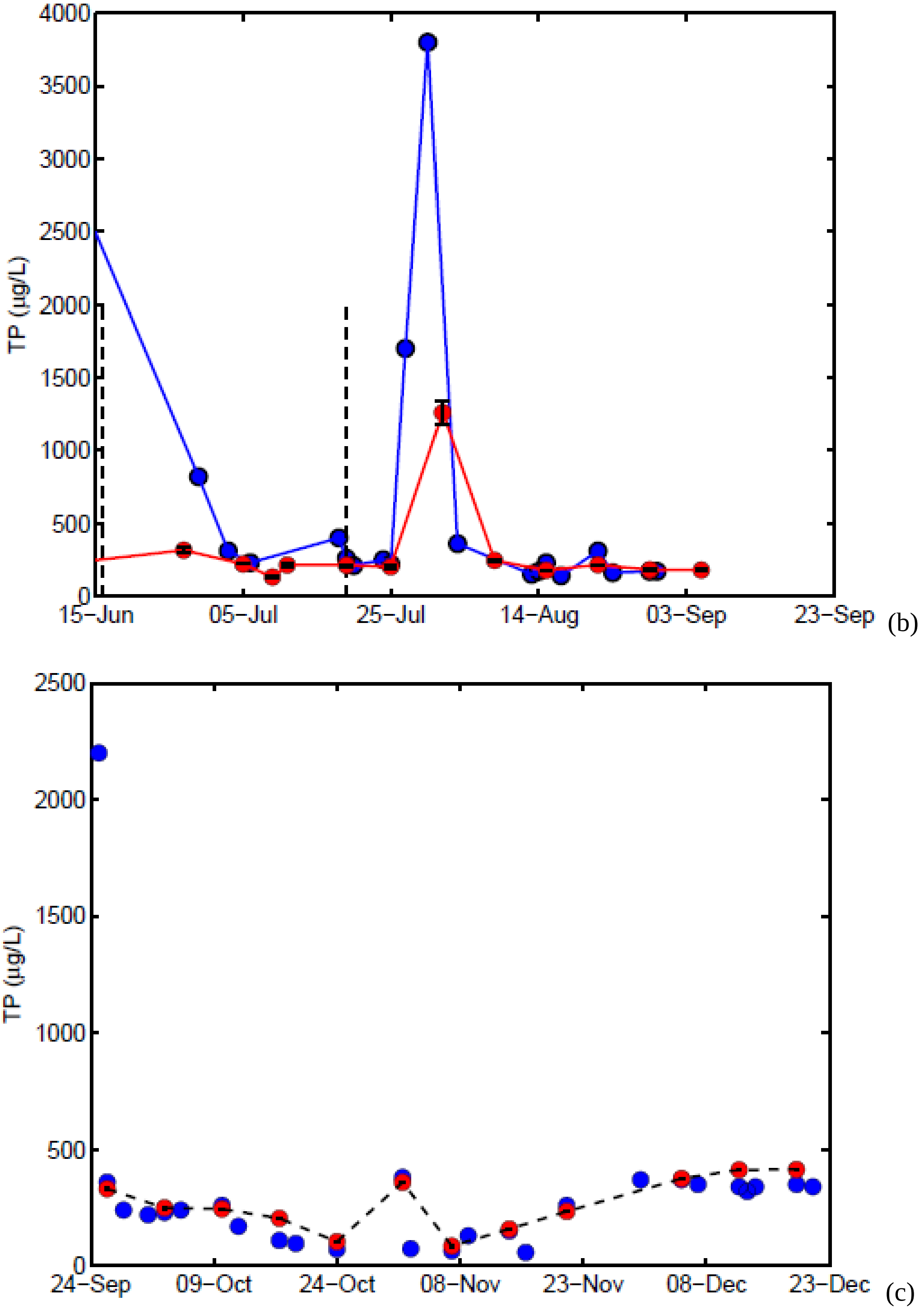
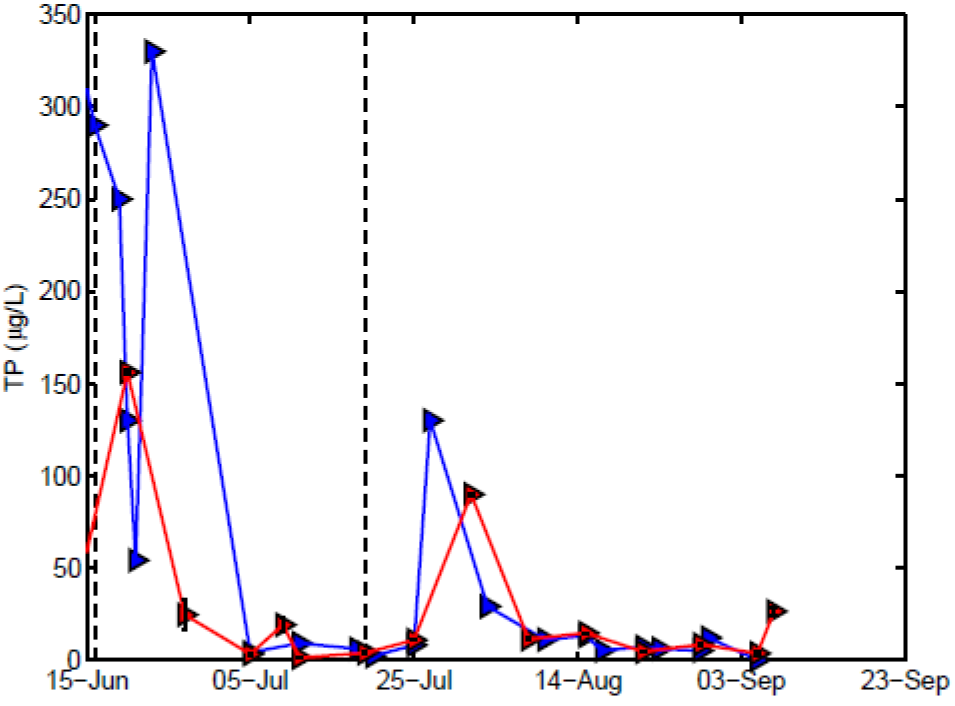


Figure C.8a-c: Total Phosphorus for ROC samples for the demonstration facility during sampling dates for the first (a), second (b) and third (c) quarter operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples

C.3 Inter-lab Comparison of Total Reactive Phosphorus in MFP and ROC

Total reactive phosphorus was not initially measured when the demonstration facility first started production for either analysis facility and therefore was excluded during comparisons between Maxxam and WLU for the first quarter, but was included for the second and third. Analyses of tRP by both labs provide consistent results within 95% confidence intervals for both MFP and ROC, regardless of the variations in analysis technique. This is likely a result of the removal of particulate matter via filtration before these samples were collected, this would remove the likelihood of any disagreement in tRP, which could result from longer incubation times. The comparison of this data is presented below.

C.3.1 Total Reactive Phosphorus—MFP



(a)

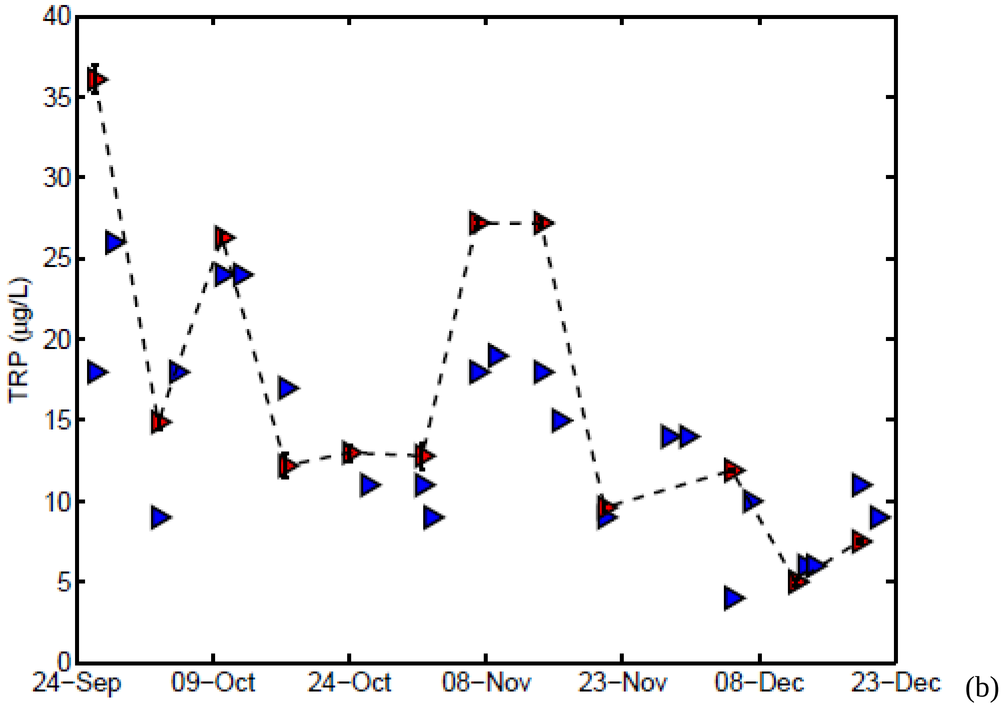
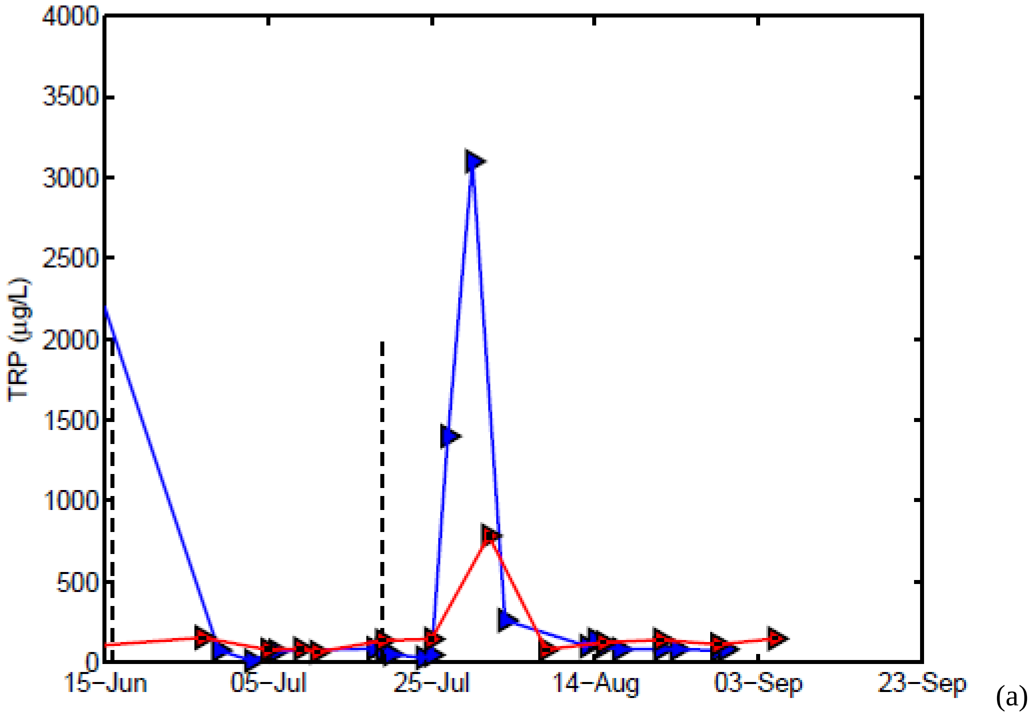


Figure C.9a and b: Total Reactive Phosphorus for MFP samples for the demonstration facility during sampling dates for the second (a) and third (b) quarter operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples

C.3.2 Total Reactive Phosphorus—ROC



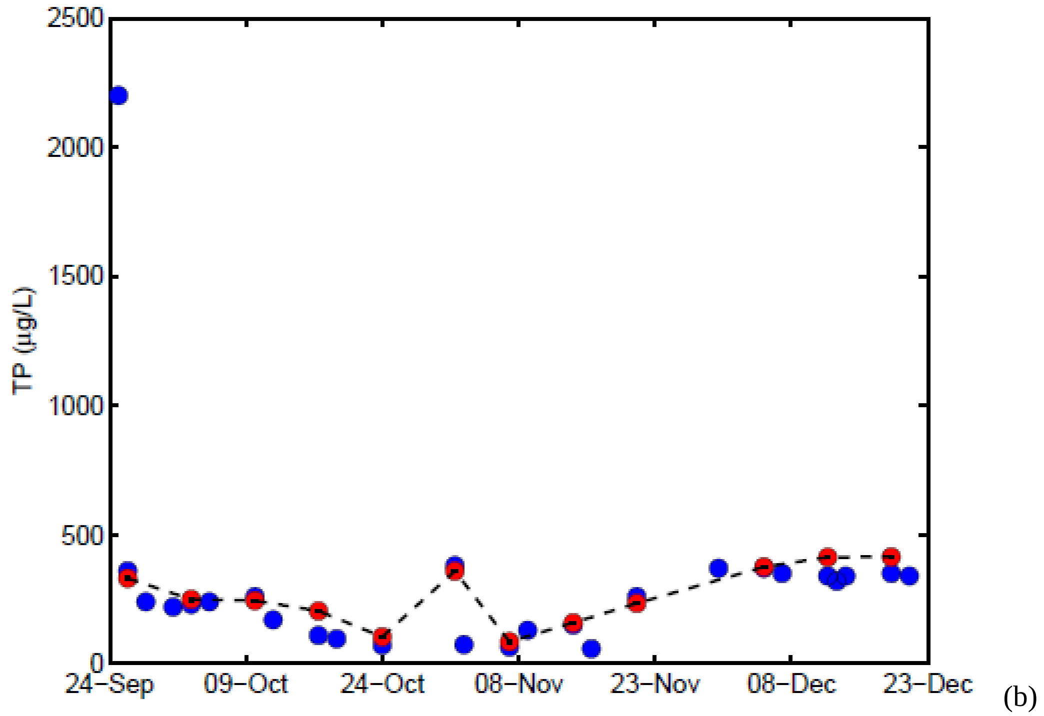


Figure C.10a and b: Total Reactive Phosphorus for ROC samples for the demonstration facility during sampling dates for the second (a) and third (b) quarter operation at the demonstration facility. Comparison between Maxxam data (blue) and that performed at WLU (red), including standard deviations on triplicate samples

C.4 Statistical Differences Summary between Maxxam and WLU

C.4.1First Quarter—TP Measurements Only for RWW, MFP, ROP and ROC

As stated previously during the first quarter only TP data was collected for each of the sample collections for the entire quarter and therefore statistical analysis was performed only on TP data. The data for each lab was compiled and used to calculate a mean TP for each sample type (RWW, MFP, ROP and ROC) over the particular time frame; 95% confidence intervals were then calculated for each sample type. As is easily observed in Figure C.11, both labs agree within 95% CI for TP analysis, which supports the accuracy of measurements provided by both labs, including the data measured only by Maxxam as more sampling events were analyzed by that facility.

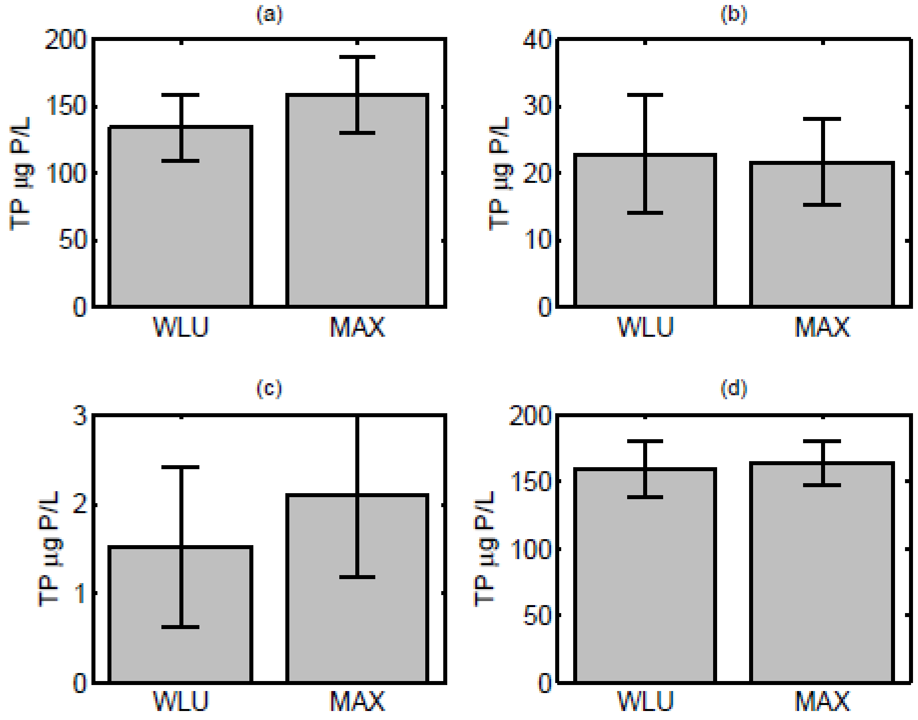


Figure C.11a-d: Total Phosphorus for (a) RWW, (b) MFP, (c) ROP and (d) ROC samples for the demonstration facility during sampling dates for the first quarter of operation. Comparison between Maxxam data and that performed at WLU, the mean of the data from both labs over the sampling times described and the error bars represent the 95% confidence intervals. Note for ROP: non-detects were considered to be 1 ppb when performing this analysis for Maxxam

Total phosphorus analysis of MFP and ROC provided the most consistent results between labs, achieving very similar means. Analyses of RWW and ROP, have varying means, but still agree within the CI selected for analysis. Again these variations are most likely resultant of the consistency in sample for the MFP and ROC, while the RWW will vary as a result of phosphorus bound to particulate and organic matter in the unfiltered sample and the ROP could vary because of the assumptions made about the large number of non-detects. Overall the data is consistent between the two analytical facilities for the first quarter of operation at the demonstration facility.

C.4.2 Third Quarter—TP and tRP Measurements for RWW, MFP, ROP and ROC

During the third quarter of operation at the demonstration facility both tRP and TP were measured for each of the sample types. As well, the new procedure using the shortened incubation time for the ROP analysis was utilized throughout this quarter. The data for each lab was compiled and used to calculate a mean TP and tRP for each sample type (RWW, MFP, ROP and ROC) over the particular time interval; 95% confidence intervals were then calculated for each sample type for the respective means. As is easily observed in Figure C.12, both labs agree within 95% CI for TP analysis all samples, which supports the accuracy of measurements provided by both labs, including the data measured only by Maxxam as more sampling events were analyzed by that facility. Total reactive phosphorus agrees within the 95% CI for all samples except RWW, which has been previously discussed in Chapter 8.3.

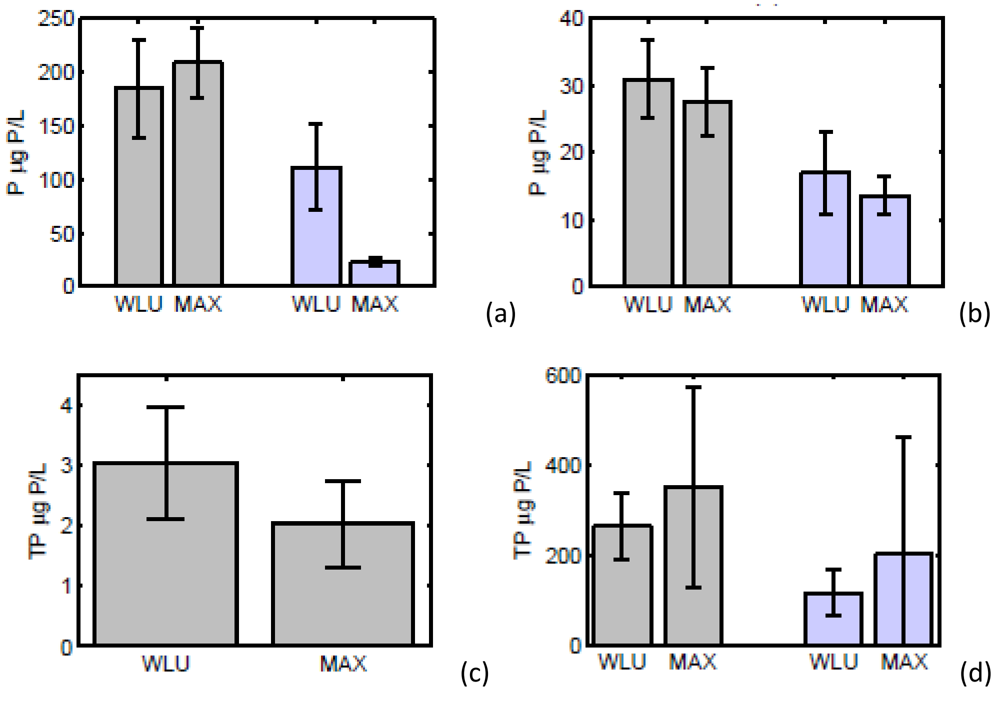


Figure C.12: Total and Total Reactive Phosphorus for (a) RWW, (b) MFP, (c) ROP and (d) ROC samples for the demonstration facility during sampling dates for the first quarter of operation. Comparison between Maxxam data and that performed at WLU, the mean of the data from both labs over the sampling times described and the error bars represent the 95% confidence intervals. Note for ROP: non-detects were considered to be 1 ppb when performing this analysis for Maxxam