Optimizing CoMag® System Operations

Billerica, MA Wastewater Treatment Plant

A Worcester Polytechnic Institute Major Qualifying Project

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Abstract

The Billerica, MA Wastewater Treatment Plant uses alum addition with CoMag® treatment for phosphorus removal before discharging to the Concord River. The plant's NPDES permit constrains levels of total phosphorus to 0.2 mg/L and total aluminum to 171 µg/L in the summer effluent water. The CoMag® system utilizes magnetite to enhance settling rates and improve removal of precipitated compounds. CoMag® is owned by Evoqua Water Technologies and due to its proprietary nature, documentation on optimal operating conditions was limited at the time of this project. Therefore, the goal of this project was to determine the optimal parameters of the CoMag® system, while meeting NPDES permit total phosphorus and total aluminum levels. A bench-scale, batch system was developed in the laboratory to simulate the multi-step CoMag® system. Alum dosing, pH, and system sludge recycle concentration were altered to determine the most effective conditions for total phosphorus and total aluminum removal. Testing was performed on samples of secondary effluent wastewater taken from the plant between October 2014 and January 2015. The most significant trend, found through bench-scale testing, was that lower sludge recycle concentrations yielded higher total phosphorus and total aluminum removal. Following bench-scale testing, recommendations for adaptations on the full-scale system were provided to the Billerica, MA WWTP.

Executive Summary

Background:
The Billerica Wastewater Treatment Plant, a municipal wastewater treatment facility located in Billerica, Massachusetts, is designed for 5.5 MGD average daily flow and 16.5 MGD peak hourly flow. The wastewater treatment plant is permitted to discharge through a NPDES permit issued by the EPA, and therefore must reduce the effluent concentrations of total phosphorus to 0.2 mg/L (from April 1-October 31) and 1.0 mg/L (from November 1-March 31). In anticipation of stricter permits, a new tertiary treatment system was designed using CoMag®. This new system came online in October 2010. In April 2014, the NPDES permit for total aluminum was revised from 357 µg/L to 171 µg/L.

The CoMag® process is used for nutrient removal during tertiary treatment. Effluent from secondary treatment enters the system and alum, the coagulant, is added via flash-mixing in the piping, reducing the pH and creating floc. Caustic is added at this time to achieve a target pH of 6.3. The CoMag® System is made of four zones of 11' x 11' x 14' tanks. The alum dosed water enters the first and second zones for coagulation and flocculation. The water flows into the third zone and experiences faster mixing. Magnetite or iron ore Fe_3O_4, a solid of a higher specific gravity than water and five times as dense as sand, is added, and binds with the floc, increasing its density. This is known as ballasted flocculation. Next, the water enters the fourth zone, with a slower mixing speed. The polymer, an anionic polyacrylamide in water-in-oil emulsion, is added, causing the flocs to agglomerate. The flow is then distributed between two clarifiers, where the ballasted floc settles quickly. Sludge from the clarifier is recycled to the third zone, or to the magnetite recovery process. The effluent water from the CoMag® clarifiers is distributed to the chlorine contact tanks for disinfection before discharge to the Concord River.

Methodology:
A bench-scale, batch system was developed for testing in the WPI laboratory. One liter samples of secondary clarifier effluent from the Billerica plant were placed in 1 L beakers. Secondary clarifier effluent was also put aside for total aluminum, total phosphorus, and orthophosphate testing. Flash mixing, zones 1-4, and clarification were replicated on the bench scale by varying the speed of the mixers. The bench-scale model also replicated the chemical addition, sludge recycle, and magnetite and polymer addition process. TSS samples were taken for analysis during the zone 4 step. Finally, 500 mL of sample was decanted and used for pH testing, total aluminum, total phosphorus, orthophosphate, and turbidity testing.

The table below outlines the variables that were manipulated during bench-scale testing:

Variables of focus for bench-scale testing

CoMag® Variables	Plant Conditions	Experimental Range
pH	6.3	5.0 – 8.0
Alum Dose	50.0 mg/L	25.0 – 78.0 mg/L
Sludge Recycle Concentration	4.0 g/L	0.0 – 6.0 g/L

The variables of pH, alum dose, and sludge concentration were chosen for their potential influence on phosphorus and aluminum removal. Sludge concentration was chosen for its effect on settling. These three variables were automated at the plant, and thus changes can be implemented relatively early. Due to the scope and time limit on this project the effects of mixing speeds, retention times, and magnetite and polymer addition were not tested.

Results:

Higher total phosphorus and orthophosphate removal was seen with sludge recycle concentrations below 2.0 g/L. As seen in the figure below, when sludge recycle was increased, the amount of final orthophosphate and final total phosphorus increased. The lowest final orthophosphate value of 0.02 mg/L P, the detection limit of the HACH DR6000, was achieved by a sludge recycle concentration of 1.0 g/L. Sludge recycle concentrations of 0.0, 0.5, and 1.0 g/L all resulted in the lowest final total phosphorous of 0.04 mg/L. At 2.0 g/L or lower, total phosphorus and total aluminum levels were below the plant's NPDES permit. Lower sludge recycle concentrations also resulted in lower turbidity levels in the system effluent.
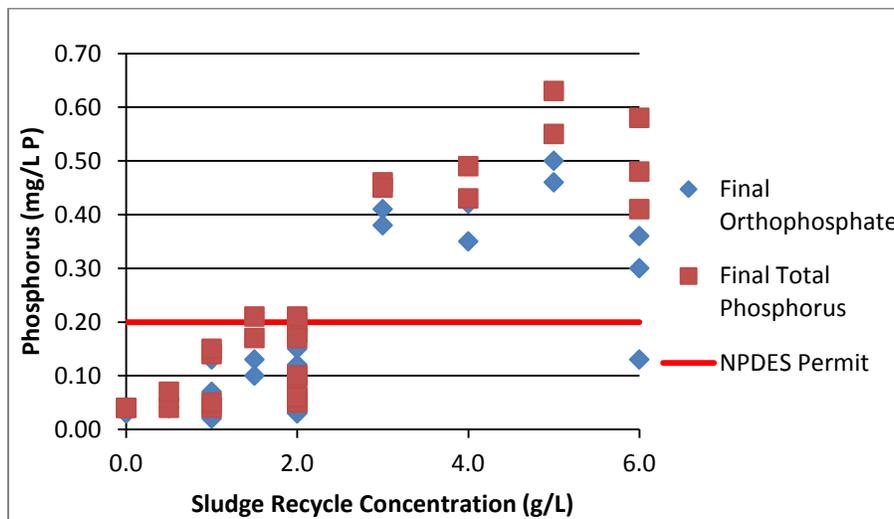
Relationship between final phosphorus level and sludge recycle concentration with a pH of 6.3 and an alum dose of 50.0 mg/L
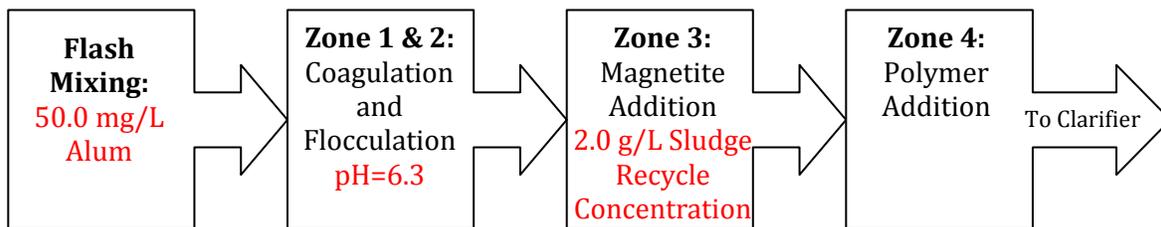
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Final total phosphorus and final orthophosphate were tested in 20 trials for the alum dose ranges stated above. When alum dose was increased both final orthophosphate and final total phosphorus levels increased as well. The lowest final orthophosphate value of 0.03 mg/L P was achieved by an alum dose of 25.0 mg/L, 37.5 mg/L, or 50.0 mg/L. This value neared the detection limit for the HACH DR6000 of 0.02 mg/L P. An alum dose of 50.0 mg/L also achieved the lowest final total phosphorus level of 0.05 mg/L P.

The pH of the system was tested at two sludge recycle concentrations, 2.0 g/L and 6.0 g/L. Tests were performed at pH levels ranging from 5.0-8.0. Results for pH testing did not follow a linear trend; however, a pH of 6.3 stood out as the most successful level for total phosphorus and total aluminum removal.

Conclusions and Recommendations:
Through bench-scale testing, it was concluded that a lower sludge recycle concentration resulted in better total phosphorus and total aluminum removal. Although results from pH and alum dose testing were inconclusive, a pH of 6.3 and alum dose of 50.0 mg/L, the plant's current operating conditions, resulted in low total phosphorus and total aluminum levels.

The figure below presents the recommended operating conditions for the CoMag® system at the Billerica WWTP that reflect a 2.0 g/L or lower sludge recycle concentration, 50.0 mg/L alum dose, and pH of 6.3.

Flash Mixing: 50.0 mg/L Alum	**Zone 1 & 2:** Coagulation and Flocculation pH=6.3	**Zone 3:** Magnetite Addition 2.0 g/L Sludge Recycle Concentration	**Zone 4:** Polymer Addition	To Clarifier

Recommended Operating Conditions for the Billerica WWTP CoMag® System

By implementing the recommended operating conditions, the plant can expect to achieve effluent levels of total phosphorus and total aluminum below the current NPDES permit levels of 0.2 mg/L and 171 µg/L, respectively. The bench-scale testing completed in this study allowed for comparison of differing treatment conditions and selection of optimal parameters for operation. Full-scale testing is still needed to confirm actual effluent concentrations of phosphorus and aluminum using these conditions.

Lastly, the parameters of magnetite dose, polymer dose, and mixing speeds should be optimized. Total suspended solids (TSS) should be tested on the system.

Acknowledgements

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Capstone Design

This Major Qualifying Project (MQP) meets the requirements for Engineering Capstone Design at Worcester Polytechnic Institute. The Accreditation Board for Engineering and Technology (ABET) defines design as the "process of devising a system, component, or process to meet desired needs" (ABET 2011). The goal of this project was to meet the needs of the Billerica Wastewater Treatment Plant (WWTP), with regards to their tertiary treatment system, CoMag®. The plant is regulated by a National Pollutant Discharge Elimination System (NPDES) permit, which was renewed on April 23, 2014. The new permit required more stringent standards on effluent water quality of total phosphorus and total aluminum levels. The plant expects future permit renewals to become stricter on these two limitations, requiring operational or procedural changes. The purpose of this MQP was to establish the optimal operating parameters of the Billerica WWTP CoMag® system, in order to meet the current permit and to recommend methods for further reducing effluent concentrations of total phosphorus and total aluminum. This was done by devising a batch, bench-scale model and testing procedures for the CoMag® system.

The ABET definition of design continues, "it is a decision-making process (often iterative), in which the basic sciences, mathematics, and the engineering sciences are applied to convert resources optimally to meet these stated needs ... [and] appropriate engineering standards and multiple realistic constraints [are incorporated]" (ABET 2011). In order to design the bench-scale system, the team toured the WWTP and took photos of the site. The team coordinated with the plant manager and Professional Engineer project sponsor to better understand the full-scale plant operation. Economic, environmental, and manufacturability constraints were taken into account during planning. The economic constraint was that the plant did not want to make a financial investment into the system for a better outcome, but instead wanted to improve their current operation of the system by changing certain parameters. The environmental constraint was that the effluent quality had to meet the required NPDES permits. The manufacturability constraint was that the bench-scale system was designed in the lab, using what the lab had, and ordering necessary parts, within budget. The design of the bench-scale system was developed using engineering principles previously learned in the team members' curriculums. The team designed the procedure for using the bench-scale model for testing, including mixing speeds, retention times, chemical addition, and the inclusion of a recycle stream. The project provided a study of the relationship between the parameters of pH, alum dose, and sludge recycle concentration with the overall quality of treated effluent for the plant to achieve permit levels for total phosphorus and aluminum.

Professional Licensure

According to the National Council of Examiners for Engineering and Surveying (NCEES), obtaining professional engineer (PE) licensure protects the public and enforces standards, restricting practice only to those meeting qualifications in education, work experience, and exam sufficiency. State licensing boards require prospective Engineers to first earn a degree from an Accreditation Board for Engineering and Technology (ABET) accredited engineering program. Next, applicants are required to pass the *Fundamentals of Engineering* (FE) exam and achieve a minimum of four years work experience under the guidance of a PE. The final step for becoming a professional engineer is to pass the *Principles and Practice of Engineering* (PE) exam.

The difference between a professional and non-professional are the types of people they serve. Non-professionals serve customers knowledgeable enough to tell them what services they want performed. A professional serves clients because of the highly technical nature of the trade by presenting a problem or opportunity and proposes what services are required to reach a solution. Professional licensure ensures clients can rightfully put their trust in the work Engineers complete. The extensive academic and occupational experience required for recognition as a professional exposes an Engineer to a wide breadth of theoretical and practical aspects of the profession.

From the academic portion of a Professional Engineer's training, aspects like the fundamentals of theory, the conventional methods of practice, and the cutting edge of technology are gained. From the occupational portion of a Professional Engineer's training, aspects like client relations, business and project management, best practice methods, and the paramount interest in public safety are obtained. Engineers in the workforce also have the ability to network with other Engineers and specialists in certain fields of engineering. All of these gained experiences, reinforced with the *Fundamentals of Engineering Examination* and the *Principle & Practice of Engineering Examination*, provide an Engineer with a very wide pool of resources to draw from in order to provide professional services for clients.

Achieving a PE licensure is vital for several logistical and legal reasons. Only licensed engineers may sign, seal, and submit engineering plans or drawings to public authorities for approval. PEs are also responsible for the lives their work affects and therefore must hold themselves to high standards of ethical practice. Requiring licensure for engineering positions in government is becoming more stringent for jobs with higher responsibilities. Many states now require teachers educating students on engineering to also be licensed in their respective practices.

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Chapter 1: Introduction

The Billerica Wastewater Treatment Plant, a municipal wastewater treatment facility located in Billerica, Massachusetts, is designed for 5.5 MGD average daily flow and 16.5 MGD peak hourly flow. The wastewater treatment plant is permitted to discharge through a NPDES permit issued by the EPA, and therefore must reduce the effluent concentrations of total phosphorus to 0.2 mg/L (from April 1-October 31) and 1.0 mg/L (from November 1-March 31). In April 2014, the NPDES permit for total aluminum was revised from 357 μg/L to 171 μg/L. The existing system could not achieve the phosphorus level reductions and meet the aluminum level, thus a new tertiary treatment system was designed using CoMag®. The new system came online in October 2010. Using a combination of magnetite, chemical coagulation, flocculation, and ballasted sedimentation, this system is a cost effective phosphorus removal process (Hazlett & Kalmes, 2012).

The CoMag® system is currently owned by Evoqua Water Technologies. Due to its proprietary nature, very little documentation verifying optimum operating conditions is available. Thus, the goal of this project was to develop parameters to optimize the CoMag® system based off a bench scale model. The WPI team collaborated with Woodard and Curran, the current consulting engineering firm for the plant, to gain access to information pertaining to the optimization of the system. Billerica WWTP discovered that as phosphorus levels were reduced, the aluminum levels were not. The goal of this project was to not only optimize CoMag® to reduce phosphorus levels, but aluminum levels as well.

The first step of this project was background research, including the wastewater treatment plant processes, the CoMag® system, phosphorus removal, and aluminum removal. Next, a laboratory procedure for bench-scale testing to study phosphorus and aluminum removal while altering alum dose, pH, and sludge recycle concentrations, was developed. The team at WPI measured total phosphorus and orthophosphate levels, while Con-Test® Analytical Laboratories tested aluminum. Tests were performed before and after treatment to determine percent reductions and also to compare actual values to the NPDES permit. The team at WPI in Worcester Massachusetts tested total suspended solids and turbidity for more comparative data. Based on these results, operational parameters for the full-scale system were drawn and recommended. The following chapters provide background information, experimental methods, findings and analysis, and conclusions and recommendations on the optimization of the CoMag® process at the Billerica WWTP.

Chapter 2: Background

This chapter provides an overview of conventional wastewater treatment, operations at the Billerica Wastewater Treatment Plant (WWTP), the CoMag® process, and wastewater constituents. The Billerica WWTP employs conventional primary and secondary treatment technologies and a proprietary technology for tertiary treatment, which is described in detail in this chapter. Finally, a brief discussion of wastewater constituents is provided, focusing on aluminum and phosphorus for the Billerica WWTP.

2.1 Conventional Wastewater Treatment

Raw sewage from a community, including residential and pre-treated industrial wastes, gets collected and enters a wastewater treatment plant (WWTP) before being discharged to a receiving water body. This WWTP effluent has to meet certain water quality requirements laid out in permits before it can be discharged to the receiving water. In a typical wastewater treatment plant, treatment begins with a screening process for bulk solids removal, including bar racks and grit chambers. The removal of light organic suspended solids occurs during primary treatment by means of gravitational forces in primary sedimentation tanks. In secondary treatment, dissolved constituents are converted to insoluble biomass followed by biological floc removal via sedimentation and clarification. Activated sludge is a common biological process for aerobic microbial growth. Nutrient removal, such as nitrogen and phosphorus, takes place during tertiary treatment and can be accomplished by various steps, including precipitation, filtration, and additional biological activity. The effluent from tertiary treatment enters a chlorine contact tank for disinfection before discharge into a body of water (Davis and Masten 2014).

2.2 Billerica Wastewater Treatment Plant

The Billerica WWTP, located between the City of Lowell and the Town of Billerica, treats an average daily flow of 5.5 MGD to a peak hourly flow of 16.5 MGD of residential wastewater from Billerica and alum sludge from the Billerica water treatment facility. The plant has headworks that direct inflow through half inch bar screens and grit channels before a Parshall flume brings wastewater to three primary clarifiers for suspended solids removal. The effluent of the primary clarifiers is sent to a series of four aeration tanks for aerobic adsorption. Bacteria within these tanks remove 60-70 percent of biochemical oxygen demand (BOD) from the wastewater by converting organic material into carbon dioxide, water, and flocs to be settled during secondary treatment. Four additional clarifiers settle out flocs generated in the aeration tanks before tertiary treatment in the CoMag® process. The CoMag® system injects alum as the coagulant. Ferric was considered, but since alum is introduced before primary sedimentation, alum was chosen as the coagulant. An outline on the technology is in Section 2.3 CoMag® Process. Before final effluent is released back into the Concord River, the water flows through chlorine contact tanks and dechlorination

channels to disinfect any residual bacteria remaining in the water and to prevent unsafe levels of chlorine from leaving the plant.

On September 9, 2005, the Town of Billerica was issued a new NPDES permit for discharging effluent into the Concord River. The mandate for this new permit was to reduce the final effluent concentration of total phosphorus to 0.2 mg/L (from April 1-October 31) and 1.0 mg/L (from November 1-March 31) and total aluminum to 357 µg/L (annually) averaged on a monthly basis. To meet this requirement, Billerica hired Woodard & Curran to conduct a feasibility study of reducing effluent phosphorus using the CoMag® process. Testing using the CoMag® pilot plant ran from July 26 to August 17, 2007 where effluent test results from the CoMag® clarifier reported on total phosphorus, sludge solids, turbidity, and pH measurements. In order to meet the total aluminum limit for the plant, caustic dosing was reduced and alum dosing was increased. This encouraged higher flocculation in aerobic adsorption and the CoMag® system.

2.3 CoMag® Process

Figure 1 illustrates the CoMag® process for nutrient removal during tertiary treatment. In the figure, "Raw Water" refers to effluent from secondary treatment. Alum, the coagulant, is added via flash-mixing in the piping, reducing the pH and creating floc. Caustic is added at this time to achieve a target pH of 6.3. The CoMag® System is made of four zones of 11' x 11' x 14' tanks. Raw Water enters the first and second zones where it is mixed and single flocs form. The fluid flows into the third zone and experiences faster mixing. A solid of a higher specific gravity than water and five times as dense as sand, known as magnetite or iron ore Fe_3O_4, is added, and binds with the floc, increasing density. This is known as ballasted flocculation. Benefits from this type of flocculation include large floc particle sizes, and higher settling rate that leads to smaller sedimentation units and lower capital investment costs (Young and Edwards 2003). Magnetite is a superior ballast because it is hydrophobic, non-abrasive, dense, fully oxidized and insoluble, inexpensive, and reusable (EvoquaWaterTechnologies 2014). Next, the fluid enters the fourth zone with a slower mixing speed. The polymer, an anionic polyacrylamide in water-in-oil emulsion, is added, causing the flocs to agglomerate. The flow is distributed between two clarifiers, where the ballasted floc settles quickly. The clarifiers have radial weirs for increased weir length. Sludge is recycled to the third zone, or to the magnetite recovery process. This includes a shear mixer to break the magnetite from the flocs. Then the sludge enters the magnetite recovery drum, which is a large magnetic drum. Recovered magnetite is combined with virgin magnetite and mixed with the sludge recycle in the third zone. The effluent water from the CoMag® clarifiers is distributed to the chlorine contact tanks for disinfection before discharge to the Concord River. Note, in Billerica, there is no polishing magnet or backflush line and polymer is added in the fourth zone instead of the third, which are depicted in Figure 1.
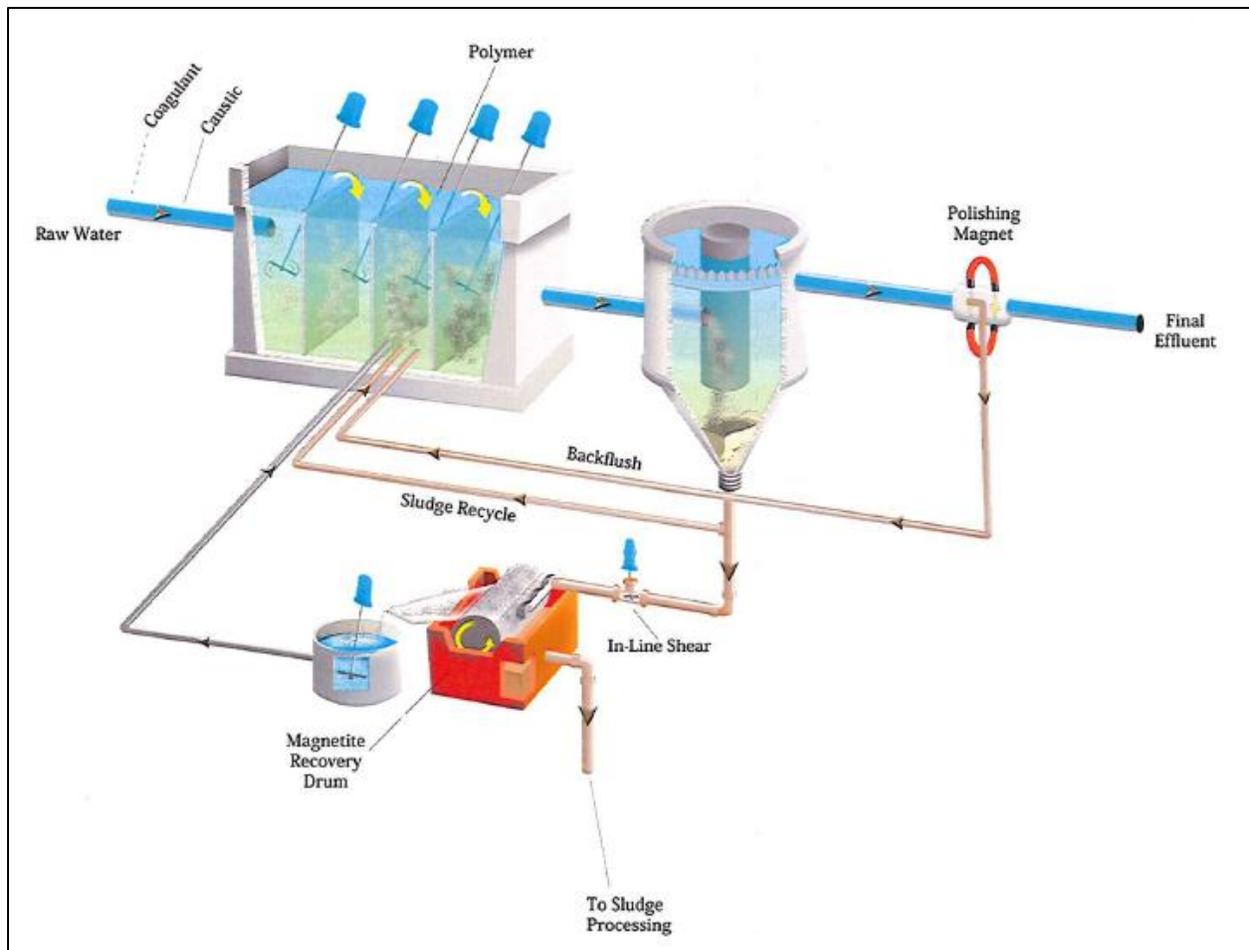
Figure 1. Evoqua Water Technologies' CoMag® System (EvoquaWaterTechnologies 2014)

2.4 Wastewater Constituents

Nutrients and other constituents are regulated in treated wastewater effluent because of their negative impacts on aquatic ecosystems and on the overall quality of water in the receiving body. Oxygen-demanding wastes are a concerning pollutant in discharge, because nutrients, such as phosphorus, contribute to the deterioration of water quality by causing excessive plant growth, like thick slime layers on rocks and dense growths of aquatic weeds (Davis and Masten 2014). This project focused on the presence of phosphorus and aluminum in the Billerica Wastewater Treatment Plant effluent, and thus these two potential pollutants are discussed further in the following sections.

2.4.1 Phosphorus

Municipal sewage contains phosphorus primarily from human excrement and industrial waste. Phosphorus is a particularly harmful constituent because it serves as a vital nutrient for algae growth. When the phosphorus availability meets the growth demands of algae, excessive algae blooms can occur. When the algae die, they are consumed in an oxygen-

demanding process, as bacteria degrade them as organic matter. This oxygen demand can overtax the dissolved oxygen supply in the receiving body, which can kill off fish species and disrupt the aquatic ecosystem (Davis & Masten, 2014).

Phosphorus is found in several different forms in the environment and in wastewater samples, including mineral forms, organic forms (such as phospholipids, nucleic acids and proteins), gaseous forms, colloidal forms and dissolved inorganic forms (pentavalent, trivalent, or univalent dissolved species) (Valls-Cantenys et al. 2012). These forms also include orthophosphates, polyphosphates, and organic phosphates. All of the different compounds present in wastewater are typically grouped and referred to as "total phosphorus". Typical untreated domestic wastewater can contain 5-20 mg/L of total phosphorus (Davis & Masten, 2014). NPDES regulations for phosphorus discharges are set as total phosphorus levels.

The Billerica Wastewater Treatment Plant currently has a seasonal NPDES total phosphorus permit. In the "Summer Season" (April 1 – October 31) the effluent total phosphorus level is 0.2 mg/L and in the "Winter Season" (November 1-March 31) the effluent total phosphorus level is 1.0 mg/L. See Appendix I for Billerica, MA NPDES total phosphorus regulations. The plant's total phosphorus discharge for the months of June, July, and August 2014 was 0.11 mg/L, 0.05 mg/L, and 0.14 mg/L respectively. Although not included in the NPDES permit, the level of reactive phosphorus or orthophosphates is also a parameter that can be tested. The plant's average orthophosphate discharge for the months of June, July, and August 2014 was 0.05 mg/L, 0.02 mg/L, and 0.05 mg/L respectively.

2.4.2 Aluminum

Several sources can contribute to the presence of aluminum in wastewater. The majority of aluminum enters wastewater in the form of aluminum sulfate, or alum, which was added by the plant, for the removal of phosphorus. The Billerica Wastewater Treatment Plant also receives discharges from the Billerica Water Treatment Plant, which contains varying levels of aluminum.

Aluminum is regulated by NPDES permits because of its potential toxic effects on fish under pH conditions where precipitation on the gill surface can occur. However, the toxicity of aluminum is heavily influenced by speciation. Species of aluminum can include dissolved free ions, soluble inorganic complexes, colloids, polymeric species, other insoluble complexes, and aluminum hydroxide. The speciation of aluminum is determined by pH value. At pH values less than 6, the speciation is dominated by $Al(OH)_2^+$, followed by $Al(OH)^{2+}$, and Al^{3+}; around pH values of 6.5 insoluble $Al(OH)_3$ dominates, and $Al(OH)_4^-$ is the main form for pH values above 7.5 (Comber et al. 2005).

The Billerica Wastewater Treatment Plant typically encounters 4.0-11.0 mg/L of total aluminum in its influent waters, as seen in Figure 2. However, the addition of alum for phosphorus removal drives those values higher. Historically, the plant was adding alum to influent water at the headworks and seeing total aluminum values of 210 µg/L to 540 µg/L in their final effluent. In May 2014 the plant increased its alum dosage at the headworks by 50 percent. The total aluminum level in the final plant effluent currently ranges from 110 µg/L to 300 µg/L. Billerica's NPDES permit allows for a discharge of 171 µg/L of total aluminum and a 7.9 lb/day as a monthly average, which the plant has exceeded on several accounts. However, the Plant's total phosphorus permits are seasonal and they will stop the addition of alum for phosphorus removal at the end of October 2014 and restart again in mid-March 2015. See Appendix I for Billerica Wastewater Treatment Facility NPDES total aluminum regulations. As seen in Figure 3, the plant has had varying success meeting these standards after the addition of the CoMag® process in September 2010.
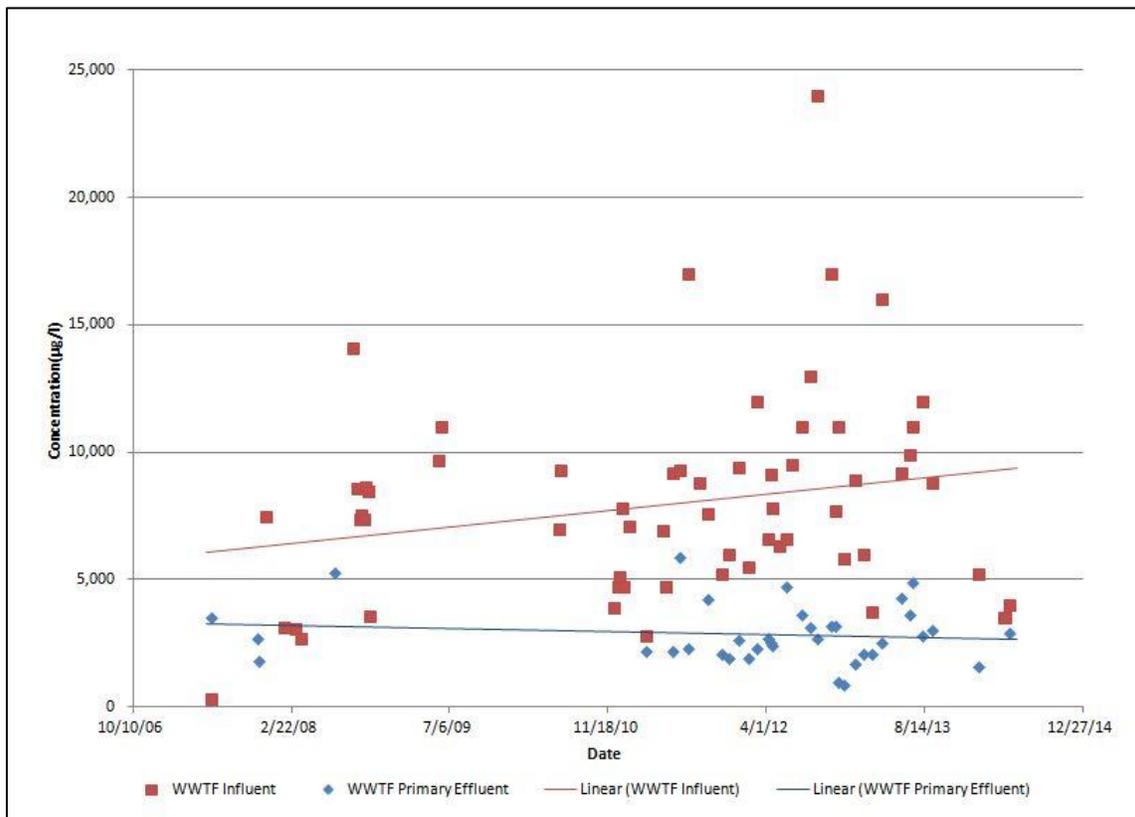
Figure 2. Billerica WWTP aluminum influent and primary effluent levels

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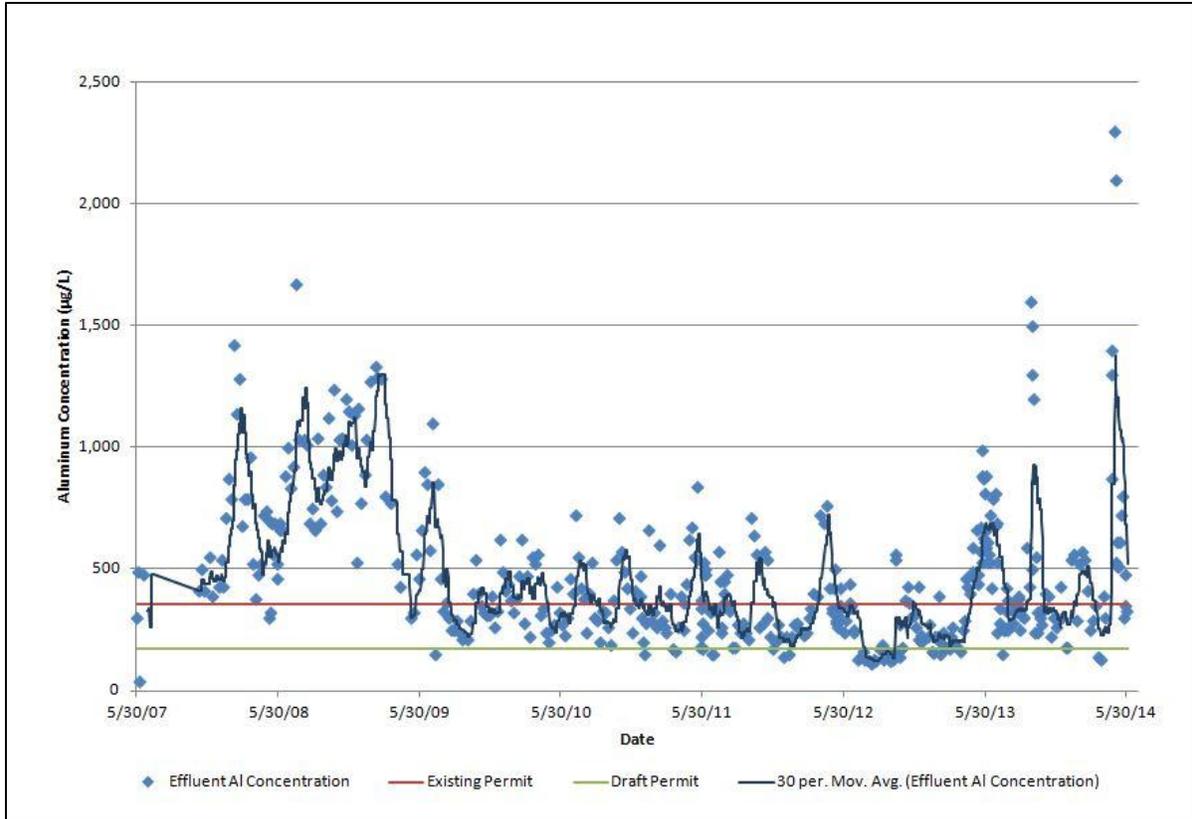
Figure 3. Billerica WWTP effluent aluminum concentrations

Chapter 3: Methodology

The project was completed by designing a bench-scale system to replicate the CoMag®
process, and testing various operational parameters. Prior to testing, retention times,
mixing speeds, pH adjustment, magnetite dosing, alum dosing, and recycle sludge dosing
were computed. For consistency, a stock of 1 L of cationic polymer and 1 L of magnetite
was collected from the Billerica plant to be used throughout the tests. The team at WPI
made acid and base solutions for pH adjustment and an alum solution as well.

Next, the bench-scale system was utilized to optimize the CoMag® system. At first, alum
dose, polymer dose, magnetite dose, and pH had the same concentrations and values as the
Billerica plant. Then, pH, alum dosage, and sludge recycle concentration were varied to find
the best operating conditions for removal of total phosphorus, orthophosphate, and total
aluminum. Total phosphorus, orthophosphate, and total aluminum concentrations were
measured before and after each bench-scale cycle of CoMag®. Total suspended solids were
measured for zone 4 of the process and turbidity levels of the effluent were also measured
for further comparison and analysis. Optimal treatment conditions were determined based
on minimizing total phosphorus, orthophosphates, and total aluminum levels.

3.1 Overview

Specific lab procedures are presented in Appendix II. The bench-scale CoMag® process
consists of batch testing as shown in Figure 4.
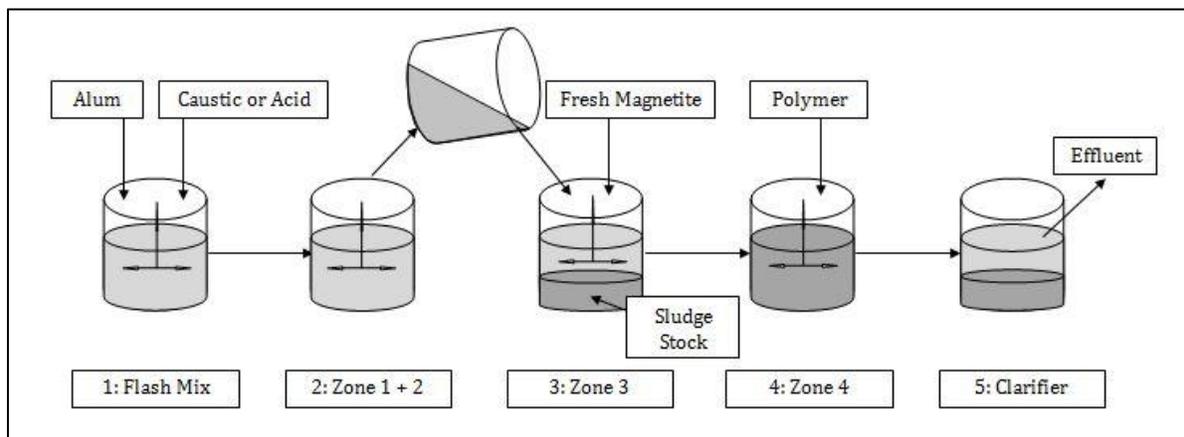
Figure 4. Bench-scale CoMag® System

One liter samples of secondary clarifier effluent from the Billerica plant were placed in 1 L
beakers. Secondary clarifier effluent was also put aside for total aluminum, total
phosphorus, and orthophosphate testing; refer to Section 3.4 for analytical methods. To
replicate flash mixing, samples received doses of alum, caustic, and/or acid to achieve a
certain pH and then mixed rapidly on a stir plate. Next, the samples were placed

underneath the mixer and mixed slowly to allow for a floc-forming period, to replicate zones 1 and 2. After zone 2, the mixer was stopped and beakers were removed from underneath the blades. Samples were poured into corresponding beakers with predetermined volumes of sludge stock from zone 4 of the plant. The combined sludge and sample beakers were placed back underneath the blades and the speed was increased greatly to replicate zone 3. Fresh magnetite was then added. After the completion of zone 3, polymer was added, and mixed gently, replicating zone 4. During the last half of zone 4, 25 mL samples were pipetted from each beaker for total suspended solids (TSS) testing; refer to Section 3.4. Following zone 4, the mixer was turned off and the samples were then left to settle, mimicking the clarification step. Finally, 500 mL of sample was decanted and used for pH testing, total aluminum, total phosphorus, orthophosphate, and turbidity testing; refer to Section 3.4.

3.2 Bench-Scale Design

Parameter conversions were made in order to construct a bench-scale model that represented the full-scale CoMag® system. These parameters included the mixing speeds and retention times for each zone, the dosing of alum in the flash mixing step, the dosing of caustic or acid to control pH, the dosing of magnetite in zone 3, the amount of sludge recycle and concentration of total suspended solids in zone 3, and the polymer dosing in zone 4.

3.2.1 Mixing Speeds

The mixing speeds were determined for the Phipps & Bird mixer, within the laboratory, through trial and error. The most important factor was to achieve well mixed conditions for magnetite during the zone 3 addition. Observably, the lowest speed the fresh magnetite stayed entrained within the mixture was at 175 rpm. After this conclusion was made, the rest of the speeds for each zone were determined, in correlation to the speeds used at the plant. Zone 1 and 2 represented the coagulation and flocculation steps of the process and both required much lower mixing speeds than zone 3. Zone 2 needed to have the lowest mixing speed overall, to allow for better flocculation. Zone 4 was the polymer addition step of the process and also required a lower mixing speed than zone 3. To allow for easier pH adjustment and alum addition in the laboratory, flash mixing was conducted on a magnetic stir plate at 700 rpm. Table 1 shows the speeds used for each zone in the bench-scale test (in rpm) and the speeds used at the plant.

Table 1. Mixer speeds for bench-scale testing

Zone	Actual Speeds (rpm)	Billerica WWTP Mixing Speeds (Hz)
1	110	38 Hz
2	50	25 Hz
3	175	48 Hz
4	110	32 Hz

3.2.2 Retention Times

In order to perform bench-scale testing, the hydraulic residence time for each step of the full-scale process was calculated. An exception was for Step 1, the Flash Mixer step. Fifty seconds was chosen as the residence time to represent flash mixing in the pipe before CoMag®, per the advice from advisors, Professor Bergendahl and Professor Plummer. The hydraulic residence time, τ, was calculated using Equation 1.

$$\tau = \frac{volume}{flowrate} \qquad \text{Equation 1}$$

The volume is the volume of the tanks, and the flow rate chosen was 2.93 MGD (7701 L/min), an average taken from Billerica's WWTP in October, 2014, seen in Table 2.

Table 2. Influent flow to CoMag® system at the Billerica WWTP

Date	Influent Flow to CoMag® (MGD)
10/1/2014	2.851
10/2/2014	2.915
10/3/2014	2.983
10/4/2014	2.909
10/5/2014	2.878
10/6/2014	2.740
10/7/2014	2.950
10/8/2014	3.110
10/9/2014	3.012
AVG	**2.930**

This average was chosen because it represented the plant conditions during one of the months in which testing occurred. The volumes of each tank are 11' x 11' x 14'. Therefore, using Equation 1, the time in each tank was calculated as 6 minutes and 15 seconds, as shown in the following sample calculation:

$$flow_{CoMag} = 2.93 MGD = 2.93 \times 10^6 \frac{gal}{day}\left(\frac{1\ day}{24\ h}\right)\left(\frac{0.00378m^3}{1\ gal}\right) = 461\frac{m^3}{h}$$

$$volume_{zone\ 1} = 11ft \times 11ft \times 14ft = 1694ft^3\left(\frac{1m}{3.28ft}\right)^3 = 48.01m^3$$

$$\tau_{zone\ 1} = \frac{flow}{volume} = \frac{461\frac{m^3}{h}}{48.01m^3}\left(\frac{60min}{1h}\right) = 6.25min$$

The last step of the process represented the clarifier, which had a diameter of 23' and height of 15'. The residence time was calculated to be 23 minutes. A summary of the residence times for the bench-scale testing is in Table 3.

Table 3. Residence time for the CoMag® bench-scale testing steps

Step	Residence Time, τ (min : sec)
Flash Mix	00:50
Zone 1	06:15
Zone 2	06:15
Zone 3	06:15
Zone 4	06:15
Clarifier	23:00
TOTAL	48:50

3.2.3 Flash Mix Alum Addition
Alum was added during the flash mixing step, to a 1 L beaker of wastewater. The initial dosage of alum for bench-scale testing was determined using plant data and mimicking that of the plant. When the flow rate of WW through CoMag® was 3.84 MGD (10,106 L/min), the flow rate of alum was automatically adjusted to 0.000191 MGD (0.504 L/min). The concentration of alum in the flash mix beaker, assuming the bulk alum was dilute and equal to the density of water, was calculated as shown in Equation 2.

$$\left(\frac{0.504\ L}{min}\right) * \left(\frac{1000\ g}{L}\right) = \frac{504\ g}{min}\ alum$$

$$\frac{504\ g}{min}\ alum * \left(\frac{1\ min}{10106\ L}\right)\left(\frac{1000\ mg}{1\ g}\right) = \frac{50\ mg}{L}\ alum \qquad \text{Equation 2}$$

A stock alum solution was prepared in the laboratory from dry chemical. Since a small volume of stock addition was desired, the concentration of the stock solution was determined using Equation 3, assuming that 1 mL of stock would be added to a 1 L sample to achieve a 50 mg/L dose.

$$C_{stock}V_{stock} = C_{dose}V_{dose}$$

$$C_{stock}(1\ mL) = \left(50\frac{mg}{L}\right)(1000mL)$$

$$C_{stock} = \left(\frac{50000\ mg}{L}\right)\left(\frac{1\ g}{1000\ mg}\right) = 50\frac{g}{L}\ alum \qquad \text{Equation 3}$$

100 mL of alum stock solution of 50 g/L alum was prepared in the laboratory, using 5 g of aluminum sulfate (Fisher Scientific, A613-500), per Equation 4. First, 5 g of aluminum sulfate were dissolved in 80 mL of purified water in a beaker on a stir plate with Teflon-coated stir bar. Then the solution was poured into a 100 mL Erlenmeyer flask. Purified water was added until the solution was 100 mL in volume. All supplies used were triple rinsed with purified water.

$$\left(\frac{50\ g}{L}\right)\left(\frac{1\ L}{1000\ mL}\right) * 100\ mL\ solution = 5g\ Al_2(SO_4)_3 \cdot 14H_2O \qquad \text{Equation 4}$$

3.2.4 Flash Mix Caustic and Acid Addition for pH Control

The target pH for CoMag®, according to the Billerica WWTP operators, was 6.3. During flash mixing, the pH was monitored. To raise the pH, 0.1 N NaOH, or caustic, was added drop wise. Similarly, to lower the pH, 1 N H_2SO_4 was added drop wise. The flash mix step was performed using a stir plate, and the beakers were transferred to the Phipps & Bird mixer.

Caustic and acid solutions were made in the laboratory. 100 mL of caustic was made using 0.4 g of NaOH (Fisher Scientific, S318-1), per Equation 5. First, 0.4 g of NaOH were dissolved in 80 mL of purified water in a beaker on a stir plate with stir bar. Then the solution was poured into a 100 mL Erlenmeyer flask. Purified water was added until the solution was 100 mL in volume. All supplies used were triple rinsed with purified water.

$$\left(\frac{0.1\ mol\ NaOH}{L}\right)\left(\frac{40\ g\ NaOH}{1\ mol\ NaOH)}\right) = \frac{4g\ NaOH}{1L\ Solution}$$

$$\left(\frac{4g\ NaOH}{1L\ Solution}\right)\left(\frac{1L}{1000mL}\right) * 100mL\ Solution = 0.4g\ NaOH \qquad \text{Equation 5}$$

100 mL of 1 N H_2SO_4 was made using 2.75 mL of a stock solution of 97% H_2SO_4 and specific gravity of 1.84 (Fisher Scientific, A300S-I212), per Equation 6. First, 2.75 mL of stock was stirred in 80 mL of purified water in a beaker on a stir plate with Teflon-coated stir bar. Then the solution was poured into a 100 mL Erlenmeyer flask. Purified water was added until the solution was 100 mL in volume. All supplies used were triple rinsed with purified water.

$$Equivalent\ Mass = \frac{gram - formula\ weight}{\#\ of\ acid\ hydrogens} = \frac{98}{2} = 49$$

$$Grams\ of\ compound\ needed = (N\ desired) * (Equivalent\ Mass) * (vol\ in\ mol\ desired)$$

$$= (1) * (49) * (0.100) = 4.9\ g$$

$$Vol\ of\ stock\ needed = \frac{Grams\ of\ compound\ needed}{(\%conc) * (specific\ gravity)}$$

$$= \frac{4.9}{(0.97)*(1.84)} = 2.75\ mL \qquad\qquad \text{Equation 6}$$

3.2.5 Zone 3 Recycle Volume

The volume of sludge recycled during bench-scale testing depended on the concentration desired in the zone 3 beaker and the concentration of the sludge stock collected from the plant. A sludge stock was collected from zone 4 of the plant and its concentration (g/L) was analyzed in the lab. This was done by weighing the mass of an empty beaker, added a known volume of well-mixed sludge stock, dried within the oven at 103 °C, cooled and weighed to obtain the mass of total solids in the sample volume, shown in Equation 7.

$$conc_{stock} = \frac{g\ solids}{L\ stock\ sample} \qquad\qquad \text{Equation 7}$$

To determine the volume of sludge stock that needed to be present in the zone 3 beaker, the desired concentration was divided by the concentration of the sludge stock and then multiplied by the desired volume of 1000 mL, shown in Equation 8.

$$V_{stock} = \frac{conc_{desired}*V_{desired}}{conc_{stock}} \qquad\qquad \text{Equation 8}$$

The volume of recycled sludge had an effect on the dosing of Magnetite and Polymer in zones 3 and 4. Equation 9 shows the corrective factor, x, to account for the relationship between the volume of recycled sludge to the dosing of Magnetite and Polymer.

Corrective Volume Factor, x, when dosing was adjusted:

$$x = \frac{1000 - Recycle\ Volume\ (mL)}{1000} \qquad\qquad \text{Equation 9}$$

3.2.6 Zone 3 Magnetite Addition

The average magnetite concentration of three grab samples in the full-scale plant was found in order to determine the dosing of magnetite in zone 3 in the bench-scale. Each grab sample was taken from the fourth tank on October 10, 2014, and poured into a graduated cylinder. The volume was then recorded. The sample was blended at high speed for a minute to separate floc from magnetite and poured into a glass beaker. A magnet was placed on the bottom of the beaker and the water was decanted. The magnetite was rinsed several times, and then added to a pre-weighed foil pan. It was dried in the oven at 104 °C for one hour, cooled and then weighed. The mass of the magnetite was recorded, by subtracting the masses collected, per Equation 10.

$$m_{mag} = m_{mag+tray} - m_{tray}$$
<div align="right">Equation 10</div>

The concentration of magnetite in zone 4 was calculated by dividing the mass of magnetite by the liquid volume of the sample. Results of the three trials are shown in Table 4.

<div align="center">Table 4. Concentration of Magnetite in Zone 4</div>

Sample	Sample Volume (mL)	Mass of Magnetite (g)	Concentration (g/L)
1	760	1.4184	1.87
2	755	1.2952	1.72
3	770	1.0698	1.39
Average	762	1.2611	1.67

For bench-scale testing, the average concentration was used, 1.67 g/L Magnetite, in conjunction with Equation 9, which adjusted for the volume of recycle addition with the Corrective Volume Factor, x, from Section 3.2.5. Therefore, Equation 11 provides the mass of fresh magnetite necessary to add in zone 3.

$$Magnetite\ (g) = 1.67x$$
<div align="right">Equation 11</div>

3.2.7 Zone 4 Polymer Addition

The volume of polymer added to the bench-scale zone 4 step was determined using plant data. The calculations were based on a polymer rate of 4 gal/day and wastewater flow of 2.93 MGD (7701 L/min). A polymer to water ratio was developed, per Equation 12.

$$\left(\frac{4\ gal}{day}\right)\left(\frac{1\ L}{0.264\ gal}\right) = 15.15\ \frac{L}{day}\ polymer$$

$$\frac{2.93x10^6\ gal}{day}\ x\ \frac{1\ L}{0.264\ gal} = 1.11x10^7\ \frac{L}{day}\ WW$$

$$\left(\frac{Polymer}{WW}\right) = \left(\frac{15.15\frac{L}{d}}{1.11x10^7\frac{L}{d}}\right) = 1.36\ x\ 10^{-6}$$

$$1.36\ x\ 10^{-6}\ x\ 1\ L\ WW = 1.36\ \mu L\ polymer \qquad\qquad \text{Equation 12}$$

These calculations show that every liter of wastewater is treated with 1.36 μL polymer.

In the laboratory, a stock solution of a 1000-fold dilution of polymer was made weekly, so that the delivery of polymer could be performed. Due to the high viscosity of the fluid, measuring milliliters of polymer was desired over microliters.

Therefore, Equation 9 was used to determine polymer addition, which adjusted for the volume of recycle with the Corrective Volume Factor, x, from Section 3.2.5. Thus, Equation 13 provides the volume necessary to add in zone 4.

$$Polymer\ (mL) = 1.36x \qquad\qquad \text{Equation 13}$$

3.3 Bench-Scale Testing

Table 5 outlines the variables that were manipulated during bench-scale testing:

Table 5. Bench-scale testing variables

CoMag® Variable	Plant Conditions	Experimental Range
pH	6.3	5.0 – 8.0
Alum Dose	50.0 mg/L	25.0 – 78.0 mg/L
Sludge Recycle Concentration	4.0 g/L	0.0 – 6.0 g/L

The variables of pH, alum dose, and sludge concentration were chosen for their potential influence on phosphorus and aluminum removal. Sludge concentration was chosen for its effect on settling. These three variables were automated at the plant, and thus changes can be implemented relatively early.

Due to the scope and time limit on this project, the following variables were kept constant throughout all tests: mixing speeds, retention times, and magnetite and polymer addition. Mixing speeds were not manipulated because a conversion from bench-scale to full-scale would require more study on the existing blades and mixing forces. Polymer was also not

explored further because of the lack of data regarding its chemical makeup due to its proprietary nature.

3.3.1 Testing pH Ranges

At the Billerica WWTP, a pH probe was located at the beginning of the CoMag® system to monitor the pH level of the influent water after being dosed with alum. The pH level of the system was automatically adjusted with the addition of caustic to the target level of 6.3. During bench-scale testing, the adjustment of pH involved adding caustic or acid drop wise, to achieve the desired pH during the flash mix step. A pH range of 5.0 – 8.0 was tested with sludge recycle concentrations of 2.0 g/L and 6.0 g/L. This range of pH values was chosen to study the effects of high and low pH values on water quality.

3.3.2 Testing Alum Dose Ranges

The plant condition of 50.0 mg/L was calculated from 50 ppmv, the automatic setting of the plant. Throughout bench-scale testing, the method for adjusting alum stock (50.0 g/L) dose was conducted by adding more or less alum during the flash mix step. The alum solubility chart also influenced the range tested.

The solubility curve of aluminum, Figure 5, was analyzed to determine the solubility of alum in water with a pH of 6.3.
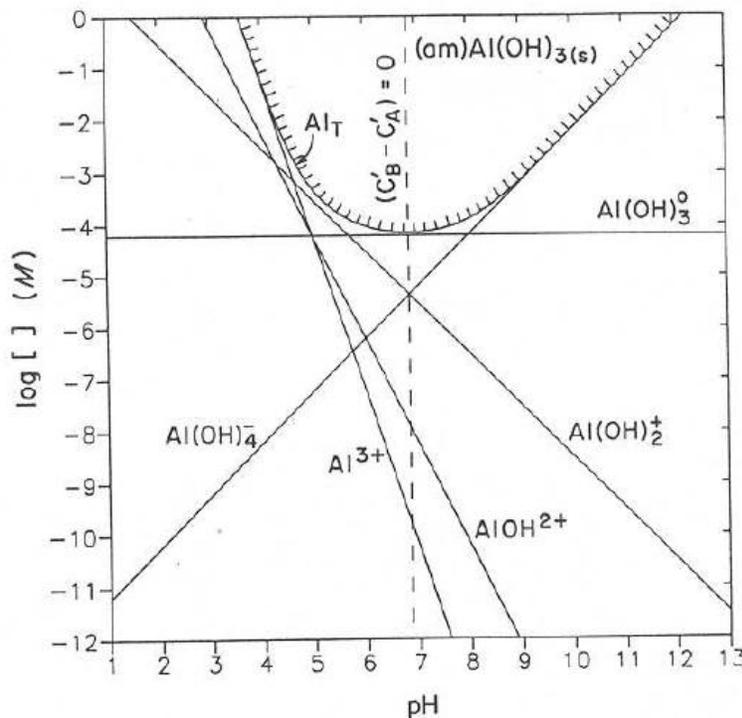
Figure 5. Solubility of aluminum in water (Crittenden et al. 2012)

The minimum dose of alum in water to precipitate Al(OH)$_3$ (s) was calculated using the curve, per Equation 14.

$$pH = 6.3$$

$$MW_{alum} = 594\frac{g}{mol}\ Al_2SO_4 \cdot 14H_2O$$

$$At\ pH = 6.3, \log(M) = -4$$

$$\log(M) = -4$$

$$M = 10^{-4}\frac{mol}{L}$$

$$\left(\frac{10^{-4}\ mol\ alum}{L}\right) * \left(\frac{594\ g\ alum}{mol}\right)\left(\frac{1000\ mg}{1\ g}\right) = 59.4\frac{mg}{L}\ alum \qquad\qquad \text{Equation 14}$$

Therefore, concentrations above, at, and below 59.4 mg/L were studied.

3.3.3 Testing Sludge Recycle Concentration Ranges

The plant condition of 4.0 g/L was determined by averaging the concentrations of eight grab samples of total solids in zone 4 of the plant, taken at various times between October and December 2014. The concentration of total solids varied depending on seasonal flow, with a high of 6.4 g/L and a low of 2.2 g/L. It was assumed that the amount of new sludge produced in the system was negligible and, therefore, the concentration of sludge recycle was equal to the total solids concentration. Throughout bench-scale testing, the method for adjusting sludge recycle concentration involved changing the volume of sludge stock added during the zone 3 step, as described in Section 3.2.5. The physical state of aluminum was studied, as discussed in Section 3.4.5 and Section 4.1, which indicated aluminum was in the particulate form. Therefore, sludge recycle concentration was chosen as a variable to study, to see what concentration yielded better settling results of aluminum.

3.4 Analytical Methods

The section describes the analytical methods used during the different tests performed for the project. Total aluminum, total phosphorus, and orthophosphate were tested prior to bench-scale CoMag® using secondary clarifier effluent. Total aluminum, total phosphorus, orthophosphate, total suspended solids (TSS), and turbidity were tested on all treated samples. Finally, the physical state of aluminum species in the plant's CoMag® clarifier effluent was determined through filtration.

3.4.1 Aluminum Testing

Aluminum was measured as total aluminum. Samples for testing were prepared in the laboratory using sample vials provided by Con-Test® Analytical Laboratories, in East Longmeadow MA. Con-Test® Analytical Laboratories, following test method EPA 200.7, performed sample testing and result generation.

3.4.2 Phosphorus Testing

Phosphorus tests for total phosphorus and orthophosphates were conducted at WPI. Tests were performed before and after treatment to determine percent reductions and also to compare actual values to the NPDES summer permit concentration of 0.2 mg/L P.

3.4.2.1 Total Phosphorus

Total phosphorus was measured using HACH Method 8190: Test 'N Tube Vials Method. For this method, a 5.0 mL sample was added to a Total Phosphorus Test Vial along with the contents of one Potassium Persulfate Powder Pillow for Phosphonate. The vial was capped and shaken until the contents of the powder pillow were dissolved. The sample was incubated for 30 minutes at 150°C. After incubation, the sample was cooled to room temperature and then 2.0 mL of 1.54 N Sodium Hydroxide Standard Solution was added. After zeroing the HACH DR 6000 spectrophotometer with the vial, the contents of one PhosVer 3 Powder Pillow were added to the vial and the sample was well mixed. After two minutes of reaction time, the total phosphorus concentration was recorded in mg/L P. Appendix III provides the detailed testing procedure.

3.4.2.2 Orthophosphates

Orthophosphate was measured using HACH Method 8048: Test 'N Tube Vials Method. For this method, 5.0 mL of sample was added to a Reactive Phosphorus Test 'N Tube Vial and then well mixed. After zeroing the HACH DR 6000 spectrophotometer with the vial, one PhosVer 3 Phosphate Powder Pillow, containing molybdate and acid, was added to the vial. After two minutes of reaction time, the orthophosphate concentration was recorded in mg/L P. Appendix IV provides the detailed testing procedure.

3.4.3 Total Suspended Solids Testing

The solid to magnetite ratio was determined after each bench-scale test. Appendix II provides the detailed testing procedures. 25.0 mL grab samples were taken before mixers were turned off for clarification. Each sample was blended separately for two minutes with an additional 150 mL of purified deionized (DI) water, which made the height of the liquid higher than the blades for effective blending. Magnetite was separated from the blended floc sample using a magnet. TSS were filtered with 1.2 μm porosity FisherBrand, Glass Fiber Filters, which had been previously weighed. The filters were then dried and re-weighed to determine the mass of total suspended solids filtered out of the treated effluent prior to clarification, as in Equation 15.

$$mass_{TSS} = mass_{floc+filter} - mass_{dry\ filter} \qquad \text{Equation 15}$$

This mass was compared with the weighed mass of dried magnetite to calculate what ratio of solids to magnetite the bench-scale tests were, per Equation 16.

$$\frac{mass_{magnetite}}{mass_{TSS}} = \text{magnetite to TSS ratio} \qquad \text{Equation 16}$$

3.4.4 Turbidity Testing

Turbidity measurements were taken using the NTU setting on the HACH 2100N Turbidimeter. A vial of supernatant was taken from each sample after bench-scale clarification. The vial was inserted into the HACH 2100N Turbidimeter and turbidity levels were recorded in NTU.

3.4.5 Physical State of Aluminum

A grab sample was taken from the plant's CoMag® system clarifier effluent. 1000 mL of effluent was measured out three times and labeled as sample 1 through 3. For each sample, 250 mL were measured out before the first filtration and added to Con-Test® Analytical Laboratories provided test bottles and labeled with the sample number and "A". The remaining 750 mL of sample was then filtered through a 1.5 µm pore filter. 250 mL of the filtrate was measured and added to a Con-Test® provided test bottle and labeled with the sample number and "B". The remaining 500 mL of sample was then filtered through a 0.45 µm pore filter. 250 mL of the filtrate was measured and added to a Con-Test® provided sample bottle and labeled with the sample number and "C". The final 250 mL of sample was passed through a 0.22 µm pore filter (a 0.10 µm pore sized filter was used for grab sample 3). The filtrate was added to a Con-Test® provided sample bottle and labeled with the sample number and "D". Sample bottles were sent out to Con-Test® for total aluminum analysis.

Chapter 4: Findings and Analysis

The CoMag® process was replicated using a bench-scale, batch system. The operating parameters of pH, alum dose, and sludge recycle concentration were tested for system optimization and produced varying degrees of success in reducing total phosphorus and total aluminum levels. In addition, the effects on orthophosphate removal, turbidity, and total suspended solids (TSS) were analyzed. Existing plant conditions were a pH of 6.3, sludge recycle concentration of 4.0 g/L, and alum dose of 50.0 mg/L. See Section 3.3 for a more detailed description of existing plant conditions. The following sections detail the physical state of aluminum in the plant's effluent and results for the bench-scale CoMag® experiment.

4.1 Physical State of Aluminum in the Plant's CoMag® Clarifier Effluent

Testing to determine the physical state of aluminum was conducted on the plant's CoMag® clarifier effluent. This was done to determine if the aluminum was in the particulate, colloidal, or dissolved state. This was done by passing the effluent samples through a series of filters with pore sizes of 1.50 μm, 0.45 μm, and 0.22 μm (0.10 μm for sample 3), with 0.45 μm acting as the cutoff between colloidal and dissolved state. Results from this testing were used in part to determine which parameters should be changed during bench-scale testing. Results from Con-Test® are summarized in Table 6. Results of samples from the pore size of 1.50 μm and smaller showed that total aluminum levels were below the detection limit (BDL) of the test, which was 50.0 μg/L. Therefore, the filtration results showed that the aluminum species present in the plant's effluent were in the particulate state and could be removed through better flocculation and settling.

Table 6. Con-Test® results for total aluminum physical state determination

Filter Size (μm)	Total Aluminum (μg/L)		
	Sample 1	Sample 2	Sample 3
None	130	130	120
1.50	BDL	BDL	BDL
0.45	BDL	BDL	BDL
0.22*	BDL	BDL	BDL

*A 0.10um pore size filter was used for sample 3

4.2 Bench-Scale Operating Parameters

The following sections discuss testing results for the bench-scale model parameters of system pH, alum dose, and zone 3 sludge recycle concentration. Throughout this section, it is important to note that the aim of each parameter optimization test was to achieve the plant's NPDES permit levels for total aluminum and total phosphorus. Appendix V provides raw data from bench-scale parameter lab tests. In addition, two statistical analyses were performed using Microsoft Excel: Correlation and ANOVA Single Factor. The correlation tests showed whether or not two parameters had a positive or negative linear relationship, or no linear relationship with each other. The ANOVA Single Factor tests showed whether or not data sets were statistically different from one another, depending on variance.

4.2.1 System pH

Although the optimal pH for the CoMag® System, according to Evoqua, is 6.3, several pH levels were tried with both 6.0 g/L and 2.0 g/L sludge recycle concentration, while keeping alum dose constant at 50.0 mg/L.

With a sludge recycle concentration of 6.0 g/L, pH levels of 6.0, 6.3, and 7.0 were tested. Figure 6 shows the final orthophosphate and total phosphorus levels achieved with the tested pH values from seven experiments. The recommended pH of 6.3 resulted in the best final total phosphorous concentration of 0.41 mg/L P in a single test and an average of 0.49 mg/L P for three replicate tests. According to correlation analysis, pH and phosphorus levels did not exhibit a linear relationship. This is consistent with the trends shown in Figure 6, where the middle pH value had the lowest final phosphorus levels. All pH values resulted in low final orthophosphate values, 0.15 to 0.36 mg/L P.

Figure 6. Relationship between final phosphorus levels and pH level, for 6.0 g/L sludge recycle concentration and alum dose of 50.0 mg/L

As seen in the figure, the final total phosphorus values from bench-scale tests exceed the plant's NPDES permit levels. The team expected a pH of 6.3 would result in the best phosphorus removal, based off of the solubility chart of alum, Figure 5 in Section 3.3.2. According to the chart, at a pH of 6.3 and dose of 50.0 g/L would result in aluminum precipitating out of solution. The team hypothesizes that because values were obtained using a higher sludge recycle concentration than present at the plant, something was necessary to counteract the addition of solids into the system. Perhaps the sludge contained a concentrated amount of phosphorus. In regards to high pH conditions, although a high pH will result in larger flocs forming, it does not correspond to greater precipitation. This is because as the pH of the solution is increased, it nears its isoelectric point, or the point at which there are an equal number of positive and negative charges and precipitation occurs. However, the isoelectric point of aluminum hydroxide is higher its solubility, meaning large flocs do not correspond with greater precipitation (Duan and Gregory 2002).

Final total aluminum concentrations were measured for the three experiments. From Figure 7, it appears pH 6.3 resulted in the highest final total aluminum concentration. However, conclusions would be premature based on three measurements. All pH values resulted in final total aluminum concentrations above the NPDES permit of 171 µg/L. Similar to phosphorus concentrations, the team hypothesizes that because values were obtained using a higher sludge recycle concentration than present at the plant, something was necessary to counteract the addition of solids into the system. Perhaps the sludge contained a concentrated amount of phosphorus. The reaction of aluminum in water is not yet completely understood (Peckham 2014). However, as pH increases, the type of aluminum present in water is less toxic to fish in the environment (Peckham 2014).

Figure 7. Relationship between final total aluminum level and pH level, for 6.0 g/L sludge recycle concentration and alum dose of 50.0 mg/L

With a sludge recycle concentration of 2.0 g/L, the pH levels of 5.0, 6.3, and 8.0 were tested. A wider pH range was chosen to see the results from testing extreme conditions. Trends were established, as shown in Figure 8, which shows final orthophosphate and final total phosphorus levels from 14 experiments. The recommended pH of 6.3 resulted in the best final orthophosphate and final total phosphorous levels, reaching 0.03 mg/L P and 0.05 mg/L P, respectively, in a single test and an average of 0.08 mg/L P and 0.12 mg/L P, respectively, for nine additional replicate tests. From statistical analysis, there was no linear relationship. This is consistent with the trends shown in Figure 8, where the middle pH value had the lowest final phosphorus levels.

As seen in the figure, all of the pH levels tested from the bench-scale resulted in final phosphorus values that met the plant's NPDES permit. However, pH values of 5.0 and 6.3 resulted in lower final orthophosphate and final total phosphorus levels than pH 8.0. The team expected a pH of 6.3 would result in the best final phosphorus levels, based off of the solubility chart of alum, Figure 5 in Section 3.3.2. According to the chart, at a pH of 6.3 and dose of 50.0 g/L would result in aluminum precipitating out of solution.
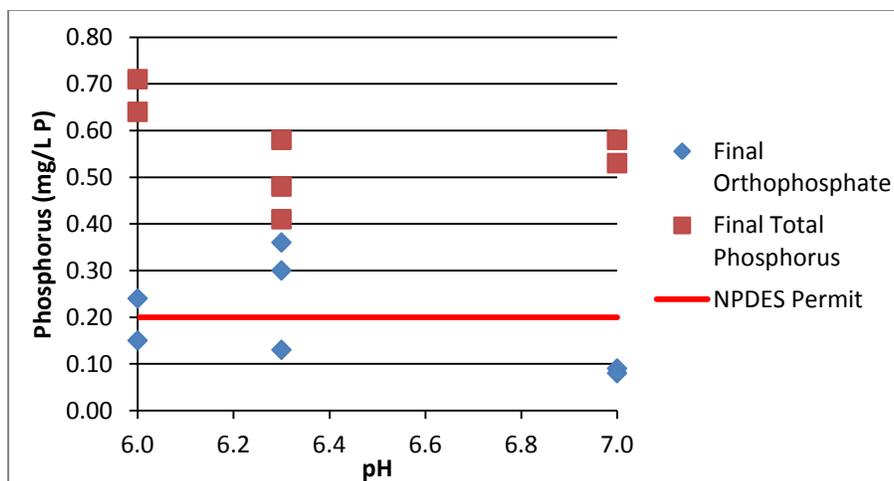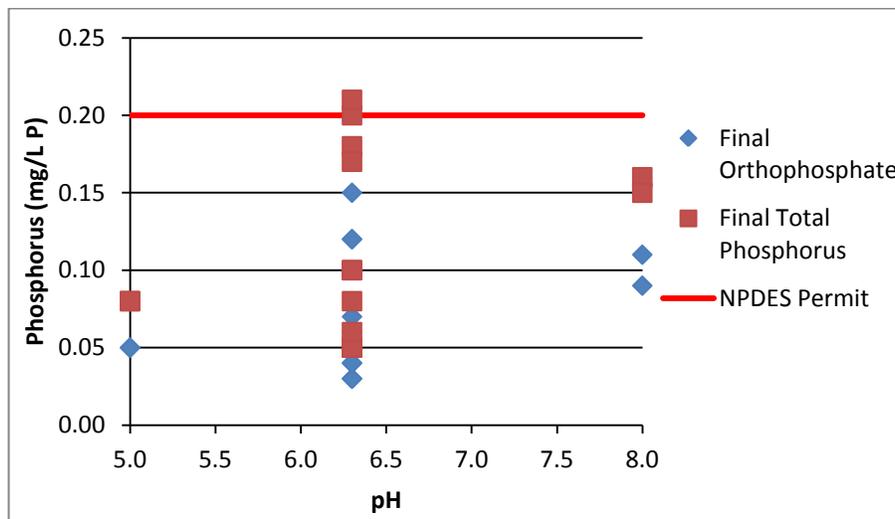

Figure 8. Relationship between final phosphorus level and pH level, for 2.0 g/L sludge recycle concentration and alum dose of 50.0 mg/L

Final total aluminum concentrations were measured, one from each test conducted at pH 5.0 and 8.0, and three for pH 6.3. From Figure 9, pH 6.3 resulted in the lowest final total aluminum concentration. However, conclusions would be premature based on five measurements. Only a pH value of 6.3 resulted in a final total aluminum concentration below the NPDES permit of 171 µg/L.
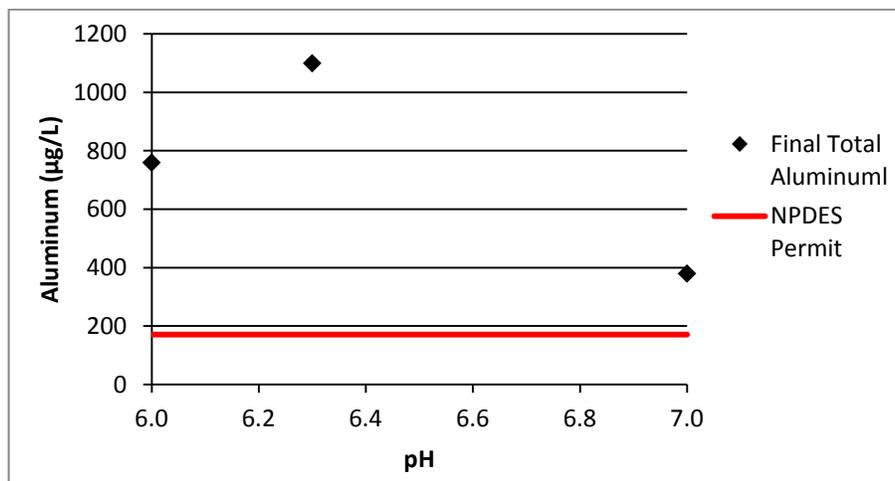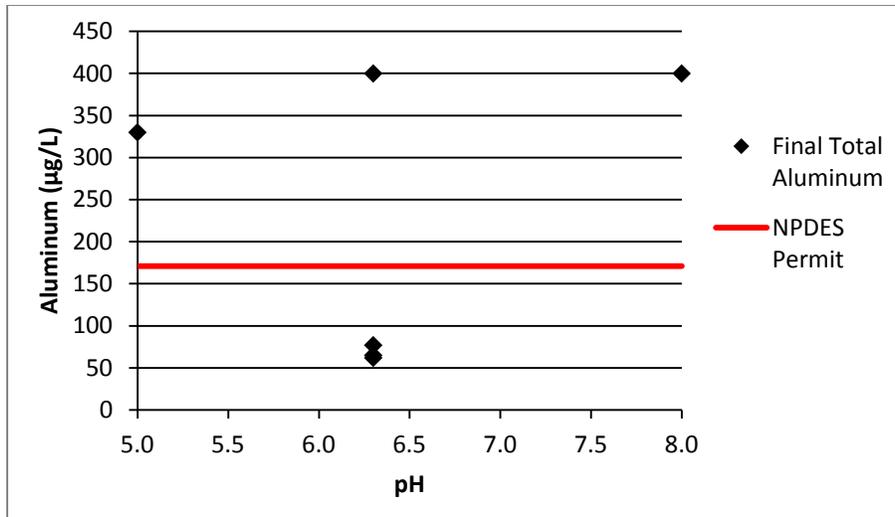
Figure 9. Relationship between final total aluminum level and pH level, for 2.0 g/L sludge recycle concentration and alum dose of 50.0 mg/L

4.2.2 Alum Dosing

The plant currently operates at an alum dose of 50.0 mg/L. A range of doses, above, equal to, and below the plant conditions, were tested. Doses of 25.0, 37.5, 50.0, 59.4, 70.0, and 75.0 mg/L were tested with a sludge recycle concentration of 2.0 g/L and a pH of 6.3. The dose of 59.4 mg/L was based off of the aluminum solubility curve and calculations found in Section 3.3.2 for the minimum dose of alum necessary for precipitation in water at pH of 6.3.

Final total phosphorus and final orthophosphate was tested in 20 trials for the alum doses stated above. As seen in Figure 10, when alum dose was increased both final orthophosphate and final total phosphorus levels increased as well. The lowest final orthophosphate value of 0.03 mg/L P was achieved by an alum dose of 25.0 mg/L, 37.5 mg/L, or 50.0 mg/L. This value neared the detection limit for the HACH DR6000 of 0.02 mg/L P. An alum dose of 50.0 mg/L also achieved the lowest final total phosphorus level of 0.05 mg/L P.
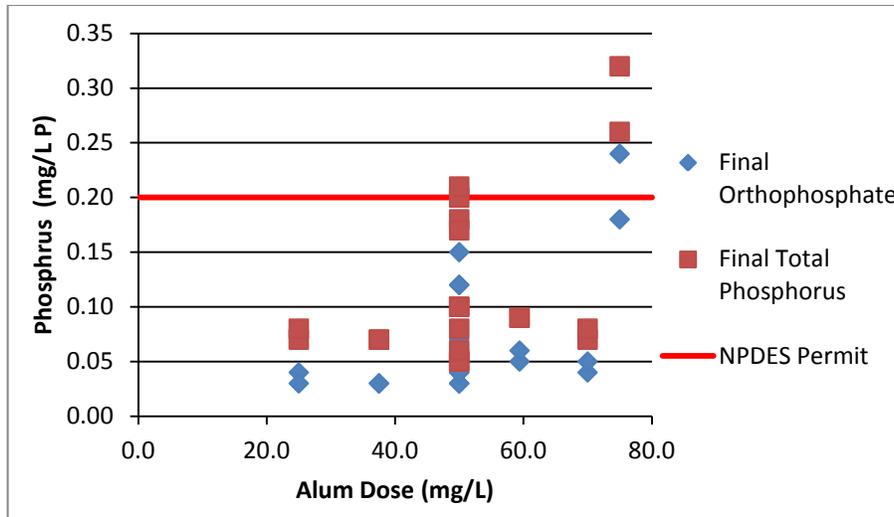
Figure 10. Relationship between final phosphorus levels and alum dose with a pH of 6.3 and sludge recycle concentration of 2.0 g/L

Table 7, presents the lowest achieved final orthophosphate and final total phosphorus values as well as the average final orthophosphate and final total phosphorus vales for each alum dose tested. As seen in the table, more tests were performed on the 50.0 mg/L. Doses between 25.0 – 70.0 mg/L all resulted in final total phosphorus levels below the NPDES permit of 0.2 mg/L P.

Table 7. Lowest achieved final orthophosphate and final total phosphorus concentrations, average final orthophosphate, and average final total phosphorus values for each alum dose tested

Dose (mg/L alum)	n (# of Trials)	Lowest Final Orthophosphate (mg/L P)	Average Final Orthophosphate (mg/L P)	Lowest Final Total Phosphorus (mg/L P)	Average Final Total Phosphorus (mg/L P)
25.0	2	0.03	0.04	0.07	0.08
37.5	2	0.03	0.03	0.07	0.07
50.0	10	0.03	0.08	0.05	0.12
59.4	2	0.05	0.06	0.09	0.09
70.0	2	0.04	0.05	0.07	0.08
75.0	2	0.18	0.21	0.26	0.29

According to correlation analysis, alum dose and phosphorus levels exhibited a positive linear relationship. This was unexpected because it was assumed that the reaction would follow Le Chatelier's Principle, where overdosing with alum would cause a reaction equilibrium shift towards products and would result in lower phosphorus levels. For coagulation with alum, a state must be achieved where the electrical charges on suspended solids in the wastewater are changed or neutralized, so that the solids can become attached to each other or another surface (Young and Edwards 2003). It had been assumed that a

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higher dose of alum would cause more particle neutralization and flocculation, which would lead to a lower final total phosphorus concentration. Additional testing could clarify results, but were not completed due to time constraints.

Final total aluminum was measured for 8 samples, with alum doses of 25.0, 50.0, 59.4, 70.0, and 75.0 mg/L. A final total aluminum sample was not taken for a dose of 37.5 mg/L due to material constraints. From Figure 11, the lowest final total aluminum level of 57.0 μg/L was achieved with an alum dose of 70.0 mg/L. This was expected because a similar trend had been experienced at the treatment plant prior to testing. Similar to final phosphorus levels, final total aluminum levels below the NPDES permit level were observed with alum doses of 27.0 – 70.0 mg/L. A statistical analysis was also performed to distinguish the relationship between alum dose and final total aluminum levels. There was no linear correlation between these values; however, no definitive relationship can be determined based on the limited data set.
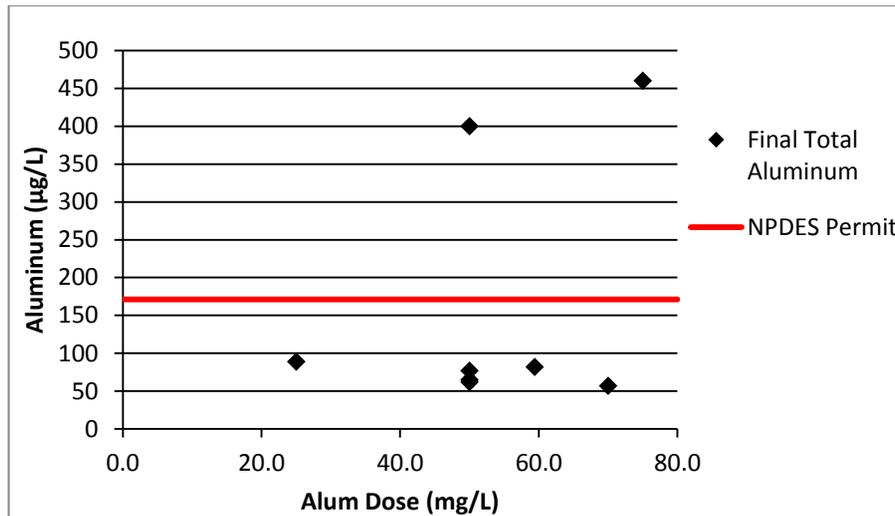
Figure 11. Relationship between final total aluminum level and alum dose with a pH of 6.3 and a sludge recycle concentration of 2.0 g/L

4.2.3 Zone 3 Sludge Recycle Concentrations

As discussed in Section 3.3.3, the plant's average sludge recycle concentration was determined to be 4.0 g/L. Sludge recycle concentrations of 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, and 6.0 g/L were tested for zone 3. Tests were also performed with sludge recycle concentrations exceeding 6.0 g/L and resulted in poor total phosphorus and orthophosphate reduction (data not shown).

Higher total phosphorus and orthophosphate removal was seen with lower sludge recycle concentrations. As seen in Figures 12, as sludge recycle increased, the amount of final orthophosphate and final total phosphorus increased. The lowest final orthophosphate

value of 0.02 mg/L P, the detection limit of the HACH DR6000, was achieved by a sludge recycle concentration of 1.0 g/L. Sludge recycle concentrations of 0.0, 0.5, and 1.0 g/L all resulted in the lowest final total phosphorous of 0.04 mg/L.

The correlation analysis also indicated that there is a strong positive relationship between sludge recycle and final phosphorus levels. One-way ANOVA showed that there was a statistically significant difference in orthophosphate concentration and sludge recycle concentrations (p value = 3.90E-09) and also a difference in total phosphorus by recycle concentration (p value = 2.42E-10).
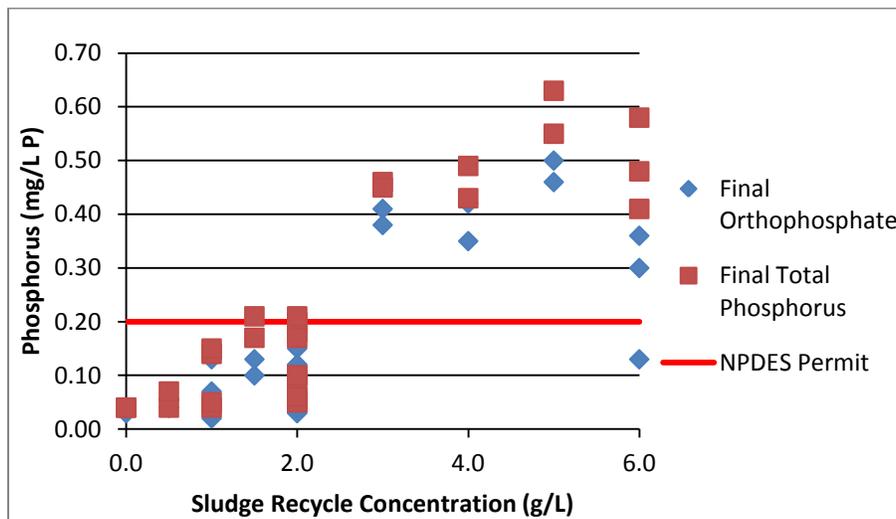
Figure 12. Relationship between final phosphorus level and sludge recycle concentration with a pH of 6.3 and an alum dose of 50.0 mg/L

This was not expected because in ballasted flocculation removal systems, "the rate of coagulation, or kinetics of floc formation, may increase if the ballasting agent dominates the agglomeration of particles" (Young and Edwards 2003). It was assumed that within systems like CoMag®, a higher solids concentration would lead to better floc formation and more successful phosphorus removal.

The implications of the difference between sludge recycle concentration in the plant's flow through system and the bench-scale, batch system are not completely understood; however, it is hypothesized that a higher sludge concentration only introduces and adds to the original amount of orthophosphate and total phosphorus. Within the bench-scale, this higher concentration of phosphorus overwhelms the system and does not flocculate and settle effectively. As seen in the figure, sludge concentrations less than 2.0 g/L resulted in a final total phosphorus level below the NPDES permit level of 0.2 g/L.

A statistical analysis was also performed to distinguish the relationship between sludge recycle concentration and final total aluminum levels. As seen in Figure 13, the lowest final

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total aluminum level of 58 µg/L was found with a sludge recycle concentration of 0.5 g/L. There was a strong positive correlation between these values; however, no definitive relationship can be determined statistically due to limited final total aluminum data. Similar to final phosphorus levels, final total aluminum levels below the NPDES permit level were observed with a sludge recycle concentration of less than 2.0 g/L. More aluminum data would provide a more definitive trend.
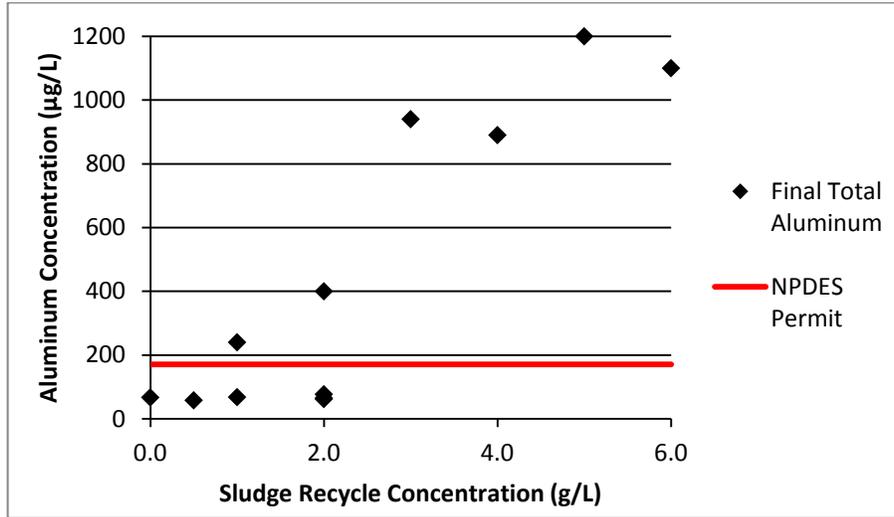
Figure 13. Relationship between final total aluminum levels and sludge recycle concentration with a pH of 6.3 and an alum dose of 50.0 mg/L

As seen in Figure 14, as the sludge recycle concentration was increased, turbidity levels in the final effluent also increased. This was a similar relationship, seen in Figure 12 and Figure 13, between sludge recycle concentration and final phosphorus and final total aluminum levels.
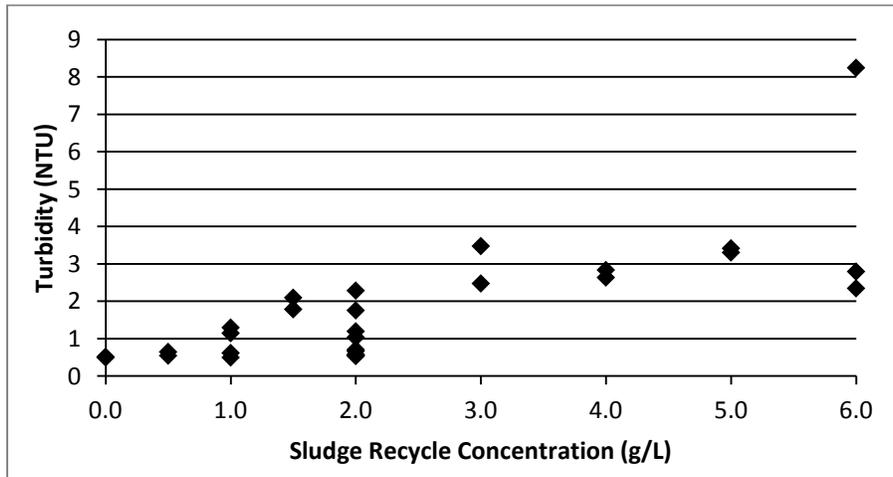
Figure 14. Relationship between sludge recycle concentration and effluent turbidity with a pH of 6.3 and an alum dose of 50.0 mg/L

4.3 Analysis of Bench-Scale Testing

Through bench-scale testing, it can be concluded that a lower sludge recycle concentration results in better total phosphorus and total aluminum removal. At 2.0 g/L or lower, total phosphorus and total aluminum levels were below the plant's NPDES permit. A lower sludge recycle concentration also resulted in lower turbidity of the system effluent. Although results from pH and alum dose testing were inconclusive, a pH of 6.3 and alum dose of 50.0 mg/L, the plant's current operating conditions, resulted in low total phosphorus and total aluminum levels. Figure 15 presents the recommended operating conditions for the CoMag® system at the Billerica WWTP that reflect a 2.0 g/L or lower sludge recycle concentration, 50.0 mg/L alum dose, and pH of 6.3.
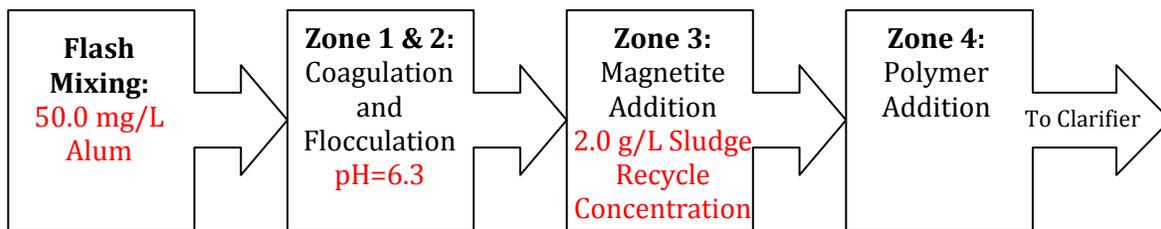
Figure 15. Recommended operating conditions for the Billerica WWTP CoMag® System

By implementing the recommended operating conditions, the plant can expect to achieve effluent levels of total phosphorus and total aluminum below the current NPDES permit levels of 0.2 mg/L and 171 μg/L, respectively. It is important to note that this study was conducted with a bench-scale, batch system that has differing mechanics than the plant's full-scale CoMag® system. However, the plant can still expect to achieve NPDES permit levels with the recommended operating conditions.

4.4 Financial Implications

The operating parameters recommended yield no additional capital cost to the Billerica WWTP. They solely require an adjustment of recycle rate if the sludge recycle concentration within zone 4 is found to be above 2.0 g/L. This, however, may result in increased operating costs for solids handling, with more sludge being wasted than recycled. Some costs to consider would be utility costs, labor costs, and transportation costs. The exact amount and impacts to the solids handling process at the WWTP with additional sludge waste would require further investigation. The recommendations allow for alum dose and pH levels to remain unchanged from current plant conditions and do not negatively impact the cost of operation.

Chapter 5: Conclusions and Recommendations

Several conclusions were drawn from the results discussed in the previous chapter including; testing methods that need to be further refined, parameters and system structures that need further study, and optimal parameters to be tested at the plant. From the bench-scale testing, the team determined recommendations for the Billerica WWTP on how to meet current and future NPDES total aluminum and total phosphorus permit levels.

5.1 Conclusions from Bench-Scale Testing

Through both qualitative and quantitative data, it was determined that lower sludge recycle concentrations result in better total phosphorus and total aluminum removal. From these conclusions, it is recommended that the Billerica WWTP lower the sludge recycle concentration to 2.0 g/L or lower if total phosphorus and total aluminum NPDES permit levels are not being met. This recommendation may create operating costs for the Billerica WWTP due to a greater amount of sludge wasting as discussed in Section 4.4. Although results from pH and alum dose testing were inconclusive, it is recommended that the plant continue to operate at a pH of 6.3 and the current alum dose of 50.0 mg/L. It is also recommended that the plant monitor sludge recycle concentration in zone 4, by following the procedure presented in Section 3.2.5.

5.2 Recommendations for Further Study at the Bench-Scale

This section provides considerations for further study on the bench-scale model. It starts by presenting system parameters that the team was not able to test, due to scope and time constraints, but consider important and potentially crucial in the removal of total phosphorus and total aluminum. The parameters of magnetite dose and polymer dose should be considered, as well as testing for total suspended solids (TSS) on the system effluent. The team also recommends that mixing speeds of the different zones throughout the system be considered. Finally, testing methods that were tried in lab but require further refinement are presented.

5.2.1 Fresh Magnetite Dosing

The magnetite dose presented in Section 3.2.6 was determined to be an adequate amount for the bench-scale system. However, through observation, the magnetite did not always stay completely entrained in the water during zone 3 mixing. It was hypothesized that this may have been due to the flat paddles on the Phipps & Bird mixer, or the amount of magnetite added. Also, the amount of fresh magnetite added at the plant is measured by the "shovel full" and may vary from day to day. This influenced the original magnetite dose calculations, found in Section 3.2.6. The dose used throughout testing was based on zone 4 grab samples taken from the plant, which included both fresh and recycled magnetite. Due to its importance in ballasted settling, different doses of magnetite should be considered during further testing.

5.2.2 Polymer Dosing

The polymer dose presented in Section 3.2.7 was determined to be adequate for the bench-scale system. Although used by the Billerica WWTP, cationic polymer is not the only option. The effects of anionic, neutral, or different cationic polymers to the system, however, are unknown and would require further testing. The optimal polymer dose in zone 4 may be influenced by sludge recycle concentration and the amount of magnetite added in zone 3. The dosage of polymer should be considered during further study.

5.2.3 Final Effluent TSS Testing

The team performed TSS testing on grab samples collected from zone 4 of the bench-scale tests in order to determine the solids to magnetite ratio of the system. It is recommended that TSS testing be performed on bench-scale final effluent, as well as in zone 4, in order to understand the amount of suspended solids and aluminum in the effluent. For final effluent TSS testing, it is recommended that the multiple filtration method used to determine the physical state of aluminum, described in Section 3.4.5, be modified to quantify both total aluminum levels and total suspended solids for each filtration step. Results from this test would provide a better understanding of the physical state of aluminum in the bench-scale effluent and affirm that the bench-scale is representative of the plant.

5.2.4 Mixing Speed of Bench-Scale System

The mixing speeds of the different zones in the CoMag® system are very important and require further study. As described in Section 3.2.1, the mixing speeds for the bench-scale test were determined empirically in the lab and were loosely based on the speed gradient seen at the plant. Further study is required to determine what the optimal mixing speed is: for flocculation in zone 2, magnetite entrainment in zone 3, and polymer-floc binding in zone 4. It is also recommended that mixers with blades more representative of the plant be used in further testing.

5.2.5 Separated, High Concentrations, and Creation of Sludge for Recycle

At the beginning of testing, few tests were performed with recycled sludge that had been separated in the blender before reintroduction into zone 3. The resulting effluent concentrations of total phosphorus and orthophosphate produced in the lab were too high compared to results before the addition of this step. This addition to the lab procedure was done to more closely mimic the plant's operation of introducing magnetite separated from flocs using the magnetic drum. This step in the designed lab methods is not recommended for bench-scale testing.

Tests were also performed with sludge recycle concentrations exceeding 6.0 g/L and resulted in poor total phosphorus and orthophosphate reduction. Concentrations of sludge recycle greater than 6.0 g/L are not recommended for bench-scale testing.

A few tests were performed using sludge that had been built up over several rounds of testing for zone 3 sludge recycle. Although this process better represented operations at the plant, it was replaced by using sludge stock taken directly from the plant due to time constraints and the introduction of unknown variables. (See procedure in Appendix II and determining sludge volume in 3.2.5).

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Appendices:

Appendix I: Billerica WWTP NPDES Permit, Abridged

CONTINUED FROM PREVIOUS PAGE

A.2. From the effective date of the permit until expiration, the permittee is authorized to discharge from treated effluent from outfall serial number **001** to the Concord River. Such discharges shall be limited and monitored as specified below.

EFFLUENT CHARACTERISTIC					EFFLUENT LIMITS	MONITORING REQUIREMENTS [3]	
PARAMETER	AVERAGE MONTHLY	AVERAGE WEEKLY	AVERAGE MONTHLY	AVERAGE WEEKLY	MAXIMUM DAILY	MEASUREMENT FREQUENCY	SAMPLE TYPE
AMMONIA-NITROGEN (May 1 – October 31)	278 lbs/day	278 lbs/day	6 mg/L	6 mg/L	9 mg/L	1/WEEK	24-HOUR COMPOSITE[5]
AMMONIA-NITROGEN (November 1 – April 30)	*********	*********	********	*********	Report mg/L	2/MONTH	24-HOUR COMPOSITE[5]
TOTAL PHOSPHORUS (April 1 – October 31)	9.3 lbs/day	*********	200 µg/L	*********	Report µg/L	2/WEEK	24-HOUR COMPOSITE[5]
TOTAL PHOSPHORUS (November 1 – March 31)	46.3 lbs/day	*********	1,000 µg/L	*********	Report mg/L	1/WEEK	24-HOUR COMPOSITE[5]
TOTAL COPPER	*********	*********	Report µg/L	*********	Report µg/L	1/MONTH	24-HOUR COMPOSITE[5]
TOTAL ALUMINUM[8]	7.9 lbs/day	*********	171 µg/L	*********	Report µg/L	2/MONTH	24-HOUR COMPOSITE[5]
WHOLE EFFLUENT TOXICITY[9,10,11,12,13]	Acute LC50 > 100% Chronic C-NOEC > 30% Hardness[13] — Report maximum daily, mg/L; Ammonia, as nitrogen[13] — Report maximum daily, µg/L; Total Cadmium[13] — Report maximum daily, µg/L; Total Lead[13] — Report maximum daily, µg/L; Total Copper[13] — Report maximum daily, µg/L; Total Zinc[13] — Report maximum daily, µg/L; Total Nickel[13] — Report maximum daily, µg/L; Total Aluminum[13] — Report maximum daily, µg/L					4/YEAR	24-HOUR COMPOSITE

Figure A. NPDES permit issued 4-23-2014

TOTAL AMMONIA NITROGEN, AS N (May 1 - Oct. 31)	***	***	***	6 mg/l	6 mg/l	9 mg/l	1/WEEK	24-HOUR COMPOSITE[3]

A.1. (continued) During the period beginning the effective date and lasting through expiration, the permittee is authorized to discharge from outfall serial number **001**, treated effluent to the Concord River. Such discharges shall be limited and monitored as specified below.

EFFLUENT CHARACTERISTIC					EFFLUENT LIMITS		MONITORING REQUIREMENTS	
		Mass Limits			Concentration Limits			
PARAMETER	AVERAGE MONTHLY	AVERAGE WEEKLY	MAXIMUM DAILY	AVERAGE MONTHLY	AVERAGE WEEKLY	MAXIMUM DAILY	MEASUREMENT FREQUENCY	SAMPLE TYPE
PHOSPHORUS, TOTAL[8,14] (April 1 - October 31)	***	***	***	0.2 mg/l[8,14]	***	Report mg/l	2/WEEK	24-HOUR COMPOSITE[3]
PHOSPHORUS, TOTAL (November 1 - March 31)	***	***	***	1.0 mg/l	***	Report mg/l	1/WEEK	24-HOUR COMPOSITE[3]
PHOSPHORUS, ORTHO (November 1 - March 31)	***	***	***	Report mg/l	***	Report mg/l	1/WEEK	24-HOUR COMPOSITE[3]
TOTAL ALUMINUM[13]	***	***	***	357 ug/l	***	Report ug/l	2/MONTH	24-HOUR COMPOSITE[3]
WHOLE EFFLUENT TOXICITY[9,10,11,12]	Acute LC50 ≥ 100% Chronic C-NOEC ≥ 24%						4/YEAR	24-HOUR COMPOSITE[3]

Figure B. NPDES permit issued 9-9-2005

Appendix II: Bench-Scale CoMag® Procedure with Plant Sludge Recycle

Calibrate pH Meter (Fisher Scientific Accumet AB150)-daily
1. Rinse probe with purified DI water, shake off excess water.
2. Open hole.
3. Place in pH 4 buffer previously inverted to mix.
4. Wait to stabilize.
5. Press STD one time.
6. Wait unit it reads "press STD."
7. Press STD one time.
8. See percent >97% (if not, redo calibration).
9. Repeat steps 1-8 with pH 7 then pH 10 buffer.
10. Keep hole open for the day's tests, then close hole.

Determine Sludge Stock Concentration:
1. Weigh and record mass of empty 500mL beaker.
2. Obtain Sludge stock sample from treatment plant.
3. Shake well to get uniform distribution of solids.
4. Obtain 50 mL of stock sample (using graduated cylinder).
5. Place 500 mL beaker in oven.
6. Weigh fully dried beaker and solids, record mass.
7. Calculate mass of solids.
8. Calculate concentration of solids in stock solution.
9. Determine amount of sludge to be recycled and amount of polymer dosing and magnetite dosing required in zones 3 and 4 (See below).

Concentration of Sludge Stock (g/L):

$$conc_{stock} = \frac{g\ solids}{L\ stock\ sample}$$

Amount of Stock to add to sample:

$$V_{stock} = \frac{conc_{desired} * V_{desired}}{conc_{stock}}$$

Determining Magnetite and Polymer Dosing in Zone 3:
Corrected Volume Factor, x, when we adjust dosing

$$x = \frac{1000 - Recycle\ Volume\ (mL)}{1000}$$

$$Magnetite\ Addition(g) = 1.67x$$

$$Polymer\ Addition\ (mL) = 1.36x$$

Sludge Beaker Set Up:
1. Add calculated amount of sludge to 6x 1L beakers that have been triple rinsed with purified DI water, labeled A, B, C, D, E, F.

Prepare Polymer-weekly
1. Add 1 mL polymer with purified water in a 1000 mL volumetric flask for a 1000-fold solution.

Bench-Scale CoMag® Procedure with Plant Sludge Recycle:
Set-up:
1. Mix carboy of WW.
2. Pour 6x 1000 mL samples into 1 L labeled beakers that have been triple rinsed, labeled A, B, C, D, E, F.

P Testing:
3. Complete initial Orthophosphate testing for the carboy using the HACH Test 'N Tube Method. Record initial value. Determine if samples need to be diluted. If not continue with Total P testing with the HACH Test 'N Tube Method. If so, retest adding 2.5 mL of sample and 2.5 mL of purified water instead of 5 mL sample and adjust reading for dilution. Follow HACH procedure, record results.

pH Adjustments:
4. Place sample on stir plate with stir bar and pH probe.
5. Stir rapidly (flash mixing) at a speed of 700 rpm.
6. Add alum (if 50 ppmv, add 1.0 mL of 50g/L stock to 1L sample).
7. Mix for 50 seconds, record pH, add caustic or acid if needed to adjust and record final pH.

CoMag:
8. Place beakers under Phipps & Bird mixer, make sure blades are in the middle of beaker and sample.
9. Start mixer speed to 110 rpm (zone1).
10. Mix for 6 minutes 15 seconds.

11. Reduce mixer speed to 50 rpm (zone 2).
12. Mix for 6 minutes 15 seconds.
13. Stop mixer and remove beaker from under blade.
14. Pour treated wastewater into corresponding sludge beakers up to 1 L mark.
15. Place beakers with sludge and treated water under blade, discard beakers with remaining waste water.
16. Raise mixer speed to 175 rpm (zone 3).
17. Add calculated amount of magnetite.
18. Mix for 6 minutes 15 seconds.
19. Reduce speed to 110 rpm (zone 4).
20. Add calculated amount of 1000-fold polymer dilution.
21. Mix for 6 minutes 15 seconds.
22. *TSS Testing: See below.*
23. Turn off mixer and let settle for 23 minutes (Clarifier).
24. Decant 500 mL from each beaker into separate triple rinsed 500 mL beakers, discard of sludge and remaining wastewater.
25. Complete initial Orthophosphate testing for each sample using the HACH Test 'N Tube Method. Mix before collecting sample to be tested. Record initial values. Determine if samples need to be diluted. If not continue with Total P testing using the HACH Test 'N Tube Method. If so, retest adding 2.5 mL of sample, and 2.5 mL of purified water instead of 5 mL sample. Follow HACH procedure, record results. Repeat dilution for Total P tests.
26. With decanted water: Send 250 mL for Al Testing by Con-Test® Analytical Laboratories, record turbidity and pH.

TSS Testing: Determining the Magnetite to Solids Ratio of CoMag®:
1. Obtain 12x 500 mL beakers in two sets labeled A, B, C, D, E, and F for floc and mag.
2. Weigh a filter paper for each sample and record the mass (for floc calculation).
3. Weigh a metal tray for each sample and record the mass (for magnetite calculation).
4. Use a 25 mL auto pipet and remove a sample from each beaker, record actual volume of each sample, and place each into a 500 mL beaker with 150 mL purified water (there for blending purposes).
5. Blend each sample+purified water for 2 minutes, separate magnetite and floc into separate beakers, using magnet.
6. For floc: Filter, dry, and reweigh filter paper for mass of floc.
7. For magnetite: dry in oven on metal tray and reweigh for mass of magnetite.
8. Calculate ratio with two mass values.
9. Calculate concentrations with volume and mass values.

Appendix III: HACH Test Methods for Total Phosphorus

HACH Method Number: 8190

EPA Method Number: 4500- P E

Test Specific Reagents:	HACH Product Number:
Total Phosphorus Test 'N Tube Reagent Set	2742645
PhosVer 3 Phosphate Reagent Powder Pillow, 10 mL	2106046
Potassium Persulfate Powder Pillow	2084766
Sodium Hydroxide, 1.54 N	2743042

Note: A HACH COD Reactor was used to incubate samples

Procedure:

1. Preheat incubator to 150°C
2. Set the Spectrometer to the correct start program for the Total Phosphorus test. For the DR 6000 use start program of 536 P Total/AH PV TNT.
3. Using an automatic pipette, measure out 5.0 mL of sample and add to a Total Phosphorus Test 'N Tube Vial.
4. Add the contents of one Potassium Persulfate Powder Pillow to the vial.
5. Shake well to dissolve the powder.
6. Insert the test vial into the incubator and allow to incubate for 30 minutes.
7. After incubating, allow the sample to cool to room temperature (The use of a water bath is recommended).
8. When cooled, add 2-mL of 1.54 N Sodium Hydroxide Standard Solution and mix well.
9. The outside of the vial should be well cleaned before inserting into the 16-mm cell holder of the spectrometer to zero the machine.
10. After zeroing, remove the vial and add the contents of one PhosVer 3 Phosphate Powder Pillow (The use of a funnel is recommended).
11. Cap the vial and shake for at least 20 seconds to mix the solution. Start a two minute reaction timer on the spectrometer.
12. When the reaction time expires, the outside of the vial should be well cleaned before inserting into the 16-mm cell holder of the instrument.
13. Push the read button on the spectrometer to obtain results shown in mg/L P
14. Repeat steps to 3-13 for each sample test.

Appendix IV: HACH Test Methods for Orthophosphates

HACH Method Number: 8048

EPA Method Number: 4500- P E

Test Specific Reagents:	HACH Product Number:
Reactive Phosphorus Test 'N Tube Reagent Set	2743545
PhosVer 3 Phosphate Reagent Powder Pillow, 10 mL	2106046

Procedure:

1. Set the Spectrometer to the correct start program for the Orthophosphate test. For the DR 6000 use start program of 535 P React. PV TNT.
2. Using an automatic pipette, measure out 5.0 mL of sample and add to a Reactive Phosphorus Test 'N Tube Vial.
3. Invert the vial to mix solution.
4. The outside of the vial should be well cleaned before inserting into the 16-mm cell holder of the spectrometer to zero the machine.
5. After zeroing, remove the vial and add the contents of one PhosVer 3 Phosphate Powder Pillow (The use of a funnel is recommended).
6. Cap the vial and shake for at least 20 seconds to mix the solution. Start a two minute reaction timer on the spectrometer.
7. When the reaction time expires, the outside of the vial should be well cleaned before inserting into the 16-mm cell holder of the instrument.
8. Push the read button on the spectrometer to obtain results shown in mg/L P
9. Repeat steps to 2-8 for each sample test.

Appendix V: Cumulative Raw Data from Bench-Scale Testing

Date	Sample Name	Recycle Conc (g/L)	Recycle Vol (mL)	pH at start of comag	Alum Stock Volume (mL)	Alum Dose (mg/L alum)	Int. OP	Fin. OP	% OP Red.	Int. TP	Fin. TP	% TP Red.	Initial Non-Reactive P	Final Non-Reactive P	Non-Reactive P Removal	Type	Mag : Solids X:1	Turbidity (NTU)	Fin. pH	Initial Al in Carboy (ug/L)	Sample Conc (ug/L Al)	% Red.
1/18/2015	F	2.0	51.78	8.30	1.400	70.0	0.54	0.05	90.74	0.66	0.08	87.9	0.12	0.03	0.09	TSS	4.29	0.70	6.54	200	57	71.50
1/18/2015	E	2.0	51.78	8.32	1.400	70.0	0.54	0.04	82.59	0.66	0.07	88.4	0.12	0.03	0.09	TSS	5.47	0.63	6.56	200		
1/18/2015	D	2.0	51.78	8.31	1.188	59.4	0.54	0.08	88.89	0.66	0.09	86.4	0.12	0.03	0.09	TSS	5.13	0.70	6.55	200	82	59.00
1/18/2015	C	2.0	51.78	8.31	1.188	59.4	0.54	0.05	90.74	0.66	0.09	86.4	0.12	0.04	0.08	TSS	4.94	0.76	6.54	200	85	67.50
1/18/2015	B	2.0	51.78	8.30	1.000	50.0	0.54	0.06	88.89	0.66	0.10	84.9	0.12	0.04	0.08	TSS	4.97	0.58	6.58	200		
1/18/2015	A	2.0	51.78	8.31	1.000	50.0	0.54	0.07	87.04	0.66	0.10	84.9	0.12	0.03	0.09	TSS	5.56	0.71	6.62	200	87	18.28
1/14/2015	F	0.0	0.00	8.32	1.000	50.0	0.57	0.03	94.74	0.68	0.04	94.1	0.11	0.01	0.10	Inconclusive	Inconclusive	0.52	6.61	83		
1/14/2015	E	0.0	0.00	8.31	1.000	50.0	0.57	0.03	94.74	0.68	0.04	94.1	0.11	0.01	0.10	Inconclusive	3.20	0.65	6.62	83	88	18.07
1/14/2015	D	0.5	11.43	8.30	1.000	50.0	0.57	0.04	92.98	0.68	0.07	88.7	0.11	0.03	0.08	Inconclusive	3.20	0.64	6.64	83		
1/14/2015	C	0.5	11.43	8.30	1.000	50.0	0.57	0.04	92.98	0.68	0.07	94.1	0.11	0.00	0.11	Inconclusive	4.94	0.55	6.64	83	58	30.12
1/14/2015	B	1.0	22.88	8.31	1.000	50.0	0.57	0.05	94.74	0.68	0.05	92.7	0.11	0.02	0.09	Inconclusive	7.87	0.50	6.68	83		
1/14/2015	A	1.0	22.88	8.31	1.000	50.0	0.57	0.02	96.49	0.68	0.04	84.1	0.11	0.02	0.09	Inconclusive	24.50	0.62	6.71	83	77	30.00
1/13/2015	F	2.0	45.70	8.02	1.000	50.0	0.54	0.09	79.63	0.82	0.15	75.8	0.08	0.04	0.04	TSS	4.24	1.25	7.42	110	400	-283.64
1/13/2015	E	2.0	45.70	8.01	1.000	50.0	0.54	0.11	83.33	0.82	0.16	74.2	0.08	0.05	0.03	TSS	5.69	1.48	7.38	110		
1/13/2015	D	2.0	45.70	6.29	1.000	50.0	0.46	0.03	93.48	0.62	0.06	90.3	0.08	0.02	0.06	TSS	3.82	0.58	6.58	110	380	-123.53
1/13/2015	C	2.0	45.70	6.31	0.750	37.5	0.46	0.03	93.48	0.62	0.08	87.1	0.08	0.04	0.04	TSS	4.55	0.80	6.59	110	89	9.18
1/13/2015	B	2.0	45.70	5.00	0.500	25.0	0.54	0.05	90.74	0.62	0.08	87.1	0.08	0.03	0.05	TSS	3.79	0.77	5.81	110	330	-200.00
1/13/2015	A	2.0	45.70	5.00	0.500	25.0	0.54	0.05	90.74	0.62	0.08	87.1	0.08	0.03	0.05	TSS	6.13	0.89	5.88	110	62	36.73
12/16/2014	F	2.0	65.00	6.30	1.000	50.0	0.46	0.03	93.48	0.50	0.05	90.0	0.04	0.02	0.02	TSS	4.24	0.55	6.61	98		
12/16/2014	E	2.0	65.00	6.32	1.000	50.0	0.46	0.03	93.48	0.50	0.05	90.0	0.04	0.04	0.02	TS	3.82	0.54	6.57	98		
12/16/2014	D	2.0	65.00	6.29	0.750	37.5	0.46	0.03	93.48	0.50	0.05	86.0	0.04	0.04	0.00	TSS	4.55	0.80	6.55	98		
12/16/2014	C	2.0	65.00	6.31	0.500	25.0	0.46	0.03	93.48	0.50	0.07	86.0	0.04	0.04	0.00	TSS	3.79	0.63	6.59	98		
12/16/2014	B	2.0	65.00	6.31	0.500	25.0	0.46	0.04	91.30	0.50	0.07	86.0	0.04	0.05	-0.01	TSS	3.98	0.71	6.62	98		
12/16/2014	A	2.0	65.00	6.30	0.500	25.0	0.46	0.04	89.30	0.50	0.08	84.0	0.04	0.03	0.01	TSS	3.69	0.82	6.68	98		
12/14/2014	F	6.0	125.00	7.01	1.000	50.0	0.58	0.09	84.48	0.70	0.58	17.1	0.12	0.49	-0.37	TSS	Inconclusive	7.21	6.70	170		
12/14/2014	E	6.0	230.00	7.01	1.000	50.0	0.58	0.09	84.48	0.70	0.53	17.1	0.12	0.45	-0.33	TSS	Inconclusive	7.99	6.70	170		
12/14/2014	D	6.0	230.00	6.30	1.000	50.0	0.68	0.08	88.21	0.70	0.46	34.3	0.12	0.38	-0.26	TSS	Inconclusive	6.50	6.56	170		
12/14/2014	C	6.0	230.00	6.31	1.000	50.0	0.58	0.13	77.59	0.80	0.17	78.8	0.22	0.45	-0.33	TSS	Inconclusive	8.25	6.54	170		
12/14/2014	B	6.0	430.00	5.98	1.000	50.0	0.58	0.15	74.14	0.70	0.64	8.6	0.12	0.49	-0.37	TS	10.10	10.10	6.41	170	760	-347.08
12/14/2014	A	8.0	430.00	5.97	1.000	50.0	0.58	0.24	58.62	0.70	0.71	-1.4	0.12	0.47	-0.35	TS	11.30	11.30	6.49	170		
12/12/2014	F	2.0	125.00	8.31	1.000	50.0	0.58	0.12	79.31	0.80	0.17	78.8	0.22	0.05	0.17	TS	3.87	1.78	6.44	160		
12/12/2014	E	2.0	125.00	8.30	1.000	50.0	0.58	0.15	74.14	0.80	0.21	73.8	0.22	0.06	0.16	TS	4.00	2.29	6.46	160		
12/12/2014	D	1.5	94.00	8.30	1.000	50.0	0.58	0.13	77.59	0.80	0.21	73.8	0.22	0.08	0.14	TS	3.57	2.10	6.52	160		
12/12/2014	C	1.5	94.00	8.30	1.000	50.0	0.58	0.10	82.76	0.80	0.17	81.3	0.22	0.07	0.15	TS	4.20	1.79	6.50	160		
12/12/2014	B	1.0	63.00	8.29	1.000	50.0	0.58	0.13	77.59	0.80	0.15	82.5	0.22	0.02	0.20	TS	4.20	1.15	6.51	160	240	-50.00
12/12/2014	A	1.0	63.00	8.29	1.000	50.0	0.58	0.07	87.93	0.80	0.14	28.8	0.22	0.07	0.15	TS	4.00	4.52	6.64	160		
12/7/2014	F	6.0	214.00	8.31	1.500	75.0	0.74	0.40	45.95	0.80	0.57	28.8	0.22	0.17	-0.11	TS	3.25	1.30	6.63	140		
12/7/2014	E	6.0	214.00	8.30	1.500	75.0	0.76	0.46	39.47	0.80	0.62	22.5	0.04	0.16	-0.12	TS	3.53	4.70	6.67	140		
12/7/2014	D	4.0	143.00	8.29	1.500	75.0	0.78	0.36	53.85	0.78	0.47	39.7	0.00	0.11	-0.11	TS	3.36	3.55	6.68	140	710	-407.14
12/7/2014	C	4.0	143.00	8.30	1.500	75.0	0.76	0.27	64.47	0.80	0.36	55.0	0.04	0.00	-0.05	TS	3.29	3.10	6.70	140		
12/7/2014	B	2.0	71.00	8.29	1.500	75.0	0.72	0.24	66.67	0.78	0.32	59.0	0.06	0.08	-0.02	TS	3.10	2.34	6.78	140	460	-228.57
12/7/2014	A	2.0	71.00	8.31	1.500	75.0	0.72	0.18	75.00	0.78	0.26	66.7	0.06	0.08	-0.02	TS	3.44	2.25	6.83	140		
12/5/2014	F	5.0	179.00	8.28	1.000	50.0	0.78	0.50	35.90	0.96	0.63	34.4	0.18	0.13	0.05	TS	4.38	3.31	6.60	170	1200	-757.14
12/5/2014	E	5.0	179.00	8.29	1.000	50.0	0.72	0.46	38.11	0.84	0.55	34.5	0.12	0.09	0.03	TS	3.80	3.42	6.74	170		
12/5/2014	D	4.0	143.00	8.27	1.000	50.0	0.72	0.35	51.39	0.96	0.43	55.2	0.24	0.16	0.08	TS	3.50	2.84	7.06	170	890	-423.53
12/5/2014	C	4.0	143.00	8.28	1.000	50.0	0.72	0.42	44.74	0.88	0.49	44.3	0.12	0.07	0.05	TS	3.43	2.84	6.95	170	1200	-605.88
12/5/2014	B	3.0	107.00	8.26	1.000	50.0	0.76	0.38	50.00	0.86	0.45	47.7	0.10	0.07	0.03	TS	3.00	2.48	6.92	170	940	-462.94
12/5/2014	A	3.0	107.00	8.35	1.000	50.0	0.80	0.41	48.75	0.86	0.46	48.5	0.06	0.01	0.01	TS	Inconclusive	3.48	6.85	170		
12/2/2014	D	2.0	84.00	8.30	1.000	50.0	0.78	0.12	84.62	0.92	0.20	78.3	0.14	0.06	0.06	TS	3.20	1.20	7.19	490		
12/2/2014	C	2.0	84.00	8.30	1.000	50.0	0.72	0.10	86.11	0.80	0.18	77.5	0.08	0.00	0.00	TS	3.30	1.04	7.15	490		
12/2/2014	B	6.0	250.00	8.30	1.000	50.0	0.78	0.18	53.85	0.88	0.32	44.2	0.08	0.12	-0.04	TS	3.53	2.80	7.05	490	400	18.37
12/2/2014	A	6.0	250.00	8.32	1.000	50.0	0.80	0.30	62.50	0.88	0.41	53.4	0.08	0.11	-0.03	TS	Inconclusive	2.35	7.23	490	1100	-124.49