2014

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STARS Citation

Salamah, Sultan, "The Effects of BAM as an Adsorptive Media on Phosphorus Removal in Stormwater" (2014). *Electronic Theses and Dissertations, 2004-2019*. 4716.
https://stars.library.ucf.edu/etd/4716

THE EFFECTS OF BAM AS AN ADSORPTIVE MEDIA ON PHOSPHORUS REMOVAL IN STORMWATER

by

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B.S. Umm Al-Qura University, 2009

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science in Environmental Engineering
in the Department of Civil, Environmental, Construction Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

Spring Term
2014

Major Professor: Andrew Randall

ABSTRACT

To maintain the quality of receiving water bodies, it is desirable to remove total phosphorus (TP) in stormwater runoff. Many media filtration technologies have been developed to achieve TP and soluble reactive phosphorus (SRP) removal. Efficient media adsorption is essential to insure control of stormwater phosphorus inputs to the receiving water body. This project develops and analyzes a functionalized Biosorption Media (BAM) to remove phosphorus species from stormwater runoff. One goal of this project is to find the BAM values for coefficients such as maximum adsorption capacity (Q_M: 4.35E-05) for the media through SRP isotherm equilibrium experiments using the Langmuir and Freundlich models. In addition, an upflow column experiment was also performed to study BAM nutrient removal from stormwater runoff. Finally, the information from the isotherm and the column experiments are used to estimate the life expectancy or quantity required of the media, and to define the effectiveness of BAM in phosphorus removal. The result of this study shows that BAM is a feasible stormwater treatment that can remove 60% SRP and >40% TP at temperature between 21-23 °C. The media is adequately modeled by both the Langmuir and the Freundlich models over the concentration range of interest in stormwater.

Dedicated to my parents (Khalid and Etimad), my wife, and all my friends.

ACKNOWLEDGMENTS

I would like to thank my master's supervisor Dr. Andrew A. Randall, Associate Professor, Department of Civil and Environmental Engineering at the University Of Central Florida for his guidance throughout my academic career. I am also grateful for Dr. Steven Duranceau, and Dr. Manoj Chopra for serving on my thesis defense committee and their valuable suggestions.

I would also like to express my appreciation to all my friends at UCF and all who worked in this project. Lastly, I would like to give my absolute thanks to my parents for their help and support throughout my life.

I would also Like to show my appreciation to The Florida Department of Transportation for funding this research project (BDK78 977-19).

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LIST OF ABBREVIATION AND ACRONYMS

A	Target Sorbate
AASHTO	American Association of Highway and Transportation Officials
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
B&G™	Bold & Gold™
BAM	Biological Adsorption Media
BET	Brunauer-Emmett-Teller Isotherm
BMPs	Best Management Practices
BPR	Biological Phosphorus Removal
C	Runoff coefficient
C_A	The equilibrium concentration of adsorbent in a solution
CO	Carbon Monoxide
D	Rainfall Duration
FDEP	Florida Department of Environmental Protection
FDOT	Florida Department of Transportation

FHH	Frenkel-Halsey-Hill Isotherm
FS	Factor of Safety
G	Green Media
g	Adsorbent Heterogeneity
G_S	Specific gravity of soils
HAB	Harmful algal blooms
IX	Ion Exchange
MCL	Maximum contaminant level
MET	MacMillan-Teller Isotherm
MOH	Mineral oil hydrocarbons
N	Nitrogen
NELAC	National Environmental Laboratory Accreditation Conference
NH3	Ammonia
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate

NOAA	National Oceanic and Atmospheric Administration
NOx	Nitrate+Nitrite
NPDES	National Pollutant Discharge Elimination System's
NSQD	National Stormwater Quality Database
NTU	Nephelometric Turbidity Units
OP	Ortho-Phosphorus
P	Phosphorus
PAHs	Polycyclic Aromatic Hydrocarbons
PAOs	phosphorus accumulating organisms
PC	Pollution Control
PO_4^{3-}	Orthophosphate
q_A	The equilibrium adsorbent-phase concentration of adsorbate
Q_M	Adsorption capacity
RL.1	Equilibrium Parameter
S*A	Bound adsorbate on the surface of the adsorbent
SRP	Soluble Reactive Phosphorus

S_v	Available site on the sorbent
TDP	Total Dissolved Phosphorus
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
TMDL	Total maximum daily load
TN	Total Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
U.S. EPA	United States Environmental Protection Agency
UCF	University of Central Florida
V/H	Vertical/Horizontal

CHAPTER ONE: INTRODUCTION

Natural watersheds are a complete system that typically can purify itself if nutrient inputs are maintained at low levels. This purification capacity has limitations, however, that are often exceeded in watersheds with increased development. Nitrogen and phosphorus species are limiting nutrients in fresh and estuary systems that stimulate the growth of photosynthetic algae in the aquatic system. Microorganisms in the water and sediments use the algae remains for food. Over growing result in harmful algal bloom (HABs) that can cause harmful effects on aquatic life via oxygen depletion, and reduction in transparency. The over growing of HABs is caused by nitrogen and phosphorus species over-enrichment which is known as Eutrophication (Walsh, 2012). The sources of excess nutrient loading from non-point sources are stormwater runoff (i.e. runoff from highways, parking lots, sidewalks, and commercial-residential structures), wet and dry air deposition, and erosion (Göbel et al., 2007; Hood et al., 2013; USEPA, 2014). Eutrophication and groundwater contamination from high nutrients potentially can pose health risks. High exposure to nitrate can cause Methemoglobinemia (a fatal blood syndrome that affects infants also known as blue-baby syndrome), spontaneous abortions, and diabetes. In addition, water with excess levels of phosphorus can result in osteoporosis and kidney or liver failure (Wanielista et al., 2008; Xuan et al., 2009). Thus, The United States Environmental Protection Agency (USEPA) considered nitrate and nitrite in the National Primary Drinking Water Regulations with a maximum contaminant level (MCL) and maximum contaminant level goal (MCLG) of 10 mg/l as N and 1 mg/l as N respectively (USEPA, 2013). To minimize the potential impact of stormwater runoff pollutants on the watershed, implementation of stormwater Best Management Practices (BMPs) has been encouraged but not required (Barrett, 2005; Shaw et al., 2001).

Several BMPs technologies were developed successfully to improve nutrient contamination control using functionalized Biosorption Activated Media (BAM) as a way to implement BMP's (Wanielista et al., 2008). The data presented in this study, intended to evaluate the effectiveness and longevity of a functionalized sorption media as a part of Bold&Gold™ media's in SRP removal using bench-scale upflow column and SRP adsorption isotherms. Bold&Gold™ is a BAM composed mainly of green and recyclable material. These engineered medias are commonly used for stormwater treatment. Bold&Gold™ was developed by the stormwater academy at University of Central Florida, Orlando, Florida (Wanielista et al., 2008).

In Florida, The Florida Department of Environmental Protection (FDEP) is developing a Statewide Stormwater Treatment Rule. The new law will require all stormwater treatment to provide at least an average annual loading reduction of TP and TN by 85% or to the level that post-development average annual loading is equal to pre-development average annual loading, as appropriate (FDEP, 2010)

Objective

The objective of this study is to determine the sorption characteristics of a specific BAM blend with respect to phosphorus removal. Sorption capacity and the appropriateness of modeling the data via the Langmuir or the Freundlich isotherms will be determined.

CHAPTER TWO : LITERATURE REVIEW

Urban and Ultra-Urban Land Characteristics

When the land is developed, it is covered with artificial structures such as highways, parking lots, sidewalks. These developments increase the imperviousness of land. The definition of the area also changes from low to high impervious percentages to follow rural, urban then ultra-urban areas in order, illustrated in Figure 1 (Shaw et al., 2001). However, urban and ultra-urban land cause more concerns that rural land. With high imperviousness, the artificial structures function as a barrier preventing rainwater from infiltrating the soil naturally and recharging the ground water causing what is called "stormwater runoff". Stormwater runoff carries many pollutants and ultimately transfers them to both surface and surficial ground water causing additional loading of pollutants and creating many environmental concerns (Brabec, 2002; Kuang, 2012). Figure 1 shows the effect of imperviousness on stormwater runoff, evaporation, and shallow and deep infiltration (Arnold et al., 1996). A land is considered urban if the imperviousness ranges between 30% - 50% while the land is considered ultra-urban if the imperviousness exceeds 50% (Arnold et al., 1996; Suntree-Technologies, 2014).

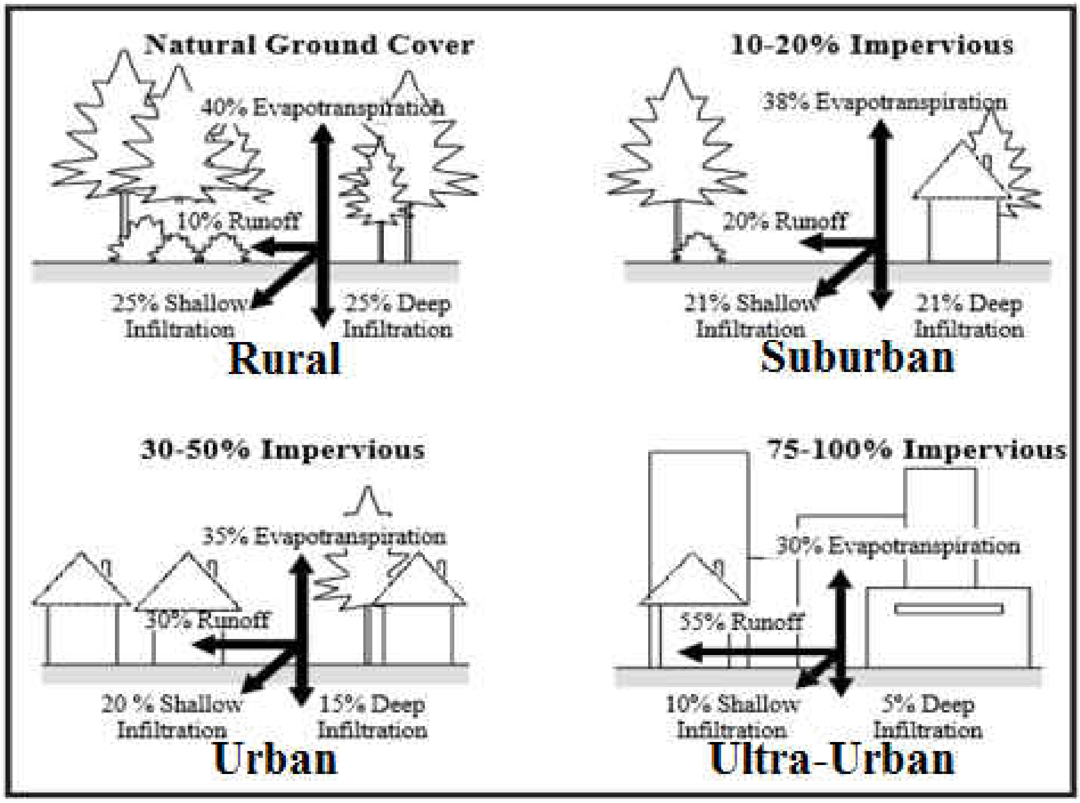


Figure 1 Impervious effect on runoff and infiltration modified from (Arnold et al., 1996)

Common Stormwater Pollutants

Before wastewater treatment and Stormwater Best Management Practices (BMPs) had been developed, society believed “dilution is the solution to pollution.” Stormwater was channeled to the closest sewers system or body of water without any further treatment (USEPA, 2012). Stormwater is highly polluted especially in urban and ultra-urban areas where there is a high population and development growth rate.

One source of pollutants is the stormwater runoff from highways, parking lots, sidewalks, and commercial-residential structures. Most times stormwater runoff has excessive levels of phosphorus and nitrogen species, heavy metals, polycyclic aromatic hydrocarbons (PAH), mineral oil hydrocarbons (MOH) and readily soluble salts which can cause serious water quality degradation (Göbel et al., 2007; Hood et al., 2013). The national average concentration of total phosphorus (TP), soluble reactive phosphorus (SRP), Ammonia (NH3), and nitrate+nitrite (NO_x) according to the national stormwater quality database (NSQD) records are 0.25 mg/l as P, 0.2 mg/l as P, 1.07 mg/l as N, and 0.28 mg/l as N respectively (Pitt et al., 2005).

Another source of contaminants and nutrients (N and P) is air deposition that can be categories in two form, dry air deposition and wet air deposition. Wet deposition occurs when dissolved compounds particles in the clouds contact the surface via precipitation such as rain, snow or fog. In contrast, dry deposition take place when particles fall to the surface without precipitation in a dry period (Burian et al., 2001; USEPA, 2014). Both dry and wet deposition deposit significant amounts of nutrients and heavy (Göbel et al., 2007). In fact, the total air deposition is responsible for an average of 20% of the Total Suspended Solids (TSS), 80% of the nitrogen species and the Total Kjeldahl Nitrogen (TKN), and 40% of the heavy metal in stormwater runoff (Wu et al., 1998).

Erosion is also a source of pollution in stormwater. Erosion is a result of high intensity storms for long duration. As a result of erosion, suspended soil transports the pollutants such as pesticides and fertilizers via stormwater runoff. Eventually, the pollutants end up in the groundwater or the surface water causing degradation of the water quality (Tsihrintzis et al., 1997).

Excessive deposition of phosphorus and nitrogen, combined with P and N transport due to erosion, can promote the growth of algal blooms. Algal blooms can cause mortality in aquatic animals via neurotoxin production and human illness by contaminated seafood consumption. Also, algal blooms may result in oxygen depletion of the water column (Hallegraeff, 1993; Smith, 2003).

Eutrophication and ground water contamination caused by high nutrient level pose many other health risks. Methemoglobinemia (blue-baby syndrome), for example, is a fatal blood disorder affecting infants caused by high levels of nitrate. In addition, above normal levels of ammonia cause moldy, earthy-tasting water. In addition, osteoposis and kidney damage can be a result of high levels of phosphorus (Xuan et al., 2009).

Stormwater management systems are required for new land developments. Stormwater ponds provide flood protection and improve water quality by removing sediments, nutrients and heavy metals. In urban stormwater, heavy metal loading is caused by highway runoff and atmospheric deposition. In addition, heavy metals in stormwater can bio-concentrate when ingested by plants or aquatic organisms near the bottom of the food chain which then accumulate in fish that may have a negative impact on public health when those fish are consumed (Campbell, 1994).

Stormwater Best Management Practices (BMPs)

As scientists continue to recognize correlations between stormwater and environmental degradation, implementation of BMPs becomes more beneficial to minimize the potential impact of stormwater runoff pollutants on the watershed (Barrett, 2005; Shaw et al., 2001).

Since the 1930s, The development of management practices to control and minimize any negative impact to the watershed was a concern. The separation of point and non-point sources of contamination and the use of BMPs for non-point pollution such as stormwater runoff was a result of the Federal Water Pollution Control Amendments of 1972 (Ice, 2004). Many BMPs were developed to improve stormwater contamination control.

One of these BMPs is Swales. Swales are a designed storm water treatment and control technology used for nutrients, heavy metals and total solids removal. Swales are sloped sides, long, and usually filled with vegetation, for soil stabilization and pollutant removal. To reduce pollutants, swales function by two principles: physical filtration and infiltration (Wanielista et al., 1992). Swales are used for low-moderate pollution control with life expectancy exceeding 20 years. The initial and maintenance costs are minimal for swales comparing with other storm water BMPs that can achieve similar results (Tsihrintzis et al., 1997).

In 1996, a 2000 foot designed swale was installed to protect Willamette River (Portland, Oregon) from stormwater runoff. The project resulted in 50% total suspended solid (TSS) reduction (France, 2002). During the same year, two swales in Virginia were studied to yield a result of 40% TSS reduction and >33% total phosphorus (TP) removal. The main specifications effecting the efficiency of the swales were : "swale length, longitudinal slope, presence of check dams, cross sectional shape, vegetative density, grass stiffness, soil infiltration rate, design flow depth, and design flow rate" (Winston et al., 2011).

Infiltration Basins (also known as recharge basins) are another example of stormwater BMPs. Infiltration Basins are a type of BMP used for stormwater runoff management, flood protection, erosion protection, and water quality improvement. The design of the infiltration basin is a shallow pond designed to infiltrate the stormwater into the aquifer through permeable soil and a flat bottom (to allow infiltration distribution).

However, infiltration is less favorable when compared with other BMPs. One problem with infiltration basins is clogging, but this can be minimized by vegetation. One limitation is that infiltration basins are not applicable in regions with karst such as limestone due to the potential of sink hole formation. Another limitation is that infiltration basins are rarely used in ultra-urban areas due to the limited free surface area. The United State Environmental Protection Agency USEPA also recommends the use of pretreatment in urban areas with high contamination levels before the use of infiltration basins (USEPA, 2014). In addition, when used in urban and ultra-urban environments, infiltration basins can contribute to ground water contamination(O'Reilly et al., 2012b).

In contrast, some studies show that the development of functionalized BAM can enhance nutrient removal compared with the native sandy soil by increasing soil moisture, and adsorption-absorption capacity while maintaining sufficient infiltration capacity (O'Reilly et al., 2012a). For example, a study used BAM in a full-scale innovative stormwater infiltration basin and compared it with the normally used sandy soil for phosphorus removal. The results indicated that after using BAM the moisture increased by 25% increasing the denitrification potential. Also, an average increase of 80% and 12% removal of TP and PO_4^{3-} respectively was observed after the use of BAM (O'Reilly et al., 2012b).

In addition, many other BMPs are used for stormwater pollution control. These BMPs are, but not limited to, retention/detention ponds (Yousef et al., 1986), green roofs (Hardin et al., 2012), dry ponds (Hossain et al., 2010), wetlands (Xuan et al., 2009), exfiltration trenches, upflow filter and skimmers, and pervious pavements (DeBusk et al., 2011; Hardin et al., 2012; Li et al., 1999; Ryan et al., 2010; Wanielista et al., 2008).

Nutrients Treatment Mechanisms in stormwater

Microbiological processes

There are two types of microbiological processes which can affect nitrogen in stormwater treatment: nitrification, and denitrification. Nitrification is a two-step bio-process that oxidizes ammonia to nitrite in the first step and oxidize nitrite to nitrate in the second step. The process is carried out by aerobic autotrophic bacteria known as nitrifying bacteria. The total oxidation reaction is as follows (Metcalf & Eddy, 2003):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

Denitrification results in the reaction of nitrate to nitrogen gas through a series of reduction steps via nitric oxide and nitrous oxide. The bacteria responsible for denitrification can be heterotrophic or autotrophic, although heterotrophic denitrification is more prevalent. The reduction steps of nitrate to nitrogen gas are shown below (Metcalf & Eddy, 2003).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Physicochemical processes

There are three types of physicochemical processes concerning stormwater treatment, adsorption, absorption and ion exchange.

Ion exchange (IX) is a process where ions from the solution are exchanged with ion from a solid or an insoluble phase (Metcalf & Eddy, 2003). IX and adsorption are similar because both occur on a solid surface. The difference between IX and adsorption, however, is that IX require a two-way equivalent exchange between the phases while adsorption has no such requirement (McBride, 1994). The ion exchanger can be of natural origin or a synthetic material, all having a fixed charge functional group on the surface with counterions (ions of an opposite charge) to maintain electro-neutrality in the IX material (Crittenden et al., 2012a). Figure 2 illustrates the ion exchange between the solution and the IX material.

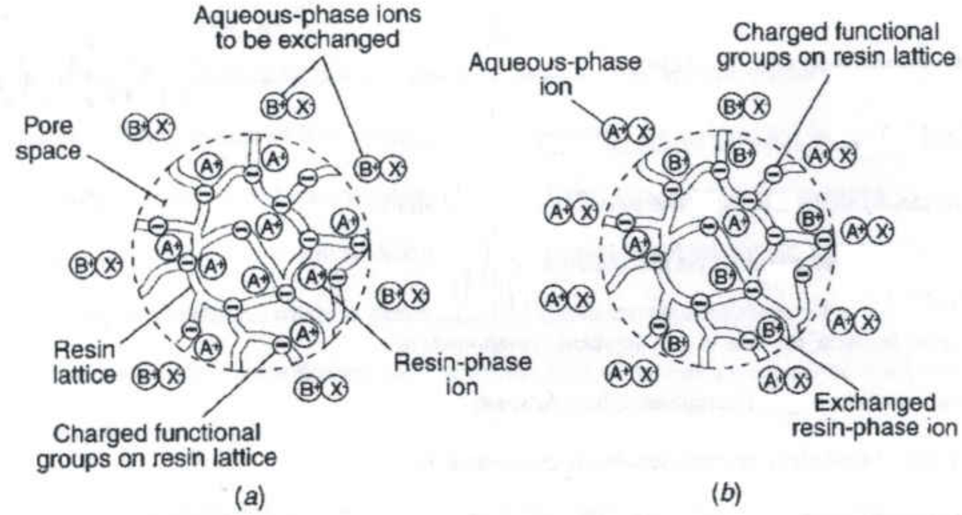


Figure 2 Ion exchange (a) initial condition, (b) equilibrium condition (Crittenden et al., 2012a)

Absorption is the physical or chemical mass transfer of a solute from a bulk phase to a homogeneous distribution throughout another bulk phase (Hossain et al., 2010). Absorption is not to be confused with adsorption processes since adsorption only occurs on the surface of the solid and not at the molecular level like absorption (Crittenden et al., 2012a). Figure 3 describes the absorption mass transfer using the two-film theory.

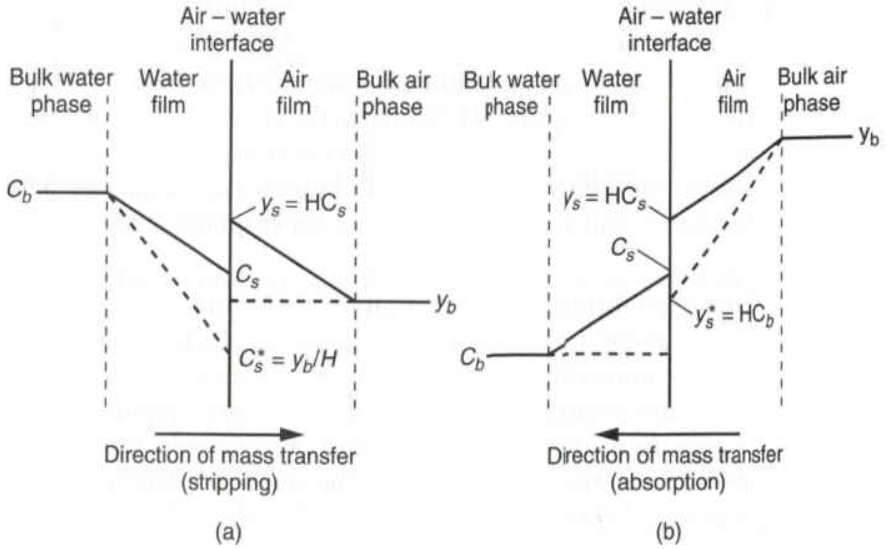


Figure 3 Two-film theory (a) desorption, (b) absorption (Crittenden et al., 2012b)

Adsorption is a mass transfer system in which a targeted constituent from the gas, liquid or solid phase is adhered to the surface of the other bulk-phase (Ruthven, 1984). Adsorbate is the target constituent that will be transferred. Adsorbent is the bulk phase to which the adsorbate is adsorbed (Clair et al., 2003). For the purpose of this research, only the adsorption between the nutrient in the stormwater (i.e. phosphorus) as the adsorbate and the adsorbent media as the adsorbent is considered.

Adsorption for Nutrient Removal in Stormwater

Removal of nitrogen and phosphorus species by adsorption is a process that involve mass transfer of the adsorbate molecule from the stormwater to the surface of the adsorbent (Crittenden et al., 2012b). Figure 4 shows the adsorption process. The constituent is adsorbed from the storm water to the liquid film between the bulk water and the adsorbent. Then, the constituent is moved to the surface of the adsorbent by chemical diffusion in the water in the pore space. Finally, the constituent is adsorbed to the internal surface area of the pores of the adsorbent. The pores adsorption function by adsorbent surface diffusion and/or molecular diffusion through the liquid (Metcalf & Eddy, 2003).

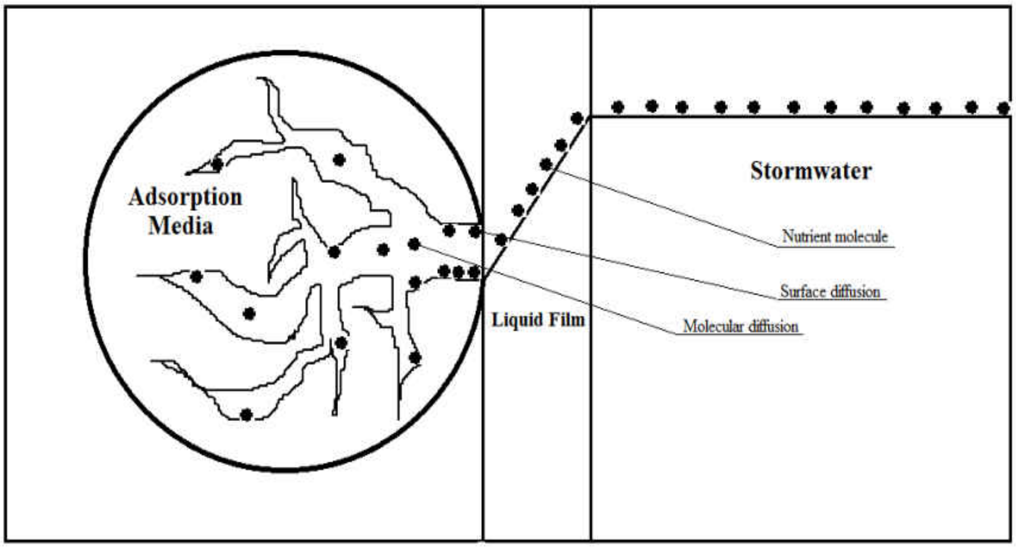


Figure 4 Adsorption process from (Metcalf & Eddy, 2003)

There are two types of adsorption, physical adsorption and chemical adsorption. Physical adsorption, known also as physisorption is a non-specific binding mechanism caused by weak binding forces. In physisorption, the process is reversible, and the molecule can be adsorbed or desorbed. The adsorbed molecules are not attached to the surface of the media but are free to relocate around the surface. However, the molecules can desorbs as a result of low nutrient concentration in the water phase. Physisorption is an exothermic reaction with an adsorption heat ranging between 4-40 kJ/mol, and the molecules can be multi-layers thick.

On the other hand, chemical adsorption (chemisorption) is a specific chemical binding mechanism that can be ionic or covalent. It is caused by much stronger forces than the physical adsorption. Chemisorption is almost irreversible, monolayer, and exothermic with an adsorption heat exceeds 200kJ/mol (Clair et al., 2003; Crittenden et al., 2012a).

Both chemisorption and physisorption are easily differentiated under extreme conditions but not so in some other cases. Table 1 list some key differences between both types of adsorption (Crittenden et al., 2012a; Metcalf & Eddy, 2003). As showing in Figure 5, usually, physical adsorption is dominant at low temperatures and chemical adsorption at high temperatures, but at very high temperature both will decrease (Chiang et al., 2001).

Table 1 Physical and chemical adsorption comparison (Crittenden et al., 2012a; Metcalf & Eddy, 2003)

Parameter	**Physical adsorption**	**Chemical adsorption**
Use in water treatment	Most popular	Rarely used
Number of layers	Multi-layer	Mono-layer
Process speed	Limited by mass transfer	Variable
Reaction type	Reversible, Exothermic	Mostly irreversible, Exothermic
Bonding type	Non-specific	Specific binding mechanism
Adsorption heat	4-40 kJ/mol	>200kJ/mol

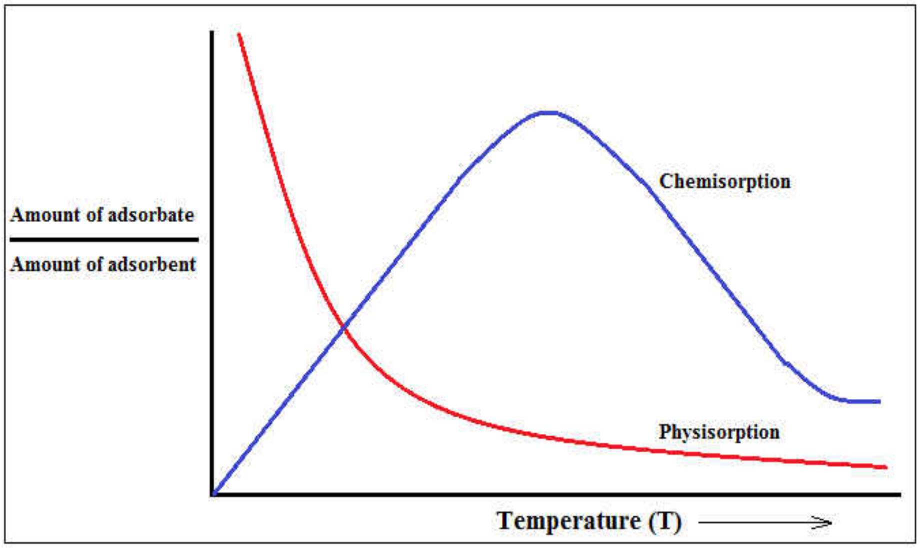


Figure 5 Adsorption capacity Vs. Temperature (Chiang et al., 2001)

Adsorption Isotherms

Adsorption Isotherms describe the relation between the adsorbent (usually a solid) and the adsorbate in equilibrium conditions to reach quantitative comparisons between different adsorbents. Isotherms are also beneficial to describe the potential adsorbents capacity, adsorption mechanisms, and surface properties. The adsorption isotherm curve is used to investigate the mobility of pollutant (sorbate) from an aqueous-phase into solid-phase at constant temperature using physiochemical parameters. Over the years, many isotherm models were developed and can be categorized into three categories two-parameter, three-parameter, and multicomponent isotherms (Foo et al., 2010).

Two-parameter isotherms

The most common models of the two-parameter isotherms are the Langmuir model and the Freundlich model.

The Langmuir isotherm was originally used to describe gas-solid adsorption when the solid is activated carbon but also has been used to investigate other adsorbents (Langmuir, 1918). The Langmuir models assume reversible chemical reactions between the surface of the sorbent and the aqueous solution in equilibrium.

$$S_v + A \leftrightarrow S * A$$

Where S_v is the available sites on the sorbent, A is the target sorbate in solution, and S*A is the bound adsorbate on the surface of the adsorbent. Another assumption is that all adsorption sites have uniform free-energy, and are capable of associating with only one molecule (Crittenden et al., 2012b).

The Freundlich Isotherm is the same as the Langmuir Isotherm in that the adsorption phenomena is reversible. However, Freundlich assumes an un-ideal distribution of adsorption (Freundlich, 1906). Early studies show that the relation between sorbate and a fixed mass of sorbent (e.g. activated carbon) changes with the change of the solution concentration (Ahmaruzzaman, 2008). Thus, this model is a better isotherm fit for activated carbon than Langmuir (Crittenden et al., 2012a).

There are many other isotherm models developed that can be included in this category such as Dubinin- Radushkevich model, Temkin model, Flory-Huggins model, and Hill model (Brdar et al., 2012; Foo et al., 2010; Sariban et al., 1987; Tosun, 2012). However, in this study only the Langmuir Isotherm and the Freundlich Isotherm will be used.

Three-parameters isotherms

The Redlich-Paterson equation can integrate three parameters, and the equation is derived from both Freundlich and Langmuir (Redlich et al., 1959; Vasanth Kumar et al., 2010). The model depends on the adsorbent heterogeneity (g). The Redlich-Paterson equation follows Henry's law when g is zero and Langmuir when g is one. When g >1, the model follows the Freundlich isotherm (Vasanth Kumar et al., 2010).

There are also other isotherm equations developed that can be categorized as three-parameters isotherm. Sips (Tosun, 2012), Toth (Brdar et al., 2012), Koble-Corrigan (Koble et al., 1952), Khan (Khan et al., 1997) and Radke-Prausnitz (Radke et al., 1972) are an example of other equations than can include three parameters.

Multi-component isotherms

Brunauer-Emmett-Teller (BET) (Brunauer et al., 1938) is an extension of the Langmuir equation where several molecule layers can exist. The BET equation allows for layers with a different thickness. In addition, the BET equation assumes that the site energy for the first layer is constant throughout the layer and equivalent to the participation free energy of the following layer (Crittenden et al., 2012a).

Frenkel-Halsey-Hill (FHH) (Hill, 1952) and MacMillan-Teller (MET) (McMillan et al., 1951) are also considered to be multi-component isotherm equations.

Nitrogen and phosphorus removal from stormwater by sorption media

Sorption media is a single or a mix of materials used to treat stormwater runoff via physicochemical and microbiological processes. The design of sorption media can be to treat a variety of constituents or functionalized to treat targeted pollutants such as nutrients (Chang et al., 2010a). Over the years, various media mixtures have been studied and used for nutrient removal. Some of medias used for nutrient removal are, wollastonite, lime-rock, peat, sand, sulfur, alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw, wood chips, and zeolite (Hossain et al., 2010).

DeBusk et al. (1997) studied the removal of various stormwater contaminants including total phosphorus (TP) using different types of medias. The materials used as sorption were quartz sand, peat soil, crushed limestone, and wollastonite (calcium silicate mineral). The results showed that wollastonite had the highest TP removal (88%) among all medias. Sand, peat soil, and limestone were not as efficient in TP removal and removed 40%, 44%, and 41% respectively (DeBusk et al., 1997).

Kim et al. (2003) conducted a column test for eight different types of media to find the best solid for stormwater nitrate removal through denitrification. They found that newspaper, wheat straw, wood chips, and alfalfa yielded a biological nitrate removal that exceeds 98% followed by sawdust with about 95% removal. However, limestone, leaf mulch, and sulfur were not as efficient and removed 60%, 55%, and 3% nitrate respectively. According to the authors, all the medias were electron donors for denitrification and a good carbon source for bio-growth, but newspaper was certainly the best electron donor (Kim et al., 2003).

Namasivayam et al. (2005) used oyster shell powder as an adsorbent for phosphate under different conditions, agitation time and adsorbent dosage. The results show that using raw oyster shell under no agitation had no effect on phosphate removal. When the oyster shell powder was agitated, the removal increased with time. At low adsorbent dose (1.2 g/50cm^3), the phosphate removal increased for the first 15 minutes and then stabilized at 45% removal, but at higher dose (25 g/50cm^3), the removal stabilized after 10 days at 80% (Namasivayam et al., 2005).

Sengupta et al. (2006) used mineral base medias such as oyster shell, marble chip, and limestone to remove nitrate via autotrophic biological denitrification. The highest removal of nitrate was registered for the crushed oyster shell. Nitrate removal for the crushed oyster shell and limestone was 80% and 53% respectively (Sengupta et al., 2006).

Hsieh et al. (2005) used sixteen bioretention columns with sixteen different mixes of sand, soil, and mulch to evaluate their effectiveness on P and N removal from an urban stormwater runoff. The research concluded that mulch removed nearly four times the nitrate removed by sand. However, mulch showed poor TP removal at less than 4%.The recommended design was using sand/soil mix with 4:1 ratio by mass. The overall removal of TP was 25-70%, nitrate 6-9%, and ammonium 11-20%. The study concluded that all the media used had poor nitrogen adsorption (Hsieh et al., 2005).

Erickson et al. (2007) studied the effectiveness of C33 sand alone and enhanced with chopped granular steel wool, three blast oxygen furnace by-products, limestone, aluminum oxide, and calcareous sand in stormwater phosphorus removal. The study used batch test and column test to evaluate the removal of dissolved phosphorus with different enhancements with C33 sand. In the patch study, C33 with no enhancement removed 45% of the dissolved phosphorus in 24 hour. When C33 sand is mixed with 0.29% - 0.31% steel wool (mix A), 50% - 10% limestone (mix B), or 50% - 10% calcareous sand (mix C) the removal of dissolved phosphorus was 60% - 90% in 24 hour with a pH between 9.8 and 10. Three blast oxygen furnace by-products removed almost all the dissolved phosphorus but increased the pH to 11 exceeding the water quality standards. The column study showed that C33 sand had only 2.1% dissolved phosphorus removal efficiency. Mix B and C caused the column to clog while mix A had no problem with clogging the column and removed about 99% of the dissolved phosphorus (Erickson et al., 2007).

Wanielista et al. (2008) used a Black&Gold Pond Media™ in a chamber up-flow filter and skimmer (CUFS) for stormwater pollution control. Figure 6 shows a schematic of the CUFS. The media was a mixture of 45% expanded clay, 45% tire crumb, and 10% sawdust. Both tire crumb and expanded clay were used to enhance phosphorus adsorption. Sawdust, however, was used to remove nitrate via denitrification as an electron donor under anoxic conditions. The result showed a reduction of TN, and TP by 33%, and 50% respectively (Wanielista et al., 2008). Ryan et al. (2010) also used the

Black&Gold Pond Media™ for stormwater treatment in a CUFS to remove TP and TN. The removal efficiency of TP and TN were 52% and 33% respectively (Ryan et al., 2010).

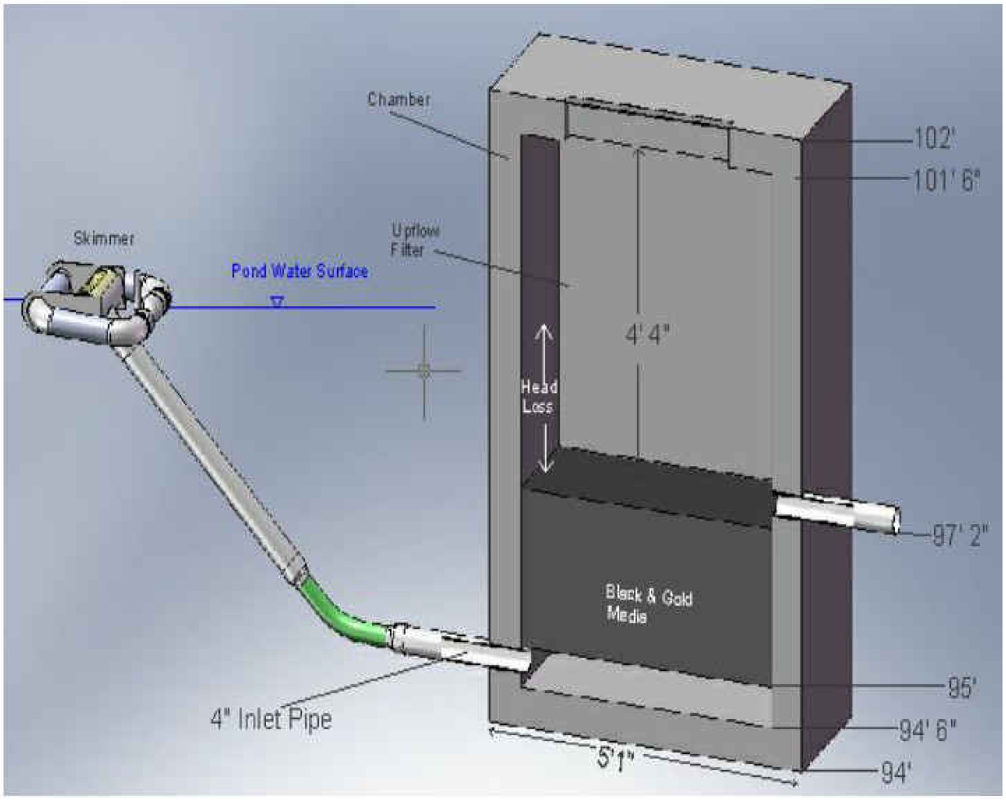


Figure 6 A schematic of stormwater chamber up-flow filter and skimmer (CUFS) from (Wanielista et al., 2008)

Chang et al. (2010b) used a green and recyclable media in a conventional field-scale underground drain field. The mix was 68% fine sand, 25% tire crumb, and 7% sawdust. The mix is one of the Bold & Gold™ medias developed by the University of

Central Florida. The sorption removal efficiency for the phosphorus forms was 81.8%, 79.1%, and 83.6% for TP, SRP, and organic-P respectively. 70.2% TN and 81.8% ammonia removal was achieved in this study and was mainly via nitrification-denitrification (Chang et al., 2010b).

Chang et al. (2011) used a two layer media mix in four small-scale up-flow wetland systems, illustrated in Figure 7, for nutrient and pathogen (fecal coliform and *E coli*) removal. The two mixes were the green media (G) and the pollution control media (PC). The first layer was a two inch G media with 75% expanded clay, 10% vermiculite, and 15% peat to support vegetation and provide a proper environment for bio-treatment. The second layer was PC media with 50% citrus grove sand, 20% limestone, 15% tire crumb, and 15% sawdust for nutrient and turbidity removal. The G and PC medias overall removal efficiency of TN, ammonia, TP, and SRP was 65.8%, 71.5%, 94.4%, and 99.4% respectively (Chang et al., 2011).

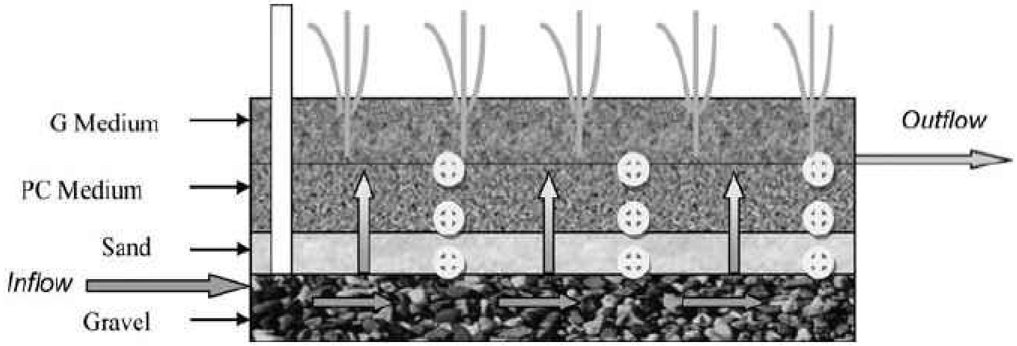


Figure 7 Small-scale up-flow wetland from (Chang et al., 2011)

O'Reilly et al. (2012b) studied the potential use of bio-sorption activated media (BAM) containing 14.3% tire crumb, 27.2% silt + clay, and 58.5% sand to remove nutrients from stormwater runoff in an innovative infiltration basin shown in Figure 8. Tire crumb was used to improve sorption capacity while silt + clay was used to increase moisture retention and sand was used to assist infiltration. The study concluded that the highest total dissolved phosphorus (TDP) removal was 90%, but nitrate showed removal less than that of TDP. The study concluded that using BAM phosphorus removal is expected to be via physicochemical processes while nitrogen removal is by biological processes (O'Reilly et al., 2012b).

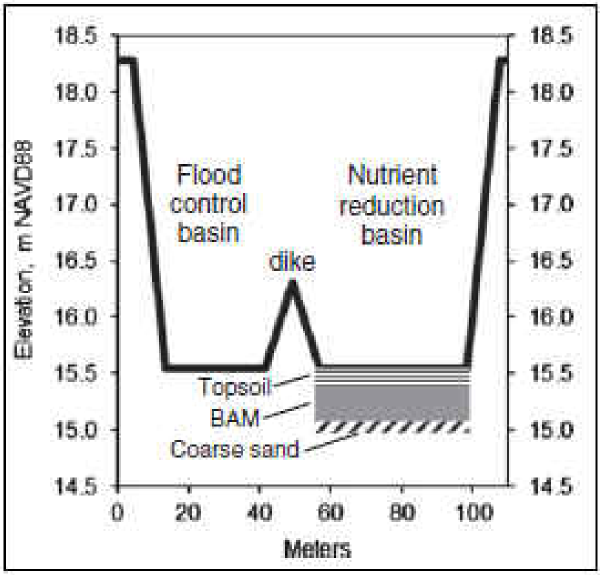


Figure 8 Innovative infiltration basin with BAM integration (O'Reilly et al., 2012b)

Hood et al. (2013) a researcher from the University of Central Florida looked into using a mix of bio-sorption media (BAM) in a comparison with the more widely used sandy-soil as a bio-infiltration system in bio-swales. The study showed 96% and 78% lower effluent concentrations of total phosphorus (TP) and soluble reactive phosphorus (SRP) using BAM compared to sandy-soil as a bio-infiltration system. The BAM mix had an average removal efficiency of 95% SRP and 71% TP (Hood et al., 2013).

Bold&Gold™

Bold&Gold™ is a functionalized bio-sorption activated media (BAM) for stormwater treatment. Bold&Gold™ was developed by the Stormwater Academy at the University of Central Florida (Wanielista et al., 2008). For the purpose of this study, a Bold&Gold™ media with 55% Fine expanded clay, 20% 3/8 expanded clay and 25% tire crumb was used.

Both fine and 3/8 expanded clay can help plant growth and provide efficient oxygen diffusion for biological nutrient removal (Xuan et al., 2009). For phosphorus, expanded clay is used mainly as adsorbent and secondary as anion exchanger (Wanielista et al., 2008) Expanded clay has a high content of silicates which provide an appropriate anion exchanger with phosphate (Douglas et al., 2004). Depending on the origin of the soil, expanded clays have a sorption capacity between 0.037 and 2.9 mg sorbate/g sorbent (Xu et al., 2006).

Tire crumb is used to increase the sorption capacity especially phosphorus adsorption (O'Reilly et al., 2012b; Wanielista et al., 2008). Tire crumb has about 30% carbon black by mass which behaves similarly to activated carbon (Hood et al., 2013).

Activated carbon is ideal for adsorption due to the large ratio of surface area to mass ratio and proven to adsorb a wide range of pollutants (Crittenden et al., 2012a). Adsorption of phosphorus to activated carbon is significant and desorption is minimal at solution pH between 4-10. Figure 9 show the effect of pH on phosphate removal and desorption at an activated carbon dose of 300mg/50mL (Namasivayam et al., 2004). Rashid (2012) compared oven-dried alum sludge to activated carbon for phosphorus removal in a breakthrough column experiment. The result show that activated carbon had a higher removal of phosphorus than the oven-dried alum sludge. The activated carbon removed >85% phosphorus at average pH of 7.2 (Rashid, 2012).

In stormwater runoff, the average national pH value is 7.2-7.5 according to the NSQD report (Pitt et al., 2005). Thus, activated carbon is a good phosphorus adsorption media in stormwater treatment.

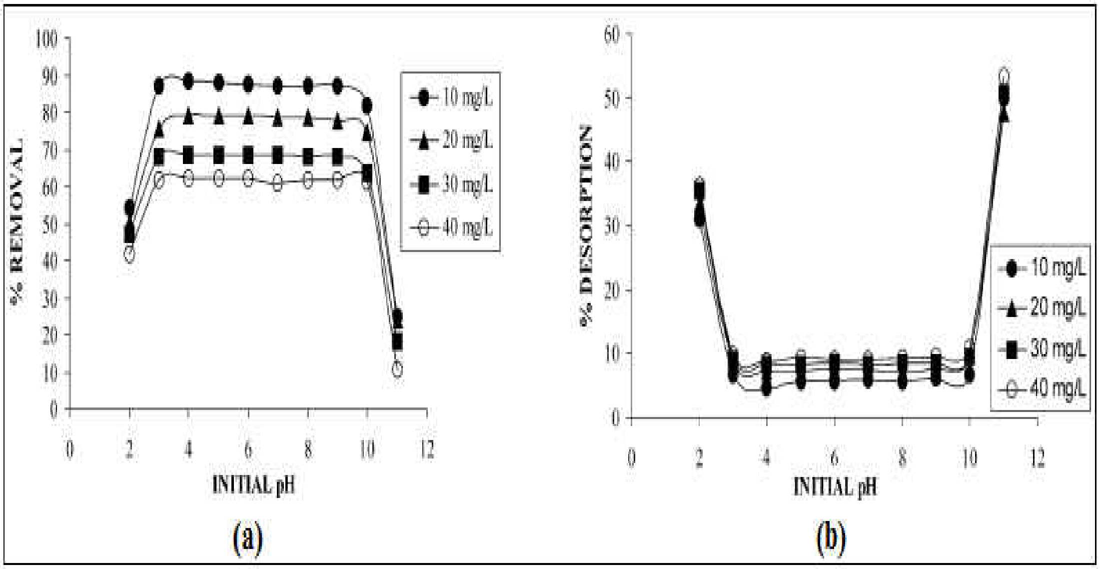


Figure 9 (a) Effect of pH phosphate removal at 300 mg activated carbon dose per 50 ml solution, (b) Effect of pH phosphate desorption 300 mg activated carbon dose per 50 ml solution (Namasivayam et al., 2004)

CHAPTER THREE: METHODS AND MATERIALS

Isotherm Batch Test

Constant Concentration of the Sorbate (2 and 12 hour experiments)

Some isotherms were conducted using a constant concentration of the sorbate (phosphorus was the sorbate for all but a few tests which showed that ammonia and nitrate did not sorbs significantly). The isotherm data was conducted using 500 ml Erlenmeyer flasks. In each of these was 300 ml of combined unfiltered pond water and a phosphorus spike. The spike volume was negligible since a 100 mg/l as PO_4^{2-} (32.7 mg/L as P) standard solution was used and the typical concentration of an experiment was around 1 mg/L as P. The standard solution was made using 0.1433g/L monopotassium phosphate salt (KH_2PO_4). The media was "leached" by washing and soaking overnight in distilled water and then dried for two days to get rid of any phosphorus or nitrogen forms that might leach out during the isotherm experiments.

Next, different masses of the sorption media consisting of 55% fine expanded clay, 20% 3/8 expanded clay and 25% tire crumb were put into each 500 ml Erlenmeyer flask along with 300 ml of spiked, unfiltered, stormwater pond water. Typical media amounts were 10, 50, and 100 grams of media (actual amounts varied from 1 to 200 grams but some amounts of media at the high and low end of the range did not yield good data). The flasks were then covered with parafilm to minimize contamination or loss of liquid and shook (on a shaker table) for either 2 or 12 hours at a constant temperature.

The samples were collected, filtered with a 0.45 µm membrane filters, and analyzed immediately using the Orbeco-Hellige™ (Sarasota, FL) low range method for phosphate concentrations between 0.02 and 1.6 mg/L as P (equivalent to HACH method 8048). Absorbance at 880 nm wavelength was measured in a HACH DR 5000 Spectrophotometer for soluble reactive phosphorus (SRP). In the early experiments HACH methods 10023 and 8192 were used for NH_3 and NO_x respectively. pH and Temperature were also measured.

Different Concentration of the Sorbate (24 hour experiments)

Other isotherms were conducted using a different concentration of the sorbate (phosphorus was the sorbate). The isotherm data was conducted using fifteen 500 ml Erlenmeyer flasks. In each of these was 300 ml of combined unfiltered pond water and a phosphorus spike. The spike volume was negligible since a 100 mg/l as PO_4^{2-} (32.7 mg/L as P) and a 1000 mg/l as PO_4^{2-} (327 mg/L as P) standard solutions ware used and the concentrations of the experiment ware 0.5, 1, 5, 10 and 20 mg/L as P. The 100 mg/l as PO_4^{2-} (32.7 mg/L as P) standard solution was made using 0.1433g/L monopotassium phosphate salt (KH_2PO_4); while, the 1000 mg/l as PO_4^{2-} (327 m/L as P) standard solution was made using 1.433g/L monopotassium phosphate salt (KH_2PO_4). The sorption media was "leached" by washing and soaking overnight in distilled water and then dried for two days to get rid of any phosphorus or nitrogen forms that might leach out during the isotherm experiments. Next, 50g of the sorption media consisting of 55% fine expanded clay, 20% 3/8 expanded clay and 25% tire crumb were put into each 500 ml Erlenmeyer flask along with 300 ml of spiked, unfiltered, stormwater pond water. The flasks were then covered with parafilm to minimize contamination or loss of liquid and shook (on a shaker table) for 24 hours at a constant temperature. The samples were collected, filtered with a 0.45 µm membrane filters, and analyzed immediately using the Orbeco-Hellige™ (Sarasota, FL) low range method for phosphate concentrations between 0.02 and 1.6 mg/L as P (equivalent to HACH method 8048). Absorbance at 880 nm wavelength was measured in a HACH DR 5000 spectrophotometer for soluble reactive phosphorus (SRP). pH, temperature, and dissolved oxygen (DO) were also measured.

Table 2 Test Methods for Nutrient Concentrations

Chemical species	***HACK Method no.***	***Measuring range ($mg \cdot L^{-1}$-P)***
Ortho-Phosphorus	Method 8048	0.02 and 1.6 mg/L as p
Nitrate+ Nitrite (NOx)	Method 8192	0.01 and 0.50 mg/L as N
Ammonia	Method 10023	0.02 and 2.50 mg/L as N

Analytical Procedures

Using the information described in Standard Methods for the Examination of Water and Waste Water Nitrate+Nitrite (NOx), ammonia (NH_3), soluble reactive phosphorus (SRP), temperature, pH and dissolved oxygen (DO) were measured throughout the research. Each procedure is described below (Eaton et al., 2005).

Nitrate+ Nitrite (NOx)

For measuring Nitrate+ Nitrite, the unfiltered spiked water sample is filtered with a Whatman™ Binder-Free Glass Microfiber Filters (PPR 47MM) to remove turbidity that can affect the result. Then NO_X is measured immediately using the cadmium reduction Orbeco-Hellige™ (Sarasota, FL) low range method for NOx concentrations between 0.01 and 0.50 mg/L as N (equivalent to HACH method 8192). Absorbance at 507 nm wavelength is measured in a HACH DR 5000 Spectrophotometer for Nitrate+ Nitrite (NOx). In addition a five point standard carve is made. In early tests Nitrate and Nitrite were measured separately and nitrite was found to be negligible.

The first step for the HACH method 8192 is transferring fifteen ml of the filtered samples using a pipet to the graduated mixing cylinders. Next, the contents of one NitraVer 6 Reagent Powder Pillow is added to the cylinders. Then, the cylinders are capped, shaken for three minutes, and given an additional 2 minutes reaction time. Then, ten ml of the 15 ml is transferred to a clean 10 ml Cuvette (HACH 2495402). Another Cuvette (HACH 2495402) is filled with sample water to zero the machine. After that, the contents of one NitriVer 3 Nitrite Reagent Powder Pillow is added to each sample cell except the one with distilled water. Then, the Cuvettes are capped, shaken for 30 seconds, and allowed 15 minutes reaction time. Then they are wiped and then the sorption readings are recorded (zeroed from the vial with the distilled water). Lastly, the concentration was measured by plotting the adsorption on the standard curve. A reagent blank (distilled water with NitraVer 6 and NitriVer 3) is prepared for each new lot of reagents and standard curves and the standard curve absorption are calculated relative to the reagent blank.

Ammonia

For measuring ammonia, the unfiltered spiked water sample was filtered with a Whatman™ Binder-Free Glass Microfiber Filters (PPR 47MM) to remove turbidity that can affect the result. Then ammonia was measured immediately using the Orbeco-Hellige™ (Sarasota, FL) low range method for ammonia concentrations between 0.02 and 2.50 mg/L as N (equivalent to HACH method 10023). Absorbance at 655 nm wavelength was measured in a HACH DR 5000 Spectrophotometer for ammonia. In addition a five point standard carve was made.

The first step for the HACH method 10023 is transferring two ml of the samples using a pipet to the AmVer™ Diluents Reagent Test 'N Tubes (one was filled with distilled water instead of the sample). Next, the contents of one ammonia Salicylate and one ammonia cyanurate powder pillows are added to each vial. Then, the vials are capped, shaken for 30 seconds, allowed 20 minutes reaction time, wiped and then the sorption readings are noted (zeroed from the vial with the distilled water). Lastly, the concentration is determined (mg/l as N) by plotting the sorption on the standard curve.

Soluble Reactive Phosphorus (SRP)

For measuring soluble reactive phosphorus (SRP) , the unfiltered spiked water sample is filtered with a Whatman™ Binder-Free Glass Microfiber Filters (PPR 47MM) to remove turbidity that can interfere with the adsorption measurement; in addition, the filtered sample is run through a 0.45 μm membrane filter be consistent with Standard Methods (Eaton et al., 2005) and exclude any colloids passing the glass fiber filter. Then Ortho-Phosphorus was measured immediately using the Orbeco-Hellige™ (Sarasota, FL) low range method for phosphate concentrations between 0.02 and 1.6 mg/L as P (equivalent to HACH method 8048). Absorbance at 880 nm wavelength is measured in a HACH DR 5000 Spectrophotometer for Ortho-Phosphorus. In addition a five point standard curve is made.

The first step for the HACH method 8048 is transferring five ml of the samples using a pipet to the Reactive Phosphorus Test ‘N Tube Dilution Vials (one is filled with distilled water instead of the sample). Second, all the vials are capped, shaken, and wiped. Then the sorption readings are taken (zeroed from the vial with the distilled water). Third, the contents of one PhosVer 3 Phosphate Powder Pillow is added to each vials. Then, the vial are capped, shaken for 30 seconds, set for two minutes, wiped and the sorption readings are taken again. The relevant sorption is the first sorption (before the powder pillow) subtracted from the second reading (after the powder pillow). Lastly, the absorbance is converted to concentration (mg/l as P) using the standard curve. The reagent blank is accounted for in the standard curve.

pH and Temperature (T°)

pH and temperature were obtained by using the Fisher Scientific (Waltham, MA) accumet dual Channel AR50 meter, an 80 ml beaker, Fisher Scientific stirring hotplate and 4, 7, and 10 pH buffering solutions. The meter was calibrated using the buffering solutions. Then, the sample was transferred to the small 80 ml beaker and positioned on the stirrer. Next, the probe on the meter was submerged into the sample and the temperature and the pH readings were taken once the values had stabilized.

Dissolved Oxygen (DO)

DO concentration were measured using Dissolve Oxygen Meter YSI Model 58 (Yellow Springs, OH) with a YSI 5905 (Yellow Springs, OH) probe and a 80 ml beaker. First, the meter was air calibrated. The saturation value was calculated using the probe reading of the temperature (no atmospheric pressure correction was required since UCF is near sea level). Following calibration, the probe was submerged into the stirred sample inside the 80 ml. Finally, the measurement was taken after the reading stabilized.

Bench-Scale upflow Column Test

The BAM column test is conducted in the Stormwater Lab of University of Central Florida in Orlando, Florida. The schematic of the columns construction is presented in. Figure 10 the columns are built using two PVC pipes each with a 4 inch inner diameter and 24 inch height. Both columns are filled with 24 inches of media which gives an approximate total volume of 300 inch3. Each column is then exposed to three two hour and one 24 hour storm events a week for about seven months in an upflow configuration using water from a stormwater pond which was spiked with ammonia, nitrite, nitrate, and soluble ortho-phosphorus. All influent and effluent samples ware preserved and sent to the certified Environmental Research & Design lab (ERD) for analysis. ERD is certified by the National Environmental Laboratory Accreditation Conference (NELAC). Table 3 summarizes the methods used in measuring SRP and TP.

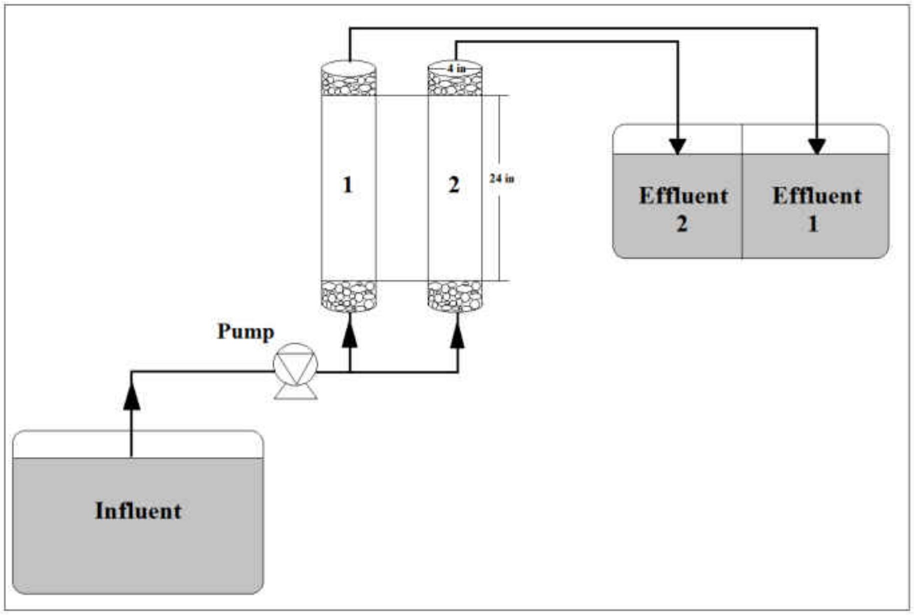


Figure 10 Schematic diagram of the column setup

Table 3 Testing methods used by ERD

Parameter	Test Method
SRP	EPA 365.1
	SM 21 4500-P F
TP	EPA 3565.1
	SM 4500-P F &SM 4500-P FB.5

CHAPTER FOUR: RESULTS AND DISCUSSION

Abstract

To maintain the quality of receiving water bodies, it is desirable to remove total phosphorus (TP) in stormwater runoff. Many media filtration technologies have been developed to achieve TP and soluble reactive phosphorus (SRP) removal. Efficient media adsorption is essential to insure control of stormwater phosphorus inputs to receiving water body. This project develops and analyzes a functionalized Biosorption Media (BAM) to remove phosphorus species from stormwater runoff. One goal of this project is to find the BAM values for coefficients such as maximum adsorption capacity (Q_M: 4.35E-05) for the media through SRP isotherm equilibrium experiments using the Langmuir and Freundlich models. In addition, an upflow column experiment was also performed to study BAM nutrient removal from stormwater runoff. Finally, the information from the isotherm and the column experiments are used to estimate quantity required of the media for representative application, and to define the effectiveness of BAM in phosphorus removal. The result of this study shows that BAM is a feasible stormwater treatment that can remove 60% SRP and >40% TP. The media is adequately modeled by both the Langmuir and the Freundlich models over the concentration range of interest in stormwater.

Introduction

Natural watersheds are a complete system that typically can purify itself if nutrient inputs are maintained at low levels. This purification capacity has limitations, however, that are often exceeded in watersheds with increased development. Nitrogen and phosphorus species are limiting nutrients in fresh and estuary systems that stimulate the growth of photosynthetic algae in the aquatic system. Microorganisms in the water and sediments use the algae remains for food. Over growing result in harmful algal bloom (HABs) that can cause harmful effects on aquatic life via oxygen depletion, and reduction in transparency. The over growing of HABs is caused by nitrogen and phosphorus species over-enrichment which is known as Eutrophication (Walsh, 2012). The sources of excess nutrient loading from non-point sources are stormwater runoff (i.e. runoff from highways, parking lots, sidewalks, and commercial-residential structures), wet and dry air deposition, and erosion (Göbel et al., 2007; Hood et al., 2013; USEPA, 2014). Eutrophication and groundwater contamination from high nutrients potentially can pose health risks. High exposure to nitrate can cause Methemoglobinemia (a fatal blood syndrome that affects infants also known as blue-baby syndrome), spontaneous abortions, and diabetes. In addition, water with excess levels of phosphorus can result in osteoporosis and kidney or liver failure (Wanielista et al., 2008; Xuan et al., 2009). Thus, The United State Environmental Protection Agency (USEPA) considered nitrate and nitrite in The National Primary Drinking Water Regulations with a maximum contaminant level (MCL) and maximum contaminant level goal (MCLG) of 10 mg/l as N and 1 mg/l as N respectively (USEPA, 2013). To minimize the potential impact of stormwater runoff pollutants on the watershed, implementation of stormwater Best Management Practices (BMPs) has been encouraged but not required (Barrett, 2005; Shaw et al., 2001).

Several BMPs technologies were developed successfully to improve nutrient contamination control using functionalized Biosorption Activated Media (BAM) as a way to implement BMP's (Wanielista et al., 2008). The data presented in this study, intended to evaluate the effectiveness and longevity of a functionalized sorption media as a part of Bold&Gold™ media's in SRP removal using bench-scale upflow column and SRP adsorption isotherms. Bold&Gold™ is a BAM composed mainly of green and recyclable material. These engineered medias are commonly used for stormwater treatment. Bold&Gold™ was developed by the stormwater academy at University of Central Florida, Orlando, Florida (Wanielista et al., 2008).

In Florida, The Florida Department of Environmental Protection (FDEP) is developing a Statewide Stormwater Treatment Rule. The new law will require all stormwater treatment to provide at least an average annual loading reduction of TP and TN by 85% or to the level that post-development average annual loading is equal to pre-development average annual loading, as appropriate (FDEP, 2010)

The objective of this study is to determine the sorption characteristics of a specific BAM blend with respect to phosphorus removal. Sorption capacity and the appropriateness of modeling the data via the Langmuir or the Freundlich isotherms will be determined.

Material and Methods

Sorption Media Evaluated

For the purpose of this study, a Bold&Gold™ media composed of 55% fine expanded clay, 20% 3/8 expanded clay and 25% tire crumb was used. Both fine and 3/8 expanded clay can help plant growth and provide efficient oxygen diffusion for biological nutrient removal (Xuan et al., 2009). For phosphorus, expanded clay is used as adsorbent and anion exchanger (Wanielista et al., 2008) Expanded clay has a high content of silicates which provide an appropriate anion exchanger with phosphate (Douglas et al., 2004). Depending on the origin of the soil, expanded clays have a sorption capacity between 0.037 and 2.9 mg sorbate/g sorbent (Xu et al., 2006).

Tire crumb is used to increase the sorption capacity especially phosphorus adsorption (O'Reilly et al., 2012b; Wanielista et al., 2008). Tire crumb has about 30% carbon black by mass which behaves similar to activated carbon (Hood et al., 2013). Activated carbon is ideal for adsorption due to the large ratio of surface area to mass ratio and proven to adsorb a wide range of pollutants (Crittenden et al., 2012a). Adsorption of phosphorus to activated carbon is significant at solution pH between 4-10. In stormwater runoff, the average national pH value is 7.2-7.5 according to the NSQD report (Pitt et al., 2005). Thus, Activated carbon is a good phosphorus adsorption media in stormwater treatment.

SRP Adsorption Isotherms

Isotherms are conducted using either a constant concentration of the sorbate and a fixed quantity of media (e.g. in this study the initial 2 hour and 12 hour equilibration isotherms), or a fixed amount of media (50 grams) and a varying concentration of the sorbate (e.g. in this study the more definitive 24 hour equilibration isotherms). Phosphorus is the sorbate for all but a few tests which show that ammonia and nitrate did not sorb significantly relative to the biological N transformations observed. The isotherm data is conducted using 500 ml Erlenmeyer flasks. In each of these 300 ml of combined unfiltered stormwater pond water and a phosphorus spike are mixed. The spike volume is negligible since a 100 mg/l as PO_4^{2-} (32.7 mg/L as P) standard solution is used and the typical concentration of an experiment is around 1 mg/L as P. The standard solution is made using 0.1433 g/L monopotassium phosphate salt (KH_2PO_4). The media is "leached" by soaking overnight in distilled water and then dried in a 105°C oven overnight to get rid of any phosphorus or nitrogen forms that might leach out during the isotherm experiments. Next, for the 2 hour and 12 hour experiments, different masses of media are put into each 500 ml flask along with 300 ml of spiked, unfiltered, pond water. Typical media amounts are 10, 50, and 100 grams of media (actual amounts vary from 1 to 200 grams, but some amounts of media at the high and low end of the range do not yield reliable data).

In the 24 hour experiments, 50 grams of media are used in all flasks and P concentrations are 0.5, 1, 5, 10, and 20 mg/l as P. The spike volume is negligible since a 100 mg/l as PO_4^{2-} (32.7 mg/L as P) standard solution is used for 0.5 and 1 mg/l as P and a 1000 mg/l as PO_4^{2-} (327 mg/L as P) standard solution is used for 5, 10, and 20 mg/l as P. The flasks are then covered with parafilm, to minimize contamination or loss of liquid, and shook (on a shaker table) for either 2, 12, or 24 hours at a constant temperature. The samples are collected, filtered with 0.45 µm membrane filters and analyzed immediately using the Orbeco-Hellige™ (Sarasota, FL) low range method for phosphate concentrations between 0.02 and 1.6 mg/L as P (equivalent to HACH method 8048). Concentrations that exceed 1.6 mg/l as P are diluted. Absorbance at 880 nm wavelength is measured in a HACH DR 5000 Spectrophotometer (Loveland, CO) for soluble reactive phosphorus (SRP). HACH methods 10023 and 8192 are used for NH_3 and NO_x respectively. pH and Temperature are also measured.

To confirm that 24 hours is sufficient to reach equilibrium, a time series test was conducted using constant amount of adsorbent (50g) and adsorbate (1mg/l as P). The last two consecutive measurement were consistent, <5% difference, over six hour interval (18hr-24hr), implying that 24 hours was sufficient to reach equilibrium.

Isotherm Modeling

The isotherm data in this paper was analyzed using two models: the Langmuir and the Freundlich isotherms. The constants from both models were then calculated using linear plotting and non-linear regression.

. The Langmuir isotherm was originally used to describe gas-solid adsorption when the solid is activated carbon but has also been used to investigate aqueous solutions and other bio-sorbents (Langmuir, 1918). The Langmuir models assume reversible chemical reaction between the surface of the sorbent and the aqueous solution in equilibrium. Both the non-linear and the linear forms of the Langmuir model are expressed as following (Crittenden et al., 2012a):

$$q_A = \frac{Q_M b_A C_A}{1 + b_A C_A} \tag{1}$$

And the linearized equation:

$$\frac{C_A}{q_A} = \frac{1}{b_A Q_M} + \frac{C_A}{Q_M} \tag{2}$$

Where q_A (i.e. x/m) is the equilibrium adsorbent-phase concentration of adsorbate, mg adsorbate/mg adsorbent. C_A is the equilibrium concentration of adsorbent in a solution, mg/l. b_A (i.e. K_{ads}) is the Langmuir adsorption or affinity constant of the adsorbent for the adsorbate, with units typically being L/mg. Q_M is the adsorption capacity, i.e. the concentration of adsorbate when surface sites are saturated with adsorbate, with units of mg adsorbate/mg adsorbent. The Langmuir equation can also be expressed in a dimensionless constant known as the equilibrium parameter ($R_{L.1}$). The equilibrium parameter is used in batch experiments to predict if sorption is a favorable process or not, and can be described as the following (Ma et al., 2011):

$$R_{L.1} = \frac{1}{1 + b_A C_i} \tag{3}$$

Where C_i is the maximum initial solute concentration in mg/L. The Value of $R_{L.1}$ can be 0, $0< R_{L.1}>1$, 1, or >1 which imply that the adsorption isotherm is irreversible, favorable, linear, or unfavorable respectively.

The Freundlich isotherm agrees with the Langmuir that the adsorption phenomena is reversible. However, The Freundlich assumes un-ideal distribution of adsorption (Freundlich, 1906). Early studies show that the relation between sorbate and a fixed mass of sorbent changes with the change of the solution concentration, proving that each site has different energy for sorbents such as activated carbon (Ahmaruzzaman, 2008).a similar relation was observed with the Langmuir model at very low concentrations. Thus, this model is typically a better isotherm fit for activated carbon than the Langmuir (Crittenden et al., 2012a). The equation used is shown below (Crittenden et al., 2012a)

$$q_A = K_a C_a^{\frac{1}{n}} \tag{4}$$

And the linearized equation is:

$$\log(q_a) = \log(K_a) + \left(\frac{1}{n}\right) \log{(C_a)} \tag{5}$$

Where K_a is the Freundlich adsorption capacity parameter, (mg/mg) and 1/n is the Freundlich adsorption intensity parameter, which is unitless.

upflow Column Test

The BAM column test is conducted in the Stormwater Lab of University of Central Florida in Orlando, Florida. The schematic of the columns construction is presented in Figure 11. The columns are built using two PVC pipes each with a 4 inch inner diameter and 24 inch height. Both columns are filled with 24 inches of media which gives an approximate total volume of 300 in^3. Each column is then exposed to three two hour and one 24 hour storm events a week for about seven months in an upflow configuration using water from a stormwater pond which was spiked with ammonia, nitrite, nitrate, and soluble ortho-phosphorus. All influent and effluent samples are preserved and sent to the certified Environmental Research & Design lab (ERD) for analysis. ERD is certified by the National Environmental Laboratory Accreditation Conference (NELAC). Table 4 summarizes the methods used in measuring SRP and TP.

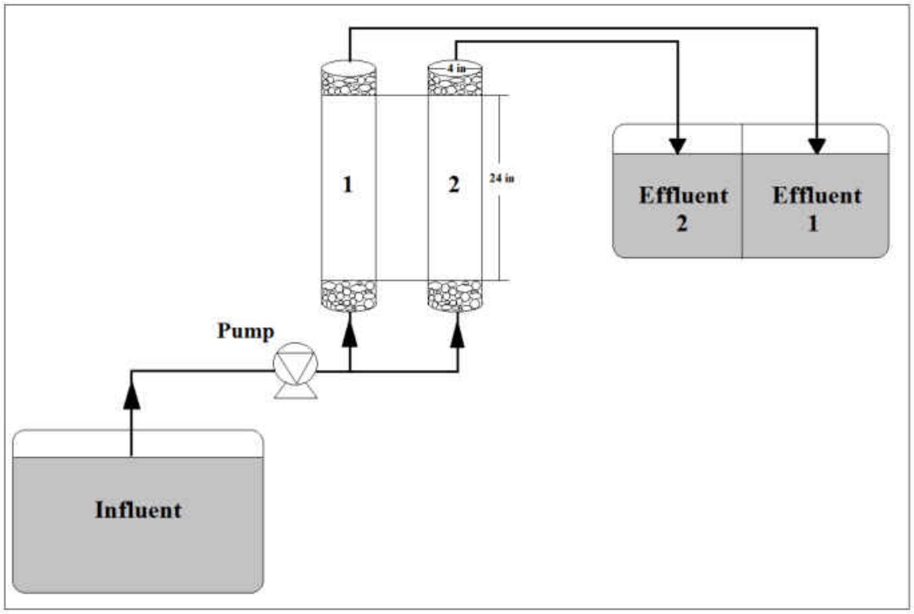


Figure 11 The column setup

Table 4 ERD test methods

Parameter	Test Method
SRP	EPA 365.1
	SM 21 4500-P F
TP	EPA 3565.1
	SM 4500-P F &SM 4500-P FB.5

Results and Discussion

pH and temperature are in a range of 7-8 and 21-23 °C respectively throughout the experiments.

Isotherms

Isotherms of SRP adsorption on Bold&Gold™ media were modeled using the Langmuir and the Freundlich isotherms using linear plotting and non-linear regression. Initial isotherms are conducted using a 2 hour equilibration time, and then a 12 hour equilibration time. It was found that 2 and 12 hour isotherms did not follow the Freundlich isotherm and only the Langmuir model was used to describe the data. Figure 12 shows the 2 hour and 12 hour isotherm data. Table 5 shows the Langmuir isotherm constants. The maximum amount of adsorbate (Q_M) is roughly 3 times higher for the 12 hour test indicating that equilibrium takes more than 2 hours to achieve.

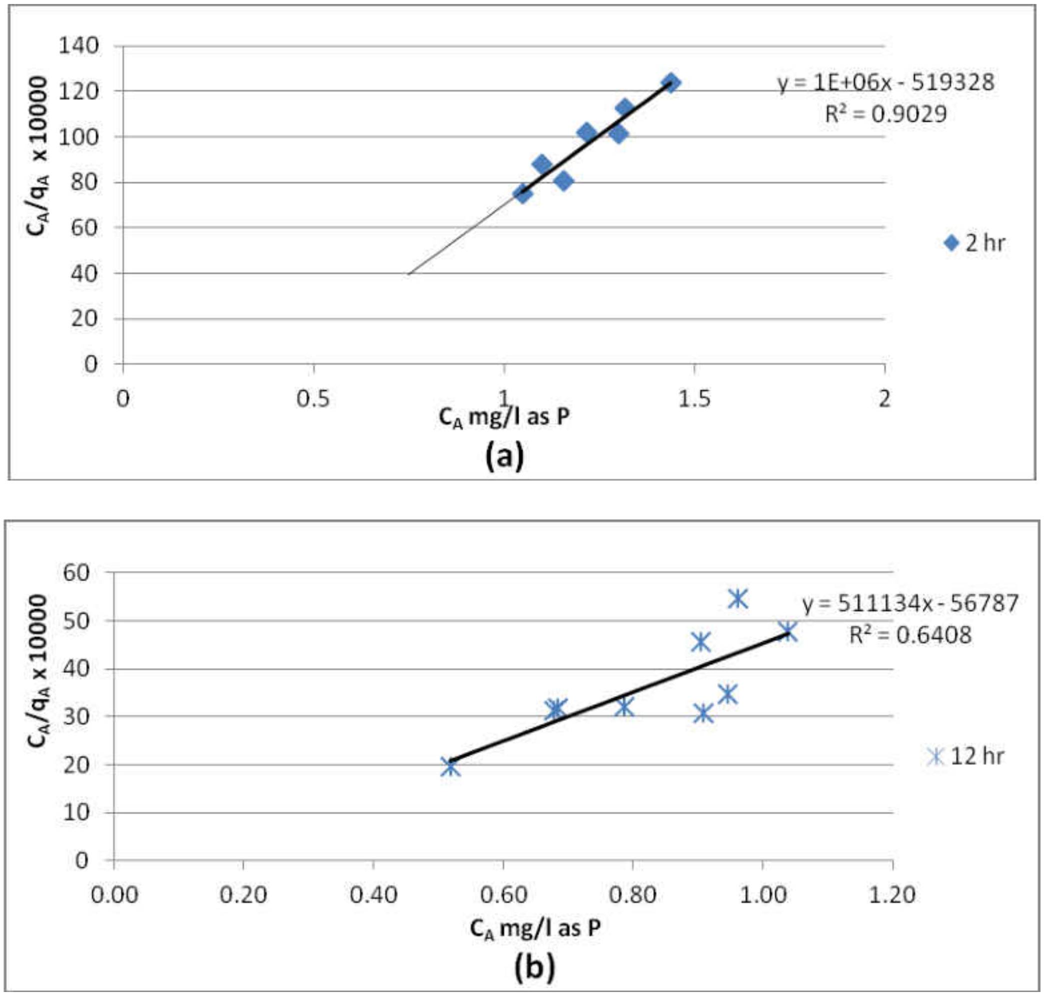


Figure 12 (a) The Langmuir graph for the 2 hour run, (b) The Langmuir graph for the 12 hour run

Table 5 The Langmuir isotherm parameters

	2hr	12hr
Slope	1.00E+06	5.11E+05
Q_m mg/mg	1.00E-06	1.96E-06
intercept	-5.19E+05	-5.68E+04
b_A, L/mg	-1.926	-9.001

A time series experiment was conducted then to try and determine how long it would take to reach equilibrium. The equilibrium test was conducted using a constant amount of adsorbent (50g) and adsorbate (1 mg/l as P). The last two consecutive measurements were constant, with <5% difference, over a six hour interval (18hr-24hr). As a result, two 24 hours Isotherm experiments are run to obtain data at equilibrium. SRP shows significant adsorption for the media at 24 hours. Figure 13 shows that there is significantly more P adsorbed in the 24 hour runs then there are in the 2 and 12 hour runs, and shows the consistent adsorption between 18 and 24 hours shaking time.

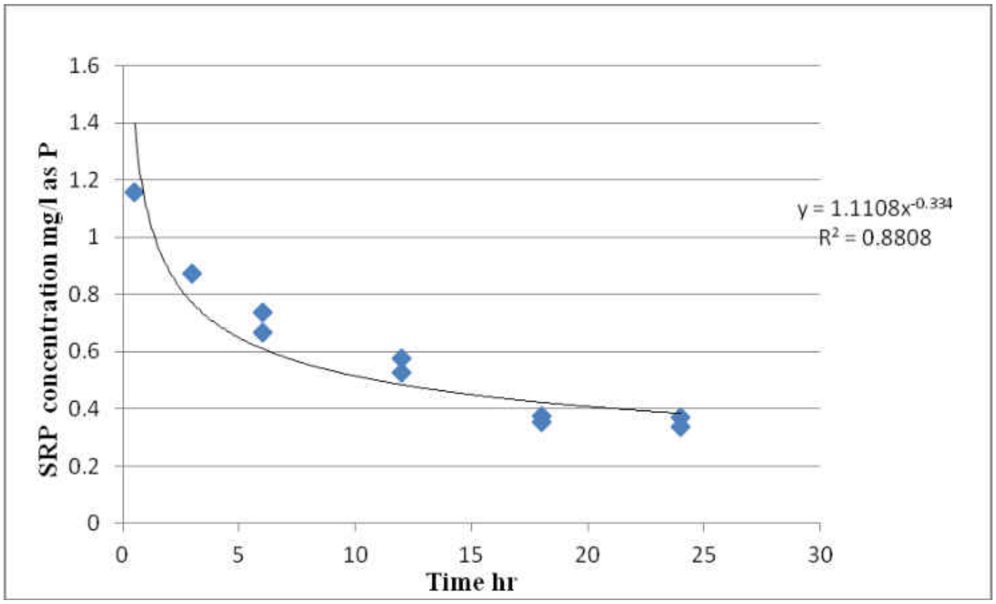


Figure 13 Time series experiment

As can be seen in Table 6 and Figure 14 a and b, the Langmuir isotherm graphs and the corresponding constants were consistent for two identical experiments. The maximum amount of adsorbate (Q_M) for the 24-1 run was almost identical to that of the 24-2's with only a 6% difference. Also, the Langmuir adsorption constant of adsorbate (bA) was similar for both runs with a 5 percent difference. The R^2 values from the linear regression indicate a proper fit for the data. The results of R^2 with respect to the Langmuir model are 0.934, and 0.895 for 24-1 and 24-2 respectively.

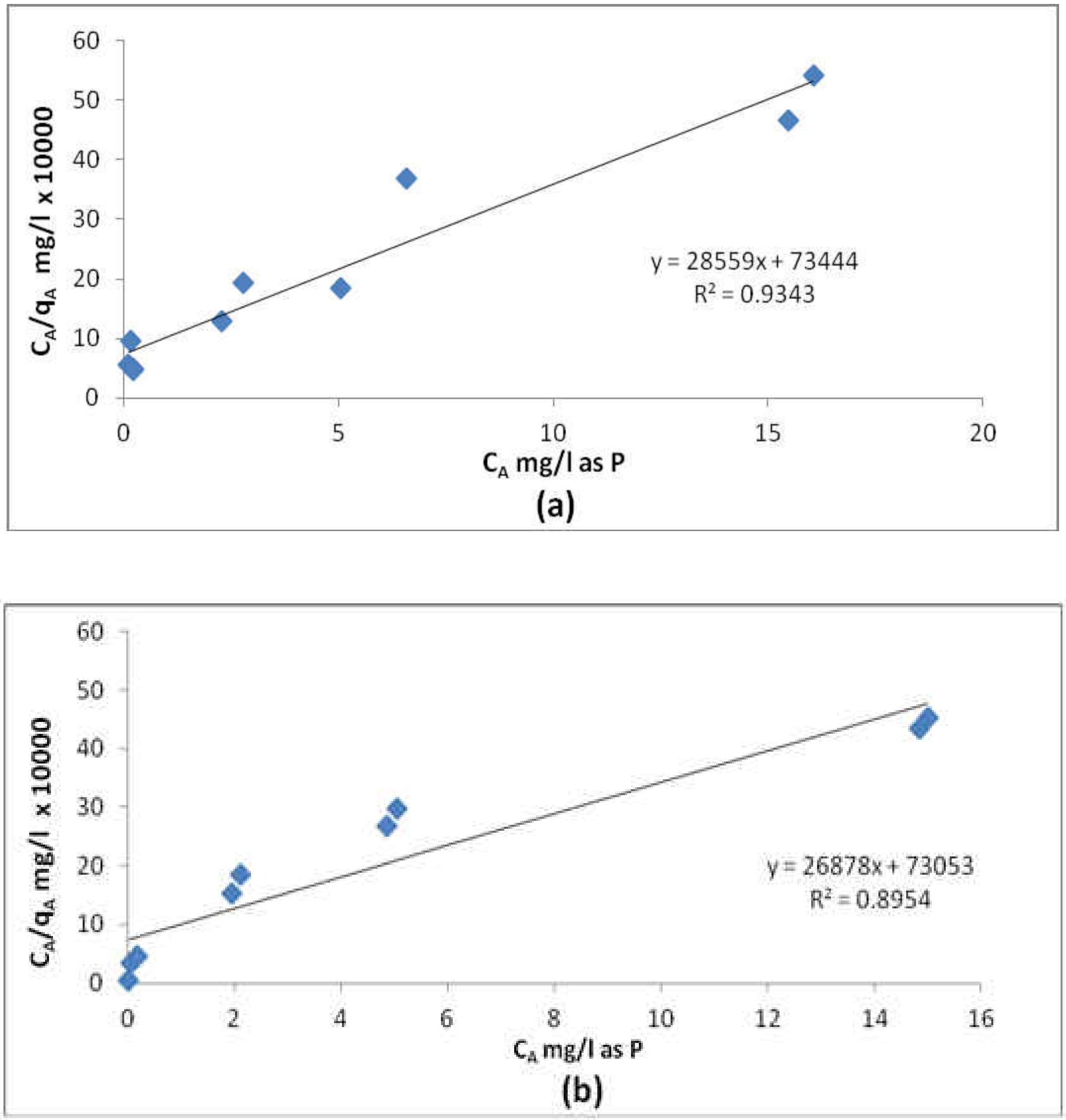


Figure 14 (a) SRP the Langmuir Isotherm run 24 hr-1, (b) SRP the Langmuir Isotherm run 24hr-2

Table 6 the Langmuir isotherm linear equation parameters run 24-1 and 24-2

	(24-1) Langmuir	(24-2) Langmuir	Average
slope	2.86E+04	2.69E+04	2.77E+04
Q_m mg/mg	3.501E-05	3.720E-05	3.611E-05
intercept	7.34E+04	7.31E+04	7.32E+04
b_A L/mg	0.389	0.368	0.378

Figure 15 and Table 7show the Freundlich isotherm graphs and the corresponding constants for the two 24 hour isotherm experiments. The adsorption capacity parameter (K_a) is almost the same for both runs with only a 10 percent difference. The R^2 values from the linear regression indicate a proper fit for the data. The results of R^2 with respect to the Freundlich model are 0.929, and 0.957 for 24-1 and 24-2 respectively.

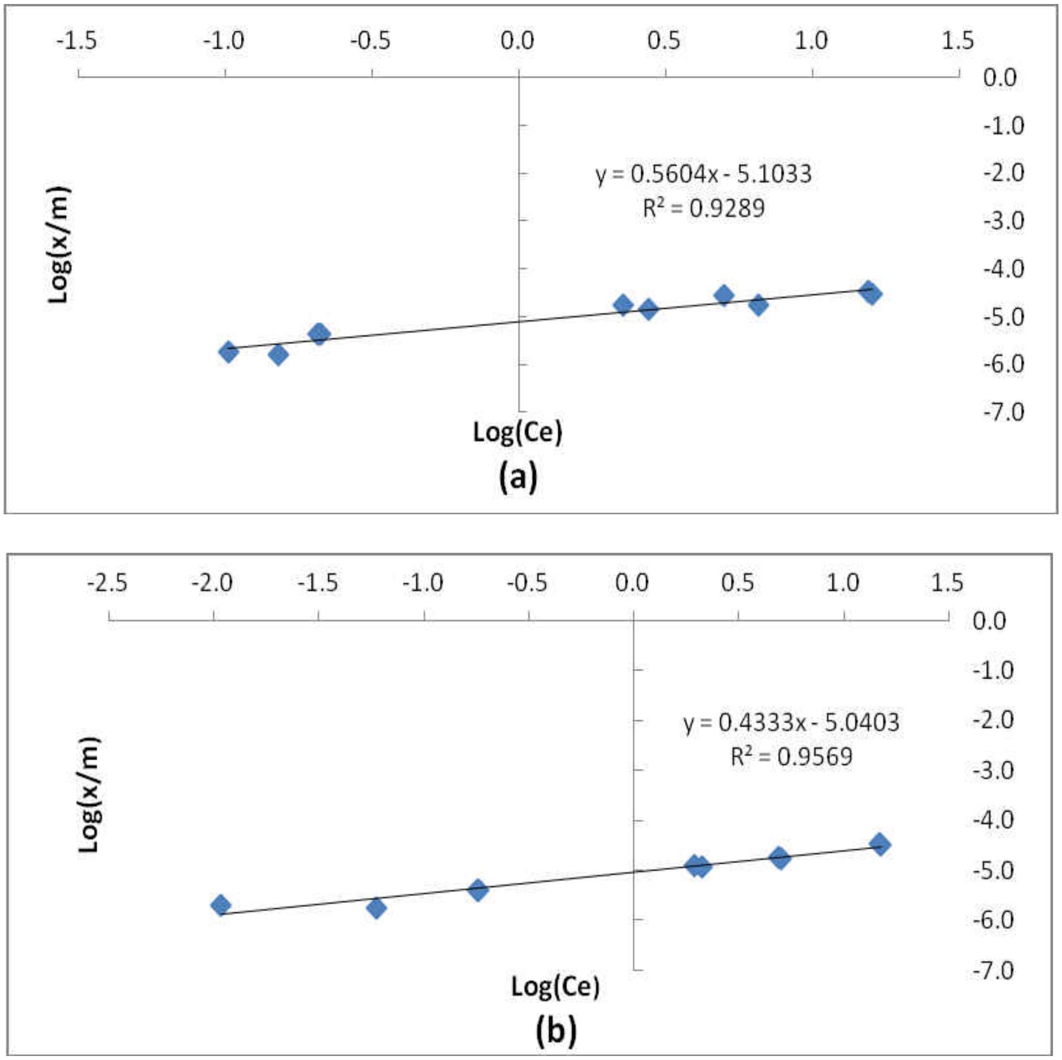


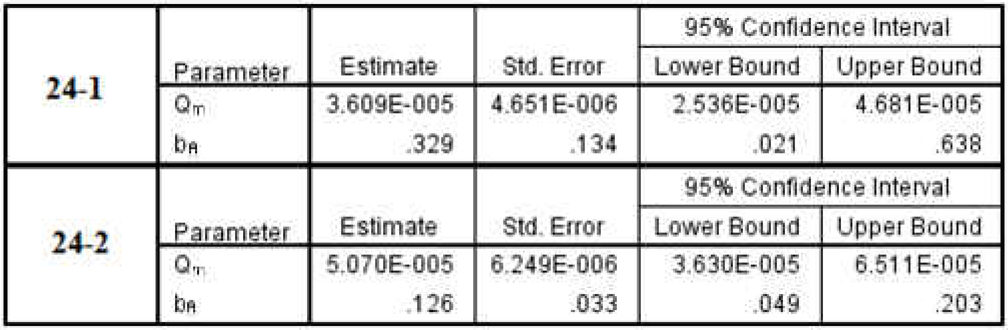
Figure 15 (a) SRP the Freundlich Isotherm run 24hr-1, (b) SRP the Freundlich Isotherm run 24hr-2

Table 7 The Freundlich isotherm equation parameters run 24-1 and 24-2

	(24-1) Freundlich	*(24-2) Freundlich*	Average
slope 1/n	0.560	0.433	0.497
n	1.784	2.308	2.046
intercept	-5.103	-5.040	-5.072
K_a *mg/mg*	7.883E-06	9.114E-06	8.498E-06

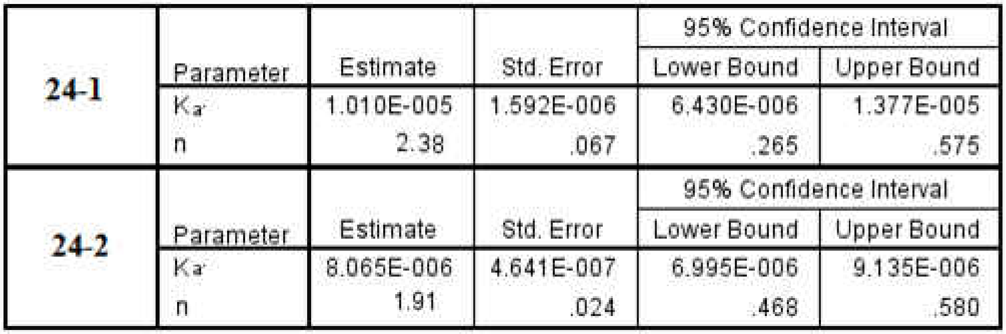
In addition, non-linear regression was used generating different values for the parameters in 24-1 and 24-2. The R^2 values from the non-linear regression indicate a proper fit for the data. The results of R^2 with respect to the Langmuir model are 0.923, and 0.970 for 24-1 and 24-2 respectively. The results of R^2 with respect to the Freundlich model are 0.916, and 0.993 for 24-1 and 24-2 respectively. Table 8 show Qm and b_A parameter estimation for both runs. Likewise, the Freundlich Ka and 1/n parameters estimation are summarized in Table 9. Furthermore, the $R_{L.1}$ was estimated for 24-1 to be 0.115 and for 24-2 to be 0.117. Both values of $R_{L.1}$ fall between 0 and 1 confirming that SRP isotherm with Bold&Gold media is a favorable adsorption process. Both models (the Freundlich and the Langmuir) are suitable for both 24-hr runs (24-1 and 24-2). However, the Langmuir model parameter values are closer to the same values for the 2 tests compared to the Freundlich parameter values. This may imply that the Langmuir model fits the data better than the Freundlich model, but both do an acceptable job.

Table 8 The Langmuir parameter estimation from the non-linear regression for 24-1 and 24-2



				95% Confidence Interval	
	Parameter	Estimate	Std. Error	Lower Bound	Upper Bound
24-1	Q_m	3.609E-005	4.651E-006	2.536E-005	4.681E-005
	b_A	.329	.134	.021	.638
				95% Confidence Interval	
	Parameter	Estimate	Std. Error	Lower Bound	Upper Bound
24-2	Q_m	5.070E-005	6.249E-006	3.630E-005	6.511E-005
	b_A	.126	.033	.049	.203

Table 9 The Freundlich parameter estimation from the non-linear regression for 24-1 and 24-2



				95% Confidence Interval	
	Parameter	Estimate	Std. Error	Lower Bound	Upper Bound
24-1	$K_{a'}$	1.010E-005	1.592E-006	6.430E-006	1.377E-005
	n	2.38	.067	.265	.575
				95% Confidence Interval	
	Parameter	Estimate	Std. Error	Lower Bound	Upper Bound
24-2	$K_{a'}$	8.065E-006	4.641E-007	6.995E-006	9.135E-006
	n	1.91	.024	.468	.580

In Figure 16 and Figure 17 the q_A is shown versus the equilibrium concentration of SRP. The curvilinear relationship is consistent with either the Langmuir or the Freundlich models rather than linear adsorption. Data at higher equilibrium concentrations would need to be obtained to determine whether q_A would reach a maximum value (the Langmuir model) or remain curvilinear (the Freundlich model).

However this would be in a concentration range not representative of stormwater so no such experiment was conducted. Either model works for the concentration range of interest. Table 10 compares the average linear and non-linear results for Langmuir and the Freundlich parameter.

Table 10 Comparison between linear and non-linear results for Langmuir and the Freundlich parameter

Langmuir	Q_m mg/mg Avg.	b_A L/mg		**Freundlich**	K_a mg/mg Avg.	n
Linear	3.61E-05	0.378		Linear	8.50E-06	2.014
non-linear	4.35E-05	0.228		non-linear	9.08E-06	2.119

Figure 16, the values of q_A and C_e were estimated using the linear and non-linear regression constants obtained by the isotherm analysis and then plotted along with the observed q_A and C_e values for the Langmuir equation. In Figure 16 the parameters obtained in the liner regression deviate from the non-linear regression values when the equilibrium SRP concentration exceeds 8 mg/l as P. In Figure 17, when the same analysis was performed using the Freundlich equation parameters the linear and non-linear regression values were virtually identical.

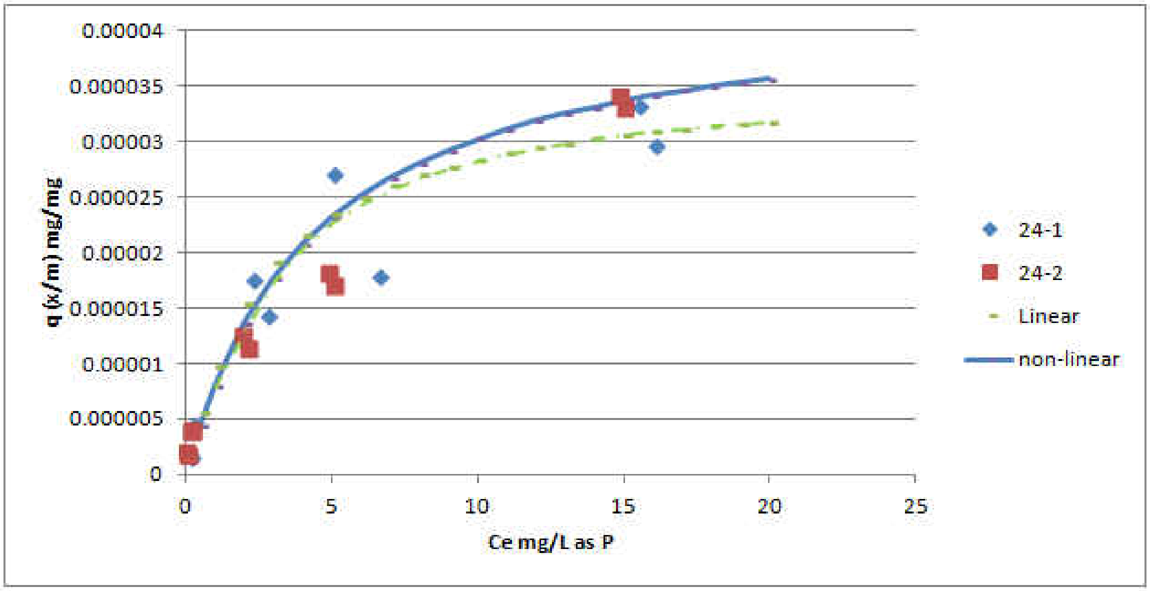


Figure 16 qA (mg/mg) versus equilibrium SRP concentration for the 24-hr tests and the lines of linear and non-linear regression estimated values using the Langmuir model

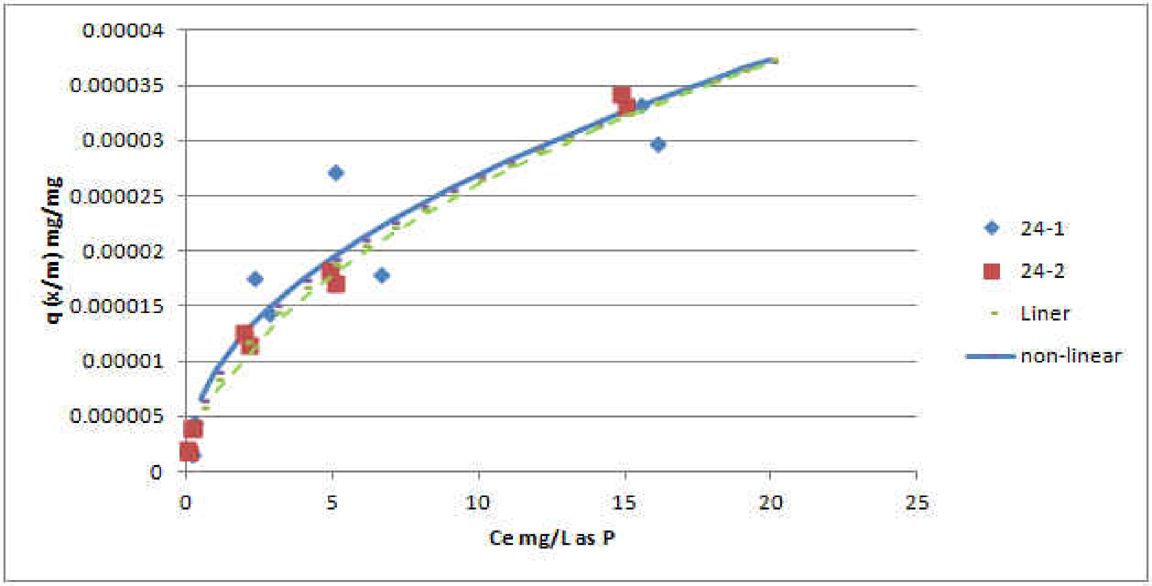


Figure 17 q_A (mg/mg) versus equilibrium SRP concentration for the 24-hr tests and the lines of linear and non-linear regression estimated values using the Freundlich model

This isotherm study was conducted for stormwater treatment purposes, and a low range SRP concentration (from 0.5 to 20 mg/l as P) was adapted to represent stormwater runoff concentrations. Adsorption isotherm experiments can be more reliable when sufficiently high SRP concentrations are tested compared to low concentrations. This can be for two reasons. First, adsorption process usually cannot be distinguished from precipitation process at low concentrations (from 0 to 50 mg/L). Precipitation can be inferred at sufficiently high SRP concentration (Ma et al., 2011). Second, the Langmuir and the Freundlich models behave similarly at low SRP concentrations. This cause uncertainty when the model with the best fit for the data is to be chosen. Data at higher equilibrium concentrations would be needed to determine whether q_A would reach a maximum value (the Langmuir model) or remain curvilinear (the Freundlich model).

Column test

Two duplicate columns were used to determine the removal efficiency of SRP and TP using Bold&Gold™ media. However, the effect of cementation on the flow rate is not addressed in this research. The columns were sampled for SRP, TP, pH, temperature and dissolved oxygen (DO) for three-2 hour and one-24 hour simulated storm events per week for seven months. pH and temperature were in a range of 7-8 and 21-23 °C respectively throughout the experiments. Average DO in the influent was 5.4 mg/L and in the effluent was 1.88 mg/L (low DO impact was out of the scope for this study). For SRP, The average influent concentration was 0.183 mg/L as P and the average effluent concentration was 0.071 mg/L as P. The removal efficiency of SRP was 60%. Bold&Gold™ media had less efficiency removing TP, at 44%. The average influent and effluent TP concentration for both columns were 0.232 mg/L as P and 0.134 mg/L as P respectively. From the column data, the highest q_A (x/m) observed at the end of the study was 8.84 X 10^{-5} mg/mg which already is significantly higher than the Q_M estimate obtained by extrapolating the Langmuir isotherm ($4.3x10^{-5}$ mg/mg from non-linear regression). In addition, no sign of column breakthrough with respect to phosphorus was observed even by running the column for about seven months which means 8.84 x 10^{-5} mg/mg simply sets a lower boundary for the maximum adsorption capacity. Moreover, the observed removal efficiency from both the batch isotherm test at equilibrium and the bench-scale upflow column were almost similar, 60% and 55% respectively.

Media Requirement For a Two Year Design Life

The isotherm data analyzed using the Langmuir isotherm indicates a Q_M of 3.6 x 10^{-5} to 5.1X 10^{-5} mg/mg. However, since the isotherm experiments were not conducted for equilibrium phosphorus concentrations above 16.1 mg/L this estimate is based on an extrapolation which assumes an almost perfect fit of the data with the Langmuir model. The constants derived describe the data remarkably well for equilibrium concentrations of 16.1 mg/L as P, but above that level it is only possible to extrapolate. The Freundlich model does not incorporate an estimate of maximum sorption capacity and can yield no information in this respect, and since it is based on the same data set it also depends on extrapolation above 16.1 mg/L as P. It is known that BAM is capable of more than 8.84 x 10^{-5} mg/mg (observed at the end of the columns test) of adsorption, but it is not known from this study how much more. Previous design experience with BAM medias indicates that 50.0 x 10^{-5} mg/mg (i.e. 0.5 mg/gram media) is a reasonable estimate of their sorption capacity with respect to phosphorus (Martin P. Wanielista et al., 2014). For SRP, observed P removals are on the order of 0.1 mg/L as P in the column study, and this also fits well with prior experience in the field with BAM. If the stormwater BAM unit receives about 6 acre-feet of runoff, and the goal is a lifespan of 2 years (i.e. a replacement time of 2 years), then there would be 7.4 million liters of stormwater treated in that time period, implying 740,000 (mg) of SRP to be removed. If the design sorption capacity of 0.5 mg/gram media is accepted then 1,480 kg (3,263 lbs) of media are needed, which at a density of 33 lbs/CF means 99 ft^3 of media would be required for a 2 year period. Using the observed q_A from the column study as though it were a maximum (which it is not) this value would increase the media requirements to 559 ft^3. The corresponding hydraulic loads would be 3.70 ft^3/ft^3*day for a maximum P sorption of 0.5 mg/gram, and 0.654 ft^3/ft^3*day for 0.0884 mg/gram. However since breakthrough was never observed a 2 year lifespan would require significantly less than 559 ft^3 of media for treatment of 6 acre-feet of runoff, and the amount might plausibly be expected to be closer to 99 ft^3 of media.

Conclusions

The media studied removed 60% of the SRP and 44% of the TP. Adsorption for the media was successfully modeled for the concentration range of interest (0.5 to 16 mg/l as P) by both the Langmuir and the Freundlich isotherms at 21-23 °C. Volume requirements of media treating 6 acre-feet of stormwater runoff for a two year design life with respect to phosphorus removal were shown to be lower than 559 ft^3 of BAM and not inconsistent with an estimated requirement of approximately 99 ft^3.

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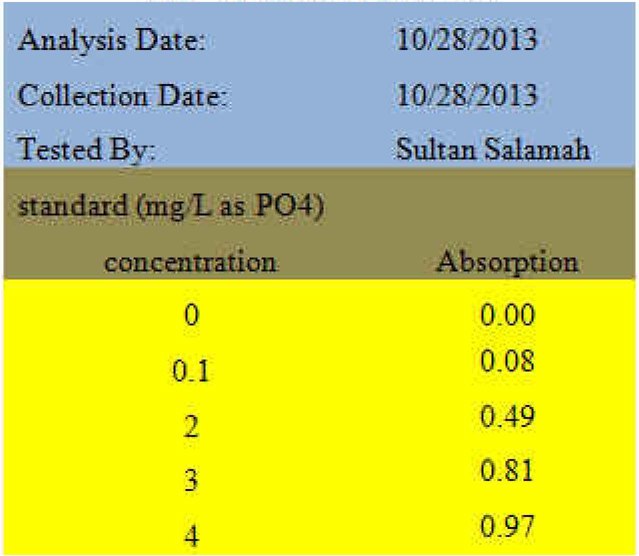
CHAPTER FIVE: CONCLUSIONS AND RECOMMENATIONS

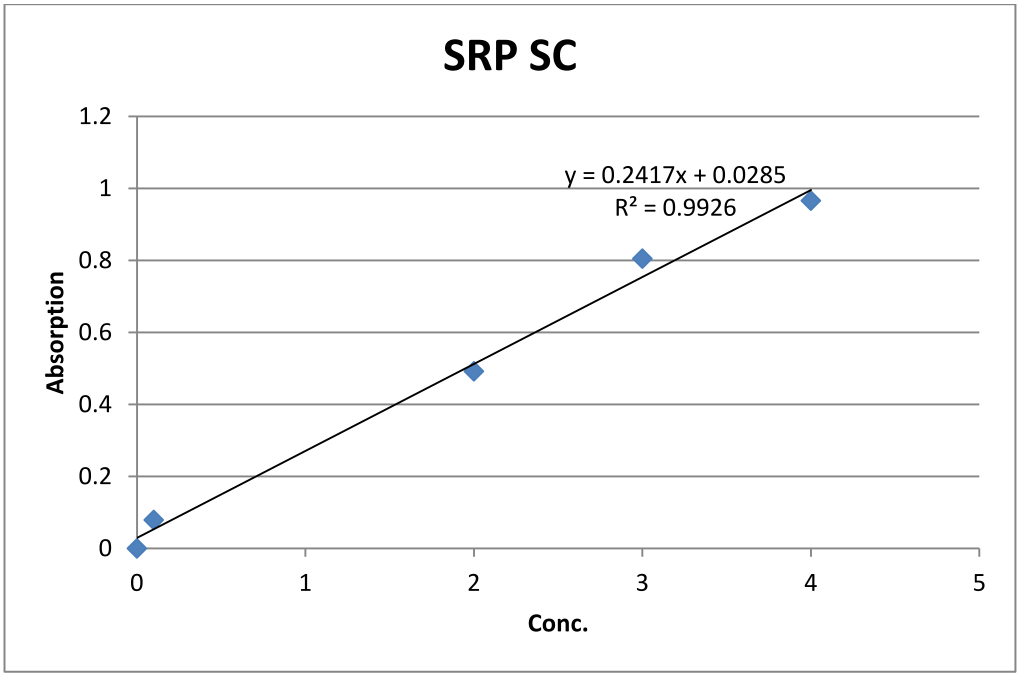
The data presented in this study, evaluates a functionalized sorption media (BAM) for phosphorus removal. The media were studied using bench-scale upflow column and SRP adsorption isotherms. The media studied using columns removed 60% of the SRP and 44% of the TP. Adsorption for the media was successfully modeled for the concentration range of interest (0.5 to 16 mg/l as P) by both the Langmuir and the Freundlich isotherms. Volume requirements of media treating 6 acre-feet of stormwater runoff for a two year design life with respect to phosphorus removal were shown to be lower than 559 ft^3 of BAM and estimated to be approximately 99 ft^3.

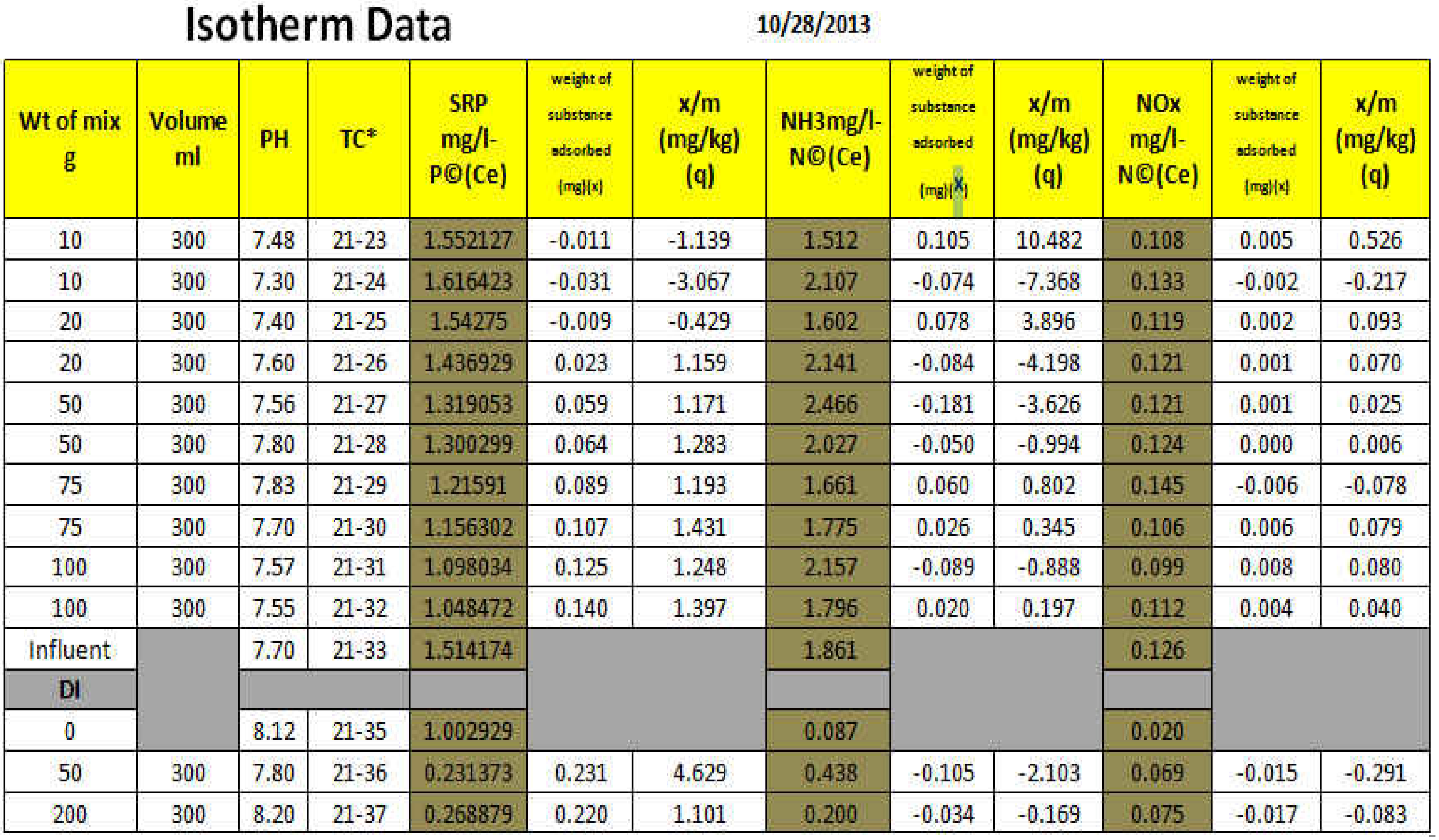
APPENDIX A:
ISOTHERM DATA

SRP Standard Curve (SC)



Analysis Date:	10/28/2013
Collection Date:	10/28/2013
Tested By:	Sultan Salamah
standard (mg/L as PO4)	
concentration	Absorption
0	0.00
0.1	0.08
2	0.49
3	0.81
4	0.97

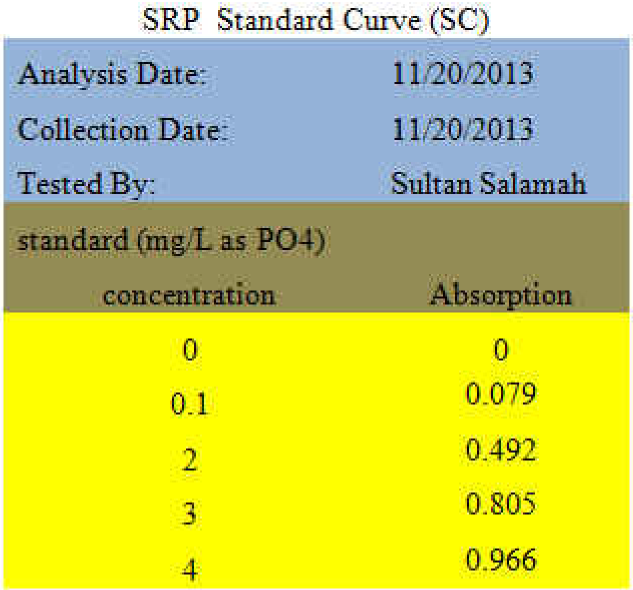




Isotherm Data

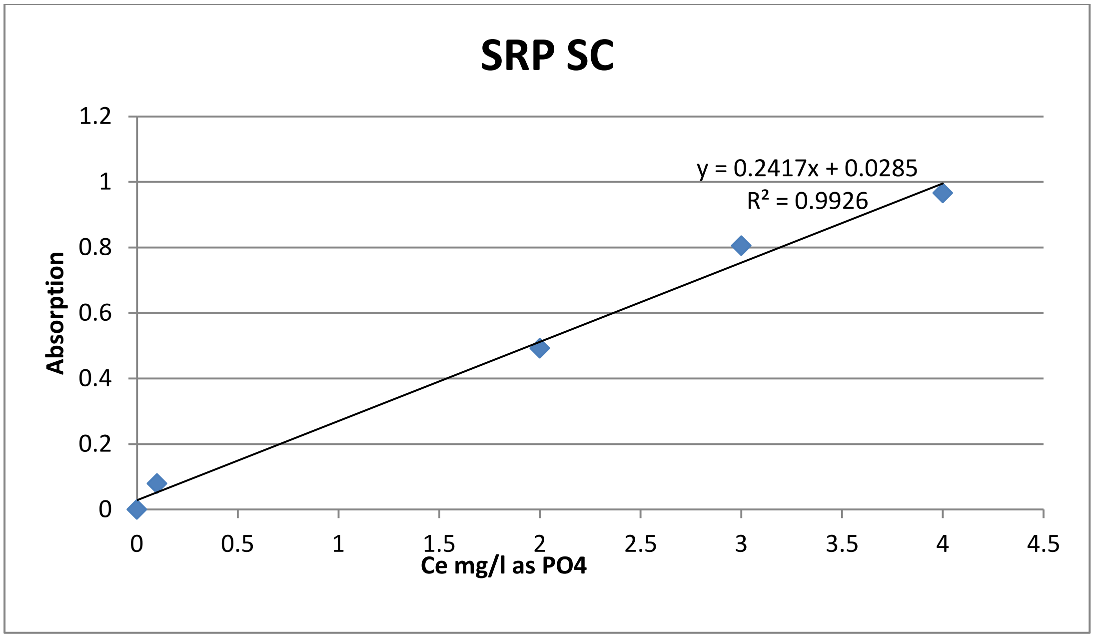
10/28/2013

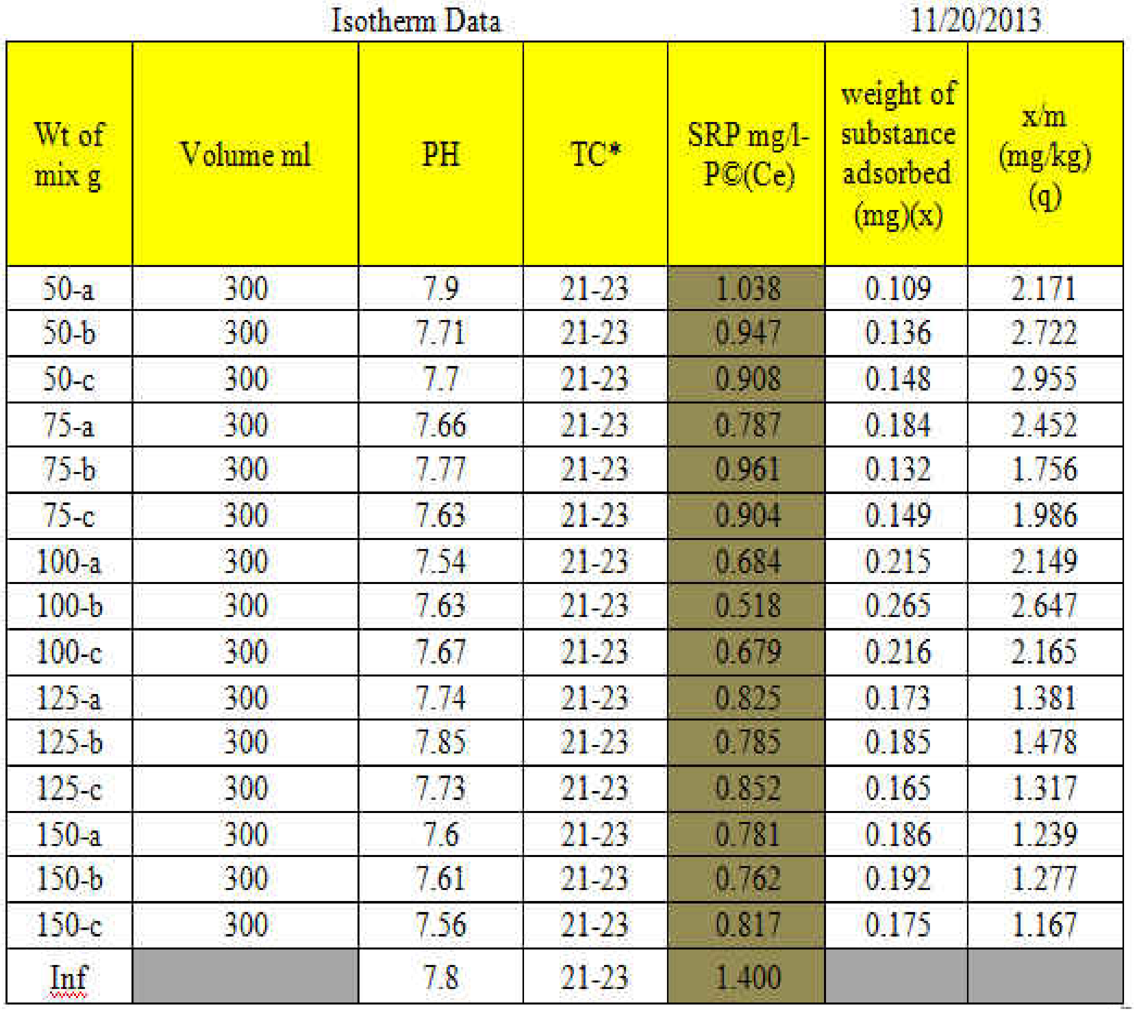
Wt of mix g	Volume ml	PH	TC*	SRP mg/l-P©(Ce)	weight of substance adsorbed (mg)(x)	x/m (mg/kg) (q)	NH3mg/l-N©(Ce)	weight of substance adsorbed (mg)(x)	x/m (mg/kg) (q)	NOx mg/l-N©(Ce)	weight of substance adsorbed (mg)(x)	x/m (mg/kg) (q)
10	300	7.48	21-23	1.552127	-0.011	-1.139	1.512	0.105	10.482	0.108	0.005	0.526
10	300	7.30	21-24	1.616423	-0.031	-3.067	2.107	-0.074	-7.368	0.133	-0.002	-0.217
20	300	7.40	21-25	1.54275	-0.009	-0.429	1.602	0.078	3.896	0.119	0.002	0.093
20	300	7.60	21-26	1.436929	0.023	1.159	2.141	-0.084	-4.198	0.121	0.001	0.070
50	300	7.56	21-27	1.319053	0.059	1.171	2.466	-0.181	-3.626	0.121	0.001	0.025
50	300	7.80	21-28	1.300299	0.064	1.283	2.027	-0.050	-0.994	0.124	0.000	0.006
75	300	7.83	21-29	1.21591	0.089	1.193	1.661	0.060	0.802	0.145	-0.006	-0.078
75	300	7.70	21-30	1.156302	0.107	1.431	1.775	0.026	0.345	0.106	0.006	0.079
100	300	7.57	21-31	1.098034	0.125	1.248	2.157	-0.089	-0.888	0.099	0.008	0.080
100	300	7.55	21-32	1.048472	0.140	1.397	1.796	0.020	0.197	0.112	0.004	0.040
Influent		7.70	21-33	1.514174			1.861			0.126		
DI												
0		8.12	21-35	1.002929			0.087			0.020		
50	300	7.80	21-36	0.231373	0.231	4.629	0.438	-0.105	-2.103	0.069	-0.015	-0.291
200	300	8.20	21-37	0.268879	0.220	1.101	0.200	-0.034	-0.169	0.075	-0.017	-0.083



SRP Standard Curve (SC)

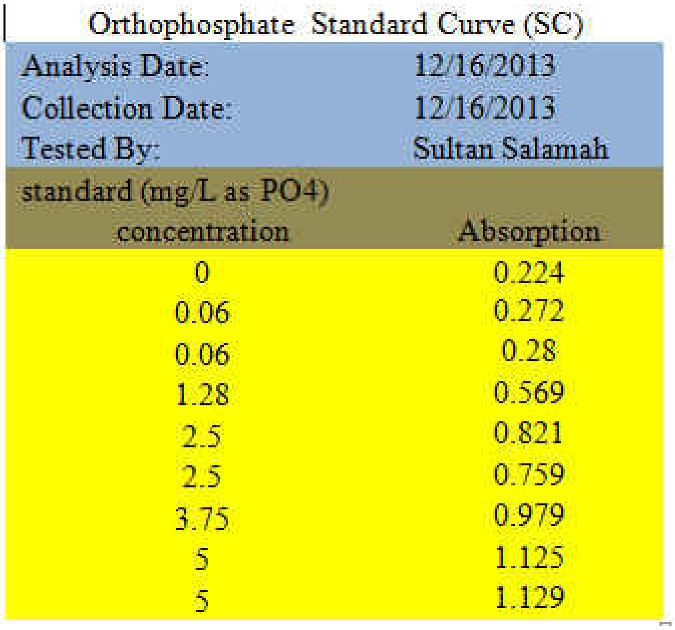
Analysis Date:	11/20/2013
Collection Date:	11/20/2013
Tested By:	Sultan Salamah
standard (mg/L as PO4)	
concentration	Absorption
0	0
0.1	0.079
2	0.492
3	0.805
4	0.966





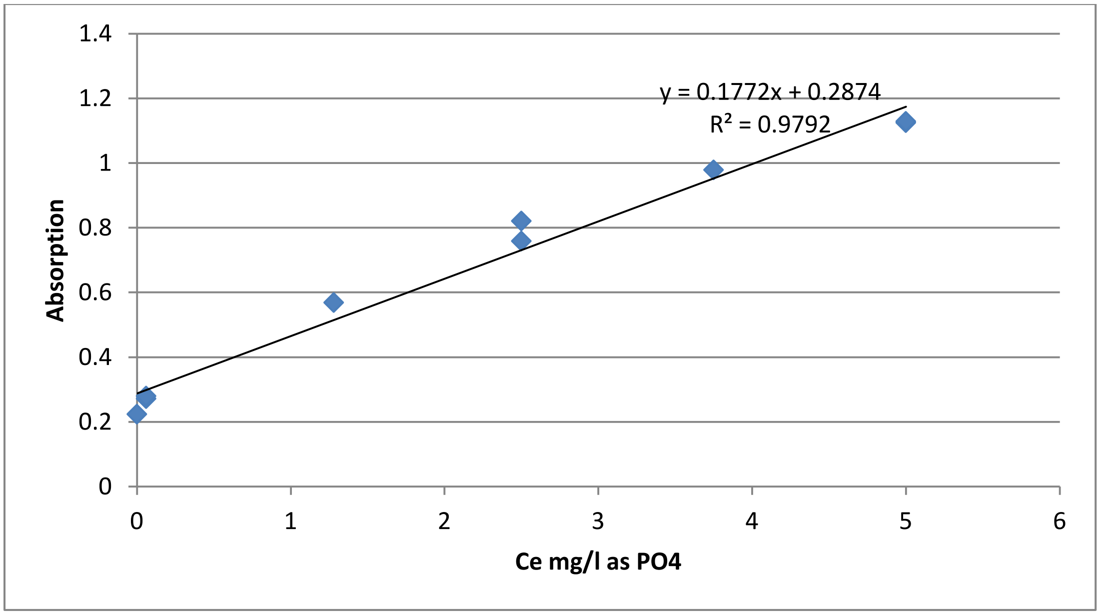
Isotherm Data 11/20/2013

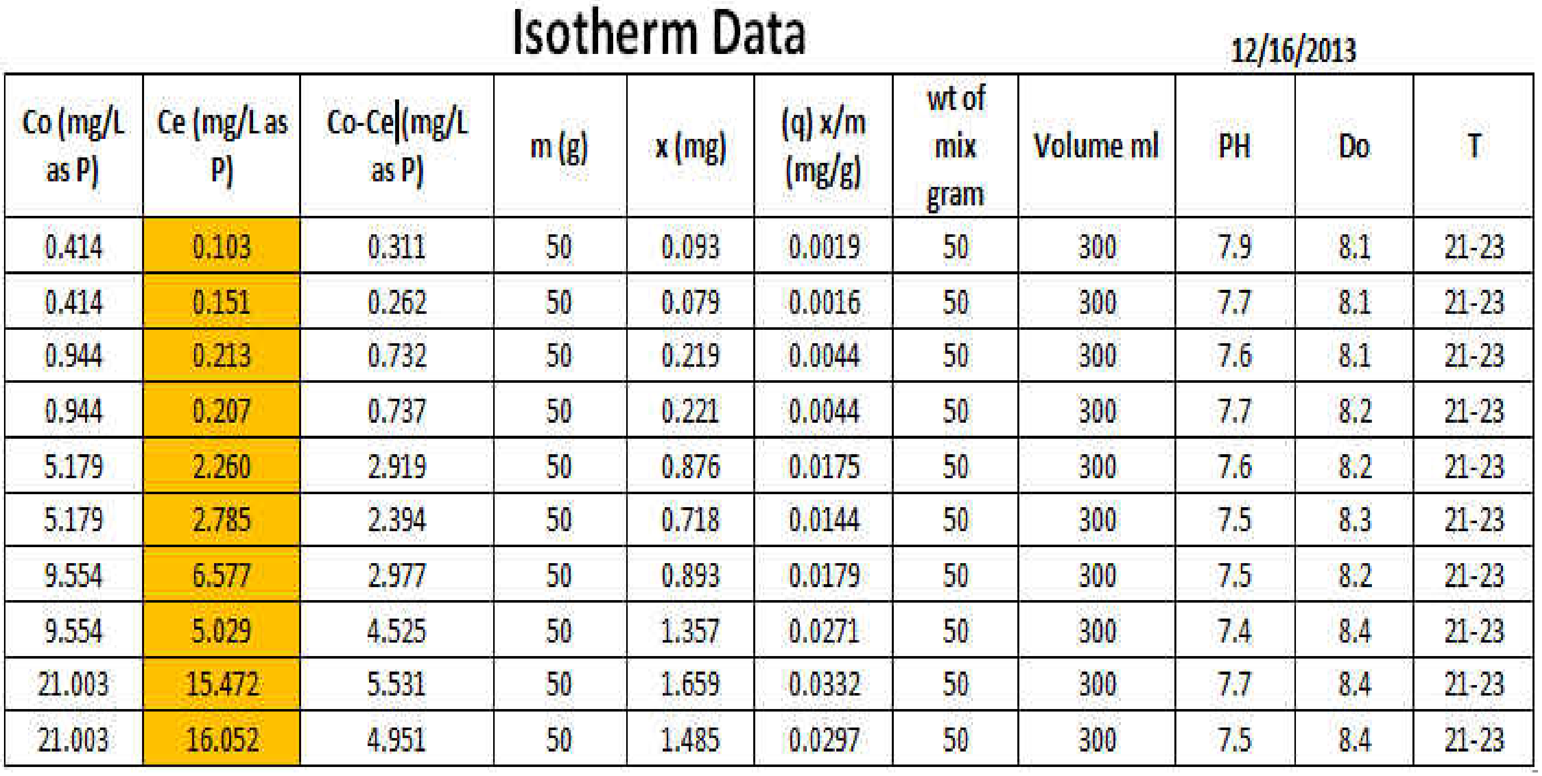
Wt of mix g	Volume ml	PH	TC*	SRP mg/l-P©(Ce)	weight of substance adsorbed (mg)(x)	x/m (mg/kg) (q)
50-a	300	7.9	21-23	1.038	0.109	2.171
50-b	300	7.71	21-23	0.947	0.136	2.722
50-c	300	7.7	21-23	0.908	0.148	2.955
75-a	300	7.66	21-23	0.787	0.184	2.452
75-b	300	7.77	21-23	0.961	0.132	1.756
75-c	300	7.63	21-23	0.904	0.149	1.986
100-a	300	7.54	21-23	0.684	0.215	2.149
100-b	300	7.63	21-23	0.518	0.265	2.647
100-c	300	7.67	21-23	0.679	0.216	2.165
125-a	300	7.74	21-23	0.825	0.173	1.381
125-b	300	7.85	21-23	0.785	0.185	1.478
125-c	300	7.73	21-23	0.852	0.165	1.317
150-a	300	7.6	21-23	0.781	0.186	1.239
150-b	300	7.61	21-23	0.762	0.192	1.277
150-c	300	7.56	21-23	0.817	0.175	1.167
Inf		7.8	21-23	1.400		



Orthophosphate Standard Curve (SC)

Analysis Date:	12/16/2013
Collection Date:	12/16/2013
Tested By:	Sultan Salamah
standard (mg/L as PO4) concentration	Absorption
0	0.224
0.06	0.272
0.06	0.28
1.28	0.569
2.5	0.821
2.5	0.759
3.75	0.979
5	1.125
5	1.129

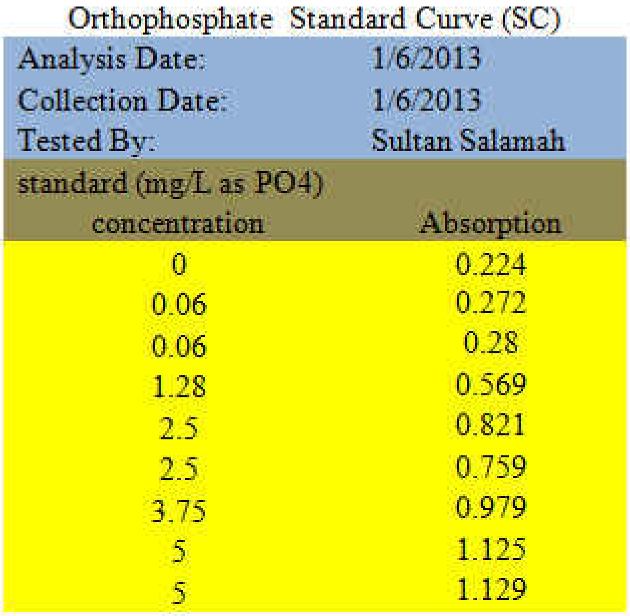




Isotherm Data

12/16/2013

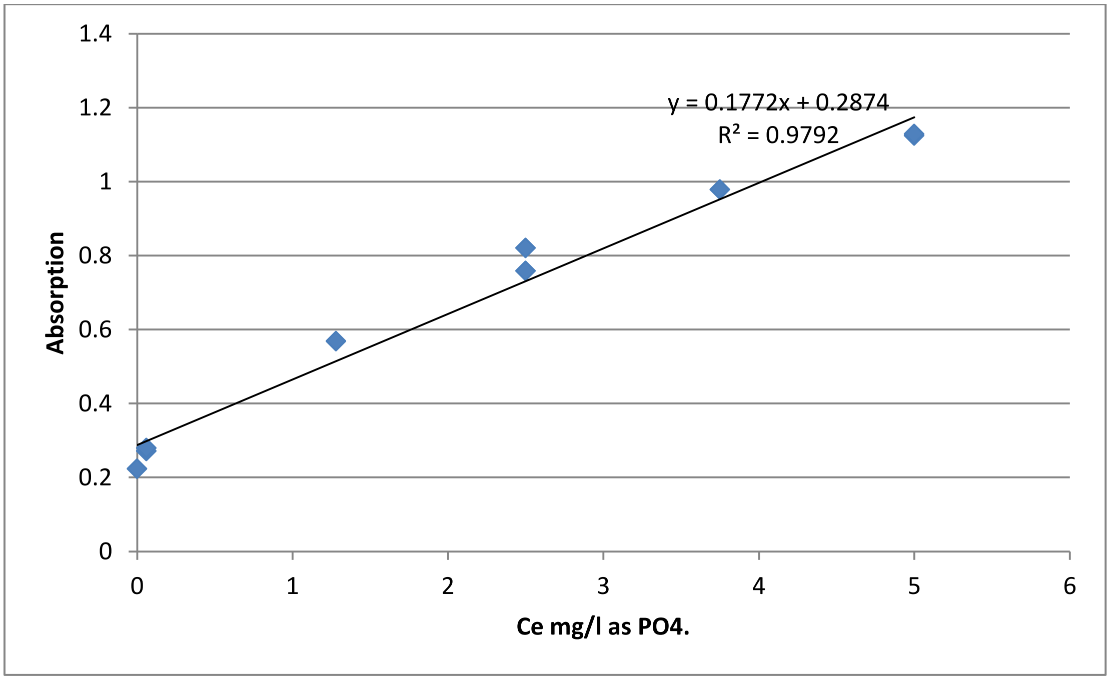
Co (mg/L as P)	Ce (mg/L as P)	Co-Ce (mg/L as P)	m (g)	x (mg)	(q) x/m (mg/g)	wt of mix gram	Volume ml	PH	Do	T
0.414	0.103	0.311	50	0.093	0.0019	50	300	7.9	8.1	21-23
0.414	0.151	0.262	50	0.079	0.0016	50	300	7.7	8.1	21-23
0.944	0.213	0.732	50	0.219	0.0044	50	300	7.6	8.1	21-23
0.944	0.207	0.737	50	0.221	0.0044	50	300	7.7	8.2	21-23
5.179	2.260	2.919	50	0.876	0.0175	50	300	7.6	8.2	21-23
5.179	2.785	2.394	50	0.718	0.0144	50	300	7.5	8.3	21-23
9.554	6.577	2.977	50	0.893	0.0179	50	300	7.5	8.2	21-23
9.554	5.029	4.525	50	1.357	0.0271	50	300	7.4	8.4	21-23
21.003	15.472	5.531	50	1.659	0.0332	50	300	7.7	8.4	21-23
21.003	16.052	4.951	50	1.485	0.0297	50	300	7.5	8.4	21-23

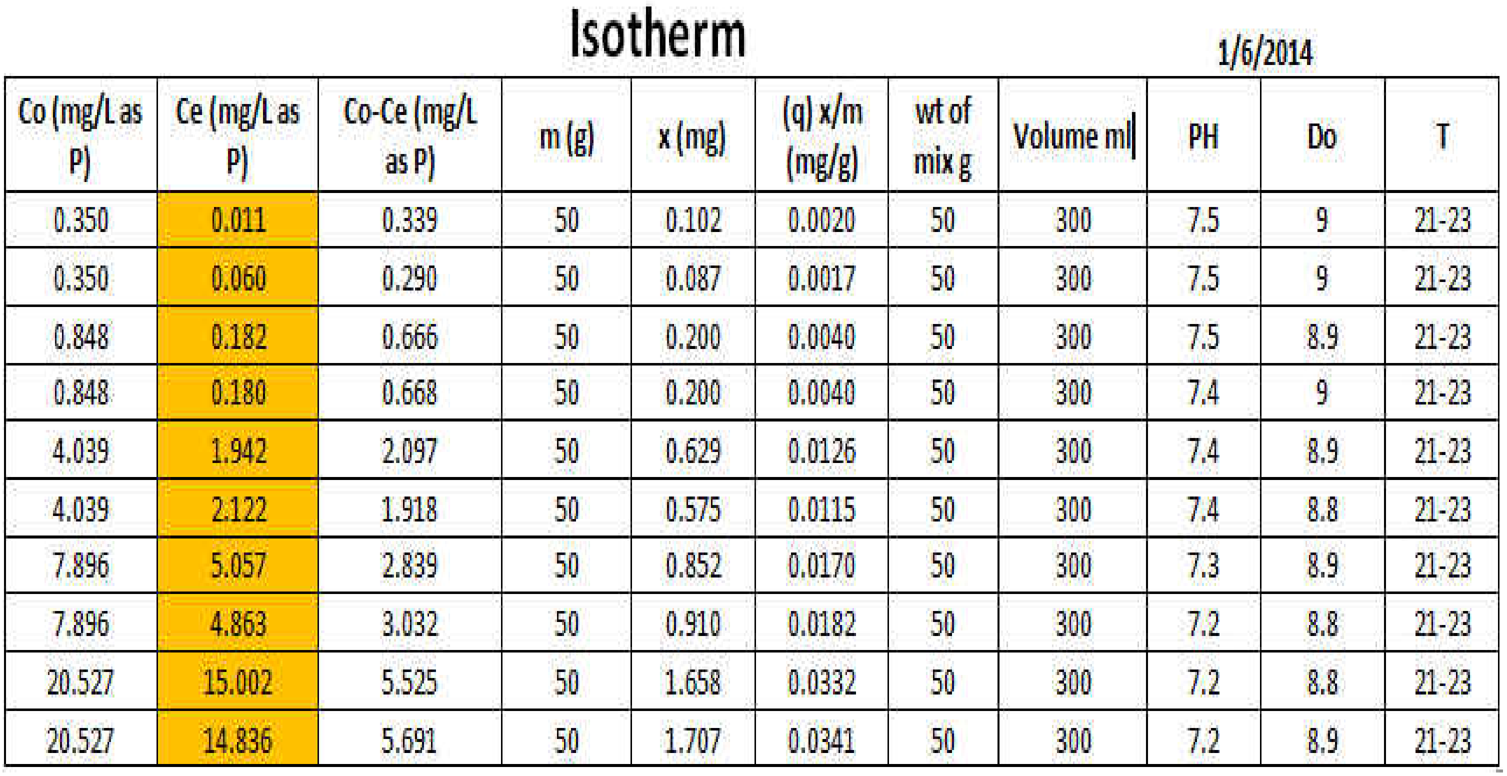


Orthophosphate Standard Curve (SC)

Analysis Date: 1/6/2013
Collection Date: 1/6/2013
Tested By: Sultan Salamah

standard (mg/L as PO4) concentration	Absorption
0	0.224
0.06	0.272
0.06	0.28
1.28	0.569
2.5	0.821
2.5	0.759
3.75	0.979
5	1.125
5	1.129





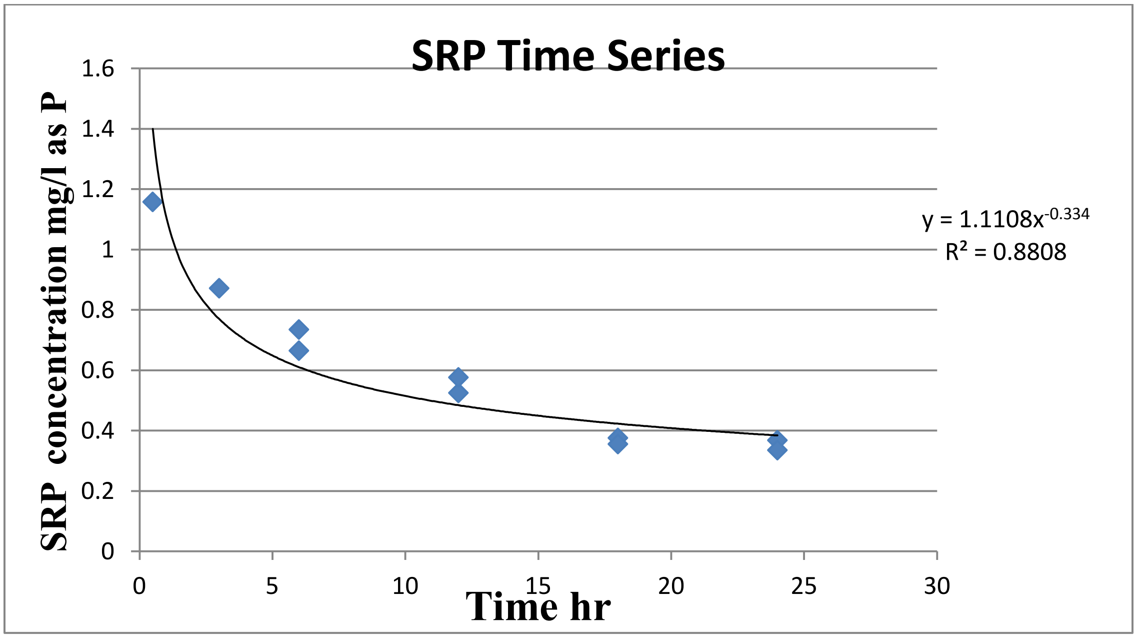
Isotherm

1/6/2014

Co (mg/L as P)	Ce (mg/L as P)	Co-Ce (mg/L as P)	m (g)	x (mg)	(q) x/m (mg/g)	wt of mix g	Volume ml	PH	Do	T
0.350	0.011	0.339	50	0.102	0.0020	50	300	7.5	9	21-23
0.350	0.060	0.290	50	0.087	0.0017	50	300	7.5	9	21-23
0.848	0.182	0.666	50	0.200	0.0040	50	300	7.5	8.9	21-23
0.848	0.180	0.668	50	0.200	0.0040	50	300	7.4	9	21-23
4.039	1.942	2.097	50	0.629	0.0126	50	300	7.4	8.9	21-23
4.039	2.122	1.918	50	0.575	0.0115	50	300	7.4	8.8	21-23
7.896	5.057	2.839	50	0.852	0.0170	50	300	7.3	8.9	21-23
7.896	4.863	3.032	50	0.910	0.0182	50	300	7.2	8.8	21-23
20.527	15.002	5.525	50	1.658	0.0332	50	300	7.2	8.8	21-23
20.527	14.836	5.691	50	1.707	0.0341	50	300	7.2	8.9	21-23

Time series (50g and 1 mg/l as P) in 300ml Spiked pond water

Time hr	SRP as Po4	SRP as P
0.5	3.552	1.159
3	2.675	0.872
6	2.255	0.736
6(Duplicate)	2.041	0.666
12	1.612	0.526
12(Duplicate)	1.769	0.577
18	1.154	0.376
18(Duplicate)	1.092	0.356
24	1.130	0.369
24(Duplicate)	1.030	0.336
Influent	3.352	1.093
Influent (Duplicate)	2.913	0.950



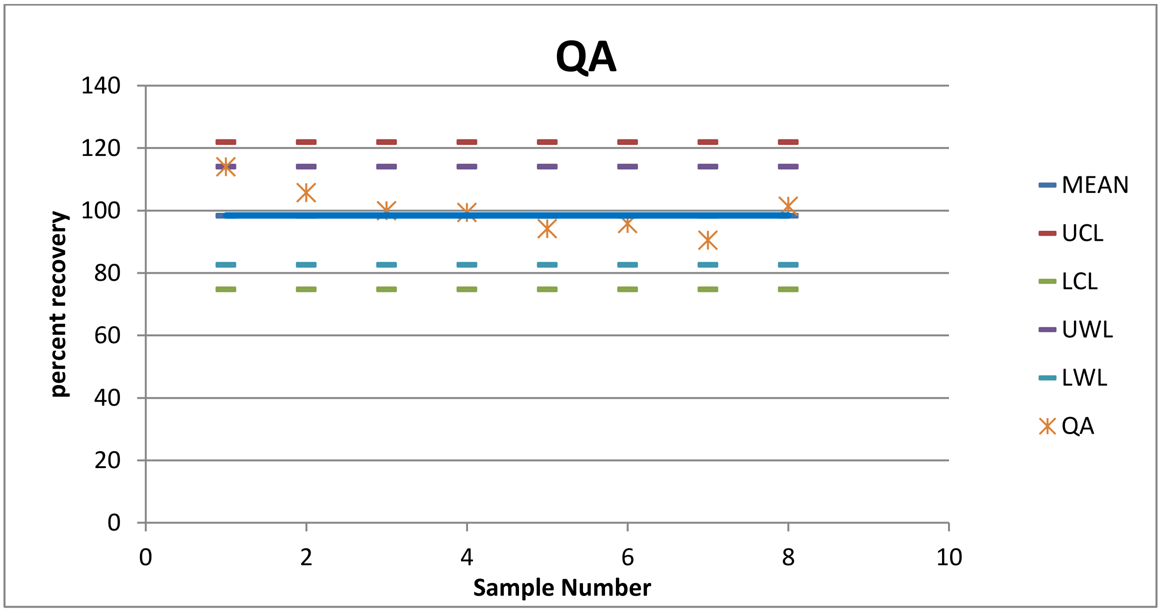
APPENDIX B:
QUALITY ASSURANCE AND QUALITY CONTROL (QA&QC)

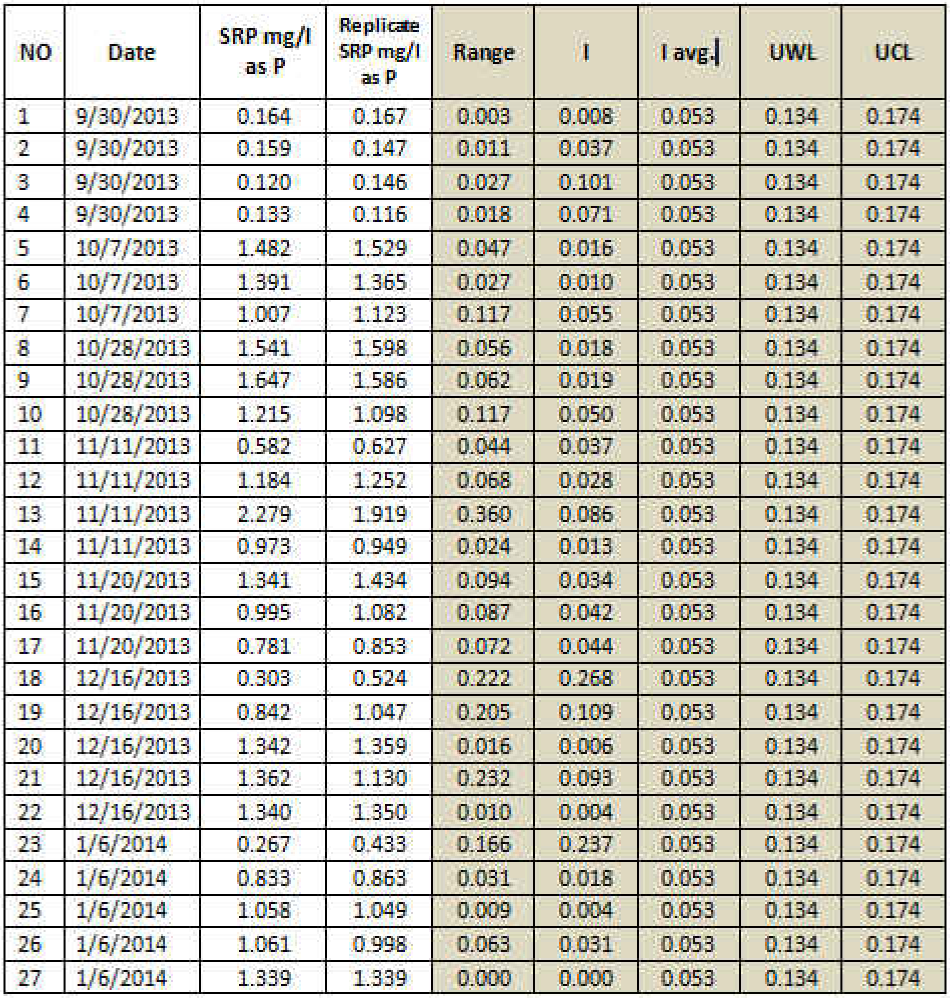
Quality Assurance - Accuracy

NO	DATE	spiked SRP mg/l as Po4	SRP mg/l as P	%	MEAN	STDEV	UCL	LCL	UWL	LWL
1	9/30/2013	3.139731	0.326793	91.4%	98.4	7.9	122	75	114	83
2	9/30/2013	2.737634	0.291569	91.0%	98.4	7.9	122	75	114	83
3	10/7/2013	6.475866	2.112041	96.5%	98.4	7.9	122	75	114	83
4	10/7/2013	6.78801	2.213843	99.6%	98.4	7.9	122	75	114	83
5	10/28/2013	6.976938	2.275461	112.5%	98.4	7.9	122	75	114	83
6	10/28/2013	2.812288	0.9172	99.4%	98.4	7.9	122	75	114	83

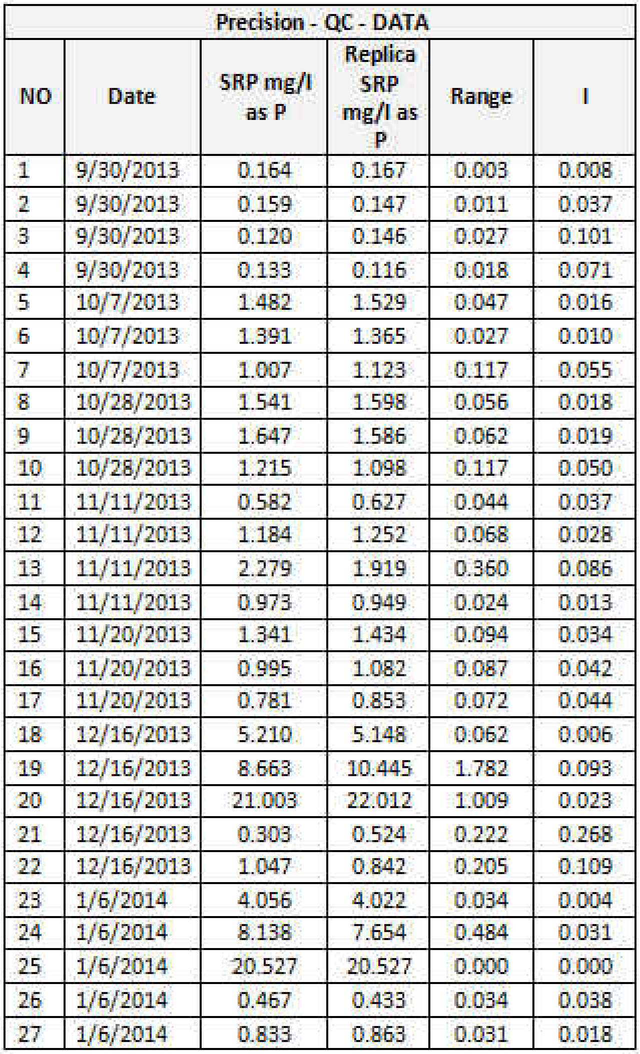
DATA

No	DATE	spiked SRP mg/l as Po4	SRP mg/l as P	%
1	11/11/2013	3.597	1.173	90.6%
2	11/11/2013	4.829	1.575	101.4%
3	11/20/2013	5.995	1.955	94.3%
4	11/20/2013	3.999	1.304	95.9%
5	12/16/2013	2.315	0.755	100.0%
6	12/16/2013	6.094	1.987	99.4%
7	1/6/2014	2.315	0.755	114.1%
8	1/6/2014	6.221	2.029	105.8%


QA
140
120
100
80
60
40
20
0
percent recovery
0
2
4
6
8
10
Sample Number
MEAN
UCL
LCL
UWL
LWL
QA

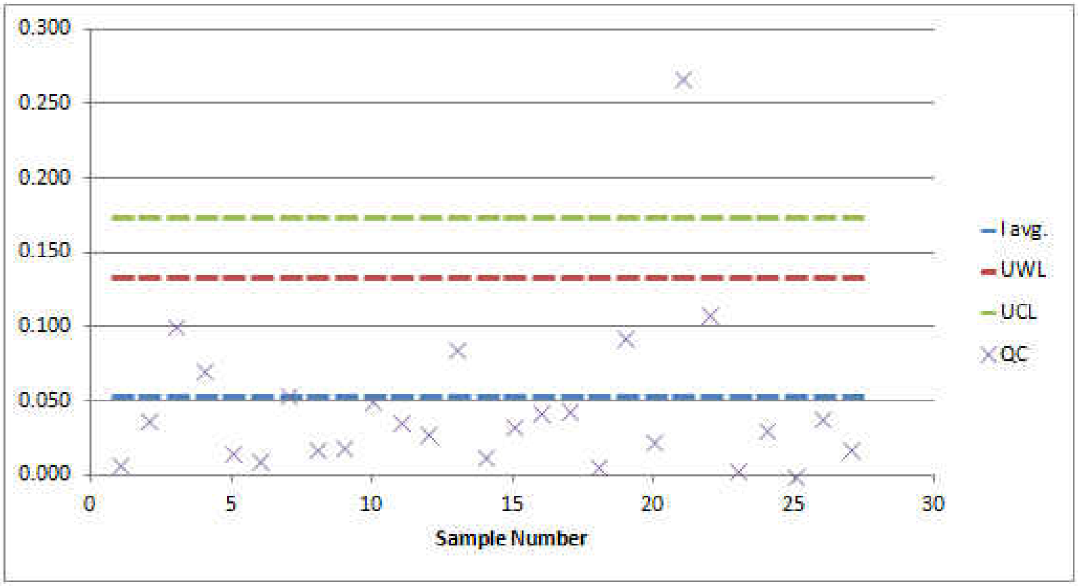


NO	Date	SRP mg/l as P	Replicate SRP mg/l as P	Range	I	I avg.	UWL	UCL
1	9/30/2013	0.164	0.167	0.003	0.008	0.053	0.134	0.174
2	9/30/2013	0.159	0.147	0.011	0.037	0.053	0.134	0.174
3	9/30/2013	0.120	0.146	0.027	0.101	0.053	0.134	0.174
4	9/30/2013	0.133	0.116	0.018	0.071	0.053	0.134	0.174
5	10/7/2013	1.482	1.529	0.047	0.016	0.053	0.134	0.174
6	10/7/2013	1.391	1.365	0.027	0.010	0.053	0.134	0.174
7	10/7/2013	1.007	1.123	0.117	0.055	0.053	0.134	0.174
8	10/28/2013	1.541	1.598	0.056	0.018	0.053	0.134	0.174
9	10/28/2013	1.647	1.586	0.062	0.019	0.053	0.134	0.174
10	10/28/2013	1.215	1.098	0.117	0.050	0.053	0.134	0.174
11	11/11/2013	0.582	0.627	0.044	0.037	0.053	0.134	0.174
12	11/11/2013	1.184	1.252	0.068	0.028	0.053	0.134	0.174
13	11/11/2013	2.279	1.919	0.360	0.086	0.053	0.134	0.174
14	11/11/2013	0.973	0.949	0.024	0.013	0.053	0.134	0.174
15	11/20/2013	1.341	1.434	0.094	0.034	0.053	0.134	0.174
16	11/20/2013	0.995	1.082	0.087	0.042	0.053	0.134	0.174
17	11/20/2013	0.781	0.853	0.072	0.044	0.053	0.134	0.174
18	12/16/2013	0.303	0.524	0.222	0.268	0.053	0.134	0.174
19	12/16/2013	0.842	1.047	0.205	0.109	0.053	0.134	0.174
20	12/16/2013	1.342	1.359	0.016	0.006	0.053	0.134	0.174
21	12/16/2013	1.362	1.130	0.232	0.093	0.053	0.134	0.174
22	12/16/2013	1.340	1.350	0.010	0.004	0.053	0.134	0.174
23	1/6/2014	0.267	0.433	0.166	0.237	0.053	0.134	0.174
24	1/6/2014	0.833	0.863	0.031	0.018	0.053	0.134	0.174
25	1/6/2014	1.058	1.049	0.009	0.004	0.053	0.134	0.174
26	1/6/2014	1.061	0.998	0.063	0.031	0.053	0.134	0.174
27	1/6/2014	1.339	1.339	0.000	0.000	0.053	0.134	0.174



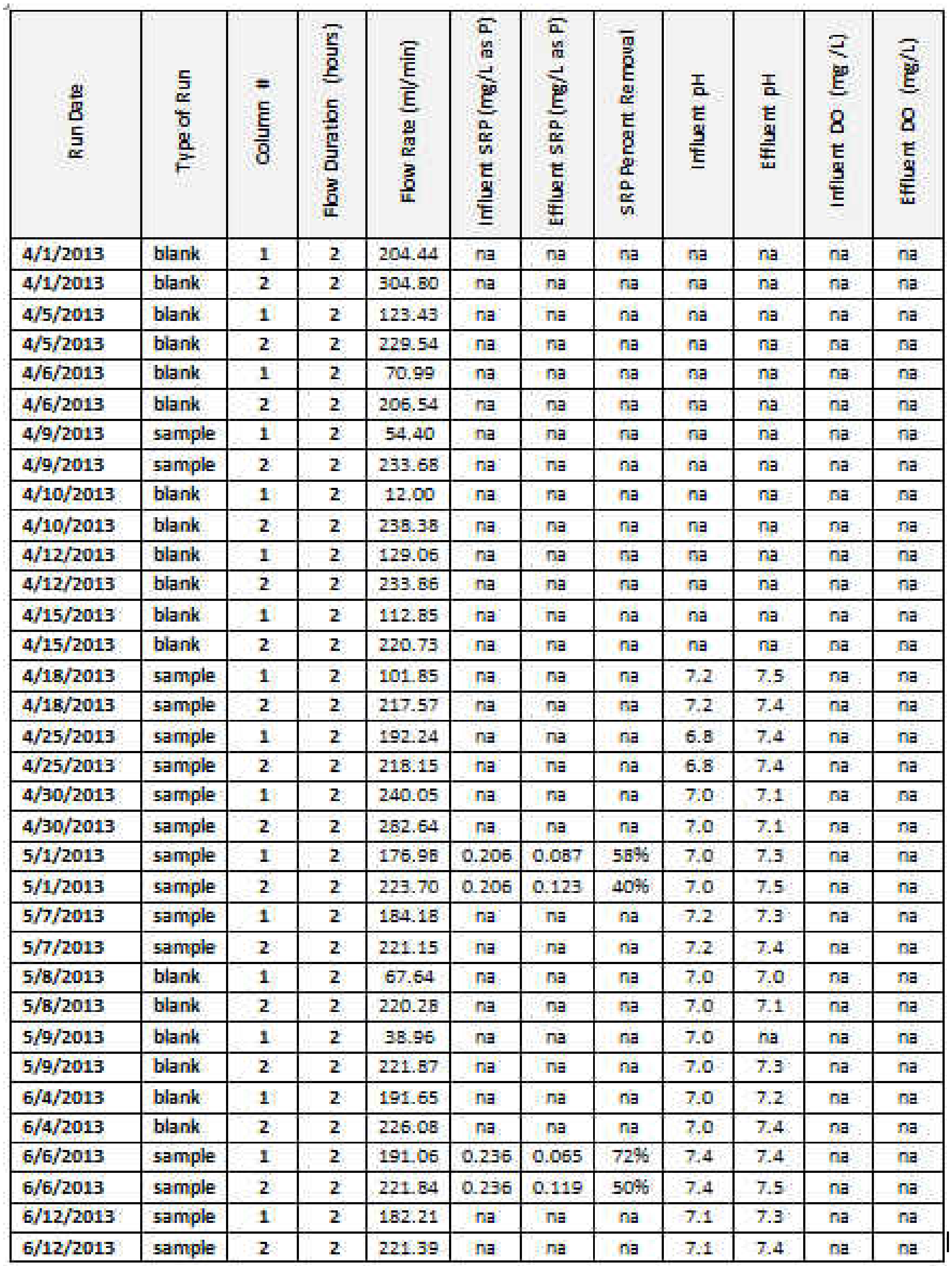
Precision - QC - DATA

NO	Date	SRP mg/l as P	Replica SRP mg/l as P	Range	I
1	9/30/2013	0.164	0.167	0.003	0.008
2	9/30/2013	0.159	0.147	0.011	0.037
3	9/30/2013	0.120	0.146	0.027	0.101
4	9/30/2013	0.133	0.116	0.018	0.071
5	10/7/2013	1.482	1.529	0.047	0.016
6	10/7/2013	1.391	1.365	0.027	0.010
7	10/7/2013	1.007	1.123	0.117	0.055
8	10/28/2013	1.541	1.598	0.056	0.018
9	10/28/2013	1.647	1.586	0.062	0.019
10	10/28/2013	1.215	1.098	0.117	0.050
11	11/11/2013	0.582	0.627	0.044	0.037
12	11/11/2013	1.184	1.252	0.068	0.028
13	11/11/2013	2.279	1.919	0.360	0.086
14	11/11/2013	0.973	0.949	0.024	0.013
15	11/20/2013	1.341	1.434	0.094	0.034
16	11/20/2013	0.995	1.082	0.087	0.042
17	11/20/2013	0.781	0.853	0.072	0.044
18	12/16/2013	5.210	5.148	0.062	0.006
19	12/16/2013	8.663	10.445	1.782	0.093
20	12/16/2013	21.003	22.012	1.009	0.023
21	12/16/2013	0.303	0.524	0.222	0.268
22	12/16/2013	1.047	0.842	0.205	0.109
23	1/6/2014	4.056	4.022	0.034	0.004
24	1/6/2014	8.138	7.654	0.484	0.031
25	1/6/2014	20.527	20.527	0.000	0.000
26	1/6/2014	0.467	0.433	0.034	0.038
27	1/6/2014	0.833	0.863	0.031	0.018


0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
5
10
15
20
25
30
Sample Number
I avg.
UWL
UCL
QC

APPENDIX C:
COLUMN TEST WATER QUALITY

SRP Data for column 1 and 2



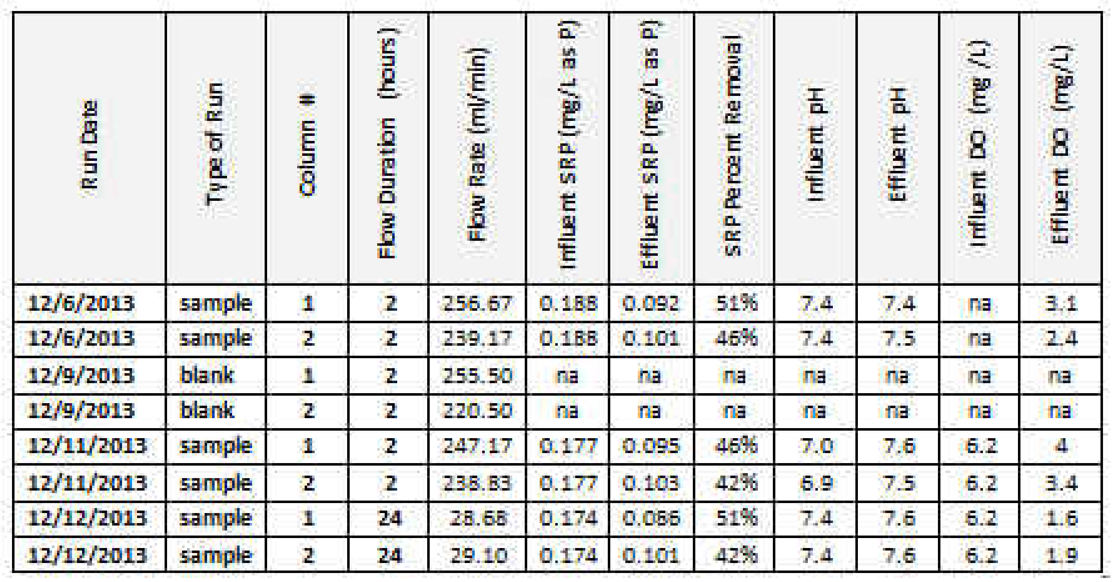
Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent SRP (mg/L as P)	Effluent SRP (mg/L as P)	SRP Percent Removal	Influent pH	Effluent pH	Influent DO (mg /L)	Effluent DO (mg/L)
4/1/2013	blank	1	2	204.44	na	na	na	na	na	na	na
4/1/2013	blank	2	2	304.80	na	na	na	na	na	na	na
4/5/2013	blank	1	2	123.43	na	na	na	na	na	na	na
4/5/2013	blank	2	2	229.54	na	na	na	na	na	na	na
4/6/2013	blank	1	2	70.99	na	na	na	na	na	na	na
4/6/2013	blank	2	2	206.54	na	na	na	na	na	na	na
4/9/2013	sample	1	2	54.40	na	na	na	na	na	na	na
4/9/2013	sample	2	2	233.68	na	na	na	na	na	na	na
4/10/2013	blank	1	2	12.00	na	na	na	na	na	na	na
4/10/2013	blank	2	2	238.38	na	na	na	na	na	na	na
4/12/2013	blank	1	2	129.06	na	na	na	na	na	na	na
4/12/2013	blank	2	2	233.86	na	na	na	na	na	na	na
4/15/2013	blank	1	2	112.85	na	na	na	na	na	na	na
4/15/2013	blank	2	2	220.73	na	na	na	na	na	na	na
4/18/2013	sample	1	2	101.85	na	na	na	7.2	7.5	na	na
4/18/2013	sample	2	2	217.57	na	na	na	7.2	7.4	na	na
4/25/2013	sample	1	2	192.24	na	na	na	6.8	7.4	na	na
4/25/2013	sample	2	2	218.15	na	na	na	6.8	7.4	na	na
4/30/2013	sample	1	2	240.05	na	na	na	7.0	7.1	na	na
4/30/2013	sample	2	2	282.64	na	na	na	7.0	7.1	na	na
5/1/2013	sample	1	2	176.98	0.206	0.087	58%	7.0	7.3	na	na
5/1/2013	sample	2	2	223.70	0.206	0.123	40%	7.0	7.5	na	na
5/7/2013	sample	1	2	184.18	na	na	na	7.2	7.3	na	na
5/7/2013	sample	2	2	221.15	na	na	na	7.2	7.4	na	na
5/8/2013	blank	1	2	67.64	na	na	na	7.0	7.0	na	na
5/8/2013	blank	2	2	220.28	na	na	na	7.0	7.1	na	na
5/9/2013	blank	1	2	38.96	na	na	na	7.0	na	na	na
5/9/2013	blank	2	2	221.87	na	na	na	7.0	7.3	na	na
6/4/2013	blank	1	2	191.65	na	na	na	7.0	7.2	na	na
6/4/2013	blank	2	2	226.08	na	na	na	7.0	7.4	na	na
6/6/2013	sample	1	2	191.06	0.236	0.065	72%	7.4	7.4	na	na
6/6/2013	sample	2	2	221.84	0.236	0.119	50%	7.4	7.5	na	na
6/12/2013	sample	1	2	182.21	na	na	na	7.1	7.3	na	na
6/12/2013	sample	2	2	221.39	na	na	na	7.1	7.4	na	na

Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent SRP (mg/L as P)	Effluent SRP (mg/L as P)	SRP Percent Removal	Influent pH	Effluent pH	Influent DO (mg/L)	Effluent DO (mg/L)
6/13/2013	sample	1	2	183.39	0.180	0.062	66%	na	na	na	na
6/13/2013	sample	2	2	213.06	0.180	0.062	66%	na	na	na	na
6/18/2013	blank	1	2	167.87	na	na	na	na	na	na	na
6/18/2013	blank	2	2	214.18	na	na	na	na	na	na	na
6/20/2013	sample	1	2	169.89	0.204	0.071	65%	na	na	na	na
6/20/2013	sample	2	2	213.37	0.204	0.066	68%	na	na	na	na
6/24/2013	sample	1	2	167.66	na	na	na	na	na	na	na
6/24/2013	sample	2	2	213.24	na	na	na	na	na	na	na
6/25/2013	sample	1	24	11.36	0.173	0.020	88%	na	na	na	na
6/25/2013	sample	2	24	23.01	0.173	0.030	83%	na	na	na	na
6/27/2013	blank	1	2	178.53	na	na	na	na	na	na	na
6/27/2013	blank	2	2	225.07	na	na	na	na	na	na	na
7/2/2013	sample	1	2	233.04	0.211	0.078	63%	na	na	na	na
7/2/2013	sample	2	2	227.41	0.211	0.057	73%	na	na	na	na
7/9/2013	blank	1	2	229.31	na	na	na	na	na	na	na
7/9/2013	blank	2	2	203.42	na	na	na	na	na	na	na
7/10/2013	blank	1	2	253.22	na	na	na	na	na	na	na
7/10/2013	blank	2	2	215.42	na	na	na	na	na	na	na
7/11/2013	sample	1	24	31.71	na	na	na	na	na	na	na
7/11/2013	sample	2	24	20.03	na	na	na	na	na	na	na
7/16/2013	blank	1	2	252.17	na	na	na	na	na	na	na
7/16/2013	blank	2	2	184.67	na	na	na	na	na	na	na
7/19/2013	blank	1	2	268.33	na	na	na	na	na	na	na
7/19/2013	blank	2	2	217.00	na	na	na	na	na	na	na
7/22/2013	blank	1	2	257.32	na	na	na	na	na	5.7	1.4
7/22/2013	blank	2	2	216.06	na	na	na	na	na	5.7	4.5
7/23/2013	blank	1	2	238.87	na	na	na	na	na	na	na
7/23/2013	blank	2	2	223.87	na	na	na	na	na	na	na
7/24/2013	sample	1	24	13.15	na	na	na	6.5	7.2	1.8	0.7
7/24/2013	sample	2	24	20.18	na	na	na	6.5	7.0	1.8	1.2
7/26/2013	sample	1	2	254.26	na	na	na	6.8	7.2	8	2
7/26/2013	sample	2	2	222.95	na	na	na	6.8	7.1	8	1.9
7/29/2013	blank	1	2	245.50	na	na	na	na	na	na	na
7/29/2013	blank	2	2	113.44	na	na	na	na	na	na	na

Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent SRP (mg/L as P)	Effluent SRP (mg/L as P)	SRP Percent Removal	Influent pH	Effluent pH	Influent DO (mg /L)	Effluent DO (mg/L)
7/30/2013	blank	1	2	254.67	na	na	na	na	na	na	na
7/30/2013	blank	2	2	218.83	na	na	na	na	na	na	na
7/31/2013	sample	1	2	250.67	na	na	na	7.3	7.2	na	na
7/31/2013	sample	2	2	219.17	na	na	na	7.3	7.4	na	na
8/1/2013	sample	1	24	22.79	na	na	na	7.2	7.4	6.5	1.3
8/1/2013	sample	2	24	16.93	na	na	na	7.2	7.9	6.5	1.6
8/5/2013	sample	1	24	14.56	na	na	na	7.1	7.4	6.8	2.1
8/5/2013	sample	2	24	16.81	na	na	na	7.1	7.6	6.8	2.2
8/7/2013	sample	1	2	248.00	na	na	na	6.7	7.3	na	na
8/7/2013	sample	2	2	202.83	na	na	na	6.7	7.3	na	na
8/8/2013	blank	1	2	248.83	na	na	na	na	na	na	na
8/8/2013	blank	2	2	201.00	na	na	na	na	na	na	na
8/9/2013	blank	1	2	247.83	na	na	na	na	na	na	na
8/9/2013	blank	2	2	199.00	na	na	na	na	na	na	na
8/12/2013	blank	1	2	250.67	na	na	na	na	na	na	na
8/12/2013	blank	2	2	199.67	na	na	na	na	na	na	na
8/13/2013	sample	1	24	19.38	na	na	na	7.3	7.1	6.6	1.4
8/13/2013	sample	2	24	21.64	na	na	na	7.3	7.6	6.6	2.3
8/15/2013	sample	1	2	257.67	na	na	na	7.2	7.8	na	na
8/15/2013	sample	2	2	204.33	na	na	na	7.2	7.7	na	na
8/16/2013	blank	1	2	252.52	na	na	na	na	na	na	na
8/16/2013	blank	2	2	204.72	na	na	na	na	na	na	na
8/23/2013	blank	1	2	263.00	na	na	na	na	na	na	na
8/23/2013	blank	2	2	199.67	na	na	na	na	na	na	na
8/26/2013	blank	1	2	251.67	na	na	na	na	na	na	na
8/26/2013	blank	2	2	200.17	na	na	na	na	na	na	na
8/27/2013	sample	1	24	16.22	na	na	na	7.1	7.2	na	1.5
8/27/2013	sample	2	24	21.18	na	na	na	7.1	7.5	na	3
8/29/2013	blank	1	2	256.83	na	na	na	na	na	na	na
8/29/2013	blank	2	2	199.33	na	na	na	na	na	na	na
8/30/2013	sample	1	2	242.67	na	na	na	7.2	7.0	4.9	3.4
8/30/2013	sample	2	2	200.08	na	na	na	7.2	7.2	4.9	2.6
9/3/2013	sample	1	24	21.36	na	na	na	6.8	7.3	5.4	2.9
9/3/2013	sample	2	24	19.10	na	na	na	6.8	7.5	5.4	2.2

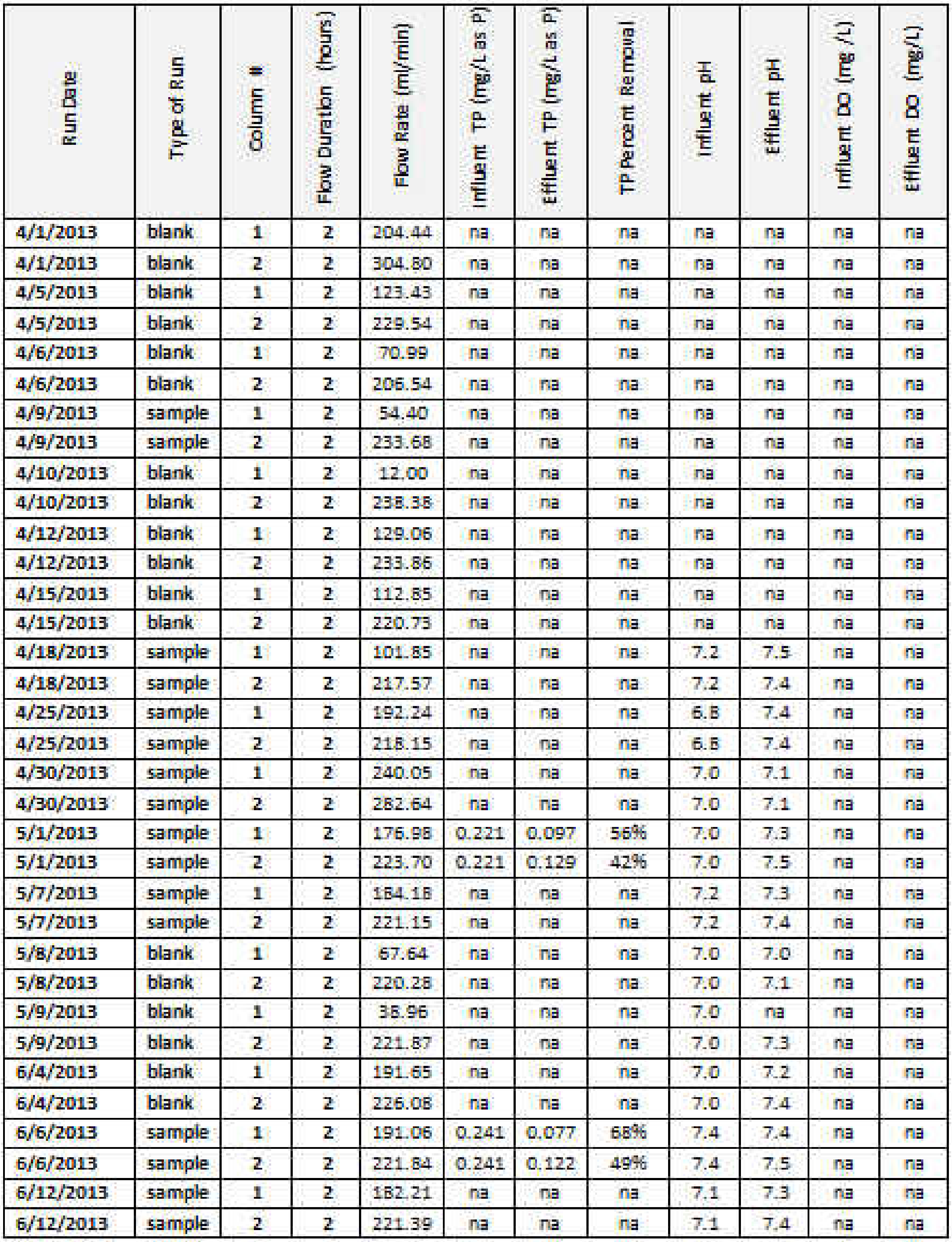
Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent SRP (mg/L as P)	Effluent SRP (mg/L as P)	SRP Percent Removal	Influent pH	Effluent pH	Influent DO (mg/L)	Effluent DO (mg/L)
9/24/2013	sample	1	24	13.96	0.190	0.026	86%	7.1	7.3	na	na
9/24/2013	sample	2	24	23.15	0.190	0.026	86%	7.1	6.9	na	na
9/26/2013	blank	1	2	254.67	na	na	na	na	na	na	na
9/26/2013	blank	2	2	250.67	na	na	na	na	na	na	na
9/27/2013	sample	1	2	241.33	0.179	0.068	62%	6.4	6.7	na	2.2
9/27/2013	sample	2	2	248.33	0.179	0.078	56%	6.4	6.8	na	2.3
9/30/2013	blank	1	2	236.33	na	na	na	na	na	na	na
9/30/2013	blank	2	2	244.83	na	na	na	na	na	na	na
10/1/2013	sample	1	24	15.99	0.132	0.079	40%	7.0	7.1	na	1.6
10/1/2013	sample	2	24	26.56	0.132	0.055	58%	7.0	6.9	na	1.8
10/3/2013	blank	1	2	193.04	na	na	na	na	na	na	na
10/3/2013	blank	2	2	189.71	na	na	na	na	na	na	na
10/4/2013	sample	1	2	249.50	0.149	0.059	60%	6.8	7.1	na	2.1
10/4/2013	sample	2	2	242.00	0.149	0.058	61%	6.8	7.0	na	1.5
10/7/2013	blank	1	2	251.00	na	na	na	na	na	na	na
10/7/2013	blank	2	2	243.83	na	na	na	na	na	na	na
10/8/2013	sample	1	24	9.89	0.213	0.128	40%	7.2	7.6	5	2
10/8/2013	sample	2	24	29.06	0.213	0.103	52%	7.2	7.4	5	1.2
10/10/2013	blank	1	2	na	na	na	na	na	na	na	na
10/10/2013	blank	2	2	242.67	na	na	na	na	na	na	na
10/11/2013	blank	1	2	216.83	na	na	na	na	na	na	na
10/11/2013	blank	2	2	202.50	na	na	na	na	na	na	na
10/14/2013	blank	1	2	245.83	na	na	na	na	na	na	na
10/14/2013	blank	2	2	234.00	na	na	na	na	na	na	na
10/15/2013	sample	1	24	24.67	0.163	0.109	33%	6.8	7.0	4.6	1.2
10/15/2013	sample	2	24	29.40	0.163	0.095	42%	6.8	6.9	4.6	1.9
10/17/2013	blank	1	2	na	na	na	na	na	na	na	na
10/17/2013	blank	2	2	225.67	na	na	na	na	na	na	na
10/18/2013	sample	1	2	217.00	0.189	0.097	49%	na	6.9	na	2.9
10/18/2013	sample	2	2	224.83	0.189	0.101	47%	na	6.9	na	1.5
10/21/2013	blank	1	2	195.08	na	na	na	na	na	na	na
10/21/2013	blank	2	2	230.50	na	na	na	na	na	na	na
10/22/2013	sample	1	24	15.81	0.164	0.030	82%	6.7	7.2	4.9	1.2
10/22/2013	sample	2	24	26.93	0.164	0.047	71%	6.7	7.0	4.9	0.7

Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent SRP (mg/L as P)	Effluent SRP (mg/L as P)	SRP Percent Removal	Influent pH	Effluent pH	Influent DO (mg/L)	Effluent DO (mg/L)
10/24/2013	blank	1	2	211.17	na	na	na	na	na	na	na
10/24/2013	blank	2	2	225.00	na	na	na	na	na	na	na
10/25/2013	sample	1	2	235.67	0.182	0.089	51%	6.9	7.3	4.6	1.5
10/25/2013	sample	2	2	235.67	0.182	0.094	48%	6.9	7.1	4.6	1.6
10/29/2013	sample	1	24	14.60	0.185	0.053	71%	6.9	7.1	5.7	0.8
10/29/2013	sample	2	24	24.26	0.185	0.066	64%	6.9	7.1	5.7	1.7
11/1/2013	sample	1	2	219.67	0.164	0.078	52%	7.3	7.3	4.5	1.8
11/1/2013	sample	2	2	224.17	0.164	0.086	48%	7.3	7.0	4.5	1.6
11/4/2013	blank	1	2	212.67	na	na	na	na	na	na	na
11/4/2013	blank	2	2	230.00	na	na	na	na	na	na	na
11/5/2013	sample	1	24	8.08	0.184	0.062	66%	7.0	6.9	5	1.1
11/5/2013	sample	2	24	21.36	0.184	0.040	78%	7.0	6.9	5	1.5
11/7/2013	blank	1	2	206.17	na	na	na	na	na	na	na
11/7/2013	blank	2	2	226.00	na	na	na	na	na	na	na
11/8/2013	sample	1	2	204.83	0.203	0.092	55%	7.1	7.0	5.7	3
11/8/2013	sample	2	2	226.67	0.203	0.078	62%	7.1	7.1	5.7	2.8
11/12/2013	sample	1	24	25.69	0.192	0.059	69%	6.8	6.9	6	0.7
11/12/2013	sample	2	24	32.39	0.192	0.061	68%	6.8	6.7	6	1.7
11/14/2013	blank	1	2	241.83	na	na	na	na	na	na	na
11/14/2013	blank	2	2	255.67	na	na	na	na	na	na	na
11/15/2013	sample	1	2	214.67	0.147	0.099	33%	7.1	7.4	4.7	1.9
11/15/2013	sample	2	2	na	na	0.084	na	7.1	na	4.7	na
11/18/2013	blank	1	2	226.83	na	na	na	na	na	na	na
11/18/2013	blank	2	2	222.67	na	na	na	na	na	na	na
11/19/2013	sample	1	24	23.21	0.158	0.033	79%	7.0	7.2	5.7	1
11/19/2013	sample	2	24	22.11	0.158	0.035	78%	7.0	7.3	5.7	1.4
11/21/2013	blank	1	2	251.33	na	na	na	na	na	na	na
11/21/2013	blank	2	2	265.00	na	na	na	na	na	na	na
11/22/2013	sample	1	2	229.17	0.163	0.096	41%	7.4	7.4	6.3	2.9
11/22/2013	sample	2	2	248.00	0.163	0.100	39%	7.4	7.4	6.3	2.2
12/3/2013	sample	1	24	21.46	0.175	0.018	90%	7.0	7.1	6.7	1.5
12/3/2013	sample	2	24	28.98	0.175	0.019	89%	7.0	7.2	6.7	1.9
12/5/2013	blank	1	2	249.50	na	na	na	na	na	na	na
12/5/2013	blank	2	2	224.75	na	na	na	na	na	na	na



Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent SRP (mg/L as P)	Effluent SRP (mg/L as P)	SRP Percent Removal	Influent pH	Effluent pH	Influent DO (mg/L)	Effluent DO (mg/L)
12/6/2013	sample	1	2	256.67	0.188	0.092	51%	7.4	7.4	na	3.1
12/6/2013	sample	2	2	239.17	0.188	0.101	46%	7.4	7.5	na	2.4
12/9/2013	blank	1	2	255.50	na	na	na	na	na	na	na
12/9/2013	blank	2	2	220.50	na	na	na	na	na	na	na
12/11/2013	sample	1	2	247.17	0.177	0.095	46%	7.0	7.6	6.2	4
12/11/2013	sample	2	2	238.83	0.177	0.103	42%	6.9	7.5	6.2	3.4
12/12/2013	sample	1	24	28.68	0.174	0.086	51%	7.4	7.6	6.2	1.6
12/12/2013	sample	2	24	29.10	0.174	0.101	42%	7.4	7.6	6.2	1.9

Total Phosphorus Data for column 1 and 2

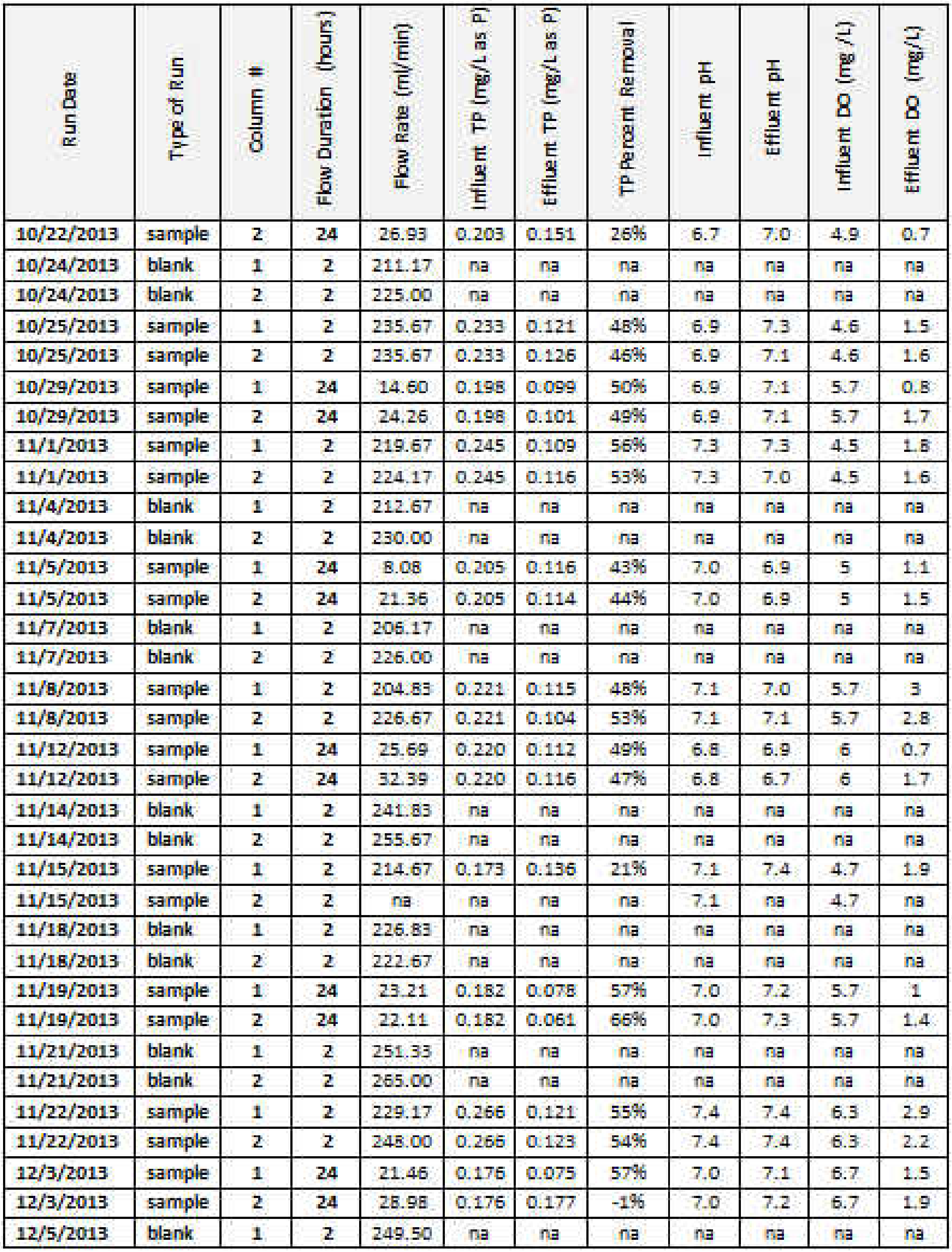


Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent TP (mg/L as P)	Effluent TP (mg/L as P)	TP Percent Removal	Influent pH	Effluent pH	Influent DO (mg /L)	Effluent DO (mg/L)
4/1/2013	blank	1	2	204.44	na	na	na	na	na	na	na
4/1/2013	blank	2	2	304.80	na	na	na	na	na	na	na
4/5/2013	blank	1	2	123.43	na	na	na	na	na	na	na
4/5/2013	blank	2	2	229.54	na	na	na	na	na	na	na
4/6/2013	blank	1	2	70.99	na	na	na	na	na	na	na
4/6/2013	blank	2	2	206.54	na	na	na	na	na	na	na
4/9/2013	sample	1	2	54.40	na	na	na	na	na	na	na
4/9/2013	sample	2	2	233.68	na	na	na	na	na	na	na
4/10/2013	blank	1	2	12.00	na	na	na	na	na	na	na
4/10/2013	blank	2	2	238.38	na	na	na	na	na	na	na
4/12/2013	blank	1	2	129.06	na	na	na	na	na	na	na
4/12/2013	blank	2	2	233.86	na	na	na	na	na	na	na
4/15/2013	blank	1	2	112.85	na	na	na	na	na	na	na
4/15/2013	blank	2	2	220.73	na	na	na	na	na	na	na
4/18/2013	sample	1	2	101.85	na	na	na	7.2	7.5	na	na
4/18/2013	sample	2	2	217.57	na	na	na	7.2	7.4	na	na
4/25/2013	sample	1	2	192.24	na	na	na	6.8	7.4	na	na
4/25/2013	sample	2	2	218.15	na	na	na	6.8	7.4	na	na
4/30/2013	sample	1	2	240.05	na	na	na	7.0	7.1	na	na
4/30/2013	sample	2	2	282.64	na	na	na	7.0	7.1	na	na
5/1/2013	sample	1	2	176.98	0.221	0.097	56%	7.0	7.3	na	na
5/1/2013	sample	2	2	223.70	0.221	0.129	42%	7.0	7.5	na	na
5/7/2013	sample	1	2	184.18	na	na	na	7.2	7.3	na	na
5/7/2013	sample	2	2	221.15	na	na	na	7.2	7.4	na	na
5/8/2013	blank	1	2	67.64	na	na	na	7.0	7.0	na	na
5/8/2013	blank	2	2	220.28	na	na	na	7.0	7.1	na	na
5/9/2013	blank	1	2	38.96	na	na	na	7.0	na	na	na
5/9/2013	blank	2	2	221.87	na	na	na	7.0	7.3	na	na
6/4/2013	blank	1	2	191.65	na	na	na	7.0	7.2	na	na
6/4/2013	blank	2	2	226.08	na	na	na	7.0	7.4	na	na
6/6/2013	sample	1	2	191.06	0.241	0.077	68%	7.4	7.4	na	na
6/6/2013	sample	2	2	221.84	0.241	0.122	49%	7.4	7.5	na	na
6/12/2013	sample	1	2	182.21	na	na	na	7.1	7.3	na	na
6/12/2013	sample	2	2	221.39	na	na	na	7.1	7.4	na	na

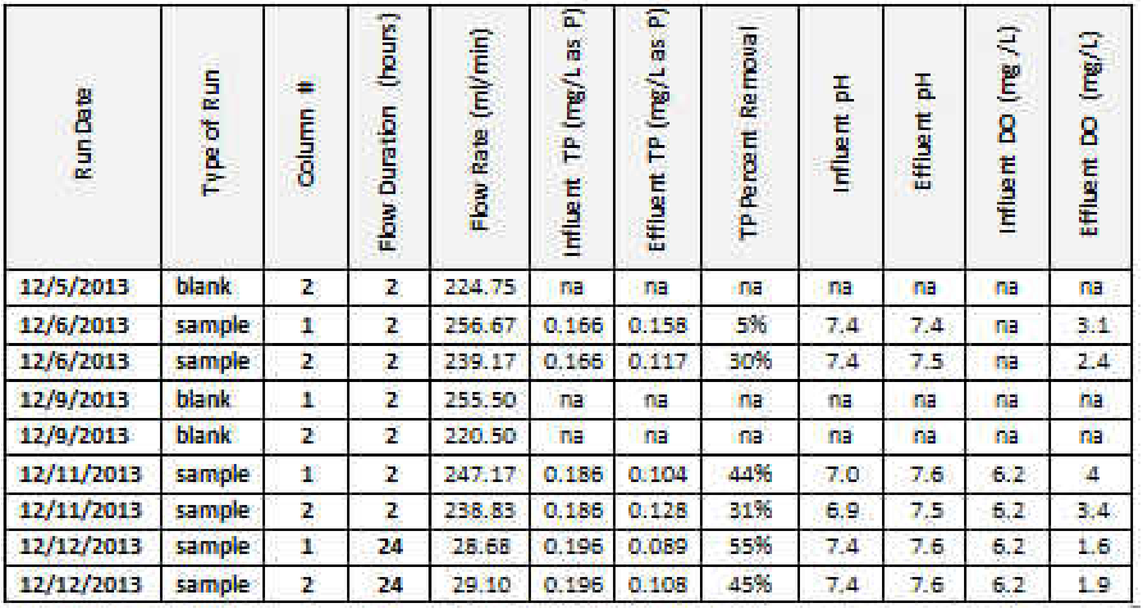
Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent TP (mg/L as P)	Effluent TP (mg/L as P)	TP Percent Removal	Influent pH	Effluent pH	Influent DO (mg/L)	Effluent DO (mg/L)
6/13/2013	sample	1	2	183.39	0.189	0.071	62%	na	na	na	na
6/13/2013	sample	2	2	213.06	0.189	0.082	57%	na	na	na	na
6/18/2013	blank	1	2	167.87	na	na	na	na	na	na	na
6/18/2013	blank	2	2	214.18	na	na	na	na	na	na	na
6/20/2013	sample	1	2	169.89	0.211	0.107	49%	na	na	na	na
6/20/2013	sample	2	2	213.37	0.211	0.105	50%	na	na	na	na
6/24/2013	sample	1	2	167.66	na	na	na	na	na	na	na
6/24/2013	sample	2	2	213.24	na	na	na	na	na	na	na
6/25/2013	sample	1	24	11.36	0.191	0.106	45%	na	na	na	na
6/25/2013	sample	2	24	23.01	0.191	0.137	28%	na	na	na	na
6/27/2013	blank	1	2	178.53	na	na	na	na	na	na	na
6/27/2013	blank	2	2	225.07	na	na	na	na	na	na	na
7/2/2013	sample	1	2	233.04	0.406	0.209	49%	na	na	na	na
7/2/2013	sample	2	2	227.41	0.406	0.220	46%	na	na	na	na
7/9/2013	blank	1	2	229.31	na	na	na	na	na	na	na
7/9/2013	blank	2	2	203.42	na	na	na	na	na	na	na
7/10/2013	blank	1	2	253.22	na	na	na	na	na	na	na
7/10/2013	blank	2	2	215.42	na	na	na	na	na	na	na
7/11/2013	sample	1	24	31.71	0.206	0.118	43%	na	na	na	na
7/11/2013	sample	2	24	20.03	0.206	0.130	37%	na	na	na	na
7/16/2013	blank	1	2	252.17	na	na	na	na	na	na	na
7/16/2013	blank	2	2	184.67	na	na	na	na	na	na	na
7/19/2013	blank	1	2	268.33	na	na	na	na	na	na	na
7/19/2013	blank	2	2	217.00	na	na	na	na	na	na	na
7/22/2013	blank	1	2	257.32	na	na	na	na	na	5.7	1.4
7/22/2013	blank	2	2	216.06	na	na	na	na	na	5.7	4.5
7/23/2013	blank	1	2	238.87	na	na	na	na	na	na	na
7/23/2013	blank	2	2	223.87	na	na	na	na	na	na	na
7/24/2013	sample	1	24	13.15	0.447	0.270	40%	6.5	7.2	1.8	0.7
7/24/2013	sample	2	24	20.18	0.447	0.315	30%	6.5	7.0	1.8	1.2
7/26/2013	sample	1	2	254.26	na	na	na	6.8	7.2	8	2
7/26/2013	sample	2	2	222.95	na	na	na	6.8	7.1	8	1.9
7/29/2013	blank	1	2	245.50	na	na	na	na	na	na	na
7/29/2013	blank	2	2	113.44	na	na	na	na	na	na	na

Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent TP (mg/L as P)	Effluent TP (mg/L as P)	TP Percent Removal	Influent pH	Effluent pH	Influent DO (mg /L)	Effluent DO (mg/L)
7/30/2013	blank	1	2	254.67	na	na	na	na	na	na	na
7/30/2013	blank	2	2	218.83	na	na	na	na	na	na	na
7/31/2013	sample	1	2	250.67	0.248	0.098	60%	7.3	7.2	na	na
7/31/2013	sample	2	2	219.17	0.248	0.111	55%	7.3	7.4	na	na
8/1/2013	sample	1	24	22.79	0.017	0.111	-553%	7.2	7.4	6.5	1.3
8/1/2013	sample	2	24	16.93	0.017	0.078	-359%	7.2	7.9	6.5	1.6
8/5/2013	sample	1	24	14.56	0.154	0.081	47%	7.1	7.4	6.8	2.1
8/5/2013	sample	2	24	16.81	0.154	0.081	47%	7.1	7.6	6.8	2.2
8/7/2013	sample	1	2	248.00	0.161	0.082	49%	6.7	7.3	na	na
8/7/2013	sample	2	2	202.83	0.161	0.095	41%	6.7	7.3	na	na
8/8/2013	blank	1	2	248.83	na	na	na	na	na	na	na
8/8/2013	blank	2	2	201.00	na	na	na	na	na	na	na
8/9/2013	blank	1	2	247.83	na	na	na	na	na	na	na
8/9/2013	blank	2	2	199.00	na	na	na	na	na	na	na
8/12/2013	blank	1	2	250.67	na	na	na	na	na	na	na
8/12/2013	blank	2	2	199.67	na	na	na	na	na	na	na
8/13/2013	sample	1	24	19.38	0.148	0.115	22%	7.3	7.1	6.6	1.4
8/13/2013	sample	2	24	21.64	0.148	0.112	24%	7.3	7.6	6.6	2.3
8/15/2013	sample	1	2	257.67	0.152	0.126	17%	7.2	7.8	na	na
8/15/2013	sample	2	2	204.33	0.152	0.125	18%	7.2	7.7	na	na
8/16/2013	blank	1	2	252.52	na	na	na	na	na	na	na
8/16/2013	blank	2	2	204.72	na	na	na	na	na	na	na
8/23/2013	blank	1	2	263.00	na	na	na	na	na	na	na
8/23/2013	blank	2	2	199.67	na	na	na	na	na	na	na
8/26/2013	blank	1	2	251.67	na	na	na	na	na	na	na
8/26/2013	blank	2	2	200.17	na	na	na	na	na	na	na
8/27/2013	sample	1	24	16.22	0.469	0.273	42%	7.1	7.2	na	1.5
8/27/2013	sample	2	24	21.18	0.469	0.397	15%	7.1	7.5	na	3
8/29/2013	blank	1	2	256.83	na	na	na	na	na	na	na
8/29/2013	blank	2	2	199.33	na	na	na	na	na	na	na
8/30/2013	sample	1	2	242.67	0.256	0.215	16%	7.2	7.0	4.9	3.4
8/30/2013	sample	2	2	200.08	0.256	0.299	-17%	7.2	7.2	4.9	2.6
9/3/2013	sample	1	24	21.36	0.252	0.149	41%	6.8	7.3	5.4	2.9
9/3/2013	sample	2	24	19.10	0.252	0.120	52%	6.8	7.5	5.4	2.2

Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent TP (mg/L as P)	Effluent TP (mg/L as P)	TP Percent Removal	Influent pH	Effluent pH	Influent DO (mg /L)	Effluent DO (mg/L)
9/24/2013	**sample**	**1**	**24**	13.96	0.209	0.262	-25%	7.1	7.3	na	na
9/24/2013	**sample**	**2**	**24**	23.15	0.209	7.854	-3658%	7.1	6.9	na	na
9/26/2013	**blank**	**1**	**2**	254.67	na	na	na	na	na	na	na
9/26/2013	**blank**	**2**	**2**	250.67	na	na	na	na	na	na	na
9/27/2013	**sample**	**1**	**2**	241.33	0.276	0.121	56%	6.4	6.7	na	2.2
9/27/2013	**sample**	**2**	**2**	248.33	0.276	0.138	50%	6.4	6.8	na	2.3
9/30/2013	**blank**	**1**	**2**	236.33	na	na	na	na	na	na	na
9/30/2013	**blank**	**2**	**2**	244.83	na	na	na	na	na	na	na
10/1/2013	**sample**	**1**	**24**	15.99	0.209	0.161	23%	7.0	7.1	na	1.6
10/1/2013	**sample**	**2**	**24**	26.56	0.209	0.207	1%	7.0	6.9	na	1.8
10/3/2013	**blank**	**1**	**2**	193.04	na	na	na	na	na	na	na
10/3/2013	**blank**	**2**	**2**	189.71	na	na	na	na	na	na	na
10/4/2013	**sample**	**1**	**2**	249.50	0.250	0.084	66%	6.8	7.1	na	2.1
10/4/2013	**sample**	**2**	**2**	242.00	0.250	0.084	66%	6.8	7.0	na	1.5
10/7/2013	**blank**	**1**	**2**	251.00	na	na	na	na	na	na	na
10/7/2013	**blank**	**2**	**2**	243.83	na	na	na	na	na	na	na
10/8/2013	**sample**	**1**	**24**	9.89	0.226	0.145	36%	7.2	7.6	5	2
10/8/2013	**sample**	**2**	**24**	29.06	0.226	0.106	53%	7.2	7.4	5	1.2
10/10/2013	**blank**	**1**	**2**	na	na	na	na	na	na	na	na
10/10/2013	**blank**	**2**	**2**	242.67	na	na	na	na	na	na	na
10/11/2013	**blank**	**1**	**2**	216.83	na	na	na	na	na	na	na
10/11/2013	**blank**	**2**	**2**	202.50	na	na	na	na	na	na	na
10/14/2013	**blank**	**1**	**2**	245.83	na	na	na	na	na	na	na
10/14/2013	**blank**	**2**	**2**	234.00	na	na	na	na	na	na	na
10/15/2013	**sample**	**1**	**24**	24.67	0.315	0.231	27%	6.8	7.0	4.6	1.2
10/15/2013	**sample**	**2**	**24**	29.40	0.315	0.450	-43%	6.8	6.9	4.6	1.9
10/17/2013	**blank**	**1**	**2**	na	na	na	na	na	na	na	na
10/17/2013	**blank**	**2**	**2**	225.67	na	na	na	na	na	na	na
10/18/2013	**sample**	**1**	**2**	217.00	0.245	0.110	55%	na	6.9	na	2.9
10/18/2013	**sample**	**2**	**2**	224.83	0.245	0.124	49%	na	6.9	na	1.5
10/21/2013	**blank**	**1**	**2**	195.08	na	na	na	na	na	na	na
10/21/2013	**blank**	**2**	**2**	230.50	na	na	na	na	na	na	na
10/22/2013	**sample**	**1**	**24**	15.81	0.203	0.116	43%	6.7	7.2	4.9	1.2



Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent TP (mg/L as P)	Effluent TP (mg/L as P)	TP Percent Removal	Influent pH	Effluent pH	Influent DO (mg /L)	Effluent DO (mg/L)
10/22/2013	sample	2	24	26.93	0.203	0.151	26%	6.7	7.0	4.9	0.7
10/24/2013	blank	1	2	211.17	na	na	na	na	na	na	na
10/24/2013	blank	2	2	225.00	na	na	na	na	na	na	na
10/25/2013	sample	1	2	235.67	0.233	0.121	48%	6.9	7.3	4.6	1.5
10/25/2013	sample	2	2	235.67	0.233	0.126	46%	6.9	7.1	4.6	1.6
10/29/2013	sample	1	24	14.60	0.198	0.099	50%	6.9	7.1	5.7	0.8
10/29/2013	sample	2	24	24.26	0.198	0.101	49%	6.9	7.1	5.7	1.7
11/1/2013	sample	1	2	219.67	0.245	0.109	56%	7.3	7.3	4.5	1.8
11/1/2013	sample	2	2	224.17	0.245	0.116	53%	7.3	7.0	4.5	1.6
11/4/2013	blank	1	2	212.67	na	na	na	na	na	na	na
11/4/2013	blank	2	2	230.00	na	na	na	na	na	na	na
11/5/2013	sample	1	24	8.08	0.205	0.116	43%	7.0	6.9	5	1.1
11/5/2013	sample	2	24	21.36	0.205	0.114	44%	7.0	6.9	5	1.5
11/7/2013	blank	1	2	206.17	na	na	na	na	na	na	na
11/7/2013	blank	2	2	226.00	na	na	na	na	na	na	na
11/8/2013	sample	1	2	204.83	0.221	0.115	48%	7.1	7.0	5.7	3
11/8/2013	sample	2	2	226.67	0.221	0.104	53%	7.1	7.1	5.7	2.8
11/12/2013	sample	1	24	25.69	0.220	0.112	49%	6.8	6.9	6	0.7
11/12/2013	sample	2	24	32.39	0.220	0.116	47%	6.8	6.7	6	1.7
11/14/2013	blank	1	2	241.83	na	na	na	na	na	na	na
11/14/2013	blank	2	2	255.67	na	na	na	na	na	na	na
11/15/2013	sample	1	2	214.67	0.173	0.136	21%	7.1	7.4	4.7	1.9
11/15/2013	sample	2	2	na	na	na	na	7.1	na	4.7	na
11/18/2013	blank	1	2	226.83	na	na	na	na	na	na	na
11/18/2013	blank	2	2	222.67	na	na	na	na	na	na	na
11/19/2013	sample	1	24	23.21	0.182	0.078	57%	7.0	7.2	5.7	1
11/19/2013	sample	2	24	22.11	0.182	0.061	66%	7.0	7.3	5.7	1.4
11/21/2013	blank	1	2	251.33	na	na	na	na	na	na	na
11/21/2013	blank	2	2	265.00	na	na	na	na	na	na	na
11/22/2013	sample	1	2	229.17	0.266	0.121	55%	7.4	7.4	6.3	2.9
11/22/2013	sample	2	2	248.00	0.266	0.123	54%	7.4	7.4	6.3	2.2
12/3/2013	sample	1	24	21.46	0.176	0.075	57%	7.0	7.1	6.7	1.5
12/3/2013	sample	2	24	28.98	0.176	0.177	-1%	7.0	7.2	6.7	1.9
12/5/2013	blank	1	2	249.50	na	na	na	na	na	na	na



Run Date	Type of Run	Column #	Flow Duration (hours)	Flow Rate (ml/min)	Influent TP (mg/L as P)	Effluent TP (mg/L as P)	TP Percent Removal	Influent pH	Effluent pH	Influent DO (mg /L)	Effluent DO (mg/L)
12/5/2013	blank	2	2	224.75	na	na	na	na	na	na	na
12/6/2013	sample	1	2	256.67	0.166	0.158	5%	7.4	7.4	na	3.1
12/6/2013	sample	2	2	239.17	0.166	0.117	30%	7.4	7.5	na	2.4
12/9/2013	blank	1	2	255.50	na	na	na	na	na	na	na
12/9/2013	blank	2	2	220.50	na	na	na	na	na	na	na
12/11/2013	sample	1	2	247.17	0.186	0.104	44%	7.0	7.6	6.2	4
12/11/2013	sample	2	2	238.83	0.186	0.128	31%	6.9	7.5	6.2	3.4
12/12/2013	sample	1	24	28.68	0.196	0.089	55%	7.4	7.6	6.2	1.6
12/12/2013	sample	2	24	29.10	0.196	0.108	45%	7.4	7.6	6.2	1.9

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