A Kinetics Study Of Selected Filtration Media For Nutrient Removal At Various Temperatures

2008

Elizabeth Henderson
University of Central Florida

STARS Citation

Henderson, Elizabeth, "A Kinetics Study Of Selected Filtration Media For Nutrient Removal At Various Temperatures" (2008). *Electronic Theses and Dissertations*. 3615.
https://stars.library.ucf.edu/etd/3615

A KINETICS STUDY OF SELECTED FILTRATION MEDIA FOR NUTRIENT REMOVAL AT VARIOUS TEMPERATURES

by

E. DEVAN HENDERSON, E.I.
B.S. University of Central Florida, 2006

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

Fall Term
2008

ABSTRACT

In recent years the nutrient levels of the Upper Floridan aquifer have been increasing (USGS, 2008). An example of this is found in Ocala, Florida where Silver Springs nitrate concentrations have risen from 0.5 mg/L in the 1960's to approximately 1.0 mg/L in 2003 (Phelps, 2004). Because stormwater is a contributor to surficial and groundwater aquifer recharge, there is an increasing need for methods that decrease nitrogen and phosphorus levels.

A laboratory column study was conducted to simulate a retention pond with saturated soil conditions. The objectives of the column studies reported in this thesis were to investigate the capabilities of a natural soil and soil augmentations to remove nitrogen and phosphorus for a range of concentrations at three different temperatures. An analytical attempt to model the columns through low order reaction kinetics and derive the corresponding temperature conversion constant to relate the rate constants is also presented.

The Media Mixes were selected through a process of research, preliminary batch testing and then implemented in column studies. Three columns measuring three feet in length and 6 inches outer diameter were packed with a control and two media mixes. Media Mix 1 consisted of 50% fine sand, 30% tire crumb, 20% sawdust by weight and Media Mix 2 consisted of 50% fine sand, 25% sawdust, 15% tire crumb, 10% limestone by weight. The control column was packed with natural soil from Hunter's Trace retention pond located in Ocala, Florida.

The reaction rates for nitrate are best modeled as first order for Media Mix 1, and zero order for the Control and Media Mix 2. The reaction rates for orthophosphate are best modeled as zero order, second order and first order for the Control, Media Mix 1, and Media Mix 2 respectively. The best overall media for both nitrate and orthophosphate removal from this study would be Media Mix 1. Media Mix 2 does have the highest average orthophosphate removal of all the mixes for all of the temperatures; however Media Mix 1 outperforms Mix 2 for the other two temperatures. The best column for Nitrate removal is the Media Mix 1 column.

The temperature conversion factors for nitrate were found to be 1.11, 1.1, and 1.01 for Media Mix 1, the Control and Media Mix 2 respectively. The temperature conversion factors for orthophosphate were found to be 1.02, 0.99, and 0.95. As well as temperature conversion factors, the activation energies and frequency factors for the Arrhenius Equation were investigated. Average values corresponding to each column, species, and temperature would be inaccurate due to the large variation in calculated values.

ACKNOWLEDGMENTS

I would like to thank Dr. Wanielista, Dr. Chang, and Dr. Randall for providing their valuable time and support in helping me achieve my graduate degree as well as sitting on my committee. As my major advisor for most of my graduate student status, Dr. Wanielista provided me with this opportunity. Dr. Chang offered me with guidance on my topic and presentation of my material. I also need to thank Dr. Randall who helped me reach this point in my academic career by providing me the chance to conduct research as an undergraduate and having faith in my abilities to achieve my goal of getting my master’s degree.

I would like to extend a very special thanks to Dr. Ammerin Makkeasorn for help with construction of experimental columns and numerous other assistance. His guidance and assistance were invaluable to my research. For their laboratory collaboration, Mikhal Moberg and Lisa Naujock deserve my gratitude.

I would especially like to thank my family and friends for their love, encouragement, patience, and moral support during my research and graduate studies; especially Dr. Erica Stone, Dr. Phillip Lintereur, Kevin Buckner and my parents, Bill and Debra Henderson.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

Introduction

The required removal of nutrients from stormwater is founded on principles with two main objectives; prevention of eutrophication and nutrient control in groundwater recharge. Eutrophication leads to a reduction in water quality that can be harmful to living organisms. Due to the use of surface water and groundwater as a potable water source, maintaining low nutrient levels are important for compliance with primary drinking water standards. Also, spring flow with high nutrient content may cause an unacceptable social condition or interfere with swimming and other recreation purposes in a spring.

Current stormwater management practices include the use of retention ponds to mitigate the effects of development. Retention allows for the collection of stormwater to another location where the water is able to infiltrate through the natural existing soil. These ponds not only allow for runoff volume reduction but for the filtration of solids and adsorption of nutrients. Retention ponds play a vital role in maintaining the delicate balance of nutrient concentrations.

Problem Statement

In recent years the nutrient levels of the Upper Floridan aquifer have been increasing (USGS, 2008). An example of this is found in Ocala, Florida where Silver Springs nitrate concentrations have risen from 0.5 mg/L in the 1960's to approximately 1.0 mg/L in 2003 (Phelps, 2004). Because stormwater is a contributor to surficial and ground water aquifer recharge, there is an increasing need for methods that decrease nitrogen and phosphorus levels.

Objectives

Soil augmentations to these ponds would be one method to help increase the filtration and adsorption functionality. The focus of the column study will be to simulate a retention pond with saturated soil conditions. The objectives of this thesis are to investigate the capabilities of a natural soil and soil augmentations to remove nitrogen and phosphorus for a range of concentrations at three different temperatures. An analytical attempt to model the columns through low order reaction kinetics and derive the corresponding temperature conversion constant to relate the rate constants will also be presented. Because this study is focused around obtaining data to represent the kinetic removals of nutrients, the columns were dosed with higher levels of nitrogen and phosphorus than would typically be found in an average stormwater pond in Florida.

Research Framework

Numerous facets will be explored over the course of this study. The work will start with extensive literary review, initial batch testing, interpretation of results, column testing, and finally analysis of the results. The following flowchart illustrates the overall outline of this research (Figure 1).

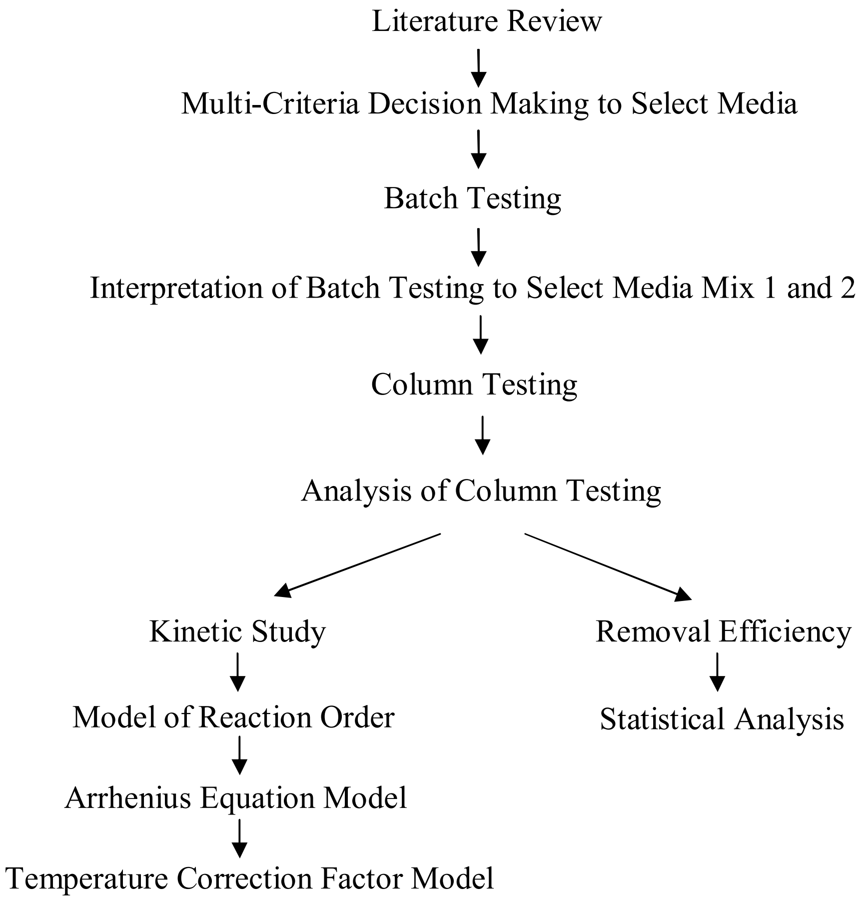


Figure 1 : Research Flowchart

CHAPTER 2: BACKGROUND AND PAST STUDIES

Nutrients

Although nutrients are essential for living organisms, high nutrient concentrations can have detrimental effects on the environment. Some of the environmental affects include decreased dissolved oxygen levels, algal blooms, toxicity, and accelerated eutrophication (USGS, 2008). When excess levels of nutrients are introduced to a system, the living organisms enter an exponential growth phase. Once all of the excess nutrient levels are depleted the organisms decompose utilizing oxygen. This process lowers the dissolved oxygen in the system which is hazardous to other living organisms. The combination of high nutrient levels and low dissolved oxygen levels create toxic conditions. Lastly, the excess nutrient concentrations lead to accelerated eutrophication. Eutrophication is the process of increased input of nutrients into a water body (USGS, 2008). Although this process can occur naturally, agricultural and commercial development can cause increased eutrophication of nearby lakes and water bodies. A survey conducted in 1993 found that 48% of North American lakes were eutrophic (ILEC, 1993).

High nutrient levels not only affect the earth's water supply, but also the humans who ingest it. Nitrates have been linked to a number of human illnesses including; methaemoglobinemia commonly known as blue baby syndrome and gastro-intestinal problems such as a build up of carcinogens of n-nitroso compounds (Rocca, 2005).

Phosphorus is naturally present in nature in the form of phosphate and in elemental form produced during manufacturing processes. The manufactured phosphorus or "white phosphorus" is extremely poisonous. A common use of white phosphorus is in rat poison. However, ingestion is not the only way for white phosphorus to cause damage, contact with the skin can cause burns and damage to the heart, liver and kidneys. In contrast, phosphates are essential for both plant and animal growth, with 1,000-2,000 mg/day recommended for human ingestion (Phosphorus, 2008). Exceeding this dosage can lead to kidney damage and osteoporosis.

Reduction of nutrients from stormwater is becoming increasingly important as nutrient levels increase and drinking water standards become more stringent. Studies show that nitrogen and phosphorus concentrations have both increased by 2-3 times in rivers worldwide (Justic, 1995). These higher concentrations are typically downstream from urban areas and are considered mostly a result of fertilizer and detergent usage (USGS, 2008, Justic, 1995). Other causes of high nutrient levels include septic systems and wastewater effluent. Therefore increases in population and development will continue to produce high concentrations in stormwater, rivers and other ending water bodies. Phosphorus is especially prevalent in Florida due to the rich phosphate sediment deposits when Florida was formed (FIPR, 2007). Because ground water and surface water are potable water sources, it is important to consider the stringent nitrogen standards. These standards currently allow for up to 10 mg/L nitrogen; however recent trends in regulations have become more severe (FDEP, 2007).

Nutrient Removal Mechanisms

The mechanisms of nutrient removal for nitrogen and phosphorus differ. Phosphorus that is present in a soluble form, known as orthophosphate or reactive phosphorus, is removed through biological organisms and sorption. Biological phosphorus removal is achieved through a variety of methods in waste water treatment. These processes typically require the use of anaerobic, anoxic and aerobic conditions. Since, the columns are going to be operated under anaerobic conditions the removal of phosphorus is expected to be the result of sorption. Nitrogen, which can be in the form of a number of species, is removed from the system via oxidation to nitrogen gas by biological activity. Two processes are responsible for this conversion; nitrification and denitrification. Nitrification occurs in two stages, first the ammonia (NH_4^+-N) is converted by nitrosomonas bacteria to nitrite (NO_2^--N) which is then converted by nitrobacter bacteria to nitrate (NO_3^--N) (Metcalf and Eddy, 2006). The stoichiometry of these reactions is shown in Equations 1 and 2. Numerous factors influence the rates of these reactions, including pH, toxicity, metals and un-ionized ammonia (NH_3). Optimal pH for nitrification bacteria is 7.5-8.0. The presence of toxic organic materials, metals and un-ionized ammonia can hinder the performance of the bacteria and in some cases prove fatal. Dissolved ammonia (NH_3) and ammonium (NH_4^+) exist in equilibrium around neutral pH but the reaction shifts toward ammonia in more alkaline pH (approximately pH = 9.25) (Metcalf and Eddy, 2006) This reaction or volatilization is dependent on mass transfer through the liquid and gas phase, with the mass transfer coefficient enhanced by wind and high temperature (Pano, 1982).

$$NH_4^+ + 1.5O2 \quad => \quad 2H^+ + 2H_2O + NO_2^- \qquad \text{Equation 1}$$

$$NO_2^- + 0.5O_2 \quad => \quad NO_3^- \qquad \text{Equation 2}$$

Denitrification is the process through which nitrate is converted to nitrogen gas. A group of bacteria, denitrifiers, are responsible for these types of bio-chemical reactions. Equation 3 is the stoichiometric equation for this reaction. The bacteria are classified as both heterotrophic and autotrophic meaning they utilize organic and inorganic carbon for growth.

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \qquad \text{Equation 3}$$

Most treatment processes go through a cycle of nitrification followed by denitrification for the removal of nitrogen as nitrogen gas. However, an exception to this is a newer technology found in an Anammox® wastewater treatment application. The Anammox® involves a process in which heterotrophic bacteria utilize oxygen and convert ammonia and nitrite straight to nitrogen gas (Zang and Flere, 2007). The focus of this thesis will be centered on the concepts of denitrification and sorption since the columns will be operated at saturated conditions with low dissolved oxygen (anaerobic conditions).

Current Stormwater Nutrient Removal Techniques

Stormwater management is especially important in Florida because of the climate. Florida gets on average 50 or more inches of rainfall annually, which can quickly accumulate in impervious areas (USGS, 2007). Stormwater management systems serve three main purposes for stormwater runoff: attenuation of peak flow, runoff volume reduction and improvement in water quality. The systems are designed to control and treat runoff that may accrue from rainfall events. Stormwater management systems typically include both structural and non-structural best management practices. Best management practices (BMPs) are cost effective techniques, measures or structural controls that manage the quantity and improve the quality of stormwater runoff (EPA, 2008). BMPs rely on a number of physical, chemical and biological processes to achieve results including sedimentation, filtration, infiltration, adsorption, biological uptake and conversion, and degradation (EPA, 2008). Both retention and detention ponds are structural BMPs. Detention ponds temporarily hold water and then allow it to travel to a different location. Retention ponds however, contain water in one location until it evaporates or infiltrates. Because consecutive, large rainfall events decrease the effectiveness of detention ponds through means of short-circuiting, the construction of detention ponds has become less common. Therefore the main focus of this study is based around retention ponds. Detention ponds have typical pollutant removals of 50-80% suspended solids, 30-65% nitrogen, and 30-65% phosphorus. While retention ponds can have surface discharge removals of all compounds in excess of 90% (EPA, 2007).

Investigation of Media

Developments in retention pond technology, such as soil augmentations, have been shown to enhance performance. Augmentations to the soil with media mixes would be excellent, versatile improvements because they can be applied to current designs and in new construction. There have been numerous studies on the removal capabilities of media and media mixes, however not all have been stormwater applications. A comprehensive list of media investigated and the corresponding sources have been provided (Table 1).

Table 1: Sorption Media Summary for the Removal of Nitrogen and Phosphorous

No.	Sorption Media	Additional environmental benefits	References
1.	Peat	Cu, Zn, Ni, and Mo, Zn, PAHs (polyaromatic hydrocarbons)	DeBusk et al., 1997; Clark and Pitt, 1999; Clark et al., 2001; Braun-Howland, 2003; Zhou et al., 2003; Kietlinska and Renman, 2005
2.	Alfalfa		Kim et al., 2000
3.	Activated carbon	copper, iron, lead, zinc	Clark et al., 2001
4.	Carbon sand, Enretech sand, or sand		Bell et al., 1995; DeBusk et al., 1997; Clark and Pitt, 1999; Clark et al., 2001; Seelsaen et al. 2006
4a	Sandy Loam (SL), Loamy Sand (LS), and Sandy Clay Loam (SCL)		Gungor and Unlu, 2005
4b	Planting soil		Hsieh and Davis, 2003
5.	Sawdust (untreated)	Pesticide and phosphate	Kim et al., 2000; Gan et al., 2004
6.	Paper, newspaper		Kim et al., 2000
7.	Lignocellulosic Materials/wheat straw		Kim et al., 2000 ; Tshabalala, 2002
8.	Tire Crumb		Lisi et al., 2004
9.	Sulfur/Limestone	TSS	DeBusk et al., 1997; Kim et al., 2000; Kim et al, 2003; Darbi et al., 2002; Zhang, 2002 ; Sengupta and Ergas, 2006
9a	Crushed oyster and sulfur		Sengupta and Ergas, 2006.
10.	Wood fiber/wood chips	Polynuclear aromatic hydrocarbons	Kim et al, 2000; Jokela et al., 2002; Boving and Zhang, 2002; Kim et al, 2003; Savage and Tyrrel, 2005; Ray et al., 2006 ; Seelsaen et al. 2006
11.	Wood compost/ leaf mulch compost	Heavy metal	Richman, 1997; Clark and Pitt, 1999; Kim et al., 2000; Kim et al, 2003; Clark et al., 2001; Savage and Tyrrel, 2005; Seelsaen et al. 2006
12.	Zeolites	Benzene, sulfate , chromate	Clark and Pitt, 1999; Li, 2003; Seelsaen et al. 2006
13.	Cotton waste		Rocca et al., 2005
14.	Perlite		Redco II, 2007
15.	Clay	phosphates, thiocyanates, cadmium, lead, nickel	Harris et al., 1996 ; Gálvez et al., 2003 ; Lazaridis, 2003
15a	Zeolites+clay	phosphates,	Gisvold, B. et al., 2000
15b	Zeolites+bark	phosphates,	Bolan et al., 2004
16.	Shale and masonry sand		Forbes et al., 2005
17.	Waste foundry sand	TCE, alachlor, and Metolachlor, Zinc	Benson, 2001
18.	Acid soils (spodosols)		USDA, 2007
19.	Opoka	Zinc	Braun-Howland, 2003
20.	Wollastonite		DeBusk et al., 1997; Hedström, 2006
21.	Iron sulfide (pyrite)		Tesoriero et al., 2000 ; Baeseman et al., 2006
22.	Limerock		DeBusk et al., 1997
23.	Polyurethane porous media		Han et al., 2001
24.	Clinoptilolite		Hedström, 2006
25.	Blast furnace slag		Hedström, 2006
26.	Emulsified edible oil substrate		Lieberman et al., 2005
27.	Allophane		AEC, 2007
28.	Chitin		AEC, 2007
29.	Pumice		AEC, 2007
30.	Bentonite		AEC, 2007
31.	Oversize “pulverized” brick		Savage and Tyrrel, 2005

Reaction Kinetics

Kinetics is the study of how a reaction proceeds as a function of time. The rate of reaction can be defined as the changes in concentration of either the reactants or products changes over a period of time. The study of kinetics is useful for knowing the reaction rate and the design of chemical or biological reactors (Cooper et. al, 1990). If the reaction rate is known, then the required retention time in a system to enable the reaction can be determined. This knowledge can then be applied to quantifying the amount of sorption media and sizing the reactor. Rates of reactions can be influenced by factors such as temperature, concentration, and the presence of a catalyst. To calculate the rate of a reaction, it is assumed that the simplified form of an equation is used for the overall reaction. In other words, the intermediate steps of chemical reactions are not taken into account. The following equations are simplified versions of the zero, first, and second order rate equations (Fine et. al., 2000).

Zero Order: $dC/dt = k[C]^0$ Equation 4

1st Order: $dC/dt = k[C]^1$ Equation 5

2^{nd} Order: $dC/dt = k[C]^2$ Equation 6

Two different equations exist that relate the rate constant to temperature; the Arrhenius Equation and the Temperature Correction Factor Model (Equations 7 and 8). For the Arrhenius Model, k is the rate constant, A is the frequency factor, E_a is the activation energy, R is the universal gas constant, and T is absolute temperature. The frequency factor attempts to define the frequency of the reaction and the activation energy is the amount of energy require to initiate those reactions (Fine, 2007). The variables in the Temperature Correction Factor Model are defined as rate constant at temperature T (k_T), the rate constant at 20°C (k_{20}), the temperature correction factor (θ), and temperature in °C (T) (Fine, et. al, 2000). The Arrhenius Equation is typically applied to chemical reactions that have large temperature variations, whereas, the Temperature Correction Factor Model is applied to biological processes that have small temperature variations (Cooper, et. al., 2000). A temperature range of around 20°C will be used follow a typical guideline for studying kinetics (Fine, 2007). Since temperature has the ability to affect a reaction drastically, it is important to understand the system.

$$k = A\exp(-E_a / RT) \qquad \text{Equation 7}$$

$$k_T = k_{20}\theta^{(T-T_{20})} \qquad \text{Equation 8}$$

CHAPTER 3: DESIGN APPROACH / METHODS

Preliminary Media Selection

Initially a screening process was used to select media to be subjected to batch testing. A master list of media was comprised from literary searching to determine the properties of different substances and previously implemented products. Any type of media that could be used for removal of nitrogen or phosphorus or both was taken into consideration at this point. It is important to note a selection of media was not completed at this point. For example the list does not take into account how well the media performs, the cost, or whether it is available in Florida etc.

A system of multi-criteria decision making was applied to the master media list to narrow down which media would have the most potential for implementation in the batch study. Five categories were used with an assigned numerical value of 1-5. These categories include relevance for nitrogen and phosphorous, permeability, cost, availability in Florida, and additional environmental benefits. Each of these categories embodies an important factor in deciding which media to choose. The relevance category is intrinsic to the purpose of the project as it is important that the media be able to remove both nitrogen and phosphorus. The permeability of the media should allow drainage for a sufficient detention time. Cost is most important for the execution of the media mix in a large scale stormwater pond study. The cost should be affordable to ensure the most wide scale employment. It is important to note that this category is flexible since the final mixture will contain a number of different media mixes which will affect the cost. Since this study is based in Florida, it is desired that the media be available in state to support the

Floridian economy. In addition to possessing the ability to remove nitrogen and phosphorus, the media mixes could provide other environmental benefits. Some examples of these benefits include utilization of recycled material and ability of the media to remove other water contaminants. An equally weighted average of all five categories allowed for the selection of the best media. A summary of each of the media and their respective scores is shown in Table 2. From this table it is apparent that Florida peat, sandy loam, sawdust/wood chip, paper/newspaper, tire crumb, limestone, crusted oyster, and compost are the best media of the group. However, upon further deliberation some of these media were eliminated. The compost was eliminated because of the difficulty in mass producing a homogenous mix and the potential leaching of toxins into the soil. Newspaper was also eliminated for its potentially toxic effects if the ink used in printing were to leach out of the mixture and into the soil (Shah, 2006). Therefore the Medias selected for the batch studies include Florida peat, sandy loam, sawdust/wood chip, tire crumb, limestone, and crusted oyster. Sandy loam soils are a general classification, thus to be more specific a sandy soil of particular mix will be used.

Table 2: Sorption Media Assessment

No.	Sorption Media	Relevance		Permeability	Cost	Available in Florida	Additional Environmental Benefits	Overall*
		P	N					
1.	Florida Peat	5	5	5	5	5	5	**5**
2.	Alfalfa	3	3	1	1	0	5	2
3.	Activated carbon	5	1	1	1	0	5	2
4.	Carbon sand, Enretech sand, or sand	5	1	1	1	0	5	2
4a	Sandy Loam (SL), Loamy Sand (LS), and Sandy Clay Loam (SCL), Planting soil	5	5	3	5	5	5	**4.6**
5.	Sawdust (untreated wood)	3	5	3	5	5	5	**4.4**
6.	Paper, newspaper	3	5	3	5	5	5	**4.4**
7.	Lignocellulosic Materials/wheat straw	3	3	1	1	0	5	2
8.	Tire Crumb /electron donor	4	5	3	3	5	5	4.1
9.	Limestone/ electronic donor	2	5	1	5	5	5	**4.88**
9a	Crushed oyster/electronic donor	2	5	1	5	5	5	**4.88**
10.	Wood fiber/wood chips/compost	3	4	1	5	5	5	**4.88**
11.	Zeolites	4	3	1	1	0	5	2.1
12.	Cotton waste	2	1	3	1	0	5	2.1
13.	Perlite	4	1	1	1	0	5	1.9
14.	Shale and masonry sand	1	1	1	1	0	5	1.6
15.	Waste foundry sand	1	1	1	3	0	5	2
16.	Opoka	2	3	1	1	0	0	0.9
17.	Wollastonite	5	1	3	1	0	5	2.4
18.	Iron sulfide (pyrite)	4	3	1	1	0	0	1.1
19.	Limerock	1	4	1	5	5	0	2.7
20.	Polyurethane porous media	1	1	1	1	0	0	0.6
21.	Clinoptilolite	4	1	3	1	0	5	2.3
22.	Blast furnace slag	3	1	1	3	0	0	1.2
23.	Emulsified edible oil substrate	1	1	5	1	0	0	1.4
24.	Allophane	1	1	5	1	0	0	1.4
25.	Chitin	4	1	3	1	0	0	1.3
26.	Pumice	1	1	1	1	0	0	0.6
27.	Bentonite	5	3	5	1	0	5	3
28.	Oversize “pulverized brick	4	2	1	3	5	5	3.4
29.	Polystyrene packaging	1	1	1	1	5	0	1.6

Relevance: P (phosphorous unsaturated and saturated)
N (nitrogen saturated)
5 (excellent), 4 (very good), 3 (good), 2 (Fair), 1 (Poor)
Permeability and Cost: 1 (Low), 3 (Medium) , 5 (High)
Available in Florida and Additional Environmental Benefits: 5 (Yes) , 1 (No)
* Overall is calculated as weighted average based on equal weight among all five criteria

Batch Tests

The next stage in the study is to conduct batch testing of some media and media mixes to further narrow down which medias have the best removal potential. The media mixes selected from this testing will be analyzed in column studies. A combination of media mixes from the preliminary media selection and sources from Delaware, Maryland, and North Carolina in the literature were used to construct a batch testing matrix. The use of this matrix will allow for the marginal affects of the addition of each media to a mix. The matrix to be used for batch testing is shown in Table 3.

Table 3: Batch Test Recipes

Test case	Recipe	Marginal effect
Control case	100% fine sand/coarse silt	-
1	50% Sand/Silt 50% Sawdust	to test the marginal effect of adding Sawdust
2	50% Sand/Silt 50% Mulch (Wood Chips)	to test the marginal effect of adding Wood Chips
3	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 25% Florida Peat	to test the marginal effect of adding Peat
4	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 25% Tire Crumb	to test the marginal effect of adding Tire Crumb
5	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 15% Tire Crumb 10% Limestone	to test the marginal effect of adding Limestone with Tire Crumb
6	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 15% Tire Crumb 10% Oyster	to test the marginal effect of adding Oyster with Tire Crumb
7	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 15% Florida Peat 10% Oyster	to test the marginal effect of adding Oyster with Florida Peat
8	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 15% Florida Peat 10% Limestone	to test the marginal effect of adding Limestone with Florida Peat
9	50% Sand/Silt 15% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 15% Florida Peat 10% Limestone 10% Tire crumb	to test the marginal effect of adding Limestone with Florida Peat/Tire Crumb
10	50% Sand/Silt 15% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 15% Florida Peat 10% Oyster 10% Tire crumb	to test the marginal effect of adding Oyster with Florida Peat/Tire Crumb
11	50% Sand/Silt 10% Sawdust or Wood Chips (pick the one which has a better performance from tests 1 and 2) 10% Florida Peat 10% Oyster 10% Tire crumb 10% Limestone	to test the marginal effect of adding Limestone with Oyster, Florida Peat/Tire Crumb

Batch Test Procedure

Pond water from a wet detention pond adjacent to the UCF police station was collected for each run. 500mL Erlenmeyer flasks containing 250 mL of pond water and 30 grams of media mix from the list in Table 3 were assembled for each of the time intervals tested. These time intervals include 1 hour, 6 hours, 12 hours, 24 hours, and 48 hours.. Selecting an appropriate time step was an important part of the batch test experiment because of the continuous uptake and release of various nutrients within the filter media. These time intervals were selected following a few test runs to ensure that equilibrium was captured. The Erlenmeyer flasks were then placed on a shaker plate that rotates at 125 revolutions per minute (Figure 2). The mixing of the samples helps ensure contact area between the mixes and the pond water. The samples were then taken off of the shaker plate at their respective time intervals and filtered using a 4.5µm glass filter to get rid of the solids. The water quality analyses for each sample and the pond water to determine the performance of the media mix are shown in Table 4. Further explanations of the Hach procedures can be found in Appendix B

Table 4: Water Quality Parameters and Methods

Parameter	**Method**	**Range***
pH	pH probe	pH units
Nitrates + Nitrites	Hach methods 8192	0.01-0.50 mg/L $NO_3^{-}N$
Ammonia	Hach methods 8155	0.01-0.50 mg/L NH_3-N
Total Phosphorus	Hach methods 8190	0.02-2.50 mg/L PO_4^{3-}
Reactive/Orthophosphate	Hach methods 8048	0.02-2.50 mg/L PO_4^{3-}

*Note: In some cases samples were diluted with DI water to fall within this range.

Figure 2: Batch Test Media on Shaker Table

Soil Tests

ASTM Standard Practices are used to determine the density, void ratio, porosity, specific gravity, surface area conductivity. The ASTM D-421-85 Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants was used. The first step in the sieve analysis was to determine the mass (grams) of dry sample that will be tested. The sieves were prepared by stack the sieves in increasing order using sieve numbers 4, 10, 20, 40, 60, 100, 140, 200, 230, and 270, from top to bottom, respectively. A bottom pan is place under the stack of sieves. The sample is then poured into the stack of sieves and covered with a sieve cover. A sieve shaker shakes the sieves for approximately 10 minutes. When the sieve shaker stops, the stack of sieves are removed. The amount of soil retained on each sieve is weighed, starting from the top sieve (No. 4) to the bottom sieve (No. 270), and the bottom pan.

The specific gravity was measured using the ASTM D-854-92 Standard Test Method for Specific Gravity of Soils. The measured volume of the media was 100 g. The pycnometer was a volumetric flask having the capacity of 1,000 mL.

The coefficient of permeability was found using the falling head test method. The preparation of the soil specimen follows the same procedure as the ASTM Standard D 2434-68 for the constant head method. After the specimen has been saturated, any air bubbles within the tubing were removed. The time for the water to flow from the two selected heads, h_1 to h_2, was measured. Several trials were run and averaged. Then the permeability was converted to a test temperature of water at 20ºC.

Column Tests

Column Design and Setup

The columns are designed to simulate retention ponds with saturated conditions. Using three columns it is possible to test the performance of two mixes as compared with a control. The control column is filled with natural soil from the Hunters Trace Pond in Ocala, Florida. The soil is sun dried and sieved with a #10 sieve to remove vegetation, rocks, and large particles.

The clear Plexiglas columns have an inside diameter of 5.8 inches and are 3 feet in length. The bottom of each column contains a filter with three inches of fish tank rocks to prevent the media and soil mixes from exiting the columns and clogging the tubes. These columns are secured onto a constructed wooded frame with straps. Two ports are installed in each column to take core samples at different heights and retention times. In addition to the ports, the water is sampled from the bottom of each column. The gaps surrounding the ports are sealed with

Rectorsell 5 and Plumbing Amazing Goop. One peristaltic pump with peristaltic tubing is used to pump water from three, five gallon reservoirs into each of the columns. A fourth reservoir is used to maintain saturated conditions by connecting the column outlet tubing at a height equal to the desired water level inside the columns.

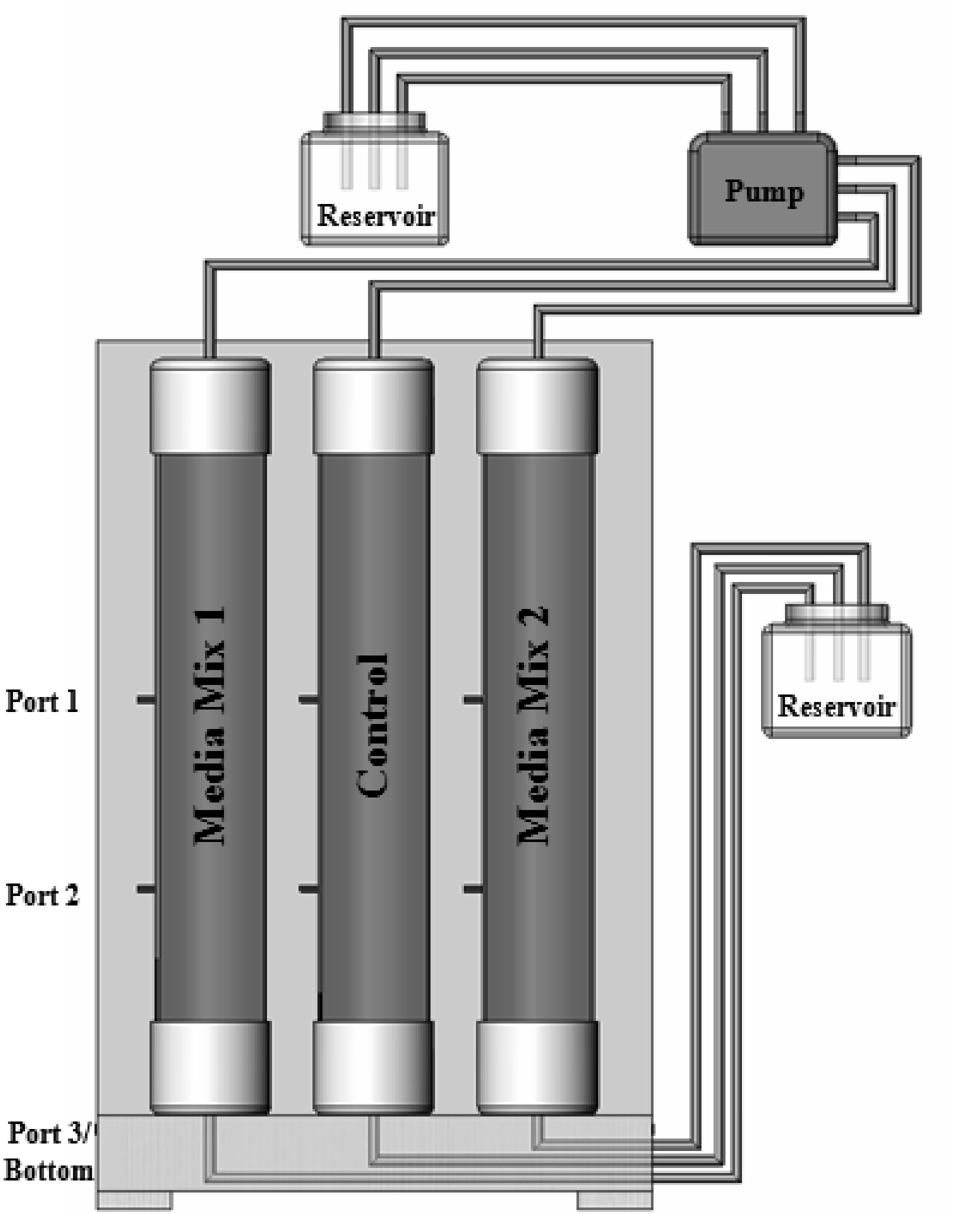


Figure 3: Experimental Column Design

The retention times for the columns is calculated using by entering the following equations into a MathCAD file so that any changes in parameters can be quickly adjusted. The contributing parameters include porosity (n), column inside diameter (d_{column}), and the height above sampling port (h). First, the volume ($V_{media(h)}$) was calculated using the following equation.

$$V_{media}(h) := \left[\frac{\pi \cdot \left(d_{column}\right)^2}{4} \cdot h\right] \cdot n \qquad \text{Equation 9}$$

Then using this volume and the desired retention time at the bottom of the column, the flow rate (Q) for the pump is calculated.

$$Q := \frac{V_{media3}}{\theta_3} = \cdot \frac{mL}{min} \qquad \text{Equation 10}$$

Lastly, using this flow rate the retention times for each port (θ) can be calculated.

$$\theta_1 := \frac{V_{media1}}{Q} = \cdot min \qquad \text{Equation 11}$$

The columns are placed in a room capable of setting a constant temperature for two of the temperatures and a refrigerator for the lowest temperature. This design will allow for the testing of the media mixes at various constant temperatures to determine the kinetics.

The pond water is first augmented with KNO_3 and HK_2PO_4 to pre-selected ranges and then pumped from each of the reservoirs through the columns. The concentration ranges were employed to validate the kinetics. Water samples are taken from three locations from each column; port 1, port 2 and port 3/the bottom. These samples are then tested for variations of nitrogen and phosphorus; a summary of these methods is in Table 5. Again, further details into the procedures can be found in Appendix B.

Table 5: Column Study Water Quality Parameters and Methods

Parameter	Method	Range*
pH	Fisher Scientific Accumet portable AP61 pH meter	pH units
Dissolved Oxygen	YSI Model 58 DO Meter	
Nitrates + Nitrites	Hach method 8192	0.01-0.50 mg/L NO_3^-N
Nitrites	Hach method 8507	0.002-0.30 mg/L NO_2^-N
Ammonia	Hach method 8155	0.01-0.50 mg/L NH_3-N
Total Nitrogen	Hach Method 10071	0.5-25.0 mg/L N
Reactive/Orthophosphate	Hach method 8048	0.02-2.50 mg/L PO_4^{3-}

*Note: In some cases samples were diluted with DI water to fall within this range.

Column Analysis

When the rate of the equation is unknown, as in this experiment, other methods for determining the rate constant can be employed. This type of analysis is often referred to as determining the rate constant from the integrated rate law. The integrated rate law involves integrating the rate law and arranging the equation in terms of the linear equation of a line (Equations 12-14). The definitions of the variables are [C] is the final concentration of the reactant, $[C_0]$ is the initial concentration of the reactant, k is the rate constant, and t stands for time.

Zero Order: $[C] = -kt$ Equation 12

1st Order: $\text{Ln}[C] = -kt + \ln[C_o]$ Equation 13

2^{nd} Order: $1/[C] = kt + 1/[C_o]$ Equation 14

This type of analysis will be applied to the columns in an attempt to describe the removal in terms of zero, first, or second order kinetics. The concentrations, inverse concentrations, and natural log of concentrations are plotted versus the retention time to show the removals as low order kinetic functions. A linear regression will be applied to each condition and the mean squared error will be displayed to determine the best fit.

To investigate the actual values for the reaction rate, the differential rate law equations will be used. The following equations were manipulated using the previously defined rate equations and will be used to model both the nitrate and orthophosphate (Equations 4-6). It is important to note that in general the reaction rate can be determined using all of the reactants. For the modeling purposes of this paper, only the investigated nutrients will be used.

Zero Order Rate Model:

$dC/dt = k[C]^0$ Equation 4

$dC/dt = k[NO^{-}{}_3 - N]^0$ Equation 4a

$dC/dt = k[PO_4^{3-} - P]^0$ Equation 4b

1st Order Rate Model:

$dC/dt = k[C]^1$ Equation 5

$dC/dt = k[NO^{-}{}_3 - N]^1$ Equation 5a

$$dC/dt = k[PO_4{}^{3-} - P]^1$$ Equation 5b

2nd Order Rate Model:

$$dC/dt = k[C]^2$$ Equation 6

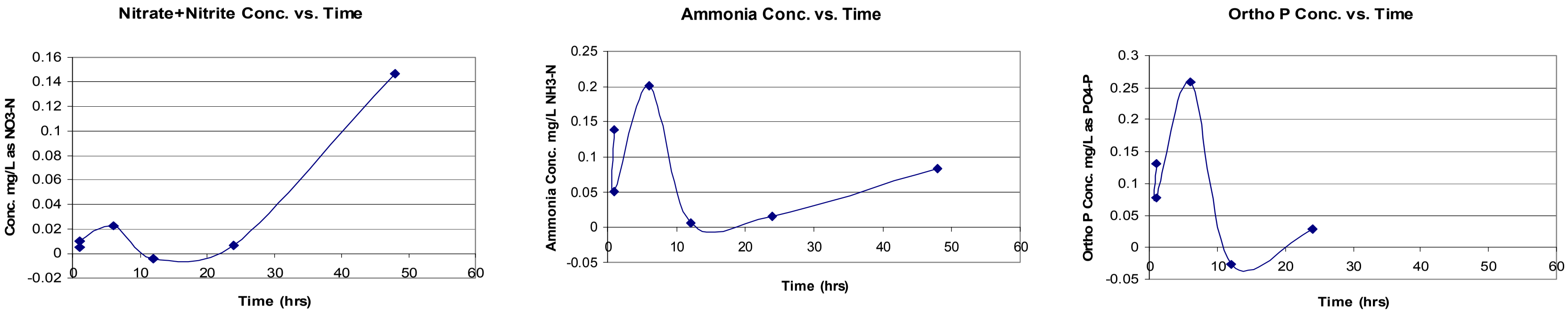
$$dC/dt = k[NO^-{}_3 - N]^2$$ Equation 6a

$$dC/dt = k[PO_4{}^{3-} - P]^2$$ Equation 6b

CHAPTER 4: RESULTS & DISCUSSION

Batch Test Results

The results of the batch test are critical for determining the type of media mix that will be studied in the column testing. An overall analysis on the media selection process based on the Batch Test results will be discussed in the following section. To provide the results from each recipe the following table was assembled (Table 6). The results of the batch test showed that the media added ammonia to the pond water. As expected the nitrate did not readily convert to nitrogen gas and leave the system, due to the aerobic conditions of testing. For each media mix the nutrient level of the initial pond water minus the nutrient level in the water after it was subjected to the media mix for the given time interval was calculated. The nutrient removal was found by subtracting the initial concentration in the pond water from the concentration after the time interval. The negative values in the graphs show removals. The following figures were selected to illustrate the best examples of the batch testing. Figure 4 demonstrates that the mixture of 50% Sand, 25% Sawdust, and 25% Tire Crumb achieved the high orthophosphate removals, however this blend adds nitrate species to the water. A comparison of this blend with one of the more complex blends (Figure 5) illustrates that the test case number 5 achieved the highest overall orthophosphate removals. The blend shown in Figure 5 contains limestone, which is suspected to have capabilities of nutrient removal and pH stabilization. This was confirmed from comparison of batch test results with all of the blends found in Table 6 and ultimately lead to it's incorporation into the media mixes selected for column studies.

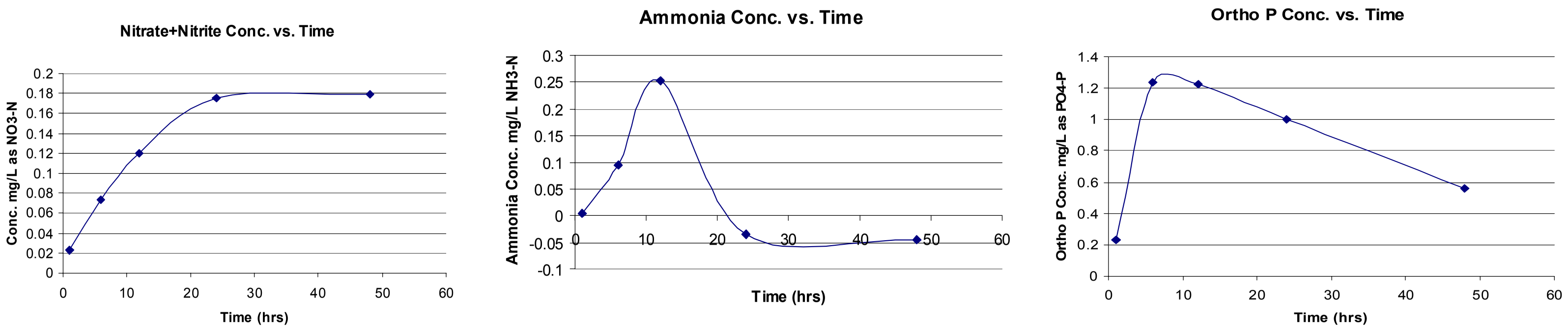


Initial Conc. = 0.17 mg/L NO_2^--N+ NO_3^--N

Initial Conc. = 0.02 mg/L NH_4^+-N

Initial Conc. = 0.02 mg/L PO_4^{3-}-P

Figure 4: Batch Test Results for 50% Sand, 25% Tire Crumb, and 25% Sawdust (Final Concentration Minus Initial Concentration)



Initial Conc. = 0.07 mg/L NO_2^--N + NO_3^--N

Initial Conc. = 0.06 mg/L NH_4^+-N

Initial Conc. = 0.16 mg/L PO_4^{3-}-P

Figure 5: Batch Test Results for 50% Sand, 15% Peat, 15% Sawdust, 10% Tire Crumb, 10% Limestone (Final Concentration Minus Initial Concentration)

Table 6: Batch Test Results

Test case	Recipe	Results
Control case	100% fine sand/coarse silt	The control case showed Nitrate, Total-P and Ortho-P removal from the water, the control case also added Ammonia to the sample.
1	50% Sand/Silt 50% Sawdust	Test 1 showed Ammonia removal and also Nitrate, Total-P and Ortho-P Addition.
2	50% Sand/Silt 50% Mulch (Wood Chips)	Test 2 showed slight Ammonia addition and significant Nitrate, Total-P and Ortho-P addition. **Sawdust had less addition of ammonia, nitrate, ortho-P and total-P than woodchips. Therefore sawdust is the preferred electron acceptor.**
3	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 25% Florida Peat	Test 3 showed Ammonia removal and the addition of Nitrate, Total-P and Ortho-P.
4	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 25% Tire Crumb	Test 4 showed decreased concentrations of ortho-P and increased concentrations of Total-P, Nitrate and Ammonia.
5	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 15% Tire Crumb 10% Limestone	Test 5 showed a decrease in Total-P, Ortho-P, Nitrate and Ammonia.
6	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 15% Tire Crumb 10% Oyster	Test 6 showed an increase in Total-P, Ortho-P, Nitrate and Ammonia.
7	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 15% Florida Peat 10% Oyster	Test 7 showed that crushed Oyster shell with Peat decreases Total-P, Ortho-P, and Nitrate concentrations.

Table 6 Continued: Batch Test Results

Test case	Recipe	Results
8	50% Sand/Silt 25% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 15% Florida Peat 10% Limestone	Test 8 showed that Limestone contributed a higher concentartion of Ortho-P than crushed oyster shell. The Limestone added less ammonia and Total-P than the crushed oyster shell.
9	50% Sand/Silt 15% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 15% Florida Peat 10% Limestone 10% Tire crumb	Comparing tests 5 and 8 the addition of tire crumb has provided for lower contribtrations of Nitrate, Total-P, and Ortho-P. Ammonia removal was uneffected by the presence of Tire Crumb.
10	50% Sand/Silt 15% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2)) 15% Florida Peat 10% Oyster 10% Tire crumb	The limestone in test 9 performs better than crushed Oyster shell in test 10 with respect to Ammonia and Total-P removal.
11	50% Sand/Silt 10% Sawdust or Wood Chips (pick the one which performs better in tests 1 and 2) 10% Florida Peat 10% Oyster 10% Tire crumb 10% Limestone	Comparing test 11 to tests 9 and 10 showed that the Limestone appears to help increase the performance of the media blend with respect to Ammonia, Ortho-P, Total-P and Nitrate.

Media Selection

When analyzing the batch test results it is important to remember a few key concepts. First, the batch tests are conducted during aerobic conditions and therefore processes that require an absence of oxygen will not occur. An example of this is denitrification. Since this is the mechanism that removes the nitrogen, nitrate removals in the batch tests are expected to be minimal. Secondly, the final media blends must contain an electron donor to facilitate this denitrification process. Ortho-phosphorous is expected to be removed via sorption, causing the main focus of the batch tests to be determining the best media for orthophosphate removal.

The results of the batch test experiments indicate that the potential electron donors Florida peat, sawdust and woodchips add considerable ortho-P, total P, nitrate and ammonia to the water sample. Out of the three electron donors that were tested sawdust added the least nutrients to the water sample and therefore is considered the best option for usage in stormwater filter media. Tire crumb was highly effective at reducing ortho P in the water samples.

The best filter media mix with respect to phosphorus and nitrate removal may be hard to attain. The denitrification process requires electron donors although it is uncertain how much is required for prolonged denitrification. The results of the batch tests show that nutrient concentrations increase as the percentage of electron donors in the media blend increase. This uncertainty lead to constructing the mixes with varying quantities of sawdust for further testing in the column study. Obviously, the nutrient additions of each media will also be taken into consideration and the media that removes the most nutrients or adds the least will be chosen.

Using the results from these criteria and the batch test results, the selected two media recipes are Media Mix 1 consisting of 50% fine sand, 30% tire crumb, 20% sawdust by weight and Media Mix 2 consisting of 50% fine sand, 25% sawdust, 15% tire crumb, 10% limestone by weight. The removal capabilities and kinetic reactions of the Mixes and a Control consisting of natural soil from Hunter’s Trace Pond were tested in column studies.

Material Characterization

Figure 6 shows the particle distribution curve for the Hunter's Trace soil. It is a well graded or evenly distributed soil. The effective size of the soil is 0.16 mm. The effective size is defined as 10 percent of the sample passing through that sieve size. According to Das 2006, effective size is a good indication of hydraulic conductivity. The selected media mixes are then packed into the other two columns. The particle size distributions and other characteristics for the media are shown in the following figures. The particle-size distribution of Media Mix 1 is poorly graded as seen in Figure 7. The effective size for Media Mix 1 is approximately 0.075 mm. The particle-size distribution of Media Mix 2 is poorly graded as seen in Figure 8. The effective size for Media Mix 2 is approximately 0.08 mm.

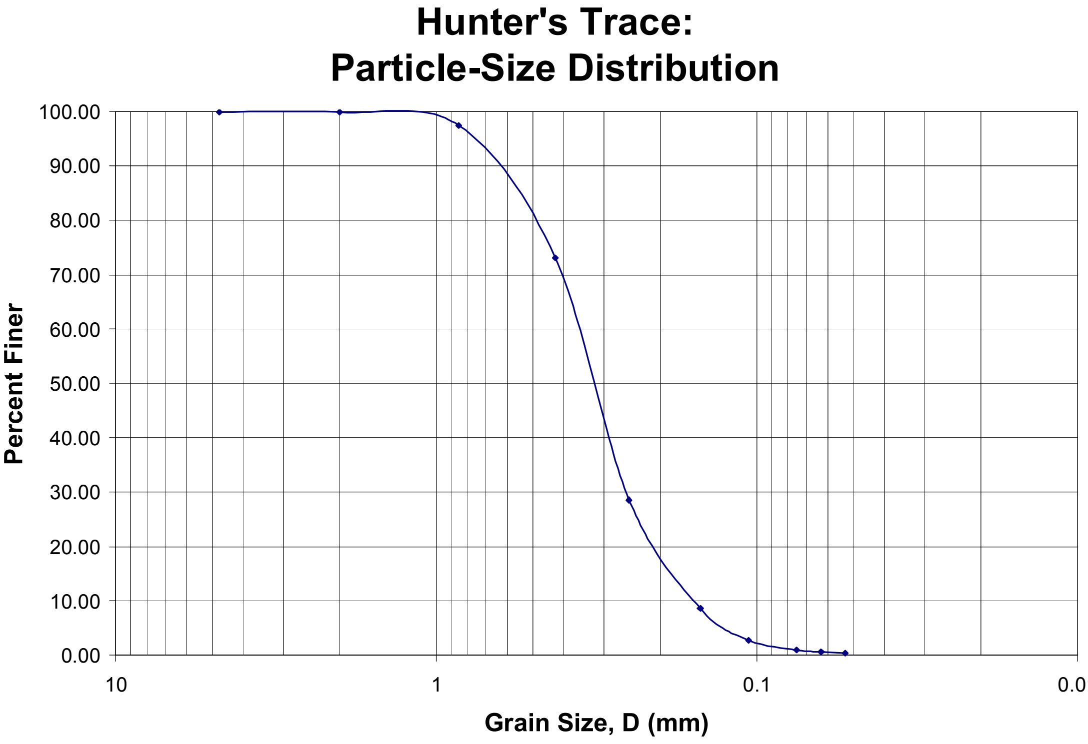


Figure 6: Control Particle-Size Distribution (Naujock, 2008)

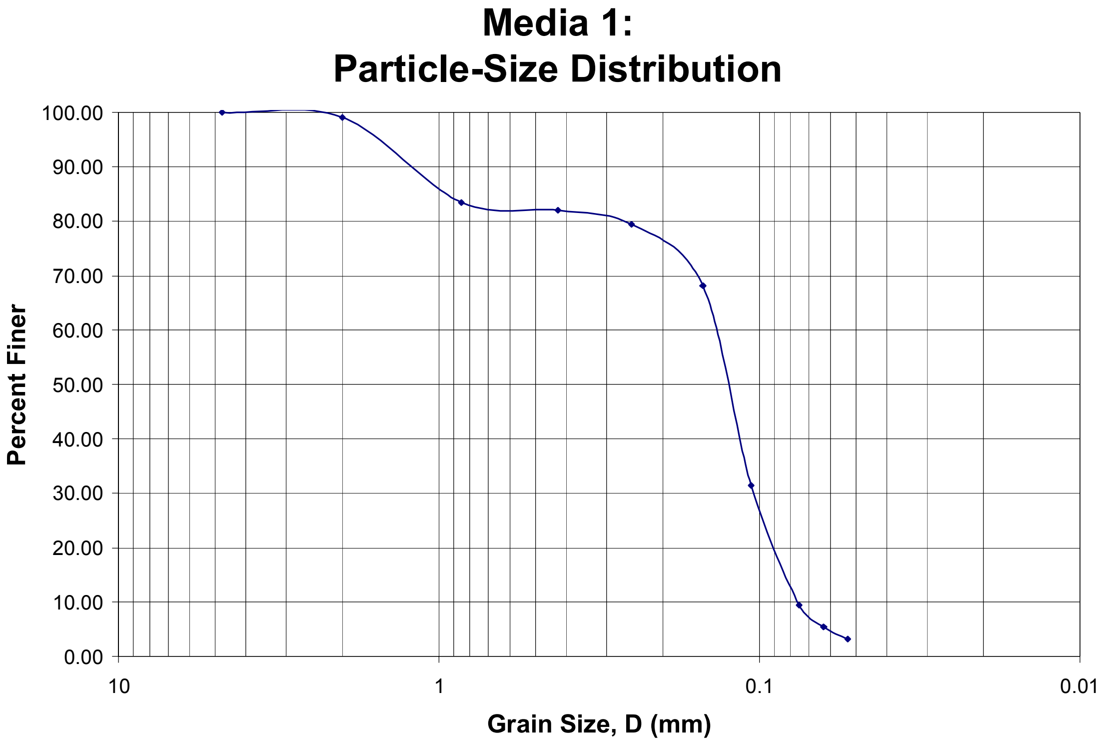


Figure 7: Media 1 Particle-Size Distribution (Naujock, 2008)

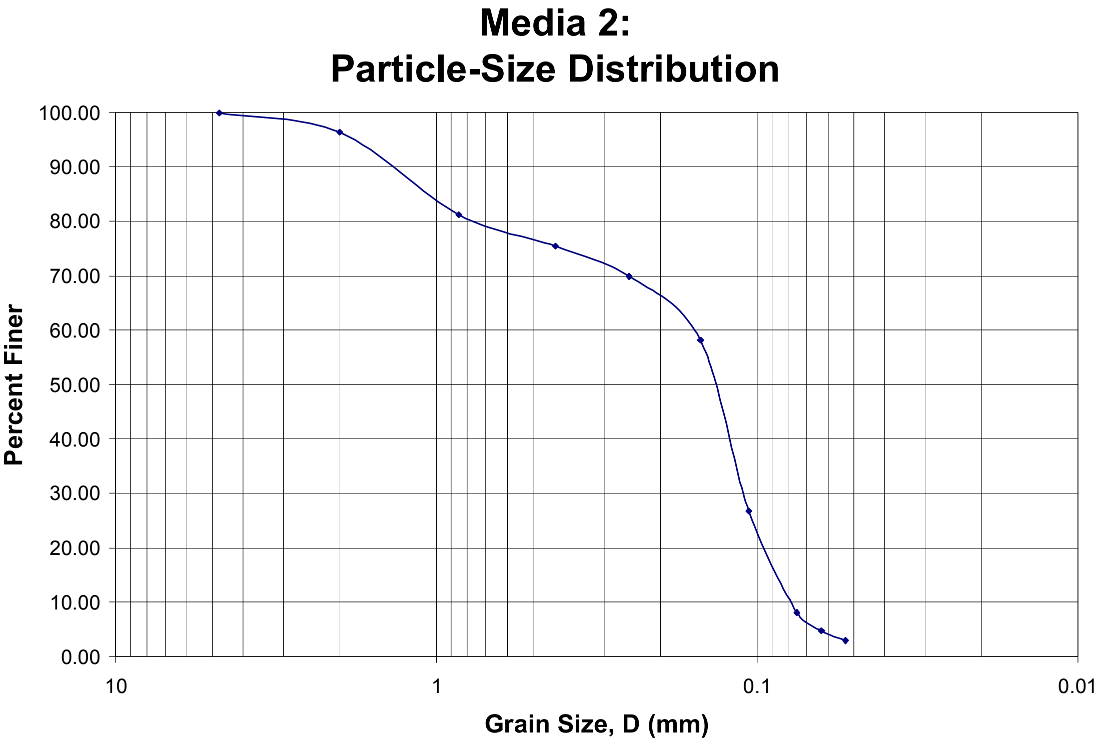


Figure 8: Media 2 Particle-Size Distribution (Naujock, 2008)

The material characteristics of the natural Hunter's Trace soil and Media amendments are shown in Table 7. The two Medias appear to be similar. The Medias have different specific gravities than the Control (Hunter's Trace Soil) due to the increased amount of organic material. The porosity of the Medias are greater than the Hunter's Trace soil and therefore may allow for a quicker flow.

Table 7: Material Characteristics (Naujock, 2008)

	Hunter's Trace (dry sample)	**Hunter's Trace (moist sample)**	**Media 1**	**Media 2**
Density (g/cm^3)	1.56	1.73	1.41	1.44
Void Ratio	0.67	0.51	0.56	0.62
Porosity	0.40	0.34	0.36	0.38
Specific Gravity (Gs)	2.62	2.62	2.19	2.33
Surface Area (m^2/g)	-	-	0.129	0.242
Conductivity (in/hr)	24.6	1.76	4.38	3.62

Column Test Results

Before the results of the column testing are presented, a few notes on how the data were obtained require discussion. Some data may appear to be missing for the control column. This is due to the fact that throughout the entire course of the experiments the first port on the control column was clogged; preventing sampling. Attempts to rectify this problem were futile as the moist porosity of the Hunter's Trace soil was small compared to the other two mixtures. Although the column data is presented in order of temperature, the columns were actually exposed to the temperatures in a different order. The lowest temperature was tested last, because it was expected to have a detrimental effect on the microbial activity. Thus, the temperatures in order of testing are 23°C, 28°C, and 10°C.

The columns will be discussed on an individual basis first, followed by a comparison of the columns by temperature and media content. Lastly, the scientific validity of the results will be tested through statistical analysis. Throughout these investigations removals are assumed to be positive; therefore a negative value would indicate an increase or addition.

The control column at 10 °C had very low removal efficiencies for nitrogen species (Table 8). When passing through the Hunter's Trace soil nitrite and ammonia levels increased for both low and high dose concentrations. However the column did achieve low removals of nitrate for both dosages, however it performed a 3% better for the higher dosage. Total nitrogen was only removed with higher nitrate dosages. The control column achieved high removal efficiencies for orthophosphate, again the high dosage exhibited out performed the low dosage.

The two Media Mix columns showed similar responses to testing for both concentrations at 10 °C (Tables 9 & 10) . Both mixes outperformed the control for nitrogen species and were outperformed by the control for orthophosphate. The media mixes had moderate removal levels for nitrate and total nitrogen. For total nitrogen both mixes were able to remove more at lower dosages. Media Mix 2 had higher removal efficiencies for nitrate at lower nitrate doses. Media Mix 1, however, removes approximately the same amount regardless of the initial nitrate dose. Media Mix 1 and 2 had higher removals of orthophosphate with higher initial phosphorus concentrations. When considering orthophosphate Media Mix 2 removed twice as much orthophosphate as Media Mix 1 for the higher dosage case, putting its removal capabilities around the average for the control column.

Table 8: Average Performance of Control Column at 10 °C

CTRL 10° C	**NO_2^-+ NO_3^-** - N		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	---	---	---	---	---	---	---	---	---	---	---	---
Port 2	-9.7%	14.1%	-241.3%	-288.8%	-9.3%	15.6%	-10.2%	20.2%	-7.5%	0.8%	32.3%	96.8%
Port 3	6.2%	9.4%	-203.7%	-47.7%	6.5%	9.5%	-64.6%	-66.9%	-23.5%	10.7%	76.0%	93.6%

*Note: Initial Dose N: Low Concentration Range (7, 13, 17 mg/L NO_3^--N) and High Concentration Range (19, 23, 24 mg/L NO_3^--N)
OP: Low Concentration Range (3, 3.5, 4 mg/L PO_4^{3-}) and High Concentration Range (6, 7, 9 mg/L mg/L PO_4^{3-})

Table 9: Average Performance of Mix 1 Column at 10 °C

MIX 1 10° C	**NO_2^-+ NO_3^-** - N		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	42.2%	30.1%	-7711.4%	-4673.5%	58.4%	45.9%	-152.6%	-185.8%	25.7%	23.5%	4.8%	32.1%
Port 2	51.8%	30.5%	-5849.1%	-3384.2%	61.3%	46.3%	-332.0%	-341.2%	36.2%	29.0%	14.7%	34.2%
Port 3	56.2%	51.8%	-8281.4%	-4124.4%	69.4%	70.1%	-180.4%	-166.5%	48.2%	38.4%	36.7%	40.3%

*Note: Initial Dose N: Low Concentration Range (7, 13, 17 mg/L NO_3^--N) and High Concentration Range (19, 23, 24 mg/L NO_3^--N)
OP: Low Concentration Range (3, 3.5, 4 mg/L PO_4^{3-}) and High Concentration Range (6, 7, 9 mg/L PO_4^{3-})

Table 10: Average Performance of Mix 2 Column at 10 °C

MIX 2 10° C	**NO_2^-+ NO_3^-** - N		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	5.2%	20.0%	-10388.5%	-223.1%	28.3%	21.0%	16.4%	15.4%	0.5%	0.6%	10.9%	10.2%
Port 2	2.3%	19.0%	-27586.0%	-548.2%	67.4%	22.0%	-108.7%	-33.4%	10.3%	13.1%	14.0%	50.0%
Port 3	38.7%	45.7%	-20280.4%	-353.0%	79.6%	46.8%	-487.9%	22.5%	33.5%	30.9%	35.4%	82.1%

*Note: Initial Dose N: Low Concentration Range (7, 13, 17 mg/L NO_3^--N) and High Concentration Range (19, 23, 24 mg/L NO_3^--N)
OP: Low Concentration Range (3, 3.5, 4 mg/L PO_4^{3-}) and High Concentration Range (6, 7, 9 mg/L PO_4^{3-})

The control column at 23 °C had moderate efficiencies for nitrogen species (Table11). When passing through the Hunter's Trace soil, nitrite and ammonia levels increased for both low and high dose concentrations. The control column did achieve moderate removals of nitrate when the initial dosage was low. For the case with the higher initial nitrate concentration the column removed around 26% of the nitrate by the time it reached the second port. But the nitrate levels increased higher than the initial dose by the time it reached the bottom causing the overall removal for the column to be zero. Nitrite levels increased in the column, however the greatest amount of nitrite was found at port 2. Approximately 28 % of the total nitrogen was removed for both dosing situations. The control column achieved high removal efficiencies for orthophosphate, again the high dosage exhibited out performed the low dosage. At this temperature dosing conditions had a greater impact on orthophosphate removals than at the lower temperature. The removals differed by 30% between the two initial dosing conditions.

At 23 °C the media mixes performed similarly in respect to removal of nitrogen species and orthophosphate (Table 12 and 13) . The actual efficiencies of the columns improved around 15% for the removal of nitrate and 30% for total nitrogen. In terms of orthophosphate removal Media Mix 1 had approximately 63% removal for both dosages, while Media Mix 2 had 53% for lower dosage and 82% for higher dosages. In this respect, the media mixes performed as well or better than the control case with lower dosages. The control column does outperform the mixtures overall with a 95% removal at high doses of orthophosphate.

Table 11: Average Performance of Control Column at 23 °C

CTRL 23° C	**NO_2^-+ NO_3^- - N**		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	---	---	---	---	---	---	---	---	---	---	---	---
Port 2	30.8%	25.3%	-157.8%	-9287.4%	31.9%	26.4%	-4788.2%	-6272.7%	38.3%	29.0%	-15.9%	95.2%
Port 3	49.1%	-8.0%	-90.3%	-414.6%	49.7%	-7.9%	-9981.5%	-8827.9%	30.0%	26.6%	64.3%	95.7%

*Note: Initial Dose N: Low Concentration Range (6.2,6.8,7.2 mg/L NO_3^--N) and High Concentration Range (19,20,31 mg/L NO_3^--N)
OP: Low Concentration Range (1,1.9,2.3 mg/L PO_4^{3-}) and High Concentration Range (3,4,5 mg/L PO_4^{3-})

Table 12: Average Performance of Mix 1 Column at 23 °C

MIX 1 23° C	**NO_2^-+ NO_3^- - N**		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	74.5%	41.6%	-1386.4%	-117960.7%	81.4%	64.1%	-3202.3%	-2167.0%	71.2%	56.8%	29.7%	40.7%
Port 2	87.5%	55.6%	-750.9%	-157321.9%	91.0%	77.3%	-2460.6%	-2932.7%	83.2%	72.0%	24.8%	55.0%
Port 3	89.6%	46.9%	-993.0%	-130481.8%	94.1%	65.4%	-2067.4%	-2282.3%	85.9%	74.5%	63.8%	62.8%

*Note: Initial Dosing N: Low Concentration Range (6.2,6.8,7.2 mg/L NO_3^--N) and High Concentration Range (19,20,31 mg/L NO_3^--N)
OP: Low Concentration Range (1,1.9,2.3 mg/L PO_4^{3-}) and High Concentration Range (3,4,5 mg/L PO_4^{3-})

Table 13: Average Performance of Mix 2 Column at 23 °C

MIX 2 23° C	**NO_2^-+ NO_3^- - N**		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	57.2%	12.3%	-821.9%	-26152.0%	60.7%	16.4%	-5269.5%	-410.7%	57.1%	32.2%	29.8%	48.7%
Port 2	63.1%	45.5%	-1065.9%	-100857%	67.6%	56.2%	-1565.3%	-575.0%	61.7%	63.0%	62.8%	62.9%
Port 3	81.8%	61.7%	-301.6%	-91019.5%	83.4%	72.4%	11.1%	-1582.2%	55.8%	71.2%	52.5%	82.4%

*Note: Initial Dosing N: Low Concentration Range (6.2,6.8,7.2 mg/L NO_3^--N) and High Concentration Range (19,20,31 mg/L NO_3^--N)
OP: Low Concentration Range (1,1.9,2.3 mg/L PO_4^{3-}) and High Concentration Range (3,4,5 mg/L PO_4^{3-})

At the last temperature tested, 28 °C, the control column performed differently than at the other temperatures (Table14). The control column reached it's highest nitrate removal at low dosage at port 2 (77%) instead of the bottom of the column (48%). The nitrate removal for high dosage was reached at the bottom of the column (44%), but was lower than the removals for low dosage. Total nitrogen removal was also greatest at port 2 in the column, and was higher for the low dosage case. Orthophosphate followed this same trend, however it had greater removal at port 2 for higher doses and greater removal at the bottom of the column for lower doses.

The media mixes also followed this new trend of achieving greater removal at port 2 instead of at the bottom of the column for some instances (Tables 15 and16). Media Mix 1 and 2 had the highest removals of nitrate at the second port for the low dose situation. But the highest removal for the high dose continued to be at the bottom of the column. Media Mix 1 had approximately the same removals for the bottom of the column at around 95%. Media Mix 2 however had a 40% difference in removal at the bottom, with the greatest removal at high doses (90%). Nitrite addition continued to be a problem for both media mixes, with nitrite levels at their highest at ports 1 and 2. Total nitrogen removals were, for the most part, at the bottom of the columns. The only exception is for Mix 1, which shows a 2% greater removal of total nitrogen at port 2. Orthophosphate removals mostly decreased as the water passed through both of the media columns. Although, Media Mix 1 has its highest removal at port 1 for the low dose concentrations. This difference however is within 1% of the removal at the bottom of the column.

Table 14: Average Performance of Control Column at 28 °C

CTRL	**NO_2^-+ NO_3^-** - N		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
28° C	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	---	---	---	---	---	---	---	---	---	---	---	---
Port 2	75.1%	29.7%	-200.7%	-251.7%	76.6%	30.3%	-320.7%	-418.6%	68.5%	32.4%	83.4%	93.8%
Port 3	47.6%	43.5%	-16.4%	-55.6%	47.8%	43.8%	-397.0%	-837.8%	48.6%	27.6%	75.0%	69.3%

*Note: Initial Dosing N: Low Concentration Range (2.8-5.8 mg/L NO_3^-) and High Concentration Range (8-12 mg/L NO_3^-)
OP: Low Concentration Range (1.6-5 mg/L PO_4^{3-}) and High Concentration Range (5.5-7.4 mg/L PO_4^{3-})

Table 15: Average Performance of Mix 1 Column at 28 °C

MIX 1	**NO_2^-+ NO_3^-** - N		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
28° C	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	55.9%	70.5%	-6869.6%	-165.3%	74.6%	71.3%	-103.6%	-298.4%	57.2%	-85.2%	62.7%	39.3%
Port 2	87.6%	81.2%	-2750.5%	-4143.6%	97.0%	86.0%	-28.4%	-564.3%	79.3%	75.9%	50.9%	52.9%
Port 3	84.2%	91.0%	-2949.7%	-2069.5%	96.7%	94.0%	-68.9%	-335.3%	82.5%	73.6%	61.4%	58.5%

*Note: Initial Dosing N: Low Concentration Range (2.8-5.8 mg/L NO_3^-) and High Concentration Range (8-12 mg/L NO_3^-)
OP: Low Concentration Range (1.6-5 mg/L PO_4^{3-}) and High Concentration Range (5.5-7.4 mg/L PO_4^{3-})

Table 16: Average Performance of Mix 2 Column at 28 °C

MIX 2	**NO_2^-+ NO_3^-** - N		**NO_2^-** - N		**NO_3^-** - N		**NH_4^+-N**		**TN-N**		**OP** (PO_4^{3-}-P)	
28° C	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.	Low Conc.	High Conc.
Port 1	41.0%	61.2%	-1671.8%	-1235.3%	46.4%	63.5%	-55.9%	-113.6%	30.2%	50.6%	36.9%	55.5%
Port 2	75.3%	85.7%	-2762.2%	-391.1%	82.8%	86.8%	-70.4%	-142.4%	79.1%	76.3%	73.7%	63.8%
Port 3	36.7%	89.2%	-753.2%	8.6%	97.8%	89.5%	-8.8%	-104.5%	86.9%	85.0%	80.4%	90.7%

*Note: Initial Dosing N: Low Concentration Range (2.8-5.8 mg/L NO_3^-) and High Concentration Range (8-12 mg/L NO_3^-)
OP: Low Concentration Range (1.6-5 mg/L PO_4^{3-}) and High Concentration Range (5.5-7.4 mg/L PO_4^{3-})

Figures 9, 10, and 11 provide a visual representation of the nitrate removal through the columns at each temperature. The values for removal efficiency at each port were calculated by averaging the removals at each port combining high and low dosages. In the case of 10°C the removal efficiencies seem to follow an increasing trend as the water travels through the column. Media Mix 1 has the greatest efficiency at each port. Nitrate removals at 23°C appear to follow a similar pattern. However, the columns responded unusually at port 3 and the efficiency of the Control and Media Mix 1 decreased slightly. In fact, the decrease for Media Mix 1 of only 0.3% could be considered negligible. Lastly, at 28°C the removal efficiencies increase as the water flows down the column and Media Mix 1 always achieved the greatest removals. The control efficiency decreased slightly between the second and third ports.

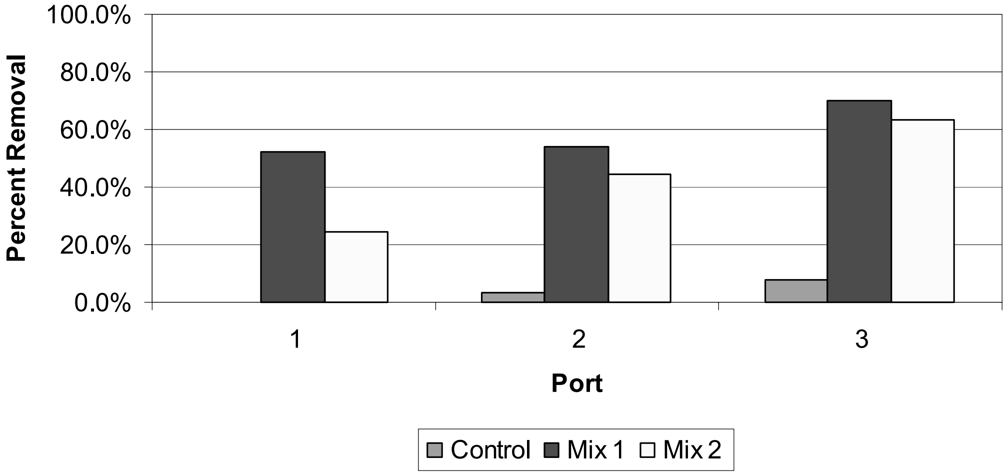


Figure 9: Nitrate Removal Through Columns at 10°C

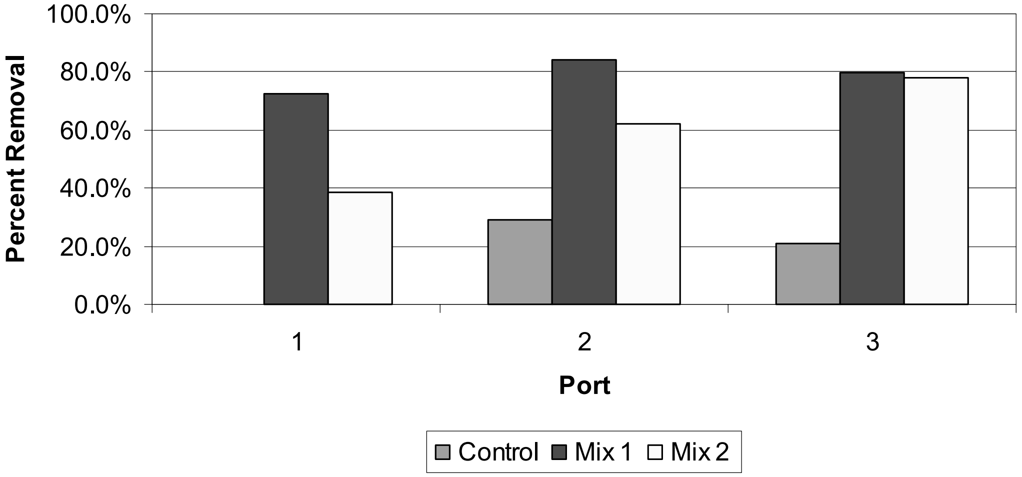


Figure 10: Nitrate Removal Through Columns at 23°C

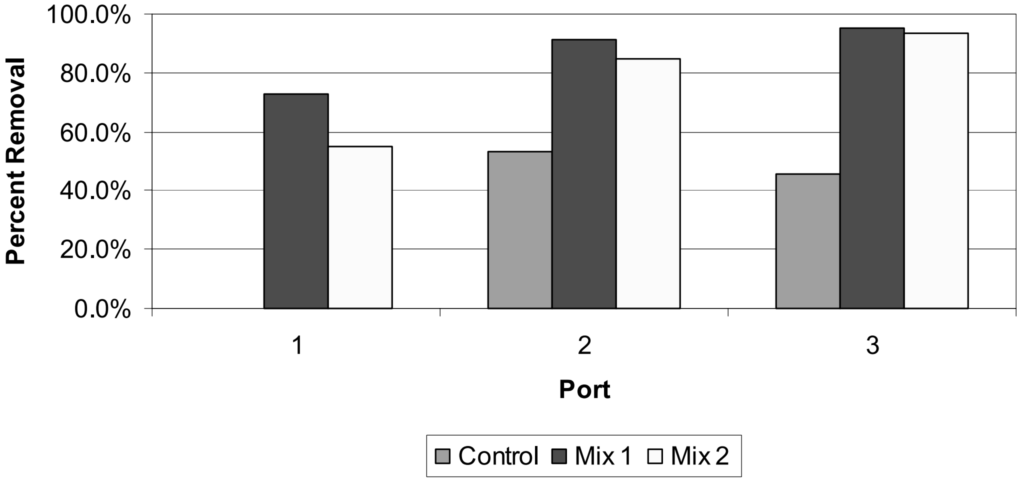


Figure 11: Nitrate Removal Through Columns at 28°C

A corresponding representation of the orthophosphate removal through the columns at each temperature was constructed (Figures 12-14). Once again, the values for removal efficiency at each port were calculated by averaging the removals at each port combining high and low dosages. The data does not appear to follow the same trends with respect to port and temperature. At the lowest temperature, the removal increases as the water passes through the columns. The Control column executes the highest removal for most cases. Media Mix 2 and 3 operated in a similar manner with Media Mix 2 having just slightly higher removals. At 23°C, all of the columns showed different reactions as the water flowed downward. The control column was outperformed by Media Mix 2 at the second port, only to achieve the highest removal of each column by the bottom. Media Mix 1 and 2 have similar removals at port 1 and 3, but Media Mix 2 has the greatest efficiency of all the columns by port 2. Lastly, the 28°C case is considered. The control achieves the highest removal of all three ports by port 2 and then decreases by port 3. Media Mix 1 efficiencies average around 56%. For Media Mix 2, the efficiency amplifies with each port, causing it to go from last place to first.

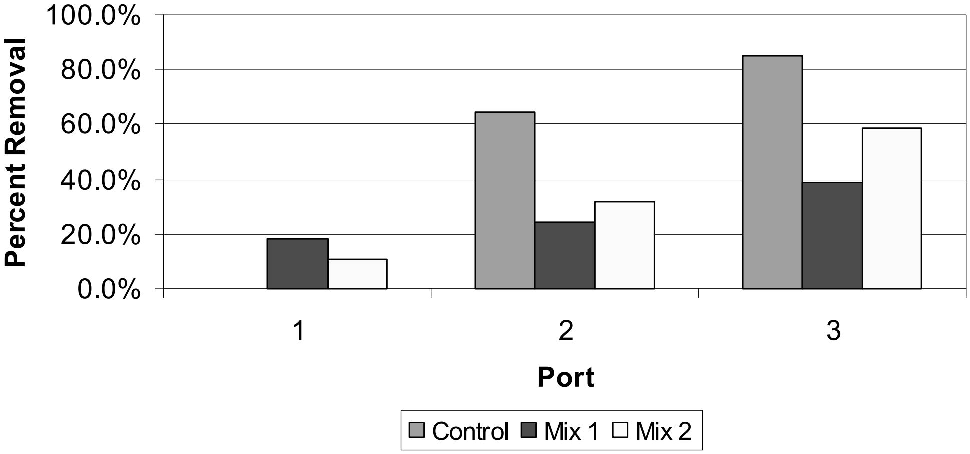


Figure 12: Orthophosphate Removal Through Columns at 10°C

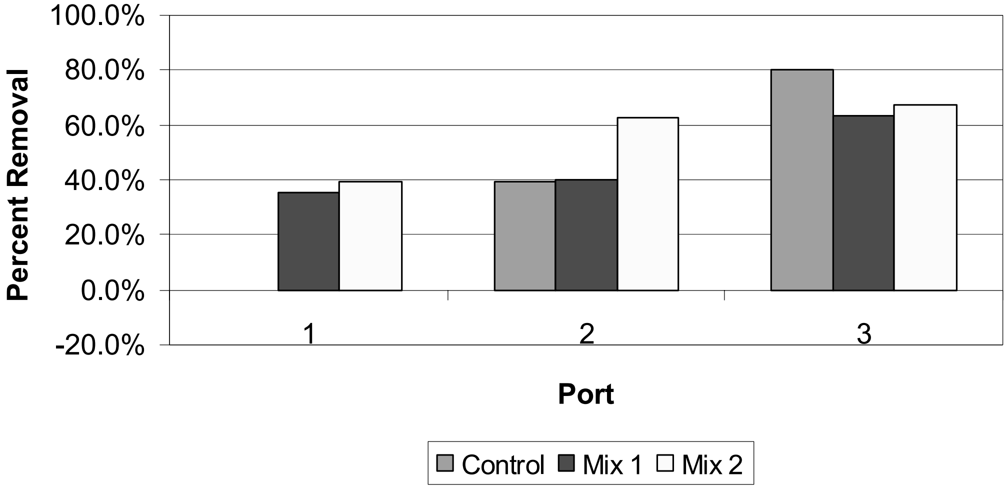


Figure 13: Orthophosphate Removal Through Columns at 23°C

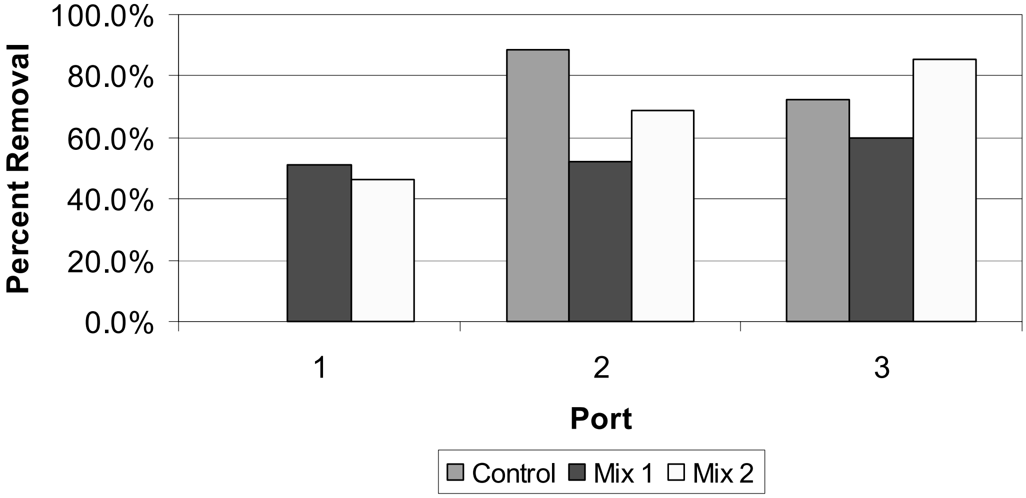


Figure 14: Orthophosphate Removal Through Columns at 28°C

A comparison of the nitrate removal for the columns at a specific temperature was constructed utilizing an average of the removals at the bottom of the columns for all doses Table 17. From this table it is easy to distinguish how the media mixtures reacted to the change in temperature in terms of nitrate removal. All of the columns achieve their highest removal at 28°C.

The nitrate performance increased with temperature. Media Mix 1 and 2 had similar increases; with approximately 10% increase from 10°C to 23°C and then a 15% increase from 23°C to 28°C. The Control column experienced a 12% increase for the first temperature gap and 25% increase between the higher temperatures. Media Mix 1 has the best removals of all three columns for 23°C, 25°C and 28°C with 69.7%, 79.7%, and 95.3% respectively. Media Mix 1 has the highest nitrate removal for all of the experiments with 95.3% nitrate removal.

Table 17: Nitrate Removal Comparison between Temperature and Column (Final Port Comparison)

NO_3^--N	Temp 1 10° C	Temp 2 23° C	Temp 3 28° C
Ctrl	8.0%	20.9%	45.8%
Mix 1	69.7%	79.7%	95.3%
Mix 2	63.2%	77.9%	93.6%

A comparison of the orthophosphate removal for the columns at a specific temperature was also constructed utilizing an average of the removals at the bottom of the columns for all doses Table 18. From this table it is easy to distinguish how the media mixtures reacted to the change in temperature in terms of orthophosphate removal. The columns all achieved the highest orthophosphate removal at different temperatures; the Control, Media Mix 1, and Media Mix 2 at 10° C , 23° C, and 28° C respectively. However, the difference between the highest and second highest removals for the Control was only 1%. The highest overall orthophosphate removal was achieved by Media Mix 2 at 28° C. The Control column outperformed the Media Mixes for 10° C and 23° C and came in at a fairly close second for 28°C.

Table 18: Orthophosphate Removal Comparison between Temperature and Column (Final Port Comparison)

OP (PO_4^{3-}-P)	Temp 1 10° C	Temp 2 23° C	Temp 3 28° C
Ctrl	84.8%	80.0%	72.1%
Mix 1	38.5%	63.3%	59.9%
Mix 2	58.8%	67.4%	85.5%

Two additional parameters were tested along with the nutrients for each column. The pH levels through the column were taken for use in consideration of real life application of the media. The pH of the stormwater should not be significantly raised or decreased; pH levels around 7 are preferable. Dissolved oxygen (DO) levels were also read for each port as the water traveled through the columns. The DO is of special importance when considering the denitrification process. In order for denitrification to occur DO levels should be less than 1.0 mg/L. This information provides insight as to whether the nitrate removals achieved throughout the column could be the result of denitrification or if the removal mechanism relies heavily on sorption. Throughout the process the testing of DO proved difficult. Levels in the following table should be analyzed such that the DO levels in the column are most likely less than measure due to errors attributed to bubbles in the tube that connected the sampling port and the DO sampling probe and some slight exposure to the atmosphere while obtaining the readings. However, attempts to keep these errors to a minimum were made by allowing the container to fill with water from the column and the reading to stabilize before recording the value. The average pH and DO values can be found in Table 19.

Table 19: Average pH and Dissovled Oxygen levels in the Columns

	Ctrl						Mix 1						Mix 2					
	10° C		23° C		28° C		10° C		23° C		28° C		10° C		23° C		28° C	
	pH	DO	pH	DO	pH	DO	pH	DO	pH	DO	pH	DO	pH	DO	pH	DO	pH	DO
R	7.3	5.4	6.8	3.7	7.6	4.1	7.3	5.4	6.8	3.7	7.6	4.1	7.3	5.4	6.8	3.7	7.6	4.1
Port 1	---	---	---	---	---	---	6.9	4.8	6.9	0.2	6.7	1.2	6.7	3.2	7.6	0.4	7.4	0.8
Port 2	7.1	5.4	6.1	0.7	7.1	1.5	6.9	0.8	3.0	0.2	7.0	1.0	7.2	4.1	7.7	1.7	7.2	1.1
Port 3	7.0	2.3	7.3	0.2	6.6	0.4	6.8	0.8	7.2	0.1	6.9	0.3	7.3	0.9	7.8	0.1	7.3	0.5
Decrease	0.3	3.2	-0.4	3.5	1.0	3.7	0.5	4.7	-0.3	3.6	0.7	3.8	0.0	4.6	-1.0	3.6	0.3	3.6

*Note: Negative values indicate increases in pH

The Control column experienced a slight drop in pH for all of the temperatures tested, except for the 23°C. The dissolved oxygen in the control column decreased as the water traveled down the column. Dissolved oxygen levels of less than or equal to 1.0 were achieved for the 23°C and 28°C cases. However, the DO levels reported for the 10C case are most likely higher than actual levels in the column due to the reduced flow and increased exposure to the atmosphere during the 10°C scenario. Media Mix 1 achieved similar results to the control in terms of pH reduction through the column. The dissolved oxygen levels in the Media Mix 1 column were almost always around the desired level. The Media Mix 2 column was the only column that was able to maintained the pH level for 10°C, increased the pH for 23°C and very slightly decreased the pH for 28°C. The dissolved oxygen levels reported are similar to the control; most likely the actual values are lower than the recorded due to errors in achieving the measurements.

In order to determine the effect temperature, dose, and media mixture have on the removal efficiency is statistically valid, two-way ANOVA analysis was conducted for each dose and nutrient. The removal efficiencies from the bottom of each column were used to standardize the data for comparison. These efficiencies were inserted into SAS® software and a two-way ANOVA was executed. Removal efficiency and media were designated as the main effects in the ANOVA model. The assumed alpha value for all of the computations was 0.1, providing 90% confidence. The assumptions associated with performance of an ANOVA test; independence, normal distributions, and equal variance were considered and the following results were obtained from this analysis. The samples were assumed to be independent since the columns are contained environments and the water travels through each one individually with no interaction. The normal assumption was assumed since only three data points for each combination were taken and thus a reliable normality test can not be performed. Lastly, statistical analysis has shown that the requirement of equal variance does not have a significant effect on the outcome of an ANOVA analysis, due to the robustness of the F distribution under unequal variance conditions when the sample sizes are the same (Neter, 1974 and Rogan, 1977).

A Two-Way ANOVA analysis was computed for the low dosage case. Table 20 provides a summary of the ANOVA analysis. The P value for column (0.0039) is less than alpha (0.1) causing rejection of null hypothesis (that there is no difference) and acceptance of the alternative. This is further shown in Table 21, where there is 90% confidence that there is a considerable difference between column 1 (Media Mix 1) and 2 (Control), as well as column 2 (Control) and 3 (Media Mix 2). Thus there is a noteworthy difference between the Media Mix columns and the Control, but not between each other. The temperature P value (0.2981) is greater than alpha (0.1) and fails to reject the null hypothesis. There is not sufficient evidence to prove there is a difference between the temperatures for the low dose nitrate case (Table 22). Lastly, the interaction term (column*temperature) is valid since it was previously determined that there was no interaction between the two. The P value (0.6386) is greater than alpha (0.1) and thus the null hypothesis can not be rejected. There is not significant evidence that there is interaction.

Table 20: Two-Way ANOVA Table for Low Nitrate Dose

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Column	2	12250	6125	8	0.004
Temperature	2	2068	1034	1	0.298
Column*Temperature	4	2053	513	1	0.639
Error	18	14363	798		
Corrected Total	26	30734			

Table 21: Column Significance for Low Nitrate Dose

Column Comparison	Difference Between Means	Simultaneous 90% Confidence		
1 – 3	11.0	-18.2	40.2	
1 – 2	49.7	20.5	78.8	***
3 – 1	-11.0	-40.2	18.2	
3 – 2	38.7	9.5	67.9	***
2 – 1	-49.7	-78.8	-20.5	***
2 – 3	-38.7	-67.9	-9.5	***

*** Indicated comparisons are significant at the 0.1 level

Table 22: Temperature Significance at Low Nitrate Dose

Temperature Comparison	Difference Between Means	Simultaneous 90% Confidence	
23 – 28	5.8	-23.4	35.0
23 – 10	20.8	-8.4	50.0
28 – 23	-5.8	-35.0	23.4
28 – 10	15.0	-14.2	44.1
10 – 23	-20.8	-50.0	8.4
10 – 28	-15.0	-44.1	14.2

*** Indicated comparisons are significant at the 0.1 level

A Two-Way ANOVA analysis was then computed for the high dosage case, to establish whether the dosage influences the results. Table 23 provides a summary of the ANOVA analysis. The P value for column (<0.001) is less than alpha (0.1) causing rejection of null hypothesis (that there is no difference) and acceptance of the alternative. Just as in the low dosage case, this is further shown in Table 24, where there is 90% confidence that there is a considerable difference between the Media Mix columns and the Control, but not between each other. However, the temperature P value (0.0066) is less than alpha (0.1) and the null hypothesis is rejected. There is sufficient evidence to prove there is a difference between 10°C vs 28°C and 23°C vs 28°C for the high dose nitrate case (Table 25). Statistically, there is not enough evidence to state that there is a difference in the removals between 10°C and 23°C. Lastly, the interaction term (column*temperature) is valid since it was previously determined that there was no interaction between the two. The P value (0.30066) is greater than alpha (0.1) and thus the null hypothesis can not be rejected. There is not significant evidence that there is interaction.

Table 23: Two-Way ANOVA Table for High Nitrate Dose

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Column	2	18657	9328	21	0.0001
Temperature	2	6011	3006	7	0.007
Column*Temperature	4	2359	590	1	0.301
Error	18	8044	447		
Corrected Total	26	35071			

Table 24: Column Significance at High Nitrate Dose

Column Comparison	Difference Between Means	Simultaneous 90% Confidence		
1 – 3	7.3	-14.5	29.2	
1 – 2	59.1	37.2	80.9	***
3 – 1	-7.3	-29.2	14.5	
3 – 2	51.7	29.9	73.6	***
2 – 1	-59.1	-80.9	-37.2	***
2 – 3	-51.7	-73.6	-29.9	***

*** Indicated comparisons are significant at the 0.1 level

Table 25: Temperature Significance at High Nitrate Dose

Temperature Comparison	Difference Between Means	Simultaneous 90% Confidence		
23 – 28	-33.4	-55.2	-11.5	***
23 – 10	-3.7	-25.6	18.1	
28 – 23	33.4	11.5	55.2	***
28 – 10	29.6	7.7	51.5	***
10 – 23	3.7	-18.1	25.6	
10 – 28	-29.6	-51.5	-7.8	***

*** Indicated comparisons are significant at the 0.1 level

A Two-Way ANOVA analysis was then computed for orthophosphate at low doses. For all of the effects tested during the orthophosphate low dose Two-Way ANOVA the P values are greater than alpha (Table 26). Thus the null hypothesis can not be rejected and there is not significant evidence that there is a difference column, difference temperature or interaction between column and temperature. Further representation can be found in Tables 27 and 28.

Table 26: Two-Way ANOVA Table for Low Orthophosphate Dose

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Column	2	1336	668	1	0.35
Temperature	2	2390	1195	2	0.17
Column*Temperature	4	2632	658	1	0.39
Error	18	10792	600		
Corrected Total	26	17151			

Table 27: Column Significance at Low Orthophosphate Dose

Column Comparison	Difference Between Means	Simultaneous 90% Confidence	
1 – 3	-2.1	-27.4	23.2
1 – 2	-15.9	-41.2	9.4
3 – 1	2.1	-23.2	27.4
3 – 2	-13.8	-39.0	11.5
2 – 1	15.9	-9.4	41.2
2 – 3	13.8	-11.5	39.0

*** Indicated comparisons are significant at the 0.1 level

Table 28: Temperature Significance at Low Orthophosphate Dose

Temperature Comparison	Difference Between Means	Simultaneous 90% Confidence	
23 – 28	-14.0	-39.3	11.3
23 – 10	8.9	-16.4	34.2
28 – 23	14.0	-11.3	39.3
28 – 10	22.9	-2.4	48.1
10 – 23	-8.9	-34.2	16.4
10 – 28	-22.9	-48.1	2.4

*** Indicated comparisons are significant at the 0.1 level

The final Two-Way ANOVA analysis was computed for ortho-phosphorus at high doses. Table 29 provides a summary of the ANOVA analysis. Similar to the high dose nitrate ANOVA test, the P value for column (0.0002) is less than alpha (0.1) causing rejection of null hypothesis (that there is no difference) and acceptance of the alternative. Table 30 further demonstrates that with 90% confidence there is a considerable difference between column 1 (Media Mix 1) and 2 (Control), as well as column 2 (Control) and 3 (Media Mix 2). The Media Mix columns vary from the Control, but not each other. The temperature P value (0.4356) is greater than alpha (0.1) and fails to reject the null hypothesis. There is not sufficient evidence to prove there is a difference between the temperatures for the low dose nitrate case (Table 31). Lastly, the interaction term (column*temperature) is valid since it was previously determined that there was no interaction between the two. The P value (0.1073) is greater than alpha (0.1) and thus the null hypothesis can not be rejected. There is not significant evidence that there is interaction.

Table 29: Two-Way ANOVA Table for High Orthophosphate Dose

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Column	2	6069	3035	14	0.0002
Temperature	2	376	188	1	0.44
Column*Temperature	4	1918	479	2	0.11
Error	18	3883	216		
Corrected Total	26	12246			

Table 30: Column Significance at High Orthophosphate Dose

Column Comparison	Difference Between Means	Simultaneous 90% Confidence		
1 – 3	-31.2	-46.4	-16.0	***
1 – 2	-32.4	-47.5	17.2	***
3 – 1	31.2	16.0	46.4	***
3 – 2	-1.2	-16.3	14.0	
2 – 1	32.4	17.2	47.5	***
2 – 3	1.2	-14.0	16.3	

*** Indicated comparisons are significant at the 0.1 level

Table 31: Temperature Significance at High Orthophosphate Dose

Temperature Comparison	Difference Between Means	Simultaneous 90% Confidence	
23 – 28	7.5	-7.7	22.6
23 – 10	8.3	-6.9	23.5
28 – 23	-7.5	-22.6	7.7
28 – 10	0.8	-14.3	16.0
10 – 23	-8.3	-23.4	6.9
10 – 28	-0.8	-16.0	14.3

*** Indicated comparisons are significant at the 0.1 level

The temperature conversion factor (θ) and Arrhenius values for each media mix with respect to each nutrient were calculated using the following methodology. The nitrate and orthophosphate removals for each column were plotted separately using a zero, first, and second order models as described by the linear forms of Equations 4-6. Because the initial dose concentrations were not exactly the same, the data from each and every run needed to be plotted individually. Next, a linear regression was executed to deduce the reaction rate of best fit. Tables 32, 33, and 34 show an example of one of the best runs for each column, species, and temperature. An average of all of the R^2 values for each column at each temperature were compared; the highest R^2 values across all three temperatures was taken to be the best model for the overall reaction order (Tables 35-7).

Table 32: Example Linear Regression Equations for the Control Column

Temp.	Species	Initial Concentration (mg/L)	Zero Order		1st Order		2nd Order	
			Equation	R^2	Equation	R^2	Equation	R^2
10	Nitrate	14	-0.017x + 14	0.55	-0.001x + 2.6	0.56	-0.0001x + .07	0.56
		17.9	-0.31x + 18	0.96	-0.002x + 2.9	0.94	0.0001x + 0.06	0.92
	Orthophosphate	3.9	-0.03x +0.4	0.97	-0.02x + 1.2	0.99	0.043x +.15	0.91
		6.4	-0.05x + 5.7	0.88	-0.04x + 1.7	0.97	0.13x -1.0	0.89
23	Nitrate	6.8	-0.015x + 7.2	0.99	0.0027x + 1.9	0.97	0.0005x + 0.13	0.95
		17.5	-0.002x + 18	0.02	-0.09x + 2.9	0.02	7e-6x + 0.06	0.02
	Orthophosphate	1	-0.004x + 1.9	0.76	-0.008x + .13	0.69	0.019x + .52	0.65
		3	-0.019x + .52	0.88	-0.03x + 0.93	0.93	0.06x + .39	0.99
28	Nitrate	17.5	-0.03x + 17.6	0.96	-0.002x +2.9	0.94	0.001x + 0.06	0.92
		19	-0.04x +18.9	0.88	-0.002x + 2.9	0.86	.0001x + 0.05	0.83
	Orthophosphate	4.2	-0.03x + 4.1	0.98	-0.03x + 1.6	0.93	0.05x -0.59	0.7
		6.2	-0.052x + 5.7	0.88	-0.038x + 1.7	0.98	0.13x - 1.0	0.89

Table 33: Example Linear Regression Equations for the Media Mix 1 Column

Temp.	Species	Initial Concentration (mg/L)	Zero Order		1st Order		2nd Order	
			Equation	R^2	Equation	R^2	Equation	R^2
10	Nitrate	13	-0.01x + 12	0.9	-0.02x + 2.6	0.98	0.008x + 0.06	0.86
		25	-0.12x + 25	0.99	-0.008x + 3.3	0.96	0.0006x + 0.03	0.88
	Orthophosphate	3.9	-0.005x + 3.6	0.92	-0.001x + 1.3	0.91	0.0004x + 0.27	0.89
		6.4	-0.017x + 7.4	0.95	-0.002 + 2	0.93	0.0005x + 0.13	0.91
23	Nitrate	6.15	-0.056x + 6	0.82	-0.03x + 2.0	0.97	0.047x -0.83	0.82
		20.6	-0.16x +.17	0.79	0.043x +2.9	0.82	0.09x - 0.75	0.68
	Orthophosphate	1	-0.008x + 0.86	0.83	-0.023x + 0.09	0.95	0.13x - 0.5	0.91
		3	-0.01x + 3	0.99	-0.005x + 1.1	0.98	0.002x + 0.3	0.94
28	Nitrate	13	-0.1x + 11.9	0.9	-0.02x + 2.6	0.98	0.008x - 0.6	0.86
		24.7	-0.4x+ 24.7	0.99	-0.008x + 3.3	0.96	0.0006x +.03	0.88
	Orthophosphate	3.7	-0.0045 x +3.7	0.92	-0.0014x +1.3	0.91	0.0004x + 0.29	0.89
		7.3	-0.017x + 7.4	0.94	-0.003x + 2.0	0.93	0.0005x + 0.013	0.91

Table 34: Example Linear Regression Equations for the Media Mix 2 Column

Temp.	Species	Initial Concentration (mg/L)	Zero Order		1st Order		2nd Order	
			Equation	R^2	Equation	R^2	Equation	R^2
10	Nitrate	8	0.06x + 8.3	0.96	-0.03x + 3.1	0.88	0.08x + -0.8	0.65
		25	-0.071x + 24	0.97	-0.004x + 3.2	0.99	0.0002x + 0.04	0.99
	Orthophosphate	3.7	-0.008x + 3.7	0.94	-0.0023x + 1.3	0.91	0.001x + 0.26	0.87
		6.4	0.03x + 6.4	0.98	-0.012x + 2	0.85	0.006x + 0.02	0.84
23	Nitrate	7.2	-0.03x + 5.8	0.75	-0.008x + 1.8	0.91	0.003x + 0.16	0.99
		31.2	-0.18x + 0.33	0.97	0.0098x + 3.6	0.95	0.0006x + 0.02	0.89
	Orthophosphate	2.3	-0.008x + 1.9	0.73	-0.007x + 0.62	0.57	0.008x + 0.66	0.34
		3	-0.014x + 0.14	0.89	-0.008x + 1.1	0.94	0.005x + 0.3	0.91
28	Nitrate	13	-0.09x + 12	0.96	-0.033x + 3.1	0.88	0.06x -1.8	0.65
		25	-0.07 + 24	0.97	-0.004x + 3.2	0.99	0.0002x +0.04	0.99
	Orthophosphate	3.7	-0.0083x + 3.7	0.94	-0.0029x +1.34	0.91	-.001x + 0.256	0.87
		6.2	-0.034x + 6.4	0.98	-.012x + 2.0	0.95	0.006x + .02	0.84

Table 35: Average R^2 Values For Each Temperature for Control

Control	**Nitrate**			**Orthophosphate**		
	10°C	**23°C**	**28°C**	**10°C**	**23°C**	**28°C**
Zero	***0.50***	***0.41***	***0.73***	***0.75***	0.65	***0.71***
1st	0.50	0.37	0.66	0.70	***0.69***	0.56
2nd	0.50	0.33	0.58	0.52	0.68	0.42

Table 36: Average R^2 Values for Each Temperature for the Media Mix 1

Media Mix 1	**Nitrate**			**Orthophosphate**		
	10°C	**23°C**	**28°C**	**10°C**	**23°C**	**28°C**
Zero	0.81	0.71	0.81	0.78	0.71	***0.73***
1st	***0.85***	***0.77***	***0.83***	0.79	0.73	0.70
2nd	0.80	0.71	0.73	***0.80***	***0.74***	0.66

Table 37: Average R^2 Values for Each Temperature for Media Mix 2

Media Mix 2	**Nitrate**			**Orthophosphate**		
	10°C	**23°C**	**28°C**	**10°C**	**23°C**	**28°C**
Zero	0.69	***0.84***	***0.62***	***0.81***	0.69	0.73
1st	***0.69***	0.82	0.60	0.78	***0.70***	***0.79***
2nd	0.56	0.73	0.59	0.72	0.60	0.77

Once the reaction order was determined, the rate constants could be calculated. The rate constant for each temperature is equal to the slope of the linear regression of the removals for the selected order. The averages of all rate constants were computed for each temperature (Tables 38-9).

Table 38: Average Nitrate Kinetic Rate Constants

k	**10°C**	**23°C**	**28°C**
Control (Zero Order)	0.014	0.007	0.03
Media Mix 1 (1st Order)	0.012	0.017	0.05
Media Mix 2 (Zero Order)	0.047	0.076	0.07

Table 39: Average Orthophosphate Kinetic Rate Constants

k	10°C	23°C	28°C
Control (Zero Order)	0.04	0.02	0.02
Media Mix 1 (2nd Order)	0.001	0.02	0.004
Media Mix 2 (1st Order)	0.08	0.01	0.01

These rate constants were then used to determine the activation energy (E_a) and frequency factors (A) for use in the Arrhenius equation for each Media Mix, nutrient, and temperature. The procedure for computing the activation energies and frequency factors involves manipulation of the aforementioned Arrhenius Equation 7. By combining two different temperatures and values, Equation 7a can be derived. Using this equation, the only variable left unknown is the activation energy. Once the activation energy is found, this value was inserted back into Equation 7 to solve for the frequency factor. The results of this type of analysis were repeated at each temperature for each media mix for both nitrate and orthophosphate (Tables 40 and 41).

$$\ln(k_2 / k_1) = E\ (T_2 - T_1) / RT_1T_2 \qquad \text{Equation 7a}$$

Table 40: Arrhenius Equation with Nitrate Kinetic Rates

NO_3^--N	K values used		Activation Energy (J/mol)	Frequency Factors
Control	0.0138	0.00743	-33169	1.04E-08
	0.00743	0.0271	191706	5.04E+31
	0.0138	0.0271	26553	1.10E+03
Media Mix 1	0.0124	0.01648	15239	8.06E+00
	0.01648	0.0499	164130	1.52E+27
	0.0124	0.0499	54781	1.60E+08
Media Mix 2	0.04715	0.07565	25328	2.23E+03
	0.07565	0.0683	-15142	1.61E-04
	0.04715	0.0683	14580	2.32E+01

Table 41: Arrhenius Equation with Orthophosphate Kinetic Rates

OP (PO_4^{3-}-P)	K values used		Activation Energy (J/mol)	Frequency Factors
Control	0.04	0.016	-50411	2.03E-11
	0.016	0.0222	62	1.64E-02
	0.041	0.0222	63	4.20E-02
Media Mix 1	0.001	0.0242	-213	9.14E-04
	0.0242	0.0039	-348	2.10E-02
	0.001	0.0039	-140	9.46E-04
Media Mix 2	0.083	0.0088	150	8.85E-02
	0.0088	0.0145	95	9.15E-03
	0.083	0.0145	179	8.92E-02

From these tables it is apparent that computing an average activation energy for each media mix would be highly inaccurate due to the large variation in magnitude. The activation energies tend to have consistent signs, however there are some exceptions. The negative activation energies could be a result of the kinetic rates decreasing with increasing temperature (Fine, 2007). The activation energies for the nitrate are typically positive, while the only approximately half of the activation energies for orthophosphate are positive.

Finally, the specific temperature conversion factors (θ) for the Media Mixes can be calculated by plugging in the values for the rate constants and their corresponding temperatures (Equation 7). The temperature conversion factor value was solved for with all three possible permutations and then an average of these produces the modeled value for θ (Table 42-43). The permutations in the table below are found by taking the kinetic constants found in Tables 38 and 39 above.

$$k_2 = k_1 * \theta^{(T_2 - T_1)} \qquad \text{Equation 8a}$$

The values of 1,2, and 3 stand for the temperatures 10, 23, and 28°C respectively, along with the kinetic values associated with those temperatures. For example, θ_{12} was found using the k values for 10 and 23°C and plugging in 10 and 23°C for the temperature.

Table 42: Temperature Conversion Constants (θ)

NO_3^--N	**Control**	**Media Mix 1**	**Media Mix 2**
$\boldsymbol{\theta}_{12}$	0.95	1.02	1.04
$\boldsymbol{\theta}_{13}$	1.04	1.07	1.02
$\boldsymbol{\theta}_{23}$	1.30	1.22	0.98
θ_{avg}	***1.10***	***1.11***	***1.01***

Table 43: Temperature Conversion Constant (θ)

OP (PO_4^{3-}-P)	**Control**	**Media Mix 1**	**Media Mix 2**
$\boldsymbol{\theta}_{12}$	0.93	1.28	0.84
$\boldsymbol{\theta}_{13}$	0.97	1.08	0.91
$\boldsymbol{\theta}_{23}$	1.07	0.69	1.11
θ_{avg}	***0.99***	***1.02***	***0.95***

Average temperature correction factors were calculated due to smaller variations in magnitude when compared with the Arrhenius Model.

CHAPTER 5: CONCLUSIONS

The results from the batch tests allowed for the narrowing down of the two media mixes to be used in column studies. The best media mixes to select were complicated by the unexpected nutrient addition by some of the media. The media mixes chosen were based on the best removal efficiencies from the batch tests and based on the electron donor that showed the least conflicting results of nutrient addition to the mixture. The selected two media recipes were Media Mix 1 consisting of 50% fine sand, 30% tire crumb, 20% sawdust by weight and Media Mix 2 consisting of 50% fine sand, 25% sawdust, 15% tire crumb, 10% limestone by weight. The control for this study was taken from Hunter's Trace Pond in Ocala, Florida, due to the overlap of multiple thesis investigations as well as the pond providing a typical example of an average retention pond in Florida.

The best media for both nitrate and orthophosphate removal in this study was Media Mix 1. The best column for nitrate removal for all temperatures is Media Mix 1. Selection of the best media in terms of orthophosphate was less straightforward. The Control Column had the best average removals at 10°C and 23°C. However, in terms of the media performance, Media Mix 1 outperforms Mix 2 for two of the temperatures; although Media Mix 2 does have the highest individual occurrence of orthophosphate removal of all the mixes for all of the temperatures.

From the ANOVA analysis, the change from low to high concentrations seemed to have an effect on the nitrate and orhto-phosphorus removals. In terms of nitrate, the ANOVA for low concentration and high concentration had the same results in terms of columns, but there were differences between the low and high concentrations in terms of temperature. This might show that the lower concentration range was near the equilibrium for the microbes. The difference in efficiency for the columns between the temperatures is interesting. Since there is seemingly no difference between 10°C and 23 C°C for the columns, it is assumed that this is the lower range for the microbial activity and removals were dictated by sorption. The difference between 23°C and 28°C would indicate that there was biological activity along with sorption. The differences between the media mixes could be due to the sorption capacity, ability to provide carbon source for denitrification, and ability to provide an ideal environment for the microbes to attach and thrive.

The reaction rates for nitrate turned out to be first order for Media Mix 1, and zero order for the Control and Media Mix 2. The reaction rates in terms of orthophosphate were different than the reaction rates for nitrate for the Media Mixes. A zero order model was selected for the Control; which is similar to nitrate. Media Mix 1 and 2 were modeled as second and first order respectively. Although the reaction rates for the Media Mixes and the Control were selected there was little difference between the models and thus it is most likely that the reactions are variable order.

The temperature conversion constants for nitrate were found to be 1.11, 1.1, and 1.01 for Media Mix 1, the Control and Media Mix 2 respectively. The temperature conversion constants for orthophosphate were found to be 1.02, 0.99, and 0.95. The activation energies and frequency factors associated with application of the Arrhenius equation were also found (Tables 39-41). An average of these values was not calculated due to the large variance in values. The kinetic rates would be helpful in determining the retention time required for the Media Mixes to achieve the best removals. Using this information, along with the media characterization information and desired removals, the depth of media that would be recommended for pilot studies in a retention pond or other high nutrient concentration application could be calculated.

The results of this research are limited to the specific media and specific composition of the media mixes eventually selected. The three temperatures selected for this study were accommodated to span the Floridian climate. Data were collected during controlled laboratory experimentation; natural conditions could potentially cause some deviations.

In the future, more aspects could be studied. Although, a carbon source is required for denitrification, the percentage of sawdust in the mixes seems to have been too high since it contributed a significant amount of ammonia. Thus, future testing of the medias should be done with a lower sawdust percentage to help alleviate the ammonia addition and investigate the required amount of electron donor for optimal denitrification. Also, the testing of the media mixes layered only a half a foot thick on top of a natural soil would be an evident progression. Lastly, the medias should be tested to see if they add anything detrimental to stormwater, such as metals. The results of this study show that the applications of the media mixtures for removal could be extended beyond just stormwater. The high removals found with such high initial concentrations could be beneficial for septic tank scenario. Also, the media could even be studied for trickling filters and other higher nutrient concentration applications.

APPENDIX A: HACH PROCEDURES

Nitrogen, Total
Method 10071

1. Turn on the DRB200 Reactor and heat to 105°C.
2. Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to each of two Total Nitrogen Hydroxide Digestion Reagent vials. Wipe off any reagent that may get on the lid or the tube threads.
3. **Prepared Sample**: Add 2mL of sample to one vial.
   Blank Preparation: Add 2 mL of the deionized water included in the kit to a second vial.

Note: Use only water that is free of all Nitrogen-containing species as a substitute for the provided deionized water.

4. Cap both vials. Shake vigorously for at least 30 seconds to mix. The persulfate reagent may not dissolve completely after shaking. This will not affect accuracy.
5. Insert the vials in the reactor. Heat for exactly 30 minutes.
6. Using finger cots, immediately remove the hot vials from the reactor. Cool the vials to room temperature.
7. Select the test. Install the Light Shield in Cell Compartment #2.
8. Remove the caps from the digested vials and add the contents of one Total Nitrogen (TN) Reagent A Powder Pillow to each vial.
9. Cap the tubes and shake for 15 seconds.
10. Press **TIMER>OK**. A three-minute reaction period will begin.
11. After the timer expires, remove the caps from the vials and add one TN Reagent B Powder Pillow to each vial.
12. Cap the tubes and shake for 15 seconds. The reagent will not completely dissolve. This will not affect accuracy. The solution will begin to turn yellow.
13. Press **TIMER>OK**. A two-minute reaction period will begin.
14. After the timer expires, remove the caps from two TN Reagent C vials and add 2 mL of digested, treated sample to one vial. Add 2 mL of digested, treated reagent blank to the second TN Reagent C vial.
15. Cap the vials and invert ten times to mix. Use slow, deliberate inversions for complete recovery. The tubes will be warm to the touch.
16. Press **TIMER>OK**. A five-minute reaction period will begin. The yellow color will intensify.
17. Wipe the reagent blank and insert it into the 16-mm round cell holder.
18. Press **ZERO**. The display will show: 0.0mg/L N
19. Wipe the reagent vial and insert it into the 16-mm round cell holder.
20. Press **READ**. Results are in mg/L N.

Phosphorus, Reactive Orthophosphate
Method 8048

1. Press **STORED PROGRAMS**
2. Select the test: 490 P React. PV
3. Fill a square sample cell with 10-mL of sample.
4. **Prepared Sample:** Add the contents of one PhosVer 3 Phosphate Powder Pillow to the cell. Immediately stopper and shake vigorously for 30 seconds.
5. Press **TIMER>OK.** A two-minute reaction period will begin. If the sample was digested using the Acid Persulfate digestion, a ten-minute reaction period is required.
6. **Blank Preparation:** Fill a second square sample cell with 10 mL of sample.
7. When the timer expires, wipe the blank and insert it into the cell holder with the fill line facing right. Press **ZERO**. The display will show: 0.00 mg/L PO_4^{3-}
8. Wipe the prepared sample and insert it into the cell holder with the fill line facing right. Press **READ**. Results are in mg/L PO_4^{3-}.

Nitrogen, Nitrate
Method 8192

1. Press **STORED PROGRAMS**
2. Select the test: 351 N Nitrate LR
3. Fill a 25-mL graduated mixing cylinder with 15 mL of sample.
4. Add the contents of one NitraVer 6 Reagent Powder Pillow to the cylinder. Stopper.
5. Press **TIMER>OK.** A 3-minute reaction period will begin.
6. Shake the cylinder vigorously during the three-minute timer.
7. When the timer expires, press **TIMER>OK** again. A 2-minute reaction period will begin.
8. When the timer expires, carefully pour 10 mL of the sample into a clean square sample cell. Do not transfer any cadmium particles to the sample cell.
9. **Prepared Sample:** Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell.
10. Press **TIMER>OK.** A 30-second reaction time will begin.
11. Cap and shake the sample cell gently during the 30-second timer. A pink color will develop if Nitrate is present.
12. Press **TIMER>OK.** A 15-minute reaction period will begin.
13. **Blank Preparation:** When the timer expires, fill a second square sample cell with 10 mL of original sample.
14. Insert the blank into the cell holder with the fill line facing right.
15. Press **ZERO**. The display will show: 0.0mg/L NO_3^--N
16. Insert the prepared sample into the cell holder with the fill line facing right. Press **READ**. Results are in mg/L NO_3^--N

Nitrogen, Nitrite
Method 8507

1. Press **STORED PROGRAMS**
2. Select the test: 371 N Nitrite LR PP
3. Fill a square sample cell with 10-mL of sample.
4. **Prepared Sample:** Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow. Swirl to dissolve. A pink color will develop if Nitrite is present.
5. Press **TIMER>OK.** A 20-second reaction time will begin.
6. **Blank Preparation:** When the timer expires, fill a second square sample cell with 10 mL of sample.
7. Wipe the blank and insert it into the cell holder with the fill line facing right. Press **ZERO**. The display will show: 0.000 mg/L NO_2^--N
8. Wipe the prepared sample and insert it into the cell holder with the fill line facing right. Press **READ**. Results are in mg/L NO_2--N.

Nitrogen, Ammonia
Method 8155

1. Press **STORED PROGRAMS**
2. Select the test: 385 N, Ammonia, Salic
3. **Prepared Sample:** Fill a square sample cell to the 10-mL mark with sample.
4. **Blank Preparation:** Fill a second square sample cell to the 10-mL mark with deionized water.
5. Add the contents of one Ammonia Salicylate Powder Pillow to each cell. Stopper and shake to dissolve.
6. Press **TIMER>OK.** A three-minute reaction period will begin.
7. When the timer expires, add the contents of one Ammonia Cyanurate Reagent Powder Pillow to each cell. Stopper and shake to dissolve.
8. Press **TIMER>OK.** A 15-minute reaction period will begin. A green color will develop if Ammonia-Nitrogen is present.
9. When the timer expires, insert the blank into the cell holder with the fill line facing right.
10. Press **ZERO**. The display will show: 0.00 mg/L NH_3-N
11. Wipe the sample and insert it into the cell holder with the fill line facing right.
12. Press **READ**. Results are in mg/L NH_3-N.

APPENDIX B: RAW DATA

Concentrations for all experiments conducted at 10°C:

Table B.1

7/8/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	13.15	0.02	13.13	0.25	2.35	4.22
Media Mix 1	1	7.52	2.32	5.20	1.63	1.68	3.01
	2	5.42	3.11	2.31	2.82	1.11	2.90
	3	5.05	4.08	0.97	0.62	0.90	2.69
Control	1	---	---	---	---	---	---
	2	13.36	0.07	13.29	0.10	2.51	1.12
	3	10.95	0.12	10.83	0.57	2.09	0.15
Media Mix 2	1	11.21	3.93	7.28	0.42	1.89	2.57
	2	8.56	5.90	2.66	0.70	1.78	2.86
	3	1.00	1.54	0.10	0.31	0.64	1.91

Table B.2

7/8/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	17.46	0.02	17.44	0.15	1.89	3.65
Media Mix 1	1	14.48	1.11	13.37	0.03	2.15	3.36
	2	16.45	0.83	15.63	0.24	2.35	3.38
	3	15.53	1.49	14.03	0.85	1.68	2.92
Control	1	---	---	---	---	---	---
	2	15.43	0.09	15.34	0.39	1.94	0.37
	3	12.85	0.07	12.79	0.33	3.08	0.14
Media Mix 2	1	11.17	0.27	10.91	0.09	2.46	3.38
	2	14.15	0.83	13.32	0.49	2.30	3.04
	3	12.72	2.42	10.30	2.40	1.94	2.24

Table B.3

7/11/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	7.69	0.02	7.67	0.58	15.64	3.54
Media Mix 1	1	2.57	1.92	0.65	0.55	5.93	4.32
	2	0.70	0.02	0.68	0.19	3.05	3.36
	3	0.32	0.02	0.30	0.18	4.39	1.63
Control	1	---	---	---	---	---	---
	2	10.70	0.07	10.64	0.19	17.70	5.90
	3	9.58	0.02	9.56	0.28	18.52	2.28
Media Mix 2	1	10.40	2.95	7.45	0.14	13.79	4.03
	2	11.30	12.55	0.10	0.12	11.17	3.79
	3	7.95	10.42	0.10	0.26	10.86	3.09

Table B.4

7/21/2008	Port	NO_2^--N + NO_3^- -N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	18.66	0.11	18.54	0.05	26.94	6.23
Media Mix 1	1	8.67	0.69	7.99	0.29	14.00	3.67
	2	8.07	0.37	7.70	0.48	11.06	3.26
	3	3.13	0.27	2.86	0.23	6.44	3.01
Control	1	---	---	---	---	---	---
	2	17.07	0.11	16.96	0.06	26.22	0.17
	3	13.77	0.09	13.68	0.10	20.28	0.06
Media Mix 2	1	13.70	0.03	13.67	0.03	27.33	5.16
	2	19.03	0.67	18.36	0.12	23.83	2.33
	3	3.84	0.33	3.51	0.03	7.67	0.91

Table B.5

7/21/2008	Port	NO_2^--N + NO_3^- -N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	24.66	0.02	24.64	0.08	26.06	7.34
Media Mix 1	1	18.94	1.36	17.58	0.11	25.72	6.14
	2	15.66	0.48	15.18	0.10	25.17	6.28
	3	9.28	0.70	8.58	0.21	23.44	4.95
Control	1	---	---	---	---	---	---
	2	20.33	0.05	20.28	0.05	25.78	0.12
	3	24.84	0.05	24.79	0.14	26.83	0.53
Media Mix 2	1	19.76	0.07	19.69	0.06	26.50	6.12
	2	15.48	0.05	15.43	0.05	27.06	4.96
	3	12.90	0.15	12.75	0.07	26.83	2.73

Table B.6

2/18/1900	Port	NO_2^--N + NO_3^- -N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	23.61	0.14	23.47	0.09	34.67	9.43
Media Mix 1	1	20.37	9.15	11.21	0.09	27.33	5.76
	2	24.04	10.43	13.61	0.15	26.11	5.62
	3	21.31	12.05	9.26	0.05	24.56	5.98
Control	1	---	---	---	---	---	---
	2	19.78	1.11	18.67	0.04	35.11	0.48
	3	22.99	0.16	22.83	0.10	31.11	1.03
Media Mix 2	1	20.38	0.82	19.56	0.10	33.00	9.72
	2	18.46	1.46	16.99	0.07	23.67	4.25
	3	21.28	0.38	20.90	0.06	26.33	0.18

Concentrations for all experiments conducted at 23°C:

Table B.7

5/22/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	6.18	0.04	6.15	0.01	15.59	2.31
Media Mix 1	1	1.82	0.60	1.22	0.30	2.94	1.91
	2	0.77	0.14	0.63	0.66	1.54	3.95
	3	0.70	0.13	0.57	0.53	1.59	1.28
Control	1	---	---	---	---	---	---
	2	0.98	0.14	0.84	0.82	3.75	3.14
	3	1.90	0.04	1.86	1.87	6.06	0.49
Media Mix 2	1	0.93	0.06	0.87	1.06	3.25	1.29
	2	1.35	0.07	1.28	0.50	1.09	0.32
	3	0.76	0.05	0.71	-0.01	1.34	0.69

Table B.8

5/22/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	19.17	0.09	19.08	0.01	29.40	3.77
Media Mix 1	1	11.91	3.82	8.09	0.01	12.83	1.99
	2	9.91	3.73	6.18	0.15	9.27	0.79
	3	15.51	3.72	11.79	0.22	9.37	0.87
Control	1	---	---	---	---	---	---
	2	16.09	0.12	15.97	0.98	16.55	0.22
	3	19.34	0.16	19.19	1.44	19.01	0.30
Media Mix 2	1	18.13	0.10	18.03	-0.08	16.15	1.58
	2	15.21	0.42	14.78	0.10	14.34	0.63
	3	10.92	1.84	9.08	0.39	13.99	0.14

Table B.9

5/11/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	7.18	0.03	7.15	0.01	13.70	1.00
Media Mix 1	1	2.17	0.53	1.64	0.04	4.82	0.28
	2	0.83	0.37	0.46	0.08	1.70	0.10
	3	0.63	0.47	0.16	0.07	2.17	0.06
Control	1	---	---	---	---	---	---
	2	5.77	0.04	5.73	0.40	11.14	0.87
	3	4.57	0.03	4.54	0.69	12.77	0.22
Media Mix 2	1	3.66	0.31	3.35	0.01	7.80	0.64
	2	2.38	0.32	2.06	0.00	7.98	0.82
	3	1.53	0.08	1.45	0.00	12.87	0.18

Table B.10

5/13/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	6.75	0.03	6.73	0.03	19.93	1.92
Control	1	---	---	---	---	---	---
	2	7.50	0.07	7.44	0.28	15.89	2.39
	3	3.94	0.09	3.85	0.62	15.52	1.21
Media Mix 1	1	1.13	0.25	0.88	1.81	6.45	1.92
	2	0.91	0.22	0.70	0.00	5.61	0.87
	3	0.75	0.32	0.43	0.06	3.24	0.90
Media Mix 2	1	4.20	0.38	3.82	1.55	10.17	1.74
	2	3.75	0.55	3.20	0.00	9.89	0.31
	3	1.41	0.21	1.20	0.08	5.98	1.80

Table B.11

6/23/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	20.69	0.02	20.67	0.01	14.44	3.08
Control	1	---	---	---	---	---	---
	2	19.37	0.18	19.19	0.70	10.97	0.18
	3	23.90	0.04	23.86	0.45	11.15	0.12
Media Mix 1	1	7.83	4.12	3.71	0.66	3.43	2.30
	2	1.70	2.66	0.10	0.74	0.45	2.23
	3	1.05	1.24	0.10	0.40	-0.35	1.59
Media Mix 2	1	15.00	1.30	13.70	0.29	8.90	1.81
	2	1.49	1.12	0.37	0.06	-0.22	1.62
	3	1.32	0.01	1.31	0.13	-1.08	0.93

Table B.12

6/23/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	31.20	0.00	31.20	0.01	20.03	4.68
Control	4	---	---	---	---	---	---
	5	14.52	0.71	13.81	0.24	16.17	0.14
	6	33.59	0.03	33.56	0.79	15.72	0.04
Media Mix 1	1	23.44	8.61	14.83	0.01	12.46	2.35
	2	22.91	11.88	11.03	0.02	9.88	1.95
	3	22.91	9.96	12.95	0.10	9.42	1.74
Media Mix 2	7	29.94	1.89	28.05	-0.05	17.39	2.48
	8	24.02	7.75	16.27	0.04	12.80	1.97
	9	16.07	7.08	8.99	-0.01	9.30	0.88

Concentrations for all experiments conducted at 28°C:

Table B.13

6/1/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	9.65	0.11	9.54	0.10	13.12	2.18
Control	1	--	--	--	--	--	--
	2	4.86	0.05	4.80	0.26	6.08	0.10
	3	4.35	0.07	4.29	0.92	7.68	0.61
Media Mix 1	1	2.22	0.05	2.17	0.02	4.44	1.19
	2	0.66	0.06	0.59	0.03	2.59	1.12
	3	0.64	0.16	0.48	0.01	2.90	1.18
Media Mix 2	1	1.30	0.02	1.27	0.05	3.72	0.93
	2	0.40	0.02	0.38	0.02	1.87	1.16
	3	0.30	0.04	0.27	0.05	2.18	0.16

Table B.14

6/2/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	13.71	0.05	13.66	0.05	15.13	2.74
Control	1	--	--	--	--	--	--
	2	11.01	0.22	10.79	0.11	10.50	0.26
	3	6.83	0.10	6.73	0.21	10.97	1.71
Media Mix 1	1	3.01	0.27	2.74	0.07	6.54	1.75
	2	3.35	0.14	3.21	0.18	3.51	1.51
	3	0.61	0.15	0.45	0.16	5.00	1.07
Media Mix 2	1	10.84	0.58	10.26	0.04	11.58	1.03
	2	4.70	0.36	4.34	0.08	6.96	0.64
	3	0.90	0.08	0.82	0.07	3.20	0.44

Table B.15

6/6/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	5.77	0.01	5.76	-0.82	14.56	3.68
Control	1	--	--	--	--	--	--
	2	1.07	0.02	1.05	-0.15	4.28	0.17
	3	4.11	0.02	4.09	0.32	6.96	0.70
Media Mix 1	1	3.26	0.35	2.92	-0.78	6.49	0.96
	2	0.37	0.14	0.23	-0.20	3.56	1.34
	3	0.52	0.23	0.29	-0.12	2.38	1.39
Media Mix 2	1	5.00	0.09	4.91	-0.81	12.15	5.07
	2	2.42	0.39	2.03	-0.31	5.62	0.81
	3	0.29	0.23	0.05	-0.31	3.51	0.51

Table B.16

6/10/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	8.56	0.01	8.55	0.09	12.05	1.67
Control	1	--	--	--	--	--	--
	2	1.24	0.02	1.22	0.29	3.15	0.49
	3	2.76	0.01	2.75	0.39	6.03	0.66
Media Mix 1	1	3.18	1.29	1.89	0.16	5.88	0.89
	2	0.19	0.04	0.15	0.13	2.43	0.80
	3	0.14	0.01	0.13	0.13	1.71	0.98
Media Mix 2	1	1.23	0.31	0.92	0.04	6.08	0.48
	2	0.89	0.44	0.45	0.18	2.07	0.55
	3	0.33	0.04	0.29	0.13	1.25	0.50

Table B.17

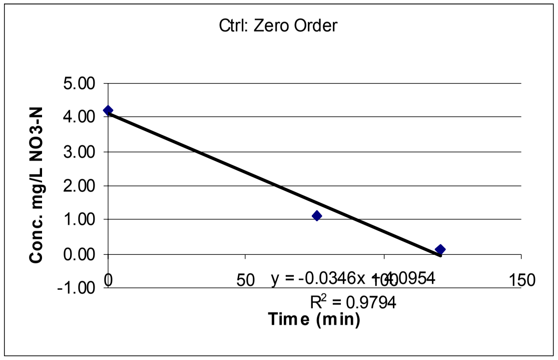
6/11/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	3.00	0.02	2.97	0.05	40.11	5.82
Control	1	--	--	--	--	--	--
	2	1.25	0.13	1.12	0.43	15.65	0.93
	3	1.61	0.02	1.59	0.51	22.59	0.94
Media Mix 1	1	1.16	1.26	0.10	0.16	13.99	1.91
	2	0.86	1.57	0.10	0.10	7.05	3.66
	3	1.11	1.64	0.10	0.16	8.81	1.12
Media Mix 2	1	2.28	0.35	1.92	0.16	30.28	1.32
	2	0.65	0.32	0.33	0.13	2.72	1.39
	3	5.43	0.13	5.30	0.06	1.92	0.86

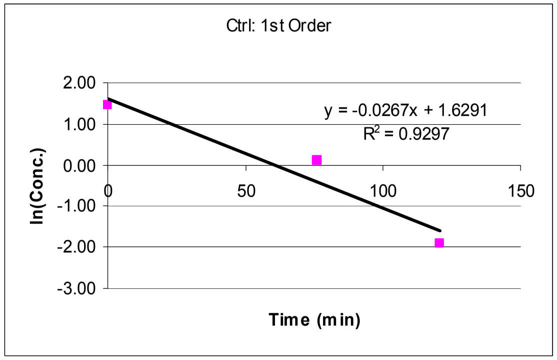
Table B.18

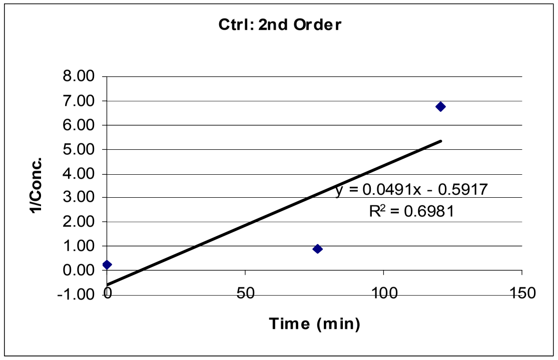
6/17/2008	Port	NO_2^--N + NO_3^--N	NO_2^--N	NO_3^--N	NH_4^+-N	TN-N	OP (PO_4^{3-}-P)
	R	28.24	0.03	28.21	0.05	30.71	4.62
Control	1	--	--	--	--	--	--
	2	22.70	0.17	22.53	0.58	26.74	0.21
	3	21.02	0.06	20.96	0.79	26.49	0.07
Media Mix 1	1	12.27	0.06	12.20	0.55	146.95	2.94
	2	7.08	3.66	3.43	0.86	9.03	1.61
	3	4.55	1.79	2.76	0.52	7.37	1.45
Media Mix 2	1	6.74	0.84	5.91	0.27	13.29	2.46
	2	1.30	0.22	1.08	0.29	3.30	1.48
	3	6.46	0.03	6.44	0.23	2.25	0.23

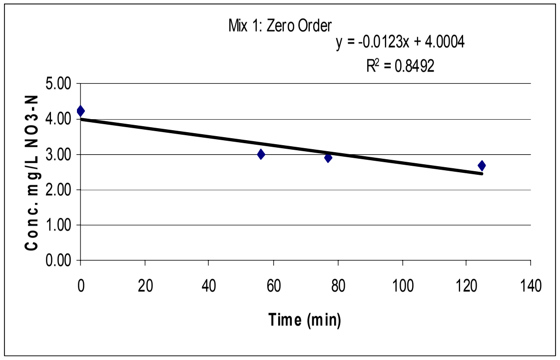
APPENDIX C: ZERO, FIRST, AND SECOND ORDER GRAPHS OF DATA

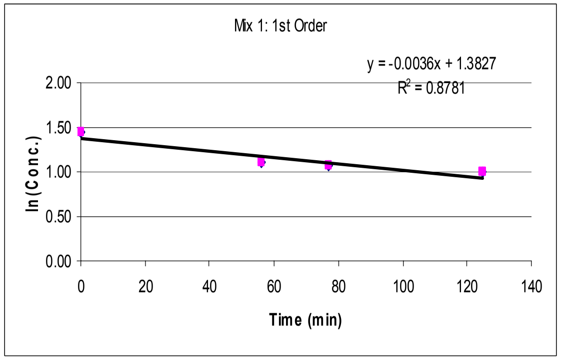
Ortho Phosphate 7/8/08

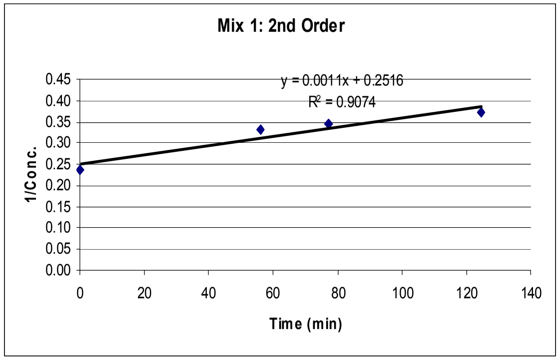




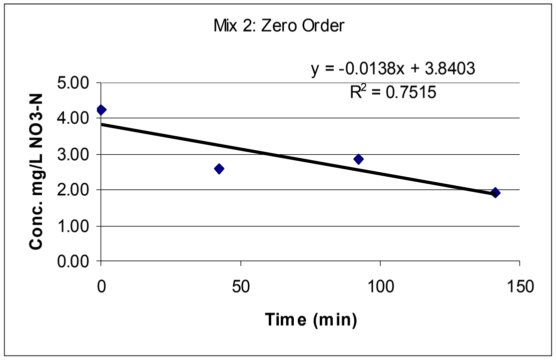


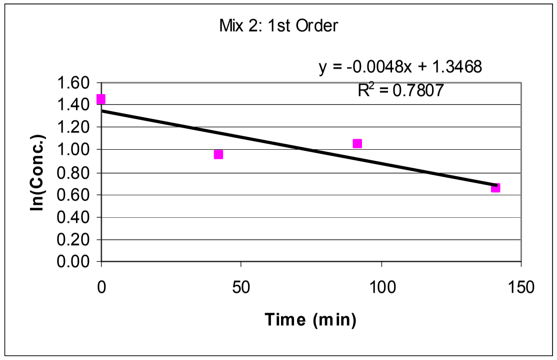


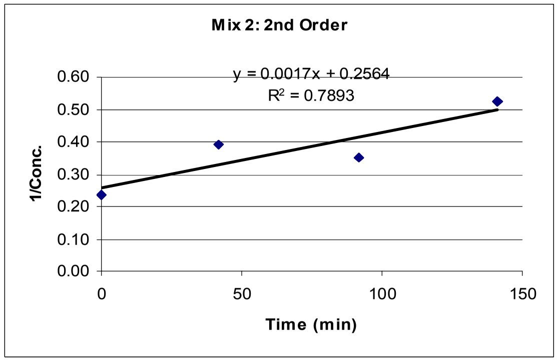




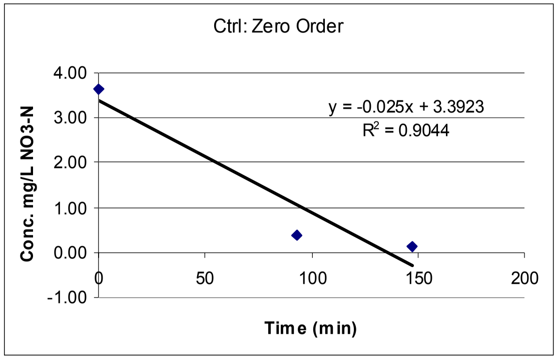
Ortho Phosphate 7/8/08 Cont.

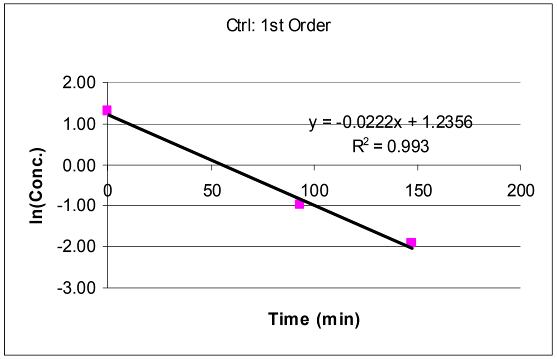


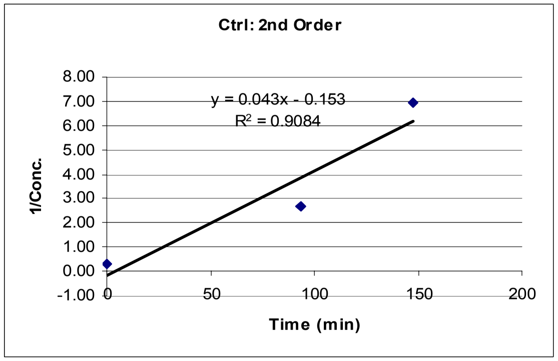


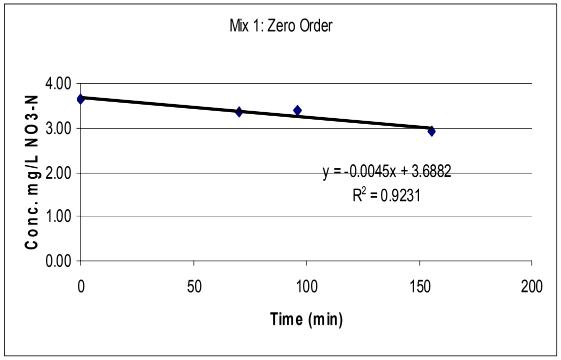


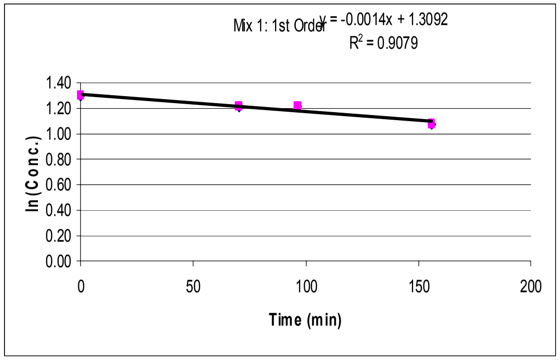
Ortho Phosphate 7/8/08 (Run 2)

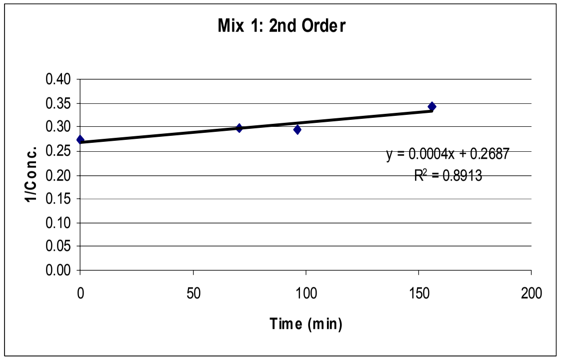




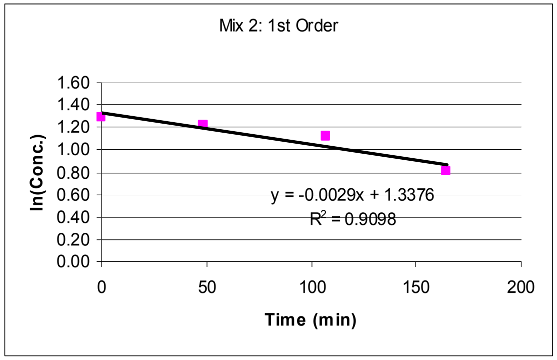


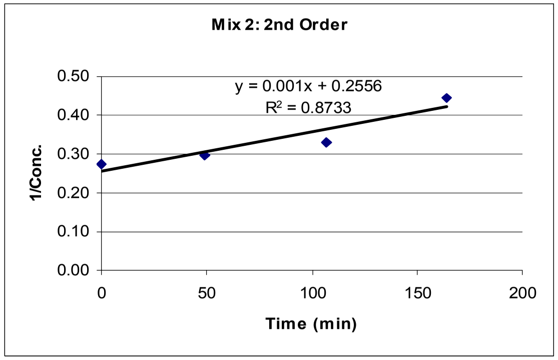




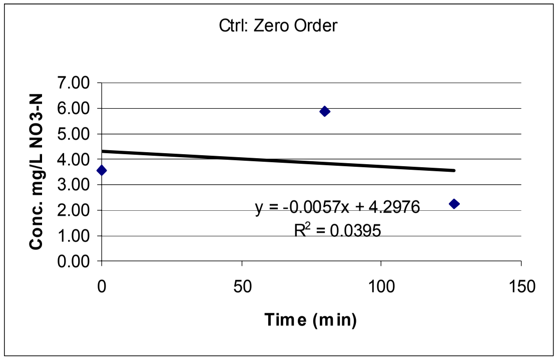


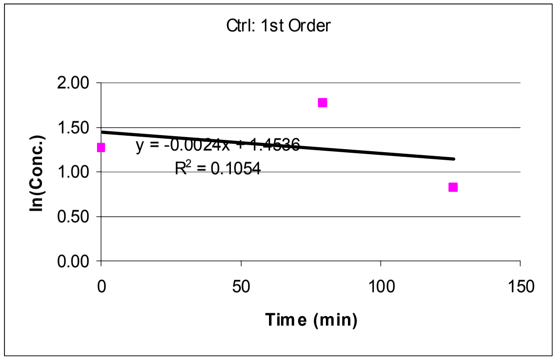
Ortho Phosphate 7/8/08 (Run 2) Cont.

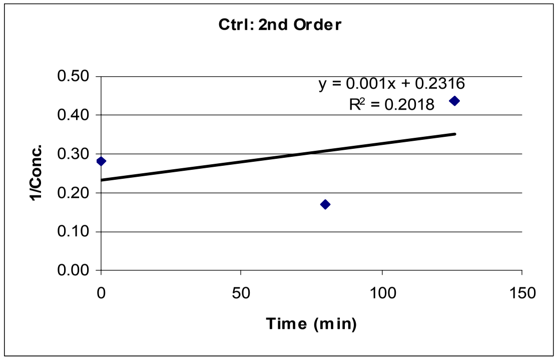


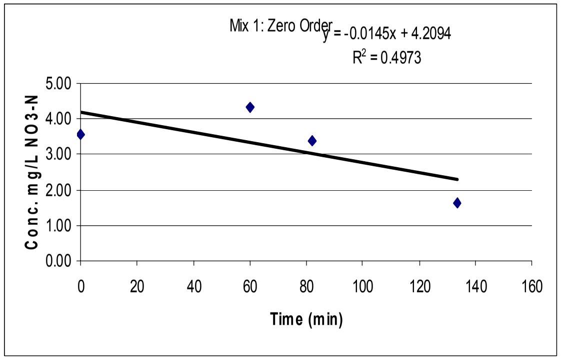


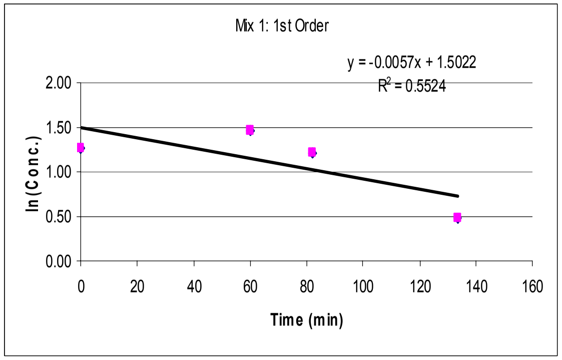
Ortho Phosphate 7/11/08

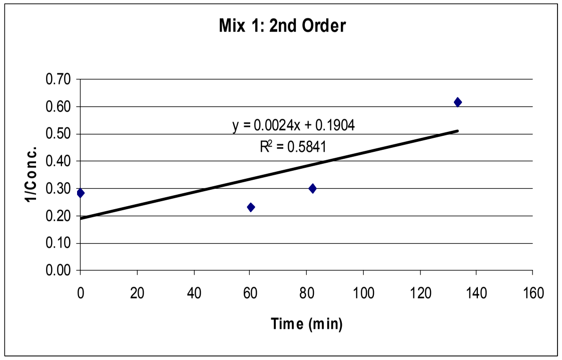




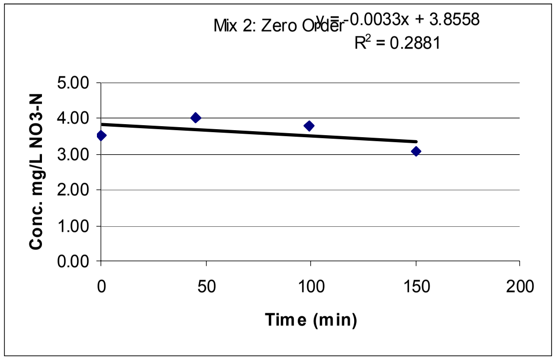


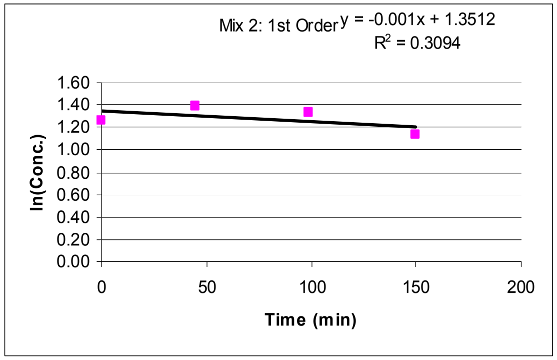




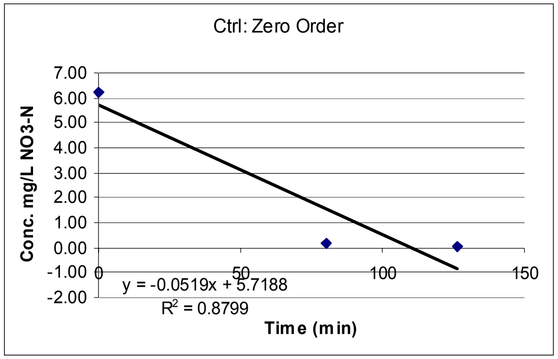


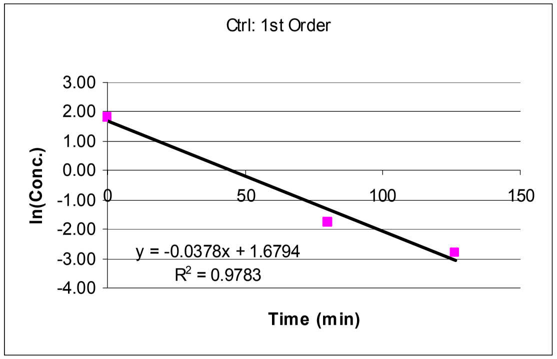
Ortho Phosphate 7/11/08 Cont.

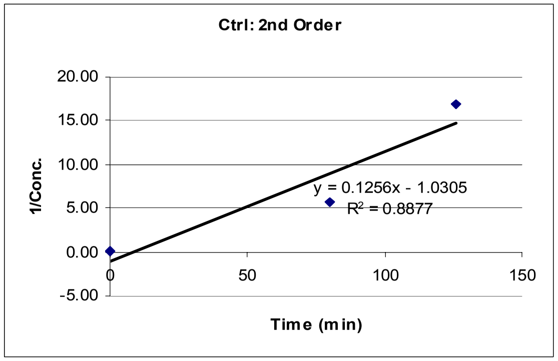


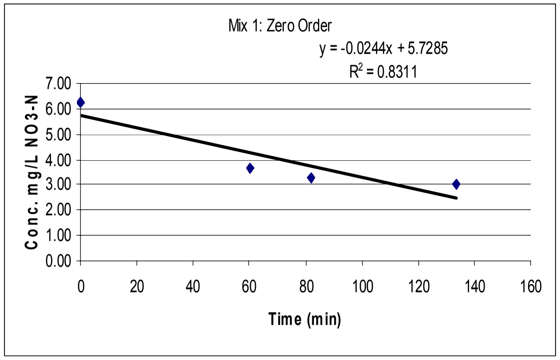


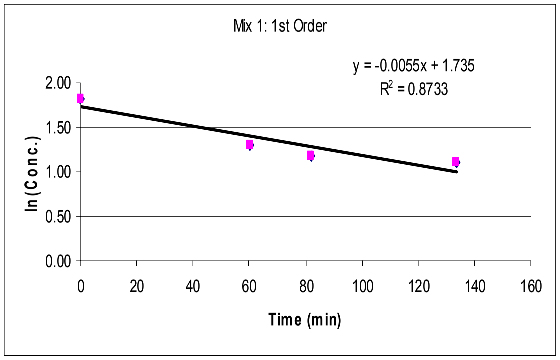
Ortho Phosphate 7/21/08



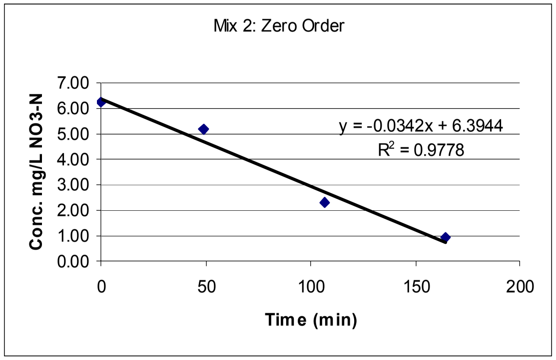


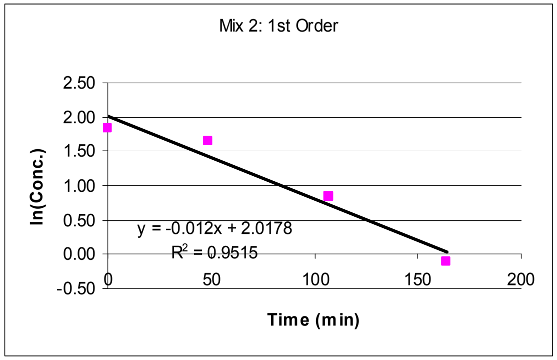


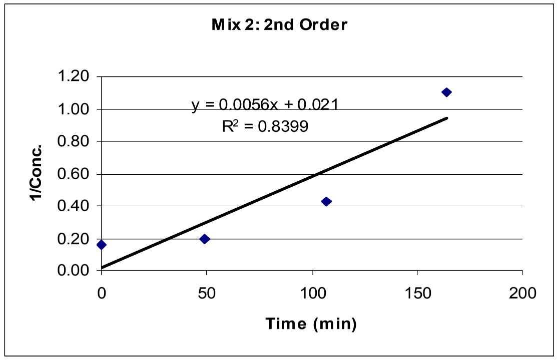




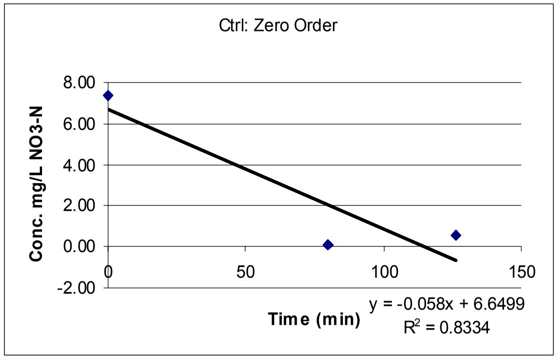
Ortho Phosphate 7/21/08 Cont.

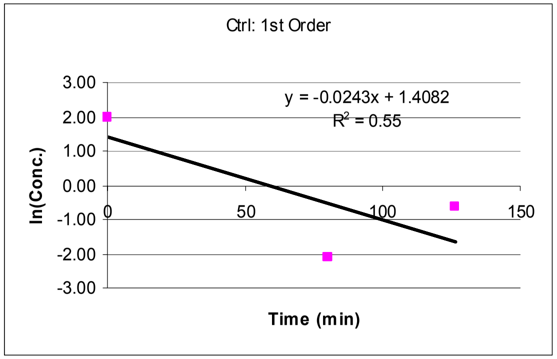


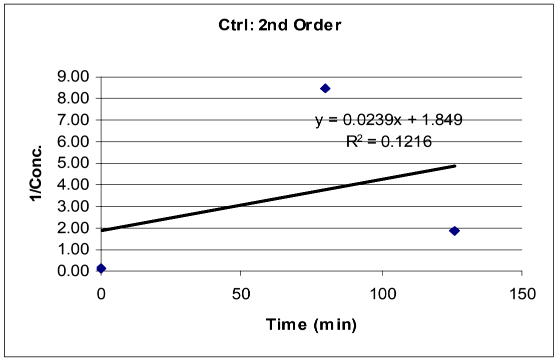


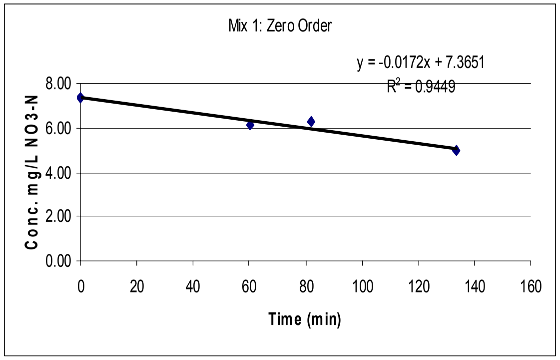


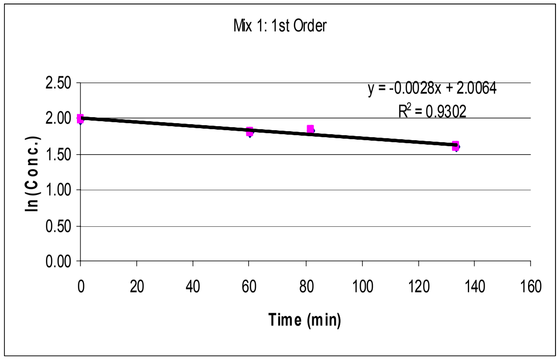
Ortho Phosphate 7/21/08 (Run 2)


Ctrl: Zero Order


Ctrl: 1st Order

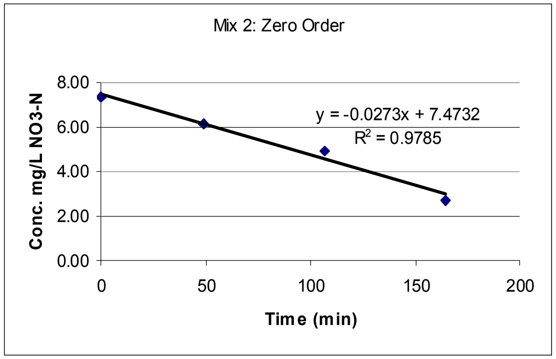

Ctrl: 2nd Order

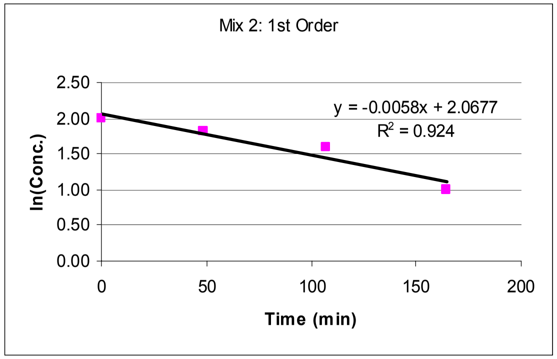

Mix 1: Zero Order

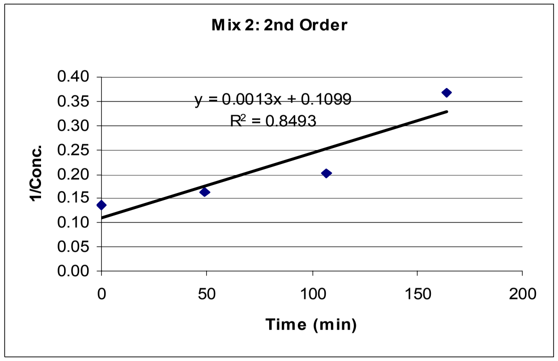

Mix 1: 1st Order


Mix 1: 2nd Order

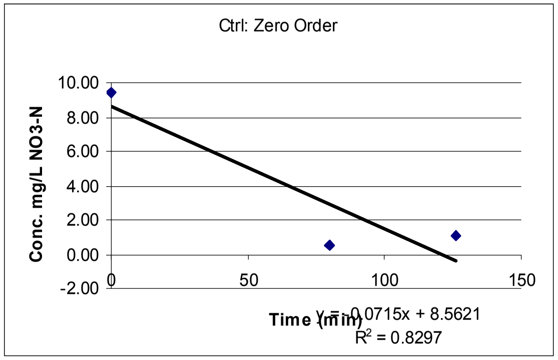
Ortho Phosphate 7/21/08 (Run 2) Cont.

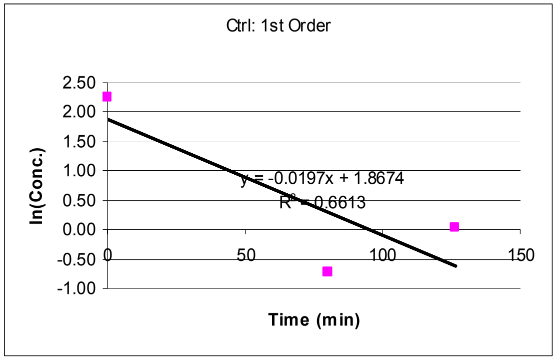

Mix 2: Zero Order

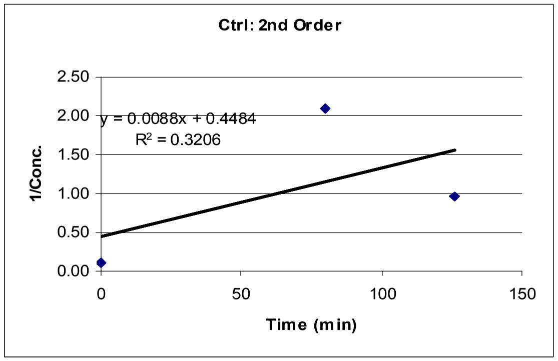

Mix 2: 1st Order

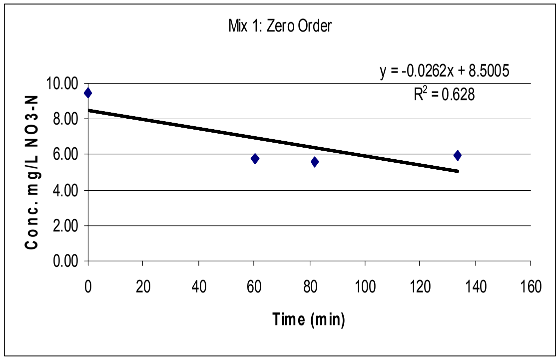

Mix 2: 2nd Order

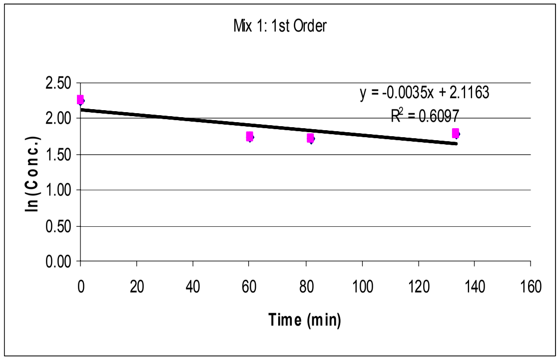
Ortho Phosphate 7/22/08

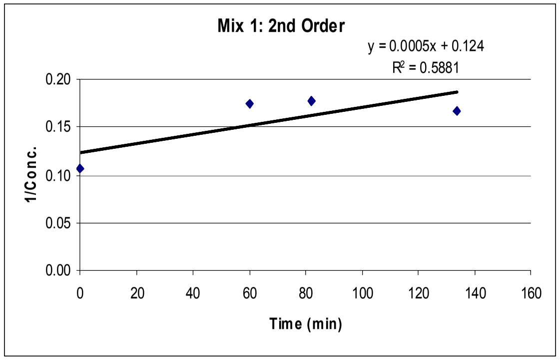




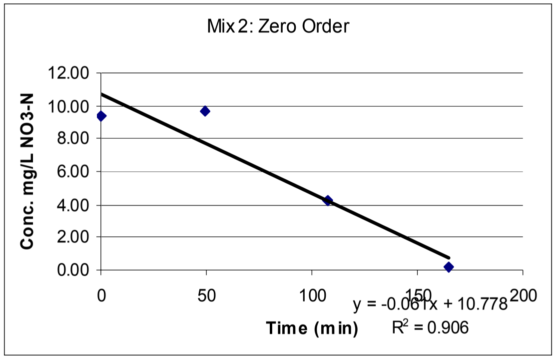


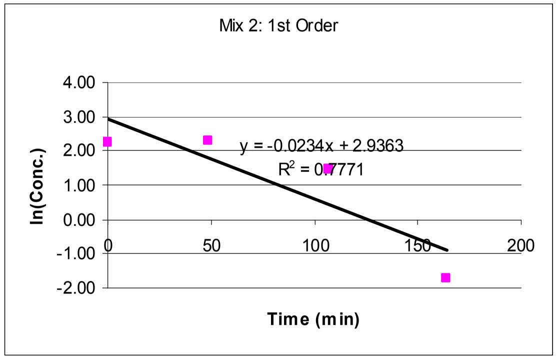


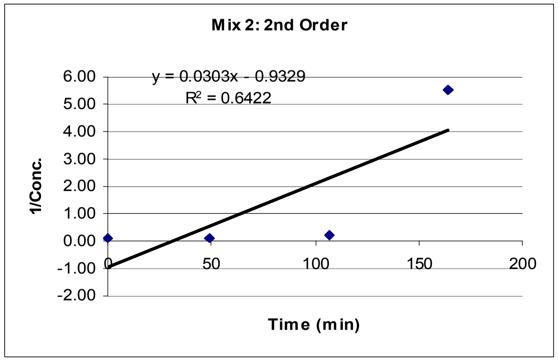




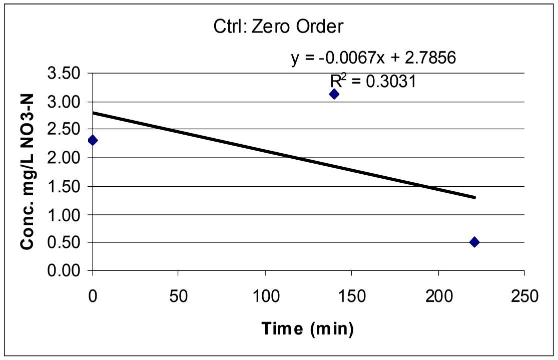
Ortho Phosphate 7/22/08 Cont.

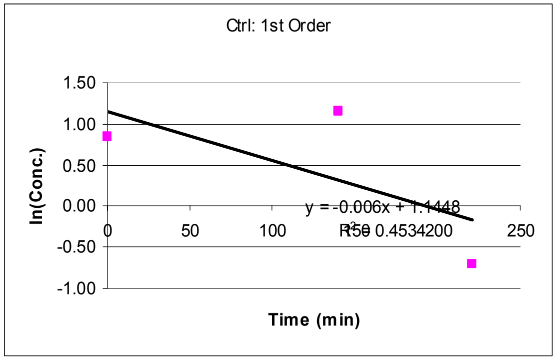

Mix 2: Zero Order
Conc. mg/L NO3-N
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0
50
100
150
200
Time (min)
y = -0.061x + 10.778
R² = 0.906

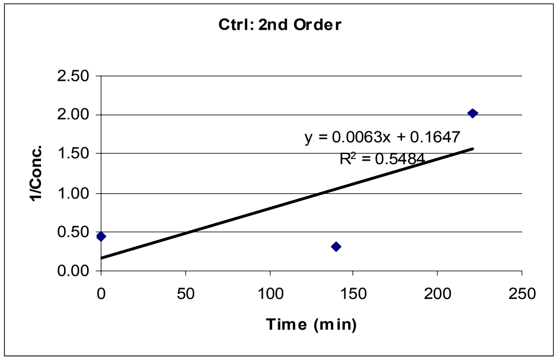

Mix 2: 1st Order
ln(Conc.)
4.00
3.00
2.00
1.00
0.00
-1.00
-2.00
0
50
100
150
200
Time (min)
y = -0.0234x + 2.9363
R² = 0.7771

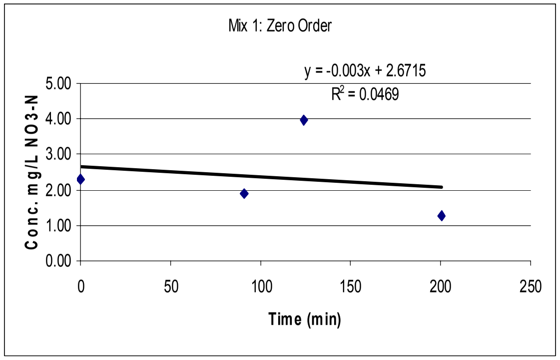

Mix 2: 2nd Order
1/Conc.
6.00
5.00
4.00
3.00
2.00
1.00
0.00
-1.00
-2.00
0
50
100
150
200
Time (min)
y = 0.0303x - 0.9329
R² = 0.6422

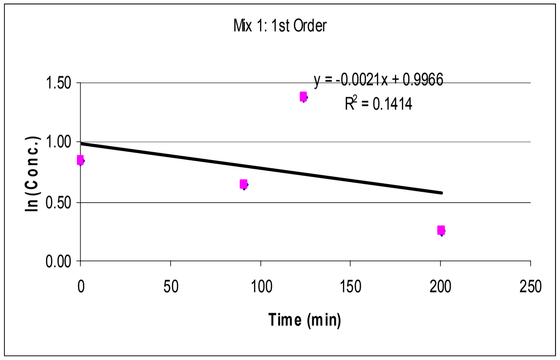
Ortho Phosphate 5/22/08

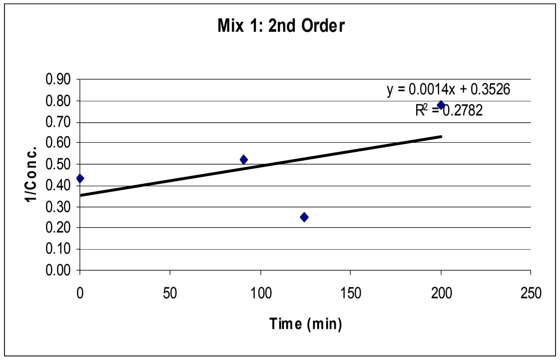




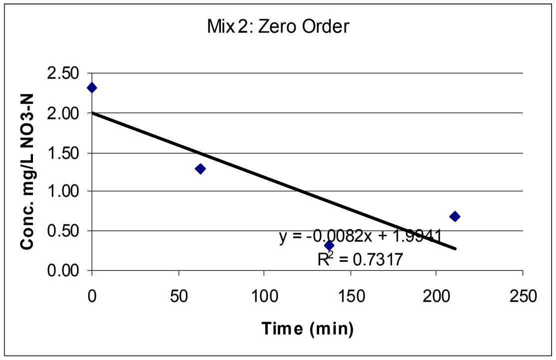


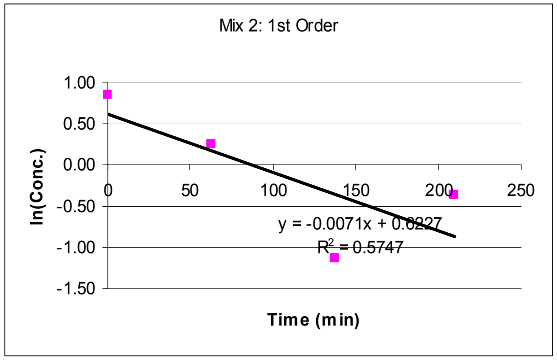


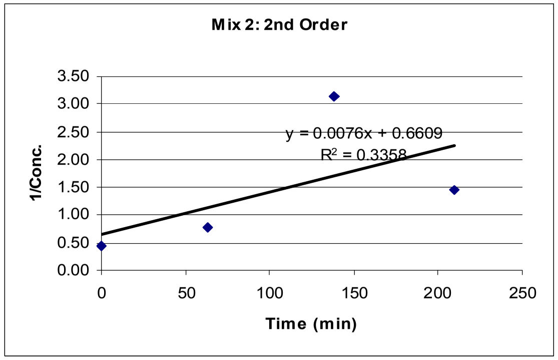




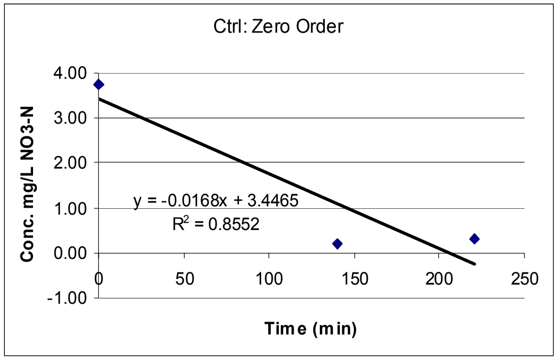
Ortho Phosphate 5/22/08 Cont.

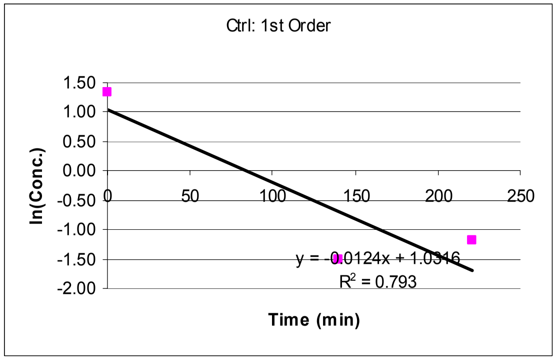


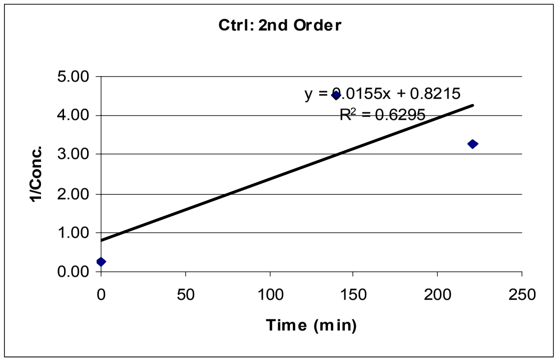


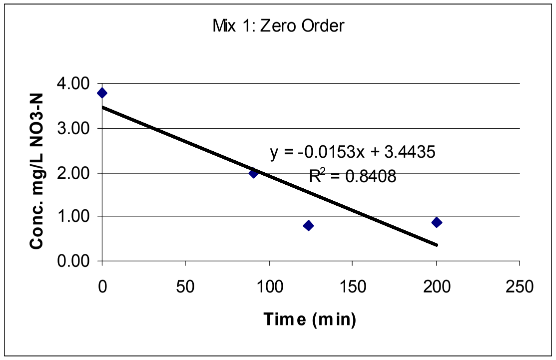


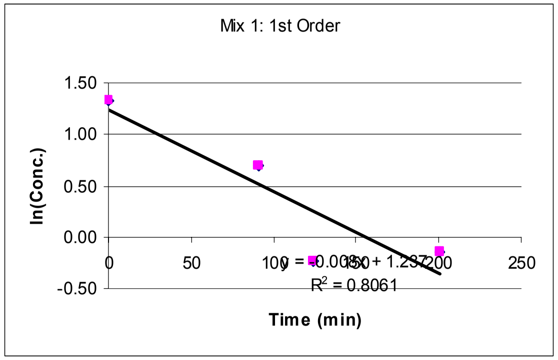
Ortho Phosphate 5/22/08 (Run 2)

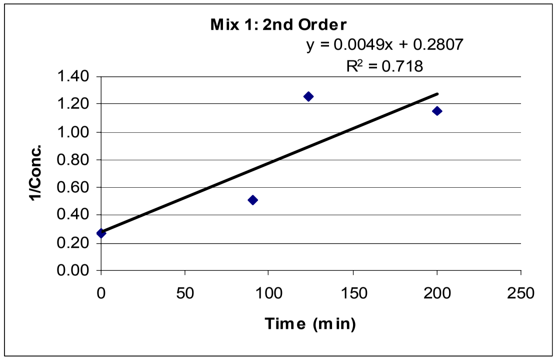

Ctrl: Zero Order


Ctrl: 1st Order

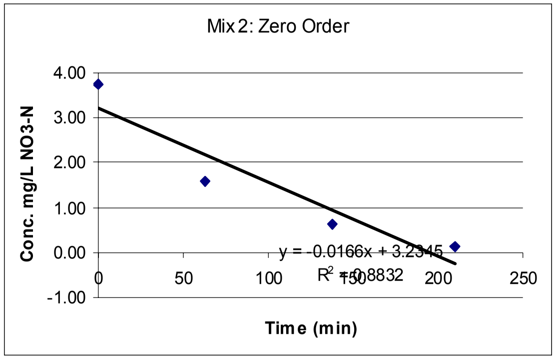

Ctrl: 2nd Order

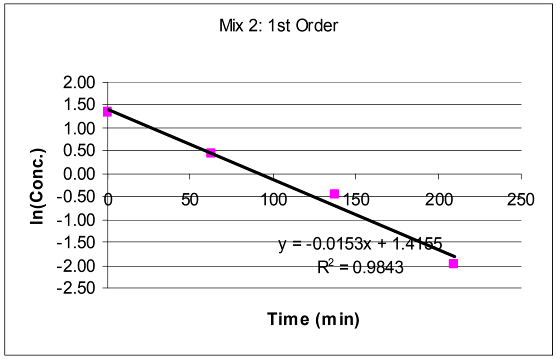

Mix 1: Zero Order

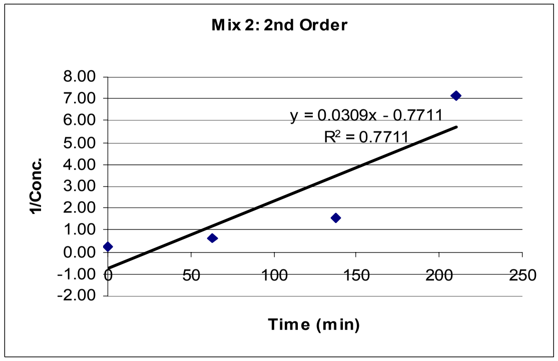

Mix 1: 1st Order


Mix 1: 2nd Order

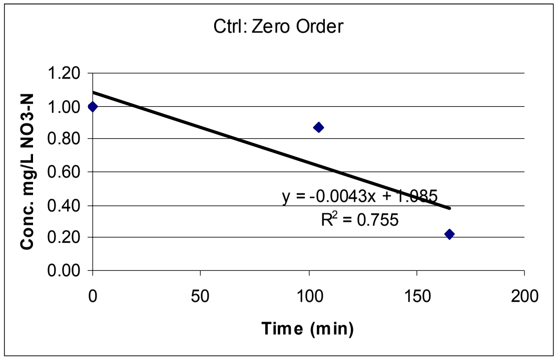
Ortho Phosphate 5/22/08 (Run 2) Cont.

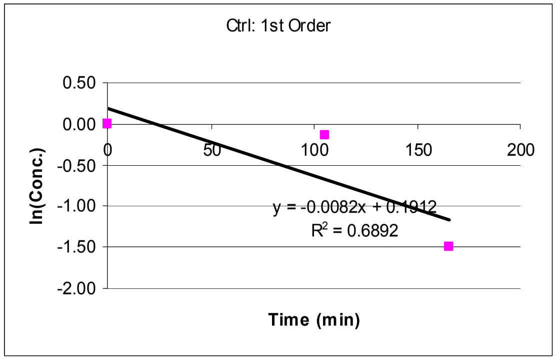

Mix 2: Zero Order
Conc. mg/L NO3-N
4.00
3.00
2.00
1.00
0.00
-1.00
0
50
100
150
200
250
y = -0.0166x + 3.2345
R² = 0.8832
Time (min)

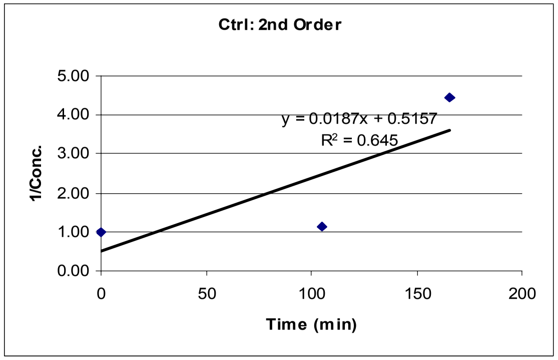

Mix 2: 1st Order
ln(Conc.)
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
0
50
100
150
200
250
y = -0.0153x + 1.4155
R² = 0.9843
Time (min)

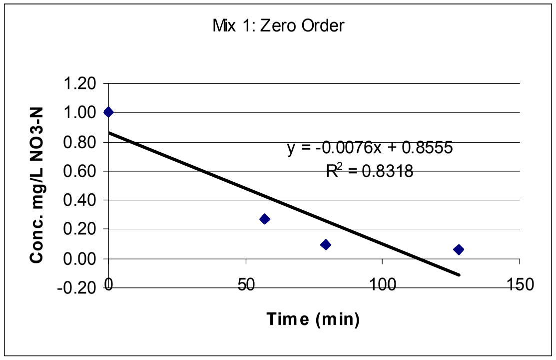

Mix 2: 2nd Order
1/Conc.
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
-1.00
-2.00
0
50
100
150
200
250
y = 0.0309x - 0.7711
R² = 0.7711
Time (min)

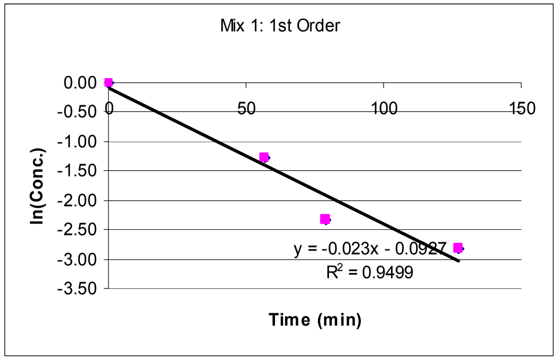
Ortho Phosphate 5/11/08

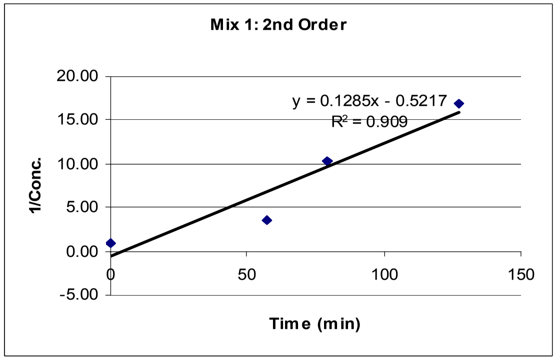




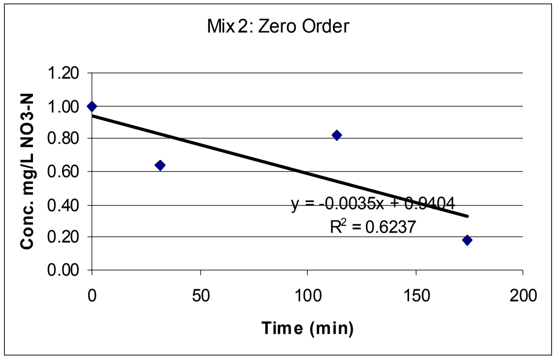




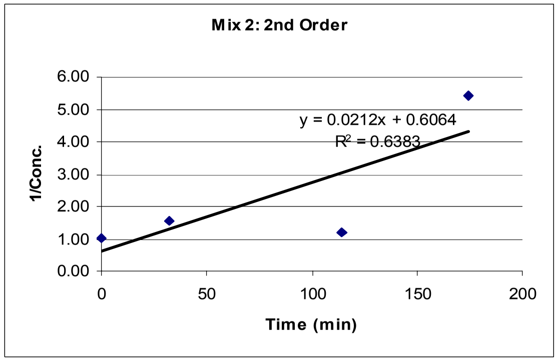




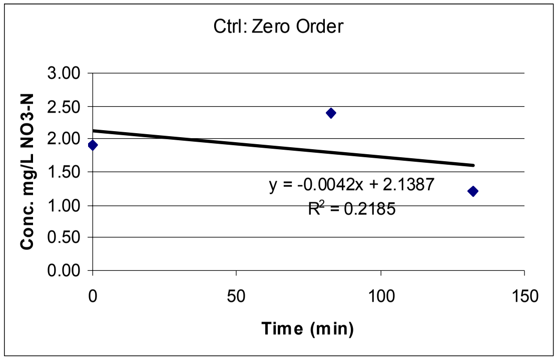
Ortho Phosphate 5/11/08 Cont.

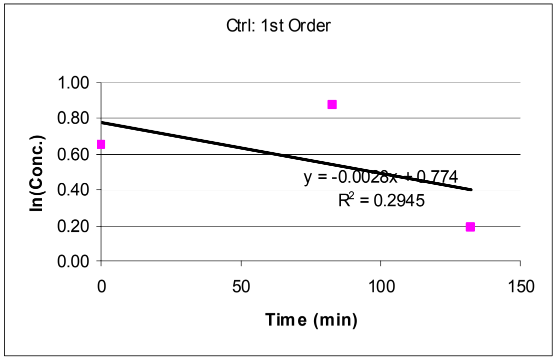

Mix 2: Zero Order
Conc. mg/L NO3-N
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
50
100
150
200
Time (min)
y = -0.0035x + 0.9404
R² = 0.6237

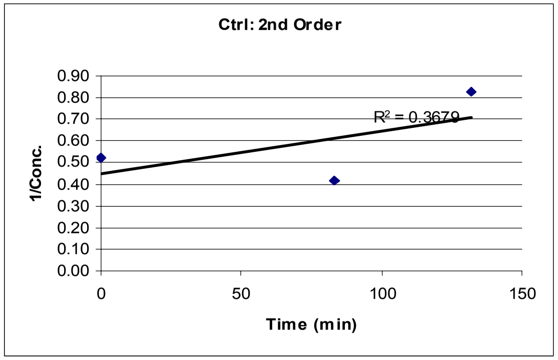

Mix 2: 1st Order
ln(Conc.)
0.50
0.00
-0.50
-1.00
-1.50
-2.00
0
50
100
150
200
Time (min)
y = -0.0077x + 0.0322
R² = 0.6419

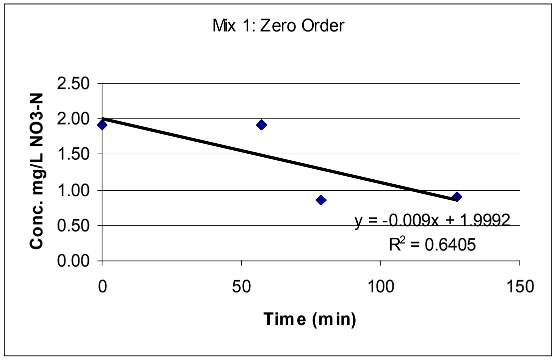

Mix 2: 2nd Order
1/Conc.
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
50
100
150
200
Time (min)
y = 0.0212x + 0.6064
R² = 0.6383

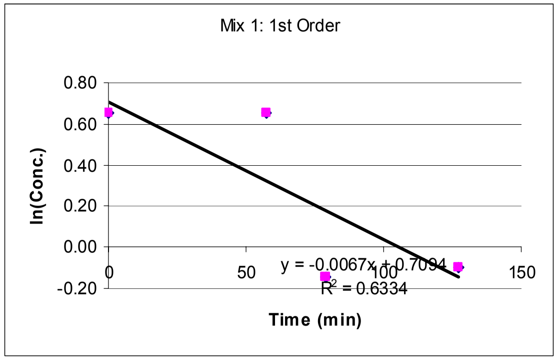
Ortho Phosphate 5/13/08

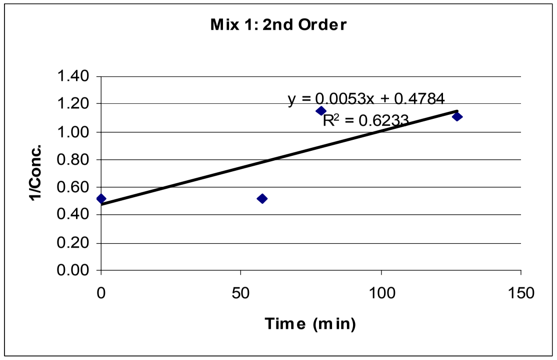

Ctrl: Zero Order


Ctrl: 1st Order

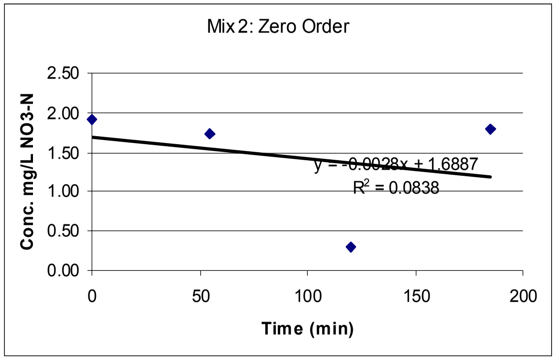

Ctrl: 2nd Order

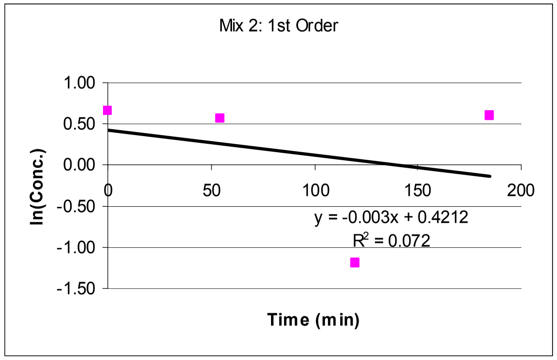

Mix 1: Zero Order

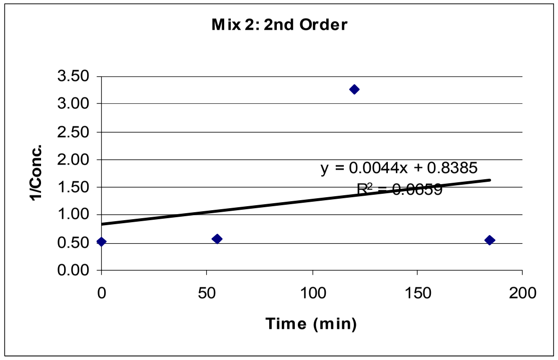

Mix 1: 1st Order


Mix 1: 2nd Order

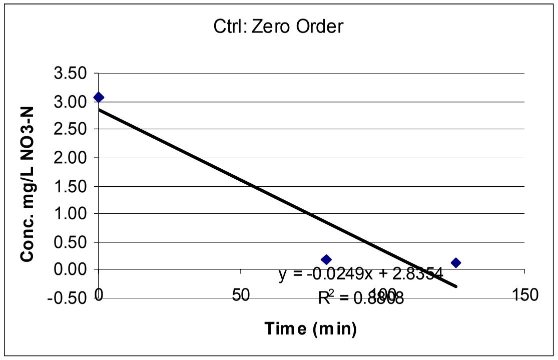
Ortho Phosphate 5/13/08 Cont.

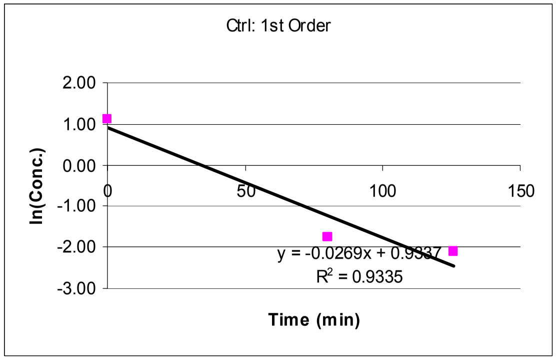


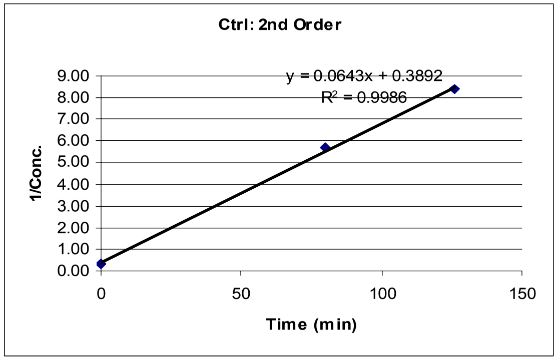


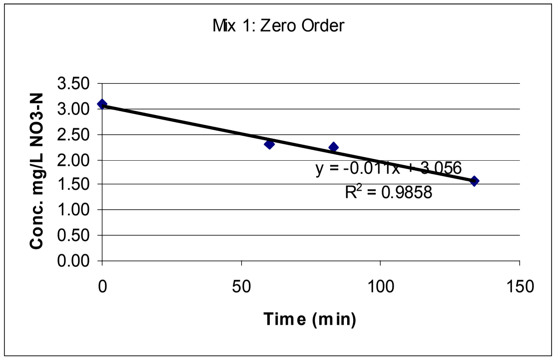


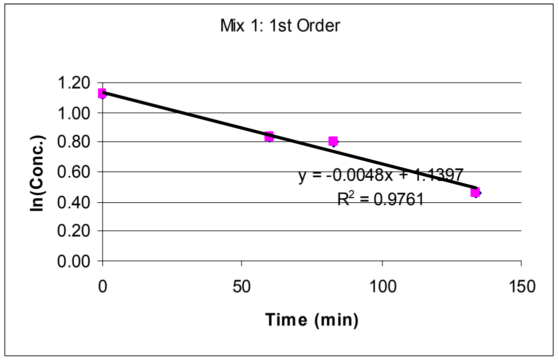
Ortho Phosphate 6/23/08

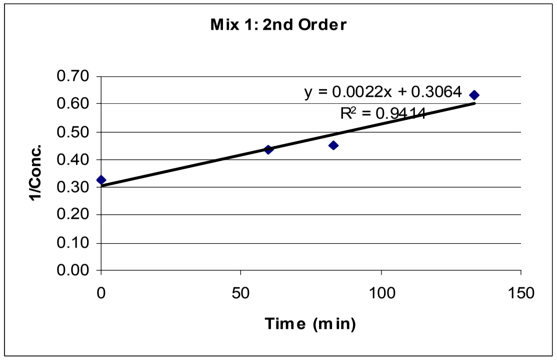




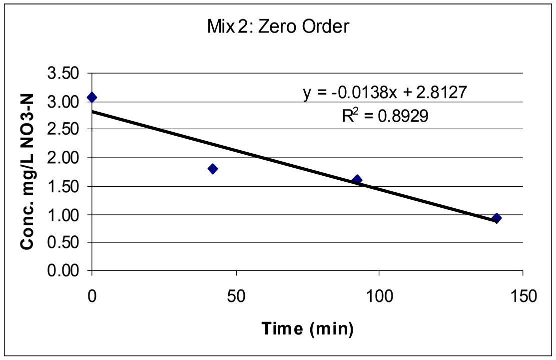


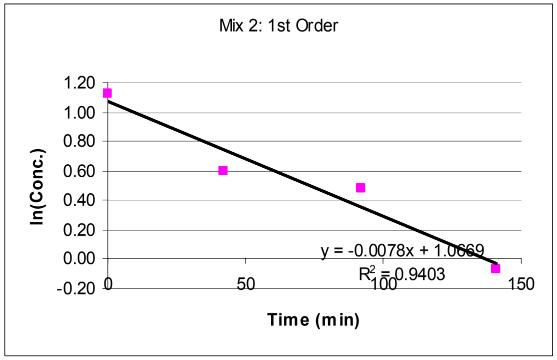


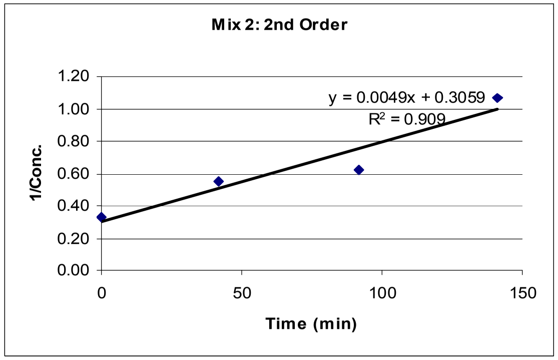




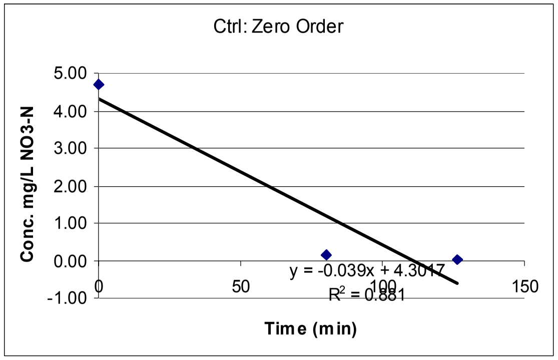
Ortho Phosphate 6/23/08 Cont.

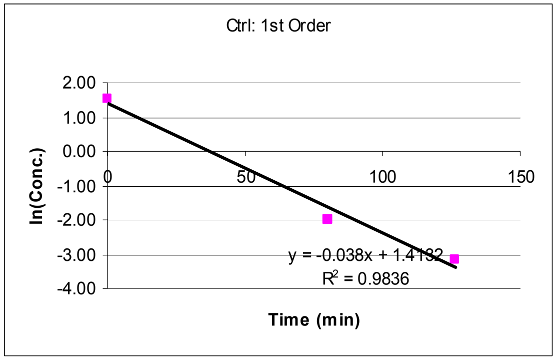


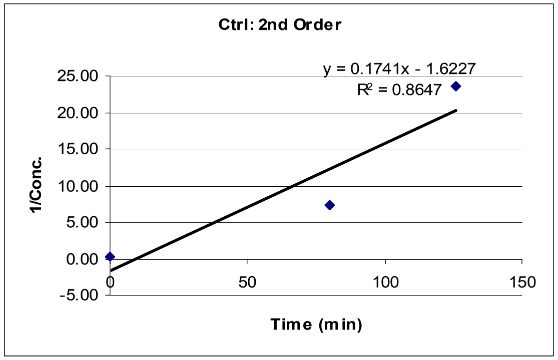


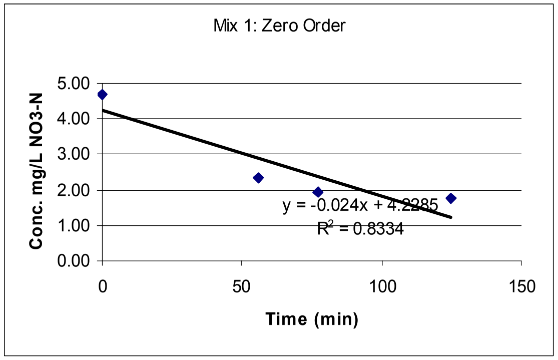


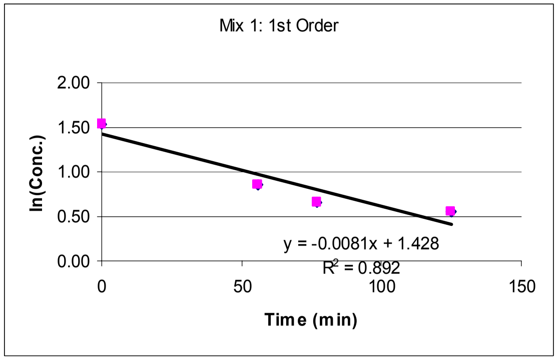
Ortho Phosphate 6/23/08 (Run 2)

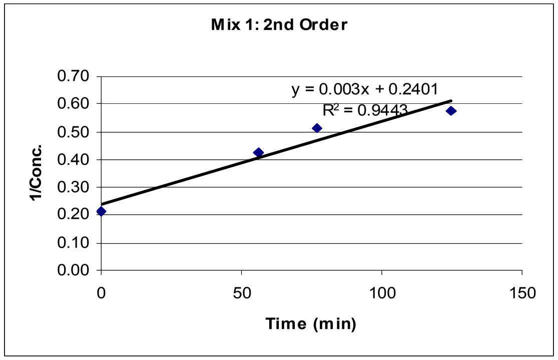




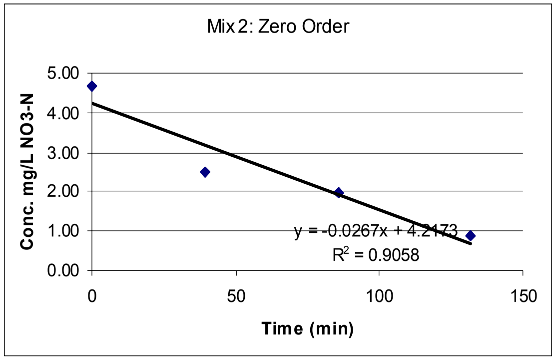


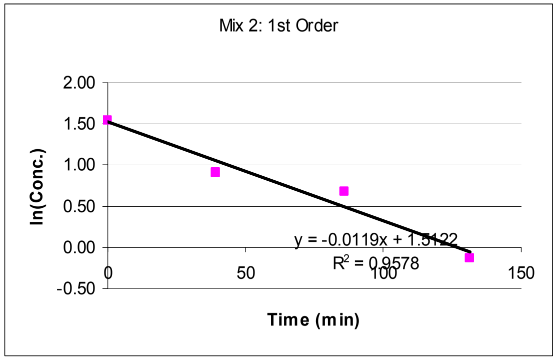


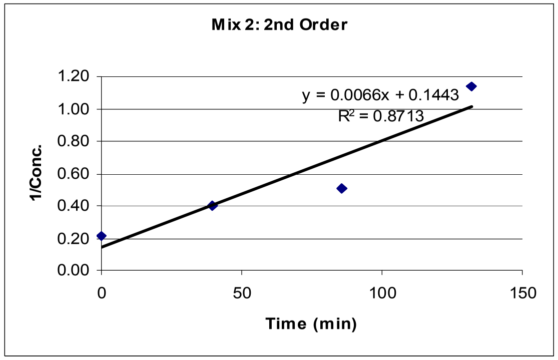




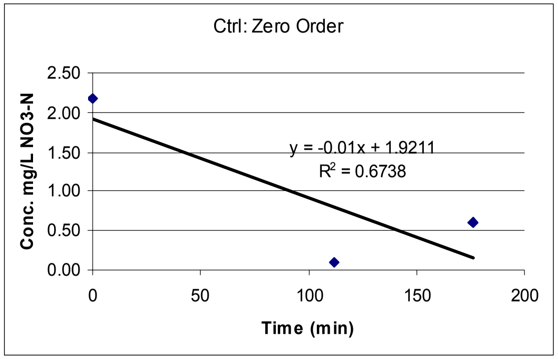
Ortho Phosphate 6/23/08 (Run 2) Cont.

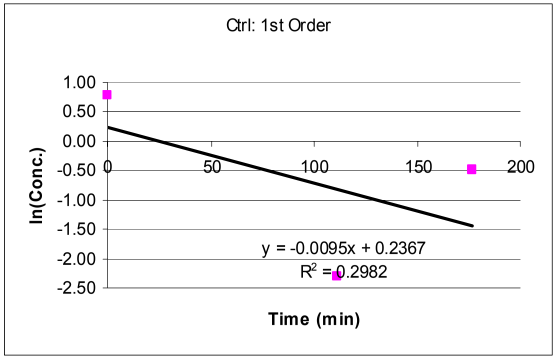


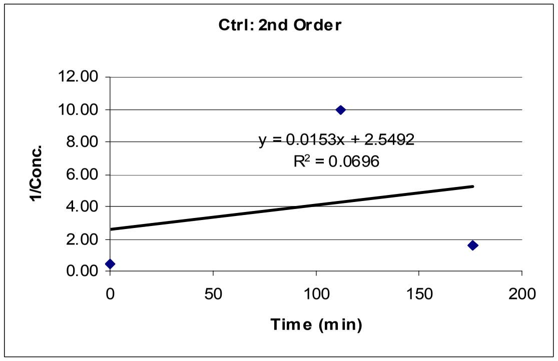


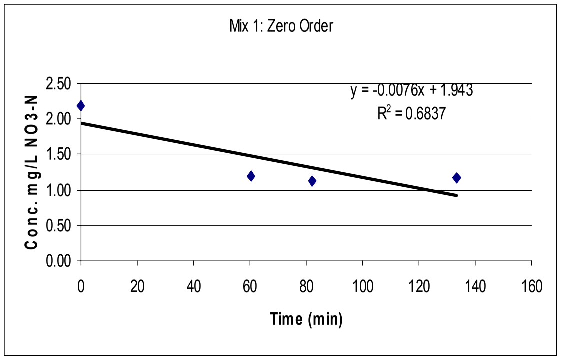


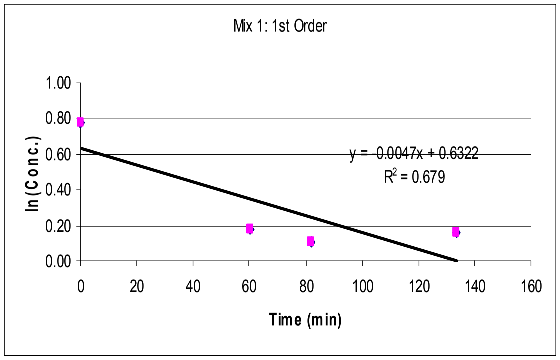
Ortho Phosphate 6/1/08

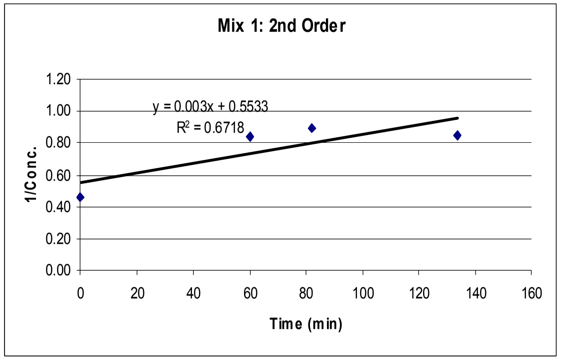

Ctrl: Zero Order


Ctrl: 1st Order

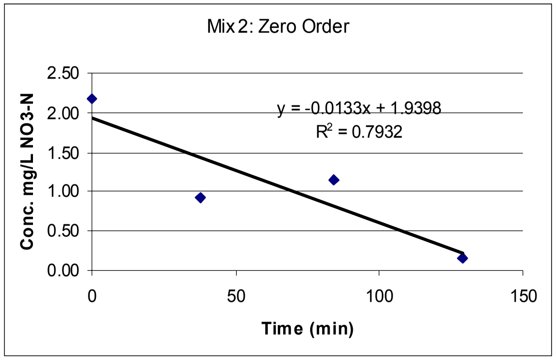

Ctrl: 2nd Order

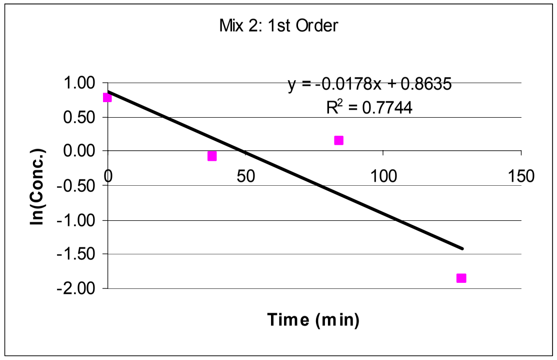

Mix 1: Zero Order

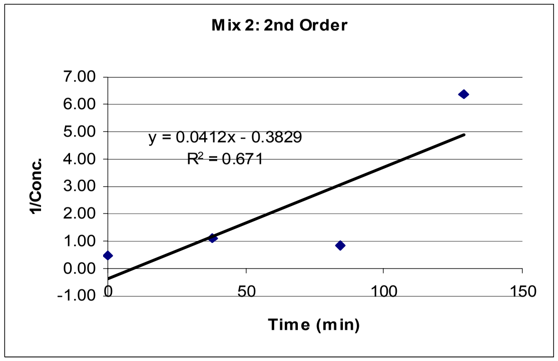

Mix 1: 1st Order


Mix 1: 2nd Order

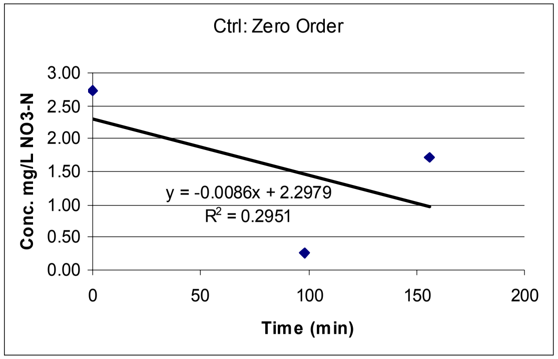
Ortho Phosphate 6/1/08 Cont.

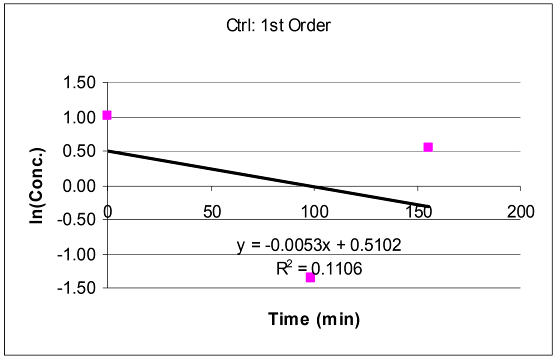


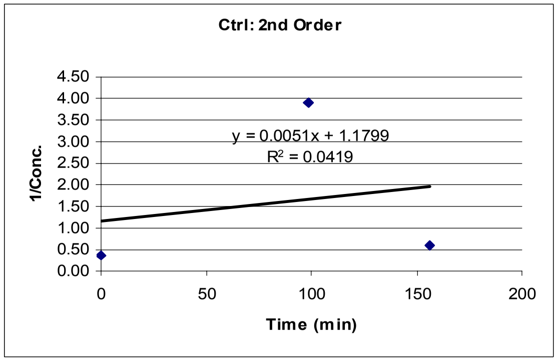


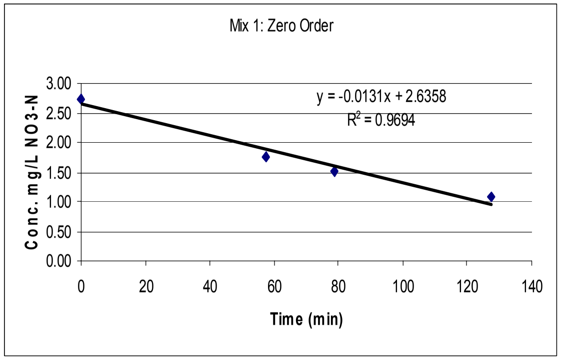


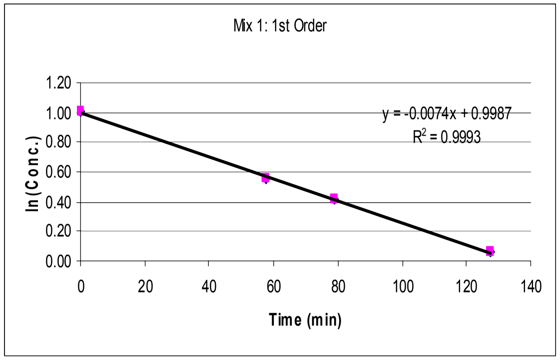
Ortho Phosphate 6/2/08

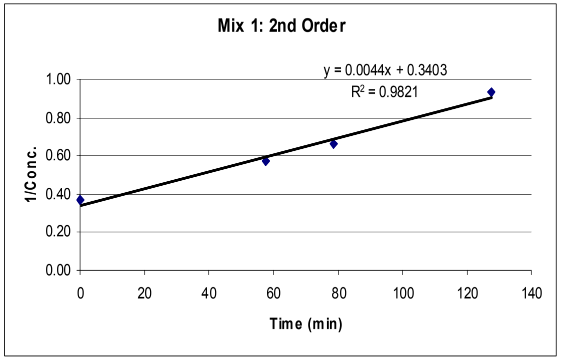




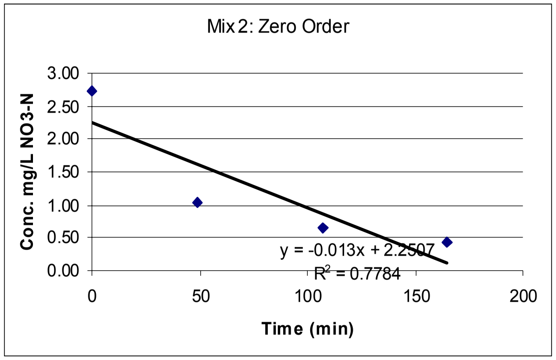


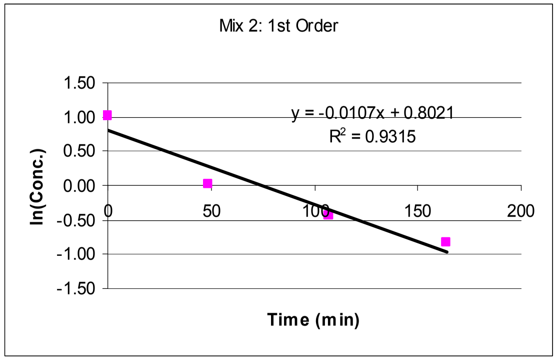


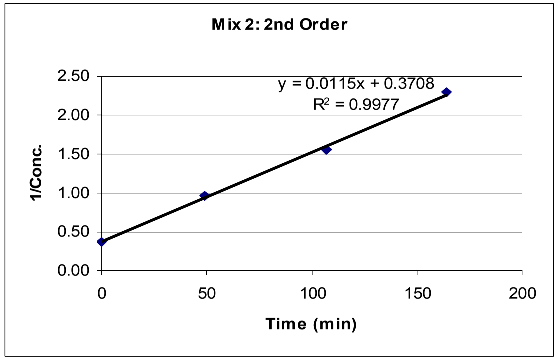




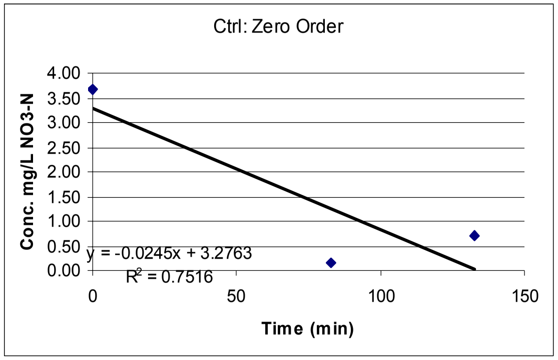
Ortho Phosphate 6/2/08 Cont.

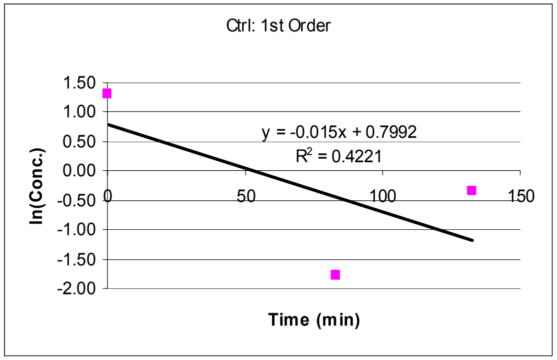


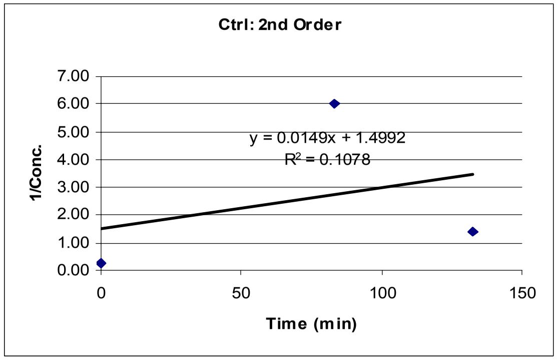


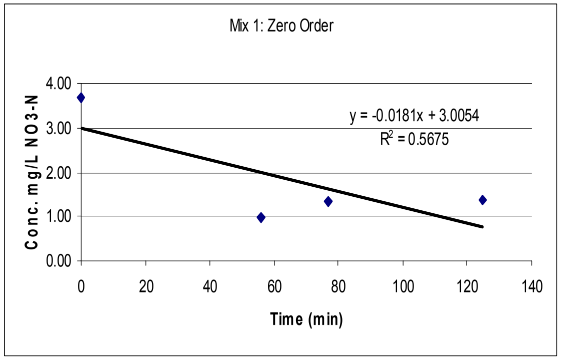


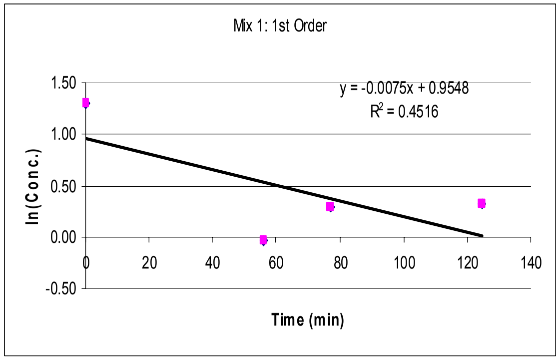
Ortho Phosphate 6/6/08

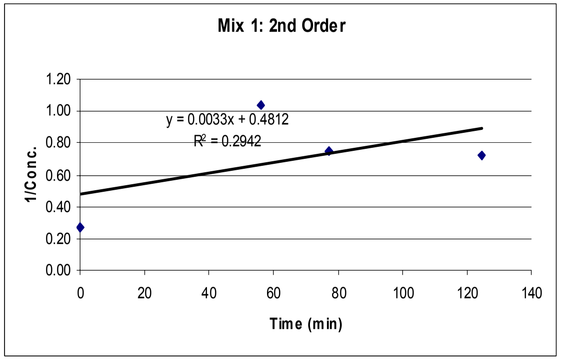




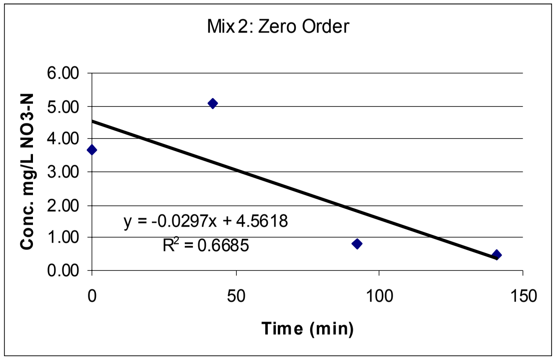


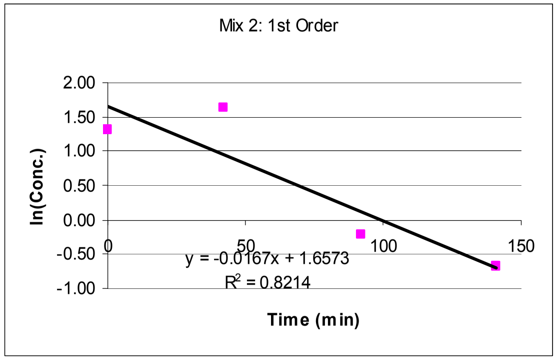


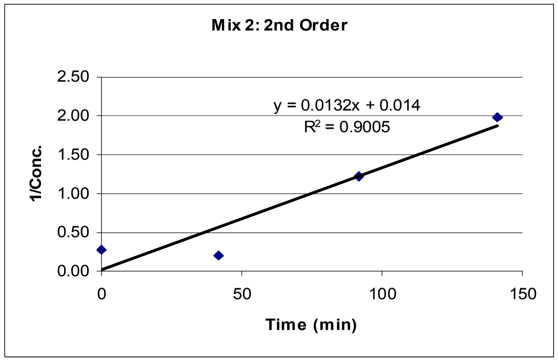




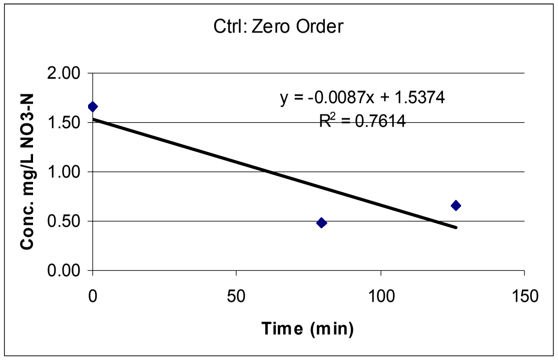
Ortho Phosphate 6/6/08 Cont.

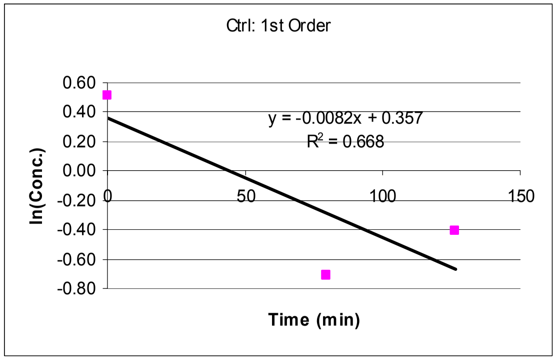


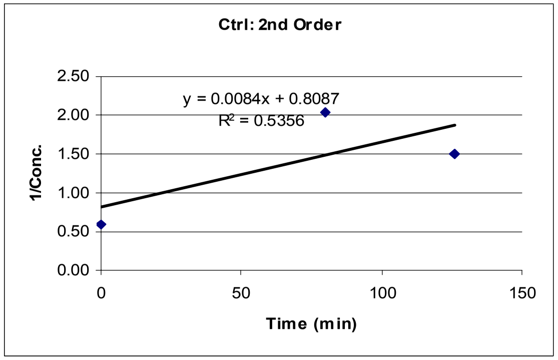


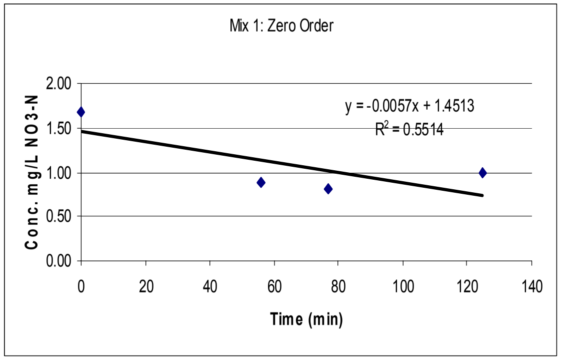


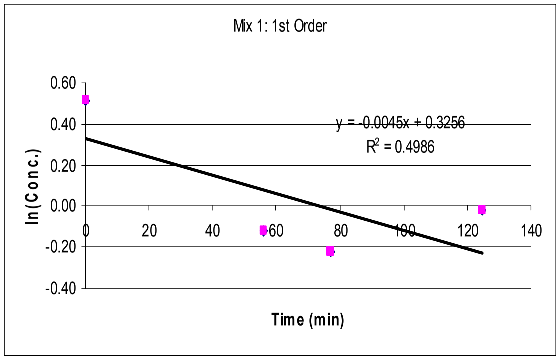
Ortho Phosphate 6/10/08

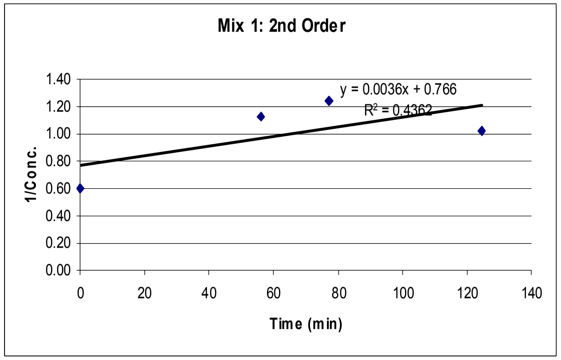




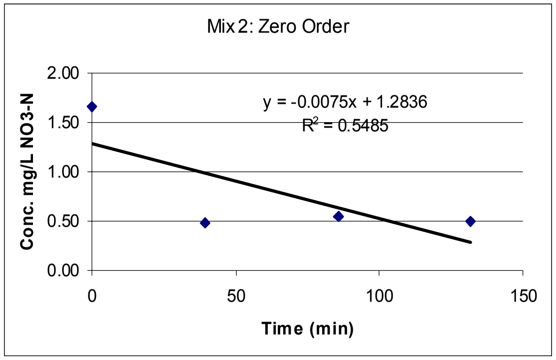


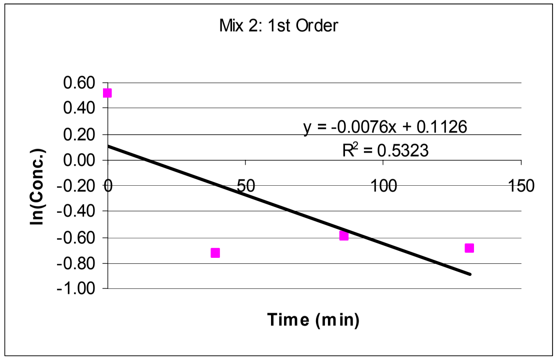


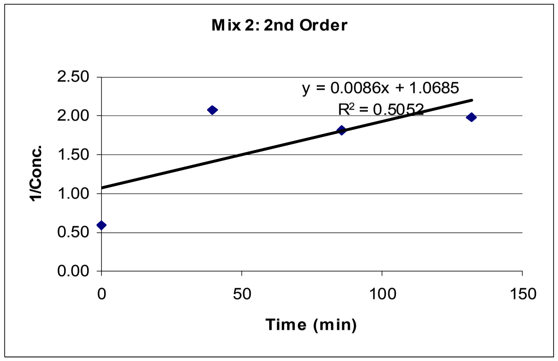




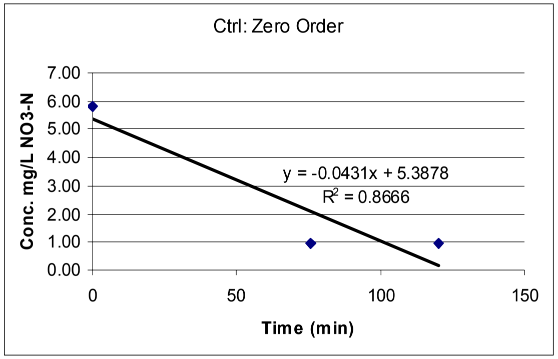
Ortho Phosphate 6/10/08 Cont.

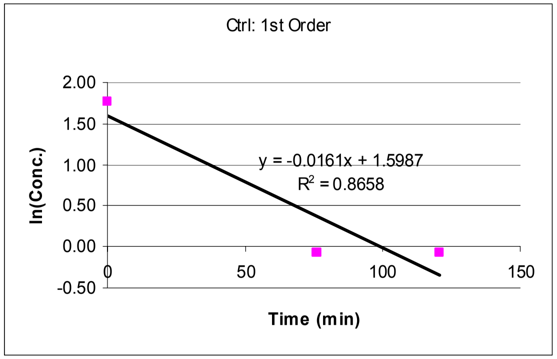


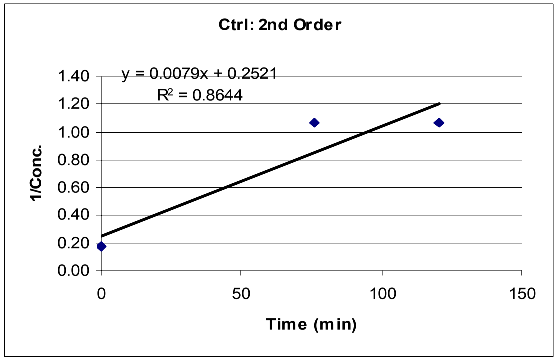


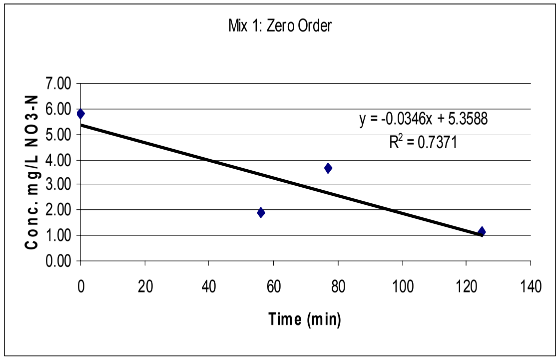


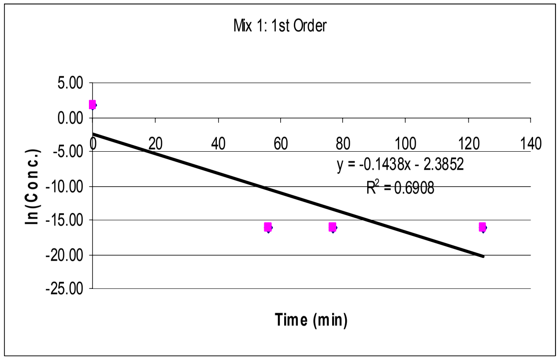
Ortho Phosphate 6/11/08

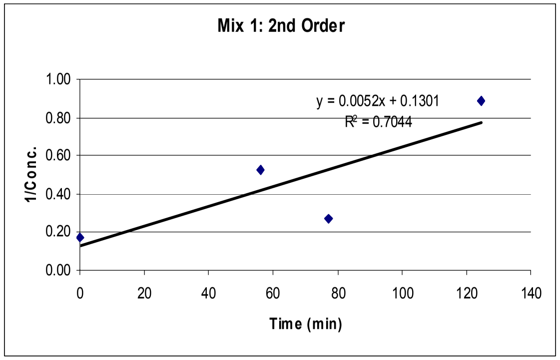




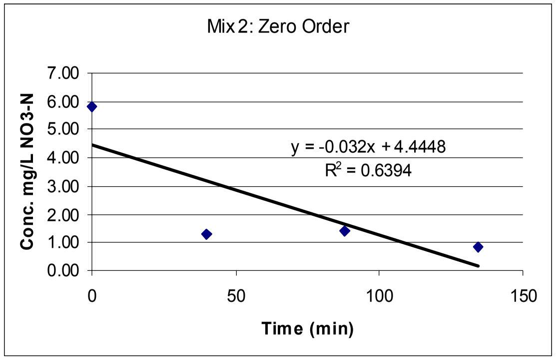


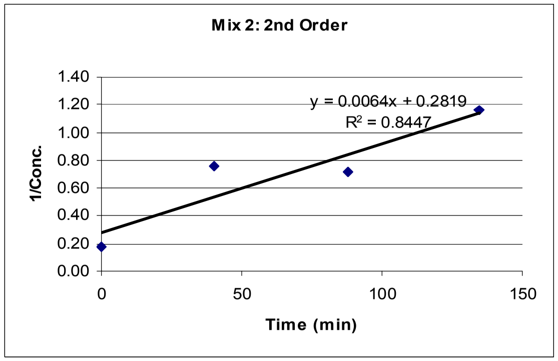




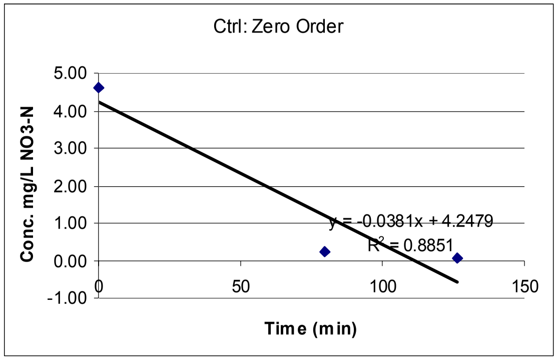


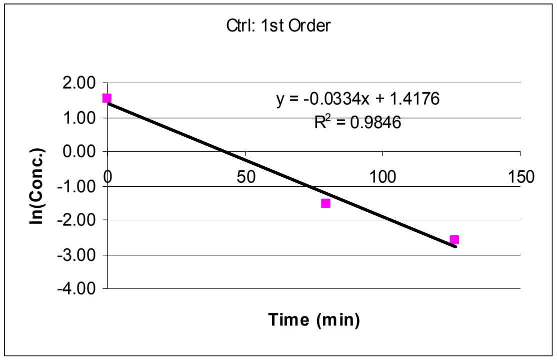
Ortho Phosphate 6/11/08 Cont.

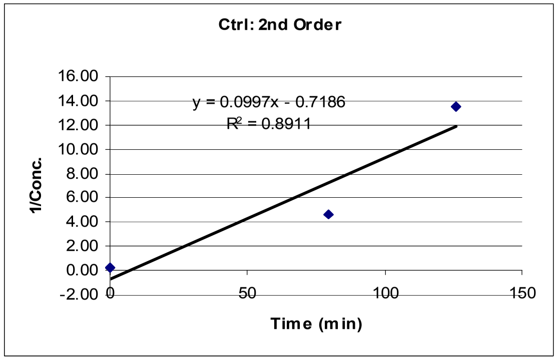


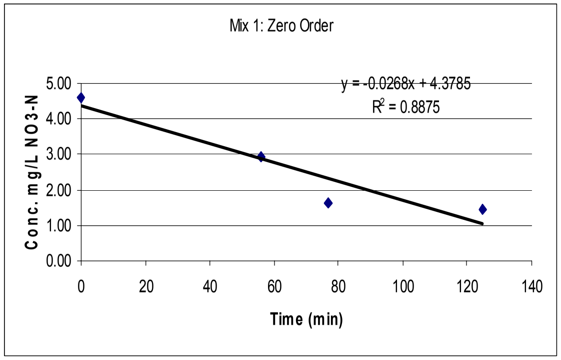


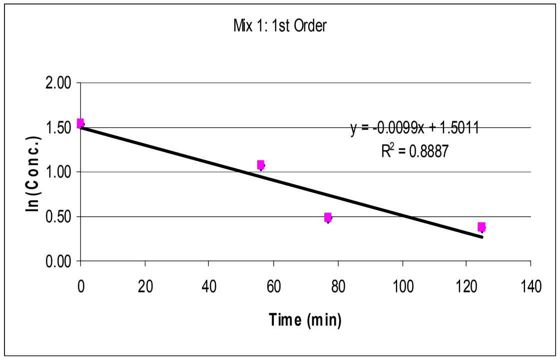
Ortho Phosphate 6/17/08

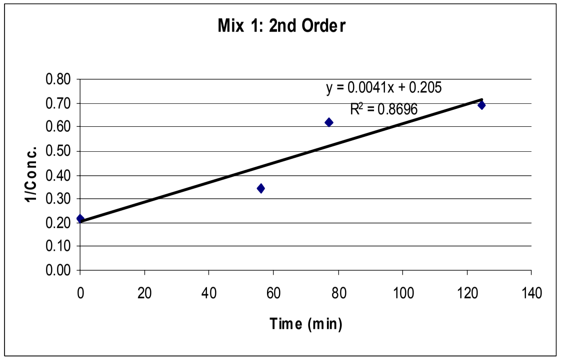

Ctrl: Zero Order


Ctrl: 1st Order

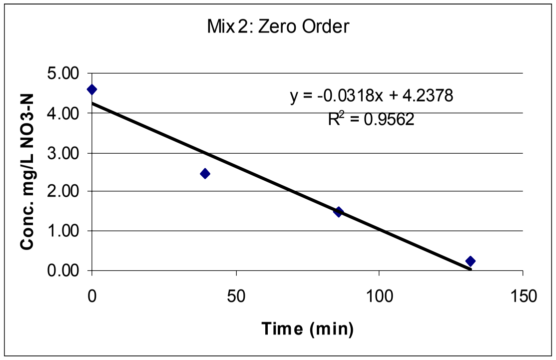

Ctrl: 2nd Order

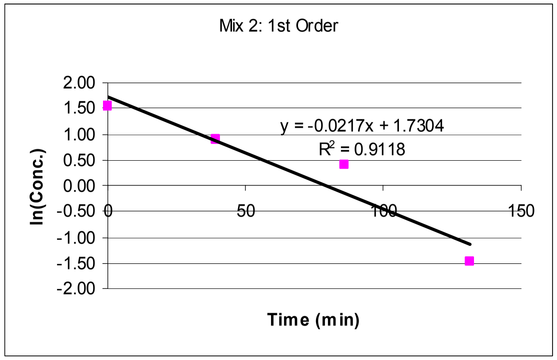

Mix 1: Zero Order


Mix 1: 1st Order

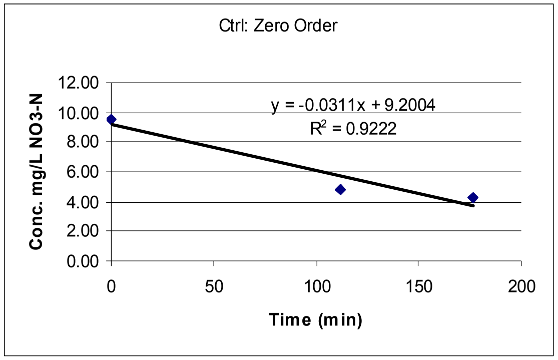

Mix 1: 2nd Order

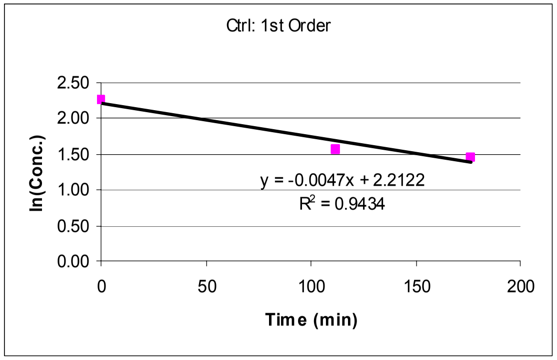
Ortho Phosphate 6/17/08 Cont.

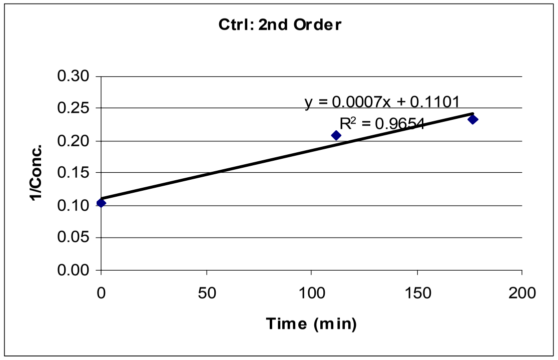


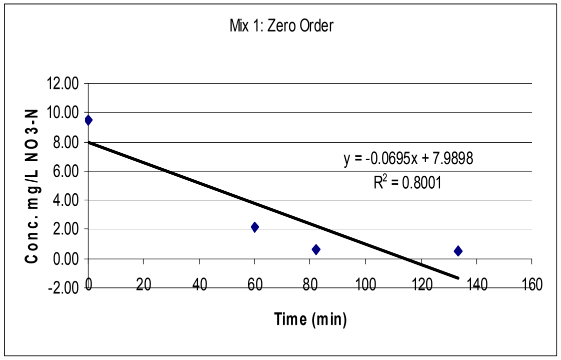


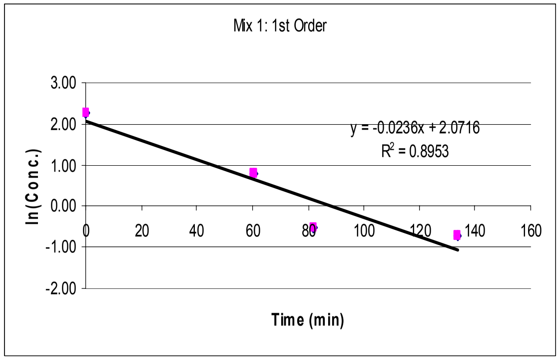
Nitrate 6/1/08

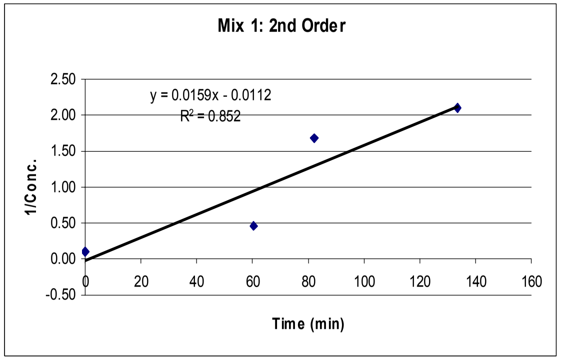

Ctrl: Zero Order


Ctrl: 1st Order

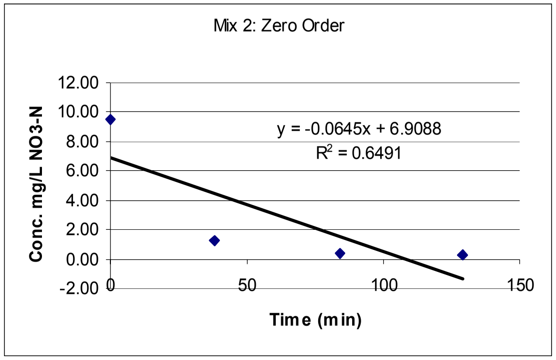

Ctrl: 2nd Order

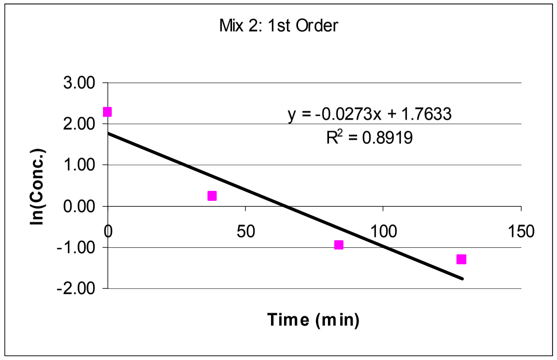

Mix 1: Zero Order


Mix 1: 1st Order

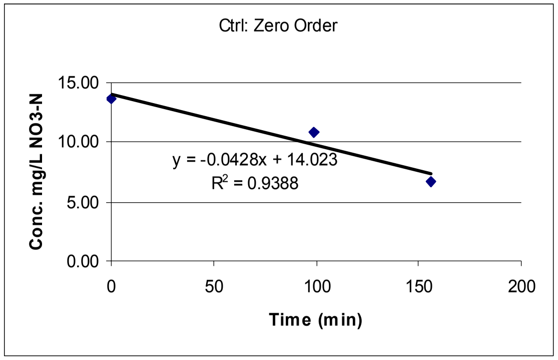

Mix 1: 2nd Order

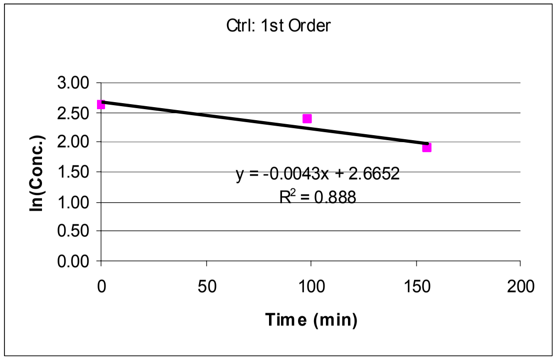
Nitrate 6/1/08 Cont.

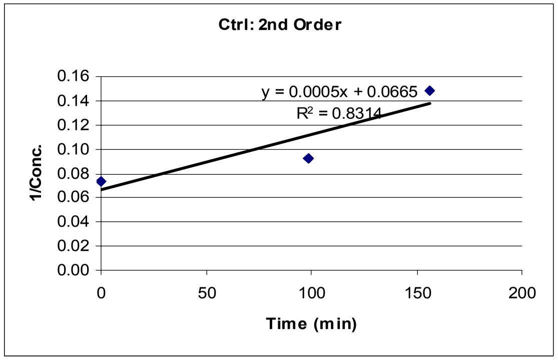


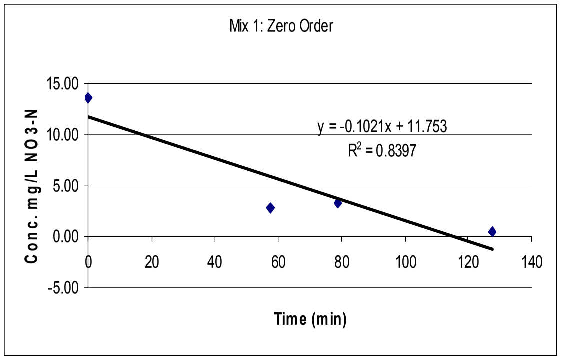


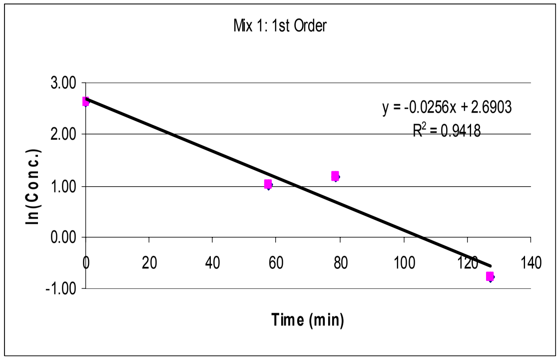
Nitrate 6/2/08

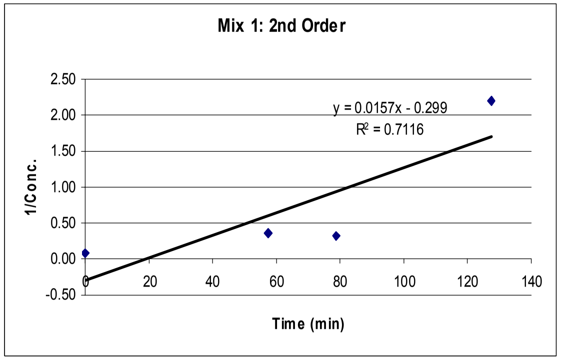




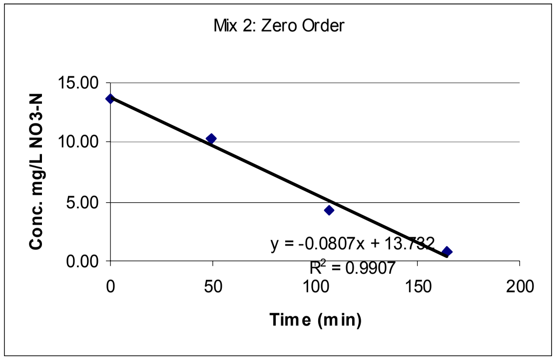


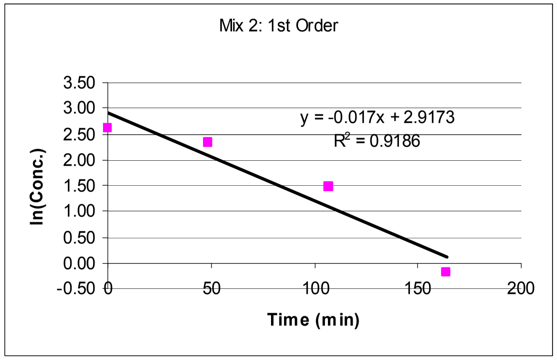


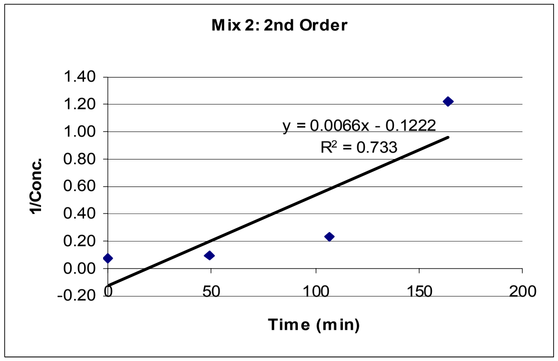




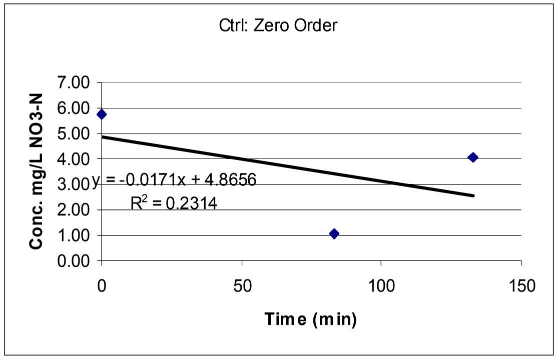
Nitrate 6/2/08 Cont.

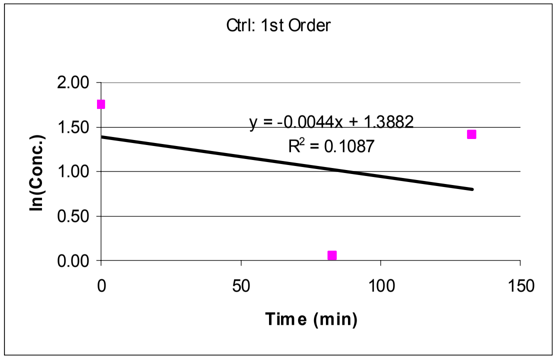


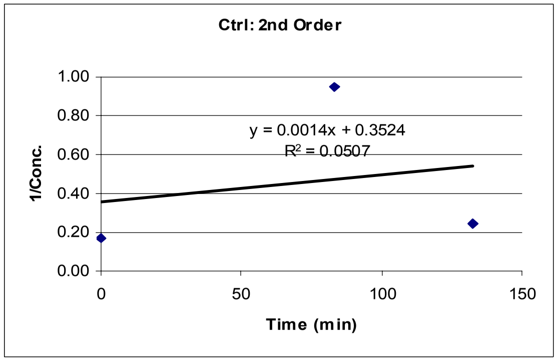


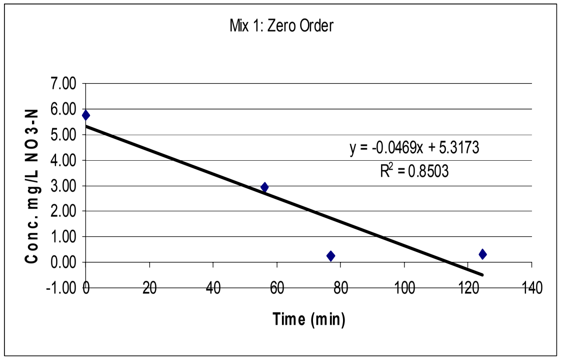


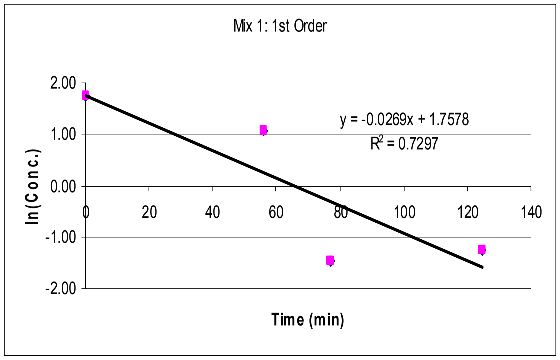
Nitrate 6/6/08

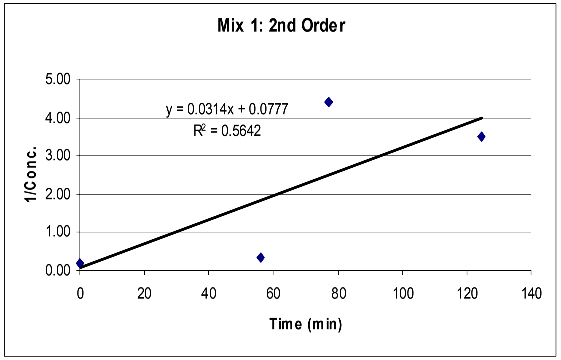




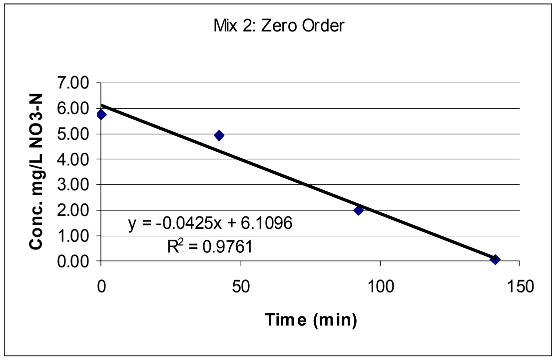


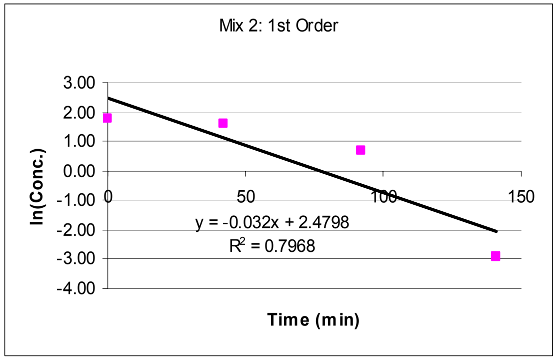


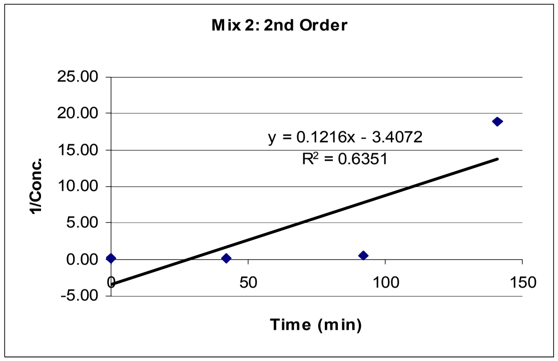




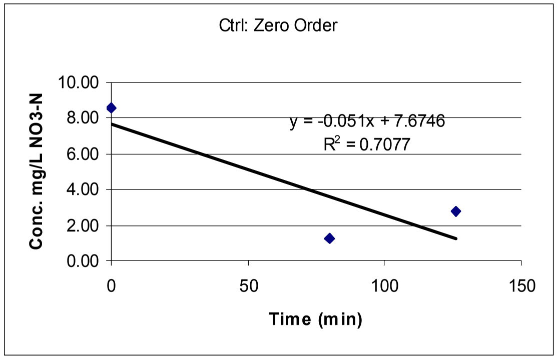
Nitrate 6/6/08 Cont.

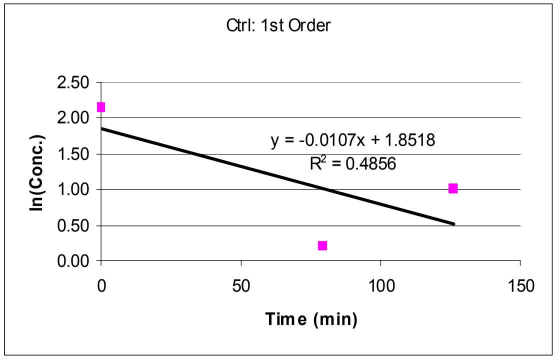

Mix 2: Zero Order

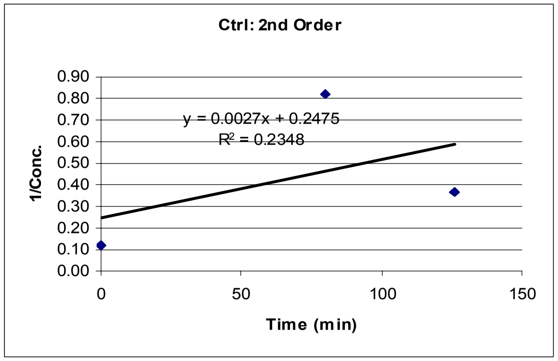

Mix 2: 1st Order

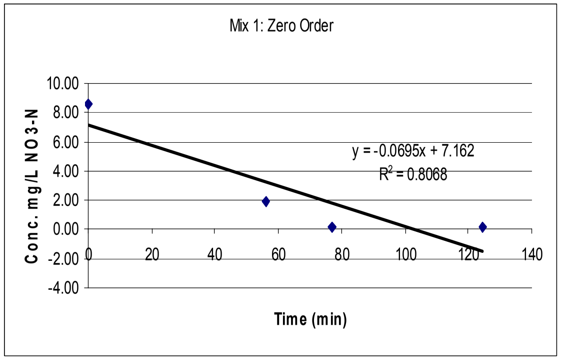

Mix 2: 2nd Order

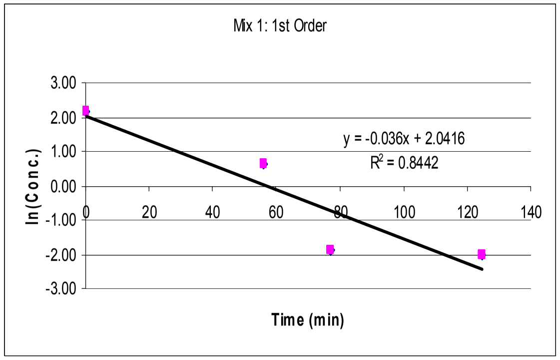
Nitrate 6/10/08

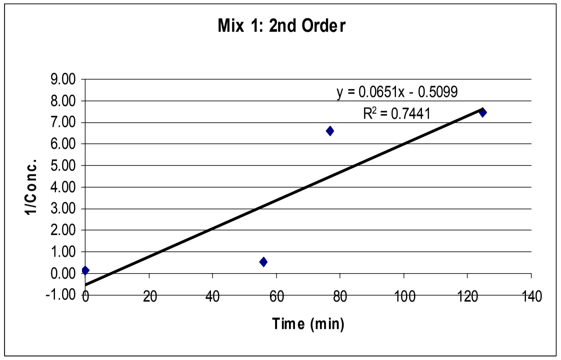




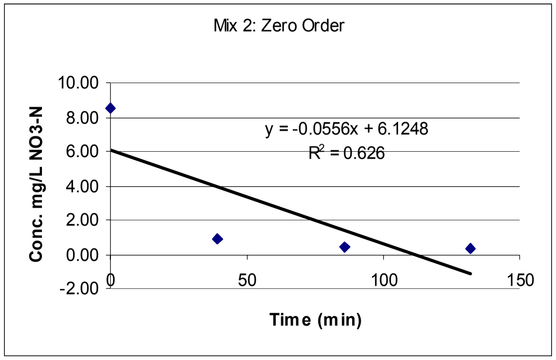


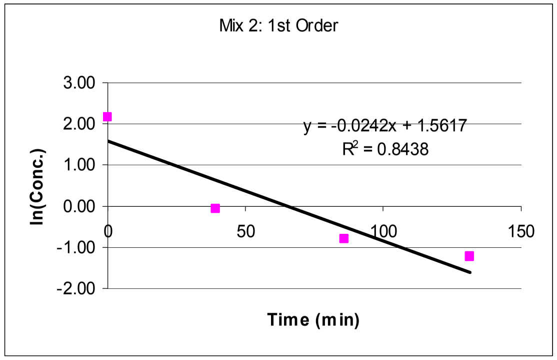


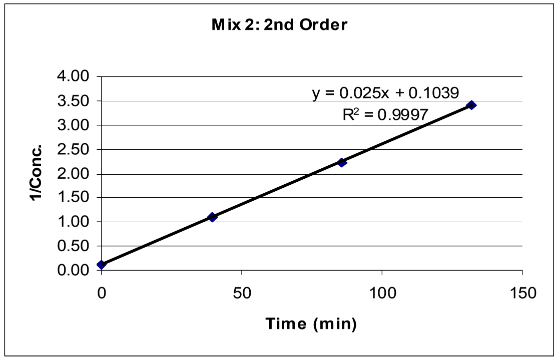




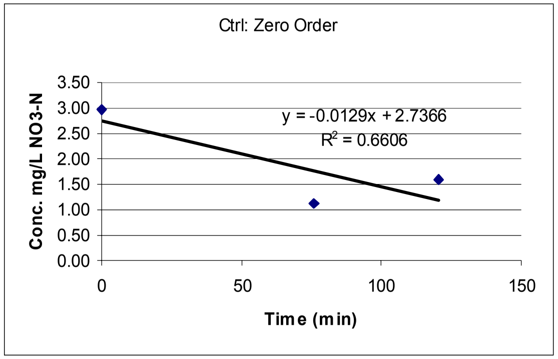
Nitrate 6/10/08 Cont.

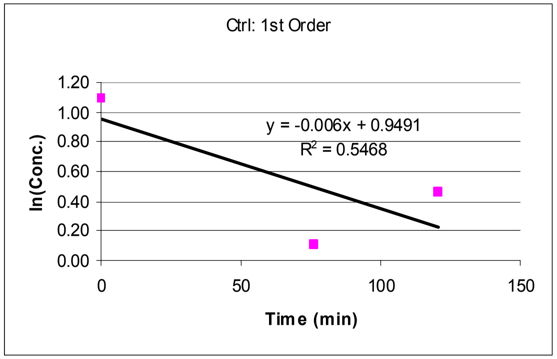


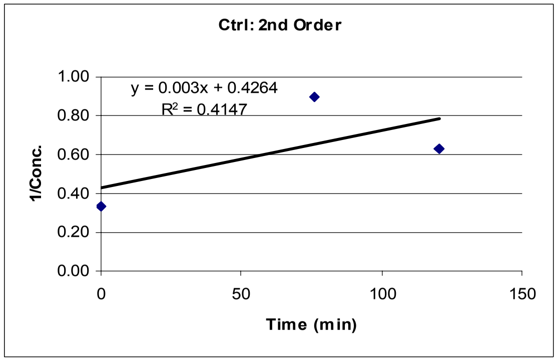




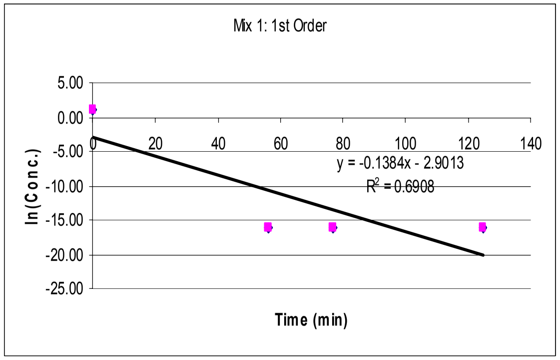
Nitrate 6/11/08


Ctrl: Zero Order


Ctrl: 1st Order

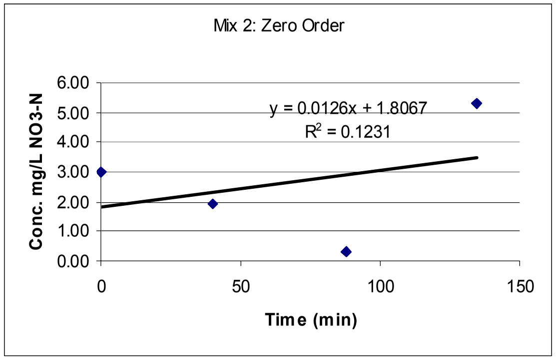

Ctrl: 2nd Order

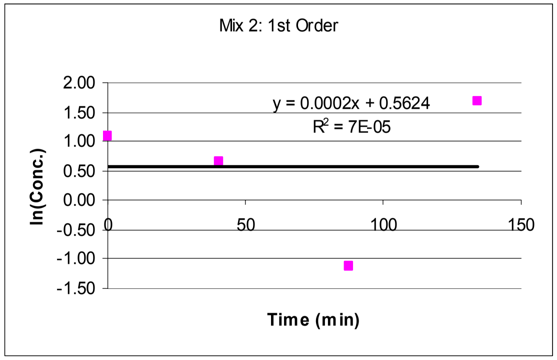

Mix 1: Zero Order

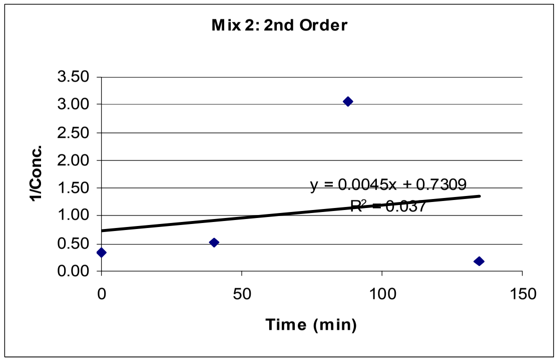

Mix 1: 1st Order


Mix 1: 2nd Order

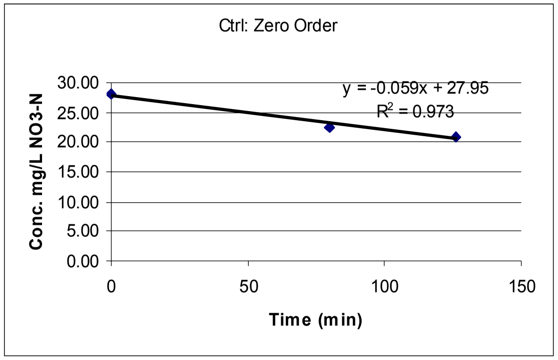
Nitrate 6/11/08 Cont.

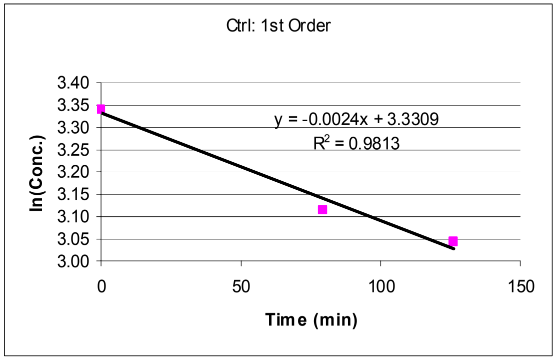


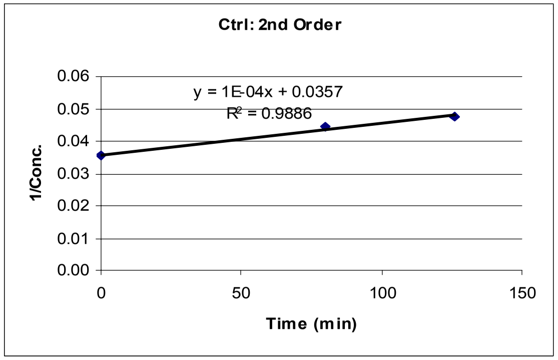


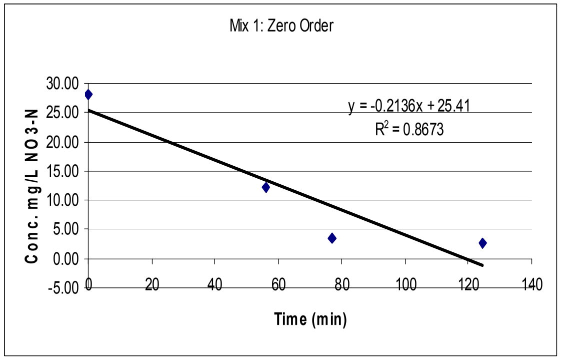


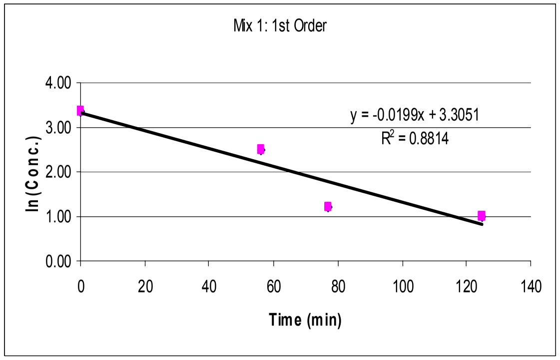
Nitrate 6/17/08

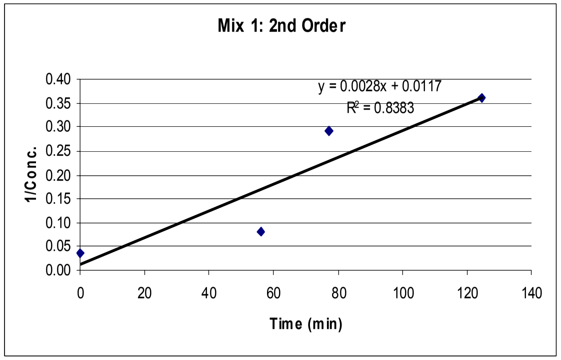




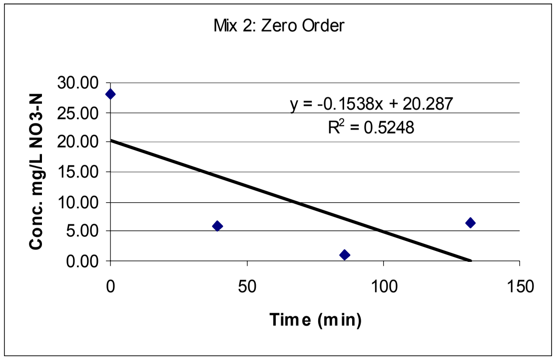


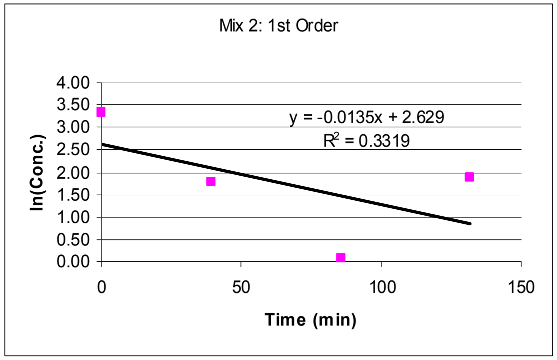


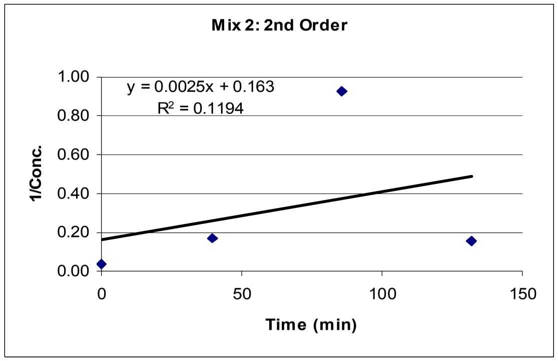




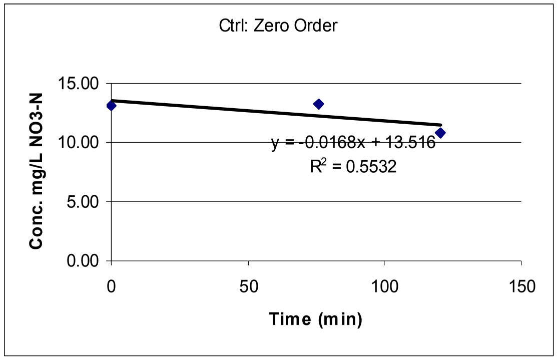
Nitrate 6/17/08 Cont.

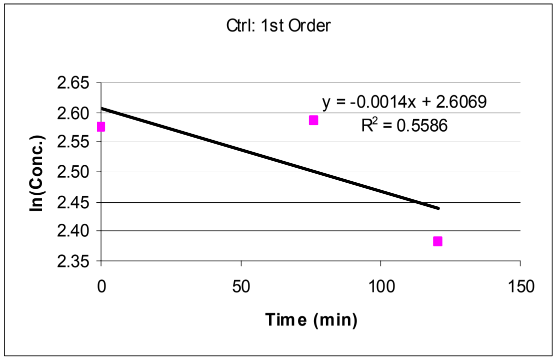


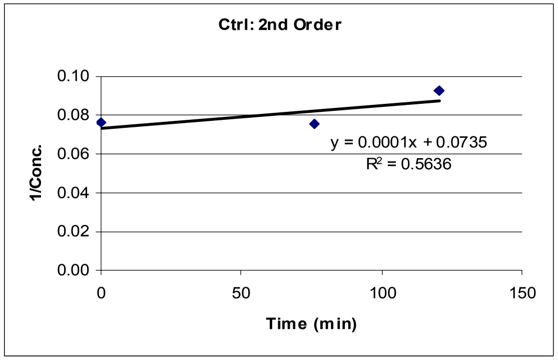


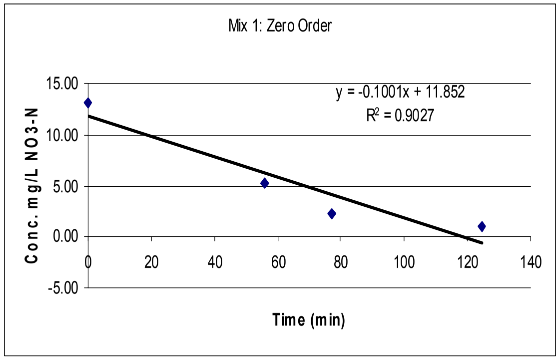


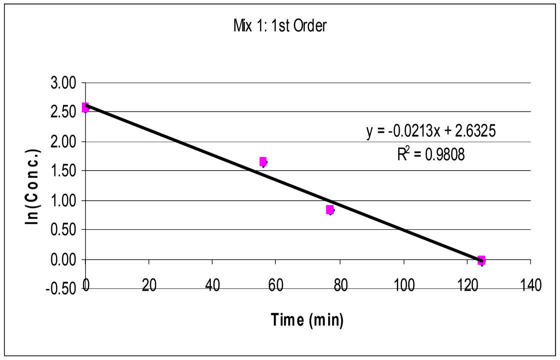
Nitrate 7/8/08

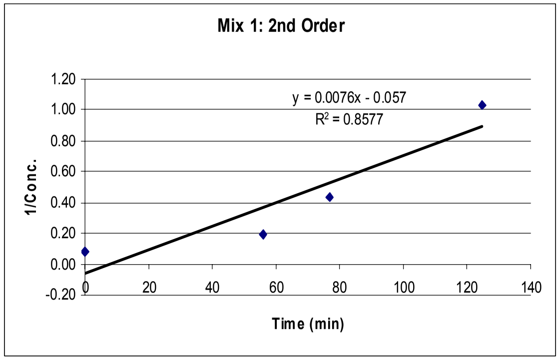




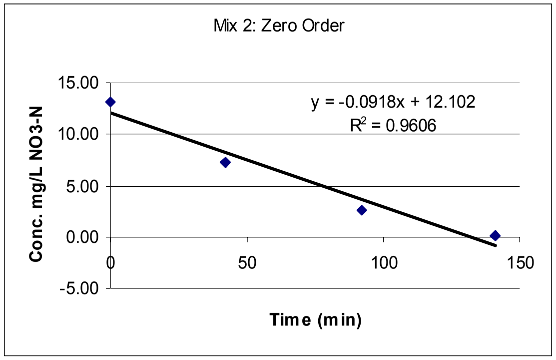


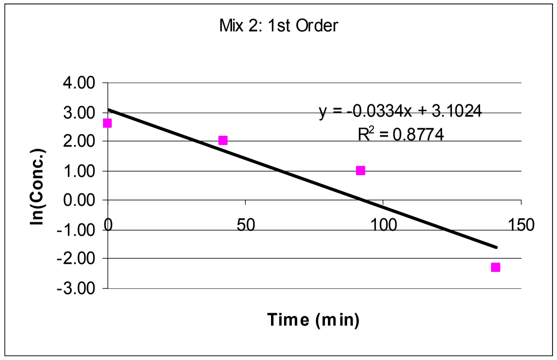


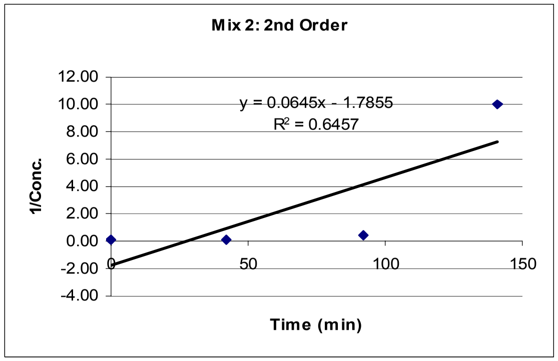




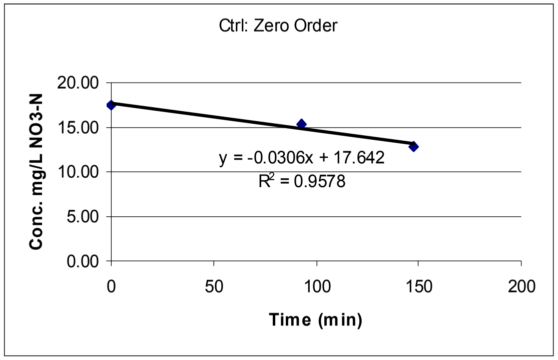
Nitrate 7/8/08 Cont.

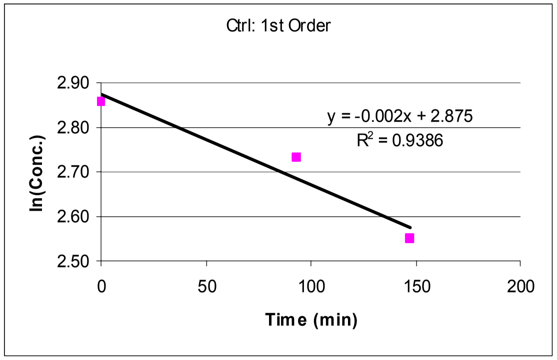


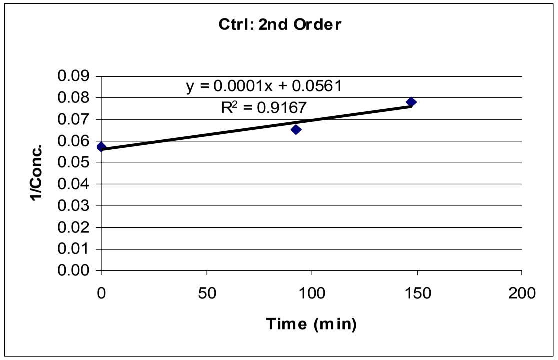


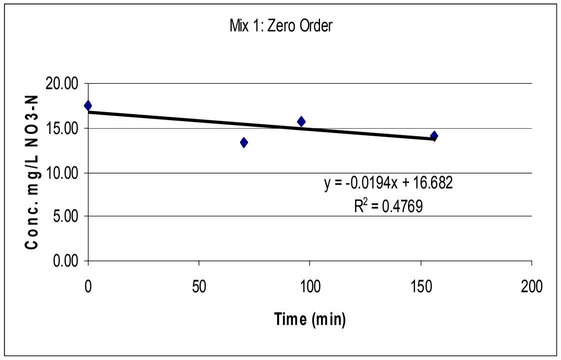


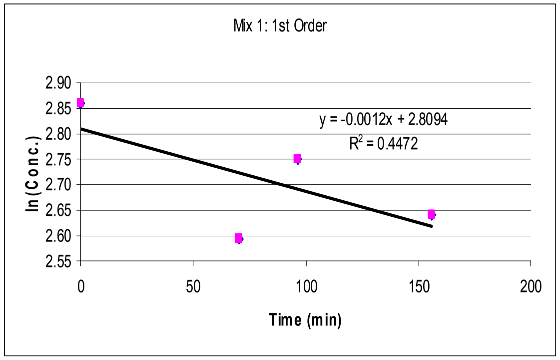
Nitrate 7/8/08 (Run 2)

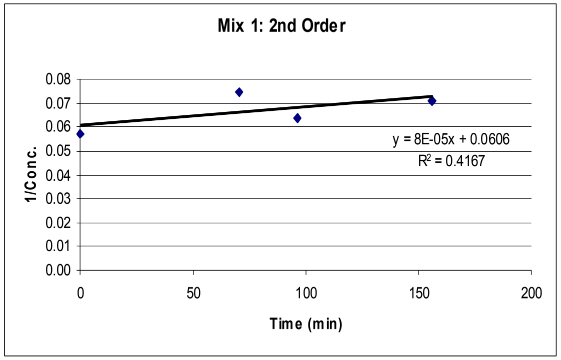




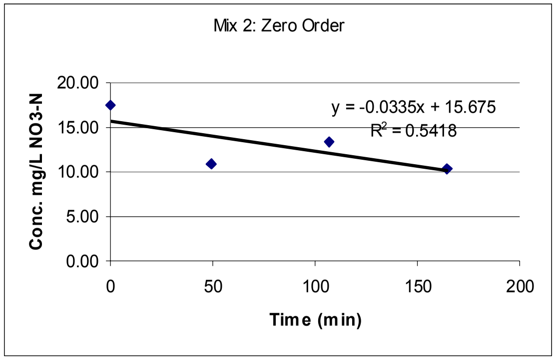


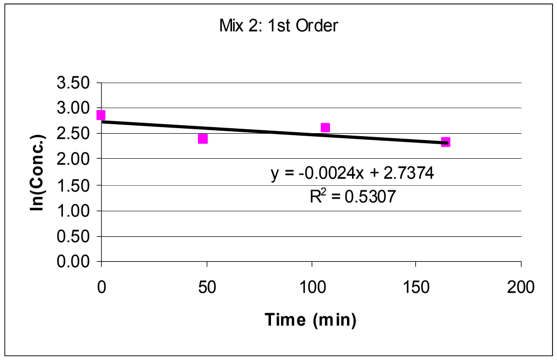


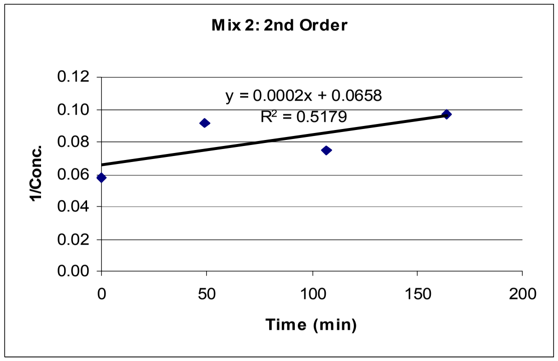




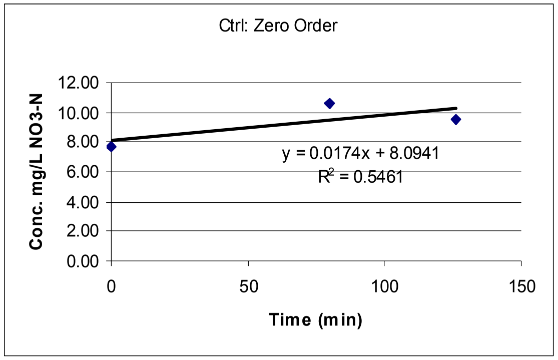
Nitrate 7/8/08 (Run 2) Cont.

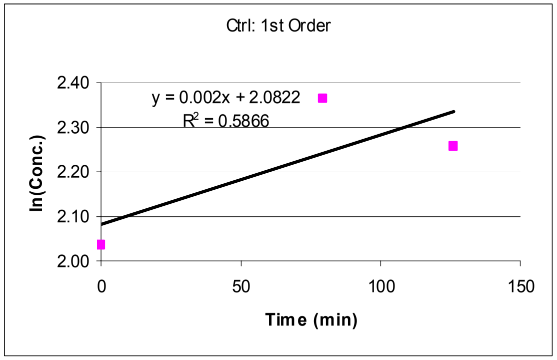


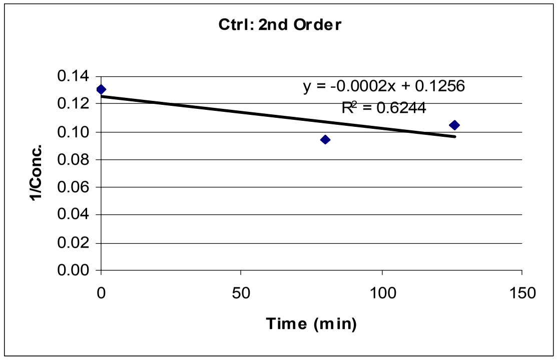


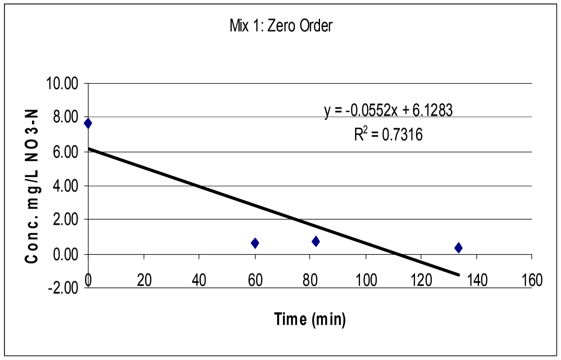


Nitrate 7/11/08

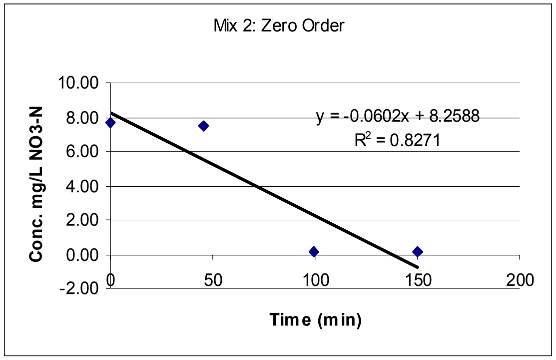


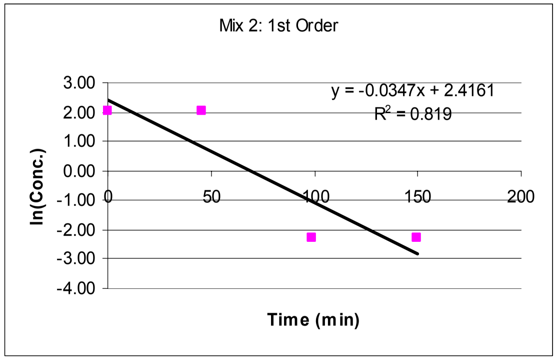


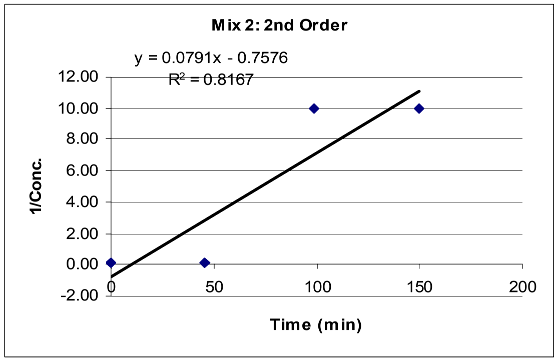




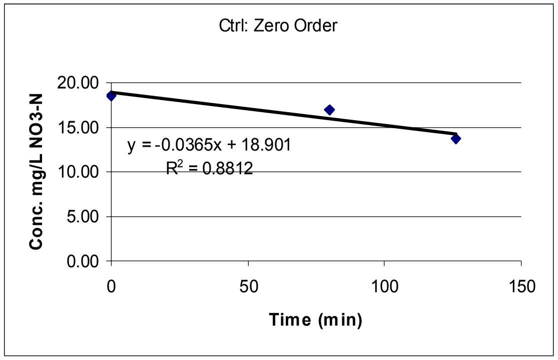
Nitrate 7/11/08 Cont.

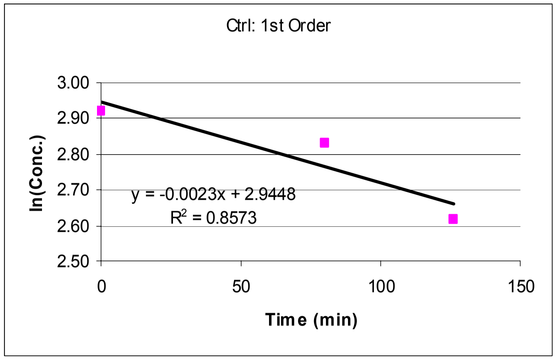


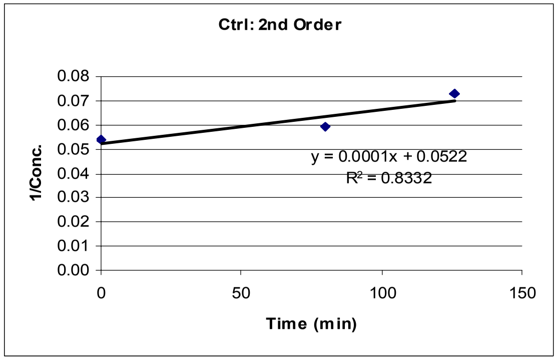


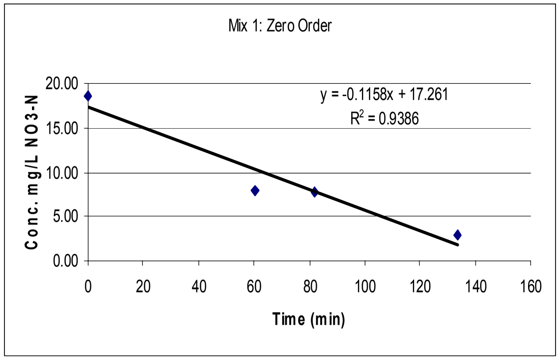


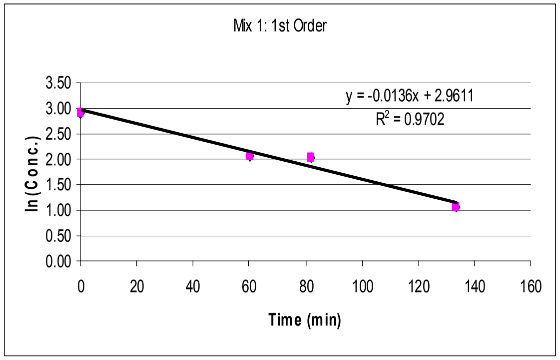
Nitrate 7/21/08

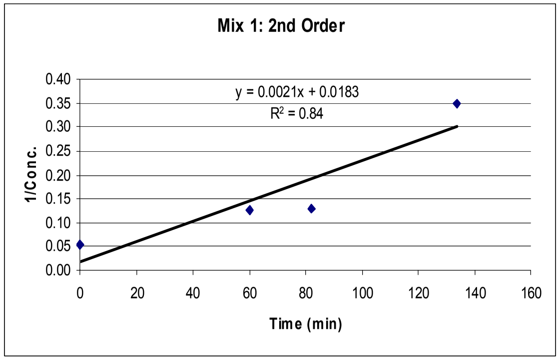

Ctrl: Zero Order


Ctrl: 1st Order

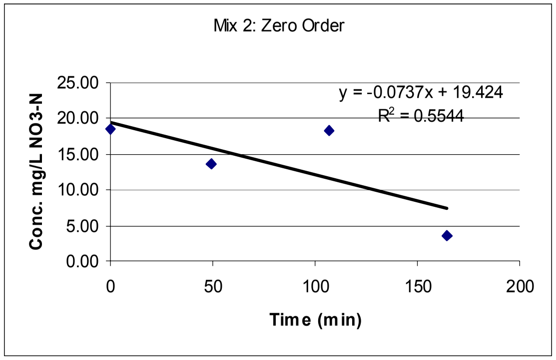

Ctrl: 2nd Order

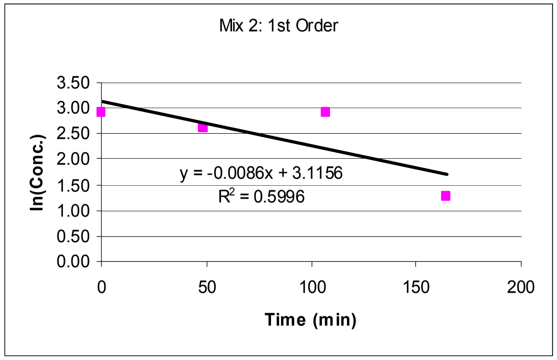

Mix 1: Zero Order

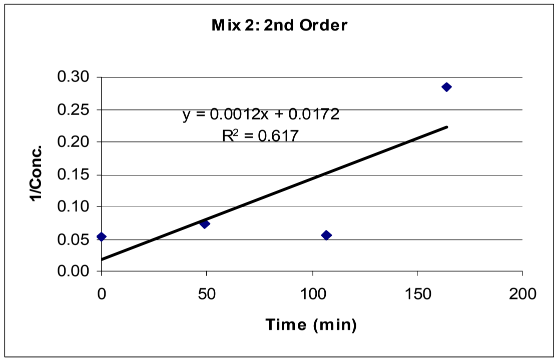

Mix 1: 1st Order


Mix 1: 2nd Order

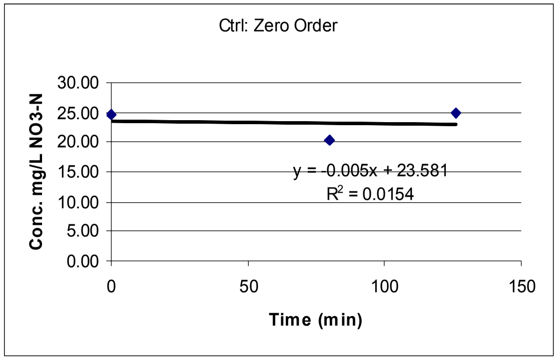
Nitrate 7/21/08 Cont.

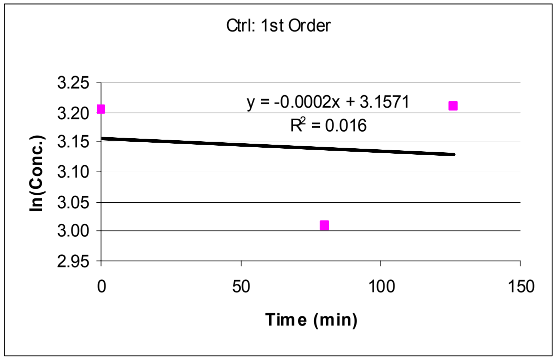


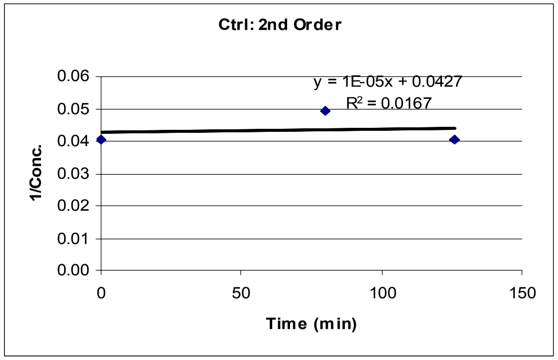


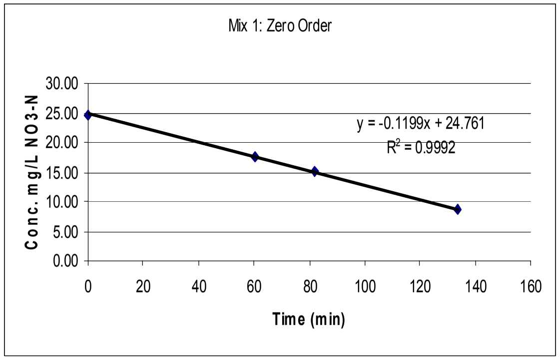


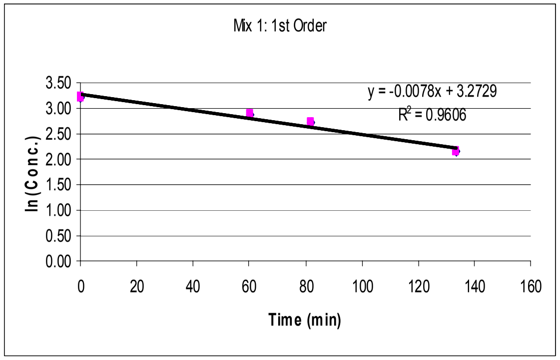
Nitrate 7/21/08 (Run 2)

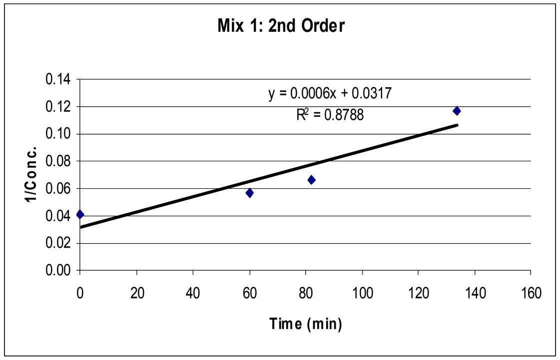

Ctrl: Zero Order


Ctrl: 1st Order

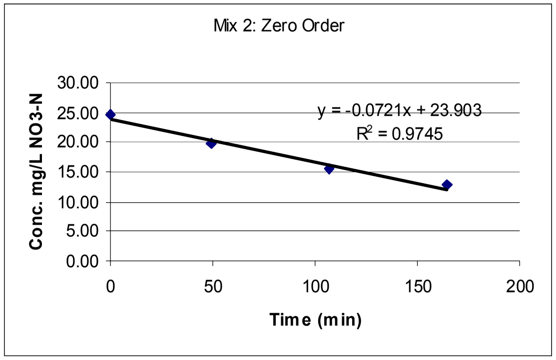

Ctrl: 2nd Order

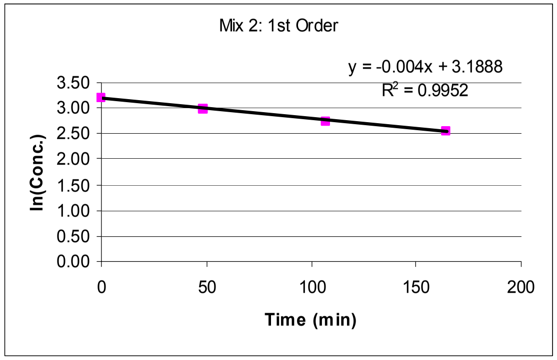

Mix 1: Zero Order

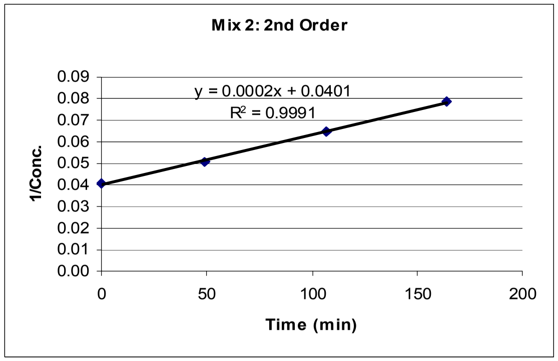

Mix 1: 1st Order


Mix 1: 2nd Order

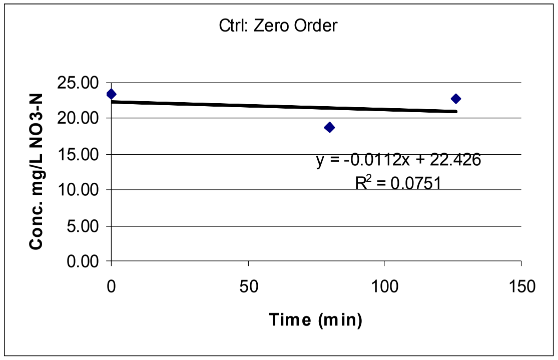
Nitrate 7/21/08 (Run 2) Cont.

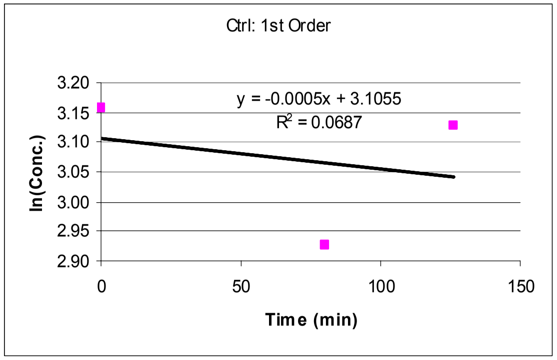


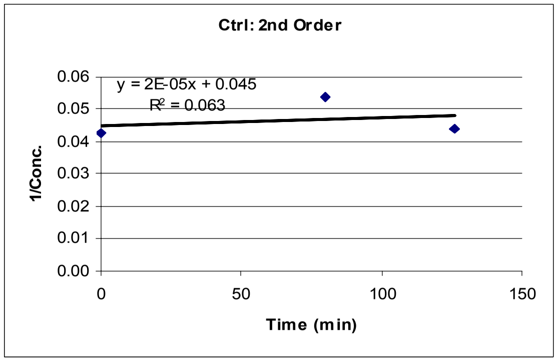


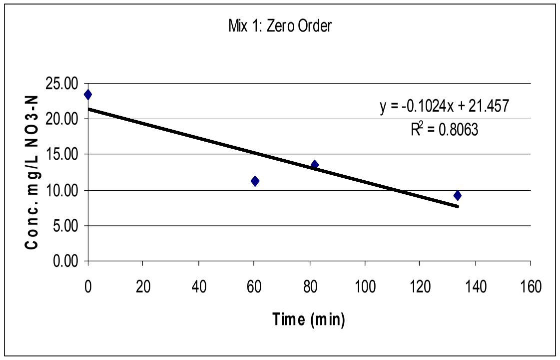


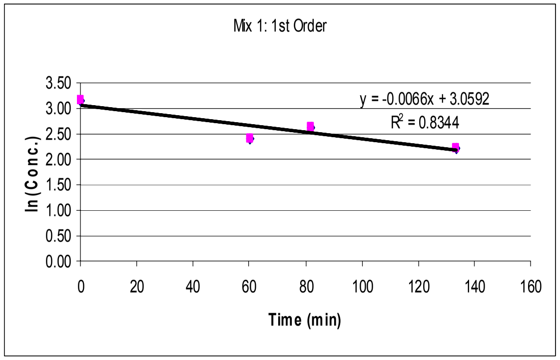
Nitrate 7/22/08

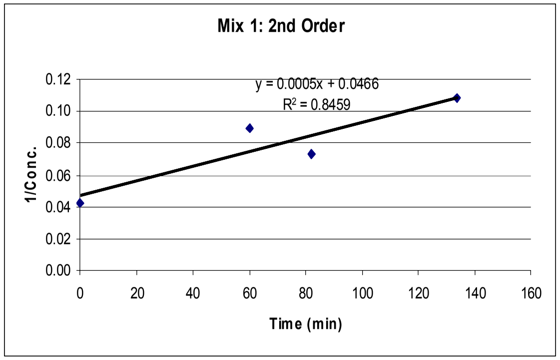




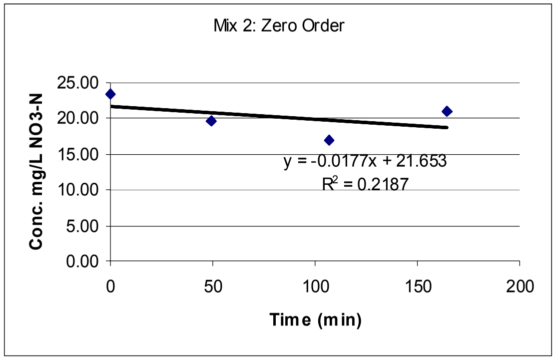


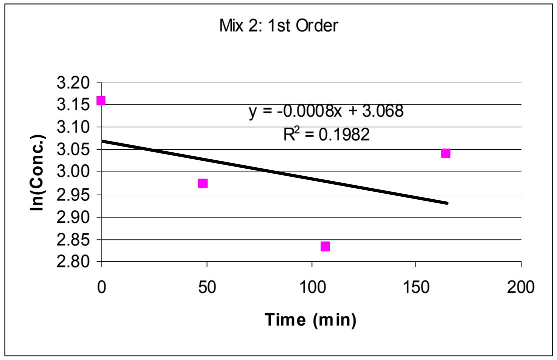




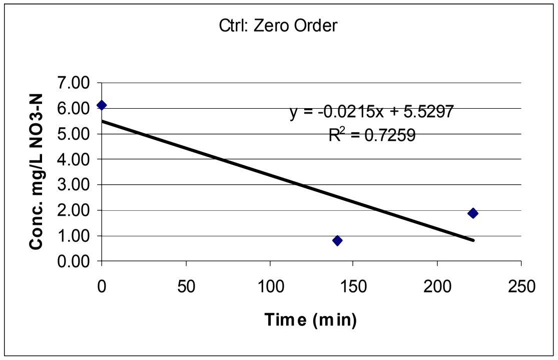


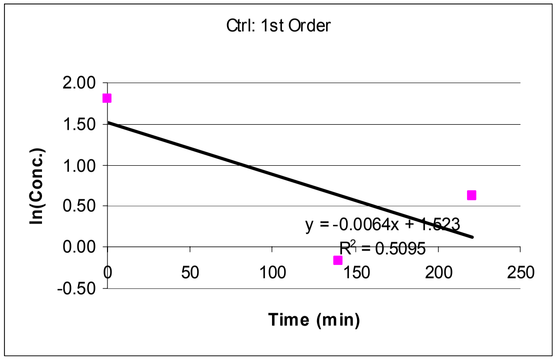
Nitrate 7/22/08 Cont.

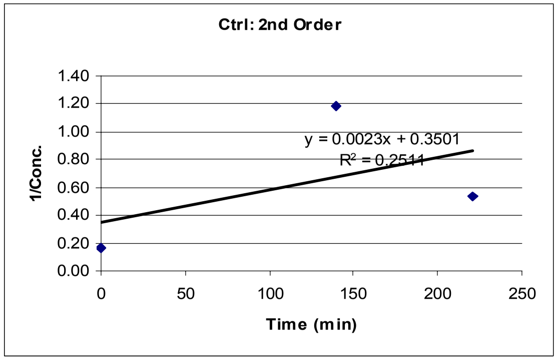


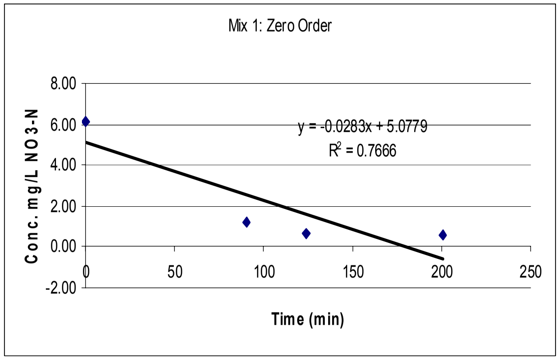


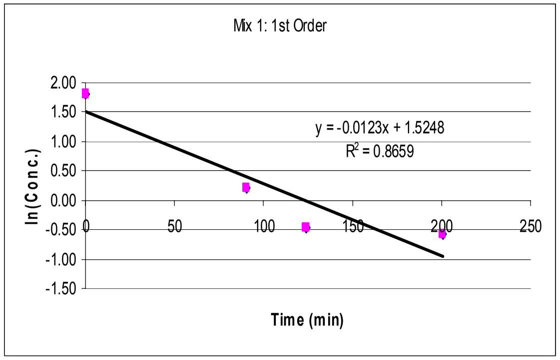
Nitrate 5/22/08

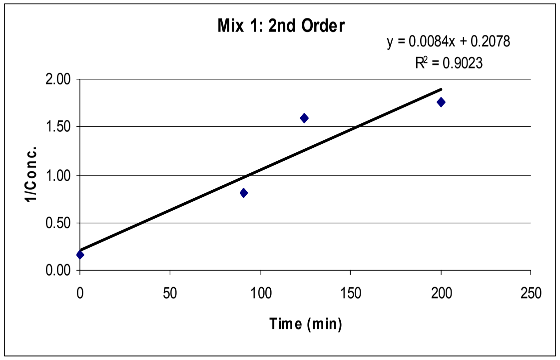




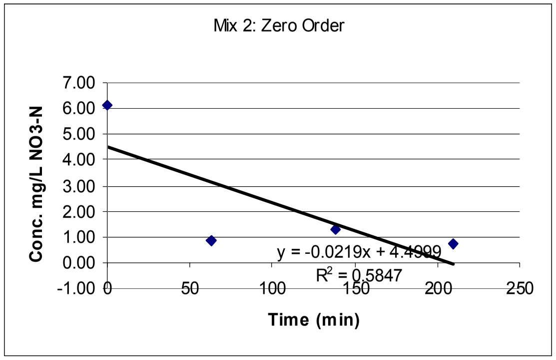


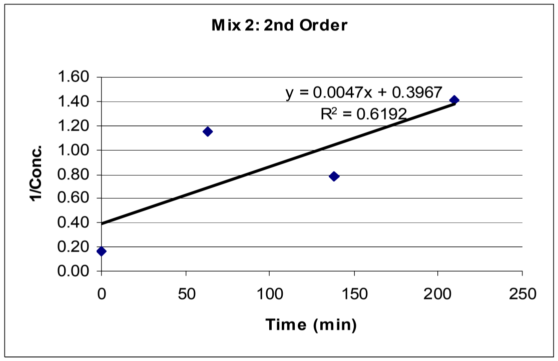




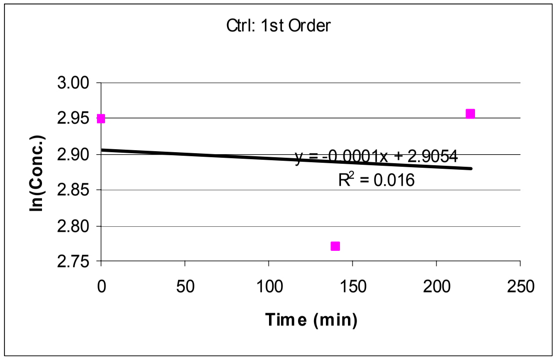


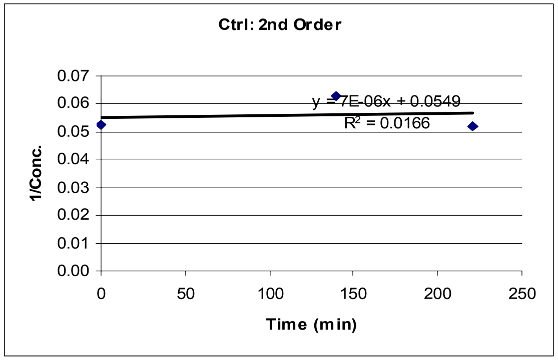
Nitrate 5/22/08 Cont.

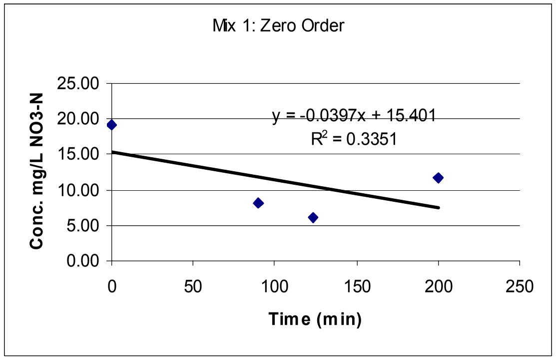


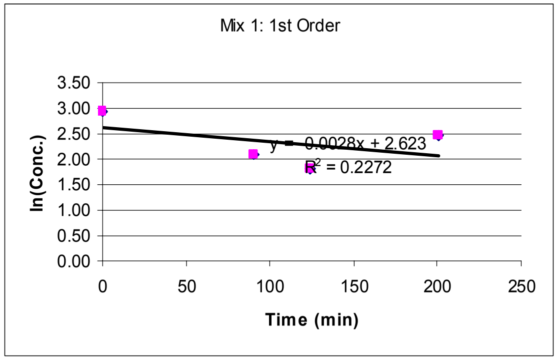


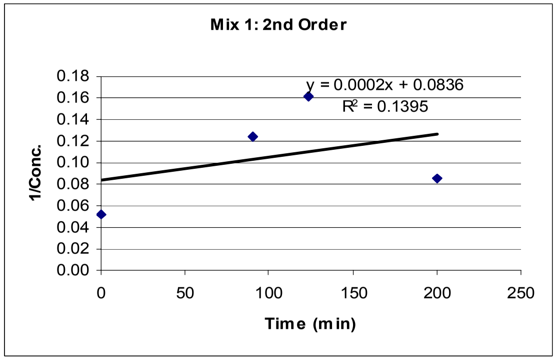
Nitrate 5/22/08 (Run 2)



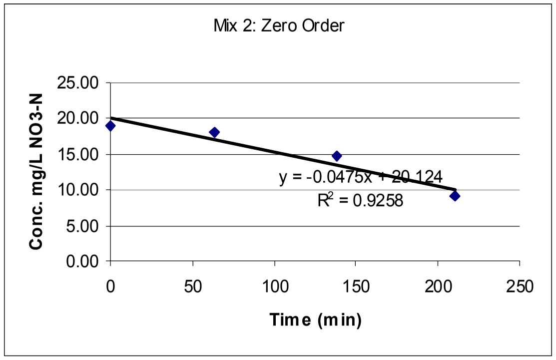


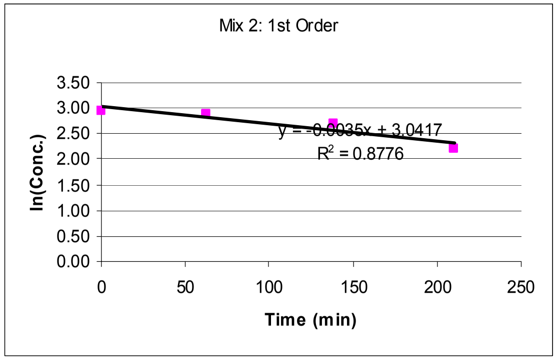


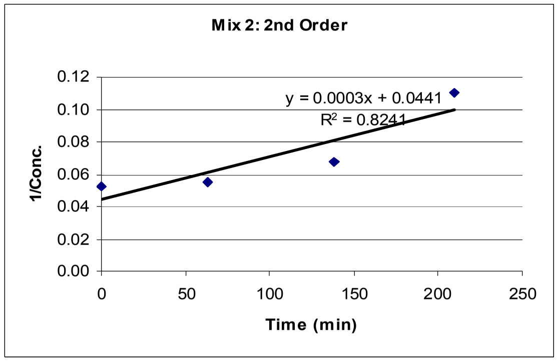




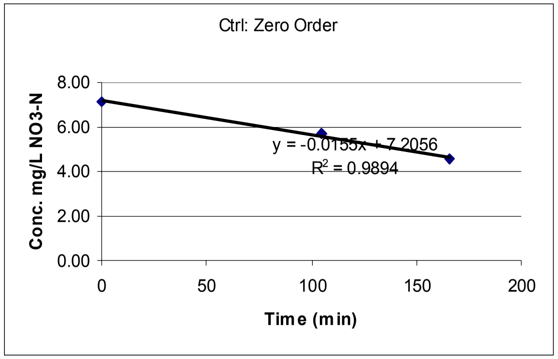
Nitrate 5/22/08 (Run 2) Cont.

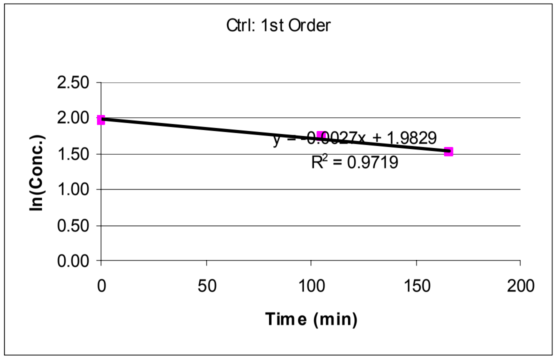


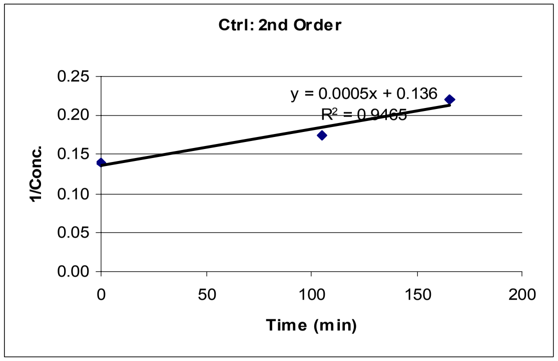


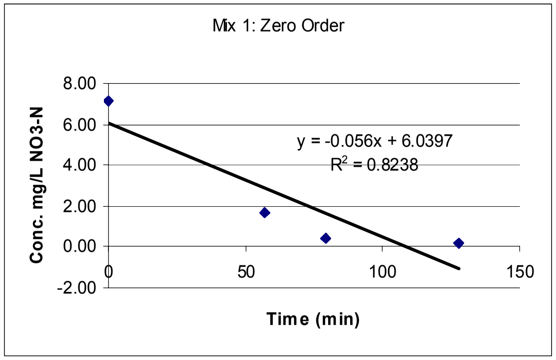


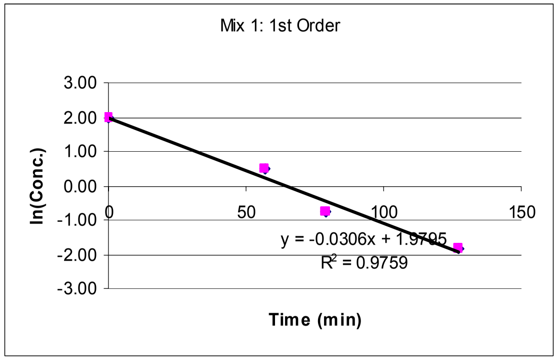
Nitrate 5/11/08

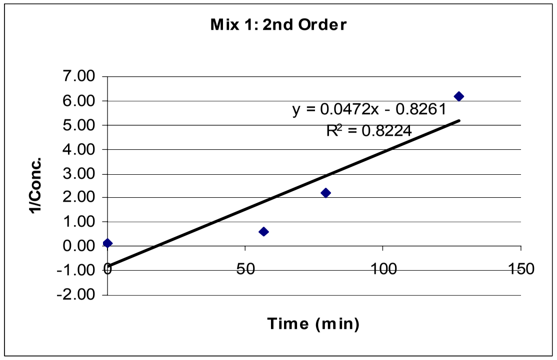

Ctrl: Zero Order


Ctrl: 1st Order

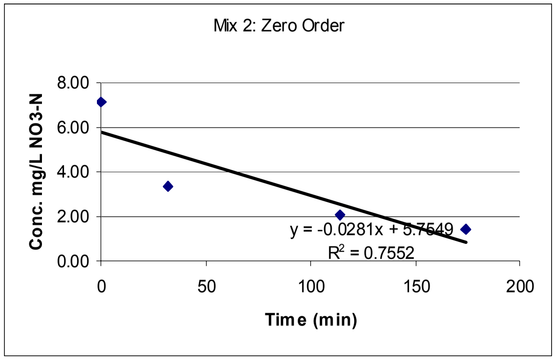

Ctrl: 2nd Order

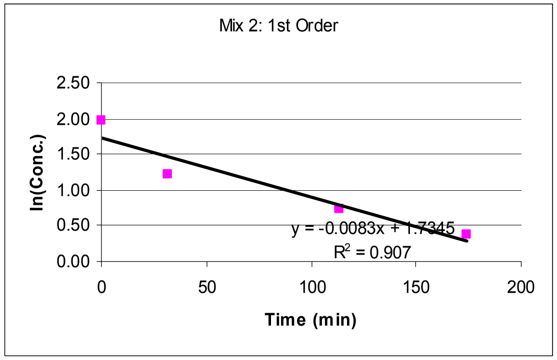

Mix 1: Zero Order

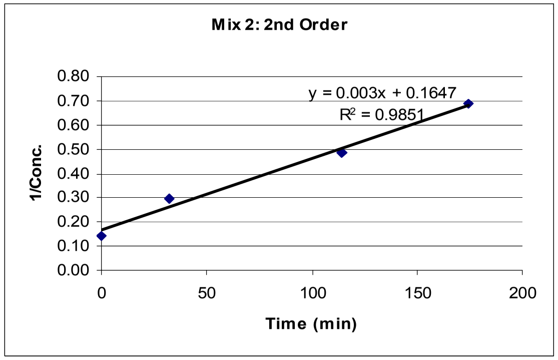

Mix 1: 1st Order


Mix 1: 2nd Order

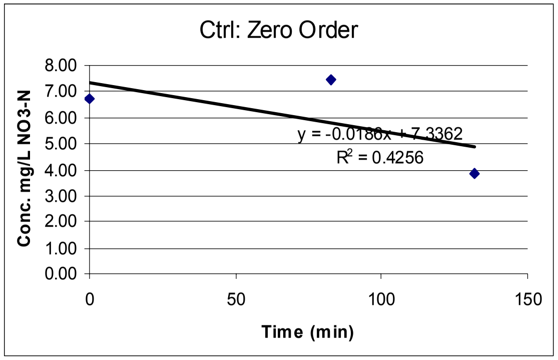
Nitrate 5/11/08 Cont.

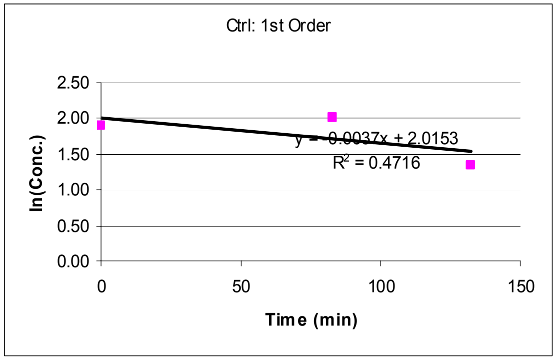

Mix 2: Zero Order

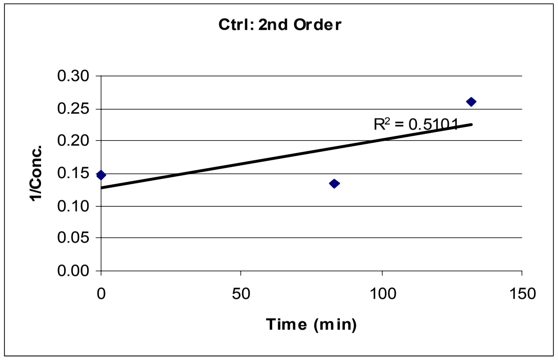

Mix 2: 1st Order

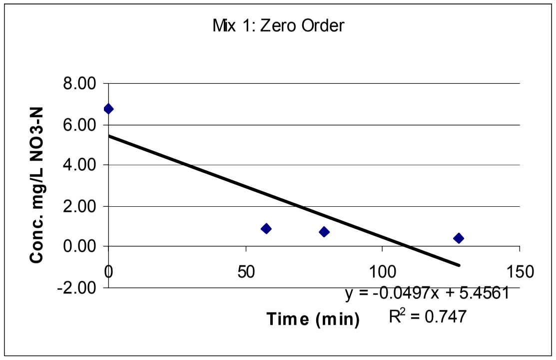

Mix 2: 2nd Order

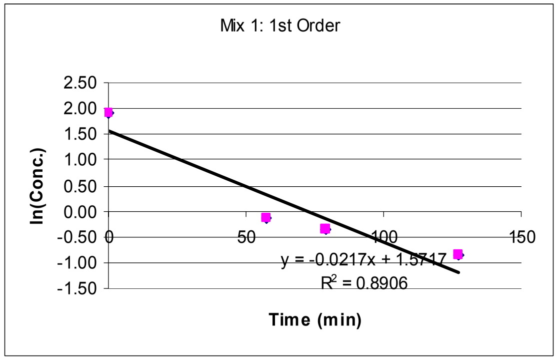
Nitrate 5/13/08

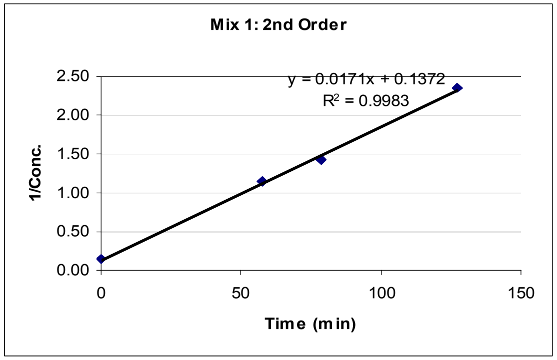




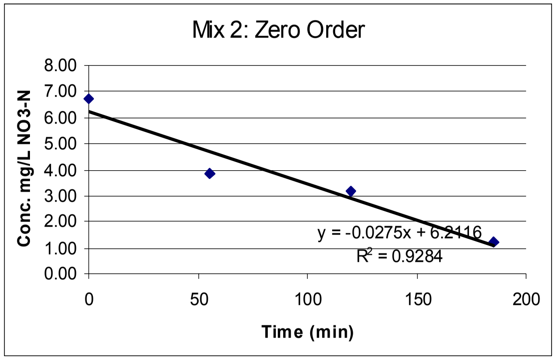


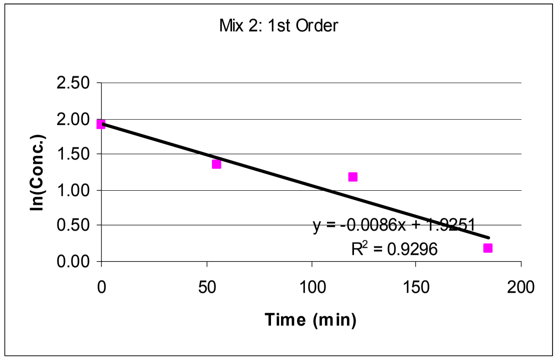


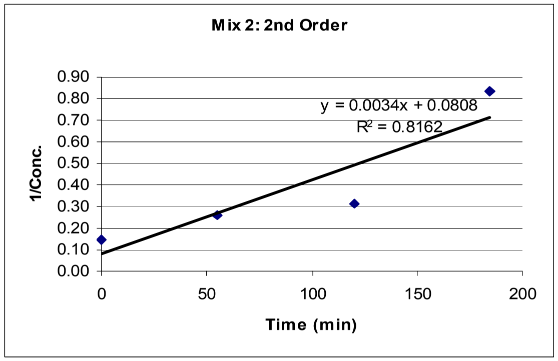




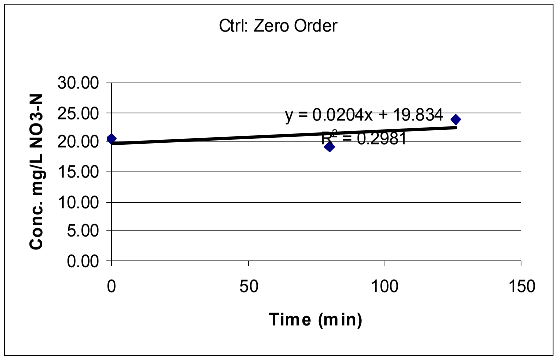
Nitrate 5/13/08 Cont.

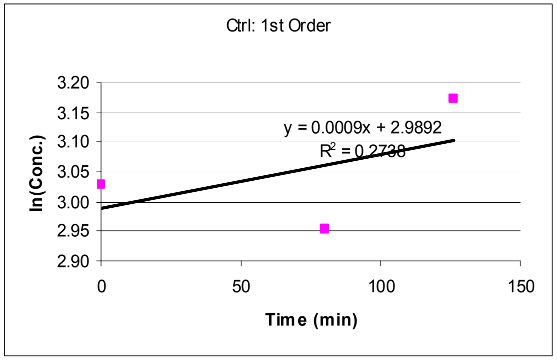


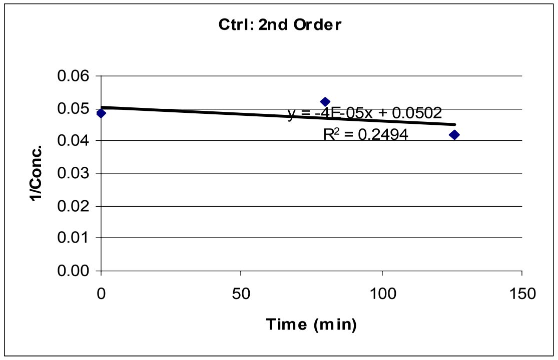


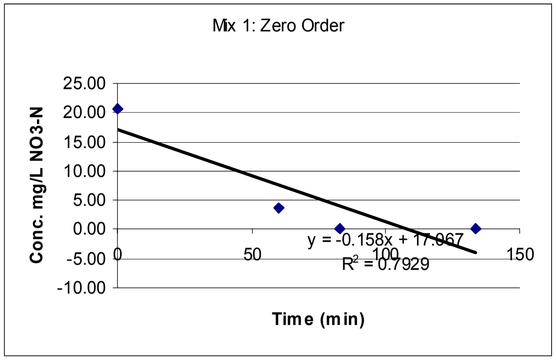


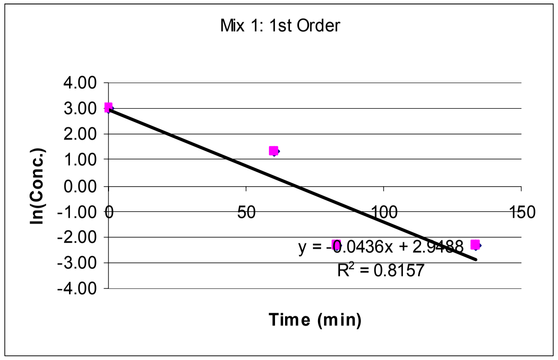
Nitrate 6/23/08

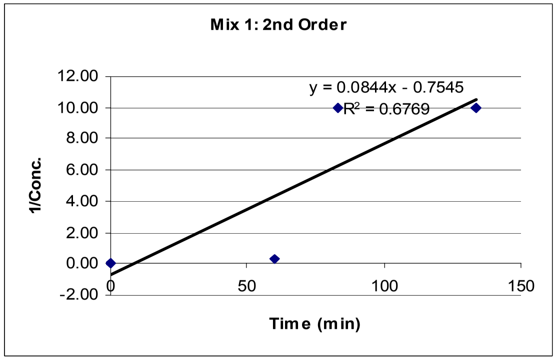




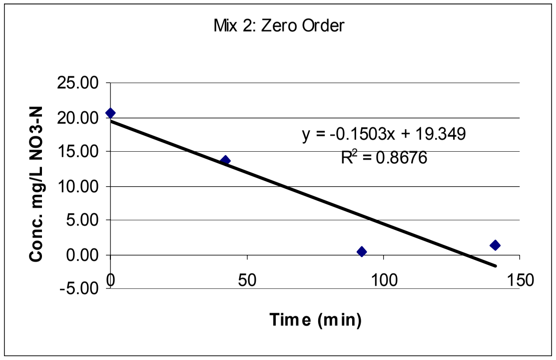


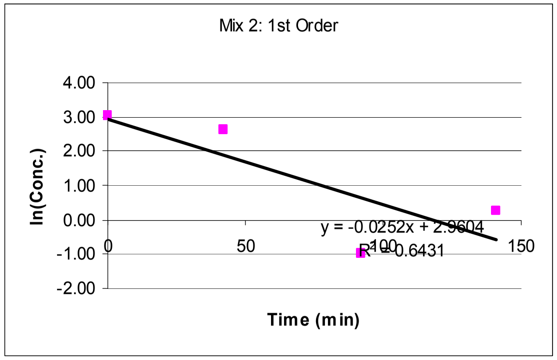


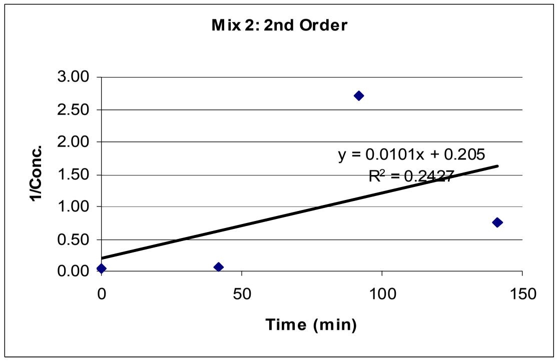




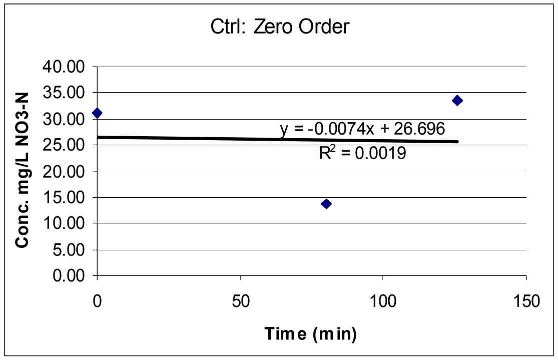
Nitrate 6/23/08 Cont.

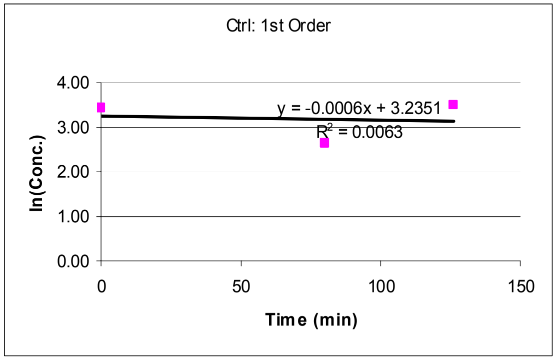


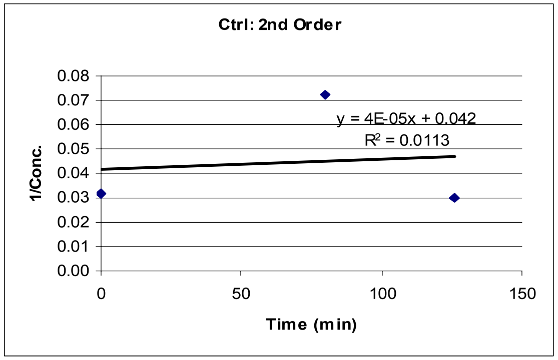


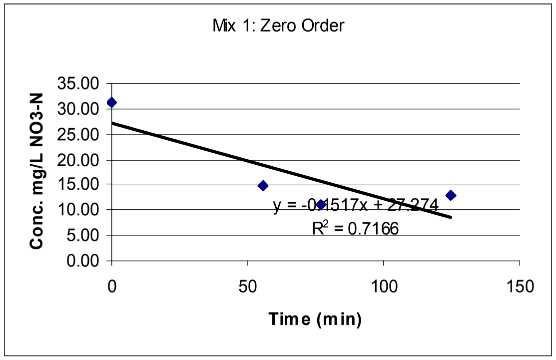


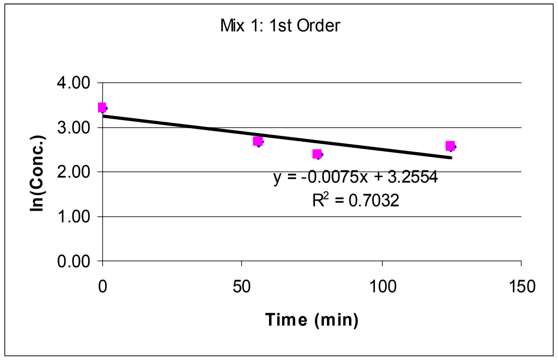
Nitrate 6/23/08 (Run 2)

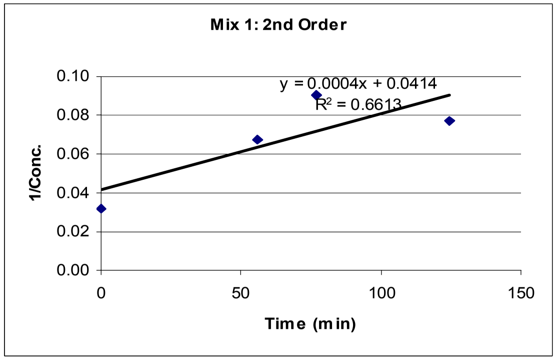




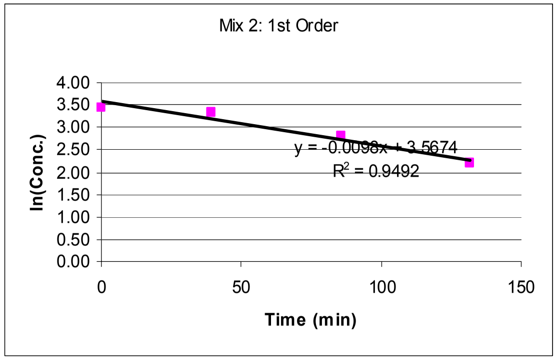


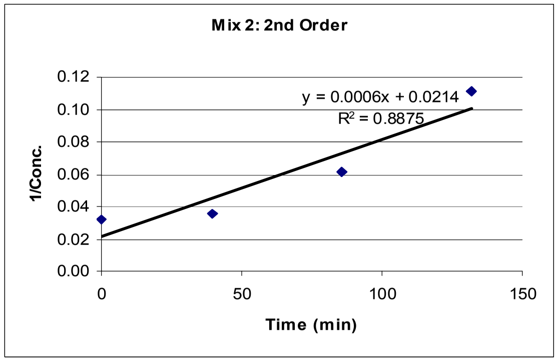






Nitrate 6/23/08 (Run 2) Cont.





LIST OF REFERENCES

Analytical & Environmental Consultants (AEC), 2005. "Locally available adsorbing materials, sediment sealing, and flocculants for chemical remediation of lake and stream water", http://www.ebop.govt.nz/media/pdf/ReportChemicalremediationstudy.pdf, accessed in April, 2007.

Bell, W., Stokes, L., Gavan, L. J., and Nguyen, T. N., 1995. "Assessment of the Pollutant Removal Efficiencies of Delaware Sand Filter BMPs", City of Alexandria, Department of Transportation and Environmental Services, Alexandria, VA.

Bolan, N. S., Wong, L., and Adriano, D. C., 2004. "Nutrient removal from farm effluents", Bioresour Technol 94(3), 251-60.

Benson, C. H., 2001. "Using Waste Foundry Sands as Reactive Media in Permeable Reactive Barriers", DNR Project #147.

Boving, T. B. and Zhang, W., 2004. "Removal of aqueous-phase polynuclear aromatic hydrocarbons using aspen wood fibers", Chemosphere, 54, 831–839.

Braun-Howland, E., 2003. "Validity Assessment of Methods to Distinguish Between Ruminant and Human Sources of Fecal Contamination in Watersheds", New York State Water Resources Institute Annual Technical Report-FY 2003, Cornell University, Ithaca, NY.

Chang, N., Wanielista, M., Hossain, F., Naujock, L., 2008. "Material Characterization and Reaction Kinetics of Green Sorption Media for Nutrient removal", ASCE World Water Environment Resource Congress, May 13-16, Honolulu, Hawaii.

Clark, S., Pitt, R.,1999."Stormwater Treatment At Critical Areas: Evaluation of Filter Media", EPA 600/R-00/010.

Clark, S., Pitt, R., and Brown, D., 2001. "Effect of Anaerobiosis on Filter Media Pollutant Retention", Engineering Foundation and the American Society of Civil Engineers Conference on Information and Monitoring Needs for Evaluating the Mitigating Effects of BMPs. Snowmass, CO, August.

Darbi, A., Viraraghavan, T., Butler, R. and Corkal, D., 2002. "Batch studies on Nitrate removal from potable water", Water SA, 28 (3), 319-322.

Das, B.M. 2006. “Principles of Geotechnical Engineering 6th ed. Toronto, ON: Thomson Canda Limited, Inc.

Engro http://www.engro-global.com/productrange.html#GGBS

FDEP 2007. “Drinking Water Standards”. < http://www.dep.state.fl.us/water/ drinkingwater/standard.htm> Date Accessed: April 2007

FIPR. “Phosphate and How Florida Was Formed.” <http://www1.fipr.state.fl.us/ PhosphatePrimer/0/C0E6FF4202BB6D685256F7700D2847> , Date Accessed: March 2007
Forbes, M. G., Dickson, K. L., Waller, W. T., 2005. “Recovery and fractionation of Phosphorus retained by lightweight expanded shale and masonry sand used as media in subsurface flow treatment wetlands”, Environ. Sci. Technol. 39, 4621-4627.

Fine, Leonard W., et. al. “Preliminary Edition Chemistry for Scientists and Engineers”. Saunders College Publishing. Orlando 2000.

Gálvez, J. M., Gómez, M.A., Hontoria, E., and González-López, J., 2003. “Influence of hydraulic loading and air flowrate on urban wastewater Nitrogen removal with a submerged fixed-film reactor”, Journal of Hazardous Materials, B101, 219–229.

Gisvold, B. et al. “Enhancing the removal of ammonia in nitrifying biofilters by the use of a zeolite containing expanded clay aggregate filter media”. Water Science and Technology Vol 41 No 9 (2000) pp 107–114 February 2007 < http://www.iwaponline. com/wst/04109/0107/041090107.pdf>

Gisvold, B. et al. “Enhanced removal of ammonium by combined nitrification/adsorption in expanded clay aggregate filters”. Water Science and Technology Vol 41 No 4–5 (2000) pp 409–416 February 2007 <http://www.iwaponline.com/wst/04104/0409/ 041040409.pdf>

Gungor, Kerm and Unlu, Kahraman. 2005“Nitrite and Nitrate Removal Efficiencies of Soil Aquifer Treatment Columns”. Turkish J. Eng. Env. Sci 29, 159-170

Gran, Q., Allen, S. J., Matthews, R., 2004. “Activation of waste MDF sawdust charcoal and its reactive dye adsorption characteristics”, Waste Management, 24, 841–848.

Han, D. W., Yun, H. J., Kim, D. J., 2001. “Autotrophic nitrification and denitrification characteristics of an upflow biological aerated filter”, Journal of Chemical Technology and Biotechnology, 76, 1112–1116.

Harris, W. G. et al. “Phosphorus Retention as Related to Morphology of Sandy Coastal Plain Soil Materials”. Soil Science Society of America Journal vol. 60, no. 5, (1996) 1513-1521 February 2007 <http://cat.inist.fr/?aModele=afficheN&cpsidt=3210322>

Hedström, A., 2006. “Reactive filter materials for ammonium and Phosphorus sorption in small scale wastewater treatment”, Doctoral Dissertation, Luleå University of Technology, ISSN: 1402-1544.

Hsieh, C. H., Davis, A. P., 2003. “Multiple-event study of bioretention for treatment of urban storm water runoff”**,** Diffuse Pollution Conference Dublin, Ireland.

Hsieh, C. H., Davis, A. P., 2005. “Evaluation and optimization of bioretention media for treatment of urban storm water runoff”, J. Envir. Engrg., ASCE, 131(11), 1521-1531.

ILEC/Lake Biwa Research Institute, eds. Survey of the state of the world's lakes. Vols. IIV. International Lake Environment Committee, Otsu and United Nations Environment Programme, Nairobi, 1988-1993.

Jokela, J.P.Y. et al. “Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification.” Water Research 36 (2002) 4079-4087.

Justic, Dubravko, et. al. “Stoichiometric Nutrient Bablance and Origin of Coastal Europhication.” <http://water.usgs.gov/nawqa/CIRC-1136.html> Date Accessed: September 2007

Kietlinska, A., Renman, G. “An evaluation of reactive filter media for treating landfill leachate.” Chemosphere 61 (2005) 933-940

Kim, H., Seagren, E. A., Davis, A. P., 2000. “Engineered Bioretention for Removal of Nitrate from Stormwater Runoff”, WEFTEC (Water Environment Federation Technical Exhibition) 2000, Water Environment Federation (WEF), Grand Rapids, MI.

Kim, H., Seagren, E.A., Davis, A.P., 2003. “Engineered bioretention for removal of Nitrate from stormwater runoff”, Water Environment Research, 75(4), 355-367.

Lazaridis, N. K., 2003. “Sorption removal of anions and cations in single batch systems by uncalcined and calcined Mg-Al-CO_3 hydrotalcite”, Water, Air, & Soil Pollution, 146(1-4), 127-139.

Lieberman, M. T., Lindow, N. L., Borden, R. C., Birk, G. M., 2005. “Anaerobic Biodegradation and Biotransformation Using Emulsified Edible Oils in Contaminated Soils”, Sediments and

Water Science in the Real World Volume 9, edited by Edward J. Calabrese, Paul T. Kostecki and James Dragun, pp. 485-500.

Lisi, R. D., Park, J. K., Stier, J. C., 2004. “Mitigating nutrient leaching with a sub-surface drainage layer of granulated tires”, Waste Management, 24, 831–839.

Moberg, Mikhal. 2008 “The Effectiveness of Specifically Designed Filter Media to Reduce Nitrate and Orthophosphate in Stormwater Runoff”, Master’s Thesis, UCF, Orlando, Florida.

Neter, J. and Wasserman, W. 1974. Applied Linear Statistical Models: Regression, Analysis of Variance, and Experimental Designs. Richard D. Irwin, Inc. Homewood Il.

Naujock, Lisa. 2008 “Development of Hydraulic and Soil Properties for Soil Amendments and Native Soils for Retention Ponds in Marion County Florida”, Master’s Thesis, UCF, Orlando Florida.

O’Reilly, A. M., 2008, Personal Communications.

Phelps, G.G., 2004, “Chemistry of Ground Water in the Silver Springs Basin,
Florida, with an Emphasis on Nitrate: U.S. Geological Survey Scientific Investigations Report”, 2004-5144, p. 54.

Phosphorus harmful : http://www.lenntech.com/Periodic-chart-elements/P-en.htm:

Pano, A. and Middlebrooks, E. J.: 1982, *Jour. Water Pollut. Contr. Fed.* 54(4), 344-351.

Rocca, Claudio Della, et. al. “Cotton-Supported Heterotrophic Denitrification of Nitrate-rich Drinking Water with a Sand Filtration Post-Treatment”. Water SA Vol. 31 No. 2 April 2005.

Rogan, R.C. and Keselman, H.J. 1977. Is the ANOVA F-Test Robust to Variance Heterogeneity When Sample Sizes are Equal?: An Investigation via a Coefficient of Variation. American Educational Research Journal., 14:4:493.

Redco II, 2007. www.perlite.net, Date accessed: April 2007.
Richman, M. 1997. “Compost media capture pollutants from stormwater runoff”, Water Environment and Technology, 9, 21-22.

Savage, A. J., Tyrrel, S. F., 2005. “Compost liquor bioremediation using waste materials as biofiltration media”, Bioresource Technology, 96(5), 557-564.

Seelsaen, N. et al. “Pollutant removal efficiency of alternative filtration media in stormwater treatment". Water Science & Technology Vol 54 No 6–7 (2006) pp 299–305

Sengupta, S., Ergas, S. J., 2006. "Autotrophic Biological Denitrification with Elemental Sulfur or Hydrogen for Complete Removal of Nitrate-Nitrogen from a Septic System Wastewater", Final Report Submitted to The NOAA/UNH Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET), August 9, 2006.

Tesoriero, A. J., Liebscher, H., Cox, S. E., 2000. "Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along groundwater flow paths", Water Resources Research, 36(6), 1545-1559.

Tshabalala, M. A., 2002. "Use of Lignocellulosic Materials as Sorbents for Pesticide and Phosphate Residues", USDA Forest Service, Madison, WI 53705-2398.

USDA, 2007. http://soils.usda.gov/technical/classification/orders/spodosols.html, Date accessed: March 2007.

USGS, 2008. "Florida Springs Interdisciplinary Science Study",
http://fl.water.usgs.gov/PDF_files/fs008_03_katz.pdf, Date accessed: January 2008.

USGS. "". http://sofia.usgs.gov/publications/circular/1134/esns/clim.html Date Accessed: November 2007

US Department of Transportation: Federal Highway Administration."Ground Granulated Blast-Furnace Slag" <http://www.fhwa.dot.gov/infrastructure/materialsgrp/ggbfs.htm> 2008

Zhang, T.C., and Flere, Joel M. "Sulfur-Based Autotrophic Denitrification Pond Systems for In-Situ Remediation of Nitrate-Contaminated Surface Water". Journal of Water Science Technology 1998. Vol. 38, No.1, pp 15-22.

Zhang, T. C., 2002. "Nitrate removal in sulfur: limestone pond reactors", J. Envir. Engrg., ASCE, 128(1), 73-84.