

THESIS

FRAC FLOWBACK WATER BLENDING AND TREATMENT REQUIREMENTS BASED
ON SPATIAL AND TEMPORAL WATER QUALITY ANALYSIS

Submitted by

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ABSTRACT

FRAC FLOWBACK WATER BLENDING AND TREATMENT REQUIREMENTS BASED ON SPATIAL AND TEMPORAL WATER QUALITY ANALYSIS

Because of the large amount of wastewater generated with oil and gas production and the complex components of produced water, associates in the human health and environmental disciplines consider the treatment and reuse of produced water as a central issue for the petroleum industry. At present, produced water recycling is one of the best ways to reduce fresh water consumption in the hydraulic fracturing process and lessen environmental impact.

This study focuses on the analysis of produced water quality and the optimization of the produced water recycling. Samples of produced water from more than two hundred horizontal wells in seven Integrated Development Plans in the Wattenberg Field were analyzed for temporal and spatial levels of total dissolved solids (TDS), sodium, chloride, calcium, and iron. Concentration of total dissolved solids, sodium, chloride and calcium were modeled to accommodate the different temporal functions in each Integrated Development Plan; the temporal logarithmic functions of each model allow prediction of produced water quality data for existing wells or new wells in certain regions. Iron concentration, however, closely correlates with geological formation, so the iron concentration of produced water must be determined spatially as an average value and maximum value in each Integrated Development Plan.

A framework for optimizing produced water reuse is presented as part of this study. Typically, some volume of fracturing fluid is retained in wells; further, portions of flowback fluids might be injected into disposal wells. Produced water must be treated to meet recycled water quality requirements. In this study, coagulation/filtration, softening/clarification, and reverse osmosis (RO) were applied to treat samples effectively for suspended solids, total dissolved solids, sodium, chloride and calcium. Following treatment, the proper amount of fresh water needed to blend with the produced water must be determined. With sources of fresh water limited, the amount of water used to optimize the recycling of produced water is one of the most significant issues in the management of produced water. Calculating the quantity of fresh water necessary can be based on the quality of the fresh water, fracturing fluids and the targeted quality of the recycled water; in some cases, it might be based on the quantity of fracturing fluids and recycled water targeted. If the result based on quality is not less than the quantity based result, additional treatment will be required. Frac fluids modification could also be used in some conditions in this program, however, the cost of additives can be high, and additional treatment may be the better option. Most of recycle produced water quality with our treatment reaches requirements of fracturing fluids after blending with certain amount of fresh water.

Produced water quality analysis of the horizontal wells in the Wattenberg Field and the established produced water recycling system program are supporting produced water management and the viability of produced water reuse. The Matlab produced water recycling program incorporates both internally sourced quality analysis data and external data uploaded from users. As a tool simulating produced water recycling, it can help users make good decisions to use in water management.

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1. INTRODUCTION

With worldwide economic development and rapidly increasing energy demand, shale-sourced gas and oil is an unconventional energy source contributing more to total oil and gas production. In the United States, total extraction of shale gas increased from five billion cubic feet per day in 2007 to 33 billion cubic feet per day in 2013—a volume representing 40% of total natural gas production in 2013[1]. Further, shale oil increased from 111,000 barrels per day in 2004 to 553,000 barrels per day in 2011[2]. The huge amount of wastewater produced by this increasing shale oil and gas production has made produced water management and treatment an even more important environmental concern in recent years.

Produced water treatment is one of the most efficient ways to decrease the amount of frac wastewater of shale oil and gas production. Wastewater recycling is becoming a means of managing produced water, and blending and treatment of fracturing flowback and produced water is always required to optimize quality prior to recycling. Blending fresh water with produced water, and then applying produced water treatment, reduces the increased concentration of water quality parameters such as total dissolved solids (TDS), sodium, chloride, calcium and iron. Adjusting the blending ratio of produced water and fresh water to minimize the demand of fresh fluids is necessary to reduce environmental impact and the draw of water supply from other uses such as irrigation.

Further, water quality analysis of fracturing flowback and produced water is necessary to effective produced water management and treatment. Modeling the quality of fracturing flowback and produced water, based on water quality analysis, can help predict water quality

data temporally and spatially. These data, then, can help determine the most appropriate method of treatment and the blending ratio appropriate for fracturing flow water reuse.

This research analyzes total dissolved solids, sodium, chloride, calcium, and iron data as key parameters of frac flowback and produced water management. Because iron concentration of produced water relates directly to geological formation and does not reflect temporal trends, it can only be compared spatially, while the other quality parameters are modeled temporally. Treatment methods examined in this study to manage and optimize quality of frac flowback water for reuse in shale oil and gas wells include reverse osmosis (RO), blending, softening, coagulation, and filtration.

The thesis reporting on produced water quality analysis, treatment, and management of the shale oil and gas industry is presented in two main parts. The first part details the modeling of water quality of fracturing flowback and produced water in Wattenberg field; the second part reports on the treatment and blending of fracturing flowback water to optimize its reuse as a fracturing fluid. Chapter 2 reviews existing literature that details shale oil and gas development and produced water quality and treatment. Chapter 3 details the objective of the research reported in this paper. Chapter 4 and Chapter 5 detail the methods of produced water quality data modeling and framework for optimization. Chapter 6 provides overall conclusions of this research, while Chapter 7 identifies all references. Chapter 8 is a comprehensive appendix of research data and graphs.

2. LITERATURE REVIEW

2.1 Unconventional Oil and Gas Development

At present, energy plays an important role in global economic growth, and unconventional oil and gas are more involved in meeting energy demand as the technology to explore these resources develops. Among the unconventional oil and gas supplies involved are shale oil and gas, which is becoming more attractive as an energy supply because of its commercial value and successful extraction and production. Driven by development of drilling and hydraulic fracturing technologies, more countries are beginning to explore and extract shale oil and gas. Comparing 2011 and 2013 numbers, the new global shale gas resource estimate has increased by ten percent and technically recoverable resources also have increased rapidly [3]. Table 2-1 compares summary data from 2011 and 2013 [3].

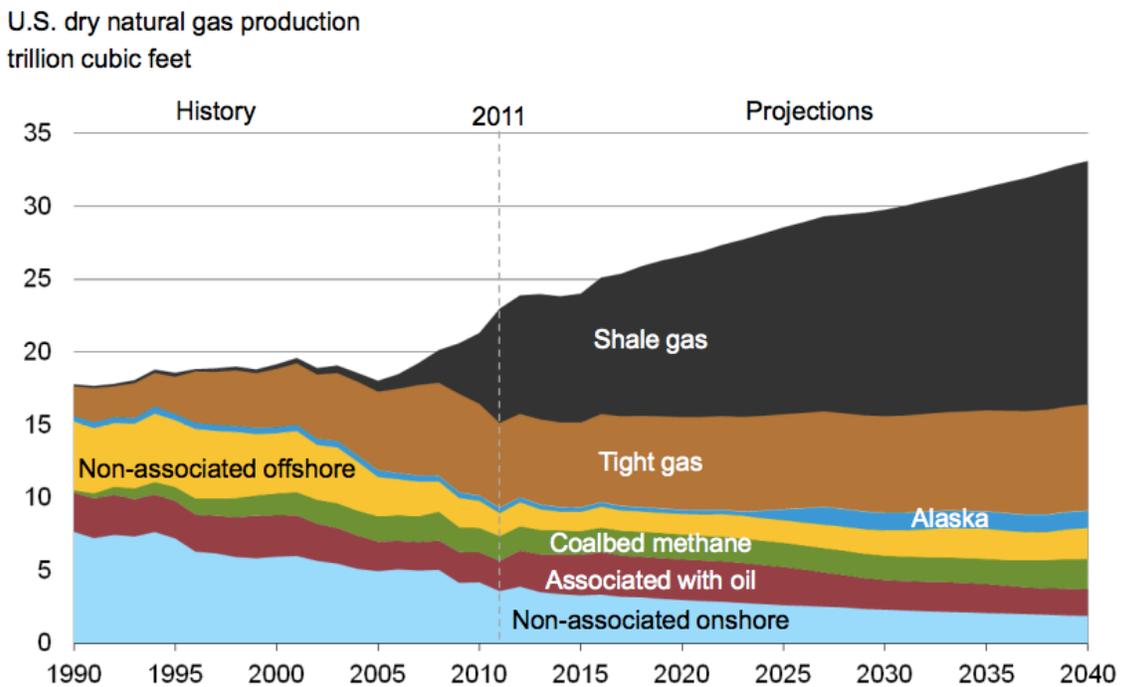
Table 2-1: Comparison of the 2011 and 2013 Reports

EIA report coverage	2011 Report	2013 Report
Number of countries	32	41
Number of basins	48	95
Number of formations	69	137
Technically recoverable resources, including U.S.		
Shale gas (trillion cubic feet)	6,622	7,299
Shale / tight oil (billion barrels)	32	345

Note: The 2011 report did not include shale oil; however, the Annual Energy Outlook 2011 did (for only the U.S.) and is included here for completeness

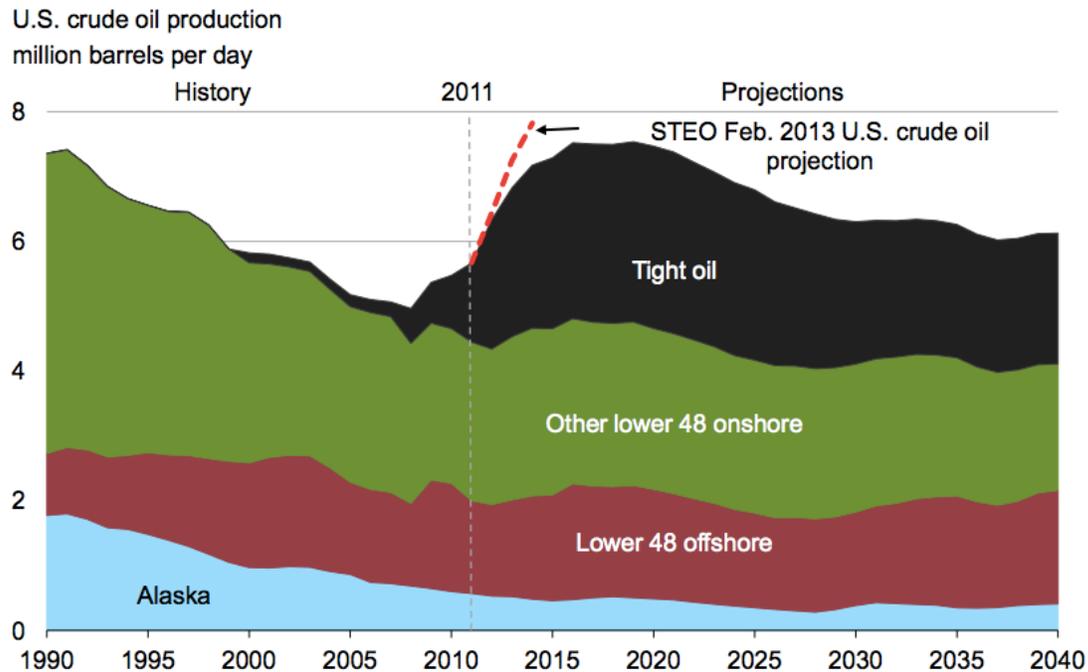
Development of shale oil and gas extraction in United States has a significant impact on both the U.S. and global oil and gas markets, resulting in lower oil and gas prices. The percentage of tight oil production increased in the U.S., where tight oil production accounted for 12% of total

crude oil production in 2008 and 35% of total production in 2012[4]. In 2013, shale gas accounted for 40% of total natural gas production, the largest contribution in U.S. natural gas production for the year[1]. The development of shale gas, tight gas, and offshore natural gas resources is expected to result in a 56% increase in total natural gas production from 2012 to 2040; shale gas production is expected to provide the largest contribution, increasing from 40% in 2012 to 53% of 2040 of total natural gas in the U.S.[4]. Further, tight oil plays a prominent role in oil production development and will become a primary unconventional energy source in the future. Figures 2-1 and 2-2 provide expected shale gas and tight oil growth trends from 1990 to 2040[5].



Source: EIA, Annual Energy Outlook 2013 Early Release

Figure 2-1: U.S. Dry Natural Gas Production, 1990-2040 (trillion cubic feet)



Source: EIA, Annual Energy Outlook 2013 Early Release and Short-Term Energy Outlook, February 2013

Figure 2-2: U.S. Crude Oil Production, 1990-2040 (million barrels per day)

Shale resources are abundant in North America; according to a U.S. Energy Information Administration study, most of the natural gas products from shale formation come from the United States and Canada[6]. The seven major shale gas plays--Bakke, Eagle Ford, Permian, Marcellus, Anadarko-Woodford, Granite Wash and Niobrara--yield most of the unconventional oil and gas production in the U.S. The oilfield services of these seven plays cost \$54.3 billion in 2012[7], reflecting the rapid development of the unconventional oil and gas industry in the last several years and the likelihood that unconventional energy will become the major energy source in U.S.

The research reported here involves oil and gas extraction from the Niobrara geologic formation, with wells drilled in the Wattenberg Field in the Denver-Julesburg Basin located in

northeastern Colorado. There, oil and natural gas can be found at depths of 3,000 to 14,000 feet below the earth's surface, with the thickness of the Niobrara geologic formation ranging from 900 to 1,800 feet. The Niobrara geologic formation consists mainly of inter-bedded organic-rich shale, calcareous shale, and marl, presenting huge oil and gas potential[8]. Oil and gas development is still in its early stages at the Niobrara play; however, the oil and gas industry, including Noble Energy, who provided the produced water quality analysis data in this study, has high expectations for the number of well fields there. Figure 2-3 shows the Niobrara play location[9].

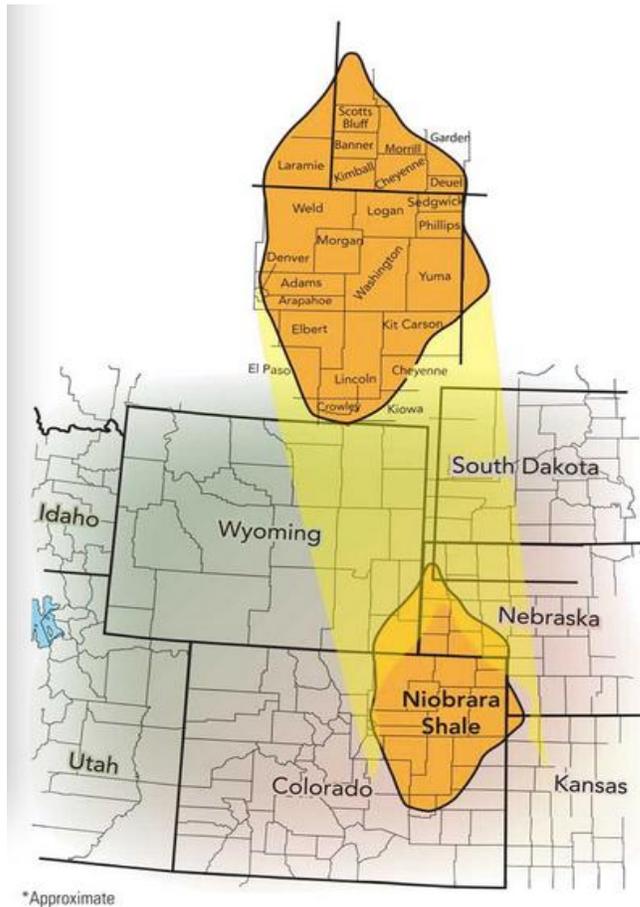


Figure 2-3: Location of Niobrara Play

2.2 Produced Water Quality

Huge volumes of water are used in the drilling and hydraulic fracturing involved in unconventional oil and gas extraction; the process also produces large volumes of wastewater. With increasing extraction activity in recent years, produced water management and treatment has become an environmental concern. Produced water quality analysis is a basic tool in reusing produced water effectively.

Produced water, the largest waste stream generated by the oil and gas industry, could be considered an industry by-product. Its composition is complex, including salt content; oil and grease; various natural inorganic and organic compounds; chemical additives used in drilling, fracturing, and operating; and naturally occurring radioactive material (NORM)[10]. Some of these constituents—such as total dissolved solids—are present in much higher concentrations than other types of water, and most components of produced water have notable impact on the environment and human health. Table 2-2 compares some typical values of produced water to other kinds of water[11].

Table 2-2: Typical Values for Produced Water Quality Compared to Some Criteria

Parameters	Drinking Water Criteria	Irrigation Water Criteria	CBM Produced Water	Natural Gas Produced Water
pH	6.5-8	-	7-8	6.5-8
TDS (mg/L)	500	2,000	4,000-20,000 *	20,000-100,000
Benzene (ppb)	5	5	<100	1,000-4,000
SAR**	1.5-5	6	Highly Varied	Highly Varied
Na⁺ (mg/L)	200	See SAR	500-2,000	6,000-35,000
Barium (mg/L)			0.01-0.1	0.1-40
Cl⁻ (mg/L)	250	-	1,000-2,000	13,000-65,000
HCO₃⁻ (mg/L)	-	-	150-2,000	2,000-10,000

* Total Dissolved Solids (TDS) range estimated for the lower 50 percentile

** SAR = Sodium Absorption Ratio -- a function of a ratio of Na to Ca and Mg Levels.

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$$

Further, the chemical constituents of produced water can break down to organic components and inorganic ions. Both organic and inorganic components consist of soluble composition, along with insoluble and separable composition that can be removed by filtration. Soluble organic components include carboxylic acids, phenols, and other compounds that are complex and difficult to analyze and reduce. Soluble inorganics can include non-ionics; cationic components such as sodium and other monovalent and multivalent elements such as potassium, calcium, magnesium, iron, barium, and boron; and anionic components such as carbonate, bicarbonate, chloride, and others. Figure 2-4 identifies typical chemical constituents of produced water[11].

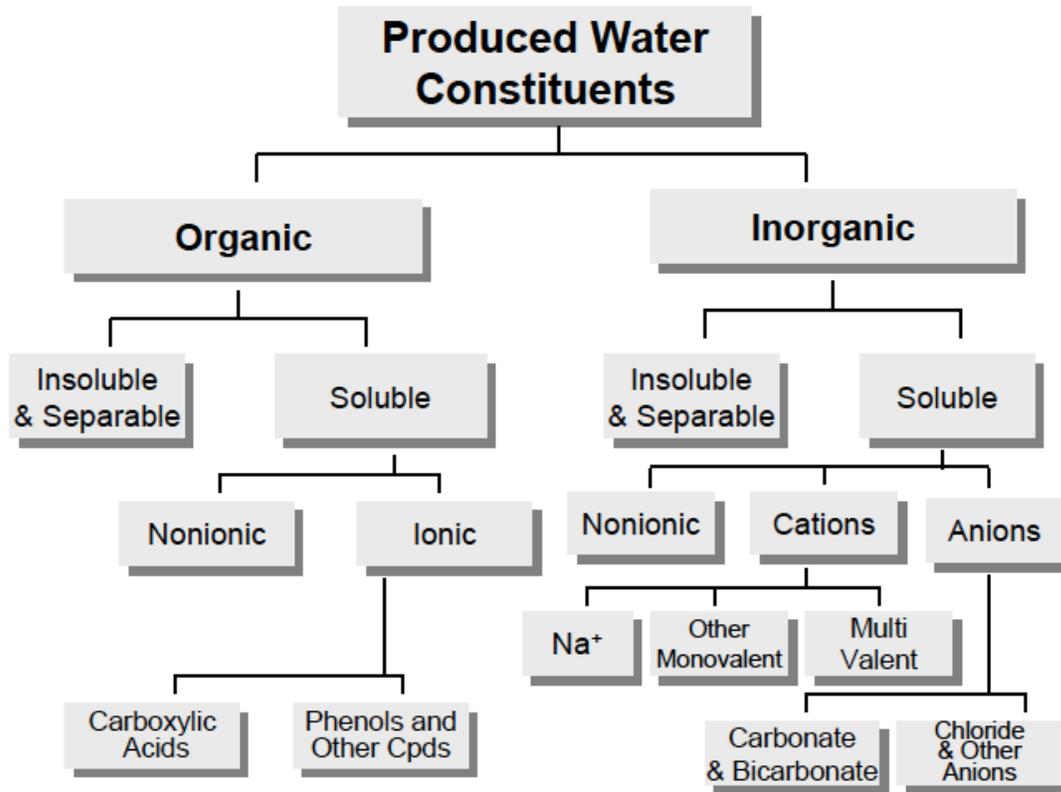


Figure 2-4: Breakdown of Produced Water Chemical Constituents

Because well field conditions and locations, geological formation of oil and gas layers, and types of production and fracturing fluid components all influence the characteristics of produced water, produced water has varying chemical composition and physical properties. The primary factors influencing produced water composition are the fracturing fluid components and geological formation characteristics. Fracturing fluid components have a large influence on produced water quality during the flowback period, while the main factor of produced water quality after the flowback period is the geological formation characteristics of the oil and gas layers.

Hydraulic fracturing fluids consist of water, sand, and chemical additives, and the relative amount of each used to maximize the recovery of hydrocarbons depends on the variable conditions of the oil and gas geological formation. The percentage of water and sand content varies from about 98 to 99.5 percent. Chemical additive content can vary from about 0.5 to 2 percent, and the categories and amounts used are chosen based on the formation contact requirements. The constituents of hydraulic fracturing fluids, while complex, might also be used in daily life; Table 2-3[12] identifies fracturing fluid ingredients and their common uses. Figure 2-5 shows the average hydraulic fracturing fluid composition for U.S. shale plays[12].

Table 2-3: Frac Fluid Additives, Main Components, and Common Uses

Additive	Chemical Ingredient	Purpose	Common Use of Chemical Ingredient
Acid	Hydrochloric acid or muriatic Acid	Helps dissolve minerals and initiate cracks in the rock	Swimming pool chemical and cleaner
Antibacterial agent	Glutaraldehyde	Eliminates bacteria in the water that produce corrosive by-products	Disinfectant; sterilizer for medical and dental equipment
Breaker	Ammonium persulfate	Allows a delayed breakdown of the gel	Used in hair coloring, as a disinfectant, and in the manufacturing of common household plastics
Corrosion inhibitor	Formamide	Prevents the corrosion of the well casing	Used in pharmaceuticals, acrylic fibres and plastics
Crosslinker	Borate salts	Maintains fluid viscosity as temperatures increase	Used in laundry detergents, hand soaps and cosmetics
Friction reducer	Petroleum distillate	"Slicks" the water to minimize friction	Used in cosmetics including hair, make-up, nail and skin products
Gel	Guar gum or hydroxyethyl cellulose	Thickens the water in order to suspend the sand	Thickener used in cosmetics, baked goods, ice cream, toothpaste, sauces and salad dressings
Iron control	Citric acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice ~7% citric acid
Clay stabilizer	Potassium chloride	Creates a brine carrier fluid that prohibits fluid interaction with formation clays	Used in low-sodium table salt substitutes, medicines and IV fluids
pH adjusting agent	Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Used in laundry detergents, soap, water softener and dishwasher detergents
Proppant	Silica, quartz sand	Allows the fractures to remain open so the gas can escape	Drinking water filtration, play sand, concrete and brick m
Scale inhibitor	Ethylene glycol	Prevents scale deposits in the pipe	Used in household cleansers, de-icer, paints and caulk
Surfactant	Isopropanol	Used to reduce the surface tension of the fracturing fluids, to improve liquid recovery from the well after the frac	Used in glass cleaner, multi-surface cleansers, antiperspirant, deodorants and hair color
Water	Water	Used to expand the fracture and deliver proppant (sand)	Landscaping, manufacturing

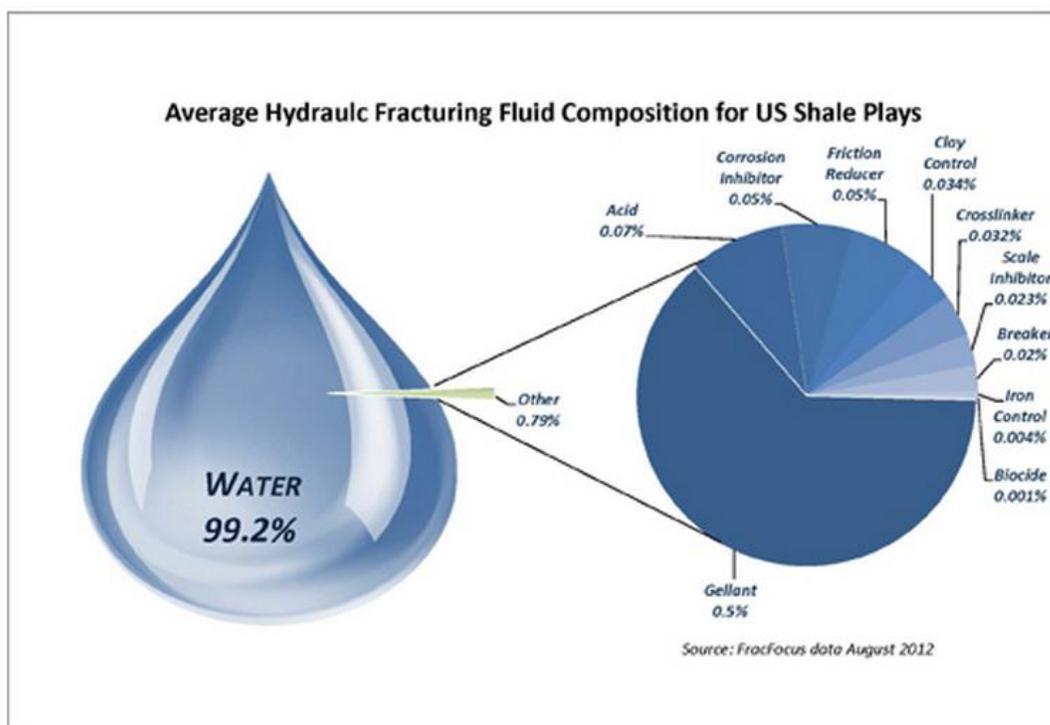


Figure 2-5: Average Hydraulic Fracturing Fluids Composition for U.S. Shale Plays

Though the chemical additives of hydraulic fracturing fluids exist in our food, drink, and daily lives, frac flowback fluids containing these chemical additives have potential impacts on environmental and human health. Extreme conditions such as high temperature and high pressure imposed on frac fluids cause chemical reactions that change their physical properties during the frac flowback period and result in produced water quality more complex than expected. The quantity of organic matter in produced water is much different from the chemical additives of hydraulic fracturing fluid, making it difficult to recognize and remove constituents such as total organic carbon (TOC) and dissolved organic carbon (DOC), the concentrations of

which should be reduced by produced water treatment to meet produced water quality standards and minimize environmental impact.

Geological formation characteristics have a large influence on produced water quality, and the concentration of total dissolved solids, ions, and even organics will vary based on the location of the basin and wells field. In the western United States, oil and grease content ranges from 40 mg/L to 2,000 mg/L and the concentration of total dissolved solids varies even more--from 1,000 mg/L to 400,000 mg/L[13]. Further, produced water from different shales will exhibit widely varying quality. In Barnett Shale, total dissolved solids and chlorides increase over time, from 50,000 ppm to 140,000 ppm and 25,000 to 80,000 ppm, respectively, while the concentration of total suspended solids (TSS) and iron tend to remain relatively low. Fayetteville Shale has “good quality water,” because the concentration of total dissolved solids, chlorides, calcium, and magnesium are much lower than other shale plays. In comparison, poor-quality produced water is seen in Haynesville Shale, where high total dissolved solids, chlorides, and total suspended solids are present in produced water immediately after fracturing, and calcium and magnesium tend to scale to higher concentrations. In Marcellus Shale, where total suspended solids values are lower, other parameters such as total dissolved solids, calcium, and magnesium are higher. Table 2-4 compares levels of total dissolved solids (TDS), chlorides, total suspended solids (TSS), calcium (Ca), magnesium (Mg), as well as the reusability potential of produced water, in Barnett Shale, Fayetteville Shale, Haynesville Shale, and Marcellus Shale[14].

Table 2-4: Comparison of TDS, Chlorides, TSS, Calcium, Magnesium and Reusability of Produced Water in Different Shale

Parameters	Barnett Shale	Fayetteville Shale	Haynesville Shale	Marcellus Shale
TDS (ppm)	50,000 - 140,000	~15,000	high	40,000-90,000 (immediately after frac) >120,000 (long term)
Chlorides (ppm)	25,000 - 80,000	~10,000	high	-
TSS (ppm)	relatively low	-	~350	~160
Ca (ppm)	-	low	~8,000	high
Mg (ppm)	-	low	~500	high
Reusability	-	excellent potential	relatively unattractive potential	attractive potential

The quality of produced water is directly associated with the chemical additives of hydraulic fracturing fluids, geological formation characteristics, and the age of produced water. Produced water quality can be modeled temporally and spatially, depending on its characteristics. Parameters such as total dissolved solids, sodium, chloride, and calcium--whose concentrations are related to the flowback period--can be modeled temporally. However, some produced water parameters—such as iron--can only be modeled spatially, because their concentrations are largely dependent on geological formation characteristics.

One of the major components of produced water is hydrocarbons, including oil and grease; organic components such as benzene, naphthalene, toluene, phenanthrene, and pentachlorophenol. The solubility of organic components can be affected by temperature and pH [15]. Hydrocarbons in produced water include inorganic acids, polycyclic aromatic hydrocarbons (PAHs), phenols, and volatiles, which contribute to the toxicity of produced water. Soluble organic compounds in produced water are difficult to remove, and the concentration of

those with lower molecular weight will be greater than the concentration of those with higher molecular weight. Generally, organic compounds are more difficult to remove by oil/water separators because of the lower weight of organic compounds[16]. The concentration of hydrocarbons and organic compounds in produced water--always at a very high level and challenging to remove or reduce--are determined by measuring total organic carbon (TOC) and dissolved organic carbon (DOC) in laboratory.

A primary constituent of produced water, salt is expressed as salinity, conductivity, or total dissolved solids. In produced water, salts are present primarily as chlorides and sulfides of calcium, magnesium, and sodium. Salinity indicates the amount of total dissolved salts and is typically measured by electrical conductivity. Produced water salinity may range from a few parts per thousand to a much higher level, and most produced water salinity concentration is much greater than that of seawater. Sodium and chloride typically represent total dissolved solids in most water; in produced water, calcium, magnesium, potassium, and bicarbonate are significant ion components. Sulfate concentration in produced water is typically lower than that in seawater, except for seawater used for oil enhancing recovery[17], while the concentration of barium and strontium is relatively high in produced water. The concentration of other ions such as ammonium, nitrite, phosphate, and sulfide are usually low in produced water and measured only when concentrations would be elevated for a specific reason [17,18]. Table 2-5 compares the concentration of salinity and some inorganic ions in seawater and in produced water[17].

Table 2-5: Salinity (%) and Concentrations (mg/L) of Selected Inorganic Ions in Typical Seawater and in Produced Water

Chemical	Seawater	Produced Water
Salinity	32-36	3-320
Sodium	10,560	65-97,000
Chloride	18,900	<5-201,000
Calcium	400	13-118,800
Strontium	13	7-3,200
Magnesium	1,270	4-11,700
Potassium	80	3-6,500
Sulfate	880	<1-1,650
Sulfide	-	0.12-256
Ammonia	-	<0.1-650

Metals also are present in produced water, with lead, chromium, and nickel typically present at lower concentrations. Other metals such as barium, iron, manganese, strontium, zinc, silver, cadmium, copper, lithium, arsenic, mercury, selenium, boron and antimony might also be found in produced water [19]. However, the concentrations of metals in different produced waters are extremely variable and depend on the age of the well and the geological formation of the oil and gas production [16].

2.3 Produced Water Treatment

At present, the main methods of managing produced water are disposal through injection, treatment for discharge, and reuse in oil and gas operation or other beneficial applications such as irrigation. Due to its high concentration of total dissolved solids, organic matter, metals, and oil and grease, produced water typically requires treatment before injection, discharge, or reuse. Physical, chemical, and biological methods are frequently combined to satisfy the general objectives for produced water treatment: de-oiling, soluble organics removal, disinfection, suspended solids removal, dissolved solids removal, softening, and other treatments[20].

Because each unit process of produced water treatment has its own limitation, a number of appropriate applications of unit processes are combined to reach the treatment required. Table 2-6 identifies these unit processes and how their application treats produced water [11].

Table 2-6: Unit Processes and Their Application to Produced Water Treatment

Treatment method	De-oiling	Suspend solids removal	Iron removal	Ca & Mg removal softening	Soluble organic removal	Trace organics removal	Desalination & Brine volume red	Adjustment of SAR	Silicate & Boron removal
API Separator	✓	✓							
Deep Bed Filter	✓	✓							
Hydrochloric	✓	✓							
Induced Gas Flotation	✓	✓							
Ultra-filtration	✓	✓							
Sand Filtration		✓							
Aeration & Sedimentation		✓	✓						
Precipitation Softening				✓					✓
Ion Exchange			✓	✓					✓
Biological Treatment					✓				
Activated Carbon						✓			
Reverse Osmosis							✓		
Distillation							✓		
Freeze Thaw Evaporation					✓		✓		
Electrodialysis					✓		✓		
Chemical Addition								✓	

✓= Indicates that the technology is applicable as a potential process as indicated by data collected from pilot or commercial scale units

Recycling produced water for use as hydraulic fracturing fluids is one of the most efficient ways of reusing process wastewater. However, typical treatment applications and blending with

fresh water must be completed to assure fracturing fluids meet produced water recycling requirements. Physical treatment, chemical treatment, biological treatment, and membrane treatment are commonly applied in produced water treatment; membrane treatment, in particular, is the promising technology for the future if costs can be decreased and chemical toxicity and pollution can be controlled [21]. Table 2-7 identifies the methodologies involved when these treatments are applied to produced water [21].

Table 2-7: Physical Treatment, Chemical Treatment, Biological Treatment, and Membrane Treatment for Produced Water

Physical Treatment	Chemical Treatment	Biological Treatment	Membrane Treatment
Adsorption of dissolved organics on activated carbon, organoclay, copolymers, zeolite, resins	Chemical precipitation	activated sludge	Microfiltration (MF)
Sand filters	Chemical oxidation	trickling filters	ultrafiltration (UF)
Cyclones	Electrochemical process	sequencing	nanofiltration (NF)
Evaporation	Photocatalytic treatment	batch reactors (SBRs)	reverse osmosis (RO)
Dissolved air precipitation (DAP)	Fenton process	chemostate reactors	Bentonite clay
C-TOUR	Treatment with ozone	biological aerated filters (BAF)	zeolite membrane
Freeze-thaw/evaporation	Room temperature ionic liquids	lagoons	Combined systems
Electrodialysis (ED)	Demulsifier	reed bed technology	Modified membrane systems to reduce fouling

Depending on water quality and reuse requirements, produced water will go through a series of treatments that might include settling, filtration, blending, coagulation, softening, and reverse osmosis (RO). This study focused on total dissolved solids, sodium, chloride, calcium and iron as key parameters for produced water quality analysis. Typically, reverse osmosis and blending

are used to reduce the concentration of total dissolved solids, sodium, and chloride in produced water treatment; while iron concentration is reduced by coagulation/filtration. Increasing pH, along with alkalinity will result in the precipitation and removal of calcium in water.

The settling process, which removes particulates by gravity, requires a large space and a relatively long time. While chemicals are not required in this process, and water detention time determines the degree and size of particles removed, chemical additives will enhance sedimentation. Settling typically is the least expensive and simplest process in produced water treatment. Filtration is widely applied in produced water treatment, and a variety of media—such as walnut shell, sand, anthracite, and others—can be used in the filtration process. Filtration can remove oil, grease, and total organic carbon in produced water, but it cannot remove dissolved ions [22]. Blending with fresh water reduces the concentration of total dissolved solids and also helps achieve the fracturing fluids volume required.

Reverse osmosis (RO) membrane technology separates dissolved and ionic components in water [23] and is a popular treatment for reducing the concentration of dissolved and ionic components from water. Compared to other treatment methods, reverse osmosis membrane filtration offers several advantages [24]:

- Can be applied for multiple industrial waters.
- Does not require chemical additions, so there is less secondary pollution.
- Does not require large spacing or high energy costs
- Can be highly automated
- Allows streams to be selected for recycling during the process.

Reverse osmosis technology has developed to a point where it is now a worldwide method for purifying saline water for reuse. Table 2-8 shows how certain water parameters in produced water from the brackish oil field were significantly reduced by reverse osmosis treatment [25].

Table 2-8: Concentration of Produced Water Parameters Prior To and After RO Treatment and Treatment Efficiency in Brackish Oil Field

Constituent	Produced water prior to treatment with RO	Produced water following to treatment with RO	Percentage of removal
Total dissolved solids (mg/L)	6554	295	95.50%
Bicarbonate alkalinity (mg/L)	528	90	82.95%
Boron (mg/L)	28	17	39.29%
Calcium (mg/L)	56	0.1	99.82%
Chloride (mg/L)	3361	106	96.85%
Electrical conductivity (µmhos/cm)	10240	350	96.58%
Iron (mg/L)	0.39	0.01	97.44%
Magnesium (mg/L)	9.1	0.1	98.90%
pH	7.7	6.7	12.99%
Potassium (mg/L)	53	0.1	99.81%
Sodium (mg/L)	2252	69	96.94%
Sodium adsorption ration (SAR)	73.4	37.8	48.50%
Total organic carbon (mg/L)	77.4	18.4	76.23%

3. RESEARCH OBJECTIVES

In the past several years, a large number of shale oil and gas wells drilled in the Wattenberg Field in the Denver-Julesburg Basin, located in northeastern Colorado. Development of the shale oil and gas industry underscores the importance of understanding the environmental impact of produced water quantity and quality. Since water resources are limited in most regions of Colorado, produced water management and treatment is a central issue for the oil and gas industry in the state. Produced water treatment and freshwater blending prior to recycling of frac flowback water allows operations to reuse water. The current study examined the close relationship between produced water quality management and its reusability, by creating models of produced water quality, blending, and treatment requirements that can support efficient and effective reuse.

The research focused on produced water quality modeling, and the blending and treatment of flowback required for optimizing produced water at an unconventional oil and gas reuse effort in Wattenberg Field. The research targeted five key parameters of produced water--total dissolved solids, sodium, chloride, calcium, and iron—by modeling them spatially and temporally in seven Integrated Development Plans, examining treatment methods and results, and recycled water quality after blending with fresh water. The main objectives of this research are:

1. Develop spatial and temporal models for identifying water quality of flowback/produced water from Noble Energy operations in the Denver-Julesburg basin

2. Develop spatial and temporal models for estimating blending and treatment requirements of flowback/produced water

4. MODELING WATER QUALITY OF FRAC FLOWBACK AND PRODUCED WATER IN WATTENBERG FIELD

4.1 Background

Produced water quality characterization is critical for effective wastewater treatment and reuse. In this research, total dissolved solids (TDS), sodium, chloride, calcium, and iron have been determined to be key water quality parameters to be considered, because total dissolved solids—typically sodium and chloride—and iron demonstrate compatibility issues with frac fluids, and calcium reflects the scaling index of fracturing fluids [26,27]. Reverse osmosis (RO) and blending are the main methods to reduce total dissolved solids in produced water [28]. Coagulation and filtration are applied to treat produced water for iron-related solids. Softening is used to reduce calcium concentration; at the same time, softening increases the water's pH value, which, in turn, precipitates iron and reduces its concentration [29, 30]. Noble Energy provided produced water quality data from its horizontal wells in the Niobrara formation in the Denver-Julesburg basin in Colorado. The entire field of wells is divided into seven Integrated Development Plans (IDPs): Core, Mustang, Greeley Crescent, East Pony, West Pony, Wells Ranch, and Cummins. Six hundred samples were collected from 225 wells that use fresh water for fracturing fluids. The produced water quality data, with outlier values removed, were used to create spatial and temporal models used in water quality data analysis.

These water quality data models provide a clear indication of the temporal variation of the total dissolved solids, sodium, chloride, and calcium in each Integrated Development Plan. There is no obvious temporal trend of iron, because the concentration of iron in produced water is closely correlated with the geological formation of the well fields; in this study, iron

concentration of fracturing flowback and produced water was analyzed spatially for average value, maximum value, and standard deviation. Water quality data for all existing wells and new wells can be predicted in each Integrated Development Plan, based on the temporal trends of total dissolved solids, sodium, chloride, and calcium. These values also identify the treatment and blending of frac flowback and produced water necessary for effective reuse and recycling.

4.2 Methods

This study compared linear and logarithmic functions with produced water quality data. Logarithmic function is used for modeling total dissolved solids, sodium, chloride, and calcium data, because the ‘R square factor’ of linear function is smaller. Noble Energy provided all data, which were collected and tested by Baker Hughes Incorporated (BHI) and Colorado State University (CSU) from 2010 to 2013. The produced water quality data provided by Noble Energy were modeled temporally for each Integrated Development Plan in the well field. Water quality data were sorted into three groups: those sampled during the 0-30 day flowback period; those sampled during the 30-165 day transition phase; and those sampled after 165 days, during the produced water phase. Because produced water quality data were collected from random wells and at random time periods, removing outlier values was necessary before water quality data modeling. Generally, the small and acceptable probability of error of the data was less than 0.05. Typically, the lower limit of water quality data was 97.5 percent of the first day data in each period. The upper limit is calculated by the following equation:

$$Upper\ limit = \bar{x} + Z_{1-\alpha/2} \frac{\sigma}{\sqrt{n}}$$

where $\frac{\sigma}{\sqrt{n}}$ is the standard error of \bar{x} and $Z_{1-\alpha/2}$ is the value of the standard normal variable that cuts off $(100\alpha/2)\%$ of the upper tail of the $N(0,1)$ distribution [31]. Since α is 0.05, the value of $Z_{1-\alpha/2}$ is 1.96.

There is no functional calculation that fits the concentration of iron in produced water, as iron concentration relates directly with the geological formation where the wells sourcing the oil and gas are drilled. All iron concentration data were analyzed by without consideration of outlier values, and the average value, maximum value, and standard deviation were compared spatially.

4.3 Results

The logarithmic function of frac flowback and produced water quality model was defined as $y = a \ln(t) + b$. Table 4-1 identifies the a , b , and R square parameters of this logarithmic function.

Table 4-1: a, b and R Square of Logarithmic Function

IDP	TDS			Sodium		
	a	b	R ²	a	b	R ²
Core	2980	4310	0.87	929	1800	0.75
Mustang	2280	10700	0.86	1600	-262	0.95
Greeley Crescent	2320	6990	0.73	788	2560	0.72
East Pony	4640	1610	0.78	2060	-929	0.79
West Pony	6130	1550	0.95	2340	105	0.94
Wells Ranch	4030	4920	0.89	1290	2650	0.86
Cummins	3240	16800	0.42	1160	6270	0.38
IDP	Chloride			Calcium		
	a	b	R ²	a	b	R ²
Core	1970	1180	0.76	61.2	-22.7	0.86
Mustang	2290	10700	0.86	52.0	0.595	0.92
Greeley Crescent	1510	3580	0.77	69.0	-20.6	0.83
East Pony	3000	-361	0.83	30.8	-2.61	0.87
West Pony	4010	-962	0.94	56.8	-9.57	0.82
Wells Ranch	2080	3500	0.76	51.7	63.9	0.82
Cummins	2030	9190	0.49	22.7	340	0.09

As shown in Table 4-1, all R square values, except those applied in the Cummins Integrated Development Plan, are greater than 0.75--indicating most of the frac flowback and produced water quality data with outlier values removed do, indeed, fit the logarithmic function well. In the Cummins Integrated Development Plan, the initial data were collected during the transition period; fracturing flowback and produced water quality data collected during those time periods varied widely and could not be used to determine an accurate slope of logarithmic function. Further, in the Cummins Integrated Development Plan area, produced water quality data values were much higher than those from the other IDPs, from the start of sampling through the sampling period. It is concluded that these two circumstances are the cause the R square value of the Cummins Integrated Development Plan to be lower than that of the other IDPs.

Figure 4-1 through Figure 4-4 graphs illustrate the temporal trends of total dissolved solids, sodium, chloride, and calcium data modeled as a logarithmic function in each IDP, based on the functions in Table 4-1.

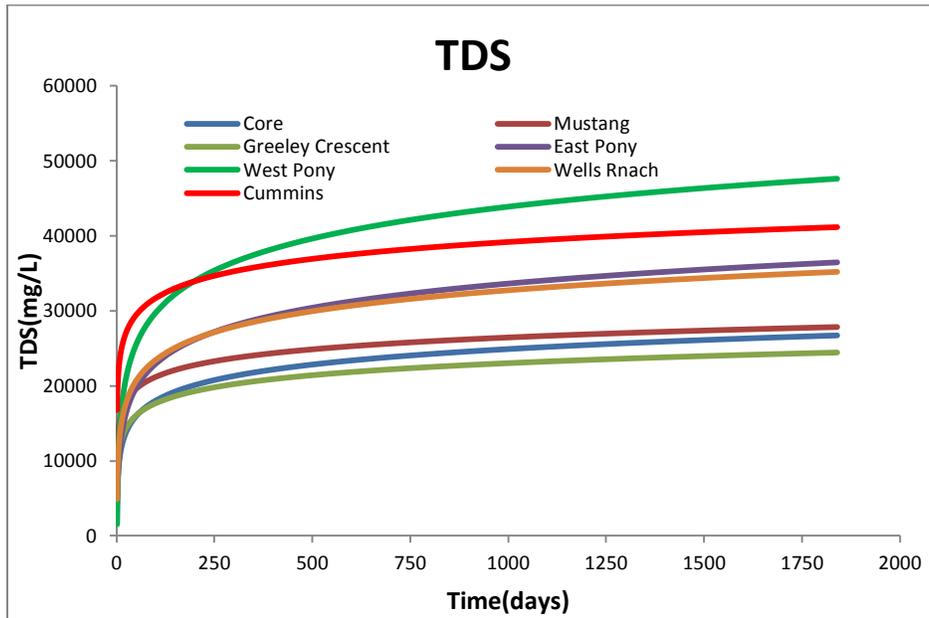


Figure 4-1: Total Dissolved Solids Temporal Trends in Different IDPs

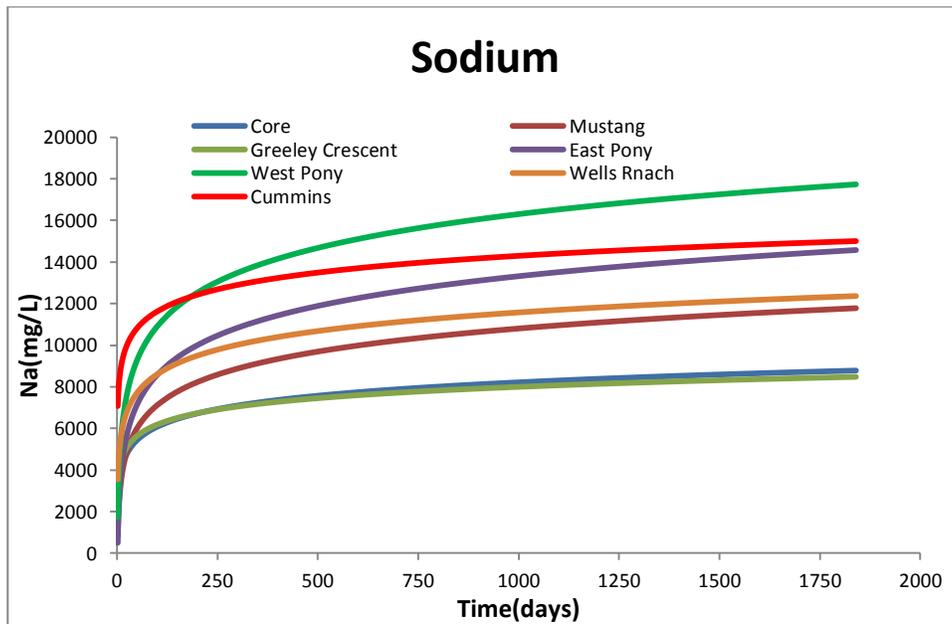


Figure 4-2: Sodium Temporal Trends in Different IDPs

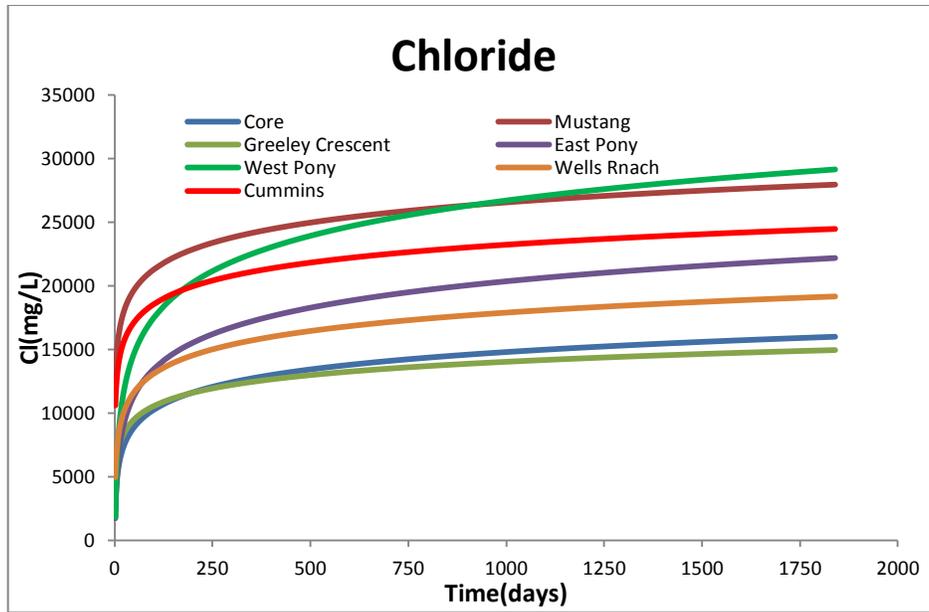


Figure 4-3: Chloride Temporal Trends in Different IDPs

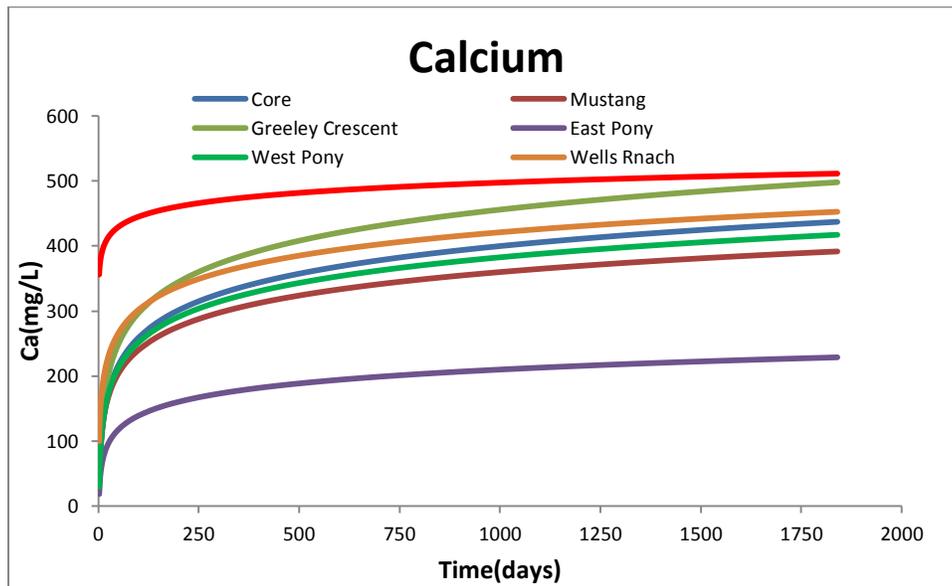


Figure 4-4: Calcium Temporal Trends in Different IDPs

Least squares means of iron concentration were compared in each Integrated Development Plan, which use two-tailed t-test. The results of t-test are shown in table 4-2 and some of p values are smaller than 0.05 which indicate differences means of iron concentration among Integrated Development Plans. Iron concentration of fracturing flowback and produced water cannot be combined with other and should be analyzed spatially. Based on Kolmogorov – Smirnov test, in seven Integrated Development Plans, none of iron concentration fits normal distribution and box and whisker plot of iron concentration is displayed in Figure 4-5.

Table 4-2: P Values compare of Iron in Different IDPs

Differences of Least Squares Means			
IDPs	IDPs(compare)	t Value	P Value
Core	Cummins	-1.34	0.1808
Core	East Pony	1.37	0.1728
Core	Greely Crescent	-0.73	0.4664
Core	Mustang	1.35	0.1773
Core	Wells Ranch	-4.96	<0.0001
Core	West Pony	-1.34	0.1815
Cummins	East Pony	2.51	0.0124
Cummins	Greely Crescent	0.28	0.7781
Cummins	Mustang	2.35	0.0189
Cummins	Wells Ranch	-3.18	0.0015
Cummins	West Pony	-0.30	0.7654
East Pony	Greely Crescent	-1.75	0.0811
East Pony	Mustang	0.15	0.8837
East Pony	Wells Ranch	-5.60	<0.0001
East Pony	West Pony	-2.32	0.0206
Greely Crescent	Mustang	1.73	0.0842
Greely Crescent	Wells Ranch	-2.49	0.0129
Greely Crescent	West Pony	-0.49	0.625
Mustang	Wells Ranch	-4.86	<0.0001
Mustang	West Pony	-2.25	0.0248
Wells Ranch	West Pony	1.90	0.058

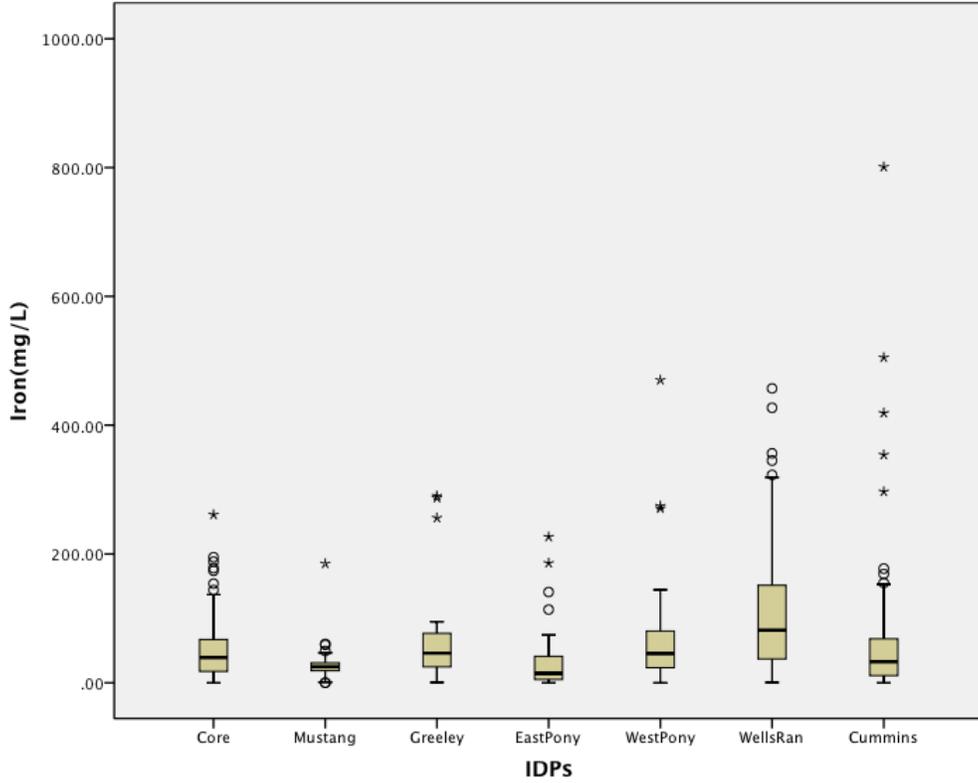


Figure 4-5: Box and Whisker Plot of Iron Concentration in Each IDP

The average value, maximum value, and standard deviation of iron concentration are presented in Table 4-3. A comparison of the maximum and average value of iron concentration in the different IDPs is provided in Figure 4-6.

Table 4-3: Average Value, Maximum Value and Standard Deviation of Iron in Different IDPs

Iron (mg/L)			
IDP	Average	MAX	σ
Core	53	261	51
Mustang	30	185	32
Greeley Crescent	66	290	74
East Pony	33	227	46
West Pony	77	470	94
Wells Ranch	106	457	86
Cummins	71	801	124

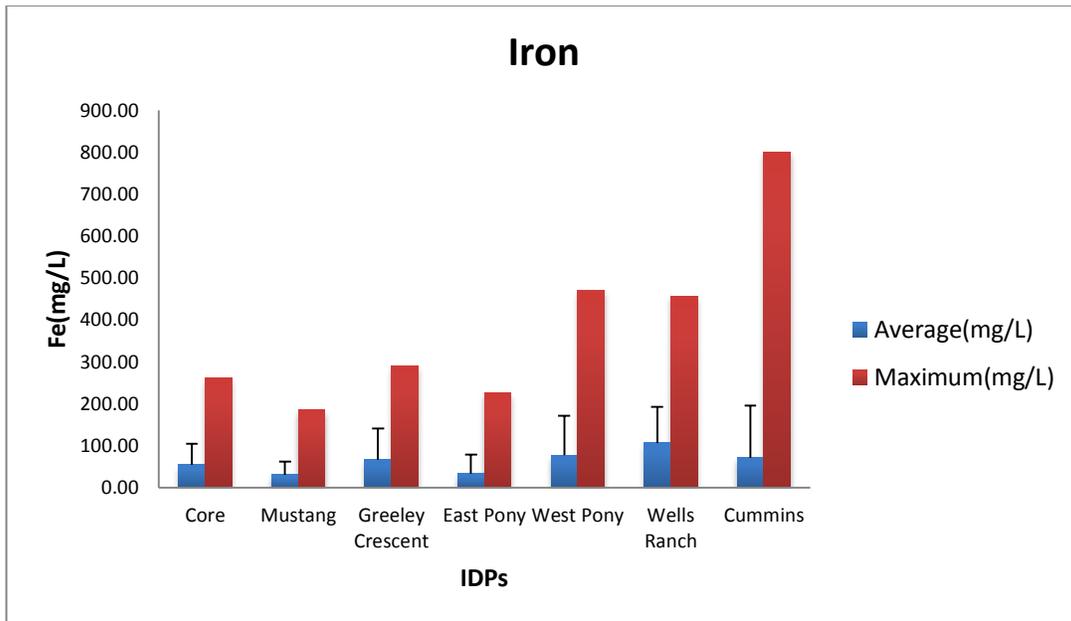


Figure 4-6: Maximum and Average Value of Iron Concentration in Each IDP

The data indicate that no temporal trends fit the iron concentration values of samples collected in each IDP. Iron concentration of frac flowback and produced water samples can only be analyzed spatially, as it relates directly to the geological formation of the well fields. Among the IDPs, those exhibiting the largest average value, maximum value, and standard deviation of iron concentration are in the Wells Ranch and Cummins IDPs. The smallest average value, maximum value, and standard deviation of iron concentrations were measured in samples from the same IDP, Mustang.

4.4 Conclusion

Noble Energy collected and provided the data identifying nearly all water quality characteristics of the frac flowback and produced water quality in the Wattenberg field. Total

dissolved solids, sodium, chloride, calcium, and iron were considered key parameters for modeling produced water quality; total dissolved solids, sodium, chloride and calcium, concentrations—which reflect temporal trends—allow comparison of linear function and logarithmic function in each Integrated Development Plan. The R square factor of the logarithmic function is larger than that of the linear function and from observing the variation tendency of water quality data, the logarithmic function is also more suitable depending on the temporal range. Analysis of the two models showed that the logarithmic function provided a better model for produced water quality in the seven IDPs. Because iron concentration of produced water relates to the geological formation of the well field instead of temporal changes in flowback characteristics, the trends in the IDPs, the average value, maximum value, and standard deviation of iron were analyzed spatially.

Temporal trends of total dissolved solids, sodium, chloride, and calcium data would be used to predict water quality data at specific times for old and new wells in the seven Integrated Development Plans. In addition, the average value, maximum value, and standard deviation of iron concentration would provide important reference values of produced water quality data in the well field. Together, the temporal and spatial modeling of frac flowback and produced water quality data would provide the basis for produced water blending and treatment on upcoming specified days and regions. Further, understanding frac flowback and produced water quality variation in the Wattenberg field will help achieve proper produced water blending and treatment in future work.

5. TREATMENT AND BLENDING OF FRAC FLOWBACK WATER FOR REUSE AS FRAC FLUID: A FRAMEWORK FOR OPTIMIZATION

5.1 Background

Produced water management and treatment are considered important issues in the unconventional oil and gas industry. Produced water is the largest volume of wastewater generated in oil and gas production, and it contains complex organic and inorganic compounds that can have significant impact on the environment and human health. Currently, produced water management consists of disposal through injection, treatment for discharge, reuse in oil and gas operation, or reuse for other purposes such as irrigation or animal feeding. This research focused on produced water recycling and reuse as the main approaches to water management optimization. Total dissolved solids, sodium, chloride, calcium, and iron were the key parameters analyzed and optimized in this study, to identify the treatment and blending with fresh water required to reduce their concentration and meet fracturing fluids quality and quantity requirements. Figure 5-1 illustrates the overall produced water treatment process, consisting of coagulation/filtration, softening/clarification, and reverse osmosis, to reduce the concentration of total dissolved solids, sodium, chloride, calcium, and iron [28,29,30]. In this treatment process, most of the iron will be removed by coagulation/filtration; softening/clarification reduces calcium hardness; and the final reverse osmosis treatment reduces concentration of total dissolved solids, sodium, and chloride in the produced water.

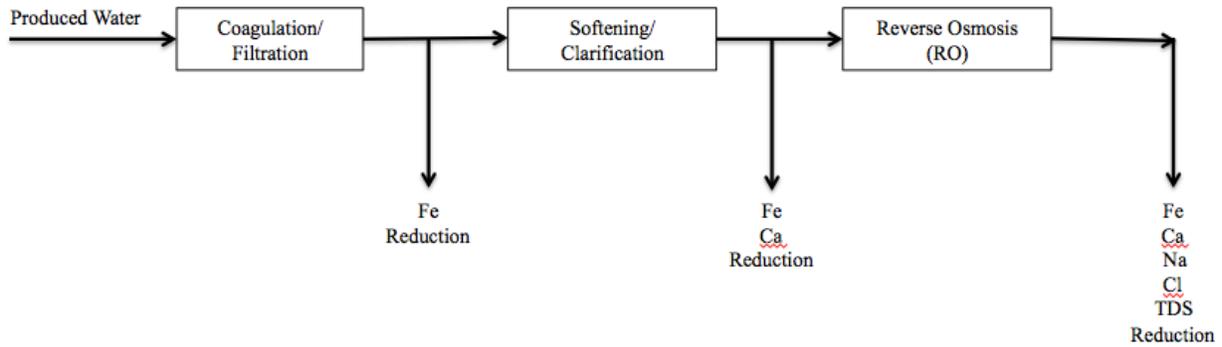


Figure 5-1: Produced Water Treatment Process

Coagulation is a commonly applied method of iron removal in the petroleum industry, and the most widely used chemical for wastewater coagulation is alum $[Al_2(SO_4)_3 \cdot 18H_2O]$ [32]. In the coagulation process, the colloidal charge of dissolved iron is neutralized by combining with countering ions, resulting in sedimentation that allows filtration of about 80% of the produced water iron content [33]. Generally in water treatment, lime softening is the least expensive and most commonly applied method of reducing hardness, and it was the method used in this study to remove calcium in produced water. While softening increased water pH to 9, chemical-equilibrium modeling predicted its effectiveness in removing at least 97% of the calcium concentration [34]. When the pH value of the produced water was increased to 7.5 to 8.0, more than 98.6% of iron content was precipitated [35]. Reverse osmosis is considered to be the an effective means of reducing total dissolved solids, sodium, and chloride concentration, usually by more than 95%[25]. Table 5-1 lists the effectiveness of treatment methods in reducing key parameters in produced water. [34,35,25]

Table 5-1: Treatment Effectiveness in Removing Key Parameters in Produced Water

Methods	Constituent	Removal Percentage
Coagulation/Filtration	Fe	80%
Softening/Clarification	Fe	99%
	Ca	97%
Reverse Osmosis (RO)	Fe	97%
	Ca	99%
	Na	97%
	Cl	97%
	TDS	96%

The volume of fresh water blended with produced water depends on the required quality and quantity of the intended fracturing fluids. The ultimate goal of produced water reuse is recycling 100 percent of frac flowback and produced water and the recycled water quality reaches the requirements of frac fluids without any blending of water. However, some treated recycled water quality is not compatible with certain frac fluids, so the recycled water must be diluted with fresh water to achieve the required quality. If the amount of dilution water required plus the available recycled water exceeds the water demand, all of the produced water cannot be used and the scenario would be considered “water quality” limited. On the other hand, if all of the recycled water is of sufficient quality that it is compatible with the frac fluid but the quantity is not high enough to supply a complete frac job (likely the case since only about 30-50% of water is recovered in the first 30 days), the scenario would be considered “quantity limited”. The tool developed with this research allows the determination of the fresh water requirements for “quality” and “quantity” under different, user defined, treatment scenarios.

5.2 Methods

Produced water that has undergone treatment and blending can be recycled as frac fluids or otherwise reused, and the primary goal of this study is to identify the means of determining the volume of fresh water necessary to blend with produced water in order to achieve reuse or recycling. As Figure 5-2 illustrates, the quantity of fresh water used correlates with the quality of that fresh water, the quality and volume of frac fluids, the quality and quantity of flowback fluids, the quality of produced water, and the targeted volume of recycled produced water. Some volume of flowback fluids might be injected in disposal wells, while another quantity of flowback fluids might be recycled for other frac jobs.

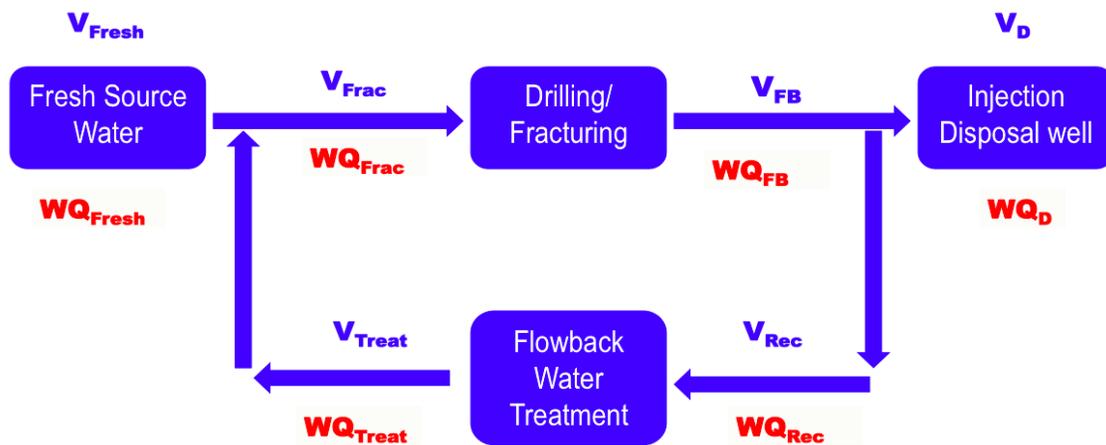


Figure 5-2: Produced Water Recycling Process Summary

In the recycling system depicted in Figure 5-2, the volume of fresh water used for blending not only is the difference of recycle produced water and volume needed to frac the well, but also can be limited by the recycle produced water quality and its diluted compatibility with the frac fluid used. The quality of the recycled/fresh water blend is an important factor influencing the volume of fresh water used since the frac fluid may need a higher degree of dilution than is accomplished if the entire volume of recycled water available is used. This scenario would result in the amount of recycled water use being limited by water, not the amount available. When the volume of fresh water based on water quality is determined to be larger than the volume based on quantity, 100% of the produced water could theoretically be recycled.

The following equations describe calculations for determining fresh water volume for “quality” and “quantity” limited scenarios:

WQ – water quality

q – flow rate

V – water volume

Frac – fracturing fluids

Fresh – fresh water

Rec – recycle water

FB – flowback fluids

D – disposal

Treat – treated water

“Quality” limited scenario

$$V_{FB} = V_{Rec} + V_D$$

$$V_{FB} = \int q_{FB}$$

$$R = \frac{V_{Fresh}}{V_{Rec}}$$

$$V_{Rec} = V_{FB} \times \text{recycle\%}$$

$$WQ_{Frac} = \frac{V_{Fresh} \times WQ_{Fresh} + V_{Treat} \times WQ_{Treat}}{V_{Frac}}$$

$$V_{Fresh,quality} = V_{Frac} \frac{WQ_{Frac,critical}}{WQ_{Fresh}} - V_{Treat} \frac{WQ_{Treat}}{WQ_{Fresh}}$$

“Quantity” limited scenario:

$$V_{Fresh,quantity} = V_{Frac} - V_{Treat}$$

$V_{Fresh,quality}$ and $V_{Fresh,quantity}$ are compared and:

$$V_{Fresh,quality} \geq V_{Fresh,quantity},$$

V_{Fresh} equals $V_{Frac} - V_{Treat}$, and

$V_{Fresh,quality}$ when the results $< V_{Fresh,quantity}$,

In the case where $V_{Fresh,quality} < V_{Fresh,quantity}$:

- If a higher fraction of produced water is desired to be used, additional treatment will be required (likely including TDS reduction)

- The percentage of produced water that is recycled will have to be reduced
- The frac fluid will need to be modified to be more tolerant to the water quality of the recycled water.

A produced water recycling program should initially identify the water quality requirements of the frac fluids, the quality and quantity of flowback water, and quality of fresh water before a systematic analysis can be done. These values have been modeled based on field data in other components of the overall project. Table 5-2 provides the quality and quantity values determined in the produced water program described in this paper. Critical fracturing fluids quality data is provided by Halliburton and Colorado State University without considering interactions and safety factor, because this is just an initial modeling of fracturing fluids quality. Figure 5-3 shows how these values are used in calculating fresh water used in the produced water recycling system.

Table 5-2: Fracturing Fluids Quantity and Quality, Flowback Fluids Quantity and Quality, and Fresh Water Quality Data

Fracturing Fluids Quality	
Constituent	Critical Concentration (mg/L)
Iron	75
Calcium	600
Sodium	9000
Chloride	9000
TDS	9000

Fracturing Fluids Quantity per Stage	
3571.428571	bbls/stage

Flowback Fluids Quality (mg/L)				
IDP	TDS	Sodium	Chloride	Calcium
Core	WQ=2982.1ln(t)+4 312.1	WQ=927.91ln(t)+1 804.4	WQ=1971.8ln(t)+1 177.2	WQ=61.173ln(t)- 22.745
Mustang	WQ=2282.5ln(t)+1 0691	WQ=1601.8ln(t)- 262.57	WQ=2293ln(t)+107 29	WQ=52.016ln(t)+0. 5952
Greeley Crescent	WQ=2322.1ln(t)+6 992.7	WQ=787.65ln(t)+2 556.2	WQ=1512.6ln(t)+3 583.6	WQ=68.964ln(t)- 20.551
East Pony	WQ=4636.6ln(t)+1 614.5	WQ=2062.2ln(t)- 928.59	WQ=3000ln(t)- 361.24	WQ=30.791ln(t)- 2.6108
West Pony	WQ=6129.5ln(t)+1 551.8	WQ=2344.5ln(t)+1 05.16	WQ=4007.2ln(t)- 961.57	WQ=56.77ln(t)- 95692
Wells Ranch	WQ=4028.5ln(t)+4 924.5	WQ=1292.2ln(t)+2 649	WQ=2084.4ln(t)+3 499.4	WQ=51.705ln(t)+6 3.865
Cummins	WQ=3244ln(t)+167 78	WQ=1161.8ln(t)+6 270.1	WQ=2033.8ln(t)+9 192	WQ=22.732ln(t)+3 40.34

Flowback Water Production Flow Rate (bbls/day)			
IDP	Frac flowback	Transition	Produced water
	(1 month)	(4 months)	(After 5 months)
Core	$Q = 1043.04t^{-0.721}$	$Q = \frac{90}{(1 + 0.0529t)^{0.769}}$	$Q = \frac{19.4084}{(1 + 0.00715t)^{0.588}}$
Mustang	$Q = 1157.61t^{-0.725}$	$Q = \frac{98.49}{(1 + 0.0693t)^{0.652}}$	$Q = \frac{22.99}{(1 + 0.0119t)^{0.682}}$
Greeley Crescent	$Q = 1406.48t^{-0.863}$	$Q = \frac{74.65}{(1 + 0.011t)^{2.083}}$	$Q = \frac{12.93}{(1 + 0.0039t)^{0.625}}$
Wells Ranch	$Q = \frac{1516}{(1 + 0.0614t)^{2.092}}$	$Q = \frac{176.33}{(1 + 0.0374t)^{1.006}}$	$Q = \frac{29.39}{(1 + 0.0034t)^{1.112}}$
East Pony	$Q = \frac{1590}{(1 + 0.2492t)^{1.055}}$	$Q = \frac{165.92}{(1 + 0.057t)^{0.7424}}$	$Q = \frac{33.62}{(1 + 0.00837t)^{0.833}}$

Fresh Water Quality	
Constituent	Concentration (mg/L)
Iron	0.1
Calcium	14.4
Sodium	3.56
Chloride	19.2
TDS	430

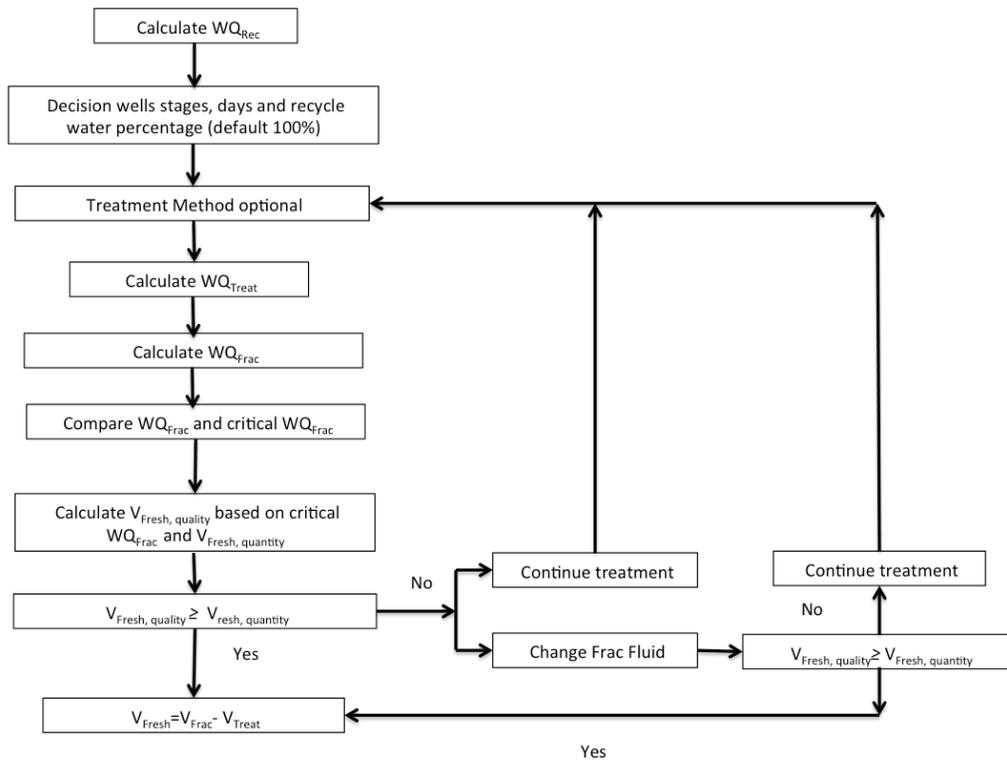


Figure 5-3: Fresh Water Calculation Process in the Produced Water Recycling System

5.3 Results

The produced water recycling program encompasses the entire recycling process: frac flowback and produced water volumes, quality and treatment; determining critical frac fluid water quality requirements, and fresh water quality. This information can lead to an estimation of fresh water volume for scenarios where there are either quality or quantity limitations. In this program, the volume of frac fluids and recycled produced water are key in determining frac fluid quality; after assessment of critical frac fluids quality, the volume of fresh water required is calculated. Figure 5-4 shows the initial produced water recycling program user interface, where inputs and default data are shown on the left side of the screen, while outputs such as well fracturing fluid volumes, fracturing fluid quality, fresh water volume, and the ratio of fresh water and recycled water volumes are available on the right side of the screen. Other data available include well locations, quality of flowback fluids and produced water, treatment methods and parameter removal percentage, critical fracturing fluid quality, and fresh water quality; all data can be edited or imported by the program user. The graph provided in this interface presents temporal trends of initial water quality, fracturing fluid quality results, and fresh water volume associated with three treatment methods.

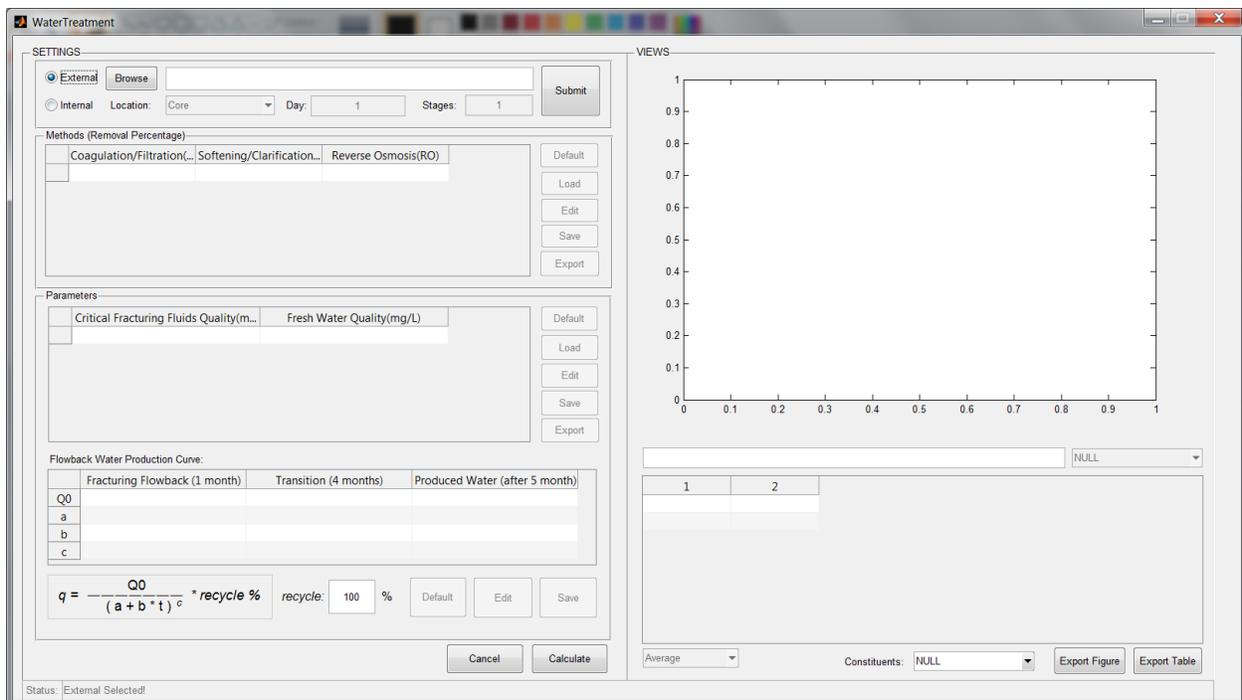


Figure 5-4: Initial User Interface of the Produced Water Recycling Program

Figures 5-5 and 5-6 provide examples of program defaults and graphic results of total dissolved solids in the Core Integrated Development Plan. Default values of the complete recycling process, and concentrations of key parameters for 20 well stages between Day 1 and Day 1000 are presented in Figure 5-5. Quantity of frac flowback and produced water are provided for three temporal periods: the flowback period (Month 1), transition (Month 2-5), and produced water (Month 6+). These data show that quantities of frac flowback and produced water decrease rapidly during the flowback period, then decrease more slowly during the transition period, and finally remain nearly constant during the produced water period. The results of fracturing fluid quality after reverse osmosis treatment are shown in Figure 5-6, along with fresh water volumes. In this figure, the blue line indicates the concentration of the key parameter while the red line indicates fracturing fluid quality or fresh water volume. Other

treatment methods, and results in other regions, reflected the same variation tendency in frac fluid quality, as reflected by other key parameters, and the same variation tendency in fresh water volume, as that illustrated in Figure 5-6 for total dissolved solids in the Core IDP.

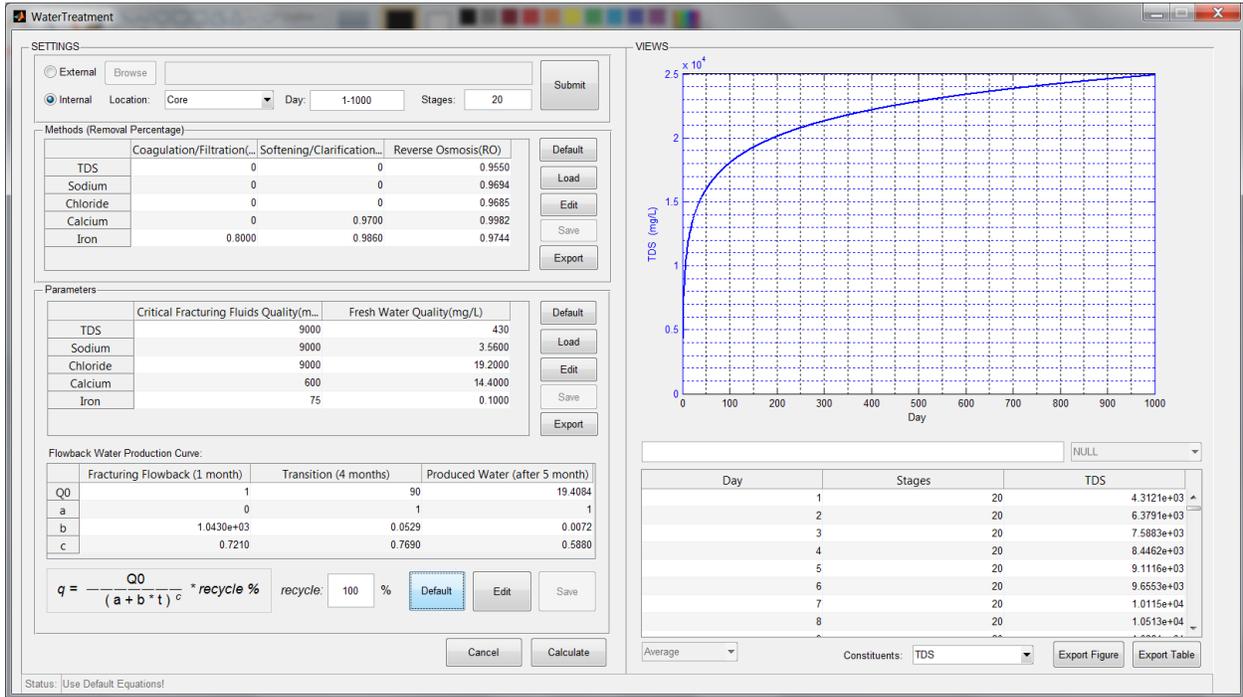


Figure 5-5: Produced Water Recycling Program, Default User Interface

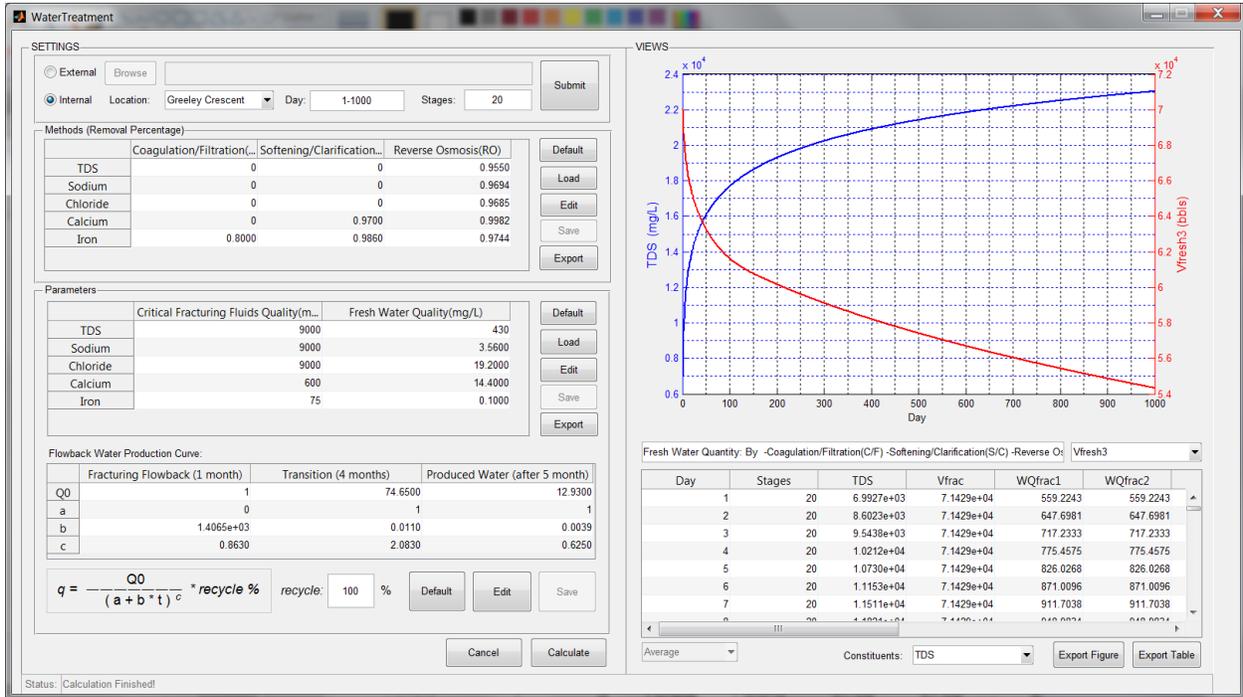
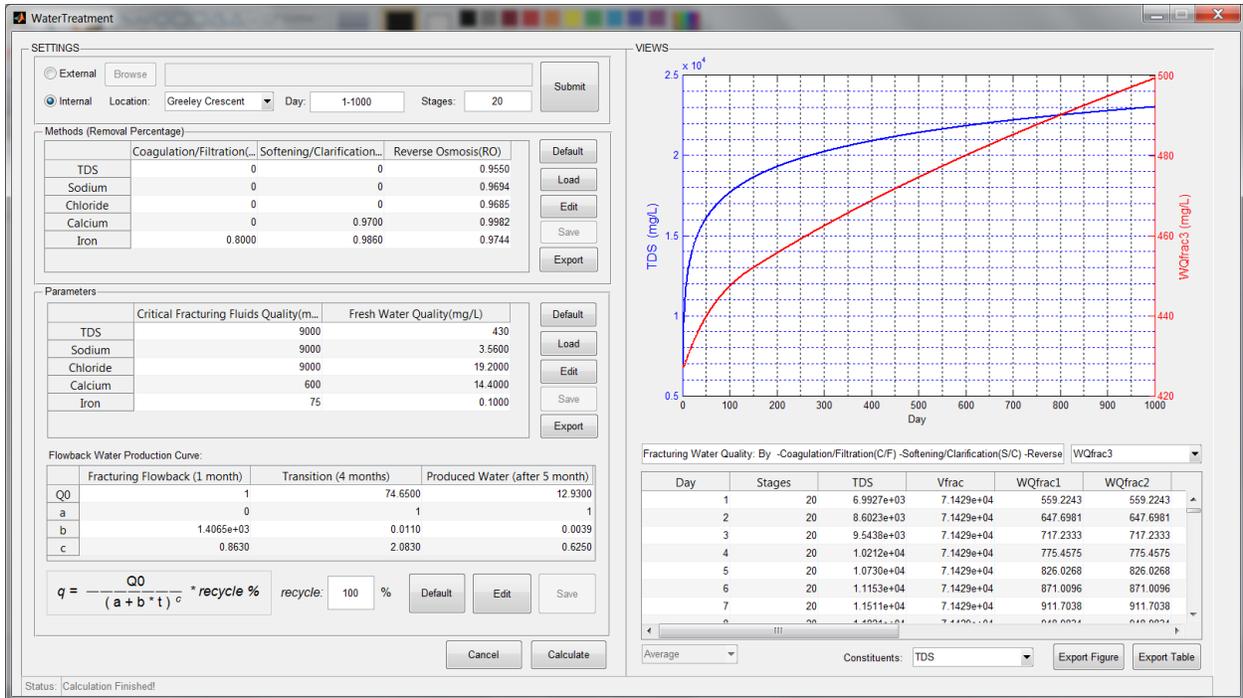


Figure 5-6: Produced Water Recycling Program, Results User Interface

Fresh water volume relates to frac fluids volume (wells stages) and recycling water quality. As frac fluid volume increases, the volume of fresh water increases and frac fluid quality tops out sooner. Fresh water volume and recycled water volume both decrease with time, resulting in a lower quality of recycled produced water.

5.4 Conclusion

One of the most efficient ways of reusing produced water, and reducing its environmental impact, is to recycle as much as possible as frac fluids. Treatment and blending with fresh water are necessary to assure the reused produced water meets quality requirements for fracturing fluids. The current study provided a framework for optimizing frac flowback and produced water reuse by treating and blending frac fluids. The study established a produced water recycling program to calculate the volume of fresh water needed for blending; it also identified which produced water treatment method--coagulation/filtration, softening/clarification, or reverse osmosis—was most appropriate to effectively reduce total dissolved solids, sodium, chloride, calcium, and iron.

This produced water recycling program enables batch computing and visualization of fresh water quantity data that supports efficient calculation. The volume of fresh water needed for blending is determined by the quality of the fresh water, the targeted quality of fracturing fluids and recycled water, and the quantity of fracturing fluids and recycled water. When the water quality and quantity of fracturing fluid is verified, the program enables efficient and accurate identification of the necessary produced water treatment and fresh water volume needed for blending. The produced water recycling program not only reduces the cost and time needed for

effective produced water management and reuse, it also make water quality and quantity predictions more practical for improved petroleum industry operations.

This produced water recycling program detects trending changes in fracturing fluid quality and fresh water volume; it also identifies the ratio between fresh water volume and recycled produced water volume--an important reference factor in produced water management and reuse. The quality of fracturing fluids, flowback fluids and produced water, and fresh water all affect the volume of fresh water and the ratio between fresh water volume and recycled produced water--all of which can be managed, considering costs.

Economic considerations apply to both produced water treatment and the chemical additives of fracturing fluids. Higher concentrations of fracturing fluid constituents require more chemical addition to those fracturing fluids to improve gas and oil exploitation. The high cost of those chemical additives sometimes makes relatively less expensive enhanced treatment or the use of more fresh water better options for produced water reuse. A produced water recycling program can predict the relationship between treatment methods and fracturing fluid quality to identify the most economical approach. Another advantage of the program is that data regarding produced water components from wells in other regions and treatment options can be added by the user.

6. CONCLUSION

This study reveals that quality analysis of produced water from the horizontal wells in the Wattenberg Field and the produced water recycling system program can enhance the effectiveness of produced water management and reuse in the petroleum industry. Modeling produced water quality can help plan water production of oil and gas wells in certain regions, reduce the cost of testing, and increase the efficiency of produced water analyses. The Matlab produced water recycling system program determines the volume of fresh water needed for blending with recycled produced water, to optimize produced water treatment and reuse.

Total dissolved solids, sodium, chloride, calcium, and iron were identified as key parameters of fracturing flowback and produced water quality and analyzed in seven Integrated Development Plans in the Wattenberg Field. Because geological formation is a factor effecting produced water quality, temporal logarithmic functions specific for the geological formation of each Integrated Development Plan were used to determine the concentration of total dissolved solids, sodium, chloride, and calcium. Because iron concentration is highly correlated with geological formation, iron was analyzed spatially as an average and maximum value for each Integrated Development Plan.

The produced water recycling system program involves produced water treatment methods, water quality data, and calculation of fresh water volume. The database details the quality of fracturing flowback and produced water, fresh water, and fracturing fluids; external data can be uploaded by the users. Three produced water treatment methods--coagulation/filtration, softening/clarification, and reverse osmosis—are applied sequentially: coagulation/filtration

reduces iron concentration, softening/clarification reduces calcium concentration, and reverse osmosis reduces concentration of all the key parameters examined. This three-step treatment allowed most of the recycled produced water to meet the quality requirements of fracturing fluid and be used to blend with certain volume of fresh water. The Matlab program simulates the produced water recycling process and helps determine the most efficient means of determining appropriate produced water treatment and the specific volume of fresh water needed to blend with recycled water.

In future work, additional fracturing flowback and produced water quality parameters will be modeled temporal and spatially, and other treatment methods will be considered for the produced water recycling process. Other factors influencing the produced water process will also be incorporated into the program.

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8. APPENDIX

A. Modeling results for water quality

Number of Wells Grouped By IDP

IDP	Flowback	Transition	Produced	Total
Core	3	9	16	23
Cummins EXTE	0	20	18	26
East Pony	3	12	4	14
West Pony	6	6	3	11
Greeley Crescent	2	4	4	9
Mustang	0	3	7	10
Wells Ranch	9	57	76	132
Overall	23	111	128	225

Number of Samples Grouped By IDP

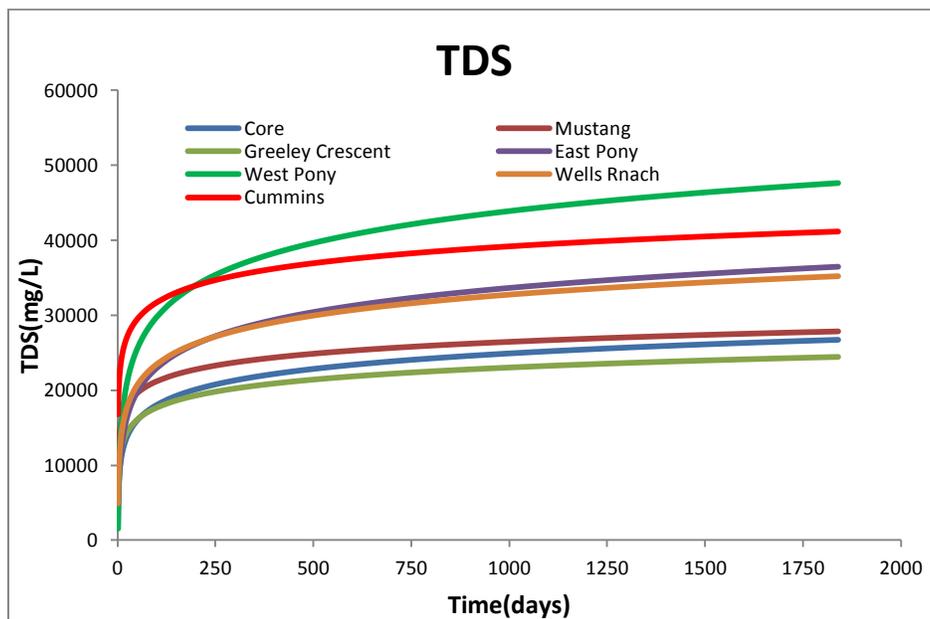
IDP	Flowback	Transition	Produced	Total
Core	15	15	53	83
Cummins EXTE	0	29	48	77
East Pony	11	20	19	50
West Pony	19	10	8	37
Greeley Crescent	14	9	10	33
Mustang	0	3	15	18
Wells Ranch	114	101	130	345
Overall	173	187	283	643

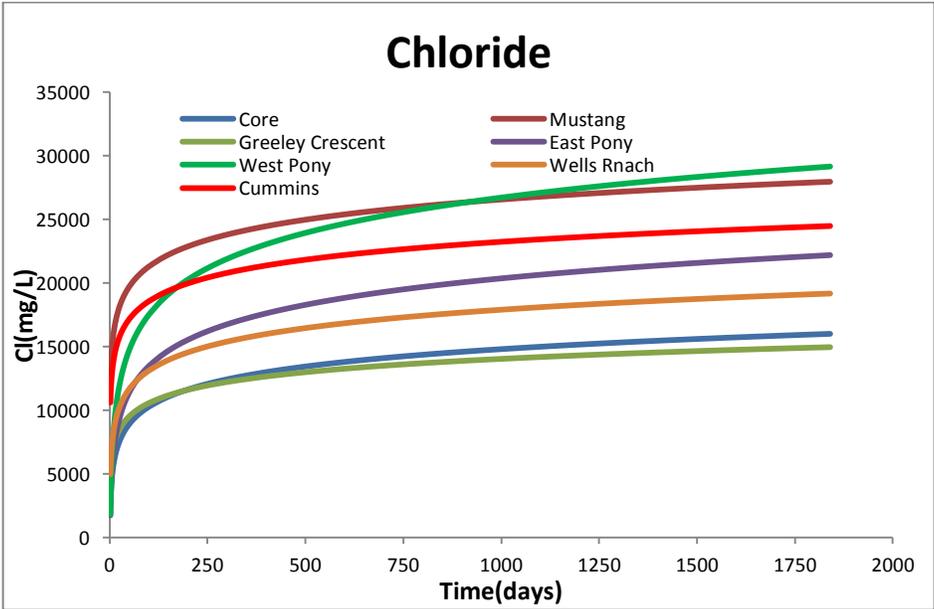
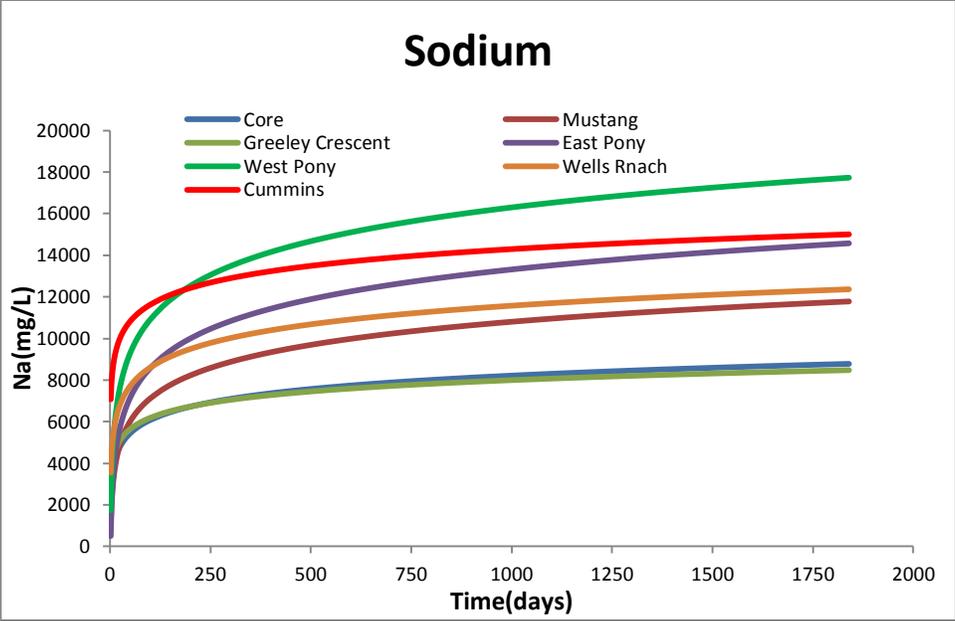
Logarithmic Functions of Total Dissolved Solids, Sodium, Chloride and Calcium in Seven Integrated Development Plansy = $a \ln(t) + b$

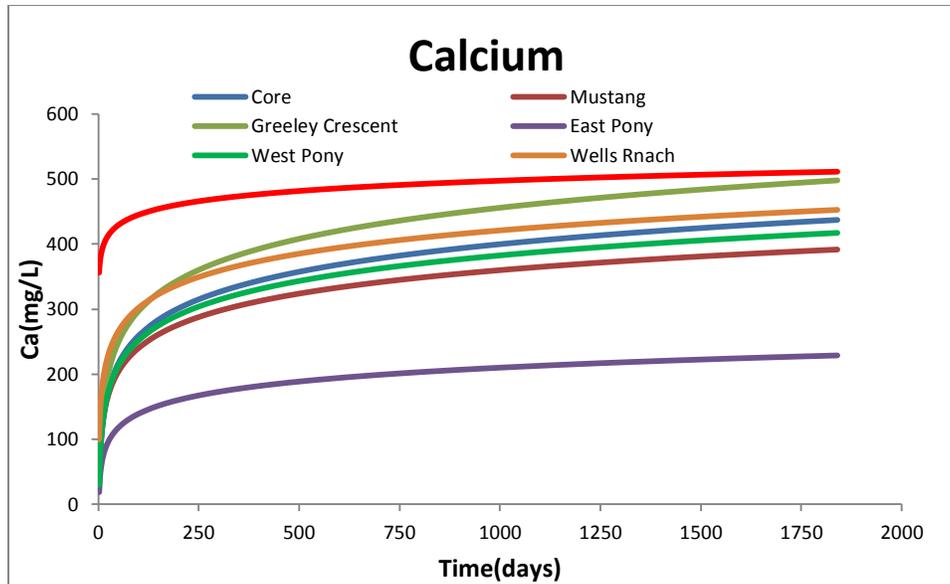
IDP	TDS			Sodium		
	a	b	R ²	a	b	R ²
Core	2982.1	4312.1	0.87168	927.91	1804.4	0.75066
Mustang	2282.5	10691	0.86322	1601.8	-262.57	0.95043
Greeley Crescent	2322.1	6992.7	0.72955	787.65	2556.2	0.72078
East Pony	4636.6	1614.5	0.78009	2062.2	-928.59	0.78895
West Pony	6129.5	1551.8	0.94993	2344.5	105.16	0.94134
Wells Ranch	4028.5	4924.5	0.88518	1292.2	2649	0.86287
Cummins	3244	16778	0.42432	1161.8	6270.1	0.3806

IDP	Chloride			Calcium		
	a	b	R ²	a	b	R ²
Core	1971.8	1177.2	0.76447	61.173	-22.745	0.85699
Mustang	2293	10729	0.86188	52.016	0.5952	0.91766
Greeley Crescent	1512.6	3583.6	0.77495	68.964	-20.551	0.83021
East Pony	3000	-361.24	0.8321	30.791	-2.6108	0.8723
West Pony	4007.2	-961.57	0.94346	56.77	-9.5692	0.81823
Wells Ranch	2084.4	3499.4	0.7589	51.705	63.865	0.82411
Cummins	2033.8	9192	0.49158	22.732	340.34	0.08822

Graphs of Total Dissolved Solids, Sodium, Chloride and Calcium in Seven Integrated Development Plans







Concentration of Total Dissolved Solids, Sodium, Chloride and Calcium in Special Days in Seven Integrated Development Plans

TDS(mg/L)						
IDP	Day 5	Day 30	Day 90	Day 180	1 year	5 year
Core	9111.60	14454.81	17730.98	19798.02	21906.18	26705.69
Mustang	14364.54	18454.23	20961.82	22543.92	24157.52	27831.06
Greeley Crescent	10729.98	14890.62	17441.71	19051.27	20692.85	24430.13
East Pony	9076.82	17384.49	22478.32	25692.16	28969.96	36432.28
West Pony	11416.85	22399.44	29133.38	33382.03	37715.22	47580.27
Wells Ranch	11408.12	18626.22	23051.98	25844.33	28692.24	35175.86
Cummins	21999.02	27811.48	31375.38	33623.95	35917.27	41138.28
Sodium(mg/L)						
IDP	Day 5	Day 30	Day 90	Day 180	1 year	5 year
Core	3297.81	4960.41	5979.82	6623.00	7278.97	8772.39
Mustang	2315.43	5185.47	6945.23	8055.51	9187.89	11765.88
Greeley Crescent	3823.87	5235.15	6100.48	6646.43	7203.25	8470.93
East Pony	2390.39	6085.36	8350.92	9780.33	11238.18	14557.16
West Pony	3878.49	8079.27	10654.96	12280.05	13937.47	17710.80
Wells Ranch	4728.72	7044.03	8463.65	9359.34	10272.85	12352.56
Cummins	8139.94	10221.61	11497.98	12303.28	13124.60	14994.45
Chloride(mg/L)						
IDP	Day 5	Day 30	Day 90	Day 180	1 year	5 year
Core	4350.69	7883.68	10049.92	11416.67	12810.62	15984.11
Mustang	14419.44	18527.95	21047.06	22636.45	24257.46	27947.91
Greeley Crescent	6018.04	8728.25	10390.01	11438.47	12507.78	14942.22

East Pony	4467.07	9842.35	13138.19	15217.63	17338.45	22166.77
West Pony	5487.77	12667.71	17070.07	19847.65	22680.50	29129.84
Wells Ranch	6854.11	10588.86	12878.80	14323.60	15797.15	19151.86
Cummins	12465.27	16109.36	18343.71	19753.44	21191.21	24464.49
Calcium(mg/L)						
IDP	Day 5	Day 30	Day 90	Day 180	1 year	5 year
Core	75.71	185.32	252.52	294.92	338.17	436.62
Mustang	84.31	177.51	234.66	270.71	307.48	391.20
Greeley Crescent	90.44	214.01	289.77	337.58	386.33	497.32
East Pony	46.95	102.12	135.94	157.29	179.05	228.61
West Pony	81.80	183.52	245.88	285.23	325.37	416.74
Wells Ranch	147.08	239.72	296.53	332.37	368.92	452.14
Cummins	376.93	417.66	442.63	458.39	474.46	511.04

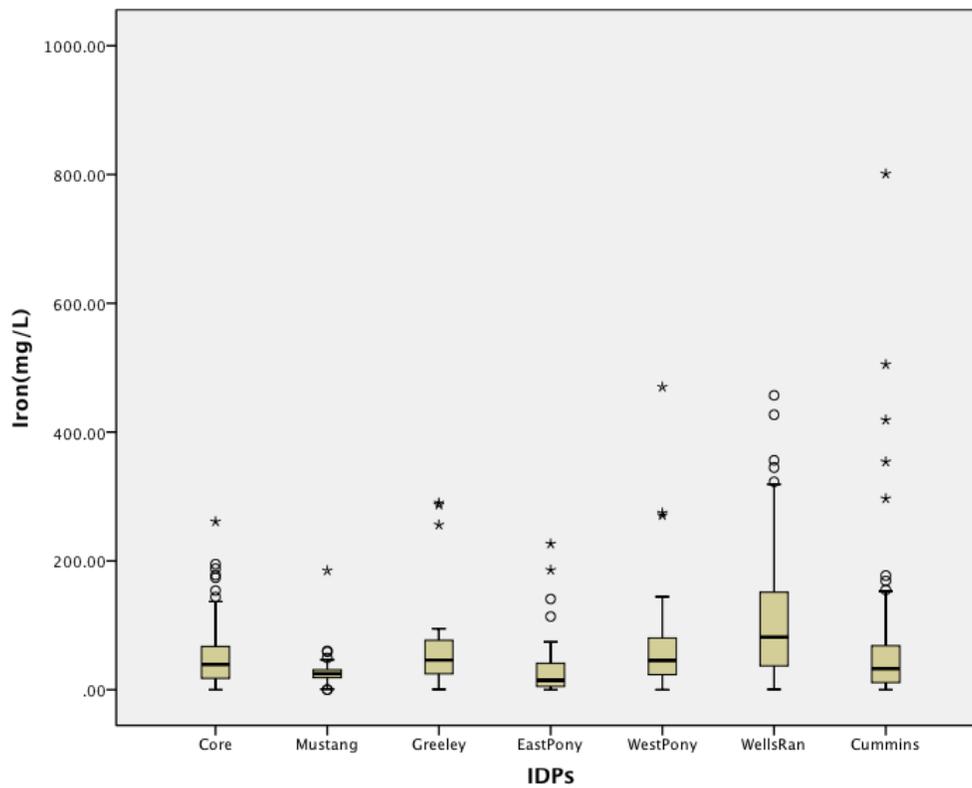
P Values compare of Iron in Different IDPs

Differences of Least Squares Means			
IDPs	IDPs(compare)	t Value	P Value
Core	Cummins	-1.34	0.1808
Core	East Pony	1.37	0.1728
Core	Greely Crescent	-0.73	0.4664
Core	Mustang	1.35	0.1773
Core	Wells Ranch	-4.96	<0.0001
Core	West Pony	-1.34	0.1815
Cummins	East Pony	2.51	0.0124
Cummins	Greely Crescent	0.28	0.7781
Cummins	Mustang	2.35	0.0189
Cummins	Wells Ranch	-3.18	0.0015
Cummins	West Pony	-0.30	0.7654
East Pony	Greely Crescent	-1.75	0.0811
East Pony	Mustang	0.15	0.8837
East Pony	Wells Ranch	-5.60	<0.0001
East Pony	West Pony	-2.32	0.0206
Greely Crescent	Mustang	1.73	0.0842
Greely Crescent	Wells Ranch	-2.49	0.0129
Greely Crescent	West Pony	-0.49	0.625
Mustang	Wells Ranch	-4.86	<0.0001
Mustang	West Pony	-2.25	0.0248
Wells Ranch	West Pony	1.90	0.058

Kolmogorov – Smirnov Test of Normal Distribution

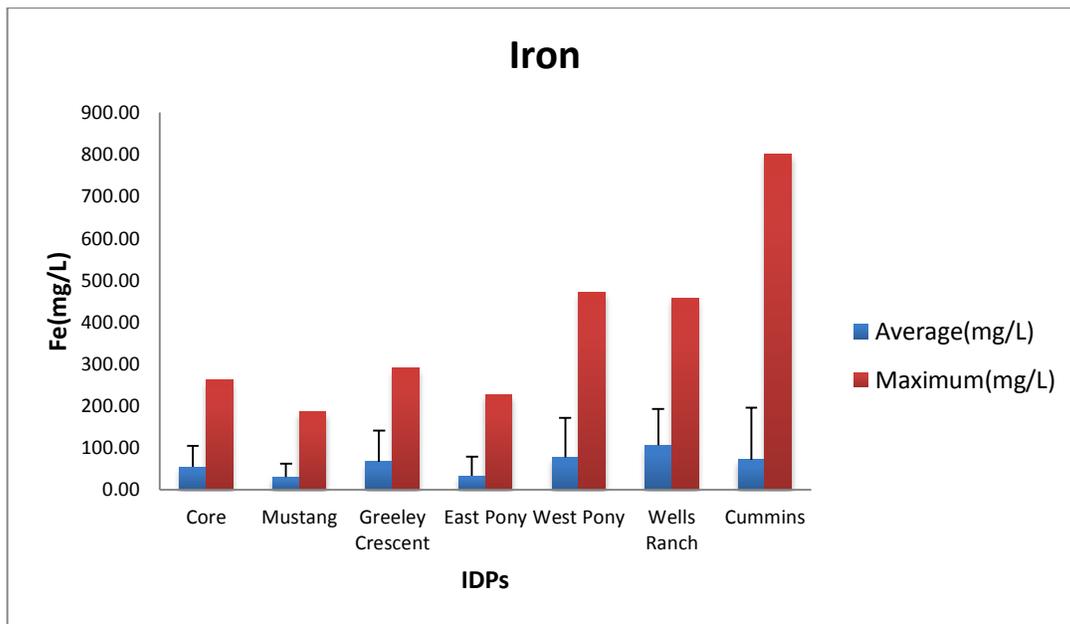
Kolmogorov - Smirnov			
IDPs	P Value	Normal Distribution	N
Core	<0.01	No	82
Mustang	<0.01	No	32
Greeley Crescent	<0.01	No	31
East Pony	<0.01	No	48
West Pony	<0.01	No	33
Wells Ranch	<0.01	No	279
Cummins	<0.01	No	76

Box and Whisker Plot of Iron Concentration in Each IDP



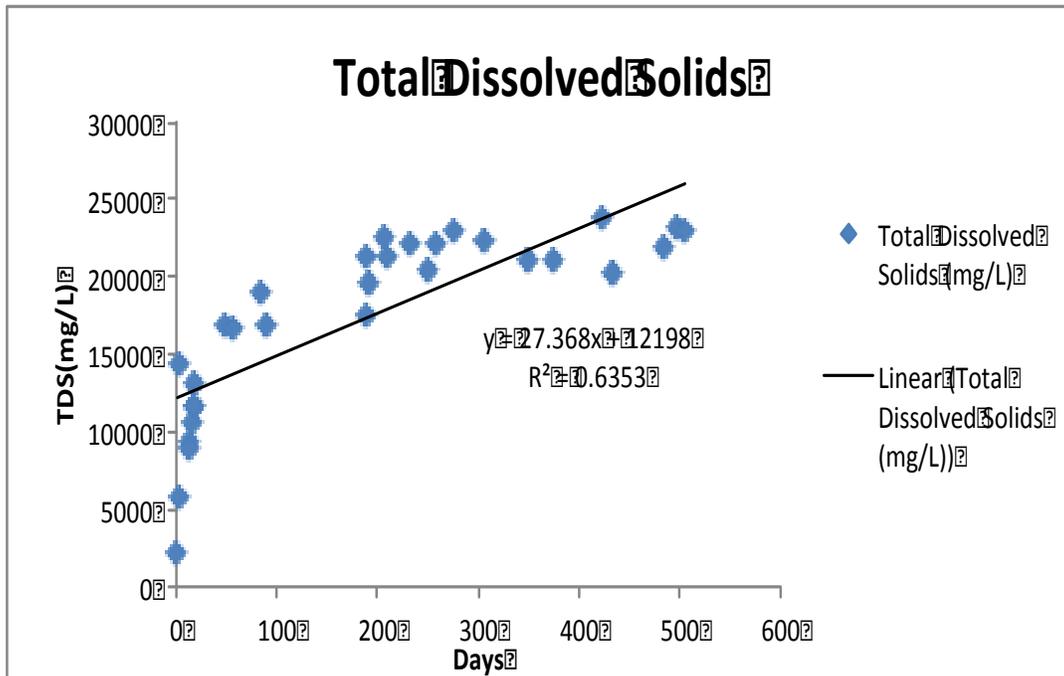
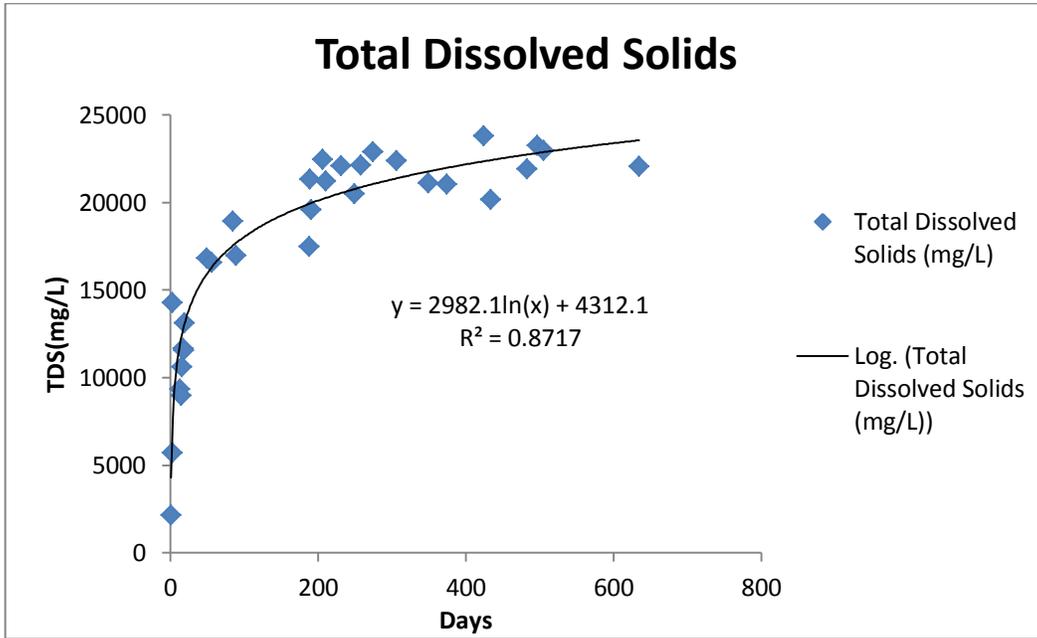
Maximum and Average Value of Iron Concentration Table and Graph in Seven Integrated Development Plans

Iron (mg/L)			
IDP	Average	MAX	σ
Core	53.46	261.00	51.31
Mustang	29.75	185.00	31.76
Greeley Crescent	66.40	290.00	74.44
East Pony	32.55	226.50	46.38
West Pony	76.68	470.10	94.33
Wells Ranch	106.11	457.00	86.23
Cummins	71.45	801.00	123.95

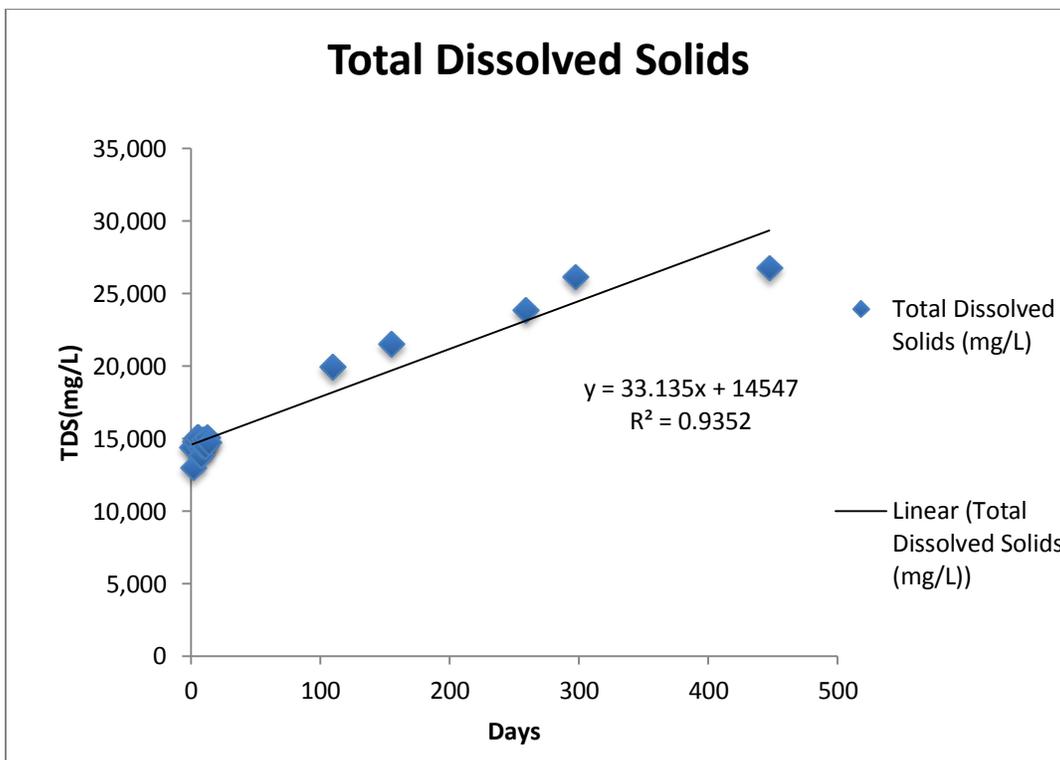
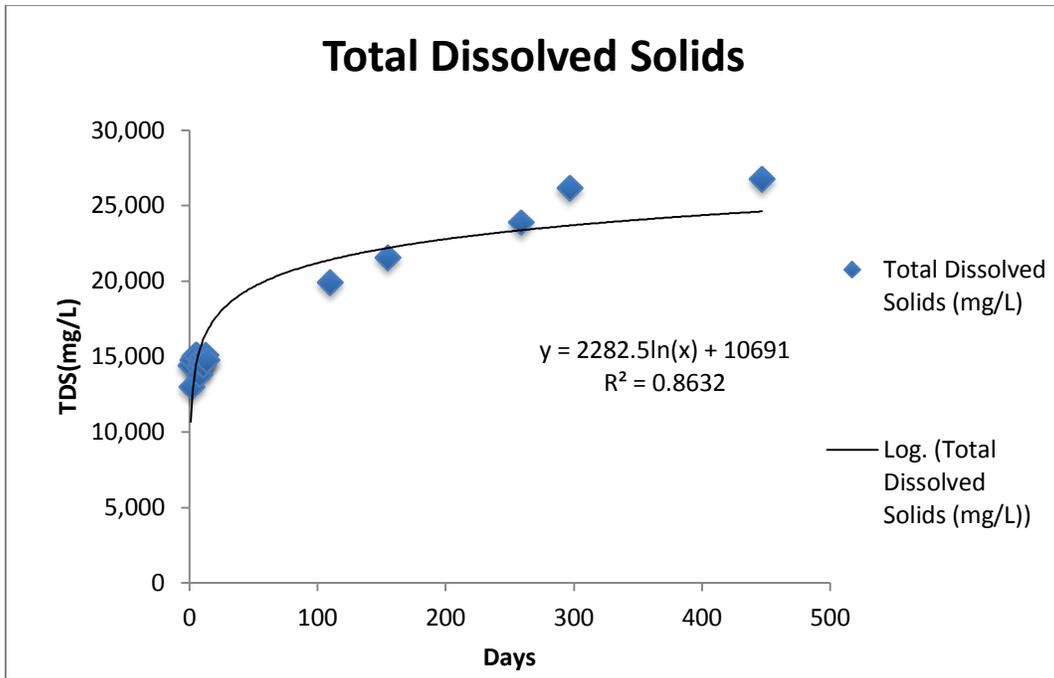


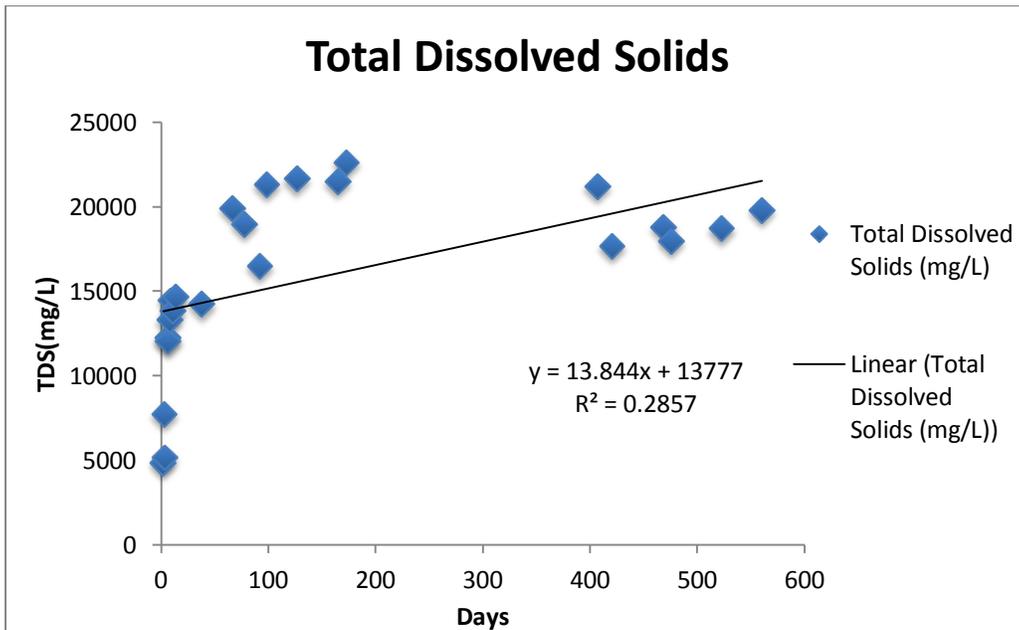
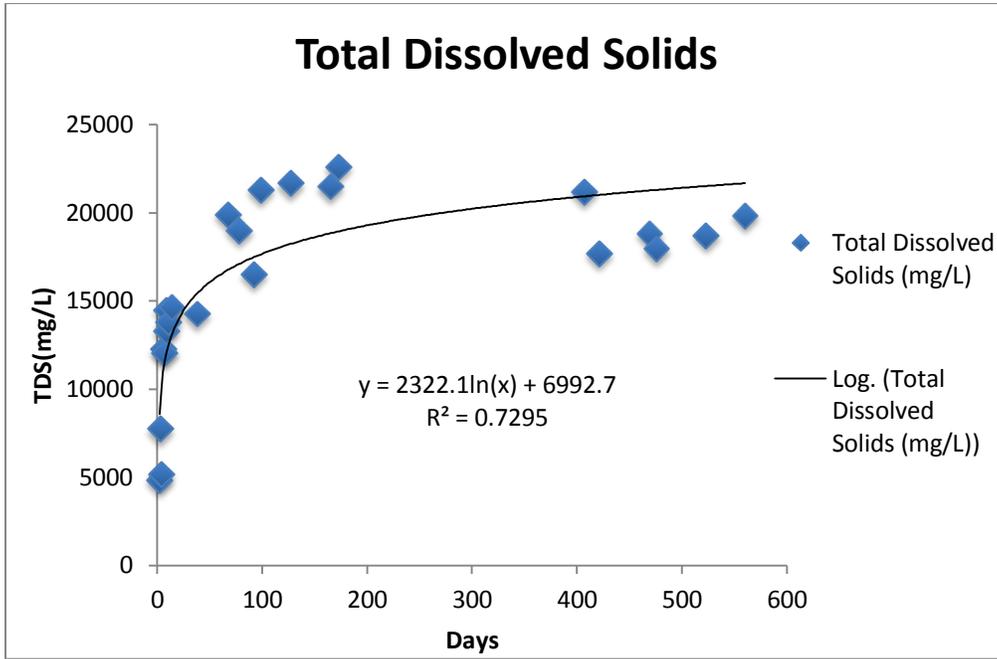
B. Comparison of Logarithmic, and Linear Functions for Water Quality
 Total Dissolved Solids Graphs in Seven Integrated Development Plans

Core

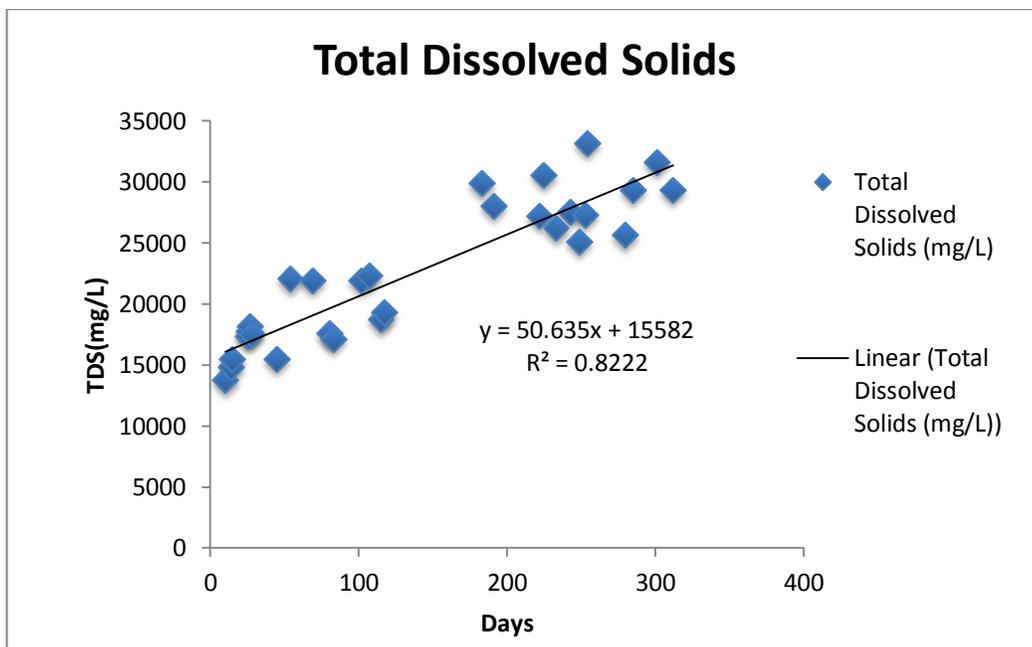
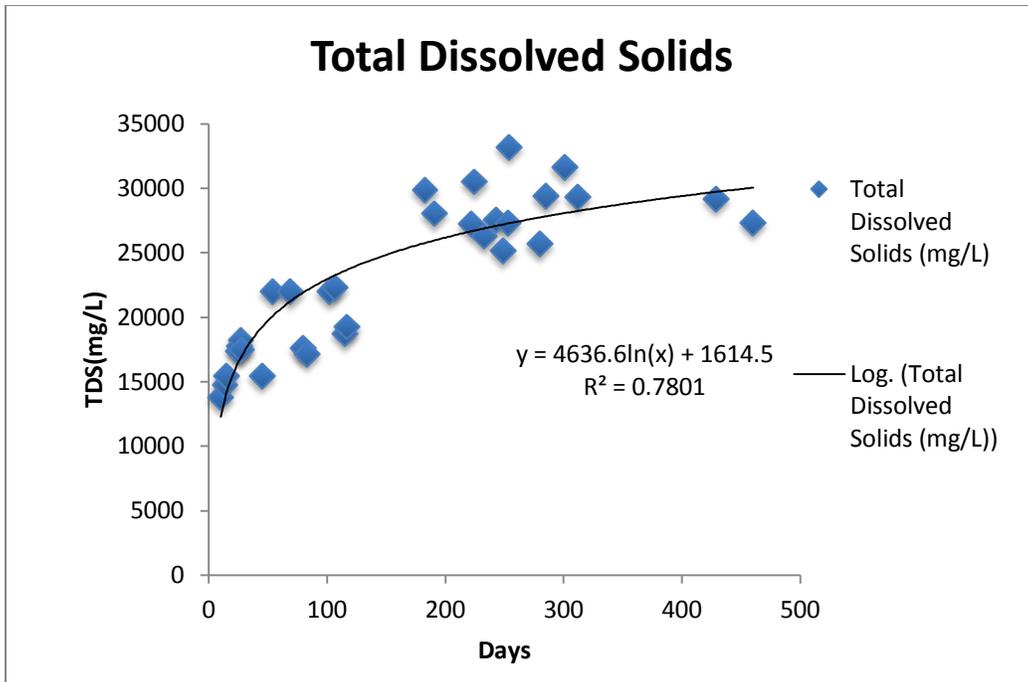


Mustang

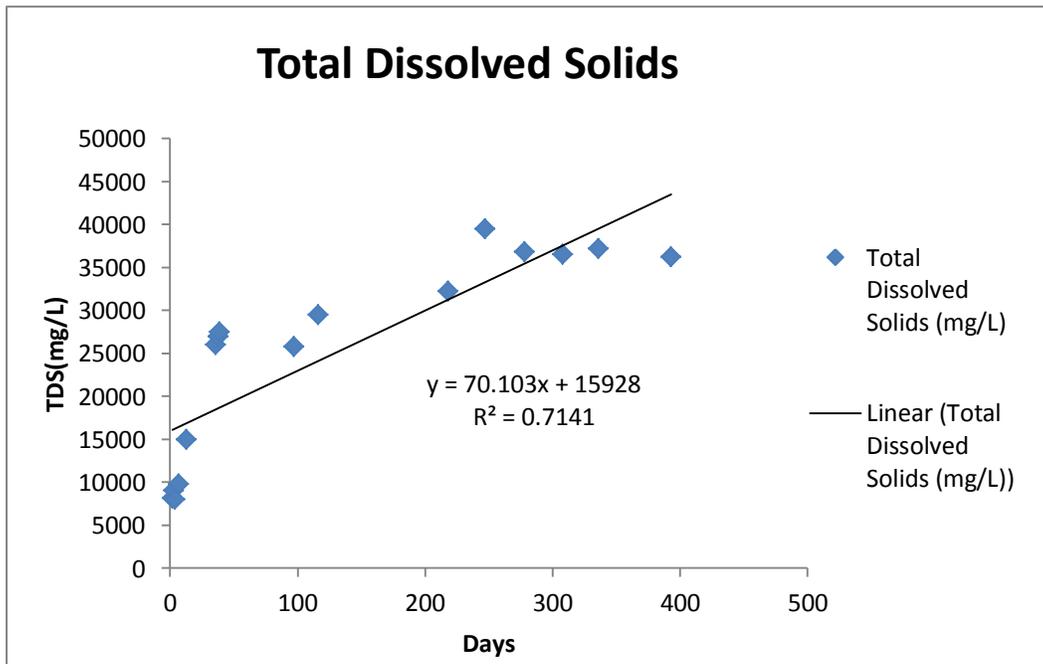
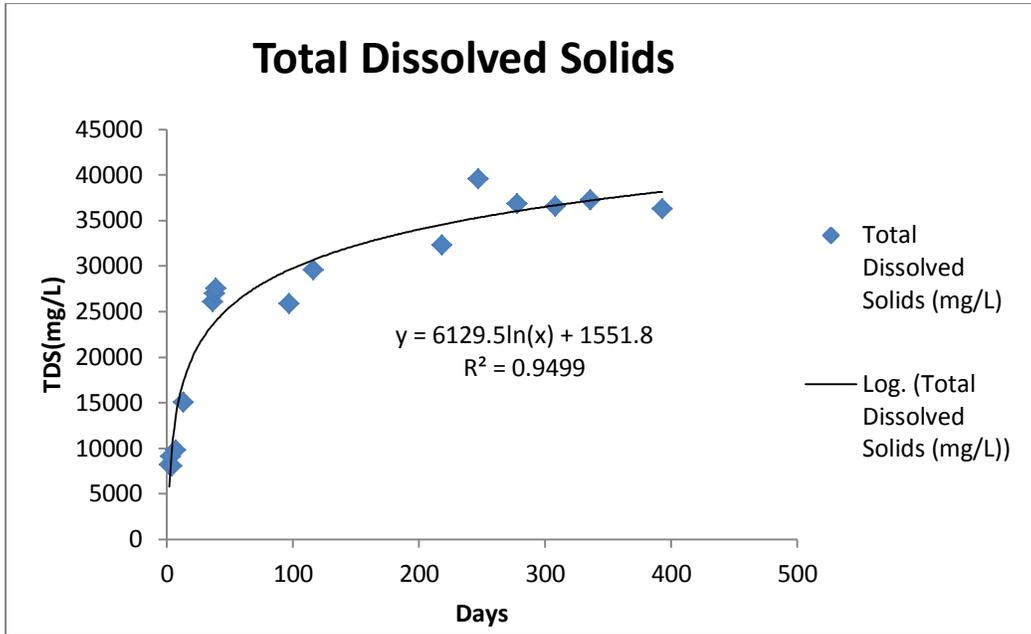




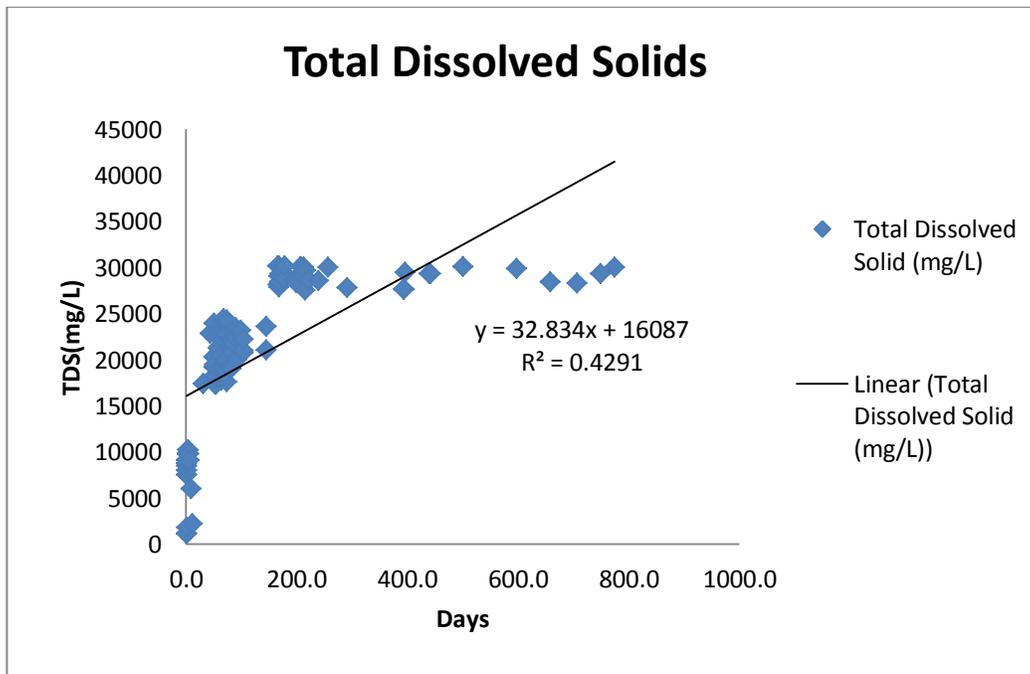
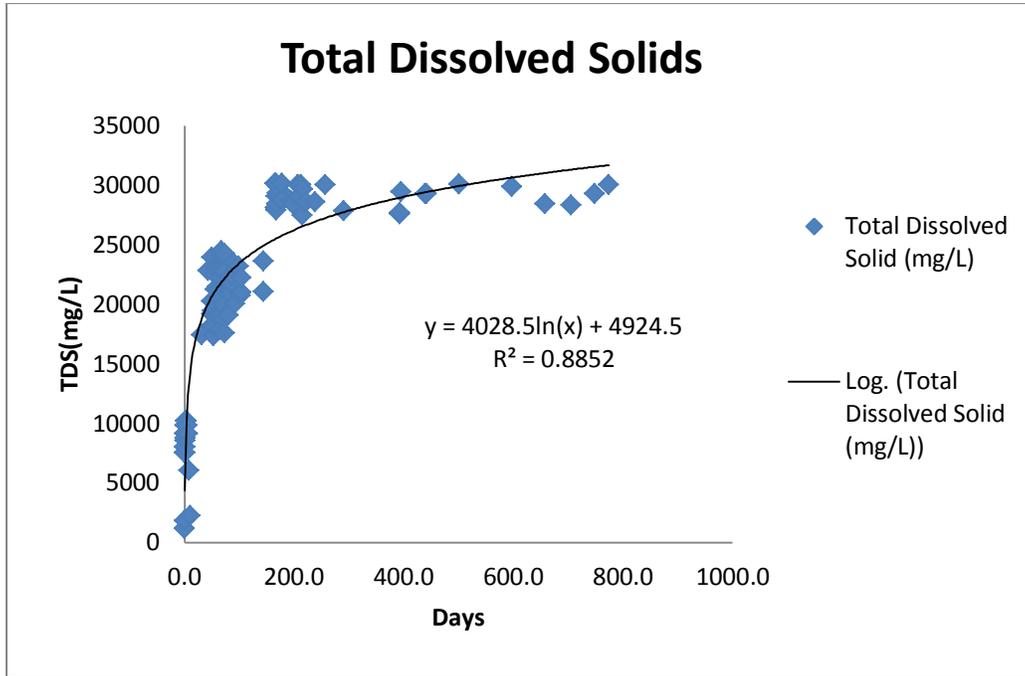
East Pony

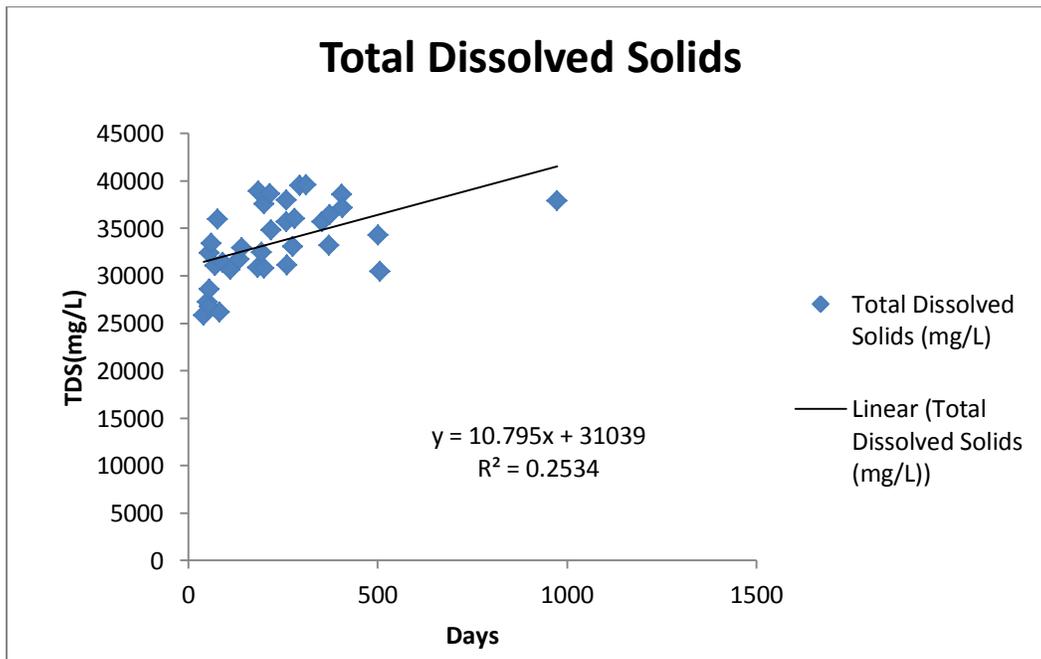
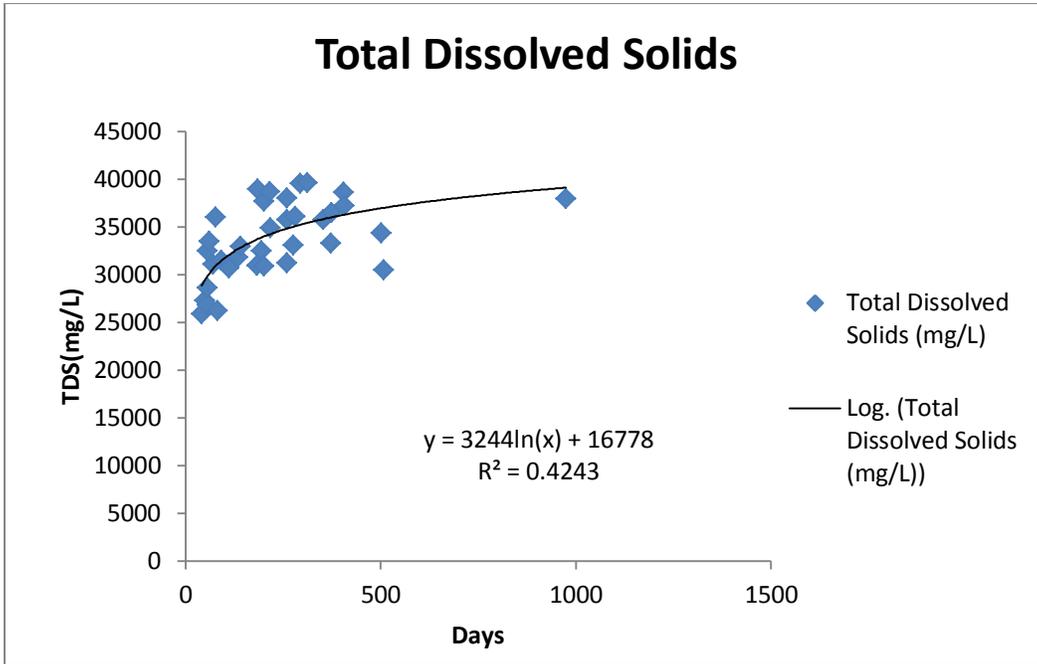


West Pony



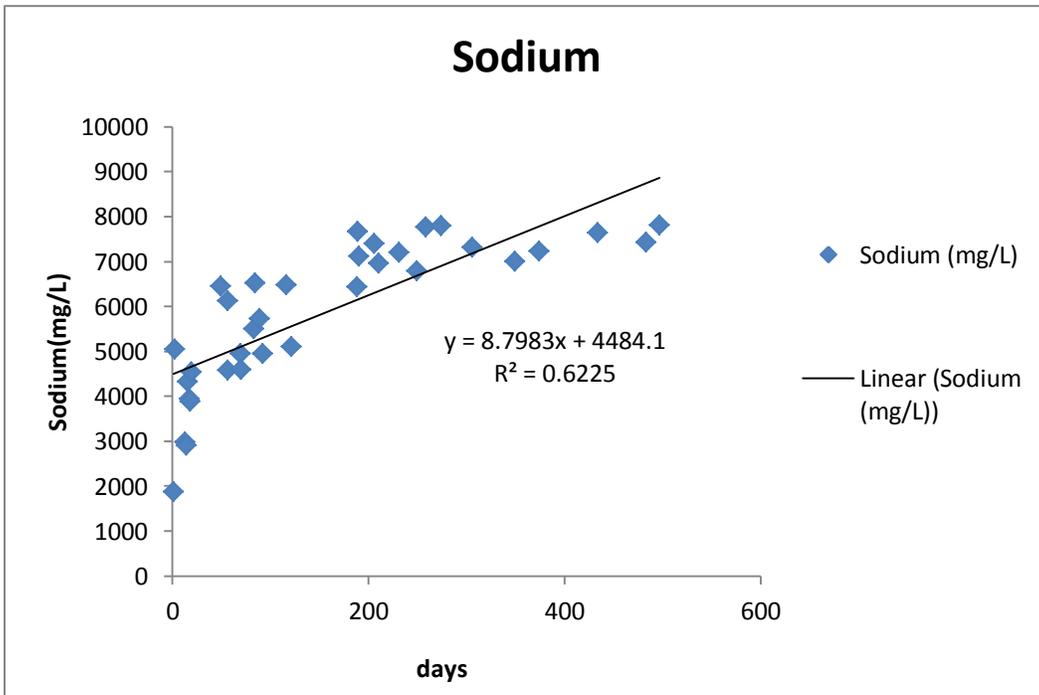
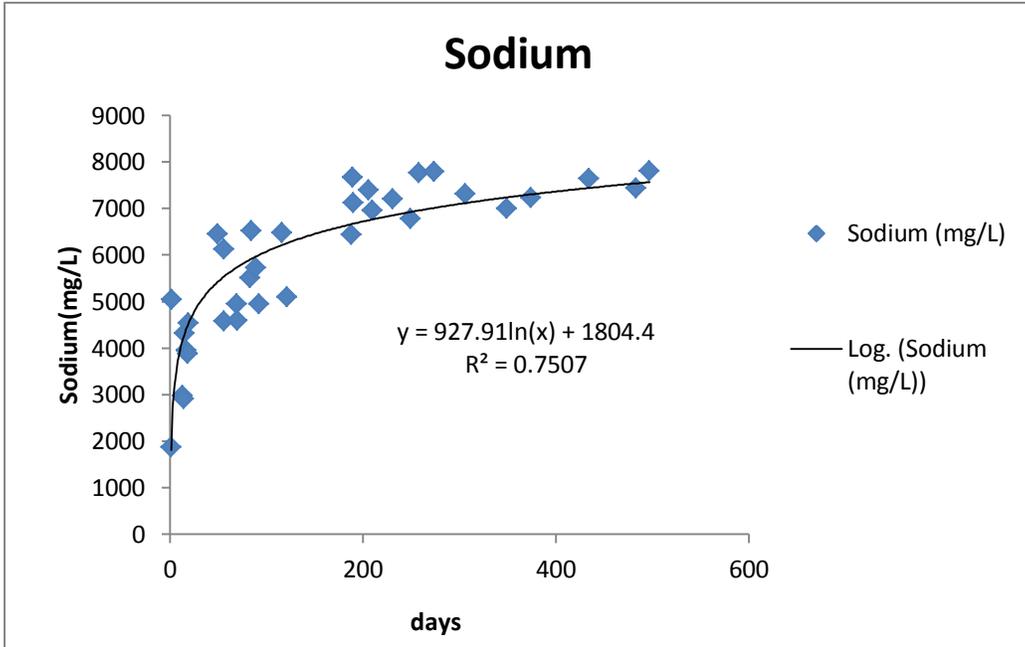
Wells Ranch



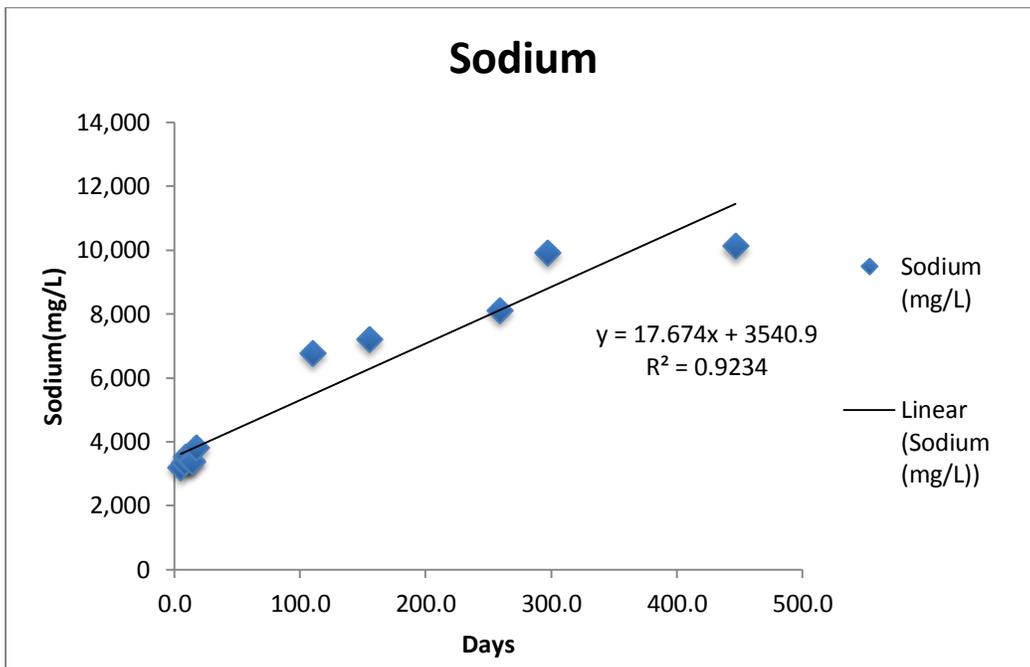
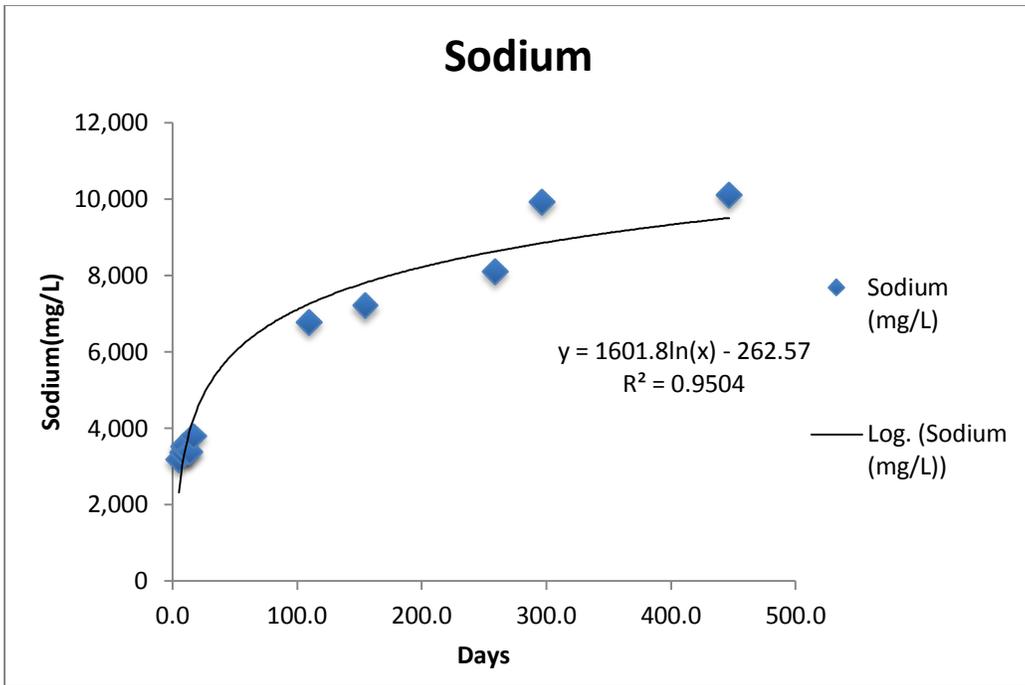


Sodium Graphs in Seven Integrated Development Plans

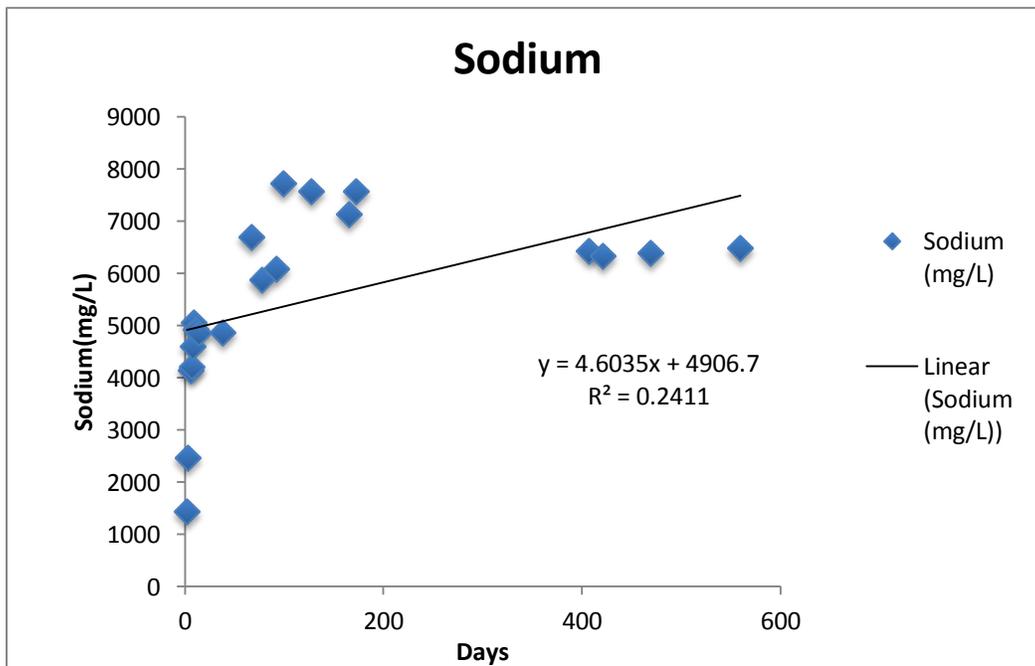
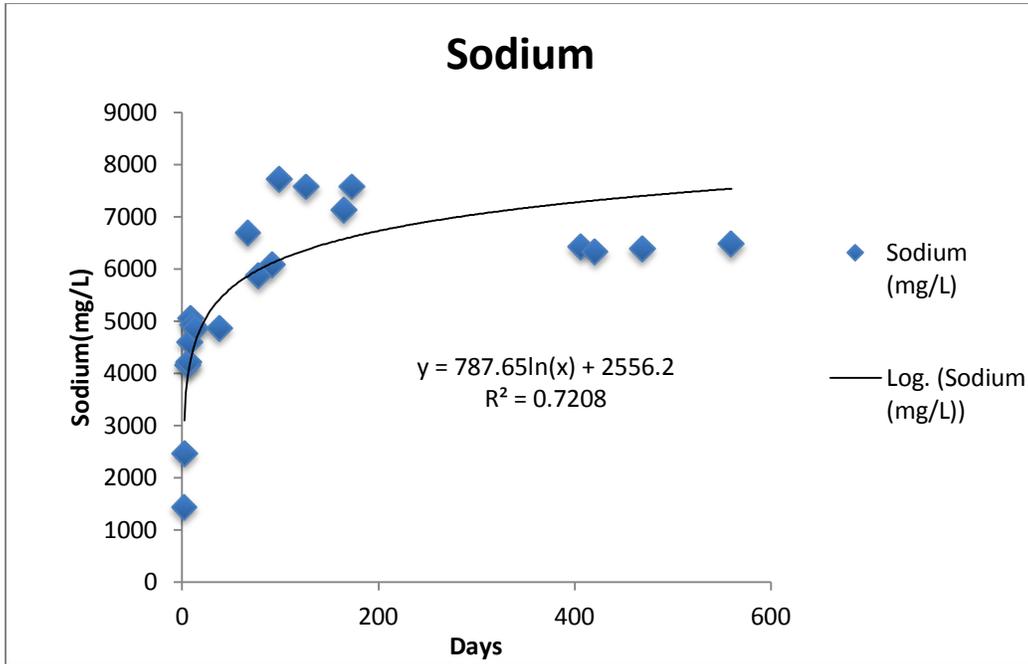
Core



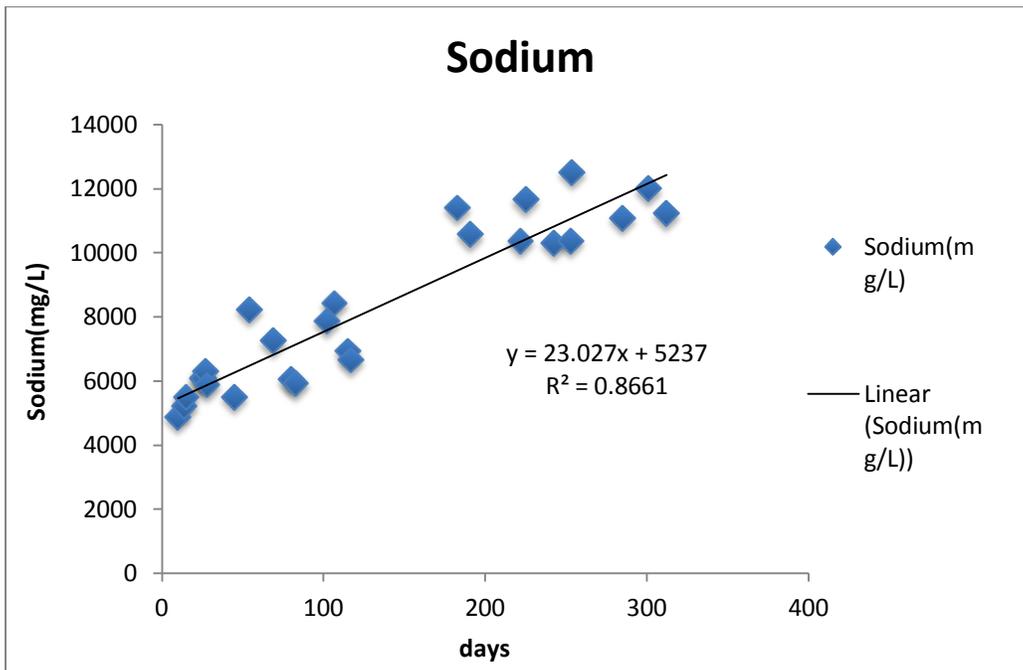
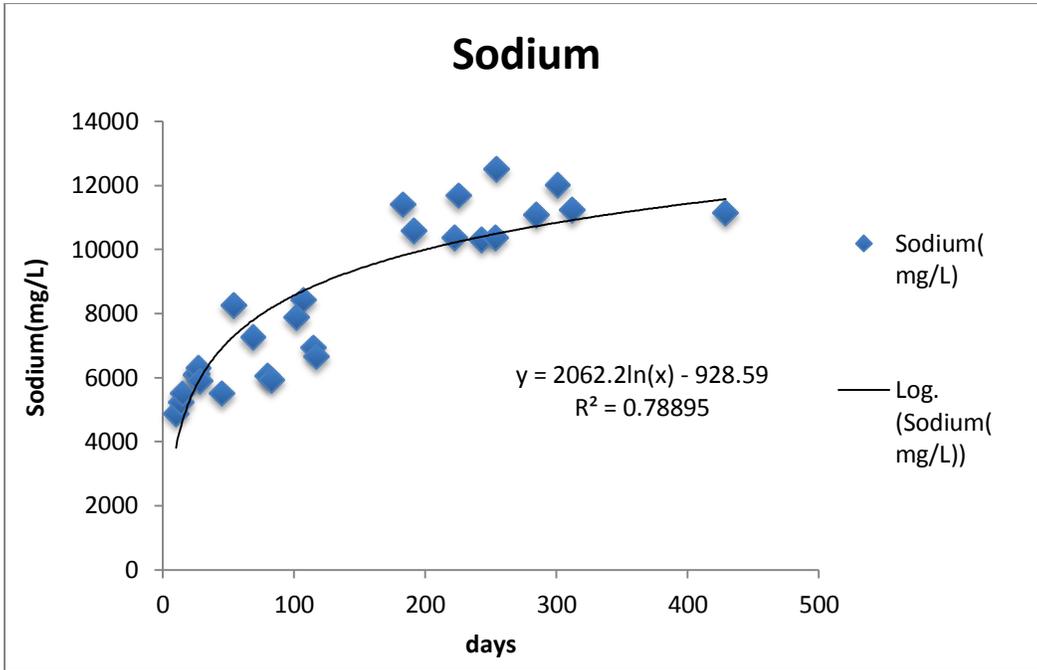
Mustang



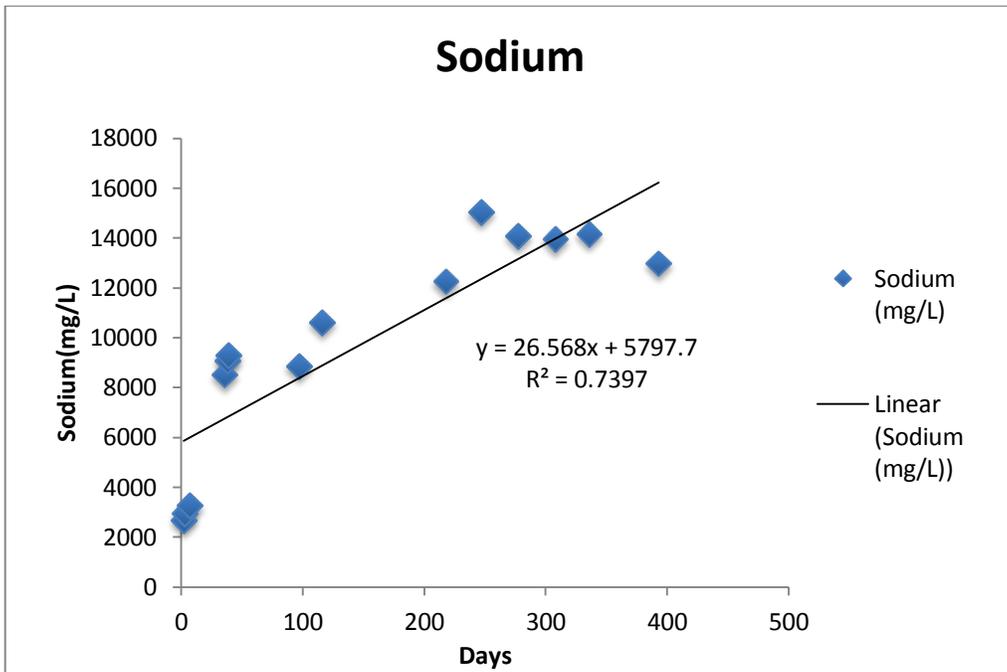
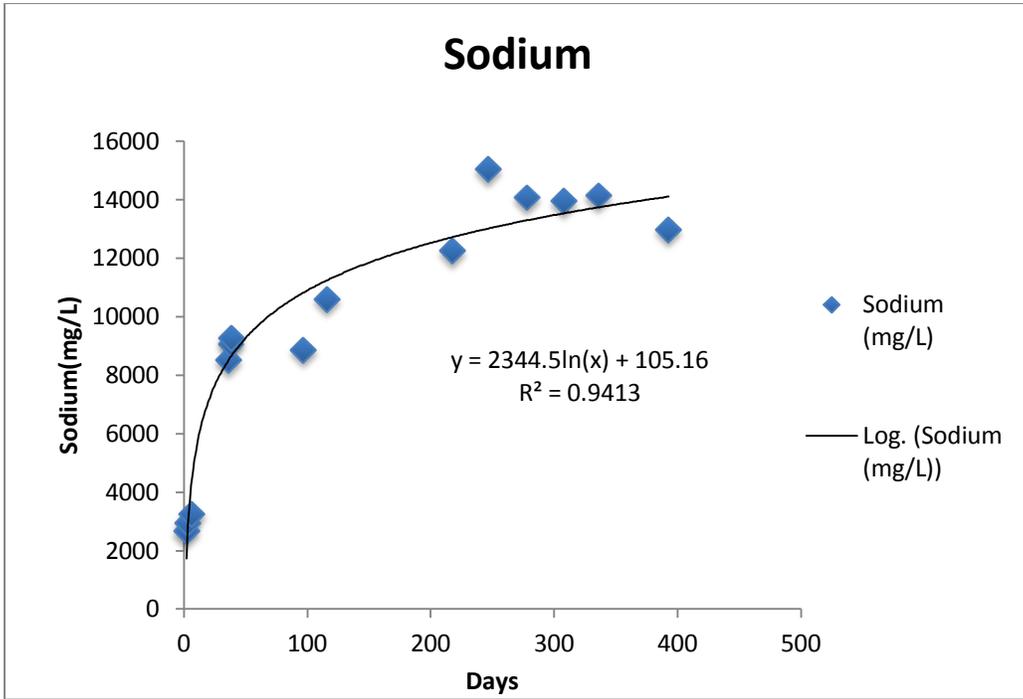
Greeley Crescent



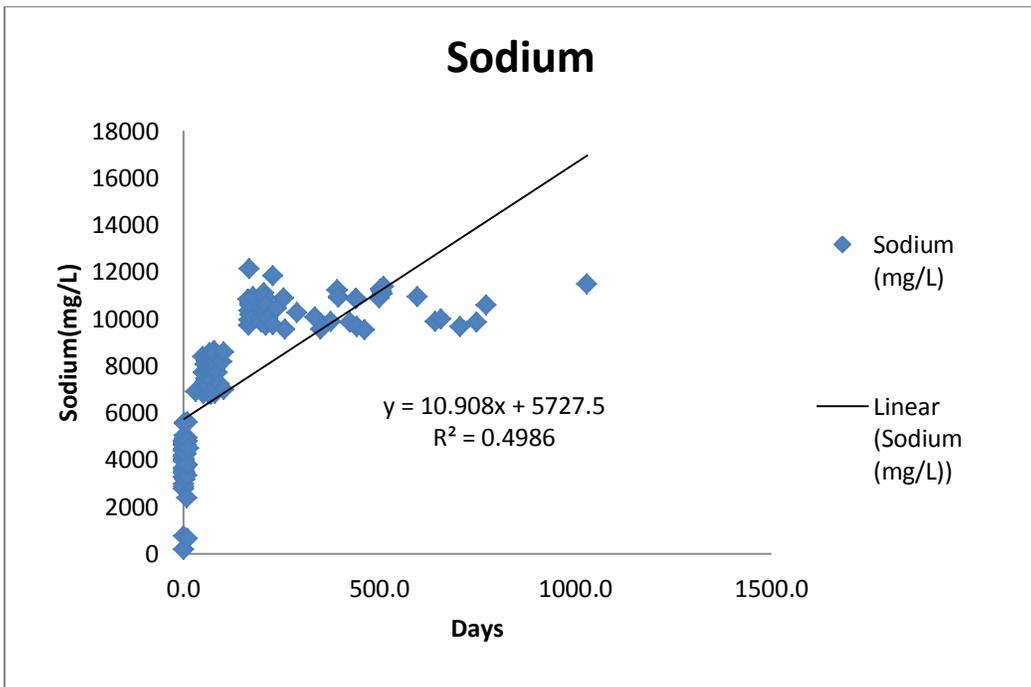
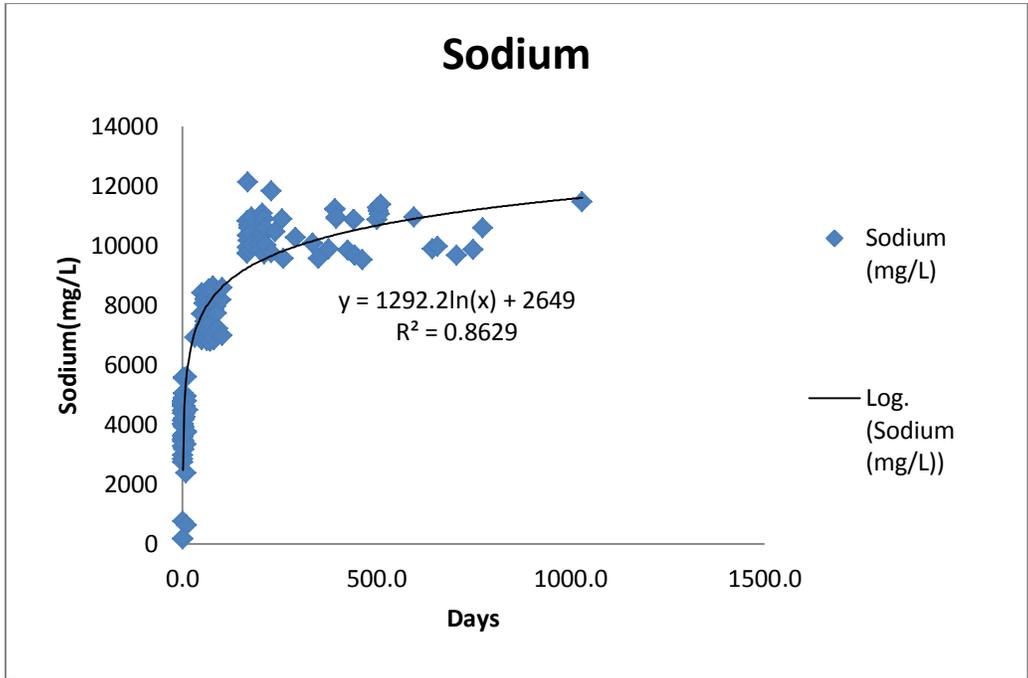
East Pony

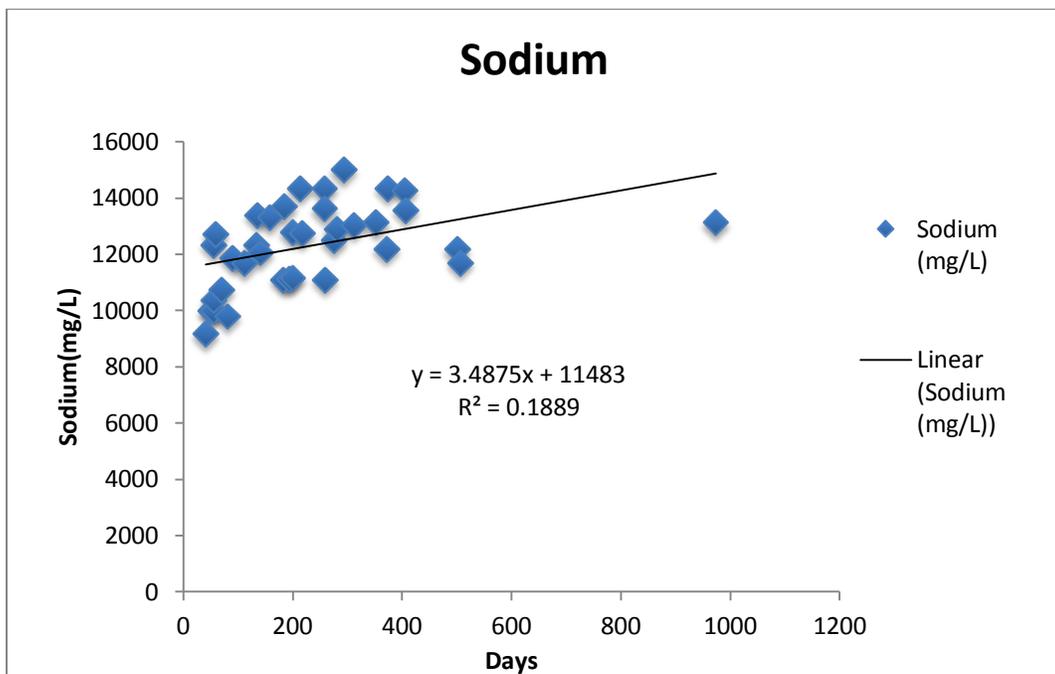
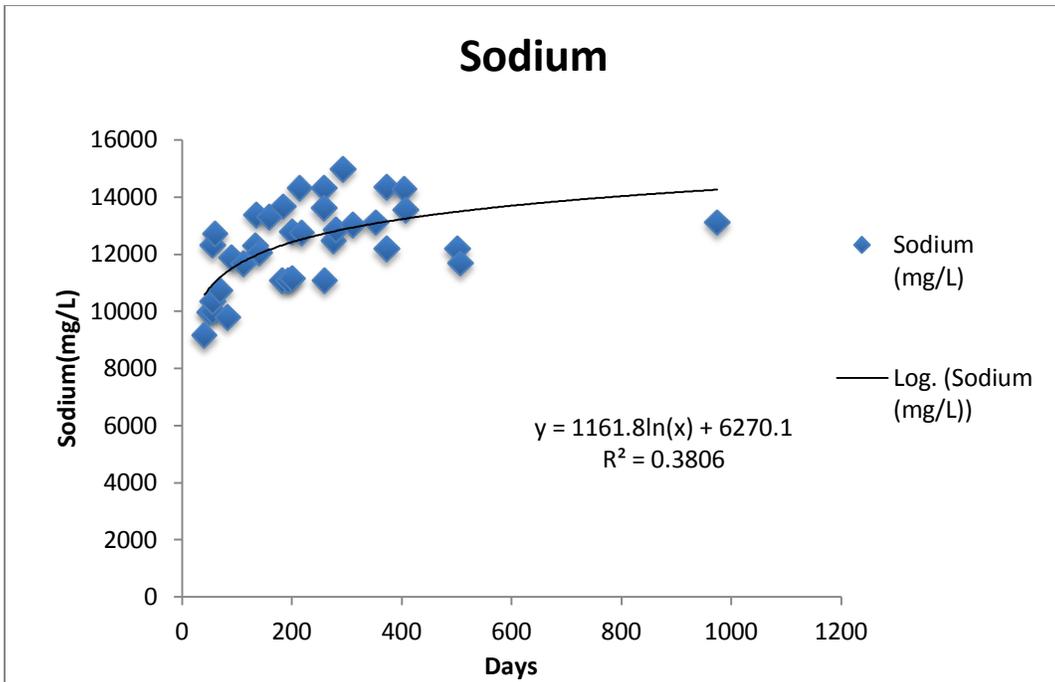


West Pony



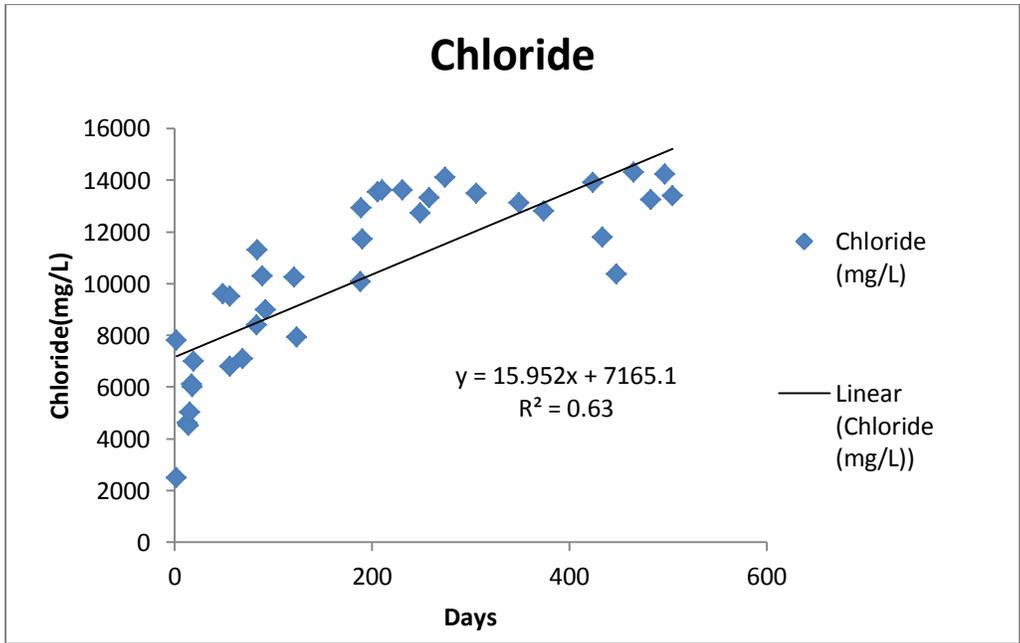
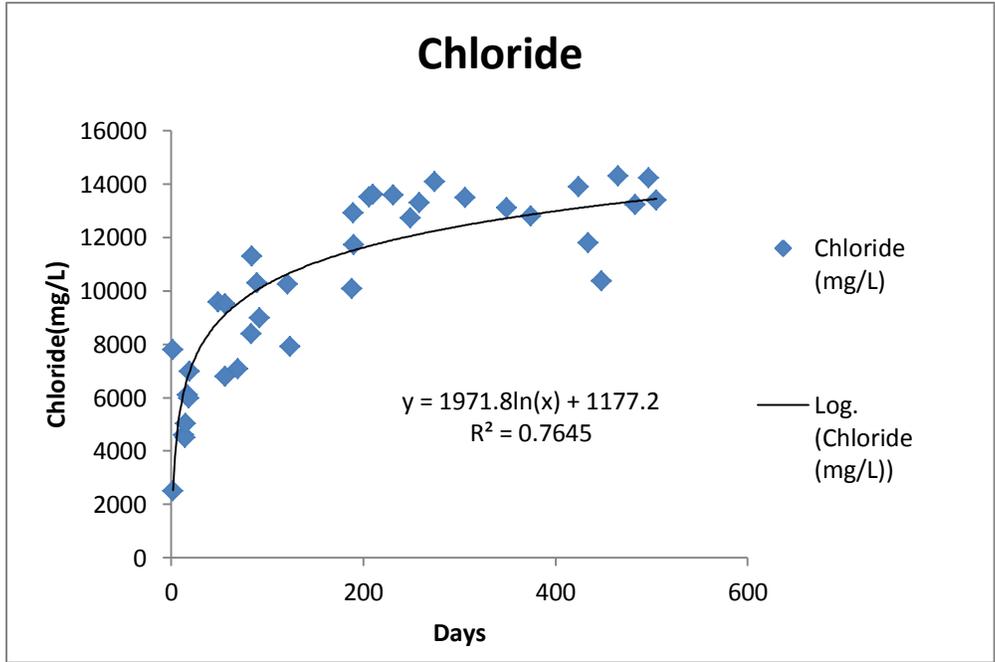
Wells Ranch



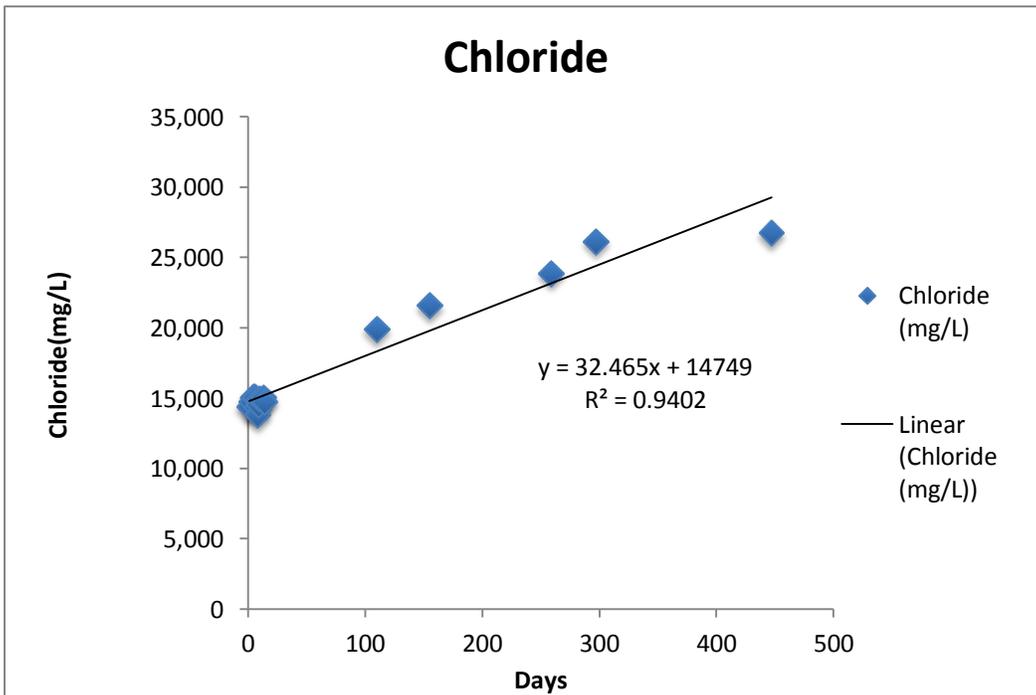
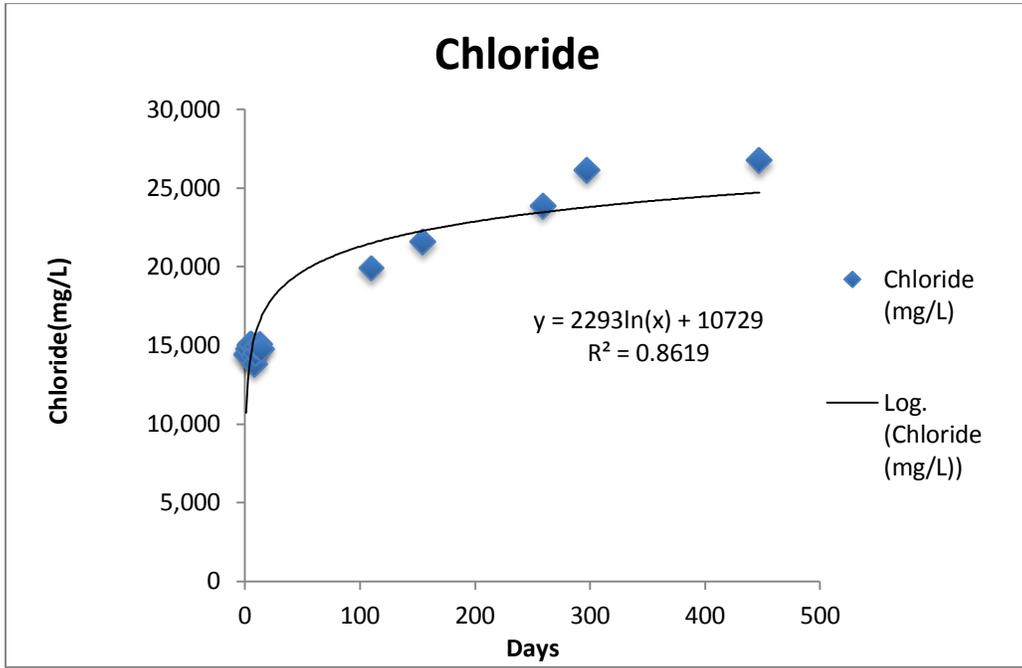


Chloride Graphs in Seven Integrated Development Plans

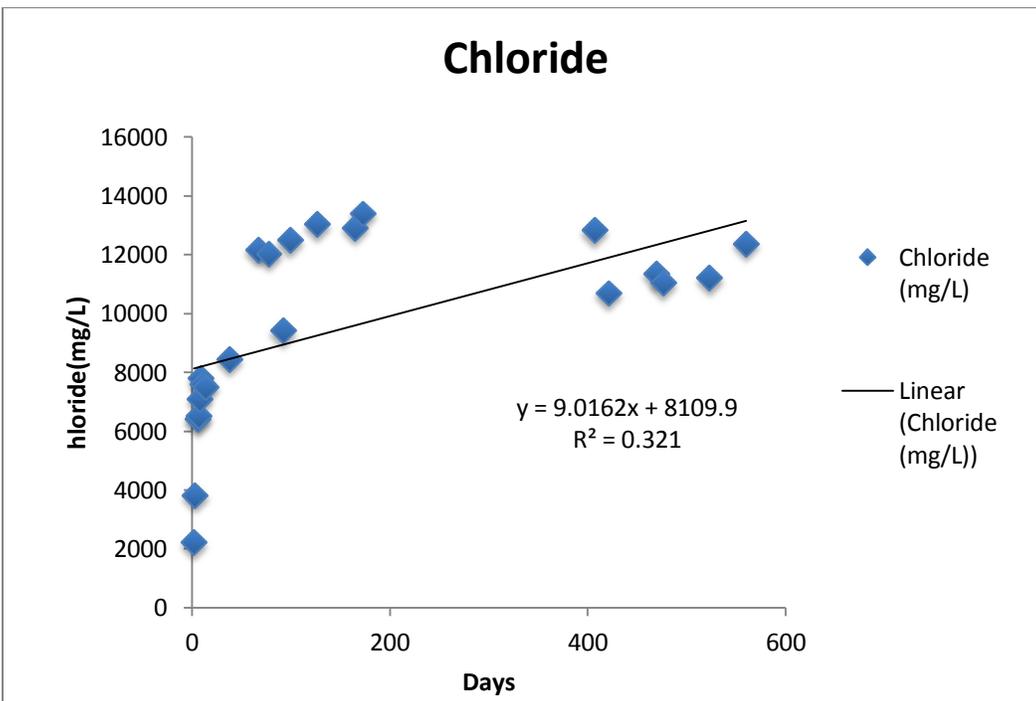
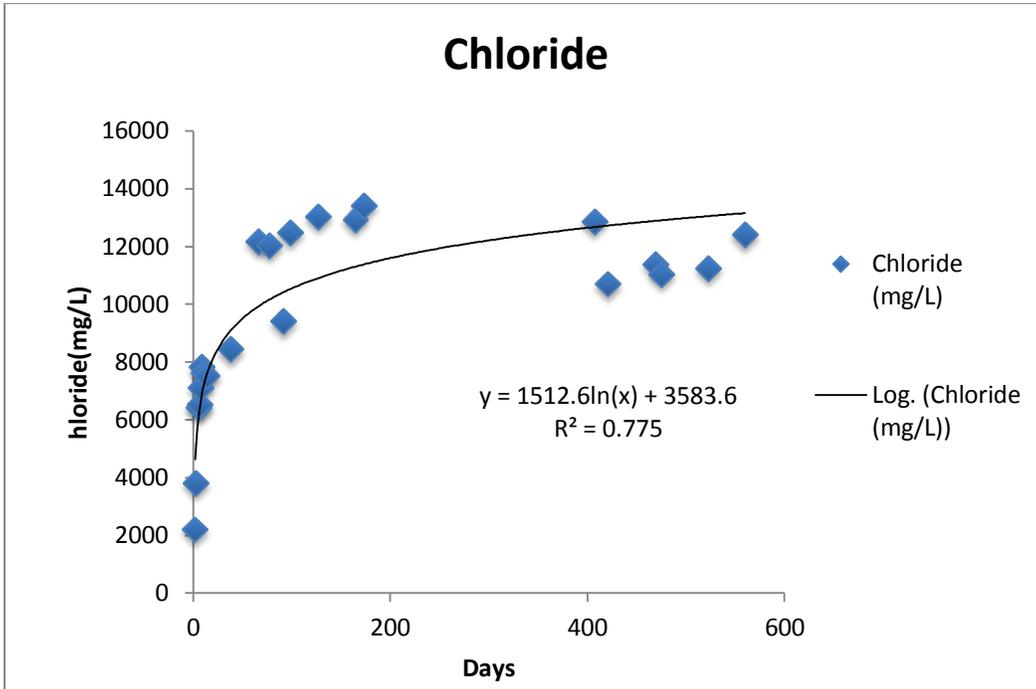
Core

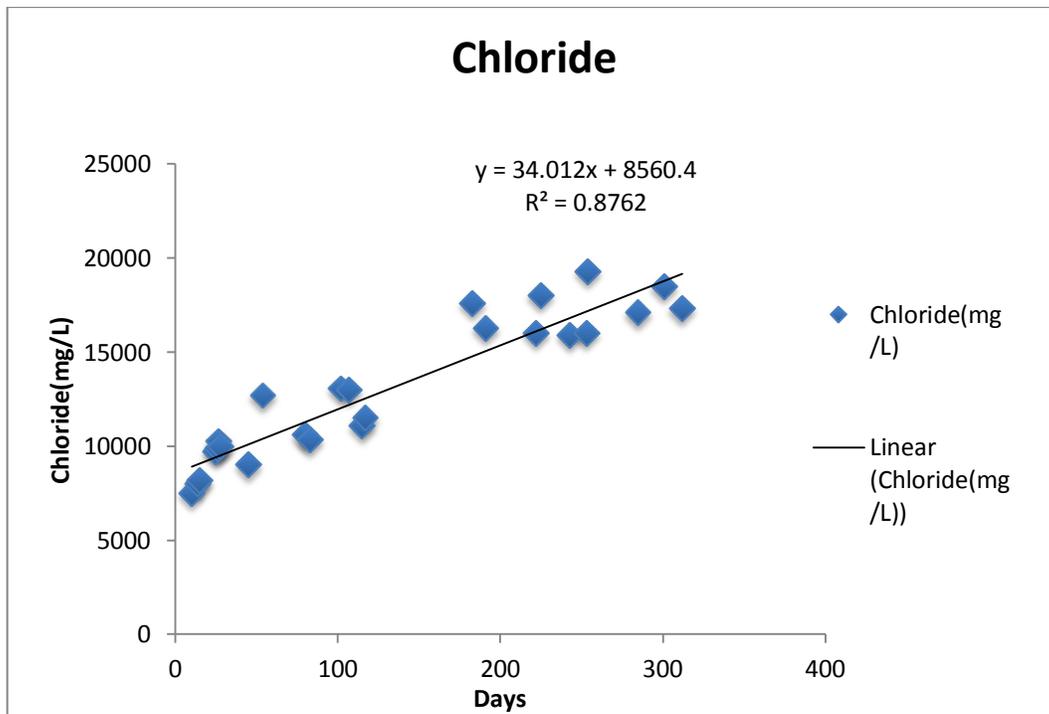
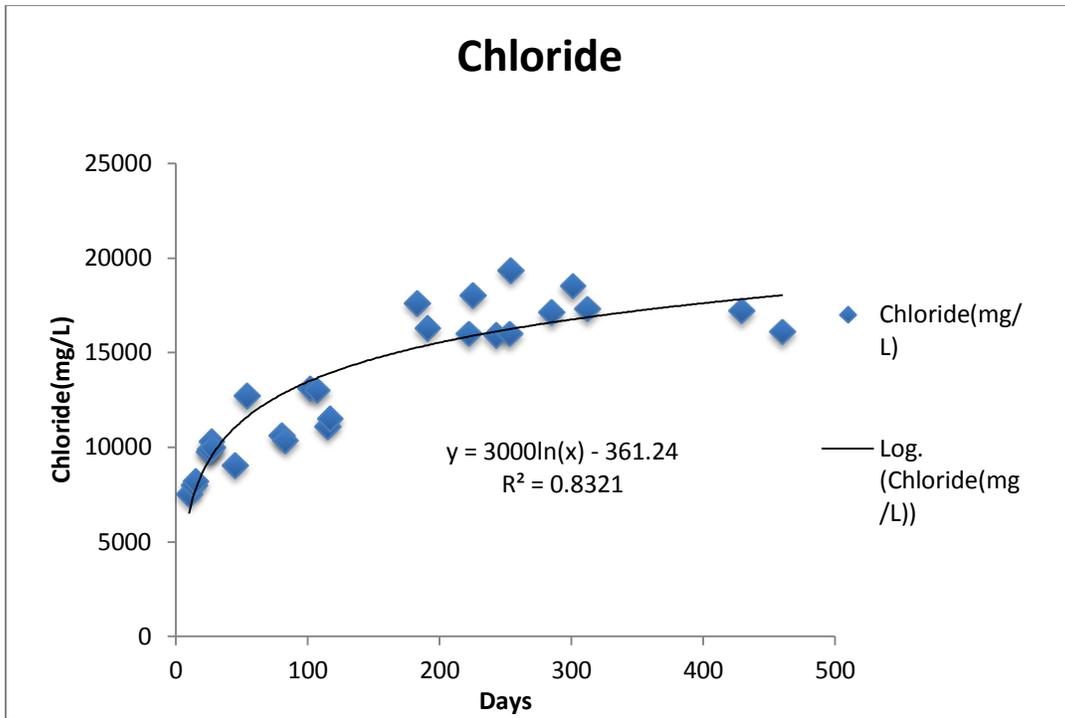


Mustang

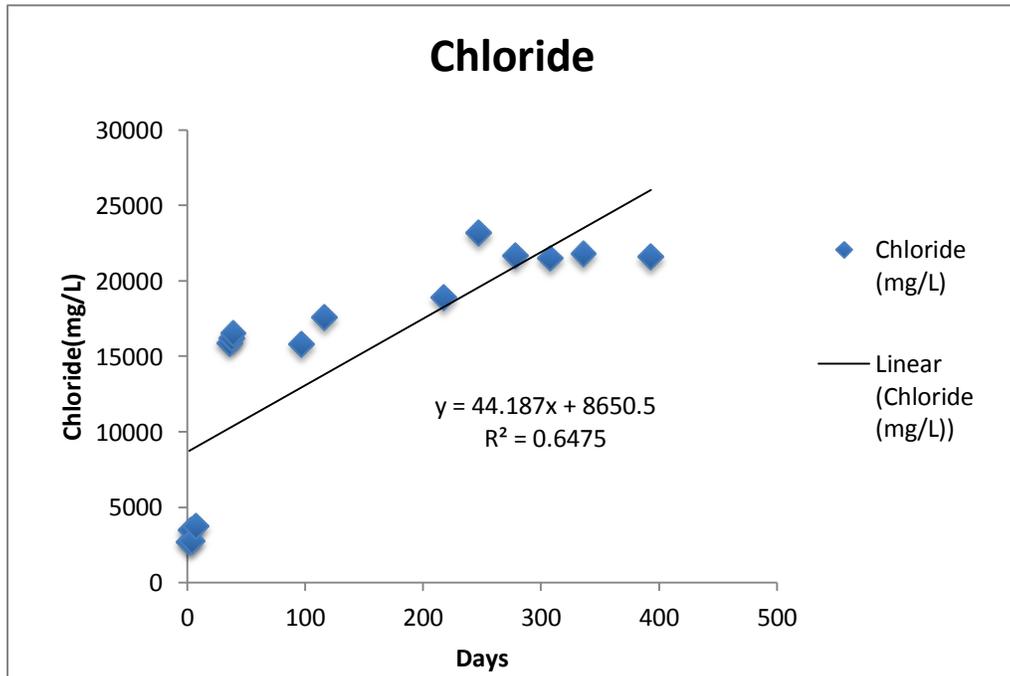
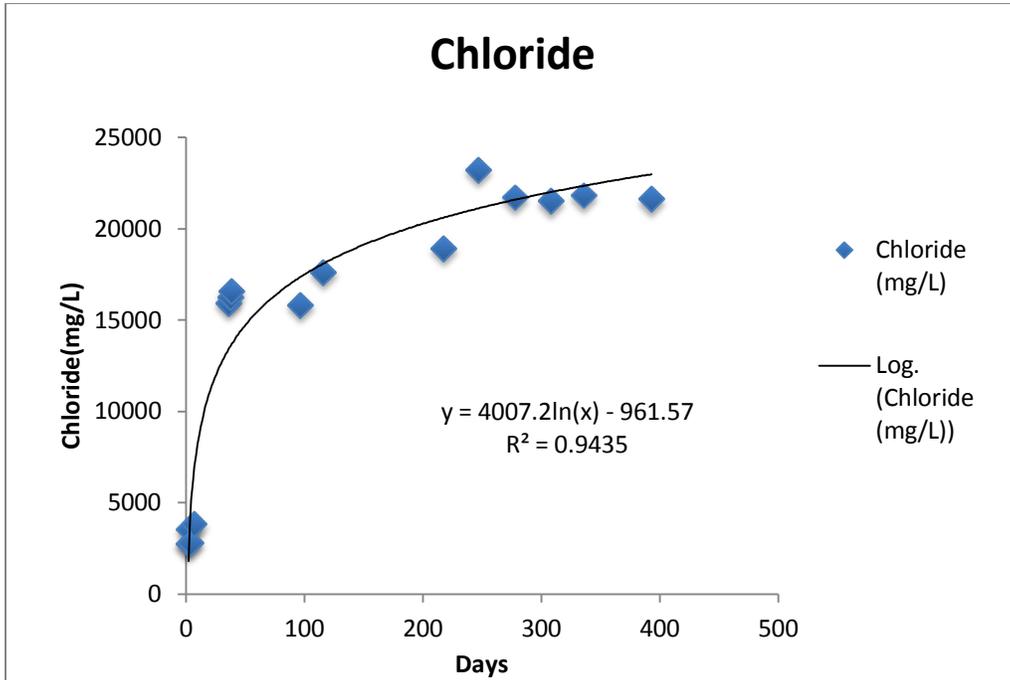


Greeley Crescent

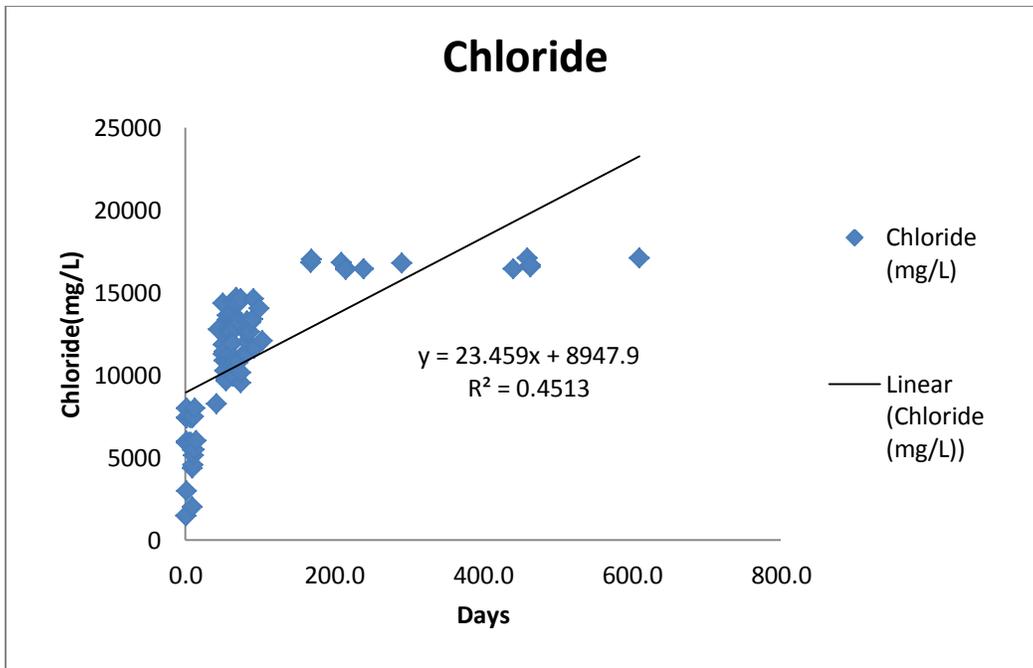
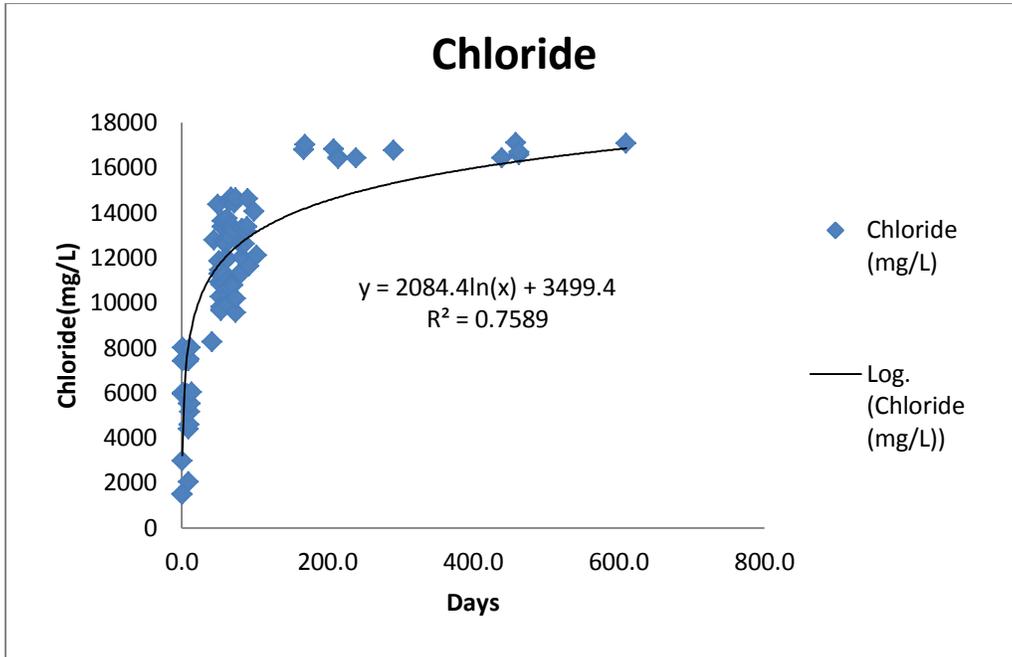


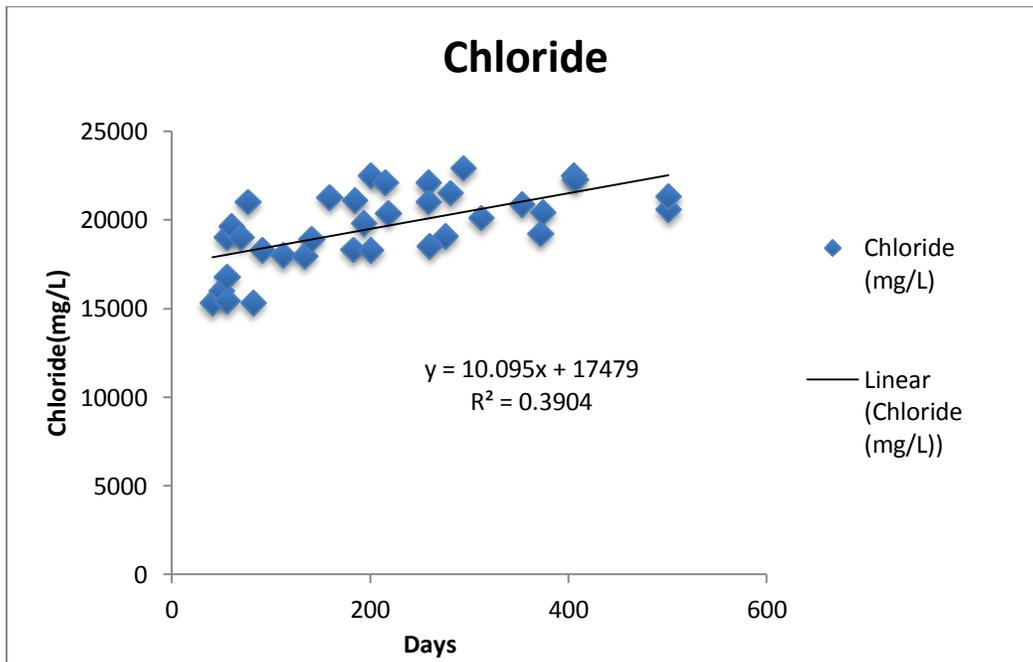
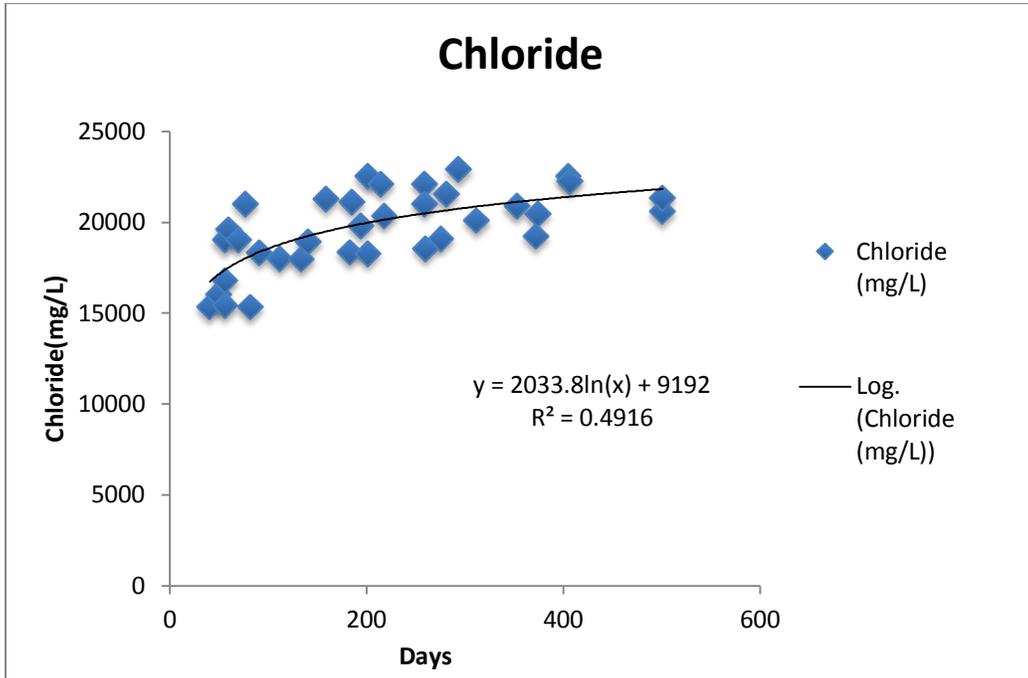


West Pony



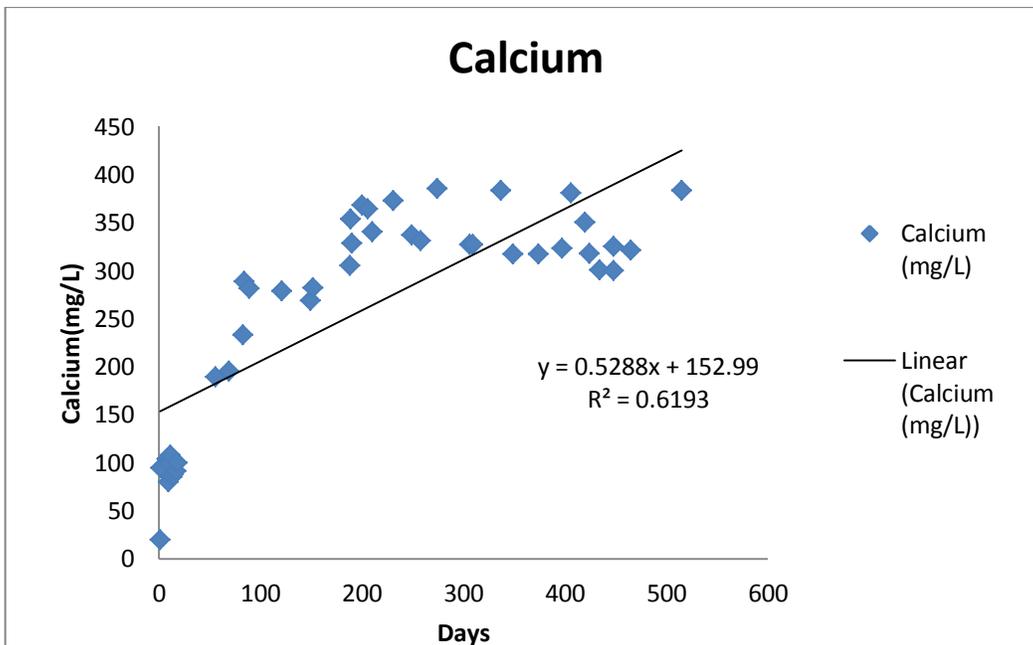
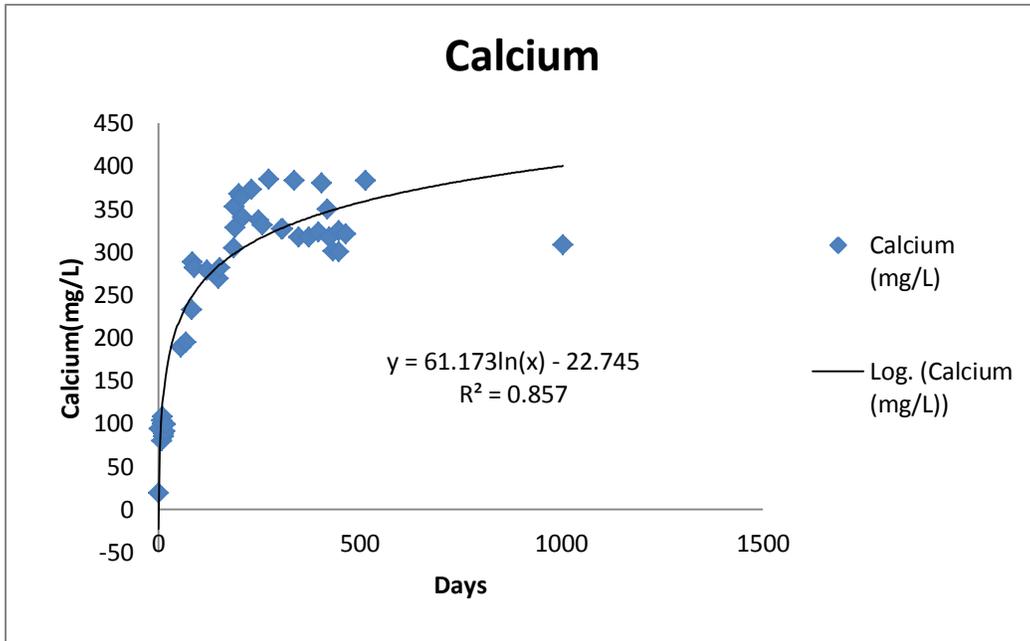
Wells Ranch



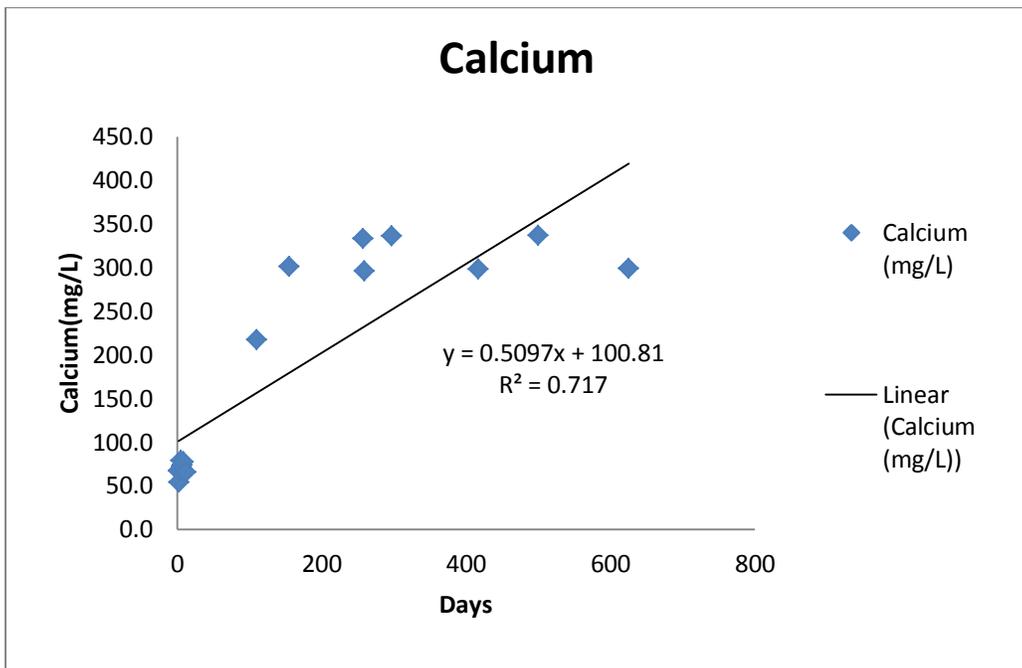
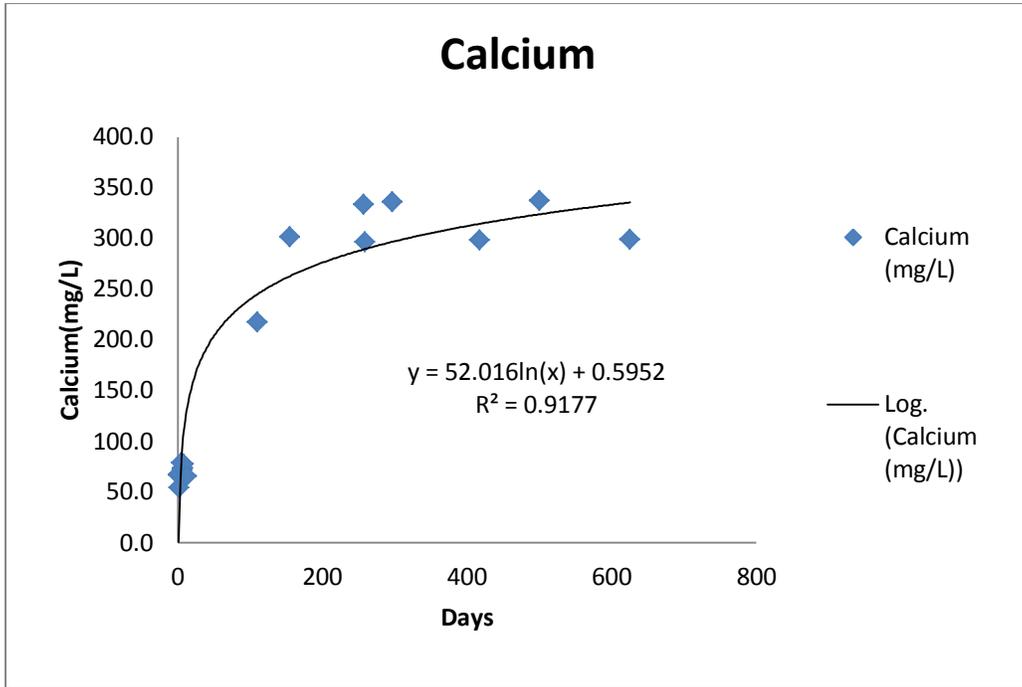


Calcium Graphs in Seven Integrated Development Plans

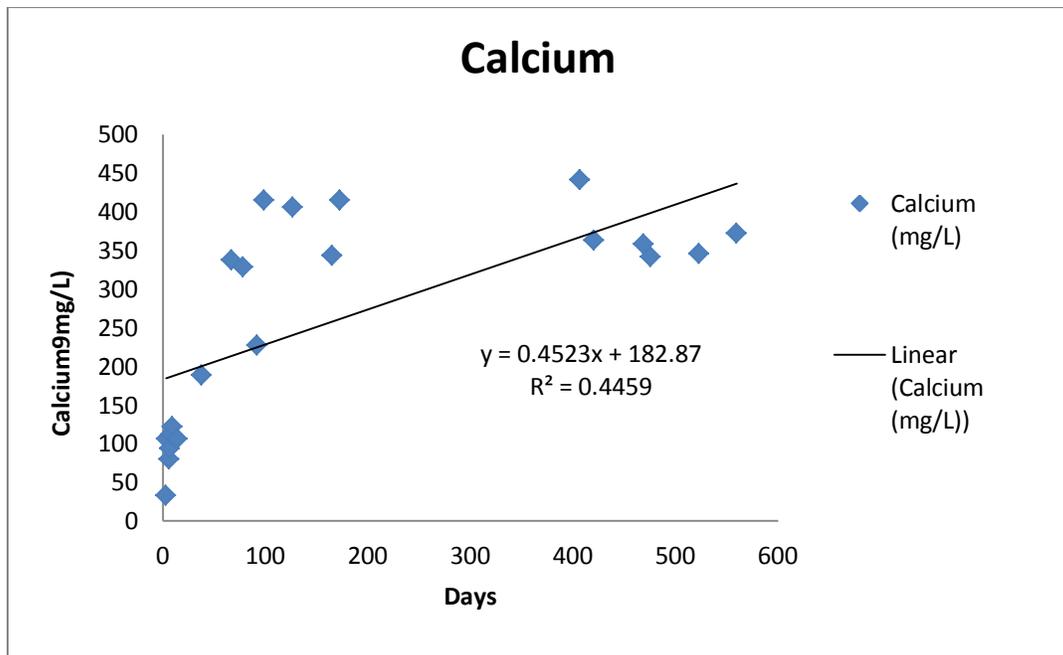
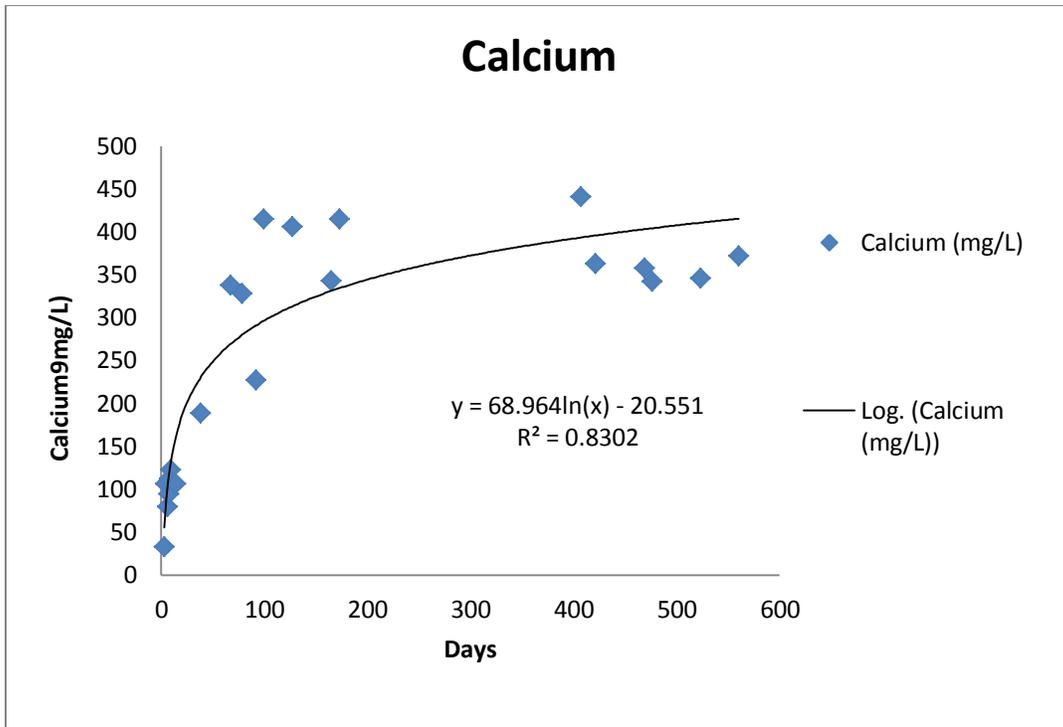
Core



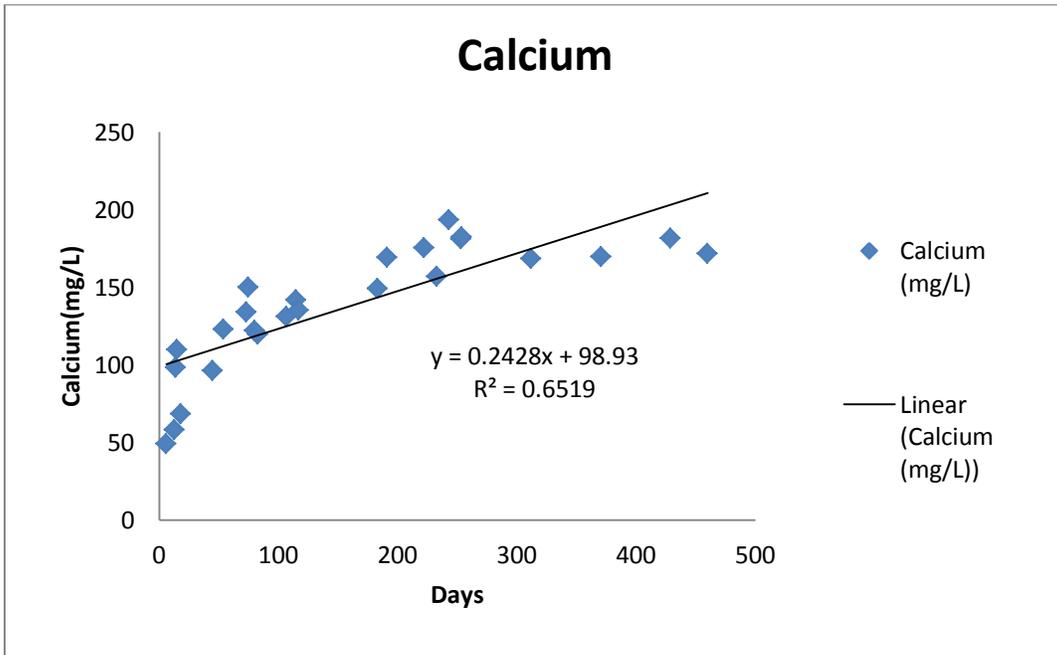
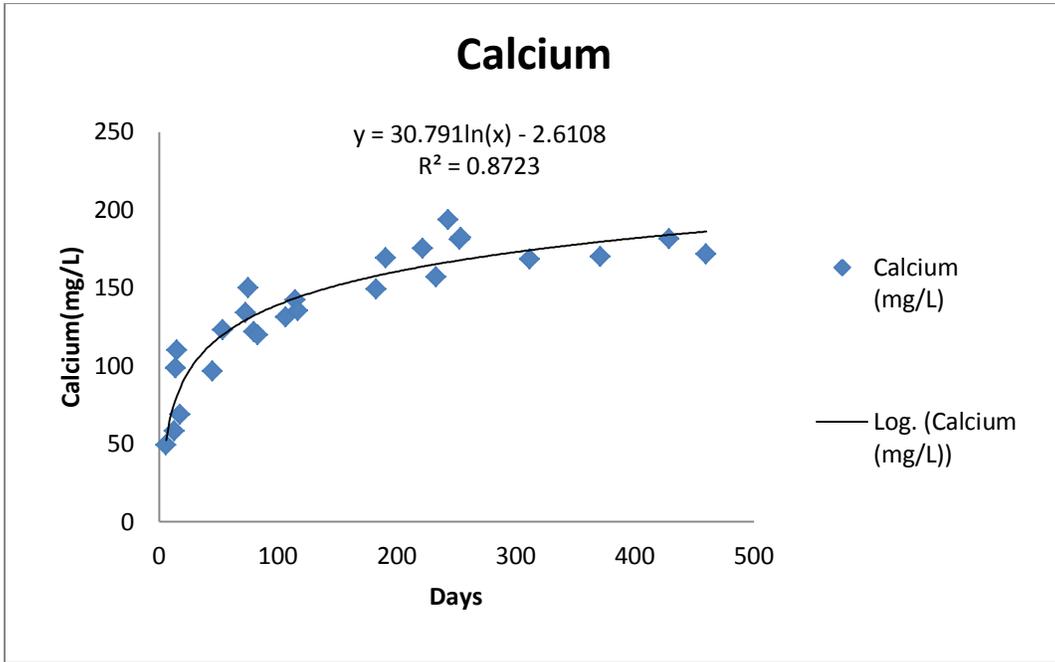
Mustang



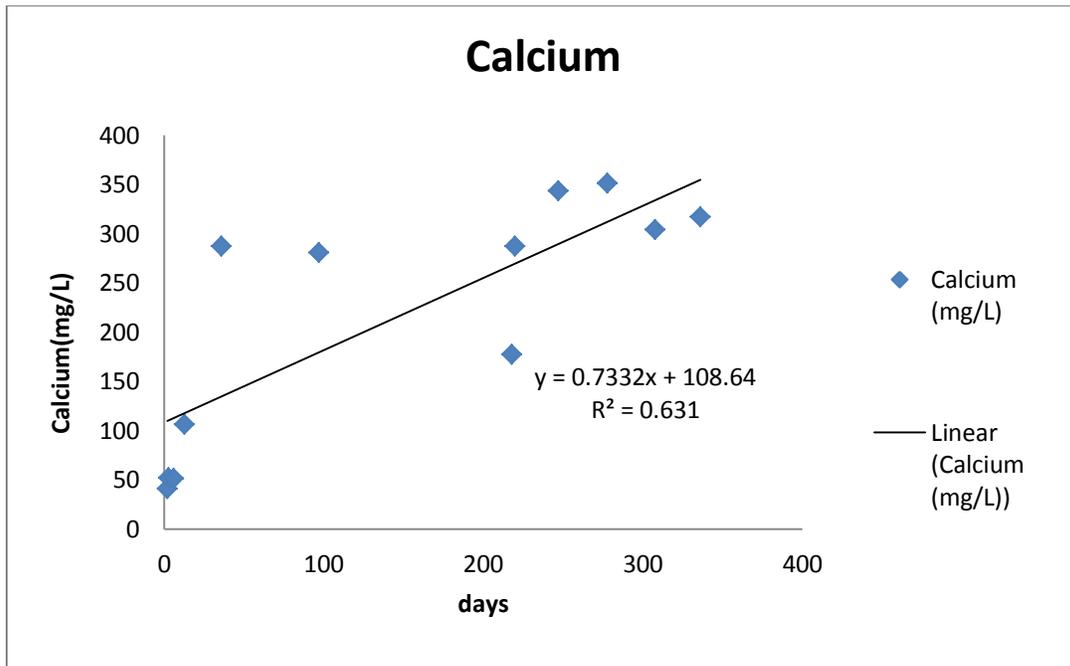
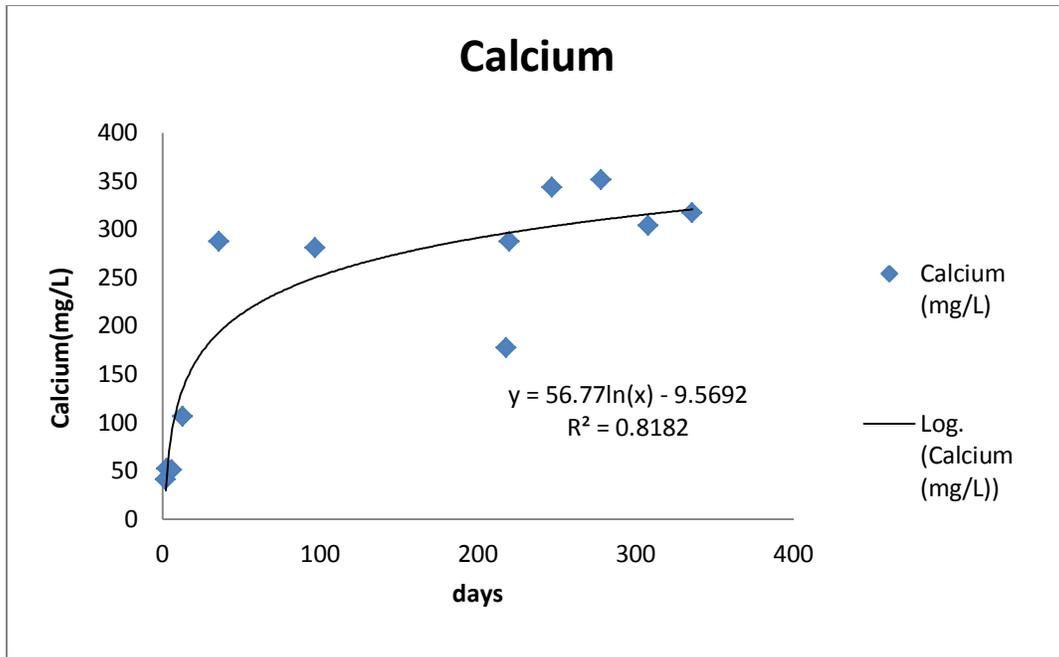
Greeley Crescent



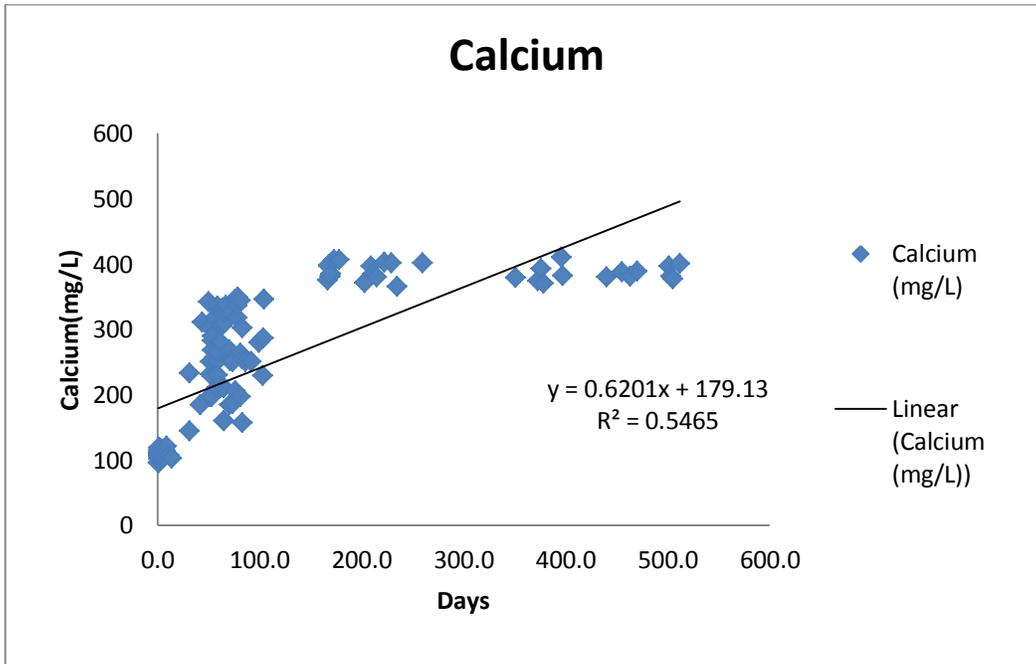
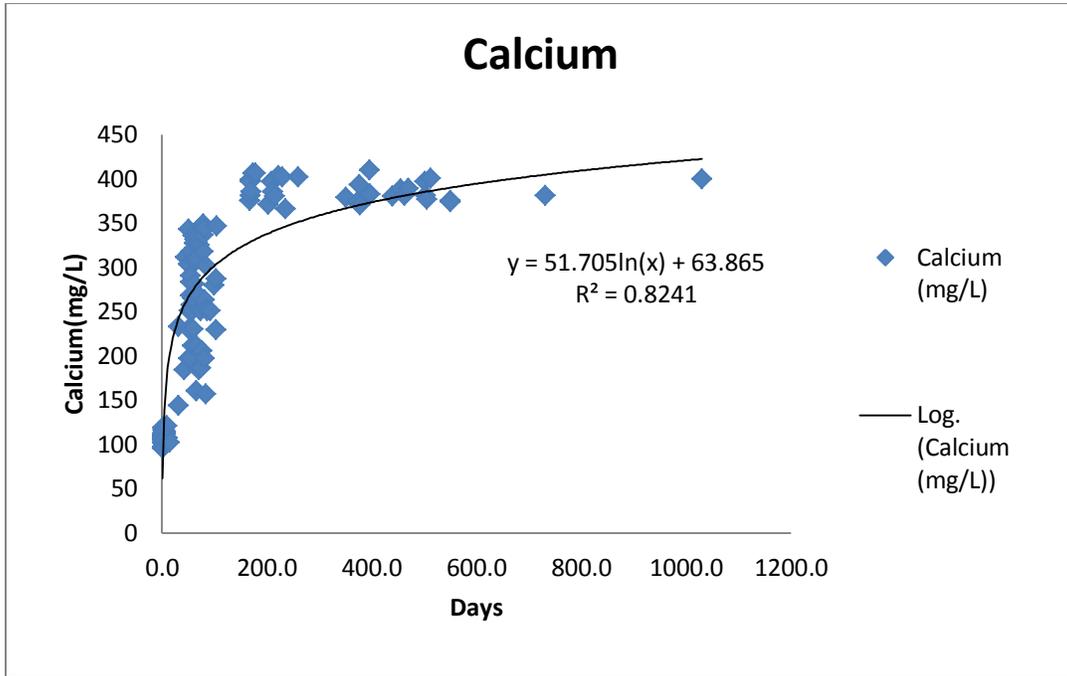
East Pony



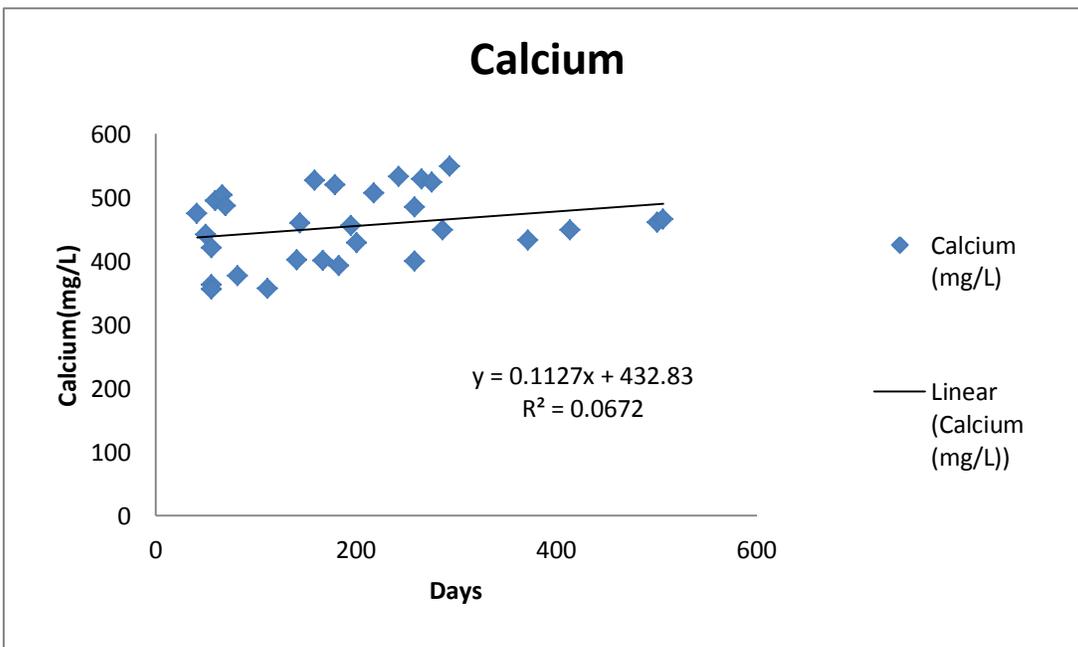
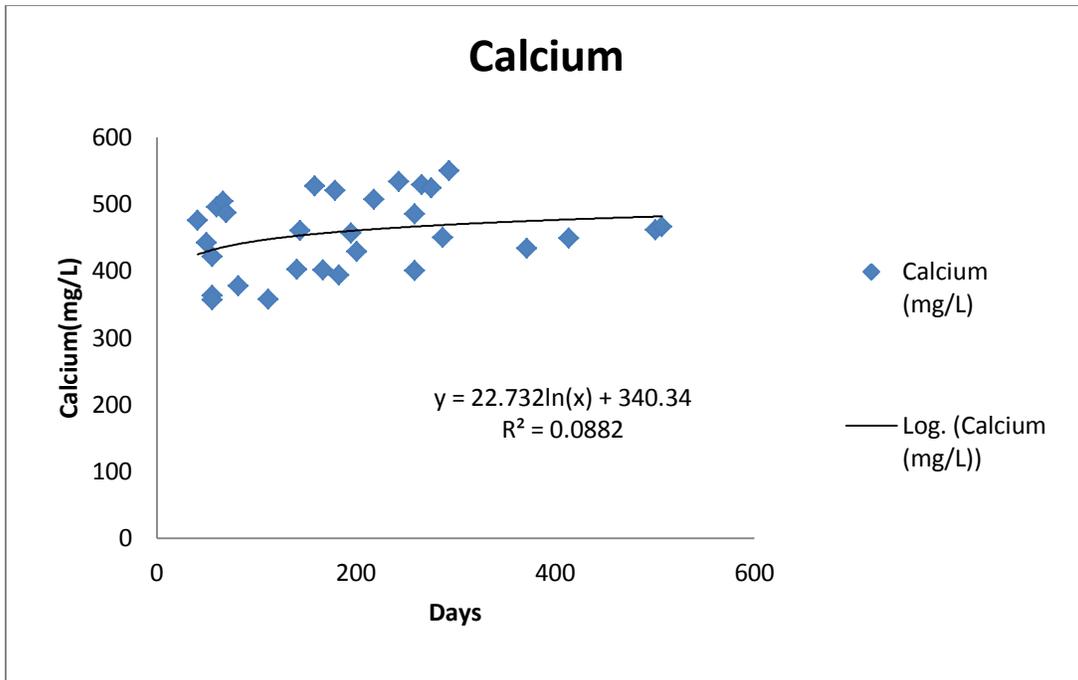
West Pony



Wells Ranch



Cummins



Tables of Logarithmic and Linear Functions of Total Dissolved Solids, Sodium, Chloride and Calcium in Seven Integrated Development Plans

Logarithmic Functions Tables $y=a\ln(x)+b$

TDS

IDP	a	b	R²
Core	2982.1	4312.1	0.87168
Mustang	2282.5	10691	0.86322
Greeley Crescent	2322.1	6992.7	0.72955
East Pony	4636.6	1614.5	0.78009
WestPony	6129.5	1551.8	0.94993
Wells Ranch	4028.5	4924.5	0.88518
Cummins	3244	16778	0.42432

Sodium

IDP	a	b	R²
Core	927.91	1804.4	0.75066
Mustang	1601.8	-262.57	0.95043
Greeley Crescent	787.65	2556.2	0.72078
East Pony	2062.2	-928.59	0.78895
WestPony	2344.5	105.16	0.94134
Wells Ranch	1292.2	2649	0.86287
Cummins	1161.8	6270.1	0.3806

Chloride

IDP	a	b	R²
Core	1971.8	1177.2	0.76447
Mustang	2293	10729	0.86188
Greeley Crescent	1512.6	3583.6	0.77495
East Pony	3000	-361.24	0.8321
WestPony	4007.2	-961.57	0.94346
Wells Ranch	2084.4	3499.4	0.7589
Cummins	2033.8	9192	0.49158

Calcium

IDP	a	b	R²
Core	61.173	-22.745	0.85699
Mustang	52.016	0.5952	0.91766
Greeley Crescent	68.964	-20.551	0.83021
East Pony	30.791	-2.6108	0.8723
WestPony	56.77	-9.5692	0.81823
Wells Ranch	51.705	63.865	0.82411
Cummins	22.732	340.34	0.08822

Linear Functions Tables $y = mx + b$

TDS

IDP	m	b	R²
Core	24.214	12605	0.59852
Mustang	33.135	14547	0.93522
Greeley Crescent	13.844	13777	0.28569
East Pony	38.755	16875	0.7106
WestPony	70.103	15928	0.71406
Wells Ranch	32.834	16087	0.4291
Cummins	10.795	31039	0.25337

Sodium

IDP	m	b	R²
Core	8.7983	4484.1	0.62247
Mustang	17.674	3540.9	0.9234
Greeley Crescent	4.6035	4906.7	0.24106
East Pony	19.733	5555.4	0.8046
WestPony	26.568	5797.7	0.73965
Wells Ranch	10.908	5727.5	0.49861
Cummins	3.4875	11483	0.18894

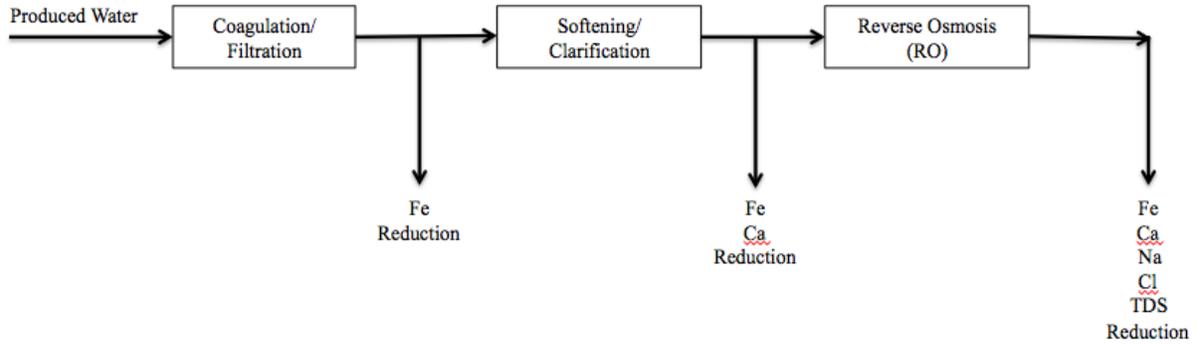
Chloride

IDP	m	b	R²
Core	15.952	7165.1	0.63003
Mustang	32.465	14749	0.94021
Greeley Crescent	9.0162	8109.9	0.32096
East Pony	24.656	9497.1	0.773171
WestPony	44.187	8650.5	0.64749
Wells Ranch	23.459	8947.9	0.45127
Cummins	10.095	17479	0.3904

Calcium

IDP	m	b	R²
Core	0.3568	183.21	0.44167
Mustang	0.5097	100.81	0.71702
Greeley Crescent	0.4523	182.87	0.44589
East Pony	0.2428	98.93	0.65188
WestPony	0.7332	108.64	0.63099
Wells Ranch	0.4502	192.28	0.47066
Cummins	0.1127	432.83	0.0672

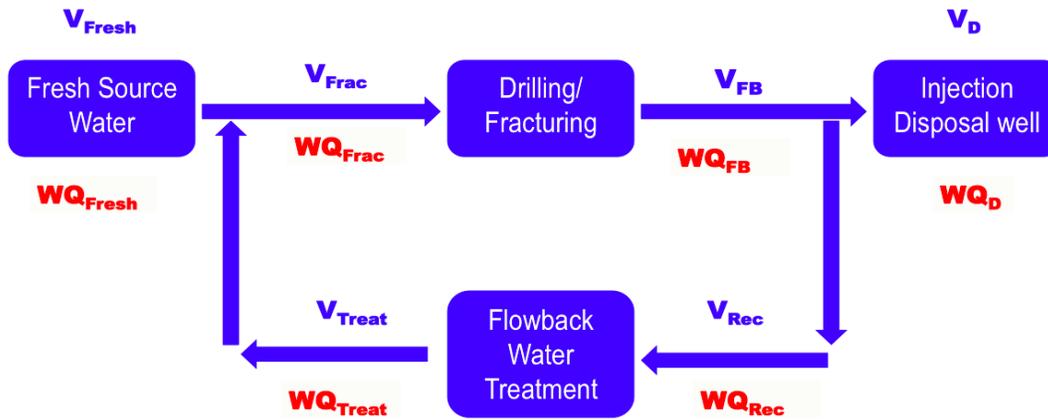
C. Produced Water Recycling Program Tables and Graphs
 Produced Water Treatment Process



Produced Water Treatment Removal Percentage

Methods	Constituent	Removal Percentage
Coagulation/Filtration	Fe	80%
Softening/Clarification	Ca	97%
Reverse Osmosis (RO)	Fe	97.44%
	Ca	99.82%
	Na	96.94%
	Cl	96.85%
	TDS	95.50%

Produced Water Recycling Process Summary



Tables of Water Quality Data

Fracturing Fluids Quality	
Constituent	Critical Concentration (mg/L)
Iron	75
Calcium	600
Sodium	9000
Chloride	9000
TDS	9000

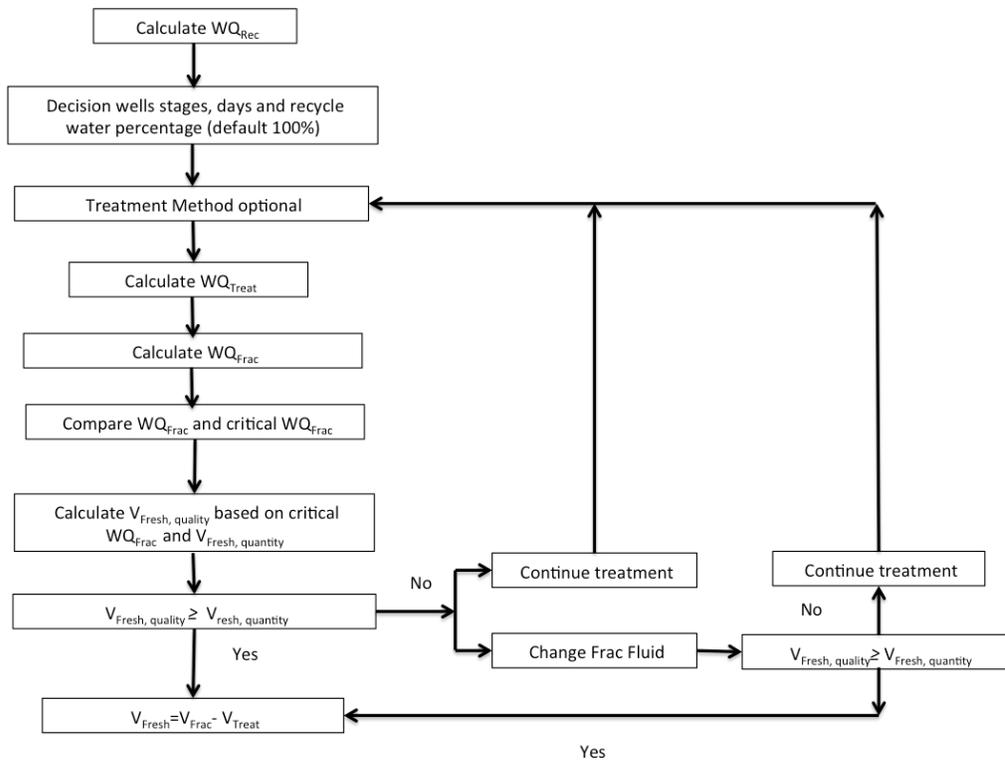
Fracturing Fluids Quantity per Stage	
3571.428571	bbls/stage

Flowback Fluids Quality (mg/L)				
IDP	TDS	Sodium	Chloride	Calcium
Core	WQ=2982.1ln(t)+4 312.1	WQ=927.91ln(t)+1 804.4	WQ=1971.8ln(t)+1 177.2	WQ=61.173ln(t)- 22.745
Mustang	WQ=2282.5ln(t)+1 0691	WQ=1601.8ln(t)- 262.57	WQ=2293ln(t)+107 29	WQ=52.016ln(t)+0. 5952
Greeley Crescent	WQ=2322.1ln(t)+6 992.7	WQ=787.65ln(t)+2 556.2	WQ=1512.6ln(t)+3 583.6	WQ=68.964ln(t)- 20.551
East Pony	WQ=4636.6ln(t)+1 614.5	WQ=2062.2ln(t)- 928.59	WQ=3000ln(t)- 361.24	WQ=30.791ln(t)- 2.6108
West Pony	WQ=6129.5ln(t)+1 551.8	WQ=2344.5ln(t)+1 05.16	WQ=4007.2ln(t)- 961.57	WQ=56.77ln(t)- 95692
Wells Ranch	WQ=4028.5ln(t)+4 924.5	WQ=1292.2ln(t)+2 649	WQ=2084.4ln(t)+3 499.4	WQ=51.705ln(t)+6 3.865
Cummins	WQ=3244ln(t)+167 78	WQ=1161.8ln(t)+6 270.1	WQ=2033.8ln(t)+9 192	WQ=22.732ln(t)+3 40.34

Flowback Water Production Flow Rate (bbls/day)			
IDP	Frac flowback	Transition	Produced water
	(1 month)	(4 months)	(After 5 months)
Core	$Q = 1043.04t^{-0.721}$	$Q = \frac{90}{(1 + 0.0529t)^{0.769}}$	$Q = \frac{19.4084}{(1 + 0.00715t)^{0.588}}$
Mustang	$Q = 1157.61t^{-0.725}$	$Q = \frac{98.49}{(1 + 0.0693t)^{0.652}}$	$Q = \frac{22.99}{(1 + 0.0119t)^{0.682}}$
Greeley Crescent	$Q = 1406.48t^{-0.863}$	$Q = \frac{74.65}{(1 + 0.011t)^{2.083}}$	$Q = \frac{12.93}{(1 + 0.0039t)^{0.625}}$
Wells Ranch	$Q = \frac{1516}{(1 + 0.0614t)^{2.092}}$	$Q = \frac{176.33}{(1 + 0.0374t)^{1.006}}$	$Q = \frac{29.39}{(1 + 0.0034t)^{1.112}}$
East Pony	$Q = \frac{1590}{(1 + 0.2492t)^{1.055}}$	$Q = \frac{165.92}{(1 + 0.057t)^{0.7424}}$	$Q = \frac{33.62}{(1 + 0.00837t)^{0.833}}$

Fresh Water Quality	
Constituent	Concentration (mg/L)
Iron	0.1
Calcium	14.4
Sodium	3.56
Chloride	19.2
TDS	430

Produced Water Recycle Program Calculation Process



Produced Water Recycling Program Interfaces

WaterTreatment
Close

SETTINGS

External Internal
 Location: Core
Day: 1
Stages: 1
Submit

Methods (Removal Percentage)

	Coagulation/Filtration...	Softening/Clarification...	Reverse Osmosis(RO)

Default
Load
Edit
Save
Export

Parameters

	Critical Fracturing Fluids Quality(m...	Fresh Water Quality(mg/L)

Default
Load
Edit
Save
Export

Flowback Water Production Curve:

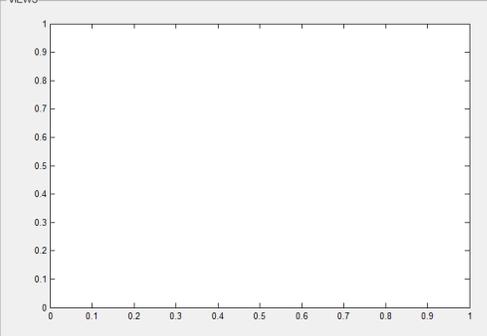
	Fracturing Flowback (1 month)	Transition (4 months)	Produced Water (after 5 month)
Q0			
a			
b			
c			

$q = \frac{Q0}{(a + b * t)^c} * recycle \%$
recycle: 100 %
Default Edit Save

Cancel Calculate

Status: External Selected!

VEWS



Average

Constituents: NULL

Export Figure Export Table

WaterTreatment
Close

SETTINGS

External Internal
 Location: Core
Day: 1-1000
Stages: 20
Submit

Methods (Removal Percentage)

	Coagulation/Filtration...	Softening/Clarification...	Reverse Osmosis(RO)
TDS	0	0	0.9550
Sodium	0	0	0.9694
Chloride	0	0	0.9685
Calcium	0	0.9700	0.9982
Iron	0.8000	0.9860	0.9744

Default
Load
Edit
Save
Export

Parameters

	Critical Fracturing Fluids Quality(m...	Fresh Water Quality(mg/L)
TDS	9000	430
Sodium	9000	3.5600
Chloride	9000	19.2000
Calcium	600	14.4000
Iron	75	0.1000

Default
Load
Edit
Save
Export

Flowback Water Production Curve:

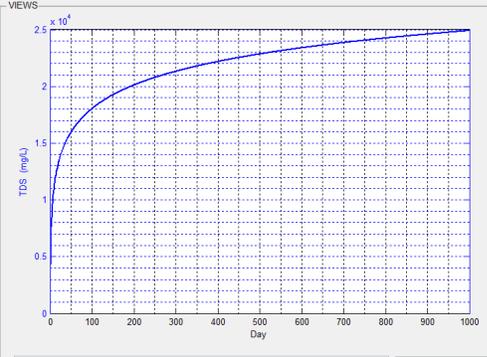
	Fracturing Flowback (1 month)	Transition (4 months)	Produced Water (after 5 month)
Q0	1	90	19.4084
a	0	1	1
b	1.0430e+03	0.0529	0.0072
c	0.7210	0.7690	0.5880

$q = \frac{Q0}{(a + b * t)^c} * recycle \%$
recycle: 100 %
Default Edit Save

Cancel Calculate

Status: Use Default Equations!

VEWS



Average

Constituents: TDS

Export Figure Export Table

Day	Stages	TDS
1	20	4.3121e+03
2	20	6.3791e+03
3	20	7.5883e+03
4	20	8.4462e+03
5	20	9.1116e+03
6	20	9.6553e+03
7	20	1.0115e+04
8	20	1.0513e+04

