

Evaluation of Oil Field Soil Brine Remediation Products

by

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## **ABSTRACT**

This study evaluated the effectiveness of three proprietary remediation products and non-proprietary gypsum to remediate brine contaminated soil. Soil was provided by Talon LPE and was collected from an oilfield with brine contaminated soil that was considered typical by Talon remediation experts. The objective of the study was to determine if additives could increase plant cover germination in soils without costly prior soil washing or dilution by clean soil addition. This research was conducted in three distinct studies: an ex-situ product application study was conducted at the Talon LPE equipment yard located in Amarillo, Texas, a controlled environment germination study conducted at the West Texas A&M University Kilgore Laboratory, and an ex-situ germination phase conducted at the Talon LPE yard. In the product application study, the soil was shredded using the Talon Soil Shredder equipped with a spray bar to apply the individual treatments of Desalt Plus, Soiltech, Chlor-rid, Calcium Sulfate (Gypsum), and Control. Treatments were placed in 40-mm high-density polyethylene cells, small drainage systems were installed in week 4 to allow removal of excess water. An initial 10-point soil composite was taken from bulk untreated soils at a depth of > 2.5cm. Five point composite soil samples were collected using randomly generated numbers within each cell's individual grid pattern. Samples were taken at a depth just below any panned sodic soil generally > 2.5 cm. Samples were collected from 2 October 2015 – 4 December 2015 and analyzed for: sodium adsorption ratio (SAR), total soluble salts (TSS), cation exchange capacity (CEC), sodium, calcium, magnesium, potassium, chlorides, and pH.

The controlled environment germination study was conducted in the Kilgore laboratory at West Texas A&M University of Dr. Jim Rogers, in coordination with the West Texas A&M Graduate School in a chamber with controlled temperature, light and watering. Contaminated soil was brought in from the ex-situ product application phase and was delineated, at a 1:1 ratio, before seeding.

The onsite growth study was conducted at the Talon LPE yard in Amarillo. The soil previously treated was seeded with a warm season grass seed mix approved by Texas Department of Transportation for disturbed roadbed seeding. The cells were then covered with 3-mil transparent Visqueen for weeks 1-3 of the research and uncovered after week three. Observations on grass seed germination and survival were recorded at weekly intervals. The study results indicated that while germination was observed in some treatments no long term plant survival was observed for any of the treatments or in the controls. Soil analysis indicated some product related improvements in soil structure and bioavailability of salts but some prior treatment such as soil washing or dilution using clean soil will be needed to revegetation.

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## **CHAPTER I: INTRODUCTION TO RESEARCH, NEED, AND REMEDIATION STRATEGIES**

### **Research**

This research evaluates the remediation capabilities of four products marketed for management of brine-contaminated soil. Brine is also referred as produced water, brackish water, saline water, or salt water. Brine is high salt-content water, comparable in salinity to ocean water, often produced from underground hydrocarbon extraction at quantities often far greater than the produced crude oil (Deuel, 1991). Brine is extracted from the crude oil prior to sale and the brine is either directed to a disposal well or to storage tanks for ultimate disposal in deep disposal wells. Due to system upsets or pipeline breaks, brines are often released to the environment and require remediation. Typically, the goal of brine site remediation is the re-establishment of grass or vegetative cover. Typical remediation methods include soil excavation and disposal with clean soil replacement, soil blending of salt contaminated soil with clean soil, soil washing to remove salts, and/or the use of products to stabilize the salts. Several products on the market claim soil remediation and plant growth can be attained by the addition of the product to the brine contaminated soil. Four products were tested in this research: Desalt Plus (D+), Soiltech (ST), Chlor-rid (CR) and calcium sulfate (Gyp). The research was conducted in three studies (I) an ex-situ product testing study, (II) a controlled environment germination study, and (III) an ex-situ germination study.

The ex-situ germination study was performed on site at the Talon LPE Amarillo yard in open environment and was performed to assess the remediation capability of the individual products on soil brine contamination via chemical composition analysis.

The controlled environment study was performed to assess the germination capability in contaminated and treated soil without environmental stressors and was conducted in a laboratory at West Texas A&M University.

The ex-situ germination study was performed on site at the Talon LPE Amarillo yard in and open environment and assessed the ability of the products to remediate brine contaminated soils to a level suitable for germination.

### **Need for remediation: Explanation of Brine Contamination**

Produced water typically contains a mixture of cations such as calcium ( $\text{Ca}^{++}$ ), potassium ( $\text{K}^{+}$ ), sodium ( $\text{Na}^{+}$ ), or magnesium ( $\text{Mg}^{++}$ ) and constituent bond groups such as ( $\text{CO}_3^{2-}$  or  $\text{SO}_4^{2-}$ ). Salinity of brine can range from nearly fresh with an electrolytic conductivity of 3 deci Siemens/meter (dS/m) or saltier than the dead sea. dS/m is measured through electrolytic conductivity (EC) or the affinity for attraction to negative (anode) and positive (cathode). A higher EC represents more affinity for bonding on these mechanical receptors. The more anions and cations that are attracted to the electrode the higher the EC. EC allows for a measurement of salt content in soil and should not be the only method of determination of remediation. The sodium adsorption ratio (SAR) is a calculation and representation of the available sodium relative to calcium and magnesium. Exchangeable sodium percent (ESP) is a value that uses the percentage of sodium relative to combined calcium, sodium, potassium, and magnesium. EC, SAR, and ESP are used to determine the salinity of soil. Table 1 illustrates how EC, SAR and ESP are used in soil structural condition characterization.

Table 1. Soil Structural Condition.

Class	EC (dS/m)	SAR	ESP	Typical soil structural condition*
Normal	Below 4.0	Below 13	Below 15	Flocculated
Saline	Above 4.0	Below 13	Below 15	Flocculated
Sodic	Below 4.0	Above 13	Above 15	Dispersed
Saline- Sodic	Above 4.0	Above 13	Above 15	Flocculated

\*Soil structural condition also depends on other factors not included in the NRCS classification system, including soil organic matter, soil texture and EC of irrigation water (*Horneck et al., 2007*).

Soil with limited toxicological effects on plants salinity effects will have an EC below 4 dS/m according to the USDA & Natural Resources Conservation Service (USDA, 1996).

When salts are dissolved in solution, they often ionize, disassociating into cations (positively-charged molecules) and anions (negatively-charged molecules) (Buckman, 1967). While salinity can affect soil in different ways, lack of water mobility through layers is most common. Specific solubility of individual salts and the composition of the mineral material through which water passes dictate the salts retained by the water (Gawel, 2006).

The most common cations present in High Plains soils are calcium, magnesium, and sodium. Mineralization of salts disrupts soil structure and reduces percolation of rainwater into soil. The commonality of these cations is due to the soil type Mollisol,

which is also the prevalent soil type for the area (Sposito, 2008). Typically, these salts dominate the exchange complex of pH neutral and alkaline soils, replacing aluminum and hydrogen on the cation exchange sites. Each of these fundamental salt cations is base-forming and contributes to an increased  $\text{OH}^-$  concentration in the soil solution and a decrease in  $\text{H}^+$  concentration (Miller, 1975). Bicarbonates and carbonates are common anions in arid and semi-arid areas of the western United States (USDA, 2016). High levels of carbonates can increase the osmotic forces exerted from brackish soils. Calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$  will decompose into calcium carbonate ( $\text{CaCO}_3$ , or lime) with a reduction in soil moisture through evaporation, plant uptake, or drainage (USDA, 2016). This interaction results in a solid precipitate,  $\text{CO}_2$ , and water. Calcium is removed from clay particles through interactions with partial negative charged clay platelets that forces calcium to soil surface while sodium is left behind, creating a sodium-dominated (sodic) soil from a calcium-dominated soil. Calcium carbonates ( $\text{CaCO}_3$ ), when present, are usually found in soil with a pH of 8 – 8.2 (Hall J. et al. 2009).

Evaporation will also cause calcium and magnesium to precipitate out of the soil pore water when the soil dries (Western Fertilizer Handbook, 1995). This allows sodium to exert a partial charged force onto soil layers. When this partial charge interacts with  $\text{H}_2\text{O}$  it creates wet but unhealthy soil conditions. Calcium and sodium cause higher levels of soil swelling when wetted. The calcium largely holds water with partial polar covalent bonding when linking clay particles, whereas sodium holds the water with partial ionic bonding when linking clay particles together (Chorom, 1995).

When a produced water spill occurs, the sodium chloride ( $\text{NaCl}$ ) disassociates slightly, allowing the sodium ( $\text{Na}^+$ ) ions to bind with the receptor points of the clays found in the

soil through partial charges. Ionic bonds are formed between cations and anions. Sodium ions binding to clay platelets cause the disassociation of the soil into dispersed soils. The soil develops a crusted surface through expulsion of salts, which prevents water percolation, leading to runoff and soil erosion. For this reason, sodium-contaminated brine soils tend to hold moisture. This effect, in combination with crusting, leads to extremely low porosity of salt-affected soils. Crusting is the drying of the top layers of soil and the excretion of unbound salts from the soil. Sodium in ionic form has the most problematic effect of soil structure (Sumner, M.E., 1998).

Vegetation grown in high-salinity soils shows physical signs of stress. The stress shown can range from germination inhibition to death of existing plants (Alam, S.M., 1994). Plants exposed to high-salinity soil will wilt due to cellular death from an inability to excrete salt buildups. Apoptosis from salts can also reduce chlorophyll production of plants (Devmarkar, et al 2014). The study “Soil Salinity Alters Growth, Chlorophyll Content, and Secondary Metabolite Accumulation in *Catharanthus roseus*” showed a direct linear correlation between salinity and reduced chlorophyll production caused by NaCl (Jaleel, S. 2008). The osmotic forces of salinity also reduce water uptake in plants (US Salinity Laboratory, 1956). High osmotic potential also has a negative impact of soil microbes (Yan, N. 2015). High osmotic potential will inhibit plant growth.

Establishing vegetative regrowth is essential for proper site remediation. Surface remediation, top 18 inches of soil, is insufficient to correct the damage caused by contamination. Full remediation is required to mitigate the pressure posed by induced chemical imbalance and brought through natural processes like wicking. Wicking is the



slow upward flow of water through semi-porous materials such as soil (Patnaik, et al. 2006).

The calcium in the gypsum reacts with the sodium chloride (NaCl), causing the chloride to switch bonds to the stronger electronegative calcium as seen in the following reaction (Abrol et al. 1979);  $2\text{NaCl} + \text{CaSO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{CaCl}_2$

The basic function of the reaction is predicated on the electronegativity of these elements. The electronegativity scale is 1-4 and predicts an elements affinity for bonding through the partial charge emitted. Electronegativity is the power of attraction for electrons in a covalent bond. This is a partial charge emitted on a sub-atomic level and the basis for fundamental remediation. The lowest calculated elemental electronegativity is cesium at 0.7 and the highest is fluorine with 4.0 (Pauling, 1970). The elements in the above equation and their respective electronegativity are listed in Table 2.

*Table 2. Electronegativity of selected elements common to brine remediation.*

Element	Electronegativity (Pauling Scale)
O	3.5
Cl	3.0
S	2.5
Ca	1.00
Na	0.9

Electronegativity is used as a method for the characterization of compounds as more ionic or covalent. Determination of electronegativity is accomplished by taking the difference in electronegativity between the two or  $X_a - X_b$ . The compound  $\text{Na}^+\text{Cl}^- = (3.0 - 0.9 = 2.1)$  and related to largely ionic bonding at 67%. The dipole moment, the point at which a bond is broken, for NaCl is  $1.58\text{\AA}$ ; derived by multiplying the bond length  $2.36\text{\AA}$  by .67 (Pauling, 1970). The power of attraction or electronegativity is used to predict the possible bonds that will occur within a solution (Abu-Shara, 1987). The effect creates the insolubility of the NaCl bonding in precipitate, when water is removed. Calcium has a stronger affinity for cation adsorption sites than sodium. Therefore, large amounts of water are required when using a high calcium-based remediation technique (Almodares et al. 2008).

The amendment of  $\text{CaSO}_4$  adds more electronegative calcium to rebind chlorides and disassociate sodium.  $\text{Ca}^{++}$  is slightly more electronegative than Na, causing the  $\text{Cl}^-$  to strip the  $\text{Ca}^{++}$  from  $\text{SO}_4^-$  and produce a stronger bond for both  $\text{Ca}^{++}$  and  $\text{Cl}^-$ . Weathered calcium minerals tend to form primary silicates and primary carbonates in the rhizosphere, or the root zone (M.R. Carter, 1990). The electronegativity of the  $\text{CaCl}_2$  is stronger than that of the NaCl bond. This allows disassociated  $\text{Na}^+$  to continuously maintain its partial bond with  $\text{SO}_4^{2-}$  (Sposito, 2007). This chemical reaction creates more force to break the sodium bond, allowing it to percolate outside of the root zone or be expelled with proper drainage. This rebind also lowers the possible partial charges that sodium exerts on soil particles.

The  $\text{CaCl}_2$  interactions on soil are less negative compared to NaCl or unbound  $\text{Cl}^-$ .  $\text{Cl}^-$  has the affinity to bond with any cations such as potassium, hydrogen, and magnesium. These

elements are important for plant growth. Plants will uptake basic minerals with chloride-attached elements (KCl, HCl, MgCl<sub>2</sub>, etc.). Chloride bonding is also why large amendments of CaSO<sub>4</sub> are required to remediate salt contaminated soils. There is an inverse correlation between solubility and the presence of CaCl<sub>2</sub>. This lack of solubility is due to the presence of various cations interacting with the SO<sub>4</sub><sup>2-</sup>.

Water is a key component for successful movement of contaminants through soil to achieve remediation. Excessive water use, however, causes the site to erode quickly and can result in an oversaturation of the root zone. Oversaturation of soil will result in reaching the osmotic potential, causing interference with plant mineral uptake and germination inhibition. The nature of brackish soil is to increase the osmotic potential. The partial electronegative bond between sodium and clay layers also causes water trapping between layers (Sposito, 2004).

### **Legal Remediation Standards for Brine:**

There is no legal remediation standard for brine-contaminated spills in Texas. Depending on the nature of the spill and receptors affected, sensitive areas (wetlands, playa lakes, etc.) are covered by state and federal standards such as the Clean Water Act, The Texas Risk Reduction Rule, Endangered Species Act and/or Migratory Bird Treaty Act. The Texas Railroad Conservation Commission has no established surface soil remediation level for brine contamination. However, most oil leasing agreements have a clause that requires oil producers to leave the site in its original condition less normal wear and tear. This standard requires soil remediation to a level that would support agricultural use for crops or grass for grazing. In some cases, an ecological risk

assessment can be used to determine the level remediation required to protect flora and fauna.

For a produced water spill, the ecological risk assessment can be used to determine the protective cleanup levels (PCLs) of the contaminants on local habitats and indicator species that reside in those habitats. The first step of an ecological risk assessment is to determine the population at risk in the area. Larger spills can put waterways at risk of becoming too brackish for local animal populations. Excess salt consumption by plants will lead to toxicity since plants will uptake less water to compensate for high osmotic pressure exerted by salt effected soils (Zhu J.K. et al. 2011). According to the Natural Resources Conservation Service, sustainable plant growth will occur at or below 4 dS/m. An EC as high as 6 dS/m can be considered suitable for remediation and would depend largely on on-site drainage, water inputs, and native plant species (United States Department of Agriculture, 1999).

Remediation to background is an option for standard of cleanup. The average background for sodium on the Northern High Plains was on average under an EC of 4 dS/m (Kharel, 2016). Background for most areas in the Panhandle will be between 2-4 dS/m.

### **Soil Characterization:**

The soil for this research was obtained from a site in Beaver County, Oklahoma selected by Talon LPE as a typical brine contaminated site. The soil was delivered to the Talon equipment staging yard. The soil was separated using a surfactant/water solution to determine the percentage makeup by particle size. The soil was composed of 45% clay, 30% sand and 25% silt. Physical characteristics and aggregate size were used in

coordination to determine soil identification. The pH of the contaminated pretreated soil was 7.5; these levels are consistent with background levels expected on site.

Ribbon and physical testing revealed that soil was equal parts gritty and smooth fringe clay-loam. The soil was identified as Pullman Clay Loam via a review of Web Soil Survey and established characteristics as defined by USDA and the area revealed that the soil is identified as a Pullman Clay Loam (Web Soil Survey). The dark brown coloration of the soil was used as a determining factor.

**According to the USDA information on Pullman clays:**

“The Pullman series consists of very deep, well-drained, slowly permeable soils that formed in clayey aeolian deposits from the Blackwater Draw Formation of Pleistocene age. These soils are on nearly level to very gently sloping plains or playa slopes. Slope ranges from 0 to 3 percent. The mean annual precipitation is about 483 mm (19 in) and the mean annual temperature is about 16 °C (60° F).” (Pullman Series, 2016)

The slope found on site consisted of 0 to 3 percent. The average annual temperature for the site is 14.4 °C (58° F). The average annual rainfall is 546.1 mm (21.5 in) yearly (Oklahoma Climatological Survey, 2003). The total bulk density of the soil was 172.1 m<sup>3</sup> (6079 ft<sup>3</sup>). The combination of small aggregate clays and high portioned sodium brine leads to partial bonding between salt and soil particles that cause further decreases in permeability (Sumner M.E. 1998). Under the USDA Soil Taxonomy system, this soil is identified as a Mollisol. Mollisol soil is found commonly in the Southern High Plains and the High Plains spanning from Texas to North Dakota. Texas, Oklahoma and North

Dakota are all high oil-producing states, according to the U.S. Energy Information Administration, and the soil represented in this study is commonly found in these states.

### **Available Remediation Strategies:**

There are currently three strategies used for brine remediation:

1: “Dig & Haul” physically removes contaminated soil, hauling it off to be disposed of either in a landfill, or through incineration.

2: “Soil Blend” removes the entire A and B horizons of soil (generally 18-24 in) and replaces them with the underlying horizons or clean soil. This method is commonly used on spills that do not have leaching issues associated with the area. Leaching issues include a high water table or soil structure that allows for wicking of saline water through soil. Soil blending will mix nutrient rich soil with nutrient deficient soil.

3: “Chemical Ex-situ” uses chemical additives, water, and irrigation systems to re-bond the Na & Cl and dilute them into other sources such as soil, the water table, or an alternative onsite water source.

4: “Soil Washing” is the method of remediation that washes soil ex-situ at a treatment facility. This type of remediation largely targets SVOCs, fuels, and heavy metals. It has not currently shown large-scale, cost-effective use for brine spill remediation. (EPA, 1989)

Most brine remediation projects require a combination of various methods to accomplish full remediation.

## CHAPTER II: EX-SITU PRODUCT APPLICATION

### Materials and Methods:

Construction of the testing site occurred on 1 October 2015 and consisted of building five 20-ft by 18-ft squares using a foot of onsite soil to create retention berms for the soils in the research area. Each cell was lined with 40-mm black high-density polyethylene. Contaminated soil from a recent spill was trucked in from Beaver County, OK on 1 October 2015; the soil was heavily impacted by brine and suspected light hydrocarbons. The soil was shredded using the Talon LPE Soil Shredder, seen in Figure 1. The Talon



*Figure 1. Soil Shredder at work during ex-situ product application study.*

LPE Shredder is a top-loaded, truck-pulled device that uses agitation to separate soil into

particles. The “shredded” soil is fed through a conveyor belt out onto the 40-mil HDPE liner in a small approx. 5ft by 5 ft. The end of this conveyor belt is equipped with a spray bar that applied desired liquid chemicals to the soils.

Each product was mixed in water and applied according to manufacturer’s instructions based on contamination level and soil amount, then extrapolated into a single 50-gal treatment for each chemical/control and applied through the shredder. The soil was covered to ensure no cross-contamination through wind movement. The shredder is a top-loaded device used to break the soils down to the smallest possible particle size and ensuring complete coverage of water and product. In theory, this reduces the required water amount to remediate soils by removing the need for product percolation. The shredder was loaded one cubic yard ( $\text{yd}^3$ ) at a time utilizing a bucket loader, to obtain approximately  $2.3 \text{ yd}^3$  of soil per cell. The shredder spray bar operated at a rate of  $10 \text{ gal/yd}^3$ . The soil tested was saline-sodic and remained at that level throughout the entirety of study I. The soil utilized in the test was found to be  $21.3 \text{ dS/m}$  in a 10-point composite sample. Each cell had 5 lbs of over-the-counter wheatgrass hay to function as low-level organic matter to facilitate improvement in soil structure for all products. Cell 3 contained  $0.8 \text{ yd}^3$  less soil due to a limiting factor of transportation of soil by Talon LPE and being filled last. The cells were then covered initially to control water inputs into the remediation site. All cell soils were spread with a bucket loader, which was washed after treated pile to ensure no cross-contamination of products. The soil was shredded in random order of cells 5, 4, 1, 2, and 3. Although the products themselves called for varying timeframes and inputs, the application was simplified to single treatment regime for research purposes. Treatment levels for SoilTech, Chlor-rid, and DeSalt Plus were all



adjusted to utilize a 50-gal treatment. Level of additive was derived from suggested dilution factors. Gypsum was applied based on a recommended 800 lb per acre application, which is considered the high range for brine remediation (Duell, 1991).

During the field phase product-testing, the cells were numbered 1 through 5 and products assigned randomly to each cell by shuffling the safety data sheet of each into a pile, leaving a blank sheet for the control, and picking at random for each number. The chemical treatments were broken down according to the volume of the soil added and in accordance with a 50-gal treatment and applied with a shred treatment.



*Figure 2. Layout of cells during ex-situ product application study.*

A 10-point random composite sample was taken first from a large soil pile on 1 October 2015 as a preliminary indication of the overall soil salinity for all cells. Treatment applications rates are shown in Table 3.

*Table 3. Soil sizes and product application rates for the ex-situ product application study.*

Cell #	Product	Amount	Pile Size	Area of Pile	Gallons of Soil
Cell 1	Gypsum	8lbs 8oz	14ftby17ft	1225ft <sup>3</sup>	520 gal
Cell 3	SoilTech	5 gal	13ftby16ft	1456ft <sup>3</sup>	454 gal
Cell 3	Chlor-rid	½ gal	11ftby15ft	866ft <sup>3</sup>	360 gal
Cell 4	DeSalt Plus	5 gal	13ftby14ft	1233ft <sup>3</sup>	397 gal
Cell 5	Control(Shredded)	-	13ftby16ft	1279ft <sup>3</sup>	454 gal

Soil depth was taken over the first 3 weeks using 4 random points and the direct center of the soil; after 3-weeks the soil lost all aeration brought by the shredding process. Aeration was created by air bubbles inlayed with the soil during the process of shredding. Initially, an average of 6 inch depth was recorded for each cell. This was reduced to 4 inches on the onset of the second week due to the structural loss from sodicity. The loss of soil depth was a vertical loss without the additional horizontal soils; this may be due to soil loss of stored gas - likely atmospheric air - and decreased the movement of air through the soil or aeration. Initially, the soil was covered with 4-mil clear plastic, however on 21 October 2015 the cover was blown free during a storm and 1.8 in of water accumulated on site, as shown in figure 3. This appears in the data, as the introduction of water correlates with a fluctuation of elements within the soil, show in Table 4 and appendix 1

(Sposito, 2004). On 23 October 2015 I collected rain data for the previous 3 days and found that 1.8 inches of rain, roughly the amount of rain seen on average for the total months of October/November/December for Amarillo, had fallen on the site as shown in Table 4. This extreme amount of water led to a failure of the plastic covering cell 2. This resulted in from 100 gal to 250 gal of water added to this cell due to the failure of the cover.

*Table 4. Local weather data for ex-situ study from October 1, 2015 thru May 4, 2016.*

<b>Date Range</b>		<b>Precip (in)</b>	<b>Snow Depth (in)</b>	<b>Snow Fall (in)</b>	<b>Avg Temp (F°)</b>	<b>Max Temp (F°)</b>	<b>Min Temp (F°)</b>	<b>Average Wind Speed (mph)</b>
2015-Oct-1	2015-Oct-10	1.33	0	0	59.875	85.16667	52	10.91667
2015-Oct-11	2015-Oct-16	0	0	0	67.83333	73.5	52.33333	14.53333
2015-Oct-17	2015-Oct-23	1.87	0	0	61.5	68	41.75	10.55
2015-Oct-24	2015-Oct-31	0.28	0	0	53.75	73.5	40.5	12.55
2015-Nov-1	2015-Nov-6	0.07	0	0	56.5	65	34.85714	13.38571
2015-Nov-7	2015-Nov-13	0	0	0	49.42857	65.28571	34.57143	13.12857
2015-Nov-14	2015-Nov-20	0.31	0	0	47.85714	61.28571	35.71429	16.84286
2015-Nov-21	2015-Dec-4	1.12	1.2	1.3	39.14286	54.35714	27.07143	11.85
2016-Dec-5	2016-May-4	5.88	13	12.1	47.91716	63.36686	34.2071	13.24142

Before removal, there were approximately 4 inches of water in the cell (from 3 random sample point average). The water did not fall directly onto the soil but rather through a 2-ft by 4-ft gap, where the wind picked up the liner and allowed the water sitting on top to drain into the cell. Flooding in cell 1 can be seen in Figure 3. An average 15 mph wind hitting the liner from N, NW, S, SW, SE & NE in a period of less than 5 hours, led to



*Figure 3. Flooding event occurred on October 21, 2015 in cell one during ex-situ product application study.*

water encroachment on the cells. Wind gusts reached as high as 25 over the two-day period. The decision was made to flood the rest of the cells. The amount of water added was calculated by taking rainfall data = 1.8 in = .623 gal. The area of each enclosed cell 20 ft x 18 ft = 360 ft<sup>2</sup>. 360 ft<sup>2</sup> x .15 ft {1.8 in} = 54 ft<sup>3</sup>. 54 ft<sup>3</sup> = 403 gal. 403 gallons of water were added to cells 2, 3, and 5. The cover for cells 1 and 4 were completely removed and both cells were flooded. Identical drainage systems were installed in all 5 cells on 25 October 2015 to remove stagnant water.

### **Sampling:**

The testing phase consisted of an initial 10 weeks of sampling after addition of the products which occurred from 2 October 2015 through 11 December 2015, as show in Table 5. The 11 December 2015 sample was missed due to extreme weather. A 6-month

sample was taken to show representative progression of each product following onsite testing on 20 May 2016.

*Table 5. Linear timeline of major events for the ex-situ product application study.*

<b>Ex-Situ Product Application Study</b>		
<b>Date:</b>	<b>Sample Type:</b>	<b>Event:</b>
1 Oct 2015	10 point composite sample	Soil delivered from Beaver Oklahoma.
2 Oct 2015	Soil added to each cell and 5 point sample	Testing area was completed
10 Oct 2015	5 point sample	
16 Oct 2015	5 point sample	
21 Oct 2015		Storm removes Visqueen cover from cells 2, 3, 5. Cells 1, 4 were flooded.
23 Oct 2015	5 point sample	
25 Oct 2015		Identical drainage systems installed into all 5 cells and stagnant water removed.
31 Oct 2015	5 point sample	
6 Nov 2015	5 point sample	
13 Nov 2015	5 point sample	
20 Nov 2015	5 point sample	
4 Dec 2015	5 point sample	
11 Dec 2015	Weather forces loss of 10 <sup>th</sup> sample period	

The cells were then covered with transparent Visqueen for weeks 1-3 of the research and uncovered after week three. Small drainage systems were installed in week 4 to allow removal of excess water. An initial 10-point soil composite was taken from bulk untreated soils at a depth of > 2.5 cm Weekly 5-point composite soil samples were

collected using randomly generated numbers within each cell's individual grid pattern. Five-point composite samples were taken at a depth just below any panned sodic soil generally > 2.5 cm.

Soil samples were collected at weekly intervals from 2 October – 4 December, and soils in each phase were analyzed for: sodium adsorption ratio (SAR), total soluble salts (TSS), cation exchange capacity (CEC), sodium, calcium, magnesium, potassium, chlorides, and pH. The 10-week sampling period was scheduled to occur from 2 October – 11 December. The 11 December date was missed due to severe weather occurring over a period of 4 days. These were 5-point composite samples taken from randomly generated grid positions of a product's sample area. Areas were created using an X & Y axis grid system (1 ft x 1 ft grid squares). East to West was designated as the X axis and North to South as the Y Axis. The sampling start point and 1 ft intervals were marked on the black 40-mil liner in each cell. Samples required at least 2 inches of soil, or the Y axis was re-randomized to a number within the area. Numbers were randomized using a random number generator application available on cellular phones on a weekly basis. The final sample was taken 6 months later to give a representative update of progression.

#### **Determination of Soil Type:**

Soil type was determined utilizing the following steps:

1. Soil was spread on dry paper towels. All organic matter (roots, sticks, plants) and rocks were removed from the soil.
2. The soil was finely pulverized using a mortar and pestle.

3. The soil was added to a large glass jar. The jar was filled to  $\frac{1}{4}$  with soil.
4. Water was added to make the container three-quarters full.
5. A teaspoon of non-foaming dish soap was added.
6. The lid was put on firmly and the jar was shaken vigorously for 10 minutes. This shaking allowed aggregates to separate in the soil.
7. After 1 minute the sand location was annotated on the jar.
8. After 3 minutes, the silt location was annotated on the jar.
9. After 20 minutes, the clay location was annotated on the jar.
10. All levels were confirmed 1, 3, and 5 hours after research.

Soil samples were prepared for ICP-MS using the following procedure.

**Testing Preparation:**

1. 4oz of soil was placed in a paper bowl.
2. Samples were placed in an incubator set up at 105°C and checked every 3-4 hours until completely dry.
3. All organic matter and stones were removed.
4. Samples were transferred to a coffee grinder and ground for 10-15 seconds or until powdered.
5. Samples were placed in a clean sample jar.
6. All equipment was washed and the process repeated.
7. Samples were transported to Servitech laboratory in Amarillo, Texas for analysis.

**Testing and Reasoning:**

The tested and reasoning for those tests are:

All samples were tested for the following: chloride ( $\text{Cl}^-$  data can be found in appendix II), potassium ( $\text{K}^+$  data can be found in appendix IX), sodium ( $\text{Na}^+$  data can be found in appendix III), calcium ( $\text{Ca}^{++}$  data can be found in appendix IV), and magnesium ( $\text{Mg}^{++}$  data can be found in appendix VII). Variables also tested were Total Soluble Salts (TSS data can be found in appendix II), Cation Exchange Capacity (CEC data can be found in appendix VI), sodium absorption ration (SAR data can be found in appendix X) and pH (pH data can be found in appendix VIII). Following is a short description of each and the reasoning for the testing.

### **Tested Variables:**

The variables analyzed for this research are:

Sodium ( $\text{Na}^+$ ): Depending on the stratigraphy of the land, total levels of naturally occurring  $\text{Na}^+$  can vary between 150 ppm and 25,000 ppm.  $\text{Na}^+$  functions similarly to potassium ( $\text{K}^+$ ) in relation to both soils and plants. Plants take up  $\text{K}^+$  via an ion transporter and sequester it within the root structure for storage.  $\text{Na}^+$  is taken up by these ion transporters that cannot differentiate the similar elements. The  $\text{Na}^+$  moves throughout the plant and, depending on the soil concentration and plant type, can be toxic. Most crops require an EC of 3 dS/m or less to have full yield (Essington, 2014). Sodium can be extremely detrimental to soil structure. A single sodium atom will partially bond with various clay particulates; this bond causes the clay to disassociate. There is a direct relationship between sodium influx and soil disassociation as well as a size dependency favoring smaller particles, due to increased effect by charge. Increasing the sodium causes further disassociation on any soil, but has an exaggerated effect on smaller soil particles (Deuel, L.E., 1991).



Calcium ( $\text{Ca}^{++}$ ): Calcium amendments to soil can improve aggregation of soils.

Improvement in aggregation is the loosening of soil structure and allowing for root growth. Improvement of soil aggregate leads to increased soil porosity due to calcium positive bonds that aid soil structure. The positive bond created by calcium results in increased soil porosity. This bottleneck creates an insolubility of the NaCl bonding in precipitate and is an effect of the Gapon selectivity coefficient. This reveals that sodium is more inclined to bond with partial soil charges and force calcium out of the structure. Therefore, large amounts of water are required when using a high calcium-based remediation technique (Almodares et al. 2008). Calcium is also a micro-nutrient for plants and its uptake is dependent on a favorable calcium-to-total cation ratio (Carter et al 1990).

Magnesium ( $\text{Mg}^{++}$ ): Magnesium is an essential nutrient for plant uptake and is used in the creation of chlorophyll. The magnesium atom is a central atom in the chlorophyll molecule. Magnesium has an affinity for motility in soil; it is thus more likely to be excreted in brackish soils (Senbayram, 2015). Increased amount of calcium increases magnesium uptake by plants (Fageria, 2009). Brine with high levels of magnesium will produce lower impacts on clay soils and they are less likely to become ionized (Alperovitch, N. 1981)

Potassium ( $\text{K}^{+}$ ): Potassium is a major nutrient in higher plants, it plays a role in turgor regulation, charge balance, leaf movement, and protein synthesis. Most terrestrial plants sustain growth at widely varying external  $\text{K}^{+}$  concentrations ranging from around 10  $\mu\text{M}$  to 10 mM. Evaluation of many experiments at millimolar  $\text{Na}^{+}$  concentrations indicates  $\text{Na}^{+}$  blockage of the  $\text{K}^{+}$  influx pathway (Zhu et al. 2011).

Chlorides ( $\text{Cl}^-$ ): Chloride exists in soils as the chloride ion ( $\text{Cl}^-$ ) at average concentrations of 100 ppm (Shulte, 2016). Plant uptake of chloride is an essential micronutrient used to control osmotic pressure in the root system, and cation exchange. The absolute threshold is specific to plant species and can occur from 300 ppm to 2000 ppm. Chloride becomes toxic as it binds to create salts ( $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$ ). Chloride-based salts are highly soluble but difficult to remove from top soil locations. Chlorides will inhibit water availability for plants and slow nutrient absorption, as well as inhibit seed germination (White, 2001).

pH: pH in soil which is a measure of hydronium ions [ $\text{H}^+$ ] in a solution. Plant success and soil activity occurs in a pH range of (5.5 - 8). pH is a confining variable to processes such as microbial activity, nutrient availability, crop production, nutrient uptake by plants, and balanced crop nutrition and health. When pH drops below 4.5, aluminum toxicity occurs by creating a favorable environment for aluminum solubility. Soluble aluminum will retard plant growth (Gazey, 2016). The amounts of soils acidic or basic cations or anions will determine the soil's pH. Drilling fluids used in hydrocarbon removal tend to be alkaline in nature and have a  $\text{pH} > 10$ . The United States has a mandated discharge range of 6-9 p.H. for oilfield waste which can include combinations of drilling fluids and produced water. (Bleckman, 1988). Plants grown in acidic soils of  $\text{pH} > 7$  will have deficiencies of  $\text{N}^+$ ,  $\text{P}^{++++}$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , or  $\text{Mo}^+$ . These deficiencies can lead to reduction of plant and root growth (Marschner, 2012).

### **Calculated Variables:**

The calculations used to test variables are:

Cation Exchange Capacity (CEC): CEC is a value given to express the cation adsorption process found within soil. The test reveals interactions between the surface functional group and the adsorbed ion. The surface functional group within this research is described as the soil itself. The focused ions for this research are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ , and  $\text{Ca}^{++}$ , though the CEC includes all partially-charged soil ions.

SAR (sodium adsorption ratio): SAR is calculated as  $\text{Na} / \sqrt{\frac{1}{2} \text{Ca} + \text{Mg}}$ . A SAR value above 13 shows an increased dispersion in soils.

Electrical Conductivity (EC): EC is another term used for soluble salt. The electrical conductivity is a measurement for levels of salinity in soil. The measured unit for EC is dS/m.

Total soluble salts (TSS): Soluble salts are inorganic soil constituents which have a high water solubility. They are accumulated through mineral degradation and carried through precipitation.

The relationship between EC and TSS is as follows:

$$\text{TSS (mg/L or ppm)} = \text{EC (dS/m)} \times 640 \text{ (Duell, 1991)}$$

### **Other Important Tests:**

Other variables are also important in brine remediation. These variables can be tested and utilized to determine the impact of brine contamination:

Boron: Plant function is limited by any deficit of boron because of its role in metabolism from production of nucleic acids (nucleic acids). Uptake occurs in plants with a neutral to

slightly acidic soil pH (5-6 pH). Most crops function with a Boron soil concentration of 1-4 ppm (Hall, 2016). Boron exists in soil in ionic forms  $B_4O_7^{2-}$ ,  $H_2BO_3^-$ ,  $HBO_3^{2-}$  and  $BO_3^{3-}$  (Essington, 2014). Boron toxicity occurs  $< 5$  ppm in areas of significantly low rainfall, resulting in minimal soil leaching through the soil. Methods for removing toxic levels of boron are similar to soil remediation of  $Na^+$  (Kelling, 1999).

Nitrogen: Availability of nitrogen for plants is only through the inorganic forms including the ammonium ion ( $NH_4^+$ ) and the nitrate ion ( $NO_3^-$ ). Ammonium is a fixed compound in the soil at quantities 2-10 ppm and serves as a transition molecule in the nitrogen cycle from organic nitrogen ( $N^+$ ) to the nitrate ion ( $NO_3^-$ ).  $NO_3^-$  found in soils concentrations of 10-30 ppm is the most mobile and available form of plant nitrogen (Masclaux-Dabresse et al. 2009). Two nitrate transport mechanisms functioning in plant roots take up and distribute Nitrogen throughout the plant. Nitrogen present in soil humus can contain up to as much as one half amino acids ( $NH_2$  amino acid). 75% of amino acids in soil are neutrally charged. These amino acids are attached to more complex R groups of largely carbon, oxygen and hydrogen (Albert et al. 2012).

Carbonates: The carbonate ion ( $CO_3^{2-}$ ) exists at a pH above 8.3 and is an important factor in the carbon cycle. The ion itself reacts within the soil to form compounds such as calcium carbonate ( $CaCO_3$ ) or magnesium carbonate ( $MgCO_3$ ). Carbonates have a vital role as a buffer to soil pH. The apportionment of carbonates in the soil correlates to impact soil fertility, erodibility, and water capacity (USDA, 2016). In plants, carbonates serve as readily available forms of essential plant nutrients such as calcium, magnesium, and iron. If a carbon source is lacking in other places,  $CO_3^{2-}$  can be taken up by plant roots as a last resort (B~Azeale 1924).

Bicarbonates: Bicarbonates ( $\text{HCO}_3^-$ ) are abundant, with a soil pH greater than 7.5.

Bicarbonates exist in soil as sodium bicarbonate ( $\text{NaHCO}_3$ ) and potassium bicarbonate ( $\text{KHCO}_3$ ). The bicarbonate ion will bind with magnesium and calcium, creating magnesium carbonate ( $\text{MgCO}_3$ ) and calcium carbonate ( $\text{CaCO}_3$ ). Bicarbonate will bind to calcium from calcium phosphates, making the phosphate ion ( $\text{PO}_4^{3-}$ ) more readily available for plant uptake. Bicarbonates reduce nutrient absorption in plants by inhibiting iron uptake, causing plants to turn a pale yellow color (Robbins et al. 1989). Bicarbonate is added to soils through irrigation water at concentrations of 0-600 ppm. Bicarbonate concentrations beyond 125 ppm can inhibit nutrient uptake in plants as well as soil crusting (Gregory 2001).

Sulfates: Sulfur is a vital macronutrient for plants used for production of amino acids and proteins (Leustek et al. 1999). It is created by oxidation of sulfur in soil organic matter. Plants consume sulfur through membranous channels at the root level in the anionic form, sulfate ( $\text{SO}_4^{2-}$ ). In soil, sulfate will appear most often as calcium, magnesium, or sodium salts. When added to the soil, sulfate will bind to sodium and help leach it through the soil (Robbins et al. 1989).

ESP (exchangeable sodium percentage):  $\text{ESP} = \{(\text{Na})/(\text{Ca} + \text{Mg} + \text{K} + \text{Na})\} \times 100$ . ESP is the percentage of sodium that is exchangeable within a tested soil. ESP gives a percentage of sodium that is exchangeable for plant uptake within soil structures. ESP is a direct indicator of sodic soils. The predicted ESP for Western states is 11.9. This is considered slightly sodic. Extreme sodicity is reached at an ESP of 25 (Bresler et al. 1983).

**Detection Methods:**

The following methods were used in the soil process of soil analysis:

Extractable chloride ( $\text{Cl}^-$ ): was prepared with  $\text{CaNO}_3$  and a flow injection analysis utilized to determine mg/kg extractable in soil.

Calcium ( $\text{Ca}^{++}$ ), magnesium ( $\text{Mg}^{++}$ ), sodium ( $\text{Na}^+$ ), and potassium ( $\text{K}^+$ ) were prepared with ammonium acetate ( $\text{NH}_4\text{CH}_3\text{CO}_2$ ) and were detected by utilizing inductively coupled plasma mass spectrometry (ICP-MS) to give a value of mg/kg of soil.

Soluble Salts were tested on a 1:1 water-to-soil ratio using a conductivity meter to give conductivity in dS/m.

Cation Exchange Capacity is the total capacity for a soil to hold exchangeable cations, reported in mEq/100 g (Rayment, 2011).

**Statistical Methods:**

The statistical analysis of the data was conducted on the following steps:

Data Normalization: The first step of statistical modeling for this research was defining the data as parametric or non-parametric. Non-parametric data skew the results of the testing and parametric data utilization brings the data closer to the true results. This normalization allows for a more concise result on the Analysis of Variance test (ANOVA), by consolidating variance within the data. The need for normalization is shown by comparing the parametric and non-parametric data. The histogram function in Excel was used for determination of data normality (Kroese et al. 2013). The results from these graphs showed that all data sets, except pH, required normalization.

The Non-parametric data show increased distribution between the highs and lows. The normalized data push the data closer to normalization by decreasing the variance of the outliers. Non-parametric data was normalized by deriving the logarithm [ $\log(\text{RESULT})$ ]. This data was then used in all statistical analyses to retrieve the truest possible results (Kroese 2013).

ANOVA: The ANOVA was utilized to determine if each product (1, 2, 3, or 4) outperformed the control (5) by determining significance between samples and within sample sets. All methods used in the field were assigned random product numbers. The control group was designated product 5. This group was the basis of comparison to accept or reject the null hypothesis. The null hypothesis is  $H_0$  and the equation for it is:

$$H_0 : \mu_1 = \mu_2 = \dots = \mu_k.$$

This would signify that all groups are equal and there is no variance between any dataset. The alternative to this is  $H_1$ : treatment level means not all equal. The ANOVA model used for this analysis omitted the 1 October 2015, which is a visualized starting point in graphic (Kroese et al. 2013). The ANOVA model, Table 6, showed the P value for soluble salts as  $> 0.05$ , which indicates significance within variance between the two groups. All ANOVA tests that revealed significance were analyzed through the Tukey-Kramer Honest Significant Difference (HSD) Test. Tukey-Kramer Honest Significant Difference (HSD) Model was chosen for its ability to display significance across product ranges (Kroese et al. 2013).

Table 6. Analysis of variance (ANOVA) statistical test utilized for determination of variance for soluble salts between product groups and the control group.

ANOVA: Two-Factor Without Replication for Soluble Salts						
<i>SUMMARY</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
2015 Oct 2	5	7.148482	1.429696	0.030083		
2015 Oct 10	5	7.070546	1.414109	0.007963		
2015 Oct 16	5	7.467543	1.493509	0.013282		
2015 Oct 23	5	7.625051	1.52501	0.022509		
2015 Oct 31	5	6.574887	1.314977	0.021742		
2015 Nov 6	5	7.770427	1.554085	0.021721		
2015 Nov 13	5	8.036431	1.607286	0.030971		
2015 Nov 20	5	7.59482	1.518964	0.010236		
2015 Dec 4	5	6.58639	1.317278	0.012989		
2016 May 20	5	7.666691	1.533338	0.014464		
Product 1	10	14.92009	1.492009	0.009667		
Product 2	10	13.41352	1.341352	0.015435		
Product 3	10	14.0553	1.40553	0.018284		
Product 4	10	16.00105	1.600105	0.028633		
Product 5	10	15.1513	1.51513	0.014907		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Rows	0.440016	9	0.048891	5.141591	0.000171	2.152607
Columns	0.401517	4	0.100379	10.5564	9.19E-06	2.633532
Error	0.342319	36	0.009509			
Total	1.183853	49				



### Statistical Analysis:

The hypotheses of interest in an ANOVA are as follows:

$$H_0: \mu_1 = \mu_2 = \mu_3 \dots = \mu_k$$

The statistical modeling used for the ANOVA analysis model is:

$$H_1: \text{Means are not all equal.}$$

If  $H_0$  is accepted, then no significant difference was found in the analysis. This result shows that compared against each other, no specific treatment performed differently than any other treatment.

If  $H_0$  is rejected, then the  $H_1$  is accepted and the data show a significant difference between two data sets. These data were run in a Tukey model to determine which group showed significant difference. All P values were set to 0.05 for all analyses and models. The ANOVA was used to determine if significant difference exists between various data sets. This test was used as a lead device to determine which data set needed to be run through the Tukey analysis. The Tukey analysis is used to compare pairwise data sets. Since all sample sizes are equal, exactly  $1-\alpha$  (Steward-Oaten, 1995).

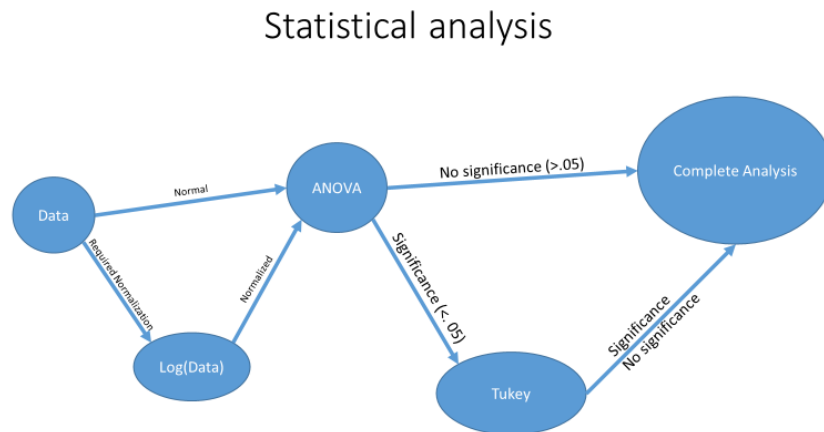
Tukey Model:

$M$  = treatment/group mean

$n$  = number per treatment/group.

### CHAPTER III: RESULTS

Statistical analysis tested each data subsets against the same subset of other products. The products D+, ST, CR, GYP and the control are defined as the groups within the Analysis of Variance Test and Tukey HSD. The weekly samples for each product represents the data subsets: sodium adsorption ratio (SAR), total soluble salts (TSS), cation exchange capacity (CEC), sodium, calcium, magnesium, potassium, chlorides, and pH. Figure 4 shows how the data was handled. All data included in analysis were samples from dates: 2 Oct 2015, 10 Oct 2015, 16 Oct 2015, 23 Oct 2015, 31 Oct 2015, 6 Nov 2015, 13 Nov 2015, 20 Nov 2015, 4 Dec 2015, and 20 May 2016. The initial 10-point sample taken on 1 Oct 2015 was omitted to reduce watering down of data analysis. A total of 10 data points are used for each analysis and each follow Figure 4.



*Figure 4. Destination of elemental data taken from 10 samples and run in product groupings.*

All statistical analysis was compared against Product 5, which was the control during the research. The P value for all tests was set to 0.05. Results  $< 0.05$  and  $> 0.10$  will be

discussed as results that could indicate research in the future and will be referred as “approaching significance”.

### **Chloride:**

The ANOVA results for chlorides (Table 7) revealed a p-value of 0.310; this value fails to reject the null hypothesis. Further evaluation of the data reveals that products all moved within the normal range of data compared to the control. All other products fell within the normal range with the averages slightly changing but lacking significance.

*Table 7. Analysis of Variance (ANOVA) comparing all product chloride levels.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.115	4	.029	1.234	.310
Within Groups	1.044	45	.023		
Total	1.158	49			

### Sodium:

The ANOVA results for sodium failed to reject the null hypothesis (Table 8). The p-value for sodium was 0.044. Significance appeared between ST and D+.

*Table 8. Analysis of Variance (ANOVA) comparing all product sodium levels.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.155	4	.039	2.673	.044
Within Groups	.654	45	.015		
Total	.809	49			

D+ increased sodium, likely through increased motility of sodium into upper soil layers.

D+ had the highest sodium content during the temperatures between 18°C and 24°C of the study and levels 3-fold higher than the other products during period of temperate rainfall. After 6 months, this product fell back into the normal range.

ST consistently had the lowest sodium levels but failed to prove significant in relation to the control. As expected, sodium levels in all soils increased following a rainfall due to the wicking back to top soil. No product showed significance when compared to Product 5 (Control) various mechanisms within the products. It is likely ST binds up small insignificant amounts of sodium, reducing their binding affinity within soil pore structure.

## Calcium:

Significance Tables are utilized to display data that has completed the statistical analysis and was significant in both tests. These tables represent significant increases or decreases in elemental levels across sample periods. The arrows indicate how the first selected product compared to the second product located on the opposite axis. The ANOVA model gave significance for calcium was below the 3 significant digits used for analysis and is displayed as 0.000. This value shows definitive significance for calcium levels across various products. Table 9 is significance table for calcium ST Decreased in calcium in relation to Gyp. Across the spectrum, ST significantly decreased the calcium

*Table 9. Significance table for calcium, results derived from positive ( $\alpha < 0.05$ ) ANOVA and Tukey results.*

Calcium	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1		↑↑↑	↑↑↑		
Product 2	↓↓↓			↓↓↓	↓↓↓
Product 3	↓↓↓				
Product 4		↑↑↑			
Product 5		↑↑↑			

against every product with exception of CR. ST significantly decreased compared to Gyp

but was unable to show significance in relation to the control.

Boxplots Figure 5, gives insight into overall range of normalized data for each product and reveals outliers.

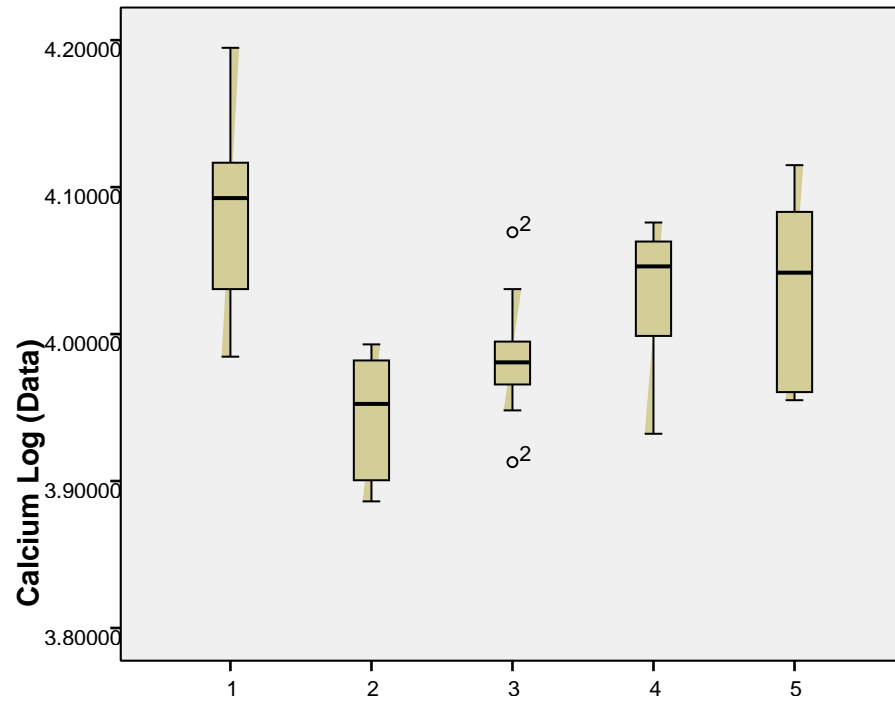


Figure 5. Normalized Boxplot for calcium.

### Total Soluble Salts (TSS):

Total Soluble Salts significance table is displayed in Table 10.

*Table 10: Significance table for total soluble salts, results derived from positive ( $\alpha < 0.05$ ) ANOVA and Tukey results.*

Table Soluble Salts	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1					
Product 2				↓↓↓	↓↓↓
Product 3				↓↓↓	
Product 4		↑↑↑	↑↑↑		
Product 5		↑↑↑			

Total Soluble Salts reveals the most about each of these products. ST showed significant decrease in TSS compared to the control and maintained reduced levels over the 6-month period.

There is an increase in total soluble salts and fluctuations within the D+ due to its extreme susceptibility to external forces, as demonstrated in the data.

On 2 October 2016, the water added during the process of application caused the first major increase. D+ saw a decrease in total value following this, but was still above all other products on 10 October 2015. On 23 October 2015, I collected rain data for the previous 3 days and found that 1.8 inches of rain, roughly the amount of rain seen on average for the total months of October/November/December for Amarillo, had fallen

Figure 6 reveals increases in TSS for D+ during large rain events.

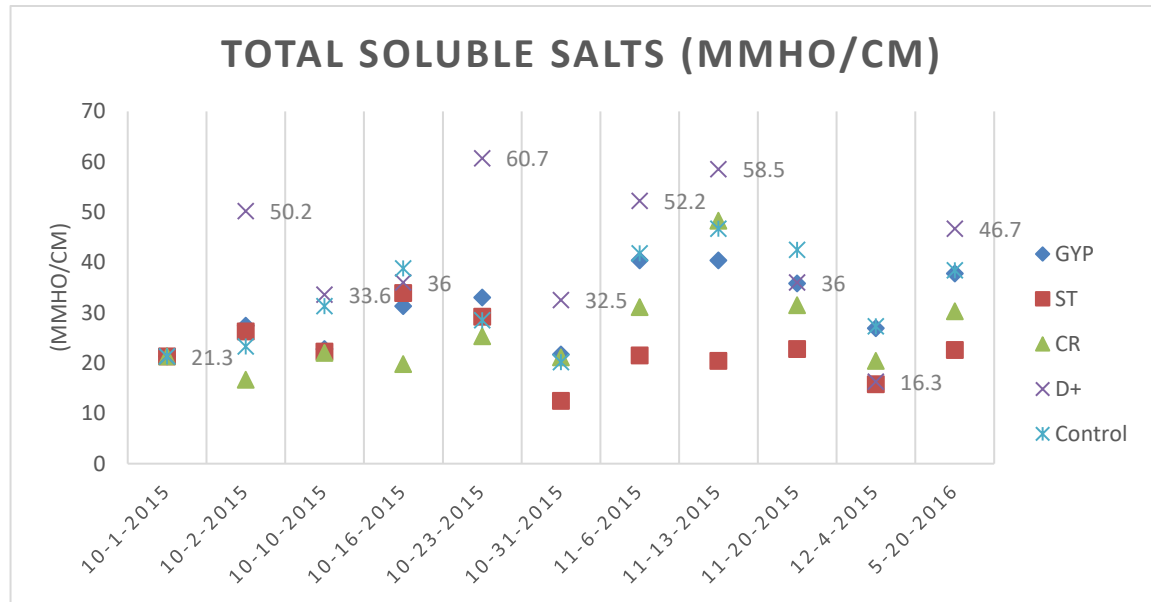


Figure 6. Total soluble salts results by date. High levels for D+ correlate with rain events.

On 4 December 2015, all cells accumulated 1.3 inches of snow, causing a final drastic dip in TSS data. This reveals that this product will increase TSS during temperatures of 18 °C and decrease TSS during snow and freezing temperature. The 4 December 2015 data point for D+ can be considered an outlier and may not be explained by temperature. Considering all products resulted in a decrease in TSS during this time, we may conclude that D+ increases variability in TSS and makes it more reactive to water and temperature. There is no doubt the other increases are explained by water. This product drastically fluctuates TSS correlative to water inputs during temperate timeframes.



### Cation Exchange (CEC):

Cation Exchange Capacity revealed significance, illustrated in Table 11, in the ANOVA model with a p-value of 0.036 observed between ST and 4.

As previous analysis showed, ST reduced the CEC in relation to D+. This value reduction appeared in 4 out of 5 significant evaluations.

*Table 11. Significance table for cation exchange capacity, results derived from positive ( $\alpha < 0.05$ ) ANOVA and Tukey results.*

CEC	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1					
Product 2					
Product 3				↓↓↓	
Product 4			↑↑↑		
Product 5					

### **Magnesium:**

The ANOVA results, Table 12, for magnesium failed to reject the null hypothesis. A p-value of 0.109 required further analysis to determine possible significance as seen in Table 12.

*Table 12. Analysis of Variance (ANOVA) comparing all product magnesium levels.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.113	4	.028	2.014	.109
Within Groups	.629	45	.014		
Total	.741	49			

The Tukey-HSD analysis revealed close significance difference in magnesium between ST and D+, as previously magnesium was slightly increased in D+ and ST saw an average decrease compared to the group. Neither the increases nor decrease were within the significant range.

### Soil pH:

ANOVA analysis, Table 13, showed no significance in the soil pH. These data were not normalized because of equal distribution of the raw data. This is the only data set that was not normalized.

*Table 13. Analysis of Variance (ANOVA) comparing all product soil pH levels.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.027	4	.007	.467	.760
Within Groups	.646	45	.014		
Total	.673	49			

### Potassium:

The ANOVA statistical analysis for potassium, Table 14, revealed a p-value of 0.027.

This value is consistent with a rejection of the null hypothesis. All means are not equal and the significance came largely from D+ showing an increase in potassium in relation to products 2 and 3. This data shift was not significant in relation to the control. D+ data outlier during cold weather saw a reduction in potassium; this reduction appeared across all treatment and in all alkali metal and alkali earth metal groups.

*Table 14. Significance table for potassium, results derived from positive ( $\alpha < 0.05$ ) ANOVA and Tukey results.*

Potassium	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1					
Product 2				↓↓↓	
Product 3				↓↓↓	
Product 4		↑↑↑	↑↑↑		
Product 5					

### CHAPTER III: STUDY II: CONTROLLED ENVIRONMENT GERMINATION

The controlled environment germination phase was conducted at West Texas A&M University utilized Texas Department of Transportation (TEXDOT) warm season mix road grow. Allow vegetation the best-case scenario for germination by mixing the contaminated soil with clean soil to dilute (1:1) the salt effects on soils structure and water adequately. An excess of salts in the soil will cause plants to react as if drought conditions were present (Blum 1988). This is due to a restriction on water uptake due to ionic bonding, by some salts, in the soil. This reduction of water availability causes stunted growth in plants, restricted root growth and general plant destruction. Salts are naturally occurring and are constantly balanced by plants, rain, wind and other functions (Blum 2005).

#### **Methods:**

The controlled environment laboratory germination phase began on 20 January 2016, show in Table 15. Contaminated soil was mixed at a 1 to 1 ratio with clean soil. The controlled environment laboratory germination phases conducted at West Texas A&M utilized Texas Department of Transportation (TEXDOT) road grow warm season mix, Green Sprangletop (*Leptochloa*), Sideoats Grama (*Haskell*), Blue Grama (*Hachita*), Buffalograss (*Texoka*), Illinois Bundleflower (*Desmanthus*). The seeds were applied at a rate of 10 pounds of seed per acre (Ogle, et al. 2010). The clean soil was a clay-loam

collected in Beaver, Oklahoma. The soil from each cell was mixed in a cement mixer and placed into a 1-gal plastic plant bowl. These plant bowls were labeled with the corresponding cell identifier. The greenhouse was constructed in a West Texas A&M University laboratory. The soil was watered until 28 March 2016. The total water added was equal to 4.5 inches of rain or equal to 25 inches yearly.

*Table 15. Timeline for controlled environment germination study.*

Controlled Environment		
20 Jan 2016	EC reading taken	Laboratory phase begins “Greenhouse” phase begins.
7 Feb 2016		Malfunction of the heater in the greenhouse.
7 Feb 2016	Germination count = 0	

## Results

These greenhouse data revealed no sustained growth for any product. On 7 February 2016, a heater malfunction was discovered. This was corrected, but did not change the outcome. The average EC per of soil before being diluted was 31.6 dS/m; when combined with non-contaminated soil background levels, this level ranged from 16.7 dS/m to 22.5 dS/m. The EC was substantially higher than the levels for sustainable plant growth which occurs at an EC of 4 dS/m according to the Natural Resources Conservation Service (Horneck et al. 2007). Some salt-resistant crops such as sorghum and wheat can withstand an EC of 15 dS/m with substantially reduced germination rates. The most salt-tolerant plant will show a 50% reduction in yield at 18 dS/m and non-

tolerant plants have the same reduction at levels below 8 dS/m (Waskom et al. 2010).

This was likely compounded by a malfunctioning temperature gauge that caused a temperature increase from 25.6 °C to 32.2 °C over a period of 2 1/2 days between watering. This occurred on 1 February 2016 and the system shock likely forced any possible growth to become dormant in the high-stress environment.

The controlled environment lab germination phase was unsuccessful in obtaining any growth due to a variety of reasons. The most influential was excessive salinity of the testing soil. Soil that is going to be tested for germination should fall between an EC of 12 dS/m and 16 dS/m if testing highly tolerant plants in a controlled environment. Other problems that occurred during research include a lack of proper lighting, system-wide crash caused by the malfunction of the thermal regulation device.

## CHAPTER IV: STUDY III: EX-SITU GERMINATION

The field phase on-site planting occurred in early spring on 5 March 2016. The timeframe was chosen for its closeness to spring/summer to allow the most suitable climate for growth during the germination phase (Long et al. 2013).

### **Methods:**

The top soil had become hardened through the panning process. The solidified top layer of brackish soil, pan, was broken up using a hand-held hoe. The seeds were applied at a rate of 10 pounds of seed per acre (Ogle, et al. 2010). West Texas A&M utilized Texas Department of Transportation (TEXDOT) warm season mix road grow. Green Sprangletop (*Leptochloa*), Sideoats Grama (*Haskell*), Blue Grama (*Hachita*), Buffalograss (*Texoka*), Illinois Bundleflower (*Desmanthus*). This was measured using a clean glass quart container with the proper weight tested and labeled in the lab. The proper weight of seeds was determined by dividing 10 lbs/43560 ft<sup>2</sup> \* cell ft<sup>2</sup>. Seeds were spread by hand, throwing equal density in each area. A water hose was used to moisturize the top soil of each cell without pooling water on the soil; this amounted to 50 gal of water in each cell. The water was applied through a large tank.

## Results

Cells 3 and 4 experienced growth (Figure 7), but this was achieved in the initial phase. It is unlikely the growth can be attributed to product D+ or CR but rather an underlying external factor. The ridge was approximately 1 in taller than the rest of the cell and formed from the collapse of the rest of the soil due to the sodicity forces. This ground contained a high number of large pebbles and rocks. The combination of these two allowed for the germination of seedlings after a heavy rain. The salinity was pushed to



*Figure 7. Ridge growth observed during ex-situ germination study in cell 4 on 24 October 2015.*

the soil below the ridge for a short time, allowing the germination of the seeds present from the application of organic matter. The growth quickly became stressed after water evaporated and sodicity returned to ridge.



## CHAPTER IV: DISCUSSION

**Product Overview:** The proprietary nature of these products prevents full knowledge or disclosure of their exact chemical composition. It is hypothesized that these products are using gypsum or mimicking the chemical reaction with varying levels. The chemical reaction for gypsum remediation is similar to the other chemicals. Thus, the chemical reaction for gypsum is explained by exchanging  $\text{Ca}^{2+}$  &  $\text{SO}_4^{2-}$  for  $\text{Na}^+$  &  $\text{Cl}^-$ . The basic interaction of the products in these cells can be assessed by comparing the chemical reaction of gypsum with the exchange of  $\text{Ca}^{2+}$  &  $\text{SO}_4^{2-}$  with unbound  $\text{Na}^+$  and  $\text{Cl}^-$ . These chemicals also have a surfactant interaction, which aids in unbinding the  $\text{Na}^+$  partial bonds to soil particles and reduce hydrocarbon interaction.

**Gyp: Calcium Sulfate ( $\text{CaSO}_4$ , gypsum):** The suggest EC product range is 4 dS/m – 7 dS/m with no soil dilution. Gypsum application is the traditional method used for produced water remediation. Its application requirements to remediate brine-contaminated soils ranges from 4 tons per acre to 10 tons per acre. (Gawel, 2006). The lack of soil solubility poses a major problem with gypsum. The leeching of the salts from soil is a process primarily performed with irrigation and addition of large amounts of water to facilitate sodium exchange within the soil pores (Gawel, 2006). A lack of rainfall and the addition of gypsum will make plant growth less likely due to increased osmotic potential and top soil panning (Abrol et al. 1979). The most conservative estimates suggest a minimum of 3 – 4 years after initial remediation steps to see substantial

progress in soil and gain growth without flooding or irrigation in sodic and saline conditions (Abrol et al. 1979). This effect is lengthier in smaller aggregate soils such as clays. The nature of the bonding makes gypsum a useful tool in a narrow and specific subset of brine spills consisting of very low-level contamination bordering on 4 dS/m. At this level, NaCl is 22.3% less soluble than at 0.65 dS/m (Sposito, 2008). This is caused by a constant bond switch within the precipitate between the constituent groups. A 2015 study testing gypsum effects on hydraulic conductivity showed that gypsum was most effective at reducing electroconductivity in larger aggregate soils such as Loamy-Sand and significantly decreased with diminishing charged particle sizes (S. Ahmad et. al, 2015). In pure H<sub>2</sub>O and NaCl precipitate, the solubility will reach a bottleneck after 0.65 dS/m. This bottleneck creates an insolubility of the NaCl bonding in precipitate and is an effect of the Gapon selectivity co-efficient, which reveals that sodium will be more inclined to bond with partial soil charges and force calcium out of the structure (Sposito, 2008). The use of gypsum can negate the effects of sodium ions on soils (L.E. Deuel, 1991). Gypsum should only be utilized in well-drained areas and as a method to decrease NaCl by incremental amounts from 6 dS/m within the germination range of the plant selected for growth (Almodares et al. 2008).

Gypsum as a single treatment needs is dependent on the nature of the brine spill: increasing the amount of Ca<sup>++</sup> if the soil is higher in Cl<sup>-</sup> or using SO<sub>4</sub><sup>-</sup> if higher in Na<sup>+</sup> concentrations (Essington, 2015). Effectiveness of this treatment is increased by allowing for a favorable solubility. Mixing the spill with small amounts of non-contaminated soil will lower the soil contamination.

Table 16 shows that Gypsum (1) did not reduce or increase the chlorides outside the

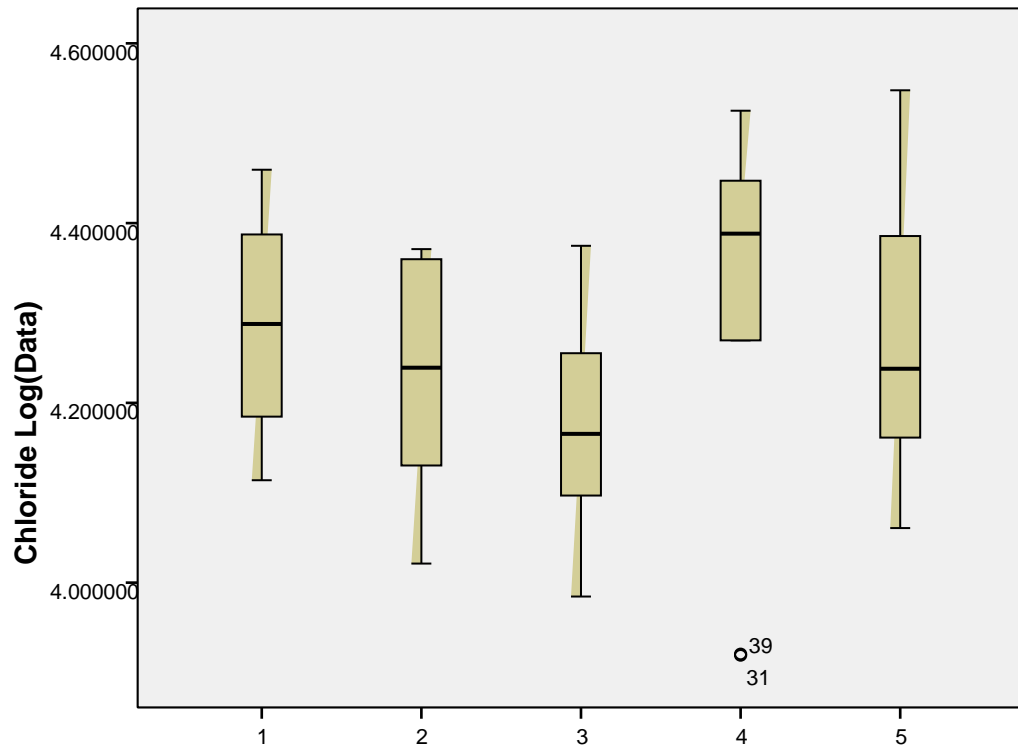


Figure 8. Boxplot of the normalized chlorine data.

normal range of the Control (5). This is due to the high soil EC and is representative of the Gapon selectivity co-efficient.

The contaminated soil tested was 21.3 dS/m at the start of the test and 37.8 after 6 months. This shows that gypsum will only compound the problem of brackish soils if the starting electronegativity is excessive, above 6 dS/m for Pullman Clay-Loam. 8 lbs 8oz of gypsum increased the tested calcium from 7819 mg/kg to 15660 mg/kg (Abrol et al. 1975). This increase took effect within only one day after treatment and was compounded by the nature of sodium contamination, which forces the calcium out of the soil structure first.

**ST SoilTech:** The suggest EC product range is 12 dS/m – 18 dS/m with no soil dilution. The ST safety data sheet indicates “proprietary blend of polyelectrolytes”. This product

uses charged polymers to bind salt. Once this chemical is added to water, it acquires a -1 charge. This charge binds with ionic salts, which carry a positive charge. It likely also partially bonds in the place of H<sub>2</sub>O and allows for a small amount of soil structure remediation, at least temporarily. The soil pH plays a large role in the effectiveness of polyelectrolytes (Abu-Sharar et al. 1987). Any modification to pH through mixture with water or other products could impact its effectiveness (Chorom et al. 1995). ST reduced chlorides in soil by an insignificant amount when compared to the control and did not outperform the control. At the 6-month mark, this product showed a minute reduction compared numerically to all other products for salt constituents' potassium and magnesium were significant reductions. ST product could approach significance, in chloride reduction, if compared to the other products in a lab setting. However, it is unlikely it would outperform the control. ST reduced upper-level contamination levels compared to D+; it did not outperform the control. This is the only product to show significance compared to the control, yielding results significantly lower in calcium and soluble salts. This product also showed significant ability to lower calcium compared to Gyp, D+, and the control. It significantly lowered potassium compared to D+. This product works as a soil flush, able to bind and remove large amounts of salts into a collection area for safe disposal. The ability for this product to remove calcium makes it unlikely to be functional in soil with high levels of naturally occurring calcium free of the gypsum compound (CaSO<sub>4</sub>). Calcareous soils will prove difficult to fully remediate with this product due to its affinity to expel calcium first.

This product would work best before rainy season, allowing it to percolate down through soil layers. I suggest reviewing the long-term effects of this product to ensure wicking

does not occur after a large-scale application. However, research shows wicking is only likely in highly calcareous soils, with large amounts of natural occurring salts. It is important to note that this product will remove important nutrients from the soils along with the contaminants. Cross-analysis between the precipitation and tested nutrient levels shows that any precipitation aids this product's ability to reduce salt levels within the first 2 in of soil. This product experienced increases above the running total for salts at times when no water was applied and decreases at times of precipitation. The increases are likely exacerbated by the 40-mm liner used to restrict leeching into soils.

**CR Chlor-rid:** The suggest EC product range is 6 dS/m – 8 dS/m with no soil dilution. Chlor-rid is a moderate acid used for the industrial removal of chloride from various materials such as steel and concrete. It has been used with a fair amount of success on bridges, jet engines, and a variety of industrial facilities. Per its safety data sheet, Chlor-rid is biodegradable, does not bio-accumulate, and has no toxicological effects, making it a safe and viable option for agricultural applications. Field and laboratory tests show it is successful in the removal of chloride. Based on its chlorine removal capability and pH of 3.5, it is reasonable to assume the mechanism involves hydrogen binding to the chloride, releasing gaseous hydrochloric acid from the surface into the surrounding air. This would also explain the high dilution factor of 1:100 needed for the product, as this would keep the acidity of the hydrochloric acid below the toxicity threshold in the environment and handling. Although testing data show that salt removal is not as effective when applied directly to a surface. This product was originally designed for application through a high pressure around 3000 psi, preventing its use in an agricultural setting in that format. This product likely functions as intended when removing salts from oilfield pipes or

equipment but is not functional for soil remediation. While this could be due to the nature of the surfaces that were previously tested, such as rusted pipes, it is possible that the energy produced by blasting water at high pressure may be needed for Chlor-rid to properly react with salts for removal. If this is the case, application of chlor-rid would damage crops, making it irrelevant for salt brine remediation, requiring an alternative application method for use in agriculture. The other possible risk is the susceptibility of plants to the gaseous hydrochloric acid and possible entrapment in soil pores. The porosity of the soil has immense impact of the effectiveness of Chlor-rid because of possible toxicity to the plants versus the successful removal of chloride. While the product has its merits when working with relatively smooth surfaces that do not have a high enough effective porosity to allow the chloride to sink, it is unlikely that it would have the same results when introduced to a porous biological medium, making it unlikely that Chlor-rid would be an effective product.

**D+ DeSalt Plus:** The suggest EC product range is 12 dS/m – 14 dS/m with no soil dilution. D+ is a product that was designed to chemically treat soil contaminated by produced water spills from oilfield accidents. The formula for D+ is proprietary; the active ingredients include surfactants, calcium ( $\text{Ca}^{++}$ ), ammonium ( $\text{NH}_4^+$ ), and potassium ( $\text{K}^+$ ) ions. Test results reveal that the underlying mechanism for this product is the increase of soluble salts. This method decreases the likelihood of sodium uptake in plants, explaining the significant growth of this product in comparison to the other products, but not in relation to the control. Viewing the data graphically shows that D+ increases the values of  $\text{Mg}^{++}$ ,  $\text{K}^+$ , and  $\text{Ca}^{++}$ . The growth was impressive, considering the test results showed sodium concentrations a level of magnitude above background levels.

Contaminated soil should be treated within 90 days of the spill for best results. D+ comes in a liquid form and should be diluted with fresh water at a minimum of 10:1. The amount of D+ required per acre is determined by the type of soil being treated and the salt concentration of the produced water (Cl ppm, TDS, or water density). Following the application, irrigation of the affected area is recommended to accelerate removal of the contamination. The calcium and potassium in D+ each have stronger ion-bonding properties than the sodium bound to the clay from contamination, as described in the introduction. The diluted solution is applied directly to the soil and the calcium and potassium ions displace the sodium ions, correcting the soil disassociation and removing the crusted surface. D+ did not show significance when compared against the control. This product largely competed with CR and showed significant increases in constituent salts sodium, calcium, potassium, and magnesium by comparison. The two products interacted in different mechanisms; CR moved salt further into soils while D+ moved salts upwards. D+ increased volatility and reactivity to external forces such as rain, snow, and temperature, compared to the others.

Physical evaluation of the soils on 20 June 2016 showed salt sequestration in a square grid pattern with approximately 0.75 inches of space between them, demonstrating the product's capability to collect and restrain salts within the soil structure. This occurred in the 4 sampled areas of the soil. This mechanism is likely the reason for increased growth in this cell, as well as increased salinity of the upper soil levels. This product does contain a sodium surfactant, making it optimal dealing with hydrocarbons within the soil. It is highly unlikely that this sodium surfactant was purely responsible for the elevated sodium soil levels. It is more plausible that this increase was caused by salt migration from lower

levels to upper layers, reducing the space available for salt storage and forcing free salts upward to the top soil.

D+ is part of a series of treatments, and instructions for application were modified as previously described. D+ appears to have the most potential, and further research is necessary to determine its effectiveness when applied as directed, including utilizing subsequent products in the treatment line to complete the remediation process. Like CR, this product showed small amounts of growth within the cell prior to the germination phase. I suggest application of this product via the soil shredder, followed by pumping the water into the subsoil at a depth of 2-3 ft. Proper drainage must be present on the topsoil to help facilitate the movement of salts upward in soil profile. Application of further products is likely required to remove remaining sequestered salts from the soil. This product appears to be effective in remediation of high brine content from contaminated soils when used properly and timely.

For ST the most significance in the study and its ability to significantly decrease potassium and insignificantly decrease sodium against D+, making both products a plausible candidate for future research on lower-level contamination. This product will thrive within the midrange of contamination 4-10 dS/m. The use of a 40-mm polyethylene liner likely impeded this product's ability to gather and move salt into the soil. Further testing on this product is suggested and should include testing its downward salinity mobility and the possibility of wicking occurring after treatment. The levels of contamination for the test were set much higher than the expected functionality of these products. This is the closest to a "silver bullet" of the products tested. Further testing is required to set the variables for remediation. The low levels of growth seen can be



partially attributed to slight mounding of soils in areas. The growth occurred in areas that were only 0.5-1.0 in above the rest of the soil in the cell. This difference reduced brine influence enough to allow the growth of seedlings. The initial germination occurred the last week of October, after heavy rains. The plants showed stress over the next weeks due to a lack of rainfall and decreased water availability in the soil. The increase in salts on the top of the soil was high enough to kill the growth.

**Control:** The control showed no growth and limited fluctuations in contamination for any variable. It is clear the Talon LPE shredder requires the proper chemical application to function properly. Across all treatments, the shredder aerated the soil and worked extremely well for product application, but the nature of sodicity combined with the shredder allowed the soil to immediately collapse from 6 in of soil depth to 4 in of soil depth within 2 weeks. Changes in soil bulk density, soil aggregates, and soil hydraulic characteristics are related to the modification of soil pore space (Blackwellet al. 1989). The increase in soils hydraulic conductivity after shredding can be explained by the collapse of soil pore space brought by soil shredding. This collapse however, can be useful in forcibly expelling salts from the soil. Further testing is required to understand which product will function best for remediation and determining a level of remediation best suited for use with the shredder. I believe proper application of D+ and ST when used at lower-level contaminations, not exceeding an EC of 25 dS/m, can be significant.

The EC was outside the scope of plausible expected remediation for all the products tested. It is advised to conduct further research at more manageable levels. Lower levels can be achieved on site through soil mixing to delineate to a level more suited for remediation.

Tillage will cause erosion of the soils. Tilling in excess will cause a hardened plow pan to form the soil surface (Adem et al. 1984). Increased organic matter in soil will lower sensitivity to soluble salts (Chiou, 2002). Soils lose carbon because of leeching, erosion, runoff, and climate change. The negative effects of sodic conditions will increase overtime. Carbon in soil is used by methanogenic bacteria, turning it into methane (Emerson, 1977). Increasing soil carbon will ultimately aid in regrowth of non-salt-resistant vegetation. The suggestion is to plant salt-resistant wheat on soils with excessive salt exposure. Wheat will not be productive at high salt concentrations but can grow in contaminated soils as high as 9 EC, in optimum conditions. Wheat is a  $\text{Na}^+/\text{H}^+$  antiporter (nhaA), meaning it is effective at avoiding sodium uptake. Wheat growth is extremely stunted by higher concentrations of salt. This concise remediation strategy will aid in the process of gaining forage crop cover in nearly all brine-contaminated spills. Remediation of brine is not a simple process that can be conducted in a single use. The best method for remediation in a single treatment is to utilize the dig and haul methodology. Proper remediation is performed over time and can be cost-effective if personnel are properly managed.

**Suggested strategy for remediation:**

The first step is determination of the constituent salts present. Blending and product application will depend on main salt group that is inhibiting growth. The process for the brine remediation includes proper identification of the spill area. This would consist of utilizing crude measurements to determine the total volume of contaminated soil. Once the volume of soil is properly calculated, it is imperative that samples be taken to identify the contamination level. This level is then used to determine the remediation process. If

the levels of contamination exceed the required levels for plant growth, then the soil must be blended. Plant selection should be based on the ecological setting of the brine contamination. Suggested plants that are feasible in most ecological conditions include a mixture of a salt-tolerant grass, such as a salt-tolerant strain of Bermuda grass (*Cynodon dactylon*), and a strong salt-resistant crop or weed, such as Crested Wheatgrass (*Agropyron cristatum*), also wheat/barley/sorghum. Barley is an extremely salt-tolerant plant that can survive in sodic conditions as high as 16 dS/m (Abdou et al. 1975). This strategy allows for germination and erosion control measures quickly during most seasons. This seeding gives the best opportunity for ground coverage regardless of the season and increases soil organic carbon over time. Wheat will increase soil organic carbon better than barley or sorghum. The combined total weight for seeding application should equal roughly 8 to 10 lbs. per acre on average and should be adjusted to correlate with the brine contamination present on site. It is important to acknowledge that as contamination levels increase the rate of germination will decrease (Waskom et al. 2010). The suggested method for soil blending consists of setting a desired achievable level, then using dimensional analysis to determine the amount of uncontaminated soil needed to lower the total to a favorable range. Gypsum has been used to lower salt concentrations and stabilize soil for thousands of years (Dick, 2011). Regardless of soil particle size, gypsum should be amended to all contaminated soil and applied in small granular form. Clay soils require larger treatment amounts. Gypsum acts as a time release for calcium into the contaminated soil. Application of gypsum in liquid form will only decrease its effectiveness due to the Gapon Coefficient. Allowing gypsum to precipitate naturally will decrease the likelihood it is expelled from the soil.

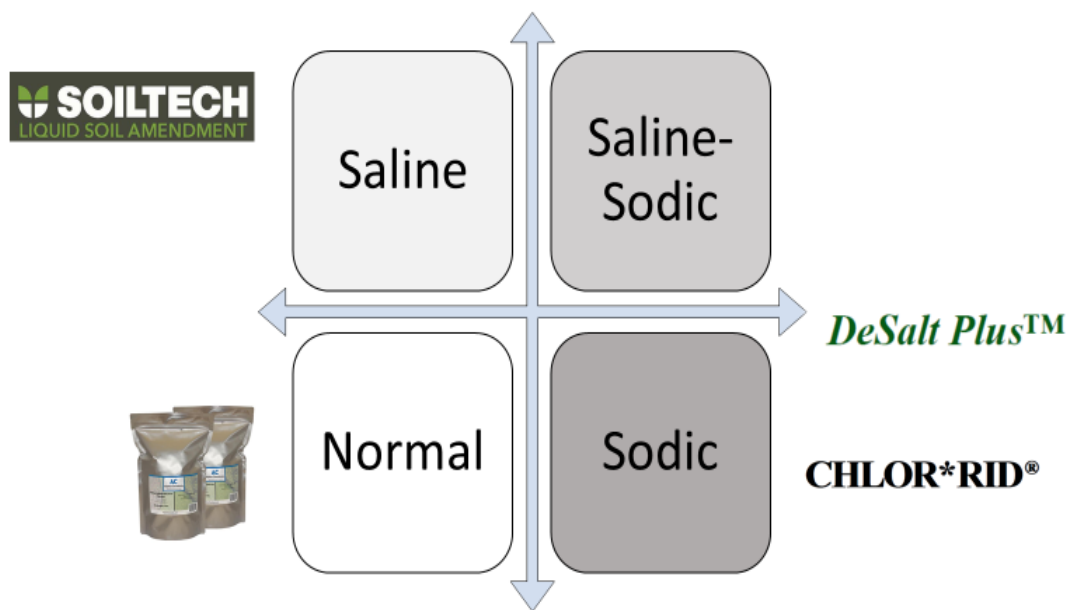
Over time, the soil shredder deteriorated the soil structure. This was due to a pancake effect, which is caused by excess levels of sodium preventing proper water flow through the soil. The use of granular gypsum is a small but important aspect. Adding the gypsum during the shredding phase in granular form will create a long-lasting semi stabilizing force in the soil. This will create a more stable base layer of contaminated soil due to the partial bonding of calcium with clay charges in soil. Gypsum adds  $\text{Ca}^{++}$  as a stabilizing force through utilization of partial bonding with soil particles and it adds Sulfate which will aid in plant growth. Utilization of gypsum in this manner will create pathways for root structures in contaminated soil by stabilizing the soil through partial bonding and giving roots needed (Abrol et al. 1979). The suggested application of gypsum is 4 tons per acre to 10 tons per acre when seeking complete remediation with exclusively gypsum. If gypsum is applied only to the A horizon, the amount is substantially lowered. Further research is necessary for a precise amount required. The amount I suggest is equal to roughly ½-1 ton per acre. The spray bar attached to the soil shredder is recommended for application chosen proprietary products. If a shredder is unavailable, then utilization of a mixing methodology is suggested for application of the gypsum (Abrol et al. 1975). D+ appears adept at disbursing sodium throughout contaminated soil. It is important to note that products containing surfactants will destroy or isolate naturally occurring carboxyl rings in the soil. If the soil is contaminated by hydrocarbon brine, then naturally occurring phenols will largely disassociate into the contamination. Utilization of the products containing a surfactant on contaminated soil without hydrocarbon contamination will affect naturally occurring phenols (Potter, 1998). Compost can be used as a topical treatment or can be mixed in low level brine contaminations in the Texas Pan Handle.

Application of compost will ensure growth at virtually any EC, if applied topically.

Compost applied in this manner will not remediate long-term for contaminations above 20 dS/m. Lignin has also showed ability to absorb chlorides in soil.

## CHAPTER V: CONCLUSION

The first step to proper remediation of salt affected soils is to identify the constituent salts. The tested products interact with different salt groups, as shown in Figure 8.



*Figure 9. Suggested product application based on soil contamination type.*

SoilTech will lower calcium in saline soils. Chlor\*rid will lower sodium in sodic soils.

DeSalt Plus gives a favorable CEC and increased upward motility of salts. Gypsum only functions in low level sodic to normal conditions.

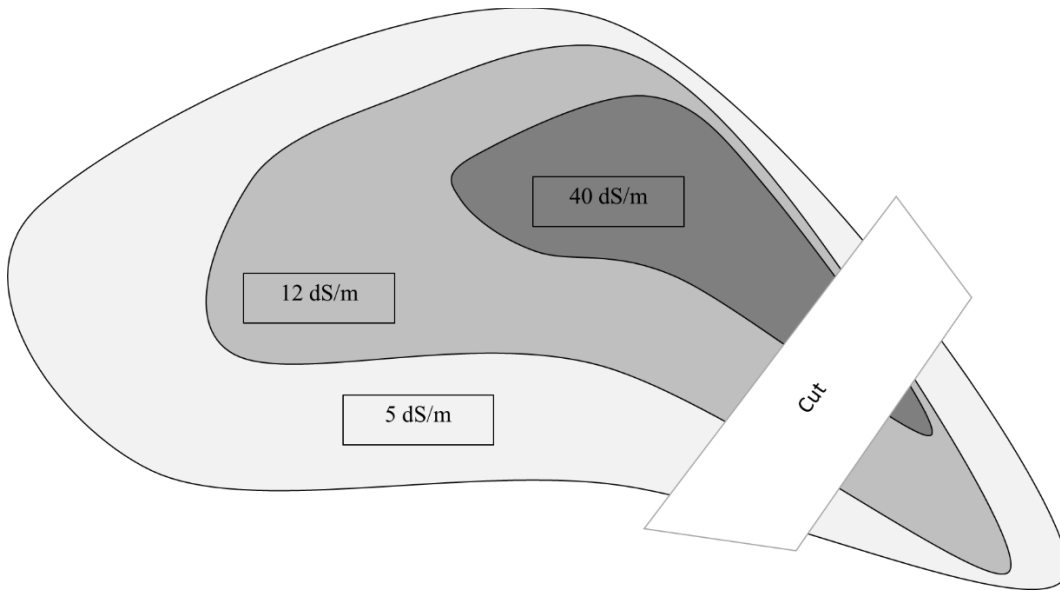
This conclusion is extrapolated from the low amounts of growth seen on testing site. A step-by-step suggested remediation guide follows:

Step 1: Analyze the contamination area to determine the average contamination level as well as the total weight of contaminated soils.

Step 2: Remove the subsurface contamination cone and replace the area with an uncontaminated similar horizon soil.

Step 3: Blend the contaminated soil with clean soil contained within the root zone.

Introduce the granular gypsum in this phase if needed. Future remediation ( $R_f$ ) is the expected result from ex-situ soil blending. Blended soil should have a  $R_f$  6 dS/m – 10 dS/m expected remediation to have vegetative growth. Blending soil should consist of soil taken from the area immediately surrounding the contamination zone. Figure 9 shows a hypothetical brine contamination mixing of a cut portion of a brine spill.



*Figure 10. Hypothetical brine contamination.*

The brine contamination cut area pictured in Figure 9.  $R_f$  is calculated as:

$$((EC^1 * Area^1) + (EC^2 * Area^2) + (EC^3 * Area^3)) \div \text{Total Area} = R_f$$

$$\text{For cut: } ((5\text{dS/m} * 40\text{yr}^3) + (12\text{dS/m} * 35\text{y}^3) + (40\text{dS/m} * 25\text{y}^3)) \div 100\text{yd}^3 = 16.2\text{dS/m}$$

Spread the blended soil over a reasonably large area. Utilization of proper irrigation techniques for this area is imperative. Water should be allowed to flow through area without causing extreme erosion.

Application of a product should be done during or immediately following the blending phase.

Seeding phase should happen approximately 3 to 6 months after product application.

Seeds should be selected based on region, Table 17 lists various crops commonly used for grazing.



Table 16. Saline-sodic plants. (United States Department of Agriculture, 1999).

Crop	EC (mmhos/cm)		Tolerance Rating
	Production Affected	Upper Limit	
Barley	8	16	High
Sugar beets	7	13	Moderate
Safflower	6	10	Moderate
Wheat	7	8	Low
Oats	4	8	Low
Corn	3	6	Low
Beans	1	2	Low
<u>Forage -Wet/Saturated (water table w/in 3 feet of soil surface) or Irrigated (well drained) Sites</u>			
Beardless wildrye	13	26	Very High
Tall wheatgrass	13	26	Very High
Newhy hybrid wheatgrass	13	26	Very High
Slender wheatgrass	10	22	Very High
Altai wildrye	10	20	Very High
Tall fescue	8	18	High
Western wheatgrass	6	16	High
Strawberry clover	6	16	High
Creeping foxtail	5	12	Moderate
Smooth brome	5	10	Moderate
Meadow brome	4	10	Moderate
Cicer milkvetch	4	10	Moderate
Birdsfoot trefoil	5	8	Low
Orchardgrass	3	8	Low
Reed canarygrass	3	5	Low
Clover (Alsike, Red, Ladino)	3	4	Low
<u>Forage - Dry (10 inch + precipitation and water table below 3 feet of soil surface) Sites</u>			
Russian wildrye	13	24	Very High
Tall wheatgrass (12 inch+)	13	24	Very High
Slender wheatgrass	10	20	Very High
Forage kochia	10	18+	High
Fourwing saltbush	10	18+	High
Winterfat	10	18+	High
Crested wheatgrass	6	14	Moderate
Siberian wheatgrass	6	14	Moderate
Pubescent wheatgrass (11 inch+)	6	12	Moderate
Intermediate wheatgrass (12 inch+)	6	12	Moderate
Yellow sweetclover	5	10	Moderate
Alfalfa (12 inch+)	4	8	Low
Small burnet (14 inch+)	2	3	Low
<u>Native Grasses</u>			
Nuttall's alkaligrass	14	30	Very High
Alkali sacaton	14	26	Very High
Beardless wildrye	13	26	Very High
Alkali cordgrass	12	24	Very High
Alkali bluegrass	12	24	Very High
Slender wheatgrass	10	22	Very High
Plains bluegrass	10	20	Very High
Western wheatgrass	6	16	High
Thickspike/Streambank wheatgrass	6	14	Moderate

This is dependent on the seeds chosen and water received (from natural or man-made sources). Seeding too early can cause the seeds to enter a state of stasis due to unsatisfactory levels of contamination. When seeding is conducted, the root zone of soil should be saturated with water and tilled. If low germination rate occurs, then further blending or increased water to the area is required. It is important to note that under perfect conditions, the suggested plants require a minimum of 10 in of rain a year. The higher level of desired contamination through blending should correlate directly with the intended application of water from unnatural sources. If it is possible to irrigate an area

using a local water source, then the levels of contamination may be higher. The plants suggested or the plants chosen should be a combination of both salt-tolerant and drought-resistant species. The application of organic matter, where possible, greatly increases the probability of a successful remediation. The successful products during this test contained small percentages of nitrogen in various forms to jumpstart the nitrogen cycle. The nitrogen cycle can be entirely lost when conditions become too sodic for microorganisms that facilitate the cycle. These microorganisms are important in the transformation of plants, microbes, and animal litter into humus. An inexpensive suggestion would be the purchase of human waste. Commonly, human waste is disposed of in landfills. Human waste would not, however, be a suggestion as a form of nitrogen amendment for land that is intended to be reclaimed for farming purposes due to the high levels of pharmaceuticals found in human waste (USGS, 2000). Farm land suggested usage would be the use of animal manure.

ST was the only product able to show a significant difference compared to the control. The dataset that showed significance was for calcium and soluble salts, which are related. These results show that this product will be effective in the removal of calcium-heavy brines and will likely have a negative effect on soil stability due to the role of calcium in removing disassociated particles. This product could show more functionality in removing sodium in proper conditions. A drainage zone is required under the contaminated soil; this area should be larger material that will allow for percolation and should have an EC sustainably lower than the soil tested. Allowing the product a porous space under the contaminated area could allow for more salt removal. It is likely calcium was expelled first from the soil and exhausted the product's use.

Further testing can also be done for D+. This product removes salts upwards, whereas ST moves them downward. The product can be functional at lower-level contaminations and suggested future research should emphasize drainage on the top soil and utilization of the entire product line.

The success of any brine remediation project will require various mechanisms to accomplish complete remediation. Ensuring the soil EC is between 10 dS/m and 20 dS/m is paramount. This level will ensure success of the project and allow the soil to eventually see growth. Plant selection must be made in correlation with specific area and expected salinity outcome. Proper drainage must be installed on site to ensure further delineation of salts in soil. Application of carbon and nitrogen will ensure plant growth, if the osmotic potential of the soil does not starve the plant growth. The factors that affect site regrowth when remediating brine are: soil particle size, nitrogen levels, carbon content, osmotic potential, microbial survivability, and salt content.

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## APPENDIX I: WEATHER DATA

*Table I-1: Raw weather data.*

DATE	PRECIP	SNW DEPTH	SNOW FALL	AVG TEMP	MAX TEMP	MIN TEMP	AWND
2015-OCT-2	0	0	0	64	73	53	17.4
2015-OCT-3	0.46	0	0	53	54	49	14.3
2015-OCT-4	0.65	0	0	52	54	50	8.5
2015-OCT-5	0.14	0	0	56	65	53	10.5
2015-OCT-6	0	0	0	63	81	51	13.4
2015-OCT-7	0.08	0	0	66	77	57	7.4
2015-OCT-8	0	0	0	63	73	56	3.8
2015-OCT-9	0	0	0	62	70	52	8.9
	1.33	0	0	59.875	68.375	52.625	10.525
2015-OCT-10	0	0	0	65	82	52	14.3
2015-OCT-11	0	0	0	70	90	57	9.8
2015-OCT-12	0	0	0	68	78	52	12.3
2015-OCT-13	0	0	0	65	85	47	8.3
2015-OCT-14	0	0	0	69	89	48	9.6
2015-OCT-15	0	0	0	70	87	56	11.2
	0	0	0	67.83333	85.16667	52	10.91667
2015-OCT-16	0	0	0	60	63	50	12.8
2015-OCT-17	0	0	0	58	76	47	14.5
2015-OCT-18	0	0	0	63	78	50	17.2
2015-OCT-19	0	0	0	65	80	53	17.9
2015-OCT-20	0.03	0	0	64	74	56	15
2015-OCT-21	1.08	0	0	60	67	55	10.5
2015-OCT-22	0.76	0	0	59	66	53	12.1
	1.87	0	0	61.5	73.5	52.33333	14.53333
2015-OCT-23	0	0	0	62	76	51	13
2015-OCT-24	0	0	0	53	63	42	8.5
2015-OCT-25	0	0	0	51	68	39	4.9
2015-OCT-26	0	0	0	52	69	39	12.1
2015-OCT-27	0	0	0	56	77	39	10.7
2015-OCT-28	0	0	0	53	63	41	10.5
2015-OCT-29	0	0	0	52	67	38	11.9
2015-OCT-30	0.28	0	0	51	61	45	12.8

	0.28	0	0	53.75	68	41.75	10.55
2015-OCT-31	0	0	0	51	69	41	8.7
2015-NOV-1	0	0	0	54	74	39	7.8
2015-NOV-2	0	0	0	57	80	39	11.4
2015-NOV-3	0	0	0	61	79	44	13.4
2015-NOV-4	0.07	0	0	62	74	52	18.1
2015-NOV-5	0	0	0	58	68	38	13.4
	0.07	0	0	57.16667	74	42.16667	12.13333
2015-NOV-6	0	0	0	47	66	31	11.2
2015-NOV-7	0	0	0	45	57	34	8.3
2015-NOV-8	0	0	0	46	60	34	15.7
2015-NOV-9	0	0	0	52	73	39	15.7
2015-NOV-10	0	0	0	57	77	41	15
2015-NOV-11	0	0	0	55	63	34	17.7
2015-NOV-12	0	0	0	44	61	29	8.3
	0	0	0	49.42857	65.28571	34.57143	13.12857
2015-NOV-13	0	0	0	46	64	33	13
2015-NOV-14	0	0	0	48	64	34	16.1
2015-NOV-15	0	0	0	52	63	46	19
2015-NOV-16	0.31	0	0	60	74	41	21
2015-NOV-17	0	0	0	43	42	35	25.9
2015-NOV-18	0	0	0	44	67	32	11.9
2015-NOV-19	0	0	0	42	55	29	11
	0.31	0	0	47.85714	61.28571	35.71429	16.84286
2015-NOV-20	0	0	0	47	72	32	16.6
2015-NOV-21	0	0	0	36	43	24	14.3
2015-NOV-21	0	0	0	37	64	23	7.8
2015-NOV-23	0	0	0	44	62	29	13.9
2015-NOV-24	0	0	0	50	76	31	14.1
2015-NOV-25	0	0	0	52	76	35	15
2015-NOV-26	0.59	0	0.2	48	59	28	16.6
2015-NOV-27	0.46	0	0.6	26	29	22	20.6
2015-NOV-28	0.07	1.2	0.5	24	29	22	9.6
2015-NOV-29	0	0	0	29	32	28	4.3
2015-NOV-30	0	0	0	37	50	28	8.9
2015-DEC-1	0	0	0	37	54	23	8.1
2015-DEC-2	0	0	0	39	56	25	7.6
2015-DEC-3	0	0	0	42	59	29	8.5
	1.12	1.2	1.3	39.14286	54.35714	27.07143	11.85
2015-DEC-4	0	0	0	43	58	32	17.2
2015-DEC-5	0	0	0	45	66	34	14.3
2015-DEC-6	0	0	0	43	57	30	8.3
2015-DEC-7	0	0	0	44	65	31	9.6
2015-DEC-8	0	0	0	47	71	30	8.1

2015-DEC-9	0	0	0	50	69	36	11.6
2015-DEC-10	0	0	0	53	69	43	10.5
2015-DEC-11	0	0	0	55	73	44	10.7
2015-DEC-12	0.35	0	0.3	50	63	33	13.4
2015-DEC-13	0.32	0	2	33	36	32	17
2015-DEC-14	0	1.2	0	38	61	24	10.3
2015-DEC-15	0	0	0	42	49	26	18.6
2015-DEC-16	0	0	0	32	43	18	6.7
2015-DEC-17	0	0	0	28	37	18	10.3
2015-DEC-18	0	0	0	31	56	18	11.6
2015-DEC-19	0	0	0	43	71	27	15.2
2015-DEC-20	0	0	0	50	65	41	20.4
2015-DEC-21	0	0	0	47	60	30	10.3
2015-DEC-22	0	0	0	46	61	38	21
2015-DEC-23	0.02	0	0	47	54	31	12.1
2015-DEC-24	0	0	0	41	47	27	10.1
2015-DEC-25	0	0	0	38	51	29	17
2015-DEC-26	0	0	0	38	44	22	25.7
2015-DEC-28	0.08	3.1	3.8	23	25	20	34.4
2015-DEC-28	0	3.1	0	26	37	20	15
2015-DEC-29	0.01	0	0.1	26	38	18	10.5
2015-DEC-30	0	0	0	32	45	23	8.5
2015-DEC-31	0	0	0	27	29	24	7.4
2016-JAN-1	0	0	0	28	37	23	6.3
2016-JAN-2	0	0	0	31	48	22	7.6
2016-JAN-3	0	0	0	35	52	22	8.5
2016-JAN-4	0	0	0	34	47	21	8.9
2016-JAN-5	0.01	0	0	30	37	23	14.8
2016-JAN-6	0	0	0	42	59	36	16.6
2016-JAN-7	0	0	0	41	49	25	11.2
2016-JAN-8	0.06	0	0.5	31	34	25	10.5
2016-JAN-9	0.01	1.2	0.3	27	32	16	12.3
2016-JAN-10	0	0	0	25	32	18	9.6
2016-JAN-11	0	0	0	30	47	21	7.6
2016-JAN-12	0	0	0	35	58	21	8.3
2016-JAN-13	0	0	0	35	57	20	8.1
2016-JAN-14	0	0	0	41	63	27	11.4
2016-JAN-15	0	0	0	39	52	24	10.1
2016-JAN-16	0.11	1.2	0.6	37	43	28	7.6
2016-JAN-17	0	0	0	31	41	20	10.5
2016-JAN-18	0	0	0	27	52	20	12.5
2016-JAN-19	0	0	0	42	53	28	14.3
2016-JAN-20	0	0	0	39	64	24	14.3
2016-JAN-21	0	0	0	41	49	25	18.6

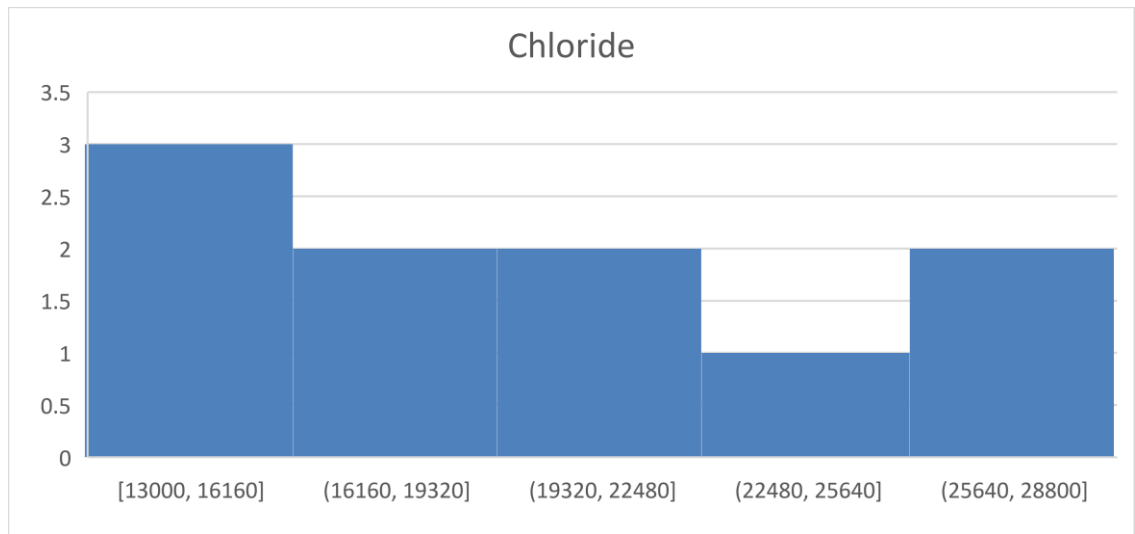
2016-JAN-22	0	0	0	34	54	21	7.6
2016-JAN-23	0	0	0	41	70	25	14.1
2016-JAN-24	0	0	0	50	70	33	15.9
2016-JAN-25	0	0	0	46	54	29	13.4
2016-JAN-26	0	0	0	36	49	24	6.5
2016-JAN-27	0	0	0	36	59	18	5.1
2016-JAN-28	0	0	0	44	66	29	7.6
2016-JAN-29	0	0	0	50	75	33	13.6
2016-JAN-30	0	0	0	52	79	30	17.2
2016-JAN-31	0	0	0	49	56	32	11.6
2016-FEB-1	0.11	0	0	38	56	27	15.2
2016-FEB-2	0	0	0	36	42	24	21.9
2016-FEB-3	0	0	0	28	42	14	8.9
2016-FEB-4	0	0	0	31	48	15	8.9
2016-FEB-5	0	0	0	35	44	26	17
2016-FEB-6	0	0	0	34	56	19	9.2
2016-FEB-7	0	0	0	41	58	25	13.2
2016-FEB-8	0	0	0	37	54	23	13.2
2016-FEB-9	0	0	0	42	65	26	11
2016-FEB-10	0	0	0	51	79	28	11.4
2016-FEB-11	0	0	0	49	68	30	7.4
2016-FEB-12	0	0	0	48	66	31	12.3
2016-FEB-13	0	0	0	45	71	28	19.7
2016-FEB-14	0	0	0	48	59	34	11.2
2016-FEB-15	0	0	0	45	65	29	10.7
2016-FEB-16	0	0	0	48	60	38	11.4
2016-FEB-17	0	0	0	50	77	34	17
2016-FEB-18	0	0	0	63	86	46	19.9
2016-FEB-19	0	0	0	66	73	50	16.1
2016-FEB-20	0	0	0	61	77	45	9.6
2016-FEB-21	0	0	0	49	60	37	13.9
2016-FEB-22	0	0	0	43	53	33	12.5
2016-FEB-23	0.39	2	3.2	37	43	30	13.6
2016-FEB-24	0	0	0	38	60	24	11.4
2016-FEB-25	0	0	0	38	50	23	8.5
2016-FEB-26	0	0	0	41	66	26	11
2016-FEB-27	0	0	0	51	76	31	16.3
2016-FEB-28	0	0	0	57	69	40	13.6
2016-FEB-29	0	0	0	54	79	37	14.8
2016-MAR-1	0	0	0	51	60	35	11.6
2016-MAR-2	0	0	0	54	82	38	16.1
2016--MAR-3	0	0	0	52	65	38	9.6
2016--MAR-4	0	0	0	55	78	42	16.1
2016--MAR-5	0	0	0	53	71	33	15

2016-MAR-6	0	0	0	60	79	51	19.7
2016-MAR-7	0	0	0	60	75	45	13.4
2016-MAR-8	0	0	0	51	63	39	10.1
2016-MAR-9	0	0	0	51	61	41	7.6
2016-MAR-10	0	0	0	49	68	36	7.6
2016-MAR-11	0	0	0	51	69	34	8.3
2016-MAR-12	0.02	0	0	53	68	42	14.8
2016-MAR-13	0	0	0	54	74	41	9.4
2016-MAR-14	0	0	0	59	82	39	14.8
2016-MAR-15	0	0	0	59	68	41	10.3
2016-MAR-16	0	0	0	50	69	33	13.4
2016-MAR-17	0	0	0	48	68	30	10.5
2016-MAR-18	0	0	0	44	47	30	17.4
2016-MAR-19	0	0	0	36	53	26	9.2
2016-MAR-20	0	0	0	38	57	18	8.1
2016-MAR-21	0	0	0	52	82	34	18.6
2016-MAR-22	0	0	0	65	85	49	20.8
2016-MAR-23	0	0	0	60	68	37	27.5
2016-MAR-24	0	0	0	43	61	31	15.2
2016-MAR-25	0	0	0	51	74	35	17.4
2016-MAR-26	0.11	0	0.4	52	65	32	17.7
2016-MAR-27	0.14	1.2	0.9	38	57	26	10.5
2016-MAR-28	0	0	0	51	76	36	20.8
2016-MAR-29	0	0	0	62	81	47	21.5
2016-MAR-30	0	0	0	64	73	46	14.8
2016-MAR-31	0	0	0	50	63	32	11.6
2016-APR-1	0	0	0	44	59	33	7.6
2016-APR-2	0	0	0	48	68	34	10.5
2016-APR-3	0	0	0	58	77	40	13.9
2016-APR-4	0	0	0	63	81	40	10.5
2016-APR-5	0	0	0	66	85	45	23
2016-APR-6	0	0	0	60	75	40	10.5
2016-APR-7	0	0	0	60	75	43	15.9
2016-APR-8	0	0	0	57	74	41	12.1
2016-APR-9	0	0	0	60	79	47	16.8
2016-APR-10	0	0	0	67	85	50	15.7
2016-APR-11	0.02	0	0	51	54	42	13
2016-APR-12	0	0	0	47	61	38	8.5
2016-APR-13	0	0	0	55	72	40	11.6
2016-APR-14	0	0	0	60	80	47	19.7
2016-APR-15	0	0	0	62	75	50	24.6
2016-APR-16	0.4	0	0	60	71	43	19
2016-APR-17	0.37	0	0	46	52	41	16.1
2016-APR-18	0	0	0	48	65	37	11.4



2016-APR-19	0.68	0	0	53	62	46	8.9
2016-APR-20	0.69	0	0	54	72	45	8.5
2016-APR-21	0	0	0	56	73	42	7.8
2016-APR-22	0	0	0	61	78	43	10.1
2016-APR-23	0	0	0	66	83	51	20.8
2016-APR-24	0	0	0	70	83	53	17.9
2016-APR-25	0	0	0	64	85	44	11.2
2016-APR-26	0	0	0	65	80	49	12.3
2016-APR-27	0	0	0	58	69	40	12.5
2016-APR-28	0	0	0	58	76	41	20.4
2016-APR-29	1.16	0	0	56	58	42	16.1
2016-APR-30	0.01	0	0	47	62	36	10.3
2016-MAY-1	0.01	0	0	45	46	39	19.5
2016-MAY-2	0	0	0	47	63	34	9.6
2016-MAY-3	0	0	0	53	73	39	10.3
2016-MAY-4	0	0	0	59	79	41	7.6
2016-MAY-5	0	0	0	66	85	46	9.8
2016-MAY-6	0	0	0	68	85	52	19
2016-MAY-7	0	0	0	71	88	55	17.7
2016-MAY-8	0	0	0	69	84	50	13.6
2016-MAY-9	0	0	0	65	80	48	13.4
2016-MAY-10	0	0	0	67	88	46	11.2
2016-MAY-11	0.38	0	0	65	76	50	15.2
2016-MAY-12	0	0	0	60	73	48	10.3
2016-MAY-13	0.08	0	0	66	86	51	14.8
2016-MAY-14	0	0	0	56	61	46	13.9
2016-MAY-15	0.04	0	0	49	51	44	14.3
2016-MAY-16	0.05	0	0	54	74	47	15.2
2016-MAY-17	0.15	0	0	54	53	48	17.7
2016-MAY-18	0.08	0	0	52	64	45	9.8
2016-MAY-19	0.02	0	0	54	65	47	12.3
2016-MAY-20	0	0	0	61	84	50	17.2
	5.88	13	12.1	47.91716	63.36686	34.2071	13.24142

## **APPENDIX II: CHLORIDE**



*Figure II-1: Chloride histogram for determination of normality.*

*Table 1: One Way ANOVA for chloride between groups.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.115	4	.029	1.234	.310
Within Groups	1.044	45	.023		
Total	1.158	49			

Table 2: Tukey HSD for chloride.

(I) Product	(J) Product	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.063170788	.068112911	.885	-	.25671022
	3	.115394347	.068112911	.448	.13036864	.30893378
	4	-	.068112911	.999	-	.17559216
	5	.017947264	.068112911	.998	.07814508	.21514248
		.021603048			-	
					.21148669	
					-	
					.17193638	
2	1	-	.068112911	.885	-	.13036864
	3	.063170788	.068112911	.939	.25671022	.24576299
	4	.052223559	.068112911	.756	-	.11242138
	5	-	.068112911	.973	.14131587	.15197169
		.081118052			-	
					.27465748	
					-	
					.23510717	
3	1	-.115394347	.068112911	.448	-	.07814508
	2	-.052223559	.068112911	.939	.30893378	.14131587
	4	-.133341611	.068112911	.303	-	.06019782
	5	-.093791300	.068112911	.645	.24576299	.09974813
					-	
					.32688104	
					-	
					.28733073	
4	1	.017947264	.068112911	.999	-	.21148669
	2	.081118052	.068112911	.756	.17559216	.27465748
	3	.133341611	.068112911	.303	-	.32688104
	5	.039550311	.068112911	.977	.11242138	.23308974

					- .06019782 - .15398912	
5	1	-	.068112911	.998	-	.17193638
	2	.021603048	.068112911	.973	.21514248	.23510717
	3	.041567741	.068112911	.645	-	.28733073
	4	.093791300	.068112911	.977	.15197169	.15398912
		-			-	
		.039550311			.09974813	
					-	
					.23308974	

*Table II-3: Chloride case validation per product.*

Product		Cases					
		Valid		Missing		Total	
		N	Percent	N	Percent	N	Percent
Chloride	1	10	100.0%	0	0.0%	10	100.0%
	2	10	100.0%	0	0.0%	10	100.0%
	3	10	100.0%	0	0.0%	10	100.0%
	4	10	100.0%	0	0.0%	10	100.0%
	5	10	100.0%	0	0.0%	10	100.0%

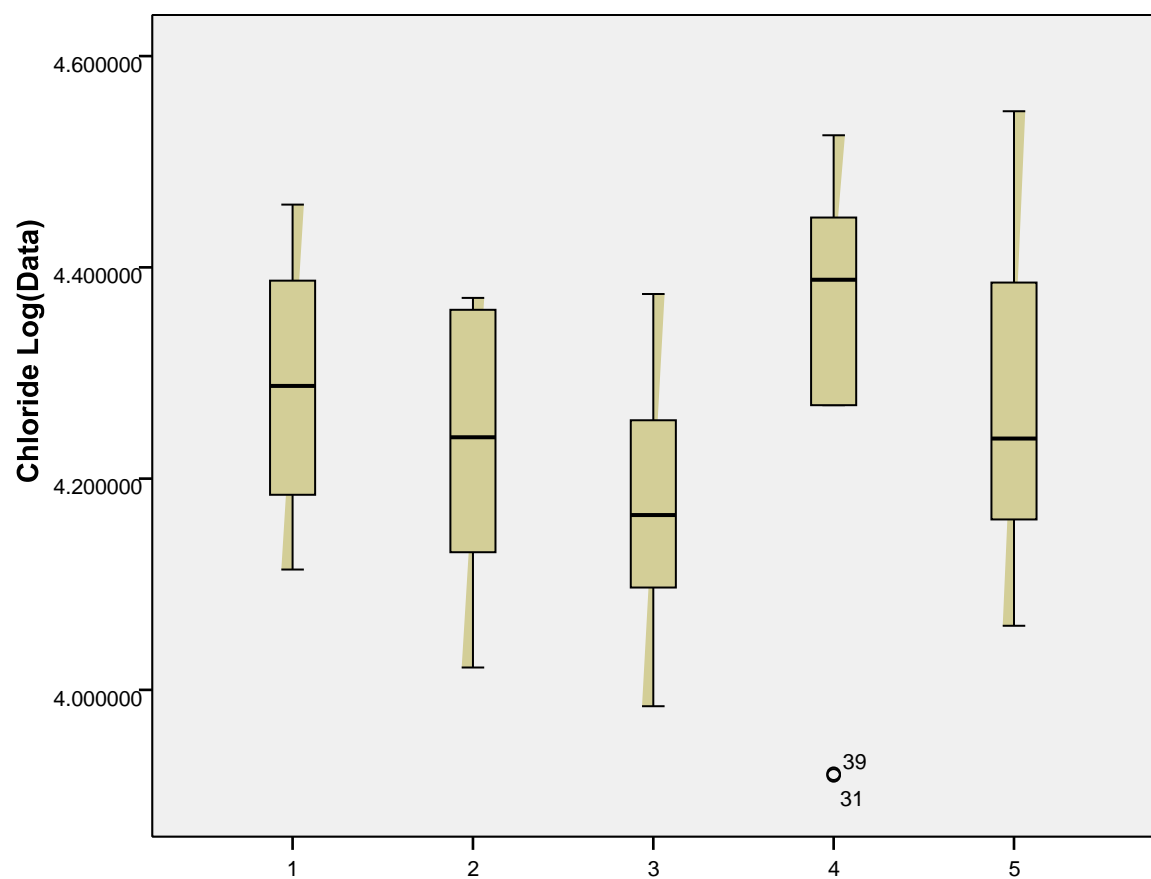


Figure II-2: Boxplot chloride concentration (mg/kg) per product.



Table II-4: Normalized chloride concentration (mg/kg) per product by date.

Chloride Log (Data)					
	Product 1	Product 2	Product 3	Product 4	Control
10-1-2015	4.113943	4.113943	4.113943	4.113943	4.113943
10-2-2015	4.184691	4.136721	4.117271	3.920645	4.079181
10-10-2015	4.158362	4.100371	4.149219	4.385606	4.190332
10-16-2015	4.294466	4.25042	4.09691	4.320146	4.285557
10-23-2015	4.281033	4.227887	4.238046	4.495544	4.161368
10-31-2015	4.113943	4.021189	3.984527	4.269513	4.060698
11-6-2015	4.326336	4.359835	4.181844	4.447158	4.376577
11-13-2015	4.459392	4.371068	4.374748	4.525045	4.547775
11-20-2015	4.451786	4.359835	4.274158	4.390935	4.385606
12-4-2015	4.232996	4.130334	4.064458	3.919078	4.167317
5-20-2016	4.38739	4.30103	4.255273	4.396199	4.419956

*Table II-5: Chloride concentration (mg/kg) per product by date.*

<b>Chloride (mg/kg)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	13000	13000	13000	13000	13000
10-2-2015	15300	13700	13100	8330	12000
10-10-2015	14400	12600	14100	24300	15500
10-16-2015	19700	17800	12500	20900	19300
10-23-2015	19100	16900	17300	31300	14500
10-31-2015	13000	10500	9650	18600	11500
11-6-2015	21200	22900	15200	28000	23800
11-13-2015	28800	23500	23700	33500	35300
11-20-2015	28300	22900	18800	24600	24300
12-4-2015	17100	13500	11600	8300	14700
5-20-2016	24400	20000	18000	24900	26300

### **APPENDIX III: SODIUM**

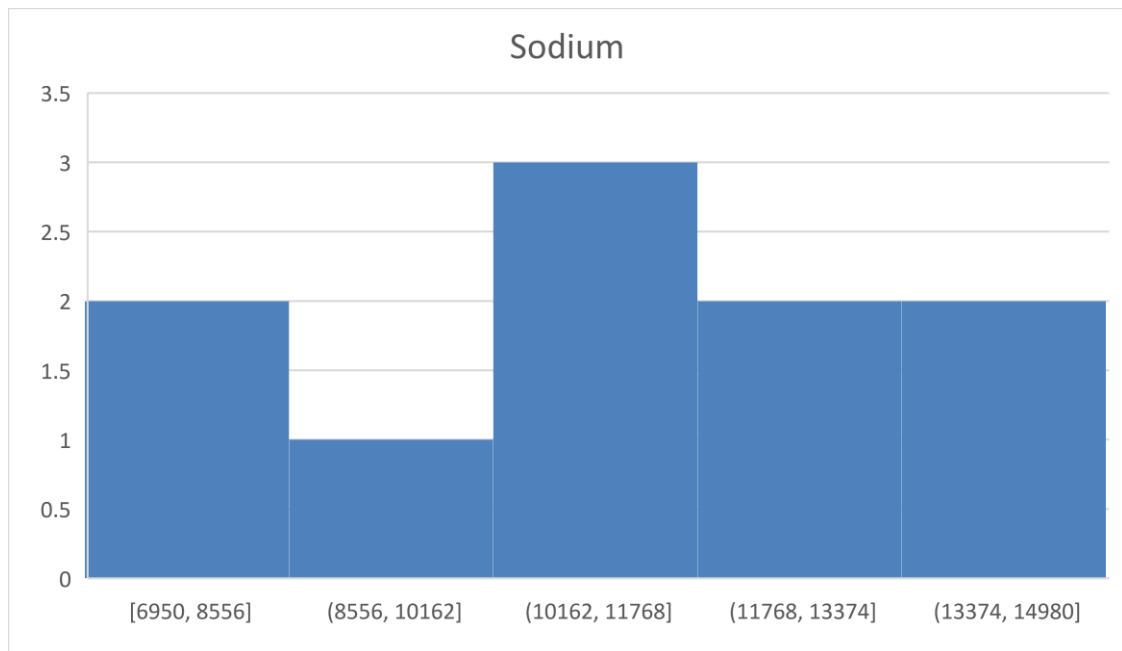


Figure III-1: Sodium histogram for determination of normality.

*Table III-1: ANOVA of sodium concentrations between groups ( $\alpha = 0.05$ ).*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.155	4	.039	2.673	.044
Within Groups	.654	45	.015		
Total	.809	49			

Table III-2: Multiple comparison Tukey HSD of sodium concentration difference between each product ( $\alpha = 0.05$ ).

(I) Product	(J) Product	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.062187735	.053905462	.777	-.09098194	.21535741
	3	.109026178	.053905462	.272	-.04414350	.26219585
	4	-.055077235	.053905462	.844	-.20824691	.09809244
	5	.016980958	.053905462	.998	-.13618872	.17015063
2	1	-.062187735	.053905462	.777	-.21535741	.09098194
	3	.046838443	.053905462	.907	-.10633123	.20000812
	4	-.117264970	.053905462	.208	-.27043464	.03590470
	5	-.045206777	.053905462	.917	-.19837645	.10796290
3	1	-.109026178	.053905462	.272	-.26219585	.04414350
	2	-.046838443	.053905462	.907	-.20000812	.10633123
	4	-.164103413*	.053905462	.030	-.31727309	-.01093374
	5	-.092045220	.053905462	.440	-.24521489	.06112445
4	1	.055077235	.053905462	.844	-.09809244	.20824691
	2	.117264970	.053905462	.208	-.03590470	.27043464
	3	.164103413*	.053905462	.030	.01093374	.31727309
	5	.072058193	.053905462	.670	-.08111148	.22522787
5	1	-.016980958	.053905462	.998	-.17015063	.13618872
	2	.045206777	.053905462	.917	-.10796290	.19837645
	3	.092045220	.053905462	.440	-.06112445	.24521489
	4	-.072058193	.053905462	.670	-.22522787	.08111148

\*. The mean difference is significant at the 0.05 level.

*Table III-3: Sodium concentration case validation per product.*

Product		Cases					
		Valid		Missing		Total	
		N	Percent	N	Percent	N	Percent
Sodium	1	10	100.0%	0	0.0%	10	100.0%
	2	10	100.0%	0	0.0%	10	100.0%
	3	10	100.0%	0	0.0%	10	100.0%
	4	10	100.0%	0	0.0%	10	100.0%
	5	10	100.0%	0	0.0%	10	100.0%

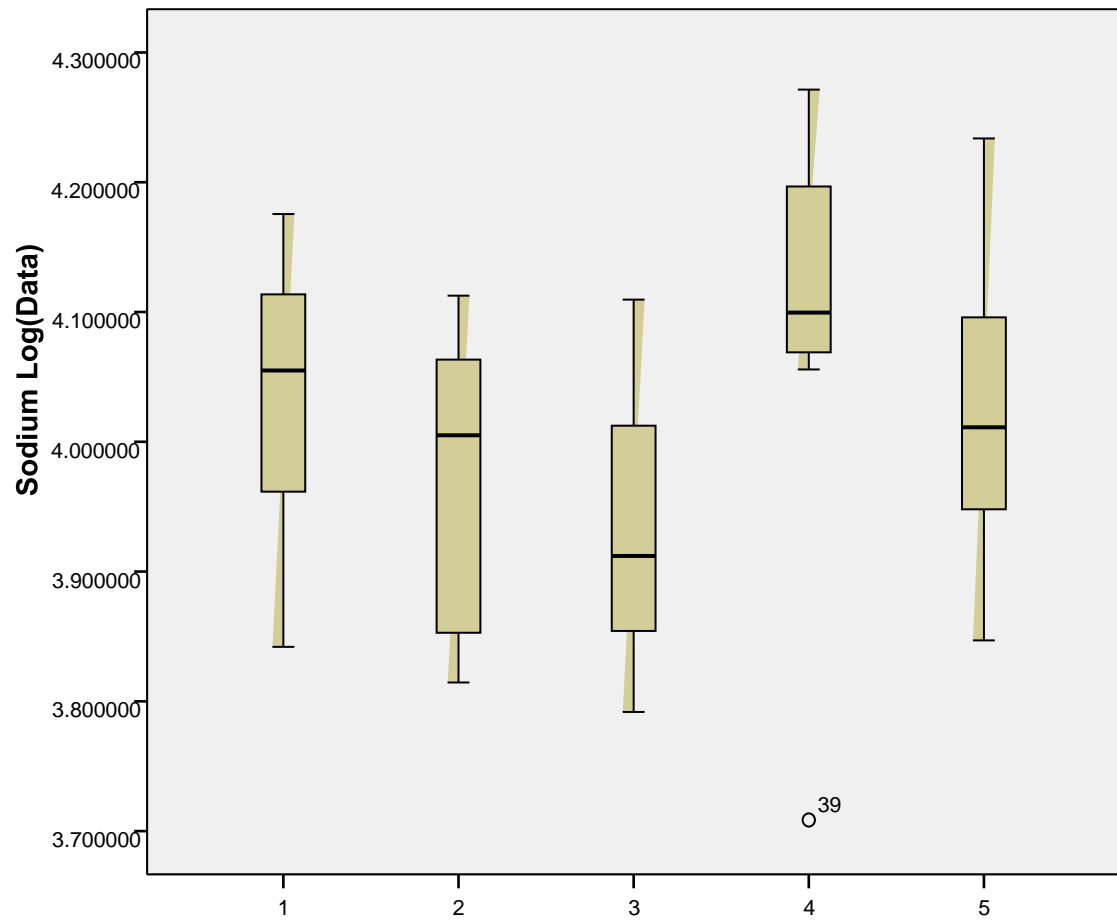


Figure III-2: Boxplot of sodium concentration (mg/kg) per product.



*Table III-4: Normalized sodium concentration (mg/kg) per product per date.*

<b>Sodium Log (Data)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	3.825296	3.825296	3.825296	3.825296	3.825296
10-2-2015	3.961563	3.880699	3.861415	4.271377	3.846955
10-10-2015	3.879841	3.852602	3.887336	4.115611	3.949439
10-16-2015	4.047275	3.999739	3.854245	4.083503	4.049993
10-23-2015	4.037825	4.063333	3.936715	4.196729	3.947973
10-31-2015	3.841985	3.814514	3.791831	4.05576	3.926548
11-6-2015	4.073352	4.05423	3.980685	4.140194	4.095866
11-13-2015	4.175512	4.101059	4.109579	4.203848	4.233757
11-20-2015	4.170262	4.112605	4.045323	4.070038	4.100715
12-4-2015	4.062582	3.852846	3.794	3.708591	3.972342
5-20-2016	4.113609	4.0103	4.012415	4.068928	4.070407

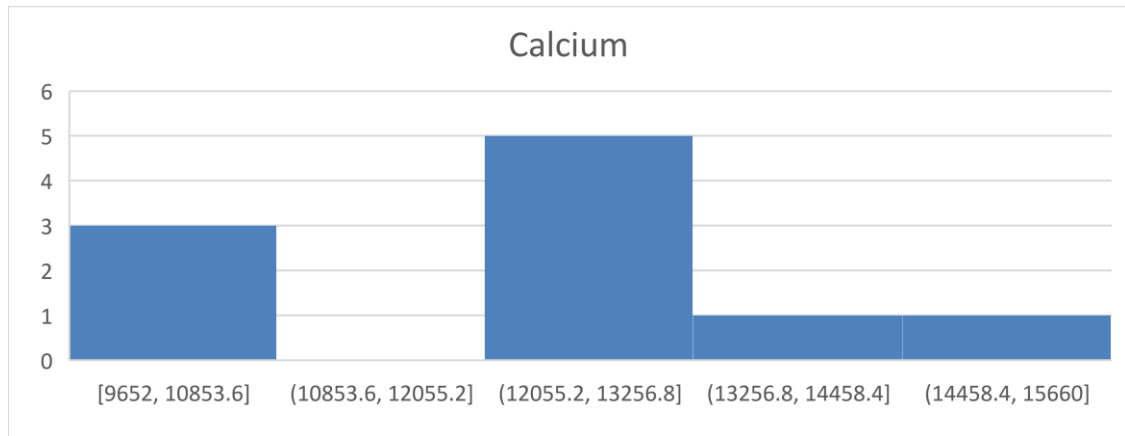
*Table III-5: Sodium concentration (mg/kg) per product per date.*

<b>Sodium (mg/kg)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	6688	6688	6688	6688	6688
10-2-2015	9153	7598	7268	18680	7030
10-10-2015	7583	7122	7715	13050	8901
10-16-2015	11150	9994	7149	12120	11220
10-23-2015	10910	11570	8644	15730	8871
10-31-2015	6950	6524	6192	11370	8444
11-6-2015	11840	11330	9565	13810	12470
11-13-2015	14980	12620	12870	15990	17130
11-20-2015	14800	12960	11100	11750	12610
12-4-2015	11550	7126	6223	5112	9383
5-20-2016	12990	10240	10290	11720	11760

*Table III-6: Statistical significance table for sodium.*

Sodium	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1					
Product 2					
Product 3				↓↓↓	
Product 4			↑↑↑		
Product 5					

## **APPENDIX IV: CALCIUM**



*Figure IV-1: Calcium histogram for determination of normality.*

*Table IV-1: ANOVA of calcium concentrations between groups ( $\alpha = 0.05$ ).*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.112	4	.028	10.400	.000
Within Groups	.121	45	.003		
Total	.234	49			

Table IV-2: Multiple comparison Tukey HSD of calcium concentration difference between each product ( $\alpha = 0.05$ ).

(I) Product	(J) Product	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.139768996*	.023231797	.000	.07375701	.20578098
	3	.099099637*	.023231797	.001	.03308765	.16511163
	4	.055238088	.023231797	.140	-	.12125008
	5	.049990188	.023231797	.217	.01077390	.11600218
2	1	-.139768996*	.023231797	.000	-.20578098	-
	3	-.040669359	.023231797	.414	-.10668135	.07375701
	4	-.084530908*	.023231797	.006	-.15054290	.02534263
	5	-.089778808*	.023231797	.003	-.15579080	-
3	1	-.099099637*	.023231797	.001	-.16511163	-
	2	.040669359	.023231797	.414	-.02534263	.03308765
	4	-	.023231797	.338	-.10987354	.10668135
	5	.043861549	.023231797	.232	-.11512144	.02215044
4	1	-.055238088	.023231797	.140	-	.01077390
	2	.084530908*	.023231797	.006	.12125008	.15054290
	3	.043861549	.023231797	.338	.01851892	.10987354
	5	-.005247900	.023231797	.999	-	.06076409

5	1	-.049990188	.023231797	.217	-	.01602180
	2	.089778808*	.023231797	.003	.11600218	.15579080
	3	.049109449	.023231797	.232	.02376682	.11512144
	4	.005247900	.023231797	.999	-	.07125989
					.01690254	
					-.06076409	

\*. The mean difference is significant at the 0.05 level.



*Table IV-3: calcium concentration case validation per product.*

Product		Cases					
		Valid		Missing		Total	
		N	Percent	N	Percent	N	Percent
Calcium	1	10	100.0%	0	0.0%	10	100.0%
	2	10	100.0%	0	0.0%	10	100.0%
	3	10	100.0%	0	0.0%	10	100.0%
	4	10	100.0%	0	0.0%	10	100.0%
	5	10	100.0%	0	0.0%	10	100.0%

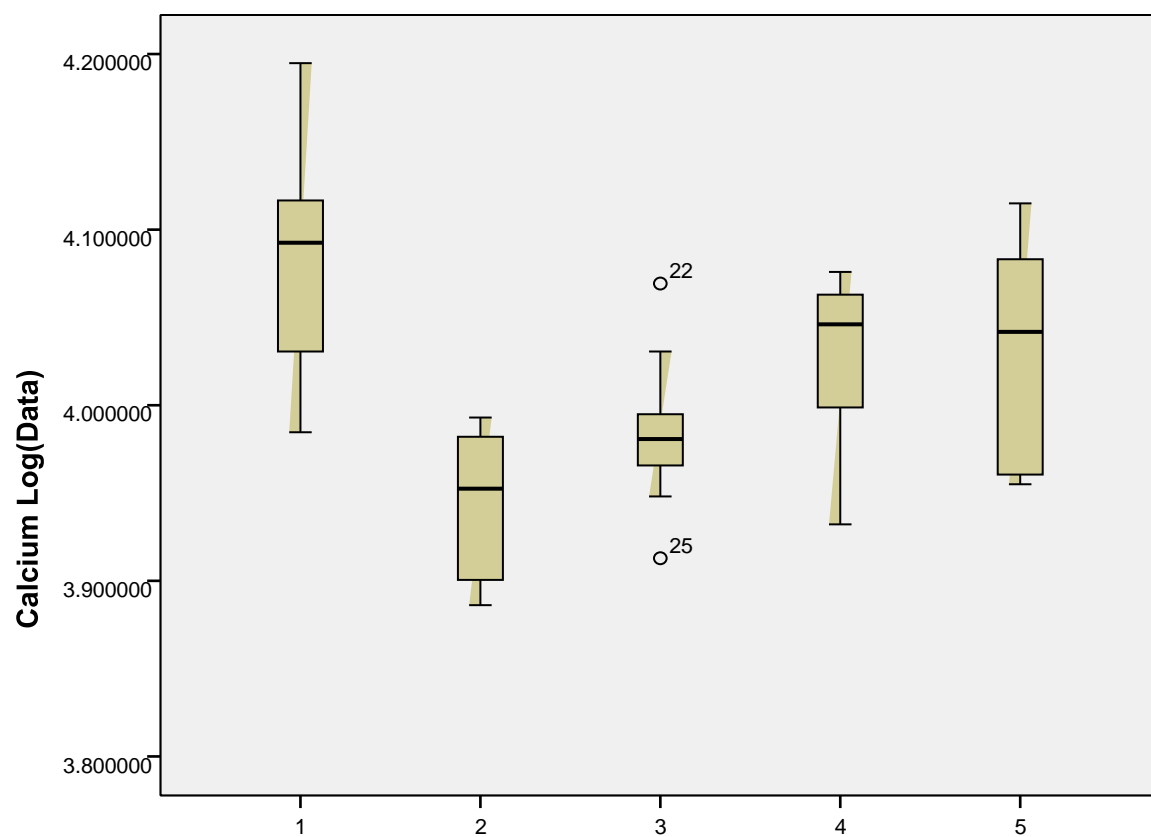


Figure IV-2: Boxplot of calcium concentration (mg/kg) per product.

*Table IV-4: Normalized calcium concentration (mg/kg) per product by date.*

<b>Calcium Log (Data)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	3.893151	3.893151	3.893151	3.893151	3.893151
10-2-2015	4.194792	3.992995	3.975845	4.062958	3.960518
10-10-2015	4.116608	3.893984	4.069298	4.051924	4.06032
10-16-2015	4.095169	3.900531	3.994889	3.998739	4.002166
10-23-2015	4.004321	3.97557	3.994757	4.040207	3.955014
10-31-2015	3.984617	3.982045	3.912859	4.012837	4.023252
11-6-2015	4.100026	3.920384	3.971183	4.057286	4.11059
11-13-2015	4.089905	3.939519	4.0306	4.075912	4.114944
11-20-2015	4.087426	3.965437	3.965719	3.99025	4.072985
12-4-2015	4.0306	3.886152	3.94807	3.932169	3.957032
5-20-2016	4.136403	3.985561	3.985651	4.065206	4.083144

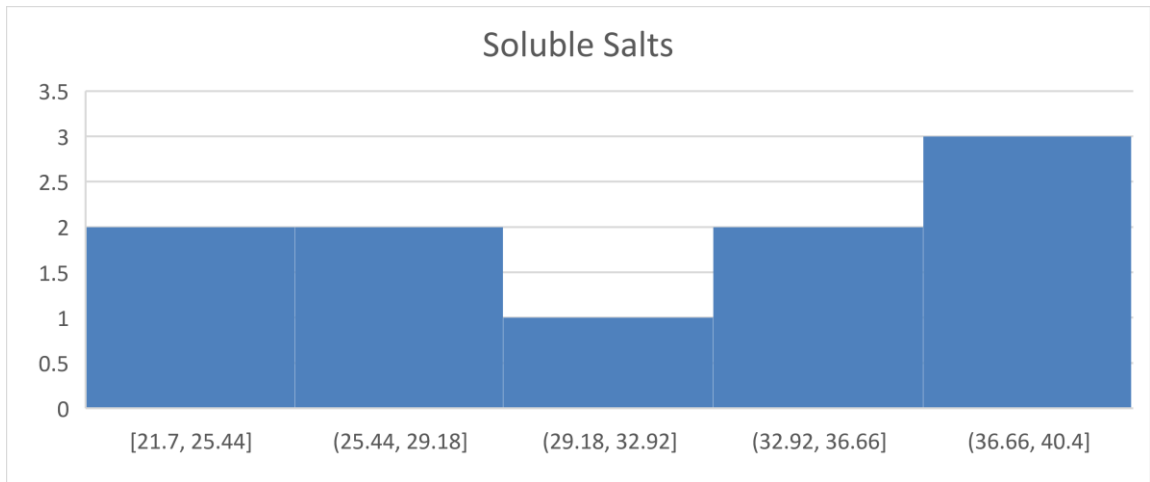
*Table IV-5: Calcium concentration (mg/kg) per product by date.*

<b>Calcium (mg/kg)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	7819	7819	7819	7819	7819
10-2-2015	15660	9840	9459	11560	9131
10-10-2015	13080	7834	11730	11270	11490
10-16-2015	12450	7953	9883	9971	10050
10-23-2015	10100	9453	9880	10970	9016
10-31-2015	9652	9595	8182	10300	10550
11-6-2015	12590	8325	9358	11410	12900
11-13-2015	12300	8700	10730	11910	13030
11-20-2015	12230	9235	9241	9778	11830
12-4-2015	10730	7694	8873	8554	9058
5-20-2016	13690	9673	9675	11620	12110

Table IV-6: Statistical significance table for calcium per product.

Calcium	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1		↑↑↑	↑↑↑		
Product 2	↓↓↓			↓↓↓	↓↓↓
Product 3	↓↓↓				
Product 4		↑↑↑			
Product 5		↑↑↑			

## **APPENDIX V: TOTAL SOLUBLE SALTS**



*Figure V-1: Soluble salts histogram for determination of normality.*

*Table V-1: ANOVA of soluble salts concentration difference between groups ( $\alpha = 0.05$ ).*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.402	4	.100	5.774	.001
Within Groups	.782	45	.017		
Total	1.184	49			



Table V-2: Multiple comparison Tukey HSD of soluble salts concentration difference between each product ( $\alpha = 0.05$ ).

(I) Product	(J) Product	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.150657109	.058966475	.097	-.01689318	.31820740
	3	.086479507	.058966475	.589	-.08107078	.25402980
	4	-.108095764	.058966475	.368	-.27564605	.05945452
	5	-.023121092	.058966475	.995	-.19067138	.14442920
2	1	-.150657109	.058966475	.097	-.31820740	.01689318
	3	-.064177601	.058966475	.812	-.23172789	.10337269
	4	-.258752873*	.058966475	.001	-.42630316	-.09120258
	5	-.173778200*	.058966475	.039	-.34132849	-.00622791
3	1	-.086479507	.058966475	.589	-.25402980	.08107078
	2	.064177601	.058966475	.812	-.10337269	.23172789
	4	-.194575271*	.058966475	.015	-.36212556	-.02702498
	5	-.109600599	.058966475	.354	-.27715089	.05794969
4	1	.108095764	.058966475	.368	-.05945452	.27564605
	2	.258752873*	.058966475	.001	.09120258	.42630316
	3	.194575271*	.058966475	.015	.02702498	.36212556
	5	.084974672	.058966475	.605	-.08257562	.25252496
5	1	.023121092	.058966475	.995	-.14442920	.19067138
	2	.173778200*	.058966475	.039	.00622791	.34132849
	3	.109600599	.058966475	.354	-.05794969	.27715089
	4	-.084974672	.058966475	.605	-.25252496	.08257562

\*. The mean difference is significant at the 0.05 level.

Table V-3: Soluble salts concentration case validation per product.

Product	Cases					
	Valid		Missing		Total	
	N	Percent	N	Percent	N	Percent
Soluble Salts 1	10	100.0%	0	0.0%	10	100.0%
2	10	100.0%	0	0.0%	10	100.0%
3	10	100.0%	0	0.0%	10	100.0%
4	10	100.0%	0	0.0%	10	100.0%
5	10	100.0%	0	0.0%	10	100.0%

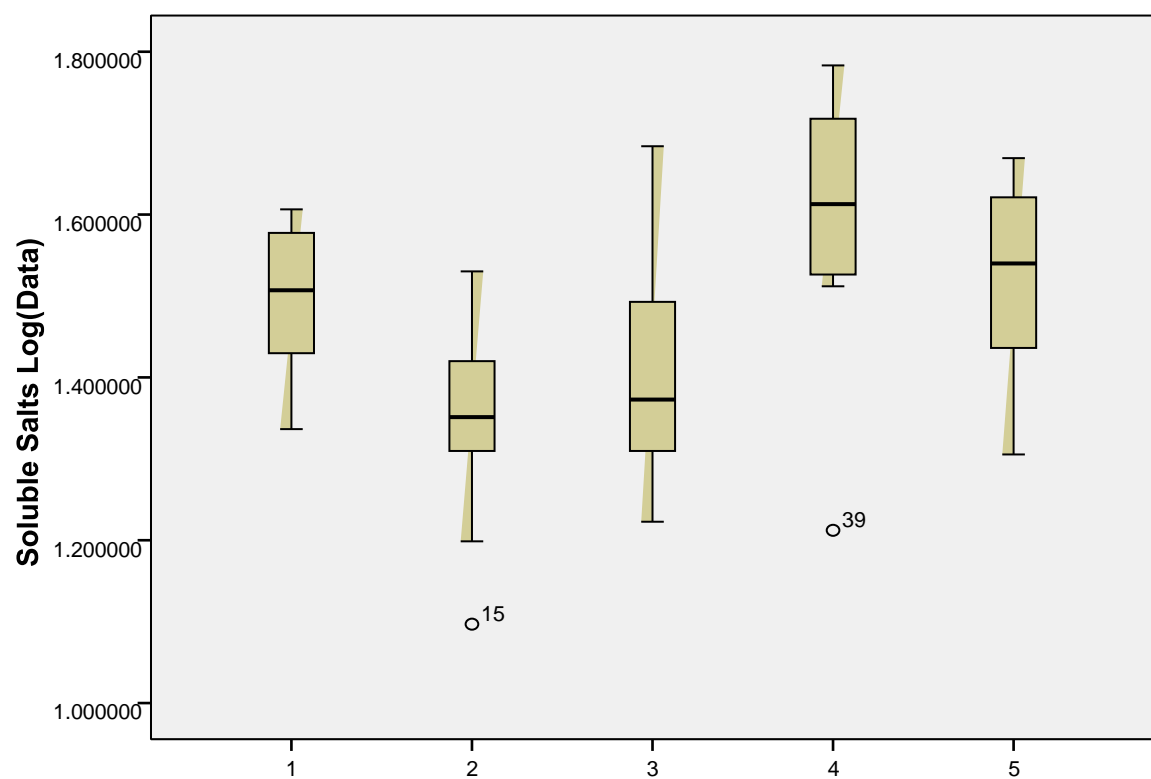


Figure V-2: Boxplot of soluble salts concentration (dS/m) per product.

*Table V-4: Concentration of soluble salts (dS/m) per product by date.*

<b>Soluble Salts (dS/m)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
2015-10-1	21.3	21.3	21.3	21.3	21.3
2015-10-2	27.4	26.3	16.7	50.2	23.3
2015-10-10	22.8	22.3	22	33.6	31.3
10-16-2015	31.3	33.9	19.8	36	38.8
10-23-2015	33	29.2	25.3	60.7	28.5
10-31-2015	21.7	12.5	21.1	32.5	20.2
11-6-2015	40.4	21.5	31.1	52.2	41.8
11-13-2015	40.4	20.4	48.3	58.5	46.7
11-20-2015	35.8	22.8	31.5	36	42.5
12-4-2015	26.9	15.8	20.4	16.3	27.3
5-20-2016	37.8	22.6	30.3	46.7	38.4

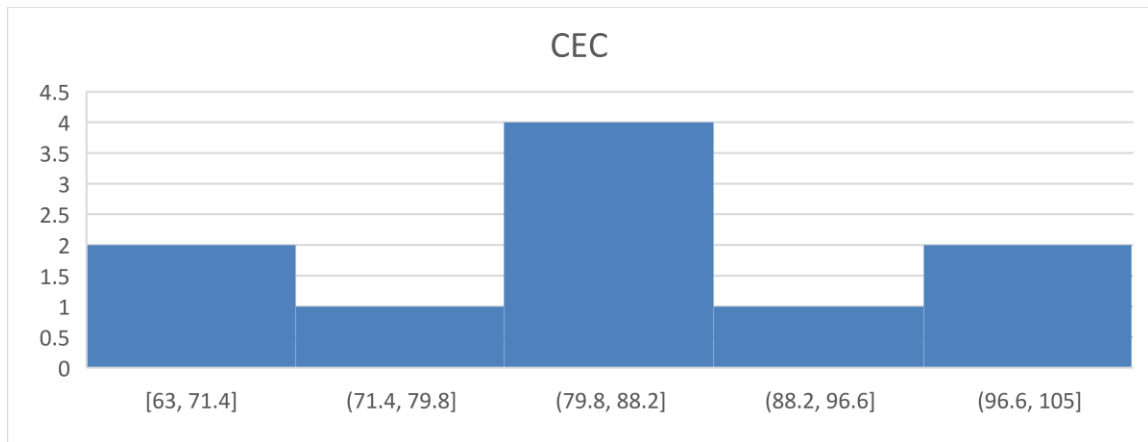
*Table V-5: Normalized concentration of soluble salts (dS/m) per product by date.*

<b>Soluble Salts Log (Data)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	1.32838	1.32838	1.32838	1.32838	1.32838
10-2-2015	1.437751	1.419956	1.222716	1.700704	1.367356
10-10-2015	1.357935	1.348305	1.342423	1.526339	1.495544
10-16-2015	1.495544	1.5302	1.296665	1.556303	1.588832
10-23-2015	1.518514	1.465383	1.403121	1.783189	1.454845
10-31-2015	1.33646	1.09691	1.324282	1.511883	1.305351
11-6-2015	1.606381	1.332438	1.49276	1.717671	1.621176
11-13-2015	1.606381	1.30963	1.683947	1.767156	1.669317
11-20-2015	1.553883	1.357935	1.498311	1.556303	1.628389
12-4-2015	1.429752	1.198657	1.30963	1.212188	1.436163
5-20-2016	1.577492	1.354108	1.481443	1.669317	1.584331

*TableV-6: Statistical significance table for total soluble salts per product.*

Soluble Salts	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1					
Product 2				↓↓↓	↓↓↓
Product 3				↓↓↓	
Product 4		↑↑↑	↑↑↑		
Product 5		↑↑↑			

## **APPENDIX VI: CATION EXCHANGE**



*Figure VI-1: CEC histogram for determination of normality.*



*Table VI-1: ANOVA of cation exchange difference between groups ( $\alpha = 0.05$ ).*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.070	4	.017	2.814	.036
Within Groups	.280	45	.006		
Total	.350	49			

Table VI-2: Multiple comparison Tukey HSD of cation exchange difference between each product ( $\alpha = 0.05$ ).

(I) Product	(J) Product	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.040463082	.035263220	.780	-.05973559	.14066176
	3	.070070858	.035263220	.289	-.03012782	.17026953
	4	-.040401637	.035263220	.781	-.14060031	.05979704
	5	.009699278	.035263220	.999	-.09049940	.10989795
2	1	-.040463082	.035263220	.780	-.14066176	.05973559
	3	.029607776	.035263220	.917	-.07059090	.12980645
	4	-.080864719	.035263220	.166	-.18106339	.01933396
	5	-.030763804	.035263220	.905	-.13096248	.06943487
3	1	-.070070858	.035263220	.289	-.17026953	.03012782
	2	-.029607776	.035263220	.917	-.12980645	.07059090
	4	-.110472495*	.035263220	.024	-.21067117	-.01027382
	5	-.060371581	.035263220	.437	-.16057026	.03982709
4	1	.040401637	.035263220	.781	-.05979704	.14060031
	2	.080864719	.035263220	.166	-	.18106339
	3	.110472495*	.035263220	.024	.01933396	.21067117
	5	.050100915	.035263220	.618	.01027382	.15029959
5	1	-.009699278	.035263220	.999	-.10989795	.09049940
	2	.030763804	.035263220	.905	-.06943487	.13096248
	3	.060371581	.035263220	.437	-.03982709	.16057026
	4	-.050100915	.035263220	.618	-.15029959	.05009776

\*. The mean difference is significant at the 0.05 level.

Table VI-3: Cation exchange case validation per product.

Product	Cases					
	Valid		Missing		Total	
	N	Percent	N	Percent	N	Percent
Cation Exchange 1	10	100.0%	0	0.0%	10	100.0%
2	10	100.0%	0	0.0%	10	100.0%
3	10	100.0%	0	0.0%	10	100.0%
4	10	100.0%	0	0.0%	10	100.0%
5	10	100.0%	0	0.0%	10	100.0%

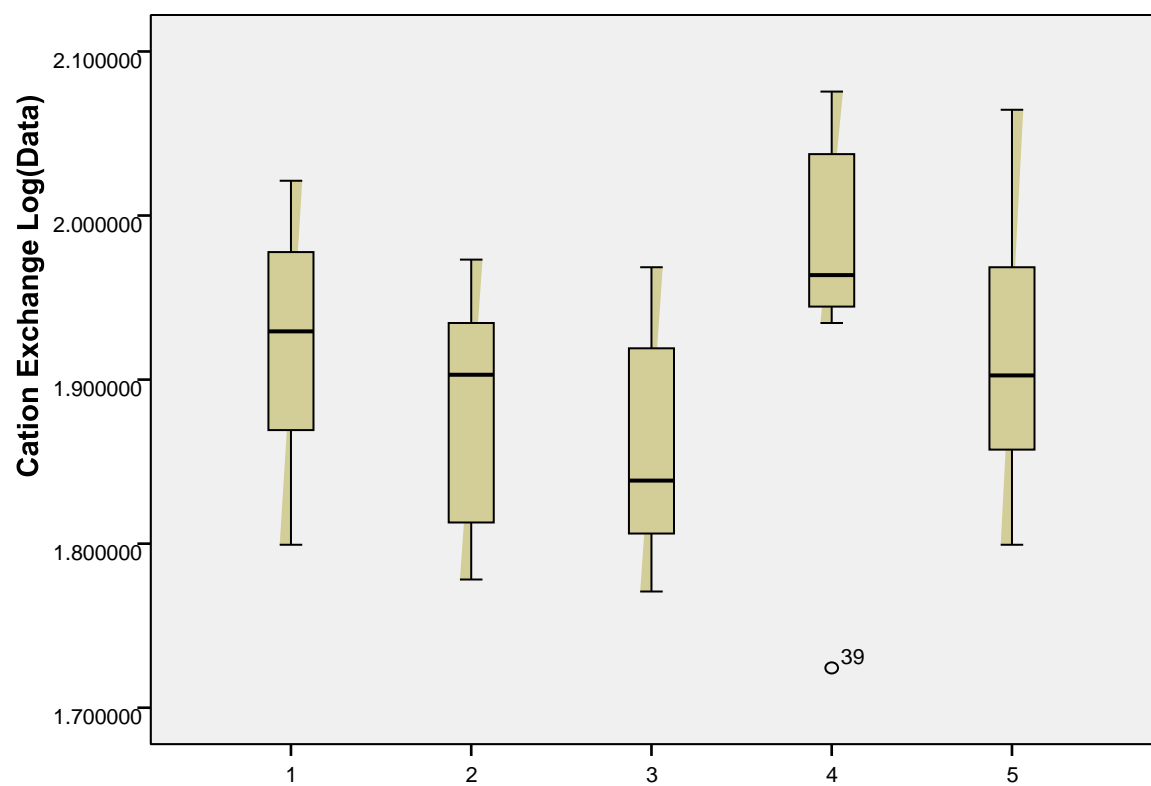


Figure VI-2: Boxplot of cation exchange capacity (mEq/100g) per product.

Table VI-4: Normalized cation exchange capacity (mEq/100g) per product by date.

<b>Cation Exchange Capacity Log (Data)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	1.78533	1.78533	1.78533	1.78533	1.78533
10-2-2015	1.869232	1.819544	1.80618	1.80618	1.799341
10-10-2015	1.819544	1.799341	1.819544	1.819544	1.857332
10-16-2015	1.924279	1.892095	1.80618	1.80618	1.924279
10-23-2015	1.919078	1.934498	1.857332	1.857332	1.857332
10-31-2015	1.799341	1.778151	1.770852	1.770852	1.845098
11-6-2015	1.944483	1.934498	1.880814	1.880814	1.963788
11-13-2015	2.021189	1.963788	1.968483	1.968483	2.064458
11-20-2015	2.017033	1.973128	1.919078	1.919078	1.968483
12-4-2015	1.934498	1.812913	1.778151	1.778151	1.880814
5-20-2016	1.977724	1.913814	1.919078	1.919078	1.968483

*Table VI-5: Cation exchange capacity per product (mEq/100g) by date.*

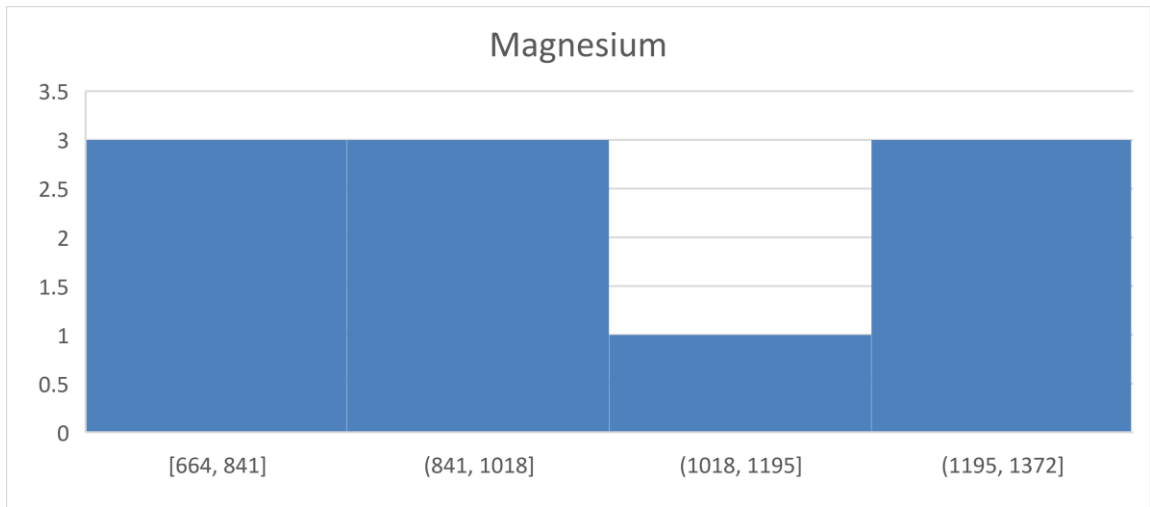
<b>Cation Exchange Capacity (mEq/100g)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	61	61	61	61	61
10-2-2015	74	66	64	119	63
10-10-2015	66	63	66	94	72
10-16-2015	84	78	64	89	84
10-23-2015	83	86	72	109	72
10-31-2015	63	60	59	86	70
11-6-2015	88	86	76	100	92
11-13-2015	105	92	93	109	116
11-20-2015	104	94	83	88	93
12-4-2015	86	65	60	53	76
5-20-2016	95	82	83	90	93

*Table VI-6: Statistical significance table for cation exchange capacity per product.*

CEC	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1					
Product 2					
Product 3				↓↓↓	
Product 4			↑↑↑		
Product 5					

## **APPENDIX VII: MAGNESIUM**





*Figure VII-1: Magnesium histogram for determination of normality.*

*Table VII-1: ANOVA of magnesium concentration difference between products ( $\alpha = 0.05$ ).*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.113	4	.028	2.014	.109
Within Groups	.629	45	.014		
Total	.741	49			

Table 2: Multiple comparison Tukey HSD of magnesium concentration difference between each product ( $\alpha = 0.05$ ).

(I) Product	(J) Product	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.047665052	.052859876	.895	-.10253364	.19786375
	3	.097239834	.052859876	.364	-.05295886	.24743853
	4	-.042485680	.052859876	.928	-.19268437	.10771301
	5	.004836738	.052859876	1.000	-.14536196	.15503543
2	1	-.047665052	.052859876	.895	-.19786375	.10253364
	3	.049574782	.052859876	.881	-.10062391	.19977348
	4	-.090150733	.052859876	.441	-.24034943	.06004796
	5	-.042828314	.052859876	.926	-.19302701	.10737038
3	1	-.097239834	.052859876	.364	-.24743853	.05295886
	2	-.049574782	.052859876	.881	-.19977348	.10062391
	4	-.139725514	.052859876	.079	-.28992421	.01047318
	5	-.092403096	.052859876	.416	-.24260179	.05779560
4	1	.042485680	.052859876	.928	-.10771301	.19268437
	2	.090150733	.052859876	.441	-.06004796	.24034943
	3	.139725514	.052859876	.079	-.01047318	.28992421
	5	.047322419	.052859876	.897	-.10287628	.19752111
5	1	-.004836738	.052859876	1.000	-.15503543	.14536196
	2	.042828314	.052859876	.926	-.10737038	.19302701
	3	.092403096	.052859876	.416	-.05779560	.24260179
	4	-.047322419	.052859876	.897	-.19752111	.10287628

Table VII-3: Magnesium concentration case validation per product.

Product	Cases					
	Valid		Missing		Total	
	N	Percent	N	Percent	N	Percent
Magnesium 1	10	100.0%	0	0.0%	10	100.0%
2	10	100.0%	0	0.0%	10	100.0%
3	10	100.0%	0	0.0%	10	100.0%
4	10	100.0%	0	0.0%	10	100.0%
5	10	100.0%	0	0.0%	10	100.0%

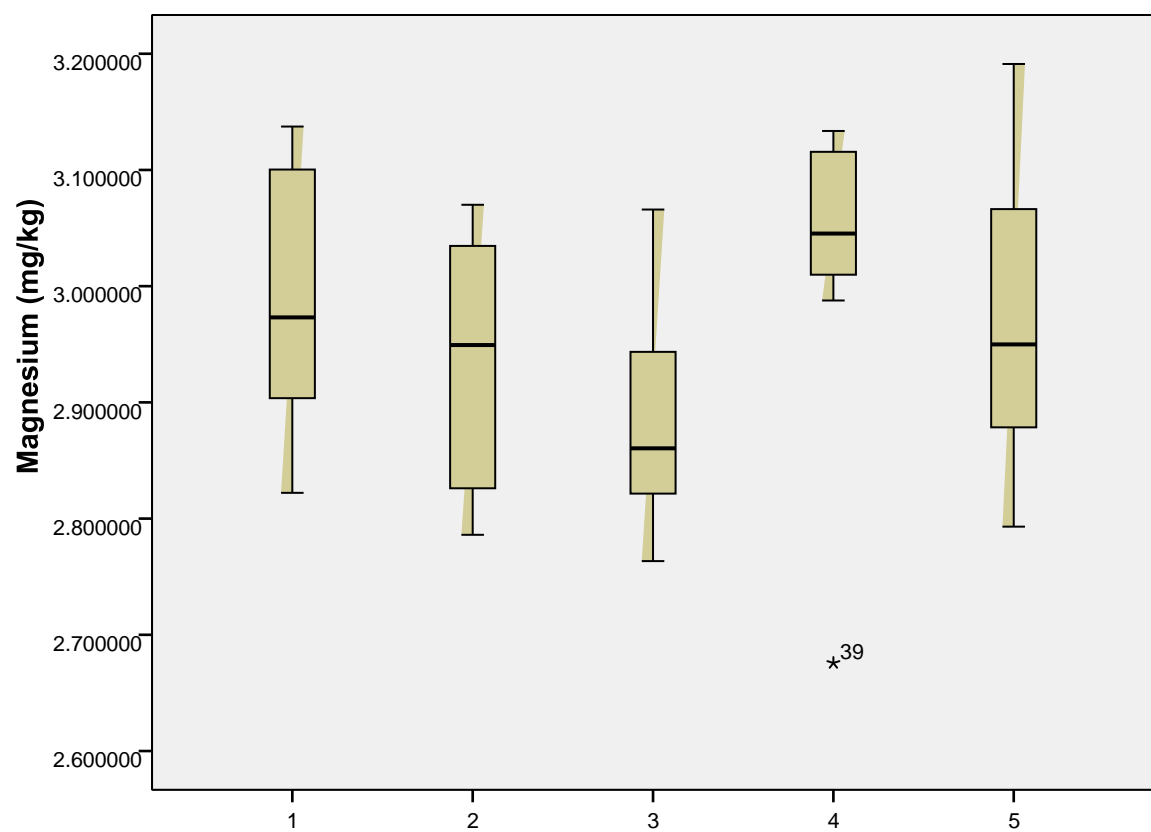


Figure VII-2:Boxplot of magnesium concentration (mg/kg) per product.

Table VII-4: Magnesium concentration (mg/kg) per product by date.

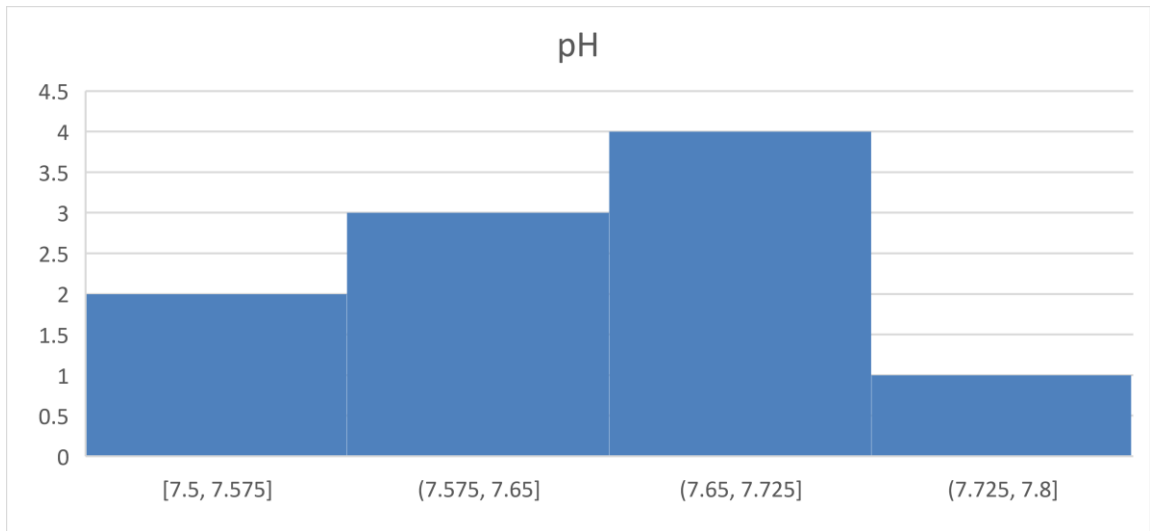
	<b>Magnesium (mg/kg)</b>				
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	598	598	598	598	598
10-2-2015	801	670	663	1125	621
10-10-2015	702	640	676	1089	756
10-16-2015	911	857	664	1023	895
10-23-2015	902	924	778	1360	756
10-31-2015	664	611	580	972	713
11-6-2015	1041	1053	782	1305	1133
11-13-2015	1291	1083	1071	1310	1502
11-20-2015	1372	1175	878	1095	1165
12-4-2015	970	743	641	474	887
5-20-2016	1260	1117	1164	1251	1553

Table VII-5: Normalized magnesium concentration (mg/kg) per product by date.

<b>Magnesium Log (Data)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-2-2015	2.903632516	2.826074803	2.821513528	3.051152522	2.7930916
10-10-2015	2.846337112	2.806179974	2.829946696	3.03702788	2.878521796
10-16-2015	2.959518377	2.932980822	2.822168079	3.009875634	2.951823035
10-23-2015	2.955206538	2.965671971	2.890979597	3.133538908	2.878521796
10-31-2015	2.822168079	2.78604121	2.763427994	2.987666265	2.85308953
11-6-2015	3.01745073	3.022428371	2.893206753	3.115610512	3.05422991
11-13-2015	3.110926242	3.034628457	3.029789471	3.117271296	3.176669933
11-20-2015	3.137354111	3.070037867	2.943494516	3.039414119	3.066325925
12-4-2015	2.986771734	2.870988814	2.80685803	2.675778342	2.94792362
5-20-2016	3.100370545	3.048053173	3.06595298	3.09725731	3.191171456

## **APPENDIX VIII: SOIL pH**





*Figure VII=1: pH histogram for determination of normality.*

*Table VIII-1: ANOVA of soil pH difference between groups ( $\alpha = 0.05$ ).*

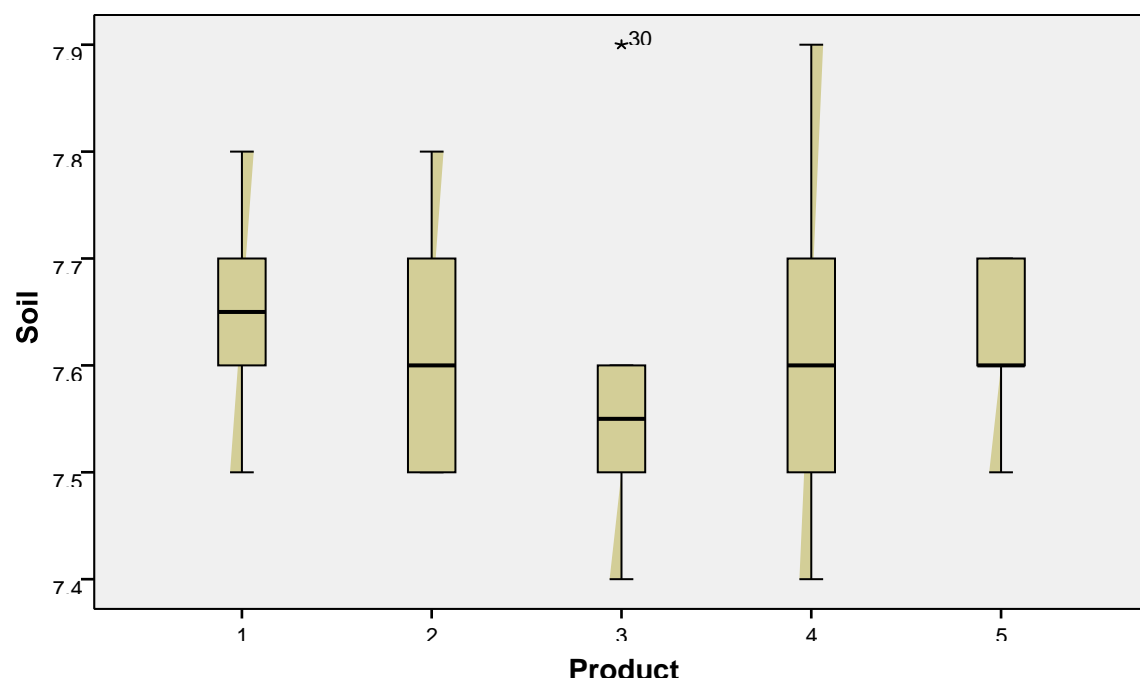
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.027	4	.007	.467	.760
Within Groups	.646	45	.014		
Total	.673	49			

Table VII-2: Multiple comparisons Tukey HAD of soil pH differences between each product ( $\alpha = 0.05$ ).

(I) Product	(J) Product	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.030	.054	.980	-.12	.18
	3	.070	.054	.689	-.08	.22
	4	.020	.054	.996	-.13	.17
	5	.020	.054	.996	-.13	.17
2	1	-.030	.054	.980	-.18	.12
	3	.040	.054	.944	-.11	.19
	4	-.010	.054	1.000	-.16	.14
	5	-.010	.054	1.000	-.16	.14
3	1	-.070	.054	.689	-.22	.08
	2	-.040	.054	.944	-.19	.11
	4	-.050	.054	.882	-.20	.10
	5	-.050	.054	.882	-.20	.10
4	1	-.020	.054	.996	-.17	.13
	2	.010	.054	1.000	-.14	.16
	3	.050	.054	.882	-.10	.20
	5	.000	.054	1.000	-.15	.15
5	1	-.020	.054	.996	-.17	.13
	2	.010	.054	1.000	-.14	.16
	3	.050	.054	.882	-.10	.20
	4	.000	.054	1.000	-.15	.15

*Table VIII-3: Soil pH case validation per product.*

Product	Cases					
	Valid		Missing		Total	
	N	Percent	N	Percent	N	Percent
Soil pH 1	10	100.0%	0	0.0%	10	100.0%
2	10	100.0%	0	0.0%	10	100.0%
3	10	100.0%	0	0.0%	10	100.0%
4	10	100.0%	0	0.0%	10	100.0%
5	10	100.0%	0	0.0%	10	100.0%

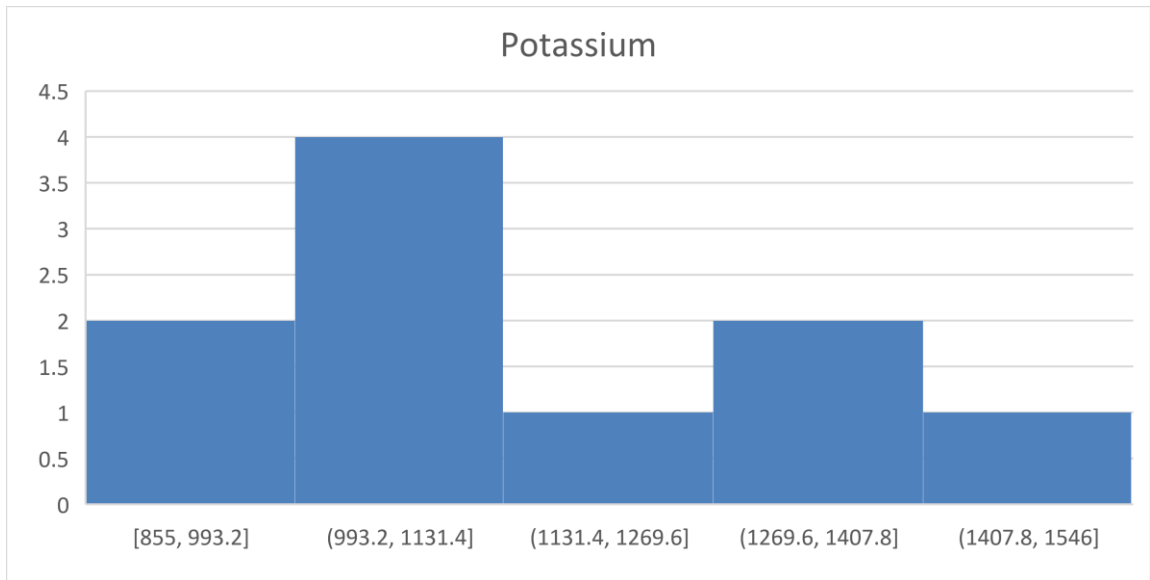


*Figure VIII-2: Boxplot of soil pH per product.*

*Table VIII-4: Soil pH per product by date.*

<b>Soil pH (units)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
2015-10-1	7.6	7.6	7.6	7.6	7.6
2015-10-2	7.6	7.6	7.5	7.5	7.7
2015-10-10	7.7	7.6	7.5	7.6	7.5
2015-10-16	7.5	7.5	7.6	7.5	7.5
2015-10-23	7.5	7.5	7.5	7.4	7.6
2015-10-31	7.7	7.8	7.6	7.7	7.7
2015-11-6	7.6	7.6	7.5	7.6	7.6
2015-11-13	7.7	7.7	7.4	7.6	7.6
2015-11-20	7.7	7.5	7.6	7.9	7.6
2015-12-4	7.6	7.6	7.6	7.9	7.7
2016-5-20	7.8	7.7	7.9	7.5	7.7

## **APPENDIX IX: POTASSIUM**



*Figure IX=1: Potassium histogram for determination of normality.*



*Table IX-1: ANOVA of potassium concentration difference between products.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.080	4	.020	3.032	.027
Within Groups	.298	45	.007		
Total	.378	49			

Table IX-2: Multiple comparisons Tukey HSD of potassium concentration difference between each product ( $\alpha = 0.05$ ).

(I) Product	(J) Product	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.05701	.03640	.526	-.0464	.1604
	3	.06330	.03640	.421	-.0401	.1667
	4	-.04622	.03640	.711	-.1496	.0572
	5	.01457	.03640	.994	-.0889	.1180
2	1	-.05701	.03640	.526	-.1604	.0464
	3	.00629	.03640	1.000	-.0971	.1097
	4	-.10323	.03640	.051	-.2067	.0002
	5	-.04244	.03640	.770	-.1459	.0610
3	1	-.06330	.03640	.421	-.1667	.0401
	2	-.00629	.03640	1.000	-.1097	.0971
	4	-.10952*	.03640	.033	-.2129	-.0061
	5	-.04873	.03640	.669	-.1522	.0547
4	1	.04622	.03640	.711	-.0572	.1496
	2	.10323	.03640	.051	-.0002	.2067
	3	.10952*	.03640	.033	.0061	.2129
	5	.06079	.03640	.462	-.0426	.1642
5	1	-.01457	.03640	.994	-.1180	.0889
	2	.04244	.03640	.770	-.0610	.1459
	3	.04873	.03640	.669	-.0547	.1522
	4	-.06079	.03640	.462	-.1642	.0426

\*. The mean difference is significant at the 0.05 level.

*Table IX-3: Potassium concentration case validation per product.*

Product		Cases					
		Valid		Missing		Total	
		N	Percent	N	Percent	N	Percent
Potassium	1	10	100.0%	0	0.0%	10	100.0%
	2	10	100.0%	0	0.0%	10	100.0%
	3	10	100.0%	0	0.0%	10	100.0%
	4	10	100.0%	0	0.0%	10	100.0%
	5	10	100.0%	0	0.0%	10	100.0%

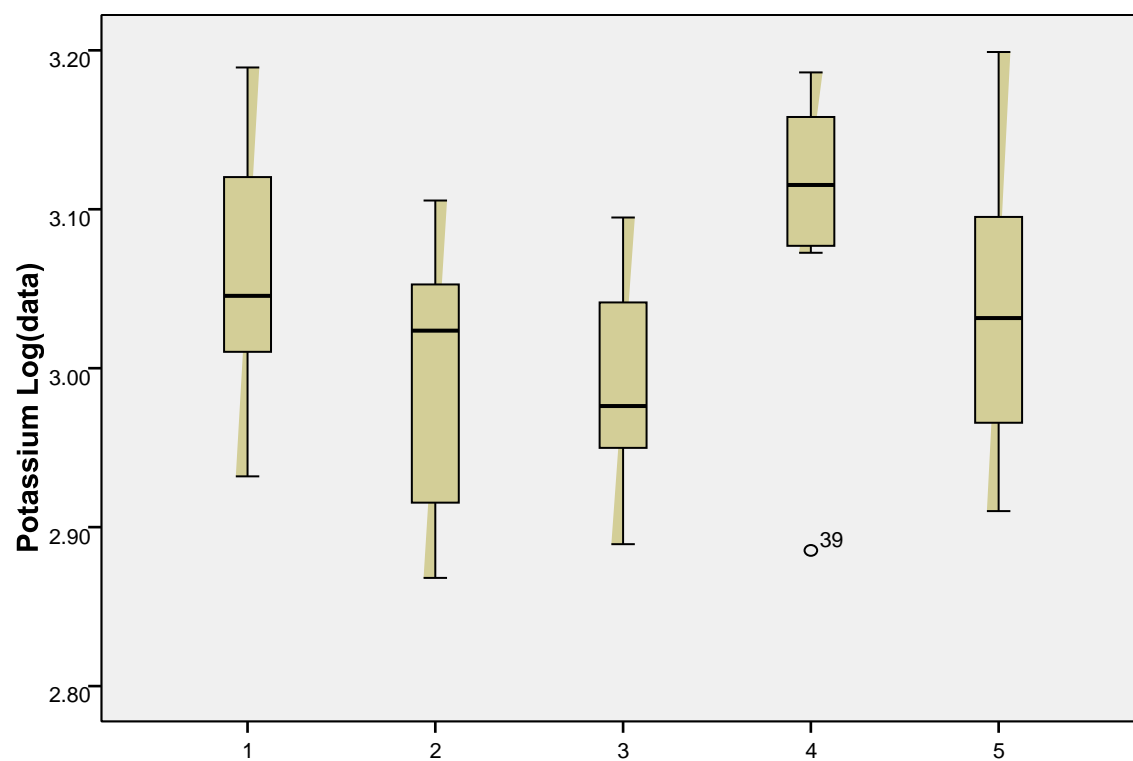


Figure IX-2: Boxplot for potassium concentration (mg/kg) per product.

*Table XI-4: Potassium concentration (mg/kg) per product by date.*

<b>Potassium (mg/kg)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	749	749	749	749	749
10-2-2015	1024	805	880	1299	813
10-10-2015	902	823	902	1309	948
10-16-2015	1110	1093	908	1235	1093
10-23-2015	1061	1044	987	1535	912
10-31-2015	855	738	775	1194	924
11-6-2015	1203	1129	1001	1486	1245
11-13-2015	1546	1068	1244	1439	1581
11-20-2015	1400	1275	1100	1182	1197
12-4-2015	1111	927	891	768	1058
5-20-2016	1319	1201	1228	1377	1434

*Table XI-5: Normalized potassium concentration (mg/kg) per product by date.*

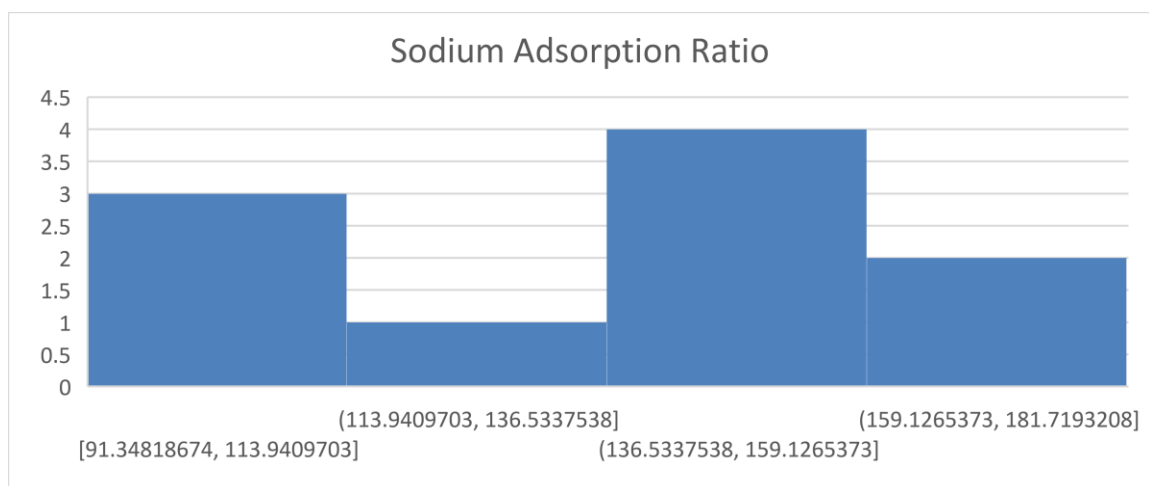
<b>Potassium Log (Data)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-1-2015	2.874482	2.874482	2.874482	2.874482	2.874482
10-2-2015	3.0103	2.905796	2.944483	3.113609	2.910091
10-10-2015	2.955207	2.9154	2.955207	3.11694	2.976808
10-16-2015	3.045323	3.03862	2.958086	3.091667	3.03862
10-23-2015	3.025715	3.0187	2.994317	3.186108	2.959995
10-31-2015	2.931966	2.868056	2.889302	3.077004	2.965672
11-6-2015	3.080266	3.052694	3.000434	3.172019	3.095169
11-13-2015	3.189209	3.028571	3.09482	3.158061	3.198932
11-20-2015	3.146128	3.10551	3.041393	3.072617	3.078094
12-4-2015	3.045714	2.96708	2.949878	2.885361	3.024486
5-20-2016	3.120245	3.079543	3.089198	3.138934	3.156549

*Table IX-6: Statistical significance table for potassium and all products.*

Potassium	Product 1	Product 2	Product 3	Product 4	Product 5
Product 1					
Product 2				↓↓↓	
Product 3				↓↓↓	
Product 4		↑↑↑	↑↑↑		
Product 5					

## **APPENDIX X: SODIUM ADSORPTION RATIO**





*Figure X-1: Sodium adsorption ratio histogram for determination of normality.*

*Table X-1: ANOVA of sodium adsorption ratio concentration difference between products.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.096	4	.024	2.098	.097
Within Groups	.516	45	.011		
Total	.612	49			

Table X-2: Multiple comparisons Tukey HSD of sodium adsorption ratio concentration difference between each product ( $\alpha = 0.05$ ).

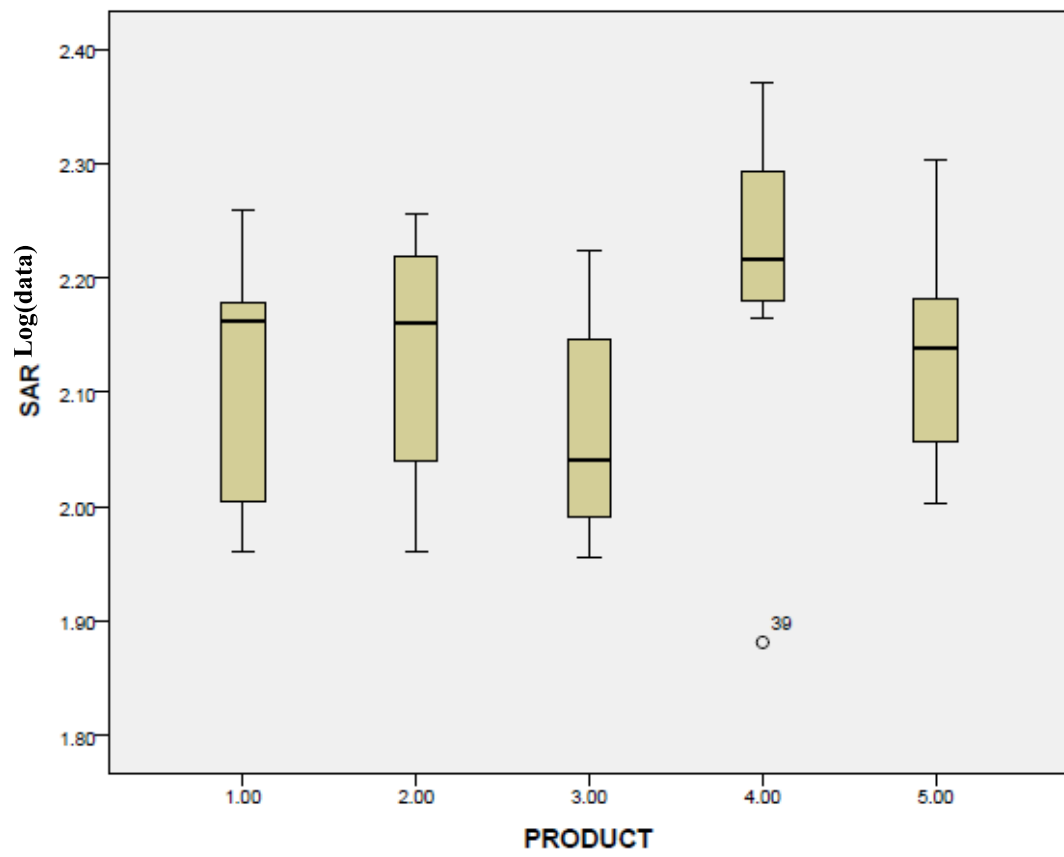
(I) Product	(J) Product	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.00391	.04789	1.000	-.1400	.1322
	3	.05942	.04789	.728	-.0766	.1955
	4	-.07879 -	.04789	.477	-.2149	.0573
	5	.00634	.04789	1.000	-.1424	.1297
2	1	.00391	.04789	1.000	-.1322	.1400
	3	.06333	.04789	.679	-.0727	.1994
	4	-.07488	.04789	.528	-.2109	.0612
	5	-.00243	.04789	1.000	-.1385	.1336
3	1	-.05942	.04789	.728	-.1955	.0766
	2	-.06333	.04789	.679	-.1994	.0727 -
	4	-.13822*	.04789	.045	-.2743	.0022
	5	-.06577	.04789	.647	-.2018	.0703
4	1	.07879	.04789	.477	-.0573	.2149
	2	.07488	.04789	.528	-.0612	.2109
	3	.13822*	.04789	.045	.0022 -	.2743
	5	.07245	.04789	.560	.0636	.2085
5	1	.00634	.04789	1.000	-.1297	.1224
	2	.00243	.04789	1.000	-.1336	.1385
	3	.06577 -	.04789	.647	-.0703	.2018
	4	.07245	.04789	.560	-.2085	.0636

\*. The mean difference is significant at the 0.05 level.

*Table X-3: Sodium adsorption ratio concentration case validation per product.*

Product		Cases					
		Valid	Missing	Total			
		N	Percent	N	Percent		
SAR	1	10	100.0%	0	0.0%	10	100.0%
	2	10	100.0%	0	0.0%	10	100.0%
	3	10	100.0%	0	0.0%	10	100.0%
	4	10	100.0%	0	0.0%	10	100.0%
	5	10	100.0%	0	0.0%	10	100.0%

Figure X-2: Boxplot for sodium adsorption concentration (mg/kg) per product.



*Table X-4: Sodium adsorption ratio concentration per product by date.*

<b>SAR</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-2-2015	101	105	102	235	101
10-10-2015	91	110	98	166	114
10-16-2015	136	151	98	163	152
10-23-2015	147	161	118	200	127
10-31-2015	97	91	94	151	113
11-6-2015	143	165	134	173	149
11-13-2015	182	180	168	197	201
11-20-2015	179	180	156	159	156
12-4-2015	151	110	90	76	133
5-20-2016	150	140	140	146	142

Table X-5: Normalized sodium exchange ratio concentration per product by date.

<b>SAR Log (Data)</b>					
	<b>Product 1</b>	<b>Product 2</b>	<b>Product 3</b>	<b>Product 4</b>	<b>Control</b>
10-2-2015	2.00	2.02	2.01	2.37	2.00
10-10-2015	1.96	2.04	1.99	2.22	2.06
10-16-2015	2.13	2.18	1.99	2.21	2.18
10-23-2015	2.17	2.21	2.07	2.30	2.10
10-31-2015	1.99	1.96	1.97	2.18	2.05
11-6-2015	2.16	2.22	2.13	2.24	2.17
11-13-2015	2.26	2.26	2.22	2.29	2.30
11-20-2015	2.25	2.25	2.19	2.20	2.19
12-4-2015	2.18	2.04	1.96	1.88	2.12
5-20-2016	2.18	2.14	2.15	2.16	2.15