



Influence of landfill leachate on growth response and mineral content of Swiss Chard

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DECLARATION

I declare that the “**Influence of landfill leachate on growth response and mineral content of Swiss Chard**” is a dissertation generated from my own work, that it has not been submitted for any degree or examination in any other University and that all sources I have used or quoted have been indicated and acknowledged by complete references.

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ABSTRACT

In this study, laboratory and greenhouse experiments were conducted to evaluate the effects of utilization of land fill leachate for irrigation purposes on potted soil and Swiss chard, to provide more insight into effects of landfill leachates on the environment. Swiss chard was grown and irrigated with different concentrations of leachates in pot experiments. For several weeks, the experimental soil and Swiss chard leaves was analyzed to assess extent of change in different chemical compositions, post-irrigation.

The leachate samples had a high electrical conductivity (mean = 383 mS cm⁻¹) and high soluble salts content (mean values, Na = 714.5 mg/L, K= 56.8 mg/L, Ca = 133.7 mg/L, Mg = 68.8 mg/L, Cl = 983 mg/L); while the composition of heavy metals in these wastewater leachates were of low concentrations. The application of leachates in irrigation resulted in increased soil cation concentrations, particularly those of Na ions (increased sodicity). Similarly, an increase in electrical conductivity and pH were recorded in the soils after irrigation with leachates. The soil metal concentrations were low and there was no significant difference in soil heavy metal concentrations between the soils irrigated with leachate and those of the controls.

The results also show significant ($p < 0.05$) reduction (up to 50%) in Swiss chard growth with application of (100%, 50% and 25%) of leachate as source of irrigation water compared to the growth observed in leachate-free (control) irrigation systems. This reduction in growth was best attributed to the high cation content in plant tissue picked up from the soil which was high in cations as a result of leachate irrigation.

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DEDICATION

I dedicate this thesis to

My parents,

My wife,

My sons and daughter

and

All my family in Libya

GLOSSARY

Abbreviations

EC	Electrical conductivity
MP-AES	Microwave plasma-atomic emission spectrometer
GLS	Green leaves Swiss chard
SEM	Scanning Electron Microscope
EPA	Environmental Protection Agency
LL	Landfill leachate
NPK	Nitrogen, Phosphate, Potassium
SAR	Sodium Adsorption Ratio
ESP	Exchangeable Sodium Percentage
OP	Osmotic Potential
%	Percentage
g m^{-3}	Gram per meter cubic

DEFINITION OF KEY TERMS

1. Heavy metals

A heavy metal is defined as any metal that has a relatively high density and is toxic at low concentration such as lead, nickel, mercury and arsenic. Heavy metals belong to a class of pollutants that produce undesirable health effects, even if present in minuscule quantities.

2. Landfill

Landfill is a disposal site where solid waste such as paper, glass and metal is buried between layers of dirt and other materials in such a way as to reduce contamination of the surrounding land. Historically, landfills have been the most common methods of organized waste disposal and remain so in many places around the world. Some landfills are also used for waste management purposes such as the temporary storage, consolidation, and transfer, or processing of waste material (sorting, treatment, or recycling).

3. Leachate

Leachate is the toxic liquid that is collected at the bottom of the landfill. Leachate is formed when water passes through the waste in the landfill cell. The precipitation can be from rain, melted snow or the waste itself. As the liquid moves through the landfill, many organic and inorganic compounds, like heavy metals, are transported in the leachate. The amount of leachate produced is directly linked to the amount of precipitation around the landfill

4. Composition of Leachate

When water percolates through the waste, it promotes and assists process of decomposition by microorganisms. These processes in turn release by-products of decomposition and rapidly use up any available oxygen creating an anoxic environment. The decomposition processes themselves release further water which adds to the volume of leachate. The leachate also reacts with materials that are not themselves prone to decomposition such as fly ash.

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CHAPTER 1

1. INTRODUCTION

1.1 Background

Landfill leachate has been, for a long time, recognized as a potential source of pollution to ground and surface waters (McDougall et al. 1980). Toxic substances which are commonly present in leachate include major ions (as sodium, potassium, sulphate, chloride and iron), heavy metals (like cadmium, chromium, copper, lead nickel and zinc), a wide range of organic compounds and micro-organisms. It is essential to collect and treat leachates before discharge in main/municipal water bodies in order to safeguard aquatic ecosystems. Utilization of municipal wastewaters on lands has been a low-cost treatment and disposal alternative. Municipal wastewater which contains considerable amounts of salts may serve as a source of nutrients for plant growth (Berry et al. 1980). Similarly, it may be possible to recycle landfill leachate by land application; this decontamination is achieved by allowing the soil to act as a filter. Bennett *et al.* (1975) reported significant water quality improvement and no serious effect on a mature hardwood forest after irrigation with landfill leachate. It has also been demonstrated that forages contained higher concentrations of macronutrients after irrigation with leachate (Menser *et al.*, 1979). However, unlike sewage effluent, landfill leachate has not been considered as a potential resource for plant growth, mainly on account of excessive Fe and Mn. Apart from Fe and Mn, other metals may be present in toxic concentrations. Landfill leachate may also contain salts and organic compounds such as organic acids and phenols in quantities that may restrict biological activity in the root zone (Artiolar-Fortuny et al., 1982). Relatively few studies had been undertaken in recent past to evaluate toxicity, deleterious effects or advantage of leachate on soil and crop yields.

Hence, this study will evaluate the use of landfill leachate as a potential source of water for irrigation purposes, and determine the degree of uptake of essential and trace elements by Swiss chard (*Beta vulgaris var. cicla*) irrigated with such landfill leachate.

1.2 Statement of research problem

The management of landfill leachate has become a major focus in landfill environmental management. The leachate is normally generated by the flow of rainfall and surface water into the landfill. Over a period of time, these waters mix with toxic and non-toxic contaminants in landfill sites and results in high concentrated wastewater found in landfill environments which may pose potential threat to the quality of groundwater. The landfill leachates contain complex compositions, such as high concentration of ammonia, nitrogen and salts, suspended solids, and heavy metals, which are also characteristic of leachate contents (Parida *et al.*, 2005).

In recent years, studies revealed that landfills are not properly managed and contamination of water bodies with heavy metals from leachates is evident. Thus, knowledge on influence of possible contamination by irrigation waters used by farmers and safety of the communities around landfill needs to be extended further. It is important to note that the escape of leachate into the main water bodies from landfill is possible under condition of heavy rainfall and improper management of landfill areas. Effect of landfill leachate on the soil properties needs to be assessed, as well as the effect on growth and nutritional composition of cultivated crops.

Hence, Swiss chard was used in a pot experiment for this study. Swiss chard merits the test crop being vegetable that matures in relatively short period and also, the deposition of photosynthate in most vegetables remains in the edible parts of the species, and if

contaminants are absorbed through the plant roots, they could easily find their way into the leaves and fruits and ultimately in human diets.

1.3 Research questions

This study seeks to provide answers to the following questions:

- What is the effect of landfill leachate on soil properties?
- Can landfill leachate be applied as an alternative source of agriculture irrigation system?
- Is there any significant difference in the growth response and mineral content of Swiss chard when different water types landfill leachate water, tap water or distilled water is used for irrigation?

1.4 Research objectives

This research aims to:

- Investigate the effect of landfill leachate on soil chemical properties and assess growth response in Swiss chard (*Beta vulgaris var. cicla*) species.
- Study the possible physiological influence of the uptake of leachate contaminants on the leaf cells of Swiss chard.
- Investigate the influence of landfill leachate on the mineral composition of Swiss chard.

1.5 Assumptions

This study is based on the following assumptions:

- There may be variation in phytochemical and mineral composition of test crop after applying leachates as irrigation water.

- The methods that will be used to analyze the presence and levels of metals in the Swiss chard species are suitable and sensitive to determine the contamination level.

1.6 Delimitations

- The effect of landfill leachate will be studied only on Swiss chard species used for the trial and not on any other vegetable crops.
- Instrumentation including Microwave plasma-atomic emission spectrometer (MP-AES) and scanning electron microscope (SEM) for analysis.
- This will be a pot experiment and not field study, and only one soil type was used.

CHAPTER 2**2. LITERATURE REVIEW****2.1 Leachate generation and composition****2.1.1 Introduction**

Landfill leachate is the wastewater that accumulates within a landfill. Leachate forms when the soluble components present in the solid wastes, dissolve and leach out as water moves through the landfill (Monroe *et al.*, 2001). The soluble components can be leached directly from the refuse or can be formed as a result of the physical, chemical and biological processes that take place during decomposition. Rainfall is the main source of water in leachate but surface water, groundwater and the moisture in the waste can also be sources. Landfill leachate is a water based solution containing dissolved organic matter, inorganic components, heavy metals and artificial organic compounds (Kjeldsen *et al.*, 2002). The exact composition of a leachate is a function of the type, age, and stabilization of the landfill waste, and the prevailing physiochemical conditions, microbiology and water content of the landfill.

2.1.2 Stabilization processes in landfills

Leachate composition is mainly a function of the age and degree of stabilization of the waste within a landfill (Reinhart *et al.*, 1998). Once buried, a complex series of chemical and biological reactions occur within a landfill as the refuse decomposes. Chemical and biological reactions stabilize the waste and proceed in a distinct series of phases. The idea of refuse decomposing in phases was first described by Farquhar *et al.*, (1973) and has been the subject of several other studies (Barlaz *et al.*, 1989; Bozkurt *et al.*, 1999). In literature, the exact number of phases involved in degradation of refuse was reported to range from three to seven (Kjeldsen *et al.*, 2002).

Similarly, it is frequently accepted that in the short term, four distinct phases of decomposition takes place (Barlaz *et al.*, 1989; Lisk, 1991; Bozkurt *et al.*, 1999). The rate of production and characteristics of the leachate produced vary from one phase to the next. Descriptions of the first four phases of refuse decomposition are given below:

Phase 1: Aerobic phase

The aerobic phase begins when the refuse lands on the landfill and only lasts a couple of days, since oxygen is not replenished once the refuse is covered (Kjeldsen *et al.*, 2002). Aerobic organisms break down the degradable material such as sugars present in the fresh refuse to produce carbon dioxide, organic compounds, heat and water (Barlaz *et al.*, 1989). Small amounts of leachate are produced during this phase as the refuse is not typically containing moisture content at field capacity or above. Most of the leachate produced is a result of moisture being released during compaction of the refuse (Kjeldsen *et al.*, 2002). Phase 1 is characterized by a neutral pH and an increase in the Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) (Taulis *et al.*, 2005).

Phase 2: Acid phase

After burial of the refuse, oxygen is not replenished and anaerobic conditions dominate. Hydrolytic, fermentative and acetogenic bacteria take over the decomposition process in the absence of oxygen. During this phase, complex organic material is degraded by hydrolysis to smaller organic molecules such as carboxylic acids, alcohols and carbon dioxide (Bozkurt *et al.*, 2000). The formation of organic acid results in a drop in pH (Kjeldsen *et al.*, 2002). The acidic leachate is chemically aggressive and will increase the solubility of many compounds including metals and other inorganic ions (Kjeldsen *et al.*, 2002; Taulis *et al.*, 2005). Carbon dioxide concentrations reach their maximum values during the acid phase and values of over 90% CO₂ have been observed in the landfill gas

(Barlaz *et al.*, 1989). The leachate from the acid phase is characterized by a pH between 5 and 6, high ammonia and BOD concentrations and a high BOD/COD ratio (Robinson *et al.*, 1989).

Phase 3: Initial methanogenic phase

The onset of the third phase begins when measurable quantities of methane are produced (Kjeldsen *et al.*, 2002). Acetogenic bacteria convert the carboxylic acids produced in the acid phase to acetate, hydrogen and carbon dioxide which raises the pH (Barlaz *et al.*, 1989). The increase in pH allows the growth of methanogenic bacteria whose growth is limited in the acidic conditions of the acidic phase (Kjeldsen *et al.*, 2002). The degradation products act as substrate for the methanogenic bacteria which convert it to methane and carbon dioxide (Bozkurt *et al.*, 2000). It is during the initial methanogenic phase that the decomposition of cellulose and hemi cellulose begins (Kjeldsen *et al.*, 2002).

Phase 4: Stable methanogenic phase

In the stable methanogenic phase, methane production reaches its maximum and decreases thereafter. Carboxylic acids are consumed at the same rate at which they are produced and methane production is dependent on the rate of cellulose and hemicellulose hydrolysis (Kjeldsen *et al.*, 2002; Taulis, 2005). There is a decline in rate of pH increment and a decrease in the BOD and COD concentrations.

2.1.3 Leachate Composition

Household waste is reasonably consistent in composition; so landfills that accept predominantly municipal solid waste and operate under anaerobic conditions tend to produce leachates with similar constituents, although concentrations vary between landfills. The major components in landfill leachate can be divided into four groups:

1. Dissolved organic matter such as volatile fatty acids, humic and fulvic compounds. These are usually measured as total organic carbon (TOC) or chemical oxygen demand.
2. Inorganic macro components such as calcium, magnesium, sodium, potassium, ammonium, sulphate, chloride, iron and hydrogen carbonate.
3. Heavy metals like cadmium, chromium, and copper, lead, nickel and zinc.
4. Xenobiotic organic compounds which can include aromatic hydrocarbons, phenols and pesticides (Christensen *et al.*, 2001; Kjeldsen *et al.*, 2002).

2.1.3.1 Dissolved organic matter

Dissolved organic matter is a bulk parameter covering a wide range of organic compounds including volatile fatty acids, and refractory products such as fulvic and humic-like compounds. The dissolved organic matter content of landfill leachate is usually expressed as biological oxygen demand (BOD), chemical oxygen demand (COD) or total organic carbon (TOC) (Kjeldsen *et al.*, 2002).

2.1.3.2 Inorganic macro-components

Inorganic macro-components are the inorganic constituents present in the leachate (Christensen *et al.*, 2001). The common cations and anions found in leachate include sodium, potassium, sulphate, chloride, and ammonia. The concentration of the inorganic macro-components can vary over time depending on the degree of stabilization in the landfill.

The higher pH enhances sorption and precipitation while lower organic matter content allows the formation of complexes with the cations. Sulphate concentrations are lower due to the microbial reduction of sulphate to sulphide (Kjeldsen *et al.*, 2002). Chloride, sodium,

and potassium concentrations are not influenced by the landfill phase as the effects of sorption, complexation and precipitation are minor for these ions (Kjeldsen *et al.*, 2002).

Most of the nitrogen present in leachate is in the form of ammonia which is produced by the degradation of proteins and amino acids. Ammonia concentrations are typically between 500 to 2000 g m⁻³ (Kjeldsen *et al.*, 2002), but concentrations in excess of 10 000 gm⁻³ have been recorded (Tatsi *et al.*, 2002). Ammonia concentrations do not decline over time as there is no mechanism for its degradation under anaerobic conditions; therefore any ammonia loss is a result of leaching out of the landfill (Bilgili *et al.*, 2006).

2.1.3.3 Heavy metals

Heavy metals are defined as metals with a density greater than 5 g cm⁻³ (Sayari *at el.*, 2005). Heavy metals present in leachate include arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) (Taulis *et al.*, 2005). Some heavy metals such as copper and zinc are essential for growth but can become toxic at high concentrations (Sayari *at el.*, 2005). Although heavy metals can be toxic, leachate heavy metals generally do not pose a groundwater pollution problem as average metal concentrations are typically low and only a small proportion of the metals that are disposed of in a landfill are leached out (Kjeldsen *et al.*, 2002). Mass balance studies have shown that less than 0.002% of heavy metals are leached from a landfill over the first 30 years of operation (Kjeldsen *et al.*, 2002). Qu *et al.* (2008), reported that total heavy metals concentration was less than 1% of that deposited in a Chinese Bioreactor landfill during a 20 month study period. Heavy metal concentrations are typically highest during the acid phase when the low pH leachate is chemically aggressive and can increase the solubility of metals (Kjeldsen *et al.*, 2002). As the pH increases and the landfill moves to the methanogenic phase, leachate heavy metal concentrations decrease. Studies

conducted on German landfills (Ehrig, 1983) and in the USA by Krug *et al.* (1995), showed that magnesium, iron, zinc and manganese concentrations are higher in the acid phase (Taulis *et al.*, 2005). Qu *et al.* (2008), examined leachate from a full scale bioreactor landfill in China over a 20 month period and reported that cadmium, chromium, copper, nickel, lead, and zinc concentrations were initially high, but after 5 months the methanogenic stage had been reached and the heavy metal concentration had dropped below the Chinese national standards. The relatively low leachate metal concentrations during the methanogenic phase are commonly attributed to adsorption and precipitation processes, binding and immobilizing the metals within the landfill.

Landfills will typically contain significant amounts of soil and organic matter, which absorb the metals, reducing their solubility and mobility (Taulis *et al.*, 2005). Absorption of metals by soil and organic matter occurs more readily at neutral to high pH values, i.e. occurs during a landfill's methanogenic phase (Taulis *et al.*, 2005).

Precipitation is the other mechanism which immobilizes metals. Heavy metals are not always immobilized within the landfill; there are also processes that are capable of increasing the concentrations of metals in the leachate. Complexation of metals to organic ligands, and adsorption onto colloids can increase the concentrations of heavy metals in leachate (Kjeldsen *et al.*, 2002). Long term landfill processes may also lead to heavy metals being mobilized from the landfill into the leachate.

2.1.3.4 Xenobiotic organic compounds

Xenobiotic Organic Compounds (XOCs) are substances derived from anthropogenic sources (Baun *et al.*, 2004). They include aromatic hydrocarbons, phenols and chlorinated aliphatic compounds (Slack *et al.*, 2007) with the most frequently found XOCs being mono-aromatic hydrocarbons and halogenated hydrocarbons (Kjeldsen *et al.*, 2002). XOCs

are commonly associated with industrial or hazardous waste but a large number occur in municipal and domestic waste. Paint, garden chemicals, household cleaning agents, motor vehicle products, batteries, waste electrical and electronic equipment are all sources of XOCs in municipal solid waste (Slack *et al.*, 2007). The number and concentration of XOCs present in leachate can vary between landfills. Baun *et al.*, (2004) monitored 10 different Danish landfills and reported the presence of 55 different XOCs plus 10 degradation products of XOCs with concentrations ranging from $<0.1 \mu\text{g/l}$ to $2220 \mu\text{g/l}$. Kjeldsen reported that concentrations of XOCs are higher in older municipal landfills compared to newer landfills. This was attributed to lower acceptance rates of XOCs in the newer landfills rather than any landfill ageing process.

2.2 Leachate irrigation

Leachate can be disposed of by spray or trickle irrigation onto vegetated land. Leachate irrigation is best suited to areas where: (1) high rainfall leads to the production of large volumes of dilute leachate, (2) there is enough suitable land available for irrigation, and (3) the landfill is too far away from any sewer network to make offsite disposal economical (Gray *et al.*, 2005). An advantage of leachate irrigation is that leachate treatment/disposal can be accomplished on site, particularly on closed landfills where irrigation can take place over the capped landfill surface. The other advantage of irrigation is that the nutrients present in the leachate can be recycled and used for plant growth.

2.2.1 Effects of leachate on plant growth

Leachate is rich in nutrients, including nitrogen needed for plant growth, and leachate irrigation has been shown to improve plant growth when managed correctly (Bowman *et al.*, 2002; Maurice *et al.*, 1999; MacDonald *et al.*, 2008; Revel *et al.*, 1999; Shrive *et al.*, 1994). Revel *et al.*, (1999) used leachate with high concentrations of NH_4^+ (1520 g m^{-3}),

Na^+ (1920 g m^{-3}), K^+ (2200 g m^{-3}) and Cl^- (2130 g m^{-3}) to irrigate pots containing ryegrass. Increased grass growth was shown when the pots were irrigated with solutions containing up to 400 gm^{-3} of leachate. Above 400 g m^{-3} the leachate had a detrimental effect on plant growth which was attributed to sodium toxicity. Shrive *et al.*, (1994) found that irrigation of a high ionic strength leachate significantly increased stem growth in hybrid poplar samplings. The authors also found that direct exposure of the leaves to the potentially phytotoxic compounds (volatile organic compounds and inorganic substances including metals) present in the leachate did not induce phytotoxic reactions in the plants.

2.3 Effects of leachate salts on soil

When discussing the influence of the soluble salts on leachate irrigation, the terms ‘salinity’ and ‘sodicity’ are commonly used. Salinity refers to the presence of soluble salts in the irrigated water or soil, while sodicity refers to the proportion of available sodium ions relative to the available calcium, magnesium, potassium and aluminum ions present in the soil or irrigated water. Salinity and sodicity are common problems in areas where irrigation is employed for agricultural purposes, especially if rainfall is low and evaporation is high (Rietz *et al.*, 2003). Soluble salts present in the irrigation water can accumulate in the soil when the rainfall is insufficient and unable to leach the salts from the soil profile (Rietz *et al.*, 2003). Increased soil sodicity and salinity can cause a reduction in soil hydraulic conductivity and reduce plant productivity.

The sodium adsorption ratio (SAR) is used to quantify the salinity of the irrigating water and the exchangeable sodium percentage (ESP) is used to quantify soil salinity (Balks *et al.*, 1998). The SAR describes the level of sodium relative to other cations (Ca and Mg) present in the irrigation water and is defined by:

$$\text{SAR} = \frac{\text{Na}^+}{\left[\frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2} \right]^{1/2}} \quad (\text{Equation 1})$$

The detrimental effects of high sodium concentrations on soils are exhibited through swelling and dispersion of clay minerals (Halliwell *et al.*, 2001).

2.3.1 Effects of leachate salts on plants

Excessive salt concentrations can affect plants in three ways (Parida *et al.*, 2005):

1. Salinity: Excessive salt concentrations affect a plant's ability to osmotically take up water. As the salt concentrations increase, the water potential between the plant and soil increases, reducing the plant-available water and making it harder for plants to take up water. If soil salinity exceeds a plant's tolerance, growth reductions occur and in extreme cases can cause plant's death (Parida *et al.*, 2005).
2. Specific ion toxicity: Excessive concentrations of specific salt such as sodium, chloride and boron can be toxic to some plants. Plants which are sensitive to these elements can be affected at relatively low levels if the soil concentrations are high enough (Seilsepour *et al.*, 2009). The effects of ion toxicities are noticeable in the leaves, particularly the leaf margins where harms including necrotic spots, leaf bronzing and, in the worst case, defoliation can occur.
3. Nutritional disorders: High salt concentrations can cause nutritional imbalances in plants. Many salts are essential plant nutrients. High soil salt concentrations can upset the nutrient balance in plants or affect the uptake of some nutrients (Seilsepour *et al.*, 2009). Plants vary in their response to high soil salinity; generally, there will be no reduction in yield up to a threshold level, which varies for different plant species. Plant species that are

able to grow and complete their life cycle in saline conditions are often termed 'salt tolerant'. Salt tolerance can be defined as the ability to survive and produce economic yields under adverse conditions caused by salinity. Salt tolerant plants are known as halophytes and can be divided into two groups; obligate halophytes which require saline conditions and facultative halophytes which can survive in saline or freshwater conditions (Parida *et al.*, 2005).

2.4 Salt stress symptoms in plants

Symptoms of salt stress in plants resemble those of plants subjected to drought conditions and are characterized by wilting and reduced growth (Seilsepour *et al.*, 2009). Salt stress affects all major processes in plants such as growth, photosynthesis, protein synthesis, and energy and lipid metabolism (Parida *et al.*, 2005). As a result, plants affected by salt stress grow more slowly and are smaller than unaffected plants. One cause of growth rate reduction is reduced photosynthesis caused by stomatal closure which limits carbon dioxide uptake (Zhu, 2001). The leaves of salt stressed plants are smaller, but may be thicker as salinity can cause increases in epidermal and mesophyll thickness, and elongation of the palisade cells (Bernstein *et al.*, 1975; Parida *et al.*, 2005). The leaves can be a different color to those of unaffected plants as generally the chlorophyll and carotenoid content of leaves decrease under salt stress (Bernstein *et al.*, 1975).

2.5 Examples of studies using leachate as irrigation systems

Hernández *et al.* (1999) investigated the effects of leachate irrigation on four wild herbaceous species in a greenhouse pot study. Three different leachates were applied to pots containing one of four plant species; two legumes (*Trifolium glomeratum* and *Trifolium tomentosum*) and two grasses (*Hordeum maurinum* and *Bromus hordaceus*). The results show Leachate irrigation significantly increased soil salinity. The plant response to

the increase in soil salinity differed for each species with the legumes more sensitive to the increase in salinity than the grasses. The dry weight of both the legumes and grasses decreased with increasing electrical conductivity of the leachate.

MacDonald *et al.* (2008) investigated the effects of leachate irrigation on the capped area of an active landfill in Michigan, USA. Six experimental plots were established and three were irrigated with leachate and left three as control. The leachate had high mean values for electrical conductivity (6000-7000 $\mu\text{S cm}^{-1}$), chloride (760-900 g m^{-3}) and ammonical nitrogen (290-390 g m^{-3}) but was low in metals and volatile organic compounds. During the first year of irrigation 320 mm of leachate was applied causing high rates of nitrate leaching and the soil electrical conductivities to rise from 500 $\mu\text{S cm}^{-1}$ to 2800 cm^{-1} in the irrigated plots compared to 700 cm^{-1} in the control plots. In the subsequent year, leachate applications rates were limited to <96 mm y^{-1} to reduce nitrate leaching and to keep soil electrical conductivities at a level which would not affect plant growth or soil structural stability. After leachate application rates were reduced, soil electrical conductivities reduced to 1400 $\mu\text{S cm}^{-1}$ in 2004 and 1600 $\mu\text{S cm}^{-1}$ in 2005. Leachate irrigation did not significantly affect soil metal concentrations and plant metal concentrations were within normal ranges.

Bowman *et. al* (2002) reported on a two year landfill leachate irrigation trial held at the Newington Landfill, Sydney, Australia. The leachate had high salinity (17,600 $\mu\text{S cm}^{-1}$) and high concentrations of sodium (3000-4000 g m^{-3}), chloride (6700-8000 g m^{-3}) and ammonium (250-330 g m^{-3}). Plots vegetated with Couch grass (*Cynodon dactylon*) and Kikuyu grass (*Pennisetum clandestinum*) was irrigated with town supply water and leachate diluted to 20%, 50% and 100% of its original concentration with town supply water. In the plots irrigated with 50% and 100% leachate, an increase in soil salinity and

bulk density was observed along with a decrease in porosity, aggregate stability and biomass production. The degradation of the soil physical properties was attributed to an increase in the sodium adsorption ratio in the soil. In the 20% leachate plot, biomass production increased while there was no significant change in the soils physical properties compared to the control plot. Nitrogen losses through leaching were significantly less in the 20% leachate plot compared to the 50% and 100% leachate plots. It was concluded that leachate irrigation is sustainable provided that management strategies, such as dilution of the leachate to reduce the electrical conductivity down to $3600 \mu\text{S cm}^{-1}$ (20% of original concentration), are adopted. Furthermore, pollution due to leaching of nitrogen to groundwater could be minimised by appropriate management of the soil to enhance denitrification (Bowman *et al.*, 2002).

2.6 Swiss Chard

Swiss chard (*Beta vulgaris var. cicla*) is an edible flowering plant that belongs to the family Chenopodiaceae. It is an annual plant that grows quickly and has the ability to survive over winter in temperate regions. Swiss chard leaves are variable in size from about 2–30 cm long and 1–15 cm broad. Larger leaves are found at the base of the plant and small leaves are found higher on the flowering stem (Gilbert *et al.*, 1996). The flowers of Swiss chard are usually yellow-green, 3–4 mm in diameter and mature into several small seeds. Plants may flower in as little as two weeks provided that they are grown in ideal conditions. Chard plants have several names in addition to Swiss chard. Leaf beet, seakettle beet and spinach beet are a few, with regional dialects adding to the list. The most common varieties of chard produce yellow, white or red stalks but there are also stems in pink, purple, orange and hues in between. All types of chard are fast growing plants that thrive in moist, humus-rich soil (Ortmann *et al.*, 2007).



Figure 2.1 Bunch of Swiss chard (<http://anrcatalog.ucdavis.edu>).

6.2.1 Origin and distribution of *Beta vulgaris*

The ancestral form of all beets (Swiss chard, beetroot, fodderbeet and sugar beet) is the wild Sea Beet (*Beta maritima*), which is distributed throughout the mediterranean and Near Asian areas. The wild form is very variable and adaptable, with branched tap-roots and varying sugar content. Swiss chard, the main root of which is not swollen, was already cultivated as a leaf vegetable in Greece around 400 BC. Through mutation, varieties have been developed with widened leaf stalks which are used as a vegetable similar to asparagus. (Pathak *et al.*, 2013). Today, China, the United States and Japan are among the largest commercial producers of Swiss chard.

2.6.2 Climatic and soil requirements of Swiss chard

Swiss chard seeds germinate at 2°C to 30°C. However, 7°C to 24°C is optimum temperature for germination. The plant requires a constant and uniform supply of water in order to obtain high quality harvest. During Swiss chard production, the soil should never be allowed to dry out. Swiss chard requires plenty of water, although the soil should have good drainage.

Swiss chard grows well on a variety of soils, although, fertile, potting soils with high organic matter content are preferred. Heavier soils can be quite productive if these are well drained and irrigated. Swiss chard is particularly sensitive to saturated soil conditions and to acidity. The optimum soil pH is 6.2 to 6.9 (Hodges, 1992). Due to the relative fast life cycle of this vegetable compared to other field crops like cereals and legumes, Swiss chard tend to vigorously take up nutrients within very short period of time and therefore has high tendency to pick heavy metals which could affect its food value (<http://anrcatalog.ucdavis.edu>).

2.6.3 Nutritional profiles of *Beta vulgaris* and effects on health

Swiss chard contains high levels of minerals and vitamins, rich in phosphorus, iron, potassium, and especially contains calcium and magnesium which are excellent bone-supportive nutrients. A commonly found vitamin in Swiss chard includes vitamin A which is a free radical-scavenger; vitamin K, vitamin B, vitamin E and vitamin C (Table 2.1). Swiss chard also contains vitamin B2, vitamin B6, folate, betaine, copper, protein, manganese, zinc, niacin, selenium and omega-3 fatty acids, which also has a more delicate texture and more nutrients than most other green-leaf vegetables. It is also very rich in antioxidants which scavenge free radicals and adjust blood pressure. These antioxidants are relatively abundant in high levels when Swiss chard is consumed fresh, steamed, or quickly boiled.

Due to its rich nutritional content, Swiss chard has many positive effects on human health. In 2005, studies showed that Swiss chard was the most protective nutrition against cancer risks (Ko et al., 2014). In addition to preventive potential of Swiss chard towards cancer, it is effective in combating cancer cell proliferation. For instance, in a related research, it was found that Swiss chard could prevent breast cancer because it contains high levels of lutein and other carotenoids (Longnecker *et al.*, 1997).

Table 2.1 Nutritional profile per 100g raw Swiss chard

Nutrients	Nutritional values
Energy	84KJ(23cal)
Carbohydrate	4.13g
Sugar	1.1 g
Dietary fiber	2.1 g
Protein	1.88 g
Vitamin A	306 mg
Folate	9 µg
Vitamin C	18 mg
Vitamin E	1.89 mg
Vitamin K	327 µg
Calcium	58 mg
Iron	2.26 mg
Fat	0.08 g

CHAPTER 3**3. MATERIALS AND METHODS****3.1 Cleaning of glassware**

All glassware and containers were thoroughly washed with detergent and tap water, rinsed with distilled water and thereafter soaked in 5% HNO₃ for a period of 48 hours after which they were thoroughly rinsed with distilled water and dried overnight in the oven.

3.2 Materials

All reagents used for this study: super-pure 65% nitric acid, 30% hydrogen peroxide, and 35% hydrochloric acid were analytical grade solvents and were obtained from Merck KGaA Company. Pots (size 15cm diameter by 20 cm high, and hold about 2.5L) were taken from the Horticulture Department in Bellville campus. Potting soil, Swiss chard seedling and organic granular fertilizers were purchased from Stodels Nurseries, Cape Town, South Africa.

3.3 Leachate collection

Leachate samples were obtained from Bellville landfill site near Cape Town. Collection of leachate was done in triplicate at specified time intervals. The leachates were collected in 25 L plastic jerry-can which was rinsed several times with the leachate before being filled with the leachate. A 500 ml sample of leachate was collected in plastic bottle and the pH was measured immediately. This was followed by immediate addition of concentrated HNO₃ for preservation. The acidified leachate sample was stored in a refrigerator at about 4 °C for the MP-AES analysis.

3.4 Experimental procedure

3.4.1 Preparation of pot experiment and trial management

Fifty pots sized 15cm diameter by 20 cm high, and hold about 2.5L of soil, were taken from Horticulture Department, which were washed with tap water and rinsed several times. Each pot was filled up with potting soil and placed inside greenhouse located in the Horticulture Department's nurseries in Bellville campus. The pots were divided into five treatments; each treatment has ten pots according to the irrigation used. Treatments were; T1 distilled water (first control); T2: Tap water (second control); T3: 100% concentration of landfill leachate (as collected from landfill); T4: 50% landfill leachate (diluted 1:1 volume by volume) and T5: 25% landfill leachate (diluted 1:3 volume by volume leachate and water, respectively). Then each group was irrigated with the respective water samples for 48h prior to transplant of seedling.



Figure 3.1 Preparation of potting soil

One seedling was planted in each pot and suitable fertilizer was added to each pot at commercial recommended rate to enhance the growth. The Swiss chard seedling was the

same cultivar and age. Treatments (leachate and controls) were applied daily at regular interval throughout the duration of the experiment.



Figure 3.2 Growing of Swiss chard seedling in potting soil

3.4.2 Soil sampling

About 2.5L of Composite soil was potted in 20 cm pots in greenhouse of the Horticulture Department in the Bellville campus of CPUT. The pH of the composite soil was measured using hand-held multi system meter. After potting, initial 80g of organic granular fertilizer was added to all pots and irrigated with the respective treatments. Treatment was applied daily to maintain good soil moisture throughout the study. Clear, unused sampling bags were used for the collection of soil samples. This process of collection was repeated each week to study the effect of irrigation system on soil properties.

3.4.3 Swiss chard sampling

Leaf samples of Swiss chard were collected from each treatment in appropriately labeled brown paper bags for tissue analysis. The Swiss chard leaves were rinsed thoroughly with

tap water and distilled water in order to remove all traces of soil and dust particles and to ensure that there is no contamination. The leaves were then dried in the oven at 60°C. Three samples of Swiss chard leaf were collected in triplicate every week from each treatment over a period of two months to investigate trend in possible accumulation of nutrients over time.

3.5 Sample preparation for different analyses

3.5.1 Soil samples

Soil samples were initially sieved with a 2 mm sieve. The soil was thoroughly mixed to achieve homogeneity and then dried in the oven at 60°C till constant weight was achieved. Once the soil had been cooled, 1.0 g of the dried soil was weighed and transferred to a 50 ml Phillips beaker. To this, 2 ml of nitric acid and 6 ml of hydrochloric acid was added. The solution was transferred to a round bottle flask and heated to approximately 85°C for approximately 30 minutes. Afterwards, the sample was cooled, filtered through Whatman GF/C filter papers, transferred to a 50 ml volumetric flask, and diluted to the mark with distilled water. The sample was then taken for analysis. (EPA Method, 2007).

3.5.2 Swiss chard samples

The Swiss chard leaves were dried in the oven at 60°C till constant weight was achieved. Moisture content was determined by difference. The dried leaves were ground in mortar and pestle, 0.1 g of each sample were weighed out accurately and transferred to a microwave digestion reaction vessel. A 2 ml of 30% hydrogen peroxide and 5 ml of 65% nitric acid were added to the contents of the vessel. The vessels were placed in the carousel digestion proceeded by means of a temperature programmer (table.1). The digestion procedure was carried out in a Milestone-MLS 1200 Mega microwave oven capable of accommodating 6 digestion vessels. After digestion, the samples were cooled, filtered

using Whatman GF/C filter paper and then transferred to the volumetric flask and made up to the mark with ultra-pure water.



Figure 3. 3 Milestone-MLS 1200 Mega microwave oven

Table 3. 1 Program for closed microwave oven procedure

Step	Power(W)	Time (min)
1	250	2
2	0	2
3	250	5
4	400	5
5	500	5

3.6 Instrumentation

3.6.1 Microwave plasma-atomic emission spectrometer (MP-AES)

Microwave Plasma-Atomic Emission Spectrometer was used for all the sample analysis to determine the concentration of metals in the samples. The MP-AES Spectrometer was chosen for this study for its multi-element capabilities and it is less subjective to chemical

and matrix interferences. The MP-AES which was used for our analysis has several advantages: Runs on air, eliminates need for source/hollow cathode lamps, and simple installation – no chiller. It has a higher resolution, it is more flexible in the number and the selection of lines is infinitely variable, automatic background correction and it is safer as no flammable gases are required.

3.6.2 pH meter

The pH of the soil and leachate samples was measured using a pH meter. The pH of the soil was determined using sieved soil samples. Three grams of soil samples was weighed in clean 50 ml glass beakers. Ultra-pure water was added to form a slurry solution from which pH measurements were done using the pH meter. Before use, the pH meter was first calibrated with standard buffer solution of pH 4 and 7.

3.6.3 Scanning electron microscopy (SEM)

A SEM can generate image for specimens with magnifications from 15X to 30,000X. The fully digital scanning electron microscope or SEM is useful for many purposes such as examining fracture surfaces. SEM was used to study the morphology of the fresh leaves samples of Swiss chard to determine possible structural changes due to heavy metals accumulation and the result was compared with the controls.

CHAPTER 4

4. RESULTS AND DISCUSSION

Experiments were carried out under greenhouse conditions from January to September, 2014. The plants were grown in the sunlight and irrigated with 50 ml/day of distilled water or tap water (for control treatments, not exposed to leachates) or with a similar quantity of different concentrations of landfill leachates (25%, 50% or 100 %) for treatments exposed to leachates). The ambient temperature in the greenhouse during the experiment was in the range of 23.8°C to 26.5°C. A total of fifty pots were sown with Swiss chard. Each treatment has ten pots. Three samples of soil and Swiss chard were collected from each treatment every week and analyzed.

4.1 Characterization of applied irrigation samples

The leachates which were collected from Bellville landfill site in Cape Town, South Africa (Fig 4.1) had orange brown to yellowish colour and a malodorous smell, which may be due to the presence of organic acids, resultant of the high concentration of organic matter (Williams, 2004).



Figure 4.1 landfill leachate site at Bellville, Cape Town, South Africa

Several parameters were analysed in the leachate, the tap water and distilled water. These parameters includes pH, electrical conductivity (EC), sodium adsorption ratio (SAR), osmotic potential (OP), and concentrations of Cl, Ca, Mg, Na, K, B, Fe and Mn (Table 4.1).

The results of analysis showed the pH ranged from very low (leachate) to medium (tap water) and neutral in the case of distilled water. Typical pH values for other studies of landfills range from 4.5 -7.5 with a mean of 6.1 for landfills in the acid phase, to 7.5- 9.0 with a mean of 8.0 in the methanogenic phase (Kjeldsen *et al.*, 2002), which would put Bellville Landfill leachate (pH of 7.8) in the methanogenic phase. Other literature reviews and studies have reported pH to be stable and near neutral during the methanogenic phase (Griffith *et al.*, 2006; Heyer *et al.*, 2001).

The electrical conductivity (EC), which defines as the concentration of total salt content in irrigation water, estimated in terms of EC, is 383 mS/m in the leachate and is higher than the considered suitable value for irrigation waters (< 225 mS/m). Leachates also have high concentration of sodium and chloride relative to the other waters.

The Sodium adsorption ratio (SAR) was calculated (using equation 1 in Chapter 2) in order to determine the sodicity or alkalinity hazard of irrigation waters. Based on the SAR (Fig.4.2) value from (Table 1), irrigation waters can be rated into different categories of sodicity as follows: Safe: < 10, moderately safe: 10–18, moderately unsafe: 19–26, unsafe: > 26 (Richards, 1954). Hence, the leachates were considered moderately safe while the tap and distilled water are safe. Analysis of the SAR and EC of the leachate can be used to predict whether dispersion or swelling of clays is likely to occur when the leachate is irrigated (Table 4.1). The SAR and EC of the leachate in the irrigation collection tank were used to assess the salinity risk for the leachate that was irrigated in potted soil. When the SAR and EC of the irrigated (Table 4.1) were compared with guidelines for the

interpretation of water quality for irrigation (Halliwell *et al.*, 2001), it appears that soil structural problems are not expected. The plot of the relationship between SAR and EC (Figure 4.2) suggests that soil structural problems are unlikely. Although the SAR of the leachate is relatively high, the EC is great enough to be above the “critical coagulation value” needed for clay dispersion to occur.

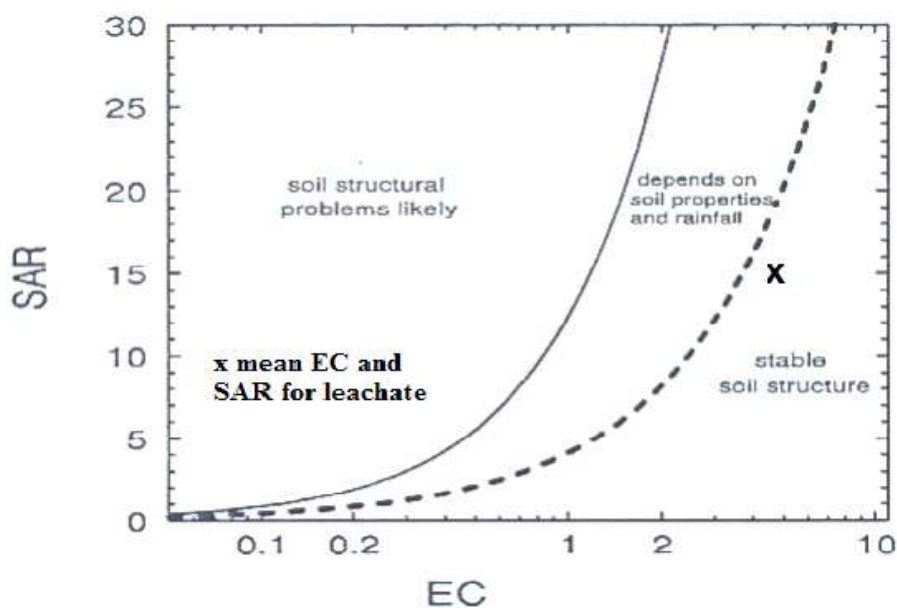


Figure 4.2 Relationship between SAR and EC of irrigation water to estimate structural stability.

The Boron concentration in the three types of irrigation water was < 1 mg/l which can be considered as low hazard. The leachate heavy metal concentrations were low (Table 4.1). This correlates with studies reported on other landfill studies (Qu *et al.*, 2008). This may be attributed to the high organic matter content from the vegetable processing waste deposited in the landfill.

Organic matter present in the landfill can absorb significant amounts of metals, hence, decreasing their solubility (Kjeldsen *et al.*, 2002). The mean pH of 7.8 may have also aided the adsorption of heavy metals; this is because the adsorption process occurs more readily

at neutral to high pH values (Taulis, 2005). The sulphate present in the leachate also contributes to the relatively low metal concentrations as metal-sulphite precipitates form readily during the methanogenic phase.

Table 4.1 Characteristics of leachate, tap water and distilled water used in the pot experiment

Type of water	Land fill leachate	Tap water	Distilled water
pH	7.8	8.5	7.1
EC(mS/m)	383	9.5	1.0
OP (kPa)	137.88	3.42	0.35
Na*	714.5	3.42	0.35
K	56.8	0.1	0.00
Cu	0.80	0.01	0.00
Zn	0.63	0.14	0.02
Cr	0.3	0.01	0.01
Ca	133.7	16.7	0.00
Cl	983.0	16.9	3.90
Fe	0.27	0.00	0.00
Mn	0.03	0.00	0.00
B	0.42	0.15	0.19
HCO ₃	1358	37.4	6.9
SO ₄	49.0	11.0	2.0
SAR	16.93	0.24	1.37

***All parameters from Na to SO₄ are measured in mg/L (ppm)**

4.2 Chemical characteristics of potting soil used in this study

The determined chemical properties of the soils included pH of soil, electrical conductance of the soil solution, exchangeable cations: Ca, Mg, Na, K, and other trace elements: B, Cu, Zn, Mn, and Fe content. The results of chemical characteristics of uncontaminated potting soil are presented in Table 4.2.

Table 4.2 Characteristics of uncontaminated soil used in pot experiment

Property the soil	pH	EC ms/m	Na	K	Ca	Mg	Mn	Cu	Zn	B	Fe
			Exchangeable cations (cmol/kg)								mg/kg
Values	7.3	80	2.06	1.87	7.31	4.2 5	43. 3	3.8 3	26. 0	3.4 1	169.4

4.2.1 The effect of leachate, tap and distilled water irrigation on potting soil properties

Irrigation of soil with leachate, tap water, de-ionized water cause changes in the chemical composition of soil pH, electrical conductivity, sodium concentration and some trace metal elements as discussed below.

4.2.1.1 Effect of leachate, tap and distilled water irrigation on soil pH

Since excessive acidity or alkalinity can be detrimental to plant, determination of soil pH is important. The experimental data of different soil pH resulting from leachate, tap and distilled water irrigations are presented in Fig. 4.3. It was observed that the pH of potting soil increased with leachate concentration (25%, 50% and 100%). The probable reason for this observation may be due to high concentration of monovalent and divalent cation contained in the leachate. The concentration of each constituent of leachate is presented in Table 4.1. The leachate also contained chloride and sulphate anions. As a result of negative charge developed by the soil particles, ions are absorbed on the surface (Li *et al.*, 2010). Any process that encourages presence of high levels of exchangeable bases such as calcium, magnesium, potassium and sodium will reduce acidity and increase alkalinity. Hence pH of the potting soils increases as the leachate concentration increased. In contrast, only a slight variation was observed in pH values of soils irrigated with tap and distilled

waters, as the concentration of these cations are low in the control treatments. There was a progressive increase in soil pH over time with every 100% increase in concentration of leachate; suggesting an accumulation of base forming salts in the treated soil compared to the control.

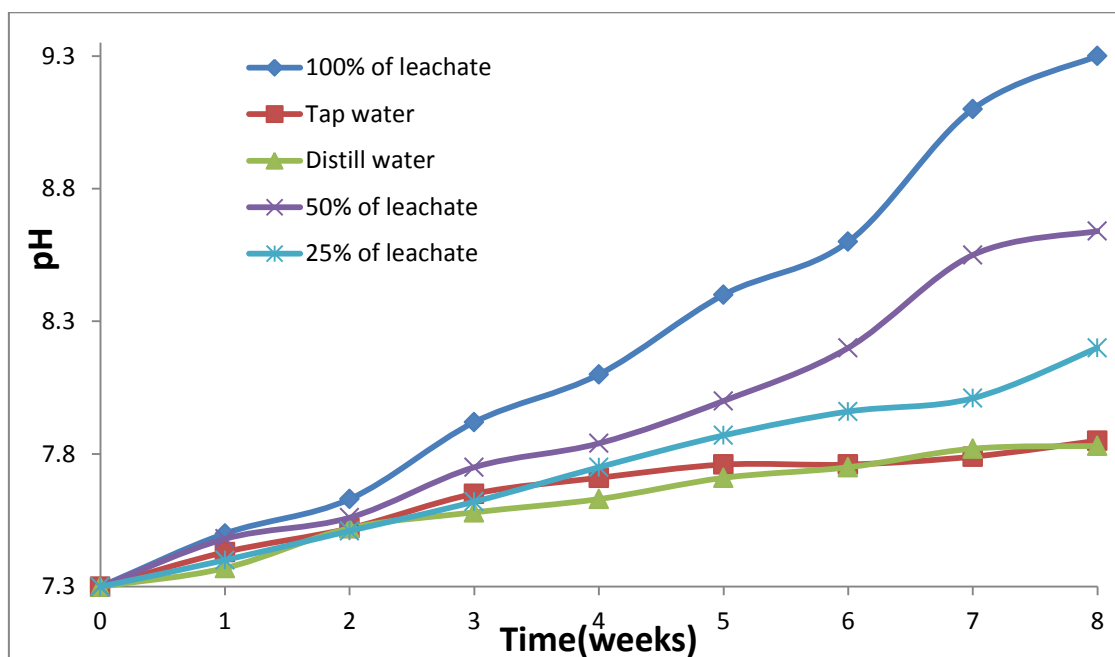


Figure 4.3 The effect of different irrigation waters on soil pH

4.2.1.2 Effect of irrigation waters on electrical conductivity of the soil (EC)

Plants are normally sensitive to soil properties such as electrical conductivity (EC). Figure 4.4 shows the change of soil EC during 8 weeks of pot experiment. The result shows continuous increase in EC of the soil when irrigated with 25%, 50%, 100% leachate. The 100% leachate irrigation shows the highest EC ~ 400 (mS/m) in the eighth week after transplant. The obvious reason for this increase is the availability of the high concentration of cations such as Ca^{2+} , Mg^{2+} , K^+ , Na^+ and anions SO_4^{2-} , Cl^- , HCO_3^- , which are responsible for carrying electrical charges and conduct electrical current (Garcia *et al.*, 1993). Consequently, the high concentration of ions in the soil leachate increases the EC of the

soil. On the other hand, the EC of soil irrigated with tap water and distilled water also show minimal to slight change during the eight weeks of the experiment as shown in Fig.4.4. This slight increase in EC from tap and distilled water irrigation may be attributed to the release of cations into soil solution due to irrigation while the significant increase was due to additive and regular accumulation of cations from the leachates treatments.

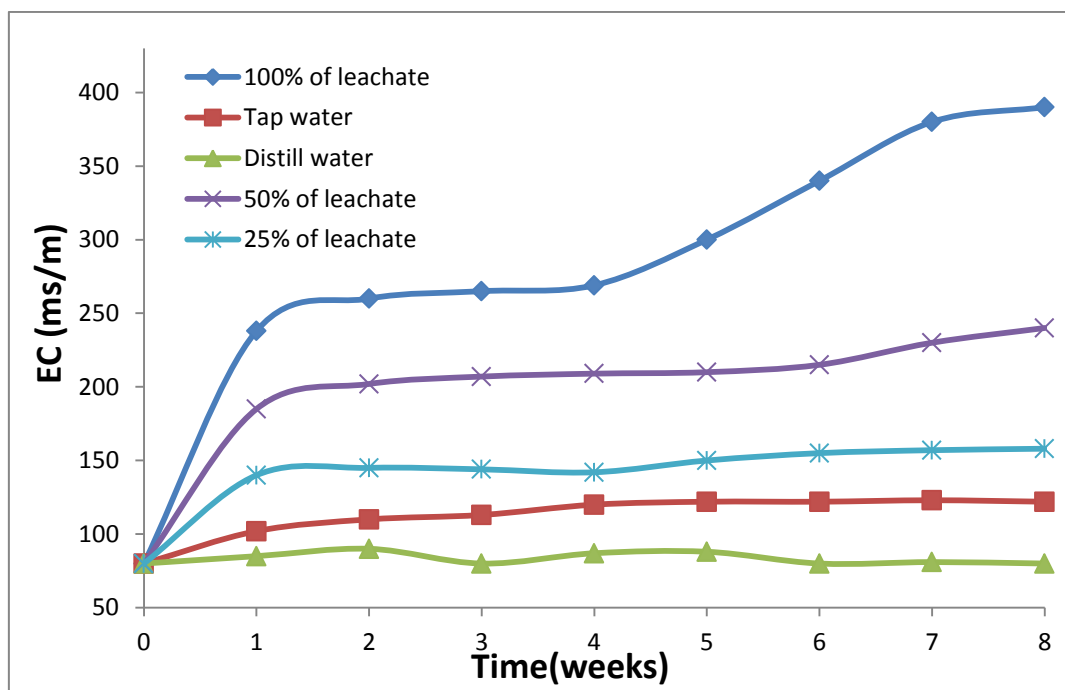


Figure 4. 4 The effect of irrigation waters on soil electrical conductivity

The EC gives an estimate of the total dissolved salts present in the leachate. Excessive salt concentrations can affect plants ability for water uptake. Therefore EC can be used for prediction if the irrigated leachate is likely to affect the crops (Table 4.3). When the mean EC leachate ($383 \mu\text{S cm}^{-1}$) was compared to Table 4.3, the Salinity Rating was high, which implies only salt tolerant plants would be unaffected by the high salt content present in the leachate. However, when the controlled sample ($95 \mu\text{S cm}^{-1}$) was compared, the Salinity Rating was very low. The Swiss chard species is moderately salt sensitive

(ANZECC *et al.*, 2000), therefore the growth rate may be affected by the presence of salts in the 100% leachate irrigated treatment.

Table 4. 3 Irrigation water ratings based on electrical conductivity

EC μScm^{-1}	Water salinity rating	Plant suitability (based on salt tolerance)
<650	Very low	Sensitive
650-1300	Low	Moderately sensitive
1300-2900	Medium	Moderately tolerant
2900-5200	High	Tolerant
5200-8100	Very high	Very tolerant
>8100	Extreme	Generally too saline

4.2.1.3 Effect of irrigation waters on the level of trace elements in the soil

The accumulation of copper, zinc and chromium in soils irrigated with different leachate concentrations and the two controlled water treatments during the experimental period are presented in Table 4.4. From the results of the analyzed potting soil, it was observed that there was increase in the concentration of zinc for all the treatments, and the relative level of increase in contamination by the irrigation waters was in the order 100% leachate > 50% leachate > 25% leachate > tap ~ distilled water. Globally, the concentration of zinc in unpolluted soils is expected to be between 10 mg/kg and 300 mg/kg, while the mean concentration is expected to be about 40 mg/kg. The results of this study fall within this range. Also copper and chromium showed gradual increase in accumulation during the treatment period. The highest copper concentration was obtained in 100% leachate irrigated soil (15.0 mg/kg) while the lowest was recorded in the distilled water irrigated soils (4.50 mg/kg). Also the highest chromium concentration was obtained in 100%

leachate irrigated soil (6.00 mg/kg), and the lowest was found in the tap water irrigated soil (3.50 mg/kg). The copper and chromium content of soils obtained in this study are similar to those reported in a study conducted in India (Shridhar *et al.*, 2014). The low accumulation of these trace elements is a resulted of their low concentration in the leachate.

Table 4.4 Trace metals content in soil during irrigation with different concentration of leachate, tap water and de-ionized water.

Trace element (mg/kg)	Water Type	100%	50%	25%	Tap water	De-ionized water
		Leachate	Leachate	Leachate		
Cu	*W2	5.00	4.00	3.00	2.00	1.50
	W5	11.8	10.0	6.0	5.00	4.0
	W8	15.0	12.5	10.5	5.50	4.50
Zn	W2	9.5	15.5	9.50	12.5	8.5
	W5	34.5	34.5	17.0	21.0	18.5
	W8	36.0	29.5	24.5	23.0	23.5
Cr	W2	1.5	2.00	2.00	1.50	1.50
	W5	4.00	3.50	4.00	3.50	4.00
	W8	6.00	5.00	4.50	3.50	4.01

*W2: Week two, W5: Week five, W8: Week eight of the experiment

4.2.1.4 Effect of irrigation waters on the exchangeable cation content of the soil

The presence of several ions in the leachates is of potential nutritional value to plants, especially when the heavy metals content are low. However, high concentrations of some ions can potentially increase salinity in soils. In general, the pollutant ions with potential of increasing soil salinity that were assessed in this study include Cl^- , SO_4^{-2} , Ca^{2+} , Mg^{2+} and Na^+ . The Na content was of greater interest since it is an important contributor to soil salinity. The Na concentrations in the three different leachate concentration had the highest cation content.

The results (Figure 4.5- 4.7) reveal that the salt content in the soils under landfill leachate treatment increased proportionally with the respective salt concentration. Increased soil salinity from week two to week eight reflected increased leachate salinity and the magnitude of the increase depends on the salt concentration in the leachate. However, there was only a slight presence of Na, Ca and Mg in potting soil when tap and distilled waters were used for irrigation, and were under the threshold level as shown in Figure 4.4- 4.6.

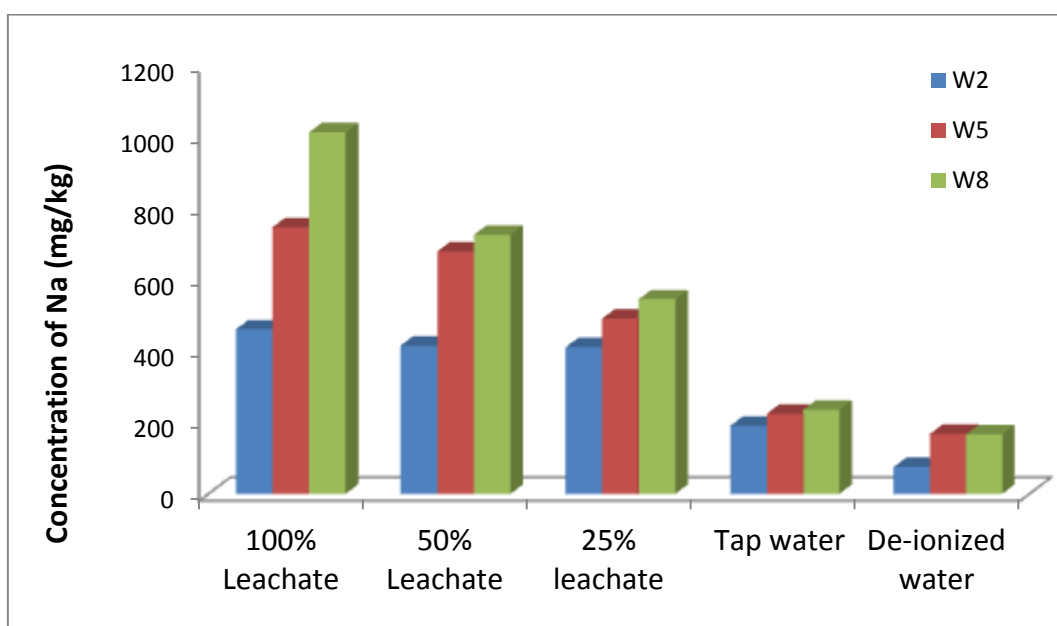


Figure 4. 5 The change in concentrations of Na in potting soils during second, fifth and eighth weeks of the experiment as affected by different concentrations of leachate

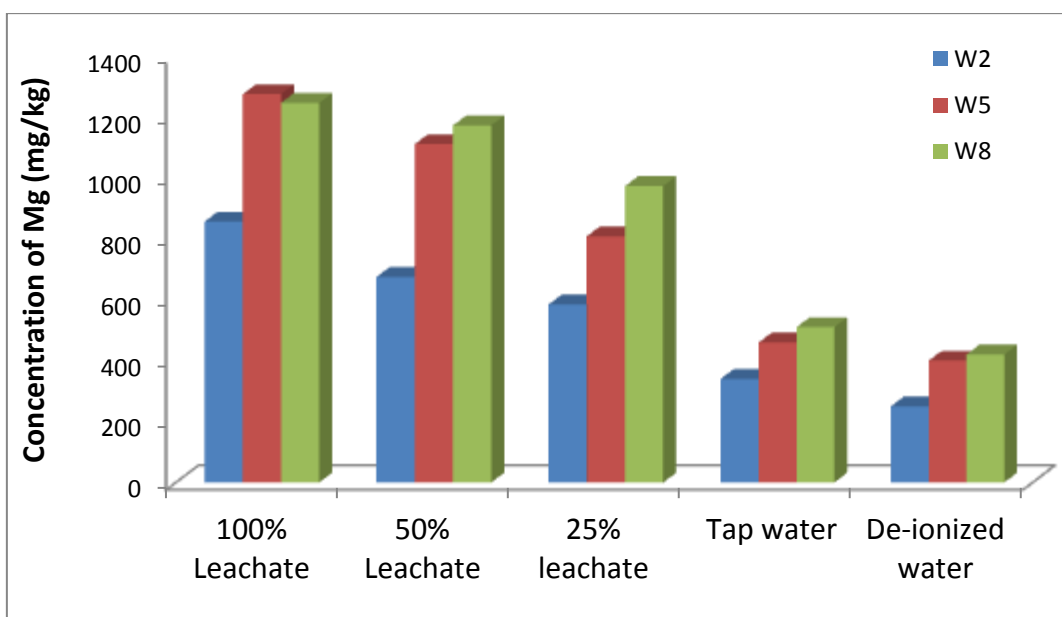


Figure 4. 6 The change in concentrations of Mg in potting soils during second, fifth and eighth weeks of treatment as affected by different concentrations of leachate

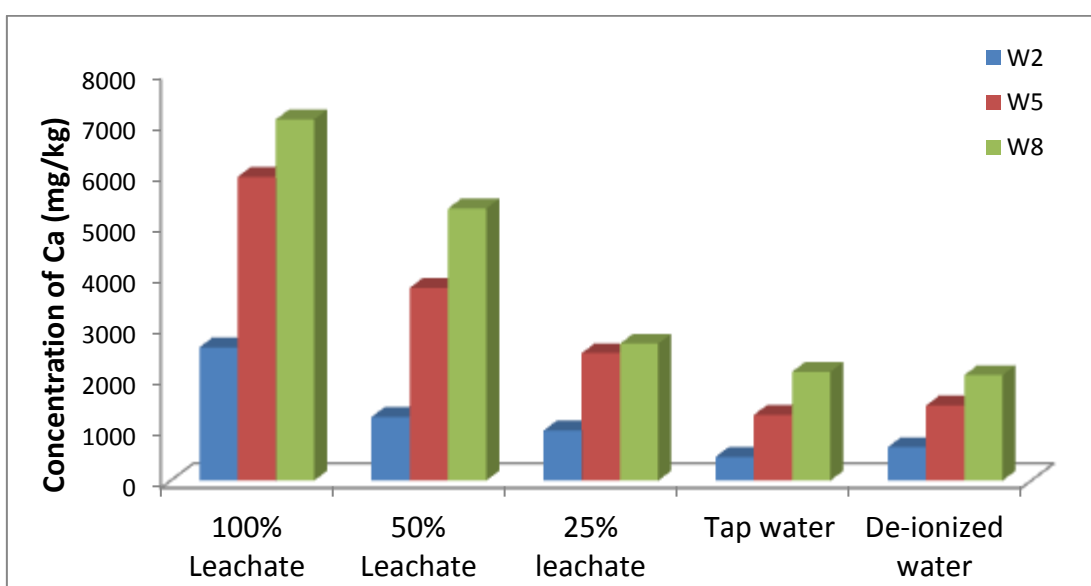


Figure 4. 7 The change in concentrations of Ca in potting soils during second, fifth and eighth weeks of the experiment as affected by different concentrations of leachate

4.2.1.5 Effects of Salinity (EC) and sodicity on Soil Physical Properties

Saline irrigation water contains dissolved salts. Soil water salinity can affect soil physical properties by causing fine particles to bind together into aggregates. This process is known as flocculation and is beneficial in terms of soil aeration, root penetration, and root growth.

Although increasing soil solution salinity has a positive effect on soil aggregation and stabilization, at high levels, salinity can have negative and potentially lethal effects on plants. On the other hand, Sodidity refers specifically to the amount of sodium present in irrigation water. Irrigating with water that has excess amounts of sodium can adversely impact soil structure, making plant growth difficult. Sodium has the opposite effect of salinity on soils. The primary physical processes associated with high sodium concentrations are soil dispersion and clay platelet and aggregate swelling (Parida *et al.*, 2005).

Sand particles are larger and therefore, have larger pore spaces for water to pass through. Under normal irrigation practices, sandy soils will naturally be able to flush more water through the root zone than clay soils. Hence, sandy soils can withstand higher saline irrigation water because more dissolved salts will be removed from the root zone by leaching. The above results also confirmed that the dispersion or swelling of the soil particle was not likely to occur as the EC was great enough to be above the “critical coagulation value” needed for dispersion to occur; although the sodium rate in the potting soil was high (Bernstein *et al.*, 1975).

4.3 The effect of irrigation waters on test crop (Swiss chard) properties

In order to investigate the changes or effects of different types of irrigation waters on growth of the test crop, leaf samples from Swiss chard were taken every week for analysis.

4.3.1 Change in the height of Swiss chard during the experimental period

Figure 4.8 shows the observed change in heights of Swiss chard species during the applications of different leachate concentrations and controls (tap, and distilled water). The result indicated the height of the Swiss chard species gradually increased for all leachate concentrations in the first weeks and reached a steady state after 4 weeks, with a recorded

maximum height of 18.5 cm. The results also showed about 50% drop in height of Swiss chard plant at 100% leachate application compared with distilled water irrigation.

The decline in growth of Swiss chard could be due to the high EC (salinity) value in the potting soil, which is resultant of high salinity of the leachate (Chiemchaisri *et al.*, 2005). As salinity increases each week due to application of irrigation waters, the amount of water available for plants' uptake decreases as the force with which the remaining water is held in the soil increases, making it progressively more difficult to withdraw water. The irrigation with tap and distilled water showed obvious growth from 9.2 cm in the first week to ~38.3 cm in the eight week of the treatment. It could therefore be conclude that the application of the leachate has a deleterious effect in photosynthate accumulation in Swiss chard species tested in this study due to accumulative toxic level of nutrients, high EC and osmotic limitations between the root and the soil solution.

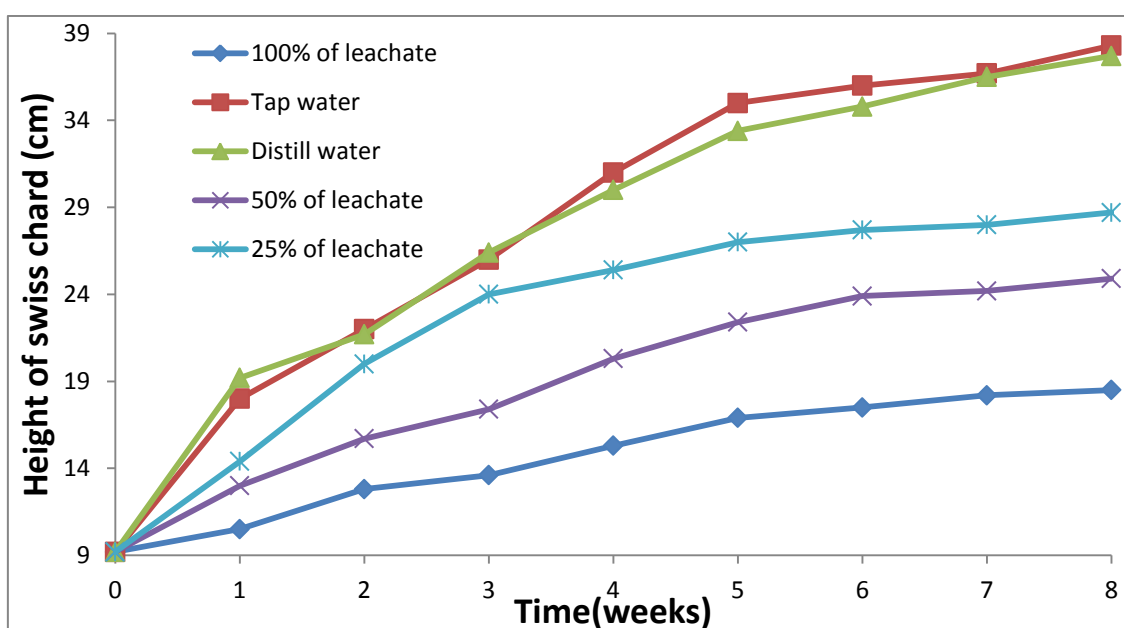


Figure 4. 8 The change of Swiss chard height resultant from different irrigation waters

4.3.2 Effect of leachates, tap and de-ionized water irrigations on level of trace elements in Swiss chard species

The illustration in Table 4.5 shows the concentration of copper, zinc and chromium in the leaves of Swiss chard irrigated with different leachate concentrations and the two controlled water treatments during the experimental period. The results show accumulation of these metals in the tissue Swiss chard leaves with the highest concentration of 2.00, 11.0 and 2.50 mg/kg for Cu, Zn and Cr respectively after eight weeks of irrigation with pure concentrated leachate (100%). Nevertheless, the concentration of these metals in plant tissue does not exceed the globally expected safe value recommended for human health.

Table 4.5 Trace metals content in Swiss chard leaves during irrigation with different concentrations of leachates, tap and de-ionized water.

Trace element (mg/kg)	Water Type	100% Leachate	50% Leachate	25% Leachate	Tap water	De-ionized water
Cu	* W2	0.00	0.00	0.00	0.00	0.00
	W5	1.00	1.00	1.50	1.50	0.50
	W8	2.00	1.50	1.55	1.06	1.00
Zn	W2	3.00	2.00	1.50	1.50	0.05
	W5	9.50	7.00	8.50	4.00	3.50
	W8	11.0	6.50	6.00	4.50	4.50
Cr	W2	0.00	0.00	0.00	0.00	0.00
	W5	1.00	1.00	1.00	1.00	1.00
	W8	2.00	1.70	1.50	1.30	1.02

*W2 :Week two, W5:Week five, W8: Week eight of the experiment

4.3.3 Effect of leachate, tap and de-ionized water on the exchangeable cation concentrations in Swiss chard leaves

The results show a differential accumulation of the three cations in Swiss chard leaves during the experimental period (Figure 4.9- 4.11). The increase in Na cation in the soils as

a consequence of leachate irrigation was clearly reflected by the content of this element in the leaves of Swiss chard species. The Na content was the most affected nutrient. The uptake of sodium by Swiss chard leaves clearly increased with time when leachate was used in irrigation system, which correlates with the concentration of this element in the leachate and ultimately in the soil .

The results also shows decrease in Ca and Mg concentrations, which has also been described for some grasses under leachate irrigations (Cureton *et al.*, 1991). Calcium deficiency was also reported by Grieve *et al.*, (1998) in salt-stressed maize shoots. This could be due to the replacement of Ca and Mg by Na (Grieve *et al.*, 1998). Such increase in the cation content (mainly Na) in the plants is one of the important aspects that must be taken into account when leachates are used as irrigation water because high concentrations of cation in the plant tissue may inhibit some biochemical processes, which are generally accompanied by a decline in growth (Greenway *et al.*, 1980).

Similarly, the Na, Ca and Mg concentrations also increased gradually in the leaf tissues of Swiss chard when tap and de-ionized water were used for irrigation (Figure 4.9 – 4.11). High Sodicity becomes a problem when enough salts accumulate in the root zone which negatively affects crops growth. As salt concentrations increase in the root zone, the water potential between the plant and soil increases, thereby reducing the plant-available water and making it harder for plants to take up water from surrounding soil. This lowers the amount of water available to the plant, regardless of the amount of water in the root zone. High salinity can also cause increases in epidermal and mesophyll thickness, and elongation of the palisade cell in the leaves. This ultimately negatively affects growth in plant.

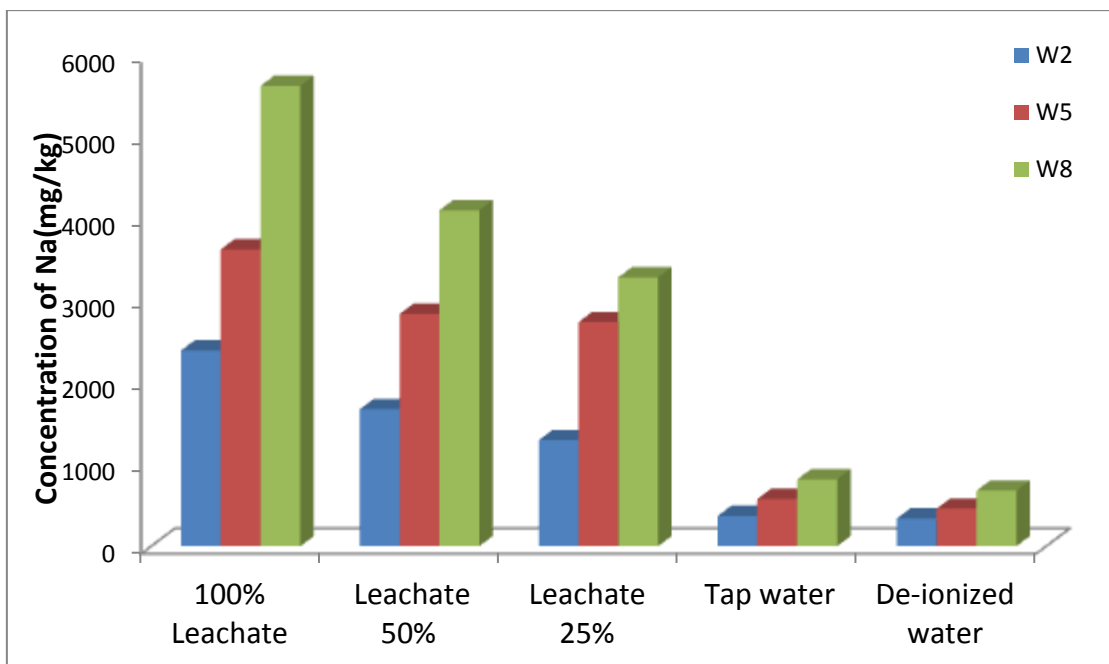


Figure 4. 9 Change in concentration of Na in Swiss chard leaves during second, fifth and eighth weeks of the experiment

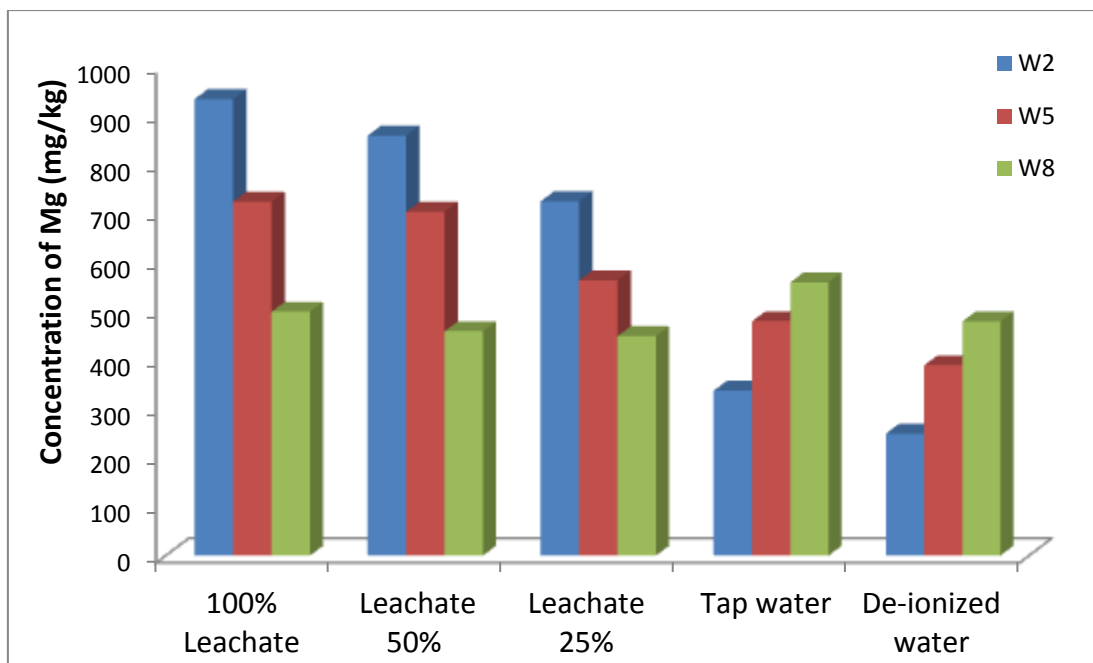


Figure 4. 10 Change in concentration of Mg in Swiss chard leaves during second, fifth and eighth weeks of the experiment

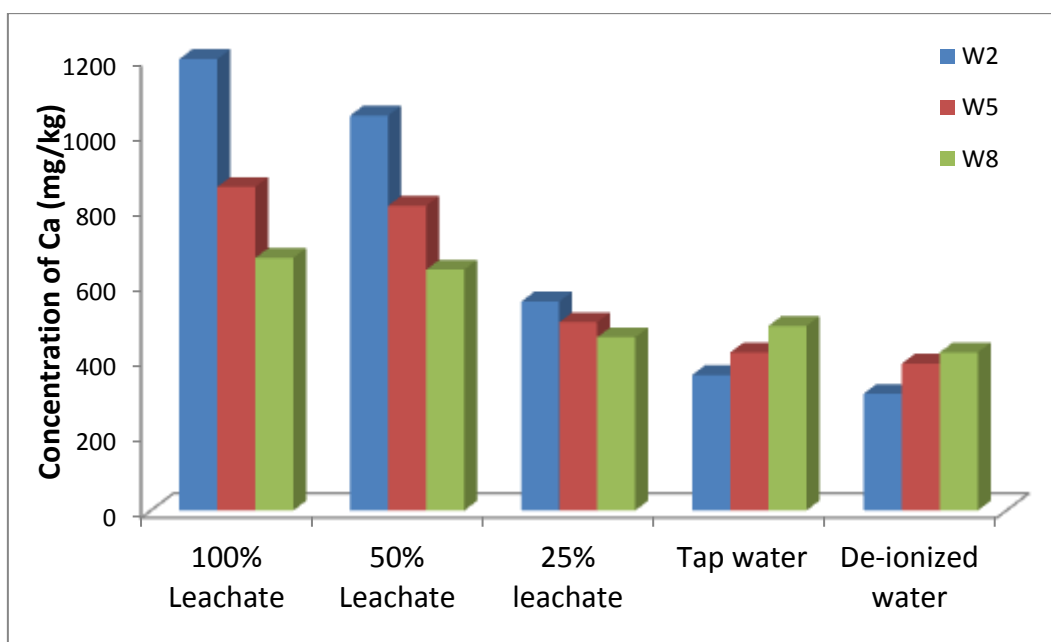


Figure 4. 11 Change in concentration of Ca in Swiss chard leaves during second, fifth and eighth weeks of the experiment

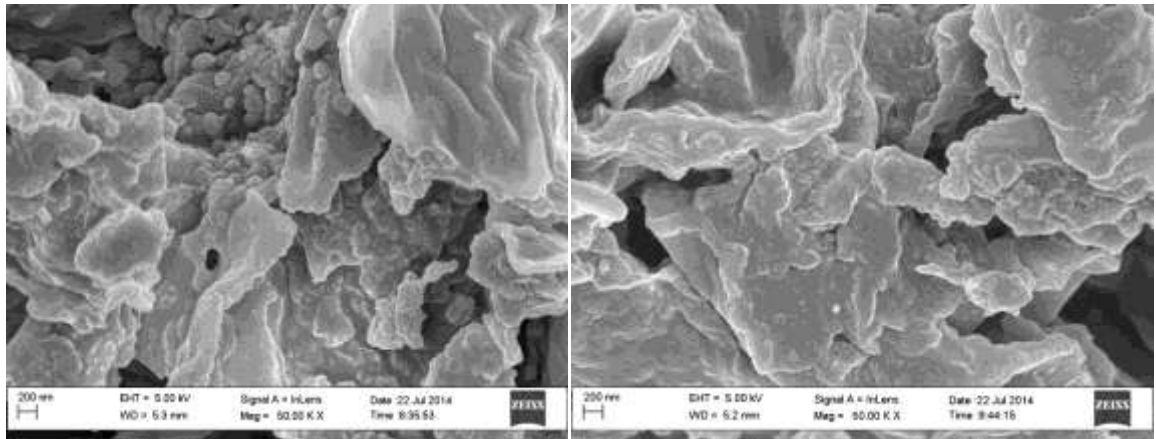
4.3.4 Effect of irrigation waters on ultra-structural leaves morphology of Swiss chard

The authentication of microscopically important ultra-structures using the Scanning Electron Microscope (SEM) plays a vital role in the identification, location and distribution of some botanical features of plants (Vaishali *et al.*, 2008). The micrographs of the Scanning Electron Microscope (SEM) revealed non-uniform granules with rough surfaces of Swiss chard leaves with probable presence of stomata as shown in Figures 4.12 a – 4.12e and Figures 4.13a – 4.13e. After irrigation with different concentrations of leachate, the leaves exhibited agglomerated smooth surfaces and the stomata may have been embedded with Na and Cl, which were confirmed by Energy Dispersive Spectroscopy (EDS). The accumulation of these metals cause increases in epidermal and mesophyll thickness, and elongation of the palisade cells. While, the tissue of Swiss chard leaves irrigated with control water show no change in the surface structure between week one and eight, irregular surface with the presence of stomata. Zooming-in further on figures 4.12a and 4.13a (100% leachate irrigated treatment), the results of the SEM analysis also

CHAPTER 4

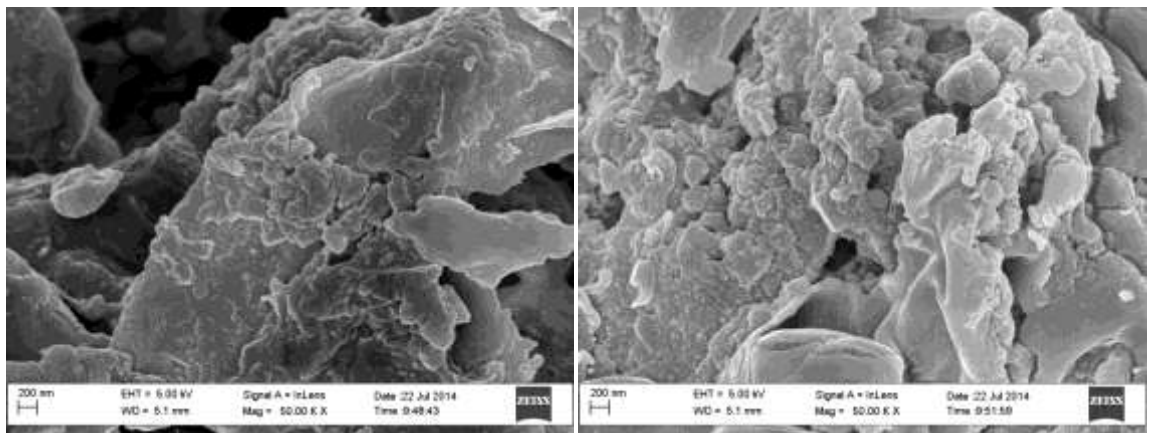
revealed possible closure of the stomata opening occasioned by osmotic pressure, deposition of metals and reduced photosynthesis; which would have limited carbon dioxide uptake (Zhu *et al.*, 2001). SEM results correlates well with the trend in plant height from week two to week eight and confirms early studies that the leaves of salt stressed plants are smaller with thick epidermal and mesophyll cells (Parida *et al.*, 2005).

CHAPTER 4



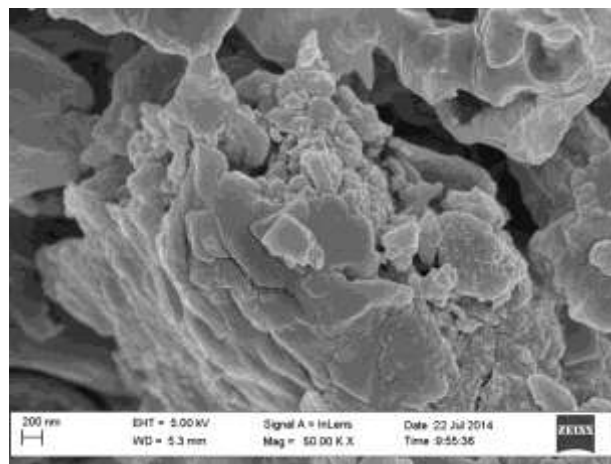
(a)

(b)



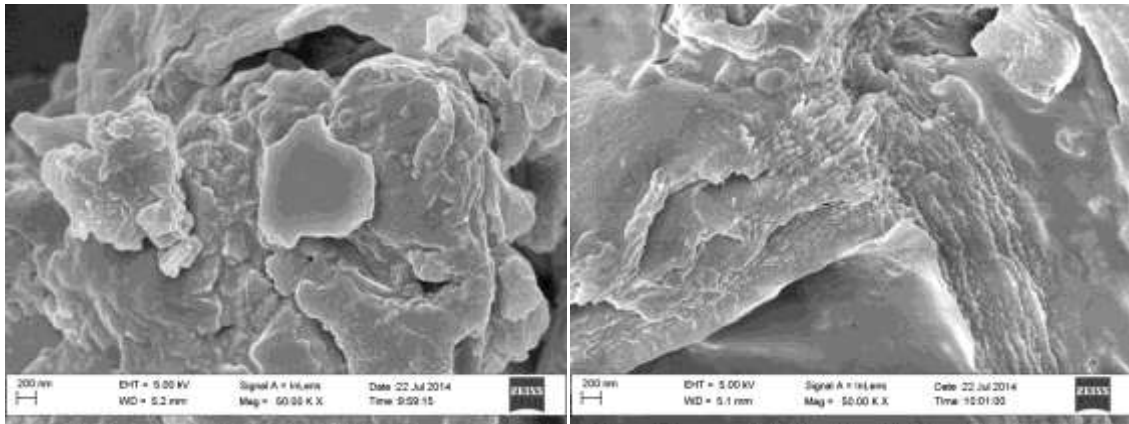
(c)

(d)



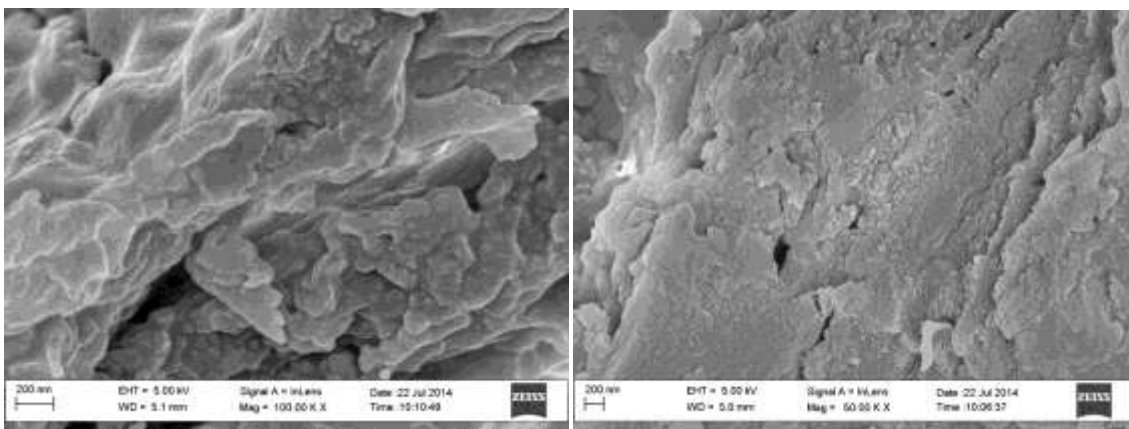
(e)

Figure 4. 12 Scanning electron micrographs of (a) 25% Leachate, (b) 100% Leachate, (c) Tap water, (d) 50% Leachate (e) Distilled water, in the first week of the experiment.



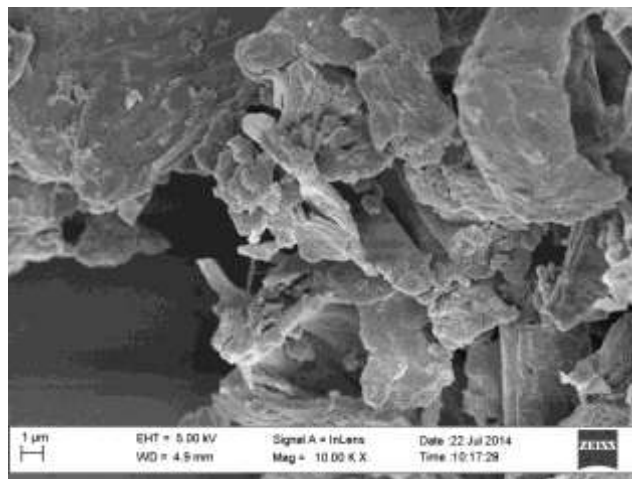
(a)

(b)



(c)

(d)



(e)

Figure 4. 13 Scanning electron micrographs of (a) 25% Leachate, (b) 100% Leachate, (c) Tap water, (d) 50% Leachate, (e) distilled water, in the eight week of the experiment.

CHAPTER 5

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

The results of this study indicate that the concentrations of cations, electrical conductivity and pH in the potted soils increased with time when the leachate was used as irrigation water compared with the utilization of tap and distilled water where little or no change was observed. However the heavy metals concentration was within allowed limits and shows no significant difference between leachate irrigated and non-irrigated one, thus indicating the low concentration of these heavy metals in leachate. Also boron toxicity was not observed; as the leachate had very low concentration of B.

The selected crop for this study shows reduction in growth in soil irrigated with 100% leachate and 50% leachate compared with the growth level observed in irrigation with tap and distilled water. This decline in growth could be attributed to the higher Na content in the leachate used for the irrigation of the crop; which tends to replace Ca and Mg in solution thereby limiting their uptake and ultimately affecting structural growth in Swiss chard.

However, Swiss chard species were able to survive up to eight weeks with the applied leachate irrigation. This may be attributed to the fact that Swiss chard has high tolerance to salinity. Furthermore, the results show the concentration of heavy metals in plant tissues over the period of this study falls within globally acceptable values which poses no harm for human consumption and health.

5.2 Future work and recommendations

In future, investigations of the effect of leachate on the other crops such as tomato, carrot and cabbage, which has variable tolerance levels, may be conducted. The study may also be extended to the utilization of different leachate sources and lower concentrations, to investigate their effect on ground water, soil and accumulation of important nutrients like Zn in crop. .

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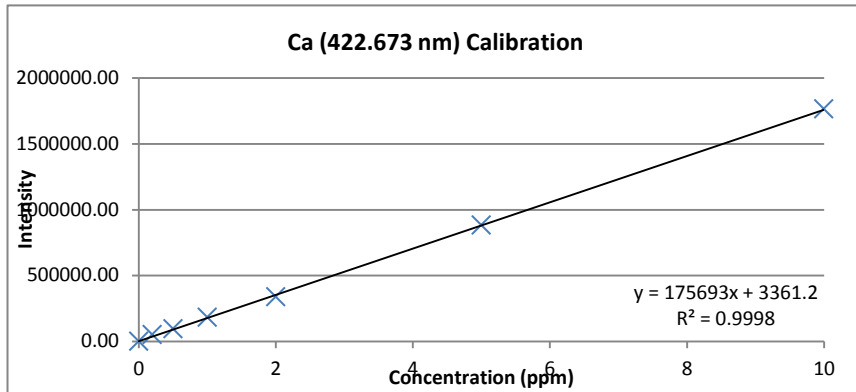
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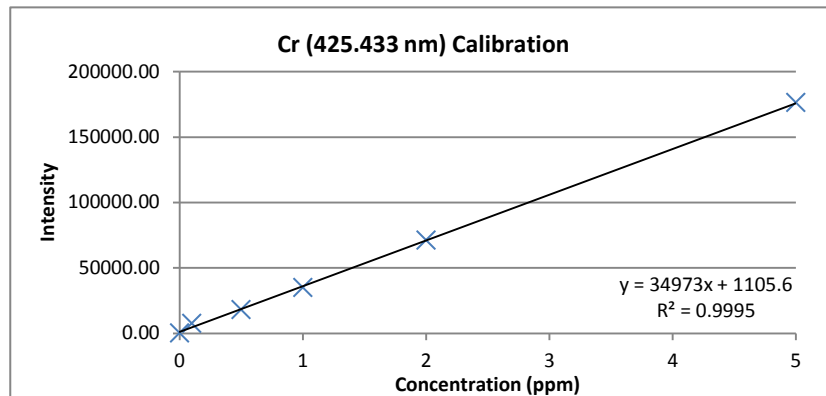
APPENDIX

APPENDIX 1:
RESULTS OF CALPRATION CURVE OF
MICROWAVE PLASMA-ATOMIC
EMISSION SPECTROMETER



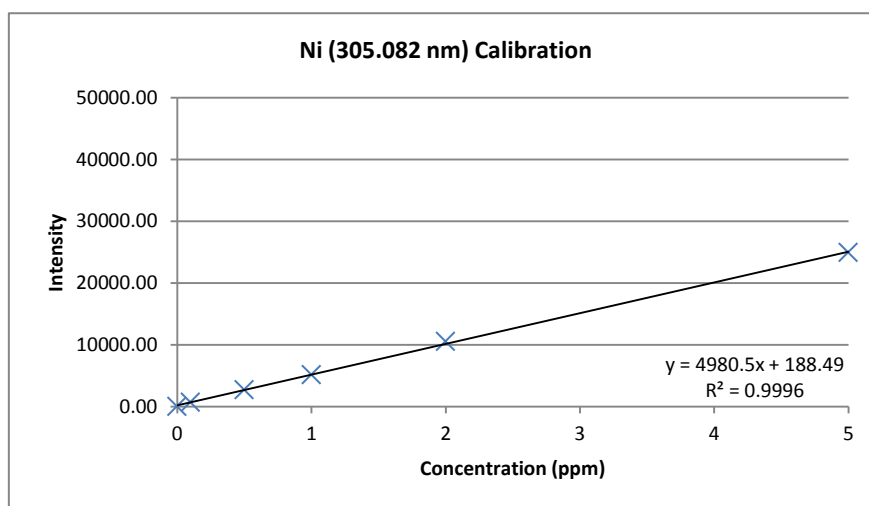
A.Ca (422.673 nm) Calibration

Label	Element	Concentration	Unit	Intensity Replicate 1	Intensity Replicate 2	Intensity Replicate 3	Ave Intensity	Std deviation
Blank	Ca 422.673	0	ppm	77.87	221.22	-284.76	4.78	260.79
Standard 1	Ca 422.673	0.2	ppm	49637.12	51093.19	50619.18	50449.83	742.66
Standard 2	Ca 422.673	0.5	ppm	94501.50	96062.67	95442.98	95335.72	786.09
Standard 3	Ca 422.673	1	ppm	183927.83	181022.87	178535.01	181161.90	2699.10
Standard 4	Ca 422.673	2	ppm	346303.94	336108.32	327962.44	336791.57	9189.82
Standard 5	Ca 422.673	5	ppm	877116.43	874754.99	894745.97	882205.80	10924.10
Standard 6	Ca 422.673	10	ppm	1776962.77	1740141.48	1771994.82	1763033.02	19979.67



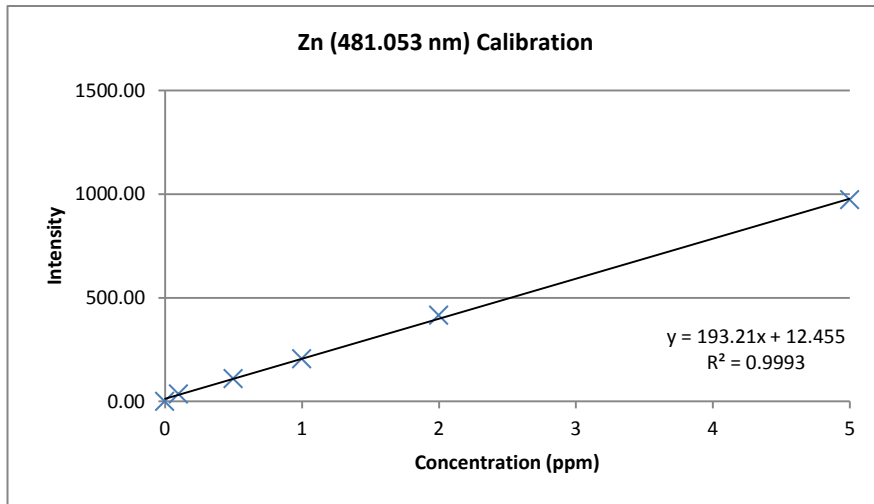
B. Cr (425.433 nm) Calibration

Label	Element	Concentration	Unit	Intensity Replicate 1	Intensity Replicate 2	Intensity Replicate 3	Ave Intensity	Std deviation
Blank	Cr 425.433	0	ppm	-13.83	9.37	4.85	0.13	12.30
Standard 1	Cr 425.433	0.1	ppm	7322.66	7374.09	7372.96	7356.57	29.37
Standard 3	Cr 425.433	0.5	ppm	18154.68	17913.72	17940.85	18003.08	131.99
Standard 4	Cr 425.433	1	ppm	34862.01	34649.26	34786.53	34765.93	107.86
Standard 5	Cr 425.433	2	ppm	71291.72	71123.80	70673.79	71029.77	319.52
Standard 6	Cr 425.433	5	ppm	177233.14	176424.22	175079.07	176245.48	1088.10



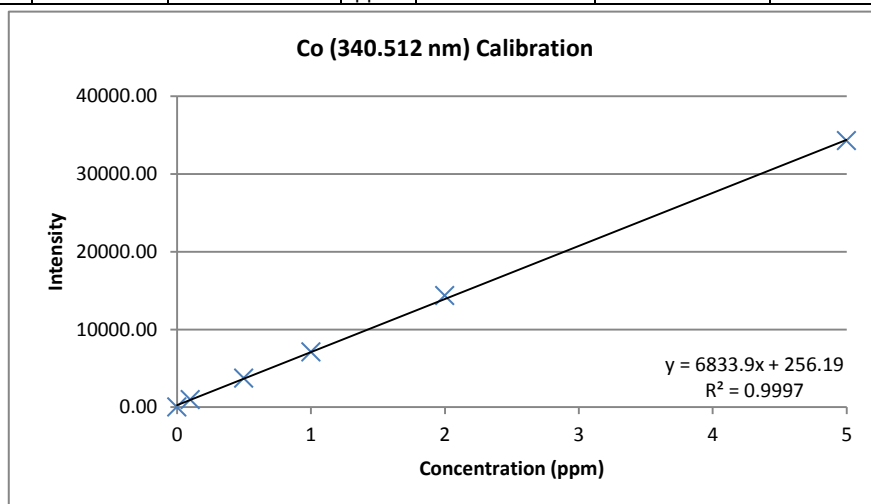
C. Ni (305.082 nm) Calibration

Label	Element	Concentration	Unit	Intensity Replicate 1	Intensity Replicate 2	Intensity Replicate 3	Ave Intensity	Std deviation
Blank	Ni 305.082	0	ppm	10.64	-5.97	-4.59	0.03	9.22
Standard 1	Ni 305.082	0.1	ppm	659.58	685.31	690.49	678.46	16.55
Standard 3	Ni 305.082	0.5	ppm	2664.62	2666.60	2726.15	2685.79	34.97
Standard 4	Ni 305.082	1	ppm	5060.07	5162.27	5169.68	5130.67	61.26
Standard 5	Ni 305.082	2	ppm	10400.54	10529.14	10621.89	10517.19	111.16
Standard 6	Ni 305.082	5	ppm	24682.14	25070.45	25100.05	24950.88	233.21



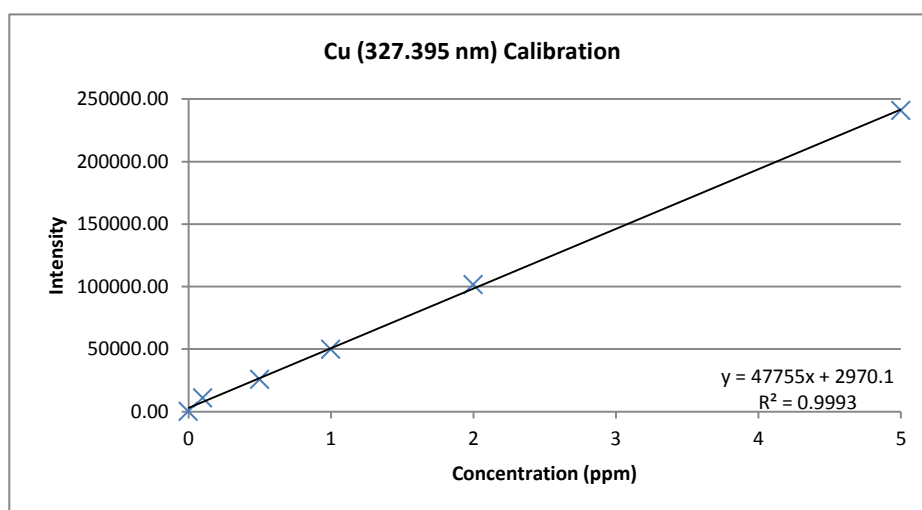
D. Zn (481.053 nm) Calibration

Label	Element	Concentration	Unit	Intensity Replicate 1	Intensity Replicate 2	Intensity Replicate 3	Ave Intensity	Std deviation
Blank	Zn 481.053	0	ppm	-0.42	0.74	-0.32	0.00	0.64
Standard 1	Zn 481.053	0.1	ppm	32.35	37.95	35.92	35.41	2.84
Standard 3	Zn 481.053	0.5	ppm	111.18	111.41	105.43	109.34	3.39
Standard 4	Zn 481.053	1	ppm	195.00	206.07	212.95	204.67	9.06
Standard 5	Zn 481.053	2	ppm	417.28	405.15	421.37	414.60	8.44
Standard 6	Zn 481.053	5	ppm	973.98	977.20	965.73	972.30	5.92



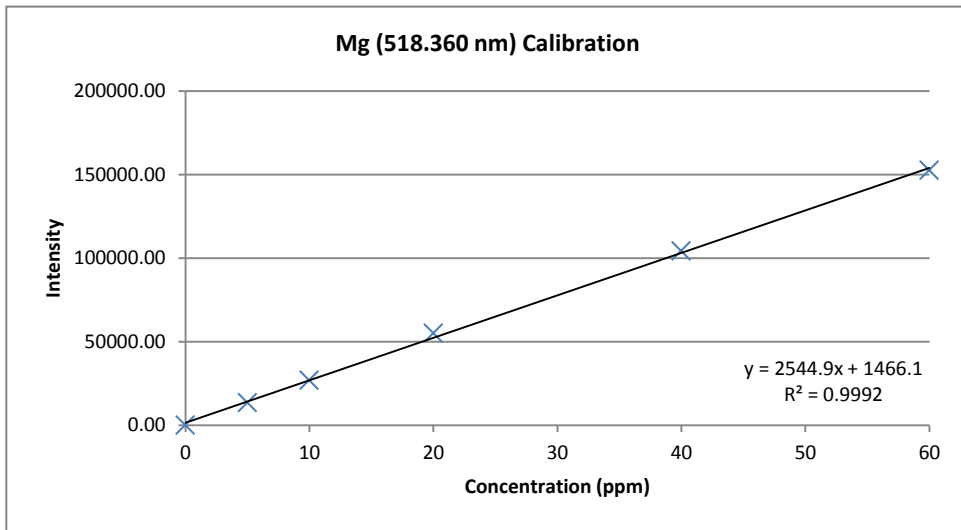
E. Co (340.512 nm) Calibration

Label	Element	Concentration	Unit	Intensity Replicate 1	Intensity Replicate 2	Intensity Replicate 3	Ave Intensity	Std deviation
Blank	Co 340.512	0	ppm	-28.94	19.76	9.15	-0.01	25.61
Standard 1	Co 340.512	0.1	ppm	940.09	960.41	968.34	956.28	14.57
Standard 3	Co 340.512	0.5	ppm	3666.99	3743.27	3699.47	3703.24	38.28
Standard 4	Co 340.512	1	ppm	7081.18	7056.93	7052.04	7063.38	15.61
Standard 5	Co 340.512	2	ppm	14277.73	14328.12	14336.51	14314.12	31.79
Standard 6	Co 340.512	5	ppm	34248.36	34195.05	34371.33	34271.58	90.40



F. Cu (327.395 nm) Calibration

Label	Element	Concentration	Unit	Intensity Replicate 1	Intensity Replicate 2	Intensity Replicate 3	Ave Intensity	Std deviation
Blank	Cu 327.395	0	ppm	23.51	19.91	-43.05	0.12	37.43
Standard 1	Cu 327.395	0.1	ppm	10967.93	10866.28	11003.39	10945.87	71.17
Standard 2	Cu 327.395	0.5	ppm	25752.86	25531.85	25661.95	25648.89	111.08
Standard 3	Cu 327.395	1	ppm	49658.02	49802.03	49707.88	49722.64	73.13
Standard 4	Cu 327.395	2	ppm	101011.55	101592.57	101408.17	101337.43	296.90
Standard 5	Cu 327.395	5	ppm	240870.76	240446.6	241256.19	240857.85	404.95



G. Mg (518.360 nm) Calibration

Label	Element	Concentration	Unit	Intensity Replicate 1	Intensity Replicate 2	Intensity Replicate 3	Ave Intensity	Std deviation
Blank	Mg 518.360	0	ppm	1.44	-3.94	2.46	-0.01	3.44
Standard 1	Mg 518.360	5	ppm	13551.79	13522.34	13501.57	13525.23	25.23
Standard 2	Mg 518.360	10	ppm	26597.66	26901.05	27028.72	26842.48	221.42
Standard 3	Mg 518.360	20	ppm	54579.30	55364.35	55129.27	55024.31	402.91
Standard 4	Mg 518.360	40	ppm	102746.50	105216.16	105083.31	104348.66	1389.10
Standard 5	Mg 518.360	60	ppm	149903.80	153664.85	154275.30	152614.65	2367.42

APPENDIX 2:
RESULTS OF
LEAVES
ANALYSIS

Code: n.d = not detected

* < 0.1
ppm

A. **Ni**
Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Concentration	Unit	Code
Sample 1	Ni 305.082	58.32	56.27	66.52	60.37	-0.03	ppm	n.d
Sample 2	Ni 305.082	198.90	214.15	214.20	209.08	0.00	ppm	n.d
Sample 3	Ni 305.082	233.68	215.00	232.71	227.13	0.01	ppm	*
Sample 4	Ni 305.082	131.09	149.52	126.06	135.56	-0.01	ppm	n.d
Sample 5	Ni 305.082	169.99	174.70	171.42	172.04	0.00	ppm	n.d
Sample 6	Ni 305.082	136.10	116.44	144.09	132.21	-0.01	ppm	n.d
Sample 7	Ni 305.082	124.76	127.34	151.31	134.47	-0.01	ppm	n.d
Sample 8	Ni 305.082	79.41	91.37	72.63	81.14	-0.02	ppm	n.d
Sample 9	Ni 305.082	106.92	136.21	134.07	125.73	-0.01	ppm	n.d
Sample 10	Ni 305.082	193.04	209.06	214.50	205.53	0.00	ppm	n.d
Sample 11	Ni 305.082	127.68	141.94	179.44	149.69	-0.01	ppm	n.d
Sample 12	Ni 305.082	211.76	185.57	182.67	193.33	0.00	ppm	n.d
Sample 13	Ni 305.082	83.60	111.80	88.38	94.59	-0.02	ppm	n.d
Sample 14	Ni 305.082	71.29	71.49	85.63	76.14	-0.02	ppm	n.d
Sample 15	Ni 305.082	425.82	429.62	417.39	424.28	0.05	ppm	*
Sample 16	Ni 305.082	106.13	123.60	111.31	113.68	-0.02	ppm	n.d
Sample 17	Ni 305.082	218.45	242.25	239.21	233.30	0.01	ppm	*
Sample 18	Ni 305.082	135.44	120.72	133.61	129.92	-0.01	ppm	n.d
Sample 19	Ni 305.082	154.15	169.15	148.28	157.19	-0.01	ppm	n.d
Sample 20	Ni 305.082	120.56	132.58	146.43	133.19	-0.01	ppm	n.d
Sample 21	Ni 305.082	-32.79	-25.51	-24.88	-27.73	-0.04	ppm	n.d
Sample 22	Ni 305.082	-43.31	-48.22	-35.79	-42.44	-0.05	ppm	n.d
Sample 23	Ni 305.082	-15.62	-22.86	-21.68	-20.05	-0.04	ppm	n.d
Sample 24	Ni 305.082	-30.44	-36.07	-38.40	-34.97	-0.04	ppm	n.d
Sample 25	Ni 305.082	-33.45	-33.15	-18.89	-28.50	-0.04	ppm	n.d
Sample 26	Ni 305.082	-19.59	-45.48	-31.63	-32.23	-0.04	ppm	n.d
Sample 27	Ni 305.082	-53.01	-17.04	-33.35	-34.47	-0.04	ppm	n.d
Sample 28	Ni 305.082	-38.03	-34.69	-26.53	-33.08	-0.04	ppm	n.d
Sample 29	Ni 305.082	-37.32	-23.48	-43.55	-34.78	-0.04	ppm	n.d
Sample 30	Ni 305.082	-42.42	-44.96	-20.83	-36.07	-0.05	ppm	n.d

Sample 31	Ni 305.082	-30.44	-3.75	-22.60	-18.93	-0.04	ppm	n.d
Sample 32	Ni 305.082	-25.44	-11.11	-28.22	-21.59	-0.04	ppm	n.d
Sample 33	Ni 305.082	-15.91	-39.68	-37.96	-31.18	-0.04	ppm	n.d
Sample 34	Ni 305.082	-24.65	-29.05	-26.59	-26.76	-0.04	ppm	n.d
Sample 35	Ni 305.082	-10.78	14.99	-34.56	-10.12	-0.04	ppm	n.d
Sample 36	Ni 305.082	-29.59	-17.23	-31.26	-26.03	-0.04	ppm	n.d
Sample 37	Ni 305.082	-23.35	-44.44	2.04	-21.92	-0.04	ppm	n.d
Sample 38	Ni 305.082	-37.64	-32.16	-28.53	-32.78	-0.04	ppm	n.d
Sample 39	Ni 305.082	-17.58	-26.06	-35.87	-26.50	-0.04	ppm	n.d
Sample 40	Ni 305.082	-24.47	-30.44	-33.46	-29.46	-0.04	ppm	n.d

**B. Cu
Concentration**

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Concentration	Unit	Code
Sample 1	Cu 327.395	5013.21	5059.95	5015.36	5029.51	0.04	ppm	*
Sample 2	Cu 327.395	6060.47	6137.86	6094.57	6097.63	0.07	ppm	*
Sample 3	Cu 327.395	10367.29	10358.62	10340.61	10355.51	0.15	ppm	
Sample 4	Cu 327.395	4588.96	4546.14	4568.26	4567.79	0.03	ppm	*
Sample 5	Cu 327.395	9324.40	9408.46	9380.10	9370.99	0.13	ppm	
Sample 6	Cu 327.395	4561.63	4593.27	4604.01	4586.30	0.03	ppm	*
Sample 7	Cu 327.395	6852.56	6874.81	6856.75	6861.37	0.08	ppm	*
Sample 8	Cu 327.395	4696.90	4725.52	4715.19	4712.54	0.04	ppm	*
Sample 9	Cu 327.395	4757.02	4691.01	4752.07	4733.37	0.04	ppm	*
Sample 10	Cu 327.395	8587.67	8544.41	8613.24	8581.77	0.12	ppm	
Sample 11	Cu 327.395	5825.18	5774.42	5760.60	5786.73	0.06	ppm	*
Sample 12	Cu 327.395	8437.64	8437.66	8415.93	8430.41	0.11	ppm	
Sample 13	Cu 327.395	4644.31	4661.12	4616.52	4640.65	0.03	ppm	*
Sample 14	Cu 327.395	4211.66	4253.81	4207.13	4224.20	0.03	ppm	*
Sample 15	Cu 327.395	5570.80	5664.18	5642.42	5625.80	0.06	ppm	*
Sample 16	Cu 327.395	5406.07	5378.48	5384.44	5389.66	0.05	ppm	*
Sample 17	Cu 327.395	10581.85	10607.38	10650.92	10613.38	0.16	ppm	
Sample 18	Cu 327.395	5554.66	5597.98	5577.12	5576.59	0.05	ppm	*
Sample 19	Cu 327.395	4153.87	4157.29	4158.68	4156.61	0.02	ppm	*
Sample 20	Cu 327.395	13228.92	13189.28	13309.65	13242.62	0.22	ppm	
Sample 21	Cu 327.395	3336.09	3287.52	3321.70	3315.10	0.01	ppm	*
Sample 22	Cu 327.395	1668.39	1714.18	1713.19	1698.59	-0.03	ppm	n.d
Sample 23	Cu 327.395	2198.01	2207.47	2223.80	2209.76	-0.02	ppm	n.d
Sample	Cu 327.395	1836.97	1820.80	1820.66	1826.14	-0.02	ppm	n.d

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Sample 25	Cu 327.395	2351.46	2365.17	2358.08	2358.24	-0.01	ppm	n.d
Sample 26	Cu 327.395	2453.46	2434.14	2408.44	2432.01	-0.01	ppm	n.d
Sample 27	Cu 327.395	1857.64	1885.20	1864.13	1868.99	-0.02	ppm	n.d
Sample 28	Cu 327.395	2183.26	2214.44	2189.76	2195.82	-0.02	ppm	n.d
Sample 29	Cu 327.395	2278.64	2369.40	2293.32	2313.79	-0.01	ppm	n.d
Sample 30	Cu 327.395	1781.49	1769.76	1790.61	1780.62	-0.02	ppm	n.d
Sample 31	Cu 327.395	2032.62	2068.91	2040.40	2047.31	-0.02	ppm	n.d
Sample 32	Cu 327.395	2087.37	2040.96	2048.65	2058.99	-0.02	ppm	n.d
Sample 33	Cu 327.395	1998.78	2031.70	2002.55	2011.01	-0.02	ppm	n.d
Sample 34	Cu 327.395	2229.65	2213.15	2208.75	2217.18	-0.02	ppm	n.d
Sample 35	Cu 327.395	1989.72	2038.40	2010.02	2012.71	-0.02	ppm	n.d
Sample 36	Cu 327.395	2019.00	2020.81	1998.80	2012.87	-0.02	ppm	n.d
Sample 37	Cu 327.395	2233.77	2238.08	2225.31	2232.39	-0.02	ppm	n.d
Sample 38	Cu 327.395	2222.46	2238.37	2211.70	2224.18	-0.02	ppm	n.d
Sample 39	Cu 327.395	2125.53	2147.12	2143.06	2138.57	-0.02	ppm	n.d
Sample 40	Cu 327.395	2345.19	2328.21	2325.90	2333.10	-0.01	ppm	n.d

**C. Mg
Concentration**

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Concentration	Unit
Sample 1	Mg 518.360	27599.32	27581.81	27528.04	27569.72	10.26	ppm
Sample 2	Mg 518.360	32207.57	32065.56	31946.93	32073.35	12.03	ppm
Sample 3	Mg 518.360	61740.93	61495.66	61578.74	61605.11	23.63	ppm
Sample 4	Mg 518.360	39455.11	39476.69	39548.64	39493.48	14.94	ppm
Sample 5	Mg 518.360	64824.92	65117.65	65155.66	65032.74	24.98	ppm
Sample 6	Mg 518.360	30692.63	31047.29	30824.67	30854.86	11.55	ppm
Sample 7	Mg 518.360	45160.90	44737.40	45318.63	45072.31	17.13	ppm
Sample 8	Mg 518.360	31193.14	31315.33	31131.18	31213.22	11.69	ppm
Sample 9	Mg 518.360	35807.52	35879.54	35781.55	35822.87	13.50	ppm
Sample 10	Mg 518.360	63470.94	63880.16	63498.32	63616.47	24.42	ppm
Sample 11	Mg 518.360	41414.26	41611.31	41978.19	41667.92	15.80	ppm
Sample 12	Mg 518.360	68383.95	68910.99	68541.85	68612.26	26.38	ppm
Sample 13	Mg 518.360	31352.58	31416.28	31429.48	31399.45	11.76	ppm
Sample 14	Mg 518.360	27251.27	27220.84	27338.72	27270.28	10.14	ppm
Sample 15	Mg 518.360	38322.53	38009.42	38131.54	38154.50	14.42	ppm
Sample 16	Mg 518.360	39673.36	39657.52	39813.75	39714.88	15.03	ppm
Sample 17	Mg 518.360	80632.24	81184.43	80587.10	80801.26	31.17	ppm

Sample 18	Mg 518.360	40807.94	41084.85	41042.13	40978.31	15.53	ppm
Sample 19	Mg 518.360	30504.24	30182.37	30233.39	30306.67	11.33	ppm
Sample 20	Mg 518.360	59214.28	58845.89	59053.02	59037.73	22.62	ppm
Sample 21	Mg 518.360	30827.50	30944.76	30948.29	30906.85	11.57	ppm
Sample 22	Mg 518.360	40905.07	41204.99	41091.83	41067.30	15.56	ppm
Sample 23	Mg 518.360	43829.75	43856.59	43901.42	43862.59	16.66	ppm
Sample 24	Mg 518.360	38452.53	38350.80	38423.40	38408.91	14.52	ppm
Sample 25	Mg 518.360	34375.24	34429.50	34313.33	34372.69	12.93	ppm
Sample 26	Mg 518.360	31391.73	31557.82	31661.18	31536.91	11.82	ppm
Sample 27	Mg 518.360	55425.31	55317.80	55379.76	55374.29	21.18	ppm
Sample 28	Mg 518.360	35025.63	35016.09	35148.63	35063.45	13.20	ppm
Sample 29	Mg 518.360	33925.01	33968.04	33910.79	33934.61	12.76	ppm
Sample 30	Mg 518.360	54016.39	53973.07	54195.60	54061.69	20.67	ppm
Sample 31	Mg 518.360	31729.94	31901.19	31748.08	31793.07	11.92	ppm
Sample 32	Mg 518.360	40566.38	40695.44	40691.76	40651.19	15.40	ppm
Sample 33	Mg 518.360	45980.88	45929.24	46020.61	45976.91	17.49	ppm
Sample 34	Mg 518.360	30917.86	31052.50	31113.20	31027.85	11.62	ppm
Sample 35	Mg 518.360	35280.93	35248.15	35529.10	35352.73	13.32	ppm
Sample 36	Mg 518.360	48256.64	48399.89	48414.96	48357.16	18.43	ppm
Sample 37	Mg 518.360	41815.21	41923.56	41924.19	41887.65	15.88	ppm
Sample 38	Mg 518.360	43000.39	43055.84	43225.09	43093.77	16.36	ppm
Sample 39	Mg 518.360	41716.40	41614.18	41886.96	41739.18	15.83	ppm
Sample 40	Mg 518.360	43503.29	43589.98	43435.80	43509.69	16.52	ppm

**D. Zn
Concentration**

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Concentration	Unit	Code
Sample 1	Zn 481.053	86.95	95.79	86.70	89.81	0.40	ppm	
Sample 2	Zn 481.053	62.58	58.73	61.68	61.00	0.25	ppm	
Sample 3	Zn 481.053	75.10	72.76	69.40	72.42	0.31	ppm	
Sample 4	Zn 481.053	-8.39	-16.62	5.68	-6.44	-0.10	ppm	n.d
Sample 5	Zn 481.053	26.89	29.90	30.43	29.07	0.09	ppm	*
Sample 6	Zn 481.053	43.36	51.17	42.92	45.82	0.17	ppm	
Sample 7	Zn 481.053	74.49	76.39	68.70	73.19	0.31	ppm	
Sample 8	Zn 481.053	60.32	57.86	62.13	60.10	0.25	ppm	
Sample 9	Zn 481.053	27.76	35.20	30.17	31.04	0.10	ppm	
Sample 10	Zn 481.053	48.46	52.71	47.44	49.54	0.19	ppm	
Sample	Zn 481.053	39.58	46.42	26.04	37.35	0.13	ppm	

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Sample 12	Zn 481.053	94.79	91.85	92.30	92.98	0.42	ppm	
Sample 13	Zn 481.053	58.40	58.85	65.93	61.06	0.25	ppm	
Sample 14	Zn 481.053	60.78	56.62	58.13	58.51	0.24	ppm	
Sample 15	Zn 481.053	58.14	50.70	59.88	56.24	0.23	ppm	
Sample 16	Zn 481.053	48.01	52.27	57.90	52.73	0.21	ppm	
Sample 17	Zn 481.053	148.50	142.76	138.82	143.36	0.68	ppm	
Sample 18	Zn 481.053	63.08	47.14	40.96	50.39	0.20	ppm	
Sample 19	Zn 481.053	57.97	52.16	52.52	54.22	0.22	ppm	
Sample 20	Zn 481.053	122.34	128.75	122.78	124.62	0.58	ppm	
Sample 21	Zn 481.053	30.04	34.66	33.19	32.63	0.10	ppm	
Sample 22	Zn 481.053	9.15	4.09	4.28	5.84	-0.03	ppm	n.d
Sample 23	Zn 481.053	8.13	9.11	7.79	8.34	-0.02	ppm	n.d
Sample 24	Zn 481.053	8.79	25.69	11.06	15.18	0.01	ppm	*
Sample 25	Zn 481.053	17.40	19.55	20.53	19.16	0.03	ppm	*
Sample 26	Zn 481.053	20.49	37.50	18.11	25.37	0.07	ppm	*
Sample 27	Zn 481.053	11.81	6.72	12.09	10.21	-0.01	ppm	n.d
Sample 28	Zn 481.053	26.68	27.74	20.60	25.01	0.06	ppm	*
Sample 29	Zn 481.053	29.28	21.90	36.46	29.21	0.09	ppm	*
Sample 30	Zn 481.053	4.07	8.83	4.05	5.65	-0.04	ppm	n.d
Sample 31	Zn 481.053	18.91	26.71	23.69	23.10	0.06	ppm	*
Sample 32	Zn 481.053	37.28	26.98	34.05	32.77	0.11	ppm	
Sample 33	Zn 481.053	23.84	24.43	23.04	23.77	0.06	ppm	*
Sample 34	Zn 481.053	29.33	29.27	22.35	26.98	0.08	ppm	*
Sample 35	Zn 481.053	34.92	22.93	21.03	26.29	0.07	ppm	*
Sample 36	Zn 481.053	16.22	22.11	10.46	16.26	0.02	ppm	*
Sample 37	Zn 481.053	25.00	19.47	16.64	20.37	0.04	ppm	*
Sample 38	Zn 481.053	34.29	35.49	41.44	37.07	0.13	ppm	
Sample 39	Zn 481.053	18.12	31.01	26.53	25.22	0.07	ppm	*
Sample 40	Zn 481.053	44.00	42.94	48.12	45.02	0.17	ppm	

**E. Cr
Concentration**

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Concentration	Unit	Code
Sample 1	Cr 425.433	2240.79	2294.58	2306.58	2280.65	0.03	ppm	*
Sample 2	Cr 425.433	2127.59	2151.13	2164.08	2147.60	0.03	ppm	*

Sample 3	Cr 425.433	4103.55	4191.85	4202.97	4166.12	0.09	ppm	*
Sample 4	Cr 425.433	2752.43	2770.85	2745.18	2756.15	0.05	ppm	*
Sample 5	Cr 425.433	4317.63	4326.48	4322.43	4322.18	0.09	ppm	*
Sample 6	Cr 425.433	2145.98	2163.26	2180.47	2163.24	0.03	ppm	*
Sample 7	Cr 425.433	2628.06	2659.7	2684.37	2657.38	0.04	ppm	*
Sample 8	Cr 425.433	2059.36	2056.16	2069.74	2061.75	0.03	ppm	*
Sample 9	Cr 425.433	2056.41	2057	2058.68	2057.36	0.03	ppm	*
Sample 10	Cr 425.433	3357.78	3362.9	3381.54	3367.41	0.06	ppm	*
Sample 11	Cr 425.433	2636.44	2642.59	2660.12	2646.38	0.04	ppm	*
Sample 12	Cr 425.433	4185.27	4199.29	4209.97	4198.18	0.09	ppm	*
Sample 13	Cr 425.433	1934.91	1982.83	1941.42	1953.05	0.02	ppm	*
Sample 14	Cr 425.433	1703.09	1726.72	1749.52	1726.44	0.02	ppm	*
Sample 15	Cr 425.433	12560.28	12538.29	12558.5	12552.36	0.33	ppm	
Sample 16	Cr 425.433	2048.8	2070.12	2076.2	2065.04	0.03	ppm	*
Sample 17	Cr 425.433	4409.22	4483.63	4455.9	4449.58	0.10	ppm	
Sample 18	Cr 425.433	1938.62	1949.29	1964.92	1950.94	0.02	ppm	*
Sample 19	Cr 425.433	1620.75	1635.56	1628.58	1628.30	0.01	ppm	*
Sample 20	Cr 425.434	4742.37	4764.67	4795.75	4767.60	0.10	ppm	
Sample 21	Cr 425.433	673.78	701.47	690.49	688.58	-0.01	ppm	n.d
Sample 22	Cr 425.433	654.72	666.64	671.85	664.40	-0.01	ppm	n.d
Sample 23	Cr 425.433	580.14	584.58	601.96	588.89	-0.01	ppm	n.d
Sample 24	Cr 425.433	596.33	611.43	603.46	603.74	-0.01	ppm	n.d
Sample 25	Cr 425.433	437.3	455.73	468.28	453.77	-0.02	ppm	n.d
Sample 26	Cr 425.433	430.57	444.47	456.68	443.91	-0.02	ppm	n.d
Sample 27	Cr 425.433	467.8	483.22	495.73	482.25	-0.02	ppm	n.d
Sample 28	Cr 425.433	394.07	402.86	401.32	399.42	-0.02	ppm	n.d
Sample 29	Cr 425.433	385.39	391.04	389.45	388.63	-0.02	ppm	n.d
Sample 30	Cr 425.433	384.34	400.25	389.95	391.51	-0.02	ppm	n.d
Sample 31	Cr 425.433	310.91	321.63	329.9	320.81	-0.02	ppm	n.d
Sample 32	Cr 425.433	459.03	476.54	500.36	478.64	-0.02	ppm	n.d
Sample 33	Cr 425.433	466.65	455.48	462.39	461.51	-0.02	ppm	n.d
Sample 34	Cr 425.433	431.98	444.71	439.87	438.85	-0.02	ppm	n.d
Sample 35	Cr 425.433	556.79	574.32	566.23	565.78	-0.02	ppm	n.d
Sample 36	Cr 425.433	422	433.67	441.99	432.55	-0.02	ppm	n.d
Sample 37	Cr 425.433	420.58	429.37	437.08	429.01	-0.02	ppm	n.d
Sample 38	Cr 425.433	419.88	406.49	420.24	415.54	-0.02	ppm	n.d
Sample 39	Cr 425.433	465.34	463.02	482.16	470.17	-0.02	ppm	n.d

Sample 40	Cr 425.433	1631.11	1641.77	1642.45	1638.44	0.02	ppm	*
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F. Co
Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Concentration	Unit	Code
Sample 1	Co 340.512	-26.02	-36.36	-21.89	-28.09	-0.04	ppm	n.d
Sample 2	Co 340.512	-36.04	-31	-39.68	-35.57	-0.04	ppm	n.d
Sample 3	Co 340.512	-60.11	-71.02	-73.58	-68.24	-0.05	ppm	n.d
Sample 4	Co 340.512	-50.27	-75.67	-68.87	-64.94	-0.05	ppm	n.d
Sample 5	Co 340.512	-75.93	-85.38	-91.14	-84.15	-0.05	ppm	n.d
Sample 6	Co 340.512	-96.88	-108.74	-127.42	-111.01	-0.05	ppm	n.d
Sample 7	Co 340.512	-79.16	-94.12	-57.16	-76.81	-0.05	ppm	n.d
Sample 8	Co 340.512	-69.91	-72.4	-86.72	-76.34	-0.05	ppm	n.d
Sample 9	Co 340.512	-90.18	-79.97	-91.67	-87.27	-0.05	ppm	n.d
Sample 10	Co 340.512	-63.65	-73.71	-75.8	-71.05	-0.05	ppm	n.d
Sample 11	Co 340.512	-72.36	-61.46	-51.93	-61.92	-0.05	ppm	n.d
Sample 12	Co 340.512	-88.75	-87.43	-111.48	-95.89	-0.05	ppm	n.d
Sample 13	Co 340.512	-74.04	-62.26	-73.65	-69.98	-0.05	ppm	n.d
Sample 14	Co 340.512	-68.79	-75.13	-77.96	-73.96	-0.05	ppm	n.d
Sample 15	Co 340.512	-82.29	-84.04	-60.21	-75.51	-0.05	ppm	n.d
Sample 16	Co 340.512	-59.06	-69.07	-70.52	-66.22	-0.05	ppm	n.d
Sample 17	Co 340.512	-99.65	-114.48	-87.94	-100.69	-0.05	ppm	n.d
Sample 18	Co 340.512	-102.31	-124.12	-119.53	-115.32	-0.05	ppm	n.d
Sample 19	Co 340.512	-63.4	-82.48	-64.75	-70.21	-0.05	ppm	n.d
Sample 20	Co 340.512	-176.5	-173.82	-174.72	-175.01	-0.06	ppm	n.d
Sample 21	Co 340.512	-17.95	-26.24	-27.27	-23.82	-0.04	ppm	n.d
Sample 22	Co 340.512	-19.26	-13.14	-29.96	-20.79	-0.04	ppm	n.d
Sample 23	Co 340.512	-32.81	-27.27	-36.57	-32.22	-0.04	ppm	n.d
Sample 24	Co 340.512	-16.71	-34	-19.34	-23.35	-0.04	ppm	n.d
Sample 25	Co 340.512	-23.69	-21.48	-22.79	-22.65	-0.04	ppm	n.d
Sample 26	Co 340.512	-9.83	-12.62	-0.04	-7.50	-0.04	ppm	n.d
Sample 27	Co 340.512	-39.37	-30.39	-29.54	-33.10	-0.04	ppm	n.d
Sample 28	Co 340.512	-22.68	-16.52	-24.76	-21.32	-0.04	ppm	n.d
Sample 29	Co 340.512	-37.47	-46.23	-30.37	-38.02	-0.04	ppm	n.d
Sample 30	Co 340.512	-33.4	-18.23	-35.98	-29.20	-0.04	ppm	n.d
Sample 31	Co 340.512	-19.6	-20.21	-34.93	-24.91	-0.04	ppm	n.d
Sample 32	Co 340.512	-32.84	-25.57	-40.69	-33.03	-0.04	ppm	n.d
Sample	Co 340.512	-30.72	-25.47	-28.64	-28.28	-0.04	ppm	n.d

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Sample 34	Co 340.512	-22.71	-42.37	-44.05	-36.38	-0.04	ppm	n.d	
Sample 35	Co 340.512	-12.17	-2.13	-18.73	-11.01	-0.04	ppm	n.d	
Sample 36	Co 340.512	-41.16	-30.28	-42.45	-37.96	-0.04	ppm	n.d	
Sample 37	Co 340.512	-20.1	-26.76	-39.05	-28.64	-0.04	ppm	n.d	
Sample 38	Co 340.512	-26.73	-31.26	-44.08	-34.02	-0.04	ppm	n.d	
Sample 39	Co 340.512	-22.91	-35.25	-20.08	-26.08	-0.04	ppm	n.d	
Sample 40	Co 340.512	-45.52	-34.49	-34.65	-38.22	-0.04	ppm	n.d	

G. Ca Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Dilution	Final Conc	Unit
Sample 1	Ca 422.673	191606.1	192753.49	190053.82	191471.14	1.07	1:50	53.53	ppm
Sample 2	Ca 422.673	247859.15	250407.05	250245.23	249503.81	1.40	1:50	70.05	ppm
Sample 3	Ca 422.673	435444.56	432558.17	430864.95	432955.89	2.45	1:50	122.26	ppm
Sample 4	Ca 422.673	227379.67	226768.64	224773.15	226307.15	1.27	1:50	63.45	ppm
Sample 5	Ca 422.673	438816.23	444671.45	444480.9	442656.19	2.50	1:50	125.02	ppm
Sample 6	Ca 422.673	188064.86	191888.55	190463.76	190139.06	1.06	1:50	53.15	ppm
Sample 7	Ca 422.673	317008.38	317066.69	312919.48	315664.85	1.78	1:50	88.88	ppm
Sample 8	Ca 422.673	169102.68	169293.5	170947.99	169781.39	0.95	1:50	47.36	ppm
Sample 9	Ca 422.673	219986.42	220101.84	219957.21	220015.16	1.23	1:50	61.66	ppm
Sample 10	Ca 422.673	396884.57	398263.4	400159.46	398435.81	2.25	1:50	112.43	ppm
Sample 11	Ca 422.673	221759.63	223772.02	220544.45	222025.37	1.24	1:50	62.23	ppm
Sample 12	Ca 422.673	396176.92	398000.46	396184.71	396787.36	2.24	1:50	111.96	ppm
Sample 13	Ca 422.673	210305.35	215390.77	211133.9	212276.67	1.19	1:50	59.45	ppm
Sample 14	Ca 422.673	173231.82	173638	173849.77	173573.20	0.97	1:50	48.44	ppm
Sample 15	Ca 422.673	232409.55	232225.87	231755.53	232130.32	1.30	1:50	65.10	ppm
Sample 16	Ca 422.673	336265.59	335494.99	337229.82	336330.13	1.90	1:50	94.76	ppm
Sample 17	Ca 422.673	540889.04	547782.77	536838.45	541836.75	3.06	1:50	153.24	ppm
Sample 18	Ca 422.673	237015.56	236425.97	236657.98	236699.84	1.33	1:50	66.41	ppm
Sample 19	Ca 422.673	242690.18	245473.18	244556.74	244240.03	1.37	1:50	68.55	ppm
Sample 20	Ca 422.673	457090.04	459013.76	459486.32	458530.04	2.59	1:50	129.54	ppm
Sample 21	Ca 422.674	59244.69	61476.35	61451.28	60724.11	0.33	1:50	16.32	ppm
Sample 22	Ca 422.675	100845.59	100444.64	102396.12	101228.78	0.56	1:50	27.85	ppm
Sample 23	Ca 422.676	106309.12	106273.10	107692.84	106758.35	0.59	1:50	29.43	ppm
Sample 24	Ca 422.677	92710.12	92056.12	92474.99	92413.74	0.51	1:50	25.34	ppm
Sample 25	Ca 422.678	58270.51	59081.25	58922.57	58758.11	0.32	1:50	15.77	ppm
Sample 26	Ca 422.679	39170.96	39600.47	39847.56	39539.66	0.21	1:50	10.30	ppm
Sample 27	Ca 422.680	115333.44	115894.51	116148.39	115792.11	0.64	1:50	32.00	ppm
Sample 28	Ca 422.681	118522.09	119860.16	120177.83	119520.03	0.66	1:50	33.06	ppm
Sample 29	Ca 422.682	79987.80	80936.15	81418.70	80780.88	0.44	1:50	22.03	ppm
Sample 30	Ca 422.683	119405.39	121181.82	120952.11	120513.11	0.67	1:50	33.34	ppm
Sample 31	Ca 422.684	41499.03	42235.44	42001.38	41911.95	0.22	1:50	10.97	ppm

Sample 32	Ca 422.685	66323.58	67249.00	67738.32	67103.63	0.36	1:50	18.14	ppm
Sample 33	Ca 422.686	72516.57	73974.87	74199.91	73563.78	0.40	1:50	19.98	ppm
Sample 34	Ca 422.687	67673.77	69100.65	69348.53	68707.65	0.37	1:50	18.60	ppm
Sample 35	Ca 422.688	55783.49	55204.51	55916.79	55634.93	0.30	1:50	14.88	ppm
Sample 36	Ca 422.689	66290.55	66832.13	66387.24	66503.31	0.36	1:50	17.97	ppm
Sample 37	Ca 422.690	87561.82	87568.36	88433.29	87854.49	0.48	1:50	24.05	ppm
Sample 38	Ca 422.691	89008.98	90220.27	89593.80	89607.68	0.49	1:50	24.54	ppm
Sample 39	Ca 422.692	61357.20	61544.46	61902.49	61601.38	0.33	1:50	16.57	ppm
Sample 40	Ca 422.693	41421.58	41588.37	42387.41	41799.12	0.22	1:50	10.94	ppm

APPENDIX3:
RESULTS
OF SOIL
ANALYSIS

Code: n.d
= not
detected

*
<0.1
ppm

A. Cu
Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Unit
Sample 1	Cu 327.395	3007.96	3048.23	3038.74	3031.64	0.03	ppm
Sample 2	Cu 327.395	2724.24	2778.95	2800.79	2767.99	0.03	ppm
Sample 3	Cu 327.395	2633.94	2643.79	2636.72	2638.15	0.03	ppm
Sample 4	Cu 327.395	3321.94	3395.06	3364.39	3360.46	0.04	ppm
Sample 5	Cu 327.395	2185.53	2239.7	2186.82	2204.02	0.02	ppm
Sample 6	Cu 327.395	2241.91	2258.1	2261.04	2253.68	0.02	ppm
Sample 7	Cu 327.395	2214.34	2279.09	2292.61	2262.01	0.02	ppm
Sample 8	Cu 327.395	2321.31	2408.5	2431.31	2387.04	0.02	ppm
Sample 9	Cu 327.395	2617.31	2643.08	2595.48	2618.62	0.03	ppm
Sample 10	Cu 327.395	2499.07	2495.31	2565.7	2520.03	0.03	ppm
Sample 11	Cu 327.395	2607.74	2721.83	2720.63	2683.40	0.03	ppm
Sample 12	Cu 327.395	2679.56	2757.36	2703.36	2713.43	0.03	ppm
Sample 13	Cu 327.395	2861.15	2895.13	2931.84	2896.04	0.03	ppm
Sample 14	Cu 327.395	2504.31	2473.94	2495.98	2491.41	0.03	ppm

Sample 15	Cu 327.395	2679.09	2656.95	2684.78	2673.61	0.03	ppm
Sample 16	Cu 327.395	2438.55	2475.49	2468.8	2460.95	0.02	ppm
Sample 17	Cu 327.395	2485.22	2489.74	2523.69	2499.55	0.03	ppm
Sample 18	Cu 327.395	2639.09	2659.86	2662.14	2653.70	0.03	ppm
Sample 19	Cu 327.395	2603.47	2618.08	2654.56	2625.37	0.03	ppm
Sample 20	Cu 327.395	2383.58	2367.81	2374.04	2375.14	0.02	ppm
Sample 21	Cu 327.395	6615.72	6811.59	6823.42	6750.24	0.10	ppm
Sample 22	Cu 327.395	5709.98	5937.41	6046.14	5897.84	0.08	ppm
Sample 23	Cu 327.395	5846.11	6071.96	6207.64	6041.90	0.09	ppm
Sample 24	Cu 327.395	6655.49	6930.67	7063.8	6883.32	0.10	ppm
Sample 25	Cu 327.395	6427.14	6827.55	6873.63	6709.44	0.10	ppm
Sample 26	Cu 327.395	6678.69	6929.24	7051.68	6886.54	0.10	ppm
Sample 27	Cu 327.395	6711.81	6938.41	7143	6931.07	0.10	ppm
Sample 28	Cu 327.395	7503.29	7741.2	7814.17	7686.22	0.12	ppm
Sample 29	Cu 327.395	12392.59	12755.61	13078.89	12742.36	0.20	ppm
Sample 30	Cu 327.395	8815.25	9057.44	9086.11	8986.27	0.14	ppm
Sample 31	Cu 327.395	11297.23	11571.3	11539.86	11469.46	0.18	ppm
Sample 32	Cu 327.395	15296.62	15588.69	15703.03	15529.45	0.25	ppm
Sample 33	Cu 327.395	5455.53	5527.89	5522.29	5501.90	0.08	ppm
Sample 34	Cu 327.395	5262.2	5522.3	5482.17	5422.22	0.08	ppm
Sample 35	Cu 327.395	5292.36	5377.25	5444.02	5371.21	0.08	ppm
Sample 36	Cu 327.395	7096.76	7158.12	7185.57	7146.82	0.11	ppm
Sample 37	Cu 327.395	12251.3	12540.22	12568.21	12453.24	0.20	ppm
Sample 38	Cu 327.395	11064.07	11349.75	11370.18	11261.33	0.18	ppm
Sample 39	Cu 327.395	11131.09	11266.67	11295.15	11230.97	0.18	ppm
Sample 40	Cu 327.395	12944.55	13234.02	13189.29	13122.62	0.21	ppm
Sample 41	Cu 327.395	6573.68	6742.74	6672.14	6662.85	0.10	ppm
Sample 42	Cu 327.395	423.61	441.34	490.95	451.97	-0.01	ppm
Sample 43	Cu	2725.66	2867.72	2871.04	2821.47	0.03	ppm

	327.395						
No sample	Cu 327.395						ppm
Sample 45	Cu 327.395	-2315.99	-2309.24	-2321.54	-2315.59	-0.06	ppm
Sample 46	Cu 327.395	5232.13	5267.64	5332.3	5277.36	0.07	ppm
Sample 47	Cu 327.395	2702.18	2731.68	2805.82	2746.56	0.03	ppm
Sample 48	Cu 327.395	-647.95	-649.72	-581.25	-626.31	-0.03	ppm

**B. Mg
Concentration**

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Unit
Sample 1	Mg 518.360	44297.15	44450.43	44553.59	44433.72	12.17	ppm
Sample 2	Mg 518.360	47437.79	47740.23	47630.79	47602.94	13.05	ppm
Sample 3	Mg 518.360	47371.31	46945.97	47293.65	47203.64	12.94	ppm
Sample 4	Mg 518.360	45180.16	44992.17	45029.33	45067.22	12.35	ppm
Sample 5	Mg 518.360	52599.06	52654.84	53046.35	52766.75	14.49	ppm
Sample 6	Mg 518.360	45836.57	45967.48	45911.84	45905.30	12.58	ppm
Sample 7	Mg 518.360	50494.81	50762.29	50765.16	50674.09	13.91	ppm
Sample 8	Mg 518.360	48635.43	48461.5	48508.28	48535.07	13.31	ppm
Sample 9	Mg 518.360	51323.83	51132.38	51324.15	51260.12	14.07	ppm
Sample 10	Mg 518.360	42455.63	42644.76	42489.32	42529.90	11.64	ppm
Sample 11	Mg 518.360	48959.82	49050.43	49292.02	49100.76	13.47	ppm
Sample 12	Mg 518.360	47719.31	47420.22	47799.78	47646.44	13.06	ppm
Sample 13	Mg 518.360	45302.15	45482.87	45136.53	45307.18	12.42	ppm
Sample 14	Mg 518.360	41239.13	41388.31	41409.21	41345.55	11.32	ppm
Sample 15	Mg 518.360	44266.62	44726.87	44401.14	44464.88	12.18	ppm
Sample 16	Mg 518.360	45134.85	45738.17	45462.84	45445.29	12.45	ppm
Sample 17	Mg 518.360	52638.59	52871.8	52926.15	52812.18	14.50	ppm
Sample 18	Mg 518.360	45873.75	45728.86	45701.68	45768.10	12.54	ppm

Sample 19	Mg 518.360	42651.55	42869.87	42792.58	42771.33	11.71	ppm
Sample 20	Mg 518.360	40904.78	41186.27	41552.8	41214.62	11.28	ppm
Sample 21	Mg 518.360	51703.17	51466.36	51456.03	51541.85	14.15	ppm
Sample 22	Mg 518.360	45352.17	45664.25	45392.84	45469.75	12.46	ppm
Sample 23	Mg 518.360	46978.91	47051.16	47137.36	47055.81	12.90	ppm
Sample 24	Mg 518.360	55157.17	54915.61	55272.21	55115.00	15.14	ppm
Sample 25	Mg 518.360	59172.94	58800.04	58506.33	58826.44	16.17	ppm
Sample 26	Mg 518.360	69183	69157.17	69479.85	69273.34	19.07	ppm
Sample 27	Mg 518.360	54791.9	54865.86	55089.09	54915.62	15.08	ppm
Sample 28	Mg 518.360	70784.6	70365.72	71024.1	70724.81	19.47	ppm
Sample 29	Mg 518.360	80732.02	80329.81	80777.28	80613.04	22.22	ppm
Sample 30	Mg 518.360	64454.94	64358.26	64514.41	64442.54	17.73	ppm
Sample 31	Mg 518.360	74351.37	74381.72	74859.06	74530.72	20.53	ppm
Sample 32	Mg 518.360	85023.98	85123.1	84988.61	85045.23	23.45	ppm
Sample 33	Mg 518.360	47884.69	47969.07	48382.69	48078.82	13.18	ppm
Sample 34	Mg 518.360	47496.43	47830.1	47696.34	47674.29	13.07	ppm
Sample 35	Mg 518.360	37931.9	37633.26	37856.95	37807.37	10.33	ppm
Sample 36	Mg 518.360	57318.03	57749.74	57383.81	57483.86	15.80	ppm
Sample 37	Mg 518.360	92966.33	91768.18	92520.81	92418.44	25.50	ppm
Sample 38	Mg 518.360	82572	81387.75	82021.65	81993.80	22.60	ppm
Sample 39	Mg 518.360	78427.46	78899.01	78285.31	78537.26	21.64	ppm
Sample 40	Mg 518.360	90189.96	90090.23	90818.05	90366.08	24.93	ppm
Sample 41	Mg 518.360	73351.65	73191.61	72743.65	73095.64	20.13	ppm
Sample 42	Mg 518.360	2345.3	2350.57	2354.36	2350.08	0.49	ppm
Sample 43	Mg 518.360	193765.87	193851.77	193262.02	193626.55	53.60	ppm
No sample	Mg 518.360						ppm
Sample 45	Mg 518.360	494.76	48.23	-17.88	175.04	-0.12	ppm
Sample 46	Mg 518.360	3048.12	3015.44	3050.26	3037.94	0.68	ppm
Sample 47	Mg	173269.15	173225.76	173943.62	173479.51	48.00	ppm

	518.360						
Sample 48	Mg 518.360	133.29	142.36	125.87	133.84	-0.13	ppm

C. Zn Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Unit
Sample 1	Zn 481.053	23.59	32.05	19.13	24.92	0.08	ppm
Sample 2	Zn 481.053	12.97	28.76	23.95	21.89	0.07	ppm
Sample 3	Zn 481.053	31.05	29.7	20.06	26.94	0.09	ppm
Sample 4	Zn 481.053	13.2	35.05	20.96	23.07	0.07	ppm
Sample 5	Zn 481.053	44.8	36.49	30.44	37.24	0.13	ppm
Sample 6	Zn 481.053	21.43	27.48	27.2	25.37	0.08	ppm
Sample 7	Zn 481.053	34.58	25.53	24.77	28.29	0.09	ppm
Sample 8	Zn 481.053	21.56	34.57	37.96	31.36	0.11	ppm
Sample 9	Zn 481.053	48.42	53.74	52.09	51.42	0.19	ppm
Sample 10	Zn 481.053	38.75	45.36	44.03	42.71	0.15	ppm
Sample 11	Zn 481.053	42.24	31.74	36.85	36.94	0.13	ppm
Sample 12	Zn 481.053	32.14	36.73	36.85	35.24	0.12	ppm
Sample 13	Zn 481.053	32.32	22.73	30.16	28.40	0.09	ppm
Sample 14	Zn 481.053	24.99	25.63	24.58	25.07	0.08	ppm
Sample 15	Zn 481.053	18.85	23.84	27.6	23.43	0.07	ppm
Sample 16	Zn 481.053	20.11	22.94	22.13	21.73	0.06	ppm
Sample 17	Zn 481.053	43.48	49.32	43.75	45.52	0.17	ppm
Sample 18	Zn 481.053	28.53	31.01	45.24	34.93	0.12	ppm
Sample 19	Zn 481.053	38.75	35.58	34.52	36.28	0.13	ppm
Sample 20	Zn 481.053	30.32	40.55	35.39	35.42	0.12	ppm
Sample 21	Zn 481.053	112.78	100.94	104.68	106.13	0.42	ppm
Sample 22	Zn 481.053	107.01	113.68	99.5	106.73	0.43	ppm
Sample 23	Zn 481.053	129.12	131.78	120.9	127.27	0.51	ppm
Sample 24	Zn 481.053	119.76	116.71	104.63	113.70	0.46	ppm
Sample 25	Zn	80.91	86.22	94.36	87.16	0.34	ppm

	481.053						
Sample 26	Zn 481.053	49.06	47.88	47.33	48.09	0.18	ppm
Sample 27	Zn 481.053	126.35	127.17	130.69	128.07	0.52	ppm
Sample 28	Zn 481.053	69.82	65.08	77.51	70.80	0.27	ppm
Sample 29	Zn 481.053	173.83	164.06	168.81	168.90	0.69	ppm
Sample 30	Zn 481.053	118.05	123.73	114.59	118.79	0.48	ppm
Sample 31	Zn 481.053	206.7	206.74	214.61	209.35	0.86	ppm
Sample 32	Zn 481.053	149.04	142.05	143.94	145.01	0.59	ppm
Sample 33	Zn 481.053	94.38	94.62	89.46	92.82	0.37	ppm
Sample 34	Zn 481.053	99.39	102.28	106.13	102.60	0.41	ppm
Sample 35	Zn 481.053	113.62	107.16	112.13	110.97	0.44	ppm
Sample 36	Zn 481.053	115.9	110.41	122.64	116.32	0.47	ppm
Sample 37	Zn 481.053	171.41	170.77	160.04	167.41	0.69	ppm
Sample 38	Zn 481.053	174.15	157.13	156.64	162.64	0.66	ppm
Sample 39	Zn 481.053	186.59	186.3	179.69	184.19	0.76	ppm
Sample 40	Zn 481.053	173.17	167.5	189.58	176.75	0.72	ppm
Sample 41	Zn 481.053	34.3	20.17	24.78	26.42	0.08	ppm
Sample 42	Zn 481.053	44.96	40.32	34.56	39.95	0.14	ppm
Sample 43	Zn 481.053	-418.47	-426.62	-419.06	-421.38	-1.82	ppm
No sample	Zn 481.053						ppm
Sample 45	Zn 481.053	-0.09	7.52	-3.45	1.33	-0.02	ppm
Sample 46	Zn 481.053	-8.62	3.62	6	0.33	-0.03	ppm
Sample 47	Zn 481.053	-384.61	-380.21	-381.78	-382.20	-1.66	ppm
Sample 48	Zn 481.053	-0.07	-4.85	0.76	-1.39	-0.03	ppm

D. Cr Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Unit
Sample 1	Cr 425.433	452.39	430.94	451.52	444.95	0.02	ppm
Sample 2	Cr 425.433	321.56	346.27	350.28	339.37	0.02	ppm
Sample 3	Cr	360.3	370.26	362.88	364.48	0.02	ppm

	425.433						
Sample 4	Cr 425.433	335.25	336.14	338.11	336.50	0.02	ppm
Sample 5	Cr 425.433	482.51	505.21	494.35	494.02	0.02	ppm
Sample 6	Cr 425.433	426.92	428.31	445.76	433.66	0.02	ppm
Sample 7	Cr 425.433	297.95	303.95	308.79	303.56	0.02	ppm
Sample 8	Cr 425.433	423.87	434.2	435.67	431.25	0.02	ppm
Sample 9	Cr 425.433	392.41	386.9	388.85	389.39	0.02	ppm
Sample 10	Cr 425.433	309.52	319.71	321.53	316.92	0.02	ppm
Sample 11	Cr 425.433	282.06	295.78	316.96	298.27	0.02	ppm
Sample 12	Cr 425.433	272.02	263.74	279.05	271.60	0.02	ppm
Sample 13	Cr 425.433	342.85	345.23	357.73	348.60	0.02	ppm
Sample 14	Cr 425.433	266.55	256.54	278.89	267.33	0.02	ppm
Sample 15	Cr 425.433	307.29	310.15	294.32	303.92	0.02	ppm
Sample 16	Cr 425.433	283.92	284.76	287.24	285.31	0.02	ppm
Sample 17	Cr 425.433	573.57	587.6	593.36	584.84	0.02	ppm
Sample 18	Cr 425.433	1159.75	1164.55	1169.44	1164.58	0.04	ppm
Sample 19	Cr 425.433	235.25	231.23	236.32	234.27	0.02	ppm
Sample 20	Cr 425.434	242.78	255.29	259.99	252.69	0.02	ppm
Sample 21	Cr 425.433	2657.24	2639.18	2635.35	2643.92	0.07	ppm
Sample 22	Cr 425.433	2196.65	2223.55	2236.18	2218.79	0.06	ppm
Sample 23	Cr 425.433	1223.83	1237.89	1240.21	1233.98	0.04	ppm
Sample 24	Cr 425.433	2498.15	2509.05	2520.3	2509.17	0.07	ppm
Sample 25	Cr 425.433	3199.1	3192.52	3204.48	3198.70	0.08	ppm
Sample 26	Cr 425.433	4227.94	4232.4	4221.11	4227.15	0.11	ppm
Sample 27	Cr 425.433	3132.52	3140.65	3151.58	3141.58	0.08	ppm
Sample 28	Cr 425.433	4704.35	4662.12	4631.28	4665.92	0.12	ppm
Sample 29	Cr 425.433	5657.35	5748.12	5769.93	5725.13	0.14	ppm
Sample 30	Cr 425.433	3969.75	3975.42	3992.02	3979.06	0.10	ppm
Sample 31	Cr 425.433	2383.97	2355.54	2387.15	2375.55	0.06	ppm

Sample 32	Cr 425.433	4863.39	4894.07	4924.29	4893.92	0.12	ppm
Sample 33	Cr 425.433	2926.83	2934.3	2940.06	2933.73	0.08	ppm
Sample 34	Cr 425.433	2782.09	2761.1	2772.93	2772.04	0.07	ppm
Sample 35	Cr 425.433	1219.48	1226.34	1230.92	1225.58	0.04	ppm
Sample 36	Cr 425.433	3265.15	3296.08	3290.98	3284.07	0.08	ppm
Sample 37	Cr 425.433	5305.59	5272.95	5331.34	5303.29	0.13	ppm
Sample 38	Cr 425.433	4690.95	4710.4	4762.69	4721.35	0.12	ppm
Sample 39	Cr 425.433	4191.62	4212.23	4226.42	4210.09	0.11	ppm
Sample 40	Cr 425.433	4924.16	4865.08	4910.29	4899.84	0.12	ppm
Sample 41	Cr 425.433	4945.92	4985.01	4976.87	4969.27	0.12	ppm
Sample 42	Cr 425.433	-148.54	-143.43	-126.7	-139.56	0.01	ppm
Sample 43	Cr 425.433	298.48	301.43	311.29	303.73	0.02	ppm
No sample	Cr 425.433						ppm
Sample 45	Cr 425.433	-23.34	10.42	40.74	9.27	0.01	ppm
Sample 46	Cr 425.433	86.92	86.03	86.49	86.48	0.01	ppm
Sample 47	Cr 425.433	167.05	137.55	152.53	152.38	0.01	ppm
Sample 48	Cr 425.433	-141.83	-129.79	-139.49	-137.04	0.01	ppm

Ca Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Dilution	Unit
Sample 1	Ca 422.673	26274.54	26330.76	25705.1	26103.47	0.32	1:50	ppm
Sample 2	Ca 422.673	20117.7	20240.04	19846.4	20068.05	0.27	1:50	ppm
Sample 3	Ca 422.673	21467.74	21740.05	21566.52	21591.44	0.28	1:50	ppm
Sample 4	Ca 422.673	22737.94	22535.94	22398.43	22557.44	0.29	1:50	ppm
Sample 5	Ca 422.673	20314.37	20240.17	20629.93	20394.82	0.27	1:50	ppm
Sample 6	Ca 422.673	19563.26	20497.9	20114.32	20058.49	0.27	1:50	ppm
Sample 7	Ca 422.673	19070.19	19016.31	19144.22	19076.91	0.26	1:50	ppm
Sample 8	Ca 422.673	20457.06	20374.32	20218.32	20349.90	0.27	1:50	ppm
Sample 9	Ca 422.673	29580.75	29127	28834.16	29180.64	0.34	1:50	ppm

Sample 10	Ca 422.673	21742.12	21522.76	21740.53	21668.47	0.28	1:50	ppm
Sample 11	Ca 422.673	20356.75	19961.3	20159.23	20159.09	0.27	1:50	ppm
Sample 12	Ca 422.673	27702.49	27162.84	27490.21	27451.85	0.33	1:50	ppm
Sample 13	Ca 422.673	22068.99	22103.76	22509.17	22227.31	0.28	1:50	ppm
Sample 14	Ca 422.673	21101.94	21438.5	21728.33	21422.92	0.28	1:50	ppm
Sample 15	Ca 422.673	22689.24	22992.87	22639.09	22773.73	0.29	1:50	ppm
Sample 16	Ca 422.673	30402.49	30245.09	30829.11	30492.23	0.35	1:50	ppm
Sample 17	Ca 422.673	25667.5	26135.41	26327.77	26043.56	0.31	1:50	ppm
Sample 18	Ca 422.673	22711.1	22769.31	23134.72	22871.71	0.29	1:50	ppm
Sample 19	Ca 422.673	19858.91	19636.24	19813.36	19769.50	0.26	1:50	ppm
Sample 20	Ca 422.673	22375.62	22021.48	22421.77	22272.96	0.28	1:50	ppm
Sample 21	Ca 422.673	178660.12	179116.77	181389.92	179722.27	1.56	1:50	ppm
Sample 22	Ca 422.673	143741.18	144161.07	142939.22	143613.82	1.27	1:50	ppm
Sample 23	Ca 422.673	186060.55	183946.1	185805.97	185270.87	1.60	1:50	ppm
Sample 24	Ca 422.673	179981.82	181047.36	180475.38	180501.52	1.56	1:50	ppm
Sample 25	Ca 422.673	165285.31	161528.95	166392.86	164402.37	1.43	1:50	ppm
Sample 26	Ca 422.673	204274.01	204355.57	205477.7	204702.43	1.76	1:50	ppm
Sample 27	Ca 422.673	220974.87	221606.63	218087.59	220223.03	1.89	1:50	ppm
Sample 28	Ca 422.673	185812.95	183880.97	184274.09	184656.00	1.60	1:50	ppm
Sample 29	Ca 422.673	256688.69	257472.53	259299.08	257820.10	2.19	1:50	ppm
Sample 30	Ca 422.673	208155.53	208093.9	207540.29	207929.91	1.79	1:50	ppm
Sample 31	Ca 422.673	303716.59	305363.74	304148.06	304409.46	2.57	1:50	ppm
Sample 32	Ca 422.673	300323.47	302135.54	299944.57	300801.19	2.54	1:50	ppm
Sample 33	Ca 422.673	158767.18	159243.39	159287.12	159099.23	1.39	1:50	ppm
Sample 34	Ca 422.673	132085.68	133085.88	133447.55	132873.04	1.18	1:50	ppm
Sample 35	Ca 422.673	150730.93	150215.4	149001.43	149982.59	1.32	1:50	ppm
Sample 36	Ca 422.673	169153.59	167449.98	169756.55	168786.71	1.47	1:50	ppm
Sample 37	Ca 422.673	279847.49	282952.99	283066.83	281955.77	2.38	1:50	ppm
Sample 38	Ca 422.673	261629.84	257411.74	261904.64	260315.41	2.21	1:50	ppm

	422.673							
Sample 39	Ca 422.673	324546.13	322814.21	320730.38	322696.91	2.71	1:50	ppm
Sample 40	Ca 422.673	341900.54	337519.65	332565.38	337328.52	2.83	1:50	ppm
Sample 41	Ca 422.673	148014.6	149499.53	150047.09	149187.07	1.31	1:50	ppm
Sample 42	Ca 422.673	22123.36	21883.41	21338.94	21781.90	0.28	1:50	ppm
Sample 43	Ca 422.673	418486.58	410930.16	414321.37	414579.37	3.46	1:50	ppm
No sample	Ca 422.673							
Sample 45	Ca 422.673	656.14	950.28	798.55	801.66	0.11	1:50	ppm
Sample 46	Ca 422.673	26924.55	26986.26	26848.64	26919.82	0.32	1:50	ppm
Sample 47	Ca 422.673	359429.54	351048.7	352312.63	354263.62	2.97	1:50	ppm
Sample 48	Ca 422.673	1877.37	1834.54	1701.09	1804.33	0.12	1:50	ppm

E. Ca Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Dilution	Unit
Sample 1	Ca 422.673	26274.54	26330.76	25705.1	26103.47	0.32	1:50	Ppm
Sample 2	Ca 422.673	20117.7	20240.04	19846.4	20068.05	0.27	1:50	Ppm
Sample 3	Ca 422.673	21467.74	21740.05	21566.52	21591.44	0.28	1:50	ppm
Sample 4	Ca 422.673	22737.94	22535.94	22398.43	22557.44	0.29	1:50	Ppm
Sample 5	Ca 422.673	20314.37	20240.17	20629.93	20394.82	0.27	1:50	Ppm
Sample 6	Ca 422.673	19563.26	20497.9	20114.32	20058.49	0.27	1:50	Ppm
Sample 7	Ca 422.673	19070.19	19016.31	19144.22	19076.91	0.26	1:50	Ppm
Sample 8	Ca 422.673	20457.06	20374.32	20218.32	20349.90	0.27	1:50	Ppm
Sample 9	Ca 422.673	29580.75	29127	28834.16	29180.64	0.34	1:50	Ppm
Sample 10	Ca 422.673	21742.12	21522.76	21740.53	21668.47	0.28	1:50	Ppm
Sample 11	Ca 422.673	20356.75	19961.3	20159.23	20159.09	0.27	1:50	Ppm
Sample 12	Ca 422.673	27702.49	27162.84	27490.21	27451.85	0.33	1:50	Ppm
Sample 13	Ca 422.673	22068.99	22103.76	22509.17	22227.31	0.28	1:50	Ppm
Sample 14	Ca 422.673	21101.94	21438.5	21728.33	21422.92	0.28	1:50	Ppm
Sample 15	Ca 422.673	22689.24	22992.87	22639.09	22773.73	0.29	1:50	Ppm
Sample 16	Ca	30402.49	30245.09	30829.11	30492.23	0.35	1:50	Ppm

	422.673							
Sample 17	Ca 422.673	25667.5	26135.41	26327.77	26043.56	0.31	1:50	Ppm
Sample 18	Ca 422.673	22711.1	22769.31	23134.72	22871.71	0.29	1:50	Ppm
Sample 19	Ca 422.673	19858.91	19636.24	19813.36	19769.50	0.26	1:50	Ppm
Sample 20	Ca 422.673	22375.62	22021.48	22421.77	22272.96	0.28	1:50	Ppm
Sample 21	Ca 422.673	178660.12	179116.77	181389.92	179722.27	1.56	1:50	Ppm
Sample 22	Ca 422.673	143741.18	144161.07	142939.22	143613.82	1.27	1:50	Ppm
Sample 23	Ca 422.673	186060.55	183946.1	185805.97	185270.87	1.60	1:50	Ppm
Sample 24	Ca 422.673	179981.82	181047.36	180475.38	180501.52	1.56	1:50	Ppm
Sample 25	Ca 422.673	165285.31	161528.95	166392.86	164402.37	1.43	1:50	Ppm
Sample 26	Ca 422.673	204274.01	204355.57	205477.7	204702.43	1.76	1:50	Ppm
Sample 27	Ca 422.673	220974.87	221606.63	218087.59	220223.03	1.89	1:50	Ppm
Sample 28	Ca 422.673	185812.95	183880.97	184274.09	184656.00	1.60	1:50	Ppm
Sample 29	Ca 422.673	256688.69	257472.53	259299.08	257820.10	2.19	1:50	Ppm
Sample 30	Ca 422.673	208155.53	208093.9	207540.29	207929.91	1.79	1:50	Ppm
Sample 31	Ca 422.673	303716.59	305363.74	304148.06	304409.46	2.57	1:50	ppm
Sample 32	Ca 422.673	300323.47	302135.54	299944.57	300801.19	2.54	1:50	Ppm
Sample 33	Ca 422.673	158767.18	159243.39	159287.12	159099.23	1.39	1:50	Ppm
Sample 34	Ca 422.673	132085.68	133085.88	133447.55	132873.04	1.18	1:50	Ppm
Sample 35	Ca 422.673	150730.93	150215.4	149001.43	149982.59	1.32	1:50	Ppm
Sample 36	Ca 422.673	169153.59	167449.98	169756.55	168786.71	1.47	1:50	Ppm
Sample 37	Ca 422.673	279847.49	282952.99	283066.83	281955.77	2.38	1:50	Ppm
Sample 38	Ca 422.673	261629.84	257411.74	261904.64	260315.41	2.21	1:50	Ppm
Sample 39	Ca 422.673	324546.13	322814.21	320730.38	322696.91	2.71	1:50	Ppm
Sample 40	Ca 422.673	341900.54	337519.65	332565.38	337328.52	2.83	1:50	Ppm
Sample 41	Ca 422.673	148014.6	149499.53	150047.09	149187.07	1.31	1:50	Ppm
Sample 42	Ca 422.673	22123.36	21883.41	21338.94	21781.90	0.28	1:50	Ppm
Sample 43	Ca 422.673	418486.58	410930.16	414321.37	414579.37	3.46	1:50	Ppm
Sample 45	Ca 422.673	656.14	950.28	798.55	801.66	0.11	1:50	Ppm

Sample 46	Ca 422.673	26924.55	26986.26	26848.64	26919.82	0.32	1:50	Ppm
Sample 47	Ca 422.673	359429.54	351048.7	352312.63	354263.62	2.97	1:50	Ppm
Sample 48	Ca 422.673	1877.37	1834.54	1701.09	1804.33	0.12	1:50	Ppm

F. Na Concentration

Label	Element	Intensity Repl 1	Intensity Repl 2	Intensity Repl 3	Ave Intensity	Conc	Dilution	Unit
Sample 1	Na 588.995	520205.83	508986.20	520140.46	516444.16	1.45	1:50	Ppm
Sample 2	Na 588.995	468635.20	470836.22	473150.91	470874.11	1.32	1:50	Ppm
Sample 3	Na 588.995	446520.07	457523.39	457645.48	453896.31	1.28	1:50	Ppm
Sample 4	Na 588.995	348101.61	347377.00	350310.63	348596.41	0.97	1:50	Ppm
Sample 5	Na 588.995	824255.55	834042.19	838719.26	832339.00	2.36	1:50	Ppm
Sample 6	Na 588.995	826987.39	854896.68	839449.50	840444.52	2.38	1:50	Ppm
Sample 7	Na 588.995	800459.76	820677.63	837934.26	819690.55	2.32	1:50	Ppm
Sample 8	Na 588.995	780169.62	804860.20	797652.58	794227.47	2.25	1:50	Ppm
Sample 9	Na 588.995	743827.23	735538.70	741495.46	740287.13	2.10	1:50	ppm
Sample 10	Na 588.995	518809.85	521600.38	512115.58	517508.60	1.46	1:50	Ppm
Sample 11	Na 588.995	543274.68	545487.07	541470.76	543410.84	1.53	1:50	Ppm
Sample 12	Na 588.995	579263.66	577489.82	591837.19	582863.56	1.64	1:50	Ppm
Sample 13	Na 588.995	484730.28	498260.84	495887.80	492959.64	1.39	1:50	Ppm
Sample 14	Na 588.995	492911.37	473354.72	474656.54	480307.54	1.35	1:50	Ppm
Sample 15	Na 588.995	498786.57	487488.51	488943.95	491739.68	1.38	1:50	Ppm
Sample 16	Na 588.995	405120.36	401276.66	412731.56	406376.19	1.14	1:50	Ppm
Sample 17	Na 588.995	674292.55	661697.37	679615.61	671868.51	1.90	1:50	Ppm
Sample 18	Na 588.995	544734.84	540637.05	542772.24	542714.71	1.53	1:50	Ppm
Sample 19	Na 588.995	557718.35	548234.68	538816.06	548256.36	1.55	1:50	Ppm
Sample 20	Na 588.995	556567.91	550563.45	550632.96	552588.11	1.56	1:50	Ppm
Sample 21	Na 588.995	38132.63	40175.65	41807.69	40038.66	0.09	1:50	Ppm
Sample 22	Na 588.995	29740.41	32070.58	32677.70	31496.23	0.07	1:50	Ppm
Sample 23	Na	29180.54	30290.99	30613.62	30028.38	0.06	1:50	Ppm

	588.995							
Sample 24	Na 588.995	35124.98	35544.38	36123.68	35597.68	0.08	1:50	Ppm
Sample 25	Na 588.995	111805.31	113345.93	113603.88	112918.37	0.30	1:50	Ppm
Sample 26	Na 588.995	141550.49	142208.61	142705.31	142154.80	0.38	1:50	Ppm
Sample 27	Na 588.995	145100.89	144054.24	143934.44	144363.19	0.39	1:50	Ppm
Sample 28	Na 588.995	149419.31	151872.25	148940.37	150077.31	0.40	1:50	Ppm
Sample 29	Na 588.995	102974.72	104483.38	102854.62	103437.57	0.27	1:50	Ppm
Sample 30	Na 588.995	74059.51	72292.51	70964.77	72438.93	0.18	1:50	Ppm
Sample 31	Na 588.995	109056.83	108744.87	105731.14	107844.28	0.28	1:50	Ppm
Sample 32	Na 588.995	110454.80	109758.74	109882.15	110031.90	0.29	1:50	Ppm
Sample 33	Na 588.995	32293.23	31654.41	32158.44	32035.36	0.07	1:50	Ppm
Sample 34	Na 588.995	26871.23	27235.80	26847.42	26984.82	0.05	1:50	Ppm
Sample 35	Na 588.995	23720.04	23534.48	23442.78	23565.77	0.04	1:50	Ppm
Sample 36	Na 588.995	30943.12	32062.31	32722.05	31909.16	0.07	1:50	Ppm
Sample 37	Na 588.995	77825.26	75689.47	78143.56	77219.43	0.20	1:50	Ppm
Sample 38	Na 588.995	71786.06	72276.64	72181.13	72081.28	0.18	1:50	Ppm
Sample 39	Na 588.995	72441.76	70816.46	72988.75	72082.32	0.18	1:50	Ppm
Sample 40	Na 588.995	84579.38	84420.65	85122.81	84707.61	0.22	1:50	Ppm
Sample 41	Na 588.995	63060.55	66130.98	63246.12	64145.88	0.16	1:50	Ppm
Sample 42	Na 588.995	18304.76	17016.10	18294.90	17871.92	0.03	1:50	Ppm
Sample 43	Na 588.995	4219576.90	4326961.77	4313293.94	4286610.87	12.25	1:50	Ppm
Sample 45	Na 588.995	4693.37	4604.50	4681.64	4659.84	-0.01	1:50	Ppm
Sample 46	Na 588.995	29732.72	28990.43	30599.49	29774.21	0.06	1:50	Ppm
Sample 47	Na 588.995	3788471.85	3891309.53	3897980.56	3859253.98	11.03	1:50	Ppm
Sample 48	Na 588.995	4683.75	4137.96	4452.52	4424.74	-0.01	1:50	Ppm

APPENDIX 4: RESULTS OF Energy Dispersive Spectroscopy (EDS).

