

**Nutrient Leaching from Switchgrass for Biofuel: Effects of Extraction  
Concentration, Temperature and Solvent**

by

**Chad Henderson**

**A Thesis  
presented to  
The University of Guelph**

**In partial fulfilment of requirements  
for the degree of  
Master of Science  
in  
Environmental Science**

**Guelph, Ontario, Canada**

**© Chad Henderson, September, 2015**

## ABSTRACT

### **LEACHING NUTRIENTS FROM SWITCHGRASS FOR BIOFUEL: EFFECTS OF EXTRACTION CONCENTRATION, TEMPERATURE AND SOLVENT**

Chad Henderson  
University of Guelph, 2015

Co-Advisors:  
Dr. Andy Gordon  
Dr. Timothy Rennie

The amount of nutrients in biomass will affect combustion efficiency. Homogenized samples of spring harvested switchgrass cv. Cave-in-Rock were ground to 1 mm, treated at varied switchgrass concentrations (25, 50, 75 and 100 g/L), temperatures (20, 40 and 60 °C) and initial mineral concentrations in several water solvents (distilled, tap and well water). After solvent removal, percent weights of nitrogen, calcium, phosphorus, potassium, magnesium, sulphur and chlorine in the switchgrass were analysed. Switchgrass concentration of 100 g/L reduced phosphorus leaching by 46 % and potassium by 54 % compared to 25 g/L. Higher temperature had a significant effect on the amount of potassium and sulphur that could be removed. Solvent type had a significant effect on leaching for calcium, phosphorus, potassium, magnesium, chloride and sulphur, but the best water type for leaching varied. Spring harvested switchgrass of this cultivar does not need to be further leached to meet combustion standards.

## **Acknowledgements**

I would like to thank all of the following for their contribution to my thesis:

Co-Advisor Dr. Andy Gordon for sharing his experience and being a voice of intellect and reason at critical times during my M.Sc. research;

Co-Advisor Dr. Timothy Rennie for introducing me to the research subject, giving me the opportunity to research with him at the Kemptville campus and providing knowledge, support and direction throughout the process;

Committee member Dr. Ashraf Tubeileh for being there throughout the process with helpful questions, insights, ideas and support to make the research a success;

Dr. Stephen Bowley for statistical guidance;

The staff at Kemptville campus for all their help and support in providing research facility and residence for my research;

And to all my family and friends which helped out immeasurably along the way.

## Table of Contents

Abstract.....	ii
Acknowledgements.....	iii
Table of Contents.....	iv
List of Tables.....	vii
List of Figures.....	x
Chapter 1- Introduction and Literature Review.....	1
1.1 Introduction.....	1
1.2 Nutrient Requirements of Bioenergy Crops.....	4
1.3 Typical Nutrient Content in Harvested Biomass and the Factors which Affect Nutrient Content.....	8
1.4 Issues with Nutrient Content in Biomass for Direct Combustion.....	10
1.5 Agronomy and harvesting Methods for Switchgrass.....	12
1.6 Effects of Harvesting Management on Nutrient Content and Yield.....	16
1.7 Effects of Weathering on Nutrient Content after Harvest and Current Knowledge of Nutrient Losses in Field Weathering.....	20
1.8 Research Opportunities to Advance Nutrient Cycling.....	23
1.9 Current Area of Research.....	25
Chapter 2 - Hypotheses and Objectives.....	27
Chapter 3 - Materials and Methods.....	28
3.1 Concentration.....	28
3.2 Temperature.....	29
3.3 Water type.....	30

Chapter 4 - Results.....	32
4.1 Concentration.....	32
4.2 Temperature.....	41
4.3 Water Type.....	52
Chapter 5 - Discussion.....	63
5.1 Concentration.....	63
5.2 Temperature.....	67
5.3 Water Type.....	71
Chapter 6 - Conclusions.....	75
Literature Cited.....	79
Appendix 1 - Percent weight of elements remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.....	86
Appendix 2 - Percent weight of elements remaining in switchgrass samples in a two factor RCBD (n=3) experiment with 4 leaching times (5, 10, 20 and 40 minutes) and 3 leaching temperatures (20, 40 and 60 °C) at 25 g switchgrass/L water.....	87
Appendix 3 - Percent weight of elements remaining in switchgrass samples in a 2 factor RCBD (n=3) experiment with 4 leaching times (5, 10, 20 and 40 minutes) and 4 water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.....	89
Appendix 4 - Statistics tables for Chapter 4.....	92

## Appendix 5 - Elemental concentrations of solvent used for water

type experiments (Distilled water, Ottawa tap water, Kemptville tap water and Well water from Carp, Ontario).....	119
--	-----

## List of Tables

Table 1.1 - Percent contribution of oxides to ash formation from switchgrass combustion (From Jenkins et al., 1996).....	11
Table 1.2 - Ash, N, K and Cl percentages in wood pellets, wheat straw and switchgrass (From Stamler, 2009).....	18
Table 4.1.1 - Means comparison of percent weight of N remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD n=3).....	33
Table 4.1.2 - Means comparison of percent weight of Ca remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).....	34
Table 4.1.3 - Means comparison of percent weight of P remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).....	35
Table 4.1.4 - Means comparison of percent weight of K remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).....	36
Table 4.1.5 - Means comparison of percent weight of Mg remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).....	37
Table 4.1.6 - Means comparison of percent weight of S remaining in switchgrass samples after leaching treatment at four concentrations of	

biomass/distilled water for 40 minutes, RCBD (n=3).....	38
Table 4.1.7 - Means comparison of percent weight of Cl remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).....	39
Table 4.1.8 - Means comparison of the sum of the percent weights of N, Ca, P, K, Mg, S and Cl remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).....	40
Table 4.3.1 - Means comparisons for the percent weight of N remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	53
Table 4.3.2 - Means comparisons for the percent weight of Ca remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	54
Table 4.3.3 - Means comparisons for the percent weight of P remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	56
Table 4.3.4 - Means comparisons for the percent weight of K remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	58
Table 4.3.5 - Means comparisons for the percent weight of Mg remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	59

Table 4.3.6 - Means comparisons for the percent weight of S remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	61
Table 4.3.7 - Means comparisons for the percent weight of Cl remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	62

## List of Figures

Figure 1.1 - Natural jurisdictional range of switchgrass in North America (USDA 2009).....	13
Figure 1.2 - Two upland varieties of switchgrass, Dacotah (left) and Sunburst (right), mature at different times of year (USDA 2009).....	14
Figure 4.2.1 - Least square means for percent weight N remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.....	42
Figure 4.2.2 - Least square means for percent weight Ca remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.....	43
Figure 4.2.3 - Least square means for percent weight P remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.....	44
Figure 4.2.4 - Least square means for percent weight K remaining in a switchgrass sample after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.....	45
Figure 4.2.5 -Surface plot of time versus temperature for the amount of K remaining in switchgrass samples over four times (5, 10, 20 and 40 minutes) and three temperatures (20, 40, 60 °C) RCBD, n=3, 25 g switchgrass/L distilled water.....	46

- Figure 4.2.6 - Means and linear regression for the response of percent weight K in switchgrass compared to temperature of leaching solution in RCBD experiment (n=3) with three temperatures (20, 40, and 60 °), averaged over four times (5, 10, 20 and 40 minutes) at 25 g switchgrass/L distilled water.....47
- Figure 4.2.7 - Least square means for percent weight Mg remaining in a switchgrass sample after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.....48
- Figure 4.2.8 - Least square means for percent weight S remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.....49
- Figure 4.2.9 - Means and linear regression for the response of percent weight S in switchgrass compared to temperature of leaching solution in RCBD experiment (n=3) with four times (5, 10, 20 and 40 minutes) and three temperatures (20, 40 and 60°C) at 25 g switchgrass/L distilled water.....49
- Figure 4.2.10 - Least square means for percent weight Cl remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.....50
- Figure 4.2.11 – Conductivity of leachate samples from RCBD experiment (n=3) with four residence times (5, 10, 20 and 40 minutes) and three temperatures (20, 40 and 60°C) at 25 g switchgrass/L of distilled water.....51

Figure 4.2.12 - Means and regression for the linear response for conductivity compared to temperature of leaching solution in RCBD experiment with four times and three temperatures at 25 g switchgrass/L distilled water (n=3).....	52
Figure 4.3.1 - Least square means for percent weight N remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	53
Figure 4.3.2 - Least square means for percent weight Ca remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	54
Figure 4.3.3 - Least square means for percent weight P remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	56
Figure 4.3.4 - Least square means for percent weight K remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	57
Figure 4.3.5 - Least square means for percent weight Mg remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	59
Figure 4.3.6 - Least square means for percent weight Ca remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).....	60
Figure 4.3.7 - Least square means for percent weight Cl remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four	

residence times, RCBD (n=3).....62

## 1.1 - Introduction

It is now considered to be extremely likely that climate change is being forced by human activities, especially the burning of fossil fuels for energy (Keeling et al. 1989; Ma et al. 2001; Lal 2004; IPCC 2013). The consequences of climate change are far ranging and difficult to quantify, but associated costs are likely to be considerable. The United States Natural Resource Defense Council estimates that at current trends, climate change will cost the US 3.8 trillion of today's dollars, per year, by the year 2100 (NRDC 2008). Climate change reduction strategies might seem costly, but doing nothing will undoubtedly be far more costly. It is imperative that steps are taken to limit the release of climate forcing pollution and help to alleviate the future cost of climate change. This will mean a step away from fossil fuel consumption and a step towards cleaner technology.

There is evidence that the discovery of new fossil fuel reserves and potential for production has already peaked, whereas global consumption continues to rise (Murphy and Hall 2011; Miller and Sorrell 2013). Chapman (2014) gives estimates for the peak of global oil production ranging from 2005 – 2035, based on various sources. Discovery of large basins of conventional oil peaked in the 1960's, forcing oil producers to move towards non-conventional oil sources with lower energy returns, such as tar sands and deep ocean wells (Chapman 2014). Most recently, however, there appears to be a surplus of oil. The price of oil dropped to around \$48 per barrel by January 2015, a six year low, due to projected surplus and stagnant oil demand growth globally (IEA 2015). Estimates for global demand growth for 2015 have since been raised considerably, and the price of oil increased 30 % between January and March 2015 (IEA 2015). The oil market is clearly volatile and hard to predict. Further, although cheap oil

alleviates stress on consumers in the short term, reliance on cheap oil hinders development towards cleaner alternatives and erodes dedication to climate change reduction strategies. If the impact of climate change is to be minimized, there needs to be a commitment to clean technology regardless of fossil fuel prices.

The options to reduce greenhouse gas emissions and to capture carbon are diverse, and many alternative energy sources such as wind, solar and biofuel are in use to various extents around the world while their efficiency continually improves. Farming crops for use as biofuel, to replace fossil fuels and contribute to a net reduction in CO<sub>2</sub>, may become an increasingly important part of climate change reduction strategies (McLaughlin and Kszos 2005).

Combustion of plant tissue for energy production is considered cleaner than fossil fuel regarding climate forcing emissions. Since plants remove carbon dioxide from the atmosphere during photosynthesis in order to grow, their net contribution of carbon dioxide to the atmosphere is lower than that of fossil fuels which are retrieved from the earth and are non-renewable on a human time-scale. However, the release of pollutants such as nitrogen and sulphur oxides during the combustion of plant material may still be an issue and needs to be minimized. Research suggests that removal of these minerals from the biomass before combustion can help alleviate this problem.

Consumption of biomass for the production of energy has become a highly researched and highly feasible alternative to the burning of fossil fuels for the production of energy (Weimer et al. 2005, Guretzky et al. 2011) and currently provides around 10 % of global energy (Khatib 2012). If the externalities associated with the release of carbon to the atmosphere were appropriately determined and affixed to the end cost of energy delivery, biomass crops would be

considerably more valuable and an increase in their production would likely follow (Alig et al. 2010). For example, a carbon tax of \$50 per tonne of CO<sub>2</sub> emissions had a projected increase in the value of switchgrass (*Panicum virgatum* L.) by 1200% and an increase in production of 1100% (Alig et al. 2010). However, it is essential that bioenergy production does not detract from food and animal feed production in an already highly stressed agricultural system (Watson et al. 1997). These concerns can be alleviated by planting bioenergy crops on marginal lands, conservation lands and land otherwise deemed unfit for agricultural production, by limiting the amount of nutrients being removed from the field and by recycling nutrients back to the field (Tilman et al. 2009; Alig et al. 2010; Guretzky et al. 2011; Song et al. 2011; Anderson et al. 2013).

Ontario has a large amount of arable land and the agricultural capacity to grow bioenergy crops on a globally significant scale. Ontario has 28,747,000 acres of land, constituting 38% of the total land area, that are within the soil classes two through six (CLI 2013). These land classes represent areas that have moderate to severe restriction on the range of crops which can be grown, but where perennial crops are still viable. This represents considerable opportunity for the production of bioenergy from home-grown biomass for Ontarians (Samson 2007, Cennatek 2011a). In order to optimize the production and use of biofuels as an alternative to fossil fuels, an understanding of the chemical properties of biomass crops and of the combustion process are necessary (Liu and Bi 2011).

Switchgrass, a perennial C<sub>4</sub> grass, has a deep root system that can provide long-term carbon storage (Lee et al. 2012). These root systems increase the organic carbon levels deep in the soil where it is not easily degraded (Chamberlain et al. 2010). Crops which grow large root

systems are often perennial and offer other advantages over crops that need to be cultivated and planted year after year. These include a reduction in net carbon emissions from farming practises, significant reductions in erosion and nutrient leaching from fields, improved soil fertility and structure, higher biological diversity, and increased levels of carbon sequestration (Ma et al. 2000; Liebig et al. 2005; Collins et al. 2010; Culman et al. 2010; Dien et al. 2006; Kell 2011). Growing biomass crops such as switchgrass to produce energy has the potential to offset 1 to 2 Pg of Carbon per year globally (Cannell 2003).

The presence of minerals in plant material can give biomass crops undesirable properties in their raw form for the production of energy by combustion or gasification (Cennatek 2011a, Ajayi and Akande 2012). Therefore, research on the removal of nutrients that contribute to these problems is important, to enhance biofuel production efficiency (Liu and Bi 2011). To help understand the process and the motivation for the current research, this literature review focuses on the basic chemistry of raw biomass material, as well as the underlying components of the agronomic process, with an emphasis on switchgrass.

## **1.2 - Nutrient Requirements of Bioenergy Crops**

No plant can survive without the presence of a range of nutrients (Marschner 1995; Jones 2003). There are 16 nutrients essential to plant life: nitrogen (N), phosphorus (P), potassium (K), sulphur (S), calcium (Ca), magnesium (Mg), boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn), as well as carbon (C), hydrogen (H) and oxygen (O) (Jones 2003). These essential nutrients are required in various amounts to allow

plants to create the organic compounds necessary for life. The concentration and accessibility of labile nutrients to plants will determine the nutritional health of a given plant (Jones 2003).

Plants acquire C, H and O from air or water in the process of photosynthesis, where plants use energy from the sun in the presence of chlorophyll, to split a water molecule and combine it with carbon dioxide, to form a carbohydrate and an O<sub>2</sub> molecule. The 13 remaining elements need to be acquired by plants through minerals in the soil and are thus classified as mineral nutrients (Jones 2003). N can also be acquired from N-fixing bacteria on root nodules in a symbiotic process found in leguminous plants (Jones 2003).

Mineral nutrients generally fit into one of two categories based on the amount of that nutrient required to sustain plant life: macronutrients and micronutrients. However, there are a few nutrients that do not fit well into these categories. For this reason macronutrients can be divided into two sub-categories: primary and secondary macronutrients. N, P and K are macronutrients: nutrients which are required in relatively large amounts. They can also be referred to as primary macronutrients. These nutrients need to be present in high concentrations, to control the growth and functions of the plant. Secondary macronutrients, which are required in high enough amounts such that they are not considered trace elements, but are not required in high enough amounts to be considered primary macronutrients include Ca, Mg and S (Jones 2003; Cennatek 2011a). Cl, B, Cu, Fe, Mn, Mo and Zn are considered micronutrients (Jones 2003).

N is often considered to be the most important nutrient for plant growth, as plant composition depends more on N than any other nutrient, and it is therefore often a main ingredient in fertilizers (Marschner 1995, Cennatek 2011a). Inorganic N, in the form of nitrate

( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) is taken into the plant and then quickly transformed into organic compounds (Marschner 1995). Ammonium is toxic to plants and therefore needs to be combined with C into non-toxic, organic compounds, such as amino acids, which are used by the plant to perform essential functions (Marschner 1995). Nitrites are also toxic to plants at very low levels, however, nitrite can be quickly transformed by plants into nitrous oxide through the process of nitrite reduction, or bacteria in the plant (nitrobacteria) can transform it into nitrate (Jones 2003).

The complex dynamic of the N cycle affects the availability of N to plants at any given time (Marschner 1995). N will undergo various states of oxidation which may or may not be available for plant uptake depending on the form (Jones 2003). A deficiency of N can cause early maturity and plant growth can be stunted (Jones 2003). Deficiency will be noticeable because the plant and leaves will be a lighter colour of green and over time leaves will turn yellow to brown and then die (Jones 2003). N is often provided to plants as a fertilizer to maintain good health, foster higher yields and avoid the problems associated with N deficiency. This adds significantly to the environmental impact of a given crop, as N fertilizer is expensive and energy intensive to produce using the Haber-Bosch process which is primarily produced through the burning of natural gas (Huo et al. 2012).

P enters the plant through the soil as hydrogen phosphate or dihydrogen phosphate and is an integral component of ATP, which plants require to produce energy (Marschner 1995; Jones 2003; Cennatek 2011a). Phosphorous compounds also help the plant carry out photosynthesis and respiration, as well as cell replication and cell growth (Marschner 1995; Jones 2003; Cennatek 2011a). P is a structural element that is necessary to form nucleic acids which make up DNA and RNA, allowing genetic information to be passed on from one generation to the next

(Marschner 1995). P deficiency can cause plants to senesce prematurely. It may also cause a reduction in the size and number of leaves on plants, as well as the number of flowers and the production of seeds (Marschner 1995).

K and Cl are essential to plants for their use in the opening and closing of stomata, thereby regulating water retention (Marschner 1995; Cennatek 2011a). K is also used in the make-up of molecules used for other plant functions including photosynthesis, respiration and protein synthesis (Marschner 1995; Cennatek 2011a). K is important for the growth of roots and helps to prevent diseases in plants (Jones 2003). It is also a factor in the size and quality of fruit produced by plants (Jones 2003). Slow and stunted plant growth can be caused by K deficiency and will be apparent by purple colouration on the underside of leaves (Jones 2003).

There is still some debate as to which nutrients are essential for plant life (Jones 2003). Silicon is not universally accepted as an essential mineral nutrient, although it can be found in switchgrass at over 3% of dry matter content and it has significant benefits to plant health when present (Jones 2003, Woli et al. 2011). Silicon is important for plants to help prevent lodging, improve drought and disease resistance, to prevent damage from pests, improve nutrient uptake, enhance fertility and improve water use efficiency (Woli et al. 2011).

Secondary macronutrients and micronutrients also help to perform plant functions and the health of plants will be negatively affected if there is a deficiency of any of the essential nutrients. The presence of a nutrient does not, however, guarantee its availability for plant uptake; the interactions among elements can affect the ability of plants to assimilate nutrients (Jones 2003).

### **1.3 - Typical Nutrient Content in Harvested Biomass and the Factors which Affect Nutrient Content**

An understanding of the nutrient content of biofuel crops is necessary when determining the feasibility of their use for energy production. The presence of higher levels of nutrients, which can cause issues with downstream processing, will ultimately affect the efficiency and feasibility of the process. Plants contain nutrients at varying concentrations but often within a similar range. Around 2-5 % of a plant's dry weight will be composed of N. P is present in plants at around 0.3-0.5 % dry weight. K is contained in similar levels to N in plants and accounts for between 1-5 % of dry weight (Marschner 1995, Cennatek 2011a). Other essential nutrients are contained at varying levels in plants.

The amount of any given nutrient available for uptake in plants is affected by various soil qualities (Jones 2003). Soil moisture is of the utmost importance, considering that water provides a vehicle for the transport of nutrients, thereby affecting the distance which any given nutrient can travel to be used in the plant. Soil pH can also be affected by soil moisture and the level of acidity in the soil can affect which nutrients can be absorbed by the plant. Fe, Al, Zn, Mn and B are more difficult for plants to absorb at a high pH, whereas Mg and P are harder for plants to absorb in more acidic soils (Jones 2003). Soil compaction also has an effect on nutrient acquisition. A heavily compacted soil will limit root growth, reducing exposure of the roots to nutrients. Heavily compacted soils will also contain less O<sub>2</sub>, which is important for roots to produce the energy necessary for nutrient absorption (Jones 2003). Soil compaction can be affected by agricultural practises such as reduced, no-till or conventional tillage (Paul 2007). Since switchgrass is a perennial species, the need for tillage is greatly reduced and its long root

structure of potentially greater than two meters helps alleviate soil compaction (Parrish et al. 2008).

There is a wide range of agronomic practices which can be implemented on any given farm that affect the nutrient content of the soil. There is evidence that different crop rotations and fertilization regimes, as well as different cultivation practices, can have an effect on organic matter content as well as nutrient levels in the soil (Janzen 1992; Paul 2007; Allison et al. 2012). Spraying pesticides or fumigation can also have an effect on nutrient levels. For example, fumigation has been shown to reduce N content resulting from necrosis of N-fixing bacteria (Janzen 1992). The resulting amount of nutrients in the field will affect the amount of nutrients that will be found in biomass grown there (Lestander and Rhén 2005).

Reduced tillage can cause layering of nutrients, since the mixture of soil by cultivation is reduced (Paul 2007). This means that any nutrient supplementation will mostly remain in the top layer of the soil and not be available for absorption in the deep root zone (Jones 2003). The plant variety determines the genetic capability for absorption of nutrients and associated yields (Jones 2003). Hybridization or genetic modification of species to maximize nutrient absorption can be used to promote higher yields. Yield is also dependent on the environmental conditions of any given site. Warmer temperatures and higher rainfall allow for maximum nutrient availability and uptake, whereas cooler, drier climates will restrict uptake of nutrients and limit plant growth (Jones 2003).

## 1.4 - Issues with Nutrient Content in Biomass for Direct Combustion

It is evident that the quality of a feedstock for bioenergy production will affect the efficiency of the combustion process (Jenkins et al. 1996; Jenkins et al. 1998). For direct combustion of biomass, the effects of excessive mineral content on the efficiency of energy production can be significant (Jenkins et al. 1998). High levels of nutrients such as K, Cl, N and S will contribute to noxious gas effluents and particulate matter pollution (REAP Canada 2008). Ca, Mg and K in the presence of Cl contribute to boiler fouling and corrosion. Therefore, the presence of these elements in biomass needs to be minimized from the field or somehow reduced by the time of biomass combustion.

When biomass is used for direct combustion, the burning of the plant residue is never 100 % complete. The inorganic material that is left behind after direct combustion is referred to as ash and contains various elements including K, Si, Ca, Na, Mg, Al, Zn and Pb (Ogden et al. 2010). The concentration of a nutrient does not always exhibit a linear relationship with boiler fouling, however, as it is often the interaction between two or more nutrients that decreases the melting point of the subsequent ash mixture by creating an eutectic compound (McKendry 2002b; Monti et al. 2008). The buildup of ash on surfaces is caused by the melting of alkali and alkaline earth metals which have a melting point that is lowered in the presence of K and Cl. K reacts with Cl to produce primary fouling compounds, while Cl acts to transport alkali and alkaline earth metals to boiler surfaces where they contribute to corrosion and fouling (Monti et al. 2008). The potential for fouling is thus higher with higher concentrations of these elements (Jenkins 1998; Tonn et al. 2011).

The formation of slag and subsequent fouling of the boiler tubes may cause reduction in flow, loss of heat transfer, increased corrosion of boiler materials, higher maintenance costs, shorter lifespan of furnace components and a subsequent increase in the overall cost of operation (Cennatek 2011a; Woli et al. 2011; Ajayi and Akande 2012). It is, therefore, important to take measures to minimize the mineral content of the feedstock, thereby reducing such issues. Jenkins et al. (1996) found that leaching in water could remove 90% of Cl and greater than 80% of the alkali metals from sugar cane bagasse, resulting in lower ash fusion temperatures and improved combustion characteristics.

Fouling is a complicated phenomenon affected by a number of variables, but the result put simply, is that the more the boiler gets fouled, the less efficient and the higher the cost of operation for the furnace or generator will be (Ajayi and Akande 2012). Table 1.1 shows the various oxides that contribute to ash formation from the combustion of switchgrass.

Table 1.1 - Percent contribution of oxides to ash formation from switchgrass combustion (From Jenkins et al., 1996).

Oxide	Percent ash
SiO <sub>2</sub>	65.18
Al <sub>2</sub> O <sub>3</sub>	4.51
TiO <sub>2</sub>	0.24
Fe <sub>2</sub> O <sub>3</sub>	2.03
CaO	5.60
MgO	3.00
Na <sub>2</sub> O	0.58
K <sub>2</sub> O	11.60
SO <sub>3</sub>	0.44
P <sub>2</sub> O <sub>3</sub>	4.50

The type of biomass being burned and the presence of nutrients within the biomass play a significant role in the level of fouling that will occur (Ajayi and Akande 2012). The type of

boiler also plays a significant role and modern boiler designs incorporate this knowledge and are now more effective at limiting the effects of fouling (Ajayi and Akande 2012). The efficient burning of nutrients is not environmentally conscious, however, if the nutrients could otherwise be recycled and returned to the field. The harvesting process can introduce impurities such as soil or even insects and small animals which can reduce production efficiency and increase issues with combustion equipment (McKendry 2002a). The amount of water left in the biomass presents issues for combustion as well and introduces the potential need for pre-drying to achieve ideal combustion moisture characteristics (McKendry 2002a).

## **1.5 - Agronomy and Harvesting Methods for Switchgrass**

Among the numerous species assessed for their potential as bioenergy crops in North America, switchgrass is deemed to have the most potential for energy production (Vogel 1996; Lewandowski et al. 2003; McLaughlin and Kszos 2005; Fike et al. 2006; Wright et al. 2010). This is in part due to its ability to produce good yields in the short growing seasons encountered in Canada (Madakadze et al. 1999; Tubeileh et al. 2014). The United States has deemed switchgrass a "model" bioenergy crop and has devoted significant resources to its study (McLaughlin and Kszos 2005). Switchgrass uses the C<sub>4</sub> photosynthetic pathway making it grow optimally during the hot summer months when C<sub>3</sub> grasses do not perform as well (Madakadze et al. 1998). Like other perennial plants, switchgrass is very water and N-use efficient, thus requiring minimal inputs (Samson et al. 2005). Due to the high efficiency of switchgrass, it can be used in water and nutrient deficient environments with good results, outperforming traditional row-crops (Bransby et al. 1989). It can also be used for regenerative growth on sites which have

been substantially decimated, making growth for other vegetation unlikely (Parrish and Fike 2005). Figure 1.1 shows the natural jurisdictional range of switchgrass in North America.



Figure 1.1 – Natural jurisdictional range of switchgrass in North America (USDA 2009).

Species selection is key when choosing bioenergy crops, as it will affect nutrient content and yields (Madakadze et al. 1999; Lewandowski et al. 2003). Switchgrass has two main morphological types: lowland and upland (Parrish et al. 2008). Lowland ecotypes originate from wet climates with mild winters and are generally capable of higher yields because they grow taller and thicker (Allison et al. 2012). Upland ecotypes are more resistant to drought and severe weather but do not grow as large and therefore provide lower yields (Allison et al. 2012). These genetic traits can make specific varieties of switchgrass good choices in regions with short growing periods such as Eastern Canada (Madakadze et al. 1998). However, certain species are going to be more productive on a given site due to climatic variables and the genetics of the plant, determined by its origin, and therefore site specific selection is important (Lewandowski et

al. 2003, Parrish et al. 2008). Figure 1.2 illustrates that differences exist within ecotypes which will affect the suitability of a species to a given site. Species within the same morphological category can still mature at different times of the year (Lee and Boe 2005, USDA 2009).



Figure 1.2 – Two upland varieties of switchgrass, Dacotah (left) and Sunburst (right), mature at different times of year (USDA 2009).

Switchgrass can potentially be harvested multiple times a year, with the aim of increasing yields, depending on the end use of the biomass. Thomason et al. (2004) found that harvesting switchgrass three times a year produced the best yields and would be suitable for a crop that was used as forage. This is due to the high nutrient levels found in the biomass before plant senescence (Samson 2007). Cutting more than once a year will increase the need for fertilizer (Guretzky et al. 2011). Multiple cutting may also reduce stand longevity, as plant density was observed to decrease over time with a multiple cutting management system (Thomason et al. 2004). A one cut management system is likely best for end use in direct combustion or gasification, so that nutrient levels in the harvested biomass can be minimized by harvesting after plant senescence when nutrient levels are low (Samson 2007).

Fertilization of switchgrass is often not considered necessary to generate sufficient yields for biomass production, and there is evidence that reduced levels of N fertilization provides a higher quality feedstock for use in direct combustion energy production (Kludze et al. 2013). Thomason et al. (2004) found that although the highest yields were attained at a high N fertilization rate (448kgN/ha), applying no fertilizer produced yields nearly as high, yielding 18Mg/ha and 16.9Mg/ha respectively. Allison et al. (2012) found, however, that on marginally productive land, switchgrass yields were significantly improved with the addition of N fertilizer, finding a 43% increase in yields with a moderate 100kg/ha application rate. Life cycle analysis of switchgrass would need to be performed to determine the validity of fertilizer application. The need to add fertilizer could clearly detract from the economic and environmental viability of switchgrass as an energy crop.

Harvesting methods for bioenergy crops such as switchgrass have mostly been limited to pre-existing practises used for the harvesting of hay crops (Venturi et al. 2004). Development of species specific harvesting equipment can be prohibitively costly. Therefore, as long as the available equipment can get the job done, new machinery will not be developed (Venturi et al. 2004). Essentially, the crop needs to be cut, dried and collected, followed by transport to bio-refineries that can use the feedstock to produce energy (Venturi et al. 2004). Switchgrass needs to be cut using some type of swathe, mower, sickle bar mower, or forage chopper (Turn et al. 1997; Venturi et al. 2004; Adler et al. 2006). These machines will leave the felled crop chopped up to varying extents, which can affect field losses from material left behind by collection implements (Turn et al. 1997) and also affects nutrient losses due to variation in the surface area exposed to leaching (Turn et al. 1997).

Kumar and Sokhansanj (2007) determined price rates for various methods of collecting switchgrass for transport to bio-refineries. The methods of collection include round or square baling, where the biomass is raked into a windrow and a baling machine follows the windrow, picks up the hay and forms it into a bale which can then be transported in this compacted form. The biomass can also be formed into a loaf after raking, whereby a loafing machine forms the biomass into a large pile and then compacts it, leaving it in dome shaped piles along the side of the field where it can dry further. The raked biomass can also be picked up by a forage harvester that shreds the biomass and then blows it into a storage wagon which is towed behind the harvester. The biomass can be left in rows before collection for varying lengths of time based on weather conditions and temperature in order to attain the desired moisture content. Depending on the moisture content, biomass collected by a forage harvester can either be collected into a large dry pile using a belt conveyor, or wet biomass can be dumped from the harvester wagon into a pit and compressed to form silage (Kumar and Sokhansanj 2007). These various forms of collection will affect the nutrient levels in the biomass as exposure to leaching will differ.

## **1.6 - Effects of Harvesting Management on Nutrient Content and Yield**

Research in some parts of the world began in the 1970's to determine which grass species might become good sources for bio-energy feedstock (Hadders and Olsson 1997). In the 1980's it became apparent that summer and early fall harvested biomass had restrictively high amounts of nutrients and ash, making the process less than economically feasible (Hadders and Olsson 1997). It was then proposed in 1989, that the stands should be left over winter to be harvested in

the spring, when plant senescence would cause the translocation of nutrients to the roots of the plant (Hadders and Olsson 1997).

The time of harvest directly affects the mineral content of the biomass (Adler et al. 2006; Ogden et al. 2010; Shahandeh et al. 2011). Allowing crops to be weathered over winter and harvested in spring can produce a feedstock which is lower in mineral nutrients and therefore more efficient for direct combustion processes, whereas harvests with high lignocellulose content are more desirable for gasification and ethanol production (Adler et al. 2006). Also, allowing switchgrass to remain standing on the field over winter and harvested in spring makes switchgrass pellets easier to mold because the grass is less waxy on the surface (Stamler 2009).

Leaving crops standing until after plant senescence and overwintering of standing or cut and windrowed plants can help achieve high levels of field leaching, but the results are not always ideal and there are associated risks. Biomass left on the field is subject to weather variability, so production and nutrient content will not be consistent year to year. Plants left standing in the field are subject to lodging and direct field losses by collection equipment in the spring can be significant. Losses of 25% or more of total yield have been observed (Stamler 2009). Organic matter can also be lost due to microbial degradation which can happen faster than nutrient removal later in the spring (Cennatek 2011a). Scheduling of other crops can be affected if harvest conditions are unpredictable (Cennatek 2011a) and late spring harvesting of switchgrass would compete for time and equipment required for grain crops, as well as affect the early nesting habits of grassland bird species (Gamble et al. 2015). This can result in direct economic losses to farmers. Therefore an industrial leaching process may be necessary to standardize the feedstock and make it more appealing to farmers.

Table 1.2 compares the energy potential and nutrient content of wood pellets and wheat straw compared to switchgrass harvested in the fall or the spring. Ash, N and K are reduced significantly over winter (Stamler 2009). Reduced nutrient and moisture content of the spring harvest would be preferable for processes requiring low levels of nutrients and for situations where moisture content is a factor in storage and transportation costs (Anderson 2013). Switchgrass is a fast growing herbaceous crop that is significantly less dense than woody biomass which makes the process of nutrient removal from the feedstock after harvest easier and more effective (Liu and Bi 2011) but also makes transport more expensive.

Table 1.2 - Ash, N, K and Cl percentages in wood pellets, wheat straw and switchgrass  
(From Stamler, 2009)

Unit	Wood pellets	Wheat straw	Switchgrass	
			Fall harvest	Spring harvest
Energy (GJ/t)	20.3	18.6-18.8	18.2-18.8	19.1
Ash (%)	0.6	4.5	4.5-5.2	2.7-3.2
N (%)	0.30	0.70	0.46	0.33
K (%)	0.05	1.00	0.38-0.95	0.06
Cl (%)	0.01	0.19-0.51	n/a	n/a

Not only can time of harvest affect mineral content, it can also affect yields. Adler et al. (2006) found that delaying switchgrass harvest until spring resulted in a 40% loss of the harvest in winters with heavy snowfall. Since the water content of plants is significantly less in the spring, increased breakage of the plant results in field losses from material being missed by the baler (Girouard and Samson 1997; Adler 2006). The plant is dead at this point and the water content is low enough that the leaves are highly sensitive to breakage. When plant tissue is dry, becomes rewetted and then dry again, the stress on the tissue can cause damage to the cell walls

and vacuoles which retain nutrients within the plant, allowing the nutrients to be leached out of the tissue more easily (Tonn et al. 2011). K and Cl are present in plants in ionic form making them highly susceptible to leaching from either rainfall in the field or mechanical leaching processes away from the field, especially when the biomass is dry (Marschner 1995; Tonn et al. 2011).

Measured differences in yields from field experiments as a result of low water content in the spring causing breakage of delicate plant parts included around 80 % seed heads, 30 % leaves, 12 % leaf sheaths and 4 % stems (Stamler 2009). Since the concentration of nutrients differs among the various plant parts, the concentration of nutrients in the harvested biomass will be affected. Monti et al. (2008) showed that the leaves of the switchgrass plant have higher concentrations of nutrients than the seed heads and stems, so if the highest losses are from seed heads overall nutrient concentrations may decrease along with yield losses. Cutting the crop in the fall and leaving it on the field until spring may provide a solution, as nutrient and water content can be reduced as well as yield losses being minimized (Stamler 2009).

Girouard and Samson (1997) found that using a cereal grain swathe as opposed to a mower conditioner could reduce field losses of overwintered crops by 74 %. Additionally, cutting and windrowing the biomass in the fall and allowing it to lie on the field over winter has been found to reduce losses by 23 % over a strictly spring harvest (REAP 2008). These losses are still significant and must be weighed against the gains of efficiency in direct combustion from reduced nutrient concentrations of field weathered material. Girouard and Samson (1997) speculated that yield losses could be less than 5 % in the future if best management practises for switchgrass harvest in spring were undertaken.

Han et al. (2011) suggested that only a certain sustainable portion of crop yields be taken from the field and the rest of the crop residue left behind in order to contribute to the soil organic matter pool and help sustain healthy microbial populations. This can affect the availability of nutrients to future crops and their subsequent nutrient content. Leaving crops standing or cut on the field over winter can also increase the soil nutrient turnover efficiency, as nutrients will leach back into soil over the winter period (Girouard and Samson 1997).

It is important to remember the effect of weather on harvest management. If time of year is important for determining nutrient and water content, then acceptable harvest times may overlap with unacceptable weather conditions for harvesting. Hwang et al. (2009) showed that there can be significant restrictions on the number of days that can actually be spent in the field. This must be taken into consideration when deciding when to harvest biomass crops.

## **1.7 - Effects of Weathering on Nutrient Content after Harvest and Current Knowledge of Nutrient Losses in Field Weathering**

If biomass can be left on the field over winter, one would expect that the amount of nutrients would be less in the spring. This would depend on the amount of rainfall and rainfall intensity as well as other factors such as freeze-thaw cycles, humidity, sun intensity and wind exposure. Tonn et al. (2011) found that the effect of rainfall intensity on nutrient leaching differs among nutrients, based on natural rainfall exposure and intensive irrigation scenarios. For ash, they found that a high intensity leaching event had a higher leaching rate. Cl had a slightly lower leaching rate with the high intensity treatment and the rate of leaching for K was largely

unaffected by rainfall intensity. This variation may be caused by differences in the amount of water able to infiltrate the tissues of plants being restricted with heavier rainfalls (Tonn et al. 2011).

The total amounts of ash, Cl and K removed by leaching in the Tonn et al. (2011) study were the inverse of their response to rainfall intensity. The removal of ash was the most difficult, and amounts removed by leaching were too low to have a beneficial effect on reduction of dust emissions during combustion processes. Concentrations of K and Cl were significantly reduced, however. Tonn et al. (2010) found that although N was not significantly leached from biomass that was left cut on the field, K and Cl were found to be leached between 55-82 %. Thus, leaching of biomass should have significant benefits for reducing slag build-up, corrosion and fouling of boilers caused by K and Cl interactions.

Excess N may cause significant problems in the combustion of biomass including the production of particulate matter and harmful nitric oxide emissions, along with the production of smog and acid rain (Cennatek 2011a). Tonn et al. (2011) found that even with hydrothermal conditioning and mechanical dewatering they could not observe significant reductions in N concentrations of dried biomass. Studies that had found reductions in N concentrations by field leaching observed this only after a five month period of field exposure with a large amount of natural precipitation. Also, they suggest that due to the non-controlled environment of this field trial, the observed losses of N may have been the result of processes other than leaching (Tonn et al. 2011). Thus, the removal of N by leaching appears to have limited potential.

Turn et al. (1997) compared the use of a John Deere Model 34 forage chopper and a Jeffco cutter for cutting banagrass into different sizes, resulting in different levels of nutrient loss

after exposure to leaching processes. The Jeffco cutter left the grass cut to a size of 1mm (standard deviation of 2.2), whereas the John Deere forage chopper cut the grass to a size of 3.9mm (standard deviation of 1.9). The Jeffco cutter combined with a press/rinse/press treatment resulted in lower ash and alkali metal concentrations compared to the John Deere forage chopper with the same treatment. Both methods of cutting followed by leaching treatments lowered the concentrations considerably resulting in high quality biogas feedstock. Reductions in the concentration of K by 90 %, Mg, Na and P by 70 % and S by 54 % were achieved with the Jeffco cutter along with almost 100 % of the Cl.

Research into nutrient recycling began in an effort to reduce the amount of nutrients removed from the field with biomass harvests which would subsequently reduce the need for the application of fertilizers and improve the long-term sustainability of biomass production (Turn et al. 1997). The research has since progressed towards limiting nutrients in biomass feedstock to improve combustion efficiency and reduce boiler fouling (Turn et al. 1997). Turn et al. (1997) showed that alkali metals and Cl could be effectively removed from straw biomass after harvest with various levels of chopping and either spraying or soaking of the material. The chopped biomass can be exposed to a process similar to the rewetting and mechanical compression process that is used to extract sugar from sugarcane (Turn et al. 1997). Cennatek (2011b) proposed processes for removal of nutrients from biomass and also recovery of nutrients from the leachate by reverse osmosis or other methods.

Some studies have shown that field leaching will result in an initial reduction in nutrients, but over time the percent weight of nutrients will actually increase, due to biological degradation of organic material happening at a faster rate than the leaching process (Cennatek 2011a). The

report by Cennatek (2011a) concluded that field leaching is not sufficient for providing a high quality combustible fuel source and thus, an industrial leaching process is necessary to sufficiently remove the nutrients.

## **1.8 - Research Opportunities to Advance Nutrient Cycling**

As climate change is projected to increase average global temperatures (IPCC 2013), the range and feasibility for production of switchgrass may increase, allowing more opportunity for switchgrass production in Ontario. Modelling programs could be used to examine long-term trends in yield increases due to climate change. If yields are likely to increase, the feasibility of various biomass production strategies might improve. The potential for increases in temperature and variability in precipitation caused by climate change could also have effects on nutrient cycling, and this has not yet been studied with a focus on switchgrass.

Lee et al. (2012) used the modeling software DayCENT to determine switchgrass yields in California, using data from across the United States to validate the model. Since the model has been well validated, it might now be used to estimate yields and various other plant and soil qualities for switchgrass production in other places such as Ontario. The model allows for the prediction of various nutrient contents in above and below ground live biomass, as well as in the soil organic matter, and if properly validated could provide valuable long-term assessment of switchgrass nutrient contents and biomass yields.

Hwang et al. (2009) showed that the length of the harvest period can significantly affect the cost of biomass production. They estimated the number of days available in Oklahoma for

cutting and baling switchgrass. These same estimates are lacking in Eastern Canada and should be expanded in order to better assess the feasibility of biomass production from switchgrass in Ontario. Completion of such a study could also help align harvest times with times of optimal biomass quality. Climate change may also have an effect on the number of days available for harvest and this could be modelled.

Shen et al. (2010) used proximate analysis to determine the concentration of C, H and O in various biomass species. They suggested that a standard method be developed in order to accurately determine elemental concentrations of plants. The extension of proximate analysis into the prediction of mineral nutrients in switchgrass and other biomass crops may be helpful in the future in order to maximize biofuel production efficiency.

The application of an industrial process for removing nutrients from switchgrass and returning it back to the field has not been thoroughly researched. There is evidence that the size of the material and associated surface area can have an effect on leaching (Cennatek 2011b, Turn et al. 1997). Turn et al. (1997) showed that with banagrass, the size distribution of the biomass was related to the resultant leaching. If the size/leaching ratio can be optimized, equipment could be used that would leave the switchgrass cut on the field within the size variation that would maximize nutrient leaching from field weathering. This research could be carried out on various plant species including switchgrass. There is also evidence that the agitation rate and intensity of exposure to water has an effect on the resultant leaching of nutrients (Cennatek 2011a, Tonn et al. 2011). There is opportunity to advance the process of in-situ and ex-situ leaching of nutrients from switchgrass, based on gaining maximum reductions in nutrient levels

of biomass with minimal amounts of energy input. This research should focus on particle size, agitation rate, biomass to water ratio, leaching temperature and solvent type.

Nutrient recovery from biomass leachate can be achieved through processes similar to that used for desalination. The specific parameters necessary to remove water from the nutrient dense leachate, in order to concentrate it into fertilizer, are not well researched. These parameters include the type of membranes necessary, the behaviour of solutes at the membrane, and clogging characteristics. Temperature, pH and trans-membrane pressures have also not been researched specifically for biomass leachate (Cennatek 2011b).

## **1.9 - Current Area of Research**

If nutrients are to be further removed from switchgrass after harvest, either after or in place of field leaching, an industrial process for their removal will be required. Literature on the process requirements to effectively remove nutrients from switchgrass is lacking. This process will require the optimization of various standards for removing the necessary nutrients in the most efficient way. This will include maximizing results while minimizing energy inputs. Some of the factors that need to be determined are the amount of time required to remove an acceptable amount of nutrients from the biomass, the concentration of solution during leaching, the temperature at which the process takes place, and the type of water and concentration of pre-existing elements in the water used.

Cennatek (2011a) compared soaking, soaking/agitation and spraying methods of liquid nutrient extraction from miscanthus (and found that soaking with agitation was the best way to

remove the nutrients. They also suggested that the water to biomass ratio be between 10:1 to 12:1 based on trials using 8:1, 10:1, 12:1 and 15:1. This study will consider the effect of changing the ratio for leaching from switchgrass. Residence times should be kept below two hours according to Cennatek. Since processing time has direct capital and energy costs, shorter residence times are desirable and the optimal time needs to be determined. This study will focus on shorter residence times to determine leaching in the early stages of exposure of switchgrass to water. This study will also explore the effect of water temperature on the leaching process, as well as the type of water and concentration of pre-existing elements in the water, and what effect these factors may have on the leaching process.

## **Chapter 2 - Hypotheses and Objectives**

Hypothesis one: Changing the concentration of switchgrass in water (grams of switchgrass per litre of water) will not affect the amount of nutrients leached into the water.

The first objective is to determine the relationship between concentration and nutrient leaching. The concentration of the leaching solution has implications regarding water usage and material throughput. Lower concentrations could extract more nutrients, but there is a limit where the amount of water used will become prohibitively costly to the process. There is a need to understand the relationship between concentration, energy input and cost.

Hypothesis two: Changing the temperature of the processing water will not affect the amount of nutrients leached from the switchgrass and into the water.

The second objective is to determine the relationship between water temperature and nutrient leaching. In this way the cost associated with heating the water can be compared to any associated gains in leaching potential.

Hypothesis three: The mineral content of the water used will not affect the ability of nutrients to leach from the switchgrass and into the water.

The third objective is to determine whether the mineral content (water quality) of water used for extraction will affect leaching potential. Accessibility and cost of well water, city water and distilled water varies by location. An analysis of commonly accessible water types and an assessment of the initial elemental concentrations of these water sources compared to the leaching potential of the water will help potential users make cost/benefit analyses.

## **Chapter 3: Materials and Methods**

All samples for this experiment were derived from a stand of Cave-in-Rock switchgrass, established in 2010, cut and windrowed on Dec 28<sup>th</sup> 2012 and baled April 21, 2013. The material was then stored in an enclosed shed until collection in September 2014. All samples were ground using a Standard Model No. 3 Wiley Mill (Arthur H. Thomas Co., Philadelphia, USA) using 1mm mesh screen then stored at room temperature in a sealed container prior to analysis. Experiments took place over a one month period. Samples were homogenized prior to use by shaking of the storage container and mixing with a lab sampling spoon. Samples were weighed to the nearest 0.01 g. Percent moisture was determined by drying a ~100 g sample in a drying oven at 105°C for 48hrs or until constant weight was achieved. Lab protocols used for elemental analysis were: Ca %: A204a, P %: A204a, K %: A204a, Mg %: A204a, Zn: A204a, Mn: A204a, Cu: A204a, Fe: A204a, S %: A221.

### **3.1 – Concentration**

Homogenized samples of switchgrass were weighed at 5, 10, 15 and 20 g to the nearest 0.01g and added to a 500mL flask. Two hundred mL of distilled water at room temperature, measured to within 1 mL, was added to the flask yielding concentrations of 25, 50, 75 and 100 g/L (without adjustment for 12.1% moisture content). The flask was stirred on a Lab Companion HP-3100 heat and stir plate with heat turned off at 65 rpm for 40 minutes, after preliminary trials showed very little leaching occurred beyond this residence time. The flask was then drained through a 250 µm (No. 60) screen into a beaker to remove the switchgrass from the water. The water was filtered through 2V (8 µm pore size) filter paper to remove fine particulate, then tested

for conductivity using an Oakton Cond6+ handheld conductivity meter. The samples were dried to constant weight at 105 °C then sealed in a plastic bag. Three replications were performed at each of the four concentrations producing 12 samples in total. The samples were sent to SGS Agrifood Laboratories (Guelph, ON) for wet chemistry analysis of N, Ca, P, K, Mg, Zn, Mn, Cu, Fe, S, Cl and B. Three control samples were also sent for analysis without treatment.

Statistical analyses were performed using SAS Version 9.3 (SAS Institute, Cary, NC). A Shapiro-Wilk's test was used to test for normality of the residuals. Levene's test of equality was used to test for heterogeneity of the residual absolute values. Lund's test for outliers was used to determine outliers. Mixed effects analysis of variance was used to determine any significance of the concentration treatment effect. Tukey's test was used for a post-hoc analysis of all possible comparisons. A covariance structure was applied to deal with heterogeneity of error over treatments if necessary.

### **3.2 – Temperature**

Homogenized samples of switchgrass were weighed to 5 g within 0.01 g and added to a 500 mL flask. Two hundred mL of distilled water was then added to the flask to within 1 mL resulting in a concentration of 25 g/L. Twenty five g/L was chosen for the temperature experiment in order to limit any effects that higher concentrations might have on nutrient extraction rates and to allow the influence of temperature to be more detectable. The water was preheated to 20, 40 or 60°C in an oven. Once the switchgrass was combined with the preheated water, it was stirred on a Lab Companion HP-3100 heat and stir plate at 65 rpm. The hot plate was calibrated to 20, 40 and 60°C and preheated prior to stirring the samples. The samples were

maintained at temperature and stirred for 5, 10, 20 or 40 minutes. The samples were then strained using a 250  $\mu\text{m}$  (No. 60) screen and filtered using a 2V (8  $\mu\text{m}$  pore size) filter. The filtrate was analysed for conductivity using an Oakton Cond6+ handheld conductivity meter. The switchgrass was dried at 105  $^{\circ}\text{C}$  until constant weight was achieved and then stored in sealed Ziploc bags. Three replications at each temperature and time combination were performed yielding 36 samples in total. The switchgrass samples were sent to SGS Agrifood Laboratories (Guelph, ON) for wet chemistry analysis of N, Ca, P, K, Mg, Zn, Mn, Cu, Fe, S, Cl and B.

Statistical analyses were performed using SAS Version 9.3 (SAS Institute, Cary, NC). A Shapiro-Wilk's test was used to test for normality of the residuals. Levene's test of equality was used to test for heterogeneity of the residual absolute values. Lund's test for outliers was used to detect outliers. Mixed effects analysis of variance was used to determine the significance of temperature and time effects. The SAS slicing technique was used for tests that showed significant interaction effects, in order to compare simple effects. Temperature and time effects were sliced to show the significance of the effect at each level, since comparison of combined means is inappropriate when interaction effects are significant. Regression responses were analysed by using contrast statements to generate variance partitions.

### **3.3 – Water Type**

Four types of water were collected for the analysis and tested for conductivity with an Oakton Cond6+ handheld conductivity meter. Well water was collected from Carp, ON, and had an initial conductivity of 940  $\mu\text{s}/\text{cm}$ . Tap water was collected from Kemptville, ON, which had an initial conductivity of 750  $\mu\text{s}/\text{cm}$  and from Ottawa, ON, which had an initial conductivity of 130  $\mu\text{s}/\text{cm}$ . Distilled water had an initial conductivity of 2.0  $\mu\text{s}/\text{cm}$ . Samples of the water were

sent out in triplicate to Caduceon Environmental Laboratories (Ottawa, ON) for analysis of chloride (Reference Method: SM4110C), total Kjeldahl nitrogen (MOEE 3367), total P (MOEE 3367), Ca, Cu, Fe, Mg, Mn, K, S and Zn (SM 3120).

Samples of switchgrass were weighed at 5 grams to the nearest 0.01 g and added to a 500 mL flask. Two hundred mL of water was added to the flask, resulting in a concentration of 25 g/L. Twenty five g/L was chosen for the water type experiment to limit any effects that concentration had on nutrient extraction and to maintain consistency with the temperature experiment. The flask was transferred to a stir plate and stirred at a rate of 65 rpm. Samples were stirred for either 5, 10, 20 or 40 minutes. Three replications were tested for each time for each of the four water types yielding 48 samples in total. The samples were then strained through a 250  $\mu\text{m}$  (No. 60) screen. The switchgrass in the screen was transferred to a tinfoil container and placed in the drying oven at 105 °C until constant weight was achieved. The samples were then sealed in plastic bags. The biomass was sent to SGS Agrifood Laboratories (Guelph, ON) for wet chemistry analysis of N, Ca, P, K, Mg, Zn, Mn, Cu, Fe, S, Cl and B.

Statistical analyses were performed using SAS Version 9.3 (SAS Institute, Cary, NC). A Shapiro-Wilk's test was used to test for normality of the residuals. Levene's test of equality was used to test for heterogeneity of the residual absolute values. Lund's test for outliers was used to detect outliers. Mixed effects analysis of variance was used to determine the significance of water type and time effects. The SAS slicing technique was used for tests that showed significant interaction effects, in order to compare simple effects. Water type and time effects were sliced to show the significance of the effect at each level, since comparison of combined means is inappropriate when the interaction effect is significant. Orthogonal regression sub-partitions were analysed.

## **Chapter 4 – Results**

In this chapter, the results of the experiments for the effects of solution concentration, temperature of the solution and mineral content of the solvent are presented. All values are given in percent weight. The conversion for percent weight to g/kg is  $(\text{percent weight}) * 10 = \text{g/kg}$ .

### **4.1 – Concentration**

The results presented are for the amount of the element remaining in switchgrass samples after leaching treatment in distilled water at 20 °C for 40 minutes at four concentrations.

Experimental design was randomized complete block with three replications.

## *Nitrogen*

Mixed effects ANOVA showed no significant effect for leaching treatment on the amount of N remaining in switchgrass samples after leaching (Appendix 4.1.1). Tukey's post hoc comparison of all possible combinations of means showed no difference in the amount of N removed at any of the four concentrations compared to the control (Table 4.1.1).

Table 4.1.1 - Means comparison of percent weight of N remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	N remaining (% weight)	se
25 g/L	0.683 a	0.028
50 g/L	0.670 a	0.028
75 g/L	0.640 a	0.028
100 g/L	0.680 a	0.028
Control	0.690 a	0.028

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

## Calcium

Mixed effects ANOVA showed that leaching had a significant effect on reducing the amount of Ca in leached samples compared to control samples (Appendix 4.1.2). Tukey's post hoc comparison of all possible combinations of treatment means showed that there was a significant amount of Ca removed at each of the four concentrations compared to the control, however, there was no significant difference between any of the four concentrations (Table 4.1.2). Fourteen percent of the Ca was removed at 25 g/L, 8 % at 50 and 100 g/L and 11 % at 75 g/L.

Table 4.1.2 - Means comparison of percent weight of Ca remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	Ca remaining (% weight)	se
25 g/L	0.207 b	0.0033
50 g/L	0.220 b	0.0033
75 g/L	0.213 b	0.0033
100 g/L	0.220 b	0.0033
Control	0.240 a	0.0033

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

## *Phosphorus*

Mixed effects ANOVA showed that leaching had a significant effect on the amount of P remaining in switchgrass samples after treatment (Appendix 4.1.3). Tukey's post hoc comparison of all possible combinations of treatment means showed a significant amount of P was removed at each of the four concentrations compared to the control (Table 4.1.3). Seventy-five percent of the P was removed at a concentration of 25 g/L. Sixty-one percent of the P was removed at both 50 and 75 g/L concentrations and 54 % was removed at 100 g/L.

Table 4.1.3 - Means comparison of percent weight of P remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	P remaining (% weight)	se
25 g/L	0.0233 c	0.0033
50 g/L	0.0367 bc	0.0033
75 g/L	0.0367 bc	0.0033
100 g/L	0.0433 b	0.0033
Control	0.0933 a	0.0033

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

## *Potassium*

Mixed effects ANOVA showed that leaching had a significant effect on the amount of K remaining in switchgrass samples (Appendix 4.1.4). Tukey's post hoc comparison of all possible combinations of treatment means showed that a significant amount of K was removed at each of the four concentrations compared to the control (Table 4.1.4). Seventy-six percent of the K was removed at 25 g/L. Sixty four percent was removed at 50 g/L and 57 % was removed at 75 g/L but the two were not significantly different. Forty-eight percent removal was achieved at 100 g/L.

Table 4.1.4 - Means comparison of percent weight of K remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	K remaining (% weight)	se
25 g/L	0.183 d	0.014
50 g/L	0.273 c	0.014
75 g/L	0.327 c	0.014
100 g/L	0.397 b	0.014
Control	0.763 a	0.014

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

## *Magnesium*

Mixed effects ANOVA showed that leaching treatment had a significant effect on the amount of Mg remaining in switchgrass samples (Appendix 4.1.5). Tukey's post hoc comparison of all possible combinations of treatment means showed that Mg was significantly removed at all four concentrations compared to the control although there were no significant differences among the four concentrations (Table 4.1.5). One third of the Mg was removed at 25 g/L and 75 g/L on average, while one quarter was removed at 50 g/L and 100 g/L.

Table 4.1.5 - Means comparison of percent weight of Mg remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	Mg remaining (% weight)	se
25 g/L	0.0533 b	0.0021
50 g/L	0.0600 b	0.0021
75 g/L	0.0533 b	0.0021
100 g/L	0.0600 b	0.0021
Control	0.0800 a	0.0021

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

## *Sulphur*

Mixed effects ANOVA showed that leaching treatment had a significant effect on the amount of S remaining in switchgrass samples (Appendix 4.1.6). Tukey's post hoc comparison of all possible combinations of treatment means showed that S was significantly removed at all four concentrations compared to the control, but that there were no significant differences between the four concentration treatments (Table 4.1.6). Fifty percent of the S was removed at 25 g/L, 38 % at 50 and 75 g/L and 29 % at 100 g/L.

Table 4.1.6 - Means comparison of percent weight of S remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	S remaining (% weight)	se
25 g/L	0.0400 b	0.0047
50 g/L	0.0500 b	0.0047
75 g/L	0.0500 b	0.0047
100 g/L	0.0567 b	0.0047
Control	0.0800 a	0.0047

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

## *Chloride*

Mixed effects ANOVA showed that leaching treatment had a significant effect on the amount of Cl remaining in switchgrass samples after leaching (Appendix 4.1.7). Tukey's post hoc comparison of all possible combinations of treatment means showed that Cl was significantly removed at 25 g/L (59 %) and 50 g/L (55 %) from the control but not significantly reduced at 75 g/L (38 %) or 100 g/L (41 %) (Table 4.1.7).

Table 4.1.7 - Means comparison of percent weight of Cl remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	Cl remaining (% weight)	se
25 g/L	0.0400 b	0.0057
50 g/L	0.0433 b	0.0088
75 g/L	0.0600 ab	0.020
100 g/L	0.0567 ab	0.0067
Control	0.0967 a	0.012

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

### *N, Ca, P, K, Mg, S and Cl Combined*

When Mixed effects ANOVA was performed on the sum of the percent weights of N, Ca, P, K, Mg, S and Cl remaining in switchgrass samples, leaching treatment was found to have a significant effect (Appendix 4.1.8). Tukey's post hoc comparison of all possible combinations of treatment means showed that all concentration treatments were significantly different than the control. The 25 g/L treatment was significantly different than the 75 and 100 g/L treatments and the 50 g/L treatment differed from the 100 g/L treatment (Table 4.1.8). Forty percent of the concentration of these elements was removed at 25 g/L and 26 % was removed at 100 g/L. This amounted to 0.81 % and 0.53 % respectively, of the total dry weight of the switchgrass.

Table 4.1.8 - Means comparison of the sum of the percent weights of N, Ca, P, K, Mg, S and Cl remaining in switchgrass samples after leaching treatment at four concentrations of biomass/distilled water for 40 minutes, RCBD (n=3).

Treatment	Estimate (% weight)	se
25 g/L	1.23 d	0.031
50 g/L	1.35 cd	0.031
75 g/L	1.38 bc	0.031
100 g/L	1.51 b	0.031
Control	2.04 a	0.031

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

## **4.2 - Temperature Results**

The results presented are for the amount of the element remaining in switchgrass samples after leaching treatment of four residence times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C). Experimental design was randomized complete block with three replications. The results do not incorporate the control in the statistics. The control is from the concentration experiment and given for reference. The concentration chosen for the temperature experiments was 25 g switchgrass per liter of distilled water.

## Nitrogen

The results for the amount of N remaining in switchgrass samples after leaching at three temperatures and four residence times are shown in Figure 4.2.1. Mixed effects ANOVA for the percent weight of N remaining in switchgrass samples after leaching had no statistically significant results (Appendix 4.2.1). Regression analysis also showed no significant responses for N to time or temperature after exposure of switchgrass to water.

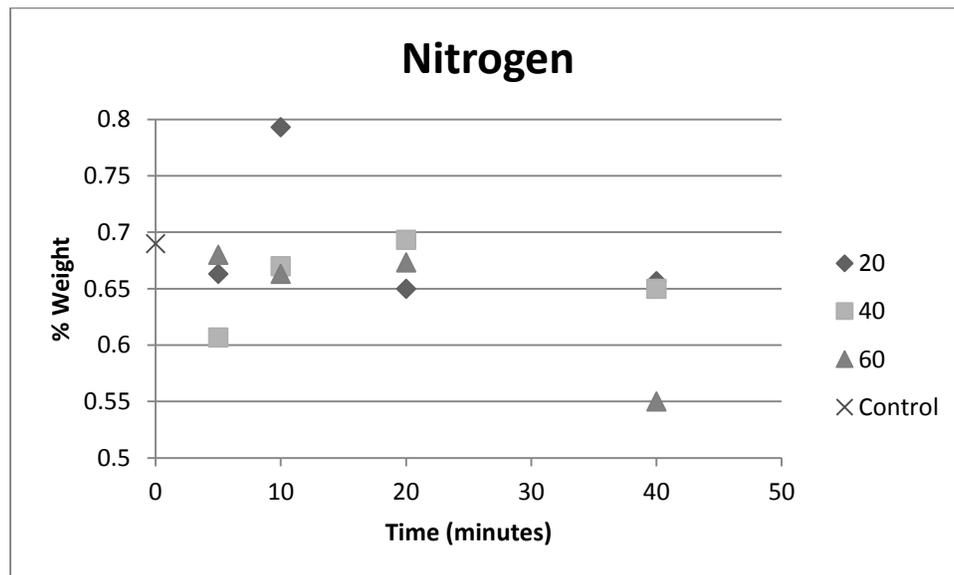


Figure 4.2.1 - Least square means for percent weight N remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.

## Calcium

The results for the amount of Ca remaining in switchgrass samples after leaching at three temperatures and four residence times are shown in Figure 4.2.2. Mixed effects ANOVA for Ca showed a significant effect for temperature but also showed a significant interaction effect between time and temperature (Appendix 4.2.2). Tests of simple effects showed that times differed significantly for 60 °C and temperatures differed significantly at 5 and 10 minutes (Appendix 4.2.3). Regression analysis of the Ca response showed that the time\*temperature linear partition was significant (Appendix 4.2.4), meaning that the temperature slopes were significantly different over time. The 40 °C slope was different than the 20 and 60 °C slopes (Figure 4.2.2, Appendix 4.2.5). The linear regression equation for 60 °C was significant (Appendix 4.2.5).

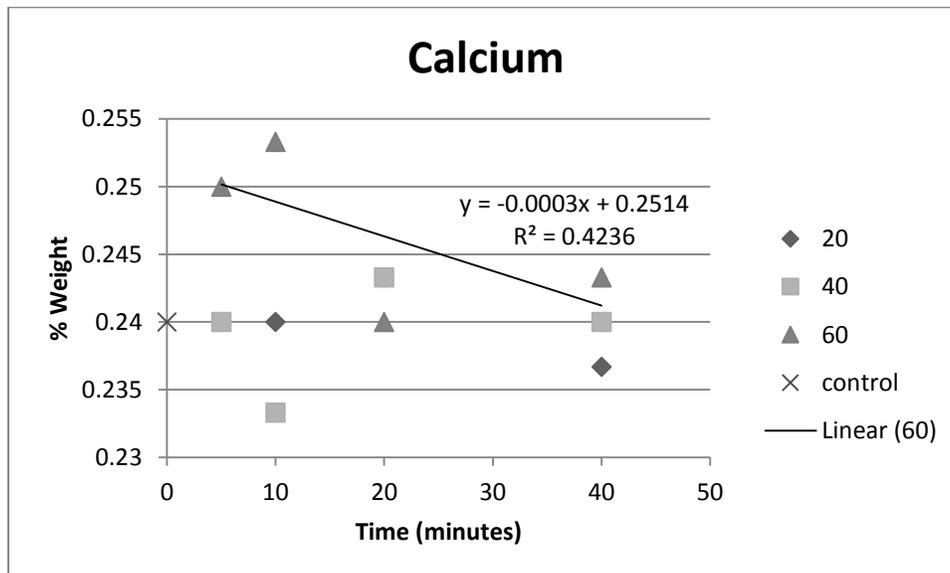


Figure 4.2.2 - Least square means for percent weight Ca remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.

## Phosphorus

The results for the amount of P remaining in switchgrass samples after leaching at three temperatures and four residence times are shown in Figure 4.2.3. Mixed effects ANOVA for P showed a significant time effect and time\*temperature interaction effect (Appendix 4.2.6). Tests of simple effects showed that times were significantly different for the 20 °C temperature and temperatures were significantly different at 5 minutes (Appendix 4.2.7). Regression analysis of the P response showed the time\*temperature linear partition to be significant (Appendix 4.2.8) meaning that the temperature slopes differed from one another over time. The three temperature slopes were significantly different from each other but only the 20 °C slope differed significantly from zero (Appendix 4.2.9) and thus was the only significant linear regression for the three temperatures.

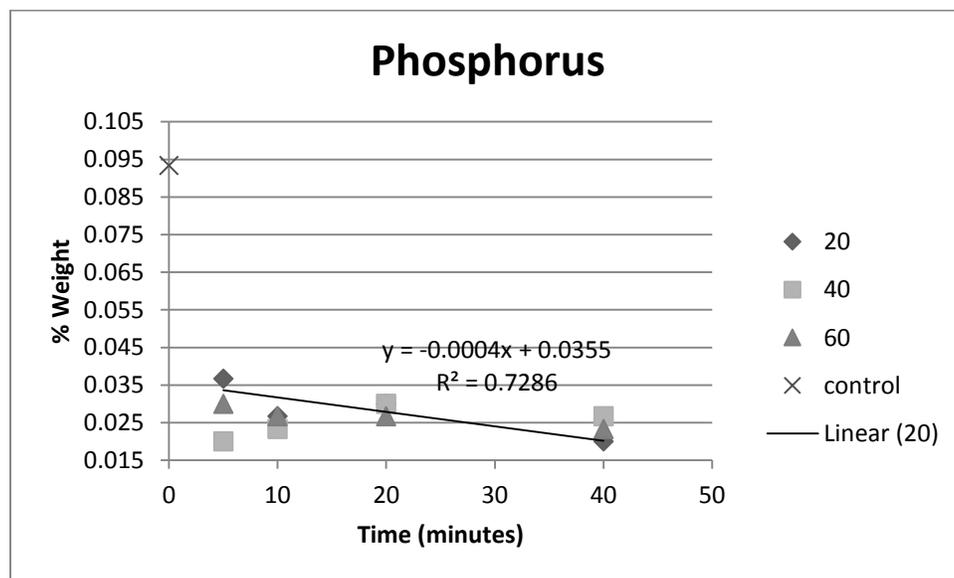


Figure 4.2.3 - Least square means for percent weight P remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60 °C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.

## Potassium

The results for the amount of K remaining in switchgrass samples after leaching at three temperatures and four residence times are shown in Figure 4.2.4. Mixed effects ANOVA for K showed there to be a significant effect for the temperature treatment as well as time (Appendix 4.2.10). The three temperature treatments were significantly different from each other and certain times differed from each other (Appendix 4.2.11). Regression analysis showed significant responses for time linear and quadratic, as well as temperature linear (Appendix 4.2.12).

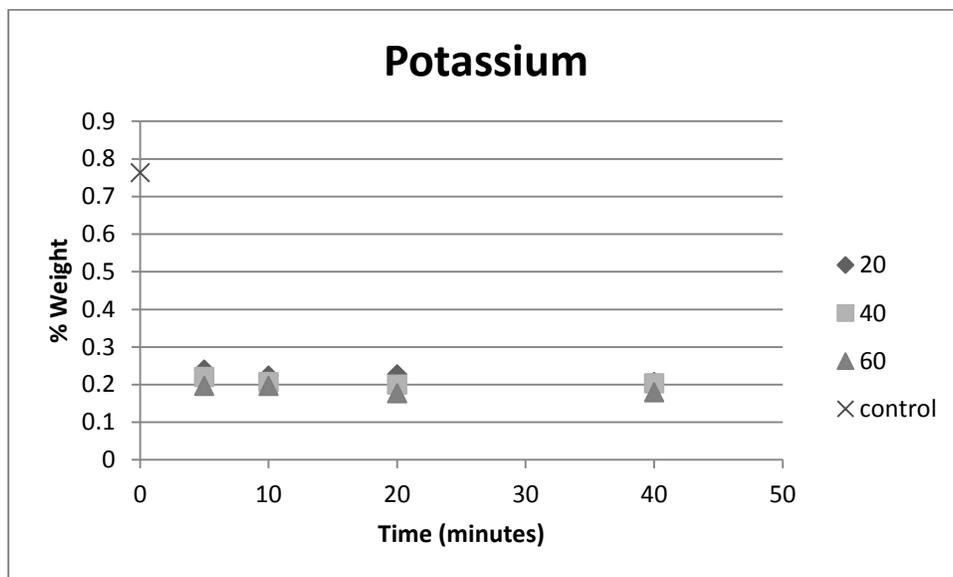


Figure 4.2.4 - Least square means for percent weight K remaining in a switchgrass sample after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.

A response surface analysis was performed in order to help visualize the two responses simultaneously. A surface plot is shown in Figure 4.2.5 and the response statistics are shown in

Appendix 4.2.13. The stationary point was a saddle point and eigenvector analysis showed the minimum response at 59.54 °C and 26.21 minutes (Appendix 4.2.14).

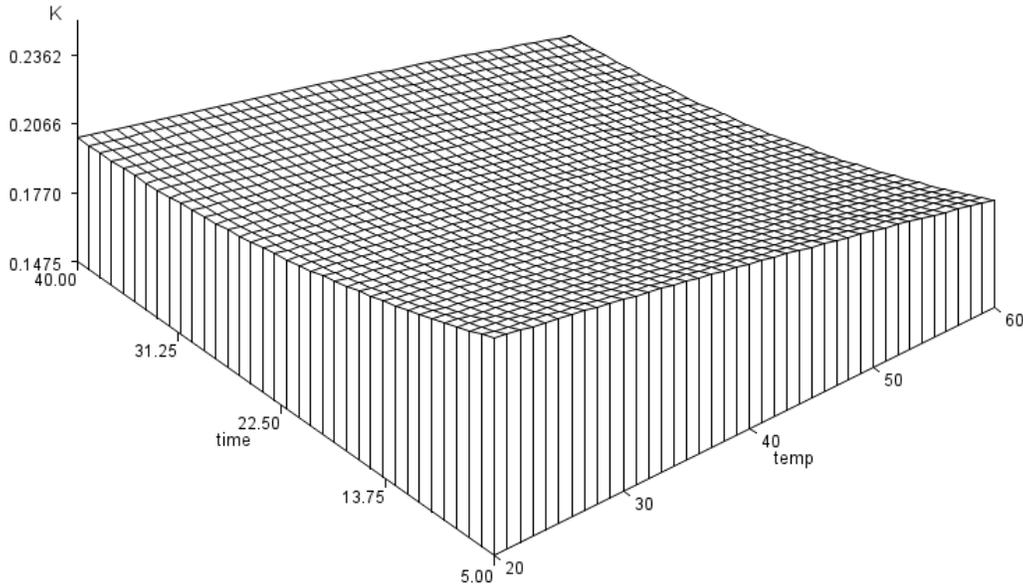


Figure 4.2.5 -Surface plot of time versus temperature for the amount of K remaining in switchgrass samples over four times (5, 10, 20 and 40 minutes) and three temperatures (20, 40, 60 °C) RCBD, n=3, 25 g switchgrass/L distilled water.

The linear regression for temperature is shown in Figure 4.2.6. The regression analysis showed the linear trend to be significant. This was evidenced by the high R-squared value (Figure 4.2.6).

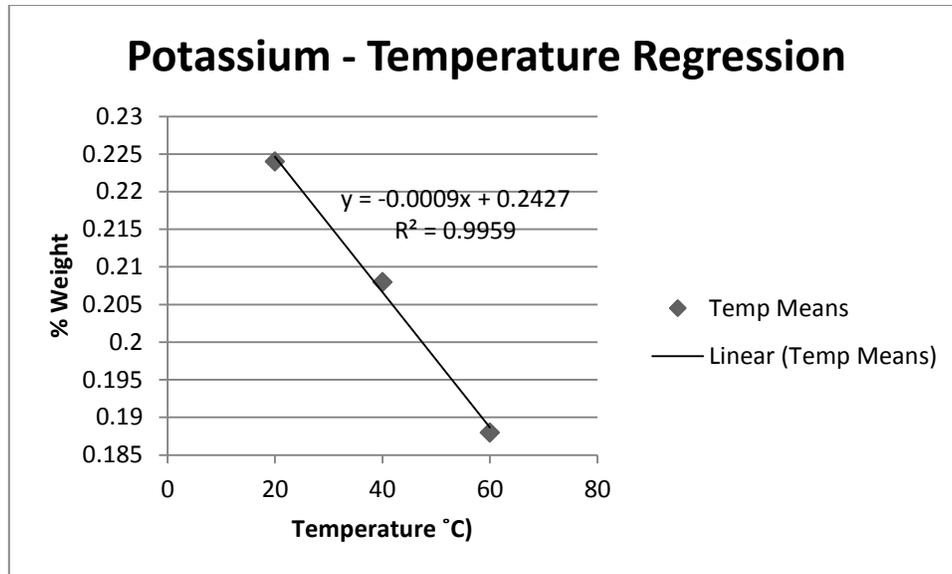


Figure 4.2.6 - Means and linear regression for the response of percent weight K in switchgrass compared to temperature of leaching solution in RCBD experiment (n=3) with three temperatures (20, 40, and 60 °), averaged over four times (5, 10, 20 and 40 minutes) at 25 g switchgrass/L distilled water.

## ***Magnesium***

The results for the amount of Mg remaining in switchgrass after leaching at three temperatures and four residence times are shown in Figure 4.2.7. Mixed effects ANOVA for Mg showed significant time, temperature and time\*temperature interaction effects (Appendix 4.2.15). Analysis of simple effects showed that times were significantly different at 20 and 40 °C and that temperatures differed at 5, 10 and 40 minutes (Appendix 4.1.16). Regression analysis showed a significant temperature\*time linear response (Appendix 4.2.17) meaning that the temperature slopes differed from one another across time. Forty degrees Celsius was significantly different from 20 and 60 °C which were not significantly different from each other. The only temperature that had a slope significantly different from zero was 20 °C making the regression model for 20 °C significant (Figure 4.2.7, Table 4.2.18)

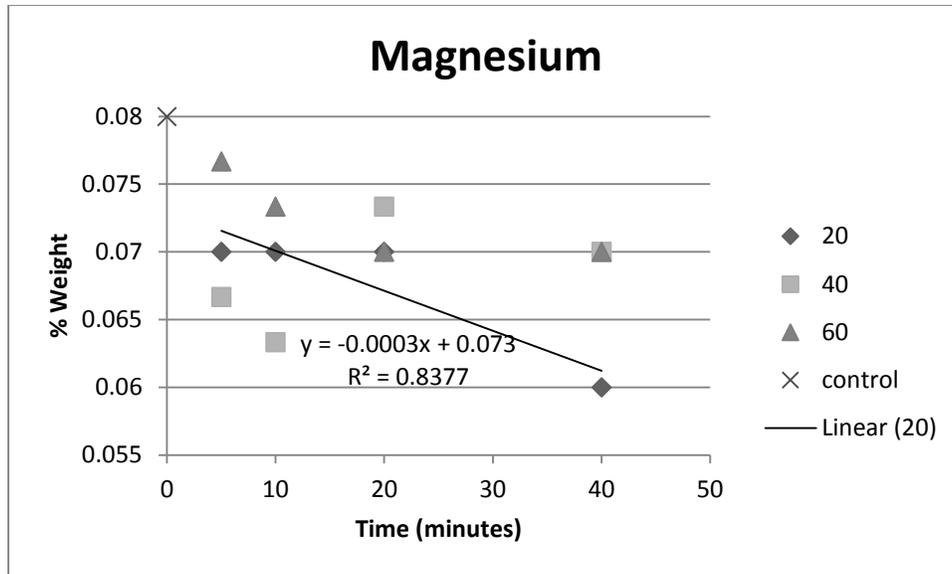


Figure 4.2.7 - Least square means for percent weight Mg remaining in a switchgrass sample after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60 °C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.

## *Sulphur*

The results for the amount of S remaining in switchgrass samples after leaching at three temperatures and four residence times are shown in Figure 4.2.8. Mixed effects ANOVA for S showed a significant effect for the temperature treatment (Appendix 4.2.19). Means for 20 and 60 °C were significantly different (Appendix 4.2.20). Regression analysis also showed a temperature linear response (Appendix 4.2.21) and the resulting linear regression comes very close to the mean values for each temperature (Figure 4.2.9).

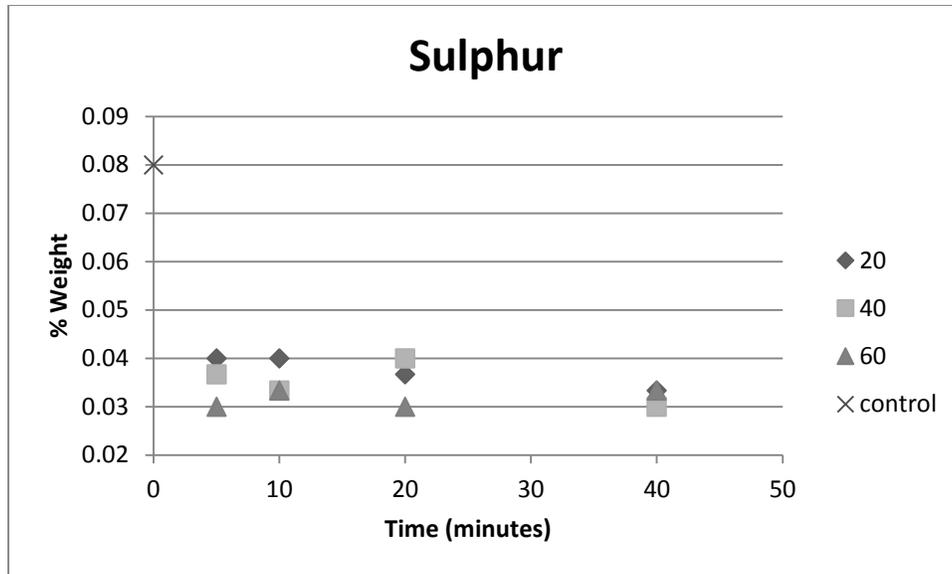


Figure 4.2.8 - Least square means for percent weight S remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.

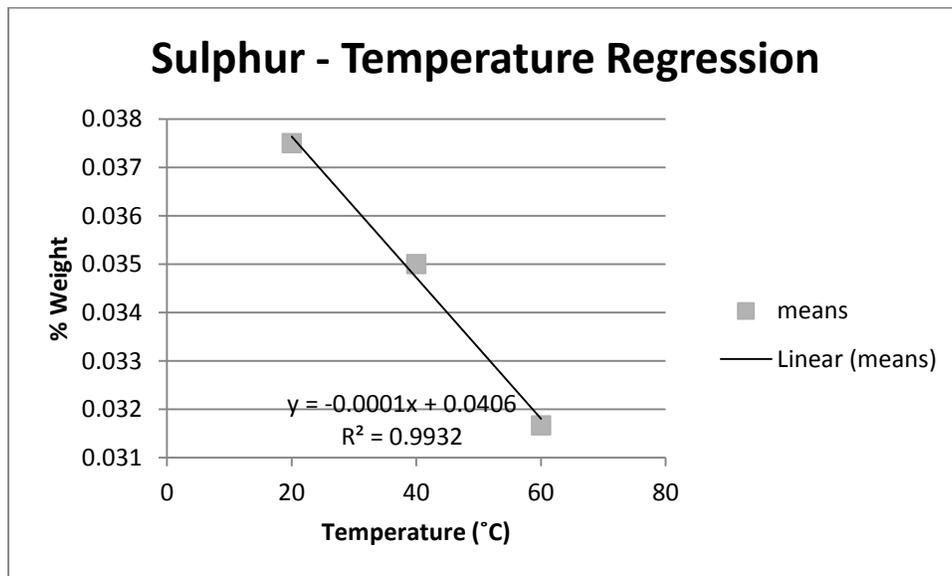


Figure 4.2.9 - Means and linear regression for the response of percent weight S in switchgrass compared to temperature of leaching solution in RCBD experiment (n=3) with four times (5, 10, 20 and 40 minutes) and three temperatures (20, 40 and 60°C) at 25 g switchgrass/L distilled water.

## Chloride

Results for the amount of Cl remaining in switchgrass are shown in Figure 4.2.10.

Analysis of variance for Cl showed no significant effects of time or temperature on the amount of Cl remaining in the switchgrass samples after leaching (Appendix 4.2.23).

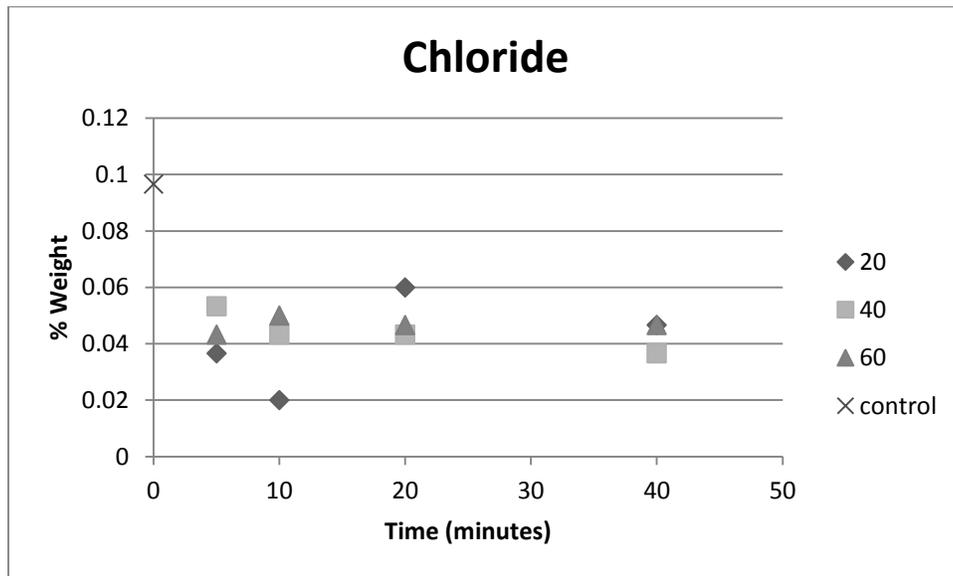


Figure 4.2.10 - Least square means for percent weight Cl remaining in switchgrass samples after leaching for four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60°C) with control shown at zero, RCBD, n=3, 25 g switchgrass/L distilled water.

## Conductivity

The results for the conductivity of filtered leachate removed from switchgrass samples treated at three temperatures and four residence times are shown in Figure 4.2.11. Mixed effects ANOVA showed time and temperature to be statistically significant predictors for conductivity (Appendix 4.2.24). Means comparisons using Tukey's test showed that the three temperatures

were significantly different from each other, and the four times were also significantly different from each other (Appendix 4.2.25). Temperature linear, time linear and time quadratic regression responses were detected (Appendix 4.2.26), modeled (Appendix 4.2.27) and plotted (Figure 4.2.11). A linear regression for temperature was also modeled (A-4.2.28) and plotted (Figure 4.2.12).

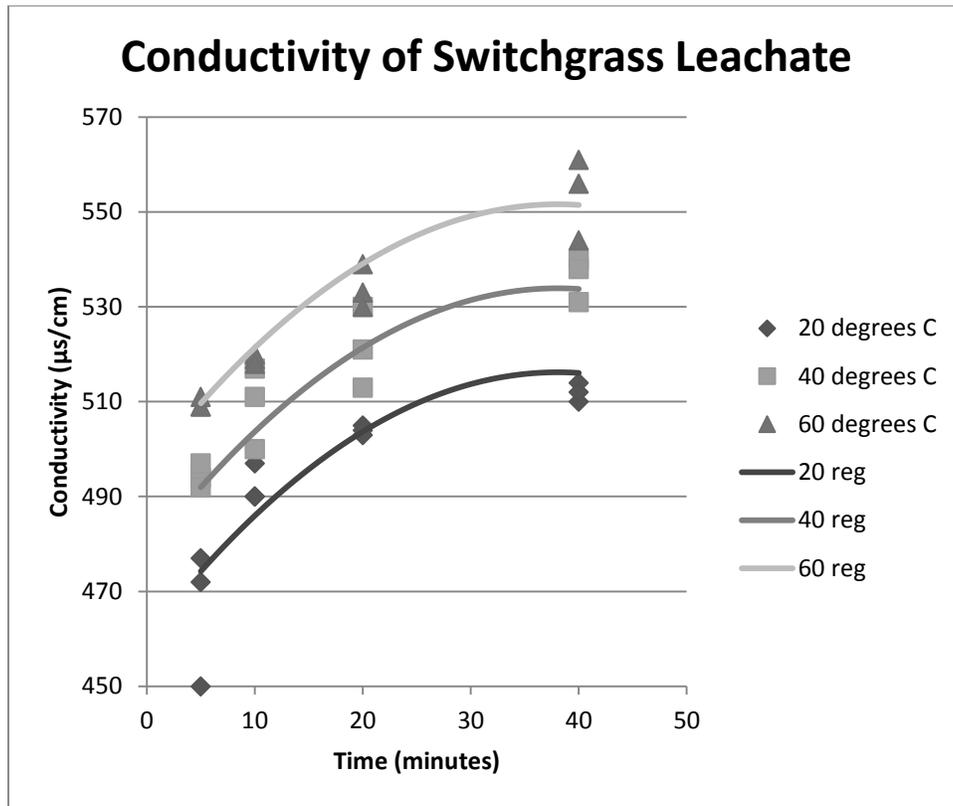


Figure 4.2.11 – Conductivity of leachate samples from RCBD experiment (n=3) with four residence times (5, 10, 20 and 40 minutes) and three temperatures (20, 40 and 60°C) at 25 g switchgrass/L of distilled water.

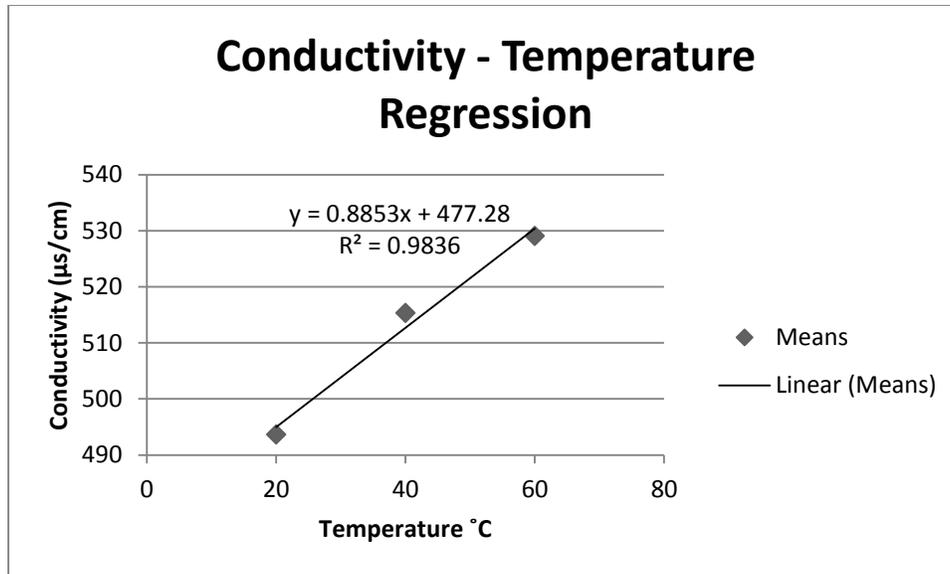


Figure 4.2.12 - Means and regression for the linear response for conductivity compared to temperature of leaching solution in RCBD experiment with four times and three temperatures at 25 g switchgrass/L distilled water (n=3).

### 4.3 Water Type Results

The results do not incorporate the control in the statistics. The control is from the concentration experiment and given for reference only. The concentration for the water type experiment was 25 g switchgrass per liter of distilled water.

#### *Nitrogen*

The results for the percent weight of N remaining in switchgrass samples after leaching in four water types at four residence times are shown in Figure 4.3.1. Mixed effects ANOVA for the percent weight of N remaining in switchgrass samples showed no significant effect for the water type on the amount of N remaining, however, the residence time was a significant effect (Appendix 4.3.1). Means comparison for residence time shows that 10 minutes differed

significantly from 20 and 40 minutes (Appendix 4.3.2). The orthogonal sub-partitions of water type and time showed time\*lack of fit time to be significant (Appendix 4.3.3), indicating a significant non-linear time relationship.

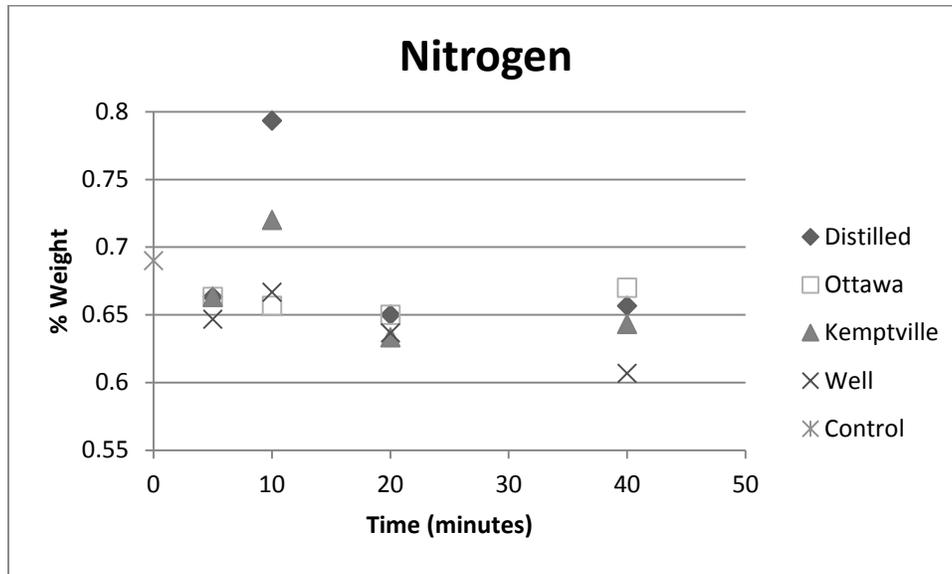


Figure 4.3.1 - Least square means for percent weight N remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

Table 4.3.1 - Means comparison for the percent weight of N remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

	Distilled	Ottawa	Kemptville	Well
Initial - water <sup>Z</sup>	<0.05	0.05	0.04	0.12
Initial - biomass <sup>Y</sup>	0.690	0.690	0.690	0.690
5 minutes	0.663 ab	0.663 ab	0.663 ab	0.647 ab
10 minutes	0.793 a	0.657 ab	0.720 ab	0.667 ab
20 minutes	0.650 ab	0.650 ab	0.633 ab	0.637 ab
40 minutes	0.657 ab	0.670 ab	0.643 ab	0.607 b
se	0.033	0.033	0.033	0.033

Means with the same letter are not significantly different with Tukey's HSD test at p<0.05.

<sup>Z</sup> Initial amount of N present in each water type before treatment (mg/L).

<sup>Y</sup> Percent weight of N in switchgrass samples before treatment.

## Calcium

The results for the percent weight of Ca remaining in switchgrass samples after leaching in four water types at four residence times are shown in Figure 4.3.2 and means comparisons are shown in Table 4.3.2. Mixed effects ANOVA for percent weight of Ca remaining in switchgrass samples after leaching showed time and water type to be significant effects (Appendix 4.3.4). The mean for 40 minutes was significantly different than the 20 minute mean (Appendix 4.3.5). The mean for samples leached in Ottawa water was significantly different from Kemptville water and well water, but not from distilled water (Appendix 4.3.5). Orthogonal sub-partitions showed time and type to have significant linear regression responses (Appendix 4.3.6). The regression solution coefficients are shown in Appendix 4.3.7.

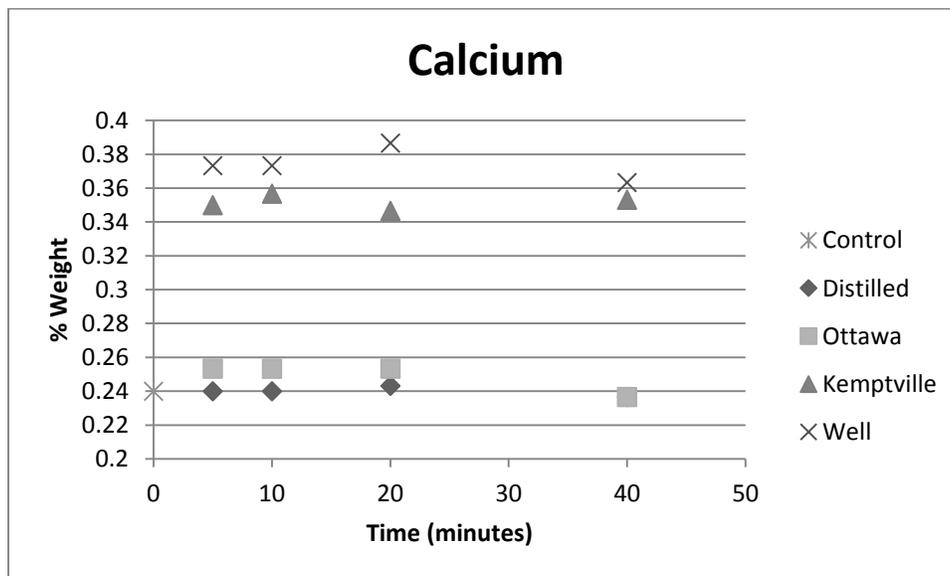


Figure 4.3.2 - Least square means for percent weight Ca remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

Table 4.3.2 - Means comparison for the percent weight of Ca remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

	Distilled	Ottawa	Kemptville	Well
Initial - water <sup>Z</sup>	0.0533	8.58	79.6	92.4
Initial - biomass <sup>Y</sup>	0.240	0.240	0.240	0.240
5 minutes	0.240 c	0.253 c	0.350 b	0.373 ab
10 minutes	0.240 c	0.253 c	0.357 b	0.373 ab
20 minutes	0.243 c	0.253 c	0.347 b	0.387 a
40 minutes	0.237 c	0.237 c	0.353 b	0.363 ab
se	0.0051	0.0051	0.0051	0.0051

Means with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

<sup>Z</sup> Initial amount of Ca present in each water type before treatment (mg/L).

<sup>Y</sup> Percent weight of Ca in switchgrass samples before treatment.

## ***Phosphorus***

The results for the percent weight of P remaining in switchgrass samples after leaching in four water types at four residence times are shown in Figure 4.3.3 and means comparisons are shown in Table 4.3.3. Mixed effects ANOVA for percent weight of P remaining in switchgrass samples after leaching showed time, water type and the time\*water type interaction to be significant effects (Appendix 4.3.8). Simple effects were significant for all times and water types except time was not a significant effect for well water (Appendix 4.3.9). The orthogonal sub-partition of time\*water type\*lack of fit time indicated a significant non-linear relationship (Appendix 4.3.10).

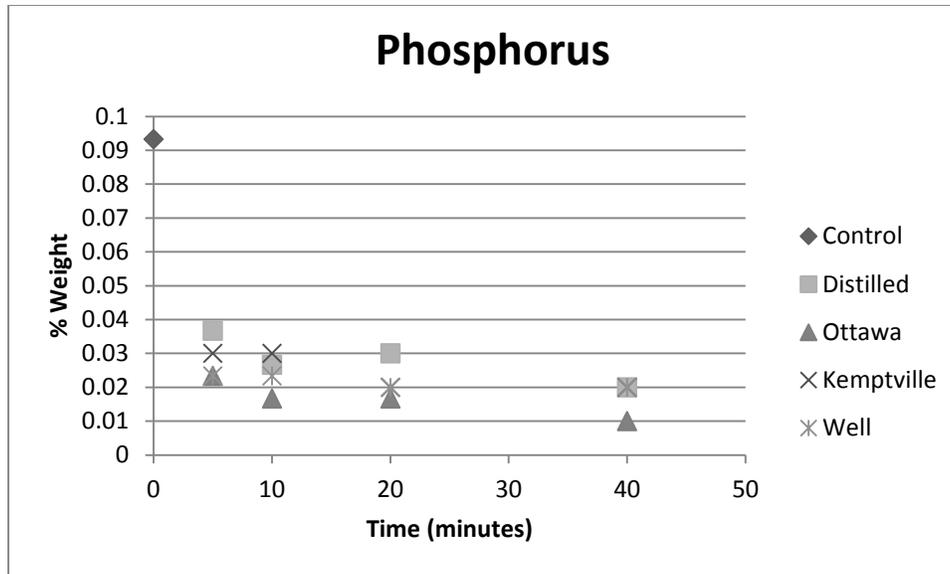


Figure 4.3.3 - Least square means for percent weight P remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

Table 4.3.3 - Means comparison for the percent weight of P remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

	Distilled	Ottawa	Kemptville	Well
Initial - water <sup>Z</sup>	<0.01	<0.01	<0.01	<0.01
Initial - biomass <sup>Y</sup>	0.0933	0.0933	0.0933	0.0933
5 minutes	0.0367 a	0.0233 bc	0.0300 ab	0.0233 bc
10 minutes	0.0267 abc	0.0167 cd	0.0300 ab	0.0233 bc
20 minutes	0.0300 ab	0.0167 cd	0.0200 bcd	0.0200 bcd
40 minutes	0.0200 bcd	0.0100 d	0.0200 bcd	0.0200 bcd
se	0.0022	0.0022	0.0022	0.0022

Means with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

<sup>Z</sup> Initial amount of P present in each water type before treatment (mg/L).

<sup>Y</sup> Percent weight of P in switchgrass samples before treatment.

## Potassium

The results for the percent weight of K remaining in switchgrass samples after leaching in four water types at four residence times are shown in Figure 4.3.4 and means comparisons are shown in Table 4.3.4. Mixed effects ANOVA for percent weight of K remaining in switchgrass samples after leaching showed time, water type and the time\*type interaction all to be significant (Appendix 4.3.11). Simple effects analysis showed the water types were significantly different at each time and that times were significantly different for Ottawa and distilled water types (Appendix 4.3.12). Orthogonal sub-partitions indicated a significant non-linear relationship (Appendix 4.3.13).

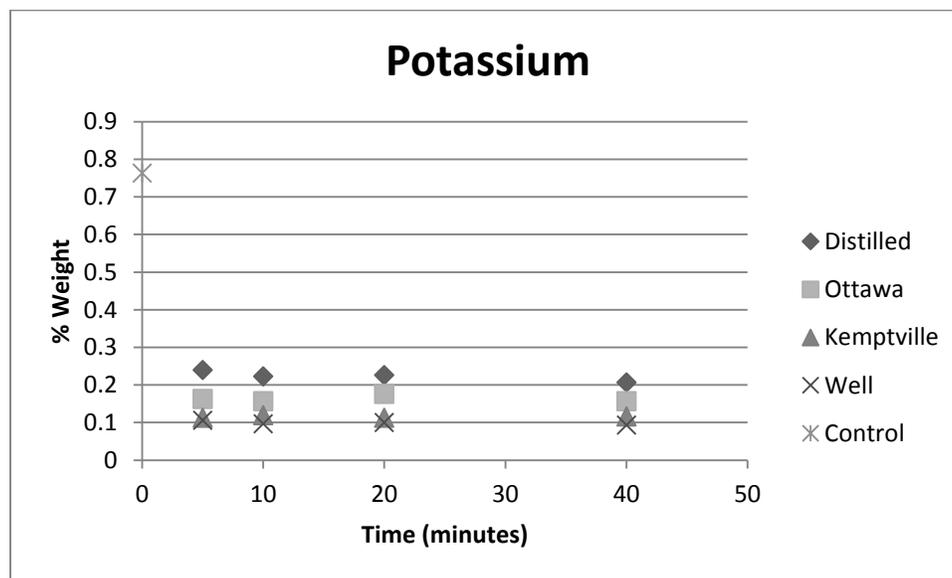


Figure 4.3.4 - Least square means for percent weight K remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

Table 4.3.4 - Means comparison for the percent weight of K remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

	Distilled	Ottawa	Kemptville	Well
Initial - water <sup>Z</sup>	<0.1	0.7	3.43	2.73
Initial - biomass	0.763	0.763	0.763	0.763
5 minutes	0.240 a	0.163 c	0.113 def	0.106 def
10 minutes	0.223 ab	0.157 c	0.120 d	0.097 ef
20 minutes	0.227 ab	0.177 c	0.113 def	0.100 def
40 minutes	0.207 b	0.157 c	0.116 de	0.0933 f
se	0.0044	0.0044	0.0044	0.0044

Means with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

<sup>Z</sup> Initial amount of K present in each water type before treatment (mg/L).

<sup>Y</sup> Percent weight of K in switchgrass samples before treatment.

## ***Magnesium***

The results for the percent weight of Mg remaining in switchgrass samples after leaching in four water types at four residence times are shown in Figure 4.3.5 and means comparisons are shown in Table 4.3.5. Mixed effects ANOVA for percent weight of Mg remaining in switchgrass samples after leaching showed time and water type to be significant (Appendix 4.3.14). The 40 minute mean differed from 5, 10 and 20 minutes, while all four water types had significantly different means (Appendix 4.3.15). Orthogonal regression partitions showed type, time and time quadratic to be significant predictors of Mg content (Appendix 4.2.16). However, the linear time coefficient for the model was not significant (Appendix 4.3.17).

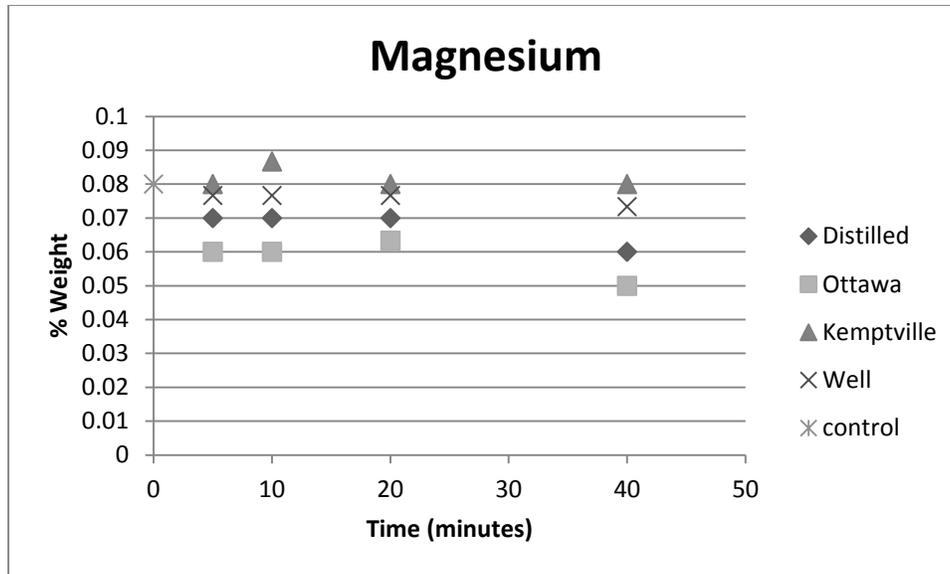


Figure 4.3.5 - Least square means for percent weight Mg remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

Table 4.3.5 - Means comparison for the percent weight of Mg remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

	Distilled	Ottawa	Kemptville	Well
Initial - water <sup>Z</sup>	0.01	2.12	37.9	34.8
Initial - biomass <sup>Y</sup>	0.08	0.08	0.08	0.08
5 minutes	0.0700 bcd	0.0600 de	0.0800 ab	0.0767 ab
10 minutes	0.0700 bcd	0.0600 de	0.0867 ab	0.0767 ab
20 minutes	0.0700 bcd	0.0633 cd	0.0800 ab	0.0767 ab
40 minutes	0.0600 de	0.0500 e	0.0800 ab	0.0733 bc
se	0.0020	0.0020	0.0020	0.002

Means with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

<sup>Z</sup> Initial amount of Mg present in each water type before treatment (mg/L).

<sup>Y</sup> Percent weight of Mg in switchgrass samples before treatment.

## Sulphur

The results for the percent weight of S remaining in switchgrass samples after leaching in four water types at four residence times are shown in Figure 4.3.6 and means comparisons are shown in Table 4.3.6. Mixed effects ANOVA for percent weight of S remaining in switchgrass samples after leaching showed water type and the time\*water type interaction to be significant (Appendix 4.3.18). Analysis of simple effects showed that the water types were significantly different at 5 and 40 minutes but not at 10 and 20 minutes and that time was a significant effect only for Ottawa water (Appendix 4.3.19). Orthogonal sub-partitions showed time and time\*type to be significant regression responses (Appendix 4.3.20). Regression coefficients are shown in Appendix 4.3.21.

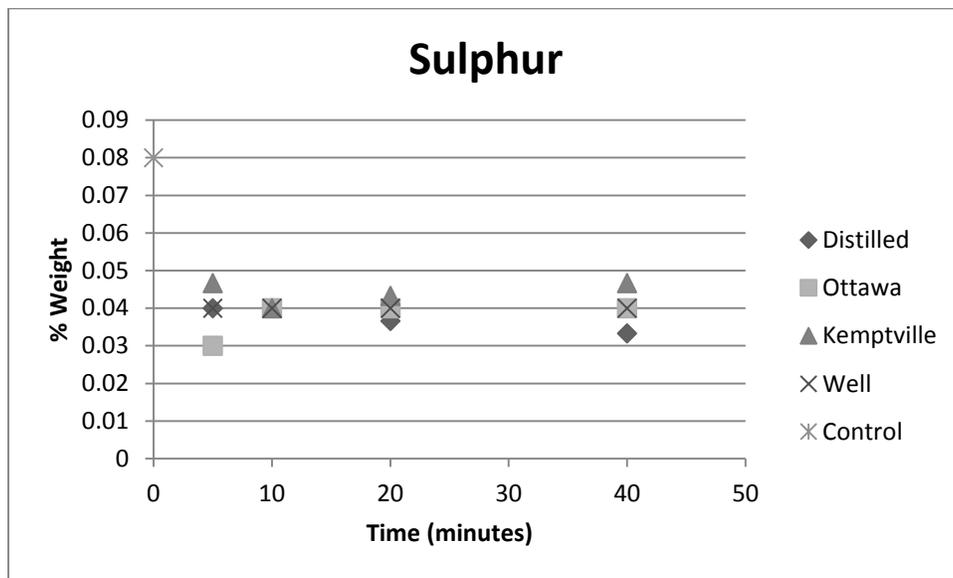


Figure 4.3.6 - Least square means for percent weight Ca remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

Table 4.3.6 - Means comparison for the percent weight of S remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

	Distilled	Ottawa	Kemptville	Well
Initial - water <sup>Z</sup>	<0.1	8.13	19.5	19.6
Initial - biomass <sup>Y</sup>	0.08	0.08	0.08	0.08
5 minutes	0.0400 abc	0.0300 c	0.0467 a	0.0400 abc
10 minutes	0.0400 abc	0.0400 abc	0.0400 abc	0.0400 abc
20 minutes	0.0367 abc	0.0400 abc	0.0433 ab	0.0400 abc
40 minutes	0.0333 bc	0.0400 abc	0.0467 a	0.0400 abc
se	0.0024	0.0024	0.0024	0.0024

Means with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

<sup>Z</sup> Initial amount of S present in each water type before treatment (mg/L).

<sup>Y</sup> Percent weight of S in switchgrass samples before treatment.

## *Chloride*

The results for the percent weight of Cl remaining in switchgrass samples after leaching in four water types at four residence times are shown in Figure 4.3.7 and means comparisons are shown in Table 4.3.7. Mixed effects ANOVA for Cl remaining in switchgrass samples after leaching showed time, water type and the time\*water type interaction to be significant (Appendix 4.3.22). Simple effects analysis showed that time was significantly different only for Kemptville water and that the water types were only significantly different at 5 minutes (Appendix 4.3.23). Orthogonal sub-partitions showed significant non-linear responses (Appendix 4.3.24).

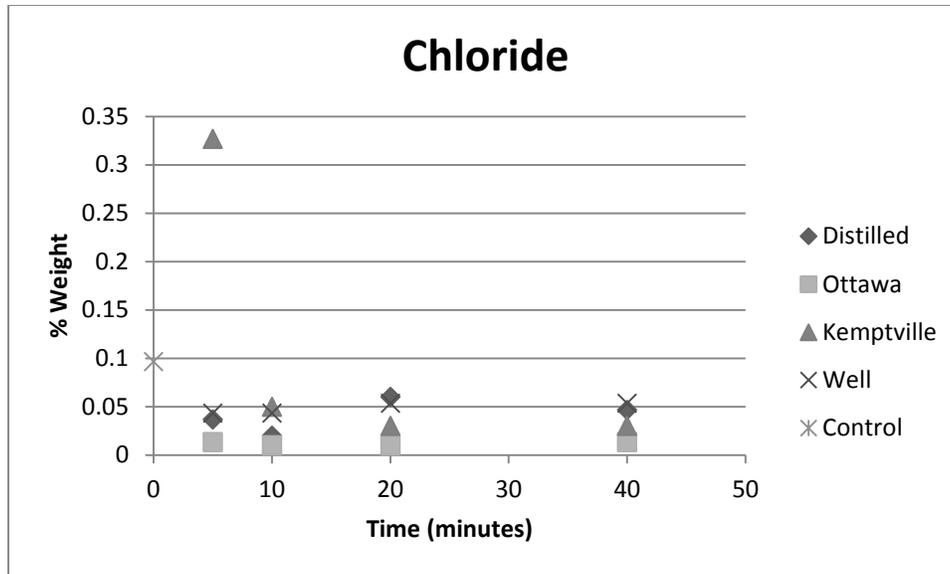


Figure 4.3.7 - Least square means for percent weight Cl remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

Table 4.3.7 - Means comparison for the percent weight of Cl remaining in switchgrass samples after leaching at 25 g switchgrass/L with four water types at four residence times, RCBD (n=3).

	Distilled	Ottawa	Kemptville	Well
Initial - water <sup>Z</sup>	<0.5	4.93	51.9	101.3
Initial - biomass <sup>Y</sup>	0.0967	0.0967	0.0967	0.0967
5 minutes	0.0367 b	0.0133 b	0.327 a	0.0433 b
10 minutes	0.0200 b	0.0100 b	0.0500 b	0.0433 b
20 minutes	0.0600 b	0.0100 b	0.0300 b	0.0533 b
40 minutes	0.0467 b	0.0133 b	0.0300 b	0.0533 b
se	0.025	0.025	0.025	0.025

Means with the same letter are not significantly different with Tukey's HSD test at p<0.05.

<sup>Z</sup> Initial amount of Cl present in each water type before treatment (mg/L).

<sup>Y</sup> Percent weight of Cl in switchgrass samples before treatment.

## Chapter 5 - Discussion

### 5.1 - Concentration

N is the only element that was not significantly leached at any one of the concentration treatments. N is likely to be bound up in organic molecules of particulate that are not broken down far enough to completely dissolve. This does not bode well for the economics of nutrient extraction for end use as concentrated fertilizer, since N is the most important element in commercial fertilizers. N also contributes to noxious emissions from combustion, but not to clinkering or slagging within boilers (Lewandowski and Kicherer 1997). Noxious emissions could potentially be captured from exhausts, but this would increase the cost of energy production accordingly. Harmful levels of N are generally considered to be anything above 1.0 % (Lewandowski and Kicherer 1997). So, although no significant amount of N could be leached in this process, the biomass is within acceptable limits at 0.69 % before treatment. Fall harvest plot-scale N levels from Adler et al. (2006) were similar at 0.62 %, and spring levels were also within range at 0.54 %.

Ca was removed at levels only up to 14 %, which was at a concentration of 25 g/L. Ca is considered to be one of the metals associated with fouling of boilers, as it lowers the ash melting point (Lewandowski and Kicherer 1997). Since this material was fairly old and had been overwintered in the field, much of the Ca may have already been returned to the soil, as the initial concentration was only 0.24 % compared to 0.436 % weight for plot-scale fall harvested switchgrass (Adler et al. 2006). Leaching does result in a slight improvement overall at each of the four concentrations compared to the control but the differences were not statistically significant.

P reductions of up to 75 % are promising, however, this was at 25 g/L. Only 54 % was removed at 100 g/L. P is one of the nutrients that is viable for concentration and resale as a liquid fertilizer, so this difference in extraction efficiency will have a direct economic impact on the feasibility of the nutrient removal process. Extraction at 50 g/L and 75 g/L were the same at 61 %, potentially allowing the 75 g/L concentration to be economically plausible. The level of P in this switchgrass feedstock was actually slightly higher at 0.093 % compared to 0.089 % for fresh fall cut at plot scale (Adler et al. 2006). Adler et al. (2006) found spring cut to be 0.052 %. This difference may be accounted for by a number of factors: field inconsistencies, prior cropping systems, different stem to leaf ratio in the representative sample, genotype, as Adler et al. (2006) used three varieties mixed together and finally, the lab method of determination.

K reductions of up to 76 % were achieved at the 25 g/L concentration. Removal at 100 g/L was significantly less at 48 %. This will clearly detract from the value of K as a recycled nutrient from the leachate for use in liquid fertilizers. K is also an alkali metal that contributes to clinkering and fouling of boilers. K levels were much higher in this study than the Adler (2006) study. The initial concentration of K was 0.763 % weight whereas Adler et al. (2006) observed 0.333 % weight in fall harvest and 0.056 % weight in plot-scale spring harvested switchgrass. The higher elemental concentration in this study may be accounted for by field inconsistencies, varying soil concentrations of K, prior cropping systems, different stem to leaf ratio in the representative sample, or different genotype. The determination methods also differed.

Mg is an alkali earth metal which can contribute to boiler fouling. Reductions of 25 and 34 % were seen. Fifty g/L and 100 g/L were equivalent at 25 % reduction while 25 g/L and 75 g/L were equivalent at 34 %, but the differences were not found to be statistically significant. This may be a result of experimental error. The numbers were also affected by the detection

limits for the test, as results were only given to one significant digit for Mg. Mg concentrations went from 0.08 % initially down to 0.05 or 0.06 % for each of the samples. The initial Mg concentration of 0.08 % weight was similar to Adler et al. (2006) spring harvest levels of 0.071 % weight.

S reductions were significant at all four concentrations compared to the control. Analysis shows reductions of up to 50 % at 25 g/L. There was high variability in the results and only one significant digit given for the percent weight. More experimentation is necessary to make broad conclusions regarding S as it contributes to noxious gas and particulate pollution. Lewandowski and Kicherer (1997) give the critical limit of S in biofuel, above which significant issues arise with S emission and raised flue-gas dew-points, to be less than 0.3 % weight. This level was achieved with all of the concentrations tested, and the initial value of 0.08 % weight was already well below the critical point making removal of S unnecessary to meet emission standards.

Reductions in Cl of up to 59 % were achieved at 25 g/L and 41 % of Cl was removed at 100 g/L, but these were not significantly different. Cl is one of the more important elements when it comes to fouling and corrosion of boilers. Cl is corrosive to boiler components. It also interacts with alkali and alkaline earth metals to facilitate fouling by lowering ash fusion temperatures. Lewandowski and Kicherer (1997) give a critical limit of 0.2 % for Cl, above which problems arise with corrosion and emissions. Control values and all concentrations in this experiment were below that critical limit. Untreated samples had an average Cl percent weight of 0.0967 %, similar to fall harvested plot-scale trials from Adler et al. (2006) which were 0.099 %. The lowest level achieved with treatment was at 25 g/L, which was 0.04 %. Adler et al. (2006) found levels were reduced to 0.027 % with a spring harvest, less than could be achieved in this experiment with spring harvested and heavily leached samples. These differences might

again be contributed to field inconsistencies, Cl concentration differences in the soil, prior cropping systems, stem to leaf ratio of the samples, genotype, and method of determination.

When the percent weights are summed together they exhibit an expected trend. At increasing concentrations, the amount of minerals left in the samples after leaching should approach the non-treatment levels, as diffusion becomes progressively more difficult when the solvent becomes increasingly saturated. Cennatek (2011a) suggested that 100 g/L to 125 g/L be used for miscanthus, in order to be economically feasible. Any concentration more dilute than this would be prohibitively costly for use with switchgrass, due to the increase in water that would have to be removed to make the nutrients concentrated enough to sell as fertilizer. An increase in concentration will clearly reduce the amount of minerals that will be able to be leached into the water, so there needs to be an assessment of which minerals are the most important, their economic value and the optimum concentration in order to maximize the economic feasibility. Furthermore, once the minerals are in the leachate there may be other methods that could be employed to economically extract the nutrients from the leachate for use as fertilizer, rather than simply concentrating the solution.

Conductivity was used as a proxy for leaching during the concentration trials and it gave a good indication as to the total amount of leaching taking place. However, wet chemistry lab results were used for the statistical analysis. When increasing the concentration of switchgrass in water there are a number of factors which could affect a potential linear trend in conductivity vs. concentration. A magnetic stir plate was used to stir the material at 65 rpm. The rpm setting of the stir plate is the rate at which the magnet within the plate spins. The rate at which the magnet within a vessel on top of the stir plate can be affected by the density of the substrate. For example, it takes more energy to stir a 100 g/L solution than it does to stir a 25 g/L solution,

therefore the agitation rate will not necessarily be consistent. The concentration of the solution also affects the rate at which the solution becomes thoroughly mixed and completely saturated. This variation could be avoided in future experiments by using a mechanical mixing mechanism as opposed to magnetic. Another challenge with the current experimental design, regarding conductivity measurements, was that using the same amount of water while increasing the amount of biomass caused reducing returns of the amount of water after filtration. This is due to the amount of water absorbed by the biomass. It was therefore necessary to analyze the biomass itself to determine accurate concentration trends.

## **5.2 - Temperature**

The amount of N remaining in switchgrass samples at all temperatures was below the 1.0 % critical limit given by Lewandowski and Kicherer (1997). Therefore, the guiding purpose for reducing N, by increasing temperature, is to recover and recycle nutrients back to the field. This could potentially reduce the amount of N fertilizer required to maintain sufficient yields, thereby increasing the efficiency of bioenergy production. Unfortunately, there is no statistically significant response of N to water temperature. Other enhancements to the process need to be considered such as increased agitation rate, decreasing particle size or an alternate solvent. Experimental error was as high as 25 % for 20 °C at 10 minutes and the analysis did contain an outlier.

Temperature had a significant effect on the amount of Ca leached from switchgrass samples and there was also an interaction effect. The slopes differed for the temperatures, and

the rate at which Ca was removed from the biomass was fastest for the highest temperature. This is the trend that one would expect to see for most minerals. The regression response for 40 °C actually showed an increase in the amount of Ca in the sample over time, although the slope did not differ significantly from zero (Figure 4.2.3). This might indicate a level of error in the sampling.

P had linear regression responses that were somewhat similar looking to Ca, although 20 °C was the only slope over time that differed significantly from zero. In the case of P, a much larger proportion of the pre-existing material was removed by the water in comparison to Ca. If control values could have been used for the regression, an exponential decay function could potentially have been found for P. This would show that almost all of the leaching occurred within the first five minutes, as indicated by Figure 4.2.3.

K and P had similar looking trends in Figures 4.2.3 and 4.2.4. Again it appears to be a decay function. By looking at Figure 4.2.4 one can infer that the decay process happens very rapidly over the first 5 minutes and then levels off to almost nothing over the next 35 minutes, even though the time means were significantly different in some cases (Appendix 4.2.11). Response surface analysis resulted in a saddle point at 59.54 °C indicating the temperature to base future experiments around in order to find the true minimum response. Economic analysis would prove that to be unnecessary. There is a linear response to temperature as depicted in Figure 4.2.6. However, at 20 °C, 71 % of the existing K is already being leached. Increasing the temperature another 40 °C nets only an additional 4.1 % removal. The cost to heat the water would far outweigh the marginal improvement in K removal.

The Mg response is somewhat less clear. There is a time\*temperature interaction effect and a significant temperature\*time linear regression response, meaning that the temperature slopes over time differ from one another and from zero in some cases. Interestingly, the greatest Mg reduction was at 20 °C (at 40 minutes). This might result from interactions with other minerals that are more readily leached into water at higher temperatures. These elements might form Mg salts that could reattach to the switchgrass. This is merely speculative, but potential for this type of dynamic interaction within the leachate over time is certainly possible, and there are other instances where it seems plausible such as with Cl. Mg is an alkaline earth metal which is known to form eutectic compounds, subsequently reducing the ash melting point, so these reactions are of interest.

S is an important contributor to noxious gas pollution from direct combustion power generation. The critical limit of S concentration in biomass for combustion is  $< 0.3\%$  (Lewandowski and Kicherer 1997). The percent weight of S in the untreated switchgrass was already considerably below this level at  $0.08\%$ . The amount of S that could be removed by increasing the heat nearly followed a linear relationship. Increasing the temperature of the water solvent reduced the amount of S at a rate of  $0.00015\%$  per degree. Since starting values were already significantly below the critical limit, and since S is not often used in fertilizers and thus will not add recycle value to the leachate, there is no need to raise the temperature of the solvent to reduce S. The cost to heat the water would outweigh any economic benefit in this case.

The amount of Cl in biomass for direct combustion is of the utmost importance, as Cl facilitates the reactions of alkali and alkaline earth metals to reduce ash melting temperatures, and Cl also directly causes corrosion of boiler components. Presence of Cl also facilitates the

release of HCL (Lewandowski and Kicherer). The critical limit for the presence of Cl to prevent these issues is 0.2 % (Lewandowski and Kicherer 1997). Concentrations between 0.1 to 0.2 % cause boiler temperatures to be kept low, in order to reduce issues caused by Cl, thereby reducing the efficiency of the process. In this case the untreated biomass had an average percent weight of Cl of 0.097 %. The leaching process decreased this to a minimum of 0.02 % which happens to occur at 20 °C. Temperature had no significant effect on the process and initial concentrations were below the critical levels. Therefore, offsite leaching is not necessary to reduce Cl in this particular feedstock.

It is interesting to note how the various minerals seemed to respond differently to leaching exposure at different temperatures. The maximum leaching response sometimes occurred at 20 °C, for example in the cases of Mg and Cl. Regression responses were quite varied across the different minerals. The measure of conductivity however, may have given a clear indication as to the collective response. Conductivity is a measure of the total ion activity and thus gives a measure of the combined response of the minerals to leaching.

Conductivity gives a clear relationship for temperature. Conductivity represents the cumulative leaching response of all the minerals in water. The minerals will contribute to the conductivity based on the ionic charge of the particle. Figure 4.2.11 and Table 4.2.26 show that, based on conductivity measurements, the collective leaching response to temperature was linear whereas the time response was quadratic. Therefore, the maximum amount that could be leached was determined by temperature. The response is based on what is leaching into the water, i.e. the conductivity of those elements, as opposed to what is remaining in the biomass, i.e. percent weight remaining. One would expect the inverse of the exponential to maximum trend seen for

conductivity for the percent weight remaining in the biomass, i.e. exponential decay. The difference in the conductivity trend compared to the trend of the individual nutrients gives evidence of complex interactions of ions in solution.

### **5.3 Water Type**

The switchgrass seemed to absorb a slight amount of N from the water initially then release it again. The amount of N remaining in switchgrass went up from 5 to 10 minutes for three of the four water types. The mean across the four water types was not significantly different for 5 and 10 minutes but it was significantly lower at 20 and 40 minutes than it was at 10 minutes (Table 4.3.2). This may potentially have been due to experimental error, however, Ca, Mg and Cl showed some indication that they may have had a similar response. Initial amounts of N in the water were similar for the four water types and the amount of leaching was similar across the four water types and four times (Table 4.3.4). The amount of N removed was fairly low, showing maximum removal of 12 % at 40 minutes with well water. It was surprising to see that the maximum response occurred with well water, as this water type generally had the highest concentration of minerals and by far the highest conductivity. The non-linear response found significant in Table 4.3.5 is likely a form of exponential decay. Figure 4.3.1 shows visually that an exponential decay response for N is likely for Ottawa and well water, and perhaps for the other two water types as well.

Ca showed an expected trend in relation to the initial amount of the given element in the water before treatment. The less Ca there was in the water initially, the less Ca was left in the grass after leaching. However, the level of Ca in the grass did not go down compared to

untreated levels (Figure 4.3.2). In fact, the percent weight of Ca in the biomass generally increased upon exposure to each of the water types, with the exception of distilled water, which maintained about the same percent weight of Ca after treatment. Ca showed linear responses that appeared to be independent of initial concentrations of Ca in the biomass (Figure 4.3.2). The response was, however, clearly affected by the water type and the concentration of minerals in the water. An increase in the amount of Ca in the material is undesirable as Ca will form eutectic compounds, thereby lowering the ash fusion temperature. This should be considered when selecting a leaching solvent.

Regression for P gave evidence of a non-linear relationship. Although it looks like a cubic relationship, it is almost certainly a case of exponential decay. P and K had very similar results. Both are likely examples of exponential decay. The element is quickly leached, exhibiting nearly all of the leaching in the first five minutes. These two minerals are important in fertilizer, so it is promising that most of the leaching happens very quickly. The interaction of time and water type was very similar for the two minerals also. Further experiments should look at time intervals between zero and five minutes to better understand the fast leaching dynamic and establish accurate values for the leaching rate.

Mg appears to follow a quadratic relationship, as quadratic regressions were significant for all of the water types. If the regression were to include the control values there might be more evidence here for a decay function. The amount of Mg in the water follows the order: distilled < Ottawa < well < Kemptville. The amount of Mg remaining in the switchgrass samples after leaching follows the order Ottawa < distilled < well < Kemptville. Kemptville water is high in Mg and leaches out the least amount, well water follows the same trend, whereas distilled and

Ottawa are reversed in order. This is potentially due to the presence of other elements in the Ottawa water which cause the interactions to be more complex.

It is possible with S that the amount went way down in the biomass in the first five minutes then slowly came back up due to reactions in the leachate, re-absorption into the tissue or residue adhering to the tissue. It was more likely another case of exponential decay. With distilled water the level did drop at 20 and 40 minutes, giving evidence for exponential decay. The other three water types had considerably higher amounts of most minerals tested so there was far more potential for reactions of ions in solution to form molecules which could bond to tissue surfaces or reabsorb into the tissue due to diffusion potential.

For Cl it appeared that the different water types displayed different relationships. All orthogonal partitions were significant, indicating that there was a significant non-linear relationship. Ottawa water looked quite linear. Distilled water looked quadratic. They were likely experiencing exponential decay. The up and down nature of the response was possibly due in part to experimental error. It also might have been due to complex interactions in solution. Cl is highly prone to ionization and interacts with many of the other minerals in this solution. The amount of leaching of Cl did not appear to be directly related to the amount of Cl in the water before treatment. However, the results for Kemptville water are intriguing. At 5 minutes the amount of Cl in the biomass was very high (0.50, 0.18 and 0.30 % mean of 0.327). At 10 minutes the mean dropped significantly to 0.0500 %. Since the biomass only started with a percent weight of 0.0967 %, it has clearly absorbed Cl after 5 minutes. Well water does not show this trend even though the initial amount of Cl in well water was around twice that of the Kemptville water samples which were analysed. This was perhaps due to inconsistency in the water used and a spike in the amount of Cl in the water that was used for the leaching treatments

compared to those sent out for analysis. The water was drawn from the tap and placed into 10 L sealed containers but some samples came from different containers.

Although there were patterns in the data that reflected a direct relationship between the amount of an element in the water type before leaching exposure and the amount of that element that was removed from the switchgrass upon exposure, this was often not the case. This was likely due to reactions between ions which created salts, and potential inconsistency in the water used for the leaching treatments. Eventually the solution should reach a point of homeostasis in relation to the solubility of the ionic compounds present.

## Chapter 6 - Conclusions

Hypothesis one was rejected since the concentration of switchgrass in water directly affected the efficiency of removal from the plant tissue for some minerals. The results for this experiment indicated that leaching treatment removed a statistically significant amount of Ca, P, K, Mg and S at all concentrations. Cl was significantly removed only at 25 and 50 g/L concentrations and N was not significantly removed at any concentration. Varying the concentration of the solution did not have a significant effect on the amount of Ca, Mg, S and Cl removed but it did have a significant effect on the amount of P and K removed. Higher amounts of leaching occurred at lower concentrations for P and K. Cumulatively, as indicated by the conductivity trend with all minerals combined, higher concentrations result in reduced leaching. This is due to a reduced opportunity for any given particle to come into contact with water that has not yet reached its ionic and particulate carrying capacity.

The amount of water used in the process will directly affect the efficiency of the process. Increasing the amount of water will increase the amount of leaching for some minerals but will also increase the amount of space required by the reactor. Higher water usage would also make the nutrient retrieval process more expensive, since more water would have to be concentrated through reverse osmosis or other methods. Any increase in size and the space used by extraction and retrieval equipment will directly increase the capital cost. The amount of water used is therefore directly cost proportionate. The associated cost will also depend on water sourcing, which is affected by local regulations, water cost and availability.

This report did not cover agitation rate. Increasing the agitation rate may reduce the amount of water necessary to extract sufficient amounts of nutrients from the switchgrass by

increasing mass transfer rates. Also, a report by Cennatek (2011b) found that 80 % of the water can be recycled through subsequent runs perpetually, without a loss of efficiency in the process, as long as 20 % new water is added for each run.

Hypothesis two was rejected since temperature did affect the amount of leaching from the switchgrass into the water for some minerals. One would expect that solvent temperature would have a direct and significant effect on the ability of any given nutrient to leach into solution. The temperature trend for leaching rate and total amount leached was often not what one would expect during these trials. Temperature did have a significant effect on the amount of Ca, K, Mg and S which could be leached, but it was not necessarily higher temperatures which caused higher leaching. For K and S, the highest average amount of leaching occurred at the 60 °C temperature. However, for Ca the trend was 40 < 60 < 20 °C and for Mg the trend was 40 < 20 < 60 °C. The maximum amount of a nutrient leached at times occurred at the lowest temperature of 20 °C (Mg at 40 minutes and Cl at 10 minutes). This may be due to the influence of other ions that were leached into solution which then reacted with the element of interest. The residence time was a significant factor for P, K and Mg but not for N, Ca, S and Cl.

No cases were found where temperature was required to reduce the amount of a nutrient in the biomass below the critical limits set out by Lewandowski and Kicherer (1997) for N, S, and Cl. However, according to said paper the levels are difficult to quantify for K, Ca and ash. Given the results from this experiment one can conclude that switchgrass of this quality should be viable for use in direct combustion energy generation without heating of solvent. Given that this material was heavily leached already from over-winter field exposure it would not require industrial leaching to be a viable fuel. Future studies should focus on fall-cut switchgrass so that

the issues with over-wintering of crops can potentially be avoided by using an industrial leaching process.

Hypothesis three was rejected since the mineral content of the water used did affect leaching ability for six of the seven minerals. The initial concentration of minerals in the water had a significant effect on the amount that could subsequently be leached into the water for Ca, P, K, Mg, S and Cl but not for N. Residence time was a significant effect for N, Ca, P, K, Mg and Cl but not for S. Interaction effects were significant for P, K, S and Cl meaning that comparisons of water type differed depending on the duration of the leaching treatment.

The ability of a mineral to leach from switchgrass into water does not appear to be determined by the amount of that particular mineral in the water before treatment. Ca mostly followed the expected trend where less Ca in the water meant more Ca could be leached into the water; K, Mg, S and Cl did not. Minerals also rarely followed the expected trend of higher leaching in water with lower cumulative mineral concentrations (conductivity). Ca showed the expected trend to some extent, where higher amounts of cumulative mineral content in the solvent meant less Ca could be leached out of the biomass. This was not the case for N, P, K, Mg, S, or Cl. K followed the opposite trend where higher cumulative mineral content of the water increased the amount of leaching from the biomass. The lack of a pattern with most of these minerals is likely due to interactions among ions in the water which are unclear from the current research. Future experiments could focus on changing the concentration of one or a few minerals in the water in order to understand the reactions. Starting by having only one mineral in the solution and varying its concentration, followed by adding in others, could help build an understanding of these reactions in a controlled manner. Undoubtedly there are many interactions taking place which are difficult to analyse with so many minerals in solution.

The removal and recovery of nutrients from miscanthus has been calculated to reduce the cost of electricity from direct combustion of biomass from \$136 to \$84/MWh (Cennatek 2011b). This is due to higher energy density of pellets and associated increases in combustion efficiency. The preceding research should help in future research and in contributing to decisions on parameters used in an industrial leaching process for switchgrass.

For this particular switchgrass under these conditions, an industrial nutrient removal process is not recommended, as the levels of the nutrients are acceptable. For switchgrass that was harvested and dried under the same conditions but still had unacceptable nutrient levels in the biomass, an industrial leaching process with 100 g/L concentration at 20 °C using distilled water, or tap water with a low conductivity (< 200 µs/cm) and a residence time of 5-20 minutes would be recommended to sufficiently remove these minerals to acceptable levels. Area specific trials should focus on concentrations greater than 100 g/L at room temperature and with the purest water source locally available in order to determine the best parameters for industrial leaching processes involving switchgrass.

## Literature Cited

- Adler, P.A., Sanderson, M.A., Boateng, A.A., Weimer, P.J. and H.G. Jung. 2006. Biomass yield and biofuel quality of switchgrass harvested in fall or spring. *Agronomy Journal*. 98: 1518-1525.
- Ajayi, K. T. and A.A. Akande. 2012. Effect of fouling on heat transfer surfaces in boilers. *Journal of Emerging Trends in Engineering and Applied Sciences*. 3(2): 383-388.
- Alig, R., Latta, G., Adams, D. and B. McCarl. 2010. Mitigating greenhouse gases: The importance of land base interactions between forests, agriculture, and residential development in the face of changes in bioenergy and carbon prices. *Forest Policy and Economics*. 12(1): 67-75.
- Allison, G.G., Morris, C., Lister, S.J., Barraclough, T., Yates, N., Shield, I. and I.S, Donnison. 2012. Effect of N fertiliser application on cell wall composition in switchgrass and reed canary grass. *Biomass and Bioenergy*. 40: 19-26.
- Anderson, E.K., Parrish, A.S., Boigt, T.B., Owens, V.N., Hong, C. and D.K. Lee. 2013. Nitrogen fertility and harvest management of switchgrass for sustainable bioenergy feedstock production in Illinois. *Industrial Crops and Products*. 48: 19-27.
- Bransby, D.I., Ward, C.Y. Rose, P.A., Sladden, S.E. and D.D. Kee. 1989. Biomass production from selected herbaceous species in the southeastern USA. *Biomass*. 20: 187-197.
- Cannell, M.G.R. 2003. Carbon sequestration and biomass energy off set: Theoretical, potential and achievable capacities globally, in Europe and the UK. *Biomass and Bioenergy*. 24:97–116.
- CLI - Canada Land Inventory: Soil Capability for Agriculture. 2013. [Online]. Retrieved May 25, 2015 from: <http://sis.agr.gc.ca/cansis/publications/maps/cli/1m/agr/index.html>.
- Cennatek - Cennatek Bioanalytical Services. 2011a. Feasibility of improving biomass combustion through extraction of nutrients. [Online]. Retrieved Sept. 25, 2013 from: <http://www.ofa.on.ca/uploads/userfiles/files/20110709%20cennatek%20ofa%20report-feasibility%20of%20improving%20biomass%20combustion%20through%20extraction%20of%20nutrients.pdf>.
- Cennatek - Cennatek Bioanalytical Services. 2011b. Optimization and scale-up of liquid nutrient extraction and recovery process. [Online]. Retrieved Sept. 25 from: <http://www.ofa.on.ca/uploads/userfiles/files/optimization%20and%20scale-up%20of%20liquid%20nutrient%20extraction%20and%20recovery%20process%20raac.pdf>.

- Chamberlain, J.F., Miller, S.A. and J.R. Frederick. 2010. Using DAYCENT to quantify on-farm GHG emissions and N dynamics of land use conversion to N-Managed switchgrass in the Southern U.S. *Agriculture, Ecosystems and Environment*. 141: 332-341.
- Chapman, I. 2014. The end of Peak Oil? Why this topic is still relevant despite recent denials. *Energy Policy*. 64: 93-101.
- Collins, H.P., Smith, J.L., Fransen, S., Alva, A.K., Kruger, C.E. and D.M. Granatstein. 2010. Carbon sequestration under irrigated switchgrass (*Panicum virgatum* L.) production. *Soil Science Society of America Journal*. 74: 2049–2058.
- Culman, S.W., DuPont, S.T., Glover, J.D., Buckley, D.H., Fick, G.W., Ferris, H. and T.E. Crews. 2010. Long-term impacts of high-input annual cropping unfertilized perennial grass production on soil properties and belowground food webs in Kansas, USA. *Agriculture, Ecosystems & Environment*. 137(1): 13-24.
- Dien, B.S., Jung, H.G., Vogel, K.P., Casler, M.D., Lamb, J.F.S., Weimer, P.J., Iten, L., Mitchell, R.B., and G. Sarath. 2006. Chemical composition and response to dilute-acid pretreatment and enzymatic saccharification of alfalfa, reed canarygrass, and switchgrass. *Biomass Bioenergy* (in press).
- Fike, J.H., Parrish, D.J. Wolf, D.D., Balasko, J.A., Green, J.T., Rasnake, M. and J.H. Reynolds. 2006. Switchgrass production for the upper southeastern USA: influence of cultivar and cutting frequency on biomass yields. *Biomass and Bioenergy*. 30(3): 207-213.
- Gamble, J.D., Jungers, J.M., Wyse, D.L., Johnson, G.A., Lamb, J.A. and C.C. Sheaffer. 2015. Harvest date effects on biomass yield, moisture content, mineral concentration, and mineral export in switchgrass and native polycultures managed for bioenergy. *Bioenergy Research*. 8:740–749.
- Girouard, P. and R. Samson. 1997. Evaluation of haymaking equipment to harvest switchgrass/Part II. REAP Canada. [Online]. Retrieved Nov. 18, 2013 from: [http://www.reap-canada.com/online\\_library/feedstock\\_biomass/12-Switchgrass%20Harvest%20Study%20\\_Girouard%20and%20Samson%201997\\_.pdf](http://www.reap-canada.com/online_library/feedstock_biomass/12-Switchgrass%20Harvest%20Study%20_Girouard%20and%20Samson%201997_.pdf).
- Guretzky, J.A., Biermacher, J.T., Cook, B.J., Kering, M.K. and J. Mosali. 2011. Switchgrass for forage and bioenergy: harvest and N rate effects on biomass yields and nutrient composition. *Plant Soil*. 339: 69-81.
- Hadders, G. and R. Olsson. 1997. Harvest of grass for combustion in late summer and in spring. *Biomass and Bioenergy*. 12(3): 171–175.
- Han, F. X., King, R. L., Lindner, J. S., Yu, T., Durbha, S. S., Younan, N. H. and M. J. Plodinec. 2011. Nutrient fertilizer requirements for sustainable biomass supply to meet U.S. bioenergy goal. *Biomass and Bioenergy*. 35(1): 253-262.

- Huo, Y., Wernick, D.G. and J. C. Liao. 2012. Toward N neutral biofuel production. *Current Opinion in Biotechnology*. 23(3): 406-413.
- Hwang, S., Epplin, F.M., Lee, B. and R. Huhnke. 2009. A probabilistic estimate of the frequency of mowing and baling days in Oklahoma USA for the harvest of switchgrass for use in biorefineries. *Biomass and Bioenergy*. 33: 103701045.
- IEA - International Energy Agency. 2015. Oil Market Report. [Online]. Retrieved Mar. 14, 2015 from: <https://www.iea.org/oilmarketreport/omrpublic/>.
- IPCC - Intergovernmental Panel on Climate Change. 2013. Climate change 2013: the physical science basis. [Online]. Retrieved Oct. 16 2013 from: <http://www.ipcc.ch/report/ar5/wg1/#.Uo90gS2EgcA>.
- Janzen, H.H., Campbell, C.A., Brandt, S.A., Lafond, G.P. and L. Townley-Smith. 1992. Division S-3 - soil microbiology & Biochemistry. *Soil Science Society of America*. 56: 1799-1806.
- Jenkins, B.M., Bakker, R.R. and J.B. Wei. 1996. On the properties of washed straw. *Biomass and Bioenergy*. 10(4): 177-200.
- Jenkins, B.M., Baxter, L.L., Miles Jr., T.R. and T.R. Miles. 1998. Combustion properties of biomass. *Fuel Processing Technology*. 54: 17-46.
- Jones, J. Benton Jr. 2003. Agronomic Handbook: Management of Crops, Soils, and Their Fertility. CRC Press: Boca Raton, Florida.
- Keeling, C.D., Bacastow, R.B., Carter, A.F., Piper, S.C., Whorf, T.P., Heimann, M., Mook, M.G. and H. Roeloffzen. 1989. A three dimensional model of atmospheric CO<sub>2</sub> transport based on observed winds: observational data and preliminary analysis .In: Peterson, D.H., editor. *Aspects of climate variability in the Pacific and the Western Americas, Geophysical Monograph*. 55: 165 –235.
- Kell, D.B. 2011. Breeding crop plants with deep roots: their role in sustainable carbon, nutrient and water sequestration. *Annals of Botany*. 108 (3): 407-418.
- Khatib, H. 2012. IEA world energy outlook 2011 – a comment. *Energy Policy*. 48: 737-743.
- Kludze, H., Deen, B. and A. Dutta. 2013. Impact of agronomic treatments on fuel characteristics of herbaceous biomass for combustion. *Fuel Processing Technology*. 109: 96-102.
- Kumar, A. and S. Sokhansanj. 2007. Switchgrass (*Panicum virgatum*, L.) delivery to a biorefinery using integrated biomass supply analysis and logistics (IBSAL) model. *Bioresource Technology*. 98: 1033-1044.
- Lal, R. 2004. Soil carbon sequestration to mitigate climate change. *Geoderma*. 123(1):1-22.

- Lee, D.K. and A. Boe. 2005. Biomass production of switchgrass in Central South Dakota. *Crop Science*. 45: 2583-2590.
- Lee, J., Pedroso, G., Linqvist, B.A., Putnam, D. VanKessel, C. and J. Six. 2012. Simulating switchgrass biomass production across ecoregions using the DAYCENT model. *GCB Bioenergy*. 4: 521-533.
- Lestander T.A. and C. Rhén. 2005. Multivariate NIR spectroscopy models for moisture, ash and calorific content in biofuels using bi-orthogonal partial least squares regression. *Analyst*. 130(8): 1182-1189.
- Lewandowski, I. and A. Kicherer. 1997. Combustion quality of biomass: practical relevance and experiments to modify the biomass quality of *Miscanthus x giganteus*. *European Journal of Agronomy*. 6(3-4): 163-177.
- Lewandowski, I., Scurlock, J.M.O., Lindvall, E. and M. Christou. 2003. The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe. *Biomass Bioenergy*. 25: 335–361.
- Liebig, M.A., Johnson, H.A., Hanson, J.D. and A.B. Frank. 2005. Soil carbon under switchgrass stands and cultivated cropland. *Biomass and Bioenergy*. 28: 347–354.
- Liu, X. and X.T.Bi. 2011. Removal of inorganic constituents from pine barks and switchgrass. *Fuel Processing Technology*. 92 (7): 1273-1279.
- Ma Z., Wood C.W. and D.I. Bransby. 2001. Impact of row spacing, N rate, and time on carbon partitioning of switchgrass. *Biomass and Bioenergy*. 20: 413–419.
- Ma Z., Wood C.W. and D.I. Bransby. 2000. Impacts of soil management on root characteristics of switchgrass. *Biomass and Bioenergy*. 18: 105–112.
- Madakadze, I.C., Coulman, B.E., Mcelroy, A.R., Stewart, K.A. and D. L. Smith. 1998. Evaluation of selected warm-season grasses for biomass production in areas with a short growing season. *Bioresource Technology*. 65: 1-12.
- Madakadze, I.C., Stewart, K., Peterson, P.R., Coulman, B.E. and D.L. Smith. 1999. Switchgrass biomass and chemical composition for biofuel in Eastern Canada. *Agronomy Journal*. 91: 696-701.
- Marschner, H. 1995. Mineral Nutrition of Higher Plants. Second Edition. Academic Press. Harcourt Brace & Company Publishers: London, England.
- McKendry, P. 2002a. Energy production from biomass (part 1): overview of biomass. *Bioresource Technology*. 83: 37-46.

- McKendry, P. 2002b. Energy production from biomass (part 3): gasification technologies. *Bioresource Technology*. 83: 55-63.
- McLaughlin, S.B. and L.A. Kszos. 2005. Development of switchgrass (*Panicum virgatum*) as a bioenergy feedstock in the United States. *Biomass and Bioenergy*. 28: 515-535.
- Miller, R.G. and S.R. Sorrell. 2013. The future of oil supply. *Philosophical Transactions of the Royal Society*. 372
- Monti, A., Di Virgilio, N., and G. Venturi. 2008. Mineral composition of six major energy crops. *Biomass and Bioenergy*. 32: 216-223.
- Murphy, D.J. and C.A.S. Hall. 2011. Energy return on investment, peak oil, and the end of economic growth in 'Ecological Economics Reviews.' Robert Costanza, Karin Limburg & Ida Kubiszewski, Eds. *Annals of the New York Academy of Science*. 1219: 52-72.
- NRDC. 2008. The cost of climate change. [Online]. Retrieved April 10, 2015 from: [www.nrdc.org/globalWarming/cost/cost.pdf](http://www.nrdc.org/globalWarming/cost/cost.pdf).
- Ogden, C.A., Ileleji, K.E., Johnson, K.D. and Q. Wang. 2010. In-field direct combustion fuel property changes of switchgrass harvested from summer to fall. *Fuel Processing Technology*. 91: 266-271.
- Parrish, D., and J. Fike. 2005. The biology and agronomy of switchgrass for biofuels. *Critical Reviews in Plant Sciences*. 24(5): 423-459.
- Parrish, D.J., Fike, J.H., Bransby, D. I., and R. Samson. 2008. Establishing and managing switchgrass as an energy crop. [Online]. Retrieved April 10, 2015 from: [http://www.nrcs.usda.gov/Internet/FSE\\_PLANTMATERIALS/publications/npmptn3-13079.pdf](http://www.nrcs.usda.gov/Internet/FSE_PLANTMATERIALS/publications/npmptn3-13079.pdf).
- Paul, E.A. 2007. Soil microbiology, ecology, and biochemistry. Third Edition. Elsevier. Burlington, MA USA.
- REAP - Resource Efficient Agricultural Production, Canada. 2008. ARF07 Project: Optimization of switchgrass management for commercial fuel pellet production. Submitted to OMAFRA. [Online]. Retrieved Nov. 18, 2013 from: [http://www.reap-canada.com/online\\_library/feedstock\\_biomass/Optimization%20of%20switchgrass%20management%20for%20commercial%20fuel%20pellet%20production%20\(Samson%20et%20al.,%202007\).pdf](http://www.reap-canada.com/online_library/feedstock_biomass/Optimization%20of%20switchgrass%20management%20for%20commercial%20fuel%20pellet%20production%20(Samson%20et%20al.,%202007).pdf).
- Samson, R., Mani, S., Boddey, R., Sokhansanj, S., Quesada, D., Urquiaga, S. and C. Ho Lem. 2005. The potential of C 4 perennial grasses for developing a global BIOHEAT industry. *Critical Reviews in Plant Sciences*. 24(5): 461-495.

- Samson, R., 2007. Switchgrass Production in Ontario: A Management Guide. Resource Efficient Agricultural Production (REAP) - Canada, 4 pages.
- Shahandeh, H., Chou, C.Y., Hons, F.M., and M.A. Hussey. 2011. Nutrient partitioning and carbon and N mineralization of switchgrass plant parts. *Communications in Soil Science and Plant Analysis*. 42(5): 599-615.
- Shen, J., Zhu, S. Liu, X., Zhang, H. and J. Tan. 2010. The prediction of elemental composition of biomass based on proximate analysis. *Energy Conversion and Management*. 51: 983-987.
- Song, F., Zhao, J., and S.M. Swinton. 2011. Switching to perennial energy crops under uncertainty and costly reversibility. *American Journal of Agricultural Economics*. 93(3): 764-779.
- Stamler, S.B. 2009. REAP Canada. [Online]. Retrieved Nov. 5 from: <http://gis.lrs.uoguelph.ca/AgriEnvArchives/bioenergy/canbio/BaileyStamler.pdf>.
- Thomason, W.E., Raun, W.R., Johnson, G.V., Taliaferro, C.M., Freeman, K.W., Wynn, K.J. and R.W. Mullen. 2004. Switchgrass response to harvest frequency and time and rate of applied N. *Journal of Plant Nutrition*. 27: 1199-1226.
- Tilman, D., Socolow, R., Foley, J.A., Hill, J., Larson, E., Lynd, L., Pacala, S., Reilly, J., Searchinger, T., Somerville, C., and R. Williams. 2009. Beneficial biofuels - the food, energy and environment trilemma. *Science*. 325: 270-271.
- Tonn, B., Dengler, V., Thumm, U., Piepho, H.-P., and W. Claupein. 2011. Influence of leaching on the chemical composition of grassland biomass for combustion. *Grass and Forage Science*. 66: 464-473.
- Tonn, B., U. Thumm, and W. Claupein. 2010. Potential of leaching to optimize fuel quality of semi-natural grassland biomass. Proceedings of the 23<sup>rd</sup> General Meeting of the European Grasslands Federation, Kiel, Germany. 307-309.
- Tubeileh, A., Rennie, T.J., Kerr, A., Saita, A. and C. Patanè. 2014. Biomass production by warm-season grasses as affected by N application in Ontario. *Agronomy Journal*. 106(2): 416-422.
- Turn, S.Q., Kinoshita, C.M. and D.M. Ishimura. 1997. Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching, *Biomass and Bioenergy*. 12: 241-252.
- USDA - United States Department of Agriculture (USDA). 2009. [Online]. Retrieved June 19, 2015 from: [http://www.nrcs.usda.gov/Internet/FSE\\_PLANTMATERIALS/publications/npmptn3-13079.pdf](http://www.nrcs.usda.gov/Internet/FSE_PLANTMATERIALS/publications/npmptn3-13079.pdf).

- Venturi, P., Monti, A., Piani, I. and G. Venturi. 2004. Evaluation of harvesting and post-harvesting techniques for energy destinations of switchgrass. 2nd World Conference on Biomass for Energy, Industry and Climate Protection.
- Vogel, K.P. 1996. Energy production from forages (or American agriculture back to the future). *Journal of Soil and Water Conservation*. 5: 137-139.
- Watson, P.A., Parton, W.J., Power, A.G. and M.J. Swift. 1997. Agricultural intensification and ecosystem properties. *Science*. 277: 504-509.
- Weimer, P.J., B.S. Dien, T.L. Springer, and K.P. Vogel. 2005. In vitro gas production as a surrogate measure of the fermentability of cellulosic biomass to ethanol. *Applied Microbiology and Biotechnology*. 67: 52-58.
- Woli, K.P., David, M.B., Tsai, J., Voight, T.B., Darmody, R.G. and C.A. Mitchell. Evaluating silicon concentrations in biofuel feedstock crops miscanthus and switchgrass. *Biomass and Bioenergy*. 35: 2807-2813.
- Wright, L.T., Wright, L. and A. Turhollow. 2010. Switchgrass selection as a "model" bioenergy crop: A history of the process. *Biomass & Bioenergy*. 34(6): 851-868.

## Appendix 1

Appendix 1 – Percent weight of elements remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Conc	Block	Cond	N(%)	Ca(%)	P(%)	K(%)	Mg(%)	Zn(ppm)	Mn(ppm)
0	1		0.7	0.24	0.1	0.77	0.08	4.18	39.94
0	2		0.7	0.24	0.09	0.75	0.08	2.27	40.21
0	3		0.67	0.24	0.09	0.77	0.08	3.02	41.1
25	1	527	0.73	0.21	0.03	0.19	0.06	0.1	31.32
25	2	512	0.73	0.2	0.02	0.18	0.05	0.1	29.91
25	3	515	0.59	0.21	0.02	0.18	0.05	0.1	30.33
50	1	956	0.63	0.22	0.03	0.28	0.06	0.1	32.41
50	2	976	0.67	0.22	0.04	0.27	0.06	0.1	32.07
50	3	967	0.71	0.22	0.04	0.27	0.06	0.1	31.91
75	1	1372	0.67	0.21	0.04	0.34	0.05	0.1	30.67
75	2	1393	0.64	0.22	0.04	0.36	0.06	0.1	32.6
75	3	1380	0.61	0.21	0.03	0.28	0.05	0.1	30.14
100	1	1776	0.62	0.23	0.04	0.42	0.06	0.1	33.39
100	2	1758	0.72	0.22	0.05	0.41	0.06	0.1	32.33
100	3	1734	0.7	0.21	0.04	0.36	0.06	0.1	31.8
Conc	Block	Cond	Cu(ppm)	Fe(ppm)	S(%)	Cl(%)	B(ppm)		
0	1		2.91	68.82	0.07	0.09	4.47		
0	2		2.46	75.37	0.09	0.11	3.23		
0	3		2.84	75.23	0.08	0.09	2		
25	1	527	2.52	33.52	0.04	0.04	0.61		
25	2	512	2.11	29.79	0.04	0.05	1.21		
25	3	515	1.84	35.21	0.04	0.03	0.61		
50	1	956	1.69	37.97	0.04	0.06	1.17		
50	2	976	1.39	38.71	0.05	0.03	1.14		
50	3	967	2.05	40.31	0.06	0.04	0.57		
75	1	1372	2.35	42.76	0.04	0.03	0.57		
75	2	1393	1.77	49.22	0.05	0.05	0.54		
75	3	1380	1.92	34.34	0.06	0.1	0.56		
100	1	1776	2.37	45.02	0.06	0.08	1.09		
100	2	1758	2	48.23	0.05	0.04	0.59		
100	3	1734	1.93	49.3	0.06	0.05	0.56		

Conc (concentration)

Cond (conductivity)

## Appendix 2

Appendix 2 – Percent weight of elements remaining in switchgrass samples in a two factor RCBD (n=3) experiment with 4 leaching times (5, 10, 20 and 40 minutes) and 3 leaching temperatures (20, 40 and 60 °C) at 25 g switchgrass/L water.

Time	Temp	Block	N%	CA%	P%	K%	MG%	ZN	MN
control	control	1	0.7	0.24	0.1	0.77	0.08	4.18	39.94
control	control	2	0.7	0.24	0.09	0.75	0.08	2.27	40.21
control	control	3	0.67	0.24	0.09	0.77	0.08	3.02	41.1
5	20	1	0.67	0.24	0.03	0.23	0.07	10.12	33.16
5	20	2	0.62	0.24	0.04	0.24	0.07	9.58	34.31
5	20	3	0.7	0.24	0.04	0.25	0.07	10.21	33.12
10	20	1	0.74	0.24	0.03	0.22	0.07	8.65	31.92
10	20	2	0.65	0.24	0.03	0.23	0.07	13.51	33.01
10	20	3	0.99	0.24	0.02	0.22	0.07	4.58	33.55
20	20	1	0.63	0.24	0.03	0.23	0.07	4.35	32.62
20	20	2	0.7	0.25	0.03	0.23	0.07	11.02	33.28
20	20	3	0.62	0.24	0.03	0.22	0.07	13.75	32.65
40	20	1	0.68	0.24	0.02	0.21	0.06	7.17	30.88
40	20	2	0.62	0.24	0.02	0.21	0.06	6	32.22
40	20	3	0.67	0.23	0.02	0.2	0.06	6.72	30.81
5	40	1	0.63	0.24	0.02	0.22	0.07	29.94	32.62
5	40	2	0.66	0.25	0.02	0.23	0.07	8.54	33.08
5	40	3	0.53	0.23	0.02	0.21	0.06	9.09	31.73
10	40	1	0.7	0.23	0.03	0.21	0.06	5.38	30.4
10	40	2	0.58	0.24	0.02	0.21	0.07	6.66	32.59
10	40	3	0.73	0.23	0.02	0.2	0.06	9.49	30.7
20	40	1	0.8	0.24	0.03	0.22	0.08	9.58	29.21
20	40	2	0.65	0.24	0.03	0.18	0.07	17.88	38.09
20	40	3	0.63	0.25	0.03	0.2	0.07	10.28	29.59
40	40	1	0.62	0.24	0.03	0.21	0.07	9.55	27.74
40	40	2	0.61	0.24	0.02	0.2	0.07	11.39	27.71
40	40	3	0.72	0.24	0.03	0.2	0.07	9.45	28.12
5	60	1	0.7	0.25	0.03	0.2	0.07	9.63	30.93
5	60	2	0.65	0.25	0.03	0.2	0.08	9.1	32.49
5	60	3	0.69	0.25	0.03	0.19	0.08	8.56	30
10	60	1	0.65	0.26	0.03	0.19	0.08	10.04	30.55
10	60	2	0.71	0.25	0.03	0.2	0.07	11.47	30.5
10	60	3	0.63	0.25	0.02	0.2	0.07	12.21	30.44
20	60	1	0.64	0.24	0.03	0.18	0.07	9.69	29.12
20	60	2	0.7	0.24	0.03	0.18	0.07	14.11	29.4
20	60	3	0.68	0.24	0.02	0.17	0.07	13.43	28.65

40	60	1	0.5	0.24	0.02	0.18	0.07	10.48	28.41
40	60	2	0.53	0.24	0.02	0.18	0.07	9.47	28.16
40	60	3	0.62	0.25	0.03	0.18	0.07	16.4	28.71
Time	Temp	Block	CU	FE	S%	CL%	B	Conductivity	
control	control	1	2.91	68.82	0.07	0.09	4.47		
control	control	2	2.46	75.37	0.09	0.11	3.23		
control	control	3	2.84	75.23	0.08	0.09	2		
5	20	1	3.91	39.66	0.04	0.02	5.55	450	
5	20	2	3.57	50.73	0.04	0.07	5.09	477	
5	20	3	2.67	44.48	0.04	0.02	4.38	472	
10	20	1	3.5	37.31	0.04	0.02	4.21	490	
10	20	2	3.18	39.11	0.04	0.02	3.93	497	
10	20	3	3.55	51.09	0.04	0.02	5.5	490	
20	20	1	3.48	37.64	0.03	0.04	4.22	505	
20	20	2	3.2	54.86	0.04	0.03	3.27	503	
20	20	3	2.52	53.66	0.04	0.11	2.66	504	
40	20	1	3.14	38.35	0.03	0.03	1.7	510	
40	20	2	2.71	45.1	0.03	0.09	3.42	514	
40	20	3	2.77	39.13	0.04	0.02	3.79	512	
5	40	1	4.24	52.63	0.03	0.05	3.58	494	
5	40	2	3.78	48.09	0.04	0.03	3.71	497	
5	40	3	3.36	40.19	0.04	0.08	3.15	492	
10	40	1	4.72	49.75	0.03	0.07	2.7	517	
10	40	2	3.07	42.85	0.03	0.02	2.59	511	
10	40	3	3.69	43.59	0.04	0.04	3.3	500	
20	40	1	6.39	36.62	0.04	0.03	5.52	530	
20	40	2	14.9	208.05	0.04	0.07	3.97	521	
20	40	3	5.81	34.89	0.04	0.03	2.34	513	
40	40	1	11.18	34.33	0.03	0.04	1.63	540	
40	40	2	6.04	33.19	0.03	0.03		538	
40	40	3	6.83	34.92	0.03	0.04	0.8	531	
5	60	1	5.87	40.63	0.03	0.02	1.73	509	
5	60	2	5.23	39.65	0.03	0.07	0.73	509	
5	60	3	4.8	44.72	0.03	0.04	0.51	511	
10	60	1	6.5	40.71	0.03	0.04		519	
10	60	2	5.29	38.8	0.04	0.09		520	
10	60	3	5.13	36.58	0.03	0.02	0.13	518	
20	60	1	5.46	72.62	0.03	0.05		539	
20	60	2	5.42	44.7	0.03	0.02	0.09	533	
20	60	3	4.36	39.04	0.03	0.07	0.06	530	
40	60	1	4.89	39.11	0.04	0.02		561	
40	60	2	4.63	43.74	0.03	0.02		556	
40	60	3	5.45	40.72	0.03	0.1		544	

## Appendix 3

Appendix 3 - Percent weight of elements remaining in switchgrass samples in a 2 factor RCBD (n=3) experiment with 4 leaching times (5, 10, 20 and 40 minutes) and 4 water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.

Time	Type	Block	Nitrogen (%)	Calcium (%)	Phosphorus (%)	Potassium (%)	Magnesium (%)	Zinc (ppm)
5	distilled	1	0.67	0.24	0.03	0.23	0.07	10.12
5	distilled	2	0.62	0.24	0.04	0.24	0.07	9.58
5	distilled	3	0.7	0.24	0.04	0.25	0.07	10.21
10	distilled	1	0.74	0.24	0.03	0.22	0.07	8.65
10	distilled	2	0.65	0.24	0.03	0.23	0.07	13.51
10	distilled	3	0.99	0.24	0.02	0.22	0.07	4.58
20	distilled	1	0.63	0.24	0.03	0.23	0.07	4.35
20	distilled	2	0.7	0.25	0.03	0.23	0.07	11.02
20	distilled	3	0.62	0.24	0.03	0.22	0.07	13.75
40	distilled	1	0.68	0.24	0.02	0.21	0.06	7.17
40	distilled	2	0.62	0.24	0.02	0.21	0.06	6
40	distilled	3	0.67	0.23	0.02	0.2	0.06	6.72
5	tap	1	0.66	0.34	0.03	0.11	0.08	7.51
5	tap	2	0.68	0.35	0.03	0.11	0.08	7.63
5	tap	3	0.65	0.36	0.03	0.12	0.08	7.39
10	tap	1	0.67	0.36	0.03	0.13	0.09	7.86
10	tap	2	0.73	0.36	0.03	0.12	0.09	6.39
10	tap	3	0.76	0.35	0.03	0.11	0.08	6.08
20	tap	1	0.66	0.35	0.02	0.11	0.08	6.63
20	tap	2	0.60	0.34	0.02	0.12	0.08	7.12
20	tap	3	0.64	0.35	0.02	0.11	0.08	6.09
40	tap	1	0.66	0.35	0.02	0.12	0.08	6.22
40	tap	2	0.64	0.36	0.02	0.12	0.08	9.28
40	tap	3	0.63	0.35	0.02	0.11	0.08	7.14
5	Ottawa	1	0.65	0.25	0.03	0.17	0.06	8.58
5	Ottawa	2	0.64	0.25	0.02	0.16	0.06	7.30
5	Ottawa	3	0.70	0.26	0.02	0.16	0.06	8.84
10	Ottawa	1	0.63	0.27	0.02	0.16	0.06	5.68
10	Ottawa	2	0.64	0.24	0.02	0.16	0.06	4.51
10	Ottawa	3	0.70	0.25	0.01	0.15	0.06	4.81
20	Ottawa	1	0.61	0.26	0.02	0.19	0.07	10.72
20	Ottawa	2	0.71	0.25	0.02	0.18	0.06	4.87
20	Ottawa	3	0.63	0.25	0.01	0.16	0.06	7.31
40	Ottawa	1	0.65	0.23	0.01	0.15	0.05	4.90
40	Ottawa	2	0.66	0.24	0.01	0.16	0.05	4.65

40	Ottawa	3	0.70	0.24	0.01	0.16	0.05	5.03
5	Well	1	0.66	0.36	0.02	0.10	0.07	9.10
5	Well	2	0.66	0.37	0.02	0.11	0.08	22.57
5	Well	3	0.62	0.39	0.03	0.11	0.08	20.35
10	Well	1	0.67	0.38	0.02	0.10	0.07	9.06
10	Well	2	0.60	0.37	0.02	0.10	0.08	6.12
10	Well	3	0.73	0.37	0.03	0.09	0.08	7.39
20	Well	1	0.65	0.40	0.02	0.10	0.08	16.52
20	Well	2	0.62	0.38	0.02	0.10	0.07	6.31
20	Well	3	0.64	0.38	0.02	0.10	0.08	8.01
40	Well	1	0.61	0.38	0.02	0.10	0.08	13.22
40	Well	2	0.64	0.35	0.02	0.10	0.07	7.94
40	Well	3	0.57	0.36	0.02	0.08	0.07	4.89

Time	Type	Block	Manganese (ppm)	Copper (ppm)	Iron (ppm)	Sulphur (%)	Chloride (%)	Boron (ppm)
5	distilled	1	33.16	3.91	39.66	0.04	0.02	5.55
5	distilled	2	34.31	3.57	50.73	0.04	0.07	5.09
5	distilled	3	33.12	2.67	44.48	0.04	0.02	4.38
10	distilled	1	31.92	3.5	37.31	0.04	0.02	4.21
10	distilled	2	33.01	3.18	39.11	0.04	0.02	3.93
10	distilled	3	33.55	3.55	51.09	0.04	0.02	5.5
20	distilled	1	32.62	3.48	37.64	0.03	0.04	4.22
20	distilled	2	33.28	3.2	54.86	0.04	0.03	3.27
20	distilled	3	32.65	2.52	53.66	0.04	0.11	2.66
40	distilled	1	30.88	3.14	38.35	0.03	0.03	1.7
40	distilled	2	32.22	2.71	45.1	0.03	0.09	3.42
40	distilled	3	30.81	2.77	39.13	0.04	0.02	3.79
5	tap	1	26.04	1.00	45.01	0.05	0.50	
5	tap	2	26.98	0.63	45.56	0.04	0.18	
5	tap	3	27.29	0.58	54.78	0.05	0.30	0.17
10	tap	1	27.76	1.76	47.23	0.04	0.04	0.24
10	tap	2	27.87	1.33	47.75	0.04	0.06	0.66
10	tap	3	26.48	0.81	44.98	0.04	0.05	0.33
20	tap	1	25.72	0.85	40.54	0.04	0.03	
20	tap	2	25.74	1.25	39.60	0.05	0.03	0.24
20	tap	3	27.23	0.81	44.31	0.04	0.03	
40	tap	1	26.16	1.54	38.02	0.05	0.03	0.91
40	tap	2	26.29	0.57	41.10	0.05	0.03	0.29
40	tap	3	27.29	0.94	42.33	0.04	0.03	
5	Ottawa	1	30.47	0.69	47.92	0.03	0.01	
5	Ottawa	2	29.01	1.14	46.68	0.03	0.01	
5	Ottawa	3	30.92	0.25	44.77	0.03	0.02	

10	Ottawa	1	31.85	0.74	49.15	0.04	0.01	
10	Ottawa	2	29.58	0.96	42.83	0.04	0.01	
10	Ottawa	3	30.07	0.61	42.36	0.04	0.01	
20	Ottawa	1	33.14	3.71	41.97	0.05	0.01	6.89
20	Ottawa	2	30.24	0.28	39.67	0.03	0.01	2.01
20	Ottawa	3	29.22	0.39	41.84	0.04	0.01	1.09
40	Ottawa	1	26.45	0.75	34.91	0.04	0.01	0.62
40	Ottawa	2	28.41	1.07	35.10	0.04	0.02	0.86
40	Ottawa	3	28.21	0.50	34.92	0.04	0.01	
5	Well	1	25.92	0.04	42.00	0.04	0.04	1.96
5	Well	2	27.45	0.60	46.65	0.04	0.05	3.34
5	Well	3	28.07	0.88	48.40	0.04	0.04	1.87
10	Well	1	26.69	1.37	45.09	0.04	0.04	2.02
10	Well	2	25.76	0.68	46.47	0.04	0.05	1.49
10	Well	3	27.84	0.84	49.00	0.04	0.04	1.30
20	Well	1	26.09	1.23	47.47	0.04	0.05	0.59
20	Well	2	27.33	1.06	46.39	0.04	0.06	1.17
20	Well	3	26.35	0.56	44.28	0.04	0.05	1.48
40	Well	1	25.13	1.27	39.43	0.04	0.06	1.78
40	Well	2	23.90	0.07	38.35	0.04	0.05	1.48
40	Well	3	25.01	0.81	35.86	0.04	0.05	1.45

---

## Appendix 4 – Statistics Tables for Chapter 4

### Concentration Results Tables

Appendix 4.1.1 - Mixed effects variance analysis of the effect of concentration on percent weight of N remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.002427	0.001085	2.24	0.0127
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	0.48	0.7527

Appendix 4.1.2 - Mixed variance analysis of the effect of concentration on percent weight of Ca remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000033	0.000015	2.24	0.0127
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	14	0.0011

Appendix 4.1.3 - Mixed effects variance analysis of the effect of concentration on percent weight of P remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000033	0.000015	2.24	0.0127
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	66	<0.0001

Appendix 4.1.4 - Mixed effects variance analysis of the effect of concentration on percent weight of K remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0.000123	0.00022	0.55	0.2896
Residual	0.00047	0.000235	2	0.0228
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	318.7	<0.0001

Appendix 4.1.5 - Mixed variance analysis of the effect of concentration on percent weight of Mg remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000013	5.96E-06	2.24	0.0127
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	27	0.0001

Appendix 4.1.6 - Mixed effects variance analysis of the effects of concentration on percent weight of S remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0.000015	0.000026	0.58	0.2809
Residual	0.000052	0.000026	2	0.0228
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	13.1	0.0014

Appendix 4.1.7 - Mixed effects variance analysis of the effect of concentration on the percent weight of Cl remaining in a switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.00044	0.000197	2.24	0.0127
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	11.47	0.0021

Appendix 4.1.8 - Mixed effects variance analysis of the effect of concentration on the sum of the percent weights of N, Ca, P, K, Mg, S and Cl remaining in switchgrass samples after leaching for 40 minutes at four concentrations (25, 50, 75 and 100 g/L) RCBD, n=3.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0.000325	0.00087	0.37	0.3543
Residual	0.002535	0.001267	2	0.0228
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Treatment	4	8	0.48	0.7527

## Temperature Results Tables

### Nitrogen

Appendix 4.2.1 - Mixed effects variance analysis of percent weight N remaining in switchgrass samples in a two factor randomized complete block experiment (n=3) with four leaching times (5, 10, 20 and 40 minutes) and three leaching temperatures (20, 40 and 60°C) at 25 g of switchgrass per 1 L of distilled water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.00511	0.001417	3.61	0.0002
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	24	2.53	0.0814
Temperature	2	24	1.52	0.2394
Time*Temperature	6	24	1.62	0.1842

### Calcium

Appendix 4.2.2 - Mixed effects variance analysis of percent weight of Ca remaining in switchgrass sample in a two factor randomized complete block experiment with four leaching times (5, 10, 20 and 40 minutes), three leaching temperatures (20, 40 and 60°C) and 3 blocks at 25 g of switchgrass per 1 L of distilled water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000023	6.40E-06	3.61	0.0002
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	24	0.76	0.5263
Temperature	2	24	8.79	0.0014
Time*Temperature	6	24	3.65	0.0102

Appendix 4.2.3 - Significance of simple effects for temperature and time on the percent weight of Ca remaining in a switchgrass sample after four leaching times at three temperatures with three randomized complete blocks and 25 g switchgrass/ 1 L water.

Effect	Slice	Num DF	Den DF	F Value	Pr > F
temp*time	20 °C	3	22	0.89	0.4623
temp*time	40 °C	3	22	2.11	0.1278
temp*time	60 °C	3	22	4.44	0.0138
temp*time	5 minutes	2	22	4	0.033
temp*time	10 minutes	2	22	12.44	0.0002
temp*time	20 minutes	2	22	0.44	0.6468
temp*time	40 minutes	2	22	1.33	0.2841

Appendix 4.2.4 – Calcium - Regression responses of time and temperature for a randomized complete block experiment with three replications with three temperatures (20, 40, and 60 °C) and four times (5, 10, 20 and 40 minutes).

Contrasts	Num DF	Den DF	F Value	Pr > F
temp linear	1	24	11.56	0.0024
temp quadratic	1	24	6.02	0.0218
time linear	1	24	2.12	0.1584
time quadratic	1	24	0.01	0.9131
time lack of fit	1	24	0.16	0.697
temp x time Linear	2	24	2.74	0.0851
time x temp Linear	3	24	3.37	0.035
time linear x temp linear	1	24	1.23	0.2782

Appendix 4.2.5 - Calcium - Regression solution coefficients for linear temperature equations over time for a randomized complete block experiment with three replications, three temperatures and four times.

Effect	Temp	Estimate	Standard Error	DF	t Value	Pr >  t
intercept	20	0.241	0.0028	28	85.07	<.0001
intercept	40	0.237	0.0028	28	83.59	<.0001
intercept	60	0.251	0.0028	28	88.49	<.0001
slope	20	-9.28E-05 a	0.00012	28	-0.75	0.4581
slope	40	8.70E-05 b	0.00012	28	0.71	0.4864
slope	60	-0.000255 a	0.00012	28	-2.07	0.0479

Slope estimates followed by the same letter do not differ significantly based on Fisher's T-test at  $p < 0.05$ .

## Phosphorus

Appendix 4.2.6 - Mixed effects variance analysis of percent weight of P remaining in switchgrass sample in a two factor RCBD experiment (n=3) with four leaching times (5, 10, 20 and 40 minutes) and three leaching temperatures (20, 40 and 60°C) at 25 g of switchgrass per 1 L of distilled water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000021	5.9E-06	3.61	0.0002
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	24	3.25	0.0394
Temperature	2	24	1.63	0.2178
Time*Temperature	6	24	3.79	0.0085

Appendix 4.2.7 – Significance of simple effects for temperature and time on the percent weight of P remaining in switchgrass samples after four leaching times at three temperatures with three randomized complete blocks and 25 g switchgrass/ 1 L water.

Effect	Slice	Num DF	Den DF	F Value	Pr > F
temp*time	20 °C	3	22	7.43	0.0013
temp*time	40 °C	3	22	2.86	0.0603
temp*time	60 °C	3	22	1.14	0.3537
temp*time	5 minutes	2	22	10.86	0.0005
temp*time	10 minutes	2	22	0.57	0.5729
temp*time	20 minutes	2	22	0.57	0.5729
temp*time	40 minutes	2	22	1.33	0.2033

Appendix 4.2.8 – Phosphorus - Regression responses of time and temperature for a RBCD experiment (n=3) with three temperatures (20, 40, and 60 °C) and four times (5, 10, 20 and 40 minutes).

Contrasts	Num DF	Den DF	F Value	Pr > F
temp linear	1	24	0.81	0.3763
temp quadratic	1	24	2.44	0.1316
time linear	1	24	4.82	0.038
time quadratic	1	24	1.07	0.3119
time lack of fit	1	24	3.86	0.0611
temp x time Linear	2	24	8.26	0.0019
time x temp Linear	3	24	1.35	0.2805
time linear x temp linear	1	24	2.55	0.1233

Appendix 4.2.9 - Phosphorus - Regression solution coefficients for linear temperature equations over time for a RCBD experiment with three replications, three temperatures (20, 40, and 60) and four times (5, 10, 20, 40).

Effect	Temp	Estimate	Standard Error	DF	t Value	Pr >  t	
intercept	20	0.03551	0.0023	28	14.86	<.0001	
intercept	40	0.02174	0.0023	28	9.1	<.0001	
intercept	60	0.02971	0.0023	28	12.43	<.0001	
slope	20	-0.000383	a	0.00010	28	-3.69	0.001
slope	40	0.000174	b	0.00010	28	1.68	0.1047
slope	60	-0.000162	c	0.00010	28	-1.57	0.1288

Slope estimates followed by the same letter do not differ significantly based on Fisher's T-test at  $p < 0.05$ .

## Potassium

Appendix 4.2.10 - Mixed effects variance analysis of percent weight K remaining in switchgrass sample in a two factor randomized complete block experiment with four leaching times (5, 10, 20 and 40 minutes), three leaching temperatures (20, 40 and 60°C) and three blocks at 25 g of switchgrass per 1 L of distilled water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000077	0.000021	3.61	0.0002

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	24	11.11	<0.0001
Temperature	2	24	52.58	<0.0001
Time*Temperature	6	24	1.83	0.1356

Appendix 4.2.11 – Means comparisons of the percent weight K remaining in switchgrass samples after leaching at four times and three temperatures using an RBCD with three blocks.

Time	Estimate	se	Temperature	Estimate	se
5 minutes	0.219 a	0.0029	20 °C	0.224 a	0.0025
10 minutes	0.201 ab	0.0029	40 °C	0.208 b	0.0025
20 minutes	0.201 bc	0.0029	60 °C	0.188 c	0.0025
40 minutes	0.197 c	0.0029			

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

Appendix 4.2.12- Potassium - Regression responses of time and temperature for a randomized complete block experiment with three replications with three temperatures (20, 40, and 60 °C) and 4 times (5, 10, 20 and 40 minutes).

Contrasts	Num DF	Den DF	F Value	Pr > F
temp linear	1	24	104.87	<.0001
temp quadratic	1	24	0.29	0.5959
time linear	1	24	26.96	<.0001
time quadratic	1	24	5.83	0.0237
time lack of fit	1	24	0.54	0.4701
temp x time Linear	2	24	1.39	0.268
time x temp Linear	3	24	2.74	0.0652
time linear x temp linear	1	24	1.09	0.3079

Table 4.2.13 - Response surface regression statistics for the amount of potassium remaining in switchgrass samples over four times (5, 10, 20 and 40 minutes) at three temperatures (20, 40 and 60 °C) in a randomized complete block experiment with three repetitions.

Fact	DF	Sum of Squares	Mean Square	F Value	Pr > F
temp	3	0.008172	0.002724	32.23	<.0001
time	3	0.002606	0.000869	10.28	<.0001

Table 4.2.14 - Eigenvector estimated ridge of minimum response coinciding with maximum nutrient leaching of K from switchgrass in a randomized complete block experiment with three replications with three temperatures (20, 40, and 60°C) and four times (5, 10, 20, 40 minutes). Stationary point is a saddle point.

Temp	Time
59.54	26.21

## Magnesium

Appendix 4.2.15 - Mixed effects variance analysis of percent weight Mg remaining in switchgrass sample in a two factor RCBD experiment with four leaching times (5, 10, 20 and 40 minutes) and three leaching temperatures (20, 40 and 60°C) at 25 g of switchgrass per 1 L of distilled water (n=3).

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000013	3.56E-06	3.61	0.0002

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	24	3.18	0.0423
Temperature	2	24	6.72	0.0048
Time*Temperature	6	24	4.69	0.0027

Appendix 4.2.16 – Significance of simple effects for temperature and time on the percent weight of Mg remaining in switchgrass samples after four leaching times at three temperatures at 25 g switchgrass/ 1 L distilled water, RCBD (n=3).

Effect	Slice	Num DF	Den DF	F Value	Pr > F
temp*time	20 °C	3	22	5.4	0.0061
temp*time	40 °C	3	22	4	0.0205
temp*time	60 °C	3	22	2.2	0.1167
temp*time	5 minutes	2	22	5.6	0.0108
temp*time	10 minutes	2	22	5.6	0.0108
temp*time	20 minutes	2	22	0.8	0.462
temp*time	40 minutes	2	22	7.2	0.0039

Appendix 4.2.17 - Magnesium - Regression responses of time and temperature for RCBD experiment (n=3) with three temperatures (20, 40, and 60 °C) and four times (5, 10, 20 and 40minutes).

Contrasts	Num DF	Den DF	F Value	Pr > F
temp linear	1	24	11.7	0.0022
temp quadratic	1	24	1.73	0.2004
time linear	1	24	5.49	0.0277
time quadratic	1	24	1.18	0.2888
time lack of fit	1	24	2.86	0.1036
temp x time Linear	2	24	8.89	0.0013
time x temp Linear	3	24	2.17	0.1182
time linear x temp linear	1	24	1.37	0.2537

Appendix 4.2.18 – Magnesium - Regression solution coefficients for linear temperature equations over time for RCBD experiment with three temperatures and four times (n=3).

Effect	Temp	Estimate	Standard Error	DF	t Value	Pr >  t
intercept	20	0.0730	0.0021	28	35.41	<.0001
intercept	40	0.0655	0.0021	28	31.75	<.0001
intercept	60	0.0757	0.0021	28	36.67	<.0001
slope	20	-0.000296 a	0.000090	28	-3.3	0.0026
slope	40	0.000151 b	0.000090	28	1.68	0.1033
slope	60	-0.000168 a	0.000090	28	-1.88	0.0708

Slope estimates followed by the same letter do not differ significantly based on Fisher's T-test at  $p < 0.05$ .

## Sulphur

Appendix 4.2.19 - Mixed effects variance analysis of percent weight S remaining in switchgrass sample in a two factor randomized complete block experiment with four leaching times (5, 10, 20 and 40 minutes), three leaching temperatures (20, 40 and 60°C) at 25 g of switchgrass per 1 L of distilled water, RCBD (n=3).

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	1.50E-06	3.19E-06	0.47	0.3197
Residual	0.000022	6.23E-06	3.46	0.0003

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	24	1.16	0.3461
Temperature	2	24	4.76	0.0181
Time*Temperature	6	24	1.67	0.1709

Table 4.2.20 – Means comparisons of the percent weight S remaining in switchgrass samples after leaching at four times and three temperatures, RCBD (n=3).

Time	Estimate	se	Temperature	Estimate	se	
5 minutes	0.0356	a	0.0014	20 °C	0.0375 a	0.0012
10 minutes	0.0356	a	0.0014	40 °C	0.0356 ab	0.0012
20 minutes	0.0356	a	0.0014	60 °C	0.0317 b	0.0012
40 minutes	0.0322	a	0.0014			

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

Table 4.2.21 - Sulphur - Regression responses of time and temperature for RCBD experiment (n=3) with three temperatures (20, 40, and 60 °C) and four times (5, 10, 20 and 40 minutes).

Contrasts	Num DF	Den DF	F Value	Pr > F
temp linear	1	24	9.46	0.0052
temp quadratic	1	24	0.06	0.8019
time linear	1	24	2.91	0.1009
time quadratic	1	24	0.55	0.4659
time lack of fit	1	24	0.01	0.9037
temp x time Linear	2	24	1.9	0.1708
time x temp Linear	3	24	1.22	0.323
time linear x temp linear	1	24	3.4	0.0776

## Chloride

Appendix 4.2.23 - Mixed effects variance analysis of percent weight Cl remaining in switchgrass samples in a two factor RCBD experiment with four leaching times (5, 10, 20 and 40 minutes) and three leaching temperatures (20, 40 and 60°C) at 25 g of switchgrass per 1 L of distilled water (n=3).

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000833	0.000231	3.61	0.0002
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	24	0.27	0.8456
Temperature	2	24	0.12	0.8845
Time*Temperature	6	24	0.47	0.8205

## Conductivity

Appendix 4.2.24 - Mixed effects variance analysis of conductivity in a two factor RCBD experiment with four leaching times (5, 10, 20 and 40 minutes) and three leaching temperatures (20, 40 and 60°C) at 25 g of switchgrass per 1 L of distilled water (n=3).

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	3.5581	6.8207	0.52	0.3010
Residual	38.3308	11.5572	3.32	0.0005

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	22	82.01	<0.0001
Temperature	2	22	99.81	<0.0001
Time*Temperature	6	22	1.43	0.2484

Appendix 4.2.25 – Means comparisons of the conductivity of samples ( $\mu\text{s}/\text{cm}$ ) after leaching at four times and three temperatures, RCBD (n=3).

Time	Estimate	se	Temperature	Estimate	se
5 minutes	490.11 d	2.3335	20 °C	493.67 c	2.0929
10 minutes	506.89 c	2.3335	40 °C	515.33 b	2.0929
20 minutes	519.78 b	2.3335	60 °C	529.08 a	2.0929
40 minutes	534.00 a	2.3335			

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$

Appendix 4.2.26 - Conductivity - Regression responses of time and temperature for RCBD (n=3) with three temperatures (20, 40, and 60 °C) and four times (5, 10, 20 and 40 minutes).

Contrasts	Num DF	Den DF	F Value	Pr > F
temp linear	1	24	196.34	<0.0001
temp quadratic	1	24	3.27	0.0842
time linear	1	24	221.22	<0.0001
time quadratic	1	24	20.97	0.0001
time lack of fit	1	24	3.83	0.0631
temp x time Linear	2	24	0.3	0.7417
time x temp Linear	3	24	2.71	0.0698
time linear x temp linear	1	24	0.48	0.4963

Appendix 4.2.27 - Conductivity - Regression solution coefficients for temperature equations over time for RCBD experiment with three temperatures and four times (n=3).

Effect	Estimate	Standard Error	DF	t Value	Pr >  t
Intercept	442.88	4.7855	2	92.55	0.0001
temp	0.8854	0.07081	30	12.5	<.0001
time	2.9219	0.4433	30	6.59	<.0001
time*time	-0.03838	0.00939	30	-4.09	0.0003

Appendix 4.2.28 - Conductivity - Regression solution coefficients for linear temperature equations over time for a randomized complete block experiment with three replications, three temperatures and four times.

Effect	Estimate	Standard Error	DF	t Value	Pr >  t
Intercept	477.28	7.8916	2	60.48	0.0003
Temperature	0.8854	0.1827	32	4.85	<0.0001

## Water Type Results Tables

### Nitrogen

Appendix 4.3.1 - Mixed effects variance analysis of percent weight N remaining in switchgrass samples in a two factor RCBD (n=3) experiment with four leaching times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.

Random effects					
Covariance	Parameter	Estimate	Standard Error	Z Value	Pr > Z
	Block	0.000135	0.000331	0.41	0.3415
	Residual	0.003071	0.000793	3.87	<0.0001
Type 3 Tests of Fixed Effects					
Effect	Num DF	Den DF	F Value	Pr > F	
	Time	3	30	3.8	0.0202
	Water type	3	30	1.76	0.1755
	Time*time	9	30	0.98	0.4767

Appendix 4.3.2 – Means comparisons of the percent weight N remaining in switchgrass samples of four times (in minutes) and four water types (distilled, Ottawa, Kemptville and well) using a RBCD experiment (n=3)

Time	Estimate		se
5	0.659	ab	0.01735
10	0.709	a	0.01735
20	0.643	b	0.01735
40	0.644	b	0.01735

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

Appendix 4.3.3 - Orthogonal sub-partitions of water type and time for the effect of four times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) on the amount of N remaining in switchgrass samples for an RCBD experiment (n=3).

Effect	Num DF	Den DF	F Value	Pr > F
type	3	30	1.76	0.1755
time	1	30	3.28	0.08
time*time	1	30	0.02	0.8847
time*type	3	30	0.59	0.6293
time*time*type	3	30	0.12	0.9497
time*loftime	1	30	8.1	0.0079
time*type*loftime	3	30	2.23	0.1046

## Calcium

Appendix 4.3.4 - Mixed effects variance analysis of percent weight Ca remaining in switchgrass samples in a two factor RCBD (n=3) experiment with four leaching times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000077	0.000019	4	<0.0001

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	30	2.99	0.0465
Water type	3	30	741.95	<0.0001
Time*type	9	30	1.43	0.22

Appendix 4.3.5 – Means comparisons of the percent weight Ca remaining in switchgrass samples at four times (in minutes) and four water types, RCBD experiment (n=3).

Time	Effect	se	Water type	Estimate	se
5	0.304 ab	0.0025	Ottawa	0.249 c	0.0025
10	0.306 ab	0.0025	Well	0.374 a	0.0025
20	0.308 a	0.0025	Distilled	0.240 c	0.0025
40	0.298 b	0.0025	Kemptville	0.352 b	0.0025

Means in the same column with the same letter are not significantly different with Tukey's HSD test at  $p < 0.05$ .

Appendix 4.3.6 - Orthogonal sub-partitions of water type and time for the effect of 4 times (5, 10, 20 and 40 minutes) and 4 water types (distilled, Ottawa, Kemptville and well) on the amount of Ca remaining in switchgrass samples for an RCBD experiment (n=3).

Effect	Num DF	Den DF	F Value	Pr > F
type	3	30	741.95	<.0001
time	1	30	5.01	0.0328
time*time	1	30	3.94	0.0563
time*type	3	30	1.37	0.2715
time*time*type	3	30	1.84	0.1617
time*loftime	1	30	0.02	0.8822
time*type*loftime	3	30	1.08	0.3711

Appendix 4.3.7 - Regression solution coefficients for the amount of Ca remaining in switchgrass samples after leaching for four times (5, 10, 20, 40 minutes) with four water types (distilled, Ottawa, Kemptville and well), RCBD experiment (n=3).

Effect	Type	Estimate	se	DF	t Value	Pr >  t
type	Ottawa	0.2531	0.003296	41	76.81	<.0001
type	Well	0.3781	0.003296	41	114.73	<.0001
type	Distilled	0.244	0.003296	41	74.02	<.0001
type	Kemptville	0.3556	0.003296	41	107.91	<.0001
time		-0.00021	0.000101	41	-2.1	0.0419

## Phosphorus

Appendix 4.3.8 - Mixed effects variance analysis of percent weight P remaining in switchgrass samples in a two factor RCBD (n=3) experiment with four leaching times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000015	3.56E-06	4	<0.0001

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	30	16.95	<0.0001
Water type	3	30	20.38	<0.0001
Time*time	9	30	2.22	0.0489

Table 4.3.9 – Test of simple effects for the amount of P remaining in switchgrass samples using four water types at four leaching times with 25 g switchgrass/ 1 L water, RCBD (n=3).

Effect	Slice	Num DF	Den DF	F Value	Pr > F
type*time	Ottawa	3	30	6.1	0.0023
type*time	Well	3	30	0.76	0.5243
type*time	Distilled	3	30	9.9	0.0001
type*time	Kemptville	3	30	6.86	0.0012
type*time	5	3	30	224.78	<.0001
type*time	10	3	30	181.26	<.0001
type*time	20	3	30	205	<.0001
type*time	40	3	30	146.37	<.0001

Table 4.3.10 - Orthogonal sub-partitions of water type and time for the effect of four times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) on the amount of P remaining in switchgrass samples for an RCBD experiment (n=3).

Effect	Num DF	Den DF	F Value	Pr > F
type	3	30	20.38	<.0001
time	1	30	46.75	<.0001
time*time	1	30	2.76	0.107
time*type	3	30	2.19	0.1097
time*time*type	3	30	0.57	0.6419
time*loftime	1	30	1.34	0.2555
time*type*loftime	3	30	3.91	0.0181

## Potassium

Appendix 4.3.11 - Mixed effects variance analysis of percent weight K remaining in switchgrass samples in a two factor RCBD (n=3) experiment with four leaching times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	7.78E-06	0.000011	0.71	0.2391
Residual	0.000051	0.000013	3.87	<0.0001

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	30	7.51	0.0007
Water type	3	30	745.98	<0.0001
Time*type	9	30	3.81	0.0026

Appendix 4.3.12 - Test of simple effects for the amount of K remaining in switchgrass samples using four water types and four leaching times with 25 g switchgrass/ 1 L water, RCBD (n=3).

Effect	Slice	Num DF	Den DF	F Value	Pr > F
type*time	Ottawa	3	30	5.27	0.0048
type*time	Well	3	30	1.92	0.1471
type*time	Distilled	3	30	11.15	<0.0001
type*time	Kemptville	3	30	0.6	0.6173
type*time	5	3	30	224.48	<.0001
type*time	10	3	30	181.26	<.0001
type*time	20	3	30	205	<.0001
type*time	40	3	30	146.37	<.0001

Appendix 4.3.13 - Orthogonal sub-partitions of water type and time for the effect of four times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) on the amount of K remaining in switchgrass samples, RCBD (n=3).

Effect	Num DF	Den DF	F Value	Pr > F
type	3	30	745.98	<.0001
time	1	30	14.48	0.0007
time*time	1	30	1.27	0.2679
time*type	3	30	5.68	0.0033
time*time*type	3	30	2.4	0.0872
time*loftime	1	30	6.79	0.0141
time*type*loftime	3	30	3.36	0.0316

## Magnesium

Appendix 4.3.14 - Mixed effects variance analysis of percent weight Mg remaining in switchgrass samples in a two factor RCBD (n=3) experiment with four leaching times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000012	3.13E-06	4	<0.0001
Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	30	11.11	<0.0001
Water type	3	30	99.11	<0.0001
Time*type	9	30	2.07	0.065

Appendix 4.3.15 – Means comparisons of the percent weight Mg remaining in switchgrass samples of the four times (in minutes) and for the four water types with 25 g switchgrass/ 1 L water, RCBD (n=3).

Time	Estimate	se	Water type	Estimate	se
5	0.0717 a	0.0010	Ottawa	0.0583 d	0.0010
10	0.0733 a	0.0010	Well	0.0758 b	0.0010
20	0.0725 a	0.0010	Distilled	0.0675 c	0.0010
40	0.0658 b	0.0010	Kemptville	0.0817 a	0.0010

Means in the same column with the same letter are not significantly different with Tukey's HSD test at p<0.05.

Appendix 4.3.16 - Orthogonal sub-partitions of water type and time for the effect of four times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) on the amount of Mg remaining in switchgrass samples with 25 g switchgrass/ 1 L water, RCBD (n=3).

Effect	Num DF	Den DF	F Value	Pr > F
type	3	30	99.11	<.0001
time	1	30	25.25	<.0001
time*time	1	30	7.66	0.0096
time*type	3	30	2.38	0.0896
time*time*type	3	30	1.42	0.2556
time*loftime	1	30	0.42	0.5211
time*type*loftime	3	30	2.42	0.0853

Appendix 4.3.17 - Regression solution coefficients for the amount of Mg remaining in switchgrass samples after leaching for four times (5, 10, 20, 40 minutes) with four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/ 1 L water, RCBD (n=3).

Effect	Type	Estimate	se	DF	t Value	Pr >  t
type	Ottawa	0.05806	0.00206	40	28.13	<.0001
type	Well	0.07556	0.00206	40	36.61	<.0001
type	Distilled	0.06722	0.00206	40	32.57	<.0001
type	Kemptville	0.08139	0.00206	40	39.44	<.0001
time		0.00034	0.000216	40	1.57	0.1232
time*time		-0.00001	4.57E-06	40	-2.51	0.0162

## Sulphur

Appendix 4.3.18 - Mixed effects variance analysis of percent weight S remaining in switchgrass samples in a two factor RCBD (n=3) experiment with four leaching times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/ 1 L water, RCBD (n=3).

### Random effects

Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.000017	4.17E-06	4	<0.0001

### Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	3	30	0.13	0.9446
Water type	3	30	7.13	0.0009
Time*time	9	30	2.68	0.0205

Appendix 4.3.19 – Test of simple effects for the amount of S remaining in switchgrass samples using four water types and four times (in minutes) with 25 g switchgrass/ 1 L water, RCBD experiment (n=3).

Effect	Slice	Num DF	Den DF	F Value	Pr > F
type*time	Ottawa	3	30	4.5	0.0101
type*time	Well	3	30	0	1
type*time	Distilled	3	30	1.83	0.1624
type*time	Kemptville	3	30	1.83	0.1624
type*time	5	3	30	8.5	0.0003
type*time	10	3	30	0	1
type*time	20	3	30	1.33	0.282
type*time	40	3	30	5.33	0.0046

Appendix 4.3.20 - Orthogonal sub-partitions of water type and time for the effect of four times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) on the amount of S remaining in switchgrass samples with 25 g switchgrass/ 1 L water, RCBD (n=3).

Effect	Num DF	Den DF	F Value	Pr > F
type	3	30	7.13	0.0009
time	1	30	0.13	0.7194
time*time	1	30	0.14	0.7107
time*type	3	30	3.55	0.0259
time*time*type	3	30	2.28	0.0995
time*loftime	1	30	0.1	0.7502
time*type*loftime	3	30	2.21	0.1079

Appendix 4.3.21 - Regression solution coefficients for the amount of S remaining in switchgrass samples after leaching for four times (5, 10, 20, 40 minutes) with four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/ 1 L water, RCBD (n=3).

Effect	Type	Estimate	se	DF	t Value	Pr >  t
type	Ottawa	0.03391	0.002166	38	15.66	<.0001
type	Well	0.04	0.002166	38	18.47	<.0001
type	Distilled	0.0413	0.002166	38	19.07	<.0001
type	Kemptville	0.04275	0.002166	38	19.74	<.0001
time*type	Ottawa	0.000191	0.000094	38	2.04	0.0488
time*type	Well	0.00E+00	0.000094	38	0	1
time*type	Distilled	-0.0002	0.000094	38	-2.16	0.0372
time*type	Kemptville	0.000075	0.000094	38	0.8	0.4276

## Chloride

Appendix 4.3.22 - Mixed effects variance analysis of percent weight Cl remaining in switchgrass samples in a two factor RCBD (n=3) experiment with four leaching times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) at 25 g switchgrass/L water.

Random effects				
Covariance Parameter	Estimate	Standard Error	Z Value	Pr > Z
Block	0	.	.	.
Residual	0.001912	0.000478	4	<0.0001

Type 3 Tests of Fixed Effects				
Effect	Num DF	Den DF	F Value	Pr > F
Time	3	30	7.75	0.0006
Water type	3	30	10.52	<0.0001
Time*type	9	30	8.63	<0.0001

Appendix 4.3.23 – Test of simple effects for the amount of Cl remaining in switchgrass samples using four water types and four times (in minutes) with 25 g switchgrass/ 1 L water, RCBD experiment (n=3).

Effect	Slice	Num DF	Den DF	F Value	Pr > F
type*time	Ottawa	3	30	0.01	0.9994
type*time	Well	3	30	0.05	0.9839
type*time	Distilled	3	30	0.45	0.722
type*time	Kemptville	3	30	33.12	<0.0001
type*time	5	3	30	34.52	<0.0001
type*time	10	3	30	0.56	0.6442
type*time	20	3	30	0.82	0.4935
type*time	40	3	30	0.5	0.6824

Appendix 4.3.24 - Orthogonal sub-partitions of water type and time for the effect of four times (5, 10, 20 and 40 minutes) and four water types (distilled, Ottawa, Kemptville and well) on the amount of Cl remaining in switchgrass samples at 25 g switchgrass/ 1 L water, RCBD (n=3).

Effect	Num DF	Den DF	F Value	Pr > F
type	3	30	10.52	<.0001
time	1	30	7.14	0.0121
time*time	1	30	7.79	0.009
time*type	3	30	10.93	<.0001
time*time*type	3	30	10.06	<.0001
time*loftime	1	30	8.31	0.0072
time*type*loftime	3	30	4.88	0.007

## Appendix 5

Appendix 5.1 – Elemental concentrations of solvent used for water type experiments (Distilled water, Ottawa tap water, Kemptville tap water and Well water from Carp, Ontario).

Water Type	Rep	Chloride	Nitrogen	Phosphorus	Calcium	Copper	Iron
Distilled	1	< 0.5	< 0.05	< 0.01	0.05	< 0.002	0.356
Distilled	2	< 0.5	< 0.05	< 0.01	0.04	< 0.002	0.102
Distilled	3	< 0.5	< 0.05	< 0.01	0.07	< 0.002	0.054
Ottawa	1	4.8	0.13	< 0.01	9.24	0.006	0.054
Ottawa	2	5	0.05	< 0.01	8.39	0.006	0.052
Ottawa	3	5	< 0.05	< 0.01	8.12	0.004	0.068
Kemptville	1	52	0.1	< 0.01	78.5	0.018	0.123
Kemptville	2	51.9	< 0.05	< 0.01	83.3	0.02	0.115
Kemptville	3	51.9	< 0.05	< 0.01	77	0.018	0.106
Well	1	101	< 0.05	< 0.01	96.2	0.017	0.007
Well	2	101	0.12	< 0.01	88.7	0.016	< 0.005
Well	3	102	0.22	< 0.01	92.3	0.023	0.012
Water Type	Rep	Magnesium	Manganese	Potassium	Sulphur	Zinc	
Distilled	1	0.01	< 0.001	< 0.1	< 0.1	0.005	
Distilled	2	< 0.01	< 0.001	< 0.1	< 0.1	0.005	
Distilled	3	0.01	< 0.001	< 0.1	< 0.1	0.005	
Ottawa	1	2.26	0.002	0.7	8.6	0.01	
Ottawa	2	2.09	0.004	0.8	8	0.016	
Ottawa	3	2.03	0.003	0.6	7.8	0.011	
Kemptville	1	37.5	0.012	3.4	19.2	0.018	
Kemptville	2	39.8	0.011	3.6	20.6	0.018	
Kemptville	3	36.3	0.011	3.3	18.7	0.058	
Well	1	36.2	< 0.001	2.9	20.4	0.011	
Well	2	33.4	< 0.001	2.6	18.8	0.009	
Well	3	34.8	< 0.001	2.7	19.7	0.013	