IOWA STATE UNIVERSITY
Digital Repository

2016

Exploration of Ion Species in Agricultural Subsurface Drainage Waters

Brett Zimmerman
Iowa State University

Exploration of ion species in agricultural subsurface drainage waters

by

Brett Andrew Zimmerman

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Agricultural and Biosystems Engineering

Program of Study Committee:
Amy L. Kaleita, Major Professor
Matthew J. Helmers
Nicola Bowler

Iowa State University

Ames, Iowa

2016

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1. GENERAL INTRODUCTION

1.1 Introduction

The 1987 USDA report, "Farm Drainage in the United States: History, Status, and Prospects", estimates nearly 110 million acres of U.S. farmland is artificially drained (Pavelis, 1987). The report also suggests that this quantity will continue to grow as there is an increasing future trend for the adoption of tile drainage on previously undrained lands. This presents environmental and human health concerns, as one unintended consequence of subsurface drainage is the efflux of nitrate-nitrogen (Bjorneberg et al 1996; Gilliam et al., 1999; Skaggs et al., 1994).

The combined nitrate-nitrogen losses from artificially drained crop lands represents a significant proportion of the total nitrate-nitrogen pollution in surface and ground waters throughout the U.S. (Kanwar et al., 1999). Iowa alone is responsible for approximately 25% of the nitrate that the Mississippi river delivers to the Gulf of Mexico, despite Iowa occupying less than 5% of its drainage basin (Shilling & Libra, 2000). Transport of nitrate-nitrogen from artificially drained crop land within the Mississippi River Basin as a whole has been identified as a primary cause of the Hypoxic Zone in the Gulf of Mexico (Rabalais et al., 2001).

Human health is at risk when nitrate in the human diet exceed natural levels. Our diet is subject to elevated nitrate levels when we are exposed to nitrate laden drinking water and dietary sources such as leafy green vegetables grown with inorganic N-fertilizers (Ward et al., 2010). The EPA reports that Blue Baby Syndrome is a concern with nitrate concentrations in excess of the drinking water standard of 10 mg $NO3-N$ L^{-1}. Additionally, Ward et al. (2010) reveals a potential link between nitrate consumption and thyroid cancer. The study found that individuals who have

consumed more than 5 mg NO3-N L^{-1} for 5 years or more were at an increased risk of developing thyroid cancer.

Ikenberry et al. (2014) suggests that drainage districts, which primarily convey agricultural subsurface drainage, could account for all of the total nitrate export in the Boone River from 2009 to 2013. Consistent nitrate-nitrogen concentrations greater than the EPA standard of 10 mg NO3-N L^{-1} in the Boone River has led to increased drinking water treatment costs for the residents of Des Moines, Iowa. In response to elevated nitrate concentrations in the Boone River, Des Moines Water Works constructed a $4.1 million nitrate removal facility. The operating cost of this facility was $7,000 per day and $900,000 annually in 2013.

Applications of N-fertilizer is a significant contributor of non-point source nitrate pollution in not only surface waters, but also ground waters (Gentry et al., 1998). High nitrate concentrations in private wells is an issue of particular concern for rural residents. Private wells are not regulated by the Clean Water Act and as a result, are infrequently monitored for pollutants. A 1980 Iowa census showed that approximately 130,000 rural Iowa residents consume drinking water from private wells that exceed the USEPA MCL (Kross, 1990). On the national scale, 20% of shallow wells in agricultural areas compared to 3% of shallow wells in urban areas exceed the USEPA MCL (Hamilton et al., 2004).

All of these issues reinforce the need for effective nitrate mitigation strategies and widespread nitrate monitoring. However, because nitrate concentrations are tightly linked to local environmental conditions and land management practices, it changes in time and space, so traditional grab sampling methods yield incomplete data. Continuous, accurate, and low-cost in-situ nitrate sensors are essential for assessing the effectiveness of nitrate mitigation strategies and widespread monitoring. Current commercially available in-situ nitrate sensors that meet research

and regulatory standards, like the NISE sc ISE Nitrate Probe ($6,973.00) (Hach, Loveland, CO) or the SUNA V2 ($25,000.00) (Satlantic LP, Halifax NS), are well outside the budget of most research efforts and rural residents with private wells. A market assessment performed by the Iowa State University College of Business suggested that wide spread nitrate monitoring is more practical with a sensor that costs $300.00 per unit. A research effort headed by Associate Professor Amy Kaleita and Professor Nicola Bowler of Iowa State University proposed that such a sensor can be attained using resonant dielectric sensing to measure the permittivity of nitrate solutions at discrete frequencies.

The research presented in this thesis is intended to support the development of this sensor by characterizing its operating environment. Specific questions to be answered by this research are: 1) what are the flow dynamics of agricultural drainage waters?; 2) what influences the concentration of not only nitrate, but also other major dissolved constituents that contribute to the bulk electrical conductivity of drainage waters?; 3) how do these parameters influence the ionic composition? By addressing these questions, this thesis provides researchers with a comprehensive understanding of component processes that affect the leaching rate of major dissolved constituents in agricultural landscapes. This information is not only valuable for the future development of a dielectric-based nitrate sensor, but also for research efforts whose focus is to adapt existing technologies like electrical conductivity for predicting solute losses in agricultural drainage waters, and development of solute mitigation strategies.

1.2 Thesis Organization

This thesis contains a review of the literature and two journal manuscripts intended for submission to referred scientific journals. The literature review presented in Chapter 2 summarizes drainage flow dynamics under different land management practices and climates characteristic to

Iowa. Chapter 2 also discusses known sources, biological and chemical processes, and general cycles of major constituents in agricultural subsurface drainage waters. Chapter 3 is a combined literature review and field investigation that identifies and evaluates relationships among drainage water constituents and individual constituent variability with different seasonal conditions, cropping systems, drainage water flow rates, temperatures, and pH. Chapter 4 is an assessment of electrical conductivity as a tool for agricultural drainage water quality monitoring. This study was intended to compliment the preceding study by quantifying each major solute's contribution to drainage water electrical conductivity, and by evaluating the effect of different environmental conditions and land management practices on the interpretations made from electrical conductivity measurements.

1.3 References

Bjorneberg, D. L., Kanwar, R. S., & Melvin, S. W. (1996). Seasonal changes in flow and nitrate-N loss from subsurface drains. *Transactions of the ASAE*,*39*(3), 961-967.

Gentry, L. E., David, M. B., Smith, K. M., & Kovacic, D. A. (1998). Nitrogen cycling and tile drainage nitrate loss in a corn/soybean watershed.*Agriculture, ecosystems & environment*, *68*(1), 85-97.

Gilliam, J. W., Baker, J. L., & Reddy, K. R. (1999). Water Quality Effects of Drainage in Humid Regions. *Agronomy, 38,* 801-830.

Hamilton, P. A., Miller, T. L., & Myers, D. N. (2004). Water quality in the nation's streams and aquifers: Overview of selected findings, 1991-2001 (No. 1265). US Geological Survey.

Ikenberry, C. D., Soupir, M. L., Schilling, K. E., Jones, C. S., & Seeman, A. (2014). Nitrate-Nitrogen Export: Magnitude and Patterns from Drainage Districts to Downstream River Basins. *Journal of Environment Quality, 43,* 6, 2024.

Kanwar, R. S., Bjorneberg, D., & Baker, D. (January 01, 1999). An Automated System for monitoring the Quality and Quantity of Subsurface Drain Flow. *Journal of Agricultural Engineering Research, 73,* 2, 123-129.

Kross, B. C., & Iowa. (1990). The Iowa state-wide rural well-water survey: Water-quality data : initial analysis. Iowa City, Iowa: Iowa Dept. of Natural Resources.

Rabalais, N. N., Turner, R. E., & Wiseman, W. J. (2001). Hypoxia in the Gulf of Mexico. *Journal of Environmental Quality*, *30*(2), 320-329.

Schilling, K. E., & Libra, R. D. (2000). The relationship of nitrate concentrations in streams to row crop land use in Iowa. *Journal of Environmental Quality*, *29*(6), 1846-1851.

Skaggs, R. W., Breve, M. A., & Gilliam, J. W. (1994). Hydrologic and water quality impacts of agricultural drainage∗. *Critical reviews in environmental science and technology*, *24*(1), 1-32.

Pavelis, G. A. (Ed.). (1987). *Farm drainage in the United States: History, status, and prospects* (No. 1455). US Department of Agriculture, Economic Research Service.

Ward, M. H., Kilfoy, B. A., Weyer, P. J., Anderson, K. E., Folsom, A. R., & Cerhan, J. R. (2010). Nitrate intake and the risk of thyroid cancer and thyroid disease. *Epidemiology (Cambridge, Mass.)*, *21*(3), 389.

CHAPTER 2. LITERATURE REVIEW

Primary dissolved constituents in agricultural subsurface drainage waters include bicarbonate (HCO_3^-), calcium (Ca^{2+}), nitrate (NO_3^-), magnesium (Mg^{2+}), chloride (Cl^-), sodium (Na^+), and sulfate (SO_4^{2-}). The rate and quantity of solute efflux from agricultural subsurface drainage is largely dependent on site specific characteristics such as soil structure, organic content, temperature, precipitation, irrigation, percolation rate, fertilizer application rate, crop uptake, and tillage (Bakhsh et al., 2002; Bjorneberg et al., 1996; Gentry et al., 1998; Helmers et al., 2005). The influence of these site specific characteristics on solute efflux is illustrated by the range of solute concentrations listed in Table 2.1, which reports several published results for solute concentrations in drainage waters from different geographic and climatic regions. Sections 2.1 and 2.2 present a detailed literature review that describes site specific conditions that influence solute efflux and identifies solute sources, sinks, and in-soil transformations.

2.1 Agricultural Subsurface Drainage Water Flow Dynamics

Helmers et al. (2005) illustrates that drainage flow rates closely mirror seasonal precipitation trends. The 15-year study of agricultural drainage flows at an experimental field site near Gilmore City, Iowa, observed a strong correlation (41%) between precipitation and drainage from April through November. June represented the greatest precipitation month (20% of annual precipitation) while October averaged the least precipitation (6% of annual). Drainage during June and October was 31% and 1% of the total annual drainage flow. During the growing season, April through August, 50% of the seasonal precipitation and 70% of the total drainage occurred in April, May and June. In July and August, evapotranspiration exceeded precipitation, leading to reduced soil moisture within the soil profile; this is recharged during September, October, November, and early spring, leading to minimal drainage in late fall. Generally, trends observed by Helmers et al.

(2005) coincide with several published results of agricultural subsurface drainage flows throughout Iowa (Table 2.2).

Baker et al. (1975), identified the primary drainage months as March, April, May, September, October, and November with over 80% of the annual drainage occurring during these months. Qi (2009) recorded an average of 45% of total annual rainfall during the drainage season (April through November) with 63% of the annual drainage occurring in April, May, and June. Bakhsh et al. (2002) found a strong correlation ($R^2 = 0.89$) between rainfall and drainage from April through November. Lawlor et al. (2008) observed an average annual drainage to precipitation ratio of 0.37 and 88% of subsurface drainage occurred between April and July in most years. As each of these studies illustrate, precipitation, evaporation, and saturation have a profound effect on drainage. Drainage flows are also influenced by subsoils, tillage, and cropping systems.

Daigh et al. (2014) concluded that cropping system significantly influenced cumulative drainage flows, approximately representing 30% of the variability in accumulated monthly flows. On an annual and event basis, variability in cumulative drainage caused by cropping system was less than 5%. In contrast, environmental conditions (precipitation depth, intensity, and frequency) accounted for approximately 67% of the monthly variability and 76% of the event variability. The study also determined that greater residue cover on continuous corn plots (cropping system: CC) caused greater soil evaporation than corn and soybean plots in annual rotation (cropping systems: C2 & S2). As a result, cumulative drainage and drainage event duration was significantly less in CC plots in comparison to C2 and S2 plots; no significant differences among cropping systems were observed in drainage duration nor drainage initiation lag time during high drainage flow events.

Ground water percolation rate is a function of soil hydraulic conductivity, which is mostly dependent on the subsoil type and tillage. Accordingly, the proportion of water intercepted by tile drains is not only influenced precipitation and cropping system, but also subsoil type and tillage. In studying the effects no-till and chisel plow practices on drainage flow rate with single N application and a corn-soybean rotation, Bakhsh et al. (2002) determined that no-till plots had over twice the drainage flow volume versus chisel plow plots. No-till practices allows for greater development of the macropore soil structure, causing increased preferential movement of water through the soil profile (Kanwar et al., 1997). Furthermore, Randall & Iragavarapu (1995) observed lower grain yields in long term no-till systems in comparison to conventionally tilled systems and suggested that these lower yields resulted in lower evapotranspiration rates, which then contributed to greater drainage flow volumes.

2.2 Major Constituents of Agricultural Subsurface Drainage Waters

2.2.1 Bicarbonate & Carbonate

In temperate weather based soils, weathering of parent minerals by carbonic acid (H_2CO_3) is the primary source of base cations and alkalinity (Markewitz et al., 2001); alkalinity is the sum of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Bicarbonate makes up the largest portion of alkalinity and DIC (dissolved inorganic carbon) in the Mississippi River (Oh & Raymond, 2006; Raymond & Cole, 2003). Carbonate can be assumed negligible for this study because CO_3^{2-} is not a significant factor in alkalinity until pH levels rise above 10 (Whisner, 2009). Alkalinity is released into the soil when natural weathering is caused by atmospheric and organically produced carbon dioxide (CO_2) which causes natural carbonic and silicate weathering by H_2CO_3 that produces Ca^{2+}, Mg^{2+}, and HCO_3^- using the equations $CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$ and $CaMg(CO_3)_2 + 2CO_2 + 2H_2O = Ca^{2+} + Mg^{2+} + 4HCO_3^-$ (Aquilina et al., 2012; Oh & Raymond,

2006). Data from Whisner (2009) show that there is a 0.95 regression fit on a graph of Ca^{2+} vs $2HCO_3^-$. If there were to be a 1:1 fit the ions would be formed completely by dissolution of $CaCO_3$, and because the recession is so close to 1, $CaCO_3$ is a main source of the ions (Whisner, 2009). The hydrologic cycle then transports the freed ions from the soil into the tile water which feeds into the river and acts as alkalinity. Approximately 60% of the HCO_3^- that enters the Mississippi river originates from atmospheric CO_2 (Raymond & Cole, 2003). This could be a result of the fact that half of the alkalinity that enters the Mississippi as a product of CO_3^{2-} weathering originates from the atmosphere because carbonate minerals produce a mole of carbon for every mole of CO_2 sequestered (Raymond & Cole, 2003).

Within the Mississippi and Ohio River basins, there is a strong correlation between land use and stream alkalinity. From "Increase in the Export of Alkalinity from North America's Largest River" the data indicates a strong negative relationship between land cover consisting of forest and stream alkalinity and a positive relationship between land cover consisting of cropland and stream alkalinity (Raymond & Cole, 2003). This suggests that forests are able to absorb and hold ions like HCO_3^-, and croplands release those ions making alkalinity levels higher in cropland areas.

Along with land types, the amount of rainfall and flow can cause a change in the alkalinity levels of tile water. In the process of weathering, water can both react with and transport minerals and ions so an increase or decrease in the water supply can cause changes in weathering rates and the concentrations of ions in tile water (Raymond & Cole, 2003). During baseflow conditions the DIC speciation is around 82.5% HCO_3^-, 17.4% H_2CO_3, and 0.1% CO_3, while in stormflow conditions it is 64.4% HCO_3^-, 35.5% H_2CO_3, and about 0.02% CO_3 (Whisner, 2009). In both cases

the CO_3 is negligible and in the second case the increase of H_2CO_3 can be attributed to slightly acidic rainfall that was not present during baseflow.

During baseflow conditions, the rate of alkalinity export for different land use sites are nearly indistinguishable suggesting that without rainfall, all sites will be consistent in alkalinity export (Whisner, 2009). However, during stormflow conditions there is an increase in the variations of alkalinity yields depending on site usage. Tilled sites showed at least twice the alkalinity export as non-tilled sites during stormflow (Whisner, 2009). This can be attributed to the surface flow impacts on total alkalinity export. In non-tilled conditions, surface flow has a lower retention time in the soil so it has lower ionic concentrations, but in tilled sites there is increased exposure to the soil and ions, so it can pick up higher ionic and alkalinity yields (Markewitz et al., 2001). In addition to flow conditions, the alkalinity export is dependent on soil composition and crop type so there may be variations simply due to differing environments (Oh & Raymond, 2006).

2.2.2   Calcium

Calcium (Ca^{2+}) is an essential macronutrient used for the development of the plant's structure, and regulates the uptake of other nutrients (White & Broadley, 2003). As with alkalinity, a primary source of the Ca^{2+} ion comes from the chemical breakdown of applied calcite ($CaCO_3$), or agricultural lime, and dolomite ($MgCa(CO_3)_2$) (West & McBride, 2005). These two sources make Ca^{2+}, on average, the most abundant cation in rivers and they contribute to 65% of Ca^{2+} export with 52% from $CaCO_3$ and 13% from $MgCa(CO_3)_2$ (Whisner, 2009). Through the weathering of $CaCO_3$ and $MgCa(CO_3)_2$, the ions Ca^{2+}, Mg^{2+}, HCO_3^-, and NO_3^- are produced (West & McBride, 2005). These shared sources could be the cause for a strong linear correlation $R^2 =$ 0.93 between Ca^{2+} and NO_3^- (Bonton et al., 2010). While there are other factors, in a graph of

Ca^{2+} versus HCO_3^-, the Ca^{2+} concentrations have a strong relationship with the CO_2 induced carbonic weathering, much like alkalinity (Aquilina et al., 2012).

Calcium is a divalent cation and aluminum (Al^{3+}) is a trivalent cation so as soils become more acidic, the Al^{3+} ions begin to dominate the cation exchange sites because they hold on more strongly than the divalent ions (Kamprath & Foy, 1985). This could cause the level of calcium ions to dwindle as the soils become more and more acidic. However, when soils are limed, the pH rises and calcium ions return and there will be much higher concentrations of Ca^{2+} in the tile water (Kamprath & Foy, 1985). Crop uptake averages 15.75 mmolc Ca^{2+} m^{-2} yr^{-1}, and is a small portion of the calcium cycle within the soil (Oh & Raymond, 2006). Calcium that is not taken up by the crops, either stays in the upper soil profile where it eventually gets washed out of the soil through water flow, or the calcium ions go deeper into the soil where they can link up with other ions and get flushed out with other ions (West & McBride, 2005). With around 40% of precipitation becoming discharge, there is a possibility that the majority of calcium ions added through liming is exported to streams in some fashion (Oh & Raymond, 2006).

The amount of calcium ions that enter into the tile drainage water can be significantly affected by agricultural practices. The more farmers apply lime to combat soil pH and fuel crops, the more calcium is present in the soil's ion exchange complex to potentially be weathered away (Pierson et al., 2009). This implies that in times of fertilizer and lime application, the levels of Ca^{2+} will increase as opposed to dormant time where all of the weathering occurs on already present calcium. Storm flow conditions can lead to an increase of calcium ions in the water, but a decrease in concentration because of the much higher levels of water flowing through the soil (Markewitz et al., 2001). Heng et al. (1991) also observed a negative correlation in Ca^{2+} losses

with drainage flow. This means that the highest levels of ions will be present in base flow conditions (Markewitz et al., 2001).

2.2.3 Nitrate and Ammonium

Nitrogen (N) is an essential macronutrient needed for plant development and growth. Nitrogen is delivered to the soil naturally through biological fixation of atmospheric nitrogen gas (N_2) and mineralization of organic-N or artificially by applications of inorganic N-fertilizers. Soybeans, like all legumes, produce nitrogen through N-fixation by Rhizobium-legume symbiosis. As a result of this attribute, legumes generally do not require external nitrogen sources. Non leguminosae crops do not have this trait and require significant amounts of N to be supplied by the soil (Peoples et al., 1995). Zea Maize (corn) for example, typically obtains 50% to 60% of the total nitrogen (TN) needed for proper plant growth, from inorganic N-fertilizers (Baker et al., 2004). Alternatively, soybean crops can generate up to 60% of its TN-requirement from N-fixation with the remaining N-needs coming from N-mineralization (Harper, 1974; Johnson et al., 1975; Olsen et al., 1970; Salvagiotti et al., 2008). The average TN requirement for corn and soybean crops is approximately 220 Kg N·ha^{-1} (Baker et al., 2004; Salvagiotti et al., 2008).

Nitrogen is supplied to the plant in the form of nitrate (NO_3^-) and ammonium (NH_4^+). Ammonium naturally accumulates in the soil through nitrogen fixation and mineralization. At the COBS research site (primary collection site for drainage water samples in this thesis), additional N inputs were supplied to corn cropping systems as urea $CO(NH_2)_2$ at annual rates of 220 kg N·ha^{-1} on corn plots in annual rotation with soybeans and 200 kg N·ha^{-1} on corn plots in continuous annual rotation. Urea is catalyzed by the enzyme urease, in a process referred to as urea hydrolysis, which converts $CO(NH_2)_2$ to ammonia (NH_3) and NH_4^+. During urea hydrolysis, significant amounts of nitrogen can be lost to the atmosphere by volatilization of NH_3. Nitrification is the

process of oxidizing NH_4^+ into NO_3^- by the autotrophic-aerobic microorganisms, Nitrosomonas and Nitrobacter. Nitrosomonas oxidizes NH_4^+ into unstable nitrite (NO_2^-), which is then quickly oxidized by Nitrobacter into NO_3^-. The rate of nitrification is influenced by temperature, soil moisture, pH, artificial nitrification inhibitors, soil texture, cation exchange capacity, aeration, and population of nitrifiers (Sabey, 1958). Optimum conditions for nitrification consist of temperatures between 25°C and 30°C, 60% soil saturation, 35% to 60% oxygen content, pH 7.0-8.5, (Sabey, 1958).

Nitrate's low affinity to the soil makes it more available for plant uptake than ammonium (Baker et al., 2004). Soil particles, especially those of clay soils, have negatively charged exchange sites that attract the positively charged ammonium ion and repel the negatively charged nitrate ion (Sabey, 1958). These forces are largely responsible for ammonium's tendency to become immobile within the soil structure and nitrate's high mobility in the soil-water. Nitrate's movement with the soil water is well documented and is illustrated by strong linear correlations ($R^2 = 0.87$ to 0.98) between subsurface drainage flow rates and the rate of nitrate export observed by Bakhsh et al. (2002), Kanwar et al. (2005), and Owens, (1960). The average NO_3^- concentration in Iowa's drainage water varies significantly among studies, but is consistently well over the EPA's 10 mg L^{-1} MCL (Table 2.3) (Bakhsh et al., 2002; Bjorneberg et al., 1996; Helmers et al., 2005; Lawlor et al., 2008; Qi, 2009). This has a profound effect on receiving waters, where the vast regions of artificially drained crop land within the Mississippi River Basin have been identified as a primary cause of the Hypoxic Zone in the Gulf of Mexico (Rabalais et al., 2001).

While the rate of nitrate export from agricultural subsurface drainage is significantly linked to the local hydrology, it is also influenced by soil structure, organic content, temperature, seasonal precipitation, fertilizer application rate, crop, and tillage (Bakhsh, et al. 2002, Bjorneberg et al.,

1996, Gentry, et al. 1998, Helmers, et al. 2005). Tillage increases aeration within soil particles, causing an increase in the rate of mineralization (Baker et al., 2004). A study comparing the agricultural drainage water NO_3^- concentrations of no-till plots with mold-board and chisel plowed plots revealed a 30% to 50% increase in the concentration of NO_3^- leached from the plowed plots (Weed & Kanwar, 1996). The influence of cropping system on the rate of nitrate export comes with mixed results. Sands et al., (2008), observed a 31% reduction in the concentration of NO_3^- export during soybean years versus corn years on plots in annual corn-soybean rotation. However, other studies have shown there is little statistical evidence to suggest the concentration of NO_3^- export to be different among corn and soybean years (Bakhsh et al., 2002; Zhu & Fox, 2003). Average annual NO_3^- concentrations (ppm) in drainage from common cropping systems, N-fertilizer rates, and tillage practices are provided in Table 2.3.

Denitrification is the process of converting NO_3^- into $N_{2\ (gas)}$ by denitrifying bacteria. The denitrifying bacteria prefer oxygen (O_2) as an electron acceptor for cellular respiration. However, in the absence of oxygen, denitrifying bacteria can alternatively utilize NO_3^- as the electron acceptor (Hoover, 2012). Low O_2 conditions occur when the soil is saturated. Denitrification is significantly influenced by temperature, pH, and organic carbon content (Smith & Tiedje, 1979; Seitzinger et al., 2006). Owens (1960), determined that 38% of the applied N (120 kg N·ha-1) was residual "unused" nitrogen, 33% was lost by denitrification, 15 to 24% was utilized by the crop, and 5 to 20% was leached from the soil.

2.2.4 Magnesium

Much like Ca^{2+}, magnesium ions (Mg^{2+}) are also added to the soil for agricultural liming purposes. However, the main source of Mg^{2+} comes from dolomite ($MgCa(CO_3)^2$) rather that calcite ($CaCO_3$) (West & McBride, 2005). With dolomite being a more secondary source of lime

to calcite, and alkalinity gaining carbon from atmospheric CO_2, Mg^{2+} is the second most abundant cation in soils and tile drainage water (Whisner, 2009).

In addition to the direct application of dolomite, a graph presented in Aquilina et al. (2012) comparing the cumulative concentration of Ca^{2+} and Mg^{2+} against alkalinity show that there is a spike in silicate weathering sources not present in the strictly Ca^{2+} versus alkalinity graph. This suggests that magnesium ions come from silicate weathering sources resulting from nitrification as opposed to carbonic weathering like alkalinity and calcium ions (Aquilina et al., 2012). The sources of silicate weathering can come from many minerals and rocks such as pyroxene (enstatite), amphibole (hornblende), or biotite which wear and break down with time and water flow which can lead to leaching losses in the soil ranging from a few pounds to over 100 pounds Mg^{2+} A^{-1} yr^{-1} in some cases (Aquilina et al., 2012; Mikkelsen, 2010).

Magnesium ions, like calcium ions, are divalent and trivalent ions, such as aluminum, have the same negative effects on the magnesium ion concentration and can also be countered by adding lime or dolomite to the soil (Kamprath & Foy, 1985). Along with competition among ions, during peak growing periods, high-yielding forages and corn silage may remove 50 lb Mg^{2+} A^{-1} (Mikkelsen, 2010). This means that there may be less magnesium ions available to be leached into tile water during prime growing season so lower equivalent concentrations could be expected. In storm flow conditions, for both tilled and non-tilled land, Mg^{2+} and Ca^{2+} equivalent concentrations were equal in drainage water suggesting that since calcium has the higher base flow concentration, magnesium must be more vulnerable to weathering due to flow conditions (Whisner, 2009).

Much like Ca^{2+}, agricultural liming sources such as dolomite, can cause an increase in the amount of Mg^{2+} in the soil and tile water (Mikkelsen, 2010). Alongside an increase of Mg^{2+}, Ca^{2+} concentrations also increase with liming. This causes competition within the ion exchange

complex, opens more ion exchange sites, and increases the solubility of the Mg^{2+} resulting in the Mg^{2+} being more susceptible to leaching (Mikkelsen, 2010). In addition to leaching from agricultural sources, Mg^{2+} also leaches easily from silicate weathering of parent materials already present in the soil. The combination of these factors allows for magnesium to have a fairly consistent concentration throughout the year, but there will be spikes during times of agricultural liming. Storm flow conditions also increase the amount of magnesium in the tile water but due to increases in the flow, the concentrations will be lower in storm flow than they are in base flow (Markewitz et al., 2001).

2.2.5 Chloride

Chloride (Cl^-) is a monovalent anion and is distinguished as the only stable ionic form of chlorine. Its concentration in the soil is dependent on vegetation, mineralization rate, proximity to the ocean, proximity to industrial activities, leaching rate, atmospheric deposition rate, soil matrix, soil amendments, soil organic matter, organic chlorine content, and irrigation. While chloride is an essential component for plant growth (Marschner, 2011), elevated levels in the soil can be toxic. High soil Cl^- concentrations can result from anthropogenic activities such as excessive use of KCl and NH_4Cl fertilizers, and intensive irrigation.

Chloride is notably susceptible to weathering, making it one of the first elements dissolved from the terrestrial rock matrix (Kafkafi, 2001; Zereini, 2008). Chloride, like NO_3^-, has a negative net charge, giving it a low affinity to soil particles and high affinity to the soil water; this is especially true in alkaline soils with a neutral pH (Kafkafi, 2001; White & Broadley, 2001; Zereini, 2008). As a result, most of the Cl^- has been weathered from terrestrial rocks and transported with runoff to the world's oceans. This is evident by the fact that on average, Cl^- accounts for approximately 55% of the major ions in the ocean (Murray, 2004). As a source overall, the world's

oceans are considered the primary source of chloride while terrestrial weathering is typically negligible (Gribble, 2003; Kafkafi, 2001; Lockwood et al., 1995).

Chloride is distributed across the land surface in the form of wet and dry deposition (Gribble, 2003). Sea spray and evaporation of ocean water incorporate Cl^- into the troposphere where it is then deposited over land as precipitation or dust (Junge & Werby, 1958). The influence of ocean water as a source of wet and dry deposition reduces significantly with increasing distance from the coastline (Gribble, 2003; Junge & Werby, 1958; Kafkafi, 2001). In coastal regions, the Cl^- concentration in precipitation can vary between 0.4 to 8 $mg \cdot L^{-1}$. However as the distance from the coastline increases to greater than 500 miles, the Cl^- content in precipitation is less variable and ranges from 0.14 to 0.49 (Junge & Werby, 1958).

Other sources of chloride ions can come from burning fossil fuels, dust and air pollution, fertilizers applied as KCl and NH_4Cl, dispersion of winter road salts, mineralization of organic chlorine deposited by litter, and nitrification inhibitors (Gribble, 2003; Matucha et al., 2010; Parker et al., 1983; White & Broadley, 2001). Chloride is lost from the soil by leaching, plant uptake, and mineralization by soil microorganisms (Gribble, 2003).

Chloride was traditionally considered a conservative ion, in that it played a limited role in biochemical processes (Matucha et al., 2010). As a conservative ion with few source natural sources, Cl^- was frequently employed as a tracer for groundwater flow and other mineral weathering rates (Lockwood et al., 1995; White and Broadley, 2001). However, more recent studies provide evidence against the traditional theory that Cl^- is conservative. Gribble (2003) notes that the soil can act as either a source or sink of Cl^- and that the chloride content is significantly influenced by the organic chlorine content. This suggests that a chemical transformation occurs within the soil. Matucha et al. (2010) found that soil enzymes and

microorganisms facilitate a reaction between soil organic matter and chloride deposited from the atmosphere.

On a global scale Cl^- losses by leaching is approximately 0.2 g Cl^- m^{-2} annually. Furthermore, because Cl^- is tightly linked the soil water, chloride leaching rates can be influenced by the rate of evapotranspiration. In dry periods where evapotranspiration exceed precipitation, chloride is driven upward with the soil water in the soil column; this is driven by the plant root system. Conversely, during wet periods, chloride tends to move downward with excess percolating water (Gribble, 2003).

2.2.6 Sulfate

Sulfate (SO_4^{2-}) is a chemically active divalent anion that originates from mineral weathering, atmospheric deposition, organic matter decomposition, and direct application of land management chemicals (Edwards, 1998; Heng et al. 1991). The negative charge on sulfate makes it highly soluble in percolating groundwater. As a result, sulfate is the primary form of sulfur leached from the soil (Edwards, 1998; Eriksen et al., 2002) and is the only available form of the essential plant micronutrient, elemental sulfur (S) (Buckman & Brady, 1922; Widdowson, 1970). In the soil-water solution, SO_4^{2-} associates with the major cations: Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, H^+, and Al^{3+} (Edwards, 1998). Sulfate rarely occurs at high enough concentrations in the soil to be toxic to plants (Bauder et al., 2007). However, when combined with water, elevated levels of SO_4^{2-} can produce concentrated sulfuric acid (H_2SO_4) spots; sulfuric acid reduces soil pH to point where the soil cannot sustain vegetation (Gough et al., 1979). Alternatively, a more common concern is reduced crop yields caused by sulfur deficiencies (Camberato et al., 2012; Schnug, 1998). Sulfur amendments are becoming a growing need as current S inputs are insufficient in providing the necessary S requirements.

Mineral weathering occurs from the breakdown of parent minerals such as iron, nickel, copper sulfides, gypsum, and calcium carbonates (Edwards, 1998). Decomposing organic matter contains residual organic sulfur that can be reincorporated into the soil as SO_4^{2-} through the process of oxidation. Organic matter decomposition is a minimal source of SO_4^{2-} with respect to the total sulfur budget (Edwards, 1998). Coal burning power plants and industrial activities introduce large quantities of sulfur dioxide (SO_2) and sulfate aerosols (SO_4^{2-}) into the atmosphere (Edwards, 1998). Atmospheric deposition of SO_4^{2-} and absorption of SO_2 by the soils and plants has been a significant S source in soils that lie within close proximity of these activities (Buckman & Brady, 1922; Widdowson, 1970). Strict emission standards, however have reduced the amount of sulfur released into the atmosphere in recent years (Camberato et al., 2012). Lower atmospheric inputs combined with increased crop uptake per unit area, transition to low-S-fertilizers, and sulfate leaching losses in subsurface drainage have consequently increased the number of sulfur deficiencies in crops throughout the United States and Europe (Camberato et al., 2012; Eriksen et al., 2002; Sawyer & Barker, 2001; Schnug, 1998; Widdowson, 1970).

Approximately 95% of the sulfur in the soil is organically bound (Schnug, 1998); the remaining S-content is primarily present as inorganic sulfates and sulfides. In-soil transformations between organic and inorganic sulfur is driven by microbial activity and chemical transformations (Buckman & Brady, 1922). Aeration, temperature, soil moisture, soil texture, vegetation, pH, and liming are factors that influence microbial activity and chemical transformations (Freney & Williams, 1983). Sulfur cycling in the soil is similar to that of nitrate; the major processes involved are immobilization, mineralization, oxidation, reduction, assimilation, absorption, and leaching.

Climatic conditions in the spring and autumn are ideal for bacterial assimilation of sulfate (Edwards, 1998). Bacterial assimilation of sulfate (or immobilization) reduces sulfate to organic

sulfur ($SO_4^{2-} \rightarrow S$). Mineralization reduces sulfate to organic sulfur, which is in turn further reduced to hydrogen sulfide ($SO_4^{2-} \rightarrow S^O \rightarrow H_2S$). In aerobic conditions, sulfate is the principal product of hydrogen sulfide oxidation by soil microorganisms (Widdowson, 1970); prokaryotes are the primary microorganisms involved (Friedrich et al., 2001). Optimal conditions for mineralization are soils temperatures between 20°C to 40°C and 60% soil saturation (Williams, 1967)

The oxidation reaction ($H_2S \rightarrow S^O \rightarrow SO_4^{2-}$) undergoes an intermittent step where hydrogen sulfide is oxidized into elemental sulfur, which is then oxidized to produce sulfate. The rate of oxidation affected by pH, soil moisture content, soil texture, and temperature (Freney & Williams, 1983). The rate of oxidation is greater when the soil moisture content is low, allowing for sufficient aeration, and temperatures range from 27 to 35°C (Edwards, 1998). The concentration of SO_4^{2-} increases in agricultural drainage as a result of increased mineralization rates during these optimal conditions. Additionally, Korentajer et al. (1983) concluded that agricultural liming can also increase the rate of SO_4^{2-} leaching by increasing the mineralization rate and decreasing the adsorption capacity on the soil colloids.

2.2.7   Sodium

Sodium (Na^+) is a monovalent cation and non-essential plant nutrient. Primary sources of sodium are weathering of parent minerals such as silicates and feldspars (Wilding et al., 1963). Wet deposition is also a source of Na^+ ions in the soil, however like Cl^-, Na^+ concentrations in precipitation decreases with increasing distance from the ocean (Junge and Werby, 1958). Extensively irrigated soils in arid regions and regions of interspersed rainfall are prone to sodic conditions (high Na^+ concentrations) caused by the use of brackish irrigation waters (Oster, 1982). Sodic conditions can lead to low soil infiltration and permeability, and reduced crop growth

(Allison, 1964; Bauder et al., 2007). Sodic soils can be remediated by amending with gypsum ($CaSO_4\ 2H_2O$).

As gypsum dissociates in the soil, Ca^{2+} effectively reduces the Na^+ content by forming sodium sulfate (Na_2SO_4) according to the equation: $2Na^+ + CaSO_4 \leftrightarrow Ca^{2+} + Na_2SO_4$ (Bower, 1974). In this equation, the divalent Ca^{2+} ion replaces the monovalent Na^+ ion on the soil exchange sites, causing soluble Na_2SO_4 to be leached from the soil (Bower, 1974; Qadir et al., 2003). Sodium leaching losses increase with anthropogenic additions of Ca^{2+} because Na^+ is held less tightly to the soil exchange sites (Oster, 1982). Similarly, natural weathering of calcite and dolomite produce excess Ca^{2+} and Mg^{2+} ions that replace Na^+ on the soil exchange sites, resulting in the exchanged Na^+ to be leached from the soil (Qadir et al., 2003; Wilding et al., 1963). Bower (1974) reports that only trace amounts of Na^+ are leached from soils in humid regions on annual basis due to minimal inputs and high drainage flow volumes.

2.3 References

Allison, L. E. (1964). Salinity in relation to irrigation. *Adv. Agron*, *16*, 139-180.

Aquilina, L., Poszwa, A., Walter, C., Vergnaud, V., Pierson-Wickmann, A. C., & Ruiz, L. (2012). Long-term effects of high nitrogen loads on cation and carbon riverine export in agricultural catchments. *Environmental science & technology*, *46*(17), 9447-9455.

Baker, J. L., Melvin, S. W., Lemke, D. W., Lawlor, P. A., Crumpton, W. G., & Helmers, M. J. (2004). Subsurface drainage in Iowa and the water quality benefits and problem. In *Drainage VIII, 21-24 March 2004* (p. 1). American Society of Agricultural and Biological Engineers.

Baker, J. L., Campbell, K. L., Johnson, H. P., & Hanway, J. J. (1975). Nitrate, phosphorus, and sulfate in subsurface drainage water. *Journal of Environmental Quality*, *4*(3), 406-412.

Bakhsh, A., Kanwar, R. S., Bailey, T. B., Cambardella, C. A., Karlen, D. L., & Colvin, T. S. (2002). Cropping system effects on NO3–N loss with subsurface drainage water. *Transactions of the ASAE*, *45*(6), 1789.

Bauder, T. A., Waskom, R. M., Davis, J. G., & Sutherland, P. L. (2011).*Irrigation water quality criteria*. Fort Collins, CO, USA: Colorado State University Extension.

Bjorneberg, D. L., Kanwar, R. S., & Melvin, S. W. (1996). Seasonal changes in flow and nitrate-N loss from subsurface drains. *Transactions of the ASAE*, *39*(3), 961-967.

Bonton, A., Rouleau, A., Bouchard, C., & Rodriguez, M. J. (2010). Assessment of groundwater quality and its variations in the capture zone of a pumping well in an agricultural area. *Agricultural water management*, *97*(6), 824-834.

Bower, C. A. (1974). Salinity of drainage waters. Drainage for Agriculture, (drainageforagri), 471-487.

Buckman, H. O., & Brady, N. C. (1922). *The nature and properties of soils* (No. 116). Macmillan.

Burford, J. R., & Bremner, J. M. (1975). Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. *Soil biology and biochemistry*, *7*(6), 389-394.

Camberato, J., Maloney, S., & Casteel, S. (2012). Sulfur deficiency in corn. Purdue University Department of Agronomy. http://www.kingcorn.org/news/timeless/SulfurDeficiency.pdf. (URL accessed April 2016)

Daigh, A. L., Zhou, X., Helmers, M. J., Pederson, C. H., Ewing, R., & Horton, R. (2014). Subsurface drainage flow and soil water dynamics of reconstructed prairies and corn rotations for biofuel production. *Vadose Zone Journal*, *13*(4).

Edwards, P. J. (1998). Sulfur cycling, retention, and mobility in soils: a review.

Eriksen, J., Olesen, J. E., & Askegaard, M. (2002). Sulphate leaching and sulphur balances of an organic cereal crop rotation on three Danish soils.European Journal of Agronomy, 17(1), 1-9.

Freney, J. R., & Williams, C. H. (1983). The Sulphur Cycle in Soil. In M. V. Ivanov & J. R. Freney (Eds.). *The Global Biogeochemical Sulphur Cycle* (129-159). Published on behalf of the Scientific Committee on Problems of the Environment of the International Council of Scientific Unions

Friedrich, C. G., Rother, D., Bardischewsky, F., Quentmeier, A., & Fischer, J. (2001). Oxidation of reduced inorganic sulfur compounds by bacteria: emergence of a common mechanism?. *Applied and Environmental Microbiology*, *67*(7), 2873-2882.

Gali, R. K., Soupir, M. L., & Helmers, M. J. (2012). Electrical Conductivity as a tool to estimate chemical properties of drainage water quality in the Des Moines Lobe, Iowa.

Gentry, L. E., David, M. B., Smith, K. M., & Kovacic, D. A. (1998). Nitrogen cycling and tile drainage nitrate loss in a corn/soybean watershed.*Agriculture, ecosystems & environment*, *68*(1), 85-97.

Gough, L. P., Shacklette, H. T., & Case, A. A. (1979). Element concentrations toxic to plants, animals, and man (No. 1466). US Govt. Print. Off.

Gribble, G. W. (Ed.). (2003). *Natural production of organohalogen compounds* (Vol. 3). Springer Science & Business Media.

Harper, J. E. (1974). Soil and symbiotic nitrogen requirements for optimum soybean production. *Crop Science*, *14*(2), 255-260.

Helmers, M. J., Lawlor, P., Baker, J. L., Melvin, S., & Lemke, D. (2005). Temporal subsurface flow patterns from fifteen years in north-central Iowa. In*2005 ASAE Annual Meeting* (p. 1). American Society of Agricultural and Biological Engineers.

Heng, L. K., White, R. E., Bolan, N. S., & Scotter, D. R., (1991) Leaching losses of major nutrients from a mole-drained soil under pasture, New Zealand Journal of Agricultural Research, 34:3, 325-334

Hoover, N. L. (2012). Denitrification woodchip bioreactor two-phase column study: Evaluation of nitrate removal at various hydraulic retention times and effect of temperature on denitrification rates.

Johnson, J. W., Welch, L. F., & Kurtz, L. T. (1975). Environmental implications of N fixation by soybeans. *Journal of Environmental Quality*, *4*(3), 303-306.

Junge, C. E., & Werby, R. T. (1958). The concentration of chloride, sodium, potassium, calcium, and sulfate in rain water over the United States. *Journal of Meteorology*, *15*(5), 417-425.

Kafkafi, U. (2001). Potassium and chloride in crops and soils: The role of potassium chloride fertilizer in crop nutrition. A. E. Johnston (Ed.). International Potash Institute.

Kamprath, E. J., & Foy, C. D. (1985). Lime-fertilizer-plant interactions in acid soils. *Fertilizer technology and use*, (fertilizertechn), 91-151.

Kanwar, R. S., Colvin, T. S., & Karlen, D. L. (1997). Ridge, moldboard, chisel, and no-till effects on tile water quality beneath two cropping systems.*Journal of Production Agriculture*, *10*(2), 227-234.

Kanwar, R. S., Cruse, R. M., Ghaffarzadeh, M., Bakhsh, A., Karlen, D. L., & Bailey, T. B. (2005). Corn-soybean and alternative cropping systems effects on NO3-N leaching losses in subsurface drainage water. *Applied Engineering in Agriculture*, *21*(2), 181-188.

Korentajer, L., Byrnes, B. H., & Hellums, D. T. (1983). The effect of liming and leaching on the sulfur-supplying capacity of soils. *Soil Science Society of America Journal*, *47*(3), 525-530.

Lawlor, P. A., Helmers, M. J., Baker, J. L., Melvin, S. W., & Lemke, D. W. (2005). Nitrogen application rate effects on corn yield and nitrate-nitrogen concentration and loss in

subsurface drainage. In *2005 ASAE Annual Meeting* (p. 1). American Society of Agricultural and Biological Engineers.

Lockwood, P. V., McGarity, J. W., & Charley, J. L. (1995). Measurement of chemical weathering rates using natural chloride as a tracer. *Geoderma*, *64*(3), 215-232.

Markewitz, D., Davidson, E. A., Figueiredo, R. D. O., Victoria, R. L., & Krusche, A. V. (2001). Control of cation concentrations in stream waters by surface soil processes in an Amazonian watershed. *Nature*, *410*(6830), 802-805.

Marschner, H. (2011). Marschner's mineral nutrition of higher plants. Academic press.

Matucha, M., Clarke, N., Lachmanová, Z., Forczek, S. T., Fuksová, K., & Gryndler, M. (2010). Biogeochemical cycles of chlorine in the coniferous forest ecosystem: practical implications. *Plant, Soil and Environment*, *56*(8), 357-367.

Mikkelsen, R. (2010). Soil and fertilizer magnesium. *Better crops*, *94*(2), 26-28.

Murray, J. (2004). Major ions of seawater. URL http://www. ocean. washington. edu/courses/oc400/Lecture_Notes/CHPT4. pdf.

Oh, N. H., & Raymond, P. A. (2006). Contribution of agricultural liming to riverine bicarbonate export and CO2 sequestration in the Ohio River basin.*Global biogeochemical cycles*, *20*(3).

Olsen, R. J., Hensler, R. F., Attoe, O. J., Witzel, S. A., & Peterson, L. A. (1970). Fertilizer nitrogen and crop rotation in relation to movement of nitrate nitrogen through soil profiles. *Soil Science Society of America Journal*, *34*(3), 448-452.

Oster, J. D. (1982). Gypsum usage in irrigated agriculture: a review. *Fertilizer research*, *3*(1), 73-89.

Owens, L. D. (1960). Nitrogen movement and transformations in soils as evaluated by a lysimeter study utilizing isotopic nitrogen. *Soil Science Society of America Journal*, *24*(5), 372-376.

Parker, M. B., Gascho, G. J., & Gaines, T. P. (1983). Chloride toxicity of soybeans grown on Atlantic coast flatwoods soils. *Agronomy Journal*, *75*(3), 439-443.

Peoples, M. B., Herridge, D. F., & Ladha, J. K. (1995). Biological nitrogen fixation: an efficient source of nitrogen for sustainable agricultural production?. *Plant and soil*, *174*(1-2), 3-28.

Pierson-Wickmann, A. C., Aquilina, L., Weyer, C., Molénat, J., & Lischeid, G. (2009). Acidification processes and soil leaching influenced by agricultural practices revealed by strontium isotopic ratios. *Geochimica et Cosmochimica Acta*, *73*(16), 4688-4704.

Qadir, M., Steffens, D., Yan, F., & Schubert, S. (2003). Sodium removal from a calcareous saline–sodic soil through leaching and plant uptake during phytoremediation. *Land Degradation & Development*, *14*(3), 301-307.

Qi, Z. (2009). Monitoring and modeling of subsurface drainage and nitrate leaching under various land covers.

Rabalais, N. N., Turner, R. E., & Wiseman, W. J. (2001). Hypoxia in the Gulf of Mexico. *Journal of Environmental Quality*, *30*(2), 320-329.

Randall, G. W., & Iragavarapu, T. K. (1995). Impact of long-term tillage systems for continuous corn on nitrate leaching to tile drainage. *Journal of Environmental Quality*, *24*(2), 360-366.

Raymond, P. A., & Cole, J. J. (2003). Increase in the export of alkalinity from North America's largest river. *Science*, *301*(5629), 88-91.

Sabey, B. R. (1958). Rate of nitrification in some Iowa soils as influenced by temperature, reaction and population of nitrifying bacteria.

Salvagiotti, F., Cassman, K. G., Specht, J. E., Walters, D. T., Weiss, A., & Dobermann, A. (2008). Nitrogen uptake, fixation and response to fertilizer N in soybeans: A review. *Field Crops Research*, *108*(1), 1-13.

Sands, G. R., Song, I., Busman, L. M., & Hansen, B. J. (2008). The effects of subsurface drainage depth and intensity on nitrate loads in the northern cornbelt. *Transactions of the ASABE*, *51*(3), 937-946.

Sawyer, J. E., & Barker, D. W. (2001). Sulfur fertilizer application to corn and soybean.

Schnug, E. (1998). Sulphur in agroecosystems (Vol. 2). Springer Science & Business Media.

Seitzinger, S., Harrison, J. A., Böhlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B., & Drecht, G. V. (2006). Denitrification across landscapes and waterscapes: a synthesis. *Ecological Applications*, *16*(6), 2064-2090.

Smith, M. S., & Tiedje, J. M. (1979). Phases of denitrification following oxygen depletion in soil. *Soil Biology and Biochemistry*, *11*(3), 261-267.

Stauffer, R. S., & Rust, R. H. (1954). Leaching losses, runoff, and percolate from eight Illinois soils. *Agronomy Journal*, *46*(5), 207-211.

Steele, K.W.; Judd, M. 1.; Shannon, P. W. 1984: Leaching of nitrate and other nutrients from a grazed pasture. New Zealand journal of agricultural research 27:5-11.

Weed, D. A. J., & Kanwar, R. S. (1996). Nitrate and water present in and flowing from root-zone soil. *Journal of Environmental Quality*, *25*(4), 709-719.

West, T. O., & McBride, A. C. (2005). The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions. *Agriculture, Ecosystems & Environment*, *108*(2), 145-154.

Whisner, C. (2009). Inorganic Carbon Cycling in Agricultural Lands, Coshocton, Ohio.

White, P. J., & Broadley, M. R. (2003). Calcium in plants. *Annals of botany*, *92*(4), 487-511.

White, P. J., & Broadley, M. R. (2001). Chloride in soils and its uptake and movement within the plant: a review. *Annals of Botany*, *88*(6), 967-988.

Widdowson, J. P. (1970). Available sulfur in some Iowa soils.

Wilding, L. P., Odell, R. T., Fehrenbacher, J. B., & Beavers, A. H. (1963). Source and distribution of sodium in solonetzic soils in Illinois. *Soil Science Society of America Journal*, *27*(4), 432-438.

Williams, C. H. (1967). Some factors affecting the mineralization of organic sulphur in soils. *Plant and Soil*, *26*(2), 205-223.

Zereini, F. (2008). Climatic changes and water resources in the Middle East and North Africa. Springer.

Zhu, Y., & Fox, R. H. (2003). Corn–soybean rotation effects on nitrate leaching. *Agronomy Journal*, *95*(4), 1028-1033.

2.4 Tables

Table 2.1. Mean and range of concentrations (ppm) of primary dissolved constituents in agricultural subsurface drainage effluent from several different geographic and climatic regions.

Reference	Statistic	HCO_3^-	Ca^{2+}	NO_3^-	Mg^{2+}	Cl^-	SO_4^{2-}	Na^+
[a]Illinois, USA;	Range	-	25 - 99	16 - 89	16 - 60	-	3 - 39	4 - 148
Stauffer (1942)	Mean	-	62	51	34	-	11	21
[b]Kaikohe, New Zealand;	Range	-	1 - 124	0.4 - 268	1 - 13	2 - 119	0.4 - 14	2 - 17
Steele et al. (1984)	Mean	-	15	32	3	18	11	7
[c]Kaikohe, New Zealand;	Range	-	3 - 80	0 - 284	1 - 21	0 - 54	0 - 29	2 - 26
Steele et al. (1984)	Mean	-	24	94	5	18	5	9
[d]Ohio, USA;	Range	44 - 206	65 - 72	-	26 - 39	14 - 17	120 - 184	0 - 5
Bower (1974)	Mean	125	69	-	33	15	152	2
[e]Iowa, USA;	Range	-	-	-	-	-	-	-
Bower (1974)	Mean	253	98	-	32	25	54	7
[e]Iowa, USA;	Range	-	-	22 - 160	-	-	38 - 103	-
Baker et al. (1975)	Mean	-	-	81	-	-	63	-
[e]Iowa, USA;	Range	-	-	24 - 55	-	-	-	-
Gali et al. (2012)	Mean	-	-	45	-	-	-	-
[f]California, USA;	Range	203 - 320	158 - 549	-	42 - 179	292 - 638	384 - 2498	131 - 752
Bower (1974)	Mean	278	297	-	92	431	1235	455

No available data is indicated by (-)

[a] Humid climate, shallow loam soils, fallow prairie, 0 kg N ha^{-1}, not irrigated.
[b] Subtropical climate, Ruatangata soils, pasture, 0 kg N ha^{-1}, not irrigated.
[c] Subtropical climate, Ruatangata soils, pasture; 57.5 kg N ha^{-1}, not irrigated.
[d] Humid climate; Tiffin & Castalia, Ohio; not irrigated.
[f] Humid climate; Boone, Carroll, and Story Counties, Iowa; corn and soybean crops, N-fertilized, not irrigated.
[f] Arid climate; Coachella Valley, Lake Mathews, and San Joaquin California; irrigated.

Table 2.2. Average annual precipitation (mm) and subsurface drainage flow (mm) reported in several published results for common cropping systems in Iowa.

| Reference | Management | | Tile Layout | | Drainage Ratio | | |
	Cropping System[a]	Tillage	Spacing (m)	Depth (m)	Precip. (mm)	Drainage (mm)	DR
Bakhsh et al., 2002	CS	Chisel	28.5	1.2	832	122	0.13
Bakhsh et al., 2002	SC	Chisel	28.5	1.2	832	122	0.13
Bjorneberg et al., 1996	CC	Moldboard	28.5	1.2	925	129	0.15
Kanwar et al., 2005	ROT	Chisel	28.5	1.2	832	179	0.20
Kanwar et al., 2005	STR	Chisel	28.5	1.2	832	178	0.20
Bjorneberg et al., 1996	CC	Chisel	28.5	1.2	925	194	0.21
Bjorneberg et al., 1996	CC	Ridge till	28.5	1.2	925	207	0.22
Bakhsh et al., 2002	CS	No-till	28.5	1.2	832	246	0.28
Bjorneberg et al., 1996	CC	No-till	28.5	1.2	925	263	0.29
Bakhsh et al., 2002	SC	No-till	28.5	1.2	832	252	0.29
Lawlor et al., 2008	C&S	Chisel	7.6	1.06	600	155	0.20
Lawlor et al., 2008	C&S	Chisel	7.6	1.06	600	137	0.22
Lawlor et al., 2008	C&S	Chisel	7.6	1.06	637	218	0.34
Lawlor et al., 2008	C&S	Chisel	7.6	1.06	637	240	0.37
Helmers et al., 2005	CS	Chisel	7.6	1.06	620	269	0.41
Lawlor et al., 2008	C&S	Chisel	7.6	1.06	600	279	0.44
Qi, 2009	CS	Chisel	7.6	1.06	771	331	0.43
Qi, 2009	SC	Chisel	7.6	1.06	771	333	0.43

[a] Cropping systems: (C&S) = alternate rows of corn and soybean; (SC) = soybean in annual rotation with corn; (CS) = corn in annual rotation with soybean; (CC) = corn in continuous rotation.

Table 2.3. Mean annual nitrate-nitrogen (NO3-N) concentrations in agricultural subsurface drainage effluent at research sites in Nashua, Iowa and Pocahontas County, Iowa.

Reference	Cropping System[a]	Tillage	N-Fertilizer Rate (kg N ha^{-1} yr^{-1})	Avg. Drainage Conc. (mg N L^{-1})
Lawlor et al., 2008	C&S	Chisel	45	5.7
Lawlor et al., 2008	C&S	Chisel	90	8.1
Bakhsh et al., 2002	SC	No-till	0	8.3
Bakhsh et al., 2002	SC	Chisel	0	10.4
Bakhsh et al., 2002	CS	No-till	110	10.7
Lawlor et al., 2008	CS	Chisel	134	11.9
Bakhsh et al., 2002	CS	Chisel	110	12.0
Qi, 2009	SC	Chisel	0	13.3
Qi, 2009	CS	Chisel	140	14.0
Lawlor et al., 2008	C&S	Chisel	168	15.5
Bjorneberg et al., 1996	CC	No-till	200	23.0
Lawlor et al., 2008	C&S	Chisel	252	23.4
Bjorneberg et al., 1996	CC	Ridge till	200	25.3
Bjorneberg et al., 1996	CC	Chisel	200	32.3
Bjorneberg et al., 1996	CC	Moldboard	200	38.0

[a] Cropping systems: (C&S) = alternate rows of corn and soybean; (SC) = soybean in annual rotation with corn; (CS) = corn in annual rotation with soybean; (CC) = corn in continuous rotation.

4

CHAPTER 3. DISSOLVED CONSTITUENTS IN AGRICULTURAL DRAINAGE WATERS

Brett Zimmerman and Amy Kaleita

3.1 Abstract

Efflux of dissolved solutes in agricultural subsurface drainage systems adversely affect ecosystems of receiving waters, degrade soil fertility, and represent economic losses to farmers. These solutes are frequently studied without regard to associated ions, which play a fundamental role in the transport characteristics of one another. Here we conduct a literature review to identify major dissolved constituents in agricultural drainage waters characteristic to Central Iowa, and pinpoint causes for variability in the leaching rate of these constituents. This literature review is complimented by a thorough field investigation that analyzes major solute concentrations with respect to seasonal conditions, common cropping systems, and relationships among ions. Results from this investigation reveal that primary dissolved constituents consist of bicarbonate, calcium, nitrate, magnesium, chloride, sodium, and sulfate (in order of decreasing ppm concentration). Analysis of seasonal drainage samples showed that bicarbonate, calcium, and magnesium were present at greater concentrations during the post growing season, while nitrate and chloride were greatest in the growing season. Seasonal variability of sulfate and sodium was negligible. Continuous corn and corn in annual rotation with soybeans had greater magnesium and chloride concentrations than that of soybeans in annual rotation with corn. Conversely, calcium was greater among soybean cropping systems compared to that of corn cropping systems. Bicarbonate and nitrate were not significantly different among any of the cropping systems. A strong correlation

between bicarbonate and calcium, suggests that agricultural lime dissolution was caused by mineral weathering, rather than acidification caused by N-fertilizer applications or nitrification. An analysis of observed drainage flows, pH, and temperature suggested that these parameters were not good indicators for differences in the ionic composition.

3.2 Introduction

Artificial subsurface drainage is common in agricultural regions with high water tables and poorly drained soils (Helmers et al., 2005). Drainage systems consist of perforated pipe networks placed below the root zone, typically at a depth of 0.9 - 1.2 meters from the soil surface, thereby providing a pathway for water to flow from the upper soil horizons. This promotes crop growth and increases crop yield in poorly drained soils (Baker et al., 2004). As water drains through the soil profile, it dissolves parent minerals and electrolytes, causing them to dissociate into their component cations and anions (Bower, 1974; Rhoades et al., 1973). Drainage systems then convey these solutes from the subsoil to surface water bodies. Solutes transported in this manner may represent an economic loss to farmers in the form of lost nutrients, and/or may adversely affect downstream ecosystems and can be expensive to remove from drinking water sources. These issues are illustrated most prominently with agricultural efflux of nitrate (NO_3^-), which is largely responsible for the Hypoxic Zone in the Gulf of Mexico (Rabalais et al., 2001; Schilling & Libra, 2000). Nitrate efflux from Iowa drainage waters account for approximately 25% of the total nitrate that enters the Gulf of Mexico from the Mississippi River (Shilling & Libra, 2000). Other solutes, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}), contribute to water hardness and soil acidity when they are leached from the soil; this increases drinking water treatment costs (Ravindra & Kaushik, 2003; Madramootoo et al., 1997) and land management costs by having to continuously apply agricultural lime (Buckman & Brady, 1922). To develop effective mitigation strategies it is

beneficial to first understand what influences solute leaching rates and how solutes interact with one another.

Land management practices and environmental conditions play a fundamental role in determining the rate of solute efflux from agricultural subsurface drainage. In the soil profile, electrolyte dissolution is a function of percolation rate and ground-water flow path, both of which are influenced by the intensity and frequency of rainfall events, soil structure, soil type, tillage, cover, evapotranspiration, and cropping system (Bower, 1974; Daigh et al., 2014; Gribble, 2003; Liard et al., 2010; Thomas & Phillips, 1979; Trudgill et al., 1983; Stauffer & Rust, 1954). While the concentration of ions leached is highly dependent on the characteristics of percolating groundwater, it is also a influenced by chemical ion-pair formations (Oster & Mcneal, 1971), availability and solubility of exchangeable bases (Liard et al., 2010; Macintire et al., 1952), soil pH (Kafkafi, 2001; White & Broadley, 2001; Zereini, 2008), ion affinity to the soil (Buckman & Brady, 1922), and drainage water exposure to the atmosphere (Rhoades et al., 1973).

The relative abundance of an ion can also influence the leaching rate of other ions (Chao et al., 2011; Heng et al., 1991; Steele et al., 1984; Terman, 1977). The addition of NH_4^+ or Ca^{2+} can displace Na^+ and Mg^{2+} from soil exchange sites, as these ions (Na^+ and Mg^{2+}) have a lower affinity to the soil (Barber, 1995; Beckett, 1965; Poss & Saragoni, 1992). Dissolution of agricultural lime (calcite and dolomite) produces the dissociated ions Ca^{2+}, Mg^{2+}, HCO_3^-, and NO_3^- (West & McBride, 2005). Baker et al., (1975) suggested that nitrate is toxic to sulfate forming microorganisms, resulting in a negative relationship between SO_4^{2-} and NO_3^- concentrations. Evidence of these interactions have been illustrated by significant correlations among ions observed in the following studies. Steele et al., (1984) reported a strong linear correlation between the equivalent concentrations of Ca^{2+} and NO_3^- leached. The study also indicates that both Ca^{2+}

and NO_3^- are good predictors for estimating the concentrations of Mg^{2+}, Na^+, and K^+; correlation coefficients from the regression of Ca^{2+}, Mg^{2+}, Na^+, K^+ on NO_3^- were 0.98, 0.90, 0.76, 0.59 for fertilized plots and slightly lower for unfertilized plots. The positive correlation between NO_3^- and major cations observed by Steele et al. (1984) was also observed by Heng et al. (1991), where a near 1:1 relationship between total cation and anion molar concentrations was maintained in all drainage samples despite increases in N-fertilization. A comprehensive review of ion leaching results from several published lysimeter studies was conducted by Terman (1977), whose conclusions further illustrate that the leaching rate characteristics of individual ions can be greatly influenced by the presence of other ions in the soil. It is important to note that not all correlations observed by these studies were solely a result of ion dependency on one another, processes such as drainage flow rate and crop uptake could have also contributed to the strong correlations. Nonetheless, given our knowledge of ion-ion interactions, we can reasonably conclude that these correlations provide at least some evidence of ion-ion dependency.

As illustrated above, the leaching rate of individual ions is function of several factors, including the presence of other ions. Complete knowledge of these processes and the leaching response of major ions is essential for development of effective mitigation strategies. However, there are few published results which have conducted a comprehensive evaluation of major dissolved constituents in agricultural drainage efflux, and even fewer have done so with real drainage samples (Heng et al., 1991). Furthermore, with increasing interest in developing dielectric sensors to monitor nitrate, it is important to have current data on the presence and dynamics of the various ion species (Gali, 2014). Therefore, in this study we will address this knowledge gap by first performing a literature review to identify the major dissolved constituents in agricultural subsurface drainage effluent; note the focus of this study will be in reference to

Iowa drainage waters. Secondly, we will complement the literature review with a field investigation of major subsurface drainage water constituents. In so doing, we hope to (1) gain insight into ion-ion relationships; (2) evaluate compositional variability with respect to growing season and post growing season drainage waters, as well as variability among three common cropping systems, drainage flow rate, pH, and temperature; (3) quantify compositional differences between plot scale and watershed scale drainage waters.

3.3 Materials and Methods

3.3.1 Literature Review

Relevant research involving ionic constituents in tile drain water, either as primary or secondary research objectives, was identified by searching the literature using Google Scholar, the Iowa State University Digital Repository, and Science Direct. A total of 7 papers were identified, spanning the years 1974 to 2012. Drainage water constituents and their corresponding concentrations were synthesized from several published results for streams and drainage waters in regions with similar environmental conditions to that of Central Iowa.

3.3.2 Field Investigation

Water samples were collected and analyzed for major ion concentrations, as determined from the literature review, from subsurface drainage flow at two locations in Central Iowa. A total of 44 samples were taken during the one year study period from May to December, 2015. Of the 44 samples, 40 were collected at the Iowa State University's Comparison of Biofuel Cropping System (COBS) research site and 4 were collected at the Hickory Grove Watershed drainage district outlet; both sites are described below. As part of parallel studies, it was important to collect samples from a variety of cropping systems, seasons, and locations. The sampling distribution is as follows: 4 samples from COBS at the end of May, 24 samples from COBS throughout June; 4

samples from both COBS and Hickory Grove throughout September and October; 8 samples from COBS in mid-December. The primary collection site, COBS, consists of several hydraulically separated no-till research plots, which allow for controlled experiments involving agricultural drainage water. By contrast, samples from Hickory Grove were of interest because they are representative of subsurface drainage effluent from a typical Iowa watershed under intensive agricultural row cropping. The proximity of Hickory Grove to COBS (approximately 21 miles NE of the COBS site) provided similar environmental conditions (ie. precipitation, temperature, soil type and leaching rate) at both locations. Samples were collected during the post growing season at Hickory Grove, as our interest in and access to this site was not realized until late in the study period.

3.3.3   COBS Study Area

The Iowa State University's Comparison of Biofuel Cropping System (COBS) research site is located in Boone County, Iowa. Soil distributions and properties were acquired from the NRCS Web Soil Survey. The soil distribution is approximately 50% Webster clay loam at 0 to 2% slopes and 50% Nicollet loam at 1 to 3% slopes. The average soil texture distribution weighted over depth (0 to 2 m) is: 41% sand, 38% silt, and 21% clay. Nicollet soils are classified as hydrologic soil group B and Webster soils are in the hydrologic soil group C. The site as described by Daigh et al. (2012), has 24 plots measuring 200 ft in length and 90 ft in width. Plots are randomized according to 6 cropping systems having 4 replicates each. Sampled cropping systems in this study are (1) C2 - corn on soybean rotation; (2) S2 – soybean on corn rotation; (3) CC - continuous corn with stover removal; (4) P - continuous unfertilized prairie. Nitrogen fertilizer was injected in the spring (prior to planting) as 32% Urea Ammonium Nitrate (UAN) at a rate of 87 kg N ha^{-1} on cropping systems C2 and CC. A second 32% UAN injection was performed in

the spring the after corn emerged; application rates were 134 kg N ha^{-1} on C2 plots and 112 kg-N ha^{-1} on CC plots. Agricultural lime was applied in the spring (prior to planting) at a rate of 13,050 kg ha^{-1} (ECCE = 7,000 kg ha^{-1}) on all corn and soybean plots (cropping systems = C2, S2, CC).

Subsurface drainage is provided by 15 cm diameter corrugated plastic pipes placed at a depth of 1.1 m along the center line, length wise, of each plot. Plots are hydraulically separated by additional drainage lines placed between plots. Each center tile drains to a sump pit where cumulative flow is recorded by a mechanical flow meter. A portion of the flow is collected in a 5-L container to provide flow proportional water samples. For this study, 30 flow-weighted samples were used. An additional 12 samples were collected using grab sampling methods. Grab samples were collected during the post growing season to maintain consistency with samples collected from Hickory Grove, described below; Hickory Grove does not have automated sampling. Grab sampling was performed by collecting drainage water directly from the tile outlet. Flow for grab samples was determined by the time required to fill a 1-liter sample container; time was recorded using a stopwatch. Flow weighted composite samples were acquired from an existing in-situ flow proportionate water collection system; flow was recorded from the flow meter at the time of collection.

3.3.4   Hickory Grove Study Area

The Hickory Grove Lake Watershed is a sub-basin of the South Skunk River Basin (HUC ID: 07080105) in Story County, Iowa. Predominant soils in this region are poorly drained fine-loam, fine-silt, and coarse-loam. Soil types consisting of Clarion, Nicollet and Webster encompass 78% of the watershed.   According to the "Hickory Grove Lake Watershed Management Action Plan", approximately 74% of the watershed's soils are classified as hydrologic soil group B with hydraulic conductivities between 11-31 mm h^{-1} (Andrews et al., n.d.). The watershed is 1633 ha

in area and has median slopes of less than 2%. The prevailing land use (84.7%) is row crops with corn and soybean being the primary crops. The remaining land uses are grass (9.8%), forest (1.6%), water (2.2%), barren (0.9%), and artificial (0.7%) (IDNR, 2014). Gali et al. (2012), reported fertilizer applications of diammonium phosphate to soybean crops at a rate of 85 kg ha^{-1} in the spring prior to planting and anhydrous ammonia was applied to corn crops at a rate of 160 kg ha^{-1} in the fall (post soybean harvest) and spring (prior to corn planting). Tillage consists of conservation, strip-till, and no-till practices (Gali et al., 2012), but the proportion and distribution of tillage practices is unknown.

A drainage district is located in the watershed's southeastern half, and drains 879 ha of the 1633 ha. The drainage district has of a network of lateral drainage pipes that connect to a drainage district main line. Lateral diameters range from 12.7 cm to 25.4 cm and are placed at a depth of approximately 1.2 m. Twenty-three surface intakes are joined to the drainage network and only flow during rainfall-runoff events and ponding. All flow within the network is routed to the drainage district outlet, which is 91.44 cm in diameter. Grab samples were collected at the drainage district outlet. Flow was determined by the depth of water from the pipe invert in conjunction with a rating curve developed by Gali et al. (2012).

3.3.5 *Analysis of Field Samples*

A Hach Pocket Pro + Multi 2 (Hach, Loveland, CO) meter was used to measure pH and temperature in collected field samples. Based on the literature review (see Results), the following ions were identified for chemical analysis of the water samples from COBS: bicarbonate (HCO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sulfate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^-), and sodium (Na^+). Chemical analyses were performed by the Iowa State Hygienic Laboratory (ISHL) in Ankeny, Iowa. Analysis methods used by ISHL are: EPA 300 for SO_4^{2-}, Cl^-, NO_3^-; EPA 200.7 for

Ca^{2+}, Mg^{2+}, Na^+; LAC 10-107-06-IJ for NH3; SM 2320B for Alkalinity as $CaCO_3$ (reports HCO_3^- and CO_3^{2-}). All ion concentrations were reported in ppm. Reported bicarbonate and nitrate concentrations were converted to mg HCO_3^- L^{-1} and mg NO_3^- L^{-1}. Ions and electrolytes not included in the chemical analysis but present in the drainage water samples were assumed to be negligible given their reported concentrations in the literature.

This assumption was verified by evaluating the charge imbalance between the total cation and anion equivalent concentrations for each sample. Rhoades et al. (1973) and Heng et al. (1991) show that the total equivalent concentration of cations in agricultural drainage waters tends to be in approximate balance with total anions. This is illustrated more precisely in observations made by Steele and Judd (1984) in which each unit increase in the equivalent concentration of NO_3^- was balanced by an equal increase of cations ($Ca^{2+} > Mg^{2+} > Na^+ > K^+$: order of increased equivalent concentration). Given these findings, it can be reasonably assumed that samples with significant charge imbalances are either incomplete in their chemical analyses or contamination occurred during sample collection. The procedure used to calculate CI follows that identified in McCleskey et al. (2012), where CI is calculated by Equation 3.1, which requires $\sum$cations and $\sum$anions to be in the form of their milli-equivalent concentration (meq L^{-1}). A negative value for CI indicates anions dominate the solution's overall charge, whereas a positive CI suggests cations dominate. A commonly accepted value of CI > ± 10% is used as the criteria for eliminating samples with erroneous or incomplete chemical analysis.

$$CI = \frac{(\sum cations - \sum anions)}{(\sum cations + \sum anions)/2}$$
(3.1)

3.3.6   Parameters that Influence Drainage Composition

Ikenberry et al. (2014) concluded that nitrate export was greatest during the early growing season and lowest in the post growing season. Bower (1974) reports crop uptake as a significant sink of major ions; the magnitude of this uptake is significant enough to affect ion leaching rate. Additionally, Terman (1977) concluded that the relative abundance of ions is the primary factor that determines ion leaching rates. In this study, we represent differences in these influential conditions with the following sampling groups: season (growing season and post growing season), and cropping systems (C2, S2, CC). Given different environmental conditions, crops, and N-fertilization rates, we expect the drainage water compositions to be significantly different among these sampling groups.

From the literature review we determined how the drainage composition was expected to change with respect to different seasonal conditions and different cropping systems. A statistical analysis was then carried out to determine if collected field samples behaved accordingly. Analyses were performed on samples collected from the COBS research site; Hickory Grove samples were not included in these tests because there is no hydraulic separation between cropping systems and samples were not collected in both the growing and post growing seasons. Appropriate statistical methods were established based on tests for normality and homogeneity of variance among sampling groups. Two-sample tests were used to compare the distribution of each major ion observed in growing season samples with samples collected during the post growing season. The ANOVA model (and the equivalent non-parametric model) were used to compare C2, S2, and CC cropping systems in growing season samples. In addition to evaluating the effect of cropping system on drainage water composition, we also looked at their effect on drainage flow volume, pH, and temperature. Significant differences in flow, pH, and temperature among

cropping systems were tested to ascertain if these parameters corresponded with the ionic compositions. Dissimilar cropping system trends between these parameters and the ionic composition would then suggest that these parameters cannot be used to make significant conclusions regarding the ionic composition. All test results were evaluated at alpha level 0.05.

3.3.7 Relationships Among Ions

Heng et al. (1984), Steele et al. (1984), and Terman (1977) show that there are significant relationships among major dissolved constituents. For example, Steele et al. (1984) found that the cumulative concentration of major cations in drainage waters responded proportionately to increased concentrations of nitrate. Furthermore, both Steele et al. (1984) and Terman, (1977) observed significant linear correlations among most major solutes. In this analysis we complement the work of Heng et al. (1984), Steele et al. (1984), and Terman (1977) by conducting a statistical analysis among ions to evaluate ion-ion relationships. Assumptions for normality and equality of variance were checked and appropriate statistical methods were applied.

3.3.8 Plot Scale vs Watershed Scale Drainage Water Analysis

A small sample set ($n = 4$) was collected from the Hickory Grove drainage district outlet for the purpose of quantifying differences in the ionic composition of watershed scale drainage with plot scale drainage from COBS. The proximity of Hickory Grove to COBS eliminates significant compositional differences caused by variations in climate and soil properties (soil properties at COBS and Hickory Grove are characteristic to the southern branch of the Des Moines Lobe). While the drainage system at COBS allows for the collection of flow proportionate sampling, only grab samples were available at Hickory Grove. To ensure accurate comparisons between COBS and Hickory Grove, grab sampling was performed at COBS during the post growing season, which correlates with the sampling period at Hickory Grove. Statistical

comparisons between Hickory Grove and the COBS research site were limited given that drainage effluent at Hickory Grove is representative of several different cropping systems, tillage, and N-fertilizer rates whereas these parameters at COBS are precisely controlled. Therefore, data gathered from Hickory Grove were used to establish baseline conditions for watershed scale drainage, and compare those to the mean drainage conditions observed across all samples at COBS.

3.4 Results

3.4.1 Literature Review

Prior to conducting the field investigation, a review of the literature was performed to identify drainage water constituents that are to be expected in field samples. Given the high costs associated with chemical analyses of sample analytes, these results were used to distinguish major constituents by their reported concentrations.

At least 12 dissociated ions can be present in Central Iowa drainage waters (Bower, 1974; Gali et al., 2012) and streams (Barnes, 2001) (Table 3.1). Note that an additional 18 electrolytes related to herbicides, pesticides, and personal care products are also known to be transported in agricultural drainage waters in humid regions throughout the United States (Table 3.1) (Gilliam et al., 1999; Gottschall et al., 2012; Muir & Baker, 1976). Assuming all of these constituents would be present in samples at COBS and Hickory Grove, we expected an average total dissolved solids concentration of 508 ppm; this was calculated as the cumulative concentration of the 30 constituents identified in published literature. Primary dissolved constituents include the following free ions: bicarbonate (HCO_3^-), calcium (Ca^{2+}), nitrate (NO_3^-), magnesium (Mg^{2+}), sulfate (SO_4^{2-}), chloride (Cl^-), sodium (Na^+), and sulfate (SO_4^{2-}). The cumulative concentration of reported HCO_3^- and Ca^{2+} ions represent a substantial portion of all dissolved constituents ($\approx$

69.1%); NO_3^-, Mg^{2+}, Cl^-, Na^+, and SO_4^{2-} account for approximately 29.7%; the remaining minor constituents account for 1.2%. Appropriate chemical analyses were selected for HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-} (see Methods) and used for analysis of samples collected from the COBS and Hickory Grove sampling locations.

3.4.2   Observed Ion Concentrations

The cumulative concentration of observed ions (HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-}) in drainage samples collected from COBS ($M = 550$ ppm) and Hickory Grove ($M = 631$ ppm) were greater than the cumulative concentration of the same ions reported in Baker et al. 1975, Bower (1974), and Gali et al. (2012) ($M = 502$ ppm) (Fig. 3.1). This difference is mostly due to differences in HCO_3^- and SO_4^{2-}. Mean observed HCO_3^- concentrations were 124 ppm greater in COBS samples and 165 ppm greater in Hickory Grove samples than the mean HCO_3^- concentration reported by Bower (1974). Conversely, Baker et al. 1975; and Bower (1974) reported substantially higher concentrations of sulfate ($M = 58$ ppm) than that which was observed at COBS ($M = 3$ ppm) and Hickory Grove ($M = 11$ ppm).

Referenced literature concentrations of Ca^{2+}, NO_3^-, and Mg^{2+} generally agree with those observed at COBS and Hickory Grove. Hickory Grove samples were slightly greater in their mean Ca^{2+} and lower in NO_3^- concentrations than in COBS samples and in the referenced literature, however as discussed in proceeding sections of this study, the magnitude of this difference is likely attributed to environmental conditions. The mean Cl^- and Na^+ content in Hickory Grove samples ($M_{Cl^-} = 20$ ppm & $M_{Na+} = 6$ ppm) were comparable to those in literature ($M_{Cl^-} = 25$ ppm & $M_{Na+} = 7$ ppm), but substantially greater than COBS samples ($M_{Cl^-} = 7$ ppm & $M_{Na+} = 3$ ppm).

The differences in sulfate concentrations could be attributed to stricter sulfur dioxide and sulfate aerosol emission standards for coal burning power plants, which have dramatically reduced

atmospheric sulfur deposition rates (Camberato et al., 2012). In fact, lower atmospheric inputs along with increased crop yields and a transition to low S-fertilizers has led to an increasing number of sulfur deficiencies throughout the United States in recent years (Camberato et al., 2012; Eriksen et al., 2002; Sawyer & Barker, 2001; Schnug, 1998; Widdowson, 1970). This reduction in sulfate could have then contributed to the greater concentrations of HCO_3^- to maintain a neutral charge balance between total cations and anions; especially considering the two primary cations (Ca^{2+} and Mg^{2+}) were approximately equal among concentrations reported in literature and those observed at COBS and Hickory Grove.

Tillage was not specified by Baker et al. 1975, however conventional tillage is reported by Bower (1974). Gali et al. (2012) reports varying tillage practices at the Hickory Grove sampling location, two of which include conservation and strip-till. Tillage can have a profound effect on the concentration of ions leached from the soil, which may explain the higher Cl^- and Na^+ concentrations reported Bower (1974) and observed in Hickory Grove samples compared to that observed in COBS samples. Drainage water solute concentrations are greater when there is a displacement of the soil water located in the main soil matrix rather than when there is rapid preferential movement of water through the soil profile (Trudgill et al., 1982). During high intensity rainfall events, infiltrating water is conveyed primarily through macropores, resulting in rapid preferential movement of the water (Thomas & Phillips, 1979). When this occurs, there is little interaction with the soil matrix and therefore minimal diffusion of solutes from the smaller pores to the macropores (Thomas & Phillips, 1979). Preferential movement is reduced by conventional tillage in comparison to no-till practices (Kanwar et al., 1997). Tillage practices shear and close off macropores at the interface of the tilled and subsoil layers (Thomas & Phillips,

1979). Subsequently, tilled lands tend to have lower drainage flow volumes (Bakhsh et al., 2002; Randall & Iragavarapu, 1995) and higher solute concentrations (Weed & Kanwar, 1996).

3.4.3   Charge Imbalance Check

To verify all major ions were captured in the chemical analysis of field samples, the charge imbalance (CI) (Eqn. 3.1) was calculated for all samples collected in the field investigation. Of the 44 total samples, one sample had a CI $> \pm 10\%$. As per our established criteria, this sample was removed from further analysis. The distribution of the remaining calculated CIs favored cations, but overall was centered close to zero ($M = 1.4\%$, $SD = 2.7\%$). This approximate neutral charge balance between total cations and total anions coincide with observations made by Heng et al. (1991), Rhoades et al. (1973), and Steele et al. (1984).

While CI was initially calculated as a quality control check, it became apparent upon reviewing the CI distribution that the slight positive skew was caused by COBS and Hickory Grove samples collected from September through December (Fig. 3.2). Calculated charge imbalance was positive for all 4 samples from Hickory Grove and 10 of the 11 COBS samples collected during this time period. In contrast, 14 of the 28 COBS samples collected in May and June were positive; note that no samples were collected from Hickory Grove in May or June.

Given the apparent seasonal difference in sample charge imbalance, a statistical analysis was conducted to determine if this difference was significant. In addition, CI was evaluated between COBS and Hickory Grove samples, and among different cropping systems (C2, S2, and CC). Groups under analysis were tested for both normality and homogeneity of variance using the Shapiro Wilk test for normality and multi group Leven's test for homogeneity of variance. Results suggest the charge imbalance is normally distributed in all groups, and equal variance was confirmed for groups in comparison (Table 3.2). An independent-samples t-test indicates that CI

was greater in COBS samples collected from September through December (post growing season - *PGS*) (*M* = 3.6%, *SD* = 1.8%) than COBS samples collected May and June (growing season samples -*GS*) (*M* = 0.1%, *SD* = 2.2%), *t*(33) = -4.665, *p-valu*e(1-sided) < 0.001 (Table 3.2). An independent-samples t-test suggests the mean CI of COBS samples (*M* = 3.6%, *SD* = %1.8) was not significantly different than that of Hickory Grove samples (*M* = 2.8%, *SD* = 1.4%), *t*(13) = 0.802, *p-valu*e(2-sided) = 0.437 (Table 3.2). The final CI analysis evaluates the influence of cropping system on CI by comparing the mean CI of drainage from corn plots in annual rotation with soybeans (C2), soybean plots in annual rotation with corn (S2), and corn plots in continuous rotation (CC); the sampling distribution for each cropping system consists of only samples collected during the growing season. An analysis of variance (ANOVA) shows that mean CI was not significantly different among cropping systems (C2, S2, CC), *F*(2, 21) = 0.305, *p-value* = 0.740 (Table 3.2).

It is important to note that samples from prairie plots were not included in the CI analysis by season because prairie plots were not sampled during the post growing season. Additionally, prairie plots are of little interest in the analysis of cropping system because prairie crops are not commonly subject to artificial subsurface drainage in Iowa. However, we will note that the mean charge imbalance of drainage from prairie plots (*M* = 3.6%, *SD* = %1.8) was moderately greater than C2, S2, and CC plots. The prairie CI distribution was skewed by one outlier, which was the second highest observed CI (6.77%) in all drainage samples. The remaining prairie samples had a negative mean CI of 0.1% and a standard deviation of 2.8%, which is more similar to that of growing season samples from C2, S2, and CC cropping systems. Given a larger sample size, it would be expected that the mean CI from prairie plots would trend toward neutral like the other sampled cropping systems.

3.4.4 Parameters that Influence Drainage Composition

The following analyses evaluate the effect of season and cropping system on the concentration of major ions in drainage water samples collected at COBS. First a literature review was performed to identify environmental conditions and land management practices that would result in different ionic compositions among growing season samples and post growing season samples, as well as among cropping systems. Then using this information, we formulated expected outcomes regarding ion concentrations with respect to different seasons and cropping systems, this was followed by hypothesis testing to identify statistically significant differences.

Seasonal temperatures and precipitation are largely responsible for either the formation or immobilization of ions. When precipitation is sufficient to saturate the soils and temperatures are above 10 °C (Gentry et al., 1998), anaerobic soil microbes may utilize the nitrate ion as an electron acceptor for respiration (Hoover, 2012). This process significantly reduces the leaching potential of nitrate and can represent as much as 33% of applied N-fertilizer losses (Owens, 1960). Alternatively, nitrate's leaching potential is increased when aerobic soil microorganism oxidize residual nitrogen, in the form of ammonium (NH_4^+), into the highly mobile form NO_3^-. This occurs when oxygen is readily available (ie. lower saturation level) and soil temperatures are between 25 and 30 °C (Sabey, 1958). As with NO_3^-, the formation or immobilization of SO_4^{2-} is driven by microorganisms (Widdowson, 1970); both nitrate and sulfate are oxidized and immobilized by microorganisms under similar soil conditions. However the leaching rate of these ions are not always positively correlated as illustrated by Baker et al. (1975), who suggested that elevated levels of nitrate were toxic to the sulfur-oxidizing bacteria.

Land management practices and seasonal changes responsible for the formation and increased leaching potential of nitrate can indirectly lead to greater losses of associated cations.

Steele et al. (1984) observed that concentrations of leached Ca^{2+}, Mg^{2+}, and Na^+ responded proportionately to changes in NO_3^-. Edwards et al. (1998) noted that SO_4^{2-} also associates with these major cations in the soil. One explanation for observations made by Steele et al. (1984) is that nitric acid (HNO_3), produced from NH_4^+ oxidization, reacts with calcium carbonate ($CaCO_3$) in agricultural lime, causing $CaCO_3$ to dissociate into Ca^{2+}, Mg^{2+}, and NO_3^- (West & McBride, 2005). When NH_4^+ is not actively being oxidized and HNO_3 is not available, $CaCO_3$ and natural carbonic minerals dissolve in the presence H_2O and gaseous or organic carbonate (CO_2) to form HCO_3^-, Ca^{2+}, and Mg^{2+} (Aquilina et al., 2012). The resulting HCO_3^- either remains in the soil or is leached out with the drained water (West & McBride, 2005). Several studies show that HCO_3^- export is positively correlated with flow (Markewitz et al., 2001; Oh & Raymond, 2006; Raymond & Cole, 2003; Whisner, 2009).

Chloride is similar to HCO_3^- and NO_3^-, in that it is tightly linked to local hydrologic conditions given their low affinities to the soil (Kafkafi, 2001; White & Broadley, 2001; Zereini, 2008). However the concentration of Cl^- in Iowa drainage waters is much lower than HCO_3^- and NO_3^- because most of the Cl^- in naturally occurring minerals has already been weathered away (Murray, 2004) and atmospheric deposition becomes negligible with increasing distance of from the ocean (Gribble, 2003; Junge & Werby, 1958; Kafkafi, 2001). Anthropogenic sources of Cl^-, such as nitrification inhibitors and Cl-fertilizers, can temporarily increase the leaching rate of Cl^- (MacIntire et al., 1952). Like, Cl^-, Na^+ concentrations are also low as a result of few natural and anthropogenic sources. Atmospheric deposition decreases with increasing distance from the ocean (Junge & Werby, 1958). Fertilizer applications as manure and sodium nitrate can cause immediate spikes in the concentration of Na^+ leached (Buckman & Brady, 1922; Laird et al., 2010). Both

Laird et al. (2010) and Heng et al. (1991) observed that leaching quantities of Na^+ and Cl^- were proportionate to their atmospheric and fertilizer inputs.

Given knowledge regarding how different parameters influence the leaching rate of ions, we expect the following:

i)   Optimal conditions for nitrification during the early growing season will result in greater concentrations of Ca^{2+}, Mg^{2+}, and NO_3^-, and lower HCO_3^- and SO_4^{2-} concentrations in growing season drainage compared to post growing season drainage.

ii)   N-fertilized cropping systems (C2 & CC) will have greater losses of Ca^{2+}, Mg^{2+}, and NO_3^- than unfertilized systems (S2), while HCO_3^- and SO_4^{2-} losses will be greatest among S2 systems.

iii)   The absence of significant and variable sources for Cl^- and Na^+ will result in consistent leaching rates among seasons and cropping systems.

3.4.5   *Seasonal Variability*

A total of 40 agricultural drainage water samples were collected and analyzed for HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-} at the COBS research site. One sample (plot 21, cropping system-CC, post growing season) was removed from the dataset due to a charge imbalance greater than $\pm10\%$. Results from the charge imbalance analysis revealed that growing season samples were significantly different in composition as compared with post growing season samples. Here we identify ions responsible for these seasonal differences with a statistical analysis of their observed concentrations. The mean total concentration of observed ions in C2, S2, and CC samples increased from 534 ppm in the growing season to 575 ppm in the post growing season. Specifically, the mean growing season concentration of HCO_3^-, Ca^{2+}, Mg^{2+}, and Na^{2+} increased by a cumulative 53 ppm in the post growing season. Alternatively, the mean concentration of NO_3^-,

Cl⁻, and SO_4^{2-} decreased by a cumulative amount of 12 ppm. Ions with the most significant shift in concentration were HCO_3^- (increased by 40 ppm), Ca^{2+} (increased by 10 ppm), and NO_3^- (decreased by 8 ppm). The magnitude of change in Mg^{2+}, Cl⁻, Na^{2+}, and SO_4^{2-} were minimal relative to that of HCO_3^-, Ca^{2+}, and NO_3^-.

Prior to testing for significantly different ion concentrations among growing and post growing season samples, the distribution of observed ion concentrations were tested for normality and homogeneity of variances. Test results listed in Table 3.3 show the significance level was sufficient to reject the null hypothesis of normal ion distributions among growing and post growing season sample populations according to the Shapiro-Wilk distribution test. Results from the Conover test support the assumption for homogeneity of variance between growing and post growing season populations of HCO_3^-, NO_3^-, Cl⁻, Na^{2+}, and SO_4^{2-}. Homogeneity of variance was rejected at alpha level 0.05 for Ca^{2+} and Mg^{2+}. The sampling distribution (Fig. 3.3) of these ions (Ca^{2+} and Mg^{2+}) illustrate that the medians of growing and post growing season sample distributions are not symmetric about the interquartile range (IQR). It should be noted that hypothesis testing on Ca^{2+} and Mg^{2+} was performed despite this departure from symmetry, therefore test results alone may not be valid for these ions.

Mann-Whitney was employed to test the null hypothesis for no differences in the median ranks of ion concentrations in growing season and post growing season samples. Test results were significant for HCO_3^- ($U = 49.5$, *p-value* = 0.003), Ca^{2+} ($U = 46.5$, *p-value* = 0.002), NO_3^- ($U = 209$, *p-value* = 0.006), Mg^{2+} ($U = 49$, *p-value* = 0.003), and Cl⁻ ($U = 234.5$, *p-value* < 0.001). Based on the median ranks (Table 3.3), observed ion distributions (Fig. 3.3), and results from the Mann-Whitney tests, there is sufficient evidence to conclude that the median concentration of HCO_3^-, Ca^{2+}, and Mg^{2+} were significantly lower in growing season samples compared to post

growing season samples. In contrast, the data suggests that median concentrations of NO_3^- and Cl^- were greater in growing season samples. The null hypotheses for no difference in the in the median ranks of Na^+ ($U = 103$, *p-value* $= 0.292$) and SO_4^{2-} ($U = 167.5$, *p-value* $= 0.213$) were not rejected, indicating that Na^+ and SO_4^{2-} concentrations in growing season and post growing season samples were not significantly different.

The expected outcome of this analysis was that optimal conditions for nitrification during the early growing season will result in greater concentrations of Ca^{2+}, Mg^{2+}, and NO_3^-, and lower HCO_3^- and SO_4^{2-} concentrations in growing season samples compared to post growing season samples. Hypothesis testing on the ranked ion concentrations using the Mann-Whitney test provided supporting evidence for the expected outcome of higher NO_3^- and lower HCO_3^- concentrations during the growing season. Alternatively, test results provided sufficient evidence against our expected outcome for Ca^{2+} and Mg^{2+}, indicating that their concentrations were greater in post growing season samples rather than growing season samples. Accordingly, this suggests that dissolution of calcite and dolomite (primary source of Ca^{2+} and Mg^{2+} ions) was not caused by HNO_3 (West & McBride, 2005), which is formed during nitrification. It was expected that no significant changes would occur in Cl^- and Na^+, however results indicated that chloride concentrations were greater during the growing season. This could have been attributed to higher mineralization rates of residual organic chlorine during the growing season (Matchua et al., 2010). Sulfate concentrations were consistent among seasons, which is more characteristic of observations by Heng et al. (1991) rather than the inverse relationship with NO_3^- observed by Baker et al. (1975). Heng et al. (1991) attributed SO_4^{2-} stability to "SO_4^{2-} buffering in the soil solution, adsorption and desorption, and transformations to and from organic forms".

3.4.6   Variability Among Cropping Systems

From the end of May through the end of June, 24 flow proportional samples were collected

from four different cropping systems: C2 = 8 samples, S2 = 8 samples, CC = 8 samples. The ionic

composition of these samples were evaluated to identify significant differences among cropping

systems. Observed concentrations (ppm) of HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-} were

tested for normality and equality of variance prior to hypothesis testing. With the exception of Cl^-

, the null hypothesis for normally distributed ion concentrations among all cropping systems was

rejected (Table 3.4) according to the Shapiro-Wilk distribution. Therefore rank based non-

parametric tests were employed to determine homogeneity of variance and equal median ion

concentrations among cropping systems. Homogeneity of variance among cropping systems was

confirmed (Table 3.4) for all ions according to the Conover test. The Kruskal-Wallis test was used

to test for identical ion population distributions (often referred to as a test for equal medians)

among the three cropping systems. Midranks of ties were automatically calculated by

Mathematica to accurately approximate the null distribution of the K-statistics by an appropriate

chi-square distribution. Significant results against the null hypothesis were then subject to an

independent two-sample Mann-Whitney test for equal medians.

Based on the approximate chi-square distribution from the Kruskal-Wallis statistic and

with 2 degrees of freedom, the significance level for HCO_3^- and NO_3^- were 0.055 and 0.400 (Table

3.4). According to the null hypothesis, this is evidence that observed concentrations of HCO_3^- and

NO_3^- in C2, S2, and CC cropping systems are from identical populations when evaluated at alpha

level 0.05. Alternatively the significance level for Ca^{2+} (0.038), Mg^{2+} (< 0.001), Cl^- (< 0.001),

Na^{2+} (0.037), and SO_4^{2-} (< 0.001) is sufficient evidence for significantly different ion distributions

in at least one sampling group (C2, S2, CC). An independent two-sample Mann-Whitney test on

the median ranks of Ca^{2+}, Mg^{2+}, Cl^-, and Na^+ provided insufficient evidence to suggest these ions were significantly different among C2 and CC cropping systems (Table 3.5). Sulfate was significantly different among all cropping systems (Table 3.5). Sodium concentrations in C2 systems were consistent with those of S2 and CC systems, but significantly different among S2 and CC cropping systems (Table 3.5).

These results are inconsistent with that which was expected based on the literature review. Bicarbonate concentrations were expected to be greatest in S2 cropping systems due to N-fertilization in C2 and CC cropping systems. However, both HCO_3^- and NO_3^- had no significant differences among all cropping systems. Test results and ion distributions (Fig. 3.3) indicate that Mg^{2+} and Cl^- were significantly greater, and Ca^{2+} was significantly lower in C2 and CC systems versus S2. Given common parent minerals for Ca^{2+} & Mg^{2+} ions, their leaching rates were expected to have a positive relationship. Perhaps Mg^{2+} replaced Ca^{2+} ions on the soil exchanges sites leading to the negative relationship between these ions in S2 cropping systems.

3.4.7 Drainage Flow, pH, and Temperature

As stated in the Introduction and literature review, several different factors influence the ionic composition of agricultural subsurface drainage waters. In the previous analysis it was determined that the ionic composition was significantly different among cropping systems. However, electrolyte dissolution and drainage composition are also dependent on the flow of water through the soil profile, soil water pH, and temperature (Bower 1974; Buckman & Brady, 1922; Kohnke et al. 1940; Stauffer & Rust, 1954; Thomas & Phillips 1979; Trudgill et al., 1983). To determine if these parameters were in some way responsible for different ionic compositions among cropping systems, observations for drainage water average daily flows, pH, and temperature were tested for significant differences among cropping systems.

Bjorneberg et al., (1996) noted that NO_3^- leaching rates were greatest during the early in the season. In mid-summer, evaporation rates often exceed precipitation, resulting infrequent drainage flows and lower ion losses. Considering that NO_3^- is an ion with significant environmental relevance, drainage flow volumes were monitored in all plot replicates of each cropping system during the month of June to capture these high leaching rates. Drainage samples were collected between rainfall events and immediately following significant rainfall events. Flows ranged from 0.0002 to 0.590 cm d^{-1}. Drainage flows during this sampling period responded proportionately to the depth of rainfall in all cropping systems (Fig. 3.4). Flows tend to be strongly correlated with precipitation during the early growing season because the ground is saturated and evapotranspiration is generally lower than precipitation (Helmers et al., 2005). From May 19th to June 26th the cumulative precipitation was 22.71 cm; this precipitation period corresponds to cumulative flows observed from May 26th to June 30th. Mean cumulative flow volumes from C2, S2, and CC systems were 6.97, 7.24, and 5.73 cm. Differences in flow volumes among cropping systems were not significant $F(2,37) = 0.726$, p-value $= 0.491$. Because the flows were not significantly different among cropping systems, but ionic compositions were, we can therefore conclude that some other factor was responsible for the difference in ionic compositions.

Helling et al. (1964) observed a positive linear correlation between external pH and soil CEC. Thus, as pH increases, the total cation leaching potential decreases. Furthermore, drainage waters typically remain in equilibrium with respect to the equivalent total concentration of cations and anions (Heng et al., 1991; Rhoades et al., 1973). Therefore, it was assumed that as pH increases, the quantity of ions leached from the soil decreases. Also, both pH and temperature are significant factors that determine the rate nitrification (Kamprath & Foy, 1985; Truog, 1947). A total of 42 drainage samples were analyzed for pH and temperature during 4 drainage events in

June. Measurements were taken from 4 different plot replicates for each cropping system C2, S2, and CC. An analysis of variance (ANOVA) test performed on measured pH among cropping systems suggests that it is not significantly influenced by C2, S2, CC cropping systems $F(2,39) = 0.726$, p-value $= 0.490$. Similarly, no differences in temperature were observed among cropping systems $F(2,39) = 0.456$, p-value $= 0.637$. Like our analysis of the drainage flow, a lack of any differences in pH and temperature among cropping systems indicates that these parameters can be ruled out as significant contributors to ion leaching variability among cropping systems.

3.4.8 Relationships Among Ions

Relationships among Ca^{2+}, Mg^{2+}, HCO_3^-, and NO_3^- observed by Heng et al. (1984), Steele et al. (1984), and Terman (1977) can be attributed to shared ion sources (Bonton et al., 2010; West & McBride, 2005). In these studies, linear regression was performed on ion concentrations to establish specific relationships. However, data observed in the present study did not allow for such regression analysis. Ranked correlations were performed on the concentration (ppm) of ions observed in growing season samples from C2, S2, & CC cropping systems at the COBS research site. Significant results from the Kendall Tau rank correlation coefficient and corresponding significance for independence are presented here. These results suggest that increases in HCO_3^- are proportionate to Ca^{2+} ($\tau = 0.645$, p-value < 0.001). Additionally, as the concentration of HCO_3^- increased, the concentrations of NO_3^- and Cl^- decreased ($\tau = -0.3460$, p-value < 0.018) & ($\tau = -0.425$, p-value < 0.003). This agrees with conclusions made from the seasonal analysis, where the concentration of both HCO_3^- and Ca^{2+} increased from the growing season to post growing season, while NO_3^- and Cl^- decreased. However these results do not coincide with those made by Heng et al. (1984), Steele et al. (1984), and Terman (1977) who observed a positive correlation between NO_3^- and major cations. No significant correlation was observed for Na^+ or SO_4^{2-}.

3.5 Conclusion

Primary dissolved ions in Central Iowa agricultural drainage waters consist of HCO_3^- > Ca^{2+} > Mg^{2+} > NO_3^- > Cl^- > Na^{2+} > SO_4^{2-} (in order of ppm concentration). These ions approximately represent 98.8% of all known dissolved constituents reported in published results for similar waters. The concentration ions in agricultural drainage water is dependent on the abundance of ions available for dissolution by percolating ground-water. The abundance of available ions in the soil is a function of inputs, losses, and immobilization. Major ion inputs are derived from mineral weathering, residual organic matter, soil enzymes and microorganisms, and anthropogenic soil amendments. Losses are primarily a result of uptake by vegetation, leaching, soil enzymes and microorganisms. Ion immobilization is dependent on ion valence, availability of soil exchange sites, chemical and biological transformations. Many of the factors that determine ion abundance in the soil and leaching potential are influenced by the climate (precipitation depth, frequency, and intensity; temperature; evaporation; etc.), soil properties, crop type, cover, crop residue and other organic matter, tillage, drainage design, and the abundance of other ions.

Agricultural lime and other parent minerals provide a common ion source for Ca^{2+}, Mg^{2+}, and HCO_3^-. When agricultural lime is dissolved by percolating ground-water, Ca^{2+}, Mg^{2+}, and HCO_3^- dissociate. When agricultural lime reacts with HNO_3 (formed during nitrification) Ca^{2+}, Mg^{2+}, and NO_3^- are produced. Therefore, we had expected the concentration of Ca^{2+}, Mg^{2+}, and NO_3^- to be greatest during the early growing season when nitrification rates would be high. Similarly, we expected HCO_3^- to be low during the growing season due to a larger portion of agricultural lime dissolving into CO_2 rather than HCO_3^-. However, the field investigation revealed that HCO_3^-, Ca^{2+}, and Mg^{2+} were present in the drainage water at greater concentrations during the post growing season, whereas NO_3^- and Cl^- were greater during the growing season. The strong

correlation between HCO_3^- and Ca^{2+} indicates that agricultural lime dissolution originated from carbonic acid (H_2CO_3), formed by residual HCO_3^- in the presence of excess hydrogen, rather than by HNO_3^- (West and McBride, 2005). This observation is contrary to those made by Heng et al. (1984), Steele et al. (1984), and Terman (1977) who show strong correlations between Ca^{2+} and NO_3^-, which is an indication that agricultural lime dissolution was caused by HNO_3^-. Despite these differences, both observations made in this present study and those of Heng et al. (1984), Steele et al. (1984), and Terman (1977) illustrate that drainage waters tend to stay in equilibrium with respect to the equivalent concentrations of total cations and total anions. Higher Cl^- concentrations during the growing season could have been attributed to increased mineralization rates. No seasonal differences were observed in SO_4^{2-} or Na^+ concentrations.

The ionic composition of sampled drainage waters were also significantly influenced by cropping system. Magnesium and Cl^- were greater in C2 and CC cropping systems than in S2 systems. Calcium and Mg^{2+} were expected to be greater in C2 and CC given that these systems were subject to external N-fertilizer applications. However, the lack of any significant correlation between NO_3^- and Ca^{2+} or Mg^{2+}, suggests that this reasoning is invalid. Assuming that Ca^{2+} and Mg^{2+} are derived from the same parent minerals, and that drainage waters tend to maintain neutral charge balances, we should expect either NO_3^- or HCO_3^- to be significant different among cropping systems as well. Results from hypothesis testing suggested otherwise, as neither NO_3^- nor HCO_3^- were significantly different among cropping systems. It was also determined that neither drainage flow volume, drainage pH, nor drainage temperature were significantly different among cropping systems; this implies that these parameters cannot be used as a descriptive variable for the ionic composition.

3.6 References

Aquilina, L., Poszwa, A., Walter, C., Vergnaud, V., Pierson-Wickmann, A. C., & Ruiz, L. (2012). Long-term effects of high nitrogen loads on cation and carbon riverine export in agricultural catchments. *Environmental science & technology*, *46*(17), 9447-9455.

Andrews, A., Soupir, M., & Gali, R., (n.d.). *Hickory Grove Lake Watershed Management Action Plan*. Retrieved from http://www.storycountyiowa.gov/index.aspx?NID=1046

Baker, J. L., Melvin, S. W., Lemke, D. W., Lawlor, P. A., Crumpton, W. G., & Helmers, M. J. (2004). Subsurface drainage in Iowa and the water quality benefits and problem. In *Drainage VIII, 21-24 March 2004* (p. 1). American Society of Agricultural and Biological Engineers.

Baker, J. L., Campbell, K. L., Johnson, H. P., & Hanway, J. J. (1975). Nitrate, phosphorus, and sulfate in subsurface drainage water. *Journal of Environmental Quality*, *4*(3), 406-412.

Bakhsh, A., Kanwar, R. S., Bailey, T. B., Cambardella, C. A., Karlen, D. L., & Colvin, T. S. (2002). Cropping system effects on NO3–N loss with subsurface drainage water. *Transactions of the ASAE*, *45*(6), 1789.

Barber, S. A. (1995). Soil nutrient bioavailability: a mechanistic approach. John Wiley & Sons.

Barnes, K., (2001). *Water Quality Assessment of the Eastern Iowa Basins: Basic Water Chemistry of Rivers and Streams, 1996-98*. U.S. Department of the Interior-U.S. Geological Survey. Available from http://ia.water.usgs.gov/projects/nawqa/abstracts/ISU2001.basicchem.html

Beckett, P. H. T. (1965). The cation-exchange equilibria of calcium and magnesium. *Soil Science*, *100*(2), 118-123.

Bjorneberg, D. L., Kanwar, R. S., & Melvin, S. W. (1996). Seasonal changes in flow and nitrate-N loss from subsurface drains. *Transactions of the ASAE*,*39*(3), 961-967.

Bonton, A., Rouleau, A., Bouchard, C., & Rodriguez, M. J. (2010). Assessment of groundwater quality and its variations in the capture zone of a pumping well in an agricultural area. *Agricultural water management*, *97*(6), 824-834.

Bower, C. A. (1974). Salinity of drainage waters. Drainage for Agriculture, (drainageforagri), 471-487.

Buckman, H. O., & Brady, N. C. (1922). *The nature and properties of soils* (No. 116). Macmillan.

Camberato, J., Maloney, S., & Casteel, S. (2012). Sulfur deficiency in corn. Purdue University Department of Agronomy. http://www.kingcorn.org/news/timeless/SulfurDeficiency.pdf. (URL accessed April 2016)

Chao, S., Changli, L., Junkun, W., Yun, Z., & Hongbing, H. (2011). Impact of the addition of a compound fertilizer on the dissolution of carbonate rock tablets: A column experiment. *Applied Geochemistry*, *26*, S170-S173.

Daigh, A. L., Zhou, X., Helmers, M. J., Pederson, C. H., Ewing, R., & Horton, R. (2014). Subsurface drainage flow and soil water dynamics of reconstructed prairies and corn rotations for biofuel production. *Vadose Zone Journal*, *13*(4).

Edwards, P. J. (1998). Sulfur cycling, retention, and mobility in soils: a review.

Eriksen, J., Olesen, J. E., & Askegaard, M. (2002). Sulphate leaching and sulphur balances of an organic cereal crop rotation on three Danish soils.European Journal of Agronomy, 17(1), 1-9.

Gali, R. K., Soupir, M. L., & Helmers, M. J. (2012). Electrical Conductivity as a tool to estimate chemical properties of drainage water quality in the Des Moines Lobe, Iowa.

Gali, R. K. (2014). Assessing monitoring and modeling approaches to improve water quality in the Hickory Grove Lake. *Graduate Theses and Dissertations.* Paper 13680. http://lib.dr.iastate.edu/etd/13680

Gentry, L. E., David, M. B., Smith, K. M., & Kovacic, D. A. (1998). Nitrogen cycling and tile drainage nitrate loss in a corn/soybean watershed.*Agriculture, ecosystems & environment*, *68*(1), 85-97.

Gilliam, J. W., Baker, J. L., & Reddy, K. R. (1999). Water quality effects of drainage in humid regions. *Agricultural drainage*, (agriculturaldra), 801-830.

Gottschall, N., Topp, E., Metcalfe, C., Edwards, M., Payne, M., Kleywegt, S., & Lapen, D. R. (2012). Pharmaceutical and personal care products in groundwater, subsurface drainage, soil, and wheat grain, following a high single application of municipal biosolids to a field. *Chemosphere, 87*(2), 194-203.

Gribble, G. W. (Ed.). (2003). *Natural production of organohalogen compounds* (Vol. 3). Springer Science & Business Media.

Helmers, M. J., Lawlor, P., Baker, J. L., Melvin, S., & Lemke, D. (2005). Temporal subsurface flow patterns from fifteen years in north-central Iowa. In*2005 ASAE Annual Meeting* (p. 1). American Society of Agricultural and Biological Engineers.

Heng, L. K., White, R. E., Bolan, N. S., & Scotter, D. R., (1991) Leaching losses of major nutrients from a mole-drained soil under pasture, New Zealand Journal of Agricultural Research, 34:3, 325-334

Hoover, N. L. (2012). Denitrification woodchip bioreactor two-phase column study: Evaluation of nitrate removal at various hydraulic retention times and effect of temperature on denitrification rates.

IDNR (2014). *Lake Restoration Report and Plan 2014*. Submitted to: Joint Appropriations Subcommittee on Transportation, Infrastructure, and Capitals and Legislative Services Agency. Available from http://publications.iowa.gov/id/eprint/20904

Ikenberry, C. D., Soupir, M. L., Schilling, K. E., Jones, C. S., & Seeman, A. (2014). Nitrate-nitrogen export: Magnitude and patterns from drainage districts to downstream river basins. *Journal of environmental quality*, *43*(6), 2024-2033.

Junge, C. E., & Werby, R. T. (1958). The concentration of chloride, sodium, potassium, calcium, and sulfate in rain water over the United States. *Journal of Meteorology*, *15*(5), 417-425.

Kafkafi, U. (2001). Potassium and chloride in crops and soils: The role of potassium chloride fertilizer in crop nutrition. A. E. Johnston (Ed.). International Potash Institute.

Kamprath, E. J., & Foy, C. D. (1985). Lime-fertilizer-plant interactions in acid soils. *Fertilizer technology and use*, (fertilizertechn), 91-151.

Kanwar, R. S., Colvin, T. S., & Karlen, D. L. (1997). Ridge, moldboard, chisel, and no-till effects on tile water quality beneath two cropping systems.*Journal of Production Agriculture*, *10*(2), 227-234.

Kohnke, H., Dreibelbis, F. R., & Davidson, J. M. (1940). A survey and discussion of lysimeters and a bibliography on their construction and performance (No. 372). US Department of Agriculture.

Laird, D., Fleming, P., Wang, B., Horton, R., & Karlen, D. (2010). Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma*,*158*(3), 436-442.

MacIntire, W. H., Young, J. B., Shaw, W. M., & Robinson, B. (1952). Nitrogen Recoveries from Applications of Ammonium Chloride, Phosphate, and Sulfate and Outgo of Complementary Ions in Rainwater Leachings through a Six-foot Soil-subsoil Column. *Soil Science Society of America Journal*, *16*(3), 301-306.

Madramootoo, C. A., Johnston, W. R., & Willardson, L. S. (1997). *Management of agricultural drainage water quality* (Vol. 13). Food & Agriculture Org.

Markewitz, D., Davidson, E. A., Figueiredo, R. D. O., Victoria, R. L., & Krusche, A. V. (2001). Control of cation concentrations in stream waters by surface soil processes in an Amazonian watershed. *Nature*, *410*(6830), 802-805.

Matucha, M., Clarke, N., Lachmanová, Z., Forczek, S. T., Fuksová, K., & Gryndler, M. (2010). Biogeochemical cycles of chlorine in the coniferous forest ecosystem: practical implications. *Plant, Soil and Environment*, *56*(8), 357-367.

McCleskey, R. B., Nordstrom, D. K., Ryan, J. N., & Ball, J. W. (2012). A new method of calculating electrical conductivity with applications to natural waters. *Geochimica et Cosmochimica Acta*, *77*, 369-382.

Muir, D. C., & Baker, B. E. (1976). Detection of triazine herbicides and their degradation products in tile-drain water from fields under intensive corn (maize) production. *Journal of Agricultural and Food Chemistry*, *24*(1), 122-125.

Murray, J. (2004). Major ions of seawater. URL http://www. ocean. washington. edu/courses/oc400/Lecture_Notes/CHPT4. pdf.

NRCS. 2016. Web Soil Survey. NRCS, Washington, DC. http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx (accessed 5 Oct. 2015)

Oh, N. H., & Raymond, P. A. (2006). Contribution of agricultural liming to riverine bicarbonate export and CO2 sequestration in the Ohio River basin.*Global biogeochemical cycles*, *20*(3).

Oster, J. D., & McNeal, B. L. (1971). Computation of soil solution composition variation with water content for desaturated soils. *Soil Science Society of America Journal*, *35*(3), 436-442.

Owens, L. D. (1960). Nitrogen movement and transformations in soils as evaluated by a lysimeter study utilizing isotopic nitrogen. *Soil Science Society of America Journal*, *24*(5), 372-376.

Poss, R., & Saragoni, H. (1992). Leaching of nitrate, calcium and magnesium under maize cultivation on an oxisol in Togo. *Fertilizer Research*,*33*(2), 123-133.

Rabalais, N. N., Turner, R. E., & Wiseman, W. J. (2001). Hypoxia in the Gulf of Mexico. *Journal of Environmental Quality*, *30*(2), 320-329.

Randall, G. W., & Iragavarapu, T. K. (1995). Impact of long-term tillage systems for continuous corn on nitrate leaching to tile drainage. *Journal of Environmental Quality*, *24*(2), 360-366.

Ravindra, K., & Kaushik, A. (2003). Seasonal variations in physico-chemical characteristics of River Yamuna in Haryana and its ecological best-designated use. *Journal of Environmental Monitoring*, *5*(3), 419-426.

Raymond, P. A., & Cole, J. J. (2003). Increase in the export of alkalinity from North America's largest river. *Science*, *301*(5629), 88-91.

Rhoades, J. D., Ingvalson, R. D., Tucker, J. M., & Clark, M. (1973). Salts in irrigation drainage waters: I. Effects of irrigation water composition, leaching fraction, and time of year on the salt compositions of irrigation drainage waters. *Soil Science Society of America Journal*, *37*(5), 770-774.

Sabey, B. R. (1958). Rate of nitrification in some Iowa soils as influenced by temperature, reaction and population of nitrifying bacteria.

Sawyer, J. E., & Barker, D. W. (2001). Sulfur fertilizer application to corn and soybean.

Schilling, K. E., & Libra, R. D. (2000). The relationship of nitrate concentrations in streams to row crop land use in Iowa. *Journal of Environmental Quality*, *29*(6), 1846-1851.

Schnug, E. (1998). Sulphur in agroecosystems (Vol. 2). Springer Science & Business Media.

Stauffer, R. S., & Rust, R. H. (1954). Leaching losses, runoff, and percolate from eight Illinois soils. *Agronomy Journal*, *46*(5), 207-211.

Steele, K.W.; Judd, M. J., Shannon, P. W. 1984: Leaching of nitrate and other nutrients from a grazed pasture. New Zealand journal of agricultural research 27:5-11.

Terman, G. L. 1977: Quantitative relationships among nutrients leached from soils. Soil Science Society of America, journal 41: 935-940.

Thomas, G. W.; Phillips, R. E. 1979: Consequences of water movement in macropores. Journal of environmental quality 8: 149-152.

Trudgill, S. T., Pickles, A. M., Smettem, K. R. J., & Crabtree, R. W. (1983). Soil-water residence time and solute uptake: 1. Dye tracing and rainfall events. *Journal of Hydrology*, *60*(1-4), 257-279.

Truog, E. M. I. L. (1947). The liming of soils. *Science in farming, US Dep Agr Yearbook, 1941-1947*, 566-576.

Weed, D. A. J., & Kanwar, R. S. (1996). Nitrate and water present in and flowing from root-zone soil. *Journal of Environmental Quality*, *25*(4), 709-719.

West, T. O., & McBride, A. C. (2005). The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions. *Agriculture, Ecosystems & Environment*, *108*(2), 145-154.

Whisner, C. (2009). Inorganic Carbon Cycling in Agricultural Lands, Coshocton, Ohio.

White, P. J., & Broadley, M. R. (2001). Chloride in soils and its uptake and movement within the plant: a review. *Annals of Botany*, *88*(6), 967-988.

Widdowson, J. P. (1970). Available sulfur in some Iowa soils.

Zereini, F. (2008). Climatic changes and water resources in the Middle East and North Africa. Springer.

3.7 Figures
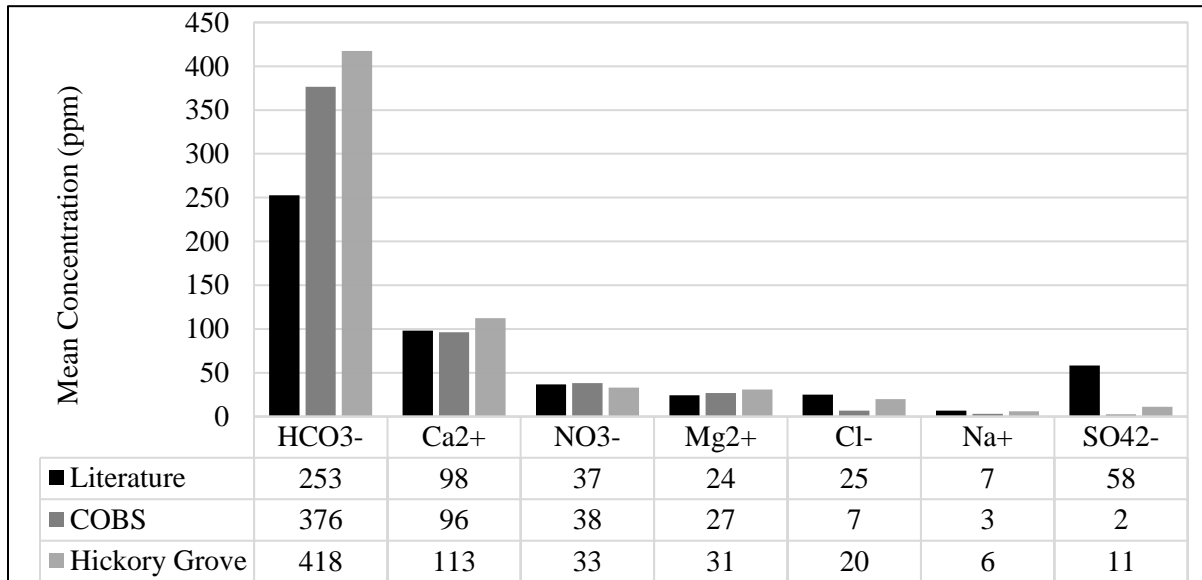
Figure 3.1. Mean ion concentrations reported in literature (Baker et al., 1975; Bower, 1974; Gali et al., 2012) for primary dissolved constituents of agricultural drainage waters in Boone and Story County, IA. Mean observed ion concentrations in samples collected at the Iowa State University's Comparison of Biofuel Cropping System research site (Boone County, IA) and Hickory Grove drainage district outlet (Story County, IA).
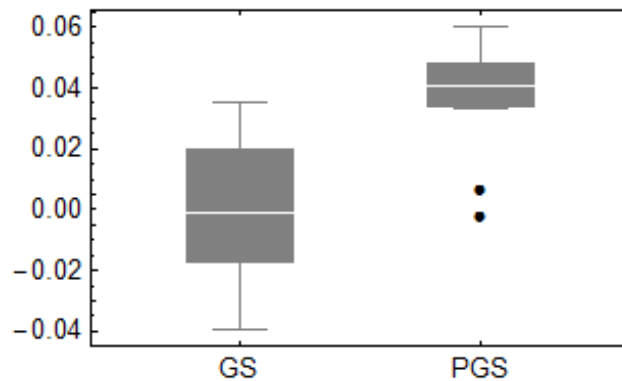
Figure 3.2. Charge Imbalance distribution for samples collected during the growing season (GS) (May and June) and post growing season (PGS) (September through December) at the COBS research site in Boone County, IA.
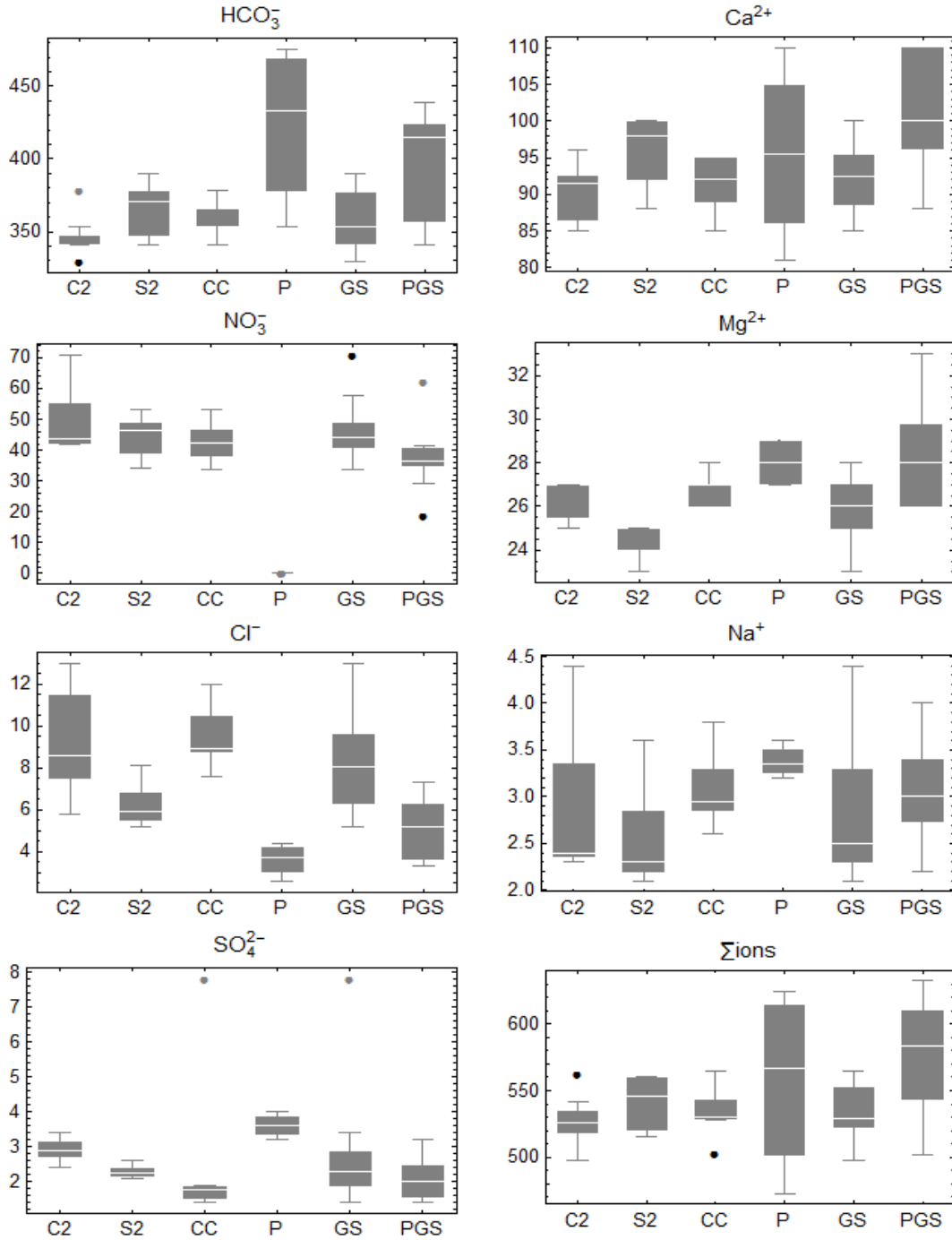
Figure 3.3. Distribution of observed ion concentrations (ppm) in drainage water samples collected at the COBS research site during the growing season (GS, n = 24) and post growing season (PGS, n = 11). Distributions are also provided for growing season samples collected from 3 different cropping system corn in annual rotation with soybeans (C2, n = 8), soybeans in annual rotation with corn (S2, n = 8), continuous corn crops (CC, n = 8), and continuous prairie crops (P, n = 8).
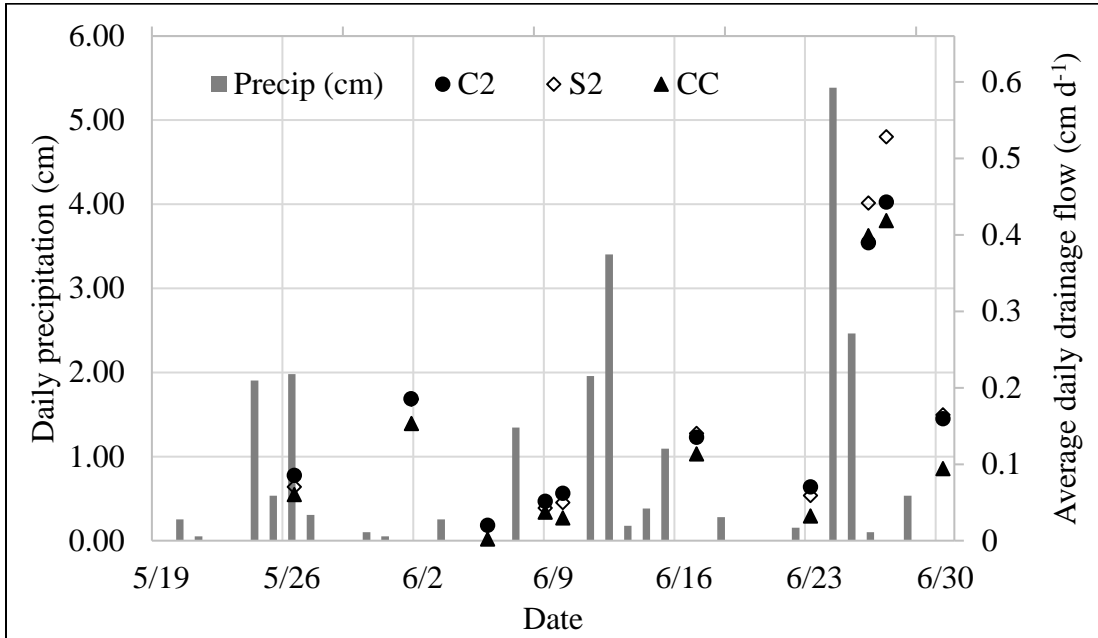
Figure 3.4. Observed growing season drainage from sampled plots at COBS and daily precipitation recorded by the AMES 8 WSW, IA US weather station located approximately 7.3 miles north of the COBS research site.

3.8 Tables

Table 3.1. Ionic constituents and associated concentrations reported in literature for waters characteristic to agricultural subsurface drainage waters in Central Iowa and similar humid regions throughout the United States.

Constituent	Conc. (ppm)	Location	Collection Period	Citation
HCO_3^-	252.60	Story & Carroll Counties, IA	April, 1970 - May 1970	Bower, (1974)
Ca^{2+}	98.20	Story & Carroll Counties, IA	April, 1970 - May 1970	Bower, (1974)
SO_4^{2-}	58.10	Boone, Carroll, & Story Counties, IA	April, 1970 - Dec., 1972	Bower, (1974), Baker et al., (1975)
NO_3^-	36.65	Story County, IA	April, 2011 - Oct., 2011	Gali et al., (2012)
Cl^-	25.20	Story & Carroll Counties, IA	April, 1970 - May 1970	Bower, (1974)
Mg^{2+}	24.30	Story & Carroll Counties, IA	April, 1970 - May 1970	Bower, (1974)
Na^+	6.70	Story & Carroll Counties, IA	April, 1970 - May 1970	Bower, (1974)
K^+	3.20	Des Moines Lobe	March, 1996 - Sept., 1998	Barnes, (2001)
NH_4^+	1.29	Story County, IA	April, 2011 - Oct., 2011	Gali et al., (2012)
Fe^{2+}	1.00	Des Moines Lobe	March, 1996 - Sept., 1998	Barnes, (2001)
F^-	0.31	Des Moines Lobe	March, 1996 - Sept., 1998	Barnes, (2001)
PO_4^{3-}	0.02	Boone County, IA	May, 1970 - Dec., 1972	Baker et al., (1975)
Other[a]	0.23	Humid regions of US and Canada	varies from (1973 - 2009)	Gilliam et al., 1999; Gotschall et al., 2012; Muir & Baker, 1976;
Total	507.79			

[a] Cumulative average of 18 constituents related to pesticides, herbicides, & personal care products

Table 3.2. Results from the distribution analysis of calculated charge imbalances (CI).

		GS	PGS	COBS	HG	C2	S2	CC
Summary	n	24	11	11	4	8	8	8
(y)	M	0.1%	3.6%	3.6%	2.8%	0.2%	-0.4%	0.4%
	σ^2	0.05%	0.03%	0.03%	0.02%	0.05%	0.02%	0.08%
Shapiro-Wilk test	H_0:	Sample parameters came from a normal distribution						
	Statistic	0.956	0.871	0.871	0.891	0.917	0.945	0.905
	p-value	0.361	0.078	0.078	0.386	0.408	0.658	0.321
Leven's test	H_0:	$\sigma^2_{GS} = \sigma^2_{PGS}$		$\sigma^2_{COBS} = \sigma^2_{HG}$		$\sigma^2_{C2} = \sigma^2_{S2} = \sigma^2_{CC}$		
	df_1, df_2	1, 33		1, 13		2, 21		
	Statistic	1.649		0.087		2.277		
	p-value	0.208		0.773		0.127		
Student t-test & ANOVA (1-way)	H_0	$\mu_{GS} < \mu_{PGS}$		$\mu_{COBS} = \mu_{HG}$		$\mu_{C2} = \mu_{CC} = \mu_{S2}$ $SS_B = 0.0003,\ SS_W =$		
	Var	$\sigma_p^2 = 0.0004$		$\sigma_p^2 = 0.0003$		0.0108		
	DOF	$df_p = 33$		$df_p = 13$		$df_1 = 2,\ df_2 = 21$		
	Statistic	$t = -4.665$		$t = 0.802$		$F = 0.305$		
	p-value	< 0.001		$= 0.437$		$= 0.740$		

Table 3.3. Statistical analysis for different ion concentrations (ppm) among growing and post growing season drainage water samples collected at the COBS research site during the growing season (GS) and post growing season (PGS).

Test	Parameter	HCO_3^-	Ca^{2+}	NO_3^-	Mg^{2+}	Cl^-	Na^+	SO_4^{2-}
Growing Season	n				24			
	M	357	93	45	26	8	3	3
	σ^2	282	23	68	2	5	0	2
	H_0:		Sample parameters came from a normal distribution					
	Shapiro-Wilk Stat	0.879	0.948	0.914	0.898	0.936	0.856	0.636
	p-value	0.008	0.244	0.042	0.019	0.135	0.003	< 0.001
Post Growing Season	n				11			
	M	397	102	37	28	5	3	2
	σ^2	1319	70	109	5	2	0	0
	H_0:		Sample parameters came from a normal distribution					
	Shapiro-Wilk Stat	0.873	0.835	0.877	0.894	0.923	0.968	0.943
	p-value	0.082	0.026	0.091	0.151	0.345	0.865	0.561
Conover test	H_0:		the ratio of the true population variances: $\sigma_1^2/\sigma_2^2 = \sigma_0^2$					
	Statistic	-1.440	-2.752	0.297	-2.036	1.404	0.188	0.137
	p-value	0.150	0.006	0.767	0.042	0.160	0.851	0.891
Group Ranks	GS: Median, IQR	15.0, 16.6	14.5, 12.1	23.5, 12.1	14.5, 15.0	23.5, 13.9	13.8, 18.1	19.5, 17.0
	PGS: Median, IQR	31.0, 14.3	27.5, 9.8	9.5, 8.5	29.0, 17.8	6.5, 10.8	23.0, 10.5	13.0, 16.3
Mann-Whitney	H_0:		Growing and post growing season parameters have the same distribution of scores (ranks)					
	U	49.5	46.5	209.0	49.0	234.5	103.0	167.5
	p-value	0.003	0.002	0.006	0.003	< 0.001	0.292	0.213

Table 3.4. Statistical analysis for different ion concentrations (ppm) among growing and post growing season drainage water samples collected at the COBS research site from cropping systems C2, S2, CC.

Test	Parameter	HCO_3^-	Ca^{2+}	NO_3^-	Mg^{2+}	Cl^-	Na^+	SO_4^{2-}
(C2) - Corn in annual rotation	n				8			
	M	346	90	49	26	9	3	3
	σ^2	210	15	108	1	7	1	0
	H_0:			Sample parameters come from a normal distribution				
	Shapiro-Wilk Stat	0.758	0.928	0.774	0.693	0.909	0.612	0.965
	p-value	0.010	0.500	0.015	0.002	0.346	0.002	0.861
(S2) - Soybeans in annual rotation	n				8			
	M	365	96	44	24	6	3	2
	σ^2	330	24	45	1	1	0	0
	H_0:			Sample parameters come from a normal distribution				
	Shapiro-Wilk Stat	0.909	0.794	0.921	0.827	0.893	0.692	0.894
	p-value	0.349	0.024	0.442	0.054	0.250	0.002	0.253
(CC) - Corn in continuous annual	n				8			
	M	358	92	42	27	9	3	2
	σ^2	167	15	42	1	2	0	5
	H_0:			Sample parameters come from a normal distribution				
	Shapiro-Wilk Stat	0.761	0.865	0.972	0.827	0.917	0.935	0.495
	p-value	0.010	0.134	0.914	0.054	0.402	0.560	< 0.001
Conover	H_0:		the ratio of the true population variances: $\sigma_1^2/\sigma_2^2 = \sigma_0^2$					
	Statistic	2.894	0.019	0.184	0.093	4.928	0.274	1.242
	p-value	0.235	0.990	0.912	0.955	0.085	0.872	0.537
Kruskal-Wallis	H_0:			C2, S2, CC are from identical populations				
	Statistic	5.565	6.140	1.922	15.260	11.992	6.218	13.031
	p-value	0.055	0.038	0.400	< 0.001	< 0.001	0.037	< 0.001

Table 3.5. Non-parametric Mann-Whitney distribution tests for differences in ion concentrations among cropping systems.

Test	Parameter	Ca^{2+}	Mg^{2+}	Cl^-	Na^+	SO_4^{2-}
Mann-Whitney	H_0:		C2 and S2 are from identical populations			
	U	11.0	61.0	57.0	49.0	61.5
	p-value	0.023	0.002	0.010	0.076	0.002
	H_0:		C2 and CC are from identical populations			
	U	26.5	26.5	28.5	16.0	56.0
	p-value	0.525	0.483	0.674	0.080	0.013
	H_0:		S2 and CC are from identical populations			
	U	50.5	0.0	1.0	13.5	56.0
	p-value	0.056	< 0.001	< 0.001	0.045	0.013

CHAPTER 4. ELECTRICAL CONDUCTIVITY OF AGRICULTURAL DRAINAGE WATER IN IOWA

A paper submitted to the Transactions of the American Society of Agricultural and Biological Engineers

Brett Zimmerman and Amy Kaleita

4.1 Abstract

Assessing the effectiveness of management strategies to reduce agricultural nutrient efflux is hampered by the lack of affordable, continuous in-situ monitoring systems. Generalized water quality monitoring is possible using electrical conductivity. However environmental conditions can influence the ionic ratios, resulting in misinterpretations of established electrical conductivity and ionic composition relationships. Here we characterize the specific electrical conductivity (k_{25}) of agricultural drainage waters to define these environmental conditions and dissolved constituents that contribute to k_{25}. A field investigation revealed that the magnitude of measured k_{25} varied from 370 to 760 µS cm^{-1}. Statistical analysis indicated that variability in k_{25} was not correlated with drainage water pH, temperature, nor flow rate. While k_{25} was not significantly different among growing and post growing season drainage waters, significant results were observed for different cropping systems. Soybean plots in rotation with corn had significantly lower conductivities than those of corn plots in rotation with soybeans, continuous corn plots, and prairie plots. In addition to evaluating k_{25} variability, regression analysis was used to estimate the concentration of major ions in solution from measured k_{25}. Regression results indicated that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, SO_4^{2-} were the major drainage constituents contributing to the bulk electrical conductivity. Calculated ionic molal conductivities of these analytes suggests that HCO_3^-, Ca^{2+}, NO_3^-, and Mg^{2+} account for approximately 97% of the bulk electrical conductivity.

4.2 Introduction

Agricultural subsurface drainage efflux of nutrients stresses ecosystems in receiving surface waters, represents economic losses to farmers, and degrades soil fertility. Continuous, low cost, and reliable in-situ monitoring is essential for the development of effective nutrient mitigation strategies, which are aimed at reducing these environmental and economic impacts. However, limitations in current available sensor technology have hindered the affordability of these sensors. Gali et al. (2012) proposed the use of electrical conductivity as a low-cost alternative means for indirectly monitoring nutrient loadings in agricultural drainage waters. The viability of this is supported by Patni et al. (1998), who found that ground water electrical conductivities at depths of 1.2 m were significantly correlated to the concentration of NO_3^- in no-till and conventionally tilled plots near Ottawa, Canada. To better understand these results and evaluate electrical conductivity's applicability to agricultural subsurface drainage water quality monitoring, we must first consider what is being measured with electrical conductivity and how it has been successfully used in the past and present.

Electrolytic solutions, like agricultural drainage waters, contain dissociated electrolytes consisting of positively and negatively charged ions (cations and anions, respectively). Under an applied external electrical current, cations will react to the electric potential gradient by migrating to the cathode and anions will respond by migrating to the anode (Miller et al., 1988). If the applied electrical field is generated by an alternating current source, the electrolytic solution obeys Ohm's Law (Eqn. 4.1) (Langford & Beebe, 1995).

$$V = iR \tag{4.1}$$

Ohm's Law defines electric potential (V) as the product of electrical current (i) and resistance (R). Resistance is directly proportional to the length (L), area (A), and resistivity (ε) of

the material in which the current is conveyed (Eqn. 4.2). Electrical conductivity (k) (Eqn. 4.3) is

the reciprocal of resistance and is expressed in units of µS cm^{-1} (Allred et al., 2008).

$$R = \frac{\varepsilon\, A}{L} \tag{4.2}$$

$$k = \frac{1}{\varepsilon} = \frac{i\, L}{V\, A} \tag{4.3}$$

The conductivity of an electrolytic solution is dependent on the mobility (μ) of ions that

carry the electrical current (Miller et al., 1988). Ion mobility (Eqn. 4.4) is proportional to the

charge (q) divided by the sum of hydrodynamic friction (ζ_H) and dielectric friction (ζ_D) (Koneshan

et al., 1998[a]; Wolynes, 1980).

$$\mu = \frac{q}{\zeta_H + \zeta_D} \tag{4.4}$$

Dielectric friction is a function of Debye relaxation time, dielectric constants of the solvent,

charge of the ion, and ion radius. Hydrodynamic friction is directly proportionate to the ion radius

and bulk viscosity of the conductor (or solvent) (Koneshan et al., 1998[b]). As the solvent's

temperature increases, bulk viscosity decreases, which in turn allows for greater ion mobility

(Miller et al., 1988). Consequently, ε is inversely proportionate to temperature, while k is directly

proportionate to temperature. Therefore, k is typically standardized to a reference temperature

(25°C is used throughout this study) with the following equation:

$$k_{25} = \frac{k}{1 + \alpha(T - 25)} \tag{4.5}$$

where measured electrical conductivity (k) is expressed in units of µS cm^{-1}, temperature (T) is in

°C, the temperature compensation factor (α) is a constant that typically ranges from 0.019 to 0.020

(Hayashi, 2004; McCleskey et al., 2012; Miller et al., 1988), and specific electrical conductivity

(k_{25}) is the k standardized to the reference temperature of 25°C (µS cm^{-1}) (McCleskey et al., 2012).

Upon performing this conversion, measured electrical conductivity becomes primarily dependent

on the cumulative concentration of total dissolved solids (TDS) in solution. The relationship

between k_{25} (μS cm^{-1}) and TDS (ppm) is most simply represented by a factor of proportionality

(*K*) (Eqn. 4.6) (Marandi et al., 2013; Walton 1989).

$$K = \frac{TDS}{k_{25}}$$ (4.6)

The relationship given in Eqn. 4.6 is commonly used by commercially available TDS

meters, which automatically calculate TDS from measured k_{25} and a standard *K* of 0.70 (Walton

1989). However, the proportionality constant, *K*, is an ambiguous variable that can range of 0.50

to 1.00 depending on the solution's ionic composition (Marandi et al., 2013; McNeil & Cox 2000;

Walton 1989). The magnitude of *K* is dependent on the concentration, size, and valence of ions

present in the solution (McNeil & Cox 2000).

For well-defined waters with relatively consistent ionic compositions, *K* can be used in

conjunction with k_{25} to reliably estimate TDS at accuracies of 95% or greater (Miller et al., 1988).

Given this attribute, along with the availability of low-cost and easily operated commercially

available meters, k_{25} monitoring has proven to be a popular and reliable alternative for monitoring

TDS in a wide variety applications. These applications include: industrial effluent (Binkley et al.,

2000), wastewater (Voichick, 2008; NWIS 2011), natural waters (Goodrich et al., 2009;

McCleskey et al., 2012; McNeil & Cox, 2000), and landfill leachate in groundwater (Abu-Rukah

& Al-Kofahi, 2001). Additionally, k_{25} is also used as quality control check for chemical analysis

of solutions (Marandi et al., 2013). In agriculture, electrical conductivity monitoring of irrigation

waters helps to reduce the risk of soil salinization (Wilcox, 1955). More recently, electrical

induction soil mapping has gained popularity in precision agriculture, as it has the ability to

accurately map spatial variations of soil properties over large areas with higher resolution and at a

lower cost than traditional grid mapping (Corwin & Lesch 2005; Kitchen et al., 1999; Sudduth et al., 2005).

Few studies have evaluated k in agricultural drainage waters and even fewer have done so with waters characteristic to Iowa. A review of the literature revealed that studies of similar scope are directed toward understanding soil salinization caused by drainage water reuse in semi-arid regions (Oster, & Grattan, 2002; Rhoades et al., 1989). However, environmental conditions in the humid regions of the Midwest produce drainage waters with significantly different compositions than those of the semi-arid regions; arid soils typically have much greater total dissolved solids concentrations (Bower, 1974). The most relevant studies include Gali et al. (2012) and Patni et al. (1998), who used k_{25} to evaluate nutrient concentrations in waters leached from agricultural landscapes. It is important to note that these studies evaluated k_{25} correlations with NH_4^+, NO_3^-, and TP without consideration of the other major dissolved constituents. Primary drainage water constituents consist of the following cations: calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^{2+}); and anions: bicarbonate (HCO_3^-), nitrate (NO_3^-), chloride (Cl^-), and sulfate (SO_4^{2-}) (Zimmerman & Kaleita, 2016). As previously stated, k_{25} is dependent on all constituents, therefore estimating the concentration of a single constituent based on k_{25} is subject to great inaccuracy. Gali et al. (2012) suggested that these inaccuracies can be reduced by understanding how environmental conditions influence relationships between k_{25} and individual constituents.

A seasonal analysis of dissolved constituents in agricultural drainage waters by Zimmerman & Kaleita (2016) quantifies how the ionic composition can vary between two time periods representing distinctly different environmental conditions. The study concluded that concentrations of HCO_3^-, Ca^{2+}, and Mg^{2+} were significantly greater in drainage samples collected after the growing season (September through December) than early growing season drainage

samples (May and June); Cl^- and NO_3^- were greater in growing season drainage; Na^+ and SO_4^{2-} remained relatively constant throughout both seasons. Furthermore, the study determined that the drainage composition was significantly different among cropping systems. Corn cropping systems had greater losses of Mg^{2+} and Cl^-; soybean cropping systems had greater losses of Ca^{2+}; SO_4^{2-} was different among all soybean and corn cropping systems; HCO_3^- and NO_3^- were consistent among all cropping systems. These results illustrate the high degree of variability among most major ions as result of seasonal changes in climate, crop uptake, relative abundance of ions, microbial activity, etc. Given that k_{25} is a function of all ion concentrations, sizes, and charges it can be expected that seasonal and cropping system variability in the ionic composition will also be reflected by the magnitude of k_{25}.

However, even if the relationships proposed by Gali et al. (2012) were established for different environmental conditions, k_{25} could not be used to confidently make accurately and reliably estimates for individual ion concentrations without frequent sampling. The exceptions to this are primary ions which contribute most to electrical conductivity, but even these estimated concentrations would be subject to error caused by the presence of other ions. These limitations again come down to the fact that k_{25} is a generalized parameter representing the ionic composition as a whole. Regardless, the composition as a whole can still be informative, and it is therefore important to understand how environmental conditions and land management practices influence k_{25}. Other environmental conditions of interest include drainage water flow, temperature, and pH.

Heng et al. (1991), Steele et al. (1984), and Terman (1977) found strong linear correlations between major cations and anions in agricultural drainage waters. In each of these studies, increasing the concentration of NO_3^- resulted in a nearly equal increase in Ca^{2+}. Zimmerman & Kaleita (2016) observed similar characteristics among HCO_3^- and Ca^{2+}. The production of both

NO_3^- and HCO_3^- is largely influenced by percolation rate, soil temperature, and pH (Raymond & Cole, 2003; Sabey, 1958; Seitzinger et al., 2006; Whisner, 2009). Therefore, it is reasonable to assume that these changes in the ionic composition would be correlated with changes in drainage rate, drainage water pH, and drainage water temperature.

In this study we perform a field investigation to characterize the electrical conductivity of agricultural drainage waters using a low cost portable electrical conductivity meter. Specifically we will: 1) cross analyze field k_{25} measurements with controlled laboratory measurements to ensure that field measurements can be performed reliably; 2) verify that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, SO_4^{2-} represent all major constituents contributing to the bulk electrical conductivity; 3) quantify each major ion's contribution toward the bulk electrical conductivity using ionic molal conductivity methods described by McCleskey et al. (2012); 4) evaluate the effect of different cropping systems and seasons on the magnitude of measured electrical conductivity; 5) determine if drainage water flow, pH, and temperature significantly influence k_{25} measurements as a result of changes in the ionic composition. In so doing we hope to complement the work performed by Gali et al. (2012) by gaining further insight to k_{25} viability and versatility as a low-cost alternative for agricultural subsurface drainage water quality monitoring.

4.3 Materials and Methods

4.3.1 Site Description

Drainage water samples and field measurements for specific electrical conductivity, pH, and temperature were collected at the Iowa State University's Comparison of Biofuel Cropping System (COBS) research site located in Boone County, Iowa. Soils at COBS consist of Webster clay loam and Nicollet loams (NRCS, 2016). Nicollet and Webster soils are classified as hydrologic soil group B and C. Drainage water sampling was performed on 16 different plots

each measuring 200-ft in length and 90-ft in width. Sampled plots represent four cropping systems: (1) C2 - corn on corn/soybean rotation; (2) S2 – soybean on corn/soybean rotation; (3) CC - continuous corn with stover removal; (4) P – continuous prairie. No-till practices were uniform across all cropping systems. Nitrogen fertilizer was applied as UAN-32 in two applications. The first application was performed in the spring, prior to seed planting, at a rate of 87 kg N ha^{-1} on C2 and CC cropping systems. After plant emergence, an additional 134 kg N ha^{-1} was applied to C2 plots and 112 kg N ha^{-1} on CC plots. Drainage is provided by corrugated tiles placed at a depth of 1.1-m along the center line - length wise. Plots are hydraulically separated by additional drainage tiles placed between plots. Drained water is conveyed to a sump pit where flow is monitored by an in-situ flow meter and flow proportionate samples are collected in a 5 L polypropylene container. Cumulative flow volumes were recorded at the time of sample collection. Average daily drainage flow rate was calculated as the cumulative flow between sampling events divided by the number of days between sampling.

4.3.2 Measured Field Parameters & Laboratory Analyses

The Hach Pocket Pro + Multi 2 meter (Hach, Loveland, CO) was used in this study to measure drainage water specific electrical conductivity ($k_{25,Field}$), pH, and temperature in degrees Celsius at the time of drainage water sampling directly from collected samples. The meter has three auto-setting operating ranges for each measurable parameter. Specifications for meter performance in the ranges applicable to measured quantities include a k_{25} range of 200 to 1999 µS cm^{-1}, resolution of 1 µS cm^{-1}, and accuracy of ± 1%. Calibrations were performed the day of sample collection with a single point (1413µS cm^{-1}) standard KCl solution. The meter automatically standardizes electrical conductivity measurements to 25°C using a temperature compensation factor of 0.05 in Eqn. 4.5.

A total 23 flow proportionate samples were collected in the months of June, September, and December, 2015. Collected samples were subject to chemical analysis by the Iowa State Hygienic Laboratory (ISHL) in Ankeny, Iowa. Analytes consisted of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+. Methods employed by ISHL include: EPA 300 for SO_4^{2-}, Cl^-, NO_3^-; EPA 200.7 for Ca^{2+}, Mg^{2+}, and Na^+; LAC 10-107-06-IJ for NH3; SM 2320B for Alkalinity as $CaCO_3$ (reports HCO_3^- and CO_3^{2-}). Selection of analytes was based on the literature review performed by Zimmerman & Kaleita (2016), who identified major dissolved constituents in drainage water samples at the COBS research site; Zimmerman & Kaleita (2016) was a parallel study and collected drainage samples overlap.

In addition to performing chemical analyses, the Iowa State Hygienic Laboratory also measured specific electrical conductivity ($k_{25,Lab}$) in 18 of the collected samples. Laboratory methods for electrical conductivity were conducted in accordance to Standard Methods 2510B. According to AWWA (2012), laboratory analyses for specific electrical conductivity have a resolution of 1 µS cm^{-1} and accuracy of ± 1%. Reported lab results, however were given at resolution of 10 µS cm^{-1}. Calibrations were performed with a (1412 µS cm^{-1}) standard KCl solution. Results from the laboratory were used to ensure quality and consistency of field measurements by performing simple linear regression to estimate the laboratory observations with field observations. The Pearson's correlation coefficient was used to describe the quality of the relationship between field and laboratory conductivities.

4.3.3   Verification of Primary Ions

To characterize drainage water electrical conductivity we first need to define the constituents that contribute its bulk electrical conductivity. A comprehensive literature review and field investigation by Zimmerman & Kaleita (2016) indicated that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-,

Na^{2+}, and SO_4^{2-} represented the major ions in COBS drainage waters; these results were not validated by any particular water quality analysis. Direct measurement of total dissolved solids (TDS) is costly, time consuming, and prone to user error (Kitto, 1938). Validation was therefore performed in the present study by using the relationship given in Equation 4.6 where measured electrical conductivity is proportionate to the cumulative TDS concentration.

First, the constant of proportionality (K) was calculated (Eqn. 4.5) for samples collected from C2, S2, and CC drainage waters at the COBS research site. Calculated K values were then evaluated to identify statistically different K factors representing sampling groups having significantly different ionic compositions, thereby ensuring a high level of accuracy in $\sum$ions:$k_{25,Field}$ regression (described below). It is important to note that the sample size of collected growing season drainage water samples were insufficient to perform a strong statistical analysis among cropping systems, therefore the following analysis was conducted on growing and post growing season samples irrespective of the cropping system in which the samples were acquired. Also, samples from prairie cropping systems were not included in the analysis since no samples were collected in the post growing season.

Total dissolved solids was calculated as the cumulative concentration (ppm) of major ions ($\sum$ions) reported by the Iowa State Hygienic Laboratory analysis of collected samples. Sample specific electrical conductivity was measured in the field ($k_{25,Field}$) using the Hach Pocket Pro + Multi 2 meter. Because theory (Eqn. 4.6) defines $k_{25,Field}$ as being proportionate to TDS ($\sum$ions), regression through the origin (RTO) was calculated to predict $\sum$ ions using measured $k_{25,Field}$. The corresponding residual error between the observed $\sum$ions and predicted $\sum$ions was then used to determine the extent to which $k_{25,Field}$ was caused by the primary ions (ie. verification of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+ as primary ions that contribute the $k_{25,Field}$).

4.3.4 Ionic Molal Conductivity

Gali et al. (2012) and Patni et al. (1998) used k_{25} to estimate the concentration of individual ions in agricultural drainage waters. While k_{25} captured general ion concentration trends, estimated values had low accuracy and precision. To better understand the causes for error in these estimated concentrations, we need to consider the magnitude of change in k_{25} caused by the concentration of all ions in solution. In the preceding section we used the relationship described by Eqn. 4.6 to validate that major ions contributing to the electrical conductivity of agricultural drainage waters consisted of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+ based on their cumulative concentration in ppm. This simplified relationship is possible because the specific electrical conductivity of an electrolytic solution is dependent on the concentration, valence, and size of ions present in the solution. Note that accurate estimation of TDS using k_{25} from Eqn. 4.6 requires a well-defined constant of proportionality which is specific to the solution's overall ionic composition, and because Eqn. 4.6 does not account for ion valence we cannot use this method to calculate each major ion's individual contribution toward the drainage water's bulk specific electrical conductivity. To calculate these individual conductivities we directly employed ionic molal conductivity methods developed by McCleskey et al. (2012). Ion speciation methods used by McClesky et al. (2012) were performed on a variety of natural waters with great accuracy; calculated conductivities were within $-0.7 \pm 5\%$ of measured conductivities in 1593 water samples. The following methods and equations are the summarized procedures used to calculate ion conductivities for drainage water samples collected in this study. Note: for additional information regarding empirical constants, detailed procedures, applicability, and discussion refer to McCleskey et al. (2012).

The calculated bulk electrical conductivity (k_{calc}) (S cm^{-1}) of an electrolytic solution is the cumulative sum of each ion's electrical conductivity (k_i), which is defined as the ion's ionic molal conductivity (λ_i) (mS kg cm$^-$1 mol^{-1}) multiplied by the speciated molality (m_i) (mol kg^{-1}).

$$k_{calc} = \Sigma\, k_i = \Sigma\, 1000 \lambda_i\, m_i \tag{4.7}$$

In Eqn. 4.8, ion molality (m_i) was determined from concentrations reported by the chemical analysis and ionic molal conductivity (λ_i) was calculated as:

$$\lambda_i = \lambda^{\circ} - \frac{A\, I^{0.5}}{1 + B\, I^{0.5}} \tag{4.8}$$

where λ° *and A* are temperature dependent equations, *B* is an empirically derived constant (λ°, *A, and B are unique to each ion, refer to McCleskey et al. (2012) for exact equations and constants*), and the solution's ionic strength (I) is a function of the speciated molality and the charge (z_i) of the ith ion.

$$I = 0.5 \Sigma\, m_i\, z_i^2 \tag{4.9}$$

4.3.5 *Effect of Cropping System and Season on Electrical Conductivity*

While k_{25} is dependent on the ionic concentration, it is also dependent on the valence and size of ions that make up the electrolytic solution. Accordingly, two solutions having different ionic concentrations could have the same measured k_{25} (Marandi et al., 2013; Walton, 1989). To effectively use k_{25} as a tool for agricultural drainage water quality monitoring, it is essential that k_{25} consistently correlates to the concentration of ions in solution. This can be achieved if the ionic composition remains relatively constant with respect to the component ion ratios (Marandi et al., 2013). However, as Zimmerman & Kaleita (2016) illustrate, the component ion ratios can be variable among different cropping systems and seasons. Here we perform analyses on $k_{25,Field}$ measured in samples collected during the growing and post growing seasons, and among cropping

systems to determine if $k_{25,Field}$ can effectively represent significant changes in the ionic composition observed by Zimmerman & Kaleita (2016).

The analysis of ionic composition among seasons and cropping systems performed by Zimmerman & Kaleita (2016) consist of overlapping samples evaluated in this study. Of the 28 growing season samples collected at COBS in that study, 12 samples had $k_{25,Field}$ measurements for the objectives of this study; these 12 samples were collected from cropping systems C2, S2, CC, and P. All 11 post growing season samples collected and evaluated by Zimmerman & Kaleita (2016) had corresponding $k_{25,Field}$ measurements; post growing season samples were collected from cropping systems C2, S2, and CC. Because $k_{25,Field}$ was not recorded in P cropping systems during the post growing season, the seasonal analysis of $k_{25,Field}$ excluded two growing season measurements of $k_{25,Field}$ from P cropping systems; this was done to maintain consistency in the statistical analysis. The influence cropping system on ionic composition is most pronounced during the growing season, which is a result of soil fertilizer amendments prior to planting and crop uptake of nutrients. We therefore conducted the cropping system analysis on $k_{25,Field}$ measurements performed during the growing season. As stated above, 12 samples were collected for chemical analysis and k_{25} analysis. Additional $k_{25,Field}$ measurements (without chemical analysis) were performed on all plot replicates of cropping systems C2, S2, CC, and P on dates corresponding to the collection of the 12 samples for chemical analysis. In total, drainage water $k_{25,Field}$ was measured 14 times for each cropping systems C2, S2, and P; only 12 observations were recorded for plots under cropping system CC due to a faulty drainage pump.

Hypothesis testing was performed to determine if $k_{25,Field}$ was statistically different among seasons and cropping systems, with the specific test determined after checking the data for normality and homogeneity of variance. Sampling groups were subject to a statistical analysis

were checked for normality and homogeneity of variance prior to group comparisons. Results for all tests were evaluated at alpha level 0.05.

4.3.6   Correlations With Flow, pH, and Temperature

In this study, drainage water electrical conductivity, pH, and temperature were monitored at the COBS research site using the Hach Pocket Pro + Multi 2 meter. A total of 54 observations were recorded for each parameter during the growing season in cropping systems C2, S2, CC, and P. These measurements correspond to $k_{25,Field}$ observations used in the cropping system analysis described in the above section. As stated in the introduction and objectives of this paper, our intention is to identify significant correlations between $k_{25,Field}$ and drainage water flow, pH, and temperature. Significant correlations are of interest since these parameters represent low cost measurements of different environmental conditions that could potentially influence k_{25}. Correlation methods were based on an analysis of variance and normality. All tests were evaluated at alpha level 0.05.

4.4 Results

4.4.1   Comparison of Field and Lab Electrical Conductivity Measurements

To ensure quality and consistency among field specific electrical conductivity measurements, 18 water samples were collected and submitted to the Iowa State Hygienic Laboratory for analysis of specific electrical conductivity. Field and laboratory observations showed a strong linear relationship, which is illustrated by (Fig. 4.1). The calculated Pearson correlation coefficient (0.962) was significant $t(16) = 14.040$, *p-value* < 0.001. However, Figure 4.1 also shows that laboratory conductivities were consistently greater than field observations. Simple linear regression was calculated to predict laboratory conductivities ($M = 661$, $SD = 32$) $\mu S\ cm^{-1}$ using the observed field conductivities ($M = 638$, $SD = 28$) $\mu S\ cm^{-1}$. Results from

regression indicated that $k_{25,Field}$ was a good estimator for $k_{25,Lab}$ F (1, 16) = 197, $p < 0.001$, R^2 = 0.925. Standard error of estimated values (9 ppm) was minimal relative to the mean and standard deviation of observed values. While these datasets disagree slightly in terms of magnitude, overall the laboratory and field measurements responded proportionately to sample compositions (regression slope of 1.08 is close to 1). McCleskey et al. (2012) noted that accurate comparisons between calculated and measured conductivities requires the use of a uniform temperature compensation factor. With calibration, resolution, and accuracy being approximately equal among both k_{25} methods, and each method uses the same linear equation (Eqn. 4.5) to calculate k_{25}, it is likely that differences in observed magnitude are due to different temperature compensation factors.

4.4.2 *Verification of Primary Ions*

The following analysis confirms that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-} are the major ions contributing to the $k_{25,Field}$ of the collected water samples. Here we use the relationship given by Equation 4.6 to estimate TDS from electrical conductivity. Because the equivalent concentration of total cations relative to total anions is greater in the post growing season (Zimmerman & Kaleita, 2016), it is expected that the mean K values will also be greater among post growing season samples because the primary cations are divalent ions. As the proportion of divalent ions increases relative to monovalent ions (primary anions are monovalent), the charge carrying capacity of the solution is increased relative to the ionic concentration (ppm). This indicates that the constant of proportionality (K), which defines the ratio of $\sum$ions:$k_{25,Field}$ (Eqn. 4.6), will have different magnitudes for growing and post growing seasons.

The Shapiro Wilk test for normality and Levene test for equality of variance were performed on the calculated K values of growing and post growing season sampling groups.

Results indicated that K is normally distributed in the growing season and post growing season, and that variances are sufficiently homogeneous. An independent-samples t-test confirmed our expected outcome, suggesting that K was greater among COBS post growing season samples ($n = 11$, $M = 0.887$, $SD = 0.012$) than growing season samples ($n = 10$, $M = 0.846$, $SD = 0.015$), $t(19) = -6.957$, p-$value$(1-sided) < 0.001. These results imply that regression of $\sum$ions:$k_{25,Field}$ should be carried separately for the growing and post growing season sampling groups.

Regression through the origin (RTO) was used to predict $\sum$ions from measured electrical conductivity ($k_{25,Field}$) for growing season samples and post growing season samples (Fig. 4.2). A significant regression model was found for growing season samples $F(1, 9) = 31452$, p-$value < 0.001$, $R^2 = 1.000$ and post growing season samples $F(1, 10) = 63449$, p-$value < 0.001$, $R^2 = 1.000$. Regression models are as follows: predicted growing season sample $\sum$ions is equal to $0.846(k_{25,Field})$ ppm when $k_{25,Field}$ is measured in units of (μS cm^{-1} @ 25 °C). Similarly, predicted post growing season sample $\sum$ions is equal to $0.888(k_{25,Field})$ ppm. The 95% for these regression slopes, K, are 0.846 ± 0.01 for growing season samples and 0.888 ± 0.01 for post growing season samples. Residuals from the estimated $\sum$ions concentration by measured $k_{25,Field}$ and seasonal proportionality factors (K) resulted in a root mean square error (RMSE) of 9 ppm and 7 ppm for the growing and post growing seasons respectively. The magnitude of these values represents a mean error of $\pm 1.7\%$ with respect to observed cumulative ion concentrations ($M = 541$, $SD = 17$) ppm and $\pm 1.2\%$ mean error in post growing season samples ($M = 575$, $SD = 43$). This is in agreement with the expected error (1.2%) caused by minor TDS constituents (Zimmerman & Kaleita 2016). Therefore, we have shown through regression and evaluation of the residuals that all major ions contributing to the electrical conductivity in COBS drainage water samples consist of HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^{2+}, and SO_4^{2-}.

It is important to note that the coefficient of determination (R^2) reduces to the sum of squared estimated values divided by the sum of squared observed values when simple linear regression is forced through the origin; causing R^2 to be unrepresentative of the true variance (Eisenhauer, 2003). This is illustrated by comparing the calculated R^2 values (1.000 & 1.000) and data about the models in Figure 4.2; the model obviously does not completely explain the observed TDS. Rather than forcing the slope through the origin, some researchers recommend performing SLR, and evaluating the model based on whether or not the resulting intercept is significantly different from the origin (Bonate & Steimer, 2006). However, given the small sample sizes of this study, SLR would have yielded constants of proportionality (*K*) unrepresentative to the true values. As stated by both Eisenhauer (2003) and Bonate & Steimer (2006), methods for statistically evaluating RTO are still debated. The R^2 was included because Eisenhauer (2003) noted that many authors consider R^2 to be equally valid in both SLR and RTO.

4.4.3 Ionic Molal Conductivity

One of the primary components of this study was to evaluate each ion's individual contribution to the bulk electrical conductivity in sampled drainage waters. To quantifying these speciated contributions, we employed the ionic molal conductivity method described in McCleskey et al. (2012) due to its wide applicability to a variety of waters having similar ionic constituents, pH ranges, and temperatures.

Ion concentrations obtained from chemical analysis of 23 drainage samples from cropping systems C2, S2, CC, and P collected at the COBS research site were used to calculate sample ionic strength (*M* = 0.0108, *SD* = 0.0008) according to Equation 4.9. Molal ionic conductivity was calculated from equations provided in McCleskey et al. (2012) at a temperature of 25°C for HCO_3^-, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^-, Na^+, and SO_4^{2-}. Individual ion conductivities were calculated as the

product of ionic molal conductivity and the speciated molality. Results for mean calculated conductivities, along with mean observed ion concentrations, are shown in Figure 4.3.

As illustrated by Figure 4.3, HCO_3^- and Ca^{2+} are the largest contributors to conductivity (μS cm^{-1}) and mass concentration (ppm). Cumulatively, these two ions represent 75% of the calculated bulk electrical conductivity ($M = 673$, $SD = 44$) μS cm^{-1} and 86% of the total concentration of major ions ($M = 557$, $SD = 41$) ppm. Magnesium and NO_3^- combined, account for a moderate proportion of the electrical conductivity (22% combined) and cumulative ion concentration (12%). Chloride, Na^{2+}, and SO_4^{2-} are minor contributors to electrical conductivity (3%) and cumulative concentration of major ions (2%). Variability among ion conductivities and concentrations was greatest in HCO_3^-, Ca^{2+}, and NO_3^-.

To ensure this molal ionic conductivity method accurately portrays the true conductivities, we evaluated the cumulative calculated electrical conductivity ($k_{25,Calc}$) (Eqn. 4.7) with respect to field and laboratory measured electrical conductivities ($k_{25,Field}$) and ($k_{25,Lab}$). The Pearson product moment correlation coefficient of $r = 0.93$, indicates there is an overall significant linear agreement between the $k_{25,Calc}$ and $k_{25,Field}$ datasets (Fig. 4.4). A strong linear relationship ($r = 0.87$) was also observed between $k_{25,Calc}$ and $k_{25,Lab}$ (Fig. 4.5). While the level of precision between $k_{25,Calc}$ and $k_{25,Field}$ was slightly higher than $k_{25,Calc}$ with $k_{25,Lab}$, $k_{25,Calc}$ yielded values that were more accurate to $k_{25,Lab}$ (RMSE = 19 μS cm^{-1}) than to $k_{25,Field}$ (RMSE = 35 μS cm^{-1}).

Figures 4.1 and 4.4 show that all $k_{25,Calc}$ and $k_{25,Lab}$ values were greater in magnitude than the corresponding values of $k_{25,Field}$. As stated in Section 4.4.1, low accuracy between $k_{25,Lab}$ and $k_{25,Field}$ was thought to have been caused by different temperature compensation factors used in Equation 4.5. This could at also partially explain the low accuracy observed between $k_{25,Calc}$ and $k_{25,Field}$ values. It is also important to note that post growing season residuals were greater than

growing season residuals in both plots of $k_{25,Field}$ and $k_{25,Lab}$ with $k_{25,Calc}$ (Fig. 4.4 & 4.5). Again, this is likely due to the temperature compensation factor not being calibrated to the ionic composition of growing and post growing season drainage water samples.

4.4.4 Effect of Cropping System and Season on Electrical Conductivity

Field measurements for drainage water electrical conductivity ($k_{25,Field}$) ranged from 387 to 760 µS cm^{-1}. Both extremes were observed within 3 days following the largest rainfall event (7.94 cm) in June. The lowest recorded $k_{25,Field}$ occurred in drainage from a continuous unfertilized prairie plot during the initial drainage period; the pH for this water sample was 6.92, which was the lowest observed pH during the study period. The highest observed conductivity was recorded in drainage from a corn plot in annual rotation with soybeans (cropping system-C2) three days following the initiation of this drainage event; measured pH (7.32) fell in the 35th cumulative percentile of all observations. Soybean plots in annual rotation with corn (S2 cropping systems) had the lowest mean conductivity ($M = 595$, $SD = 76$) µS cm^{-1}, while drainage from C2 plots had the largest mean conductivities ($M = 685$, $SD = 42$) µS cm^{-1}. Variability in $k_{25,Field}$ was lowest among continuous corn plots (cropping system-CC) ($M = 663$, $SD = 26$) µS cm^{-1}, and greatest among continuous prairie plots (cropping system-P) ($M = 623$, $SD = 127$) µS cm^{-1}. Mean $k_{25,Field}$ across all drainage samples was 642 µS cm^{-1} with a standard deviation of 79 µS cm^{-1}. Distributions for sampling groups are provided in Figure 4.6.

4.4.5 Cropping System Analysis

As previously stated, the ionic composition of drainage water is influenced by cropping system. Because k_{25} is dependent on the ionic composition, it was of interest to evaluate $k_{25,Field}$ variability among different cropping systems. Sample $k_{25,Field}$ populations of cropping systems C2 ($n = 14$), S2 ($n = 14$), CC ($n = 12$), and P ($n = 14$) were subject to a test for normality and equality

of variance prior to conducting inferential analyses regarding differences among sampling distributions. A Shapiro-Wilk test indicated the S2 and P $k_{25,Field}$ data were not normally distributed. A non-parametric rank-based Conover test was used to check for equality of variance among all sampling groups, with results indicating the variances were sufficiently homogeneous. The Kruskal-Wallis test was therefore used to determine that there is a statistical difference in at least one of the sampling groups (C2, S2, CC, P). Given these results, independent two-sample comparisons were then carried out on the ranks using the Mann-Whitney test for equal medians. Results from the two sample tests suggest that the median $k_{25,Field}$ measured in cropping system, S2, is significantly different than the median $k_{25,Field}$ of C2 ($U = 182$, *p-value* < 0.001), CC ($U = 20$, *p-value* < 0.001), and P ($U = 53$, *p-value* = 0.036) cropping systems. The $k_{25,Field}$ of C2 was not significantly different from CC ($U = 106$, *p-value* = 0.269) or P ($U = 111$, *p-value* = 0.566) cropping systems. Similarly, the median $k_{25,Field}$ of CC was not significantly different from the P ($U = 70.5$, *p-value* = 0.504) cropping system. These results coincide with those of Zimmerman & Kaleita (2016) who observed significantly higher concentrations of Mg^{2+} and Cl^- in COBS drainage samples from C2 and CC cropping systems in comparison to that of S2 systems. These specific differences in the ionic composition could explain why $k_{25,Field}$ was similar among C2 and CC cropping systems but different than S2 systems.

4.4.6 Seasonal Analysis

Assumptions for normality and homogeneity of variance among GS and PGS populations were tested to ensure appropriate statistical methods for conducting independent two-sample comparisons. The assumption for normality among growing season data ($W = 0.946$, *p-value* = 0.226) and post growing season data ($W = 0.944$, *p-value* = 0.573) was not violated according to the Shapiro-Wilk distribution. However, the Levene's test provided sufficient evidence to reject

the null hypothesis for equality of variances ($W(1, 33) = 5.590$, *p-value* = 0.024). An independent samples Welch's t-test was therefore employed to evaluate the effect of season on measured $k_{25,Field}$ in agricultural drainage water. Results from the Welch's t-test were not significant at alpha level 0.05, indicating that $k_{25,Field}$ was not different among growing season ($M = 650$, $SD = 23$) µS cm^{-1} and post growing season ($M = 648$, $SD = 42$) µS cm^{-1} drainage waters $t(12.78) = 0.118$, *p-value* (2-sided) = 0.908. These results are contrary to what was expected, given that Zimmerman & Kaleita (2016) observed significant differences in the ionic composition among GS and PGS samples at the COBS research site.

4.4.7   Correlation With Drainage Flow rate, pH, and Temperature

A correlation analysis was performed on drainage rate, drainage water pH, and drainage water temperature with respect to $k_{25,Field}$ to quantify this influence. The sampling population ($n = 54$) for this analysis were obtained from the combined sample population of observed values during the month of June. Assumptions for normality were tested using the Shapiro-Wilk test. Test results indicated that our assumption for normality was rejected for drainage water k_{25} ($M = 641$, $SD = 85$) cm d^{-1} ($W = 0.791$, *p-value* < 0.001), and drainage flow rate ($M = 0.231$, $SD = 0.181$) µS cm^{-1} ($W = 0.875$, *p-value* < 0.001). Therefore, the Kendall-Tau ranked correlation test was calculated to evaluate k_{25} dependency on temperature, pH, and flow. Results from the correlation test suggest measured electrical conductivity, k_{25}, is independent of drainage water temperature ($\tau = 0.115$, *p-value* = 0.223), pH ($\tau = -0.178$, *p-value* = 0.059), and flow ($\tau = 0.118$, *p-value* = 0.207). It is important to remember that temperature in this analysis represents an indicator for different ionic compositions, which can influence the magnitude of measured electrical conductivity. This is different than temperature's influence on the solvent's viscosity, which is automatically accounted for using Equation 4.5.

4.5 Conclusion

Hand held multi-parameter meters, like the one used in this study, are a cost effective, reliable and accurate tool for generalized water quality monitoring of TDS. In this study, a Hach Pro + Multi 2 meter was used to collect 54 growing season and 11 post growing season measurements for specific electrical conductivity, pH, and temperature in agricultural subsurface drainage water at the COBS research site in Boone County, IA. A total of 23 of these drainage waters were collected and analyzed for HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, Na^+. Of the 23 collected samples, 18 were analyzed for specific electrical conductivity in accordance with SM 2510B. Laboratory conductivities exhibited the same trend as the field measurements ($r = 0.970$), but were 23 μS cm^{-1} greater on average; this may be due to inconsistent temperature compensation factors among the two methods. We therefore concluded that field electrical conductivity measurements had high precision, but suffered from low accuracy. Further investigation with calculated electrical conductivities provided additional evidence that field measurements tended to underestimate the drainage water electrical conductivity. However the level of error observed in field conductivity measurements was acceptable, given that the error was consistent with respect to laboratory and calculated conductivities.

Based on a comprehensive literature review and field investigation, Zimmerman & Kaleita (2016) determined that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^+, and SO_4^{2-} were the sole primary ions in agricultural drainage waters at COBS. This was verified in the present study by performing regression to estimate the cumulative concentration of these major ions using measured electrical conductivity and the relationship described by Equation 4.6, which states that the cumulative concentration of major ions is proportionate to k_{25}. Analysis of the constant of proportionality (K) indicated that regression should be carried out using separate K values for the growing season (K

= 0.846) and post growing season ($K = 0.888$). Results from regression through the origin (RTO) show that measured electrical conductivity was a good estimator for the cumulative concentration of major ions. Analysis of the estimated concentration yielded an average residual RMSE of 9 ppm for the growing season and 7 ppm for the post growing season; this represents an average error of $\pm 1.7\%$ and $\pm 1.2\%$ with respect to the average observed total ionic concentration. The magnitude of these values coincide with the 1.2% (Zimmerman & Kaleita, 2016) contribution of minor dissolved constituents to the total dissolved solids concentration. Therefore, through regression analysis, we have quantitatively shown that HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, Na^+ are the major ions responsible for the bulk electrical conductivity of these drainage water samples.

Each major ion's individual contribution to the bulk electrical conductivity was calculated using molal conductivities. Procedures for this evaluation were taken directly from McCleskey et al. (2012) who presented a method for calculating ionic molal conductivities for various natural waters. Results showed the majority of the bulk electrical conductivity was a produced by HCO_3^-, Ca^{2+}, and Mg^{2+}, which cumulatively accounted for 90% of the total calculated electrical conductivity. Calculated conductivities for the NO_3^- and Cl^- averaged approximately 7% and 2% of the bulk electrical conductivity, while SO_4^2 and Na^+ were less than 1% each. Furthermore, calculated conductivities indicated that variability was least among Mg^{2+}, SO_4^{2-}, Cl^-, and Na^+.

Several published results have shown that the composition of agricultural drainage water is dependent on cropping system, season, pH, temperature, and drainage flow rate. Since electrical conductivity is a function of the water's ionic composition, we had expected k_{25} to also be influenced by these parameters. Statistical analysis of observed data indicated that k_{25} was not significantly different among growing and post growing season drainage, nor was k_{25} dependent on pH, temperature, or drainage flow rate. Significant results were obtained for different cropping

systems. Specifically, the median of k_{25} distributions from observed drainage in cropping systems

C2, CC, and P were statistically different from the median of S2 systems. These results coincide

with results in Zimmerman & Kaleita (2016), which suggested that ionic composition (indicated

by the concentrations of Ca^{2+}, Mg^{2+}, and Cl^-) of S2 cropping systems we significantly different

than C2 and CC systems. By performing these analyses, we have qualitatively described the

variability of bulk electrical conductivity in agricultural drainage waters with respect to different

environmental and land management conditions. The most important aspect to note is that

different seasonal conditions significantly influence the ionic ratios to an extent that can result in

a misinterpretation of the estimated ionic composition. This knowledge is essential for the future

research attempting to implement electrical conductivity as a tool for water quality monitoring.

4.6 References

Abu-Rukah, Y., & Al-Kofahi, O. (2001). The assessment of the effect of landfill leachate on ground-water quality—a case study. El-Akader landfill site—north Jordan. *Journal of Arid Environments*, *49*(3), 615-630.

Allred, B., Daniels, J. J., & Ehsani, M. R. (Eds.). (2008). *Handbook of agricultural geophysics*. CRC Press.

AWWA (2012). Standard Methods 2510B. In E. W. Rice, R. B. Baird, A. D. Eaton, & L. S. Clesceri (Eds. 22), *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association Publications

Binkley, J., Simpson, J. A., & McMahon, P. (2000). Characterisation of textile aerobic-activated sludge plant by conductivity and pH measurement. Journal of the Textile Institute, 91(4), 523-529.

Bonate, P. L., & Steimer, J. L. (2006). *Pharmacokinetic-pharmacodynamic modeling and simulation* (pp. 205-265). New York: Springer.

Bower, C. A. (1974). Salinity of drainage waters. Drainage for Agriculture, (drainageforagri), 471-487.

Corwin, D. L., & Lesch, S. M. (2005). Apparent soil electrical conductivity measurements in agriculture. Computers and electronics in agriculture, 46(1), 11-43.

Daigh, A. L., Zhou, X., Helmers, M. J., Pederson, C. H., Ewing, R., & Horton, R. (2014). Subsurface drainage flow and soil water dynamics of reconstructed prairies and corn rotations for biofuel production. *Vadose Zone Journal*, *13*(4).

Eisenhauer, J. G. (2003). Regression through the origin. *Teaching Statistics*,*25*(3), 76-80.

Gali, R. K., Soupir, M. L., & Helmers, M. J. (2012). Electrical conductivity as a tool to estimate chemical properties of drainage water quality in the Des Moines Lobe, Iowa. In *2012 Dallas, Texas, July 29-August 1, 2012* (p. 1). American Society of Agricultural and Biological Engineers.

Goodrich, B. A., Koski, R. D., & Jacobi, W. R. (2009). Monitoring surface water chemistry near magnesium chloride dust suppressant treated roads in Colorado. *Journal of environmental quality, 38*(6), 2373-2381.

Hayashi, M. (2004). Temperature-electrical conductivity relation of water for environmental monitoring and geophysical data inversion. *Environmental monitoring and assessment*, *96*(1-3), 119-128.

Heng, L. K., White, R. E., Bolan, N. S., & Scotter, D. R., (1991) Leaching losses of major nutrients from a mole-drained soil under pasture, New Zealand Journal of Agricultural Research, 34:3, 325-334.

Kitchen, N. R., Sudduth, K. A., & Drummond, S. T. (1999). Soil electrical conductivity as a crop productivity measure for claypan soils. Journal of Production Agriculture, 12(4), 607-617.

Kitto, W. H. (1938). A contribution to water analysis. *Analyst*, *63*(744), 162-175.

Kohnke, H., Dreibelbis, F. R., & Davidson, J. M. (1940). A survey and discussion of lysimeters and a bibliography on their construction and performance (No. 372). US Department of Agriculture.

Koneshan, S., Rasaiah, J. C., Lynden-Bell, R. M., & Lee, S. H. (1998). Solvent structure, dynamics, and ion mobility in aqueous solutions at 25 C.*The Journal of Physical Chemistry B*, *102*(21), 4193-4204.

Koneshan, S., Lynden-Bell, R. M., & Rasaiah, J. C. (1998). Friction coefficients of ions in aqueous solution at 25 C. *Journal of the American Chemical Society*, *120*(46), 12041-12050.

Langford, C. H., & Beebe, R. A. (1995). *The development of chemical principles*. Courier Corporation.

Marandi, A., Polikarpus, M., & Jõeleht, A. (2013). A new approach for describing the relationship between electrical conductivity and major anion concentration in natural waters. *Applied geochemistry*, *38*, 103-109.

McCleskey, R. B., Nordstrom, D. K., Ryan, J. N., & Ball, J. W. (2012). A new method of calculating electrical conductivity with applications to natural waters. *Geochimica et Cosmochimica Acta*, *77*, 369-382.

McNeil, V. H., & Cox, M. E. (2000). Relationship between conductivity and analysed composition in a large set of natural surface-water samples, Queensland, Australia. Environmental Geology, 39(12), 1325-1333.

Miller, R. L., Bradford, W. L., & Peters, N. E. (1988). Specific conductance: theoretical considerations and application to analytical quality control. US Government Printing Office.

NRCS. 2016. Web Soil Survey. NRCS, Washington, DC. http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx (accessed 5 Oct. 2015)

NWIS (2011) National Water Information System: USGS Water-Quality Data for the Nation. Available from: <http://waterdata.usgs.gov/nwis/qw>.

Oster, J. D., & Grattan, S. R. (2002). Drainage water reuse. *Irrigation and Drainage Systems*, *16*(4), 297-310.

Patni, N. K., Masse, L., & Jui, P. Y. (1998). Groundwater quality under conventional and no tillage: I. Nitrate, electrical conductivity, and pH. *Journal of environmental quality*, *27*(4), 869-877.

Raymond, P. A., & Cole, J. J. (2003). Increase in the export of alkalinity from North America's largest river. *Science*, *301*(5629), 88-91.

Rhoades, J. D., Bingham, F. T., Letey, J., Hoffman, G. J., Dedrick, A. R., Pinter, P. J., & Replogle, J. A. (1989). Use of saline drainage water for irrigation: Imperial Valley study. *Agricultural Water Management*, *16*(1), 25-36.

Sabey, B. R. (1958). Rate of nitrification in some Iowa soils as influenced by temperature, reaction and population of nitrifying bacteria.

Sands, G. R., Song, I., Busman, L. M., & Hansen, B. J. (2008). The effects of subsurface drainage depth and intensity on nitrate loads in the northern cornbelt. *Transactions of the ASABE*, *51*(3), 937-946.

Steele, K.W.; Judd, M. 1.; Shannon, P. W. 1984: Leaching of nitrate and other nutrients from a grazed pasture. New Zealand journal of agricultural research 27:5-11.

Seitzinger, S., Harrison, J. A., Böhlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B., ... & Drecht, G. V. (2006). Denitrification across landscapes and waterscapes: a synthesis. *Ecological Applications*, *16*(6), 2064-2090.

Sudduth, K. A., Kitchen, N. R., Wiebold, W. J., Batchelor, W. D., Bollero, G. A., Bullock, D. G., ... & Thelen, K. D. (2005). Relating apparent electrical conductivity to soil properties across the north-central USA. Computers and Electronics in Agriculture, 46(1), 263-283.

Terman, G. L. 1977: Quantitative relationships among nutrients leached from soils. Soil Science Society of America, journal 41 : 935-940

Voichick, N. (2008). Specific conductance in the Colorado River between Glen Canyon Dam and Diamond Creek, Northern Arizona, 1988-2007 (No. 364). Geological Survey (US).

Walton, N. R. G. (1989). Electrical Conductivity and Total Dissolved Solids—What is Their Precise Relationship?. *Desalination*, *72*(3), 275-292.

White, R. E.; 1988: Leaching. pp. 193-211 in: Advances in nitrogen cycling in agricultural ecosystems, Wilson, J. R. ed. Wallingford, CAB.

Wilcox, L. (1955). Classification and use of irrigation waters.

Whisner, C. (2009). Inorganic Carbon Cycling in Agricultural Lands, Coshocton, Ohio.

Wolynes, P. G. (1980). Dynamics of electrolyte solutions. *Annual review of physical chemistry*, *31*(1), 345-376.

Zimmerman & Kaleita, (2016). Dissolved Constituents in Agricultural Drainage Waters.
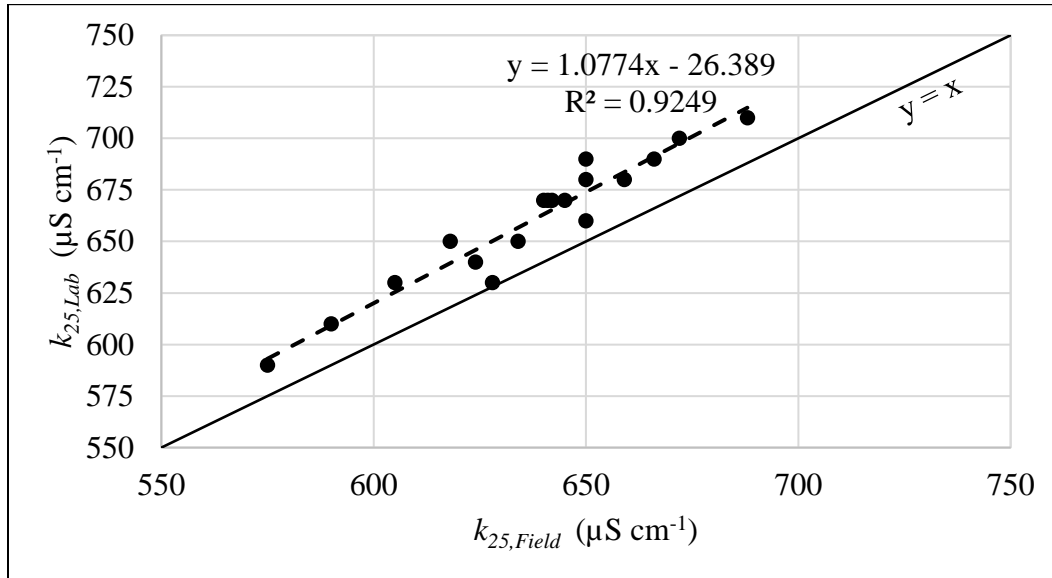
4.7 Figures

Figure 4.1. Comparison of field and laboratory specific electrical conductivity measurements on sampled drainage water at the COBS research site. The two agree closely but the laboratory measurements are consistently slightly higher.
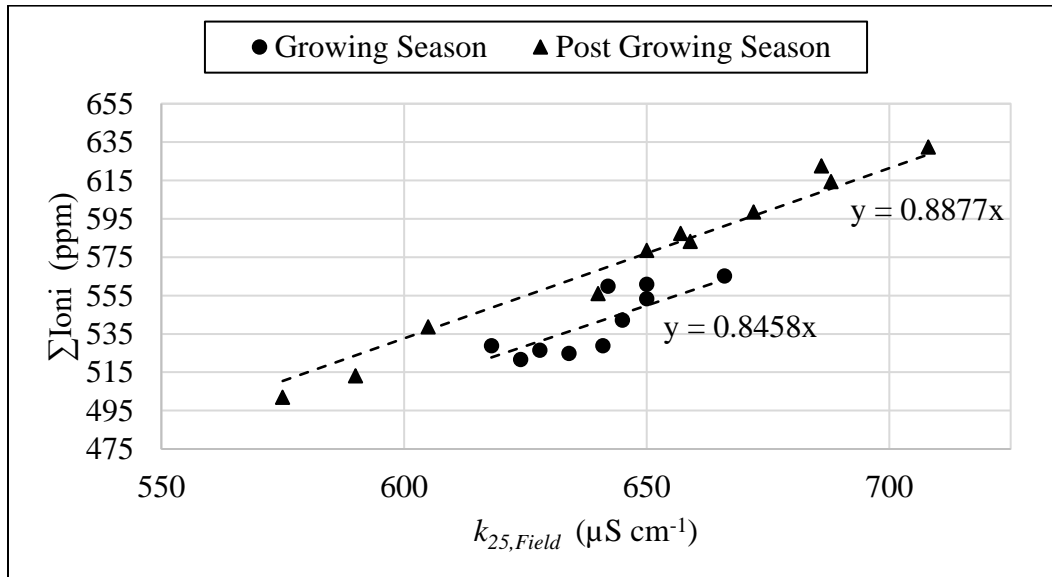

Figure 4.2. Measured specific electrical conductivity ($k_{25,Field}$) plotted against the cumulative concentration of HCO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, and Na^+ in drainage water samples collected during the growing and post growing season at the COBS research site.
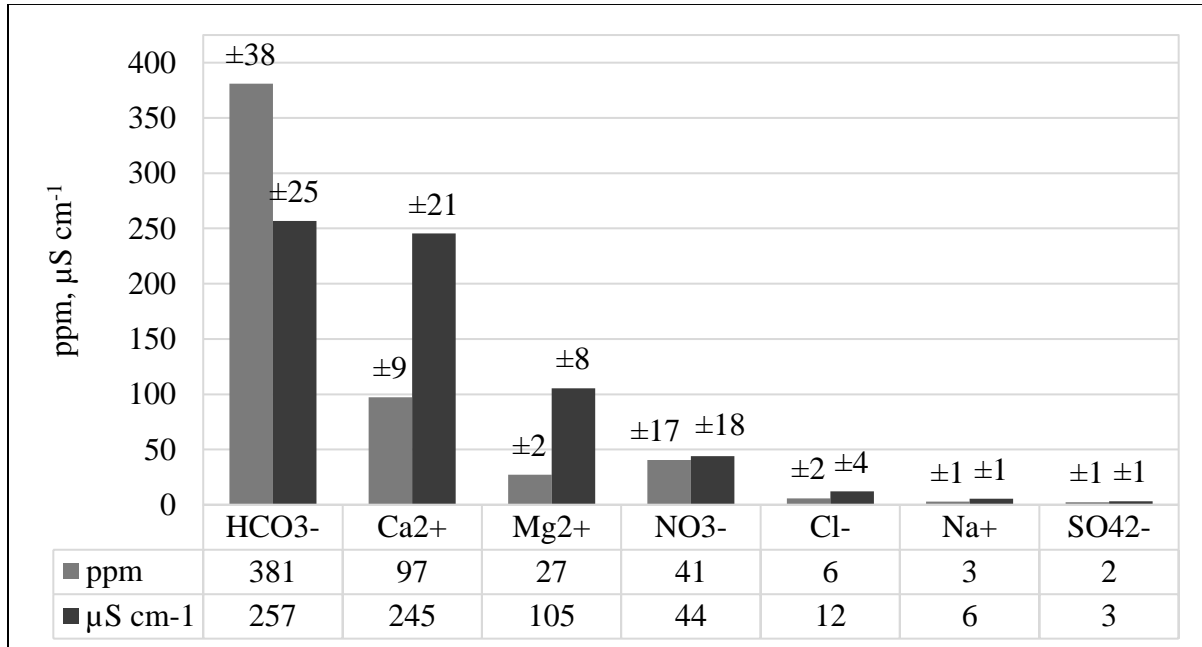
Figure 4.3. Mean calculated conductivities (µS cm^{-1}) and mean observed concentrations (ppm) of major ions observed in 23 drainage water samples from the COBS research site located in Boone County, IA. Standard deviations are listed above each bar.
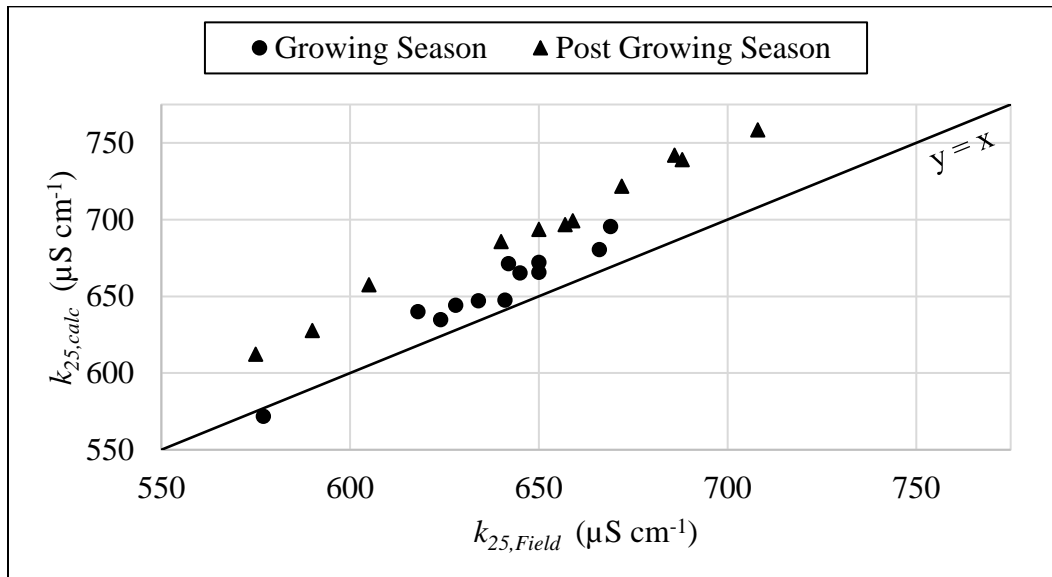

Figure 4.4. Calculated electrical conductivity at 25°C ($k_{25,Calc}$) against field measured specific electrical conductivity ($k_{25,Field}$).
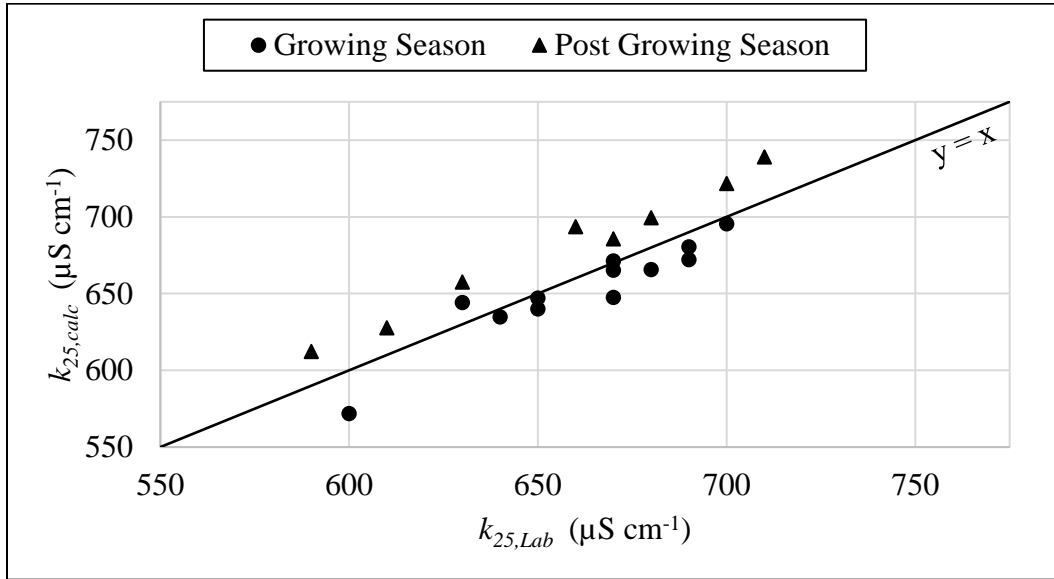
Figure 4.5. Calculated electrical conductivity at 25°C ($k_{25,Calc}$) against laboratory measured specific electrical conductivity ($k_{25,Lab}$).
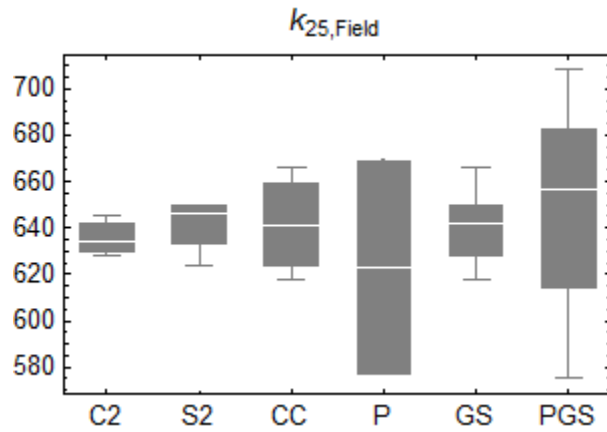

Figure 4.6. Drainage water specific electrical conductivity (μS cm^{-1}) observed in cropping systems C2, S2, CC, and P during the growing (GS) and post growing season (PGS).

CHAPTER 5. GENERAL CONCLUSIONS

A review of the literature identified a total of 12 dissociated ions (HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^+, SO_4^{2-}, K^+, NH_4^+, Fe^{2+}, F^+, and PO_4^{3-}) reported in published results for agricultural subsurface drainage waters characteristic to Iowa. Based on the reported concentrations (ppm) in cited literature, major ions include HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^+, and SO_4^{2-}, as these ion cumulatively represent 98.8% of the total dissolved solids (TDS) concentration; assuming TDS is defined as the cumulative reported concentration for all 12 ions.

Results from the field investigation presented in Chapters 3 and 4 confirmed that HCO_3^-, Ca^{2+}, NO_3^-, Mg^{2+}, Cl^-, Na^+, and SO_4^{2-} approximately represent all major dissolved constituents in sampled drainage waters at the COBS and Hickory Grove locations. Supporting evidence was provided by a charge imbalance analysis and regression on the cumulative concentration of major ions and measured specific electrical conductivity. The charge imbalance showed that on average, the ionic composition of sampled drainage waters had a near 1:1 relationship between the equivalent concentration of total cations and total anions. It was noted that post growing season samples tended to be weighted more heavily on the side of total cations. Root mean square error of the estimated cumulative major ions concertation from regression with measured specific electrical conductivity was ±1.2% and ±1.7% with respect to the mean observed cumulative concentration of major ions during the post growing season and growing season. Observed error from the regression analysis was consistent with the expected error of 1.2% caused by minor constituents, which were not chemically tested for in collected field samples.

In COBS samples with field measured electrical conductivities, the average observed concentration of major ions as a percentage of their cumulative concentration ($M = 557$, $SD = 41$) ppm was greatest among HCO_3^- (68%), Ca^{2+} (17%), NO_3^- (7%), and Mg^{2+} (5%). Chloride, Na^+,

and SO_4^{2-} accounted for approximately 2% of the observed cumulative major ions concentration. Similarly, the calculated conductivities for each major ion as a percentage of total calculated conductivity ($M = 673$, $SD = 44$) $\mu S\ cm^{-1}$ @ 25°C were greatest among HCO_3^- (38%), Ca^{2+} (36%), NO_3^- (7%), and Mg^{2+} (16%). Chloride, Na^+, and SO_4^{2-} accounted for approximately 3% of the observed total major ion concentration. Calculated and laboratory conductivities were on average 30 and 23 $\mu S\ cm^{-1}$ greater than measured field conductivities in the same drainage samples. While field measurements appear to have suffered from low accuracy compared with calculated and laboratory conductivities, a strong correlation between calculated ($r = 0.934$) and laboratory ($r = 0.962$) conductivities shows that a high degree of precision was maintained. Given these strong linear correlations, low accuracy between all three conductivity methods was attributed to differences in the linear temperature compensation factors.

Results from the field investigation illustrated that estimating the mass concentration of total ions from measured specific electrical conductivity is subject to error if a uniform constant of proportionality (K) is used for drainage waters with significantly different ionic ratios. Ionic ratios can be significantly influenced by environmental conditions (precipitation depth and frequency, temperature, soil type, etc.) and land management practices (N-fertilization, liming, crop, tillage, cover, etc.). In the field investigation, several of the most influential parameters were accounted for by grouping drainage samples according to the time of year (ie. growing season or post growing season) and cropping system (C2, S2, CC, and P). Results from Chapter 3 show that sampled drainage waters had significantly different ionic compositions among seasons and among cropping systems. Specifically, the seasonal analysis found that HCO_3^-, Ca^{2+}, and Mg^{2+} were present at greater concentrations during the post growing season, while NO_3^- and Cl^- were greater during the growing season; no differences were observed in the concentration of Na^+ and SO_4^{2-}.

Analysis of the ionic composition among cropping systems revealed that SO_4^{2-} was significantly different among all cropping systems, S2 cropping systems had higher concentrations of Ca^{2+} and lower concentrations of Mg^{2+} and Cl^- than C2 and CC cropping systems; no significant differences were observed for the concentrations of HCO_3^- or NO_3^- among cropping systems.

Agricultural lime applications and natural carbonic minerals at the COBS research site provided a common parent ion source for HCO_3^-, Ca^{2+}, and Mg^{2+}. Evidence for these shared ion sources was illustrated by a strong relationship ($\tau = 0.645$) between the observed HCO_3^- and Ca^{2+} concentrations, and similar seasonal trends among all three ions. The fact that HCO_3^-, Ca^{2+}, and Mg^{2+} concentrations were lowest during the growing season, while nitrate concentrations were greatest during this time period, provided further evidence that carbonic mineral weathering was not significantly influenced by nitric acid produced during nitrification. Understanding these relationships among ions are essential for predicting the characteristics of drainage waters.

Since the ionic composition is a function of environmental conditions, it was thought that measured drainage water flow, pH, and temperature would complement measured electrical conductivity by providing secondary data for making interpretations about the ionic composition. However, results suggested otherwise, as none of these parameters corresponded with differences in the ionic composition nor measured specific electrical conductivity among seasonal and cropping system sampling groups.

Results presented in this thesis characterize the major dissolved constituents of agricultural subsurface drainage waters with respect to typical concentrations and the impact of different environmental and land management practices. This knowledge is essential for the further advancement of existing and future agricultural drainage water quality monitoring efforts and development of mitigation strategies.

ACKNOWLEDGEMENTS