Assessing the Implications of Chloride from Land Application of Manure for Minnesota Waterways

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Table of Contents

List of Tables

List of Figures

Chapter 1

Literature Review

1.1 Chloride in Minnesota Waterways

Chlorine is a relatively abundant natural element on Earth; it is the eighteenth most abundant element found on the planet (Graedel & Keene, 1996). Chlorine is introduced to the pedosphere from various natural pathways. Decomposition of chlorine bound to organic matter, the weathering of inorganic chlorine from mineral surfaces, and atmospheric and oceanic deposition are large contributors (Barnum & Coates, 2022). As chlorine is a reactive element, it quickly experiences biogeochemical transformations that reduce it into the chloride anion. Chloride, however, is considered a conservative ion and undergoes few biogeochemical transformations. Chloride is the only stable form of chlorine and as a result, is the dominating chlorine species in the environment (Svensson et al., 2021). Due to chloride's solubility in water, once it is in soil, it is more likely to be transported via leaching than chlorine, making it a larger threat to water quality (Öberg, 1998). As chloride is leached below the root zone, it cannot be taken up by plants and is more likely exported into ground and surface waters where it permanently pollutes waterbodies as there is no feasible way to remove it (MPCA, 2020a). While there are natural cycles in which chloride is input into the environment, anthropogenic influence has accelerated chloride deposits into soil and water (Barnum & Coates, 2022).

While chloride naturally occurs in ground and surface waters in concentrations below 50 mg L^{-1} (Wu et al., 2021), chloride contamination of water is a rising concern in Minnesota. In 2022, 54 waterbodies were listed as impaired for chloride by the Minnesota Pollution Control Agency (MPCA), exceeding concentrations allowed by the Environmental Protection Agency (EPA) of 230 mg L^{-1} (Anderson et al., 2022; MPCA, 2022). Specifically outlined in these reports, over 221 miles of river, 55 acres of wetlands, and 1,400 acres of lake are impaired by chloride, and an additional 75 waterbodies are being monitored for nearing the chloride standard. Chloride has become a more widespread issue in groundwater as well (MPCA, 2020b). In 2017, 40% of shallow groundwater monitoring wells tested had a significant upward trend in chloride concentration compared to recent analyses done in 2005, with some monitoring wells increasing by over 100 mg L^{-1} (MPCA, 2020b). With 8.4% of Minnesota covered by water and 75% of the state's drinking water sourced from groundwater (USGS, 2018), the threat of widespread chloride contamination is high. Pollution from chloride salts presents a regional issue as 1,972 waterbodies and 1,329 groundwater monitoring wells in 17 other states in the Midwest and Northeast United States are at risk of salinization (Dugan et al., 2020; Mullaney et al., 2009).

Per 2020 estimates for chloride loading in Minnesota, livestock manure is one of the potential anthropogenic sources of chloride loading; however, there is insufficient data to understand and fully represent its role in surface and ground water contamination (MPCA, 2020b; Overbo et al., 2021). The objective of this review is to provide a background on chloride loading into Minnesota waters, understand its transport and fate through the environment, and highlight potential research gaps surrounding manure-based chloride and its part in chloride pollution in Minnesota. This review will justify the need for increased chloride monitoring in manure to help implement best management practices to reduce environmental, agricultural, and health concerns from chronic chloride exposure. A chloride mass balance for the state of Minnesota will benefit from a better understanding of manure-based chloride.

1.2 Health and Environmental Impacts of Chloride Contamination

1.2.1 Chloride's Function in Human, Livestock, and Crop Health

Chloride is an essential micronutrient that supports human, animal, and plant life (Soetan et al., 2010). It is essential in human diets as it facilitates proper balance of electrolytes, supports muscular activity, and maintains pH in the body (O'Connor & Ahmad, 2015). Similar to humans, chloride is an important anion in livestock health and maintains a proper balance of bodily fluids, regulates food intake and weight, and maintains osmotic pressure in cells (Harty, 2022; Neathery et al., 1981). Chloride is also a necessary component of crop production. Crops need chloride to support proper uptake of essential cations including calcium, potassium, magnesium, and ammonium into plant tissues (Kafkafi & Xu, 2002; Mengel et al., 2009). Chloride salts have also been utilized to suppress disease in crops grown in the Midwest (Heckman, 2006). Reid et al. (2001) demonstrated that soil amended with sodium chloride (NaCl) was effective in reducing root rot in asparagus while not affecting yield. A similar study by El-Mougy & Abdel-Kader (2009) showed that calcium chloride ($CaCl_2$) salts reduced the incidence and severity of early blight disease in potatoes by inhibiting pathogen growth. However, chloride use in excessive amounts can have negative effects on human, crop, and soil health (MPCA, 2020a).

1.2.2 Health and Environmental Impacts Related to Long-Term Exposure to Chloride

Long-term exposure to drinking water contaminated with chloride in concentrations greater than the EPA drinking water standard of 250 mg L^{-1} can be detrimental to human health (US EPA, 2009). Elevated levels of chloride in drinking water cause hypertension, a weakened immune system and kidney failure in severe cases (Wu et al., 2021). Chloride pollution can indirectly affect human health as well. When chloride leaches from the soil surface into groundwater aquifers, it interacts with latent toxic metals present in the soil including nickel, copper, cadmium, lead, and mercury (Hahne & Kroontje, 1973). Chloride associates with toxic metals to form molecules called chlorocomplexes, which are mobile in soil and easily carried into groundwater, allowing chloride along with toxic heavy metals to pollute drinking water (Doner, 1978). Health effects from drinking chloride contaminated drinking water are associated with adverse socioeconomic consequences as models show that long-term exposure could cause a loss of 19 working days per year due to related health concerns (Das et al., 2019). This would be a particular burden for individuals who cannot afford medical costs or time off from associated illnesses.

Soil becomes saline when high concentrations of soluble chloride salts accumulate in the soil (Fitzpatrick et al., 2000). Soil salinity is measured by the soil electrical conductivity (EC), or a soil's ability to transmit an electrical charge (Corwin & Lesch, 2003). EC values greater than 4 deciSiemens per meter are considered saline (Silvertooth, 2001). While chloride is a naturally occurring micronutrient in soil, crop requirements are typically low, so small amounts applied to soil create a saline environment which results in plant toxicity over time (Geilfus, 2018). White (2001) determined that chloride toxicity occurs in leaf tissue from ranges of 4 – 7 and 15 – 50 mg kg^{-1} of dry weight of crop in chloride-sensitive and chloride-tolerant crop species, respectively. When toxicity occurs, chloride accumulates in leaf and shoot tissues causing leaf burn, yield reductions, and photosynthesis suppression (Geilfus, 2018; Li et al., 2017; Tavakkoli et al., 2010).

Saline soils also have negative effects on essential soil microbial communities, thus influencing soil function and health. A study by Song et al. (2019) found that increasing salinization of soil reduces relative abundance of important phylum of soil bacteria such as Proteobacteria, Actinobacteria, Firmicutes, and Nitrospirae. Reductions in soil microbial biodiversity affect ecosystem functions that aid crop production including soil fertility, nutrient cycling, carbon sequestration, decomposition, and respiration (Kennedy & Smith, 1995; Maestre et al., 2015; Müller et al., 2002). Enzymatic activity of soil microbes in saline soil are inhibited, thus reducing their productivity in biogeochemical cycling (Dinesh et al., 1995; Omar et al., 1994; Zhang et al., 2018).

Chloride salts affect the overall soil structure, especially in soils with inadequate drainage to remove salts from the soil profile. Structural changes to the soil profile alter soil hydraulic processes and crop growth in affected soils (Essington, 2015). Saline soils are more easily compacted, resulting in reduced water infiltration and altered water flow through the soil profile (Short, 2019). A study by Black & Abdul-Hakim (1984) applied NaCl to soil and showed that excessive inputs deteriorated soil aggregate stability, an important indicator of soil health. Their study found that aggregate slacking, the destruction of aggregates caused by soil swelling and dispersion from chloride ions, occurred up to 30-cm in depth and that soil crusting was evident on the soil surface (Black & Abdul-Hakim, 1984). Increased compaction, reduced aggregate stability, and soil surface crusting affect crop germination and root penetration, decreasing overall crop yield (Lemos & Lutz, 1957; Machado & Serralheiro, 2017).

1.3 Sources of Chloride into Waterways

1.3.1 Urban Sources of Chloride Loading

Chloride has many point and non-point pathways into the Minnesota environment. Urban and suburban areas within the state contribute the greatest amount of chloride overall. Road salt de-icing and wastewater treatment plant (WWTP) discharge from water softening, and industrial sources account for 42% and 25% of chloride loading into the state respectively (MPCA, 2020b). Road salt (commonly applied as NaCl) is used for winter road maintenance in many northern states. Minnesota applies roughly 403,600 tons of chloride from road salt application (Overbo et al., 2021). Seventy-eight percent of road salt applied is lost to groundwater or accumulates in local waterbodies after application, highlighting a direct pathway of chloride into water (MPCA, 2020a).

Wastewater intercepted by WWTPs is treated for pollutants before being discharged back into waterways. Wastewater originates from two major sources: residential and industrial sources. Residential sources of chloride include water softening. Minnesota is considered a “hard water” state, where 72% of the state population softens their water. Hard water is high in concentrations of calcium and magnesium leaving an unpleasant taste in drinking water and harms appliances and pipes over time (McVean, 2019; Sengupta, 2013). Sodium chloride is commonly used as a water softener to make water more desirable for consumption and household use by removing calcium and magnesium. Softened water waste contains high concentrations of chloride as a result, which cannot be easily removed before being discharged into the environment. Of all the chloride being discharged from WWTP, 132,500 tons was estimated to be from water softening discharge, and 29,500 tons originated from industrial sources including waste management and food processing facilities (MPCA, 2020b; Overbo et al., 2021). Chloride is also introduced into septic systems which originates from human excreta, drinking water, and household product use. Effluent from septic systems is discharged into drain fields where it carries chloride into the environment. Overall, 33,100 tons were estimated to be from residential septic system discharge (Overbo et al., 2021).

1.3.2 Rural Sources of Chloride Loading

In addition to urban sources of chloride, agricultural practices also contribute to chloride contamination. Commercial fertilizer application accounts for roughly 23% of chloride loading in Minnesota (MPCA, 2020b). Chloride salts, such as potassium chloride (KCl), $CaCl_2$, or magnesium chloride ($MgCl_2$) are commonly added to fields to meet crop nutritional requirements of K, Ca, Mg among other nutrients. As KCl provides many agronomic benefits to crop production, and exchangeable K is often limiting in Minnesota soils, many producers utilize it as a fertilizer amendment making it an important source of chloride loading in densely cropped areas (Kaiser, 2018; Overbo et al., 2021). Minnesota croplands as a whole receive roughly 220,000 – 260,000 tons of chloride per year from KCl fertilizer application (MPCA, 2020b).

Manure is commonly applied as fertilizer and hosts a variety of agronomic and soil health benefits that cannot be met by synthetic fertilizers (Xia et al., 2017; Zhang et al., 2020). Manure is rich in nutrients essential for plant growth. Although considered heterogenous, manure is typically high in the macronutrients nitrogen, phosphorus, and potassium, as well as in the micronutrients copper (Cu), iron (Fe), manganese (Mn), and molybdenum (Mo) among others (Kumar et al., 2013). When applied to fields, manure is beneficial to overall soil structure by improving soil aggregate stability, water-holding capacity, bulk density, and water infiltration (Moral et al., 2005; Zingore et al., 2008). Manure also has high concentrations of organic matter. Triberti et al., (2016) found that land-applied manure increases soil organic matter (SOM) content, thus drastically increasing carbon sequestration, an important method to mitigate climate change.

When manure is land applied as a nutrient dense fertilizer, non-point source chloride contamination is a persistent threat due to chloride's presence in manure. In Minnesota, 62,600 tons of chloride, or 6% of the total load, was estimated to be applied by the land application of manure (Overbo et al., 2021). This manure is primarily sourced from the state's 1,200 concentrated animal feeding operations (CAFOs) which sometimes contain 5% - 10% chloride salts (University of Arizona, 2000). This estimation does not account for manure inputs other than land application. While much of manure is intentionally land applied, improper disposal, open feedlot runoff, and leaching from waste lagoons occur as well (Minnesota Groundwater Association, 2020). For example, it was found that preferential flow of water off hard packed feedlot surfaces carried manure-based chloride onto permeable ground where it is able to infiltrate (García et al., 2012; Olson et al., 2005).

1.3.2.1 Sources of Chloride in Manure

There are many avenues in which chloride can be introduced into manure, both before and after excretion, thus increasing the salinity of manure fertilizer. Livestock feed is often supplemented with vitamins and minerals to efficiently and cost effectively make up for nutrient deficiencies of forage and grain-based diets, especially trace minerals (cobalt (Co), Cu, Fe, Mn, Mo, and zinc (Zn)) and macro minerals (Na, sulfur (S), K, Ca, and Mg) (López-Alonso, 2012; Suttle, 2022). This process helps producers maintain high livestock productivity and meet market demands (Udo et al., 2011). Chloride most commonly is amended to feed in the form of NaCl, but can also be added via KCl and $MgCl_2$ depending on nutritional requirements of the livestock (Berger & Cunha, 2006). NaCl in feed, for example, aids proper digestion of other nutrients by supporting enzymatic function, and $CaCl_2$ supplementation reduces risk of hypoglycemia (Afshar Farnia et al., 2018; Argüelles-Ramos & Brake, 2020). However, livestock commonly have trouble digesting chloride and associated salts. This results in higher concentrations found in excreta when fed a high salt diet. Many trace minerals, including chloride salts, are only soluble in specific pH environments (Genther & Hansen, 2015). The mineral tribasic copper chloride ($Cu_2(OH)_3Cl$) is more soluble at a lower pH and cannot be properly absorbed in ruminant digestive environments which range in pH from 6.0 – 6.8 (Spears, 2003; Spears et al., 2004). Chloride experiences interactions with other dietary supplements that change the digestibility of chloride salts. The solubility and absorption of chloride salts in poultry digestion is facilitated by the presence of dietary fiber. If absent, or low in fiber, poultry will utilize less mineral salts during digestion and excrete excess

(Jha & Mishra, 2021). Li-Xian et al. (2007) reported ranges of chloride in chicken and swine manure at 17.3% and 7% of total soluble salts in manure respectively in their study measuring manure salinity. These values were largely attributed to salt supplementation of feed to improve flavor and maintain a balance of cations and anions in livestock.

Chloride salts may be added in low concentrations to manure storage systems to offset other environmental concerns. Chloride in the form of aluminum chloride ($AlCl_3$) inhibits ammonia (NH_3) volatilization by nearly 57%, making it an effective chemical additive to reduce gaseous emissions from swine manure storage systems (Nahm, 2005; Smith et al., 2004). When added to poultry litter and swine manure, $AlCl_3$ reduces phosphorus solubility by 36%, thus decreasing P concentrations in runoff by 84% when applied to fields (Choi & Moore, 2008; Smith et al., 2004). Chloride amendments create conflicting interests as they reduce nitrogen and phosphorus losses but increase the salinity of manure fertilizers before field application causing unintended chloride contamination.

Bedding materials are essential in barns to help maintain overall health and production of livestock. Proper bedding insulates the barn floor in cold environments, absorbs excess waste and moisture, and keeps animals clean preventing infection and disease (Carroll, 2020). Old bedding material is added to manure in storage systems as an organic amendment rather than disposal or spreading it immediately over croplands (Bollwahn, 2014). Research is available showing that bedding materials amended into manure affect the nutrient content, although much of the work is focused on nitrogen and phosphorus concentrations (Arnold, 2021; Keskinen et al., 2017; Sawyer & Mallarino, 2016). For example, bedding helps sequester and retain nitrogen in manure as it inhibits ammonium volatilization (Anderson et al., 2006). Limited research is available to determine if chloride interacts within bedding manure mixtures and influences chloride movement. Meyer & Robinson (2007) report that bedding makes up roughly 4% of the total chloride input to dairy manure, however, frequent analysis of bedding materials and manure is needed to accurately account for this input. These results are highly dependent on bedding material used as well. Research shows that when using wood bedding as opposed to straw, chloride concentration in manure is significantly lower and risk to groundwater contamination when land applied is reduced (Miller et al., 2005, 2011).

There has been very little research done to determine how manure handling practices affect chloride concentrations. Composted manure offers many environmental benefits to producers, as it stabilizes nutrients to reduce their mobility in soil, reduces manure's weight by 50-60% which decreases hauling costs, and kills pathogens and parasites making manure safer to handle and apply (Keena, 2022). Composting manure, however, reduces moisture and organic matter content through evaporation and decomposition, which concentrates chloride salts that are then land applied (Larney et al., 2006). Despite there being evidence that composting affects chloride concentrations, there are few studies that research chloride concentrations during composting and other handling processes.

Manure nutrient concentration data is notoriously variable, owing to feed, animal, storage, and handling practice differences between farms and over time (Lorimor et al., 2004). Chloride concentration measurements of manure are not a typical practice, so baseline data is lacking. The MPCA reports chloride values as high as 215 mg L^{-1} for liquid manures and 9,061 mg kg^{-1} for solid manures (Ground Water Monitoring and Assessment Program, 2001). Other studies have reported manure values ranging from 86 – 1,980 mg L^{-1} with region, sampling regime, species, and diet accounting for variation in chloride concentrations (Minnesota Groundwater Association, 2020; Panno et al., 2006). Recent unpublished data from an Upper Midwest Agriculture Service lab highlights variability in chloride concentration by species in both solid (Figure 1.1a) and liquid (Figure 1.1b) manure.

1.3.2.2 Manure Application and its Environmental Impacts

An estimated fifty million tons of manure was produced in Minnesota annually and spread over 1.69 million acres of cropland in 2017 (*2017 Census of Agriculture*, 2019; Porter & Cox, 2020). When facilitated according to nutrient best management practices, manure application provides a sustainable way for livestock operations to recycle nutrients, especially the three essential macronutrients (nitrogen, phosphorus, and potassium), from crops used for livestock rearing back onto croplands (Spiegal et al., 2020). Even so, nutrient losses persist, due to the nature of nutrient flow into ground and surface waters (Hamilton et al., 2016). Both nitrogen and phosphorus are root causes to eutrophication in water bodies, impairing freshwater for drinking and recreational use due to harmful algal blooms (Davis et al., 2006). Drinking eutrophic water is toxic to human and animal health and has been attributed to stomach cancer and livestock deaths (Dodds & Welch, 2000). Harmful algal blooms from eutrophication also deteriorate aquatic environments by creating low-oxygen hypoxic zones that kill fish and plant life, harm essential habitat, and disrupt food webs in aquatic systems (NOAA, 2021). As of 2020 in Minnesota, 693 lakes and 814 miles of river are impaired and experience eutrophication due to high nitrogen and phosphorus inputs (Anderson, 2020).

A majority of cropland in Minnesota is in the southern and western part of the state. In these areas, croplands dominate land use, with some counties designating over 75% of land cover to agriculture (Gunderson et al., 2019). An evaluation of nitrate leaching into Minnesota waters by the MPCA determined 70% of nitrate in surfaces waters originates from surface runoff, leaching, and tile drainage from crop and pasture lands. In the Minnesota, Missouri, Cedar, and Lower Mississippi River Basins located in southern Minnesota, croplands contributed 89 – 95% of the total nitrate loads (Wall, 2013). Approximately 37% of the contribution of phosphorus originated from cropland runoff and is primarily located in the Minnesota, Red, Upper Mississippi, and Lower Mississippi River Basins in southern and western Minnesota (Anderson, 2020; Mulla et al., n.d.; Wasley, 2007).

Application rate guidelines are also set forth by University of Minnesota – Extension to mitigate nutrient losses from manure and fertilizer use. These guidelines consider nutritional needs of the crops being fertilized and how manure/fertilizer application can supplement these needs alongside other nutritional inputs including irrigation water, organic nutrient sources in the soil, and credits from previous crops (Wilson, 2019). However, nutrient application rates can only balance application and uptake for one nutrient, and nutrients not accounted for can be applied in excess of what the crop can utilize resulting in contaminated runoff and leachate (Sadeghpour et al., 2016, 2017; Toth et al., 2006). There are restrictions in place, however, to prevent the over application of nitrogen more than crop needs regardless of application rate, but other nutrients do not have these restrictions. Nitrogen based application rates for manure, for example, sometimes apply 3 – 6 times the amount of phosphorus that the crop can take up causing phosphorus accumulation in the soil and eventual loss into water (Moore & Ippolito, 2009). Potassium chloride fertilizer application rates are determined based on soil tests to assess K concentration available in soil for plant growth (Kaiser, 2018). While this supplies enough K to make up for deficiencies, this does not account for chloride being applied during application. As KCl is made up of approximately 47% chloride by mass, this could potentially add large amounts of chloride onto croplands in excess of crop needs that leach into groundwater (Bero et al., 2016; Heng et al., 1991; Stites & Kraft, 2001). The chloride concentration of manure is not consistently monitored or considered in application rate calculations prior to field application.

Nitrogen and phosphorus are the forefront of water quality management in Minnesota, while other nutrients, such as chloride, receive less attention. In Minnesota's most recent Nutrient Reduction Strategy report released in 2014, no plans were outlined to reduce chloride pollution from manure or fertilizer inputs (MPCA, 2014). If and when more research-based demonstration of manure-applied chloride impacts become available, regulatory limits may be necessary to reduce unintended chloride contamination from manure and fertilizer application.

1.4 Pathways from Soil to Water After Fertilizer/Manure Application

Nutrient and water transport are highly dependent on soil physical and chemical characteristics of soil (Schoonover & Crim, 2015). Cation exchange capacity (CEC) is a measure of a soil's total negative charge and determines the amount of positively charged ions that can be held in the soil root zone, and influences how negatively charged ions move through the soil profile with the flow of water (Sumner & Miller, 1996). Agricultural soils in the United States, and especially in the northern Midwest, contain high amounts of negatively charged clay minerals and soil organic matter, resulting in a greater CEC and higher capacity to repel anions (Anderson & Khaleel, 2022). While nutrients such as nitrate and sulfate are at greatest risk for leaching due to their negligible interactions with other elements in a soil profile, chloride is also susceptible to leaching from soils with high CEC values, especially in times of high precipitation as it is highly soluble in water (Schroth & Lehmann, 2002). It should also be noted that CEC is a pH-dependent soil characteristic. Acidic soils tend to have lower CEC values compared with more alkaline soils, resulting in less rapid chloride leaching (Bache, 1976).

Soil structure and texture interacts with rainfall intensity and frequency to affect leaching behaviors, as well. Whereas horizontal surface runoff is typical in soils with low permeability during intense or frequent rainfall rates which exceed infiltration rates, subsurface leaching is typical in soils with high permeability during less intense or infrequent rainfalls which do not exceed infiltration rates (Huddleston, 1996). Low permeable soils include finer texture clay soils with smaller pores, while high permeable soils are typically coarse-textured sands with large pore space (Ramakrishna & Viraraghavan, 2005). Chloride transport is influenced by these interactions. A study by Cichota et al. (2016) showed that chloride transport through leaching was greater in intense irrigation regimes in permeable soils when water was able to infiltrate. A study measuring the interaction between frequency and intensity of precipitation's ability to transport chloride determined that more frequent small-scale precipitation events were more prone to displace chloride below the rooting zone as opposed to less frequent, but more intense precipitation events (Kirda et al., 1974).

Leaching patterns can be altered when certain land use practices affecting soil structure are utilized on agricultural landscapes. While integral in supporting soil health, research suggests that no-till practices increase the presence of macropores in a soil and alters leaching patterns of contaminated water (Amin et al., 2016; Dalal, 1989; Tyler & Thomas, 1977). This can make leaching through the soil profile, as opposed to surface runoff, the dominant pathway for water movement carrying greater amounts of chloride into groundwater (Jarvis et al., 1991).

After application as manure or commercial fertilizer on or near the soil surface, the rate of chloride movement into groundwater via leaching is dependent on weather and water management practices. Although hydrologic discharge is typically rapid, chloride accumulation in surface soil can occur during periods of drought, in arid regions where evapotranspiration exceeds precipitation, or when land use changes are implemented that reduce groundwater recharge (Huang & Pang, 2011; Miller et al., 2011). Following precipitation, accumulated surface soil chloride is redistributed into the subsurface region where it is more at risk of being transported into groundwater aquifers (Geilfus, 2019). In a study evaluating manure-based chloride's movement in the soil profile, Miller et al. (2011) found that subsurface redistribution of accumulated chloride can occur below the rooting zone at depths up to 150-cm. Ultimately, chloride-contaminated groundwater can leach into aquifers where it resides until discharged into surface water bodies (MDNR, 2000).

Tile drainage is a significant source of point source pollution into agricultural watersheds (Schilling & Wolter, 2001). Common in croplands in the Midwest, this land management practice drains water from the soil sub-surface (Davis et al., 2000). As a result, water soluble nutrients are exported into streams via effluent. However, there is conflicting evidence as to whether tile drainage is a significant source of chloride in agricultural watersheds following manure or fertilizer application. A long-term study by David et al. (2016), found that chloride was exported via drainage water from uncontrolled drainage systems from tile drained fields quickly after KCl application and that soil chloride concentrations decreased through the duration of the study as it was exported from tile lines. Another study reported that high concentrations of chloride were rapidly exported from tile drains on recently fertilized fields in just hours following precipitation (Richard & Steenhuis, 1988). Other studies, however, report that chloride is not lost through tile effluent, rather accumulates in soil despite wet conditions (Frey et al., 2012; Gast et al., 1974). These differences may be a result of study scale, length of study, climactic conditions, or geology of the study site. More research is needed to understand chloride pathways through tile drained fields.

1.5 Conclusions

While applying manure onto croplands is an efficient way for producers to utilize nutrients from livestock operations, it may be associated with unintended chloride pollution of ground and surface waters in Minnesota. Research suggests there is a clear pathway for chloride to be introduced to manure and that it can leach into Minnesota waterways. While there are estimates of the amount of chloride being applied to Minnesota croplands, they may be misrepresenting actual chloride loading as there is little research to quantify standard chloride concentrations at a statewide scale. Minnesota does not require monitoring of manure for chloride, so there is little data to accurately estimate chloride contributions from manure inputs. Monitoring data that is available shows large variability in chloride concentrations by species and type. Without further research to understand chloride's presence in manure and its ability to leach through different soils, it will be difficult to fully understand manure's role in chloride contamination of Minnesota's ground and surface waters or create an accurate chloride mass balance for the state.

1.6 Figures

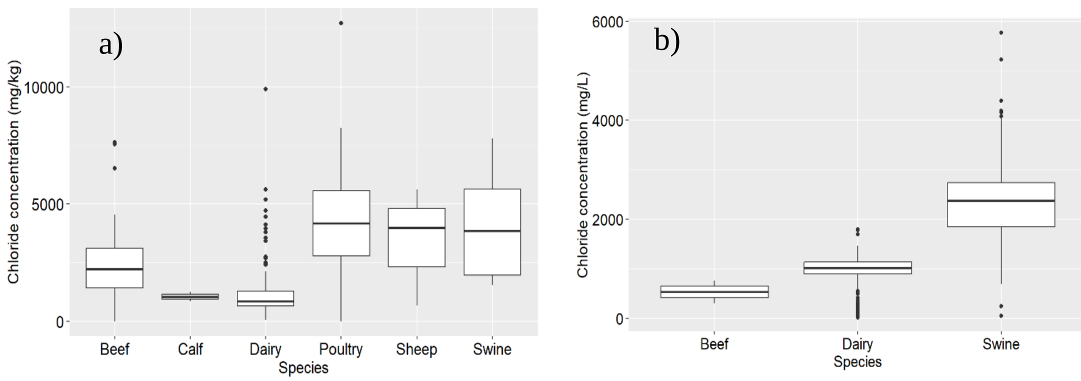

Figure 1.1: *Manure chloride concentration by species in* ***a)*** *solid manure and* ***b)*** *liquid manure based on analyses of random manure samples by a commercial laboratory.*

Chapter 2

Collecting and Constructing Intact Soil Columns via Soil Drilling

2.1 Abstract

Leaching column studies are an effective method for measuring water and solute transport through soil profiles. Undisturbed, intact soil columns are commonly collected using downward force from heavy equipment which can impact the soil structure if care is not taken and can be too costly and time intensive for practical use in large-scale, lab-based studies. An alternative method for collecting undisturbed soil columns, which reduces the risk of harming the natural soil structure, uses a rotating drill to slowly push through the soil profile. Here we present a method for extraction and assembly of large (0.3 m depth × 0.3 m diameter) soil column lysimeters via drilling. The accompanying leaching study simulated three, 5-cm irrigation events to four soil types in Minnesota, USA (Estherville sandy loam, Waukegan silt loam, Nicollet clay loam, and a Floam-Aazdahl-Hamerly complex soil). Cumulative leachate volume from each column for the duration of the study was compared between soil types and replicates within soil types to determine how drilling impacted leaching behavior. A small demonstration on drainage rates using one replicate from the Estherville sandy loam and Floam-Aazdahl-Hamerly complex soil types further illustrated differences in drainage behaviors. Soil bulk density measurements were taken to evaluate how soil column drilling affected soil structure and compaction. While cumulative leachate volume showed variability by soil type, replicates within soil types did not differ in the volume of water leached. Average drainage rates between the Estherville and Floam-Aazdahl-Hamerly soils emphasized that soil types still showed independent leaching patterns during irrigation. Soil bulk density values from soil columns also did not indicate any signs of compaction or damage to the soil

structure. Our results indicated that soil columns extracted via drilling are representative of natural soil conditions and are practical for lab-based leaching studies.

2.2 Introduction

The uses of fertilizers and pesticides are important for improving crop productivity by supplementing nutrient deficient croplands with essential macronutrients (nitrogen, phosphorus, and potassium) and protecting crops from pests and disease (Hemathilake & Gunathilake, 2022). However, high nutrient and chemical inputs onto croplands threaten water quality as excess nutrients and pollutants are leached below the root zone and into groundwater causing groundwater contamination (Messiga et al., 2020; Singh & Sekhon, 1979). Nutrient and chemical leaching is spatially variable and is driven in part by soil physical and chemical properties. Soil texture, class, and structure all affect a soil's ability to transport water and carry pollutants into groundwater (Manjula, 2017). Chemical properties, including soil pH and cation exchange capacity (CEC), are also important in determining a soil's capacity to retain nutrients or release them deeper into the soil profile (Lehmann & Joseph, 2009). Understanding soil properties and their effects on water and solute flow is essential to inform fertilizer and pesticide application and land best management practices that maximizes crop productivity and reduces nutrient and chemical losses into groundwater (Huang et al., 2017; Ozlu et al., 2022).

Soil column/lysimeter leaching studies are effective techniques to simulate water and solute movement through soil, which helps assess the risk of groundwater contamination following fertilizer or pesticide application (Feyereisen et al., 2010; Katagi, 2013). Lysimeter studies are conducted both in the field and in the lab with field based studies being effective in mimicking field conditions while the latter are carried out in a controlled environment where variables can be more easily managed (Belford, 1979; Winton & Weber, 1996). Soil columns for lysimeter studies can be collected as disturbed or undisturbed columns. While disturbed columns are uniformly packed with sieved soil, undisturbed columns are typically collected using force with a drop hammer, a hydraulic press, or sledgehammer to push the column into the soil and then excavated to provide an intact soil column from fields (Holten et al., 2019; Saporito et al., 2016; Walker et al., 1990). Undisturbed soil columns are the preferred method of soil column collection as disturbed soil columns have altered soil physical and chemical properties, including bulk density, water holding capacity, biogeochemical cycling, and hydraulic flow paths, which are essential properties in understanding natural water and solute leaching patterns (Belford, 1979; Cassel et al., 1974; Powelson et al., 2023).

Undisturbed soil columns installed using downward force, however, can compact soil, collapse macropores, and destroy the soil edges along the lysimeter wall if care is not taken during the collection process, making them less representative of in-field conditions (Allaire & Bochove, 2006; Bowman et al., 1994). These changes to the soil structure make soil columns more susceptible to preferential flow along the column sidewalls disrupting the natural flow of water (Cameron et al., 1992). This is especially prevalent with finer textured soils and soils with high soil moisture content, making comparisons between soil textures and moisture regimes challenging (Allaire & Bochove, 2006). Undisturbed soil columns must also be large enough to fully represent the soil profile and leave macropore distribution undisturbed (Iversen et al., 2012). Soil columns with a small surface area (<0.05 m^2) have greater risk of sidewall flow and shallow soil columns (<0.3 m) do not include the whole drainage depth of a soil, limiting their application to real leaching scenarios (Bergström, 1990). Additionally, undisturbed soil columns large enough to be representative - which are collected by downward force - are costly to excavate from fields and transport, making them less feasible for lab-based studies where a controlled environment is necessary and/or studies requiring multiple treatments and replications (Brown et al., 1985; Dabrowska & Rykala, 2021).

An alternative method of collecting undisturbed soil columns uses a drilling technique for column collection rather than downward force. First used in a study by Persson & Bergström (1991), this technique showed success in installing in situ soil column lysimeters which retained natural soil physical properties and reduced sidewall flow of water, while also being large enough to be representative of soil conditions. Soil column drilling requires less equipment and less labor which reduces the overall cost and time investment of column collection compared to the downward force method (Persson & Bergström, 1991). For these reasons, large undisturbed soil columns extracted via drilling are a feasible option for laboratory studies when compared with columns collected with downward force. Soil columns collected with a drilling apparatus allow researchers to conduct soil column leaching studies in a controlled environment without sacrificing representative soil columns from extraction procedures. The objective of this study is to show that soil column lysimeters collected with a drilling apparatus are reproducible, structurally intact, and mimic hydraulic flow patterns of soils in field settings.

Here, we present a method for constructing and collecting large (0.3 m depth × 0.3 m diameter) undisturbed soil columns for use in a lab-based leaching study via the drilling technique. We collected 48 undisturbed soil columns from fields in Minnesota with different soil types following soybean (*Glycine max* L.) harvest. Four soil types were chosen for this study: a Waukegan silt loam (Silt L) (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludolls), a Nicollet clay loam (Clay L) (Fine-loamy, mixed, superactive, mesic Aquic Hapludolls), an Estherville sandy loam (Sandy L) (Sandy, mixed, mesic Typic Hapludolls), and a Floam-Aazdahl-Hamerly complex (Silty Clay L) (Fine-loamy, mixed, superactive, frigid Aquic Hapludolls) (Table 2.1). Soil columns were brought into a laboratory at the University of Minnesota – Twin Cities campus, brought to field capacity, and subjected to three weekly irrigation events simulating 5-cm of rainfall per event. Water was allowed to percolate through the soil and leachate was collected from the bottoms of the soil column lysimeters.

Leachate volume (liters) was tracked per irrigation event and used to calculate cumulative leachate volume per column for the duration of the leaching study. Cumulative leachate volume was compared both among soil types and among replicates within soil types. Cumulative leachate volume, both among soil types and among replicates within soil types were compared using a one-way analysis of variance statistical test (ANOVA). To further demonstrate that this method did not alter hydraulic flow patterns, we measured leachate weights through time from one replicate from the Sandy L and the Silty Clay L soils to calculate the average drainage rates per column. Average drainage rates for each column were calculated by dividing the total weight of leachate (grams) by the elapsed time drainage occurred (minutes) for each soil type. Following the completion of the leaching experiment, soil bulk density (BD) was measured from each column from two depths in the soil profile (0 – 15 cm, and 15 – 30 cm). The BD values were compared with ideal BD values reported on the United States Department of Agriculture – Natural Resources Conservation Service (USDA-NRCS) soil quality indicator fact sheet for each respective soil texture (USDA-NRCS, 2008).

2.3 Protocol

1. **Preparing the materials**

    1. Create the supporting PVC structure for the soil column.

        i. Cut 30 cm diameter PVC pipe to 60 cm in length. The PVC should be Schedule 35 (SDR 35) (Figure 2.1a).

        ii. Designate a top side for the PVC pipe. Drill four 2.5 cm holes equidistant around the perimeter of the pipe, 1.5 cm down from the top of the pipe. These holes will be used to lock the PVC pipe into the drill apparatus (Figure 2.1b).

        iii. The PVC pipe is now ready to be used in the field.

    2. Create the baseplate for the supporting PVC structure using PVC board.

        i. Cut a 30 cm diameter circular baseplate from 10 mm thick PVC board using a jigsaw (Figure 2.2a).

        ii. Confirm that the baseplate will fit within the inside diameter of the PVC pipes. Use a hand router to shave excess material (Figure 2.2b).

iii. Drill a 3.8 cm hole in the approximate center of the PVC baseplate.

3. Install a fiberglass wick for leachate collection. (Note: the material for the wick must be chosen with intended purpose of leaching in mind. For example, fiberglass wicks must be used when studying nitrogen and phosphorus to avoid chemical interference during the leaching process.)
   i. Cut a 3.8 cm diameter fiberglass wick to 30 cm in length.
   ii. Slip the wick through the drilled hole in the PVC baseplate, leaving roughly 15 cm on either side of the plate (Figure 2.3a).
   iii. On the segment of the wick that will be in the interior of the column (the side of the baseplate that will be touching the soil column bottom), cut away the plastic netting holding the wick together down to the base. Cut away excess plastic netting from the interior segment of the wick and discard.
   iv. Pull apart individual strands of the wick on the interior side of the baseplate and lay them evenly around the circular baseplate.
   v. Glue individual strands to the interior of the baseplate using all-purpose adhesive (Figure 2.3a). Allow the adhesive to dry for 24-hrs.

2. Setting up the soil column drill machine

1. Become familiar with the components of the soil column drill machine (Figure 2.4).

2. Remove the metal plate for the bottom of the soil column drill machine. Set the plate aside where it will not be run over by the tractor or other farm equipment.
3. Attach the soil column drill machine to a tractor with a 3-point hitch.
4. Bring the lifting mechanism to the ground. Using the four drill pin locks, detach the drill cylinder from the machine.
5. Raise the lifting mechanism, leaving the drill cylinder standing upright on the ground. Continue to raise the lifting mechanism until it is at least 0.5 m above the drill cylinder.
6. Slip a PVC pipe from Step 1.1, without a baseplate, onto the lifting mechanism. Align the marked guide hole in the PVC pipe to the marked PVC pin locks. Slide the pins, attaching the PVC pipe to the machine.
7. Ensuring that the PVC pipe is aligned with the drill cylinder on the ground, lower the lifting mechanism into the drill cylinder until the drill pin locks are aligned with the holes of the drill. If necessary, use a rubber mallet to align drill pin locks with the holes on the drill cylinder.
8. Raise the lifting mechanism so that drill cylinder and PVC are no longer touching the ground.
9. Reattach the metal plate of the soil column drill machine. Ensure that the plate is secure in its metal holds.
10. Drive the tractor and soil column drill machine to the collection site
.

3. Collecting a soil column

1. Remove the metal plate for the bottom of the soil column drill machine. Set aside where it will not be run over by the tractor or other farm equipment.
2. Locate a flat parcel of land within the area of interest for drilling.
3. Use tractor hydraulics to lower the soil column drill machine to the ground. Continue to adjust the machine's positioning with tractor hydraulics to ensure the machine is vertical and level with the ground on the sample site.
4. Remove surface debris, vegetation, and/or rocks from the collection area.
5. Using the controls on the drill machine, spin the soil column drill clockwise at a consistent speed and begin lowering the lifting mechanism to the ground. Maintain a consistent speed while lowering the drill into the ground.
6. Continue the downward movement of the spinning drill into the soil column. Drill several centimeters deeper than the desired depth to ensure there is enough soil within the column for the experiment. For example, for a 30 cm soil column, drill roughly 45 cm deep.
7. Prior to lifting the soil column from the ground, break the soil column bottom from the soil for extraction. Locate the lever atop the lifting mechanism. Slowly rotate the drill counterclockwise ½ turn until the lever catches the metal divot attached to the soil column mechanism.

8. While holding the lever up, slowly spin the soil column clockwise for a quarter turn.
9. Leaving the machine in its current place in the ground, detach the drill cylinder from the lifting mechanism by unlocking the four drill pin locks.
10. Slowly raise the lifting mechanism out of the ground leaving the drill cylinder in the hole and only removing the PVC pipe filled with soil.
11. As it is pulled out of the ground and above the drill cylinder, have another person check the bottom of the PVC pipe to ensure that soil has been extracted and has not fallen out of the PVC pipe back into the hole.
12. Once the PVC pipe has been raised at least 30-cm above the top of the drill cylinder, slide a wooden board under the PVC pipe. Slowly lower the lifting mechanism until the PVC pipe is atop the wooden board.
13. While having a person holding the PVC pipe with soil in place, unlock the PVC pin locks from the PVC pipe.
14. Have another person use ratchet straps to hold the wooden board firmly in place. This will prevent the loss and/or destruction of the soil column during transport.
15. Remove the intact column from the area. If collecting more columns, lock the next PVC pipe into the machine following steps 2.4 – 2.7.
16. Raise the lifting mechanism with the attached PVC and drill cylinder from the ground. Once removed, brush away excess soil from the exterior and interior of the drill.

17. Using tractor hydraulics, lift the machine from the ground and drive forward to the next site.
18. Fill in hole from the previous column extraction with excess soil.
19. Repeat steps 3.2 – 3.18 if doing subsequent soil column extractions.

4. Column assembly

1. Assemble the column in an interior workspace in proximity to where the study will take place. Each column weighs approximately 45 kg, and limited movement is desired.
2. Measure the depth of soil within the column based on the distances of the top and bottom of the pipe respective to soil surfaces. Determine how much excess soil you have which needs to be removed from the bottom of the column.
3. Insert a piece of cardboard cut to fit the interior of the column. Insert the carboard into the top of the soil column ensuring it is snug against the soil to prevent disturbing the surface as you tip the column on its side.
4. Tip the soil column onto its side. Remove the ratchet strap holding the wooden board to the bottom of the soil column. Remove the wooden board strapped to the bottom from the area.
5. Using a small trowel, gently chip away excess soil until the column has its desired amount of soil, taking care not to smear the soil, which can interfere with the leaching process.

6. Take baseplate fitted with a wick from Step 1.3 and push it into the interior of the PVC pipe from the bottom of the column so the glued wick is touching the soil.
7. Gently press the baseplate into the column until it is flush with the bottom of the soil.
8. Apply a thick layer of acrylic caulk around the circumference of the baseplate to seal the gaps between the baseplate and soil column wall. Use a finger to spread the caulk evenly (Figure 2.3b).
9. Allow the caulk to dry overnight.
10. Once dry, stand the soil column upright.
11. Set up two 40 cm × 20 cm × 20 cm cinder blocks on the floor roughly 25 cm apart.
12. Place the constructed soil column on top the two cinder blocks so that the wick hanging from the baseplate hangs in the middle (Figure 2.5).
13. Warm several 4 oz tubes of petroleum jelly in water atop an electric hotplate. Once liquified, squeeze roughly 4 ounces of petroleum jelly (one tube) per column between the soil and column wall. Allow petroleum jelly to slide down the column wall. This will prevent lateral flow of water during the leaching experiment.
14. Allow petroleum jelly to resolidify (Figure 2.6).

15. Place a 4 L pail roughly 15 cm in height on the floor below the soil column between the two cinder blocks. Ensure the wick is hanging within the pail so that leachate is collected.
16. Cut a 35 cm × 35 cm square from a plastic painter's tarp. Cover the top of the column with a tarp cover to prevent evaporative losses during the experiment.

5. Irrigating intact soil columns

1. Bring the soil column to field capacity to ensure that they are all at a similar initial moisture content prior to the start of the experiment.
    i. Using deionized water, slowly and gently pour 1 L of water onto the soil surface of each column.
    ii. Allow water to absorb into the soil before pouring more water onto the columns.
    iii. Repeat these steps until drainage from the soil column bottom occurs.
2. After columns are brought to field capacity, simulate the 5 cm irrigation event (3.78 L of water) following the guidelines in step 5.1.i – 5.1.ii.
3. Allow soil columns to drain until water stops (anywhere between 7 - 12 hours depending on soil texture).
4. Once drainage stops, measure the volume of leachate from each column.
5. Repeat steps 5.2 - 5.4 weekly to simulate multiple irrigation events.

6. **Measuring drainage rate from soil columns**

    1. Place a scale underneath the container used for leachate collection.
    2. Set up a game camera on a tripod to monitor the weight of the leachate through time. In this instance, the camera took a photo every minute until drainage became less rapid and was switched to every 10 minutes until drainage stopped.
    3. Periodically monitor the fill of the leachate collection container to ensure that the scale is not over the scale's weight capacity. When the scale is near its weight capacity, document the current weight of the collection bucket and quickly empty leachate into a secondary container and place the bucket back underneath the column on the scale.
    4. Note: This component can be conducted in other ways, including a data logging scale. The important piece is to ensure that the weight of leachate is logged through time for the duration of drainage in each column.

2.4 Results

Cumulative leachate volume for the duration of the leaching study ranged from 8.25 L to 10.25 L of the 11.35 L of water applied and varied by soil type (Figure 2.7). The Silt L soil generally drained the greatest volume of water, while the Sandy L soil generally retained the most. Statistical analysis showed that soil type had a significant effect on the volume of water that was drained from the soil columns during the study ($P < 0.0001$). When cumulative leachate volumes were compared between replicates within individual soil types, however, no significant differences in leachate volumes were observed ($P > 0.05$).

The Sandy L and Silty Clay L soil columns demonstrated several differences in drainage patterns during the drainage rate test. Over the duration of the irrigation event, the Sandy L soil column had more rapid drainage and drained less water than the Silty Clay L soil column overall (Figure 2.8a). The Sandy L soil finished draining after 284 minutes and only leached 2,797 g of water, whereas the Silty Clay L soil stopped drainage after 428 minutes and leached 3,224 g of water. Drainage began more quickly in the Sandy L soil column, starting only 4 min after water application, as opposed to starting after 11 min in the Silty Clay L soil column (Figure 2.8b). The drainage rate in the Sandy L soil column plateaued after roughly 20 minutes following water application where the drainage rate plateaued after roughly 35 minutes in the Silty Clay L soil column (Figure 2.8b). The drainage rate for each soil column for the duration of the irrigation event was 9.85 g min $^{-1}$ and 7.53 g min $^{-1}$ for the Sandy L and Silty Clay L soils, respectively, and indicated that the Sandy L soil had a more rapid drainage rate for the entirety of the irrigation event.

Mean BD values from soil columns were all within the ideal soil bulk density range that is reported by the USDA-NRCS (Table 2.3). In each soil type, the BD in the bottom layer of the soil column (15 – 30 cm), had a slightly higher SBD than the top layer (0 – 15 cm). The Sandy L soil columns had the greatest mean BD, followed by the Silt L, Silty Clay L, and Clay L soil columns.

2.5 Discussion

Maintaining soil structure is essential when collecting soil columns for lab-based water and nutrient leaching studies. Here we present a method to collect large (0.3 m depth × 0.3 m diameter) intact soil columns for a laboratory-based leaching study. We evaluated the method's effect on soil structure by measuring key soil physical properties including soil bulk density and evaluated hydraulic flow patterns from columns from drainage volumes following irrigation.

Soil bulk density was used as an indicator of soil compaction during the soil column collection process. In all soil types from this study, average BD values were within the appropriate range of reported ideal BD values where compaction and reduced plant growth occur as described by the USDA-NRCS (USDA-NRCS, 2008), suggesting that soil was not significantly compacted during the drilling process or, alternatively, loosened by the drilling process. Average BD values from columns also mimicked variability reported by soil texture. Natural BD values are typically highest in sandy soils, and lowest in clay soils, with silty soils having intermediate BD values (MPCA, 2023). Results from this study reflected that pattern as the Sandy L, which had the highest proportion of sand, had the highest BD values, followed by Silt L and Silty Clay L which contained high proportions of silt, followed by the Clay L soils with a high proportion of clay (Tables 2.1 and 2.3).

Cumulative leachate volume for each soil type was also an important indicator that the drilling process did not significantly alter soil structure and that soil columns were representative of natural soils. As leaching is affected by soil physical properties such as water holding capacity and pore space, which vary by soil texture (Irmak, 2019; O'Geen, 2013), we would expect variation in cumulative leachate volume to occur across our soil types. Furthermore, the lack of significant differences in cumulative leachate volume among replicates within soil types suggests that the soil column drilling technique extracted soil columns with consistency and that soil columns were reproducible within soil type.

Our demonstration measuring drainage from the Sandy L and Silty Clay L soils found that drainage patterns and rates mimicked drainage patterns from soils in field conditions. Whereas the Sandy L soil is characterized by a high infiltration rate and excessive drainage, the Silty Clay L soil has less drainage and a slower infiltration rate according to the USDA Web Soil Survey (Table 2.1) (USDA-NRCS, 2007, 2019). This was evident in this demonstration as the Sandy L experienced more rapid drainage and drained more quickly overall than the Silty Clay L soil which took longer to begin drainage and slowly drained over a longer period (Figure 2.8a). For the duration of irrigation event, the Sandy L soils drained 2.32 g of leachate per minute more than the Silty Clay L soil column, supporting that drainage was quicker in the Sandy L column and reflective of drainage patterns that would be observed in field conditions (Table 2.2).

Large scale soil columns were collected from the field via drilling and had a low risk of soil profile disruption, thus reducing the possibility of altering water and nutrient flow. Representative results for this study support that this method had minimal influence on key soil physical properties that would affect soil hydraulic properties and that leaching behavior of soil columns was unaffected.

One potential limitation of this method involves acquiring the soil column drill machine. While this method is cost efficient and effective in collecting representative soil samples, the machine required may be difficult to source as it is a niche piece of equipment. Additionally, soil moisture content at the time of extraction is an important consideration when attempting soil column collection. Soils in dry conditions were more difficult to collect as they were more prone to slipping from the soil column drilling machine or falling apart during extraction. Soils in ideal field conditions will be moist enough to adhere to the sidewalls of the PVC pipe when being raised out of the ground at the same time maintaining the integrity of the whole profile. Sandy soils were especially sensitive to field conditions as they were more prone to crumbling during extraction, provided they were not at ideal moisture contents.

2.6 Tables

Table 2.1: *Soil physical properties of each soil type as reported by the USDA Web Soil Survey (WSS) (USDA-NRCS, 2019).*

Soil Type †	% clay	% silt	% sand	Hydraulic Group	Drainage Class
Sandy L	17	26	57	A – high infiltration rate	Somewhat excessively drained
Silt L	22.5	68	9.5	B – moderate infiltration rate	Well drained
Clay L	30	39	31	C/D – low infiltration rate	Moderately well drained
Silty Clay L	30	53	17	C/D – low infiltration rate	Moderately well drained

† *Estherville sandy loam (Sandy L), Waukegan silt loam (Silt L) soils, Nicollet clay loam (Clay L), and Floam-Aazdahl-Hamerly complex (Silty Clay L) soils.*

Table 2.2: *Average drainage rates over the duration of the irrigation event in Estherville sandy loam (Sandy L) and Floam-Aazdahl-Hamerly complex (Silty Clay L) soil columns.*

Soil Type	Average Drainage Rate (g min^{-1})
Sandy L	9.85
Silty Clay L	7.53

Table 2.3: *Comparison between mean soil bulk density measured in soil columns and ideal soil bulk density values that promote plant growth reported by the United States Department of Agriculture – Natural Resources Conservation Service (NRCS) (USDA-NRCS, 2008).*

Soil Type †	Soil Layer	Average Soil Bulk Density (g cm^{-3})	Ideal Soil Bulk Density (g cm^{-3})
Sandy L	0 – 15 cm	1.35	< 1.60
	15 – 30 cm	1.40	
Silt L	0 – 15 cm	1.18	< 1.40
	15 – 30 cm	1.26	
Clay L	0 – 15 cm	1.09	<1.10
	15 – 30 cm	1.12	
Silty Clay L	0 – 15 cm	1.18	< 1.40
	15 – 30 cm	1.23	

† *Estherville sandy loam (Sandy L), Waukegan silt loam (Silt L) soils, Nicollet clay loam (Clay L), and Floam-Aazdahl-Hamerly complex (Silty Clay L) soils.*

2.7 Figures

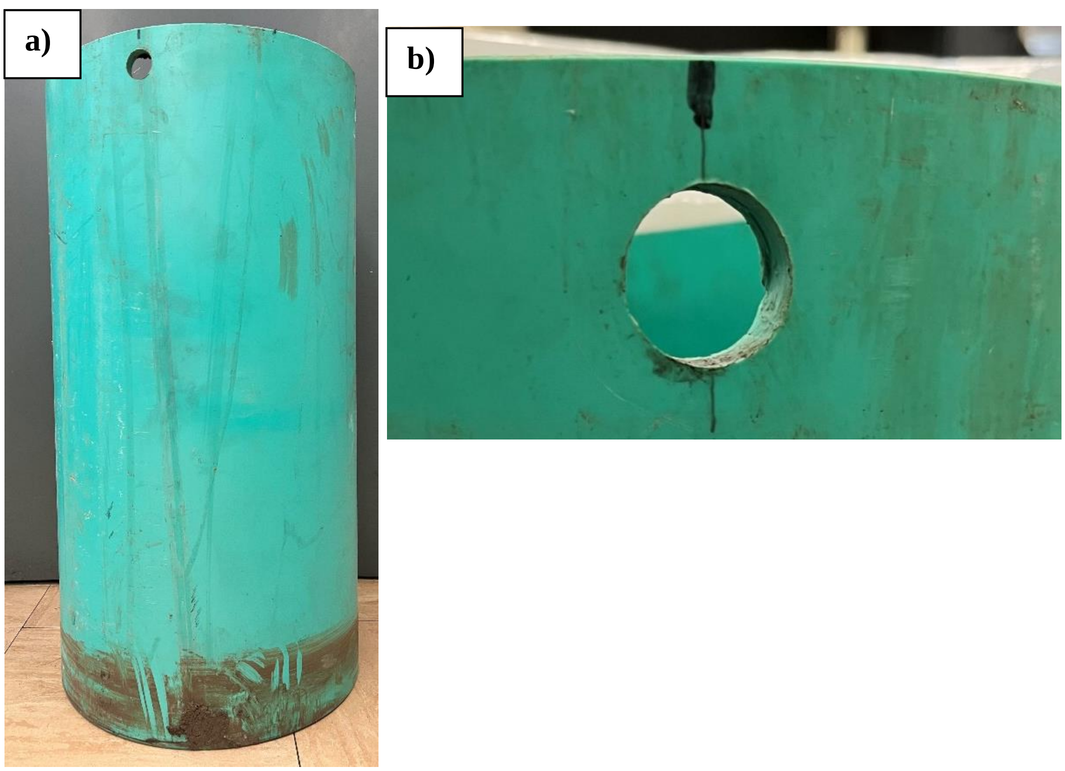

Figure 2.1: a) *Soil column casing cut to 60 cm from PVC pipe.* ***b)*** *3.85 cm hole drilled near the top of the PVC pipe to lock onto the soil column drill apparatus.*

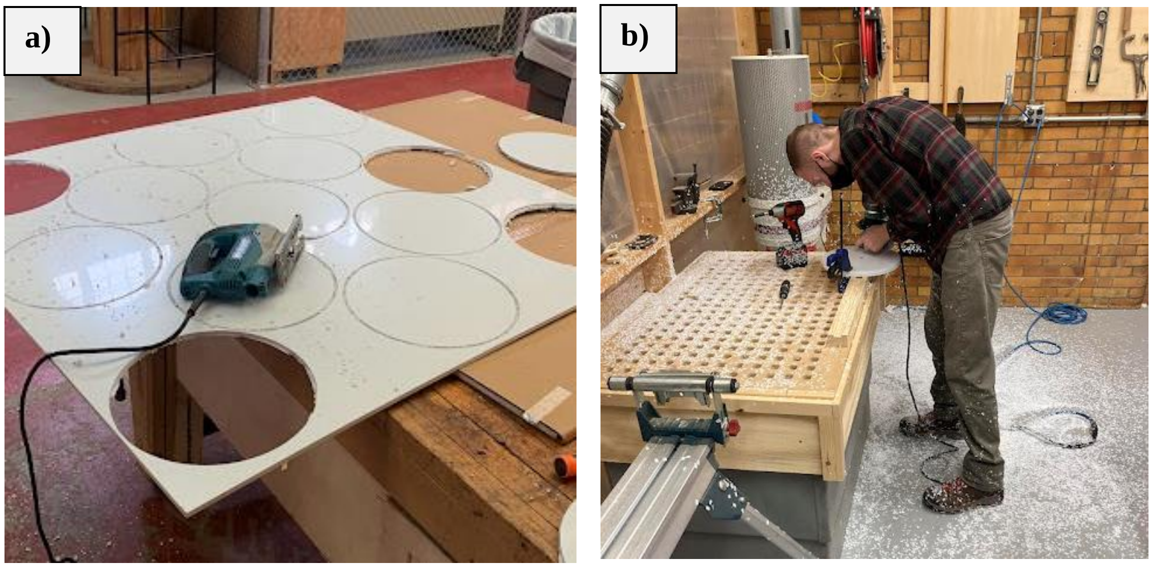

Figure 2.2: a) *Cutting soil column baseplates from PVC board using a jigsaw.* ***b)*** *Shaping the soil column baseplate with a hand router.*

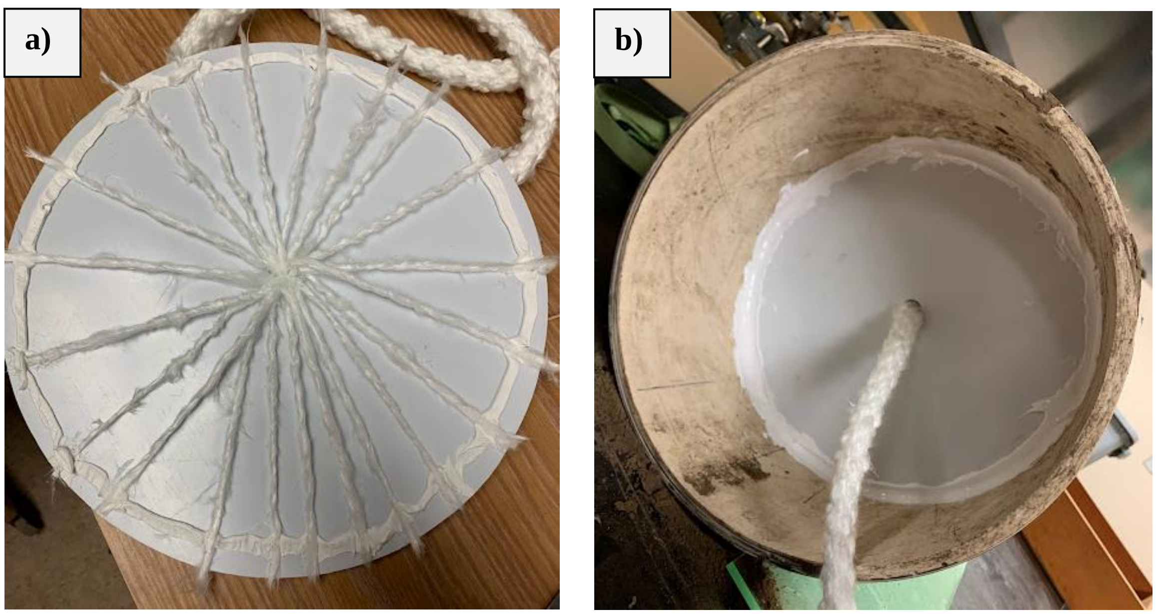

Figure 2.3: a) *Top of soil column baseplate with fiberglass wick laid out and glued to surface prior to sealing in soil column.* ***b)*** *Bottom of soil baseplate with wick hanging from soil column after sealing baseplate to the walls with caulk.*

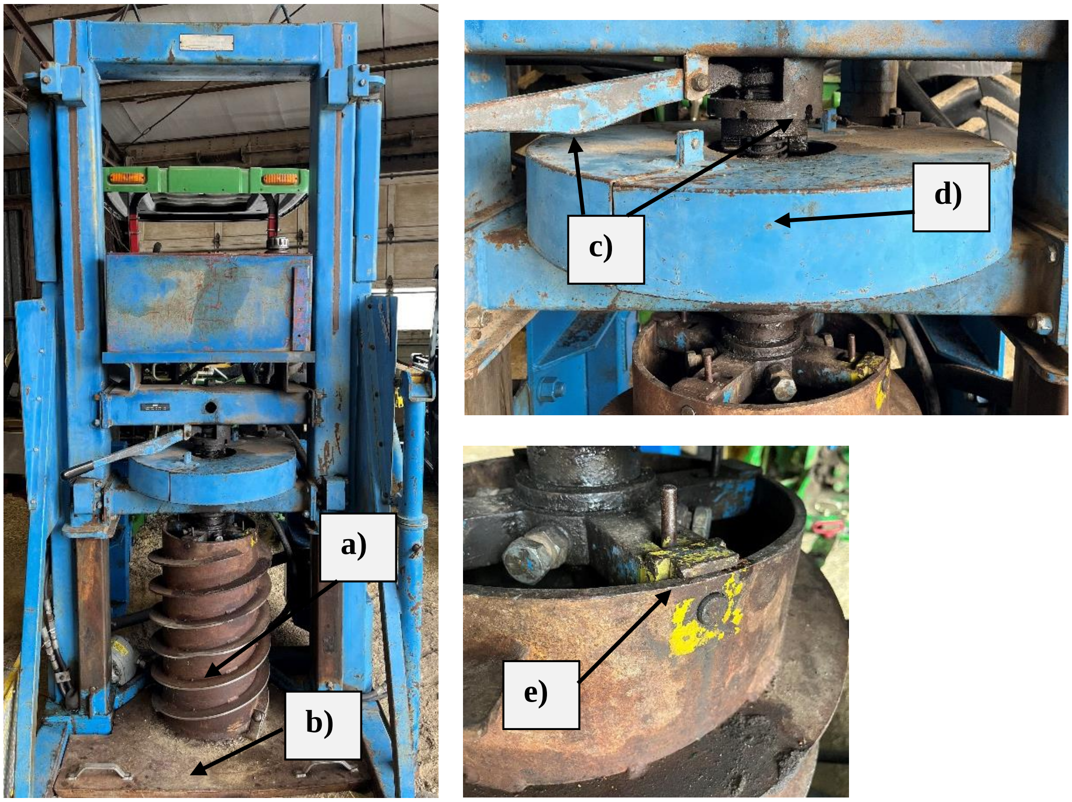

Figure 2.4: *Major components of the soil column drilling machine:* ***a)*** *drill cylinder;* ***b)*** *metal baseplate;* ***c)*** *lever for breaking soil column and metal divot;* ***d)*** *lifting mechanism;* ***e)*** *drill lock pins.*

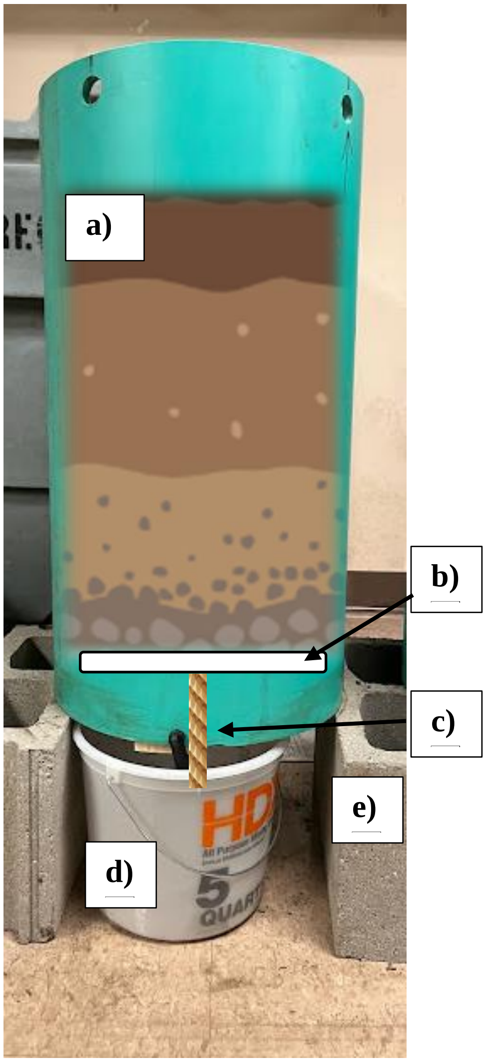

Figure 2.5: *Schematic of the interior of a fully constructed soil column lysimeter* ***a)*** *intact soil column within PVC;* ***b)*** *PVC baseplate securing the soil column within the PVC pipe;* ***c)*** *3.8 cm diameter fiberglass wick;* ***d)*** *leachate collection container;* ***e)*** *cinder block stands.*

Figure 2.6: *Liquified petroleum jelly surface applied around the circumference of the soil column to prevent sidewall flow of water during irrigation events.*

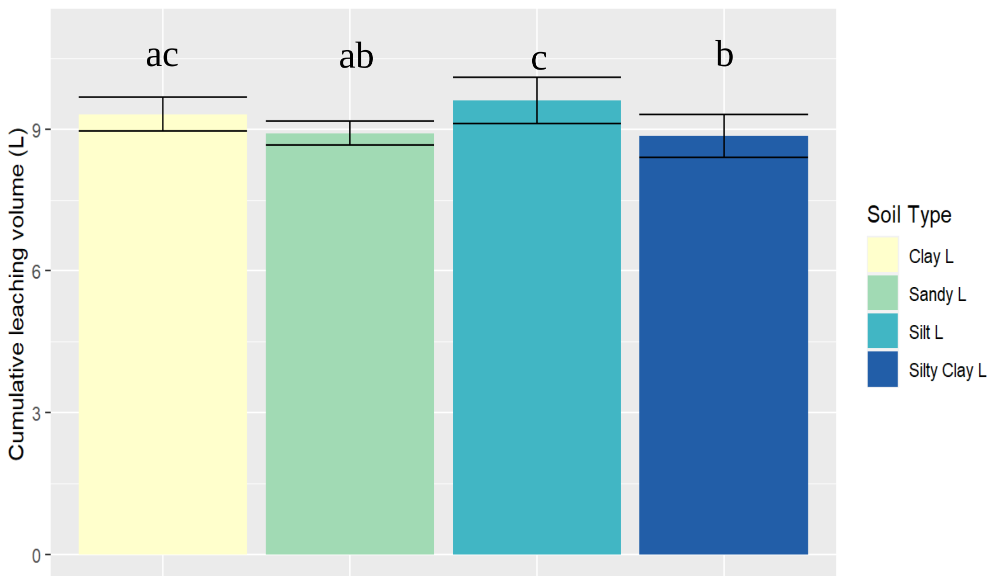

Figure 2.7: *Average* **c***umulative leachate volume (liters) for each soil type for the duration of the leaching study. Letters indicate significant differences in cumulative leachate volume (P < 0.05). Error bars represent standard error of the mean.[Estherville sandy loam (Sandy L), Floam-Aazdahl-Hamerly complex (Silty Clay L), Nicollet clay loam (Clay L), and Waukegan silt loam (Silt L) soils].*

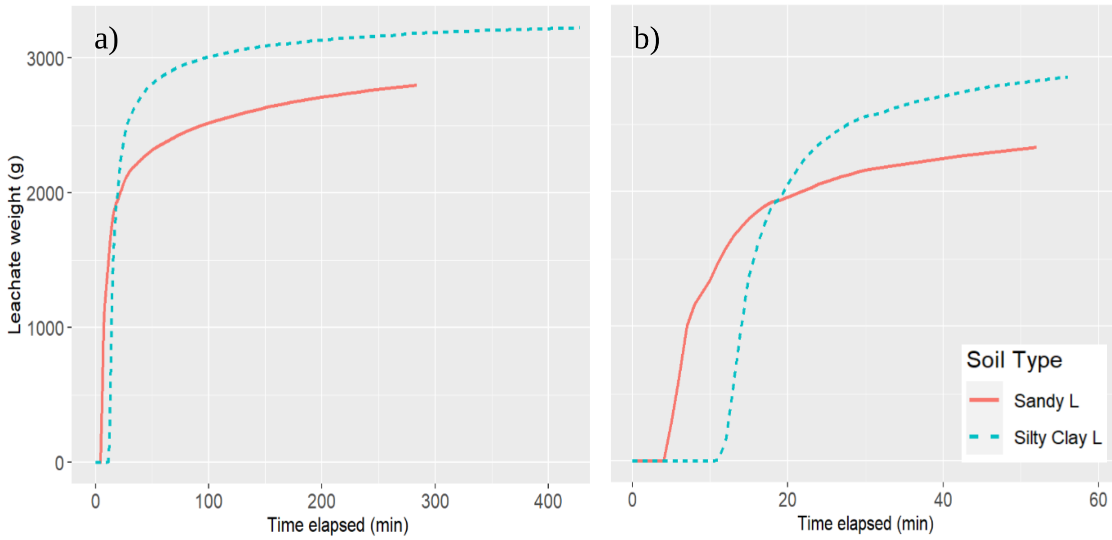

Figure 2.8: *Leachate weight (g) documented every minute from one replicate from the Estherville sandy loam (Sandy L) and Floam-Aazdahl-Hamerly complex (Silty Clay L) soils for* ***a)*** *the entire duration of the irrigation event and* ***b)*** *the initial 60 minutes of the irrigation event.*

Chapter 3

Chloride Leaching Potential Following Land Application of Manure to Minnesota Soils

3.1 Abstract

Chloride concentration in the environment is a growing concern for ground and surface water quality in many regions in the northern United States. While the land application of manure is an important strategy for agricultural producers to fertilize croplands, it could be a source of chloride, and it is unclear how manure and soil characteristics interact to affect chloride leaching into groundwater, which makes understanding manure's role in groundwater contamination difficult. We conducted a series of large intact column (0.3 m depth × 0.3 m diameter) leaching studies to evaluate manure and soil type interactions on chloride leaching potential after manure application. Four soil types (sandy loam, silt loam, silty clay loam, and clay loam) around Minnesota were chosen for this study. Columns were surface applied with four treatments (swine manure, turkey litter, KCl, or control) before carrying out three 5-cm irrigation events on day 4, 11, and 18 of the study following treatment application. We measured chloride concentration of leachate after each irrigation event, the percentage of chloride leached relative to amount of chloride applied, and the percent change in soil chloride storage from the beginning to the end of the experiment. Our results showed that surface treatment and soil type interacted to affect chloride concentration in leachate, and that chloride concentrations varied through time. While soil type did not affect the percentage of chloride lost to groundwater, surface treatment type did, with swine manure leaching 87% of chloride applied compared to turkey litter and KCl treatment which leached 57% and 49% of chloride applied respectively. These results are likely due to swine manure's low dry matter content which allowed it to be flushed out of the soil more rapidly compared to other

treatments. Before data can be used at a field scale, future studies should evaluate chloride leaching potential at a longer timescale with additional irrigation events, as well as from a wider variety of manure types and application methods.

3.2 Introduction

Excessive chloride loading into the environment presents several issues for ecosystem services, water quality, and human health (Dugan et al., 2017). In many parts of the northern United States, chloride concentrations in ground and surface waters have been rapidly increasing since the 1960s, and are projected to continue to rise (Kelly et al., 2012; USGS, 2014). Quantifying chloride inputs into the environment is important to appropriately outline reduction strategies and implement chloride focused best management practices (BMPs) (Azad et al., 2022). Regional chloride management plans attempt to determine contributions of chloride into the environment and assess environmental impacts of chloride pollution. The Minnesota Statewide Chloride Management Plan (SCMP) was published by the Minnesota Pollution Control Agency (MPCA) in 2020 and is an example of a management plan which cites potential sources of chloride contamination in ground and surface waters in Minnesota, lists recommendations to reduce water pollution, and measures long-term chloride trends (MPCA, 2020b). The SCMP outlines chloride inputs from livestock waste, both from open feedlot runoff and land applied manure as a fertilizer source, to be a minute source of chloride into the environment, accounting for roughly 6% of the total load (MPCA, 2020b; Overbo et al., 2021). However, many questions persist as to how much chloride is in land applied manure, and how chloride moves through the soil into groundwater.

Although the contribution of chloride from manure is thought to be low, the estimate outlined by the SCMP may be misrepresenting actual chloride loading from manure as it generalizes manure inputs from both open feedlot runoff and land applied manure. Unlike feedlot runoff, land applied manure is considered a non-point source of chloride and is more difficult to accurately quantify than point source pollution (García et al., 2013). Additionally, data used in the SCMP was compiled from daily chloride excretion rates measured from a variety of livestock species, however, much of this data is outdated and has not been updated since 2003 and does not account for manure storage in its calculations (ASAE, 2003; Sherwood, 1989). As manure storage systems are known to impact nutrient compositions in manure (Harrison & Smith, 2004), and standard manure nutrient concentration values have changed over time compared to established standard values created by the Midwest Plan Service (MWPS) in 2004 (Bohl Bormann et al., 2022), data used in the SCMP estimate may not be accurately representing values of chloride applied to fields from manure.

When applied to soil through manure or fertilizer application, nutrients are carried through the soil via percolating water through a process called leaching (Lehmann & Schroth, 2002). Excess nutrients unable to be utilized by crops are leached below the crop root zone and can be a risk of contaminating groundwater aquifers (Nieder & Benbi, 2008). The leaching potential, or likelihood a pollutant applied to soil is introduced into groundwater, of chloride is variable by soil type as physiochemical properties, including pore space, water holding capacity, permeability, pH, and cation exchange capacity, affect water and nutrient flow through soil (Huddleston, 1996). Climactic conditions, especially precipitation, also influence water flow through soil affecting the quantity of nutrient leaching occurring. The frequency and severity of nutrient leaching is greater with increased rainfall as higher soil moisture contents allow for increased water movement through soil (Bowles et al., 2018; Martinez-Feria et al., 2019). Since research on leaching potential is primarily focused on nitrate, there is little research on chloride, specifically from manure, which makes it difficult to predict how manure-based chloride leaching patterns vary.

It remains unclear how the type of manure applied and soil characteristics interact to affect chloride movement through soil and into groundwater. The objective of this study was to evaluate chloride leaching potential from different types of manure applied to different soil types found in Minnesota. This research aims to aid efforts in developing a chloride-based fertilizer mass balance and understand the impact that non-point source chloride from land applied manure has on groundwater quality.

3.3 Methods

3.3.1 Site Descriptions

Intact soil columns were collected from recently harvested soybean (*Glycine max* L.) fields. Columns were sampled from a clay loam, silt loam, sandy loam, and a silty clay loam soil with a high pH. Silt loam soil columns were collected at the Rosemount Research and Outreach Center in Rosemount, MN (44°42'44.5"N, -93°05'24.2"W) in November of 2021. Soil at this site was a Waukegan silt loam (Silt L) (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludolls). The crop was soybean in 2020 and 2021, corn in 2019, and a corn-soybean rotation prior to 2019. Fields received 222 kg K ha

$^{-1}$ in the form of KCl, 222 kg P ha $^{-1}$ in the form of P_2O_5, and anhydrous ammonia in the spring of 2019. Prior to 2019, fertilizer was applied every other year on corn years. Clay loam soil columns were collected at the Southern Research and Outreach Center in Waseca, MN (44°03'40.4"N, -93°31'27.3"W) in early December of 2021. The soil at this site was a Nicollet clay loam (Clay L) (Fine-loamy, mixed, superactive, mesic Aquic Hapludolls) and was in corn-soybean rotation for the 10 years prior to sampling. In even numbered years, this soil was used for nitrogen (N) research studies with varying rates of N additions to the field. Sandy loam clay soil columns were collected from at the Rosemount Research and Outreach Center in Rosemount, MN (44° 41' 44.5"N, -93° 3' 22.78"W) in November 2022. The soil at this site was an Estherville sandy loam (Sandy L) (Sandy, mixed, mesic Typic Hapludolls). This field has been in a long-term corn-soybean rotation for the past 10 years. Corn received 144 kg anhydrous N ha $^{-1}$, 222 kg K ha $^{-1}$ in the form of KCl, 222 kg P ha $^{-1}$ in the form of P_2O_5, and 84 kg S ha $^{-1}$ via ammonium sulfate prior to planting. High pH soil columns were collected at the West Central Research and Outreach Center in Morris, MN (45° 35' 56.9"N, -95° 54' 40.69"W) in late November 2022. Soil at this site was a Floam-Aazdahl-Hamerly complex (Silty Clay L) (Fine-loamy, mixed, superactive, frigid Aquic Hapludolls). This field had been in a corn-corn-soybean rotation for the past 10 years. Fields received 178 kg N ha $^{-1}$, 55 kg P ha $^{-1}$, and 17 kg S ha $^{-1}$ in 2020 and 2021 and were not fertilized in 2019 or 2022.

3.3.2 Soil Column Collection and Construction

The method and materials for soil column construction and collection are presented in more detail in Chapter 2 of this thesis and are briefly summarized here. Soil columns were collected using an intact column sampling machine with help from the United States Department of Agriculture (USDA). The intact column sampling machine was equipped with a large metal drill and fitted with a polyvinyl chloride (PVC) pipe 30 cm in diameter and 60 cm in length. The machine was attached to tractor hydraulics and controlled by research staff to drill into the soil profile. Columns were drilled to a depth of roughly 45 cm in depth and extracted from the ground. Columns that crumbled, fell apart, or showed disruption to the soil profile in any way were discarded. Extracted columns were brought to the laboratory for the leaching experiment.

Soil columns were encased in the PVC pipe for the duration of the experiment. Excess soil from extraction was chiseled away from the bottom of the column until soil within the PVC column was 30 cm deep. Soil column bottoms were fitted with PVC baseplates against the bottom of the soil profile within the PVC tube. PVC baseplates were equipped with 3.8 cm diameter fiberglass wick to assist with drainage and sealed with silicone caulk around the perimeter of the PVC disk. Liquified petroleum jelly was applied from the top of the soil profile between the column wall and the soil to prevent lateral flow of water during the experiment. Fiberglass wicks drained into 4-L plastic buckets for leachate collection. Both columns and leachate collection containers were covered with plastic tarp to prevent evaporation from soil columns.

3.3.3 Manure Collection and Analysis

Swine manure (SM) and turkey litter (TL) samples were collected from producers around Minnesota in November 2021. A total of 90 L of SM was collected from deep pit storage from a farm located near Le Sueur, MN. Roughly 12 L of TL was collected from stockpiled litter storage from a farm located in Northfield, MN. For each manure type, multiple grab samples were collected, composited in a large container, and brought back to the University of Minnesota – Twin Cities campus and stored at 15 ºC until the start of the experiment. Prior to column application each year, 100-mL subsamples of both the SM and TL were sent to Agvise Laboratories Inc., for analysis. Dry matter content in manures were determined by oven drying manure samples for 24 hours at 110 ºC (Hoskins et al., 2003). Chloride concentration in manure samples was measured by potentiometric analysis (Table 3.3) (Wilson et al., 2022).

3.3.4 Experimental Design

To examine the movement of manure-based chloride through soil, this experiment was conducted as a completely randomized design with four soil types, four nutrient treatments, and three replications for each soil type and nutrient treatment combination (n=48). Columns were then exposed to three irrigation events simulating 5-cm rainfall during each event for a total of 15 cm of simulated rainfall for the entire study. Clay L and Silt L soils were used for the first year of leaching studies, while Sandy L and Silty Clay L soils were used in the following year. Leachate samples following each irrigation event were then analyzed for chloride concentration. Soil samples before and after were also analyzed for chloride content.

Nutrient treatments were broadcast applied onto the top of the soil columns. Nutrient treatments included TL, SM, or synthetic KCl fertilizer (KCl), while columns with no nutrient application served as controls. Application rates of manure and fertilizer were calculated following the University of Minnesota Extension guidelines (Kaiser et al., 2022;

Wilson, 2022). To represent standard agricultural practices in the region, manure treatments were applied on a nitrogen-based application rate, while the KCl treatment was applied on a potassium-based application rate (Table 3.1). The same two manures were used for each study with the second-year manure being stored in freezers at -15 ºC between the first and second year.

Manure and fertilizer treatments were broadcast applied the day following bringing the columns to field capacity. The treatments were allowed to sit on the soil for three days before simulating the first irrigation event. Irrigation events were simulated on day 4, 11, and 18 of the experiment.

3.3.5 Bulk soil collection and analysis

Soil plugs were collected by hand with a 2-cm diameter soil probe within 5-cm of the soil column extraction locations to determine baseline soil nutrient concentrations of soil columns at time of collection. Six soil plugs were taken in bulk at two depths and composited separately; the first depth comprised the plow layer at a depth of 0 – 15 cm and the other was sampled from the same sampling locations at a depth of 15 – 30 cm. Following the final irrigation event, six soil plugs were collected within each soil column for post-experiment nutrient concentration comparisons. Six soil plugs were extracted from each column at the same two depths as baseline soil plugs taken from the fields. Samples were then composited and processed in the lab. After soil plugs were collected, columns were sampled for soil bulk density (BD) with a soil column sampler at the same two depths.

Prior to being sent for analysis, composited soil plug samples were oven dried for 48 hours at 35 ºC. Dried composited soil samples were sent to the Research and Analytical

Laboratory at the University of Minnesota – Twin Cities for nutrient analysis (Table 3.2). Soil samples were crushed and sieved through a 2-mm mesh and then analyzed for chloride concentration on a Lachat QuikChem 8500 Flow Injection Analyzer by the mercury (II) thiocyanate method (Gelderman et al., 1998; USEPA, 1979).

3.3.6 Leachate Collection and Analysis

Prior to broadcast applying manure and fertilizer, each column was brought to field water capacity on day 1 of the experiment by applying 4 L of deionized water to each column until drainage occurred to ensure that columns were at a similar initial water content. Once drainage stopped, the volume of leachate in collection buckets was measured, thoroughly mixed, and 100 mL was sampled for baseline leachate analysis. Another 3.78 L of deionized water was applied to each column at each irrigation event interval on days 4, 11, and 18. Once drainage stopped, leachate volumes were measured, water was thoroughly mixed, and another 100 mL of leachate was collected. Leachate samples were then vacuum filtered through a 0.45-μm filter paper and stored in a freezer at -15 ºC until being sent to the Research and Analytical Laboratory at the University of Minnesota – Twin Cities for analysis. Leachate samples were analyzed for chloride concentration using the flow injection colorimetry analysis from the Quikchem 10-117-07-1-H method on a Thermo Fisher Scientific Integrion Ion Chromatograph (Thermo Fisher Scientific, 2001).

3.3.7 Calculations and Statistical Analyses

Total chloride inputs (g) from each treatment were derived by multiplying the chloride concentration by the total amount of treatment applied which was determined from the application rate (Table 3.4).

The chloride load leached (g) per irrigation event was calculated by multiplying chloride concentration (mg L^{-1}) by the leachate by volume of water leached (L). Every chloride load for each individual column was added together to calculate cumulative chloride load per column for the duration of the experiment. The average cumulative chloride leached from control columns of each soil type was subtracted from the cumulative chloride leached for each respective soil type to account for chloride already present prior to treatment application which would naturally be flushed from the soil. Then, cumulative chloride leached, without the control values, was divided by the total chloride inputs from each treatment application to determine the percentage of chloride leached from the soil. This metric was used to compare chloride losses by treatment and soil type.

The chloride concentration following each irrigation event was used to determine how the interaction between treatment application, soil type, and time since application affected chloride leaching potential through time.

The change in chloride storage (g) in the soil following the completion of the experiment was found by subtracting the initial chloride load in soil at the beginning of the experiment from the final chloride load in soil following the completion of the experiment. The change in chloride storage was then divided by the total chloride inputs to determine the percent change of chloride concentration in the soil.

The total chloride inputs minus the cumulative chloride losses (without subtracting the loss from controls) in leachate was plotted against the change in soil chloride storage. A regression line was plotted against the two variables and was used to demonstrate the mass balance of chloride and determine where imbalances occurred.

Data from this study were analyzed using The R Project for Statistical Computing (R Core Team, 2021). The effect of the soil type and treatment interaction on the percentage of chloride leached and the percent change in soil chloride were both analyzed using a Two-Way Analysis of Variance (ANOVA). The effect of the interaction between soil type, treatment, and days since application on chloride concentration in leachate were analyzed using a Three-Way Repeated Measures ANOVA with days used as the repeated measure using a compound symmetry model. Data for each test was determined to be normal using a Shapiro-Wilk Test following logarithmic transformation.

3.4 Results

Leachate from soil columns varied in chloride concentration (mg L^{-1}) through the duration of the study (Figure 3.1). Statistical analysis showed that the three-way interaction between soil type, treatment, and days since treatment application had a significant effect on chloride concentration in leachate ($P < 0.05$). Generally, SM produced the highest chloride concentration in leachate for each soil type at each sampling date following application, which was followed by the KCl treatment in Clay L soils and the TL treatment in the Sandy L and Silty Clay L soils which were statistically similar to each other ($P < 0.05$). Control soils always had the lowest chloride concentration in leachate from each soil type. The SM and KCl in Clay L soils, SM in the

Silt L soils, and TL and KCl soils in the Silty Clay L soils followed similar patterns where chloride concentrations in leachate were highest following the second irrigation event on Day 4 and gradually decreased in concentration until the end of the study on day 18. Alternatively, leachate from the SM, TL, and KCl treatments in Sandy L soils and the KCl treatment in Silt L soil gradually increased in chloride concentration in leachate from the beginning to the end of the study.

The interaction between soil type and treatment did not have a significant effect on cumulative chloride losses (with respect to applied chloride; Fig. 3.2) which was lost to leachate following irrigation ($P > 0.05$); however, soil type ($P < 0.01$) and treatment ($P < 0.0001$) were both found to have a significant effect individually. While not statistically different than the Clay L and Silty L soils, the Sandy L soils showed the most variability compared to the other soil types, where 32% to 109% of chloride applied was lost in leachate (Figure 3.2a). Silt L soils, however, had the lowest percentage of chloride lost following irrigation events and had the least variability. Soil columns with the SM treatment leached the highest percentage of chloride, while the TL and KCl treatments did not leach as high of a percentage and did not show significant differences between each other (Figure 3.2b).

The interaction between soil type and treatment had a significant effect on the percent change in soil chloride storage – the change in soil chloride content (g) with respect to total chloride inputs (g) – in the columns ($P < 0.01$) (Figure 3.3). The greatest percent change in soil chloride storage occurred in the Sandy L and Silty Clay L soils applied with the SM treatment where storage of soil chloride increased by values as high as 327% and 591% respectively. This result (and the percentage leached in the previous paragraph), however, may be influenced by questionable manure nutrient analysis results from the second year's SM nutrient analysis. The Year 2 manure sample analysis indicated higher solids and lower chloride content than Year 1; if the chloride concentration of the manure was actually higher than analyzed in Year 2, the difference between SM and other nutrient types would likely be lessened. The interactions shown in the other treatments are reflected by each soil type retaining variable amounts of chloride relative to their surface treatment, which are unaffected by the Year 2 SM data. If the SM × Sandy and SM × Silty Clay L results are ignored, the surface treatment appears to produce consistent changes in soil chloride storage for the different soil types, with Silt L retaining the most chloride.

The regression evaluating the chloride mass balance within columns by comparing the relationship between total chloride inputs minus cumulative chloride losses in leachate against the final soil chloride content minus the initial soil chloride content showed a weak relationship when all the data was included ($R^2 = 0.09$) (Figure 3.4a). However, this was determined to be largely driven by outliers from SM treated columns from the Sandy L and Silty Clay L soils. The removal of these outliers (n = 6) demonstrated a significant improvement in the relationship between the two elements of the mass balance ($R^2 = 0.57$) (Figure 3.4b).

3.5 Discussion

Each soil type and treatment combination had distinctive chloride leaching patterns throughout the duration of the study which indicates that chloride leaching potential is highly variable and dependent upon several factors including manure/fertilizer and soil characteristics. Chloride leaching potential was typically greatest in the SM treatments compared to the TL and KCl treatments. Manure characteristics, such as low dry matter % (DM) and chloride content, are potential drivers which increased chloride leaching potential from SM manures.

Manures with lower DM content tend to be more mobile in soils and improper application or heavy rainfall after application can flush these manures and their nutrients deeper into the soil profile and into groundwater (Fulhage, 2018; Hoorman et al., 2009). The SM treatment had a low DM relative to the other treatments applied (Table 3.3). By observation, SM manure tended to quickly infiltrate into the soil profile when applied, regardless of soil type, compared to the TL and KCl treatments, which sat atop the soil surface for the duration of the study. It is likely that this allowed the manure-based chloride from the SM treatments to mix with irrigation water, and more quickly flush out of the soil profile compared to the other two treatments.

This behavior was evident in the trends of chloride concentration in leachate through time (Figure 3.1). In Clay L and Silt L soils from the first year of the study, highly mobile chloride from the SM treatment was likely flushed out during the first irrigation event, with subsequent irrigations events flushing out less manure-based chloride. This is reflected by the large spike in chloride concentration of leachate on day 4, and the gradual decrease in chloride concentration of leachate in following irrigation events. The TL and KCl treatments on Clay L and Silt L soils showed a consistent concentration of chloride in leachate through time. It is possible that since the manure sat atop the surface, the chloride was only able to dissolve into leachate during wetting events. The SM treatment, which infiltrated deep into the soil profile, was more easily carried out of the columns by irrigation water.

This behavior may be reflected in the amount of chloride leached relative to the amount of chloride applied as well. The chloride in the TL and KCl treatments was unable to rapidly move through the soil profile with irrigation water and was not rapidly leached, reducing the percentage lost (Figure 3.2). However, as this study was a short scale and did not fully represent the amount of precipitation/ irrigation which could occur during a field season, it is possible the TL and KCl treatments could leach greater amounts of chloride over time with added wetting events. Further research is needed to fully understand how much chloride would leach from manure with a high DM content over the entire course of a field season. It is possible the TL and KCl treatments could flush out greater amounts of chloride provided a longer study time and added irrigation events.

While the SM treatment leached a greater percentage of chloride overall, this may have been influenced by inaccurate estimations of chloride content in the second year of the study, which misrepresented the amount of chloride being applied to columns. This phenomenon is reflected in the evaluation of the mass balance for the study. A chloride mass balance states the total inputs minus the cumulative chloride losses for each column should be a one-to-one relationship with the calculated change in soil chloride derived from the final chloride content minus the initial chloride content of the soil column. While the first comparison showed a weak relationship between the inputs minus the outputs as the explanatory variable and the change in storage as the response variable (Figure 3.4a), removing the six outlier points of SM applied to Sandy L and Silty Clay L soils from the second year significantly improved the relationship between the two sides of the mass balance (Figure 3.4b). For the six outlier values, the calculated soil chloride content derived from the final minus initial soil chloride content was much higher than the chloride retention derived from total inputs minus the cumulative chloride losses in leachate. The manure analysis in Year 2 for SM, wherein the SM was applied to Sandy L and Silty Clay L soils, may explain the imbalance. The Sandy L and Silty Clay L soils retained well above 100% of chloride relative to what was applied (Figure 3.3), suggesting that the soils gained additional chloride aside from that applied as a treatment. We hypothesize that the imbalance in the six outlier samples was due to heterogenous nutrient content in manure. The hypothesis that the issue lies with the SM treatment in the second year of the study is supported by the outliers only representing SM treatments on Sandy L and Silty Clay L soils, which increased the chloride retained in soil relative to what was applied by upwards of 300% (Figure 3.2). Manure is highly variable and heterogenous in its chemistry and can be difficult to collect a representative sample, particularly for manures with low DM contents (Manitoba Agriculture, Food and Rural Initiatives, 2009).We believe that the sample sent for analysis directly prior to application had a significantly lower chloride content than that applied to soil columns.

Soil characteristics did not affect chloride leaching potential of manure and fertilizer treatments as originally expected. While the amount of chloride leached was generally similar across soil types, aside from Silt L soils, which leached a lower amount of chloride in the study timeframe, the speed at which chloride leached from columns showed differences which affect the risk of chloride leaching following treatment application. Sandy L soils, which would be expected to leach chloride most rapidly due to its high permeability and low water holding capacity (Huddleston, 1996), initially leached a lower amount of chloride from each treatment at the beginning of the study followed by a gradual increase in chloride concentration in leachate on columns from each treatment application. Clay L and Silt L soils, specifically those applied with the SM treatment, have a greater risk of leaching chloride immediately after application, followed by a decreased risk with each subsequent irrigation event. This suggests that the risk in the amount of chloride leached is generally similar across soil types, however, certain soil types may transport certain types of manure more rapidly than others.

This data has implications for manure management in Minnesota. This study suggests manures with low DM content are more likely to quickly leach chloride at higher concentrations, at least from the top 30-cm of the soil profile, following a rain event. While manures with high DM content and KCl fertilizer are at a lesser risk of rapid chloride leaching, they are at a greater risk of consistent chloride leaching with persistent irrigation or precipitation. However, while not evaluated in this study, manure-based chloride from these fertilizer types may be carried away in surface runoff if the manure is not properly incorporated into the soil (Jokela et al., 2016), and remain a water quality risk.

This study demonstrated the implications associated with sampling manure prior to land application following guidelines from regional land-grant universities. Currently, manure chloride is not well understood and varies in concentrations based on manure characteristics, especially DM content (Table 3.3), which makes chloride loading estimates difficult. Like with other nutrients, manure could be sampled for chloride annually for at least the first three to four years to understand baseline manure chloride values. Once baseline manure chloride values are understood, manure only needs to be sampled for chloride again every three years or when drastic changes in livestock diet occur as this can affect chloride excretion. For a more representative estimate of actual chloride applied at the time of field application, multiple manure samples should be taken from properly agitated manure storage systems prior to application, as well as directly from the applicator during application (Modderman, 2021). While chloride is not a limiting nutrient, and unlikely to be accounted for in manure application rates from producers, a general understanding of chloride content in manure at the time of application, as well as the change in soil chloride storage over the course of the growing season will be useful in calculating a rough estimate of chloride losses. Nutrient and water quality managers can utilize this data in a mass balance approach to get a better understanding of manure application's impact on groundwater contamination of chloride.

Future lab-scale research can address some remaining questions. While DM content seemed to be influential in chloride leaching potential, this study did not pick a wide variety of manures with differing DM contents as there was only high and low content DM manures. Future studies could conduct similar leaching studies targeting a wider range of DM contents from manure to determine to what extent DM content affects chloride leaching potential.

There remains a lack of reliable data available to assess chloride leaching at field scale. Studies which attempt to make a regional estimate of chloride losses into groundwater have utilized a mass balance approach to create a chloride budget. By having a general understanding of the amount of chloride in manure at application, and an estimate of how much manure is applied onto croplands onto the area of interest, a chloride budget can be made to determine the amount of chloride that could be leached into groundwater (Overbo et al., 2021).

This study also did not attempt to determine how chloride leaching potential is affected by manure application technique, and only focused on surface application. While primarily focused on nitrogen, application technique is an important consideration when concerned about nutrient losses as both surface application and soil incorporation affect nutrient movement through the soil and uptake by crops (University of Minnesota - Extension, 2021). For manures with low DM contents, for example, soil incorporation as opposed to surface application, has shown to reduce gaseous nitrogen emissions, but increase the leaching potential of nitrogen into groundwater (Smith & Chambers, 1993). Evidence suggests that increased nutrient leaching from incorporated low DM manures could be due to preferential flow paths created by injection machinery, but it is unclear if this is the sole driver of increased leaching (Dell et al., 2011). Alternatively, soil incorporation has shown to reduce leachate losses of phosphorus as opposed to surface application (Kleinman et al., 2009). There is little to no research available as to how manure application technique affects the chloride leaching potential, and future work should be done to determine how it would influence these results.

3.6 Conclusions

Our results indicate that chloride leaching from manure and soil type are both important considerations when accounting for chloride leaching following manure application. Chloride concentration of leachate is driven by soil type and treatment application interactions and changes through time with added irrigation. The amount of chloride which was retained in the soil following application could also be affected by soil type and treatment. Finally, the proportion of chloride applied which is lost to leachate is independently affected by soil type and treatment application. While questionable chloride contents in the SM samples for the second year of the study make interpretation of the mass balance and comparisons between years and treatments difficult, the TL and KCl treatments are comparable and show their tendency to leach chloride less rapidly in all soil types. While this is a demonstration of how chloride leaching potential differs between a subset of manure and soil types, more research is needed to create a more precise chloride mass balance for manure fertilizer and fully understand manure's role in chloride loading. Similar leaching studies evaluating a wider variety of manure types, a timescale mimicking leaching throughout an entire field season, and manure application methodology would all be beneficial in providing more insight into chloride leaching potential from manure application.

3.7 Tables

Table 3.1: *Application rates for manure and fertilizer treatments.*

Treatment †	Application rate (L ha $^{-1}$)	Application rate (kg ha $^{-1}$)
TL	-	18256.1
SM	65736.1	-
KCl	-	168.1

† Turkey litter (TL), Swine manure (SM), potassium chloride fertilizer (KCl).

Table 3.2: *Baseline soil nutrient analysis results at time of soil column extraction.*

Soil Type	Depth (cm)	Chloride (mg kg $^{-1}$)
Silt L	0 – 15	14.7
	15 – 30	11.9
Clay L	0 – 15	11.2
	15 – 30	16.1
Silty Clay L	0 – 15	12.4
	15- 30	7.1
Sandy L	0 - 15	11.3
	15 - 30	7.4

Table 3.3: *Manure and fertilizer chloride concentrations and % dry matter at the time of column application.*

Year	Treatment †	Dry Matter (%)	Chloride (mg L $^{-1}$)	Chloride (mg kg $^{-1}$)
1	TL	53	-	3700
	SM	1.3	2280	-
	KCl	-	-	470000
2	TL	45	-	3900
	SM	4.3	1116	-
	KCl	-	-	470000

† Turkey litter (TL), Swine manure (SM), Potassium chloride (KCl)

Table 3.4: *Total chloride inputs from manure and fertilizer treatment application.*

Year	Treatment †	Chloride (g)
1	TL	0.49
	SM	1.09
	KCl	0.57
2	TL	0.51
	SM	0.53
	KCl	0.57

† Turkey litter (TL), Swine manure (SM), Potassium chloride (KCl)

3.8 Figures

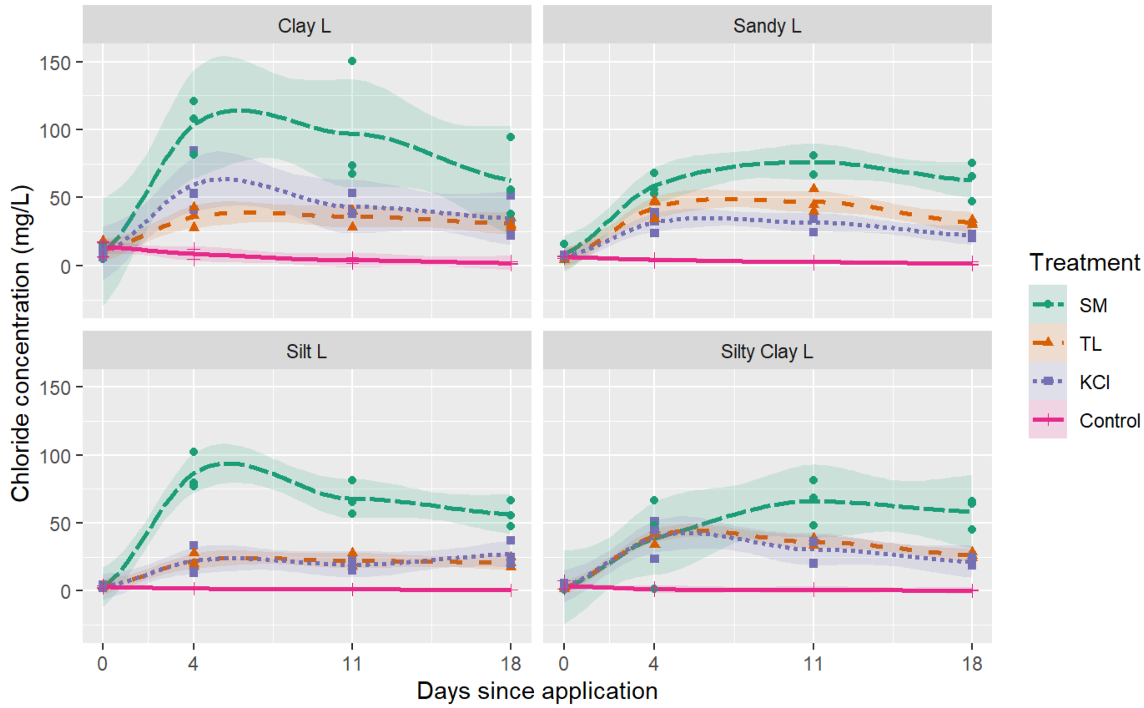

Figure 3.1: *Chloride concentration of leachate through the duration of the leaching study with respect to soil type and nutrient treatment. Shaded regions represent standard error. [Swine Manure (SM), Turkey Litter (TL), Potassium chloride (KCl)]*

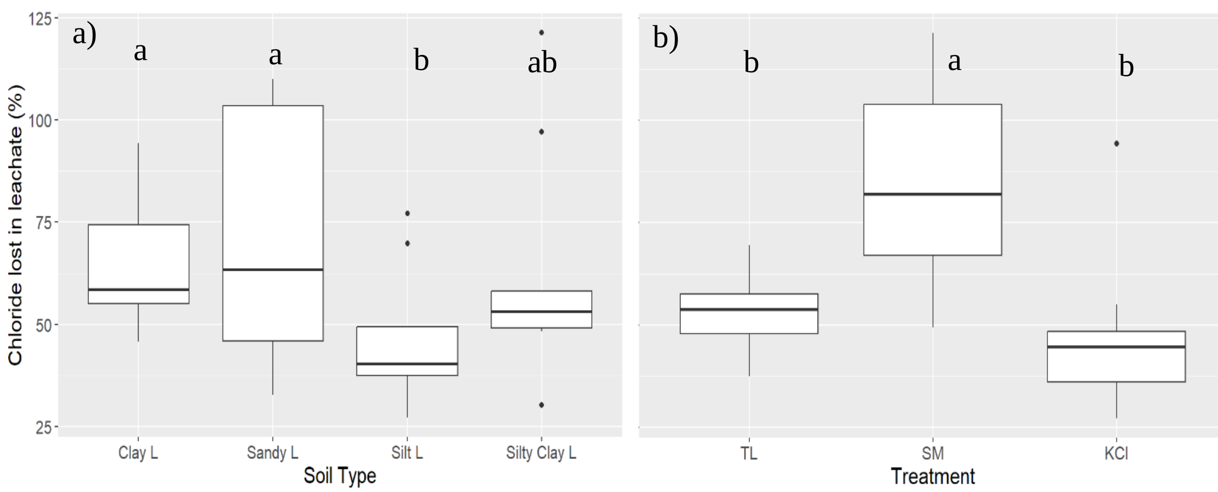

Figure 3.2: *Boxplots representing the percentage of chloride lost via leachate with respect to total chloride applied by* ***a)*** *soil type and* ***b)*** *treatment. Letters denote significant differences [Swine Manure (SM), Turkey Litter (TL), Potassium chloride (KCl)]*

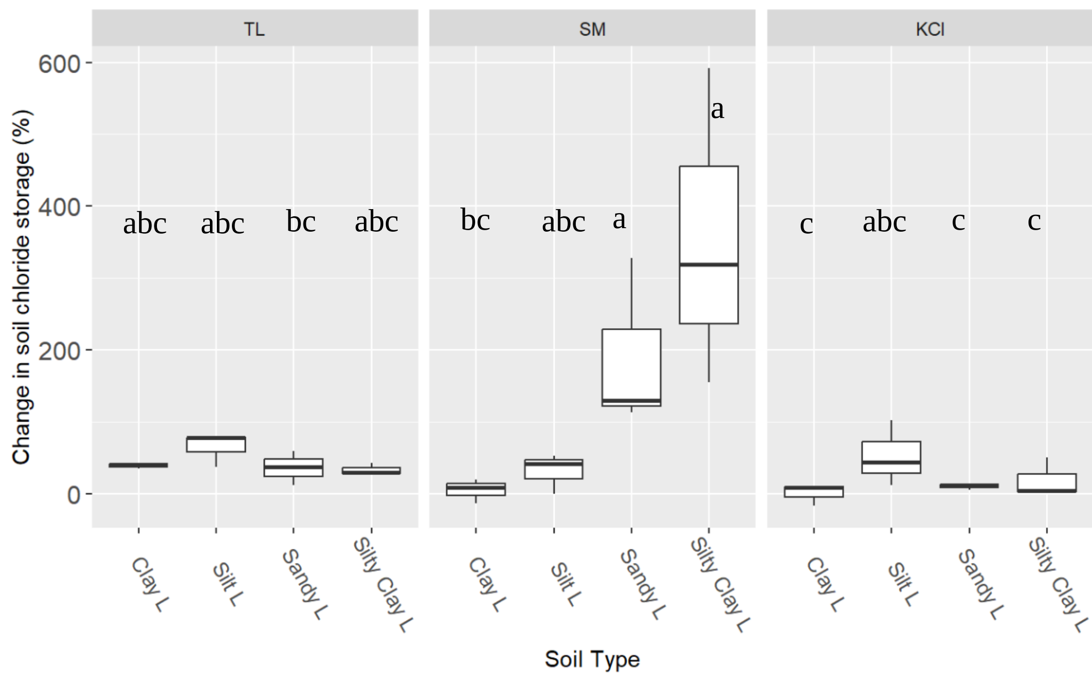

Figure 3.3: *Boxplots representing the change in soil chloride storage with respect to total chloride applied by soil type and treatment. Letters denote significant differences [Swine Manure (SM), Turkey Litter (TL), Potassium chloride (KCl)]*

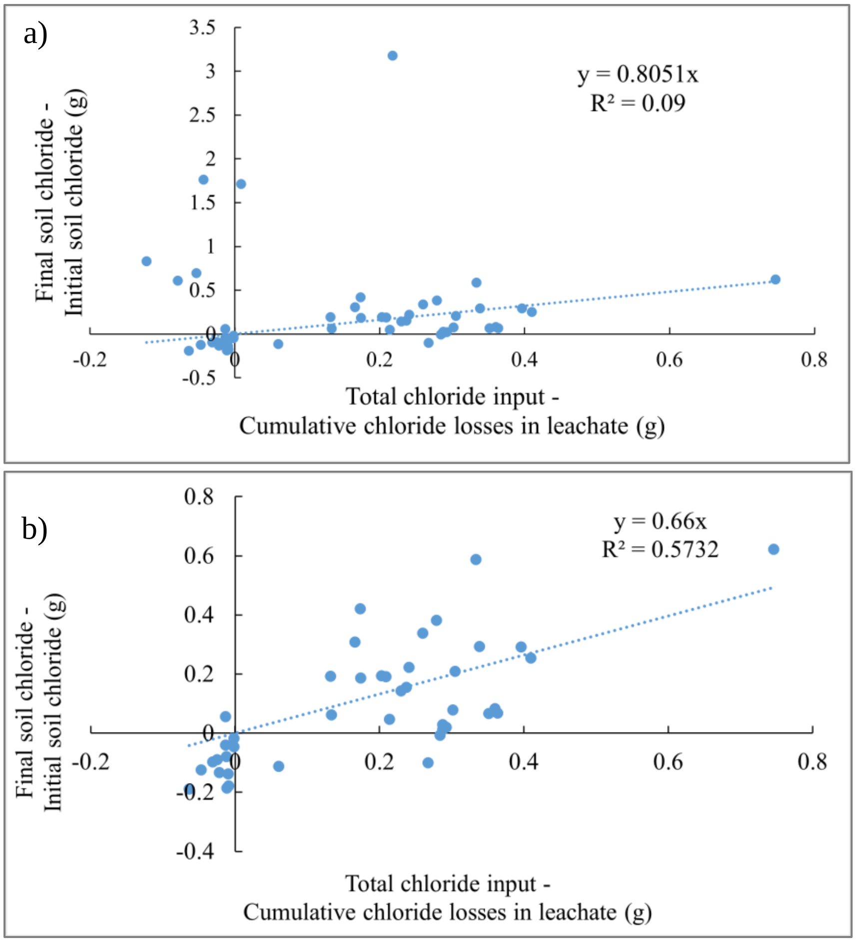

Figure 3.4: *Comparison of change in soil chloride (final – initial) to soil chloride retention (based on chloride inputs – leachate losses) including* ***a)*** *all the data available and* ***b)*** *six outlier values from Swine Manure (SM) treated Silty Clay L and Sandy L soils omitted.*

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