Migration of Roadway Deicer Through Soils: A Clear Roads Study

Final Report

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research for winter highway maintenance

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16. Abstract This study investigated the fate and transport of chloride-based roadway deicers in sandy loam soil representative of common northern U.S. roadside conditions. The work focused on sodium chloride and magnesium chloride solutions, with and without a beet juice-based agro-additive used in winter road maintenance operations. Methods included a survey of state DOT practices, laboratory batch sorption tests, vertical and horizontal soil-column experiments, elemental analysis, and data-driven modeling to supplement experimental interpretation. The results showed that chloride was weakly retained by the tested soil and migrated readily under both vertical and horizontal flow configurations. Sodium and magnesium interacted more strongly with soil exchange sites, but their retention was limited and could be exhausted over time. Compared with chloride-only solutions, the beet juice additive altered soil interactions and increased the mobility of chloride salt ions, likely through coating of soil particles and interaction between additive functional groups and salt ions. Differences between vertical and horizontal columns indicate that flow direction and soil structure can affect transport behavior. The findings support relative risk assessment and site-specific winter maintenance decisions, especially for permeable soils and areas with shallow groundwater.			
17. Key Words Roadway deicers; chloride salts; sodium chloride; magnesium chloride; beet juice additive; agro-based additives; roadside soils; sandy loam; solute transport; soil column testing; sorption; groundwater; winter maintenance; Clear Roads; environmental impacts.	18. Distribution Statement No restriction. This document is available to the public through the Clear Roads Organization and the Minnesota Department of Transportation.		
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Executive Summary

This study investigates the behavior of chloride-based deicers, including those with a common beet juice additive, in sandy loam soils typical of U.S. roadside environments. Using a combination of controlled laboratory experiments and data-driven modeling, this Clear Roads project provides new evidence to help state Departments of Transportation (DOTs) assess the subsurface environmental implications of their winter maintenance practices.

This summary presents the key findings, their operational significance, and a practical path for DOTs to apply the results responsibly.

Key Findings

1. Chloride moves quickly through common roadside soils. Laboratory column tests confirmed that chloride ions are only weakly retained by the tested sandy loam soil, migrating readily under both vertical and horizontal flow conditions.
2. Sodium and magnesium interact more with soil, but retention is limited. While batch and column tests showed measurable retention of Na^{+} and Mg^{2+} on soil exchange sites, this capacity is finite and can be exhausted, allowing these ions to migrate downward over time.
3. Beet juice additive altered soil interactions, increasing the mobility of cations. When compared to chloride-only solutions, the beet juice additive modified soil surface properties, reduced chloride adsorption, and led to faster chloride migration through the soil columns. The report identifies two probable mechanisms: surface coating of soil particles and complexation of chloride ions by the additive itself.
4. Flow direction and soil structure influence transport. Observed differences between vertical and horizontal column tests underscore that real-world transport is sensitive to

flow configuration, meaning preferential pathways and soil layering in the field can significantly affect migration rates.

5. The project used machine learning models to predict concentrations beyond the range of direct measurements and to manage datasets with frequent non-detects. The modeling was explicitly designed to support the physical experiments, not to replace them, and its use required careful correction and interpretation.

Significance for DOT Operations

These findings are operationally relevant for three primary reasons:

- Roadside soil is a primary pathway. Survey data confirms that coarse to medium-grained soils like the sandy loam tested are commonly encountered along U.S. roadways, making them a direct receptor for applied deicers.
- Performance additives are not inherently low risk. While agro-based additives like beet juice are used to enhance deicer performance, this study demonstrates they can also alter subsurface chemistry in a way that increases the mobility of chloride salts and associated ions, with potential implications for shallow groundwater and long-term soil salinity.
- Field conditions may accelerate migration. The controlled laboratory setting does not capture the full complexity of the roadside subsurface, where soil heterogeneity, preferential flow paths, and seasonal freeze-thaw cycles can lead to even faster transport than observed in the lab.

Actionable Guidance for DOTs

DOTs should consider the following practical steps:

- Use findings for relative comparison. Apply these results to understand relative risks (e.g., additive vs. no additive) rather than to generate precise, site-specific predictions of contaminant travel.
- Exercise added caution with additives in permeable soils. In soils similar to those tested, deicers containing agro-based additives as having a potentially higher mobility. This is particularly important in coarse-textured soils, areas of repeated application, and locations with shallow groundwater.
- Do not assume additives reduce subsurface risk. The study provides direct evidence that an additive can increase environmental mobility. Site-specific data should be required to support claims of reduced risk.
- Apply the modeling approach cautiously. Use machine learning as a supplementary tool for extending laboratory analyses, not as a standalone predictive model for regulatory or high-stakes decisions.

Report Limitations

The conclusions are bound by the study's scope:

- Results are based on controlled tests using homogenized soil, not on heterogeneous field-scale profiles.
- Critical field factors like freeze-thaw cycling, variable infiltration, and long-term accumulation were not directly tested.
- Findings are most directly applicable to soils with texture and properties similar to the sandy loam used in the experiments.

Conclusion for Practitioners

This study provides credible, experimental evidence that chloride salts are inherently mobile in a common roadside soil and that adding a beet juice-based performance additive can increase its migration potential. For DOT engineers and maintenance planners, the most prudent application of this work is to inform risk-aware decision-making, especially in environmentally sensitive areas. These laboratory insights should be paired with local site knowledge and monitoring to develop effective, context-specific winter operations strategies.

Scholarly Abstract

In this study, we examined the fate and transport of chloride (Cl^-) salts with and without the use of organic additives in roadside soils that are commonly encountered in the United States. Chloride (Cl^-) salts with agro-based additives have been increasingly used as anti-icers or deicing chemicals on roadways in North America for improved safety and mobility during the winter season. They facilitate improved road pavement surface conditions during the harsh winter season and reduce traffic accidents and hindrance to socio-economic activities. In many cases, however, roadside soils are often the recipients of these chloride salts through runoff actions and deposition from snow ploughing activities. While their use provides immense benefits to commuters, their fate and transport through roadside soil haven't been examined. There is no holistic study that has investigated the fate and transport of this composite material (i.e., chloride salts and agro-based additives) in roadside soils. In this study, we examined the fate and transport of two chloride salt (sodium and magnesium) ions and the effect of beetroot juice additive on them. To achieve this, we conducted extensive laboratory soil column and batch experiments and evaluated the effect of the direction of flow on the fate and transport of these chloride salt ions by utilizing vertical and horizontal soil columns. Results obtained from this study suggest that beetroot juice altered the surface properties of the soil. This influenced the adsorption capacity and affinity of the ions on the soil particles, thus increasing the probability of chloride salt ion migration to groundwater at a faster rate. The mechanism of alteration was explained to have resulted from (1) surface coating of the soil particle and increasing the functional group for ion interaction. (2) binding of the chloride salt ion within the functional group of the beetroot juice, thereby limiting the interaction of these ions with the soil particle surfaces.

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AEC	Anion exchange capacity
CEC	Cation exchange capacity
CMA	Calcium magnesium acetate
DI	Deionized water
EC	Electrical conductivity
HC	Hydraulic conductivity
NaCl	Sodium chloride
OM	Organic matter
SAR	Sodium adsorption ratio
SOM	Soil organic matter
SWRC	Soil water retention curve
USDOT	United States department of transportation
WHC	Water Holding Capacity

CHAPTER ONE

1.0 Introduction

1.1 Background and Problem Statement

In the last decade, chloride (Cl^-) salts have been increasingly used as anti-icers or deicing chemicals on road pavement surfaces in North America to improve transportation safety and mobility during the winter season (Miller, 2008; Fay & Shi, 2012). Sodium (Na), magnesium (Mg), and calcium (Ca) chlorides are common types of chloride salts used by transportation agencies for deicing, prewetting and anti-icing operations (Shi et al., 2013). They lower the freezing point of water and reduce the bond strength between ice and the road pavement surface (Shi et al., 2009). This mechanism helps in maintaining the traction between the road pavement surface and vehicle tires, thereby reducing road accident occurrences and hindrance to socio-economic activities. Despite the advances in the use of chloride salts for winter maintenance operations on road pavement surfaces, there are concerns about the environmental impacts of these salts in the environment.

Chloride salts are often transported from their point of application (i.e., pavement surface) to rivers, streams or stormwater management facilities by different mechanisms such as runoff with precipitation and snow melt (Falk-Pedersen et al., 2000). In many cases however, roadside soils are often the recipients of these chloride salts through runoff actions, deposition from snow ploughing activities (Buttle & Labadia, 1999), and wind action (Gustafsson & Blomqvist, 2004).

Environmental concerns resulting from the use of chloride salts have been listed as one of the challenges in a report by the National Cooperative Highway Research Program (NCHRP) for winter maintenance operations (Nixon, 2010). Increased roadside soil salinity, leaching of metal

cations and chloride anions are common conditions that have been observed from chloride salts use (Baraza & Hasenmueller, 1991). In addition, increased concentrations of these chloride salt ions can alter the physicochemical properties of the receiving roadside soil and increases their potential to migrate to ground and surface waters. Presently, the United States Environmental Protection Agency (USEPA) does not consider chloride salts a contaminant and therefore, they do not regulate their use (Kaushal et al., 2005). Consequently, there are no federal policies regulating the amount of chloride salts that can be used for roadway maintenance operations. With increased acceptance and widespread use of chloride salts by transportation agencies for deicing and anti-icing operation and maintenance, concerns about the environmental and hydro-mechanical response of roadside soils are gaining more attention by practitioners and the research body in general.

In recent years, chloride salts are often augmented with agro-based materials as additives to improve their deicing capabilities and anti-corrosion effects on transportation infrastructures and maintenance equipment's of transportation agencies (Nazari et al., 2020). These agro-based materials are produced from the fermentation of molasses, corn, beetroot, and other agricultural products (Cheng & Guthrie, 1998). Besides the associated additional cost to winter maintenance operations, environmental implications with respect to their degradation, toxicity and interaction with the chloride salts have not been reported. Despite several studies that have examined the environmental implications of chloride salts in soils (e.g., Cui et al., 2015; D'Itri, 1992; Erickson et al., 2019; Lee et al., 2017; Lundmark & Olofsson, 2007; Ramakrishna & Viraraghavan, 2005), an holistic understanding of its' fate and transport in soils commonly encountered near roadways in the United States and the effect of agro-based organic additives on this in still far-fetched. For

the rest of this thesis, “chloride salt”, “chloride-based salt” or “salt” is used interchangeably to represent chloride salt deicers and anti-icers, including those used for prewetting operations.

Previous attempts have been made to understand the interaction and mechanism of corrosion inhibition between agro-based corrosion inhibitor (from apple pomace) and sodium chloride (NaCl) brine (e.g., Nazari et al., 2020) on buried pipes. Chemical analysis of the agro-based materials showed that its major corrosion-inhibiting agent can attach to steel surfaces and form a barrier layer. Its adsorption followed the Langmuir isotherm, and physical adsorption was dominant over chemical adsorption. This result is in synergy with previous studies that observed that the physicochemical properties of corrosion inhibitors such as the functional groups, electronic structure, or electron density influenced the interaction between the corrosion surface and corrosion causing agents (Ryl et al., 2019).

In a related study, Cheng and Guthrie (1998) observed that organic materials (e.g., agro-based additives) can be broken down by soil microorganisms and temporarily create anoxic (anaerobic) conditions in the soil. At cold temperatures, the decomposition rate of these organic materials in soil is reduced, thus increasing their migration or transport potential into groundwater (Cheng & Guthrie, 1998). Findings from these studies suggest the following: (1) similar mechanisms of adsorption of the agro-based corrosion inhibitor ions unto steel surfaces can be initiated on soil particle surfaces, (2) ions present in these inhibitors will compete for adsorption site with those in the deicer salts especially in fine grained soils having active mineral surfaces, and this might influence which ions migrates to groundwater and the rate of their transport.

Estimating the fate and transport of solutes through the vadose zone is imperative for understanding its potential impact to surface and groundwater including vegetations and subsurface soil properties. However, subsurface soil is spatially heterogenous and an estimation of

the fate and transport of solute through them often requires rigorous field, and laboratory studies. A full-scale experiment would be expensive, time-consuming, and constrained in difficult-to-access terrains or depths below the ground. While the history of the system can be extrapolated from the available field and laboratory records, there is no way of predicting the future behavior of the full-scale system unless it is subject to conditions and assumptions. Therefore, a practical option is to develop a model based on past field and laboratory results that reasonably represents the behavior of a full-scale system, replicates the pertinent physical parameters, and defines the significant characteristics of the transport phenomenon.

Several modeling approaches have been developed to complement field and laboratory data in describing the fate and transport of solutes, including future predictions that are not readily available from field and laboratory data. Whatever model is used, one of the challenges in solute transport is determining the relevant parameters and coefficients, such as source concentration and size, seepage velocity, and time since the solute first entered the soil (Bear 1972). Analytical approaches (e.g., Liu et al., 2000) often consider one or two governing processes, usually in a simplified flow domain with uniform transport characteristics. In contrast, numerical simulation of solute transport provides a system that can approximately incorporate the impacts of numerous controlling processes; and it is the only approach that can handle geometries and parameter distributions.

Much evidence (e.g. Wheatcraft & Cushman, 1991) suggests that solutions of classical solute transport models (analytical and numerical), no matter how refined they are to include the most relevant chemical and microbiological processes and soil properties, often fail to accurately describe transport processes in most natural field soils. A major reason for this failure is that the subsurface environment is overwhelmingly heterogeneous. Heterogeneity occurs at a hierarchy of

spatial and time scales (Wheatcraft & Cushman, 1991), ranging from microscopic scales involving time dependent chemical sorption and precipitation/dissolution reactions, to intermediate scales involving the preferential movement of water and chemicals through macropores or fractures, and to much larger scales involving the spatial variability of soils across the landscape. Hence, recent studies have explored other methods that do not try to represent the solute transport in exact detail as this is practically impossible. An example is the use of stochastic models that incorporate certain assumptions about the transport process in the heterogeneous system (e.g., Sposito & Barry, 1987).

1.2 Research Need and Objectives

Chloride (Cl^-) salts and agro-based additives have been increasingly used as anti-icers or deicing chemicals on roadways in North America, for improved safety and mobility during the winter season (Miller, 2008; Fay & Shi 2012). They facilitate improved road pavement surface conditions during harsh winter season and reduce traffic accidents and hindrance to socio-economic activities (Shi et al., 2009). While the use of chloride salts provides immense benefits to commuters, the environmental implications and detriments to soil and groundwater are often overlooked. Several studies have examined the migration rate of few chloride salts, however, to our best knowledge, there is no holistic study that has investigated the fate and transport of this composite material (i.e., chloride salts and agro-based additives) in roadside soils.

With increased acceptance and widespread use of chloride salts and agro-based additives by transportation agencies for deicing and anti-icing operation and maintenance, concerns about the environmental and hydro-mechanical response of roadside soils are gaining more attention by practitioners and the research body in general. Hence, this study intends to provide additional information on the effect of agro-based additives on the fate and transport of chloride salts in

commonly encountered roadside soils in the United State using extensive laboratory experiments and modeling approaches. The objectives are to.

(1) Evaluate the transport of the ions of two chloride salts and the effect of agro-based additives on them.

(2) Explore transport models that describe the transport phenomena of this composite material through the test soil.

(3) Identify fundamental mechanisms that influence the transport of chloride salt ions in the presence of an agro-based additive.

1.3 Research Hypothesis

The review of past literature has provided useful insight into how the use of agro-based additives with chloride salts influenced its physicochemical interaction with steel pipes. Hence, we hypothesize that a similar mechanism of adsorption for the agro-based corrosion inhibitor ion to soil surface might be induced as observed by Nazari et al. (2020) on steel surfaces. We believe that this will limit the interaction and adsorption of chloride salt ions on soil surfaces. To validate this, control experiments with only chloride salt solutions as infiltrating fluid were carried out and compared with those having an addition of an agro-based additives.

CHAPTER TWO

2.0 Literature Review

2.1 Chloride Salt Migration from Road Pavement Surfaces

Chloride salts are often transported from their point of application (i.e., pavement surface) to roadside soils by different mechanisms such as runoff with snow melt (Falk-Pedersen et al., 2000), direct deposition from snow ploughing activities (Buttle & Labadia, 1999), wind (Gustafsson & Blomqvist, 2004), or improper handling during their application (See Fig. 1 and 2). Chloride salts deposition has been documented in various literature to be transported as far as 30 meters from the sides of a road pavement and 110-meter depth (e.g. Evan & Frick 2001). Continuous application of chloride salts leads to their prolong accumulation in roadside soils with an increased potential of migrating to ground water after they saturate the soil (Lundmark & Olofsson, 2007). The type and characteristics of the road, including traffic conditions, have been listed as key influences in the transport distance of these salts. For example, in wet conditions, road traffic generates salt spray actions that lead to their transportation to considerable distances (e.g., Blomqvist & Johansson, 1999). Furthermore, during road ploughing activities, the snowpack that is created by the sides of the road often acts as reservoir for these deicer salts and when they are melted at increased temperatures or by precipitation action, they find their way to the surrounding soils as runoffs before infiltrating into the ground (Bartosova & Novotny, 1999). Often, these mechanisms occur simultaneously, and it is difficult to isolate a single process responsible for chloride salts deposition in roadside soils under field conditions.

Past literature has examined regions where multiple types of chloride salts have been applied over time (e.g., Evan & Frick 2001). Findings from these studies indicate that the concentration of the chloride salt ions was higher in snow packs and soil near the road pavement but decreased with

increasing distance from the pavement (Foster & Maun, 1978; Hull & Bishop, 2004; Baraza & Hasenmueller, 2021). Furthermore, chloride salt ion concentrations were observed to vary seasonally in roadside soils with higher concentrations observed during seasons of deicer salt use for winter maintenance operations. These concentrations were observed to decrease at warmer seasons for the same depths and distances with a few exceptions where the concentrations remained unchanged through the year (Foster & Maun, 1978). The observations from the results from these studies indicate that chloride salt ions migrate at different rates in roadside soils under varying conditions.

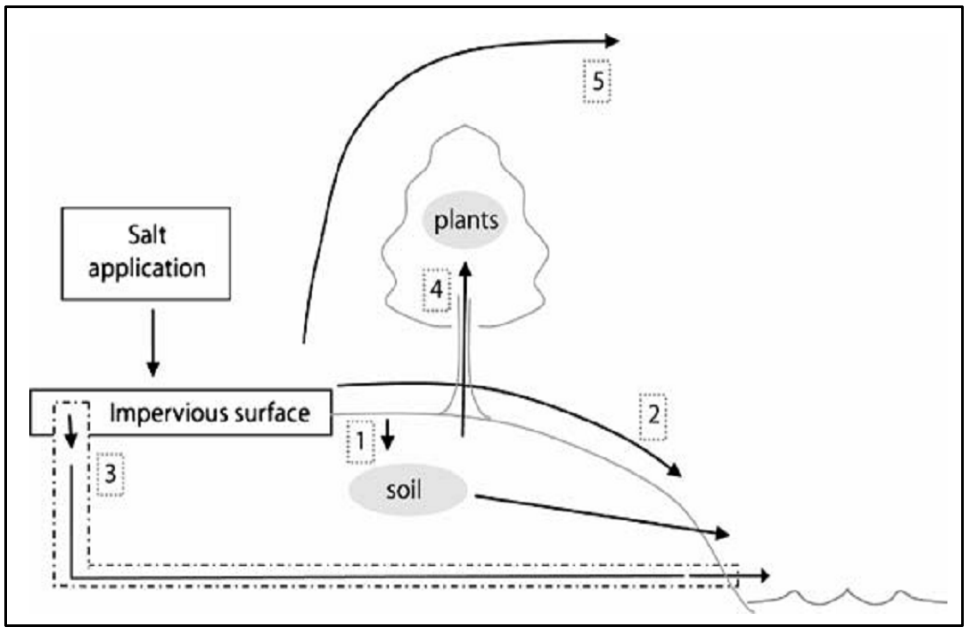


Figure 1. Various pathways for chloride salts migration from road pavement surfaces; (1) movement through roadside soils to groundwater or surface water (2) surface runoff with rain or snowmelt into water bodies; (3) transport through storm drains; (4) uptake by plants, with temporary or long-term storage in plant tissues; (5) airborne movement of dry dust or liquid droplets (After Cunningham et al., 2008).

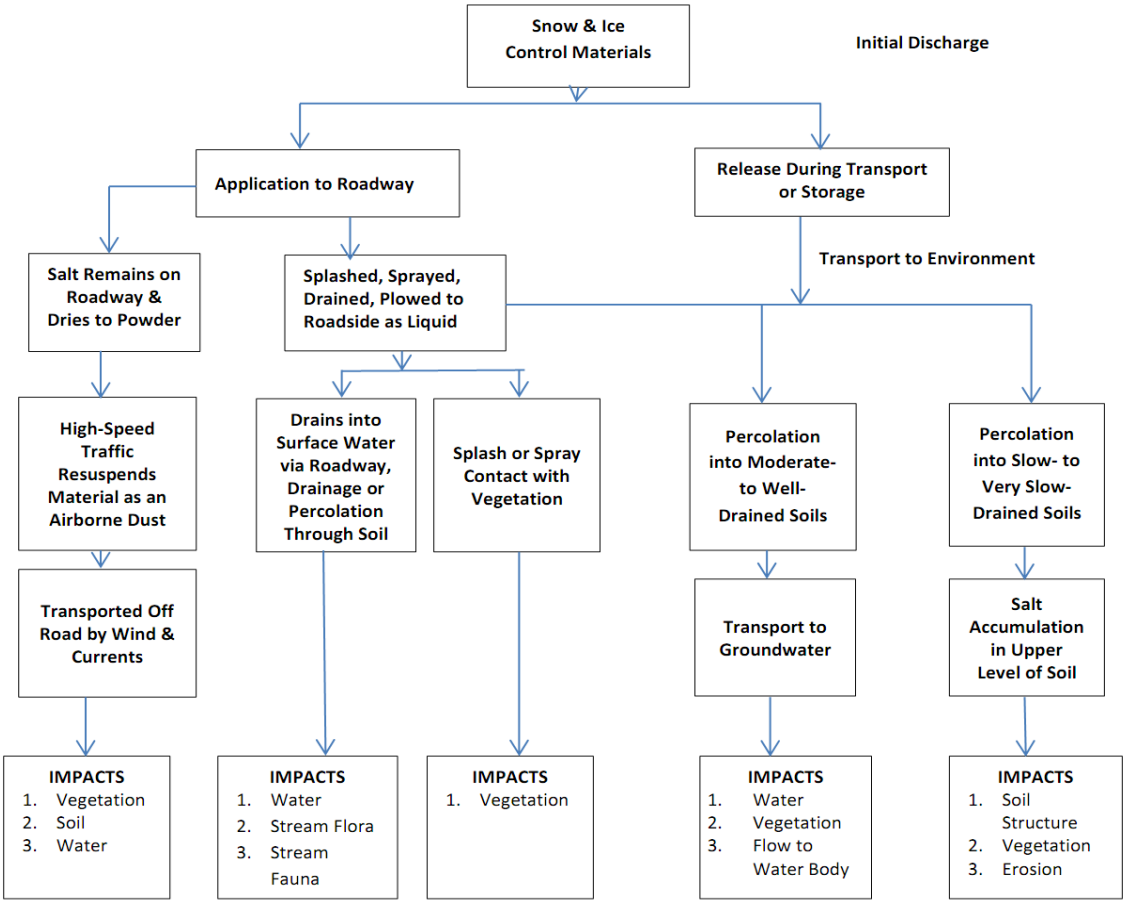


Figure 2. Migration path and impacts of deicing salts on the environment (Casey et al., 2014; Transportation Research Board & National Academies of Sciences, Engineering, and Medicine, 2007)

2.2 Influences of Soil Properties on Chloride Salt Migration

Chloride salt solutions are often transported through roadside soils with precipitation or snowmelt at a rate that is dependent on the soil and deicer/anti-icer solution properties. The physical (e.g., density, porosity, permeability, water content/saturation and soil type), and chemical (cation exchange capacity, minerology, and elemental composition) properties of soil contribute to the fate and transport of these salts through the soil (Lundmark & Olofsson, 2007).

Likewise, their retention and accumulation in turn influences the physical and chemical properties of the soil (Sarsembayeva & Zhussupbekov, 2021).

2.2.1 Permeability and Pore Size Distribution

Soil permeability is an intrinsic property of the soil that is dependent on the particle size and pore size distribution of the soil. Soils with high permeability ($> 10^{-6}$ m/s) are often characterized with a higher fraction of coarse-grained particle sizes and a corresponding relatively larger pore or void ratio. The distribution and connectivity of the macro (0.08-5 mm diameter), meso (0.03-0.08 mm diameter), and micropores (0.005-0.03 mm diameter) are important characteristics that influences the infiltration or flow of water in such highly permeable soil (Weil & Brady, 2016). In soils with large fractions of macropores, transport of such chloride salt solutions may occur by gravitation (freely through macropores) or capillary force (Mitchell & Soga, 2005). Irrespective, the non-homogenous pore size distribution creates uncertainty when assessing flow trends in in-situ soils (Lu & Likos, 2004). In addition, shrinkage cracks created by wetting (precipitation) and drying (evaporation) or freezing and thawing cycle contributes to flows through soils. With regards to chloride salt solution, it is expected that with an increase in the permeability of the soil, there is corresponding increase in the infiltration rate and an increased potential of the chloride salt ions to migrate to groundwater at a relatively shorter time duration. Under increased infiltration or flow in higher permeable soils, the contact time for interaction between the chloride ions and soil particle surface will be minimized (Mitchell & Soga, 2005). Hence, the influent concentration gradient will be relatively maintained throughout the soil profile for the duration of flow.

2.2.2 Mineralogy and Chemical Composition

Mineralogy is a primary factor that influences the physical and chemical properties of the soil (Mitchell & Soga 2005). The influence of mineralogy and chemical properties of soil on the

transport of electrolyte solutions (e.g., salt solutions) is often complex and difficult to isolate individual mechanisms. This is more pronounced in fine grained soils especially clays and silt with charged surfaces. Thus, the mineralogy of the soils often determines the composition of these active surfaces and in return the type of interaction including adsorption and desorption processes that take place at the soil particle surfaces and interlayers. For example, in a soil-water-electrolyte system, there are often unbalanced force fields between the soil particles and dissolved ions in the soil water (Israelachvili, 2011; Lu & Likos, 2005; Mitchell & Soga 2005). This phenomenon is well described by the Gouy-Chapman (Gouy, 1910; Chapman, 1913) theory that describes the distribution of ions near a charged surface in an electrolyte solution forming diffused layers as a function of the mineralogical, chemical properties of the soil and electrolyte composition. In such soil-water-electrolyte system, it is the formation and arrangement of these layers that enables (1) the movement of ions and charge through particle surfaces; (2) the transfer of charge between particle surfaces and electrolytes in solution. This diffused layer results in relative motion between the soil and its pore fluid. It does suggest that adsorption-desorption processes in a soil-electrolyte system are dependent on chemical and mineralogical properties of the soil which in return influence the formation of these diffuse layers and influence the migration rate of ions (e.g., chloride salt ions) through the soil. Detailed description of the electrical double layer and fundamental flow process in soil-electrolyte system are described by Reddy and Cameselle (2009).

2.2.3 Soil Saturation and Water Content

Initial water content or saturation contributes to the fate and transport of water and electrolyte solutions (e.g., chloride salts) through soils. At high water content, the liquid phase is more connected in the voids and thus a corresponding increase in the potential of water to flow through the voids (Lu & Likos, 2005). The vadose zone is always in an unsaturated state, and the hydraulic

conductivity (HC) depends on the amount and connectivity of the pore fluid (Mitchell & Soga, 2005). However, the hydraulic conductivity in a soil profile can vary by 2 to 3 orders of magnitudes owing to ununiform void ratio, water content, soil fabric arrangement and particle size distribution within the soil profile. Thus, in the vadose zone, there is a spatial distribution of saturation and water content that results from the previously mentioned properties in addition to environmental conditions of wetting (precipitation) and drying (evaporation) cycles.

Flow laws with respect to hydraulic and chemical transport are governed by Darcy's law and Fick's law. The water to about 1.0 nm, that is, three molecular layers, from the soil surface is strongly adsorbed (Sposito, 1984;1989) and has a structure different from that of free water. Thus, at low water contents, there is increased competition for adsorption of water between the ions in the soil and the soil mineral surface. This tightly adsorbed water is mostly immobile and thus limits any flow within such system. At increased saturation however, the effect of such binding force reduces with increased distance from the soil surface and thus, the pore fluid has more potential to flow (Mitchell & Soga 2005). In coarse grain soils, advection is the main mechanism for chemical transport i.e., dissolved, or suspended materials are carried with the flowing water or liquid. While in fine-grained soils, the dominant mechanism for chemical transport is by diffusion.

2.3 Fate of Chloride Salts in Soil

Previous literature (e.g. Lax & Peterson, 2009; Nelson et al., 2009; Schweiger et al., 2015) has evaluated the fate of chloride salts in soils following soil column tests. As these salt solutions infiltrate through the soil, several reactions were observed to be initiated including adsorption-desorption, ion exchange, precipitation and/or biological processes. Adsorption-desorption of the cation and anion of the chloride salt between the pore fluid and soil were observed to be both linear and nonlinear. This resulted from varying cation exchange capacity (CEC) of the soil, particle size

and valence of ion present in the pore fluid solution. The hierarchy of exchange for the ion within such system is described by the lyotropic series (i.e., aluminum ion (Al^{3+}) > hydrogen ion (H^{+}) > Ca^{2+} > magnesium ion (Mg^{2+}) > potassium ion (K^{+}) > sodium ion (Na^{+}) (Reddy & Cameselle, 2009). Generally, the cation exchange capacity of soils can range from as little as having large proportions of clay and soil organic matter (Holtz et al., 2011; Fanun, 2014; Balasubramanian, 2017). For soils rich in organic colloids, anion exchange capacity (AEC) may also be observed.

In previous literatures (e.g. Lax & Peterson, 2009; Nelson et al., 2009; Schweiger et al., 2015) that evaluated the fate of sodium chloride (NaCl) deicer using soil column tests, sodium ion was observed to bind to the negatively charged soil surface and replaced existing cations or metals on the soil and organic matter surface (e.g., clays or organic matter) thereby initiating their release into the pore fluid. Sodium ion concentration was mostly found to be maximum at the upper part of the soil's profile and after the soil adsorptive capacity was exhausted, and the adsorption site moved down gradient (e.g. Howard & Beck, 1993). On the other hand, chloride adsorption on soil was low and it was observed to rapidly diffuse through the soils (e.g. Öberg et al. 2005). While the mechanism for chloride adsorption were not reported in these studies, chlorination of organic matter, microbial or plant uptake, anion adsorption on cations, are evidences of chloride retention in soils as reported in similar studies (Bastviken et al., 2007, 2009; Mason et al. 1999). Chloride often bind temporarily or semi-permanently with SOM and organically bound chloride in soil may be correlated to the organic carbon content (e.g., Erickson et al., 2019).

2.4 Metal Mobilization in Soils from Chloride Salt Use

Metals (e.g., lead-Pb, copper-Cu, zinc-Zn, and cadmium-Cd) are often introduced to soils from the operation of automobiles and other anthropogenic activities (Elliot & Chénier, 2001). In addition, trace metals (up to 5% wt.) are sometimes the constituents of rock salt (NaCl) that is used as deicers

for winter maintenance operations (Elliot & Chénier, 2001). Increased desorption of heavy metals from soil has been a concern for chloride salt use in recent years. They migrate to ground and surface waters when desorbed into the soil pore fluid (Backstrom et al., 2004; Norrstrom, 2005). Several studies have examined the release of metals, from high sodium chloride concentration exposure, in roadside soils (e.g., Amrhein & Strong, 1990; Backstrom et al., 2004; Norrstrom, 2005). Lead (Pb), cadmium (Cd) and Zinc (Zn) were observed to be released from soils where sodium chloride salt was applied (Amrhein & Strong, 1990; Norrstrom, 2005). For most metals, cation exchange, chloride complex formation, and colloid dispersion were common mechanisms that facilitated their release and mobilization (Nelson et al., 2009). The formation of metal-chloride complexes and competition for cation exchange sites were precursors for increasing water-soluble metal concentration when chloride salts were applied (Rasa et al., 2006).

The mobilization of organic matter has also been observed to be a precursor for increased dissolution and mobility of metals such (e.g., Nelson et al., 2009; Norrstrom,2005). In a study by Norrstrom (2005), it was observed that soils leached with sodium-chloride solution, experienced the release and colloidal transport of cadmium (Cd) and zinc (Zn) metals. In other studies, the proportion of heavy metals that were bioavailable, and the rates of transformation from unavailable to bioavailable metals in roadside soils increased when sodium chloride salts were applied (e.g., Amrhein & Strong, 1990; Amrhein et al., 1992). Amrhein et al. (1993) also confirmed the mobilization of soil organic matter and trace metals by leaching the soil with rock salt (NaCl) solutions. Dissociation of sodium ions, soil organic matter mobilization and formation of metal complexes were observed. While many studies have reported that the transport of trace metals are associated with colloidal particles of mostly soil organic matter and iron oxides (e.g., Amrhein et

al., 1993), ion exchange has been documented extensively to be the major mechanism for heavy metal release and mobilization through soils (Amrhein et al., 1993; Bäckström et al., 2004).

2.5 Effect of Chloride Salts on Soil Properties

2.5.1 Electrical Conductivity

The presence of chloride salts increases the electrical conductivity of soils (Surabian, 2017). For example, the measured electrical conductivity increased by 350% in a study by Wang et al. (2012) when the soil was leached with 0.5% wt. of chloride salt solution. Previous studies (Warrence et al., 2002; KesslerS et al., 2010; Mavi et al., 2012; Gerasimov et al., 2021; Akinleye et al., 2022) also observed a correlation between electrical conductivity and salt concentration in soils. Measured electrical conductivity values were higher in soils leached with chloride salts solutions when compared to other salts (e.g., glycerin and nitrates) at the same concentration (Eppard et al., 1992). Electrical conductivity measured across a soil matrix often accounts for the contribution from ions present in the soil-pore fluid, those in the soil-mineral interlayers, and those absorbed on the soil surface (Mitchell & Soga, 2005). However, the bulk of the measured electrical conductivity value is reflective of those in the soil-pore fluid. This is because ions have higher conductivity in solutions than when adsorbed to soil surfaces or soil-mineral interlayers (Akinleye et al., 2021, Reddy & Camselle, 2009).

2.5.2 Salinity and Sodicity

Soil salinity has been observed to increase with an increase in the accumulation of water-soluble salt in soils. This condition is exacerbated in soils where drainage is impeded, and surface evaporation is excessive (Buckman & Brady, 1967; Warrence et al., 2002). Soils with increased water-soluble salt concentration are classified as either saline, saline-sodic, or sodic soils (Warrence et al., 2002). The presence of chloride salts are not exceptions to these. For saline soils,

less than 15% of the soil is often occupied by sodium ions and the pH is usually below 8.5. For saline-sodic soils, more than 15% of the cation exchange capacity of the soil is occupied by sodium and their pH is often below 8.5. Sodic soils, on the other hand, contain relatively lower concentration (< 15%) of soluble salts, with more than 15% of exchangeable sodium and a correspondingly high pH value typically about or above 10.0. At such high pH value, soil organic matter can be dissolved.

When chloride salts are dissolved into solutions, they often ionize, disassociating into cations and anions molecules (Buckman & Brady, 1967; Warrence et al., 2002). Common chloride salt dissociated cations in arid and semi-arid areas include calcium, magnesium, and sodium. These cations have been described as base-forming (e.g., Buckman & Brady, 1967), meaning that they can contribute to an increase in hydroxyl ion (OH^-) concentration in the soil and a decrease in the hydrogen ion (H^+) concentration. They typically dominate the ion exchange surfaces of soil by displacing aluminum and H^+. Furthermore, anions and cations from dissociated chloride salts can cause an increase in soil salinity by their formation of carbonates or bicarbonates. For example, sodium bicarbonate has been reported to often exist as solid salts (Buckman & Brady, 1967). Conversely, calcium and magnesium bicarbonates have been found to exist more in the soil-pore solution with calcium being more soluble. When soil moisture becomes reduced, either by evaporation, plant uptake, or drainage, calcium bicarbonate decomposes into calcium carbonate (lime); a solid precipitate, carbon dioxide (CO_2) and water (H_2O). Increased dissociation and dissolution of calcium or magnesium from soil surface into soil pore solution causes an increase in the relative proportion of sodium in the soil, thereby creating a sodium-dominated (sodic) soil.

When, sodium ions (Na^+) are adsorbed on negatively charged soil particle surfaces and mineral interlayers, they can be retained for a prolong time and released long after the deicing period (Kelly

et al., 2008). A study on sodium accumulation in soils along roadsides in Massachusetts indicated a decrease in sodium concentration from 101 mg/kg to 16 mg/kg at a lateral distance of 5 to 15 feet (Casey et al., 2014). Similar studies observed that sodium can also be weakly adsorbed in calcareous soils (i.e., soils with high calcium carbonate content $CaCO_3$) (e.g., Eimers et al., 2015; Kelting & Laxson, 2010; Norrström & Bergstedt, 2001). Once sodium displaces other cations (like Ca^{2+} or Mg^{2+}), those exchanged cations are lost by leaching during precipitation. In addition, increased concentration (~15% of the total cation exchange capacity of the soil) of sodium in clays can affect the soil structure. At this concentration, the clay soil loses its ability to aggregate, and its permeability, water holding capacity (WHC), and aeration is decreased (Kelting & Laxson, 2010).

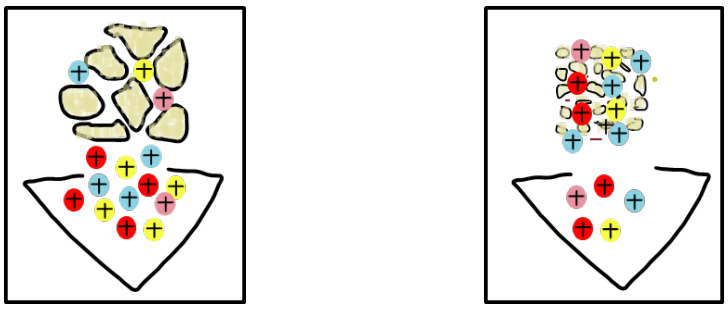
The retention rate of sodium have been determined from soil column tests and sodium adsorption ratio (SAR), providing useful information of sodium, calcium, and magnesium concentration in soils as described by equation 1. Sun et al. (2010) observed a reduction in the rate of sodium retention as the flow rate of water was increased and sodium retention was found to be higher than the total cation exchange capacity of the soil. This effect was attributed to physical adsorption of sodium due to van der Waals forces and the transient entrapment of sodium in the soil pore spaces during the transport of sodium chloride salt solution. Their result thus suggests that the cation-exchange capacity of soils may not be a good indicator for the total retained sodium in soils. Historical data of sodium and chloride retention in the Delaware river basin (DRB), United States provided addition useful information to this study. Increased sodium chloride deicer application for over five decades, decreased the molar ratio of sodium to chloride (i.e., Na/Cl) in the river basin. This suggest that sodium was largely retained in the soil while chloride leached out at a higher fraction (Sun et al., 2010).

$$\text{SAR} = \frac{[Na+]}{(0.5[Ca^{2+}]+0.5[Mg^{2+}])^{1/2}} \quad (1)$$

where Na^+, Ca^{2+} and Mg^{2+} are the concentrations of sodium, calcium and magnesium ions in the soil solution (Weil & Brady, 2016).

2.5.3 Cation Exchange Capacity (CEC) and pH

Fine-textured soils (i.e., silt and clay) are more susceptible to changes in their cation exchange capacity when leached with chloride salt solutions. This is because they possess active soil mineral surfaces due to their mineralogical formation (Lu & Likos, 2004) and relatively high specific surface area (i.e., surface area available for ion adsorption). In precipitation events, ions in chloride salt solutions are likely to migrate faster through coarse-grained soils to ground water because of the limited adsorption surface area and increased dilution of deicer salt concentration (Fig. 3a). However, there is an increased tendency for the formation of salt precipitates in soil-pore spaces at sufficiently high concentration.



(a) (b)

Figure 3. Migration of deicers through soil (a) Coarse-textured soils with low CEC and (b) Fine-textured soils with higher CEC (After Surabian, 2017)

In a stratified soil (i.e., soil profile with different soil types or composition at varying depths), cation exchange capacity is often maximum at layers with higher soil organic matter and clay

content. In a study by Cunningham et al. (2008), the long-term application of chloride salt decreased the cation exchange capacity of the soil. Similar results were obtained by Backstrom et al. (2004) and Cui et al. (2015).

The influence of chloride salt on the pH of soil has also been examined. An increase in the soil's pH was observed with a corresponding increase in the concentration of the salt solution (Wang et al., 2012) (Fig. 4a). A conflicting result was however observed by Ke et al. (2013) that examined the effect of chloride salts (NaCl) on the pH of a bulk soil sample. For example, there was an initial decrease in pH at the topsoil layer for the initial 7 days, but the pH increased after 7 days to an observation period of 14 days (Fig. 4b). The decrease in pH was attributed to leaching of chloride ion from the soil, thereby reducing the relative concentration of sodium in the pores of those layers.

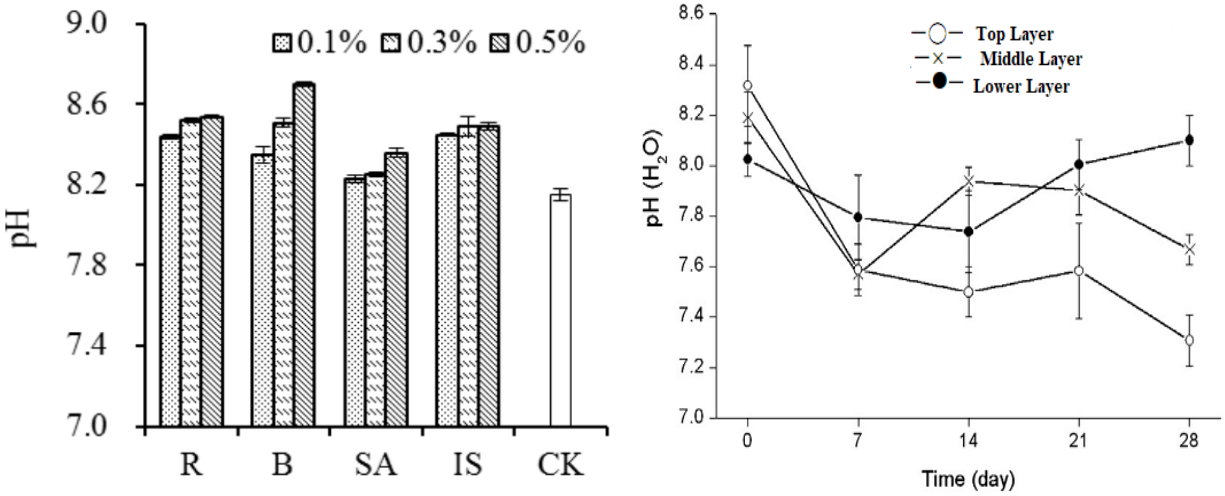


Figure 4. Effect of deicer on soil pH (a) pH response of soils to different deicer types at varying concentrations; chloride (R), nitrate (B), organic (SA), industrial (IS) and control (CK). (Wang et al., 2012) (b) pH response to chloride salt solution dosage in three layers of a Chinese soil (Ke et al., 2013).

2.5.4 Density and Soil's Structure

Changes in the engineering properties and structure of soil often arise from the changes in the physiochemical forces in the soil matrix. Adsorption and desorption of ions from soil surfaces and soil-mineral interlayers are often a precursor to the changes in soils' physical and chemical behavior. For example, applying deicer salt (mainly NaCl) to sodic soils, can further spike the concentration of sodium thereby inducing a high pH condition in the soil (e.g., in medium to fine textured soils). This high pH condition then initiates the dissolution of organic soil matter that binds soil particles together hence leading to soil-particle disaggregation (Mitchell & Soga, 2005). Disaggregation of soil particles leads to a decrease in the soil pore sizes and a potential consequence of this is the reduction in the soils' permeability and increased water holding capacity (i.e., increased soil surface area for water adsorption) (Jones et al., 1993; Shi et al., 2009). Conversely, in some fine-textured soils, adsorption of higher valence cations form deicer salt solutions can affect the soil plasticity (i.e., consistency of soils). On the other hand, ions exchanged between deicer salts and soils can increase the tendency for water-molecule attraction into the soil-mineral interlayer (e.g., clays of high plasticity). This can lead to soil swelling and a corresponding increase in the soil porosity (volume fraction of voids in the soil) (Mitchell & Soga, 2005). In a similar manner, the presence of deicer ions in soil pore fluids increases the osmotic suction (i.e., dissolved ions contribution to water potential) of the soil. In this condition, soil has increased tendency to absorb more moisture from the atmosphere (Wang et al., 2012; Lu & Likos, 2004). Increase retention of deicer salt ions in soils beyond equilibrium condition (i.e., complete adsorption of cations and anions on available surfaces) can induce salt precipitate formation at concentrations ideal for their formation in the soil-pores. These precipitates can fill, clog the soil pores, and increase the soil density (Fig. 5), decrease the permeability, and change the water

holding/retention capacity of the soil. A logical deduction from these described conditions implies that the introduction of deicer salt solutions in soils can instigate several physical and chemical interactions within the soil particles that can ultimately affect the soil density and structure.

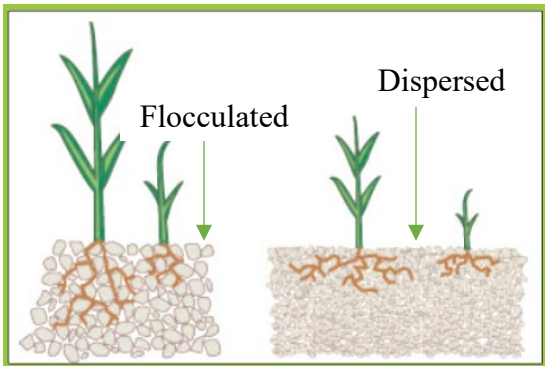


Figure 5. Effect of salts on soil's structure and plant health (Cunningham et al., 2008; Surabian, 2017)

2.5.5 Infiltration Rate and Hydraulic Conductivity

Changes in the hydraulic conductivity of soils was evaluated by Amrhein and Strong (1990) after leaching with sodium chloride (NaCl) and/or calcium magnesium acetate (CMA) solution for a winter season. Result obtained showed that the hydraulic conductivity for the sodium chloride leached soil was 88 times lower than that leached with CMA. Sodium ion was hypothesized to alter the soil's structure and reduce the hydraulic conductivity. This is because increased retention of sodium causes the dispersion of the particles and a corresponding reduction in the soil-pore sizes (Warrence et al., 2002; Lu & Likos, 2004; Shannon et al., 2020). Relationships between infiltration rate or hydraulic conductivity with soil dispersion, sodium adsorption ratio and concentration of salt solutions are different in swelling soils, mainly because of the complex nature of the clay minerals and soil-water interactions (Mitchell & Soga, 2005). Chaudhari et al. (2010) leached two clay soils with chloride salts and observed soil swelling. Their soil-pore sizes,

permeability, and hydraulic conductivity increased correspondingly. In both soils, they observed a change in the hydraulic conductivity of the soils as the salt concentrations were varied. A positive correlation between their experiment result and their model prediction validated their findings. Yousaf et al. (1987) also had a similar observation where increasing chloride salt concentration resulted in soil dispersion and a corresponding decrease in the hydraulic conductivity of the soil.

2.5.6 Water Retention Capacity of Soils

Application of deicer salts can alter the physiochemical characteristics of soil over time. Associated mechanisms for these changes include: (1) ion exchange between the deicer salt solution and soil (2) increased concentration of salt ions in pore water after equilibrium conditions (Mitchell & Soga, 2005). One of such changes in the soil's characteristics is its water retention capacity and it is often described using a soil-water retention curve. The soil water retention curve provides useful information between the gravimetric (mass) or volumetric (volume) water content in the soil and the soil suction (chemical potential of the soil-pore water) (Lu & Likos 2004). When deicer salts are applied to soils, ions from the salt solution can be retained on the soil surface, within interlayer of the soil minerals or exist in dissolved states or as precipitates in the soil-pore fluid. The retention of these deicer ions can alter the soil-water retention behavior of the soil through different mechanisms. For example, at a given water content or saturation in the soil, introduction of deicer salt ions into the soil can increase the soil suction, i.e., reduces the potential of soil water. Similarly, dissolved ions in the soil-pore fluid can increase the soil suction (from osmotic effect on the soil suction) (Lu & Likos, 2004; Akinleye et al., 2022). Also, if precipitates are formed within the soil pores, they can clog the pores, reduce the pore sizes and increase the soil suction at any given water content (mostly influencing the capillary regime of the soil-water retention curve) (Xing et al., 2017). Xing et al. (2017) evaluated the soil-water retention behavior

of loamy soils (having montmorillonite as the dominant clay mineral), that were leached with different chloride-based deicer salts at varying concentrations. The chloride salt crystals ($MgCl_2$, $CaCl_2$, NaCl, and KCl) were dissolved in distilled water to different concentrations and soil samples were soaked (saturated) in the salt solutions. The results obtained exhibited a dynamic correlation between deicer salt concentration and the soil-water retention behavior (Fig. 6).

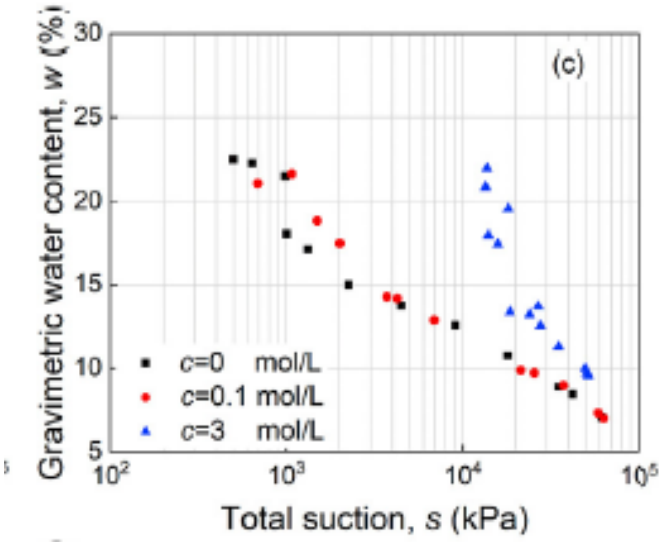


Figure 6. Effect of salinity on the water retention capacity of soil. c: concentration

Generally, when the salt concentration was increased, there was a corresponding increase in the soil suction. These behaviors were attributed to variation in the water adsorption capacity of the respective deicer salt ions, specific surface area (SSA) of the soil affected by the adsorbed ions on the soil surface including their water hydration kinetics (e.g., Akin & Akinleye, 2021). Soil-water retention curve, the various factors and mechanisms that influence it are fully described by Van Genuchten (1980).

2.6 Agro-based Addictive and Corrosion Inhibitors

Agro-based materials have received increased attention in recent years for use as deicers or additives with chloride-based deicers in improving the deicing capabilities and anti-corrosion effect on transportation infrastructure and the maintenance equipment of transportation agencies (Muthumani & Shi, 2017; Naziri & Shi, 2020). These agro-based materials are often produced from fermentation processes of molasses, corn, beet juice and other agricultural products (Cheng & Guthrie, 1998). Asides the associated increased cost to winter maintenance operations, they also pose environmental concerns of increased toxicity via biodegradation or interaction with other chemicals and materials in their applied environment (Naziri & Shi, 2020). Previous attempts have been made to understand the interaction between agro-based corrosion inhibitor (from apple pomace) and NaCl brine including the mechanism of corrosion inhibition (Honarvar et al., 2019). Chemical analysis on the agro-based materials showed that its major corrosion inhibiting agent can attach to steel surfaces and form a barrier layer. In addition, its adsorption followed the Langmuir isotherm while physical adsorption was dominant over chemical adsorption. This result is in synergy with previous studies that defined the efficiency of corrosion inhibitors to be related to their physiochemical properties such as their active functional groups, electronic structure, or electron density (Ryl et al., 2019). Cheng and Guthrie (1998) observed that organic materials (e.g., agro-based additives) can be broken down by soil microorganisms and temporarily create anoxic (anaerobic) conditions in the soil. Also, at cold temperatures, decomposition of the organic material in soil is reduced, and this condition increases their migration or transport potential into groundwater (Cheng & Guthrie, 1998). Findings from these literatures suggests the following: (1) similar mechanism of adsorption of the agro-based corrosion inhibitor ion to soil surface might be induced (2) physical adsorption mechanism of these inhibitors might contribute to reduced

chemical interaction/transformation induced by the presence between deicer cations (3) ions present in these inhibitor will compete for adsorption site with those in the deicer salts especially in fine grained soils having active mineral surfaces, and this might influence which ion migrates to groundwater. Elemental composition of beet juice has been found to include carbon, oxygen, sodium, chlorine, and potassium and thus might increase the concentration of ions from additives in deicing solutions.

2.7 Solute Transport Modeling

Estimating solute transport through the vadose zone is imperative for understanding its potential impact to surface and groundwater. However, subsurface soil is spatially heterogenous and an estimation of solute transport through them often requires rigorous field, and laboratory studies. While the history of the system could be extrapolated from the available field and laboratory records, there is no way of computing the future behavior of the full-scale system unless it is subject to conditions and assumptions (Šimůnek & van Genuchten, 2016). However, a full-scale field and laboratory experiment would be expensive, time-consuming, and constrained in difficult-to-access terrains or depths below the ground. Therefore, one practical option is to develop a model that reasonably represents the behavior of a full-scale system, replicates the pertinent physical parameters, and defines the significant characteristics of the transport phenomenon.

Several modeling approaches have been developed to complement field and laboratory data in describing the fate and transport of solutes including future predictions that are not readily available from field and laboratory data. Numerous analytical and numerical models are available for instantaneous pulses and continuous solute sources in the literature (e.g., Leij & Toride, 1997; Leij et al., 2000; Liu et al., 2000). Whatever model is used, one of the challenges in solute transport is determining the relevant parameters and coefficients (Bear, 1979). Analytical approaches (e.g.,

Liu et al., 2000) consider one or two governing processes, usually in a simplified flow domain with uniform transport characteristics. In contrast, numerical simulation of solute transport provides a system that can approximately incorporate the impacts of numerous controlling processes; and it is the only approach that can handle geometries and parameter distributions (Simone, 2006).

Irrespective, classical solute transport models (analytical and numerical) often fail to adequately describe solute transport mechanisms in most natural field soils because the subsurface environment is heterogeneous. Heterogeneity occurs at a hierarchy of spatial and time scales (Wheatcraft & Cushman, 1991), from microscopic scales involving time-dependent chemical sorption and precipitation/dissolution reactions to intermediate scales involving water and chemical preferential movement through macropores or fractures to much larger scales involving soil spatial variability across the landscape. Since solute transport is difficult to accurately model, numerous research often explores alternate methods like stochastic models that incorporate certain assumptions in the transport process in the heterogeneous system (Sposito & Barry, 1987).

The transport of solute in the sub-surface is often dependent or related to water flux in the soil. This condition is exacerbated with evaporation and precipitation processes including physicochemical interactions of the solute and soil particle. Generally, flow processes in soils are often described using Darcy's (Eq. 2) equation and Richard's (Eq. 3) equation that combined the Darcy-Buckingham equation for variably saturated flow with a mass balance equation.

$$Q = -KA\frac{\Delta h}{L} \tag{2}$$

Where, Q is the flow, L is the length, A is the cross-sectional area, K is the hydraulic conductivity and Δh is the potential gradient.

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[k(\Psi)\left(1 + \frac{\partial \Psi_m}{\partial z}\right)\right] \tag{3}$$

Where, θ is the volumetric water content,Ψ is the total potential, Ψ_m is the matric potential, K is the hydraulic conductivity and z is the distance.

The diverse scale from microscopic to macroscopic typically causes preferential flow processes that are difficult to characterize with Richard's equation. Water and dissolved solutes rapidly migrate via macropores (e.g., between soil aggregates, earthworm, or decaying root channels) or rock cracks, bypassing the soil or rock matrix. Other factors include soil textural changes, water repellency (Hendrickx & Flury, 2001; Ritsema & Dekker, 2005), lateral funneling of water due to sloped or other textural boundaries (Kung 1990). Such complex conditions often present saturated flow conditions as alternatives for experimental studies and model validation that can be extrapolated to variable saturated flow conditions.

As with water flow, mathematical formulations for solute transport are usually based on a mass balance that allows the solute to reside in all three phases of the soil (gaseous, liquid, and solid), allows a wide range of transport mechanisms (including advective and diffusive transport), and facilitates any chemical reaction that leads to losses or gains in the total concentration. Common solute transport modeling approaches are briefly described herewith.

2.7.1 Analytical Models

Analytical methods solve differential equations to find an exact solution. Analytical solute transport models usually yield a concentration equation for a specific time and location. Thus, one may immediately estimate concentration without numerical approaches involving time stepping. However, analytical solutions can only be derived for simplified transport systems with linearized governing equations, homogeneous soils, simplified transport domain geometries, and constant or highly simplified initial and boundary conditions (Liu et al., 2000). Analytical solutions for more complex circumstances, such as transient water flow or nonequilibrium solute transport with non-

linear reactions, are rarely accessible and must be obtained using numerical models (Šimunek, 2006). Furthermore, analytical solutions are commonly achieved by applying Laplace, Fourier, or other transforms to the governing equations, separating variables, or utilizing Green's function technique (Leij et al., 2000). Over the past 40 years, many analytical solutions of the linear advection–dispersion solute transport equations (Eqn. 4) (e.g., Ogata and Banks, 1961; Lindstorm et al 1967; Sauty 1980; van Genuchten & Wagnet, 1989; Toride et al., 1993) or their two- and three-dimensional equivalents have been developed and used for prediction and analysis of laboratory and field concentration distributions. Most of these solutions use solute transport equations with constant water content, and flux, q, for steady-state water flow in a homogeneous medium.

$$R_d \frac{\partial \theta}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial^2 c}{\partial x} \quad (4)$$

Where, R_d is the retardation factor, D is the dispersion coefficient, v is the velocity of the fluid, c is defined as either the resident concentration or volume average concentration, x is the distance.

2.7.2 Numerical Models

Numerical models are generally more practical than analytical models (Šimunek, 2006). They allow complex geometries to reflect natural geologic and hydrologic conditions, govern parameters in space and time, prescribe more realistic boundary conditions, and apply nonlinear constitutive relationships. Numerical approaches frequently subdivide the time and spatial coordinates into finite differences, elements, and volumes and reformulate the continuous form of governing partial differential equations in terms of a system of algebraic equations. Numerical methods typically involve intermediate simulations (time-stepping) between the initial condition and the desired time the solution is needed. Reviews of the history of development of various

numerical techniques used in solute transport modeling are given by van Genuchten & Wagnet, 1989; Šimunek, 2006).

2.7.3 Transfer Function Models

There is a substantial body of evidence indicating that classical solute transport models (analytical and numerical), despite their representations of pertinent chemical and microbiological processes as well as soil properties, frequently fall short in accurately depicting transport phenomena in most field soils. This is often attributed to the highly heterogeneous nature of the subsurface environment spatially and time scale (Wheatcraft & Cushman, 1991). This heterogeneity spans from microscopic scales, characterized by time-dependent chemical sorption and precipitation/dissolution reactions, to intermediate scales, encompassing the preferential flow of water and chemicals through macropores or fractures, and finally to larger scales, which encompasses the spatial variability of soils across the landscape. However, the issue of subsurface heterogeneity can be examined through process-based descriptions that aim to account for the impacts of heterogeneity at one or multiple scales. It can be addressed through the utilization of stochastic methodologies that integrate specific assumptions regarding the transportation process within the heterogeneous system (e.g., Sposito & Barry, 1987).

Jury (1982) developed an alternative formulation for solute transport called the transfer function model (Eqn. 5). This approach measures the distribution of solute travel times from the soil surface to a reference depth i.e., it is a function of a single variable. It was developed based on two main assumptions about the soil system: (a) the solute transport is a linear process, and (b) the solute travel time probabilities do not change over time. These two assumptions lead to the following transfer function equation that relates the solute concentration at the outflow end of the system with the time-dependent solute input into the system:

$$C_{out}(t) = \int_0^t C_{in}(t - t')\, f(t')dt' \quad (5)$$

Where C_{out} is the outflow concentration, C_{in} is the solute concentration, and t is time.

The outflow at time *t*, $C_{out}(t)$ [ML^{-3}], consists of the superposition of solute always less than *t,* $C_{in}(t - t')$ [ML^{-3}], weighted by its travel-time probability density function (pdf) *f (t)* [T^{-1}] (Jury and Horton, 2004). One important advantage of the transfer function approach is that it does not require knowledge of the various transport processes within the flow domain. By representing the transfer process through a probability density, all the physical mechanisms which contribute to variations in chemical transport are assumed to be unique function of the net amount of the solution.

CHAPTER THREE

3.0 Survey of USDOT Chloride Salt Use and Commonly Encountered Roadside Soils

3.1 Key Findings from Online Survey

A total of twenty-one (21) valid responses were obtained from the United States department of transportation (USDOT) personnels across sixteen states. Sodium and magnesium chloride were identified as the main chloride salts that are used for anti-icing, deicing, and pre-wetting winter maintenance operation. These salts have been adopted for use by various United States department of transportation (USDOT) agencies across various states based on several factors that are applicable to their region. For example, environmental conditions like snow intensity and road pavement temperature. A summary of some chloride salts adopted by some states for snow and ice maintenance activities are presented in Table 1. Commercially available chloride salts (deicers) often contain some corrosion inhibitors (e.g., organic amines, triethanolamine, and agro-based products). The corrosion inhibitors vary with the brand of salt (deicer) used. Furthermore, result from past evaluation indicates that these salts often contain trace concentrations of metals. For example, copper, cyanide, phosphorous, and nitrates were found in a 23% (w/v) sodium chloride salt brine solution (Mussato and Guthrie 2000). Copper, lead, zinc, arsenic, cadmium, and phosphorus were present in a magnesium chloride (30%-w/v) salt evaluated by Lewis (1997). Mussato and Guthrie (2000) also found phosphorus, sulfates, and nitrate in a 30% (w/v) calcium chloride salt.

Table 1. Commonly used chloride-based salts in the United States (survey response from DOT personnels)

State	Chloride Deicers (Salts)		
	Anti-icing	Deicing	Pre-wetting
Indiana	NaCl	NaCl	NaCl
Idaho	NaCl, $MgCl_2$	$MgCl_2$	NaCl, $MgCl_2$
Vermont	N/A	$CaCl_2$, $MgCl_2$	NaCl, $MgCl_2$
Connecticut	NaCl	NaCl; $MgCl_2$	$MgCl_2$
South Dakota	N/A	NaCl, $MgCl_2$	NaCl, $MgCl_2$
Maryland	$CaCl_2$, NaCl, $MgCl_2$	NaCl, $MgCl_2$	NaCl
Michigan	NaCl	NaCl	$CaCl_2$, NaCl
North Dakota	NaCl	NaCl	NaCl
Montana	NaCl, $MgCl_2$	NaCl, $MgCl_2$	NaCl, $MgCl_2$
Massachusetts	NaCl, $MgCl_2$	NaCl, $MgCl_2$	$MgCl_2$
Rhode Island	$CaCl_2$, NaCl, $MgCl_2$	NaCl	$CaCl_2$, NaCl, $MgCl_2$
Utah	NaCl	NaCl	NaCl, $MgCl_2$
Oregon	$MgCl_2$	NaCl, $MgCl_2$	$MgCl_2$
New Hampshire	NaCl, $MgCl_2$	NaCl, $CaCl_2$, $MgCl_2$	NaCl, $MgCl_2$
Ohio	NaCl	NaCl, $CaCl_2$	NaCl, $CaCl_2$
Maine	NaCl, $MgCl_2$	NaCl, $MgCl_2$	NaCl, $MgCl_2$

3.2 Chloride Salt Application

A study by Fischel (2001) examined the application rates of some chloride salts used by the Colorado Department of Transportation (CDOT). Magnesium chloride was the most common

chloride salt used in the state and the application rate for anti-icing operation was about 35-45 gal/lane-mile. For deicing operations, the application rate varied from 40 to 60 gal/lane-mile. Under heavy snowpack conditions, the application rate was about 60 gal/lane-mile. Similar application rates are used in other states; however, this is dependent on the environmental conditions (snow, ice, temperature, etc.) peculiar to each region. Ultimately, deicer application methods and rates change from one place to another.

3.3 Commonly Encountered Soil Types in the United States

With respect to the most encountered roadside soil 20 ft from the road pavement, coarse to medium-grained soils (i.e., particle gradation) and sandy loam (United States department of agriculture soil classification system) were predominant as indicated from the online survey responses. The soil contains a larger fraction of sand (50 - 2000 μm) and smaller fractions of silt (2 - 50 μm) and clay (< 2 μm) particles, and this raises concern for increased migration rate of the chloride salts through soil to ground water.

3.4 Agro-based Additive

Beet juice (i.e., by-product of the fermentation of beet fruit) is the most used agro-based organic additive, and corrosion inhibitor for winter maintenance operations across the United States department of transportation (USDOT). A summary of agro-based addictive adopted by several USDOT agencies is presented in Table 2. More often, beet juice was applied at 20% wt. of the chloride salt solution.

Table 2. Commonly used agro-based deicer additives in the United States (survey response from DOT personnel)

State	Agro-based Additives	Percent Per Weight (%) (Tons)
Indiana	Beet Heet	20
South Dakota	Beet Juice	-
Michigan	Boost	1
North Dakota	Beet Juice	20
New Hampshire	Ice Be Gone	20
Ohio	Beet Heet	10
Maine	Magic-0	70-100

CHAPTER FOUR

4.0 Experiment Method and Processes

4.1 Soil Selection

With respect to the findings from the online survey, a replica of sandy loam soil was formulated in the laboratory. Topsoil that was excavated from the new Pullman-Moscow regional airport construction site in the Pacific Northwest, Washington state, was purchased from SYG Nursery and Landscaping Inc, Pullman, WA. The topsoil was mixed with Sakrete sand that was purchased from the Pullman building supply, Pullman WA. The soil samples were mixed and formulated to include less than 8% of clay (Table 3), with a larger fraction of silt and sand to obtain a loam soil with similar soil particle fractions like those commonly encountered in roadside soils in the United States as reported in the survey response.

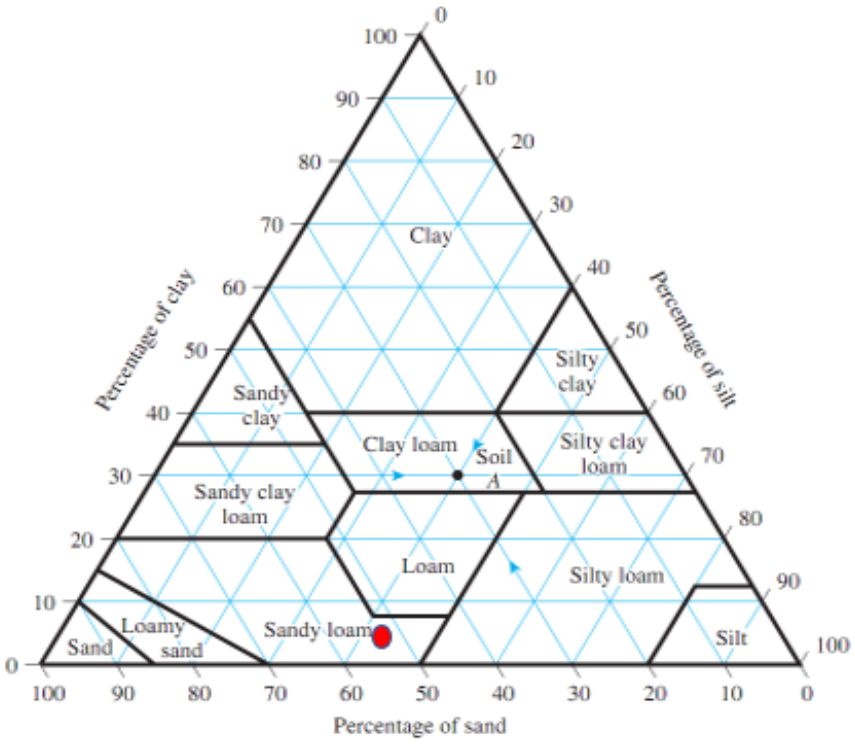


Figure 7. Soil classification following USDA standard

Table 3. Particle size fraction of test soil

Soil Particle Fraction	Lab Soil (50% Topsoil + 50% Sand)
Clay (%)	7.46
Silt (%)	40.35
Sand (%)	52.17
Gravel (%)	0.00

4.2 Sieve Analysis and Hydrometer Test

Sieve analyses were conducted on the soil to determine its particle size distribution in accordance with ASTM standard (ASTM D6913). The fine contents (< 75 μm) collected in the pan were evaluated using hydrometer analysis in accordance with ASTM D7928-21 (or the active standard during testing) to determine the fraction of clay and silt in the soil. The combined result from the sieve analysis and hydrometer test was used to plot the particle size distribution (PSD) curve. Other parameters that were obtained from the combined data and PSD curve are the uniformity coefficient (Cu), coefficient of curvature (Cc), the effective grain size (mm), and the medium grain size (mm) of the soil.

4.3 Soil Compaction, Maximum and Minimum Void Ratio

Soil compaction was carried out to determine the maximum dry density and optimum moisture content of the soil. They gave an idea on the packing density to utilize during soil column experiment or a density relative to the maximum dry density of the soil. Compaction of the soil was done using the standard proctor compaction tests in accordance with ASTM D698. Results from this experiment provided information on the maximum dry density (MDD) (g/cm^3) and optimum moisture content (OMC) of the soil. Soil was compacted in the columns at a relative value to the MDD and OMC or in-situ values representative of field condition. The maximum (e_{max}) and minimum (e_{min}) void ratio of the soil was determined in accordance with ASTM D4254 and ASTM D4253. These values were used to obtain the relative density of the in-situ soil.

4.4 Specific Gravity

The specific gravity of the soil was determined in accordance with ASTM D854-14. The result from this experiment provided information on the density of the soil and this value was utilized when calculating the degree of saturation of the soil, before and after the soil column test.

4.5 Loss of Ignition Test

Organic matter (OM) content in the soil was measured using the loss of ignition (LOI) test following procedure described by Scalia et al. (2014) and ASTM D7348-21. Oven-dried (105° C) soil samples will be kept in a muffle furnace (550° C) for 4 h. The mass difference before and after the furnace was used to calculate LOI and related to soil organic content.

4.6 Soil pH

The average pH of the soil samples was measured using a digital Milwaukee MW102 PRO+ integrated with a temperature meter with ATC. 1 g of homogenized biochar samples were added to 50 ml plastic vial tubes. 10 ml deionized water was added, vortexed, and allowed to equilibrate for 24 h before measurement in triplicates.

4.7 Cation Exchange Capacity

The cation exchange capacity of the soil was determined by using the ammonium displacement method in accordance with ASTM D7503-18. In addition, other parameters like the soluble and bound cations were obtained using this method.

4.8 Batch Experiment for Sorption Isotherm and Kinetics

Batch experiment on test soil was done in accordance with ASTM D4646. To obtain the sorption isotherm, about 1g of the test soil was weighed and transferred into 50 ml vial tubes. A series of sorbate solutions (Table 4) were prepared at different concentrations (~10) at room temperature,

and their pH was adjusted to neutral (7). About 20 ml of the sorbate solution were then added to the vial tubes and capped appropriately. Each sorbate concentration/experiment was carried out in triplicates to obtain an average value. The tubes were then placed in a sample shaker at 30 rpm for 24 hrs. for equilibrium to be achieved. Afterwards, the samples were left to stand on a table for another 24 hrs. The mix was then filtered using a 0.22μm pore diameter glass fiber filters through 0.00 um and about 10 ml of filtrate was collected for elemental testing. The concentration of the ions in the filtrate was then measured using a TSTAR XRF. The equilibrium adsorption data were fitted to two common isotherm models: Langmuir and Freundlich isotherms (Eqns. 4 and 5 respectively)(Fig. 8).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F \mathrm{C}_e^{\frac{1}{n}} \tag{5}$$

$$q_e \; is \; obtained \; as$$

$$q_e = \frac{(C_o - C_e)V}{m} \tag{6}$$

Where: q_e is the adsorbed amount at equilibrium (mg/g), C_e is the equilibrium concentration (mg/l), C_o is initial concentration (mg/l), q_m maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F is the adsorption capacity (mg/m), n is the adsorption intensity, V is the solution volume(L) and m is the biochar mass (g).

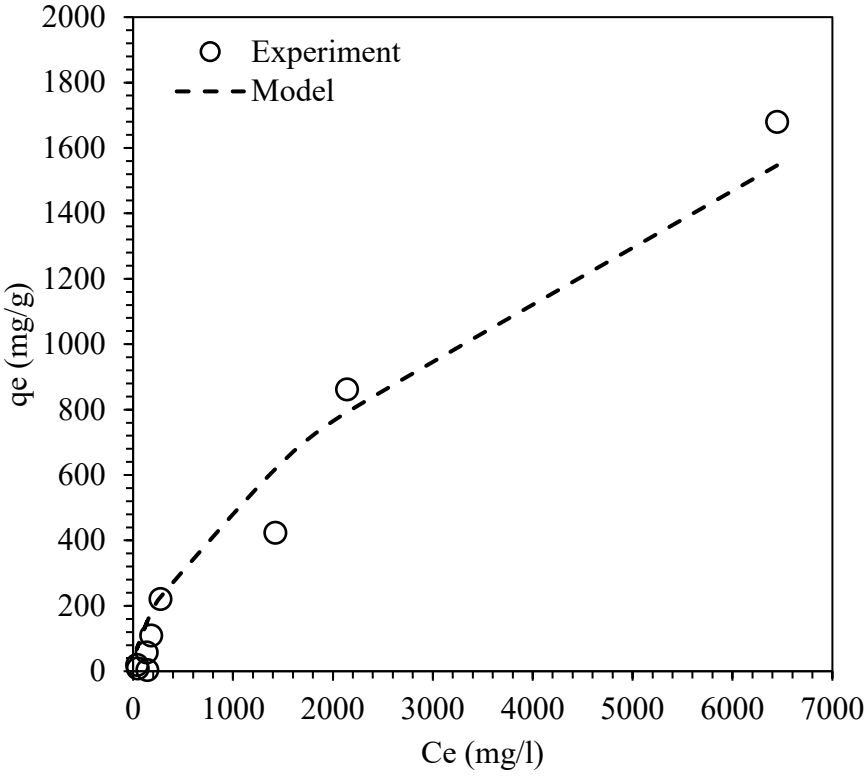


Figure 8. Non-linear experiment data fit to Langmuir isotherm model

4.9 Soil Column Experiment

Vertical and horizontal rigid wall soil columns with a height of 32 inches and diameter of 4 inches were designed and fabricated (Fig. 9). Both ends of the soil column were fitted with flexible tubes for inlet of the influent solution and outlet for the effluent solution. A reservoir for the influent solution with an outflow opening was placed at same height as the top of the soil column to allow gravity flow of the influent solution from the reservoir into the soil column.

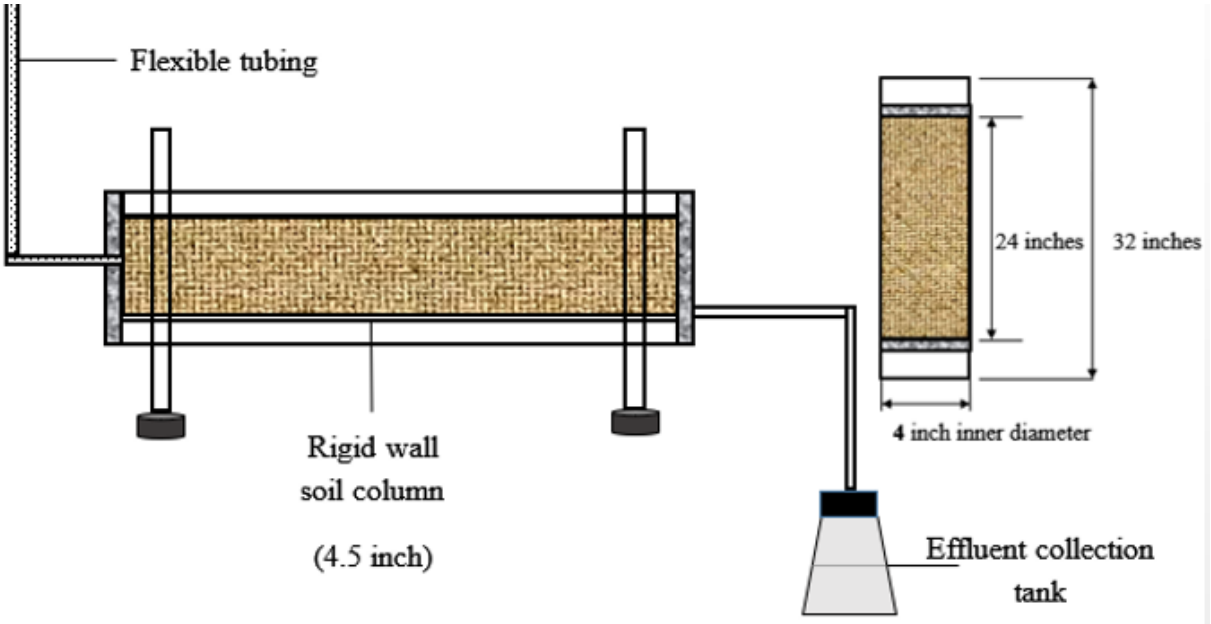


Figure 9. Laboratory soil column setup

For both the vertical and horizontal soil columns, the test soil was compacted to the same predetermined density and moisture content in the rigid wall columns i.e., using disturbed soil samples. The column was designed to allow for inflow and outflow of the infiltrating fluid i.e., no ponding of water. The compacted soil in the columns was slowly saturated from the outflow tube opening using a low ionic strength solution (i.e., sodium and magnesium chloride solution) to remove entrapped air. To ensure complete saturation, the low ionic strength solution was allowed to overflow. After column saturation, the flow was reversed under a constant hydraulic head using a Marriot tube. Once the steady-state condition was verified, that is, when flux (Q) variations were below about 5%, the influent solution was then replaced with those of the actual concentration regimes as described in Table 4. Effluent samples were collected from the outflow tube at predetermined time and pore volume (5 samples per pore volume) for elemental testing.

Table 4. Chloride salt concentration and dilution

Solute	Condition 1	Condition 2	Condition 3
NaCl	23% (w/v)	1:30 dilution of condition 1	1:90 dilution of condition 1
NaCl + Beet Juice	23% + 20% Beet Juice (wt.)	1:30 dilution of condition 1	1:90 dilution of condition 1
$MgCl_2$	30% (w/v)	1:30 dilution of condition 1	1:90 dilution of condition 1
$MgCl_2$ + Beet Juice	30% + 20% Beet Juice (wt.)	1:30 dilution of condition 1	1:90 dilution of condition 1

4.10 Elemental Measurement Using TSTAR X-ray fluorescence Device

Effluent samples collected from the outflow tube from the soil column were vortexed for 1 min to homogenize the sample. 1 ml of the vortexed samples were collected using a pipette into clean eppendorph tubes (epi tube). The tubes were spun in a centrifuge for 3 mins at 4000 rpm to pellet soil particles that might be present in the sample. 100 ul of the supernatant was then transferred to a new epi tube. The supernatant was then diluted with 100 ul of 100 ug/mL scandium standard and 800 ul of deionized water to make a final dilution ratio of 1:10. The diluted samples were then vortexed again to homogenize the solution.

Quartz discs were cleaned thoroughly by first washing under running tap water for about 30 secs. The washed discs were cleaned using 99% assay ethanol solution, submerged in RBS solution and 4% nitric acid solution respectively for 1.5 hrs. and 2 hrs. and heated at a temperature of 80^{o} c

under a fume hood. The cleaned discs were dried in a 60^{o} c oven for 12 hrs. After drying, the quartz disc surfaces were coated with 10 ul of serva solution (silicon based) to achieve a hydrophobic surface for high-quality sample deposit. The serva coated disc surfaces were placed under a heat lamp to dry out. 10 ul aliquot from the vortexed sample were then dropped on the center of the discs using a centering device and placed under a heat plate to dry out. Prior to coating the disc surfaces, blank measurements were obtained using a Bruker S4-T-STAR XRF (Fig. 10) device to check the cleaned discs for contamination.

For sample testing, the dried discs were placed in the XRF trays and slotted into the device. Elemental concentrations were measured by selecting the tungsten light (W-L) x-ray tube compactable with the scandium standard solution that is integrated with the device. The scandium standard added served as quality control and internal standard to verify results and device efficiency throughout testing.

Figure 10. Elemental analysis using a Bruker S4-TSTAR XRF device

4.11 Machine Learning Modeling of trained test data

A physics-based machine learning approach was utilized to train and predict the experiment data to be able to predict experiment results beyond measured experiment pore volume (See Fig. 11). The predicted data provided useful information that was used in this study to estimate model fitting parameters when result are projected to beyond the measure pore fluid volume. We employed separate hybrid modeling approaches for the three output variables (Y_1 - Na^+ concentration; Y_2 - Mg^{2+} concentration; Y_3 - Cl^- concentration) with each model considering all four input variables. Based on the data characteristics, variables X_1(chloride salt), X_2(beet juice), and X_3(dilution) were defined as discrete categorical variables, whereas X_4(pore volume) and all output variables (Y_1—Y_3) were treated as continuous numerical features.

Given the significant presence of zero values in Y_1 (Na^+ concentration) and Y_2 (Mg^{2+} concentration), a two-stage modeling framework was adopted: (1) a classification stage to distinguish zero from non-zero values, followed by (2) a regression stage to predict the magnitude of non-zero values. In contrast, Y_3 (Cl concentration) exhibited continuous distribution without zero inflation, and thus only a regression model was trained.

Considering the inclusion of categorical input variables, we utilized the CatBoost library-a gradient boosting framework based on decision trees-implemented in Python for both classification and regression tasks (Dorogush et al., 2018). The CatBoostClassifier was trained on the full dataset to identify zero and non-zero cases, while the CatBoostRegressor was subsequently fitted on the subset of samples where the target values (Y_1 and Y_2) were greater than zero.

Tree-based models generally lack extrapolation capability for unseen values (Cai et al., 2023), which is, however, required for X_4 in this study. As a result, an additional polynomial ridge regression was fitted using the CatBoostRegressor predictions and X_4 as input features. The final

output predictions were then adjusted through this correction model to enhance the extrapolation performance. The specific hyperparameters configured for the models are detailed as in the following Table 5.

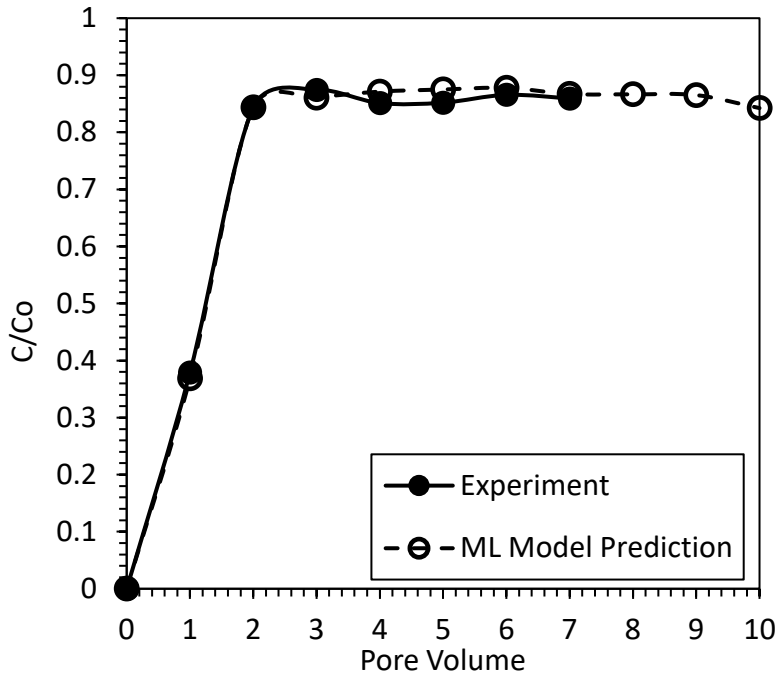


Figure 11. Machine learning prediction of trained test data

During data preprocessing, the “Vertical” dataset, consisting of 230 samples, was divided into a training set (186 samples, 81%), a validation set (21 samples, 9%), and a testing set (23 samples, 10%). Similarly, the “Horizontal” dataset, containing 172 samples, was divided into a training set (138 samples, 80%), a validation set (16 samples, 9%), and a testing set (18 samples, 11%). The training and validation sets were used for model development, while the testing set was used to evaluate the final model’s performance, particularly its predictive accuracy.

Table 5. Hyperparameter setting for both classification and regression models

Model	Hyperparameter	Value
CatBoost	iterations	500
	depth	6
	Learning rate	0.05
	verbose	0
	random seed	42
Ridge Regression	polynomial degree	2
	alpha	1.0

During data preprocessing, the “Vertical” dataset, consisting of 230 samples, was divided into a training set (186 samples, 81%), a validation set (21 samples, 9%), and a testing set (23 samples, 10%). Similarly, the “Horizontal” dataset, containing 172 samples, was divided into a training set (138 samples, 80%), a validation set (16 samples, 9%), and a testing set (18 samples, 11%). The training and validation sets were used for model development, while the testing set was used to evaluate the final model’s performance, particularly its predictive accuracy.

CHAPTER FIVE

5.0 Result and Discussion

5.1 Particle Size Distribution

The particle size distribution of the test soil is presented in Figure 12. Result was obtained from a combined extrapolation of wet sieve analysis and hydrometer analysis of the test fraction passing the sieve #200. Result shows that the test soil is composed of ~52.2% sand, 40.4% silt and 7.4% clay. Using the USDA classification system, the soil is classified as sandy loam soil. This is the same as the commonly encountered roadside soil observed and reported by the DOT personnels.

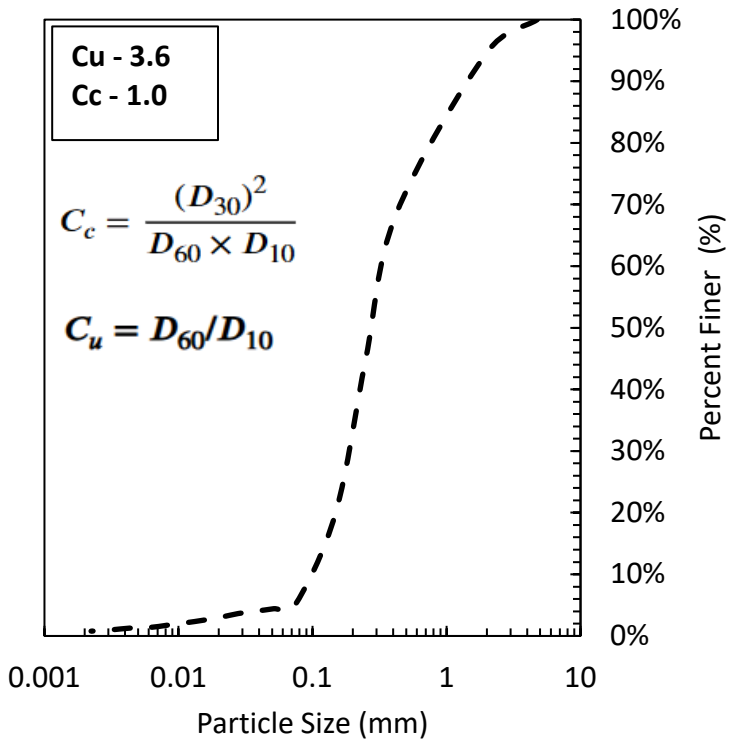


Figure 12. Particle size distribution of the test soil

With a uniformity coefficient of 3.6 (obtained as the ratio of diameter of particle size with 60% finer to the diameter of particle size with 30% finer) and coefficient of curvature of 1, it is ascertained that the soil is well graded with a wide range of particle sizes (sand to clay).

5.2 Soil Density and Specific Gravity

The maximum dry density and optimum water content of the test soil obtained from the standard proctor compaction test was 1.73 g/cm^3 and ~15% respectively (Fig. 13). The specific gravity of the soil was obtained as 2.7 and this value is typical for soils formed from the soil mineral, quartz e.g. sand.

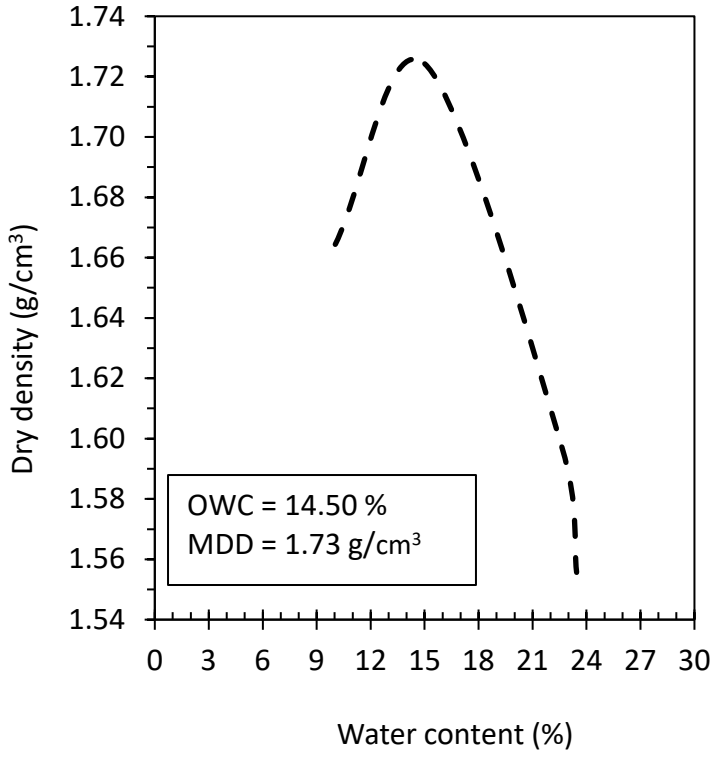


Figure 13. Standard proctor compaction curve for test soil

The relatively low MDD value is characterized by high percentage of fines (~54.8%) that is influenced by the shapes of the particles (e.g., plate-like or angular for clays and silts) limiting

interlock of the soil particle in the presence of water to achieve a higher density. Also, the OWC value obtained is indicative of the presence of cohesive soil (clay and silt) requiring a significant amount of water to achieve its MDD.

5.3 Soil Organic Matter, pH and Cation Exchange Capacity

Cation exchange capacity of the test soil was obtained as 8.82 meq/100g. This CEC value is typical of sandy loam soil (5 -10 meq/100 g) and clay content derived from the clay mineral kaolinite (3-15 meq/100 g) (Mitchell & Soga, 2005). The organic content of the test soil was found to be 4% by dry weight of the soil. As described by Brady and Ray (1996), this value falls within soils having a medium organic matter content. The average pH of the soil was 6.2 and can be classified as having a near neutral pH value.

5.4 Sorption Isotherm of the Test Soil

Result from the batch experiments were fitted to the Langmuir and Freundlich isotherm models nonlinearly as presented in Table 6. The Langmuir isotherm model assumes monolayer sorption on a homogenous surface, while Freundlich adsorption model describes those on a heterogenous surfaces. Generally, both models were a good fit for the experiment data with R^2 values ranging between 0.96 – 0.98 except, in a case where the R^2 value was 0.55 and 0.76 for Na^+ adsorption in sodium chloride with beet solution. Adsorption of the ions on the soil particle surface exhibited characteristics of homogenous and non-homogenous adsorption. Thus, the chloride salt ions were adsorbed on monolayers of the soil surface, but these surfaces weren't uniformly distributed i.e., there is a distribution of ion adsorptions on the nonhomogeneous surfaces having different affinity and energy of adsorption to different ions. The test soil exhibited this dual adsorption behavior as a result of the following possible reasons: (1) the presence of multiple clay minerals (Fig. 14) that possess different structures, surface charge and arrangement (2) the metal oxide and hydroxide

content as observed in the XRF result that have different affinity for adsorption of specific ions often termed as ligand exchange (3) the complexity of the soil organic matter structure present in the soil that is often complexed with several surface functional groups with varying binding strength (4) carbonates in the soil that often contributes to anion adsorption (5) the arrangement and presence of a spectra of pore sizes that are accessible to the ions from sorbates (ions) (Mitchell & Soga, 2005).

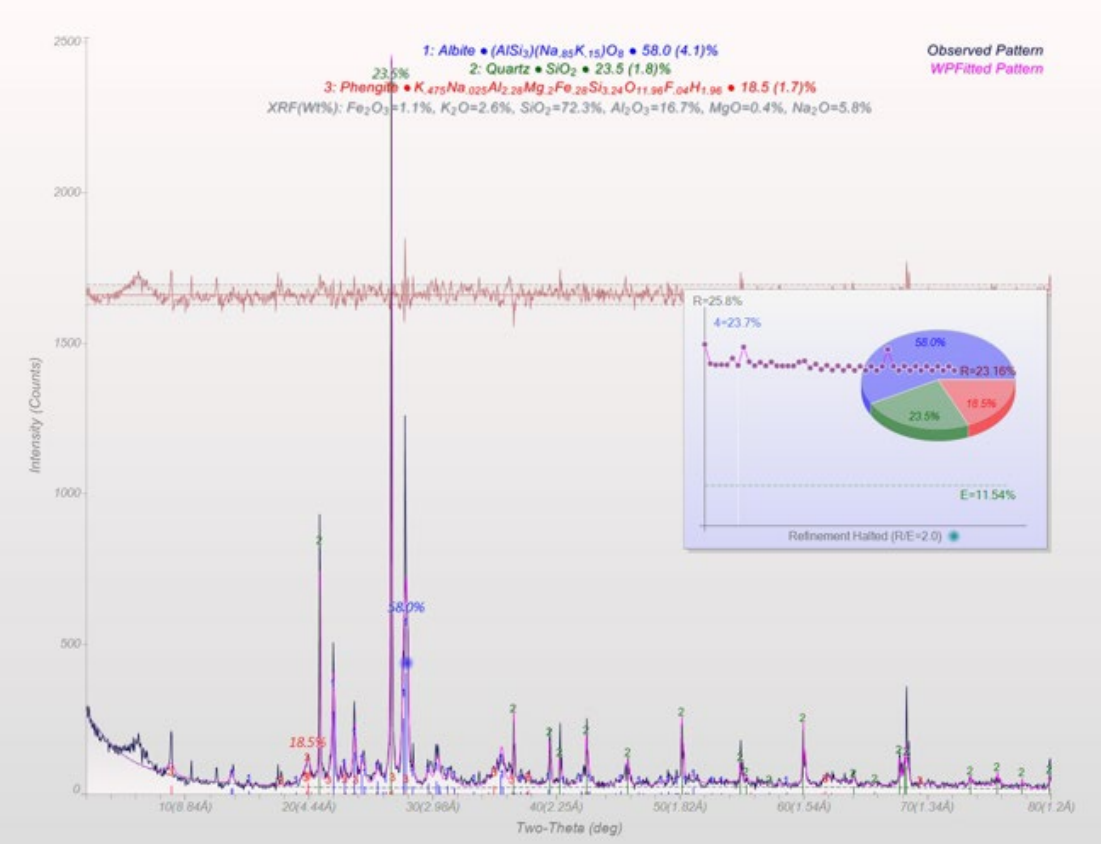


Figure 14. Mineralogy of the test soil

An example of the sorption isotherm models fit to the experiment data tested at 25^0 C and pH of 7 is shown on Fig. 15. Sorption capacity of the test soil from the Langmuir isotherm model is reflected by the Q_m parameter provided the adsorption data of the experiment fits the model. The Q_m parameter is a theoretical maximum number of ions that can be adsorbed per unit mass of the

adsorbate (soil in this study) when all the adsorption sites are occupied. This is also indicative of the number of sites available for sorption. As seen in the result presented in Table 6, the region that defines the Q_m parameter which is the plateau defining the adsorption saturation in a typical Langmuir isotherm model isn't reached. Hence the Q_m values described here are an extrapolated estimate and not the measured capacity. Without the presence of beet juice, the adsorption of Na^+ on average had the highest adsorption capacity on the test soil. However, this result is in contrast with conventional knowledge on the hierarchy of ion adsorption where cations with higher valence charge adsorb better than those with lower valence charge (i.e., $Mg^{2+} > Na^+$) (Mitchell & Soga, 2005). Conversely, considering the value of the K_L parameter that is Related to the binding energy/affinity between the adsorbate and adsorbent surface, Mg^{2+} had a higher affinity for adsorption on the test soil.

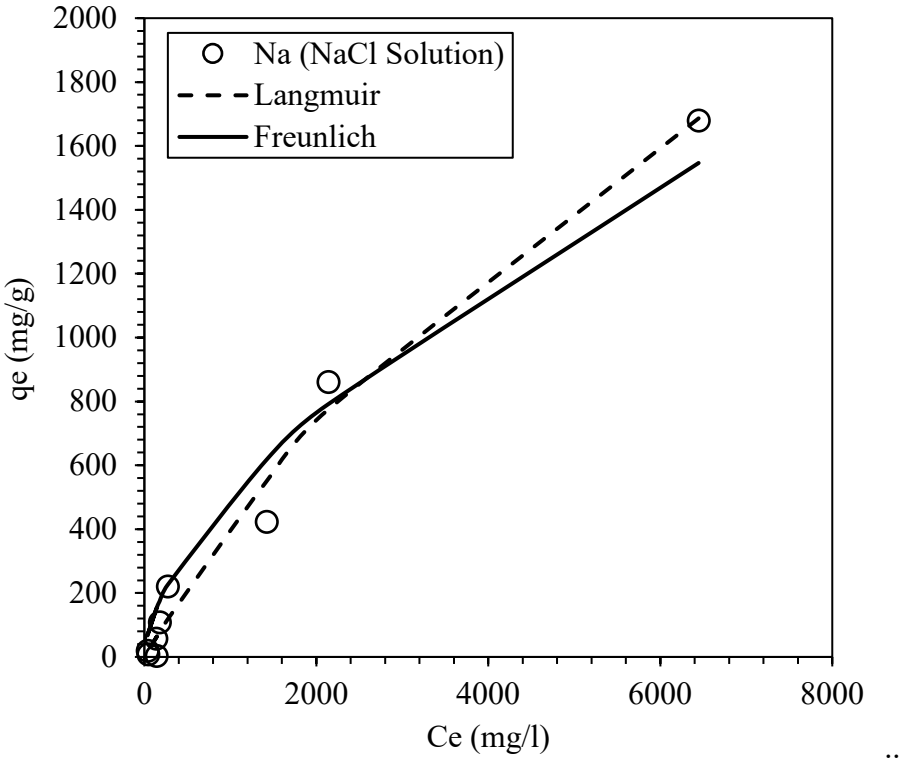


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Figure 15. Langmuir and Freundlich model fit to adsorbate sorption on test soil

Table 6. Test soil parameter from sorption isotherm models

Sample (pH =7)		Langmuir			Freundlich		
		$q_{max\ (mg.g^{-1})}$	K_L ($L.mg^{-1}$)	R^2	K_f ($mg^{1-n}L^ng^{-1}$)	n	R^2
NaCl	Na^+	4.06	1.0E-4	0.98	2.09	1.31	0.98
	Cl^-	4.07	3.0E-4	0.98	13.40	1.65	0.97
NaCl + Beet	Na^+	4.36	2.36	0.55	3.2E-05	0.50	0.76
	Cl^-	4.05	3.0E-5	0.91	7.9E-04	0.60	0.98
$MgCl_2$	Mg^{2+}	8.73	0.01	0.92	4.60	0.96	0.99
	Cl^-	4.45	2.7E-4	0.98	3.68	1.25	0.99
$MgCl_2$ + Beet	Mg^{2+}	9.45	2.0E-3	0.99	18.70	0.98	0.98
	Cl^-	3.86	0.03	0.94	448.96	2.79	0.96

Several conditions have been described to produce exceptions where cations with lower charge valency have higher adsorption on the adsorbent. For example, in acidic soils where H^+ compete for adsorption sites, hydrolyzation of cations that makes their adsorption more complex (e.g., Mitchell & Soga, 2005). Also, in soils with high oxide content, cations with lower valence charge are favorable of the formation of inner-sphere complexes. Furthermore, the presence of soil organic matter can be a precursor to the formation of soluble complexes with organic ligands and a consequent reduction in the concentration of free ions. The test soil in this study had a pH value of 6.2 and thus cannot be considered acidic. In addition, batch experiments for the sorption tests were carried out at a neutral pH (7) hence, the hydrolyzation of the cations is unlikely. The oxide content of the test soil and the formation of soluble complexes with organic ligands were not

evaluated hence, associating the anomaly in the sequence of adsorption of the cations cannot be established.

With the addition of beet juice, the adsorption capacity (Q_m) for Mg^{2+} increased by over 10 folds. However, considering the K_L parameter that defines the affinity between the adsorbent and the adsorbate, the affinity for Mg^{2+} adsorption was more pronounced without the presence of beet juice. A possible explanation for this will be the modification of the soil surface with the addition of beet juice. Beet juice is an organic molecule that contains functional groups including phenols, carboxylic and many others (Nazari et al., 2020). We infer that it is possible that the soil particle surfaces were coated with beet juice molecules (functionalization) thus creating a denser layer of adsorption with functional surface groups. This type of surface coating was observed by Nazari et al. 2020 where the addition of beet juice to chloride salt used as deicer reduced the corrosion effect on buried steel pipes. With introduction of these surface functional groups, a corresponding increase in the Qm value will be observed. With respect to the paradox of a decrease in affinity (K_L) of Mg^{2+} when the soil particle surface is coated with beet juice, the new layer of adsorption form by the beetroot molecules may possess a weaker electrostatic attraction. Hence while there is more adsorption of the cation on the organic surface, the strength of adsorption is however weak. Thus, it can be likened to trading the quality of adsorption on the soil particle surface with quantity of adsorption of the beat root coated surface.

This same phenomenon wasn't observed with Na^+. It is more probable that with Na^+ having a lower valence charge, there is a corresponding weaker electrostatic bond. Hence the new surface created by the beet juice might be quite ineffective at binding the sodium ion leading to no significant change in Q_m value with or without the addition of beetroot. Furthermore, the presence of functional groups such as the carboxyl group has been reported (e.g., Mitchell & Soga, 2005) to

preferentially and strongly bind to divalent cations like Mg^{2+} than with monovalent cations like H^{+}. For Cl^{-}, there was no observed trend in the Q_m values and affinity (K_L) for adsorption test with beetroot and without beetroot. At neutral pH, the molecules of beet juice should be complexed negative charges owing to the presence of the functional group. In addition, soil particle surfaces are often negatively charged especially with the presence of clay particles. Hence electrostatic repulsion of the Cl^{-} ion is expected and should be pronounced with the introduction of beetroot juice because of its functional groups. However, if an increase in adsorption affinity is observed, other mechanisms except electrostatic attraction like the formation of specific chemical bonds e.g., ligands formation with specific metals present in the soil. Such examples of chloride adsorption have been documented by (Brady and Weil, 2008).

5.5 Soil Column Result

The parameters of the soil column for the experiment are presented in Table 7. The average time for achieving 1 pore volume of flow through the vertical soil column was three days (72 hrs.) while the horizontal soil lasted for five days (120 hrs.). Five (5) samples were collected per pore volume, and a total of 7-10 pore volume was achieved for each experiment. The pressure head of the influent solution was adjusted as required to achieve a continuous flow throughout the soil column. An example of the breakthrough curve for one of the soil column experiments is presented on Fig. 16. The breakthrough of the solute was achieved at about 1 pore volume, and this is typical for each of the soil column experiments. After the solute breakthrough, the effluent solution maintained a relatively constant concentration for the rest of the soil pore volume. This result exemplifies the complete adsorption and desorption of the ions in the chloride salt solution on the soil particle surfaces after about 1 pore volume. The result agrees with theoretical understanding

of breakthrough curves of solute from a continuous flow source that exhibits a constant concentration gradient after the breakthrough pore volume.

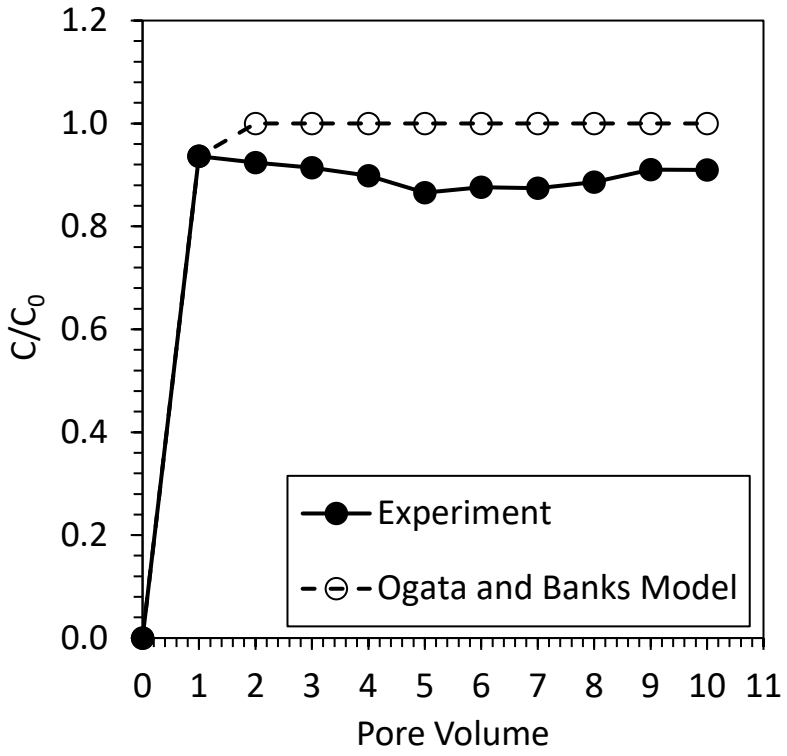

Figure 16. Solute breakthrough curve

Table 7. Soil column parameters

Diameter (cm)	10.795	
Length (cm)	72	
porosity (n)	0.48	
Total Volume (cm^3)	6625	
Pore Volume	3215.697	
	Initial Concentration of Solute (g/l)	
	Cl^-	Na^+
1:90 NaCl	1.54	1.0
1:30 NaCl	4.60	3.0
1:90 NaCl + Beet	1.24	0.80
1:30 NaCl + Beet	3.72	2.41
	Cl^-	Mg^{2+}

1:90 MgCl2	2.46	0.86
1:30 MgCl2	7.40	2.60
1:90 MgCl2+ Beet	1.99	0.68
1:30 MgCl2 + Beet	5.96	2.04

The plot of the breakthrough curve also hints on advection as the main transport process that dominated the soil column. Hence no dispersion front was observed in all the soil column experiments. This is typical in sandy soil with dispersivity values of about 1 cm. The advection-dispersion parameters from the soil column results are presented in Table 8.

Table 8. Advection-dispersion parameters from soil column experiment

Chloride Salt	Vertical Soil Column			
	Cl^-		Na^+	
	Dispersion Coefficient	Retardation Factor	Dispersion Coefficient	Retardation Factor
1:90 NaCl	0.03	0.83	0.02	1.09
1:30 NaCl	0.02	1.02	0.01	1.55
1:90 NaCl + Beet	0.03	0.73	0.02	1.05
1:30 NaCl + Beet	0.02	0.98	0.02	1.00
	Cl^-		Mg^{2+}	
1:90 $MgCl_2$	0.02	0.99	0.01	1.15
1:30 $MgCl_2$	0.02	0.98	0.01	1.17
1:90 $MgCl_2$+ Beet	0.02	0.95	0.01	1.09
1:30 $MgCl_2$ + Beet	0.02	0.90	0.01	1.16
	Horizontal Soil Column			
	Cl^-		Na^+	
	Dispersion Coefficient	Retardation Factor	Dispersion Coefficient	Retardation Factor
1:90 NaCl	0.01	1.23	0.01	1.09
1:30 NaCl	0.01	1.15	0.01	1.09
1:90 NaCl + Beet	0.01	1.24	0.01	1.05
1:30 NaCl + Beet	0.01	1.09	0.01	1.05
	Cl^-		Mg^{2+}	
	Dispersion Coefficient	Retardation Factor	Dispersion Coefficient	Retardation Factor
1:90 $MgCl_2$	0.01	1.01	0.01	1.16

1:30 $MgCl_2$	0.01	1.17	0.01	1.22
1:90 $MgCl_2$+ Beet	0.01	0.99	0.01	1.04
1:30 $MgCl_2$ + Beet	0.01	1.13	0.01	1.07

In the vertical soil column, the retardation factor for the chloride ion was between 0.73 – 1.02. The retardation factor describes the delay experienced by a solute because of its interaction with the absorbent (soil). A retardation factor of 1 often signals little or no interaction with the soil as it travels through the column. This results of the chloride ion represents a typical example of a conversative or tracer ion with no interaction with soil particle surfaces. The chloride ion has a negative charge and thus experiences electrostatic repulsion with the soil particle surfaces that are also often negatively charged. Hence, it is expected that such conservative ions will experience its breakthrough faster than other ions with positive charge.

For the Na^+, the highest retardation was observed in the 1:30 NaCl influent into the soil. This is a higher concentration of Na^+, and this is expected to have increased interaction with the soil as compared to the 1:90 dilution Na^+. However, in comparison with the Mg^{2+}, an opposite trend is expected where Mg^{2+} should have an increased adsorption on the soil particle surface. A similar trend was observed in the sorption isotherm result in section 2.4 however, the fundamental mechanism for the anomaly in this trend cannot be established and further evaluation is required for a defined conclusion. For both Na^+ and Mg^{2+}, when beetroot juice was introduced, there were slight reductions in the retardation factors. For the 1:30 $MgCl_2$ and 1:90 NaCl solutions, this reduction is minute and thus a definite change in retardation factor cannot be inferred. For the other solutions, the addition of beetroot juice is believed to have interacted with the soil particle surfaces to cause a reduction in the interaction with the cations. As observed in the isotherm data where the addition of beetroot juice increased the adsorption of Mg^{2+}, the opposite trend in the soil column

experiment data can be explained as follows; (1) the soil column experiment is a dynamic experiment consisting of continuously flowing beetroot and salt solution. Beetroot juice, being a more viscous fluid, can clog tiny pores within the soil and reduce the accessible surface area within the soil and cause preferential flow (2) the isotherms measures the concentrations of these ions at equilibrium, however, with the high porosity to the test soil, the probability for an equilibrium condition is reduced (3) the beetroot juice can compete with soil for cation adsorption owing to the presence of functional groups in it. Thus, the cations are held tightly to the beet juice thus reduction the interaction of these cations with the soil. This reduction in the retardation of the cations through the soil column is also exhibited in the horizontal soil column results. A reduction in the retardation factor was observed to all cations at the different solute concentration.

CHAPTER SIX

6.1 Summary and Conclusion

In the last decade, chloride (Cl^-) salts have been increasingly used as anti-icers or deicing chemicals on road pavement surfaces in North America to improve transportation safety and mobility during the winter season. They lower the freezing point of water and reduce the bond strength between ice and the road pavement surface. In many cases, however, roadside soils are often the recipients of these chloride salts through runoff actions, deposition from snow ploughing. With increased acceptance and widespread use of chloride salts by transportation agencies for deicing and anti-icing operation and maintenance, concerns about the environmental and hydro-mechanical response of roadside soils are gaining more attention from practitioners and the research body in general. In recent years, chloride salts are often augmented with agro-based materials as additives to improve their deicing capabilities and anti-corrosion effects on transportation infrastructures and maintenance equipment's transportation agencies. Besides the associated additional cost to winter maintenance operations, environmental implications with respect to their degradation, toxicity and interaction with the chloride salts have not been reported.

In this study, we examined the fate and transport of chloride salt ions in roadside soils that are commonly encountered in the United States. We further evaluated the effect of beetroot juice that is added as an additive to chloride salt for winter maintenance operation on the fate and transport of these chloride salt ions. To achieve this, we conducted extensive laboratory soil column experiments. In addition, we evaluated the effect of the direction of flow on the fate and transport of the chloride salt ions by utilizing vertical and horizontal soil columns. We also examined the adsorption and desorption mechanisms of these ions at equilibrium concentration in the soil using

batch experiments and fitting to sorption isotherm models. From the results obtained from the various experiments, we have the following deductions:

- Adsorption of the chloride salt ions on the soil particle surface exhibited characteristics of homogenous and non-homogenous adsorption. The soil was complexed with surfaces having different affinity and energy of adsorption to different ions.
- Beetroot juice altered the adsorption properties of the chloride salts ions on the soil particle surfaces. Results showed that it influences the adsorption capacity and affinity of the ions on the soil particle surfaces.
- The Cl^- exhibited conservative properties and least interaction with the test soil. In addition, the presence of beet juice did not influence the fate and transport of Cl^- through the soil considerably.
- The addition, and prolonged use of beetroot juice with chloride salt clogs small soil pores because of the increased viscosity as observed in the experiment of this study. In road soil, this condition can initiate increased surface runoffs following precipitation events.

6.2 Practical Use of the Machine Learning Models

The project employed a specialized machine learning (ML) approach to extend analysis beyond the direct laboratory measurements. Its role is specific and should be understood within the following context.

Model Purpose and Design: The ML model was designed to predict experimental results beyond the measured pore-volume range and to aid parameter estimation for these projections. It used a two-stage process to manage datasets where some ions (Na^+, Mg^{2+}) had many zero-concentration

measurements. Recognizing that tree-based models poorly extrapolate, the team applied a polynomial ridge regression correction to improve projections.

Realistic Application for DOTs: The ML component serves as a decision-support tool for extending laboratory datasets, not as a standalone predictive model or a replacement for mechanistic understanding. Appropriate uses aligned with the report's methodology include: (1) Extending laboratory-derived breakthrough curves to support scenario comparisons and parameter fitting.(2) Managing sparse or zero-inflated data in a structured, transparent manner.

Limitations for Implementation: For practitioners, this means:

- Model performance is tied to the specific data it was trained on. It should not be assumed transferable to new soils, additives, or conditions without additional validation.
- Even with correction techniques, extrapolated outputs must be used cautiously and as supporting evidence, not as the sole basis for environmental decisions.

6.3 Implementation Recommendations for Practitioners

This section translates the study's laboratory and modeling findings into practical guidance for state DOTs. It distinguishes clearly between conclusions directly supported by the research and outcomes that remain uncertain under field conditions.

6.3.1 Translating Laboratory Evidence to Field Decisions

The project evaluated chloride fate and transport, with and without a beetroot juice additive, using controlled batch and soil column experiments on a sandy loam. While these methods are effective for isolating key mechanisms, implementing the results requires consideration of real-world complexities highlighted in the report. The key considerations for field application include:

- *Account for soil heterogeneity.* Natural roadside soils are highly variable, with heterogeneity occurring from the micro-scale to the landscape scale. Laboratory-derived transport behavior should be treated as representative of controlled conditions, not as a site-specific prediction.
- *Recognize preferential flow.* Subsurface transport in the field can be dominated by flow through macropores, cracks, or other preferential pathways influenced by wet-dry or freeze-thaw cycles. Consequently, field transport can be locally faster than suggested by uniform laboratory columns. A conservative interpretation is warranted.
- *Use results for screening, not prescription.* Field conditions, including soil layering, compaction, drainage, and moisture, often diverge substantially from laboratory setups. Therefore, these findings are best used for: (1) Relative comparisons, e.g., deicer-only vs. deicer with additive; vertical vs. horizontal flow). (2) Screening-level risk evaluation to identify settings where chloride mobility may be elevated. For high-stakes decisions involving shallow groundwater, sensitive aquifers, or protected water resources, these findings should be paired with site-specific characterization or monitoring.

6.3.2 Implications for Winter Operations Using Agro-Based Additives

A central finding is that the beetroot juice additive altered soil-solute interactions, increasing chloride mobility relative to chloride salts alone. Our findings suggest that the additive modifies soil surface properties, potentially reducing chloride adsorption and increasing migration potential.

A pragmatic approach for integrating this research into practice involves the following steps:

1. Use the results to inform relative risk comparisons (e.g., additive versus no additive) rather than to generate absolute predictions of travel time or concentration.

2. In conditions comparable to the study, treat agro-based additives as a potential factor for increased chloride mobility, particularly in coarse-grained roadside soils.
3. Employ the modeling approach strictly as an extension tool for laboratory data to support projections, where suitable.
4. Explicitly recognize subsurface variability and the associated challenges for transport modeling when discussing these results internally or with stakeholders.

In summary, this report provides laboratory evidence that chloride transport is sensitive to both soil-solute interactions and flow direction, and that a beetroot juice additive can alter these interactions in a manner that may increase chloride migration. For DOT engineers, the most defensible implementation strategy is to use these findings for risk-informed screening and comparative assessment. This should be coupled with a clear acknowledgment of the subsurface heterogeneity and extrapolation limits detailed throughout the study.

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APPENDIX

APPENDIX I: Test soil characteristics

Table A1 . Elemental composition of the test soil expressed as their oxides

Elemental Composition			
Major Element	Weight(%)	Trace Element	ppm
SiO_2	65.85	NiO	19.60
TiO_2	1.16	Cr_2O_3	24.70
Al_2O_3	15.70	Sc_2O_3	19.88
FeO*	6.14	V_2O_3	178.40
MnO	0.11	BaO	1261.99
MgO	2.20	Rb_2O	74.43
CaO	3.71	SrO	778.18
Na_2O	2.93	ZrO_2	317.09
K_2O	1.92	$Y2O_3$	25.64
P_2O_5	0.28	Nb_2O_5	19.60
Total (%)	100	Ga_2O_3	28
		CuO	64.34
		ZnO	113
		PbO	14
		La_2O_3	45
		CeO_2	86
		ThO_2	8
		Nd_2O_3	33
		U_2O_3	1
		Sum of trace element	2251
		in %	0.31

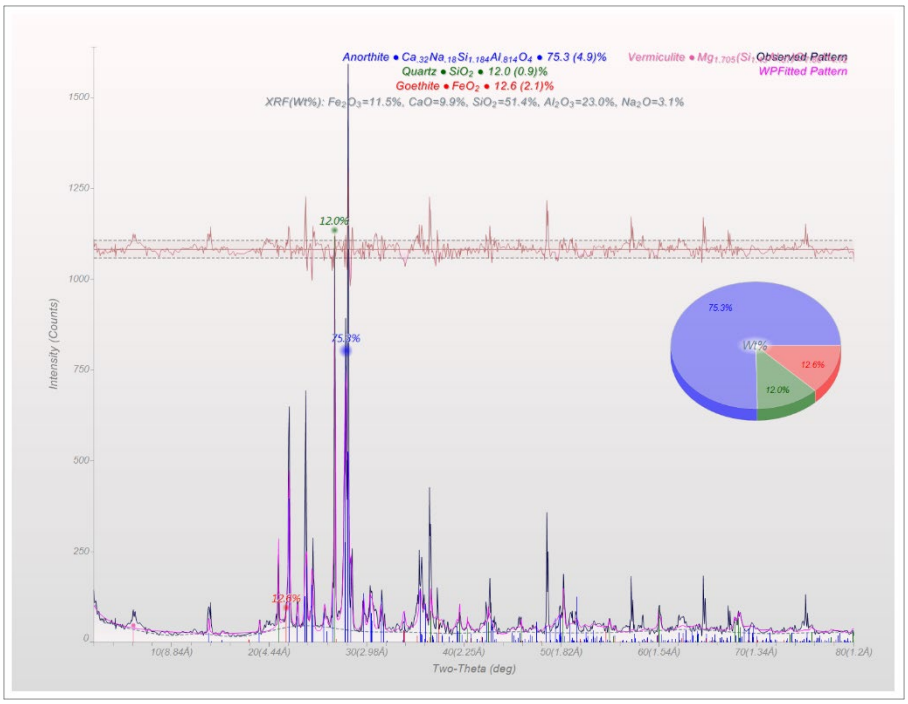

Figure A1. XRD for sand

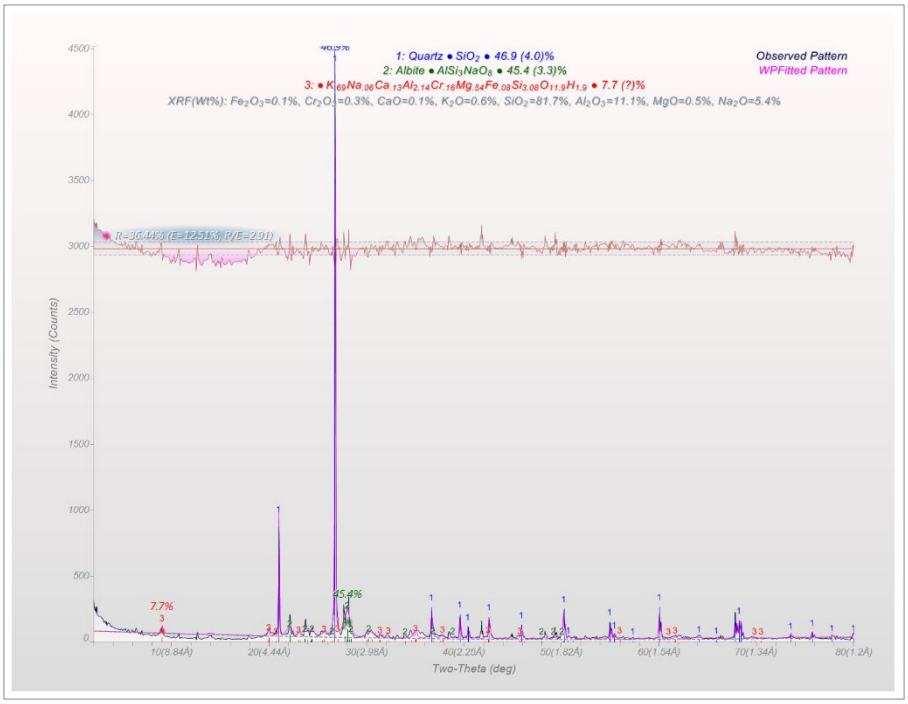

Figure A2. XRD for topsoil

APPENDIX II: Sorption isotherm model fit to experiment data

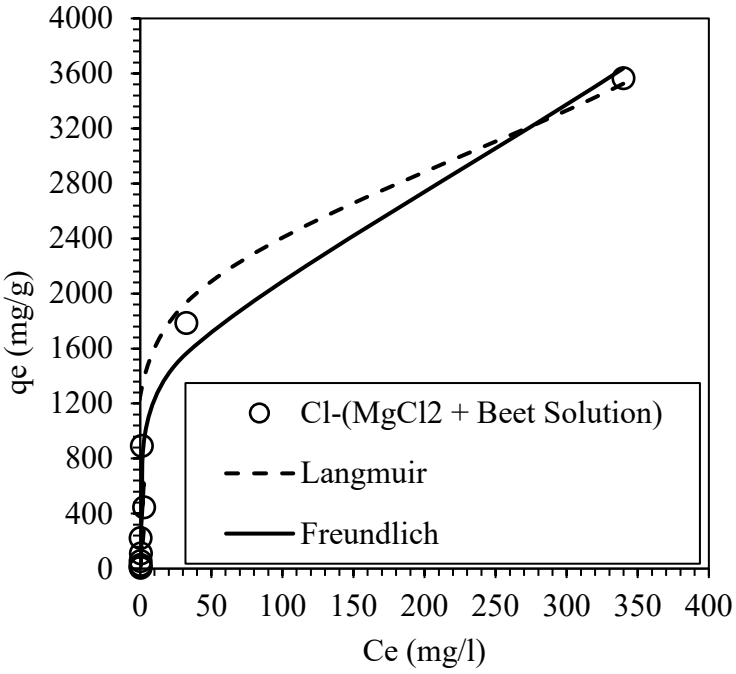

Figure A3. Sorption isotherm models fit to Cl^- experiment data in $MgCl_2$+Beet solution

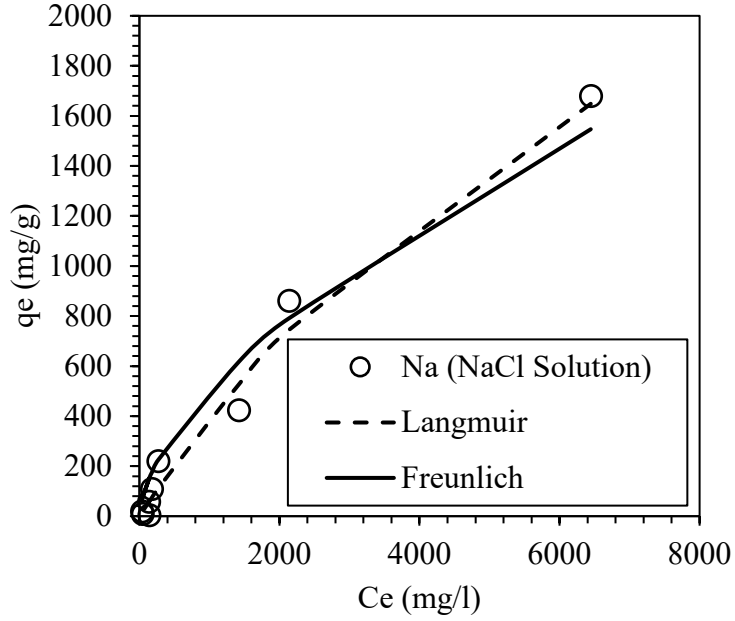

Figure A4. Sorption isotherm models fit to Na^+ experiment data in NaCl solution

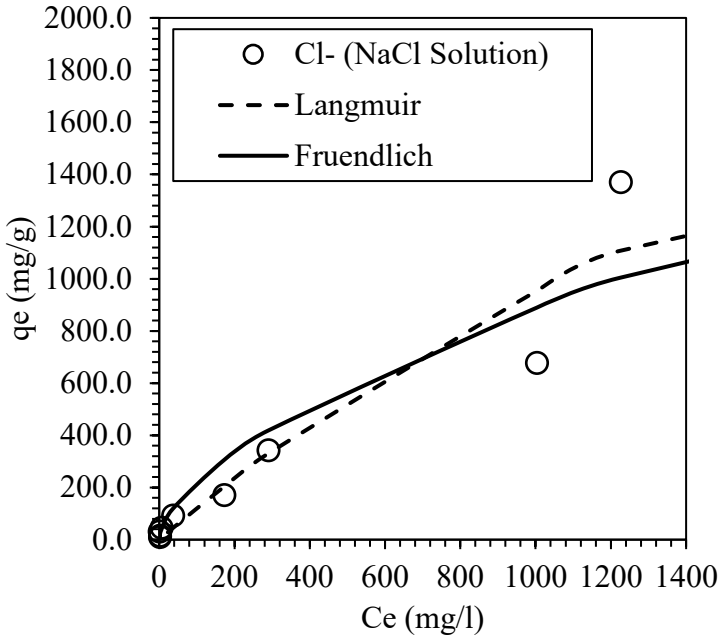

Figure A5. Sorption isotherm models fit to Cl^- experiment data in NaCl solution

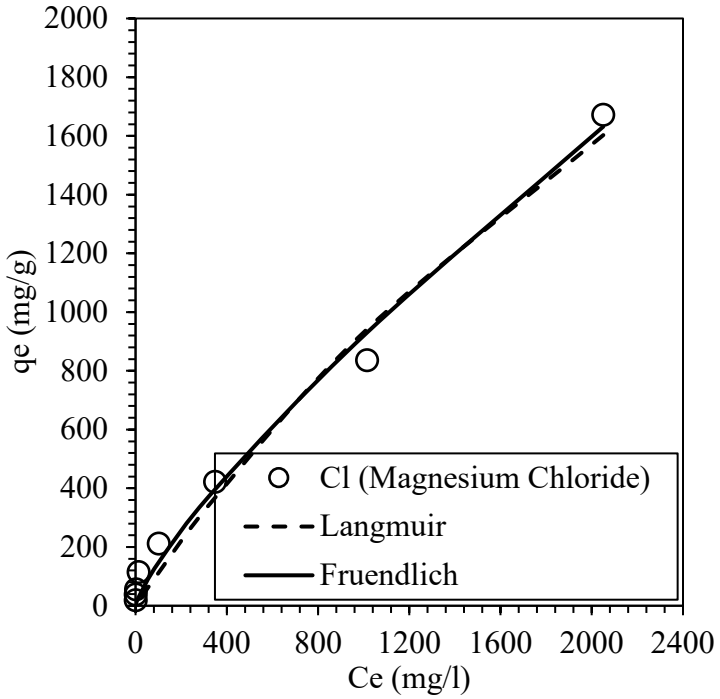

Figure A6. Sorption isotherm models fit to Cl^- experiment data in $MgCl_2$ solution

APPENDIX III: Machine Learning Prediction of experiment data

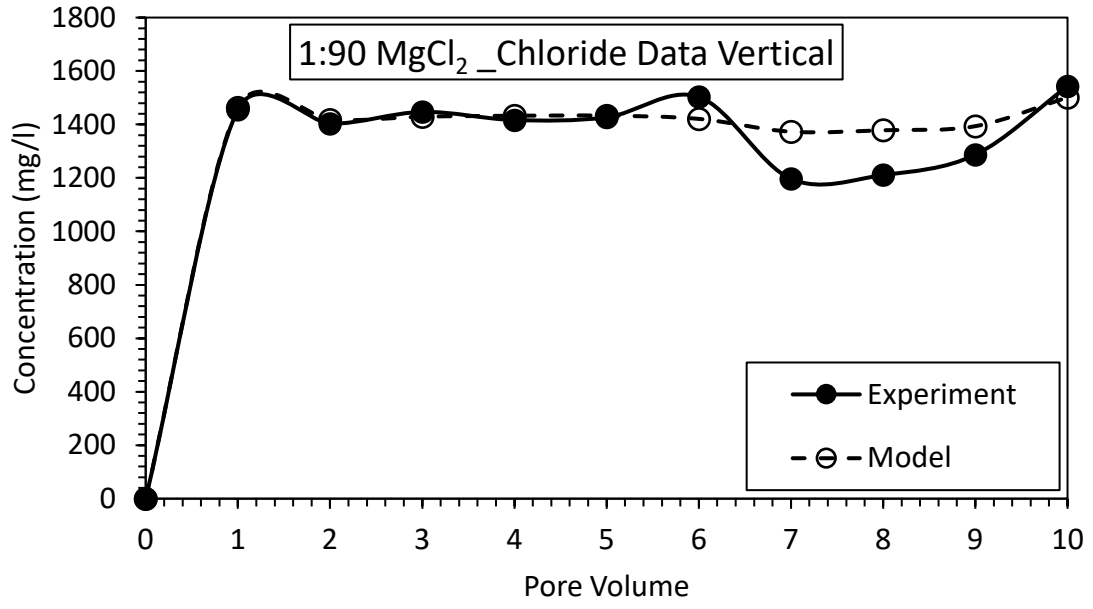

Figure A7. 1:90 $MgCl_2$ _chloride data for vertical soil column

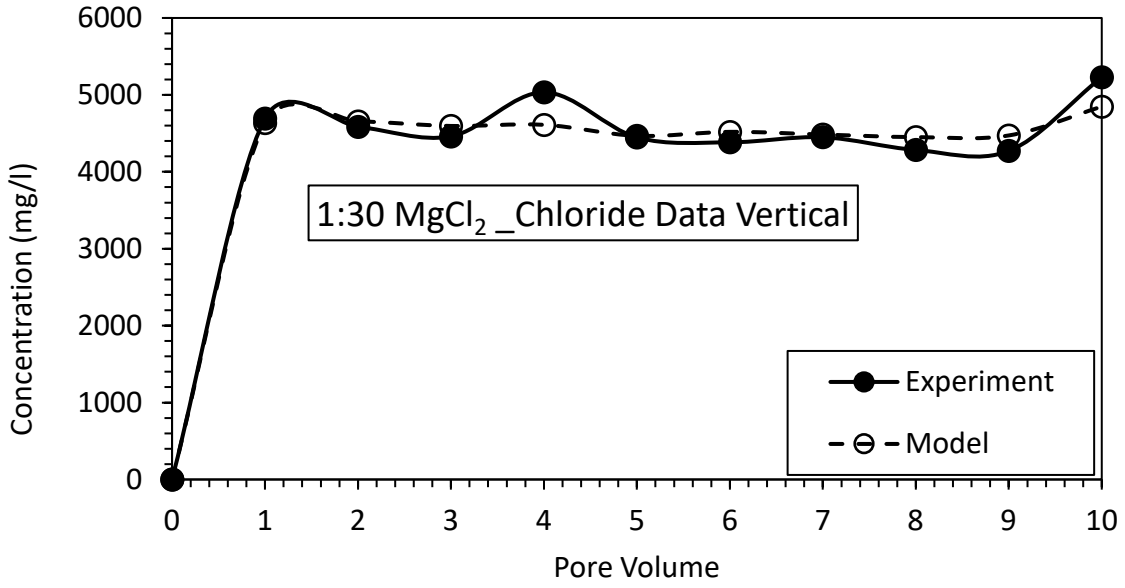

Figure A8. 1:30 $MgCl_2$ _chloride data for vertical soil column

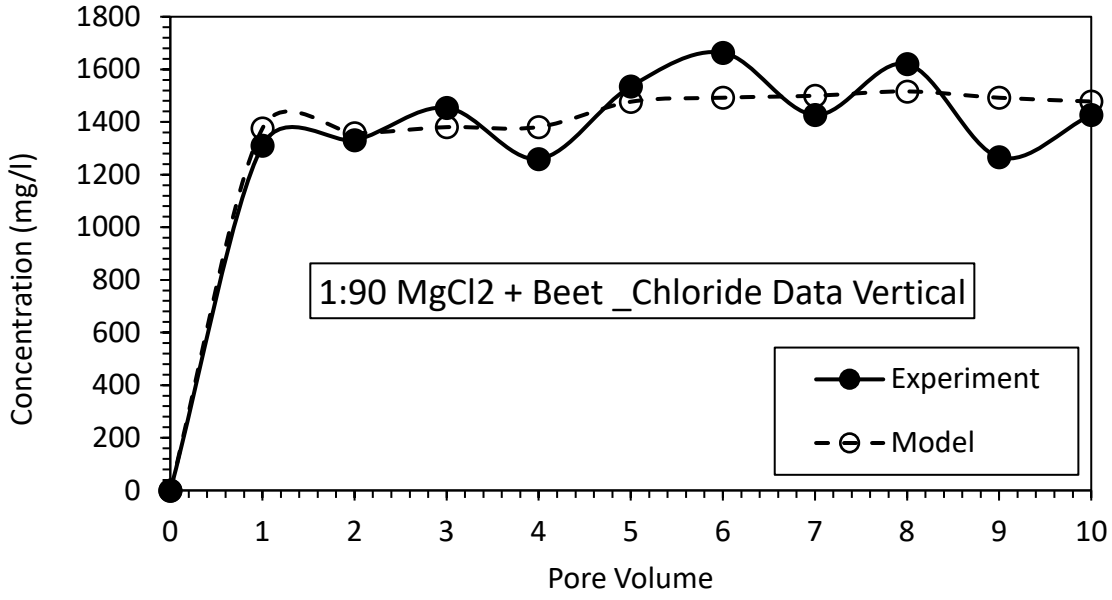

Figure A9. 1:90 MgCl2 + beet _chloride data for vertical soil column

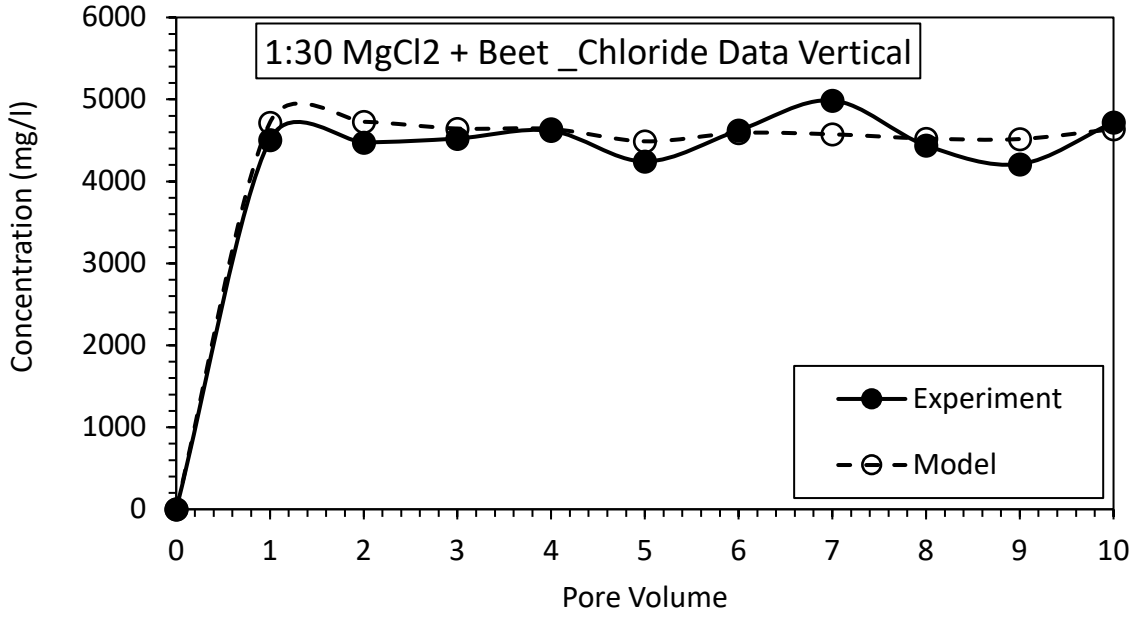

Figure A10. 1:30 MgCl2 + beet _chloride data for vertical soil column

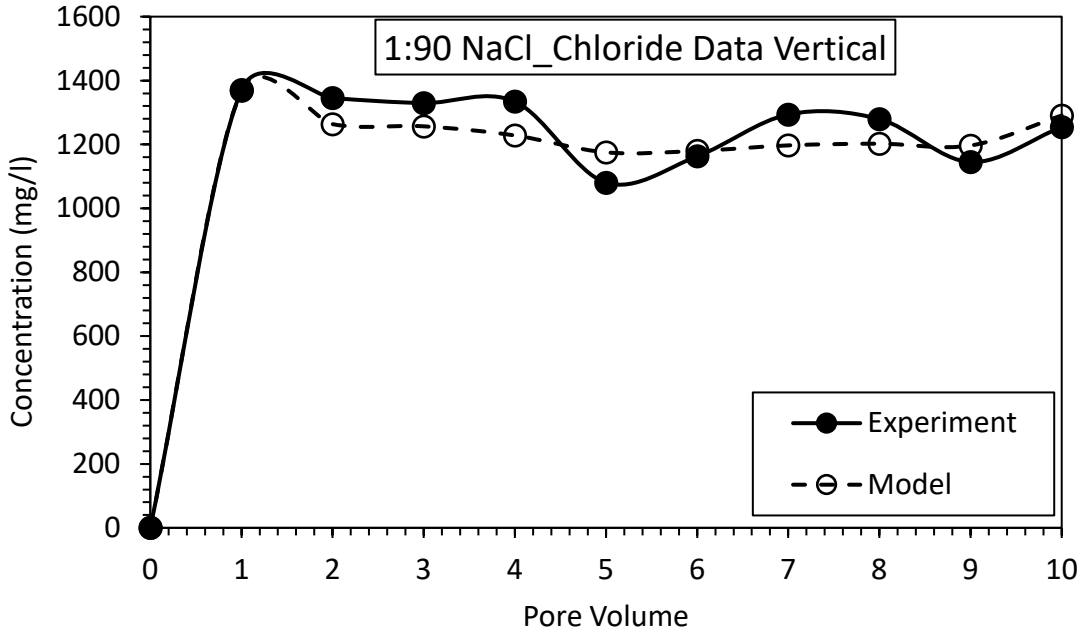

Figure A11. 1:90 NaCl_chloride data for vertical soil column

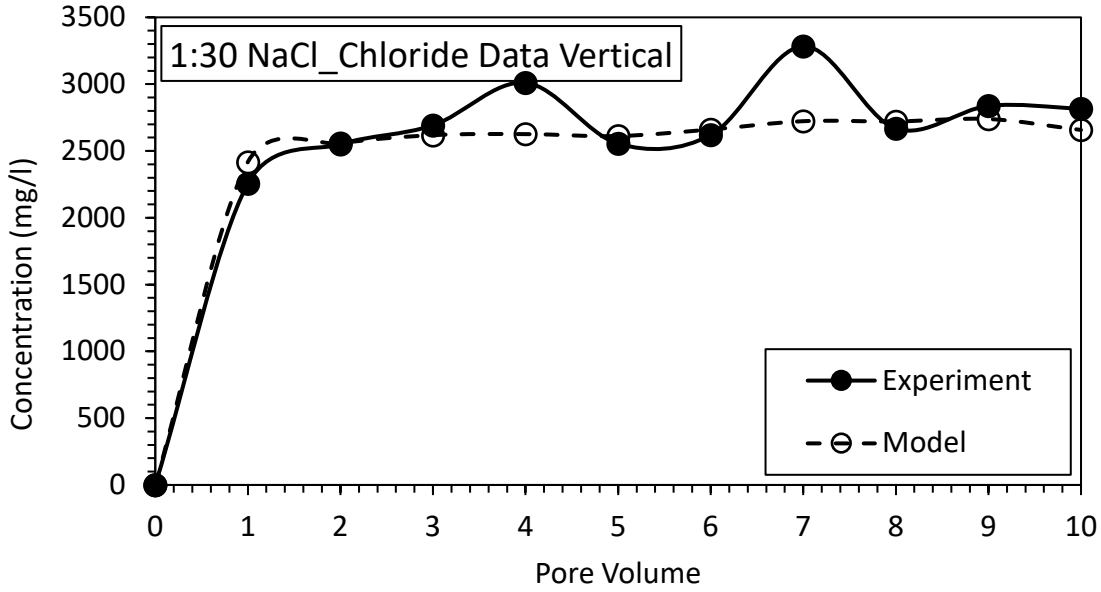

Figure A12. 1:30 NaCl_chloride data for vertical soil column

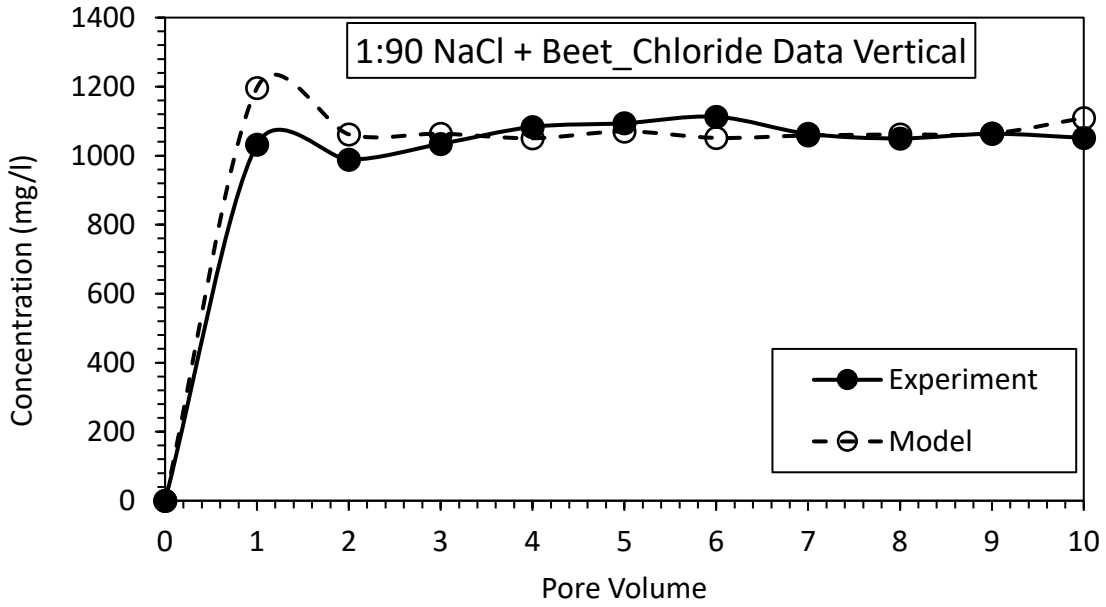

Figure A13. 1:90 NaCl + beet_chloride data for vertical soil column

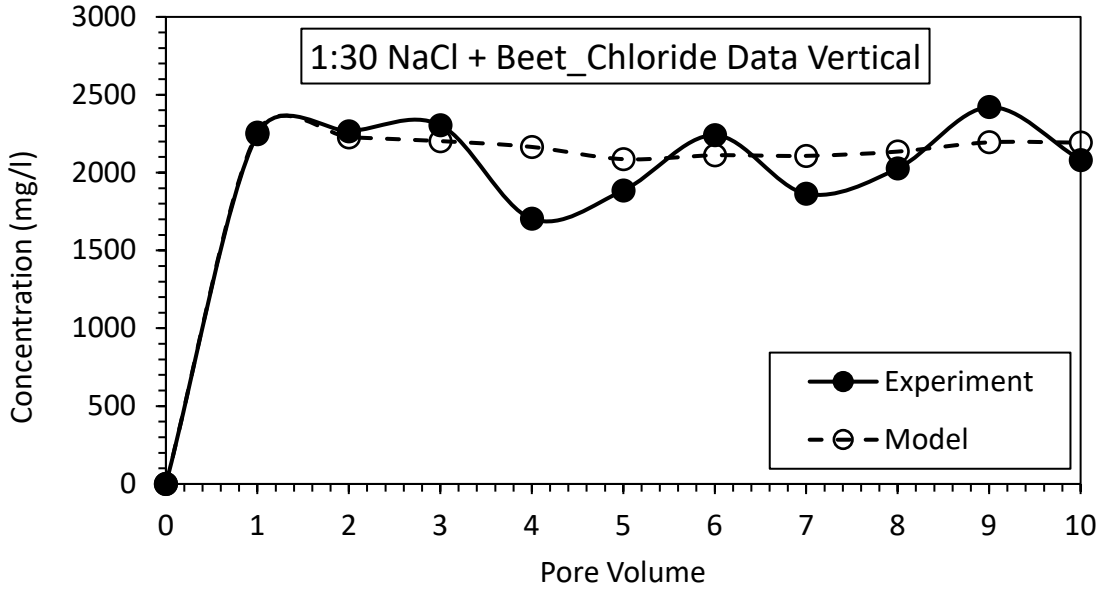

Figure A14. 1:30 NaCl + beet_chloride data for vertical soil column

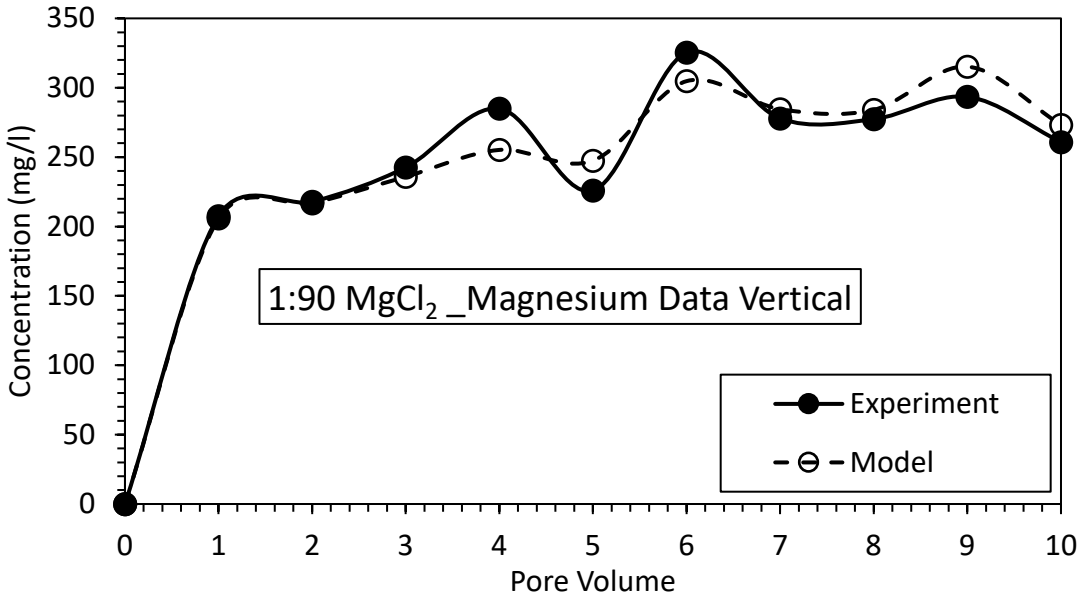

Figure A15. 1:90 $MgCl_2$ _magnesium data for vertical soil column

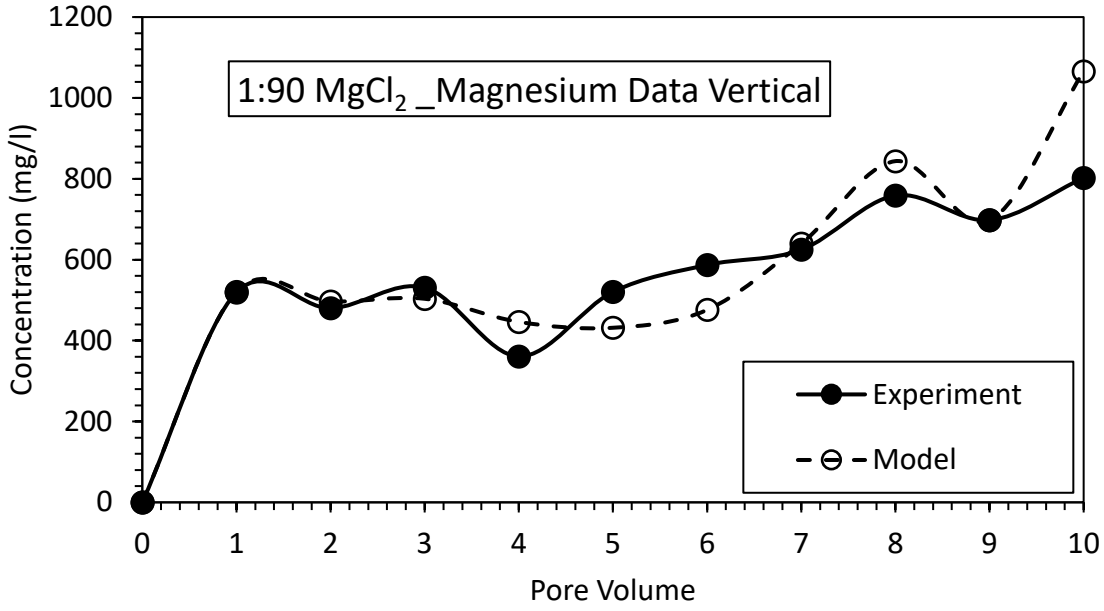

Figure A16. 1:30 $MgCl_2$ _magnesium data for vertical soil column

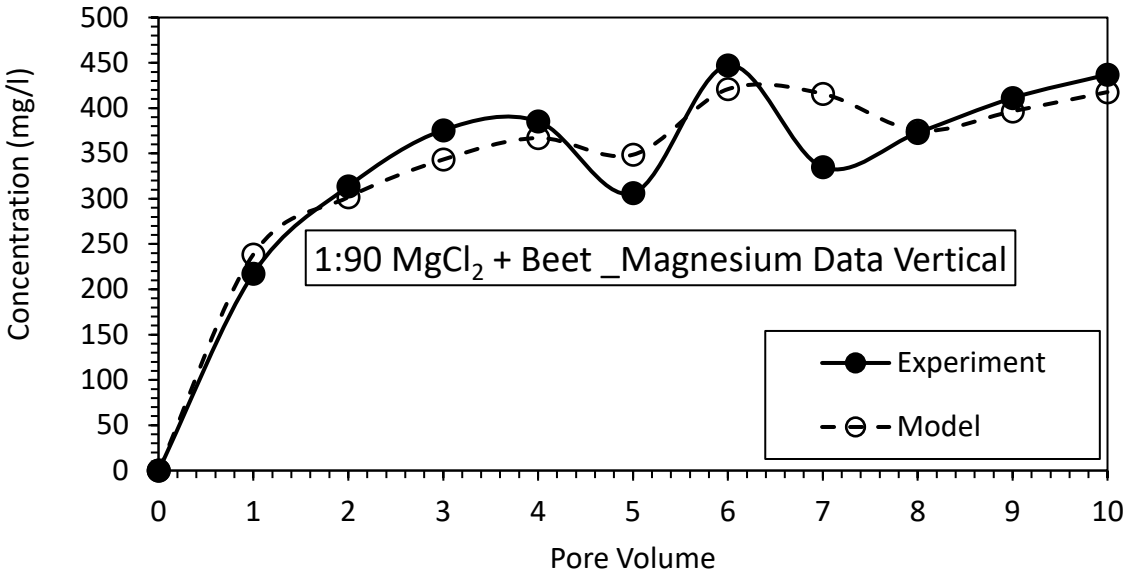

Figure A17. 1:90 $MgCl_2$ + beet _magnesium data for vertical soil column

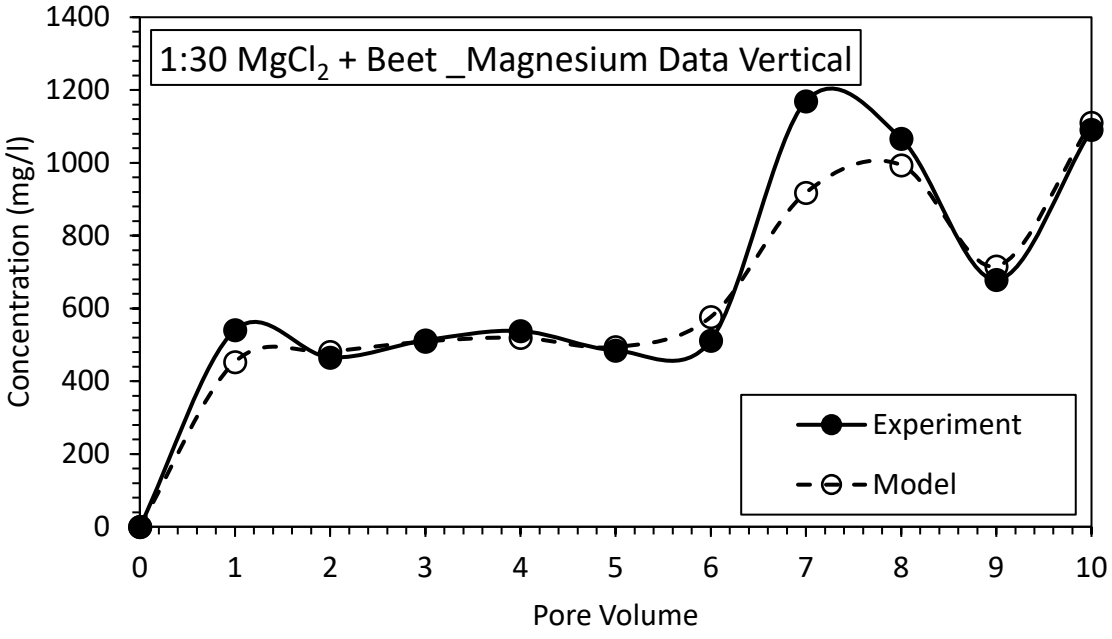

Figure A18. 1:30 $MgCl_2$ + beet _magnesium data for vertical soil column

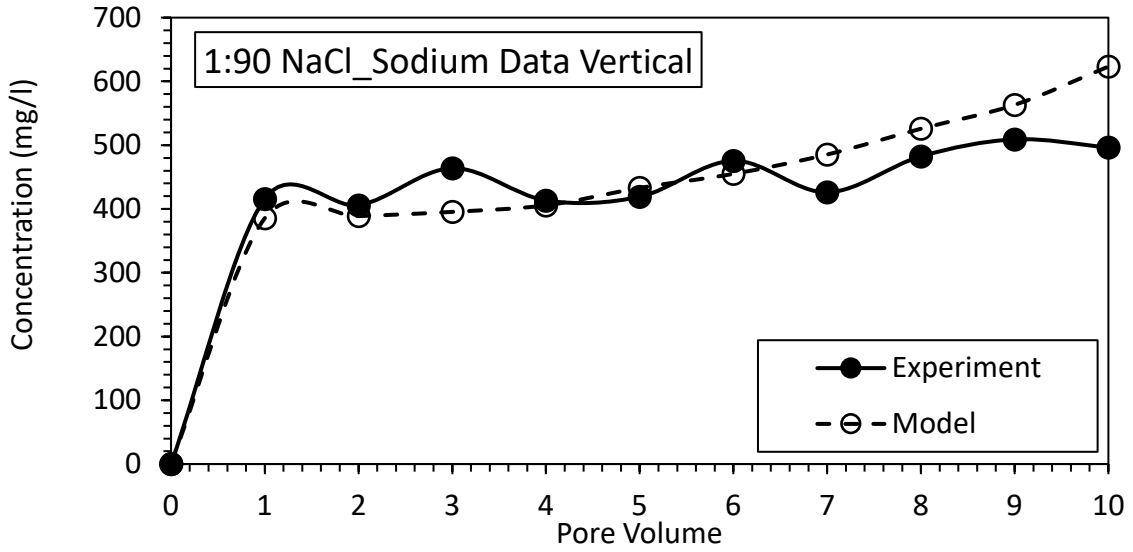

Figure A19. 1:90 NaCl_sodium data for vertical soil column

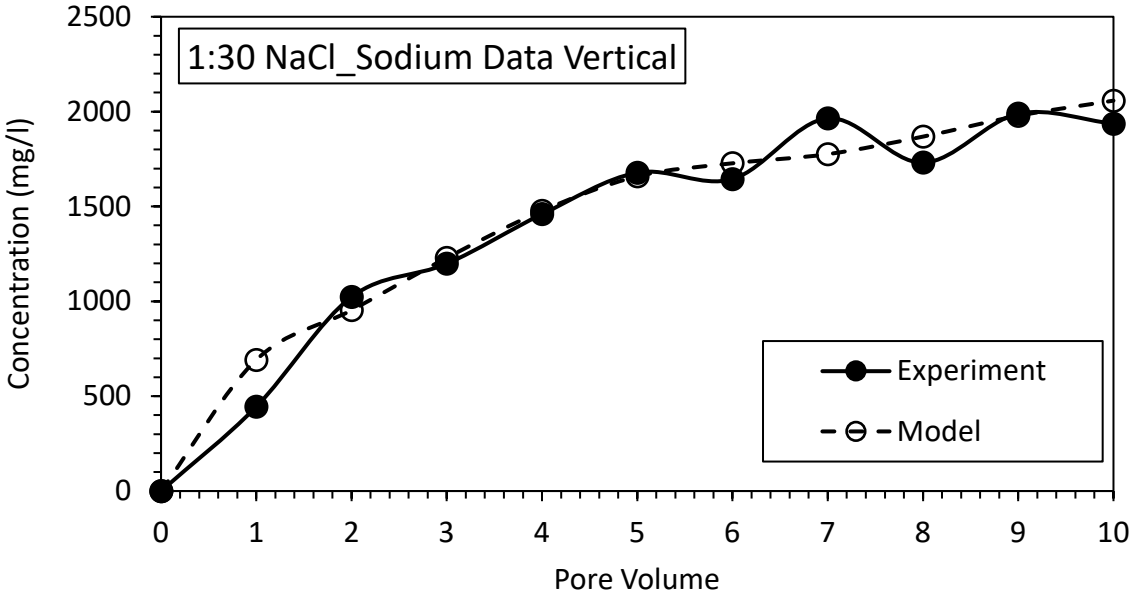

Figure A20. 1:30 NaCl_sodium data for vertical soil column

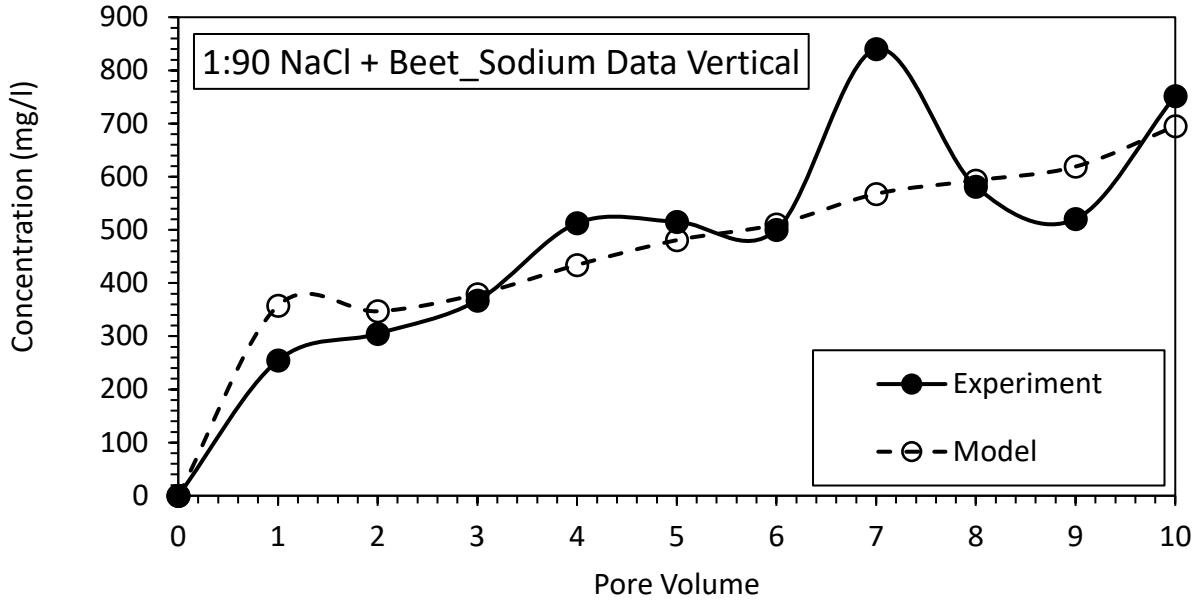

Figure A21. 1:90 NaCl + beet_sodium data for vertical soil column

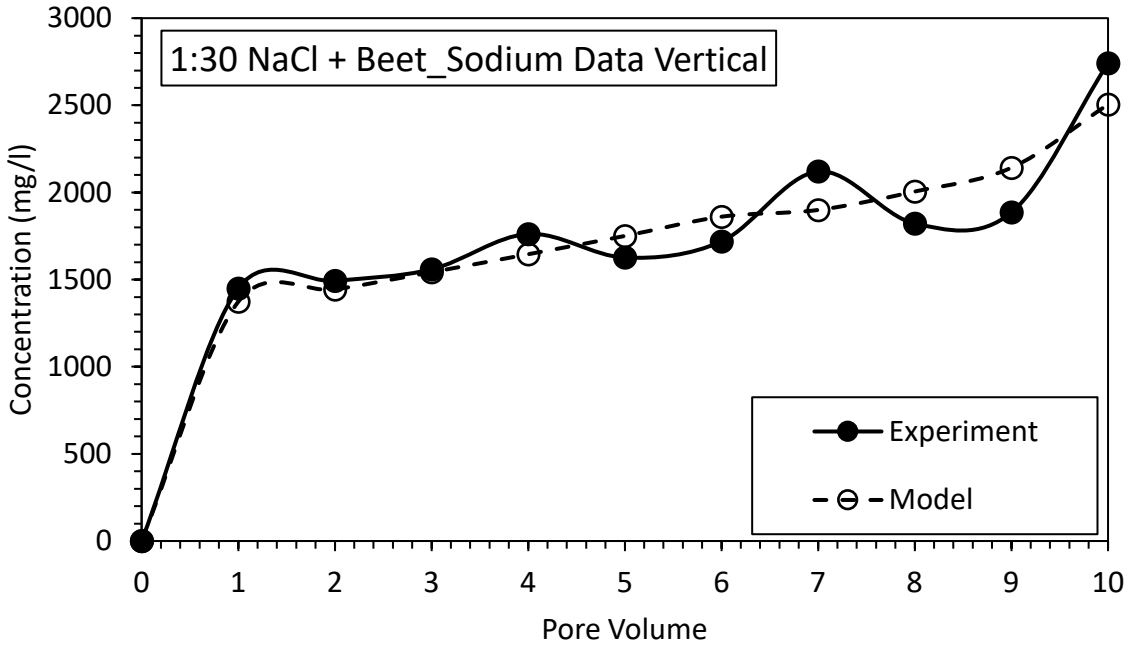

Figure A22. 1:30 NaCl + beet_sodium data for vertical soil column

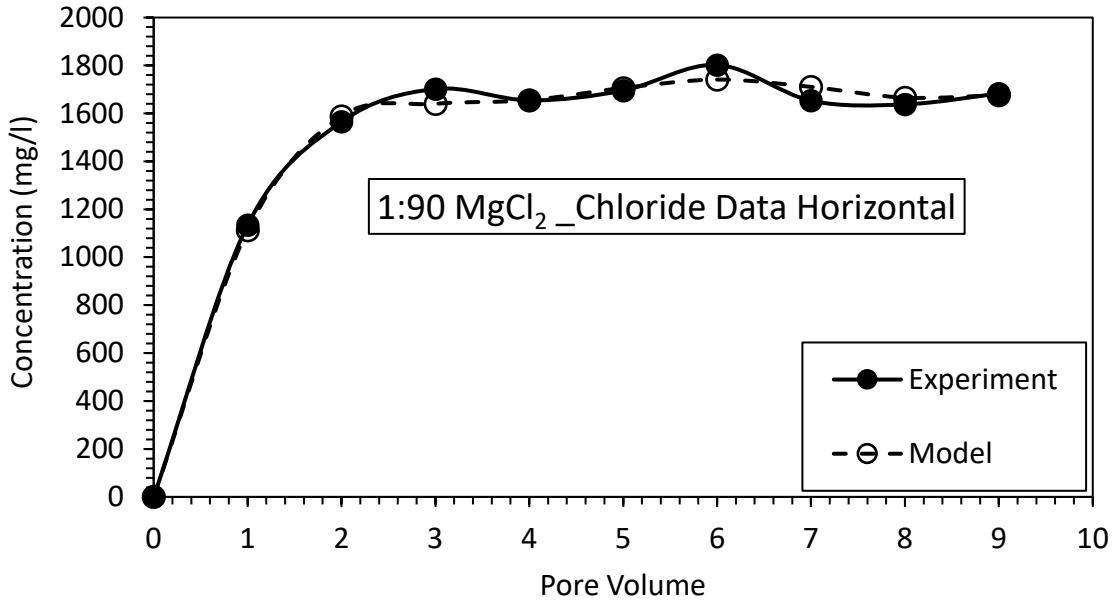

Figure A23. 1:90 MgCl2 _chloride data for horizontal soil column

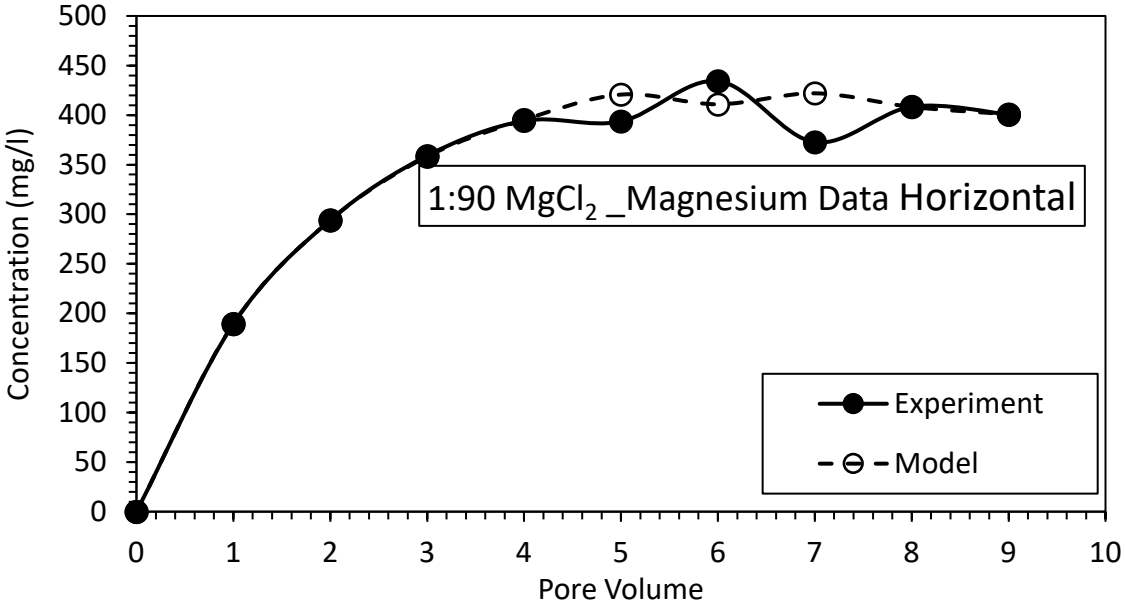

Figure A24. 1:90 $MgCl_2$ _magnesium data for horizontal soil column

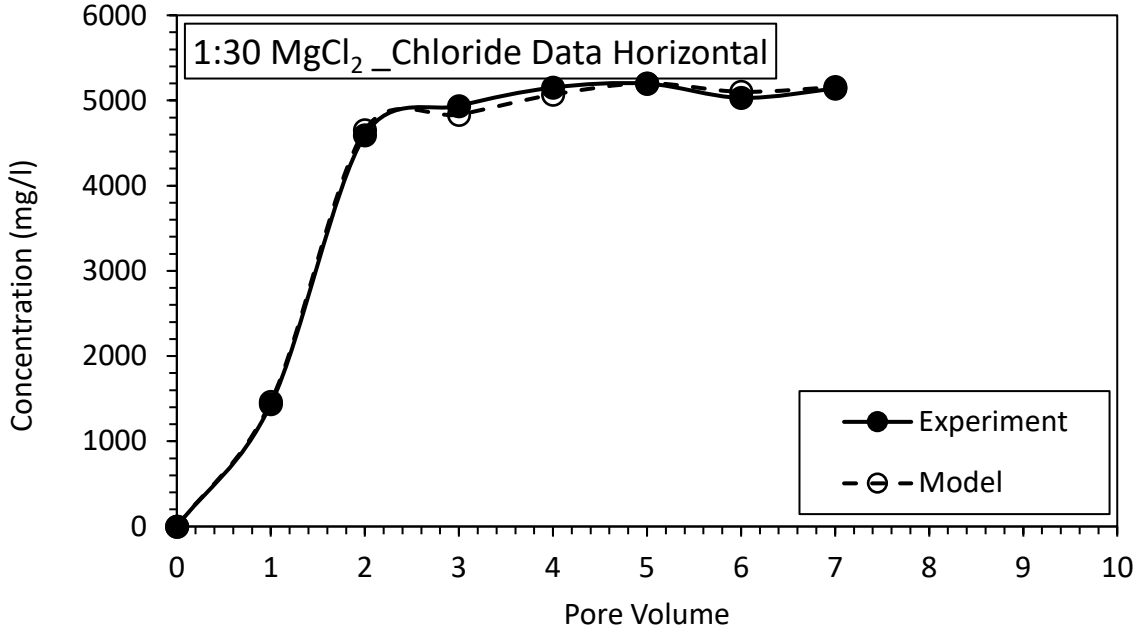

Figure A25. 1:30 $MgCl_2$ _chloride data for horizontal soil column

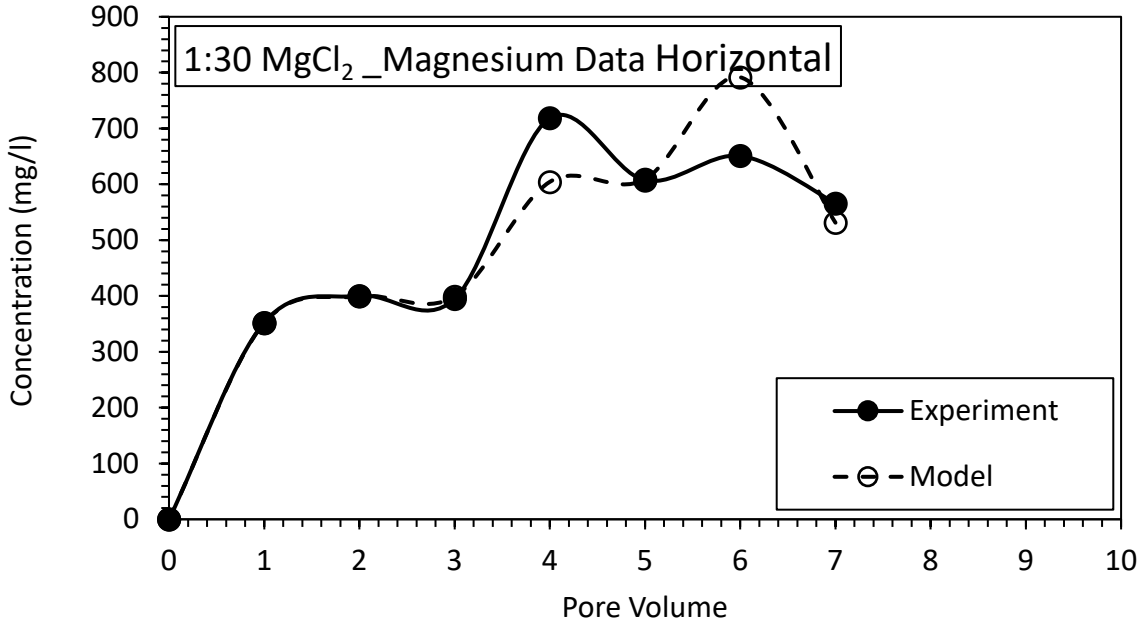

Figure A26. 1:30 $MgCl_2$ _magnesium data for horizontal soil column

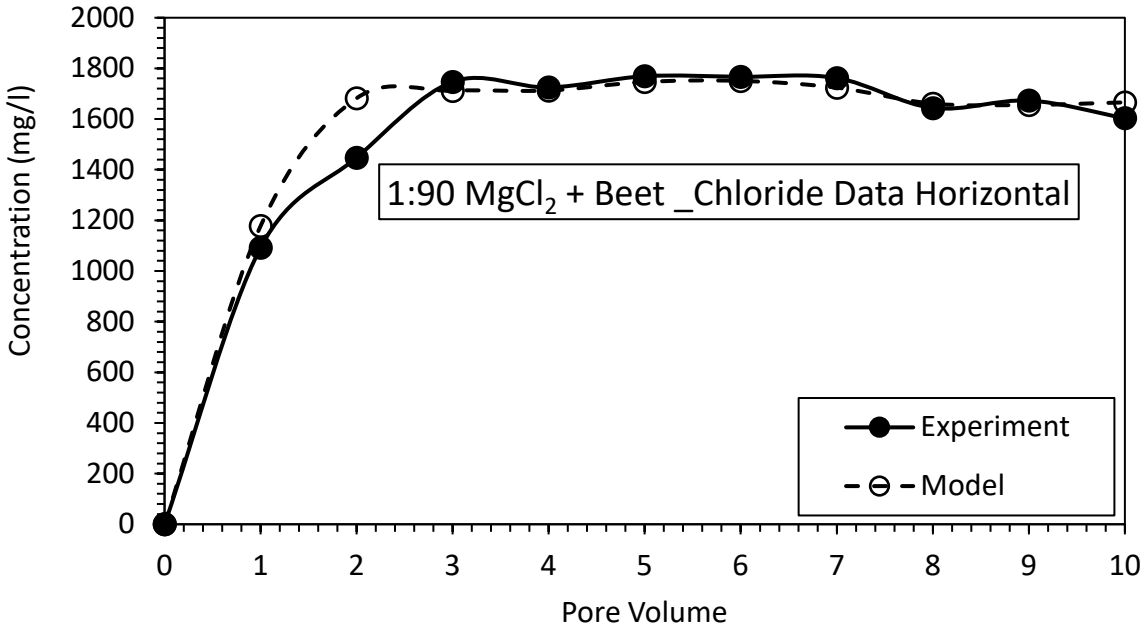

Figure A27. 1:90 $MgCl_2$ + beet _chloride data for horizontal soil column

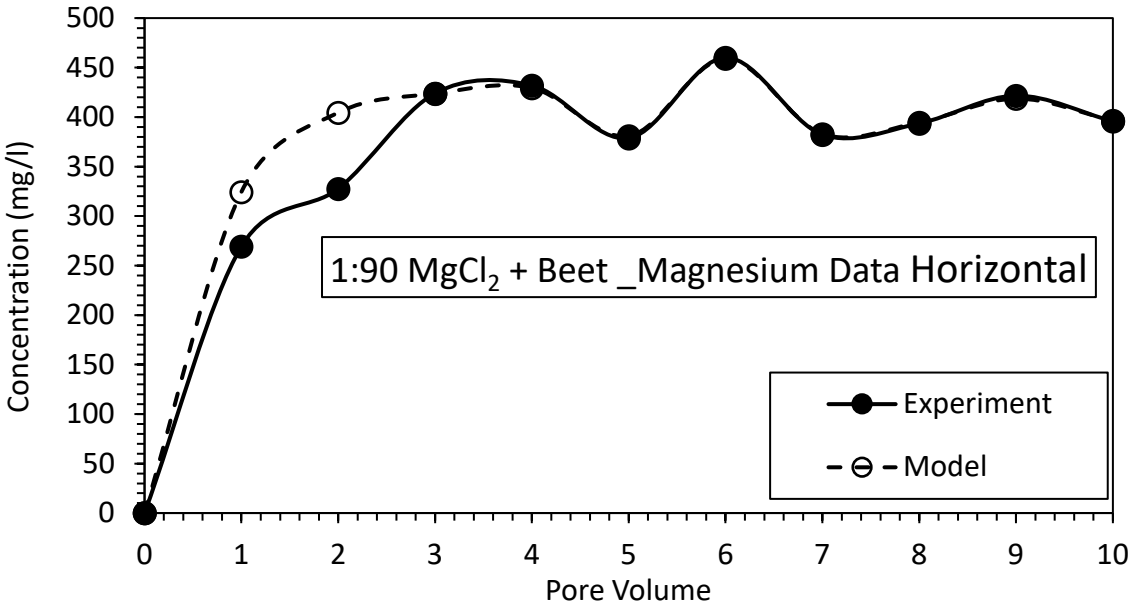

Figure A28. 1:90 $MgCl_2$ + beet _magnesium data for horizontal soil column

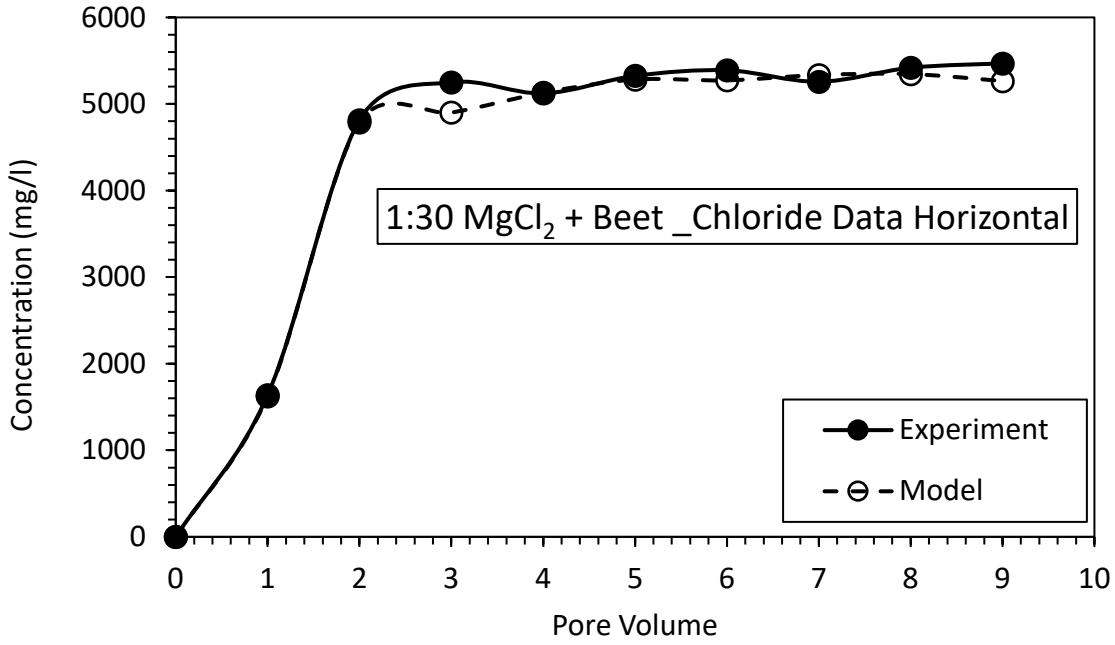

Figure A29. 1:30 $MgCl_2$ + beet _chloride data for horizontal soil column

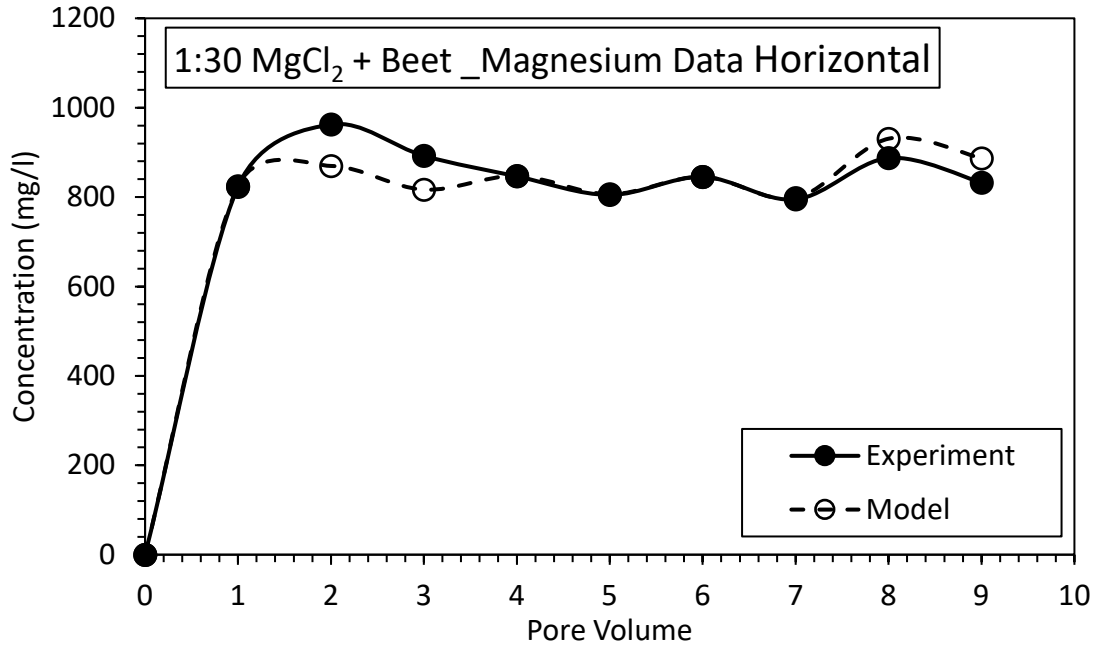

Figure A30. 1:30 $MgCl_2$ + beet _magnesium data for horizontal soil column

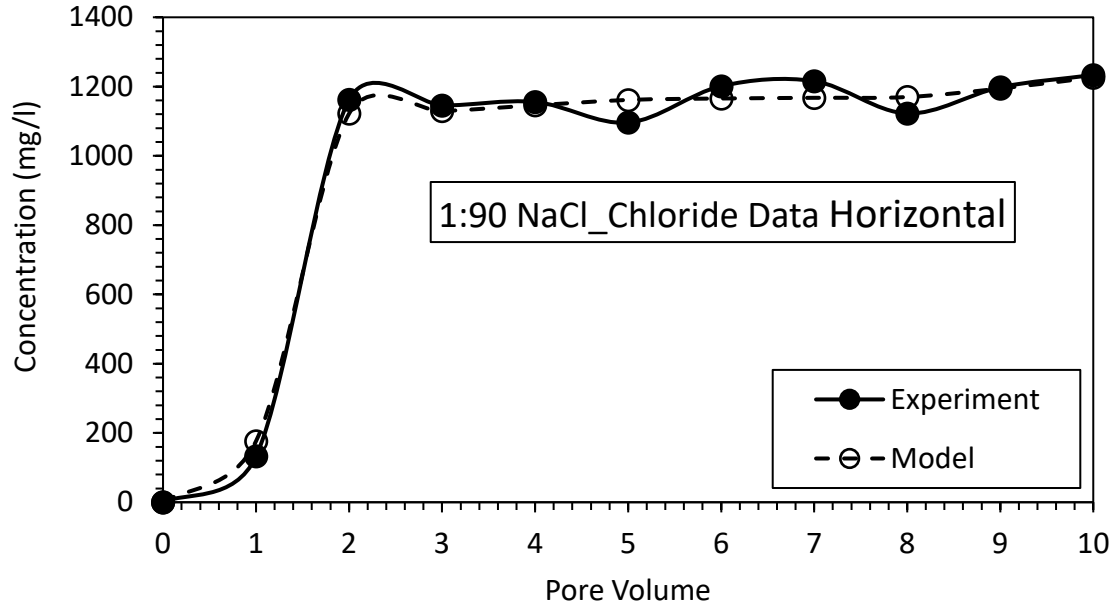

Figure A31. 1:90 NaCl_chloride data for horizontal soil column

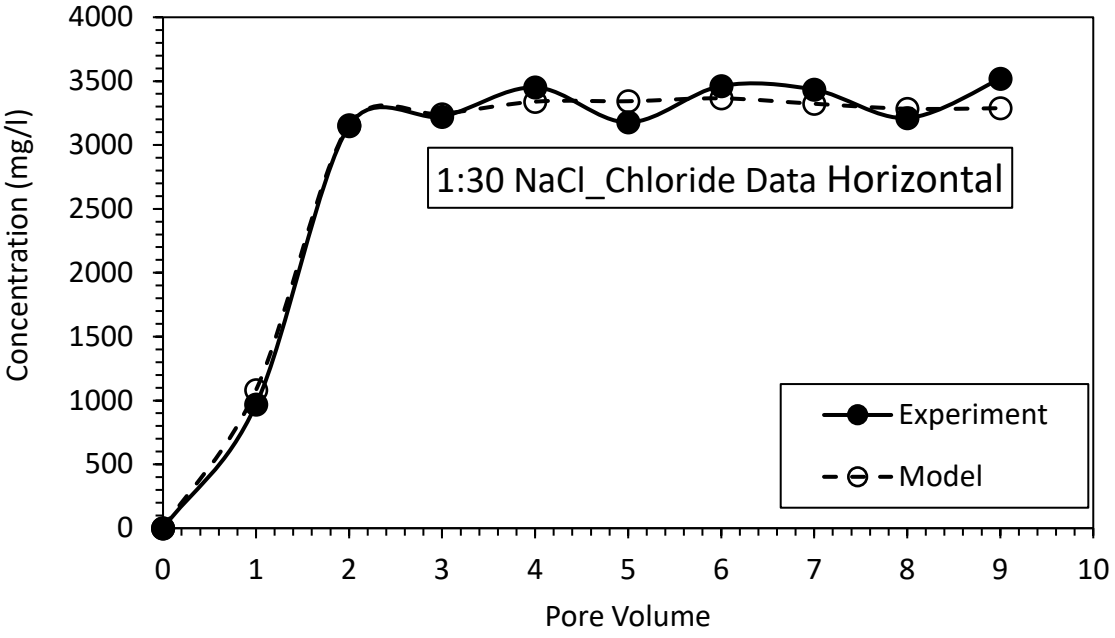

Figure A32. 1:30 NaCl_chloride data for horizontal soil column

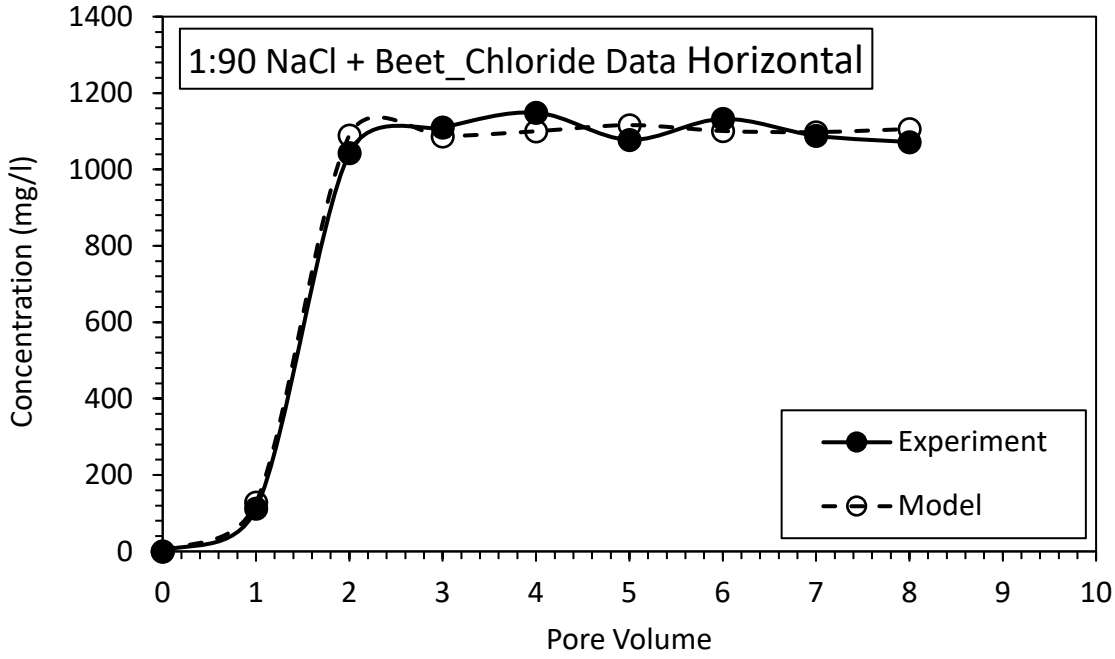

Figure A33. 1:90 NaCl + beet_chloride data for horizontal soil column

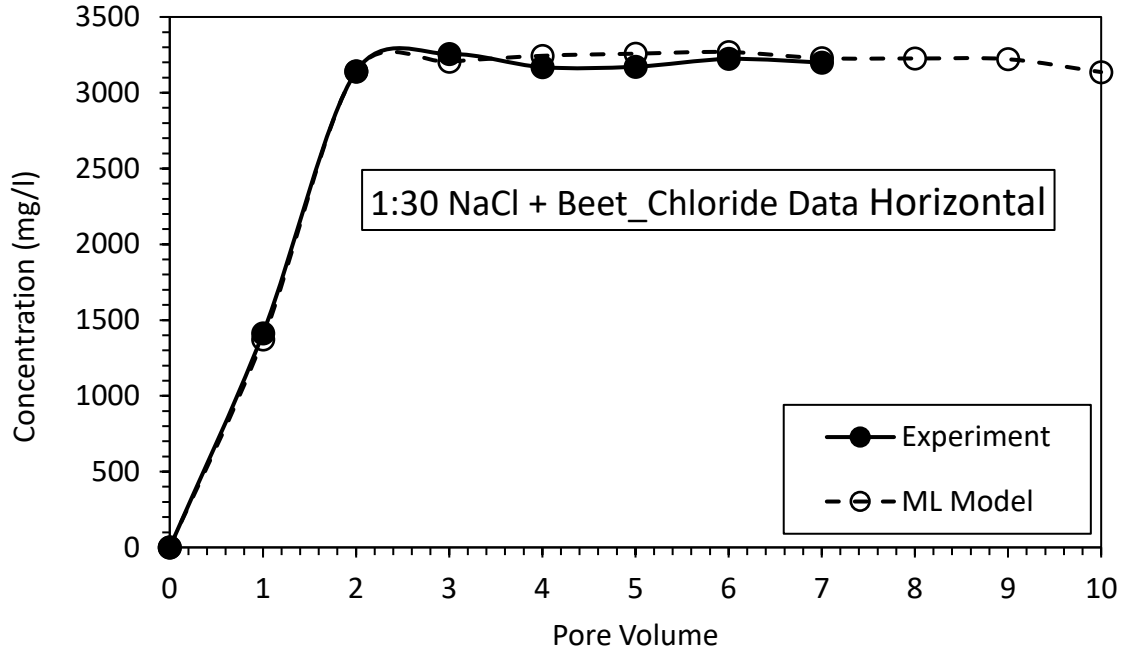

Figure A34. 1:30 NaCl + beet_chloride data for horizontal soil column

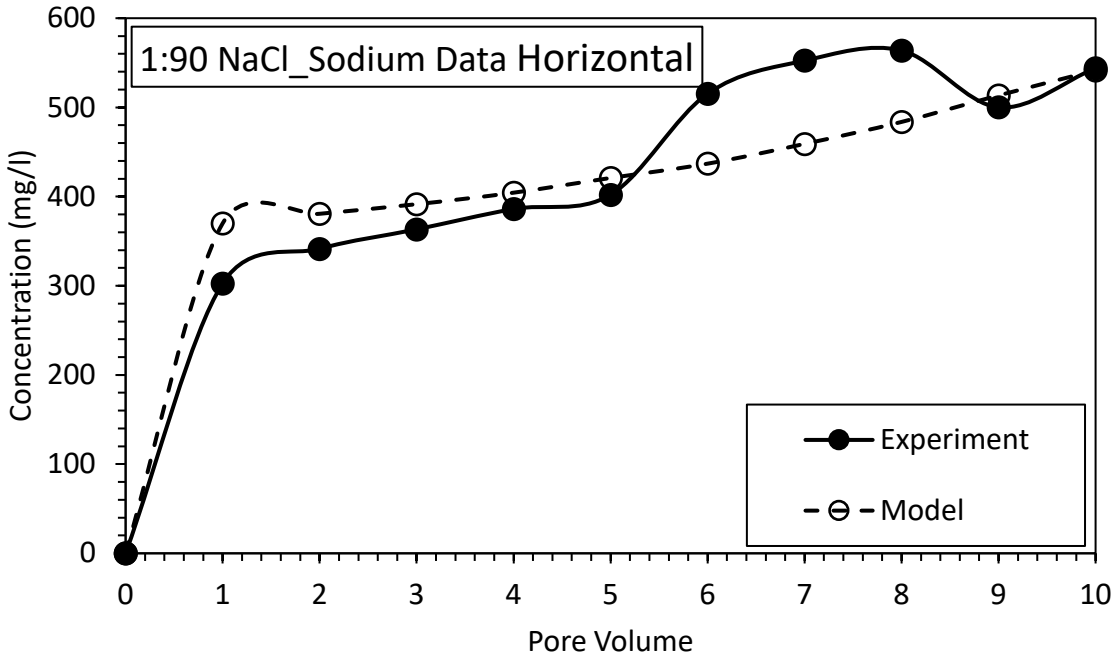

Figure A35. 1:90 NaCl_sodium data for horizontal soil column

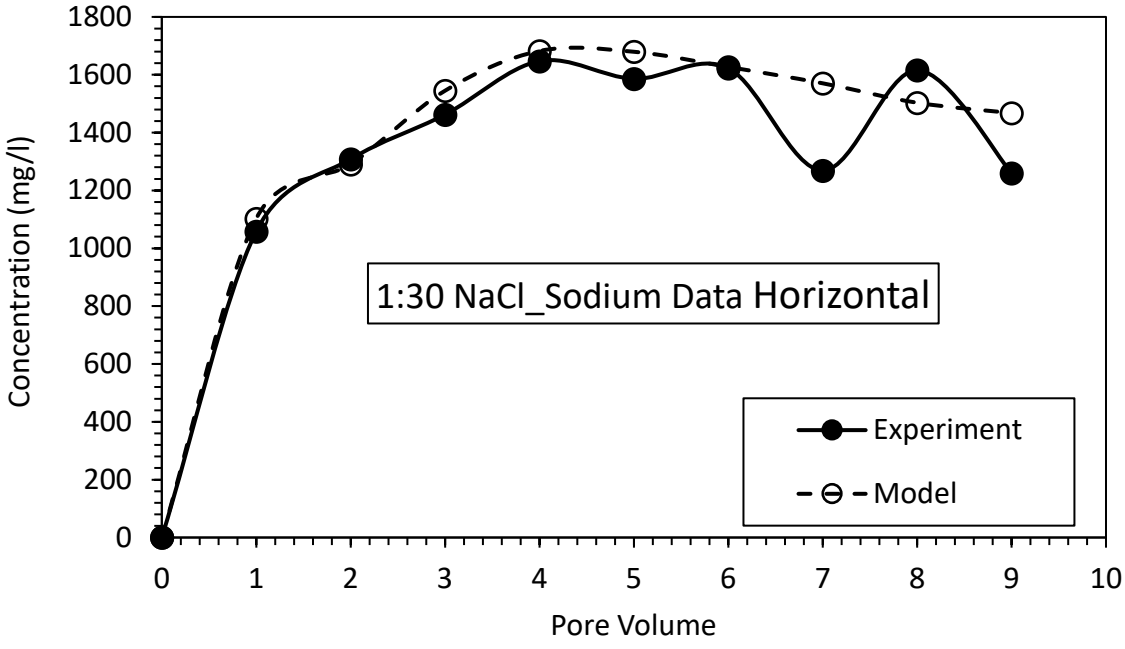

Figure A36. 1:30 NaCl_sodium data for horizontal soil column

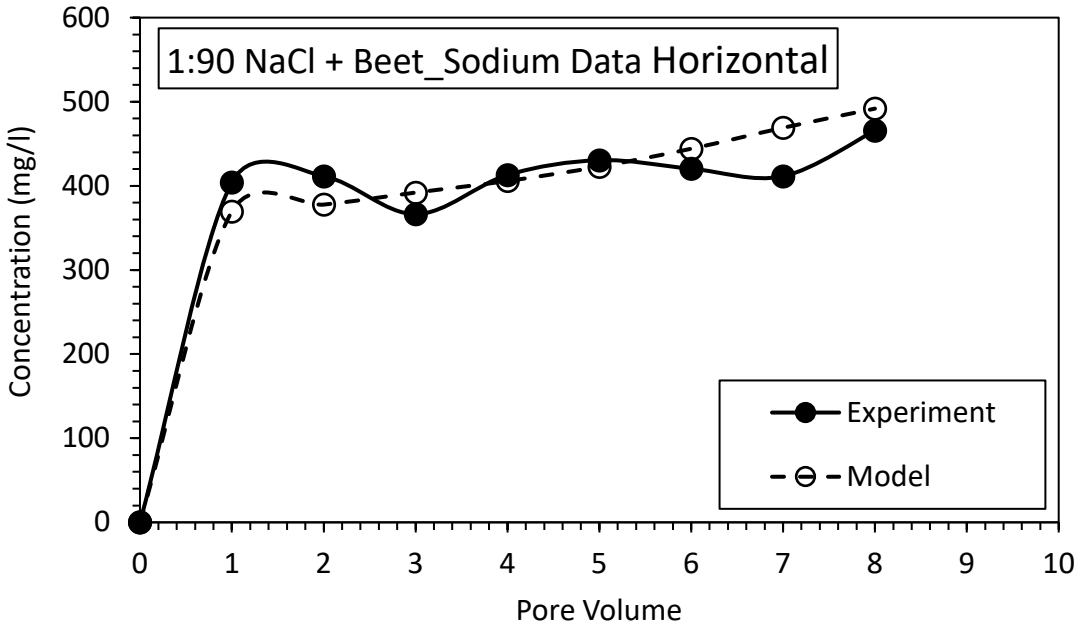

Figure A37. 1:90 NaCl + beet_sodium data for horizontal soil column

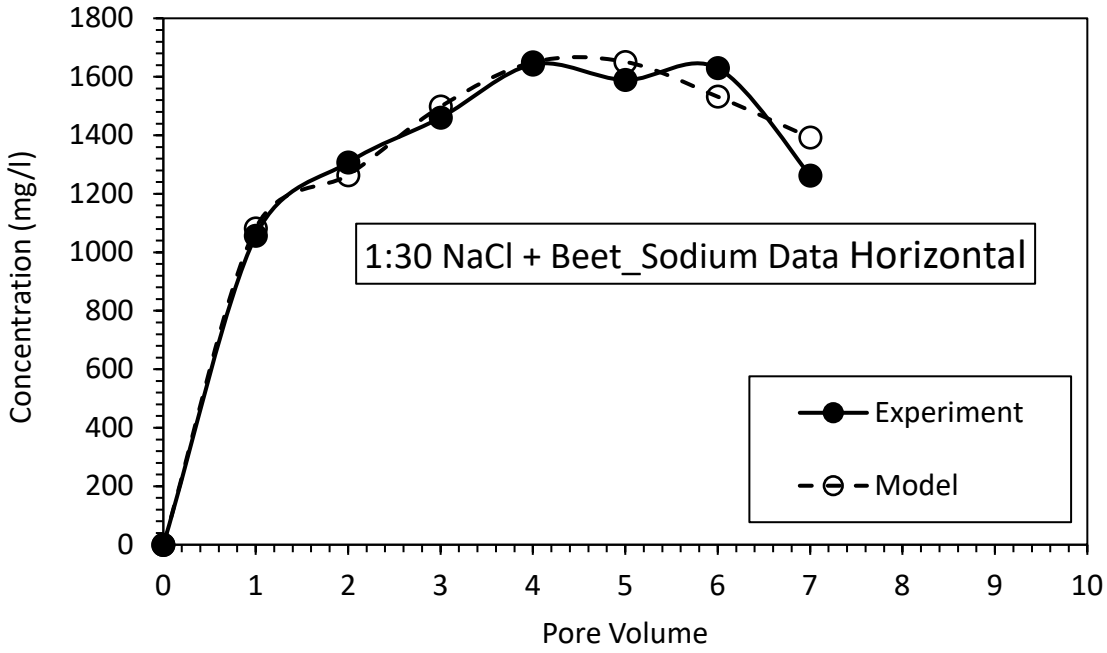

Figure A38. 1:30 NaCl + beet_sodium data for horizontal soil column

research for winter highway maintenance

Lead state:
Minnesota Department of Transportation
Research Services
395 John Ireland Blvd.
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