



Hydraulic property modification of saline-sodic soils by addition of calcium chloride
by Bryan Lee Woodbury

A thesis submitted in partial fulfillment of requirements for the degree of Master of Science in Soils
Montana State University

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Abstract:

Saline-sodic soils have developed in some irrigated areas of eastern Montana, due in part to increasing total dissolved solids of irrigation water and sodium accumulation in these irrigated soils. This accumulation has resulted in reduced yields, prompting farmers to consider application of amendments without evaluating the potential impact on irrigation return flow quality and/or soil physical properties other than sodium displacement.

Previous greenhouse experiments have been conducted with intact soil columns of loam, silt loam, and silty clay loam textures. *Medicago sativa* L. was grown in soil columns irrigated with an accelerated salt-loading schedule using past, present and projected future irrigation water qualities from the Powder River. Following the final harvest, two studies were conducted. One study utilized undisturbed soil cores from two of the five replicated soil columns to characterize long-term irrigation and subsequent calcium chloride application effects on soil hydraulic properties and drainage water quality. Identical cores were treated with two rates of calcium chloride, 6.42 kg m⁻² and 7.73 kg m⁻². Calcium chloride solution was applied to the cores and passed through with a pressure head of 33.0 kPa to simulate free drainage. Leachate was collected and analyzed for sodium concentration. Following amendment application and leaching, replicated Tempe cell measurements in the pressure range 0-100. kPa were made to determine the effect of calcium chloride on soil hydraulic properties. Water outflow data were used to prepare moisture release curves and calculate pore size distribution.

The second study utilized the remaining undisturbed soil columns to evaluate the effect of calcium chloride application on soil hydraulic properties. Calcium chloride was applied at a rate of 6.42 kg m⁻² to soil columns. Following calcium chloride application, a 5 cm irrigation was applied and allowed to drain below soil surface. Intact cores were taken from surface and placed in Tempe cells to determine effect of treatments on soil hydraulic properties.

Irrigation of the soils with present and projected future water qualities resulted in decreased macro-porosity and reduced soil hydraulic conductivity. Addition of calcium chloride increased the macro-porosity but resulted in significantly elevated sodium concentration in drainage water. This elevated sodium concentration would likely have deleterious effects on groundwater quality.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Date 13 May 1993

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LIST OF SYMBOLS

Symbol	Meaning
EPSR	Effective pore size radius
PAW	Plant available water
n	Number of hydrogen bonded molecules in polymer
σ	Surface tension of water (dynes cm^{-2})
r	Radius of pore (cm), radius of curvature
P_e	Pressure greater than atmospheric
g	Acceleration due to gravity (980 cm sec^{-1})
ρ	Temperature dependent density of water (g cm^{-3})
γ	Contact or wetting angle
h	Height of water rise in capillary tube (cm)
V_{max}	Terminal velocity
ν	Coefficient of velocity
F	Tangential force exerted on massless plate
A	Cross-sectional area of capillary tube
W	Distance between plates
F_s	Shear force
dV/dy	Velocity gradient perpendicular to stationary plate
C	Ion concentration at a specific distance from a charged surface
C_0	Ion concentration of bulk solution
Z	Ion valence
q	Electrostatic unit charge

LIST OF SYMBOLS- Continued

Symbol	Meaning
ψ_e	Distance dependent colloid electrical potential
k	Boltzmann constant
F_{ic}	Force of ion-clay interaction
D	Dielectric constant of solution
$q^{+/-}$	Electrostatic unit of cation/anion
d	Distance
ψ_z	Gravitational potential
ψ_m	Matric potential
ψ_p	Pressure potential
ψ_s	Solute potential
ψ_h	Hydraulic potential
F_p	Force between two points in a capillary tube
P_a	Pressure at point a
P_b	Pressure at point b
ΔP	Change in ψ_h between two points
R	Radius of capillary tube
L	Length of capillary tube (cm)
τ	Tangential force per unit area
v	Velocity of fluid flow
dv/dR	Change in velocity perpendicular to tube wall
T	Absolute temperature

LIST OF SYMBOLS-Continued

Symbols	Meaning
Q	Quantity of water
J_w	Water flux
K_i	Intrinsic permeability
HC	Hydraulic conductivity
ϵ	Water-filled porosity
f	Fluidity
η	Viscosity of water (poise)
HC_s	Saturated hydraulic conductivity
EC	Electrical conductivity
ESP	Exchangeable sodium percentage
SAR	Sodium adsorption ratio
MRC	Moisture release curve
PDTP	Percent of total porosity
TDS	Total dissolved solids
θ_v	Volumetric water content
θ_m	Mass water content
h_m	Matric head

ABSTRACT

Saline-sodic soils have developed in some irrigated areas of eastern Montana, due in part to increasing total dissolved solids of irrigation water and sodium accumulation in these irrigated soils. This accumulation has resulted in reduced yields, prompting farmers to consider application of amendments without evaluating the potential impact on irrigation return flow quality and/or soil physical properties other than sodium displacement.

Previous greenhouse experiments have been conducted with intact soil columns of loam, silt loam, and silty clay loam textures. Medicago sativa L. was grown in soil columns irrigated with an accelerated salt-loading schedule using past, present and projected future irrigation water qualities from the Powder River. Following the final harvest, two studies were conducted. One study utilized undisturbed soil cores from two of the five replicated soil columns to characterize long-term irrigation and subsequent calcium chloride application effects on soil hydraulic properties and drainage water quality. Identical cores were treated with two rates of calcium chloride, 6.42 kg m^{-2} and 7.73 kg m^{-2} . Calcium chloride solution was applied to the cores and passed through with a pressure head of 33.0 kPa to simulate free drainage. Leachate was collected and analyzed for sodium concentration. Following amendment application and leaching, replicated Tempe cell measurements in the pressure range 0-100 kPa were made to determine the effect of calcium chloride on soil hydraulic properties. Water outflow data were used to prepare moisture release curves and calculate pore size distribution.

The second study utilized the remaining undisturbed soil columns to evaluate the effect of calcium chloride application on soil hydraulic properties. Calcium chloride was applied at a rate of 6.42 kg m^{-2} to soil columns. Following calcium chloride application, a 5 cm irrigation was applied and allowed to drain below soil surface. Intact cores were taken from surface and placed in Tempe cells to determine effect of treatments on soil hydraulic properties.

Irrigation of the soils with present and projected future water qualities resulted in decreased macro-porosity and reduced soil hydraulic conductivity. Addition of calcium chloride increased the macro-porosity but resulted in significantly elevated sodium concentration in drainage water. This elevated sodium concentration would likely have deleterious effects on groundwater quality.

CHAPTER 1

INTRODUCTION

Many ancient civilizations came into power by forming an agricultural-based economy through extensive use of irrigation. These same civilizations experienced difficulty when their soils became too salty to sustain continued crop production (Schafer, 1982). Salinization of irrigated cropland not only has a serious impact on the economy of a nation but can influence quality of the environment.

It is generally assumed there is a direct relationship between irrigation of arid and semiarid soils and crop yield. About one-third of the earth's land is arid or semiarid (James et al., 1982). With the earth's population expanding exponentially, there is increasing need to bring this land under production. Irrigation is the key for enabling these regions to produce food necessary to feed this expanding population.

For the most part, all soil parent materials contain some salts (Schafer, 1982). Natural weathering processes release these salts, and water moving through this material solubilizes these salts (Rhoades, 1968a). Irrigation water containing excessive salts can have a deleterious effect on structure and physical properties of soil.

Fine-textured soils are adversely affected when sodium becomes the predominant cation on the exchange sites of clay minerals. Shrinking and swelling of the clay double layer in response to decreases and increases in soil water content weaken soil aggregates (Abu-Sharar et al., 1987 and Barnes, 1980). This weakening decreases overall effective pore size radius (EPSR). Soils with relatively smaller EPSR retain soil water at more negative potential than soils with larger EPSR for a given volumetric water content. Since plants are limited in the potentials they are able to generate for extracting soil water, this decrease in EPSR reduces the amount of plant available water (PAW) in soil.

The Montana Department of Natural Resources and Conservation is concerned about sodium accumulation in soils irrigated with Powder River water. This accumulation has resulted in reduction of irrigated crop yields over the past two decades (Gallagher, 1986). These yield reductions have prompted irrigators to consider various land management alternatives, including the use of surface-applied soil amendments.

Numerous studies have evaluated the effect of surface-applied amendments on crop yield, performance, and soil properties (Richards, 1969; Brock, 1991; Anderson et al., 1972). Farmers along the Powder River have considered application of amendments without evaluating the potential impact on irrigation return flow quality and/or soil

physical properties other than sodium displacement.

Previous studies in this area have shown limited benefit from addition of either calcium sulfate (CaSO_4) or elemental sulfur (S) (Brock, 1991). The lack of consistent response to these amendments is due in part to the fact that many of the soils along the Powder River are saturated with respect to calcium carbonate (CaCO_3), and S is a common constituent of the irrigation water. Calcium chloride and/or MgCl_2 have been considered as alternative amendments (Bond et al., 1984). However, little is known about the effect of either of these amendments on soil hydraulic property modification or the effect on irrigation return flow qualities. Excessive Mg^{2+} cations on clay exchange sites can have a more deleterious effect than sodium on soil structure.

Objectives

The objective of this study was to evaluate the effect of reclaiming sodium-damaged soils from along the Powder River on water quality of irrigation return flows and shallow groundwater. This thesis provides baseline data for predictive modeling of irrigation leachate quality and return flow of sodium by soil type into the Powder River water table. Also, an attempt was made to quantify the potential impact of future irrigation and reclamation efforts on vadose zone salt loading.

Specific objectives were:

1. To determine the impact of CaCl_2 on the physical and hydraulic properties of three soils irrigated with simulated past, present, and expected future irrigation water qualities of the Powder River;
2. Evaluate the effect of CaCl_2 addition on quality of irrigation return flow.

CHAPTER 2

LITERATURE REVIEW

Much work has been done to examine effects of surface-applied amendments on soil physical properties, but little work has been done to assess the impact amendment rates have on the quality of groundwater and irrigation return flow. Sodium, the cation usually targeted for displacement by amendments, though not commonly considered a hazardous chemical, is deleterious to freshwater aquatic systems at high concentrations (Rhoades et al., 1973).

Soil water retention curves are used in models predicting non-saturated flow through soil, since fluid movement takes place only in those areas occupied by water. This approach is partially incorrect since part of the total soil water content is located in isolated pockets or dead-end pores not contributing to the overall hydraulic conductivity. Current methods for predicting solute transport rates have come under much scrutiny recently with the detection of hazardous chemicals in groundwater ahead of prediction.

It is necessary to understand concepts of water and its movement through soils before understanding amendment rate effects on groundwater quality and irrigation return flow.

Properties of Water

Molecular Properties

A water molecule consists of two hydrogen and one oxygen atoms, with a H-O bond length 9.7×10^{-11} m (Figure 1). The valence shell of the oxygen atom in the water molecule has two bonding and two nonbonding pairs of electrons. The four electron pairs are arranged in a tetrahedral shape with a bond angle of 105° , which gives the molecule an angular configuration. This configuration places the hydrogen atoms approximately 1.54×10^{-10} m apart (Figure 1).

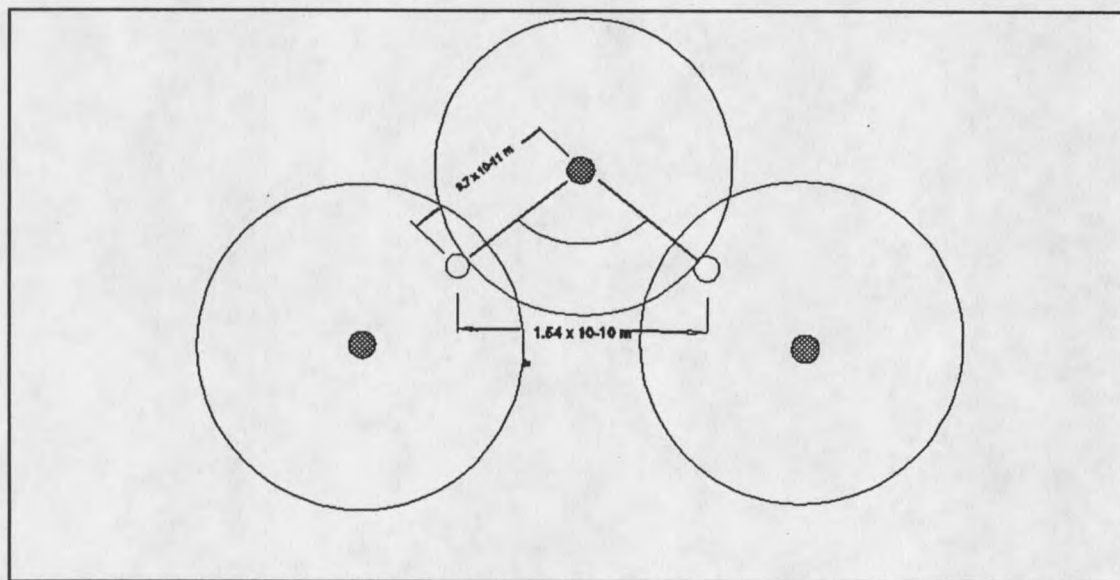


Figure 1. Structure of water molecule. Straight lines represent bonds, shaded circles are oxygen molecules, small open circles are hydrogen, and large open circles are electron cloud orbitals.

Water molecules exhibit distinct intermolecular forces

called hydrogen bonding (Mortimer, 1986). Hydrogen bonding occurs when hydrogen is covalently bonded to the small, strongly electronegative oxygen atom. The oxygen atom pulls the center of the electron cloud from the hydrogen, resulting in a significant partial positive charge on the almost exposed hydrogen proton. The electropositive hydrogen atom of water is attracted to unshared electrons of an electronegative atom, resulting in an electrostatic bonding force. Hydrogen bonds are relatively weak in comparison to covalent and ionic bonds. These bonds are, however, crucial to many important properties of water.

States of Water

Water molecules in vapor phase have a structure that is independent of other water molecules; although dimers and trimers structures are possible, they are very rare (Hillel, 1980). Water molecules in the solid phase have a rigid lattice structure with a tetrahedral configuration (Figure 2).

Liquid phase (state) water is somewhere between these two structures. When ice melts, the rigid lattice structure does not totally disappear. Hydrogen bonds between liquid water molecules hold the molecules in small, transient crystal configurations called "flickering ice crystals"

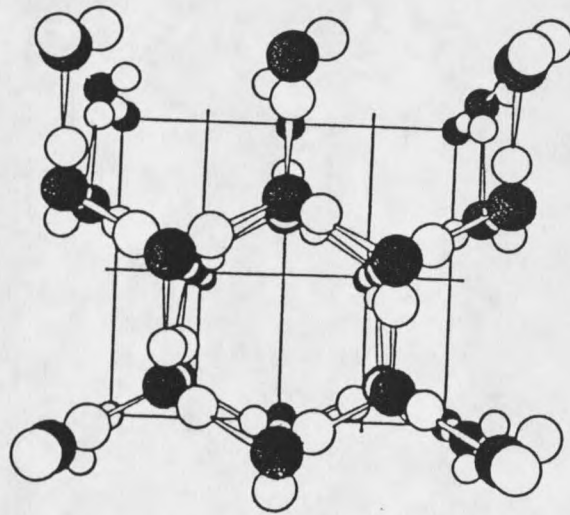


Figure 2. Schematic structure of an ice crystal. Oxygen atoms are shown in black and hydrogen atoms in white. Pegs linking adjacent molecules represent hydrogen bonds (from Hillel, 1980).

(Hillel, 1980). Molecules of water form and separate hydrogen-bonded polymers repeatedly in a random and transitory pattern designated as $(\text{H}_2\text{O})_n$, where n is the number of hydrogen-bonded water molecules in a polymer at any one particular moment in time. These polymers have a quasi-crystalline structure with an average n of about 40; however, these polymers associate and dissociate so rapidly that liquid water behaves as a homogenous liquid (Hillel, 1980). The average n size is dependent on temperature, since n decreases as temperature increases.

Fluid Properties of Water

Water has many unusual properties including: density

greater as a liquid than a solid; high heat of fusion; high heat of vaporization; high specific heat; high dielectric constant (Table 1). These unusual fluid properties for water are best explained by the frequency of hydrogen bonding taking place between individual molecules.

Table 1. Selected physical properties of pure water (from Jury et al., 1991)

Properties	Value	Units	Temperature (°C)
Density			
(liquid)	0.998	g cm ⁻³	20
(solid)	0.910	g cm ⁻³	0
(vapor)	1.73 x 10 ⁻⁵	g cm ⁻³	20
Heat of fusion	3.34 x 10 ⁸	erg g ⁻¹	0
Heat of vapor.	2.45 x 10 ⁹	erg g ⁻¹	20
Specific heat	0.999	erg g ⁻¹ °C ⁻¹	20
Dielectric con.	80		20
Thermal cond.	6.03 x 10 ³	erg cm ⁻¹ s ⁻¹ °C ⁻¹	20
Viscosity	1.00 x 10 ⁻²	g cm ⁻¹ s ⁻¹	20
Surface tension	72.7	erg cm ⁻²	20

Fluid Properties

Surface Tension

When water has an interface with another fluid like air, molecules near the interface are subject to many forces. Molecules of water in the bulk fluid are hydrogen bonded to adjacent molecules in all directions. There is no net tension pulling bulk fluid molecules in any particular

direction. The molecules exposed to an air-water interface do not have tension in all directions since no hydrogen bonding exists between the molecules of the air and the molecules of water at the water surface. The water molecules at the interface have a net tension pulling them toward the bulk fluid, thereby forming a crystalline-like structure at the surface. The density of water at the air-water interface is greater than that of the bulk fluid. Since the arrangement of the molecules at the surface has greater order, the molecules at the surface have more energy per unit area than molecules in the bulk fluid. This force exhibited on the surface molecules is referred to as surface tension (σ).

Surface tension is the reason water will form a dome at the top of an over-filled glass. This curved surface at the air-water-solid interface is the basis for another important property of water--pressure gradient across a curved interface. The pressure is greater on the convex side of a curved fluid interface than on the concave side (Kirkham and Powers, 1972). This pressure difference is the result of tension created by stretching of the hydrogen bonds in the surface layer, changing the surface area on the opposing sides of this layer. The pressure at the surface at equilibrium can be described by Equation 1.

$$\frac{2\pi r\sigma}{g\rho} = \pi r^2 P_e \quad [1]$$

where r is the radius of curvature, and P_e is the pressure greater than atmospheric, σ is surface tension, ρ is fluid density, and g is the acceleration due to gravity (see Figure 2). Rearranging and solving Equation 1 for pressure yields Equation 2.

$$P_e = \frac{2\sigma}{rg\rho} \quad [2]$$

Contact Angle

When water is present in a three phase system, the angle measured from the water-solid interface to the water-air interface is called the contact angle (γ). When water is preferentially attracted to a solid phase with more force than the cohesive attraction to adjacent water molecules, the solid phase is considered "wetable" (Figure 3).

When the cohesive force between adjacent water molecules is greater than the attractive force between water molecules and the liquid phase, the solid is considered "non-wetable" (Figure 4).

Capillary Rise

When a small, glass capillary tube is placed in a reservoir of water exposed to atmospheric pressure, the adhesive force between the liquid and solid phase causes the water to move up the sides of the glass tube, forming a curved surface at the interface (Figure 5).

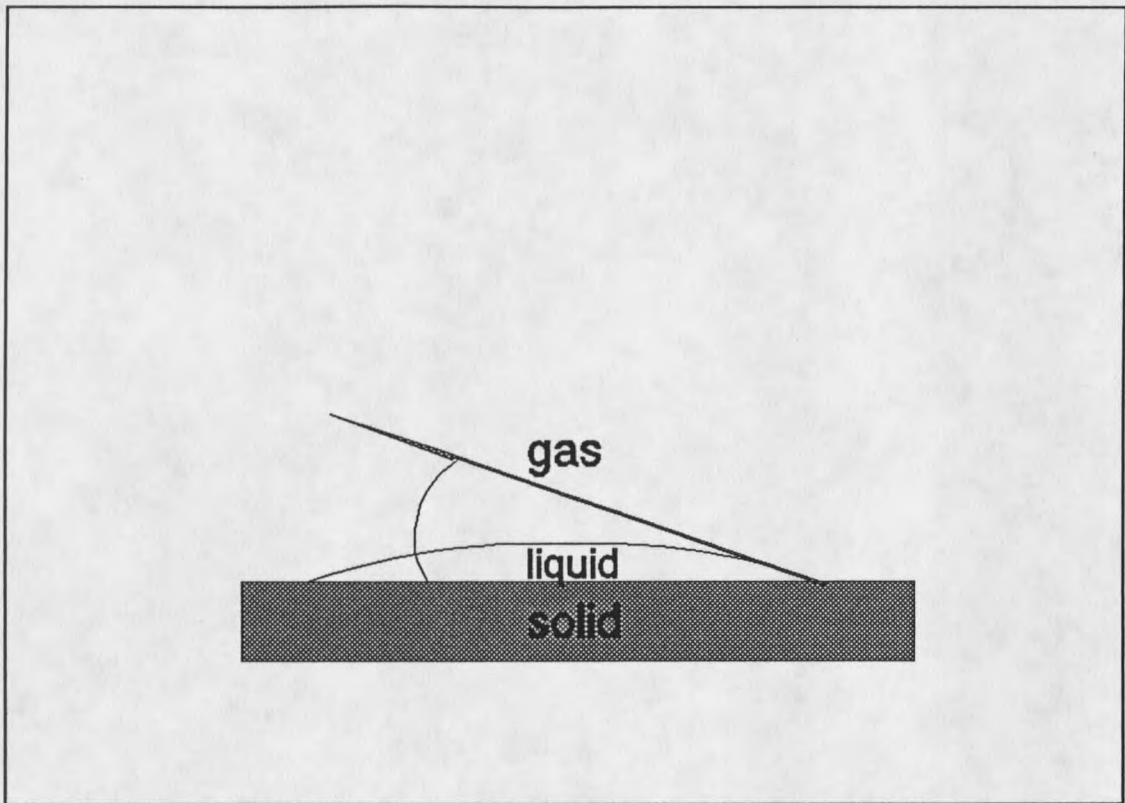


Figure 3. Illustration of the contact angle for a wettable solid.

This curved surface results in a pressure gradient, and atmospheric pressure pushes water up the tube. Water will rise up the capillary tube until the weight of the column of water equals the pressure gradient across the curved surface. Magnitude of the rise is dependent on the radius of the capillary tube and is described by Equation 3.

$$h = \frac{2\sigma \cos \gamma}{r \rho g} \quad [3]$$

where h is height of water rise in capillary tube, σ is surface tension of water, γ is the wetting angle, r is the radius of the tube, g is acceleration due to gravity, ρ is

