AMELIORATION OF SODIC TEXTILE WASTEWATER WITH GYPSUM BEFORE LAND APPLICATION

by

DANILO ARMANDO RODRIGUEZ

(Under the direction of Dr. Malcolm Sumner)

ABSTRACT

Textile plants produce wastewaters that are frequently high in Na and relatively low in Ca and Mg; such waters are termed sodic. When such wastewaters are applied to land, the Na/(Ca+Mg) imbalance, which is measured by the sodium adsorption ratio or SAR, is detrimental to the soil. One management practice used to counter this effect is the addition of gypsum ($CaSO_4 \cdot 2H_2O$) to the wastewater. In this research, the long-term effects of land application of textile wastewaters with different SAR values on the physical and chemical properties were studied. Soil columns using a Cecil series soil were prepared and leached with wastewaters having SAR values of 2, 5, 10 and 20. Soil cation exchange capacity increased at all SAR levels. Soils treated with SAR 10 and 20 wastewaters showed the largest decline in hydraulic conductivity.

INDEX WORDS: Textile wastewater, Sodicity, SAR, Land application, Gypsum, Cation exchange capacity, Hydraulic conductivity.

AMELIORATION OF SODIC TEXTILE WASTEWATER WITH GYPSUM BEFORE LAND APPLICATION

by

DANILO ARMANDO RODRIGUEZ

Licenciate, Universidad del Valle de Guatemala, Guatemala, 2000

A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2002

AMELIORATION OF SODIC TEXTILE WASTEWATER WITH GYPSUM BEFORE LAND APPLICATION

by

DANILO ARMANDO RODRIGUEZ

Approved:

Major Professor: Dr. Malcolm Sumner

Committee: Dr. William Miller
Dr. David Radcliffe

Electronic Version Approved:

Gordhan L. Patel
Dean of the Graduate School
The University of Georgia
August 2002

DEDICATION

I would like to dedicate this thesis to God and to my parents Danilo and Aura Marina, because without them I would not have accomplished all the things that I have done. To my family, my sisters Karina and Marialejandra for their support and care, my grandmothers and all the people that have helped me along the way.

ACKNOWLEDGMENTS

I would like to give thanks to my major professor Dr. Sumner, for giving me the opportunity to expand my knowledge of soils and for his advice in every aspect of my degree. To my friends at the department of Crop and Soil Sciences, especially John Rema and Gene Weeks, thank you, for your help and advice throughout my master's degree. I like to thank also my friends, John, Jeff, Monte, Jen, Shelby, Zack, Patty, Jodi, Patrick, thank you for your support and friendship.

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

During the last 20 years there has been growing pressure to dispose of municipal and industrial effluents on land instead of disposing of them in natural waterways (Bond, 1998). Textile plants produce wastewaters that are frequently high in Na and relatively low in Ca and Mg; such waters are termed sodic. When such wastewaters are applied to land either directly or via city sewer systems, the Na/(Ca+Mg) imbalance, which is measured by the sodium adsorption ratio or SAR, defined as $[Na]/([Ca + Mg]/2)^{1/2}$ where brackets [] reflect cation concentration in $mmol_c/L$ is detrimental to the soil (Sumner et al., 1998). When wastewaters of high SAR are applied to land, the extent of soil degradation will depend on the level of electrolyte present. However, under humid conditions, rainfall dilutes the electrolyte in the soil, increasing the susceptibility of the soil to hydraulic degradation (Levy et al., 1998).

In the United States, 55% of all textile mills are located in the states of Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee. North and South Carolina, Georgia, and Alabama are four of the five major states for employment in the textile industry. Textile mills can discharge their wastewater directly to streams (direct dischargers) or through a water treatment plant (indirect dischargers) where the wastewater is treated before being applied to the land or discharged into

streams. Indirect dischargers comprise 96% of all textile mill dischargers (U.S. EPA, 1997).

Land application of sodic textile wastewater can have both economical and environmental advantages, but only if it is accompanied by judicious soil management practices. One management practice is the addition of gypsum ($CaSO_4 \cdot 2H_2O$) to the wastewater to reduce the SAR and increase the electrolyte concentration (Oster and Jayawardane, 1998). In cases where high SAR waters were not ameliorated with gypsum and subsequently applied to agricultural and industrial land, severe soil degradation occurred (Shainberg and Letey, 1984; Keren et al., 1990).

Although a large number of studies have investigated the impact of saline and sodic irrigation waters on soil sodicity, research on the effect of sodic wastewater (including textile mill effluent) on soil physical and chemical properties in Ultisols is scarce. Preliminary studies with sodic wastewaters conducted by Jayawardane (1995) and Surapaneni et al. (1998) suggest the need for research programs to develop management systems. Still, there are great limitations. For example, it is not well understood how sodic wastewaters change soil chemical properties and how these changes affect soil physical properties and subsequent soil behavior.

The objective of this study is: To quantify and determine the long-term effect of land application of textile wastewater with different SAR on physical and chemical soil properties.

References:

Bond, W.J. 1998. Effluent irrigation – An environmental challenge for soil science. Aust. J. Soil Res. 36:543-55.

Levy, G.J., I. Shainberg, and W.P. Miller. 1998. Physical properties of sodic soils. p. 77-94. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Jawardane, N.S. 1995. Wastewater treatment and reuse through irrigation: With special reference to the Murray Basin and adjacent coastal areas. Australian Commonwealth Scientific and Industrial Research Organization Division of Water Resources. Divisional Rep. 95-1. Griffith, Australia.

Keren, R., D. Sador, H. Frenkel, I. Shainberg, and A. Meiri. 1990. Irrigation with sodic and brackish water and its effects on the soil and on cotton yields. Hassadeh 70:1822-1829.

Oster, J.D., and N.S. Jayawardane. 1998. Agricultural management of sodic soils. p. 125-146. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Shainberg, I., and J. Letey. 1984. Response of soils to sodic and saline conditions. Hilgardia 52:1-57.

Sumner, M.E, W.P Miller, R.S. Kookana, and P. Hazelton. 1998. Sodicity, dispersion, and environmental quality. p. 149-172. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Surapaneni, A., D.P. Burrow, K.A. Olsson, D.R. Hill, and R.J. Wrigley. 1998. Impact of wastewater irrigation on soil sodicity and structure: A preliminary survey. p. 17-20. *In* Proc. of the Natl. Soils Conf. Aust. Soc. of Soil Sci., Brisbane, Australia.

U.S. Enviromental Protection Agency (U.S. EPA). 1997. Profile of the textile industry. USEPA Rep. 310-R-97-009. U.S. Gov. Print. Office, Washington, DC.

CHAPTER 2

LITERATURE REVIEW

Soils in numerous areas of the world are adversely affected by the presence of excess Na in the soil solution and as an exchangeable cation. Sodium–affected soils exhibit poor soil water and air relations which adversely affect soil water movement, stunt root growth and plant production, and make soil difficult to farm when it is either dry or wet. Consequently, in many cases, such soils have to be abandoned (Levy, 2000).

Drainage water and recycled municipal wastewater, are significantly more sodic than normal fresh water, but are rapidly becoming a common water source for agriculture in many areas of the world. In particular, there has been an increase in the past 10 years in land application of sodic wastewater as an alternative means of disposal of municipal and industrial (e.g., food and textile industry) effluents (Bond, 1998).

In order to better understand the effect of sodium on the physical and chemical properties of the soil, it is necessary to define the parameters by which sodic soils are evaluated.

Two important parameters are generally used. The first is the exchangeable Na percentage (ESP), which describes the level of adsorbed Na in the soil, and is defined as:

ESP = 100 * (Exchangeable Na/Cation Exchange Capacity (CEC))

where the CEC is normally determined at a reference pH (7.0 or 8.2).

The second parameter reflects the sodicity level of the irrigation water or soil solution and is termed the Na adsorption ratio (SAR); it is defined as:

$$SAR = [Na]/([Ca+Mg]/2)^{1/2}$$

where brackets [] reflect cation concentrations in $mmol_c/L$. It should be emphasized that the sodicity hazard of solutions is related to the ratio of Na to the divalent cations present in the water and not to the Na concentration alone (Levy, 2000).

Exchange reactions take place between the soil solution and the exchange phase. Thus, soil ESP can be estimated from the SAR of saturated soil paste extracts using the following empirical relationship (USSL Staff, 1954):

$$ESP = 100(-0.0126+0.01475SAR)/(1+[-0.0126+0.01475SAR]).$$

When more dilute extracts are used (e.g., 1:5 soil:water ratio), then a different relationship holds (Rengasamy et al., 1984):

$$ESP = 1.95SAR + 1.8.$$

In terms of the suitability of water for irrigation, this is determined by the potential for water to cause problems to soils and crops and is related to the management practices needed. The quality of water for irrigation is determined mainly by the concentration and composition of solutes present. Consequently, the most important water quality parameter for irrigation is the total salt concentration, most commonly measured as electrical conductivity (EC). The relation between EC ($S\ m^{-1}$) and electrolyte concentration (C_e) of a given salt ($mol_c\ m^{-3}$) is given by:

$$\wedge = EC/C_e$$

where $\wedge$ is the equivalent conductance ($S\ mol_c^{-1}\ m^2$).

The EC of an aqueous electrolyte solution increases at a rate of approximately 2% C^{-1}. Although the factor for converting EC (dS m^{-1}) to C_e ($mmol_c$ L^{-1}) depends on the type of electrolyte, a useful approximation is:

EC(dS m^{-1})*10 = C_e ($mmol_c$ L^{-1}) (Keren, 2000).

To date there is no widely accepted definition of a sodic soil. The USSL Staff (1954) define a sodic soil as one whose physical properties are adversely affected by the presence of Na or where the ESP is >15, adding the reservation that this limit must be regarded as somewhat arbitrary and tentative. For this reason, Sumner (1993) expressed doubts about referring to a soil as "sodic" on the basis of ESP and SAR or on SAR alone. In his review, he used the term "sodic soil" to refer to situations where soil physical behavior is appreciably affected by the presence of exchangeable Na, irrespective of the amount present. He suggested the terms "sodic" and "sodicity" should become obsolete as their definition has become imprecise. Rather, soils should be described in terms of their behavior and should be classified as "spontaneously dispersive" in water at very low salt contents, "mechanically dispersive" with energy inputs at higher salt contents, and finally "flocculated" in high salt contents.

In terms of properties of the soil, the hydraulic aspects of sodic soils are fundamental in determining their capacity for agricultural and industrial use. The hydraulic conductivity is an important parameter to determine the rate of water movement through the soil profile. The hydraulic conductivity of a soil is determined by the pore size distribution, clay mineralogy, clay content, sodicity and EC (Shainberg and Letey, 1984).

The constant head method is commonly used to measure hydraulic conductivity under saturated conditions (K_s). In this method, a constant head of water is maintained at the top or bottom of a soil core and the steady water flux is recorded (Klute and Dirksen, 1986). Using Darcy's equation:

$$K_s = J * L/(H_2 - H_1)$$

where L (>0) is the length of the core, and H_1 and H_2 are the total potentials at the top and bottom of the core, respectively. The flux, J, is negative in the downward direction so K_s must always be positive (Radcliffe and Rasmussen, 2000).

Clay dispersion as affected by sodium

When Na is involved in the association among clay particles, soils tend to form micro- and macro-aggregates without any hierarchical arrangement of different particle size (Barzegar et al., 1994). Upon wetting, the swelling and dispersion of soil clay particles within the aggregates proceed through a number of different stages, as seen on Figure 1. Initial hydration of cation-saturated clays leads to swelling while continuous (extensive) hydration of highly sodic clays results in the liberation and spontaneous dispersion of clay particles from the aggregates. The extent of the hydration depends on the nature of bonding between the cations and the clay surfaces. In Figure 2 we can see three types of bonds between clay surfaces and cations. The linkage between Al-hydroxy cations and clay surfaces is dominated by covalency because of the high polarizing power of Al (Figure 2a). Thus Al and Fe hydroxy species are specifically adsorbed or inner spherically coordinated to the clay surfaces. Hence, hydration of Fe and Al in such linkages becomes difficult. Calcium forms polar covalent bonds (Figure 2b) in which the

hydration of Ca is limited and determined by the polarity of the bond. For Na, the linkage of clay surfaces is ionic (Figure 2c), and hence, hydration is extensive for Na-saturated clays (Rengasamy and Sumner, 1998).

To better understand this process, it is necessary to explain the magnitude and direction of energy changes taking place during wetting of an aggregate, the hydration mechanism for soil clays, the repulsive and attractive forces in clay-water systems, and spontaneous versus mechanical dispersion.

In the initial wetting of dry aggregates, clay particles are bound together by inorganic and organic compounds involving several mechanisms and types of bonding (van der Waals forces, ionic, hydrogen, covalent, and hydrophobic bonds and coordination complex), which produce strong attractive pressures (Rengasamy and Olsson, 1991). The water stability of an aggregate depends on the strength and persistence of these types of bonds. Bond strength in the presence of water generally decreases in the order: covalent, hydrophobic, Lifshitz-van der Waals, coordination complexing, hydrogen, and finally ionic bonds (Huheey et al., 1994). The degree of covalency in a bond involving metal cations is characterized by the Misono softness parameter *Y* derived from ionization and ionic potentials (Misono et al., 1967):

$$Y = 10(I_z/I_{z+1})(r_i/z^{1/2})$$

where

r_i = ionic radius of metal ion

z = its formal charge

I_z = z^{th} ionization potential ($M^{(z+1)+} \rightarrow M^{z+}$)

Consequently, the tendency to form covalent bonding and complexes increases in the order: Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Hg^{2+}.

In the hydration mechanism for soil clays, the attractive forces between clay particles depend on the nature of bonding mediated through the cations (Na, K, Ca, Mg, Fe and Al) commonly found in soils. The degree of ionicity (or covalency) of such bonds depends on the nature of the cations as characterized by the Misono factor, with Na contributing more to ionicity than Ca. For Na, the linkage of clay surfaces is ionic, and hence, hydration is extensive (Rengasamy and Sumner, 1998).

Only charged clay particles exhibit swelling and dispersion, which depend on the ability of the water molecules to solvate the cations or anions involved in clay–clay bonding and are related to electron–acceptor and electron–donor interactions. It is important to note that the extent to which free (solution) versus adsorbed cations and anions are hydrated are different. For example, the hydration of cations by hydration numbers follows the order $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$, whereas the extent of swelling of smectites caused by the hydration of cationic clays in pure water at zero matric potential follows the order $Na^{+} > K^{+} > Mg^{2+} > Ca^{2+}$ (Rengasamy and Sumner, 1998).

During extensive hydration, as is observed in sodic clays, separation of clay particles > 7 nm depends on both ionic strength, and electron acceptor and electron donor interactions. When the ionic strength of the equilibrium solution is decreased, water molecules enter between the clay particles. The magnitude of pressure developed during macroscopic swelling, usually known as clay dispersion, depends on the difference in chemical potential of water in the equilibrium and inner (i.e., in the space between the particles) solutions. Once the clay particles are dispersed (i.e., separated into distinct

individual entities), electrostatic repulsive forces, as predicted by the Derjaguin-Landau-Verwey-Overbeek (DVLO) theory, come into play and Lifshitz-van der Waals attractive forces are negligible (Rengasamy and Sumner, 1998).

In repulsive and attractive forces in clay–water systems, the DVLO theory approach on the stability of dispersed clays is based on opposing forces of attraction due to van der Waals interaction and repulsion arising from electrostatic forces in the double layer. To further understand this process one needs to define the electrical double layer.

In an aqueous suspension, the charge of the clay particles is neutralized by hydrated ions of opposite charge. The electrical double layer consists of the surface charge and the surrounding ion swarm. Various theories (Gouy-Chapman, Stern) and modifications thereof (multiple layer models) have been proposed in an attempt to predict the behavior of the electrical double layer present in dispersed colloidal systems, but all have failed to predict behavior quantitatively except under very limited equilibrium conditions (Rengasamy and Sumner, 1998).

However, once clays become dispersed, either spontaneously or mechanically, the different forces operating in colloidal suspensions can be described adequately by these models (discussed in detail by van Olphen, 1977; McBride, 1989; Gregory, 1989; Iwata et al., 1995). According to the Gouy-Chapman theory, the relationship between the electrical potential ψ and the charge Φ at the particle surface, and the nature and concentration of the equilibrium solution are given by:

$$\Phi = (2,nkT)^{1/2}\ \pi\ \sinh\ (ze\psi_o/2kT)$$

where:

σ = surface charge on particle

ψ_o = surface potential

n = electrolyte concentration in equilibrium solution

z = valence of the counter ions (cations)

e = electronic charge

$\in$ = dielectric constant of solvent

k = Boltzmann's constant

T = temperature in ^oK

The effective thickness $1/k$ of the double layer is given by:

$$1/k = (\in kT/8\pi z^2 e^2 n)^{1/2}$$

Because of the exponential nature of the relationship between ion concentration and distance, theoretically the double layer is infinite in thickness (Rengasamy and Sumner, 1998).

The surface charge σ, the surface potential ψ_o and the effective thickness of the double layer change between permanent, variable, and mixed charged systems.

In permanent charge systems, where the charge in the clays arises from isomorphous substitution (e.g., smectites), the surface charge is constant, and consequently, changes in electrolyte composition and concentration (z and n) cause the surface potential ψ_o and the distribution of ions in the diffuse layer to change. On increasing the electrolyte concentration (or the valence) of the cations, the double layer thickness is reduced, but the total area formed by the counter ions and co-ions remains constant (Rengasamy and Sumner, 1998).

In variable charge systems (e.g., kaolinites and oxides of Fe and Al) the charge is dependent on pH, electrolyte concentration, and counter ion valence. When n or z are

changed, the surface charge increases or decreases while the surface potential ψ_o remains constant. Thus, except for a difference in the magnitude of the charge, variable charge systems react in essentially the same way to changes in *n* and *z* as do permanent charge systems, namely, increasing *n* and *z* reduce the effective thickness of the double layer but increase the total surface charge (Rengasamy and Sumner, 1998).

In mixed charge systems (i.e., mixtures of permanent and variable charge; e.g., inorganic and organic colloids), the surface charge σ, the surface potential ψ_o, and the effective thickness of the double layer ($1/k$) will all change simultaneously with changes in solution composition and pH of the suspension (Rengasamy and Sumner, 1998).

Because repulsion between particles increases with an increase in $1/k$ in a system of uniform polarity, the nature and concentration of the cations control the behavior in negatively charged systems and anions in their positively charged analogues. In mixed charged systems, charge reversal can be affected by changing pH and/or adsorption of organic and inorganic ligands (e.g., phosphate on positively charged sites) by innersphere complexation to the surface (specific adsorption) or both. In terms of sodic soils, in which there are elevated levels of Na, expansion of the double layer and hence repulsion between particles is promoted (Sumner, 1992).

Soils can be either spontaneously or mechanically dispersed. Spontaneous dispersion often takes place without energy inputs when sodic clay is placed in water of very low electrolyte concentration. When the bridging between clay particles involves Na and the EC is low, the interparticle distance continuously increases, with continued wetting to > 7 nm. The proportion of clay particles separated in this way depends on the

number of Na ions involved in the clay linkages and hence on the SAR of the soil-water system (Rengasamy and Olsson, 1991).

Mechanical dispersion occurs when hydrated clay particles which have undergone limited separation can be pushed further apart by applying external mechanical pressure in the range of Pascals to kilopascals (e.g., raindrops). At distances of separation greater than $2/k$, where k is the thickness of the electrical double layer in nanometers, electrostatic repulsive forces predominate over attractive forces. Hence, on continued wetting, which reduces electrolyte concentration and increases double layer thickness, the particles become progressively more separated, finally reaching the state of dispersion (Rengasamy and Sumner, 1998).

SAR and EC stability diagrams for different clay minerals and soils

Soil stability has been commonly assessed by laboratory hydraulic conductivity (Quirk and Schofield, 1955; McNeal and Coleman, 1966) or dispersion tests (Emerson, 1967; Rengasamy et al., 1984). The general consensus is that soil stability is a function of threshold electrical conductivity (TEC) and ESP or SAR, which affect attractive and repulsive forces between clay particles during wetting and inputs of energy. This relationship is illustrated on Figure 3 (Rengasamy and Olsson, 1991). Soils with high sesquioxide and organic contents or with high organic contents alone are more stable.

Quirk and Schofield (1955), who were the first to introduce the concept of TEC to determine the boundary between stable and unstable permeability, chose an arbitrary 15% reduction in hydraulic conductivity relative to that at an initially high electrolyte concentration as the TEC value. Cass and Sumner (1982a, b, c) developed a Na stability

model that was based on the slope of the linearized response curves for a series of hydraulic conductivity reductions.

Two processes which affect stability are soil swelling and clay dispersion (Frenkel et al., 1978). Soil swelling has a marked effect on reducing hydraulic conductivity, and the enhanced swelling of sodic soils results in reduced subsoil wetting, and hence, reduced available water storage. Pore swelling has been attributed to dispersion of clays, which also leads to reduce hydraulic conductivity and subsoil wetting. These processes can be related to clay mineralogy. Thus, the type of clay mineral is important since, while dispersion can occur with all clays, slaking, swelling, and consequent aggregate breakdown, or swelling into pore space, will only be significant with swelling clays (Shaw et al., 1998).

Soils with high contents of expansible 2:1 layer silicates (e.g., smectites) have a higher degree of response to sodic conditions while those high in kaolinite and sesquioxides are the least labile (McNeal and Coleman, 1966; Yaron and Thomas, 1968). Acidic kaolinitic soils have been considered insensitive to changes in soil ESP; however, upon addition of smectitic impurities to these soils, their susceptibility to sodic conditions increased markedly (Frenkel et al., 1978). The hydraulic conductivity of nonacidic arid land kaolinitic soils has been reported to decrease significantly upon exposure to sodic conditions (Frenkel et al., 1978; Abu Sharar et al., 1987). Among the 2:1 layer silicates, smectitic soils have greater sensitivity to ESP than their vermiculite counterparts (Rhoades and Ingvalson, 1969). Figure 4 illustrates the combinations of salt concentrations and ESP required to produce a 25% reduction in hydraulic conductivity for different types of soils.

In relation to texture, mobile clay in the leachate is usually only observed in sandy soils. When clay content is high, the small size of the conducting pores usually ensures that dispersed clay moves only short distances before it clogs the pores, thus leading to a low hydraulic conductivity. Conversely, in sandy soils, the dispersion mechanism and macroscopic clay movement become evident particularly at higher ESP levels (Pupisky and Shainberg, 1979).

Review of cases where amelioration of sodic irrigation waters with gypsum occurred

Gypsum ($CaSO_4 \cdot 2H_2O$), both from natural and anthropogenic sources (byproducts), is the most commonly used amendment for sodic soil reclamation, primarily because of its low cost, reasonable solubility, and availability. Gypsum added as an amendment to sodic irrigation water can prevent a decrease in the soil's hydraulic conductivity due to the accumulation of Na by means of increasing the electrical conductivity and cation exchange effects in the soil (Loveday, 1976).

The addition of gypsum to the soil surface or to the irrigation water for the purpose of maintaining the structure and infiltration rate of the soil is a common practice in many areas of the world.

In California, Mace and Amrhein (2001) applied gypsum to the soil surface after irrigation with sodic water of SAR values (1,3,5 and 8) and reported an increase in hydraulic conductivity of the soil for all SAR values following application of gypsum to the soil surface. In Iran, Sameni and Morshedi (2000) also reported that gypsum application to soils modified the suppressing effect of sodicity on the hydraulic

conductivity, and the decrease in suppression was more pronounced for higher rates of gypsum applied.

In Israel, Frenkel and Hadas (1981) and Keren et al. (1990) suggested that surface application of phosphogypsum in cotton production is efficient in maintaining an adequate hydraulic conductivity in the soil even after years of subsequent cycles of irrigation with saline-sodic water in the summer and low electrolyte rainwater in the winter.

In India, the use of sodic irrigation water in crop production is growing, which results in a deterioration of the soil physical properties during the monsoon season. Many studies have reported a positive impact of surface-applied gypsum on wheat, rice and maize yields due to an improvement of the soil structure and hydraulic conductivity and a decrease of the soil ESP (Joshi and Dhir, 1994; Bajwa et al., 1993; Ali et al., 1991; Singh and Bajwa, 1991; Bajwa and Josan, 1989; Manchanda et al., 1988).

Furrow erosion and low rate of water intake caused by sodic conditions in the soil is a growing problem of crop production systems in Latin America. In Venezuela, Ramirez et al. (1999) used phosphogypsum as an amendment to low electrolyte irrigation water in onion production. Improved drainage and infiltration rates were reported after amending the soil with phosphogypsum, which consequently increased onion yields.

Review of sodic wastewater disposal

Wastewater effluents generally contain high concentrations of suspended and dissolved solids, both organic and inorganic (e.g., sodium, chloride, boron and selected heavy metals). Most of the salts added to the wastewater during domestic and industrial

usage are only minimally removed during conventional sewage treatment, so they remain in the irrigation water that may eventually reach the soil.

The sodium adsorption ratio (SAR) values for wastewater effluents are generally higher than those for the associated potable water, and, as a result, the exchangeable sodium percentage (ESP) of soils irrigated with reclaimed wastewater increases (Tarchitzky et al., 1999).

The potential use of land-applied wastewater specifically from the food, textile and paper industry in agriculture has emerged as one promising solution (Vasconcelos and Cabral, 1993; Ritter et al., 1992; Zibilske, 1987). In many parts of the world, treated municipal wastewater has been successfully used for the irrigation of various crops including agronomic (Bielorai et al., 1981; Bole and Bell, 1978; Campbell et al., 1983; Feigin et al., 1984; Al-Jaloud et al., 1995; Clark et al., 1999) and horticultural (Basiouny, 1984; Nielsen et al., 1989a, 1989b, 1989c, 1991; Howe and Wagner, 1996; Mancino and Pepper, 1992).

These studies have reported that municipal wastewater can be used in crop production systems, because it increases the cation exchange capacity (CEC) and the amount of organic matter in the soil; but they also reported that it could be detrimental to the soil structure and crop growth due to the high concentration of sodium.

In drier areas, the problem of high concentrations of sodium in the wastewater, may pose a limitation to the sustainability of its use on land (Bond, 1998). The use of sodic wastewater in these conditions may cause not only problems in crop production but can cause the soil to become sodic. Under conditions where sodicity develops, soil and

wastewater management must be adapted to prevent such soil degradation (Bresler et al., 1982; Oster and Jayawardane, 1998).

The use of gypsum to ameliorate the sodium imbalance in the wastewater or to prevent crust or seal formation at the soil surface due to the high concentrations of sodium has been proposed (Mancino and Pepper, 1992; Sumner and Stewart, 1992).

However, no laboratory or field scale tests have been conducted to determine the effect of gypsum in ameliorating sodic wastewater for land disposal or agricultural production.

There is much scope for greater use of land disposal or agricultural use of sodic wastewater provided that in each particular situation, it can be shown to be environmentally sustainable and economic (Sumner, 2000).

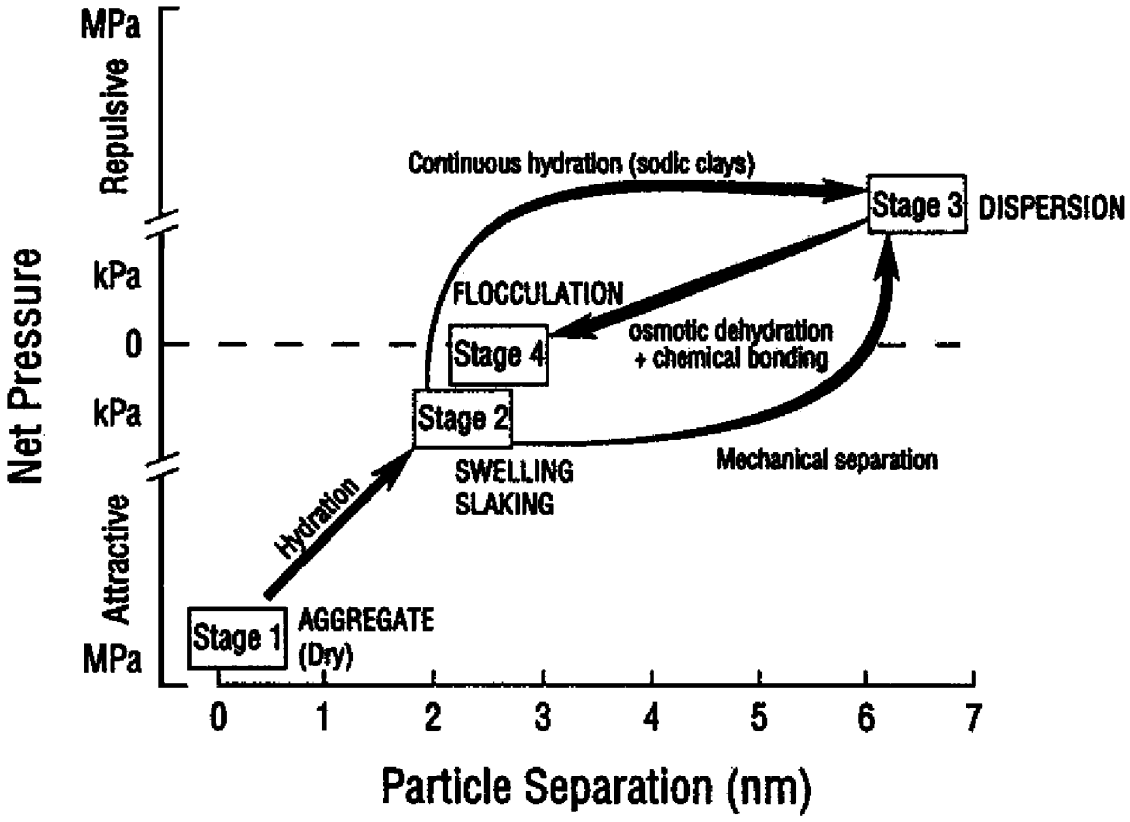


Figure 1. Schematic illustration of processes that take place and intensity of attractive and repulsive forces involved when a dry aggregate of a soil is wetted. [Sumner and Naidu, Sodic soils: Distribution, properties, management and environmental consequences (1998)].

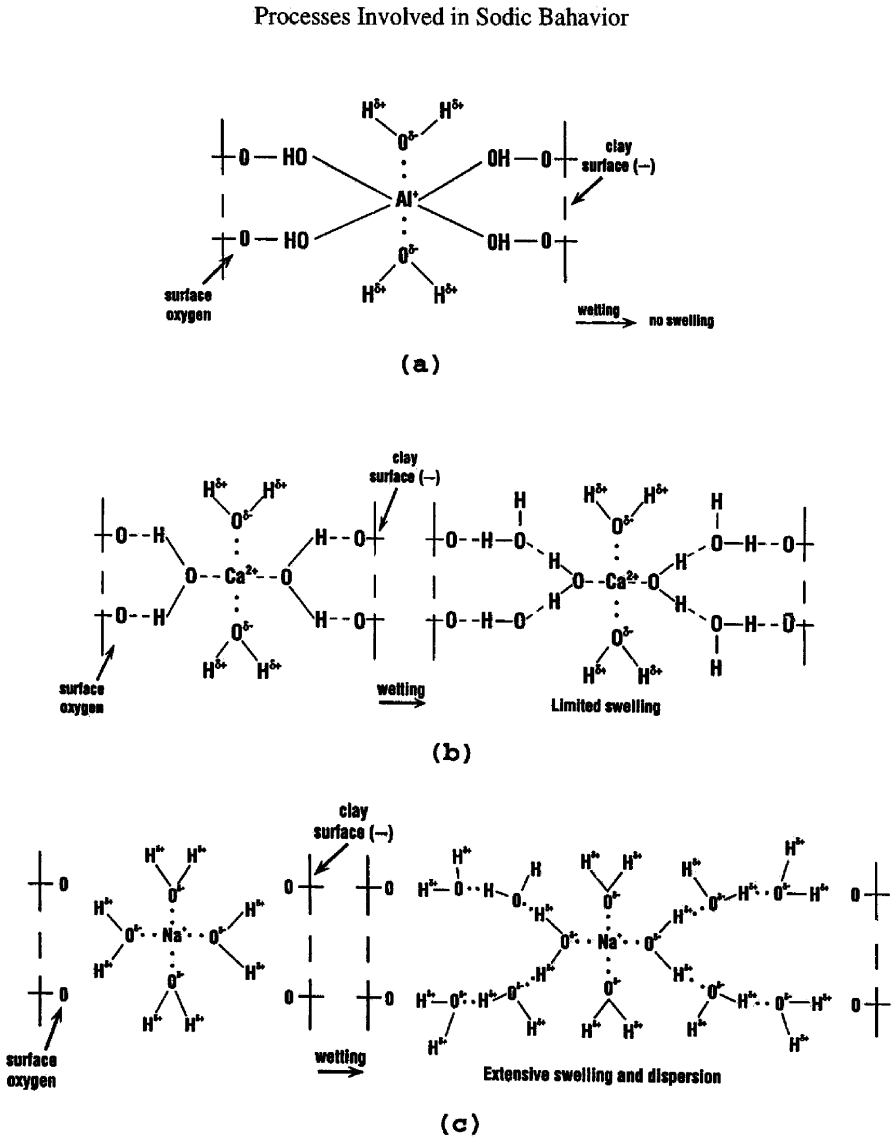


Figure 2. Schematic representation of the effect of wetting and nature of bonding between cations and clay surfaces on swelling and dispersion: (a) ($[Al(OH)_2]^+$) ion linking clay particles by covalent bonding (-) (b) Ca^{2+} aquo ion linking clay particles by polar covalent bonding (--) and (c) Na^+ aquo linking clay particles by ionic bonding. Water molecules are linked to cations by hydrogen bonding (●●). [Sumner and Naidu, Sodic soils: Distribution, properties, management and environmental consequences (1998)]

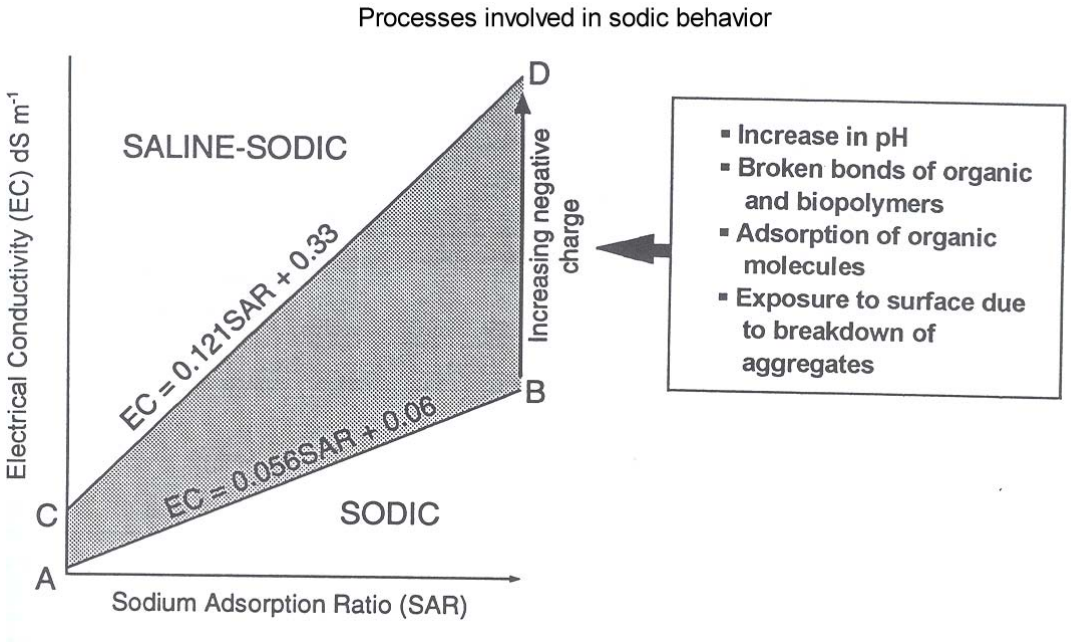


Figure 3. Schematic illustration of factors affecting threshold electrolyte concentration (TEC) [Rengasamy and Olsson, Aust. J. Soil Res. 29:935-952 (1991)]

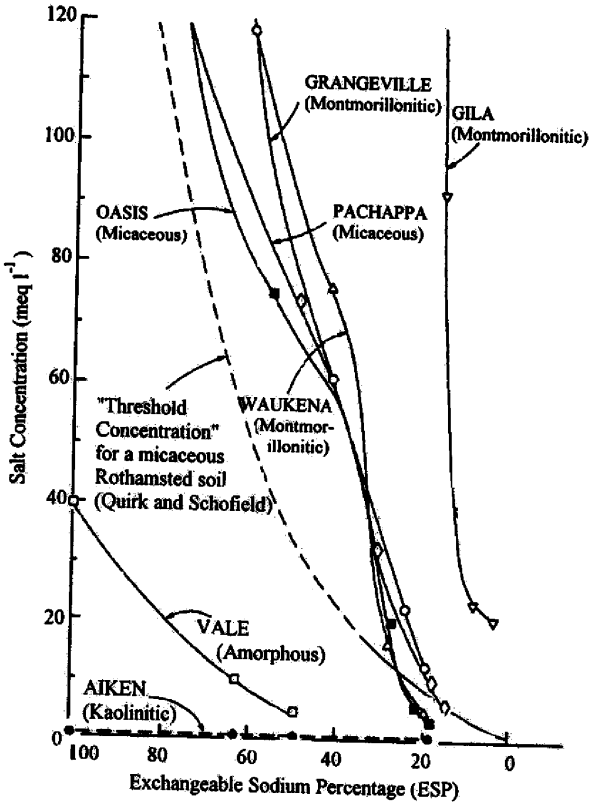


Figure 4. Combinations of salt concentration and ESP required to produce a 25% reduction in hydraulic conductivity for selected soils [McNeal and Coleman, Soil Sci. Soc. Am. Proc. 20:308-312 (1966)]

References:

Abu-Sharar, T.M., F.T. Bingham, and J.D. Rhoades. 1987. Stability of soil aggregates as affected by electrolyte concentration and composition. Soil Sci. Soc. Am. J. 51:309-314.

Al-Jaloud, A, G. Hussain, A.J. Al-Saati, and S. Karimulla. 1995. Effect of wastewater irrigation on mineral composition of corn and sorghum plants in a pot experiment. J. Plant Nutrition. 18:1677-1692.

Ali, R., A. A. Cheema, M. Niazi, and Z. Saleem. 1991. Sodic water irrigation effect with and without gypsum on wheat and maize yields and soil properties. J. Agric. Res. 29:373-383.

Barzegar, A.R., J.M. Oades, P. Rengasamy, and L. Giles. 1994. Effect of sodicity and salinity on disaggregation and tensile strength of an Alfisol under different cropping systems. Soil Tillage Res. 32:329-345.

Bajwa, M.S., and A.S. Josan. 1989. Effect of gypsum and sodic irrigation water on soil and crop yields in a rice-wheat rotation. Agric. Water Manage. 16:53-61.

Bajwa, M.S., A.S. Josan, and O.P. Choudhary. 1993. Effect of frequency of sodic and saline-sodic irrigations and gypsum on the buildup of sodium in soil and crop yields. Irrig. Sci. 14:21-26.

Basiouny, F.M. 1984. The use of municipal treated effluent for peach tree irrigation. Proc. Fla. State Hort. Soc. 97:345-347.

Bielorai, H., I. Vaisman, and A. Feigin. 1984. Drip irrigation of cotton with treated municipal effluents: I. Yield response. J. Environ. Qual. 13:231-234.

Bole, J.B., and R.G. Bell. 1978. Land Application of municipal sewage wastewater: Yield and chemical composition of forage crops. J. Environ. Qual. 7:222-226.

Bond, W.J. 1998. Effluent irrigation – An environmental challenge for soil science. Aust. J. Soil Res. 36:543-55.

Bresler, E., B.L. McNeal, and D.L. Carter. 1982. Saline and sodic soils: Principles, dynamics, modeling. Springer-Verlag. New York, NY.

Clark, D.R., C.J. Green, V.G. Allen , and C.P. Brown. 1999. Influence of salinity in irrigation water on forage sorghum and soil chemical properties. J. Plant Nutrition. 22:1905-1920.

Campbell, W.F., R.W. Miller, J.H. Reynolds, and T.M. Schreeg. 1983. Alfalfa, sweet corn, and wheat responses to long term application of municipal wastewater to cropland. J. Environ. Qual. 12:243-249.

Cass, A., and M.E. Sumner. 1982a. Soil pore structural stability and irrigation water quality: I. Empirical sodium stability model. Soil Sci. Soc. Am. J. 46:503-506.

Cass, A., and M.E. Sumner. 1982b Soil pore structural stability and irrigation water quality: II Sodium stability data. Soil Sci. Soc. Am. J. 46:507-512.

Cass, A., and M.E. Sumner. 1982c. Soil pore structural stability and irrigation water quality: III. Evaluation of soil stability and crop yield in relation to salinity and sodicity. Soil Sci. Soc. Am. J. 46:513-517.

Emerson, W.W. 1967. A classification of soil aggregates based on their coherence in water. Aust. J. Soil Sci. 5:47-57.

Feigin, A., I. Vaisman, and H. Bielorai. 1984. Drip irrigation of cotton with treated municipal effluents: II. Nutrient availability in soil. J. Environ. Qual. 13:234-238

Frenkel, H., and A. Hadas. 1981. Effects of tillage and gypsum incorporation on rain runoff and crust strength in field soils irrigated with saline-sodic water. Soil Sci. Soc. Am. J. 45:156-158.

Frenkel, H., J.O. Goertzen, and J.D. Rhoades. 1978. Effects of clay type and content, exchangeable sodium percentage, and electrolyte concentration on clay dispersion and soil hydraulic conductivity. Soil Sci. Soc. Am. J. 42:32-39.

Gregory, J. 1989. Fundamentals of flocculation. Crit. Rev. Environ. Control 19:185-230.

Howe, J., and M. Wagner. 1996. The effect of papermill wastewater and organic ammendments on sodium accumulation by potted cottonwoods. Environ. Pollut. 92:113-118.

Huheey, J.E., E.A. Keiter, and R.L. Keiter. 1994. Inorganic chemistry. Harper Collins, New York.

Iwata, S., T. Tabuchi, and B.P. Warkentin. 1995. Soil-water interactions: Mechanisms and applications. Marcel Dekker, New York.

Joshi, D.C. and R.P. Dhir. 1994. Amelioration and management of soils irrigated with sodic water in the arid region of India. Soil Use Manage. 10:30-34.

Keren, R. 2000. Salinity. p. G-3 to G-25. *In* M.E. Sumner (ed.) Handbook of soil science. 1st ed. CRC Press, Boca Raton, FL.

Keren, R., D. Sador, H. Frenkel, I. Shainberg, and A. Meiri. 1990. Irrigation with sodic and brackish water and its effects on the soil and cotton yields. Hassadeh 70:1822-1829.

Klute, A. and C. Dirksen. 1986. Hydraulic conductivity and diffusivity: Laboratory methods. p. 687-734. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Soil Science Society of America, Madison, WI.

Levy, G.J. 2000. Sodicity. p. G-27 to G-63. *In* M.E. Sumner (ed.) Handbook of soil science. 1st ed. CRC Press, Boca Raton, FL.

Loveday, J. 1976. Relative significance of electrolyte and cation exchange effects when gypsum is applied to a sodic clay soil. Aust. J. Soil Res. 14:361-371.

Mace, J.E., and C. Amrhein. 2001. Leaching and reclamation of a soil irrigated with moderate SAR waters. Soil Sci. Soc. Am. J. 65:199-204.

Manchanda, H.R., S.K. Sharma, H.R. Malik, and B.K. Suneja. 1988. Technology for using sodic water for guar and bajra. Indian Farming. 38:11-15.

Mancino, C.F., and I.L. Pepper. 1992. Irrigation of turfgrass with secondary sewage effluent: Soil quality. Agron. J. 84:650-654.

McBride, M.B. 1989. Surface chemistry of soil minerals. p. 35-88. *In* J.B. Dixon and S.B. Weed (ed.) Minerals in soil enviroments. 2nd ed. Soil Science Society of America, Madison, WI.

McNeal, B.L., and N.T. Coleman. 1966. Effect of solution composition on soil hydraulic conductivity. Soil Sci. Am. Proc. 30:308-312.

Misono, M., E. Ochiai, Y. Saito, and Y. Yoneda. 1967. A new dual parameter scale for the strength of Lewis acids and bases with evaluation of their softness. J. Inorg. Nucl. Chem. 29:2685-2691.

Neilsen, G.M., D.S. Stevenson, and J.J. Fitzpatrick. 1989a. The effect of municipal wastewater irrigation and rate of N fertilization on petiole composition, yield and quality of Okanagan Rieslin grapes. Can. J. Plant. Sci. 69:1285-1294.

Neilsen, G.H., D.S. Stevenson, J.J. Fitzpatrick, and C.H. Brownlee. 1989b. Yield and plant nutrient content of vegetables trickle-irrigated with municipal wastewater. HortScience. 24:249-252.

Neilsen, G.M., D.S. Stevenson, J.J. Fitzpatrick, and C.H. Brownlee. 1989c. Nutrition and yield of young apple trees irrigated with municipal wastewater. J. Amer. Soc. Hort. Sci. 114:377-383.

Neilsen, G.M., D.S. Stevenson, J.J. Fitzpatrick, and C.H. Brownlee. 1991. Soil and sweet cherry responses to irrigation with wastewater. Can. J. Sci. Soil Soc. 71:31A1.

Oster, J.D., and N.S. Jayawardane. 1998. Agricultural management of sodic soils. p. 125-146. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Pupisky, H., and I. Shainberg. 1979. Salt effects on the hydraulic conductivity of a sandy soil. Soil Sci. Soc. Am. J. 43:429-433.

Quirk, J.P., and R.K. Schofield. 1955. The effect of electrolyte concentration on soil permeability. J. Soil Sci. 6:163-178.

Radcliffe, D.E., and T.C. Rasmussen. 2000. Soil water movement. p. A-113 to A-115. *In* M.E. Sumner (ed.) Handbook of soil science. 1st ed. CRC Press, Boca Raton, FL.

Ramirez, H., O. Rodriguez, and I. Shainberg. 1999. Effect of gypsum on furrow erosion and intake rate. Soil Sci. 164:351-357.

Rengasamy, P., and K. A. Olsson. 1991. Sodicity and soil structure. Aust. J. Soil Res. 29:935-932.

Rengasamy, P., and M.E. Sumner. 1998. Processes involved in sodic behavior. p. 35-50. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Rengasamy, P., R.S B. Greene, and G.W. Ford. 1984. The role of clay fraction in the particle arrangement and stability of soil aggregates: A review. Clay Res. 3:53-67.

Rengasamy, P., R.S.B. Greene, G.W. Ford, and A.H. Mehammi. 1984. Identification of disperse behavior and the management of red–brown earths. Aust. J. Soil Res. 22:413-431.

Rhoades, J.D., and R.D. Ingvalson. 1969. Macroscopic swelling and hydraulic conductivity properties of four vermiculite soils. Soil Sci. Soc. Am. Proc. 33:364-369.

Ritter, W.F., J.G. McDermott, and A.E.M. Chirnside. 1992. Use of paper mill residuals as soil ammendments. Commun. Soil Sci. Plant Analysis. 23:469-488.

Sameni, A.M. and A. Morshedi. 2000. Hydraulic conductivity of calcareous soils as affected by salinity and sodicity. II. Effect of gypsum application and flow rate of leaching solution. Commun. Soil Sci. Plant Anal. 31:69-80.

Shainberg, I., and J. Letey. 1984. Response of soils to sodic and saline conditions. Hilgardia 52:1-57.

Shaw, R.J., K.J. Coughlan, and L.C. Bell. 1998. Root zone sodicity. p. 95-106. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Singh, H., and M.S. Bajwa. 1991. Effect of sodic irrigation and gypsum on the reclamation of sodic soil and growth of rice and wheat plants. Agric. Water Manage. 20:163-171.

Sumner, M.E. 1992. The electrical double layer and clay dispersion. p. 1-32. *In* M.E. Sumner and B.A. Stewart (ed.) Soil Crusting: Chemical and physical processes. Lewis Publishers, Boca Raton, FL.

Sumner, M.E. 1993. Sodic soils: New perspectives. Aust. J. Soil Res. 31:683-750

Sumner, M.E. 2000. Beneficial use of effluents, wastes and biosolids. Commun. Soil Sci. Plant Anal. 31:1701-1715.

Sumner, M.E., and B.A. Stewart. 1992. Soil crusting: Chemical and physical processes. Lewis Publishers. Boca Raton, FL.

Tarchitzky, J., Y. Golobati, R. Keren, and Y. Chen. 1999. Wastewater effects on montmorillonite suspensions and hydraulic properties of sandy soils. Soil Sci. Soc. Am. J. 63:554-550.

U.S. Salinity Laboratory Staff (USSL Staff). 1954. Diagnosis and improvement of saline and alkali soils. USDA Handb. 60, US Gov. Print. Office, Washington, D.C.

van Olphen, H. 1977. An Introduction to clay colloid chemistry. 2nd ed. John Wiley, New York.

Vasconcelos, E., and F. Cabral. 1993. Use and environmental implication of pulp mill sludge as an organic fertilizer. Environ. Pollut. 80:159-162.

Yaron, B., and G.W. Thomas. 1968. Soil hydraulic conductivity as affected by sodic water. Water Resour. Res. 4:545-552.

Zibilske, L. M. 1987. Dynamics of nitrogen and carbon in soil during papermill sludge decomposition. Soil Sci. 143:26-33.

CHAPTER 3

MATERIALS AND METHODS

Soil:

The soil used for the experiment was obtained from the irrigation field area located next to the wastewater treatment plant in the city of Greensboro, Georgia (Piedmont region). The water treatment plant is located at coordinates 33° 34' 14" N latitude and 083° 14' 01" W longitude. The sampling site is located on field 4 of the irrigation area, which is comprised of nine different fields with a total area of 125 acres (Figure 5). The soil sampling was made in the month of August, 2000. A hydraulic Giddins auger mounted on a truck was used in the soil sampling to obtain 20 sampling cores to a depth of 105 cm. Once the sampling cores were extracted they were divided into seven 15-cm long sections, to obtain a sample from the soil at 15-cm depth increments, as seen in Figures 7 and 8. Once collected, the soil samples were air-dried and sieved through a 2 mm mesh sieve. The soil belongs to the Cecil series (clayey, kaolinitic, thermic Typic Kanhapludults) (Soil Survey Staff, 1997). Textural class was determined for each soil section using the pipette method and following the procedure described by NRCS National Soil Survey Center (1996). Soil pH was determined using a 1M KCl solution at a 1:2.5 soil solution ratio. The extractable bases (Na, Ca, Mg and K) were determined by extraction with neutral 1M NH_4Oac following the procedure described by Knudsen et al. (1982) and Lanyon and Heald (1982). Aluminum was determined by titration following the procedure described by Thomas (1982). Organic

carbon content was determined by dry combustion using a Shimadzu TOC-5050 Total Organic Carbon Analyzer following the procedure described by Nelson and Sommers (1982). Cation exchange capacity (CEC) was determined using a 1M NaCl solution following the procedure described by NRCS National Soil Survey Center (1996). Percent water dispersible clay was determined by weighing a 5g sample of air-dried 2mm-sieved soil in a 50 ml centrifuge tube and adding 30 ml of deionized water. The centrifuge tubes were shaken in an Eberbach reciprocating shaker for 30 minutes. After removal from the shaker, the mixture was allowed to stand for 4 hours, at which time a 1ml sample of the supernatant was placed in a pre-weighed aluminum pan and dried in a Thelco oven for two hours, after which the pan was weighed again. The amount of clay was determined by the difference. The percent water dispersible clay was obtained using the following formula:

$$\% \text{ water dispersible clay} = \frac{\text{Amount of clay in the 1ml sample)}}{[(\% \text{ clay content} * 5)/30]} * 100\%$$

The exchangeable sodium percentage (ESP) of the soil was determined using the following two formulas:

(1) $$ESP = \frac{[Na]}{[Na] + [Ca] + [Mg] + [K]} * 100$$

(2) $$ESP = \frac{[Na]}{CEC\ (cmol_c\ kg^{-1})} * 100$$

where [] represent ion concentrations in $cmol_c\ kg^{-1}$.

The Effective Cation Exchange Capacity (ECEC) of the soil was determined using the following formula:

$$ECEC = [Na] + [Ca] + [Mg] + [K] + [Al]$$

where [] represent ion concentrations in $cmol_c\ kg^{-1}$.

The results of the analysis performed on the soil used in this experiment are presented in Tables 1 and 2.

Wastewater effluent:

Wastewater from the water treatment plant located in the city of Greensboro, Georgia was used in the experiment. This wastewater is the result of a secondary treatment, following the precipitation of all the solids in the settling tanks, as seen in Figure 8. The wastewater sampling was performed in the month of August, 2000 and two plastic drums (each containing 50 gallons) were collected. Various chemical characteristics of the wastewater effluent are presented in Table 3. Using the wastewater recollected, four solutions representing SAR values of 2, 5, 10 and 20 were prepared by adding 0.56 g L^{-1} and 0.015 g L^{-1} of $CaSO_4 \cdot 2H_2O$ and 0.195 g L^{-1} and 0.53 g L^{-1} of NaCl respectively.

Soil columns:

To determine the effect of wastewater effluent SAR on soil hydraulic conductivity and chemical composition, soil columns were prepared by evenly packing air-dried, 2-mm sieved soil into cylindrical Plexiglas tubes of 39 cm in height and 5 cm in diameter. The tubes were divided into seven sections and in each section a sample from the soil collected from the seven 15-cm deep sections was packed, thus, representing in one column the entire soil profile to a depth of 105 cm. All of the columns were prepared by packing 0.15 kg of soil in each section of the column and they were filled from the

bottom upwards. Soil columns were packed to a bulk density of 1.4 g cm^{-3}. Sand (20 g) and mesh cloth was applied at both ends of the column to ensure an even wetting front. At both ends, the columns were closed with a metal cap fitted with an opening where a Tygon plastic tube (3mm interior diameter) was connected, as seen in Figure 9.

In this manner four soil columns were prepared and then placed in a horizontal position, then each of the columns were leached from the end representing the topsoil with 1 L of wastewater effluent from one of the four SAR values (2, 5, 10 and 20). This volume represents 18 inches of precipitation in the field. The leaching was performed using an ISCO Wiz peristaltic pump. Subsequently, 1 L of deionized water was then leached thru the soil column. This procedure was repeated three times. The reason is to simulate 3 years of land application of wastewater with different SAR value and winter rains. The leachate coming out of the columns was collected in an ISCO Advanced Retriever II and Spectra/Chrom CF1 fraction collectors at 12 min intervals. The volume of each fraction was determined to estimate changes in the flow rate. A sample of each fraction was also collected and EC and SAR were determined to estimate changes over the leaching period. The EC was determined using a Radiometer Copenhagen CDM 80 electric conductivity meter and the SAR was determined by obtaining the Na, Ca and Mg concentrations in the water sample using a Perkin Elmer Atomic Absorption Spectrophotometer and replacing them in the following formula:

$$SAR = [Na] / (([Ca] + [Mg])/2)^{1/2}$$

where [] represent concentrations in $mmol_c\ L^{-1}$.

After the three wastewater-deionized water cycles, the columns were taken apart and divided into the same seven sections as before. For each section pH, extractable bases

(Ca, Mg, Na, K and Al), % water dispersible clay, % organic carbon, cation exchange capacity (CEC) and exchangeable sodium percentage (ESP) were measured using the same procedures described in the analysis of the original soil. In the same manner, another four columns were prepared, with six wastewater-deionized water cycles leached through them. The same procedure was performed to analyze the effluent and the soil in these columns.

Hydraulic conductivity

To determine the hydraulic conductivity of a sample representing the entire soil profile to a depth of 105 cm, another set of four soil columns (three replicates) were built and each was leached with wastewater effluent of a certain SAR value (2, 5 10 or 20) and deionized water. First, all of the columns were leached with 1 L of 5 meq $CaCl_2$ solution and then with six cycles of 1 L wastewater-1 L deionized water using an ISCO Wiz peristaltic pump. The columns were prepared in the same manner as described in the preliminary studies. In order to determine the hydraulic conductivity, the pressure of the water flow coming from the peristaltic pump into the column was determined using a water manometer. The water manometer was constructed using three glass tubes connected to Tygon plastic tubes attached to the soil columns using plastic T-connectors. The glass tubes were attached using plastic tubing to two capillary glass stopcocks. The two glass stopcocks were joined to a third capillary glass stopcock in a pyramidal formation. The last glass stopcock was joined using plastic tubing to a Netech Digimano pressure meter. All of the joints were sealed with Dow Corning vacuum grease to prevent any air leaks. Capillary glass stopcocks were used to minimize the air volume and to

allow the measurement of the air pressure in one glass column without disturbing the others. The water flow pressure was determined by obtaining the pressure of the air inside the glass columns being compressed by the ascending water column using the air pressure gauge. The water manometer can be seen in Figure 10. The leachate coming out of the columns was collected in an ISCO Advanced Retriever II a Spectra/Chrom CF1, and a LKB 2112 Redirac fraction collectors at 12 min intervals. The volume of each fraction was determined to estimate changes in the flow rate. A sample of each fraction was also collected and EC and SAR were determined to estimate changes over the leaching period. The EC and SAR were determined using the same procedure as described in the preliminary studies.

After leaching the six wastewater-deionized water cycles through the columns, they were taken apart and divided into the same seven sections. For each section pH, extractable bases (Ca, Mg, Na, K and Al), % water dispersible clay, % organic carbon, cation exchange capacity (CEC) and exchangeable sodium percentage (ESP) were measured using the same procedures utilized for the analysis of the original soil.

The hydraulic conductivity of the soil columns was determined by using the flow rate data combined with the water flow pressure from each soil column using the following equation:

Saturated hydraulic conductivity (K_s) = J * L / $H_2 - H_1$

where:

J = water flux (cm min^{-1}) = flow rate (cm^3 min^{-1}) / cross-section area (cm^2)

L = length of the soil column (cm)

H_2 = Potential at the outlet of the soil column (cm water)

H_1 = Potential at the inlet of the soil column (cm water)

The potential at the bottom of the soil column (H_2) was assumed as zero, because the outlet at this end was open to the atmosphere in order to record the flow rate coming out of the column. The potential at the top of the soil column (H_1) was assumed as equal to the pressure of the water flow coming from the peristaltic pump to the column, obtained from the water manometer connected to the top of the column.

Afterwards, another soil column was prepared in the same manner as described before and leached with 12 liters of 5 meq $CaCl_2$ solution. The flow rate and pressure of the water coming into the column through out the leaching period was obtained. This was realized in order to determine a base hydraulic conductivity for the original soil.

Statistical analysis

Significant differences in the chemical and physical parameters measured due to the different wastewater SAR treatments were determined using an analysis of variance (P#0.05) and an lsd mean comparison test (P#0.05) using SAS (SAS, 1988).

Table 1. Textural class, pH, organic carbon (OC), water dispersible clay, effective cation exchange capacity (ECEC) and measured cation exchange capacity (CEC) of the Cecil series soil used in these experiments.

Sample depth	Textural class	pH	OC	Water dispersible clay	ECEC	CEC
cm			----------%----------		----$cmol_c\ kg^{-1}$----	
0-15	loam	4.55	1.84	4.56	5.09	4.90
15-30	clay	4.21	0.43	0.71	3.69	3.50
30-45	clay	4.29	0.25	0.71	3.89	3.81
45-60	clay	4.41	0.16	0.40	3.61	3.70
60-75	clay	4.31	0.11	0.43	3.58	3.30
75-90	clay	4.32	0.05	0.41	3.59	3.20
90-105	clay	4.33	0.06	0.56	3.40	3.10

Table 2. Exchangeable cation concentration (Na, Ca, Mg, K and Al) and exchangeable sodium percentage (ESP) of the Cecil series soil used in these experiments.

Sample Depth	Na^+	Ca^{2+}	Mg^{2+}	K^+	Al^{3+}	ESP
cm	----------$cmol_c\ kg^{-1}$----------					%
0-15	0.024	3.78	1.10	0.36	0.08	0.48
15-30	0.023	2.37	1.02	0.43	0.12	0.62
30-45	0.020	2.37	1.09	0.58	0.15	0.52
45-60	0.022	2.33	1.09	0.34	0.15	0.63
60-75	0.025	2.31	1.10	0.28	0.18	0.72
75-90	0.025	2.31	1.13	0.27	0.22	0.71
90-105	0.029	2.32	1.05	0.16	0.25	0.86

Table 3. Chemical composition of the original Greensboro wastewater effluent and the four different SAR solutions used in these experiments.

	Total organic carbon (TOC)	Electrical conductivity (EC)	Na^+	Ca^{2+}	Mg^{2+}	K^+	SAR
	mg L^{-1}	$\mu S\ cm^{-1}$	----------$mmol_c\ L^{-1}$----------				
Wastewater effluent	290.1	650	4.13	0.76	0.29	0.43	5.7
Wastewater effluent (SAR 2)	290.1	1100	4.13	7.90	0.29	0.43	2.0
Wastewater effluent (SAR 5)	290.1	690	4.13	1.05	0.29	0.43	5.0
Wastewater effluent (SAR 10)	290.1	928	7.25	0.76	0.29	0.43	10.0
Wastewater effluent (SAR 20)	290.1	1115	14.4	0.76	0.29	0.43	20.0

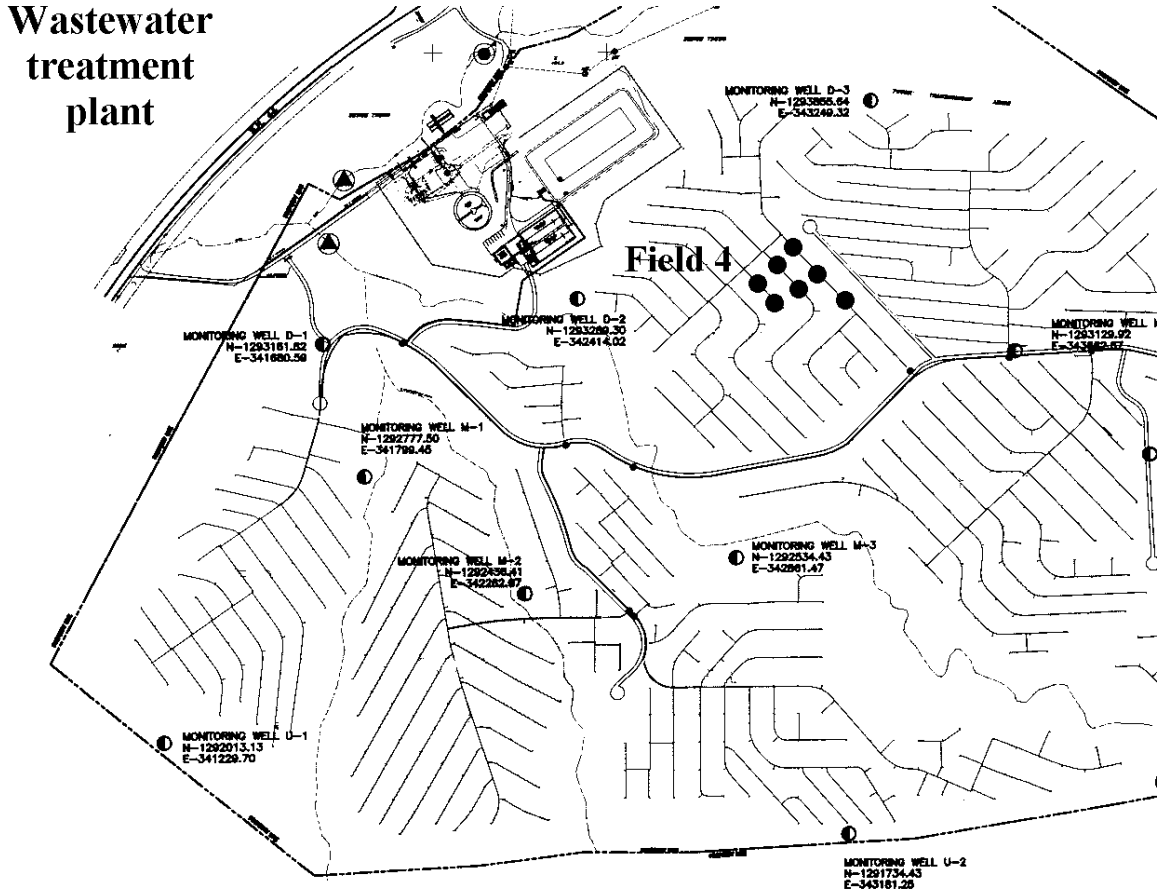


Figure 5. Map of the wastewater treatment plant located in Greensboro, Georgia and adjacent irrigation fields. The solid circular dots (●) indicate the soil sampling areas located in field 4.

Figure 6. Method of soil sampling used for this experiment. Soil cores to a depth of 105 cm were obtained using a Giddins hydraulic auger mounted in a truck.

Figure 7. Partitioning of the soil cores obtained in the soil sampling into seven sections each 15-cm wide

Figure 8. Wastewater pond located in the Greensboro water treatment plant, where the wastewater used in this experiment was sampled.

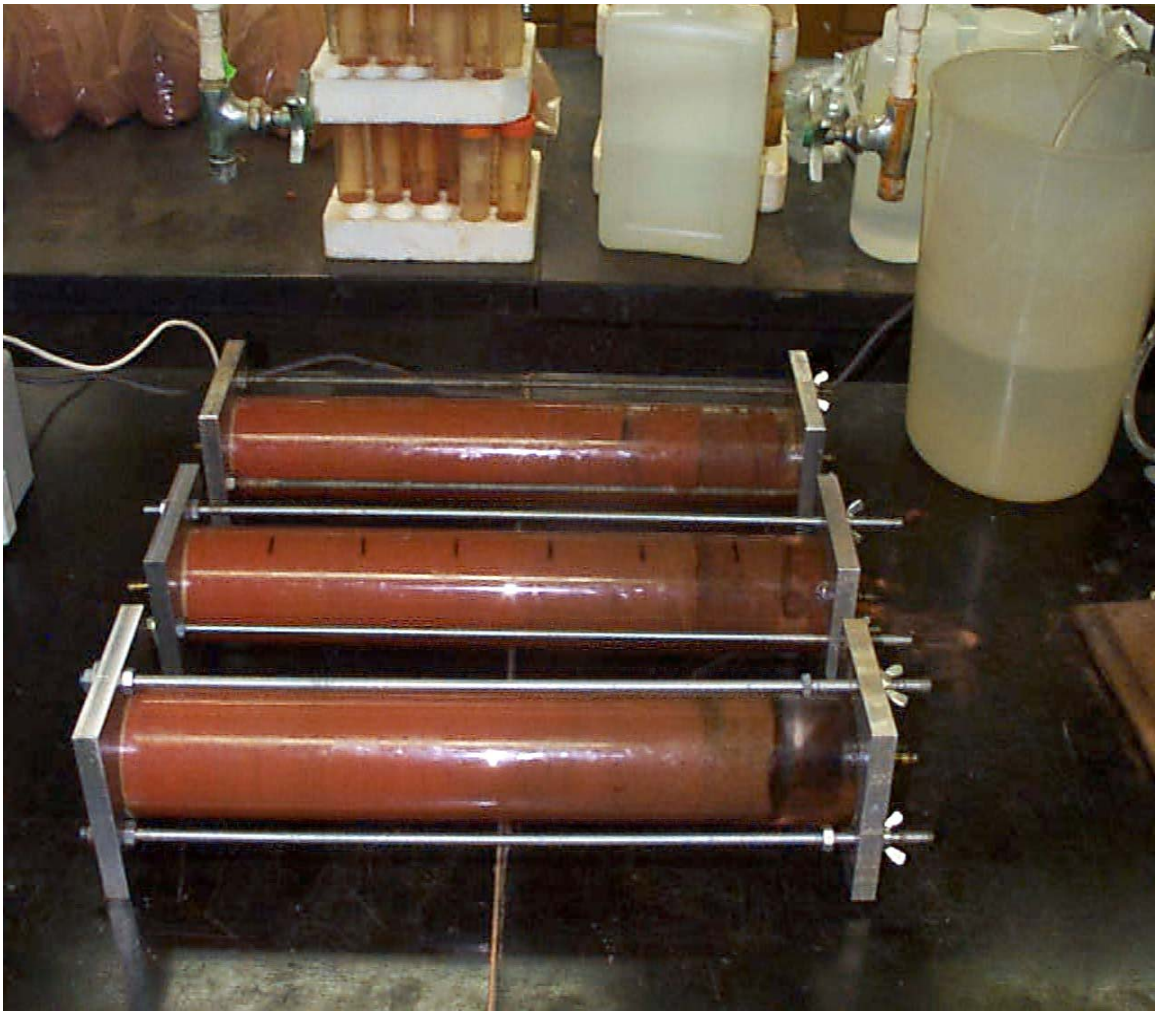


Figure 9. Soil columns. The soil was packed in a plastic cylinder, which at both ends was closed using a metal cap fitted with an opening where a plastic tube was connected. One end was connected to the water manometer and the peristaltic pump, and the other end was connected to the fraction collector.

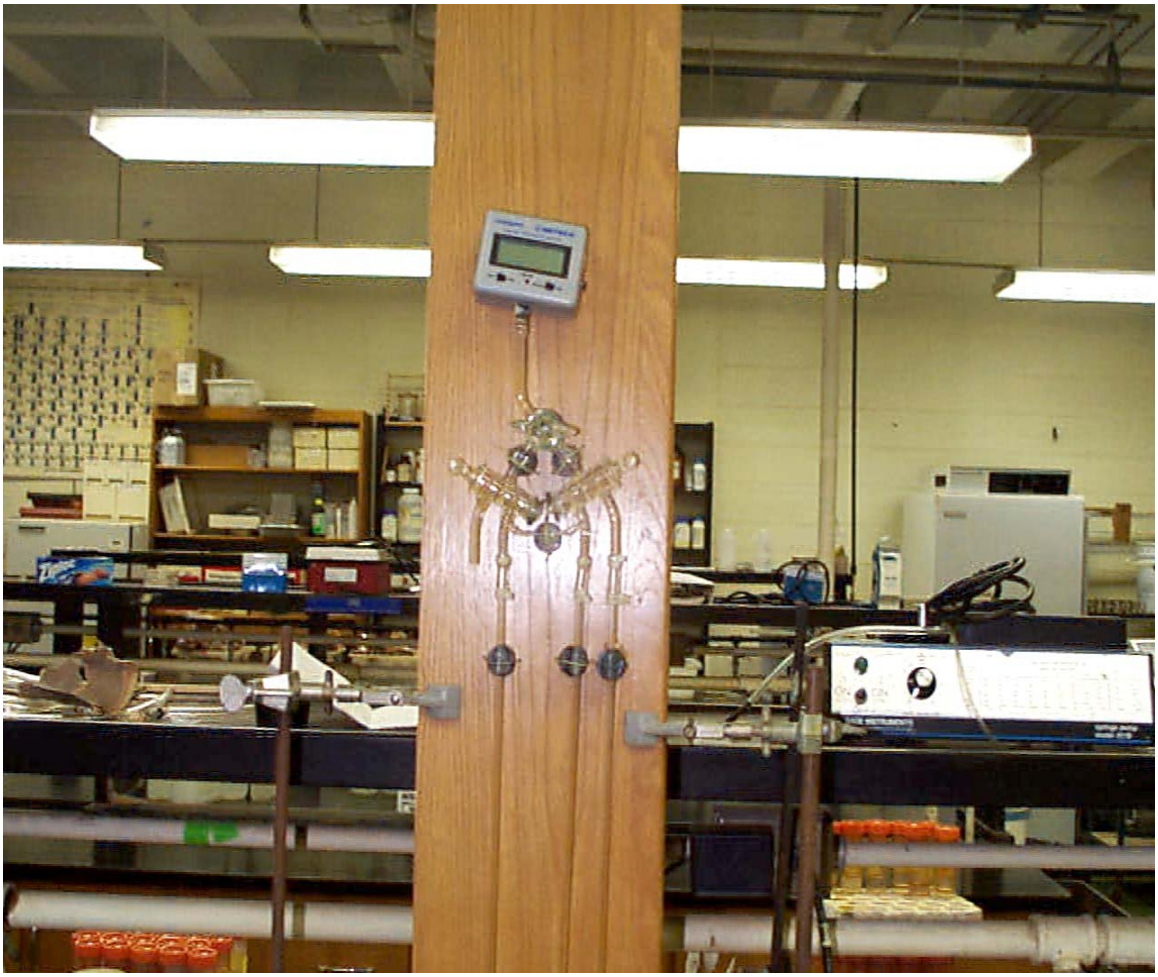


Figure 10. Water manometer used in this experiment to measure the pressure of the water flow at the top of the soil column. The pressure meter is connected to the different glass tubes using capillary stopcocks.

References:

Knudsen, D., G.A. Peterson, and P. F. Pratt. 1982. Lithium, sodium, and potassium. p. 225-246. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

Lanyon, L.L., and W.R. Heald. 1982. Magnesium, calcium, strontium, and barium. p. 247-262. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-579. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

NRCS National Soil Survey Center. 1996. Soil Survey Laboratory Methods Manual. USDA, Washington, DC.

Soil Survey Staff. 1997. Keys to soil taxonomy. 7th ed. Pocahontas Press. Blacksburg, VA.

Thomas, G.W. 1982. Exchangeable cations. p. 159-165. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

CHAPTER 4

RESULTS AND DISCUSSION

Organic carbon

The wastewater effluent increased the total amount of organic carbon in the soils leached with wastewater when compared to the original soil (Figure 11). The amount of total organic carbon present in the wastewater was 290.1 mg L^{-1}. In the soil leached with wastewater and deionized water, the increase in organic carbon occurred throughout the soil column and this increase ranged from 20 to 600% from the original soil values. This increase was larger in the subsoil than in the topsoil. This can be explained by the fact that the fine size organic particles, which constitute most of the total organic carbon content in the wastewater, were leached from the topsoil to the subsoil when deionized water was applied. The organic carbon content present in the leachate from all of the columns was very small (~ 10 mg L^{-1}), so most of organic matter present in the wastewater was bonded in the subsoil. According to the mass balance analysis (Table 4), about 93% of the organic matter added in the wastewater remains attached to the soil in the columns. This can be the result of anionic components in the organic matter being attracted to positive charges on the inorganic colloids, especially iron oxides (Oades, 1989). Other investigations conducted by Mancino and Pepper (1992) and Juwarkar and Subrahmanyam (1986) reported an increase in total organic carbon in the soil after application of wastewater. In terms of the wastewater's SAR, based on an analysis of

variance, there is no significant change in organic matter accumulation due to SAR of the wastewater at a 0.05 significance level.

pH:

The pH of the wastewater used in these experiments ranged from 6.89 to 7.01. Soil pH (1M KCl) values were consistently higher in the soils leached with wastewater at the four different SAR values (2, 5, 10 and 20) followed by deionized water when compared to the original field soil, for 6 cycles of leaching (Table 5). The soil leached with wastewater had an increase of pH from 0.1 to 1.7 units and was more pronounced in the first three sections of the soil column corresponding to the first 45 cm of soil. Soil corresponding to the 75 to 105 cm depth range (last two sections of the soil columns) showed the smallest increase in pH. This effect is consistent with results obtained by Mancino and Pepper (1992) and Juwarkar and Subrahmanyam (1986) where land application of secondary sewage effluent and paper mill wastewater, respectively increased soil pH. This increase in pH can be attributed to neutralization of H and Al ions and the ligand exchange cations added from the wastewater. According to the analysis of variance performed, there were no significant differences in pH values between different SAR treatments for all soil depths at a 0.05 significance level.

Measured CEC and Effective CEC (ECEC)

The measured (CEC) and the effective cation exchange capacities (ECEC) were higher in all of the soils leached with wastewater when compared to the original soil (Figures 12 and 13). This increase ranged from 2.1 to 7.5 $cmol_c\ kg^{-1}$ with the SAR 2 and

5 treatments showing the biggest increase. For all of the treatments, CEC and ECEC decreased with depth. The increase in CEC and ECEC arises from the addition of organic matter present in the wastewater and the increase in pH after wastewater was applied. Organic matter is the biggest contributor to the CEC, providing 25 to 90% of topsoil CEC in mineral soil (Stevenson, 1992). Also, the increase in pH promotes the development of variable negative charge in the organic matter and clay colloids, thus resulting in greater cation adsorption (Sparks, 1995). As observed in Figures 12 and 13, this increase in CEC and ECEC is not only limited to the topsoil, but occurs all through the subsoil. It correlates with the increase in organic matter and pH in the subsoil, which facilitates cation adsorption on the clay minerals, thus increasing the CEC. As seen in Figures 14 and 15, the relationship between CEC, ECEC, pH and organic carbon is best described by a positive linear relationship, where pH and organic carbon are highly significant in determining CEC and ECEC, those two variables are able to account for 55% and 36% of the total variability present in the CEC and ECEC values respectively. Also, according to the analysis of variance, there were significant differences for CEC and ECEC between the different SAR treatments for all soil depths, with the SAR 2 and 5 treatment showing the highest CEC and ECEC values (Figures 16 and 17). This effect could be the result of higher Ca concentration in the SAR 2 and 5 treatments.

Exchangeable cations:

Sodium:

The Na levels in the soils leached with wastewater increase with increasing SAR (Figure 18). The Na content of the wastewater used to leach the soil columns ranged from

94.9 to 331.06 mg L^{-1}. According to the analysis of variance performed, the Na levels were significantly different between the different SAR treatments for all soil depths at a 0.05 significance level (Figure 19). Tarchitzky et al. (1999) and Mancino and Pepper (1992) also reported increase levels of Na in sandy soils after being irrigated with wastewater. In all of the four treatments (SAR 2, 5, 10, and 20), the Na levels where slightly higher in the last three portions of the columns, corresponding to a soil depth from 60 to 105 cm when compared to the top section of the columns. This could be due to the fact that in the topsoil portion of the soil columns Ca and Mg are preferentially being absorbed over Na. The free Na ions are then leached and adsorbed by the newly added organic matter and iron oxides in the deeper soil layers. According to the mass balance analysis (Table 5), about 10% of the Na added in the wastewater is attached in the soil.

Calcium:

The Ca levels in the soils leached with wastewater were higher than the original soil (Figure 20). The Ca content of the wastewater used to leach the soil columns ranged from 15.24 to 158.39 mg L^{-1}. The Ca concentration in the soil was positively related to the Ca content of the wastewater used for leaching. Therefore, the Ca levels were higher for the soils leached with wastewater of SAR 2 and 5, and lower for soils leached with wastewater of SAR 10 and 20. According to the analysis of variance performed, the Ca levels were significantly different between the SAR 2 and 5 treatments when compared to the SAR 10 and 20 treatments at a 0.05 significance level for all soil depths (Figure 21). Clark et al. (1999) also reported increased levels of Ca in a sandy loam soil after being

irrigated with saline irrigation waters with high levels of Ca. In all of the four treatments (SAR 2, 5, 10, and 20), the Ca level was higher in the top portion of the soil columns, corresponding to the first 15 cm of soil. This can be attributed to the fact that most of the Ca ions are bonded to the organic matter present in the topsoil. Ca is preferred to Na in bonding with organic matter because of its higher ionic potential (Marshall, 1964). Also, this selectivity of organic exchange sites for Ca over Na increases with increase CEC of the organic matter and an increase in soil pH (Nelson and Oades, 1998). Although most of the Ca bonding occurs in the topsoil, the levels of Ca in the subsoil also show a significant increase, especially for the SAR 2 and 5 treatments. This can be the result of saturation of the complex sites in the topsoil, which causes the excess Ca ions to leach into the subsoil where most of them are adsorbed by the newly attached organic matter from the wastewater. According to the mass balance analysis (Table 4), about 95% of the Ca added in the wastewater is attached to the soil in the columns.

Magnesium:

The Mg levels in the soils treated with wastewater varied from the original soil (Figure 22). The Mg content of the wastewater is 7.05 mg L^{-1}. All of the sections of the columns showed an increase in Mg levels when compared to the original soil. This could be the result of bonding of Mg ions to the organic matter present in the topsoil and to the new organic matter attached in the subsoil. Zekri and Koo (1994) and Clark et al. (1999) reported also an increase in levels of Mg in soils after application of wastewater. An increase in the leaching cycles from 3 to 6, did not increase the amount of Mg in the soil in all of the treatments, instead, the amount of Mg in the subsoil decrease slightly. This

could be the result of leaching of excess Mg ions that were not absorbed in the top or subsoil. According to the analysis of variance performed, the Mg levels were not significantly different between the different SAR treatments at a 0.05 significance level. This effect is logical considering the fact that no Mg was added in any of the treatments. One important aspect to mention is that the increase in Mg levels in the soils treated with wastewater could have helped in incrementing the clay dispersion effect in the SAR 10 and 20 treatments. van der Merwe and Burger (1969) found that Na-Mg saturated soil was structurally less stable than the Na-Ca counterpart. Also, there have been studies documenting the inability of Mg in irrigation waters to counter the accumulation of Na in soils (Chi et al., 1977; Rahman and Rowell, 1979).

Potassium:

The K levels in the soils leached with wastewater of SAR 2, 5, 10 and 20 did not vary consistently from the levels in the original soil (Figure 23). Mancino and Pepper (1992) reported that values of K in wastewater irrigated soils did not vary considerably from non-irrigated soil. One notable trend is the reduction in the amount of exchangeable K in the 60 to 105 cm depth soil (last three portions of the column) treated with wastewater of SAR 2 and 20. This could be the result of these two treatments having the highest electrical conductivities, due to the addition of high amounts of Ca or Na. In both cases the high cation concentration could have replaced some of the K in the deeper soil layers, which then was leached out. This fact is substantiated by the analysis of variance performed, which resulted in no significant differences of the K values between the different SAR treatments for the first two soil sections, but at deeper soil depths were

found significant differences between treatments at a 0.05 significance level (Figure 24). At a soil depth range from 70 to 105 cm, there is no significant differences in K levels between the SAR 2 and 20 treatments, which in turn are lower than the other treatments.

Aluminum:

The Al levels in the soils leached with wastewater and deionized water were notably lower than the original soil. The level of Al increased with depth in all of the treatments and in the original soil (Figure 25). Clark et al. (1999) also found a decrease in Al soil levels after application of wastewater. This decrease in Al levels can be the result of an increase in Al precipitation due to higher soil pH values resulting in lower levels of exchangeable Al. The analysis of variance also showed no significant differences in Al levels between the different treatments at a 0.05 significance level.

Water dispersible clay:

The percent of water dispersible clay increases with an increase in wastewater SAR as seen in Figure 26, with the effect being more pronounced in the upper parts of the column. In the soils leached with wastewater of SAR (2, 5, 10 and 20) and deionized water, percent water dispersible clay in the first section of the columns (15 cm) did not vary much and ranges from 19 to 24%. The amount of water dispersible clay increases to 25 to 32% in the next section of the column, (15 to 30 cm) in the soils treated with wastewater of SAR 10 and 20. Water dispersible clay approaches zero in the soils treated with wastewater of SAR 2 and 5 at soil depths from 15 to 105 cm. The soil treated with wastewater of SAR 20 exhibits water dispersible clay up to a soil depth of 60 cm. At

deeper soil depths, clay dispersion is not observed even in the SAR 20 treatment, which could be the result of high amounts of iron oxides bonding clay particles together and behaving as silt size particles. El- Swaify (1973) determined that Fe oxides form a coating around soil aggregates restricting their swelling and dispersion. As described above, an increase in the amount of Na in the wastewater results in an increase in the amount of clay dispersed through the soil profile, due to its inhibiting effect on macroaggregation and by increasing the osmotic and hydration forces during wetting. The effect of Na in clay dispersion has been reviewed extensively in van Olphen (1977); Shainberg and Letey (1984); Shainberg and Levy (1992); Sumner (1993); and Rengasamy and Sumner (1998).

It is important to mention that the added organic matter from the wastewater also plays an important role as either a bonding or a dispersing agent, depending on the sodicity level of the wastewater and the ESP of the soil. In the soils treated with wastewater of SAR 10 and 20, where the Na content in the wastewater and in the soil is high, anionic organic matter may act as a dispersing agent. Organic anions are known to increase clay dispersion, especially where variable charge minerals are present (Oades, 1984; Durgin and Chaney (1984); Gu and Doner (1993); and Kretzschmar et al. (1993)). Gupta et al. (1984) added farmyard manure to a soil equilibrated with solutions having different SAR values. Manure increased dispersion of fine clay at all levels of sodicity, but the effect was greatest at high SAR. For the soils treated with wastewater of SAR 2 and 5, where the Na content in the wastewater and in the soil is low, organic matter acts as a bonding agent. Organic matter has a beneficial effect on the structure of sodic soils, but its effect is much greater following displacement of Na by Ca (Muneer and Oades,

1989; and Rengasamy and Olsson (1991)). Also, this effect tends to be greatest when ESP is low and the Ca content in the soil is high (Rengasamy and Sumner, 1998). Based on the analysis of variance performed, the amount of water dispersible clay is not significantly different between the different SAR treatments at the 0 to 15 cm soil depth; but is significantly different a the 15 to 60 cm soil depth (Figure 27).

Exchangeable sodium percentage (ESP):

The ESP levels in the soils increased with an increase in the SAR of the wastewater used for leaching (Figure 28). The ESP increased from top to subsoil. The ESP values ranged from 0.9 to 2.1 in the soil treated with wastewater of SAR 2 to 5.6 to 11.9 for soil leached with wastewater of SAR 20. This increase in soil ESP when leaching with wastewater was also observed by Juwarkar and Subrahmanyam (1986), Hayes et al. (1990) and Mancino and Kopec (1989). Although, the increase in ESP was higher for the soil treated with wastewater of SAR 20, the final soil ESP levels ranging from 5.1 to 11.9 still are considered moderate sodicity levels (Levy et al. 1998). This is the result of the leaching of most of the Na ions during the period when deionized water was applied. Even so, these moderate sodicity levels have a marked, and often irreversible effect on physical and hydraulic conductivities of most soils under conditions of low levels of electrolyte concentration (winter rains) (Levy et al. 1998). Based on the analysis of variance performed, soil ESP levels vary significantly between the different SAR treatments at all soil depths (Figure 29).

Effluent parameters:

Flow rate, electrical conductivity (EC) and cation composition:

As seen in Figure 30, the flow rate of the effluent from the columns leached with wastewater of SAR 2 and 5 remains constant at the original rate for the entire leaching period. In the column leached with SAR 20 wastewater, the flow rate decreases to 54% of its original value after 3 pore volumes of solution leached. This coincides with the point at which the wastewater is replaced by deionized water. This decreasing trend continues in the subsequent leaching cycles to a final flow rate that constitutes only 20% of its original value. In the column leached with SAR 10 wastewater the flow rate takes longer to decrease. The flow rate decreases to 50% of its original value after eight pore volumes. This coincides with the second time the wastewater is replaced by deionized water. After decreasing the flow rate by half a slight recovery occurs when wastewater is again leached, but then it decreases rapidly to a final flow rate that is only 25% of its original value. The reduction of effluent flow rate and final flow rate with increased wastewater SAR can be seen in Figures 31 and 32. As seen in these figures the breaking point for the flow rate occurs between SAR 5 and 10. This reduction of water flow in the columns leached with wastewater of SAR 10 and 20 is the result of two processes: clay dispersion and some swelling due the addition of high amounts of Na relative to other divalent cations (e.g, Ca and Mg) present in these wastewaters and by the subsequent application of low electrolyte solution (deionized water). As seen in the flow rate distribution for the SAR 10 and 20 wastewater, the decline occurs when the Na-saturated clays from the wastewater are hydrated when deionized water is applied, which produces swelling and breaking of bonds. This process of reduction of water flow through a soil with low (< 5)

or moderate (5 to 10) ESP when leached with a low electrolyte solution (deionized water) has been reviewed extensively (McNeal and Coleman, 1966; Yaron and Thomas, 1968; Cass and Sumner, 1982; Shainberg and Letey, 1984). Although, clay dispersion is the most important factor for reducing water flow, there was no presence of clay colloids in the effluents from these columns. This may be due to the fact that mobile dispersed clay in the leachate is usually only observed in sandy soils (Levy et al., 1998). In this case, the Cecil soil used in the columns has a high clay content, which ensures that the dispersed clay moves only short distances, before it clogs the pores, thus becoming entrapped. In the columns leached with SAR 2 and 5 wastewater, the ESP through out the soil profile remains low, making the soil less susceptible to clay dispersion and swelling when leached with a low electrolyte solution.

In Figures 33 to 36, the electrical conductivity (EC) of the effluents from the columns and cation composition for selected points are shown. The EC of the effluent from the soil columns present similar patterns. As expected, the EC of the effluents increases when wastewater is being applied to the columns and decreases when deionized water is leached. This increase in the EC is related to the ions that are leached out of the soil columns. One important aspect to mention is the fact that the SAR values for the peaks in the EC graphics are higher that the corresponding wastewater SAR. This signifies that when the wastewater is being replaced in the column by deionized water, most of the Na ions are leached out but most of the Ca and Mg are adsorbed by the newly attached organic matter in the soil columns and by oxides in the subsoil. Also, the SAR of the effluent increases throughout the leaching period, this is the result of the Na levels in the effluent from the columns remaining constant while the Ca and Mg levels decreasing

throughout the leaching period, attached by increasing amounts of organic matter in the soil. In the field, this aspect is important due to possible contamination of groundwater reservoirs with high amounts of Na originated from the successive land applications of wastewater.

Hydraulic conductivity

The effect of wastewater effluent of different SAR on the hydraulic conductivity of the soil is shown on Figure 37. As seen, the soils treated with wastewater of SAR 10 and 20 showed the steepest decrease in hydraulic conductivity over the entire leaching period. On the other hand, the soils treated with wastewater of SAR 2 and 5 also showed a decrease in soil hydraulic conductivity but it was less pronounced that the SAR 10 and 20 treatments. In Figure 38 we can see that the final hydraulic conductivity for both SAR 10 and 20 treatments falls below 5% of its original value, for SAR 2 and 5, the final hydraulic conductivity represents 80% and 59% respectively of its original value. This pronounced effect on hydraulic conductivity for the SAR 10 and 20 treatments appears to be the result of mainly clay dispersion and to a lesser extent of swelling. As discussed earlier, these two processes are the result of Na saturation of soil clays due to the high amounts of Na in these wastewaters. These Na saturated clays are mainly bonded by ionic bonds, which tend to swell and ultimately break when hydrated (Rengasamy and Sumner, 1998). The swelling process decreases soil pore size distribution and restricts water flow. In the case of the packed soil columns constructed for this experiment, a decrease in water flow from the columns was accompanied by an increase in water flow pressure coming into the column. This increase in water flow pressure was the result of

backpressure created by the sealing of soil pores in the column. Another factor that could have been involved in the sharp decrease in hydraulic conductivity was the addition of high amounts of organic matter from the wastewater to the soil columns. In addition to being a dispersing agent in situations where the Na soil content is high, the organic matter could have also have also played an important role in plugging soil pores. As discussed earlier, most of the organic matter from the wastewater was retained in the soil, and most of that organic matter was fine size algae particles that when bonded to the clay could have blocked soil pores. This factor could have played a relatively large role in decreasing the hydraulic conductivity of the soil columns treated with SAR 2 and 5 wastewater. Although clay swelling and dispersion were likely to be very limited in these soils, the decrease in hydraulic conductivity observed was probably the result of the blocking of soil pores by organic matter. As seen in Figures 39 and 40, the total decrease and final hydraulic conductivity for the four SAR treatments showed that the biggest increase occurs between SAR 5 and 10 treatments. Also, as seen in Figure 37 the rate of decline for the hydraulic conductivity in the SAR 20 column is much sharper and occurs earlier than the SAR 10 column. This may be the result of the different degrees of Na saturation, in the SAR 20 column the amount of Na saturated clays caused by the first application of wastewater probably were higher than in the SAR 10 column, so the consequent swelling of these clays produced an earlier bigger decline in soil pore size in the SAR 20 column. As seen in Figure 37, this process of clay dispersion and swelling is irreversible and even when the soil column is again leached with a high electrolyte solution (wastewater), the hydraulic conductivity does not return to its previous value. In Figure 38, if we consider a 25% reduction of hydraulic conductivity from its original

value as the boundary between stable and unstable permeability, we can see that this occurs at 3, 5 and 20 pore volumes of solution leached for the soils treated with SAR 20, 10 and 5 wastewater respectively. The soil treated with SAR 2 wastewater does not reach this level during the entire leaching period.

Table 4. Mass balance analysis for organic carbon (OC), Na and Ca for the four different SAR treatments.

Element	Amount added	Increase in the column	Amount in the effluent
	----------mg----------		
Organic carbon (SAR 2)	1740.6	1646	120.2
Organic carbon (SAR 5)	1740.6	1676	119.3
Organic carbon (SAR 10)	1740.6	1546	127.6
Organic carbon (SAR 20)	1740.6	1566	125.2
Na (SAR 2)	569.69	42.76	506.1
Na (SAR 5)	569.69	59.77	492.3
Na (SAR 10)	1000.06	114.95	875.11
Na (SAR 20)	1986.36	186.22	1782.14
Ca (SAR 2)	950.34	922.3	20
Ca (SAR 5)	326.31	320.2	16.2
Ca (SAR 10)	102.4	115.5	11.3
Ca (SAR 20)	102.4	105.2	10.5

Table 5. Final pH values (1M KCl) for each soil depth for the original soil and for the soil used in the columns leached with wastewater of SAR 2, 5, 10 and 20 and deionized water (6 cycles†).

Depth	Original	Wastewater SAR			
(cm)	Soil	2	5	10	20
0-15	4.55	5.62 a‡	5.59 a	5.75 a	5.42 a
15-30	4.21	5.71 a	5.59 a	5.93 a	5.45 a
30-45	4.29	5.92 a	5.87 a	6.02 a	5.77 a
45-60	4.41	5.79 a	6.02 a	6.02 a	6.05 a
60-75	4.31	5.72 a	5.75 a	5.87 a	6.07 a
75-90	4.32	5.4 a	5.48 a	5.45 a	5.31 a
90-105	4.33	4.56 a	4.66 a	4.78 a	4.47 a

† 1 Cycle = 1 L of wastewater + 1 L of deionized water leached thru the soil column.

‡ = Values with the same letter are not significantly different at 0.05 significance level.

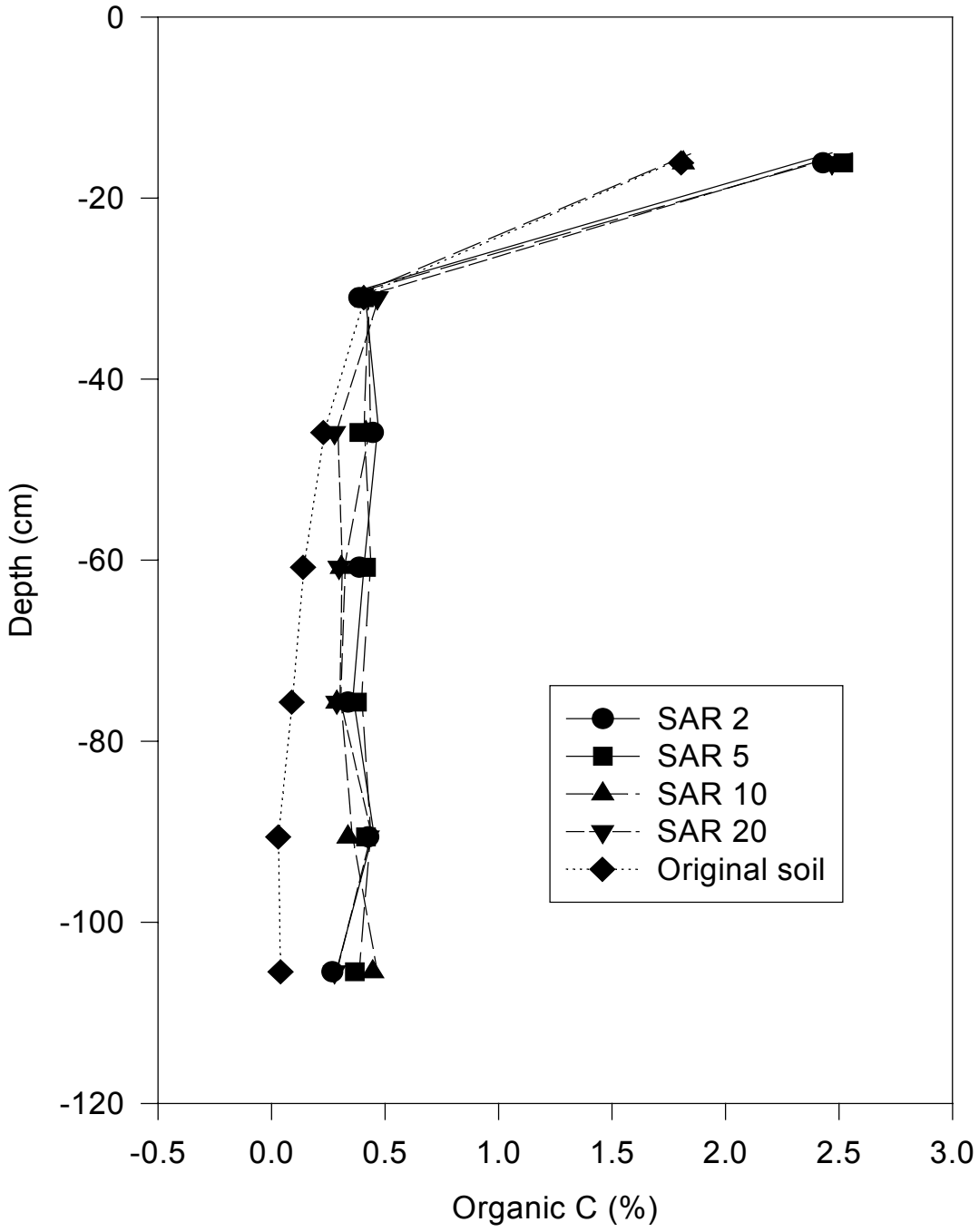


Figure 11. Organic C in the soil as a function of column soil depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

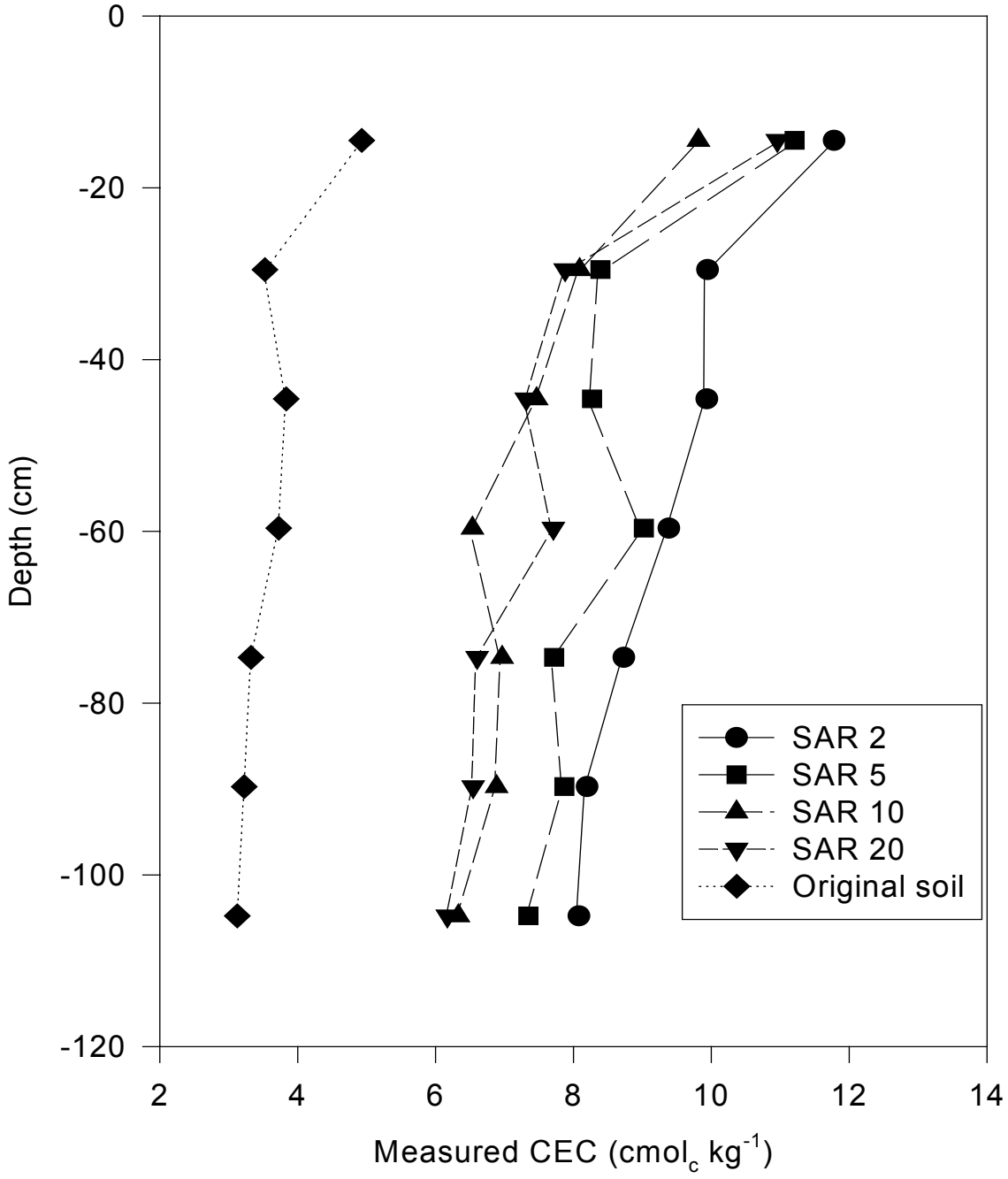


Figure 12. Measured CEC in the soil as a function of column soil depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached, CEC = cation exchage capacity

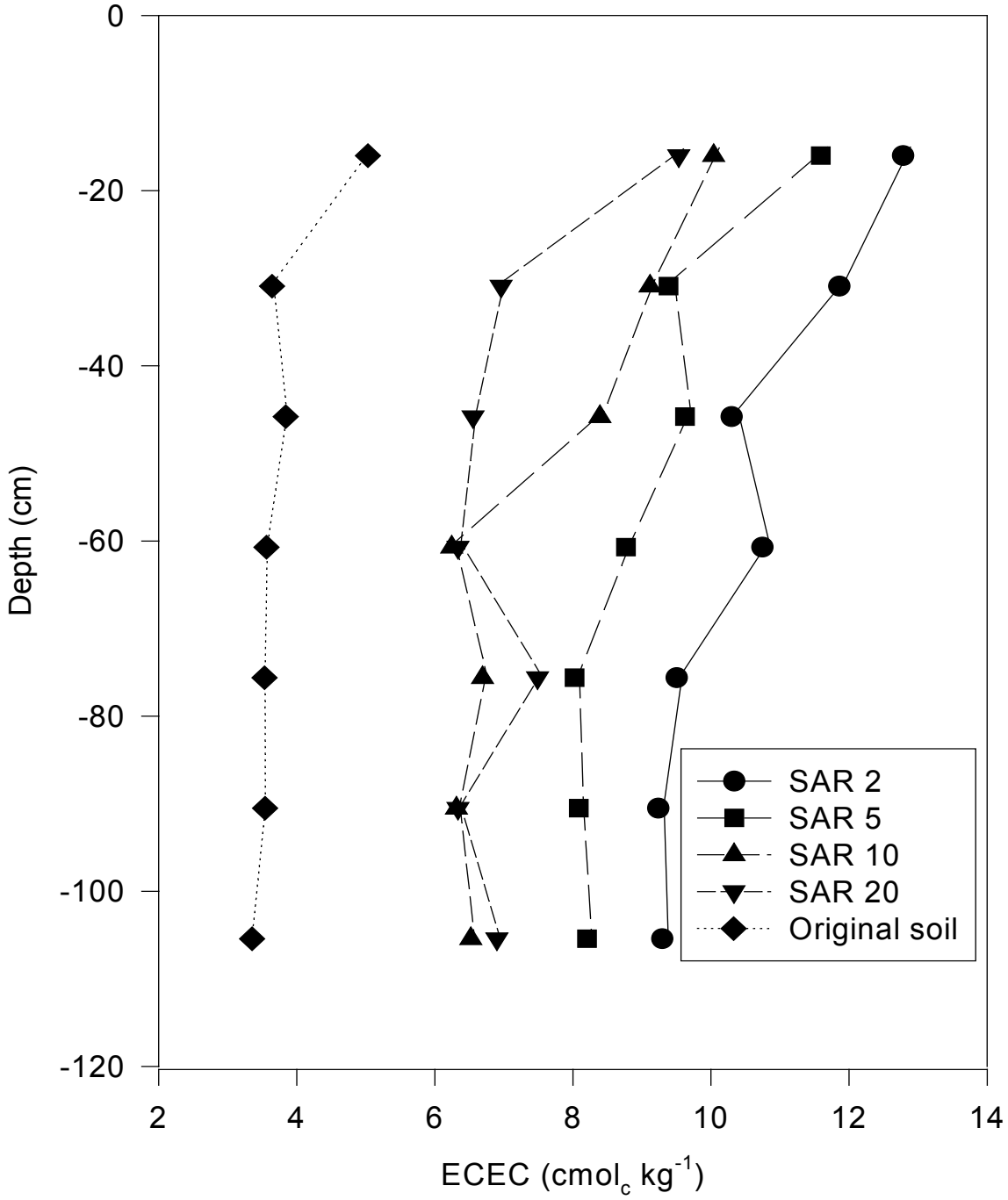
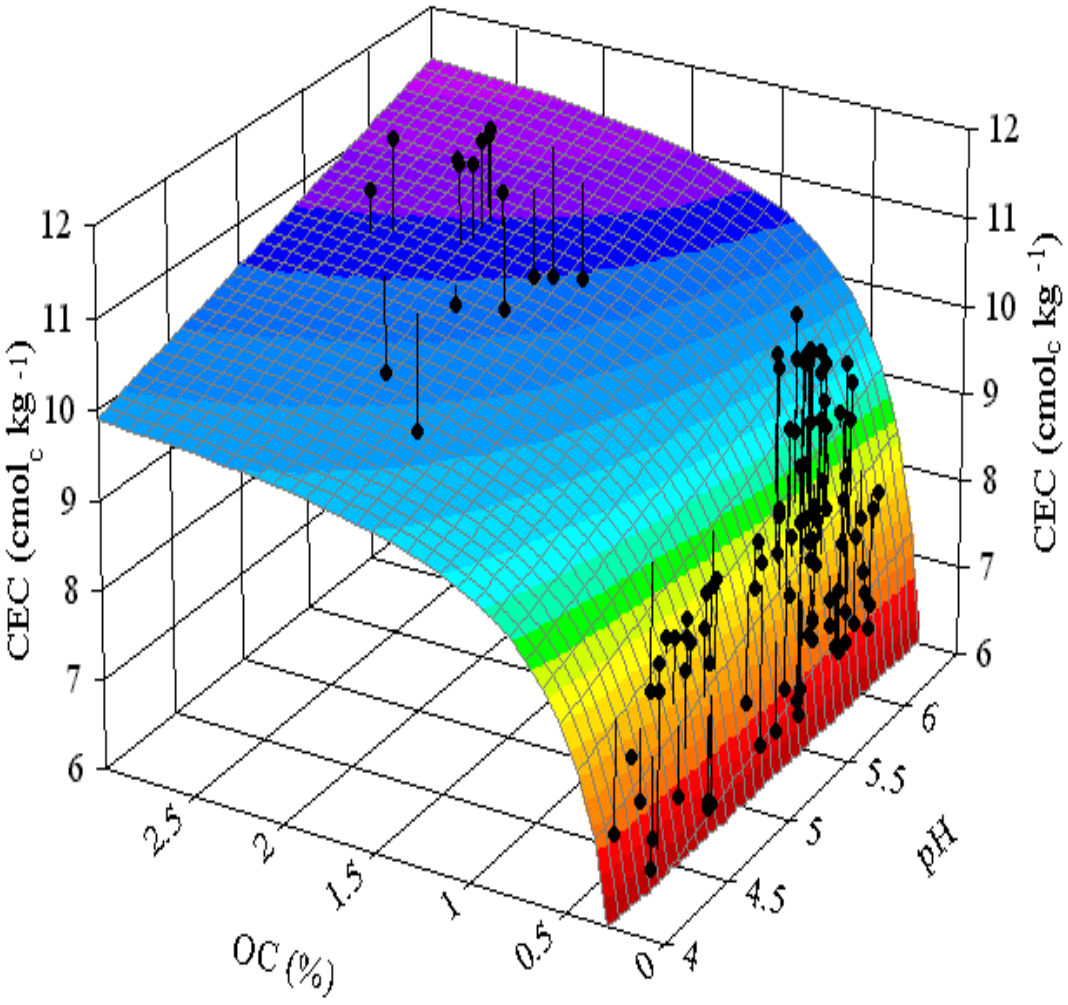
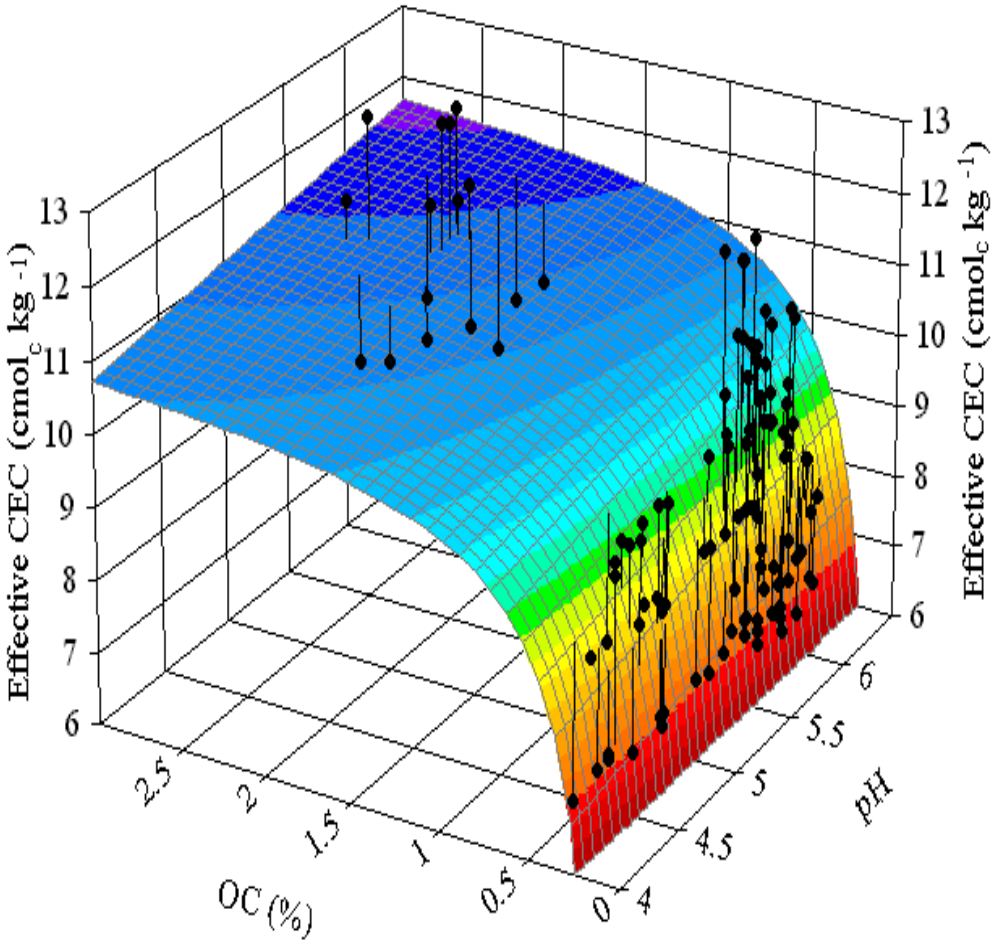


Figure 13. Effective CEC in the soil as function of column soil depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached, CEC = cation exchage capacity



$$CEC = 7.90 + 0.6pH - 1.2(OC^{-1})$$

Figure 14. Regression analysis for the measured cation exchange capacity (CEC) at different pH and organic carbon (OC) values.



$$ECEC = 9.64 + 0.37pH - 1.18\ (OC^{-1})$$

Figure 15. Regression analysis for the effective cation exchange capacity (ECEC) at different pH and organic carbon (OC) values.

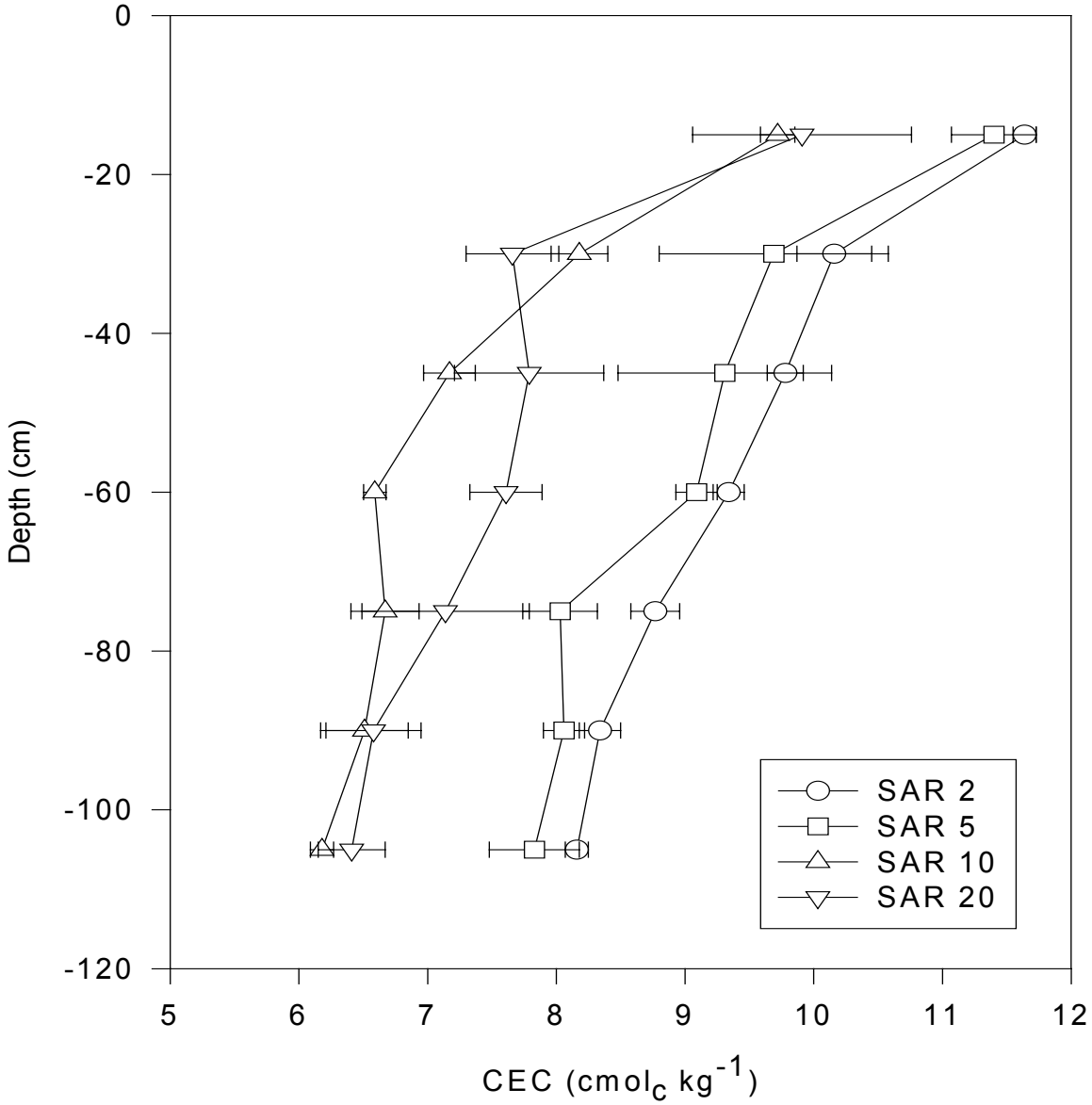


Figure 16. Means ± standard deviation for cation exchange capacity (CEC) values as a function of soil depth for the four different wastewater's SAR treatments.

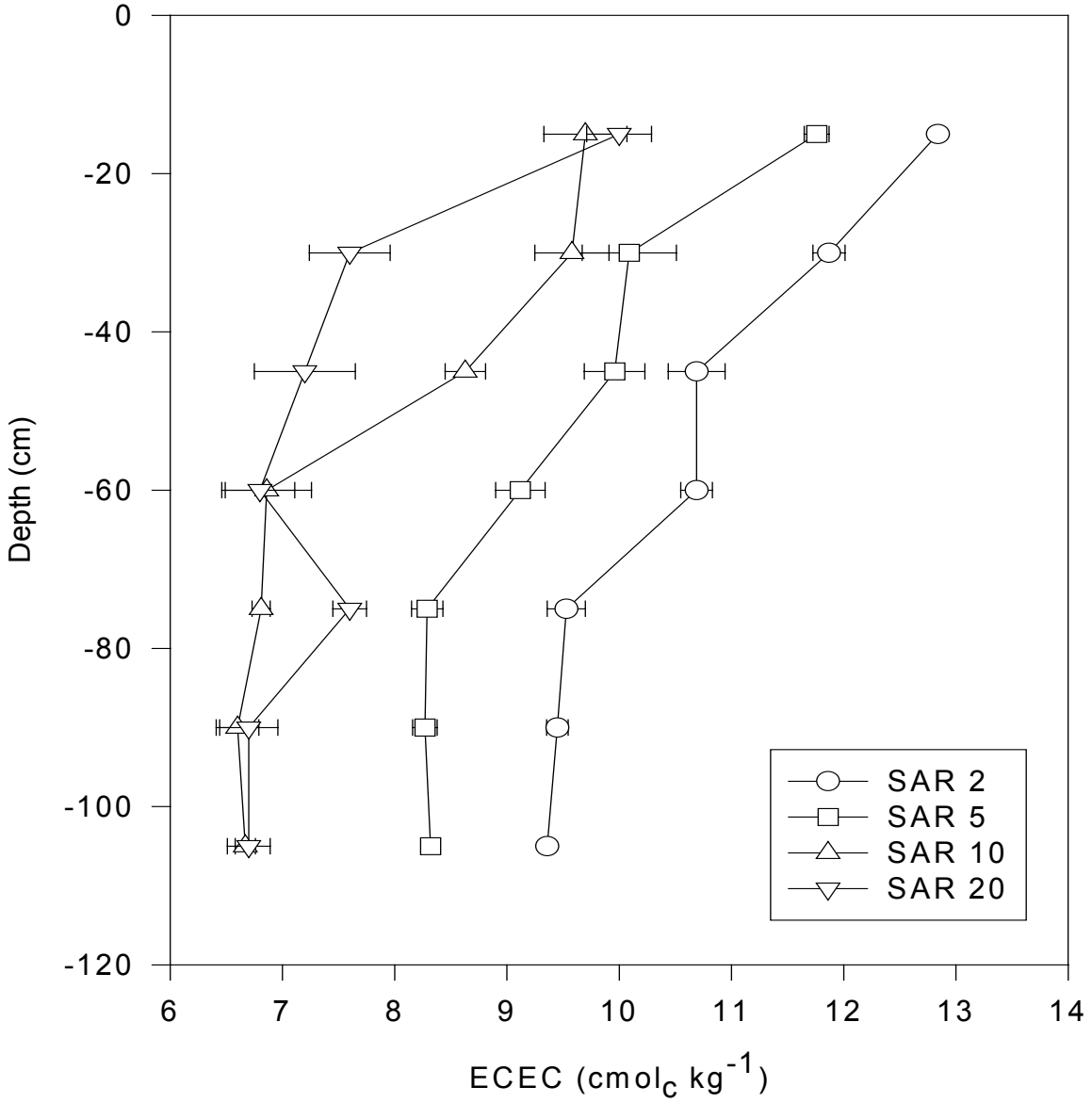


Figure 17. Means ± standard deviation for effective cation exchange capacity (ECEC) values as a function of soil depth for the four different wastewater's SAR treatments.

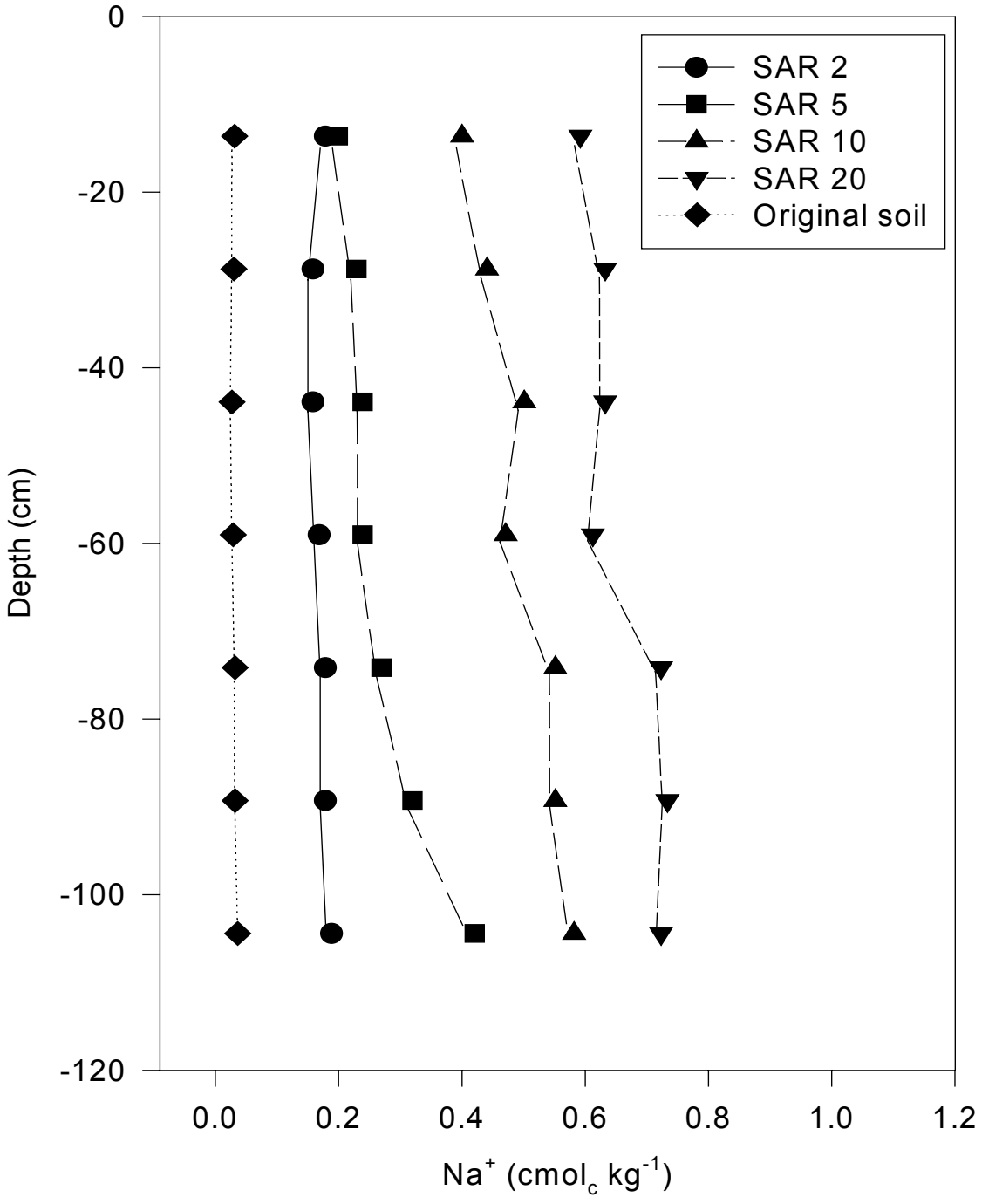


Figure 18. Exchangeable Na composition in soil as a function of soil column depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

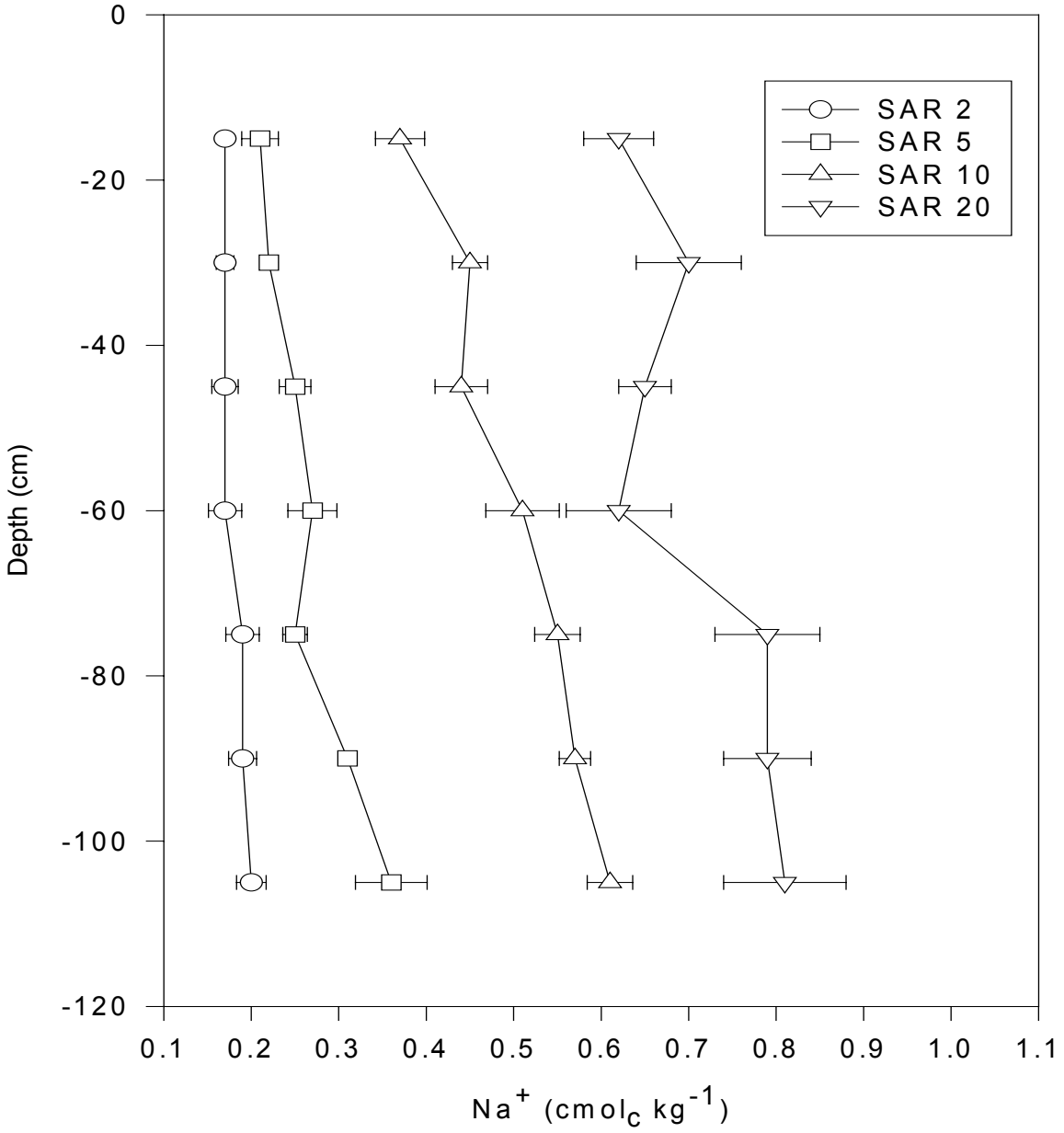


Figure 19. Means ± standard deviation for exchangeable Na values as a function of soil depth for the four different wastewater's SAR treatments.

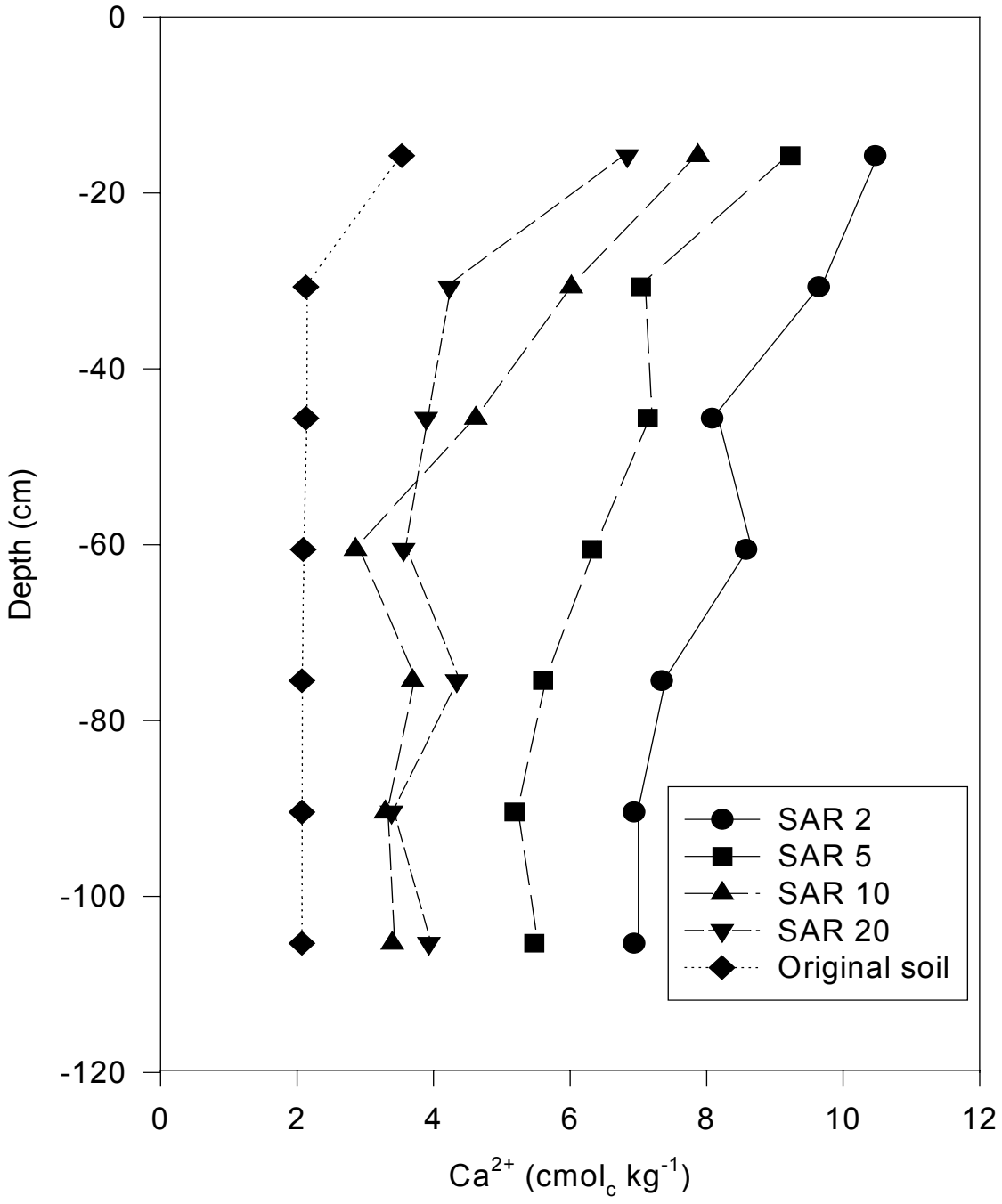


Figure 20. Exchangeable Ca composition in soil as a function of soil column depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

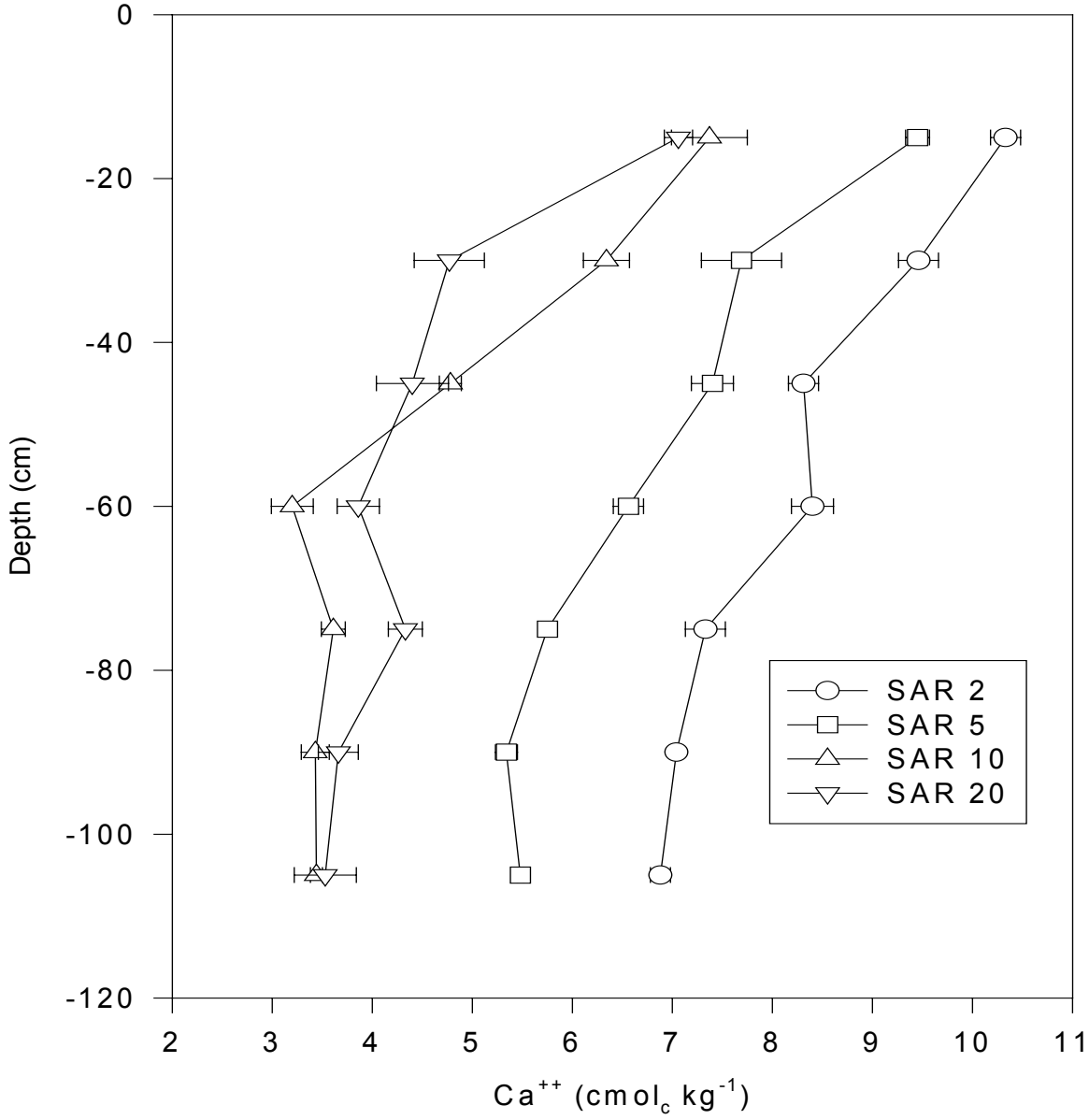


Figure 21. Means ± standard deviation for exchangeable Ca values as a function of soil depth for the four different wastewater's SAR treatments.

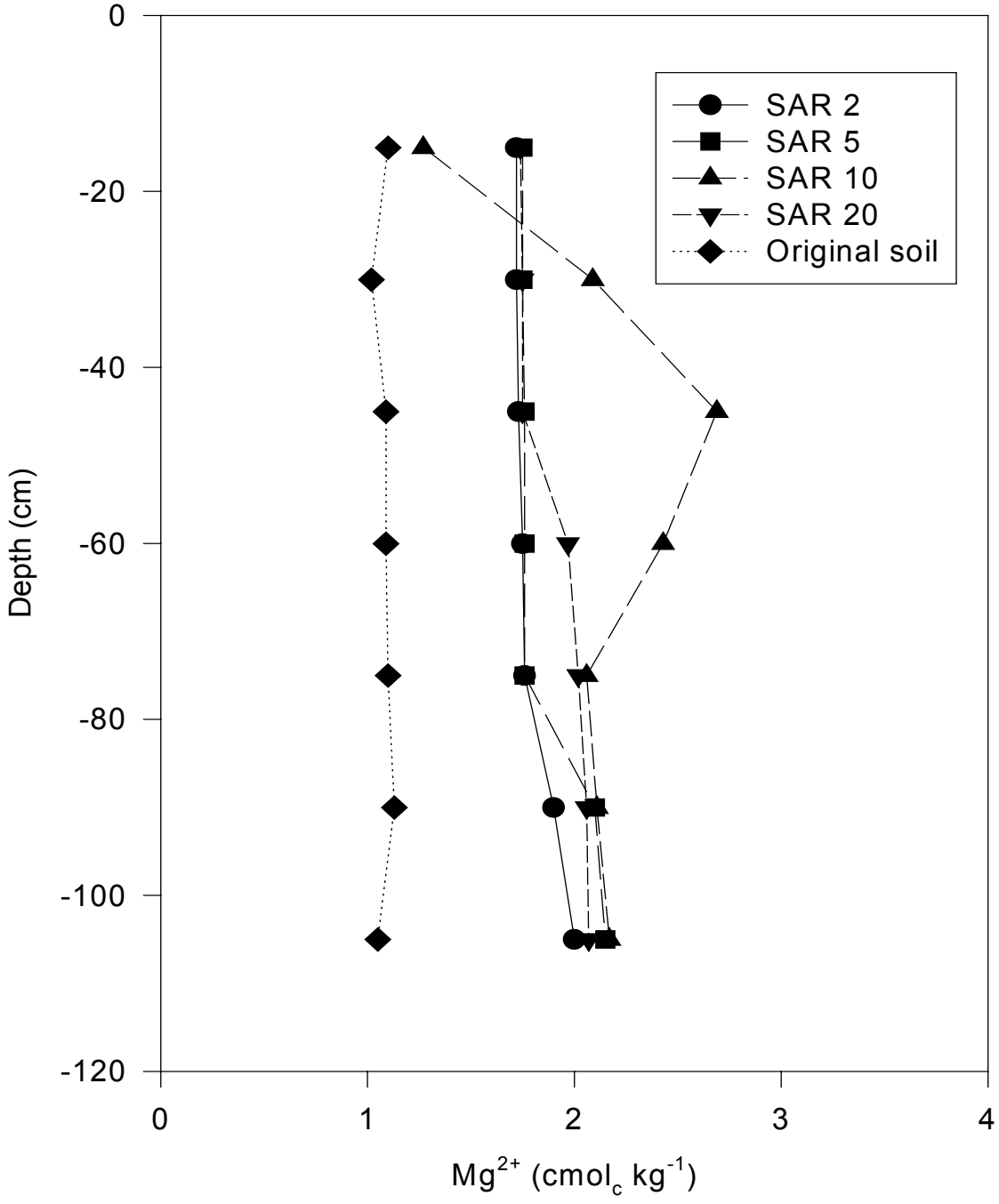


Figure 22. Exchangeable Mg composition in soil as a function of soil column depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

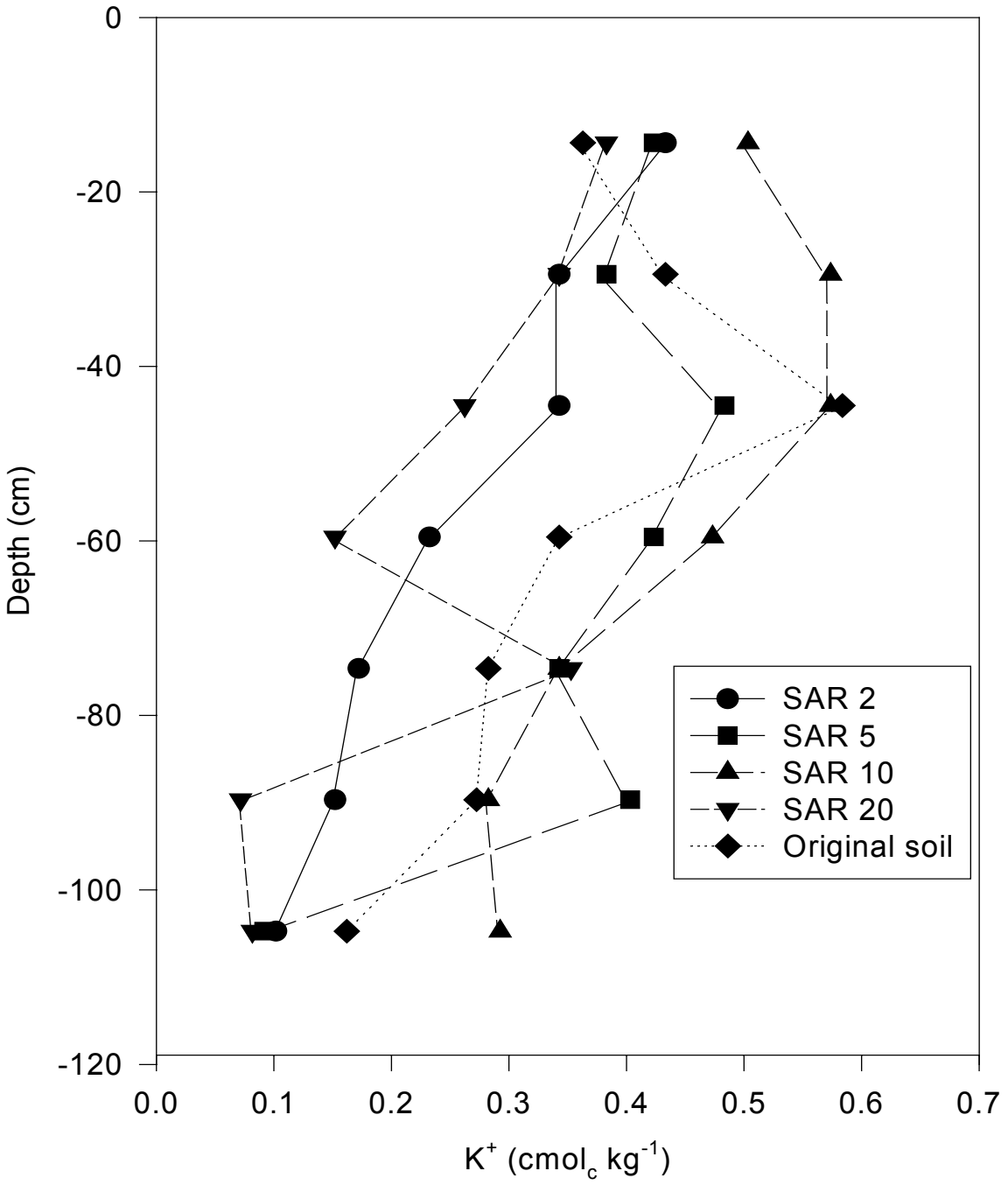


Figure 23. Exchangeable K composition in soil as a function of soil column depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

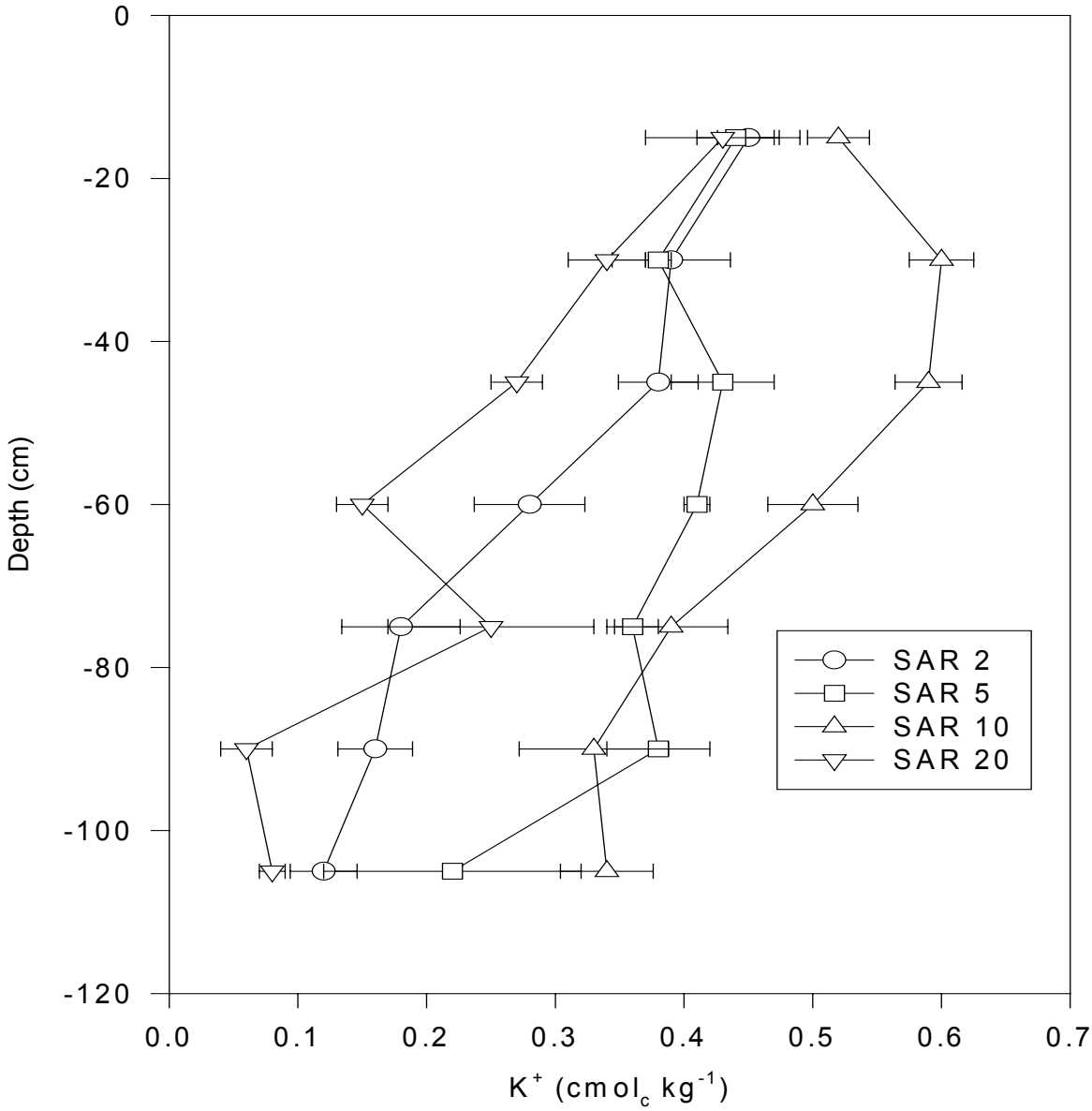


Figure 24. Means ± standard deviation for exchangeable K values as a function of soil depth for the four different wastewater's SAR treatments.

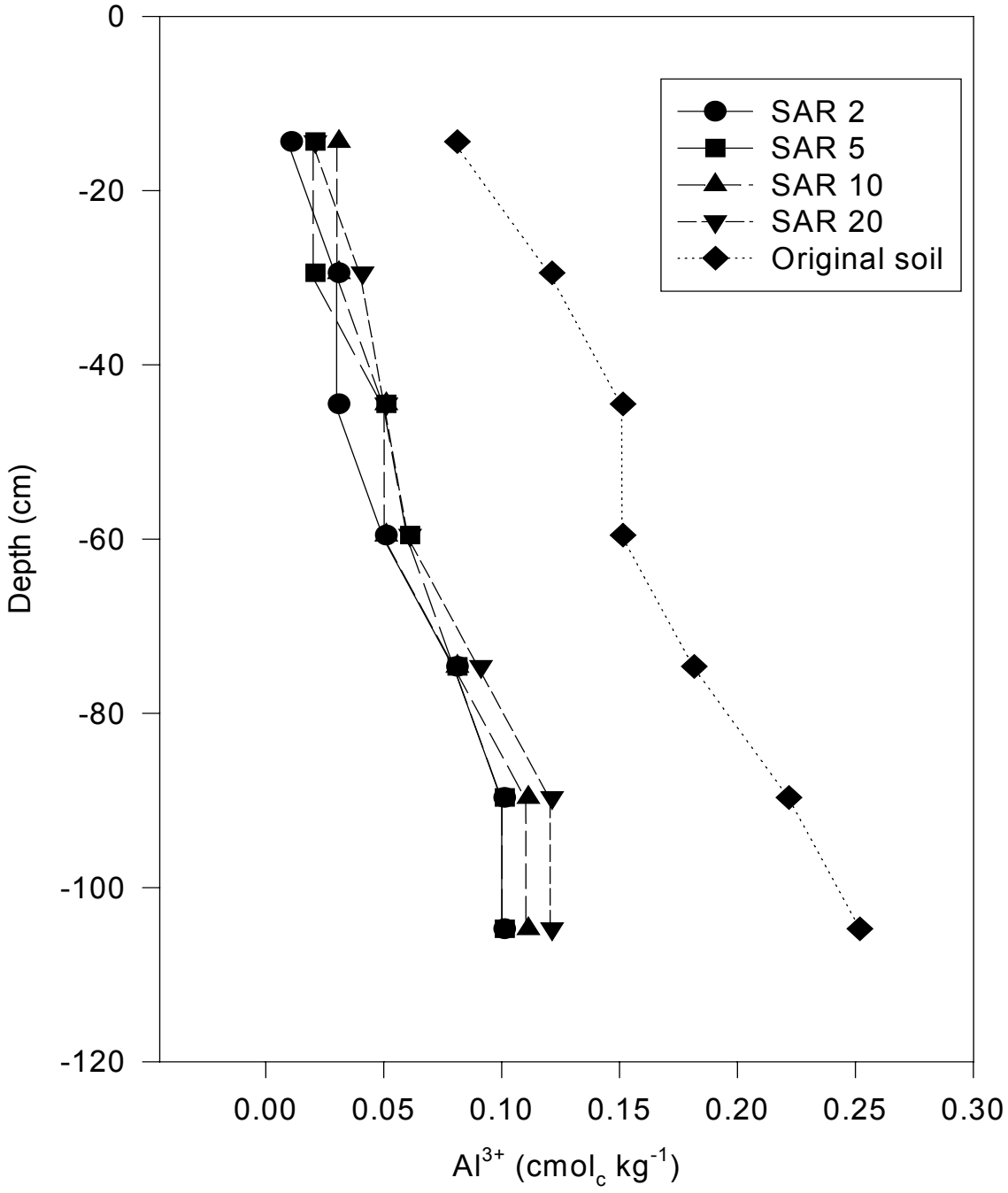


Figure 25. Exchangeable Al composition in soil as a function of soil column depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

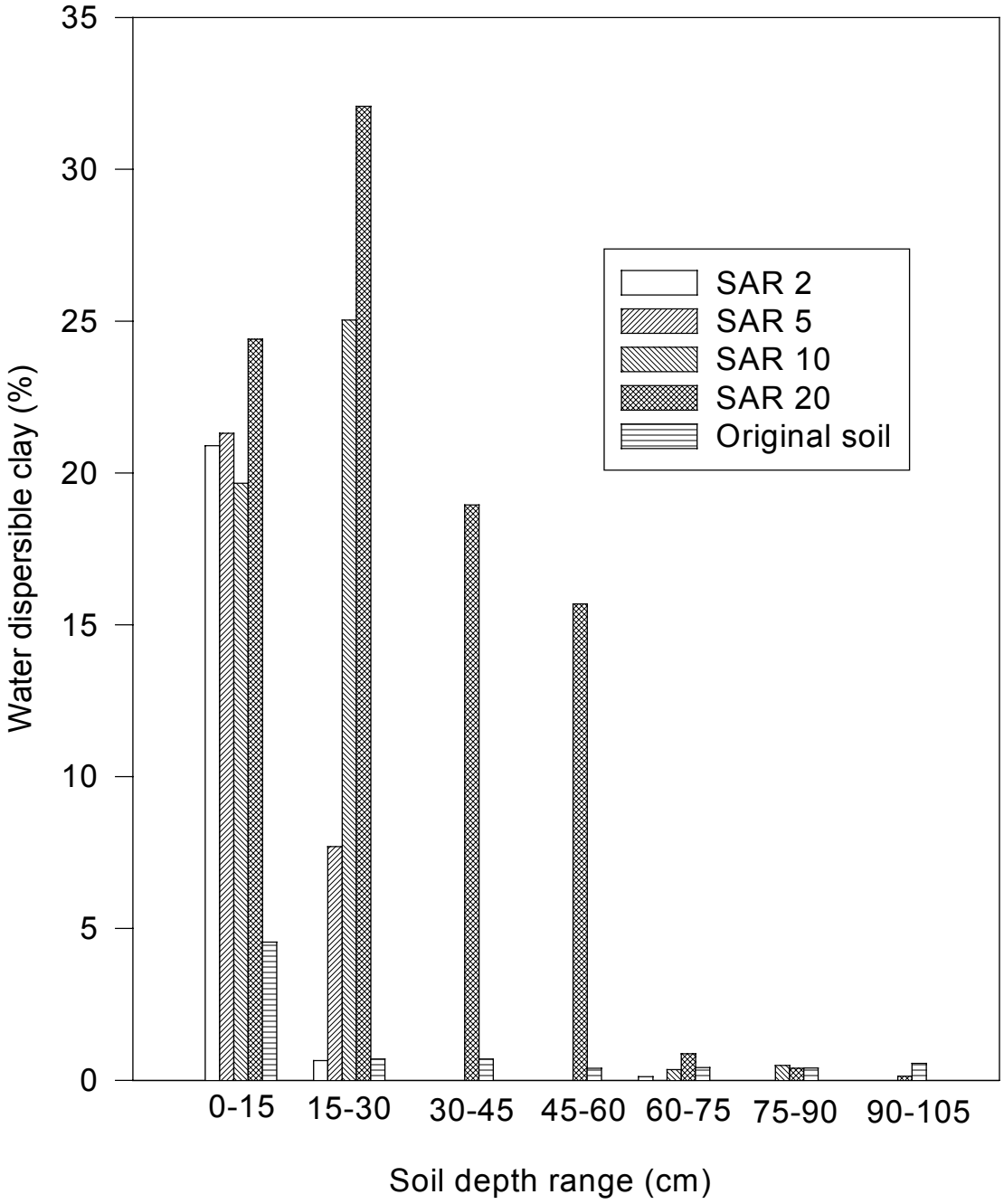


Figure 26. Water dispersible clay in the soil as a function of range of soil depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

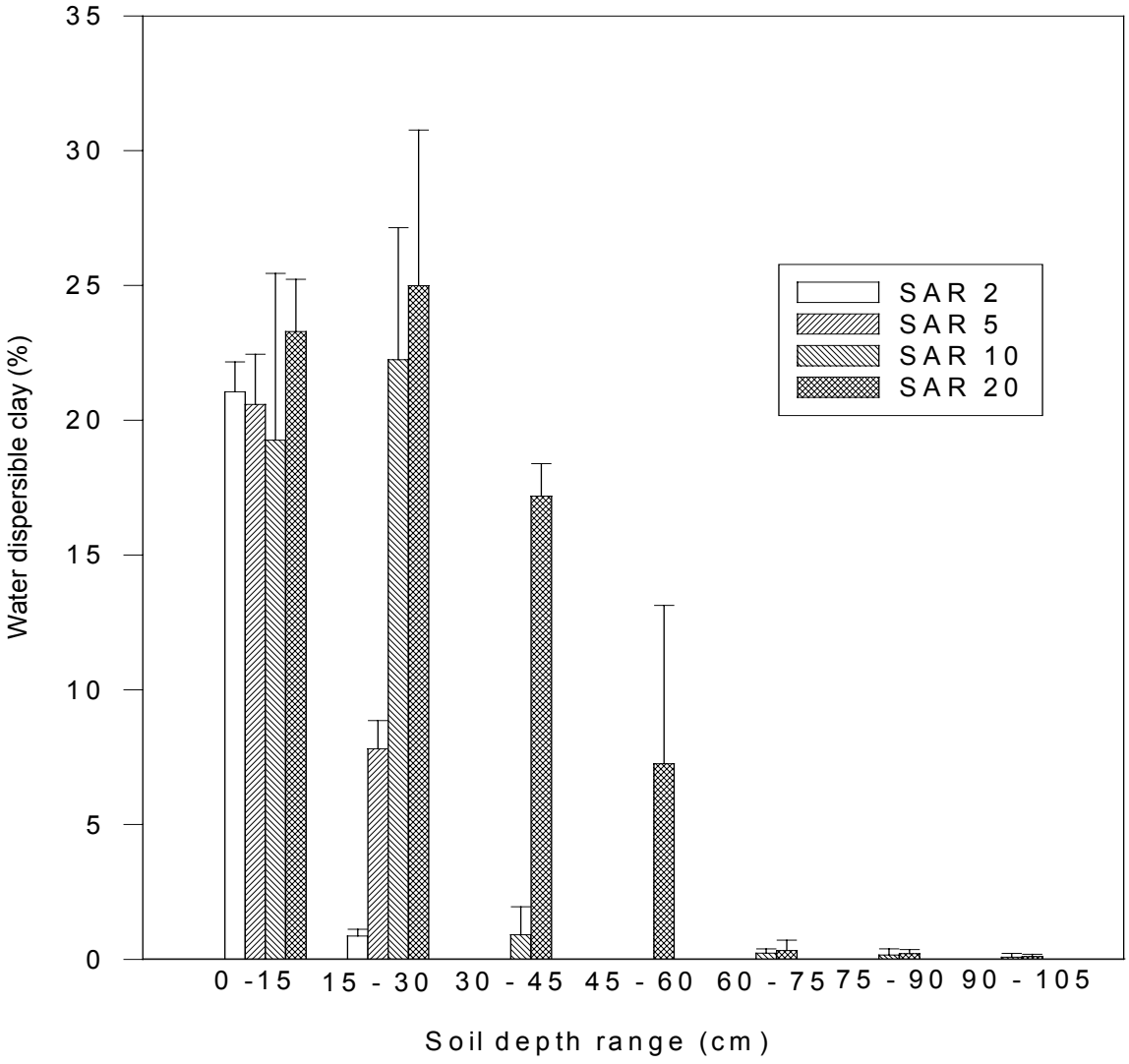


Figure 27. Means ± standard deviation for water dispersible clay values as a function of soil depth range for the four different wastewater's SAR treatments.

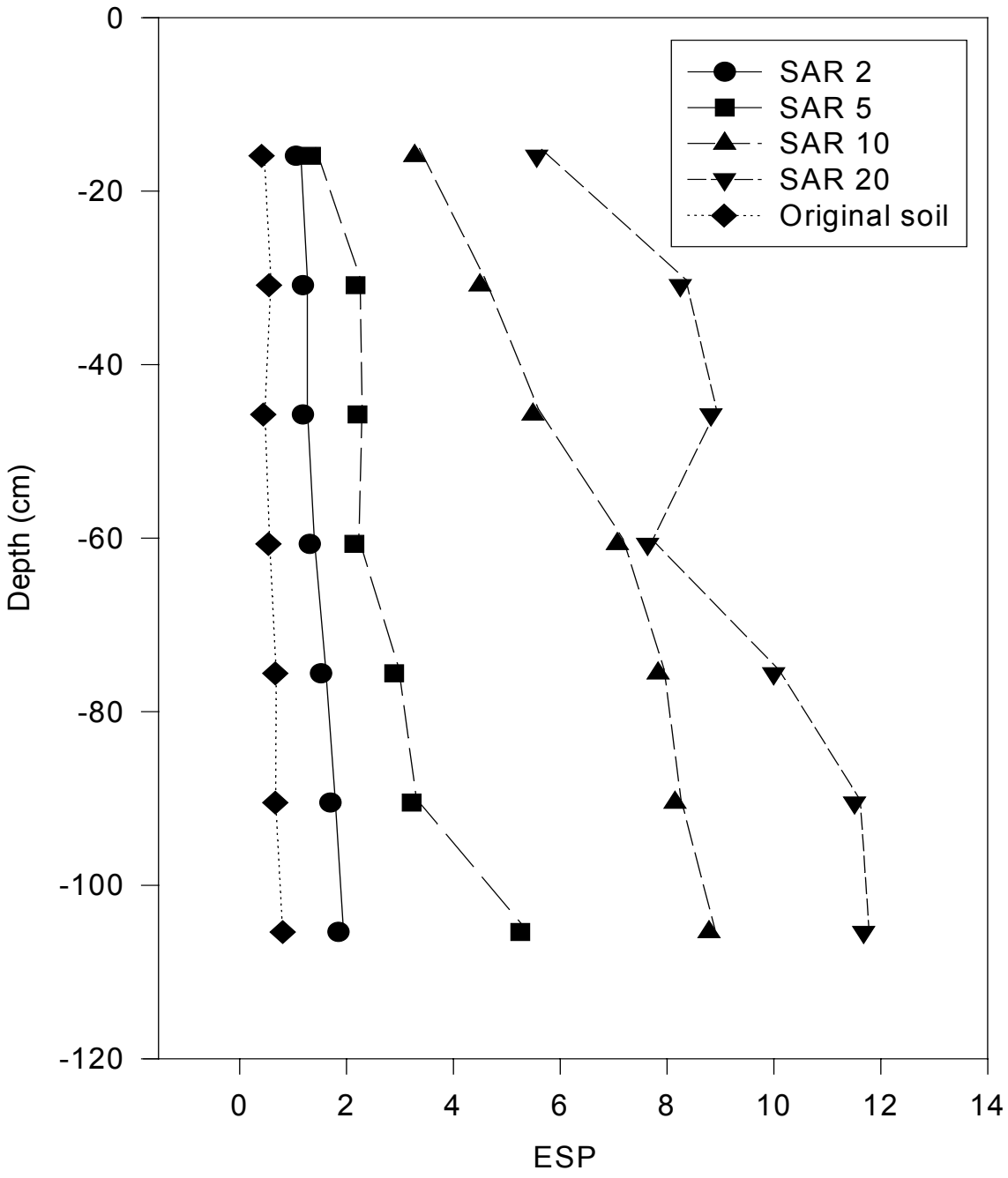


Figure 28. Exchangeable sodium percentage (ESP) in soil as a function of soil column depth after 6 leaching cycles with wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

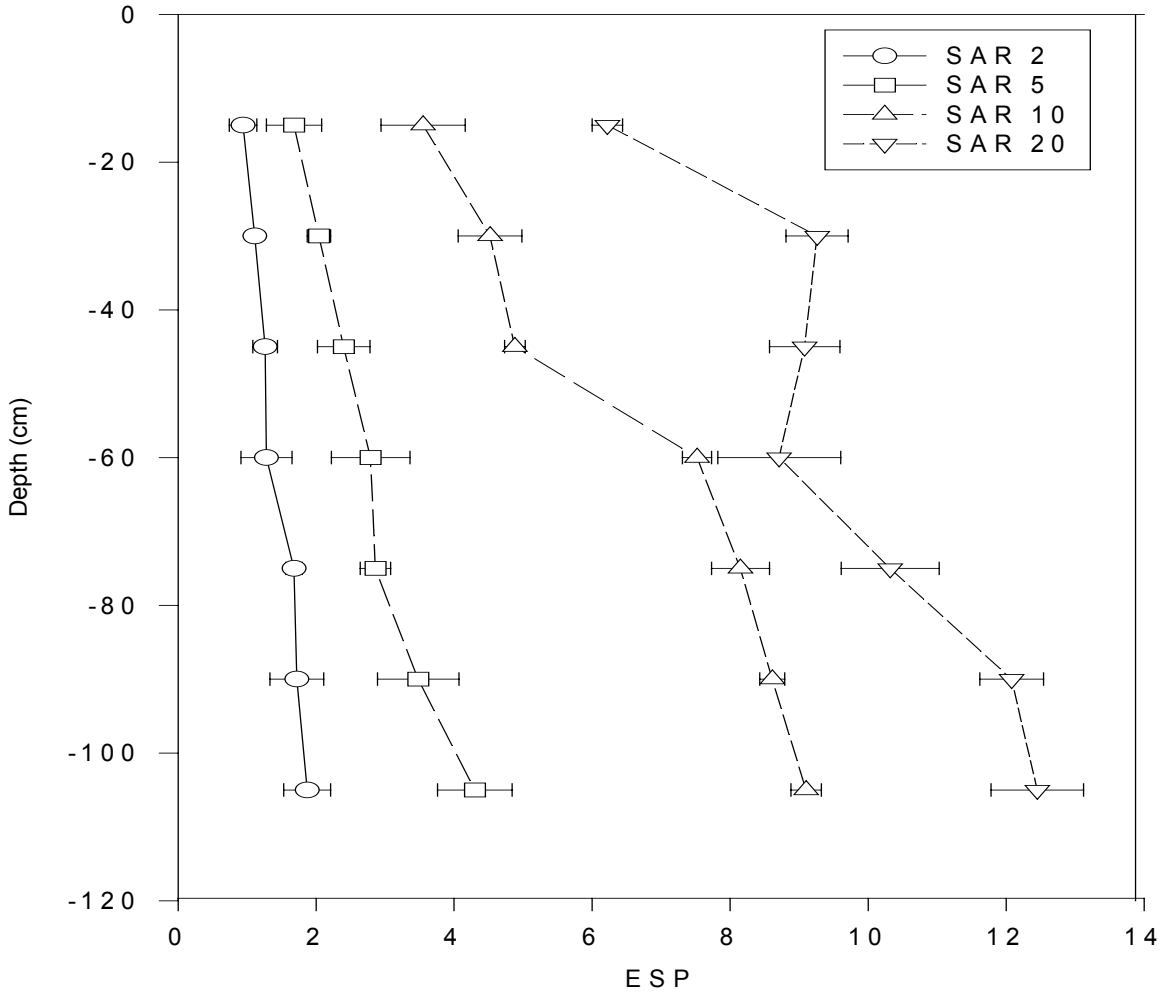


Figure 29. Means ± standard deviation for exchangeable sodium percentage (ESP) values as a function of soil column depth for the four different wastewater's SAR treatments.

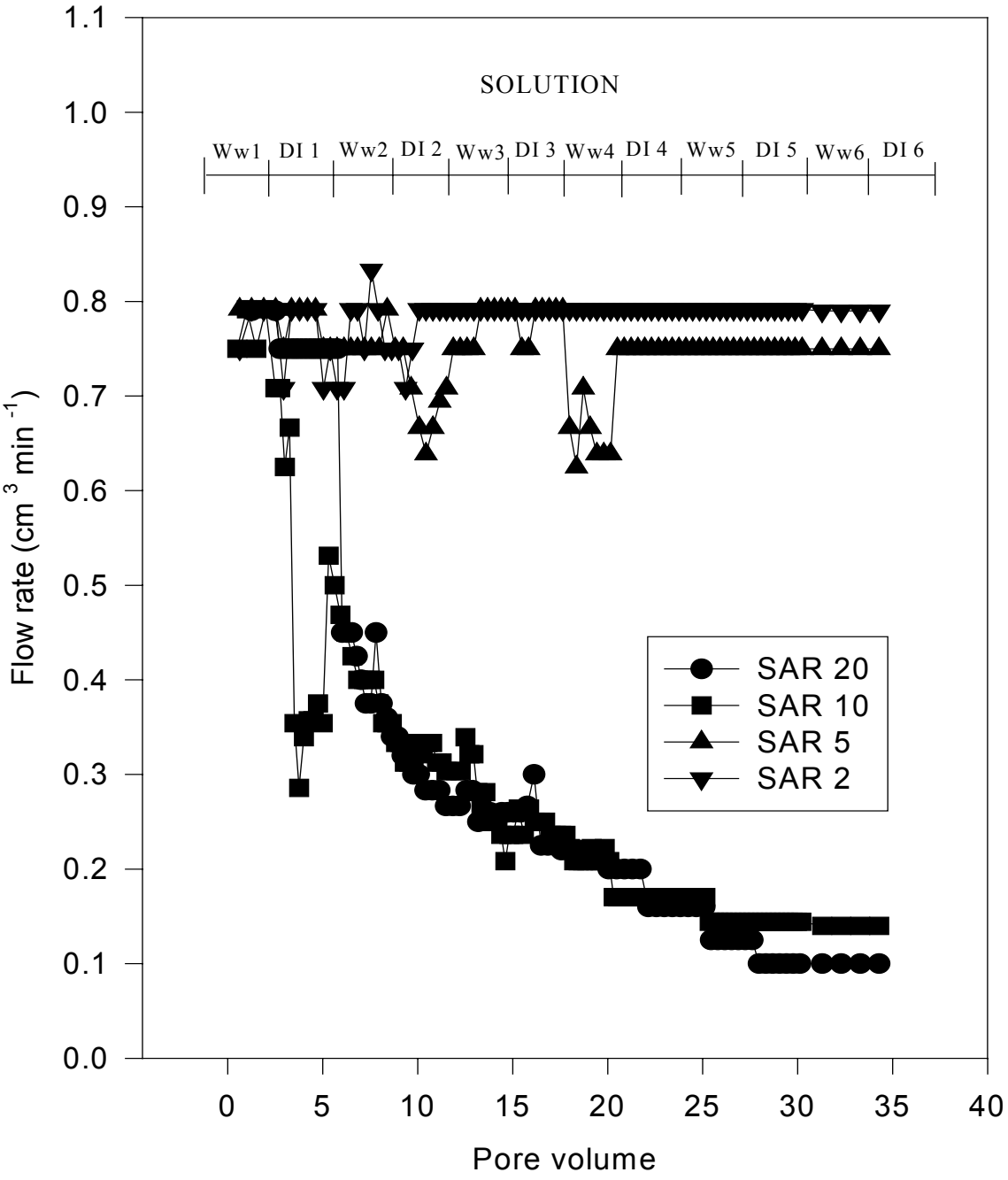


Figure 30. Effluent flow rate from the columns leached with 6 cycles of wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached, Ww = wastewater, DI = Deionized water

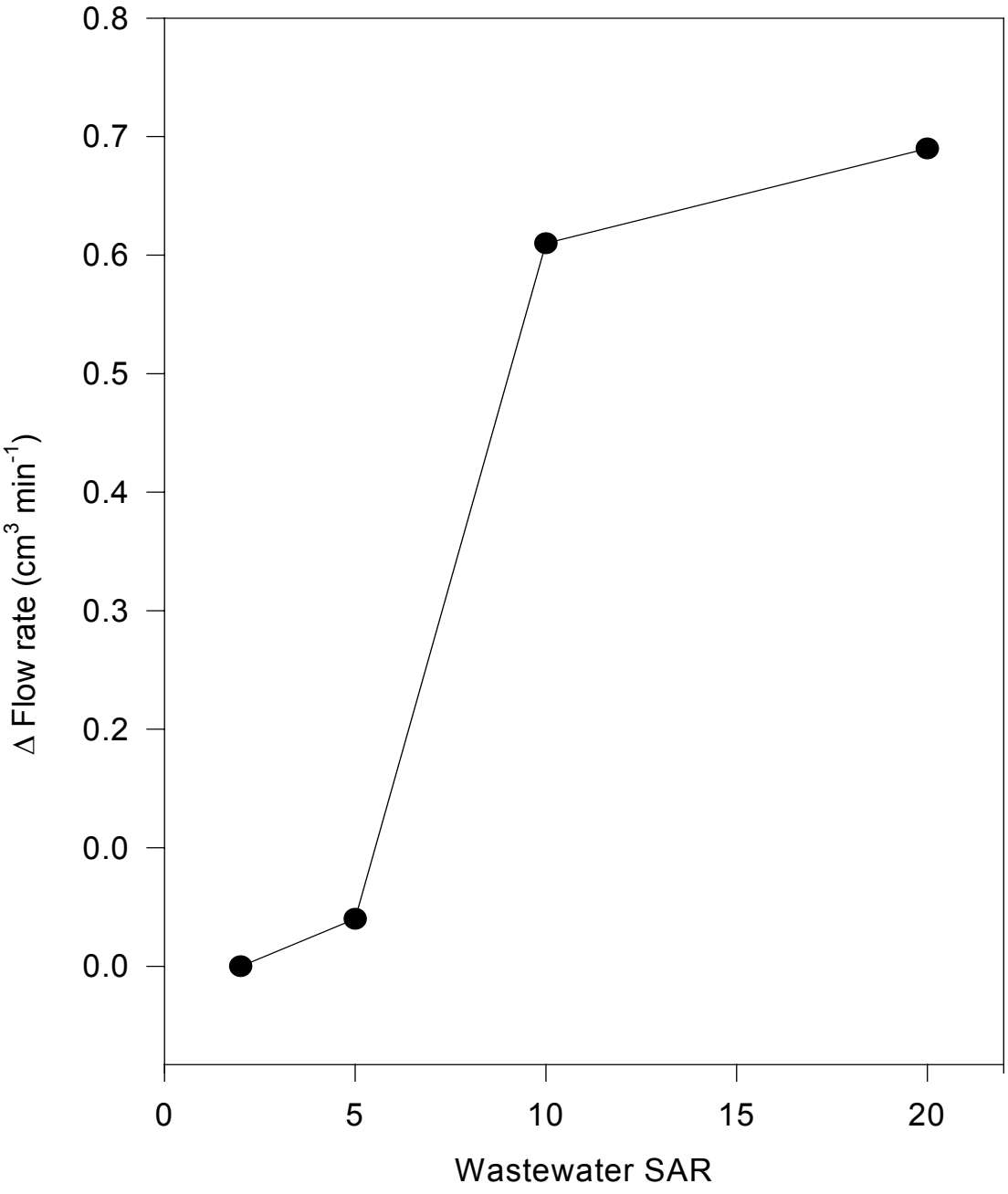


Figure 31. Total decrease in effluent flow rate from the columns leached with 6 cycles of wastewater of various SAR and deionized water.
1 cycle = 1L wastewater + 1L deionized water leached.

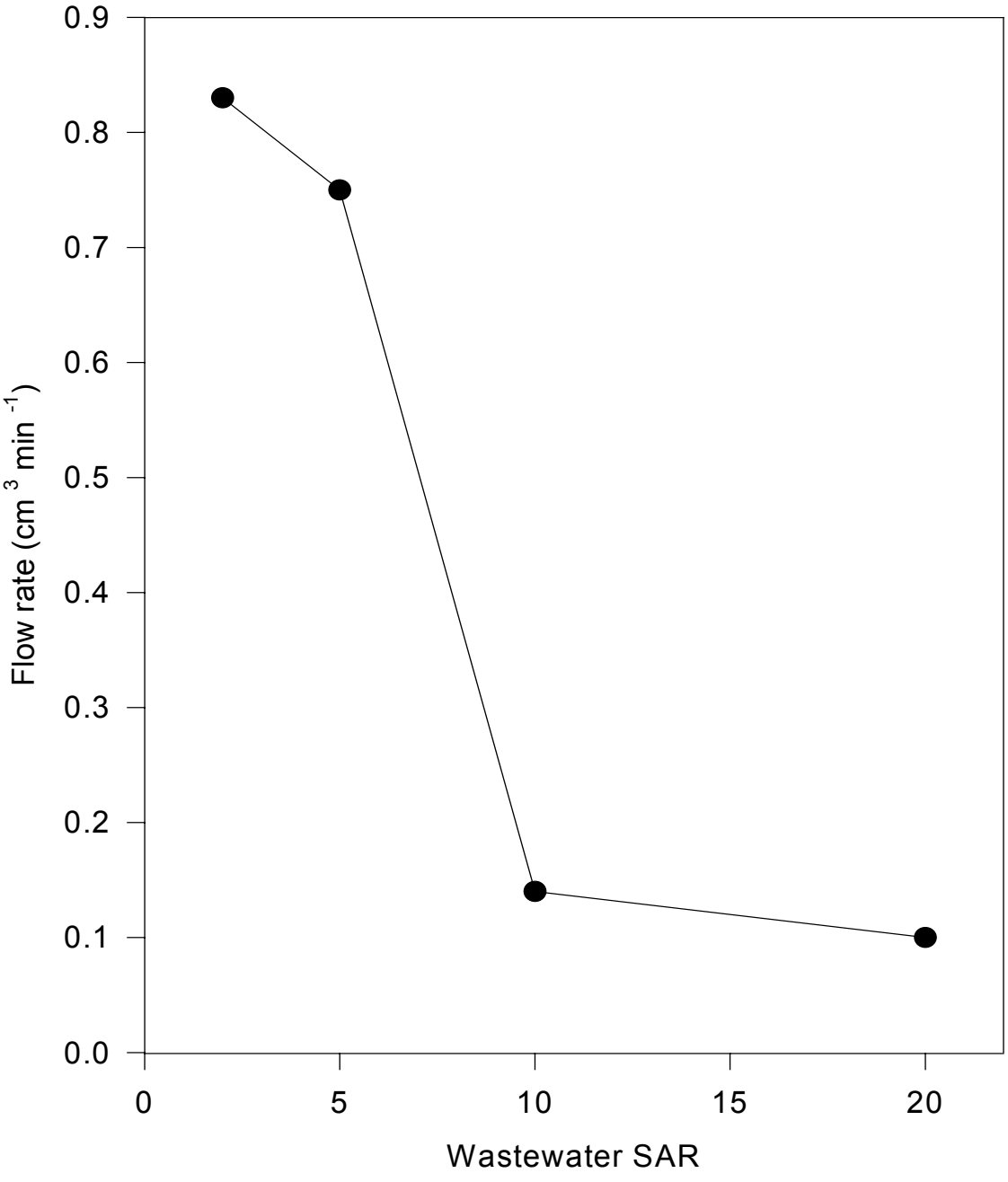


Figure 32. Final effluent flow rate from the columns leached with 6 cycles of wastewater of various SAR and deionized water.
1 cycle = 1L wastewater + 1L deionized water leached.

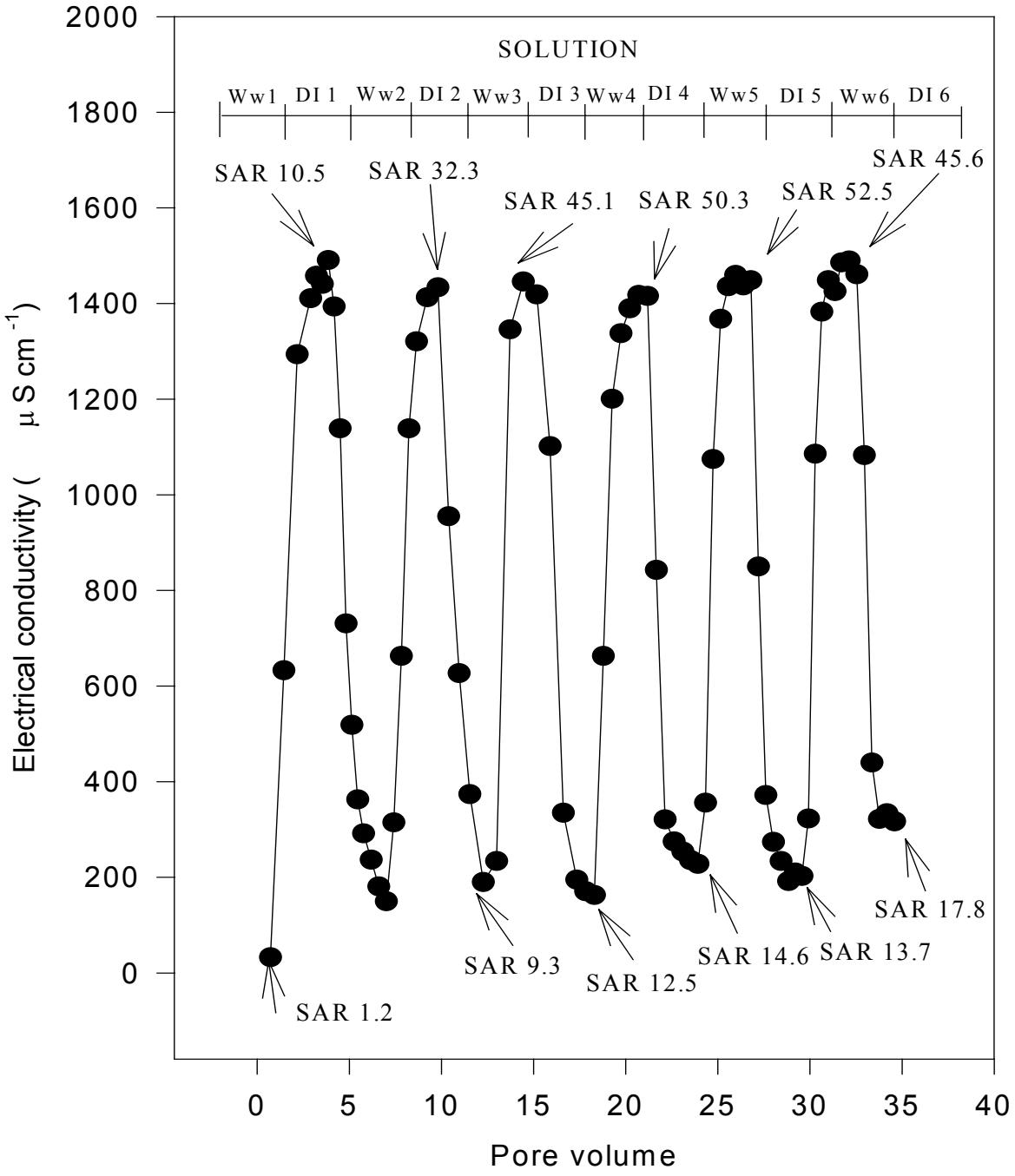


Figure 33. Electrical conductivity (EC) of the flow rate from the column leached with 6 cycles of SAR 20 wastewater and deionized water 1 cycle = 1L wastewater + 1L deionized water leached, Ww = wastewater, DI = deionized water.

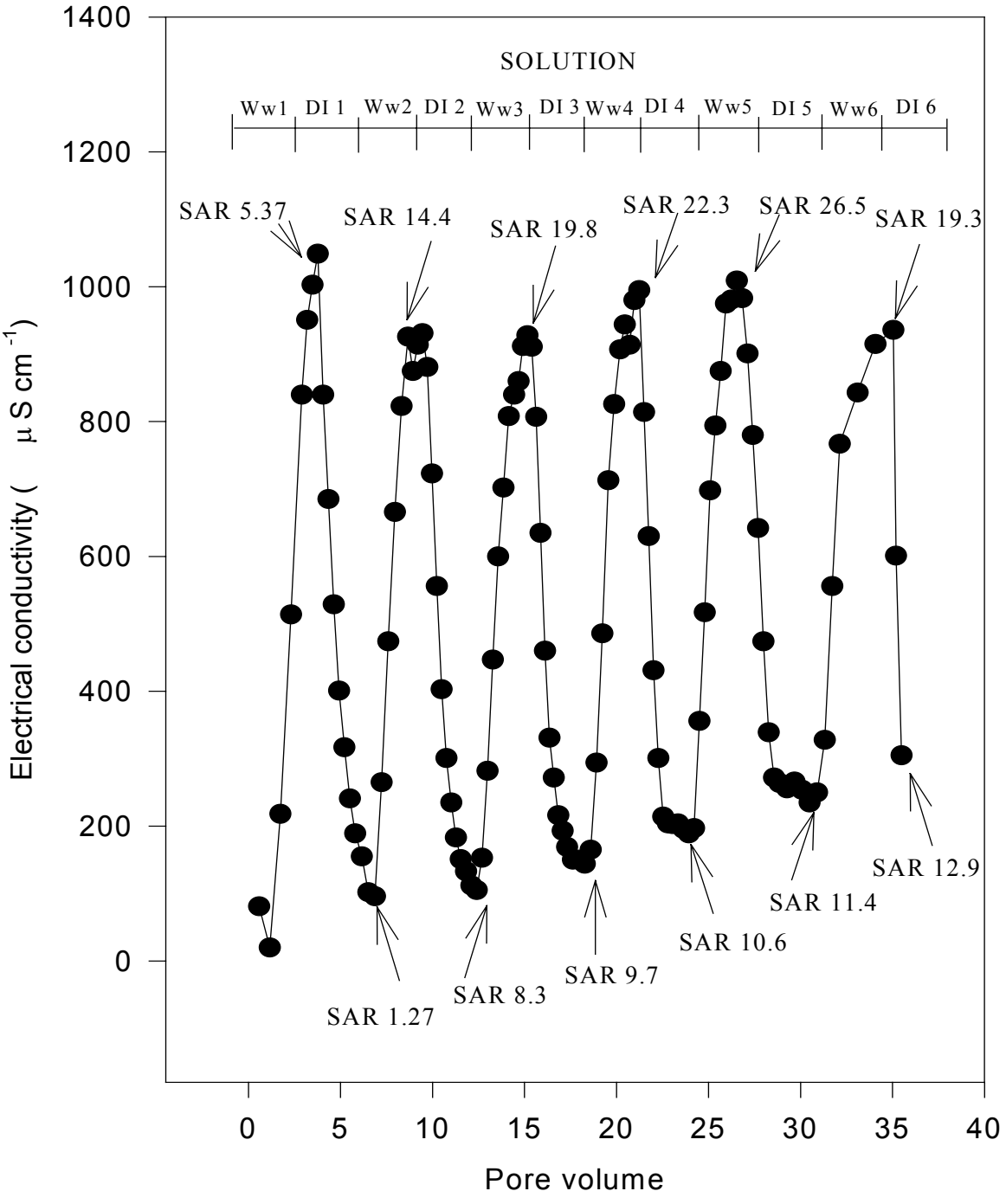


Figure 34. Electrical conductivity (EC) of the flow rate from the column leached with 6 cycles of SAR 10 wastewater and deionized water 1 cycle = 1L wastewater + 1L deionized water leached, Ww = wastewater, DI = Deionized water.

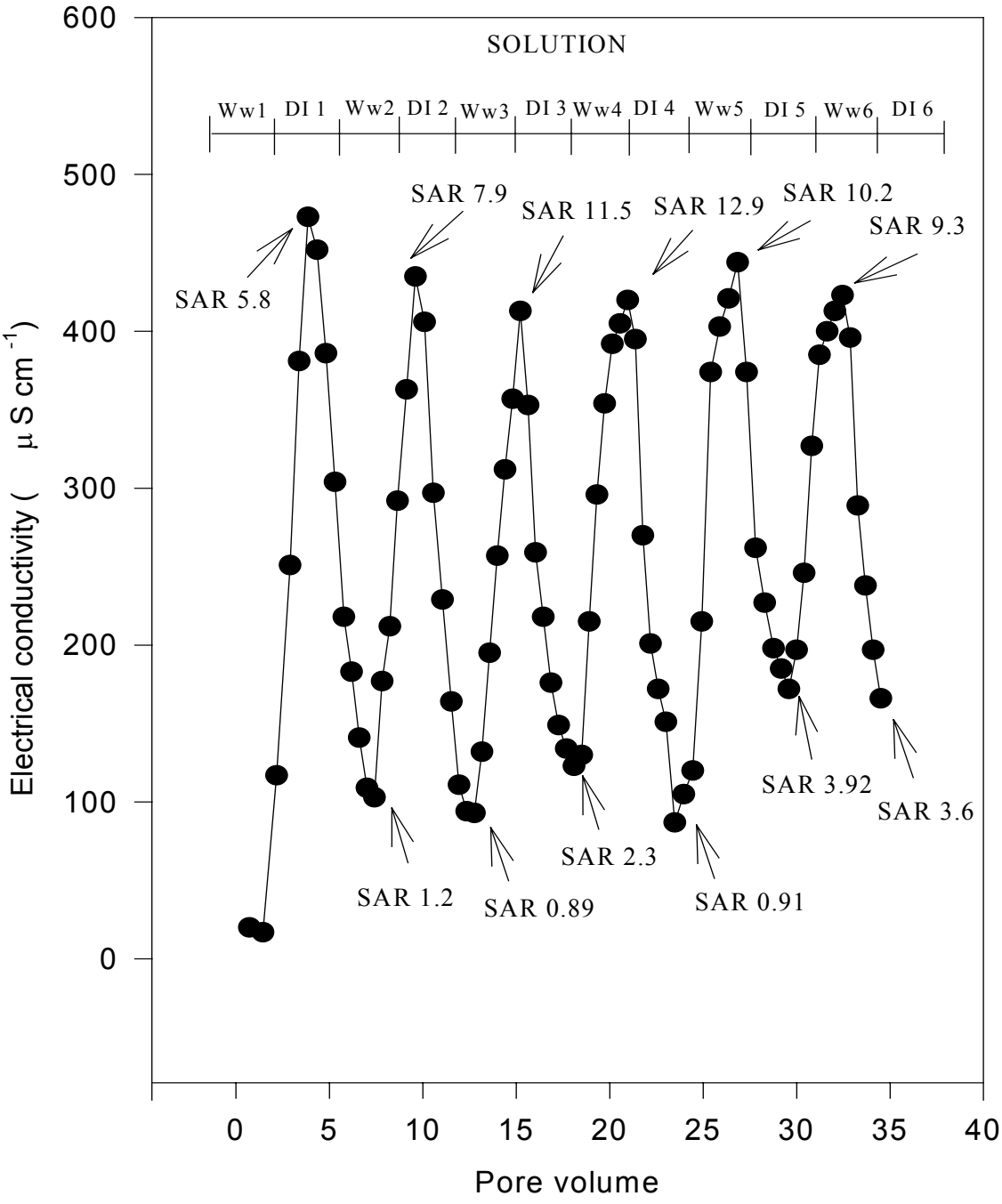


Figure 35. Electrical conductivity (EC) of the flow rate from the column leached with 6 cycles of SAR 5 wastewater and deionized water 1 cycle = 1L wastewater + 1L deionized water leached, Ww = wastewater, DI = Deionized water.

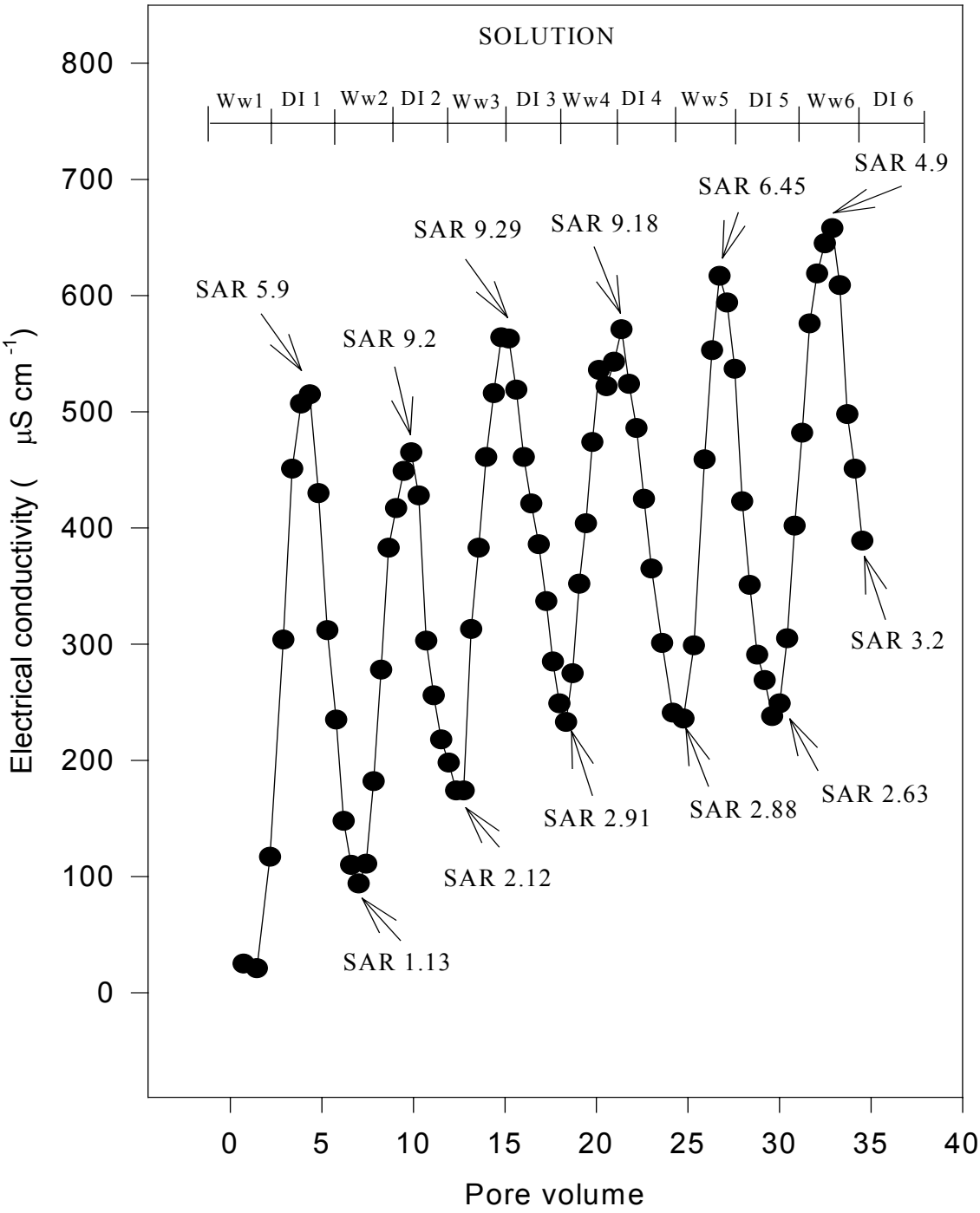


Figure 36. Electrical conductivity (EC)of the flow rate from the column leached with 6 cycles of SAR 2 wastewater and deionized water 1 cycle = 1L wastewater + 1L deionized water leached, Ww = wastewater, DI = Deionized water.

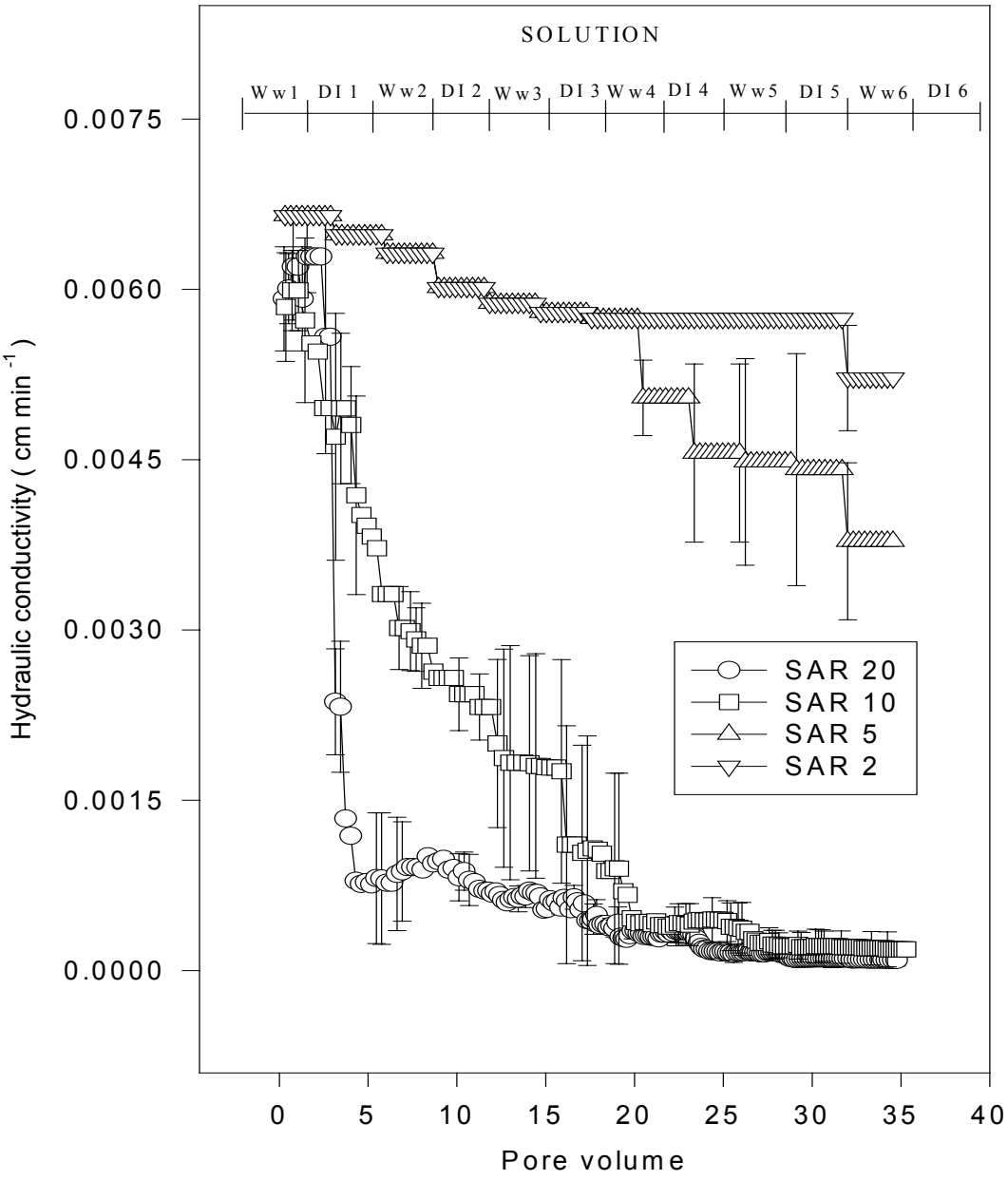


Figure 37. Means ± standard deviation for the hydraulic conductivity values as a function of pore volume for the four different wastewater's SAR values.

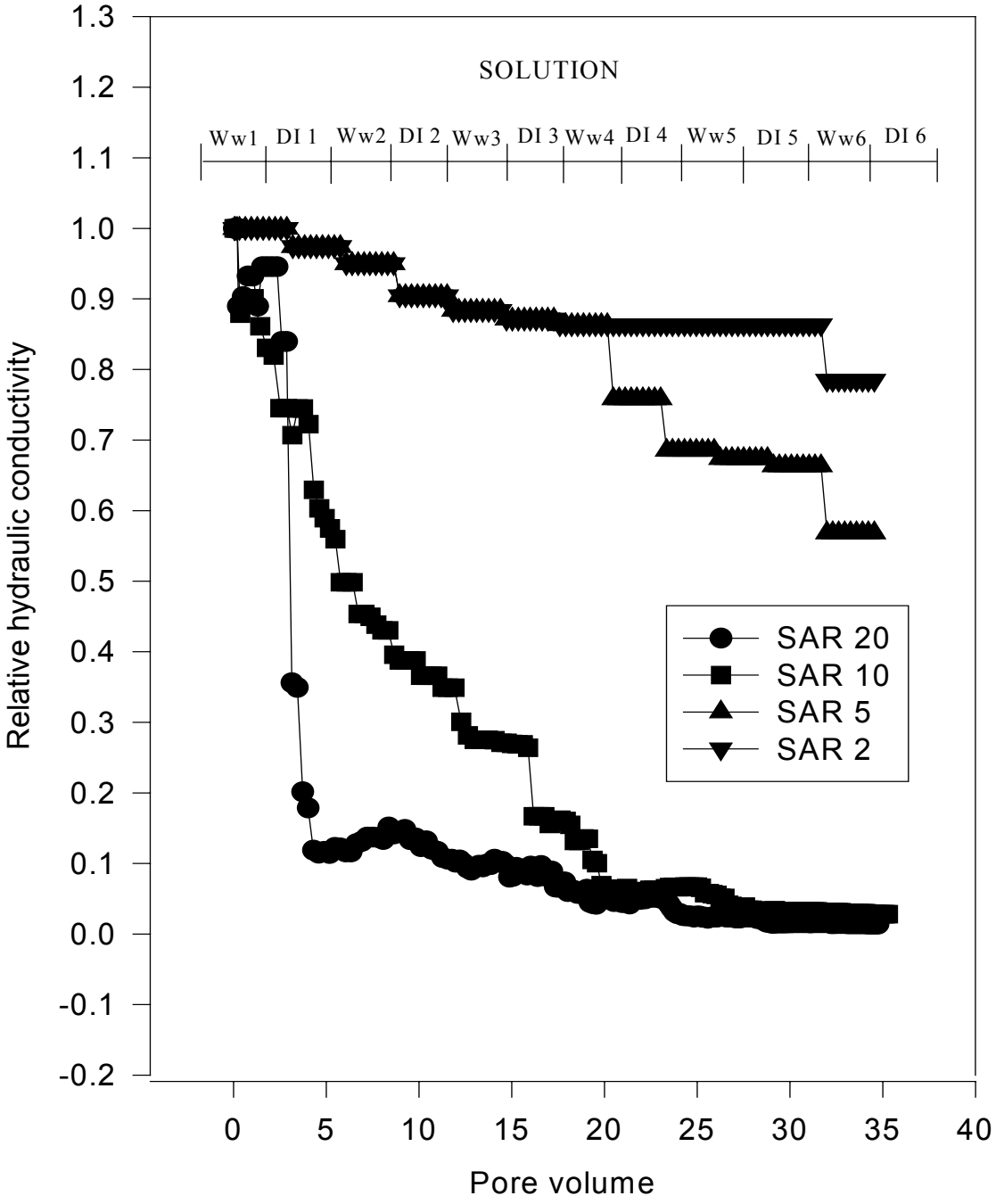


Figure 38. Relative hydraulic conductivity from the columns leached with 6 cycles of wastewater of various SAR and deionized water. 1 cycle = 1L wastewater + 1L deionized water leached.

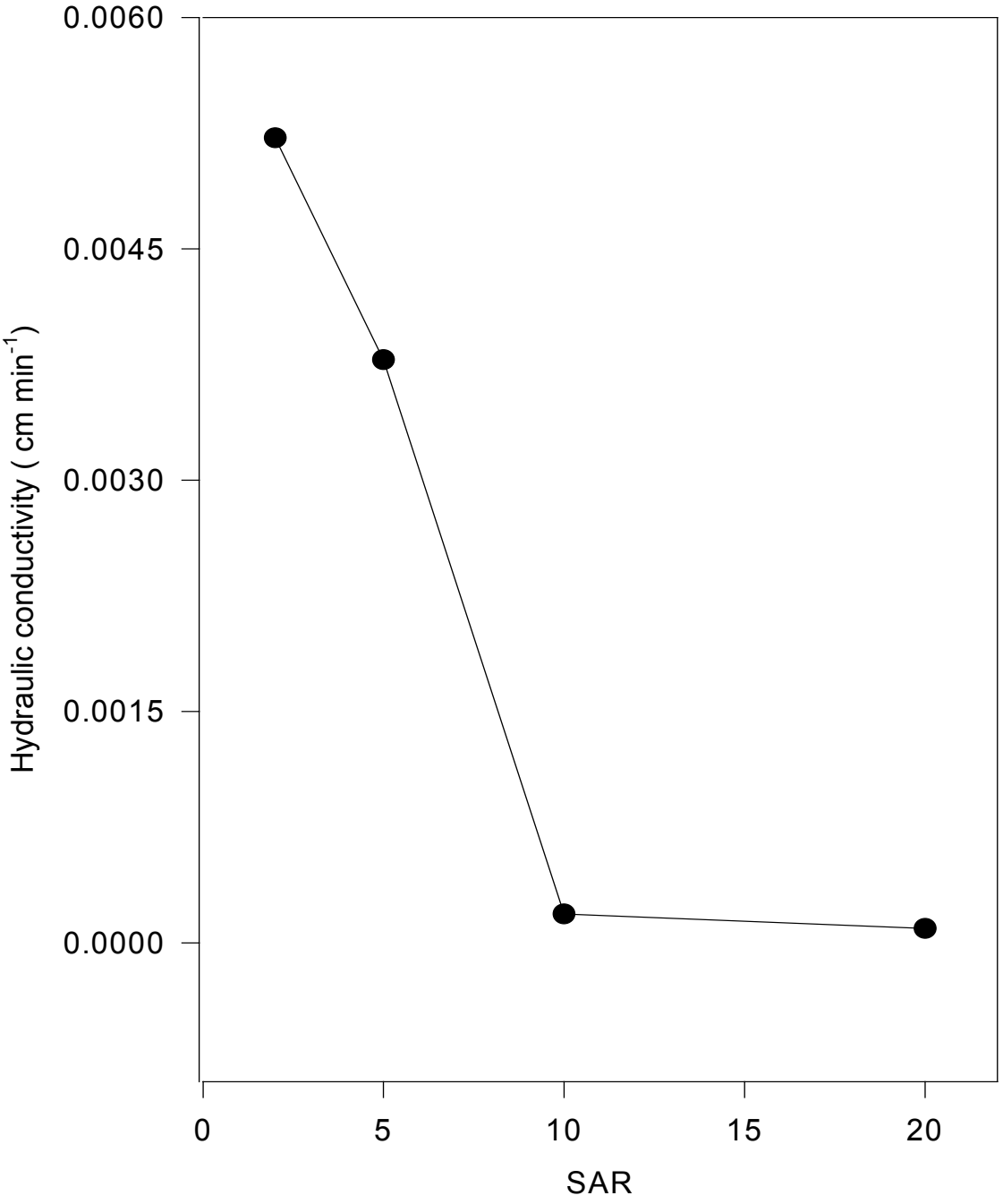


Figure 39. Final hydraulic conductivity from the columns leached with 6 cycles of wastewater of various SAR and deionized water.
1 cycle = 1L wastewater + 1L deionized water leached.

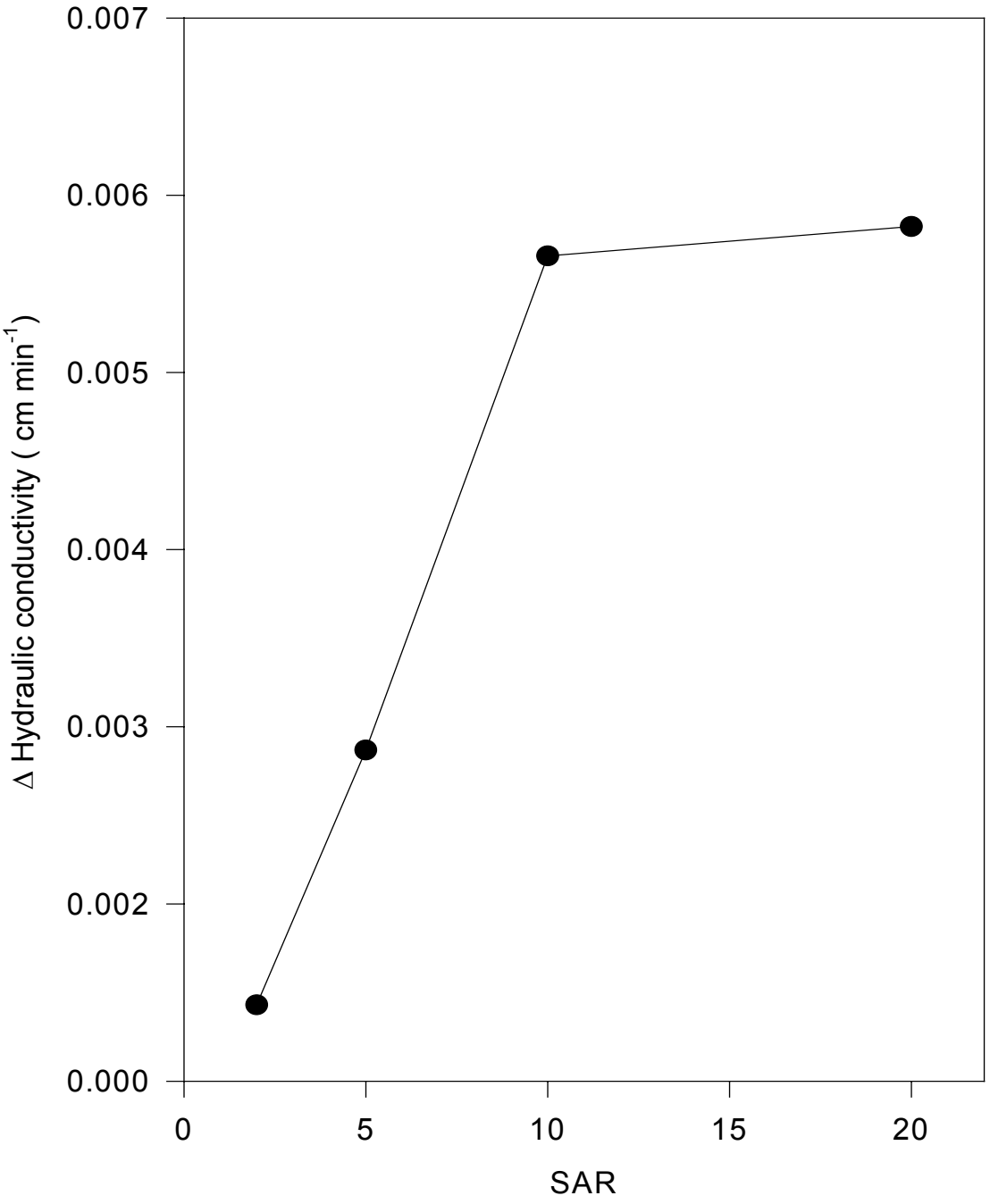


Figure 40. Total decrease in hydraulic conductivity from the columns leached with 6 cycles of wastewater of various SAR and deionized water.
1 cycle = 1L wastewater + 1L deionized water leached.

References:

Aylmore, L.A.G., and I.D. Sills. 1982. Characterization of soil structure and stability using modulus of rupture-exchangeable sodium percentage relationships. Aust. J. Soil Res. 20:213-224.

Cass, A., and M.E. Sumner. 1982. Soil pore structural stability and irrigation water quality: III. Evaluation of soil stability and crop yield in relation to salinity and sodicity. Soil Sci. Soc. Am. J. 46:513-517.

Chi, C.L., W.W. Emerson, and D.G. Lewis. 1977. Exchangeable calcium, magnesium and sodium and the dispersion of illites in water. I. Characterization of illites and exchange reactions. Aust. J. Soil Res. 15:243-253.

Clark, D.R., C.J. Green, V.G. Allen , and C.P. Brown. 1999. Influence of salinity in irrigation water on forage sorghum and soil chemical properties. J. Plant Nutrition. 22:1905-1920.

Durgin, P.B., and J.G. Chaney. 1984. Dispersion of kaolinite by dissolved organic matter from Douglas-fir roots. Can. J. Soil Sci. 64:445-455.

El-Swaify, S.A. 1973. Structural changes in tropical soils due to anions in irrigation water. Soil Sci. 24:137-144.

Gu, B., and H.E. Doner. 1993. Dispersion and aggregation of soils as influenced by organic and inorganic polymers. Soil Sci. Soc. Am. J. 57:709-716.

Gupta R.K., D.K. Buhmbla, and I.P. Abrol. 1984. Effect of sodicity, pH, organic matter, and calcium carbonate on the dispersion behavior of soils. Soil Sci. 138:109-114.

Hayes, A.R., C.F. Mancino, and I.L. Pepper. 1990. Irrigation of turfgrass with secondary sewage effluent: I. Soil and leaching water quality. Agron. J. 82:939-943.

Juwarkar, A.S., and P.V.R. Subrahmanyam. 1986. Impact of pulp and paper mill wastewater on crop and soil. Wat. Sci. Tech. 19:693-700.

Kretzschmar, R., W.P. Robarge, and S. B. Weed. 1993. Flocculation of kaolinitic soil clays: Effects of humic substances and iron oxides. Soil Sci. Sco. Am. J. 57:1277-1283.

Levy, G.J., I. Shainberg, and W.P. Miller. 1998. Physical properties of sodic soils. pp 77-94. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Mancino, C.F., and D.M. Kopec. 1989. Effects of gypsum wastewater-irrigated Turfgrass soil. p. 55-66. *In* D.M. Kopec (ed.) Turfgrass and ornamentals research summary. Zona Agric. Exp. Sta. Series P-86.

Mancino, C.F., and I.L. Pepper. 1992. Irrigation of turfgrass with secondary sewage effluent: Soil quality. Agron. J. 84:650-654.

Marshall, C.E. 1964. The physical chemistry and mineralogy of soils. 1. Soil materials. John Wiley, New York, NY.

Muneer, M., and J.M. Oades. 1989. The role of Ca-organic interactions in soil aggregate stability. I. Laboratory studies with ^{14}C-glucose, $CaCO_3$ and $CaSO_4 \cdot 2H_2O$. Aust J. Soil Res. 27:389-339.

McNeal, B.L., and N.T. Coleman. 1966. Effect of solution composition on soil hydraulic conductivity. Soil Sci. Am. Proc. 30:308-312.

Nelson, P.N., and J.M. Oades. 1998. Organic matter, sodicity, and soil structure. pp 51-75. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Oades, J.M. 1984. Soil organic matter and structural stability: Mechanisms and implications for management. Plant Soil 76:319-337.

Oades, J.M. 1989. An introduction to organic matter in mineral soils. pp 89-160. *In* Dixon, J.B., and S.B. Weeds (eds.). Minerals in soils environments.. Soil Science Society of America, Madison, WI.

Rahman, A.W., and D.L. Rowell. 1979. The influence of magnesium in saline and sodic soils: A specific effect or a problem of cation exchange? J. Soil Sci. 30:535-546.

Rengasamy, P., and K. A. Olsson. 1991. Sodicity and soil structure. Aust. J. Soil Res. 29:935-932.

Rengasamy, P., and M.E. Sumner. 1998. Processes involved in sodic behavior. p. 35-50. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Shainberg, I., and J. Letey. 1984. Response of soils to sodic and saline conditions. Hilgardia 52:1-57.

Shainberg, I., and G.J. Levy. 1992. Physico-chemical effects of salts upon infiltration and water movement in soils. *In* Wagenet, R.J., P. Baveye, and B.A. Stewart (eds.) Interaction processes in soil science. Pp. 37-94. Lewis Publishers, Boca Raton, FL.

Sparks, D.L. 1995. Environmental soil chemistry. 1st. ed. Academic Press, San Diego, CA

Stevenson, F.J. 1992. Humus chemistry: Genesis, composition, reactions. 2nd ed. John Wiley, New York, NY.

Sumner, M.E. 1993. Sodic soils: New perspectives. Aust. J. Soil Res. 31:683-750

Tarchitzky, J., Y. Golobati, R. Keren, and Y. Chen. 1999. Wastewater effects on montmorillonite suspensions and hydraulic properties of sandy soils. Soil Sci. Soc. Am. J. 63:554-550.

van Beekom, C.W.C., C. van den Berg, T.A. De Boer, W.H. van der Molen, B. Verhoeven, J.J. Westerhoff, and A.J. Zuur. 1953. Reclaiming land flooded with salt water. II. Exchangeable cations. Neth. J. Agric. Sci. 1:225-244.

van der Merwe, A.J., and R. Burger. 1969. The influence of exchangeable cations on certain physical properties of a saline-alkali soil. Agrochemophysica 1:63-66.

van Olphen, H. 1977. An Introduction to clay colloid chemistry. 2nd ed. John Wiley, New York.

Yaron, B., and G.W. Thomas. 1968. Soil hydraulic conductivity as affected by sodic water. Water Resour. Res. 4:545-552.

Zekri, M., and R.C.J. Koo. 1994. Treated municipal wastewater for citrus irrigation. J. Plant Nutrition. 17:693-708.

CHAPTER 5

CONCLUSIONS

The observed effects of the long term land application of textile wastewaters with different sodium adsorption ratios (SAR) on chemical and physical parameters on a Cecil soil are varied.

In relation to the chemical parameters, the main effect of the application of wastewater is that it increases the cation exchange capacity (CEC) of the soil. This increase in CEC varies from topsoil to subsoil and with the SAR of the wastewater, but ranges from 100 to 140%, with the soils leached with SAR 2 and 5 wastewater showing the biggest increase. Two processes can mainly explain this effect: (i) an increase in organic matter content in the soil and, (ii) an increase in pH. The wastewater used contained high amounts of total organic carbon (290.1 mg L^{-1}), made up mainly of fine size particles. When applied, the organic matter present in the wastewater attached to organic and clay sites present in the top and subsoil, increasing the available exchange sites for cation adsorption. The pH also increases throughout the soil profile by 0.1 to 1.7 units. The increase in pH can be related to neutralization of H and Al ions and by ligand exchange cations present in the wastewater. This increase in pH favored creation of negatively charged sites in organic and clay exchange sites, thus increasing the propensity for cation adsorption.

The amounts of exchangeable cations present throughout the soil profile also varied with the application of wastewater. The amount of exchangeable Na, Ca and Mg increased throughout the soil profile in relation to the original soil and was related to the SAR content of the wastewater. Therefore, the soil leached with the highest SAR (SAR 20) had the highest increase in exchangeable Na and the one leached with the wastewater with the smallest SAR (SAR 2) had the highest increase in exchangeable Ca. In relation to the exchangeable Mg, this increase was not related to the SAR content of the wastewater but to the Mg content in the wastewater. This increase in the amount of exchangeable Na, Ca, and Mg is due to the addition of those cations to the soil from the wastewater; in the soil these cations are retained by the newly attached organic matter and in clay adsorption sites. In regard to the amount of exchangeable K in the soil, it increased in most of the soil profile for soils treated with SAR 5 and 10 wastewater, but decreased in most of the soil profiles with the SAR 2 and 20 wastewater. This increase or decrease could be related to the cation composition in the wastewater; in the case of the soil treated with SAR 2 it was possibly replaced by the high amounts of Ca and with the SAR 20, replaced by Na. As for exchangeable Al in the soil, it decreased throughout the soil profile with addition of wastewater to the soil. This was the result of increased pH in the soil.

The amount of water dispersible clay and exchangeable sodium percentage (ESP) in the soil varied in relation to the SAR content of the wastewater. The amount of water dispersible clay was higher in the soils leached with SAR 10 and 20 wastewater in relation to the soils leached with SAR 2 and 5 wastewater. This is the result of the high amounts of Na present in the SAR 10 and 20 wastewater; when added to the soil the Na

has an inhibiting effect on macroaggregation and when the soil is leached with a low electrolyte solution (deionized water) it increases the osmotic and hydration forces between clay particles resulting in their dispersion. Also, the organic matter added to the soil from the wastewater plays a role as a bonding or dispersing agent depending on the Na content in the wastewater. For the soils treated with SAR 2 and 5 wastewater where the Na content is low, the organic matter acts as a bonding agent. In the cases where the Na content is high (SAR 10 and 20), the organic anions enhance dispersion. One important aspect to mention is the absence of dispersed clay below 60 cm soil depth even at soils leached with SAR 20 wastewater. This could be the result of Fe oxides forming a coating around clay particles preventing their swelling and consequent dispersion when hydrated. The ESP of the soils, as expected, increased with an increase in SAR of the wastewater. The ESP was highest for the soil leached with SAR 20 wastewater and in all the cases increased from top to subsoil.

In relation to physical parameters, the hydraulic conductivity of the soil decreased sharply when leached with wastewater of SAR 10 and 20, in contrast to a smaller gradual decrease observed in the soils leached with wastewater of SAR 2 and 5. Reduction of hydraulic conductivity appears to result from pore size diminution via two processes: (i) a change in soil pore size distribution due mainly to dispersion and to a lesser extent to swelling of clay particles, which increases with an increase in SAR of the wastewater, and, (ii) retention of most of the organic matter particles added from the wastewater which leads to blocking of soil pores. The final hydraulic conductivity for the soils treated with wastewater of SAR 20 and 10 falls below 5% of its original value, for SAR 2 and 5, the final hydraulic conductivity represents 80% and 59% respectively of its

original value. For all the treatments, the decrease in hydraulic conductivity is irreversible and even when the soil column is again leached with wastewater, the hydraulic conductivity does not return to its previous value.

The chemical composition of the effluent from the columns showed that about 10% of the Na added throughout the leaching period is being leached out mainly when deionized water is applied and that the Ca and Mg added are almost a 100% bonded. In a land application site, this could be an important aspect to consider, due to possible contamination of groundwater reservoirs with high amounts of Na originated from land applications of wastewater.

The amelioration of sodic textile wastewater with gypsum before land application is a viable option to limit the deleterious effect of high SAR wastewater on structure and hydraulic conductivity of the soil. Based on the results obtained, lowering the SAR to 5 or less can have a great beneficial effect on hydraulic conductivity of the soil and can help in maintaining the ESP and amount of dispersible clay of the soil at manageable levels. In conjunction with an increase in CEC, the option of applying gypsum-ameliorated sodic textile wastewater can be beneficial not only to the structure of the soil but its possible subsequent use for agriculture or forestry purposes.

APPENDICES

Table 6. Analysis of variance (ANOVA) table for soil pH values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	5.62 (0.355)† a‡	5.59 a	5.75 a	5.42 a
15-30	5.71 (0.296) a	5.59 a	5.93 a	5.45 a
30-45	5.92 (0.227) a	5.87 a	6.02 a	5.77 a
45-60	5.79 (0.264) a	6.02 a	6.02 a	6.05 a
60-75	5.72 (0.214) a	5.75 a	5.87 a	6.07 a
75-90	5.4 (0.427) a	5.48 a	5.45 a	5.31 a
90-105	4.56 (0.249) a	4.66 a	4.78 a	4.47 a

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level.

Table 7. Analysis of variance (ANOVA) table for soil Na ($cmol_c\ kg^{-1}$) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	0.17 (0.041)† a‡	0.21 b	0.37 c	0.62 d
15-30	0.17 (0.048) a	0.22 b	0.45 c	0.70 d
30-45	0.17 (0.038) a	0.25 b	0.44 c	0.65 d
45-60	0.17 (0.061) a	0.27 b	0.51 c	0.62 d
60-75	0.19 (0.05) a	0.25 b	0.55 c	0.79 d
75-90	0.19 (0.044) a	0.31 b	0.57 c	0.79 d
90-105	0.20 (0.067) a	0.36 b	0.61 c	0.81 d

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 8. Analysis of variance (ANOVA) table for soil Ca ($cmol_c\ kg^{-1}$) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	10.33 (0.348)† a‡	9.45 b	7.37 c	7.06 c
15-30	9.46 (0.471) a	7.69 b	6.34 c	4.77 d
30-45	8.31 (0.349) a	7.4 b	4.78 c	4.4 d
45-60	8.4 (0.265) a	6.56 b	3.2 c	3.86 d
60-75	7.33 (0.227) a	5.75 b	3.61 c	4.33 d
75-90	7.04 (0.205) a	5.34 b	3.43 c	3.66 d
90-105	6.88 (0.256) a	5.48 b	3.44 c	3.53 c

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 9. Analysis of variance (ANOVA) table for soil Mg ($cmol_c\ kg^{-1}$) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	1.87(0.269)† a‡	1.63 a	1.4 a	1.82 a
15-30	1.82 (0.083) a	1.78 a	1.95 a	1.7 a
30-45	1.79 (0.127) a	1.82 a	2.06 a	1.84 a
45-60	1.79 (0.11) a	1.82 a	2.58 b	2.06 b
60-75	1.75 (0.118) a	1.85 a	2.17 b	2.16 b
75-90	1.96 (0.063) a	2.14 b	2.17 b	2.07 b
90-105	2.08 (0.092) a	2.17 a	2.19 a	2.19 a

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 10. Analysis of variance (ANOVA) table for soil K ($cmol_c\ kg^{-1}$) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	0.45 (0.054)† a‡	0.44 a	0.52 a	0.43 a
15-30	0.39 (0.048) a	0.38 a	0.42 a	0.34 a
30-45	0.38 (0.047) a	0.43 b	0.59 c	0.27 d
45-60	0.28 (0.05) a	0.41 b	0.38 b	0.15 c
60-75	0.18 (0.078) a	0.36 b	0.39 b	0.25 c
75-90	0.16 (0.057) a	0.38 b	0.33 b	0.06 c
90-105	0.12 (0.085) a	0.22 b	0.34 b	0.13 a

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 11. Analysis of variance (ANOVA) table for soil Al ($cmol_c\ kg^{-1}$) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	0.02 (0.009)† a‡	0.03 a	0.04 a	0.02 a
15-30	0.03 (0.014) a	0.03 a	0.04 a	0.05 a
30-45	0.03 (0.013) a	0.06 b	0.05 b	0.05 b
45-60	0.05 (0.017) a	0.06 a	0.06 a	0.08 b
60-75	0.08 (0.018) a	0.08 a	0.08 a	0.11 b
75-90	0.09 (0.012) a	0.10 a	0.10 a	0.11 a
90-105	0.09 (0.0097) a	0.10 a	0.11 a	0.12 a

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 12.Analysis of variance (ANOVA) table for estimated CEC ($cmol_c\ kg^{-1}$) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	12.84 (0.38)† a‡	11.76 b	9.7 c	9.96 c
15-30	11.87 (0.51) a	10.09 b	9.58 c	7.56 d
30-45	10.69 (0.47) a	9.96 b	8.63 c	7.21 d
45-60	10.69 (0.43) a	9.12 b	6.86 c	6.76 c
60-75	9.53 (0.21) a	8.29 b	6.81 c	7.63 d
75-90	9.45 (0.27) a	8.27 b	6.6 c	6.71 c
90-105	9.36 (0.16) a	8.32 b	6.67 c	6.75 c

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 13.Analysis of variance (ANOVA) table for ESP (1) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	0.94 (0.6)† a‡	1.68 b	3.55 c	6.22 d
15-30	1.11 (0.52) a	2.04 b	4.52 c	9.26 d
30-45	1.26 (0.52) a	2.40 b	4.88 c	9.08 d
45-60	1.28 (0.84) a	2.79 b	7.52 c	8.71 d
60-75	1.68 (0.69) a	2.86 b	8.15 c	10.32 d
75-90	1.72 (0.61) a	3.48 b	8.61 c	12.08 d
90-105	1.87 (0.7) a	4.3 b	9.10 c	12.45 d

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 14.Analysis of variance (ANOVA) table for ESP (2) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	1.42(0.61)† a‡	1.87 a	3.81 b	6.30 c
15-30	1.66 (0.79) a	2.27 a	5.53 b	9.16 c
30-45	1.74 (0.43) a	2.71 b	6.19 c	8.4 d
45-60	1.81 (0.81) a	2.96 b	7.8 c	8.12 c
60-75	2.18 (0.96) a	3.12 a	8.3 b	11.06 c
75-90	2.32 (0.96) a	3.89 b	8.71 c	12.07 d
90-105	2.48 (0.90) a	4.58 b	9.8 c	12.53 d

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 15.Analysis of variance (ANOVA) table for organic carbon (OC) (%) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	2.2 (0.28)† a‡	2.2 a	2.01 a	2.23 a
15-30	0.44 (0.07) a	0.39 a	0.36 a	0.52 b
30-45	0.40 (0.07) a	0.40 a	0.34 a	0.34 a
45-60	0.39 (0.05) a	0.41 a	0.36 a	0.35 a
60-75	0.37 (0.04) a	0.39 a	0.34 a	0.31 a
75-90	0.40 (0.06) a	0.41 a	0.36 a	0.36 a
90-105	0.34 (0.07) a	0.37 a	0.37 a	0.35 a

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance level

Table 16.Analysis of variance (ANOVA) table for water dispersible clay (%) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	21.05 (5.26)† a‡	20.58 a	19.25 a	23.26 a
15-30	0.86 (5.89) a	7.8 b	22.23 c	24.96 c
30-45	0.0 (1.23) a	0.0 a	0.90 a	17.15 b
45-60	0.0 (1.31) a	0.0 a	0.0 a	14.73 b
60-75	0.0 (0.31) a	0.0 a	0.22 a	0.31 a
75-90	0.0 (0.21) a	0.0 a	0.15 a	0.19 a
90-105	0.0 (0.13) a	0.0 a	0.07 a	0.08 a

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance

Table 15.Analysis of variance (ANOVA) table for measured CEC ($cmol_c\ kg^{-1}$) values.

Depth (cm)	Wastewater SAR			
	2	5	10	20
0-15	11.64 (0.71)† a‡	11.4 a	9.72 b	9.91 b
15-30	10.16 (0.50) a	9.69 b	8.18 c	7.66 d
30-45	9.78 (0.63) a	9.31 b	7.17 c	7.79 c
45-60	9.34 (0.28) a	9.09 a	6.59 b	7.61 c
60-75	8.77 (0.60) a	8.03 b	6.67 c	7.14 c
75-90	8.34 (0.42) a	8.06 a	6.51 b	6.58 b
90-105	8.16 (0.35) a	7.83 a	6.18 b	6.41 b

† = Least significant difference
‡ = Values with the same letter are not significantly different at 0.05 significance

REFERENCES

Abu-Sharar, T.M., F.T. Bingham, and J.D. Rhoades. 1987. Stability of soil aggregates as affected by electrolyte concentration and composition. Soil Sci. Soc. Am. J. 51:309-314.

Al-Jaloud, A, G. Hussain, A.J. Al-Saati, and S. Karimulla. 1995. Effect of wastewater irrigation on mineral composition of corn and sorghum plants in a pot experiment. J. Plant Nutrition. 18:1677-1692.

Ali, R., A. A. Cheema, M. Niazi, and Z. Saleem. 1991. Sodic water irrigation effect with and without gypsum on wheat and maize yields and soil properties. J. Agric. Res. 29:373-383.

Aylmore, L.A.G., and I.D. Sills. 1982. Characterization of soil structure and stability using modulus of rupture-exchangeable sodium percentage relationships. Aust. J. Soil Res. 20:213-224.

Barzegar, A.R., J.M. Oades, P. Rengasamy, and L. Giles. 1994. Effect of sodicity and salinity on disaggregation and tensile strength of an Alfisol under different cropping systems. Soil Tillage Res. 32:329-345.

Bajwa, M.S., and A.S. Josan. 1989. Effect of gypsum and sodic irrigation water on soil and crop yields in a rice-wheat rotation. Agric. Water Manage. 16:53-61.

Bajwa, M.S., A.S. Josan, and O.P. Choudhary. 1993. Effect of frequency of sodic and saline-sodic irrigations and gypsum on the buildup of sodium in soil and crop yields. Irrig. Sci. 14:21-26.

Basiouny, F.M. 1984. The use of municipal treated effluent for peach tree irrigation. Proc. Fla. State Hort. Soc. 97:345-347.

Bielorai, H., I. Vaisman, and A. Feigin. 1984. Drip irrigation of cotton with treated municipal effluents: I. Yield response. J. Environ. Qual. 13:231-234.

Bole, J.B., and R.G. Bell. 1978. Land Application of municipal sewage wastewater: Yield and chemical composition of forage crops. J. Environ. Qual. 7:222-226.

Bond, W.J. 1998. Effluent irrigation – An environmental challenge for soil science. Aust. J. Soil Res. 36:543-55.

Bresler, E., B.L. McNeal, and D.L. Carter. 1982. Saline and sodic soils: Principles, dynamics, modeling. Springer-Verlag. New York, NY.

Campbell, W.F., R.W. Miller, J.H. Reynolds, and T.M. Schreeg. 1983. Alfalfa, sweet corn, and wheat responses to long term application of municipal wastewater to cropland. J. Environ. Qual. 12:243-249.

Cass, A., and M.E. Sumner. 1982a. Soil pore structural stability and irrigation water quality: I. Empirical sodium stability model. Soil Sci. Soc. Am. J. 46:503-506.

Cass, A., and M.E. Sumner. 1982b Soil pore structural stability and irrigation water quality: II Sodium stability data. Soil Sci. Soc. Am. J. 46:507-512.

Cass, A., and M.E. Sumner. 1982c. Soil pore structural stability and irrigation water quality: III. Evaluation of soil stability and crop yield in relation to salinity and sodicity. Soil Sci. Soc. Am. J. 46:513-517.

Chi, C.L., W.W. Emerson, and D.G. Lewis. 1977. Exchangeable calcium, magnesium and sodium and the dispersion of illites in water. I. Characterization of illites and exchange reactions. Aust. J. Soil Res. 15:243-253.

Clark, D.R., C.J. Green, V.G. Allen , and C.P. Brown. 1999. Influence of salinity in irrigation water on forage sorghum and soil chemical properties. J. Plant Nutrition. 22:1905-1920.

Durgin, P.B., and J.G. Chaney. 1984. Dispersion of kaolinite by dissolved organic matter from Douglas-fir roots. Can. J. Soil Sci. 64:445-455.

El-Swaify, S.A. 1973. Structural changes in tropical soils due to anions in irrigation water. Soil Sci. 24:137-144.

Emerson, W.W. 1967. A classification of soil aggregates based on their coherence in water. Aust. J. Soil Sci. 5:47-57.

Feigin, A., I. Vaisman, and H. Bielorai. 1984. Drip irrigation of cotton with treated municipal effluents: II. Nutrient availability in soil. J. Environ. Qual. 13:234-238

Frenkel, H., and A. Hadas. 1981. Effects of tillage and gypsum incorporation on rain runoff and crust strength in field soils irrigated with saline-sodic water. Soil Sci. Soc. Am. J. 45:156-158.

Frenkel, H., J.O. Goertzen, and J.D. Rhoades. 1978. Effects of clay type and content, exchangeable sodium percentage, and electrolyte concentration on clay dispersion and soil hydraulic conductivity. Soil Sci. Soc. Am. J. 42:32-39.

Gregory, J. 1989. Fundamentals of flocculation. Crit. Rev. Environ. Control 19:185-230.

Gu, B., and H.E. Doner. 1993. Dispersion and aggregation of soils as influenced by organic and inorganic polymers. Soil Sci. Soc. Am. J. 57:709-716.

Gupta R.K., D.K. Buhmbla, and I.P. Abrol. 1984. Effect of sodicity, pH, organic matter, and calcium carbonate on the dispersion behavior of soils. Soil Sci. 138:109-114

Hayes, A.R., C.F. Mancino, and I.L. Pepper. 1990. Irrigation of turfgrass with secondary sewage effluent: I. Soil and leaching water quality. Agron. J. 82:939-943.

Howe, J., and M. Wagner. 1996. The effect of papermill wastewater and organic ammendments on sodium accumulation by potted cottonwoods. Environ. Pollut. 92:113-118.

Huheey, J.E., E.A. Keiter, and R.L. Keiter. 1994. Inorganic chemistry. Harper Collins, New York.

Iwata, S., T. Tabuchi, and B.P. Warkentin. 1995. Soil-water interactions: Mechanisms and applications. Marcel Dekker, New York.

Jawardane, N.S. 1995. Wastewater treatment and reuse through irrigation: With special reference to the Murray Basin and adjacent coastal areas. Australian Commonwealth Scientific and Industrial Research Organization Division of Water Resources. Divisional Rep. 95-1. Griffith, Australia.

Joshi, D.C. and R.P. Dhir. 1994. Amelioration and management of soils irrigated with sodic water in the arid region of India. Soil Use Manage. 10:30-34.

Juwarkar, A.S., and P.V.R. Subrahmanyam. 1986. Impact of pulp and paper mill wastewater on crop and soil. Wat. Sci. Tech. 19:693-700.

Keren, R. 2000. Salinity. p. G-3 to G-25. *In* M.E. Sumner (ed.) Handbook of soil science. 1st ed. CRC Press, Boca Raton, FL.

Keren, R., D. Sador, H. Frenkel, I. Shainberg, and A. Meiri. 1990. Irrigation with sodic and brackish water and its effects on the soil and cotton yields. Hassadeh 70:1822-1829.

Klute, A. and C. Dirksen. 1986. Hydraulic conductivity and diffusivity: Laboratory methods. p. 687-734. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Soil Science Society of America, Madison, WI.

Knudsen, D., G.A. Peterson, and P. F. Pratt. 1982. Lithium, sodium, and potassium. p. 225-246. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

Kretzschmar, R., W.P. Robarge, and S. B. Weed. 1993. Flocculation of kaolinitic soil clays: Effects of humic substances and iron oxides. Soil Sci. Sco. Am. J. 57:1277-1283.

Lanyon, L.L., and W.R. Heald. 1982. Magnesium, calcium, strontium, and barium. p. 247-262. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

Levy, G.J., I. Shainberg, and W.P. Miller. 1998. Physical properties of sodic soils. p. 77-94. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Levy, G.J. 2000. Sodicity. p. G-27 to G-63. *In* M.E. Sumner (ed.) Handbook of soil science. 1st ed. CRC Press, Boca Raton, FL.

Loveday, J. 1976. Relative significance of electrolyte and cation exchange effects when gypsum is applied to a sodic clay soil. Aust. J. Soil Res. 14:361-371.

Mace, J.E., and C. Amrhein. 2001. Leaching and reclamation of a soil irrigated with moderate SAR waters. Soil Sci. Soc. Am. J. 65:199-204.

Manchanda, H.R., S.K. Sharma, H.R. Malik, and B.K. Suneja. 1988. Technology for using sodic water for guar and bajra. Indian Farming. 38:11-15.

Mancino, C.F., and D.M. Kopec. 1989. Effects of gypsum wastewater-irrigated Turfgrass soil. p. 55-66. *In* D.M. Kopec (ed.) Turfgrass and ornamentals research summary. Zona Agric. Exp. Sta. Series P-86.

Mancino, C.F., and I.L. Pepper. 1992. Irrigation of turfgrass with secondary sewage effluent: Soil quality. Agron. J. 84:650-654.

Marshall, C.E. 1964. The physical chemistry and mineralogy of soils. 1. Soil materials. John Wiley, New York, NY.

Misono, M., E. Ochiai, Y. Saito, and Y. Yoneda. 1967. A new dual parameter scale for the strength of Lewis acids and bases with evaluation of their softness. J. Inorg. Nucl. Chem. 29:2685-2691.

Muneer, M., and J.M. Oades. 1989. The role of Ca-organic interactions in soil aggregate stability. I. Laboratory studies with ^{14}C-glucose, $CaCO_3$ and $CaSO_4 \cdot 2H_2O$. Aust J. Soil Res. 27:389-339.

McBride, M.B. 1989. Surface chemistry of soil minerals. p. 35-88. *In* J.B. Dixon and S.B. Weed (ed.) Minerals in soil enviroments. 2nd ed. Soil Science Society of America, Madison, WI.

McNeal, B.L., and N.T. Coleman. 1966. Effect of solution composition on soil hydraulic conductivity. Soil Sci. Am. Proc. 30:308-312.

Neilsen, G.M., D.S. Stevenson, and J.J. Fitzpatrick. 1989a. The effect of municipal wastewater irrigation and rate of N fertilization on petiole composition, yield and quality of Okanagan Rieslin grapes. Can. J. Plant. Sci. 69:1285-1294.

Neilsen, G.H., D.S. Stevenson, J.J. Fitzpatrick, and C.H. Brownlee. 1989b. Yield and plant nutrient content of vegetables trickle-irrigated with municipal wastewater. HortScience. 24:249-252.

Neilsen, G.M., D.S. Stevenson, J.J. Fitzpatrick, and C.H. Brownlee. 1989c. Nutrition and yield of young apple trees irrigated with municipal wastewater. J. Amer. Soc. Hort. Sci. 114:377-383.

Neilsen, G.M., D.S. Stevenson, J.J. Fitzpatrick, and C.H. Brownlee. 1991. Soil and sweet cherry responses to irrigation with wastewater. Can. J. Sci. Soil Soc. 71:31A1.

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-579. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

Nelson, P.N., and J.M. Oades. 1998. Organic matter, sodicity, and soil structure. pp 51-75. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

NRCS National Soil Survey Center. 1996. Soil Survey Laboratory Methods Manual. USDA, Washington, DC.

Oades, J.M. 1984. Soil organic matter and structural stability: Mechanisms and implications for management. Plant Soil 76:319-337.

Oades, J.M. 1989. An introduction to organic matter in mineral soils. pp 89-160. *In* Dixon, J.B., and S.B. Weeds (eds.). Minerals in soils environments.. Soil Science Society of America, Madison, WI.

Oster, J.D., and N.S. Jayawardane. 1998. Agricultural management of sodic soils. p. 125-146. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Pupisky, H., and I. Shainberg. 1979. Salt effects on the hydraulic conductivity of a sandy soil. Soil Sci. Soc. Am. J. 43:429-433.

Quirk, J.P., and R.K. Schofield. 1955. The effect of electrolyte concentration on soil permeability. J. Soil Sci. 6:163-178.

Radcliffe, D.E., and T.C. Rasmussen. 2000. Soil water movement. p. A-113 to A-115. *In* M.E. Sumner (ed.) Handbook of soil science. 1st ed. CRC Press, Boca Raton, FL.

Rahman, A.W., and D.L. Rowell. 1979. The influence of magnesium in saline and sodic soils: A specific effect or a problem of cation exchange? J. Soil Sci. 30:535-546.

Ramirez, H., O. Rodriguez, and I. Shainberg. 1999. Effect of gypsum on furrow erosion and intake rate. Soil Sci. 164:351-357.

Rengasamy, P., and K. A. Olsson. 1991. Sodicity and soil structure. Aust. J. Soil Res. 29:935-932.

Rengasamy, P., and M.E. Sumner. 1998. Processes involved in sodic behavior. p. 35-50. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Rengasamy, P., R.S B. Greene, and G.W. Ford. 1984. The role of clay fraction in the particle arrangement and stability of soil aggregates: A review. Clay Res. 3:53-67.

Rengasamy, P., R.S.B. Greene, G.W. Ford, and A.H. Mehammi. 1984. Identification of disperse behavior and the management of red–brown earths. Aust. J. Soil Res. 22:413-431.

Rhoades, J.D., and R.D. Ingvalson. 1969. Macroscopic swelling and hydraulic conductivity properties of four vermiculite soils. Soil Sci. Soc. Am. Proc. 33:364-369.

Ritter, W.F., J.G. McDermott, and A.E.M. Chirnside. 1992. Use of paper mill residuals as soil ammendments. Commun. Soil Sci. Plant Analysis. 23:469-488.

Sameni, A.M. and A. Morshedi. 2000. Hydraulic conductivity of calcareous soils as affected by salinity and sodicity. II. Effect of gypsum application and flow rate of leaching solution. Commun. Soil Sci. Plant Anal. 31:69-80.

Shainberg, I., and J. Letey. 1984. Response of soils to sodic and saline conditions. Hilgardia 52:1-57.

Shainberg, I., and G.J. Levy. 1992. Physico-chemical effects of salts upon infiltration and water movement in soils. *In* Wagenet, R.J., P. Baveye, and B.A. Stewart (eds.) Interaction processes in soil science. Pp. 37-94. Lewis Publishers, Boca Raton, FL.

Shaw, R.J., K.J. Coughlan, and L.C. Bell. 1998. Root zone sodicity. p. 95-106. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Singh, H., and M.S. Bajwa. 1991. Effect of sodic irrigation and gypsum on the reclamation of sodic soil and growth of rice and wheat plants. Agric. Water Manage. 20:163-171.

Soil Survey Staff. 1997. Keys to soil taxonomy. 7th ed. Pocahontas Press. Blacksburg, VA.

Sparks, D.L. 1995. Environmental soil chemistry. 1st. ed. Academic Press, San Diego, CA

Stevenson, F.J. 1992. Humus chemistry: Genesis, composition, reactions. 2nd ed. John Wiley, New York, NY.

Sumner, M.E. 1992. The electrical double layer and clay dispersion. p. 1-32. *In* M.E. Sumner and B.A. Stewart (ed.) Soil Crusting: Chemical and physical processes. Lewis Publishers, Boca Raton, FL.

Sumner, M.E. 1993. Sodic soils: New perspectives. Aust. J. Soil Res. 31:683-750

Sumner, M.E. 2000. Beneficial use of effluents, wastes and biosolids. Commun. Soil Sci. Plant Anal. 31:1701-1715.

Sumner, M.E., and B.A. Stewart. 1992. Soil crusting: Chemical and physical processes. Lewis Publishers. Boca Raton, FL.

Sumner, M.E, W.P Miller, R.S. Kookana, and P. Hazelton. 1998. Sodicity, dispersion, and environmental quality. p. 149-172. *In* M.E. Sumner and R. Naidu (ed.) Sodic soils: Distribution, properties, management and environmental consequences. Oxford University Press, New York.

Surapaneni, A., D.P. Burrow, K.A. Olsson, D.R. Hill, and R.J. Wrigley. 1998. Impact of wastewater irrigation on soil sodicity and structure: A preliminary survey. p. 17-20. *In* Proc. of the Natl. Soils Conf. Aust. Soc. of Soil Sci., Brisbane, Australia.

Tarchitzky, J., Y. Golobati, R. Keren, and Y. Chen. 1999. Wastewater effects on montmorillonite suspensions and hydraulic properties of sandy soils. Soil Sci. Soc. Am. J. 63:554-550.

Thomas, G.W. 1982. Exchangeable cations. p. 159-165. *In* A.L. Page et al. (ed.) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy 9. ASA. Madison, WI.

U.S. Enviromental Protection Agency (U.S. EPA). 1997. Profile of the textile industry. USEPA Rep. 310-R-97-009. U.S. Gov. Print. Office, Washington, DC.

U.S. Salinity Laboratory Staff (USSL Staff). 1954. Diagnosis and improvement of saline and alkali soils. USDA Handb. 60, US Gov. Print. Office, Washington, D.C.

van Beekom, C.W.C., C. van den Berg, T.A. De Boer, W.H. van der Molen, B. Verhoeven, J.J. Westerhoff, and A.J. Zuur. 1953. Reclaiming land flooded with salt water. II. Exchangeable cations. Neth. J. Agric. Sci. 1:225-244.

van der Merwe, A.J., and R. Burger. 1969. The influence of exchangeable cations on certain physical properties of a saline-alkali soil. Agrochemophysica 1:63-66.

van Olphen, H. 1977. An Introduction to clay colloid chemistry. 2nd ed. John Wiley, New York.

Vasconcelos, E., and F. Cabral. 1993. Use and environmental implication of pulp mill sludge as an organic fertilizer. Environ. Pollut. 80:159-162.

Yaron, B., and G.W. Thomas. 1968. Soil hydraulic conductivity as affected by sodic water. Water Resour. Res. 4:545-552.

Zekri, M., and R.C.J. Koo. 1994. Treated municipal wastewater for citrus irrigation. J. Plant Nutrition. 17:693-708.

Zibilske, L. M. 1987. Dynamics of nitrogen and carbon in soil during papermill sludge decomposition. Soil Sci. 143:26-33.