

DISSERTATION

SALT CHEMISTRY EFFECTS ON SALINITY ASSESSMENT AND  
SOIL SOLUTION MODELING IN THE ARKANSAS RIVER BASIN,  
COLORADO

Submitted by

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In partial fulfillment of the requirements  
for the Degree of Doctor of Philosophy  
Colorado State University  
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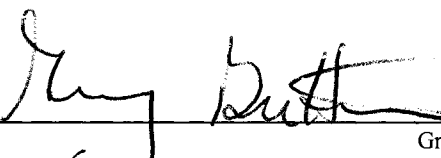
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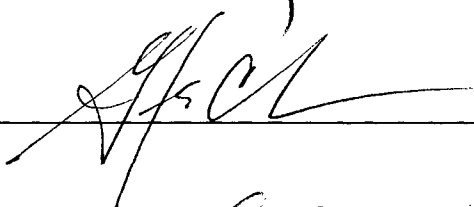
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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY CURTIS ALLEN COOPER ENTITLED SALT CHEMISTRY EFFECTS ON SALINITY ASSESSMENT AND SOIL SOLUTION MODELING IN THE ARKANSAS RIVER BASIN, COLORADO BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

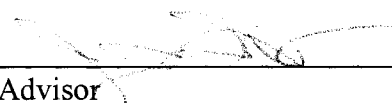
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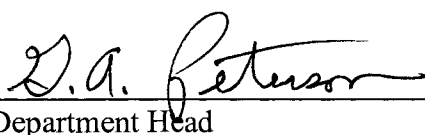
  
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## Abstract of Dissertation

### SALT CHEMISTRY EFFECTS ON SALINITY ASSESSMENT AND SOIL SOLUTION MODELING IN THE ARKANSAS RIVER BASIN, COLORADO

Electrical conductivity is an essential indicator of soil quality. Methods used to measure electrical conductivity (EC) were examined to determine the effects of laboratory analysis and extrapolations to in-situ conditions. Methods were tested using combinations of (1) surrogate irrigation waters (SI) to saturate soils over a range of chemical concentrations, (2) soils with different salinity levels, and (3) soils ground or retaining aggregates. Baseline soil EC levels were measured from soil extracts that were saturated with distilled water ( $EC_e$ ) and showed no significant difference between ground and aggregated treatments for the low salinity soil  $EC_e$ .

When the low salinity soils were saturated with SI waters, the response ECs varied as SI concentrations increased. The sum of the baseline  $EC_e$  and SI EC were not equal to the measured EC above approximately  $3.5 \text{ dS m}^{-1}$ , suggesting that gypsum dissolution was becoming limited. Soils with high salinity ( $EC_e > 8 \text{ dS m}^{-1}$ ) lacked structure and aggregates and could not be compared to ground soils. None of the tests with the high salinity ground soils had the sum of the baseline (distilled water)  $EC_e$  and the SI EC equal to the measured EC of soils saturated with SI.

Multiple extractions from the same soil sample were processed to determine salt removal potential from calcareous/gypsiferous soil. The Ca concentrations remained

relatively constant over 14 extractions while Na concentrations decreased. The  $EC_e$  decreased from above  $8 \text{ dS m}^{-1}$  in the initial extraction to approximately  $4 \text{ dS m}^{-1}$  by the 9<sup>th</sup> extraction, and remained stable to the 14<sup>th</sup> extraction. This stable  $EC_e$  suggests that mineral reservoirs of gypsum and calcite remain in the soils. These mineral reservoirs have implications for salinity removal, which becomes limited to the more soluble salts and minerals (e.g. Na and mirabilite).

Examination of the multiple extraction data suggests that improved leaching will not successfully lower the EC level below approximately  $4 \text{ dS m}^{-1}$  due to the gypsum and calcite reservoirs in the soil. Combinations of the irrigation water chemistry and precipitation and dissolution chemistry can potentially complicate or negate expected leaching potential.

Mineralogical variations associated with salinity influence the calibration of the electromagnetic induction meter because the ions are the primary carriers of the electromagnetic resonance. Soils in the high plains of the lower Arkansas River Basin of Colorado are reservoirs of calcite and gypsum. When ions in solution precipitate, their influence on the electromagnetic resonance is decreased. Current EM-38 (Geonics, Ontario, Canada) calibration equations for the lower Arkansas River Basin rely upon electromagnetic measurements in the vertical position ( $EM_v$ ) and water content measurements to predict saturated paste electrical conductivities ( $EC_e$ ).

Calibration equations developed in this research, use either depth averaged or depth weighted salt concentrations and/or predicted pore water salt concentrations from Visual Minteq. For example, the current Downstream sub-region calibration equation relating EM readings to soil  $EC_e$  has an  $R^2$  is 0.54 with an root mean square error

(RMSE) of  $2.16 \text{ dS m}^{-1}$ . The equation from this research, using depth weighted Mg concentrations and SAR with Visual Minteq has an  $R^2$  of 0.93 with a RMSE of  $1.34 \text{ dS m}^{-1}$ , and is effective for both the Upstream and Downstream sub-regions. Validation of these equations suggests that predictability is equivalent between the initial sub-region model and the models for the entire region. The inclusion of the chemistry/mineralogy in the calibration equations serves to resolve some of the unevenness of the  $EM_v$ - $EC_e$  calibration, but at the cost of more complex computing and data requirements. However, the inclusion of the chemical data offers an alternate approach not yet utilized in extrapolating the calibration of the EM-38 from a field to a regional scale.

Calcareous soils in the Lower Arkansas River Basin are impacted by salt concentrations in irrigation water and high ground water tables. Leaching many of these impacted soils is not effective in reducing salinity due to capillary rise at locations with high water tables. Modeling of management options for these soils can predict potential changes in the salt accumulation in the soil. Three locations with different levels of salinity chemistry and electrical conductivities were modeled in the Hydrus-1D version 3.0 (H1D) computer program, which has been coupled with UNSATCHEM. This H1D program allows modeling of soil hydraulic properties, root growth, carbon dioxide production and transport, as well as primary ion reactions and flux both in solution and as solids. Surface water quality was varied in the model runs, along with the depth to ground water and cropping options.

Soil surface evaporation led to evaporites forming on the soil surface for most model runs, particularly for the fallow runs. The ground water was predicted as a source

of salts in the modeled soil profile. The uptake of water by the crop was found to be a driving factor in the location of the salt accumulation within the soil profile.

Changes in irrigation water quality influenced the magnitude of the peak salt concentrations but not the depth of those peaks. The volume of water applied altered the depth to the peak salt concentrations; additionally, the ground water also contributed to the depth to the peak salt concentrations. Precipitates of gypsum and calcite were the primary repositories of precipitated salts in the soil profile and were subject to redistribution within the soil profile. It is concluded that no single management option will lead to the salinity decreases needed to improve crop production. Potentially costly management options are required to improve soil salinity problems.

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## Abbreviations

AGG	Soils retaining aggregates
AVG	Depth averaged salt chemistry
AVG-VM	Depth averaged salt chemistry adapted by Visual Minteq (VM)
EC	Electrical conductivity (generic meaning)
EC <sub>a</sub>	Bulk electrical conductivity
EC <sub>e</sub>	Electrical conductivity (saturated soil paste extracts with distilled water)
EC <sub>SI</sub>	Electrical conductivity (saturated soil paste extracts with surrogate irrigation water)
EC <sub>w</sub>	Electrical conductivity (water quality – also surrogate irrigation water)
EM	Electromagnetic induction
EM <sub>v</sub>	Electromagnetic induction measured in the vertical placement
GRD	Soils ground and sieved
HESP	High EC soil profile
HIGH	High EC <sub>e</sub> soils
H1D	Hydrus 1-D 3.0
L-CL	Las clay loam
LESP	Low EC soil profile
LOW	Low EC <sub>e</sub> soils
MESP	Medium EC soil profile
Mg-VM	Magnesium concentrations adapted by Visual Minteq (VM)
PET	Potential evapotranspiration
RF-CL	Rocky Ford clay loam
SAR-VM	Sodium adsorption ratio adapted by Visual Minteq (VM)
SI	Surrogate irrigation water
VM	Visual Minteq
WC	Water content
WGT	Depth weighted salt chemistry
WGT-VM	Depth weighted salt chemistry adapted by Visual Minteq (VM)

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## **Chapter 1 Introduction and Background**

Water resources are limited in Colorado. The lower Arkansas River Basin has been losing water to the Denver Metro area, often to the city of Aurora through trans-basin diversions (Hartman, 2003). The change in this water use means less water is available for irrigated agriculture in the lower Arkansas River Basin, an area that has the largest problem with salt build-up in the state of Colorado (Schwien, 1985).

Combined with the water diversions is the interstate compact with Kansas that limits ground water pumping and sets forth guidelines for surface water availability in the lower Arkansas River Basin (Gates et al., 2002). While these socio-political aspects are not solely responsible for the current salinity issues in the basin, these aspects have implications for potential remediation and management options by affecting water availability.

Since 1999, the Salinity and Waterlogging Project, a team of faculty and researchers from Colorado State University, the Natural Resources Conservation Service, and other groups, has been examining the salinity and waterlogging issues in the basin. This group has been examining wide-ranging topics, from surface and ground water quality, regional and field-scale salinity, modeling regional changes in irrigation supply and delivery methods, and irrigation application. The group developed calibration equations for electromagnetic inductance meter (EM) for each of the two sub-regions in the lower basin to provide rapid in-situ salinity measurements using EM (vertical) and

soil moisture measurements to predict soil electrical conductivity (Wittler et al., In Press). The project divides the lower Arkansas River Basin into two sub-regions in Colorado, the Upstream reach between Manzanola and La Junta, and the Downstream reach below the John Martin Reservoir and between Lamar and the Colorado/Kansas border. Multiple salinity sources and causes in the basin have been proposed, ranging from geologic, urban, agricultural return flows and waterlogging (Konikow and Person, 1985; Hukkinen, 1993; Goff et al., 1998; Gates et al., 2002).

Previous in-basin monitoring and modeling efforts have typically relied upon smaller stream reaches than the current research region (Gates et al., 2002; Burkhalter and Gates, 2005). Goff et al. (1998) used a 2-dimensional flow and transport model to examine changes to alluvial aquifer quantity and quality from modifications in irrigation from either surface or ground waters. The study found that river and ground water salinity would decrease with limited and/or cessation of alluvial aquifer pumping for irrigation and that return flow volumes to the river would increase (Goff et al., 1998). Additionally, Goff et al. (1998) found that changes in lower Arkansas River Basin irrigation practices in Colorado would lead to improved water quality for downstream users, but the study did not examine waterlogging issues associated with decreases in ground water pumping.

Hukkinen (1993) analyzed the sociological and political issues with water management and modeling approach scenarios. Hukkinen cuttingly stated that economic viability was the central issue that required immediate resolution, and that the Soil Conservation Service's approach was flawed, as it did not account for the sources of salinity in the basin. Konikow and Person (1985) refuted an early 1970's modeling effort

that predicted an increase in salinity in a segment of the lower Arkansas River Basin. They concluded that the earlier model was created and calibrated over a period of salinity increase, but long-term data suggested that the 11-mile study reach had attained a dynamic equilibrium in terms of salinity.

The U.S. Geological Survey (USGS) produced several reports regarding the lower Arkansas River basin. A study of irrigation return flows concluded that in the study area 75% of the return flow was as ground water, which then transported 88% of the applied salts (Cain, 1985). Another study examined the irrigation use from and around the Fort Lyon Canal. This study concluded that conveyance losses from the canals constituted the primary loss from the surface water system, and that the crop consumptive use was estimated at 227,530 acre-feet in 1989 and 251,130 acre-feet in 1990 (Dash and Crawford, 1995).

There is a lack of site-specific soil chemical data in the lower Arkansas River Basin. Much of the current salinity understanding is based on the use of electrical conductivity (EC). Since plant and chemical reactions vary depending upon the dominant salt forms (Bower, 1963; Hardie and Eugster, 1970; Steppuhn et al., 2005a), a baseline understanding of salinity chemistry is required to confirm presumptions and interpretations as well as offer an understanding soil chemistry variability. Initial observations found that the salinity constituents were characteristic of calcareous soils. Calcareous soils are typical of arid and semi-arid environments and contain primary precipitates such as calcite and gypsum (Hillel, 2000; Suarez, 2005). Calcareous soil mineral composition leads to variable chemical processes dependent upon the dominance

of either Cl or SO<sub>4</sub> (Skarie et al., 1987b). Therefore, baseline soil salinity chemistry is needed to analyze chemical processes and for modeling.

Salinity determination may be made via direct and indirect measurements. The most common direct measurement utilizes the saturated paste extraction method. Suction is applied to a saturated soil, leading to release of effluent waters, which are analyzed for conductivity and/or chemical composition (Richards, 1954). Indirect methods such as Time Domain Reflectometry or an EM meter can be used in-situ.

Measuring EC is an essential procedure in soil analysis and in agriculture in general. Soil EC is a predictor used to estimate productivity and select crops (Francois and Maas, 1978; Francois and Maas, 1985; Maas, 1993; Steppuhn et al., 2005a; Steppuhn et al., 2005b). EC methods have been consistent for many years, and the use of the saturated paste extract (EC<sub>e</sub>) method has been the method of choice (Richards, 1954). In-situ field conditions may vary drastically from laboratory conditions; soil water content is typically significantly lower in the field than in the saturated soil pastes used for chemical analysis and EC measurements. The use of 1:1 (or greater) soil:water extracts are even less representative than results from saturated paste extracts (Richards, 1954; Longnecker and Lyerly, 1964; Yadav et al., 1979; Hogg and Henry, 1984; Hillel, 2000; Zhang et al., 2005). However, promoted methods for creating soil pastes cause alterations to the soil properties by typically destroying soil aggregates. Loveday (1972) found that grinding soils influenced sample saturation levels. These results confirmed the findings by Jacober and Sandoval (1971) where the grinding/sieving size had a significant impact on saturation levels. Additionally, Jacober and Sandoval (1971) found that the suction levels applied and the time of suction caused significant changes in the salt concentrations of

the extracts. Therefore, a better understanding of the soil EC/chemistry testing methods is needed for comparison to field conditions.

In this research, it is hypothesized that calcite and gypsum precipitation/dissolution reaction effects on the indirect measurements of the electromagnetic induction meter may account for the variability of the EM predictive capacity. Limiting this variability would allow an expansion of the EM calibration from a site-specific to a regional calibration in the lower Arkansas River Basin. The EM meter (Geonics, Mississauga, ON, Canada; [www.geonics.com](http://www.geonics.com)) utilized in the Salinity and Waterlogging project functions by producing a series of electromagnetic pulses that are conical in nature with the largest portion closest to the meter. The meter then measures the resistance produced by this wave (McNeill, 1980a; McNeill, 1980b). Researchers have been attempting to calibrate the EM measurement of bulk soil electrical conductivity to a saturated paste conductivity extract through empirical relationships (Rhoades and Corwin, 1981; Rhoades et al., 1989; Hendrickx et al., 2002; Wittler et al., In Press). There are two types of EM measurements, the vertical and the horizontal, which describes the position of the meter/coil on the soil surface. The significant differences between the measurements are the depth to which the wave is created and variations in the volume of near surface soil measured (McNeill, 1980a). Developed calibration equations for the EM meter are either site-specific in the data used for their creation or highly generic (Rhoades and Corwin, 1981; Slavich, 1990; Triantafilis et al., 2000). There is a need to expand EM measurements for calibration to  $EC_e$  on a regional scale, with salinity chemistry hypothesized to add the necessary component for this expansion.

Over the past 40 years, there have been many attempts to model soil/water electrical conductivities as a function of chemical constituents. These efforts have primarily relied upon mathematical equations, graphical methods or computer models based upon the Debye-Hückel equation (Oster and McNeal, 1971; Suarez, 1982; Mualem and Friedman, 1991). The continuous changes in the soil saturation percentage affect a model's ability to predict electrical conductivity (Oster and McNeal, 1971). Modeling attempts have been hampered by the complex nature of dissolution/precipitation reactions in mixed-salt solutions (McNeal et al., 1970) and a need for activity coefficients (Adiku et al., 1992). Recent models (and computing power) have allowed for the combination of necessary chemical and hydraulic components together with root growth and temperature factors (Simunek et al., 2005b).

Due to the solubility of gypsum, it is possible for it to be dissolved and redistributed within the soil profile (Skarie et al., 1987b; Skarie et al., 1987a). The high water tables in the lower Arkansas River Basin limit the effective leaching potential of this dissolved gypsum or other salt species. Thus, there is a need to predict changes due to modification of management practices through modeling. Changes in water applied, the depth to the water table (which can be modified by tile drain installation), and the quality of the water applied all influence soils salinity levels. Predictions are based upon model results from the Hydrus 1-D version 3.0 program and will be used to understand the relative differences between management options (Simunek et al., 2005a).

## Objectives

The goal of this research was to examine the processes and methods associated with salinity monitoring and analysis in the lower Arkansas River Basin. It was hypothesized that salinity issues in the basin are influenced and controlled by the accumulation of precipitates in the soils. Understanding the influential processes governing precipitate formation will help direct management practices for improved agricultural productivity. Specific research objectives were to:

- Analyze calcareous soils for potential salinity chemistry remediation using laboratory methods for a baseline understanding (Chapter 2)
- Analyze laboratory methods that have the potential to influence the measurement of  $EC_e$  due to manipulations of the soil properties, and subsequent variations from in-situ conditions such as using a surrogate irrigation water quality to saturate soils (Chapter 2)
- Utilize soil salinity chemical data to develop EC-EM calibrations (Chapter 3)
- Model various management options to predict salinity changes in the soil profile (Chapter 4)

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## Chapter 2 Analysis of soil EC methods and chemistry

### Summary

Electrical conductivity is an essential indicator of soil quality. Methods used to measure electrical conductivity (EC) were examined to determine the effects of laboratory analysis and extrapolations to in-situ conditions. Methods were tested using combinations of (1) surrogate irrigation waters (SI) with a range of chemical concentrations to saturate soils, (2) soils with different salinity levels, and (3) soils ground or retaining aggregates. Baseline soil EC levels were measured from soil extracts that were saturated with distilled water ( $EC_e$ ).

When low salinity soils were saturated with SI waters, the response EC varied as SI concentrations increased. The sum of the baseline  $EC_e$  and SI EC were not equal to the measured EC above approximately  $3.5 \text{ dS m}^{-1}$ , suggesting that gypsum dissolution was becoming limited. Soils with high salinity ( $EC_e > 8 \text{ dS m}^{-1}$ ) lacked structure and aggregates and only ground soils were tested. None of the tests with the high salinity ground soils had the sum of the baseline (distilled water)  $EC_e$  and the SI EC equal to the measured EC of soils saturated with SI.

Multiple extractions from the same soil sample were processed to determine salt removal potential from calcareous/gypsiferous soil. The Ca concentrations remained relatively consistent over 14 saturated paste extractions while Na concentrations decreased. The  $EC_e$  decreased from above  $8 \text{ dS m}^{-1}$  in the initial extraction to approximately  $4 \text{ dS m}^{-1}$  by the 9<sup>th</sup> extraction, and remained stable to the 14<sup>th</sup> extraction.

This stable  $EC_e$  suggests that mineral reservoirs of gypsum and calcite remain in the soils. These mineral reservoirs have implications for salinity removal, which is limited to the more soluble salts and minerals (e.g. Na and mirabilite).

Examination of the multiple extraction data suggests that improved leaching will not successfully lower the EC level to below approximately  $4 \text{ dS m}^{-1}$  due to gypsum and calcite reservoirs in the soil. Combinations of the irrigation water chemistry and precipitation and dissolution chemistry can potentially complicate or negate expected leaching potential.

## **Introduction**

Measuring electrical conductivity (EC) is an essential procedure in modern soil analysis and for agriculture in general. Soil EC is a predictor used to help estimate crop productivity and to select crops (Francois and Maas, 1978; Bresler et al., 1982; Francois and Maas, 1985; Maas, 1993; Steppuhn et al., 2005a; 2005b). Electrical conductivity methods have been consistent for many years, with the use of the saturated paste extract ( $EC_e$ ) method as the method of choice (Richards, 1954). Soil salinity laboratory measurements using distilled water do not represent in-situ EC, where soils are saturated with an irrigation water containing salts. An understanding of the variations between in-situ and laboratory salinity measurements is required to determine the influences and direction of change in EC measurements.

In-situ conditions vary drastically from laboratory conditions. In particular, soil water content is typically significantly lower than in the saturated soil pastes used for EC measurements and chemical analysis. The use of saturated paste and 1:1 (or greater)

soil:water extracts has long been a concern, as the results may not be representative of field conditions (Richards, 1954; Longnecker and Lyerly, 1964; Yadav et al., 1979; Hogg and Henry, 1984; Hillel, 2000; Zhang et al., 2005). Many tests have been proposed to measure the in-situ soil EC condition, including vacuum extraction using ceramic cups buried in the soil, imbibition-type sensors (Yadav et al., 1979; Rhoades et al., 1999), the use of a centrifuge to remove soil water from soil samples (Mubarak and Olsen, 1977), and other methods. These methods have not proven to be applicable outside of research settings.

Several EC methods using greater than saturation water contents have been proposed and analyzed. Work by Hogg and Henry (1984) compared 1:1 and 1:2 soil:water suspensions and extracts against saturated paste extracts, finding that there were good correlations. Slavich and Petterson (1993) used empirical equations to estimate  $EC_e$  from 1:5 soil:water suspensions, this method also required the inclusion of texture. Zhang et al. (2005) found that  $EC_e$  and 1:1 soil to water extracts were correlated, and that the regressions developed could accurately assess soil salinity, with the caveat that the adjusted 1:1 results were approximations and might not be a sound substitution. In the end, the saturated paste extract method has proven sufficiently reliable, repeatable and robust enough to withstand variations within  $\pm 5\%$  from saturation (Rhoades, 1996), and remains the standard index despite the inconsistencies reported previously.

The methods for testing saturated pastes cause alterations to the soil properties. Loveday (1972) found that grinding soils had a significant effect on the saturation level. Loveday used a capillary wetting method and either a float valve or Mariotte bottle set at 1 cm, rather than traditional saturation paste methods in Richards (1954). Loveday

confirmed that the 2 mm size was the preferred soil sieving particle size, and that the variations in water contents, attributed to different levels of grinding and saturation, were considered significant and influenced the extraction of soluble salts. These results confirm the findings by Jacober and Sandoval (1971) where comparison between grinding/sieving size was significant. Additionally, they found that the vacuum suction/tension applied and the time of suction/tension caused significant changes between the methods, and recommended that these methods and grinding equipment be standardized.

Air-drying, grinding and sieving are typical methods used to create a soil media conducive for EC and/or chemical analysis assessment (Richards, 1954; Janzen, 1993; Rhoades, 1996). Janzen (1993) states that soils should be processed by the methods in *Diagnosis and Improvement of Saline and Alkali Soils* (Richards, 1954) or by methods proposed by J.D. Rhoades (1982), which has since been updated (Rhoades, 1996). Saturated paste electrical conductivity serves as the baseline for other EC methods, direct or indirect, and from which recommendations are developed. The EC at water contents of field capacity and wilting point can be estimated from  $EC_e$  (Bower, 1963), but is not always reliably reproducible (Longnecker and Lyerly, 1964; Loveday, 1972).

Grinding has been found to alter soil properties and effect salt mineral precipitates. Soil gypsum and calcite precipitates are known to form either together, on top of one another, and/or at the same location (Lindsay, 1979; Keren and Kauschansky, 1981; Doner and Lynn, 1989). These crystalline nodules are broken down during grinding, creating a precipitate powder with greater surface area than occurs in field situations. Since gypsum dissolution is improved by increased surface area or fragment

diameter (Kemper et al., 1975), grinding can increase gypsum dissolution in saturation paste extracts. The ionic strength of the irrigation or soil water can influence dissolution as well, since gypsum has a conditional solubility product, where its solubility increases as a function of increasing ionic strength of the solution (Kemper et al., 1975; Sposito, 1989).

Under field conditions, soil water content is variable and never at a “true” saturation condition, even with irrigation, as there will always be trapped air in the soil matrix. As soils dry or drain, water content and solution chemical concentrations are affected. Reitemeier (1946) found that influences of soil moisture changes on soil solution chemistry was complex, so that Na increased with dilutions due to cation exchange. In some soils, Ca increased with increasing water content as related to dissolution of calcite and gypsum, and Ca decreased with dilution in other soils. Reitemeier (1946) recommended that arid soil dissolved ions be tested at the water contents for which the results will be applied.

Distilled water used for creating soil pastes is essentially electrically neutral and not representative of in-situ conditions where soils are wetted with irrigation water. The assumption that the leaching fraction can/should be based solely upon  $EC_e$  measurements may fail to capture the entire spectrum of salts based upon dissolution kinetics, solubilities, and the reservoir of gypsum and calcite in calcareous soils.

This research consisted of two parts. The first part analyzed laboratory methods to determine if those methods altered EC significantly from field conditions in these calcareous/gypsiferous soils. Soil samples were air-dried, either ground or left retaining their aggregates, and then saturated with either distilled or surrogate irrigation water. The

second part estimated the potential for leaching calcareous soils using a saturated paste extract electrical conductivity ( $EC_e$ ) and salt concentrations. Soils were repeatedly saturated with distilled water then had tension applied to remove the solution.

## **Methods**

Two soils were selected for the  $EC_e$  test, a low salinity soil (LOW) and a high salinity soil (HIGH). The LOW soil was a Fort Collins Loam and the HIGH soil was a Las Clay Loam. The soils were processed as both a ground soil sieved through a 2 mm mesh (GRD) or as a soil retaining soil aggregates (AGG), where efforts were made to maintain the soil structure.

For each of the GRD LOW and GRD HIGH soil groups, 5 replicate samples were saturated using distilled water based upon methods in Rhoades (1996) and Janzen (1993). From these samples, the average saturated water content was used as the baseline water content. Baseline water contents for each soil type were used for all the tested samples. The AGG soils were not stirred and were minimally processed to decrease the destruction of soil aggregates. It was assumed that the saturated percentage would remain constant between the GRD soils and the AGG soils, and the baseline water content was used. This assumption was made because other methods were not effective at saturating the AGG soils. For example, wetting from the bottom up did not saturate in the larger pore spaces. Soil water extracts were removed under tension at approximately 400 mm Hg for approximately 5 minutes.

Samples were processed to contrast LOW and HIGH soils, and between GRD and AGG soils. Additionally, surrogate irrigation waters (SI) were used to saturate the soils for each of the LOW and HIGH groups, the extracts were then removed and tested for electrical conductivity ( $EC_{SI}$ ) to further identify changes between the soil properties as a function of irrigation water quality.

Surrogate irrigation water was created in the laboratory, based upon USGS water quality data for the Arkansas River at Las Animas (Station 07124000) (USGS, 2004). The average concentration of the primary ions (Na, K, Ca, Mg, Cl and  $SO_4$ ) was used as the baseline for the surrogate irrigation water development, with concentrations based upon 0.25, 0.5, 1.0, 1.5 and 2.0 times the average (1.0) concentrations (Table 2.1). These five surrogate irrigation waters were used for making saturated paste extracts to measure  $EC_{SI}$ .

To examine potential removal of salts and to estimate leachable salts in soils from saturated paste extracts, a Las Clay Loam (L-CL) and a Rocky Ford Clay Loam (RF-CL) were analyzed for ion concentrations in saturated paste extracts created with distilled water. Soil samples for each of the extractions were saturated with distilled water, stirred and equilibrated overnight. These soils were then extracted under 400 mm Hg tension to a uniform dryness for each of the extractions. The clay loam soils were collected from the lower Arkansas River Basin in southeast Colorado, which has the largest problem with salt build-up in the state from both surface and high ground water tables (Miles, 1977; Schwien, 1985; Sutherland, 2002). Samples were processed according to methods in Rhoades (1996) and Janzen (1993). These samples were then repeatedly saturated and extracted with extract water composition were analyzed at the Colorado State University

Soil, Water and Plant Testing Laboratory using inductively coupled plasma (ICP) for cation and ion chromatograph (IC) for the anion determination.

## **Results and Discussion**

### *Laboratory Methods*

The low salinity (LOW) soil had an average water saturation percentage of 56%, with a range of 55.4% to 56.8%. The LOW  $EC_e$  averaged  $1.4 \text{ dS m}^{-1}$  with a range of 1.0 to  $1.7 \text{ dS m}^{-1}$ . The high salinity (HIGH) soil had an average saturated percentage of 58% with a range 55.0% to 58.9%. The  $EC_e$  of the HIGH soil averaged  $10.0 \text{ dS m}^{-1}$  with a range of 9.75 to  $10.12 \text{ dS m}^{-1}$ . All subsequent samples for each soil were based upon the 56% and the 58% saturation levels.

When saturated with distilled water the LOW  $EC_e$  of the ground (GRD) soils averaged less than the LOW soils retaining their aggregates (AGG). The average LOW GRD  $EC_e$  was  $1.4 \text{ dS m}^{-1}$ , while the LOW AGG averaged  $1.7 \text{ dS m}^{-1}$  with a range of 1.5 to  $1.9 \text{ dS m}^{-1}$  (Figure 2.1). The variability in the samples leads to the average difference not being statistically significant between the LOW GRD and the LOW AGG soils. The higher  $EC_e$  associated with the AGG soils were believed to be due to the solubility chemistry.

In the HIGH soil, however, there was no comparison between the GRD and AGG soils since there was not sufficient soil structure to represent a soil retaining aggregates (Figure 2.2). The HIGH AGG soils either formed hard lumps that would not “wet up,” or

collapsed to a fine powder, suggestive of Na dispersion destroying soil structure (Lebron et al., 1994). Therefore, the HIGH GRD soils were only tested for the effect of surrogate irrigation waters (SI) and were not compared against the AGG soil. Based upon the finding of a lack of soil structure in the high  $EC_e$  soils, issues with infiltration and water flow may compound any efforts to leach these soils.

During the air-drying process, the last salts predicted to precipitate (primarily Na minerals such as mirabilite and halite) would do so on the surface of aggregates. This migration of salts from the pores would be driven by capillary processes causing highly soluble minerals to be precipitate in a location where they would be more likely to re-dissolve and be removed in the extraction process. This process would not occur to the same degree in the GRD soils. Thus, the drying process may have unduly influenced the test toward the more soluble salts that are predicted in the soils by not reincorporating them back into the soil media in the AGG soils. The high mineral solubility of the predicted mirabilite ( $NaSO_4 \cdot 10 H_2O$ ) would add  $SO_4$  to the pore waters and then the common ion effect would limit gypsum dissolution. This common ion effect would be more pronounced above an EC of approximately  $3.5 \text{ dS m}^{-1}$  (Arndt and Richardson, 1989). Based on the expected mineralogy in the LOW soils, below an EC of  $3.5 \text{ dS m}^{-1}$  there would not be limits on gypsum dissolution. While for the AGG soils the Na salts would be dissolved into the pore space allowing a greater Na flux from the AGG soils than from the GRD soils where the Na salts are incorporated into the mixed soil media. The samples with EC above of approximately  $3.5 \text{ dS m}^{-1}$  would have a limited dissolution of gypsum because of the greater  $SO_4$  concentrations from the preferential dissolution of mirabilite and from SI waters, especially in the AGG soils where the

mirabilite would have precipitated last in the drying process. During analysis the stirring of the GRD soils would negate or limit the preferential dissolution of the Na salts (predicted as halite and mirabilite). Further analysis is required to confirm this process.

Surrogate irrigation waters (SI) were created in the laboratory using the primary cations (Table 2.1). Slight variations from the average occur as a function of meeting overall electrical neutrality and cation/anion balance. The  $EC_w$  of these SI solutions increased from  $0.7 \text{ dS m}^{-1}$  in the 0.25 SI to  $4.6 \text{ dS m}^{-1}$  in the 2.0 SI, with the 1.0 average  $EC_w$  at  $2.5 \text{ dS m}^{-1}$  (Table 2.1).

The SI waters were added at the previously developed saturation percentages of 56% for the LOW soils. Results of the LOW testing are presented in Figure 2.1, where the average values are plotted so that the sum of SI  $EC_w$  and soil  $EC_e$  are expected to be equivalent to the measured  $EC_e$  or  $EC_{SI}$  and fall on the 1:1 line if the sum SI  $EC_w$  and  $EC_e$  is additive. A good relationship existed for the LOW AGG and LOW GRD soils between the summed and measured EC up to approximately  $3.5 \text{ dS m}^{-1}$ , or roughly at the 0.5 SI (Figure 2.1). For the 1.0 SI and larger the measured  $EC_{SI}$  was less than the expected summation. Therefore, the salts from the soils were not dissolving as had occurred for the lower SI concentrations and/or there were precipitates that formed from the SI waters.

In comparing the LOW soil types, the AGG soils response was variable in comparison to the GRD soils (Figure 2.1). For the DI solution and at low SI concentrations, the measured AGG  $EC_e$  or  $EC_{SI}$  were greater than the measured GRD  $EC_e$  or  $EC_{SI}$ . At the 0.5 SI level the  $EC_{SI}$  were essentially equivalent, while at 1.0 SI or greater the GRD soils had greater  $EC_{SI}$ . These differences can be explained by the preferential dissolution of mirabilite that is predicted to form under low water contents.

In all the HIGH soils tests, using a baseline of a saturated percentage of 58%, the summation of the  $EC_w$  and the  $EC_e$  failed to equal the  $EC_{SI}$  (Figure 2.2). The sum of the  $EC_w$  and the  $EC_e$  was greater than the measured  $EC_{SI}$ . This result was similar to the findings for the LOW GRD and LOW AGG at the greater than 1.0 SI concentrations. This result occurs when the EC summation is greater than the saturation/equilibrium EC of gypsum minerals. As the  $EC_{SI}$  increases it is believed that the common ion effect may decrease the dissolution of soil minerals, may promote precipitation of some of the solution salts most likely as Ca minerals, or have both occurring at once (Hardie and Eugster, 1970; Wigley, 1973; Kemper et al., 1975).

This research supports the findings of Jacober and Sandoval (1971), where the soil properties influenced the measurements of salinity and  $EC_e$ . In that study, the soils retaining their aggregates were not sieved to below 12.7 mm; however, most aggregates were below that size.

### *Multiple Extraction Analysis*

The multiple saturated paste extraction was designed to examine the change in the leachable salts with repeated extractions. The soil saturated paste method was used to allow consistent results that could be compared to the literature and other recommendations. Soil L-CL was a saline-sodic soil based upon the first extraction, while RF-CL was a saline soil (Figures 2.3 and 2.4).

The first extract was dominated by Na cations for both soils (Figures 2.3 and 2.4). Based upon solubilities, this was the expected result. The Mg and Na concentrations decreased through extraction 8 and then concentrations became constant. The decrease in the  $EC_e$  closely follows the decreases in the Na and Mg concentrations. Over the 14

extractions, the Na concentration decreased by more than 3700 mg L<sup>-1</sup> for L-CL and more than 1500 mg L<sup>-1</sup> for RF-CL (Figures 2.3 and 2.4).

Potassium, SO<sub>4</sub> and Cl decreased similarly to the Na and Mg concentrations (data not shown). Potassium concentrations in the extract waters decreased from 42.0 mg L<sup>-1</sup> in the first extraction to 10.8 mg L<sup>-1</sup> in the 14<sup>th</sup> extraction for L-CL. For RF-CL, the K concentrations decreased from 29.4 mg L<sup>-1</sup> in the first extraction to 15.6 mg L<sup>-1</sup> in the 14<sup>th</sup> extraction. The SO<sub>4</sub> concentrations in the extract waters decreased from 22,100 mg L<sup>-1</sup> in the first extraction to 5080 mg L<sup>-1</sup> in the 14<sup>th</sup> extraction for L-CL. For RF-CL, the SO<sub>4</sub> concentrations decreased from 12,580 mg L<sup>-1</sup> in the first extraction to 5140 mg L<sup>-1</sup> in the 14<sup>th</sup> extraction. Chloride concentrations in the extract waters decreased from 1700 mg L<sup>-1</sup> in the first extraction to below detection (10 mg L<sup>-1</sup>) in the 14<sup>th</sup> extraction for L-CL. For RF-CL, the Cl concentrations decreased from 840 mg L<sup>-1</sup> in the first extraction to below detection (10 mg L<sup>-1</sup>) in the 14<sup>th</sup> extraction. The SAR in the extract waters decreased from 19.8 in the first extraction to 0.7 in the 14<sup>th</sup> extraction for L-CL, and dropped below an SAR of 13 after the first extraction and thus reclassified this soil as saline. For RF-CL, the SAR decreased from 11.5 in the first extraction to 0.6 in the 14<sup>th</sup> extraction.

There was an asymptotic EC<sub>e</sub> level at approximately 4 dS m<sup>-1</sup> at approximately extraction number 9 for both L-CL and RF-CL (Figures Figure 2.3 and Figure 2.4). The Ca salts, however, were essentially stable, or increased slightly, throughout the 14 extractions. For L-CL and RF-CL, the average Ca concentration was approximately 860 mg L<sup>-1</sup>, or at 21.5 mmol L<sup>-1</sup>, which is within the expected range for Ca dissolution for the saturation level for gypsum in a mixed chemical solution (Nakayama, 1971). In addition,

the asymptote for the  $EC_e$  was approximately at the level associated with gypsum solubility in a mixed solution (Arndt and Richardson, 1989). The slight increase in Ca concentration was caused by decrease in  $SO_4$  concentration, allowing more gypsum to dissolve because the  $SO_4$  ion is not limiting the gypsum dissolution. However, after 9 extractions, both soils are on the borderline of being classified as a saline or a normal soil based on the  $EC_e$ .

Over the course of multiple extractions, the chemical composition of the extract waters changed. The ratios of the salts in the extract solutions are shown in a ternary plot (Figure 2.5). The first extraction of L-CL had 56% of the cation composition as a combination of Na and K, with 26% as Mg and the remaining 18% as Ca. However, for the 14<sup>th</sup> extraction L-CL had 9% of the cation composition as a combination of Na and K, with 23% as Mg and the remaining 68% as Ca. Similar results were measured for RF-CL. Based upon the sum of all 14 extractions, L-CL had 36% of the cation composition as a combination of Na and K, with 26% as Mg and the remaining 38% as Ca (as depicted by the white diamond in Figure 2.5), and similar results were found for RF-CL (as depicted by the white circle in Figure 2.5). This implies that the SAR values decreased with continued extractions and that CEC would be dominated by Ca and Mg salts, and the summation provides an understanding of the overall salt composition of the tested soils.

Extrapolating this multiple extraction analysis to field conditions must be done with caution, because soils are composed of aggregates and cannot be as thoroughly mixed in-situ as occurred in this analysis. Based upon the approximately steady Ca concentrations, these soils act as a reservoir of gypsum ( $CaSO_4 \cdot 2 H_2O$ ) and calcite

(CaCO<sub>3</sub>), and extractions were limited by the solubilities of these salt minerals in basic solutions. The waters available for irrigation were basic (as are the soils) and will do little to increase the solubility of calcite. Gypsum has a solubility of 15.4 mmol L<sup>-1</sup> in pure water (Nelson, 1982; Seelig, 2000), but can be nearly twice that in high chloride soils (Nakayama, 1971). The multiple extraction Ca concentrations were within the molar dissolution concentrations of gypsum. These solubility levels are dependent upon the total ions, particularly Cl concentrations (Nakayama, 1971; Skarie et al., 1987). Therefore, dissolution and removal of these minerals would require more water than is likely to be available under current water limitations in the lower Arkansas River Basin and other semi-arid and arid locations.

Since the initial EC<sub>e</sub> of the multiple extraction soils were 9.0 dS m<sup>-1</sup> for L-CL and 8.1 dS m<sup>-1</sup> for RF-CL, irrigation with an average water quality from the Arkansas River (Table 2.1) would not dissolve the reservoir minerals as might be expected, based upon the analysis of Figure 2.2. The combination of field soil moisture levels and irrigation water quality suggests that there is a potential that even effective leaching volumes would not be sufficient to adequately remove the Ca salts. This is likely not an issue since gypsum salts are considered less detrimental to crops than Cl salts (Maas and Grattan, 1999), but sufficient available water to overcome osmotic differences is required, once the Na salts are removed.

Remediation of saline soils requires the leaching of salts to below the root zone. This is only effective in situations where the ground water is sufficiently deep to not have hydrologic connection with the root zone (Barica, 1972). There is also the risk that the

salts can be drawn back up to the root zone through capillary action with high water tables, thus negating the benefits of leaching (Hoffman, 1990).

## **Conclusions**

Use of distilled water to make saturated soil paste extracts for electrical conductivity measurements does not represent in-situ conditions. The combination of surrogate irrigation water  $EC_w$  and soil  $EC_e$  influence mineral dissolution and are not additive when their summed EC are greater than approximately  $3.5 \text{ dS m}^{-1}$ . However, below approximately  $3.5 \text{ dS m}^{-1}$  total EC, the  $EC_w$  and  $EC_e$  can be summed for ground and sieved soils. Gypsum saturation is the demarcation point where irrigation water and soil EC are no longer additive.

Grinding soils removes preferential flow paths and creates uniform pore spaces. Grinding also increases the surface area and increases the dissolution of gypsum. Whereas in soils retaining aggregates, the larger pore spaces between aggregates are prime locations for mineral precipitation, dissolution, and pore water/solute flow. Grinding also alters the dissolution of precipitates that would form on soil aggregates in-situ and then become readily dissolved with changing water contents.

The multiple extraction analysis of the same soil sample found that these calcareous soils essentially maintained a continuous Ca concentration in the saturated paste extract waters at a level consistent with gypsum dissolution for all 14 extractions. The average dissolved Ca concentrations were approximately  $860 \text{ mg L}^{-1}$  for all the extractions. The Na concentrations, however, decreased with each subsequent extraction,

from above  $3700 \text{ mg L}^{-1}$  to less than  $100 \text{ mg L}^{-1}$  for L-CL. The  $\text{EC}_e$  levels decreased in a similar manner to the Na concentrations, with an initial  $\text{EC}_e$  of  $9 \text{ dS m}^{-1}$  and remaining stable at approximately  $4 \text{ dS m}^{-1}$  between extractions 9 and 14.

Implications of this research suggest that remediation of these calcareous and gypsiferous soils through improved leaching will not be successful in lowering the EC level to below approximately  $4 \text{ dS m}^{-1}$  due to the calcite and gypsum reservoirs in the soil. The use of irrigation water and the effects of precipitation and dissolution chemistry can potentially complicate or negate expected leaching potential by adding to the gross calcite and gypsum reservoirs or limiting dilution of those mineral reservoirs. It is recommended that caution be used in extrapolating laboratory EC and chemical analyses to in-situ conditions in calcareous and gypsiferous soils.

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## Tables

Table 2.1. Surrogate irrigation water, chemical concentrations and electrical conductivity at 25° C.

	<u>Multiplier of Average Concentration</u>				
	0.25	0.5	1.0	1.5	2.0
Na, mg L <sup>-1</sup>	66	130	261	390	523
K, mg L <sup>-1</sup>	1	3	6	8	11
Ca, mg L <sup>-1</sup>	63	125	251	376	501
Mg, mg L <sup>-1</sup>	23	47	93	141	186
Cl, mg L <sup>-1</sup>	19	38	75	114	151
SO <sub>4</sub> , mg L <sup>-1</sup>	317	634	1267	1902	2538
Electrical Conductivity, dS m <sup>-1</sup>	0.7	1.3	2.5	3.6	4.6

Note: Carbonate and bi-carbonate concentrations were not included, as interactions with the atmosphere were expected to modify results.

## Figures

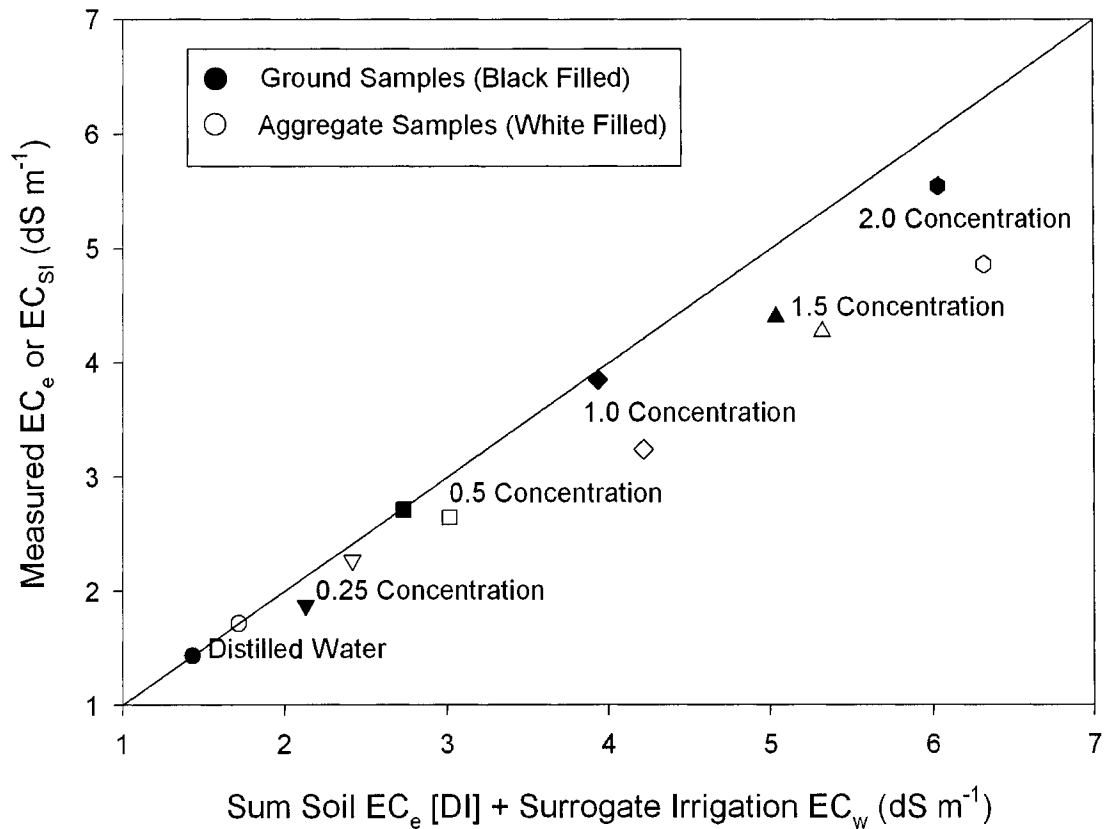


Figure 2.1. Average of measured  $EC_{SI}$  values for the LOW  $EC_e$  soils, against the sum of the baseline  $EC_e$  and SI  $EC_w$ . Soils were saturated with surrogate irrigation waters or with distilled water for a reference. The black filled markers represent the ground soils while the white filled markers represent the soils retaining aggregates. Marker shapes are for pairs of Ground (GRD) and Aggregates (AGG) to designate the solution used to develop saturation paste extracts. A 1:1 line is added to delineate ideal correlation.

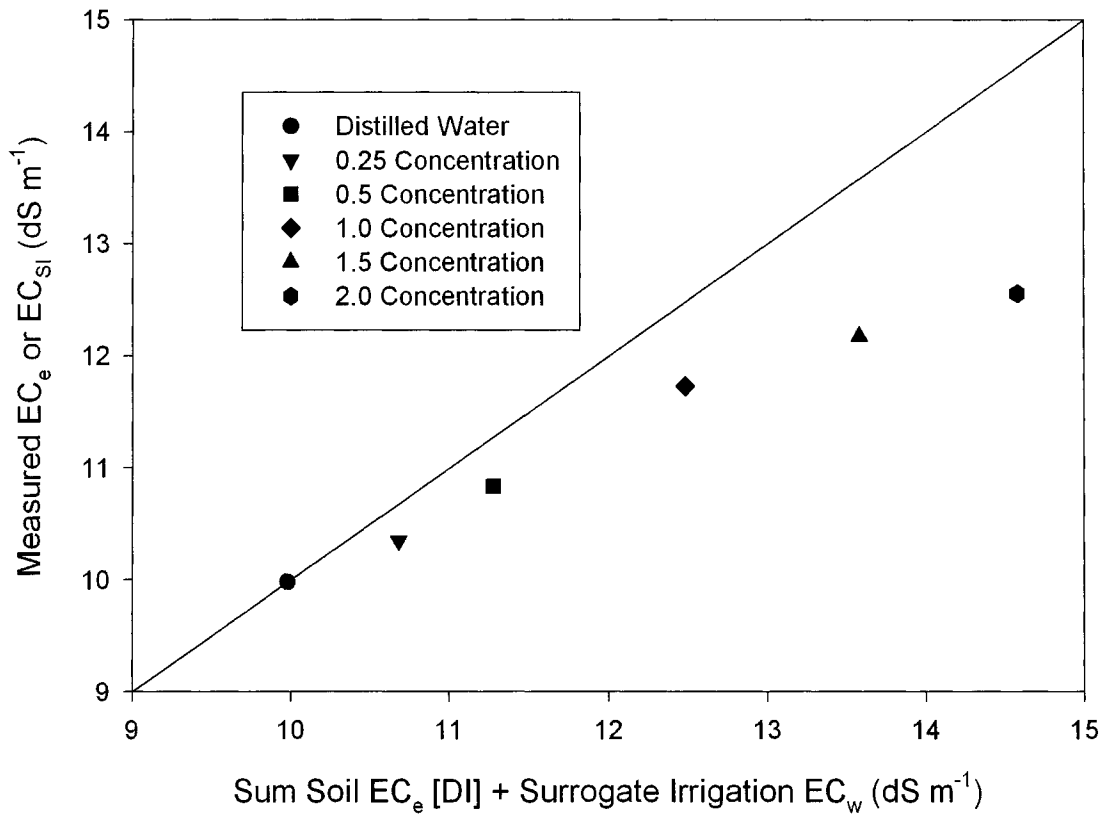


Figure 2.2. Average of measured EC<sub>SI</sub> values for HIGH EC<sub>e</sub> soils, against the sum of the baseline EC<sub>e</sub> and the SI EC<sub>w</sub>. Soils were saturated with surrogate irrigation waters, with the distilled water saturation for reference. A 1:1 line is added to delineate ideal correlation.

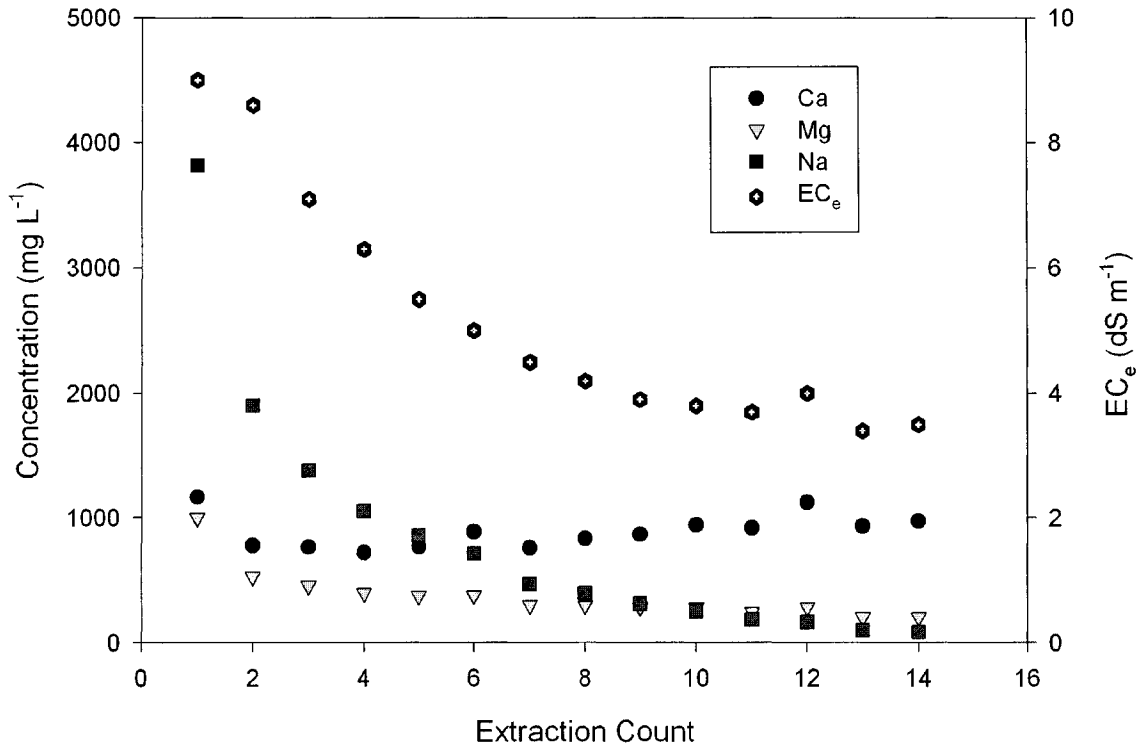


Figure 2.3. Las (L-CL) cations measured over 14 extractions from the same soil sample, with EC<sub>e</sub> measurements on the right axis.

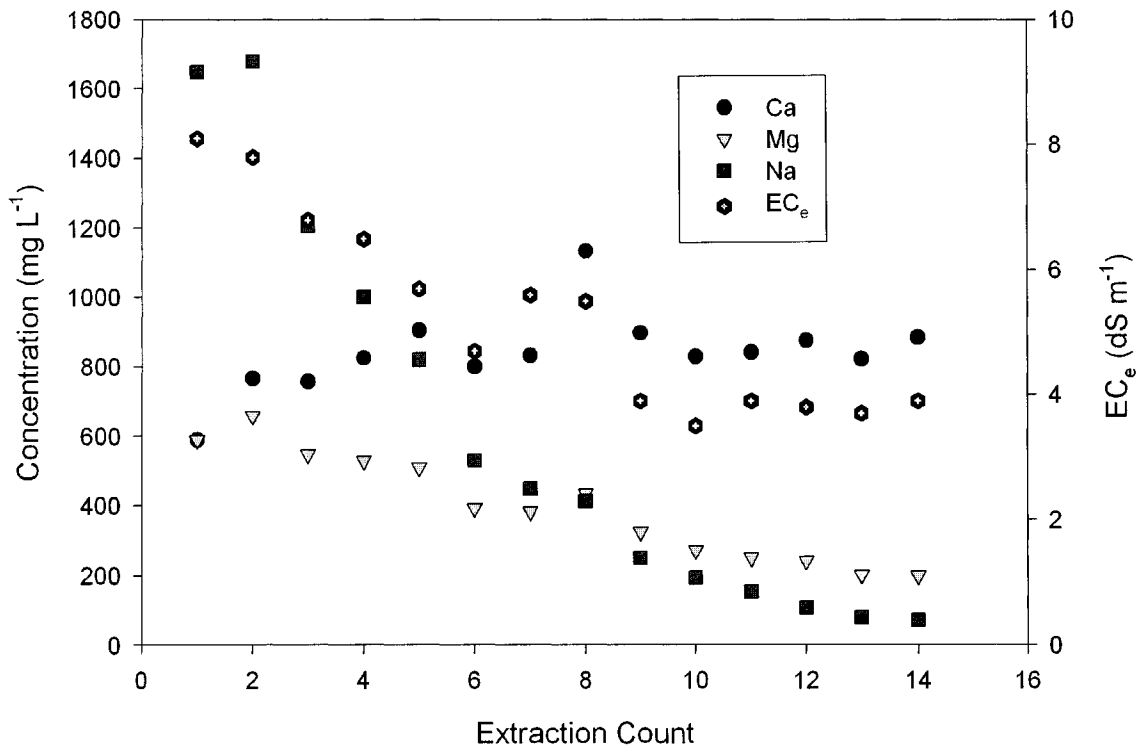


Figure 2.4. Rocky Ford Clay Loam (RF-CL) cations measured over 14 extractions from the same soil sample, with EC<sub>e</sub> measurements on the right axis.

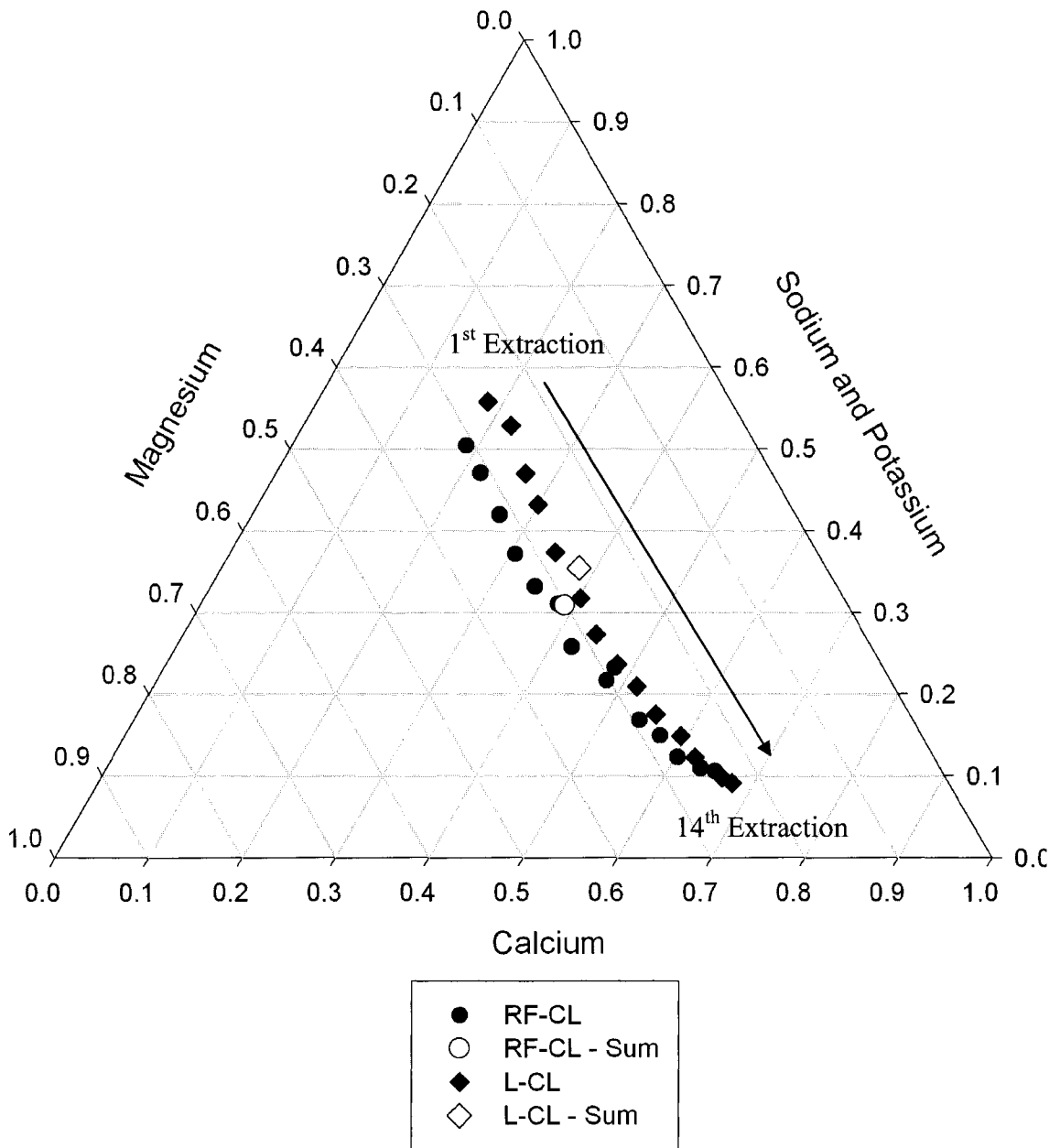


Figure 2.5. Ternary plot of extract soil water composition of the percent of the sum of the cations and the overall percent of the sum of the extractions, Mg values on the down and right oriented lines, while the Na and K values follow the horizontal lines.

## **Chapter 3 Calibration of an EM-38 to predict EC<sub>e</sub> using salinity chemistry**

### **Summary**

Mineralogical variations associated with salinity influence the calibration of the electromagnetic induction meter because the ions are primary carriers of electromagnetic resonance. Soils of the high plains in the lower Arkansas River Basin of Colorado are reservoirs of calcite and gypsum, influencing pore water solution chemistry as wetting and drying occurs. When ions in solution precipitate, their influence on the electromagnetic resonance is decreased. Current EM-38 (Geonics, Ontario) calibration equations for the for the lower Arkansas River Basin rely upon electromagnetic measurements in the vertical position (EM<sub>v</sub>) and water content measurements to predict saturated paste electrical conductivities (EC<sub>e</sub>). Multiple calibration equations were developed in this research using either depth averaged or depth weighted salt concentrations and/or predicted salt concentrations in the pore water using Visual Minteq. For example, the current Downstream sub-region calibration equation had an R<sup>2</sup> of 0.54 with an RMSE of 2.16. The equation from this research, using depth weighted Mg concentrations and SAR with Visual Minteq had an R<sup>2</sup> of 0.93 with a RMSE of 1.34, and was effective for both the Upstream and Downstream sub-regions. Validation of these equations suggests that predictability is equivalent between the initial sub-region model and the models for the entire region. The inclusion of the chemistry, the mineralogy or both in the calibration equations served to resolve some of the unevenness of the

EM<sub>v</sub>-EC<sub>e</sub> calibration, but at the cost of more complex computing and data requirements. However, the inclusion of the chemical data offers an alternate approach not yet utilized in extrapolating the EM-38 calibration from a field to a regional scale.

## **Introduction**

The impacts of soil salinity on agricultural production are well documented (FAO, 1984; FAO, 1990; Tanji, 1990; Rhoades et al., 1999; Hillel, 2000). The ability to measure and monitor salinity, however, is in a constant state of flux, often driven by technological advances using saturated paste extracts, time domain reflectometry, four-probe, and more recently, electromagnetic induction meters. Technological advances have influenced the manner in which soil salinity is measured and quantified. Often overlooked in salinity monitoring is the underlying influence of chemistry and mineralogy on salinity measurements.

Electrical conductivity (EC) is an accepted indicator of salinity for use in crop productivity and management (Richards, 1954; Steppuhn et al., 2005a; 2005b), but EC is only an indicator and exemplifies the disconnect between salinity and chemistry. Since multiple combinations of chemistry can lead to the same EC measurement, SAR and EC have been used in combination, as well as CEC and ESP (Richards, 1954). Multiple methods have also been used to measure soil EC (e.g. saturated paste extracts, 1:1 or 1:5 soil:water extracts). In addition, multiple computer models have been developed to predict chemistry/mineralogy/thermodynamics and ion pair interactions (i.e. Minteq,

Phreeq, Unsatchem, SatChem, Expresso). The same is true for models that include transport/leaching functions (i.e. Watsuit, Hydrus 1D 3.0).

The question arises on how to transfer site-specific measurements to a field or regional scale representative of regional chemistry. Quick and inexpensive methods are required to adequately measure and map salinity in agricultural areas. Salinity data that are transferable to GIS programs for use in Precision Agriculture to better calculate or estimate expected yields for appropriate nutrient management are needed (Corwin and Lesch, 2003). The electromagnetic induction meter (e.g. Geonics EM-38) is a tool that can help satisfy this requirement. Precision Agriculture has benefited from the development of the EM meter and associated GIS equipment, adding to the ease of EC mapping (Sudduth et al., 2001; Corwin and Lesch, 2003; Corwin and Plant, 2005; Corwin et al., In Press). However, the EM meter data output is in terms of bulk electrical conductivity ( $EC_a$ ) and requires calibration to reference criteria, which are often in terms of electrical conductivity from saturated paste extracts ( $EC_e$ ). Bulk electrical conductivity is representative of a large soil area, but can require transformations using texture and/or water content to be compared to  $EC_e$  (de Jong et al., 1979; Rhoades, 1981; McKenzie et al., 1989; Rhoades et al., 1989; Diaz and Herrero, 1992; Triantafilis et al., 2000; Wittler, 2005).

The EM sensor utilized (EM-38) is produced by Geonics (Mississauga, ON, Canada; [www.geonics.com](http://www.geonics.com)) and functions by producing a series of electromagnetic pulses. The sensor then measures the secondary wave produced, which is a measure of bulk soil electrical conductivity (McNeill, 1980a; 1980b; Robinson et al., 2004).

Researchers have been attempting to calibrate EM readings to saturated paste extract

electrical conductivities using empirical relationships (Rhoades and Corwin, 1981; Rhoades et al., 1989; Hendrickx et al., 2002). There are two types of EM measurements, vertical and horizontal. Differences between the measurements are the depth to which the EM wave is emitted and variations in the measured volume of near surface soil (McNeill, 1980a). Calibration equations for the EM sensor have been developed, but are either site-specific or highly generic (Rhoades and Corwin, 1981; Slavich, 1990; Triantafyllis et al., 2000; Corwin et al., 2003; Corwin and Lesch, 2005b; 2005c).

The uses of the EM-38 are thoroughly documented, as are the wave promulgations and the effective depth; Corwin and Lesch (2005a) thoroughly reviewed the current literature. There has been discussion of the uses of the EM-38 beyond  $EC_a$ , such as analysis of how it is affected by soil-water content and in recharge investigation (Cook et al., 1989; Cook and Walker, 1992; Hanson and Kaita, 1997), soil properties (Friedman, 2005) and for depth and inverted profiles (Corwin and Rhoades, 1984; Rhoades et al., 1989; Slavich and Petterson, 1990). Unfortunately, EM sensors are influenced by soil moisture content and to a limited degree soil mineralogy (McNeill, 1980a; 1980b). Wittler et al. (In Press) found that water contents are a principle component to the development of EM sensor calibration equations in the lower Arkansas River Basin, CO. Extrapolations from these findings suggest that salt chemistry influences the EM calibration based upon mineral solubility, which in turn is affected by changing soil water contents.

This project is a continuation of research begun by James Wittler (2005) to calibrate an EM-38 in the vertical position ( $EM_v$ ) and to predict  $EC_e$  for sub-regions, all part of a larger project currently monitoring and modeling salinity and management

options (Gates et al., 2002; Burkhalter and Gates, 2005). Portions of the study region have an elevated EC, often above  $8 \text{ dS m}^{-1}$ . These fields remain productive, but less productive than fields with lower EC and yet with greater productivity than expected from the literature (Ayers and Westcot, 1985; Maas, 1993; Sutherland, 2002; Steppuhn et al., 2005a; 2005b). The most plausible reason is because of the calcareous nature of the soils. In Na dominated soils, the pore water ionic strength combined with the Na toxicity can severely reduce productivity. Therefore, water chemistry models can be used to predict pore water chemistry changes as the extract water is reduced to in-situ conditions. Visual Minteq is equipped with a “simulate evaporation/concentration” function that is a multiplier of the input chemical concentrations based upon the change in the water content (Gustaffson, 2005).

Soil chemical dilution/precipitation reactions are affected by the water content. Since only pure water evaporates and plant uptake of salts is minimal, as the water content decreases the salts concentrate in the remaining pore water; this is especially true for the more soluble Na salts. However, the Ca salts are more prone to precipitation associated with  $\text{CO}_3$  or  $\text{SO}_4$ , typically as calcite and gypsum minerals (Hardie and Eugster, 1970). Since these precipitated minerals are not readily soluble when compared to the expected Na precipitated salts, they are likely to remain in a solid form under field conditions due to the basic pH levels of both the irrigation and soil waters of the research area.

Calcareous soils have precipitation/dissolution effects that influence EM and EC measurements. These effects have impacts on two distinct levels, 1) Ca that is expected to exchange out Na on soil exchange sites may actually be tied up as calcite or gypsum,

thus negating some of the expected benefits (Nakayama, 1969); and 2) the salts measured from saturated pastes may not represent the salts under field conditions, so that in-situ conditions experienced by crops may have diluted (as a function of precipitates) or concentrated pore water salinity.

A change in the salt mineralogy is proposed as the primary influence for alterations in the EM wave as soil water content changes in calcareous/gypsiferous soils. It was expected that the change in root zone water contents would lead to calcite and gypsum crystal growth. The limited solubility of these precipitates has the potential to influence the EM sensor calibration that measures in-situ pore water salinity, while the calibration is to a saturated paste extract. Therefore, the inclusion of chemical data would serve to explain some of the variability found in the calibration curves derived by Wittler (2005). It was hypothesized that since the EM measurements are made under less than saturated soil conditions, that the inclusion of chemical data, some of which were transformed via Visual Minteq to in-situ water contents, would improve the precision of the use of EM data to predict  $EC_e$ .

## **Location**

Soil chemical sampling and EM measurements were made in the lower Arkansas River Basin, CO. Two sub-regions have previously been identified for salinity-based studies (Gates et al., 2002; Burkhalter and Gates, 2005; Wittler, 2005). Currently, both sub-regions have individual EM calibration equations incorporating  $EM_v$  and water content (Wittler, 2005). Each sub-region is approximately 50 thousand hectares and

approximately half of those hectares are irrigated. The sub-regions are separated by John Martin Reservoir, a main stem reservoir in the Arkansas River that was completed in 1948. Both sub-regions are in the High Plains of Colorado, on the western edge of the Great Plains (Figure 3.1). The climate is dominated by summer precipitation with an average annual precipitation of approximately 38 cm (Miles, 1977). Additional water for plant growth is provided from irrigation, with source water coming primarily from the Rocky Mountains west of Pueblo, CO. Of the two regions, the Upstream sub-region begins near Manzanola, CO and ends upstream of John Martin Reservoir. The Downstream sub-region begins near Lamar, CO and ends at the State line of Colorado/Kansas. A more complete description of the sub-regions is available in associated research literature (Gates et al., 2002; Burkhalter and Gates, 2005; Wittler et al., In Press).

In Colorado, the Arkansas River Basin extends from the Continental Divide to the Colorado/Kansas border. Additional water is brought from the western half of the divide into the Arkansas River to augment the natural flows in the basin. In the basin, there are mountain peaks above 4267 meters (14,000 ft), and the Arkansas River departs the state at an elevation of below 1036 meters (3400 ft).

Water resources are limited in Colorado. The lower Arkansas River Basin has been losing waters through transbasin diversions to the Denver Metro area, most often to the city of Aurora (Hartman, 2003). The change in this current water use results in less water available for irrigated agriculture in the lower Arkansas River Basin, an area with the largest problem with salt build-up in the state of Colorado (Miles, 1977; Schwien, 1985).

Salinity levels in the lower Arkansas River Basin of southeastern Colorado have led to changes in cropping patterns (Miles, 1977). Multiple sources and causes of the salinity have been proposed, ranging from geologic, urban, agricultural return flows and waterlogging (Konikow and Person, 1985; Hukkinen, 1993; Goff et al., 1998; Gates et al., 2002). Salinity is one of the most significant water issues in the valley (Miles, 1977; Ward and Waskom, 2002) with salinity levels in the lower Arkansas River Basin increasing (Gates et al., 2002).

## **Methods**

Approximately 70 fields were sampled at one location to 1.20 m depth using a Giddings soil sampler (Fort Collins, CO, USA; [www.soilsample.com](http://www.soilsample.com)). The cores were separated into 0.3 m segments. Based on associated work, a stratified random sampling approach was used to select field sites. Fields were categorized by depth averaged  $EC_e$  values into four groups, ranging from low to very high  $EC_e$ . The Low group had average soil  $EC_e$  between 0 and 2  $dS\ m^{-1}$ , the Medium group with  $EC_e$  between 2 and 5  $dS\ m^{-1}$ , the High group with  $EC_e$  between 5 and 8  $dS\ m^{-1}$ , and the Very High group with  $EC_e > 8\ dS\ m^{-1}$ . For the calibration equation validation, individual fields were randomly removed from the database within each group to ensure that chemical composition across the range of  $EC_e$  values was adequately measured/sampled, and reserved to test the calibration equations.

Samples were processed according to methods in Janzen (1993). Soil water from saturated pastes was extracted using 500 mm mercury tension. Extract waters were

filtered through a 0.45  $\mu\text{m}$  filter and were tested at the Colorado State University Soil Water and Plant Testing Laboratory. Cations (Ca, Mg, K and Na) were tested with inductively couple plasma spectroscope (ICP). The anions (Cl and  $\text{SO}_4$ ) were tested with ion chromatography (IC).

The saturated paste chemical data was analyzed with Visual Minteq using the “simulation evaporation/concentration” function (Gustaffson, 2005). Each chemical data point was adapted to all the changes in water content available for each sample field and depth. Chemical data was assumed to be representative of the entire field and to calibration points collected for associated research across several years and locations in each field, thus expanding the database from the single chemistry location to previous EM and  $\text{EC}_e$  measurements (Wittler et al., In Press).

The saturated paste chemical data, the Visual Minteq adapted data, along with physical parameters (e.g. soil texture, soil moisture, water table depth) were analyzed in Minitab (Release 14.2, Minitab, Inc. State College, PA, USA). The Best Subset Regression was used to process selected chemical and physical parameters to determine the most influential parameters, using a Mallows’  $C_p$  function. Multiple regression equations were developed to predict depth averaged  $\text{EC}_e$  and depth weighted  $\text{EC}_e$ . Regression equations were validated against data not used in the equation development.

For regression analysis, available  $\text{EC}_e$  and chemical data were treated first by averaging across depths, and second, by using a weighted value. The somewhat inverted conical nature of the EM pulse is suggestive of root growth models, therefore weighting was based upon 40% in the upper 0.3 m, 30% in the second 0.3 m depth, 20% in the third 0.3 m depth, and 10% in the final 0.3 m depth, to a total depth of 1.2 m. Regression

equations were developed for the entire lower Arkansas River Basin research region, rather than the sub-region approach utilized by Wittler et al. (In Press).

### *Visual Minteq Methods*

Visual Minteq was used to estimate pore water chemistry and mineralogy under in-situ conditions versus the measured saturated paste water contents. The measured Ca, Mg, Na, K, SO<sub>4</sub> and Cl concentrations were entered into the Visual Minteq program in units of mmol L<sup>-1</sup>. The partial pressure of the CO<sub>2</sub> (g) was inserted at two-times atmospheric concentration. Both CaCO<sub>3</sub> and CaSO<sub>4</sub> minerals are known to coexist in soils (Doner and Lynn, 1989), and are found together in the lower Arkansas River Valley soils (D. Huber, personal communication, 2005). Therefore, a balance between these precipitates was necessary as water contents were modeled as decreasing from saturated to measured in-situ conditions. Two-times atmospheric concentration of the CO<sub>2</sub> (g) was chosen as the best representation that allowed precipitation of either or both CaCO<sub>3</sub> (as calcite) and CaSO<sub>4</sub> (as gypsum) minerals. Since soil chemical compositions have formed over many years, in addition to approximately 150+ years of irrigated agriculture (Sutherland, 2002), it was assumed that precipitation of calcite-gypsum was preferable to “mimic” the overall conditions rather than use greater CO<sub>2</sub> – HCO<sub>3</sub> concentrations as suggested in the literature (Lindsay, 1979; Sposito, 1989; Suarez and Simunek, 1997). Since Steinwand and Richardson (1989) found that gypsum accumulation in the soil was a long-term event resulting from a combination of climate, hydrology and geomorphology, ensuring gypsum precipitation was an important factor in mimicking in-situ/actual conditions. Visual Minteq inputs that exceeded two-times the atmospheric

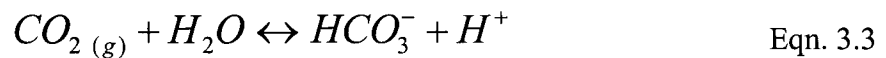
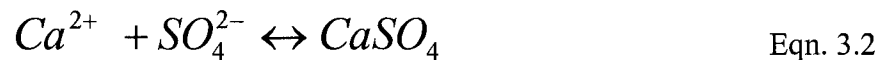
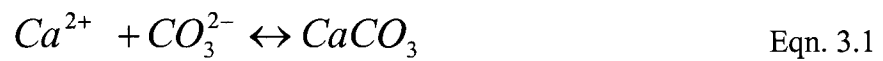
CO<sub>2(g)</sub> concentration often led to mineral precipitates consisting primarily of calcite and failed to be representative of the system as a whole.

The Visual Minteq thermodynamic databases were modified to meet current kinetic understanding and modeling preferences. The databases used were based upon the properties presented in Lindsay (1979). To better predict actual conditions and expectations, dolomite was removed from the database. Dolomite is thermodynamically predicted to precipitate, but unlikely (Deelman, 1981; Jurinak and Suarez, 1990). Additionally, magnesite was also removed as “precipitates in soils is not documented” (Jurinak and Suarez, 1990). Anhydrite typically forms from marine evaporates (Kinsman, 1974; Jurinak and Suarez, 1990), aragonite is chemically unfavorable under surface conditions (Doner and Lynn, 1989), and huntite were all removed from the database to prevent these minerals from forming.

### *Theory*

The theory behind the precipitate chemistry is included to depict the connection of the EM measurement and the potential implications of precipitates on EM sensor calibration. The mineralogical component of the EM calibration is based upon ion pair formation leading to precipitates, particularly for Ca species. This pathway, associated with water evaporation and transpiration, drives the constituent chemicals in the pore water towards concentration so that Ca species reach saturation/supersaturation levels and precipitate (Hardie, 1968; Hardie and Eugster, 1970; Suarez, 1977; 1983; Inskeep and Bloom, 1986; van den Ende, 1991; Amrhein et al., 1993). The pathways to this saturation point will vary with pore water dissolved CO<sub>2(g)</sub> and the subsequent

bicarbonate/carbonate concentrations. A pathway dependent upon elevated ( $\text{CO}_2 - \text{HCO}_3$ ) concentrations is detailed in Eqn. 3.1. This equation is slightly modified under acidic conditions, but acidic conditions are not relevant for the study area (Table 3.1). The second pathway is dependent upon a slightly lower concentration of ( $\text{CO}_2 - \text{HCO}_3$ ) and a greater  $\text{SO}_4$  concentration for precipitates to form  $\text{CaSO}_4$  (Eqn. 3.2). The  $\text{CO}_2 - \text{HCO}_3$  pathway is presented (Eqn. 3.3), but for the carbonate species most likely to be found in solution at the pH levels of these soils, not the simplified pathway of Eqn. 3.1



The most important factor in the  $\text{CaCO}_3$  (calcite) system is the reduced solubility of this mineral. Calcite is relatively insoluble, especially in the alkaline soils and basic waters found in the lower Arkansas River Basin and has a solubility of  $0.00014 \text{ moles liter}^{-1}$  (Seelig, 2000). However, gypsum solubility is often used as the demarcation between soluble and insoluble minerals in salt affected areas (Seelig, 2000). Eqn. 3.2 does not include the various hydration levels that can occur in conjunction with the  $\text{CaSO}_4$  product, so that the mineralogy can potentially vary between an amorphous  $\text{CaSO}_4$  to a fully hydrated  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  (gypsum). It can be assumed that the  $\text{CaSO}_4$  precipitates will occur as gypsum since gypsum is the most stable and dominant of the  $\text{CaSO}_4$  mineralogical species (Nettleton et al., 1982; Doner and Lynn, 1989). Gypsum

has a solubility of 0.0154 moles liter<sup>-1</sup> in pure water (Nelson, 1982; Seelig, 2000), but can be nearly twice that in Cl dominated soils (Nakayama, 1971).

The importance of these Ca phase changes from ions in solution to solid precipitates has implications for the measurement of EC with non-invasive methods, such as the EM sensor. Based upon the thermodynamics of the predicted precipitates in the calcareous soils of the study region, Ca precipitates leave more soluble salts in solution to concentrate as the soil water content decreases, thus the salts remaining in solution drive the relationship between EM and EC. Results from multiple studies have found that soil water content influences the calibration of the EM sensor. Wittler et al. (In Press) found that moisture content was an essential factor in creating a model to calibrate the EM sensor to saturated paste EC<sub>e</sub> in the lower Arkansas River Basin, CO. Hanson and Kaita (1997) found that water contents were highly influential on EM measurements and recommended that EM measurements be taken at times of relatively high water contents. They also found that the EM sensor was more sensitive to changes in the soil-water content at high salinities.

The variability in calcareous soils Ca mineral solubility suggests the use of Mg as a more effective indicator of soil chemistry. Magnesium does form some precipitates, primarily as epsomite (MgSO<sub>4</sub> \* 7 H<sub>2</sub>O) in the study region, but typically at very low water contents. The high solubility of epsomite leads to it and its component chemistry being leached from the rootzone in areas of high precipitation, but in arid and semi-arid locales there is not sufficient water to effectively leach the soluble salts from the soil profile (Doner and Lynn, 1989).

An alternate view of the salt chemistry is to group the soils by their anion components, since Cl or SO<sub>4</sub> dominance in the chemistry can lead to different effects on the Ca relationship in the soils (Skarie et al., 1987). In Cl dominated systems, it was found that Ca increased with EC, whereas in SO<sub>4</sub> systems the Ca was controlled by gypsum solubility (Skarie et al., 1987). Calcium chemistry is variable as a function of the surrounding chemistry and water contents.

## **Results and Discussion**

### *Chemistry*

The chemistry of the lower Arkansas River Basin is typically dominated by SO<sub>4</sub>/HCO<sub>3</sub> based salts (Table 3.1), but some locations were dominated by Cl salts (data not shown). The SO<sub>4</sub>/HCO<sub>3</sub> were typically associated with Ca, and Cl salts with Na. Often the 0.3 - 0.6 m depth and the 0.6 - 0.9 m depth had highest salt concentrations (data not shown). Whether these depth concentrations were due to poor leaching from irrigation water or from capillary action above the water table was beyond the scope of this study, but either action could have the same effect. Calcium cations in saturated paste extracts were typically limited by gypsum solubility, and the Na and Mg cations were highly soluble.

A relationship between EC<sub>e</sub> and EM<sub>v</sub> existed, but the data was highly variable as shown by the R<sup>2</sup> values (Figure 3.2). The best-fit line based upon the depth averaged EC<sub>e</sub> explained over half of the variation found in the data (R<sup>2</sup> = 0.59). The best-fit line for the depth weighted EC<sub>e</sub> explained slightly less than the averaged EC<sub>e</sub> line (R<sup>2</sup> = 0.55).

Neither equation explained enough variation to be satisfactory for a predictive equation, but showed promise as the base for a multilinear model.

There was a distinct change in the slope of the  $EC_e$  – SAR relationship at approximately  $4 \text{ dS m}^{-1}$  (Figure 3.3), which is at approximately the  $EC_e$  of gypsum saturation (Arndt and Richardson, 1989). Gypsum saturation would limit Ca dissolution, decreasing its influence in the SAR equation and leading to a sharp increase in SAR values above an EC of  $4 \text{ dSm}^{-1}$ . There was also a strong relationship between  $EC_e$  and Mg concentrations (Figure 3.4), suggesting that Mg would be an effective predictor for adapting EM measurements to  $EC_e$ .

### *Visual Minteq*

In adapting the saturated paste extract chemistry to measured in-situ water contents, the Visual Minteq output often reduced the dissolved Ca concentrations through precipitation of calcite and gypsum, dissolved Mg concentrations decreased due to Soil-Mg binding, and Na concentrations were typically increased as a function of the level of evapoconcentration. Other precipitates that were predicted from the Visual Minteq modeling included Soil-Ca and mirabilite, although other minerals were predicted to be dissolved in solution.

The Visual Minteq adapted SAR values (SAR-VM) are plotted against the  $EC_e$  of the saturated paste data to demonstrate the increase in the SAR-VM values with decrease in the modeled water content from the saturated paste data (Figure 3.5). The SAR-VM values are approximately an order of magnitude greater than the saturated paste SAR values (Figure 3.3). However, the sorption of soil-bound Mg was apparent in the Visual

Minteq adapted Mg concentrations (Mg-VM) (Figure 3.6) that are an order of magnitude lower than the measured Mg concentrations (Figure 3.4).

### *Equation Development*

Four equations were developed from the available data, two using saturated paste chemistry data and two using Visual Minteq adapted data. For convenience the four equations were renamed: the depth averaged equation as AVG (Eqn. 3.4); the depth weighted equation as WGT (Eqn. 3.5); the depth averaged equation with Visual Minteq adapted data as AVG-VM (Eqn. 3.6); and the depth weighted equation with Visual Minteq adapted data as WGT-VM (Eqn. 3.7).

$$EC = 1.41 + 2.18EM_v + 0.027Mg + 0.217SAR \quad \text{Eqn. 3.4}$$

$$EC = 1.16 + 2.55EM_v + 0.033Mg + 0.197SAR \quad \text{Eqn. 3.5}$$

$$EC = -1.16 + 3.03EM_v + 0.023Mg + 0.298Mg-VM + 0.017SAR VM \quad \text{Eqn. 3.6}$$

$$EC = -1.13 + 3.29EM_v + 0.023Mg + 0.286Mg VM + 0.017SAR VM \quad \text{Eqn. 3.7}$$

Selection of the parameters for the equation development was based upon the Mallows'  $C_p$  statistic. Beyond the salt chemistry (Ca, Mg, Na, K, Cl and  $SO_4$  as measured by saturated paste and/or Visual Minteq adapted), the Mallows'  $C_p$  also included the average depth water table, water contents, soil texture (silt, sand and clay) and coupled with the measured  $EM_v$ . The selection process aimed for lowest Mallows'  $C_p$  combined with the highest  $R^2$ , while limiting the number of variables. The best variables, having the lowest Mallows'  $C_p$ , highest  $R^2$  and justifiable through multiple locales, relied upon Mg (from the saturated paste extract and/or the Visual Minteq adapted data), and the SAR, (from the saturated paste extract and/or the Visual Minteq adapted data), in combination with the  $EM_v$  measurements (Table 3.2). The behavior of

soil Mg and the fact that SAR values are composed of Na, Ca and Mg enhanced the acceptance of these as the preferred variables for regression equation development. There was a high regression coefficient ( $R^2$ ) suggesting an effective fit for all four equations developed (Table 3.2).

The inclusion of the Visual Minteq Mg and SAR data slightly improved the  $R^2$  values for both the AVG-VM and for the WGT-VM equations compared to the saturated paste equations (Table 3.2). This suggests that there was an added benefit of processing chemical data through the Visual Minteq program adding to the predictive power of these developed equations.

The average predictive equations were then used to back predict  $EC_e$  from the original data used to create the equations. A 1:1 relationship was expected for precise predictive equations; the relationship was relatively close (Figure 3.7). An analysis of the absolute value of the AVG residuals found that they ranged between 0.06  $dS\ m^{-1}$  and 4.18  $dS\ m^{-1}$  with a mean of 1.48  $dS\ m^{-1}$ . An analysis of the absolute value of the AVG-VM residuals found that they ranged between 0.03  $dS\ m^{-1}$  and 4.37  $dS\ m^{-1}$  with a mean of 1.23  $dS\ m^{-1}$ . There was variability around the predicted  $EC_e$ , but the mean predicted  $EC_e$  was within  $\pm 1.5\ dS\ m^{-1}$ .

Data from both WGT and WGT-VM equations were also not a precise 1:1 relationship (Figure 3.8). An analysis of the absolute values of the WGT residuals found that they ranged between 0.04  $dS\ m^{-1}$  and 3.74  $dS\ m^{-1}$  with a mean of 1.29  $dS\ m^{-1}$ . An analysis of the absolute value of the WGT-VM residuals found that they ranged between 0.03  $dS\ m^{-1}$  and 3.50  $dS\ m^{-1}$  with a mean of 1.04  $dS\ m^{-1}$ . There was variability around the predicted  $EC_e$ , but the mean predicted  $EC_e$  was within  $\pm 1.3\ dS\ m^{-1}$ .

### *Equation Validation*

Validation of the prediction equations was accomplished with data not utilized in the development of those equations (Tables 3.3 and 3.4). Visual Minteq utilized the same methods in the validation as were used in the model development. Validation data ( $n = 14$ ) were processed for each of the four equations. For the AVG data the absolute value of the residuals ranged between  $0.13 \text{ dS m}^{-1}$  and  $3.00 \text{ dS m}^{-1}$ , with a mean of  $1.48 \text{ dS m}^{-1}$  (Table 3.3). For the WGT data the absolute value of the residuals ranged between  $0.25 \text{ dS m}^{-1}$  and  $3.45 \text{ dS m}^{-1}$ , with a mean of  $1.45 \text{ dS m}^{-1}$  (Table 3.4). For the AVG-VM data the absolute value of the residuals ranged between  $0.35 \text{ dS m}^{-1}$  and  $3.17 \text{ dS m}^{-1}$ , with a mean of  $1.63 \text{ dS m}^{-1}$  (Table 3.5). For the WGT-VM data the absolute value of the residuals ranged between  $0.10 \text{ dS m}^{-1}$  and  $3.43 \text{ dS m}^{-1}$ , with a mean of  $1.70 \text{ dS m}^{-1}$  (Table 3.6).

Based upon the validation datasets (Tables 3.3 to 3.6), apparently the predictive capacities of the four equations were essentially equal. When the assumptions of database combination were accounted for (associating data points with  $\text{EC}_e$  within  $\pm 4 \text{ dS m}^{-1}$ ), all equations succeeded in predicting within that  $\pm 4 \text{ dS m}^{-1}$  parameter. Additionally, all equations mean residuals were approximately the same as the mean residuals of the developing datasets (Table 3.2).

### *Management Categories*

The residuals from each of the four equations offered insight into their ability to predict  $\text{EC}_e$  from  $\text{EM}_v$  and chemistry. However, application of this data requires the use of management goals and recommendations. A two-part article by Stepphun et al. (2005a; 2005b) developed management recommendations based upon baseline EC,

salinity tolerance and other information and equations. Below are management expectations, using Stepphun's equations and methods as utilized in Wittler et al. (In Press).

Category 1 – soil water salinity expected to cause negligible crop yield loss ( $EC_e < 4 \text{ dS m}^{-1}$ ), Category 2 – soil water salinity expected to cause 0 to 20% crop yield loss ( $4 \text{ dS m}^{-1} < EC_e < 6 \text{ dS m}^{-1}$ ), Category 3 – soil water salinity expected to cause 20 to 40% crop yield loss ( $6 \text{ dS m}^{-1} < EC_e < 10 \text{ dS m}^{-1}$ ), Category 4 – soil water salinity expected to cause 40 to 60% crop yield loss ( $10 \text{ dS m}^{-1} < EC_e < 17 \text{ dS m}^{-1}$ ), and Category 5 – soil water salinity expected to cause > 60% crop yield loss ( $EC_e > 17 \text{ dS m}^{-1}$ ).

The predictive capacity of the four equations were analyzed against the change in category, which will directly affect management goals. For the AVG validation, the absolute value of the mean change in category was 0.6, with 6 of the 14 category predictions within the actual category, and only one sample point with a two-category change (Table 3.3). For the WGT validation, the absolute value of the mean change in the category was 0.5, with 7 of the 14 category predictions within the actual category, and all of the errors being within  $\pm 1$  category (Table 3.4). For the AVG-VM validation, the absolute value of the mean change in the category was 0.4, with 8 of the 14 category predictions within the actual category, and all of the errors being within  $\pm 1$  category (Table 3.5). For the WGT-VM validation, the absolute value of the mean change in the category was 0.7, with 4 of the 14 category predictions within the actual category, and all of the errors being within  $\pm 1$  category (Table 3.6).

### *Equation Comparisons*

Since this analysis came from the lower Arkansas River Basin, the primary comparison will be to the sub-regional equations developed by Wittler et al. (In Press) in the basin. The Wittler Upstream (Eqn. 3.8) and Downstream (Eqn. 3.9) equations were

used to predict the  $EC_e$  of the validation dataset (Table 3.7), where the gravimetric water content (WC) is required. For the Wittler equations, the absolute value of the residuals ranged between  $0.18 \text{ dS m}^{-1}$  and  $3.17 \text{ dS m}^{-1}$ , with a mean of  $1.34 \text{ dS m}^{-1}$ . The absolute value of the mean change in the category was 0.5, with 7 of the 14 category predictions within the actual category, and all of the errors being within  $\pm 1$  category.

$$EC_e = 0.45 + 7.23EM_v^{1.78} + 19.54WC - 34.06EM_v(WC) \quad \text{Eqn. 3.8}$$

$$EC_e = 2.33 + 7.16EM_v^{1.44} + 9.41WC - 23.18EM_v(WC) \quad \text{Eqn. 3.9}$$

When comparing the residuals between the four chemical based equations and the Wittler sub-region equations, there was no significant difference. Therefore, the equations all offered approximately the same result. When comparing the prediction of management categories, the equations were all approximately equivalent, with no distinct difference between any of the equations.

The chemistry does not offer significant improvement to predict  $EC_e$  from  $EM_v$  data when compared to sub-region equations, nor does weighted or VM improve the predictive capacity. However, the significant difference was that the current equations are effective for the entire study region (over 100,000 hectares) with no loss in predictive capacity, not for just the Upstream sub-region (53,100 hectares) or the Downstream sub-region (55,200 hectares). Therefore, the averaged or weighted equations can be considered an improvement since the equations have an increased capacity to account for spatial variability. Additionally, including chemical parameters negates the need for WC in predictive equations, where WC appears to be a surrogate for salinity chemistry.

Pore water chemistry, as modeled by Visual Minteq, did not offer equation prediction improvement. This was potentially due to the lack of model kinetics, so that

supersaturation of both  $\text{CaSO}_4$  and  $\text{CaCO}_3$  are possible in the pore water, but not in the Visual Minteq predicted waters. Additionally, the random selection of fields for the validation may have biased the model results for all the equations. The extremely low soil water contents for several points may have led to erroneous measurements by the EM sensor. McKenzie et al. (1989) suggested that the soil moisture be greater than 30%, but many of the validation points were below that soil water value (Table 3.7). Additionally, the assumption of a  $\pm 4 \text{ dS m}^{-1}$  acceptance level to combine and expand the databases may have introduced a level of error that could be removed through a larger, more comprehensive database.

The depth weighting in this study differed from that proposed in the literature based upon the response by the EM-38. Johnston et al. (1996) used a weighting that had an effective depth of 1.8 m, was based upon soil texture and where the second 0.3 m depth had 30% weighting factor, and the largest weight of that profile. However, in this research, the inclusion of texture did not significantly add to the best subset in the Mallows'  $C_p$  for the weighted equations.

The spatial scale of this research in the  $\text{EM}_v\text{-EC}_e$  calibration was unique and specific to the requirements of a regional model for management. The spatial variability issues are well documented (Clay et al., 2001), but this research found that they can be partially overcome by inclusion of chemistry in the  $\text{EM}_v\text{-EC}_e$  calibration and use of management categories (Steppuhn et al., 2005b). Typically, the approach has been to effectively calibrate the  $\text{EM}_v$  to a single location (often field scale) by statistically calculating the number of calibration sites necessary (Diaz and Herrero, 1992; Lesch et

al., 1995a; 1995b; Lesch, 2005), or by using the ESAP program developed by the United States Salinity Lab (Riverside, CA).

This research supports the statement by Corwin and Lesch (2005a) that  $EC_a$  is influenced by the chemistry, as determined in the response of predicting  $EC_e$ . Additionally, the work of Friedman (2005) is also supported; however, this research does not imply that the use of texture is deemed as insignificant to the  $EM_v$ - $EC_e$  calibration, just that it had a lesser effect than the chemical properties potentially due to the spatial scale issues.

## **Conclusions**

Developing calibration equations for an electromagnetic induction meter so data can be related to saturated paste electrical conductivity compatible with recommendations and typical measurements is vital for management purposes. Since the EM-38 is based upon an  $EC_a$  (bulk/apparent electrical conductivity), calibrations are needed to convert the results to  $EC_e$ , which are typically used. Equations in this paper were developed to regionally calibrate  $EM_v$  to  $EC_e$  for the lower Arkansas River Basin, CO, and possibly being related to other locations with calcareous/gypsiferous soils.

Four equations were developed, using either depth averaging or depth weighting. Each depth scheme also used data output from Visual Minteq, attempting to add an in-situ moisture and chemical concentration to the time when the  $EM_v$  measurement was determined. All the equations used  $EM_v$  measurements and saturated paste Mg concentrations. The SAR was used either as a saturated paste based calculation or as

calculated from the Visual Minteq data, and Visual Minteq adapted Mg concentrations were also used in conjunction with the saturated paste Mg concentrations. In the validation procedures, however, it was found that the use of the Visual Minteq adapted data did not improve the prediction power of the  $EC_e$  when compared to the equations using saturated paste chemistry.

All of the equations were equivalent to the current sub-regional calibrations, except that with the addition of salinity chemistry in the calibration equations the spatial scale was doubled while precision was held constant. The equations were moderately successful in predicting and placing the  $EC_e$  into a management category. Additionally, the chemically based equations were robust enough to account for significant differences in regional soil quality, across a range of initial saturated paste extract chemistry. Equation improvement might be achieved by using a more intensive sampling protocol and using a single comprehensive database where all chemistry and EM measurements are directly correlated, rather than combining two databases used in this approach.

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## Tables

Table 3.1. Individual sample point soil chemical descriptive statistics by sub-region and EC range.

Variable	Upstream				Downstream				Upstream and Downstream			
	N	Mean	Median	StDev	N	Mean	Median	StDev	N	Mean	Median	StDev
<b>Low EC category (0 - 2 dS m<sup>-1</sup>)</b>												
EC, dS m <sup>-1</sup>	31	1.4	1.3	0.3	18	1.2	1.15	0.4	49	1.3	1.3	0.4
pH, su	31	7.9	7.8	0.3	18	8.3	8.3	0.4	49	8.1	8	0.4
Na, meq L <sup>-1</sup>	31	4.87	4.48	1.48	18	5.05	4.13	2.48	49	4.92	4.44	1.87
Ca, meq L <sup>-1</sup>	31	6.89	6.69	2.00	18	5.09	4.79	1.95	49	6.24	5.94	2.15
Mg, meq L <sup>-1</sup>	31	3.79	3.37	1.48	18	2.96	2.55	1.23	49	3.46	3.29	1.40
Cl meq L <sup>-1</sup>	31	6.54	5.08	6.60	18	1.04	0.93	0.54	49	4.51	1.52	5.87
SO <sub>4</sub> , meq L <sup>-1</sup>	31	9.70	8.99	4.10	18	10.56	10.33	5.52	49	10.01	9.81	4.62
<b>Medium EC category (2 - 5 dS m<sup>-1</sup>)</b>												
EC, dS m <sup>-1</sup>	28	3.0	3.0	0.8	31	3.4	3.7	1.0	59	3.2	3.2	0.9
pH, su	28	7.8	7.9	0.3	31	8.1	8.1	0.3	59	8	7.9	0.3
Na, meq L <sup>-1</sup>	28	11.40	9.18	6.00	31	16.10	15.83	6.22	59	13.88	13.92	6.53
Ca, meq L <sup>-1</sup>	28	19.06	15.27	13.87	31	21.56	17.07	10.38	59	20.36	16.57	12.13
Mg, meq L <sup>-1</sup>	28	14.07	10.62	11.52	31	13.41	11.93	6.17	59	13.74	11.77	9.05
Cl meq L <sup>-1</sup>	28	17.66	13.06	18.36	31	4.46	3.39	3.41	59	10.72	4.37	14.42
SO <sub>4</sub> , meq L <sup>-1</sup>	28	35.27	29.25	28.25	31	61.44	54.03	37.48	59	49.01	39.87	35.66
<b>High EC category (5 - 8 dS m<sup>-1</sup>)</b>												
EC, dS m <sup>-1</sup>	9	6.1	5.9	1.0	28	6.8	6.6	1.2	37	6.6	6.3	1.2
pH, su	9	7.6	7.6	0.1	28	8	7.9	0.3	37	7.9	7.8	0.3
Na, meq L <sup>-1</sup>	9	46.68	40.80	20.45	28	53.90	51.16	18.66	37	52.11	46.24	19.10
Ca, meq L <sup>-1</sup>	9	28.49	31.34	4.94	28	32.78	33.88	7.29	37	31.74	31.94	6.99
Mg, meq L <sup>-1</sup>	9	33.33	31.11	8.39	28	34.07	32.92	10.04	37	33.90	32.18	9.55
Cl meq L <sup>-1</sup>	9	75.43	23.19	102.15	28	17.97	14.67	13.57	37	31.93	15.23	55.49
SO <sub>4</sub> , meq L <sup>-1</sup>	9	86.55	80.26	21.99	28	184.17	183.84	53.17	37	160.44	172.81	63.48
<b>Very High EC category (&gt;9 dS m<sup>-1</sup>)</b>												
EC, dS m <sup>-1</sup>	16	14.9	13.3	4.1	20	12.7	12.0	2.7	36	13.7	12.5	3.5
pH, su	16	7.7	7.8	0.2	20	8	8	0.2	36	7.9	7.9	0.3
Na, meq L <sup>-1</sup>	16	281.79	244.08	156.30	20	223.24	197.66	111.88	36	249.26	206.36	134.68
Ca, meq L <sup>-1</sup>	16	42.42	44.71	18.01	20	40.07	40.07	9.98	36	41.12	40.07	13.97
Mg, meq L <sup>-1</sup>	16	156.84	135.12	86.57	20	104.59	99.65	58.10	36	127.80	107.64	75.71
Cl meq L <sup>-1</sup>	16	192.84	89.09	227.71	20	82.40	77.58	43.05	36	131.49	80.74	162.26
SO <sub>4</sub> , meq L <sup>-1</sup>	16	423.19	383.82	191.79	20	550.46	510.09	250.19	36	493.89	454.81	232.08

Table 3.2. Predictor equation multilinear regression for the four equations and for the combined dataset of Upstream and Downstream sub-regions; including the R<sup>2</sup>, RMSE and Mallows' C<sub>p</sub> values for each equation, and covariate t-values and p-values.

Equation Type	Covariates	Coefficient	t-value	p-value	Mallows' C <sub>p</sub> †	R <sup>2</sup>	RMSE
Averaged (AVG)	Constant	1.41	3.36	0.001	23.9	0.89	1.64
	EM <sub>v</sub>	2.18	3.99	<0.001			
	Mg	0.027	3.46	0.001			
	SAR	0.217	4.91	<0.001			
Weighted (WGT)	Constant	1.16	2.63	0.011	11.5	0.91	1.58
	EM <sub>v</sub>	2.55	4.52	<0.001			
	Mg	0.033	4.38	<0.001			
	SAR	0.197	4.29	<0.001			
Averaged plus Visual Minteq (AVG-VM)	Constant	-1.16	-2.12	0.038	1.1	0.93	1.35
	EM <sub>v</sub>	3.03	6.61	<0.001			
	Mg	0.023	3.81	<0.001			
	Mg VM	0.298	5.42	<0.001			
	SAR VM	0.017	5.69	<0.001			
Weighted plus Visual Minteq (WGT-VM)	Constant	-1.13	-1.97	0.054	0.6	0.93	1.34
	EM <sub>v</sub>	3.29	6.42	<0.001			
	Mg	0.023	3.37	0.001			
	Mg VM	0.286	4.51	<0.001			
	SAR VM	0.015	5.27	<0.001			

† Some differences occurred in the Mallows' C<sub>p</sub> due to the number of variables included in the analysis.

Where:

EM<sub>v</sub> = Electromagnetic Induction in the Vertical

Mg = Magnesium concentration (meq L<sup>-1</sup>)

SAR = Sodium Adsorption Ratio

VM = Visual Minteq designator for Mg and SAR

RMSE = Root Mean Square Error

Table 3.3. Averaged validation (AVG) dataset including  $EM_v$ , Mg and SAR with categories for prediction within management units (n=14).

Field Code	Measured Averaged		Predicted Averaged		Predictors			Residuals	
	EC †	Category	EC <sub>e</sub>	Category	EM <sub>v</sub>	Mg	SAR	EC Difference	Category Change
	dS m <sup>-1</sup>		dS m <sup>-1</sup>		dS m <sup>-1</sup>	meq L <sup>-1</sup>		dS m <sup>-1</sup>	
US99-001	3.6 (3.0)	1	3.2	1	0.55	7.92	1.96	0.4	0
UF00-043	2.3 (2.8)	1	5.3	2	1.18	23.66	2.89	-3.0	1
US99-043	4.7 (2.8)	2	5.1	2	1.11	23.66	2.89	-0.8	0
US03-077	3.5 (6.8)	1	6.3	3	0.62	35.10	11.80	-2.8	2
US99-077	4.7 (6.8)	2	5.8	2	0.41	35.10	11.80	-1.1	0
DF02-318	6.4 (6.0)	3	5.3	2	0.68	37.96	6.54	1.0	-1
DF03-318	6.1 (6.0)	3	5.2	2	0.62	37.96	6.54	0.9	-1
DS03-318	5.5 (6.0)	2	6.1	3	1.02	37.96	6.54	-0.6	1
DS02-348	1.7 (3.5)	1	3.7	1	0.43	12.96	4.65	-2.0	0
DS03-348	5.0 (3.5)	2	3.8	1	0.48	12.96	4.65	1.2	-1
DS02-360	3.1 (1.9)	1	3.0	1	0.28	5.10	3.78	0.1	0
DS03-360	5.8 (1.9)	2	2.9	1	0.26	5.10	3.78	2.8	-1
DF02-350A	9.5 (8.1)	3	8.0	3	1.22	34.92	13.87	1.5	0
DS02-350A	5.2 (8.1)	2	7.7	3	1.07	34.92	13.87	-2.5	1
Mean								1.48 ‡	0.6 ‡

† Numbers in parenthesis are the measured EC<sub>e</sub>.

‡ Mean of the absolute values.

Table 3.4. Weighted validation (WGT) dataset including  $EM_v$ , Mg and SAR with categories for prediction within management units (n=14).

Field Code	Measured Weighted		Predicted Weighted		Predictors			Residuals	
	EC †	Category	EC <sub>e</sub>	Category	EM <sub>v</sub>	Mg	SAR	EC Difference	Category Change
	dS m <sup>-1</sup>		dS m <sup>-1</sup>		dS m <sup>-1</sup>	meq L <sup>-1</sup>		dS m <sup>-1</sup>	
US99-001	3.8 (2.6)	1	3.2	1	0.55	7.11	1.86	0.6	0
UF00-043	2.1 (2.6)	1	5.5	2	1.18	24.19	2.77	-3.4	-1
US99-043	4.4 (2.6)	2	5.3	2	1.11	24.19	2.77	-0.9	0
US03-077	2.8 (5.6)	1	5.4	2	0.62	27.62	9.05	-2.6	0
US99-077	4.0 (5.6)	2	4.9	2	0.41	27.62	9.05	-0.9	0
DF02-318	5.9 (5.8)	2	5.2	2	0.68	34.15	6.19	0.6	0
DF03-318	5.7 (5.8)	2	5.1	2	0.62	34.15	6.19	0.6	-1
DS03-318	5.0 (5.8)	2	6.1	3	1.02	34.15	6.19	-1.1	0
DS02-348	1.5 (3.2)	1	3.6	1	0.43	11.89	4.63	-2.0	1
DS03-348	4.5 (3.2)	2	3.7	1	0.48	11.89	4.63	0.8	0
DS02-360	2.5 (1.9)	1	2.8	1	0.28	5.14	3.70	-0.3	1
DS03-360	5.3 (1.9)	2	2.7	1	0.26	5.14	3.70	2.5	1
DF02-350A	10.1 (8.8)	4	8.6	3	1.22	38.06	15.61	1.5	-1
DS02-350A	5.8 (8.8)	2	8.2	3	1.07	38.06	15.61	-2.4	0
Mean								1.45 ‡	0.5 ‡

† Numbers in parenthesis are the measured EC<sub>e</sub>.

‡ Mean of the absolute values.

Table 3.5. Averaged validation (AVG-VM) dataset using Visual Minteq adapted data including  $EM_v$ , Mg and SAR with categories for prediction within management units (n=14).

Field Code	Measured Averaged		Predicted Averaged		Predictors				Residuals	
	EC † dS m <sup>-1</sup>	Category	EC <sub>e</sub> dS m <sup>-1</sup>	Category	EM <sub>v</sub> dS m <sup>-1</sup>	Mg meq L <sup>-1</sup>	Mg-VM meq L <sup>-1</sup>	SAR-VM	EC Difference dS m <sup>-1</sup>	Category Change
US99-001	3.6 (3.0)	1	2.5	1	0.55	7.92	6.08	3.33	1.1	0
UF00-043	2.3 (2.8)	1	5.2	2	1.18	23.66	7.37	9.64	-3.0	-1
US99-043	4.7 (2.8)	2	5.0	2	1.11	23.66	7.15	8.62	-0.8	0
US03-077	3.5 (6.8)	1	4.9	2	0.62	35.10	9.23	40.04	-1.4	-1
US99-077	4.7 (6.8)	2	4.3	2	0.41	35.10	9.40	41.96	0.3	0
DF02-318	6.4 (6.0)	3	7.8	3	0.68	37.96	18.37	39.05	-1.4	0
DF03-318	6.1 (6.0)	3	7.6	3	0.62	37.96	18.33	38.58	-1.5	0
DS03-318	5.5 (6.0)	2	8.1	3	1.02	37.96	16.74	27.64	-2.6	-1
DS02-348	1.7 (3.5)	1	3.7	1	0.43	12.96	10.14	16.74	-1.9	0
DS03-348	5.0 (3.5)	2	3.3	1	0.48	12.96	8.89	11.31	1.6	1
DS02-360	3.1 (1.9)	1	2.6	1	0.28	5.10	8.83	12.54	0.5	0
DS03-360	5.8 (1.9)	2	2.6	1	0.26	5.10	9.09	13.11	3.2	1
DF02-350A	9.5 (8.1)	3	9.0	3	1.22	34.92	16.66	51.01	0.4	0
DS02-350A	5.2 (8.1)	2	8.1	3	1.07	34.92	15.78	40.52	-3.0	-1
Mean									1.63 ‡	0.4 †

† Numbers in parenthesis are the measured EC<sub>e</sub>.

‡ Mean of the absolute values.

Table 3.6. Weighted validation (WGT-VM) dataset using Visual Minteq adapted data including  $EM_v$ , Mg and SAR with categories for prediction within management units (n=14).

Field Code	Measured Weighted		Predicted Weighted		Predictors				Residuals	
	EC †	Category	EC <sub>e</sub>	Category	EM <sub>v</sub>	Mg	Mg-VM	SAR-VM	Absolute Difference	Category Change
	dS m <sup>-1</sup>		dS m <sup>-1</sup>		dS m <sup>-1</sup>	meq L <sup>-1</sup>	meq L <sup>-1</sup>		dS m <sup>-1</sup>	
US99-001	3.8 (2.6)	1	2.5	1	0.55	7.11	5.75	3.31	1.2	0
UF00-043	2.1 (2.6)	1	5.5	2	1.18	24.19	7.16	9.95	-3.4	-1
US99-043	4.4 (2.6)	2	5.2	2	1.11	24.19	7.01	8.92	-0.8	0
US03-077	2.8 (5.6)	1	4.4	2	0.62	27.62	8.54	29.23	-1.6	-1
US99-077	4 (5.6)	2	3.9	1	0.41	27.62	8.77	33.15	0.2	1
DF02-318	5.9 (5.8)	2	7.7	3	0.68	34.15	18.26	37.80	-1.8	-1
DF03-318	5.7 (5.8)	2	7.5	3	0.62	34.15	18.34	38.39	-1.9	-1
DS03-318	5 (5.8)	2	8.3	3	1.02	34.15	17.05	29.14	-3.4	-1
DS02-348	1.5 (3.2)	1	4.0	1	0.43	11.89	10.95	18.92	-2.4	0
DS03-348	4.5 (3.2)	2	3.6	1	0.48	11.89	9.45	12.56	0.9	1
DS02-360	2.5 (1.9)	1	2.6	1	0.28	5.14	8.79	13.09	-0.1	0
DS03-360	5.3 (1.9)	2	2.5	1	0.26	5.14	8.74	12.68	2.7	1
DF02-350A	10.1 (8.8)	4	9.6	3	1.22	38.06	17.34	60.11	0.4	1
DS02-350A	5.8 (8.8)	2	8.7	3	1.07	38.06	16.59	48.20	-2.9	-1
Mean									1.70 ‡	0.7 ‡

† Numbers in parenthesis are the measured EC<sub>e</sub>.

‡ Mean of the absolute values.

Table 3.7. Validation dataset using equations from Wittler et al. (In Press) including  $EM_v$ , and Gravimetric water content (WC) with categories for prediction within management units.

Sub-region	Field Code	Measured Averaged		Predicted Averaged		Predictors			Residuals	
		EC	Category	EC <sub>e</sub>	Category	EM <sub>v</sub>	WC	EM <sub>v</sub> (WC)	EC Difference	Category Change
		dS m <sup>-1</sup>		dS m <sup>-1</sup>		dS m <sup>-1</sup>			dS m <sup>-1</sup>	
Upstream										
	US99-001	3.6	1	3.2	1	0.55	0.27	0.15	0.47	0
	UF00-043	2.3	1	3.9	1	1.18	0.30	0.36	-1.63	0
	US99-043	4.7	2	2.5	1	1.11	0.36	0.40	2.17	1
	US03-077	3.5	1	3.3	1	0.62	0.14	0.08	0.18	0
	US99-077	4.7	2	2.8	1	0.41	0.15	0.06	1.91	1
Downstream										
	DF02-318	6.4	3	5.4	2	0.68	0.16	0.11	0.96	1
	DF03-318	6.1	3	5.0	2	0.62	0.18	0.11	1.10	1
	DS03-318	5.5	2	6.1	3	1.02	0.25	0.25	-0.63	-1
	DS02-348	1.7	1	4.3	2	0.43	0.20	0.09	-2.60	-1
	DS03-348	5.0	2	4.4	2	0.48	0.23	0.11	0.58	0
	DS02-360	3.1	1	3.8	1	0.28	0.12	0.03	-0.70	0
	DS03-360	5.8	2	3.7	1	0.26	0.09	0.02	2.11	1
	DF02-350A	9.5	3	6.3	3	1.22	0.29	0.36	3.17	0
	DS02-350A	5.2	2	4.6	2	1.07	0.37	0.39	0.58	0
Mean									1.34 †	0.5 †

† Mean of the absolute values.

## Figures

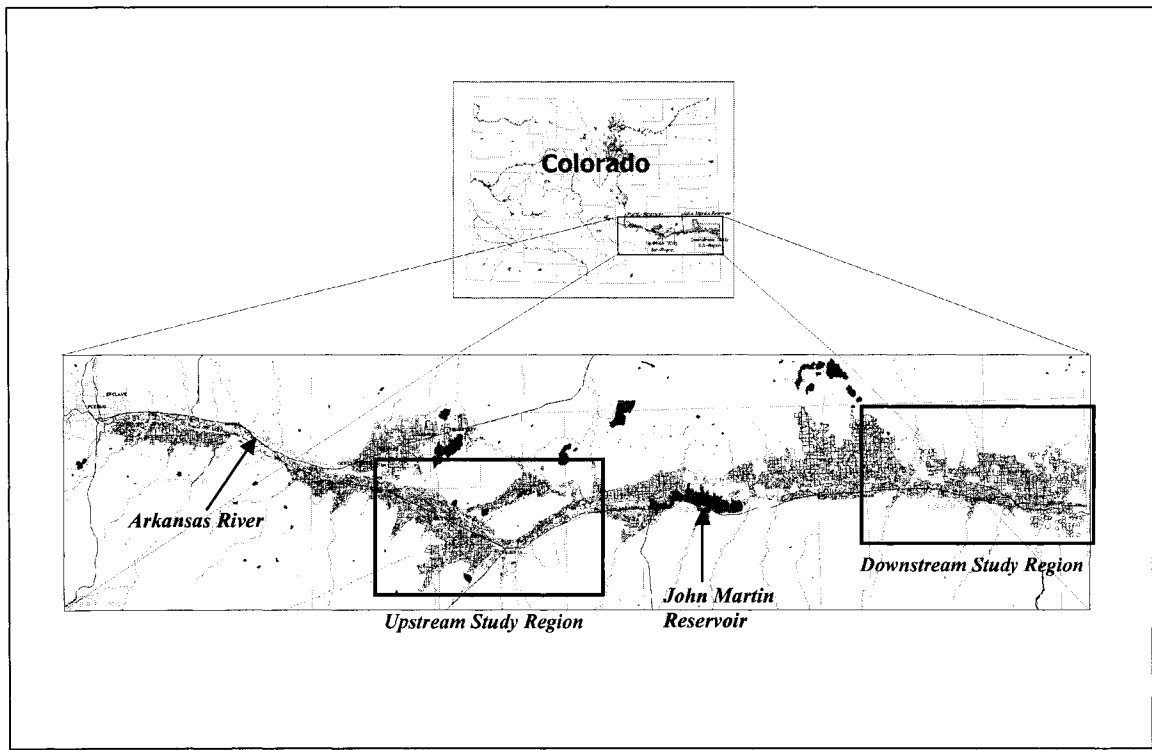


Figure 3.1. Map of the study region with the Upstream and Downstream sub-regions designated.

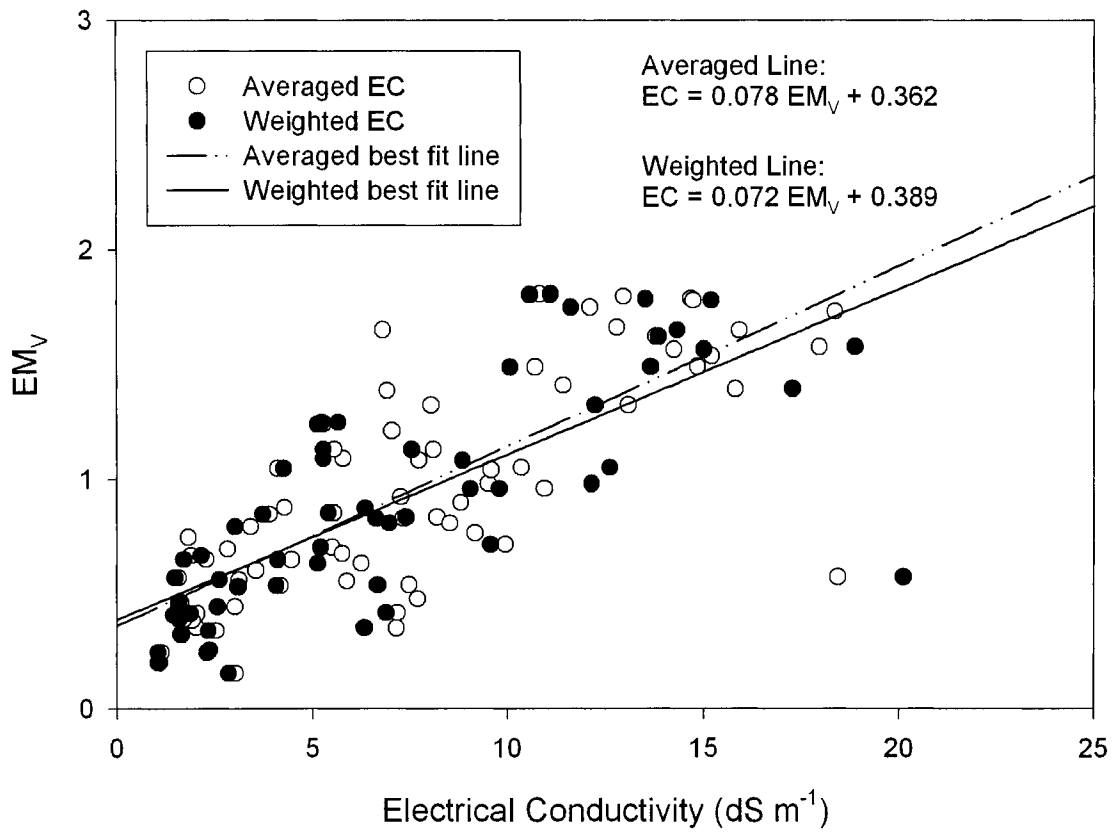


Figure 3.2.  $EM_v$  plotted against electrical conductivity with best fit lines to suggest a regression fit. The depth averaged  $EC_e$  best fit line had an  $R^2$  of 0.59, whereas the depth weighted best fit line had an  $R^2 = 0.55$ .

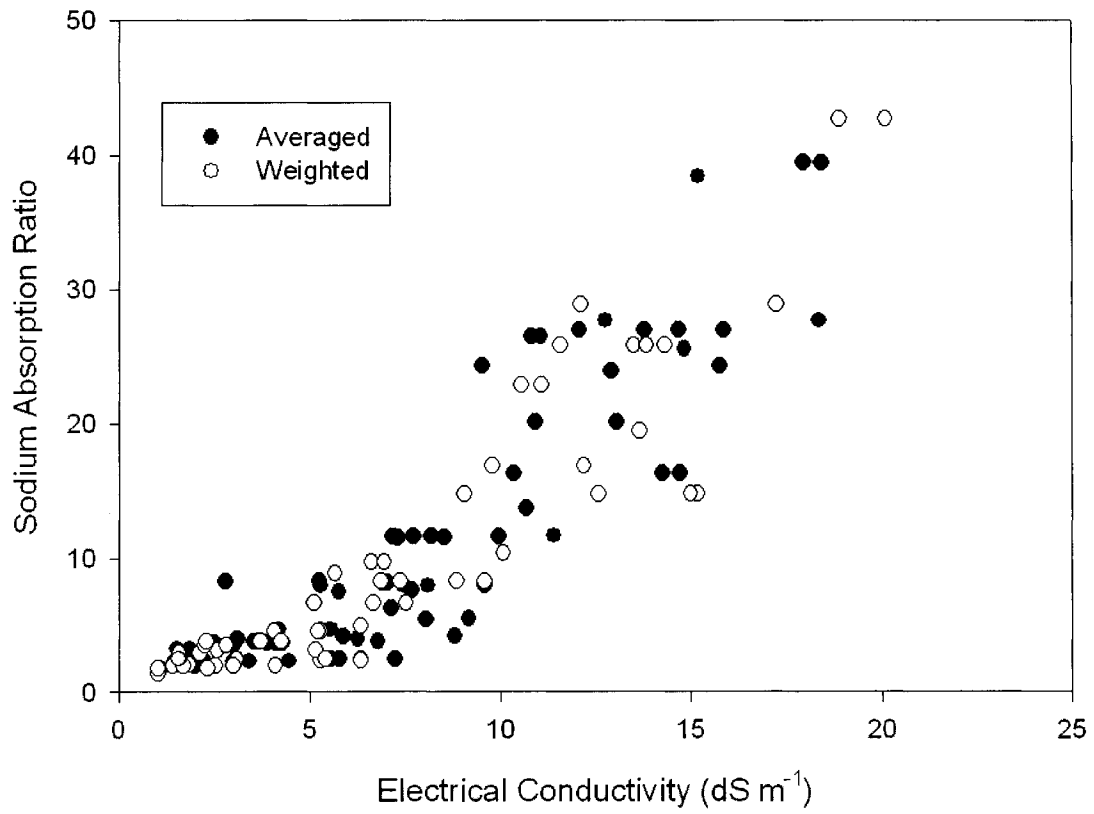


Figure 3.3. Sodium adsorption ratio (SAR) in the saturated paste samples as a function of electrical conductivity.

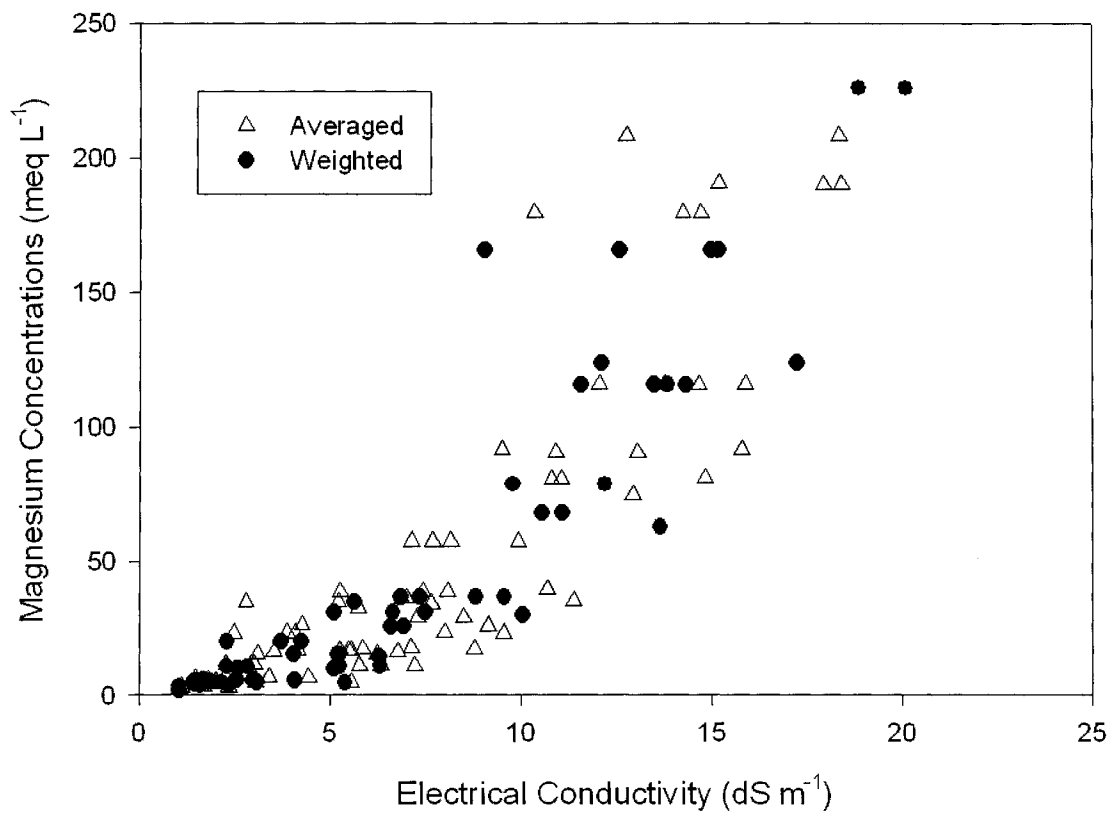


Figure 3.4. Magnesium concentrations as a function of electrical conductivity in saturated paste extract.

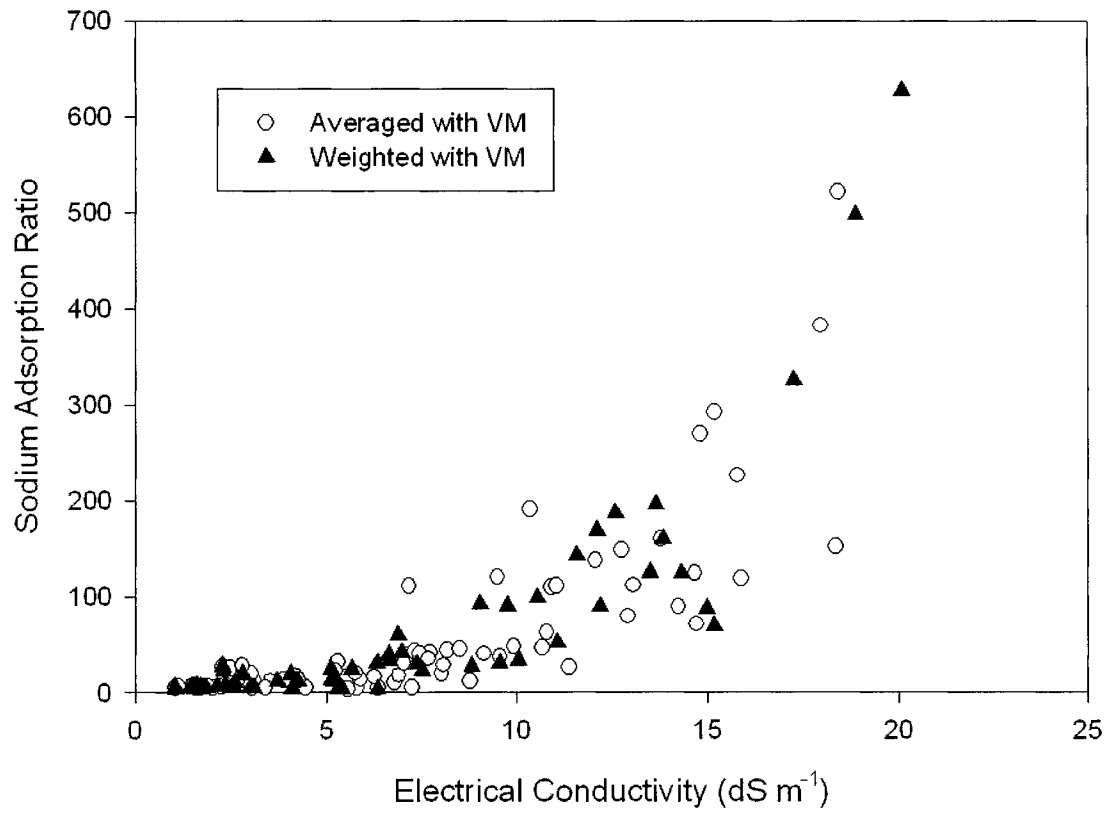


Figure 3.5. Sodium adsorption ratio (SAR) of the Visual Minteq (VM) adapted data as a function of electrical conductivity.

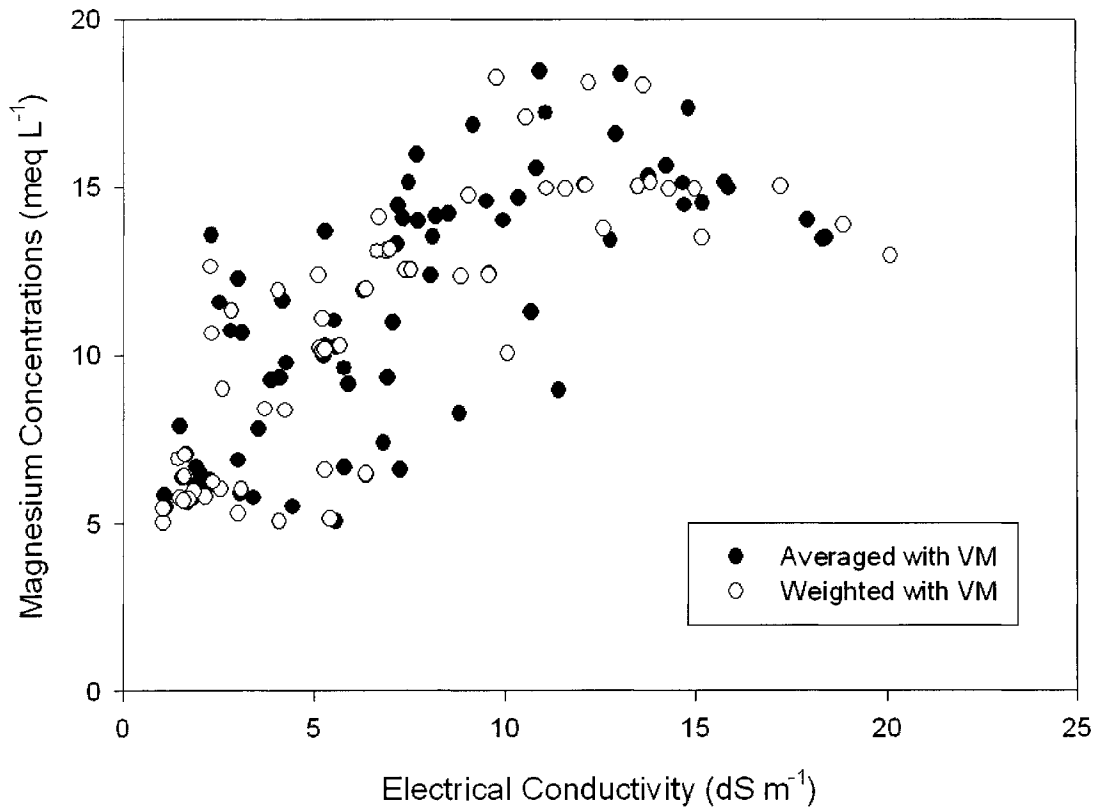


Figure 3.6. Magnesium of the Visual Minteq (VM) adapted data as a function of electrical conductivity.

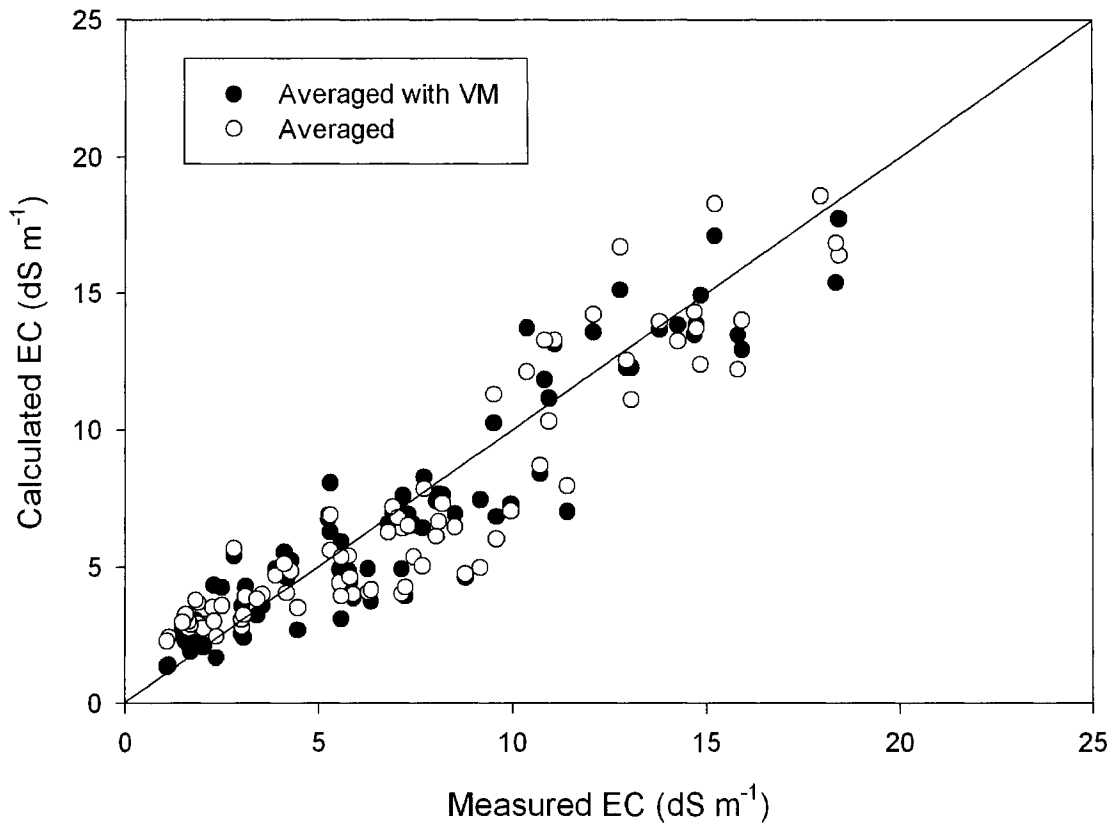


Figure 3.7. Calculated/predicted EC from the Averaged dataset (AVG) plotted against the Measured EC, using equations from both the saturated paste data and the Visual Minteq (VM) adapted data. A 1:1 line is added to delineate ideal correlation.

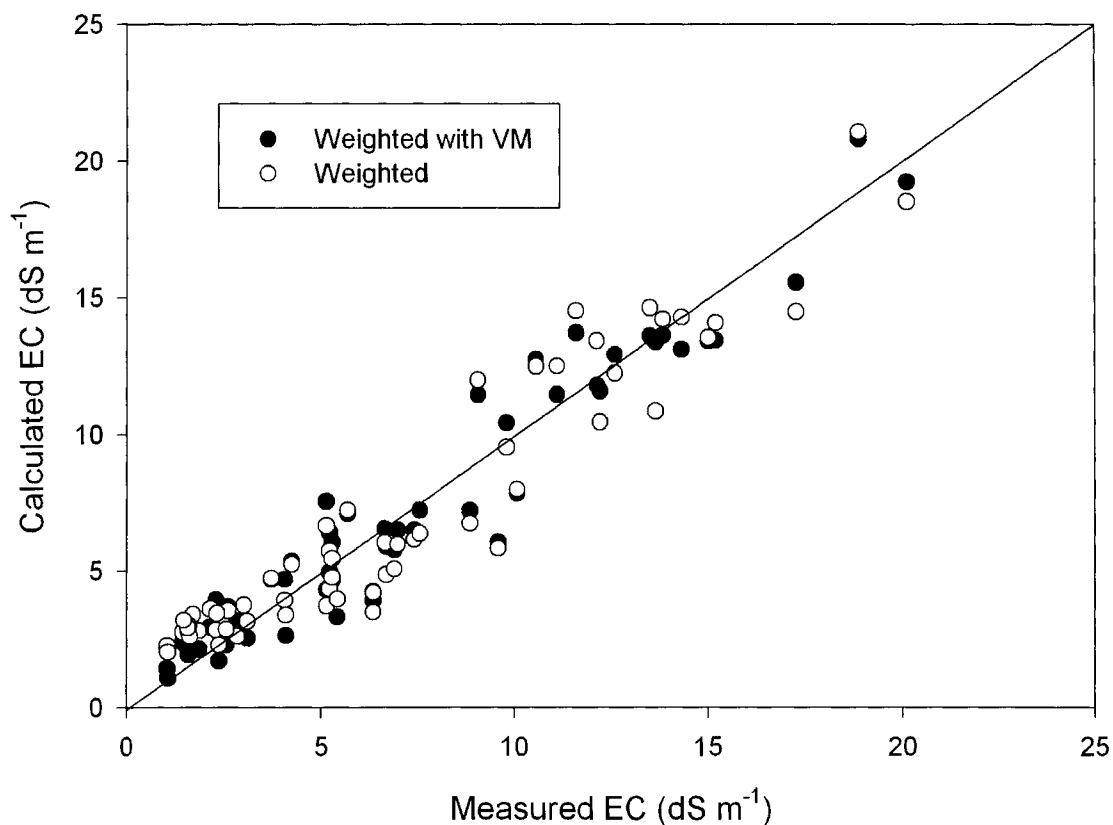


Figure 3.8. Calculated/predicted EC from the Weighted dataset (WGT) plotted against the Measured EC, using equations from both the saturated paste data and the Visual Minteq (VM) adapted data. A 1:1 line is added to delineate ideal correlation.

## **Chapter 4 Prediction of soil salinity management options using a chemical and flow based model**

### **Summary**

Calcareous soils in the lower Arkansas River Basin are impacted by salt concentrations in irrigation water and high ground water tables. Leaching many of these impacted soils is not effective in reducing salinity due to capillary rise at locations with high water tables. Modeling of management options for these soils can predict potential changes in the salt accumulation in the soil. Three locations with different soil salt concentrations and electrical conductivities were modeled in the Hydrus-1D version 3.0 (H1D) computer program. The H1D program allows modeling of soil water flow, root growth, carbon dioxide production and transport, as well as primary ion reactions. Simulations were performed examining the affect of changes in surface/irrigation water quality, depth to ground water and cropping options on salt accumulation.

Measured field soil properties, saturated paste extract chemistry, and Arkansas River water quality data were used in conjunction with climate data from Rocky Ford, CO in the modeling. Cropping patterns included plant growth or fallow without irrigation. Sufficient irrigation water, to avoid the wilting point, was applied to all irrigated model runs.

Evaporation was responsible for evaporites forming on the soil surface for most model runs, particularly in the simulations of fallow soil. The ground water was often a

source of salts in the 120 cm soil profile. Crop water uptake was found to be a primary factor in the location of the salt accumulation within the soil profile.

Changes in irrigation water quality influenced the magnitude of the peak salt concentrations but not the depth of those peaks. The volume of water applied altered the depth of the peak salt concentrations. Additionally, the ground water contributed to the depth to peak salt concentration. Gypsum and calcite precipitates were the primary repositories of precipitated salts in the soil profile and were subject to redistribution within the soil profile. It is concluded that no single management option will lead to salinity decreases needed to improve crop production. Potentially costly management options are required to improve soil salinity problems.

## **Introduction**

Salinity is one of the most significant agricultural issues in the lower Arkansas River Basin of southeastern Colorado (Ward and Waskom, 2002) (Figure 4.1). Multiple salinity sources and causes in the lower Arkansas River Basin have been proposed, ranging from geologic, urban, agricultural return flows and waterlogging (Miles, 1977; Konikow and Person, 1985; Hukkinen, 1993; Goff et al., 1998; Gates et al., 2002). Over time, these sources have led to salt accumulations in the soils throughout the basin.

The interdepartmental and interagency Salinity and Waterlogging Project has collected electromagnetic induction, electrical conductivity (EC), and other soil property measurements since 1999 in the lower Arkansas River Basin (Figure 4.1). This group has been examining wide-ranging topics, from surface and ground water quality, regional and

field-scale salinity, modeling regional changes in the irrigation supply and delivery methods, and irrigation application.

Gates et al. (2002) presented preliminary results of modeling strategies to maintain irrigated agriculture in the lower Arkansas River Basin. This work was expanded upon by Burkhalter and Gates (2005) who presented modeling results for the study region for 1999 to 2001. Both papers discussed the issues of management practices, such as waterlogging/drainage and canal lining as options to improve salinity management.

Colorado water law follows the Prior Appropriation Doctrine which determines how waters are adjudicated based upon the initial date of a water right (Radosevich et al., 1976). Thus during dry years, or drought, water may only be supplied for crop irrigation once or twice in the lower Arkansas River Basin (Miles, 1977). Much of the basin is subject to high ground water levels leading to waterlogging (Miles, 1977; Gates et al., 2002; Burkhalter and Gates, 2005). Waterlogging can act as a salinity source, and through capillary action transport salts to the soil surface or into the root zone (Hillel, 2000).

Calcite and gypsum are believed to dominate the salinity related mineralogy of the Upstream research area (D. Huber, personal communication, 2005), as is typical for arid and semi-arid lands (Bresler et al., 1982; Hillel, 2000; Suarez, 2005). Calcite ( $\text{CaCO}_3$ ) is composed of calcium and carbonate ion pairs, and its solubility is primarily controlled by pH and  $\text{HCO}_3^-$  concentrations (Olsen and Watanabe, 1959; Lindsay, 1979). Gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ) is composed of calcium and sulfate ions joined with two water molecules. In pure water, gypsum solubility is controlled by the solubility product of its

solid phase (Glas et al., 1979), but in salt solutions (e.g. irrigation waters) the solubility of gypsum is subject to the ionic strength and chemical composition of the waters (Kemper et al., 1975; Gobran and Miyamoto, 1985; Hem, 1985). Gypsum can be dissolved and precipitated within the soil profile because of its solubility (Skarie et al., 1987a; Skarie et al., 1987b). Gypsum and calcite precipitates equilibrate and co-exist in soils at a pH of approximately 7.8 (Lindsay, 1979).

Effective management of soil salinity requires adequate leaching (Hoffman, 1990). Issues associated with salt accumulation in the soil and for crop production are with specific ion toxicity, typically Na, and increases in osmotic potential affecting root uptake of water and essential nutrients (Bresler et al., 1982). Salinity also affects the soil physical properties since Na causes dispersion and swelling of soils (Bresler et al., 1982). Exchanging and leaching of the Na through application of Ca as gypsum is a recommended option (Keren and O'Connor, 1982), but in calcareous soils the use of gypsum is not feasible, and leaching is the primary tool for salt removal (Bresler et al., 1982; Hoffman, 1990; Hillel, 2000). Effective leaching in the lower Arkansas River Basin is limited to locations without high ground water levels.

Models, mathematical and computer based, have attempted to use soil hydraulic properties, such as tortuosity, to help predict soil electrical conductivities (Mualem and Friedman, 1991). Other attempts have been based upon divalent systems containing gypsum, but required expansion to include other reactions (Dutt, 1962). Many EC models are based upon the assumption that individual salts in a solution are additive to the EC. However, at high concentrations interactions among chemicals may invalidate this assumption (Adiku et al., 1992).

Various models have been proposed for predicting salinity, using individual ions in soils for both transport and chemical reactions. The calculation of soil salt balance and transport have been done either as a steady-state system (Oster and Rhoades, 1990) or under varying field conditions (Bresler, 1967). Hutson et al. (1990) described multiple approaches to modeling and the necessary components that models require to be effective, such as hydraulic properties, boundary conditions and solute transport. Other authors have discussed specific models and model parameters in various levels of detail (Robbins et al., 1980; Suarez and Goldberg, 1994; Rieu et al., 1998; Ali et al., 2000a; 2000b). Most models have issues with computing power and the interconnectedness of predictive soil hydraulic parameters, root growth, chemical reactions and CO<sub>2</sub> production and reaction (Hutson et al., 1990; Oster and Rhoades, 1990; Suarez and Simunek, 1997).

Details of chemical equilibrium models and the development of UNSATCHEM are found in Suarez and Simunek (1997). UNSATCHEM was developed in the late 1990's (Simunek et al., 1996) and was combined with Hydrus-1D in 2005 as Hydrus-1D version 3.0 (Simunek et al., 2005b). The Hydrus-1D version 3.0 (H1D) program (Simunek et al., 2005a) was utilized in this research to model management options for three locations in the lower Arkansas River Basin, near Rocky Ford, CO.

The objectives of this research were to examine the impact of management options on soil salinity in the lower Arkansas River Basin during an irrigation season. The specific goals were to examine the effects of crops or fallow management, irrigation applications at different water quantity and quality levels, and the influence of ground water depth. These specific goals were tested at three locations with initial salinity levels of low, medium and high. The goals were set forth to determine the potential magnitude

of remediation that may be possible under various management options and combinations.

## **Methods**

### *Data Sources*

Climate data were downloaded from the CoAgMet webpages for *CSU Rocky Ford Expt* location (CoAgMet, 2004). The selected weather station is located on the Colorado State University Experiment Station, 4 km southeast of Rocky Ford, CO. Climate data were downloaded for 2004, beginning in March and continuing through October. A total of 245 days were downloaded to include precipitation, temperature (daily average and amplitude) and potential evapotranspiration (PET) in the modeling. The PET was separated into categories of transpiration and evaporation to fit the H1D model input requirements. Separation was based upon the probable soil surface evaporation as a function of plant cover development. A baseline of  $0.5 \text{ cm day}^{-1}$  was used as the potential maximum soil evaporation. This level decreased as a function of the assumed root growth as a surrogate for above ground growth, beginning on day 30. A linear decrease in evaporation continued until the transpiration was approximately 85% of the PET on day 75.

Three locations were selected for the modeling based upon their chemistry and EC levels. The Low EC Soil Profile (LESP) was selected for its low initial EC and chemical concentrations, High EC Soil Profile (HESP) had the highest EC and chemical concentrations, whereas Medium EC Soil Profile (MESP) was in between LESP and

HESP for EC and chemical concentrations (Figure 4.1). Chemical and soil properties data were obtained from soils sampled to 120 cm depth using a Giddings soil sampler (Fort Collins, CO, USA; [www.soilsample.com](http://www.soilsample.com)). The cores were separated into 30 cm segments for chemical, texture and bulk density analyses. Samples were processed according to methods in Janzen (1993). Extract waters were filtered through a 0.45  $\mu\text{m}$  filter and were tested at the Colorado State University Soil Water and Plant Testing Laboratory. Cations (Ca, Mg, K and Na) were tested with inductively couple plasma spectroscope (ICP). The anions (Cl and  $\text{SO}_4$ ) were tested with ion chromatography (IC).

Ground water chemical data were supplied from research through the overall project (Salinity and Waterlogging Project, unpublished data, 2005). The depth to ground water was based upon results of the overall monitoring (Gates et al., 2002; Burkhalter and Gates, 2005). The irrigation/surface water quality was downloaded from USGS water quality monitoring of the Arkansas River at Las Animas, CO (Station 07124000). Approximately 58 years of record were available from the USGS website (USGS, 2004). Average and maximum concentrations were used to model irrigation water quality.

Estimations of the mass of solids (mineral precipitates) in the soil profiles were determined by iteration so that the EC during initial time steps for each location was roughly equivalent to measured  $\text{EC}_e$ , and the minerals were not a source of additional soil solution salts. At LESP there were estimated calcite additions, but no gypsum additions were added to the soil profile. There were increasing gypsum and calcite estimated concentrations utilized at both MESP and HESP.

Soil properties (texture and bulk density) were used to estimate soil hydraulic parameters used in the H1D model using the Rosetta subroutine (Simunek et al., 2005a). Soil properties were developed for each 30 cm increment to a depth of 120 cm. Irrigation events began on day 15 (to wet the soil prior to initial root growth on day 30) and continued until day 195 with irrigation occurring on a 10 day cycle. Irrigation levels were entered at 0, 3, 5 or 10 cm applications. The level of irrigation was selected to allow soil water depletions between irrigation events so that wilting point was not reached (using a soil-water pressure of -1500 cm of water). The soils were not waterlogged from the combination of surface applications and ground water additions. Model convergence difficulties arose when soil-water contents were below wilting point, thus to ensure model run completions sufficient irrigation water application was used in the model to avoid wilting point.

#### *Hydrus – 1D Parameters and Designations*

Model parameters used in the H1D program included all available main processes including water flow, solute transport (major ion chemistry), heat transport, root water uptake, root growth and CO<sub>2</sub> transport. This section details the parameters required for model runs in the H1D program (Simunek et al., 2005a). The modeling was for a one-dimensional profile 120 cm long in a vertical direction, consisting of four soil layers (30 cm each) but one comprehensive layer for mass balance calculations. The model was run for 245 days with a one day maximum time step interval, although the time step for both the solute and water transport calculations was considerably less than the maximum time step. Eight months (245 days) of data were used in the modeling to allow an equilibration to be reached for temperature, soil moisture and salinity chemistry inputs,

before root growth began, and to avoid issues with frozen soils and precipitation other than rain.

The van Genuchten-Mualem model for single porosity models was selected, with no air-entry values and without hysteresis. Hydraulic boundary conditions were altered to meet model run requirements. The upper boundary was an atmospheric boundary condition with surface run off, whereas the lower boundary conditions were either free drainage or variable pressure head (to mimic ground water levels).

Seven chemical solution concentration combinations were used, the first four represented the soil layers, the fifth for irrigation water quality inputs, the sixth as a chemically free precipitation input (rain), and the seventh was ground water quality. Chemical boundary conditions varied based upon the model run goals, but were typically an upper concentration flux boundary condition and a lower concentration flux boundary condition or zero gradient. The zero gradient designation assumed that the condition below the boundary was similar to that above the boundary. The time weighting selected was the Crank-Nicholson scheme, while the space weighting scheme selected was Galerkin finite elements. Cation exchange capacity (CEC) composition was unchanged throughout all the runs for a field.

Heat transport modeling was based on a loam default parameter for the entire depth, with an upper temperature flux boundary condition and a lower zero gradient boundary condition. All the  $\text{CO}_2$  (g) transport and production parameters were based upon the model default values. Root water uptake parameter was selected for a grass using the Feddes' model, with no solute stress (to maximize transpiration). The root growth began on day 30, finished on day 75, with harvest (or plant cessation) on day 210.

Model runs were designed to test for the implications of management changes by manipulating the H1D program input. There were tests of the ground water depth, mimicked at the lower boundary with either a constant -300 cm of water pressure or as free draining, two irrigation water qualities, and the factors of crop growth and subsequent removal of soil water from the root zone (Table 4.1). Each run was modeled on all three fields, with slight modifications to meet irrigation demands as soil texture and water holding capacity altered between locations.

Each model run result was presented along with the original composition as measured/calculated from saturated paste extracts, labeled Initial. Run 1 modeled a ground water table and upper boundary water inputs from precipitation in a field left fallow; no root uptake and no transpiration values. Run 2 modeled a grass crop, in an irrigated location without a ground water table, but with an average irrigation water quality. Run 3 modeled a grass crop, in an irrigated location with a ground water table, and with an average irrigation water quality. While Run 4 modeled a grass crop, in an irrigated location with a ground water table, and with the maximum expected irrigation water quality concentrations from the Arkansas River (Table 4.2).

## **Results and Discussion**

The climate station at Colorado State University Rocky Ford Experiment Station at Rocky Ford, CO, measured 32.4 cm of precipitation in 2004 over the 245 days used in the modeling (Table 4.1). The average of the mean daily temperature was 16.6 °C for the 245 days in 2004. The mean of the daily amplitude in the temperature was 9.4 °C. For

modeling purposes the daily climate data were used (data not presented). Both the surface irrigation and ground waters were dominated by  $\text{SO}_4$  anions, and not Cl anions, which suggested that Ca levels in the soil solution were controlled by  $\text{SO}_4$  (Skarie et al., 1987b). The Ca and Na were roughly equivalent in the irrigation water concentrations (Arkansas River water) for both the average concentrations and the maximum expected concentrations, but ground water Na concentration was  $11.1 \text{ meq L}^{-1}$  and Ca concentration was  $8.1 \text{ meq L}^{-1}$  (Table 4.2). Soil textures range between clay and silt loams, with the majority of the soils falling into the loam category (Table 4.3). Bulk densities ranged between a maximum of  $1.65 \text{ g cm}^{-3}$  and a minimum of  $1.30 \text{ g cm}^{-3}$  (Table 4.3).

Initial soils water contents were entered at -1 cm of pressure (as water), to approximate saturated paste extract measurements. As the soils dry down through evaporation/transpiration, the initial soil solution chemistry was expected to modify as some salts become saturated and minerals precipitated while other salts would concentrate, and/or the soil profile would drain, leaching some chemical constituents below the modeled profile (Oster and Rhoades, 1990). The initial water contents varied because of the soil textures utilized. The initial water contents at LESP were approximately 0.4 initially, but for each of the four runs there was a decrease in the water content by day 245 (Figure 4.2).

The LESP – Runs 1, 3 and 4 the water content at the lower boundary (120 cm depth) were all at approximately a water content of 0.27, which corresponds to the -300 cm of pressure as water used to represent the influence of the ground water table (Table 4.1). The LESP – Run 2 had a decrease in the water content to approximately 0.18, due

to the free drainage designation for the lower boundary (Figure 4.2 and Table 4.1). Similar results occur at MESP, except for Run 2 which was above the -300 cm pressure since the clay layer at the 90 to 120 cm depth (Figure 4.3 and Table 4.3). At HESP, the final water content results were similar to LESP in that the lower boundary/ground water influence was apparent (Figure 4.4). All three locations had a predicted surface/near surface drying effect due to the evaporation leading to salts being drawn upward through capillary rise and then precipitated at the soil surface. This was similar to measured results in North Dakota (Timpson et al., 1986; Skarie et al., 1987b; Steinwand and Richardson, 1989).

### *Salinity Indicators*

The initial input, along with the four runs, were presented for each of the three fields. The LESP was the field with the lowest initial EC (Figure 4.5), MESP was between the LESP and HESP for EC (Figure 4.6), and HESP had the highest EC levels (Figure 4.7). Ground water effects and influences were apparent by the convergence in the EC in Runs 1, 3 and 4 at MESP and at HESP at the 120 cm depth (Figures 4.6 and 4.7).

The approximate EC convergence of all the runs at LESP was coincidental (Figure 4.5) because the apparent convergence occurred for SAR values for LESP – Runs 1, 3 and 4, but not for Run 2 (Figure 4.8). At LESP, there was a difference between the depths with the highest SAR values. For Runs 2, 3 and 4 the maximum SAR values were between 20 and 70 cm depth, but for Run 1 the maximum SAR value was at 120 cm below the surface and associated with the lower boundary layer pressure and

concentrations of the ground water. The depth of the peak SAR values in LESP – Runs 2, 3 and 4 were due to the crop uptake and transpiration of water, thus selectively leaving the salts in the soil profile (Figure 4.8). Results similar to those at LESP for SAR also occurred for the matching runs at MESP (Figure 4.9). For the HESP runs, there was a peak SAR value for Run 1 at 100 cm below the surface, due to incomplete leaching of the initial salt concentrations (Figure 4.10).

Wienhold and Trooien (1995) studied salinity management options in lysimeters, with alterations to water volumes applied and water quality. They found that sodicity changes were persistent, and that irrigation was a viable option if the water quality was not an issue. Salt accumulation on the soil surface was a potential issue. There were similar patterns to the SAR values in the soil profiles between these modeled parameters and those measured by Wienhold and Trooien (1995).

### *Salinity Ions*

Chemical mass balances from the model runs are listed in Tables 4.4 through 4.6. Calcium solid concentrations at LESP for Run 1 decreased from the initial input value, due to calcite dissolution based upon the decrease of the “mass in solid” for both the Ca and the  $\text{HCO}_3$  (Table 4.4). (NOTE: In order to remain consistent with H1D output and labels, mass will be used to describe the chemical/mineral concentrations.) There was an accumulation of Ca on the soil surface (outside of the soil profile upper boundary) due to soil surface evaporation, which led to the net positive (upward) values of the Ca, as well as the other constituents in Run 1.

At LESP – Runs 2, 3 and 4 there were increases in the net Ca solid concentrations as calcite and gypsum precipitates formed in the soil profile (Table 4.4). For example, at

LESP – Run 3 there was a net increase in the total mass in the profile of 27,000 meq cm<sup>-2</sup> of Ca. (NOTE: The units of meq cm<sup>-2</sup> represents a hypothetical surface expression of 1 cm by 1 cm for the profile modeled, or for 120 cm depth, thus offering a 3-D unit from a 1-D model.) The sum of the Ca as a solid and the Ca in solution approximately equaled the overall net increase of 27,000 meq cm<sup>-2</sup> of Ca, since there was an increase of 24,000 meq cm<sup>-2</sup> of Ca as a solid (or precipitates as calcite or gypsum), and 2500 meq cm<sup>-2</sup> of Ca in solution. There was an error of approximately 2800 meq cm<sup>-2</sup> added to the system, or a 0.7 % error in the Ca mass balance. The negative value of the cumulative upper flux designates that Ca crossed the upper boundary (downward) into the soil profile with 21,100 meq cm<sup>-2</sup> from surface irrigation water inputs. Whereas the positive value for the lower boundary indicated an 2800 meq cm<sup>-2</sup> input from the ground water to the soil profile. Gypsum precipitates were apparent from the SO<sub>4</sub> increases in the solid concentrations when compared to the initial concentration. Changes in the calcite precipitates were apparent from the HCO<sub>3</sub> increases in the solid concentrations when compared to the initial mass of the HCO<sub>3</sub> as a solid. The initial HCO<sub>3</sub> mass in solution was based upon atmospheric concentrations of CO<sub>2</sub> and initial calcite inputs (Table 4.4).

Chemical mass balance results are listed for MESP (Table 4.5) and HESP (Table 4.6). There was an increase in the relative error as the concentrations increased along with the greater concentrations of the modeled factors between the runs and the locations. Calcium concentrations in the soil solution were variable between locations and runs. The LESP – Run 1 had decreases in the Ca in solution when compared to the initial value (Figure 4.11). This decrease was primarily due to salt transport to the soil surface caused

by evaporation, since Run 1 did not have irrigation water inputs to effectively leach salts out of the profile. The LESP – Runs 2, 3 and 4 all had peak soil solution Ca concentrations in the root zone. There were Ca inputs into the profile from irrigation in these runs but not sufficient volumes to effectively leach the inputs to below the lower boundary in Run 2, while Runs 3 and 4 also had Ca inputs from the ground water (Table 4.4). Patterns similar to LESP runs occurred at MESP and at HESP (Figures 4.12 and 4.13). At MESP and HESP – Run 1 there were indications of the Ca flux to the soil surface based upon the high levels of Ca at the upper boundary, as well as the positive values for the ions in the mass balance calculations (Tables 4.5 and 4.6).

A lack of peak concentrations in the Ca, at all three locations, was due to the tendency for Ca to precipitate out of solution causing Ca concentration profiles to appear flattened at greater concentrations (Figures 4.11 to 4.13). Additionally, the variation in gypsum solubility also affected the peak concentrations, since gypsum solubility is influenced by the ionic strength of the solution (Nakayama, 1971). Calcium accumulation as a solid will be discussed in later.

Sodium soil solution concentrations at LESP – Run 1 indicated a loss of Na to both the surface and to below the lower boundary (Table 4.4 and Figure 4.14), with the Na concentrations converging toward the ground water influenced concentration. For LESP – Runs 3 and 4 had almost identical peak Na soil solution concentrations in the profile at approximately 50 cm depth, but separated by the magnitude of their concentrations (Figure 4.14). This was due to the variation in the irrigation water quality used, suggesting that the processes were essentially the same for salt accumulation in the soil for similar physical conditions (e.g. root uptake, irrigation rates and evaporation), but

were unique due to salt concentrations. Extrapolation from this result suggests that changes in irrigation or ground water quality primarily affect the magnitude of Na accumulation, not the location in the profile, assuming that there were no detrimental effects upon the crop to reduce plant uptake of soil water. For LESP – Run 2 had incomplete leaching of the Na from the soils, due in part to irrigation water inputs and root water uptake. Run 2 did have a deeper peak Na concentration in the soil profile than did Runs 3 and 4 due to the lack of water and additional salts from the ground water (Figure 4.14).

Results similar to the LESP runs occurred in the Na solution concentrations for MESP and HESP runs (Figures 4.15 and 4.16). There were some slight differences with depth, related to the variations in the soil textures, but the essential comparison of the concentration peaks between Run 3 and 4 was similar to runs at LESP. At HESP, however, the large initial Na soil solution concentrations influenced the final shape of the Na soil solution concentrations in the soil profile, especially for Run 1 which had limited water inputs (Figure 4.16).

Results for the Mg, K and Cl in the soil solution are not presented graphically, as the results were similar to the Na concentrations. Since there were no changes in these constituents due to solid formation in the soil profile, and as part of the initial conditions, CEC exchanges were not allowed to change, the essential mass balance data are presented in Tables 4.4 through 4.6.

Sulfate in the soil water solution behaved similarly to the sodium concentrations, in that the peak concentrations occurred in the root zone, and that there was a potential source from the ground water (Figures 4.17 to 4.19). At LESP – Run 1 there was a net

loss of  $\text{SO}_4$  to the soil surface (Table 4.4). For Runs 1 and 2 there was a downward flux of  $\text{SO}_4$  to below the lower boundary. For Runs 2, 3 and 4 there was a loss of  $\text{SO}_4$  from the soil solution to solids, but the net flux into the soil from the upper boundary does not imply that there was not a flux of  $\text{SO}_4$  to the surface during times of limited water inputs, such as after the irrigation stopped on day 195. For Runs 2, 3 and 4 there was a net increase in the  $\text{SO}_4$  in the soil profile (Table 4.4).

At MESP, there were increases in the  $\text{SO}_4$  with depth for the initial condition (Figure 4.18). This sequential increase with depth, coupled with the initial Ca concentrations in the soil solution (Figure 4.12) suggested that there was a significant source for both Ca and  $\text{SO}_4$  initially in the soil profile. Based on ion pairing, gypsum mineral accumulations were assumed to exist in the soil and were dissolved during chemical analysis. In the MESP location, the results were similar to LESP runs, but for MESP – Run 3 the net flux of  $\text{SO}_4$  was to the soil surface not downward into the soil profile. There was a net loss of  $\text{SO}_4$  from the lower boundary for all runs at MESP (Table 4.5). There were indications of a concentrating effect for Run 1 in the shallow depths for  $\text{SO}_4$  due to soil surface evaporation and a lack of irrigation for this run (Figure 4.18).

Similar results occurred at HESP, except that for HESP – Runs 2, 3 and 4 the net  $\text{SO}_4$  flux in the soil solution was downward through the soil profile and from solids (calcite and gypsum mineral precipitates), with a net loss of  $\text{SO}_4$  overall (Table 4.6). There were indications of  $\text{SO}_4$  concentrating at the soil surface for Run 1, even though there was a net flux into the soil profile (Figure 4.19).

## *Precipitates*

Calcite and gypsum were the primary salt minerals predicted to form in the calcareous soils of the lower Arkansas River Basin. The precipitation of both gypsum and calcite can occur together, on top of one another and can be unavoidable with sufficient evaporation (Wigley, 1973; Keren and Kauschansky, 1981). The precipitation and dissolution reactions in the H1D model for both calcite and gypsum influenced the total salt mass in the profile. At the LESP location, calcite concentrations decreased for Run 1, but increased for Runs 2, 3 and 4, based upon changes in the mass of both the Ca and HCO<sub>3</sub> concentrations (Table 4.4). There was significant redistribution of calcite from the initial distribution for all the model runs (Figure 4.20). All the runs at LESP had calcite precipitates forming at the top of the profile, but Runs 1, 2 and 3 all had little to no calcite for the next several centimeters into the soil profile. Run 4 maintained a calcite concentration throughout the profile, with no locations where calcite was completely dissolved (Figure 4.20).

The LESP – Run 2 had the largest accumulation of calcite at the bottom of the soil profile, but this accumulation may have been due to the slight change in assumptions of the model since this run had a free drainage lower boundary condition (Figure 4.20). Calcite dissolution appeared to be strongly connected to the change in the soil texture at LESP since at the 30 cm depth there was a change from a loam to a clay loam, which created conditions that allowed for calcite precipitation. Calcite precipitation was most likely because of a change in the hydraulic conductivity leading to a “perching” of soil water and chemical concentrations along the boundary between soil layers (Table 4.3).

At LESP there were no gypsum minerals in the initial condition and no gypsum precipitates formed during Run 1. However, gypsum can be assumed to form as a soil surface evaporite (above of the model boundary) during Run 1, based upon the flux upward for both Ca and SO<sub>4</sub> (Table 4.4). Gypsum precipitated in Runs 2, 3 and 4 in the soil profile (Figure 4.21). The solubility of gypsum offers clues to the transport of salts and associated water contents, since it typically precipitates as water contents decrease (Hardie and Eugster, 1970). Additionally, gypsum formation occurs during winter and under freezing conditions and contributes to long-term accumulation (Hardie and Eugster, 1970; Marion and Farren, 1997). There were similar patterns between gypsum accumulation and depth of the highest EC (Figure 4.5) and the depths where the Ca concentrations in the soil solution had “flattened” peak values (Figure 4.11). This combination of events suggested that soil solution Ca concentrations reached saturation levels and precipitated calcite and gypsum minerals, thus flattening the peak Ca concentrations.

At MESP, there were calcite and gypsum minerals in the initial conditions that were redistributed between the model runs (Figures 4.22 and 4.23 ). There was a net loss of solids for Runs 4 and 6, but increases in the precipitated solids for Runs 2 and 4 based upon the mass in solution and as solids. There was a decrease in gypsum concentrations in the profile for all the runs, and Runs 2 and 4 had an increase in the calcite mineral based upon changes of the HCO<sub>3</sub> and SO<sub>4</sub> allocated to the solids (Table 4.5). Similar to LESP, there was an accumulation of calcite at the upper boundary for all the runs apparent from the large calcite deposits near surface (Figure 4.22), but Run 1 had a layer of gypsum that also formed (Figure 4.23). The accumulation of Ca minerals near the

upper boundary indicated that the Ca losses from the upper boundary would lead to similar salts forming a salt evaporite crust outside of the modeled profile. Influence of the clay soil was apparent in the lack of change in both the calcite and gypsum for the 90 to 110 cm depth maintained by the high water contents (Figure 4.3), and did not increase in the gypsum precipitates as occurred from the 20 cm to approximately 90 cm depth (Figure 4.23).

Like the MESP runs, at HESP there were increases and decreases between the model runs for the solids, and indications of salt crust forming on top of the upper boundary; however, there were no losses in the mass of calcite during any of the runs (Table 4.6). Calcite concentrations increased for all the HESP runs between 30 cm and 110 cm below the surface, with most of the initial mineral dissolution from the uppermost 30 cm of the profile. Runs 2 and 3 had significant calcite precipitates between 10 cm and 30 cm depth (Figure 4.24). For gypsum, the primary additions occurred at approximately 20 cm depth and the concentrations decreased to approximately the 90 cm depth. Peak concentrations occurring at 22 cm depth, at approximately  $70 \text{ meq kg}^{-1}$  for HESP – Run 4 which suggested that the greater chemical concentrations in the irrigation water for Run 4 influenced the gypsum precipitation (Figure 4.25).

#### *Analysis of Assumptions and Error Sources*

It was assumed that irrigation water would be available, both in time and in the quantities required. Treatment of the chemical constituents had assumptions based upon soil and chemical interactions and that surface and ground water qualities and/or depths did not fluctuate with time. It was assumed that soil properties did not fluctuate on less than a 30 cm scale.

Since water resources are limited in Colorado, water rights may not be fulfilled for junior rights, and during severe droughts, senior rights as well (Radosevich et al., 1976). The assumption that water was available in sufficient quantities to meet the modeled irrigation levels may be inappropriate throughout the basin. In many cases irrigation opportunities are based upon availability in the canals, which is determined by the irrigation company and their goals of seeking to minimize seepage losses and maximize calls by growers (Radosevich et al., 1976; Miles, 1977; Hartman, 2003). Issues with limited available water for crop uptake led to some issues with model convergence and completion of H1D model runs, thus leading to the assumption that crop requirements would be met in these model runs.

The Gapon selectivity parameters in the H1D program, which determine the exchange ratios associated with CEC, were set for zero exchange (e.g. Ca:Na) for the three parameters and all depths. The Gapon selectivity parameters were zeroed because of a lack of model convergence when both ground water and irrigation water quality were included in the model at the input concentrations.

Infiltration rates estimated by the H1D program for HESP may not represent actual infiltration rates. Wittler, J.M., (unpublished, 2004) found that after 24 hours of furrow irrigation the depth of the wetting front was shallow; however, actual infiltration rates were not measured. This observation suggests that the actual infiltration was not as deep or as effective as modeled, thus the pattern of the initial salt concentrations and EC were due to long-term accumulation coupled with poor infiltration.

Multiple years of climate data were also tested (not reported), but were found to offer little in the understanding of the soil chemical profiles, since the volume of applied

irrigation water significantly surpassed the precipitation/rain for all locations for Runs 2, 3 and 4 (Table 4.1). Differences between 2003 and 2004 rain/precipitation were significant, with 2003 receiving 19.7 cm of precipitation with 153.5 cm of PET during the modeling period of 245 days, versus 32.4 cm of precipitation and 141 cm of PET in 2004. For Run 1, where there was no irrigation, the salt profiles typically varied only in the depth of the final profile and not in the general shape and pattern.

Additional ground and surface water qualities were processed, but these typically resulted in changes in the magnitude of the salts in solution but not the depths, and therefore, were not included in this discussion. Changes in ground water depth also were modeled, but these runs typically changed the depth of the peak salt concentrations in the soils as is apparent in the differences in Runs 2 and 3, but from a bottom upward direction.

## **Conclusions**

Modeling results of the salt concentrations in calcareous/gypsiferous soils of the lower Arkansas River Basin imply that the current salinity levels developed over time and are redistributed on an annual basis, but not removed. Management of these soils is a complex issue that is compounded by multiple factors and continually changing variables, as water contents in the soils affect the salts in solution. This modeling effort assumed that both the surface and ground water qualities would not vary over the irrigation season; this is not an adequate assumption since quality in the river does change as flow volume changes due to spring snowmelt.

The two factors that are potentially manageable for salinity-impacted agricultural fields in the lower Arkansas River Basin are the amount of irrigation water applied over the irrigation season and the depth to the ground water. Modeling results show that changes in applied water volumes influenced the depth of the peak salt concentrations in the soil solution, as solids in the soils or as evaporites on the soil surface. Fallow runs without irrigation had little to no leaching of salts from the profile, especially in the locations with higher salt concentrations. Changes in the depth to the water table also shifted the peak salt accumulations in the soil, but the ground water also acted as source of salts. Over a meter of irrigation water was applied during irrigated model runs and often adequate water contents for plant growth were barely maintained. Water availability limits agricultural productivity in the lower Arkansas River Basin, even under irrigation.

Changes in the quality of the irrigation water did not change the depth of the peak accumulation of salts in the soil profile. As irrigation water salt concentrations increased, the magnitude of soil solution salt concentrations increased, but the depth of those peak concentrations was related to the water input, either from surface or ground water sources. Therefore, a “better quality” of water is not sufficient for the remediation of these soils if the quantity of water is not also increased. Additionally, adequate water supplies are only effective for remediation if infiltration at the soil surface is not hindered by silting in of the pore spaces, dispersion, clogging by salt accumulation (evaporites), or by the expansion of the shrink-swell clays that occur in the basin and/or by high ground water tables.

Implications of this modeling effort suggest that remediation of the salinity impacted soils in the lower Arkansas River Basin are unlikely to be successful without a multiple pronged approach. It is concluded that no single management option will lead to the improvements needed to improve crop production, especially at the higher EC locations that require remediation. Active and potentially costly (in terms of time and/or water that could be used elsewhere) management options are required to improve soil salinity problems.

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## Tables

Table 4.1. Model run parameters and boundary conditions, where LESP is the Low EC Soil Profile, MESP is the Medium EC Soil Profile and HESP is the High EC Soil Profile..

Location	Run	Crop	Precipitation	Irrigation	Irrigation Water Concentration	PET †	Actual Transpiration	Lower Boundary Pressure
			cm	cm		cm	cm	cm
LESP	Run 1	Fallow	32.4	0	--	108 (0)	0	-300 cm
	Run 2	Grass	32.4	80	Average	141 (87)	65.3	Free Drainage
	Run 3	Grass	32.4	77	Average	141 (87)	66.1	-300 cm
	Run 4	Grass	32.4	77	Maximum	141 (87)	66.1	-300 cm
MESP	Run 1	Fallow	32.4	0	--	108 (0)	0	-300 cm
	Run 2	Grass	32.4	80	Average	141 (87)	65.8	Free Drainage
	Run 3	Grass	32.4	75	Average	141 (87)	65.7	-300 cm
	Run 4	Grass	32.4	75	Maximum	141 (87)	65.6	-300 cm
HESP	Run 1	Fallow	32.4	0	--	108 (0)	0	-300 cm
	Run 2	Grass	32.4	91	Average	141 (87)	65.3	Free Drainage
	Run 3	Grass	32.4	91	Average	141 (87)	65.5	-300 cm
	Run 4	Grass	32.4	91	Maximum	141 (87)	65.5	-300 cm

† Potential Transpiration in parenthesis.

Table 4.2. Water quality concentration parameters for model runs, surface and ground waters.

Water Type	Quality	Ca	Mg	Na	K	HCO <sub>3</sub>	SO <sub>4</sub>	Cl
		-----meq L <sup>-1</sup> -----						
Irrigation Water	Average	12.8	8.2	11.8	0.14	4.2	26.4	2.12
	Maximum	19.1	14.2	21.8	0.22	5.4	44.6	3.95
Ground Water	Average	8.1	2.3	11.1	0.10	5.9	49.5	2.14

Table 4.3. Soil parameters for model runs and hydraulic conductivity estimations, where LESP is the Low EC Soil Profile, MESP is the Medium EC Soil Profile and HESP is the High EC Soil Profile..

Location	Depth	Sand	Clay	Silt	Class	Bulk Density
	cm	%	%	%		g cm <sup>-3</sup>
LESP	0 to 30	32.5	22.5	45.0	Loam	1.32
	30 to 60	27.5	32.5	40.0	Clay loam	1.65
	60 to 90	30.0	25.0	45.0	Loam	1.56
	90 to 120	25.0	17.5	57.5	Silt loam	1.42
MESP	0 to 30	41.3	22.5	36.3	Loam	1.55
	30 to 60	43.8	22.5	33.8	Loam	1.40
	60 to 90	12.5	46.3	41.3	Silty clay	1.43
	90 to 120	5.0	70.0	25.0	Clay	1.48
HESP	0 to 30	45.0	23.8	31.3	Loam	1.56
	30 to 60	38.8	17.5	43.8	Loam	1.57
	60 to 90	36.3	17.5	46.3	Loam	1.46
	90 to 120	28.8	15.0	56.3	Silt loam	1.30

Table 4.4. Low EC Soil Profile (LESP) chemical mass balance concentrations and errors.

Run	Constituent	Cumulative Upper Flux	Cumulative Lower Flux	Mass in Solution	Mass Adsorbed	Mass in Solid	Total Mass	Absolute Error	Relative Error
							-----meq cm <sup>-2</sup> -----		%
Initial		--	--	35000	125000	188000	348000	--	--
	Ca	--	--	22200	53500	0	75800	--	--
	Mg	--	--	30600	17800	0	48400	--	--
	Na	--	--	1380	17800	0	19200	--	--
	K	--	--	4510	--	188000	193000	--	--
	HCO <sub>3</sub>	--	--	70900	--	0	70900	--	--
	SO <sub>4</sub>	--	--	60500	--	--	60500	--	--
	Cl								
Run 1		22900	2300	17300	125000	186000	329000	-1050	0.3
	Ca	6380	-6560	9340	53500	0	62900	-34	0.1
	Mg	8840	-5140	17000	17800	0	34900	-473	1.4
	Na	642	-210	544	17800	0	18400	-13	0.1
	K	15000	11100	3670	--	186000	190000	-1330	0.7
	HCO <sub>3</sub>	17600	-3760	51500	--	0	51500	-2010	3.9
	SO <sub>4</sub>	26400	-17000	16600	--	--	16600	491	1.9
	Cl								
Run 2		-27000	11600	39300	125000	232000	396000	-9340	2.4
	Ca	-25700	-9950	41300	53500	0	94800	-3280	3.5
	Mg	-37300	-13400	59200	17800	0	77100	-4750	6.2
	Na	10	-381	1110	17800	0	19000	-115	0.6
	K	3790	26000	2230	--	219000	221000	-6680	3.0
	HCO <sub>3</sub>	-85600	-34000	120000	--	12500	133000	-9970	7.5
	SO <sub>4</sub>	15300	-22100	25500	--	--	25500	-2370	9.3
	Cl								
Run 3		-21100	2810	37500	125000	212000	375000	-2760	0.7
	Ca	-23000	-7510	38100	53500	0	91600	-421	0.5
	Mg	-33300	-2710	62400	17800	0	80200	-1170	1.5
	Na	59	-272	1090	17800	0	18900	-35	0.2
	K	6430	12000	3190	--	198000	201000	-3060	1.5
	HCO <sub>3</sub>	-76800	12600	150000	--	14300	164000	-3790	2.3
	SO <sub>4</sub>	16100	-19700	25100	--	--	25100	-440	1.7
	Cl								
Run 4		-99100	9410	37900	125000	293000	456000	608	0.1
	Ca	-42400	-7570	56400	53500	0	110000	637	0.6
	Mg	-65600	-2770	92600	17800	0	110000	718	0.7
	Na	-178	-274	1290	17800	0	19100	-6.6	0.0
	K	-57500	18700	3280	--	267000	270000	-1080	0.4
	HCO <sub>3</sub>	-135000	12500	192000	--	26400	218000	558	0.3
	SO <sub>4</sub>	9870	-19800	30500	--	--	30500	284	0.9
	Cl	--	--	35000	125000	188000	348000	--	--

Units (meq cm<sup>-2</sup>) designate a hypothetical region with a surface area of 1 cm<sup>2</sup> for the designated depth, in this case 120 cm and is termed as a mass to remain consistent with model output.

Negative values designate a flux in a downward direction.

Table 4.5. Medium EC Soil Profile (MESP) chemical mass balance concentrations and errors.

Run	Constituent	Cumulative Upper Flux	Cumulative Lower Flux	Mass in Solution	Mass Adsorbed	Mass in Solid	Total Mass	Absolute Error	Relative Error
-----meq cm <sup>-2</sup> -----									
Initial									
	Ca	--	--	126000	125000	1750000	2000000	--	--
	Mg	--	--	124000	53500	0	177000	--	--
	Na	--	--	83500	17800	0	101000	--	--
	K	--	--	10300	17800	0	28200	--	--
	HCO <sub>3</sub>	--	--	3800	--	918000	922000	--	--
	SO <sub>4</sub>	--	--	312000	--	836000	1150000	--	--
	Cl	--	--	107000	--	--	107000	--	--
Run 1									
	Ca	113000	-54000	76300	125000	1630000	1830000	4540	0.2
	Mg	14800	-53600	53300	53500	0	107000	2350	2.2
	Na	13500	-27700	41800	17800	0	59600	568	1.0
	K	1300	-4260	4600	17800	0	22400	169	0.8
	HCO <sub>3</sub>	24800	17900	5530	--	912000	918000	-2820	0.3
	SO <sub>4</sub>	112000	-137000	171000	--	720000	891000	7160	0.8
	Cl	14400	-32600	59400	--	--	59400	341	0.6
Run 2									
	Ca	71300	388000	71300	125000	2180000	2380000	-55500	2.3
	Mg	-19400	-52200	96300	53500	0	150000	-5140	3.4
	Na	-34200	-30600	93900	17800	0	112000	-6850	6.1
	K	-4470	-4140	11500	17800	0	29300	-811	2.8
	HCO <sub>3</sub>	29200	431000	3270	--	1370000	1380000	-51400	3.7
	SO <sub>4</sub>	-1910	-121000	235000	--	809000	1040000	-15000	1.4
	Cl	2180	-32700	75500	--	--	75500	-3540	4.7
Run 3									
	Ca	65900	-62800	55700	125000	1700000	1880000	-3890	0.2
	Mg	-17200	-69600	73000	53500	0	127000	-1420	1.1
	Na	-30500	-35900	81300	17800	0	99100	-3140	3.2
	K	-4000	-5580	9060	17800	0	26900	-313	1.2
	HCO <sub>3</sub>	23200	22100	2190	--	921000	924000	-2730	0.3
	SO <sub>4</sub>	3610	-168000	205000	--	778000	983000	-6920	0.7
	Cl	2060	-47000	58400	--	--	58400	-674	1.2
Run 4									
	Ca	-120000	-62900	53600	125000	1890000	2070000	-4830	0.2
	Mg	-37500	-69700	94900	53500	0	148000	-3160	2.1
	Na	-64100	-36100	117000	17800	0	135000	-5660	4.2
	K	193	-5590	4600	17800	0	22400	-57	0.3
	HCO <sub>3</sub>	-156000	22200	2230	--	1100000	1100000	-2870	0.3
	SO <sub>4</sub>	-60100	-168000	264000	--	788000	1050000	-12400	1.2
	Cl	-4090	-47100	65400	--	--	65400	-1580	2.4

Units (meq cm<sup>-2</sup>) designate a hypothetical region with a surface area of 1 cm<sup>2</sup> for the designated depth, in this case 120 cm and is termed as a mass to remain consistent with model output.  
 Negative values designate a flux in a downward direction.

Table 4.6. High EC Soil Profile (HESP) chemical mass balance concentrations and errors.

Run	Constituent	Cumulative Upper Flux	Cumulative Lower Flux	Mass in Solution	Mass Adsorbed	Mass in Solid	Total Mass	Absolute Error	Relative Error
					-----meq cm <sup>-2</sup> -----				
%									
Initial									
	Ca	--	--	116000	125000	2690000	2930000	--	--
	Mg	--	--	160000	53500	0	213000	--	--
	Na	--	--	299000	17800	0	317000	--	--
	K	--	--	1040	17800	0	18900	--	--
	HCO <sub>3</sub>	--	--	4120	--	1810000	1820000	--	--
	SO <sub>4</sub>	--	--	483000	--	872000	1360000	--	--
	Cl	--	--	356000	--	--	356000	--	--
Run 1									
	Ca	99600	-66900	67900	125000	2560000	2760000	4620	0.2
	Mg	4410	-116000	33700	53500	0	87200	5870	6.7
	Na	5240	-233000	49800	17800	0	67600	11600	17.1
	K	98	-657	255	17800	0	18100	31	0.2
	HCO <sub>3</sub>	28100	18500	4480	--	1810000	1810000	-2940	0.2
	SO <sub>4</sub>	72800	-371000	136000	--	757000	892000	19300	2.2
	Cl	16400	-228000	102000	--	--	102000	9990	9.8
Run 2									
	Ca	53800	37400	44800	125000	2760000	2930000	-19100	0.7
	Mg	-34900	-148000	44400	53500	0	97900	2200	2.2
	Na	-51200	-282000	63100	17800	0	80900	5610	6.9
	K	-590	-926	727	17800	0	18600	-23	0.1
	HCO <sub>3</sub>	34300	127000	4180	--	1930000	1930000	-17800	0.9
	SO <sub>4</sub>	-58100	-445000	127000	--	836000	963000	5560	0.6
	Cl	3140	-315000	31900	--	--	31900	5930	18.6
Run 3									
	Ca	54600	-98600	54300	125000	2600000	2770000	811	0.0
	Mg	-35700	-147000	41900	53500	0	95400	6610	6.9
	Na	-52100	-273000	66500	17800	0	84300	11900	14.1
	K	-605	-875	752	17800	0	18600	18	0.1
	HCO <sub>3</sub>	37300	30200	4950	--	1810000	1820000	-4050	0.2
	SO <sub>4</sub>	-60900	-452000	166000	--	784000	950000	14100	1.5
	Cl	1690	-311000	27800	--	--	27800	15200	54.8
Run 4									
	Ca	-212000	-94600	51700	125000	2870000	3040000	4200	0.1
	Mg	-64300	-151000	64900	53500	0	118000	8650	7.3
	Na	-99400	-279000	105000	17800	0	122000	15200	12.4
	K	-951	-910	1020	17800	0	18900	63.7	0.3
	HCO <sub>3</sub>	-221000	35500	6280	--	2070000	2080000	-3540	0.2
	SO <sub>4</sub>	-149000	-462000	227000	--	792000	1020000	22400	2.2
	Cl	-6950	-314000	35300	--	--	35300	13600	38.6

Units (meq cm<sup>-2</sup>) designate a hypothetical region with a surface area of 1 cm<sup>2</sup> for the designated depth, in this case 120 cm and is termed as a mass to remain consistent with model output.

Negative values designate a flux in a downward direction.

## Figures

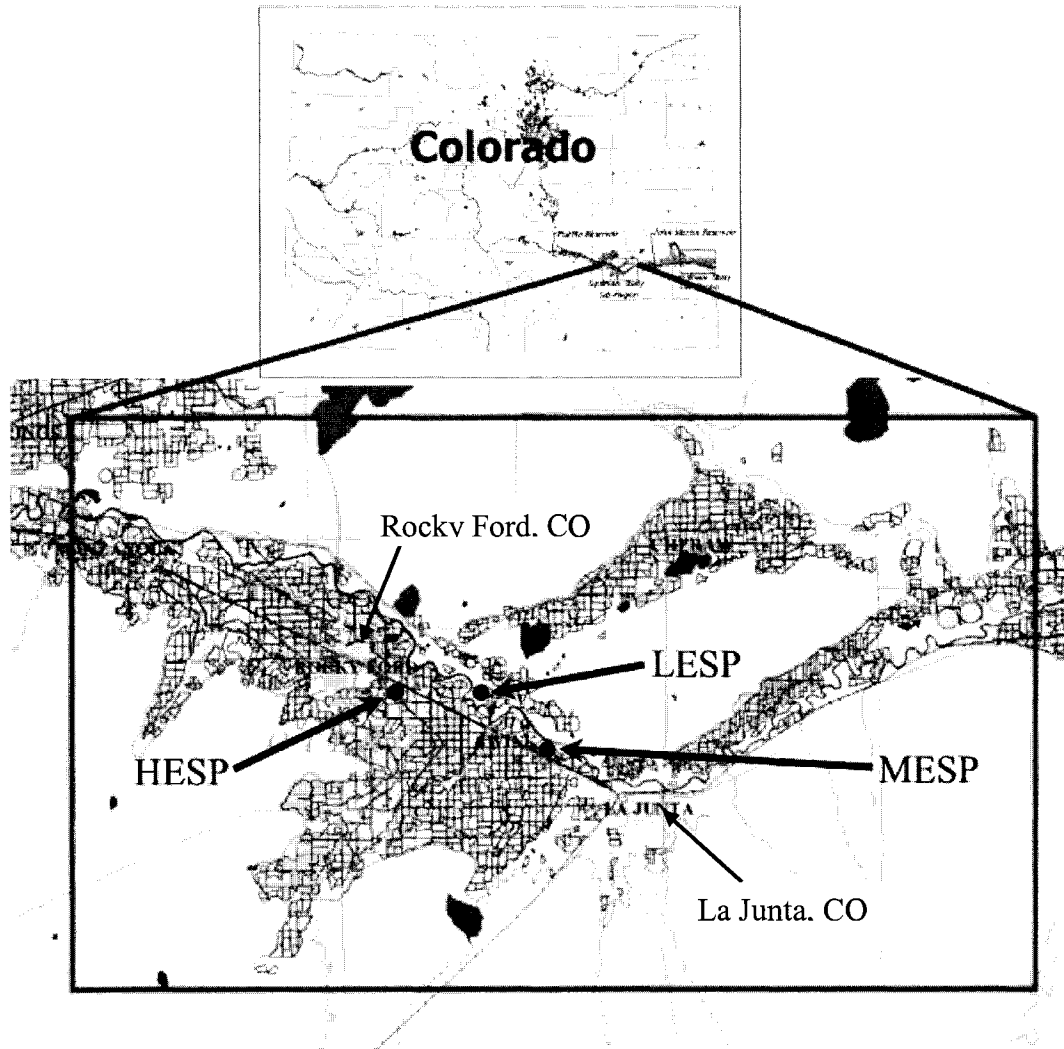


Figure 4.1. Map of the monitoring region of the Salinity and Waterlogging Project. Locations of soil chemical and property data in the Upstream sub-region are shown, where LESP is the Low EC Soil Profile, MESP is the Medium EC Soil Profile and HESP is the High EC Soil Profile.

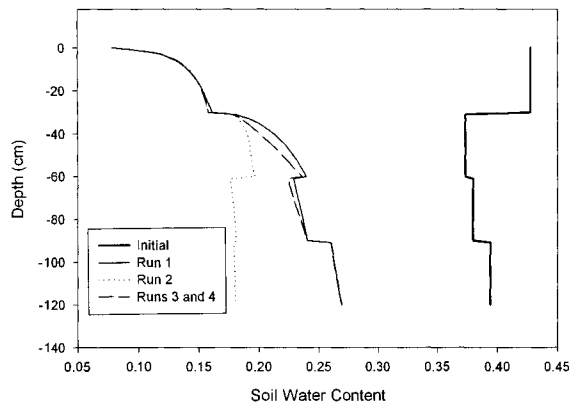


Figure 4.2. Low EC Soil Profile (LESP) initial soil water contents in the soil profile, and after 245 days.

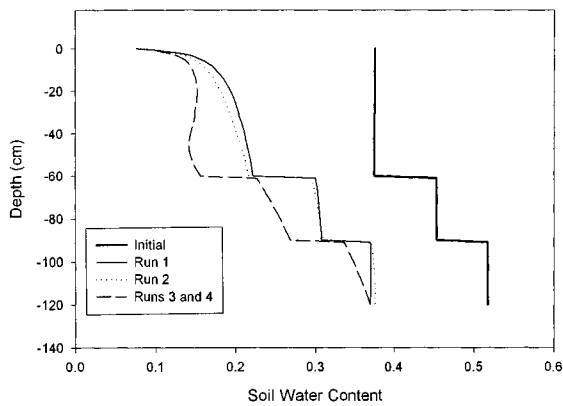


Figure 4.3. Medium EC Soil Profile (MESP) initial soil water contents in the soil profile, and after 245 days.

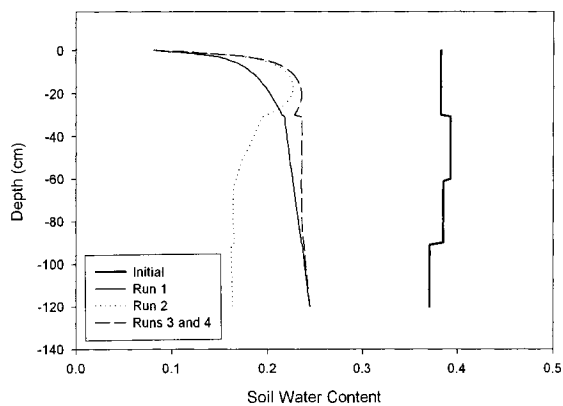


Figure 4.4. High EC Soil Profile (HESP) initial soil water contents in the soil profile, and after 245 days.

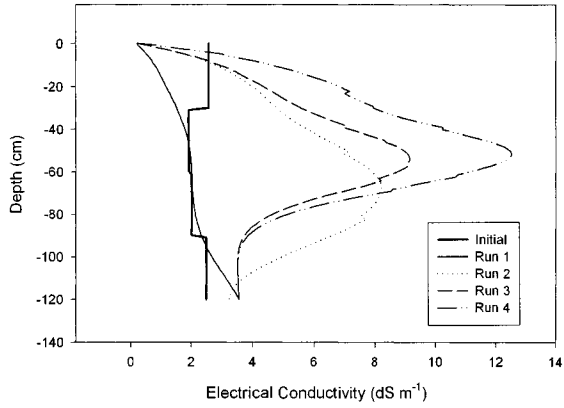


Figure 4.5. Low EC Soil Profile (LESP) initial electrical conductivity of the soil solution in the soil profile, and after 245 days.

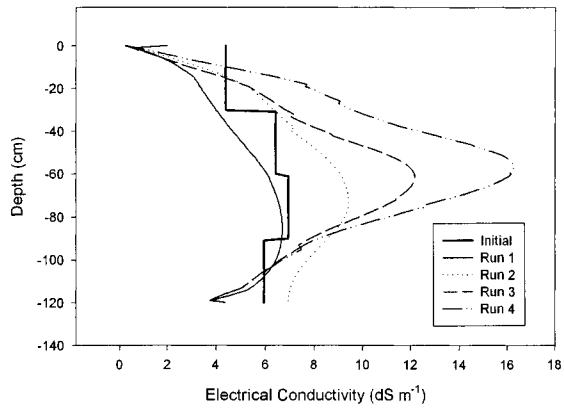


Figure 4.6. Medium EC Soil Profile (MESP) initial electrical conductivity of the soil solution in the soil profile, and after 245 days.

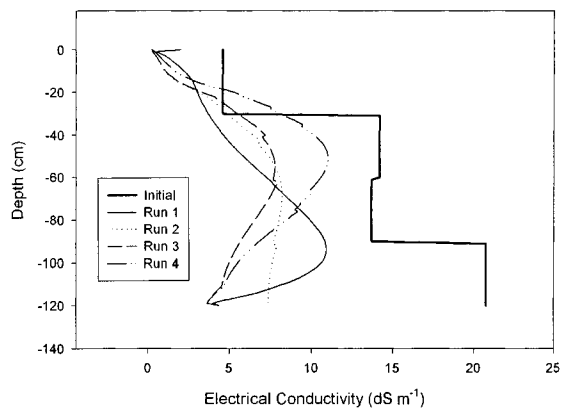


Figure 4.7. High EC Soil Profile (HESP) initial electrical conductivity of the soil solution in the soil profile, and after 245 days.

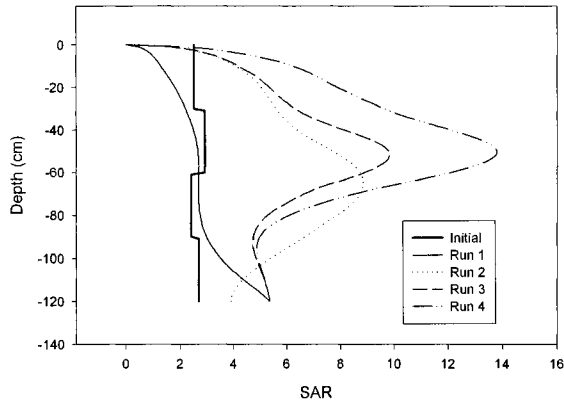


Figure 4.8. Low EC Soil Profile (LESP) initial sodium adsorption ratio of the soil solution in the soil profile, and after 245 days.

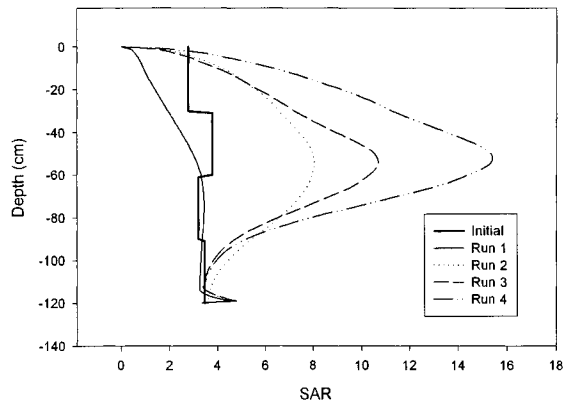


Figure 4.9. Medium EC Soil Profile (MESP) initial sodium adsorption ratio of the soil solution in the soil profile, and after 245 days.

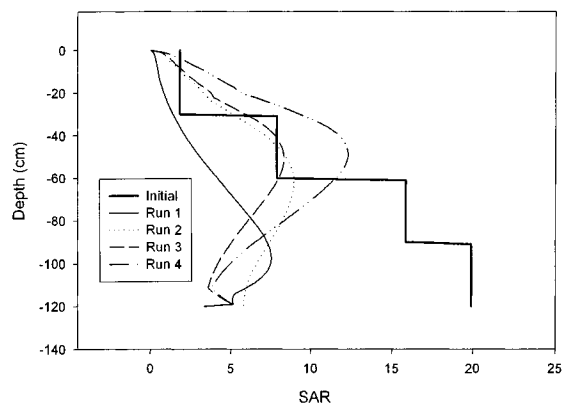


Figure 4.10. High EC Soil Profile (HESP) initial sodium adsorption ratio of the soil solution in the soil profile, and after 245 days.

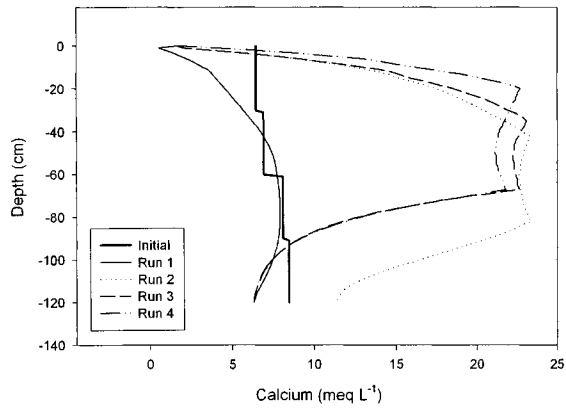


Figure 4.11. Low EC Soil Profile (LESP) initial calcium soil solution concentrations in the soil profile, and after 245 days.

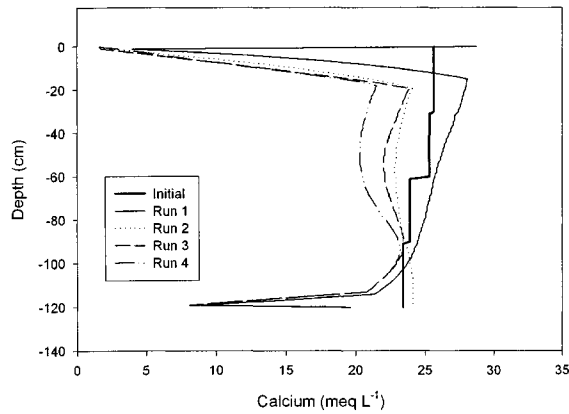


Figure 4.12. Medium EC Soil Profile (MESP) initial calcium soil solution concentrations in the soil profile, and after 245 days.

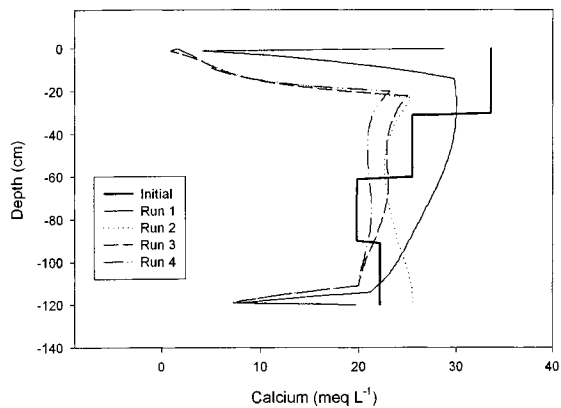


Figure 4.13. High EC Soil Profile (HESP) initial calcium soil solution concentrations in the soil profile, and after 245 days.

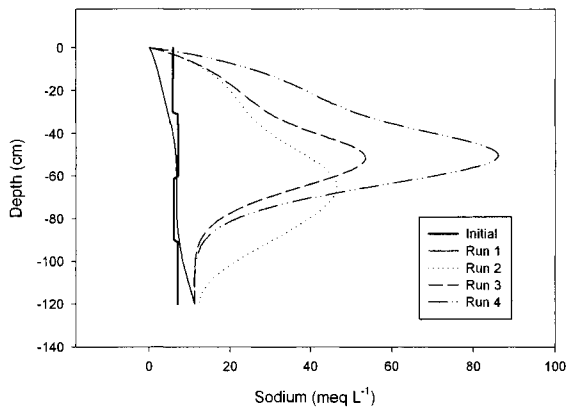


Figure 4.14. Low EC Soil Profile (LESP) initial sodium soil solution concentrations in the soil profile, and after 245 days.

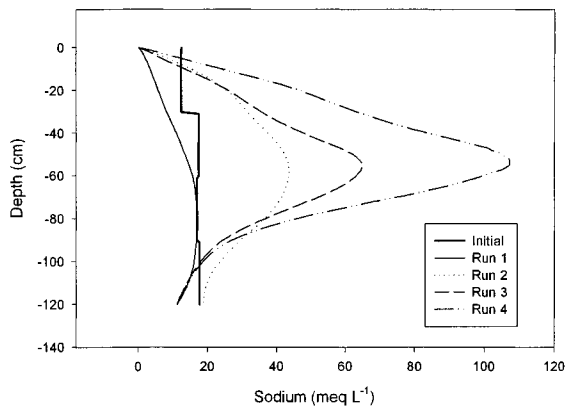


Figure 4.15. Medium EC Soil Profile (MESP) initial sodium soil solution concentrations in the soil profile, and after 245 days.

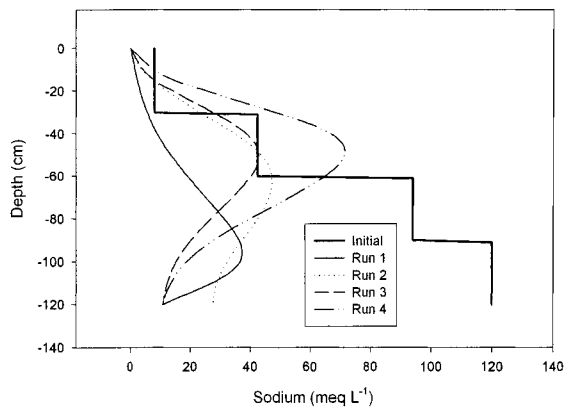


Figure 4.16. High EC Soil Profile (HESP) initial sodium soil solution concentrations in the soil profile, and after 245 days.

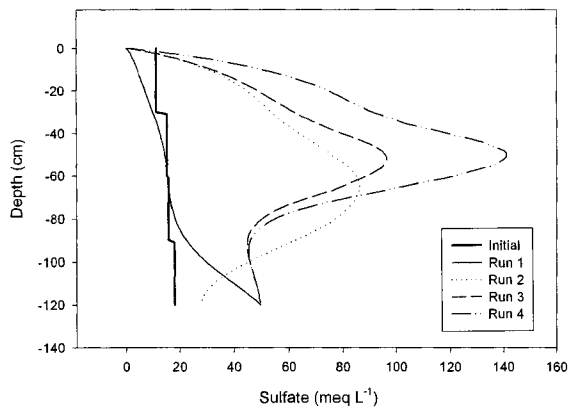


Figure 4.17. Low EC Soil Profile (LESP) initial sulfate soil solution concentrations in the soil profile, and after 245 days.

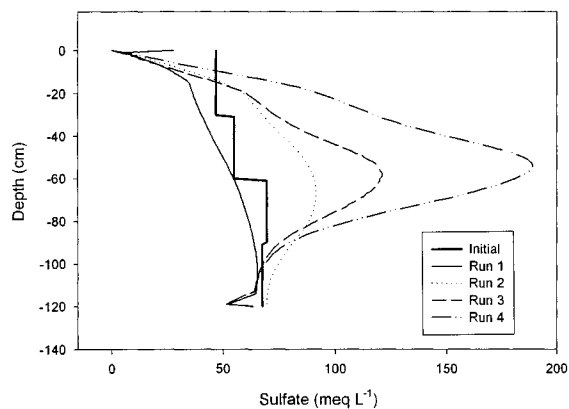


Figure 4.18. Medium EC Soil Profile (MESP) initial sulfate soil solution concentrations in the soil profile, and after 245 days.

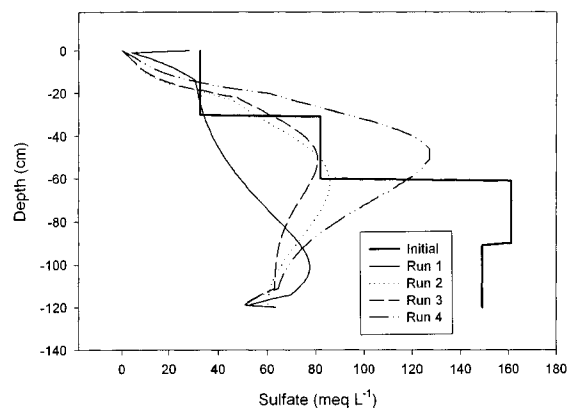


Figure 4.19. High EC Soil Profile (HESP) initial sulfate soil solution concentrations in the soil profile, and after 245 days.

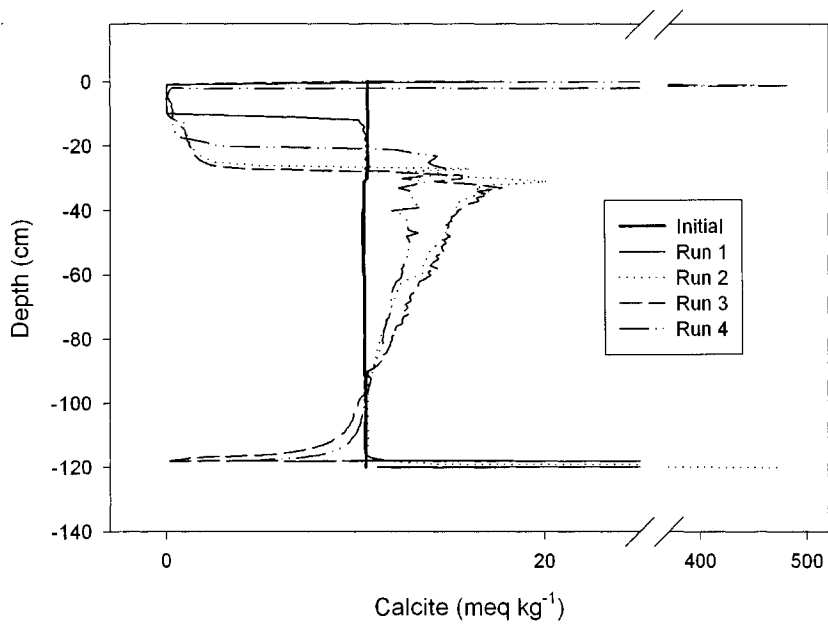


Figure 4.20. Low EC Soil Profile (LESP) initial calcite precipitates in the soil profile, and after 245 days.

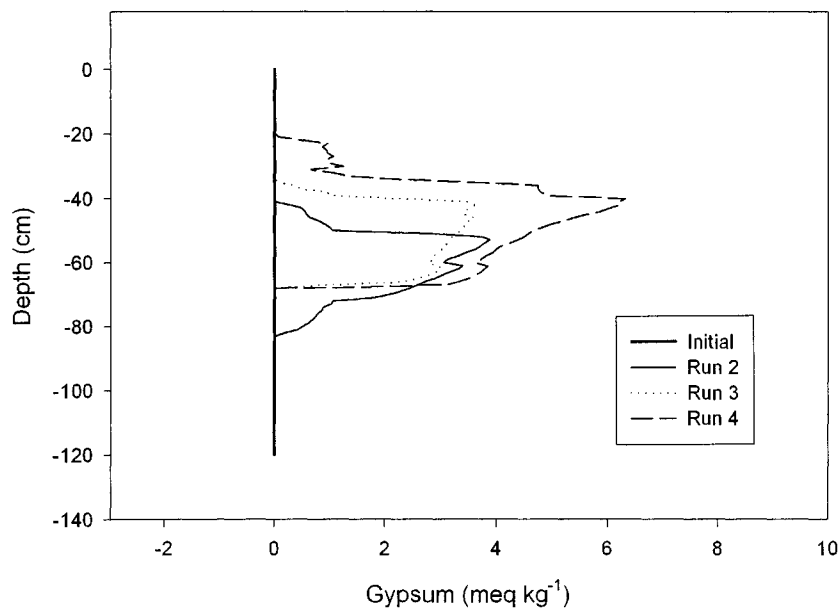


Figure 4.21. Low EC Soil Profile (LESP) initial gypsum precipitates in the soil profile, and after 245 days.

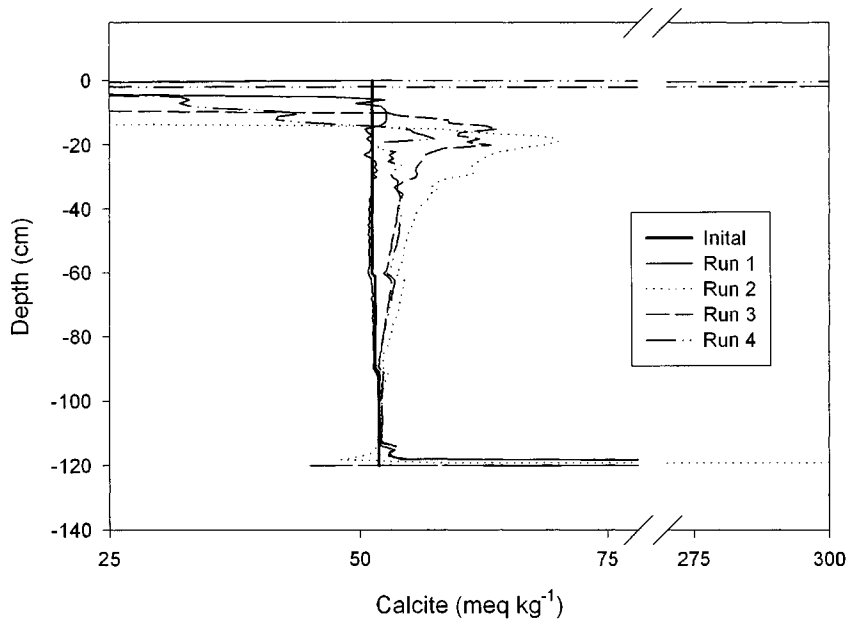


Figure 4.22. Medium EC Soil Profile (MESP) initial calcite precipitates in the soil profile, and after 245 days.

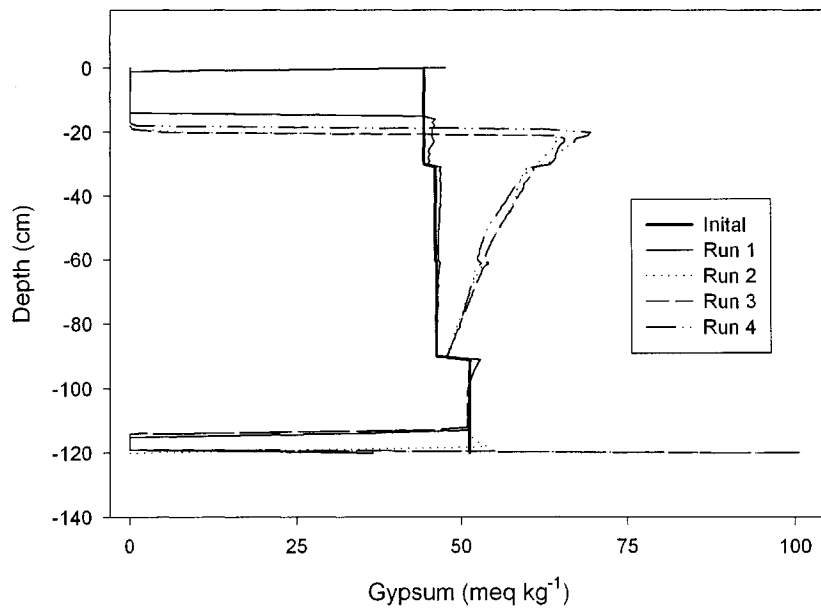


Figure 4.23. Medium EC Soil Profile (MESP) initial gypsum precipitates in the soil profile, and after 245 days.

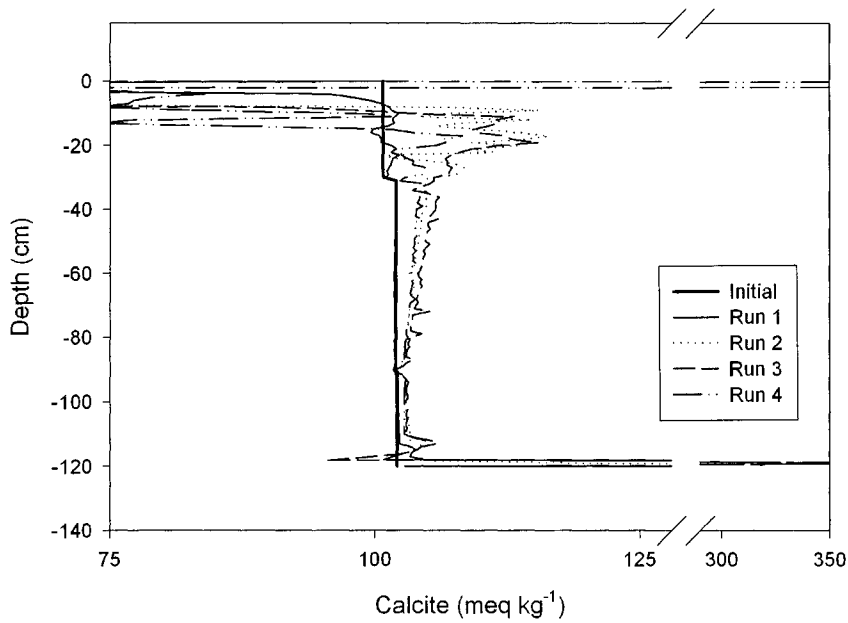


Figure 4.24. High EC Soil Profile (HESP) initial calcite precipitates in the soil profile, and after 245 days.

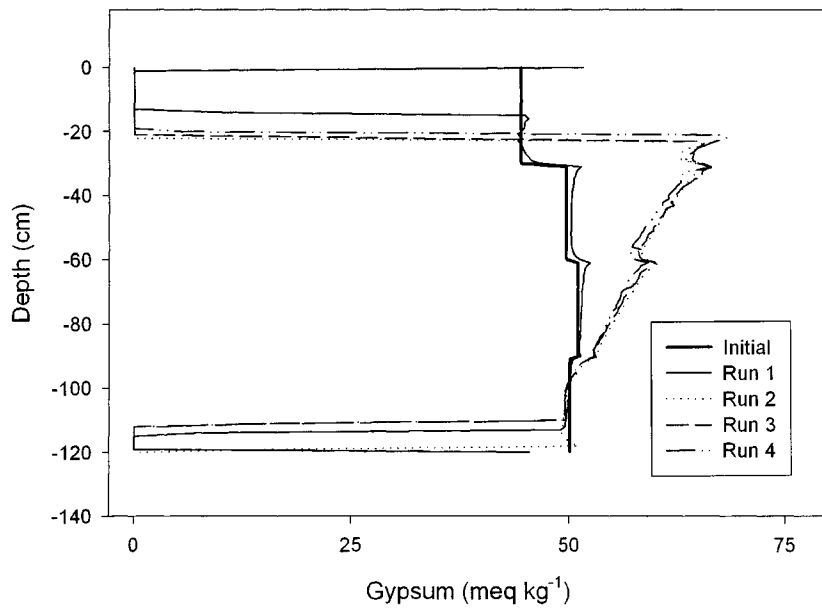


Figure 4.25. High EC Soil Profile (HESP) initial gypsum precipitates in the soil profile, and after 245 days.

**Appendices**

Appendices A to C contain descriptive statistics for all the salt chemistry collected for this research. Additionally, there is included the summarized statistical analysis performed on this data, but not included in any of the chapters.

## **Appendix A Upstream descriptive statistics and ANOVA by depth**

Appendix Table 1. Upstream Low EC category (0 - 2 dS m<sup>-1</sup>) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, mg L <sup>-1</sup>	0.3	7	169	23	60	169	0.3
	0.6	6	122	16	39	113	-0.7
	0.9	6	125	19	47	120	0.4
	1.2	6	200	47	115	175	3.4
Cl, mg L <sup>-1</sup>	0.3	7	241	98	259	242	1.5
	0.6	6	130	51	124	83	-1.5
	0.9	6	249	122	298	173	3.3
	1.2	6	296	116	284	230	0.3
EC, dS m <sup>-1</sup>	0.3	7	1.5	0.1	0.4	1.6	-0.19
	0.6	6	1.2	0.1	0.3	1.1	2.21
	0.9	6	1.2	0.1	0.3	1.2	0.59
	1.2	6	1.8	0.4	0.9	1.5	3.20
Mg, mg L <sup>-1</sup>	0.3	7	54	6	15	52	-0.8
	0.6	6	38	6	14	36	-0.5
	0.9	6	36	5	11	33	1.9
	1.2	6	70	24	58	51	5.1
Na, mg L <sup>-1</sup>	0.3	7	107	13	33	99	-2.3
	0.6	6	106	12	30	100	3.1
	0.9	6	100	9	23	90	0.7
	1.2	6	159	43	105	119	4.6
pH, su	0.3	7	8.0	0.1	0.4	8.0	-0.64
	0.6	6	7.9	0.1	0.3	7.8	4.85
	0.9	6	8.0	0.2	0.4	8.1	-1.07
	1.2	6	7.7	0.1	0.2	7.8	1.26
SO <sub>4</sub> , mg L <sup>-1</sup>	0.3	7	396	62	163	312	-1.6
	0.6	6	441	69	168	393	1.8
	0.9	6	439	78	190	404	1.1
	1.2	6	861	273	670	631	4.5

Appendix Table 2. Upstream Medium EC category (2 - 5 dS m<sup>-1</sup>) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, mg L <sup>-1</sup>	0.3	9	202	20	61	228	-1.3
	0.6	9	493	149	448	336	4.6
	0.9	8	348	69	196	360	-1.4
	1.2	7	333	87	229	229	-2.1
Cl, mg L <sup>-1</sup>	0.3	9	416	110	329	431	-0.6
	0.6	9	970	298	894	937	-1.4
	0.9	8	658	245	693	483	2.1
	1.2	7	215	73	194	102	-1.5
EC, dS m <sup>-1</sup>	0.3	9	2.1	0.2	0.5	2.1	-1.4
	0.6	9	3.1	0.4	1.2	3.3	-0.5
	0.9	8	3.2	0.4	1.1	3.3	-0.1
	1.2	7	2.8	0.4	1.1	3.0	0.9
Mg, mg L <sup>-1</sup>	0.3	9	79	12	36	71	5.3
	0.6	9	215	68	204	171	4.6
	0.9	8	174	43	122	155	0.2
	1.2	7	151	42	111	113	1.0
Na, mg L <sup>-1</sup>	0.3	9	152	22	65	146	0.9
	0.6	9	336	73	217	215	-0.8
	0.9	8	289	72	204	233	4.3
	1.2	7	231	34	90	206	2.2
pH, su	0.3	9	7.9	0.1	0.3	7.9	-1.52
	0.6	9	7.8	0.1	0.3	7.7	0.11
	0.9	8	7.8	0.1	0.1	7.8	-1.19
	1.2	7	7.8	0.1	0.3	7.8	-0.81
SO <sub>4</sub> , mg L <sup>-1</sup>	0.3	9	668	130	389	473	-1.7
	0.6	9	2191	703	2109	1412	5.4
	0.9	8	1769	341	964	1704	-0.2
	1.2	7	1596	392	1036	1540	0.1

Appendix Table 3. Upstream High EC category (5 - 8 dS m<sup>-1</sup>) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, mg L <sup>-1</sup>	0.3	3	304	60	103	332	*
	0.6	3	547	68	118	582	*
	0.9	3	531	68	118	566	*
	1.2	3	585	41	71	609	*
Cl, mg L <sup>-1</sup>	0.3	3	769	102	176	822	*
	0.6	3	1563	1331	2305	254	*
	0.9	3	3794	3499	6060	366	*
	1.2	3	7117	4514	7818	5587	*
EC, dS m <sup>-1</sup>	0.3	3	3.6	1.3	2.2	2.9	*
	0.6	3	6.6	0.7	1.1	6.1	*
	0.9	3	8.9	2.5	4.3	7.5	*
	1.2	3	9.1	1.6	2.8	10.5	*
Mg, mg L <sup>-1</sup>	0.3	3	174	102	177	84	*
	0.6	3	410	53	92	393	*
	0.9	3	629	151	262	613	*
	1.2	3	564	63	110	616	*
Na, mg L <sup>-1</sup>	0.3	3	464	277	479	189	*
	0.6	3	1116	175	303	969	*
	0.9	3	2278	810	1403	2160	*
	1.2	3	2153	658	1139	2764	*
pH, su	0.3	3	7.9	0.1	0.1	7.8	*
	0.6	3	7.7	0.1	0.1	7.6	*
	0.9	3	7.7	0.0	0.1	7.7	*
	1.2	3	7.6	0.1	0.2	7.6	*
SO <sub>4</sub> , mg L <sup>-1</sup>	0.3	3	1714	1060	1836	682	*
	0.6	3	4249	582	1008	3855	*
	0.9	3	6972	1806	3128	6321	*
	1.2	3	6548	1375	2381	7158	*

Appendix Table 4. Upstream Very High EC category ( $>9$  dS m<sup>-1</sup>) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, mg L <sup>-1</sup>	0.3	4	1075	210	420	1190	2.0
	0.6	4	1047	105	210	1102	1.0
	0.9	3	936	146	253	1039	*
	1.2	3	425.3	27.8	48.2	448	*
Cl, mg L <sup>-1</sup>	0.3	4	8374	4068	8136	7521	-2.3
	0.6	4	11405	5981	11962	7579	2.0
	0.9	3	1946	648	1122	2332	*
	1.2	3	2831	1606	2782	1979	*
EC, dS m <sup>-1</sup>	0.3	4	11.4	3.1	6.2	10.4	1.94
	0.6	4	17.2	1.8	3.5	18.3	-0.35
	0.9	3	16.5	2.6	4.6	18.3	*
	1.2	3	14.7	2.5	4.3	12.9	*
Mg, mg L <sup>-1</sup>	0.3	4	1682	598	1196	1587	0.7
	0.6	4	2910	461	922	3180	2.9
	0.9	3	2192	492	853	2293	*
	1.2	3	1246	334	579	1437	*
Na, mg L <sup>-1</sup>	0.3	4	5416	2450	4900	4460	2
	0.6	4	9733	1686	3372	9039	-2
	0.9	3	7415	1660	2876	5922	*
	1.2	3	3995	817	1416	3195	*
pH, su	0.3	4	8.1	0.1	0.1	8.0	4.00
	0.6	4	7.8	0.1	0.3	7.9	2.23
	0.9	3	7.6	0.1	0.2	7.7	*
	1.2	3	7.6	0.1	0.2	7.6	*
SO <sub>4</sub> , mg L <sup>-1</sup>	0.3	4	17899	6451	12901	17345	1.5
	0.6	4	29093	2977	5955	29813	-1.8
	0.9	3	23362	3018	5228	21999	*
	1.2	3	14579	3049	5282	17328	*

Appendix Table 5. Upstream One-way ANOVA at 95% as a function of depth per EC category.

Variable	F statistic	P - critical	Result
Low EC category (0 - 2 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	1.68	0.203	Depth Not Significant
Cl, mg L <sup>-1</sup>	0.47	0.706	Depth Not Significant
EC, dS m <sup>-1</sup>	1.55	0.231	Depth Not Significant
Mg, mg L <sup>-1</sup>	1.60	0.220	Depth Not Significant
Na, mg L <sup>-1</sup>	1.38	0.276	Depth Not Significant
pH, su	1.27	0.309	Depth Not Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	2.27	0.110	Depth Not Significant
Medium EC category (2 - 5 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	1.66	0.198	Depth Not Significant
Cl, mg L <sup>-1</sup>	2.31	0.097	Depth Not Significant
EC, dS m <sup>-1</sup>	2.35	0.093	Depth Not Significant
Mg, mg L <sup>-1</sup>	1.62	0.207	Depth Not Significant
Na, mg L <sup>-1</sup>	2.15	0.115	Depth Not Significant
pH, su	0.54	0.660	Depth Not Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	2.16	0.115	Depth Not Significant
High EC category (5 - 8 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	4.44	0.041	Depth IS Significant
Cl, mg L <sup>-1</sup>	0.94	0.466	Depth Not Significant
EC, dS m <sup>-1</sup>	2.40	0.143	Depth Not Significant
Mg, mg L <sup>-1</sup>	4.08	0.050	Depth IS Significant
Na, mg L <sup>-1</sup>	2.51	0.132	Depth Not Significant
pH, su	2.02	0.189	Depth Not Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	3.55	0.068	Depth Not Significant
Very High EC category (>9 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	3.73	0.049	Depth IS Significant
Cl, mg L <sup>-1</sup>	1.10	0.395	Depth Not Significant
EC, dS m <sup>-1</sup>	1.12	0.385	Depth Not Significant
Mg, mg L <sup>-1</sup>	2.05	0.171	Depth Not Significant
Na, mg L <sup>-1</sup>	1.76	0.219	Depth Not Significant
pH, su	3.74	0.049	Depth IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	2.03	0.173	Depth Not Significant

## **Appendix B Downstream descriptive statistics and ANOVA by depth**

Appendix Table 6. Downstream Low EC category (0 - 2 dS m<sup>-1</sup>) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, mg L <sup>-1</sup>	0.3	6	134	16	40	142	-1.8
	0.6	6	138	41	100	106	1.3
	0.9	6	261	97	236	207	2.1
	1.2	6	323	76	185	308	-0.7
Cl, mg L <sup>-1</sup>	0.3	6	48	12	30	37	-0.5
	0.6	6	50	7	17	55	-1.5
	0.9	6	69	20	50	67	1.7
	1.2	6	178	58	142	130	-1.4
EC, dS m <sup>-1</sup>	0.3	6	1.4	0.2	0.4	1.5	1.20
	0.6	6	1.3	0.2	0.6	1.2	-1.42
	0.9	6	2.1	0.5	1.2	2.0	-1.41
	1.2	6	2.8	0.5	1.1	2.9	-1.82
Mg, mg L <sup>-1</sup>	0.3	6	50	9	21	51	1.7
	0.6	6	51	18	45	30	1.2
	0.9	6	85	30	74	65	0.2
	1.2	6	98	22	53	105	-2.3
Na, mg L <sup>-1</sup>	0.3	6	124	28	68	105	-1.0
	0.6	6	156	44	107	120	0.1
	0.9	6	219	59	144	198	-2.1
	1.2	6	271	54	132	280	-0.6
pH, su	0.3	6	8.4	0.2	0.4	8.5	3.73
	0.6	6	8.0	0.1	0.2	8.0	0.07
	0.9	6	8.0	0.2	0.4	8.0	0.76
	1.2	6	8.2	0.2	0.5	8.1	2.66
SO <sub>4</sub> , mg L <sup>-1</sup>	0.3	6	556	120	294	670	-1.3
	0.6	6	857	304	744	496	-1.0
	0.9	6	1592	555	1360	1264	-1.0
	1.2	6	1948	417	1023	2115	-2.7

Appendix Table 7. Downstream Medium EC category (2 - 5 dS m<sup>-1</sup>) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, mg L <sup>-1</sup>	0.3	7	247	46	121	278	-0.5
	0.6	7	481	99	262	518	-1.8
	0.9	6	691	39	95	673	0.1
	1.2	5	577	61	136	629	3.7
Cl, mg L <sup>-1</sup>	0.3	7	71	15	39	60	-2.1
	0.6	7	196	68	179	144	3.9
	0.9	6	361	200	489	175	4.4
	1.2	5	257	71	160	200	-2.4
EC, dS m <sup>-1</sup>	0.3	7	2.7	0.5	1.2	2.7	-0.84
	0.6	7	3.8	0.6	1.5	4.1	-0.55
	0.9	6	4.9	0.4	1.0	4.8	1.28
	1.2	5	4.9	0.5	1.2	4.8	-1.34
Mg, mg L <sup>-1</sup>	0.3	7	111	24	64	112	0.4
	0.6	7	195	44	117	150	-1.5
	0.9	6	280	12	30	283	1.6
	1.2	5	258	42	94	239	-0.4
Na, mg L <sup>-1</sup>	0.3	7	263	57	152	182	0.9
	0.6	7	467	96	254	392	-0.6
	0.9	6	664	134	328	637	3.3
	1.2	5	704	161	360	586	-2.5
pH, su	0.3	7	8.4	0.1	0.4	8.4	-0.64
	0.6	7	7.9	0.1	0.2	7.9	0.62
	0.9	6	7.9	0.1	0.4	7.9	-1.65
	1.2	5	7.9	0.1	0.3	7.8	0.13
SO <sub>4</sub> , mg L <sup>-1</sup>	0.3	7	1643	327	865	1595	0.2
	0.6	7	3756	907	2401	2660	-0.9
	0.9	6	5383	998	2446	5580	0.1
	1.2	5	5726	1282	2867	5270	-2.4

Appendix Table 8. Downstream High EC category (5 - 8 dS m<sup>-1</sup>) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, mg L <sup>-1</sup>	0.3	7	347	95	250	317	-1.9
	0.6	6	730	32	78	721	-0.3
	0.9	6	673	43	105	650	-0.7
	1.2	6	567	58	141	587	0.9
Cl, mg L <sup>-1</sup>	0.3	7	248	91	241	172	-0.6
	0.6	6	876	265	649	820	-1.8
	0.9	6	740	200	491	740	-1.5
	1.2	6	1053	551	1350	480	4.4
EC, dS m <sup>-1</sup>	0.3	7	4.0	1.1	2.8	3.1	-1.16
	0.6	6	7.5	0.8	2.0	6.6	3.25
	0.9	6	8.6	0.8	1.9	8.3	3.30
	1.2	6	7.7	1.3	3.2	7.1	1.64
Mg, mg L <sup>-1</sup>	0.3	7	202	64	168	152	-2.1
	0.6	6	478	42	103	440	3.3
	0.9	6	582	55	134	564	0.8
	1.2	6	644	221	542	458	3.8
Na, mg L <sup>-1</sup>	0.3	7	717	285	755	351	0.5
	0.6	6	1379	323	792	994	3.3
	0.9	6	1695	209	511	1666	0.5
	1.2	6	1851	690	1690	1395	4.5
pH, su	0.3	7	8.4	0.1	0.3	8.5	0.72
	0.6	6	8.2	0.1	0.3	8.2	0.59
	0.9	6	7.9	0.1	0.2	7.9	1.28
	1.2	6	7.9	0.1	0.2	7.9	-2.15
SO <sub>4</sub> , mg L <sup>-1</sup>	0.3	7	4607	1853	4901	2355	-1.5
	0.6	6	11587	2448	5997	9170	5.5
	0.9	6	10702	901	2208	11240	4.0
	1.2	6	12353	3431	8405	9430	3.3

Appendix Table 9. Downstream Very High EC category ( $>9 \text{ dS m}^{-1}$ ) descriptive statistics.

Variable	Depth (m)	N	Mean	SE Mean	StDev	Median	Kurtosis
Ca, $\text{mg L}^{-1}$	0.3	6	769	42	104	769	-1.0
	0.6	6	834	84	207	855	-0.3
	0.9	6	817	150	368	813	0.8
	1.2	5	731	54	120	797	-2.8
Cl, $\text{mg L}^{-1}$	0.3	6	1805	875	2143	1050	3.9
	0.6	6	2372	494	1209	2160	0.5
	0.9	6	2873	775	1899	3110	-0.6
	1.2	5	2872	716	1602	2600	-1.2
EC, $\text{dS m}^{-1}$	0.3	6	8.7	2.3	5.7	6.7	4.53
	0.6	6	12.0	0.9	2.3	11.9	1.17
	0.9	6	12.1	1.3	3.2	12.5	1.94
	1.2	5	12.0	1.4	3.1	11.4	2.68
Mg, $\text{mg L}^{-1}$	0.3	6	775	422	1035	394	5.7
	0.6	6	923	158	388	793	-0.6
	0.9	6	1376	403	988	1281	2.2
	1.2	5	1160	194	433	1177	2.2
Na, $\text{mg L}^{-1}$	0.3	6	2770	1662	4072	1213	5.7
	0.6	6	3574	291	713	3527	-2.2
	0.9	6	5462	1189	2914	5329	-1.1
	1.2	5	5647	1258	2813	5686	0.9
pH, su	0.3	6	8.04	0.12	0.29	8.13	-1.61
	0.6	6	7.89	0.07	0.18	7.95	-1.64
	0.9	6	8.03	0.12	0.29	8.10	-1.71
	1.2	5	8.08	0.15	0.33	8.10	1.22
SO <sub>4</sub> , $\text{mg L}^{-1}$	0.3	6	14611	7041	17247	8970	5.6
	0.6	6	19808	2111	5170	19335	-0.6
	0.9	6	27933	7138	17484	26800	0.4
	1.2	5	26884	5033	11253	28300	0.6

Appendix Table 10. Downstream One-way ANOVA at 95% as a function of depth per EC category.

Variable	F statistic	P - critical	Result
Low EC category (0 - 2 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	2.06	0.138	Depth Not Significant
Cl, mg L <sup>-1</sup>	3.89	0.024	Depth IS Significant
EC, dS m <sup>-1</sup>	3.14	0.048	Depth IS Significant
Mg, mg L <sup>-1</sup>	1.30	0.303	Depth Not Significant
Na, mg L <sup>-1</sup>	1.89	0.163	Depth Not Significant
pH, su	1.19	0.337	Depth Not Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	2.81	0.066	Depth Not Significant
Medium EC category (2 - 5 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	7.85	0.001	Depth IS Significant
Cl, mg L <sup>-1</sup>	1.33	0.292	Depth Not Significant
EC, dS m <sup>-1</sup>	4.43	0.015	Depth IS Significant
Mg, mg L <sup>-1</sup>	5.29	0.007	Depth IS Significant
Na, mg L <sup>-1</sup>	3.4	0.037	Depth IS Significant
pH, su	4.83	0.010	Depth IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	4.51	0.014	Depth IS Significant
High EC category (5 - 8 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	7.06	0.002	Depth IS Significant
Cl, mg L <sup>-1</sup>	1.30	0.301	Depth Not Significant
EC, dS m <sup>-1</sup>	4.17	0.018	Depth IS Significant
Mg, mg L <sup>-1</sup>	2.98	0.055	Depth Not Significant
Na, mg L <sup>-1</sup>	1.58	0.224	Depth Not Significant
pH, su	6.27	0.003	Depth IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	2.50	0.087	Depth IS Significant
Very High EC category (>9 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	0.22	0.878	Depth Not Significant
Cl, mg L <sup>-1</sup>	0.49	0.696	Depth Not Significant
EC, dS m <sup>-1</sup>	1.11	0.371	Depth Not Significant
Mg, mg L <sup>-1</sup>	0.67	0.579	Depth Not Significant
Na, mg L <sup>-1</sup>	1.36	0.284	Depth Not Significant
pH, su	0.53	0.669	Depth Not Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	1.19	0.340	Depth Not Significant

## **Appendix C Comparison of Upstream and Downstream sub-regions**

Appendix Table 11. Descriptive Upstream and Downstream Statistics a Combination of Upstream and Downstream Data.

Variable	N	Mean	SE Mean	StDev	Median	Kurtosis
Low EC category (0 - 2 dS m <sup>-1</sup> )						
Ca	49	125	6	43	119	-0.8
Cl	49	160	30	208	54	2.9
EC	49	1.3	0.1	0.4	1.3	-0.90
Mg	49	42	2	17	40	4.2
Na	49	113	6	43	102	0.5
pH	49	8.1	0.1	0.4	8.0	-0.27
SO <sub>4</sub>	49	481	32	222	471	-0.5
Medium EC category (2 - 5 dS m <sup>-1</sup> )						
Ca	59	408	32	243	332	7.7
Cl	59	380	67	511	155	5.8
EC	59	3.2	0.1	0.9	3.2	-1.12
Mg	59	167	14	110	143	8.9
Na	59	319	20	150	320	0.3
pH	59	8.0	0.0	0.3	7.9	-0.28
SO <sub>4</sub>	59	2354	223	1713	1915	3.5
High EC category (5 - 8 dS m <sup>-1</sup> )						
Ca	37	636	23	140	640	1.4
Cl	37	1132	323	1967	540	16.9
EC	37	6.6	0.2	1.2	6.3	-0.98
Mg	37	412	19	116	391	0.1
Na	37	1198	72	439	1063	-0.7
pH	37	7.9	0.1	0.3	7.8	-0.20
SO <sub>4</sub>	37	7706	501	3049	8300	-1.0
Very High EC category (>9 dS m <sup>-1</sup> )						
Ca	36	824	47	280	803	-0.8
Cl	36	4661	959	5752	2862	8.4
EC	36	13.7	0.6	3.5	12.5	-0.78
Mg	36	1553	153	920	1308	-0.2
Na	36	5730	516	3096	4744	0.4
pH	36	7.9	0.0	0.3	7.9	0.05
SO <sub>4</sub>	36	23722	1858	11147	21845	1.0

Appendix Table 12. Upstream and Downstream One-way ANOVA at 95% as a function of depth per EC category.

Variable	F statistic	P - critical	Result
Low EC category (0 - 2 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	1.68	0.184	Depth Not Significant
Cl, mg L <sup>-1</sup>	1.40	0.257	Depth Not Significant
EC, dS m <sup>-1</sup>	2.07	0.117	Depth Not Significant
Mg, mg L <sup>-1</sup>	3.28	0.029	Depth IS Significant
Na, mg L <sup>-1</sup>	0.45	0.715	Depth Not Significant
pH, su	1.30	0.287	Depth Not Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	1.52	0.221	Depth Not Significant
Medium EC category (2 - 5 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	1.51	0.223	Depth Not Significant
Cl, mg L <sup>-1</sup>	1.97	0.130	Depth Not Significant
EC, dS m <sup>-1</sup>	1.75	0.167	Depth Not Significant
Mg, mg L <sup>-1</sup>	1.06	0.375	Depth Not Significant
Na, mg L <sup>-1</sup>	1.39	0.254	Depth Not Significant
pH, su	4.44	0.007	Depth IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	1.97	0.129	Depth Not Significant
High EC category (5 - 8 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	0.85	0.478	Depth Not Significant
Cl, mg L <sup>-1</sup>	0.22	0.883	Depth Not Significant
EC, dS m <sup>-1</sup>	0.70	0.560	Depth Not Significant
Mg, mg L <sup>-1</sup>	1.05	0.383	Depth Not Significant
Na, mg L <sup>-1</sup>	1.29	0.293	Depth Not Significant
pH, su	3.20	0.036	Depth IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	1.16	0.339	Depth Not Significant
Very High EC category (>9 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	4.86	0.007	Depth IS Significant
Cl, mg L <sup>-1</sup>	1.29	0.296	Depth Not Significant
EC, dS m <sup>-1</sup>	0.17	0.916	Depth Not Significant
Mg, mg L <sup>-1</sup>	0.83	0.487	Depth Not Significant
Na, mg L <sup>-1</sup>	0.44	0.728	Depth Not Significant
pH, su	0.2	0.899	Depth Not Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	0.34	0.797	Depth Not Significant

Appendix Table 13. Upstream and Downstream One-way ANOVA at 95% as a function of EC category and sub-region.

Variable	F statistic	P - critical	Result
Low EC category (0 - 2 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	9.06	0.004	Sub-region IS Significant
Cl, mg L <sup>-1</sup>	12.37	0.001	Sub-region IS Significant
EC, dS m <sup>-1</sup>	2.53	0.118	Sub-region Not Significant
Mg, mg L <sup>-1</sup>	4.73	0.035	Sub-region IS Significant
Na, mg L <sup>-1</sup>	0.12	0.734	Sub-region Not Significant
pH, su	13.89	0.001	Sub-region IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	0.38	0.539	Sub-region Not Significant
Medium EC category (2 - 5 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	0.62	0.436	Sub-region Not Significant
Cl, mg L <sup>-1</sup>	15.45	0.000	Sub-region IS Significant
EC, dS m <sup>-1</sup>	2.35	0.131	Sub-region Not Significant
Mg, mg L <sup>-1</sup>	0.07	0.786	Sub-region Not Significant
Na, mg L <sup>-1</sup>	8.66	0.005	Sub-region IS Significant
pH, su	8.29	0.006	Sub-region IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	9.02	0.004	Sub-region IS Significant
High EC category (5 - 8 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	2.68	0.111	Sub-region Not Significant
Cl, mg L <sup>-1</sup>	8.90	0.005	Sub-region IS Significant
EC, dS m <sup>-1</sup>	2.30	0.139	Sub-region Not Significant
Mg, mg L <sup>-1</sup>	0.04	0.835	Sub-region Not Significant
Na, mg L <sup>-1</sup>	0.97	0.332	Sub-region Not Significant
pH, su	11.48	0.002	Sub-region IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	28.33	0.000	Sub-region IS Significant
Very High EC category (>9 dS m <sup>-1</sup> )			
Ca, mg L <sup>-1</sup>	0.25	0.623	Sub-region Not Significant
Cl, mg L <sup>-1</sup>	4.54	0.040	Sub-region IS Significant
EC, dS m <sup>-1</sup>	3.59	0.067	Sub-region Not Significant
Mg, mg L <sup>-1</sup>	4.68	0.038	Sub-region IS Significant
Na, mg L <sup>-1</sup>	1.72	0.199	Sub-region Not Significant
pH, su	9.21	0.005	Sub-region IS Significant
SO <sub>4</sub> , mg L <sup>-1</sup>	2.81	0.103	Sub-region Not Significant

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