

# **Salt Chemistry Effects on Salinity Assessment in the Arkansas River Basin, Colorado**

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SALT CHEMISTRY EFFECTS ON SALINITY ASSESSMENT IN THE  
ARKANSAS RIVER BASIN, COLORADO

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Colorado Water Resources Research Institute  
Completion Report 206

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## Abstract

### SALT CHEMISTRY EFFECTS ON SALINITY ASSESSMENT 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  $R^2$  of 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.

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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
HIGH	High EC <sub>e</sub> soils
L-CL	Las clay loam
LOW	Low EC <sub>e</sub> soils
Mg-VM	Magnesium concentrations adapted by Visual Minteq (VM)
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)

### Chemicals and Minerals

Ca	Calcium
Mg	Magnesium
Na	Sodium
SO <sub>4</sub>	Sulfate
CO <sub>3</sub>	Carbonate
Cl	Chloride
CaCO <sub>3</sub>	Calcium Carbonate/Calcite
CaSO <sub>4</sub> * 2 H <sub>2</sub> O	Calcium Sulfate/Gypsum
Na <sub>2</sub> SO <sub>4</sub> * 10 H <sub>2</sub> O	Sodium Sulfate/Mirabilite
MgSO <sub>4</sub> * 7 H <sub>2</sub> O	Magnesium Sulfate/Epsomite

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## **Introduction and Background**

Water resources are limited in Colorado. The lower Arkansas River Basin has been losing water to urban areas through transbasin 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 (Figure 1). 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 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<sub>e</sub>) 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.

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, Espresso). 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; Triantafilis 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  $\text{EC}_e$ .

## **Objectives**

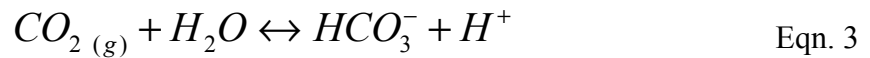
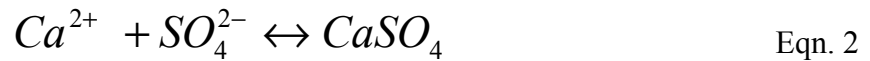
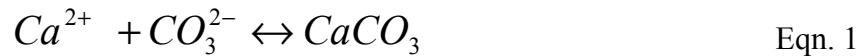
The goal of this research was to examine the processes and methods associated with salinity monitoring and analysis in the lower Arkansas River Basin. It was hypothesized that salinity issues in the basin are influenced and controlled by the accumulation of precipitates in the soils. Understanding the 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
- Analyze laboratory methods that have the potential to influence the measurement of  $\text{EC}_e$  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
- Utilize soil salinity chemical data to develop EC-EM calibrations.



## 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  $\text{CO}_2(\text{g})$  and the subsequent bicarbonate/carbonate concentrations. A pathway dependent upon elevated ( $\text{CO}_2 - \text{HCO}_3$ ) concentrations is detailed in Eqn. 1. This equation is slightly modified under acidic conditions, but acidic conditions are not relevant for the study area (Table 2). 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. 2). The  $\text{CO}_2 - \text{HCO}_3$  pathway is presented (Eqn. 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. 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. 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  $0.0154 \text{ moles liter}^{-1}$  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  $\text{EC}_e$  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 ( $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ ) 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  $\text{SO}_4$  dominance in the chemistry can lead to different effects on the Ca relationship in the soils (Skarie et al., 1987b). In Cl dominated systems, it was found that Ca increased with EC, whereas in  $\text{SO}_4$  systems the Ca was controlled by gypsum solubility (Skarie et al., 1987b). Calcium chemistry is variable as a function of the surrounding chemistry and water contents.

## 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<sub>v</sub> 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 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 urban areas, 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

### Analysis of Soil EC methods and Chemistry

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 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.

## **Calibration of an EM-38 to predict $EC_e$ using salinity chemistry**

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  $\mu m$  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  $SO_4$ ) 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  $EC_e$  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  $EC_e$  and depth weighted  $EC_e$ . Regression equations were validated against data not used in the equation development.

For regression analysis, available  $EC_e$  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,  $SO_4$  and Cl concentrations were entered into the Visual Minteq program in units of  $mmol\ L^{-1}$ . The partial pressure of the  $CO_2(g)$  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(g)</sub> 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.

## Results and Discussion

### Analysis of Soil EC methods and Chemistry

#### *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<sub>e</sub> averaged 1.4 dS m<sup>-1</sup> with a range of 1.0 to 1.7 dS m<sup>-1</sup>. The high salinity (HIGH) soil had an average saturated percentage of 58% with a range 55.0% to 58.9%. The EC<sub>e</sub> of the HIGH soil averaged 10.0 dS m<sup>-1</sup> with a range of 9.75 to 10.12 dS m<sup>-1</sup>. All subsequent samples for each soil were based upon the 56% and the 58% saturation levels.

When saturated with distilled water the LOW EC<sub>e</sub> of the ground (GRD) soils averaged less than the LOW soils retaining their aggregates (AGG). The average LOW GRD EC<sub>e</sub> was 1.4 dS m<sup>-1</sup>, while the LOW AGG averaged 1.7 dS m<sup>-1</sup> with a range of 1.5 to 1.9 dS m<sup>-1</sup> (Figure 2). 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<sub>e</sub> 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 3). 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<sub>e</sub> 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 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<sub>4</sub> \* 10 H<sub>2</sub>O) would add SO<sub>4</sub> 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 dS m<sup>-1</sup> (Arndt and Richardson, 1989). Based on the expected mineralogy in the LOW soils, below an EC of 3.5 dS m<sup>-1</sup> 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 dS m<sup>-1</sup> would have a limited dissolution of gypsum because of the greater SO<sub>4</sub> 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 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 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, 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). 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). 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 3). 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 **Error! Digit expected.** and **Error! Digit expected.**).

The first extract was dominated by Na cations for both soils (Figures **Error! Digit expected.** and **Error! Digit expected.**)). 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 **Error! Digit expected.** and **Error! Digit expected.**).

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  $EC_e$  level at approximately 4 dS m<sup>-1</sup> at approximately extraction number 9 for both L-CL and RF-CL (Figures Figure 4 and Figure 5). 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<sub>4</sub> concentration, allowing more gypsum to dissolve because the SO<sub>4</sub> 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 6). 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 6), and similar results were found for RF-CL (as depicted by the white circle in Figure 6). 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 ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ) and calcite ( $\text{CaCO}_3$ ), 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  $15.4 \text{ mmol L}^{-1}$  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., 1987a). 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  $\text{EC}_e$  of the multiple extraction soils were  $9.0 \text{ dS m}^{-1}$  for L-CL and  $8.1 \text{ dS m}^{-1}$  for RF-CL, irrigation with an average water quality from the Arkansas River (Table 1) would not dissolve the reservoir minerals as might be expected, based upon the analysis of Figure 3. 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).

## **Calibration of an EM-38 to predict $\text{EC}_e$ using salinity chemistry**

### *Chemistry*

The chemistry of the lower Arkansas River Basin is typically dominated by  $\text{SO}_4/\text{HCO}_3$  based salts (Table 2), but some locations were dominated by Cl salts (data not shown). The  $\text{SO}_4/\text{HCO}_3$  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  $\text{EC}_e$  and  $\text{EM}_v$  existed, but the data was highly variable as shown by the  $R^2$  values (Figure 7). The best-fit line based upon the depth averaged  $\text{EC}_e$  explained over half of the variation found in the data ( $R^2 = 0.59$ ). The best-fit line for the depth weighted  $\text{EC}_e$  explained slightly less than the averaged  $\text{EC}_e$  line ( $R^2 = 0.55$ ). 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 8), 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  $4 \text{ dS m}^{-1}$ . There was also a strong relationship between  $EC_e$  and Mg concentrations (Figure 9), 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 10). The SAR-VM values are approximately an order of magnitude greater than the saturated paste SAR values (Figure 8). However, the sorption of soil-bound Mg was apparent in the Visual Minteq adapted Mg concentrations (Mg-VM) (Figure 11) that are an order of magnitude lower than the measured Mg concentrations (Figure 9).

### *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. 4); the depth weighted equation as WGT (Eqn. 5); the depth averaged equation with Visual Minteq adapted data as AVG-VM (Eqn. 6); and the depth weighted equation with Visual Minteq adapted data as WGT-VM (Eqn. 7).

$$EC = 1.41 + 2.18EM_v + 0.027Mg + 0.217SAR \quad \text{Eqn. 4}$$

$$EC = 1.16 + 2.55EM_v + 0.033Mg + 0.197SAR \quad \text{Eqn. 5}$$

$$EC = -1.16 + 3.03EM_v + 0.023Mg + 0.298Mg-VM + 0.017SAR \quad \text{Eqn. 6}$$

$$EC = -1.13 + 3.29EM_v + 0.023Mg + 0.286Mg-VM + 0.017SAR \quad \text{Eqn. 7}$$

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). 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).

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). 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 12). An analysis of the absolute value of the AVG residuals found that they ranged between  $0.06 \text{ dS m}^{-1}$  and  $4.18 \text{ dS m}^{-1}$  with a mean of  $1.48 \text{ dS m}^{-1}$ . An analysis of the absolute value of the AVG-VM residuals found that they ranged between  $0.03 \text{ dS m}^{-1}$  and  $4.37 \text{ dS m}^{-1}$  with a mean of  $1.23 \text{ dS m}^{-1}$ . There was variability around the predicted  $EC_e$ , but the mean predicted  $EC_e$  was within  $1.5 \text{ dS m}^{-1}$ .

Data from both WGT and WGT-VM equations were also not a precise 1:1 relationship (Figure 13). An analysis of the absolute values of the WGT residuals found that they ranged between  $0.04 \text{ dS m}^{-1}$  and  $3.74 \text{ dS m}^{-1}$  with a mean of  $1.29 \text{ dS m}^{-1}$ . An analysis of the absolute value of the WGT-VM residuals found that they ranged between  $0.03 \text{ dS m}^{-1}$  and  $3.50 \text{ dS m}^{-1}$  with a mean of  $1.04 \text{ dS m}^{-1}$ . There was variability around the predicted  $EC_e$ , but the mean predicted  $EC_e$  was within  $1.3 \text{ dS m}^{-1}$ .

### *Equation Validation*

Validation of the prediction equations was accomplished with data not utilized in the development of those equations (Tables 4 and 5). 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 4). 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 5). 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 6). 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 7).

Based upon the validation datasets (Tables 4 to 7), apparently the predictive capacities of the four equations were essentially equal. When the assumptions of database combination were accounted for (associating data points with  $EC_e$  within  $4 \text{ dS m}^{-1}$ ), all equations succeeded in predicting within that  $4 \text{ dS m}^{-1}$  parameter. Additionally, all equations mean residuals were approximately the same as the mean residuals of the developing datasets (Table 3).

### *Management Categories*

The residuals from each of the four equations offered insight into their ability to predict  $EC_e$  from  $EM_v$  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 4). 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 1 category (Table 5). 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 1 category (Table 6). 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 1 category (Table 7).

### *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. 8) and Downstream (Eqn. 9) equations were used to predict the  $EC_e$  of the validation dataset (Table 8), 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 1 category.

$$EC_e = 0.45 + 7.23EM_v^{1.78} + 19.54WC - 34.06EM_v(WC) \quad \text{Eqn. 8}$$

$$EC_e = 2.33 + 7.16EM_v^{1.44} + 9.41WC - 23.18EM_v(WC) \quad \text{Eqn. 9}$$

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 8). Additionally, the assumption of a  $4 \text{ dS m}^{-1}$  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  $\text{EC}_a$  is influenced by the chemistry, as determined in the response of predicting  $\text{EC}_e$ . 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  $\text{EM}_v\text{-EC}_e$  calibration, just that it had a lesser effect than the chemical properties potentially due to the spatial scale issues.

## 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  $EC_e$  levels decreased in a similar manner to the Na concentrations, with an initial  $EC_e$  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.

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.



## Tables

Table 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.

Table 2. 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. Predictor equation multilinear regression for the four equations and for the combined dataset of Upstream and Downstream sub-regions; including the  $R^2$ , RMSE and Mallows'  $C_p$  values for each equation, and covariate t-values and p-values.

Equation Type	Covariates	Coefficient	t-value	p-value	Mallows' $C_p$ †	$R^2$	RMSE
Averaged (AVG)					23.9	0.89	1.64
	Constant	1.41	3.36	0.001			
	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)					11.5	0.91	1.58
	Constant	1.16	2.63	0.011			
	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)					1.1	0.93	1.35
	Constant	-1.16	-2.12	0.038			
	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)					0.6	0.93	1.34
	Constant	-1.13	-1.97	0.054			
	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'  $C_p$  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 4. 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		Category Change
	EC †	Category	EC <sub>e</sub>	Category	EM <sub>v</sub>	Mg	SAR	EC Difference	dS m <sup>-1</sup>	
US99-001	3.6 (3.0)	1	3.2	1	0.55	7.92	1.96	0.4	0.4	0
UF00-043	2.3 (2.8)	1	5.3	2	1.18	23.66	2.89	-3.0	-3.0	1
US99-043	4.7 (2.8)	2	5.1	2	1.11	23.66	2.89	-0.8	-0.8	0
US03-077	3.5 (6.8)	1	6.3	3	0.62	35.10	11.80	-2.8	-2.8	2
US99-077	4.7 (6.8)	2	5.8	2	0.41	35.10	11.80	-1.1	-1.1	0
DF02-318	6.4 (6.0)	3	5.3	2	0.68	37.96	6.54	1.0	1.0	-1
DF03-318	6.1 (6.0)	3	5.2	2	0.62	37.96	6.54	0.9	0.9	-1
DS03-318	5.5 (6.0)	2	6.1	3	1.02	37.96	6.54	-0.6	-0.6	1
DS02-348	1.7 (3.5)	1	3.7	1	0.43	12.96	4.65	-2.0	-2.0	0
DS03-348	5.0 (3.5)	2	3.8	1	0.48	12.96	4.65	1.2	1.2	-1
DS02-360	3.1 (1.9)	1	3.0	1	0.28	5.10	3.78	0.1	0.1	0
DS03-360	5.8 (1.9)	2	2.9	1	0.26	5.10	3.78	2.8	2.8	-1
DF02-350A	9.5 (8.1)	3	8.0	3	1.22	34.92	13.87	1.5	1.5	0
DS02-350A	5.2 (8.1)	2	7.7	3	1.07	34.92	13.87	-2.5	-2.5	1
Mean									1.48 ‡	0.6 ‡

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

‡ Mean of the absolute values.

Table 5. 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		Category Change
	EC †	Category	EC <sub>e</sub>	Category	EM <sub>v</sub>	Mg	SAR	EC Difference	dS m <sup>-1</sup>	
US99-001	3.8 (2.6)	1	3.2	1	0.55	7.11	1.86	0.6	0.6	0
UF00-043	2.1 (2.6)	1	5.5	2	1.18	24.19	2.77	-3.4	-3.4	-1
US99-043	4.4 (2.6)	2	5.3	2	1.11	24.19	2.77	-0.9	-0.9	0
US03-077	2.8 (5.6)	1	5.4	2	0.62	27.62	9.05	-2.6	-2.6	0
US99-077	4.0 (5.6)	2	4.9	2	0.41	27.62	9.05	-0.9	-0.9	0
DF02-318	5.9 (5.8)	2	5.2	2	0.68	34.15	6.19	0.6	0.6	0
DF03-318	5.7 (5.8)	2	5.1	2	0.62	34.15	6.19	0.6	0.6	-1
DS03-318	5.0 (5.8)	2	6.1	3	1.02	34.15	6.19	-1.1	-1.1	0
DS02-348	1.5 (3.2)	1	3.6	1	0.43	11.89	4.63	-2.0	-2.0	1
DS03-348	4.5 (3.2)	2	3.7	1	0.48	11.89	4.63	0.8	0.8	0
DS02-360	2.5 (1.9)	1	2.8	1	0.28	5.14	3.70	-0.3	-0.3	1
DS03-360	5.3 (1.9)	2	2.7	1	0.26	5.14	3.70	2.5	2.5	1
DF02-350A	10.1 (8.8)	4	8.6	3	1.22	38.06	15.61	1.5	1.5	-1
DS02-350A	5.8 (8.8)	2	8.2	3	1.07	38.06	15.61	-2.4	-2.4	0
Mean								1.45 ‡		0.5 ‡

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

‡ Mean of the absolute values.

Table 6. Averaged validation (AVG-VM) dataset using Visual Mintage adapted data including EM<sub>v</sub>, Mg and SAR with categories for prediction within management units (n=14).

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

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

‡ Mean of the absolute values.

Table 7. Weighted validation (WGT-VM) dataset using Visual Mintage adapted data including EM<sub>v</sub>, 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 8. 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	$EM_v$	WC	$EM_v(WC)$	EC Difference	Category Change
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

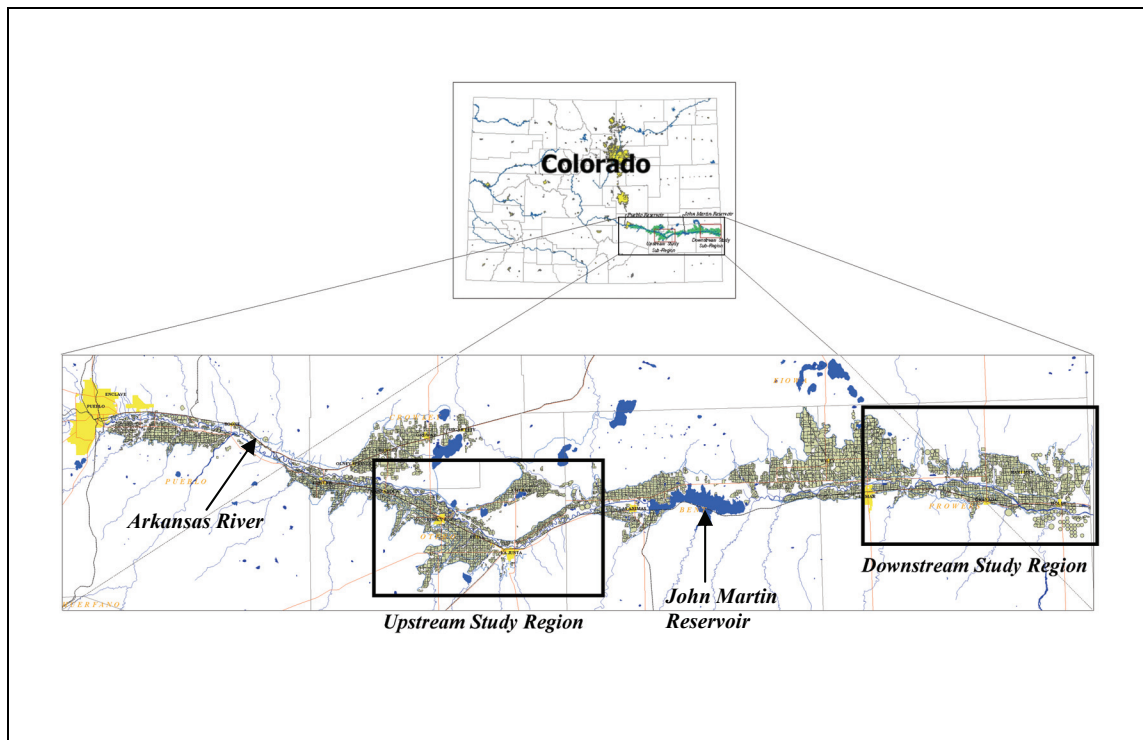


Figure 1. Map of the study region with the Upstream and Downstream sub-regions designated.

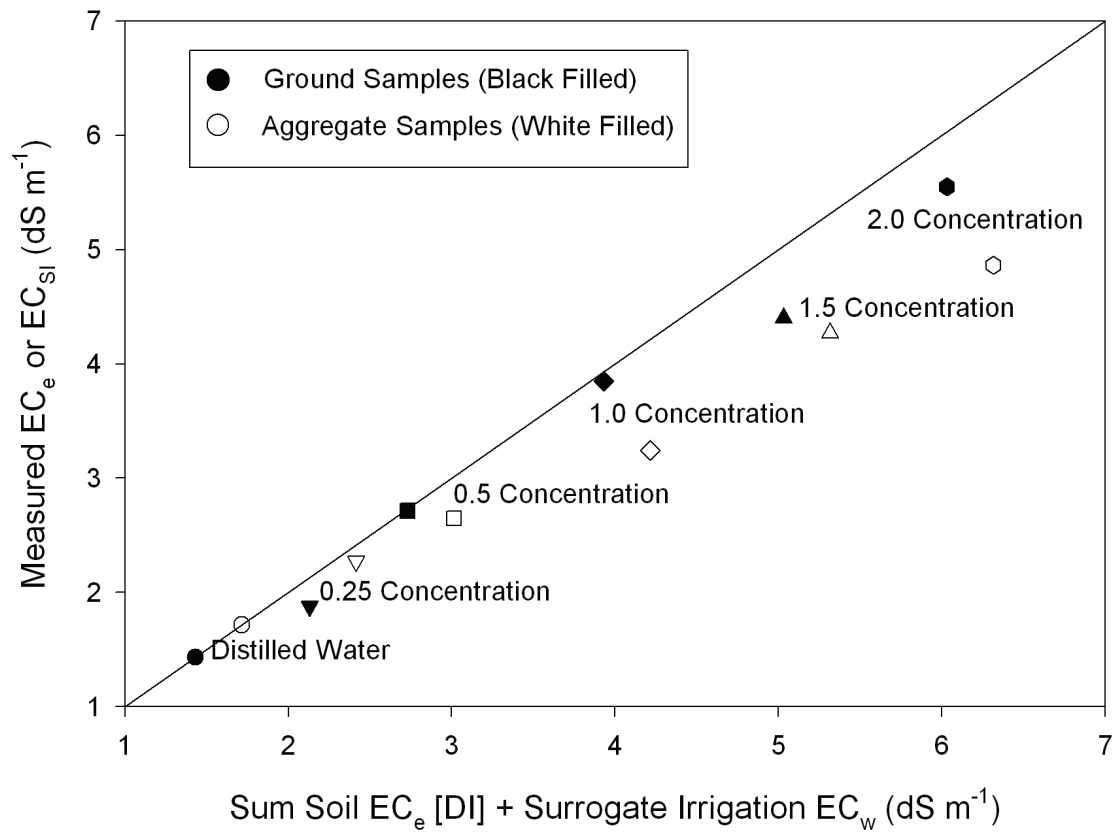


Figure 2. Average of measured  $EC_{SI}$  values for the LOW  $EC_e$  soils, against the sum of the baseline  $EC_e$  and SI  $EC_w$ . Soils were saturated with surrogate irrigation waters or with distilled water for a reference. The black filled markers represent the ground soils while the white filled 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.

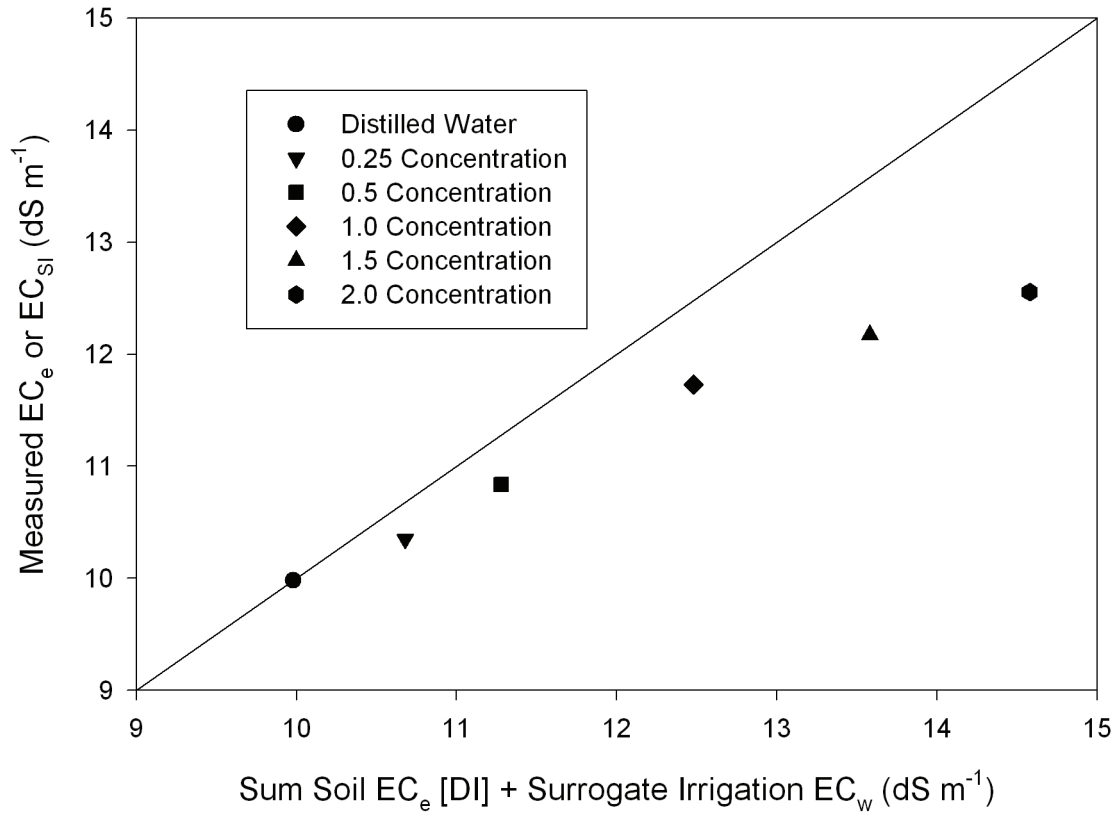


Figure 3. Average of measured EC<sub>SI</sub> values for HIGH EC<sub>e</sub> soils, against the sum of the baseline EC<sub>e</sub> and the SI EC<sub>w</sub>. Soils were saturated with surrogate irrigation waters, with the distilled water saturation for reference. A 1:1 line is added to delineate ideal correlation.

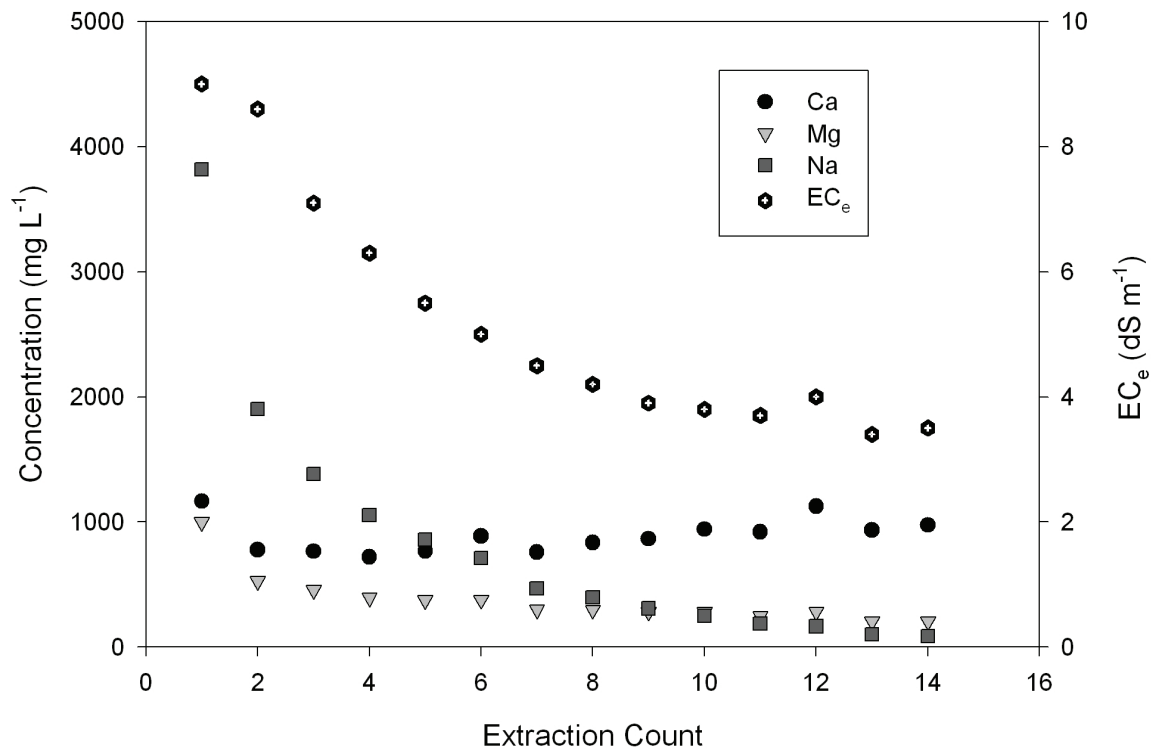


Figure 4. Las (L-CL) cations measured over 14 extractions from the same soil sample, with EC<sub>e</sub> measurements on the right axis.

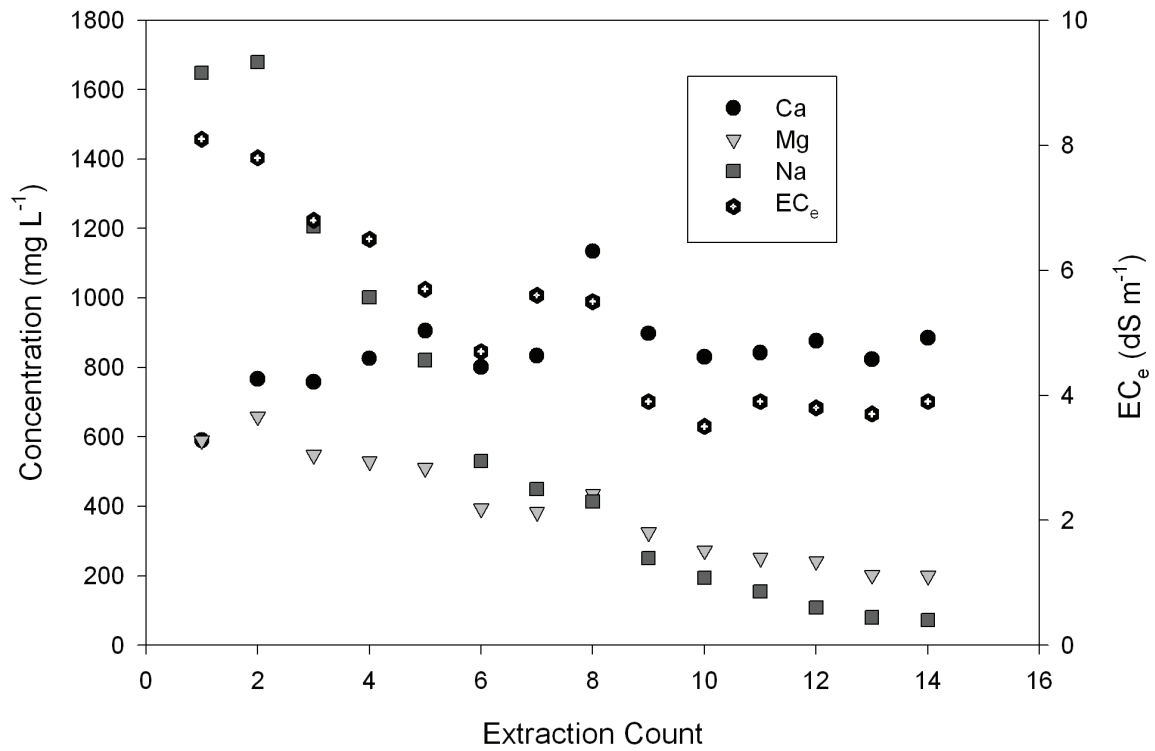


Figure 5. Rocky Ford Clay Loam (RF-CL) cations measured over 14 extractions from the same soil sample, with EC<sub>e</sub> measurements on the right axis.

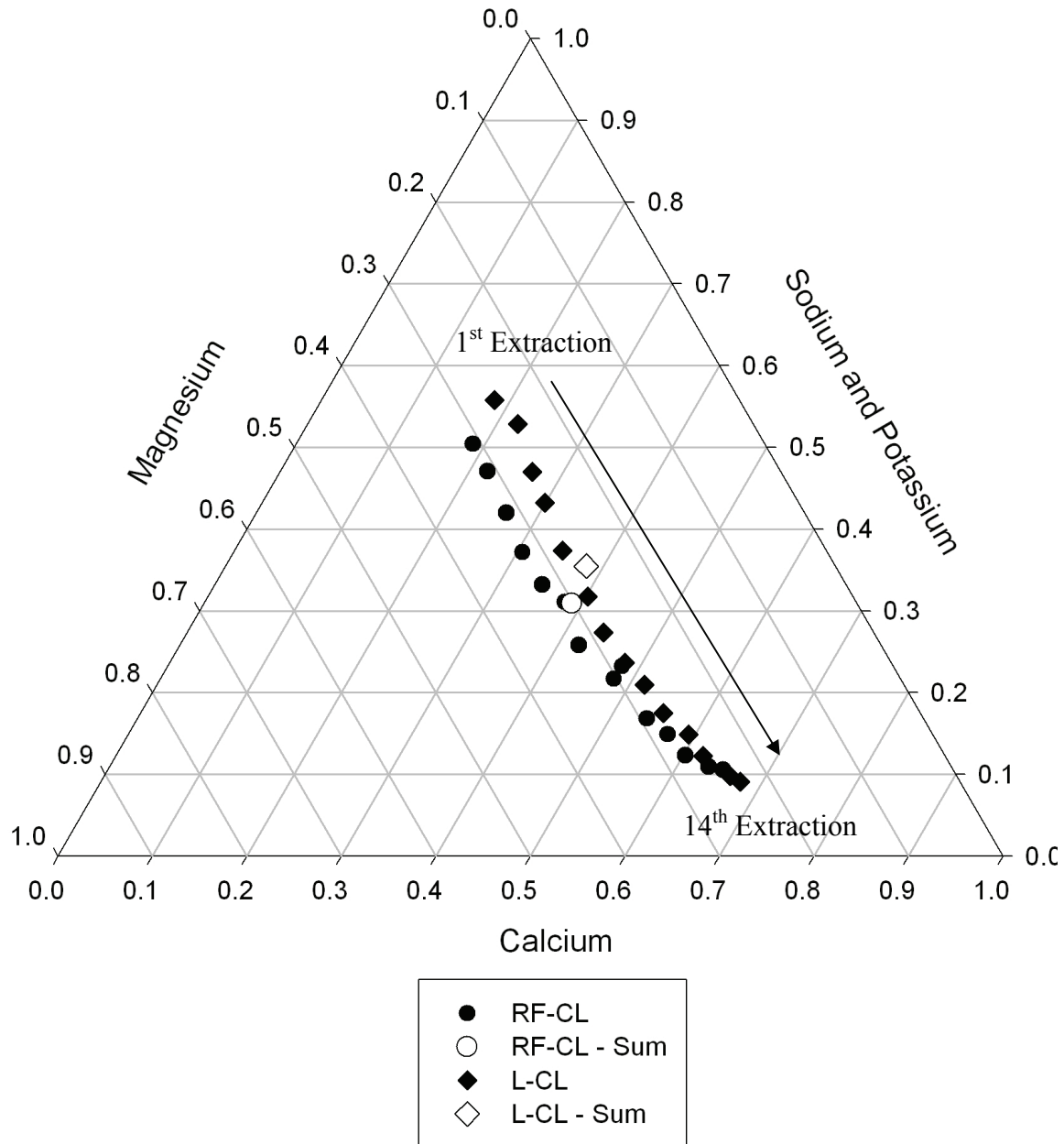


Figure 6. Ternary plot of extract soil water composition of the percent of the sum of the cations and the overall percent of the sum of the extractions, Mg values on the down and right oriented lines, while the Na and K values follow the horizontal lines.

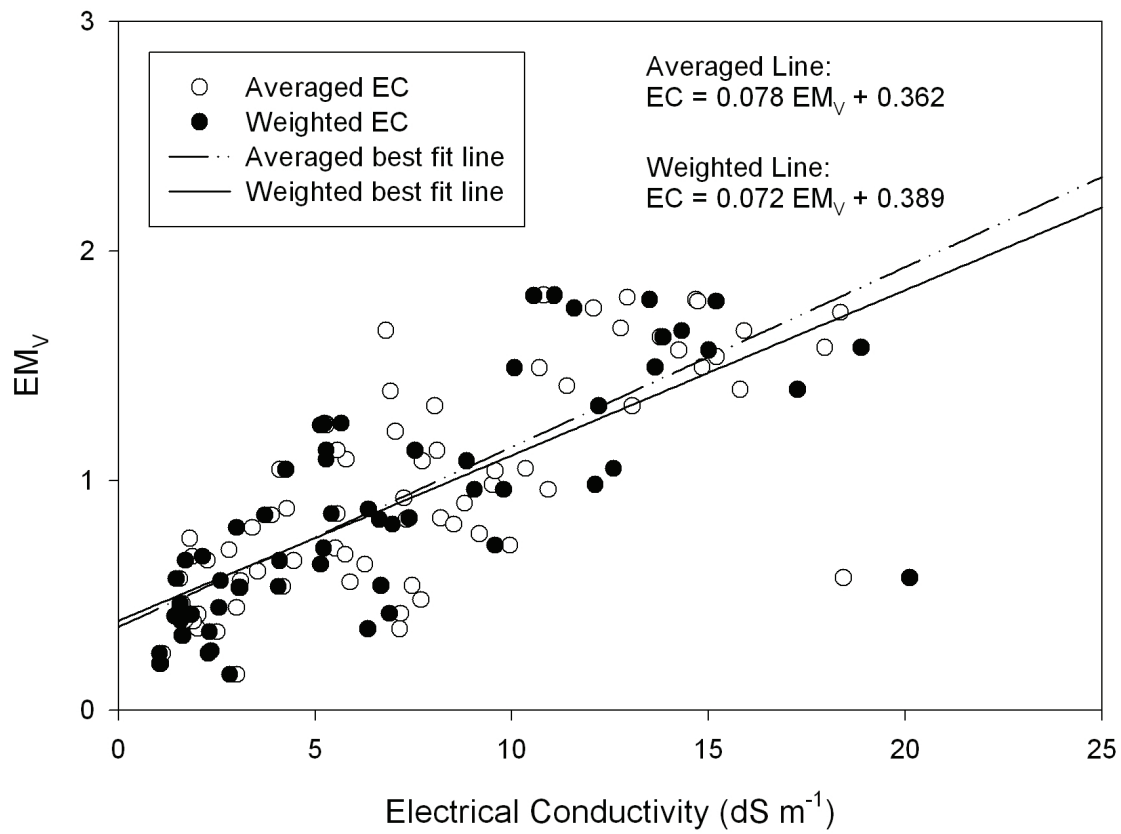


Figure 7.  $EM_v$  plotted against electrical conductivity with best fit lines to suggest a regression fit. The depth averaged  $EC_e$  best fit line had an  $R^2$  of 0.59, whereas the depth weighted best fit line had an  $R^2 = 0.55$ .

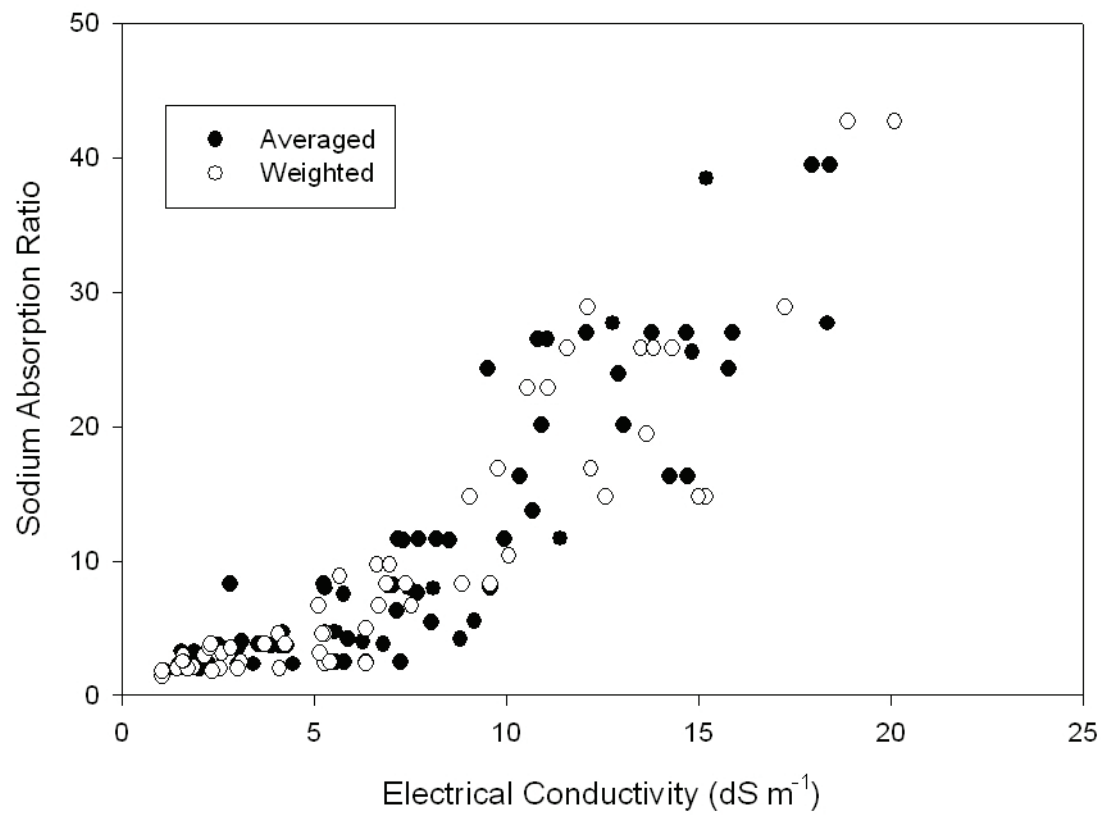


Figure 8. Sodium adsorption ratio (SAR) in the saturated paste samples as a function of electrical conductivity.



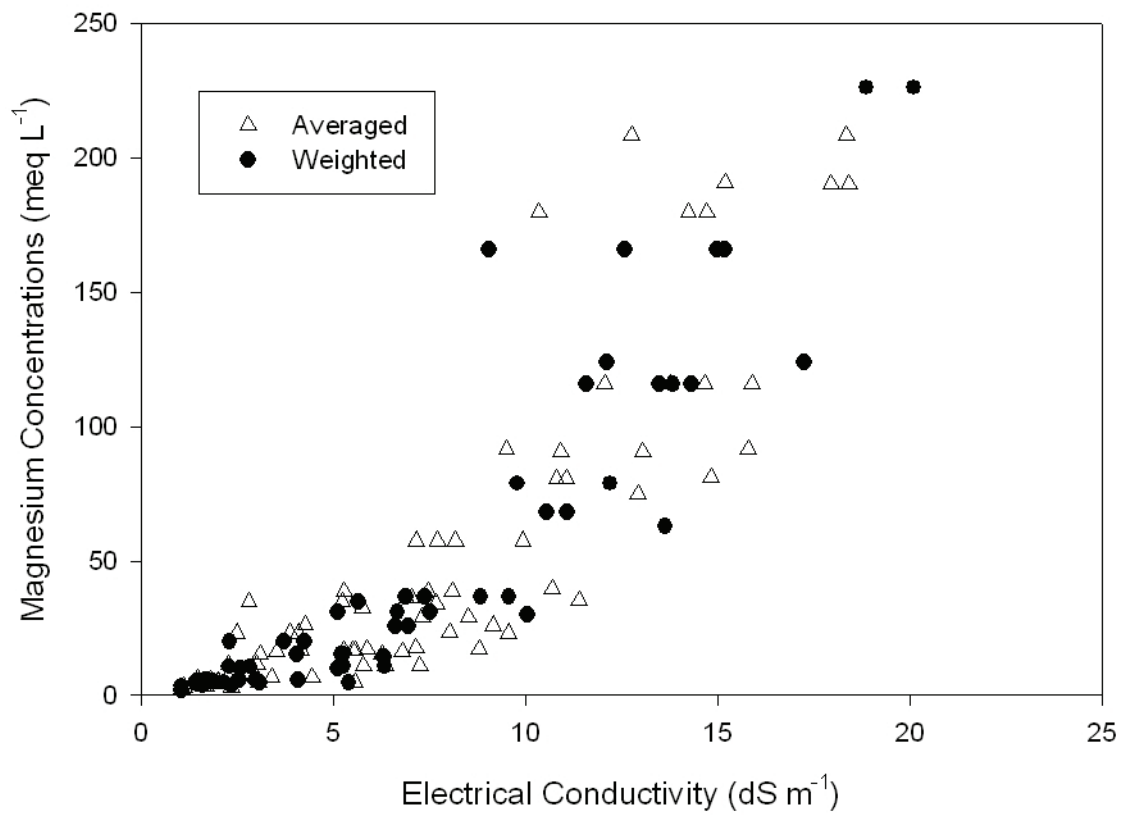


Figure 9. Magnesium concentrations as a function of electrical conductivity in saturated paste extract.

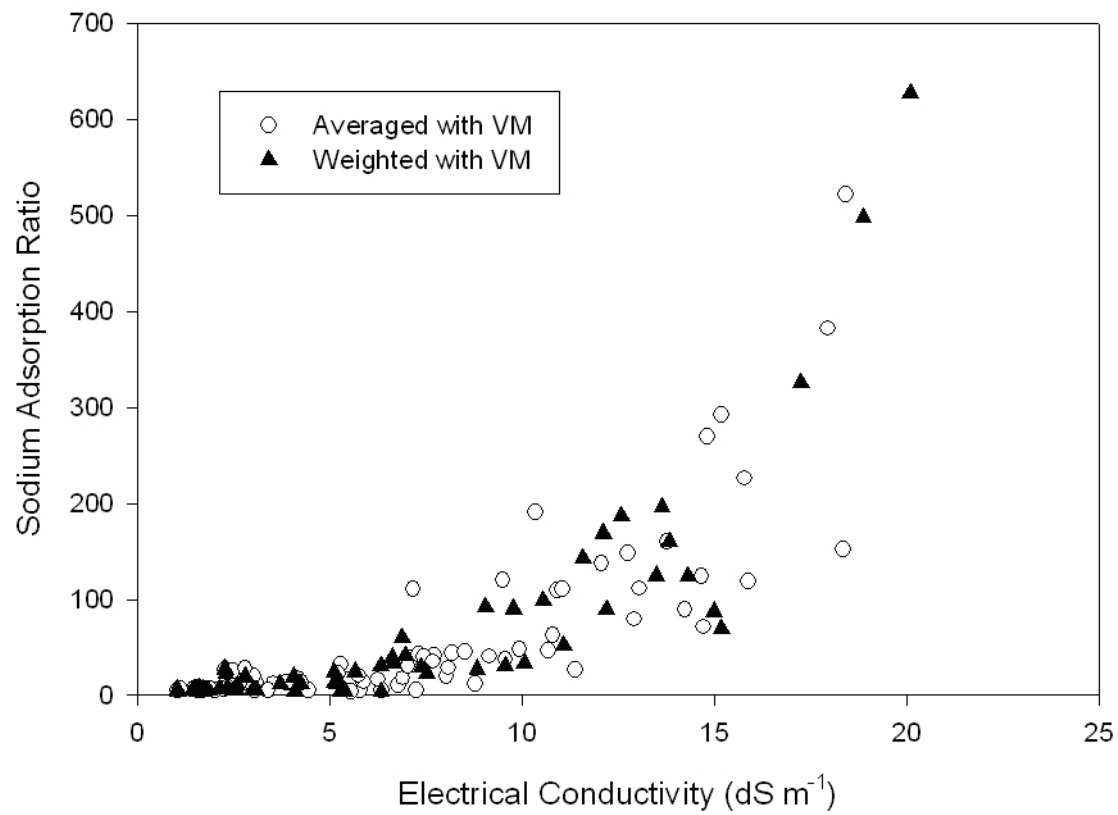


Figure 10. Sodium adsorption ratio (SAR) of the Visual Minteq (VM) adapted data as a function of electrical conductivity.

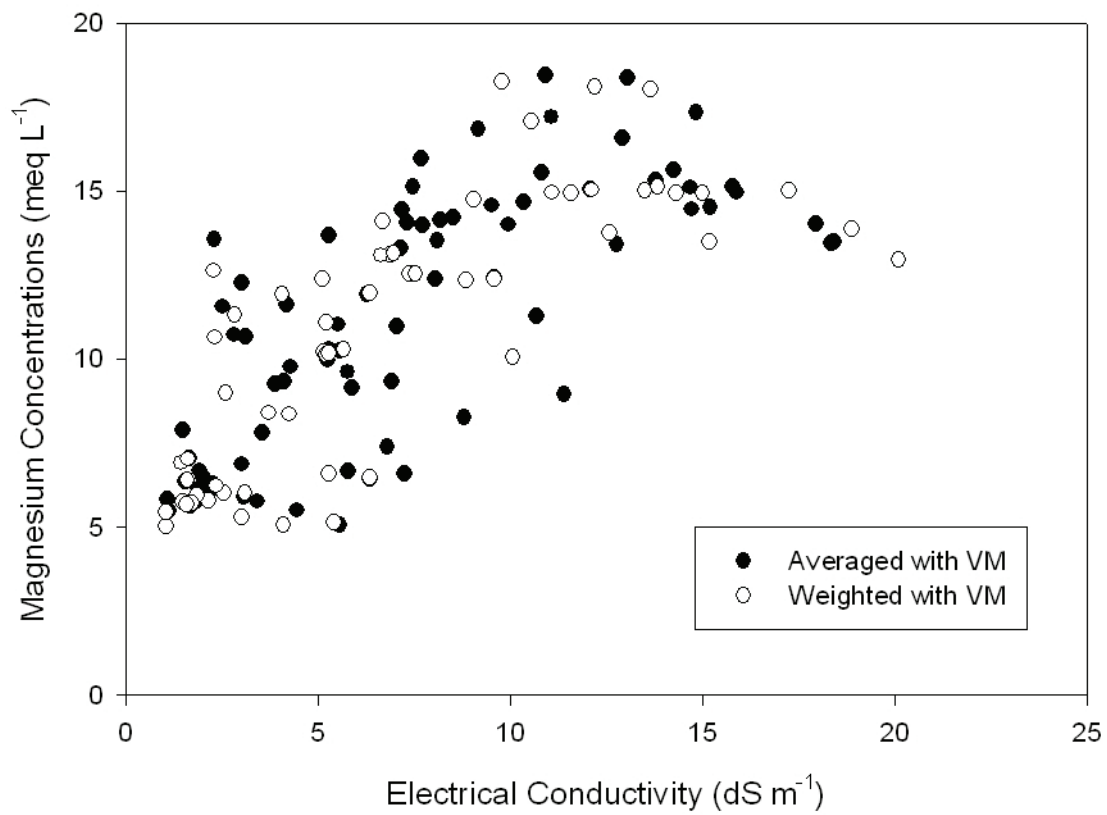


Figure 11. Magnesium of the Visual Minteq (VM) adapted data as a function of electrical conductivity.

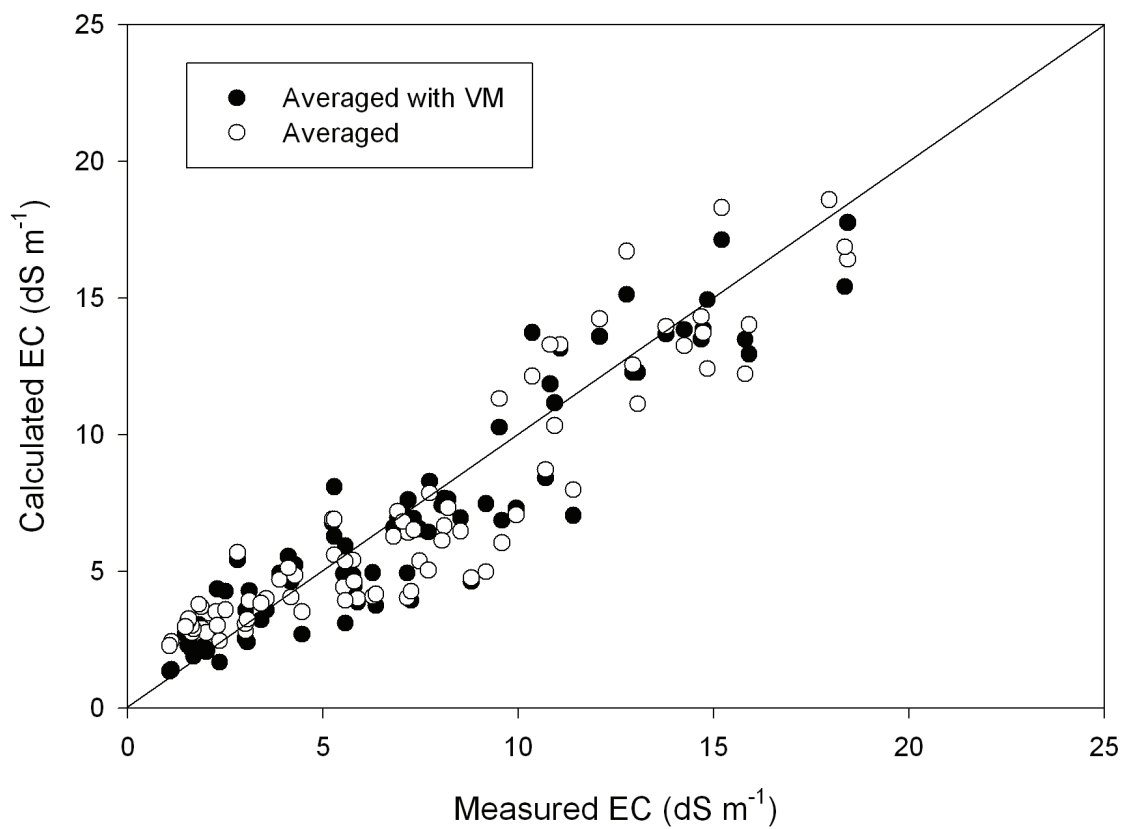


Figure 12. Calculated/predicted EC from the Averaged dataset (AVG) plotted against the Measured EC, using equations from both the saturated paste data and the Visual Minteq (VM) adapted data. A 1:1 line is added to delineate ideal correlation.

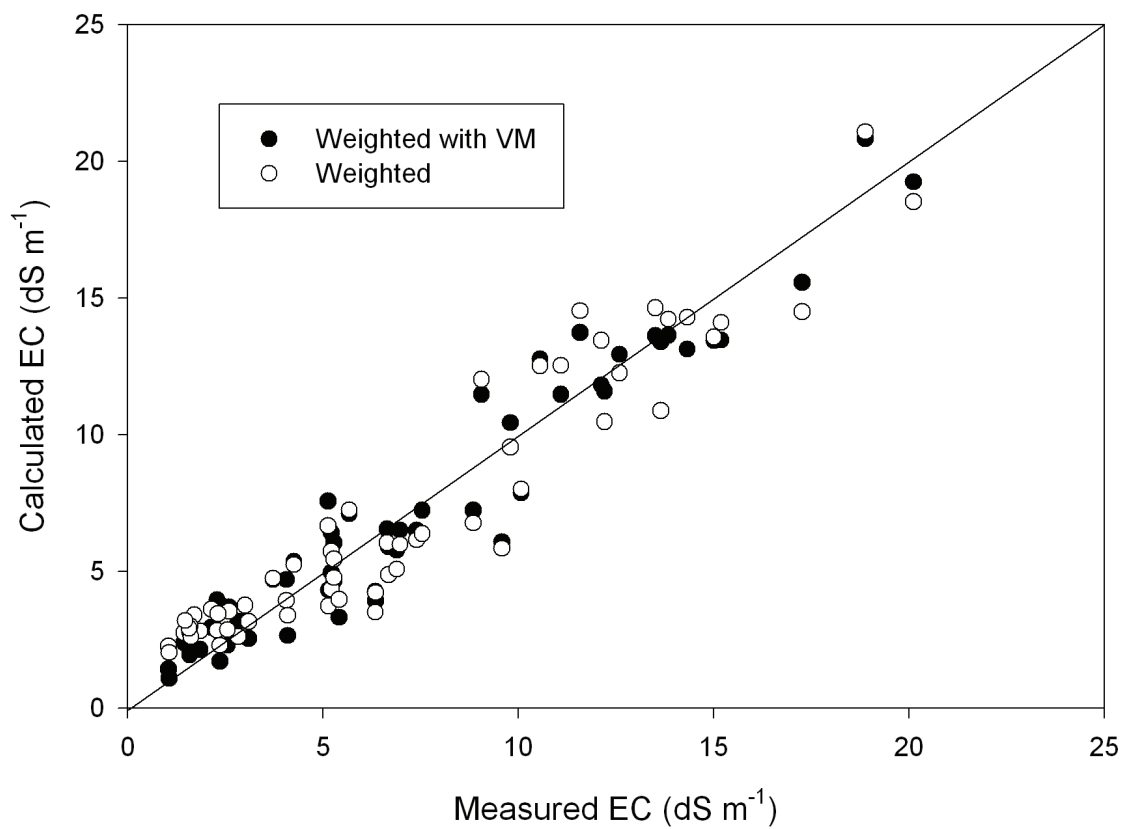


Figure 13. Calculated/predicted EC from the Weighted dataset (WGT) plotted against the Measured EC, using equations from both the saturated paste data and the Visual Minteq (VM) adapted data. A 1:1 line is added to delineate ideal correlation.

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