Methods of Soil Analysis

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Salinity: Electrical Conductivity and Total Dissolved Solids

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The measurement of soil salinity is a quantification of the total salts present in the liquid portion of the soil. Soil salinity is important in agriculture because salinity reduces crop yields by reducing the osmotic potential, making it more difficult for the plant to extract water, by causing specific-ion toxicity, by upsetting the nutritional balance of plants, and by affecting the tilth and permeability of a soil. A discussion of the principles, methods, and equipment for measuring soil salinity is presented. The discussion provides a basic knowledge of the background, principles, equipment, and current accepted procedures and methodology for measuring soil salinity in the laboratory using electrical conductivity of aqueous extracts from soil samples and measurement of total dissolved solids in the saturated soil extract. Attention is also given to the use of suction cup extractors, porous matrix or salinity sensors, electrical resistivity, and electromagnetic induction to measure salinity in soil lysimeter columns and small field plots (<10 by 10 m). Land resource managers, producers, extension specialists, Natural Resource Conservation Service field staff, undergraduate and graduate students, and university, federal, and state researchers are the beneficiaries of the information provided.

Abbreviations: DI, deionized; DPPC, dual pathway parallel conductance; EC, electrical conductivity; EC $_{\rm e}$, apparent soil electrical conductivity; EC $_{\rm e}$, electrical conductivity of the saturation extract; EC $_{\rm p}$, electrical conductivity of the saturated soil paste; EC $_{\rm w}$, electrical conductivity of the soil solution; EC $_{\rm 1:1}$, electrical conductivity of a 1:1 soil/water ratio extract; EC $_{\rm 1:2}$, electrical conductivity of a 1:5 soil/water ratio extract; EC $_{\rm 1:3}$, electrical conductivity of a 1:5 soil/water ratio extract; EMI, electromagnetic induction; ER, electrical resistivity; SP, saturation percentage; TDR, time domain reflectometry; TDS, total dissolved solids.

DEFINITION, SOURCES, EFFECTS, AND GLOBAL IMPACT

Soil salinity refers to the total salt concentration in the soil solution (i.e., the aqueous liquid phase of the soil and its solutes) consisting of soluble and readily dissolvable salts including charged species (e.g., Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, HCO₃⁻, NO₃⁻, SO₄⁻² and CO₃⁻²), non-ionic solutes, and ions that combine to form ion pairs (Corwin, 2003). The primary source of salts in soil and water is the geochemical weathering of rocks from the Earth's upper strata, with atmospheric deposition and anthropogenic activities serving as secondary sources. Salts accumulate in the root zone of agricultural soils primarily as a consequence of the process of evapotranspiration, which is the combined processes of evaporation from the soil surface and plant transpiration. Evapotranspiration selectively removes water, leaving salts behind. Soil salinity can also accumulate as a consequence of poor irrigation water quality, poor drainage due to a high water table or low soil permeability, and topographic effects where an upslope recharge results in a downslope discharge of salts. In addition, salts can accumulate from saltwater spills associated with oil field activities, from high rates of manure and sludge applications, and from seawater intrusion in coastal areas.

There are a variety of agricultural impacts that salt accumulation in the root zone can have. Salts in the root zone can reduce plant growth, reduce yields, and, in severe cases, cause crop failure. Salinity impacts on plant yield occur for several reasons. Salinity limits plant water uptake by reducing the osmotic potential, making it more difficult for the plant to extract water. Salinity may also cause specific-ion toxicity (e.g., Na⁺ and Cl⁻) or upset the nutritional balance of plants. The composition of the salts in the soil solution influences the composition of cations on the exchange complex of soil particles, which subsequently influences soil permeability and tilth.

The global impact of soil salinity is daunting. Squires and Glenn (2009) estimated the global extent of saline soils to be 412 Mha, which closely agrees with the FAO estimate of 397 Mha (http://www.fao.org/soils-portal/soil-management/management-of-some-problem-soils/salt-affected-soils/more-information-on-salt-affected-soils/en/). The estimate of Szabolcs (1989) is more conservative at 352 Mha. Of the estimated 230 Mha of irrigated land worldwide, from 20 to 50% may be salt affected (Szabolcs, 1992; Ghassemi et al., 1995; Flowers, 1999). Ghassemi et al. (1995)

estimated that salinization of irrigated soils causes an annual global income loss of US\$12 billion. Soil salinity is a crucial soil chemical property for soil health and quality that is routinely measured and monitored due to its impact on agriculture.

There are a variety of techniques to measure soil salinity. In the laboratory, the determination of soil salinity involves three different approaches: (i) the measurement of the mass of total dissolved solids (TDS, mg L⁻¹), (ii) the electrical conductivity (EC, dS m⁻¹) of soil water extracts, or (iii) the proportion and composition of salt species using spectrophotometry. In the field, soil salinity is generally measured by geospatial measurements of the apparent soil electrical conductivity (ECar dS m⁻¹), which are calibrated to salinity, because EC_a is a rapid, reliable, and easy to take measurement that is easily mobilized (Corwin and Lesch, 2005a). At intermediate scales (e.g., soil lysimeter columns to field plots, ranging from 2–200 m³) soil solution extractors, salinity sensors, capacitance sensors or frequency domain reflectometry, time domain reflectometry (TDR), and combinations of ECa and solution extracts from soil samples are used. Here we focus on soil salinity measurements of volumes <200 m³ with greatest emphasis on laboratory analysis of soil samples for salinity by measuring EC or TDS. For a comprehensive discussion of field-scale salinity assessment using ECa, see Corwin et al. (2012) and Corwin and Scudiero (2016).

RATIONALE FOR GENERAL PROCEDURE

The most common technique for the measurement of soil salinity is laboratory analysis of aqueous extracts of soil samples. Soil salinity is quantified in terms of the concentration of total salts in the soil. The measurement of the total salt concentration of the aqueous extracts of soil samples can be done either directly through chemical analysis of the chemical constituents that constitute the soil salinity (or mass of the TDS) or indirectly through the measurement of the EC. The chemical species of primary interest in salt-affected soils include: four major cations (i.e., Na+, K+, Mg2+, and Ca2+) and four major anions (i.e., Cl⁻, HCO₃⁻, SO₄²⁻ and CO₃²⁻) in the soil solution, exchangeable cations (i.e., Na+, K+, Mg²⁺, Ca²⁺), and the precipitated salts CaCO3 (lime) and CaSO4 (gypsum). Other soil properties of concern in salt-affected soils include pH, water content of the saturation paste, Na adsorption ratio, and exchangeable Na percentage. Detailed analytical techniques for measuring all of these salinity-related properties can be found in Sparks (1996), Dane and Topp (2002), and Corwin and Scudiero (2016). A chemical analysis of the chemical constituents that constitute the soil salinity is too labor and cost intensive to be practical, particularly when large numbers of samples are involved; consequently, the salinity of aqueous extracts of soil samples has been most often measured by EC. Even the measurement of the mass of the TDS is not as rapid as measuring the EC.

It is well-known that the EC of water is a function of its chemical salt composition and total salt concentration (US Salinity Laboratory Staff, 1954). In the laboratory, soil salinity is invariably determined from the measurement of the EC of soil solution extracts, where the current-carrying capacity of the soil solution is proportional to the concentration of ions in the solution. The total concentration of the soluble salts in soil is measured by the EC of the soil solution (in dS m⁻¹). Across a range of mixed salt concentrations commonly found in soils

(i.e., $1-50 \text{ mmol}_c \text{L}^{-1}$), total salt concentration (*C*, in mmol_c L^{-1}) is linearly related to electrical conductance of the solution by

$$C \approx 10 \times EC_{\text{w@25}^{\circ}\text{C}}$$
 [1]

where $EC_{w@25^{\circ}C}$ is the electrical conductivity of the soil solution referenced to 25°C (dS m⁻¹). If C is measured in milligrams per liter, then C is related to $EC_{w@25^{\circ}C}$ by a factor of 640 (i.e., $C\approx 640\times EC_{w@25^{\circ}C}$) for EC between 0.1 to 5.0 dS m⁻¹ and by a factor of 800 for EC > 5.0 dS m⁻¹. Across a broader range of salt concentrations (i.e., 10–500 mmol_c L⁻¹), the relationship between C and $EC_{w@25^{\circ}C}$ is no longer linear and is best fit with a third-order polynomial or an exponential equation. Another useful relationship is between osmotic potential (ψ_p) and EC, where ψ_p in megapascals is related to $EC_{w@25^{\circ}C}$ by a factor of -0.036 (i.e., $\psi_p\approx -0.036\times EC_{w@25^{\circ}C}$ for $3\leq EC_{w@25^{\circ}C}\leq 30$ dS m⁻¹). However, because of differences in the equivalent weights, equivalent conductivities, and proportions of major solutes in soil extracts and water samples, each of the above relationships is only an approximation.

Theoretical and empirical approaches are available to predict the EC of a solution from its solute composition. An example of a theoretical approach based on Kohlrauch's Law of independent migration of ions, where each ion contributes to the current-carrying ability of an electrolyte solution, is

$$EC = \sum_{i} EC_{i} = \sum_{i} \frac{c_{i} \left(\lambda_{0}^{i} - \beta \sqrt{c_{i}} \right)}{1000}$$
 [2]

where EC is the specific conductance (dS m⁻¹), EC_i is the ionic-specific conductance (dS m⁻¹), c_i is the concentration of the ith ion (mmol_c L⁻¹), λ_0^i is the ionic equivalent conductance at infinite dilution (cm² S mol_c⁻¹), and β is an empirical interactive parameter (Harned and Owen, 1958). An empirical equation was developed by Marion and Babcock (1976):

$$log(TSS) = 0.990 + 1.055log(EC) (r^2 = 0.993)$$
 [3]

where TSS is the total soluble salt concentration (mmol_c L^{-1}).

Temperature influences EC; consequently, EC must be referenced to a specific temperature to permit comparison. Electrolytic conductivity increases at a rate of approximately 1.9% °C⁻¹ increase in temperature. Customarily, EC is expressed at a reference temperature of 25°C. The EC measured at a particular temperature t (in °C), EC $_t$, can be adjusted to a reference EC at 25°C, EC $_t$ 25°C, using (US Salinity Laboratory Staff, 1954)

$$EC_{25^{\circ}C} = f_t \times EC_t$$
 [4]

where f_t = 0.4470 + 1.4034 exp(-t/26.815) from Sheets and Hendrickx (1995) and is referred to as the temperature correction factor.

Historically, four principal methods have been used for measuring soil salinity in the laboratory, in soil columns (i.e., <2 m³) and weighing lysimeters (2–9 m³), and at field-plot (i.e., <200 m³) scales: (i) the EC of the soil solution at or near field capacity, of extracts at higher than normal water contents (i.e., including saturation and soil/water ratios of 1:1, 1:2, and 1:5), or of a saturation paste; (ii) in situ measurement of electrical

resistivity (ER); (iii) noninvasive measurement of EC with electromagnetic induction (EMI); and (iv) in situ measurement of EC with TDR or capacitance probes.

REVIEW OF EXISTING APPROACHES: STRENGTHS AND LIMITATIONS

Electrical Conductivity

Electrical conductivity is a surrogate measure of salinity in which the salt content of the soil water extract (or soil water suspension) is determined by the ability of the extract (or suspension) to conduct electricity between two electrodes, i.e., the greater the salt concentration in the extract (or suspension), the more current that is conducted between electrodes. To determine the EC of a soil solution extract, the solution is placed in a cell containing two electrodes of constant geometry and separation distance. An electrical potential is imposed across the electrodes, and the resistance of the solution between the electrodes is measured. The measured conductance is a consequence of the solution's salt concentration and the electrode geometry, whose effects are embodied in a cell constant. At constant potential, the current is inversely proportional to the solution's resistance:

$$EC_t = \frac{k}{R_t}$$
 [5]

where EC_t is the electrical conductivity of the soil solution (in dS m⁻¹) at temperature t (°C), k is the cell constant, and R_t is the measured resistance (in W) at temperature t (1 dS m⁻¹ = 1 mS cm⁻¹ = 1 mmho cm⁻¹, which is the obsolete units of EC).

Except for the measurement of the EC of a saturated soil paste (EC_p), the determination of soluble salts in disturbed soil samples consists of three basic steps (Fig. 1): (i) preparation of a soil paste, (ii) extraction of the water from the soil paste, and (iii) measurement of the salt concentration of the extract using EC. Customarily, soil salinity has been defined in terms of laboratory measurements of the EC of the extract of a saturated soil paste (EC_e). This is because it is impractical for routine purposes to extract soil water from samples at typical field water contents; consequently, soil solution

extracts must be made at saturation or higher water contents. The saturation paste extract is the lowest soil/water ratio that can be easily extracted with vacuum, pressure, or centrifugation while providing a sample of sufficient size to analyze. The water content of a saturation paste is roughly twice the field capacity for most soils. Furthermore, EC_e has been the standard measure of salinity used in plant salt-tolerance studies. Most data on the salt tolerance of crops has been expressed in terms of the EC of the saturation paste extract (Bresler et al., 1982, p. 174–181; Maas, 1986); consequently, EC_e is regarded as the standard for the measurement of soil salinity. However, because greater time and effort is needed to obtain the saturation extract, soil solution extracts of higher soil/water ratios are often found in the scientific literature, including 1:1, 1:2, and 1:5 soil/water extracts.

Unfortunately, the partitioning of solutes across the three soil phases (i.e., gas, liquid, and solid) is influenced by the soil/water ratio at which the extract is made so that the ratio needs to be standardized to obtain results that can be applied, interpreted, and compared universally. Commonly used extract ratios, other than a saturated soil paste, are 1:1, 1:2, and 1:5 soil/water mixtures. These extracts are easier to prepare than saturation paste extracts. With the exception of sandy soils, soils containing gypsum, and organic soils, the concentrations of salt and individual ions are approximately diluted by about the same ratio between field conditions and the extract for all samples, which allows conversions between water contents using dilution factors. The conversion of EC from one extract to another is commonly done using a simple dilution factor. For example, if the gravimetric saturation percentage (SP) is 100%, then $EC_e = EC_{1:1} = 5 \times EC_{1:5}$, or if SP = 50%, then $EC_e = 2 \times EC_{1:1} = 10 \times EC_{1:5}$. However, this is not recommended, particularly in arid and semiarid soils, because of potential dissolution-precipitation reactions that may occur. At best, the use of a dilution factor to convert from one extract to another is an approximation.

Any dilution above field water contents introduces errors in the interpretation of data. The greater the dilution, the greater the deviation between ionic ratios in the sample and the soil solution under field conditions. These errors

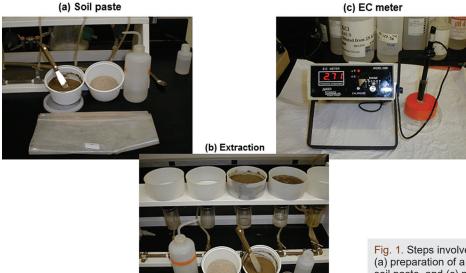


Fig. 1. Steps involved in the preparation of a soil solution extract: (a) preparation of a soil paste, (b) extraction of the water from the soil paste, and (c) measurement of the salt concentration of the extract using electrical conductivity (EC).

are associated with mineral dissolution, ion hydrolysis, and changes in exchangeable cation ratios. In particular, soil samples containing gypsum deviate the most because the Ca²⁺ and SO_4^{2-} concentrations remain nearly constant with sample dilution, while the concentrations of other ions decrease with dilution. The standardized relationship between the extract and the conditions of the soil solution in the field for different soils is lost with the use of soil/water ratios above saturation. However, software developed by Suarez and Taber (2007) allows the accurate conversion from one extract ratio to another, provided that sufficient chemical information is known (i.e., knowledge of the major cations and anions and presence or absence of gypsum). The disadvantage of determining soil salinity using a soil sample is the time and labor required, which translates into high cost. However, there is no more accurate way of measuring soil salinity than with extracts from soil samples.

Prior to the 1950s, much of the data on soil salinity was obtained by using a 50-mL cylindrical conductivity cell, referred to as a Bureau of Soils cup, filled with a saturated soil paste to estimate soluble-salt concentrations by measuring the EC_p. This approach was fast and easy; consequently, it was used to map and diagnose salt-affected soils. When Reitemeier and Wilcox (1946) determined that plant responses to soil salinity correlated more closely with the EC values of the saturation paste extract, the use of the paste was discontinued. A theoretical relationship between EC_p and EC_e has since been developed to overcome the cell's shortcomings. This was done by developing a simple method of determining the volumetric water and volumetric solid contents of the saturation paste, the conductance of the sample surface, and the current pathway of the water in the cell (Rhoades et al., 1999a). Even so, the relationship between EC_p and EC_e is complex; consequently, the measurement of EC_p is not recommended except in instances where obtaining an extract of the saturation paste is not possible or is impractical. Figure 2 graphically illustrates the theoretical complexity of the relationship between EC_p and EC_e based on the dual parallel pathway conductance (DPPC) model of Rhoades et al. (1989a, 1989b).

Soil salinity can also be determined from the measurement of the EC of a soil solution (EC $_{\rm w}$), where the water content of the soil is less than saturation, usually at field capacity. Ideally, EC $_{\rm w}$ is the best index of soil salinity because this is the salinity actually experienced by the plant root. Nevertheless, EC $_{\rm w}$

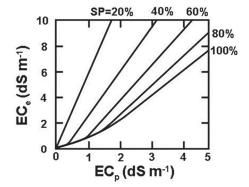


Fig. 2. Theoretical relationship between saturation extract and soil paste electrical conductivities (EC $_{\rm e}$ and EC $_{\rm p}$, respectively) for different saturation percentages (SP) based on the dual parallel pathway conductance model of Rhoades et al. (1999a).

has not been widely used to express soil salinity for various reasons: (i) it varies throughout the irrigation cycle as the soil water content changes so it is not single valued; and (ii) the methods for obtaining soil solution samples at typical field water contents are too labor, time, and cost intensive to be practical (Rhoades et al., 1999a). For disturbed soil samples, soil solution at water contents less than saturation can be obtained in the laboratory by displacement, compaction, centrifugation, molecular adsorption, and vacuum- or pressure-extraction methods. Figure 3 shows displacement equipment. A soil sample is placed in a large plastic syringe with a displacement solution (usually containing a dye) above the soil sample followed by compression of the syringe, which causes a couple of drops of soil solution to be displaced into a vial beneath the syringe. The EC_w of the displaced drops is measured using a drop EC meter. For undisturbed soil samples, EC_w can be determined with a soil-solution extractor (Fig. 4a), often referred to as a porous cup extractor, or using an in situ, imbibing-type porous-matrix salinity sensor (Fig. 4b).

Porous cup soil solution extractors include zero-tension and tension (or suction) cups. Historically, suction cups have been more widely used. Soil solution extractors are generally used for large soil columns, weighing lysimeters, or small field plots (<10 by 10 m). No single soil solution sampling device will perfectly sample under all conditions, so it is important to understand the strengths and limitations of a sampler to determine when to apply certain sampling methods in preference to other methods. In structured soils, suction cups do not sample water in preferential flow paths. Zero-tension cups will almost always sample just saturated flow, which is more closely associated with preferential flow channels, and tension samplers will more efficiently sample unsaturated flow within soil aggregates. Zero-tension cups represent the flux concentration, whereas the tension samples are approximations of resident concentrations.

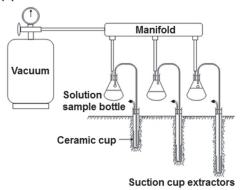
The basic design of a suction cup apparatus consists of a suction cup, sample collection bottle, manifold (if there is more than one suction cup), an overflow trap, an applied vacuum, and connective tubing (Fig. 4a). The general principle behind the operation of suction cup extractors is simply that suction, preferably the suction at field moisture capacity, is placed against the porous cup. This suction opposes the





Fig. 3. Displacement method for measuring soil salinity showing (a) the syringes containing soil samples and displacement solution in a handmade press and (b) the drop electrical conductivity (EC) meter used to measure the EC of one or two drops of displaced soil solution.

(a) Soil solution extractor



(b) Porous-matrix salinity sensor

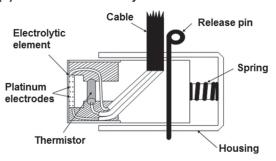


Fig. 4. Schematic of instruments for obtaining soil solution extracts at water contents less than saturation, including (a) a soil solution extractor (source: Corwin, 2002a) and (b) a porous-matrix salinity sensor (source: Corwin, 2002b).

capillary force of the soil at field capacity, causing soil solution to be drawn across the porous wall of the cup as a result of the induced pressure gradient. The imbibed solution is stored in a sample collection chamber. This approach for extracting soil solution is viable when the soil-water matric potential is greater than about $-30~\mathrm{kPa}$.

The salinity sensor consists of a porous ceramic substrate with an embedded platinum mesh electrode, which is placed in contact with the soil to measure the electrical conductivity of the soil solution that has been imbibed by the ceramic (Fig. 4b). The method assumes that the salt concentration in the ceramic is in equilibrium with the ionic constituents of the soil solution. A housing covers the sensor, with a stainlesssteel spring between the housing and sensor, which ensures good physical contact of the ceramic and soil. The salinity sensor contains a thermistor designed to temperature correct the electrical conductivity readings. Both the electrolytic element and thermistor of a salt sensor (Fig. 4b) must be calibrated for proper operation. Calibration is necessary because of (i) the variation in water retention and porosity characteristics of each ceramic and (ii) the variation in electrode spacing, both of which cause the cell constant to vary for each salt sensor. The calibration provides a functional relationship between the conductance measured by the salinity sensor (C_{se}) and the EC of the adjacent soil solution preferably at field capacity (EC_w), i.e., $C_{se} = a + bEC_{w'}$ where a and b are coefficients of the linear relationship. The calibration can change with time, so periodical recalibration is necessary. The reliability and limitations of salinity sensors were addressed by Aragüés (1982). Salinity

sensors are generally used in soil columns (i.e., <2 m³) and weighing lysimeters (i.e., 2–9 m³) because of their relatively small volume of measurement.

There are various advantages and disadvantages to measuring EC using soil solution extractors or soil salinity sensors. The obvious advantage is that EC_w is being measured, but this is outweighed by the disadvantages. Even though the sample volume of a soil-solution extractor (10–100 cm³) is roughly an order of magnitude larger than a salinity sensor (1–2 cm³), both measure very limited sample volumes; consequently, there are serious doubts about the ability of soil solution extractors and porous-matrix salinity sensors to provide representative soil water samples, particularly at field scales (England, 1974; Raulund-Rasmussen, 1989; Smith et al., 1990). Soil heterogeneity significantly affects chemical concentrations in the soil solution. Because of their small sphere of measurement, both solution extractors and salt sensors do not adequately integrate spatial variability (Amoozegar-Fard et al., 1982; Haines et al., 1982; Hart and Lowery, 1997). Biggar and Nielsen (1976) suggested that soil solution samples are "point samples" that can provide a good qualitative measurement of soil solutions but not adequate quantitative measurements unless the field-scale variability is adequately established. Furthermore, salinity sensors demonstrate a response time lag that is dependent on the diffusion of ions between the soil solution and the solution in the porous ceramic, which is affected by (i) the thickness of the ceramic conductivity cell, (ii) the diffusion coefficients of both soil and ceramic, and (iii) the fraction of the ceramic surface in contact with soil (Wesseling and Oster, 1973). The salinity sensor is generally considered the least desirable method for measuring EC_w because of its low sample volume, unstable calibration with time, and slow response time (Corwin, 2002b). Soil solution extractors have the drawback of requiring considerable maintenance due to cracks in the vacuum lines and clogging of the ceramic cups with algae and fine soil particles. Both solution extractors and salt sensors are considered slow and labor intensive.

Obtaining the EC of a soil solution when the water content is at or less than field capacity, which are the water contents most commonly found in the field, is considerably more difficult than obtaining extracts for water contents at or above saturation because of the pressure or suction required to remove the soil solution at field capacity and lower water contents. The EC of the saturated paste is the easiest to obtain followed by the EC of extracts greater than SP, followed by the EC of extracts less than SP. However, it is EC $_{\rm e}$ above all others that is most preferred; consequently, either measuring EC $_{\rm e}$ or being able to relate the EC measurement to EC $_{\rm e}$ is critical.

Electrical Resistivity

Because of the time and cost of obtaining soil solution extracts and the lag time associated with porous ceramic cups, developments in the measurement of soil EC shifted in the 1970s to the measurement of the EC of the bulk soil, referred to as the apparent soil electrical conductivity (EC_a). Apparent soil electrical conductivity provides an immediate, easy-to-take measurement of conductance with no lag time and no need to obtain a soil extract. However, EC_a is a complex measurement that has been misinterpreted and misunderstood by users in the past due to the fact that it is a measure of the electrical conductance of the bulk soil and not just a measure

of the conductance of the soil solution, which is the desired measurement because the soil solution is the soil phase that contains the salts affecting plant roots. The techniques of ER, EMI, and TDR measure $\mathrm{EC_a}$. The most comprehensive body of research concerning the adaptation and application of geophysical techniques to the measurement of soil salinity within the root zone (top 1 to 1.5 m of soil) was conducted by scientists at the US Salinity Laboratory. The most recent reviews of this body of research were provided by Rhoades et al. (1999a), Corwin (2005), and Corwin and Lesch (2005a, 2013).

Because EC_a measures the conductance of the bulk soil, it measures anything conductive in the soil. Apparent soil electrical conductivity is a measure of the conductance through three pathways in the soil (see Fig. 5): (i) solid–liquid (Pathway 1), (ii) liquid (Pathway 2), and (iii) solid (Pathway 3) conductance pathways. Because of these pathways of conductance, EC_a is influenced by a complex interaction of several edaphic properties including salinity, water content, texture (or SP), bulk density (ρ_b), cation exchange capacity, clay minerology, organic matter, and temperature. When interpreting EC_a data, these influencing factors must be kept in mind.

There are a variety of models that relate EC_a to edaphic properties. However, the most practical model is the DPPC model of Rhoades et al. (1989b), later extended by Lesch and Corwin (2003). This model is based on multi-pathway parallel electrical conductance (Fig. 5). The DPPC model has been shown to be applicable to a wide range of typical agricultural situations (Corwin and Lesch, 2003). The DPPC model demonstrates that EC_a can be reduced to a nonlinear function of five soil properties: salinity as measured by $EC_{e'}$, SP, volumetric soil water content, $\rho_{b'}$, and soil temperature. The DPPC model of Rhoades et al. (1989b) is

$$EC_{a} = \frac{\left(\theta_{ss} + \theta_{ws}\right)^{2} EC_{ws} EC_{s}}{\theta_{ss} EC_{ws} + \theta_{ws} EC_{s}} + \left(\theta_{w} - \theta_{ws}\right) EC_{wc}$$
[6]

where $\theta_{w}=\theta_{ws}+\theta_{wc}=$ total volumetric water content (cm³ cm⁻³); θ_{ws} and θ_{wc} are the volumetric soil water content in the soil-water pathway (cm³ cm⁻³) and in the continuous liquid pathway (cm³ cm⁻³), respectively; θ_{ss} is the volumetric water content of the surface conductance (cm³ cm⁻³); EC $_{ws}$ and EC $_{wc}$ are the specific electrical conductivities of the soil-water pathway (dS m⁻¹) and continuous liquid pathway

Pathways of Electrical Conductance Soil Cross Section

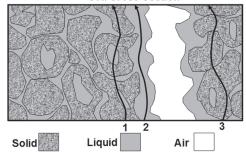


Fig. 5. Schematic illustrating the three conductance pathways for the apparent soil electrical conductivity (EC_a) measurement: solid–liquid (Pathway 1), liquid (Pathway 2), and solid (Pathway 3) (modified from Rhoades et al., 1989b).

(dS m⁻¹), respectively; and EC_s is the electrical conductivity of the surface conductance (dS m⁻¹). Equation [6] is not easily parameterized, but soil EC_a is easily converted into EC_e by substituting the following equations, originally developed by Rhoades et al. (1989b), into Eq. [6]:

$$\theta_{\rm w} = \frac{PW \times \rho_{\rm b}}{100} \tag{7}$$

$$\theta_{ws} = 0.639\theta_{w} + 0.011$$
 [8]

$$\theta_{ss} = \frac{\rho_b}{2.65} \tag{9}$$

$$EC_s = 0.019(SP) - 0.434$$
 [10]

$$EC_{w} = \left(\frac{EC_{e} \times \rho_{b} \times SP}{100 \times \theta_{w}}\right) = EC_{e} \left(\frac{SP}{100 \times \theta_{g}}\right)$$
[11]

where PW is the percentage of water on a gravimetric basis, ρ_b is the bulk density (Mg m $^{-3}$), SP is the saturation percentage, EC $_{\rm w}$ is the average electrical conductivity of the soil water assuming equilibrium (i.e., EC $_{\rm w}$ = EC $_{\rm ws}$ = EC $_{\rm wc}$), and EC $_{\rm e}$ is the electrical conductivity of the saturation extract (dS m $^{-1}$). The DPPC model is a module in the ESAP software by Lesch et al. (2000), which can be downloaded from http://www.ars.usda.gov/Services/docs.htm?docid=15992.

Electrical resistivity was originally used by geophysicists to measure the resistivity of the geological subsurface. Electrical resistivity methods involve the measurement of the resistance to current flow across four electrodes inserted in a straight line on the soil surface at a specified distance between the electrodes (Corwin and Hendrickx, 2002). The electrodes are connected to a resistance meter that measures the potential gradient between the current and potential electrodes (Fig. 6). These methods were developed in the second decade of the 1900s by Conrad Schlumberger in France and Frank Wenner in the United States for the evaluation of near-surface ER (Rhoades and Halvorson, 1977; Burger, 1992).

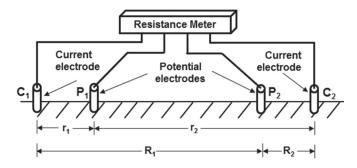


Fig. 6. Schematic of four-electrode probe electrical resistivity used to measure apparent soil electrical conductivity (modified from Corwin and Hendrickx, 2002). Schematic shows the electrical resistivity method with an array of four electrodes: two outer current electrodes (C_1 and C_2) and two inner potential electrodes (P_1 and P_2). When the electrodes are equally spaced, the electrode array is referred to as a Wenner electrode configuration.

Even though two electrodes (one current and one potential electrode) can be used, the stability of the reading is improved with the use of four electrodes. With two electrodes, measurements are obscured by electrode polarization resulting from the interaction of the charged electrode surface with free charges in the electrolyte forming an electrical double layer on the electrode surface with a large capacitance. Four electrodes mitigate the problem of electrode polarization by providing a second pair of electrodes to measure the voltage across the soil.

The resistance is converted to EC using Eq. [5], where the cell constant, k, in Eq. [5] is determined by the electrode configuration and distance. The depth of penetration of the electrical current and the volume of measurement increase as the interelectrode spacing increases. The four-electrode configuration is referred to as a Wenner array when the four electrodes are equidistantly spaced (inter-electrode spacing = a). For a homogeneous soil, the depth of penetration of the Wenner array is a and the soil volume measured is roughly πa^3 .

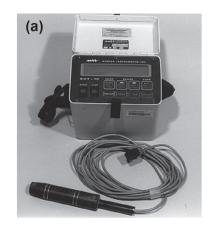
There are additional four-electrode configurations that are frequently used, as discussed by Burger (1992), Telford et al. (1990), and Dobrin (1960). The influence of the inter-electrode configuration and distance on EC_a is reflected by

$$EC_{a,25^{\circ}C} = \frac{1000}{2\pi R_t} \left\{ \frac{f_t}{1/(1/r_1 - 1/r_2 - 1/R_1 + 1/R_2)} \right\}$$
[12]

where $EC_{a,25^{\circ}C}$ is the apparent soil electrical conductivity temperature-corrected to a reference of 25°C (dS m⁻¹) and r_1 , r_2 , R_1 , and R_2 are the distances (in cm) between the electrodes as shown in Fig. 6. For the Wenner array, where $a = r_1 = r_2 = R_1 = R_2$, Eq. [12] reduces to $EC_a = 159.2 f_t/aR_t$ and 159.2/a represents the cell constant (k).

There are a variety of commercially developed four-electrode probes, reflecting diverse applications. Burial and insertion four-electrode probes are used for continuous monitoring of EC_a and to measure soil profile EC_a, respectively (Fig. 7a and 7b). These probes have volumes of measurement roughly the size of a football (i.e., about 2500 cm³), while bedding probes with small volumes of measurement of roughly 25 cm³ were used to monitor EC_a in seed beds (Fig. 7c). However, these probes are no longer commercially available. Only the Eijelkamp conductivity meter and probe are commercially available, which is similar in use and basic design to the insertion probe in Fig. 7b. Rhoades and van Schilfgaarde (1976) and Austin and Rhoades (1979) provided details for the construction of a four-electrode probe and circuitry for reading the four-electrode probe, respectively.

Electrical resistivity is an invasive technique that requires good contact between the soil and four electrodes inserted into the soil; consequently, it produces less reliable measurements in dry or stony soils than a noninvasive measurement such as EMI. Nevertheless, ER has a flexibility that has proven advantageous for field application, i.e., the depth and volume of measurement can be easily changed by altering the spacing between the electrodes. A distinct advantage of the ER approach is that the volume of measurement is determined by the spacing between the electrodes, which makes a large volume of measurement possible. For example, a 1-m interelectrode spacing for a Wenner array results in a volume of measurement of >3 m³. This large volume of measurement



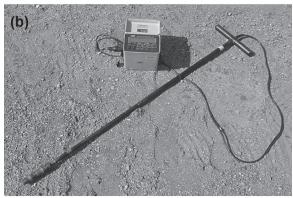




Fig. 7. Examples of various four-electrode probes: (a) burial probe, (b) insertion probe, and (c) bedding probe.

integrates the high level of local-scale variability often associated with EC_a measurements.

Because EC_e is regarded as the standard measure of salinity, a relation between EC_a and EC_e is needed to relate EC_a to salinity. The relationship between EC_a and EC_e is linear when EC_a is >2 dS m⁻¹ and is dependent on soil texture, as shown in Fig. 8. Rough approximations of EC_e from EC_a (in dS m⁻¹) when $EC_a \geq 2$ dS m⁻¹ are: $EC_e \approx 3.5 EC_a$ for fine-textured soils, $EC_e \approx 5.5 EC_a$ for medium-textured soils, and $EC_e \approx 7.5 EC_a$ for coarse-textured soils. For $EC_a < 2$ dS m⁻¹, the relation between EC_a and EC_e is more complex. In general, at $EC_a \geq 2$ dS m⁻¹ salinity is the dominant conductive constituent; consequently, the relationship between EC_a and EC_e is linear. However, when $EC_a < 2$ dS m⁻¹, other conductive properties (e.g., water and clay content) and properties influencing conductance (e.g., bulk density) have greater influence. For this

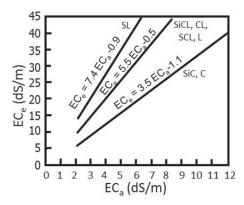


Fig. 8. Relationships between apparent and saturation extract electrical conductivities (EC $_{\rm a}$ and EC $_{\rm e}$, respectively) for representative soil types found in the US Northern Great Plains (modified from Rhoades and Halvorson, 1977), including sandy loam (SL), silty clay loam (SiCL), clay loam (CL), sandy clay loam (SCL), loam (L), silty clay (SiC), and clay (C).

reason, it is recommended that below an EC_a of 2 dS m⁻¹, the relation between EC_a and EC_e be established by calibration. The calibration between EC_a and EC_e is established by measuring the EC_e of soil samples reflecting a range of EC_a values and collected throughout the volume of measurement for the EC_a technology used (i.e., ER or EMI).

There are also low-cost insertion and burial sensors that measure EC_a through two-probe ER to obtain soil salinity and measure dielectric permittivity of the surrounding soil or medium through capacitance–frequency domain technology to obtain the volumetric water content. These sensors include Decagon's 5TE and GS3 sensors. Both sensors measure electrical conductivity, volumetric water content, and temperature. The sensors consist of three prongs.

The Decagon 5TE uses a two-electrode array (i.e., two screws on the surface of the sensor) to measure the EC_a of the surrounding medium, with an accuracy of $\pm 10\%$ from 0 to 7 dS m⁻¹, which is adequate for most field, greenhouse, and nursery applications. Special considerations must be made for salt-affected soils outside the sensors' upper limit of 23.1 dS m⁻¹, and user calibration is required above 7 dS m⁻¹. Using an oscillator operating at 70 MHz, the sensor measures the dielectric permittivity of the surrounding soil or medium to determine the volumetric water content. A thermistor located underneath the sensor overmold in contact with one of the sensor prongs provides the soil temperature. The GS3 is similar to the 5TE in most respects, but the GS3 provides an increased range of accuracy in the measurement of EC_a (±10% from 0–10 dS m⁻¹).

Electromagnetic Induction

Apparent soil electrical conductivity can be measured non-invasively with EMI. Electromagnetic induction is used on field plots or larger spatial extents. A transmitter coil located at one end of the EMI instrument induces circular eddy-current loops in the soil, with the magnitude of these loops directly proportional to the electrical conductivity in the vicinity of that loop (Fig. 9). Each current loop generates a secondary electromagnetic field that is proportional to the value of the current flowing within the loop. A fraction of the secondary induced electromagnetic field from each loop is intercepted by the receiver

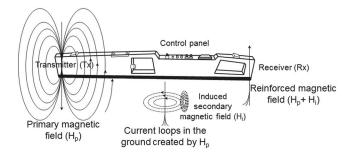


Fig. 9. Schematic showing the operation of an electromagnetic induction conductivity meter (adapted from Corwin et al., 2012).

coil of the instrument, and the sum of these signals is amplified and formed into an output voltage, which is related to a depthweighted EC_a. The amplitude and phase of the secondary field will differ from those of the primary field as a result of soil properties (e.g., clay content, water content, salinity), spacing of the coils and their orientation, frequency, and distance from the soil surface (Hendrickx and Kachanoski, 2002).

The most commonly used EMI conductivity meters in soil science and in vadose zone hydrology are the Geonics EM-31 and EM-38 (Geonics Ltd.) and the DUALEM-2 (Dualem Inc.). The EM-38 has had considerably greater application for agricultural purposes because the depth of measurement corresponds roughly to the root zone (generally 1–1.5 m). When the instrument is placed in the vertical coil configuration (EM,, i.e., coils are perpendicular to the soil surface), the depth of measurement is about 1.5 m, and in the horizontal coil configuration (EMh, i.e., coils are parallel to the soil surface), the depth of the measurement is 0.75 to 1.0 m. The EM-31 has an intercoil spacing of 3.66 m, which corresponds to a penetration depth of 3 and 6 m in the horizontal and vertical dipole orientations, respectively. Both depths extend well beyond the root zone of most agricultural crops. However, the EM-38 has one major pitfall, which is the need for field calibration (i.e., zeroing), which the DUALEM-2 does not require. The dual-dipole EM-38 and DUALEM-2 are multiple core orientation instruments that obtain both the EM_v and EM_h EC_a measurements simultaneously. Further details about and operation of the EM-31 and EM-38 equipment are discussed in Hendrickx and Kachanoski (2002). Information concerning the DUALEM-2 can be found at http://www.dualem.com/documents.html (accessed 1 Sept. 2016). For a detailed discussion of EMI conductivity equipment, protocols, methodology, and guidelines for three-dimensional mapping of the spatial variability of soil properties using EC_a-directed sampling at the field scale and larger spatial extents, see Corwin and Scudiero (2016).

Apparent soil electrical conductivity measured by EMI at $EC_a < 1.0 \text{ dS m}^{-1}$ is given by (McNeill, 1980)

$$EC_a - \frac{4}{2\pi\mu_0 fs^2} \left(\frac{H_s}{H_p}\right)$$
 [13]

where EC_a is measured in siemens per meter; $H_{\rm p}$ and $H_{\rm s}$ are the intensities of the primary and secondary magnetic fields at the receiver coil (A m⁻¹), respectively; f is the frequency of the current (Hz); μ_0 is the magnetic permeability of free space $(4\pi 10^{-7}~{\rm H~m^{-1}})$; and s is the intercoil spacing (m).

Both ER and EMI are rapid and reliable technologies for the measurement of $\mathrm{EC}_{\mathrm{a'}}$ each with its advantages and disadvantages. The primary advantage of EMI over ER is that EMI is noninvasive, so it can be used on dry and stony soils that would not be amenable to invasive ER equipment. The disadvantage is that EC_{a} measured with EMI is a depth-weighted value that is nonlinear, whereas ER provides an EC_{a} measurement that is more linear with depth. More specifically, EMI concentrates its measurement of conductance throughout the depth of penetration at shallow depths, while ER is more uniform with depth. Because of the linearity of the response function of ER, the EC_{a} for a discrete depth interval of soil, $\mathrm{EC}_{x'}$ can be determined with the Wenner array by measuring the EC_{a} of successive layers by increasing the inter-electrode spacing from a_{i-1} to a_i and using, for resistors in parallel (Barnes, 1952),

$$EC_{x} = EC_{a_{i} - a_{i-1}} = \frac{EC_{a_{i}} a_{i} - EC_{a_{i-1}} a_{i-1}}{a_{i} - a_{i-1}}$$
[14]

where a_i is the inter-electrode spacing, which equals the depth of sampling, and a_{i-1} is the previous inter-electrode spacing, which equals the depth of previous sampling. This approach is an estimation of the conductance profile and has been improved with the use of inverse modeling. Improved accuracy in conductance profiling is possible by combining inverse modeling with EMI instrumentation having dual-geometry receivers at multiple separations from the transmitter (e.g., DUALEM-421) or electrical resistivity tomography. This was discussed in greater detail by Corwin and Scudiero (2016).

Measurements of $\mathrm{EC_a}$ by ER and EMI at the same location and throughout the same volume of measurement are not comparable because of the nonlinearity of the response function with depth for EMI and the more linear response function for ER. An advantage of ER over EMI is the ease of instrument field calibration. Field calibration of the EM-31 and EM-38 is more involved than for ER equipment. However, there is no need to field calibrate the DUALEM-2.

There is also a low-cost insertion and burial sensor that measures EC_a through an electromagnetic field, Delta-T Devices' WET-2 sensor. Like the Decagon sensors, the WET-2 sensor is a three-prong sensor that measures electrical conductivity, volumetric water content, and temperature. However, in contrast to the Decagon sensors, the WET-2 sensor applies a 20-MHz signal to the central rod, which produces a small electromagnetic field within the soil. The water content, electrical conductivity, and composition of the soil surrounding the rods determines its dielectric properties. The sensor detects these dielectric properties from their influence on the electromagnetic field and calculates the water content and pore-water electrical conductivity (EC_{pw} dS m⁻¹). For all three sensors (i.e., 5TE, GS3, and WET-2), EC_{pw} is derived from Hilhorst (2000) using

$$EC_{pw} = \frac{\varepsilon_{pw}EC_{a}}{\varepsilon_{a} - \varepsilon_{EC, =0}}$$
 [15]

where ε_{pw} is the real portion of the dielectric permittivity of the soil pore water (unitless), ε_a is the real portion of the dielectric permittivity of the bulk soil (unitless), and $\varepsilon_{ECa=0}$ is the real portion of the dielectric permittivity of the soil when the EC_a is 0 (unitless).

Time Domain Reflectometry and Capacitance Sensors

Time domain reflectometry and capacitance sensors are grouped together because both measure the dielectric permittivity of the surrounding porous medium or soil. Time domain reflectometry determines the characteristics of electrical lines by observing reflected waveforms. An impulse of energy is propagated into the soil, followed by the subsequent observation of the energy reflected by the porous medium. An analysis of the shape, duration, and magnitude of the reflected waveform determines the nature of the impedance variation of the porous medium. In contrast, capacitance sensors determine the dielectric permittivity of the soil by measuring the charge time of a capacitor, which uses the soil as a dielectric.

Time domain reflectometry was initially adapted for use in measuring water content, θ (Topp et al., 1980, 1982; Topp and Davis, 1981). The TDR technique is based on the time for a voltage pulse to travel down a soil probe and back, which is a function of the dielectric permittivity (ε , F m⁻¹) of the porous medium being measured. Later, Dalton et al. (1984) demonstrated the utility of TDR to also measure EC_a. The measurement of EC_a with TDR is based on the attenuation of the applied signal voltage as it traverses the medium of interest, with the relative magnitude of energy loss related to EC_a (Wraith, 2002).

By measuring ϵ , θ can be determined through calibration (Dalton, 1992). The value of ϵ is calculated as (Topp et al., 1980)

$$\varepsilon = \left(\frac{ct}{2l}\right)^2 = \left(\frac{l_{\rm a}}{lv_{\rm p}}\right)^2 \tag{16}$$

where c is the propagation velocity of an electromagnetic wave in free space (2.997 \times 10^8 m s⁻¹), t is the travel time (s), l is the real length of the soil probe (m), $l_{\rm a}$ is the apparent length (m) as measured by a cable tester, and $v_{\rm p}$ is the relative velocity setting of the instrument. The relationship between θ and ε is approximately linear and is influenced by soil type, $\rho_{\rm b}$, clay content, and organic matter (Jacobsen and Schjønning, 1993).

By measuring the resistive load impedance across the probe ($Z_{\rm I}$), EC_a can be calculated as (Giese and Tiemann, 1975)

$$EC_{a} = \frac{\varepsilon_{0}c}{l}\frac{Z_{0}}{Z_{I}}$$
 [17]

where ε_0 is the permittivity of free space (8.854 \times 10⁻¹² F m⁻¹), Z_0 is the probe impedance (W), and $Z_{\rm L}$ = $Z_{\rm u}$ [(2 $V_0/V_{\rm f}$) – 1]⁻¹, where $Z_{\rm u}$ is the characteristic impedance of the cable tester, V_0 is the voltage of the pulse generator or zero-reference voltage, and $V_{\rm f}$ is the final reflected voltage at a very long time. The value of EC_a can be referenced to 25°C by

$$EC_{a} = K_{c} f_{t} Z_{L}^{-1}$$
 [18]

where K_c is the TDR probe cell constant $(K_c \text{ [m}^{-1}] = \varepsilon_0 c Z_0/l)$, which is determined empirically.

For a parallel plate capacitance sensor, the capacitance (C, F) is a function of the dielectric permittivity (ε) of the soil between the capacitor plates:

$$C = \frac{\varepsilon A}{S}$$
 [19]

where A is the area of the capacitor plates (m²) and S is the distance between the plates (m). The charge time on the capacitor is a simple linear function of the dielectric permittivity of the surrounding soil expressed by

$$\varepsilon = \frac{t}{\left(RA/S\right)\ln\left[\left(V - V_{\rm f}\right)/\left(V_{\rm i} - V_{\rm f}\right)\right]}$$
[20]

where t is the time it takes to charge the capacitor (s) from a starting voltage of $V_{\rm i}$ to a voltage V with an applied voltage $V_{\rm f'}$ and R is the series resistance (W).

The complex permittivity (i.e., dielectric permittivity) of soil measured by dielectric sensors (i.e., TDR and capacitance sensors) is the sum of the soil real (ϵ) and imaginary (ε'') permittivity (i.e., $\varepsilon = \varepsilon' + i\varepsilon''$, where *i* is the imaginary part, $i^2 = -1$). Water content is related to e' only, while ε'' changes according to salinity, soil temperature, and the operating frequency of the dielectric sensor. A drawback of both TDR and capacitance sensors is that the interpretation of their output can be problematic at high salinity (e.g., the Decagon ECH₂O-5TE capacitance probe has an upper limit of about 10 dS m⁻¹). Consequently, capacitance sensors and TDR are primarily used to measure water content and have not been the instruments of choice for the measurement of salinity, whether in the laboratory or in the field. However, improved calibration models and dielectric sensors with higher operating frequencies are extending the range and accuracy of soil water content and salinity determination (Scudiero et al., 2012).

The advantages of TDR for measuring EC_a include (i) a relatively noninvasive nature because there is only minor interference with soil processes, (ii) an ability to measure both soil water content and $EC_{a'}$ (iii) an ability to detect small changes in EC_a under representative soil conditions, (iv) the capability of obtaining continuous unattended measurements, and (v) a lack of a calibration requirement for soil water content measurements in many cases (Wraith, 2002). Capacitance sensors have many of the same advantages. However, because c and l in Eq. [16] are constant and a fixed length, respectively, TDR measurements are considered less susceptible to soil conditions than capacitance sensors.

Soil $\rm EC_a$ has become one of the most reliable and frequently used measurements, particularly to characterize field variability, due to its ease of measurement and reliability (Corwin and Lesch, 2003). Although TDR has been demonstrated to compare closely with other accepted methods of $\rm EC_a$ measurement (Heimovaara et al., 1995; Mallants et al., 1996; Spaans and Baker, 1993; Reece, 1998), it is still not sufficiently simple, robust, or fast enough for the general needs of field-scale soil salinity assessment (Rhoades et al., 1999a). Only ER and EMI have been adapted for the georeferenced measurement of $\rm EC_a$ at field scales and larger (Rhoades et al., 1999a, 1999b). Capacitance sensors and TDR are most often used in soil columns or small field plots where spatial variability is not a particular concern, thereby minimizing the need for numerous sensors to characterize variability.

PROCEDURE FOR LABORATORY MEASUREMENT OF SALINITY FROM SOIL SAMPLES

Soil salinity is quantified in terms of the total salt concentration of the soil solution of a soil sample. The soil solution may be obtained from an aqueous extract of the soil sample

or from a sample of displaced soil solution. The most common laboratory technique for measuring soil salinity is the analysis of aqueous extracts of soil samples using either direct or indirect analysis. Direct analysis involves the measurement of the total salt concentration through the chemical analysis of the individual chemical constituents that constitute the soil salinity for a soil sample or through the residue weight of the soil solution or aqueous extract following evaporation to dryness after filtration. The total salt concentration is the sum of the chemical constituents. Indirect analysis involves the measurement of the EC of the aqueous extract of a soil sample.

The primary chemical species in salt-affected soils include: four major cations (Na⁺, K⁺, Mg²⁺, and Ca²⁺) and four major anions (Cl⁻, HCO₃⁻, SO₄²⁻, and CO₃²⁻) in the soil solution, exchangeable cations (i.e., Na⁺, K⁺, Mg²⁺, and Ca²⁺), and the precipitated salts CaCO₃ (lime) and CaSO₄ (gypsum). Soluble fertilizers also contribute additional ions that constitute the salinity, including NH₄⁺ and NO₃⁻. To determine the contribution of these anion and cation concentrations to soil salinity, a variety of approaches are used: ion chromatography, colorimetric methods, flame-atomic absorption spectroscopy, titrimetric methods, induced coupled plasma-atomic emission spectroscopy, and induced coupled plasma-mass spectrometry.

Soil salinity can also be measured as TDS by evaporating a known filtered volume of water to dryness and weighing the residual solids. However, this method is subject to error as a consequence of incomplete filtration of clay platelets and inclusion of dissolved organic compounds in the evaporite. Rhoades (1996) provided the tedious procedure for determining TDS based on residual weight following evaporation to dryness after filtration. There is no exact quantitative relationship between EC and TDS because the chemical constituents and salt species influence the conversion values. However, there is an approximation when NaCl is the dominant salt, in which case TDS (mg L⁻¹) is obtained by multiplying EC (dS m⁻¹) by a factor of 500 to 670; the factor commonly used is 640.

In most instances, the laboratory analysis of the individual chemical constitutes that comprise soil salinity or of the residue-weight after evaporation is too resource intensive to be practical, particularly when large numbers of samples are involved; consequently, the salinity of aqueous extracts of soil samples has been most often measured by EC. Electrical conductivity is measured in the laboratory using a conductivity meter. In lysimeter columns, field plots, and entire fields, EC is most commonly determined from the measurement of the bulk soil EC or EC $_{\rm a}$ (dS m $^{-1}$).

Partitioning of solutes across the three soil phases (i.e., gas, liquid, and solid) is influenced by the soil/water ratio at which the extract is made, so the ratio must be standardized to obtain results that can be applied and interpreted universally. Customarily, soil salinity has been defined in terms of laboratory measurements of the EC_e because it is impractical for routine purposes to extract soil water from samples at typical field water contents. One widely used technique is to obtain an extract by vacuum filtration of a saturated soil paste made with distilled water. Commonly used extract ratios other than the saturation extract from a saturated soil paste are 1:1, 1:2, and 1:5 soil/water mixtures. However, extracts at these ratios provide only relative salinity because the soils are adjusted to

unnaturally high water contents not found in the field. Soil salinity can also be determined from the measurement of the EC of the soil solution at some defined field water content (EC $_{\rm w}$). An example would be the EC at field capacity, which represents the water content of the soil 2 to 3 d after irrigation when free drainage is negligible. Ideally, EC $_{\rm w}$ is the best index of soil salinity because this is a salinity actually experienced by the plant root. Nevertheless, EC $_{\rm w}$ has not been widely used for two reasons: (i) it varies throughout the irrigation cycle as the soil water content changes; and (ii) methods for obtaining soil solution samples are too labor and cost intensive to be practical for most applications.

Soil solution extracts can be obtained by various means. For disturbed samples, the soil solution can be obtained in the laboratory by displacement, compaction, centrifugation, molecular adsorption, and vacuum- or pressure-extraction methods. For undisturbed samples, EC_w can be determined either in the laboratory from a soil solution sample collected with a soil-solution extractor (see Fig. 4a) or directly in the field using in situ, imbibing-type porous-matrix salinity sensors (see Fig. 4b). The following detailed procedures focus on the measurement of soil salinity through the analysis of aqueous extracts of disturbed soil samples using indirect analysis of the EC, which is the prevalent and most common means of determining soil salinity. The soil-water extracts from disturbed soil samples include saturation, 1:1 soil/water ratio, 1:2 soil/water ratio, and 1:5 soil/water ratio extracts as well as the EC of the saturated soil paste. For a detailed discussion of measurements of solute concentrations (including soil salinity) from undisturbed volumes of soil ranging from soil columns to field plots (i.e., 2–200 m³) using soil solution extractors, salinity sensors, and TDR, see Dane and Topp (2002, p. 1253–1536).

Electrical Conductivity of Soil Extracts Saturation Extract

Soil solution samples at water contents typically found in the field are too time, labor, and cost intensive to be practical; consequently, aqueous extracts of soil samples are taken at higher than normal water contents (i.e., saturation and above) for routine soil salinity analysis. Standardization of the soil/water extract ratio is necessary to obtain results that can be interpreted and compared because the absolute and relative amounts of solutes are influenced by the soil/water extract ratio (Reitemeier, 1946). The saturation extract has become the standard because it is the lowest water content for most soils that provides sufficient extract for determination of chemical composition and analysis, causing it to be the soil water content for the measurement of soil salinity (i.e., EC_e) used in all plant salt tolerance studies (Maas and Hoffman, 1977; Maas, 1986, 1990; Grieve et al., 2012).

Materials needed:

- 500-mL (or greater) capacity plastic containers with snaptight lids
- deionized (DI) water
- a spatula
- · oven-safe weighing tins
- · labeling tape
- marker pen

- a balance or scale accurate to 0.1 g
- a vacuum-line extraction rack (see Fig. 1) consisting of a Buchner funnel, vacuum flask, filter paper (e.g., Whatman no. 1 medium flow), and extract bottles for collecting and storing the solution extract sample.

Reagent:

Sodium hexametaphosphate [(NaPO₃)₆] solution, 0.1%.
Dissolve 0.1 g of (NaPO₃)₆ in DI water and dilute the solution to 100 mL.

Method:

Using a laboratory marker and labeling tape, label the lidded plastic container with a unique ID code for the sample. Using the marker pen, label the oven-safe weighing tin with the same ID code. Weigh out 350 to 450 g of air-dried soil (ground to pass 10-mesh sieve, i.e., <2.0 mm) of known water content into a lidded plastic container. Make certain that the 350 to 450 g of air-dried soil subsample is obtained from a homogeneously mixed soil sample to assure that it is representative of the entire soil sample. Add incremental volumes of DI water to the soil, stirring the sample with a spatula after each increment of DI water. Add sufficient DI water until nearly saturated. Allow the mixture to stand covered for a couple of hours to allow the soil to imbibe water and the readily soluble salts to dissolve. Add more water with continued stirring to bring it to saturation and to get a uniformly saturated paste. Characteristic signs of a saturated paste are: (i) the surface of the paste will glisten, (ii) the saturated paste flows slightly when the plastic container is tipped, (iii) the paste slides freely off a smooth spatula, (iv) running a thin stick or spatula through the paste will create a groove that will hold its shape (if additional DI water is added and the groove folds in on itself, then the point of saturation has been exceeded), and (v) the paste consolidates easily and the groove folds in on itself by tapping the container. Be sure there are no dry clumps of soil and the soil paste is homogeneous. Seal the container with the snap-tight lid and place in cold storage (4°C) overnight. If microbial activity is a concern with regard to the saturation extract composition, then thymol $(C_{10}H_{14}O)$ can be added to the paste (Carlson et al., 1971).

In the morning remove the saturated paste from cold storage; let the paste sit until it reaches room temperature. Recheck the paste for saturation: (i) free water should not collect on the soil surface, (ii) the paste should not have stiffened, and (iii) the paste should still glisten. Stir the soil paste with a spatula to ensure that it is homogeneous. Record the weight of an empty weighing tin. Add a subsample (40–50 g) of the saturated soil paste to the weighing tin and record the weight of the weighing tin with the wet subsample. Place the tin into the laboratory oven set to $105^{\circ}\mathrm{C}$. Oven dry for 24 h, allow the weighing tin to cool, and weigh the weighing tin with the oven-dried subsample. (Note: If EC $_{\mathrm{p}}$ is desired, then see below for detailed procedural information.) Calculate the saturation water percentage (SP) of the saturated paste using

$$SP = 100 \frac{W_{w} - W_{s}}{W_{s} - W} = 100 \frac{W_{water}}{W_{soil}}$$
 [21]

where W is the weight of the weighing tin (g), $W_{\rm s}$ is the dry weight of the oven-dried saturated soil paste subsample including weight of weighing tin (g), $W_{\rm w}$ is the wet weight of

the saturated soil paste subsample including weight of weighing tin (g), W_{water} is the weight of the water (g), and W_{soil} is the weight of the oven-dried soil (g).

Apply vacuum suction and add the saturated soil paste to the Buchner funnel fitted with Whatman no. 1 filter paper (if the extract is turbid, then a more highly retentive filter paper such as Whatman no. 5 may be needed). Make sure to evenly and completely cover the filter paper with the soil paste. As moisture is removed from the soil paste, cracks in the soil cake will form. If left unchecked, air will be drawn through the cracks in the soil cake and through the extraction flask into the vacuum system. Air drawn through the soil cake will prematurely dry the cake at the cracks. Likewise, air traveling through the extraction flask will cause extract to evaporate. To prevent these from happening, the extraction process should be monitored from time to time, and cracks in the soil cake should be smoothed with a spatula. Once the extract is obtained, add 1 drop of 0.1% (NaPO₃)₆ solution for each 25 mL of extract, which prevents the precipitation of CaCO₃. Extracts that are turbid containing soil particulates will need to be filtered a second time. The second filtration is achieved by decanting the extract through a highly retentive, slow-flow filter paper (Whatman no. 5) in a laboratory funnel.

Samples that contain substantial clay may require the transfer of the unextracted soil paste to another extraction funnel or may require multiple days to extract. In the former case, the soil paste at the bottom of the soil cake dries, sealing the extract above from getting through. Transfer the unextracted soil to another extraction funnel and continue extracting. In the latter case, cover the top of the Buchner funnel with Parafilm, a watch glass, and a wet paper towel, turn off the vacuum, and leave it overnight. In the morning, unwrap and continue extracting.

The soil extract should be placed in cold storage (4°C) when not being analyzed.

1:1, 1:2, and 1:5 Soil/Water Extracts

Even though the saturation extract is the standard, there are several other soil/water extracts that are used including 1:1 and 1:5 soil/water extracts. The 1:2 soil/water extract has found occasional use in European countries and is recommended in place of 1:5 soil/water extracts for soils with appreciable amounts of gypsum. The reason for using soil/water extracts that are generally above saturation is because the procedure is faster, enabling the water extraction of large numbers of soil samples in less time with less labor.

Materials:

- 500-mL (or greater) air-tight flask or bottle
- DI water
- spatula
- · oven-safe weighing tins
- labeling tape
- marker pen
- balance or scale accurate to 0.1 g
- mechanical shaker
- vacuum-line extraction rack (see Fig. 1) consisting of a Buchner funnel, vacuum flask, medium to highly retentive filter paper (Whatman no. 1–5), and extract bottles

for collecting and storing the solution extract sample.

Reagent:

 Sodium hexametaphosphate [(NaPO₃)₆] solution, 0.1%. Dissolve 0.1 g of (NaPO₃)₆ in DI water and dilute the solution to 100 mL.

Method:

Determine the gravimetric water content of the air-dried soil by drying a subsample at 105°C for 24 h: gravimetric water content of air-dried soil = (g of air-dried soil - g of oven-dried soil)/g of oven-dried soil. Weigh out 350 to 450 g of air-dried soil ground to pass a 10-mesh sieve (<2.0 mm) and transfer to a labeled flask or bottle. Make certain that the 350 to 450 g of air-dried soil subsample is obtained from a homogeneously mixed soil sample to assure that it is representative of the entire soil sample. Add the required amount of DI water to bring the soil and water to an equal weight for a 1:1 extract, taking into account the water content in the air-dried soil when determining the amount of DI water to add. For example, an air-dried sample containing 2% water (i.e., a gravimetric water content of 0.02 g g⁻¹) on an oven-dried basis can be adjusted to a 1:1 soil/water ratio by adding 98 mL of water to 102 g of air-dried soil. For the 1:2 soil/water extract, the weight of the water should be two times the weight of the soil, and for the 1:5 soil/water extract, the weight of the water should be five times the weight of the soil. At a soil/water ratio of 1:5, no correction for the water content of the air-dried soil is generally needed because the water content is so high that the correction becomes insignificant.

Stopper the container and shake it on a mechanical shaker, preferably an end-over-end shaker, for 1 h to dissolve soluble salts. In the absence of a mechanical shaker, shake the container vigorously by hand for several minutes at least five to six times at 30- to 60-min intervals. Filter the suspension with a highly retentive filter paper (Whatman no. 5). If filtration is too slow with the highly retentive filter paper, then filter with Whatman no. 1 filter paper (if extract is turbid, then filter again with a more highly retentive filter paper such as Whatman no. 5). Once the final extract is obtained, add 1 drop of 0.1% (NaPO₃) $_6$ solution for each 25 mL of extract. All extracts should be stored at 4°C until analyzed.

Comments Regarding Soil Extracts

Selection of the mass of soil to use to obtain a water extract depends on several factors: (i) the volume of extract needed for chemical analyses as determined by the number and type of analyses conducted and (ii) the salt content of the soil. As a general rule, 25 to 30% of the water in a saturation soil paste can be removed by the vacuum extraction and filtration process.

As discussed by Reitemeier (1946), salinity and chemical constituent errors due to mineral dissolution, dispersion, hydrolysis, and cation exchange increase as the soil/water ratio increases from 1:1 to 1:5. Even though extract ratios of 1:1, 1:2, and 1:5 require less labor and usually provide greater extract volume, they are less representative of field soil water compositions and contents. Sonneveld and van den Ende (1971) suggested the use of a 1:2 soil/water extract because it (i) is closer to the saturation extract ratio, (ii) provides greater extract volume, and (iii) is faster. However, 1:2 soil/water extracts are not as common as 1:1 and 1:5. Gypsiferous soils

are particularly problematic at various extract ratios. Due to dissolution reactions, the EC of extracts of gypsiferous soils decreases less as the soil/water ratio increases from 1:1 to 1:5. Gypsum dissolution exaggerates the soluble salt concentration at lower soil water contents, especially at water contents found under field conditions. Inaccuracies due to dissolution reactions can be dealt with through the use of the ExtractChem software of Suarez and Taber (2007), which enables the conversion of EC from any soil/water extract ratio to the EC of the saturation extract (i.e., EC_e). However, ExtractChem requires knowledge of the SP and major cations and anions, which is considerable work to obtain, making the preparation of saturation extracts more appealing in many cases.

Air-dried soil should be used rather than oven-dried soil when preparing extracts for the determination of EC. This is due to the fact that heating to 105° C converts a portion of the gypsum (i.e., $CaSO_4 \cdot 2H_2O$) to $CaSO_4 \cdot 1/2H_2O$, which has a higher solubility in water than gypsum. Furthermore, other salts and minerals are affected by heating.

Special consideration should be given to the preparation of saturation extracts from peat or muck soils, very fine-textured soils, and very coarse-textured soils (Prichard et al., 1983). Peat and muck soils need to remain moist after sampling; consequently, they should not be air dried like mineral soils. Once brought to near saturation, both peat and muck soils must sit overnight to obtain a more accurate saturation point by adding DI water and remixing the following morning. In the case of very fine-textured soils, DI water should be added with a minimum of mixing to bring the sample to nearly saturation. The wetted soil should sit overnight. In the morning, DI water should be added and mixed to bring the soil to saturation. This will help obtain a more definitive endpoint for saturation and reduce the likelihood of overwetting. Similarly, caution should be taken to prevent the overwetting of very coarse-textured soils. An indicator of oversaturation is the presence of any free water standing on the surface of the soil paste. The effect of oversaturation has a small effect on the EC_e but can result in appreciable error in the SP.

Electrical Conductance of Soil Extracts

Materials:

- EC meter
- calibration standard solution (if available)
- wash bottle with DI water
- Kimwipes
- · shell vials
- 100-mL beaker

Reagent:

• If a calibration standard solution is not available, then make a 0.010 M KCl reference solution. Dissolve 0.7455 g of reagent-grade anhydrous KCl (i.e., KCl should be dried at 110°C for 2 h) in CO₂–free distilled or DI water (EC < 0.001 dS m⁻¹) and make to a volume of 1.0 L in a glass-stoppered borosilicate glass volumetric bottle. The reference solution EC is 1.413 dS m⁻¹ at 25°C. If the soil solution extract has an EC significantly higher than 1.413 dS m⁻¹, then a higher EC calibration standard solution is needed.

Method:

Remove soil solution extracts from 4°C cold storage and bring to room temperature. Calibrate the EC instrument using the calibration standard solution. Calibration procedures vary by instrument; consequently, following the manufacturer's instructions is recommended. No single probe can measure the entire range of soil solution extracts; consequently, the appropriate EC probe must be selected that will cover the range of ECs for the soil solution extracts of interest. An EC probe range of 0.001 to 50 dS m⁻¹ is generally sufficient. Calibration is done using one or two calibration standard solutions depending on the EC instrument. Rinse the conductivity probe thoroughly before and after calibration using DI water, and carefully blot the probe dry using a Kimwipe. Choose a calibration standard solution that approximates the range of your extracts. If the range is broad, then select a calibration standard solution that is 65% of the full range. Gently agitate the calibration standard solution and add about 5 mL of solution to a shell vial. With the EC meter set to an appropriate range, dip the probe into the shell vial. The probe should not rest at the bottom of the vial, and the tip of the probe should be submerged about 2.5 cm. Gently move the probe up and down a few times to dislodge any air bubbles. Allow the reading to equilibrate. Adjust the calibration control until the display reads the value of the standard solution used. Using the wash bottle, rinse the outside and inside of the conductivity probe; use the 100-mL beaker to catch the rinse water. Shake off the excess water and gently pat dry with a Kimwipe. The conductivity meter should be recalibrated if changing ranges. For this reason, it is recommended to set aside extracts that are of a different range to be analyzed later.

Gently agitate the extract sample and pour about 5 mL of soil extract into a shell vial. Dip the probe into the shell vial. The probe should not rest at the bottom of the vial, and the tip of the probe should be submerged about 2.5 cm. Gently move the probe up and down a few times to dislodge any air bubbles. Allow the reading to equilibrate and record the EC reading of the extract. Use the wash bottle and Kimwipes to rinse and dry the probe between extracts. Many EC meters have automatic temperature correction, which adjusts the EC to 25°C. If the meter does not have any means of temperature correction, then the temperature of the extract must be obtained and the EC must be adjusted to 25°C using Eq. [4]. If the EC reading is erratic, it may be necessary to clean the probe. Follow the cleaning instructions provided by the manufacturer. This often requires soaking the probe in a cleaning solution overnight.

Electrical Conductance of Saturated Soil Paste

Materials:

- EC meter
- calibration standard solution (if available)
- · wash bottle with DI water
- Kimwipes
- 100-mL beaker

Reagent:

 If a calibration standard solution is not available, then make a 0.010 M KCl reference solution. Dissolve 0.7455 g of reagent-grade anhydrous KCl (i.e., KCl should be dried at 110° C for 2 h) in CO₂–free distilled or DI water (EC < 0.001 dS m⁻¹) and make to a volume of 1.0 L in a glass-stoppered borosilicate glass volumetric bottle. The reference solution EC is 1.413 dS m⁻¹ at 25°C. If the saturated soil paste has an EC significantly higher than 1.413 dS m⁻¹, then a higher EC calibration standard solution is needed.

Method:

Conductivity of the soil paste is determined before the soil solution is extracted from the saturated soil paste. Use an EC probe that is easy to clean and doesn't require the soil paste to flow into the probe. A probe should be selected that will enable good contact with the saturated soil paste.

Gently agitate the calibration standard solution. Follow the same EC instrument calibration procedure described above for soil extracts.

Remove the saturated soil paste from overnight 4°C cold storage; let the paste sit until it reaches room temperature. Stir the soil paste to make it homogeneous just prior to measuring the EC_p. Dip the probe into the soil paste, moving the probe around to ensure good contact with the soil paste. Wait for reading to equilibrate and record measurement. Use the wash bottle and Kimwipes to rinse and dry the probe between pastes. Many EC meters have automatic temperature correction, which adjusts the EC to 25°C. If the meter does not have any means of temperature correction, then the temperature of the paste must be obtained and the EC must be adjusted to 25°C using Eq. [4]. If the EC reading is erratic, it may be necessary to clean the probe. Follow the cleaning instructions provided by the manufacturer. This often requires soaking the probe in a cleaning solution overnight.

Total Dissolved Solids in Soil Saturation Extract

Total dissolved solids refers to any salts, minerals, metals, cations, or anions dissolved in a soil saturation extract, composed primarily of inorganic salts consisting of the major cations (i.e., Na⁺, K⁺, Ca²⁺, and Mg²⁺), major anions (i.e., Cl⁻, NO_3^- , HCO_3^- , CO_3^{2-} , and SO_4^{2-}), and small amounts of organic matter that are dissolved in water. These inorganic and organic substances are dissolved in water in molecular, ionized, or microgranular suspended form. The amount of TDS in a soil sample is measured by weighing the residue remaining after evaporating a soil or water sample that has been filtered. The general methodology consists of filtering a soil sample that has been brought to a specified water content (usually saturation) through a membrane filter (usually 0.45-μm pore size), evaporating the filtrate to dryness in a ceramic weighing dish placed in a drying oven at 103°C, and finally drying to a constant weight at 180°C to remove occluded water, which is water trapped in the mineral matrix. In general, the TDS concentration is the sum of the cations and anions in water. The units of TDS are milligrams per liter. Because some colloids are not removed by filtration and the composition of the residue differs from the dissolved material initially present in the water, the definition is operational.

Materials:

- evaporation dish
- temperature-controlled electrical hot plate (capable of temperature control near but not exceeding boiling)

- muffle furnace (capable of operation at 600 ± 25 °C)
- desiccator
- drying oven (capable of operation at $180 \pm 2^{\circ}$ C)
- analytical balance (accuracy ± 0.1 mg)
- filtration apparatus (capable of removing particulates >0.45 mm in diameter)
- distilled deionized (DDI) water

Method:

Heat an evaporation dish for 1 h to 600 ± 25 °C. Cool and store the evaporation dish in a desiccator. Precisely measure the volume (in mL) of the soil saturation extract needed to yield on evaporation a minimum of 25 mg of residue. Pass the measured volume of extract through a filter membrane, followed by three successive 15-mL volumes of DDI water. Weigh the evaporation dish. Transfer the complete filtered sample to an evaporation dish. Heat the evaporation dish to evaporate the filtered sample but do not bring it to a boil and don't heat to the point where the filtered sample is dry. When the filtered sample is nearly dry, transfer it to a 103°C drying oven and complete the evaporation. Dry the evaporation dish and residue for 1 h at 180 \pm 2°C, cool in a desiccator, and weigh the evaporation dish and residue. Repeat the 1-h drying, cooling in the desiccator, and weighing cycle until a constant weight is attained (or until the weight loss is <4% of the previous weight or 0.5 mg, whichever is less). Record the weight of the dried residue plus dish. The TDS (in mg L^{-1}) is calculated by

$$TDS = 1000 \frac{A - B}{V_{sc}}$$
 [22]

where A is the weight of the dried residue plus the evaporation dish (mg), B is the weight of the evaporation dish (mg), and $V_{\rm se}$ is the volume of soil saturation extract (mL).

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