CENTRAL ARIZONA SALINITY STUDY—PHASE I

Technical Appendix A

SALINITY AND TOTAL DISSOLVED SOLIDS

Introduction

Salinity or Total Dissolved Solids (TDS) is a measure of the total ionic concentration of dissolved minerals in water. Owing to broad variation in the TDS of both imported and local water supplies, water resource managers for many years have been forced to balance the consumer's demand for high quality water with the quality of available water supplies. This issue paper provides brief background information related to the chemical constituents comprising TDS and their analytical determination, and includes discussions on the limitations of these chemical constituents relative to their ultimate uses. The purpose of this issue paper is to provide a background reference guide on the threshold concentrations of salinity that impact various uses.

Chemical Components of TDS and Their Measurement

TDS is composed of the following principal cations (or positively charged ions): Sodium (Na^+), Calcium (Ca^{2+}), Potassium (K^+), Magnesium (Mg^{+2}), and anions (or negatively charged ions): Chloride (Cl^-), Sulfate (SO_4^{2-}), Carbonate (CO_3^{2-}), Bicarbonate (HCO_3^-), and, to a lesser extent by Nitrate (NO_3^-), Boron (B^{3+}), Iron (Fe^{3+}), Manganese (Mn^{2+}) and Fluoride (F^-). TDS can be readily estimated in the field or laboratory by measuring the electrical conductivity (EC) of an aqueous solution. Electrical conductance is a measure of the electrical current produced (typically in micromhos per centimeter (μmhos/cm) or microsiemens per centimeter (μS/cm) by the dissolved ions. For water containing less than 5,000 milligrams per liter (mg/l) TDS, the ratio of EC:TDS generally ranges from about 1.04:1 to 1.85:1 and averages about 1.56:1. In the laboratory, TDS is typically determined by evaporating a known quantity of filtered water at 18^o C then weighing the residue. The TDS of a water sample may also be estimated by summing the concentrations of the principal cations and anions. However, to accurately obtain, by summation, a result comparable to that determined by the evaporation method, only one-half of the HCO_3 value is to be used since, under the evaporation method, carbon dioxide (CO_2) and water of hydration (H_2O) which make up approximately one-half of the HCO_3 would be driven off and not included in the residue.

The individual cations and anions comprising TDS, with the exception of CO_2 and HCO_3, are measured by specific analytical methods in the laboratory. Carbonate and HCO_3 are typically determined by means of a calculation based on the results of alkalinity analyses and the associated pH at the titration endpoints. Nitrate, Fe, Mn, F and B concentrations are also determined through specific chemical analyses.

Other Related Analyses

Another item of concern to water resources managers is the hardness of the water supply. Hardness results from the presence of divalent metallic cations, of which Ca and Mg are the most abundant. Excessive hardness causes scale formation in boilers and reacts with soap to form a scum which prohibits lathering. Hardness can be measured experimentally or calculated through the formula: $H = 2.5\ Ca + 4.1\ Mg$ (Todd, 1980) where Ca and Mg concentrations are in mg/l. Hardness may also be calculated by multiplying the sum of the milliequivalents per liter of Ca and Mg by 50 [As reference, the milliequivalent of an ionic species calculated based on the atomic weight of the ionic species divided by its valence (e.g., Ca = 40.08/2 = 20.04) which is then divided by the concentration (in mg/l) of the ionic species in water].

Limitations of TDS and Related Chemical Constituents to Water Use

The beneficial uses of imported water and local water supplies generally consist of domestic or municipal, industrial, and agricultural. The concentration of TDS and/or the related chemical constituents comprising TDS in water supplies can limit the beneficial use of these waters. The following sections provide information on the limitations of water supplies based on TDS and related chemical constituent concentrations.

Drinking Water Quality Standards

The Safe Drinking Water Act (SCWA) was signed into law in 1974. The SDWA has been amended several times since, most recently in 1996 (Safe Drinking Water Act Amendments of 1996, Public Law 104-182). The SDWA mandates that the United States Environmental Protection Agency (USEPA) develop maximum contaminant levels (MCLs) or treatment techniques for drinking water constituents that may be of a health or aesthetic concern. MCLs for a wide range of constituents have been established, some of which are summarized in Table 1 for drinking water relative to TDS and related chemical constituents. Primary standards are for substances with a health risk. Secondary standards are recommended levels for substances, which can affect the aesthetic quality of water such as color, taste, or odor: but have no health risk.

Table 1 - Summary of Primary and Secondary State and Federal Drinking Water Standards for Total Dissolved Solids and Related Chemical Constituents

Chemical Constituent	Arizona Department of Environmental Quality MCL (mg/l)	USEPA MCL (mg/l)
Primary MCLs		
Fluoride	4.0	4.0
Nitrate	10	10[1]
Secondary MCLs		
Iron	--	0.3
Manganese	--	0.05
Chloride	--	250
Sulfate	--	250
TDS	--	500
1. Measured as N. In addition, the MCL for total nitrate/nitrite = 10 mg/l.		

Domestic/Industrial Limitations

Presented in Table 2 is a summary of the various limitations of TDS and related chemical constituents for domestic and industrial use. It should be noted that some types of industry (e.g., computer microchip manufacturers) require water that exceeds drinking water standards and therefore must treat the water supply prior to use.

Table 2 - Principal Chemical Constituents Related to TDS, their Natural Concentrations in Water and Suitability for Use [1]

Chemical Constituent	Concentration in Natural Water	Suitability for Industrial and Domestic
Calcium (Ca^{2+})	Generally less than 100 mg/l; brine may contain as much 75,000 mg/l.	Calcium and magnesium combine with bicarbonate, carbonate, sulfate and silica to form heat retarding, pipe clogging scale in boilers and in other heat-exchange equipment. Calcium and magnesium combine with ions of fatty acid in soaps to form soap scum; A high concentration of magnesium has a laxative effect, especially on new users of the supply.
Magnesium (Mg^{2+})	Generally less than 50 mg/l; ocean water contains more than 1,000 mg/l, and brine may contain as much as 57,000 mg/l.	
Sodium (Na^{-})	Generally less than 200 mg/l; about 10,000 mg/l in seawater; about 25,000 mg/l in brine.	More than 50 mg/l sodium and potassium in the presence of suspended solids causes foaming which accelerates scale formation and corrosion in boilers. Sodium and potassium carbonate in recirculating cooling water can cause deterioration of wood cooling towers. More than 65 mg/l of sodium can cause problems in ice manufacture.
Potassium (K^{+})	Generally less than about 10 mg/l; as much as 100 mg/l in hot springs; as much as 25,000 mg/l in brine.	
Carbonate (CO_3^{2-})	Commonly less 10 mg/l in groundwater. Water high in sodium may contain as much as 50 mg/l of carbonate	Upon heating, bicarbonate is changed into steam, carbon dioxide, and carbonate. The carbonate combines with

Bicarbonate (HCO_3^-)	Commonly less than 500 mg/l; may exceed 100 mg/l in water highly charged with carbon dioxide.	alkaline earth – principally calcium and magnesium – to form crust like scale of calcium. Carbonate that retards flow of heat through pipe walls and restricts flow of fluids in pipes. Water containing large amounts of carbonate alkalinity is undesirable in many industries.
Sulfate (SO_4^-)	Commonly less than 300 mg/l except in water supplies influenced by acid mine drainage. As much as 200,000 mg/l in some brine	Sulfate combines with calcium to form an adherent, heat-retarding scale. More 250 mg/l is objectionable in water in some industries. Water containing about 500 mg/l of sulfate tastes bitter; water containing about 1,000 mg/l may have a laxative effect.
Chloride (Cl^-)	Commonly less than 10 mg/l in humid regions but up to 1,000 mg/l in more arid regions. About 19,300 mg/l in seawater; and as much as 200,000 mg/l in brine.	Chloride in excess of 100 mg/l imparts a salty taste. Concentrations greatly in excess of 100 mg/l may cause physiological damage. Food processing industries usually require less than 250 mg/l. some industries – textile processing, paper manufacturing, and synthetic rubber manufacturing – desire less than 100 mg/l.
Fluoride (F^-)	Concentrations generally do not exceed 10 mg/l. Concentrations may be as much as 1,600 mg/l in brine.	Fluoride concentration between 0.6 and 1.5 mg/l in drinking water has a beneficial effect on the structure and resistance to decay of children's teeth. Fluoride in excess of 1.5 mg/l in some areas causes "mottled enamel" in children's teeth. Fluoride in excess of 6.0 mg/l causes pronounced mottling and disfiguration of teeth.

Nitrate (NO_3^-)	Commonly less than 10 mg/l.	Water containing large amounts of nitrate (more than 100 mg/l) is bitter tasting and may cause physiological distress. Water containing more than 45 mg/l has been reported to cause methemoglobinemia in infants. Small amounts of nitrate help reduce cracking of high-pressure boiler steel.
Iron (Fe^{3+})	Generally less than 0.50 mg/l in fully aerated water. Groundwater having pH less than 8.0 may contain 10 mg/l; rarely as much as 50 mg/l may occur. Acid water from thermal springs, mine wastes, and industrial wastes may contain more than 6,000 mg/l.	More than 0.1 mg/l Fe^{2+} precipitates after exposure to air; causes turbidity, stains plumbing fixtures, laundry, and cooking utensils, and imparts objectionable tastes and colors to foods and drinks. More than 0.2 mg/l is objectionable for most industrial uses. Precipitates if the iron is in the Fe^{2+} (Ferrous) valence state. Not all iron and manganese precipitate out.
Manganese (Mn^{2+})	Generally 0.20 mg/l or less. Groundwater and acid mine water may contain more than 10 mg/l.	More than 0.2 mg/l Mn^{2+} precipitates upon oxidation; causes undesirable tastes, deposits on foods during cooking, stains plumbing fixtures and laundry, and foster growth of Iron/Mn bacteria in reservoirs, filters, and distribution systems. Most industrial users object to water containing more than 0.2 mg/l.

Dissolved Solids	Commonly contain less than 5,000 mg/l; some brine contains as much as 300,000 mg/l.	Less than 500 mg/l is desirable for drinking. Less than 300 mg/l is desirable for dyeing of textiles and the manufacture of plastics, pulp paper, rayon. Dissolved solids cause foaming in steam boilers; the maximum permissible content decreases with increases in operating pressure.
[1] Modified after Todd (1980)		

As indicated previously, the concentrations of Ca and Mg ions are used to calculate hardness. The effects of hardness (i.e., hard water producing scale or soap scum) are directly related to the concentrations of Ca and Mg ions in the water supply (described above in Table 2). Owing to these observed reactions, hard water is considered undesirable for most domestic and industrial uses. In order to determine if water softening is required prior to beneficial use, several researchers have developed hardness classification to assess these potential deleterious impacts. Table 3 presents two of these hardness classification schemes.

Table 3 - Hardness Classification

Hardness Range mg/l (as $CaCO_3$)	Hardness Range mg/l (as $CaCO_3$)[2]	Description
0 – 60	0 – 75	Soft
61 – 120	75 – 150	Moderately Hard
121 – 180	150 – 300	Hard
Over 180	Over 300	Very Hard

In the water softening industry, hardness is expressed in grains per gallon (one grain per gallon equals 17.1 mg/l). No State of Federal drinking water MCL has been established for hardness due to lack of unequivocal data relating to public health.

Crop Irrigation Limitations

The suitability of the water supply for crop irrigation is contingent upon the ability of the dissolved constituents to be consumptively used by the crops for maintaining proper growth. Adequate drainage of applied water is also an important facet of proper crop irrigation. Two principal limitations to crop growth are salt tolerance and sodium content. Table 4 list various crop families by relative salt tolerance and provides a range of salinity in (μ S/cm) and mg/l) in which the various crops in each crop family are capable of growing.

Table 4 - Relative Tolerances of Crops to Salt Concentrations [1,2]

Crop Division	Low Salt Tolerance	Medium Salt Tolerance	High Salt Tolerance
Fruit Crops	Avocado Lemon Strawberry Peach Apricot Almond Plum Prune Grapefruit Orange Apple Pear	Cantaloupe Date Olive Fig Pomegranate	Date Palm
Vegetable Crops	3,000 μ S/cm (1,900 mg/l) Green bean Celery Radish 4,000 μ S/cm (2,550 mg/l)	4,000 μ S/cm (2,550 mg/l) Cucumber Squash Peas Onion Carrot Potato Sweet corn Cauliflower Bell pepper Cabbage Broccoli Tomato 10,000 μ S/cm (6,400 mg/l)	10,000 μ S/cm (6,400 mg/l) Spinach Asparagus Kale Garden beet 12,000 μ S/cm (7,700 mg/l)
Forage Crops	2,000 μ S/cm (1,300 mg/l) Burnet Ladino clover Red clover Alsike clover Meadow foxtail White Dutch clover 4,000 μ S/cm (2,550	4,000 μ S/cm (2,550 mg/l) Sickle milkvetch Sour clover Cicer milkvetch Tall meadow oat grass Smooth brome Big trefoil Reed canary	12,000 μ S/cm (7,700 mg/l) Birdsfoot trefoil Barley (hay) Western wheat grass Canada wild rye Rescue grass Rhodes grass Bermuda grass Nattal alkali grass

	mg/l)	Meadow fescue Blue grame Orchard grass Oats (hay) Tall fescue Alfalfa Huban clover Sudan grass Dallis grass Strawberry clover Mountain brome Perennial rye grass Yellow sweet clover White sweet clover 12,000 μ S/cm (7,700 mg/l)	Salt grass Alkali sacaton 18,000 μ S/cm (11,500 mg/l)
Field Crops	4,000 μ S/cm (2,550 mg/l) Field bean 6,000 μ S/cm (3,850 mg/l)	6,000 μ S/cm (3,850 mg/l) Castor Bean Sunflower Flax Corn (field) Sorghum (grain) Rice Oat (grain) Wheat (grain) Rye (grain) 10,000 μ S/cm (6,400 mg/l)	10,000 μ S/cm (6,400 mg/l) Cotton Rape Sugar beet Barley (grain) 16,000 μ S/cm (10,250 mg/l)

1. Crops are listed in order of increasing salt tolerance.
2. Electrical conductance values represent salinity levels of the saturation extract at which a 50 percent decrease in yield may be expected as compared to yields on nonsaline soils under comparable growing conditions. The saturation extract is the solution extracted from a soil at its saturation percentage.

Table 5 provides a listing of irrigation water salt tolerances for a select group of crops, some of which are also shown in Table 4. It is noted that for some of the crops shown in Tables 4 and 5 (e.g. tomatoes), the range of eletroconductivities (EC) in Table 4, when converted to TDS, do not correspond with the indicated TDS values shown in Table 5. This may be due , in part, to the fact that the EC ranges shown in Table 4 reflect the crop salt tolerances of extract saturation of the soil corresponding to a 50 percent reduction in crop yields: whereas, the TDS values in Table 5 correspond to an irrigation water salinity level that causes no reduction or a 10 percent reduction in crop yields. The salt tolerance ranges in Table 5 will depend on the salinity content in the soil and the salinity of water applied to reach saturation.

Table 5 - Irrigation Water Salt Tolerances for Selected Crops [1,2]

Crop	Irrigation Water TDS (mg/l)
Apples	725
Avocado	555
Citrus	768
Grapes	640
Macadamia	840
Persimmons	768
Strawberries	427
Roots, bulbs, tubers	640 – 2,560
Carnations	640 – 1,280
Gladiolas	429 – 840
Poinsettias	1,058 – 1,728
Roses	1,472
Beans	427
Corn	726
Cucumbers	1,087
Mushrooms	Highly Insensitive
Potatoes	725
Squash	853
Tomatoes	1,067
Fescue	1,864
Bermuda Grass	2,944

1. Under normal conditions, soil moisture salinity (ECe) is approximately 1.5 * irrigation water salinity (ECw), i.e., (ECe = 1.5 * ECw)
2. Under drought conditions, soil salinity can be as much as 3 * Ecw. Salinity tolerance levels assume no yield reductions.

Boron

Boron, in minute concentrations, is essential to the normal growth of all plants. However, when present in larger concentration boron becomes toxic. Table 6 provides a list of crops based on their relative tolerance to boron. Boron in excess of 2.0 mg/l in irrigation water is deleterious to certain plants and some plants may be affected adversely by concentrations as low as 1.0 mg/l.

Table 6 - Relative Tolerance of Plants to Boron (Listed in Order of Increasing Tolerance)

Sensitive	Semi-tolerant	Tolerant

Lemon Grapefruit Avocado Orange Thornless blackberry Apricot Peach Cherry Persimmon Kadota fig Grape Apple Pear Plum American elm Navy bean Jerusalem artichoke English walnut Black walnut Pecan	Lima bean Sweet potato Bell pepper Pumpkin Zinnia Oat Milo Corn Wheat Barley Olive Ragged robin rose Field pea Radish Sweetpea Tomato Cotton Potato Sunflower	Carrot Lettuce Cabbage Turnip Onion Broadbean Gladioulus Alfalfa Garden beet Date palm Palm Asparagus Athel

Exchangeable Sodium Content (Percent Sodium) and Sodium Adsorption Ratio

The concentration of sodium in irrigation water supplies is important because sodium reacts with soil causing a reduction in soil permeability. Exchangeable Sodium Content (%)in irrigation water supplies is usually expressed as percent sodium using the equation:

$$ESP = \quad ((Na)/(Ca + Mg + K + NH_4 + Na)) * 100\ (\%)$$

Where all ionic concentrations are expressed in milliequivalent per liter.

The Sodium Adsorption Ratio (SAR) is also used to estimate the probable impact of sodium adsorption by soils for irrigation of crops. The SAR is calculated using the formula:

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

Where the concentrations of the chemical constituents are expressed in milliequivalents per liter. SAR is used in conjunction with the salinity of the irrigation water. The higher the salinity the lower the SAR should be.

Classification of Irrigation Water Quality

A typical water quality classification scheme for irrigation water supplies is presented in Table 7. The data shown in the table are useful in the these numerical ranges may be compared with the relative tolerances to salinity, e.g., EC, in Tables 4 and 5 and boron in Table 6.

Table 7 - Quality Classification of Water for Irrigation

Water Class	Percent Sodium	Electrical Conductivity /TDS [(μ S/cm)/(mg/l)]	Boron (mg/l)		
			Sensitive Crops	Semi-Tolerant Crops	Tolerant Crops
Excellent	<20	<250/(160)	<0.33	<0.67	<1.00
Good	20 – 40	250 – 750/(160 – 480)	0.33 – 0.67	0.67 – 1.33	1.00 – 2.00
Permissible	40 – 60	750 – 2,000/(480 – 1,300)	0.67 – 1.00	1.33 – 2.00	2.00 – 3.00
Doubtful	60 -- 80	2,000 – 3,000/(1,300 – 1,900)	1.00 – 1.25	2.00 – 2.50	3.00 – 3.75
Unsuitable	>80	>3,000/(1,900)	>1.25	>2.50	>3.75

Other Issues

The relationship between TDS and related chemical constituents to the taste of water supplies has emerged as an issue. However, the regulation of TDS (or other related chemical constituents) to meet a particular range of taste thresholds (which is not in itself a public health issue, but rather for aesthetic purposes) would most likely raise concerns among water resources managers regarding the potential additional levels of water treatment required and the associated potential costs for such enhanced water treatment.

References

1. Salinity Management Study, Final Report, Technical Appendix: Salinity and Total Dissolved Solids", Metropolitan Water District of Southern California and U.S. Department of the Interior, Bureau of Reclamation, prepared by Bookman-Edmonston Engineers Inc., June 1999.