

Strategies for Addressing Salt Impacts of Produced Water Releases to Plants, Soil, and Groundwater

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Cover photo:

A produced water-impacted plot (left) contrasts with an adjoining salt-flat remediation plot (right) where the thriving halophyte, marsh hay cordgrass (<u>Spartina</u> sp.), was planted as plugs about five years previously in the Smackover oilfield of south Arkansas.

Photo courtesy of David J. Carty, GreenBridge EarthWorks



Strategies for Addressing Salt Impacts of Produced Water Releases to Plants, Soil, and Groundwater

CHARLES J. NEWELL AND JOHN A. CONNOR GROUNDWATER SERVICES, INC.

PURPOSE OF THIS GUIDE

The exploration and production (E&P) industry uses great care during the handling and disposal of the produced water that is generated as part of oil and gas production. However, unintentional releases can occur. Depending on the chemical composition of the produced water and the nature of the local environment, salts associated with such releases can impair soils, vegetation, and water resources.

This guide provides a collection of simple rules of thumb, decision charts, models, and summary information from more detailed guidance manuals to help you address the following assessment and response issues:

- 1) Will a produced water release cause an unacceptable impact on soils, plants, and/or groundwater?
- 2) In the event of such an impact, what response actions are appropriate and effective?



HOW TO USE THIS GUIDE

Determining when a response action will likely be needed to protect soil, plants, or groundwater.

- Protecting Soil/Plants: See Rules of Thumb on Page 2 and more detailed decision charts on Pages 4 to 5.
- **Protecting Groundwater:** See Rules of Thumb on Page 3 and Planning Model on Pages 9 to 14.

Selecting and implementing an appropriate remedial measure for impacted soils or plants.

- Remedy Selection: See decision charts on Pages 4 to 5.
- Remedy Implementation: See simple guidelines for natural remediation, in-situ chemical amendments, and mechanical remediation on Pages 6, 7, and 8, respectively.

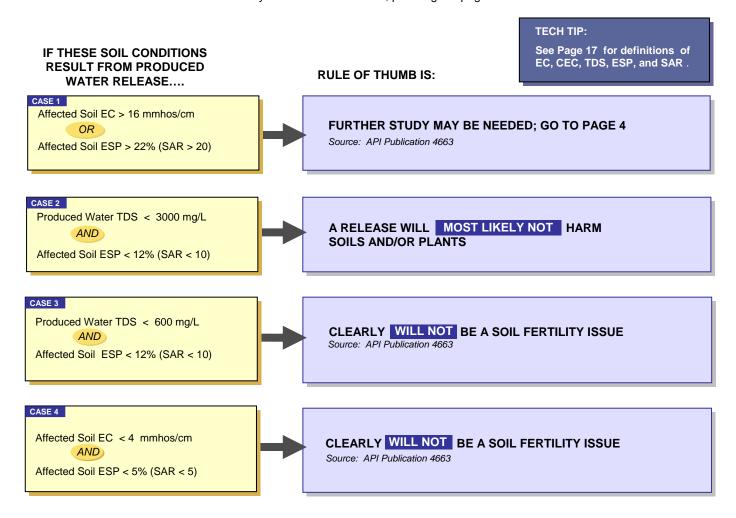
Evaluating potential impacts on groundwater resources.

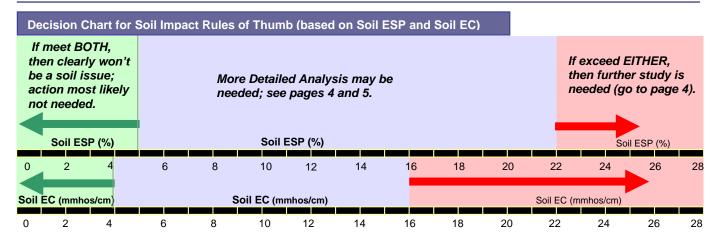
- **Planning Model:** See simple procedures for assessing potential effects on groundwater quality on Pages 9 to 14.
- Beneficial Use Criteria: See general criteria for evaluating the potential use of water resources on Page 15.

Background information on produced water and its potential effects.

- Produced Water Production and Disposal in the U.S.: Page 16
- Definition/ Measurement of Key Parameters: Pages 17 and 21
- Potential Impacts on Plants: Page 18
- Potential Impacts on Soil: Page 19
- Key Factors for Assessing Groundwater Impacts: Page 20
- Example Site Assessment: Pages 22 and 23

Information from API Publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities and other sources was compiled to develop the following "Rules of Thumb" for response to impacts by produced water. Each Rule of Thumb describes a set of conditions associated with a produced water release and the typical response to such conditions. These Rules of Thumb are for typical rangeland and farmland areas, but may not be applicable to environments with naturally high salinity. For further discussion of conditions not covered by these Rules of Thumb, please go to page 4.

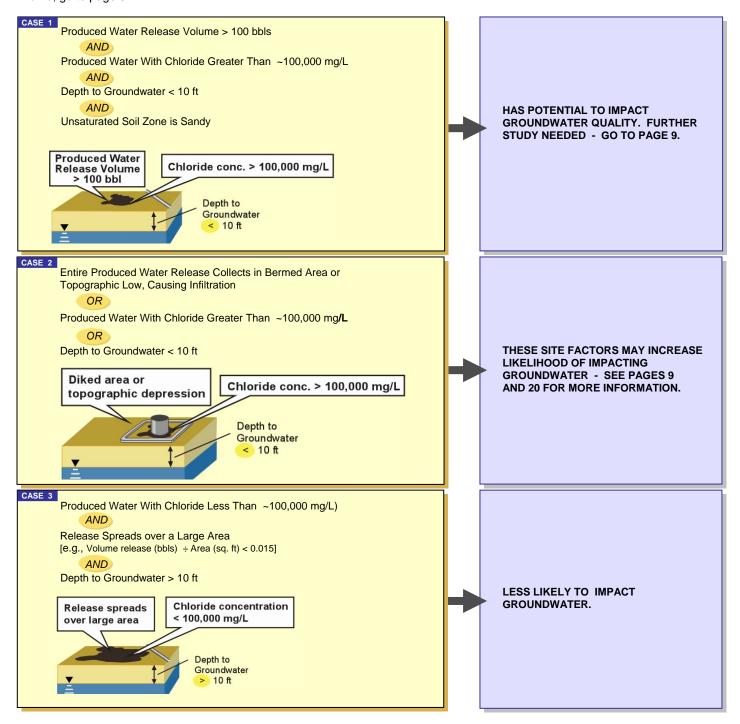




GROUNDWATER IMPACT RULES OF THUMB

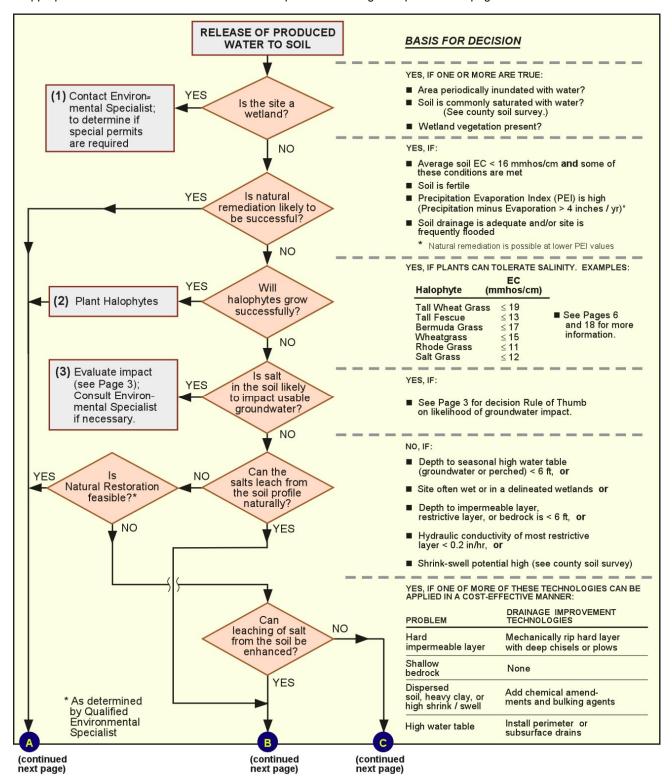
Evaluating Impacts - GROUNDWATER

The following Rules of Thumb for response to groundwater impacts by produced water were developed as guidance using information from API Publication 4734, *Modeling Study of Produced Water Release Scenarios*. In that study, the authors performed several hundred computer simulations with the HYDRUS-1D model to determine the sensitivity of groundwater underlying a produced water release to various factors such as release volume, chloride concentration of the produced water, depth to groundwater, soil type, rainfall and hydrology of the area, and other factors. Each Rule of Thumb describes a set of site conditions associated with a produced water release and assesses the likelihood of an impact to groundwater. These Rules of Thumb may not be applicable to environments with naturally high salinity or areas with multiple releases over several years. For cases not covered by these Rules of Thumb, go to page 9.

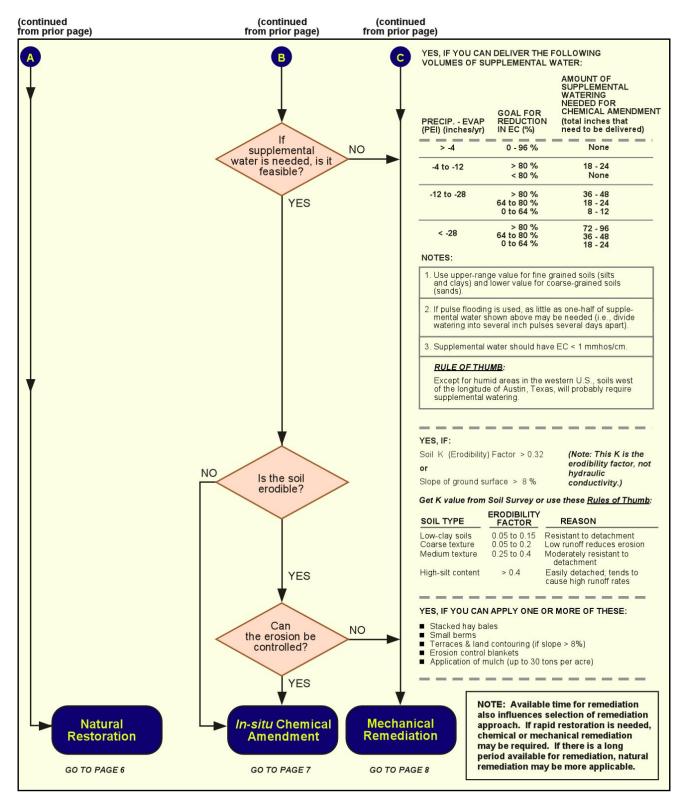


DECISION CHART FOR SOIL/PLANT IMPACTS

For those sites where produced water impacts to soils requires a corrective action, the following decision chart can be used to select appropriate remedial measures. More detail on specific technologies is provided on pages 7 - 8.



Decision Chart for Salt-Impacted Soils (Adapted from API Publication 4663)



Decision Chart for Salt-Impacted Soils - Continued (Adapted from API Publication 4663)

NATURAL REMEDIATION OF SOIL IMPACTS Responding to Impacts - SOIL Mechanical **Natural** In-situ Chemical Remediation Remediation Amendment Soil Remediation Alternative 1: Natural Remediation Use plants and natural water flushing to restore salt-impacted soils. This option is preferable in cases Concept: where remediation equipment can create additional soil damage (such as wetlands). OPTION A. Approach: Allow natural revegetation to occur over 1-to 3-year time period and monitor the revegetation Monitored Natural process. The affected area should be monitored for barren zones and stressed vegetation over time. If monitoring shows revegetation process is too slow, consider other methods. This method Revegetation works best with sandy soils and soils containing limited clay. In some cases adding mulch, fertilizer, and water (see Option B, below) can speed up revegetation. OPTION B. = Approach: Plant halophytic vegetation that is suitable for the climate and the soil conditions and that can tolerate elevated salinity (see table below for examples of halophytic grasses). Add mulch and fertilizer as Plant Salt-Tolerant necessary: Vegetation Till in 2 to 4 inches of mulch over affected area (less for coarse soils, Mulch Rule of Thumb: more for fine-grained soils, about five 60-lb bales of hay for every 1000 sq. feet). Fertilizer Rule of Thumb: Add about 28 pounds of 13-13-13 fertilizer for every 1000 sq. feet. (For more detail, see API Publication 4663) (Don't add too much fertilizer in a soil; fertilizers can act like salts.) Watering Rule GENERALLY DO NOT ADD WATER BY ITSELF IF SALT IMPACT HAS ALREADY ENTERED SOILS CONTAINING CLAY. IF YOU ARE GOING TO of Thumb: ADD WATER, FIRST ADD CHEMICAL AMENDMENTS (see next page). For more detailed information on mulch / fertilizer addition, see API Publication 4663.



Halophyte-assisted natural remediation Photo Courtesy of David Carty

EXAMPLES OF GRASSES THAT MAY BE USED FOR REVEGETATION

| | | ACCEPTABLE PRECIPITATION RATES | | SOIL TYPE | U.S. PLANTING | SEEDING RATE | SEEDING DRILL DEPTH |
|-----------------------|-------|--------------------------------|------------------|--------------|----------------------|-------------------------|---------------------------------|
| GRASS | HABIT | Min (in/yr) | Max (in/yr) | L-M-H | SEASON | (lbs/ac PLS drilled) | (inches) |
| Alkali Sacaton | Bunch | 8 | 18 | L-M-H | Summer | 1/5 | 1/4 |
| Basin Wildrye | Bunch | 9 | Irrigation OK | L-M-H | Late Fall/Spring | 5 | 1 |
| Western Wheatgrass | Sod | 10 | 20 | M-H | Early Fall/Spring | 8 | ¹ / ₂ - 1 |
| Beardless Wildrye | Sod | 20 | Irrigation OK | M-H | Late Fall/Spring | 8 | 3/4 |
| Tall Wheatgrass | Bunch | 5 | 20 | L-M-H | Spring | 8 | 1/2 - 2 |

NOTES: This table only presents a few of the grasses that can be used for revegetation. A number of other grasses (such as Bermuda grass) are presented in API Publication 4663 and other literature.

SOIL TYPE: L = LIGHT - sands, loamy fine sands, sandy loams

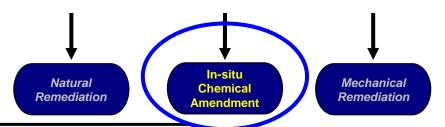
M = MEDIUM - silty loams, loams, very fine sandy loams, sandy clay loams

H = HEAVY - clay loams, silty clays, clay

PLS = Pure Live Seeds.

IN-SITU CHEMICAL AMENDMENT OF SOIL IMPACTS

Responding to Impacts - SOIL



Soil Remediation Alternative 2: In-Situ Chemical Amendment

Concept: Add a calcium-containing compound, such as gypsum, which serves to replace sodium (which changes the structure and porosity of clays in salt-impacted soils) with calcium and restores the structure of the soil. (See page 19.)

Add Gypsum or Other Amendment

Approach:

- 1) Improve drainage, if necessary.
- Calculate how much gypsum to add using Calculation Method 1 or Method 2 (below) or use this Rule of Thumb:

Add 13 pounds of gypsum per 100 sq. feet of impacted soil

- 3) Add chemical amendments to affected soil.
 - <u>Solid Amendment</u>: Incorporate from surface to depth of 1 to 2 ft using plow. Make sure amendment is in powdered or granular form.
 - <u>Liquid Amendment</u>: Apply over soil surface with or without mechanical incorporation.
- **4)** Adding mulch and fertilizer may enhance rapid restoration (see page 6).
- 5) Use perimeter berms to contain rainfall or use sprinkler irrigation in affected area to increase infiltration and leach salts (sodium) from affected soils.

Rules of Thumb:

- ADD CHEMICAL AMENDMENTS BEFORE IRRIGATION OR A PERIOD OF HEAVY RAIN.
- Pulse flooding (watering with a few inches of water every few days) can reduce water requirements by half.
- A final top dressing of gypsum or mulch can protect the soil surface from dispersing after a rainfall or water event.
- See page 5 for amount of supplemental irrigation that is needed.
- Install erosion controls, if necessary.



Addition of Chemical Amendment Photo Courtesy of David Carty

TECH TIP 1:

If soil pH is between 5.5 and 8.5, and if chloride or nitrate will not impact groundwater, you can replace gypsum with:

- Calcium Chloride [CaCl₂:2H₂0] at 0.85 pounds per pound gypsum requirement
- Calcium Nitrate [Ca(NO₃)₂] at 0.95 pounds per pound gypsum requirement

TECH TIP 2:

Adding more than the calculated amount of calcium will not hurt the soil.

Calculation Method 1: Amount of Gypsum Needed Based on Soil ESP and CEC

Formula:

No. of lbs of gypsum to add per square foot of impacted soil [ESP - 5] x [CEC] x [0.00078]

(in %) (in meq/100 grams)

(in pounds $/ ft^2$)

Calculation Steps:

- 1. Perform calculation for 0 to 1 ft layer.
- 2. Perform calculation again for 1 to 2 ft layer.
- 3. Add lbs per sq. ft. numbers together.
- 4. Multiply lbs of gypsum per sq. ft. by area of spill in sq. ft. to get lbs of gypsum.
- If soil pH is <5.5, then may need to add CaCO₃ to replace some of the gypsum. See API Publication 4663.
- If soil pH > 8.5, then may need to add sulfur or alternative chemical to decrease pH. See API Publication 4663.

Calculation Method 2: Amount of Gypsum Needed Based on Sodium Concentration in Produced Water Release

Formula:

No. of lbs of gypsum to add to affected area

[sodium concentration] x [6.94] x [volume spilled] x [0.00019]

(sodium concentration in mg/L) (volume spilled in bbl; 42 gallons per bbl)

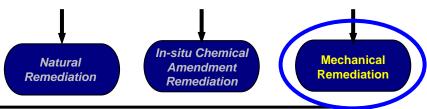
(in pounds)

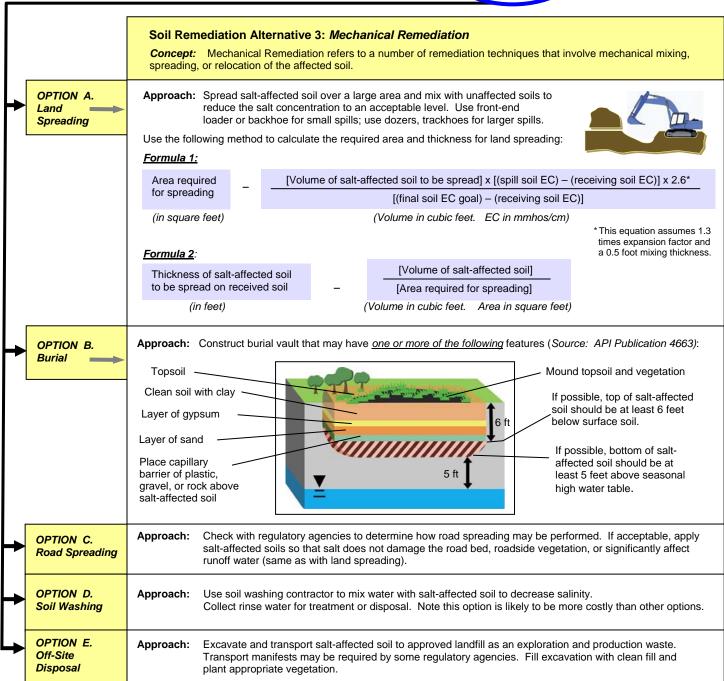
Calculation Steps:

- Calculate lbs of gypsum to add using formula shown above.
- Note that sodium typically comprises 20-35% of the TDS concentration, and can be estimated as (0.2 to 0.35) x TDS (mg/L).

MECHANICAL REMEDIATION OF SOIL IMPACTS

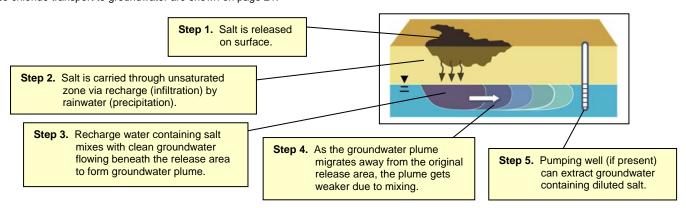
Responding to Impacts - SOIL





Chloride Transport Pathway

Chloride associated with a produced water release to the surface can impact surface soils and be transported to underlying groundwater. The transport process can be separated into four separate steps as shown below. This guide provides a Planning Model (see below and pages 10-14), that can be used to evaluate this migration process. Information on Beneficial Uses of groundwater is provided on page 15. A summary of key parameters that influence chloride transport to groundwater are shown on page 21.



Using the Planning Model

Results of this modeling are combined with other site-specific information to determine the potential effects on groundwater.

To use the Planning Model, perform the following steps:

- Step 1: Estimate <u>Mass of Chloride</u> using volume and chloride concentration of a produced water release, *OR*Estimate <u>Mass of Chloride</u> using the area of produced water release (area of affected soil) and the chloride concentration of the soil (page 10)
- Step 2: Estimate Chloride Loading Rate to Groundwater using the Annual Precipitation, (page 11)
- Step 3A: Estimate Increase in Chloride Concentration in Groundwater at the Release Point using the width of the release area, (page 12)
- Step 3B: Refine the estimate from Step 3A using site-specific information (either the site location, or more detailed hydrogeologic info), (page 13)
- Step 4: (Optional) Estimate the <u>Increase in Chloride Concentration in Groundwater at a Downgradient Point</u> using the distance from the release area (and other parameters), (page 14)

Key assumptions and limitations of the Planning Model include: 1) salts are mixed evenly throughout the soil; 2) the *percentage* of the rainfall that infiltrates through the soil to groundwater is proportional to the amount of rainfall; 3) the recharge rate is the 80th percentile of recharge rates from data compiled from API Publication 4643; 4) almost all the salts in affected soils can be flushed out with 12 inches of recharge (from API 4663); 5) no capillary effects, evaporation, or other transport processes except advection, mixing, and dispersion in the saturated zone are present; 6) no density effects are assumed in transport of chloride in groundwater; 7) salt is mixed throughout the water-bearing unit; 8) a 2x safety factor is assumed; and 9) potential impacts only apply to the uppermost water-bearing unit, and NOT to deeper, regional aquifers. When applied to site conditions presented in API Publication 4734, the Planning Model was more likely to show higher chloride concentrations in groundwater than chloride concentrations predicted by HYDRUS, a much more sophisticated leaching model.

Other Methods

Other approaches can also be used to provide more accurate estimates of chloride migration. Key resources include:

- API Publication 4734: In this study, the authors performed several hundred computer simulations with the HYDRUS model to determine the sensitivity of groundwater underlying a produced water release to various factors such as release volume, chloride concentration of the produced water, depth to groundwater, soil type, rainfall and hydrology of the area, and other factors. Review of this document can provide additional information regarding the impact of produced water releases on groundwater.
- More Detailed Computer Models: Models such as VADSAT or HYDRUS can be applied to investigate potential groundwater impacts from produced water releases.
- **Site Investigation:** A groundwater site investigation involving the collection of groundwater samples from monitoring wells or direct push sampling techniques can show if a produced water release has actually affected groundwater at a given site.

Factors That May Influence Remediation of Saltwater Releases

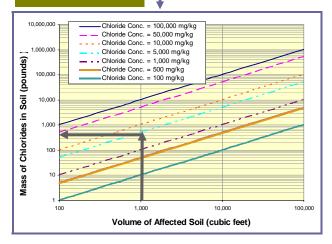
For the purposes of this guide, the principal objective of groundwater remediation is to *maintain the beneficial use of the groundwater* resource. However, remediation of saltwater releases can be influenced by a variety of non-technical factors that are not directly addressed in this guide. These **non-technical factors** include (API Publication 4663):

- Landowner claims
- Lease agreements
- Federal, state, and local regulations
- Reduction of long-term liabilities
- Company policies

STEP 1: Estimate MASS OF CHLORIDE RELEASED by either Method A or Method B below:

METHOD A. You know Volume of Affected Soil and its Chloride Concentration...

USE THIS GRAPH

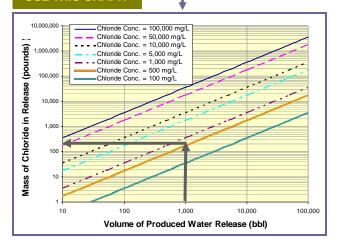


OR USE THIS EQUATION

 $\begin{array}{ll} \text{Mass} &= \left(\begin{array}{c} \text{Area of} \\ \text{Affected Soil} \end{array} \right) x \left(\begin{array}{c} \text{Depth of} \\ \text{Affected Soil} \end{array} \right) X \left(\begin{array}{c} \text{Chloride Conc.} \\ \text{of Affected Soil} \end{array} \right) \div (9500) \\ \text{(in lbs} & \text{(in sq feet)} \end{array} \right) \left(\begin{array}{c} \text{in feet} \\ \text{(in feet)} \end{array} \right) X \left(\begin{array}{c} \text{Chloride Conc.} \\ \text{of Affected Soil} \\ \text{(in mg/kg)} \end{array} \right) \div (9500) \\ \text{(in mg/kg)} \end{array}$

METHOD B. You know Volume of Produced Water Release and its Concentration...

USE THIS GRAPH



OR USE THIS EQUATION

 $\begin{array}{ll} \text{Mass Chloride} &= & \text{(Volume Released)} \times \text{(Chloride Concentration)} \div \text{(2900)} \\ \textit{(in lbs chloride)} & \textit{(in barrels)} & \textit{(in mg/L or ppm)} \end{array}$

GO TO STEP 2 WITH MASS OF CHLORIDE

METHOD A EXAMPLE

Example: Mass of chloride in 50 ft x 10 ft area of affected soil with 5000 ppm chloride in soil to 2 feet deep.

Mass Chloride = (50 ft) x (10 ft) x (2 ft) x (5000 ppm) ÷ (9500) (*lbs chloride*)

Mass Chloride = 526 pounds

METHOD B EXAMPLE

Example: Mass of chloride from 1000 bbl release with 500 mg/L chloride:

Mass Chloride = $(1000 \text{ bbl}) \times (500 \text{ mg/L}) \div (2900)$ (*lbs chloride*)

Mass Chloride = 172 pounds

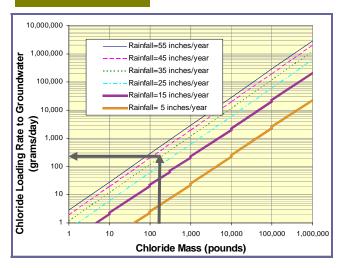
BACKGROUND

These graphs and equations are based on conventional mass calculations for affected water and soil. See page 9 for more information about the assumptions and limitations related to the Planning Model. NOTE: 1 bbl = 42 gallons = 159 liters.

STEP 2: Estimate the CHLORIDE LOADING RATE TO GROUNDWATER (in grams per day):

Start with CHLORIDE MASS...

USE THIS GRAPH



OR USE THIS EQUATION

Chloride Loading

Rate to $\overline{GW} = (Mass Chloride) \times (Annual Rainfall)^2 \div 1000$ (in grams/day) (in lbs) (in in/yr)

(Note: Using the square of the rainfall is correct; the higher the annual rainfall, the higher the fraction of rainfall that reaches groundwater. GW = groundwater)

THEN ADJUST THE ANSWER FOR SOIL TYPE

If SANDY SOIL:

Use chloride loading rate shown in the graph or equation.

If SILTY SOIL:

Divide the chloride loading rate from graph or equation by 2 (i.e., \div 2).

If CLAYEY SOIL:

Divide the chloride loading rate from graph or equation by 10 (i.e., ÷ 10).

GO TO STEP 3A WITH CHLORIDE LOADING RATE

BACKGROUND:

This graph and this equation are based on:

- 1) An empirical equation to estimate the recharge rate to groundwater due to rainfall developed by Connor et al., 1997, for the Texas Commission on Environmental Quality. The recharge equation was derived from a study of numerous recharge studies in API Publication 4643, and represents a conservative estimate for recharge (i.e., overpredicts).
- It is assumed that the excess salinity in an affected soil can be fully flushed from soil by 12 inches of recharge (API Publication 4643).
- A safety factor has been applied (i.e., the chloride loading rate is increased by a factor of 2 to ensure that the planning model generally overpredicts results compared to the HYDRUS model).
- 4) See Page 9 for more information about the assumptions and limitations associated with the Planning Model.

EXAMPLE

Example: Take results from Example B on page 10. Assume SILTY SOIL and 40 inches per year of rainfall.

Chloride Loading

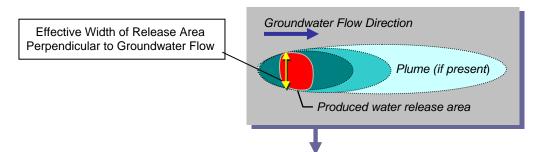
Rate to GW = $(172 \text{ lbs}) \text{ x } (40 \text{ in/yr})^2 \div (1000) \div (2)$ (in grams/day)

<u>Chloride Loading Rate to GW</u> = 138 grams per day (about 0.3 pounds per day)

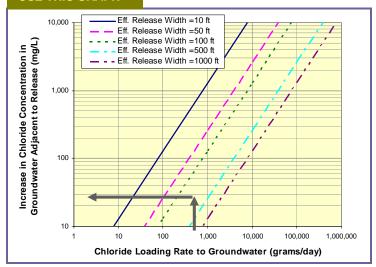
Step 3A: Estimate the increase in concentration of chloride in groundwater next to the release (at a generic site) by dividing the chloride loading rate by an estimate of the groundwater flow that mixes with the chloride:

Start with CHLORIDE LOADING RATE...

DETERMINE THE WIDTH OF THE RELEASE AREA



USE THIS GRAPH



OR USE THIS EQUATION

Increase in Chloride Conc. = { (Chloride Loading Rate) \div (Eff. Width) } x (13) at a Generic Site (in mg/L) (in g/day) (in ft)

Note: This assumes a national average groundwater Darcy velocity from a statistical study of 400 hazardous waste sites (from API Publication 4476). For more information regarding uncertainty and differences in discharge rate between regions, see page 13.

GO TO STEP 3B WITH INCREASE IN CHLORIDE CONCENTRATION

BACKGROUND

To estimate the increase in chloride concentration in groundwater, the chloride loading rate is divided by an estimate of the groundwater flow that mixes with the chloride. The groundwater flow is assumed to be the groundwater Darcy velocity (hydraulic conductivity times hydraulic gradient) multiplied by the estimated mixing zone thickness for the water-bearing unit underlying the release area. For this method, a typical value for groundwater discharge of 1000 cubic feet per year per foot of water-bearing unit width was derived from: i) a statistical study of 400 hazardous waste sites prepared by API (API Report No. 4476) when a mid-range Darcy groundwater velocity of 33 ft/yr was indicated; and ii) an estimated value for the mixing zone thickness of 30 feet.

EXAMPLE

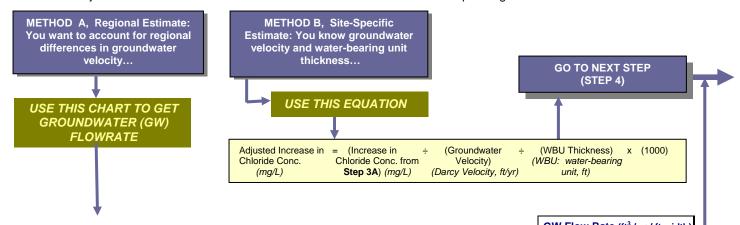
Assume a chloride loading rate of 138 grams per day and a release area effective width of 100 ft:

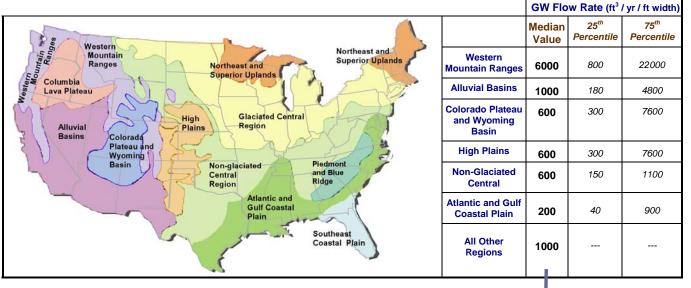
Increase in Chloride Conc. (mg/L) = $[(138 \text{ grams/day}) \div (100 \text{ ft})] \times (13)$ at a Generic Site

Increase in Chloride Concentration (mg/L) = 18 mg/L

See Page 9 for more information about the assumptions and limitations of the Planning Model.

STEP 3B: Adjust the increase of concentration in chloride to account for more site-specific groundwater conditions:





THEN USE GW FLOWRATE IN THIS EQUATION

Adjusted Increase in Chloride Concentration (mg/L) = Increase in Chloride Concentration (mg/L) from Step 3A ÷

Value from Chart

x 1000

BACKGROUND

The groundwater dilution capacity estimate can be improved by utilizing groundwater velocity and water-bearing unit thickness several ways:

- METHOD A: Use regional values derived from the HGDB Hydrogeologic Database (Newell et al., 1990), a statistical study of 400 hazardous waste sites prepared by API (API Report No. 4476). Median values and upper-range (75th percentile) values are presented. This method assumes a 30-ft mixing zone thickness and the effective source width entered during STEP 3A (see the previous page).
- METHOD B: Use site-specific data from near-by water supply or monitoring wells.

EXAMPLE

Option A. Assume site is in Atlantic and Gulf Coastal Plain.

Adjusted Increase in Chloride Conc. = (Increase in Chloride Conc. from Step 3A \div Value from Chart) x 1000

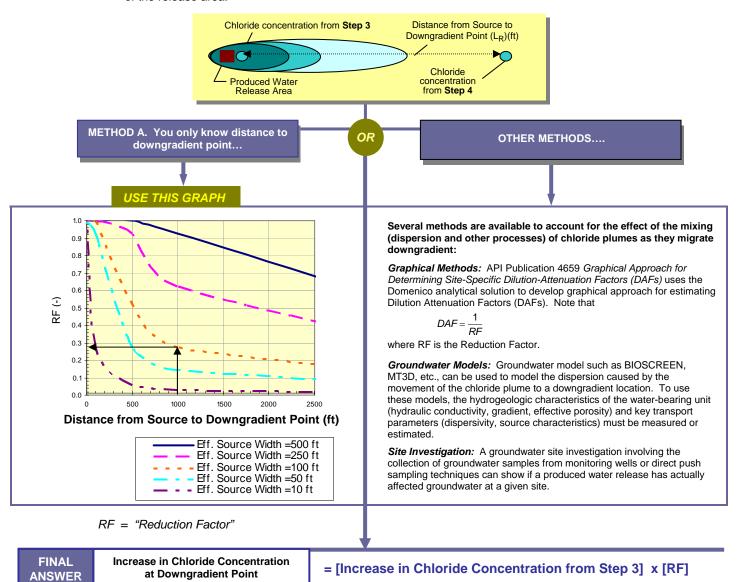
Adjusted Increase in Chloride Conc. = $(18 \text{ mg/L} \div 200) \times 1000$

Adjusted Increase in Chloride Conc. = 90 mg/L

NOTE: This is likely to over-estimate the increase in chloride concentration. See Page 9.

See Page 9 for more information about the assumptions and limitations of the Planning Model.

STEP 4 (Optional): Estimate the change in concentration in groundwater after it has mixed with groundwater at a point downgradient of the release area:



BACKGROUND

METHOD A: The steady-state Domenico analytical transport model was used to develop a family of computer simulations. Two-dimensional aquifer conditions were assumed. Longitudinal dispersivity was assumed to be equal to 10% of the modeled distance. Transverse dispersion was assumed to be 10% of longitudinal dispersion.

EXAMPLE

To predict the groundwater concentration at a point 1000 ft downgradient of a release area that is 100 ft wide and has increased the chloride concentration by 90 mg/L:

Increase in Chloride

 $\underline{\text{Concentration}} \ \overline{\text{(mg/L)}} = 90 \ \text{mg/L} \ \text{x} \ \underline{\text{RF}}$

RF 1000 ft downgradient from = 0.28

Method A Chart

Increase in Chloride

Concentration $(mg/L) = 90 \text{ mg/L} \times 0.28$ (from

METHOD A chart)

1000 ft downgradient = 25 mg/L

EVALUATING GROUNDWATER IMPACTS

Responding to Impacts - GROUNDWATER

Beneficial Uses of Groundwater

If an increase in the chloride concentration in groundwater is known or estimated (i.e., by using the Planning Model, more sophisticated model, or sampling wells), the impact on the beneficial use of the groundwater can be determined. Beneficial uses MAY include:

- drinking water supply;
- industrial water supply;
- · irrigation or livestock water; and
- discharge to surface water (aquatic life).

KEY POINT:

There is no impairment to the resource unless the actual beneficial use of the water is restricted or impaired.

The applicability of a given groundwater resource for these beneficial uses may depend, in part, on the concentrations of salt-related constituents, such as chloride and/or total dissolved solids (TDS). In the United States, groundwater is often regulated by the state governments on the basis of the use of the groundwater. Examples of beneficial uses are shown below:

Drinking Water and Industrial Uses

The Safe Drinking Water Act sets standards for drinking water quality to be achieved for public water supplies. Total dissolved solids and chloride are not considered by the U.S. EPA to present a risk to human health at the Secondary Maximum Concentration Level (SMCL) but are considered "nuisance chemicals" and have the following SMCLs:

Industrial water quality requirements vary significantly, depending on the particular industry. For most industries, the acceptable concentrations of chloride and TDS are significantly higher than drinking water standards in most cases.

| Constituent | Secondary MCL * (mg/L) | Noticeable Effects Above Secondary MCL |
|---------------------------------|------------------------------|--|
| Total Dissolved Solids (TDS) | 500 | hardness; deposits; colored water; staining; salty taste |
| Chloride | 250 | salty taste |

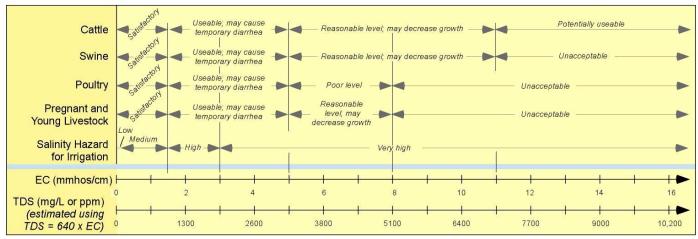
^{*} The U.S. EPA does not consider these constituents to present a risk to human heath at these levels. These levels are established only as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, odor, and color.

Aquatic Life Protection

The U.S. EPA (1988; 2006) developed ambient aquatic life criteria for chloride for acute exposures (860 mg/L) and chronic exposure (230 mg/L). Several states developed aquatic life criteria for non-priority pollutants including TDS that range from 250 mg/L (lowa, 2003).

Agricultural Uses of Water

There is a wide variety of research that summarizes the effect of salinity on livestock and irrigation. Data compiled by USDA-NCRS and presented in API Publication 4663 is summarized below:



Groundwater Response Actions

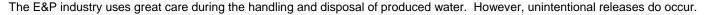
If groundwater is impacted adversely, there are a wide variety of approaches that can be taken to manage the problem, including installation of an engineered solution, providing an alternative water supply, implementing a passive remediation approach, evaluating the actual risk associated with the impact and/or combining approaches. Example technologies include: Natural Attenuation; Alternative Water Supply; Plume or Source Containment; Point of Use Treatment; and Groundwater Pump and Treat.

PRODUCED WATER OVERVIEW

Produced Water

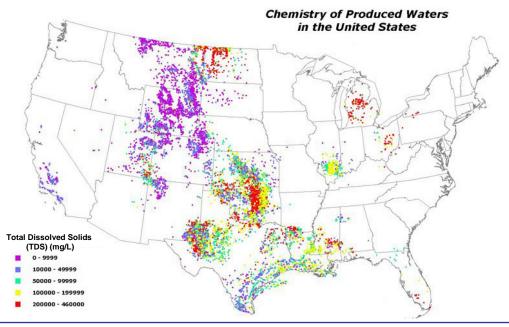
Produced water refers to water from underground geologic formations that is brought to the surface (or "produced") in the process of oil or natural gas production. This formation water has been in contact with the geologic strata for many thousands of years and, as a result, may contain elevated concentrations of natural minerals that have dissolved from the rock or soil. The resulting chemical composition of the produced water can vary from fresh to very saline, as follows (USGS):

- **Brine** (total dissolved solids (TDS) greater than 35,000 mg/L (ppm))
- Highly saline (TDS between 10,000 and 35,000 mg/L)
- Moderately saline (TDS between 3,000 and 10,000 mg/L)
- Slightly saline (TDS between 1.000 and 3.000 mg/L)
- Freshwater (TDS less than 1,000 mg/L)



How Does Produced Water Quality Vary Across The U.S.?

This map from the U.S. Geological Survey (Breit and Otton, 2002) based on almost 60,000 produced water analyses taken across the country, shows the Total Dissolved Solids (TDS) content to vary significantly among the various oil and gas regions of the U.S. Such variations are explained by the age, geochemistry, and hydrology of the specific formation(s) from which the water comes. In the Powder River Basin of Wyoming, gas production zones can yield produced water with a TDS < 1000 mg/L, corresponding to freshwater, while in some areas of Oklahoma and West Texas, the TDS content can exceed 200,000 mg/L, corresponding to strong brine.



Key Produced Water Statistics

HOW MUCH PRODUCED WATER IS GENERATED IN THE U.S.?

18 billion barrels of water in 1996, down from 21 billion barrels in 1985 (API, 2000). For comparison, U.S. oil production in 1996: 2.4 billion barrels of oil.

HOW IS IT MANAGED?

In the United States in 1995, produced waters were managed in accordance to state regulations (API, 2000).

92% Injected (three-fourths for enhanced oil recovery, one fourth in Class II injection wells)

- 3% Discharged to surface water (mostly low salinity water from coalbed methane production)
- 3% Disposed (in percolation pits, on-site evaporation, and treatment plants)
- 2% For Beneficial Use

TECH TIP:

Concentrations of salts in groundwater are usually reported in **milligrams per liter** ("mg/L").

For water samples, this is approximately the same as a "part per million" (ppm). The difference between "mg/L" and "ppm" increases as the salt concentration of the water sample increases.

DEFINITION OF KEY PARAMETERS

EC: Electrical Conductivity

Description: EC represents the ability of a solution to carry an electrical current through ions in the water. In practice, EC is proportional to the amount of inorganic ions (primarily sodium, chloride, sulfate, calcium, potassium, magnesium, and bicarbonate) dissolved in the water. EC is the opposite of resistivity and may also be called specific

Units: EC is measured in milli-mhos per centimeter (mmhos/cm), or deciSiemens per $\overline{\text{meter}}$ (dS/m). Note that 1 mmhos/cm = 1 dS/m.

Method: For Liquid: Use Method 120.1 (Black, 1965). For Soil: Use the Paste Extract Method 62-2.2 (Black, 1965).

TDS: Total Dissolved Solids

Description: TDS is the total sum of all dissolved constituents in the water.

This test is performed by: 1) filtering the water to remove suspended solids, 2) heating the sample to drive off all the water, and 3) weighing the residue.

Units: TDS is reported in milligrams per liter (mg/L). For most applications, mg/L can be assumed to be equivalent to parts-per-million (ppm).

Method: 160.1 (U.S. EPA, 1983) or estimated from liquid EC.

DATA TIP 1:

Some meters and laboratories report specific conductance in units of micro-mhos per centimeter (µmhos/cm), particularly for water samples.

Make sure to convert micro-uhos/cm (µmhos/cm) to millimhos per centimeter (mmhos/cm) by dividing micro-mhos/cm by 1000 to use some of the rules in this guide!

Many ions available Few ions available to carry electrical to carry electrical charge through charge through water or soil paste water or soil paste Low EC **High EC** CI Ca** Na+ Na+ CI Mg++ CI Na+ Na+ Na+ CI CI Ca CI CI Na+ CINA SO4 Na+ SO4 Na+ Water Sample or Soil Paste Extract

DATA TIP 2:

EC and TDS are two different measurements for the same water quality characteristic. EC is an indirect measurement that can be performed in the field with a meter, while TDS is a direct measurement performed in the lab. You can convert between them with:

IF EC < 5 mmhos/cm: EC (mmhos/cm) x 613 = TDS (mg/L or ppm) IFEC > 5 mmhos/cm: EC (mmhos/cm) x 800 = TDS (mg/L or ppm)

CEC: CATION EXCHANGE CAPACITY OF SOIL

Description: A cation is a positively charged ion. For evaluation of soil sodicity, the key cations are calcium, potassium, magnesium, and sodium. CEC is the total amount of exchangeable cations that can be held in the soil (i.e., cations that can be removed and exchanged for other cations in waters infiltrating through the soil).

Units: Milliequivalents per 100 grams soil.

Method: 57-3 (Black, 1965)

ESP: EXCHANGEABLE SODIUM PERCENTAGE OF SOIL

Description: The percentage of CEC of a soil sample that is comprised

of sodium. Similar to SAR (sodium adsorption ratio).

Units: Percent (%) Exchangeable Sodium (meq/100 grams soil) x 100 Calculation: ESP = CEC (meg/100 grams soil)

SAR: SODIUM ADSORPTION RATIO OF SOIL

Description: An indication of the sodium hazard to a soil. Similar to ESP.

Units: unitless (-)

[Sodium(meq/I)] Calculation: SAR = $\left[Calcium(meq/I) + Magnesium(meq/I) \right]$

(in concentrations of meq/L), or use DATA TIP 3.

Importance of CEC, ESP, and SAR

Clays and organic soils have a large number of negatively-charged sites that can hold cations such as sodium. During a salt spill, the calcium, potassium, and magnesium can be replaced by sodium, which changes the structure of the clays.

DATA TIP 3:

ESP and SAR are two expressions for the fraction of the soil's cations that are comprised of sodium. You can convert between ESP and SAR using the following approximation:

- 0.0126 + 0.01475 x SAR ESP(in %) = 100 x -1+ (-0.0126 + 0.01475 x SAR)





Low CEC

High CEC





Low ESP

High ESP

DATA TIP 4:

The chloride concentration and sodium concentration of produced water can be estimated by assuming all of the TDS is comprised of salt, and using the following equations:

= TDS (mg/L) x 0.2 (low end estimate) concentration (mg/L) = TDS (mg/L) x 0.35 (high end estimate)

Chloride

= TDS (mg/L) x 0.3 (low end estimate) = TDS (mg/L) x 0.6 (high end estimate) Concentration (mg/L)

SALT IMPACT ON PLANTS

How Salt Can Affect Plants

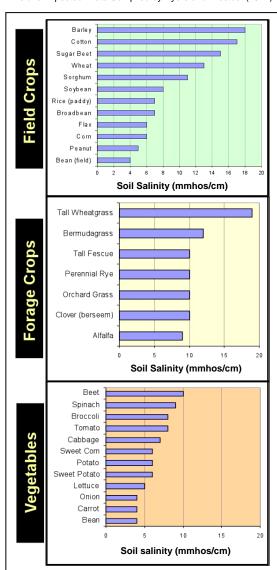
Water present within the soil pores is subject to several forces related to: i) the soil solid phase; ii) the dissolved salts; and iii) the gravitational field. Plants work against the capillary tension of water within the soil pores in order to draw in water. An increase in the TDS of the soil pore water increases the osmotic effect, thereby increasing the force a plant must exert to extract water from the soil. This can cause plants to go into drought stress even though a substantial amount of water may still be present in the soil.

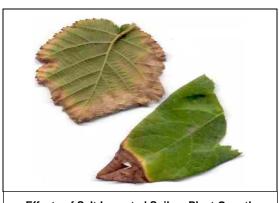
Plants are more sensitive to salinity during germination than in later stages of growth. Sprigging, sodding, or transplanting of plant materials is a way to avoid the sensitivity of the seedling stage.

Symptoms of Plant Stress Caused by Salt

Excessive soil salinity can result in barren spots, stunted vegetative growth with considerable variety in size, and a deep blue-green foliage (USDA, 1954). Plants that are stunted due to low fertility are usually yellow-green, while those stunted due to elevated salinity are characteristically blue green. The bluish appearance is the result of an unusually heavy waxy coating on the surface of the leaves, and the darker color is due to increased chlorophyll content. Some plants may develop dead areas or tipburn or exhibit cupping or rolling of the leaves.

Soil Salinity Levels at Which 50% Decrease in Plant Yield is Expected. Data Compiled by Ayers and Westcot (1977).





Effects of Salt-Impacted Soil on Plant Growth Use with permission of www.laspilitas.com

| Tolerance of Specific Plant to Sodicity (excess sodium) of Soil (adapted from Keech, 1995) | | | | | | | |
|--|------------------------|-------------------|--------------------|--|--|--|--|
| SENSITIVE | MODERATELY TOLERANT | TOLERANT | VERY TOLERANT | | | | |
| SOIL ESP = 2-20% | SOIL ESP = 20-40% | SOIL ESP = 40-60% | SOIL ESP > 60% | | | | |
| Deciduous Fruit | Clover | Wheat | Crested Wheatgrass | | | | |
| Nuts | Oat | Cotton | Tall Wheatgrass | | | | |
| Citrus Fruit | Tall Fescue | Alfalfa | Rhodegrass | | | | |
| Avocado | Rice | Barley | | | | | |
| Bean | Dallisgrass | Tomato | | | | | |
| | | Beet | | | | | |

KEY POINTS: OSMOTIC STRESS

Cause: High Soil EC/Salinity Values

Mechanism: As salinity increases, osmotic

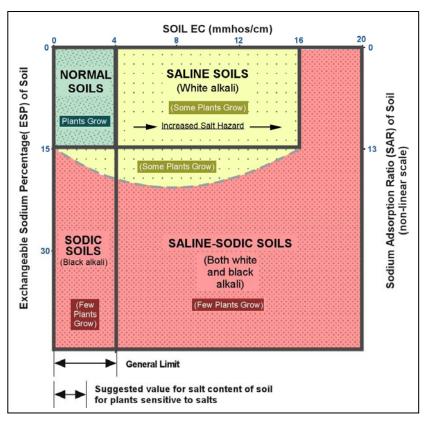
forces hinder transport of water from soil pores to plant roots.

Potential Impacts:
Plants can be stressed or killed.

SALT IMPACTS ON SOILS

The Impact of Salt on Clay in Soils

When salt migrates through soils containing clay minerals (see soil texture triangle to the right), the non-sodium ions present in the clays (e.g., potassium, calcium, and magnesium) can be removed and replaced (exchanged) by the sodium in the salt water. This results in *dispersion*, an electro-chemically induced process which causes soil clay particles to repel each other, physically move apart, and clog soil macropores (i.e., clog the large openings in the soil). Dispersed soils have lower permeability to water than non-dispersed soils. In addition, the repulsive forces acting among the soil particles reduce the soil cohesion and make the dispersed soil more susceptible to erosion.



Soil Classification Based on ESP (%) (Y-Axis) and EC (mmhos/cm) (X-Axis) (API Publication 4663); adapted from Donahue et al., 1983).

Soil Descriptions:

Normal Soils: (EC< 4, ESP < 15) No adverse effect due to salinity

Saline Soils: (EC>4, ESP < 15) Plants can experience osmotic stress.

No dispersion and no damage to soil structure.

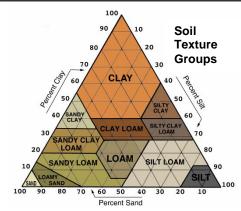
Sodic Soils: (EC<4, ESP > 15) Plants will not experience osmotic stress.

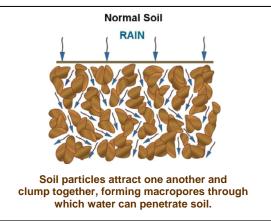
Soil is dispersed, damaging soil structure.

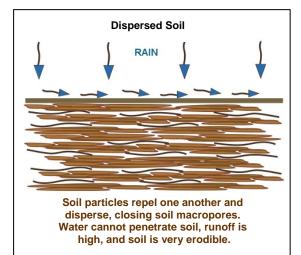
Saline-Sodic (EC>4, ESP > 15) Plants will likely experience osmotic stress.

Soils: Soil is dispersed, damaging soil structure.

Note: Soil dispersion is only a factor for clayey soils.







KEY POINTS: SOIL DISPERSION

Indicator: High ESP (> 15%)

Mechanism: Increased proportion of sodium in clays

disperses clay particles, damaging soil

structure.

Potential Soil structure is affected, drainage through soil is reduced, and soils are easier to erode.

Groundwater Sensitivity Analysis

In a modeling study of potential impacts to groundwater (API Publication 4734), nine technical factors were evaluated as part of a sensitivity analysis. The objective of this study was to determine which of the nine factors were the most important and which were the least important in terms of predicting whether a produced water release could impact shallow groundwater (i.e., the uppermost water-bearing unit, not deeper regional aquifers). The nine factors evaluated and the range of values used in the sensitivity analysis are show below.

| | | Nine Factors Evaluated | | | | | | | | |
|--------------|------|--|--|--------------------|------------------------------------|------------------------|---------------------------------------|--|-----------------------------------|--|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Range Values | | Chloride Mass Loading "L" (grams/ft²) | Thickness of Aquifer "b" (ft) | Soil "S" (-) | Aquifer Flux "Q" (ft/day) | Climate "C" (-) | Ground- Water Depth "D" (ft) | Volume of Brine Release "V" (ft ³) | Dispersion Length "AL" (ft) | Ambient CI Concentration in Groundwater "AC" (mg/L) |
| Level | Low | 76.20 | 9.84 | Sand | 0.003 | Humid (Shreveport, LA) | 9.843 | 421.094 | 0.328 | 0 |
| | High | 18,288 | 98.43 | Clay | 0.164 | Arid (Hobbs, NM) | 98.425 | 42,109 | 6.562 | 100 |

Sensitivity Analysis Approach

The sensitivity analysis used a " 2^k factorial" approach, where a total of 512 model simulations ($2^9 = 512$) were performed, one for each combination of "High" and "Low" values for the nine factors. This procedure is described below, and shown in the figure to the right.

- To assess the importance of Chloride Mass Loading, 256 simulations were run with the Chloride Mass Loading set at "Low", and all High/Low combinations of the other eight factors. The average increase in chloride concentration to shallow groundwater was calculated to be 89 mg/L (see diagram to the right).
- An additional 256 simulations were run where the "High" Chloride Mass Loading was used, resulting in an average chloride concentration increase in the shallow groundwater of 8357 mg/L.
- 3) Subtracting out the average of the "Low" runs from the average of the "High" runs gave a difference of (8357-89) = 8268 mg/L.

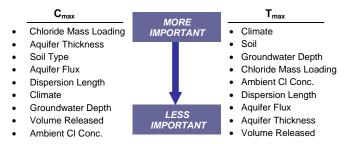
When this same approach was used for the *Groundwater Depth* factor, the difference between the "Low" and "High" runs was only 1827 mg/L, compared to 8268 mg/L for *Chloride Mass Loading*. Therefore *Chloride Mass Loading* is likely to have a greater effect than *Groundwater Depth* on chloride concentration in shallow groundwater.

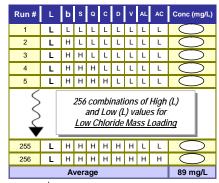
This type of sensitivity analysis was performed to evaluate key factors for:

- C_{max}, the increase in chloride concentration in shallow groundwater; and
- T_{max}, the time to reach the maximum increase in chloride concentration in shallow groundwater.

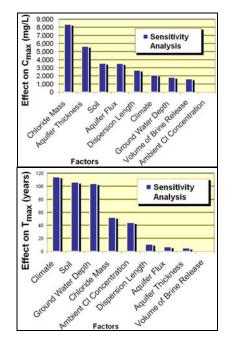
Results of the sensitivity analysis are shown in the bar charts to the right. Note the values shown on the Y axis (C_{max} , or increase in chloride concentration in shallow groundwater, and T_{max} , average time to reach C_{max} concentration in groundwater) are only meaningful in a relative sense (to compare factors). The absolute value (such as 8268 mg/L for *Chloride Mass Loading*) does not correspond to an expected value for actual site conditions.

A summary of the relative importance of the nine factors is shown below:





Schematic: 2^k Factorial Method Used in API Publication 4734.



KEY DATA INPUTS FOR IMPACT ASSESSMENT AND REMEDY SELECTION

Background - DATA

| PARAMETER | USED ON PAGE(S) | USED FOR | HOW TO GET THIS DATA | |
|--|-----------------|--|--|--|
| SOIL CHEMICAL DATA | | | | |
| EC of impacted soil (saturated paste method) | 2, 4, 5 | Rule of thumb for soil impact Soil response decision charts | Method 62-2.2 (Black, 1965) See pages 18, 23 | |
| Chloride concentration of impacted soils | 9, 10 | Rule of thumb for groundwater impact Groundwater planning model | Method 325.2 (U.S. EPA, 1983) See page 18 | |
| ESP (or SAR) of impacted soils | 2, 7 | Rule of thumb for soil impact Design of chemical amendment project | Calculated. See page 18 | |
| CEC of impacted soils | 7 | Design of chemical amendment project | Method 57- 3 (Black, 1965) See page 18 | |
| EC goal for soils (saturated paste method) | 8 | Design of mechanical remediation project | (See page 24 for related information) | |
| SOIL PHYSICAL DATA | | | | |
| Depth to impermeable layer in unsaturated zone | 4 | Soil response decision charts | Site-specific knowledge, site characterization data, County Soil Surveys ** | |
| Hydraulic conductivity of unsaturated zone | 4 | Soil response decision charts | | |
| Shrink-swell potential of soil | 4 | Soil response decision charts | | |
| Slope of land | 5 | Soil response decision charts | | |
| Depth to groundwater | 3 | Rule of thumb for groundwater impact | | |
| Type of soil (first 36 inches) | 5, 6 | Soil response decision charts Natural remediation design | | |
| Type of unsaturated zone (36 inches deep to water table) | 3 | Rule of thumb for groundwater impact | + | |
| PRODUCED WATER RELEASE DATA | | | | |
| Volume of produced water release | 3, 7, 10 | Rule of thumb for groundwater impact Design of chemical amendment project Groundwater planning model | Site-specific knowledge | |
| Sodium concentration of produced water release | 7 | Design of chemical amendment project | Method 200.7 (U.S. EPA, 1983) See page 18 | |
| TDS concentration of produced water release | 2 | Rule of thumb for soil impact | Method 160.1 (U.S. EPA, 1983) See page 18 | |
| Chloride concentration of produced water release | 3 | Rule of thumb for groundwater impact Groundwater planning model | Method 325.2 (U.S. EPA, 1983) See page 18 | |
| Area of produced water release (area of affected soil) | 3 | Rule of thumb for groundwater impact Groundwater planning model | Site-specific knowledge | |
| GENERAL DATA | | | | |
| Release area wetland? | 4 | Soil response decision charts | API Publication 4663 | |
| Annual precipitation | 5, 6 | Soil response decision charts Natural remediation design Groundwater planning model | Web page* or API Publication 4663 | |
| Annual evaporation | 5 | Soil response decision charts | Web page* or API Publication 4663 | |
| GROUNDWATER DATA | | | | |
| Effective width of source | 12 | Groundwater planning model | Sketch of site (see pages 12 and 22) | |
| Groundwater (Darcy) velocity | 13 | Groundwater planning model | Site-specific knowledge, site characterization data, or approximation method (see page 13) | |
| Thickness of water-bearing unit | 13 | Groundwater planning model | Site-specific knowledge, site characterization data, or approximation method (see page 13) | |
| Distance to point of interest | 14 | Groundwater planning model | Site-specific knowledge and/or site characterization data | |
| Transverse dispersivity | 14 | Groundwater planning model | Estimated | |
| Groundwater concentration goal for chloride | 15 | Groundwater planning model | Site-specific knowledge (see page 24 for related information) | |

^{*} Get precipitation and evaporation maps over the web.
One source:
http://jan.ucc.nau.edu/~doetqp-p/courses/env302/lec3/LEC3.html

**Order soil survey reports for your county at: <u>http://soils.usda.gov/survey/</u>

OR

Call the USDA National Resources Conservation Service

DRAW A SKETCH OF THE SITE:

Typically, the sketch should show:

Natural Features

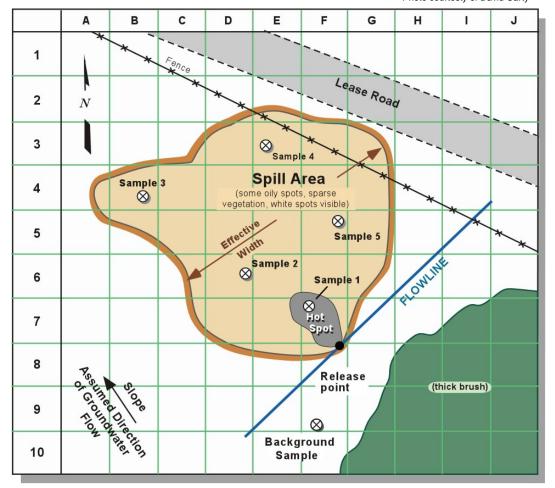
- Different soil types
- Different plant types
- Slope
- Rocky features
- · Extent of stressed vegetation

Release Data

- Sampling locations
- Approximate area of spill
- Release location



Use of Electromagnetic Conductivity Tool (EM-31) to Delineate Areas of Salt-Impacted Soil Photo courtesty of David Carty



Sample Location
Sample 1 at 0-1 and 1-2 ft
Sample 2 through 5 at 0-1 ft
Background sample 1 at 0-1 ft

Example of Spill Area Sketch

SOIL SAMPLING AND TESTING GUIDELINES

Lab Data That May Be Needed for Remediation

- Screening studies or quick field assessments need fewer of these lab tests.
- Detailed remediation designs need more of these tests.
- <u>Site-specific conditions</u> may determine actual data needs. At some sites, very limited data are needed to evaluate impacts and determine appropriate response. At other sites, more complicated tests (e.g., soil column studies) can be helpful.

DATA NEEDS:

Basic:

These tests are used for screening and to select between natural, chemical, and mechanical remediation.

Design:

These tests are used to design chemical amendment remediation projects (such as adding gypsum).

Compare:

These tests are used to determine if background conditions will limit plant growth.

TECH TIP 1: COMPOSITING SAMPLES

The objective of the sampling exercise is to determine the <u>average</u> condition of the soil. Compositing samples from 3 to 5 locations together can be an effective method to reduce analytical costs and define average soil conditions.

Rules of thumb: These general rules are typically applicable:

- Sample only when the soil is relatively dry.
 Clumps should be broken and the soil easy to mix.
- Collect samples from the surface to the depth where the EC is no longer elevated, to a maximum depth of 4 feet.

| Data Need | Soil Lab Test | Hot Spot | Full Spill Area | Background Samples |] | |
|--------------|---|--------------|--------------------|--------------------|--|--|
| | | | | | | |
| Basic | EC (saturated paste; see Tech Tip 2 below) | ✓ | \checkmark | ✓ | A B C D E | F G H |
| Basic | As-Received Moisture % | ✓ | / | | 1 1 1 | Lease Road |
| Basic | Saturated paste moisture % | \ | ✓ | | 2 N | |
| Basic | рН | \ | / | | 3 Sample 3 Spill 4 | 100 |
| | | | | | 4 Sample 3 Spill is one offy spill s | s, sparse pots visible) |
| Design | SAR | \checkmark | | | 5 ments | Sample 5 |
| Design | CEC | ✓ | ✓ | ✓ | 6 Sample | Sample 1 |
| Design | ESP | \ | | | 7 | One Control of the Co |
| Design | Chloride | \ | / | | 8 % | 7 |
| | | | | | 2011/19 | Release point on |
| Compare | Basic soil fertility (N, P, K, Ca, Mg, Na, S, EC) | ✓ | ✓ | ✓ | 9 Tolko Back 10 Back San | ground sple |
| | | | | | | 1 |

TECH TIP 2: MEASURING SOIL EC

To measure the EC of a soil sample, you must add water to convert the dry soil to a saturated paste as described below:

- 1) Place an amount of soil in a wide-mouth container.
- If you want to calculate the % moisture, weigh the container with soil.
- 3) Slowly add distilled water to the soil while gently tapping the container on a hard surface and gently stirring the soil. The water should be added until all the soil pores are filled, without any standing water on the surface. When the soil is saturated, the top of the saturated soil mass should glisten, the paste should fill the hole left by the stirring rod, and the paste should slide off the stirring rod. There should be no free water on the surface.
- Cover with aluminum foil and let stand for one hour so the salts and water can reach equilibrium.
- 5) If free water has appeared after an hour, add more soil and stir. If the paste has stiffened, add more water and stir. Repeat Step 4.

- 6) Extract water from the paste using positive pressure (such as a filter and syringe, or under a vacuum (such as with a Buchner funnel)).
- Use a conductivity meter to measure the EC of the extract. This
 value is used as the EC of the soil.

ALTERNATIVE METHOD 1: 1:1 SOIL EXTRACT METHOD. Mix 100 grams of dried soil with 100 grams of pure water. Let sit for minimum of 16 hours. Vacuum filter water through qualitative filter paper, recover extract, and measure EC of extract.

NOTE: Alternative Method 1 is easier but may not be as comparable to salt tolerance values that were determined using the saturated paste method.

ALTERNATIVE METHOD 2: IPEC SOIL SALT ANALYSIS KIT. (See www.ipec.utulsa.edu.)

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