NORTH DAKOTA REMEDIATION RESOURCE **MANUAL**

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FURTHER, the EERC and each of the contributing authors, reviewers, companies, and organizations expressly acknowledge that while the North Dakota Remediation Resource Manual (“Resource Manual”) identifies several options for remediation methods and procedures for various types of spills, the Resource Manual is not intended, nor should it be relied upon by any party, as *requiring* a specific remediation process for any particular spill event. Recognizing each spill event may require unique or different remediation efforts, together with future technologies and advancements in remediation, any remediation plan, after consultation between the company, landowner, and appropriate state, federal, and/or tribal governmental agency having regulatory jurisdiction, should consider any appropriate and relevant factors, options, methods, and mitigating circumstances, whether described in the Resource Manual or not.

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PURPOSE OF THE MANUAL

This manual was created to be a technical resource summarizing remediation techniques and the decision processes associated with selecting remediation options as well as other useful information and should not be assumed to be an all-inclusive summary. This manual is intended for a variety of audiences including, but not limited to, the following hypothetical users:

- Seasoned environmental professionals may utilize this document as a technical resource to be referenced along with their many other resources during hydrocarbon and brine remediation.
- Entry-level environmental practitioners may use this manual as an introductory training and educational tool as they develop remediation experience in the field.
- The general public may use this manual to develop a better understanding of the process of remediating hydrocarbon and brine spills.

Regardless of the user, the content provided in this manual is in no way intended to dictate or prescribe any specific remediation decisions or standardized practices. The specific remediation approach and process can only be done with careful consideration and analysis of site-specific conditions on a case-by-case basis.

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PROLOGUE

The current version of the resource manual is a product of existing successful practices currently being utilized in the oil fields of North Dakota as well as, but not limited to, the most relevant concepts from previous work by the following:

- American Petroleum Institute
- Environment Sciences Division of Alberta Environment
- U.S. Department of Agriculture
- Kerry Sublette, Ph.D.
- Len Gawel, Ph.D. (work funded by the North Dakota Industrial Commission and Hess Corporation)

Man—despite his artistic pretensions, his sophistication, and his many accomplishments—owes his existence to a six-inch layer of topsoil and the fact that it rains." – *Author Unknown*

The "North Dakota Remediation Resource Manual" is dedicated to the North Dakota landowner. It was the landowner who asked that remediation, especially for saltwater spills, be an option for returning the topsoil back as close to original productivity as possible. The oil and gas industry of North Dakota, having been engaged in spill response efforts for decades and recognizing the value of topsoil as a nonrenewable resource, was receptive to landowner desires, recognizing the importance of landowner relationships in resource development.

"The Nation that destroys its soils destroys itself." – *President Franklin D. Roosevelt, February 26, 1937*

In 2013, members of the North Dakota Petroleum Council (NDPC) created a working group to collaborate with the Energy & Environmental Research Center (EERC) to create two documents: a public education booklet entitled "Spills Cleanup Primer" and this document, the "North Dakota Remediation Resource Manual."

Media across North Dakota have done their part to shape public perception of spills. Some perceptions of spills include the idea that spills are common, produced water is laden with metals and other harmful chemicals, and once a spill occurs, the soil and surrounding land is ruined forever.

Based on data from the North Dakota Department of Mineral Resources (DMR), only 0.01% of the produced water (brine) or oil volume produced is ever involved in a spill, and 75%–80% of spills are contained on the well pad. In addition, remediation techniques have evolved to put the land back to its previous productivity in a shorter time period and more effectively than ever before, often within one season.

As early as 1760, George Washington used crushed limestone, manure, and gypsum fertilizers and plowed crops of grass, peas, and buckwheat back into his fields.

The method of remediation is determined by the type of spill—hydrocarbon, brine, or other—as well as the site conditions, soil type, and risk to public and environment. Once remediation has been performed, surface reclamation is undertaken to reestablish vegetation. Although complete restoration is the goal of everyone involved in the spill remediation process, it should be recognized by all that remediating the impacted land back to its original, prespill condition may not be achievable.

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NOMENCLATURE

API	American Petroleum Institute
BLM	U.S. Bureau of Land Management
BTEX	benzene, toluene, ethylbenzene, and xylene
C	carbon
Ca^{2+}	calcium ion
CEC	cation exchange capacity
CFR	Code of Federal Regulations
cfs	cubic feet per second
Cl^{-}	chloride
COC	chemicals of concern
CSM	conceptual site model
DC	direct current
DMR	Department of Mineral Resources
DRO	diesel-range organics
dS/m	decisiemens per meter
E&P	exploration and production
EC	electrical conductivity
EC_e	electrical conductivity by saturated paste method
EERC	Energy & Environmental Research Center
EM	electromagnetic
EPA	U.S. Environmental Protection Agency
ESP	exchangeable sodium percentage
FBIR	Fort Berthold Indian Reservation
GPS	global positioning system
GRO	gasoline-range organics
GW	groundwater
K	erodibility factor
K^{+}	potassium ion
LEPC	Local Emergency Planning Committee
MassDEP	Massachusetts Department of Environmental Protection
Mcf	thousand cubic feet
MCL	maximum contaminant level
meq	milliequivalent
MHA	Mandan, Hidasta, and Arikara Nation
mg/L	milligrams per liter
Mg^{2+}	magnesium ion
N	nitrogen
Na^{+}	sodium ion
NDDES	North Dakota Department of Emergency Services
NDDH	North Dakota Department of Health

Continued. . .

NOMENCLATURE (continued)

NDIC	North Dakota Industrial Commission
NDPC	North Dakota Petroleum Council
NDSU	North Dakota State University
NO_3^-	nitrate
NRC	National Response Center
P	phosphorus
PAHs	polycyclic aromatic hydrocarbons
PEI	precipitation evaporation index
pH	potenz hydrogen
PID	photoionization detector
ppb	parts per billion
ppm	parts per million
QA	quality assurance
QC	quality control
RBCA	risk-based corrective action
RBSL	risk-based screening level
RCRA	Resource Conservation and Recovery Act
SAR	sodium adsorption ratio
SAR_e	sodium adsorption ratio by saturated paste method
SARA	Superfund Amendments and Reauthorization Act
SDS	safety data sheet
SO_4^{2-}	sulfate
SPCC	spill prevention, control, and countermeasure
SSTL	site-specific target levels
TDS	total dissolved solids
TPH	total petroleum hydrocarbons
UND	University of North Dakota
USDHHS	U.S. Department of Health and Human Services
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
WOTUS	Waters of the United States

DEFINITION OF TERMS

A horizon: A mineral soil horizon formed at or near the surface in the zone of removal of materials in solution and suspension or maximum in situ accumulation of organic carbon or both.

active site: A description of a site where activities are being performed in association with the investigation, assessment, and remediation of a spill.

adsorption: The electrostatic attraction of ions or compounds to a surface (i.e., nutrients in solution [ions] carrying a positive charge become attached to [adsorbed by] negatively charged soil particles).

aeration: The process by which air in the soil is replaced by air from the atmosphere. The rate of aeration depends largely on the size, volume, and continuity of pores from the surface and within the soil. Compaction, sodic-induced clay dispersion, and texture have a direct influence on aeration.

aerobic: Processes that occur only in the presence of molecular oxygen, i.e., aerobic decomposition.

aggregation (as in soil): A description of soils where the fine particles are bonded together, usually with humus, in a single mass or cluster.

alkali soil: 1) A soil with a high degree of alkalinity (pH of 8.5 or higher), a high exchangeable sodium content (15% or more of the exchange capacity), or both. 2) A soil that contains sufficient alkali (sodium) to interfere with the growth of most crop plants.

anion: A negatively charged ion (i.e., chloride [Cl^-] and sulfate [SO_4^{2-}]).

B horizon: A mineral soil horizon characterized by one or more of the following:

1. An enrichment in silicate clay, iron, aluminum, or humus.
2. A prismatic or columnar structure that exhibits pronounced coatings or staining associated with significant amounts of exchangeable sodium.
3. An alteration by hydrolysis, reduction, or oxidation to give a change in color or structure from the horizons above or below or both.

bioremediation: A process by which naturally occurring or deliberately introduced organisms in the soil consume and break down soil contaminants.

brine: Water produced in the extraction of oil and gas, typically high in sodium chloride. Commonly considered water with total dissolved solids (TDS) > 30,000 mg/L. Also referred to as produced water.

bulk density: The mass of dry soil per unit bulk volume, expressed in grams per cubic centimeter. Soil compaction increases the bulk density of soil and can impact soil porosity, water infiltration, and root penetration.

C horizon: A mineral soil horizon comparatively unaffected by the soil formation processes operative in A and B horizons, except gleying and the accumulation of carbonates and soluble salts.

cation: A positively charged ion (i.e., sodium [Na^+], calcium [Ca^{2+}], magnesium [Mg^{2+}], and potassium [K^+]).

cation exchange capacity: The total amount of exchangeable cations that can be adsorbed or held by the soil, expressed in terms of milliequivalents per 100 grams of soil at pH 7.0 or at some other stated pH value.

chemicals of concern: Specific chemicals, whether they be hydrocarbon, brine compounds, or both, that are identified as potentially persisting or having an impact to the environment.

colloidal material: Organic and inorganic material with a very fine particle size (about 0.1 to 0.001 µm) and, therefore, high surface areas, which usually exhibits exchange properties.

diesel-range organics: Hydrocarbons present in a sample with carbons ranging from C10 to C28.

dispersion (as in soil): The breaking down of soil aggregates into individual particles. A description of soil in which the clay has dispersed. A dispersed soil consists of discrete soil particles that are not bonded together and are highly erodible. Dispersion is the opposite of aggregation.

electrical conductivity: A measure of how well a substance conducts electricity. It is a measure of the amount of soluble salts (salinity) in a soil, expressed in dS/m.

exchangeable sodium percentage (ESP): The extent to which the adsorption complex of a soil is occupied by sodium or the amount of exchangeable sodium expressed as a percentage of total exchangeable cations (Equation 1):

$$\mathrm{ESP} = \frac{\text{Exchangeable Sodium (meq/100 g soil)}}{\text{Cation Exchange Capacity (meq/100 g soil)}} \times 100 \qquad \text{[Eq. 1]}$$

The approximate relationship between the ESP and the sodium adsorption ratio (SAR) at equilibrium can be calculated as follows (Equation 2):

$$\mathrm{ESP} = \frac{100\ (-0.0126+0.01475\ \mathrm{SAR})}{1+(-0.0126+0.01475\ \mathrm{SAR})} \qquad \text{[Eq. 2]}$$

extractable petroleum hydrocarbons: Refers to an analytical method developed by the Massachusetts Department of Health with results representing C9 to C36 aliphatic hydrocarbons plus C11 to C22 aromatic hydrocarbons, similar in carbon range to DRO analysis.

field capacity: The amount of soil water remaining in a soil after the free water has been allowed to drain away (1 or 2 days) after the root zone has been previously saturated. It is the greatest amount of water that the soil will hold under conditions of free drainage and is related to the saturated paste extract.

free-phase product: Petroleum product in the environment as a separate layer "floating" on the groundwater or surface water or pooled on the ground surface.

gasoline-range organics: Hydrocarbons present in a sample that have carbons ranging from C6 to C12.

gleyed soil: Soil that formed under poor drainage, resulting in the reduction of iron and other elements in the profile and in gray colors and mottles.

groundwater: Subsurface water that fills the pore space of the soil to the extent that it is considered water-saturated.

halophytes: Plants that are highly tolerant of saline conditions.

hydraulic conductivity: The rate at which water will move through soil under a unit hydraulic gradient.

hydraulic gradient: The change in hydraulic head per unit distance. In groundwater this would be the slope of the groundwater table.

illuviation: The introduction of salts or colloids into one soil horizon from another by percolating water.

in situ remediation: A description of remediation that is performed on soil and/or water in place without requiring removal of the material to treat the impacted material.

landfarming: A bioremediation process where an environment is created to allow naturally occurring or deliberately introduced organisms in the soil to break down hydrocarbons (primarily in an aerobic environment). This is accomplished by incorporating nutrients, amendments, and oxygen in the soil with tillage while maintaining adequate moisture.

milliequivalent (meq): One-thousandth of the equivalent weight of an element, radical, or compound. Concentrations of electrolytes are often expressed as milliequivalents per liter, which is an expression of the chemical combining power of the electrolyte in a fluid.

natural attenuation: The reduction of contamination toxicity due to natural processes over time, including dispersion, dilution, sorption, and biodegradation.

no further action: A description of site status where sufficient remediation has been performed at the site such that the state regulatory agency deems there is no risk to receptors.

osmotic pressure: The pressure exerted by the flow of water through a semipermeable membrane separating two solutions with different concentrations of solute.

percent sodium: The percentage of the CEC occupied by sodium.

perched groundwater: Unconfined groundwater that is separated from an underlying body of groundwater by an unsaturated zone and a confining bed.

permeability: A measure of the ability for water or air to move through a soil profile. It is dependent on grain size, pore size, fracture size, and orientation but is not dependent on fluid viscosity and density like hydraulic conductivity.

pH: A measure of the degree of acidity or alkalinity of a soil. Expressed in terms of the pH scale ranging from 0 to 14 (pH < 7 being acidic, pH $= 7$ being neutral, and pH > 7 being basic or alkaline).

photoionization detector: A field instrument used to detect and measure certain petroleum hydrocarbon vapors.

phytoremediation: The specific use of plants and their associated microorganisms to reduce contamination in soils, surface water, and groundwater.

pore space: Total space not occupied by soil particles in a bulk volume of soil, commonly expressed as a percentage.

porosity: The volume percentage of the total bulk volume not occupied by solid particles.

produced water: See *brine*.

receptor: A term used to describe a person, plant, animal, or environment that could be adversely affected by a release of petroleum or brine.

reclamation: The process of returning disturbed land to a natural productive ecosystem or economically usable purpose.

remediation: Removal, conversion, or concentration reduction of contaminants from soil or water by physical, mechanical, or biological methods to minimize the impacts of these contaminants to the environment.

root zone: A term used to describe the soil depth that is penetrated by plant roots. Although the root zone can vary greatly depending on the specific plant or crop, for the purposes of this document, the root zone is considered to be the upper 4 feet of soil.

saline: Having elevated concentrations of total dissolved solids (i.e., Ca, Mg, Na, K, Cl, NO_3, and SO_4).

saline soil: Nonsodic soil containing sufficient soluble salts to impair its plant growth productivity. Commonly considered to be soil that exhibits a saturated paste extract EC > 4 dS/m and a pH < 8.5.

saline–sodic soil: Soil that contains sufficient exchangeable sodium to interfere with the growth of most crop plants and also contains appreciable quantities of soluble salts. Commonly considered to be soil with a SAR > 13 (ESP > 15%) and a saturated paste extract EC > 4 dS/m.

salinity: A term describing water solutions containing dissolved solids.

saturated paste: A mixture of soil and water that occurs when all soil pores are just filled with water. At saturation, the soil paste glistens as it reflects light and flows slightly when the container is tipped. The paste slides freely and cleanly from a spatula for all soils except those with high clay content. In undersaturated soil, deionized water is added to the soil sample with minimal mixing until all soil pores are filled with water and there is negligible air in the pores. The saturated paste moisture content is directly related to the field percent moisture range between permanent wilting and field capacity. It is useful as a reference because it represents the actual concentration and ratios of dissolved constituents available for uptake by plant roots.

saturated paste extract: Soil pore water containing dissolved constituents (soluble salts) that have been removed from the saturated paste with a suction filter for analysis.

sodicity: Sodium concentration.

sodium adsorption ratio: A measure of the sodic content of soil, expressed empirically as Equation 3:

$$\mathrm{SAR} = \frac{[\mathrm{Na}]}{\sqrt{(([\mathrm{Ca}]+[\mathrm{Mg}])/2)}} \qquad \text{[Eq. 3]}$$

sodic soil: Soils that contain sufficient sodium to interfere with the growth of most crop plants. Commonly considered to be soil that exhibits a SAR ≥ 13 (ESP ≥ 15%). Also referred to as alkali soil.

soluble salts: Determined by EC as measured in the extracts from saturated paste, 1:1 or 1:5 extracts (soil:water). The reliability of salinity estimates based on the conductivity of 1:1 and 1:5 extracts depends upon the kind of salts present. Highly soluble chloride salts will be only slightly affected by solutions with higher moisture content. In salts with lower solubilities such as sulfate or carbonate salts, the apparent amount of soluble salts (EC) will be higher in soils with higher moisture content.

subsoil: The B horizon of soils with distinct illuviation. Located below the A horizon and normal plowing depth, it is very important for rooting depth, soil moisture, and fertility.

subsoiling: The tillage of subsurface soil (subsoil) without inversion, for the purpose of breaking up dense layers that restrict water movement and root penetration.

surface soil: The uppermost part of the soil often mechanically affected by tillage in cultivated soils ranging in depth from 5 to 8 inches. Frequently designated as the plow layer (Ap) or the A horizon.

tile drain: Pipe made of perforated flexible plastic pipe to collect and carry excess water from the soil to a sump or other drainage feature. Usually laid at depths between 1 and 5 feet and spaced laterally depending on soil texture and horizonation.

total dissolved solids: Mineral matter suspended and dissolved in solution which passes a standard glass filter and 0.45-µm filter and does not evaporate below 180°C. Generally used as a gross indicator of the mass of dissolved salts in a solution, but the analytical method is subject to interferences from colloidal material.

total petroleum hydrocarbons: A measure of the quantity of oil-related compounds in a given quantity of soil.

volatile petroleum hydrocarbons: Refers to an analytical method developed by the Massachusetts Department of Health with results representing C5 to C12 aliphatic hydrocarbons plus C9 to C10 aromatic hydrocarbons, similar in carbon range to GRO analysis.

NORTH DAKOTA REMEDIATION RESOURCE MANUAL

INTRODUCTION

This document was prepared to aid those involved in the remediation and reclamation of sites impacted by oil field-related spills. Remediation information included in this document is for spills limited to soil impacts and does not address remediation related to groundwater impacts. In addition, the information is specific to the execution of these activities in North Dakota and may not be wholly applicable to other areas of the country.

This Resource Manual is organized much like an instruction manual or reference document with distinct sections for different topics (listed below). This manual is based on practical, reproducible, and field-friendly procedures. The document is prepared so that users can reference individual sections specific to their needs without requiring them to read the entire document. The North Dakota Petroleum Council (NDPC), and those whose efforts this manual represents, is confident that technology advancement in the future will create additional options for more effective remediation, and this manual will be revised to incorporate those technological advances. The distinct sections are as follows:

Regulation Overview

Spill remediation and reclamation regulations, for the most part, are at the discretion of the various regulatory agencies. North Dakota Industrial Commission (NDIC) regulations require operators to respond with appropriate resources to contain and clean up spills. Discharged fluids must be promptly and properly removed unless otherwise approved. Remediation standards are determined on a case-by-case basis, depending on the contaminant involved and the potential for risk to human health and the environment.

Depending on the severity of the spill or accidental discharge, the North Dakota Department of Health (NDDH) may require the owner or operator to do one or all of the following:

- Take additional actions necessary to protect human health and the environment.
- Take immediate remedial measures.
- Determine the extent of pollution to waters of the state.
- Provide alternate water sources to water users impacted by the spill or accidental discharge.

Depending on if federal lands are impacted and what agency governs the remediation efforts, reclamation requirements will vary. As indicated below in spill reporting, for tribal lands in North Dakota, the MHA (Mandan, Hidatsa, and Arikara Nation) Energy Division requires preapproval for spill remediation activities. The U.S. Forest Service (USFS) dictates activities on Forest Service lands.

SPILL REPORTING

Spill reporting varies based on the spill volume, severity of the impacts, and site location. These variables determine when/what agencies will respond to an event. A breakdown of who needs to be contacted depending on these mentioned variables is provided in Figure 1.

State Spill Reporting

In general terms, NDIC requires verbal and online spill reporting based on specific spill volume thresholds and time lines. Spills above the regulated reported threshold must be reported to NDDH or the NDIC and the North Dakota Department of Emergency Services (NDDES). Additional reporting requirements exist throughout the remediation/reclamation process. Additional notifications may be required depending on location and spill impact. See Figure 1 for the North Dakota release notification procedure flowchart for further information. See Appendix A for an example of a spill response notification form as well as other useful field forms. For details regarding spill reporting volume thresholds and time lines, as well as other pertinent information, the user should access the Web site below or contact the state agencies listed below.

Online Initial Notification Report:
www.dmr.nd.gov/oilgas/mvc/wincident/

North Dakota Industrial Commission:
Oil and Gas Division
(701) 328-8020

North Dakota Department of Health:
Environmental Health Section
(701) 328-5210 or 5166

North Dakota Department of Emergency Services:
(800) 472-2121 (24-hour hotline)

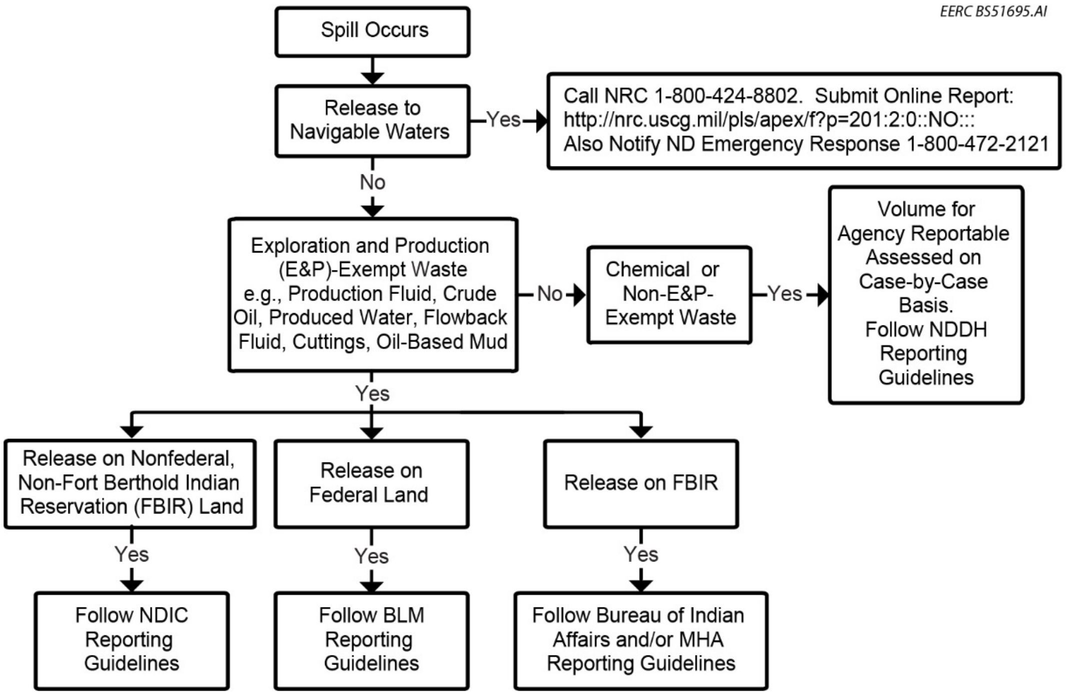


Figure 1. North Dakota release notification procedure flowchart.

Federal Mineral Impact

Any well impacting federal royalties, whether on federal or private land, is subject to Bureau of Land Management (BLM) reporting regulations. For details regarding spill reporting volume thresholds and time lines, as well as other pertinent information, the user should access the Web site below or contact BLM.

Bureau of Land Management:
(701) 227-7700
North Dakota Field Office
99 23rd Avenue West, Suite A
Dickinson, ND 58601

Notice to Lessees and Operators of Onshore Federal and Indian Oil and Gas Leases (NTL-3A – Reporting of Undesirable Events):
www.blm.gov/style/medialib/blm/mt/blm_programs/energy/oil_and_gas/operations/ntls.Par.36263.File.dat/ntl3a.pdf

Tribal Land Impact

Spills occurring on tribal land have additional requirements from state or federal requirements. For details regarding spill reporting volume thresholds and time lines, as well as other pertinent information, the user should access the Web site below or contact the MHA Energy Division.

MHA Energy Division:
(701) 627-5154
Compliance Department
227 West Main Street
New Town, ND 58763

MHA Energy Division: Accidental Release or Spill Requirements:
www.mhanation.com/main2/departments/mha_energy_division/mha_energy_website/Information%20Spill%20Response%20Requirements.pdf

Federal Reportable Spills

Any operator responsible for a release or spill is required to notify the federal government when the amount reaches a federally determined limit. See chemical-specific safety data sheets (SDS) for reportable quantity. For petroleum hydrocarbons, discharges in such quantities that have been determined may be harmful to the public health or the environment must be reported to the National Response Center (NRC) if one of the following occurs:

1. Spill reaches navigable water or direct tributaries/adjoining shorelines
2. Discharge violates water quality standards
3. Discharge leaves a sludge or emulsion beneath the surface

U.S. Environmental Protection Agency (EPA) National Response Center:
(800) 424-8802

EPA Region 8:
(303) 312-6384 or (800) 227-8917
8OC-EISC
1595 Wynkoop Street
Denver, CO 80202-1129

EPA Reporting Requirements:
www2.epa.gov/emergency-response/reporting-requirements-oil-spills-and-hazardous-substance-releases

Other Reporting

Depending on the location and magnitude, USFS, the U.S. Army Corps of Engineers (if the spill impacted waters of the United States [WOTUS]), affected landowners, and local community agencies must also be notified. USFS will oversee any remediation activities on USFS land. For spills occurring close to a community, the Local Emergency Planning Committee (LEPC) and fire department may need to be contacted to respond to the incident. Through annual Tier II reporting, LEPC and the fire department already know the hazardous chemicals located within their counties.

USFS:
(701) 250-4443
Supervisor’s Office
240 West Century Avenue
Bismarck, ND 58503

LEPC Contact List:
www.nd.gov/des/uploads%5Cresources%5C815%5Cnd_em_list_9-23-2015.pdf

Fire Department Contacts:
www.nd.gov/des/uploads%5Cresources%5C667%5Cfiredeptlisting.pdf
As part of emergency response plans, operators should have spill or incident response notification forms. These forms can be used as a resource during an event to track who was contacted when and what response efforts are already under way.

IMPACT OF CRUDE OIL AND BRINE SPILLS ON SOIL

Impact of Hydrocarbons on Soil

Crude oil is a complex mixture of organic compounds of which greater than 95% is carbon and hydrogen (Pinnella and Alstad, 2013). Crude oil from the Bakken and Three Forks Formations has an API gravity of approximately 42° and is classified as a light sweet crude. Crude oil is less dense than water and is sparingly soluble in water, with solubility increasing with API gravity (American Petroleum Institute, 2001).

Crude Oil Chemistry

Crude oil, like other petroleum hydrocarbons, is generally divided into two groups: aliphatic hydrocarbons and aromatic hydrocarbons. Aliphatic and aromatic hydrocarbons are further defined by their molecular structure. Figure 2 illustrates the hydrocarbon nomenclature and structure.

Aliphatic hydrocarbons are classified as either straight-chain, branched-chain, or cyclic. Straight-chain aliphatics are known as normal alkanes (or paraffins); branched-chain aliphatics are called isoalkanes; and cyclic aliphatic compounds are referred to as cycloalkanes (or cycloparaffins). The common characteristic of these alkanes is that they contain only single carbon–carbon bonds. On the other hand, the other classes of aliphatic compounds, alkenes (olefins) and alkynes (acetylenes), contain double and triple carbon–carbon bonds, respectively.

Aromatic hydrocarbons have either a single or multiple benzene-ring structure. Single benzene-ring hydrocarbons include benzene, toluene, ethylbenzene, and xylenes (or BTEX) and multiple benzene-ring hydrocarbons are referred to as polycyclic aromatic hydrocarbons (or PAHs). Naphthalene, which contains two benzene-ring hydrocarbons, is an example of a PAH.

Crude oils contain less BTEX than gasoline and the USGS (U.S. Geological Survey, 2006) reported that, on average, BTEX compounds represent about 2% of the crude oil by weight. Aromatic hydrocarbons, especially BTEX, tend to be the most water-soluble fraction of crude oil with benzene being the most water soluble of the BTEX compounds. BTEX compounds, are also the most volatile of the aromatic compounds and are considered to be in the class of volatile organic compounds (VOCs).

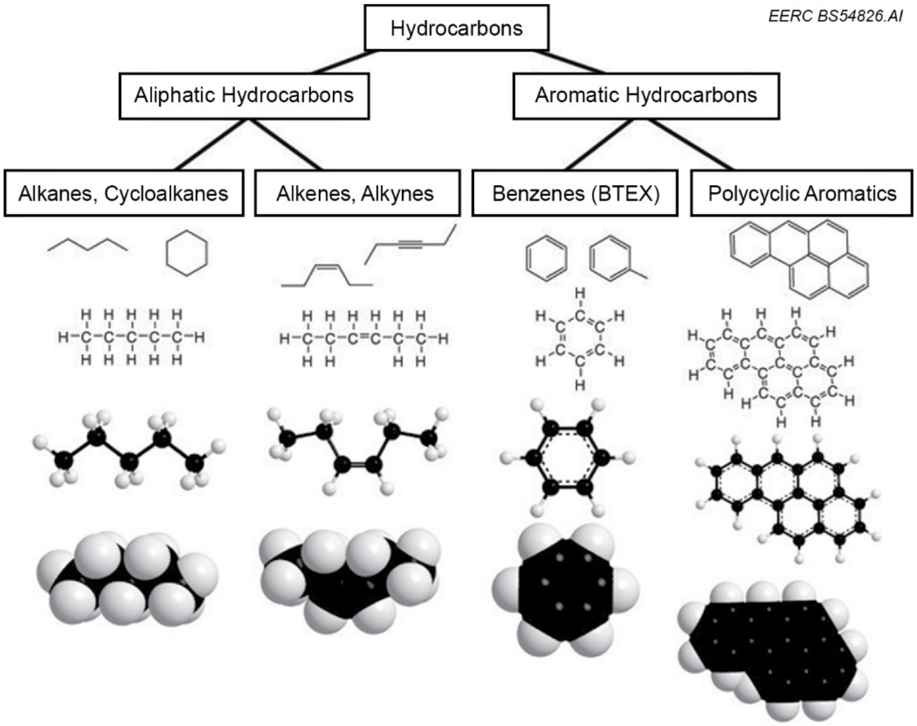


Figure 2. Hydrocarbon structure diagram.

The Massachusetts Department of Environmental Protection [MassDEP] (Massachusetts Department of Environmental Protection, 2015), while studying Bakken crude oil spills, published that light crude oil contains a greater amount of volatile organic compounds and will lose up to 20% to 40% of its mass immediately following a release. Similarly, up to 1/3 of a medium-grade crude oil will evaporate in the first 24 hours; the material that remains will be much more viscous.

In addition, MassDEP indicated that some of the lower-molecular-weight oil components are soluble in water; however, these soluble components are also volatile and evaporate rapidly at rates 10 to 1000 times faster than their dissolution in water. Dissolution occurs within the first day after a release and is not a major fate and transport process as most crude oil components are relatively insoluble.

The key physical characteristics of hydrocarbons that affect their movement in the environment include solubility in water, volatility, density, viscosity, and pour point (U.S. Geological Survey, 2006).

Crude Oil in the Environment

Once introduced to the environment, the hydrocarbon compounds in crude oil can volatilize, adsorb to soil particles, dissolve into soil pore water, or remain as part of the free product (Spence and others, 2001). The impact of hydrocarbon spills can vary but is largely a function of the following factors (Pinnella and Alstad, 2013):

- Spill volume
- Type of crude oil (density, viscosity, and interfacial tension)
- Dispersion rate
- Surface terrain
- Soil type (porosity and permeability)
- Weather

Crude oil released to the environment can migrate through soil via two general pathways: 1) as bulk oil flow infiltrating the soil under the forces of gravity and capillary action, and 2) as individual compounds that separate from the bulk petroleum mixture and partition to air or water (U. S. Department of Health and Human Services, 1999). These migration pathways are briefly discussed in the remainder of this section.

Migration of Bulk Oil

When bulk oil flow occurs, it results in little or no separation of the individual compounds from the hydrocarbon mixture and its infiltration rate into the subsurface is usually fast relative to its dissolution rate in water. Since many of the individual hydrocarbon compounds in crude oil are insoluble in water, their only means of migration is as part of the bulk oil flow. Factors affecting the rate of bulk oil infiltration include soil moisture content, vegetation, terrain, climate, rate of release, soil particle size, and oil viscosity (U.S. Department of Health and Human Services, 1999).

Over time, as bulk oil migrates through the soil column, a small portion of the oil is retained by soil particles and is no longer mobile. The concentration of bulk oil retained by the soil particles at this time is known as “residual saturation.” Depending upon the persistence of the bulk oil in the subsurface environment, it can be present at residual saturation for long periods of time, depending on site conditions and remedial action taken. Residual saturation is important as it represents long-term soil impacts that can act as a continuing source of contamination to groundwater and soil vapor as individual hydrocarbon compounds separate from the bulk oil (U.S. Department of Health and Human Services, 1999).

Migration of Individual Hydrocarbon Compounds

As the bulk oil migrates through the soil column, some individual hydrocarbon compounds will separate from the mixture and partition to the soil, soil vapor, or soil pore water, where they can migrate independent of the bulk oil. Chemical properties such as volatility, solubility, and sorption potential are often used to evaluate and predict which compounds will likely separate from the mixture via these pathways (U.S. Department of Health and Human Services, 1999). Each of these potential partitioning phenomena is discussed in more detail below.

Volatility

Volatility can be described as the propensity of a chemical to evaporate or partition into the vapor phase. Lower-molecular-weight hydrocarbon compounds, containing 1 to 10 carbon atoms, evaporate or volatilize into the air more readily than intermediate-molecular-weight compounds, containing 11 to 22 carbon atoms, which volatilize slowly over several days. High-molecular-weight compounds, containing 23 or more carbon atoms, volatilize only minimally or not at all

(Massachusetts Department of Environmental Protection, 2015). In addition, given a similar molecular weight, alkanes and alkenes tend to be more volatile than aromatic hydrocarbons (U.S. Geological Survey, 2006).

Solubility

Solubility, specifically water solubility, is a measure of the tendency of crude oil (or individual hydrocarbons) to dissolve into water. In general, less than 5% of crude oil will dissolve in water (U.S. Geological Survey, 2006). Solubility generally decreases with increasing molecular weight of the hydrocarbon compounds. For compounds of similar molecular weight, the aromatic hydrocarbons are more water soluble than the aliphatic hydrocarbons, which are more water soluble than the branched aliphatic hydrocarbons. (U.S. Department of Health and Human Services, 1999).

Analogous to volatility, lower-molecular-weight components, containing 1 to 10 carbon atoms, dissolve more readily and to a greater extent into water than intermediate-molecular-weight components, containing 11 to 22 carbon atoms. High-molecular-weight components, containing 23 or more carbon atoms, dissolve much more slowly and to a lesser extent than these lower-molecular-weight components (Massachusetts Department of Environmental Protection, 2015).

It is important to understand that the solubility of a pure compound in water is higher if the pure compound is in contact with water than if that same compound is present in a hydrocarbon mixture. As an example, Figure 3 shows the various solubility limits of benzene in water for pure benzene, a 50% mixture of benzene and toluene, and a diesel fuel containing 0.05 mole % benzene. (Alaska Department of Environmental Conservation, 2006).

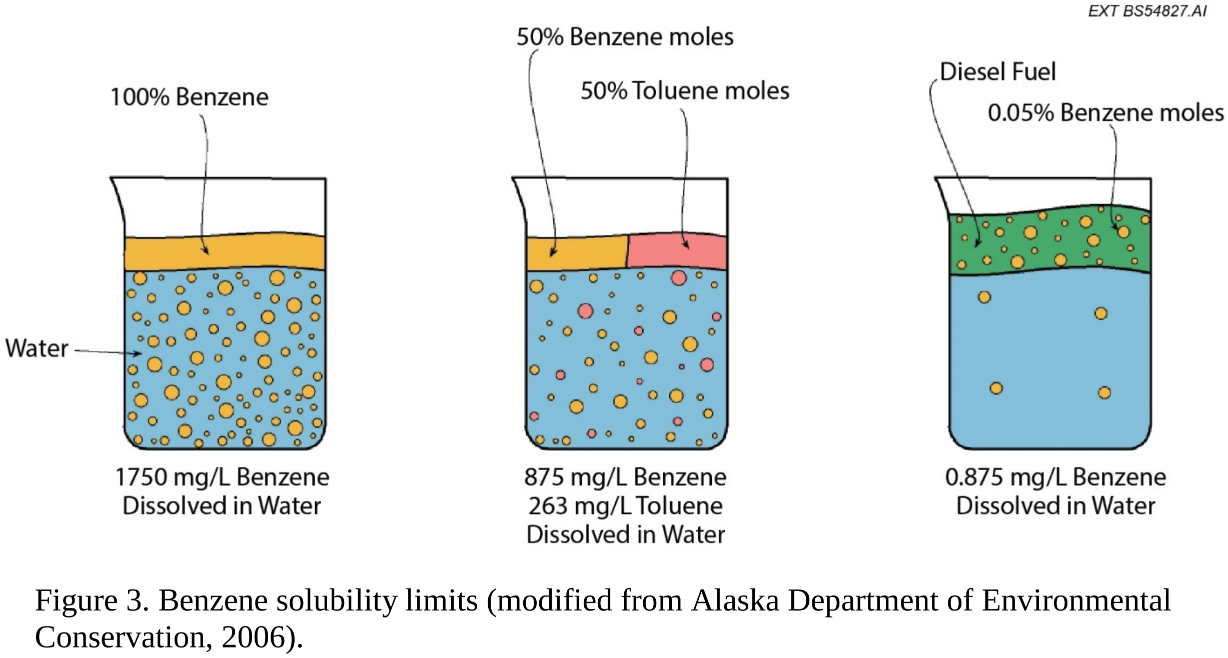


Figure 3. Benzene solubility limits (modified from Alaska Department of Environmental Conservation, 2006).

Sorption

Sorption potential can be defined as the propensity of constituents in the bulk oil to attach (or adsorb) to organic matter in the soil. If the chemical is strongly associated with the organic matter in the soil (i.e., strongly sorbed), the chemical is relatively immobile as it will not volatilize or leach from the soil. If the chemical is weakly sorbed to the organic matter in soil, this is not the case and the chemical has the potential to be transported, providing a greater chance for it to come into contact with human or ecological receptors.

Other Important Factors Affecting Presence/Migration of Hydrocarbons in the Environment

Phase Partitioning

Phase partitioning, i.e., the distribution of the crude oil and its components between the soil, soil vapor, and soil pore water, is an important factor that influences the fate and transport of hydrocarbons in the subsurface environment.

The ability of a soil to hold hydrocarbons in the dissolved, vapor, and sorbed states is finite, and the maximum holding capacity of the soil for dissolved-, vapor-, and sorbed-phase hydrocarbons is designated as the soil saturation concentration, which is abbreviated as C_{sat}. C_{sat} is dependent on the soil properties (such as moisture content, bulk density, and porosity) and the properties of the hydrocarbon compounds (Alaska Department of Environmental Conservation, 2006).

At hydrocarbon concentrations below C_{sat}, all hydrocarbon present in the soil is distributed between the dissolved, vapor, and sorbed phases. At hydrocarbon concentrations above C_{sat}, nonaqueous phase hydrocarbon (i.e., crude oil) is present in addition to the dissolved, vapor, and sorbed phases. Above C_{sat}, any additional hydrocarbons will only increase the mass of the nonaqueous phase (Alaska Department of Environmental Conservation, 2006). This phase partitioning is important as it dictates which of the above hydrocarbon migration phenomena are in play and dominating the fate of the hydrocarbons in the subsurface.

Figure 4 graphically shows the relationship between C_{sat}, the concentratrions of hydrocarbons in the dissolved, vapor, and sorbed phases, and the presence of a non-aquous phase hydrocarbon liquid (Alaska Department of Environmental Conservation, 2006). Figure 4 illustrates that prior to the hydrocarbon concentration in the bulk soil reaching C_{sat}, the total hydrocarbon mass is distributed between the dissolved, vapor, and sorbed phases. However, as more hydrocarbon is introduced to the soil and the bulk soil concentration exceeds C_{sat}, no additional hydrocarbon reports to these three phases, i.e., the concentration remains the same, but a fourth, nonaqueous liquid phase appears.

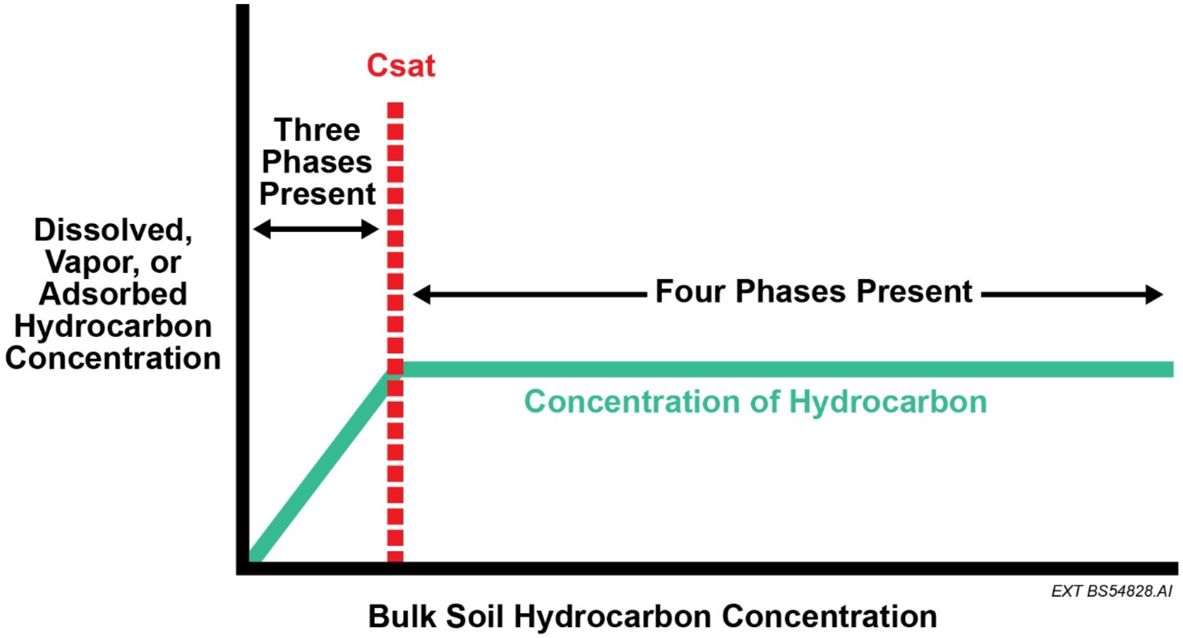


Figure 4. Soil saturation concentration (modified from Alaska Department of Environmental Conservation, 2006).

Biodegradation

The biodegradation of hydrocarbons is well established and involves the destruction of the hydrocarbons by microorganisms that naturally exist in the soil and use the hydrocarbons as a food source. This action of the microorganisms creates additional biomass as it breaks down the hydrocarbons into CO_2 and water. In almost all cases, the presence of oxygen is essential for effective biodegradation of crude oil. However, decomposition of petroleum hydrocarbons in the absence of oxygen, i.e., anaerobic biodegradation, also can occur but typically at much lower rates of degradation. Unlike other fate processes that disperse contaminants in the environment, biodegradation is important because it can eliminate the contaminants from the subsurface, leaving behind only CO_2 and water (U.S. Department of Health and Human Services, 1999).

The MassDEP developed a list of hydrocarbon classes in order of increasing difficulty of biodegradation (Massachusetts Department of Environmental Protection, 2015):

1. n-alkanes
2. Isoalkanes
3. Alkenes
4. Benzene and its alkyl derivatives, e.g., toluene, ethylbenzene, and xylene (BTEX)
5. Polycyclic aromatic hydrocarbons (PAHs)
6. High-molecular-weight cycloalkanes

Other literature that supports this biodegradation assessment are listed below:

- McMillen and others (2002) report that crude oils with an API gravity greater than 20 are readily biodegradable, with BTEX being the most readily degraded compounds (Ohio Environmental Protection Agency, 2014).

- U.S. Department of Health and Human Services (U.S. Department of Health and Human Services, 1999) noted the following:

    1. Generally, normal alkanes and BTEX are degraded more readily than highly branched isoalkanes.

    2. *n*-alkanes, *n*-alkyl aromatics, and aromatics in the C_{10}–C_{22} range are the most readily biodegradable.

    3. n-alkanes, *n*-alkyl aromatics, and aromatics in the C_5–C_9 range are biodegradable at low concentrations by some microorganisms but are generally preferentially removed by volatilization and thus are often absent in many environments.

    4. *n*-alkanes in the C_1–C_4 range are biodegradable but only by a narrow range of specialized hydrocarbon degraders.

    5. *n*-alkanes, *n*-alkyl aromatics, and aromatics above C_{22} are generally not available to degrading microorganisms.

    6. Hydrocarbons with condensed ring structures, such as PAHs with four or more rings, have shown to be relatively resistant to biodegradation, although the biodegradation of PAHs with only two or three rings has been routinely observed.

Impact of Salt on Soil

Brine, when released into the environment, can have a detrimental effect on soil both chemically and physically. This is a result of the increase in the amount of salts in the soil (salinity) and the total sodium concentration (sodicity). Depending on the amount of salts or sodium in the brine, saline, saline–sodic, or sodic soil conditions may result. The different classifications each have specific mitigation requirements.

Most often, saline–sodic soil conditions will be present following a brine spill; as such, saline–sodic soils will be covered in this document. Soil is classified as saline–sodic when the electrical conductivity (EC) is greater than 4 decisiemens per meter (dS/m), the pH is greater than 8.5, and the sodium adsorption ratio (SAR) is greater than 13 (unitless).

There are three major impacts on soil and plants when saline–sodic conditions are present:

1. Soil particles are dispersed, reducing soil aggregation (**sodic soil**).
2. Osmotic potential inhibits the plant’s ability to uptake water (**saline soil**).
3. Ionic imbalance of the soil solution reduces nutrient absorption (**saline–sodic soil**).

Soil Aggregation

One of the major impacts of a brine spill is the physical destruction of the soil aggregates by dispersion and swelling. Dispersion/swelling can occur when the sodium ion occupies more than 15% of a clay particle's exchange sites and when the total EC in the soil solution is low (it is important to note that dispersion and swelling are dependent on the clay mineralogy and content, organic matter, and soil moisture among other field conditions). The summations of the total number of clay exchange sites and exchange sites from organic matter are referred to as the clay's cation exchange capacity (CEC). When brine, dominated by the sodium ion (Na^+) of the sodium chloride molecule, is released into the environment in elevated concentrations, the Na^+ is more available to the clay exchange sites because of "mass action" than are the other common ions (e.g., calcium [Ca^{2+}] and magnesium [Mg^{2+}]), resulting in an ion imbalance. When these conditions are present, the Na^+ ion is able to exchange with a sufficient number of the Ca^{2+} and Mg^{2+} ions on the clay particles to weaken the hydrated bonding strength, as the Na^+ is a larger ion and has a weaker valence charge than Ca^{2+} and Mg^+. Basically, Na^+ prefers to be hydrated (surrounded by water), and Ca and Mg prefer to be coordinated (bound) to the clay layer, thus keeping the soil clay flocculated (held together). The general order of exchangeability of some important hydrated exchangeable cations is as follows:

$$\mathrm{Al^{3+}} > \mathrm{Ca^{2+}} > \mathrm{Mg^{2+}} > \mathrm{K^+} = \mathrm{NH_4^+} > \mathrm{Na^+}$$

Soil Dispersion/Swelling

As the Na ion begins to dominate the clay exchange sites and when water is introduced, the clay particles can swell and lose structure. The loss of soil structure decreases the pore space within the soil profile. This process limits water infiltration, percolation, bioactivity, and nutrient transfer within the soil profile. As this process continues, water will be unable to enter the soil profile and will run off the soil surface and start to erode away topsoil.

Figure 5 illustrates the process of soil dispersion/swelling from a natural (flocculated) soil to an unflocculated or dispersed soil. Left untreated, a Na-dominated, brine-impacted soil could result in the total loss of soil structure. The potential dispersion of impacted soil can be determined analytically by the exchangeable sodium percentage (ESP), SAR, or the percent of the Na^+ in the soil solution.

Soil dispersion/swelling results in the following:

- Loss of soil structure
- Loss of pore structure
- Soil compaction
- Reduced infiltration of precipitation or irrigation waters
- Reduced air and water movement
- Reduced bioactivity
- Reduced nutrient transfer
- Increased water runoff and soil erosion

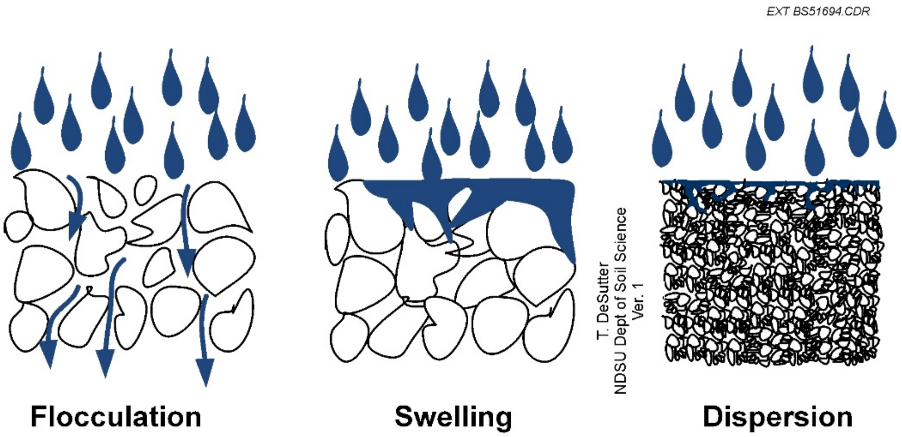


Figure 5. Example of dispersion in sodium-impacted soil (courtesy of North Dakota State University Department of Soil Science).

Osmotic Potential

Salts decrease the soil’s osmotic pressure and can starve plants of water if the pressure drops below the osmotic pressure of the plant roots (i.e., the osmotic gradient leads away from the plant root). Also, the lowering of the osmotic potential of soil water can negatively impact soil microbe communities by preventing cell growth/division (Emerson and Breznak, 1997). Similar to plant roots, soil microbes will experience water loss of cells in high saline conditions. Soil microbe and plant root symbiosis is important for nutrient cycling.

Ionic Imbalance of Soil Solution

Chloride can have a direct toxicity effect on plants depending on the chloride concentration relative to the other negatively charged ions in the released brine. Sensitivity of different plant species to the ions in the brine solution will vary (refer to Appendixes E and F for the tolerance levels of different plant species). The chloride and other negatively charged ions are highly mobile in soil solution and, consequently, can percolate below the root zone of most perennial plants under normal annual precipitation conditions (12–14 inches of rain) in parts of North Dakota. It should be noted that to ensure that brine impacts remain below the root zone, sufficient water, either natural or introduced, must be applied to the site to translocate salts to the deep soil. Without sufficient translocation via applied waters, salts will likely move back into the root zone via capillary rise.

SPILL AND SITE ASSESSMENT

When a sampling plan is developed, it is important to consider the unique nature of the spill and complexity of the site. Soil sampling, coupled with field and laboratory analysis, can provide accurate information on the extent and severity of the brine contamination if samples are taken, handled, and analyzed correctly. Sampling and analysis can provide information on depth and lateral extent of salt contamination, type, age, source, and concentration of salts in soil. It can also be used to confirm whether other contaminants such as hydrocarbons or metals are present in the soil. Users should consider the following when developing a sampling plan.

Sampling Strategy

The first step in developing a sample strategy for a release site is to conduct a paper or electronic search for the area of interest (landowner/operator interviews, historical aerial photographs, Web Soil Survey), identify all potential sensitive receptors, and then conduct a visual site assessment. This could include a geophysical survey (electromagnetic [EM] induction survey) and/or soil sampling program which can be used to determine the variability of salt distribution and document the site characteristics and distance to sensitive receptors. A more detailed discussion regarding the use of EM induction as a site characterization tool is provided later in this section (see "Geophysical Survey").

Once the site features have been documented, a systematic sampling strategy should be developed. This could include a variety of sampling collection strategies employing consistent grid pattern, transects, or a stratified random sample selection. Regardless of the systematic sampling strategy deployed, it must be reproducible. Examples of forms for the systematic collection of field data are provided in Appendix A. Table 1 is a list of potential analytical parameters for consideration when conducting the site assessment or remediation/reclamation phases of a release site. The user must determine which parameters are appropriate for the user's specific situation.

Table 1. Analytical Parameters (example)

Project Phase	Soil Lab Test	Hot Spots	Full Spill Area	Background Sample
Site Assessment				
	EC (saturated paste, 1:1, or 1:5)	X	X	X
	Chloride concentration	X	X	X
	Bromide concentration	X	X	X
	SAR and/or %Na	X	X	X
	Total petroleum hydrocarbons, DRO[1]	X	X	
	Total petroleum hydrocarbons, GRO[2] with BTEX[3]	X	X	
	pH	X	X	X
	RCRA[4] metals	X	X	
Remediation/Reclamation				
	CEC	X	X	X
	SAR and/or %Na	X	X	X
	Particle size and texture class	X	X	
	Exchangable sodium percent (ESP – if necessary)	X	X	X
	Basic soil fertility (N, P, K, Ca, Mg, Na, S, EC)	X	X	X

[1] Diesel-range organics.
[2] Gasoline-range organics.
[3] Benzene, toluene, ethylbenzene, and xylene.
[4] Resource Conservation and Recovery Act.

Sample Type

The two common types of sampling methods are grab and composite sampling. Grab sampling involves the collection of single samples from specific locations at a site. Grab sampling is best for delineating variations in salinity and can be very effective when used in conjunction with an EM survey. Narrow linear sampling of wetlands or stream channels is also well suited for single grab samples because of the potential transport of contaminants downstream from the source of the spill.

Composite samples are generated by combining/collating portions of multiple samples (usually five subsamples) taken from different locations of a target area. This sampling technique is best suited for monitoring larger areas of previously characterized soils or areas containing similar soils or impacts. Generally, only samples that are expected to have the same range of contaminant concentration are composited. For subsurface samples, it is best to form composite samples from samples taken at the same depth profile.

Note: Collection of composite samples can be used to minimize laboratory expense.

Representative control (background) samples should be collected as either grab or composite samples from sites adjacent to the contaminated area that are unaffected by the release. It is best to use the same sampling techniques for characterizing both control and salt-affected soils. EM induction surveying can be used to assist in selecting control sample locations. Controls are used for comparative purposes and should be taken from similar landscape settings or soil types, land uses, etc., to the spill area. Controls are essential for salt characterization in areas where soils may have a natural, background salinity.

Number of Sample Locations

Depending on the complexity of the spill/site, it may be necessary to select a range of samples to characterize the different conditions in the spill area. Fewer samples may be required if an EM induction survey is conducted and used to guide the soil sampling effort. Since different remediation methods may be appropriate for different parts of a large spill, it may be necessary to divide the spill area into areas of low, medium, and high contamination and/or by landscape settings within the contaminated area. If the area is small and uniform, two sets of samples, one near the edge and one near the center or most impacted area, may be adequate to characterize the site. The reader is referred to NDDH's "Guidelines for the Assessment and Cleanup of Saltwater Releases" for additional guidance on sample collection.

Note: Each sampling location should be assigned a unique name, which should be recorded clearly on a diagram of the site, and its position marked using GPS (global positioning system).

Depth of Sampling

Sufficient sampling is necessary to determine the nature and extent of the site impacts. Common practice is to sample the impacted area vertically at 12-inch intervals at each sample location until clean soil is reached. Since it is extremely important to understand the impacts in the upper soil profile from 0 to 12 inches, one might also consider sampling the upper 12 inches of soil at 0–6-inch and 6–12-inch intervals at each of the sample locations. Appendix B presents field screening methods that can be employed to limit the amount of soil samples that must be submitted to an analytical laboratory. Once clean samples have been identified in the soil column using field screening techniques, a sample can be collected from just above and below the field-screened sample and submitted for laboratory analysis.

Sample Containers and Labeling

For salinity analysis, soil samples can be collected in heavy-duty plastic bags and sealed with either a ziplock or twist tie. Most soil-testing laboratories are able to supply soil-sampling bags.

For hydrocarbon analysis, soil samples should be collected in precleaned glass jars with Teflon-lined lids. Again, most laboratories will supply the necessary sample container, preservative material, and labels for the appropriate analytical parameters and matrix as well as chain-of-custody forms. Soil with organic compounds should be stored at 4°C (39°F) or colder, and the laboratory should receive samples within 24 hours of sampling, if possible.

When sampling, the following information should be recorded:

- Project name
- Sample identification number (assigned by the sample plan)
- Date the sample was collected
- Time the sample was collected
- Name or initials of the person collecting the sample
- Sample depth or interval sample was collected from

Other information that will be required by the laboratory includes chain of custody, sample site name, preservative (if used), time of preservation, and any relevant sample site observations. An adequate volume of each sample must be secured to allow for the the analysis of multiple parameters, as recommended in Table 1. The analytical laboratory should be consulted prior to sampling to ensure the required amount of sample is collected to conduct the required analytical tests.

Note: Consider acquiring laboratory-supplied bottle orders when responding to large spills.

Sample Quality Assurance and Quality Control

Quality assurance (QA) is a systematic process for guaranteeing that collected data and decisions based on these data are technically sound, statistically valid, and properly documented. Quality control (QC) procedures are methods used to measure the degree to which QA objectives are met. Appropriate QA/QC measures are based on the data quality requirements of the project, which set the limit for overall uncertainty of results. General QA and QC measures that are employed for subsurface investigation include:

- Use of proven and appropriate methods by trained field and laboratory personnel.

- Care, cleanliness, maintenance, and calibration of field equipment and analytical instruments.

- Documentation of all field and laboratory activities.
- Use of field QC measures, including field blanks and duplicate sample analyses, to detect contamination during handling and transport and analytical precision, respectively. Coordination with analyzing laboratory for preparation of sampling containers, preservation, packaging, shipping, and receipt of samples.

Note: Develop a formal QA/QC plan when responding to larger spills.

Geophysical Survey

A number of geophysical tools can be used to make indirect measurements of salinity. The most commonly used of these are EM induction meters. These meters detect differences in the bulk EC of subsurface materials by generating an EM field that passes through the soil. The response of the EM meter is largely influenced by soil salinity but also, to a lesser extent, by soil temperature, moisture, and texture. Pipelines, overhead wires, other metals, and electrical fields may also interfere with EM results. Electrical resistivity surveys represent another approach to delineate salt-contaminated areas. The surveyed geophysical area should extend well into the surrounding noncontaminated area to adequately characterize both spill and nonspill (control) areas. Data quality may be impacted by infrastructure interference caused by utility lines, steel fences, or other large metallic objects.

In summary, geophysical surveys can be used for the following at a spill site:

- To determine relative differences in EC values throughout the site for initial delineation of soil salinity. If required, site-specific correlation between EM and field and/or laboratory-saturated paste extract EC values can be made to ground-truth the survey results. This technology is especially useful when determining impacts on large sites.
- To determine “hot spots” or areas of highest contaminant concentration.
- To aid in targeting sample locations for the collection of grab or composite soil samples.

This information will support the development and implementation of a cost-effective sampling strategy at a spill site which will characterize the magnitude and variability of the pre- and postspill salt distribution in both soil and groundwater.

RISK ASSESSMENT

Risk assessment is used to determine if site contaminants result in unacceptable impacts to human and/or ecological receptors. It involves identifying the sources of contaminants, potential human and/or ecological receptors, and the exposure pathways whereby the receptors can come into contact with the source contaminants. Figure 6 provides a flowchart that describes a risk assessment framework for a crude oil/brine spill site. As shown in Figure 6, the sources of interest in this manual are hydrocarbon and brine fluids associated with the exploration and production of crude oil (i.e., produced water and crude oil). The exposure pathways include migration of these contaminants on the surface, through the soil, and via leaching to groundwater. The

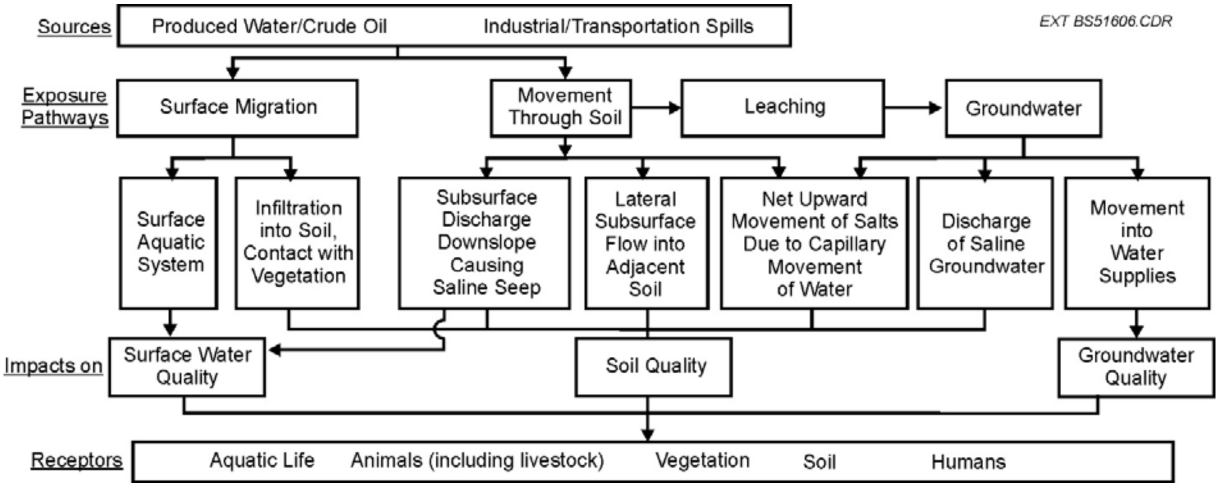


Figure 6. Risk assessment flowchart (modified from Alberta Environment, 2001).

For the purposes of this doument:

Sources discussed are hydrocarbon and brine fluids associated with the exploration and production of crude oil (i.e., produced water and crude oil).

Pathways describe how the source reaches the receptor, which is most often over the land surface and through the soil.

Receptors describe the thing that is impacted by a release. Receptors are most often humans but may include surface water and groundwater, soil and plants, and livestock and native animals.

potential receptors that may come into contact with these contaminants via these exposure pathways are also identified and include humans, animals (domestic and nondomestic), aquatic life, and vegetation. Both soil and groundwater, which are mediums for the transport of the contaminants, also represent receptors in their own right and must be considered as such during the risk assessment.

Risk-Based Corrective Action (RBCA)

The formal application of a risk assessment is typically performed as part of a Risk-Based Corrective Action (RBCA). The RBCA process, created by the American Society of Testing of Materials (ASTM) and adopted by EPA, is a scientific, risk-based decision-making process for making environmental management decisions based on the potential risk to human health and the environment (American Society of Testing of Materials, 2000). Risk-based approaches to site management permit the evaluation and prioritization of site actions based on the actual reduction in risk that would be achieved, resulting in a more optimal allocation of both technical and financial resources.

The RBCA process is a three-tiered process with increasingly sophisticated levels of data collection and risk analysis as one moves from Tier 1 through Tier 3. Figure 7 provides a flowchart illustrating the three tiers of assessment and the critical decision points associated with each tier.

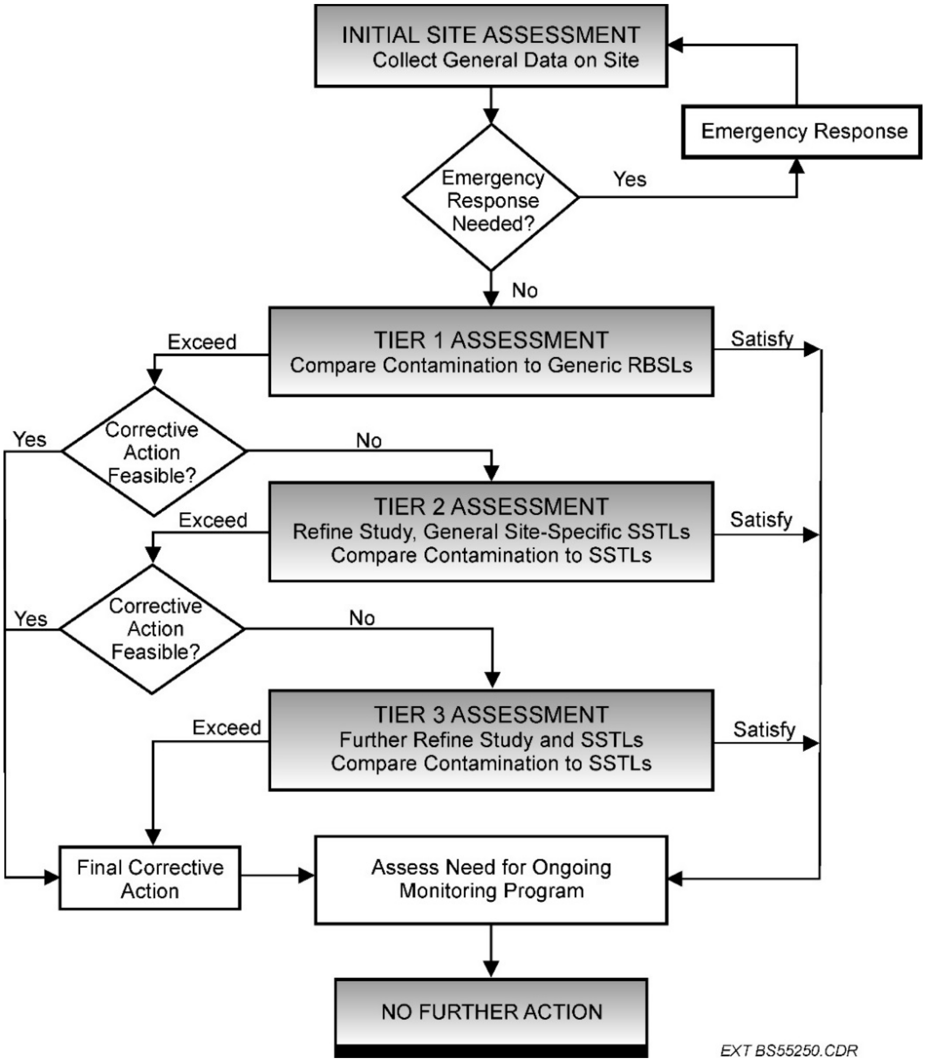


Figure 7. RBCA flowchart illustrating tiers and decision points (modified from McMillen and others, 2001).

The general sequence of steps in the RBCA process, as shown in Figure 7, are discussed in detail in American Petroleum Institute, 2001, and are briefly summarized below:

1. Perform an initial site assessment.

2. Determine if an emergency response is required and, if necessary, implement it and repeat the initial site assessment until no further emergency action is required.

3. Complete a Tier 1 comparison of concentrations of chemical(s) of concern at the site with a set of conservative, generic risk-based screening levels (RBSLs), i.e., a set of predetermined risk-based contaminant concentrations for different exposure pathways and different land uses. Tier 1 RBSLs can be obtained from other related studies or evaluations or by conducting a risk assessment of the site, per Figure 7, using generic, conservative assumptions.

4. Decide whether a second tier of evaluation (i.e., Tier 2) is warranted, i.e., the Tier 1 RBSLs are exceeded; however, at this point, the decision can be made to remediate the site to the Tier 1 RBSLs and forego any further risk-based analysis at the site.

5. If the decision is made not to remediate to Tier 1 RBSLs, collect additional site-specific information, as necessary, and complete a Tier 2 comparison of the concentrations of the chemical(s) of concern at the site with site-specific target levels (SSTLs) determined for specific point(s) of compliance. SSTLs are determined by conducting a site-specific risk assessment per Figure 7 but with fewer generic assumptions and more site-specific details built into the analysis. It is likely that the SSTLs of the Tier 2 analysis will be greater than the Tier 1 RBSLs as the generic assumptions used in the Tier 1 analysis are replaced with more relevant site-specific assumptions or data.

6. Decide whether a third, and final, tier of evaluation is warranted, i.e., the Tier 2 SSTLs are exceeded; however, similar to following the Tier 1 analysis, the decision can be made to remediate the site to the Tier 2 SSTLs and forego any further risk-based analysis at the site.

7. If the decision is made not to remediate to Tier 2 SSTLs, collect additional site-specific information, as necessary, and complete a Tier 3 comparison of the concentrations of the chemical(s) of concern at the site with SSTLs that have been determined using additional site data and more sophisticated risk analysis and/or modeling, again using the risk framework shown in Figure 7.

8. Compare the concentrations of chemical(s) of concern at the determined point(s) of compliance with the Tier 3 SSTLs.

9. If the Tier 3 SSTLs are exceeded, design and implement a corrective action plan to achieve the Tier 3 contaminant concentrations.

10. Following the remediation of the chemicals of concern, regardless of which RBSLs or SSTLs are targeted, assess the need for implementing an ongoing monitoring plan to ensure that the concentrations of the chemicals of concern at the point of compliance have been achieved and remain at acceptable risk-based levels over time.

The RBCA process is designed with several off ramps, at which time the site manager can review the results and recommendations following each tier of analysis, i.e., Tiers 1 and 2, and decide if the cost of conducting the additional site-specific risk analyses of the next tier is warranted. Using this approach, the flexibility exists to forego the detailed risk characterization effort of a site-specific Tier 2 or Tier 3 assessment, both of which have the potential to yield higher clean-up goals than the previous tier of analysis, and to proceed directly to site remediation and closure.

Source of Potential Tier 1 RBSLs for Hydrocarbon and Brine Spills

The RBSLs used as part of the RBCA Tier 1 assessment are not site-specific; rather, they are derived either by 1) drawing from other impact assessments that involve the chemicals of concern but at other spill sites or hypothetical constructs of spill sites or 2) by applying the risk framework of Figure 7 to the site using generic exposure assessment parameters and receptors. To be protective of human health and environment, the Tier 1 RBSLs are usually conservatively low, recognizing that many, if not most of site spill evaluations, will proceed to the site-specific Tier 2 and Tier 3 analyses.

Impacts to the environment from brine and hydrocarbon spills have been studied by a number of governmental agencies, scientific institutions, and trade groups and have shown that cleanup standards depend on land use, soil type, vegetation, and landscape position. These variables significantly influence the migration potential, and hence the risks, to groundwater, surface water, and other receptors. Furthermore, the user should recognize that, when impacts and associated risks of brine and hydrocarbon spills are discussed, each party involved in the discussion will likely have different goals related to remediation direction and success. Regulators and much of the literature available related to risk-based corrective action and cleanup targets for these impacts are focused on protecting waters (both surface water and groundwater) as well as humans, while landowners are primarily motivated by a desire to restore land to prespill conditions. These two perspectives do not always align with each other and can result in very different remediation requirements and costs.

Brine Spill Risk Metrics

Based on a review of studies and regulation related to the remediation of brine spills and releases, there is broad recognition of the complexity of remediating brine-impacted soils and the difficulty in returning the site to productive health. As a means of highlighting some of these works as well as actions recommended or required based on salinity concentrations in the soil, examples are provided in the following paragraphs.

The API in its 2006 Publication 4758, “Strategies for Addressing Salt Impacts of Produced Water Releases to Plants, Soil, and Groundwater,” summarizes brine impacts to the environment as follows:

- Vegetation impacts are likely if the produced water spill alters EC: EC between 4 and 15 mmhos/cm may require cleanup dependent on drainage, climate, and vegetation; EC > 16 mmhos/cm requires cleanup.
- Groundwater impacts are dependent on the volume of the release, chloride concentration, depth to groundwater, soil type, and release footprint.
- Potential groundwater impact varies based on receptors (human health, aquatic life, irrigation, livestock).

Figure 8 provides some rules of thumb associated with the potential impact of brine spills on soil and plants based on API Publication 4758. Specific EC_e and SAR_e thresholds are intended to be rules of thumb only, and the user should determine whether these thresholds are valid as Tier 1 RBSLs for the specific project based on the analytical results from the site assessment.

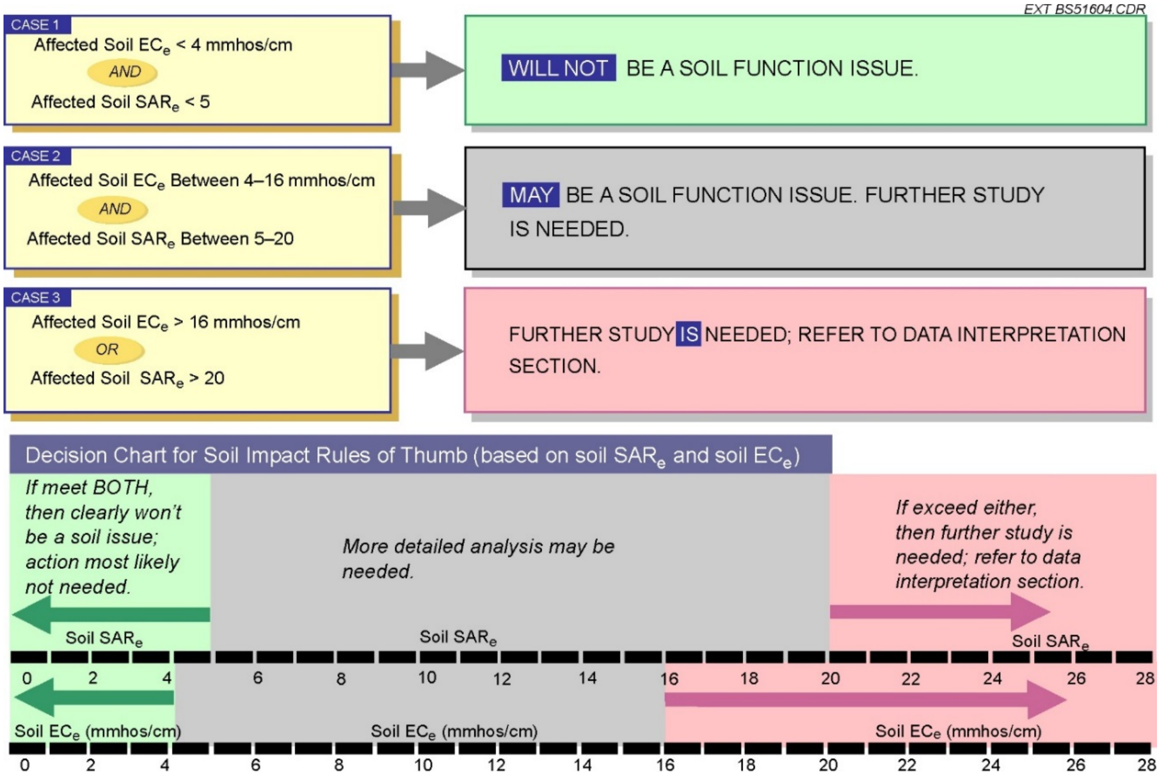


Figure 8. Soil impact rules of thumb (source: American Petroleum Institute Publication 4758, Strategies for Addressing Salt Impacts of Produced Water Releases to Plants, Soil, and Groundwater, 2006 [“reproduction courtesy of the American Petroleum Institute”]).

In addition, other potential Tier 1 RBSLs can be found in the July 2014 “Guardian Guidance for the Assessment and Cleanup of Complex Crude Oil, Condensate, and Other Hydrocarbon Release Sites, Including Historically Impacted Sites” of the Oklahoma Corporation Commission, Pollution Abatement Department, Oil and Gas Conservation Division. This guidance is directed toward the regulation of brine cleanup actions based on the following parameters:

- EC ≤ 4 mmhos/cm and ESP 0–15: no cleanup required.
- EC 6–8 mmhos/cm and ESP 0–15: treatment required only for certain vegetation/crops.
- EC > 8 mmhos/cm and ESP 0–15: treatment required to 3 feet (root zone).
- ESP > 15 mmhos/cm: soil replacement required.

Hydrocarbon Spill Risk Metrics

Many states follow a risk-based approach when addressing hydrocarbon cleanups, including the remediation of crude oil. Studies have illustrated that >10,000 mg/kg total petroleum hydrocarbons (TPH) from crude oil did not adversely impact the growth of most plants nor pose an unacceptable risk due to leaching to groundwater. Based on these results, some states have adopted a TPH clean-up level of 10,000 mg/kg (1% by weight). However, other states used TPH standards as low as 100 mg/kg in soil that are similar to those developed for gasoline leaks at underground storage tank sites for the protection of groundwater (American Petroleum Institute, 2001), even though the fate and transport of crude oil in the environment is significantly different than that of gasoline.

Although a 1% TPH soil concentration threshold may be utilized as a Tier 1 screening level in the RBCA process, it is not necessarily a remediation end point since the risk associated with a TPH concentration in soil can vary dramatically based on the detailed hydrocarbon composition of the TPH. For example, further analyzing the TPH impacts of petroleum in terms of GRO (gasoline range organics), DRO (diesel range organics), or volatile petroleum hydrocarbons and extractable petroleum hydrocarbons provides a better understanding of the chemical composition of the impacts, which has important risk implications. More specifically, because light-end hydrocarbons are more mobile in the environment, they are more likely to migrate from the site and represent a risk to offsite human or ecological receptors compared to the heavier-end hydrocarbons that are far less mobile and less likely to migrate offsite. For this reason, it is important to understand the chemical composition of the TPH at a site to properly assess the risk of those impacts and determine a target concentration for remediation that is protective of both human health and the environment.

Several studies that involve TPH impact on plants and animals have suggested that TPH concentrations in soil in excess of 1% can result in acceptable risks to these receptors:

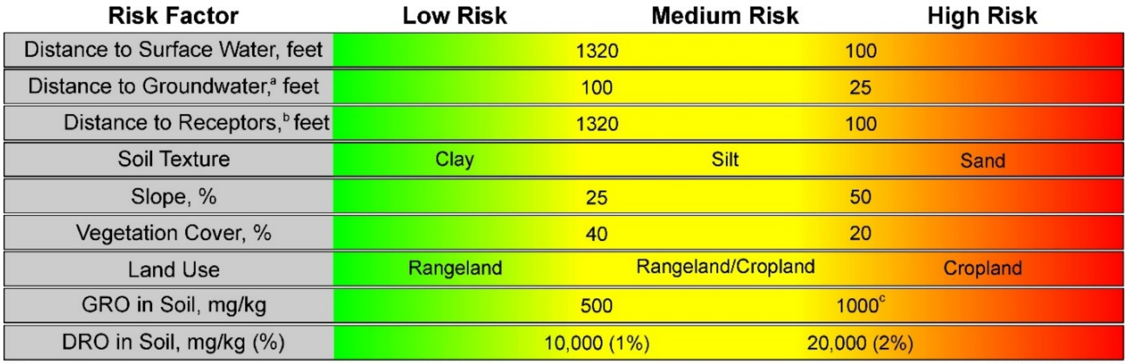
- Hamilton, Sewell, and Deeley in their report “Technical Basis for Current Soil Management Levels of Total Petroleum Hydrocarbons” concluded that if the amount of petroleum hydrocarbons in soil is kept at or below 1%, and there are acceptable salt and pH levels, there should not be significant reductions in plant yield (1999). In addition, the 1% soil TPH guidance value was below the minimum level required for hydrocarbon mobility, thereby preventing movement toward groundwater receptors.

- White and others concluded from their research that vegetation was successfully established at a field site contaminated with 2.5% weathered crude oil. Significant reductions in TPH concentrations were observed in vegetated fertilized plots as compared to nonvegetated plots after 6 months. These reductions were attributed to the presence of significantly higher total bacterial, fungal, and PAH degrader levels in vegetated fertilized plots as compared to the nonvegetated, nonfertilized plots (2001).

- Regarding risk to livestock from petroleum spills, Pattanayek and DeShields in their report “Risk-Based Screening Levels for the Protection of Livestock Exposed to Petroleum Hydrocarbons” concluded that risk-based screening levels for crude oil in soil range from 17,600 to 47,200 mg/kg for livestock typical in the United States (2004). These values were based on two exposure pathways: drinking water ingestion and incidental soil ingestion.

Finally, a review of the risk-based corrective action regulations of several states, including Kansas, Montana, New Mexico, Oklahoma, South Dakota, Texas, Utah, and Wyoming, is provided in Figure 9, which summarizes the risk factors that influence the impact potential of hydrocarbon spills. Users should consider these risk ranges as a point of reference, and site-specific factors may supersede the risk ranges.

Note: On a case-by-case basis, the following risk factors may be used to aid in evaluating and recommending the appropriate remediation approach and possible alternative cleanup standards in agreement with the landowner, operator, and the jurisdictional regulator.



Risk Factor	Low Risk		Medium Risk		High Risk
Distance to Surface Water, feet		1320		100	
Distance to Groundwater,[a] feet		100		25	
Distance to Receptors,[b] feet		1320		100	
Soil Texture	Clay		Silt		Sand
Slope, %		25		50	
Vegetation Cover, %		40		20	
Land Use	Rangeland		Rangeland/Cropland		Cropland
GRO in Soil, mg/kg		500		1000[c]	
DRO in Soil, mg/kg (%)		10,000 (1%)		20,000 (2%)	

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[a] Groundwater in the case is specific to beneficial use groundwater.

[b] Receptors would include water wells, residences, schools, and other occupied buildings.

[c] For GRO analysis results in the high-risk area, a fractionated analysis of GRO to obtain BTEX concentrations is recommended.

Figure 9. Summary of risk factors influencing hydrocarbon spill impact potential.

DATA INTERPRETATION

Figure 10 represents a remedial options decision tree that can be used as a tool to develop remediation strategies for site cleanup. Specific numbers used in the “Basis for Decision” section are to be considered rules of thumb. Users should determine whether these values are valid for their specific project.

REMEDIATION OPTIONS – HYDROCARBON IMPACTS

This section is intended to provide a brief overview of the various remediation options available and when they might be utilized.

In Situ Remediation Option

Natural Attenuation

Natural attenuation is the scientific term for letting the natural systems already in place remediate the spill contaminant. Natural attenuation is only applicable for hydrocarbon spills of relatively low concentration when no sensitive receptors are threatened.

Bioremediation

In situ bioremediation is only effective on hydrocarbons and, therefore, would only be a remediation option if the spill is only hydrocarbons or a mixed release with minimal brine present.

This option involves the use of microorganisms already present in the soil to remediate the impacted soil. Usually this also involves the implementation of specific enhancements to optimize the effectiveness of the natural degradation of the hydrocarbons.

In situ bioremediation is a process where naturally occurring organisms in the soil are allowed to break down the hydrocarbons (primarily in an aerobic environment). The soil is prepared and maintained to promote this process during the remediation phase.

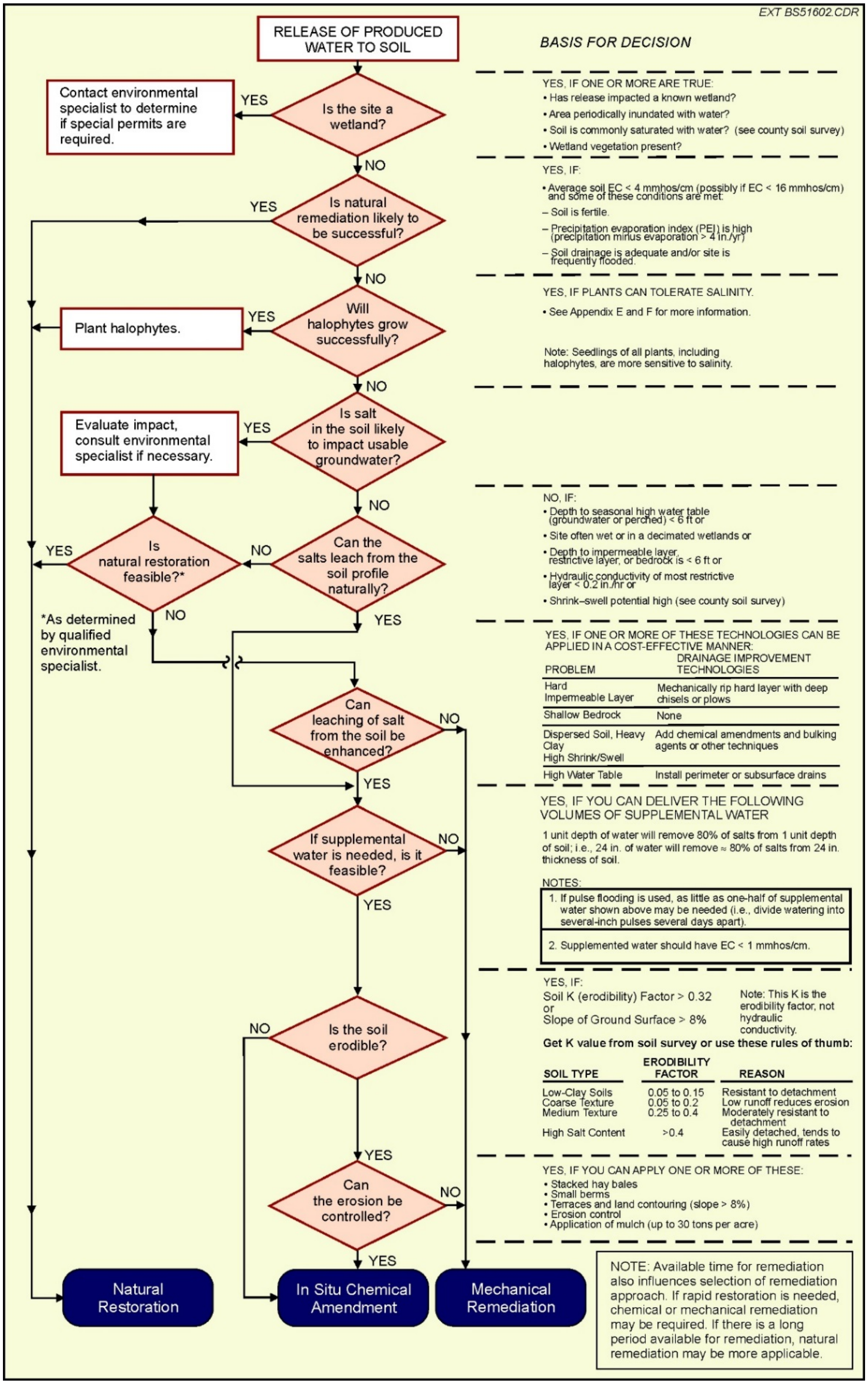

Figure 10. Remedial options decision tree (source: American Petroleum Institute Publication 4758, Strategies for Addressing Salt Impacts of Produced Water Releases to Plants, Soil, and Groundwater, 2006 [“reproduction courtesy of the American Petroleum Institute”]).

The following factors are vital to a successful bioremediation project:

- Contact between the bacteria and the hydrocarbons
- Available nutrients
- Presence of oxygen
- Adequate moisture
- Appropriate pH
- Proper soil temperature

Soil–Hydrocarbon Contact

Contact between the bacteria and the hydrocarbons is achieved by tilling or disking the hydrocarbon-impacted soil (and amendments if needed). In addition, working the spill area also creates a more even vertical distribution of hydrocarbons and nutrients, eliminates any surface crusting, and increases soil pore space for the transport of oxygen from the atmosphere to bacteria and removal of bacterial respiration by-products (e.g., carbon dioxide) from the soil environment which could become toxic for bacteria if aeration removal rates are not adequate.

After initial soil sampling is complete, tillage should be performed to incorporate “clean” soil (if needed) and pH amendments (if needed). A second tillage event should be performed to incorporate nutrients and organic matter. Tillage should then be performed every other week for the first 3 months and monthly thereafter to maintain proper soil aeration because of soil settling over time.

Nutrient Addition

Nutrient requirements will most likely not be sufficient to maximize biodegradation rates in the native soil, and additional nutrients will be required. The primary nutrients required are nitrogen (N), phosphorus (P), and potassium (K). Application of commercial fertilizers is the most effective method for supplementing nutrients. Nitrogen requirements are typically based on suggested carbon (C) to N ratios, and C can be assumed to be 80% of the TPH concentration.

EPA suggests a C:N:P:K ratio of 100:10:1:1 (U.S. Environmental Protection Agency, 1996), while others have suggested it is more appropriate to use a C:N ratio of 150:1 to avoid excess salinity and a corresponding N:P:K ratio of 4:5:1 (Hodges and Simmers, 2006; Sublette, 2014).

Care must be exercised when the application amount of N, P, and K is determined for the site, as the potential of adding salinity exists when commercial fertilizers are introduced (these commercially available nutrients come in the form of salts). Sandy soils and soils with low moisture tend to be susceptible to fertilizer salinity, whereas clays and soils with high organic matter tend to be less susceptible to fertilizer salinity (Sublette, 2014).

If the N requirement exceeds 150 pounds/acre, an operator should consider splitting up the applications and applying the required N in two or three applications performed 30 days apart.

Oxygen

Introduction of oxygen into the bioremediation process is achieved with tillage of the site. Oxygen content does not need to be measured, as properly scheduled tillage should accomplish adequate oxygen transfer.

Moisture

Most in situ bioremediation sites will only rely on natural precipitation for moisture addition. References sourced for preparation of this document indicate that optimal moisture content is 40%–80% (Hodges and Simmers, 2006) or 60%–80% (Sublette, 2014) of the soil's water-holding capacity or field capacity. This is equal to about 12%–30% on a weight basis (U.S. Environmental Protection Agency, 1996).

The use of organic matter can greatly increase the moisture-holding capacity of the soil and help prevent compaction issues. Typical organic amendments used include manure (preferably aged manure), hay, straw, cornstalks, and biosolids.

When used as an organic matter bulking source, fully composted manure is preferred over fresh manure for several reasons but mainly because it tends to be lower in N, P, and K (thereby not affecting fertilizer calculations), contains little salt, and any weed seeds are no longer viable.

pH Adjustment

A soil pH of 6 to 8 is optimal for microbial activity. A soil sample should be taken initially to determine the soil pH, and adjustments should be made by the incorporation of amendments (lime or elemental sulfur) at the time of first tillage. An operator should consult with agricultural experts, soil testing laboratories, or the North Dakota State University (NDSU) Extension Service to determine the appropriate type and quantity to apply.

Soil Temperature

In an in situ bioremediation site, an operator can do little to control soil temperature. Being aware that soil temperature has an impact on microbial performance is the important factor. Microbes are considered to be active when the soil temperatures are between 40° and 90°F (4° and 32°C). With that said, bioremediation projects should be considered active from April through October.

Ex Situ Remediation Options

Excavation and Disposal

Although often not considered a remediation practice, the excavation of impacted soils does remove the contaminant from the environment. This practice is the most aggressive and, in North Dakota, is one of the most common practices for addressing hydrocarbon spills.

The benefits of excavation and disposal include the following:

- Immediate removal of source and impacted soils

- Landowner satisfaction
- Potentially less long-term liability at the spill site

The potential disadvantages of excavation and disposal include the following:

- Cost required to haul and dispose of hydrocarbon-impacted soil at a special waste landfill
- Potential liability of hauling impacted soil from the spill site
- Added expense of fill material, typically uncontaminated topsoil of similar textural class and quality
- The potential introduction of weeds not previously observed at the site prior to the spill

The extent of the excavation is dictated primarily by the cleanup action threshold guidance provided by the regulatory agency. In most cases, soils are excavated to a point where the vertical and horizontal extent of contamination above the action threshold is removed. This would assume that groundwater is not impacted and sensitive receptors are not present, such as groundwater wells, within a distance of concern.

To determine the areal extent of hydrocarbon impacts/excavation limits, a photoionization detector is typically used for surface spills. For brine spills, the extent of impacts is determined by a field EC measurement. In both cases, confirmation samples from the bottom and sides of the excavation would be collected and submitted to an approved laboratory. Appendix B contains field screening methods for collecting hydrocarbon confirmation samples.

The contaminated soils are manifested and transported to an approved special waste landfill for disposal. A current list of special waste landfills can be viewed at the NDDH Web site (www.ndhealth.gov/wm/Publications/SpecialWasteLandfills.pdf).

To replace the excavated material, "clean" subsoil and topsoil of similar mineral textural class and quality should be brought in and placed in the excavation. Care should be taken to place replacement subsoil and then replacement topsoil with minimal mixing of the subsoil and topsoil.

Note: consider working with the property owner when selecting a source for the borrowed material.

Bioremediation/Landfarming

Ex situ bioremediation or landfarming involves the removal of impacted soil and treatment of the soil either at the spill site or at a separate landfarming site. This option would only be applicable for hydrocarbon spills that are not impacted by brine.

Ex situ bioremediation involves the same process as in situ bioremediation except impacted soils to be remediated are excavated and hauled from the spill site and taken to an approved landfarming site. Ex situ bioremediation may also be performed by composting the excavated soil. The primary difference between landfarming and composting is the soils are windrowed and often aerated (and sometimes covered), watered, and fertilized to more aggressively facilitate biological activity.

Ex Situ Thermal Treatment

Ex situ thermal desorption is used to treat light and heavy-end hydrocarbon contamination. The process works by heating soil in a rotating kiln to temperatures between 350°C (low-temperature thermal desorption) to 850°C (high-temperature thermal desorption). The temperature of the desorber is dependent upon what contaminants are being targeted, but the preference (fuel and capital costs) is to use the lower-temperature systems where possible.

Essentially, at elevated temperatures, contaminants that are adsorbed to or within the pores of soils are driven into the vapor phase. The vapors are subsequently drawn through a filter under vacuum prior to being combusted in a thermal oxidizer unit prior to exhaust to atmosphere. Cleaned soils are quenched for cooling and lost moisture added prior to reuse.

There are limitations with thermal desorption, specifically with the type soil. Soil that is too clayey or silty will reduce the process efficiency, as will oversaturated soil. Soil that has a high contaminant load will also need to be carefully considered prior to treatment. However, if the soil can be properly processed/handled through appropriate pretreatment steps, thermal desorption can be an effective treatment method, often resulting in a very high standard of cleanup.

REMEDIATION OPTIONS – BRINE IMPACTS

In Situ Remediation Option

Natural Attenuation

Natural attenuation, with brine-impacted soil, could be an appropriate option if the salt's effects to the soil chemical and physical properties are within the tolerance of the dominant plant species or desired crop (refer to the rule of thumb flowchart [Figure 7] and Appendices E and F for more information). Natural remediation should only be considered after careful review of site-specific conditions.

Occasionally, situations occur where any attempt to enhance remediation may cause greater environmental damage than the brine released. These situations include highly erosive soils or wetland settings where any attempt to bring in equipment may cause significant and/or long-lasting habitat loss. In these situations, the operator may choose to monitor the site to verify that natural remediation is occurring at an acceptable rate and with limited risk to environmental and sensitive receptors.

In Situ Chemical Amendment Remediation

The objective of in situ chemical amendment remediation is to restore the soil's natural chemical and physical properties and decrease the salt concentration in the upper soil profile to a level that no longer impedes plant growth. This technique involves the introduction of calcium-based (Ca^{2+}) chemicals and water that facilitate the remobilization of Na^{+} Cl^{-} so they can be carried by percolating water deeper into the subsoil or to a tile system for removal and disposal (Figure 11). It is imperative that these salts be mobilized to a soil profile depth greater than the potential upward capillary movement of soil water by evaporation and transpiration forces. These forces could potentially transport the removed salts back into the plant rooting zone.

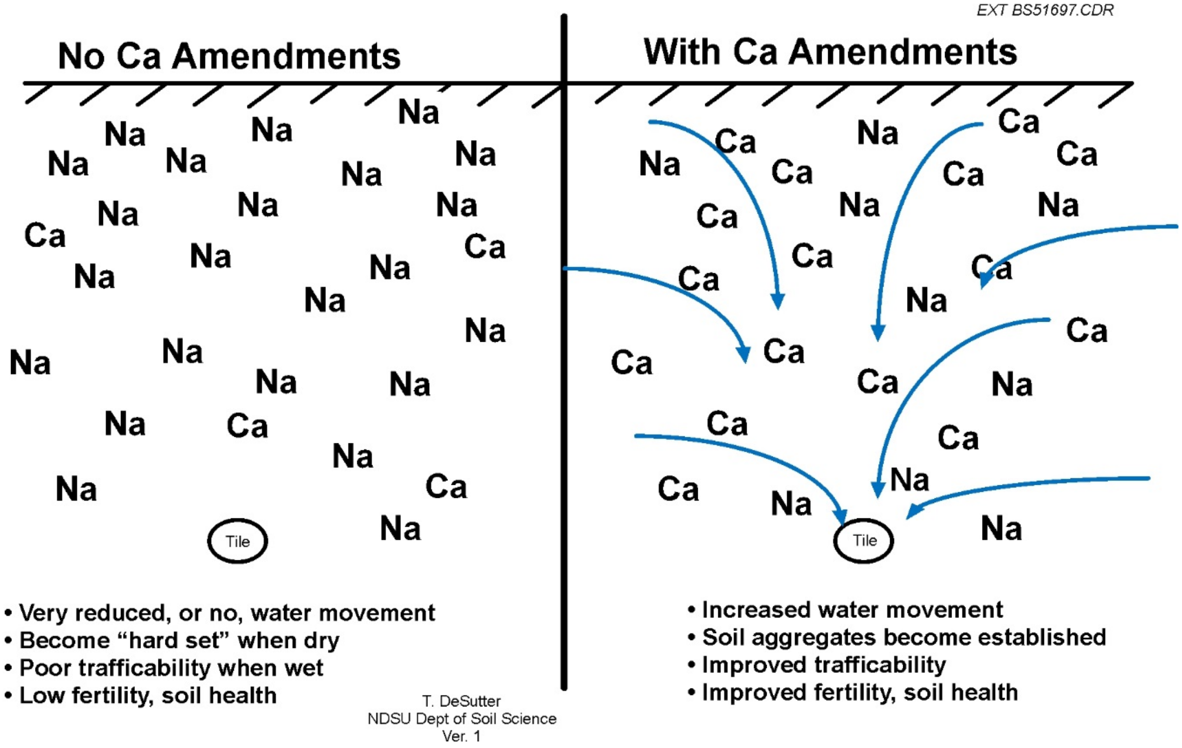

Figure 11. Comparison of soil with and without calcium amendments (Courtesy of North Dakota State University Department of Soil Science).

As discussed in the decision tree (Figure 10), a net downward movement of water and salts is required in order to be successful. These conditions require sufficient precipitation and soil and groundwater conditions to allow sufficient internal soil drainage. If precipitation is limited, application of irrigation and/or improved drainage may be required. The decision tree concentrateson the process of determining when this technique is an appropriate option and on developing the data required to select specific amendments and techniques that increase the probability of success.

Physical replacement of soil cations such as Ca, K, and Mg with Na results in the dispersion and swelling of clays, resulting in the loss of soil aggregation/structure. This physical breakdown reduces aeration, water infiltration, and permeability, leading to surface crusting, runoff, and erosion. As previously stated, the replacement of exchangeable Na ions can be accomplished by increasing the amount of Ca concentration in the soil solution by the addition of a Ca amendment. A variety of chemical amendments can be added to remobilize Na. These include granular gypsum ($CaSO_4$), liquid gypsum, liquid calcium nitrate ($CaNO_3$), calcium chloride ($CaCl_2$), and citric acid with calcium amendments. With the addition of calcium in the soil, the ions of the soil particles are in a dynamic equilibrium with the soil solution. Therefore, a high concentration of Ca in the soil solution will result in Ca replacing Na on the clay exchange sites. This process lowers the SAR and %Na and begins to balance the chemistry of the soil solution, which facilitates the improvement of the soil's physical properties.

On a fresh release, the ionic concentration (EC) of the soil solution should not be allowed to fall below the level at which clay swelling or dispersion (Figure 6) occurs until sufficient calcium has been applied to replace most of the sodium on the soil's exchange sites and lower the SAR to acceptable levels. Swelling and/or dispersion will occur when the SAR or %Na is 5 or greater and the $EC_{1:1}$ is less than 1.5 mmhos/cm. This maintenance of high EC will promote infiltration and soil water movement. The critical level will be site-specific (different types of clay behave differently to Na and EC) but may be estimated by means of a laboratory treatability study. It may take several years and treatments to return an area to its previous productive capacity, especially in areas with high clay content.

Calcium amendments can be added to the soil in dry or liquid form. Liquid calcium amendments are faster acting and have a deeper initial penetration depth. Commercial formulations of liquid calcium are available in concentrated and finely ground forms. Liquid amendments can also be made by dissolving calcium sources in water. The most commonly used dry amendments are gypsum and calcium nitrate, although calcium chloride may be used if adequate drainage is in place and leachate is collected for disposal. Use of calcium amendments may require subsequent irrigation and leachate collection.

The amount of calcium nitrate applied is often limited by concerns about nitrate contamination of groundwater. The amount that should be applied will depend on the potential for movement of nitrates into groundwater. Sites of greater concern are those with high-permeability soils (sandy), shallow groundwater, high rainfall, or applied irrigation water.

It is important to note that in the remediation process it is very important to treat the soil as soon as possible. Rain on the spill site before it has been amended with a calcium-based product will increase the potential for soil dispersion and clogging of soil pores, thus sealing pores and limiting water infiltration/movement.

Phytoremediation

Phytoremediation involves the introduction of specfic halophytic plant species that are capable of surviving (and in some cases thriving) in saline environments. The use of plants to perform remediation is usually most applicable to brine spills. It should be noted that most of the extremely salt tolerant plant species are not typically considered beneficial use plants and, in some cases, are the same plants (weeds) that the agricultural community works very hard to eliminate. Appendixes E and F contain information about halophytic forages and crops as well as their respective salt tolerances.

Electrokinetics

Electrokinetics technology involves the application of direct current (DC) electric fields in conjunction with relatively inexpensive direct-push wells. When soil and groundwater are subject to DC electric fields, the pore water moves toward the cathode via electroosmosis while cations also migrate toward the cathode and anions migrate toward the anode by electromigration. A series of anode and cathode wells placed in the soil can be used to separate and recover chloride (anion) and sodium (cation), respectively, from brine-impacted soil. Figure 12 provides an illustration of this process.

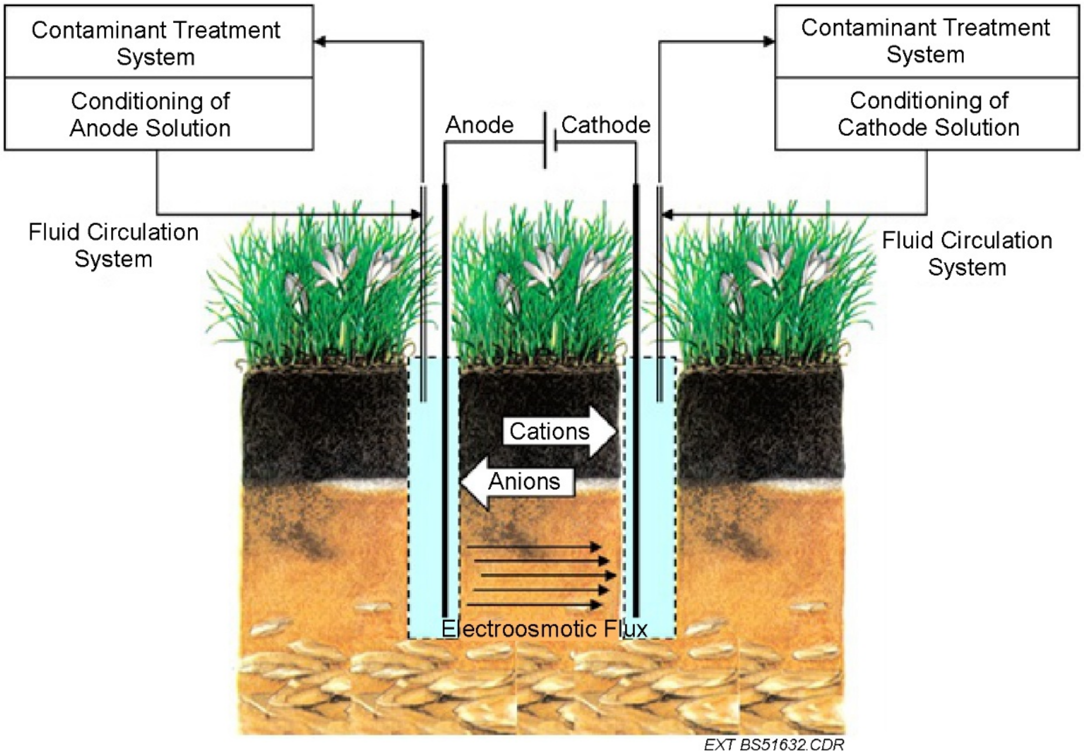

Figure 12. Example of electrokinetic process (Cameselle and others, 2013).

The advantages to this technology include moderate expense and noninvasive passive soil remediation, especially when remediating small, confined, high-value habitats such as wetlands. Disadvantages include time and equipment. Consulting with a technical expert is suggested when exploring this technology.

NDSU Crystallization Inhibitor Technology

NDSU is studying the use of crystallization inhibitors, such as the chemical hexacyanoferrate for use in reclamation of oilfield land impacted by saltwater (Daigh and Klaustermeier, 2016). The crystallization inhibitor is surface-applied as a colloidal suspension with a solvent if the inhibitor's counter ion (e.g., K, Na, Fe, etc.) is not readily soluble in water. During subsequent evaporation of water in soil pores, the salts are transported to the soil surface and then inhibited from crystallizing and forming a cemented salt crust near the soil surface. Instead, soft dendritic salt growths form above the soil surface so that it can be easily removed without physical disturbance to the soil. The salt would then be disposed of or injected into an approved site.

Laboratory research conducted at NDSU showed that application of the ferric hexacyanoferrate, which is mixed with water and ammonia (a solvent), brought 29% to 70% of the salt on high-salt soil to the surface which varies based on the soil texture. One advantage of using crystallization inhibitors such as ferric hexacyanoferrate on salt-impacted soil is that they are available on the market and are nonproprietary. Refer to the open-access publication by Daigh and Klaustermeier (2016) for more details on crystallization inhibitors for use in remediating brine spills.

Ex Situ Remediation Options

Excavation and Disposal

Mechanical remediation may be appropriate when natural remediation and in situ chemical amendment remediation options are not advisable. When dealing with a small release, mechanical remediation could be the least complex and costly option.

Most mechanical remediation options involve the excavation and relocation of the brine-impacted soil to a suitable treatment facility or certified special waste landfill. Following excavation, clean soil is typically brought in to replace the excavated soil. Imported subsoil can be used for deeper excavations, but the uppermost 6 to 12 inches of the excavation is generally replaced with clean and productive topsoil as similar as possible in texture and quality to the impacted soil.

This option is often selected for sites with extremely high salt concentrations or sites that are located near sensitive waters or shallow soils or when treating soil with poor drainage or permeability and where regulatory, lease, or legal considerations favor this option.

Field screening, as presented in Appendix B, could be employed to guide excavation activities to determine when the impacted soil has been removed. Refer to the NDDH's Guidance Document for directions when collecting soil closure sample.

Soil Washing

Soil washing involves the excavation of the impacted soil, putting the soil through a "washing" process to remove the contaminants, and replacing the soil in the original excavation. This process is only applicable to brine-impacted soils. Soil washing may be done at the location. This technology involves chemical remediation with intensive mechanical agitation to speed up the reaction and for better control of the leachate.

In the initial phases of soil washing, freshwater or brackish water may be mixed with the brine-affected soil to decrease salinity if the relationship between EC and SAR is monitored closely to avoid clay dispersion. When EC and SAR relationships begin to approach dispersion (i.e., low EC and high SAR or high %Na), then the salty washwater can be removed for disposal. Additional chemical amendments and freshwater can then be reapplied to further displace sodium from the cation exchange sites. When the sodium has been displaced sufficiently to meet the remediation goal, the soil water containing the displaced sodium and chloride may be removed for disposal. The soil may require fertilization and organic amendments postwashing to replace the nutrient balance following treatment.

In addition to rapid and complete remediation, the advantage of soil washing includes close control of soil chemistry through chemical additions and water. This can result in material cost savings. Disadvantages are the expense that is required for specialized equipment.

POSTREMEDIATION MONITORING AND SITE CLOSURE

Site Monitoring and Maintenance

After reclamation activities are completed, ongoing monitoring is necessary to ensure adequate vegetation establishment: a minimum of two visits a year is suggested, one in mid- to late spring and one in early fall. The spring visit provides a preview of plant emergence and is the first indication of long-term growth. Monitoring during the initial growing season(s) can consist of simple visual observations to ensure that germination has occurred and seedlings are beginning to establish. Any areas of poor seedling emergence should be noted for further evaluation. Inspections should also include checking for noxious weeds, erosion problems, and grazing impacts. Grazing should be excluded from reclaimed sites until they are well established.

Fall and spring visits should also be used to plan weed management efforts. Appropriate herbicides should be spot-applied to prevent the establishment and spread of noxious weeds on the reclaimed area. Note that many broadleaf-selective herbicides can still have impacts on emerging grass seedlings and should be applied with care. Noxious weed management efforts should be conducted a minimum of twice a year, as needed. Noxious weeds, by law, must be controlled by mowing or spraying before they spread or produce seed. If annual weed competition is inhibiting establishment of the desired plant species, annual weeds can be mowed in initial growing seasons. However, it is important that mowing height be (at a minimum) about 6 inches to avoid impacting establishing grasses.

During monitoring, any areas of instability or erosion should be identified. Uncontrolled wind and water erosion can rapidly degrade a reclamation project, destroying the integrity of the land and the quality of water downgradient. If areas of erosion are found, incorporate control measures that slow and divert runoff. Erosion control best management practices include successful stands of vegetation, erosion control fabric, wattles, silt fences, straw bales, and trenches. Wind erosion is more difficult to evaluate than water erosion; however, if best management practices are implemented for water erosion control, wind erosion control is highly likely.

Any persistent bare spots should be tested for remaining salt or hydrocarbons. If they are determined to be impacted, soil amendments or suitable alternative treatments previously discussed should be considered.

After establishment, quantitative vegetation monitoring may be required to demonstrate revegetation success. If vegetation monitoring is performed, the user may want to consider the following guidelines.

Monitoring should be conducted by a qualified professional who is well versed in the native flora, pasture grasses, or crops that are being reestablished on the site. Monitoring should occur at the peak of seasonal growth as determined by a qualified professional.

In addition to monitoring the reclaimed area, a nearby unimpacted area should be monitored at the same time for comparison purposes. Using a reference area instead of a fixed vegetation standard to determine revegetation success allows for annual and seasonal environmental variations (i.e., precipitation) and a direct comparison with a target vegetation community. The reference area should be a nearby existing pasture, native grassland, or crop with similar species composition and soil type. For pasture or cropland, it may be appropriate to seed a nearby similar area at the same time as the reclamation with the same seed mix to use this area for comparison.

Revegetation success standards should be based on the reference area. Depending on the vegetation type (cropland, native grassland, or pasture), various measures of vegetation cover and/or production should be taken. Recommended revegetation success standards are described in Table 2.

Table 2. Suggested Revegetation Success Standards

Revegetation Standard	**Cropland**	**Native Grassland**	**Pasture**
Cover	None	Native perennial vegetation cover greater or equal to 90% of reference for two consecutive growing seasons	Desired* perennial vegetation cover greater or equal to 90% of reference
Production	Yields greater or equal to 90% of reference	Productivity greater or equal to 90% reference for two consecutive growing seasons	Productivity greater or equal to 90% reference

* In pasture areas, introduced perennial grasses may be included as appropriate vegetation cover depending on the specific land use of the area.

Monitoring Methods

Vegetation cover (if appropriate) should be measured using the point intercept method with a minimum of ten points per sample unit (frame or transect). Production should be measured using crop-harvesting techniques or standard plot clipping with a minimum plot size of 0.25 m^2, Table 3.

Samples should be located arbitrarily on the reclaimed and reference areas. Best practices include plotting the sample locations in advance of monitoring using mapping software to eliminate bias.

It is important to collect an adequate number of cover samples to ensure the data are representative of the vegetation on the entire site. Table 4 provides recommended sample sizes and adequacy calculations. Statistically adequate samples should be collected on both the reclaimed and reference areas.

Table 3. Recommended Postremediation Sampling Methods

Sampling Methods	**Cropland**	**Native Grassland**	**Pasture**
Cover	None	Basal or first hit by species + litter + rock + bare Minimum of ten points per sample unit	Basal or first hit by species + litter + rock + bare Minimum of ten points per sample unit
Production	Whole field harvest, representative strips with equipment, or hand harvest	Plot clipping by life-form 0.25-m^2 frames	Whole field harvest, representative strips with equipment, or plot clipping by life-form 0.25-m^2 frames

Table 4. Recommended Postremediation Sample Size and Adequacy Calculations

Sample Size and Adequacy	Cropland	Native Grassland	Pasture	Adequacy Calculation*
Cover	None	Minimum 15 Sample to adequacy on sites larger than 5 acres	Minimum 15 Sample to adequacy on sites larger than 5 acres	$n = \frac{t^2\ pq}{d^2}$ Poisson or binomial distribution $n = \frac{t^2 s^2}{d^2}$ Normal distribution
Production	Minimum 15 if hand harvest is used	Minimum 15	Minimum 15 if plot clipping is used	None

* n = number of samples required.
t = t-distribution value for a given level of confidence.
p = cover percentage.
q = 100 – p.
d = level of accuracy desired for the estimate of the mean.
s = the estimate of the variance from sampling.

Site Closure

After the site is seeded, monitored, and maintained for vegetation success and site stability, the final step in spill remediation is the process of site closure. Site closure documentation shows how effective the remediation efforts are as discussed above in the monitoring methods section. Depending on the impact of the spill, various agencies may be involved in the spill closure process. Landowners should also be consulted as part of the spill closure process.

Stakeholder Consideration

Stakeholder satisfaction is key in determining when site closure is final. Multiple stakeholders should be considered throughout the reclamation and site closure process. Landowners, particularly, should be consulted throughout the entire remediation process and sign off on the site closure whenever possible.

Documentation

Documentation provides written proof of proper reclamation activities. Seed tags should be collected and stored with site files to provide proof that the proper seed mix and quantities have been used. Written inspections should occur during site monitoring and should include dated pictures. The inspections and pictures provide a dated record of site conditions. This is especially important during remediation and reclamation activities to show how the site has improved from the original spill conditions. Any chemicals or herbicides used during reclamation should also be documented, including what was applied, area applied to, and quantities used. A final inspection should occur once the site is fully reclaimed. As part of this final inspection, site conditions should be documented with dated pictures and comments.

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APPENDIX A

FIELD FORMS

SPILL RESPONSE NOTIFICATION FORM (EXAMPLE)

Reporter's Name:_____________________________Reporter's Position:____________________________

INCIDENT DETAILS:

Date of Incident:_______________Approximate Time Incident Occurred:___________________________
Material Discharged:_________________________Estimated Quantity (with units):___________________
Incident Description:____
____
Material Released in Water? If so, estimate quantity (include units):_______________________________
Media Affected: Soil_____ Water_____ Other (list)____
Spill Location:____Nearest City:____________________

IMPACT:

Description of Injuries (quantity/type):____
How many people were evacuated?____
Was there any damage:__________________ (Y/N)? If yes, describe damage including the medium affected and the approximate dollar amount of damage. (Be complete):________________________________
____
____

RESPONSE ACTION:

Actions Taken to Correct, Control, or Mitigate Incident:____
____
____

EXTERNAL NOTIFICATIONS:

Agency:_____________________________Contact Name:___________________Date/Time:___________
Agency:_____________________________Contact Name:___________________Date/Time:___________
Agency:_____________________________Contact Name:___________________Date/Time:___________
Agency:_____________________________Contact Name:___________________Date/Time:___________
Landowner:__________________________Contact Name:___________________Date/Time:___________

(based on severity of the incident, consider calling the following: National Response Center, U.S. EPA, state agencies, local fire department, LEPCs, hospitals, etc.)

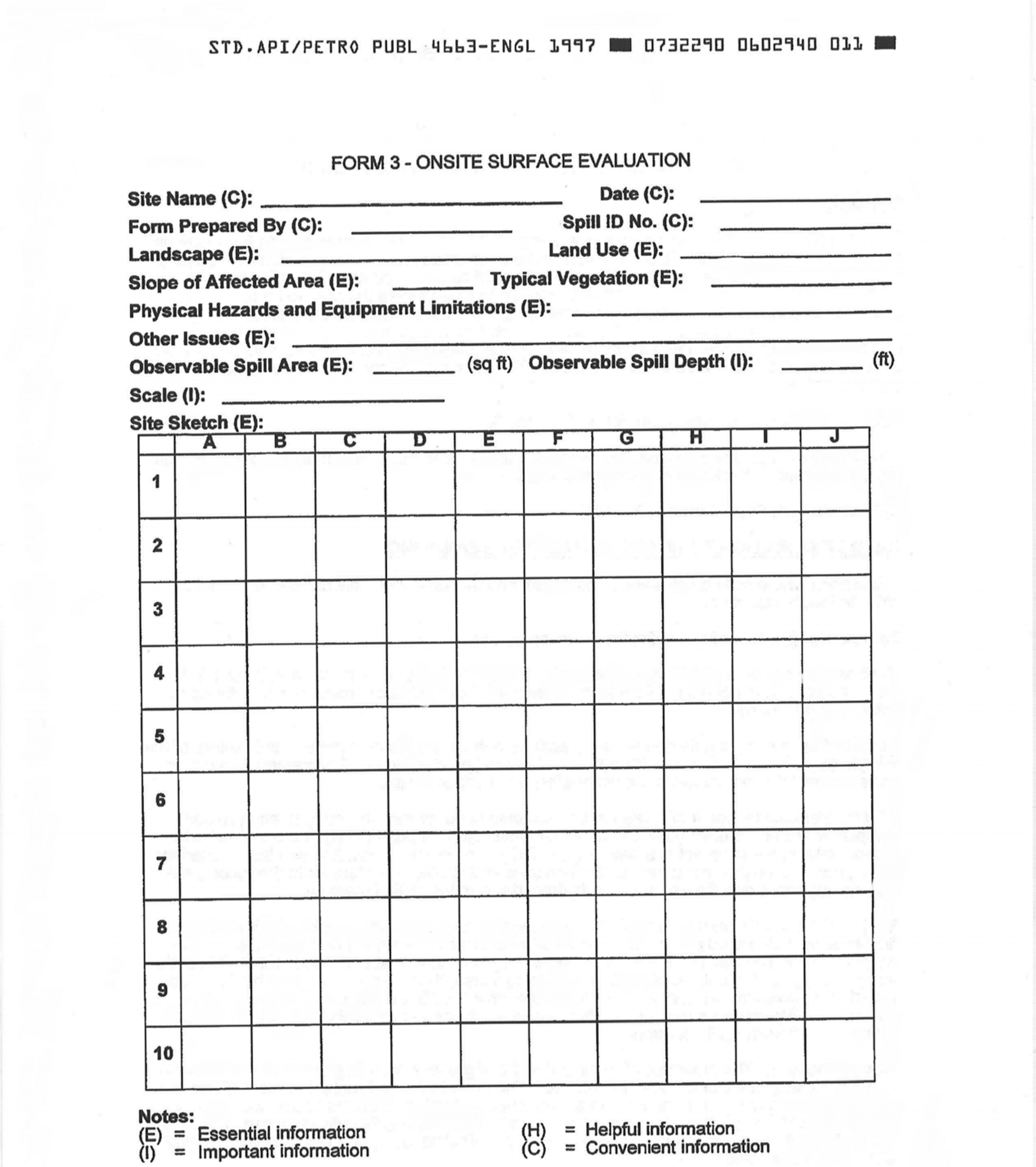
RESPONSE CONTRACTORS:

Company:____________________________Contact Name:___________________Date/Time:___________
Company:____________________________Contact Name:___________________Date/Time:___________
Company:____________________________Contact Name:___________________Date/Time:___________

ADDITIONAL COMMENTS:

____
____
____
____

NOTE: DO NOT DELAY NOTIFICATION (INTERNAL OR EXTERNAL) PENDING COLLECTION OF ALL INFORMATION.



FORM 3 - ONSITE SURFACE EVALUATION

Site Name (C): ______________________ **Date (C):** ______________

Form Prepared By (C): ____________ **Spill ID No. (C):** ____________

Landscape (E): ________________ **Land Use (E):** ______________

Slope of Affected Area (E): ______ **Typical Vegetation (E):** ____________

Physical Hazards and Equipment Limitations (E): ______________________

Other Issues (E): ______________________________________

Observable Spill Area (E): ______ (sq ft) **Observable Spill Depth (I):** ______ (ft)

Scale (I): ________________

Site Sketch (E):

	A	B	C	D	E	F	G	H	I	J
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										

Notes:

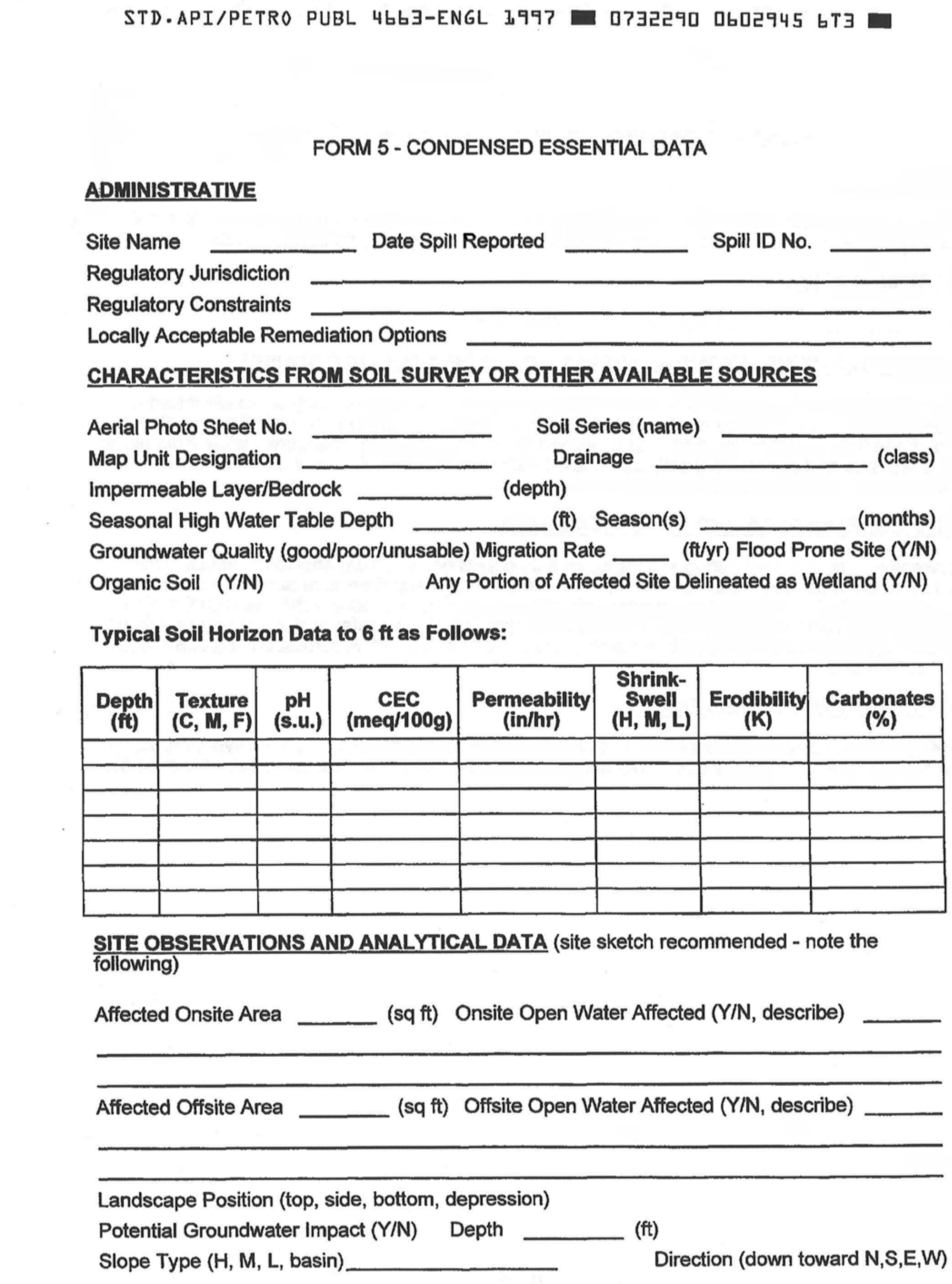
(E) = Essential information

(I) = Important information

(H) = Helpful information

(C) = Convenient information

(source: American Petroleum Institute Publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities, 1997 [“reproduction courtesy of the American Petroleum Institute”])



FORM 5 - CONDENSED ESSENTIAL DATA

ADMINISTRATIVE

Site Name ____________ Date Spill Reported __________ Spill ID No. ________

Regulatory Jurisdiction ____

Regulatory Constraints ____

Locally Acceptable Remediation Options ________________________________

CHARACTERISTICS FROM SOIL SURVEY OR OTHER AVAILABLE SOURCES

Aerial Photo Sheet No. _______________ Soil Series (name) _______________

Map Unit Designation _______________ Drainage __________________ (class)

Impermeable Layer/Bedrock ___________ (depth)

Seasonal High Water Table Depth ___________ (ft) Season(s) ___________ (months)

Groundwater Quality (good/poor/unusable) Migration Rate _____ (ft/yr) Flood Prone Site (Y/N)

Organic Soil (Y/N) Any Portion of Affected Site Delineated as Wetland (Y/N)

Typical Soil Horizon Data to 6 ft as Follows:

Depth (ft)	Texture (C, M, F)	pH (s.u.)	CEC (meq/100g)	Permeability (in/hr)	Shrink-Swell (H, M, L)	Erodibility (K)	Carbonates (%)

SITE OBSERVATIONS AND ANALYTICAL DATA (site sketch recommended - note the following)

Affected Onsite Area _______ (sq ft) Onsite Open Water Affected (Y/N, describe) _______

____

____

Affected Offsite Area ________ (sq ft) Offsite Open Water Affected (Y/N, describe) _______

____

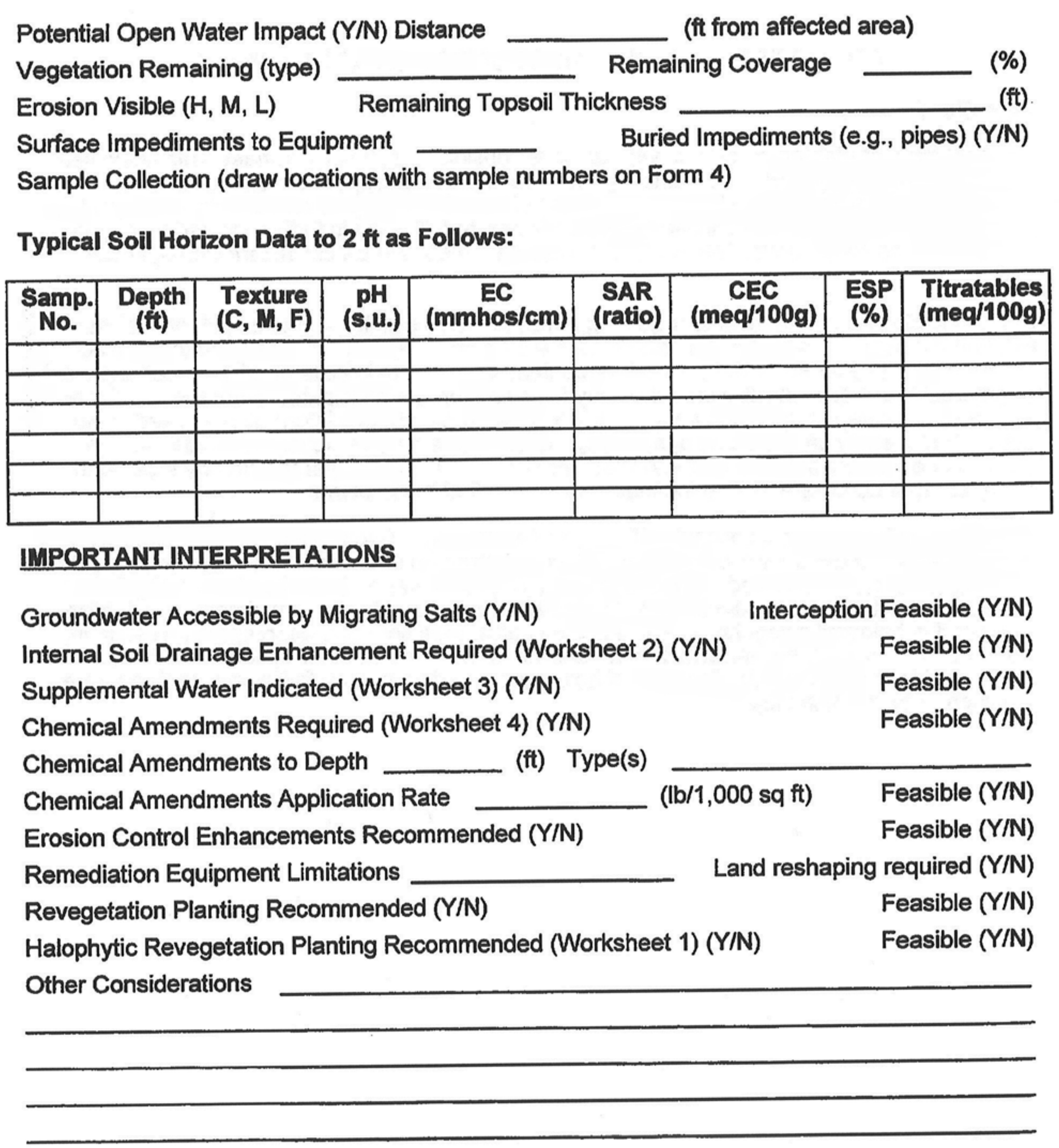
____

Landscape Position (top, side, bottom, depression)

Potential Groundwater Impact (Y/N) Depth _________ (ft)

Slope Type (H, M, L, basin)__________________ Direction (down toward N,S,E,W)

(source: American Petroleum Institute Publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities, 1997 ["reproduction courtesy of the American Petroleum Institute"])



Potential Open Water Impact (Y/N) Distance ____________ (ft from affected area)
Vegetation Remaining (type) __________________ Remaining Coverage ________ (%)
Erosion Visible (H, M, L) Remaining Topsoil Thickness ______________________ (ft)
Surface Impediments to Equipment _________ Buried Impediments (e.g., pipes) (Y/N)
Sample Collection (draw locations with sample numbers on Form 4)

Typical Soil Horizon Data to 2 ft as Follows:

Samp. No.	Depth (ft)	Texture (C, M, F)	pH (s.u.)	EC (mmhos/cm)	SAR (ratio)	CEC (meq/100g)	ESP (%)	Titratables (meq/100g)

IMPORTANT INTERPRETATIONS

Groundwater Accessible by Migrating Salts (Y/N) Interception Feasible (Y/N)
Internal Soil Drainage Enhancement Required (Worksheet 2) (Y/N) Feasible (Y/N)
Supplemental Water Indicated (Worksheet 3) (Y/N) Feasible (Y/N)
Chemical Amendments Required (Worksheet 4) (Y/N) Feasible (Y/N)
Chemical Amendments to Depth _________ (ft) Type(s) ______________________
Chemical Amendments Application Rate _____________ (lb/1,000 sq ft) Feasible (Y/N)
Erosion Control Enhancements Recommended (Y/N) Feasible (Y/N)
Remediation Equipment Limitations ____________________ Land reshaping required (Y/N)
Revegetation Planting Recommended (Y/N) Feasible (Y/N)
Halophytic Revegetation Planting Recommended (Worksheet 1) (Y/N) Feasible (Y/N)
Other Considerations ____
____
____
____
____

(source: American Petroleum Institute Publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities, 1997 ["reproduction courtesy of the American Petroleum Institute"])

PARAMETER: Plant Production

METHOD: meter (0.5m x 2m rectangle)

LOCATION:

EXAMINER:

AREA:

DATE:

TRANSECT NUMBER:			**TRANSECT NUMBER:**		
SPECIES/ LIFE FORM	**WET WEIGHT**	**DRY WEIGHT**	**SPECIES/ LIFE FORM**	**WET WEIGHT**	**DRY WEIGHT**
Cool Perennial Grass			Cool Perennial Grass		
Warm Perennial Grass			Warm Perennial Grass		
Annual Grass			Annual Grass		
Grasslike			Grasslike		
Perennial/Biennial Forb			Perennial/Biennial Forb		
Noxious Weeds			Noxious Weeds		
COMMENTS:			COMMENTS:		

Point Intercept Ground Cover (50 m at 1 m spacing); Shrub Density (50 m x 2 m belt)

Sampling Area:

Date:

Observer:

Sample No.-->	Species Total	Photo:	Secondary Hits	Species Total	Photo:	Secondary Hits
Graminoids						
Forbs						
Woody		Density			Density	
Total Plant Cover						
Rock						
Litter						
Bare Ground						
100%						

NOTES:

REPORT OF:___________________________

Time: _________ AM PM to _________ AM PM _________ Total Hours Mileage: _________ Total Round Trip

To: ____

____

____

Job No.:____________________ Date: _______________

Daily Report No.: ___________Sheet ________of _____

Invoice No.: ______________________________________

Project:

Copies: ______________________________________

____

Field Observer: ___________________________________

Approved By: ____________________________________

INCIDENT BRIEFING (ICS 201)

1. Incident Name:	**2. Incident Number:**	**3. Date/Time Initiated:** Date: Time:

4. Map/Sketch:

5. Situation Summary and Health and Safety Briefing (for briefings or transfer of command)**:** Recognize potential incident Health and Safety Hazards and develop necessary measures (remove hazard, provide personal protective equipment, warn people of the hazard) to protect responders from those hazards.

6. Prepared by: Name: ___________________ Position/Title: __________________Signature: ___________________

ICS 201, Page 1 Date/Time: ____

INCIDENT BRIEFING (ICS 201)

1. Incident Name:

2. Incident Number:

3. Date/Time Initiated:
Date: Time:

7. Current and Planned Objectives:

8. Current and Planned Actions, Strategies, and Tactics:

Time:	Actions:

6. Prepared by: Name: ____________________ Position/Title: ____________________ Signature: ____________________

ICS 201, Page 2

Date/Time: ____

INCIDENT BRIEFING (ICS 201)

1. Incident Name:

Sample ID	EC (mmhos/cm)	Chloride (ppm)	Notes (location/assignment/status)

APPENDIX B

FIELD SCREENING METHODS

FIELD SCREENING METHODS

SPECIFIC CONDUCTIVITY AND CHLORIDE CONCENTRATION FIELD TEST

Materials Needed:
Distilled water
Scale
Plastic soil tray for scale
Shaker bottle
Shot glass
Liquid measuring cup (mL)
Filters
Funnel
Conductivity meter
Chloride Quantab titration strips
Data sheets

Method:
Step 1: Gather supplies.

Step 2: Decontaminate items, wash out any residual material with potable water, and rinse with distilled water. Remove any excess distilled water by snap shaking. DO NOT USE TOWELS TO DRY.

Step 3: Calibrate electrical conductivity (EC) meter with appropriate calibration solution range that you expect to encounter in the field. If EC readings occur outside the range of the calibration solution, rerun the calibration to the appropriate calibration solution.

Step 4: Thoroughly homogenize field sample making sure the sample is not separated into chunks.

Step 5: Turn on scale, set plastic soil tray on scale, reset to zero, measure 25 g of soil, and add to shaker bottle.

Step 6: Measure 100 mL of distilled water, and add to shaker bottle for a 1:5 dilution. Record the dilution factor. A 1:1 dilution factor can also be used and may be more representative of a saturated paste extract conducted in the laboratory.

Step 7: Mix by shaking bottle for 60 seconds, until the sample is sufficiently liquefied. Heavy clay soils will not generally mix in 60 seconds, and you may have to stir with a porcelain spatula to break up the clods.

Step 8: Set funnel with filter on shot glass, and pour liquefied mixture into the funnel so it will drain through the funnel into the glass.

Step 9: Once drained, remove funnel, measure and record conductivity of the sample using the conductivity meter. Multiply the recorded value by five to compensate for the 5:1 dilution. Record dilution factor and the EC value in either µS/cm or mS/cm.

Steps 9 and 10: Place a Quantab in the shot glass, and wait for the yellow band near top to turn black. It should be noted that where the tip of the white chloride peak falls on the numbered Quantab scale, this represents the Quantab unit value. Refer to the table on the back of the Quantab bottle, and multiply the recorded value by five to compensate for the 5:1 dilution.

Step 11: Quantab test strip scales are available in low range (30 to 600 mg/L) and high range (300 to 6000 mg/L). If the low-range scale is exceeded, either perform a carefully measured dilution with distilled water of 5:1 or 10:1 (distilled water:aliquot) or use the high-range tab. Record the dilution factor.

Step 12: Record this value as the sample chloride concentration as mg/L.

Step 13: Decontaminate all equipment used by method explained in Step 2.

HEATED HEADSPACE

Two commonly used field instruments for detecting organic vapors at petroleum sites are photoionization detectors (PIDs) and flame ionization detectors (FIDs).

Heated headspace organic vapor monitoring involves the measurement of volatile organics emitted from soil samples in a sealed container. The container is typically warmed and then tested for volatile organic vapors using photo- or flame-ionization techniques. The results generated by this method are qualitative to semiquantitative and are limited to compounds that readily volatilize.

Conduct headspace analysis in glass jars or resealable polyethylene bags. If using resealable polyethylene bags, a blank sample should be tested prior to field screening to account for potential interferences caused by the bags themselves. In addition, the presence of moisture may interfere with instrument readings. Results should be presented in the report.

The following heated headspace field screening procedure must be used:

- Calibrate PID and FID field instruments according to the manufacturer's specifications and requirements.
- Partially fill (one-third to one-half) a glass jar or resealable polyethylene bag with the sample to be analyzed. Total capacity of the jar or bag may not be less than eight ounces (approximately 250 mL), but the container should not be so large as to allow vapor diffusion and stratification effects to significantly affect the sample.
- If the sample is collected from a split-spoon, transfer it to the jar or resealable polyethylene bag for headspace analysis immediately after opening the split-spoon.
- Collect the sample from freshly uncovered soil if is collected from an excavation or soil stockpile.
- If a jar is used, quickly cover the top with clean aluminum foil or a jar lid. Use screw tops, strong rubber bands, or other methods that will tightly seal the jar. If a resealable polyethylene bag is used, it must be quickly sealed shut.
- From the time of collection, allow headspace vapors to develop in the container for at least 10 minutes but no longer than 1 hour.
    - Shake or agitate containers for 15 seconds at the beginning and end of the headspace development period to assist volatilization. Temperatures of the headspace must be warmed to at least 40°F (approximately 5°C).
- After headspace development, insert the instrument sampling probe to a point about one-half the headspace depth. The container opening must be minimized, and care must be taken to avoid uptake of water droplets and soil particulates.

- After probe insertion, record the highest meter reading. This normally will occur between 2 and 5 seconds after probe insertion.

- Complete headspace field screening within 1 hour from the time of sample collection.

- Document all field screening results in the field record or log book.

Department of Environmental Protection
Bureau of Remediation & Waste Management
RCRA Program
Standard Operating Procedure Change Record

Title: FIELD SCREENING OF SOIL SAMPLES UTILIZING PHOTOIONIZATION AND FLAME-IONIZATION DETECTORS

Identification #: **RWM-DR 011**

SOP Originator: Brian Beneski

Author	Revision Number	Description of Change	Date
Deb Stahler	RCRA 01	Substitute MEDEP/RCRA in the place of MEDEP/DR, and Division of Oil and Hazardous Waste Facilities Regulation in the place of Division of Remediation. Section 2.0: Change first sentence to "MEDEP/RCRA is responsible for the investigation and subsequent corrective actions for RCRA facilities throughout Maine." Section 7.0 Procedure: Include the updated PID/FID calibration set-points guidance. For key project decisions and site closure, use all procedures listed in Appendix Q of Chapter 691 as attached. Section 8.0 Additional Considerations with Use of PID/FID: Add sentence "When using the PID/FID to determine clean-up standards for petroleum use the attached set-points." Section 10.0 Documentation: All sampling events must be documented in a field notebook or field note forms. Chain of custody forms must be completed, and a completed, signed copy retained in the project file.	8/1/2009
	RCRA 02	New Set Points	8/19/04
	RCRA 03	New Set Points	9/13/06
	RCRA 04	New Set Points	11/24/08

Approved by:

Scott Whittier, RCRA Program Manager Date:

Appendix Q: Field Determination of Soil Hydrocarbon Content by Jar/Poly Bag Headspace Technique

1. **Introduction.** The following is a procedure acceptable to the commissioner for determination of the hydrocarbon content of soils contaminated only by oil and petroleum products. A soil sample is placed in a sealed jar or polyethylene bag, and the volatile hydrocarbons are allowed to come to equilibrium with the jar headspace. The headspace hydrocarbon concentration is then measured with a calibrated photo- or flame-ionization (PID or FID) instrument approved by the commissioner.

2. **Applicability.** This procedure is intended for estimating gasoline, No. 2 heating oil, diesel fuel, kerosene, and other chemically and physically similar oil contamination in mineral soils, having water contents between bone-dry and saturation. The procedure is not intended for estimating concentrations of heavy oils, lubricating oils, waste oil, and other low volatility hydrocarbon products. Soil grain size distribution and organic carbon content may affect the partitioning of hydrocarbon between soil, liquid, and vapor phases. Weathering of the hydrocarbon product also will decrease the proportion of volatile and soluble constituents, thereby decreasing instrument response. None of these limitations invalidate the method as a technique for approximation of low-level petroleum hydrocarbon concentrations.

3. **Equipment Required.**

   A. Shovel; trowel.

   B. Lab containers (VOA or SVOA) of type and quantity for hydrocarbon to be sampled at expected concentrations.

NOTE: laboratory should be consulted in advance to determine its needs.

   C. Metal dial-type thermometer, –10° to 50°C.

   D. (Jar headspace method only) Glass, wide-mouthed, metal screw-top, 16-oz jars, with cardboard lid liner removed, and ¼-inch hole drilled through center of lid.

   E. (Jar headspace method only) Roll of heavy-duty aluminum foil.

   F. (Poly bag method only) 1-quart, ziplock-type polyethylene bags.

   G. Means of measuring 250-g soil sample, plus or minus 10 g (e.g., a “calibrated” container, a “Weight Watchers” spring balance).

   H. Photoionization (PID) or flame ionization (FID) instrument approved by the commissioner.

NOTE: A list of approved instruments and their calibration set points is available from the commissioner. The department also has developed a protocol whereby manufacturers of other instruments may generate calibration data for commissioner evaluation and approval. Copies are available from the Bureau of Remediation and Waste Management.

I. Calibration equipment for instrument chosen.

J. Decontamination equipment including soapy water and clean distilled water in squirt bottles or pressurized canisters.

4. Analytical Procedure.

A. Determine the location at which the sample is to be taken. If possible, identify an uncontaminated location at the same site from which soil of similar texture and moisture content can be obtained, to serve as a field "blank."

B. Measure a 250-g sample of the soil into a wide-mouthed jar or polyethylene bag. In so far possible, samples should be mineral soil free of vegetation and stones larger than ½ inch in diameter. Seal the samples immediately in the jars by placing a square of foil over the mouth and screwing on the lid and the bag by zipping the closure. Sufficient air should be left in the bag so that the instrument can withdraw an adequate headspace sample.

C. Repeat this procedure for three (3) more samples, all gathered within a 2-ft × 2-ft area.

D. Shake the jars for 30 seconds to thoroughly mix the contents. If bags are used, they may be kneaded until the contents are uniform.

E. Measure the samples' temperature by sacrificing one jar or bag. If necessary, adjust all sample temperatures to between 15° and 25°C by bringing sample containers into a warm vehicle or immersing in a water bath. In warm weather, samples should be kept in a shaded, ventilated area during headspace development and analysis.

F. Allow at least 15 minutes but not more than 1 hour for soil hydrocarbons to reach equilibrium with the headspace.

G. If samples are to be taken for laboratory analysis, they should be collected and preserved per laboratory protocols at this time. Preferably, these samples should bracket a wide range of hydrocarbon concentrations, including the highest and lowest concentration at the site.

H. Warm up and calibrate the PID or FID instrument to be used to the calibration set point determined by the commissioner for the make of instrument in use and the product(s) present at the facility.

NOTES: 1. These calibration set points have been established by testing the instruments against weathered petroleum headspace surrogates. Therefore, no conversion of the readings to their benzene equivalent is necessary.

2. The UV source in PID instruments should be cleaned at least weekly per the manufacturer's recommended procedure. Both PID and FID instruments must be recalibrated after 4 hours of continuous use, as well as at the beginning of field use, since their calibration may drift with battery condition.

I. Shake the jars or knead the bags again for thirty (30) seconds.

J. Measure the samples' headspace concentration. If the jar headspace technique is used, break the foil seal through the drilled hole in the jar lid using a pencil or nail. Insert the instrument's probe about ½ inch into the jar. If using the poly-bag technique, insert the probe through the bag opening while squeezing the bag tight around the probe. Record the highest reading that remains steady for 1 to 2 seconds (i.e., that is not due to instrument needle inertia). Repeat this step until all jars have been measured.

NOTE: Both PID and FID instruments withdraw a headspace sample from the jar. In the jar headspace technique, air replaces this sample, diluting the headspace as it is being measured. In the poly bag technique, the bag collapses as its headspace is used by the instrument. In either case, it is important to obtain an instrument reading immediately after the seal is broken – preferably within 10 seconds. Once a jar or bag has been used, it may not be used again, even if sufficient time is allowed to reestablish headspace equilibrium.

K. Repeat all steps at each other location of interest at the site. Finally, repeat all steps for the "field blank" obtained from the uncontaminated location.

L. Average the three readings obtained from each soil sample within each 2-ft × 2-ft area. Blank results must be reported but must not be used to adjust the readings obtained on other samples.

NOTE: Because calibration set points have been established by testing the instruments against weathered petroleum headspace surrogates, no conversion of the readings to their benzene equivalent is necessary.

CALIBRATION SET POINTS
November 2008 Update

DATE: November 24, 2008

TO: All Persons Performing Site Assessments Pursuant To "Regulations for Registration, Installation, Operation & Closure of Underground Oil Storage Facilities (Appendix P of CMR, Chapter 691)"

FROM: George Seel, Director Division of Technical Services, Bureau of Remediation & Waste Management

SUBJ: Calibration Set Points For Photoionization- (PID) and Flame Ionization- (FID) Detectors Used in Field Headspace Determinations at Maine Petroleum Remediation Sites

****

The following table gives the set points for various PIDs and FIDs when calibrated with manufacturer-recommended span gas. The listed set points were determined for each make and model of PID using the lamp normally supplied by the manufacturer for petroleum investigations, usually in the 10.2 – 10.6 eV range. The set points are not valid for lamps of other energies.

Please note that the set points previously established for several instruments have changed (new or changed values are shown in red). This was necessary due to a recent change in the test gas formulation. Set points are intended only to normalize response of various PID and FID models to complex petroleum mixtures, not to evaluate the cleanup level achieved at most sites. DEP's guidance for determining cleanup standards, *DEP Procedural Guidance For Establishing Standards For The Remediation Of Oil-Contaminated Soil And Groundwater In Maine* ("Decision Tree") requires laboratory analysis of soil or groundwater for the closure of any Stringent (ST) or Intermediate (IN) site. These changes, therefore, should seldom affect the extent of a remediation or produce outcomes inconsistent with past practices.

Only the makes and models of instrument listed below may be used in Maine site assessments pursuant to Chapter 691 closure requirements. The notification level using instruments adjusted to these set points is 100 ppm for motor vehicle fuels, aviation fuel, marine diesel fuel, and middle distillate heating products. The headspace method is not appropriate and should not be used for evaluating heavy oil or waste oil sites.

Instruments calibrated to the listed set points **may** be used to determine compliance with the cleanup standards at Baseline (BL) sites, where a petroleum discharge poses minimal risk to human and ecological health or environmental resources.

Instruments may be made to read directly by entering the appropriate set point when the calibration routine requests the span gas concentration. Alternatively, the instrument may be calibrated to the actual span gas concentration and its readings later multiplied by the set point divided by 100. Concentrations obtained by either method should not be corrected to "benzene equivalents," as suggested by some instrument manufacturers.

This list is periodically updated as set points are established for additional instruments. For the most current listing, please contact the Division of Technical Services, Bureau of Remediation & Waste Management (BRWM) at (207) 287-2651.

Photoionization Instruments (PIDs)

Make	Model	Gasoline Set Point	Fuel Oil Set Point
GasAlert	Micro 5 PID	260	385
Hnu Systems	HNu 101 Series	320	400
	HNu 102 Series	210	290
Ion Science	PhoCheck Series	140	130
MSA	Photon Gas Detector	225	225
	Passport PID II OVM	200	220
	Sirius Multigas Detector	285	385
Photovac	MicroTIP Series	225	225
	2020 ProPLUS	120	130
RAE Systems	MiniRAE 2000	130	140
	MiniRAE 3000	220	260
Thermo Environmental	OVM 580 Series	210	240
Foxboro	TVA-1000 (PID mode)	210	250

Flame Ionization Instruments (FIDs)

Make	Model	Gasoline Set Point	Fuel Oil Set Point
Photovac	MicroFID	100	90
Thermo Environmental	OVM 680	80	45
Foxboro	TVA-1000 (FID mode)	100	90

COVERSHEET
STANDARD OPERATING PROCEDURE

OPERATION TITLE: **FIELD SCREENING OF SOIL SAMPLES UTILIZING PHOTOIONIZATION AND FLAME-IONIZATION DETECTORS**

Originator: **Brian Beneski**
Quality Assurance Coordinator
Division of Remediation
Bureau of Remediation and Waste Management

Standard Operating Procedure: *DR#011*

REVISION: **02**
DATE: **March 16, 2009**
Written/Revised by: **Nick Hodgkins**
Reviewed by: **Troy Smith**

Five Year Review No Changes Needed:

Print Name: Signature: Date:

Print Name: Signature: Date:

Print Name: Signature: Date:

Print Name: Signature: Date:

1.0 PURPOSE

The purpose of this document is to describe the Maine Department of Environmental Protection, Bureau of Remediation and Waste Management, Division of Remediation’s (MEDEP/DR) procedure for field screening volatile organic content of soils using a closed container and a photoionization detector (PID) or a flame ionization detector (FID).

2.0 APPLICABILITY

MEDEP/DR is responsible for the investigation and remediation of uncontrolled hazardous substance sites throughout Maine. The procedure described herein will provide a screening tool for determining relative levels of volatile organic compounds (VOCs) present in soil with a field PID or FID instrument.

3.0 RESPONSIBILITES

This procedure applies to all staff in the MEDEP/DR who are involved with performing field activities in the investigation of uncontrolled hazardous substance sites. Generally, it is the field personnel of MEDEP/DR and MEDEP/Technical Services (MEDEP/TS) (the Oil and Hazardous Materials Specialist and Geologist positions) who will be responsible for performing this task. Project managers of MEDEP/DR can assist and/or perform this task with field personnel present, or after receiving specific training in this activity.

All managers and supervisors are responsible for ensuring that staff who are responsible for performing this procedure understand and adhere to it for all events.

4.0 INTRODUCTION

In conducting this procedure, a soil sample is placed in an approved container and the volatile constituents are allowed to come to equilibrium. The headspace is then measured with a calibrated PID or FID, with a result expressed in parts per million (ppm). Due to the different ionization potentials of various compounds, actual levels of contamination cannot be determined. However, this technique provides an effective means of screening soil to determine “hot spots”, extent of contamination, and as a means of screening samples for submittal for laboratory analysis.

This methodology is not a substitute for actual laboratory analysis; it is a screening tool in the field for determining “hot spots” and other areas of high or low concentrations of VOCs present in soil, or for when choosing samples from a site to submit for laboratory analysis.

5.0 PLANNING

As with any sampling event, a sampling and analysis plan (SAP) and a health and safety plan (HASP) must be developed. Protocol for the development of a Sampling and Analysis Plan can be found in DSR’s SOP #014 – Development of a Sampling and Analysis Plan.

6.0 EQUIPMENT

The following equipment is required for conducting the procedure:

- Soil sampling equipment (shovel, bucket auger, soil borer)
- Approved containers (one quart freezer zip lock bags are most commonly used, see section 6.1)
- A PID or FID
- Calibration equipment, including user's manual, for particular PID or FID to be used.

6.1 SPECIAL CONSIDERATIONS REGARDING CONTAINERS

Currently, the most commonly used (and recommended) containers are one quart sized polyethylene zip lock freezer bags (various manufacturers make these types of bags). Freezer bags are recommended as they are usually constructed from thicker material, and have better quality zip locks. Also used are wide mouthed, metal screw top 16 oz jars, with a ¼ inch hole drilled through center, with foil over the top to provide the seal.

7.0 PROCEDURE

1) Collect the soil sample, as outlined in the site specific Sampling and Analysis Plan (SAP) (See SOP DR#014 - Development of a Sampling and Analysis Plan) with appropriate soil sampling equipment.

2) Place approximately 250 grams of the soil sample into a approved container as stated in the SAP. The same type of container should be consistently used at the site for comparison purposes; do not mix or reuse headspace containers (unless the approved container is reusable and cleaned appropriately between uses). In so far as possible, samples should be mineral soil free of vegetation and stones larger than ½ inches in diameter. If soil samples are of different type (loam, sand, silt), this should be identified in the field log book. If a duplicate sample is to be submitted to the laboratory for analysis, this sample should be containerized and preserved as appropriate **immediately**. Soil that has been screened with this procedure should not be submitted for laboratory analysis, unless so documented. If using jars, the jars should be sealed now by placing a square of foil over the mouth and screwing on the lid. If using a bag, the bag should be zipped closed leaving sufficient air in the bag so that the instrument can withdraw an adequate headspace sample.

3) Shake the container for 30 seconds to thoroughly mix the contents. If bags are used, they may be kneaded until the contents are uniform.

4) Let Sample equilibrate. Allow at least fifteen minutes but not more than two hours for VOCs to reach headspace equilibrium with the headspace. An attempt should be made to allow the same amount of equilibration time for each sample.

5) Warm up and calibrate the PID and FID instrument to be used according to the manufacturers recommended procedure (See Section 8 - Additional Considerations With Use of PID/FID). The PID and/or FID should be ready for use prior to collection of the first sample.

6) Shake containers/knead bags again for thirty seconds.

7) Measure and record the samples headspace concentration with the instrument. Collect a sample of the headspace by inserting the PID/FID probe into the appropriate opening for the container you are using. Record the highest reading on the instrument after allowing the probe to “sniff” the container for 10 – 15 seconds. It is important to obtain insert the probe as quickly as possible after the seal to the container has been broken. Documentation of headspace results should be outlined in the SAP.

8.0 ADDITIONAL CONSIDERATIONS WITH USE OF A PID/FID

Use of a PID/FID can be found in SOP DR#019 – Protocol for Use of a PID/FID.

There are limitations of PIDs and FIDs. A PID or FID cannot detect all VOCs, nor do they detect all VOCs equally. Factors that influence the response of the particular compound include ionization potential of compound, particular energy rating of lamp, calibration standard used, response factor, response curve, etc. In some instances, such as when the contaminant of concern is a single known compound, it is possible to calibrate the instrument so that a relatively accurate measurement, when compared to laboratory analysis, can be obtained. Because of this, it is recommended that the operator of the particular instrument that will be conducting this procedure take the time before the sampling event to familiarize themselves with the particular instrument that will be used, if they are not already familiar with that instrument. This includes reviewing the specific user manual, and calibration and practice with the instrument prior to the sampling event.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

Data quality objectives (DQOs) should be stated in the SAP (See SOP DR#014). QA/QC samples may be collected if needed to meet your data quality objectives. The following are typical QA/QC samples or tasks conducted for PID/FID field screening. Additional sampling or tasks may be added based on the DQO requirements of the project.

9.1 RECALIBRATION DURING USE

During the course of the work day, the PID/FID should be recalibrated after all long work stoppages (such as lunch break). Additionally, the TVA’s response should be periodically tested by challenging it with calibration gas. If the TVA does not read within 15% of the calibration gas, it should be recalibrated. All recalibration and meter challenges must be documented in the field notebook.

9.2 DUPLICATE SAMPLES

Duplicate samples may be collected at a rate of 5% to assess sample location variability.

10.0 DOCUMENTATION

Field notes should be collected following the standard procedures outlined in SOP DR#013 - Documentation of Field Activities and Development of a SETR. It is important that documentation include the specific lamp energy rating, calibration standard, and special response factors or curves that may be employed for the particular sampling event. When documenting such a sampling event, one should include enough information so that a person at a later date can easily duplicate the sampling and be able to compare the results.

As this type of screening is done in the field by the sampling team conducting the sampling, no chain of custody is required.

Specialized forms may be developed for recording field screening data. Additionally, some PID/FIDs have software which can record data. Any special method of recording and documenting results must be outlined in the SAP.

APPENDIX C

LABORATORY METHODS

Guidelines for the Assessment and Cleanup of Saltwater Releases – NDDH
Recommended Alternative Methods

	North Dakota Cleanup Standards			Recommended Alternative Methods	
Constituent	**Analytical Method**	**Soil Concentration**	**GW Concentration**	**Soil Analytical Method**	**Water Analytical Method**
Chloride	EPA[1] 300.0	250 mg/kg	250 mg/L	Saturated paste prep	
Sodium, %	Calc			Saturated paste prep	EPA 200.8, 200.7, 6010C, 6020A
Sulfate	EPA 300.0	NA[2]	250 mg/L	NA	
Alkalinity	SM 2320B	NA	600 mg/L	NA	
Conductivity/EC[3]	SM 2510B	2 mmhos/cm	1.5 mmhos/cm	Saturated paste prep	
TDS[4]	Calc	NA	500 mg/L	NA	SM 2540C
Benzene	5035/8021	NA	5 µg/L	5035/8260B/8021B	5035/8260B/8021B
TPH[5]-GRO[6]	8015C	100 mg/kg	10 µg/L	8260B	8260B
TPH-DRO[7]	8015D	100 mg/kg	40 µg/L	8015D	8015D
Bromide	EPA 300.0	NA		NA	
Lead	7421*	250 µg/kg	15 µg/L	EPA 200.8, 200.7, 6010C, 6020A	EPA 200.8, 200.7, 6010C, 6020A
Mercury	7471A	10 µg/kg	2 µg/L	7471B	245.1
Arsenic	7060A*	250 µg/kg	10 µg/L	EPA 200.8, 200.7, 6010C, 6020A	EPA 200.8, 200.7, 6010C, 6020A
Barium	6010B	2500 µg/kg	2000 µg/L	EPA 200.8, 200.7, 6010C, 6020A	EPA 200.8, 200.7, 6010C, 6020A
Cadmium	7191A*	500 µg/kg	5 µg/L	EPA 200.8, 200.7, 6010C, 6020A	EPA 200.8, 200.7, 6010C, 6020A
Chromium	7191*	250 µg/kg	100 µg/L	EPA 200.8, 200.7, 6010C, 6020A	EPA 200.8, 200.7, 6010C, 6020A
Selenium	7740*	250 µg/kg	50 µg/L	EPA 200.8, 200.7, 6010C, 6020A	EPA 200.8, 200.7, 6010C, 6020A
Silver	7761*	250 µg/kg	100 µg/L	EPA 200.8, 200.7, 6010C, 6020A	EPA 200.8, 200.7, 6010C, 6020A
SAR[8]	EPA 200.7	12	NA	Saturated paste prep	NA

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[1] U.S. Environmental Protection Agency.
[2] Not applicable.
[3] Electrical conductivity.
[4] Total dissolved solids.
[5] Total petroleum hydrocarbons.
[6] Gasoline-range organics.
[7] Diesel-range organics.
[8] Sodium adsorption ratio.
* No longer EPA-promulgated.

APPENDIX D

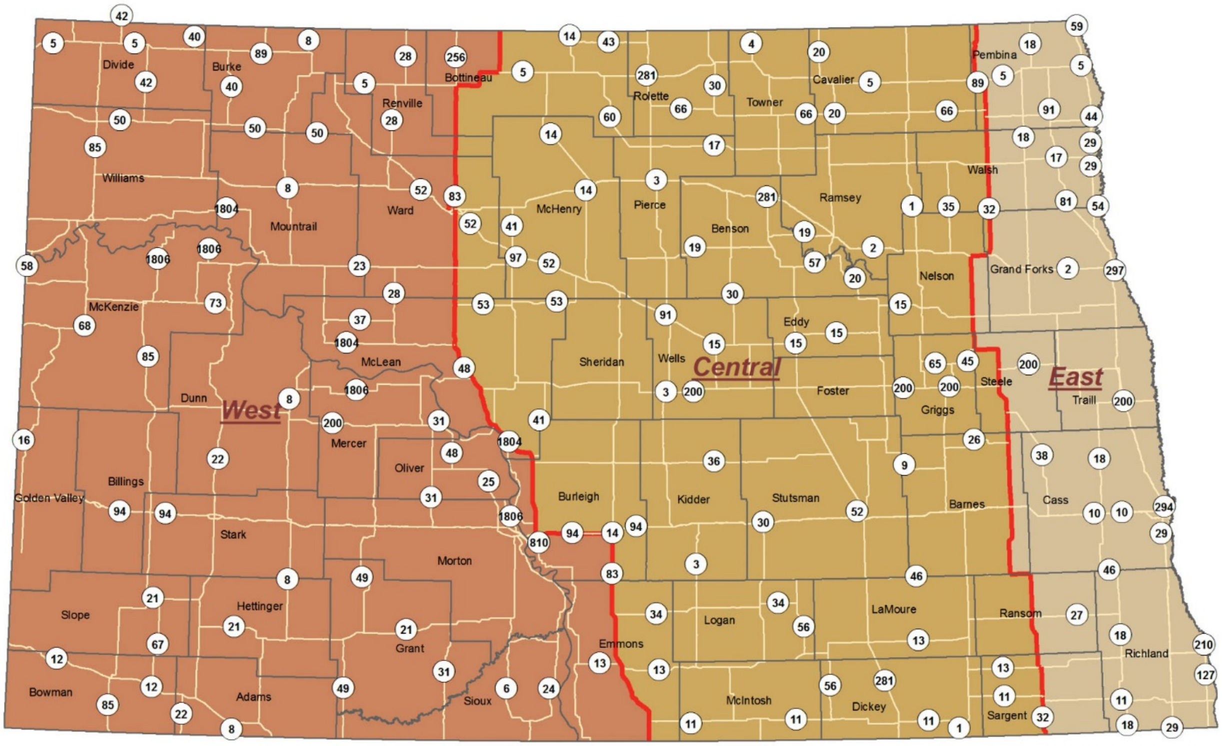
SEED MIX INFORMATION FOR DISTURBED AND HYDROCARBON-IMPACTED AREAS

(source: North Dakota State University Extension Service, 2014, Successful reclamation of lands—distributed by oil and gas development and infrastructure construction)

SEED MIXTURES AND RATES FOR RANGELAND, CONSERVATION RESERVE PROGRAM LANDS, HAY LAND, TAME PASTURE AND RIGHT OF WAY FOR DISTURBED AND HYDROCARBON-IMPACTED AREAS

We divided the state into three major areas for seed mixtures and separated them by major roadways (Figure D-1). Major highways were used to simplify the decision making of remediation and reclamation. The boundaries were delineated on general rangeland types and precipitation relative to a region. Each section will have a recommended native rangeland seed mixture for *loamy/clayey sites, thin loamy/shallow loamy/limy sites, sandy/sands sites, and wet meadow, saline, and/or sodic sites.*

For the *upland rangeland sites*, select a minimum of three forbs/legumes from the recommended species list to complement the recommended grass-seeding mixtures. For the *wet meadow, saline, and/or sodic rangeland sites*, select at least one forb species from the list that best fits the site.



EERC BS50447.CDR

Figure D-1. Location of west, central, and east zones, with the boundary, to be used for recommended seeding mixtures and rates in North Dakota. The *West* is an area from the Montana border east to U.S. Highway 83, *Central* stretches from U.S. Highway 83 to North Dakota Highway 32 and the *East* lies east of North Dakota Highway 32 to the Minnesota border.

Government agencies may have more rigorous restrictions on seed cultivars, origins, seeding dates, or other specifications than those listed here. Consult with the corresponding agency before designing and purchasing a seed mixture.

It is ***NOT*** *recommended to apply fertilizer to native plant seeding. Fertilizers enhance exotic grasses and annual weeds, reducing the success of the establishment.*

Upland Grass Seed Mixture Option for Rangeland Reclamation

Loamy and Clayey Sites			
Grass Species	West	Central	East
PLS lb/ac[1]			
Western Wheatgrass	5.0	3.0	2.0
Green Needlegrass	2.5	2.0	2.0
Slender Wheatgrass	1.0	1.0	1.0
Sideoats Grama	2.0	2.0	2.0
Blue Grama	0.5	0.25	0.25
Big Bluestem	–	1.0	1.5
Switchgrass	–	0.25	0.5
Canada Wildrye	–	1.0	1.0
Indiangrass	–	–	1.0
Total Seed Mixture	11.0	10.5	11.25
Thin Loamy, Shallow Loamy, and Limy Sites			
PLS lb/ac[1]			
Western Wheatgrass	2.5	3.0	2.0
Green Needlegrass	1.5	1.5	1.5
Slender Wheatgrass	1.5	1.0	1.0
Little Bluestem	1.0	1.0	1.0
Prairie Sandreed	1.0	1.0	1.0
Sideoats Grama	2.0	2.0	2.0
Blue Grama	0.5	0.5	0.25
Big Bluestem	–	1.0	1.5
Total Seed Mixture	10.0	11.0	10.25
Sandy and Sands Sites			
PLS lb/ac[1]			
Western Wheatgrass	2.5	2.5	2.0
Needle-and-Thread	2.0	2.0	1.0
Canada Wildrye	1.0	1.0	1.0
Little Bluestem	1.0	1.0	1.0
Prairie Sandreed	1.5	1.5	1.0
Sideoats Grama	2.0	2.0	2.0
Blue Grama	0.5	0.5	0.25
Sand/Big Bluestem	–	1.5	2.0
Total Seed Mixture	10.5	12.0	10.25

[1] PLS = pure live seed: Seeding rates are 1.5 times the normal seeding rate based on 30 seeds/ft^2.

Upland Forb Seed Options (select 3) to Seed with the Grass Seed Mixture for Rangeland Reclamation

Forb and Legume Mixture (loamy, clayey, sandy, sands, shallow loamy, thin loamy, limy)	
Forb and Legume Species[1]	North Dakota
PLS lb/ac[2,3]	
Purple Prairieclover	0.1
White Prairieclover	0.1
Purple Coneflower	0.1
Maximilian Sunflower	0.1
Blanket Flower	0.2
Black-Eyed Susan	0.05
Stiff Sunflower	0.1
Goldenrod	0.05
Lewis Flax	0.1
Scarlet Globemallow	0.05
Prairie Coneflower	0.1

[1] Select a minimum of three forb/legume species from the list. The seeding rate of three selected forbs/legumes at the prescribed rate will equal approximately 5% of the total mixture.

[2] Seeding rates are 1.5 times the normal seeding rate based on 30 seeds/ft^2.

[3] Drill calibration is critical when seeding low rates because seed may be expensive.

Wet Meadow and Saline/Sodic Site Grass and Forb Species Seed Mixture Options for Rangeland Reclamation

Wet Meadow, Saline and/or Sodic Sites			
Plant Species[1,2]	West	Central	East
PLS lb/ac[3]			
Western Wheatgrass	8.0	5.0	5.0
Slender Wheatgrass	2.0	2.0	2.0
Prairie Cordgrass	2.0	2.0	2.0
Inland Saltgrass	1.0	1.0	1.0
Switchgrass	–	1.0	1.0
Total Grass Seed Mixture	13.0	11.0	11.0
Western Yarrow	0.05	0.05	0.05
Gardner Saltbush[4]	0.3	0.3	0.3
Fourwing Saltbush[4]	0.45	0.45	0.45
Lewis Flax	0.1	0.1	0.1

[1] Select a minimum of one forb/legume species from the list.

[2] Drill calibration is critical when seeding low rates because seed may be expensive.

[3] PLS = pure live seed: Seeding rates are 1.5 times the normal seeding rate based on 30 seeds/ft^2.

[4] Gardner and fourwing saltbush should be used only on the saline/sodic sites.

Varieties/Cultivars/Ecovars

Approved Named Varieties		
Species		Recommended Varieties for North Dakota
		Origin of nonvarietal (common) native and introduced grass seed is limited to North Dakota, South Dakota, Nebraska, Montana, Wyoming, Minnesota, and Canada.
Introduced Cool-Season Grasses		
Meadow Bromegrass		Fleet, Paddock, Regar, Montana, MacBeth, Cache
Crested Wheatgrass	Type: standard	Nordan, RoadCrest, Summit
	Fairway	Ephraim, Ruff, Parkway, Fairway, Douglas
	Hybrid	HyCrest II, HyCrest, NU-ARS AC2
Intermediate Wheatgrass		Reliant, Clarke, Slate, Chief, Oahe, Haymaker, Beefmaker, Manifest
Pubescent Wheatgrass		Manska, Greenleaf
Native Warm- and Cool-Season Grasses		
Green Needlegrass		Lodorm, AC Mallard, Fowler
Needle-and-Thread		Common, AC Sharptail
Nutall Alkaligrass		Common
Porcupine Grass		Common
Prairie Junegrass		Common
Slender Wheatgrass		Adanac, Pryor, Revenue, Primar, Firststrike
Western Wheatgrass		Rodan, Walsh, Flintlock, Rosana, W.R. Poole, Recovery
Canada Wildrye		Mandan
Big Bluestem		Sunnyview, Bison, Bonilla, Bounty
Little Bluestem		Badlands, Itasca
Blue Grama		Bad River
Sideoats Grama		Killdeer, Pierre, Butte
Indiangrass		Tomahawk
Prairie Cordgrass		Red River
Prairie Sandreed		Goshen, Bowman, Koch
Switchgrass		Dacotah, Forestburg, Sunburst, Summer
		Nonvarietal (common) native forbs and legumes will originate or be grown in North Dakota, South Dakota, Nebraska, Montana, Wyoming, Idaho, Washington, Oregon, Minnesota, Wisconsin, Iowa, Colorado and Canada.
Native Legumes/Forbs		
Black-Eyed Susan		Common
Blanket Flower		Common
Grayhead Coneflower		Common
Narrow-Leaved Purple Coneflower		Bismarck
Prairie (yellow) Coneflower		Stillwater
Purple Coneflower		Common
Canada Goldenrod		Common
Missouri Goldenrod		Common
Stiff Goldenrod		Common
Lewis Flax		Appar, Maple Grove
Maximilian Sunflower		Medicine Creek

Approved Named Varieties		
Species		Recommended Varieties for North Dakota
Purple Prairieclover		Bismarck
Scarlet Globemallow		Common
Stiff Sunflower		Bismarck
Western Yarrow		Great Northern
White Prairieclover		Antelope
Introduced Legumes		
Alfalfa [1]		Fall dormancy rating or winter survival index (WSI) of 3 or less [2]
Native Shrubs		
Fourwing Saltbush	Dewinged	Wytana, Snake River
Gardner Saltbush		
Winterfat		Open Range
WY Big Sagebrush		Common

[1] A partial list of grazable-type alfalfas can be found in "Developing Alfalfa Adapted to Grazing in the Northern Great Plains," available at www.ag.ndsu.edu/archive/streeter/99report/berdahl99.htm.

[2] The following Web sites are approved for use in determining approved alfalfa varieties: www.alfalfa.org/ and www.maes.umn.edu/. Varieties should have a fall dormancy rating or WSI of 3 or less. Note: Alfalfa varieties with a WSI of 2 or 3 may experience some winter kill. The origin of nonvarietal (common) alfalfa types is limited to North Dakota, South Dakota, Minnesota, Montana, and Canada.

NOTE: Approved alfalfa varieties that may not be shown on these Web sites include Alogonquin, Anik, Blazer, Champ, Drylander, Grim, Ladak, Ladak 65, Prowler, Rambler, Rangelander, Ramsey, Ranger, Spredor 2, Teton, Travois, Vernal, and Wrangler. Alfalfa varieties not listed here or shown on these Web sites will require documentation from the distributor or developer to determine suitability.

Conservation Reserve Program (CRP)

Seed CRP fields back to the predominant species found within the stand. Contact the local NRCS office for help with seed mixtures in your construction area. Some CRP is seeded to native species. Take care to seed all areas to appropriate species.

Hay Land Reclamation

Hay Land Sites			
Plant Species[1]	West	Central	East
PLS lb/ac[2]			
Crested Wheatgrass	3.0	–	–
Pubescent/Intermediate Wheatgrass	4.0	3.0	–
Meadow Bromegrass	–	7.0	10.0
Alfalfa[3]	4.0	3.0	5.0
Total Seed Mixture	11.0	13.0	15.0

[1] These hay land recommendations are to be used as examples. Always consult with the landowner/manager, and plant what he or she prefers or needs for future use.

[2] PLS = pure live seed: Seeding rates are 1.5 times the normal seeding rate based on 30 seeds/ft^2.

[3] Use alfalfa varieties with a fall dormancy rating of 3 to 4 and a winter hardiness rating of 2 to 2.5 when reseeding pure stands of alfalfa. Recommended seeding rates are 8 pounds/acre of PLS in the west, 9 pounds/acre of PLS in the central, and 10 pounds/acre of PLS in the eastern portions of North Dakota.

Tame Pasture Reclamation

Hay Land Sites			
Plant Species[1]	West	Central	East
PLS lb/ac[2]			
Crested Wheatgrass	4.0	–	–
Pubescent/Intermediate Wheatgrass	5.0	6.0	6.0
Western Wheatgrass	5.0	–	–
Meadow Bromegrass	–	15.0	15.0
Alfalfa[3]	–	–	–
Total Seed Mixture	14.0	21.0	21.0

[1] These tame pasture recommendations are to be used as examples. Always consult with the landowner/manager, and plant what he or she prefers or needs for future use.

[2] PLS = pure live seed: Seeding rates are 1.5 times the normal seeding rate based on 30 seeds/ft^2.

[3] Use alfalfa varieties with a fall dormancy rating of 3 to 4 and a winter hardiness rating of 2 to 2.5 when reseeding pure stands of alfalfa. Recommended seeding rates are 8 pounds/acre of PLS in the west, 9 pounds/acre of PLS in the central, and 10 pounds/acre of PLS in the eastern portions of North Dakota.

Rights of Way

Use specifications for Class II seed specifications in North Dakota Department of Transportation Manual Section 708.02B.

Seeding Dates

Recommended Seeding Dates	
Species Type and Season of Planting	**North Dakota**
Cool-Season Species	
Spring	Prior to June 1[1]
Late Summer [2]	Aug. 1 to Sept. 1
Late Fall (dormant)	See footnote[3]
Warm/Cool-Season Mix	
Spring	April 20 to June 15[1]
Late Summer[2]	Not recommended
Late Fall (dormant)	See footnote[3]

[1] Seeding may be extended with adequate soil moisture and when favorable precipitation and temperatures are forecast.

[2] Weather and soil moisture conditions permitting. If soil moisture levels and forecasted precipitation amounts are not favorable, this time period of seeding is not recommended.

[3] Seed after October 10 when ground temperatures at a depth of 4 inches are 45°F or lower and cooler air temperatures are forecast.

APPENDIX E

SALT-TOLERANCE INFORMATION OF GRASSES, FORBS, AND LEGUMES

Table E-1. Relative Saline Tolerance Levels (EC) of Selected Grass, Forb, and Legume Species[1,2]

	EC (mmhos/cm) Production Affected – Seedling Stage	EC (mmhos/cm) Production Affected – Vegetative Stage	Upper Limit	Tolerance Rating	Palatability
Grass					
Nuttall's Alkaligrass	8	14	32	Very high	Medium
Inland Saltgrass	12	16	32	Very high	Medium
Alkali Sacaton	10	32	32	Very high	Medium
Beardless Wildrye		13	26	Very high	Medium
Tall Wheatgrass		13	26	Very high	Low
Green Wheatgrass (Newhy)		13	26	Very high	High
Russian Wildrye		13	24	Very high	Medium
Alkali Cordgrass		12	24	Very high	–
Alkali Bluegrass		12	24	Very high	–
Slender Wheatgrass		10	22	Very high	Medium
Altai Wildrye		10	20	Very high	Medium
Plains Bluegrass		10	20	Very high	Medium
Tall Fescue		8	18	High	Medium
Western Wheatgrass	4	8	16	High	High
Thickspike/Streambank Wheatgrass		6	14	Moderate	Medium
Crested Wheatgrass		6	14	Moderate	High
Siberian Wheatgrass		6	14	Moderate	Medium
Pubescent Wheatgrass		6	12	Moderate	Medium
Intermediate Wheatgrass		6	12	Moderate	High
Little Bluestem	6	6	10	Moderate	Medium
Creeping Foxtail		5	12	Moderate	High
Smooth Brome		5	10	Moderate	Highest
Meadow Brome		4	10	Moderate	Highest
Orchardgrass		3	8	Low	Highest
Switchgrass		–	6	Low	Medium
Reed Canarygrass		3	5	Low	Highest
Blue Grama	4	4	6	Low	Highest
Buffalograss		–	3	Low	Highest
Forbs and Shrubs					
Forage Kochia		10	18+	High	Medium
Fourwing Saltbush		10	18+	High	Medium
Winterfat		10	18+	High	High
Strawberry Clover		6	16	High	Highest
Yellow Sweetclover		5	10	Moderate	High
Cicer Milkvetch		4	10	Moderate	Highest
Birdsfoot Trefoil		5	8	Low	High
Alfalfa		4	8	Low	Highest
Clovers (red, alsike, ladino)		3	4	Low	Highest
Small Burnet		2	3	Low	Highest

[1] Source: Ogle, D., and St. John, L., 2009, Plants for saline to sodic soil conditions: TN Plant Materials No. 9A (Rev.), USDA, NRCS, October 2009.

[2] Source: Thomlinson, H, 2016, Project data.

APPENDIX F

SALT-TOLERANCE INFORMATION OF AGRONOMIC CROPS

Table F-1. Relative Saline Tolerance Levels (EC) of Agronomic Crops[1,2]

Crop	EC (mmhos/cm) Production Affected	Upper Limit	Tolerance Rating
Canola	10	14	High
Barley	8	16	High
Wheat (durum)	7	14	Moderate
Wheat (semidwarf)	7	14	Moderate
Sugar Beets	7	14	Moderate
Sunflower	6	14	Moderate
Safflower	6	10	Moderate
Oats	4	8	Low
Soybean	4	8	Low
Alfalfa	4	8	Low
Corn	3	6	Low
Flax	2	4	Low
Edible Beans	1	2	Low

[1] Source: Ogle, D., and St. John, L., 2009, Plants for saline to sodic soil conditions: TN Plant Materials No. 9A (Rev.). USDA, NRCS, October 2009.

[2] Source: Franzen, D., 2013, Managing saline soils in North Dakota: Circ. SF1087 (Rev.), NDSU Extension Service.

APPENDIX G

USEFUL INFORMATION

CONVERSIONS AND STANDARDS

Electrical Conductivity

decisiemen per meter (dS/m)	mmhos/cm

Chemical Concentration

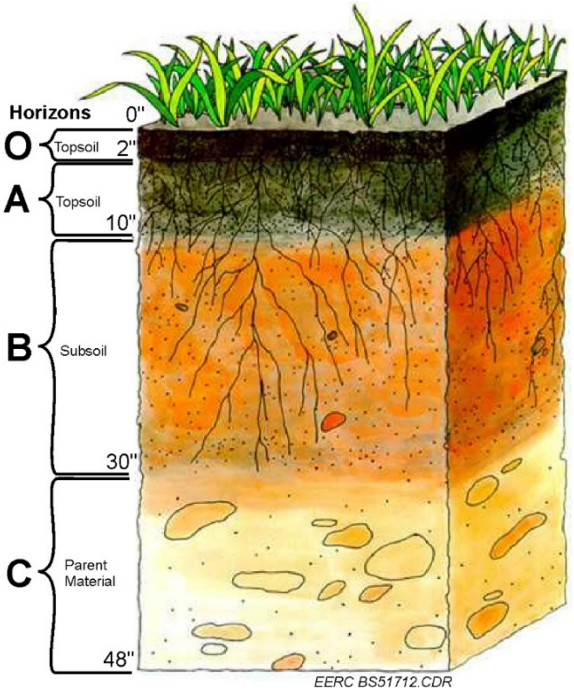
parts per million (ppm)	mg/kg (in soil) mg/L (in liquids)
parts per billion (ppb)	µg/kg (in soils) µg/L (in liquids)

Area

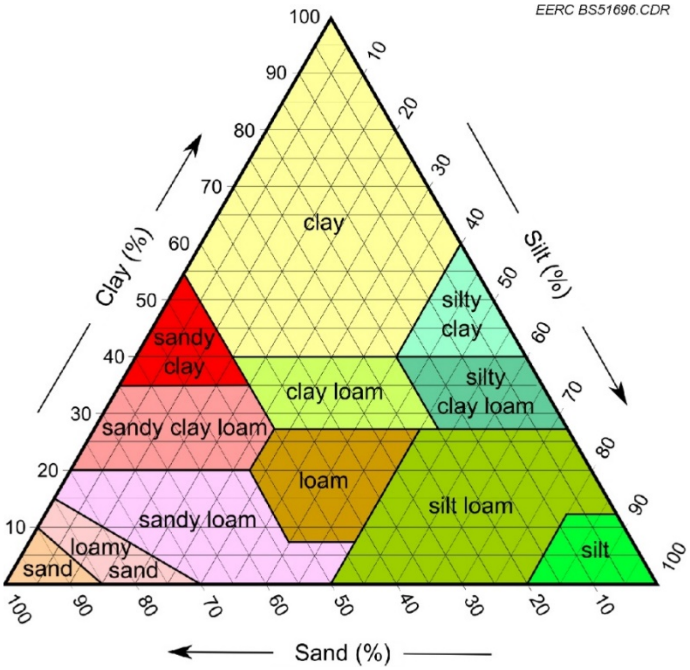
acre	43,560 square feet
1 ha	2.471 acres

Volume

barrel	42 gallons
acre-foot	325,851 gallons
1 cfs/day	1.98 acre feet



Soil profile image (source: U.S. Department of Agriculture).



Soil texture triangle (source: U.S. Department of Agriculture).

Criteria Used with the Field Method for Determining Soil Texture Classes (source: Brady, 1990)

Criterion	Sand	Sandy loam	Loam	Silt Loam	Clay Loam	Clay
1. Individual grains visible to eye	Yes	Yes	Some	Few	No	No
2. Stability of dry clods	Do not form	Do not form	Easily broken	Moderately easily broken	Hard and stable	Very hard and stable
3. Stability of wet clods	Unstable	Slightly stable	Moderately stable	Stable	Very stable	Very stable
4. Stability of "ribbon" when wet soil rubbed between thumb and fingers	Does not form	Does not form	Does not form	Broken appearance	Thin, will break	Very long, flexible

Infiltration Rates of Various Soils

Soil Type	Steady Infiltration Rate
	(inch/hour)
Sands	>0.79
Sandy and Silty Soils	0.39-0.79
Loams	0.20-0.39
Clayey Soils	0.04-0.20
Sodium Clayey Soils	<0.04

Adapted from Hillel, D., 1998, Environmental Soil Physics: Academic Press, San Diego, California, p. 403.

APPENDIX H

API INFORMATION AND WORKSHEETS

(source: American Petroleum Institute Publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities, 1997 [“reproduction courtesy of the American Petroleum Institute”])

API INFORMATION AND WORKSHEETS

DRAINAGE

Many spill circumstances will require some amount of attention to internal soil drainage. Unattended poor internal soil drainage may be the most common reason for failure of remediation projects. Soil drainage factors can be combined into hydrologic soil groups, as shown in Table H-1.

Table H-1. Hydrologic Soil Groups

Hydrologic Soil Groups	Definition
A.	Soils having a high infiltration rate even when thoroughly wetted and consisting chiefly of deep, well to excessively drained sands or gravels (low runoff potential). These soils have a high rate of water transmission.
B.	Soils having a moderate infiltration rate when thoroughly wetted and consisting chiefly of moderately deep to deep, moderately well to well-drained soils with moderately fine to moderately coarse texture. These soils have a moderate rate of water transmission.
C.	Soils having a slow infiltration rate when thoroughly wetted and consisting chiefly of soils with a layer that impedes downward movement of water or soils with moderately fine to fine texture. These soils have a slow rate of water transmission.
D.	Soils having a very slow infiltration rate when thoroughly wetted and consisting chiefly of clay soils with a high swelling potential, soils with a permanent high water table, soils with a clay pan or clay layer at or near the surface, and shallow soils over nearly impervious material. These soils have very slow rates of water transmission.

Source: U.S. Department of Agriculture Soil Survey Division Staff, 1993; USDA-SCS, 1979.

In order to remediate a salt-affected soil chemically, salts must have a pathway through which they can migrate out of the root zone during leaching. Impediments to salt migration out of the root zone include bedrock, an impermeable layer, a water table, or a very slowly permeable soil within 6 feet of the soil surface. Unless these conditions are altered, chemically displaced salts will be unable to migrate out of the root zone.

There are six basic ways to create a path for soil pore water to migrate below the root zone:

- Chemical amendments
- Plant growth
- Mulching
- Deep plowing
- Installing subsurface drains
- Establishment of intensive-water-demand plants around the spill-affected area to lower the water table

In most spill circumstances which require attention to improve drainage, several or all of these methods may be utilized simultaneously.

CHEMICAL AMENDMENT

Application of appropriate chemical amendments to sodic soil causes the dispersed soil to aggregate. A period of years may be required for organic matter and slowly soluble amendments, such as granular gypsum, to aggregate soil sufficiently to create macropores, whereas typically a few weeks or months may be required for very soluble amendments, such as liquid calcium nitrate or calcium chloride. These reactions are dependent on soil moisture conditions.

In order to aggregate the soil, the chemical amendment must come into contact with the salt-affected soil. If the soil has already dispersed, the chemical amendment may require a mechanical method to incorporate it into the salt-affected areas. This can be done with plowing to shallow depths, deep ripping, or by hydraulic injection as a slurry or solution for deeper depths.

All forms of chemical amendment should be incorporated into the soil. A final topdressing of gypsum and organic mulch may protect the surface from dispersion and crusting.

PLANT GROWTH

During remediation, the roots of any vegetation present will help physically to move soil particles. If the soil chemistry has been adjusted with an effective chemical amendment, the soil particles will aggregate. If the salt concentration is high (electrical conductivity [EC] >8–12 mmhos/cm) at the outset of remediation, establishment of interim, salt-tolerant vegetation will help generate macropores. If the water table is also high, then wetlands plants may be advisable. Vegetation also occurs in conjunction with other soil biota, such as invertebrate animals, fungi, and microbes, all of which will help aggregate soil. If required, addition of fertilizer and organic matter will stimulate these organisms, and the soil will be remediated more quickly. Appendices E and F contain a list of salt-tolerant plants.

MULCHING

The use of mulch (such as native hay or straw) can assist in facilitating soil aggregation, improve aeration, minimize surface soil crusting, and reduce evaporation and erosion. Mulch should be incorporated into the soil as deeply as possible. Chemical amendments (previously discussed) should be applied at least as deeply as the mulch is placed. Mulch and chemical amendments can be incorporated with a variety of plows and rototillers. Mulch has been shown to accelerate the rate of remediation substantially and improve the effectiveness of chemical amendments.

The interface between the mulch and the soil usually acts as a water channel or macropore. Then, as the mulch decomposes, larger macropores are left where the mulch had been. If the chemical amendment has had time to promote soil aggregation, these pores will remain open for some time. If the chemical amendment has not reacted by the time the mulch decomposes, then the clay particles may disperse again and refill the macropores. Mulch with high C:N ratios will decompose slowly, and mulch with low C:N ratios will decompose quickly. Refer to API Manual 4663 Appendix L for more information on mulch.

DEEP PLOWING

Impermeable layers can be broken up by deep plows, deep dozer ripping, or by hydraulic fracturing. Breaking up this layer will promote internal soil drainage and removal of soluble salts. Deep plows are mechanical implements pulled by a tractor or tracked vehicle and are most functional to a depth of 3 ft below ground surface. If considering deep plowing, also consider plowing in a cross pattern.

SUBSURFACE DRAINS

Subsurface drains can be used to lower the water table and/or intercept downward-migrating salts if the receiving groundwater is sensitive to salts. Consultation with a drainage expert is recommended if subsurface drains are contemplated.

For very small plots, one or two open trenches may suffice. Trench drains may be most effective for a coarse soil over a finer-textured subsoil where the water table is higher than the finer-textured subsoil. The trench is dug slightly lower than the top of the fine-textured subsoil, and “perched” water runs into it. The salty water is collected in the trench for transfer to a processing or disposal unit. The trench drain would not be appropriate for intercepting salts to prevent migration into groundwater if there is no barrier layer between the topsoil and the groundwater.

In larger areas, or if a greater intensity of drain spacing is required, a temporary mole drain or more permanent drain tubing can be installed. These subsurface drains can be used both to lower the water table and intercept salts. Both mole drains and subsurface tubing drains terminate in a sump. Saltwater collected in the sump is disposed in an approved manner.

Mole drains involve pulling a 4-inch-diameter, bullet-shaped implement through the subsoil. This drain is temporary and will usually close and seal off within a couple of years as the soil settles. Figure H-1 portrays a mole drainage system.

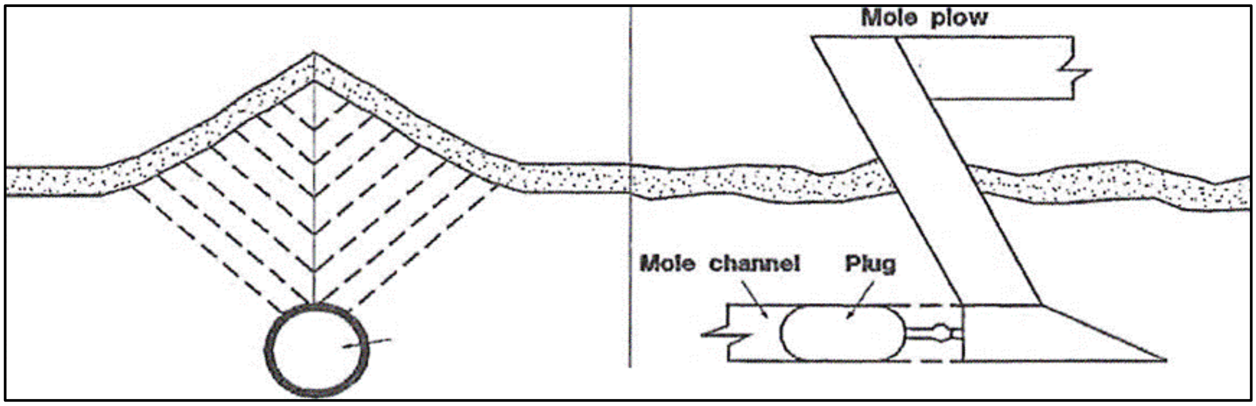


Figure H-1. Diagram showing how an underground mole drainage system is put in place (Hughes, 1980) (reproduction by permission of Deere & Company ©1980, Deere & Company. All rights reserved).

To install subsurface drain tubing, a trench approximately 8 inches wide is dug. Sand may be placed in the bottom of the trench in addition to 4-inch-diameter perforated plastic drain tubing. The drain tube should be surrounded with a filter sock to minimize clogging the drain interior with soil particles. The lengths of 4-inch lateral tubing snap together, and also snap into the main, which can be 4 or 6 inches in diameter. A diagram depicting lateral and main configurations is shown in Figure H-2.

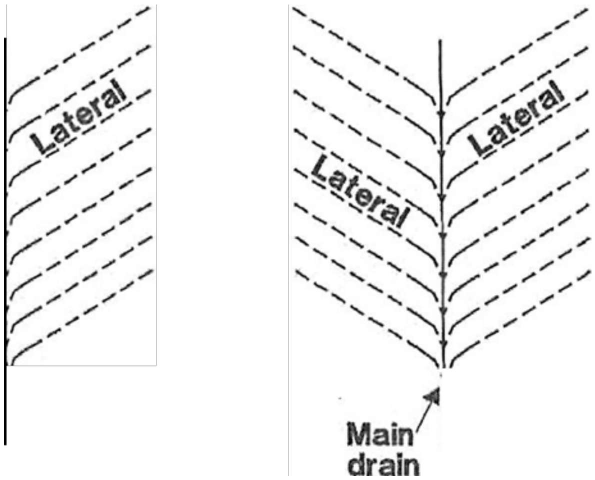


Figure H-2. Example layer of subsurface laterals and main (adapted from Brady, 1984).

Subsurface drain tubing is placed at the depths and lateral spacing shown in Table H-2. However, laterals should not be placed more than twice as deep as the surface layer of a stratified soil. Drains should also be placed above a transmissive subsoil layer if this layer is within the saturated zone and underlies a finer texture. The reason is to avoid collecting water primarily from the surrounding area instead of from the salt-affected soil above.

Table H-2. Approximate Depth and Spacing of Subsurface Drain Lines

Soil Texture, group	Drainage Depth, ft	Lateral Spacing, ft
Coarse	3	30
Coarse	6	60
Medium	3	20
Medium	6	40
Fine	3	10
Fine	6	20

CHEMICAL AMENDMENTS AND APPLICATION PROCEDURES

Chemical amendments are used to displace sodium from soil clay exchange sites. In a dilute electrolyte solution (low EC), soil clays with more than 10% to 15% sodium on cation exchange sites will cause soil dispersion. In smectitic soils, the critical sodium adsorption ration (SAR) or sodium (Na) % is as low as 5. The dispersion of soil particles results in structural disintegration and a reduction of drainage which greatly impedes remedial efforts. Dispersion can be avoided by applying a chemical amendment before leaching begins. Chemical amendments will prevent the soil from dispersing until the Na has been displaced from cation exchange sites. As the SAR and Na % decreases, the need for soil electrolytes (e.g., total soluble anions and cations) also decreases. After the SAR and Na % has decreased to a suitable level (note, suitability is dependent on field conditions; refer to pages 7–9 of this manual for more discussion), the leaching in most soils can be completed without concern for additional dispersion.

The chemical amendments discussed below include materials to be used at relatively neutral pH (5.5 to 8.5) and in more acidic (pH <5.5) and more alkaline (pH >8.5) solutions. A variety of chemical amendments typically applied as both solids and liquids is discussed below (see also Table H-3).

Concentrated amendment solutions (e.g., liquid chemical amendments and fertilizers) may shorten the remediation time and require less water compared to solid amendments like agricultural gypsum. However, they are typically more expensive, thus making them less practical in most situations than solid amendments. Concentrated amendments can often be applied with irrigation water, but it is important that the irrigation process equally distribute the chemical amendment over the affected area.

With the exception of the acidifying amendments and calcium nitrate, an efficiency correction factor should be used for increasing the amount of the chemical amendment applied. Often, unrepresentative sampling and inaccurate analytical results cause chemical amendment calculations to underestimate the amount of amendment actually needed. Practice has shown that about **1.25** times the amount calculated using the laboratory analyses will provide sufficient chemical amendment to accomplish remediation objectives. As noted below, regardless of other chemical amendments used, a final topdressing of gypsum and organic matter will provide long-lasting protection of the soil surface while the soil recuperates.

Table H-3. Chemical Amendments Used to Remediate Salt-Affected Soils

Amendment	Chemical Formula	Commercial Availability	Purpose	Positive Attributes	Application Method	Follow-Up Procedures	Warnings or Cautions
Bulk or Sack Gypsum/Calcium	$CaSO_4 \cdot 2H_2O$	Bulk or sack	Sodium displacement	Slow release; residual benefits	Surface spread, then till	Light surface application	Poor solubility; about 1 vertical ft of water is required to dissolve about 50 lb of gypsum/100 ft^2 of very salt affected soil
Calcium Chloride	$CaCl_2 \cdot 2H_2O$	Bulk, sack, or liquid	Sodium displacement: supplies Ca	Quick acting; faster results	Slurry or dissolved in water	Surface apply gypsum for residual benefit	Increases chlorides; protect shallow groundwater
Calcium Nitrate	$Ca(NO_3)_2$	Bulk, sack, or liquid	Fertilizer: sodium displacement: supplies Ca and N	Quick acting; enhances biodegradation and vegetation growth	Broadcast on surface and incorporate, or apply as liquid	Surface apply gypsum for residual benefit	Protect drinking water, nitrate toxic to some animals
Calcium Carbonate	$CaCO_3$	Bulk or sack	Soil alkalizer: sodium displacement: supplies Ca	Good for use in acidic soils	Broadcast on surface	Surface apply gypsum for residual benefit	Will not work in alkaline soils
Dolomite	$CaCO_3 \cdot MgCO_3$	Bulk or sack	Soil alkalizer: sodium displacement: supplies Ca and Mg	Good for use in acidic soils	Broadcast on surface	Surface apply gypsum for residual benefit	Will not work in alkaline soils
Calcium Oxide	CaO	Sack	Soil alkalizer: sodium displacement	Quick acting; good for use in acidic soils	Broadcast on surface, then incorporate; coapply with gypsum	Surface apply gypsum for residual benefit	Will not work in alkaline soils; can burn skin and eyes, reactive with water; overuse can cement soil; determine quantity by titration
Calcium Hydroxide	$Ca(OH)_2$	Bulk or sack	Soil alkalizer: sodium displacement	Quick acting; good for use in acidic soils	Broadcast on surface, then incorporate; coapply with gypsum	Surface apply gypsum for residual benefit	Will not work in alkaline soils; can burn skin and eyes, reactive with water; overuse can cement soil; determine quantity by titration
Sulfur	S	Bulk or sack	Soil alkalizer: sodium displacement	Slow release	Apply as slurry or powder, then incorporate; coapply with gypsum	Surface apply gypsum for residual benefit	Corrosive to metals after oxidation; requires water and thiobacillus; determine quantity by titration
Sulfuric Acid	H_2SO_4	Bulk, drum, or liquid	Soil alkalizer: sodium displacement	Rapid response	Apply liquid to surface, then incorporate; coapply with gypsum	Surface apply gypsum for residual benefit	Corrosive to metals; use with caution; determine quantity by titration
Aluminum Sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	Bulk or sack	Soil acidifier: enhanced drainage: sodium displacement	Rapid response in developing soil macropores	Broadcast on surface then incorporate; coapply with gypsum	Surface apply gypsum for residual benefit	Can become toxic to plants at pH <5; determine quantity by titration
Iron Sulfate	$FeSO_4 \cdot 7H_2O$	Sack	Soil acidifier: drainage enhancement: sodium displacement	Provides iron and sulfate to vegetation	Broadcast on surface then incorporate; coapply with gypsum	Surface apply gypsum for residual benefit	Determine quantity by titration
Diammonium Phosphate	$(NH_4)_2(HPO_4)$	Bulk or sack	Fertilizer: sodium displacement: soil binder	Provides nitrogen and phosphate to vegetation	Broadcast on surface then incorporate; coapply with gypsum	Surface apply gypsum for residual benefit	Very water soluble; protect shallow groundwater
Displace Polymers	Various chemicals	Bucket or drum	Drainage enhancement: aggregate stabilizer	Fast acting	Apply sodium displacer first, then broadcast or spray on surface, incorporate, allow to dry	Surface apply gypsum for residual benefit	Soil must be allowed to dry after wetting for polymers to bind soil

CHEMICAL AMENDMENTS FOR RELATIVELY NEUTRAL SOILS

Gypsum ($CaSO_4 \cdot 2H_2O$)

Gypsum is the most commonly used amendment. It dissolves slowly to provide low but adequate electrolyte (as expressed by EC) and a slow release of calcium. Various particle sizes of gypsum physically keep pore sizes open while soil chemistry is slowly converted from the dispersive to aggregative condition. The solubility of gypsum increases as salt concentration increases. Gypsum is twice as soluble when EC is 15 mmhos/cm compared to when EC is 3.5 mmhos/cm and is about four times more soluble when exchangeable sodium percentage (ESP) is 100% compared to when ESP is near 0%. Because of low solubility, gypsum must be mechanically mixed into the soil to be effective. For various reasons, the solubility of industrial-grade gypsum is several times more than mined gypsum. One foot of water is required to dissolve each 10-ton/acre application of gypsum under optimal dissolving conditions (e.g., high EC, high ESP, and gypsum in powdered form).

Gypsum is normally applied by broadcasting, followed by incorporation via disking. Gypsum should be mixed throughout the upper 2 feet of soil (when possible) if salts occur throughout that depth. In most reclamation circumstances, at least 50% of the gypsum applied should be placed within the upper 1 foot.

A final topdressing of gypsum is suggested to protect the soil surface from dispersion, regardless of the principal type of chemical amendment used. A topdressing of gypsum provides the slow release of calcium to the uppermost clay particles which incorporated chemical amendments may have bypassed. The following topdressing rates are suggested in pounds per acre: coarse, 200; medium 80; fine 4 mesh size. Some practitioners recommend that the maximum single application of gypsum not exceed **5 tons/acre** for each **6-inch depth** into which it will be incorporated. If additional gypsum is required, it can be applied at 6-month intervals until all required gypsum has been applied.

Gypsum can also be applied as a slurry and deep-injected with modified ripper shanks or a handheld hydrolance. Gypsum rocks placed along the irrigation water route line will slowly dissolve, supplying calcium to the irrigation water.

Calcium Chloride ($CaCl_2 \cdot 2H_2O$) and Calcium Nitrate ($Ca[NO_3]_2$)

Calcium chloride and calcium nitrate are very soluble and provide solutions of high electrolyte concentration. The reaction time of these chemicals is very rapid, and they penetrate the soil at approximately the same rate as water, except for the fraction that becomes adsorbed onto clay. For this reason, they provide for rapid remediation as long as the solution they are in can penetrate the soil.

These chemicals are typically applied as a slurry or as dissolved ions in water. They are preferred by remediation contractors because they show rapid results. Gypsum may be coapplied to provide more residual benefits, especially at the soil surface.

Because the anions of calcium nitrate (NO_3) and calcium chloride ($CaCl_2$) are very mobile and move at the same rate as water, it is very important to have an understanding of where application and subsequent leaching water will go. If the receiving groundwater is to be sacrificed (because it is already too salty to reclaim), this may be an acceptable location for additional chloride (and Na). However, it is not usually an acceptable location for nitrate, as noted below.

Calcium nitrate supplies nitrogen in a plant available form and also improves the biodegradation rate of petroleum hydrocarbons. However, the amount applied may exceed the ability of the plants or microbes to consume it before it leaches into groundwater. Only **10 mg/L nitrate** is allowed in drinking water because of its extreme toxic effects on animals. Therefore, nitrate must be contained to the extent possible and not allowed to migrate overland into surface water or leach into groundwater. This is difficult because nitrate is one of the most mobile ions in soil. As a general rule, use of calcium nitrate is not advised in coarse-textured soils and only with caution in medium- and fine-textured soils. It should never be used close to surface water or where nitrate can migrate into usable groundwater.

Calcium chloride and calcium nitrate are expensive, except that sometimes calcium chloride can be obtained as a waste by-product. Both are also corrosive, and consideration should be given to the type of application equipment to be used. The amount of calcium chloride and calcium nitrate equivalent to 1 lb of gypsum is 0.85 and 0.95 lb, respectively. This means that 0.85 lb of calcium chloride and 0.95 lb of calcium nitrate can displace the same amount of sodium as 1 lb of gypsum in a soil if the entire amount of each chemical is dissolved and used appropriately.

CHEMICAL AMENDMENTS FOR ACID SOILS (pH <5.5)

Limestone ($CaCO_3$) and Dolomite ($CaCO_3 \cdot MgCO_3$)

Limestone (calcium carbonate) and dolomite are only effective in acid soils because these amendments are not very soluble at alkaline pH levels. The soil pH should be less than 6.0 if limestone is to be used. These liming agents are usually applied as a powder or in crushed form but can also be applied as a slurry. Dolomite (also known as dolomitic limestone) is slightly less soluble than calcium and also supplies magnesium (Mg^{++}), which is a divalent cation capable of displacing sodium and is an important plant nutrient.

Both lime and dolomite are relatively inexpensive. They are easy to apply and not corrosive. In addition, they constitute excellent pH buffers in the soil at a 200-mesh particle size, and overapplication is not as much of a concern as it is for calcium oxide, calcium hydroxide, and the acidifying amendments.

Calcium Oxide (CaO) and Calcium Hydroxide ($Ca[OH]_2$)

Calcium oxide (burned lime, quick lime, oxide, or burned oyster shell lime) and calcium hydroxide (hydrated lime or slaked lime) are concentrated liming agents. Their use is not recommended in a general sense because they may cause some soil cementation and are reactive with organic matter. However, they are very fast-acting and can be used to raise the pH of acid soils. Both present handling problems and cause a burning sensation when they come into contact with water (or perspiration). They are also serious hazards to the eye and have a high heat of reaction. When calcium oxide first comes into contact with water, it can actually raise the temperature of nearby paper and wood to ignition temperature. Calcium oxide and calcium hydroxide are, respectively, 1.6 and **1.25** times as effective by weight as calcium carbonate for neutralizing soil acidity.

CHEMICAL AMENDMENTS FOR ALKALINE SOILS (pH > 8.5)

Sulfur (S)

Elemental sulfur must be oxidized in the soil to be effective. In the presence of certain types of bacteria which occur in most soils, the sulfur oxidizes and combines with soil pore water to become sulfuric acid. The soil must contain sufficient water to assist in the microbial oxidation of the sulfur. The acid dissolves calcium carbonate in the soil and releases calcium for exchange with sodium on exchange sites. The soil pH is simultaneously decreased as the hydrogen ions are released from the sulfuric acid. Remediation time usually requires several months.

Sulfur can be applied at the soil surface as a dry powder, then mechanically incorporated into the soil. However, the dust may be problematic. Sulfur can also be applied as a slurry, typically as a solution of about 55% to 60% sulfur. Typically, sulfur should not be applied to a soil which does not contain calcium carbonate.

It is important to not over apply the acidifying amendments, and generally, they should be applied only when calcium carbonate is present in the soil layers being treated. Incorporation of manure with acidifying amendments has been especially efficient at improving the soil for plant growth and improving drainage of salt-affected soils.

Sulfuric Acid (H_2SO_4)

Sulfuric acid also reacts with calcium carbonate to produce a soluble source of calcium and sulfate. Water intake and percolation rates are increased because of increased electrolyte concentration and dissolution of aluminum and iron compounds which promote aggregation.

As a liquid, sulfuric acid can move at a rate in the soil similar to the rate of water percolation. Because downward movement in soil may be slow if the soil is dispersed, incorporation of elemental sulfur to greater depths may be more rapid. However, elemental sulfur must be in oxidizing conditions to form sulfuric acid.

Sulfuric acid is generally inexpensive because it can be obtained as an industrial by product. Approximately 3.06 lb of sulfuric acid is equivalent to 1 lb of elemental sulfur. However, special handling, equipment, and PPE (personal protection equipment) are required for safe application. Caution should be exercised when working with sulfuric acid, and because it is corrosive, selection of application equipment should be appropriate.

Sulfuric acid is less damaging to the soil when applied in concentrated form directly to the soil, instead of as a diluted solution. It can also be applied by spray equipment or in irrigation water.

Aluminum Sulfate ($Al_2[SO_4]_3 \cdot 18H_2O$) and Iron Sulfate ($FeSO_4 \cdot 7H_2O$)

Aluminum sulfate and iron sulfate act like dilute sulfuric acid in the soil, and they supply a trivalent cation (Al^{+++}) or divalent cation (Fe^{++}) Both aluminum and iron are very strong aggregating agents and can rapidly create macropores in a soil. Although iron is an important plant nutrient, especially at high pH where it is not very soluble, aluminum has no fertility value and, in fact, can be toxic when the pH is less than 5.0.

These chemicals would be expected to work faster than elemental sulfur and at about the same rate as sulfuric acid, calcium nitrate, or calcium chloride. Approximately 6.94 and 8.69 lb of aluminum sulfate and iron sulfate, respectively, are equivalent to 1 lb of elemental sulfur. In other words, 6.94 lb of aluminum sulfate and 8.69 lb of iron sulfate can displace the same amount of sodium in soil as 1 lb of elemental sulfur if the entire amount of each chemical reacts or is dissolved and used appropriately.

OTHER CHEMICAL AMENDMENTS

Polymers

Several organizations manufacture and distribute or use their own staff to apply salt remediation materials which contain polymers. Several different types of polymers (such as polyvinyl alcohols, polyacrylamides, and natural plant polymers) are currently on the market. Initial studies indicate that polymers may aid in remediation of salt-affected soils by rapidly aggregating soil particles. These polymers are usually applied in a mix of other salt-remediating chemical amendments, most often being calcium nitrate.

Proprietary Chemicals

A number of organizations are working on proprietary chemical amendments for salt remediation. These materials should not be given widespread use without prior performance demonstrations.

Diammonium Phosphate ($[NH_4]_2[HPO_4]$)

Although technically a fertilizer, diammonium phosphate provides a unique opportunity to speed remediation of a salt-affected soil. The ammonium ion (NH_4^+) will behave similarly to potassium (K^+) as a mild displacing agent for sodium. However, the ammonium is also a plant-available form of nitrogen. The phosphorus supplied with diammonium phosphate is also an important plant nutrient and has been demonstrated to help plants withstand stress because of excessive salts and sodium. Rapid growth of plant seedlings is especially stimulated. Diammonium phosphate is also completely water-soluble and can move quickly into the soil.

Diammonium phosphate should be applied only at a rate indicated by fertility testing. When fertilizer results are to be reported, the analytical laboratory should be asked to recommend a rate which will utilize diammonium phosphate.

Diammonium phosphate is usually provided in the fertilizer grade 18–46–0. This means that the fertilizer contains 18% nitrogen, 46% phosphate as P_2O_5, and no potassium. Fertilization application rates are site-specific depending on soil type and can be readily identified by the analytical laboratory conducting the soil analysis.

Chemical Oxidation Amendments

In situ chemical oxidation (ISCO) is a chemical oxidation technology used in environmental remediation of soil and/or groundwater to reduce the concentrations of organic compound contaminants to acceptable levels as determined by state and federal regulators. ISCO is accomplished by injecting or otherwise introducing strong chemical oxidizers directly into the contaminated medium (soil or groundwater) to alter/change the contaminant(s) at the molecular level (via oxidation/reduction reactions), in place.

Common oxidants used in this process are permanganate (both sodium permanganate and potassium permanganate), Fenton's Reagent, persulfate, ozone and calcium peroxide (*Cool-Ox*®). Some of these oxidants are discussed below.

Fenton-type chemistry (liquid hydrogen peroxide) is clean, effective, and straightforward ISCO. This treatment involves injecting hydrogen peroxide (H_2O_2) with ferrous iron (Fe^{2+}) to form Fenton's Reagent. In the presence of Fe^{2+}, the H_2O_2 is decomposed to produce hydroxyl radicals ($OH\cdot$) that are short-lived and react rapidly and nonspecifically with organic compounds in an exothermic reaction. An acidic environment is preferred to keep the Fe^{2+} soluble in aqueous solutions because oxidation occurs more rapidly. The OH· has been effective in oxidizing both free and dissolved-phase petroleum hydrocarbons; however, there are few discussions in the literature of applying it both safely and effectively at sites with light nonaqueous-phase liquid (LNAPL) plumes.

The limitations with this technology are its short (microseconds) useful life under practical application circumstances. Therefore, when it is applied, if it does not immediately contact the target contaminant, it will react with anything (mainly site soils or natural organic matter [NOM]). Additionally, Fenton chemistry can be unstable to handle and may result in extreme pH drift.

Calcium peroxide, when reacted with water, produces hydrogen peroxide. Additionally, the sparing solubility of calcium peroxide retards the production of hydrogen peroxide as the calcium peroxide is hydrolyzed. This reaction facilitates available hydrogen peroxide in the remedial target zone for up to 90 days postapplication. The character of this reaction prolongs the useful life and increases the probability of contact with the target contaminant.

Some potential problems to consider:

1. Sulfates should never be used for remediation where ferrous metals are present.
2. Chemical oxidation is not the most effective method to remediate halogenated organics.
3. Permanganate does not work well with hydrocarbons and may be cost-prohibitive.
4. High concentrations of calcium peroxide may poison the sites because of the generation of quicklime.
5. Soil vapor extraction (SVE) systems are limited because of the volatile organic compound’s (VOC’s) affinity for heavier hydrocarbons adsorbed to the soil.

Humic Amendments

Humic substances are NOMs that remain after the process of humification, which is the biodegradation of biomatter that then recombines and synthesizes into dark-colored complex compounds with no definite chemical structure.

Two distinct characteristics of humic substances are their highly heterogeneous molecular structure and their resistance to further biodegradation. These qualities are important in the context of ecosystems because humic substances play critical roles in ecosystem function and health. Healthy ecosystems are resistant to degradation and contamination as well as fit to carry out ecosystem functions, including sufficient cation exchange capacity and water-holding capacity and providing an environment for a diverse and healthy population of soil microorganisms.

A vast array of humic products includes naturally occurring mined materials such as leonardite, oxidized lignite, carbonaceous shales, humates, or liquid products such as liquid humic acids and liquid fulvic acids, soluble or suspendable powders, and gels (source: www.humictrade.org/humic-products-explained).

Zeolite Amendments

Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. About 40 natural zeolites have been identified, and more than 150 zeolites have been synthesized. The most common naturally occurring zeolites are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties (source: www.minerals.usgs.gov/minerals/pubs/commodity/zeolites/index.html).

Other Amendments

Citric Acid

Citric acid and gypsum amendments have been successfully used to remediate brine spills. A food-grade citric acid amendment will react with the natural soil calcium carbonate, gypsum, and calcium carbonate amendments to produce soluble calcium. The soluble calcium cations (Ca^{2+}) will displace the sodium cations (Na^{+}). Since citric acid is much more water-soluble than gypsum, less water is required to drive the the release of calcium from amendments of gypsum or calcium carbonate and/or native soil carbonates.

Sulfur

Where soil pH is high (>8.6), sulfur may be added with the other amendments to lower the soil pH and increase the solubility of gypsum (i.e., calcium) and, in turn, may reduce the remediation time line. It should be noted that sufficient water must be present in the soil to facilitate the microbial oxidation of the sulfur.

INSTRUCTIONS FOR TABLE H-4 – RECLAMATION PRACTICES

For relatively uncomplicated saltwater release sites, Table H-4 may be used to estimate the amounts of amendments to be applied if chemical remediation is found to be a viable remedial option.

How to Use Table H-4

1. Determine Moisture Deficit (Sections A, B, or C in Table H-4)
   Find the section of Table H-4 that matches the rainfall characteristics for the site (select either adequate rainfall [Section A], marginal rainfall [Section B], or inadequate rainfall [Section C]). To select the appropriate section, estimate the net annual moisture condition. Use the precipitation evaporation index (PEl). Appendix I contains the information needed to calculate the net annual moisture condition. For the site of interest, obtain the normal annual precipitation and mean annual Class A pan evaporation rate from the maps in Appendix I. Calculate the net annual moisture condition as follows:
   - Annual precipitation (inches) minus annual evaporation (inches) = net annual moisture condition.
   - If the net annual moisture condition is (select Table H-4 section):
     - Less negative or more positive than –12 inches (e.g., –4 inches or +7 inches) A, adequate rainfall
     - Between –12 and –28 inches (e.g., –19 inches) B, marginal rainfall
     - More negative than –28 inches (e.g., –33 inches) C, inadequate rainfall

2. Locate soil EC (Column 1)
   Within the appropriate section of Table H-4, find the EC value in Column 1 that matches the site conditions. If EC levels are < 4 mmhos/cm and there is evidence that the salt-affected soil will not support natural vegetation, chemical amendments may be needed to alleviate dispersed soil conditions. At low soil EC values, soil dispersion may occur if ESP > 5% in soils with smectite clays or ESP > 15% in soils containing clays other than smectites (e.g., illites).

3. Calculate chemical amendment (gypsum) requirement
   To calculate the amount of chemical amendment (expressed as gypsum) required, use the equation provided in Column 2:
   a. Use the values for CEC (cation exchange capacity) and ESP from the 0–1-ft depth interval to calculate the gypsum requirement for the 0–1-ft depth interval (to convert SAR to ESP, use Figure H-3, Equation 1, or Equation 2).

   b. Repeat the calculation using the CEC and ESP for the 1–2-ft depth interval.

   c. Add the results from the two calculations to get the amount of gypsum to treat the upper 2 ft of soil. An additional topdressing of gypsum will help prevent soil crusts from forming at the ground surface.

   d. If the pH is < 5.5 or > 8.5, or chemical amendments other than gypsum are to be applied; consult manual.

Table H-4. Reclamation Practices for Adequate, Marginal, and Inadequate Rainfall Areas

Column 1 EC, mmhos/cm	Column 2 Calculate Gypsum Application Rate,[1] lb/100 ft^2	Column 3 Mulch Rate,[2] depth in inches before incorporation[3]	Column 4 N-P-K Fertilizer Rate,[2] lb/100 ft^2	Column 5 Remedial Actions
Section A, Adequate Rainfall (net annual moisture condition less negative or more positive than –12 inches)				
0–4[4]	If (CEC)(ESP-5)(0.078) = then, 0–1 + 1–2 ft = total	2c, 3m, 4f	3 lb of 13-13-13	Incorporate gypsum (to displace sodium and prevent dispersion) and mulch. Surface apply fertilizer. Plant.
4–8	If (CEC)(ESP-5)(0.078) = then, 0–1 + 1–2 ft = total	2c, 3m, 4f	3 lb of 13-13-13	Incorporate gypsum and mulch. Surface-apply fertilizer. Plant with semi-salt-tolerant vegetation.
8–16	If (CEC)(ESP-5)(0.078) = then, 0–1 + 1–2 ft = total	2c, 3m, 4f	3 lb of 13-13-13	Incorporate gypsum and mulch. Surface-apply fertilizer. Plant with salt-tolerant vegetation.
>16	=>	=>	=>	Consult environmental specialist.
Section B, Marginal Rainfall (net annual moisture condition between –12 and –28 inches)				
0–4	If (CEC)(ESP-5)(0.078) = then, 0–1 + 1–2 ft = total	2c, 3m, 4f	3 lb of 13-13-13	Incorporate gypsum (to displace sodium and prevent dispersion) and mulch. Surface-apply fertilizer. Plant. Irrigate, if required.
4–8	If (CEC)(ESP-5)(0.078)= then, 0–1 + 1–2 ft = total	2c, 3m, 4f	3 lb of 13-13-13	Incorporate gypsum and mulch. Surface-apply fertilizer. Plant with semi-salt-tolerant vegetation. Irrigate, if required.
8–16	If (CEC)(ESP-5)(0.078)= then, 0–1 + 1–2 ft = total	2c, 3m, 4f	3 lb of 13-13-13	Incorporate gypsum and mulch. Irrigate, if required. Surface-apply fertilizer. Plant with salt-tolerant vegetation. Irrigate again, if required.
>16	=>	=>	=>	Consult environmental specialist.
Section C, Inadequate Rainfall (net annual moisture condition more negative than –28 inches)				
0–4	If (CEC)(ESP-5)(0.078)= then, 0–1 + 1–2 ft = total	2c, 3m, 4f	2 lb of 13-13-13	Incorporate gypsum (to displace sodium and prevent dispersion) and mulch. Surface-apply fertilizer. Plant. Irrigate.
4–8	If (CEC)(ESP-5)(0.078)= then, 0–1 + 1–2 ft = total	2c, 3m, 4f	2 lb of 13-13-13	Incorporate gypsum and mulch. Surface-apply fertilizer. Plant with semi-salt-tolerant vegetation. Irrigate, if required.
8–16	If (CEC)(ESP-5)(0.078)= then, 0–1 + 1–2 ft = total	2c, 3m, 4f	2 lb of 13-13-13	Incorporate gypsum and mulch. Irrigate. Surface-apply fertilizer. Plant with salt-tolerant vegetation. Irrigate again.
>16	=>	=>	=>	Consult environmental specialist.

[1] Example gypsum calculation: A site characterization found that the 0-1–ft depth interval had a CEC = 14 meq/100 g and an SAR = 32. The 1–2-ft depth interval was found to have a CEC = 17 meq/100 g and an SAR = 20. Using Figure H-3, the SAR values of 32 and 20 convert to ESP values of 37% and 26%, respectively. Using the equation in Column 2 (and ignoring the CEC denominator), calculate the pounds of gypsum per 100 ft^2 of soil as follows:

0–1-ft depth interval: (14 meq)(37 – 5)(0.078) = 35 lb gypsum/100 ft^2
1–2-ft depth interval: (17 meq)(20 – 5)(0.078) = 20 lb gypsum/100 ft^2

To find total gypsum requirement:

(35 lb gypsum/100 ft^2) + (20 lb gypsum/100 ft^2) = 55 lb gypsum/100 ft^2

If a chemical amendment other than gypsum is to be used, consult manual.

About 1 vertical ft of water will be required to dissolve 50 pounds of gypsum per 100 ft^2 of salt-affected soil. Therefore, slightly over 1 vertical ft of water will be required to dissolve 55 lb of gypsum per 100 ft^2 of soil in this example.

[2] Mulch and fertilizer improve soil drainage and fertility and may speed the remediation process. Consult your company policy or environmental specialist regarding the use of these amendments.

[3] c = coarse-textured soil, m = medium-textured soil, f = fine-textured soil.

[4] See instructions on the use of Table H-4 regarding gypsum application to soils with EC < 4 mmhos/cm.

$$\mathrm{ESP} = 1.25 \times \mathrm{SAR} \qquad \text{[Eq. 1]}$$

$$\mathrm{ESP} = 1.95 + 1.03 \times \mathrm{SAR} \qquad \text{[Eq. 2]}$$

Note: For SAR concentrations above 30, Eq. 1 and Eq. 2 may not be sufficiently accurate.

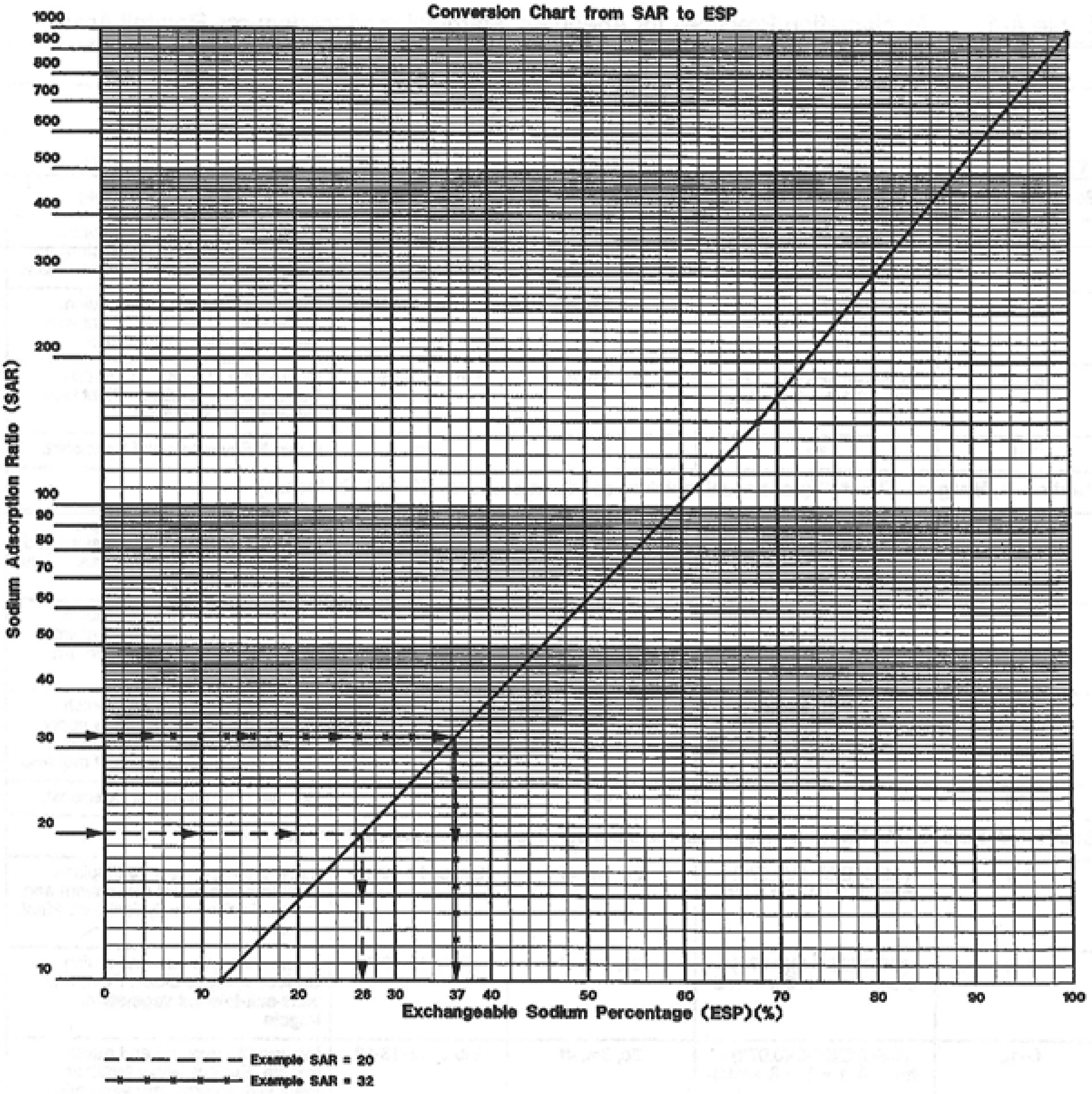


Figure H-3. Correlation of ESP and SAR.

Example Gypsum Calculation

A site characterization found that the 0–1-ft depth interval had a CEC = 14 meq/100 g and an SAR = 32. The 1–2-ft depth interval was found to have a CEC = 17 meq/100 g and an SAR = 20. Using Figure H-3, the SAR values of 32 and 20 convert to ESP values of 37% and 26%, respectively. Using the equation in Column 2 (and ignoring the CEC denominator), calculate the pounds of gypsum per 100 ft^2 of soil as follows:

0–1-ft depth interval: (14 meq)(37 – 5)(0.078) = 35 lb gypsum/100 ft^2
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To Find Total Gypsum Requirement

(35 lb gypsum/100 ft^2) + (20 lb gypsum/100 ft^2) = 55 lb gypsum/100 ft^2

If a chemical amendment other than gypsum is to be used, consult manual. About one vertical foot of water will be required to dissolve 50 lb of gypsum per 100 ft^2 of salt-affected soil. Therefore, slightly over one vertical foot of water will be required to dissolve 55 lb of gypsum per 100 ft^2 of soil in this example:

4. Note mulch and fertilizer application rates (Columns 3 and 4)
   Mulch and fertilizer improve drainage and fertility of soil. Mulch (Column 3) and fertilizer (Column 4) may be applied at the rates indicated.

5. Note remedial actions (Column 5)
   Remedial actions noted in Column 5 provide additional information and cautions applicable to the spill site circumstances within the same row. The steps provided are in approximate chronological order (there may be some site-specific exceptions).

CHEMICAL AMENDMENTS (INSTRUCTIONS)
(Worksheet H-1)

Summary
Chemical amendments can be used to displace sodium from soil cation exchange sites. This worksheet provides a step-by-step process whereby soil or spilled produced water analytical data are used to calculate the quantity and type of chemical amendment required to remediate the spill-affected soil. This worksheet may be modified to be consistent with operator policy.

Step 1: The quantity of chemical amendment to apply may be calculated based on soil measurements (Step 2A) or measurements from the spilled material (Step 2B). The first step is to decide which of these two methods will be used. Using the calculations based on spilled material (Step 2B) has the following inherent disadvantages:

- Assumes the entire spill is contained in the upper 2 ft of soil.
- Assumes all sodium is retained on clay cation exchange sites.
- Assumes uniform distribution of spilled material over the entire spill-affected area.
- Does not address soil responses to salt over time.

As a result, this option should be used only when soil data cannot be obtained and only if the spill occurred within the previous 6 months. Use of the calculations based on soil measurements (Step 2A) is always acceptable, regardless of the age of the spill. Therefore, Step 1 guides the user into either Step 2A for calculations based on soil measurement or into Step 2B for calculations based on spilled material.

Step 2A: Following the soil measurement option, Step 2A involves collection of the data shown. Soil pH, CEC, and ESP are determined separately at the analytical laboratory for the 0–1- and 1–2-ft depth increments. The 0–1- and 1–2-ft depth intervals can be substantially different in physical and chemical properties which are important to chemical amendment selection. The spill area is also determined.

Step 3A: In Step 3A, the comprehensive gypsum requirement is calculated. Gypsum is used as a reference material to determine how much calcium should be applied to displace sodium to an end point ESP of 5%. An ESP of 5% accounts for smectite, which is especially sensitive to exchangeable sodium, and sampling and analytical inefficiencies. The final calculation in this step is the total calculated pounds of pure gypsum required to displace sodium in the affected area. However, because of sodium displacement inefficiencies with gypsum, it is generally recommended to apply about 1.25 times the amount of gypsum calculated in Step 3A. Thus if gypsum is the material selected for application, then 1.25 times that amount should be applied and incorporated into the spill area. If the pH is between 5.5 and 8.5, and neither calcium nitrate nor calcium chloride is to be applied, then this is the actual amount of gypsum to apply. The principal disadvantage of gypsum is that 1 ft of water is required to dissolve the gypsum applied at a rate of 10 tons/acre under optimal dissolution conditions (high EC and high ESP).

Step 4A (neutral-pH soil): The corresponding alternative amount of calcium chloride or calcium nitrate to apply when the pH is between 5.5 and 8.5 is given in Step 4A (neutral-pH soil). Although the equivalent weight of calcium chloride and calcium nitrate is less than that of gypsum, these two materials are usually much more expensive than gypsum. They also have potential disadvantages associated with the addition of nitrates or yet more chlorides. However, with these disadvantages understood, both of these amendments are fast acting and require less water to dissolve compared to gypsum.

High- or Low-pH Amendments: If the pH is less than 5.5, as an option, it may be advisable to apply lime as a chemical amendment unless plant pH preference is lower than 5.5. Calcium and magnesium from lime dissolving in acid soil will displace sodium in acid soils, and it will raise the pH to a level more suitable to the growth of many plants. If the pH is more than 8.5, an acidifying amendment may be used to displace sodium in soils with carbonates. Acidifying amendments can decrease the soil pH to a level more suitable to the growth of most plants, but over time, gypsum will also tend to lower pH. The acidifying amendments usually work best in topsoil and when the soil contains carbonates because calcium and magnesium are released when the carbonates dissolve in the acid. However, it may be better to use gypsum, calcium chloride, or calcium nitrate if the pH is above 8.5 or if the soil has insufficient carbonates to buffer the pH change. Any adjustments made in soil pH should be consistent with the pH preference or tolerance range of the vegetation present.

Step 4A (acid soil): Data required to calculate the amount of lime to apply for an acid soil are calculated in Step 4A (acid soil). If the soil analytical results show that the soil pH is less than 5.5 and the deliberate liming option is chosen, the analytical laboratory should be asked to provide a lime requirement to raise the pH to 7.0. The laboratory should perform a titration procedure and report the results in pounds of calcium carbonate ($CaCO_3$) required to raise the pH of the soil to 7.0 in 1000 lb of soil. This should be done separately for the 0–1- and 1–2-ft depth intervals. The total amount of calcium carbonate to apply is calculated at the bottom of Step 4A (acid soil).

Step 5A (acid soil): The lime requirement to raise the pH to 7.0 may not supply enough calcium to displace the amount of sodium necessary. Lime applied in excess of the pH 7.0 end point does not dissolve and, therefore, supplies little calcium or magnesium at a pH level above 7.0. Therefore, in Step 5A (acid soil), the lime requirement value is converted into a gypsum-equivalent value. In Step 6A (acid soil), the renaming sodium displacement required is calculated so that it can be supplied by gypsum.

Step 6A (acid soil): In Step 6A (acid soil), the gypsum equivalent value of lime from Step 5A (acid soil) is subtracted from the total comprehensive gypsum value required to displace sodium calculated in Step 3A. The result is the amount of gypsum that should be coapplied with the calcium carbonate to provide the total amount of calcium required to displace sodium. For more rapid response, strong and very soluble liming agents, such as calcium oxide (CaO) and calcium hydroxide ($Ca[OH]_2$), can be used but they are both dangerous to handle, and they could have a cementing effect on the soil. In contrast, it is always acceptable to apply limestone or dolomite to raise pH. Unlike calcium oxide and calcium hydroxide, limestone and dolomite will not cause chemical burns or raise the soil pH above 8.5. In addition, limestone and dolomite are usually readily available, inexpensive, and relatively easy to handle. Their reaction rate in soil can be accelerated by applying in small grain sizes.

Step 4A (alkali soil): Data required to determine the amount of acidifying amendment to apply to an alkali soil are shown in Step 4A (alkali soil). If this option is chosen, the laboratory is asked to provide a sulfur (S) requirement in pounds of sulfur per 1000 lb of soil to decrease the pH to 8.3. The total amount of sulfur to apply is calculated at the bottom of Step 4A (alkali soil).

Step 5A (alkali soil): In Step 5A (alkali soil), the gypsum equivalent of the sulfur is calculated.

Step 6A (alkali soil): The amount of gypsum to coapply with sulfur to supply the total amount of calcium required is calculated in Step 6A (alkali soil).

Step 7A (alkali soil): Acidifying alternatives to sulfur are given in Step 7A (alkali soil). These include aluminum sulfate ($Al_2[SO_4] \cdot 18H_2O$); iron (II or ferrous) sulfate ($FeSO_4 \cdot 7H_2O$); and sulfuric acid (H_2SO_4). Sulfuric acid is dangerous to handle and is applied as a liquid. Use of elemental sulfur should be restricted to sites that have topsoil remaining because the oxidation of sulfur to sulfate requires the presence of a soilborne bacterium which will usually be more abundant and amid more growth support factors in topsoil in contrast to surface-exposed subsoil. To avoid undesired results, it is important to apply no more of these acidifying chemicals than is calculated here.

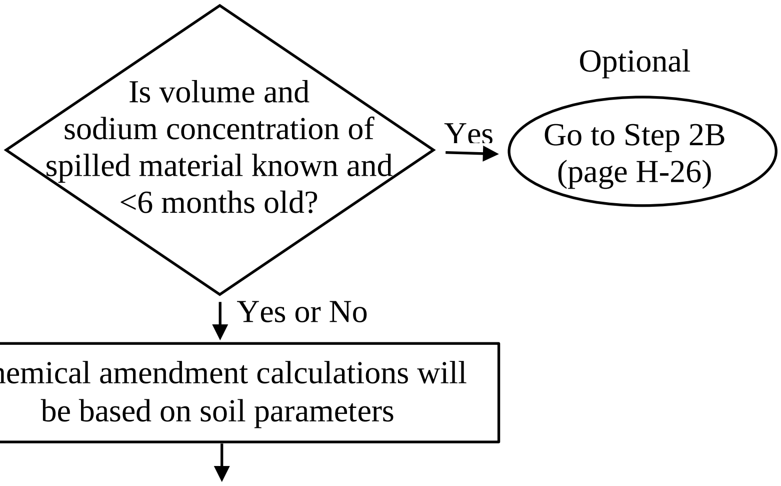
Step 2B: Data required to calculate the chemical amendment equivalent and requirement based entirely on the concentration and quantity of spilled material are listed in Step 2B. These data include the volume spilled (in barrels) and the sodium concentration (in mg/L) in the spilled material. The sodium concentration is typically between 20% to 35% of the total dissolved solids (TDS) (in mg/L) in produced waters, and the TDS data are requested as a check function. The spill area is also recorded here as a matter of convenience.

Step 3B: The gypsum equivalent and requirement based on the concentration and quantity of spilled material are calculated in Step 3B. The amount of gypsum to apply to the spill area is the last calculation in Step 3B. Calculating the gypsum requirement in this manner does not address potentially high or low soil pH conditions. For reasons listed in Step 1 of this worksheet, calculation of the chemical amendment requirement based on soil data is preferred over calculations based on the concentration and quantity of spilled material.

Worksheet H-1
Chemical Amendments Worksheet

Chemical amendment for displacing sodium and adjusting pH is calculated for upper 2 ft of spill-affected soil*

Step 1



Step 2A

Collect Data

Spill Area =		ft^2
pH (0–1 ft) =		s.u.
pH (1–2 ft) =		s.u.
CEC (0–1 ft) =		meq/100 g
CEC (1–2 ft) =		meq/100 g
ESP (0–1 ft) =		%
ESP (1–2 ft) =		%

Step 3A

Calculate Comprehensive Gypsum Requirement
Calculate Separately for 0–1 and 1–2 ft

For 0–1 ft

Gypsum requirement = ESP-5 × CEC × 0.00078 = ____ lb gypsum/ft^2

____ lb gypsum/ft^2× ____ ft^2 spill area = ____ Total lb gypsum

For 1–2 ft

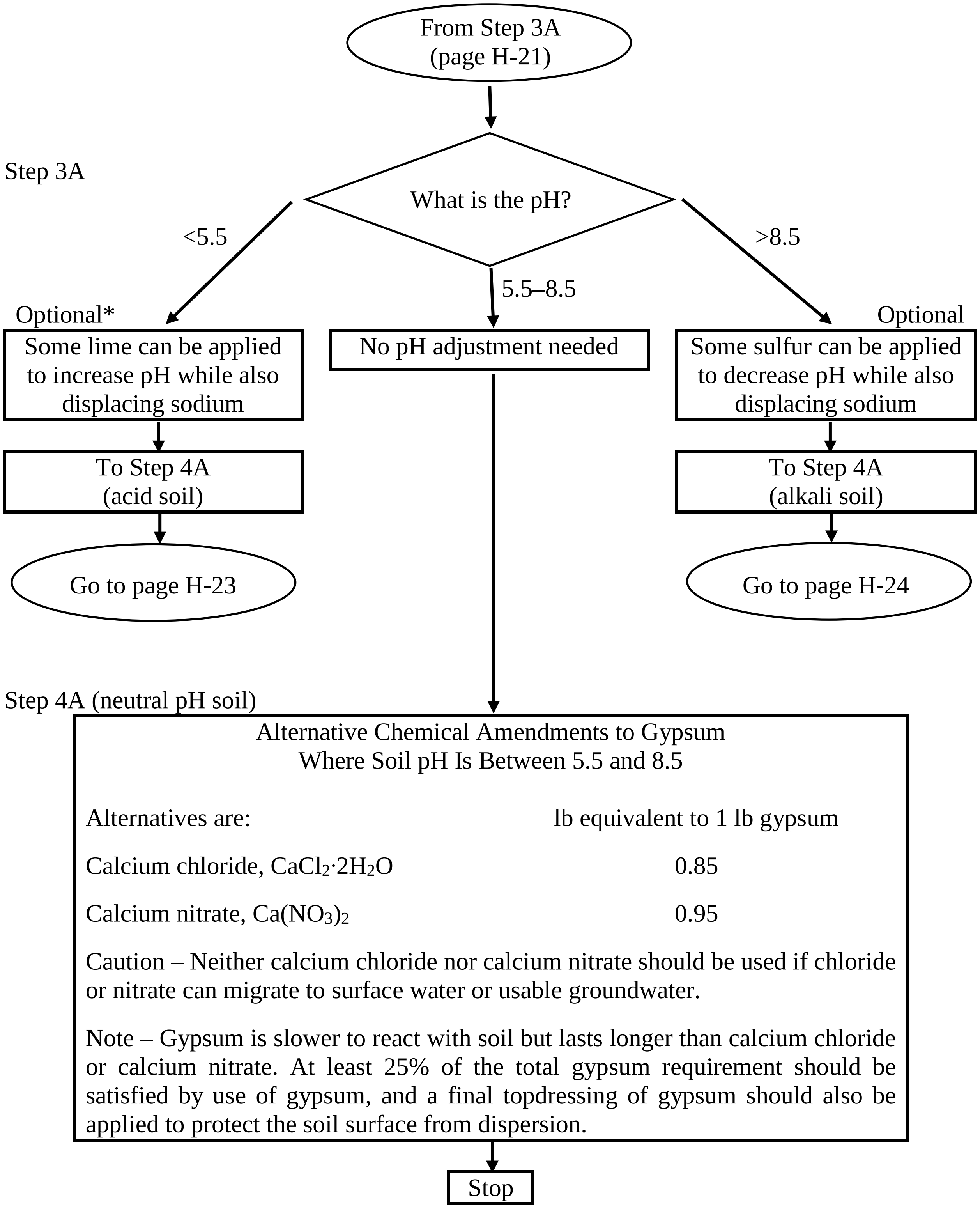
Gypsum requirement = ESP-5 × CEC × 0.00078 = ____ lb gypsum/ft^2

____ lb gypsum/sq ft × ____ ft^2 spill area = ____ Total lb gypsum

For combined 0–2 ft

0–1 ft ____ total lb gypsum + 1–2 ft ____ total lb gypsum = 0–2 ft ____ Total lb gypsum to apply

Go to page H-22



Alternative Chemical Amendments to Gypsum
Where Soil pH Is Between 5.5 and 8.5

Alternatives are:	lb equivalent to 1 lb gypsum
Calcium chloride, $CaCl_2 \cdot 2H_2O$	0.85
Calcium nitrate, $Ca(NO_3)_2$	0.95

Caution – Neither calcium chloride nor calcium nitrate should be used if chloride or nitrate can migrate to surface water or usable groundwater.

Note – Gypsum is slower to react with soil but lasts longer than calcium chloride or calcium nitrate. At least 25% of the total gypsum requirement should be satisfied by use of gypsum, and a final topdressing of gypsum should also be applied to protect the soil surface from dispersion.

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* Most plants prefer pH 5.5–8.5. pH should be adjusted to within 5.5 and 8.5 as part of salt remediation of most soils, but there may be exceptions in certain locations and agricultural situations. Applications of pH-neutral amendments will usually improve yields in both strongly acid and strongly alkaline soils.

From Step 3A
(page H-22)

↓

(To increase pH while displacing sodium)

↓

Step 4A (acid soil)

Collect Data

Have laboratory titrate acidity up to pH 7.0 and provide
a lime requirement in lb $CaCO_3$/1000 lb soil

Determine 0–1 and 1–2 ft separately

From 0–1 ft ____ lb $CaCO_3$/1000 lb soil

+

From 1–2 ft ____ lb $CaCO_3$/1000 lb soil

=

Total 0–2 ft ____ lb $CaCO_3$/2000 lb soil

0–2 ft
(____ lb $CaCO_3$/2000 lb soil) × 0.092 × (____ ft^2 soil) = ____ Total lb $CaCO_3$ to apply

↓

Step 5A (acid soil)

Calculate Gypsum Equivalent

For 0–1 ft
(____ lb $CaCO_3$/1000 lb soil) × 0.158 × (____ sq ft soil) = ____ Total lb gypsum equivalent

For 1–2 ft
(____ lb $CaCO_3$/1000 lb soil) × 0.158 × (____ sq ft soil) = ____ Total lb gypsum equivalent

For combined 0–2 ft

0–1 ft ____ lb gypsum equivalent + 1–2 ft ____ lb gypsum equivalent = 0–2 ft ____ Total lb gypsum equivalent

↓

Step 6A (acid soil)

Calculate Gypsum to Coapply with Calcium Carbonate ($CaCO_3$)

From Step 3A: (0–2 ft ____ total lb comprehensive gypsum required) − From Step 5A (acid soil): (0–2 ft ____ total lb gypsum equivalent) = ____ Total lb gypsum to coapply

↓

Stop

From Step 3A
(page H-22

(To decrease pH while displacing sodium)

Step 4A (alkali soil)

Collect Data

Have laboratory titrate alkalinity to pH 8.3 and provide an acid requirement in lb S/1000 lb soil

Determine 0–1 and 1–2 ft separately

From 0–1 ft ______ lb S/1000 lb soil

+

From 1–2 ft ______ lb S/1000 lb soil

=

Total 0–2 ft ______ lb S/2000 lb soil

0–2 ft
(______ lb S/2000 lb soil) × 0.092 × (______ ft^2 soil) = ______ Total lb S to apply

Step 5A (alkali soil)

Calculate Gypsum Equivalent

For 0–1 ft
(______ lb S/1000 lb soil) × 0.495 × (______ sq ft soil) = ______ Total lb gypsum equivalent

For 1–2 ft
(______ lb S/1000 lb soil) × 0.495 × (______ sq ft soil) = ______ Total lb gypsum equivalent

For combined 0–2 ft
0–1 ft ______ lb gypsum equivalent + 1–2 ft ______ lb gypsum equivalent = 0–2 ft ______ Total lb gypsum equivalent

Step 6A (alkali soil)

Calculate Gypsum to Coapply with Sulfur (S)

From Step 3A: (0–2 ft ______ total lb comprehensive gypsum required) − From Step 5A (alkali soil): (0–2 ft ______ total lb gypsum equivalent) = ______ Total lb gypsum to coapply

Go to page H-25

From Step 6A (alkali soil)
(page H-24)

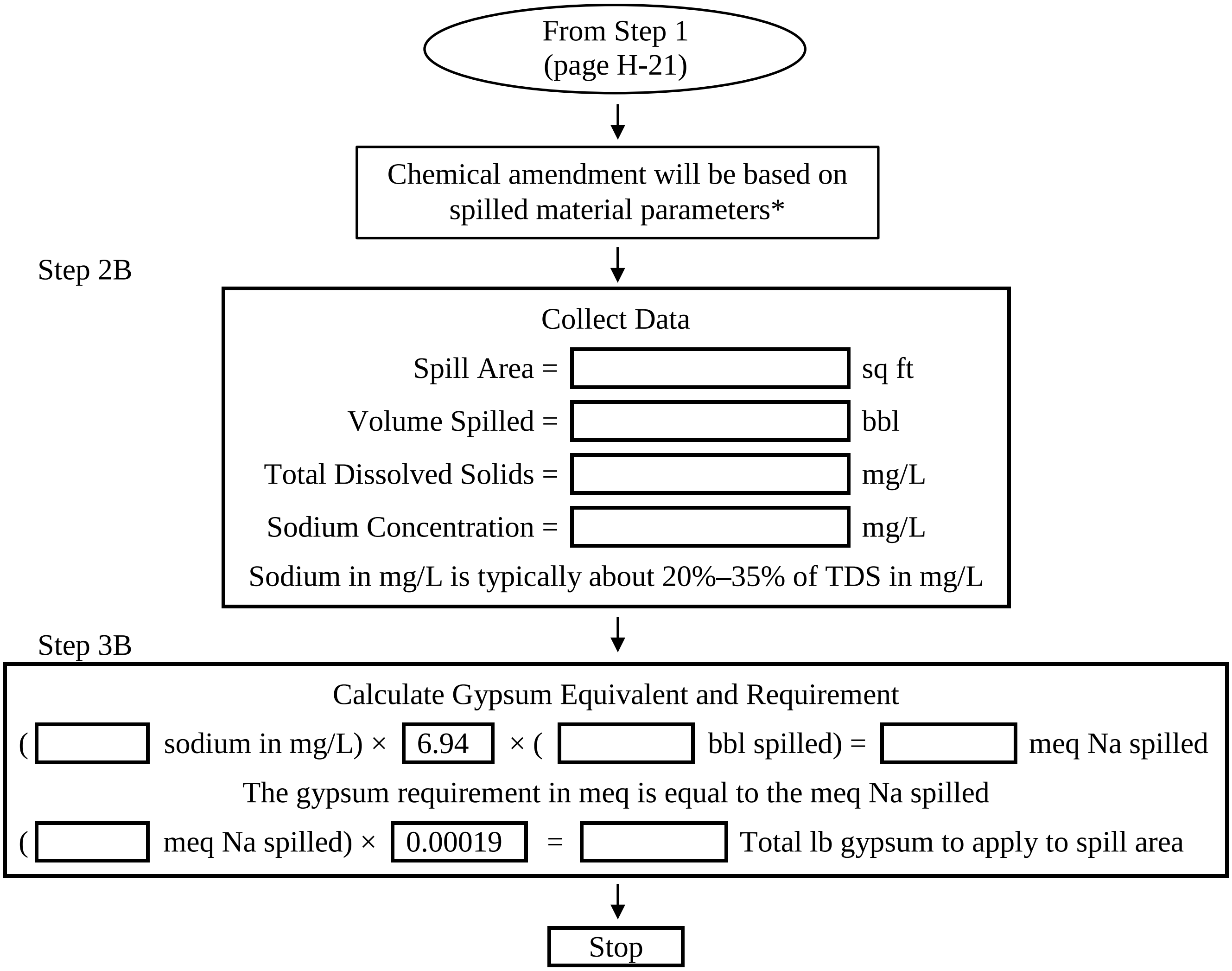
Step 7A (alkali soil)

Alternative Chemical Amendments to Sulfur (S) Where pH Is >8.5

Alternatives are:	lb equivalent to 1 lb sulfur
Aluminum sulfate (alum), $Al_2(SO_4)_3 \cdot 18H_2O$	6.94
Iron sulfate, $FeSO_4 \cdot 7H_2O$	8.69
Sulfuric acid, H_2SO_4	3.06

Caution – These acid-forming amendments including elemental sulfur (S) are typically recommended only if carbonates are present in the soil. Sulfuric acid can cause burns and must be used with care. Use of elemental sulfur also requires the presence of topsoil.

Stop



From Step 1
(page H-21)

Chemical amendment will be based on spilled material parameters*

Step 2B

Collect Data

Spill Area = sq ft

Volume Spilled = bbl

Total Dissolved Solids = mg/L

Sodium Concentration = mg/L

Sodium in mg/L is typically about 20%–35% of TDS in mg/L

Step 3B

Calculate Gypsum Equivalent and Requirement

(sodium in mg/L) × 6.94 × (bbl spilled) = meq Na spilled

The gypsum requirement in meq is equal to the meq Na spilled

(meq Na spilled) × 0.00019 = Total lb gypsum to apply to spill area

Stop

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