

Evaluation of Limiting Constituents Suggested for Land Disposal of Exploration and Production Wastes

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
AND
EXPLORATION AND PRODUCTION DEPARTMENT

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SECTION 1

INTRODUCTION AND EXECUTIVE SUMMARY

Onshore exploration and production (E&P) activities generate a limited variety of wastes. Ninety-eight percent of E&P waste (by volume) is composed of produced water, most of which is disposed of via Class II injection wells. The remaining 2% is composed of drilling wastes (drilling muds and wellbore cuttings that yield pit solids and liquids) and associated wastes which include production solids, tank bottoms, oily emulsions, and so forth. E&P wastes that are not recycled or managed at off-site facilities are commonly disposed of on site in pits or landspread over larger areas.

The objective of this study was to develop salinity and petroleum hydrocarbon threshold values for one-time landspreading, on-site burial, or road spreading of these E&P wastes. Definition, technical justification and guidance for the application of these threshold values is provided. Measurable parameters which serve as indices for proper management of salinity and petroleum hydrocarbons include: electrical conductivity (EC), sodium adsorption ratio (SAR), and exchangeable sodium percentage (ESP) for salinity; and oil and grease (O&G) for petroleum hydrocarbons.

The threshold guidance values generally recommended for land-applied waste:soil mixtures are EC <4 millimho per centimeter (mmho/cm), SAR <12, ESP <15%, and O&G <1%. The parameter

thresholds have been developed to be generally applicable for any waste containing salts or petroleum hydrocarbons including E&P wastes under ordinary conditions. Previous studies cited within this document provide supporting technical justification for selection of the threshold values.

In general, waste:soil mixtures that test below the threshold values are shown to have minimal impact to soil and vegetation for one-time applications. Yield reductions for many crops is less than 15% in the first year after application. Under certain restrictive conditions, the guidance threshold values have to be adjusted or crops temporarily changed to more tolerant species. Depending on drainage, crop cover, and soil amendments (gypsum and fertilizer), a soil with a loading no greater than that recommended should recover over a few seasons. **The operator must determine whether the guidance values apply over the short- or long-term, or whether site-specific conditions warrant more or less restrictive values.**

In general, the references cited within this report provide support for the recommended guidance values to avoid potential groundwater contamination. In addition, API is developing a contaminant fate and transport model to verify the appropriateness of the threshold values for a range of hydrogeologic environments found at E&P sites.

SECTION 2

TECHNICAL JUSTIFICATION AND LITERATURE REVIEW

2.1 Limiting Constituents

Salts and hydrocarbons have been identified as the principal limiting constituents of concern relative to onshore E&P operations because they may induce a phytotoxicity or, in the case of sodium salts, may deteriorate soil structure interrupting normal soil-plant-water relationships and causing excessive erosion (Miller and Honarvar, 1975; Ferrante, 1981; Freeman and Deuel, 1984; Nelson et al., 1984). Salts and hydrocarbons associated with E&P wastes may pose a significant threat to surface and groundwater resources when not properly managed (Henderson, 1982; Murphy and Kehew, 1984).

2.2 Salinity

Salinity is a general term reflecting the levels of available cations and anions in aqueous solution. Major ions include sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), chloride (Cl), sulfate (SO_4), bicarbonate (HCO_3), carbonate (CO_3) and hydroxide (OH). EC reflects the ionic strength or total level of these constituents, while SAR and ESP consider the influence that specific ions may have under particular circumstances.

2.2.1 Definitions

Charged particles in solution will conduct an electric current to an extent determined primarily by the concentration and type of ionic species present, hence the term electrical conductivity. EC is measured directly in reciprocal units of resistance and conveniently reported in mmho/cm. Since dissolved solids are predominately dissolved salts in the form of dissociated charged particles, EC may be used as an indirect, approximate measure of total dissolved solids (TDS).

TDS is defined in chemical terms as the unfilterable residue associated with aqueous fluids resulting from the evaporation of a known quantity of water, and is reported in terms of mass per unit volume (mg/liter). This residue is predominately composed of salts, but may include organic materials (humic substances or anthropogenic compounds) or mineral colloids passing through the filter.

An exact relationship exists between concentration of a specific salt in pure water and electrical conductance of that solution (Barrow, 1966). However, this relationship is inaccurate at high-salt concentration, solutions of mixed salt species, or presence of nonionic dissolved species. Of more immediate use have been empirical correlations between TDS and EC for various aqueous solutions:

$$\text{TDS} = (\text{A}) \times (\text{EC})$$

with the regression constant "A" (slope), being used as a conversion factor. Values of "A" have been found to range naturally from 540 to 960 cm.mg/mmho.liter (Hem, 1985). For naturally occurring saline/sodic soils a constant of 640 may be assumed (U.S. Salinity Laboratory Staff, 1954). Using the above equation, one calculates a TDS of 2560 mg/liter at a corresponding EC of 4 mmho/cm, and "A" of 640 cm.mg/mmho.liter. A recent analytical review of E&P wastes by the EPA (1987), and parallel review by the API (1987), suggested that an "A" value of 613 more accurately estimates TDS in E&P wastes when calculated from EC. This value is used in subsequent TDS calculations within this document.

TDS is generally not an accurate measure of salinity for many E&P wastes, due to errors associated with hydrocarbons and fine clay passing the filtration step. If one wants the perspective of salinity on a mass basis, it is best estimated from EC. EC has long been the parameter of choice in defining salinity hazards associated with production agriculture.

2.2.2 Concerns

2.2.2.1 Plants and Soil

Although some elements, such as boron, are toxic to plants, generally the ill effects of salinity are caused by increased osmotic pressure of soil solution in contact with plant roots (Haywood and Wadleigh, 1949; U.S. Salinity Laboratory Staff, 1954). Osmosis is a process that controls the movement of water between solutions and depends upon the number of dissolved molecules or ions (salinity). Water flows from lower to higher

osmotic pressure. Plants have an osmotic pressure associated with their cell solution which varies greatly between plant species and to some degree between cultivars within species. If the osmotic pressure in soil solution outside the plant exceeds that inside, the plants wilt. The point of permanent wilting is reached when the plant can not recover even when exposed to less saline water. There is a direct relationship between osmotic pressure and EC:

$$\text{Osmotic Pressure (OP), atm.} = 0.36 \times \text{EC, mmho/cm}$$

Salts also affect plants by disrupting normal nutrient uptake and utilization (Kramer, 1969). The mechanism is one of simple antagonism, whereby a given salt specie in excess inhibits the plant intake of required elements. The effect is usually manifested as a deficiency resulting in lowered yield expectations or overall crop quality.

There is no one critical or threshold salinity level where all plants fail to grow or maintain acceptable yields (Maas and Hoffman, 1977). General crop response to soil salinity is shown in Table 1 (U.S. Salinity Laboratory Staff, 1954). The sensitivities of various agricultural crops to salt are shown in Figures 1 through 3 generated from equations and data in Maas (1986). For example: At an EC of 4 mmho/cm, barley, cotton, and bermuda grass are not affected by salt, whereas yields are expected to decrease for rice and corn (0-15%), alfalfa and sugarcane (15-30%) and beans (30-50%). Yield response intervals shown in Figures 1 through 3 were developed from agricultural

Table 1. General Crop Response as a Function of EC.

(After U.S. Salinity Laboratory Staff, 1954)

EC (mmho/cm)	Effect on Crop Yield
0 - 2	None
2 - 4	Slight to none
4 - 8	Many crops affected
8 - 16	Only tolerant crops yield well
> 16	Only very tolerant crops yield well

systems receiving salt-containing irrigation over the long term and may overestimate the anticipated response for a one-time land disposal of E&P wastes. Based on Lunin (1967), the authors believe that salinity guidelines for continual use systems can reasonably be doubled for a one-time application; the rationale being that salt accumulated outside the bulk soil mass (in pores and on ped surfaces) is more easily displaced than that penetrated into and reacted with the bulk soil mass.

If the salinity is initially too high for a given crop after land applications of waste, soils will generally recover following rainfall or irrigation containing less salt because excess salts are leached when adequate drainage is present. Growth of more salt tolerant plants may be desirable during the interim

Fiber, Grain, and Special Crops

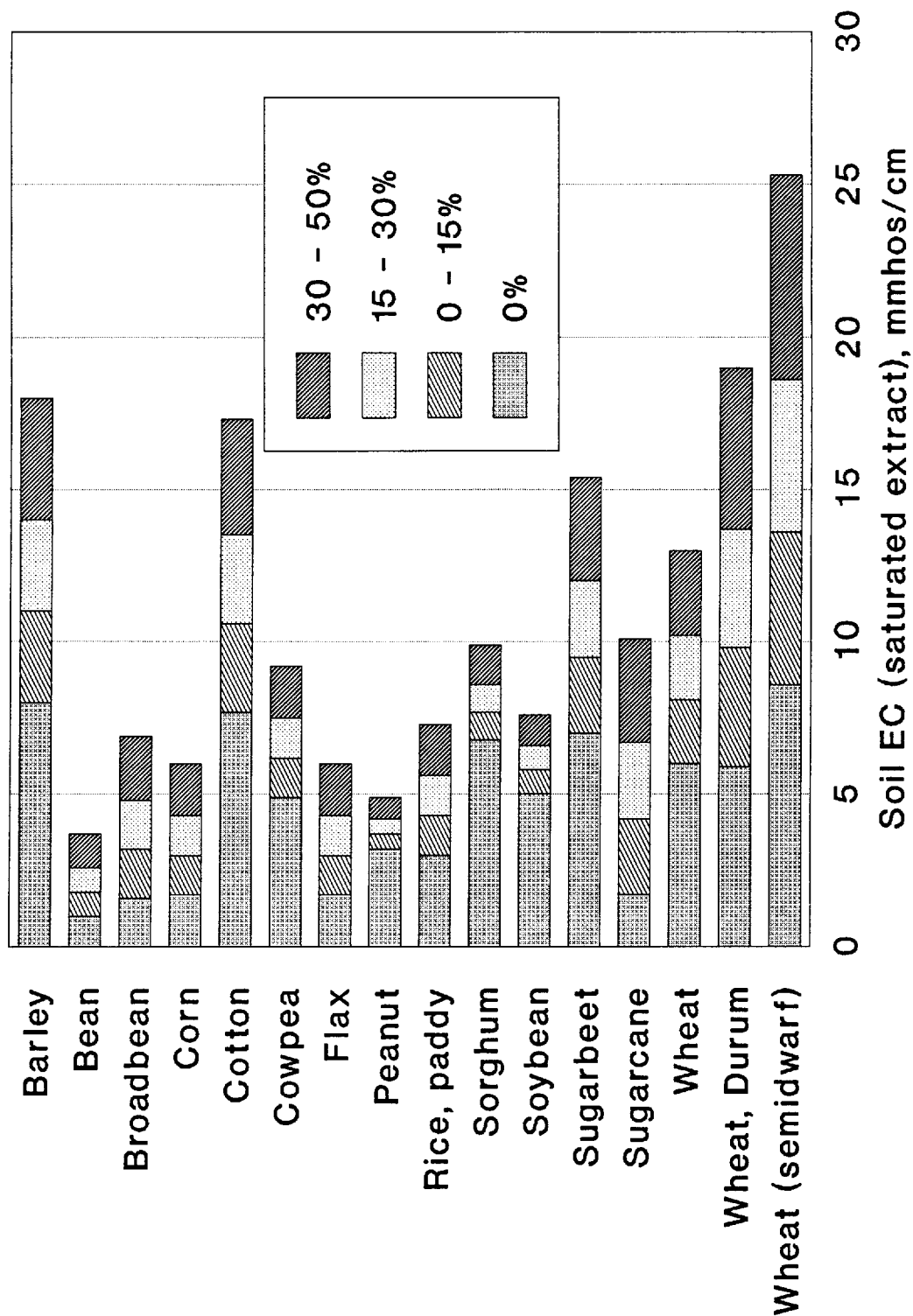


Figure 1. Yield decrease due to soil salinity (Maas, 1986)

Grasses and Forage Crops

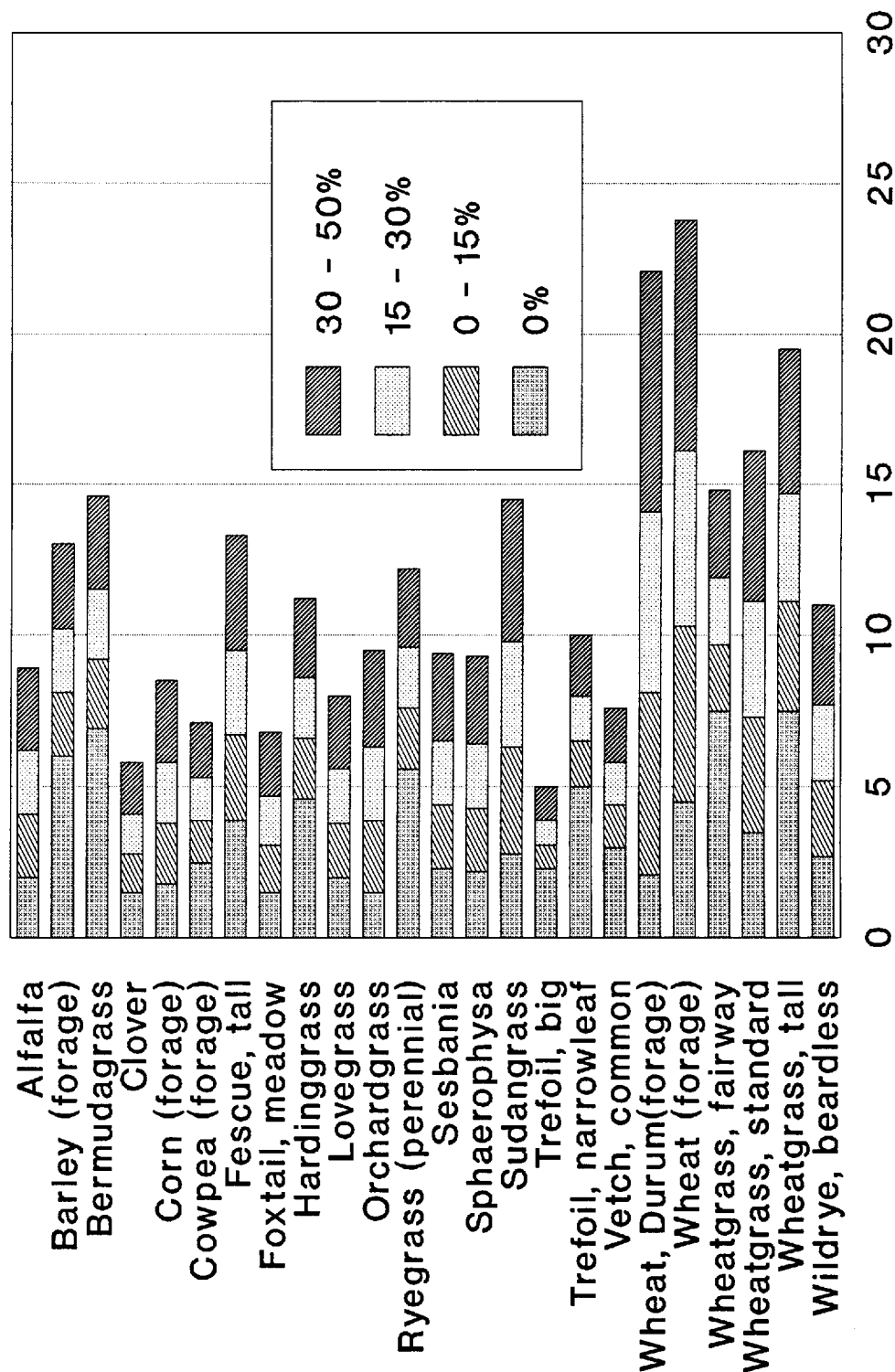


Figure 2. Yield decrease due to soil salinity (Maas, 1986)

Vegetable and Fruit Crops

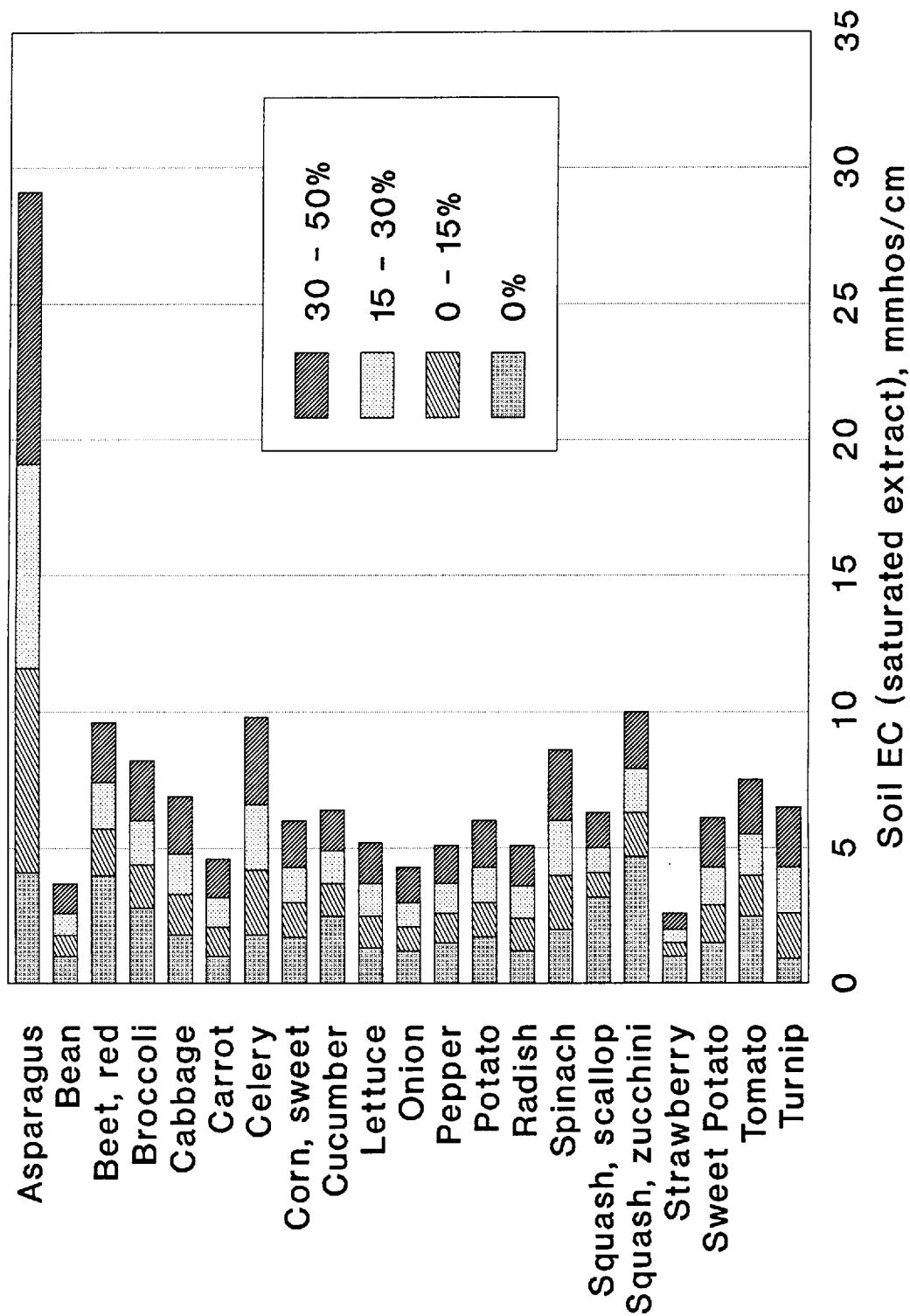


Figure 3. Yield decrease due to soil salinity (Maas, 1986)

between application and recovery (Foth and Turk, 1972). Reclamation of salt-containing soils may be hastened through the application of calcium sulfate (gypsum) which results in the replacement of exchangeable sodium by calcium (Oster and Rhoades, 1984). Plants grown on gypsiferous soils will tolerate an EC approximately 2 mmho/cm higher than those shown in Figures 1 through 3 (Mass, 1986). This is because gypsum is dissolved at moisture equivalents used in preparing saturated soil extracts for analysis but not at moisture equivalents normal to field conditions.

USDA Handbook 60 (U.S. Salinity Laboratory Staff, 1954) classifies water with EC values above 2.25 mmho/cm as unfit for agricultural purposes except under very special circumstances. Soils with salinity levels > 4 mmho/cm are considered saline. The recommended criteria of 4 mmho/cm is too high for the more salt sensitive crops (Table 1), and some adjustments may have to be made relative to intended land use. Miller and Pesaran (1980) found that high concentrations of soluble salts in mud-treated soil hindered plant growth in a 1:1 mud:soil mixture. Extracting their data where EC of the mud:soil mixture was < 8 mmho/cm, yield decreases averaged only 7% for green beans and 13% for sweet corn. Nelson et al. (1984) measured average yield decreases of 20% and 38% for swiss chard and rye-grass, where EC ranged from 6.3 to 18.6 mmho/cm. In these studies EC was above the recommended criteria of < 4 mmho/cm. Tucker (1985) reported adding drilling mud with resulting EC values from 1.3 to 5.3

mmho/cm with no adverse effect on bermudagrass and at 1.7 mmho/cm with no adverse effect on alfalfa. He also reported a significant decrease in EC with time following application, reflecting the leaching of salts out of the root zone.

The expected yield decrease associated with a one-time EC application guideline of 4 mmho/cm is <15% for most crops. In those cases where precipitation, drainage, or crop type places special restrictions on waste management, some adjustments may have to be made relative to waste addition levels or intended land use while the soil recovers.

2.2.2.2 Water Resources

In areas of net infiltration, the soluble salts are transported from the surface to lower soil zones. Murphy and Kehew (1984) found that soluble salts from a pit containing saturated brine drilling fluids (EC > 200 mmho/cm) posed a threat to localized groundwater resources. However, the EC of 200 mmho/cm greatly exceeds the recommended threshold of 4 mmho/cm. Bates (1988), working with a freshwater drilling fluid, demonstrated that Cl was not retained in the zone of incorporation when mixed with surface soil.

The criteria of 4 mmho/cm (2452 mg/liter TDS for "A" = 613) can be expected to have no measurable impact on groundwater even in the most sensitive hydrological settings. Water and associated dissolved constituents do not move through soils as an isolated unit (plug flow), instead there is a natural redistribution controlled by water potentials, pore dynamics, dispersion, and

diffusion (i.e., chromatographic effect). Recent field research studies conducted by Owens et al. (1985) and Bruce et al. (1985) perhaps best illustrate this principal in that they were conducted at concentrations comparable in magnitude to the 4 mmho/cm threshold. Both studies observed the redistribution of surface-applied bromide (Br) by rainfall infiltration and percolation.

The Owens group demonstrated better than a 7-fold decrease in Br after passing through only 2.4 m of well-drained silt loam and fractured shale due to attenuation processes mentioned above. Under conditions similar to their study, a surface loading of NaCl equivalent to 4 mmho/cm (2452 mg/liter TDS) would result in an EC < 0.6 mmho/cm and corresponding Cl of < 213 mg/liter at a depth of 2.4 m. Bruce et al. (1985) showed Br redistribution from as great as 1800 mg/liter at the surface to < 20 mg/liter below a depth of 3 m after nearly 4 years and 4.7 m of rainfall. The Br level was 100 mg/liter at a depth of 1.5 after 4 years with none detected below 3.8 m. If one substitutes Cl for the Br salts used in these studies it becomes apparent that percolating water will be at or below the EPA secondary drinking water quality standard of 250 mg/liter Cl (40 CFR, Part 143, Sec. 143.3) within a few feet of the source at controlled land applications (EC < 4 mmho/cm).

2.2.3 Criteria

In summary, the EC criteria of 4 mmho/cm based on a one-time application serves to protect vegetation, land and groundwater resources at most drilling and production locations, including

those located in sensitive regions, if amenable to a temporary adjustment in plant species. The criteria may be adjusted to meet special requirements.

2.3 Sodicity (ESP and SAR)

2.3.1 Definitions

2.3.1.1 Exchangeable Sodium Percentage (ESP)

The capacity of a soil to adsorb positively charged ions (cations) is called the cation exchange capacity (CEC) and may be expressed in meq/100 g.

It follows that the exchangeable cations in a soil are those positively charged ions held on the surface exchange sites and in equilibrium with the soil solution. The major cations calcium (Ca), magnesium (Mg), sodium (Na), and K (potassium) are called basic cations, and the percentage of the CEC occupied by these cations is called the base saturation. Fertile soils have a base saturation greater than 80% with the cations distributed mainly as Ca and Mg.

ESP is a measure of the degree to which the soil exchange sites are saturated with sodium and is calculated as follows:

$$\text{ESP, \%} = (\text{NaX} / \text{CEC}) \times 100$$

where NaX (exchangeable Na) and CEC are expressed in meq/100g.

2.3.1.2 Sodium Adsorption Ratio (SAR)

Ca and Mg are generally needed in relatively large amounts to maintain good soil structure (physical status relative to tilth and permeability) and fertility, but they form salts of low solubility in soils. Na salts are much more soluble and readily dominate soil solutions, often with a detrimental impact.

SAR is an empirical mathematical expression developed by the USDA Salinity Laboratory as an index to detrimental sodium effects in soils (U.S. Salinity Laboratory Staff, 1954). SAR is computed as follows:

$$SAR = Na / \sqrt{(Ca + Mg)/2}$$

where concentrations are expressed in meq/liter. Concentrations are determined by direct chemical analysis of pit liquids or aqueous extracts of waste solids or soils. An empirical equilibrium expression developed by the USDA Salinity Laboratory relating the ESP of the solid phase to the SAR of irrigation water or soil solution is given below:

$$ESP = 100 (-.0126 + .01475 SAR) / 1 + (-.0126 + .01475 SAR)$$

2.3.2 Concerns

High Na levels (SAR >12) in soil solution cause Ca and Mg deficiencies in plants by both antagonistic reactions and shifting of solubilities by common ion effect (Kramer, 1969; U.S. Salinity Laboratory Staff, 1954).

Soils reacted with solutions of high SAR are at risk of becoming sodic. A soil is termed sodic when the ESP exceeds 15% of the CEC (U.S. Salinity Laboratory Staff, 1954). The most distinguishing feature of sodic soils is their lack of structure and tendency to disperse in water. A dispersed soil condition has a devastating impact on plants by limiting the free exchange of air and infiltration of water (Reeve and Fireman, 1967; Bresler et al., 1983).

Research conducted by Tucker (1985) involving land disposal of waste drilling fluids indicated that $SAR < 10$ and $ESP < 15\%$ are required for maintaining good soil structure and normal plant growth. Miller and Pesaran (1980) measured ESP for 1:1 and 1:4 mud:soil mixtures and found average yield decreases of 12% for green beans and 20% for sweet corn at an average ESP of 11.5%. These results are from samples with ESP ranging from 0.6-19.7% and $EC < 8$ mmho/cm.

SAR is somewhat less critical in that it represents the more easily altered solution phase. Deuel and Brown (1980) showed that the detrimental effect for water with an EC of 2.6 mmho/cm and SAR of 16.1 was directed proportionate to the solid-phase Ca in receiving soil. The occurrence of appreciable amounts of gypsum in the soil, either naturally or by amendment, may permit the disposal of highly sodic E&P wastes, particularly if the ionic strength of total salt is relatively low. Freeman and Deuel (1984) reported the successful pit closure in terms of the soil and plant environment ($SAR < 15$, $ESP < 15\%$) by land disposal of E&P waste solids with SARs > 200 and $ESP > 90$, when salinities were < 4 mmho/cm. Treatment consisted

of blending waste solids with native soils at chemically defined mix ratios in conjunction with gypsum and fertilizer amendments.

2.3.3 Criteria

Therefore, the API Environmental Guidance Document recommends a SAR of <12 and ESP of <15% for a single application land disposal of E&P wastes. These values are widely accepted thresholds recommended by the USDA for preventing soil sodicity (U.S. Salinity Laboratory, 1954). Field and laboratory studies with drilling muds have also shown them to be reasonable values.

It is important to note that guidance values pertain to final disposition or closure status: These values do not limit the composition of the wastes that can be land disposed. However, operators must be prepared to provide necessary management inputs for wastes applied to land in exceedance of recommended values.

2.4 Hydrocarbons

2.4.1 Composition and Analysis

Crude oil and diesel are the principal hydrocarbons associated with E&P wastes (Miller et al., 1980; Thoresen and Hinds, 1983; Whitfill and Boyd, 1987). They are sometimes added to water base drill systems to lubricate the drill bit and pipe string. O&G levels in freshwater drilling wastes are generally < 4% (Freeman and Deuel, 1986). Other E&P waste such as tank bottoms, emulsions, and oil-contaminated soil may have higher concentrations of O&G.