ASSESSMENT AND REMEDIATION OF EARTHEN PITS ASSOCIATED WITH OIL AND GAS PRODUCTION IN ALBERTA

Soil Protection Branch
Wastes and Chemicals Division
Alberta Environment

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Code of practice for the land treatment of soil containing hydrocarbons

KEA 421 C669 L23 2001 Draft

2. Alberta soil and water quality guidelines for hydrocarbons at upstream oil and gas facilities, 3 volumes

TD 195 P4 A299 2001 Draft Also available on the Internet

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Introduction

Flare and blowdown pits are a common feature at older well sites, compressor stations and pumping batteries throughout Alberta. Most such pits are simple excavations lacking liners or other containment features, which receive wastes such as condensates (combusted or non-combusted), blowdown from well workovers and other maintenance tasks, production water and small volumes of miscellaneous fluids. These waste pits are largely obsolete and many companies are decommissioning and replacing them with superior technology such as flare stacks. It is important, however, that decommissioning of pits be conducted in an environmentally sound manner and there is a need for general guidance on procedures for assessment and remediation steps.

This document provides a framework for contaminant assessment and it's use in identification of remedial options. Particular attention is paid to potential roles for land treatment and backfilling. These operations are likely to be considered early in the decommissioning process because of their perceived economy and frequent historical use. Whereas land treatment is expected to play a role in future decommissioning, it is appropriate only in certain instances and is but one of many tools available to the land manager. Because inappropriate spreading of wastes on land damages soil that currently is not degraded, it is paramount that circumstances leading to this result be avoided. Proposals following are designed to minimize the occurrence of unnecessary environmental damage.

Guiding Concepts

The framework developed below is guided by the environmental objective of preservation or restoration of *equivalent capability* on the leased land. Therefore decommissioning of a pit or pond now must not compromise land capability in future.

In the case of earthen pits located on agricultural land, the principal capability that must be recovered is the ability to sustain, at approximate pre-construction yields, crops or forages that are suitable for human or animal consumption, respectively. Such suitable crops and forages will contain contaminants below concentrations at which any adverse health effects would be expected.

Other important aspects of environmental quality embodied in the equivalent capability concept include protection of 1) soil biota, and 2) groundwater chemistry.

The approach taken to achieve decommissioning objectives is entirely of the proponent's choice and creative solutions are desirable. The framework presented in this document strives to minimize land management errors through a phased characterization-decision tree. It is not an endorsement of any particular remediation technology.

Terminology

Land treatment as discussed in this document is defined as a once-only implementation of:

An accepted waste treatment option, which through planning and controlled management of optimized surface soil-waste mixing, utilizes recognized inherent soil processes (biotic, abiotic) to dissipate organic waste constituents and decomposition/transformation products. Carbon dioxide, water and nontoxic residue compounds are the expected products.

Land treatment is <u>not</u> equivalent to: 1) landfarming, which involves serial spreading and manipulation at a planned, dedicated and monitored facility, or 2) land disposal aimed at dilution of non-degradable wastes through mixing with un-contaminated soil - including "squeezing out".

Overview of Approach

A phased approach to assessment of pit and lease, and identification of remedial options is presented in Figure 1. In the *Preliminary Assessment Phase* fundamental information on the quantity and quality of both lease and pit is gathered. The type of information gathered is aimed at early identification of land treatment incompatibilities so as to minimize investment in analyses tailored to this assumed remedial option. A preliminary assessment may lead to classification of a pit as a candidate for land treatment, in which case a *Salinity-Sodicity-Acidity (SSA) Assessment Phase* may be entered. In this phase information on the amount and type of salts present and pH of the pit material is gathered and evaluated. This information is necessary to protect: 1) plants from osmotic shock, 2) soils from dispersion and other structure problems, and

3) against increases in the mobility and bioavailability of toxic metals. Again, a pit may emerge from the SSA assessment as a land treatment candidate and, if so, would finally be subjected to an *Organics Assessment Phase* wherein a screen for highly toxic and poorly bioremediated organohalogens is performed and, for hydrocarbons, an index of biodegradability is obtained.

Preliminary Assessment

Steps in the Preliminary Assessment are outlined in Figure 2. The first job in this phase is to evaluate the site for land treatment suitability. The general properties of sites appropriate for land treatment are discussed in the draft Guidelines for Land Treatment of Industrial Waste (Alberta Environment 1992). Briefly, an appropriate site is characterized by good but not excessive permeability (saturated hydraulic conductivity), a seasonally high water table at a depth of at least one meter; and for the 0-15 cm depth of soil, moderate to high cation exchange capacity, pH in the range 6.5 to 8.5. In addition, sodium adsorption ratio (SAR) should not exceed 6. Taken together these requirements eliminate all organic or podzolic soils and many gleysolic or solonetzic soils. Classification of soils (Agriculture Canada Expert Committee on Soil Survey 1987) and evaluation against the appropriate soil survey report (surveys to 1985 summarized in Alberta Energy and Natural Resources 1985) is an efficient means of gathering the necessary site information while reducing laboratory analysis.

Given that the lease site has acceptable properties for land treatment, system capacities must be determined. The mass of contaminated material considered for land treatment is calculated from the bulk density and the depth and lateral dimensions having oil and grease concentrations in excess of 0.1%. Specifically, the mass in tonnes is the product of the bulk density (tonne m⁻³) and the waste volume in m³. The waste mass is then compared to the area available for treatment to determine whether sufficient capacity exists. An acceptable spread rate of 750 tonne ha⁻¹ is based on a nominal waste bulk density of 1 and remedial depth of 15 cm, of which 50% is waste material.

^{*} more recent soil surveys available from: Agriculture Canada - Soil Survey 653 Terrace Plaza Tower 4445 Calgary Trail South Edmonton, Alberta T6H 5R7

If the mass of material to be remediated exceeds the acceptable loading rate it may still be attractive to perform land treatment up to the recommended limit and find alternative treatment/disposal for the remaining waste.

Assuming a favorable waste/lease area ratio, assessment now proceeds to a consideration of the potential metal loading. This is accomplished by calculating the mass-weighted mean of strong acid-digestible metal concentrations in the waste and lease surface soil. For example, given the following waste and lease properties one may estimate the Cu loading:

Waste Characteristics	Lease Characteristics	
[Cu] = 120 ppm = 120 g tonne ⁻¹	[Cu] = 20 ppm = 20 g Tonne ⁻¹	
mass = 110 tonne ($\approx 100 \text{ m}^3$)	surface bulk density = 1.0 tonne m ⁻³	
	potential landspreading area = 40 m X 50 m	

1. Lease area

$$40 \text{ m X } 50 \text{ m} = 2000 \text{ m}^2 = 0.2 \text{ ha}$$

2. Spread capacity

110 tonne waste/ $0.2 \text{ ha} = 550 \text{ tonne ha}^{-1}$

- 3. Depth of waste after spreading
 - assume waste and receiving soil managed to bulk density = 1 tonne m^{-3} 110 tonne/ 1 tonne m^{-3} = 110 m^3 waste

$$110 \text{ m}^3 / 2000 \text{ m}^2 = 0.055 \text{ m} = 5.5 \text{ cm}$$

- 4. Mass of lease soil
 - assume depth of remedial system = 15 cm

depth of lease soil = 15 cm - 5.5 cm = 9.5 cm = 0.095 m
mass = density X volume
=
$$(1 \text{ tonne m}^{-3})(0.095 \text{ m X } 2000 \text{ m}^2) = 190 \text{ tonne}$$

5. Expected [Cu] in remedial system

[Cu] =
$$\frac{20 \text{ g tonne}^{-1} \text{ X } 190 \text{ tonne} + 120 \text{ g tonne}^{-1} \text{ X } 110 \text{ tonne}}{190 \text{ tonne} + 110 \text{ tonne}}$$

= 56.7 g tonne⁻¹ = 57 ppm

In this illustration the result for Cu is well within draft Alberta Tier I Guidelines and therefore would not restrict a land treatment exercise. Parallel calculations must be carried out for all metal contaminants.

6

Assuming no metals are limiting to land treatment, the oil and grease content of the potential remedial system is now calculated in a similar fashion. If oil and grease in the proposed remedial system is below 2%, land treatment remains a possible option and consideration should now be given to salinity, sodicity and acidity concerns.

Salinity-Sodicity-Acidity (SSA) Assessment

The SSA assessment provides information necessary to 1) protect surface soil from degradation in physical properties, 2) prevent accumulations of salts that adversely affect plant growth, and 3) control bioavailability and mobility of heavy metals. Poor soil physical properties promote overland flow of precipitation and meltwater, which mediates off-site movement of hydrocarbon contaminants and reduces plant available moisture. Soils with EC>4 are classed as saline (SSSA 1984) and affect salt-sensitive vegetation. High osmotic potentials in such soils constrain water uptake by many plants, including agronomic species. In addition, saline soils with high chloride contents may have significantly increased mobility of certain heavy metals owing to the formation of low charge-to-radius ratio ion pairs (Sposito 1989). Finally, low soil pH increases movement and bioavailability of most heavy metals by raising their solubilities.

The following discussion assumes a non-saline lease surface soil and a loading of pit waste at the maximum rate of 750 tonne ha⁻¹.

SSA assessment begins with the determination of electrical conductivity (EC) and pH (Figure 3). If EC exceeds 4 the waste is saline and inappropriate for land treatment unless desalinized. Electrical conductivities greater than 12 suggest salinization to levels that may: 1) be a hazard to plants even when left at depth, and 2) have caused or will cause a saline plume in groundwater. Where pit EC>12 amount and origin of

salts should be determined through chloride analysis and assessment of salinity status at a control location out of the zone of potential influence from the pit. Once extent and origin of salinization is known the need for further action, if any, can be assessed.

If EC is between 2 and 4 some sulfate or chloride salts are present and may or may not be of concern depending on the balance among basic cations. For wastes in this range it is recommended that the sodium adsorption ratio (SAR) be determined. If SAR < 6 there is little danger of clay dispersion and acidity assessment may proceed. If, however, 6 < SAR < 10 management of sodicity will be necessary if the waste is to be land treated. Gypsum (CaSO₄) has been an effective amendment to manage sodicity in Alberta soils. Wastes with SAR > 10 are considered unsuitable for land treatment because, even with gypsum amendment coupled to scheduled irrigation, a prohibitive amount of time is required to effect improvement in SAR and structure (Alberta Environment 1987).

In situations where the amount of suitable pit waste is small and therefore, loading of contaminated material to the lease surface is less than the maximum of 750 tonne ha⁻¹, the salt tolerance can be increased. As a first approximation the electrical conductivity and SAR of a potential remedial system may be calculated as the mass-weighted means of those properties recorded in the pit waste and lease surface soil. However, due to the non-linear relationship between SAR and basic cation concentrations, as well as lack of additivity across composites in soil properties affecting soluble ion status, calculations of EC and SAR in a potential remedial system should be made more rigorously when the outcome of a first approximation calculation breaches or approaches the management criteria of EC<2 and SAR<6. A computer program that performs robust mixing calculations to support a potential land treatment exercise is under development through the Reclamation Research Technical Advisory Committee (RRTAC). It is expected that this tool can be modified to accommodate calculations necessary for the consistent application of this Guideline.

Assuming salinity concerns, if present, are manageable the waste acidity must be assessed. Waste pH should be between 6.5 and 8.5. Acidic waste can be ameliorated with high grade lime (low dolomite content). It is unlikely that many pits having salinity problems will also be acidic.

If management of salts and acidity is expected to be successful assessment now proceeds to characterization of organic components.

Organics Assessment

Organics assessment is undertaken for three reasons. First, a mechanism is needed to limit human and environmental health hazard resulting from spreading of high toxicity organohalogens. Second, confirmation is needed that organic contaminants are susceptible to biodegradation within a reasonable time frame. Third, some indication of the inherent toxicity and potential for off-site movement of contaminant hydrocarbons is provided that may temper the choice of management system.

A history of use of certain organohalogens at a lease, as indicated by a thorough search of management records, leads to an extractable organic halogens (EOX) screen (Figure 4). Not all organohalogens pose a concern for surface bioremediation. Targeted organohalogens are mainly those that appear on the U.S. EPA priority pollutants list -- for example, PCBs, banned or de-listed sterilants or biocides such as chlordane, lindane, 1,3 dichloropropene, DDT etc. Continuous operation of transformers, compressors, or hydraulics that used PCBs should be considered a positive history for priority halogenated organics use. Use of short half-life organohalogens does not indicate a need for the EOX test unless evidence exists that mismanagement of these has occurred. If an EOX screen is carried out and concentrations in excess of 2 ppm are found it is necessary to identify the source. If the source compound(s) is found to be of low toxicity to humans, is known to biodegrade, and is in sufficiently low concentration (e.g. 2,4-D) land treatment may remain as an option. If, however, the organohalogens are either high toxicity, non-degradable, or both, land treatment is an inappropriate practice.

Fractionation Characterization

Assuming organohalogens are not a factor on the site, a final recommended step is to confirm that hydrocarbons in the waste material can be successfully managed through land treatment. This information can generally be obtained through treatability studies but may be bypassed provided certain patterns exist in proximate chemical analyses in a fractionation characterization (e.g. Williams 1981, Fuhr et al. 1988). On the basis of differing polarity and therefore, mobility in different solvent systems, fractionation characterization separates hydrocarbon constituents into broad classes: asphaltenes,

saturates, resins (or polars) 1 and 2, and aromatics. The balance among these fractions can be used to give a qualitative to semi-quantitative prediction of 1) biodegradation rates, and 2) potential risk of toxic exposure or off-site transport.

Interpretation of results of fractionation characterization procedures relies on: 1) the generalized chemical composition of the fractions, and 2) knowledge of the fate, transport and toxicity of these components. The general composition found in oily wastes for the fractions listed above are as follows:

Saturates. Mixture of straight-, branched-chain and cyclic alkanes and alkenes.

- Aromatics. Mono- and polycyclic aromatic hydrocarbons lacking heteroatoms. Examples include toluene, naphthalene, phenanthrene, benzo[a]pyrene, fluorene, chrysene, and substituted PAH such as 7,12-dimethylbenzanthracene.
- Polars 1. Relatively low molecular weight (compared to asphaltenes) amorphous polymers of various hydrocarbons including alcohols, acids and hydroxyacids; fatty acids.
- Polars 2. N- and S-rich heterocyclic aromatic compounds including pyrroles, quinolines, diazoles, carbazoles, thiophenes, benzothiophenes and thiazoles.
- Asphaltenes. Complex, highly condensed, high molecular weight, heterogeneous hydrocarbons including both aliphatic and aromatic structures. Very poorly characterized due to lack of appropriate purification and separation technology.

Discussion of the intrinsic and environmental factors regulating biodegradation rates of substances listed above can be found in Atlas (1981), Leahy and Colwell (1990), Sims et al. (1990) and Blum and Speece (1991). In soils relying on a native microbial community the following patterns normally prevail:

- Saturates. Intermediate to short chain unbranched alkanes and alkenes rapidly degraded. Very long (= C25 and greater) straight chain compounds less degradable. Branched chain, especially methyl-substituted, alkanes more resistant. Cyclic alkanes slowly degraded.
- Aromatics. Aerobic biodegradability inversely related to molecular size and, therefore, numbers of fused rings. Essentially non-degradable under anaerobic

conditions. Many 4, 5 and 6 ring PAH are both poorly degradable (half-life > 100 d) and carcinogenic. Benzene both mobile and a confirmed carcinogen.

- Polars 1. Fatty acids rapidly degraded, amorphous resins less degradable but varies with molecular size.
- Polars 2. Many compounds in this category are highly toxic or carcinogenic and degrade very slowly under aerobic conditions. Under anaerobic conditions degradation is negligible.
- Asphaltenes. Very slowly degraded due to lack of regular pattern in chemical structure, hydrophobicity, and very high molecular weight.

Kinetic Analysis

Mathematical description of the time-course of contaminant dissipation is a type of kinetic analysis. Kinetic studies in a variety of environments provide a basis for prediction of contaminant fate in, as yet, unstudied environments. Currently, availability of kinetic data is limited for all but polyaromatic compounds.

Aromatic fractions contain, and can be dominated by, polycyclic aromatic hydrocarbons; whose biodegradation kinetics have recently been studied in detail. Park et al. (1990) found that half-lives of PAH with four or more rings varied from about 200 to 400 d in two sandy loam soils incubated at 25° C. Even greater half-lives were reported by Coover and Sims (1987) for PAH in agricultural soils that were incubated 240 d. Half-lives are influenced by soil moisture and temperature as well as management factors such as nutrient and organic matter additions. Manipulation of nutrients and organic matter can double the decomposition rate (Sims et al. 1990), however, under field conditions in Alberta lack of moisture and low temperatures may offset such gains.

Management of a potential bioremedial system can be improved by combining fractionation/characterization information with biodegradation kinetic parameters for representative constituent compounds. Asphaltenes may be used as an example. Studies in the Soil Protection Branch and elsewhere indicate that the asphaltenes are probably even more slowly degraded than PAH. Assuming a soil concentration of 2% oil and grease, 40% of which is asphaltenes (8000 ppm) with a first order half-life of 300 d the following analysis may be applied:

The rate of asphaltene dissipation is given by

$$\frac{dC}{dt} = -kC$$
 [1]

where

C = concentration of asphaltenes in soil at time, <math>t = t

k = first order degradation constant

Integration of [1] yields

$$C = C_0 e^{-kt}$$
 [2]

where

 C_0 = concentration of asphaltenes in soil at time, t = 0

e = base of natural logarithms

Taking logarithms and rearranging [2] we have

$$t = \frac{\ln C_0/C}{k}$$
 [3]

The half-life is defined as the time required for the initial concentration to be halved (i.e. $C_0/C = 2$)

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$
 [4]

Rearranging [4] to solve for k given $t_{1/2} = 300 \text{ d}$

$$k = \frac{0.693}{300} = 0.00231 \text{ d}^{-1}$$

And the time required to reduce asphaltenes to a concentration of 0.1% (1000 ppm) may be calculated from [3]:

$$t = \frac{\ln(8000/1000)}{0.00231} = 900 \text{ d}$$

Because Alberta climatic conditions provide for no more than 8 months (240 d) when soil temperatures allow any significant biodegradation, land treatment of contaminated soil in the above example could be expected to require 4 years -- assuming other fractions have a negligible contribution to total extractable hydrocarbons at the end of this period.

Similar calculations may be carried out for other hydrocarbon fractions. Mean kinetic parameters must be nominated for fractions based on available literature and combined with masses determined from the fractionation characterization and gross hydrocarbon data (oil and grease or total extractable hydrocarbons). The greatest management benefit is likely to be achieved by concentrating on recalcitrant fractions that are most likely to limit bioremedial success (i.e. asphaltene, aromatic, polar 2 fractions).

The above information leads to the following generalizations for hydrocarbon contaminated soils:

- 1. Bioremedial success expected to be greatest when saturates, polar 1 and low molecular weight aromatics predominate.
- 2. Systems with high concentrations of polar 2 or high MW aromatics should not be applied to land without treatability studies establishing fate of parent compounds and toxicity time-course as related to production of intermediates.
- 3. Systems with high concentrations of asphaltenes may be remediated by land treatment but time required (years) may be unacceptable. Treatability study is indicated.

Because information from fractionation characterization may be inconclusive, a proponent may wish to perform waste-specific treatability studies in order to identify appropriate management practice and predict remediation progression.

Treatability Studies

Treatability studies can establish whether a proposed bioremedial method can deliver the degree of clean-up required for the particular waste and site under consideration. The studies can be carried out in laboratory microcosms or in the field. Whether such studies are a useful alternative to other remedial options such as excavation and disposal, incineration, solvent extraction etc. will depend on factors such as the site sensitivity, mass of waste, access to treatment or disposal facilities, time available for remediation, and desired remedial endpoint.

Procedures in common use for treatability studies are discussed in Sims et al. (1990) and Sims (1990). These papers stress that treatability studies are most useful in comparing performance of management alternatives. Normally, such comparisons are made under optimum conditions and therefore, if a particular system cannot achieve desired levels within an acceptable time frame in the testing environment, it is highly unlikely that performance will be acceptable in the field. Management factors for land treatment systems that might be explored in treatability studies include contaminant loading, nutrient element additions, aeration, and organic matter amendments.

Alternative Remedial Options

Characterization will show some pit wastes to be inappropriate for land treatment. Remediation technologies for wastes containing high concentrations of heavy metals, salts, or hydrocarbons have recently been evaluated by the Canadian Petroleum Association (CPA 1989, CPA 1990). Options include soil washing, solvent extraction, ex-situ bioremediation, thermal desorption/incineration, stabilization/solidification, land disposal in a secure landfill.

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Appendix - Characterization Parameters and Methodology

Analytical Parameter	Procedure Outline	Reference
bulk density	core method	McKeague 1978
cation exchange capacity (CEC)	NH ₄ ⁺ determined by AutoAnalyzer or equivalent colourimetric method	Rhoades 1982, Technicon Industrial Method No. 98- /70WA 1977
electrical conductivity (EC)	measured on saturated paste extract with conductivity cell	APHA. 16th ed. 1980 Standard Methods
extractable organic halogens	after extraction total halides determined by neutron activation analysis	Helmke 1982
fractionation characterization	separated into several fractions by chromatography on alumina column (or on Amicon Sep-Pak cartridges containing neutral alumina) using eluting solvents of increasing polarity	Williams 1981, Fuhr 1988
oil and grease	measured gravimetrically after Soxhlet extraction with methylene chloride	McGill and Rowell 1977
pH	2:1 slurry in 0.01 M CaCl ₂	McKeague 1978
saturated hydraulic conductivity	core method	McKeague 1978
saturated paste and paste extraction solution	prepared by USDA Soil Salinity lab method. Vacuum filtered through 0.45 µm Millipore	USDA 1954, Rhoades 1982
sodium adsorption ratio (SAR)	calculated from soluble ions in saturated paste extract	McKeague 1978
total elemental analysis (heavy metals)	ICP-AES preceded by strong acid digestion	McKeague 1978 or Abboud 1988

Additional Methodological References

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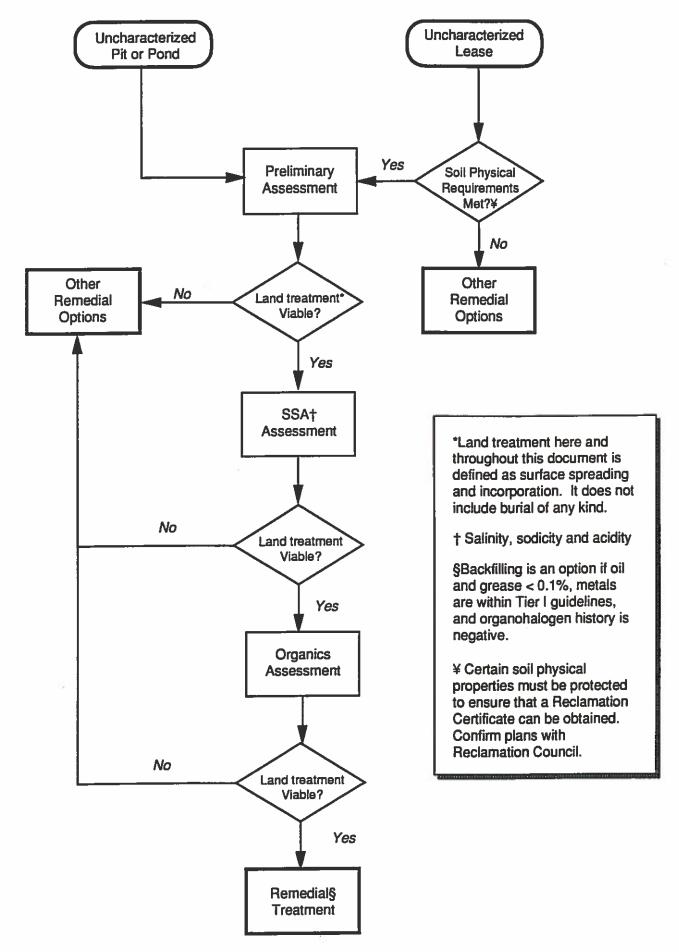
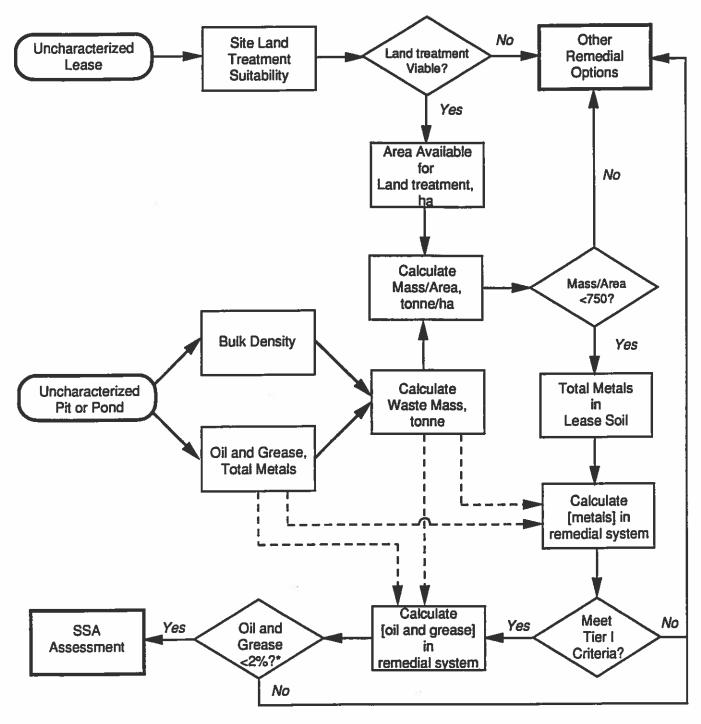
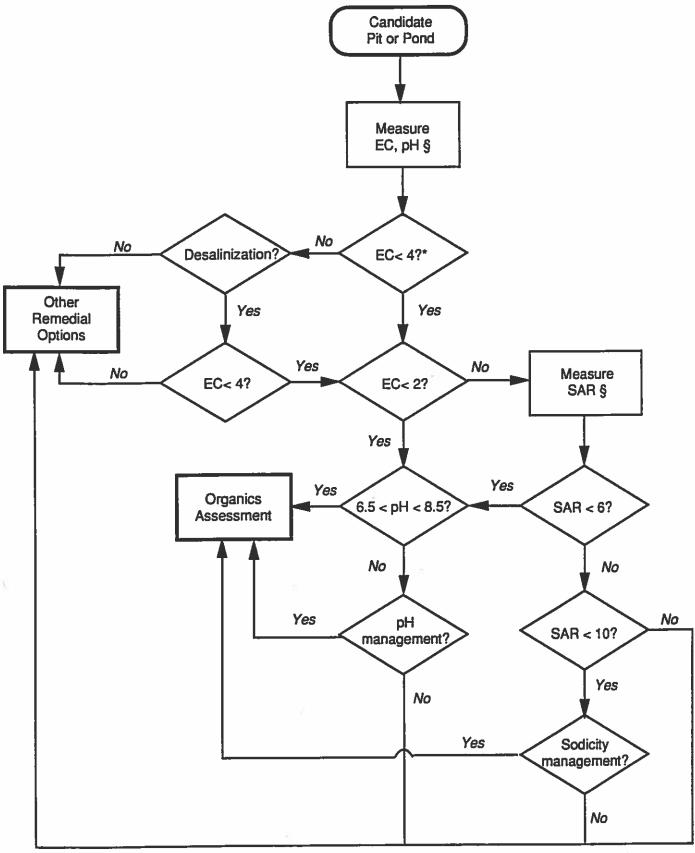


Figure 1. Proposed approach to characterization and identification of remedial options, including land treatment, for earthen pits associated with oil and gas production



^{*}Backfilling is an option if oil and grease < 0.1%, metals are within Tier I guidelines, EC<12, and organohalogen history is negative.

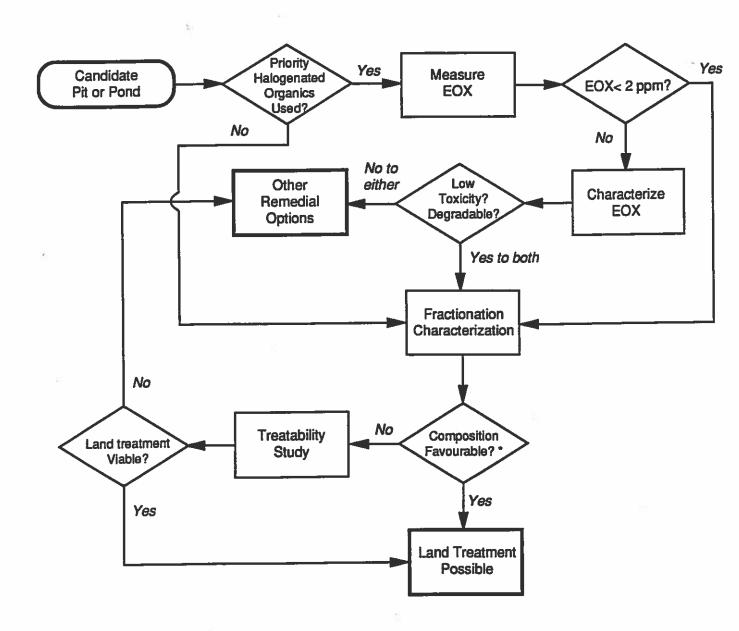
Figure 2. Preliminary assessment for evaluation of land treatment as a remedial option for earthen pits and ponds associated with oil and gas production



§ Waste criteria based on maximum loading rate of 750 tonne/ha. See text for procedures for lower loading rates.

Figure 3. Assessment of salinity, sodicity and acidity for evaluation of land treatment as a remedial option for earthen pits and ponds associated with oil and gas production

^{*} If EC>12 further investigation of salt types and distribution is necessary



^{*} Interpretation of balance among fractions is discussed in Guideline.

Figure 4. Assessment of organic contaminants for evaluation of land treatment as a remedial option for earthen pits and ponds associated with oil and gas production