Kill•Spill

Integrated Biotechnological Solutions for Combating Marine Oil Spills

Deliverable D8.6

Experimental protocol for ex situ sand treatments

This project is supported by the European Union under the Food, Agriculture and Fisheries and Biotechnology theme of the 7th Framework Programme for Research and Technological Development under GA no. 312139

Work package	WP8 Field Testing of Most Promising Technologies and Benchmarking with existing products
Deliverable no	D8.6
Deliverable title	Experimental protocol for ex situ sand treatments
Due date:	Month 30 (2015-06-30)
Actual submission date:	Month 33 (2014-10-05)
Start date of project:	2013-01-01
Deliverable Lead Beneficiary (Organisation name)	Technical University of Crete
Participant(s) (Partner short names)	TUC
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Dissemination Level: (PUblic, Restricted to other Programmes Participants, REstricted to a group specified by the consortium, COnfidential only for members of the consortium)	PU
Deliverable Status:	final

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1 About this deliverable

This protocol is a guide for anyone who needs to conduct ex-situ treatment of oil polluted sand through landfarming. Landfarming provides a platform where soil conditions (pH, nutrient, moisture, and tilling) can be optimized to promote microbial activities and thus desired degradation of soil pollutants can be achieved. The factors under which landfarming is applicable and leads to increased effectiveness are reviewed (Pope and Matthews, 1993; Eweis et al.,1998; Dupont et al., 1998; US EPA, 2003; US EPA, 2004; Environment Canada, 2013; NSW EPA 2014) and design parameters for successful landfarming applications are suggested.

2 Introduction –Landfarming Technique

Landfarming, typically used for remediating refinery petroleum sludges, is among the bioremediation technologies that have been also used for the remediation of crude oil contaminated marine beach sand and sediments (Nikolopoulou and Kalogerakis, 2011).

Landfarming, also known as land treatment or land application, is an aboveground remediation technology for soils that reduces concentrations of petroleum constituents through volatilization and biodegradation. This technology usually involves spreading excavated contaminated soils in a thin layer on the ground surface and stimulating aerobic microbial activity within the soils through aeration and/or addition of minerals, nutrients, and moisture (US EPA, 2004).

Landfarming utilizes commercially available farm equipment such as tractors, rotary tillers, chisel plows, soaker hoses and rotary sprinklers. The nature of the technology is such that requires open large areas which should be prepared for drainage management, operation equipment access and materials management. Landfarming has been successfully practiced for over 100 years in treating mostly hydrocarbon contaminated soils. Lighter petroleum hydrocarbons are mainly removed from soil through volatilization and to a lesser extent due to microbial degradation. On the other hand, heavier petroleum hydrocarbons like lubricating oils and diesel fuel do not evaporate and their removal is due to microbial breakdown, which takes longer (Khan et al., 2004).

Nonetheless it has become more attractive than other soil remediation methods because it has low cost, energy consumption, risk of contaminant migration and low environmental impact, but most importantly landfarming complies with government regulations and is very versatile to any climate and location (Besaltatpour et al., 2011). Major benefits and drawbacks of landfarming are summarized in Table 1. Landfarming can be in situ or ex situ; if contaminated soils are shallow (i.e., $<$ 1 m below ground surface), it may be possible to effectively stimulate microbial activity without excavating the soils, if petroleum contaminated soil is deeper than 1.7 m, the soils should be excavated and reapplied on the ground surface (US EPA, 2004). Soil is treated until the contaminant concentrations are below or at acceptable limits as established by environmental control agencies.

Table 1 Advantages and Disadvantages of Landfarming

Advantages*	Disadvantages
Technology simple to design and implement	Reductions of concentration greater than 95% and concentrations lower than 0.1 ppm are difficult to achieve
Short treatment times (6-24 months under optimal conditions)	May not be effective for high constituent concentrations (greater than 80,000 ppm total petroleum hydrocarbons)
Very low capital and operation input required	Applicable only to biodegradable pollutants
Large soil volumes can be treated	Large treatment area is needed
Can be applied ex-situ	Volatile constituents tend to evaporate rather than biodegrade during treatment
Effective on organic constituents with slow biodegradation rates	Involves risk of pollutant exposure
Has small environmental impact	Adsorbents like clay and organic matter can decrease the bioavailability and therefore lower biodegradation efficiency as contaminants are tightly bound to the soil matrix
Energy efficiency	Substantial cost can be incurred during excavation

* adapted from US EPA (2004) and Maila and Cloete (2004).

3 Technology Requirements

As mentioned earlier, landfarming is a simple *ex-situ* technique which although takes advantage of several mechanisms of contaminant loss (volatilization of low molecular weight compounds or surface degradation by UV light or humification of PAHs), it is primarily concerned with optimization of biological contaminant degradation as it is the primary mechanism of removal of most organic contaminants.

Thus, successful landfarming requires the addition of nitrogen (N) and phosphorous (P) based-nutrients in addition to other growth-limiting substrates as well as oxygen, which is provided by regular tiling, and water to maintain the moisture at the desired levels (Nikolopoulou et al., 2013). Several studies also suggest supplementation with specialized cultures of allochtonous contaminant-degrading prokaryotes during the startup phase of a landfarming facility (Kalogerakis, 2005). Overall, the effectiveness of landfarming depends on a number of parameters (Table 2) which influence biodegradation, the main mechanism of contaminants removal and are grouped into three categories: soil characteristics, constituent characteristics, and climatic conditions. These parameters are usually monitored or/and controlled and evaluated before implementation of a land treatment Unit (US EPA, 2004).

Table 2 Major factors influencing landfarming performance (US EPA, 2004)

Soil characteristics	Constituent characteristics	Climatic conditions
Microbial Population Density	Volatility	Ambient Temperature
pH	Chemical Structure	Rainfall
Moisture	Concentration	Wind
Temperature		
Oxygen		
Nutrient Concentrations		
Texture		

3.1 Soil Characteristics

3.1.1 Microbial Population Density

Microbial population densities in typical soils range from 10^4 to 10^7 CFU/g dry weight of soil. According to US EPA (2004), for landfarming to be effective the minimum heterotrophic plate count should be 10^3 CFU/g. Plate counts below this indicate the presence of toxic concentrations of organic or inorganic (e.g., metals) compounds, still though landfarming may be effective as long as soil is amended to increase the bacterial population or is supplemented with suitable consortia. If the contaminated soil lacks a significant population of degraders it is possible to use bioaugmentation. The population of microorganisms should be monitored in soil by plate count, most probable number technique, phospholipid fatty acid (PLFA) analysis, or denaturing gradient gel electrophoresis (DGGE).

3.1.2 Soil pH

Desired soil pH values to support bacterial growth should be within the 6 to 8 range, with a value of about 7 (neutral) being optimal. When soil pH values fall outside this range it can be raised through the addition of lime or lowered by adding elemental sulfur, aluminum sulfate preferably prior to landfarming operation (US EPA, 2004).

3.1.3 Moisture Content

Too much water in the soil will hinder the supply of oxygen and as a result will decrease microbial activities and subsequently the rate of biodegradation. On the other hand, too little water will inhibit microbial activities. The optimal soil moisture range for supporting the microbes is between 40 and 85% of the water-holding capacity (field capacity) or soil moisture content between 12 and 30% by weight (US EPA 2004).

3.1.4 Temperature

Biological activity is promoted when soil temperature is kept within the range of 10–45°C (US EPA 2003). Microbial activity of most bacteria diminishes at temperatures below 10°C or greater than 45°C and hence, special temperature-controlled enclosures or special bacteria required for areas with extreme temperatures should be incorporated.

3.1.5 Oxygen

Aeration of landfarmed soils is crucial so that there is sufficient oxygen to promote optimal microbial degradation of contaminants, though it should be low enough to prevent excessive volatilization of compounds, such as BTEX (NSW EPA 2014). Moreover, aeration creates a more homogenous distribution of contaminants, nutrients, water, air and micro-organisms and increases biodegradation rates. On the contrary when it is applied to a very wet or saturated soil tends to destroy the soil structure, which generally reduces oxygen and water intake and reduces microbial activity. The normal method of aerating land treatment units is to regularly till, plough or turn the material to increase oxygen infiltration (US EPA 2003). A tractor-mounted rotary tiller provides more aeration during soil mixing and is recommended for optimum results.

3.1.6 Nutrient Concentrations

Nutrients such as nitrogen and phosphorus are essential to support cell growth and sustain biodegradation processes. Effective biodegradation requires the carbon to nitrogen to phosphorus ratios to be between 100:10:1 and 100:1:0.5 depending upon the specific constituents and microorganisms involved in the biodegradation process (US EPA, 2004). Fertilizers may be added in pellet form or dissolved in the irrigation water added to the landfarm. The amount and frequency of fertilizer addition depend upon field conditions.

3.1.7 Soil texture

Soil texture affects the permeability, moisture content, and bulk density of the soil. Soils (such as clays) that clump together are difficult to aerate and result in low oxygen concentrations. The distribution of nutrients and moisture can also be hampered in clayey soils. It is also difficult to uniformly distribute nutrients throughout these soils and can retain water for extended periods following a precipitation event (US EPA, 2004). On the other hand, very coarse soils are not suited to landfarming, as they do not retain moisture and nutrients. Volatilization of compounds occurs more readily from coarse-grained soils than from those with fine grains. Using bulking agents (woodchips, sawdust, straw) can reduce bulk density and improve soil structure and oxygen infiltration and increase the moisture-holding capacity of sandy soils (NSW EPA 2014).

3.2 Contaminant Characteristics

3.2.1 Volatility

Control, capture and treatment of the release to the atmosphere of VOCs using covers (plastic sheet), structural enclosures (greenhouse or plastic tunnel) which can then be sequestered on activated carbon filters may be required particularly during tilling or plowing operations if volatile constituents are present in the soils being landfarmed. Emissions should present no health risks and compliance with air quality standards and occupational exposure standards is required (US EPA 2004, NSW EPA 2014).

3.2.2 Chemical Structure

The chemical structure of the contaminants to be treated by landfarming determines their potential biodegradation rate. Typically, nearly all constituents in petroleum products found underneath underground storage tanks are biodegradable; however, the higher the molecular weight and complexity of constituents structure (polyaromatic compounds) the lower the biodegradation rate. Thus the evaluation (biotreatability studies) of the chemical structure of the constituents proposed for degradation by landfarming determines which constituents will be the most degradable and to what extent (US EPA 2004).

3.2.3 Concentration and Toxicity of Contaminant

High concentrations of total petroleum hydrocarbons (TPH> 80 g/kg or 8%) or heavy metals (>2.5 g/Kg) in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation in landfarms. However, concentrations of petroleum product up to 25% by weight of soil could be treated by mixing with clean or less contaminated soils to dilute the contaminants concentrations to desirable ranges (Pope and Matthews, 1993). The final TPH levels attainable vary based on waste streams, site conditions, and the component properties of the waste oil. For example, if the oil is highly weathered and contains very little biodegradable hydrocarbons remaining, then it is not amenable to bioremediation.

3.3 Climatic Conditions

Exposure to climatic factors (rain, snow, wind, temperature) is typical for ex-situ uncovered landfarms.

3.3.1 Ambient Temperature

The ambient temperature is important since it is directly related to soil temperature. Favorable temperatures for bacterial activity and thus biodegradation are in the range 10°C to 45°C.

3.3.2 Rainfall

Rainfall can increase the moisture content of the soil to saturation level and excess water can cause erosion of the landfarm area. Landfarming is not suitable in areas where the annual rainfall exceeds 762 mm. In any case Water Management systems for control of runon and runoff should be installed. Runon is usually controlled by earthen berms or ditches that intercept and divert the flow of stormwater. Runoff can be controlled by diversion within the bermed treatment area constructed with a slope <5% to a retention pond where the runoff can be stored, treated, or released. A leachate collection system at the bottom of the landfarm and a leachate treatment system may also be necessary to prevent groundwater contamination from the landfarm (US EPA 2004).

3.3.3 Wind

Erosion of landfarm soils can occur during windy periods and particularly during tilling or plowing operations. Wind erosion can be limited by terracing the soils into windrows and spraying periodically to minimize dust (US EPA 2004).

4 Land treatment unit design and construction

4.1 Site preparation

4.1.1 Soil preparation

Contaminated soil contains often a wide variety of debris including rocks, roots, trees, and miscellaneous metal and wood items. So the excavated contaminated soil is screened to remove debris (greater than about 2.5 cm diameter) with for instance a portable trommel plant (i.e. de-rocking equipment commonly used in road construction), and then is placed on top of the porous sand or soil subbase. Most tractor-mounted tilling devices can till only to a depth of about 30cm. Large tractors with specialized equipment that can till to depths of 1 m or more have been used for in situ land treatment. Large augers are now available that can move soil from 15 to 35 m depths to the surface. Any debris (for example, wood shavings) occurring in the contaminated soil that may adsorb the contaminants should be removed if possible and treated separately (Pope and Matthews, 1993; Dupont et al., 1998).

4.1.2 Size estimation of Land Treatment Area

In general the volume of soil due to fluffing and soil disturbance during excavation increases approximately 1.25 and 1.4 times its initial volume (Eweis et al.,1998). If the estimated volume to be excavated is 535.7 m^3 then the increased volume (V) due to “fluffing” is 1.4 ×535.7 m^3= 750 m^3

The depth of the treatment zone is generally 15 to 30 cm (6 to 12 in.) and is based on the depth of soil that can be effectively tilled and treated (Dupont et al., 1998).If the resulting soil depth (d) is decided to be 0.3 m then the needed surface area is going to be A=soil volume (V)/ soil depth (d) = $750m^3/0.3m = 2500\ m^2$.

However, most of the times the availability of land for LTU construction may ultimately determine its size.

4.1.3 Liners- Leachate Control system

The LTU is constructed by preparing the base. Large debris is removed to protect liners placed on it, and grading is necessary in order to control runoff from the LTU.

The purpose of the liner system is to prevent leachate from migrating below the LTU and to provide a collection point for leachate recovery. The liner system design will vary depending on performance and design criteria. The liner .system described below is a double liner-leachate collection system, which represents conservative design requirements (Dupont et al., 1998).

Liners/barriers are not required at sites with more than 5 m of native underlying soil with low hydraulic conductivity (<10^{-6} cm/s). A liner/barrier should be used if there is less than 5m of native underlying soil or if the hydraulic conductivity is >1×10^{-6} cm/s (Environment Canada, 2013).

The bottom layer of the liner system consists of 30 to 60 cm of compacted, low-permeability (10^{-7} cm/s) clay material. Permeability, sieve size, and moisture content requirements for the clay material are usually necessary. The clay liner is graded (2%) towards the gravel drain, located along the central axis of the LTU and also graded (1%) to a collection sump located at one end of the LTU. A flexible membrane liner is placed on top of the compacted clay liner. A variety of materials may be used for this liner, but usually, 1mm high-density polyethylene (HDPE) is selected due to its durability and compatibility with leachate (Dupont et al., 1998). A schematic view is given in Figure 1.

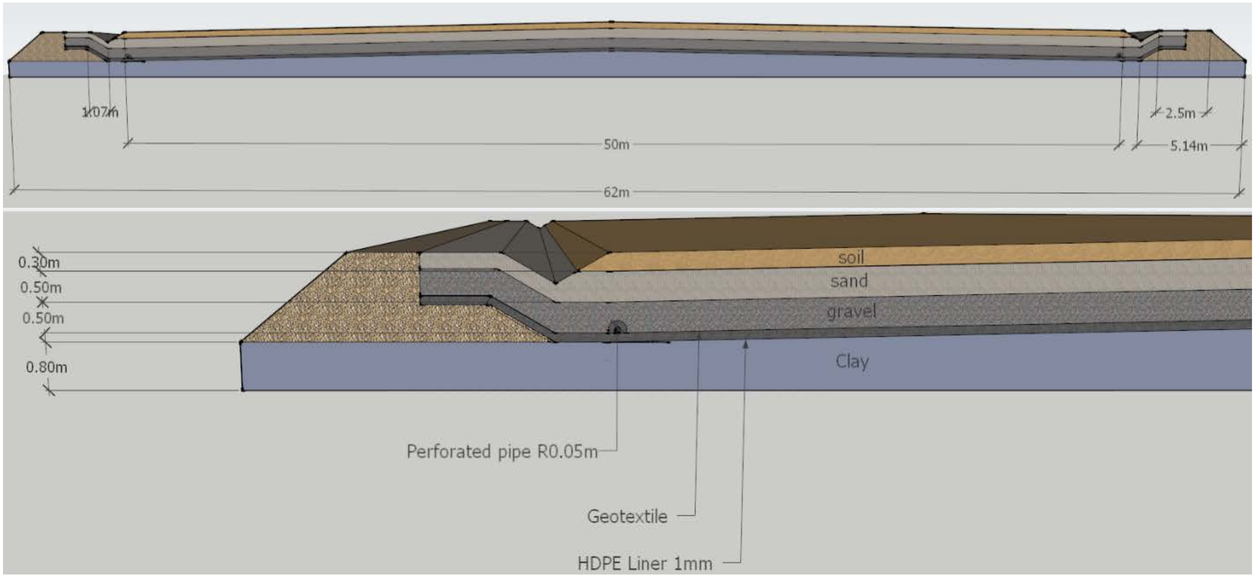

Figure 1 Design details of Landfarming Units (top) overall diagram – width view and (bottom) berm details.

A drainage system is then installed above the liners for leachate collection. The leachate col lection system consists of a drainage layer that lies on top of the HDPE liner to convey the flow of leachate to the central collection system. A geotextile, filter fabric (15 cm) is placed over the drainage net to capture migrating particles that can clog the leachate collection system. Drainage network consists of perforated HDPE pipes 10 to 15 cm in diameter and wrapped in filter fabric is placed along the longitudinal axis of the LTU in the drainage trough and covered with gravel and again with filter fabric. Non angular < 13 mm gravel is used to prevent puncture of the synthetic liner material. A gravel sump is constructed at the low end of the leachate collection system for central leachate collection. A riser pipe extends from the bottom of the collection sump to the exterior of the LTU from which leachate can be removed and analyzed. (Dupont et al., 1998).

A sand or soil layer, ranging from 0.6 to 1.2 m thick, is placed above the liner(s) and drainage system to protect them from heavy equipment (Cookson 1995). The minimum thickness though is usually 0.3 to 0.6 m. Ditches or berms at least 0.8 m high and 0.5 m thick are installed at the periphery of the cell in order to prevent run-on and to capture runoff. Requirements for the site will vary depending on local regulatory authorities. The system suggested and shown in Fig. 2a and 2b should be considered a general guideline; there are different versions of this design that will successfully contain leachate within the boundary of the LTU.

4.2 Optimization of soil properties

The land treatment unit (LTU) provides a platform where soil conditions (pH, nutrient, moisture, and tilling) can be optimized to promote microbial activities and should be constantly monitored and controlled.

4.2.1 Soil pH

The desired soil pH ranges from 6 to 8 for Optimum biodegradation. The pH of soil affects microbial activity, availability of nutrients, plant growth, immobilization of metals, rate of abiotic transformation of organic waste constituents, and soil structure. Ammonia nitrogen is the form of nitrogen most bioavailable. At high pH (> 8.5), ammonia predominates and may escape into the atmosphere in significant quantities. The solubility of phosphorus, an important nutrient in biological systems, is maximized at a pH of 6.5 (Sims, Sims, and Matthews 1989; Pope and Matthews, 1993; Dupont et al., 1998).

Soil pH can be adjusted by addition of chemical reagents (see Table 3). For acidic soils liming agents like CaO and agriculture lime ($CaCO_3$) may be used to raise the pH (see Table 4); aluminum sulfate or ferrous sulfate or elemental sulfur (a slow acting chemical that requires microbial activities to generate acid) or inorganic acids (sulfuric, phosphoric) may be used to lower the pH of alkaline soils.

Table 3 Amount of Sulfur Needed to Lower Soil pH by 1*

Material	pH Change	kg/100 m^2
Sulfur	7.5 to 6.5 8.0 to 6.5 8.5 to 6.5	7.3 17.1 19.5
Iron sulfate	7.5 to 6.5 8.0 to 6.5 8.5 to 6.5	61.0 14.2 16.2
1 Effective only on soils without free lime 2 Higher rates will be required on fine-textured clayey soils and soils with a pH of 7.3 and above		

Table 4 Lime Application Rates to Raise Soil pH to Approximately 7.0 *

Existing Soil pH	Lime Application Rate (kg/100 m^2)		
	Sandy	Loamy	Clayey
5.5 to 6.0	9.76	12.2	17.1
5.0 to 5.5	14.6	19.6	24.4
3.4 to 5.0	19.5	26.8	39.1
3.5 to 4.5	24.4	34.2	39.1

Lime application rates shown in this table are for dolomite, ground, and pelletized limestone and assume a soil organic matter level of approximately 2% or less. On soils with 4 to 5% organic matter, increase limestone application rates by 20%.

* Source: http://www.ext.colostate.edu/mg/gardennotes/222.html

4.2.2 Tilling-Oxygen supply

A tractor-mounted rotary tiller is commonly used in agriculture and is commercially available. The rotary tiller is recommended since it creates a thorough soil-waste mixture and aerates the soil, in one pass. Other techniques include discing and moldboard plowing. In addition, flotation tires, for farm equipment, such as spreaders and tank wagons; and equipment for hauling and spreading solid wastes are commercially available for use in LTU applications (Dupont et al., 1998).

Tilling should be conducted in all possible directions (i.e., cross length and width and diagonally to achieve maximum mixing and stirring of the LTU soils). Tilling frequency should also be considered as a factor when operating in the LTU. Tilling should be performed near the lower end of recommended soil moisture content and should be performed to depths up to 30 cm. Tilling very wet or saturated soil tends to destroy the soil structure, which generally reduces oxygen and water intake and reduces microbial activities thus tilling should not begin until at least 24 hours after the irrigation or a significant rainfall event. (Pope and Matthews 1993)

4.2.3 Moisture requirements-control

Specifying important soil parameters in order to determine the application water volume needed in the first irrigation of the LTU

Determination of soil moisture content

4.2.4 Water Holding Capacity

The water-holding capacity of the soil can be determined by placing duplicate 20 g field-moist soil samples in funnels fitted with folded Whatman 2V filter paper on the inside and mounted on preweighed 250 ml flasks as described by Forster, 1995. Percentage water-holding capacity is calculated with the following formula:

$$\%\, Water\ holding\ capacity = \frac{(100-W_p)+W_i}{d_{wt}} \times 100,$$

where W_p is the weight of the percolated water in grams, W_i is the initial amount of water in grams contained in the sample, and d_{wt} is the soil dry weight in grams (Forster, 1995).

4.2.5 Soil Gravimetric Water Content and Soil Dry Mass

Water content in sand samples can be determined gravimetrically after desiccation at 105°C overnight. The differences in masses before and after drying are a measure for the water content of soils. The water content is calculated on gravimetric (*g* water/*g* soil) or on volumetric basis (cm^3 water/cm^3 soil) (Wilke, 2005).

The dry mass content (w_{dm}) or water content (w_{H2O}) on a dry mass basis expressed as percentages by mass to an accuracy of 0.1% (*m/m*) are calculated using the following equations:

$$W_{dm} = \frac{m_2 - m_0}{m_1 - m_0} \times 100 \qquad (2)$$

$$W_{H_2O} = \frac{m_1 - m_2}{m_2 - m_0} \times 100 \qquad (3)$$

where $m_{0=}$ mass of the empty container (g), m_1 =mass of the container with field-moist soil (g) and $m_{2=}$ mass of the container plus oven-dried soil (g).

The soil is classified as sandy and its estimated water-holding capacity for the soil was 33.73%. The optimal soil moisture range for supporting the microbes is between 40 and 85% of the water-holding capacity (field capacity) and as was estimated the optimal soil moisture content should be between 13.5% and 28.7%.

Determination of the water addition requirement for soil bioremediation

4.2.6 Moisture requirement (Kuo J., 1999)

The following formula can be used to determine the volume of water needed for bioremediation.

$$V_{water} = (V_{soil})(\Phi_{w,f} - \Phi_{w,i}) = (V_{soil})[(\eta)(S_{w,f} - S_{w,i})]$$

where, $\Phi_{w,i}$= initial soil moisture content, $\Phi_{w,f}$ = desired soil moisture content, η = porosity of soil, $S_{w,i}$= initial degree of saturation, and $S_{w,f}$= desired degree of saturation. In order to determine the amount of water needed for the first spray applied to the excavated 750 m^3 oil-contaminated soil we use the following measured data: soil porosity is 43.7% and initial saturation is 20%.

Solution:

a. The optimal moisture content for soil bioremediation as already mentioned is 40 to 85% of the water-holding capacity. Without conducting an optimization study, the middle value of this range, 60%, is selected.

b. Water needed = 750×0.437×(60%-20%)=131.1 m^3

The frequency of moisture additions depends heavily on the climate of the project site.

Soil moisture is usually applied via sprinkler systems where a supply of pressurized water is available. In remote locations, water may be pumped from nearby water bodies or trucked in and surface applied.

4.2.7 Nutrient requirements

To sustain microbial growth nutrients should be applied following the optimal C:N:P ratio of 100:10:1. The ratio is on a molar basis. It means that every 100 moles of carbon requires 10 moles of nitrogen and 1 mole of phosphorous. For bioremediation, a feasibility study is always recommended. Determination of an optimal nutrient ratio should be part of the feasibility study. If no other information is available, the ratio mentioned above can be used. Nutrients are often dissolved in water first and then applied to the soil by spraying or irrigation.

To determine the nutrient requirements, two different procedures can be followed as presented in the preceding examples and the needed information is:

- The mass or concentration of the organic contaminants

- The chemical formula of the contaminants or % w/w carbon content in contaminants
- The optimal C:N:P ratio
- The chemical formula of the nutrients

Determine the nutrient requirement for soil bioremediation

We are going to estimate the amount of nutrients needed to remediate the contaminated soil aforementioned and thus we are going to need the following data in our calculation:

a) Volume of excavated soil in pile =750m^3
b) Initial concentration of oil in the pile = 1000mg/kg
c) Soil porosity = 0.437
d) Soil bulk density = 1.04 g/cm^3 (1040 kg/m^3)
e) The amounts of N and P naturally occurring in the excavated soil is insignificant
f) Trisodium phosphate ($Na_3PO_4 \times 12H_2O$) as the P source
g) Ammonium sulfate ($(NH_4)_2SO_4$) as the N source
h) One-time nutrient addition only

Solution:

A conservative approximation of the amount of nitrogen and phosphorus required for optimum degradation of petroleum products can be calculated by assuming that the total mass of hydrocarbon in the soil represents the mass of carbon available for biodegradation. This simplifying assumption is valid because the carbon content of the petroleum hydrocarbons commonly encountered at underground storage tank sites is approximately 85% carbon by weight.

Crude oil is a complex mixture of mainly organic compounds comprised from 1 to 60 carbon atoms and hydrogen atoms (approximately 85% carbon, 15% hydrogen).

a. Determine the mass of contaminated soil. Contaminated soil is equal to its volume and bulk density:
   Soil mass = 750 m^3 × 1040 kg/m^3= 7.8 × 10^5 kg
b. Determine the mass of the contaminant (and carbon), which is equal to the product of the mass of contaminated soil and the average TPH concentration in the contaminated soil:
   Contaminant mass (Carbon) = 7.8 × 10^5 kg × 1,000 mg/kg= 780 kg
c. Determine the mass of N needed (using the C:N:P ratio).
   Mass of N needed = (10/100)×780 = 78 kg
   Nitrogen molar ratio in $(NH_4)_2SO_4$ = 28/132 (each mole of ammonium sulfate contains two moles of N).
   Amount of $(NH_4)_2SO_4$ needed = (132/28)×78 = 367.7 kg.
d. Determine the mass of P needed (using the C:N:P ratio).
   Mass of P needed = (1/100)×780 = 7.8 kg
   Phosphorous molar ratio in $Na_3PO_4 \times 12H_2O$ = 31/380.
   Amount of $Na_3PO_4 \times 12H_2O$ needed = (380/31)×7.8 = 95.6 kg.

In the case where contaminants formula is known then the procedure is as follows:

Let's assume that the soil excavated is contaminated with gasoline. We are going to estimate the amount of nutrients needed to remediate the gasoline-contaminated soil so we are going to need the following data in our calculation:

a) Volume of excavated soil in pile =750m3
b) Initial mass of gasoline in the pile = 158 kg
c) Soil porosity = 0.437
d) Formula of gasoline (assumed) = C7H16

e) The amounts of N and P naturally occurring in the excavated soil is insignificant
f) Trisodium phosphate (Na3PO4 ×12H2O) as the P source
g) Ammonium sulfate ((NH4)2SO4) as the N source
h) One-time nutrient addition only

Solution:

a. Determine the number of moles of gasoline. Molecular weight of gasoline = 7×12+1×16 = 100 and moles of gasoline = 158/100 = 1.58 kg-mole.

b. Determine the number of moles of C in soil. Since there are seven carbon atoms in each gasoline molecule, as indicated by its formula, C_7H_{16}, then Moles of C = 1.58× 7 = 11.06 kg-mole

c. Determine the number of moles of N needed (using the C:N:P ratio).
Mole of N needed = (10/100)×11.06 = 1.106 kg-mole
Mole of $(NH_4)_2SO_4$ needed = 1.106/2 = 0.553 kg-mole (each mole of ammonium sulfate contains two moles of N).
Amount of $(NH_4)_2SO_4$ needed = 0.553×[(14+4)×2+32+16×4] = 73 kg.

d. Determine the number of moles of P needed (using the C:N:P ratio).
Mole of P needed = (1/100)×11.06 = 0.111 kg-mole
Mole of Na_3PO_4 ×12H_2O needed = 0.111 kg-mole. Amount of Na_3PO_4 ×12H_2O needed = 0.111×[(23×3)+31+(16×4)+(12×18)] = 42 kg.

However, if ones need to be more precise a third more accurate option would be to measure total organic carbon and nitrogen in soil by Dry Combustion Method ("Elemental Analysis") using a CHNS Analyzer. Combustion technique calculates all the carbon in a sample.

4.3 Irrigation requirements

The irrigation system should be sized to allow application of at least 25, 5 mm of water in 10-12 hours. The rate of water application should never be more than the soil can absorb with little or no runoff since LTUs consist of bare soil and excessive runoff can rapidly cause significant erosion. Generally, coarser (sandy or loamy) soils can take up water at faster rate than finer textured clay or clay loam soils. Usually application rates of more than 13mm/h of water are not recommended. A water meter to measure the volume of water applied is helpful in controlling application (Pope and Matthews, 1993)

Irrigation rate depends on soil properties, which correspond to certain infiltration capacity. Soil infiltration can be estimated through either Horton's or Green-Ampt's method (Chow et al., 1988). However moisture can be estimated on a regular basis through installed hydrometers.

4.4 Monitoring

When monitoring the soils on the landfarm, samples should be taken at regular intervals from various parts of the landfarm, dependent upon the scale of the landfarm operations. A sampling plan should include sampling methods (grid, composite) and frequency (No of samples /surface area). Since landfarmed material is relatively thinly applied and homogenized through tilling, only one depth of sample collection is required (Environment Canada, 2013). Soil parameters that should be checked in regular basis include pH, moisture content, bacterial population, nutrient content, and contaminant concentrations. The results of these analyses, which for some of them can be done using electronic instruments, field test kits, or in a field laboratory are critical to the optimal operation of the landfarm. The results should be used to adjust aeration frequency, nutrient application rates, moisture addition frequency and quantity, and pH. Optimal ranges for these parameters should be maintained to achieve maximum degradation rates (US EPA, 2004).

5 Treatability/feasibility studies of land treatment

Where there is uncertainty about the effectiveness of landfarming to remediate a particular site, treatability studies should be undertaken to determine whether any reduction in concentration will be due to biochemical processes and not just chemical processes alone, such as volatilisation and photo-decomposition. These studies will also provide important design information required for the success of the landfarm as well as an estimate of the potential time frames for achieving the remedial target concentrations (US EPA 2003). Treatability studies can involve both laboratory and field trials.

5.1 Soil Biotreatability study

A set of laboratory experiments using contaminated soil can be carried out in order to investigate the feasibility of land treatment of such soil. Biodegradation potential of a particular hydrocarbon waste can be determined by the extensive chemical characterization of the petroleum-contaminated soil. Here we provide some useful guidelines on carrying out laboratory feasibility studies on potential of land treatment of petroleum-contaminated soil.

Figure 2 Mesocosm biotreatability study of soil contaminated with petroleum hydrocarbons

Laboratory mesocosms to study biodegradation of petroleum hydrocarbons in contaminated soil are shown in Figure 2 and they can be prepared in open trays (glass or metal) as follows:

1. Soil is screened to remove particulates greater than 2 mm in size.
2. Trays containing 2–5 kg of contaminated or spiked soil are prepared.
3. Oil or TPH content is determined and adjusted in the range of 0.5–5% w/w by diluting with clean soil.
4. To obtain optimal soil moisture content for the microbial activity, soil moisture is adjusted to between 40 and 85% of the field capacity (water holding capacity). A water content adjusted to 60% of the field-holding capacity is suitable.
5. Adjust the pH to around 7.0 using lime, caustic soda, elemental sulfur or ammonium sulfate.
6. The trays should be incubated at the optimum temperature range for microbial degradation of 10–35 ^{o}C depending though on the site to be remediated environmental conditions.
7. Nutrients are added to such amount that results a final concentration equivalent to a C:N:P molar ratio of 100:10:1. The amount of each nutrients can be estimated using the procedure given in section 3.2.4.
8. The duration of the biotreatability study depends on the overall objective of the project. In general, it is recommended to run for 2–6 months.

9. Two basic treatments should be included: A) control no nutrient additives only aeration by mixing every week and addition of water to maintain 60% of the field holding capacity, B) Sterile control under the same conditions as in control but using sterile soil.
10. Oil or TPH content, moisture and pH should be periodically monitored.
11. The soil should be mixed at least twice a week to provide proper aeration, mixing, and moisture control.
12. The moisture content should be monitored at 1 week interval and the soil should be sprayed with water to adjust to the optimum moisture content.
13. Monitoring the disappearance of oil or TPH with chromatographic techniques (gas chromatography–mass spectrometry), as well as moisture, pH, and nitrogen is important during the treatability studies. Total heterotrophic or hydrocarbon-degrading microbial counts may also be monitored to evaluate the biodegradation process. It is important to use the same sampling strategy and methods throughout the treatment period.

6 References

http://www.esaa.org/wp-content/uploads/2015/06/03-Balba.pdf
http://www.ext.colostate.edu/mg/gardennotes/222.html

Besaltatpour A, Hajabbasi M, Khoshgoftarmanesh A and Dorostkar V (2011) Landfarming process effects on biochemical properties of petroleum contaminated soils. *Soil and Sediment Contamination: An International Journal*. 20: 234-248.

Chow V.T., Maidment D. R., Mays L. W (1988) Applied Hydrology. Tata McGraw-Hill Education.

Cookson J.T. (1995) Bioremediation Engineering Design and Application. McGraw-Hill, Inc., New York, NY.

Dupont R. R., Bruell C. J., Downey D. C., Huling S. G., Marley M. C., Norris R. D.,and Pivetz B. (1998) Innovative site remediation technology: design and application,v. 1: Bioremediation. U.S. Environmental Protection Agency, EPA 542-B-97-004

Environment Canada (2013). Federal Guidelines for Landfarming Petroleum Hydrocarbon Contaminated Soils. Available at http://www.federalcontaminatedsites.gc.ca/B15E990A-C0A8-4780-9124-07650F3A68EA/Landfarming_en.pdf

Eweis J.B., Ergas S., Chang P.D.Y., Schroeder D. (1998). Bioremediation Principles. McGraw-Hill, New York, United States.

Forster JC (1995) Determination of the gravimetric water content and soil dry mass. In Alef K and Nannipieri P (eds.) Methods in Applied Soil Microbiology and Biochemistry. pp. 105-106. London: Academic Press.

Kalogerakis N. (2005) Ex-situ Bioremediation of Contaminated Soils. In: Liens, P., Grotenhuis, T., Tabak, H. (Eds.), Soil and Sediment Remediation, IWA Publishing, pp 151-175.

Khan FI, Husain T, Hejazi R (2004) An overview and analysis of site remediation technologies. Journal of Environmental Management. 71: 95–122.

Kuo J (1999) Practical Design Calculations for Groundwater and Soil Remediation. CRC Press LLC

Maila MP and Cloete TE (2004) Bioremediation of petroleum hydrocarbons through landfarming: Are simplicity and cost-effectiveness the only advantages? Reviews in Environmental Science & Bio/Technology. 3: 349–360.

Nikolopoulou M and Kalogerakis N (2011) Petroleum Spill Control with Biological Means. In Moo-Young M (ed.) Comprehensive Biotechnology. pp. 263–274. Elsevier B.V.: Amsterdam The Netherlands.

Nikolopoulou M, Pasadakis N, Norf H. and Kalogerakis N (2013) Enhanced ex situ bioremediation of crude oil contaminated beach sand by supplementation with nutrients and rhamnolipids. Marine Pollution Bulletin 77: 37–44

NSW EPA (2014) Best Practice Note: Landfarming. Environment Protection Authority, Australia, available at http://www.epa.nsw.gov.au/clm/140323landfarmbpn.htm

Pope, Daniel F., and J.E. Matthews. 1993. Environmental Regulations and Technology: Bioremediation Using the Land Treatment Concept. Ada, OK: U.S. Environmental Protection Agency, Environmental Research Laboratory. EPA/600/R-93/164

Sims J. L., Sims R. C., and Matthews J. E. (1989) Bioremediation of Contaminated Surface Soils. U.S. Environmental Protection Agency, Environmental Research Laboratory. EPA/600/9-89/073

US EPA (2003) Aerobic Biodegradation of Oily Wastes: A field guidance book for federal on-scene coordinators, Version 1.0, United States Environmental Protection Agency, Region 6 South Central Response and Prevention Branch, Washington DC; available at http://www2.epa.gov/sites/production/files/2013-07/documents/aerobic_biodegradation_of_oily_wastes.pdf

US EPA (2004) Chapter V (Landfarming) of OUST's publication: How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers. (EPA 510-B-95-007). http://www.epa.gov/swerust1/pubs/tums.htm.

Wilke BM (2005) Determination of Chemical and Physical Soil Properties. In Margesin R and Schinner F (Eds.) Soil Biology, Volume 5 Manual for Soil Analysis p.44 -95. Springer-Verlag Berlin Heidelberg.