Centre for Ecology & Hydrology

Disposal of oiled beach sand in coastal soils

Final Report to Maritime and Coastguard Agency

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ITE is one of four Institutes which form the Centre for Ecology and Hydrology, a part of the UK Natural Environment Research Council. The mission of CEH is to advance the sciences of ecology, environmental microbiology (including virology) and hydrology. It will do this through high-quality and internationally recognised research which will lead to a better understanding and quantification of the physical, chemical and biological processes relating to land and freshwater, and of living organisms within these environments. ITE is responsible for research into all aspects of the terrestrial environment and its resources, and has specialist staff based at six research stations, each with its own particular expertise and regional emphasis.

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

Background

Disposal of oiled sand removed from beaches contaminated as a result of oil spills at sea poses a major problem. Regulatory and environmental constraints are increasingly limiting the use of landfill sites to dispose of such material. In many remote areas the only acceptable disposal method is the long-distance transport of the OBS to an officially licensed disposal site.

A research programme to investigate the feasibility and environmental acceptability of an alternative method of disposal was instigated by the Maritime and Coastguard Agency (formerly Marine Pollution Control Unit of the Coastguard Agency). Its purpose was to assess the practicality and environmental acceptability of using naturally occurring populations of soil micro-organisms to degrade weathered oil residues incorporated into sandy coastal soils. Especially in low grade, non-sensitive areas of coastal sand dunes and dune pastures. If the method proved successful it would facilitate disposal of oiled beach sand (OBS) in remote areas where disposal is difficult and expensive.

The work was carried out by a consortium led by The Institute of Terrestrial Ecology and began in 1994.

Main conclusions

- **Microbial action can rapidly reduce the concentration of hydrocarbons in oiled sand. Under favourable conditions, the original hydrocarbon content can be more than halved in less than a year.**

- **The process has produced no adverse environmental effects. There was no movement of hydrocarbons to groundwater, and plant and animal communities were not affected by the presence of weathered oil residues in the soil.**

Methodology

An initial feasibility study showed that the problem of OBS disposal in coastal areas required an ecological rather than a technical approach. Observations were made in the laboratory and in the field to obtain information on the processes involved in microbial degradation of petroleum hydrocarbons and their ecological consequences. Experiments to study the factors identified in the literature as being important in controlling rates of decomposition were conducted in the laboratory and in the field. Potential for movement of the introduced hydrocarbons, or their breakdown products was measured in laboratory scale experiments and in field trials. Toxic effects of oil residues on plants were examined in glasshouse tests and the capacity for site recovery was measured in field trials. Towards the end of the project, issues of selection and management of suitable sites were explored with representatives of local authorities, statutory conservation agencies and the Environment Agency.

Experimental Work

Laboratory experiments

Microbiological studies examined the stimulation of respiration of microbial communities when challenged with introduced hydrocarbons and the ability of cultured organisms to break aromatic ring structures.

Small-scale experiments were used to examine the responses of plants found in coastal dunes and dune pastures to the presence of different concentrations of weathered and unweathered oil residues.

A lysimeter facility (consisting of 30 tubes 2 m deep x 27.5cm diameter) at ITE Merlewood was used to examine the influence of a number of factors on the rate of hydrocarbon degradation and the composition of drainage water in replicated experiments.

Field Trials

A field trial at Eskmeals, Cumbria was used to compare degradation rates in replicated plots containing buried and landfarmed OBS. Measurements were also made of air and soil temperatures, and rainfall and water table fluctuations. Groundwater samples taken from beneath the plots were analysed to determine whether hydrocarbons were present.

A larger scale monitoring trial, following oil residue decomposition, was conducted at Pendine, where OBS prepared from a stranding of tar balls was placed in a dune hollow. The deposit was characterised by uneven distribution of highly weathered oil residues. This site was also used to examine the progress of plant colonisation and sand stabilisation within the dune area.

A second experiment at Pendine was designed to measure the decomposition of a homogeneous OBS prepared with a high concentration of fuel oil to detect any movement of hydrocarbons from the deposit to groundwater.

Geographical Variation
Because areas of the coast differ in climatic conditions and in the type of sand found, an extensive trial was carried out, in which small bags of OBS were buried at fifteen sites around the British coast from Shetland to Devon. These bags were recovered at intervals and analysed for remaining hydrocarbon content. A collateral trial at a single site (Eskmeals) contained bags of OBS made from sands collected at all fifteen sites.

Results and observations

Main findings
Trials at all scales showed that micro-organisms (principally bacteria) with a capacity for hydrocarbon degradation were present in coastal sandy soils and that these populations responded rapidly to the presence of oil residues. In all cases, a rapid build-up of the microbial hydrocarbon degrader populations was accompanied by enhanced soil respiration and a reduction in the concentration of hydrocarbons present in the soil.

Pattern of Decay
A common pattern of degradation was found, with an initial rapid reduction in hydrocarbon content of OBS, followed by a progressive slowing of the rate of loss with time. This pattern of decomposition can best be described by the power function ($Y = A . X^n$). Actual equations defining the decay curves varied depending on the type and concentration of the oil residue and a number of external factors, including temperature, moisture and nature of the sand into which the oil residues were incorporated. The shape of the decay curve may be a result of the more readily decomposable components of the oil residues being degraded quickly, whilst more recalcitrant compounds persist. There may also be some rate limiting factor related to microbial nutrition or to changes in buffering capacity of the soil which means that the bacteria operate in progressively less favourable nutrient or pH conditions.

If the nature of the oil residues is the main determinant, then there is little that can be done in practical terms to increase the efficiency of natural breakdown. However, if the rate limiting factor is related to physical or chemical properties of the sand containing the oil residues some form of treatment may be possible which is capable of enhancing the rate and completeness of breakdown. For example, the addition of nutrients may increase the rate of decay but investigations into such additions were outside the scope of this project.

Effect of oil concentration
Extensive weathering of oil residues reduced the initial decomposition rate, indicating that the most volatile or soluble components were those which are likely to be most readily metabolised by micro-organisms. Increasing concentration of hydrocarbons in OBS, up to about 7.5% increased the rate of decomposition, but above this concentration there was rapid decrease in degradation rate. This suggests there is an optimum starting concentration (between 5% and 7.5%), for OBS to obtain maximum breakdown of hydrocarbons.

Effect of Temperature
Temperature had a clear influence on degradation rate, as demonstrated in laboratory and lysimeter experiments, where temperature could be controlled or measured continuously. Seasonal temperature dependence is more likely to be important than diurnal in terms of site management, and timing of disposal may be important in establishing the precise nature of the decay curve.

Effect of moisture
As aerobic decomposition is the predominant process by which hydrocarbons are degraded, it was considered important to examine factors influencing water content of the OBS. Waterlogging after periods of rain appeared to be responsible for reductions in measured microbial activity in lysimeter experiments. The influence of waterlogging in reducing hydrocarbon decomposition was also seen in the field plots at Eskmeals. Those plots at the foot of the sloping dune pasture area (where groundwater penetration of the OBS deposits was more frequent and prolonged) showed a slower rate of hydrocarbon degradation than those at the top of the slope and in drier dunes. In contrast, within the unstructured, free draining, sand of the first Pendine experiment, microbial respiration was enhanced by periods of rain, suggesting that water may have been a limiting factor at this site.

Microbial differences between sites
Differences were found between the initial populations of hydrocarbon-degrading bacteria in beach and dune sands from the same site, and between sands taken from different beaches or dunes. However, initial bacterial counts did not necessarily reflect the patterns of decomposition found. The results suggest that there may be large differences in adaptability of microbial populations between sites.

Comparing burial with land farming
The Eskmeals trials showed that, landfarming with frequent ploughing, was more efficient in reducing the concentration of hydrocarbons present in a given weight of OBS than burial. However, for the same land area the total amount of oil residues degraded was greater in burial plots than in landfarming plots.

Migration of hydrocarbons to ground water
Hydrocarbons from OBS deposits only migrated a few centimetres into underlying sand deposits. No evidence was found of the increased presence of hydrocarbons above background concentrations in groundwater.

Ecological impacts
The main environmental impacts arise from mechanical disturbance of sites rather than from the presence of hydrocarbons. At all the field sites, colonisation of experimental areas by plants was observed. At those sites where disturbance was minimal rapid recovery of vegetation was observed. Animal colonisation of the plots at Eskmeals followed development of near-complete plant cover.

Discussion and Consultation

To explain the results and demonstrate the low environmental impact of this alternative method of disposal for OBS a series of meetings, presentations and site visits was arranged. Organisations consulted included: English Nature, Scottish Natural Heritage, The Countryside Council for Wales. The Environment Agency, Scottish Environmental Protection Agency and local authorities.

Site selection criteria

A site selection procedure has been developed together with a preliminary set of guidelines on site management designed to maximise the efficiency of degradation of OBS.

Future work

This project has demonstrated the feasibility of this method for disposal of OBS and has covered most of the background scientific aspects. Future work needs to concentrate primarily on the regulatory and environmental protection issues. Additional research should also be directed at refining the site selection and management procedures, and at identifying more precisely the relationships between particular controlling factors and degradation efficiency.

1. INTRODUCTION

1.1 Aims of the project

The need to find an effective and environmentally-acceptable means for disposal of oiled beach sand prompted the Marine Pollution Control Unit to commission a project to investigate the possibility of using a natural bioremediation method. A one-year Feasibility Study produced a report in 1993 and, on the basis of information obtained, an experimental programme began in January 1994. The project had two major aims:

- To test the suitability of burial and landfarming of weathered oil residues in coastal sandy environments, as a practical alternative to disposal in landfill sites.

- To assess whether such operations would be environmentally acceptable.

1.2 The incidence of spills

When oil from spills at sea comes ashore on a sandy beach, it poses a number of environmental and practical problems. Considerable publicity accompanies accidents involving oil tankers at sea or in coastal waters and the consequent release of, occasionally, large quantities of crude oil or refined products. Although such incidents may result in the beaching of large volumes of oil emulsion at one time, there is also a more continuous problem of small quantities of weathered oil coming ashore on many beaches in the vicinity of busy shipping lanes. The products of either type of spill will have consequences along the affected shoreline, involving wildlife, economic and recreational activity. They also pose disposal problems.

1.3 The problems of disposal

The arrival of the products of a spill on the shore inevitably threatens wildlife conservation on affected coastal sites; though vulnerability will depend on shore type (Gundlach & Hayes, 1978; Gray, 1985). In some instances clean-up may be undesirable because, for example, attempts to remove oil from salt marshes may be more damaging in the long term than allowing the oil to remain and degrade naturally. On high energy, rocky coastlines removal may not be practical and, in any case, wave action may assist the process of self-cleaning of rocks. In contrast, oil washed ashore on sandy beaches on low-energy coasts is likely to stay there and degrade slowly or be redistributed by successive tides. It then remains a physical threat to wildlife and a problem for human use of the beaches. There may also be significant economic impacts where commercial fisheries or popular tourist beaches are impacted. For which ever of these reasons, clean-up and disposal become priorities.

Although clean-up of such beaches is not practically difficult, given ease of access, disposal of the material removed does pose an increasingly serious problem. The options for disposal fall into three broad categories:

- Recovery and re-use
- Stabilisation and storage
- Degradation

Recovery
It may be possible, in some cases to remove oil emulsions from the beach and to recover some of the hydrocarbons present, following removal of the water component. This is a preferred option, both economically and environmentally, though the appropriate, necessary, facilities may not exist in the vicinity of a spill site.

Stabilisation
Material recovered may be used in civil engineering works, usually following stabilisation with a binding agent or quicklime. The stabilised oils may then be used as part of land reclamation infill, may be incorporated in tarmac or be used in other construction materials. A prime example of this disposal route was the use of oiled sand, recovered following the *Torrey Canyon* spill, in the reconstruction of Brest harbour. Again, the possibility of disposal by this means cannot be assured.

Storage
Final disposal of oily waste has frequently been to landfill sites. Such disposal has involved either pre-treatment with a stabilising agent or no treatment (especially where oil residues were well-weathered and contained few low-molecular weight compounds). Such disposal may have taken place into sites also receiving domestic refuse (as in the case of beached oil from the *Eleni V* in 1978) or specially licensed sites. Such sites would normally be sealed to reduce the risks of groundwater contamination. The major problem with disposal to

landfill is the development of anaerobic conditions, which lead to partial decomposition of oil residues and the production of a range of intermediate compounds, whose environmental effects are poorly known. Where there is potential for contamination of water resources, the practice becomes increasingly unacceptable. This unacceptability has been emphasised by recent policy decisions at the British and European level, backed by the introduction of such measures as strict site licensing regulations and a landfill tax.

Degradation

Destruction of oil residues may be achieved by high temperature incineration but efficient burning requires the provision of appropriate specialist facilities nearby. On-site burning would be less efficient and create additional problems of air pollution.

In recent years there has been increased interest in bioremediation, predominantly *in situ*, on shorelines (Venosa *et al.* 1996; Oudot *et al.* 1998). Bioremediation involves enhancement of natural rates of hydrocarbon degradation by the addition of micro-organisms, the addition of nutrients, or promoting the transport of oxygen to reaction sites. The oldest method of encouraging natural biodegradation is by ploughing a thin, superficial layer of oily waste into underlying soil. This process (known as landfarming) and means of maximising its efficiency, have been described by a number of authors including; Knowlton & Rucker (1979), Amaral (1987) and Bleckmann *et al.* (1997).

The two major problems associated with landfarming are:

- the large area of land required to accommodate material in a thin layer
- the potential for accumulation of heavy metals where a landfarm site is used repeatedly.

Mixing hydrocarbons with some other forms of organic matter is thought to aid the process of degradation and this is the rationale behind landfill operations where oily waste is incorporated with domestic refuse. An alternative is to mix the oil with natural sorbents such as straw, to promote so-called "composting." Surface area (and hence access to oxygen) is increased and some nutrient addition may be achieved, depending on the nature of the organic material used as the composting agent.

Proponents of bioremediation suggest the addition of nutrients (principally nitrogen, phosphorus and potassium) with or without the addition of cultures of hydrocarbon degrading micro-organisms. Considerable publicity was given to this type of bioremediation during clean-up operations following the *Exxon Valdez* spill (Bragg *et al.* 1994). However, the success of these procedures has been questioned following an initial wave of enthusiasm, and the need for critical examination of the techniques and their efficacy has been advocated by a number of authors, including Mearns (1997).

Two problems arise in the use of bioremediation agents. First, the need for cultured organisms is highly questionable when native microbial floras with hydrocarbon–degrading capacity already exist and, second, the wider environmental effects of introducing nitrates and phosphates into environments which are naturally nutrient poor.

2. NATURAL BIOREMEDIATION

2.1 Hydrocarbon degradation

Hydrocarbons, naturally occurring compounds containing only carbon and hydrogen, are ubiquitous in the environment. Low-molecular weight hydrocarbons are gases but those of higher molecular weight occur as liquids or solids at normal temperatures. Bacteria and fungi are known to degrade hydrocarbons but it is generally considered that the former assume the major role. If protected from microbial degradation, mixtures of hydrocarbons can accumulate in vast quantities as oil deposits, which may be found throughout the world. Oils are complex mixtures of many types of hydrocarbon and the individual compounds are more, or less, susceptible to microbial degradation depending on their precise molecular structure. Generally, the saturated alkanes (straight chain molecules) can be degraded most rapidly but resistance to microbial activity increases with increasing chain length, and as the ratio of carbon atoms to hydrogen atoms increases because of the presence of unsaturated (double) bonds and branched chains. Aromatic compounds (with ring structured molecules) tend to be more resistant as cleavage of ring structures (essential for degradation) is less easily accomplished. Multiple ring structure compounds and those containing nitrogen or sulphur groups are even more recalcitrant. Such compounds are, therefore, degraded more slowly. The biochemical mechanisms for metabolism of hydrocarbons are diverse. The degradation of different components of oil may be carried out by different species or consortia of species within a microbial population.

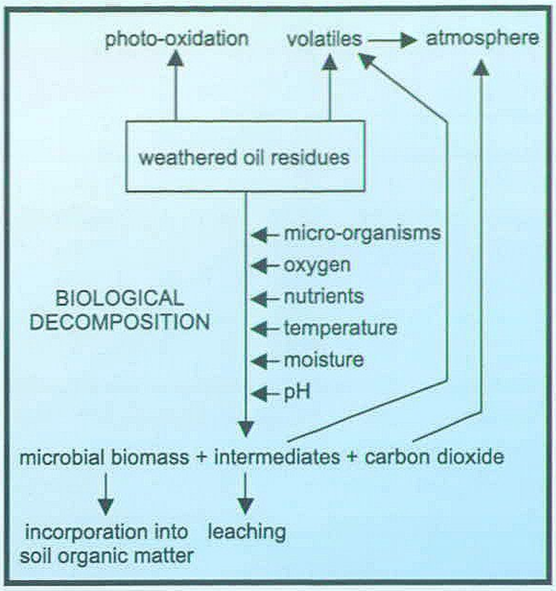


Figure 2.1. Processes, factors influencing them, and fates of products resulting from degradation of oil residues by micro-organisms.

The rate at which hydrocarbons are degraded is subject to several controlling factors. These are summarised in Figure 2.1. The generally accepted theory is that oxygen is essential for the rapid degradation of hydrocarbons. There is evidence of some loss of hydrocarbons in anaerobic environments and laboratory trials have demonstrated anaerobic degradation potential using nitrate or sulphate instead of oxygen (e.g. Coates *et al.* 1996). However, it is still not clear if degradation is complete under anaerobic conditions and the possible accumulation of stable, and potentially toxic, end products should not be discounted.

More complete degradation is to be expected under aerobic conditions and that is the premise adopted in the present study. As many hydrocarbons are hydrophobic, degradation will only occur at the interface of oil and aqueous phases.

In a practical context, decomposition will depend on the availability of oxygen and a supply of essential nutrient elements for the growing microbial populations. For a microbial population to respond to a large excess of hydrocarbon, mineral nutrient requirements must be satisfied. Nitrogen and phosphorus in particular are thought to be limiting, as oil residues have very low N & P contents. Concentrations of these elements may also be low in some environments. The natural environment tends to maintain a balance between different chemical processes as reactions within the major biogeochemical cycles counteract one another. The stimulation of organic carbon decomposition can perturb this equilibrium and result in major environmental change. For example, the production of acidity by excessive aerobic decomposition may saturate the natural buffering capacity of the medium in which micro-organisms are growing. Microbial activity may then decrease in response to falling pH. Hydrocarbon decomposition may, therefore, become self-limiting as a result of this negative feedback mechanism.

2.2 The distribution of hydrocarbon degraders in the environment

Hydrocarbons, and micro-organisms capable of degrading them, occur in marine, freshwater and terrestrial ecosystems.

There has always been a discrepancy between bacterial cell numbers obtained from total counts and those found through the use of culturable counting methods. Under natural conditions the culturable count is only 0.01% to 12.5% of the total count which means that the vast majority of bacteria in the environment cannot be grown under laboratory conditions. This has severely restricted the advance of microbial ecology and only recently has progress been made. Despite this limitation there is good evidence that the distribution of hydrocarbon degrading bacteria correlates well with sources of hydrocarbon in ecosystems (Leahy & Colwell, 1990; Benka-Coker & Ekundayo, 1997)). The proportion of the population able to degrade hydrocarbons appears to be quantitatively related to the degree or extent of exposure of that ecosystem to hydrocarbon contaminants. A number of studies have shown that areas subject to recent or frequent spills have larger populations of hydrocarbon-degraders than similar "clean" sites (Atlas 1984; Barkay & Pritchard 1988).

Bacterial populations are not static and can become adapted to degrade specific hydrocarbons when the supply of those hydrocarbons increases. Native microbial populations have the capacity to metabolise a range of compounds and generally contain the appropriate genotypes enabling them to break down most hydrocarbons. In many cases this potential may not be organised into definitive enzyme systems but exchange of genetic material within the population, and the induction of appropriate enzyme systems, will allow degradation pathways to evolve rapidly. Because of this adaptability, significant populations of hydrocarbon-degrading micro-organisms show a high degree of variability in both time and space.

2.3 Biodegradation following spills

There is evidence from a number of oil spill incidents that hydrocarbons are degraded as a result of microbial activity. Changes were reported to have begun within days of beaching, in the case of the *Amoco Cadiz* spill in 1978. Almost all the n-alkanes were found to have disappeared within 4 years from oil spilled by the *Irish Stardust*, which ran aground on Vancouver Island in 1970. Even where conditions were found to be unfavourable, e.g. in the Strait of Magellan, there was slow degradation of oil spilled from the *Metula* in 1974 (though this was considered to be the result of nutrient limitation rather than low temperature). More recently, even without the extensive use of bioremediation techniques, there was marked decomposition of oil spilled from the *Exxon Valdez* in Prince William Sound and of the vast amounts of oil beached in the Persian Gulf during the Gulf War of 1992. Microbial decomposition thus operates over a wide range of climatic conditions.

In late 1992, during the Feasibility Study phase of this project, a visit was made to the MoD site at Pendine. Beached oil emulsion from the accident in 1978 involving the *Christos Bitas* had been buried at this site. No accurate estimates of the original hydrocarbon content of this material had been made, though improbable concentrations as high as 20% have been quoted. Core samples revealed a concentration of 0.45% of extractable hydrocarbons remaining in the deposit. Even allowing for a low (e.g. 5%) starting concentration, this represented a loss of over 90% of the oil residues in 14 years. Core samples showed that bacteria capable of mediating the breakdown of hydrocarbons were present in the deposit in significantly higher numbers than in the adjacent sand dunes.

There is, thus, evidence that microbial activity can act to decompose a large proportion of the compounds present in weathered oils reaching the shore.

2.4 The starting material

Some microbial communities are able to survive in, and mediate the breakdown of, crude oil or refined petroleum products. However, unless a spill occurs following grounding of a vessel directly on a beach, any oil reaching shore will have undergone physical and chemical transformation at sea. Figure 2.2 shows the major processes involved and the time scales over which they operate. Since the more volatile and more "soluble" components will have been dispersed to the atmosphere and the sea, respectively, they will be largely absent from any oil that is beached. The remaining residues can be solid (tar balls), liquid or, most commonly, an emulsion produced by mixing of oil and seawater. These will lack the most reactive (and hence the most biologically active) components which may

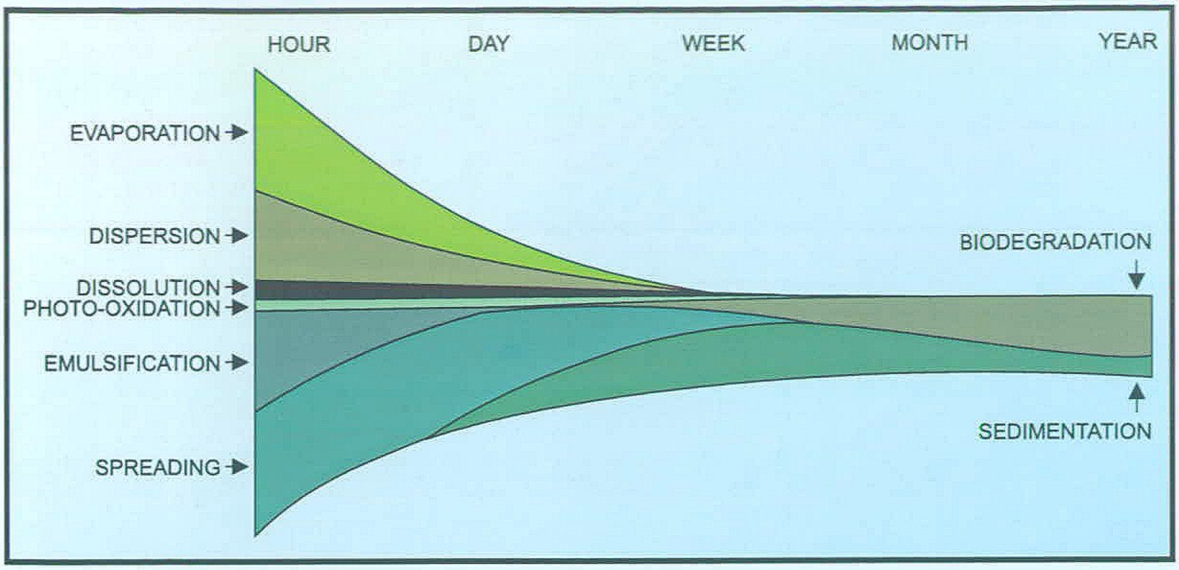


Figure 2.2. Weathering processes influencing oil spill composition and time scale over which they operate (Courtesy of ITOPF).

have been present in the original oil. Disposal will therefore involve what might be best referred to as "oil residues" rather than oil. This term will be retained throughout this report. The longer a slick is at sea, the more it will be weathered and the greater will be the change in its nature (both chemical and physical). In addition, any microbial populations present in the weathered oil will begin to degrade the hydrocarbons present. Because of wave action, some of the oil residue on the shore will become mixed with the materials of which the beach is composed. Subsequent removal of the oil residues will also involve removal of part of the surface layer of the beach (largely sand, but with possible addition of seaweed, shells or pebbles). The resulting mixture is referred to as Oiled Beach Sand (OBS).

3. EXPERIMENTAL APPROACH

3.1 General Philosophy

The project specification called for examination of what was considered to be a simple, cheap and environmentally acceptable disposal method. The need to adopt this strategy dictated that technological input at the field scale was minimal and that the design of experiments should be such that they would resolve practical questions.

That nutrient addition is capable of enhancing degradation has been shown by a number of studies (Atlas1984; Swannell *et al.* 1993). Other workers have examined the possibilities of selecting particular microbial organisms (Jason *et al.* 1995) or of modifying them through molecular genetic techniques (Padmanabhan *et al.* 1998). However it has been suggested (Chapelle, 1999) that introduced micro-organisms might not compete successfully with the, indigenous, populations. The objective of this project has not been to design new bioremediation techniques, so addition of fertilisers or cultures has played no part in the work programme.

In the past there has been a lack of integration between field observation and laboratory-based experimentation under highly artificial, and often unrealistic, conditions. In an attempt to remedy this mismatch, this project was designed to examine the processes involved in hydrocarbon degradation in a co-ordinated manner. The approach adopted was one in which systematic studies were integrated over a range of experimental scales.
Because of this, it was considered possible to have some confidence in any upscaling from experimental to field trials and to extend this to practical aspects of real disposal operations.

3.2 Experimental scales

Experiments have been conducted at a range of scales, each designed to provide the appropriate level of control over factors thought to influence the process of oil residue degradation. Each scale was capable of being linked readily to findings from the next scale up or down, as appropriate.

Microbiological studies looked at the stimulation of respiration when microbial communities were challenged with hydrocarbons. In addition, the ability of cultured organisms to degrade aromatic molecules (a key process in oil degradation) was also examined. The inclusion of appropriate control samples at all experimental scales allowed critical examination of these data.

In order to assess the responses of plants to oil residues and gain insight into the possible toxic effects of disposal, pot experiments were set up at ITE Banchory and performance was recorded.

A series of experiments used a purpose-built set of lysimeters installed in a trench at Merlewood to monitor the processes of oil residue decomposition under controlled conditions. Lysimeter experiments offered the capacity to study the decomposition of buried OBS under natural climatic conditions in close proximity to laboratory facilities. This allowed immediate analysis of leachates collected from the bases of the lysimeters following precipitation events, and the possibility of monitoring (e.g. gas sampling) at more regular intervals than was feasible at the remote field locations. From these studies, it was possible to derive a much greater understanding of the processes and mechanisms controlling the oil degradation.

Small quantities of OBS buried in the ground at a number of locations were used to relate geographical, and attendant climatic and edaphic, conditions to oil residue breakdown. These experiments again allowed control of starting conditions and replication, but no control over external variables. A collateral trial at Eskmeals, using the same procedures, eliminated climate variables whilst retaining variation attributable to sand type.

Larger field plots were established at the MoD (DERA) site at Eskmeals, Cumbria, and used to compare breakdown rates in landfarming and burial plots. Control of initial conditions and replication at a larger scale was still possible in these experiments.

Two operational scale experiments, one the product of a real spill and one a simulation of a spill, were set up at the MoD (DERA) site at Pendine, Carmarthenshire. Within these experimental sites, data were collected to predict the rates of breakdown from different starting OBS type and concentration, and to detect any movement of hydrocarbons towards the water table. A re-vegetation trial was also established on the real spill site (first Pendine experiment). At this site there was less control of starting conditions in the real spill experiment than in the simulated one and no control over environmental variables.

A number of common analytical techniques were applied across all scales of experiment (see sections 3.9-3.11).

3.3 Toxicity trials

Trials set up to assess the toxicity of weathered oil residues used the grass *Festuca rubra* (red fescue - a species found as a major component of dune pastures) collected from a number of locations around the British coast. For each species, five replicate pots were set up for each of five different OBS types, prepared from each of three different oils (Forties crude, Kuwait crude and medium fuel oil). The oils were artificially weathered for different lengths of time before being mixed with beach sand to provide growing media containing 5% oil residues. Young plants of comparable size were planted into the OBS and the proportion of healthy foliage present was assessed at monthly intervals for six months.

A second trial, using only a single oil (Forties) given a single weathering treatment, compared the effect of OBS on the performance of eleven vascular plants and one moss growing in dunes and dune pastures. Six replicates were used and the monitoring methods were the same as in the first trial.

The effect of different concentrations of oil residues in OBS on germination success was also tested using *Festuca rubra* and comparisons were made between three grasses and three herb species at a single oil residue concentration.

3.4 Lysimeter experiments

Overall design

Large lysimeters (cylindrical PVC tubes 150cm x 30cm internal diameter) were filled from the base with gravel (30cm), dune pasture sand (80cm), 12.5 kg OBS (20cm) or beach sand as a control sample, and 15cm dune pasture topsoil (over-burden). This left a headspace of 5cm between the surface of the sand and the top of the lysimeter tube. The water table was set at 100cm below the sand surface, and designed to allow a small amount of fluctuation.

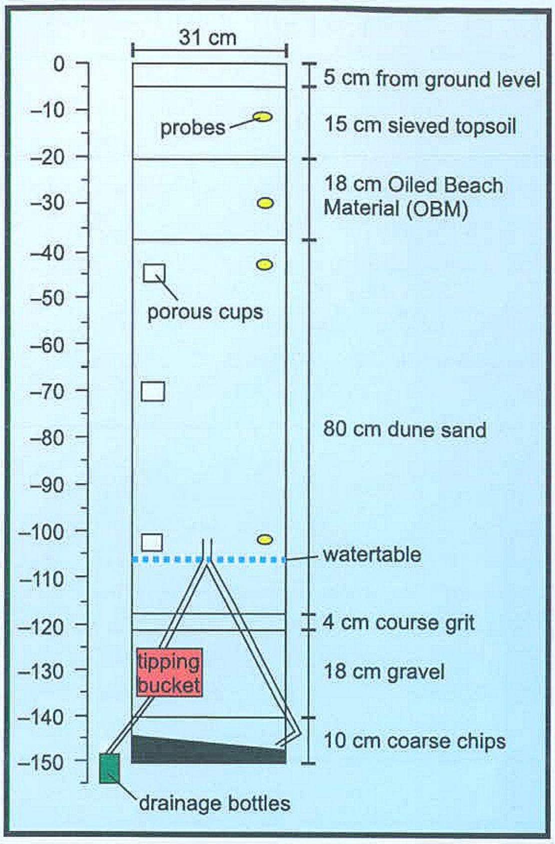


Figure 3.1. Cross section of a lysimeter, showing main design features.

Climatic variables were monitored constantly by an adjacent meteorological station with an integral data logger. Hourly values for rainfall and air temperature were recorded together with sand temperature at four depths (8, 22 (OBS layer), 38 and 98 cm) in selected lysimeters. Suction samplers were inserted immediately below the OBS layer to collect rainfall as it percolated through, and tipping bucket devices at the base of the lysimeter measured and collected through-flow. Leachates from the base of each lysimeter tube were sampled at intervals and analysed using an oil -in-water meter, or forwarded to ITE Monks Wood for PAH analysis. Between collection and analysis these samples were maintained at 4°C.

First experiment

The first lysimeter experiment was set up in June 1994 to examine differential breakdown of three oils under three weathering treatments. Forties crude, Kuwait crude and medium fuel oil were given three different treatments: untreated; washed in three changes of seawater in a cement mixer; washed in seawater and then exposed on an artificial beach for 10 days. A 5% OBS was prepared from each of the differently weathered oils. The experiment was set up as three blocks with 3 oils x 3 weathering treatments (= 9 combinations) + 1 control in each block. Overall respiration (as CO_2 flux from the soil samples) was measured and leachates were tested for hydrocarbons. Microbial populations and their activity were assessed when the experiment was terminated.

Second experiment

The second lysimeter experiment was designed to determine how oil residue concentration might influence decomposition rate and potential for the leaching of hydrocarbons. Only partially weathered Kuwait crude was used in this experiment, with six nominal concentrations of OBS being prepared (0%, 2.5%, 5%, 7.5%, 8.5%, 10%). Again a randomised three block design was used, giving three replicates of each treatment. Carbon dioxide flux was measured and leachate waters were collected for analysis. Samples were also collected at the end of the experiment for microbiological examination.

Third experiment

The third lysimeter experiment was closely linked into the extensive trial (see 3.6, below) examining differences in site characteristics. Following preliminary examination of the nature and microbial activity of sands from the fifteen experimental sites, five (Askernish, Cresswell, Largo, Pendine, Tain) were selected for inclusion in a lysimeter experiment where they could be compared under the same climatic conditions.

Washed and lightly weathered Forties oil was used to prepare 12.5 kg of OBS with 2-3% concentrations of oil residues. The experiment was set up in three randomised blocks, each block containing factorial combinations of five beach sands with two treatments (with OBS and without OBS). This design allowed comparison of background activity within beach sands and a measurement of the stimulation provided by the addition of hydrocarbons to each beach sand type.

3.5 Eskmeals field trials

Three types of trial were conducted at Eskmeals; dune burial, dune pasture burial and landfarming. All used the same starting material, an artificial OBS prepared from local quarry sand and a topped Russian oil supplied as an emulsion containing 38% sea water. Quarry sand was used because it was not possible to obtain a permit to remove sand from nearby beaches.

OBS Preparation

The first stage in OBS preparation was to make an artificial beach on which the oil was to be weathered. A 40m x 20m area was excavated and lined with a 1.5mm thick polyethylene membrane overlain by a geotextile fleece. A drainage sump and the necessary pipework were installed, then a gravel filter (300mm deep) and a 300mm layer of coarse sand were placed on top of the fleece. Finally, a layer of quarry sand (used for OBS preparation) was spread over the surface and sprayed with sea water at a rate of $5\ l\ m^{-2}$.

OBS was prepared on two occasions; January 1995 for winter burial trials and July 1995 for summer burial trials. On each occasion the oil emulsion was spread evenly over the surface of the artificial beach using rubber spreaders and allowed to remain for two days before being mixed into the surface layer of the artificial beach with a rotovator to give an oil residue concentration of 5%. This OBS was used for the burial trials. Subsequently, a 10% mix was prepared for incorporation into landfarming trials.

The experimental site

The pasture burial and landfarming trials were established using a randomised block design within a stock-proof exclosure in an area that had previously been grazed by sheep and cattle. Dune burial plots were contained within a separate enclosed area in nearby, disturbed, mature dunes.

In the summer of 1994, before the setting up of the plots, soil, vegetation and invertebrate surveys were conducted to provide a baseline against which subsequent changes could be measured.

Dune burial plots

Dune burial plots were set up in winter only, with no equivalent burial in summer. Four replicated blocks were established. Within each block, four holes (each 1m square and 0.7m deep) were excavated after removal of the surface turf. Each hole was filled to within 0.2m of the surface with OBS, and backfilled with material previously excavated. Turf was replaced over the surface of all plots. In April 1995, transplants of *Ammophila arenaria* (marram), *Hippophaë rhamnoides* (sea buckthorn) or *Hypochoeris radicata* (cat's-ear) were made into three plots in each block: the fourth remained as an untreated control.

Landfarming plots

The landfarming plots were set up on 31st January and 7th June 1995. A randomised block design was

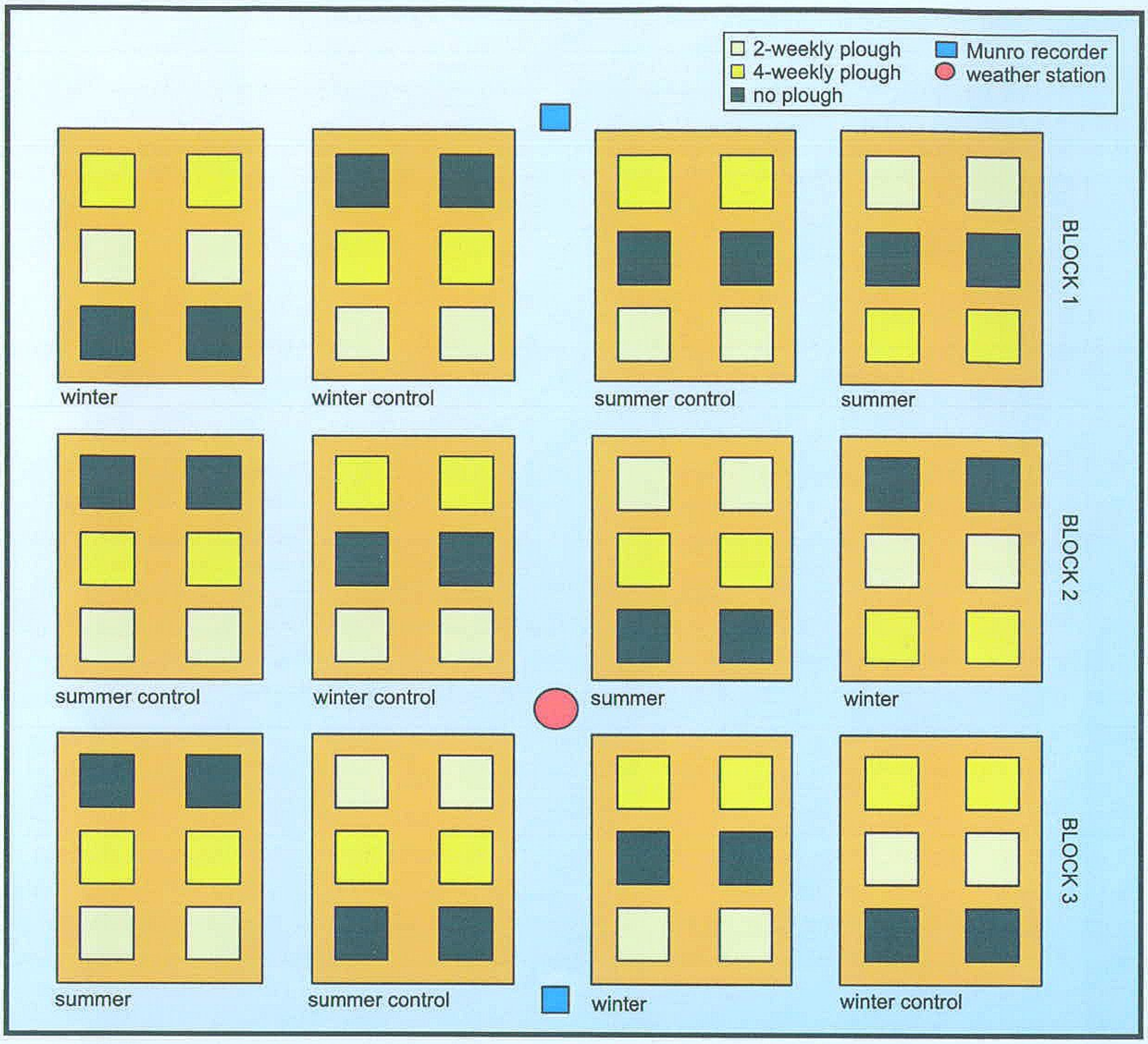


Figure 3.2. Layout of landfarming plots in field trial at Eskmeals

used with six replicate sub-plots of each main treatment (winter and summer landfarmed, and winter and summer control) in each main plot of each block.

Subplots were paired and each pair was assigned to one of three ploughing treatments:

- no ploughing;
- ploughed at two-weekly intervals;
- ploughed at four-weekly intervals.

Stakes were used to mark the corners of each 2m x 2m subplot. For the controls, quarry sand was applied as a 75mm layer and ploughed into the surface to a total depth of 150mm, using a rotovator. For experimental plots, a 75mm layer of OBS was applied after all control plots had been established and ploughed in to a depth of 150mm. The schedule of ploughing began on 13th March and on each occasion control plots were ploughed before OBS plots, using a clean rotovator. For winter plots, ploughing ceased in January 1996 and for the summer plots on 24th April 1996. Revegetation treatments (application of rye-grass seed mixture and control with no seeding) were applied randomly to pairs of plots.

Dune pasture burial plots

Within the main enclosure, dune pasture burial plots were set up on 2nd February and 7th June 1995 in an area adjacent to that used for the landfarming plots. For winter burial plots, two areas (each 7m x 5m) within each block were excavated to a depth of 0.7m. Six heavy duty plywood frames (1m x 1m x 0.7m) were put in place within the excavated area to delimit the individual sub-plots. The area between the frames was backfilled with the native sand excavated from the site.

Quarry sand was placed in the control plot frames and prepared OBS in the burial frames, both to within 0.2m of the surface (giving an OBS depth of 0.5m). The frames were then removed and the plots were covered by 0.2m of native topsoil. The same procedure was followed for the summer burial plots. Revegetation trials included transplants of rye-grass tillers, in addition to the seeding and control treatments used in landfarming plots.

Environmental monitoring

Changes in water table height were measured using Munro recorders installed adjacent to the dune burial plots, and close to the upper and lower blocks of the landfarming trial. A Delta-T automatic weather station was installed close to the centre of the dune pasture site to collect air temperature, soil temperature at different depths, and rainfall data. Comparisons of temperature between plots were made using TinyTalk data loggers installed in a number of plots across the site. Piezometer tubes, with bottom end-caps and 0.3mm slotted tubing at their lower ends, were installed in and around all plots in both landfarming and burial trials to allow sampling of groundwater.

Carbon dioxide emission was measured using static gas chambers put in place shortly before a set of measurements was taken. Each chamber consisted of a 200mm length of 170mm diameter rigid plastic pipe, threaded at the top, which was sunk into the ground, leaving a headspace of 120mm between the soil surface and the top of the tube. An airtight screw cap fitted over the top of the pipe. After a timed period, bungs fitted into two 8mm diameter holes in the cap were removed and the inlet tube to a portable infra-red gas analyser was inserted in one of them.

A peak reading for carbon dioxide concentration was noted, compared with background concentration, and used to calculate the emission rate over the timed period.

Vegetation change, over a two year period, was monitored by recording the species present in each plot and estimating the percentage cover for the most common species found.

Pitfall traps placed in and around all plots were used to collect samples of ground-dwelling invertebrates. Their covers were removed at the beginning of each sampling round and replaced afterwards. Samples were then returned to the laboratory and examined in order to determine the number of different taxa (at the species or genus level) present in each sample.

3.6 Extensive study

Following a desk study, supported by a subsequent, selective, field survey, 15 sites were chosen for burial of small quantities of OBS, as a means of testing variations in decomposition attributable to local site conditions. The choice of sites (Figure 3.3.) was not intended to imply any designation as potential locations for future disposal. On two occasions (autumn and spring), at each selected site, OBS was prepared using topped Russian oil emulsion (the same as that used for the Eskmeals trials) and local beach sand. A 1:10 w/w mixture was calculated to give a final oil residue concentration of 6%. The prepared OBS was weighed into nylon mesh bags that were sealed and tagged with wire or string to aid recovery, and buried 30cm deep in prepared pits. Three additional bags were taken for analysis of initial hydrocarbon concentration.

The trials were set up as three replicate blocks at each site. Within each block six bags were buried in two parallel rows in March 1996. At one end of the row a slotted piezometer tube was installed to a depth of at least 2 metres. Adjacent to this a bag of sand, without addition of emulsion was buried. Close to the piezometer tube in the central block a pair of TinyTalk automatic temperature data loggers were buried, one 10cm and one 30cm deep. A further set of four bags (two per row) was buried in September 1996.

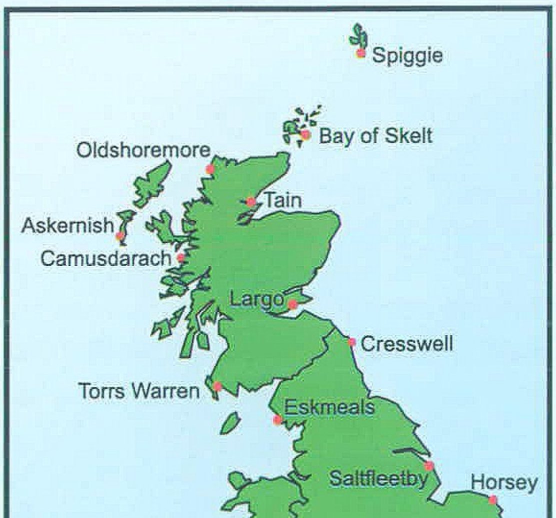


Figure 3.3. Locations of extensive study sites

At intervals replicate bags from each block were removed and returned for analysis of hydrocarbon content. TinyTalk loggers were removed for downloading of data and new ones were buried in the same positions. Water table depth was measured and vegetation was recorded (species presence and cover value). At the end of the experiment the "blank" bags of beach sand were removed with the final samples. On 2nd April 1996, a collateral trial was established at Eskmeals. Using sand collected from the dispersed set of field sites, five replicate bags of OBS, comparable to that in the field sites, were prepared. These were buried in five blocks, one replicate per block.

Locations of individual OBS types were randomised within each block. Adjacent to each OBS bag, a bag of beach sand from the same site was buried. These plugs of OBS and beach sand were removed at the same time as the last set of samples from the field plots.

3.7 First Pendine deposit

Initial establishment

Between Christmas 1993 and new Year 1994 a quantity of well-weathered oil was washed up as tar balls of varying size on the beaches of Pendine and Laugharne Sands. Following agreement between MOD, EA and CCW, the oil residues were removed, together with the surface layer of beach sand, by Carmarthen District Council and buried in a dune hollow adjacent to the old *Christos Bitas* deposit. A monitoring programme was begun involving, initially, the collection of core samples in a stratified manner from random locations within selected squares of a 5m grid set up on the site. The core samples, taken with a 5cm bipartite Ejkelkamp corer, were analysed for hydrocarbon content and microbial activity. At intervals, measurements were made of CO_2 flux at random points across the site.

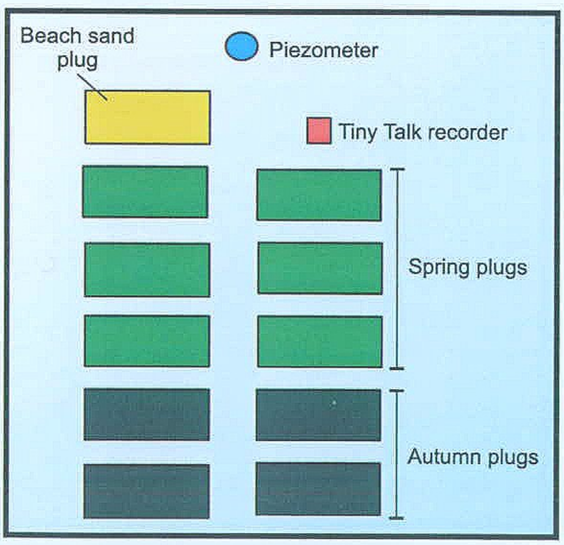


Figure 3.4. Plan of individual plot layout within an extensive study site.

Groundwater monitoring

Because of the problems of ensuring absence of munitions in the vicinity of the site, the installation of piezometer tubes to allow measurement of water table depth and the collection of groundwater samples for hydrocarbon analysis was delayed for six months. However, a set of nine holes was drilled in July 1994, using a hydraulically-operated percussion drill.

Lengths of 30mm diameter piezometer tubing (sufficiently long to give at least 1m penetration of the ground water table) were installed. The bottoms of these tubes were capped and the lowest sections had 0.3mm horizontal slots: upper sections were unslotted.

Revegetation trial

Because of the problems of wind erosion carrying sand from the surface of the deposit, it was decided that a surface vegetation cover should be established. Although some marginal invasion of plants from the adjacent dunes had been observed, this was not rapid enough the stabilise the sand surface. The opportunity was taken to combine the need for surface stabilisation with a trial of the effectiveness of different vegetation types in achieving this stabilisation. In November 1994 the trial was set up using a series of replicated plots each 4m square, set up within the cells of the sampling grid established earlier. The following treatments were applied:

1) control
2) surface raking
3) surface raking and incorporation of 70g m^{-2} of an alginate soil stabiliser
4) seeding with a *Festuca rubra* mix after addition of 70 g m^{-2} of soil stabiliser
5) seeding with a *Festuca rubra* mix after addition of 135 g m^{-2} of soil stabiliser
6) seeding with a Festuca juncifolia mix after addition of 70 g m^{-2} of soil stabiliser
7) planting of marram tillers at 0.5m intervals
8) planting of marram tillers at 0.5m intervals after addition of 70 g m^{-2} of soil stabiliser

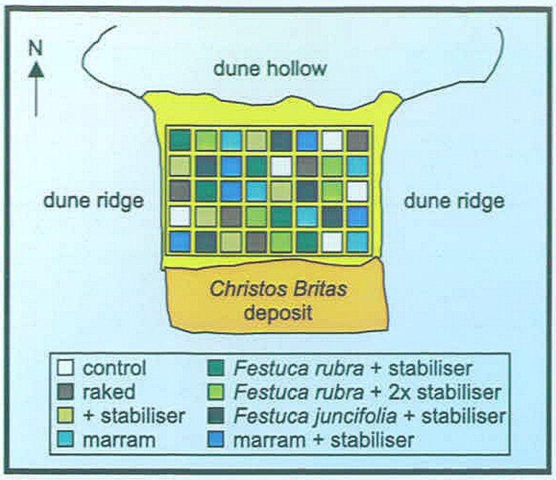


Figure 3.5. Layout of experimental plot and revegetation trial in the first Pendine experiment.

Plant species present within the plots were recorded, together with measurements of their cover and vegetation height, at yearly intervals. At the same time, measurements of sand accumulation were made by recording height differences at 1m intervals along a horizontal line stretched between diagonally opposite marker posts of each grid square.

3.8 Second Pendine deposit

The site

In early 1996, two adjacent hollows were selected within an area of mature dunes that had been subject to disturbance in the past. The smaller, landward, hollow was designated as the control, to be filled with beach sand, and the larger, deeper, hollow (the experimental hollow) on the seaward side of a low ridge was to contain prepared OBS.

Pre-establishment procedures and baseline sample collection

In February 1996 a series of 12 piezometer tubes was installed in the hollows and the surrounding dunes using a percussion drill and tubing similar to that installed at the site of the first Pendine experiment.

The site was levelled to give relative heights of the tube tops and the ground surface. The depths to water table were measured and contour maps were constructed showing the relationship between surface contours and ground water levels.

The consulting engineers (Sir William Halcrow & Partners) produced a contour map of the site, tied into a benchmark in Pendine village.

A series of samples of groundwater, sand and seawater was taken at intervals between installation of the piezometer tubes and incorporation of the OBS some 13 months later.

Experiment establishment and early sampling

Work began on setting up the experiment in March 1997. Sand was collected from the mid shore part of the nearby beach as a skim of up to 10cm thickness over an area approximately 100 m x 50 m. An area 10m x 5m was levelled and a 300mm high bund was built up around its margin. The enclosure produced was lined with damp-course quality Nesqueen polythene, the individual sheets of which were double tucked together to provide a seal capable of preventing contamination of underlying sand. At the edges of the area, the polythene was raised and incorporated into the bund to provide lateral containment of any oil spilled. The polythene lining forming the floor of the enclosure was then covered with a 40mm layer of sand. This area was designed to receive 12 skips for temporary storage of oil and preparation of emulsion.

Once the emulsion preparation area had been completed, an area 49m x 33m was similarly levelled, bunded and lined with Visqueen and covered with a 200mm layer of beach sand. This formed the artificial beach. The actual width of the mixing area on the artificial beach was set as 45m x 29m, giving a total area of 1305m^2 and leaving a 2m buffer zone around the margin to further reduce the risk of contamination of the surrounding area.

23,000 litres of medium fuel oil, delivered by tanker from BP Llandarcy, was maintained in lined skips within the bunded containment area.

Emulsion was produced in 2000 litre batches in a skip dedicated to this function. Equal volumes of oil and seawater (collected and delivered using a bowser) were pumped into the mixing skip and combined using a submersible TK150 hydraulic pump. After initial trials, a standard procedure was adopted which produced a stable, thick, emulsion.

Turves were removed from the control hollow, a layer of beach sand (1m thick) was placed in the hollow and the turves were replaced. Two Theta probes were buried at approximately 0.2m above the base of the beach sand layer to allow the moisture status of the sand to be measured.

Following completion of the control hollow, the experimental hollow was prepared by removal of turf. A layer of beach sand was placed in the hollow and levelled off (0.4m thick over the deepest part of the hollow). Two Theta probes were buried mid-way down this beach sand layer. A thermistor probe, for temperature measurement, was laid on the surface close to the middle of the hollow. The connecting wires from all probes were laid back to the ridge between the two hollows, which had been designated to receive the data logger and rainfall gauge.

Emulsion was pumped from the skips into the bucket of a dumper truck and taken to the artificial beach, where it was dribbled over the lip of the bucket as the dumper made a pass. A single pass of the dumper across the artificial beach delivered the appropriate quantity of emulsion to give an even spread over the sand surface. This method of application prevented contamination of the dumper wheels and ensured containment of the emulsion.

Mixing of the emulsion into the upper layer of the artificial beach was carried out using a tractor-mounted rotovator. The OBS was considered to be thoroughly mixed after two complete rounds by the tractor. After 48 hours of weathering on the artificial beach, the OBS was transferred to the experimental hollow and spread using a long-arm excavator. Within the deepest part of the hollow the depth of the slightly domed OBM deposit was 1.3m. A set of samples (four of OBS and four of the underlying buffer layer) was collected from the artificial beach and sent to the Environment Agency laboratory at Llanelli for analysis.

Once placing of the OBM had been completed, the artificial beach was removed. Sand which had formed the buffer layer was transported to the experimental hollow and placed over the OBM to form what we have termed overburden. This overburden was 0.6m deep over the central part of the hollow, but reduced in thickness towards the margins.

Delta-T automatic data logging equipment and a solar cell to provide its main power source (plus backup batteries) were set up on the ridge between the two hollows. Previously installed instruments were connected up. Remaining temperature probes were installed within the hollows; water table measuring probes were inserted within two piezometer tubes (one in the centre of the experimental hollow and one toward the margin of the control hollow). A tipping bucket rain gauge was also set up on the ridge close to the control hollow.

At regular intervals, samples of groundwater were taken from the piezometer tubes and core samples were also taken from the control and experimental

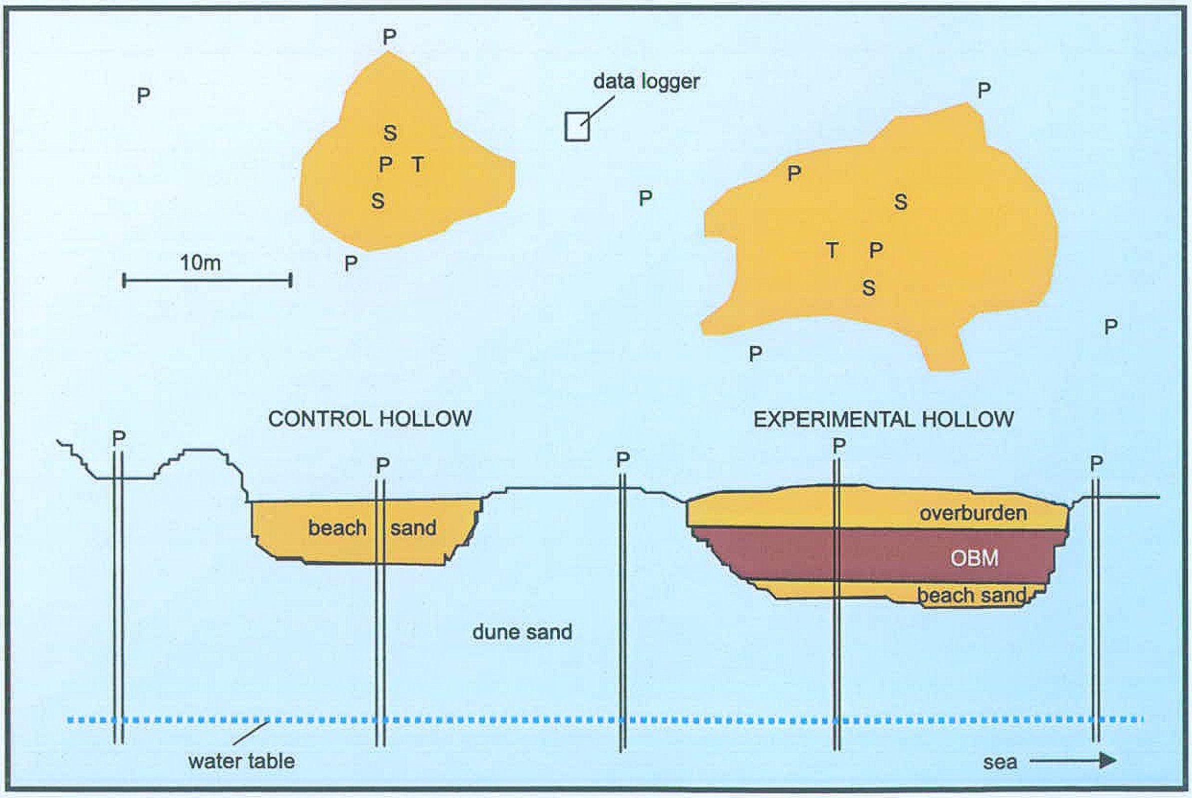


Figure 3.6. Layout of second Pendine experiment

hollows. Overburden was sampled using a 7cm diameter bipartite corer; the OBS using a 5cm diameter bipartite corer and the underlying layer of beach sand (underburden) using a 2.5cm diameter gouge auger. Samples were sent to Llanelli, Monks Wood, Windermere or Merlewood for appropriate analysis.

3.9 Microbiological techniques

The experimental designs used to compare treatments and sites required a large number of samples. It was important, therefore, that microbiological methods were simple and yet provided sufficient information on oil residue decomposition processes and potential within experiments and trials sampled.
The sand dune environment (especially in its less mature phases) is characterised by low concentrations of organic matter and inorganic nutrients. The addition of oil residues to the sand represented a large input of organic carbon. Measurement of the metabolic activity of the microbial populations provided a representative estimate of their response to the challenge of hydrocarbons. Sand dune soils are well drained so that, given a low water table, only aerobic respiration needs to be considered. Replicate samples of sand or OBS were incubated in sealed glass vials and the accumulation of carbon dioxide in the headspace gases was used as an estimate of respiratory activity. The inclusion of control plots in all experimental designs allowed comparison of activity between oiled and non-oiled samples. Some respiratory activity should be expected in the control sands as they contain small quantities of naturally decomposing organic matter from other sources (e.g. plant and animal remains).

The overall activity of the microbial population provided no indication of the range of hydrocarbon compounds being degraded and a method was required, which would demonstrate if more stable compounds, particularly those with aromatic ring structures, were being metabolised. Degradation of aromatic compounds involves modification of side-groups on the carbon ring to aromatic acids then conversion to catechols. This is followed by oxidative cleavage of the carbon ring. One pathway (the meta-pathway), for this oxidative step, results in the formation of hydroxy-muconic semi-aldehyde. This reaction can be observed as the colourless catechol is transformed to the yellow semi-aldehyde derivative.

The ability of the bacterial community to mediate this key reaction was followed using laboratory culture techniques. Using ultra-sound, bacteria were dislodged from the sand particles after suspending a known weight of sample in water. The supernantant was diluted and small volumes spread onto the surface of nutrient agar plates. The culturable bacteria were allowed to grow for 7 days at 20°C after which the colonies were counted. The plate was then flooded with a 1% (w/v) solution of catechol and colonies capable of degrading the aromatic ring structure turned yellow. These were then counted separately. It is accepted that there may be other metabolic pathways resulting in the cleavage of the carbon ring structure, and that the culturable count is likely to be only a small proportion of the total bacterial population active within the sample. However, despite these limitations, it was considered that the catechol screening method provided useful information on the adaptation of microbial populations to hydrocarbon decomposition.

3.10 Decomposition activity

Decomposition activity is defined as non-destructive measurement of the components of the degradation process. As in the case of measurements of microbial activity, this consisted predominantly of measurements of carbon dioxide fluxes.

In the first lysimeter experiment, we used a volatile organic compound (VOC) monitor to detect the extent of direct evaporation of hydrocarbons from OBS. Only trace quantities of VOC's were detectable at the beginning of the experiments, during periods of hot weather, and thereafter none. Because of low and infrequent emissions, measurements were not continued on a regular basis.

In contrast, it was possible to detect differences in fluxes of CO_2 resulting from microbial respiration in the head-space above the surface of sand in capped lysimeters. Initially the head-space was sampled via a syringe and injected into an infrared gas analyser (IRGA). Later, a 24-channel, automated, facility was developed for sampling lysimeters sequentially and measuring CO_2 flux using an IRGA.

Protocols were devised to determine the CO_2 concentrations in the 30 lysimeters containing the OBS and control treatments. Lysimeters were capped with a gas-tight lid and allowed to equilibrate for one hour prior to obtaining a single value integrated from a 15 second reading at 10:00 hrs. On each occasion, the instrument was calibrated from prepared 0, 1000 and 2000 ppm (v/v) CO_2-C mixtures in nitrogen, and flux concentrations derived from a linear regression. Net flux from the lysimeter was computed following deduction of ambient atmospheric concentration.

A similar principle was used in the field, where static gas chambers with screw caps (see section 3.5) were installed in bare sand overlying the experimental deposits. Portable IRGA monitors were used at the Pendine and Eskmeals field trials, although the data was more difficult to interpret due to the greater variability in the plots, and the influence of other factors such as plant root respiration.

3.11 Assessment of degradation

The main method for estimating the oil residue content of OBS used a gravimetric procedure to determine changes in the concentration of hexane-extractable hydrocarbon. This procedure was applied to core samples taken from the Eskmeals landfarming and burial plots, and the two Pendine field trials. It was also used to determine the hydrocarbon content of OBS recovered from lysimeter experiments and the extensive study (including its collateral trial).

A 10g sample of pre-dried OBS (dried for 3 hours at 105°C) was refluxed with 25ml hexane for 30 minutes. The mixture was filtered and the filter residue washed with 3 x 25ml volumes of hot hexane. The filtrate and washings were combined in a weighed evaporating basin, and the extracted hydrocarbon determined gravimetrically after evaporation of the hexane. It is possible that some volatile, low molecular weight, hydrocarbons were lost during sample preparation for hexane extraction. Moreover, asphaltenes and resins are known to precipitate when oil is dissolved in hexane. Therefore, it was expected that the measured hydrocarbon content of the sands would be lower than the calculated value.

Analysis of oil residues for PAH content in selected samples was undertaken at ITE Monks Wood. Hydrocarbon residues were extracted from water samples using hexane, followed by reduction of the hexane component at 80°C after separation from the aqueous phase and drying with anhydrous sodium sulphate. The extract was cleaned on a glass column containing 0.8g of alumina deactivated with 5% water and reduced further under a stream of nitrogen. Hexane extracts of OBS were filtered through anhydrous sodium sulphate. In both cases, Dichlobenil was added as an internal standard before extracts were transferred to chromatography vials. Extracts were analysed using GC-MS. A recovery sample and a blank were included in each analysis and limits of detection were defined as the concentration giving a signal twice that of the baseline noise.

OBS samples from the second (1997) Pendine experiment were also sent to the Environment Agency laboratory at Llanelli, where they were analysed for total hydrocarbon content and abundance of individual components using fluorescence spectrometry and GC-MS, with Forties and Ekofisk oils as the calibration standards.

3.12 Assessment of leaching

Direct evidence of leaching was obtained by analysis of water samples taken from below the field trials and from the bases of the lysimeters. Water collected from the lysimeters was initially tested using an oil-in-water monitor but because of its lack of resolution, later samples were tested for the presence of hydrocarbons by smell. PAH content was measured at Monks Wood using GC-MS.

Fluorescence spectrometry was also used by the EA Llanelli laboratory to estimate the total concentration of hydrocarbons present in groundwater samples taken at the site of the second Pendine experiment. The procedure used was that developed for analysis of oil residue samples recovered following the *Sea Empress* incident. Samples of groundwater from the second Pendine trial were analysed for chloride concentration as a means of tracing the movement of water displaced from the OBS and beach sand. That seawater would also be expected to act as a carrier for "soluble" hydrocarbon fractions from the artificial OBS. The British Geological Survey, Wallingford, analysed groundwater samples collected from the second Pendine experiment using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). These measured concentrations of inorganic elements providing indications of changes in groundwater chemistry resulting from deposition of OBS.

4. FACTORS AFFECTING DEGRADATION

4.1 Pattern of degradation

All experiments, at all scales, showed a progressive reduction of hydrocarbon content in OBS samples. There was, with some exceptions in the case of the extensive trial, rapid development of populations of hydrocarbon-degrading micro-organisms, and an increase in CO_2 flux in samples containing oil residues, compared with that in controls.

The longest period of sampling was for the first Pendine experiment, where six sample dates were spread over four and a half years. From these results it has been possible to construct a decay curve showing the decline in concentration of hexane-extractable hydrocarbons present in the OBS.

From the position of the points on the graph it is clear that the relationship is curvi-linear rather than linear. An exponential line cannot be fitted with confidence ($R^2 = 0.23$). However, a power curve better fitted the data and gave an R^2 value of 0.87, indicating a statistically significant result.

By extrapolation from this curve, the starting concentration of the OBS was estimated to be c. 0.4%. Even given this low starting concentration, it does mean that within less than 5 years some 97.5% of the original hexane extractable hydrocarbon had been degraded. In terms of actual quantities, this is equivalent to a loss of 78 tonnes from an original estimated 80 tonnes present in the OBS. The large loss of hydrocarbon is notable as the original material consisted of well weathered fuel oil and hence was expected to contain a relatively low proportion of the more easily degradable components.

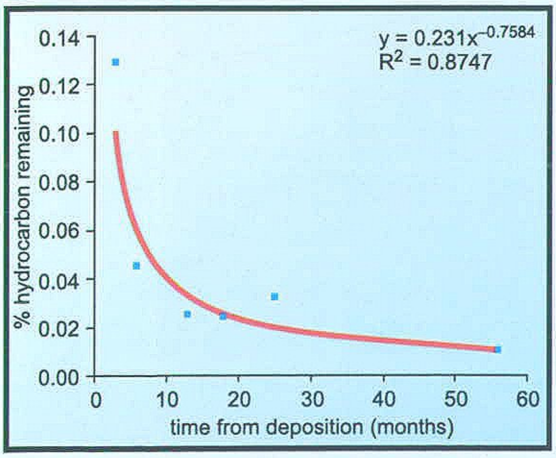


Figure 4.1. Reduction in hydrocarbon content of OBS with time at the first Pendine experiment. A power curve has been fitted to the field data.

As suspected at the time of the beach cleaning operation, an unnecessarily high proportion of sand was removed and the low concentration of oil residue remaining in the OBS did not make this a realistic test of the power of the disposal technique. The concentrations of oil residue used in other experiments approached more closely that expected from a normal clean-up operation, whilst the use of less heavily weathered oils produced a starting product more comparable with that from a fresh spill.

The initially rapid decline in hydrocarbon content, followed by a slowing of that rate, agrees with studies undertaken by other workers. The fitting of a power function to degradation curves, as in this project, appears to be new. The power function, has the general form:

$$Y = A \,.\, X^n$$

where Y = concentration of hydrocarbons remaining, X = time since incorporation of the OBS, A = initial hydrocarbon content of the OBS and n = the rate function.

This implies that decomposition will depend on the initial concentration, time and some rate limiting factor. However, the initial concentration of oil residues may help determine some of the factors contributing to the rate limiting function (e.g. ease of penetration of oxygen or nutrients). The nature of the residues (the ratio of easily decomposed compounds to those, which are more recalcitrant) may also be expected to help determine the rate limiting function. Because of this, we may expect that there will be a family of curves defining the behaviour of different types of OBS under different environmental conditions. These different conditions and the influence they have on the decomposition processes have formed the basis of much of the project.

4.2 Effects of oil type and concentration

The first two lysimeter experiments addressed the question of the influence of oil type, including weathering history (which influences composition of the initial staring material) and oil concentration on the degradation process. Results (Table 4.3) showed that overall there was a significant difference between the starting and final hydrocarbon concentrations (paired student 't' test gave t=3.67: p=0.005). However, statistical analysis

Table 4.1. Starting concentrations of hydrocarbon in OBS prepared from different oils and subjected to different treatments.

Oil type	unweathered	washed	washed and weathered
Forties	1.96	2.23	0.73
Kuwait	2.93	2.67	1.33
Medium fuel	4.4	3.73	0.64

Table 4.2. Microbial activity (measured as CO_2 flux) in OBS prepared using different oils with different degrees of weathering.

Oil type and treatment	CO_2 flux (nM CO_2 g dry wt^{-1} day^{-1}) Topsoil	OBS	Sand
Medium fuel oil			
unweathered	0.42	0.52	0.09
washed	0.16	0.42	0.03
washed & weathered	0.23	0.11	0.04
Kuwait crude oil			
unweathered	0.52	0.31	0.10
washed	0.38	0.50	0.10
washed & weathered	0.29	0.22	0.08
Forties crude oil			
unweathered	0.63	0.21	0.08
washed	0.38	0.23	0.09
washed & weathered	0.29	0.19	0.09
Control	0.26	0.05	0.04

of variance (ANOVA) also showed significant differences between treatments ($F=82.9$: $p<0.001$). With all three oil types the washing and weathering treatment produced a significantly lower hydrocarbon content in the starting OBS than washing alone or no treatment. The amount of reduction depended on oil type. Even without artificial weathering, there were clear differences in the final hydrocarbon content of samples taken. This reflected differential loss through processes such as evaporation during the preparation of the OBS.. Starting concentrations are given in Table 4.1.

Differences in decomposition between residues derived from the three oil types varied depending on the initial starting material and the treatment given. Washing reduced the hydrocarbon concentration by a relatively small amount, but exposure on an artificial beach produced a much larger reduction. Increasing weathering reduced the degradation due to microbial activity and that degradation varied between oil types, being greatest in Forties and least in fuel oil.

Weathering treatment influenced respiration rate in the lysimeters during the summer of 1994, with OBS prepared with unweathered oils producing a greater flux of CO_2 than that from washed oil. Washed and weathered oil residues produced the least amount of CO_2. During the winter of 1994/95 there was very little flux of CO_2 but, during the spring and summer of 1995 rates rose again. However, although an overall significant effect of treatments was detected in measurements made in July 1995 ($F=3.2$: $p<0.02$), the only significant difference between individual treatments was that between untreated Forties, and washed and weathered Forties. Flux rate from untreated Forties oil residues was some five times as high as that from the washed and weathered equivalent (40 mg C m^{-2} h^{-1} compared with 8 mg C m^{-2} h^{-1}).

Table 4.3. Lysimeter experiment: effect of starting hydrocarbon concentration on degradation after eight months and on carbon dioxide flux in summer and spring.

Nominal starting concentration (%)	Actual concentration (%) Initial	Final	% degraded	Net flux of CO_2 August	March
2.5	2.77	2.83	0	11.27	7.32
5	5.12	2.83	45	19.21	7.11
7.5	7.17	3.2	55	23.87	11.12
8.5	8.3	7.83	6	4.48	0
10	9.51	6.17	35	7.00	1.01

The results suggest that the lighter components of the oil, which are lost during the washing and weathering processes, may be those which are subject to initial and more rapid degradation by micro-organisms.

Although microbial activity measured in the laboratory (samples taken from lysimeters in November 1994) showed overall differences between treatments, within the OBS prepared with crude oil residues, no differences were attributable to weathering treatment. This is unlike the fuel oil residues, where weathering significantly reduced the CO_2 emission rate compared with washing only and no treatment. An incidental effect of the use of different oils was to produce different oil residue concentrations in the starting OBS. The second lysimeter experiment was designed to investigate more rigorously the effect of differences in starting concentration.

After eight months of this experiment, the effect of different starting concentrations of oil residues in OBS was to produce differences in the proportion of hydrocarbon degraded; from zero (though this may be a spurious result) to 55%. No consistent pattern was found to relate decomposition directly to starting concentration. The results do, however, suggest that there was a progressive rise in decomposition rate with increasing concentration, followed by a fall, as concentrations rose above 7.5%. A further indication that this may be the case was shown by the pattern of emission rates of CO_2 from the lysimeters. During August 1996 net flux measurements over a 24 hour period, at a time of expected high microbial activity, increased progressively with increasing oil residue concentration up to 7.5% and then decreased to values below those for a 2.5% starting concentration. The pattern in March was similar although the actual values obtained were lower. There was no difference between flux rates from OBS with starting concentrations of 2.5% and 5% but, above 7.5%, (where maximum rates were achieved) flux was again reduced significantly.

The most likely explanations are:

- at high concentrations, much of the pore space is filled by oil which, allied to the increasing frequency of flooding on the surface of these lysimeters following periods of rainfall, leads to development of anaerobic conditions and reduction in aerobic microbial activity.

- at concentrations greater than 7.5%, the oil residues show a toxic effect.

4.3 Effects of temperature

Because microbial activity is normally affected strongly by temperature, it is to be expected that hydrocarbon degradation and carbon dioxide emission would be influenced by this factor. Such a relationship was demonstrated in a microcosm experiment in which OBS samples taken from the dune burial plots at Eskmeals were incubated at different temperatures in the laboratory. Respiratory activity was measured as CO_2 flux.

The results showed a more or less linear increase in CO_2 emission with rise in temperature, up to 20°C and a more rapid response above that. Samples of OBS from two depths showed similar, elevated, respiration rates compared with controls. The control sample taken from 30-35cm deep showed a higher rate of respiration than that from 60-65cm because of the presence of other organic matter in the surface horizons of the dune soil.

Temperature strongly influenced weekly CO_2 emission rates within lysimeters containing OBS made with sands from different locations around the coast, confirming the findings of the laboratory incubation study (Fig 4.2). The relationship between net CO_2 flux and temperature within the OBS layer was highly significant.

Comparison of the increase in flux between 5 and 15°C (of 31 mg C m^{-2} h^{-1}) and between 15 and 25°C (104 mg C m^{-2}. h^{-1}) demonstrated a Q_{10} value of approximately 3. That is, a rise in temperature of ten degrees from 5 to 15°C or 15 to 25°C increased microbial activity by a factor of three (Fig 4.3). Values of Q_{10} greater than two are usually taken to indicate enhanced biological activity. Confirmation of the effect of temperature over a smaller time scale was also demonstrated in lysimeters. Carbon dioxide fluxes followed a diurnal pattern over a period of 48 hours, reflecting changes in temperature recorded in the OBS layer and tracking variation in air temperature (Fig 4.4).

4.4 Effects of moisture

Within the first few weeks of the start of the third lysimeter experiment it became obvious that rainfall affected the evolution of carbon dioxide into the headspace above the sand surface. Recent rainfall events appeared to coincide with much lower flux values, resulting in highly variable between-week measurements. These "quenching" effects continued to be observed through to the

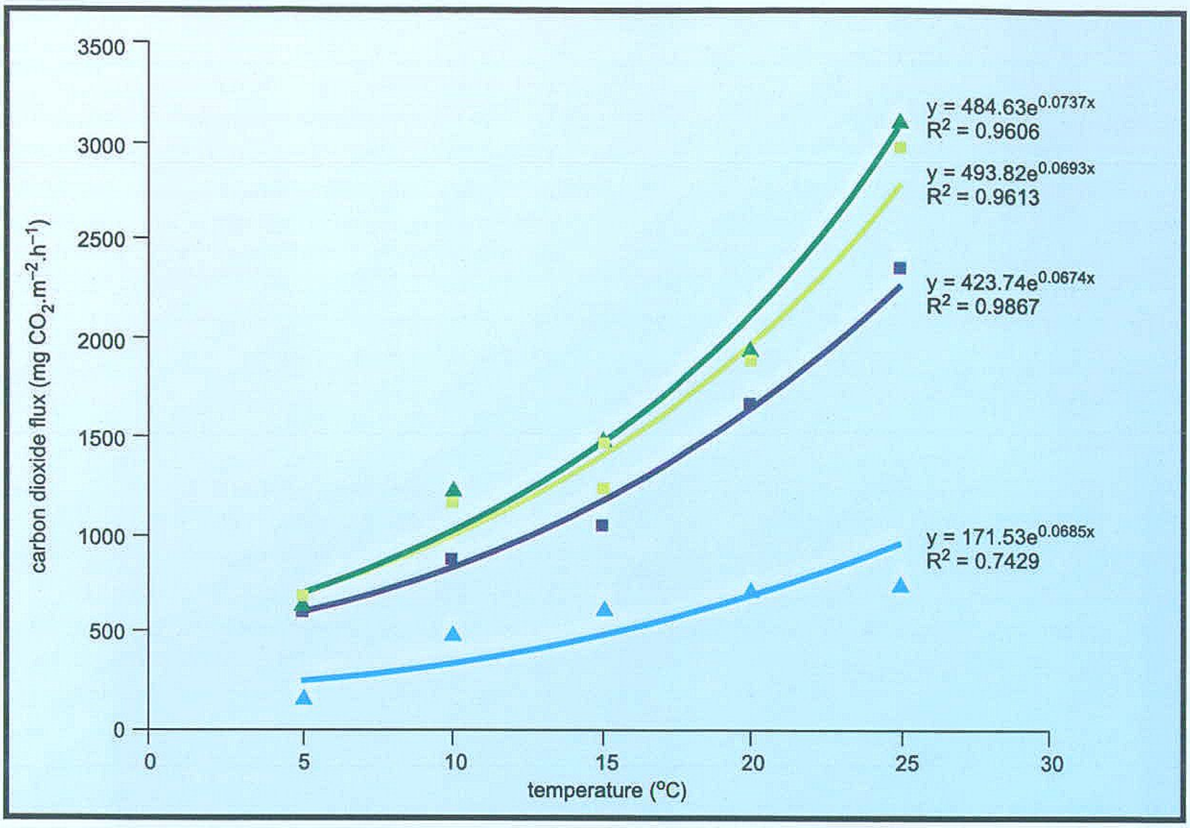


Figure 4.2. Effect of temperature on carbon dioxide flux from incubated OBS (green) and control sand (blue) samples taken from dune burial sites. Samples from 30cm are indicated by triangles; those from 60cm by squares.

conclusion of the experiment and affected both control and treatment lysimeters. However, because of decreasing microbial activity within the OBS, the effects were not as pronounced during the latter part of the experimental period. During periods of light rain, presumably when steady infiltration and through-flow were sufficient to counteract the tendency for waterlogging to occur, the rate of emission of carbon dioxide was unaffected.

The influence of moisture on microbiological activity in the field has also been demonstrated in two trials. Continuous measurements made in the first Pendine experiment showed that, in a well drained system with a low concentration of aggregated oil residues, a period of rainfall enhanced the rate of carbon dioxide emission (Fig 4.5).

Variation in water table fluctuation within the Eskmeals trial appeared to influence oil residue degradation directly in the dune pasture burial experiment. Power curves fitted to hydrocarbon decay data are based on the following equations, but have been adjusted to give a constant starting point of 5% concentration of oil residues in the OBS at 1 month and so allow easier comparison:

Winter burial

Block 1

$Y=4.67.X^{-0.219}$ $R^2=0.96$

Block 2

$Y=4.98.X^{-0.181}$ $R^2=0.82$

Block 3

$Y=5.09.X^{-0.163}$ $R^2=0.74$

Summer burial

Block 1

$Y=4.59.X^{-0.239}$ $R^2=0.88$

Block 2

$Y=4.78.X^{-0.200}$ $R^2=0.90$

Block 3

$Y=4.93.X^{-0.163}$ $R^2=0.97$

In both winter and summer burial treatments, plots in block 1 showed the fastest rate of hydrocarbon degradation and those in block 3 the slowest (Fig 4.6). Because of the way the experiment was arranged, with block 3 on the lower part of a sloping site and block 1 on the upper part, groundwater rose towards the OBS layer more frequently in block 3. The water table rose and

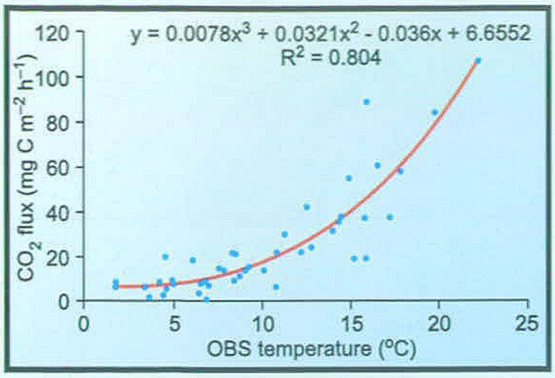


Figure 4.3. Change in carbon flux with rising temperature in lysimeter experiment using different sands.

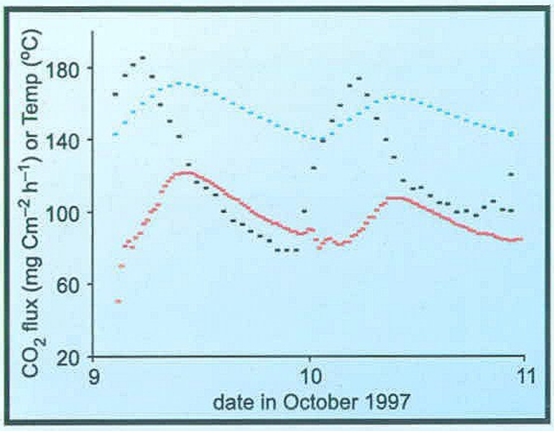


Figure 4.4. Diurnal variation in air (black) and OBS (blue) temperature, and its influence on carbon dioxide flux (red). Temperatures are shown as actual values x 10 in order to achieve a common scale.

penetrated into both OBS deposits during winter periods of all three years of the experiment (Figure 4.7). However, this penetration was higher and more prolonged in block 3, producing longer periods when anaerobic conditions prevailed and so restricted degradation activity.

Soil moisture was also one of the measurements made to characterise sands from different sites in the extensive field trial. Although overall there was no relationship between initial moisture content and amount of hydrocarbon degraded, there appear to be two groups of sites. One had a relatively low water content and showed a range of capabilities for decomposition of oil residues, whilst the other had a wider range of soil moisture and a lower overall capacity to degrade oil residues. If the two groups are taken separately, each shows a positive relationship between water content and capacity to degrade hydrocarbons. This result appears to

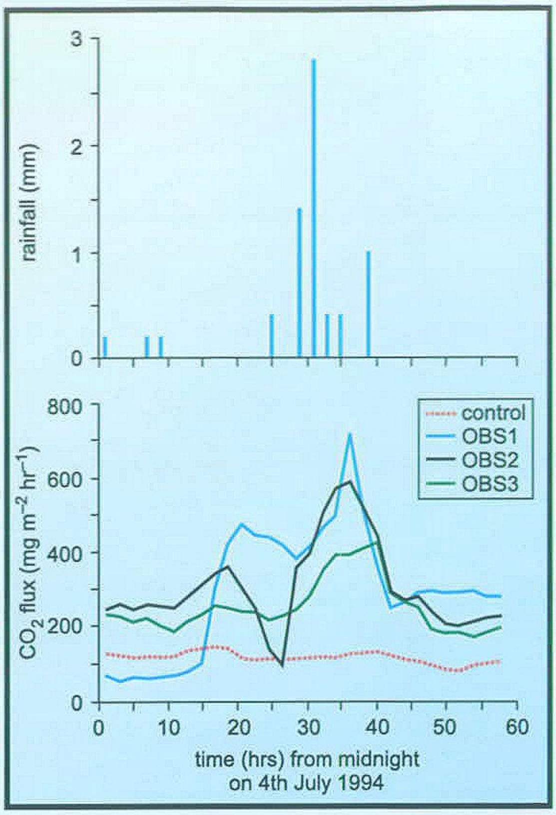


Figure 4.5. Rainfall and carbon dioxide flux over two days in first Pendine experiment.

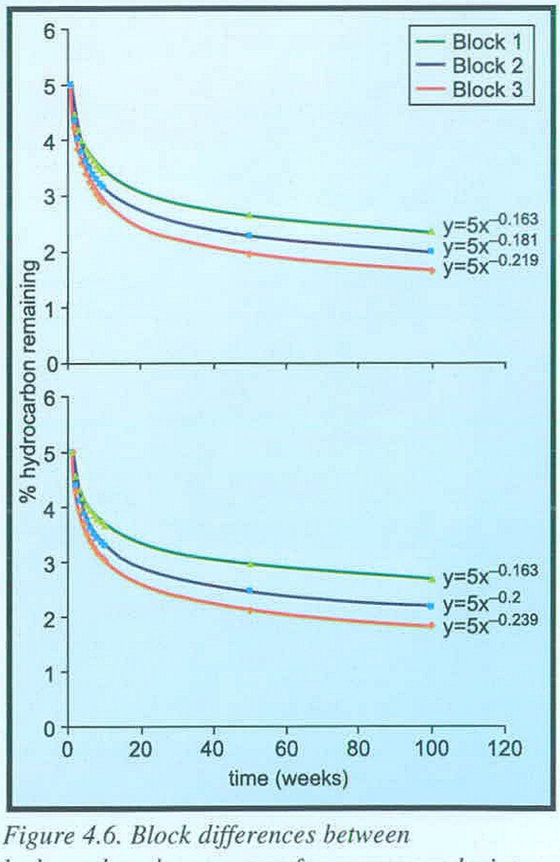


Figure 4.6. Block differences between hydrocarbon decay curves for summer and winter burial in dune pasture at Eskmeals.

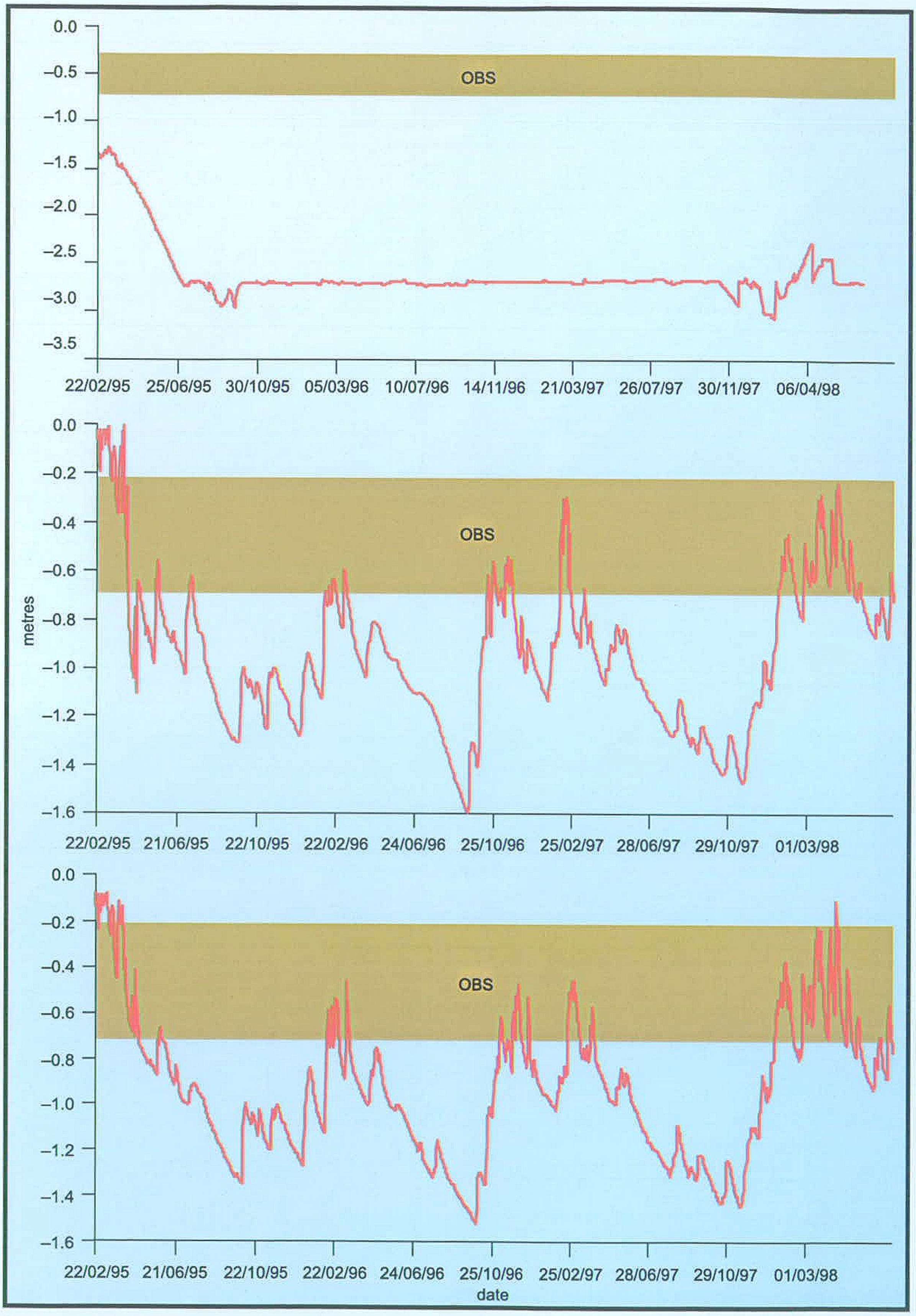


Figure 4.7. Water table fluctuations in relation to OBS in; a) dune, b) block 1 and c) block 3 of burial experiment at Eskmeals.

contradict the findings of the lysimeter experiment. However, in well-drained, coarse-textured systems, such as those found in coastal dunes, moisture availability may be a factor limiting degradation at times. Where fine material is incorporated in the sand, or the sands are well cemented, there may be a greater tendency for temporary waterlogging and reduced degradation.

4.5 Effects of sand type

The burial trials established at Eskmeals used quarry sand as the bulking medium in preparation of OBS. The rate of degradation was observed to be lower than that in the first Pendine experiment. It is possible that a lack of buffering in the Eskmeals quarry sand, compared with the Pendine beach sand contributed to this difference. The presence of calcium carbonate in shell fragments in the beach sand incorporated in the Pendine trial could have provided the necessary buffering to prevent a fall in pH unfavourable to bacterial growth.

Variation in the native sand into which OBS was introduced appeared to have little effect at a local scale. No significant differences were observed between burial plots in dune and dune pasture soils at Eskmeals. Results show that the driest of the three blocks in the dune pasture burial trial matched the dune burial plots in terms of the degradation rate function and the total amount of hydrocarbon degraded over a two year period. Equations for the two locations were:

$$Y=4.67.X^{-0.219}$$

for the dune pasture burial and

$$Y=4.67.X^{-0.214}$$

for the dune burial..

The extensive trial was undertaken to determine whether differences on a larger scale did influence the degradation process. Results from this trial were assessed in conjunction with those from a collateral trial at Eskmeals using sand from all extensive trial sites. and from a lysimeter experiment in which sands from five of the locations were used to prepare OBS to a common starting concentration. These trials, where external conditions were common, revealed differences in the rate of hydrocarbon degradation.

Field trial

Because of confounding factors in oil preparation, site location and site characteristics, it was difficult to relate rates of hydrocarbon decomposition to specific factors. However, differences were found (Table 4.4) and these appeared to be related more to characteristics of the sands used in preparation of OBS than to local climatic factors. This seems somewhat surprising given that temperature is clearly an important factor controlling hydrocarbon degradation and clear differences were found in temperature regime between sites. Another confounding factor was the tendency of some sites to flood, though the extent and duration of such flooding is not known. However, at one site (Spiggie) final sampling was not possible because the site was inundated.

The results of a principal components analysis showed a strong inter-correlation among ten variables used to describe each site, though no single variable played a dominant role. Three components produced by the analysis accounted for 70% of the variation encountered. These were:

- calcium-magnesium-organic matter content of beach sand used;
- moisture content of OBS and pH of beach sand;
- site rainfall and a possible association with water table.

Table 4.4. Variation in chemical and physical characteristics of sands from extensive trial sites used in the third lysimeter experiment.

Site	pH	Loss on ignition (%)	Calcium (%)	Nitrogen (%)	Moisture content (%)	Particle size (% composition) >2mm	>1mm	>0.2mm	>0.2mm
Askemish	8.3	1.2	14.0	0.015	22.0	0.0	0.3	94.0	5.4
Cresswell	6.9	0.7	2.5	0.002	1.9	0.0	1.5	98.0	0.1
Largo	8.4	0.9	4.5	0.006	6.1	0.1	1.6	96.0	2.6
Pendine	8.2	0.7	3.6	0.006	3.0	0.0	0.5	76.0	24.0
Tain	7.9	1.4	0.1	0.041	20.0	0.0	4.8	65.0	30.0

Table 4.5. Variation in microbial activity (measured as carbon dioxide flux) in OBS prepared using sands from different extensive trial sites. Values are expressed as mg C m^{-2} h^{-1}

Site	Treatment	Summer	Autumn	Winter	Spring
Askernish	OBS	93.7	32.8	23.4	73.9
	Control	13.6	5.2	3.9	9.2
Cresswell	OBS	68.6	19.2	12.5	39.8
	Control	13.7	5.8	4.6	10.1
Largo	OBS	79.1	24.6	15	48.4
	Control	18.7	5.6	4.4	9.7
Pendine	OBS	78.6	20.5	15.5	42.1
	Control	21.6	6.3	4.7	9.4
Tain	OBS	86.1	14.5	4.4	22.5
	Control	27	5.7	4.9	11.5

Collateral trial

Within the collateral trial at Eskmeals, effects of differences in sand type were revealed. A significant relationship was found between the proportion of hydrocarbon degraded and the final moisture content of the OBS mixture. Soil moisture content is dependent on a number of intrinsic features of the sand: grain size and organic matter content are two of the more important. The influence of water content in this trial re-enforced the results from earlier lysimeter experiments, and the burial and landfarming field trials at Eskmeals. A high water content inhibited aerobic degradation of oil residues by micro-organisms.

Lysimeter experiment

Under the standardised conditions of lysimeter experiment 3, there was considerable variation in the rate of oil residue decomposition in sands collected from five of the locations used for the extensive field trial.

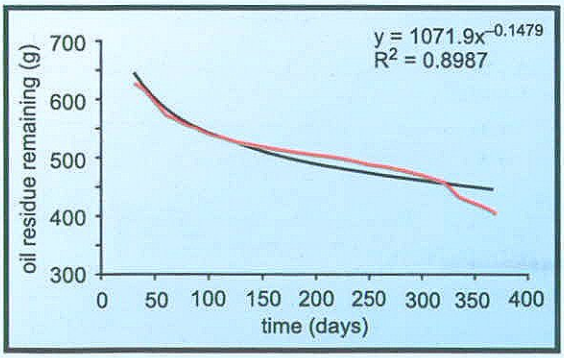


Figure 4.8. Hydrocarbon degradation in OBS prepared using Askernish sand. Calculated values are based on measured carbon dioxide flux values. A power curve has been fitted to the data.

Three of the sands (Askernish, Cresswell and Largo) were characterised by relatively large grain size, though Askernish also had a high calcium and organic matter content. Cresswell differed from Largo principally in its lower calcium content and lower pH. Of the two sands with a high proportion of fine particles, Tain had much more organic matter and nitrogen than Pendine, but a lower calcium content.

Measurements of carbon dioxide flux after one week showed that lysimeters containing Askernish OBS gave the highest rates of carbon dioxide production.
These lysimeters continued to produce the highest flux values throughout the experiment (Table 4.5). However, OBS prepared using sand from Tain showed a high initial rate of microbial activity but, on autumn, winter and spring sampling occasions it consistently produced the lowest values of all five sands tested. Sands from Largo and Pendine gave consistently similar values approximately two thirds that of Askernish. Cresswell samples were consistently somewhat lower than Largo and Pendine. In control samples, Askernish and Cresswell had similar, low, rates of microbial activity, with Largo and Pendine having slightly higher activity. The highest rate was found in Tain controls.

A possible explanation is that this sand contained a suitable carbon substrate for microbial decomposition, though this need not have been based on petroleum hydrocarbons. Tain sand was known from analysis to have been finer than the others sampled and had a higher organic matter content (as measured by loss on ignition).

Carbon dioxide flux has been used to calculate degradation rates without the need for destructive sampling. ANOVA showed that, for individual samples, variances about the mean in carbon dioxide flux were comparable over time. This meant that random errors were consistent between one set of measurements and another and we could have confidence in using these mean values in the predictive model. A matched pair t-test confirmed that only Askernish gave a significantly different (higher) rate of respiration among all tested pairs. Plots of change in estimated oil residue mass with time have thus been possible assuming a starting weight of 625g of oil residue (5%) in the OBS (Fig 4.8).

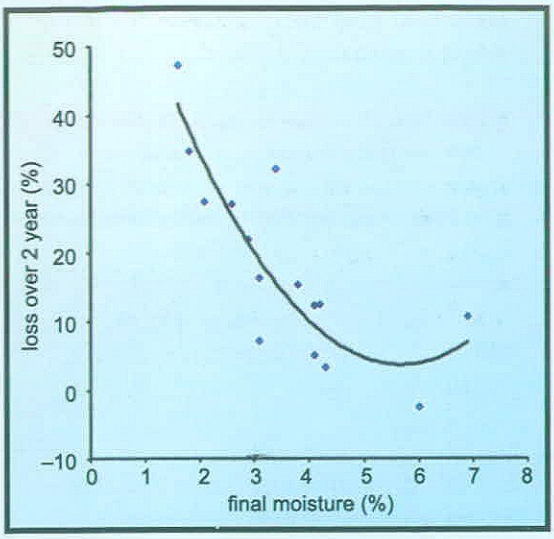


Figure 4.9. relationship between final moisture content of OBS, prepared using different sands, and hydrocarbon loss.

After eight months the estimated reduction in oil residues was 43% for Askernish and 28% for Cresswell, Largo, and Pendine. Although Tain OBS lost a similar percentage, carbon dioxide production ceased after 130 days of the experiment. This suggests a very high level of initial activity but that some factor limiting that activity came into operation subsequently.

The results obtained did not precisely match expectations from laboratory incubation of sands from the different sites, which predicted that Cresswell would show low activity, Pendine and Largo would show intermediate activity, and that Askernish and Tain would be the most active. Tain samples, in particular, did not behave as expected. Although an initial active population of micro-organisms was present in Tain sand, it would appear that other factors in the field or in lysimeter experiments limit actual degradation. Among the more important of these factors may be the fineness of the sand itself, where a small pore size, may retain water, and limit the movement of the oxygen and nutrients necessary for microbial growth. That water content may be important is indicated by the results, after two years, from the collateral trial, where there was a clear relationship between hydrocarbon loss and moisture content of the OBS (Fig 4.9).

It has also been suggested (Ellis & Adams 1961) that the presence of some other organic compound in soil may provide an alternative, preferred, substrate which means that the full hydrocarbon-degrading potential of the microbial populations present may not be achieved. However, this contention is open to argument as almost any population of bacteria is capable of adapting to degrade hydrocarbons and the presence of one active community does not lead to exclusion of another.

4.6 Effects of microbial differences

Based on colony morphology, which may not always be reliable, differences were seen in the composition of the bacterial communities from beach sand and OBS. Some colony types disappeared after the addition of oil residues, which could suggest differential toxicity. Whilst prediction of activity may not yet be possible, our results show that, generally, microbial populations adapt rapidly and become capable of degrading hydrocarbons.

The rate, and extent, of degradation in the extensive trial will have depended on many factors, not least of which would have been the pollution history of the beach sand used to prepare the OBS. The inability to detect a capacity for degrading aromatic molecules might suggest the beach sand came from a relatively unpolluted location, but exposure to oil residues still allowed populations with this ability to develop.

Table 4.6. Culturable bacterial counts obtained from samples taken from the extensive study sites in spring 1996. Counts are given in terms of number of colonies x 10^6 per gram dry weight of material sampled. ns = no sample.

Site	Beach sand	OBS mix	native sand
Askernish	17.9	124	3.7
Camusdarach	3.8	1.6	6.5
Climping	0.8	0.9	69.2
Cresswell	1.1	0.4	21.4
Eskmeals	2.6	1.1	1.4
Horsey	8.9	8.3	12.3
Largo	4.6	4	ns
Northam	3.2	3.3	31.7
Oldshoremore	2.6	21.8	9.1
Pendine	5	6.4	8.7
Bay of Skelt	2.2	0.3	18.1
Saltfleetby	2.6	8.4	35.8
Spiggie	9.9	14.6	9.4
Tain	1.8	8.1	18.1
Torrs Warren	3.6	15.7	1.6

Microbial respiratory activity was generally greater in dune soils in which the OBS bags were buried in the extensive trial than in beach sand (Table 4.7). However, the reverse was true for samples from Askernish, Bay of Skelt, Tain and Torrs Warren where high respiratory activity was associated with incubated samples of beach sand. One possible explanation is that this may have been related to the recent pollution history of the beaches concerned. As noted in Section 2.2, oil-polluted sites tend to have larger populations of hydrocarbon-degraders than unpolluted sites. However, the beaches in question are not those where there is a high expectation of oil pollution.

Spring burial

With the exception of Saltfleetby, microbial respiration was stimulated after the addition of oil residues (indicating metabolism, i.e. degradation of those residues). The level of stimulation varied. It was high in samples from Askernish, Largo and Tain, but low in samples from Camusdarach, Cresswell, Horsey and Saltfleetby. It was moderate in all other samples (Table 4.8).

Although there was considerable variation between replicate samples removed from each site, the data showed similar trends, with four observable patterns of microbial response to oil residue addition:

- Immediate, moderate, stimulation of activity, which was maintained (Bay of Skelt, Climping, Northam, Pendine, Spiggie) or increased (Eskmeals, Oldshore More, Torrs Warren) over 3 or 6 months of burial.
- Immediate, large, stimulation of activity that was maintained for 3 to 6 months (Askernish, Largo, and Tain).
- Little immediate stimulation, but an increase in activity after 3 months (Cresswell, Horsey) or 6 months (Camusdarach) exposure to OBS.
- No stimulation within the first six months (Saltfleetby).

These findings suggest that there may be large differences in the adaptability of microbial populations between sites. We have not investigated whether this is related to site specific differences in the species, or to the balance between bacteria, fungi, yeasts and algae (all of which taxonomic groups have species capable of degrading hydrocarbons). The capacity to maintain any activity which is stimulated is also variable and this may be a function of the physical and chemical nature of the deposits within which the micro-organisms are found, rather than a property of the microbes themselves. Any feature which reduces the availability of nutrients or oxygen, or which prevents the dispersal of breakdown products and so leads to changes in the local environment, may

Table 4.7. Respiratory activity of samples taken from extensive study sites in spring 1996. Values given are micromoles CO_2 g^{-1} dry weight day^{-1}. ns = no sample.

	beach sand	OBS mix	native sand
Askernish	0.341	0.928	0.179
Camusdarach	0.022	0.032	0.066
Climping	0.037	0.17	0.8
Cresswell	0.013	0.059	0.068
Eskmeals	0.024	0.12	0.054
Horsey	0.017	0.03	0.085
Largo	0.141	0.591	ns
Northam	0.023	0.101	0.306
Oldshoremore	0.043	0.117	0.241
Pendine	0.038	0.147	0.333
Bay of Skelt	0.177	0.246	0.075
Saltfleetby	0.129	0.054	0.285
Spiggie	0.032	0.116	0.112
Tain	0.279	1.165	0.134
Torrs Warren	0.107	0.148	0.032

Table 4.8. Bacterial respiratory activity in samples taken from OBS buried in spring 1996 at different locations. Values are micromoles CO_2 g^{-1} dry weight day^{-1}

	Time (months) from burial			
	0	3	6	12
Askernish	0.928	0.345	0.663	1.550
Camusdarach	0.032	0.044	0.256	0.930
Climping	0.170	0.685	0.314	1.970
Cresswell	0.059	0.170	0.147	0.490
Eskmeals	0.120	0.173	0.317	0.530
Horsey	0.030	0.164	0.253	0.790
Largo	0.591	0.499	0.681	1.660
Northam	0.101	0.110	0.172	0.670
Oldshoremore	0.117	0.124	0.261	0.590
Pendine	0.147	0.259	0.315	0.600
Bay of Skelt	0.246	0.320	0.229	1.220
Saltfleetby	0.054	0.052	0.061	0.480
Spiggie	0.116	0.324	0.187	1.890
Tain	1.165	1.329	0.983	2.940
Torrs Warren	0.148	0.225	0.317	0.580

Table 4.9. Bacterial respiratory activity in samples taken from OBS buried in autumn1996 at different locations. Values are micromoles CO_2 g^{-1} dry weight day^{-1}

	Time (months) from burial			
	0	3	6	12
Askernish	0.57	0.90	0.30	0.76
Camusdarach	0.08	0.16	0.17	0.76
Climping	1.14	1.80	0.57	0.63
Cresswell	0.28	0.29	0.10	0.53
Eskmeals	0.28	0.22	0.07	0.38
Horsey	0.27	0.79	0.17	0.75
Largo	0.80	0.21	0.13	0.40
Northam	0.21	0.69	0.14	0.23
Oldshoremore	0.21	0.09	0.04	0.46
Pendine	0.41	0.54	0.10	0.32
Bay of Skelt	0.52	0.99	0.49	1.30
Saltfleetby	0.09	0.51	0.51	0.39
Spiggie	0.52	1.52	0.57	1.43
Tain	1.95	1.52	0.39	1.02
Torrs Warren	0.36	0.48	0.12	0.32

inhibit microbial activity. The sands do differ in a number of physical and chemical characteristics.

Autumn burial

As in the spring burial, addition of oil residues stimulated microbial activity. The level of stimulation was high in OBS buried at Askernish, Bay of Skelt, Largo and, possibly, Pendine, low at Camusdarach, and intermediate at the other sites. There were three notable differences in response of beach sand populations compared with spring burial.

1) High activity at Bay of Skelt
2) Moderate stimulation at Saltfleetby
3) Low activity at Largo.

In addition, catechol degraders were found in samples of beach sand from Tain and OBS from Climping.

Fungi

Examination of samples taken from OBS, which had been buried for six months at each of six sites showed different patterns of fungal colonisation.

Plates prepared using beach sand had few, if any fungal colonies, and those using OBS consistently showed many more colonies and species. There were large differences in actual numbers recorded depending on site of origin of the sand. In general, those sites with high bacterial counts had low fungal counts.

Table 4.10. Fungal distribution in beach sand and OBS samples from 5 sites around Britain. Bacterial counts are 10^6 g^{-1} dry weight of material sampled. Fungal species and colonies are total numbers per plate.

	bacterial	fungal spp.		colonies	
	counts	sand	OBS	sand	OBS
Askernish	57.8	0	5	0	149
Cresswell	7.7	0	8	0	25
Eskmeals	26	3	7	6	126
Largo	69.1	1	10	1	48
Pendine	45.4	0	7	0	35
Tain	120	0	2	0	2

It is known that, in general, bacteria are favoured by growth media which are circum-neutral, whilst fungi tend to grow in more acidic conditions. However, no correlation was found between pH of initial beach sand and fungal growth. No data exists on the pH of OBS at the time of sampling for fungi because the presence of oil residues makes accurate measurement difficult.

4.7 Effects of treatment

In translating experiments at a small scale to realistic and practical application at the operational scale, it is necessary to take account of different management procedures, which may be adopted, and the effects that these will have on the degradation process. Minimal differences occurred between the patterns of breakdown of OBS in burial plots, whether these were in dunes or dune pasture.

The establishment of burial and landfarming trials side by side at Eskmeals gave the opportunity for comparisons between such treatments.

The two major differences between burial and landfarming plots were:

- Whilst OBS in burial plots was not exposed directly to the atmosphere, landfarming plots were.
- OBS in burial plots remained undisturbed once in place, but in landfarming plots it was mixed at regular intervals.

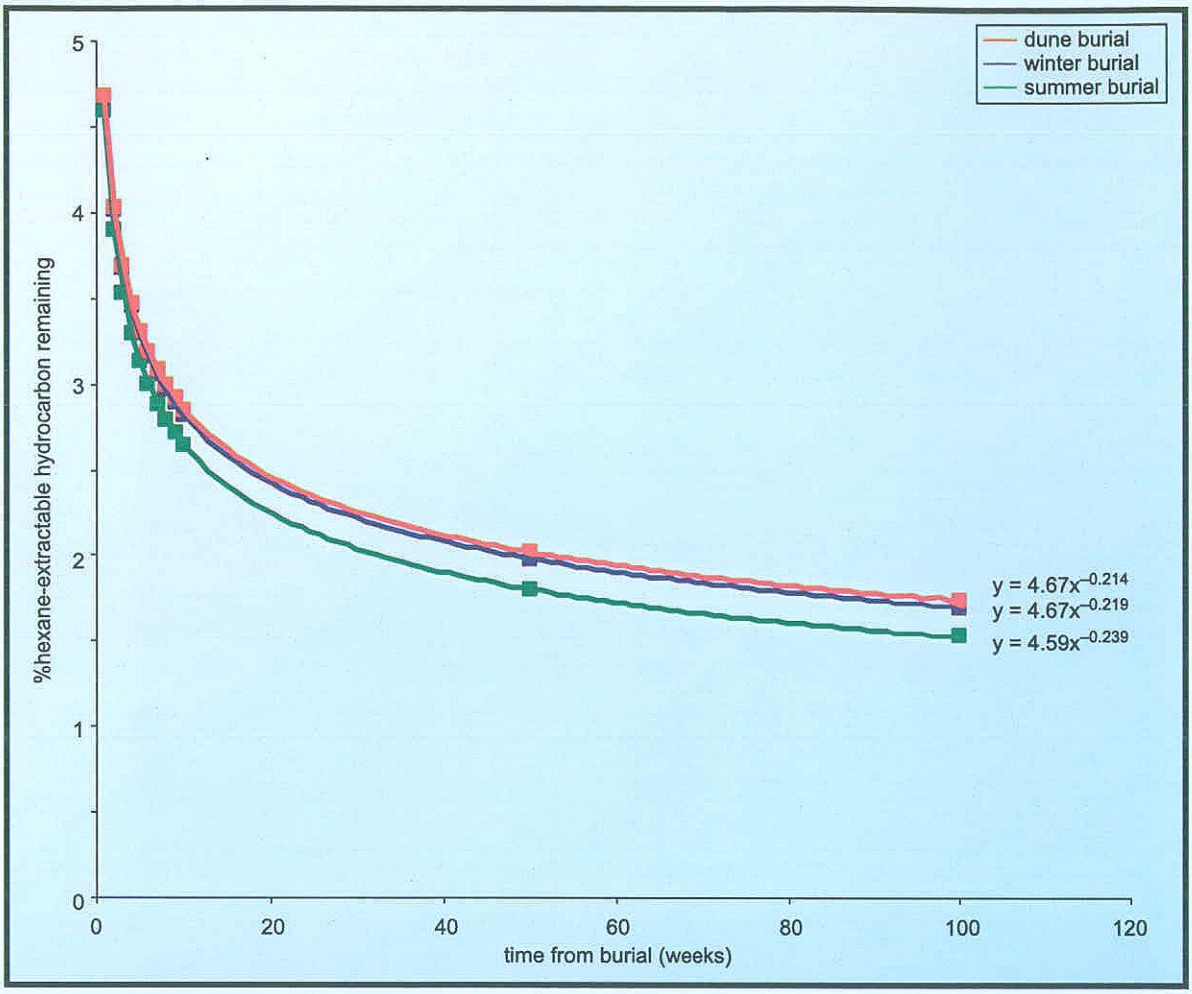


Figure 4.10. Comparison of fitted decay curves for dune burial plots, and winter and summer dune pasture burial in block 1 within the drier part of the pasture.

However, for a given land area, burial plots were capable of accepting greater volumes of OBS than landfarming plots. Hence, two different comparisons have been made: between rates of degradation and total amount of oil residue degraded per unit area of land occupied.

Decay curves for incorporated oil residues in both burial and landfarming plots showed rapid initial falls in hexane-extractable hydrocarbon concentration, followed by subsequent slowing of the rate of loss. As in other experiments, a series of power equations best explained the patterns of degradation. However, the rate function in the equations differed depending on treatment applied.

Comparison between landfarming treatments

The rate of loss of hydrocarbons from OBS in landfarming plots depended on both the time of incorporation (winter or summer) and the frequency of ploughing. In both winter and summer burial plots the rate of decomposition of the oil residues was in the order: 2-weekly plough>4 weekly plough>no plough. Clearly, frequent ploughing had a major effect on hydrocarbon breakdown rate, possibly because it increased OBS aeration by bringing buried material to the surface, and also redistributed, moisture, nutrients and microbial populations.

Winter burial appeared to be more favourable for degradation than summer burial. This may be a real effect, resulting from the creation of more suitable moisture conditions in winter, or an artifact produced as a result of incomplete incorporation of the OBS into the upper layer of sand in the summer treatment. In summer treatments there was a tendency for the topsoil to dry as large clods. Such drying may have produced conditions where water became a rate limiting factor (cf. first Pendine experiment).

Based on an initial hydrocarbon concentration of 4.8% within the OBS incorporated into the landfarming plots, calculation of the amounts of oil residues degraded, by weight, have been made.

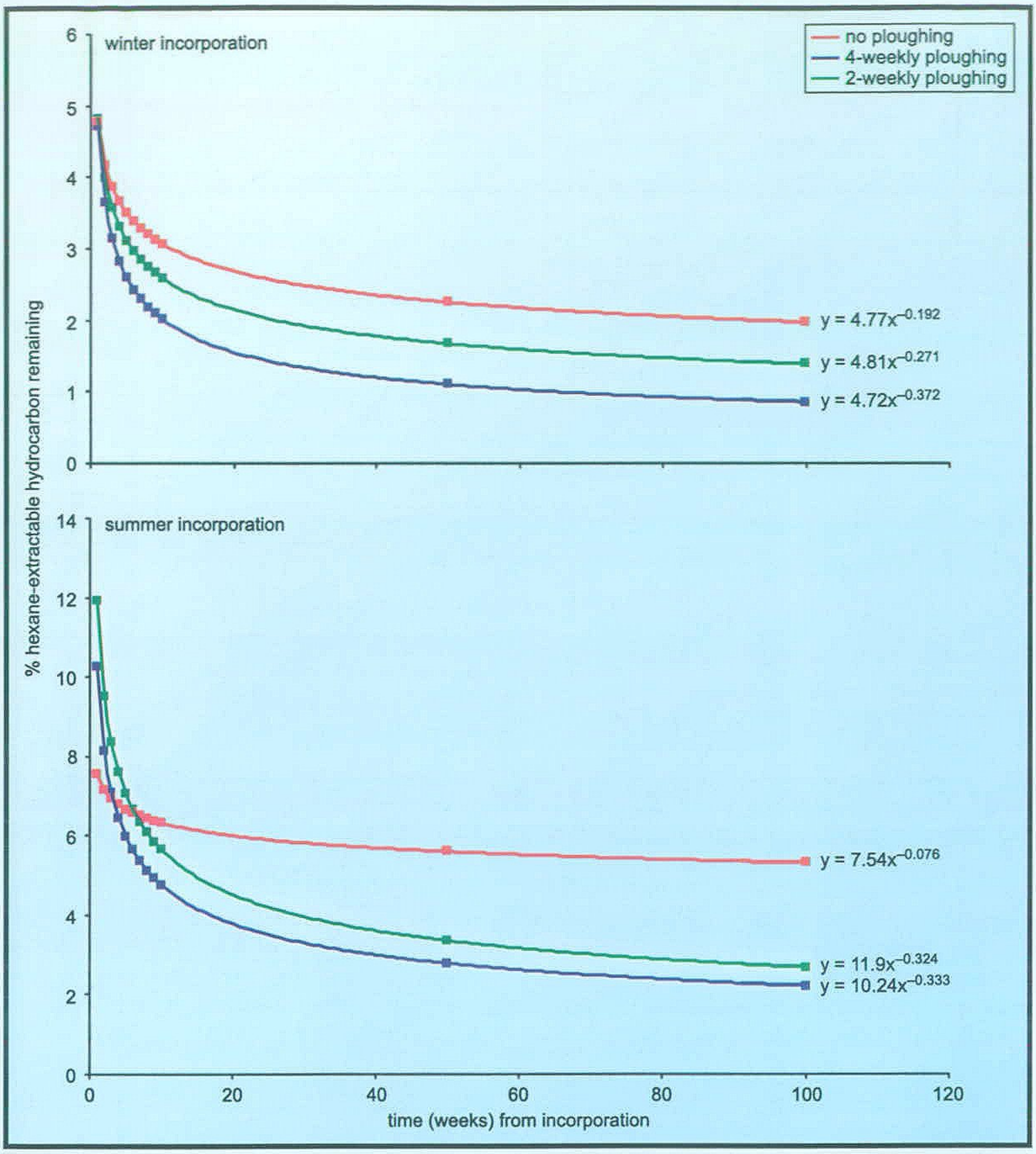


Figure 4.11. Progress of OBS breakdown in landfarming plots established in winter and summer, and subjected to different ploughing treatments (mean values for all three blocks).

These show that ploughing every two weeks increased by 35% the efficiency of hydrocarbon breakdown compared with that in the no-plough treatment in winter plots. The efficiency of degradation was doubled by rotovation every two weeks in the summer incorporation plots (Fig 4.11).

Comparison of landfarming and burial

The degradation rate was consistently higher in ploughed landfarming plots than in burial plots. The process of degradation was more rapid and more complete over two years in ploughed landfarming plots than in burial plots, though not in unploughed landfarming plots. Unploughed winter plots showed similar degradation curves to burial plots, but unploughed summer plots appeared to retain high concentrations of oil residues. Landfarming with frequent ploughing was, thus, more efficient at hydrocarbon removal than burial.

Calculation of total quantities of oil residue degraded showed that burial plots could accept a larger quantity of material initially. Burial plots also degrading a larger absolute amount of hydrocarbon than landfarming plots of equivalent area.

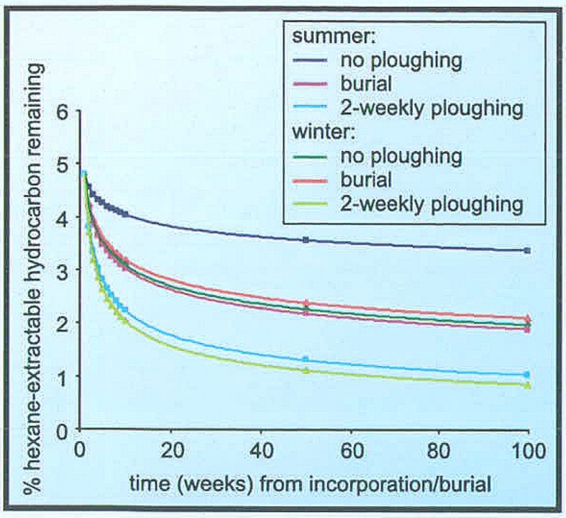


Figure 4.12. Fitted decay curves for breakdown of OBS in landfarming and burial plots at Eskmeals.

4.8 Interactions

The results of the field trials and the lysimeter experiments indicate that there is no single controlling factor that determines the rate of decomposition of oil residues. This is not an unexpected conclusion, bearing in mind the initial proposition (Figure 2.1) that moisture, oxygen supply, temperature, micro-organisms, pH and nutrients were likely to be key factors controlling degradation. From a practical point of view, bearing in mind the starting materials used, temperature and moisture appear to be the most important variables. The lysimeter experiments, in particular, illustrated the interaction of these two climatic variables and a relationship has been derived which links rainfall within the previous twelve hours and soil temperature with the flux of carbon dioxide:

$$\mathrm{Log}_{10}(F) = 0.93 + 0.058(T) - 0.042(P)$$

where F is CO_2 flux (mg $C.m^{-2}.h^{-1}$)
T is temperature within the OBS (°C)
P is precipitation over the previous 12 hours (mm).

This equation would not apply to all situations because the depth of OBS and the initial oil type present would have an influence on degradation potential. However, the degradation pattern would follow the general "power curve" relationship over time in each case.

A fully predictive equation would need to be based on measurements made of all the interacting factors which influence the microbial degradation of petroleum hydrocarbons.

Table 4.11. Comparison of percentage decomposition of hydrocarbons under burial and landfarming treatments.

Disposal method	% degraded after 2 years
Dune burial	60.1
Winter burial	18.0
Summer burial	20.0
Winter landfarming	
2-weekly plough	82.1
4-weekly plough	71.6
no plough	41.0
Summer landfarming	
2-weekly plough	54.5
4-weekly plough	44.8
no plough	29.1

Table 4.12. Comparison of total weights (tonnes per hectare) of hydrocarbon degraded in burial and landfarming plots at Eskmeals.

	Oil residues in OBS	
Disposal method	initial weight	degraded after 2 years
Dune burial	334	201
Winter burial	1008	182
Summer burial	1029	210
Winter landfarming		
2-weekly plough	134	110
4-weekly plough	134	96
no plough	134	55
Summer landfarming		
2-weekly plough	134	73
4-weekly plough	134	60
no plough	134	39

5. DEGRADATION PRODUCTS AND THEIR FATE

5.1 Introduction

Some of the compounds present in the unweathered parent oils are known to be biologically active and to produce toxic effects. Acute effects are shown by exposure to the BTEX group of cyclic compounds (benzene, toluene, ethylbenzene and xylene). Polycyclic aromatic hydrocarbons (PAHs), which are ubiquitous in the environment, may be particularly toxic and some are known carcinogens or mutagens. However, because many of the more volatile, low molecular weight, compounds (including the BTEX compounds) are not present in weathered oil residues, these residues may not pose a significant threat to the environment.

Hydrocarbons consist almost entirely of carbon and hydrogen atoms and the main product of oxidation is carbon dioxide, which poses no pollution threat. Complete degradation of hydrocarbons is desirable, but it is possible that partial biological transformation could result in the release of potentially toxic intermediate compounds.

The production of intermediate compounds during the course of degradation and the existence of PAHs in weathered oils may pose threats to microbial, plant and animal communities, if released into the environment at concentrations above known critical thresholds.

In order for a disposal method to be environmentally acceptable, the risks of producing and releasing significant quantities of toxic compounds must be reduced to a minimum. Concentrations must remain below the critical thresholds. As well as release, the problem of transport of potentially toxic compounds to groundwater, and hence their wider dispersal, has had to be addressed. Because of this, the project included a major component designed to determine whether there was any movement of environmentally unacceptable materials from the OBS to surrounding soil or underlying groundwater. In the Feasibility Study phase of the project, heavy metals, some hydrocarbons and PAHs were identified as possible sources of concern. For reasons given below, heavy metal ion concentrations were not measured. Samples were taken on a regular basis to detect and monitor the concentrations of hydrocarbons in drainage water from OBS in lysimeters and in groundwater below field trials. A more restricted sampling programme was carried out to determine the presence of PAHs in these waters.

5.2 Heavy metals

Although crude oils contain heavy metals, principally vanadium (V) and nickel (Ni), the concentrations found are not normally above a few parts per million. In some oils, e.g. Boscan crude from Venezuela, the concentrations of Ni may reach 100ppm and V may be as high as 1,000ppm (Stencel & Jaffe, 1998). Such high concentrations are rare, however. More typical values are shown in Table 5.1 together with the WHO drinking water guideline value for Ni (though none have yet been set for V by WHO). Environment Assessment Levels (EALs) set by the Environment Agency vary depending on water hardness. For nickel, they range from 50µg l^{-1} in the softest waters (containing less than 50mg l^{-1} of calcium carbonate) to 200µg l^{-1} for very hard waters (with more than 200 mg l^{-1} of calcium carbonate). For vanadium, water with less than 200 mg l^{-1} of calcium carbonate, the EAL is 20µg l^{-1} and for harder waters it is 60µg l^{-1}. In coastal waters, the EAL is 100µg l^{-1} of vanadium. In the context of the current study, heavy metal contamination was not considered to pose a serious environmental hazard because of the low concentrations involved. They are not easily eluted as free ions and pH values are high enough in seawater and coastal sandy soils to prevent mobilisation in the dune environment.

Table 5.1. Concentrations of nickel and vanadium in some typical oils and calculated concentrations in 5% OBS prepared using those oils. ns = no standard.

	Concentration (mg kg^{-1})			
	In oil		In 5% OBS	
Oil type	Ni	V	Ni	V
Kuwait crude	9.6	31	0.48	1.55
Nigerian crude	5	<0.5	0.25	<0.03
Libyan crude	4.3	1.7	0.21	0.08
Forties crude	2	3	0.1	0.15
range in 6 fuel oils	1.5 - 66	2.7 - 180	0.07 - 3.3	0.13 - 0.16
WHO guidelines (mg l^{-1})			0.02	ns

5.3 Changes in hydrocarbon composition

As oil residues degrade, the more readily decomposed hydrocarbon components, e.g. short chain alkanes, disappear first, leaving progressively more recalcitrant compounds behind. The current project did not investigate the changes in composition of oil residues in detail as the overall process is well recorded (Kennicut 1988, Blenkinsopp *et al.* 1995). Instead, samples were taken at intervals from a limited number of the experiments and were subjected to analysis to determine the overall hydrocarbon composition and, more specifically, the concentration of representative PAH's. In particular, samples from the second Pendine trial have been analysed by GC-MS.

The result of the analyses of samples from the second Pendine trial, over a period of eighteen months, followed the expected course. There was a reduction in the concentration of hydrocarbons over a large part of the range and virtual loss, as a result of microbial degradation, of short chain compounds within the upper layer of the OBS deposit. Whilst hydrocarbons were also removed from the lower layers of the OBS, larger quantities of short chain compounds remained in this part of the deposit. In both parts of the OBS deposit, molecules with carbon chain lengths of 20-21 produced maximum peak heights throughout the period of measurement.

Table 5.2. PAH concentrations ($\mu g\ g^{-1}$) in fuel oil, emulsion and OBS prepared for second Pendine experiment. Note: $\mu g\ g^{-1}$ = parts per million).

PAH compound	oil	emulsion	OBS
Naphthalene	2067.300	1386.500	346.625
Acenaphthalene	10.500	6.300	1.575
Acenaphthylene	98.800	66.600	16.650
Flourene	382.100	257.200	64.300
Phenanthrene	1374.700	910.900	227.725
Anthracene	140.100	95.800	23.950
Fluoranthene	90.700	61.100	15.275
Pyrene	690.700	458.100	114.525
Benzo(a)anthracene	18.300	114.500	28.625
Chrysene	489.500	283.300	70.825
Benzo(b)fluoroanthene	5.100	2.800	0.700
Benzo(k)fluoranthene	25.800	19.800	4.950
Benzo(a)pyrene	6.300	1.200	0.300
Dibenz(a,h)anthracene	7.800	1.500	0.375
Benzo(g,h)perylene	9.800	4.200	1.050
Ideno(1,2,3-cd)pyrene	62.300	41.400	10.350

Within the OBS, some polycyclic aromatic hydrocarbons were found. On the basis of concentrations found in the original oil, it is possible to calculate the concentrations in the OBS deposit at the start of the experiment.

No significant hydrocarbon peaks were present in the control samples and this pattern was repeated in material taken from beneath the OBS deposit after 10 months. In some samples, traces of weathered fuel oil were found, but this may be attributable to some cross-contamination in sampling.

5.4 Vertical migration

One objective of the second lysimeter experiment was to examine whether the starting concentration of oil residue in OBS influenced the potential for downward movement of hydrocarbons through the soil to groundwater. Microbial respiration by samples of sand from beneath the OBS under laboratory conditions was used to detect the presence of such hydrocarbons and the potential for their removal. In all lysimeters there was greater activity beneath those containing OBS than in the controls and evidence of a trend of increasing respiratory activity with increasing concentration of oil residues incorporated in the OBS, despite variation between individual lysimeters.

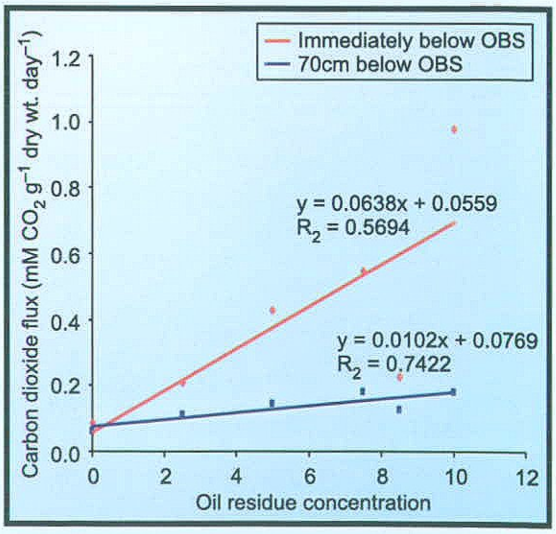


Figure 5.1. Variation in microbial respiration rate in sand from two depths beneath OBS in lysimeters, with different starting concentrations of oil residues.

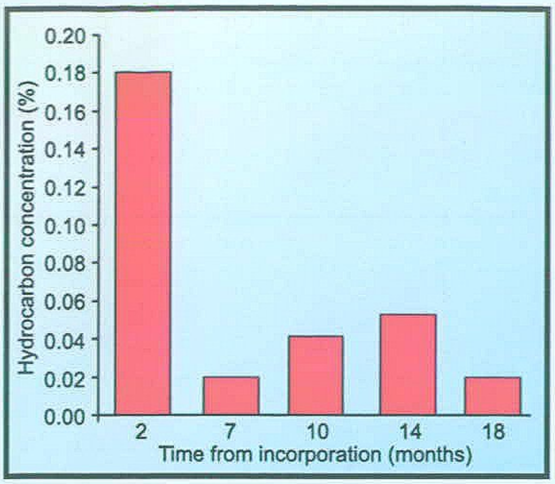


Figure 5.2. Hydrocarbon content of sand samples taken from beneath OBS deposit at second Pendine experiment site. Samples taken from 1-5cm below the base of the OBS.

With increasing depth, the rate of respiration decreased, indicating a combination of lower microbial activity and lower concentrations of substrate hydrocarbons. Although there was some movement of hydrocarbons from the OBS into the underlying sand, this was accompanied by populations of hydrocarbon-degrading micro-organisms. At 70cm below the OBS there was virtually no respiratory activity or detectable hydrocarbon substrate. The presence of micro-organisms in the layer of sand immediately beneath the OBS resulted in breakdown of the migrating hydrocarbons so that, within 70cm, there was virtually none remaining.

In the second Pendine experiment, core samples showed a clear boundary between OBS and underlying beach sand, suggesting there had been no mass movement of oil residues from the OBS. However, analysis of the underburden showed the presence of very low concentrations of hydrocarbon after the first sampling two months after burial of OBS. This suggested a limited amount of initial downward movement and the possibility that bacterial populations subsequently degraded hydrocarbons leaching from the OBS. Samples taken at seven and eighteen months were at the limits of detection (0.02%).

5.5 Leaching of mineral ions to groundwater

Changes in the concentration of mineral ions in groundwater beneath the second Pendine experiment confirmed that leaching of these ions from beach

Table 5.3. Changes over time in the concentration of chloride in groundwater samples taken from piezometer tubes located on the landward side of the experimental area, within the control and experimental hollows and on the seaward side of the experimental hollow.

	Chloride content (mg l^{-1})			
Weeks from burial	landward hollow	control hollow	OBS hollow	seaward of OBS
1	46	72	46	86
9	55	47	240	1400
25	82	75	1500	500
28	65	67	740	470
34	67	68	770	290
44	42	37	58	290
48	49	50	65	920
59	44	100	38	150
69	44	41	47	340
77	61	29	53	410

sand and its included seawater had occurred. Measurements made of chloride (an easily leached ion) concentration showed that an initial flush of inorganic anions had taken place. The rise in concentration within areas adjacent to the control hollow showed a distinct pulse, despite superimposed variations between seasons.

Groundwater from beneath the control hollow and its margins showed enhanced levels of chloride, but the pattern in concentrations occurring below and around the margins of the OBS deposit suggested that direct percolation of water through the OBS did not take place. Rather, precipitation was penetrating only a limited distance into the OBS, and percolating water was shed from within its upper layers to groundwater around the margins of the infilled hollow. This suggests that where the oil residue concentration is high, complete penetration of water is not possible, and this may inhibit the degradation process, as suggested by the flooding found to follow periods of rainfall in the lysimeter experiments containing high concentrations of oil residue in OBS.

5.6. Leaching of hydrocarbons to groundwater

Leachates draining from the lysimeters were odourless, suggesting a minimal hydrocarbon content. In line with this observation, low concentrations (below the levels considered toxic

Table 5.4. PAH concentrations in water draining from lysimeters containing different starting concentrations of OBS.

	Starting OBS concentration (%)			
	2.5	5.0	7.5	10.0
PAH compound	PAH concentration (ng ml^{-1})			
Naphthalene	<0.017	1.600	0.298	0.538
Acenaphthalene	0.097	0.018	0.003	0.003
Acenaphthylene	1.860	0.805	0.224	0.828
Flourene	<0.031	0.876	0.012	0.034
Phenanthrene	<0.022	0.468	0.008	<0.008
Anthracene	0.177	0.338	0.009	0.055
Fluoranthene	<0.019	0.106	<0.015	<0.005
Pyrene	0.425	0.151	<0.007	<0.006
Benzo(a)anthracene	<0.023	<0.010	<0.008	<0.008
Chrysene	1.450	0.130	0.015	0.013
Benzo(b)fluoroanthene	<0.022	<0.010	0.010	0.011
Benzo(k)fluoranthene	<0.019	<0.010	<0.007	<0.007
Benzo(a)pyrene	0.200	<0.013	0.009	0.021
Dibenz(a,h)anthracene	<0.053	<0.018	<0.020	<0.018
Benzo(g,h)perylene	<0.025	<0.008	<0.009	<0.009
Ideno(1,2,3-cd)pyrene	<0.011	<0.004	<0.005	<0.004

for algae and most invertebrates) of PAHs were also found.

No hydrocarbons were detected in groundwater samples collected from piezometer tubes around the trial plots at Eskmeals. Analysis for PAHs similarly failed to reveal the presence of these compounds in groundwater samples taken from the same piezometer tubes.

This lack of movement of hydrocarbons from OBS to groundwater was confirmed in water samples taken at the second Pendine site. Although concentration of hydrocarbons in groundwater tended to show a slight increase, the amounts present were not significantly above background concentrations. Samples taken after 60 weeks from beneath dunes 2km to the east of the site (close to the first Pendine experimental site) showed hydrocarbon concentrations ranging from 0.007 to 0.014 mg l^{-1}, whilst seawater and water issuing from the springline on the beach gave values of 0.005 and 0.011 mg l^{-1} respectively.

Samples taken at Pendine before the establishment of the second experiment show background PAH concentrations varying in both time and space. The higher concentrations were not significantly exceeded following the placing of OBS in the experimental hollow. Comparison shows that the concentrations of some compounds found were far

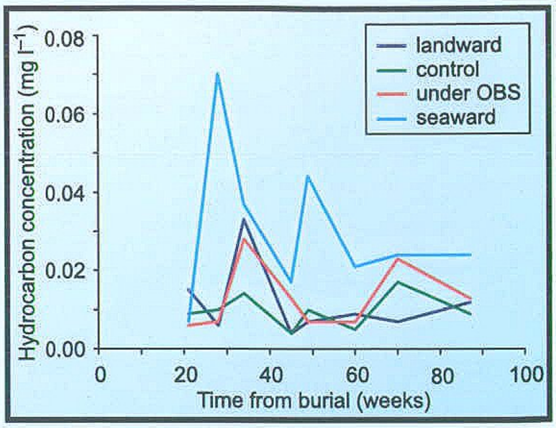


Figure 5.3. Changes in hydrocarbon concentration in groundwater samples taken from piezometer tubes at the second Pendine experiment site.

exceeded in seawater in spring 1997. The rise in concentration of some PAHs in the control hollow following placing of beach sand reflects high concentrations of these same compounds in seawater and appears to be the product of leaching of that seawater from the sand. Analysis of samples taken in January, May, July and September 1998 failed to show PAHs in water from any of the piezometer tubes. Thus, leaching of these compounds from OBS deposits in the field appears to be, at most, a temporary phenomenon giving rise to no problems of groundwater contamination.

6. SITE RECOVERY

6.1 Nature conservation value of dunes

Dunes not only form part of natural coastal defence systems, but also have high inherent nature conservation value. This results from their structural features and edaphic characteristics. Dune systems consist of sequential series of ridges and hollows showing increasing maturity with increasing distance from the sea. Young dunes composed of accumulated wind-blown sand along the upper margins of beaches, are well-drained and frequently contain high concentrations of calcium but little organic matter. They are, generally, sparsely vegetated. As dune systems mature, the calcium content is leached away, but there is surface accumulation of organic matter and, hence, water-holding capacity of the sand increases. This nutrient poor system supports a specific range of plant species and the invertebrate fauna dependent upon them.

The biological diversity of dune systems is further increased by the topographic pattern of dry ridges and intervening wet hollows, where the water table may approach, or rise above, the ground surface. Within these wet hollows, an additional range of freshwater communities is able to develop.

Within mature dune systems there may be some redistribution of wind-blown sand, but large scale disturbance of the surface can lead to excessive erosion.

Sand dune systems are, thus, sensitive to disturbance, which disrupts the delicate balance between erosion and deposition, and to nutrient inputs which allow the development of more mesotrophic (often weedy) vegetation. Despite this, many dune systems have been subjected to extensive use in the past and the majority of the remaining areas of relatively undamaged dune complexes have some form of nature conservation designation as Sites of Special Scientific Interest or National Nature Reserves.

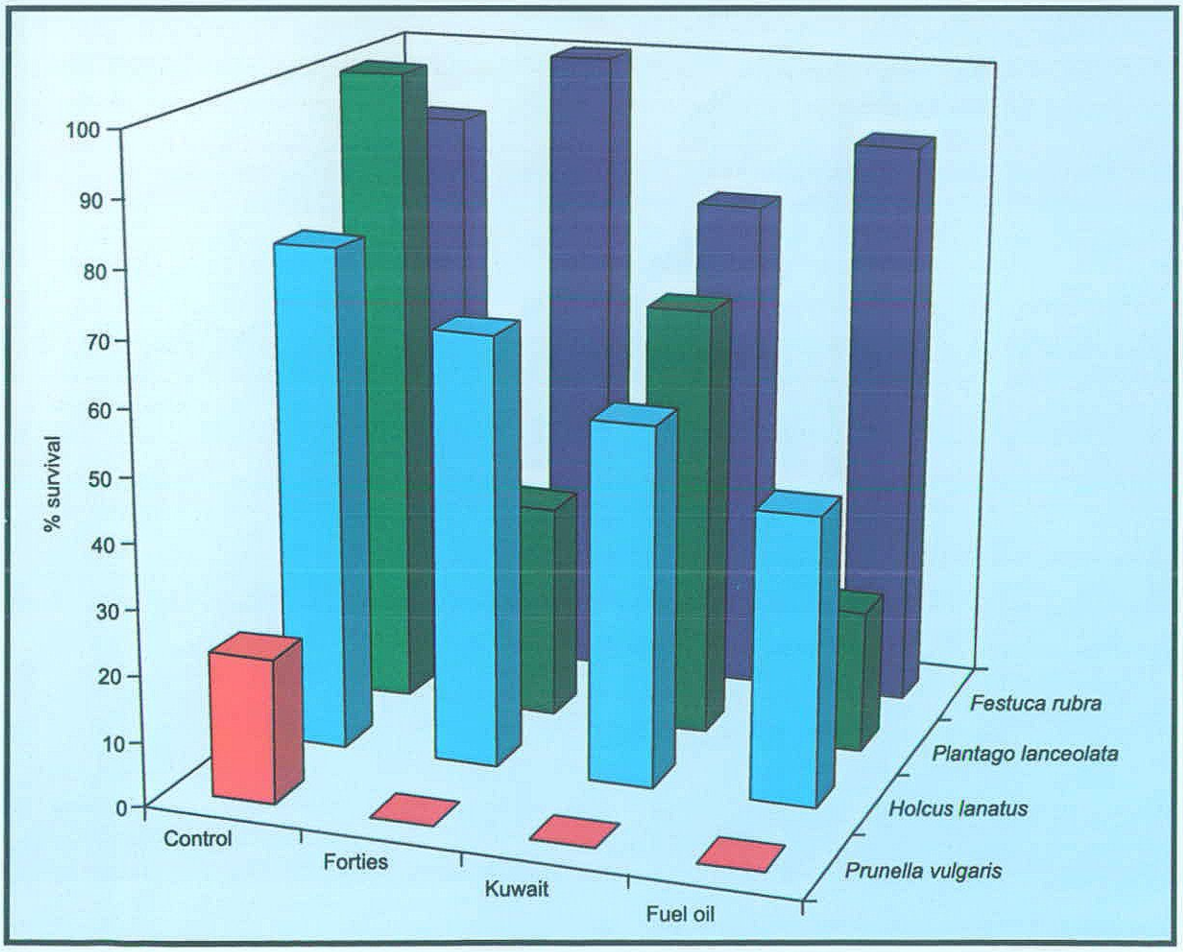


Figure 6.1. Survival of four plant species in OBS prepared using different oils.

In seeking to find suitable areas for disposal of oil residues, the sensitivity of dune systems has to be taken into account. As part of the process of assessing effects of disposal of OBS in dune systems, glasshouse experiments were carried out and field observations on vegetation and fauna were made on field trial plots.

6.2 Toxicity testing of plants

Results from the trial using four different species commonly found in dune systems showed differential survival when planted in 3.6% OBS prepared from different oils. Of the two grasses used, red fescue (*Festuca rubra*) showed good survival after six months in all oil residue types, but Yorkshire fog (*Holcus lanatus*) appeared to survive less well, especially in medium fuel oil OBS (Fig 6.1).

Ribwort plantain (*Plantago lanceolata*) showed a considerable reduction in survival in all oil types and the result for the other broad-leaf species self-heal (*Prunella vulgaris*) was thought to be affected by drought during one hot, dry, weekend: this species is less tolerant of dry conditions than the others used.

Tillers of red fescue obtained from coastal dunes and planted directly into 5% OBS prepared using different weathered oils showed significant reductions in the proportion of healthy leaves, compared with control plants.

Table 6.1. Effect of different weathering treatments of different oils on growth of red fescue. Results expressed as percentage compared with control plants.

	Forties crude	Fuel oil	Kuwait crude
No weathering			
Healthy foliage	15	22	33
Tillers produced	33	44	57
Plant mortality	20	0	0
Weathered for 9 hours			
Healthy foliage	16	23	42
Tillers produced	33	46	64
Plant mortality	27	7	0
Weathered for 74 hours			
Healthy foliage	21	38	27
Tillers produced	36	56	39
Plant mortality	13	0	0

Both oil type and period of weathering affected the severity of this effect. After six months, OBS prepared using Forties oil had a greater effect than that prepared using medium fuel oil or Kuwait crude.

Plants of the same species (red fescue) collected from different locations around the British coast, or even from different parts of the same population at a single site, showed different responses to the presence of oil residues. This suggests that there is a genetic component to tolerance of oil residues, which, in practical terms, may be difficult to take into account in the field.

Because of somewhat variable results from these experiments, any overall conclusion on general toxicity is difficult to draw. However, experience in the extensive field trial suggested that the presence of oil residues was not a common problem, because roots of dune plants were found to have penetrated many of the bags excavated. These roots showed no apparent adverse effects.

6.3 Recovery of dune sites

Groundwater chemistry

There is no long term effect on groundwater chemistry resulting from the introduction of a large volume of sand and emulsion, both containing seawater. Following an initial flush of anions and cations from the deposits, the chemistry of groundwater beneath dune systems returned quickly to its initial status. This was demonstrated effectively at the site of the second Pendine experiment, where groundwater, characterised by the dominance of calcium and bicarbonate, passed through a phase in which sodium and chloride became the major ions, before returning to calcium bicarbonate waters once again. The speed of change and its extent depend on the quantity of material incorporated into the dune system, rainfall patterns, infiltration rate, and the rate of release of ions from the OBS which will, in turn, depend on emulsion composition and concentration of emulsion.

Because the changes observed were rapid and reversible, there is no reason to believe that they would adversely affect the long term survival of dune plant and animal communities though, in the short term, some species may be favoured locally by the temporary introduction of more saline conditions.

Plant colonisation

Clear changes in vegetation were seen in the dune burial plots at Eskmeals. Although no control plots had been established, comparable observations were made on the plots themselves, the disturbed area within the experimental enclosure and in undisturbed dune vegetation nearby. The results of observations made after two years, indicated that the undisturbed dune community was one in which marram (*Ammophila arenaria*) and red fescue had similar, high, levels of relative abundance, with false oat-grass (*Arrhenatherum elatius*) and sand sedge (*Carex arenaria*) as common associates. Disturbance reduced the abundance of marram and false oat-grass dramatically, whilst common bent (*Agrostis capillaris*) increased in abundance. Within the OBS plots, the abundance of marram and fescue was reduced much further, whilst three grasses, Yorkshire fog, common bent and smooth meadow-grass increased, together with false oat-grass. This indicates a change from dune vegetation to open, acid grassland. Yorkshire fog, common bent and smooth meadow-grass are typical early colonists of disturbed sandy soils in general.

Dune vegetation at the site of the second Pendine experiment had already shown signs of past disturbance, in particular the presence of garden plants in the vicinity of the dune hollows, though these did not extend into the hollows themselves. The closed vegetation present before the OBS and control deposits were put in place, contrasts with the open vegetation, containing a large number of colonising species, which developed subsequently.

Within the dune pasture at Eskmeals, significant changes also took place in vegetation on the burial plots. At the beginning of the trial the field consisted of improved grassland with a high stocking rate of grazing sheep. The result was a pasture dominated by perennial ryegrass (*Lolium perenne*). Establishment of the trial plots resulted in disturbance to the established sward and loss of grazing. The vegetation developing on the plots reflected these changes.

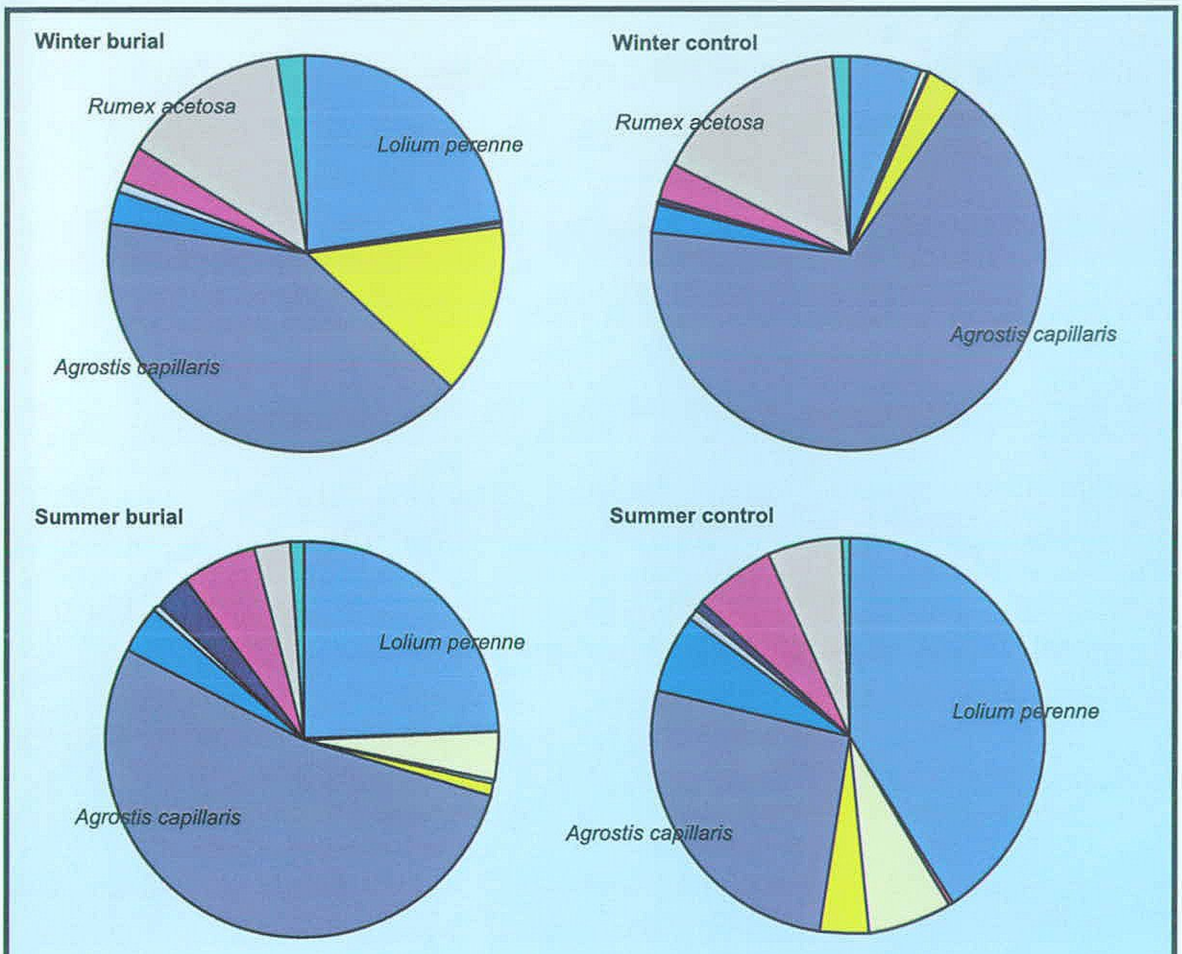


Figure 6.2. Relative proportions of different plant species in control and burial plots at Eskmeals. Only the more abundant species are named.

Table 6.2. Relative cover-abundance of species on OBS and control plots at Eskmeals. Values expressed as percentage of total vegetation cover in plots.

	Winter burial	Summer burial	Winter control	Summer control
Lolium perenne	22.5	24.4	6.1	41.1
Senecio jacobaea	0.0	0.1	0.0	0.4
Holcus lanatus	0.3	3.9	0.4	6.9
Festuca rubra	0.2	0.1	0.1	0.0
Trifolium repens	13.9	2.8	2.8	3.8
Agrostis capillaris	40.2	52.8	67.2	26.4
Cerastium fontanum	3.0	4.1	2.1	6.5
Erodium cicutaria	0.8	0.4	0.3	0.6
Medicago lupulina	0.0	3.0	0.4	0.8
Poa annua	2.8	6.2	2.9	6.7
Rumex acetosa	14.0	2.6	16.3	6.3
Viola tricolor	2.2	1.2	1.3	0.4

No undisturbed vegetation was monitored, but vegetation characteristics were assessed on OBS and control plots.

The results show that, although perennial ryegrass persisted, common bent was the most abundant species present, as in the case of the disturbed dune burial site. There was no consistent difference in the response of different species to either the presence of OBS in the deposit or the timing of disturbance. However, winter burial of OBS or control sand produced a more complete vegetation cover after two years. This may have been because winter burial disturbed any seed present in the seed bank without affecting its capacity to germinate, whilst summer burial removed newly germinated plants and left a dry surface upon which germination was not possible. Nevertheless, by July 1996, summer plots had a vegetation cover in excess of 70%, compared with almost complete cover in the winter plots.

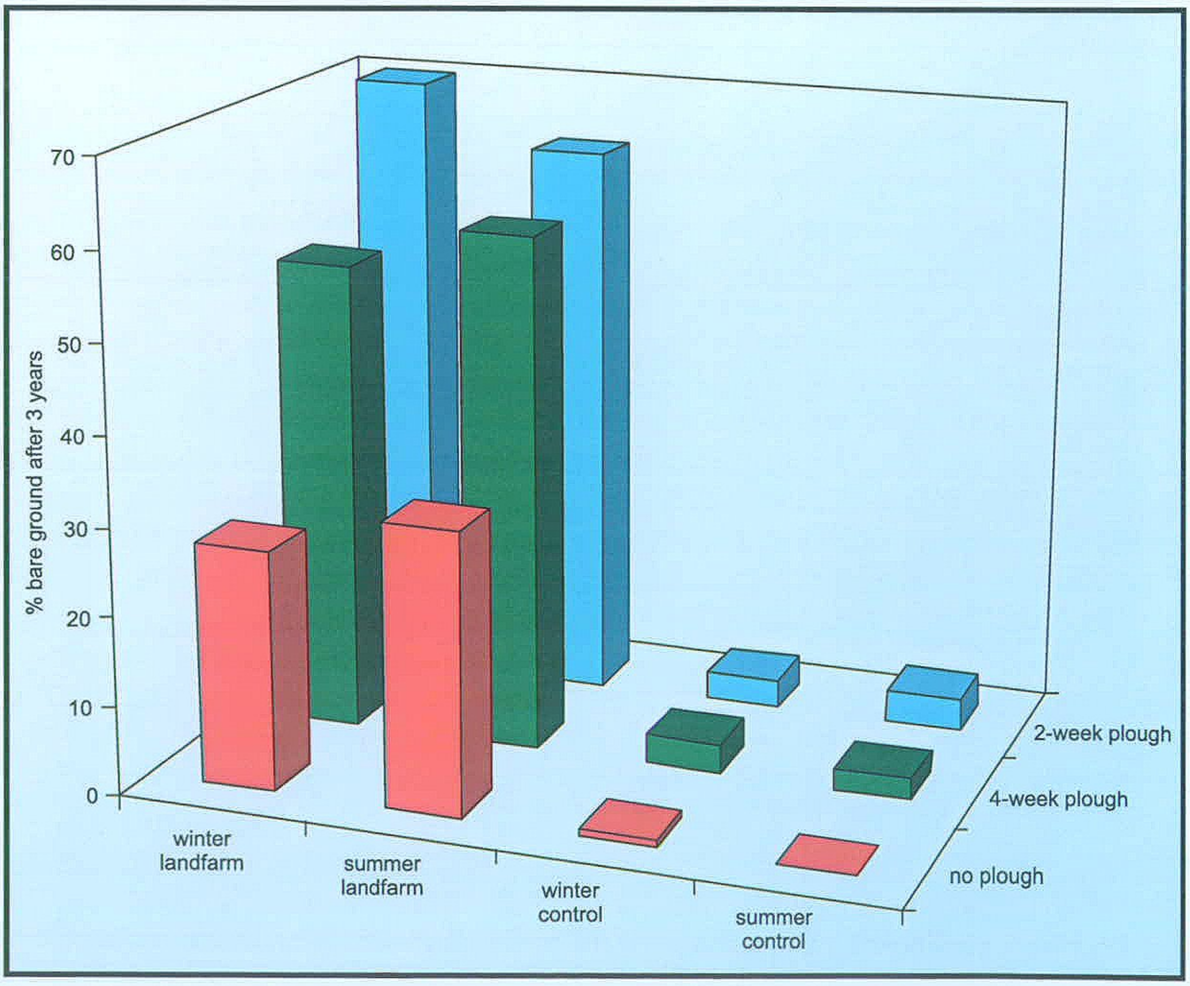


Figure 6.3. Effect of landfarming treatments on percentage of bare ground remaining in plots at Eskmeals after three years.

The effect of landfarming was different and related to two factors; disturbance and retention of oil residues at the surface. Frequent ploughing was expected to delay the establishment of permanent vegetation and this appears to have been the case in the plots at Eskmeals. Almost complete vegetation cover had established in control plots by January 1998 (after three years), whilst in ploughed plots an average 50% of the plot was still bare ground. This overall value has hidden considerable differences attributable to different ploughing treatments, with more frequent ploughing resulting in less successful colonisation (Fig 6.3).

Differences between blocks were also found but these were not consistent across all treatments.

Where no natural dune or dune pasture soil is returned to the surface, colonisation of a disposal site may need to be managed through seeding or planting with appropriate species. Although some marginal invasion from adjacent communities may occur, this may be slow and irregular, and where there is a significant area, may leave a central core exposed to loss of sand by wind erosion. Planting with appropriate species will help to stabilise bare sand and to encourage its accumulation rather than loss. The results of the planting trial at the first Pendine trial site have shown that the planting of marram tillers may be used as a successful method of producing an almost complete vegetation cover within four years. Sowing with a red fescue seed mix also helps stabilise sand and produce sites for accumulation. However the effectiveness of this sward in trapping sand is not as great as the presence of marram tussocks.

Animal colonisation

At the first Pendine experimental site, observations suggest that the margins of the large deposit were colonised by both ants and spiders within the first six months. A range of invertebrates was also observed during the first summer at the second experimental site at Pendine.

Detailed surveys of surface-dwelling invertebrate animals have only been carried out on the Eskmeals experimental plots.

Results from pitfall traps indicates that site disturbance and a reduction in vegetation cover, rather than presence of oil residues, have been responsible for a reduction in number of animals found

Table 6.3. Mean number of invertebrates per pitfall trap within, and adjacent to, different types of field plot at Eskmeals, September 1995.

	mean number	
	outside plots	inside plots
Dune burial	168	56
Pasture burial		
winter	60.7	47.3
winter control	150.3	125.7
summer	20.7	23.3
summer control	29.6	82
Landfarming		
winter	60.7	47.3
winter control	150.3	125.7
summer	20.7	23.3
summer control	29.6	82

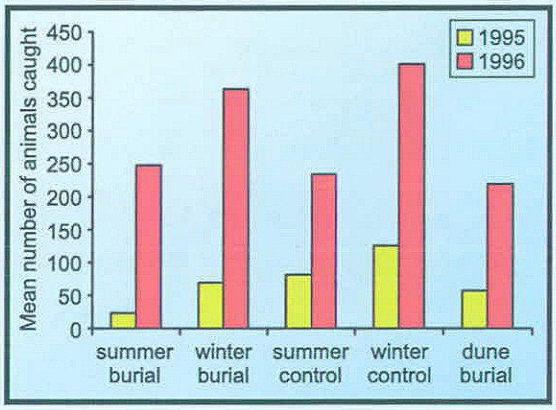


Figure 6.4. Numbers of animals caught in 1995 and 1996 in pitfall traps within trial plots at Eskmeals.

Dunes appear to support larger populations than the dune pasture and the effect of disturbance has been to reduce the number of animals significantly. The reduction in number of animals trapped, from a smaller starting base, was less pronounced in dune pasture burial plots than in landfarming plots.

As vegetation re-colonised the plots, numbers of invertebrates captured in pitfall traps placed within the plots increased dramatically. The increase was found across all types of plot, suggesting that, at least in terms of overall number of animals, the presence of oily residues at the surface in the landfarming plots was not a factor inhibiting colonisation.

7 CONCLUSIONS

The main conclusions from the project are:

1 The disposal method works, because:
- Micro-organisms present in sandy coastal soils have the capacity to degrade petroleum hydrocarbons.
- There is only limited migration of hydrocarbons from OBS to underlying sand.
- There is no significant leaching of hydrocarbons from OBS deposits to groundwater.

2 The process of degradation proceeds rapidly at first but declines with time.
- The pattern of degradation can be expressed most accurately by a power function.
- Low molecular weight compounds (with fewer than 10 carbon atoms) are lost from oil residues more quickly than those of higher molecular weight.

3. A number of factors influence the rate of degradation.
- The type of oil and the degree of weathering influence the rate of degradation.
- The two main external influences on decomposition rate are temperature and soil moisture.
- Higher temperature, within the normal climatic range, encourages faster degradation of oil residues.
- The presence of a high water table or infiltration of heavy rainfall inhibits degradation.
- Characteristics of the soil also influence degradation rate.
- Grain size and organic content of soil may affect degradation rate by influencing soil water holding capacity
- Buffering capacity (observed as calcium carbonate concentration) appears to be particularly important.

4 Environmental risks are low
- Leaching of ions from seawater contained within the OBS is short term and groundwater chemistry quickly returns to its former status.
- Hydrocarbon-degrading populations of microbes develop in sand immediately below OBS deposits.
- Although polycyclic aromatic hydrocarbons are found in low concentrations within degrading OBS, they do not migrate to groundwater.

5 Ecological risks are low
- Although in experimental situations toxic effects of weathered oils on dune pasture plants can be demonstrated, such toxicity was not found in field trials.
- In field trials, disturbance has a greater effect in slowing the development of colonising plant communities than the presence of oil residues.
- The number of invertebrate animals is also affected by disturbance more than the presence of oil residues.

8. IMPLEMENTATION

Although the objective of the project was to examine the efficacy of a natural method for degradation of oil residues, the application of the method to the treatment of the products of real spills requires some positive management. This should aim to maximise the rate function controlling decomposition of oil residues contained in OBS.

The technical objectives may be partly met by appropriate selection of disposal sites and partly by manipulation of starting conditions. Other practical considerations, based on factors such as location and status of potential sites will also need to be taken into account.

8.1 Site considerations

Habitat type and conservation designation

There would be a presumption against the use of high quality sites for the disposal of OBS. Sites with a nature conservation designation (and accepting a hierarchy of importance such that e.g. sites of international importance would rate more highly than those designated for local interest only) would be considered only in extreme circumstances and after other possibilities have been exhausted. In all cases, a competent agent should carry out an ecological impact assessment. Suitable areas within designated sites may be capable of use provided there is no threat to the integrity of those sites from either the burial or associated activity.

Access

Any site considered for burial should have suitable access for the type of machinery required for moving the quantities of material to be dealt with. Such access should be, for preference, served by a tarmac road or other suitable track and should, in all cases avoid direct traversing of active dune systems or other areas of high environmental value. If sites of different capacity for burial are defined, it may be that the access criteria may be modified for smaller vehicles (e.g. small unattributable spills may by removed by dumper truck rather than by large lorry). This consideration, together with the possibility of installing temporary trackways could have consequences for assessment of accessibility in particularly difficult locations.

Area

A disposal site needs to be of sufficient size to accommodate the OBS to be disposed of and any ancillary works associated with such disposal. No additional engineering is envisaged in burial sites (other than temporary storage of turves, should their removal and replacement be seen as an essential part of site rehabilitation).

Volume

Each disposal site, or component of a disposal site, should have sufficient available volume to accommodate the amount of material to be received, without excavation. In practice, for burial sites there will need to be, as part of the site specification, a stated limit on the volume of material, which that site, or each component of it can accept. This would mean that for any site, there might be a range of identified individual areas capable of taking different volumes and so, be appropriate for use with different sizes of spill.

Stability

Sites where the dunes are accumulating sand will provide more acceptable locations than those where dune erosion is active. In eroding sites, there is a greater possibility of subsequent exposure before decomposition of hydrocarbons has been completed.

8.2 Site factors influencing degradation

The features of sites, which are most likely to influence degradation, have been identified in the different experiments and trials undertaken in this project.

Water Table Depth

Soil aeration or the possibilities of waterlogging causing anaerobic conditions within any OBS deposit are key factors in determining site suitability. Sites where there is a permanently high water table, or where fluctuations in water table would bring it into close proximity to OBS, are inherently unsuitable. Sites where the water table is less than 1m below ground level for all or part of the year should be rejected. Sites with a water table at 1 - 2m below OBS level for all or part of the year should be regarded as probably suitable and those where the water level is below 2m for all or part of the year should be considered as most suitable.

In most cases of disposal in near-shore locations, water tables will slope towards the sea. However, where the groundwater slope is inland (as on the landward side of some dune systems) any migration of hydrocarbons under conditions of high water table could present difficulties for wetland sites. Hence parts of dune systems with included wet slacks should always be avoided.

Climate

All areas of Britain are likely to be suitable climatically, but actual rainfall and temperature conditions may need to be taken into account in defining management procedures at any particular location.

OBS type

The rate of degradation will depend on the type of OBS to be buried. This will be determined by the type of oil and its weathering history, and the grain size and chemistry of sand. Although there is no control over this, management prescriptions may be dependent on factors within the OBS.

Timing of disposal

Research results indicate that the timing of disposal influences the rate of degradation and that summer and winter incorporation of OBS may lead to different patterns of decomposition. It would not be possible, nor advisable to separate clean-up operations and disposal (because age of material can also influence breakdown rate). However the timing of disposal may play an important role in determining management strategies for the deposit, and in influencing any projections of the rate of the decay process and the time taken to reach any pre-determined final concentrations.

Beach pollution history

A beach with a history of oil pollution is likely to have larger populations of micro-organisms adapted to hydrocarbon degradation than a beach with no such history. Because of this, degradation may be expected to begin more quickly at such a site. Again, there is no control over this, but it may influence projections of degradation rates.

8.3 Management factors

Oil concentration

Given that efficacy of oil degradation is reduced as hydrocarbon content rises above 7-8%, it may be necessary to dilute the OBS to an appropriate concentration with beach sand before burial. A set of optimal concentrations should be set for specific oil types and main geoclimatic regions of the country in order to optimise degradation rates and end points.

Thickness of oil layer

This may be linked to oil concentration. A lower concentration of oil in the OBS may permit a greater thickness of that OBS to be deposited. Options may be related to land configuration such that a shallow depression may be best suited to a thin layer of more concentrated oil residues (within the limits imposed by penetration of air, water and nutrients) whilst a small, deep hollow may require the deposition of a thick, but less concentrated layer of OBS. Once individual locations have been identified, it will be necessary to try to build in tailored specifications.

Fertiliser Application

In naturally nutrient-poor locations (which dunes systems are) the addition of fertiliser is generally to be avoided (especially where semi-natural dune communities are present and their maintenance is to be valued). However, in certain circumstances, some addition may be recommended for particular sand types in particular situations. The efficacy of nutrient supplements, usually N & P (but possibly including Ca in sands with low Ca concentrations) has been demonstrated in bioremediation applications elsewhere. At present there are no rules governing the application of fertilisers in dune systems, but minimal applications would be demanded. There are different possibilities for application techniques (incorporation with OBS, subsequent drilling and filling, surface dressing where vegetation is absent)

Aeration

Under normal circumstances there is not expected to be any need for aeration. In general sands are well aerated, unless the water table is high. There may only be a need for aeration where high concentrations of oil are used, or there has been some concentration of oil within lower layers of OBS deposits leading to anaerobic conditions. Passive aeration could be achieved by incorporation of porous pipes within OBS or sandwiching layers of OBS and clean sand. Forced aeration requires special engineering solutions and the use of pumps on site.

Revegetation

The need for specific revegetation measures is very much dependent on site characteristics and disposal method. For burial sites, a standard recommendation is for removal of surface layers prior to deposition and subsequent return of these as turves. Any other operations must be seen as only "emergency repairs" to be undertaken when problems arise. In the absence of such a turfing procedure, two different approaches suggest themselves, depending on site size. For a small site, marginal invasion would accomplish revegetation within a comparatively short period, so a *laissez-faire* approach is all that is required. For larger sites, a planting programme would be required, following standard practices for dune restoration, or reseeding.

8.4 Public perception

With all technologies involving materials considered to be potentially capable of damaging the environment or public health, certain precautions need to be taken to ensure that any risk (perceived or actual) is minimised and that the procedures adopted are subject to control and scrutiny by appropriate authorities. The main aspects of concern in this context would be:

Public sensitivity
Areas seen as especially sensitive in terms of public opinion would be considered only after examination of the potential of other suitable, but less sensitive, locations in the vicinity. Any operation would need a programme of public education and the public would need to be assured of the low and short term risk element attached to disposal of OBS by burial.

Security
Site security has two facets: maintaining any monitoring equipment installed on site, and safety of the public. Sites offering some measure of security for, e.g. water sampling wells, would be viewed more favourably than those open to public access. Such sites would also be favoured because of the possible risks of disturbance to the deposit and human contact with OBS (especially early in the life of the deposit). Although such contact is not likely to cause any serious health problems, it should still be considered as a risk to the public. At some locations new fencing may be required. Sites exposed to particular threats or risks of erosion should also be avoided.

Ownership
Site ownership would need to be considered carefully, particularly where any special conditions apply to that ownership, or where there are perceived threats to the value of private land. For reasons of access, security and, public sensitivity, certain types of site in public or commercial ownership may be more suitable than those in private ownership or considered as part of the public domain. However, it is hoped that any problems arising could be resolved by negotiation.

Monitoring
Monitoring schemes pose no practical problems, but do have a cost implication. Any monitoring scheme needs to obtain baseline data before deposition of OBS. A requirement for any monitoring programme is the setting of clear objectives. In practice, in the case of burial of OBS, this means establishing pre-defined limits to hydrocarbon content which, once met, mean that the site can be decommissioned, as any remaining materials would no longer be regarded as special waste, and monitoring can cease.

9. FUTURE RESEARCH NEEDS

The current project has established that microbial degradation of OBS provides a practical answer to problems of disposal of oil residues from spills. It has also shown that there are no significant environmental risks from the release of toxic compounds during the breakdown process. The main focus of any future research should be directed at two topics:

- Methods of enhancing the process. This means determining both conditions under which the initial rate of hydrocarbon break-down can be maximised and investigating possible means by which decomposition rates may be maintained or improved during the latter part of the process.
- Investigations to determine availability and suitability of potential disposal sites around the British coast.

9.1 Enhancement of degradation

The second lysimeter experiment indicated that there may be an optimal concentration of oil residues in OBS, which would

- maximise aerobic degradation
- minimise the downward movement of hydrocarbons
- minimise interference with site hydrology

The object of future research in this area would be to determine this optimum concentration and any patterns of variation attributable to oil type or weathering history. Although initial experiments might be on a small, lysimeter, scale, they would also need to be scaled up to field trials to ensure effective translation of experimental scale results.

As an adjunct to this area of research, it would be valuable to determine the behaviour of similar starting OBSs in other light-textured soils, e.g. sandy loam, sandy clay loam. This proposal arises from suggestions made during the early part of the project that the possibility of including soils other than sands might increase the potential number of sites along parts of the coastline where dunes and dune pasture systems are not present or are unavailable because of their high conservation value. Under this proposal it would be necessary to determine both differences in oil residue decomposition rates and possible modification of mobility characteristics. In the first instance such research should be concentrated on lysimeter experiments, with subsequent field-testing.

Although we have derived a general function to describe the course of hydrocarbon degradation in buried OBS, the reasons for the decline in breakdown rate with time will be related to some rate limiting factor. This may related to the substrate itself or to some other, external, limiting factor. Once the small molecular weight components of oil residues have been metabolised, the process may slow because micro-organisms with the capacity for degrading long chains or ring structures are not present in sufficient numbers in the soil medium. Alternatively, the decline may result from progressive exhaustion of one of the major controlling external resources, e.g. oxygen or nutrients. Research directed at determining which of the factors may be causing the decline could provide guidance on management of deposits to enhance degradation at an appropriate stage, thus ensuring more rapid and more complete decomposition.

One specific measure which has been suggested as providing a means of enhancing degradation is the mediation of plants – phytoremediation. Some plant species are thought to be able to stimulate hydrocarbon-degrading micro-organisms, particularly those associated with the rhizosphere, and so promote breakdown of oil residues. Research to follow up this line of enquiry would involve pot trials in the first phase and determination of the role of plants in promoting hydrocarbon degradation, via stimulation of rhizosphere bacteria and mycorrhizal fungi. Such a programme would involve a microbiological component, quantifying the extent of any such stimulation. This would be linked to assessment of differing potential among plants with different morphological or physiological characteristics (e.g. grasses, legumes, and non-legume herbs), and measurement of the effectiveness of the plants in promoting degradation.

9.2 Site selection

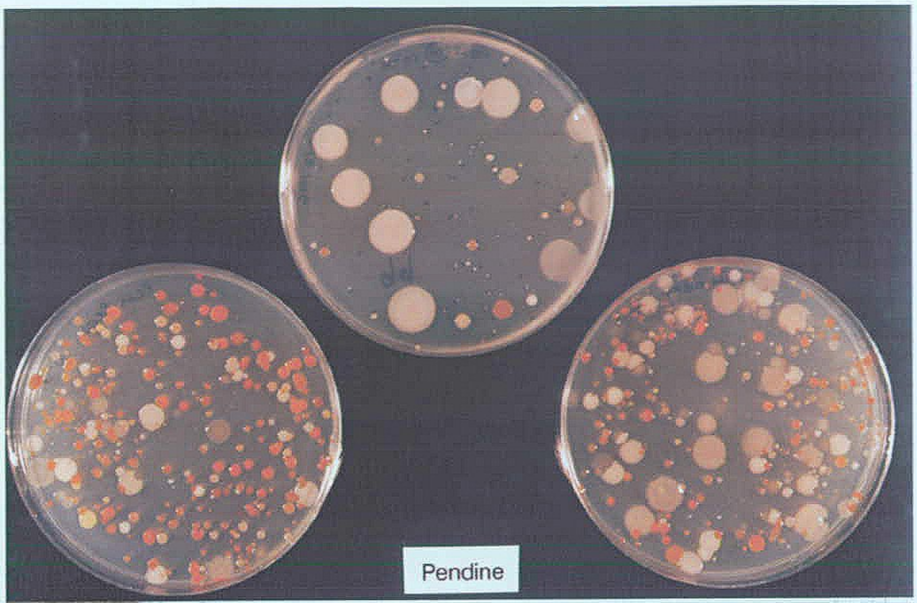
Although some indication has been given of the questions to be considered in selecting and managing disposal sites, further work is needed to identify and characterise locations, which might be available to receive oil residues following future oil spills. Any work in this field must be carried out in a manner that provides clear guidance on criteria for selection and the rigorous application of guidelines produced. Only with a clearly defined protocol in place can selection be seen to be based on objective assessment.

The site selection exercise needs to be conducted independently of any immediate need arising from a spill in which oil is washed ashore. Only in this way will it be possible to conduct the survey in an independent manner, free from the pressure which a particular incident or situation is bound to provoke.

Choice of potential disposal sites is seen as an exercise which would be a combination of ecological, hydrogeological, environmental conservation and logistic studies, combined with awareness of local social and economic constraints, and the legal requirements associated with disposal of oily waste materials.

10. ILLUSTRATIONS

First Pendine experiment. Bacteria colonies cultured from dune sand, beach sand and OBS.



First Pendine experiment. Planting marram grass shoots in a trial plot, November 1994.

First Pendine experiment. Revegetation of trial plots after two years.

Eskmeals field trial. Preparing plots within dune pasture for receipt of OBS,February 1995.

Eskmeals field trial. ploughing oil residues into sand on the artificial beach, February 1995.

Eskmeals field trial. Taking sequential core samples.

Lysimeter facility at ITE, Merlewood.

Extensive study. Removing turves for burial of OBS

Second Pendine experiment. Mixing emulsion, March 1997.

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