# Response to Spills Involving Ground Penetration and Contaminated Land Remediation

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## Abstract

The objective of the paper is to examine the behaviour and remediation of oil and chemical spills on the soil surface and in the sub-surface. The aim is to contrast this with the behaviour of contaminating materials on the coastline, and evaluate whether any remediation approaches used inland have potential application along the shore.

Initially, the behaviour of a contaminating liquid following a spill is examined, with consideration given to the dominant physico-chemical properties of the contaminant, the properties of the substrate and the presence of groundwater. A variety of remediation approaches that do not involve the excavation of contaminated materials is then introduced. These include in-situ processes that can treat both contaminated solids and contaminated groundwater.

A discussion of the characteristics of the shoreline area and a comparison of this drawn with more typical inland areas then follows. This is extended to evaluate the potential for the various remediation processes to be used along the shoreline.

It is concluded that many remediation approaches are unlikely to be used on the shoreline, while the application of others is likely to be restricted as a result of operational difficulties in implementing the technology and controlling it. This applies particularly to in-situ technologies where the introduction of reagents/chemicals is required. Those methodologies involving bioremediation approaches are likely to be most easily transferred to the shoreline coastline.

A case study is presented which suggests that in situations where the physical oil removal rates are low (and therefore the threat of oil migration to uncontaminated beaches is slight), and there is little pressure to clean the shore for amenity or economic purposes, or because the residual oil poses a threat to animal or bird populations, bioremediation should be considered as a treatment technology.

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# 1 INTRODUCTION

The transport, handling, distribution and use of liquids can result in accidental or deliberate releases to the ground. Once such a spillage occurs then the environmental consequence is dependant on a variety of factors. These include:

- the hazardous nature of the liquid
- the physico-chemical properties of the liquid
- the nature of the surface onto which it is spilled
- the nature of the substrate under the area upon which it is spilled
- the sensitivity of the environment which it might impact.

Spillages of this nature can occur both inland or at sea, where the spilled liquid can ultimately impact the shoreline. This paper is primarily concerned with the former but provides a comparison with marine spillages that have impacted the shoreline. It provides an introduction to contaminant behaviour on the ground surface, and below the ground in both the unsaturated and saturated zones, and while moving along with the groundwater. A comparison is then drawn between inland spills and shoreline contamination. Remediation options for the in-situ treatment of inland spills are then introduced and their applicability to the shoreline discussed. Relevant case studies are presented for technologies that might be applicable to the shoreline and finally some conclusions drawn.

# 2 CONTAMINANT BEHAVIOUR

Following the release of a liquid contaminant its behaviour and subsequent impact on the environment is influenced by a range of processes. These processes are in turn influenced by the physico-chemical properties of the contaminant and the properties of the substrate onto which it is spilled. Additional factors that come into play are environmental factors influencing contaminant properties, and factors controlling natural attenuation.

The following sections introduce the general behaviour of spilled liquid contaminants:

- on the ground surface
- in the unsaturated zone
- in the saturated zone
- during movement within the groundwater.

## 2.1 On The Ground Surface

Liquids spilled onto the ground surface will do one or more of the following:

- evaporate
- spread out and flow
- penetrate the ground surface.

Evaporation processes will act on any volatile liquids or volatile components of a liquid of mixed chemical constituents and start to transfer these to the atmosphere. Factors affecting evaporation rate include the volatility of the liquid, the surface area that it covers, the ambient temperature and wind conditions. With very volatile liquids a large proportion of the spilled liquid might evaporate if conditions are favourable. Under certain conditions, gas phase concentrations of volatile compound can represent an explosion risk, especially if the volume spilt is large.

The mobility of a liquid is influenced by viscosity which is a measure of the resistance of a liquid to flow. Consequently the viscosity of a spilled liquid will influence its mobility both across the surface of which it is spilled and into the substrate upon which it has been spilled. A low viscosity liquids is more mobile and so will move across surfaces more readily, is likely to cover a larger surface area and will penetrate into substrates more rapidly.

The viscosity of any particular liquid can also change following spillage. Two main causes of viscosity change are:

- change in composition; where the spilled liquid is a mixture of different components evaporative processes will act to selectively remove the more volatile components leaving the a residue of different composition and often with a different viscosity and density. Hydrocarbon mixtures, particularly crude oils are especially prone to such changes and the viscosity of the residual spilled material will generally increase significantly as evaporation proceeds.
- changes in temperature; ambient temperature conditions will also influence viscosity with higher temperature producing lower viscosities and therefore resulting in greater mobility. Some liquids that have very high viscosities at ambient temperatures might be transported or stored at elevated temperatures e.g. HFO might be transported at temperatures in the region of 60 °C. However, in most instances, unless very large quantities are spilled, the temperature of these materials will rapidly fall to ambient following spillage, resulting in significant increases in viscosity. It should also be remembered that temperature can also influence evaporation rates.

The degree of spreading and rate of flow will also be influenced by the permeability of the surface and the presence of any slope. Spreading will be less on permeable surfaces as more liquid will penetrate into the ground, and a spill in a topographical low or depression will spread less than one on a slope. Where flow rates are relatively high there is an increased risk of the contaminant entering surface water bodies such as rivers or lakes.

The amount of liquid penetrating the ground surface will depend on the permeability of the surface material and also the moisture content of it. Penetration into concrete and low permeability materials such as clays will be considerably less than in course sands or made ground. Permeability is considered in more detail in the next section.

## 2.2 In The Unsaturated Zone

Once a spilled liquid has entered the ground its movement through the unsaturated zone is influenced primarily by gravity and capillary processes. In substrates of homogenous permeability gravitational forces will result in the vertical movement of the liquid to deeper areas. As this occurs, capillary processes will act to cause some horizontal spreading of the contaminant as it penetrates deeper. The result is an area of contamination that increases with depth of penetration. In general with homogeneous soils, the maximum depth of penetration will occur where there are surface pools of oil to provide a pressure head that drives penetration.

In materials with variable permeability this picture becomes more complex as the percolating liquid preferentially follows zones of higher permeability or, alternatively, may even be arrested when a low-permeable horizon is encountered.

The actual process of liquid penetration through permeable substrates is complex and is influenced by a variety of properties of either the liquid or the substrate. Macroscopic properties include permeability, while pore scale processes include interfacial tension, wettability and capillarity (Pankow and Cherry, 1996). The main requirements for movement through such substrates are that the liquid is able to deform to enter the pore spaces and is able to displace any other liquid (primarily water) that is there. On a macroscopic level, the permeability of the substrate is dominant, with high permeability materials enabling greater rates of penetration. At the pore scale level for example, liquids with low interfacial tensions are more able to enter water wet pores and crevices and some are more likely to penetrate low permeability materials more readily (Pankow and Cherry, 1996).

The permeability of any substrate can vary considerable both vertically and horizontally. Generally, well sorted course materials such as gravels and course sands are more permeable than poorly sorted fine materials such as silty clays or clays. Table 1 indicates the permeability of some more common substrates. Additional factors influencing permeability include the degree of any fracturing, the presence of any solution features or the presence of other geological features such as bedding planes, jointing systems or faulting. Such features can result in very rapid transfer of contaminants as they act as preferential pathways. Certain similar high permeability features of anthropogenic origin, such as underground drains, loose backfill around services and shafts or addits etc. can have similar impacts.

The rate at which a contaminating liquid moves through a permeable material can also be influenced by the density of the liquid. High density liquids will tend to penetrate more readily under the influence of gravity (Pankow and Cherry, 1996) and so can be expected to contaminate to greater depths than low density liquids.

**Table 1: Generalised Permeability of Selected Substrates**

| Substrate | Permeability Range, cm/s |
|---|---|
| **Unconsolidated materials:** | |
| • Gravel | 1 - 100 |
| • Clean sand | $10^{-3}$ - 1 |
| • Silty sand | $10^{-5}$ - $10^{-1}$ |
| • Glacial till | $10^{-10}$ - $10^{-4}$ |
| • Clay | $10^{-12}$ - $10^{-7}$ |
| **Consolidated materials:** | |
| • Fractured and jointed rocks | $10^{-6}$ - 1 |
| • Limestone | $10^{-7}$ - $10^{-4}$ |
| • Sandstone | $10^{-8}$ - $10^{-4}$ |
| • Shale | $10^{-11}$ - $10^{-7}$ |
| • Igneous and metamorphic rocks (un-fractured) | $10^{-12}$ - $10^{-8}$ |

However, it should also be realised that not all liquid penetrating the ground continues to penetrate to depth, even if conditions are favourable. Two major influences inhibiting penetration through permeable materials are the volatility of the liquid and the retention capacity of the substrate. Volatility is influenced by the air-water partitioning coefficient (Henry's Law constant); if liquids are volatile then volatile components will continue to be lost to the soil atmosphere and so limit the overall quantity of contaminant that is available in the liquid phase. The density of the subsequent vapour can in turn influence the contaminant behaviour. Low density vapour will tend to migrate to the surface with time and might be lost to the atmosphere, while high density vapours may continue to move to greater depths (Pankow and Cherry, 1996). Additionally, as the contaminant moves vertically through the substrate residual quantities of it may remain behind as coating on individual particles, in pore spaces or adsorbed/absorbed onto particles. The capacity of substrates to retain residual contamination can be substantial and will depend upon the characteristics of the contaminant as well as the substrate. Fine materials with a high organic content will generally have higher retention capacities. For example, the retention capacity for some oils can be 25 litres/m³ for medium/fine sand and up to 40 litres/m³ for fine sand/silt (CONCAWE, 1981).

## 2.3 In The Saturated Zone

Once a spilled liquid has penetrated the ground and percolated down to the groundwater table a range of things can happen to it depending on a variety of factors, particularly its miscibility with water and it density. Liquids that are miscible with water are likely to become solubilised and will result in contamination of the groundwater. This contamination will move under the influence of local and regional groundwater flow conditions and will result in a contaminated plume moving away from the source of the contamination (see next section). Table 2 indicates the water solubility of some selected liquids.

## Table 2: Solubility and Density of Selected Liquids

| Liquid | Water Solubility*, mg/l | Density*, g/cm$^3$ |
|---|---|---|
| Water | - | 1.00 |
| Benzene | 1791 | 0.88 |
| Toluene | 421 | 0.87 |
| m-Xylene | 146 | 0.88 |
| Heptane | 3 | 0.68 |
| Acetone | completely miscible | 0.79 |
| Ethanol | completely miscible | 0.79 |
| Methanol | completely miscible | 0.79 |
| Carbon tetrachloride | 805 | 1.59 |
| Tetrachloroethylene | 150 | 1.62 |
| Trichloroethylene | 1100 | 1.46 |

\* Source: Pankow and Cherry, 1996

If the liquid is non-miscible its behaviour upon reaching the groundwater table is dominated by its density compared with water. The non-miscible liquid does not mix with the groundwater and is termed a non-aqueous phase liquid or NAPL. If the density if less than water then it is refereed to as a light non-aqueous phase liquid or LNAPL, while if the density is higher it is refereed to as a dense non-aqueous phase liquid or DNAPL. Table 2 also indicates the densities of some liquids.

LNAPL's tend to accumulate on the surface of the groundwater table and subsequently spread out to form a lens of free product. This free product generally moves along in the general direction of the groundwater flow but can also flow down any irregularities in the water table such as might be created by drawdown. LNAPL's can result in the smearing of contamination within the substrate above the groundwater table if fluctuations in the level of the water table occur.

DNAPL's will tend to enter directly into the groundwater and continue downwards under the influence of gravity until they reach a low permeability horizon. Here, they can flow down gradient and can accumulate in topographical lows on the top of the low-permeability layer. DNAPL's are not necessary influenced by groundwater flow and can move in the opposite direction under the influence of gravity.

In practice, the distinction between miscible and non-miscible liquids, DNAPL's and LNAPL's is often not distinct as some liquids may contain a range of chemical components.

## 2.4 During Movement Within The Groundwater

Contaminants that reach the groundwater, especially those occurring as a free phase product or as a dissolved phase, become influenced by groundwater flow which is generally the main factor controlling contaminant movement (Pankow and Cherry, 1996). As such the contaminant can move away from the original area of the spillage in the form of a lens of free product or as a plume. As the contaminant moves through the

sub surface in this manor it is subject to the processes of natural attenuation (Brady et al, 1998; Allerman and Leson, 1999; Wood, 1999).

Natural attenuation is defined by the US Environmental Protection Agency as "the biodegradation, dispersion, dilution, sorption, volatilisation, and/or chemical and biochemical stabilisation of contaminants to effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the ecosystem" (Brady et al, 1998).

There are many processes combining to achieve natural attenuation and these can be grouped under the three main categories of physical, chemical and biological. Table 3 indicates the main processes that might act upon liquid contaminants.

**Table 3: Summary of Main Natural Attenuation Processes Acting Upon Liquid Contaminants\***

| Physical | Chemical | Biological |
|---|---|---|
| Dilution<br>Dispersion<br>Adsorption<br>Absorption | Gas dissolution/exsolution | Aerobic degradation<br>Anaerobic degradation |

\*Sources: Brady et al, 1998; Wood, 1997; Thibodeaux, 1996; Tan, 1993; Young et al, 1992; DoE, 1986; Alleman and Leeson, 1999.

2.4.1 Physical Processes

Dilution and Dispersion

Dispersion can be considered as the smearing out of the contaminant plume by a combination of physical and chemical factors as it moves away from the source (Brady et al, 1998). The result is a dilution of the contaminant concentration but an increase in the overall volume of water contaminated. Factors influencing dispersion include local variations in hydraulic conductivity within a substrate, recharge by infiltrating rainwater, and other physical and chemical processes. For example, groundwater movement will not be uniform across the entire cross section of the plume. Both variations in velocity and some lateral movement of fluids will occur in both porous and fractured rocks as a result of variations in porosity and flow path geometry. Additionally, any large fluctuations in the water table such as may occur seasonally will encourage dilution and dispersion of contaminants.

Sorption

Absorption is the process whereby one substance penetrates into the body of another. Adsorption is the process whereby one substance is taken up at the surface of another. Absorption enables substances to penetrate into solids such as minerals thus providing access to internal adsorptive surfaces.

Sorption processes can result in contaminants adhering to mineral or non-mineral particles, so reducing their mobility and possibly removing them from a contaminant plume. The adsorption process is complex although surface area of the adsorbing agent is very important. The amount of material that can be adsorbed is directly proportional to the surface area. The mechanisms responsible for adsorption reactions include physical forces, hydrogen bonding, hydrophobic bonding, electrostatic bonding co-ordination reactions and ligand exchange (Tan, 1993). In general, it is the least water soluble chemicals that are the most likely to sorb (Brady et al, 1998).

Fine particles and porous materials such as clay minerals and porous sedimentary rocks tend to provide good adsorption surfaces and are thus capable of removing contamination from a contaminant plume as it moves through such materials.

## 2.4.2 Chemical Processes

### Gas Dissolution/Exsolution

Volatile organic contaminants either dissolved in a contaminant plume or occurring as a free phase product floating on the groundwater table might transfer to the vapour phase. The vapour phase might then move into the atmosphere above the soil where natural degradation process such as photolysis are often more effective than in soils. Alternatively, a vapour phase may travel at a different speed within the soil than the groundwater plume, and may indeed travel in a different direction (Brady et al, 1999). These process combine to provide an attenuation of the contamination and also a potential for a reduction in the overall amount.

## 2.4.3 Biological Processes

Biodegradation involves the breakdown of complex compounds into less complex compounds by naturally occurring organisms. Biodegradation of certain types of contaminants, particularly organics, can occur within a contaminated plume thus reducing their concentration in the groundwater over time, and as the plume moves away from the source. The biodegradation of organic contaminants is a complex and the various processes involved need to be understood. However, degradation half-lives (resulting from a combination of hydrolysis and biodegradation) have been identified for several contaminants (Brady et al, 1998).

Biodegradation can result in an overall reduction in the total amount of a specific contamination present in a system. However, the process might also result in formation of intermediate metabolic products that are more toxic, or more mobile than the parent contaminant (Wood, 1997).

## 3 COMPARISON OF INLAND AND COASTAL AREAS

The sections above have reviewed the generalised behaviour of contaminants following a spill on land. However, whereas there may be some similarities between this and the behaviour materials on the shoreline that are derived from liquids spilled at sea, there will

also be some differences. Table 4 draws a comparison of inland spills and shoreline contamination.

**Table 4: Comparison of Inland Spills and Shoreline Contamination**

| Inland Spills | Shoreline Contamination |
|---|---|
| Contaminant<br>• unweathered<br>• volatiles generally present<br>• oil not emulsified<br>• surface and subsurface<br>• distribution from point source<br>• lower opportunity for remobilisation | Contaminant<br>• weathered<br>• volatiles often lost<br>• oil emulsified<br>• surface and subsurface<br>• distribution from non-point source<br>• higher opportunity for remobilisation |
| Substrate<br>• variable permeability (e.g. high for river gravels and sandy drift; low for concrete and clays)<br>• organic content can be low or high<br>• water content can be low or high | Substrate<br>• variable permeability (e.g. high for pebble beaches; low for marshes and mud flats)<br>• organic content can be low or high<br>• water content can be low or high |
| Water table<br>• shallow or deep<br>• little fluctuation<br>• fresh water | Water table<br>• shallow<br>• daily fluctuation<br>• salt/brackish water |
| Natural attenuation<br>• potential opportunity | Natural attenuation<br>• restricted opportunity |
| Energy<br>• low | Energy<br>• high |
| Sensitivity of site<br>• generally high | Sensitivity of site<br>• can be high |

If any contaminating liquids resulting from a marine spillage reach the shoreline and become stranded they are likely to have undergone a degree of weathering which can change their physical and chemical nature. This is particularly the case with oil. Additionally, material on the shoreline is less likely to be water soluble, miscible with water or a DNAPL as these materials would be less likely to reach the shoreline in the first case.

Once on the shoreline the contaminant might remain on the surface or penetrate into it, depending on the characteristics of the contaminant and the substrate as outlined above. Material remaining on the surface does offer the potential for remobilisation by a subsequent tide of sufficient magnitude. Alternatively, if conditions are right the stranded contaminant might penetrate into shoreline substrate.

Figures 1 and 2 provide a conceptual model of LNAPL contaminant behaviour following stranding and penetration on a shoreline with homogeneous and heterogeneous permeability respectively. If penetration does occur then it will continue until a low permeability horizon is encountered or the water table is reached. Residual

concentrations of contamination could occur in the unsaturated zone along the path through which the material penetrated. Given that the water table is unlikely to be very deep then penetration will be restricted. Once at the water table the contaminant will behave as a LNAPL and/or might result in dissolved phase contamination of the groundwater. The opportunity for extensive free phase contaminant occurring on the groundwater table is restricted unless very large quantities of contaminant were initially stranded. Note that, as the groundwater is likely to be under the influence of tidal fluctuations, some horizontal and vertical transport of contaminated groundwater is likely. Smearing of any free phase product in the unsaturated substrate immediately above the saturated zone might become extensive. Contaminants will be transported upwards and landwards during the flood tide and might be lost to the sea on the ebb tide. Opportunities for extensive natural attenuation will generally be restricted. The largest volumes of contaminated substrate are likely to occur where deep permeable shore deposits (such as a storm beach) are under the influence of a large tidal range. Additionally, any contaminants that were stranded at neap tides are likely to contaminate larger volumes of material with successive high waters until the spring tide is reached.

Figures 3 and 4 provide a conceptual model of DNAPL contaminant behaviour following stranding and penetration on a shoreline with homogeneous and heterogeneous permeability respectively. With homogeneous permeability the DNAPL will continue to penetrate the groundwater and may eventually form a DNAPL pool once a less permeably horizon is encountered. With heterogeneous permeability the DNAPL will move down the surface of any low permeability stratum under the influence of gravity. If the slope of this surface is seawards then DNAPL might be released from the ground, either in the intertidal zone or below the low water level. Additionally, depending on the degree of tidal fluctuation, it is possible that some DNAPL at the surface of the impermeable stratum might get entrained during flood or ebb conditions.

## 4 REMEDIATION OPTIONS

If the risk management strategy to be applied to any area contaminated by an inland spill requires remediation to be undertaken then the technology or technologies must be able to tackle those aspects of the contamination of concern. It has been shown earlier that contamination can occur in a variety of forms:

- contamination of the ground surface
- contamination of the substrates within the unsaturated zone
- contamination of the soil atmosphere within the unsaturated zone
- contaminated of the substrate within the saturated zone
- contamination of the groundwater by LNAPL, DNAPL or dissolved phase.

Additionally the remediation process selected will need to be able to deal with the:

- specific type of contaminant - different contaminants might require different remediation processes
- type of substrate - remediation processes are not applicable to all substrates.

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A wide range of remediation technologies have been developed to tackle specific occurrences of contamination, types of contamination and types of substrate. These have been well reviewed by Riser-Roberts (1998). While many are proprietary variations of particular approaches there is a more restricted range of generic technologies. Table 5 provides a summary of the more established technologies that might be used for the in-situ treatment of contaminated ground following a spill.

## 4.1 Application to the Shoreline

The selection of the best remedial option for any given contamination conditions is a complicated affair. Factors to be considered include applicability, effectiveness, limitations, costs, development status, availability, operational requirements, information requirements, monitoring needs, potential environmental impact, health and safety needs and post-treatment management needs (Wood, 1997). A major consideration for the shoreline would be the constraints of the operating conditions and environment, especially the presence of any unconsolidated/course sediments and a fluctuating water table, and the cost of competing alternatives that are already used. Difficulties in controlling the hydraulic regime as a result of tidal fluctuations would also mean that those technologies that involve the addition of chemicals/reagents to the groundwater would be difficult to control. Table 6 summarises the applicability of the main generic in-situ treatment technologies to the shoreline. In theory the majority of treatment would have potential application although in practice they are unlikely to be used unless the amount of contamination is extensive, both in area and depth, and generally in special situations when the environmental risks are severe.

## 5 CASE STUDY: BIOREMEDIATION OF OILED SHORELINE

The *Sea Empress* ran aground in Milford Haven on 15 February 1996. Over the course of the next 7 days an estimated 72,000 tonnes of Forties Blend crude oil and 300 tonnes of heavy fuel oil were released into the Haven, contaminating around 200 km of the south-west coastline of Wales. A wide range of clean-up techniques were used to treat the oiled shorelines. The choice of technique depended on the level of contamination, beach substrate, degree of exposure and environmental considerations (MPCU, 1996; Lunel et al, 1995). However for the first time after an oil spill in western Europe, a detailed evaluation was carried out to determine whether any of the contaminated shorelines were amenable to treatment with bioremediation.

Bioremediation has been shown to have potential to treat oiled shorelines (Prince, 1993; Swannell et al, 1995 & 1996; Jones 1998). Field experiments in the UK (Swannell et al, 1997a), Canada (Lee et al, 1995; Lee and Levy, 1992) and the USA (Venosa et al, 1996) have demonstrated that bioremediation can stimulate in-situ oil biodegradation. Work following oil spill incidents in Israel (Rosenberg et al, 1992) and Alaska (Pritchard and Costa, 1991; Bragg et al, 1994) have also shown that bioremediation could stimulate oil biodegradation on oil-contaminated shorelines. However, although the scientific understanding of the use of bioremediation has improved considerably, there have been few trials which tackle the operational use of bioremediation after spill incidents (Prince, 1993; Swannell et al, 1996; Head, 1998). It was recognised that a well-constructed test of the use of bioremediation to treat oil contamination arising from the *Sea Empress*

**Table 5: Selection of Generic In-situ Treatment Technologies Applicable to Contaminated Ground Following Penetration of a Spilled Liquid**

| Technology | To Treat | Comments |
|---|---|---|
| Containment | Substrate atmosphere and groundwater | Installation of low permeability barriers to reduce migration of soil vapours and contaminated groundwater |
| Soil Vapour Extraction | Substrate atmosphere | Removes VOC's from soil atmosphere by vacuum pumping and encourages further volatilisation from soil particles and groundwater surface |
| Bioventing | Substrate in unsaturated zone | Aerates soils by air injection to encourage biodegradation of contaminants. Can be augmented by addition of nutrients |
| Soil heating | Substrate in unsaturated zone | Heat is applied underground to thermally desorb contaminants from particle surfaces or increase volatilisation rates of volatiles/semi-volatiles. Heating mechanisms include hot air, steam and radio frequency heating |
| Bioremediation (ground) | Substrates in unsaturated zone | Range of methods to encourage biodegradation of contaminants at any depth from surface to groundwater table. Can involve addition of nutrients, oxygen sources and water |
| Soil flushing | Substrate in saturated zone | Reagents are injected into the soil to remove contaminants from particles and into cleaning solution. Solution is then pumped to surface. |
| In-situ chemical treatment | Substrate in unsaturated zone and groundwater | Addition of reagents to achieve a chemical change in the contaminant to make it less toxic or less mobile/bioavailable. Approaches include oxidation/reduction, neutralisation, hydrolysis |
| Pump and Treat | Groundwater | Removes contaminated groundwater by pumping for treatment on the surface. Treated groundwater can subsequently be returned |
| Air sparging | Groundwater | Air is pumped through groundwater to air strip volatile contaminants which are then removed by soil vapour extraction |
| Biosparging | Groundwater and substrate in saturated zone | Addition of air/oxygen and nutrients below groundwater to encourage biodegradation of contaminants. Also brings about air sparging and potentially improved biodegradation in the substrate in the unsaturated zone |
| Bioremediation (groundwater) | Groundwater | Addition of nutrients and/or oxygen sources into contaminated plume to encourage biodegradation |
| Active barriers or in-situ reactors | Groundwater | Introduction of reagents into the ground to treat contaminated plume as it migrates through the barrier or treatment zone (includes bioremediation of groundwater) |
| LNAPL recovery | LNAPL free product | Pumping of free product to surface by a variety of methods |
| DNAPL recovery | DNAPL pools | Pumping of DNAPL to surface |

**Table 6: Applicability of Generic In-situ Treatment Technologies Applicable to the Shoreline**

| Technology | To Treat | Application |
|---|---|---|
| Containment | Substrate atmosphere and groundwater | Unlikely - possible application to contain liquids or to prevent groundwater fluctuations associated with tidal flow. Has been used to prevent migration of contaminant plumes from the land seawards |
| Soil Vapour Extraction | Substrate atmosphere | Unlikely - possible application to recover vapour from thick unsaturated substrates if the risks are sufficient. In thin unsaturated substrates air exchange resulting from tidal fluctuations will remove much vapour |
| Bioventing | Substrate in unsaturated zone | Unlikely - a fluctuating water table is likely to encourage sufficient air movement although the addition of nutrients may be advantageous in certain situations |
| Soil heating | Substrate in unsaturated zone | Unlikely - but possible in certain situations, especially if depth of contamination is great. Possible problems on establishing an appropriate thermal gradient |
| Bioremediation (ground) | Substrates in unsaturated zone | Potential application, especially in sensitive environments were normal clean-up procedures may cause damage |
| Soil flushing | Substrate in saturated zone | Unlikely - but possible if substrate below water table is itself contaminated and there is a need to treat. Potential problems in controlling hydraulic regime due to tidal influences on saturated zone |
| In-situ chemical treatment | Substrate in unsaturated zone and groundwater | Potential application to unsaturated zone but operational problems might arise. Unlikely application to groundwater due to operational problems in controlling groundwater |
| Pump and Treat | Groundwater | Potential application but possible operational difficulties |
| Air sparging | Groundwater | Potential application although it may not be necessary to remove stripped volatiles by soil vapour extraction as air movements resulting from tidal fluctuations may be sufficient |
| Biosparging | Groundwater and substrate in saturated zone | Potential application although operational difficulties would mean that use of any nutrients needs to be carefully considered |
| Bioremediation (groundwater) | Groundwater | Potential application although operational difficulties would mean that use of any nutrients needs to be carefully considered |
| Active barriers or in-situ reactors | Groundwater | Unlikely - possible application to migrating contaminant plume, especially a bioremediation approach |
| LNAPL recovery | LNAPL free product | Potential application if free product layer is sufficiently thick and if operational issues allow |
| DNAPL recovery | DNAPL pools | Potential application if DNAPL pools can be located. Possibility of recovery from areas where DNAPL may emanate onto beach at low tide |

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might improve the operational understanding of bioremediation, clarifying more precisely the role of bioremediation as an oil spill treatment technology (Mearns, 1997). This section describes the field evaluation of two bioremediation strategies in triplicate on a shingle and pebble beach, and their effect on the shoreline and nearshore environments using a similar methodology to that employed by Venosa et al (1996). Full details of this case study have been published elsewhere (Swannell et al, 1999).

## 5.1 Site Selection

The south-west coastline of Wales consists of a wide variety of shoreline types (mudflats, coarse and fine sands, shingle, pebble and rocky shorelines). An initial survey identified 4 beaches (Pwllcrochan, Gelliswick, Popton Beach and Bullwell Bay) where the level of oil contamination, the beach substrate, and the low level of tidal and wave energy rendered the sites potentially suitable for bioremediation (Lee and Levy, 1992). Further investigations were carried out on these beaches to determine local nutrient concentrations, and the numbers of hydrocarbon-degrading micro-organisms present in the beach sediment (as determined using a sheen screen method (Brown and Braddock, 1990) modified by Venosa et al (1993), and using weathered Forties crude oil as a carbon source with weathered Forties crude oil as the substrate). On the basis of the data obtained from these investigations, Bullwell Bay, a beach of limited amenity use, was considered the most suitable site for a demonstration project. The substrate was a mixture of free-draining shingle and pebble (mean density = 1.6 kg/l) overlaying clay (depth to clay layer= 10-40 cm), and had a gradient of 10-12.5% (n= 4). The interstitial water was poorly retained on the beach owing to substrate porosity and the gradient of the beach. The mean water holding capacity of the beach material was found to be 0.09 g water/g wet weight of sediment. The beach faced north, had a short fetch of <1 km, and was normally subject to low wave and tidal energy. As such, physical removal of oil was thought to be slow, and oil biodegradation by indigenous micro-organisms was thought likely to be a significant mechanism for oil removal from this site.

Preliminary analyses showed that the beach possessed a hydrocarbon-degrading population ($>10^5$ cells/g) and suggested that the levels of N and P present in the beach substrate (< 1.0 mg /kg) may be limiting oil biodegradation.

## 5.2 Experimental Design

A randomised block design was utilised with 3 blocks of 3 plots (each 9 m long by 0.9 m wide) placed perpendicular to the sea 1.25 m apart; a distance proven by tracer experiments to be adequate to mitigate the effects of cross contamination by the migration of mineral nutrients across the beach. Lithium chloride was selected as a tracer because of its chemical similarity to the mineral fertilisers which were to be evaluated, and because its natural shoreline concentration was low (Swannell et al, 1997b). In each block, one plot was treated with inorganic fertiliser (1.15 kg $NaNO_3$ and 0.08 kg $KH_2PO_4$ in 9 litres of seawater/plot/week), the second with a pelleted slow release fertiliser (15% N, 4.8% P, 13% K and 2% Mg, as $NH_4NO_3$, $(NH_4)_3PO_4$, $Ca_3(PO_4)_2$, $K_2O$ and MgO in casing derived from soya oil). These pellets were placed in mesh bags (1 m long x 0.2 m wide) and secured to the beach with steel pegs at 1 m intervals along the length of the treated plot. Sufficient slow-release fertiliser was added to provide the same

amount of N and P over the length of the experiment as was supplied to the plots treated with liquid fertiliser. The weekly fertiliser addition was equivalent to 1% N and 0.1% P of the mean oil concentration on the beach (9030 mg/kg, range= 2230-20260 mg/kg), an addition rate which has been used successfully previously (Swannell et al, 1997a). The third plot was left untreated as a control.

## 5.3 Monitoring

Beginning on 6th August 1996, the plots were monitored on a monthly basis, 2 days after the last weekly addition of liquid inorganic nutrients. Each plot was divided into three equal zones (i.e. upper, middle and lower intertidal zone), and one composite sample was taken from each zone. To produce a composite sample, each zone was subdivided into 6 regions of equal area. A sub-sample of sediment (300 ml) was taken at random from within each region by excavating oiled substrate to a depth of 10 cm and placing it into a pre-cleaned aluminium container. The 6 sub-samples were transferred to an aluminium foil container and mixed thoroughly. Samples (250 ml) were then removed from the container for oil residue analysis, mineral nutrient analysis and sediment toxicity. For Microtox™ analysis, 100 ml samples were taken from each zone and mixed together thoroughly to form 1 sample per plot.

The composition and concentration of residual hydrocarbons were analysed by GC/MS according to a method described by Swannell et al (1997b). Toxicity of the sediment was assessed using Microtox™ and oyster embryo assays. As the concentration of toxicants within the weathered oil stranded at Bullwell Bay was expected to be low, the Microtox™ Organic Solvent Extract - Basic Test was carried out according to a method described in the manufacturer's testing manual (Microbics Corporation, 1994). The oyster embryo test measured toxic effects on the development of the larvae of the Pacific oyster *Crassostrea gigas*.

Seawater samples were also taken at 3 points from the surf zone within Bullwell Bay (at the eastern end, the centre and the western end of the bay), and at 6 points in the Milford Haven Waterway directly outside Bullwell Bay, to determine whether the bioremediation treatments were elevating nutrient levels in the nearshore environment. The results were compared with those taken from the centre of the waterway by the Environment Agency (the environmental regulatory authority for England and Wales in the UK) as part of their routine monitoring programme. Beach height and sediment temperature were measured daily. Beach height was monitored relative to fixed markers placed at three equidistant points along the experimental area.

## 5.4 Results

### 5.4.1 Residual Hydrocarbon Analysis

At the start of the experiment no significant difference was found in the mean TPH levels (Figure 5), whereas at the end of the experiment the levels were significantly lower on the plots treated with liquid fertiliser (p=0.024) and on the plots treated with the slow release fertiliser (p=0.074). The TPH/hopane ratios were also reduced on the treated plots (Figure 5 & 6). Given the weathered state of the oil seven months after the spill,

any changes in this ratio could be attributed to biodegradation rather than to any other weathering process (Bragg et al, 1994; Douglas et al, 1996). After 2 months TPH/hopane and Total GC Resolvable Hydrocarbon (TRH)/hopane ratios were significantly reduced ($p < 0.001$) on the bioremediated plots relative to the controls. There was no difference in the average ratios at Day 0, and the magnitude of the difference between controls and treated plots increased with time (Figure 6). At the end of the experiment, the oil on the control plots was on average 13% more biodegraded than at the beginning. In contrast the oil on the treated plots was on average between 35 and 43% more biodegraded. There was no statistical difference in the degree of oil biodegradation on the bioremediated plots.

The results suggest that the treatments stimulated oil biodegradation most substantially in the upper intertidal zone (as any biodegradation in the control plots was too small to quantify), the zone which was influenced least by the tide, whereas the smallest relative influence of the treatment was noted in the middle zone (Table 7). The reason for these differences on the control plots is unclear from the data and requires further investigation. Certainly there was no evidence of markedly different sediment nutrient levels (Figure 8). In contrast, the mean reduction in TPH/hopane ratio was surprisingly consistent between zones, with the liquid fertiliser addition resulting in marginally more oil biodegradation. These observations perhaps suggest that factors other than nutrient levels were limiting biodegradation on the bioremediated plots. ·

**Table 7: Influence of Bioremediation on Biodegradation in Different Zones of the Experimental Plots**

| Position in Plot | Mean TPH/hopane ratio (n=3) | | Reduction |
|---|---|---|---|
| Treatment | Day 0 | Day 60 | In Mean Ratio |
| *Upper Intertidal Zone* | | | |
| Control | 2600 | 2600 | 0 |
| Liquid Fertilizer | 2500 | 1400 | 1100 |
| Slow Release Fertilizer | 2300 | 1600 | 700 |
| *Middle Intertidal Zone* | | | |
| Control | 2500 | 1700 | 800 |
| Liquid Fertilizer | 2300 | 1300 | 1000 |
| Slow Release Fertilizer | 2000 | ·1300 | 700 |
| *Lower Intertidal Zone* | | | |
| Control | 2200 | 2000 | 200 |
| Liquid Fertilizer | 2100 | 1100 | 1000 |
| Slow Release Fertilizer | 1900 | 1100 | 800 |

The concentration of hopane did decrease slightly over the course of the experiment (Figure 7) suggesting that some of the reduction in TPH could have been attributed to physical oil processes. However, these changes were not statistically significant, and most importantly, were not influenced by treatment. Thus, the oil chemistry results strongly suggests that the bioremediation treatments stimulated oil biodegradation thereby reducing the TPH concentrations and the TPH/hopane ratio. The treatments did not have a significant effect on the physical removal of oil. Detailed analysis of the

hopanoid biomarkers in the samples recovered from the beach indicated that the oil was a mixture of cargo and fuel oil from the *Sea Empress*. These data are consistent with analyses conducted on nearby beaches on the southern shore of Milford Haven (Pwllcrochan and Kilpaison) which also showed that the oil contamination was a mixture of oils spilled from *Sea Empress* (Swannell et al, 1997b). The ratio of cargo oil and fuel oil was variable but on average was 50:50 w/w (Bowes, 1997).

### 5.4.2 Mineral Nutrient Levels

The liquid fertiliser applications elevated the nitrate concentrations on the sediment substantially and this effect persisted for at least 4 tidal cycles (Figure 8). By contrast, the plots treated with the slow-release fertiliser showed only marginally higher levels of nitrate than were observed in the control. A similar pattern was noted for phosphate distribution (Figure 9). Similar results were obtained directly after the first nutrient addition, and at the 1 and 2 month sampling points. The lower levels of mineral nutrients within the plots treated with slow-release fertiliser may have been due to: 1) inefficient nutrient released from the fertiliser pellets into the beach substrate, 2) consumption of mineral nutrients by biological processes, and/or 3) physical removal of nutrients (wave and tidal action) at a rate similar to their release rate from the pellets.

In order to confirm that mineral nutrients were being released from the slow release fertiliser, separate experiments were carried out on Bullwell Bay. Over a period of 16 weeks a median loss of fertiliser from the pellets within the analysed mesh bags was 60% (n= 9, standard deviation = 14%). The manufacturer quoted an expected lifetime of 3-4 months. It should however be noted that the landward ends of the plots were only subjected to tidal water irregularly, and thus the release rate here would be consequently lower. At the seaward ends of the plots the mean loss from the pellets was 81% (n= 3, standard deviation = 11%) indicating the importance of tidal inundation for effective release of nutrients from the pelleted fertiliser.

### 5.4.3 Toxicity Assessment

Two assessments of the toxicity of the recovered samples were made. Microtox™ Organic Extract - Basic Tests were completed on all samples taken at the start of the experiment and at 1 and 2 month intervals. Acute toxicity within the extracted sediment samples contaminated with the 6-month weathered oil was low. Indeed, $EC_{50}$ values for sediment extracts expressed as units of sediment (wet weight) equivalent per unit of solvent (mg eq/mL) could only be identified in 3 of the 9 sediment samples recovered on the first (mean = 52.8 mg eq/mL) and last day (mean = 53.0 mg eq/mL) of the study. These mean values are close to the value reported in the literature as reflecting "uncontaminated" sediments (i.e. 49.5 mg eq/ml. See Johnson (1998)). With the restricted number of positive samples, variation in toxicity between samples could not be correlated to treatment. Remaining samples were below the $EC_{50}$ detection limit of the Microtox™ Basic Test.

Using the oyster larvae assay, residual toxicity could be detected in some samples of contaminated sediment (Figure 10). All plots showed residual toxicity in the samples taken at the beginning of the study. However on Days 30 and 60, only samples from

certain plots gave a toxic response, and this was not related to treatment. Overall the bioremediation treatment had no significant influence on the reduction in toxicity seen on all plots over the course of the experiment.

## 5.4.4 Seawater Nutrient Concentrations

Generally, low background levels of nitrogen were seen at all the sites (Figure 11), although on Day 16, one sample was high skewing the data from within Bullwell Bay. The levels for total inorganic nitrogen at the reference sites within Milford Haven for the sample period ranged from 25-184 µg/l (n= 18), which were consistent with the results obtained within and near to Bullwell Bay. Similarly, low levels of phosphate were found at all the reference sites (range = 6-36 µg/l, mean = 15 µg/l; n= 18), and there was no evidence of an increase within Bullwell Bay over the course of the experiment (range = 4-46 µg/l, mean = 18 µg/l; n=12). Whilst there was some variability, looking at the totality of the data, and comparing with the data for Milford Haven as a whole it is clear that the bioremediation treatments had minimal impact on nutrient levels in the nearshore environment, an finding that would be expected given the large dilution available within the adjacent waterway.

## 5.5 Conclusions of Case Study

This study clearly shows that the addition of both liquid inorganic and slow-release mineral fertiliser were capable of significantly stimulating the natural biodegradation of oil in sediment on Bullwell Bay, resulting in significantly less oil on average on the treated plots than on the controls. This beach was contaminated with a mixture of cargo oil (Forties Blend) and heavy fuel oil spilled during the grounding of the *Sea Empress*. Forties Blend is a light crude oil and known to be biodegradable whereas heavy fuel oil is regarded as being relatively resistant to biodegradation (Bowes, 1997; Atlas, 1975; Leahy and Colwell, 1990). Whilst there may be differences in the rates at which these oils degraded in-situ, the results clearly show that both bioremediation treatments were effective in stimulating the biodegradation of the oil mixture. The effect of the treatment could be observed both on the total resolvable hydrocarbons and also on the concentration of total petroleum hydrocarbons.

The consequences for the beach habitat of the two treatments were strikingly different. Levels of mineral nutrients detected in the plots treated with liquid fertiliser were upto 100 fold higher than those treated with the slow release agent, depending on the exposure of the sediment to the tide. Nutrients were more likely to persist in the upper intertidal zone, where exposure to waves occurred only during Spring tides. Despite the lack of evidence for increased nutrient levels on the sediment treated with slow-release pellets, oil biodegradation was significantly stimulated on these plots, in comparison to the controls. Moreover, subsequent experiments have shown that nutrients were released from the pellets secured in mesh bags on the beach at Bullwell Bay. Therefore, we can only propose that microbial utilisation and physical removal of nutrients were equivalent to the release rate of the nutrients from the pelleted fertiliser. The slow-release agent was much less labour-intensive to apply and required re-application only every four months. For this reason, we see the use of such slow release mineral fertilisers as a promising

operational bioremediation strategy for treating shorelines from the standpoint of cost, convenience and efficacy.

This trial has also demonstrated that bioremediation has a minimal impact on the surrounding environment in line with the observations made after the *Exxon Valdez* incident (Bragg et al, 1994; Pritchard et al, 1991). In this work, there was little detectable impact on nutrients levels in nearshore seawater and in the Milford Haven Waterway as a whole, which is unsurprising given the scale of the project and the dilution available in the adjacent waterway. Moreover, the bioremediation treatments had no detectable affect on the toxicity of the oiled sediment. These are important considerations, especially as the use of some bioremediation products has been found to have detrimental consequences (Lee et al; 1995). Addition of ammonium and nitrate near aquatic resources is of significant regulatory concern, and in some areas may be key to the acceptance of bioremediation as an operational tool. This study has shown that while such concerns are understandable, mineral bioremediation products when used carefully should not have detrimental consequences for the beach or nearshore habitats. Nonetheless, it is very important that the scale of the nutrient addition, the type of nutrient added and the toxicity of the nutrient is related to the dilution available in the nearshore environment, before bioremediation is undertaken in the field (see Swannell et al (1996)). It is also our view that nutrient concentrations should be monitored in the nearshore environment during application to confirm that any treatment is not posing any toxicological threats to the environment. Our results suggest that the use of a slow release fertiliser may reduce the concentration of N and P that is washed off the beach, although this will have to be confirmed by further research.

The use of bioremediation to treat oil-contaminated shorelines has been the subject of much research, and is increasingly being accepted as a response tool. Field trials have been conducted both experimentally and after spill incidents (e.g. Swannell et al, 1995 & 1997a; Lee and Levy, 1992; Venosa et al, 1996; Rosenberg et al, 1992; Bragg et al, 1994; Oudot et al, 1998). The promising results from many of these studies, and the statistical evaluations completed by Bragg et al (1994), Venosa et al (1996) and undertaken in this study, demonstrate that bioremediation can significantly increase oil biodegradation in-situ on contaminated shorelines. What is less clear, particularly to the oil spill responder, is by how much the oil biodegradation can be increased, and whether any increase results in a net environmental benefit. This field research and the results of those reported elsewhere suggest that bioremediation can increase oil biodegradation rates on shorelines by between 2 and 7 times (Swannell et al, 1996; Venosa et al, 1996; Bragg et al, 1994). However, this potential increase in rate has to be considered in the context of other natural oil removal processes. For example, if physical processes (such as tide and wave action) will remove the oil naturally within 6 months, then even increasing the in-situ rate of oil biodegradation 5 fold may well have little net environmental benefit (although used carefully it will cause little harm, and could still be considered). However, on shorelines where physical removal rates are slow (for example, *Sea Empress* oil remained on Bullwell Bay, and on Pwllcrochan and Kilpaison, 18 months after the oil spill (Swannell et al, 1997b)), then increasing the rate of oil biodegradation could reduce the residence time of the oil on the shoreline substantially. In the upper intertidal zone of Pwllcrochan, the residual oil was more biodegraded in June 1997 than in September 1996 (median degree of biodegradation = 53 %,

interquartile range = 43-60%), with the microbial community biodegrading alkanes, branched alkanes and aromatics (Swannell et al, 1997b). On such shorelines, bioremediation could substantially increase oil removal rates.

It is our contention therefore, that when physical oil removal rates are low (and therefore the threat of oil migration to uncontaminated beaches is slight), and there is little pressure to clean the shore for amenity or economic purposes, or because the residual oil poses a threat to animal or bird populations, bioremediation should be considered as a treatment technology. Having reviewed the relevant literature, Sell et al (1995) have suggested that physical and chemical shoreline treatment methods used during experimental spills and spill incidents around the world have generally had little, if any, positive effect on natural rates of shoreline recovery on rocky shorelines and salt marshes. Given that bioremediation seeks to stimulate natural biodegradative processes, then it seems likely that this approach could increase the natural rate of shoreline recovery, bringing net environmental benefits. This comment presupposes that the bioremediation strategy is conducted carefully, and is supplying the nutrients that are limiting natural rates of oil biodegradation. However, the precise effect of bioremediation on the recovery of the natural shoreline biota (such as the micro- and meio-fauna) has not been studied, and any effect will have an important influence on the operational use of bioremediation.

## 6 CONCLUSIONS

This paper has examined the behaviour and remediation of oil and chemical spills on the soil surface and in the sub-surface. It has also contrasted this with the behaviour of contaminating materials on the coastline, and evaluated whether any remediation approaches used inland have potential application along the shore.

It is concluded that many remediation approaches are unlikely to be used on the shoreline, while the application of others is likely to be restricted as a result of operational difficulties in implementing the technology and controlling it. This applies particularly to in-situ technologies where the introduction of reagents/chemicals is required. Those methodologies involving bioremediation approaches are likely to be most easily transferred to the shoreline coastline.

A case study has been presented which suggests that in situations where the physical oil removal rates are low (and therefore the threat of oil migration to uncontaminated beaches is slight), and there is little pressure to clean the shore for amenity or economic purposes, or because the residual oil poses a threat to animal or bird populations, bioremediation should be considered as a treatment technology.

## 7 ACKNOWLEDGEMENTS

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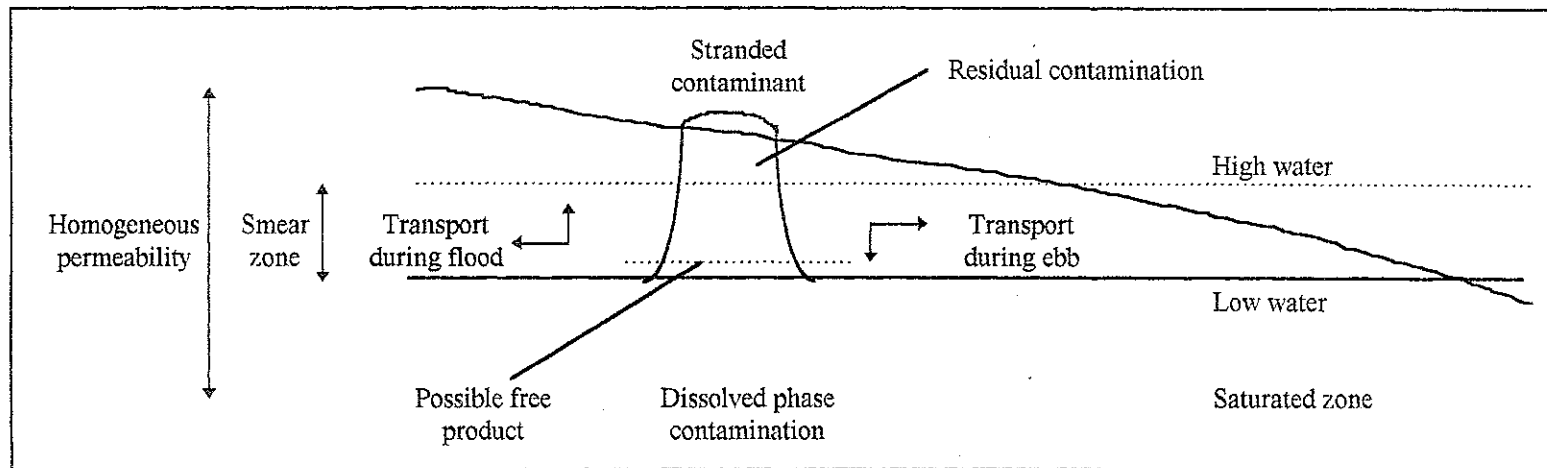
**Figure 1: Conceptual Model of LNAPL Behaviour on a Shoreline with Homogeneous Permeability**
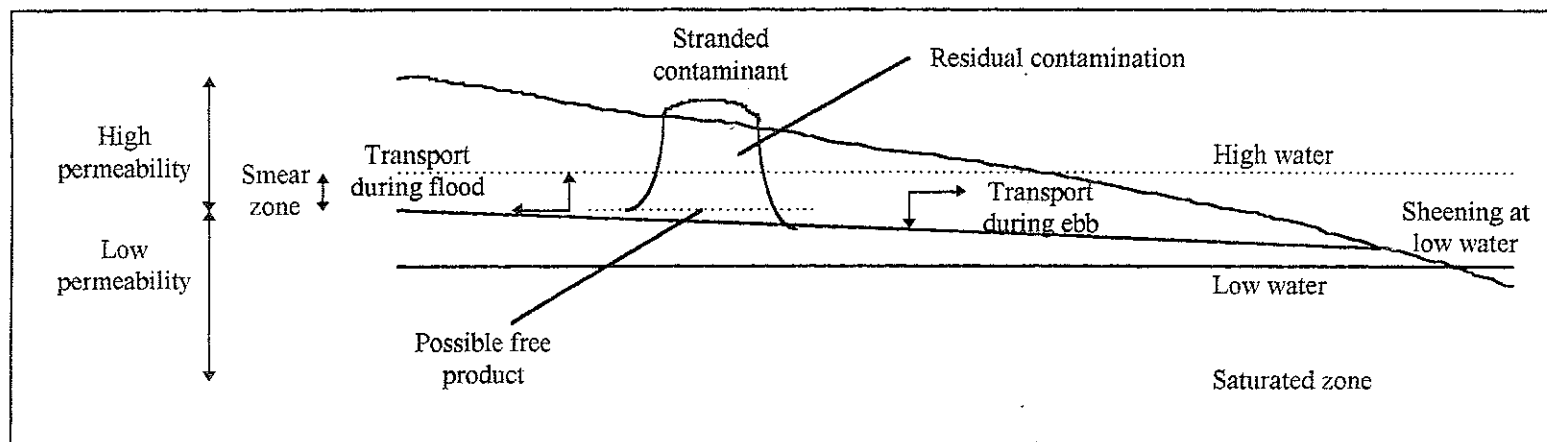


**Figure 2: Conceptual Model of LNAPL Behaviour on a Shoreline with Heterogeneous Permeability**
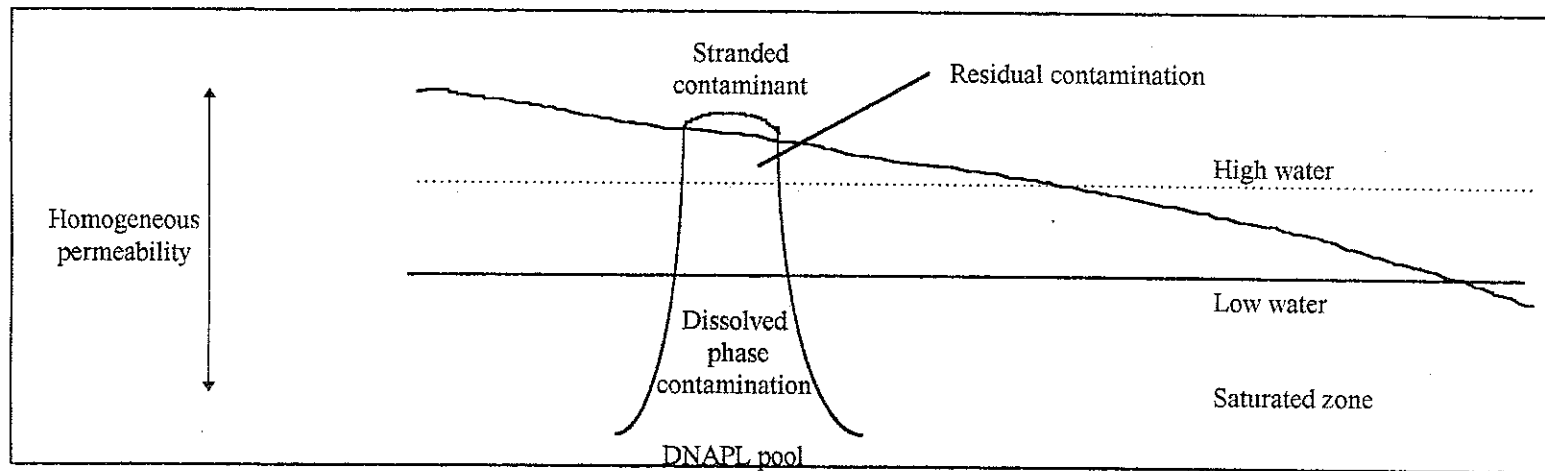
**Figure 3: Conceptual Model of DNAPL Behaviour on a Shoreline with Homogeneous Permeability**
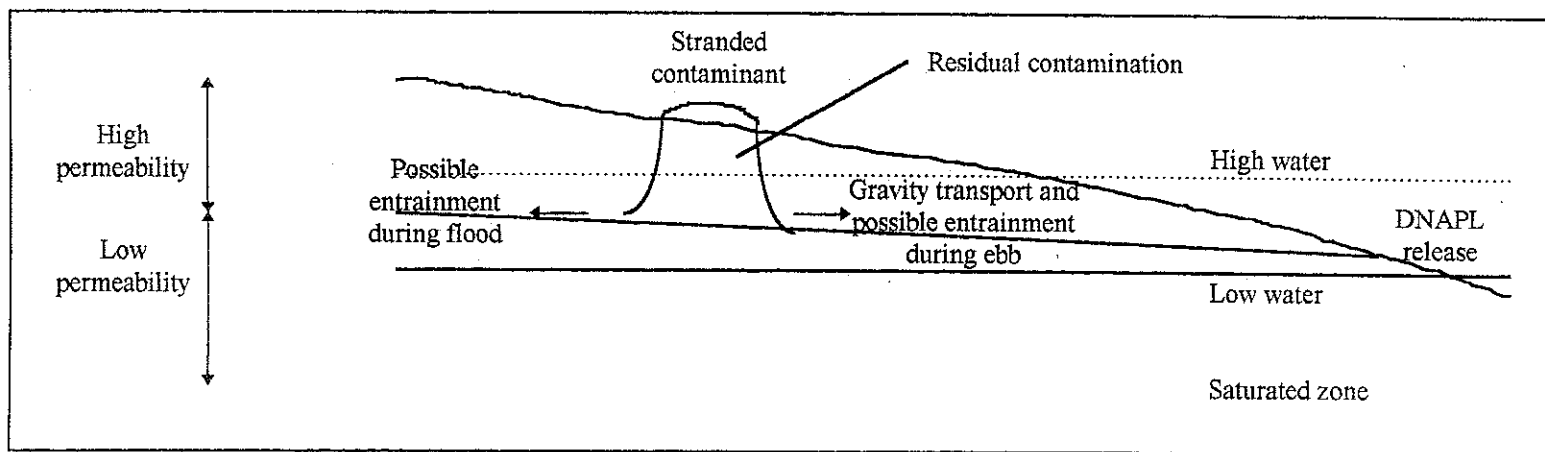
**Figure 4: Conceptual Model of DNAPL Behaviour on a Shoreline with Heterogeneous Permeability**
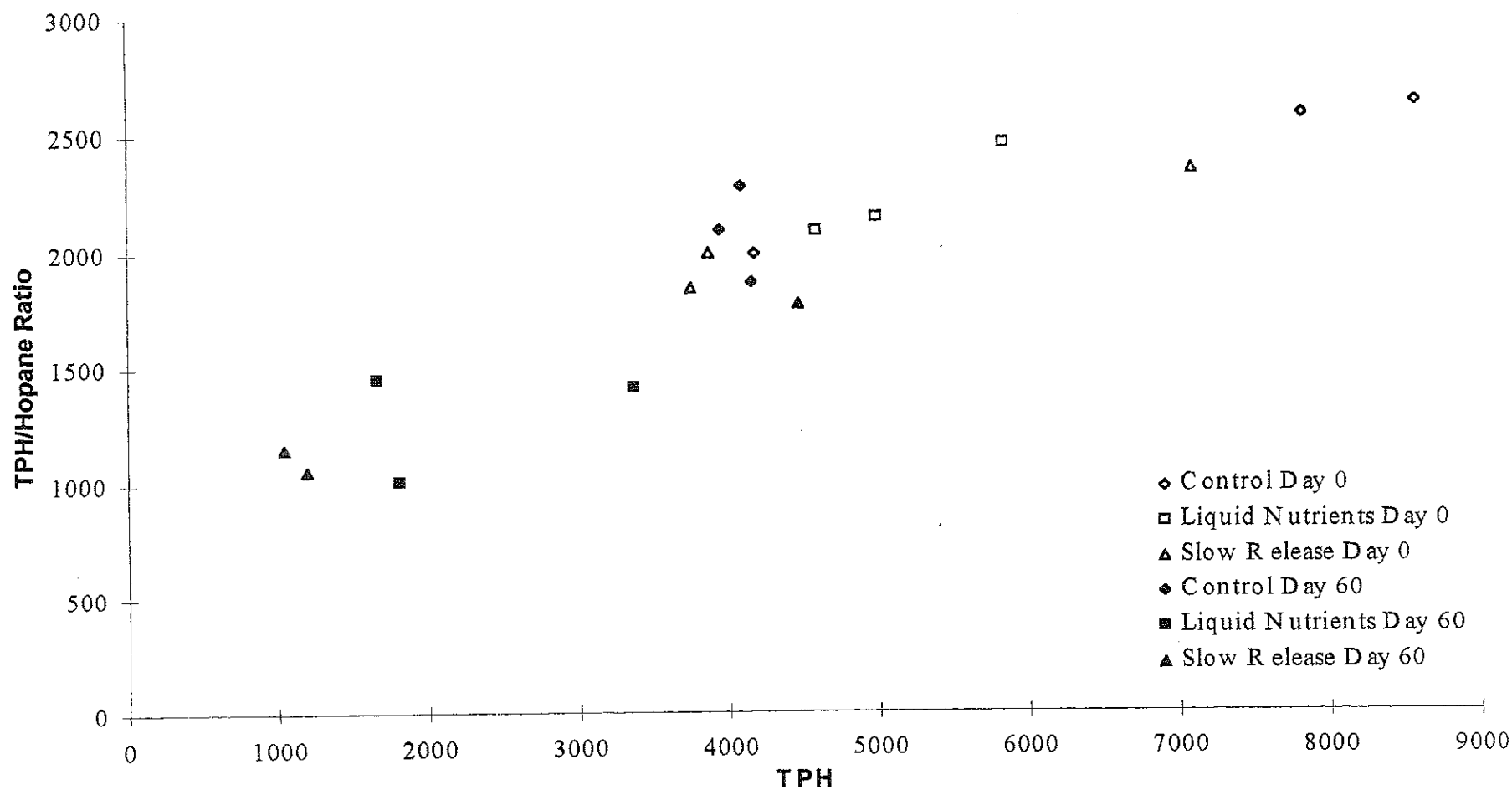
**Figure 5: Effect of the Treatment on Oil Concentration and Composition.** Changes in the content of biodegradable residues were indicated by changes in the mean ratio of the total petroleum hydrocarbons (TPH):17α(H),21β(H) hopane. Each point represents the mean content on each plot (n=3)
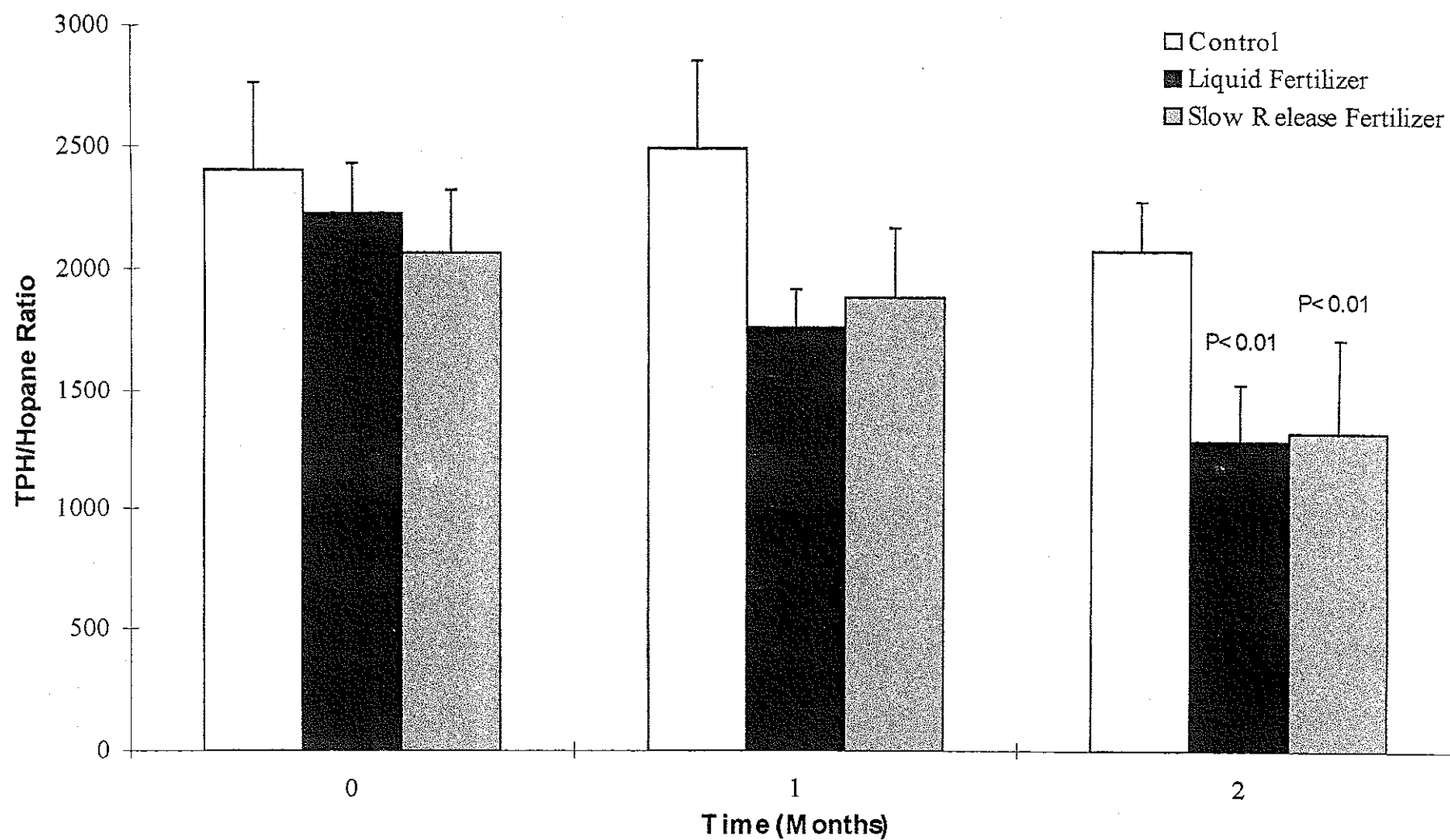
**Figure 6: Effect of Treatment on the Biodegradation of Oil.** Biodegradation was monitored by determining changes in the mean ratio of the total hydrocarbons (TPH):$17\alpha$(H),$21\beta$(H) hopane
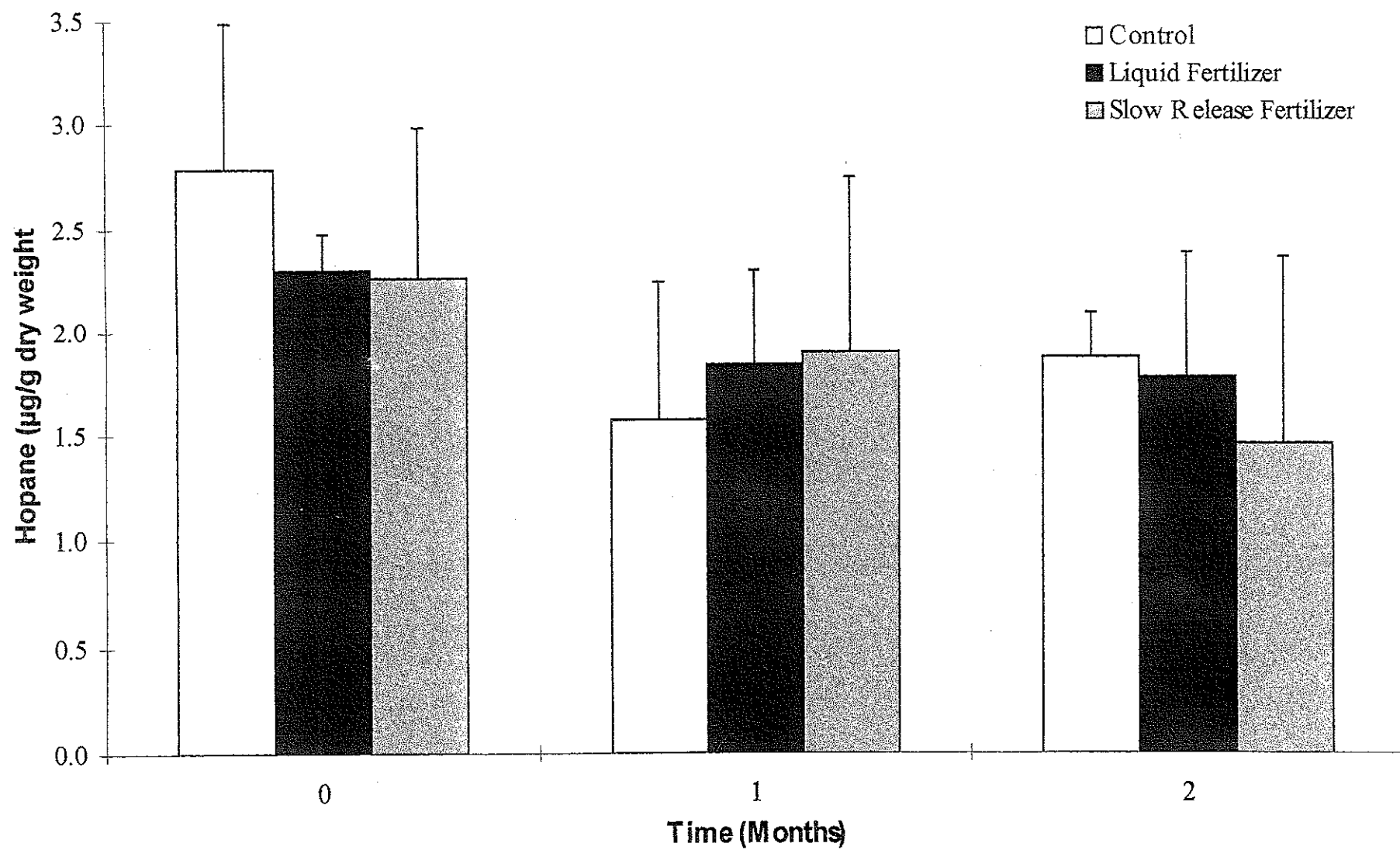
Figure 7: Effect of Treatment on the Concentration of $17\alpha(H),21\beta(H)$ hopane
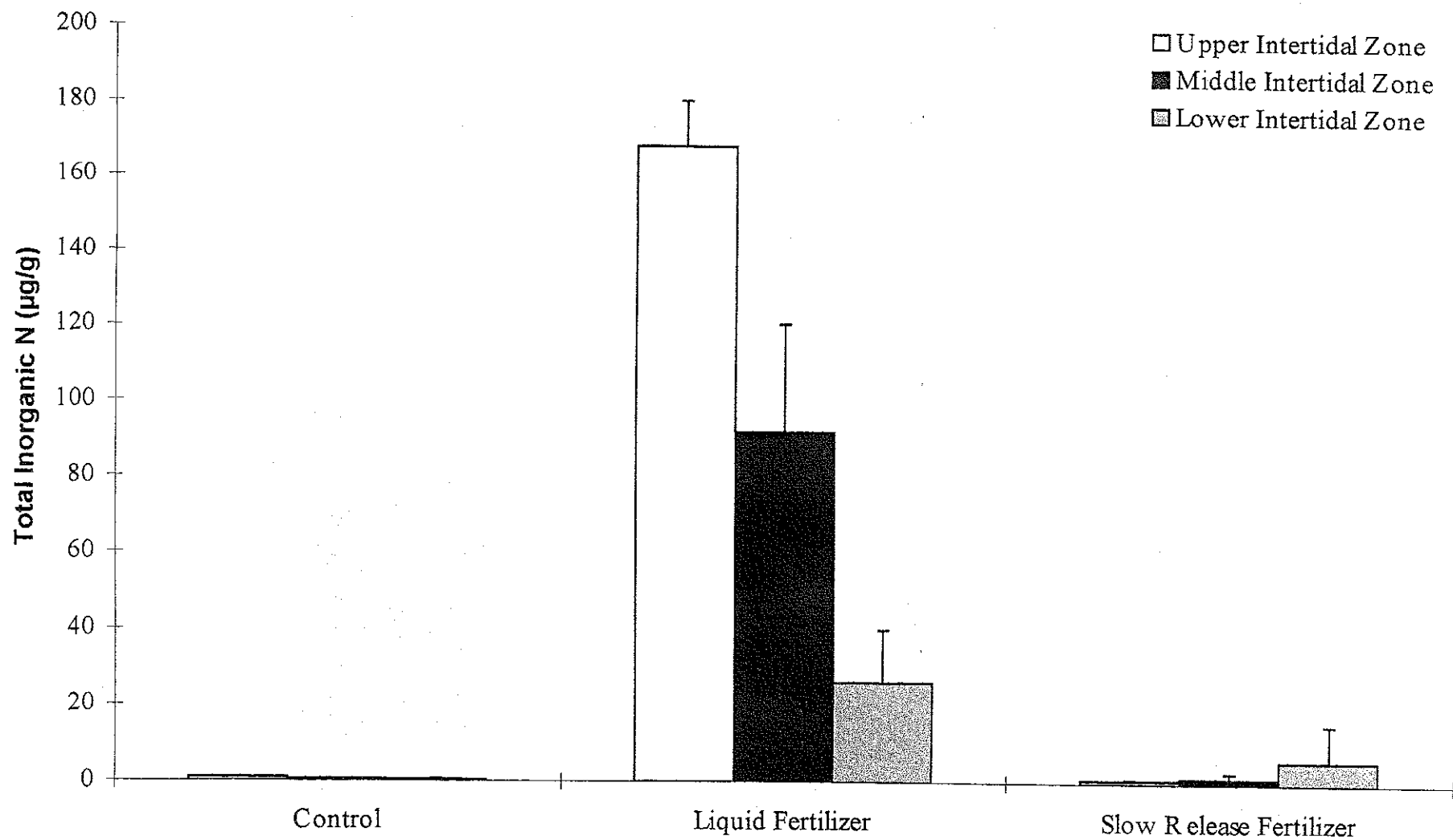
**Figure 8: Mean Total Inorganic Nitrogen Concentration in Beach Sediment from the Experimental Plots after One Month.** Samples were taken 4 tidal cycles after the most recent addition of liquid fertiliser
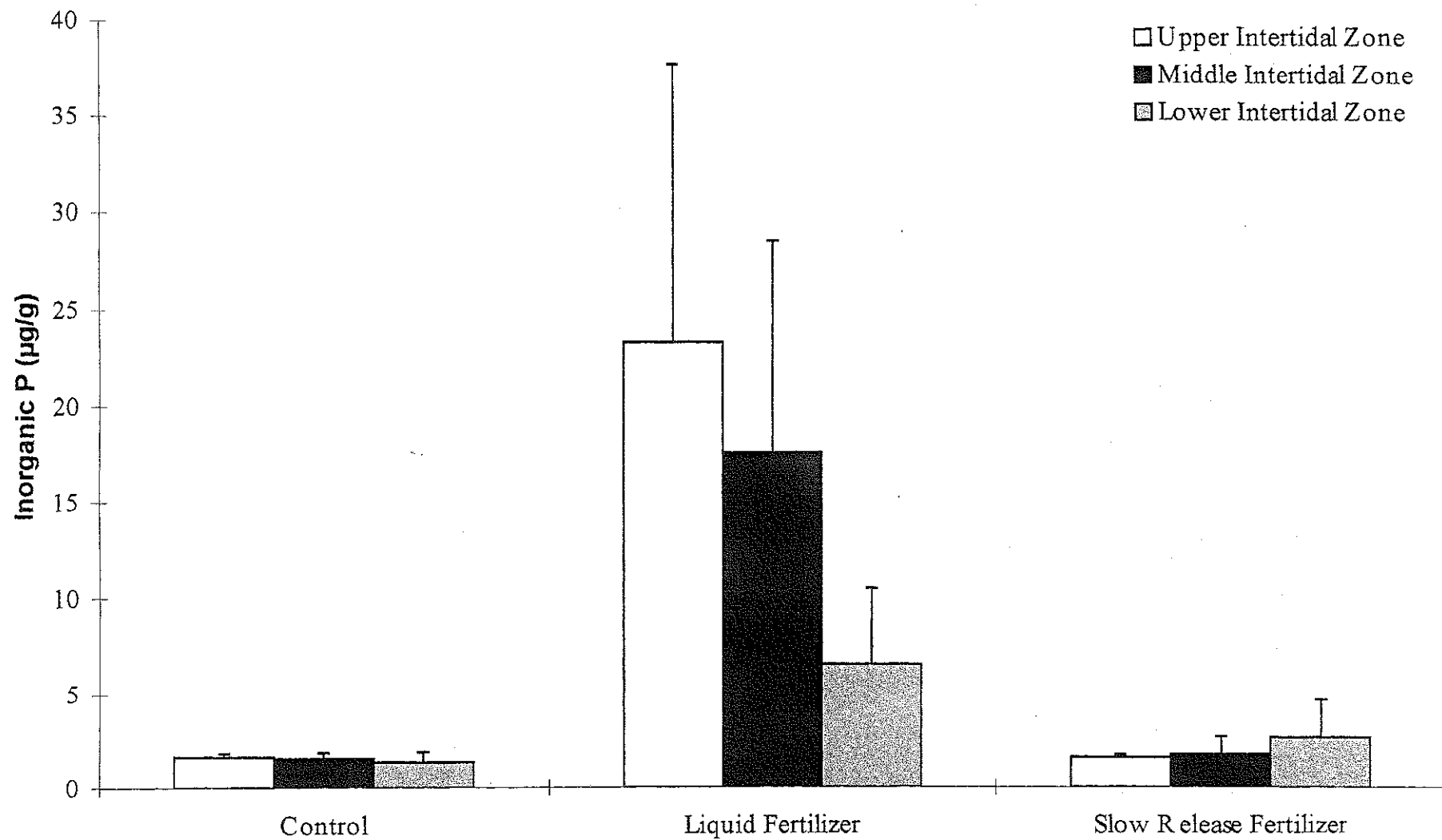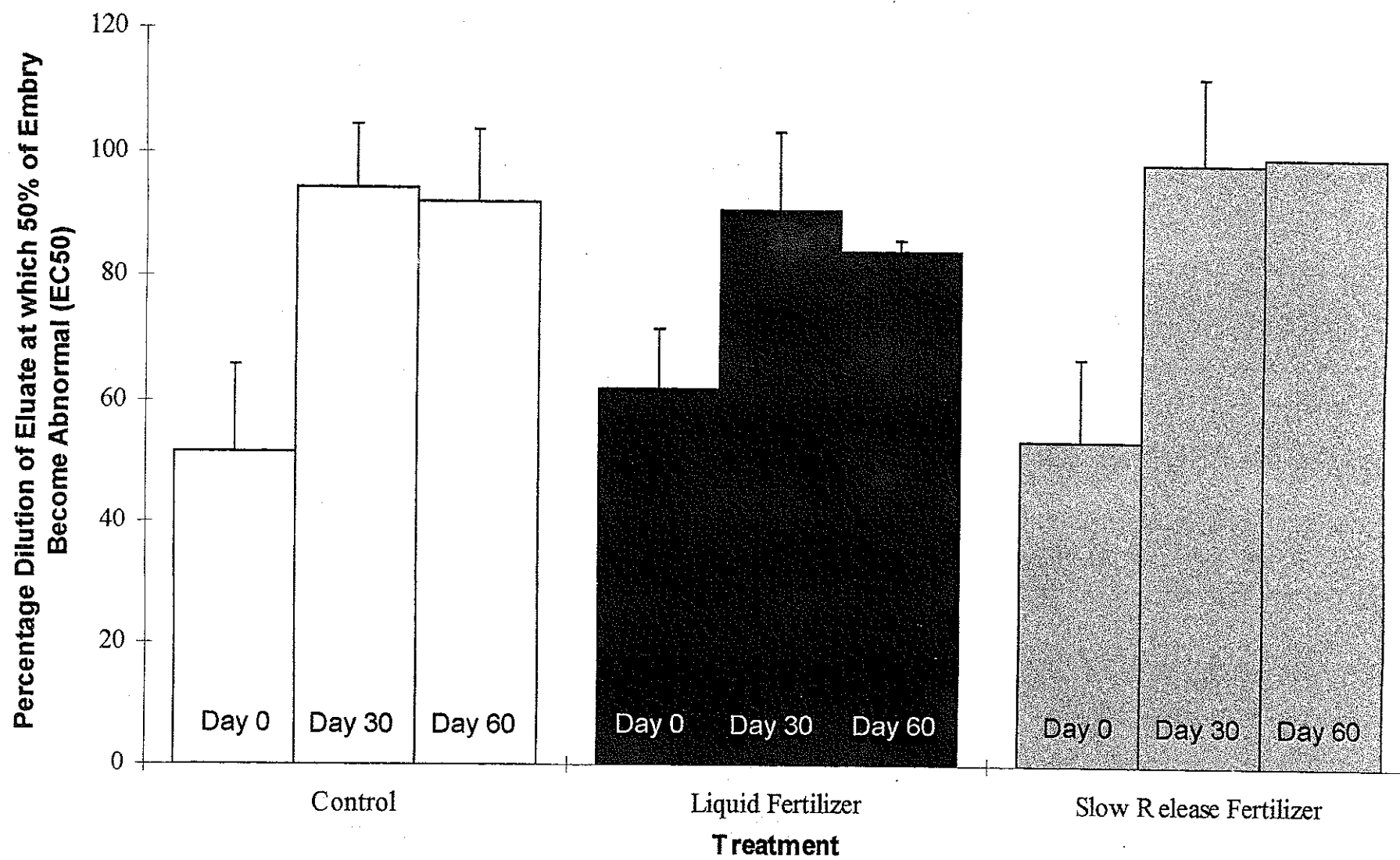
**Figure 9: Mean Inorganic Phosphorous Concentration in Beach Sediment from the Experimental Plots after One Month.** Samples were taken 4 tidal cycles after the most recent addition of liquid fertiliser

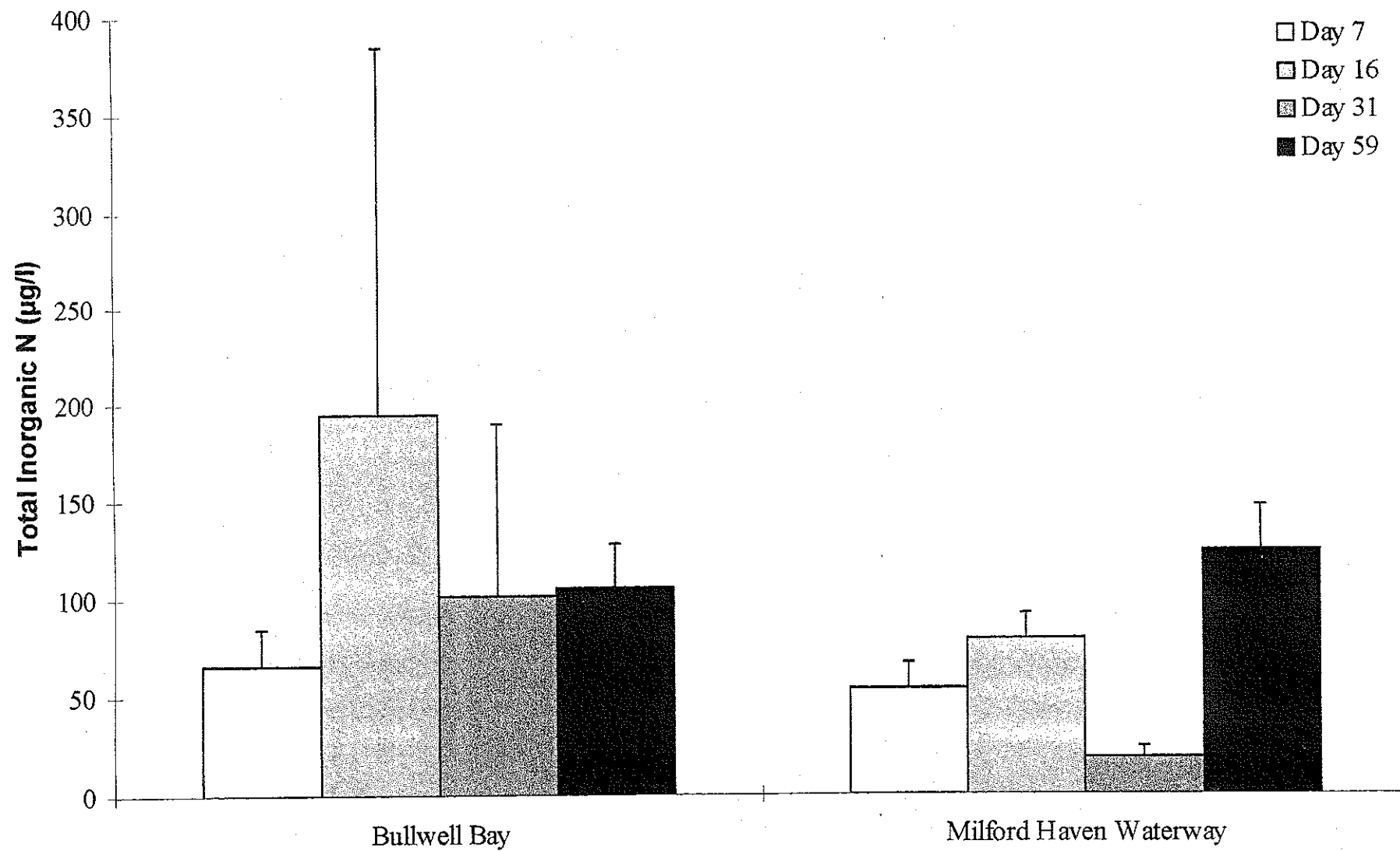**Figure 10: Toxicity of Sediment Samples Determined by the Oyster Larvae Assay**

**Figure 11: Inorganic Nitrogen Levels in Seawater Sampled in Bullwell Bay and Milford Haven**