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Environmental Management of the Waste Stream with Specific Reference to Marine Oil Spills

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Abstract:

Development and expansion of renewable energy generation is one of the highest political and environmental priorities facing today's Governments. Due to increased demand for green technology, the range of options for generating clean energy has expanded. In the case of energy generation from waste sources, it has been further fuelled by increasing pressure for environmentally benign waste disposal systems, burgeoning waste volumes and concerns over secondary pollution from disposed waste. An industry that is integral to energy production, and has a high profile in terms of environmental protection and pollution remediation, is oil spill response. There is scope for expanding the environmental management of the oil spill response industry to incorporate using waste oil from spill incidents as a source of fuel. In order for potential markets (in terms of environmental protection, waste management and energy generation) to be exploited, the necessary range of education and training demands must be established, developed and delivered. Education and training from grass roots to strategic management and Government levels are essential aspects in establishing the knowledge base, compliance, maintaining standards and ongoing development.

This thesis examines the integration of the management of the waste stream, energy generation from waste and focuses specifically on the disposal of oil spill waste. The outputs of the research fall into two categories. (i) A series of laboratory and *ex-situ* field trials to quantify the potential of oil from marine spill incidents as a fuel source, to evaluate the effectiveness of pixel analysis as a mechanism to monitor the efficacy of oil spill response technologies, and to record the percentage recovery of oil and sorbent from the environment as a measure of clean up effectiveness. (ii) To examine the role and impact of education and training initiatives in disseminating scientific, technical and legislative material on bioremediation of marine oil spills.

The research demonstrated that there are sufficient levels of carbon present in range of compounds of oils and sorbents from marine oil spill incidents to be utilised as fuel. Pixel analysis was established as an effective technique, oil and sorbent compound dependent, to quantify the extent to which oil had been removed from the environment. Percentage recovery was deemed a value-added data set to analyse the effectiveness of sorbents at recovering oils with varying viscosities. In terms of education and training, feedback from distance learning initiatives specifically developed for the research pathway, including undergraduate modules, and workshops and training courses for professionals and industry was analysed and integrated into the distance learning material on bioremediation. The positive nature of the feedback and subsequent suggestions for expanding the courses from all target audiences, demonstrated their impact, importance and effectiveness within the scope of the environmental management process. These recommendations contributed to the development and design of the bioremediation research.

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Abbreviations

2050	2050 refined oil
ANOVA	Analysis of variance
AONB	Area of Outstanding Natural Beauty (UK)
ASEAN	Association of South East Asian Nations
BIOREM	Bioremediation of Marine Oil Spills in Vietnam
BiWaRE	Biomass and Waste for Renewable Energy
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
CDROM	Compact disc read only memory
CHP	Combined heat and power
CO_2	Carbon dioxide
Cr	Crude oil
DEFRA	Department for Food, Rural Affairs and Agriculture (UK)
DL	Distance Learning
DLM	Distance Learning Material
DSS	Decision Support System
DTI	Department of Trade and Industry (UK)
DVD	Digital versatile disc
EC	European Comission
EHWS	Extreme high water springs
EIA	Environmental Impact Assessment
EMAS	Eco-Management and Audit Scheme
ESG	Bangalore Environmental Services Group (India)
EU BAP	European Union Best Available Practice Policy
EU	European Union
FUND	International Fund for Compensation for Oil Pollution Damage
GDP	Gross Domestic Product
H_2S	Hydrogen sulphide
HE	Higher education
HWD	The Hazardous Waste Directive
IEA	International Energy Agency
IMO	International Maritime Organisation
INVENT	Innovative Education Modules and Tools for the Environmental Sector, Particularly in Integrated Waste Management
IPIECA	International Petroleum Industry Environmental Conservation Association
IPPC	Integrated Pollution Prevention and Control
ISO	International Organisation for Standardisation
IT	Information technology
ITOPF	International Tanker Owner's Pollution Federation
Kl	Klausorb absorbent
KMUTT	King Monkut's University of Technology, Thornburi (Thailand)
kWh	Kilo-watts/hour
LEP	Law on Environmental Protection (India)

MARPOL	International Convention for the Prevention of Pollution from Ships
MBT	Mechanical/biological treatment (waste)
Mg/kg	Milligrams per kilogram
MNR	Marine Nature Reserve (UK)
MPN	Most probable number
MSW	Municipal solid waste
MW	Mega-watt
NEA	National Environmental Agency (Vietnam)
NEBA	Net Environmental Benefit Analysis
NGO	Non-governmental organisation
NIMBY	Not In My Back Yard
NOAA	National Oceanic and Atmospheric Administration
NOS	United States National Ocean Service
NO_x	Nitrogen Oxide
OPA90	Oil Pollution Act 1990 (United States)
ORS	Old Red Sandstone
OSRL	Oil Spill Response Limited
PAH	Polycyclic aromatic hydrocarbon
PCNPA	Pembrokeshire Coast National Park Authority (UK)
pH	Potential hydrogen
PPM	Parts per million
PROTEKT	Development of guidelines for the handling and treatment of oil contaminated water in industries and trades in Thailand
PVC	Polyvinyl chloride
RDF	Refuse derived fuel
Re	RecoverIt adsorbent
SAC	Special Area of Conservation (UK)
SACODI	Segregation, collection and disposal of hazardous waste
SEM	Scanning Electron Microscope
SL	Smooth limestone
SME	Small to medium enterprise
SO_2	Sulphur dioxide
SPA	Special Protection Area (UK)
SRF	Secondary recovered fuel
SSSI	Site of Special Scientific Interest (UK)
TDS	Total dissolved solids
TROPICS	Tropical Oil Pollution Investigations in Coastal Systems
UK	United Kingdom
UKMCA	United Kingdom Maritime and Coastguard Agency
UN	United Nations
UNDP	United Nations Development Organisation
UNEP	United Nations Environmental Programme
US	United States
UV	Ultra violet
WHO	World Health Organisation
WL	Weathered limestone

1 Chapter One

1.1 Introduction

This chapter introduces the scope of the thesis which is based around the integration of the management of the waste stream and the generation of energy from waste, with specific reference to waste from marine oil spill incidents. The principles and definitions used in the research pathway are stated, and the need for such research in the field is justified. The research aims and objectives are presented followed by the structure of the thesis.

The primary research outputs are:

- A conceptual analysis and summary of the waste management and energy from waste industries to provide the framework for the research into the management of oily waste from marine spills.
- A series of laboratory experiments and *ex-situ* field trials to determine the feasibility of using oil spill waste as fuel, and to trial a novel application of pixel analysis to quantify the efficacy of oil spill sorbents.
- An investigation into the role of education and training in the dissemination of related scientific and technical material, and the development and delivery of Distance Learning Modules (DLM).

The development of the research pathway was achieved through conceptual integration of the research areas.

Waste management is a wide field in terms of the range and scope of operational activities and their associated research requirements. The logistics of waste production, transport, treatment and disposal, legislation and regulation, are all established research areas. This research focuses on the utilisation of the waste product from marine oil spill incidents as one facet of waste management. Within the scope of managing the end of product of waste management, challenges facing the industry include pressure on disposal systems, increasing waste volumes, the environmental imperative and burgeoning legislation.

A factor that can contribute to the alleviation of such pressures is that of the utilisation of waste products as sources of fuel. The integration of energy demands and waste production is an established yet topical subject. The papers of Bebar L (2005), Chaya W (2006) and Murphy JD (2004) discuss options for the use of a range of waste products as fuel. It can be said that priority areas in some current political agendas are high crude oil prices, climate change, increasing public awareness and increasing waste volumes. Considering these factors, research into waste reduction and energy production from waste oil is timely. The benefits of waste as fuel include the potential to reduce waste volumes, the production of a profitable end product, a cleaner environment, reduction of energy costs and a reduced reliance on fossil fuels.

An area of limited research in terms of the integration of waste management, energy production and the environment was identified in marine oil spill response. The research considered the options for clean up of marine oil spills, the logistics of managing a response and the potential of the waste oil. The paper of Otay E 2000 identified the calorific value of waste oil from a spill incident (Otay E 2000). However, the utilisation of waste oil as fuel has been subject to relatively few research programmes. This was identified as an opportunity to integrate further the concepts of waste management and energy from a novel perspective. For the sake of the research in this thesis, waste oil from marine spill incidents is not considered to be a source of renewable fuel, more a value added stage in the logistic chain of waste management and oil spill response.

If the concept of implementing these technologies at operational level is considered, an issue that has challenged at all geographical and political levels is that of the transition from legislation and policy to functional implementation and operation (Jordan A 1998). One of the most cost effective and efficient tools for dissemination of technical and legislative material is education and training (Vastag G 1996). It can be argued that effective implementation at an operational level is a substantive aspect of environmental management. During the period of research, the author was personally responsible for the design, execution and reporting of selected components of research activity dedicated to dissemination and promulgation of waste management methodologies in support of current EC research programmes. This was achieved through design and delivery of education and training material specific to waste management, energy from waste and oil spill response in selected countries in the Far East. The skills acquired directly contributed to the development of the Distance Learning material in chapter five of the thesis. (Green J 2005, Green J 2006, Green J 2006 (1), Green J 2008, BiWaRE Handbook 2005, BIOREM Handbook 2006, SACODI Handbook 2007, http://www.protekt.hs-bremen.de (1))

1.2 Research aims and objectives

Aim One:

To establish the conceptual structure of the waste management and energy from waste industries.

Objectives:

- To establish current operational and technical concepts, and legislative structure of the waste management and energy from waste industries
- To provide the framework for the research into the management of oily waste

Aim Two:

To investigate the potential of waste oil-sorbent compounds from oil spill incidents as sources of fuel

Objectives:

- To quantify the percentage carbon in samples of oil and biodegradable sorbents.
- To compare data sets for data collected in laboratory conditions and *ex-situ* field trials.

Aim Three:

To examine the efficacy of a range of biodegradable sorbents commercially available for oil spill response

Objectives:

- To assess the efficacy of pixel analysis as a technique to quantify oil removal from a range of substrata after sorbent application.
- To quantify the success of oil spill sorbents using pixel analysis
- To use percentage recovery of sorbent as a technique with which to quantify the efficacy of a range of sorbents.

Aim Four:

To evaluate the role of DLM in the transfer of knowledge and expertise in the production and management of energy from oily waste.

Objectives:

- To investigate the validity of distance learning in disseminating information on waste management and energy from waste.
- To design and construct, deliver and appraise a Distance Learning Model in bioremediation of marine oil spills.

1.3 Structure of thesis

Chapter two presents and interprets the key concepts and framework of waste management and energy from waste; and progresses to a focus on oil spill management. The conceptual basis of waste and energy from waste are discussed and legislation and policy are deatailed as drivers for compliance. This leads to a section on marine oil spill incidents which includes key considerations in the delivery of an oil spill response program. This is followed by an overview of the impact of education and training in disseminating scientific and technical detail on waste and energy generation specific to oil. The chapter concludes by outlining the research pathway and detailing the research methodology.

Chapter three discusses the options for the clean up in marine oil spill response operations. Major spill incidents that have changed oil spill response practice are discussed prior to flagging the fate of oil in marine spills. The impacts of oil in the environment and the most effective mechanisms to manage spilled oil are examined followed by a focus on disposal of oily waste. The chapter concludes with a study into the implementation of bioremediation studies in Vietnam through education and training. The *Volgoneft 248* spill is discussed as an example of a spill incident where the calorific value of the waste oil was used as an indicator of response success.

Chapter four contains the laboratory and *ex-situ* field trials research. The research focused on the value of waste oil as fuel using pixel analysis to quantify the efficacy of sorbents. The chapter contains the concept of research, details of the materials and products used, the preliminary data collection and feasibility research, the methodology, results of the laboratory and field research, discussion and analysis, and conclusions and recommendations

Chapter five is a study into the role of education and training in disseminating scientific and technical material to specific target groups. The chapter begins with a brief introduction to the role of education and training. The core of the chapter is composed of a trialled example of a distance learning model developed and designed by the author on bioremediation of marine oil spills. The research into education and training was designed as a functional output of the research pathway and a synthesis of the research objectives.

Chapter six draws the research themes and primary data collection results and analysis together. The major conclusions of the research are flagged and discussed.

2 Chapter Two: Environmental Management and the Waste Stream

2.1 Introduction:

This chapter addresses the philosophical and conceptual structure of the thesis - the integration of oil spill response into waste management and energy production, as one facet of the environmental management process. Specifically, the research focuses on the disposal of associated residues of oil spills as one aspect of the 'cradle to grave' process of waste management.

This chapter is composed of the following sections: An introduction to the key concepts and framework of waste management and energy from waste; and a focus on oil spill management including the fate of oil in marine spills, environment specific response to incidents, and the disposal and wider use of oil spill waste. This is followed by an overview of the impact of education and training in disseminating scientific and technical detail on waste and energy generation specific to oil. The chapter concludes by outlining the research pathway and detailing the research methodology.

2.2 Waste Management and Energy from Waste:

The management of the waste stream is an international industry as demonstrated by the Basel Convention on Trans-boundary Movement of Hazardous Wastes and their Disposal (http://www.basel.int (4)). The Convention came about as a result of increasing amounts of waste, higher disposal costs, and tighter environmental regulations. These factors resulted in an increase in shipping vessels known as "toxic traders" transporting hazardous cargo to countries with less stringent legislation and cheaper disposal options.

Waste legislation is a driver for compliance and regulation through the development of protocols, selection of appropriate options and the adoption of best practices. Major initiatives on legislation and policy have established the framework within

which waste management needs to operate. The technical options to manage the waste stream are well established and include a diverse range of biological, chemical and physical treatment options. One option to alleviate the issue of growing waste amounts is the utilisation of waste as an energy source. It can be said that the combination of pressure on fossil fuel reserves and environmental concerns regarding carbon emissions have contributed to the development of options for utilising waste products as fuel. Advantages of this process include waste volume reduction, a positive energy yield and a profitable end product. The production of energy from waste incineration in compliance with EU standards may be considered in some cases to be a relatively low risk, environmentally benign method of recycling waste. It can lead to the recovery of 500 kWh_e per ton of waste (Porteous A 2005). In other examples, it may be considered to be extremely controversial in terms of emissions and overall impact. Research by Upreti B (2004) suggested that key issues regarding the location of energy from waste and in particular biomass power plants in the UK included: plant location, emissions, odour, public health and accidents (Upreti B 2004). There are a range of challenges, both legislative and technical, involved in exploiting the potential of energy from waste. In some Western countries, one driver for the utilisation of waste is the increasing pressure on disposal and storage systems (King AM 2005). In economies with less advanced waste management legislation, similar pressures may exist but the issue may be a lack of technology and enforcement of efficient disposal. (BiWaRE Handbook 2005).
The research considered the multi-disciplinary natures of waste management and energy from waste, this provided the structural context for justification into the research into energy generation from oil spill waste.

Oil spill waste was selected as a specialist area of research in order to examine both the use of waste oil and sorbents from spill incidents as fuel, and the role of distance learning in promulgating best practice. Oil is one of the driving forces behind world economic growth. It is used to power homes, businesses, industry and transport. Its influence can be emphasized by fluctuations in stock markets and the political instability in oil rich-countries affecting the price of crude oil on a daily basis (Hallcock JL 2004). In 2002, global consumption of oil was 75 million barrels a day, by 2010 even with moderate levels of development predicted, that is expected to rise to 90 million barrels per day (IPIECA 2002). There has been a recent drive to find alternative sources of fuel, due partly to concern over global oil supplies and also by an increasing concern over greenhouse gases, and the impact that the oil industry is having on global warming (Moore TG 2008). These factors have been exacerbated through the impact of the global recession and uncertainty regarding predicted recovery times. It can be argued that from the perspective of energy from waste generation, a long term perspective is required regarding global energy supply, demand and inherent security of fuel sources.

As the rate of oil consumption has increased, so has demand, and transportation rates have also shown volatility. 60% of the World's oil is transported by sea (Burgherr P 2007) and despite substantive transportation developments in the last twenty years, accidental spillages are still a threat. Statistics from ITOPF (The International Tanker Owner Pollution Federation) state that 1,138,000 tons of oil was spilled in recorded accidents worldwide in the 1990's. Figures for the current decade show that 192,000 tons have been spilled thus far (http://www.itopf.com (2)). In light of these statistics, the research acknowledged that as a percentage of the oil spilled into the sea *per annum*, the contribution of large scale spillage is small. It is estimated that 5% of the oil that enters the oceans every year comes from major spill incidents http://response.restoration.noaa.gov (1).

A significant role of the environmental management oil spills, regardless of the treatment techniques used, is the organisation of the disposal of oily waste. After the *Sea Empress* incident off Milford Haven, Wales in 1996, 20,000 tons of liquid waste and 11,000 tons of solid waste required disposal (Law RJ 2004). The techniques used were: landfill, stabilisation in asphalt, processing in oil refineries and land farming (Law RJ 2004). In terms of energy production, one occurrence of the calorific value of the waste oil being used as a benchmark of oil quality was found in the literature review (Otay E 2000). These factors suggest that there may be potential to derive energy from such incidents as shipping-related oil spills, however depending on the condition of the oil with regard to contaminants, pre-treatment may be required in order for it to suitable as fuel (Champ A 2003). Considering this factor, the laboratory and *ex-situ* field trials were designed to explore options and logistical requirements to assess the potential through a series of scaled-down incineration experiments quantifying carbon levels in waste oil and sorbent compounds. A key conceptual point to the philosophy of the research into energy from waste oil from marine spills is that it is not considered a source of renewable energy, rather a value added stage in the environmental management of the waste stream, energy production and the development of oil spill response.

If the concept of utilising the waste oil from spills as a source of energy is taken one step further, there is scope for expansion from the research in this thesis. Based on the results of the laboratory and *ex-situ* field trials, and the acknowledgement that in terms of global spill volumes, large scale marine incidents contribute a small percentage, the concepts and research could be expanded to include small scale industrial and other terrestrial spill incidents.

The delivery of education and training may be considered to be a core component in equipping the next generation of students and trainees with the tools and knowledge necessary to make the transition into the working environment. It is also essential in establishing and maintaining standards, implementing methodologies and developing practicable protocols at industry level. Within the range of education and training strategies, the effectiveness of distance learning as tool to disseminate knowledge, maintain standards and demonstrate best practice was examined through research-led delivery programmes. The range of delivery options in distance learning initiatives has become increasingly interactive and arguably more effective. Teaching and learning resources have benefited from the growth in e-learning (Newton R 2007). The importance and potential of education and training is demonstrated by its inclusion in a range of legislative initiatives and organisations, including: the IPPC Directive, EMAS, ISO 14001, Agenda 21, NOAA, the IMO and ITOPF.

Throughout the thesis, education is considered as a process with the capacity to improve technical or professional qualifications, develop further the abilities of participants, and to enrich knowledge and training in any formal, post-compulsory activity that develops knowledge, skills and attitude (http://www.unesco.org (1)). During the research, the role and implementation of education and training were examined as functional outputs of technical and scientific material through a series of education and training packages. In order to determine the most effective techniques with which to disseminate the material, pedagogy and the conceptual development of distance learning were studied within the literature review.

If the role of education and training in developing and implementing energy from waste strategies is considered, it is not contained in either of the EU Directives that are related to energy from waste (The Waste Incineration Directive, Directive on Renewable Energy: the Promotion of Electricity from Renewable Energy Sources). (http://europa.eu (8), http://europa.eu (6), http://eurlex.europa.eu (2), http://europa.eu (5), http://europa.eu (1)).

From a demand perspective, energy sources that reduce dependency on fossil fuels and contribute to emission reduction are attractive to industry and Governments (Asifa M 2007). The potential of energy from waste may be demonstrated by the fact that in 2006, 8% of the UK's municipal solid waste was processed in energy from waste generators, and the UK Government's Waste Strategy for England 2007 predicts that this level will increase to 25% by 2020. Energy from waste replaced the equivalent of 776,000 tons of oil in the UK in 2006. (http://www.esauk.org (1)).

Emissions from the incineration of waste include carbon dioxide, dioxins, antimony, lead, magnesium, chromium and cobalt (Porteous A 2001). However, their release into the environment is strictly managed by the Waste Incineration Directive (http://europa.eu (8)). The combination of fears over pollution and the 'NIMBY Syndrome' have led to opposition to the development of incinerators (Upreti B 2004). The issue of resistance to energy from waste technologies can be addressed by interactive communication, public participation, education through stakeholder involvement and training of personnel (Upreti B 2004). In order to achieve these objectives, education and training policies, and activities for a specific target audience can be utilised to increase knowledge through dissemination of information to local communities. The use of education and training as tools to facilitate use of energy from waste technologies was implemented in case studies coordinated and organized as part of the EU BiWaRE Project (BiWaRE Handbook 2005). During the period of research, the author was directly responsible for a range of distance learning models, and contributed to the design and implementation and delivery of workshops and training courses specific to energy from waste and renewable energy. (BiWaRE Handbook 2005, Green J 2005, Green J 2006, Green J 2006 (1)). The distance learning initiatives were designed to be delivered to students in higher education establishments, workers, professionals and industrial partners in Vietnam, India, Thailand and Cambodia. The workshops and training courses were designed to be delivered to industrial partners and professionals to increase their knowledge and awareness of technology options that may be appropriate for their companies.

The structure of the research pathway and methodology can be seen in figure 2 in section 2.7.

2.3 Policy and Legislation related to Waste Management

This section considers the major factors in the management of the waste stream, that is, the functional organization and understanding necessary to deliver effective treatment and disposal of waste to the highest standards of compliance and environmental quality. It is broken down into a summary of the core concepts of waste management and an overview of the legislative and regulatory control of waste management.

It is widely acknowledged that the key to effective waste management is a holistic approach to the chain of processes (Dijkema GPJ 2000). Individual stages cannot be interpreted or treated as autonomous entities but need to be addressed as one aspect of the environmental management process. In terms of integrating the disposal and utilisation of oil spill waste into waste management, key concepts and the legislative structure are provided to establish the boundaries within which oil spill waste can operate.

The management of waste is an inter-disciplinary industry is demonstrated by the existence of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes http://www.basel.int (3). Policy and legislation are key drivers for developing and implementing environmental management strategies, thus key pieces of legislation for waste management from International to National level were considered.

As a case study of implementing waste management policies and highlighting the potential for integrating waste management and energy policy, the UK perspective on energy from waste is flagged.

2.3.1 Definition of waste

The identification of one definition of waste that encompasses all relevant activities to be controlled and items that are considered as waste is not feasible. There are a range of perspectives from which the issue of defining waste is addressed. One approach is to define waste by developing a list of descriptions of activities or substances that fall within that definition. This includes descriptions of industrial pollutants and the concentrations of substances that are emitted in industrial processes. Potential issues with using this type of definition include having to constantly update lists of substances and advances in technology affecting substances or emissions. These issues are a necessary exercise to avoid exploitation of gaps in definitions (Cheyne I 1995). An alternative to this technique is to define by compliance with, or breach of, legislation. This can be demonstrated in the UK Environmental Protection Act 1990, whereby the definition of a statutory nuisance is dependent on the activity within, or the state of the premises in question, resulting in damage to health or constituting a nuisance (Cheyne I 1995).

A key theoretical component is separation of the concept of waste from the concept of pollution. It can be said that pollution is caused by waste, yet waste may not always lead to pollution. Considering this factor, the nature and definition of waste and waste management is affected by the cycle of waste management from waste formation, collection, transport, treatment and final disposal. Problems with waste will only occur if the inherent risk of the management process is inappropriately handled (Cheyne I 1995). For this research, the definition of waste in Article 1a of the Waste Framework Directive is used:

"waste" is "...any substance or object...which the holder discards or intends or is required to discard" http://eurlex.europa.eu (1).

2.3.2 International legislation

The Basel Convention is a global agreement, ratified by member states and the European Union for addressing the issues and challenges posed by hazardous waste. It provides assistance and guidelines on legal and technical issues, gathers statistical data, and conducts training on the appropriate management of hazardous waste http://www.basel.int (3). The key objectives of the convention are:

- To minimize the generation of hazardous wastes in terms of quantity and hazardousness.

- To dispose of them as close to the source of generation as feasible.

- To reduce the movement of hazardous wastes http://www.basel.int (1).

The Convention has been updated since its introduction in 1992 http://www.basel.int (4). Recent developments include the enhancement of information exchange, education and awareness-raising in all sectors of society and co-operation and partnership at all levels between countries, public authorities, international organizations, the industry sector, non-governmental organizations and academic institutions (Draft Strategic Plan for the Implementation of the Basel Convention 2002).

The Convention has aided the development of Regional Centres for Training and Technology Transfer as training and technology transfer are highlighted as policies that are particularly effective at implementing its objectives. Article 14 details the education and training requirements for signatories:

> *"The Parties agree that, according to the specific needs of different regions and subregions, regional or sub-regional centres for training and technology transfers regarding the management of hazardous wastes and other wastes and the minimization of their generation should be established."*

http://www.basel.int (2)

2.3.3 European Legislation

At a European perspective, there is one key directive on waste management and a number of more specific directives regarding specific waste types. Member states of the European Union are legally obliged to comply with all EU legislation.

The five European Directives that are relevant to waste management are:

- The Waste Disposal Directive
- The Hazardous Waste Directive
- The IPPC Directive

- The Landfill Directive
- The Waste Incineration Directive (discussed in Chapter Four)

(http://europa.eu (1), http://www.defra.gov.uk (3), http://ec.europa.eu (1), http://ec.europa.eu (2), http://europa.eu (3))

Table 1: Summary of EU waste legislation Directives.

Directive	Key considerations
Waste Disposal Directive	- Member states must prohibit abandonment, dumping or uncontrolled disposal of waste and promote waste prevention, recycling and reuse. - They must inform the Commission if rules give rise to technical difficulties and excessive disposal costs - The use of certain types of waste for energy production must be explored
Hazardous waste directive	- Provides provisions to control the movement of hazardous wastes - To provide a precise and uniform European-wide definition of hazardous waste and to ensure the correct management and regulation of such waste - Defines hazardous waste as wastes featuring on a list drawn up by the European Commission, because they possess one or more of the hazardous properties set out in the HWD
The IPPC Directive	- To minimise pollution from various industrial sources throughout the European Union - Operators of industrial installations covered by Annex I of the IPPC Directive are required to obtain a permit from the authorities in the EU countries. - Permits must take into account the whole environmental performance of the plant.
The Landfill Directive	- To prevent or reduce as far as possible negative effects on the environment from the landfilling of waste, during the whole life-cycle of the landfill - To reduce pollution of surface water, groundwater, soil and air, and on the global environment, including the greenhouse effect, as well as any resulting risk to human health

Sources: http://europa.eu (1), http://www.defra.gov.uk (3), http://ec.europa.eu (1), http://ec.europa.eu (2), http://europa.eu (3)

Table 1 summarises the key considerations and focus of each Directive. Key factors the Directives cover include: mechanisms for regulating the waste stream, the environmental impacts of waste and inappropriate handling and treatment of waste, and environmental management of waste.

2.3.4 UK legislation

The situation in the UK is included as a case study in order to examine the influence of international and European legislation at a national level. There are two perspectives to examine: (i) the extent to which international law affects policy at national level and (ii) the contribution of the UK to developing international environmental law and policy (Bell and McGillivray 2006). In the UK, international agreements are transposed into National Law through legislation. They create legal boundaries that bind the UK within its international obligations as opposed to enforcing regulations on individuals or businesses. Since the advent of the EU, the role of developing international law within the UK has been integrated into generic EU responses (Bell and McGillivray 2006).

The latest document to date published by the UK Government is the Waste Strategy 2007. It outlines a 'Waste Hierarchy' for treating waste products. The philosophy of the Waste Hierarchy is predominantly environmental but includes financial incentives through encouraging production with fewer natural resources and reducing the cost of treatment and disposal. The Hierarchy can be seen in Figure 1.

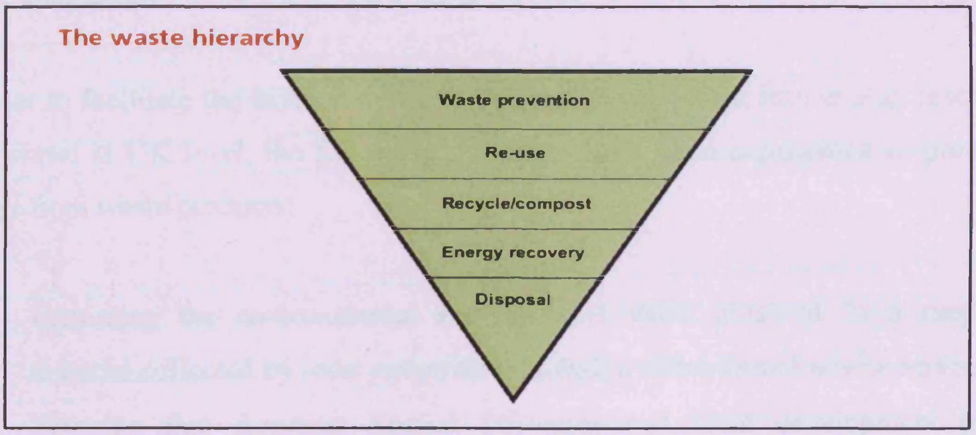


Figure 1: UK Waste Hierarchy
Source: Waste Strategy for England 2007

A key aspect of the Strategy is to promote the environment through increased recycling of resources and recovery of energy from residual waste using a range of technologies. An incentive has been developed to introduce enhanced capital allowances for investment involving the use of secondary recovered fuel (SRF) for combined heat and power facilities.

In terms of energy generation from waste, DEFRA (Department of Environment, Food and Rural Affairs) has identified a range of techniques for energy retrieval from waste. DEFRA considers the incineration of waste as a source of energy to be an integral aspect of waste management. Renewable energy and CHP (combined heat and power) are exempt from the Climate Change Levy and this boosts the financial feasibility of waste to energy schemes. The rationale behind CHP technology is that heat and power are produced from the same plant. Currently, around 30-50% of the input energy is converted into energy in a power plant; the remainder of the energy is lost as waste heat. If the waste heat can be utilised, it is possible that between 80 and 90% of the input energy could be harnessed and fuel bills could be cut by 40% (Waste Strategy 2000).
A further potential source of fuel for energy recovery from waste is a product that is derived from Municipal Solid Waste (MSW). Refuse derived fuel (RDF) is composed of MSW with recyclable and non combustible elements removed (http://www.defra.gov.uk (4)). It can be incinerated and the heat given off used to power generators.

In order to facilitate the extension of research and development into energy recovery from waste at UK level, the following initiatives have been highlighted to promote energy from waste products:

- Increasing the environmental and financial value obtained from recycled material collected by local authorities through a strengthened advice service,
- Ensuring that Regional Spatial Strategies and local development plans conform to national planning guidance on waste
- Improving procurement and investment by local authorities through comprehensive support and strengthened central and regional coordination

DEFRA have highlighted three possible techniques to harness energy from waste material.

(i) The use of individual waste streams directly as a fuel source,

(ii) To separate recyclables from existing waste streams. This can either be done a source or through some mechanical means, the residue is then incinerated and the resulting energy is sold to the National Grid.

(iii) To use a mechanical or biological treatment (MBT) to turn the waste product into Refuse Derived Fuel (RDF).

If these factors are considered regarding the integration of oil spill waste as fuel, it can be stated that incineration is one of the conventional techniques for disposing of waste oil (Boopathy R 2000). If an energy yield can be harvested from the incineration process, space in landfill sites can be freed for other waste.

It is estimated that 30,000 tons of oil was recovered from Welsh beaches after *Sea Empress* ran aground in 1996 (Law RJ 2004). The oil was dispersed through wave action and the addition of chemical dispersant agents to the shore. Laboratory tests showed that the presence of water in an emulsion did not affect the oil's ability to dry out or combust (see Chapter Six). Statistics for the UK show that there were 5049 incidents of oil spills from offshore installations in 2005, and 664 incidents from discharges attributed to vessels and offshore oil and gas installations in 2004. These figures suggest there is a 'supply' of waste oil from spillages that could be utilised as fuel (http://www.defra.gov.uk (5)).

As compliance with legislation and conformance with policy objectives tend to drive management response, their framework is fundamental to the way in which the industry has developed. Environmental law operates at a range of geographical levels: national, European and international. International environmental law predominantly functions to negotiate a combined response to the threat of international environmental issues. European law is more specific and aims at achieving common standards among member states. National laws are the most specific and outline specific functions in order that countries comply with both European and international standards (Bell S 2006).

2.4 Policy and Legislation related to Energy from Waste

Having flagged key themes and the legislative structure of waste management, this section focuses on deriving energy from the disposal of waste, Core concepts and the legislative structure are considered.

If the waste and energy industries are considered from the perspective of supply and demand, it is acknowledged that crude oil is not a feasible long term solution to our energy needs (Tjernström E 2008). It is an inevitability that the world's largest oil users will look to alternative sources of energy in the future (Salameh M 2003). A further issue that has arisen is the potential impact of carbon emissions on climate change (Tjernström E 2008, Thuiller W 2008) The emissions of greenhouse gases in the last half century have increased four fold (http://www.dti.gov.uk (1)) and carbon emissions have been identified as a significant contributor to this. It is estimated that currently fossil fuels are providing 80% of the worlds energy needs, this factor, combined with the fact that global economic output doubles every 30 years, provides strong evidence for expansion into other fuel sources (Asifa M 2007). Research illustrates that the global consumption of energy is expected to rise by 57% between 2002 and 2025, if fossil fuels continue to be used at their current rate, the reserves of North America, Europe and Eurasia, and Asia-Pacific are predicted to disappear in 10, 57 and 40 years respectively (Asifa M 2007).

The challenge is twofold, to reduce and regulate carbon emissions while providing a secure supply of energy to match increasing global demand. Current research on stabilisation of emissions is divided; the paper of Green C (2006) suggests that the largest issue facing the energy climate issue is whether technology exists to facilitate stabilisation of emissions. While Metz *et al*, (2001), O'Neill *et al*, (2003) and Swart *et al*, (2003) propose that the stabilisation of emissions can be achieved at a relatively low cost and that the major barriers are socio-economic and institutional. However, the current generation of academics and professionals view the issue of emission reduction, the incineration of waste as a fuel source and the introduction of waste oil from spill incidents, can contribute to reducing pressure on landfill sites and ease dependence on fossil fuels.

The integration of waste management into the energy industry has developed due to two factors. (i) The increasing demand for energy and concerns over the impact of carbon emissions on climate change. (ii) The increasing volumes of waste being produced and associated issues with disposal. In the UK, municipal waste volumes are increasing by 3-4% *per annum* and total volumes are predicted to double by 2020 (Bulkeley H 2005). Traditionally, landfill has been the dominant option. However, the decline of new sites due to fewer 'extractive' industries operating, combined with the fact that regulations governing landfill operations have tightened, have reduced its feasibility (Bulkeley H 2005). The EU Landfill Directive states that the volume of municipal waste sent to landfill is to be reduced to 75% of the 1995 level produced by 2010, 50% by 2013, and by 35% by 2020 (Bulkeley H 2005). These statistics, together with a review of technology undertaken in the initial phase of the research provided a section of the justification framework of the author's research into energy from oil spill waste.

2.4.1 International Legislation

With regard to International legislation, the Kyoto Protocol is one of the highest profile global commitments to climate change and reduction of greenhouse gas emissions. The Protocol was developed at the UN Framework Convention on Climate Change at the Earth Summit in Rio de Janeiro in 1992. It was formally agreed five years later and commits developing countries to reduce greenhouse gases to below 1990 levels by between 2008 and 2012 (http://www.dti.gov.uk (1)). Data from the International Energy Agency (IEA) shows that between 1990 and 2003, the world's emissions of greenhouse gases increased by 20% and the world economy grew by 49%. This shows a reduction of energy consumption relative to economic growth but the IEA have estimated that 85% of the worlds energy needs over the next 25 years will be provided by fossil fuels. This will lead to an increase in the amount of carbon in the atmosphere through emissions of 60% (http://www.dti.gov.uk (1)). A potential solution to alleviating this issue is exploring alternative sources of fuel, in particular, renewable sources that have a low 'carbon footprint'.

2.4.2 European legislation

The first landmark document detailing the EU commitment to renewable energy was the White Paper for a Community Strategy and Action Plan in 1997. White Papers are not legislatively binding but contain proposals for action in a specific area. A substantive driver for this was environmental concern over fossil fuel consumption (http://ec.europa.eu (5)). A target of 12% of gross inland energy consumption from renewable energy sources was set to be achieved by 2010, of which electricity would represent 22.1%. With the 2004 expansion of commitments to renewable energy sources, the EU's target became 21% (http://ec.europa.eu (5)). The White Paper highlights the necessity for change at a global level to reduce greenhouse gas emissions and warns of environmental consequences in the future if levels are not reduced. It highlights a range of issues with energy production that require regulation including spills, waste, noise, amenity damage and atmospheric pollution from emissions (http://ec.europa.eu (5)).

There is no specific piece of legislation at European level focused on developing energy from waste sources. The two policy areas of EU law that relate to energy from waste are waste incineration and renewable energy.

Table 2: EU waste management Directives

Act	Scope	Targets
The Waste Incineration Directive	- To prevent or reduce pollution of air, water or soil resulting from the incineration of waste - Covers 'co-incineration' plants designed to produce energy or material products using waste as core or additional fuel - Not specific to energy generation from waste, does not cover all wastes that are incinerated - No legal requirement to utilise the resulting heat as energy - Heat generated from the incineration process must be put to good use as far as possible	By 31 December 2008, the Commission must report on the application of the Directive, progress achieved in emission control and with waste management. Other reports on the implementation of the Directive will also be produced.
Renewable energy: the promotion of electricity	- Constitutes an essential part of the package of measures needed to comply with the commitments made by the EU under the Kyoto Protocol on the reduction of greenhouse gas emissions.	- All Member States should be required to set national targets for the consumption of electricity produced from

from renewable energy sources.	- Includes electricity produced from wind, solar, geothermal, wave, tidal, hydroelectric, biomass, landfill gas, sewage treatment gas and biogas - National targets for the proportion of electricity produced from renewable sources in each Member State as part of an overall objective of 20% for the EU.	renewable sources - The Member States must publish every five years, a report setting targets for future renewable energy consumption for the following ten years and showing what measures have or are to be taken to meet those targets

Sources: http://europa.eu (7), http://europa.eu (6), http://eurlex.europa.eu (2), http://europa.eu (5), http://europa.eu (1)

Table 2 provides a structural outline of the Waste Incineration Directive and EU renewable energy policy. The Waste Incineration Directive was implemented in 2000 and was the first piece of European legislation that covered the use of co-incineration plants. (http://europa.eu (1)) The regulation of co-incineration facilities included monitoring of the amount of hazardous and non-hazardous waste being incinerated, the plants capacity and monitoring of performance. Although it is not legally binding to utilise the heat from the incineration process as fuel, the Directive states that the heat must be put to as good a use as feasible (http://europa.eu (1)). The renewable energy legislation highlights the use of biomass, landfill gas and biogas as options for facilitating member states renewable obligations. Members are obliged by EU law to set targets and develop action plans to increase the use and scope of renewable energy technologies. Biomass currently accounts for between 44 and 65% of renewable energy used in the EU. It currently meets 4% of the EU's energy needs, equivalent to 69 million tonnes of oil, and the EU has set a target of increasing this to 150 million tonnes by 2010. It is estimated that an increase of this magnitude could reduce greenhouse gas emission *per annum* by 209 million tonnes.

2.5 Marine oil spills

Having examined key concepts and the legislative background to the waste management industry and energy from waste, this section provides contextual background to the oil spill response industry and considers the existing framework within which waste oil from marine spill incidents may be used as fuel. Key considerations include: the fate of oil in marine spill incidents, environment specific response to oil spills, disposal of oil spill debris and the use of oil spill waste.

The fate of oil in terms of its physical form and the environments it is deposited in, in the wake of a spill incident, are critical factors that affect every stage of the response operation. It can be said that the techniques, timeframes and efficacy of spill response operation are fundamentally affected by the volume and physical form of the oil. There are a diverse range of factors that can affect the fate and distribution of oil once spilled, these include: the volume and type of oil, geography, geomorphology, hydrography, hydrodynamics, prevailing meteorological conditions, and the chemical and physical processes that the oil undergoes when spilled. Typically, the logistics of an oil spill response operation will be determined by how these factors have affected the nature and distribution of the spilled oil.

If the physical nature of the oil is considered, the extent to which it is emulsified and weathered affect factors including: its persistence in the environment, its ability to spread, its behaviour when it is washed onto shore and the type of equipment required to remove it. In terms of gaining this information prior to implementing an appropriate spill response, a range of information can be collated and analysed. This includes information regarding the type and volume of oil spilled which provides information on the likely state of the oil once it has grounded and the extent to which it will spread. The sea state at the time of the incident can be used to estimate the extent to which the oil has spread and become emulsified. Satellite tracking is used as a tool to monitor and predict spill movement and the likely timing and location of beaching. If this information is combined with site specific data on predicted oil beaching sites including substrate, exposure and sensitivity; a timely and appropriate response can be formulated and implemented.

If the concept of taking environment specific response to an oil spill incident is taken further, there are a range of factors both conceptually and practically that have changed within the industry. If the conceptual development of response technology over time is considered, the case studies of the *Torrey Canyon, Exxon Valdez* and *Braer* each had substantive impacts in either the development of technology or legislative and regulatory controls. In the case of *Torrey Canyon* the use of toxic dispersants to break down beached oil was reviewed and the legal and legislative boundaries of fault and blame for spill incidents were developed. The impact of the *Exxon Valdez* led to the Government of the United States developing OPA90 which phased out the use of single hulled tankers in American waters over a set time period. Lord Donaldson's report in the wake of the *Braer* incident reviewed procedures regarding the reporting of vessels in difficulty and designing a response operation specific to the circumstances of the spill.

The advancement of science, technology and our understanding of the impacts of oil in the environment have led to a more diverse range of procedures and products being made available to respond to oil spills. This includes a higher variety of options and more effective technology. This has been combined with tighter legislative requirements regarding pollution prevention and waste minimisation and treatment.

Considering these factors, oil spill response strategies focus on selecting the most appropriate strategy from environmental and economic perspective to remove the oil. Factors including oil persistence, oil volume, site accessibility, site sensitivity and the size of area affected are considered. Two theories have been developed to formalise appropriate responses, Net Environmental Benefit Analysis (NEBA) and Time Windows of Response are discussed in more detail in chapter three of the thesis.

It can be said that a critical stage in the efficacy of an oil spill response operation is effective containment, removal and treatment of the spilled oil. A critical stage of the research pathway into determining whether waste oil from spill incidents is suitable as fuel was to examine current options and procedures for waste oil removal and treatment. If the logistic chain of waste oil removal, treatment and disposal is considered there are two core factors. The initial collection of oil and storage on-site, and the decision making process required to determine how the waste is treated and disposed. If the on-site removal and storage is considered, key factors include maximising the efficiency of oil collection to minimise the volume of contaminants collected, oil and contaminant segregation on-site and effective containment of waste oil. The decision making process to determine the most appropriate technique with which to dispose of the oil depends on available technology, the physical form and volume of the oil and the options for oil transportation. If this process is taken one step further, oil spill waste can be used in a variety of ways that can reduce the volume of the waste product and in some cases end in a financial; gain. The possible further use of oil spill waste largely depends on its physical form, this is particularly applicable to using it as fuel as the more pre-treatment that is required on a fuel source the more expensive the process is and the fewer facilities exist to refine it.

These options are all discussed further in chapter three of the thesis.

2.6 The role of education and training

Having discussed the conceptual background to the thesis and outlined core concepts in waste management, energy from waste generation and the oil spill response industry, this section of the chapter focuses on the application of education and training in disseminating environmental policy, best practise and delivery from the legislative and policy level to functional delivery and implementation.

The research into education and training in improving environmental performance is a functional output of the research pathway and a synthesis of the integration of waste management, energy from waste and a focus on marine oil spills. In chapter five of the thesis, a DLM on oil spill bioremediation developed for the thesis is examined. It's structure and delivery was informed by Distance Learning strategies in waste management, renewable energy and oil spill response developed by the author and delivered in Vietnam/India and Thailand. The research in Vietnam/India and Thailand provided the opportunity to design, develop, implement and review a series of education and training packages. These were used to 'ground truth' the efficacy of education and training as mechanisms to disseminate scientific and technical material, and inform the development of the distance learning model on bioremediation. The techniques developed as an output of this research have the potential to be used to disseminate and educate personnel regarding the use of waste oil as fuel.

In the fields of waste management and oil spill response, education and training strategies are designed to inform and improve the decision making process through dissemination of information and facilitation of communication. The benefits of dissemination of data and education and training are value added in as much that they can:

- Act as a catalyst for further action.
- Raise awareness of key issues.
- Assist continuity of activities and the adoption of best practice.
- Disseminate the importance of concepts, tools and methodologies to a wider audience.
- Encourage the development of local or internal capacity and competence to continue and enhance further objectives of the taught material.
- Demonstrate commitment and progress where evidence of performance is intrinsic to funding and support.
- Recruit support and resources to sustain the activity for the future.
- Maintain ongoing interest and support in projects.

(PROTEKT Handbook 2007, SACODI Handbook 2007)

For these concepts to be effectively implemented through distance learning, a range of factors including the following need to be considered: the stated target audience, course duration and delivery mechanisms, student support infrastructure, the range and scope of assessments and resource availability. (Sherry L 1996, ACSB 1999).

In terms of the benefits and cautions associated with distance learning, they are stated in Table 3:

Table 3: Benefits and cautions of DL

Benefits	Cautions
- Fees for training, conferences, seminars and consultants can be reduced by DL. - DL enables organisations to cross borders, cut costs and share knowledge - Provide businesses the opportunity to keep employees up to date - Students can study at their own pace	- Cost effectiveness. The creation and operation of networks to maintain DL must be funded - There is a risk of students falling behind with reduced tutor contact - Potential student social isolation - Technical problems can delay progress - Quality of instruction

- Employers gain from increased knowledge and understanding of employees without releasing them for long periods - DL can be integrated within an organisation - Location is not an issue	

Sources: Harper KC 2004, Barratt RS 2006, Cook DA 2007, Valentine D 2002

The role of education and training is implicit in ongoing environmental management. Organisations and companies maintain ongoing training and improvement in environmental performance to meet policy and legislative requirements and further professional development (Barratt R 2006). Evidence of the application, role and efficacy of distance learning can be demonstrated by its inclusion in internationally recognised environmental management systems and legislation.

The IPPC (Integrated Pollution Prevention and Control) Directive 1996 is a piece of European legislation regarding minimising waste from point sources (http://ec.europa.eu (4)). Under the IPPC, operators will apply standards to ISO 14001 or EMAS (the EC's Eco-Management or Audit Scheme) standards. They both require that the management system provides a commitment to ongoing improvement in environmental performance (DEFRA (3rd ed.), 2004). Other commitments to education and training found within EMAS include organisations acknowledging the need for staff information and training on environmental issues. It flags that staff directly involved in environmental performance should be provided with an upgraded level of environmental qualifications (Official Journal of the European Communities L 247/1 2001).

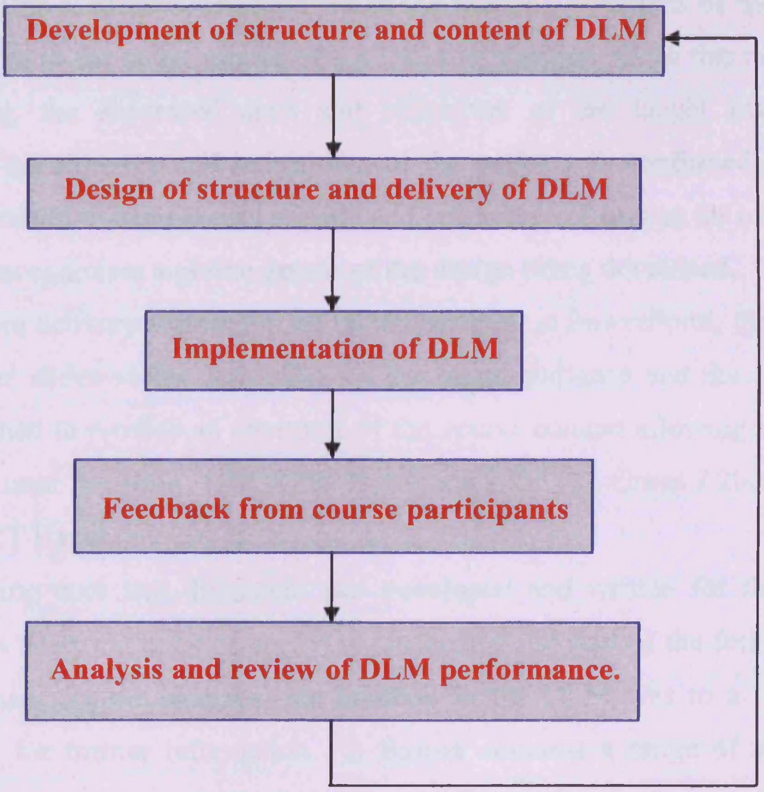
Education and training is further included in Agenda 21, a UN initiative dedicated to political commitment in development and environmental cooperation. There is an emphasis on public participation and the active involvement of the non-governmental organizations (http://www.unep.org (1)). Agenda 21 is spilt into chapters of which number 36 is titled 'Promoting education, public awareness and training' (http://www.unep.org (1)).

What originated as a fundamentally formal education tool has expanded into an intrinsic aspect of progressive environmental management. Maintenance of standards and protocol, compliance with legislation and policy and ongoing development of environmental performance can all be supplemented and maintained by the integration of education and training initiatives. They can be applied from grassroots level at schools and in HE to management and industry level research.

2.6.1 Development and delivery of DLM's

This section provides a summary of the development, design, implementation and feedback for the distance learning material developed to analyse the efficacy of DL strategies for the research pathway of the thesis (Green J 2006, Green J 2005, Green J 2006 (2), Green J 2008, BIOREM Handbook 2006, and SACODI Handbook 2007). The process of constructing a DLM from conceptual development to review and critical analysis is a cyclical process where feedback is fed into ongoing review and development.

Table 4: DLM structure



The development of the DLM in bioremediation of marine oil spills:

- Identification of material to populate DLM and target groups

- Development of aims and objectives
- Identification of learning outcomes
- Structure and format of taught material

The first stage is sourcing the material with which to populate the package and identification of target groups. During this process the nature, format and extent of available material is analysed and considered for inclusion in the taught material. The DLM on bioremediation was populated from sources including: technical and scientific reports, the literature review for this thesis, independent internet research and scientific journals. Identification of the target audience is necessary at this stage as it affects balance of technical, scientific and case study material and aims, objectives and learning outcomes. The target audience for the DLM includes local authorities, port and harbour personnel, oil companies and regional government.

The information selected to populate the DLM is then divided into modules, sections and chapters. This facilitates development of the learning outcomes of the material which are tailored to the target groups of the DLM in question. Once this process has been completed, the expressed aims and objectives of the taught material are developed and the structure and breakdown of the package is confirmed. The full proposal is submitted to independent experts and academic colleagues for review prior to the assessment exercises and fine details of the design being developed. In terms of delivery, the core delivery format for the taught material is PowerPoint, the extent of the detail on the slides varies depending on the target audience and the tutor. The slides are designed to provide an overview of the course content allowing students to scribe what the tutor is saying. (BIOREM Handbook 2006 (1), Green J 2006, Green J 2008, PROTEKT Handbook 2007).

An accompanying core text document was developed and written for the training package. It was designed to be presented to students at the start of the full DLM as a working document for the lectures. Its function in the DLM was to act as a first reference point for further information. It further contains a range of assessment exercises that are found at the beginning and end of each chapter that are designed to test student's knowledge, understanding and ability to analyze the information they are taught. Learning outcomes and self assessment questions are designed to reinforce understanding and knowledge of key concepts and summary and suggestions and tutor marked assessments are designed to test students ability to analyse and interpret what they have learned.

As the full DLM is designed to be taught remotely, a support system was designed for the staff delivering the content and the course participants. Staff notes were developed and designed to support the staff in the delivery of the course. They include information such as which equipment to use and sources of additional information to adapting the content for different target audiences. Student notes were provided to accompany the lecture and to elaborate on each part of the taught course.

2.7 Methodologies

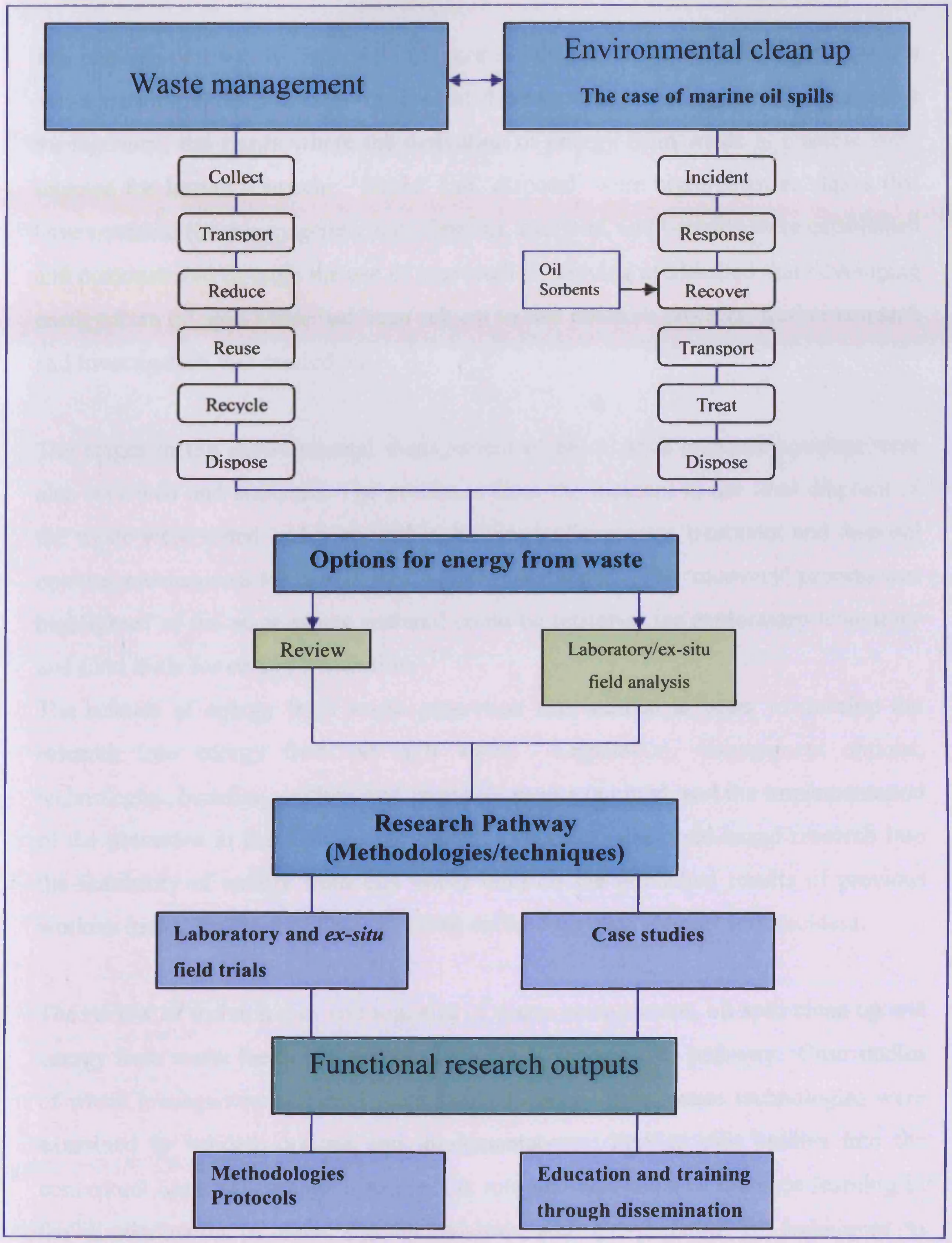


Figure 2: Research pathway

2.7.1 Research methodology

The research pathway is displayed in Figure 2. The principles of, and stages in, waste management and oil spill clean up are stated. From within the logistic chain of waste management, the stages where the derivation of energy from waste is feasible were selected for further research. 'Reuse' and 'disposal' were highlighted as stages that have potential for energy generation. Options, cautions, and benefits were established and demonstrated through the use of case studies. Having established that developing energy from oil spill waste had been subject to few research projects, further research and investigation was carried out.

The stages in the environmental management of an oil spill response incident were also reviewed and analysed. The processes from the incident to the final disposal of the waste were stated and from within the range of recovery, treatment and disposal options, mechanisms for energy derivation were flagged. The 'recovery' process was highlighted as the stage where material could be retrieved for exploratory laboratory and field trials for energy generation.

The science of energy from waste generation was studied in order to develop the research into energy from oil spill waste. Legislation, management options, technologies, benefits, cautions and protocols were examined, and the implementation of the processes in the field was reviewed. Laboratory and field-based research into the feasibility of energy from oily waste built on the published results of previous workers including those of Otay E (2000) on the *Volgoneft 248* oil spill incident.

The review of technologies and logistics of waste management, oil spill clean up and energy from waste facilitated the development of the research pathway. Case studies of waste management, oil spill response and energy from waste technologies were examined to validate options and implementation. Further case studies into the conceptual basis of distance learning, the role and relevance of distance learning in the dissemination of data, and the analysis and interpretation of techniques to implement distance learning were studied.

A series of laboratory tests and *ex-situ* field trials were specifically designed to evaluate the carbon content of a range of compounds of commercially available oil spill sorbents and oil. Carbon was recorded as a quantifiable measure of the compounds ability to ignite and thus be used as fuel. The oils that were selected exhibited different properties in terms of their behaviour, viscosity and composition. In the course of the review of literature, the role and use of image pixel analysis was identified as an analytical technique with which to monitor environmental performance. The papers of Lee JH 2005 and Pettorelli N 2005 discuss the role of pixel analysis in environmental monitoring. It was considered that the technique could provide a quantitative data set for the efficacy of shoreline response techniques in the wake of an oil spill incident (Lee JH 2005, Pettorelli N 2005). The research pathway identified that the sole use of image analysis in oil spill response to date was satellite tracking of oil at sea (Kozai K 2003).

The data from the laboratory and *ex-situ* field trials, and the delivery and review of the education and training packages form the functional research outputs of the thesis. Throughout the duration of the research a series of Distance Learning Modules, workshops and training courses were delivered to communities, industrial partners and academic colleagues. Post delivery, the packages were reviewed and critically appraised from scientific, technical and pedagogic perspectives prior to the development of the next project. This process informed the research contained in the thesis on distance learning. The data from the laboratory and *ex-situ* field trials consisted of a series of Scanning Electron Microscope (SEM) images of the sorbents before and after oiling. Time lapse photographs taken at pre-determined points through the oil recovery operation, and a comparison of three pixel distribution images in unpolluted, polluted and cleaned states were analysed as part of the programme. The relationships between the various pixel distributions provided a quantitative indicator of sorbent performance and environmental recovery. An extension to the data set was incorporated into the analysis through weighing the quantity of oil and sorbent before and after application. This gave a further quantitative data set regarding the performance of the sorbent. The relative successes of combinations of oils and sorbents, in terms of proportion of oil removed, are discussed through their percentage recovery results. Table 5 summarises the data sets.

Table 5: Outputs of laboratory and *ex-situ* field trial research

Research stage	Outputs
Preliminary research	A review of sorbent application, scope and role in oil spill response.
	An investigation into the range of options of image and pixel analysis.
Core research	Scanning Electron Microscope (SEM) imagery of sorbents pre and post oiling.
	Laboratory trials of products and procedures prior to data collection.
	Data collection in the laboratory and Southampton.
Analysis and interpretation	Critical review and analysis of results and procedure. Statistical analysis and discussion.

2.7.2 Evaluation of implementation

The application of case studies to the science of oil spill response and energy from waste enabled critical analysis and review of best practise and performance. Selected data and case studies were extracted, analysed and interpreted from a series of technical reports to which this research programme contributed (BIOREM Handbook 2006 (1), PROTEKT Handbook 2007, SACODI Handbook 2007). Substantive outputs from the material in the technical reports were the workshops, training packages and DLM's. The expertise acquired in their development was used to develop a DLM for bioremediation of marine oil spills.

The review of literature provided a further range of case studies that were analysed, interpreted and integrated throughout the thesis. The case studies ranged from local and regional, to national, European and International. Issues related to, legislation, policy, environment, socio-economic aspects and industrial technology were considered. The case studies were used to illustrate and investigate the options and challenges to the implementation of policy and legislation, to demonstrate the efficacy of techniques in the field, and to examine commercial performance.

2.8 Conclusion

This chapter has detailed a brief introduction to the field of the research and flagged the conceptual background of the research in this thesis. The over-riding concepts of waste management and energy from waste have been discussed to provide a framework for the substantive output of the thesis - an investigation into the integration of oil spill response into waste management and energy production. The substantive outputs of the research are: laboratory and *ex-situ* field analysis to quantify the potential of waste oil from marine spill incidents to be used as fuel, to examine the efficacy of pixel analysis as a tool to quantify the efficacy of oil spill sorbents and research the impact of education and training in marine oil spill research using bioremediation as a working case study.

The next chapter of the thesis provides a detailed examination of the management of marine oil spills, treatment techniques used and a series of case studies specifically selected to support the research pathway.

3 Chapter Three: Oil spill management

3.1 Introduction

An area of limited research in terms of the integration of waste management, energy production and the environment was identified in the management of marine oil spills. This chapter examines the link between the management and disposal of oily waste from spill incidents and options for utilising oil spill waste. The following concepts are stated and reviewed: oil spill incidents that have changed the science and implementation of oil spill response, the fate and impact of oil in the environment, and environment - specific response to oil spill incidents. The potential use of a range of waste oils as fuel is established (Bebar L 2002) and the contextual background of energy from waste generation has been stated and reviewed in chapter two of the thesis. Bioremediation in Vietnam is evaluated as a case study of appropriate responses to a spill incorporating socio-economic and environmental factors. The chapter concludes by reviewing and analysing the energy potential in waste oil and evaluating a case study where the calorific value of the waste oil was quantified.

The structure of oil spill response procedures and implementation is established, tried and tested. However, restricted dissemination and availability of data can affect effective management and implementation (Kirkland LH 1999). It may be considered that the following factors affect oil spill response management:

- Lack of studies, examples and explanations of EMS implementation.
- Lack of technical data for options and management.
- Lack of skills and knowledge.
- Application of inappropriate solutions.
- Multiple stakeholders with conflicting interests
- Reactive as opposed to proactive environmental policy.

(Kirkland LH 1999)

An option to increase knowledge and awareness, and to facilitate effective management is education and training of personnel (Vastag G 1996). Concepts including proactive policy towards environmental issues and communication between stakeholders can be introduced into training schemes as core skills to be incorporated into management.

The successful management of the response to an oil spill incident relies on an accessible technical and scientific body of knowledge, comprehensive response structures, appropriately trained personnel, coordinated management, effective communications and the ability to adapt to changing situations and circumstances. For the sake of this research, oil spill response was selected as a field where education and training can enhance strategies for clean up. Within oil spill response, there is scope for training and information dissemination regarding oil type, behaviour and impact, environmental variables, options for containment and recovery and implementation of policy. An essential aspect of education and training is working within a framework of knowledge, protocol and implementation. Regarding oil spill incidents, a typical response operation can be broken down into the following stages:

- The management of the response from initial deployment of personnel to post recovery analysis of objectives and performance.
- Identification, maintaining and managing, recovery, transportation, treatment and disposal of waste.
- Environmental and economic targets of the response operation.
- The timing of field operations.
- An understanding of the complex terrestrial, coastal and marine conditions that can impact the geographical footprint of the spill, the spread and behaviour of the oil, oil persistence in the environment and the logistics of clean up.

Vietnam was selected as a case study to evaluate the role of bioremediation in a country with a relatively undeveloped oil spill response system. This provided an opportunity to examine the impact of developing oil spill response protocol through education and training in a society with limited prior experience of either. The objectives of the research in Vietnam were to develop a set of scientific and technical

Guidelines on bioremediation of oil spills in Vietnam and to design, construct and deliver a series of education and training packages on bioremediation to Vietnamese personnel.

3.2 Case histories

As a percentage of the oil spilled into the sea *per annum*, the contribution of large scale spillage is small. It is estimated that 5% of the oil that enters the oceans every year comes from major spill incidents http://response.restoration.noaa.gov (1). In the last 50 years, there have been a number of large scale oil spills that have received widespread media coverage including: *Amoco Cadiz, Prestige, Exxon Valdez, Sea Empress* and *Braer.* It can be said that this attention to the industry has contributed to further research and develop the techniques used to remove oil from the environment (Kim I 2002). A high profile example of this is the pressure that was exerted on the US Government post-*Exxon Valdez*, to only permit double hulled vessels into US waters (Kim I 2002). In order to evaluate the suitability of response procedures to a given environment and the potential of energy recovery from the resulting waste, it was necessary to examine selected spills to investigate the manner in which their responses were managed. Three high profile spills that led to a shift in regulation and management of tankers, and response to oil spills were *Torrey Canyon, Exxon Valdez* and *Braer.*

3.2.1 *Torrey Canyon*

Torrey Canyon ran aground on Seven Stones Reef, off Cornwall, UK on 18 March 1967 (Figure 3). The vessel's tanks ruptured on impact and in the following 12 days the full cargo of 119,000 tonnes of Kuwait crude oil was spilled (http://www.itopf.com (1)). One of the features of the *Torrey Canyon* incident that places it above other similar incidents in terms of severity, was the use of first generation dispersants that were more toxic to sessile marine flora and fauna than the oil. In total, 22,500 gallons were applied to the oiled shores per day and the sandy beaches were ploughed up with bulldozers prior to application of the dispersant (O'Sullivan A 1967). Laboratory experiments conducted after *Torrey Canyon* showed that the concentration required to kill 50% of intertidal organisms in 24 hours of exposure was between 5 and 100 ppm (parts-per-million) with limpets in the genus *Patella* being particularly vulnerable. These lethal concentrations are lower than those needed to disperse oil. As a consequence, communities of flora and fauna disappeared in areas of the shore that were subject to dispersant spraying (http://www.ukmarinesac.org.uk (1)). Due to an unsuccessful salvage operation on the tanker and worsening weather, the decision was taken to bomb the hull to burn the remaining 19,000 tons of oil on board. In total, 160 1,000lb bombs were dropped, 11,000 gallons of kerosene, 2000 gallons of napalm and 16 rockets were dropped on the tanker. *Torrey Canyon* eventually sank in heavy seas (Burrows P 1974).

Figure 3: *Torrey Canyon*
Source: http://www.livingmemory.org.uk (1)

In the wake of the response to the *Torrey Canyon* incident, the legal and legislative boundaries of whom to blame for such an incident were raised. An *ad-hoc* committee was established to manage the impacts of the incident and it became a permanent role of the IMO (International Maritime Organisation) thereafter. In 1969, a conference held by the IMO adopted a convention regarding the civil liability of the ship or cargo for damage caused by a pollution incident. It was designed to ensure compensation was paid to victims and the liability placed on the ship owner (http://www.imo.org (2)). Two further conferences in 1973 (The International Convention for the Prevention of Pollution from Ships) and 1978 (Tanker Safety and Pollution Prevention) led to the International Convention for the Prevention of Marine Pollution from Ships (MARPOL), 1973 as modified by the Protocol of 1978, which entered into force on 2 October 1983 (http://www.imo.org (4)).

Table 6 has further details on the implications of the post spill committee meetings.

Figure 4: ***Torrey Canyon*** **post bombing**
Source: http://www.axfordsabode.org.uk (1)

3.2.2 *Exxon Valdez*

Exxon Valdez grounded on Bligh Reef, Prince William Sound, Alaska on the 24th March 1989. 37,000 tons of Alaska North Slope Crude Oil spilled into Prince William Sound (Figure 5). In terms of volume, the incident was 35th on the list of major oil spills since 1967 (http://www.itopf.com (8)). However, the fragility of the environment in which the oil was spilled, and the impacts on flora and fauna, raised its profile above other spills of a greater volume (Paine RT 1996, http://www.itopf.com (4)). The strategies implemented in the wake of *Exxon Valdez* were as follows:

- Booms deployed to prevent oil contaminating salmon fisheries.
- Fishing banned in areas affected by oil.

- Oiled birds and mammals were removed and brought to rehabilitation centres for clean up.
- 1500 vessels involved in assessment, clean up, wildlife rescue and logistics.
- 12,000 people removed oil from beaches.
- 500km of shoreline in Prince William Sound sprayed at high pressure with heated sea water.
- 110km of shoreline were treated with fertiliser to stimulate biodegradation. (Paine RT 1996).

The combined efforts of all the strategies removed between 10 and 14% of the total oil spilled (Paine RT 1996). The clean up required 40 times that much oil to operate the boats and equipment. Burning was not deemed an option due to the volatile components of the oil evaporating and the risk of disrupting local communities. It is estimated that up to 50% of the oil could have been burned with no danger to the vessel (Paine RT 1996). Exxon paid post-spill costs of $2300 million to fishermen and cleanup workers and reached an out-of-court settlement with Federal and State officials to pay $900 million more over 10 years to "restore the resources injured by the spill, and the reduced or lost services (human uses) they provide" (Paine RT 1996, Trustee Council, Exxon Valdez Oil Spill 1995).

Due to the fragile nature of the environment where the spill occurred and the images that spread through the media; the public reaction to the *Exxon Valdez* was extensive, and this triggered demands for changes in policy and legislation regarding tanker movements in US waters (Birkland A 2002). As a result of the incident, the US Government drew up the OPA 1990 (Oil Pollution Act). OPA90 created a coordinated structure and response unit to manage spills in US waters. In the 1980's, the House and the Senate were deadlocked on whether federal spill policy would pre-empt state laws (Birkland A 2002). The oil industry supported pre-emption, citing that is would be more effective to have one regulatory regime managing an incident as opposed to several. For example, an oil spill near Philadelphia could expose a vessel to liability in New Jersey, Pennsylvania, and Delaware and Federal pre-emption would prevent problems with multiple liability regimes. A significant outcome of the *Exxon Valdez* incident was the House's turnaround on pre-emption. The impacts and subsequent public reaction to *Exxon Valdez* led to the House to shift from supporting pre-emption to an adoption of the Senate position that no pre-emption be permitted. As a result of this, the OPA was drawn up and signed by the President on August 18 1990 (Birkland A 2002). What OPA90 introduced were tougher penalties and liability for the spillers of oil, the allocation of more funds to be made available to manage spills, and the decision that over a pre-determined timeframe, single hulled tankers would be phased out from operating in US waters (Birkland A 2002).

Figure 5: ***Exxon Valdez***
Source: http://darkwing.uoregon.edu (1)

3.2.3 *Braer*

On the 5th February 1993, the Liberian registered tanker *Braer* ran aground following engine failure in severe weather on Garth's Ness, Shetland. Over a period of 12 days, 84,700 tons of Norwegian Gulfaks crude oil and 1500 tons of heavy bunker oil spilled into the sea (Figure 6) (http://www.itopf.com (3)). Response operations for the *Braer* incident were unusual as a result of a minimal proportion of the oil reaching the coast. A combination of a light crude, high winds and rough seas dispersed the oil through the water column before a surface slick formed. Once in the water column, the oil droplets were adsorbed onto sediment particles which sank to the sea bed. Sub-surface currents spread the oil over a wide area, although deposits were found in two deep, fine sediment 'sinks' (http://www.itopf.com (3)). Severe weather conditions limited mechanical recovery of the oil at sea so 130 tons of chemical dispersant were sprayed onto the slick. Oiling of shorelines was minimal relative to the size of the spill and cleanup involved the collection of oiled debris and algae by a small workforce (http://www.itopf.com (3)).

The *Braer* incident led to the Donaldson Report being commissioned by the UK Government into marine salvage operations designed to prevent the escape of pollutants into the environment and to limit their effects should spillage occur. The report was an inquiry into the adequacy and most effective methods of employing intervention powers in the context of pollution from shipping and offshore installations. The recommendations that the Donaldson Report had in relation to the *Braer* incident are in Table 6 (Edgell N 1994).

Figure 6: *Braer*

Source: http://gruppen.greenpeace.de (1)

Table 6: Legislative and regulatory changes after oil spill incidents.

Cause of spill	Response	Recommendations	Implications
Braer Engine failure	Lord Donaldson's report	1) The requirement for internationally agreed rules requiring the early reporting of difficulties experienced by laden tankers. 2) The necessity to arrest the decline in the number of professional salvage companies. 3) The value of well planned and rehearsed emergency response plans 4) The requirement for whatever action is taken to be appropriate to the circumstances of each particular incident	1) Since 1994 the UK Government has published details of foreign flag vessels in UK ports in accordance with Recommendation 41. 2) Introduction of the Merchant Shipping (Salvage and Pollution) Act 1994. Strict liability for oil pollution in UK waters to covers spills from all ships 3) Measures and recommendations to be put into place for tankers in UK waters to protect sensitive areas from the risk of pollution. This was submitted to and adopted by the IMO. 4) EU restrictions on tanker traffic in sensitive areas 5) EU Common Policy on Safe Seas – enhancing safety in maritime transport.
Torrey Canyon Human error	International Convention for the Prevention of Pollution from Ships 1973.	1) Determine who is to be held responsible for damage caused by oil pollution, 2) Determining liability and the level of compensation for damage	1) Introduction of the International Convention for the Prevention of Marine Pollution from Ships, 1973 as modified by the Protocol of 1978 relating thereto (MARPOL 73/78) 2) Introduction of the International Convention on the Establishment of an International Fund for Compensation for Oil Pollution Damage (FUND), 1971

Exxon Valdez Human error	Oil Pollution Act (OPA) 1990	1) Tougher penalties and liability for the spillers of oil, 2) The requirement for the allocation of more funds to be made available to deal with spills, 3) Over a pre-determined timeframe, single hulled tankers to be phased out from operating in US waters	1) In the 1980's the Senate was divided over whether spill policy would pre-empt state regulations. 2) *Exxon Valdez* led the House and Senate to resolve their differences on the pre-emption issue and the OPA was drawn up and signed by the President on August 18 1990. 3) The OPA led to stricter penalties and liability for spillers of oil, allocated resources for dealing with spills, and placed responsibility on the federal executive branch to respond to oil spill incidents promptly.

Sources: Plant G 1995, Kim I 2002, Edgell N 1994, Negro MC 2007, Kim I 2002, A Common Policy on Safe Seas 1993, Birkland A 2002, Booth S 1995, http://www.imo.org (2), http://www.imo.org (3)

3.2.4 Analysis

The circumstances surrounding the impacts of and responses to, the *Torrey Canyon, Exxon Valdez* and *Braer* incidents were fundamental to the subsequent changes in the philosophy and regulation of oil spill response. Pieces of legislation such as MARPOL and OPA 90 were the first policy related steps in oil spill response history designed to prevent future incidents from occurring. The impact of phasing out single hulled tankers in American waters as stipulated in OPA 90, was reflected in statistics that showed oil spills declined in US waters from 2,383 for the 1981-1990 period to 1,375 for the 1991-2000 period. The volume of tank ship (barge) oil spills declined from 27,651,000 gallons for the period 1981-90 to 1,390,138 gallons for the period 1991-2000. Double hulled tankers have subsequently been incorporated into MARPOL, it is a requirement that all new tankers built after 1993 of 5,000 dwt and above are to be fitted with double hulls separated by a space of up to 2 metres (on tankers below 5,000 dwt the space must be at least 0.76m) (Talley WK 2004).

Lord Donaldson's Report focused on prevention of incidents and control of associated pollution. A key finding was that the concepts of pollution and safety are closely linked and that a fundamental aspect of maintaining safety and preventing pollution is to maintain the structural and operational integrity of the vessel. It was further proposed that explanations of why guidance is being given, as opposed to imposing mandatory guidelines that are difficult to enforce, is an efficient method of maintaining standards. Regarding response to marine oil spills, Donaldson's Report concluded that the UK is correct to maintain the capability to spray dispersants from the air but this should be followed where necessary with additional techniques. Strict liability for oil pollution in UK waters to covers spills from all ships was also introduced and this has become a key aspect of the logistics of spill response (Corbet AG 1995). As a direct result of Lord Donaldson's report, restrictions on tanker traffic in sensitive areas, measures and recommendations for tankers in UK waters to protect sensitive areas from oil were implemented (Warren LM 1994, Corbet AG 1995).

It was the response to the *Torrey Canyon* incident that first highlighted the potential damage that inappropriate response options can cause the environment. The lethal concentrations of dispersants were lower than those needed to disperse the oil. Grazing species such as *Patella* and barnacle species are key species in structuring shore communities and the loss of grazers caused algal blooms in the months after the spill. *Fuciod* cover took 15 years to return to pre spill levels but oiled shores that were not treated at all recovered to pre-spill conditions within three years (Hawkins SJ, Southward AJ 1992, Southward and Southward 1978, O'Sullivan A 1967). These statistics give an indication of the environmental consequences that can be caused by inappropriate environmental management. When developing the methodology for the laboratory and *ex-situ* field work in the thesis, it was intended to remove the oil from the substrata using environmentally benign techniques. By calculating the percentage recovery of oil and sorbent it was possible to quantify sorbent efficacy, thus commenting on the optimum combination of oil-sorbent-substrata and associated oil recovery.

3.3 The fate of oil in marine spills

Factors that influence the fate and distribution of spilled oil include: the volume and type of oil, geography, geomorphology, hydrography, hydrodynamics, and prevailing meteorological conditions of the area, and the chemical and physical processes that the oil undergoes when spilled. Typically, the logistics of an oil spill response operation will be determined by how these factors have affected the nature and distribution of the spilled oil. With regard to the research carried out in this thesis, the behaviour of the oil is critical because information on environmental factors that affect oil state and behaviour can affect its ability to combust and thus be suitable for use as fuel (Allen B 1999). Figures 7 to 10 illustrate a series of environments affected by oil and their impact on oil movement and behaviour.

Figure 7: Oil slick at sea in Alaska

Source: http://www.evostc.state.ak.us (1)

Figure 8: oiled rocky shore after *Prestige* incident

Source: http://whyfiles.org (1)

Figure 9: oiled sandy beach in Lebanon
Source: http://www.jadedthea.com (1)

Figure 10: oiled mangroves in the Philippines
Source: http://weblog.greenpeace.org (1)

As Figures 7 to 10 shows, the required response to a spill incident is fundamentally influenced by the environment in which the oil is present. In highly sensitive environments such as mangrove swamps, minimising environmental damage as a consequence of clean up is as critical as reducing oil volume. Oil on sandy beaches may be absorbed and pollution on rocky shores leads to rock pools, boulders and shingle being oiled. It can be said that the influence of marine and coastal processes on spilled oil has a substantial impact on its behaviour, persistence in the environment and the techniques used to remove it from the environment. The next section of this chapter examines the processes oil undergoes when spilled and presents four case studies in terms of oil impact in the environment.

3.3.1 Processes

Oil at sea, if left, will break up and disperse into the environment over time. This dispersion is due to a range of chemical and physical processes that the oil undergoes following release. Collectively, the processes are known as weathering - the in situ breakdown through mechanical or chemical means (http://www.itopf.com (6)). Its viscosity and persistence in the environment determines how the oil breaks up. Light oils such as kerosene evaporate rapidly and disperse over a wide area in a relatively short time frame. Heavier oils including a range of bitumens, asphaltanes and resins do not evaporate and are more persistent in the environment. They are referred to as persistent oils; the lighter fractions such as propane and benzene are known as non-persistent oils (http://www.itopf.com (6)). The major types of weathering, the behaviour of weathered oil and associated implications for clean up are presented in Table 7.

Table 7: Types of weathering and their implications for clean up

Weathering type	Behaviour of oil	Implications for clean up
Spreading	- oil spreads fast and becomes thinner - speed of spreading depends on oil viscosity - after time slick splits and forms bands parallel to the wind direction	- thin slicks reduce the possibility of *in situ* burning - slicks can spread hundreds of kilometres in 2-3 days limiting the possibility of offshore clean up
Evaporation	- light compounds evaporate quickly - speed of evaporation depends on volatility of oil	- faster spreading leads to a high surface area and faster evaporation rates. - refined products (kerosene, gasoline) can evaporate completely - up to 40% of light crude oils can evaporate in 24 hours - spills of volatile oils in confined spaces represent a fire hazard - remaining residue post evaporation has high viscosity and density which complicates removal operations.
Dispersion	- extent of dispersion dependant on sea state - the higher the sea state the higher the rate of dispersion - large droplets rise to the surface and form a slick, small droplets stay in water column.	- increased surface area due to dispersion can aid processes such as biodegradation - viscous oils do not disperse readily, are highly persistent in the environment and if left to dry at the coast form asphalt like 'pavements' if not removed.
Emulsification	- water droplets become mixed with oil and form a 'mousse' - increases volume of oil by 3 or 4 times.	- increases volume of oil and subsequent storage requirements - decreases oil's buoyancy making it more likely to sink - increases viscosity and oil 'stickiness' complicating pumping and storage options. - decreases oil's ignitability - decreases oil's surface area reducing effectiveness of biodegradation
Dissolution	- water soluble compounds within the oil dissolve into	- only the lightest compounds of crude oil are soluble, these compounds are lost

	surrounding water.	quickly through evaporation. - heavy ends of crude oil are insoluble in sea water.
Oxidation	- oils react chemically with oxygen - high viscosity oils form 'tar' - the presence of 'tar' increases the persistence of the oil in the environment	- leads to formation of soluble products or persistent tars - overall impact on oil dissipation is minor
Sedimentation/sinking	- oil can adhere to pieces of suspended sediment and sink - shallow water that is often high in suspended particles is an ideal environment for sedimentation.	- when mixed with sediment, oil forms dense tar 'mats' on the shore - once mixed with sediment oil will sink if washed offshore - if mixed with fine particles on sheltered shores, oil becomes persistent in the environment.
Biodegradation	- sea water contains bacteria that can degrade crude oil - availability of nitrogen, phosphorous and oxygen are the main limiting factors.	- restricted by availability of nitrogen, phosphorous and oxygen - is most efficient at oil-water interface where bacteria in the water have access to the oil and oxygen is available - oil on shores with a low surface area restricts biodegradation efficiency - oil mixed with sediment is limited due to a lack of oxygen and nutrients.

Sources: API, NOAA, USCG, USEPA 2001, http://www.itopf.com (6), http://www.itopf.com (9)

These processes are significant contributing factors to the nature, extent and eventual degree of success of a response operation. Regarding types of weathering, there are three listed in Table 7 that can assist the clean up process (evaporation, dispersion and biological weathering). Light oils evaporate soon after release onto the surface of the water, high rates of evaporation reduce the volume of oil requiring recovery and removes a significant proportion of the oil's toxic volatile compounds http://www.itopf.com (6). Light oils are also prone to dispersion; the rate of dispersion depends on the viscosity of the oil and the sea state. The increase in surface area of the surface slick as a result of dispersion can aid natural degradation of the oil compounds. Light oils disperse into the water column and spread over a wide area reducing their environmental impact. Biological weathering in the form of biodegradations can reduce oil volume. The process is most effective at the oil-water interface where bacteria can access the oil and an oxygen supply to facilitate metabolism. The significant limiting factor of this process is availability of nitrogen, oxygen and phosphorous which are essential to bacteria's ability to metabolise oil.

The remaining types of weathering (spreading, emulsification, oxidation and sedimentation) adversely affect the efficacy of a recovery operation. In spite of spreading increasing slick surface area and thus exposure to bacteria, it can complicate recovery at sea. The thinner the layer of oil on the surface, the less likely ignition will be possible. Oil can also travel for many kilometres in a relatively short space of time which can complicate mobilising shore clean up and prioritising sites for recovery. Emulsification of oil multiplies the volume of material requiring recovery and disposal by 3-4 times http://www.itopf.com (6). It also decreases the oils ability to float on the surface and its ignitability. The increased volume has consequences for recovery and storage and final disposal of the waste product. Regarding the use of waste oil as fuel, the water content is a critical factor in determining its potential. Heavily emulsified oils may require extensive pre-treatment prior to incineration as fuel; this will have consequences for the financial viability of any waste oil as fuel projects. Sedimentation becomes a factor in response when oil droplets adhere to sediment particles. This increases the volume of material to be recovered and can lead to the formation of 'mats' of oil on the shoreline. If the oil is washed offshore after beaching the additional weight of the sediment causes it to sink and thus it can become persistent in the environment (API, NOAA, USCG, USEPA 2001, http://www.itopf.com (9)).

3.3.2 Impact of oil in the environment

Regarding the physical, chemical and biological impact of oil in the environment, it can be said that it is affected not only by the circumstances of the spill but also by the nature of the clean up methods used. This section focuses on selected oil spill incidents and identifies the techniques used to remove the oil and their associated environmental implications. Regarding specific tools and methods to remove oil from the environment, each technique has benefits and cautions. Figures 11 to 15 display the range of options for oil containment and recovery and the environments they operate in.

Recovery methods that may be appropriate include:

- Booms and skimmers in open water. A containment and recovery system is used whereby a boom is placed on the water surface to contain the slick and a skimmer removes the oil from the surface within the confines of the boom.
- Dispersants, that are capable of removing certain oil types from the sea by dispersing the oil into the water column. Wave and tidal energy cause the oil to break up into small droplets that are diluted and biodegraded by micro-organisms naturally occurring in the marine environment.
- Absorbents, materials that are capable of absorbing the oil into their structure.
- Adsorbents, materials that are capable of condensing the oil into a layer on their surface.
- Mechanical techniques including high temperature water pressure and scrubbing.

Figure 11: oil containment boom

Source: http://www.pcs.gr.jp (1)

Figure 12: Oil skimming unit

Source: http://www.pcs.gr.jp (2)

Figure 13: Oil dispersant application

Source: http://www.noaanews.noaa.gov (1)

Figure 14: aerial dispersant application

Source: http://www.oceansatlas.org (1)

Figure 15: shoreline clean up techniques
Source: http://www.saa.org (1)

3.3.2.1 Impacts: *Torrey Canyon*

The circumstances of the *Torrey Canyon* incident are stated in section 3.2.1. The subsequent patterns of species distribution and recolonisation reflected the extent of the damage the spill caused. The first evidence that *Patella* had re-colonised shores was in the winter of 1967/8. The limpets had begun to re-establish themselves under the dense canopy of *Fuchoids* thus preventing further *Fuchiod* plants colonising. As the plants aged, limpet grazing of their holdfasts weakened them further and between 1971 and 1975, the shores became bare to the extent where there was less algal coverage than before the spill. Interactions between communities in the littoral zone are finely balanced between algal species, grazers and species that rely on them for both food and shelter. The variations in their distribution in the wake of *Torrey Canyon* provides evidence of the impact oil has on these communities, and further flags the impacts of using the chemical dispersants available in 1967 which were deemed appropriate and effective (http://www.ukmarinesac.org.uk (1)). Research showed that the timescale for recovery at these sites was 10 years with treatment; this was longer than first thought by ecologists at the time. It was wrongly assumed that dense growth of algae was an indication of recovery and some ecologists proposed that the sites had fully recovered in 2 years (Southward AJ 1978). However, Southward and Southward (1978) dismissed these assumptions and the expected rapid recovery. Evidence shows that some sites heavily treated with dispersants did not returned to pre-spill conditions in 10 years, and in the most affected cases it took 15 years for the sites to recover fully (Southward AJ 1978, http://www.ukmarinesac.org.uk (1), http://www.itopf.com (10)).

The differences in opinion highlight the complications that occurred regarding monitoring recovery of the oiled shores. In the case of *Torrey Canyon* the issue was to be able to differentiate between the effects of human intervention and natural remediation.

3.3.2.2 Impacts: *Exxon Valdez*

The environmental impacts on the flora and fauna of Prince William Sound were extensive and a pattern of acute mortality followed the release of the oil. Oiling of marine mammals and seals caused loss of insulating capacity, hypothermia, oil smothering, drowning and ingestion of toxins (Peterson C 2003). Estimated figures for mass mortalities were:

- 1000-2800 sea otters
- 250,000 sea birds
- 302 harbour seals

(Peterson C 2003)

Mass mortality of macroalgae, microalgae and benthic organisms also occurred. This was attributed to a combination of exposure to toxins, oil smothering and displacement by high pressure water application. Oil was trapped in many coastal types of sediment including mussel beds and this provided a biological route for the oil into a range of producers and heterotrophs. Long term chronic exposure was recorded in fish species, sea otters and ducks. This was particularly associated with species reliant on sediment foraging for food and sediment environments for nesting (Peterson C 2003).

Exxon Valdez was the first major spill incident where bioremediation was trialed as a response operation (Lee K 1999). The process involved the application of nitrogen-containing fertilisers to stimulate growth of indigenous hydrocarbon degrading microorganisms.

Following laboratory trials, field experiments were carried out in order to evaluate the effectiveness of bioremediation agents. The impact of the bioremediation agents was recorded by monitoring changes over time in the oil composition relative to hopane, which is a stable high-molecular weight hydrocarbon present in the oil. The field data sets showed that fertilizer additions accelerated the rate of oil removal by a factor of five (Lee K 1999). Analysis of the results showed this was due to the level of nitrogen present in the pore water of the intertidal sediments. The results of the study showed that the rate of bioremediation can be improved by measuring nutrient levels in sediments to ensure sufficient levels of nutrients are maintained during microbial application (Lee K 1999).

3.3.2.3 Impacts: *Sea Empress*

Sea Empress ran aground off the Welsh coast in 1996 in the UK's only predominantly coastal National Park. The flora, fauna and habitats of the National Park and surrounding area are regulated and managed through the National Park and additional designations including an MNR (Marine Nature Reserves), 7 SAC's (Special Area of Conservation), 3 SPA's (Special Protection Area), 6 NNR's (National Nature Reserve), and 75 SSSI's (Sites of Special Scientific Interest). (PCNPA: The State of the Park 2004).

One of the most high profile species that was affected by the spill was the Cushion Star *Asterina* which had a population of 150 individuals at West Angle Bay prior to the spill. This number was reduced to 13 in the wake of oil beaching at West Angle. However, removal of egg masses to specialist incubators increased numbers to 45 by 1998. The population has subsequently recovered and removal of individuals during the oil recovery phase significantly increased understanding of *Asterina* reproductive biology (Edwards R 1999). The tourist industry is also of significant value to the area contributing an estimated £343 million *per-annum* to the County's economy (Edwards R 1999). A significant attraction of Pembrokeshire to the tourist is its coastal and marine scenery and wildlife and access to popular activities include walking, SCUBA diving, canoeing, kayaking, coasteering, fishing and sailing. It was feared that the impact of the oil would significantly reduce tourist numbers in the years after the incident (Edwards R 1999, http://www.visitpembrokeshire.com (1)).

In spite of the highly sensitive geography of the area, the anticipated environmental damage was less severe than initially predicted. This was due to:

- The spill occurring in February, this was a time of low use from a tourist and environmental perspective. The majority of the seabirds had not returned to the area to nest and many of the fish species had migrated offshore or were inactive.
- On the day of the spill, the wind was blowing northerly thus carrying the oil away from the coast.
- Forties Light Crude is a light fraction of crude oil, 40% of the spill evaporated off the surface of the seawater before it was blown to the coastal areas. The application of chemical dispersants from the air proved to be successful, it was estimated that 28% of the oil dispersed naturally and 24% was dispersed through chemical use (Edwards R 1999).
- The damage was less than anticipated due to the techniques used to remove the oil from the beaches (priority to amenity beaches and mass removal of bulk oil from accessible shores by a workforce of over 1000 individuals.) (Edwards R 1999).

Due to the weather conditions and the light oil type that was spilled, between 5-7% of the spill reached the shoreline (3,700-5,300 tons which transformed into 11,000-16,000 tons of emulsion). Within 6 weeks of the oil beaching, beaches were visibly cleaner and open to the public. Clean up operations carried on for 18 months and were focused on pockets of oil exposed on beaches or washed ashore (Edwards R 1999). The range of options used to recover oil from the surface of the water and shores after *Sea Empress* were:

- Offshore dispersant spraying,
- Mechanical recovery on beaches and rocky shores
- Protective booms to retain the oil offshore and facilitate dispersant spraying.

(http://www.itopf.com (10), Lunel T 1998)
These measures, in addition to a high rate of evaporation and natural dispersion, reduced the quantity of oil reaching inshore waters and beaching. It is estimated that 200km of coastline was contaminated and a shoreline cleanup operation was initialised involving mechanical recovery, trenching, beach washing, and the use of dispersants and sorbents (Lunel T 1998).
A range of techniques were employed for bulk and residual cleaning including manual removal and the application of 12 tonnes of dispersant. At the height of the response 50 vessels, 19 aircraft and 25 organisations were directly involved with 250 staff working on the response at sea and 950 working on the shoreline (Edwards R 1998).
Due to the proximity of the spill to high amenity coastal areas, there were a range of impacts that affected humans, both from a health and economic perspective.
Regarding human health, short term effects of the oil were noted in the aftermath of the clean up operation. Conditions such as nausea, dermatological irritation and headaches were noted. This was particularly the case in personnel who had not worn adequate safety clothing during the clean up. Crops and other agricultural products had been deemed safe.

The expected impact on the tourism industry was substantial but due to the success of the clean up and to the loyalty of returning visitors, the impact on tourist numbers in the summer of 1996 were less than predicted (Lunel T 1998).
Fishing and lobster potting are a traditional source of income and employment in Pembrokeshire. As a precaution, a closure order was put in place for all commercial and recreational fishing in the area affected. The orders were implemented to ensure the survival of the fisheries and to prevent any tainted fish being sold. The orders were lifted progressively and no mortalities of fin-fish, crustaceans or molluscs were attributed to the spill (Edwards R 1999). In the absence of mortalities, it was decided to carry out biological and chemical analysis on the fish, invertebrate and mollusc populations. The immune systems of species including *Mytulis edulis* (the Common Mussel) was impaired and improved with contamination decrease, other impacts such as growth impairment and alteration in DNA were tested for and anomalies in the data sets were found. However, whether these differences were due to the effects of the oil or other environmental contaminants was not established (Edwards R 1999).

Amphipod communities showed little impact of contamination by oil, although some changes were evident at the population level. A decline in the populations of amphipod fauna as the genera *Ampelisca* and *Harpinia* and the family *Isaeidae* was recorded. This was accompanied by increases in the diversity and abundance of *polychaete* populations as opportunist species colonised in the absence of amphipod fauna. Within five years of the spill the amphipod fauna had shown clear signs of recovery (Nikitik C 2003).

3.3.2.4 Impacts: *Prestige*

On the 19th November 2002, *Prestige* sank 160km off the coast of North West Spain in waters 3600m deep (http://www.spillcon.com (1)). The vessel had sustained a 50m gash on her starboard side and under tow at the direction of the Spanish authorities; she broke up in heavy seas and spilled a total of 64,000 tons (www.panda.org (1)). Of the 64,000 tons spilled, 20,000 tons were washed up on the shoreline of Cantabria, the region most affected. These contaminants were mainly removed from sandy beaches and rocky intertidal areas (Juanas JA 2007). A large scale offshore cleanup operation was carried out. The response was complicated by adverse weather conditions and by the inability of fishing vessels that lacked cargo heating capability to discharge recovered oil. Over a thousand vessels participated in the cleanup in sheltered coastal waters and during favourable weather. The open-sea recovery operation off Spain removed 50,000 tonnes of oil-water mixture. Despite this and the deployment of 20km of booms, 1,900 km of shoreline were oiled. The shorelines of Spain were cleaned manually by a workforce of over 5,000 military and local government personnel, contractors and volunteers. Issues raised included the time-consuming nature of the process in rocky areas and secondary oiling of previously cleaned areas by re-mobilised oil (Juanas JA 2007, http://www.itopf.com (7)).

Preliminary studies on the effect of the *Prestige's* oil on the shorelines show evidence of substantial damage. The damage extended to areas of the shore above the EHWS (Extreme High Water Spring) mark, particularly to lichens which were affected by oil droplets being carried by onshore winds. In the littoral zone disappearance of the brown alga *Pelvetia canaliculata, Fucus spiralis, Fucus vesiculosus* and *Rhodothamniella floridula* was recorded (www.panda.org (1)). Over the 12 months following the spill, benthic macrofaunal species that are known to be sensitive to crude oil declined and were replaced by opportunistic species, most commonly *polychaetes*. This decline was followed by a three year decrease in populations known to be vulnerable to oil. It was in the fourth year after the spill that pollution sensitive species reappeared on the shore (Suarez *et al* 2005). One of the issues that made responding to the spill logistically complex was the nature of the oil the *Prestige* had been carrying. It was a heavy fuel that had a high density and low viscosity and thus did not evaporate or disperse naturally. The health issues flagged by the response personnel included headaches, rashes, eye redness, respiratory problems, nausea, trauma and dizziness (Suarez *et al* 2005).

3.3.2.5 Analysis:

The case studies illustrate the range of impacts that oil can have in terms of its interactions with the environment (weathering), the species balance of the shore, the specific environment in which it is spilled and the techniques used to recover it. It can be said that the range of impacts, environments and possible options are diverse and demand a multi-disciplinary response. There is no one set of definitive guidelines for spill response. However, there are a set of common denominators that may be considered for each incident, regardless of location. Documents that can be utilised in these scenarios are guidelines detailing best practice, options, protocol, benefits and cautions. Location-specific material can be added as appendices or case studies to focus the mechanics and logistics of the operation. If the mechanisms used to remove oil from the environment in each of the four incidents discussed are interpreted in further detail, it is possible to comment on how the oil spill response industry has developed over time.

Torrey Canyon was the first major tanker incident that was brought to the widespread attention of the public (Southward AJ 1978), what set it apart from other incidents was the indiscriminate use of toxic dispersants. In terms of removing oil from the shores, they were largely successful; however, they were often applied undiluted direct onto substrata which caused widespread mortality in littoral flora and fauna. (http://www.itopf.com (10)). Initial predictions by ecologists at the time that the shores had recovered within 2 years of the incident proved inaccurate. Further analysis of species diversity and distribution in the years after the incident suggested that the shores took between 10-15 years to recover where dispersants had been applied (Southward AJ 1978).

Exxon Valdez is the largest oil spill in American waters to date. It attracted intense interest from the public and media due to its size and the fact that it occurred in an area of pristine wilderness that supports species including Sea Otters and Bald Eagles. As a result of these factors and the fact that the oil was threatening an important fishing area; the response was the most expensive ever recorded for an oil spill incident. At its height, over 10,000 workers were involved at a cost of US$2billion http://www.itopf.com (4). Despite the expense and level of manpower involved, the amount of oil recovered was equivalent to between 10-14% of the total spilled, as previously stated. The machinery used to remove and transport the oil used 40 times more oil than had been spilled (Payne RT 1996). The level of hot water, high pressure washing used to remove oil from coastal substrata was also the most extensive to date. In spite of most oiled shores being visibly cleaner one year after the spill, studies at the time suggested that the application of high pressure hot water substantially delayed recovery on a range of shores through the removal of algal species and grazers http://www.itopf.com (4). *Exxon Valdez* was the first major spill incident to trial bioremediation as an oil removal strategy. The science of bioremediation and its application to oil has been subject to extensive laboratory research; the challenge facing the industry has been to extend this research to field conditions (Head I 1999). *Exxon Valdez* provided an opportunity to study the efficacy of bioremediation at a scale not previously encountered. What the studies from *Exxon Valdez* proved was that in order to effectively implement bioremediation in the field, it was necessary to quantify the amount of fertiliser required by the amount of nutrients present in the environment, not as pre-determined dosage for a given area of shore. This could be monitored by on-site recording of ground water nutrient levels throughout fertiliser application (Bragg JR 1994).

Due to the fragility and high amenity value of the coast where *Sea Empress* ran aground, the subsequent response and clean up operation was subject to extensive scrutiny from the public and media. Regarding the efficacy of response measures, *Sea Empress* can be used as a direct comparison to *Torrey Canyon* in terms of dispersant application. If the figures from *Sea Empress* are examined in further detail, the amount of oil spilled was 72,000 tons, of this, 40% (28,800 tons) evaporated which meant there was in excess of 40,000 tons of oil at sea that could have come ashore. Forties Blend Crude has a tendency to produce a 70% water-in-oil emulsion which could have translated into 130,000 tons of emulsion beaching on the South Wales coastline (Lunel T 1995). The reality of the situation was that between 11-16,000 tons washed ashore (Edwards R 1998). The mechanisms responsible for this reduced amount were mechanical recovery at sea which removed 4,000 tons and the effective use of dispersants (Lunel T 1995). It is estimated that 50% of the total oil spilled was dispersed, 80% of which was dispersed by chemicals. Research carried out by Lunel *et al* stated that the application of dispersants significantly enhanced natural degradation rates and resulted in a net environmental benefit through reduction of surface oil (Lunel T 1995).

The *Prestige* incident is an example of factors that can reduce the efficacy of a response operation. The oil spilled from *Prestige* was heavy fuel oil, it was viscous and highly persistent in the environment and due to this factor, the oil drifted on the sea surface with winds and currents. It came ashore in Galicia, where the predominantly rocky coastline was heavily contaminated, the Bay of Biscay and the Atlantic coast of France. The initial response to the oil beaching was hampered by severe weather and by the inability of the fishing vessels first on the scene, lacking the cargo heating capability necessary to discharge recovered oil (Albaiges J 2006). The at-sea recovery operation removed 50,000 tonnes of oil-water emulsion. However, this and the deployment of over 20kms of boom did not prevent extensive coastal contamination. The high levels of contamination were attributed to poor weather conditions restricting the deployment and efficacy of booms (http://www.itopf.com (7), Albaiges J 2006). In total, 1,900 km of shoreline were affected (http://www.itopf.com (7)).

In the aftermath of the incident, what emerged as a factor behind the ineffective initial response was a lack of a decision making framework and organisational ability to implement a strategy (Albaiges J 2006). In the absence of a strategic contingency plan, the first responders on-site were fishing vessels and volunteers on the beaches. As a result of the organisational failure, the Spanish Governments Ministry of Science and Energy devised an Urgent Strategic Action and Scientific Response Plan to manage funds and implement response strategies (Albaiges J 2006). It was organised and implemented in six stages that included: the behaviour of the oil in the sunken tanks, seismic risks for the wreck, the fate of the oil, biological impacts of the oil, socio-economic impacts and the definition and implementation of contingency planning (Albaiges J 2006).

The response to the *Prestige* incident highlighted the need for a coordinated and planned response to future incidents. Research by Albaiges *et al.* 1996 suggested that due to the persistence of the oil spilled and the nature of the environments contaminated, it was necessary to continue environmental impact assessments beyond 2 years immediately after an incident. However, it was stated that release of hydrocarbons into the sea from other sources could skew the analysis of impacts from a major spill. It was proposed that a strategy of continual development and expansion of knowledge and techniques to predict impacts and provide guidance was necessary (Albaiges J 2006).

3.4 Environment specific response to oil spill incidents

This section covers two options recognized by industry to facilitate appropriate response to oil spill incidents; these are Time Windows of Response and Net Environmental Benefit Analysis (NEBA). Bioremediation is also discussed as an option suited to oil spill response in the coastal habitats and ecosystems in Vietnam.

3.4.1 Time windows of response:

The concept of 'Time Windows of Response' application to an oil spill incident is that there is a specific window of time in the response operation where any one technique will be at its most effective. A key factor in spill response is reacting to the changes that the oil undergoes when spilled and adjusting the response accordingly. It is an understanding of these changes and how they are influenced by environmental factors that leads to a 'time window' being calculated for a response strategy. With regard to the clean up operation, it can be said that oil spreading, emulsification and evaporation dictate the nature of clean up. Oil thickness, flash point, pour point density and viscosity are all altered when oil undergoes one of these processes (Nordvik A 1999). Oil viscosity is a substantive factor in the efficacy of dispersant application and mechanical recovery. The flash point and water content influence ignitability and the length of time oil will burn; density affects the effectiveness of separation techniques. Table 8 shows oil spill response technology and factors influencing their time window. It is noted that where emulsification is flagged as a factor, it is possible to partly reverse the process by the application of heat or chemicals (Nordvik A 1999).

Table 8: Response techniques and factors affecting response

Technique		Factor affecting response
Skimmers	weir	Extent of emulsification Oil thickness
	adhesion	Oil thickness Viscosity
Oil and water separation (mechanical)		Density Emulsification Viscosity
Dispersants		Viscosity Pour point Water content Emulsification (water content and stability)
In situ burning		Flash point Release of combustible vapour Rate of evaporation prior to combustion Emulsification

Source: Nordvik A 1999

The factors highlighted in Table 8 are specific to spills at sea where variations in the oil's characteristics and behaviour can complicate response operations more so than responses on land due to the inherent dynamics and interactions between the oil and the environment. Weir and adhesion skimmers use different mechanisms but oil thickness and the extent to which it has emulsified affect the ability of the skimmer to remove the oil from the surface of the water (Nordvik A 1999). Separators operate on the difference in density between oil and water, and evaporation and emulsification both reduce this difference. A further consideration is that the weight of crude and refined oils varies and the extent to which they separate can be affected. The use of chemical dispersants is one of the most established techniques for responding to oil on water (Chapmana H 2007). If the viscosity of the oil, its pour point, water content or stability are increased then the oil becomes less dispersible. The higher the amounts of wax and asphaltanes present in the oil the higher the likelihood that dispersant effectiveness will be compromised (Nordvik A 1999).

A caution with *in situ* burning of oil is the resulting smoke and if the oil is emulsified, ignition may not be possible. Ignition and continued combustion of oil relies on the flash point and the release of combustible vapour. It is the vapour, not the liquid oil that burns during the process. The most flammable components of the oil burn at below 150°c but they are also the first to evaporate. The heavier ends in the oil burn at around 350°c and require a higher ignition temperature. Another factor that affects the combustibility of oil is the droplet thickness on the surface of the water. It is possible to alleviate this by booming the slick but this requires specialist fire proof booms. It can be said that *in situ* burning as a response is highly oil and environment specific (Nordvik A 1999).

3.4.2 Net Environmental Benefit Analysis (NEBA)

The conceptual basis of Net Environmental Benefit Analysis (NEBA) is to respond to a spill situation while minimising environmental impacts and ensuring that the clean up mechanisms can justify further environmental consequences. The advantages and disadvantages of natural clean up are introduced as an option from socioeconomic and environmental perspectives. There are four stages to a NEBA:

- Research of available information on the physical characteristics of the area,
- A review of previous local incidents.
- Development of a database of information regarding the environmental outcomes for each possible response strategy.
- Advantages and disadvantages of natural and engineered responses are assessed (IPIECA Report Volume Ten 2000).

Within NEBA, both oil on water and the shore are covered. With regard to managing oil on water, predicting the speed and direction of travel is critical. The assumption that the slick will reach sensitive shore areas covers the worst case scenario. It is often the case that using low toxicity dispersants is the most suitable strategy as they are deemed low risk to fish stocks and they can reduce the amount of oil beaching (IPIECA Report Volume Ten 2000). Oil on the shore presents a multi-disciplinary challenge and response. There are a range of considerations regarding oiled shoreline response within NEBA:

Table 9: NEBA considerations

Issue	Considerations
Severity of oiling	- heavy mechanical recovery can cause more damage than oil - heavily weathered mousse can persist in the environment for up to 25 years if not removed. - low pressure hoses can remove oil from sediments without extensive mixing occurring.
Interacting systems	- interacting systems (nearshore ecosystems/breeding birds) are vulnerable to oil is the shore is not cleaned - high pressure hot water may be used to remove sticky oil in a seal breading area - the resultant long recovery time for intertidal grazers is deemed to be accepted as seals have a higher clean up priority.
Socio economic values	- Prioritizing between amenities such as beaches with a high tourist value and marinas and sensitive environmental areas is a priority - If oil is running off the shore onto a shellfish bed which is used as source of local food the shellfish will survive the tainting but will be unsuitable for consumption. ↓ - The issue raised is whether this justifies heavy cleaning of the shore to prevent the runoff when it may be the case that natural cleanup has already started and artificially speeding the clean up may damage the shore

Source: IPIECA 2000

NEBA aims to highlight scenarios where it is justifiable to cause further damage through response options if the perceived advantages to the environment and the economy are deemed high enough. The advantages and disadvantages of each clean up option are analysed against natural clean up, and it can be the case that the recovery time is extended by using aggressive clean up techniques. This was demonstrated after the *Torrey Canyon* incident (O'Sullivan A 1967). If it is the case that a clean up is focused on the short term health and appearance of the shore, NEBA may highlight there is no long-term ecological justification for clean-up and that operations should cease (IPIECA 2000, Kerambrun L, 1998). As the over-riding philosophy of NEBA is that it may be justifiable to cause further damage to the environment through specific response options, it is essential to analyse past incidents and the outcomes of their responses, the net value of socio-economic and environmental amenities in the area and the predicted impact of an incident.

In an effort to quantify the application and efficacy of NEBA, a 20 year long study was carried out in Panama (Baca B 2005). In 1984, non-treated Prudhoe Bay crude oil and dispersed crude oil were deliberately released into sites representative of mangrove, seagrass and coral ecosystems as part of the TROPICS (Tropical Oil Pollution Investigations in Coastal Systems) research project. The effects of the non-treated and dispersed oil were recorded and analysed over a 20 year period. In the immediate aftermath of oil application, mortality of invertebrates, seagrass and coral was observed at both sites, and it was noted that mortality in the mangrove forest was significantly higher in the non-treated oil site. Observations over the 20 year scope of the project showed continued presence of oil, diminished mangrove population and substrata erosion in the untreated site. At the dispersed oil site, no oil was detected and no long term toxicological impacts noted in flora and fauna (Baca B 2005).
The data set for the NEBA study consisted of biological data to quantify the impact of oil on the ecosystem and physical data to measure hydrocarbon levels and substrata erosion. In order to analyse the results further, flora, fauna and ecosystems were spilt into parameters representative of their overall importance to the community. PIL1 were considered highly important and consisted of key organisms, PIL2 were considered secondary in importance yet represented a significant proportion of field measures. PIL3 were considered to not be directly important to the community, they were predominantly transient species that results suggested were not significantly affected by the presence or otherwise of oil (Baca B 2005). The core results of the study can be seen in Tables 10 and 11.

Table 10: NEBA 1984 compared to 1994.

Habitat	Component	Parameter	**PIL	Crude 1984	Crude 1994	Disp 1984	Disp 1994	Ref 1984	Ref 1994	NEB?
Mangrove	Trees	Number Living	1	149	80	72	70	108	108	YES
	Trees	Mean Trunk Diameter (cm)	2	5.3	*6.9	8.9	9.4	7.5	9.0	YES
	Trees	Mean Height (m)	2	4.4	5.0	5.0	4.9	4.4	4.7	NO
	Trees	Open Canopy (LAI#)	2	2.7	*3.9	3.1	3.6	2.4	2.6	YES
	Trees	Canopy Density (%)	2	NM	*38.1	NM	44.1	NM	56.1	YES
	Trees	Leaf Production (#/mo)	2	0.64	0.47*	0.67	0.40*	0.78	0.73	NO
	Trees	Leaf L/W Ratios	3	2.21	2.16	2.19	2.16	2.37	2.24	NO
	Trees	Mean % Herbivory	3	NM	24.0	NM	18.4	NM	20.1	NO
	Trees	Mean Lenticels/cm²	3	0.44	0.61	0.37	0.52	0.42	0.52	NO
	Mangrove sediment	Hydrocarbons (mg/l)	3	0.9	19.4	0.6	*30.8	0.6	1.1	NO
	Seedlings	Number Living	3	13	*89	33	19	26	21	NO
	Tree Snails	Mean #/tree	3	297	*879	766	*690	445	927	NO
	Tree Oysters	Mean #/m root	3	53	*184	48	83	61	64	NO
	Cup Oysters	Mean #/m root	3	16	*77	33	58	23	35	NO
Seagrass	Seagrass	Mean Shoot Density (#/m²)	2	841.7	*440.0	816.7	516.0	666.7	452.0	YES
	Seagrass	Mean Growth (cm/da)	3	0.48	0.53	0.38	0.48	0.46	0.58	NO
	Seagrass	Mean Leaf Area (cm²)	3	22.2	17.6	24.4	18.6	27.6	20.4	NO
	Urchins	Mean #/line intercept	3	1.93	1.69	1.53	0.57	0.77	1.00	NO
Coral	Corals	Total Cover (%)	1	30.5	35.6	33.5	26.9	21.3	12.8	NO
	Fauna	Total Cover (%)	3	50.3	50.8	50.3	49.3	49.3	48.5	NO
	Flora	Total Cover (%)	3	7.0	18.5	3.8	*26.9	19.3	34.5	NO
	Organisms	Total Cover (%)	3	57.3	69.3	54.0	*76.1	68.5	83.0	NO

Source: Baca B 2005

Table 11: NEBA 1984 compared to 2001 and 2002.

Habitats (1984/2001)	Component	Parameter	**PIL	Crude 1984	Crude 2001	Disp 1984	Disp 2001	Ref 1984	Ref 2001	NEB?
Mangrove	Trees	Number Living	1	149	141	72	60	108	85	NO
	Trees	Mean Trunk Diameter (cm)	2	5.3	*2.3	8.9	10.2	7.5	9.0	YES
	Trees	Mean Height (m)	2	4.4	*3.1	5.0	5.4	4.4	4.3	YES
	Trees	Open Canopy (LAI #)	2	2.7	*2.3	3.1	5.0	2.4	3.6	YES
	Trees	Leaf L/W Ratios	3	2.21	2.38	2.19	2.08	2.37	2.14	NO
	Trees	Mean % Herbivory	3	NM	12.6	NM	*22.3	NM	10.2	NO
	Seedlings	Number Living	3	13	*75	33	*13	26	21	NO
Habitats (1984/2002)	Component	Parameter	**PIL	Oiled 1984	Oiled 2002	Disp 1984	Disp 2002	Ref 1984	Ref 2002	NEB?
Seagrass	Seagrass	Mean Shoot Density (#/m²)	2	841.7	*228.0	816.7	*412.0	666.7	593.3	YES
	Seagrass	Mean Growth (cm/da)	3	0.48	0.43	0.38	*0.47	0.46	0.40	NO
	Seagrass	Mean Leaf Area (cm²)	3	22.2	*28.5	24.4	20.2	27.6	17.4	YES
Coral	Corals	Total Cover (%)	1	30.5	*67.5	33.5	45.5	21.3	16.8	YES
	Fauna	Total Cover (%)	3	50.3	*79.5	50.3	53.3	49.3	37.3	YES
	Flora	Total Cover (%)	3	7.0	6.0	3.8	31.0	19.3	42.0	NO
	Organisms	Total Cover (%)	3	57.3	85.5	54.0	84.3	68.5	79.3	NO

Source: Baca B 2005

A net environmental benefit was believed to exist if results from all PIL1 values and a majority of PIL2 values were significantly different between the non-treated oil and dispersed oil data sets.

The key patterns in the data between 1984 and 1994 were as follows:

- The use of dispersant use in the mangroves is supported by all PIL1 species and 60% of PIL2 species.
- The seagrass data showed a significant reduction in shoot density between 1984 and 1994. As a result of seagrass growth and leaf area not being positively or negatively affected by dispersant application, it was concluded that there was a net environmental benefit to dispersant application over seagrass beds.
- Application of dispersants showed no long term positive or negative effects on coral recovery. Significant increases in flora and total organism cover at the dispersed site were not deemed to be applicable to the experiment as the control site experienced similar trends (Baca B 2005).

Key patterns in the data between 1984 and 2001 showed the following:

- The mangrove data showed a net environmental benefit in PIL2 species, it was noted that a significant proportion of the trees that were oiled had died and had been replaced by seedlings. This led to a return of tree numbers but a reduction in trunk diameter, canopy cover and tree height.
- Shoot density for seagrass was highest at the dispersed oil site. Density was significantly lower at the untreated and dispersed oil site in comparison to the control but the untreated site was the only one that was still significantly low compared to the 1984 data. This supports the use of dispersant use for seagrass beds using NEBA to quantify the results.
- The most significant result from the coral data was a significant increase in coral cover from the untreated oil site, this may have been partially attributed to a decrease in seagrass cover, but the results supported the use of dispersant application in nearshore coral environments (Baca B 2005).

The most recent data collected from the site (2004), further supported the use of dispersant application using NEBA as a quantifiable benchmark for efficacy. The findings of the study concluded that oil contamination remained at the untreated oil site but was not evident at the dispersed oil or control site. Oil originating from the untreated site leached into adjacent environments, erosion and sediment re-distribution occurred at the untreated site but not at the dispersed or control site. These findings provide positive evidence in the use of dispersants in nearshore environments and that they can lead to a net environmental benefit in comparison to sites that are not treated for oil contamination (Baca B 2005).

3.4.3 Case study: Oil spills in ecologically sensitive environments

With regard to environment specific response to oil spills, an alternative to determining time periods for each response option or perceived socio-economic and environmental gains is to base the decision making process for clean up on the vulnerability of the affected environment.

Bioremediation is an option that utilises microbial populations that are either naturally occurring or introduced into the contaminated environment to degrade oil. Bioremediation can be defined as: "the use of living organisms, primarily microorganisms, to degrade environmental contaminants into less toxic forms" (Vidali M 2001). It utilises naturally occurring bacteria and fungi or plants to degrade or detoxify substances hazardous to human health and/or the environment, the process is an environmentally friendly technique to remediate oil spills (Odokuma LO 2003). Research was carried out in Vietnam to facilitate implementation of *in-situ* and *ex-situ* bioremediation technologies and demonstrate the dissemination of bioremediation technology to universities and oil spill response personnel (BIOREM Handbook 2006, Green J 2006).

3.4.3.1 Introduction:

The main outputs of the research in Vietnam were a series of practically orientated guidelines on decision making and implementation of *in-situ* and *ex-situ* techniques for bioremediation of contaminated shorelines. The material was disseminated through a workshop, training scheme and distance learning package which the author researched, developed and designed (Green J 2005, Green J 2006 (2) BIOREM Handbook 2006). The objectives of the research were to:

- Promote environmental awareness,
- Contribute to the implementation of bioremediation as a feasible technology for pollution remediation,
- Facilitate networking, coordination and collaboration between stakeholders,
- Promote integrated planning, coastal zone management and waste management
- Integrate the science into higher education to train future generations of professionals in Vietnam (BIOREM Handbook 2006).

Vietnam was selected due to its sensitive coastal and marine habitats and its expanding economy. It has 3,400km of coastline, over 300 islands and in excess of 1,000,000km^2 of exclusive economic waters; it covers less than 1% of the worlds landmass yet is home to 10% of the world's species (BIOREM Handbook 2006). Within the ASEAN (Association of South-Eastern Asian Nations) network, Vietnam has been highlighted as a medium priority for expansion in the oil and gas industries, it is also reliant on the tourist industry in coastal areas for income and employment opportunities. The most frequently occurring types of shoreline are mangrove swamps, wetlands, tidal flats, marshes and sandy beaches - these are all high sensitivity shores vulnerable to oil spill damage. Over half of Vietnamese cities are found on the coast, coastal communities contribute 40% towards Vietnams GDP and provide jobs for 10 million people. Many of the smaller communities rely on inshore fishing for their livelihoods. Recently, the number of ships using Vietnamese waters has increased and the oil and gas industry has expanded. A gap between policy and implementation of legislation and policy has been flagged and training has been highlighted as an option to facilitate further integration (BIOREM Handbook 2006).

Figure 16: Vietnam

Figure 17: South East Asia

Source fig 16: http://www.reisenett.no (1)

Source fig 17: http://www.lib.utexas.edu (1)

3.4.3.2 Vulnerability:

Tourism is critical to the Vietnamese economy and the diversity of coastal and marine habitats; scenery and biodiversity are a key attraction. It is estimated that 70% of attractions aimed at tourists are in coastal areas, between 1995 and 2000 the number of tourists increased from 4.5 to 10.7 million *per annum* (Figure 18). Fisheries and aquaculture are highly developed in Vietnam and are important to the Vietnamese traditionally, culturally and economically (Figure 19). The Government treats fisheries as a valuable asset, in 2000, the export value increased 35% to US$1.3 billion and total output production increased 20% (BIOREM Handbook 2006).

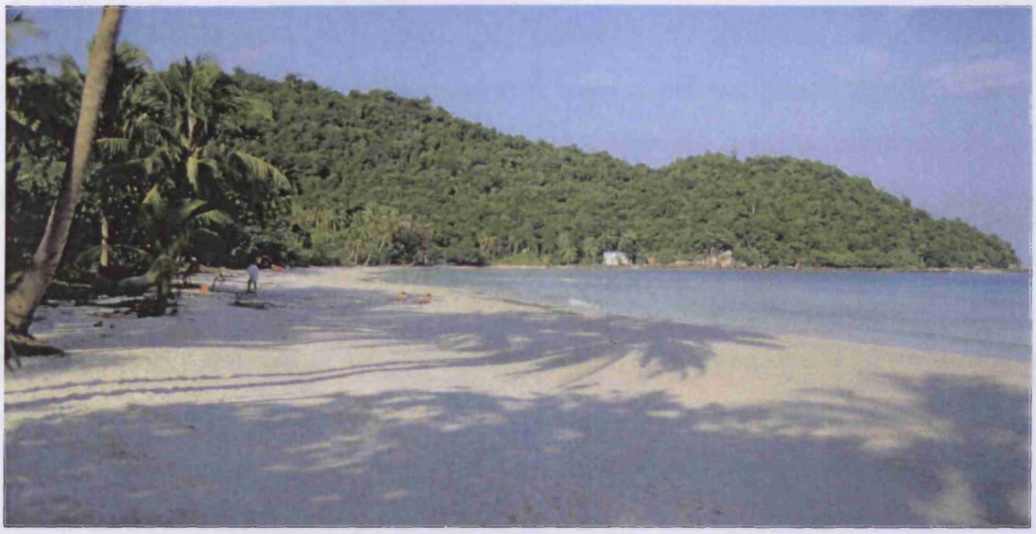


Figure 18: Vietnamese coastal scenery
Source: http://www.discoverphuquoc.com (1)

Figure 19: inshore Vietnamese fishing boats
Source: http://www.seacology.org (1)

Aside from the physical, chemical and biological impact oil can have on the environment; humans are vulnerable to spilled oil at a number of levels. Health is an issue, not solely through contact with spilled oil but through the risk of ingesting oil that has been taken up by a tainted organism. Vulnerability of a society to an oil spill can be quantified by the ability of that society to adapt and manage the circumstances of the spill (BIOREM Handbook 2006). Economically, oil spills can cause disruption to livelihoods, damage fishing and agricultural areas and force a community to adapt to a changing environment. The social impact of an oil spill is most influenced by the resource dependency on coastal and marine flora and fauna of the affected communities.

Research into the feasibility of bioremediation in sheltered vulnerable shoreline environments has been carried out (Wright A 1997, Burns K 2000, Duke N 2000). The results of the studies carried out on mangrove swamps and salt marsh environments showed that in salt marshes up to 72% of the hydrocarbons spilled were removed by microbial action. It was noted that air temperature affected the speed of microbial degradation and in lower temperatures the rate reduced to 56% (Wright A 1997). Mangrove swamps are particularly vulnerable to oil and in the event that the oil is not treated it can persist for decades (Wright A 1997). It is noted that absence of oxygen in mangroves is an inhibiting factor for microbial action. Results from studies by Burns K *et al* 2000 in Australia stated that bioremediation accounted for a 20% decrease in oil presence and the addition of fertilisers further contributed to degradation. It was noted during the study that species of tree and worm which are vital to the ecological balance of the mangroves studied were not adversely affected by the presence of bioremediation agents (Burns K 2000). Considering these factors, it can be said that a range of Vietnamese coastal ecosystems are suited to bioremediation as a mechanism to remove oil while minimising the potential environmental damage associated with mechanical oil removal. The Vietnamese coastal zone can also be classified vulnerable due to a dependency on tourism and coastal and marine resources.

3.4.3.3 Oil spills

If the issue of vulnerability is aligned with that of oil spill management, an economic diversification program can be implemented where alternative employment opportunities are promoted in areas highly dependant on fisheries and marine and coastal resources. In Vietnam, poverty is defined by food security; if the amount of rice per capita per month is below 25kg in urban areas, 20kg in rural areas and 15kg in highland areas, the person in question is deemed to be below the poverty line. By these standards over 90% of Vietnam's rural population is poor. This factor suggests that diversification of the workforce can not be achieved prior to addressing the poverty levels (BIOREM Handbook 2006). The increase in Vietnam's industrial activity poses a further oil related threat to Vietnam as it has led to an increase in wastewater production of which the majority is pumped into rivers with minimal treatment. This has resulted in a situation where Vietnam's coral population has deteriorated. With regard to the number of marine oil spills that have occurred in Vietnamese waters recently the volumes have been relatively low. Between 1992 and 2004 all spills that were recorded and led to the loss of over 700 tons of oil per incident were caused by collision, spills below 700 tons were caused either by shipwrecks, collision or loss during loading or through discharge. Of the 29 spills recorded, only 12 had full details available for spill volume, oil type and damage assessment (BIOREM Handbook 2006). This data is key to implementing effective strategies to respond to an incident and to judge the potential impacts of the oil in the short, medium and long term. Spill information and statistics are further core components of developing and implementing oil spill management training and strategies.

The most frequent cause of oil pollution in Vietnam is through maritime transport incidents involving either collision or accidents in ports. Between 1987 and 2001 there were 90 spills in Vietnamese waters of which over 50% came from collisions or loading and unloading related accidents. A further source of oil pollution is the drilling and production industry. There are two types of pollution that are associated with this activity (i) operational pollution involving spillages from day to day activities, and (ii) accidents due to mechanical failure of equipment. Spills of this nature are rare in Vietnam; in 1999 there were 10 recorded incidents. With regard to future developments that may affect the nature shipping and oil spills in Vietnam, the economy and associated industrial activities are growing. The strategic position of Vietnam in the Far East is a significant factor as it is situated on many major shipping routes. It is currently home to 110 ports and with the increase in shipping this is predicted to further rise (BIOREM Handbook 2006).

3.4.3.4 Dissemination of legislation and policy

Vietnamese legislation concerning environmental management and specifically oil pollution is a recent addition to the legislative framework. The key act is the National Plan for dealing with oil spill response. By 2010 the plan aims to be able to respond promptly and effectively to spill incidents with the core aim of minimising damage to the environment and the economy. It also aims to have established mechanisms, policies and organisations from central government to grass roots levels in place (BIOREM Handbook 2006).

The Plan includes facilities designed for different levels of response across the country. The response centres are either 'establishments' or 'regional centres'. Establishments have facilities and equipment available to manage spills of a limited magnitude. The Regional Centres are larger and hold technical information and communication equipment to facilitate and coordinate a response; they also hold spill response equipment and safety equipment for workers (BIOREM Handbook 2006).
Oil spill response activities are implemented at three levels in Vietnam – grassroots, regional and national. Grassroots level strategies are aimed to achieve a degree of self-sustainability in companies that handle oil. The companies devise oil spill contingency plans internally and fund equipment and training needs. In the event of a spill on a larger scale, they are expected to form part of a larger task force. If the facilities of any one company are limited the scheme is designed for them to work with other local companies to respond to a spill incident. Each regional area has a specialist 'oil spill response coping centre'. The centres are controlled and funded by the state and have dedicated professionally trained response personnel. Two centres in the central and southern regions of Vietnam have been developed and based on feedback on their performance, a northern centre has been proposed. It is intended that by 2010 all three will be fully operational. In the event of a spill that is beyond the capability of a regional centre the State mobilizes forces from other regions and organisations. Should the magnitude of the spill be beyond the National response units, the Government would seek the aid of foreign response units and personnel (BIOREM Handbook 2006).

3.4.3.5 Recommendations

With regard to dissemination of data and development of oil spill response centres throughout Vietnam, the following recommendations were developed through analysis of the EU research and the literature review.

- Widespread promulgation of standards on oily waste management and treatment.
- Promulgation of technical guidelines on oily waste management and treatment.
- The use of specialist technology to treat hazardous waste. It has been noted in some cases older technology is attractive to businesses due to reduced cost. Incentives can be introduced to encourage use of more efficient 'green' technology.
- Improvement of monitoring and enforcement of hazardous waste management and treatment procedures. This can be seen to be a partnership between government and industry as opposed to strict policy-led enforcement. Education and dissemination of data regarding environmental and human impacts of untreated hazardous waste can be made available.
- Increased recycling and reuse of treated waste.
- Improvement of public awareness and perception on collection, separation and recycling of contaminated waste. This can be extended further to increasing industry awareness and the provision of further training for personnel who work with oily waste.
- Dissemination and communication of the fundamental principles of the dangers of hazardous waste and associated options for treatment into the curriculum
- Positive incentives, including: reductions in the cost of new equipment, financial offers, positive company image in the public domain prior to fines and warnings being implemented.
- Inclusion of local people in waste management and recycling decision making and implementation in their neighbourhoods.

In order to develop the feasibility of bioremediation as an option for oil spills in Vietnam, a set of guidelines and a training package were designed for managers, decision makers, foremen and students at HE institutions (BIOREM Handbook 2006 (1), Green J 2006, Green J 2006 (1)). The guidelines consisted of technical and scientific material related to bioremediation and site specific input from Vietnamese research partners on the state of the coastal environment, oil spill response and contingency planning and legislation in Vietnam. It can be said that there is a value to having generic guidelines present with the addition of site specific expertise that can be manipulated into training and education packages. The structure of the bioremediation guidelines were as follows:

Table 12: Guidelines for bioremediation

Structure of Guidelines	Conceptual outline
1) Introduction to marine oil pollution *- Environmental impacts* *- Socio economic impacts* *- Case histories* *- Response options* *- Sensitive areas* *- Contingency planning*	- Scientific and technical background - Best practise response options and contingency planning - Implementation of response options in previous case histories
2) Framework conditions in Vietnam *- Oil pollution* *- Contingency planning and legislation* *- Management*	- Vietnam as working example - Current legislation and management options
3) Non biological treatment of oily sand, soil and sediment	- Technical data - Options - Best practise - Relevant companies in Vietnam
4) Bioremediation of oily sand, soil and sediment	- Technical data - Options - Best practise - Relevant companies in Vietnam
5) Guidelines for implementation of bioremediation of oil spills	- Implementation of 11 steps of guidelines - Flow chart in the form of a 'Decision Tree' to aid the decision making process
6) Workshops and training package: Bioremediation of Oil Spills in Vietnam.	- Manipulation of the guidelines into modules for education and training.

	- 2 day training course for professionals in Vietnam - Dissemination of data through project website

Sources: BIOREM Handbook 2006, Green J 2006 (1)

The Guidelines were designed to provide a holistic view of the issue and industry, to focus on Vietnam with regard to protocol and legislation, and to implement scientific and technical information through education and dissemination programmes. The structure of the guidelines is flexible and in theory could be applied to any country, industry or government department. Screenshots of the Guidelines and Training Course can be seen in Figures 20, 21, and 22.

2.2 Sources of Oil Pollution

The precise contribution of individual contaminants by the shipping industry remains obscure and uncertain, mainly due to the quality of the data and the sources from which they are derived. However, it remains a public misconception that oil spills following collisions or tanker accidents are the biggest cause of marine and port pollution. They account only for 5%, or 0.12 million tons, of the 2.60 million tons of oil which end up quietly in the seas each year, while oil and oily waste entering the marine environment from traditional, both, legal and illegal, routine ship maintenance and other operations are more than four times larger (1996: 0.52 million tons) than amounts from accidental cargo spills:

Table 2.2-1: Sources of oil and oily wastes in seawater

SOURCES OF OIL AND OILY WASTE ENTERING THE SEAS		TONS PER YEAR (millions)	%
DOWN THE DRAIN	• used engine oil • oil runoff and wastes from land-based industrial sources • other land-based sources	1.38	53
ROUTINE SHIP MAINTENANCE AND OPERATION	• bilge and tank cleaning • fuel leakages • oily ballast water • oily and wastes • cargo residues	0.52	20
UP IN SMOKE	• atmospheric deposition of hydrocarbons in the seas through air pollution from vehicles and industry	0.34	13
NATURAL SEEPS	• oil released from the ocean bottom and eroding sedimentary rocks	0.24	9
BIG SPILLS	• tanker accidents • accidents of other types of ships	0.12	5
TOTAL		2.60	100

[Wesnigk, Johanna B.; Universitat Bremen: 2005]

Figure 20: Guidelines screenshot

Source: author

Table 2.6-2 Different response options and their advantages and disadvantages

OPTION:	HYPERLINK	METHOD OF APPLICATION	ADVANTAGES	DISADVANTAGES
Sorbents (Offshore)	Oil Spill Responses Summary - sorbents	Can be applied manually or mechanically using blowers or fans For use on sea or land	Useful in clean up operations in inaccessible locations Inexpensive and usually available in large quantities Can be used at sea and on land Synthetic absorbents can absorb up to 70 times their own weight in oil	Used sorbents present are a toxic waste hazard and need to be disposed of property Some absorb water as well as oil and can sink Some lose particles in the water and are hard to collect after use Can be used once only. once absorbed, the oil cannot be released Can be hard to apply in windy conditions
Shoreline clean up	Oil Spill Response Summary - shoreline clean up	Manual or mechanical	Good political strategy Aids recovery of amenity beaches and protected areas of shore	Potential cause of environmental damage Requires extensive communication and logistics Inaccessible areas of shore may be impossible to reach Care must be taken not to remove excessive amounts of substrate Aggressive techniques such as high pressure water jets and sand blasting harm flora and fauns

Figure 21: Guidelines screenshot 2

Source: author

The Environmental Impact of Marine Oil Spills:

This section contains information in the three tiers of detail.

Tier One	Environmental Impacts of Marine Oil Spills
Tier Two	Environmental Impact of Spills overview of content
Tier Three	Environmental Impact Links

Contingency Planning for Marine Oil Spills:

This section contains the three tiers of information and additional reports on the ITOPF and IPIECA perspectives on contingency planning. It also includes a link to the EPA guidelines for bioremediation report (163 pages) and a link to the contents of the report for quick reference.

Tier One	Contingency Planning for Marine Oil Spills
Tier Two	Contingency Planning overview of content
Tier Three	Contingency Planning References
ITOPF	The ITOPF Perspective
IPIECA	The IPIECA Perspective
EPA Contents	EPA Bioremediation guidelines contents
EPA Report	EPA bioremediation guidelines report

Figure 22: Training course screenshot

Source: author

It may be considered that the biggest challenges facing personnel in an oil spill response operation are the unpredictability of the event, the volumes and dynamics of the oil and environmental variables. These factors necessitate the need for a comprehensive, holistic management system that starts in advance of, and finishes beyond, the timescale of the incident and the clean up. Dissemination of protocol, procedure, practical, skills and best practise is a cost effective technique to develop the next generation of environmental managers (Vastag G 1996).

3.5 Disposal of oil spill debris

Disposal of oil spill waste was investigated as one aspect of the preliminary research into the laboratory and *ex-situ* data collection. Options, procedures, best practice and cautions were researched for integration into the investigative rationale. Environmentally friendly disposal of debris collected off the shore and water surface after an incident is a substantive undertaking. Post *Torrey Canyon*, 4,000 tons of oil and oil emulsion was removed from Guernsey and 4,200 tons from French beaches. (http://greennature.com (1)) Post *Prestige*, data shows that 23,428 birds were affected by the pollution by May 2003, of these, 75% were found dead. (www.panda.org (1)) The *Tasman Spirit* ran aground off the coast of Karachi, Pakistan in 2003, on August 14th between 500-600kg of dead fish were recovered. (http://www.reliefweb.int (1))

Figure 23: Oily waste bagged ready for incineration after *Exxon Valdez* - Alaska
Source: http://www.adn.com (1)

The impact of oil spill waste can affect:

- The aesthetic appeal of a coastal area
- Economic value
- Human health
- Safety
- Living conditions for surviving wildlife?
- Physical quality of the natural environment?

The IPIECA (International Petroleum Industry Environmental Conservation Association) has developed a package designed to aid responders with disposal of waste after an oil spill.

3.5.1 IPIECA perspective

The IPIECA have devised a 'waste hierarchy' that is focused on waste reduction and recycling to minimise the amount of waste produced after an incident. (IPIECA/Energy Institute/Cedre 2004). In the case of a marine oil spill, this can be affected by circumstances surrounding the spill over which the clean up operators will have little or no control. An example of this would be emulsification of the oil offshore which leads to a higher volume of material requiring collection and disposal. Other factors that affect the amount of oil that reaches a given coastline include: the rate of evaporation, spreading, dispersion, solution, emulsification, biodegradation and photo-oxidation (http://www.amsa.gov.au (1)). The resultant debris is classified into two groups (IPIECA/Energy Institute/Cedre 2004).

1) *Recovered oil.* This can turn into oil-and-water emulsions *post*-spillage and can be difficult to pump and store. If the pour point of the oil is higher than the ambient temperature, heavy residues of oil are left if *in situ* burning is carried out.

2) *Oil spill debris.* This can include oiled algae, pebbles, rocks, sorbent materials, wood, plastics and moribund flora and fauna. This additional volume of material can complicate collection and disposal of oil. It has been estimated that after a spill, the amount of debris requiring disposal is five times the amount of oil spilled taking into account the entrained water (IPIECA/Energy Institute/Cedre 2004).

A key factor in managing oil spill waste is separation. The IPIECA have devised a 'classification by source of pollution' technique. In this system, waste is channelled into separate storage depending on the most suitable containment option (http://www.amsa.gov.au (1)). It is recommended that vulnerable beaches are highlighted in local and national contingency plans and strategies put in place to clear these beaches of waste before the oil grounds. Segregation of waste types at source, covered containment sites to prevent rainwater and contaminant infiltration and re-use of recovery equipment are advised techniques. Sorbents are most efficient if used sparingly and effectively (IPIECA/Energy Institute/Cedre 2004).

Figure 24: Waste oil collection
Source: http://www.dec.state.ak.us (1)

In the immediate aftermath of a spill, facilities for emergency storage of waste are necessary. Emergency storage areas should be:

- Close to the centre of operations,
- Easily accessible,
- A flat pan area with one access route in and out to minimise further contamination.
- Sorbents should be easily accessible should there be any spillage.
- Storage sites are recommended to be above high water springs.

It is possible to store large quantities of liquids by digging large pits and lining them with heavy gauge oil impermeable materials such as PVC or oil resistant rubber. If there is material mixed in with the liquids then it must be filtered and disposed of separately. Remaining issues include the financial and logistic aspects of providing storage pits and appropriate measures transport and disposal of the liquids. There are a range techniques available for the final disposal of treated waste.

Table 13: Options and implications for oil spill waste disposal

Option	Application	Cautions	Benefits
Land farming	waste is spread and mixed in with soils to aid aerobic microbial degradation	- site to be located away from water - low soil permeability necessary - flat land necessary to reduce leaching	- aerobic nature of land farming is more efficient that anaerobic landfill sites - contaminated material can be applied directly - site can be reused or used for other purposes - suitable for building on post remediation
Landfilling with refuse	oil is incorporated into a landfill site with municipal or industrial waste	- overloading can lead to leaching of oil - sites with sufficient capacity to accept and cover waste should be chosen - potential ignition – volatile components must be dispersed.	- few arrangements have to be made to take oily waste at existing sites - oiled debris can be mixed with other waste and used an a sorbent
Burial	oil is buried in pits, or other depressions prepared for disposal, the excavated soil is used as a final cover for the waste.	- oil toxicity - oil leaching to groundwater - long term presence of oil - disruption to flora and fauna	- burial close to site of origin lessens costs and time - no mixing required
Bioremediation	Metabolic utilisation of organic compounds by microorganisms	- inexpensive with low energy requirements - technically sophisticated is not required	- rate of oxidation is temperature dependant - presence of toxins or lack of oxygen, nitrogen or phosphorous can inhibit degradation - large land areas are necessary - no energy is recovered from the oil
In-situ burning	Burning the oil at the site of the incident	- simple - fast - can remove high quantities of oil - cheap - versatile - reduces volume for storage	- requires specialist equipment - air pollution - flashback - secondary fires - burn residue is highly viscous
Incineration.	Waste is removed and incinerated at a dedicated facility	- cost of transportation- - pre-treatment of waste may be required - cost of using dedicated facility	- efficient - volume reduction of waste - filters on chimneys reduce air pollution

Sources: Champ A 2003, Nordvik A 1996, AMSA 2004

If the options displayed in Table 13 are considered, the most effective option for an incident will depend on the circumstances of the spill, and the facilities and budget available for clean up. Regarding the composition and volume of waste material produced, and methods of disposal, options were researched in the conceptual design of the lab and *ex-situ* data collection. If oil is to be used as fuel, quality restrictions are stringent and restricted by safety, corrosion (due to a high chloride content) and the presence of toxic suspended solids can affect the suitability of a product as a fuel source. High water content may restrict combustion to the point where auxiliary fuel is needed (IPIECA/Energy Institute/Cedre 2004). Regardless of the treatment technique, environmental monitoring is necessary to manage environmental pollution such as surface runoff and settlement of oily residues, contamination of groundwater, retarded oil degradation and contaminated vegetation. Strategies can be put in place to counter these threats including monitoring of groundwater and oil-soil mixtures http://www.amsa.gov.au (1). The health and safety of the workers involved in the clean up can be addressed through health and safety equipment and clothing being made available to all personnel. The risk of secondary contamination can be reduced the designation of 'clean' and 'dirty' sites at the work site, decontaminating personnel and equipment, lining all containment vehicles and checking all storage is oil proof.

The UK MCA (Maritime and Coastguard Agency) provides technical guidance on waste minimisation and segregation in the UK for oil spill situations and their recommendations are as follows:

Table 14: MCA guidance on waste minimisation

Wastes generated	Stages of clean up	Logistics
Oiled equipment Recovered oil Oiled seawater and vegetation	Waste segregation	- Classification of waste type and source - Waste to be channelled into separate storage areas - Appropriate containers for waste type sourced
Oily water Oily sorbents Oiled beach material Oiled flotsam and jetsam Seabird and shore life carcasses	Waste minimisation	- Potential impact sites identified before oil reaches the shore - Impact sites to be cleared of rubbish before oil has beached - wastes segregated at source - contaminated sites to be covered to minimise runoff in the event of rain - Oiled recovery equipment reused not discarded - Sorbents used sparingly and effectively
	Secondary contamination	- Potential spread of oil by people, transport and equipment - designated 'clean' and 'dirty' sites designated - Personnel and equipment decontaminated before leaving clean up zone

Source: http://www.mcga.gov.uk (1)

For waste oil from a spill incident to be considered an economically viable source of fuel, the purer the oil recovered the higher the chance of it being suitable (Otay E 2000). If the range and composition of waste collected in the wake of an oil spill is considered, factors including the amount of flora and fauna, sediment and beach detritus will affect the value of the recovered oil as a fuel source. The key factor to consider is the extent to which the oil has emulsified as the higher the water levels in the oil, the higher the volume of the waste and the less likelihood that the oil will combust. The decision making process regarding whether an oil that has been spilled is a suitable source of fuel is ideally started prior to clean up so that oil collection and contaminant reduction can be maximised. The *Volgoneft 248* spill incident used the calorific value of the waste oil as a benchmark for cleanup. It is discussed later in the chapter.

3.6 Use of oil spill waste:

Waste from a spill can be utilised in a variety of ways that results in reduced volume and in some cases, financial profit. Research has showed that there are a number of microorganisms present in soil that have an ability to degrade components of crude oil (Genouw G 1994). The concept of using these micro-organisms as an oil treatment technology was first developed in the USA 40 years ago (Genouw G 1994). The process of refining crude oil requires large amounts of water, and if this water becomes contaminated it may then contain chemicals from the crude oil and a range of additives that are used in the fracturing and refining processes (Shailubhai K 1984). Soil provides a natural environment that is capable of breaking down such chemicals through bioremediation. Micro-organisms that are present in oil degrade the oily sludge into intermediate substances such as alcohols, phenyls and fatty acids and these are converted into carbon dioxide, water and basic cellular materials (Venosa D 2000). An issue with the treatment of oily waste is that the variety of materials in the sludge makes the composition and the efficacy of subsequent treatment variable. The most common techniques for treatment of the sludge are gravity thickening, vacuum filtration, dumping into lagoons, the ocean or landfill. Dumping into the ocean is no longer deemed a viable option as many marine organisms rapidly accumulate heavy metals. Incineration is not generally considered an option as the energy cost and emissions make the process unattractive to industry (Venosa D 2000).

3.6.1 Energy potential of waste oil

3.6.2 Technology

This section covers the potential energy value of waste oil recovered from spill incidents. The first section details options for treating marine and coastal oil spills with heat, further case studies are then studied analysing the use of alternative types of oil as fuel. This research was carried out as the feasibility study into the laboratory and *ex-situ* field work.

With regard to oil spills in coastal and marine environments, several options have been researched to reduce oil volume and toxicity using heat.

3.6.2.1 Thermal desorption:

Thermal desorption is a process whereby pollutants are removed from sand, soil or other material by the application of heat to alter the pollutants from a solid to a liquid. The resulting flue gases are collected and the dust and toxic components are separated for disposal. The principle behind thermal desorption is that it increases the speed and efficiency of removing pollutants from the environment and reduces costs. The process can be carried out both *in situ* and *ex situ* (Araruna JT 2004). The *in situ* process involves heating either the surface of the contaminated material or applying heat through wells. The heat converts both groundwater and any water in the soil catena or sand profile to steam which evaporates the hazardous chemicals in the pollutant. The length this process requires depends on:

- Nature and amount of chemicals present
- Nature and depth of the polluted area
- Type of soil and conditions present (Araruna JT 2004).

Research by Arajuana JT *et al.* in Brazil trialed *in situ* and *ex situ* thermal desorption. The *ex-situ* tests were carried out to determine the required temperature and timeframe of clean up for an efficient response. The tests were conducted on 50g oil samples and were exposed to temperatures between 100 and 500°c for between 2 and 8 hours. The relative success of this technique was quantified by analysing the total oil and grease content exposed to the range of temperatures. To test this approach, samples were tested at two wavelengths, one that is strongly absorbed by hydrocarbons and the other where limited absorbtion occurs (Araruna JT 2004). The results of this test show that the oil and grease content decrease rapidly with increasing temperature. When the samples were exposed to temperatures of over 850°c, trace amounts of oil remained in the debris.

The *in-situ* tests were carried out on polluted material that had been placed in a masonry tank. A thermal 'blanket' was placed on the tank with two heating elements at 1200°c. The results from the wavelength tests showed that the oil coating the debris had been 100% removed to a depth of 20cm. Lower than 20cm, the technique was less effective due to the rapid decrease in temperature away from the heating elements. The results showed that only material that had been exposed to temperatures over 300°c had been cleaned (Araruna JT 2004). The issue of depth and a related drop in temperature can be resolved by placing the heating elements at varied depths; however, this may limit the effectiveness of cleaning at the surface due to it being over the desired temperature. This is one of the substantive cautions of the system and limits the rate of success for subsurface cleaning. Despite this, the results from the tests show that desorption is an effective technique for cleaning contaminated sediments as it also further avoids the costly process of having to remove the contaminated sediment for treatment elsewhere (Araruna JT 2004).

3.6.2.2 Land farming:

Land farming has been identified as a successful treatment option on-site at oil refineries (Venosa D 2000). The technology involves spreading oily sludge in 10-15cm layers, allowing it to dry for seven days, adding fertilisers and mixing the sludge into the soil. Breakdown of the waste is achieved by aerobic micro-organisms in the top layers of the soil where there is sufficient oxygen available (Genouw G 1994, Venosa D 2000). There are a range of parameters to be considered in this process. The breakdown of oil in soil is a slow process that involves a complex mix of chemical, physical and biological factors. The impacts of tillage, soil texture, temperature fluctuations all change the rate of degradation.

A study into the landfarming of oily waste was carried out at Ghent harbour in Belgium (Genouw G 1994). The purpose of this study was to determine the optimum treatment for the process, to demonstrate that the process is an appropriate technology for the remediation of oil sludge, and to illustrate that landfarming had no deleterious effects on the environment in terms of groundwater quality, toxicity to micro-organisms and plant growth. Field trials were carried out after the laboratory experiments. The test site was excavated and the oily sludge (40% hydrocarbons) was mixed with soil from the upper 30cm of the site and fertilisers and a starter inoculum were added. Regarding the different fractions of crude oil, the following observations were recorded: the fraction of aromatic compounds decreased strongly, the fraction of asphaltic hydrocarbons proportionally increased, and the levels of saturated hydrocarbons stayed constant. The explanation for the stable level of saturated hydrocarbons is attributed to the degradation of aromatic hydrocarbons involving the production of saturated hydrocarbons (Genouw G 1994). Experimental design such as that carried out by Genouw *et al.* highlight the range of fractions that are degradable and the necessity for knowledge of the oil constituents with regard to potential degradation through landfarming.

A variable that was tested by Genouw *et al.* was the presence of leaching from the trial site. The movement of oil, nitrogen and phosphorous over the first four years of the experimental work was minimal. Percolation levels of hydrocarbons, nitrogen and phosphate increased minimally *post* oil application. Analysis of variance showed that there were no significant defences between the sampling sites and times (Genouw *et al.* 1994).

Having established the range of possibilities in landfarming and detailed the extent to which the technology works, the following conclusions were drawn: The addition of minerals increases the rate of biodegradation, in view of its low toxicity and effectiveness; acetone was highlighted as an effective solvent for the extraction of soils and sediments polluted with hydrocarbons. The research further highlighted that varying fractions of crude responded to microbial action to greater and lesser extents. Fractions such as aromatic compounds degraded to a greater extent than heavy saturated hydrocarbons. With regard to the environmental impact of landfarming, the research showed that leaching of contaminated material from the test site was minimal and was not deemed to be a threat to local groundwater. If appropriate technical and structural procedures are followed and sufficient time for degradation is provided (minimum 15 years) the research stated that biodegradation of petroleum hydrocarbons through landfarming was an effective way to treat crude oil (Genouw *et al.* 1994).

3.6.3 The *Volgoneft 248*

3.6.3.1 Background

On 29 December 1999, the Russian tanker *Volgoneft 248* broke in two off the Sea of Mamarra near Istanbul spilling 1578 tons of heavy fuel oil (Moller T 2002). The storm force winds that led to the incident played a key role in spreading the oil along the coast. Five kilometres of coast were affected including rocks and concrete structures at the resort of Florya. The majority of the oil was deposited above the high water mark and formed a continuous band of oil between 2 and 10 metres wide and up to 5cm thick. Due to the low temperatures that prevailed in December, the oil was viscous but soon penetrated into the spaces between the sand grains; it was covered by fresh sand on the next high tide. At a number of points along the beach a 1-3cm layer of oil was prevalent between 3 and 30 centimetres below the surface of the sand (ITOPF 1999). The heavy fuel oil that was spilled had a specific gravity close to that of sea water and as a consequence, substantial amounts of oil were mixed in with sand, mussel shells and other debris. The gravity of the oil also led to the un-recovered portion of the spill sinking either through attachments to water molecules or sediment, or due to turbulent sea conditions. The residual contamination resulting from this process led to long term contamination (Otay EN 2002).

3.6.3.2 The Clean up

What sets the response to *Volgoneft 248* spill apart from a standard containment and removal operation was the nature of the payment method used in the clean up. The amount of money paid to the workers was determined by the calorific value of the oil they collected.

Figure 25: The hull of the *Volgoneft* 248 *post* impact
Source: http://www.riverships.ru (1)

An action plan was put in place by ITOPF (International Tanker Owner Pollution Federation) on January 1 2000 outlining the shoreline clean up strategy. An average of 133 men worked every day, their core priority was to remove the accumulations of oil on beaches and concrete platforms, and to ensure the most efficient clean up strategy - this was done using hand-held tools and shovels. The waste was stored in plastic bags prior to transportation to the disposal site; the average rate of removal was 50m² per man per day. The main deposits of oil were removed but small tar pieces remained. The technique employed to remove these was to sieve the upper layers of the sand, a time consuming yet effective technique (Figures 26 and 27). Every effort was made to remove the oily waste with minimal contamination; this was partly due to the cost issue and for this reason front end loaders were not used to remove large amounts of oil due to the amount of sand they collect. By March 14th, 4,535 tons of waste had been transported in 314 trucks (ITOPF 1999). The oily waste was delivered to a local incineration plant.

Figure 26: Florya Municipality Recreation Facilities (29 December 2000)
Source: Moller TH 2002

Figure 27: Florya Municipality Recreation Facilities (7 April 2001)
Source: Moller TH 2002

The technique used to manage the recovery operation was known as a 'no cure-no pay' contract. The contractors in charge of the recovery operation charged an agreed rate for the amount of pure oil that was recovered. This approach proved a success for a variety of reasons: It maximised the efficiency of the response operation whilst discouraging the recovery of material other than oil. As soon as the calorific value dropped below an economically viable level, the clean up ceased. The commercial incentive provided by this approach can also quantify the issue of 'how clean is clean?' The cut off point for collection when there are only small pockets or widely distributed sheens of oil remaining is simpler to determine if there is an incentive of contaminant reduction in the collected material (Moller TH 2002). Approximately a quarter of the waste collected was pure oil and its overall value was quantified by determining the known calorific value of the total cargo. It was assumed that the calorific value of the spilled oil and the original cargo was the same and that the calorific value of the contaminants in the spilled oil (including: water, beach materials and sediment) was insufficient to skew the results. The highest calorific value recorded was 22,070 kJ/kg implying an oil content of 55%. The batch of oil this result came from appeared visually to be pure oil with no sand or debris. The remaining 45% was composed of water droplets contained in the oil. The average oil content in the material sent for testing was 11,627kJ/kg or 29%. Any waste that recorded an oil content of less than 1000kJ/kg was sent to landfill (Moller TH 2002). In phase one of the initial clean up, the equivalent of 654 tons of oil was collected by 133 men taking 8919 man days of work. In phase two, the systematic clean up of beaches was initiated using manual sieving techniques and rakes. Of the 968 tons of material that were recovered, 73 tons were oil; this is roughly equivalent to 5% of the total spill volume. Calculations carried out over the entire clean up operation showed that 50% of the spilled oil was unaccounted for. The data suggested that the majority of it sunk and was lying on the seabed close to shore (Otay E 2002).

Attempts were made to collect the oil from the seabed; a total of 1488 tons was recovered with an oil content of 25%. This is around 14% higher than the level of recovery in the shoreline cleanup. Of the 1488 tons that were collected around 368 tons were pure oil (23% of the spill volume). The collection rate was higher than the terrestrial work, this was though to be due to the sunken oil lay in thick deposits on the seabed and was often more accessible than the oil on the shoreline (Otay E 2002). The payment rate was US$7000 per ton and it was recognised that the clean up would become more complex and restricted as it progressed, so an 'escalator system' in the payments was implemented. The payment rate would increase in certain defined areas dependent on the quantity of pure oil that had been recovered. This process served as an incentive to the contractors to recover oil that had been buried under the sand (Otay E 2002). It was thought that the 'no cure-no pay' technique employed was an effective way of measuring the effectiveness of the response operation. The aims of maximising the amount of oil recovered and reducing the amount of shoreline pollution in times of onshore winds was achieved. It also set the financial boundaries for all parties involved prior to the clean up commencing; this reduced any potential delay in complications to the clean up being further held up by discussions over pay. Regarding the use of this method to other incidents, the research by Otay E *et al.* suggested that it would be feasible to utilise the technique for bulk removal of oil from shorelines. It was not deemed suitable for fine scale shoreline oil removal, as the benchmark for success of such operations is typically based on visual aesthetics as opposed to the calorific value of the oil recovered.

3.7 Conclusions

Having reviewed selected oil spill response incidents from the last 50 years, it is possible to comment on how the philosophy of spill response incidents has changed over time. It can be said that in the era of *Torrey Canyon* and to some extent, *Exxon Valdez,* the response operations were a series of reactions to an incident as opposed to the results of pre-determined development and research. This statement can be supported by the resulting changes in policy and response implementation in the wake of *Torrey Canyon, Exxon Valdez* and *Braer*. A relatively recent change in the science and philosophy of responding to an oil spill is the concept that each spill incident and the inter-relationships between the environment, oil and associated impacts demands a highly specific response operation. Emphasis has swung away from rapid mechanical and chemical treatment of oiled shores based on the philosophy that use of heavy machinery and chemicals was justified by an oil free environment in a relatively short time frame. The concepts of NEBA and Time Windows of Response highlight the fact that rapidly ensuring an oil-free environment in the wake of a response operation is insufficient and that in some cases leaving the oil *in-situ* can be an environmentally benign option. If this is not the case then the response can be designed specifically for the oil type, extent of oil weathering and environments that have been affected. This is highlighted by the case study examining the role of bioremediation in responding to oil spills in Vietnam. As an option for breaking hydrocarbons down into their constituent properties with minimal environmental disturbance, bioremediation is well established. An environment that is particularly vulnerable to oil spills due to its anaerobic state and subsequent inability to metabolise oil, mangrove swamps are ideal environments for hydrocarbon bioremediation. This is further supported by the fact that they are highly sensitive to disturbance and thus unsuitable for mechanical removal of oil.

Typically, the waste from a marine oil spill is either disposed of in landfill, incinerated, or treated through options including thermal desorption or landfarming (IPIECA/Energy Institute/Cedre 2004, Araruna JT 2004, Venosa D 2000, Genouw G 1994). An area of limited research in terms of disposal of oil waste is utilising it as a source of fuel. The response to the *Volgoneft 248* incident highlighted the potential of waste oil in terms of its calorific value. However, the oil was either disposed of in landfill or incinerated (Moller TH 2002). The science and logistics of generating energy from waste sources is established, the papers of a range of researchers including: Kumar S 2000, Umberto D 2003, Ferrer E 2005 and Pacey J 1999, demonstrate the protocols, techniques and options for utilising energy from waste. This research aims to bridge the gap between the management of an oil spill response operation and generating energy from waste sources through quantifying the application of oil spill waste as a fuel source. A data set of the carbon content of a range of oil-sorbent compounds can provide a benchmark for further research and investigation into waste oil use. Comparisons between oil-sorbent-substrata and associated efficacy of oil removal can provide a preliminary database of the optimum combinations of oil, environment and response strategy.

The efficacy of education and training as a technique with which to disseminate and promulgate information is established (Vastag G 1996). In light of the distance learning initiatives, training courses and workshops that were designed and implemented in the Far East; it would be feasible to use these options and approaches to further develop the concept of using oil from marine spills as fuel. There is potential to integrate the concept into environmental management strategies, oil spill response research, energy generation and waste disposal through the integration the management of marine oil spill waste with small scale industrial and terrestrial spillages. From this there is scope to view energy from oil spills as part of the wider waste oil industry, this is further reinforced by the point flagged in Section 3.2 that only 5% of the worlds oil spills are sourced from major spill incidents. The substantive contributor to this statistic is small scale industrial and commercial spillage.

The next chapter of the thesis contains the laboratory and *ex-situ* field data that was collected and analysed to determine whether waste oil from marine spills is a potential source of fuel.

4 Chapter Four: Potential of energy from oil spill waste.

4.1 Concept of research

The experimental design for the laboratory and simulated *ex-situ* field trials was developed to determine the efficacy of a range of commercially available oil sorbents and to determine whether there is a potential for recovered oil and associated wastes from an oil spill to be used as fuel. The study was designed to provide a full data set regarding the range of oils and sorbents and interactions between them used in the tests. This was achieved by:

- Research into their structure and characteristics.
- Research into sorbents ability to retain oil and the behaviour of the spilled oil. A selection of oils was chosen with varying weights, viscosities and behaviour.
- Analysing the structure of the sorbents under an SEM (Scanning Electron Microscope).
- Designing a series of tests (pixel analysis, carbon content and percentage recovery) to analyze their performance.

The substrata used were selected to determine how their porosity and the degree of weathering affected the results. An aspect of the decision making process into carrying out the research was the decision whether to deliberately pollute with the aim of further developing responses or to react to an incident and trial a potentially less effective option. Waiting for an incident was not deemed an option as it was possible that the 'right' type of spill would not have occurred for the scope of the research, additionally it would have only provided the opportunity to sample in the environmental conditions at the time of the incident. This would limit the validity of the application of this research in the wider field.

Deliberate pollution was not deemed feasible as there was no way to guarantee 100% retention of all materials spilled. With these factors in mind it was decided to carry out simulated *ex-situ* fieldwork at a specialist facility in Southampton.
The conceptual development of the research was composed of the following stages:

- A study of the structure of crude, refined and weathered oils.
- Analysis of behaviour of spilled oil at sea.
- Principals, techniques and application of absorption and adsorption.
- Case histories.

Oil type, sorbent and substratum were kept constant in all data sets. Every combination of the three was tested in each environment and five replicates of each combination were collected. The data collection was focused in three core areas:

- Analysis of the pixel distribution of unoiled, oiled and cleaned substrata. Images were taken before, during and after oiling and the distribution of pixels analysed to determine how close the cleaned image was to the control.
- Compounds of oil and sorbent were collected, dried and incinerated to quantify their carbon and moisture contents.
- The total weight of oil and sorbent was weighed prior to application to a substratum and re-weighed post recovery to quantify the percentage recovery of the oil-sorbent compound.

4.2 Materials and products used

4.2.1 Oil

The oils used were selected to cover the widest spectra of oil types that are recovered using absorbents or adsorbents. It was decided to test both crude and refined oils. The crude that was chosen was Statfjord Light Crude. Statfjord is a light low sulphur North Sea crude, it is transported from the oil field off the Norwegian coast to destinations throughout Europe, approximately 180,000 barrels are produced a day. Its pour point is -2°c. Light crude oils have a tendency to be highly fluid, they spread rapidly on water and solid surfaces, they have a high evaporation rate and are flammable. If they are spilt on porous substrata, they have a tendency to soak in; this can restrict the amount of oil which is recoverable from an incident. They do not adhere to surfaces and can be removed by flushing with water. They are highly toxic to humans and marine and coastal flora and fauna http://www.epa.gov (1). The second type of oil used in the study was a refined motor oil. 2050 grade oil is designed for modern high performance car and marine engines. It is available for use on all types of suitable engines. It disperses quickly, its flash point is 220°c and its pour point is -15°c. It is highly persistent in the environment (http://www.epa.gov (3)). The third type of oil used was provided by OSRL (Oil Spill Response Limited) in Southampton. It had been recovered from a spill and was composed of a range of crude and engine oils, it had been subjected to weathering and had become an oil-in-water emulsion prior to recovery.

The oils were chosen to firstly highlight the behaviour of different oils under different environments and environmental conditions, and secondly to illustrate the difference in behaviour of a spilled crude and refined oil. When the oil comes into contact with the surface of the water it is subjected to a range of weathering processes, this factor formed part of the justification to source and include oil recovered from the environment following an oil spill incident.

4.2.2 Sorbents

A range of adsorbents and absorbents were used to recover the oil from the substrata. Absorbents draw the oil off the surface of the rock or water and in the case of the products used in the research either soak the oil up into a porous structure or use a complex folded structure and a high surface area to trap the oil. Adsorbents attract the oil to their surface but do not take it into their structure. This can make separation easier than with absorbents.

The first absorbent is Olyjn peat, it is produced as a by-product of the energy industry in Finland and sold as a specialist absorbent for oil. It has a porous structure that absorbs oil, if the spill occurs on water it is possible to compress the peat post application, the water drains out and the oil remains bound in the peat structure. The second product, Klausorb, is commercially manufactured by a company called Paulex. Klausorb is a recycled product made from old fridges and freezers. It is hydrophobic meaning oil, not water will be absorbed. It can be disposed of by residue free incineration or by landfill and is non toxic. The third product is an adsorbent called Recoverit, it is commercially produced in the USA by Robinsons. Recoverit can adsorb up to ten times its own weight in oil and is biodegradable under ultra-violet (UV) light (i.e. sunlight). It is environmentally friendly and can be reused. Once the product has adsorbed the oil it can be placed in a centrifuge for separation. The oil (if of a sufficient quality) and adsorbent can be reused.

4.2.3 Substrata

Milford Haven Port Authority part funded the laboratory and *ex-situ* simulation trials. The Haven supports two oil refineries, this combined with a high concentration of flora and fauna, ecosystems and protected sites, makes Pembrokeshire an area where spill response has high profile and priority. The rocks selected are typical of Pembrokeshire's geology; two rock types typical of Pembrokeshire are Old Red Sandstone and Carboniferous Limestone. It was decided to carry out the experimental work on a piece of Old Red Sandstone, a piece of smooth weathered Carboniferous limestone and a piece of rough pitted Carboniferous limestone. Carboniferous Limestone was laid down in Great Britain and Ireland in the Dinantian stage of the Carboniferous period. It is a sedimentary rock and is characterized by being jointed in the form of horizontal joints, or bedding planes, and vertical joints. The joints are weaknesses in the rock and are thus exploited by agents of denudation and weathering. They also lead to the most significant characteristic of carboniferous limestone, particularly with reference to oil spill response, its permeability. Old Red Sandstone is a sedimentary rock from the Devonian period. It is a porous rock, with a greater porosity than Carboniferous limestone. The *ex-situ* field trials offered the opportunity to increase the scope of the research in terms of substrata type. OSRL had blocks of stone wall and concrete slabs, representative of sea walls and other coastal concrete structures and a stockpile of marine shingle to simulate pollution in beach environments. These were used in the tests to simulate field conditions as accurately as possible and to further test the validity of the methodology in terms of transferring laboratory analysis to the field.

4.3 Data collection

4.3.1 Pixel analysis

The ability to quantify the success or shortcomings of an oil spill response operation is critical in ongoing analysis of protocol and performance. One technique that has not been utilised to test the performance of oil spill response products is image analysis using pixel distribution as an indicator of product performance. The theory behind this technique is to take a series of images before, during and after a spill and analyze the difference in pixel distribution to analyse whether the response has been successful. The software used for the analysis was Scion Image, designed by Scion Corporation. A breakdown of how the software works is discussed later in this chapter.

4.3.2 Percentage recovery

The purpose of sorbents is to reduce residual contamination by stabilising the waste oil and facilitating recovery of spilled oil. A simple yet effective technique to quantify the success of a clean up is to weigh the material that is recovered from the spill site and compare it to that which was spilled. The accuracy of this technique depends on there being sufficient data on how much oil was spilled and how much of any chosen recovery product was used. In addition, there will be experimental inaccuracies in such an operation. This technique is most suited to onshore operations, laboratory testing of products and terrestrial industrial spills. The higher the percentage recovery the more successful the operation has been.

4.3.3 Carbon content of oil and sorbent compounds.

Tests were carried out on a compound of oil and sorbent to quantify the amount of carbon present. Disposal of waste oil after a spill is an integral part of the recovery operation and incineration is sometimes used as an option to reduce volume of waste oil. There is potential to utilise the energy given off in the incineration process.

4.4 Preliminary data collection and feasibility research

Preliminary research and two series of tests were performed prior to data collection to trial and critically assess techniques and gain more information on the products to be used. A range of behavioural traits of fluid mechanics and the oils physical behaviour were noted prior to each experimental treatment. There are three main factors that affect the behaviour of oil when it is spilled: surface tension, specific gravity and viscosity. The rate at which these factors vary determines the movement and characteristics of the oil and its impact on the environment. The surface tension of a liquid can be described as the measure of attraction between the layer of molecules on the surface of the liquid and the layer directly beneath. The higher the surface tension, the more likely the oil is to remain *in-situ*. The lower the surface tension, the more likely the oil is to flow and spread, if low enough this can happen without the impact of such processes as wind and tide. An increase in temperature can reduce a liquids surface tension, thus oil is more likely to spread on water and substrata in warmer waters than cooler waters http://hyperphysics.phy-astr.gsu.edu (1). The specific gravity of a liquid is the relative density of the substance in question in relation to the density of water. The majority of oils are less dense than water and thus float on it. The specific gravity of an oil can increase if the lighter fractions evaporate http://www.epa.gov (4). Viscosity can be described as the property of a fluid that resists the force that causes it to flow http://www.epa.gov (4). Viscosity affects fluids exerting force on each other or another surface as they move against each other. Viscosity is a critical consideration when responding to oil pollution as it affects the oils ability to adhere to and be removed from a substratum. It also affects thickness and flow rates that affect prediction of oil slick movement and using equipment such as skimmers. The higher the viscosity the thicker and more sticky the oil, this makes it harder to recover from substrata but restricts the amount an oil slick spreads.

In addition to the characteristics of the oil affecting its behaviour at sea, environmental processes affect the nature and composition of the spilled oil. As both absorbents and adsorbents were used in the data collection it was decided to observe them with and without oil under a Scanning Electron Microscope (SEM) to further develop understanding of how they behave when in contact with oil.

4.4.1 SEM analysis of sorbent structure:

This section of the chapter covers the broad concepts of sorbent materials and focuses on the products used for research in this study. From the oil spill clean up perspective, sorbents offer the possibility of comprehensive collection and removal of oil from the contaminated site. The addition of sorbents to oil changes the oils state from liquid to semi-solid, this simplifies handling and collection. It is possible with some absorbent materials to recycle the waste (Adebajo MO 2003). An effective sorbent material must have the following properties: hydrophobicity and oleophilicity, a high uptake capacity, retention over time, reusability and biodegrability. Absorbent materials for oil spills can broadly be classified into three categories: inorganic mineral products (zeolites, silica, graphite and sorbent clay), synthetic organic products (polymeric materials such as polypropylene and polyurethane foams) and organic vegetable products or natural sorbents (straw, wood fibre, and peat moss) (Adebajo MO 2003). Klausorb and RecoverIt are synthetic organic products and peat is a naturally occurring sorbent.

4.4.2 Site selection for *ex-situ* field trials:

OSRL is a specialist Oil Spill Response Facility in Southampton; it is joint owned by 32 international oil companies. The facility is designed to offer training for oil spill response operators and has the capability to dispose of oily waste. Due to Environment Agency regulations and the risk of causing unnecessary pollution, it was not feasible to carry out any research into spilling and collecting oil in the environment. As a training centre with fresh and salt water tanks as well as a range of artificially constructed substrata for training purposes, OSRL offered an alternative to fieldwork. The purpose of the work carried out at OSRL was to scale up from the laboratory work to gain a broader data set and understanding into the role of energy from oil spill waste when a range of systems and processes have acted upon the oil and the environment. The methodology for the work carried out at OSRL was constant with that used in the laboratory. It was decided to keep the amounts of oil and absorbent the same so as to eliminate any inaccuracies with regard to data comparison. The sample area used and oil storage tanks at OSRL can be seen in Figures 28 and 29.

Figure 28: Oil storage tanks at OSRL

Source: author

Figure 29: Sampling area at OSRL
Source: author

4.5 Aims

1) To investigate the efficacy of a range of absorbents in terms of their ability to absorb a given volume of oil spilled on a range of substrata.
2) To determine whether a range of compounds of oil and sorbents are suitable for use as fuel.

4.6 Objectives:

Aim one objectives:

1) Determine the extent to which sorbents remove oil from rocks by analysing the pixel distribution of images of the rocks before, during and after oiling.
2) Determine the efficacy of the sorbents by recording percentage recovery of sorbent and oil after clean up through a comparison of weights pre-application and post-recovery.
3) Compare the data sets from lab and field data to determine the effects of contaminants on the data.

Aim two objectives:

1) To determine the amount of carbon in a compound of oil and sorbent through a series of drying and incineration trials.
2) To compare the results of the carbon trials from lab and field data to determine whether the presence of contaminants in the compound affected its ability to combust.

4.7 Methodology

4.7.1 SEM analysis of sorbent structure

As part of the preliminary research into sorbent structure and the ways in which sorbents retain material, it was decided to analyse their structure under a Scanning Electron Microscope (SEM). The sample preparation process for the SEM was as follows: Samples of the sorbent with and without oil were mounted on a 12.5mm pin stub. They were coated in a gold palladium layer to minimise the effects of charging in the SEM chamber. Once coated, the samples were placed in the SEM and a range of images were taken at different resolutions to visualise the structure of the sorbents with and without oil.

4.7.2 Pixel analysis

Laboratory methodology:

The first stage of the data collection was to obtain control images of the three substrata. They were wetted to simulate tidal coverage, photographed and placed in a large plastic dish; 50ml of oil was weighed and then poured onto the surface of the rock from a height of 10cm. 50 ml was deemed an amount sufficient to cover the rock and assessed as being satisfactory for the scope of the project. The oil was left to settle for three minutes and then photographed. 20g of sorbent was weighed and applied to the rock. Rock and sorbent were left for three minutes to allow the sorbents to act; the mixture of both was then collected and weighed. The techniques used to remove the oil and sorbent from the substratum were brushing, washing with cold water and washing with cloths. The rocks were washed for two reasons, firstly to simulate the effect of tidal washing on the clean up and secondly to prepare the rock samples for further tests. Once cleaned, the rocks were photographed again and the distribution of pixels compared with the control image. It was decided that the refined oil would be used first as this left little or no stain on the rocks after clean up. This was followed by the weathered product and the crude oil. Had the crude been used first staining would have affected the validity of the results for the refined oil. Preliminary tests were carried out to determine the amount of oil necessary to cover the rock and the amount of sorbent required to soak up the oil.

OSRL methodology:

This technique was applied to the tests carried out in the laboratory and the tests carried out in Southampton on the stone wall and concrete slab. Due to the difference in size and the behaviour of the shingle in the environment, an alternative technique was used to clean the shingle. A wooden frame was constructed with a steel mesh attached to it (Figure 30). Once the oil and sorbent had been applied, the shingle was placed on the mesh frame and shaken for one minute, the debris that fell through the frame was collected in a tray below and measured. The aggravation time was calculated by carrying out trials on the materials and deciding the most appropriate time to collect the sorbent. For the tests that involved aggravation and washing the shingle was placed in a plastic container and washed using the same techniques as the laboratory tests.

Figure 30: Mesh grid for aggravation of shingle samples
Source: author

Figure 31: Split tank for shingle washing
Source: author

The tests were run 5 times as to eliminate any anomalous results and for the sake of statistical analysis. The samples were photographed after clean up and a database of all possible combinations of oil, absorbents and rocks was complied.

It is noted that the techniques used to clean the rocks were less aggressive than others that could have been used. These techniques were selected to demonstrate that high pressure hoses and other intensive mechanical options are not always necessary to clean substrata. A further reason was that a high proportion of the rocks on a rocky shore will be covered in a biofilm of microalgae, the less harsh the oil recovery technique used the higher the proportion of microalgae that will survive. Inter-tidal grazers such as the limpet *Patella spp* graze on microalgae and themselves are a source of food for a range of bird species.

4.7.3 Scion Image analysis of oil recovery

The first stage of the data collection process using Scion was to obtain control images of the substrata prior to pollution. These images provided the first opportunity analyse the applicability of the software to the tests. The substrata were photographed in their unpolluted state and once again when oil was applied. The images were uploaded into Scion and the shape of the rock isolated using a cutting tool to minimise inaccuracies by removing pixels from areas around the rock. Point A in Figure 32 shows the dotted line drawn by the cutting tool in Scion. Had the pixels in areas B and C been counted, the distribution of pixels for the substratum would have become skewed.

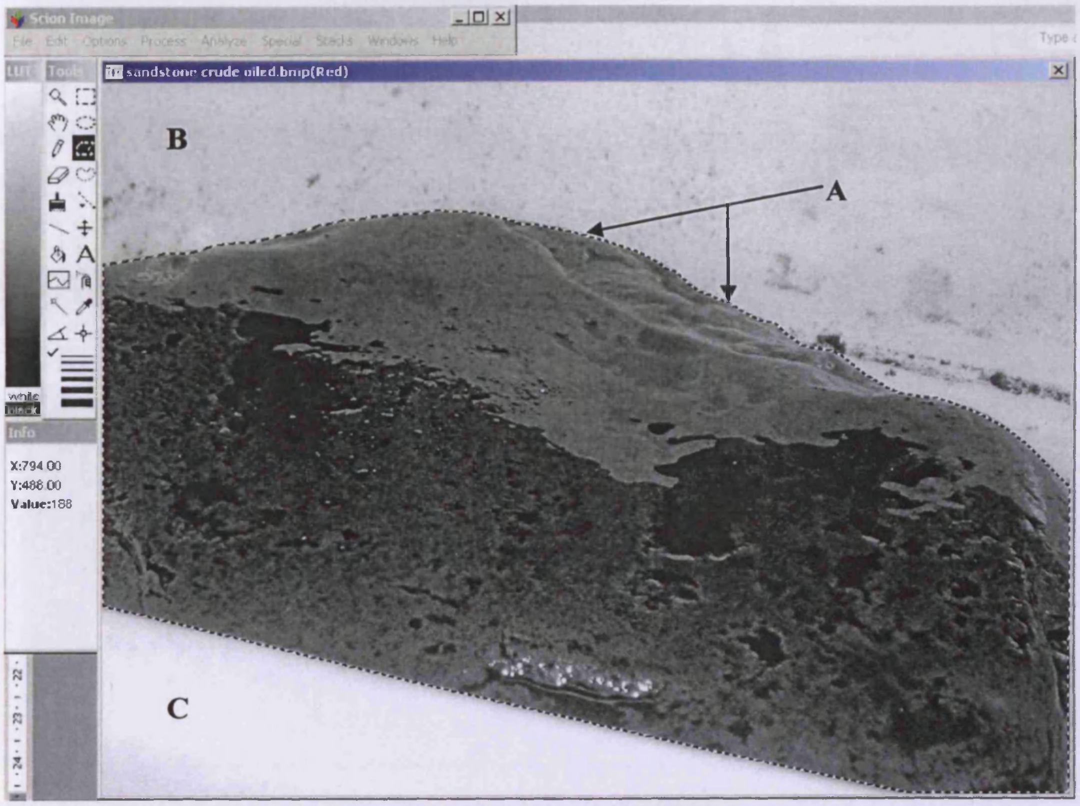


Figure 32: Input of image into Scion Image – the dashed line (A) around the rock represents the cutting tool
Source: author

Once the shape of the substratum had been isolated, the image was split into 256 pixels where pixel 0 is 100% white and pixel 255 is 100% black. Scion plots a histogram of the data that shows the pixel distribution of the image, a corresponding picture of the rock that the histogram data represents, and tabular data comparing counts from a range of pixel values across the spectrum. The histograms and the tables were manipulated to compare and contrast a selection of the results. The histogram (D) and data table (E) can be seen in Figure 33.

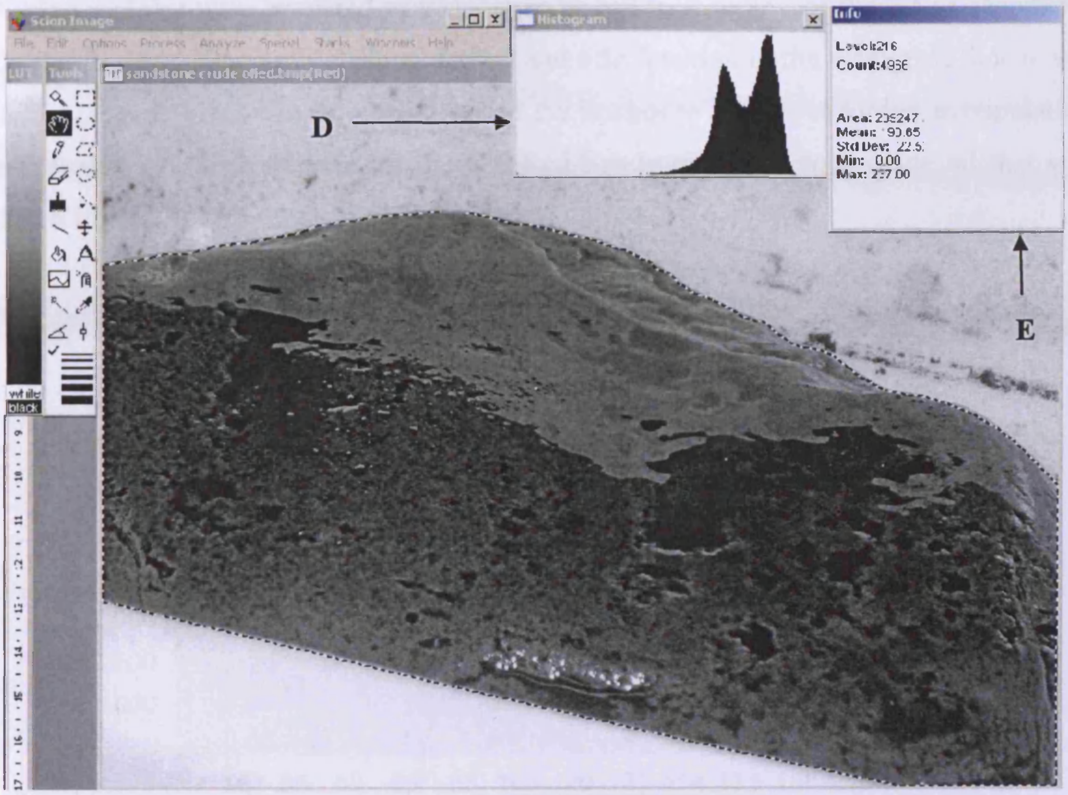


Figure 33: Image trimmed and histogram and data table displayed.

Source: author

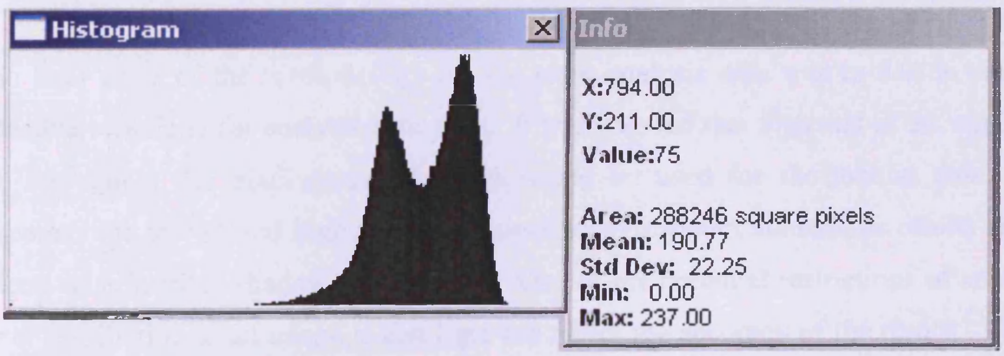


Figure 34: Histogram and data table in Scion Image

Source: author

All the samples were prepared in a vessel so as not to lose any of the oil or absorbent. Due to the lack of an axis labelling, legend and title function in the histogram function in Scion, (Figure 34) it was decided to export the images to Excel for further manipulation and analysis. The histogram for the Old Red Sandstone oiled with crude oil that was drawn in Excel can be seen in Figure 35.

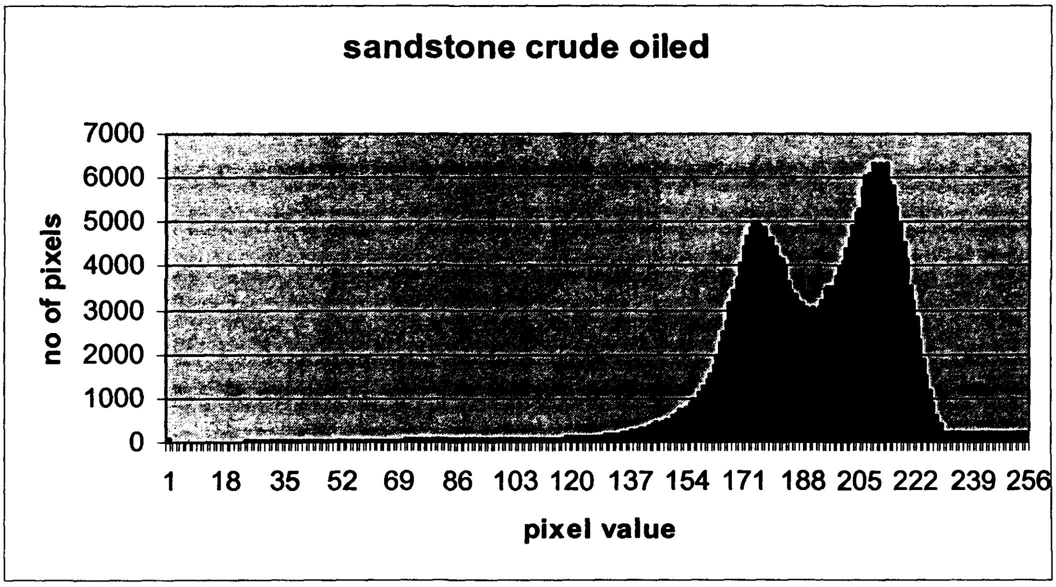


Figure 35: Histogram in Excel
Source: author

The final stage of the methodology for the pixel analysis data was to decide the most effective technique for analysing the data. It was decided that intervals of 20, starting at 20, throughout the pixel range of 0-255 would be used for the tabular data. This discounts the lowest and highest of the values so to discount anomalous results and the effects of reflection, shadows or pooling. One of the potential restrictions of analysing pixel distribution of an image is that light can affect the accuracy of the results. Natural light or the flash from the camera can give abnormally high values of the pixels near the white end of the spectrum.

4.7.4 Percentage recovery methodology

The oil and sorbents were weighed prior to application to the substratum for two reasons. One, to ensure accuracy and consistency, and two, to facilitate calculation of their efficacy through percentage recovery. The recovered mixture was recovered, placed in a glass vessel and weighed. A percentage recovery of the material was calculated. A cross analysis of pixel mapping and percentage recovery was carried out on the products. The results from this can be found later in the chapter.

4.7.5 Carbon and moisture content methodology

The procedure necessary to quantify the carbon and moisture content of the compound of oil and sorbent has two stages. The sample preparation procedure is as follows: a ceramic crucible was weighed and the weight recorded. Ten millilitres of oil and five grams of sorbent were added to the crucible, the compound and crucible were weighed again before being placed in a drying oven for 24 hours at 80°c. The crucible was left to cool, removed and re-weighed to quantify the percentage moisture of the compound. The crucible was then put on a ceramic tray in a muffle furnace for one hour at 550°c and once cooled weighed again. An equation was applied to the differences in weight throughout the process, the results of which gave a percentage water content and carbon reading for the compound. The oils and sorbents used in the efficacy tests in Southampton were collected and brought back to Cardiff to undergo measurement of moisture and carbon content.

4.7.6 Statistical analysis

A series of statistical tests were carried out on the results from the pixel analysis and carbon content results. However, due to negative values in the percentage recovery data, it was not possible to analyse that data statistically. The test chosen for the analysis was Analysis of Variance (ANOVA) test. Two types of tests were carried out, a two-way ANOVA and a multivariate nested ANOVA where 4 variables were accounted for.

Two-way ANOVA.

The two-way ANOVA test was carried out on the data from the drying and incineration tests on the compounds of oil and sorbent from the laboratory. The results showed whether there was a significant difference between the different oils and sorbents with regard to the carbon content and whether the relationship between the oil and sorbent was affecting the carbon content. The process of converting the data from weights and percentages to a decimal for analysis is described below. The raw data collected for this test was in grams, the weights were converted into a percentage for carbon content and moisture content. This was transformed, or normalised using an arcsine transfer into decimal data for ANOVA.

Fully nested ANOVA

Due to the number of variables that were tested in the pixel analysis work, it was necessary to carry out a fully nested ANOVA with 4 variables. The results of the nested ANOVA provide a statistical result each for the pixel data against the substratum, oil type and sorbent. The 4 results for the fully nested ANOVA present whether there was a significant difference between the substratums and the pixel distribution, the oil types and the pixel distribution and the sorbents and the pixel distribution. The fourth piece of data represents whether there is a difference between the polluted and cleaned samples and pixel distribution. A fully nested ANOVA test was also used for the results from the carbon tests carried out in Southampton. The reason the two way analysis was not used was that the Southampton data included the substratum which represented an additional variable in the statistics.

4.8 Results

This section of the chapter provides the results for:

- The SEM analysis.
- Pixel analysis, percentage recovery and carbon and moisture content from the laboratory analysis and *ex-situ* field trials in Southampton.
- Results from the statistical tests.

4.8.1 SEM

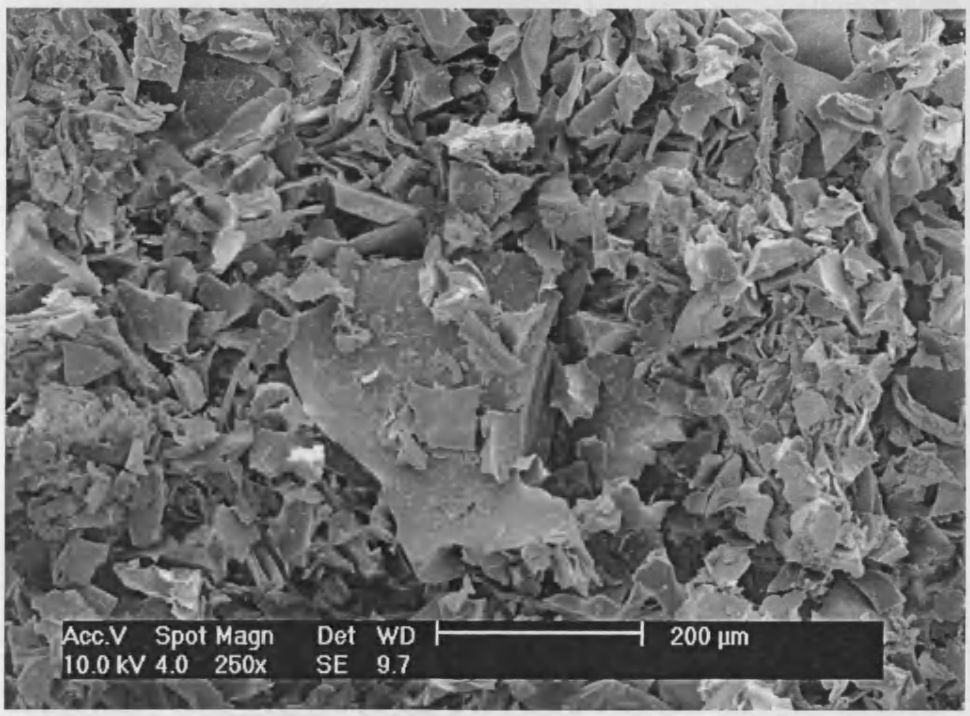


Figure 36: Klausorb unoiled

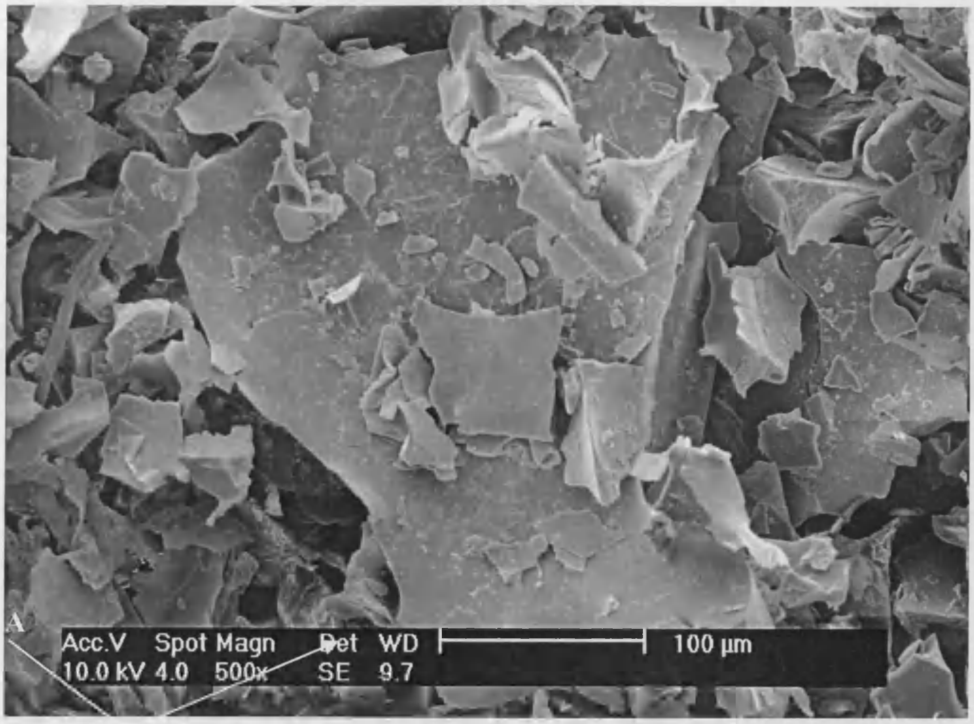


Figure 37: Klausorb unoiled

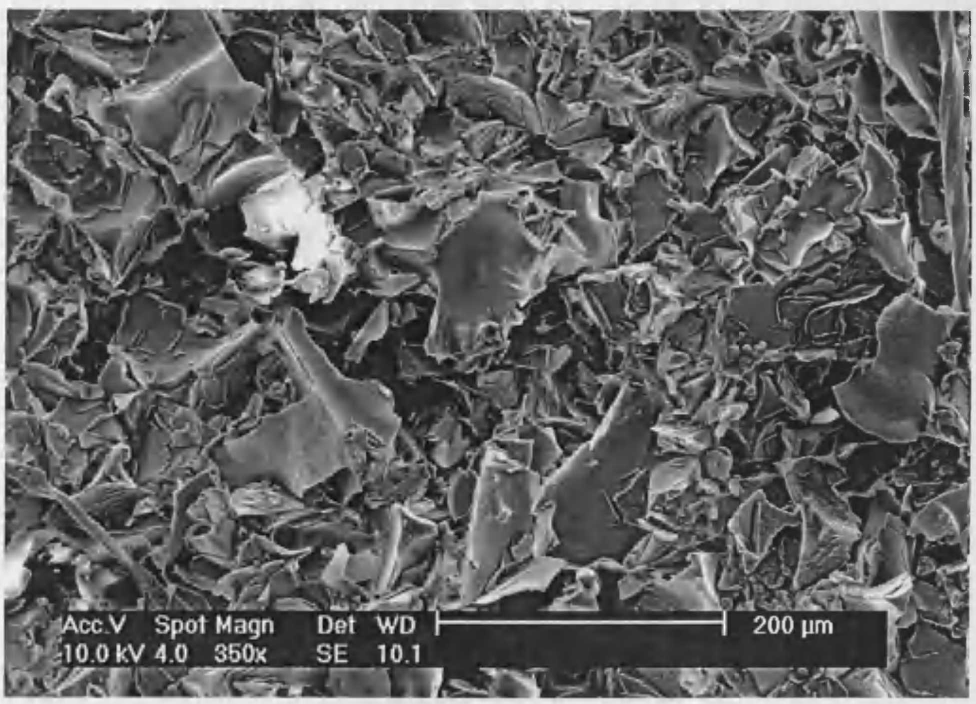


Figure 38: Klausorb oiled

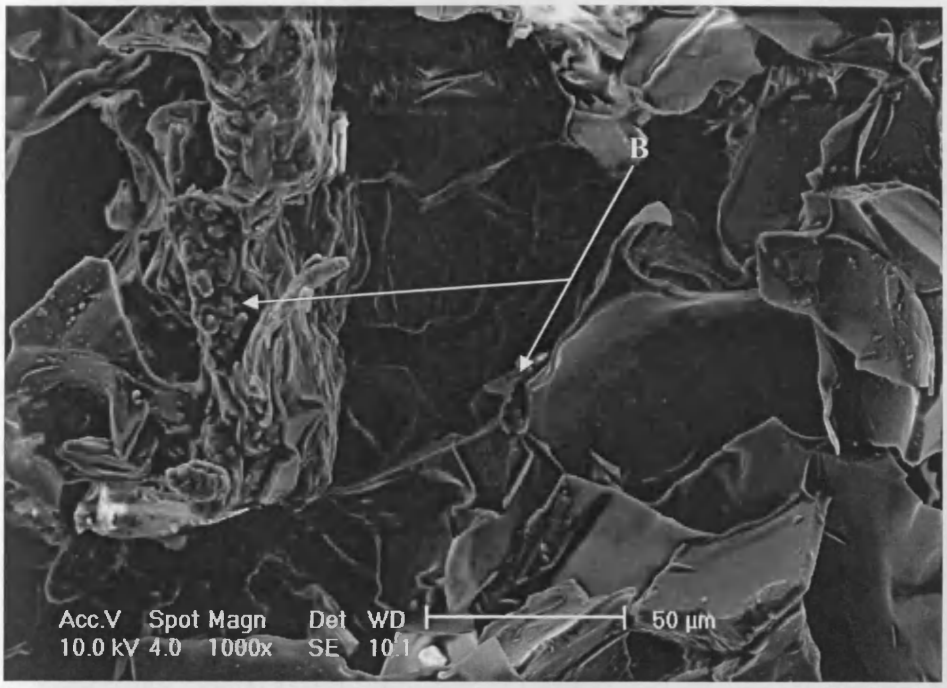


Figure 39: Klausorb oiled

Figures 36 and 37 show Klausorb prior to application of oil. The images show that Klausorb uses a high surface area to 'trap' oil between many layers and prevent its release. Point A in Figure 37 illustrates the particulate structure of Klausorb and the many 'pits' and layers in the product that trap the oil. The oiled images of Klausorb show the oil adhered to the surface of the sorbent, Point B in Figure 39 shows oil bound to the layers preventing release of the oil. Absorption is achieved through a combination of the viscosity of the oil and the high surface area of the product

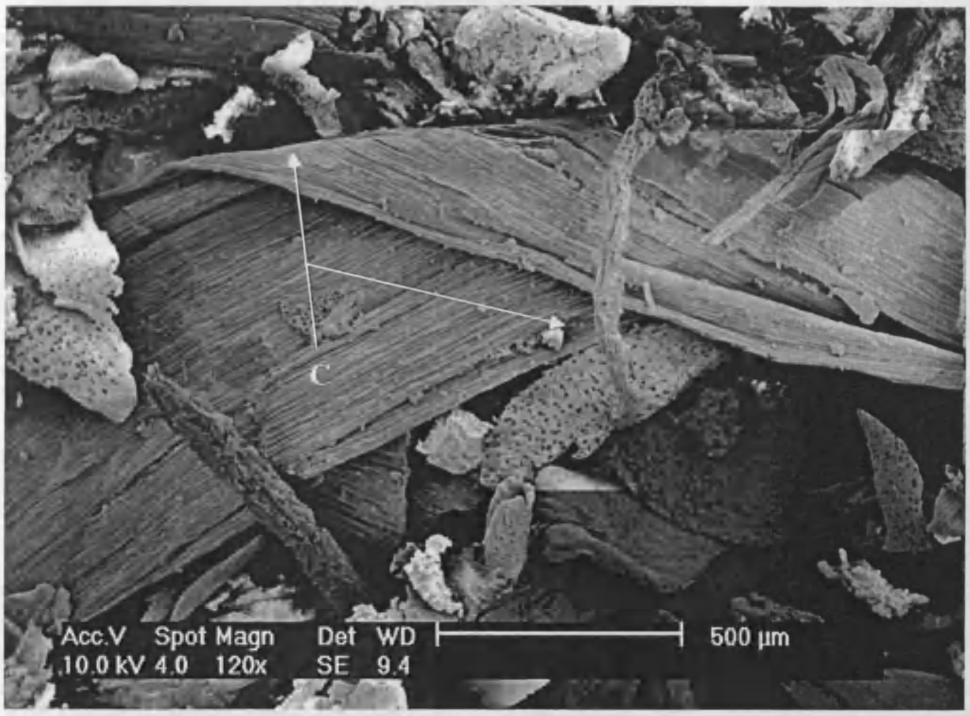


Figure 40: Peat unoiled

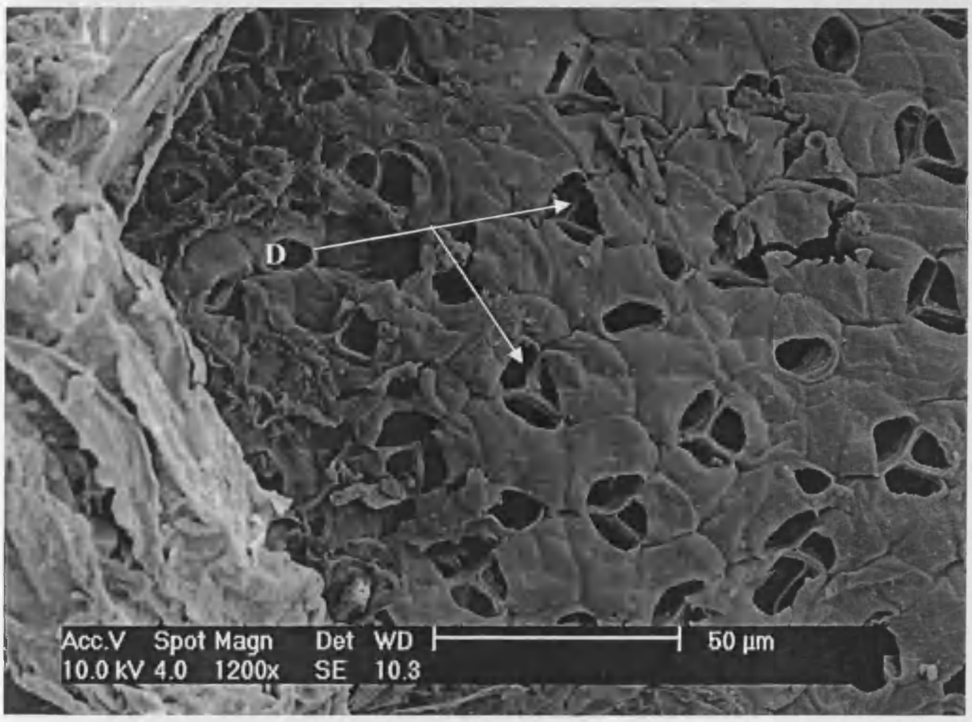


Figure 41: Peat unoiled

Figures 40 and 41 represent the peat prior to oiling. It can be seen from points C and D that the peat absorbs the oil through a high surface area (point C) and a porous structure (point D). When the oil is applied it fills the pores in the peat and is bound between the layers in the peat's structure. The porous structure of the peat binds the oil to the extent that when squeezed water drains out and the oil remains bound in the pores.

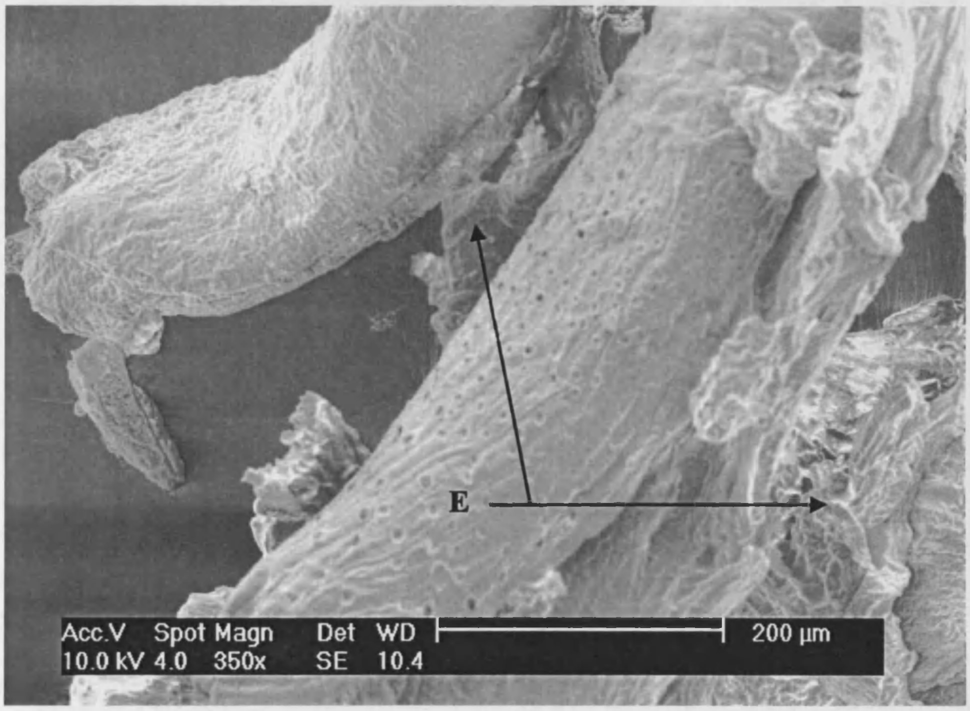


Figure 42: Peat oiled

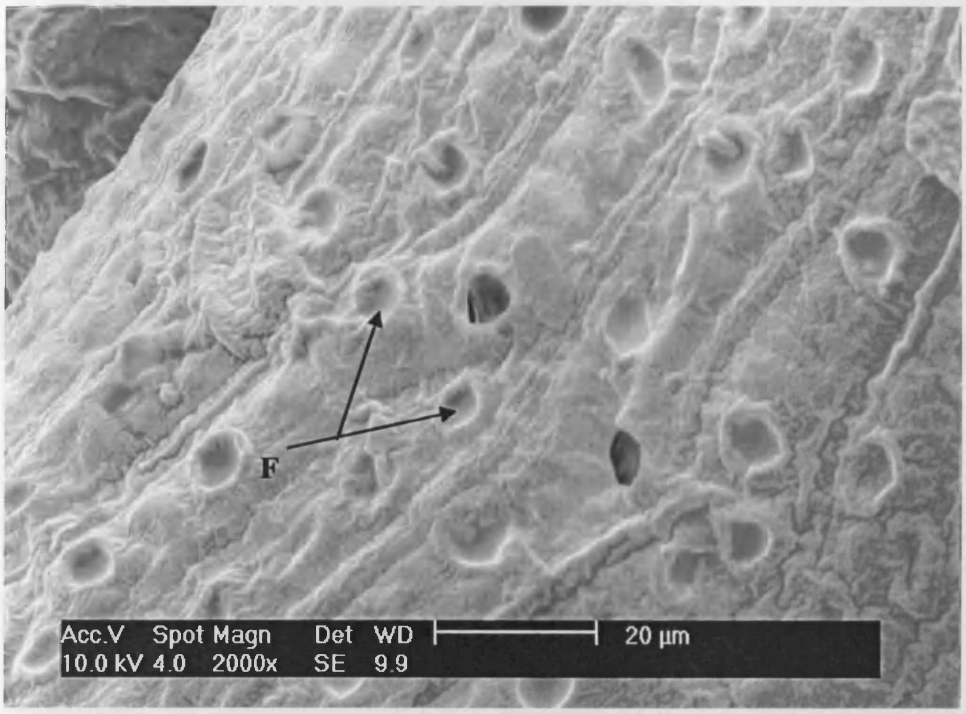


Figure 43: Peat oiled

Point E in Figure 42 shows the oil bound to the layers of the peat, the three dimensional structure and high surface area is clearly evident in the image. Point F in Figure 43 shows the pores in the peat filled with oil. If this is compared with Point D in Figure 41, the effectiveness of the porous nature of the peat is evident.

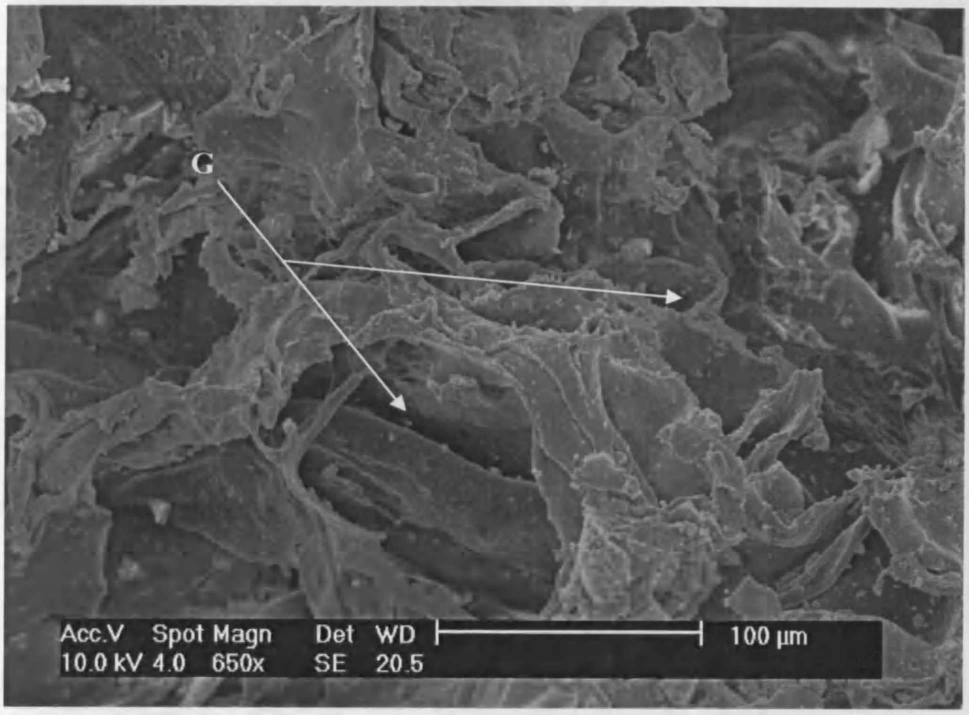


Figure 44: RecoverIt unoiled

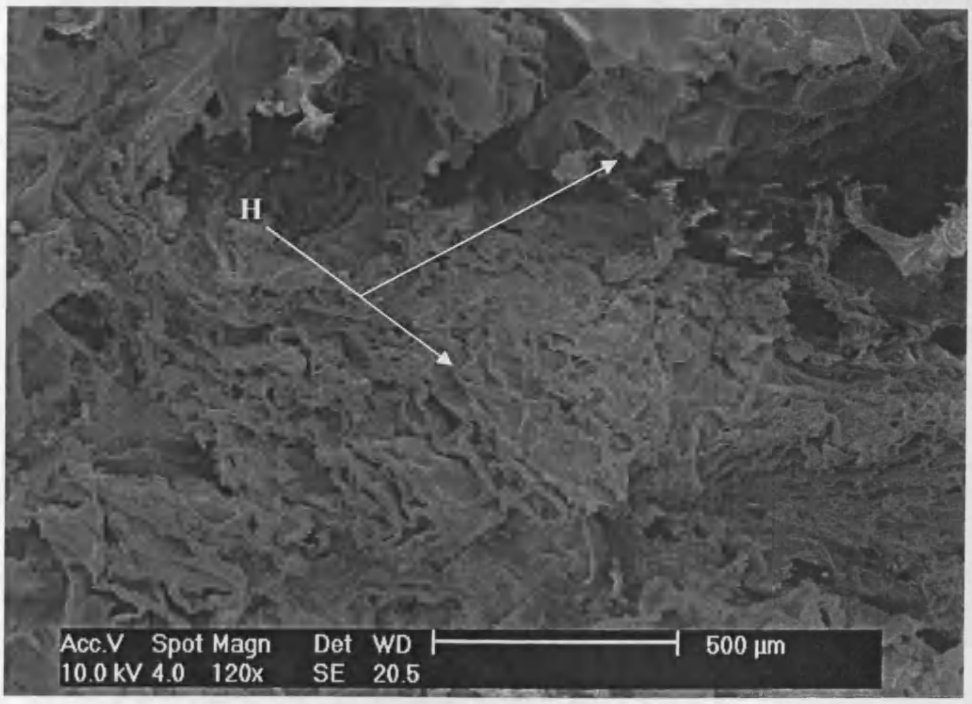


Figure 45: RecoverIt unoiled

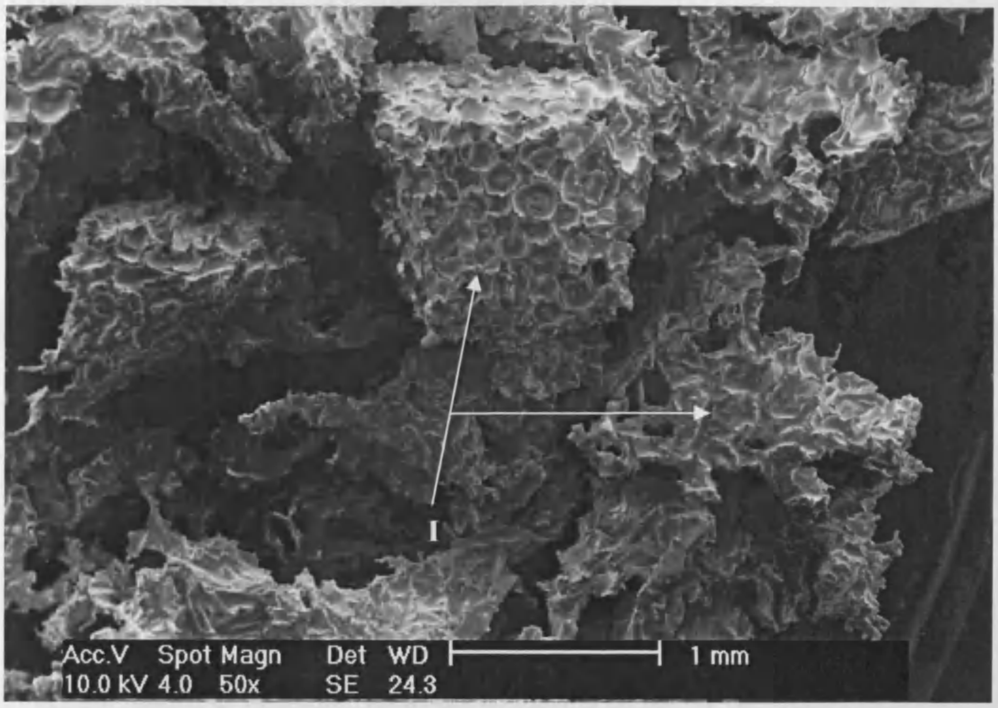


Figure 46: RecoverIt oiled

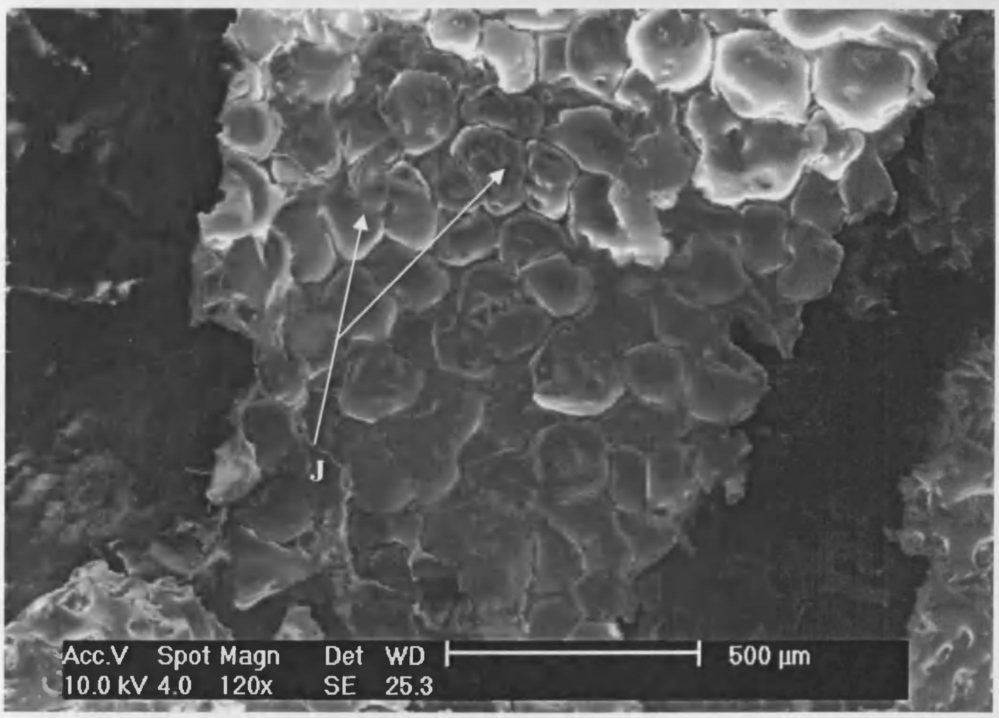


Figure 47: RecoverIt oiled

Points G and H in Figures 44 and 45 shows that the structure of RecoverIt is less particulate than Klausorb but has a more convoluted structure and a higher surface area. RecoverIt was the only adsorbent to be tested. Points I and J (Figures 46 and 47) show the complex structure covered in the layer of oil (point I) and the individual oil droplets that are attached to the surface of the product (point J).

4.8.2 Pixel analysis:

4.8.2.1 Control Images and histograms:

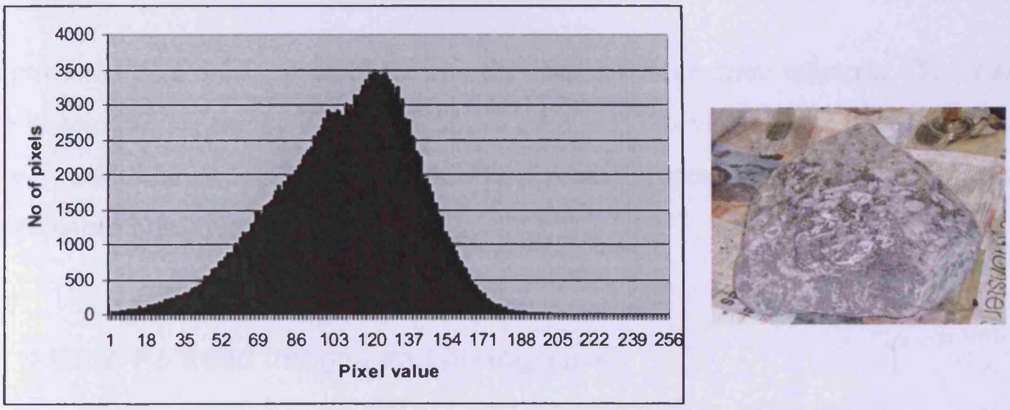


Figure 48: Weathered limestone unpolluted.

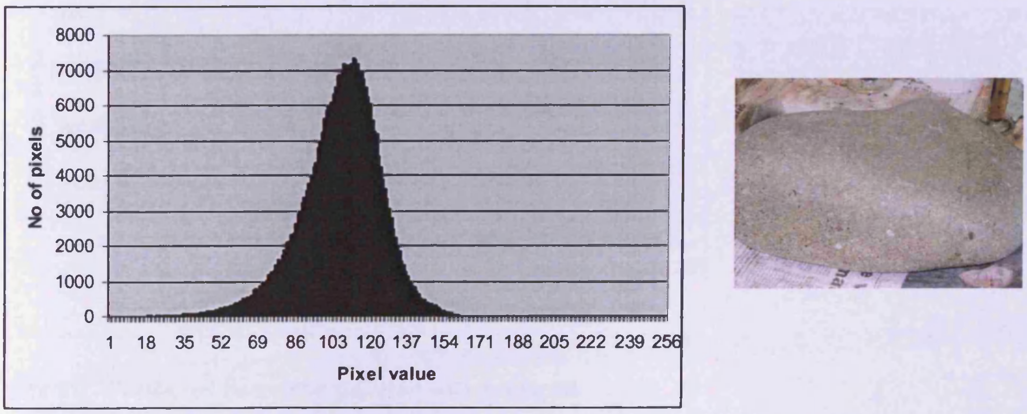


Figure 49: Smooth limestone unpolluted.

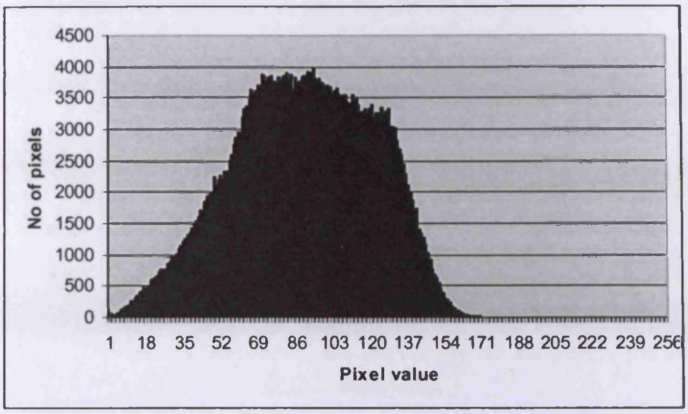


Figure 50: Sandstone unpolluted

Figures 48, 49 and 50 represent the control images for the three substrata. The *x* axis on the histograms represents the total number of pixels of every colour in the 0-255 range. The *y* axis represents the colour of the pixels. 0 represents a white pixel and 255 represents a black pixel.

4.8.2.2 Polluted images and histograms

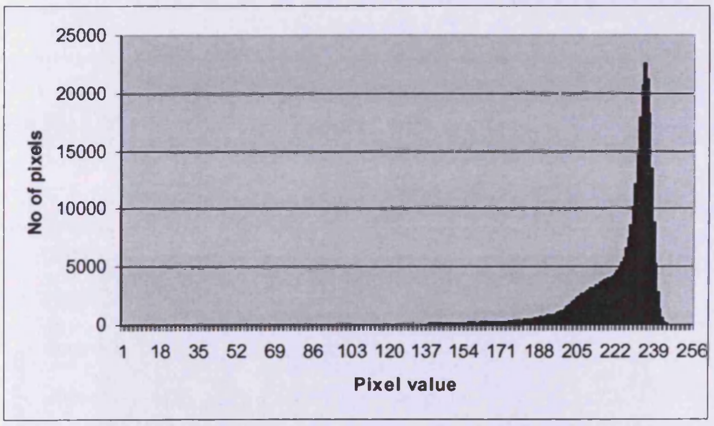


Figure 51: Weathered limestone polluted with crude oil.

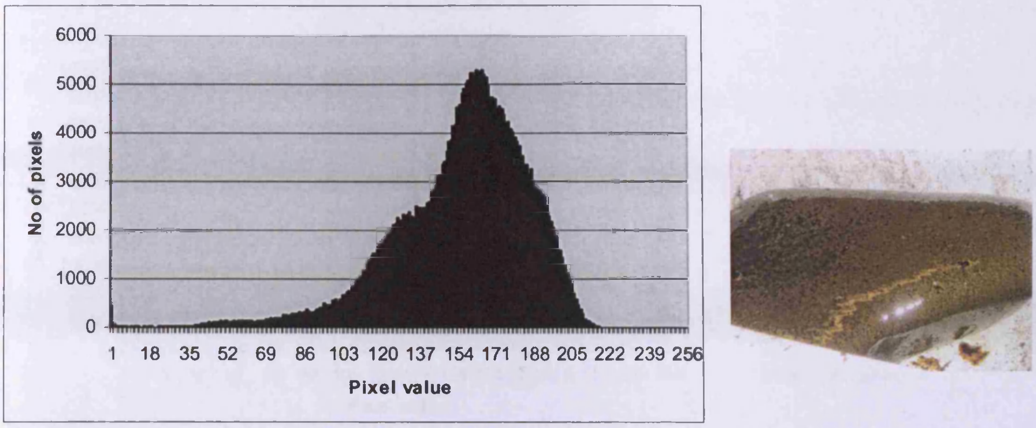


Figure 52: Smooth limestone polluted with crude oil.

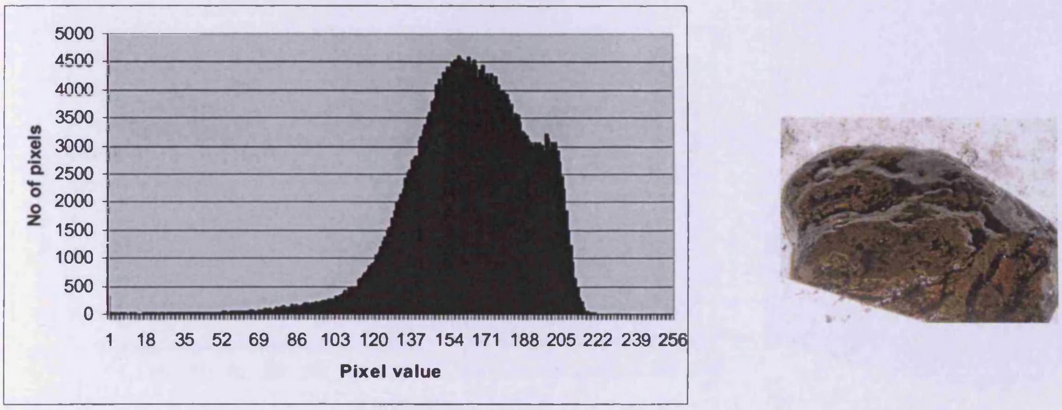


Figure 53: Old red sandstone polluted with crude oil.

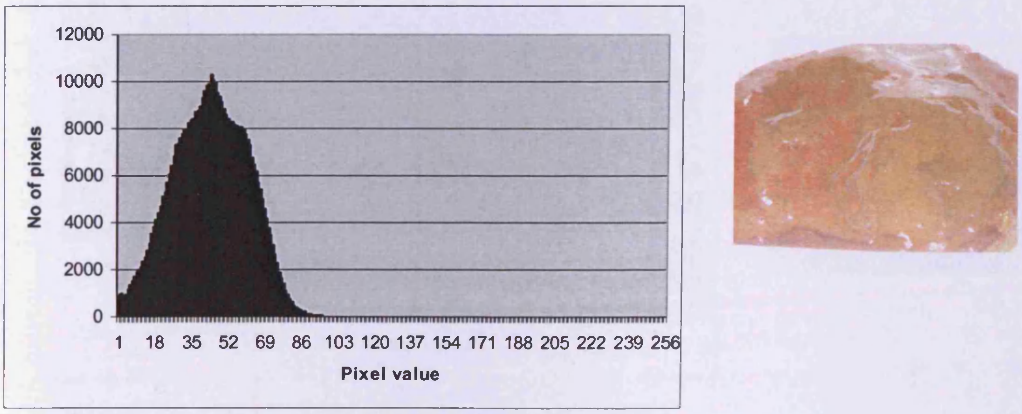


Figure 54: Old red sandstone polluted with refined oil.

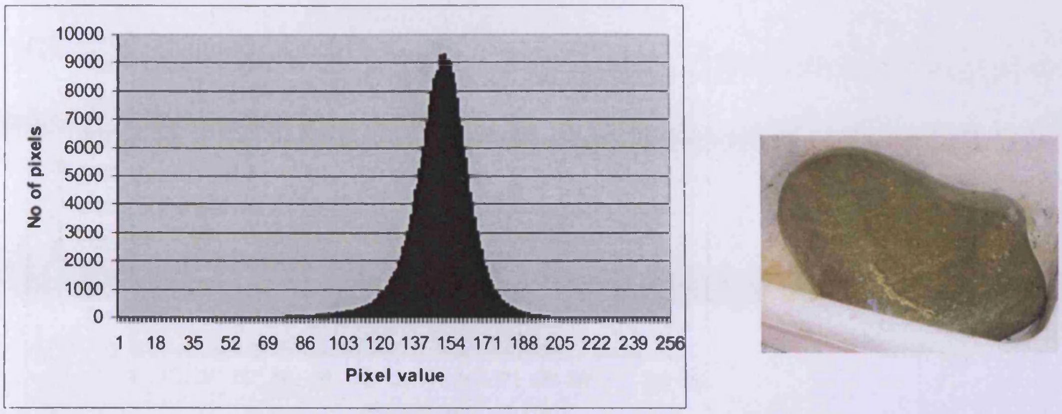


Figure 55: Smooth limestone polluted with refined oil.

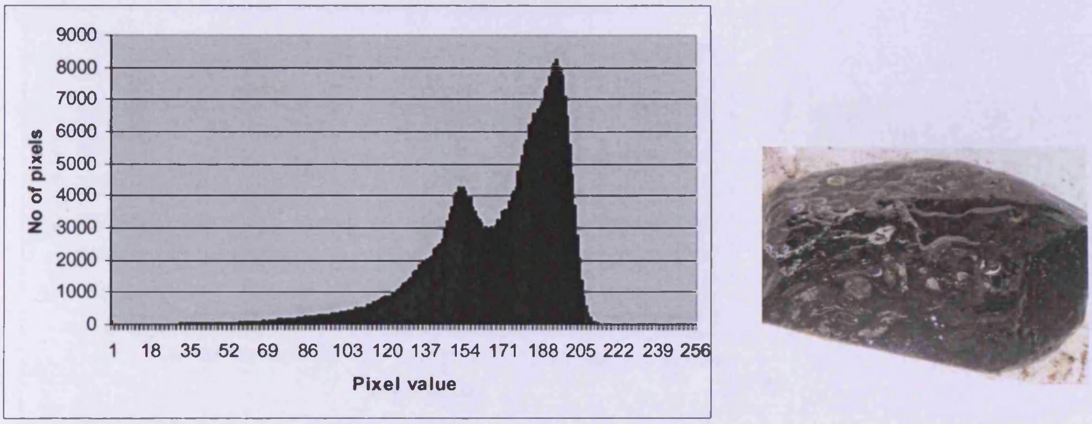


Figure 56: Weathered limestone polluted with refined oil.

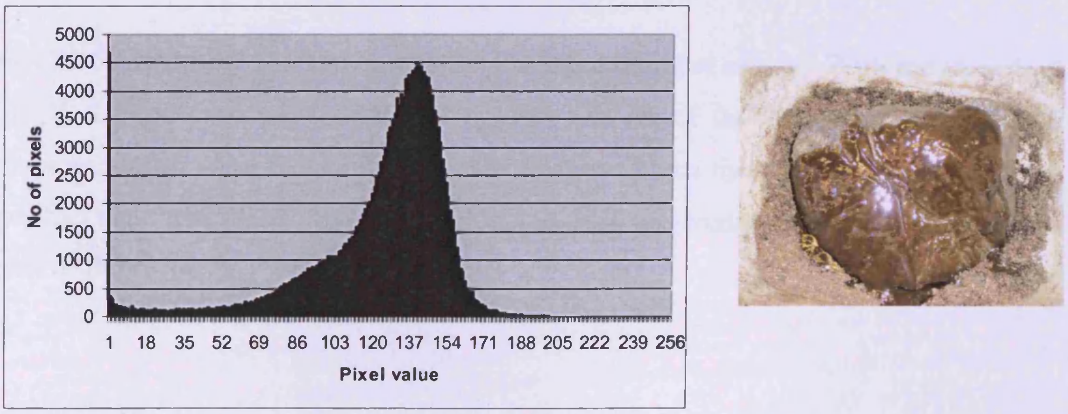


Figure 57: Weathered Limestone polluted with weathered oil

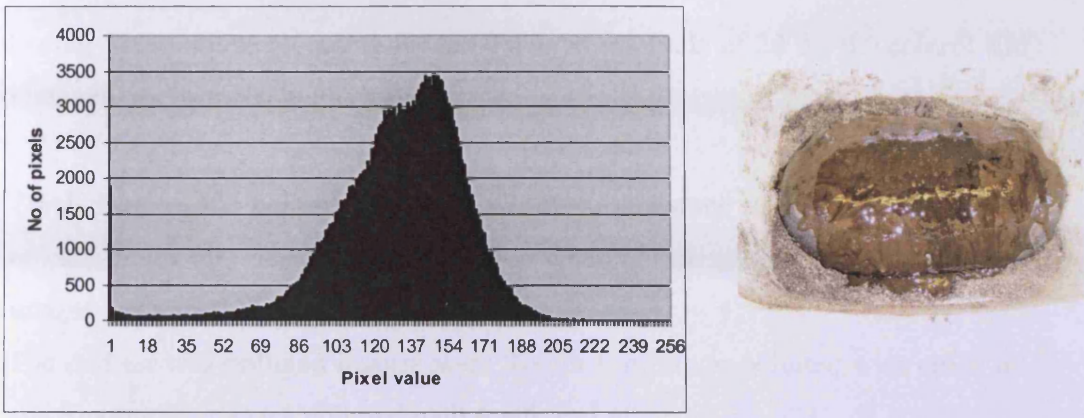


Figure 58: Smooth Limestone polluted with weathered oil

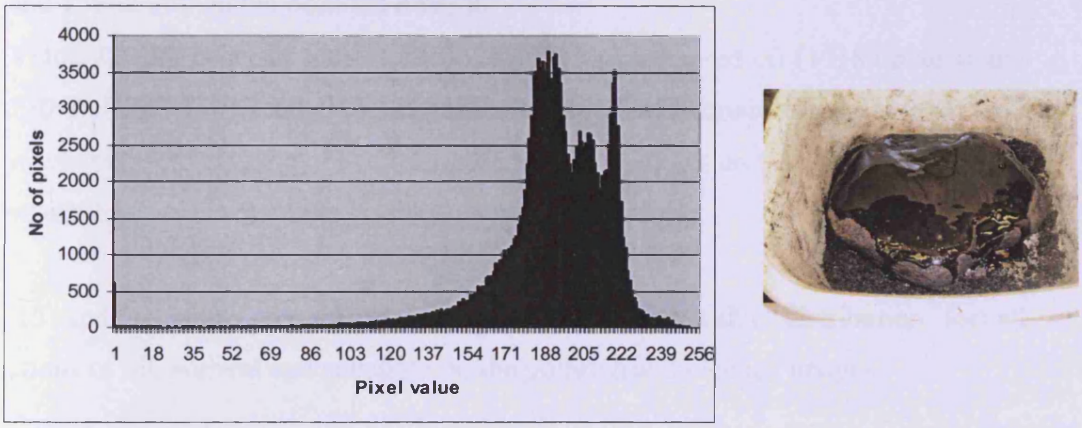


Figure 59: Old Red Sandstone polluted with weathered oil

Figures 51-59 represent the histograms for the substrata post oiling. With the exception of Old Red Sandstone oiled with 2050 motor oil, all of the images of the polluted substrata are darker than those of the control images. Once the results from the cleaned images had been processed, they were compared with the control images to quantify the efficacy of the sorbents.

4.8.2.3 Laboratory pixel analysis:

The following observations regarding the pixel data in intervals of 20 for the control and polluted images can be made at this stage:

- The lightest of the polluted images is Old Red Sandstone polluted with the 2050 refined motor oil. This is a consideration when comparing cleaned and polluted images.
- The darkest two polluted images were Rough Limestone polluted with crude oil and Smooth Limestone polluted with weathered oil.
- The majority of the pixels are found between 40 and 160 on the control images and 100 to 200 on the polluted images.
- Value 220 for Smooth Limestone polluted with weathered oil (10189 pixels) and 220 and 240 for Weathered Limestone polluted with crude oil (4075 and 5262 pixels respectively) may have been affected by shadows and pooling of oil on the substrata.

Tables 15 and 16 show the results for the mean pixel value distribution for all combinations of oil, sorbent and substrata on the polluted and cleaned images

Table 15: Mean pixel value (20-120) distribution of oil and cleaned rocks – laboratory results

pixel value →	20		40		60		80		100		120	
Image state →	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	Cleaned
substratum/oil/recovery ↓												
SL klausorb 2050	16	29.6	77.2	27.6	65.4	60	134.6	213	301.4	1461.4	1147.2	3561.6
SL Klausorb weathered	15.2	76.8	31.4	146.6	56.6	327	98.6	688.6	125	1011	157.2	1561.2
SL klausorb crude	11.2	31.6	21.4	31	37.8	59.4	61.6	122.2	70.6	234	113.4	518.4
SL peat 2050	20.6	45.4	33.6	59	26.2	74.4	32.2	106.2	75.6	167.8	222	389.4
SL peat crude	46.6	34.8	76.6	118.6	115.2	335.2	197.8	495.2	336.8	930.2	1209.2	1717.4
SL peat weathered	17.4	32	29	40	57.8	68.6	86.6	103	167.4	193	316.6	498.4
SL recit 2050	39.8	169.8	126	228.2	156.2	270	78.6	370.2	137	595.6	2190.2	1441
SL recit crude	165.4	83.6	383	152.8	400.2	258.2	1046.4	456.2	2700.4	853.6	1330.4	1612.2
SL weathered recit	30.6	62	52	80	96.8	123.2	288	194.4	494	301.6	727	551
RL 2050 paulex	270.8	463	845.8	715	2646	1287.2	5828.8	2723.8	4646.6	5081.4	1441.4	6165.8
RL paulex crude	161.8	175.4	403.6	295.2	970.6	592	2043.8	1477.8	2795.6	2993.4	2989	4596.8
RL paulex weathered	30.8	33.6	76.4	48.4	178.2	73.6	415.6	124.8	1357.4	297.6	3615.6	807.2
RL peat 2050	87.6	245.4	339	365.4	1303.4	639.6	3073.4	1282.4	4646.4	2051.6	4173.4	3388.6
RL peat crude	55.6	212.8	82.4	382.2	153.4	844.4	292.4	1581.2	706.6	2481.4	1497.2	2469.4
RL peat weathered	63.8	219.2	134.4	327.8	227.8	556.4	470.8	1081.8	1589	1887.6	2130	2335.6
RL recit 2050	218.8	460.4	701.6	787.8	1846.8	1286.4	5961.4	2286	7996.4	3852.8	4716.6	5893
RL recit crude	162.4	279.6	346.4	330	799.4	479.2	1494.4	955.8	2225	2359.8	2751.6	5484.4
RL weathered recit	159	105.4	304.6	153.2	600.6	244.8	2015	550	1655.6	1426	673.4	3777.6

ORS Paulex 2050	198.4	322.4	812	874.2	4118.6	1578	6833.4	2595	3988.4	2928.4	2282.6	1411.4
ORS Paulex crude	5.2	7.2	4.8	18	56.2	15	181.4	33.4	366.6	75.2	762	339.2
ORS Paulex weathered	1	8.4	5.4	11.8	7.6	27.8	13.6	96.8	23.6	394	43	2123.6
ORS Peat 2050	972	80.2	1975.2	180.6	1656.2	357.2	749.6	946.8	2067.4	2559.8	1518.4	2700.6
ORS Peat crude	27	324.4	63.6	791.6	129.6	1891.2	248	2306.8	369	2116	591	2014.6
ORS Peat weathered	2.6	4.6	5.6	7.6	9.6	9.6	6.8	15.2	12.2	25.6	20	48.2
ORS recit 2050	632.6	326.6	3877	764.4	6222.2	1861.8	5470.4	2922.2	3267.4	3415.2	566.8	3665.8
ORS recit crude	125.4	820.2	207.6	3311.6	313	5018.6	526.2	5076.4	1042	2979.6	1689.2	356.6
ORS Recit weathered	283.2	403.2	529.4	1039.6	972.6	2718.4	1562.6	5198.6	1935	5380.2	4200	3380.4

Legend:

WL: Weathered limestone

ORS: Old red sandstone

Re: Refined oil

2050: 2050 refined motor oil

SL: Smooth limestone

Kl: Klausorb absorbent

Cr: Crude oil

Table 16: Mean pixel value (140-240) distribution of oil and cleaned rocks – laboratory results

pixel value →	140		160		180		200		220		240	
substratum/oil/recovery ↓	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	Cleaned
SL klausorb 2050	2775.2	3140.4	7314	3775	3638.4	2180.8	56	164.8	21.2	17.4	0	2.6
SL Klausorb weathered	345	2351.4	1340.2	2258.2	2152.8	3225.4	2246.4	3686.8	6173.2	413.6	2575.8	10.2
SL klausorb crude	326	1704	1366.8	5387.8	4007.6	4139.8	2656.4	1287.8	2820.2	962.4	53.2	1466.8
SL peat 2050	1408.2	1429	2591.2	3557.6	5171.4	4860.4	3734.8	3805	376.2	1530.4	11.8	159.6
SL peat crude	1321.6	1405.2	3647.6	2961.4	4229.6	3817.4	2367.4	2082.6	2878.8	561.2	341.6	32.8
SL peat weathered	776.6	1980.2	1930.8	3890.8	2139.6	4033.4	6862.4	4318.8	4699.4	1104.6	46.8	57.25
SL recit 2050	2543	3793.4	4957.4	8496.4	6411.2	4189.6	744.6	650	2	64.4	0	11.4
SL recit crude	607.8	3195.6	839.2	5506.4	1538.4	5503.8	3266.6	2366.4	4019	135.4	2599	15.6
SL weathered recit	1803.4	1220.4	2663.6	3408.4	1269.2	6143	4619.4	6207.2	6362.2	421.2	4813.8	44.4
RL 2050 paulex	2098.6	3781.2	2096.4	898.6	623.2	206.8	158.4	55.8	22	8.2	2	1.4
RL paulex crude	2967	5025	3162.4	3158.4	2074	961.4	1169.2	272.2	588.8	105.6	15.4	4.6
RL paulex weathered	3107.8	1688.6	566.6	2704.4	1107	3525.8	3343.6	2254.2	2383	340.4	934	28.8
RL peat 2050	2734.8	4243	1914.2	2845.6	1669.4	1814	1527.6	999.6	27.8	320.2	2.8	43.6
RL peat crude	2417.8	2098.6	2493.8	2224.2	2129.8	2058.8	2038.6	2032.6	2828	2832.2	3248.6	165.4
RL peat weathered	977.2	1763.8	5035.6	1968.8	2604.4	2495.8	1850.8	2777.6	3661.4	2075.4	1347.6	486.4
RL recit 2050	1534.6	4410.2	290.4	1660.4	30.8	323	1.8	45.2	0.4	7.2	0	2
RL recit crude	2642.8	5644.6	2439.4	2371.8	2204.4	1712.6	1839	115.8	1533.4	181.2	1572.6	17.2
RL weathered recit	1328.6	6120.2	4246.2	4663.8	2780.4	1085.8	2348.4	95.2	2694.6	11	1173.6	1.4

ORS Paulex 2050	117	2254.8	24.8	3233.4	26.2	1204.2	100.6	18.4	2671.6	0	279.4	0
ORS Paulex crude	1092.8	2747.8	1177.2	3831.6	2671.4	1678.2	4614.2	4362	2751	1111.2	176.2	6.8
ORS Paulex weathered	156.8	1478.4	991	1548	2210.2	6514.2	5905.2	3218.4	7251.4	560.2	0.8	33
ORS Peat 2050	1428	1885.4	2256.4	1743.4	1984.6	1811.6	2902.2	2194.6	631.2	1453.6	36	56.6
ORS Peat crude	1315	2066.2	2563.8	2797	5156.8	2090.2	2734.2	1012.4	2584.4	239	1299.2	8
ORS Peat weathered	39	121.8	131	641.6	800.6	3403.4	2903.2	8068.4	9314.4	2521.4	395.6	138.6
ORS recit 2050	519.2	6014.6	1565.8	1018	1571.2	231.8	295.8	36	10.8	1.8	0.2	0.2
ORS recit crude	2333	150	2915.2	1036.2	2585.6	2313	3065.2	295.8	4107.6	54.2	2211.4	2
ORS Recit weathered	5360.6	1588.6	2780	752.6	530.2	1550	536	127.4	2202.6	51.4	0	15.2

Legend:

WL: Weathered limestone

ORS: Old red sandstone

Re: Refined oil

2050: 2050 refined motor oil

SL: Smooth limestone

Kl: Klausorb absorbent

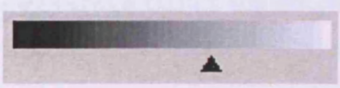
Cr: Crude oil

Tables 15 and 16 show the results for the mean pixel value distribution for all combinations of oil, sorbent and substrata on the polluted and cleaned images.
The results have been split into different 'shades' in the 0-255 spectrum, the trends in the results are as follows:

Shade 20: 

256 **0**

- The first shade to be discussed is 20. As one of the lightest colours in the spectrum it would be expected that the images from the cleaned substrata would have a higher pixel tally than those of the polluted substrata. Of the twenty seven combinations of sorbent, oil and substratum, twenty two (81.4%) have a higher tally in the cleaned data than the polluted.
- Of the 5 results that have a higher polluted tally there are no dominant oil types or substrata. RecoverIt accounts for 3 of the results and peat for 2. At this colour on the pixel spectrum the high tallies on the polluted images are most likely attributed to reflection.
- The average percentage decrease between the cleaned and polluted tallies for the twenty two results with a higher cleaned tally was -222.2%. The average increase between the polluted and cleaned tallies for the 5 results that had a higher polluted value was 49.7%.
- The average values at this shade were 141.5 for the polluted images and 187.3 for the cleaned images.

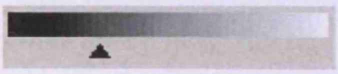
Shade 100: 

256 **0**

- At shade 100 it would be expected that the images from the cleaned substrata would be higher than that of the polluted data. On nineteen of the twenty seven images (70.3%) this was the case.

- 4 of the 8 results that had a higher polluted tally were Rough Limestone. There is no distinguishable pattern between sorbents. RecoverIt was the most dominant of the sorbents. However if differences between polluted and cleaned pixel tally is considered, RecoverIt was the most effective sorbent and peat the least effective.
- The data suggests that oil type did affect pixel distribution as the refined 2050 oil showed the highest pixel count. The Old Red Sandstone responded least well to clean up.
- The average percentage decrease between the cleaned and polluted tallies for the nineteen results with a higher cleaned tally was -253.2%. The average increase for the 8 results where the polluted tally was higher than the cleaned was 51.6%.
- The average tallies for pixels in the polluted data set was 1670.3 and for the cleaned data 1779.9.

Shade 180:



256 **0**

- At shade 180 twelve of the twenty seven images (44%) had a higher pixel tally for the polluted images than the cleaned ones.
- The results showed that Smooth Limestone had responded best to clean up. Substrata that had been cleaned with peat showed the highest difference in pixel tally between the polluted and cleaned images.
- The average percentage decrease between the polluted and cleaned tallies for the twelve results with a higher polluted tally was -597.3%. The average percentage increase for the fifteen results with a higher cleaned tally was 33.5%.
- The average tallies for the polluted images was 2345.1 and for the cleaned images 2706.4

Shade 240: 

256 0

- At this shade it would be expected that the pixel tally on the polluted images would be higher than the cleaned images. This was the case in sixteen of the twenty seven results (60%)
- The results show that the peat performed least well of the sorbents and the RecoverIt performed most effectively. The weathered oil was the hardest to remove. There were no distinctive trends in the distribution of the substrata through the data set.
- The average percentage increase between the cleaned and polluted tallies was 1180% and the average decrease between the polluted and cleaned tally was -82.5%.
- The average pixel tally for the polluted images was 856.9 and 104.1 for the cleaned images.

The statistical analysis for the data was carried out on the substrata, oil and sorbent as opposed to pixel shades. The results for the substrata ($F_{(2,3239)} = 0.821$ N/S) shows there was no statistically significant difference in the distribution of pixels through the spectrum due to the different substrata. This is supported by observations made at 20 and 240 where there were no clear patterns in the spread of the substrata through the data set. At 100 and 180 2 of the 3 substrata showed no clear patterns. The statistical result for the sorbents ($F_{(6,3239)} = 6.016$, $P = 0.01$) showed a statistical difference in the results due to the sorbent used to remove the oil. This is supported by there being a pattern in the data set when sorted by sorbent in all 4 pixel shades observed. At shade 20, Klausorb performed least well of the sorbents. At 100 and 240 RecoverIt performed most effectively and peat least effectively. Peat was most effective at shade 180. There was a statistically significant difference in the data due to oil type. ($F_{(18,3239)} = 2.011$, $P = 0.049$). This is supported at 2 of the 4 shades that were observed. The weathered oil was the hardest of the 3 to remove and the 2050 refined motor oil the easiest.

Having discussed the differences in pixel distribution between the polluted and cleaned images, the next stage of the analysis compared the cleaned images with the control. Tables 17, 18 and 19 represent each of the substrata and display the average values for the cleaned, polluted and control images at shades 20, 100, 180 and 240. Table 17 displays the data for the Smooth Limestone.

Table 17: Smooth limestone average values – laboratory results

Data →	SL Cont.	IS	SL Kl 2050	SL Kl Crude	SL Kl Wea	SL RecIt 2050	SL Recit Crude	SL Recit Wea	SL Peat 2050	SL Peat Crude	SL Peat Wea
PV ↓											
20	24	Cle	29.6	31.6	76.8	169.8	83.6	62	45.4	34.8	32
		Poll	16	11.2	15.2	39.8	165.4	30.6	20.6	46.6	17.4
100	5829	Cle	167.8	930.2	2993.4	1887.6	2051.6	5081.4	301.6	853.6	193
		Poll	75.6	336.8	2795.6	1589	4646.4	4646.6	494	2700.4	167.4
180	3	Cle	2180.8	4139.8	3225.4	4189.6	5503.8	6143	4860.4	3817.4	4033.4
		Poll	3638.4	4007.6	2152.8	6411.2	1538.4	1269.2	5171.4	4229.6	2139.6
240	0	Cle	2.6	1466.8	10.2	11.4	15.6	44.4	159.6	32.8	57.2
		Poll	0	53.2	2575.8	0	2599	4813.8	11.8	341.6	46.8

Legend:

PV = pixel value	**SL = smooth limestone**	**IS = image state**
Cont. = control value	**Kl= Klausorb**	**Cle = cleaned**
Wea = weathered oil	**Recit – RecoverIt**	**Poll = polluted**

It is clear that in Table 17 value 100 is the dominant shade in the pixel distribution of the control image. At shade 20 it would be expected that there would be a higher pixel tally in the cleaned images than the polluted. Seven of the nine results (78%) display this. At shade 100 due to the dominance of the pixel distribution in the control, a pixel count in the cleaned image near the control tally would indicate a level of success in the clean up. Six of the nine results (67%) have a higher cleaned pixel tally. Five of the nine results (55%) at shade 180 and 240 have a higher pixel count in the cleaned image. This data suggests that the sorbents have removed a proportion of the oils from the substrata but not to the extent that the shade of the cleaned images reflects the control image.

Table 18: Weathered limestone average values – laboratory results

Data →	SL Cont.	IS	WL Kl 2050	WL Kl Crude	WL Kl Wea	WL RecIt 2050	WL Recit Crude	WL Recit Wea	WL Peat 2050	WL Peat Crude	WL Peat Wea
PV ↓											
20	130	Cle	463	175.4	33.6	460.8	279.6	105.4	245.4	212.8	219.2
		Poll	270.8	161.8	30.8	218.8	162.4	159	87.6	55.6	63.8
100	2781	Cle	2979.6	7996.4	137	3267.4	75.2	2481.6	2928.4	2359.8	1426
		Poll	1042	2286	370.2	2922.2	366.6	706.6	3988.4	2225	1665.6
180	101	Cle	206.8	961.4	3525.8	323	1712.6	1085.8	1814	2058.8	2495.8
		Poll	623.2	2074	1107	30.8	2204.4	2780.4	1669.4	2129.8	2604.4
240	0	Cle	1.4	4.6	28.8	2	17.2	1.4	43.6	165.4	486.4
		Poll	2	15.4	934	0	1572.6	1173.6	2.8	3248.8	1347.6

Legend:

PV = pixel value **WL = weathered limestone** **IS = image state**

Cont. = control value **Kl= Klausorb** **Cle = cleaned**

Wea = weathered oil **Recit – RecoverIt** **Poll = polluted**

Table 18 represents the data from the Weathered Limestone images. Shade 100 is dominant in the control image. At shade 20 the pixel count is higher on the cleaned image on 11 out of 12 results (91%). The presence of pixels in the polluted images can be attributed to reflection from natural light or the camera. At shade 100 it was expected to have a higher cleaned than polluted tally, five of the nine results (55%) reflect this. Two of the results with a higher polluted tally were from data with weathered oil and two were from peat. This suggests peat was less effective than the other two sorbents and weathered oil was less responsive to sorbent application. The results for shade 180 were three of the nine results (33%) having a lower cleaned tally. Two of these results represented 2050 refined motor oil. This suggests it is the least responsive to sorbent application on Weathered Limestone. It was found that the high surface area of the substratum affected the efficacy of the oil removal as oil pooled and was harder to recover. There were no pixels with a value of 240 on the control image and with the exception of one of the results there were fewer pixels on the cleaned images than the polluted ones. This suggested the clean up had lightened the rocks successfully from the darker end of the spectrum.

Table 19: Old Red Sandstone average values – laboratory results

Data →	ORS Cont.	IS	ORS Kl 2050	ORS Kl Crude	ORS Kl Wea	ORS RecIt 2050	ORS Recit Crude	ORS Recit Wea	ORS Peat 2050	ORS Peat Crude	ORS Peat Wea
PV ↓											
20	600	Cle	322.4	7.2	8.4	326.6	820.2	403.2	80.2	324.4	4.6
		Poll	198.4	5.2	1	632.6	125.4	283.2	972	27	2.6
100	3668	Cle	394	1011	234	2116	5380.2	25.6	297.6	2559.8	1461.4
		Poll	23.6	125	70.6	369	1935	12.2	1357.4	2057.4	301.4
180	3	Cle	1204.2	1678.2	6514.2	231.8	2313	1550	1811.6	2090.2	3403.4
		Poll	26.2	2671.4	2210.2	1571.2	2585.6	530.2	1984.6	5156.8	800.6
240	0	Cle	0	6.8	33	0.2	2	15.2	56.6	8	138.6
		Poll	279.4	176.2	0.8	0.2	2211.4	0	36	1299.2	395.6

Legend:

PV = pixel value **ORS = Old Red Sandstone** **IS = image state**

Cont. = control value **Kl= Klausorb** **Cle =cleaned**

Wea = weathered oil **Recit – RecoverIt** **Poll = polluted**

Table 19 represents the data from the Old Red Sandstone results. 100 is the dominant shade in the control image.

Seven of the nine results (78%) at pixel shade 20 have a higher cleaned than polluted tally. It is noted that both results with a higher polluted tally were from data with 2050 refined motor oil. The anomalous result (Old Red Sandstone, peat and 2050 refined motor oil) is explained by the combination of the sandstone and the pale oil resulting in a high number of pale pixels. At shade 100 eight of the nine results (89%) have a higher cleaned than polluted tally. This is a clear indication based on the dominance of pixel distribution in the control that the application of sorbents has successfully removed the oil. The result with a higher polluted tally had 2050 refined motor oil, its pale colour explains this result. The high numbers of pixels in comparison to the control image can be attributed to the porous structure of the Sandstone, its capability to absorb oil has been reflected in the high pixel tally of both polluted and cleaned data. Six of the nine results

(67%) at shade 240 had higher tallies in the polluted images. The low values in the cleaned images are an indication of the efficacy of the sorbents.

The histograms in Figures 60, 61 and 62 display the averages of the data sets from the control, polluted and cleaned images.

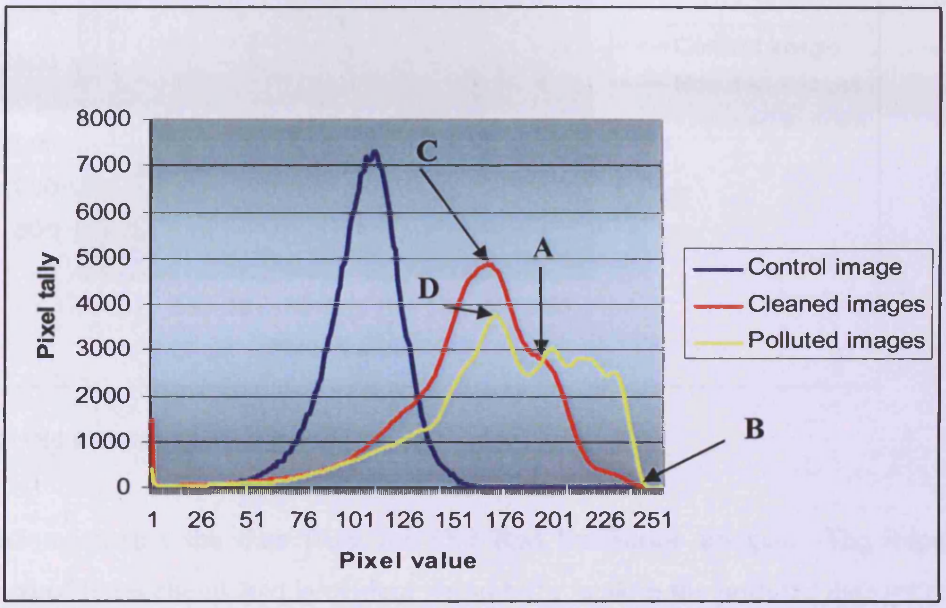


Figure 60: Smooth Limestone summary graph

The data from the Smooth Limestone results (Figure 60) shows the control image (blue line), the average results for the polluted images (yellow line) and the average for the cleaned images (red line). The area between the red and yellow line at point A and point B shows the reduction in dark pixels between the polluted and cleaned images. The differences in height between the peaks of the lines at point C and point D at the 170 pixel shade illustrate the reduction in pixels of that colour post-cleaning.

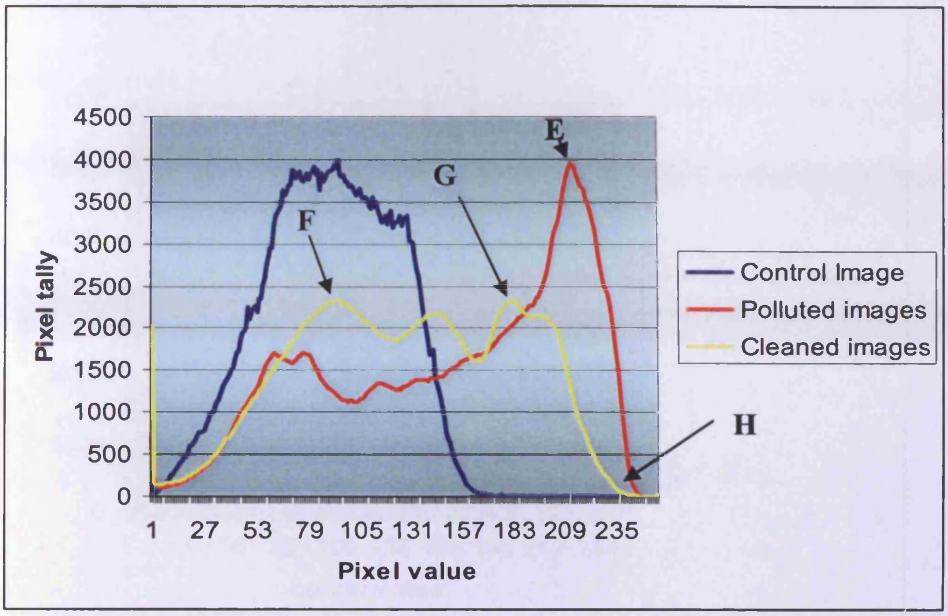


Figure 61: Old Red Sandstone summary graph

Figure 61 represents the data from the Old Red Sandstone images. The impact the application of the sorbents had is evident through the peak in the polluted data set at point E and the peak in the cleaned images at point F. The area between the yellow and red lines at points G and H illustrate the drop in dark pixels post-sorbent application.

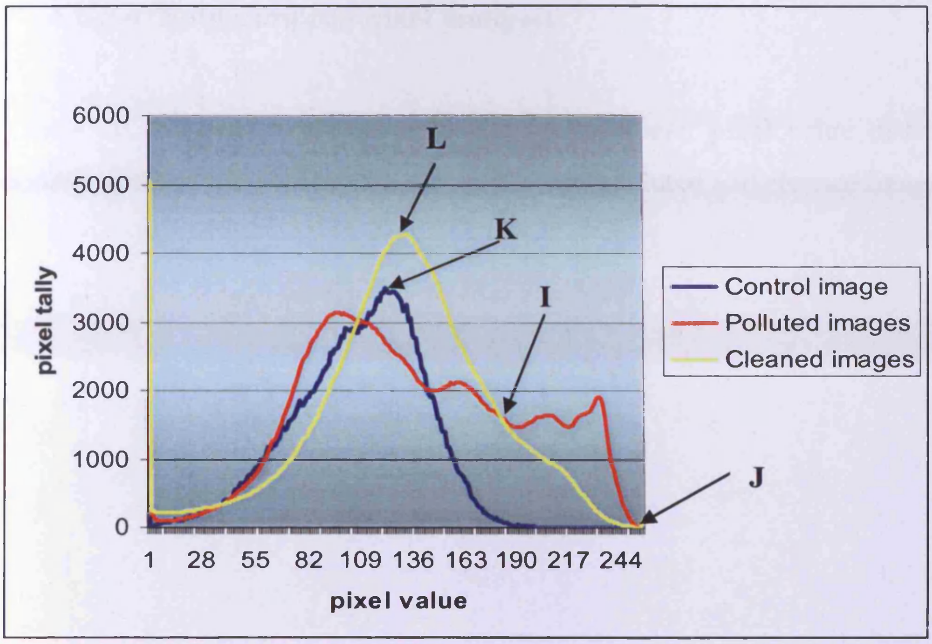


Figure 62: Weathered Limestone summary graph

Figure 62 represents the data for the Weathered Limestone results. The area between the red and yellow lines at point I and J illustrate the impact of the sorbents. The difference in the height of the peaks of the data (points K and L) in the polluted and cleaned images is a further indication of the effectiveness of the sorbents.

4.8.2.4 Southampton pixel analysis:

Tables 20, 21 and 22 show the results for the mean pixel value distribution for all combinations of oil, sorbent and substrata on the polluted and cleaned images

Table 20: Pixel value distribution on unpolluted and oiled rocks – Southampton data

Pixel value → / Rock type ↓	20	40	60	80	100	120	140	160	180	200	220	240
St Wa Cont	93	1099	3718	6404	6628	4683	1723	657	249	111	82	31
Concrete Cont	61	1187	6755	10132	3714	868	321	123	85	38	21	10
Shingle Cont	2	35	36	32	6	3	1	0	0	0	0	0
St Wa Crude	33	69.6	135.6	344	2154.2	1592	443.4	199.6	384.4	263.3	1275.2	204.8
St Wa 2050	16.6	35	251	249	680.4	1158.8	1238.2	690	768.6	503.4	368	13.6
St Wa weath	26.4	153.2	563	1146.4	1648.6	1349.8	895.6	629.4	396.2	234	92.8	24.4
Concrete crude	10.2	33.2	124	907.6	1473.8	630.8	230.4	591.2	839.2	92	333	1116.8
Concrete 2050	119.6	199.6	380.2	882	1213.2	1008	819.2	551.4	160	47.4	20.6	5.6
Concrete weath	0	0	0.4	9	149.6	316	608.2	107.4	6	0.4	0	0
Shingle crude	0	0.2	1.2	3	6.2	17.2	35.6	166.6	223.8	343.2	211.6	337.6
Shingle 2050	0.4	0.8	2	5.2	18.4	72.9	312.4	679.4	445.2	174.8	7.8	0.6
Shingle weath	219.4	311.2	220.8	193.2	91.2	48.6	152.6	218	332.6	225.2	239	109.6

The following trends in the average values for the pixel distribution for the control and polluted images from Southampton can be observed:

- The pixel distribution in the control images of the concrete slab and piece of stone wall is concentrated between 40 and 140.
- The distribution of the pixels for the control image of the shingle is concentrated between 40 and 80.
- It is noted that the number of individual pixels is lower on the shingle control than the concrete or stone wall, this is due to the size of the piece of shingle.
- The addition of oil darkened the images with the exception of concrete with 2050 oil and shingle with weathered oil.
- This is due to the shade of the 2050 oil and the composition of the weathered oil including various oils and water.
- The surface areas of the substrata were larger than the ones used in the laboratory,

Table 21: Mean pixel value distribution (20-120) of oil and cleaned rocks – Southampton results

pixel value →	20		40		60		80		100		120	
	Polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned
substrate/oil/recovery ↓												
conc 2050 klau	5.8	35.4	32.2	170.4	533.2	866.8	1193	2380	1357.2	1538.6	652.6	407.2
conc 2050 recit	119.6	138.6	199.6	209.6	380.2	493.2	882	1185.6	1213.2	1972.4	1008	1958.8
conc crude klau	13.2	32.6	52.6	94.4	147.4	250.2	285	744	400.8	1876	1535	2139.6
conc crude recit	10.2	7.4	33.2	38.6	124	204.4	907.6	707	1473.8	1898	630.8	994
st wall 2050 klau	16.6	68.8	35	168.4	251	380.8	249	721.2	680.4	1368.2	1158.8	2183.6
st wall 2050 recit	25.4	109.4	96.6	257.8	345.6	577	883.4	1045.2	1005.8	1083.2	708.4	1024.4
st wall crude klau	33	73.6	69.6	127.2	135.6	218.8	344	412.2	2154.2	820.2	1592	1571
st wall crude recit	0.2	1	0	1.6	0.4	5.4	8.6	32	30	130.2	141.6	273.2
weathered conc klau	0	0	0	0.2	0.4	0.4	9	5.6	149.6	134	316	660.6
weathered conc recit	0	0	0	0.4	0	0.2	0.4	7.2	853.4	401.6	258	704
2050 conc peat	0	26.4	12.8	92.6	342	292	579.6	681.6	999.2	949.2	1296	659.2
crude peat concrete	0	103	0.6	295.6	2.4	605.6	6.8	875.6	43.8	1117.8	513.6	1133.4
crude peat stone wall	13.8	33.6	28.4	99.6	70	197.2	225.2	338.4	915.2	483	327.6	661.8
2050 peat stone wall	12	35.6	151.2	95.8	196	205.4	437.4	377	478	599	342.6	849.4
2050 peat shingle agg	1.6	4.2	4	10.2	7.6	9.8	13.2	26.6	21.6	57.8	86.6	125.8
2050 peat shingle a+w	2	2	2.4	3	3.2	5.4	65.4	4.6	321	16.6	300	135.6
crude peat shingle agg	1	1.8	1.2	0.4	3.2	3	2.8	3.8	9.2	6.6	21.2	34.8
weathered peat shingle agg	0.8	0	1	1.2	5.4	2	17	2.8	48.4	9.6	116.2	32.6

shingle weathered peat aw	3.6	0	8.2	0	28.6	0.6	54.4	1.2	170.6	3	331	33
weathered peat concrete	36	49.2	92.4	26.4	244.4	153.2	930	563	721.6	1146.4	389.6	1648.6
weathered stone wall klausorb	26.4	18.6	153.2	46.4	563	158.4	1146.4	762.8	1648.6	536.6	1349.8	402.2
weathered stone wall peat	24.6	43	59.2	156.2	260	398.6	614.2	753.2	737.2	1076.8	445.4	1104
weathered stone wall recit	14.8	10.2	35.2	37.8	104.4	187	640.2	767.2	575.8	1625	296.4	1502.6
shingle klausorb 2050 agg	0	0.6	0	0.8	0.8	1.2	3.6	2.4	66	4.6	468.4	11.8
shingle klausorb crude agg	0.4	0.6	1.2	0.6	2.2	2.2	4.2	3.8	8.8	6.8	31.4	30.2
shingle klausorb crude aw	0.8	3	1.6	5.6	2.4	13.4	7.2	32.2	23.2	80.8	48.8	104.6
shingle klausorb weathered agg	1.2	3.4	0.6	3.8	2.2	7.2	2.4	12.2	3.4	18.6	8.4	43.8
shingle klausorb weathered aw	1.8	2.2	2.2	0.8	2.2	2.8	5	4.6	24.2	11.4	78.2	34.4
shingle recit 2050 agg	0.4	1.6	0.8	4.6	2	14	5.2	25.8	18.4	61.4	79.2	295.4
shingle recit 2050 aw	0.4	0.2	0.6	0.4	2.2	2.2	3.2	4.6	10.6	14.6	22	45.2
shingle recit crude agg	0.6	0.8	0.2	1.2	0.6	2.2	0.8	5.6	3	9.4	9.6	43.8
shingle recit crude aw	0	0.6	0.2	2.6	1.2	3.2	3	8.4	6.2	14.6	17.2	36.6
shingle recit weathered agg	219.4	1.8	311.2	5.6	220.8	6.8	193.2	15	91.2	33.2	48.6	85.4
shingle recit weathered aw	1.2	0.4	1.2	0.8	1.2	2.8	4.4	1.8	3	4.2	7.8	24
shingle peat crude aw	0	0	0	0	0	0	0	0.2	0	0.8	0.8	0.8

Legend:

St Wall = stone wall, AW = cleaned by aggravation and washing, Recit = RecoverIt, Agg = cleaned by aggravation

Table 22: Mean pixel value distribution (140-240) of oil and cleaned rocks – Southampton results

pixel value →	140		160		180		200		220		240	
	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned	polluted	cleaned
substrate/oil/recovery ↓												
conc 2050 klau	1154	130	362.4	49	31.2	13.2	4	5.8	2	2	0.2	0.2
conc 2050 recit	819.2	1100.8	551.4	499.6	160	214.6	47.4	95.2	20.6	38.4	5.6	10.2
conc crude klau	204.8	1354.2	160.6	782.8	155.4	408.6	236.2	174.4	1153.6	82.2	2305.2	725
conc crude recit	230.4	652.8	591.2	416	839.2	289.4	92	209.6	333	282.4	1116.8	452
st wall 2050 klau	1238.2	2290.4	690	1716.2	768.6	1023.6	503.4	438.8	368	143.4	13.6	37.6
st wall 2050 recit	446.8	850	374.6	545.2	268.6	301	180	153.4	47.6	57.6	4.6	24.2
st wall crude klau	443.4	2227.6	199.6	1679.2	384.4	691.2	263.6	244.6	1275.2	87.8	204.8	21.2
st wall crude recit	736.8	384.6	353	287	104.6	143	69.8	107.8	62.8	81.8	123.8	112.2
weathered conc klau	608.2	392	107.4	116.8	6	2	0.4	0	0	0	0	0
weathered conc recit	275.2	46.2	14	2.8	1	0	0	0	0	0	0	0
2050 conc peat	742.2	631.4	289.2	448.2	116.2	334.8	58.6	208.6	27.2	129.4	3.6	47.6
crude peat concrete	864.8	975	1120.6	823.2	38	671	57.8	489.4	96	290	4854.6	112.6
crude peat stone wall	348.8	718.4	77.6	645	57.8	530.6	78.4	339.6	335.2	156.8	380.2	38.6
2050 peat stone wall	406.2	899.4	392.4	745.6	363.4	475	205.2	260.2	64.4	124.2	3.2	41.2
2050 peat shingle agg	369.2	529.8	886	634.8	463.6	352.8	266.6	221.6	21.8	108.6	4	83.4
2050 peat shingle a+w	373	377.8	482.2	575	370	344.8	93.2	245.2	39	146.2	7	46.2
crude peat shingle agg	79.6	186.6	233.4	223	376.4	237	497.2	230.6	376.8	219.4	199.6	182.4
weathered peat shingle agg	205.6	166.2	421.2	372.6	264.2	291	208.8	158	132.4	117.2	0.4	30.6

shingle weathered peat aw	340.6	212	135.2	556	96.2	434.6	46.6	154.8	4.6	74.6	0.6	1.6
weathered peat concrete	433.4	1349.8	975	895.6	787.6	629.4	431.4	396.2	137.8	234	30.4	92.8
weathered stone wall klausorb	895.6	656.4	629.4	554.2	396.2	196.2	234	62.8	92.8	16.2	24.4	1.4
weathered stone wall peat	795.6	978.2	409.8	648.2	125.4	361	49	151.8	19.8	45.4	4.8	13.4
weathered stone wall recit	531.2	916.6	398.6	405.2	192.6	129	95.4	25.2	33.4	3.4	10.2	0.4
shingle klausorb 2050 agg	437.4	39.8	804.6	260.6	177.6	670.6	146.6	405	32.2	74.8	2	3
shingle klausorb crude agg	167.2	148.4	426.4	375.8	241.6	384.4	230	283.6	234	229.6	544.6	55
shingle klausorb crude aw	429.4	106.2	357.8	276	192	362	164.4	190.6	301	86.2	397.4	17.4
shingle klausorb weathered agg	35.6	135	126.4	308.8	318.8	203.6	205	108.6	497.2	33.8	62.4	3.8
shingle klausorb weathered aw	120.6	114.4	183.2	268.2	364	466.2	312.6	326.6	337	183	57.2	19.4
shingle recit 2050 agg	312.4	297.4	679.4	368.6	445.2	323.8	174.8	268.2	7.8	50.8	0.6	5
shingle recit 2050 aw	180.6	190.4	1013.8	464	525.2	385.8	268	306.8	13.8	77.6	0.2	3
shingle recit crude agg	35.6	188	166.6	438.2	223.8	494.6	343.2	250.6	211.6	84.8	337.6	15.2
shingle recit crude aw	40.6	199.6	120.6	533.6	235	333	267	116.2	319	106.6	204.6	12
shingle recit weathered agg	152.6	262.2	218	580.4	332.6	392.8	225.2	113.4	239	26.8	109.6	2.6
shingle recit weathered aw	27	239.4	126.4	464.8	888.8	272	174.8	94.8	463.2	11	13.2	1
shingle peat crude aw	4.8	26.2	103.8	85.6	234.8	161.8	205.4	165.4	66.2	57	4	8

Legend:

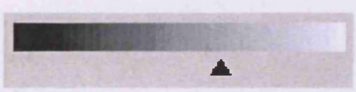
St Wall = stone wall, AW = cleaned by aggravation and washing, Recit = RecoverIt, Agg = cleaned by aggravation

Tables 20, 21 and 22 show the results for the mean pixel value distribution for all combinations of oil, sorbent and substrata on the polluted and cleaned images. The comments below reflect the difference in the pixel tallies between the polluted and cleaned images. The next set of results discusses the cleaned images in relation to the control image.

Shade 20: 

256 **0**

- As with the results from the laboratory work it would be expected that the pixel tally at shade 20 would be higher on the cleaned imaged than the polluted one. This was the case in twenty seven of the thirty six combinations (75%).
- Of the 6 results which have a higher polluted tally the shingle and weathered oil are dominant.
- The average percentage increase between the cleaned and polluted tallies for the 9 results with a higher polluted tally was 67%. The average decrease between the polluted and cleaned tallies for the twenty seven results with a higher polluted tally was 169.9%.
- The average pixel tally for the cleaned images was 23.13 and for the polluted images 16.76.

Shade 100: 

256 **0**

- At shade 100 it was expected that the pixel tally for the cleaned substrate would be higher than that of the polluted. This was the case in twenty one of the thirty six (58.3%) combinations.
- Of the fifteen results with a higher polluted tally, shingle is the dominant substratum and peat the dominant sorbent.
- The average percentage increase between the cleaned and polluted tallies for the fifteen results with a higher polluted tally was 54.5%. The average

decrease between the polluted and cleaned tallies for the twenty one results with a higher polluted tally was -252.5%.

- The average pixel tally for the polluted images was 464.76 and for the cleaned images 546.

Shade 180: 

256 **0**

- At shade 180 it would be expected to have a higher pixel count on the polluted images. This was the case in sixteen of the thirty six results (44%).
- There were no clear patterns regarding oil type in the twenty results that had a higher cleaned tally, the crude was the dominant oil and RecoverIt was the least dominant sorbent, the remaining results were split between peat and Klausorb.
- The average percentage increase between cleaned and polluted image tallies in the twenty results with a higher cleaned tally was 212.2%. The percentage decrease between polluted and cleaned was -41.5%
- The average pixel tallies for the cleaned images were 357.84 and the polluted images 301.31.

Shade 240 

256 **0**

- At shade 240 eighteen of the thirty six results (50%) had a higher tally on the polluted images.
- In the data that had a higher cleaned tally crude oil only accounted for a single result, 2050 refined motor oil was the dominant oil type. Peat was the dominant sorbent and there were no patterns in the distribution of substrata.
- The average percentage decrease between the polluted and cleaned tallies for the twelve results with a higher polluted tally was -79.6%. The average percentage increase for the fifteen results with a higher cleaned tally was 1001.4%.

- The average pixel tally for the polluted results was 315.17 and for the cleaned images 63.43.

The results for the statistical analysis carried out on the substrata, oil ad sorbents showed the following: The results for the substrata ($F_{(3,4248)} = 9.925$ $P < 0.01$) shows there was a statistically significant difference in the distribution of pixels through the spectrum due to the different substrata. The results showed that at shades 20 and 100, the shingle was the least successfully cleaned substratum as it had the lowest cleaned pixel tallies. At the darker end of the spectrum, the concrete has the highest cleaned counts suggesting it was the most responsive to sorbent application. The results for C_2 (oil type) showed a non significant difference in the distribution of pixels between the polluted and cleaned images. ($F_{(3,4248)} = 1.908$ N/S). Despite the non significant result the results suggested that the weathered and the crude oils were the hardest to remove and the refined 2050 motor oil the easiest. There was a statistically significant difference between the sorbents used and pixel distribution. C_3 ($F_{(3,4248)} = 4.166$ $P < 0.001$). At shade 20 RecoverIt was the most effective sorbent at removing oil from the substrata. 140 was used due to lack of patterns at 100 and this showed RecoverIt to be most effective. Peat was observed to be the least effective.

Table 23: Stone wall averages – Southampton results

Data →	SW Cont.	IS	SW Kl 2050	SW Kl Crude	SW Kl Wea	SW RecIt 2050	SW Recit Crude	SW Recit Wea	SW Peat 2050	SW Peat Crude	SW Peat Wea
PV ↓											
20	93	Cle	68.8	73.6	18.6	109.4	1	10.2	35.6	33.6	43
		Poll	16.6	33	26.4	25.4	0.2	14.8	12	13.8	24.6
100	6628	Cle	1368.2	820.2	536.6	1083.2	130.2	1625	599	483	1076.8
		Poll	680.4	2154.2	1648.6	1005.8	30	575.8	478	915.2	737.2
180	249	Cle	1023.6	691.2	196.2	301	143	129	475	530.6	361
		Poll	768.6	384.4	396.2	268.6	104.6	192.6	363.4	57.8	125.4
240	31	Cle	37.6	21.2	1.4	24.4	112.2	0.4	41.2	38.6	13.4
		Poll	16.6	204.8	24.4	4.6	123.8	10.2	3.2	380.2	4.8

Legend:

PV = pixel value | **SW = Stone Wall** | **IS = image state**

Cont. = control value | **Kl= Klausorb** | **Cle = cleaned**

Wea = weathered oil | **Recit – RecoverIt** | **Poll = polluted**

Table 23 represents the averages of the control image and all the polluted and cleaned data for the stone wall data set. It is clear from the table that shade 100 was the dominant colour in the control image. At shade 20 it would be expected to find a higher pixel count in the cleaned image than in the polluted, this is the case in 7 of the 9 (78%) of the results. The low number of pixels at this shade reduces the relevance of the 2 results with a higher polluted pixel count. As shade 100 is dominant on the control image, a higher cleaned pixel count would imply successful oil removal. 6 of the 9 results (67%) have a higher cleaned tally. 2 of the 3 results with a higher polluted tally have Klausorb as a sorbent suggesting it was the least effective product in this test. At shade 180 it would be expected that the polluted pixel tally would be higher than the cleaned. This is the case in 2 of the 9 (22%) results. This data suggests that the clean up had not been successful. It was observed through the course of the work that the application of oils and sorbents spread the distribution of pixels thinner over the colour spectrum. The two results with a higher polluted tally were both from weathered oil data sets, this suggest at this shade weathered oil was the easiest to remove. As with 180, it would be expected that at shade 240 the polluted image pixel count would be higher than the cleaned. This was the case in 5 of the 9 results (55%). The pixel tallies for the polluted images for crude recovered with peat and crude recovered with Klausorb are 380.2 and 204.8 respectively, the cleaned images results are 38.6 and 21.2 respectively. This suggests that the crude oil was the easiest of the three oils to remove. 3 of the 4 results with a higher cleaned count had 2050 refined motor oil as the oil type. This suggests these results were affected by the pale colour of the 2050 oil.

Table 24: Shingle averages cleaned by aggravation – Southampton results

Data →	Sh Cont.	IS	Sh Kl 2050	Sh Kl Crude	Sh Kl Wea	Sh RecIt 2050	Sh Recit Crude	Sh Recit Wea	Sh Peat 2050	Sh Peat Crude	Sh Peat Wea
PV ↓											
20	3425	Cle	0.6	0.6	3.4	1.6	0.8	219.4	4.2	1.8	0
		Poll	0	0.4	1.2	0.4	0.6	1.8	1.6	1	0.8
100	373	Cle	4.6	6.6	18.6	61.4	9.4	33.2	54.8	6.6	9.6
		Poll	66	8.8	3.4	18.4	3	91.2	21.6	9.2	48.4
180	11	Cle	670.6	384.4	203.6	323.8	494.6	392.8	352.8	237	291
		Poll	177.6	241.6	318.8	445.2	223.8	332.6	463.6	376.4	264.2
240	0	Cle	3	55	3.8	5	15.2	2.6	4	182.4	0.4
		Poll	2	544.6	62.4	0.6	337.6	109.6	83.4	199.6	30.6

Legend:

PV = pixel value **SW = Stone Wall** **IS = image state**
Cont. = control value **Kl= Klausorb** **Cle = Cleaned**
Wea = weathered oil **Recit – RecoverIt** **Poll = Polluted**

Table 24 represents the control image and the average values from the shingle data set cleaned by aggravation only. The dominant shade of the shingle is 20. It would be expected that this would be reflected in the data by a higher average in the cleaned results. In 8 of the 9 (89%) results this is the case. Despite this, if the tallies of the polluted and cleaned images are observed it can be said that aggravation alone is insufficient as a technique to clean the shingle. The data for shade 100 supports this observation as only 4 of the 9 results (45%) have a higher cleaned value. There are no patterns in the distribution of oils and sorbents in the data set. At shade 180, a successful clean up would be demonstrated by the polluted images would have a higher average than the cleaned. This is the case in 4 of the 9 results (45%). There was no evidence of any strong patterns in the distribution of sorbent or oil. The data at 240 showed 7 of the 9 results (78%) having a higher polluted tally. This suggests in 78% of cases the sorbents have lightened the substrata however this is not backed up by results at 180 suggesting that aggravation is only suitable for removal of the thick oil deposits and pools that are highlighted at pixel value 240.

Table 25: Shingle averages cleaned by aggravation and washing – Southampton results

Data →	Sh Cont.	IS	Sh Kl 2050	Sh Kl Crude	Sh Kl Wea	Sh RecIt 2050	Sh Recit Crude	Sh Recit Wea	Sh Peat 2050	Sh Peat Crude	Sh Peat Wea
PV ↓											
20	3425	Cle	0.72	3	2.2	0.2	0.6	0.4	2	0	0
		Poll	44.2	0.8	1.8	0.4	0	1.2	2	0	3.6
100	373	Cle	12.4	80.8	11.4	14.6	14.6	4.2	16.6	0.8	3
		Poll	20.6	23.2	24.2	10.6	6.2	3	321	0	170.6
180	11	Cle	330.8	362	466.2	385.5	333	272	344.8	161.8	434.6
		Poll	383	192	364	525.2	235	888.8	370	234.8	96.2
240	0	Cle	7.7	17.4	19.4	3	12	1	7	4	1.6
		Poll	133.8	397.4	57.2	0.2	204.6	13.2	42.6	8	0.6

Legend:

PV = pixel value **Sh = shingle** **IS = image state**

Cont. = control value **Kl= Klausorb** **Cle = Cleaned**

Wea = weathered oil **Recit – RecoverIt** **Poll = Polluted**

Table 25 shows the results for shingle cleaned by aggravation and washing. At shade 20, 2 of the 9 results (22.2%) had a higher cleaned pixel tally. This data suggests that the addition of washing to aggravation did not improve the efficacy of the clean up. However, the low pixel tallies at this shade reduce the relevance of further analysis. At shade 100, 5 of the 9 results (55%) have a higher cleaned tally. All results from shingle cleaned with RecoverIt have a higher cleaned tally; this suggests RecoverIt was the most effective sorbent. All results where crude oil was used also have a higher cleaned tally. This suggests the crude oil at this shade was removed most effectively. At shade 180 it would be expected that the polluted tally would be higher. This is the case in 5 of the 9 results (55%). There were no occurrences of 2050 refined motor oil in the 4 results where the cleaned tally was higher. This suggests that at this shade the 2050 oil was most effectively cleaned.

Table 26: Concrete averages – Southampton results

Data →	Con Cont.	IS	Con Kl 2050	Con Kl Crude	Con Kl Wea	Con RecIt 2050	Con Recit Crude	Con Recit Wea	Con Peat 2050	Con Peat Crude	Con Peat Wea
PV ↓											
20	61	Cle	35.4	36.2	0	138.6	10.2	0	26.4	103	49.2
		Poll	5.8	13.2	0	119.6	7.4	0	0	0	36
100	3714	Cle	1538.6	1876	134	1972.4	1898	401.6	949.2	1117.8	1146.4
		Poll	1357.2	400.8	149.6	1292.2	1473.8	853.4	999.2	43.8	721.6
180	85	Cle	13.2	408.6	116.8	214.6	289.4	0	334.8	671	629.4
		Poll	31.2	155.4	107.4	160	839.2	1	116.2	38	787.6
240	10	Cle	0.2	725	0	5.6	452	0	47.6	112.6	30.4
		Poll	0.2	2305.2	20	10.2	1116.8	0	3.6	4854.6	92.8

Legend:

PV = pixel value **Con = concrete** **IS = image state**
Cont. = control value **Kl= Klausorb** **Cle = Cleaned**
Wea = weathered oil **Recit – RecoverIt** **Poll = Polluted**

Table 26 represents the results from the concrete substratum. It can be seen that shade 100 was dominant in the control image. In 7 of the 9 results (78%) the cleaned tally is higher than the polluted one at shade 20. It is noted that the remaining 2 results have a pixel tally of 0 for both cleaned and polluted images. This suggests that every combination of sorbent and oil has been effectively removed from the concrete. At shade 100, 6 of the 9 results (66%) have a higher cleaned tally. 2 of the 3 results with a higher polluted tally have weathered oil as an oil type. This suggests that weathered oil was removed least effectively. There is no pattern in the distribution of sorbents. At shade 180, 4 of the 9 results (44%) have a higher polluted tally, results from weathered oil account for 2 of the 4 results. This supports results from shade 100 suggesting removal of weathered oil was least successful. 1 of the 5 results with a higher polluted tally had RecoverIt as a sorbent. This suggests RecoverIt performed most effectively of the sorbents. Shade 240 shows 6 of the 9 results (66%) with a higher polluted tally. There were no clear trends in the distribution of sorbent or oil in the results with a higher polluted tally. 2 of the results had even numbers for polluted and cleaned, the only result with a higher cleaned tally was 2050 refined motor oil removed with peat.

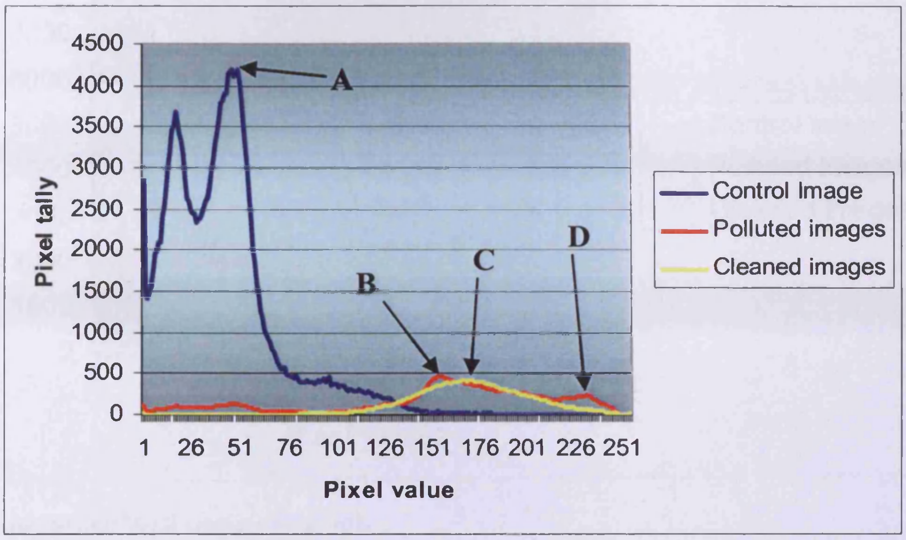


Figure 63: Shingle cleaned by aggravation summary graph

Figures 63 to 66 display the data from the control image and an average of the polluted and cleaned images for the various substrata. The patterns shown in the data are not as pronounced as with the laboratory data but there are various trends that can be discussed. What can be seen from all of these figures is that the application of oil and sorbent to the substrata spread the distribution of pixels over the full colour range. Figure 63 displays the data from the shingle cleaned by aggravation, it was observed when comparing values from the control and the polluted and cleaned images that the technique was ineffective. This can be reinforced by the peaks of the data shown at points A, B and C. Point D illustrates where the cleaned data has a lower average than the polluted data at the dark end of the spectrum suggesting that the sorbents have removed a proportion of the oil.

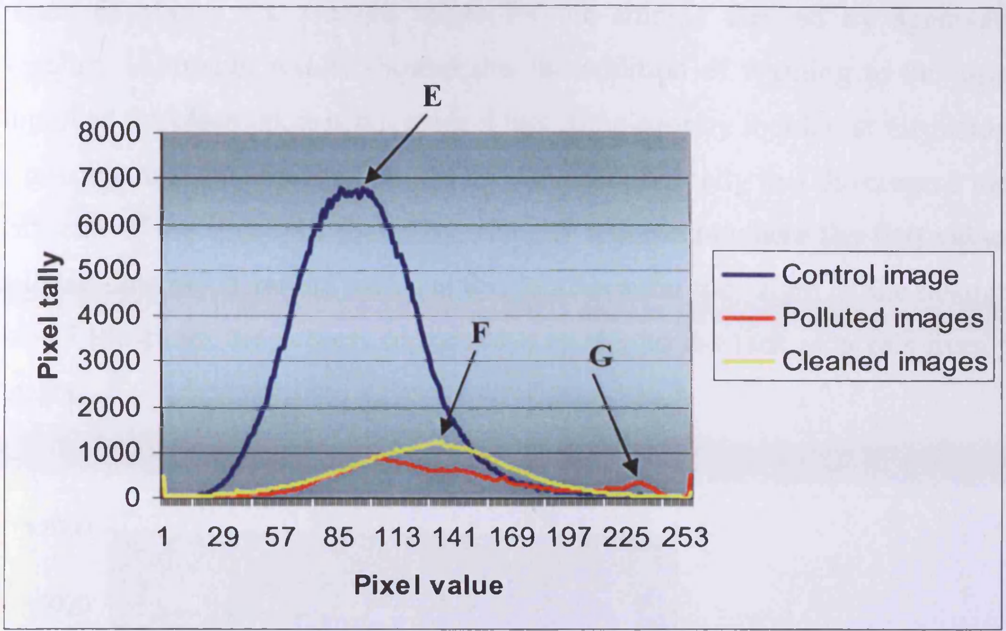


Figure 64: Stone Wall summary graph

Figure 64 displays the results from the stone wall data. The dominant shade on the stone wall control was 100 as shown by point E. Evidence that the clean up on the stone wall had succeeded in removing a proportion of the oil can be seen by the peak of the cleaned averages at point F and by there being a higher polluted pixel count at the dark end of the spectrum (point G)

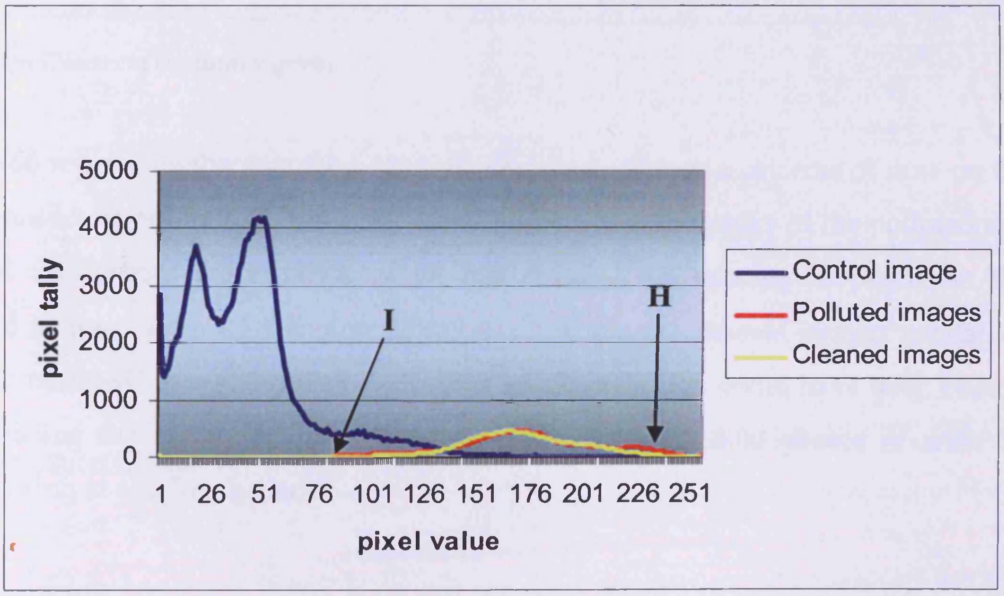


Figure 65: Shingle cleaned by aggravation and washing summary graph

Figure 65 shows the average values for the shingle cleaned by aggravation and washing. Although results showed that the addition of washing to the aggravation improved the clean up, it is not evident this is the case by looking at the histogram. It is possible to see where the polluted data has a higher tally that the cleaned data at the dark end of the spectrum (point H). Point I represents where the first value for the polluted data is. It can be said that the data between the origin of the histogram and point I illustrates the success of the clean up due to the lack of pixels from polluted images.

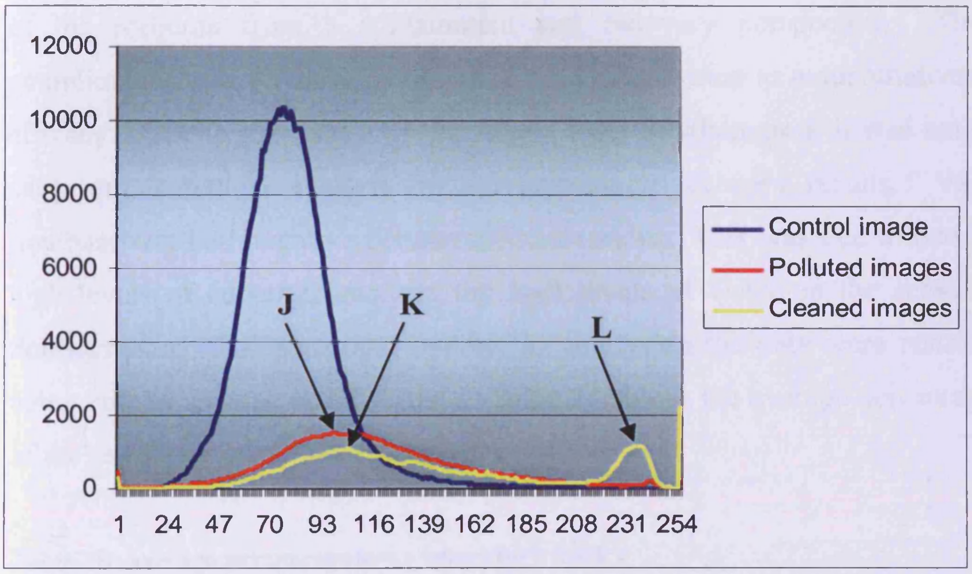


Figure 66: Concrete summary graph

Figure 66 represents the data from the concrete data. The two patterns of note on the histogram are at points J, K and L. Points J and K show the peaks of the polluted and cleaned data where the removal of oil has reduced the number of pixels on the polluted images. Point L is an anomalous result where the cleaned images are darker than the polluted ones at the dark end of the spectrum. This could have been caused by spreading the oil on the concrete slab leading to individual photos or areas of photos being anomalously dark.

4.8.3 Percentage loss results

4.8.3.1 Laboratory results

Percentage recovery tests were carried out on all combinations of the oils and sorbents from the laboratory and Southampton. It was expected that the results would show a lower percentage recovery for the Southampton results due to a range of factors affecting both oil and sorbent that were not present in the laboratory. The purpose of the percentage recovery exercise was to analyse the effectiveness of the performance of the sorbents from a containment and recovery perspective. These results compliment the work carried out on the pixel distribution as a quantitative measure of efficacy. Due to the nature of the results from Southampton, it was not possible to carry out statistical analysis on the percentage recovery results. Various from Southampton had negative percentage loss results. This was due to two factors, the high levels of contaminants and the high levels of water on the substrata used in Southampton. The statistical options for analysing the data were restricted by not being able to analyse negative data. Table 27 shows the average percentage loss data of the results from the laboratory work.

Table 27: Average percentage loss - laboratory work

Substratum	Oil type	Sorbent	% loss
ORS	2050	Klausorb	10.77
ORS	2050	Peat	10.14
ORS	2050	RecoverIt	5.50
ORS	Crude	Klausorb	24.63
ORS	Crude	Peat	24.06
ORS	Crude	RecoverIt	3.36
ORS	Weathered	Klausorb	33.73
ORS	Weathered	Peat	7.32
ORS	Weathered	RecoverIt	15.42
RL	2050	Klausorb	40.90
RL	2050	Peat	41.82
RL	2050	RecoverIt	3.93
RL	Crude	Klausorb	54.41
RL	Crude	Peat	28.64
RL	Crude	RecoverIt	1.82
RL	Weathered	Klausorb	25.54

RL	Weathered	Peat	6.74
RL	Weathered	RecoverIt	11.92
SL	2050	Klausorb	8.35
SL	2050	Peat	11.29
SL	2050	RecoverIt	4.69
SL	Crude	Klausorb	5.30
SL	Crude	Peat	16.19
SL	Crude	RecoverIt	3.49
SL	Weathered	Klausorb	13.95
SL	Weathered	Peat	13.06
SL	Weathered	RecoverIt	22.52

Legend:
RL – Rough Limestone
SL – Smooth Limestone
ORS – Old Red Sandstone

All the results in Table 27 are positive i.e. less material was recovered than applied. In order to further analyze the efficacy of individual oils and sorbents, it was necessary to average the results and sort them by oil type and sorbent. The averages are displayed in Table 28.

Table 28: Percentage loss summary of averages - laboratory data

Factor	Average % loss
ORS	14.99
SL	10.98
RL	23.96
RecoverIt	8.07
Klausorb	24.17
Peat	17.69
Weathered	16.68
2050	15.26
Crude	17.98

It can be seen from Table 28 that of the three substrata, the Rough Limestone has highest percentage loss figures (23.96%). This was expected and in trials in the experimental design phase of the study shown to be the case. The reason for the high percentage loss is related to the high surface area of the Rough Limestone and subsequent complications in removing the oil. It was noted that the surface of the Old Red Sandstone had a higher porosity than either of the Limestone samples. This combined with its surface being more abrasive than Limestone led to it having percentage loss figures of 14.99%. The Smooth Limestone had the lowest percentage loss results (10.98%), this is due to the smoothness of its surface and its low surface area. It was observed during the study that containment and recovery of the oil and sorbent was most effective on the Smooth Limestone.

The highest standard deviation in the results was from the sorbent data set. Klausorb recorded the highest percentage loss (24.17%) and RecoverIt the lowest (8.07%). Klausorb is structurally the finest of the sorbents, on contact with the oils, particularly the weathered and 2050 refined motor oil it formed a paste like substance and became sticky. The peat's ability to absorb oil was not the reason for a percentage loss figure of 17.69%. The fine material in the peat structure spread rapidly and became sticky post application, this complicated containing and recovering the product. The highest average percentage loss of the Klausorb data was when the rough limestone was polluted with the 2050 refined motor oil. This is the combination of the substratum with the highest surface area, the most viscous oil and the finest sorbent. The RecoverIt was the most efficient sorbent due to it having the largest particle size of the three sorbents; it maintains its structure post oiling and becomes less pasty and sticky than Klausorb.

The results for the oils had the smallest standard deviation of the 3 data sets. The crude oil had the highest percentage loss (17.98%) and the 2050 refined motor oil the lowest (15.26%). Observations made while collecting the data suggest this was due to the crude oil having the ability to soak into the substrata and due to its lack of viscosity it spread rapidly. The weathered oil result is related to its water content which aided spreading. Containing the weathered oil as it was composed of a range of products of varying viscosity contributed to the percentage loss. Once contained, recovering it was manageable. The 2050 motor oil was viscous and spread the least of the 3 oils and this aided the containment but due to the paste like substance forming complicated recovery. This is illustrated by two of the rough limestone results polluted with 2050 refined motor oil are over 40% loss.

4.8.3.2 Southampton results:

The results for the Southampton data set are displayed in Tables 29 and 30. Table 29 displays the data from all combinations of substrata, sorbent and oil. The negative results are due to more material being collected than applied. This was due to the presence of water and contaminants being mixed with the oil-sorbent compound.

Table 29: Average percentage loss – Southampton data

Substratum	Oil type	Sorbent	% loss
Concrete	2050	Klausorb	14.39
Concrete	2050	Peat	3.41
Concrete	2050	RecoverIt	10.29
Concrete	Crude	Klausorb	26.00
Concrete	Crude	Peat	10.47
Concrete	Crude	RecoverIt	11.37
Concrete	Weathered	Klausorb	-16.33
Concrete	Weathered	Peat	-15.99
Concrete	Weathered	RecoverIt	-63.45
Stone Wall	2050	Klausorb	51.65
Stone Wall	2050	Peat	19.84
Stone Wall	2050	RecoverIt	27.70
Stone Wall	Crude	Klausorb	37.80
Stone Wall	Crude	Peat	29.58
Stone Wall	Crude	RecoverIt	32.54
Stone Wall	Weathered	Klausorb	11.05
Stone Wall	Weathered	Peat	-48.39
Stone Wall	Weathered	RecoverIt	-39.30
Shingle agg	2050	Klausorb	31.70
Shingle agg	2050	Peat	-20.24
Shingle agg	2050	RecoverIt	14.36
Shingle agg	Crude	Klausorb	43.73
Shingle agg	Crude	Peat	-12.23
Shingle agg	Crude	RecoverIt	-3.29
Shingle agg	Weathered	Klausorb	23.59
Shingle agg	Weathered	Peat	-22.37
Shingle agg	Weathered	RecoverIt	-6.68
Shingle aw	2050	Klausorb	-5.23
Shingle aw	2050	Peat	3.84
Shingle aw	2050	RecoverIt	-8.97
Shingle aw	Crude	Klausorb	41.43
Shingle aw	Crude	Peat	-91.03

Shingle aw	Crude	RecoverIt	9.38
Shingle aw	Weathered	Klausorb	16.30
Shingle aw	Weathered	Peat	-35.22
Shingle aw	Weathered	RecoverIt	-4.69

The averages for the Southampton data era displayed in Table 30.

Table 30: Percentage loss summary of averages - Southampton data

Factor	Average % loss
Concrete	-2.2
Stone wall	13.60
Shingle agg	5.39
Shingle aw	-8.24
RecoverIt	-1.72
Klausorb	23.00
Peat	-14.80
Weathered	-16.79
2050	11.89
Crude	11.31

The two results with positive values from the substrata data are stone wall and shingle cleaned by aggravation. The stone wall had the highest surface area and recurrent complications were observed recovering the oil and sorbent as were found with Rough Limestone in the laboratory. This was noted when using Klausorb, the paste it formed in contact with the oil was persistent on the Stone Wall during clean up. The shingle that was cleaned by aggravation had recorded an average percentage loss of 5.39. Klausorb recorded the highest percentage loss; it was the presence of negative results in the data that brought the overall average down.

The shingle tests that were cleaned using aggravation and washing recorded an average percentage loss of -8.24. As with all the tests conducted cleaning the shingle in this way the reason more material was collected than spilled was due to the sorbents retaining the water used to wash the substratum as well as the spilled oil. The concrete had an average of -2.2%, of the nine tests conducted with the concrete, three had a negative percentage loss and they were all from the data using the weathered oil. It was observed that the weathered oil spread fastest on the concrete and in doing so it came into contact with contaminants and any water that was present on the substratum. On several occasions, the uniform surface of the concrete led to pooling of water while the irregular surface of the stone wall enabled water to drain off.

Of the three sorbents used, RecoverIt was the most effective with regard to ease of recovery. The highest percentage loss with RecoverIt was when it was applied to crude oil on Stone Wall. This was due to the substratum and oil type as opposed to the sorbent; the 2050 oil had a 27.70% loss and the weathered oil -39.30% loss. Klausorb had the highest average percentage loss (23.00%), this was due to its particle size and the inherent difficulties of recovering fine particles mixed with oil. The peat's overall negative average is largely due to one result. When crude was applied to the shingle and recovered with peat by aggravation and washing there was a percentage loss of -91.03%. This is due to the peat's ability to absorb water at the same rate as oil so any of the water that was used to wash the shingle that came into contact with the peat was included in the calculation. This was reflected in the peat's results as seven of the twelve results yielded a negative value.

Two of the three oils used have a positive percentage recovery; the 2050 refined motor oil has an average loss of 11.89% and the crude 11.31%. The 2050 refined motor oil was the most viscous of the three; it spread less and took longer to mix with water, the crude spread faster than the 2050 but not as rapidly as the weathered product. The weathered oil had an average loss of -16.79; this is due to its high water content and spreading. To put these figures in perspective, the *Exxon Valdez* incident in Alaska in 1989 saw a total of 9% of the oil on the surface of the sea recovered (White I 1998)

4.8.4 Carbon and moisture content tests

4.8.4.1 Laboratory results

The results from the carbon and moisture content tests carried out on compounds of oil and sorbent are as follows. Table 31 displays the average values for carbon and moisture content for the laboratory samples.

Table 31: Average carbon and moisture content – Laboratory results

Sorbent	Oil type	%/100 moisture	%/100 carbon
Peat	Crude	22.76	91.61
Peat	weathered	47.86	94.59
Peat	20/50 motor	8.49	94.33
Klausorb	Crude	11.32	88.98
Klausorb	weathered	43.8	90.53
Klausorb	20/50 motor	5.19	92.99
Recit	Crude	31.80	92.47
Recit	weathered	53.99	86.72
Recit	2050 motor	5.05	97.16
Overall average		**25.59**	**92.15**

The oil with the highest moisture percentage (47.6%) was the weathered oil. The water in the oil came from it being recovered from offshore and the coast after it had formed an oil-in-water emulsion. The average moisture percentage result for the crude oil was 21.30% and for the 2050 refined weathered oil 0.2%. The likelihood is that the water found in the crude oil samples came from the drilling, extraction or transportation phase http://crudemarketing.chevron.com (1). The refining process involves boiling the oil which accounts for the 0.2% result for the 2050 refined motor oil. The statistical test for the moisture results ($F_{(2,44)}$ = 2.15 N/S) showed there was no significant difference between the compounds of oil and sorbent and their moisture content. With regard to using the compounds as fuel, moisture levels can be a limiting factor. The non significant result with moisture content is a positive statistic to support the argument.

The results for the carbon tests show that the weathered oil has an average carbon percentage of 90.61%, the 2050 refined motor oil 94.83% and the crude oil 90.02%. The statistical test showed there was a statistically significant difference between the carbon levels in the oil-sorbent compounds. ($F_{(2,44)}$ = 5.00 $P<0.05$) An overall average of 92.15% provides support for the research into using these products as fuel.

The final statistical test was an interaction test to determine whether the carbon or moisture content was affected by the interaction between oil and sorbent. The result showed there was a statistically significant interaction. ($F_{(2,44)}$ = 3.28 $P<0.05$). This may have been caused by the high moisture levels being affected by the efficacy of the sorbents.

4.8.4.2 Southampton results

Table 32 displays the % moisture and carbon content from the Southampton data set.

Table 32: Average carbon and moisture content – Southampton results

Substratum	sorbent	oil type	% wt weight/100	%carbon content/100
Concrete	Peat	2050	7.32	97.04
Concrete	Recoverlt	2050	5.46	94.85
concrete	Klausorb	2050	3.88	93.89
stone wall	Klausorb	2050	6.10	88.74
stone wall	Peat	2050	6.14	96.96
stone wall	Recoverlt	2050	13.39	94.57
Shingle	Peat	2050 agg	18.25	98.52
Shingle	Recoverlt	2050 agg	18.10	94.14
shingle	Klausorb	2050 agg	9.50	96.83
Shingle	Peat	2050 aw	7.12	98.03
Shingle	Recoverlt	2050 aw	36.43	96.38
shingle	Klausorb	2050 aw	17.72	98.14
Concrete	Klausorb	Crude	4.57	94.05
Concrete	Peat	Crude	12.04	96.18
Concrete	Recoverlt	Crude	22.29	94.53
stone wall	Klausorb	Crude	7.81	89.87
stone wall	Peat	Crude	16.68	97.69
stone wall	Recoverlt	Crude	30.81	93.99
Shingle	Klausorb	Crude agg	13.74	95.51
Shingle	Peat	Crude agg	13.43	92.14
Shingle	Recoverlt	Crude agg	38.18	84.63
Shingle	Peat	Crude aw	59.49	96.63
Shingle	Klausorb	Crude aw	22.33	92.79
Shingle	Recoverlt	Crude aw	40.37	94.65
Shingle	Peat	Weathered aw	69.02	97.46
Shingle	Klausorb	Weathered aw	38.93	97.04
Concrete	Klausorb	Weathered	51.49	95.01
Concrete	Recoverlt	Weathered	66.88	92.62
concrete	Peat	Weathered	30.07	98.16
stone wall	Klausorb	Weathered	31.80	95.00
stone wall	Peat	Weathered	65.20	97.16
stone wall	Recoverlt	Weathered	60.31	90.92
Shingle	Peat	Weathered agg	66.45	96.90
Shingle	Recoverlt	Weathered agg	26.99	94.60
Shingle	Klausorb	Weathered agg	39.22	93.83
shingle	Recoverlt	Weathered aw	57.80	85.07

Overall average	28.76	94.57

In order to analyze these results, the average values from the Southampton data set were calculated and compared with then laboratory results. Table 33 displays the average moisture content results.

All three results from Southampton have higher moisture content than the laboratory results. The increase in the percentage can be attributed to water on the substrata when the data was being collected. The weathered oil has the highest percentage moisture content and the 2050 refined motor oil had the lowest. The most noticeable increase in the moisture contents is in the data with 2050 refined motor oil. The result that has led to this high average is from the shingle using RecoverIt as the sorbent and recovered by aggravation and washing. The crude and weathered oil results show a difference of 3.37% and 2% between the laboratory and field data respectively. This shows that the field conditions did not significantly affect the moisture levels in the compounds.

The test carried out on the moisture readings showed a statistically significant difference between oil type and moisture content ($F_{(8,144)} = 6.513$ $P = 0.000$), there was no statistically significant difference between substrata and oil type ($F_{(8,144)} = 0.250$ N/S). The result for the sorbent showed a significant difference ($F_{(8,144)} = 18.326$ $P = 0.000$). This is due to the fact that the statistics were carried out on the compounds, the high moisture levels in the oils led to the sorbent test being significant.

Table 33: Average % moisture content – laboratory and Southampton

Oil type	Average moisture content %	
	Lab	Southampton
Weathered	47.60	49.60
2050 motor	0.20	12.45
Crude	21.30	24.67

The results for the carbon test data averages in the laboratory and Southampton can be seen in Table 34. In all three of the results, the carbon levels are higher in the Southampton data set. The 2050 refined motor oil has the highest carbon percentage in both samples. The source of the additional carbon in the samples was most likely sourced in contaminants collected with the compound.

The statistical results show there was no significant difference in the levels of carbon due to the different substrata. ($F_{(3,144)} = 0.246$ N/S) or oil type ($F_{(3,144)} = 0.686$ N/S).

The statistics for the sorbent results show a significant difference in carbon levels due to the sorbents. ($F_{(3,144)} = 9.500$ $P = 0.000$). A standard error test was carried out to determine the standard deviation of the error in the data set. The result of the standard error test was 0.055. This illustrates that the variations between the carbon content of the sorbents is sufficiently large to yield a statistically significant difference.

Table 34: Average % carbon content - laboratory and Southampton

Oil type	Average carbon content %	
	Lab	Southampton
Weathered	90.61	94.25
2050 motor	94.83	95.68
Crude	91.02	93.82

Table 35: % carbon results for statistical analysis

Sorbent	Oil type	%/100 carbon
Peat	Crude	91.61
Peat	weathered	94.59
Peat	20/50 motor	94.33
Klausorb	Crude	88.98
Klausorb	weathered	90.53
Klausorb	20/50 motor	92.99
Recit	Crude	0.924784
Recit	weathered	0.867231
Recit	2050 motor	0.971655
Overall average		**0.921583**

4.9 Discussion

4.9.1 SEM analysis of sorbent structure

In order to further understand the properties and behaviour of the sorbents used in the laboratory work, a scanning electron microscope (SEM) was used to analyse the differences in the structure of the products before and after sorption. The results of the SEM analysis provided the means to analyse the methods by which the sorbents retained the oil. During the course of the laboratory and field trials, RecoverIt was the easiest sorbent to retain and collect of the three tested. This was due to its particles being a uniform spherical size and it maintaining its structure during oiling and collection. The particulate structure of the peat varied in size. The smaller components formed a paste like substance with the oil and spread quickly over and around the oiling site. A benefit peat had over the other two products was that it retained the oil if it was compressed post oiling to drain any absorbed water out. Klausorb is composed of a high number of fine particles, some as small as 5 μm across. This provided the necessary surface area to absorb the oil but the product quickly formed a paste post-oiling which complicated clean up. The only technique found to remove all traces of the sorbent from the substrata was application of high pressure water.

4.9.2 Pixel analysis

The use of pixel analysis is a novel technique for assessing the efficacy of response operations. Image analysis of oil spills was researched as part of the literature review, it is used to detect and track the trajectory and speed of offshore slicks but no evidence of research was found quantifying the efficacy of spill response products. The discussion section covers two aspects of the data collection. Firstly it analyses the results as indicators of sorbent performance, secondly it analyses the relative success of pixel analysis as a tool in oil spill response.

4.9.2.1 Laboratory results:

If the results from the laboratory data are discussed first, it was expected that at the lighter end of the spectrum a higher pixel tally would be observed in the cleaned over the polluted image. This was the case in 81.4% of the images at shade 20 and 70.3% at shade 100. A higher count in the polluted image was expected at the darker end of the spectrum and at shade 180 this was the case in 44% of the images. 60% of the images at shade 240 were darker in the polluted data set. These figures suggest that overall the application of sorbents to the substrata restored the pixel distribution of the cleaned image to a level between the control and the polluted. This is supported by the patterns shown in the summary graphs observed. Figure 60 showing the results from the Smooth Limestone shows the data cleaned images nearer the control than the polluted. A trend that was observed during data entry and analysis was that the distribution of pixels in the spectrum of the cleaned images was spread wider than that of the control or polluted. This can be seen in the distribution of the cleaned data in the Old Red Sandstone and Rough Limestone graphs.

Overall, the RecoverIt performed most effectively of all the products and peat the least effective. Of the trends found in the substrata, the Smooth Limestone proved the easiest substratum to clean. In comparison to the other two substrata, it was flatter and smoother, the reduced surface area and smooth surface aided the recovery process of oil and sorbent. The relative lack of patterns in the substrata data was supported by there being no statistically significant difference in the pixel distribution based on substrata. The performance of the Recoverit supports what was noted when handling the sorbents in the field. Its ability to maintain its structure when applied and its relatively large grain size enable effective containment and recovery of oil. The peat dispersed rapidly on application and its high variation in grain size (≈1cm - 250µm) complicated recovery. The statistically significant in pixel distribution due to sorbent type supports these observations. RecoverIt consistently performed more effectively than peat and Klausorb. Over the three oils that were applied, the 2050 refined motor oil was the easiest to recover and the weathered oil the hardest. This is supported by the statistical analysis. It was observed during data collection that the weathered oil spread quickly on application, this was enhanced by the presence of water in the oil.

The 2050 refined motor oil was the most viscous of the three products and spread the least. The viscosity reduced the amount of oil absorbed into the substrata.

4.9.2.2 Southampton results:

The purpose of the investigation at OSRL Southampton was to analyse the impact of field conditions on the efficacy of the sorbents and test the validity of pixel analysis in the field. A similar pattern to the results from the laboratory analysis was expected. At shade 20, 75% of the results had a higher pixel count on the cleaned over the polluted data. At shade 100, 58.7% were higher. These are lower than the laboratory results (81.45% and 70.3% respectively) but demonstrate that the application of sorbents restored the pixel distribution of the cleaned images closer to the control. The results at shades 180 and 240 showed 44% and 50% of the images had a higher count on the polluted images. This is in comparison to the laboratory results (44% and 60% respectively). The relative proximity of the results between the laboratory and Southampton suggest that the influence of field conditions did not adversely affect the performance of the sorbents by a significant margin. However this technique does illustrate the necessity of ground truthing laboratory analysis of oil spill response products. What is evident from the summary graphs is that as a tool for visualising the efficacy of the technique the Southampton graph is not as clear as the one from the laboratory. It is possible to see peaks of polluted and cleaned pixels on the three graphs but if return to the distribution of the control image is a benchmark of success, the graphs display little evidence. Despite this, the statistics and results display patterns of the performance of substrata, oil and sorbent.

The statistical test for the substrata showed a significant difference. The trends in the data suggested that the shingle was the least responsive to clean up and the concrete the most. This was due to the smoothness and impermeability of the surface of the concrete. Recovery was efficient and none of the three oils soaked in. The shingle had the highest surface area of the substrata and was porous. Oil and sorbent became trapped between the pieces of shingle complicating recovery. It was noted that recovery of the oils was further hindered by the persistent nature of the oil-sorbent compound among the pieces of shingle. The most effective technique to use was application of high pressure water. The statistics for oil type showed a non significant difference, differences in the behaviour of the oils were noted during data collection and there are some trends in the data to reflect this. The 2050 refined motor oil was the easiest to remove and the crude and refined products the most difficult. The crude and refined products spread rapidly in the field and this affected the sorbent performance.

The sorbent statistics showed a significant difference. It was observed that over the four shades analysed that the RecoverIt was the most effective and the peat the least effective. This supports the data from the laboratory analysis. It was noted in the field that the spherical nature of the RecoverIt granules was a factor in increasing the ease of recovery. The peat dispersed quickly and due to the variation in size and shape of its particles it adhered to the surfaces it came into contact with.

4.9.2.3 Appraisal of pixel analysis technique

This study was partly designed to assess the efficacy of pixel analysis as a technique to quantify oil spill response. The use of satellite imagery is an established technique to predict and track the trajectory of offshore oil spills (Brekkea C 2005). The use of pixel analysis of images to quantify environmental performance is an untested technique in oil spill response. An analysis of the use of pixel analysis and Scion Image undertaken throughout this study highlighted a range of cautions and benefits to the technique (Figure 67).

Benefits	Cautions
- Simple to collect primary data - Cost effective - Simple visual results available - Quantifiable output - Large data set - Effective as an indicator of environmental performance - Ability to monitor change over time - Possible to assess success of clean up and analyse individual products - Potential to build a database of most effective combinations of substrata, oil and sorbent.	- Limited scope of software - Accuracy of photography - Limited to shore response - Only provides aesthetic perspective - Graphical output limited in field data - Limited in circumstances where oil and substrata are similar shades

Figure 67: Benefits and cautions of pixel analysis technique

The benefits of the technique include: The only primary data needed from the incident site is photos of oiled substrata. These are uploaded direct in Scion Image for analysis. Scion is available free of charge online, it is a cost effective analysis technique as all that is required is a digital camera and a computer. Once processed, it can provide fast and accurate indication of the progress of the cleanup. On completion of the analysis the data can be manipulated in spreadsheets and inputted into statistics packages to quantify whether variations in oil, clean up technique or substrata have significantly affected the pixel distribution. The data can be easily manipulated into tables and histograms that can be made available as indicators of progress in clean up operations.

An important aspect of spill response is monitoring change of polluted environments over the duration of the clean up period. A series of time lapse photos taken at locations in the affected area can provide an indication of how the environment is changing over the course of the clean up. The philosophy behind Net Environmental Benefit Analysis can be supported by the addition of a breakdown of pixel distribution over time. The technique has two major applications. Firstly, it can be used to quantify the efficacy of a specific spill response product or combination of product, oil and substrata in laboratory conditions. Secondly, it can be used over time to quantify the efficacy of a clean up operation in field conditions. With further analysis, it would be possible to use the technique to contribute to a database of 'optimum combinations' of oil, sorbent and substrata. This could be used as a decision making tool based on the circumstances surrounding the oil spill.

During the course of the study, a range of limitations and cautions of using the technique were experienced. At a number of points in the analysis of results it was noted that glare on the images from the flash of the camera or natural reflection affected the pixel balance of the image. Scaled up to field investigations, intensity of sunlight and extent of cloud cover may affect the balance of pixel distribution. This may especially be an issue if images are being taken over a period of time. The technique is not applicable for spills on water and would be most beneficial to onshore operations. The range of techniques used to assess the impact and recovery of oil spill response includes physical, biological and chemical indicators. The use of pixel analysis only provides an aesthetic perspective of shore clean up. However, this is a key indicator of progress and a quantifiable output of a response. A caution that was flagged as the experimental study developed was a potential limitation in analysing oil and substrata of similar colours. It may be the case that the technique would be limited if pale coloured oils were spilled on sandstone and shale. For the sake of the experimental work it was observed that cross comparison of different oils, sorbents and substrata was not applicable.

Having discussed a range of benefits and cautions of using pixel analysis in oil spill response the following observations can be made: It is a cost effective and rapid technique to quantify the impact of oil spill response techniques. It can be used to validate products in laboratory conditions or provide an indication of the extent and speed of response over time in the field. With the advent of NEBA and Time Windows of response, it can contribute to the body of knowledge of different products performing more effectively on specific oils and substrata. It is limited through primarily being an aesthetic technique and may not be suitable with certain types of oils and substrata. However, it can be said that as one aspect of the management of oil spill response it can provide a systematic and substantive, quantitative data set to assess the efficacy of response options.

4.9.3 Percentage loss

The calculation of the percentage loss of oil and sorbent from the field provides two data sets. It enables spill responders to quantify how much oil and sorbent material is left in the environment post recovery and it gives an indication of the efficacy of a product. The ranges of sorbents used in the experimental work were environmentally benign. However, some chemical sorbents used are not and may pose further environmental issues if left *in-situ.* With regard to percentage recovery being an indication of product efficacy, it can be used to judge the effectiveness of a product with regard to its absorbing or adsorbing properties. It can also be used to quantify the extent to which the product can be removed from the site once it has been oiled.

4.9.3.1 Laboratory results

If the impact of the substrata is analysed first, it was expected that the high surface area of the Rough Limestone would complicate recovery and lead to a higher percentage loss. The results show that the Rough Limestone has the highest percentage loss of the three substrata. Its surface was pitted and grooved and proved the most difficult substratum to recover the oil-sorbent compound from. In comparison, the surfaces of the Smooth Limestone and the Old Red Sandstone were smooth and substantially less sorbent remained on their surfaces. It was noted that the Old Red Sandstone had the most porous surface of the three substrata. This was identified as a potential factor in reducing percentage recovery in the experimental design and this most likely explained the variation between the Old Red Sandstone and Smooth Limestone results. These trends have been reflected in the data where the Rough Limestone had the highest percentage loss followed by the Old Red Sandstone and the Smooth Limestone.

It can be said from this data that the characteristics of the substrata have an impact on the clean up when using non abrasive techniques. Had the samples been cleaned by high pressure water or steam, the oil and sorbent would have been removed but the percentage loss would have been substantially higher and any flora or fauna present may have suffered damage from the pressure of the water.

The largest variation in percentage recovery data was the sorbents. Of the three, the Klausorb recorded the highest percentage loss (24.17%) and the RecoverIt the lowest (8.07%). Klausorb was the finest of the three sorbents and on contact with the more viscous oils it formed a paste like substance and became sticky. This complicated recovery and left noticeable deposits on the substrata. The highest average percentage loss using Klausorb was when the rough limestone was polluted with the 2050 refined motor oil. This is the combination of the substratum with the highest surface area, the most viscous oil and the finest sorbent. The RecoverIt was the most efficient sorbent. Based on its structure observed in the SEM and its behaviour when oiled, it was concluded that is spherical particulate structure and ability to maintain this when oiled eased the process of retrieving it from the environment. The peat was restricted by the shape and variation in particle size. The pieces of peat were more elongated and narrow than the RecoverIt which led it to stick to the substrata; it also complicated recovery of the product. The advantage peat has over the other two sorbents is that once it has absorbed oil and water, if compressed it will retain the oil in its structure as the water drains out.

The variation in the percentage loss results for the oils was 1.6%. The crude oil had the highest percentage loss and the refined 2050 motor oil the lowest. Observations made while collecting the data suggest this was due to the crude oil having the ability to soak into the substrata and due to its lack of viscosity spread more rapidly than the 2050. The presence of water in the weathered oil enabled it to spread the oil component rapidly over the substrata. The water drained off the substrata rapidly after application. The 2050 refined oil spread least of the three however the paste that formed when it was recovered made it difficult to recover from the substrata, in particular from the Rough Limestone where two of the results are over 40% loss.

4.9.3.2 Southampton Results

It was expected that the results from Southampton would yield a higher percentage loss due to operating in field conditions. However, the impact of the field conditions led to the opposite being true in a number of data sets. The amount of additional material collected with the oil and sorbents led to more material being collected than was applied. The two results with positive values from the substrata are stone wall and the shingle that was cleaned by aggravation. The stone wall had the highest surface area and the same problems recovering the oil and sorbent were found as with the Rough Limestone. This factor was exaggerated when using Klausorb. The shingle that was cleaned by aggravation had recorded an average percentage loss of 5.39. Klausorb recorded the highest percentage loss and it was only the presence of negative results in the data that brought the overall average down. The shingle tests that were cleaned using aggravation and washing recorded an average loss of -8.24%. The sorbents retained the water used to wash the substrata in addition to the oil. The concrete had an average of -2.2%, of the nine tests conducted with the concrete, three had a negative percentage loss and they were all from the data using the weathered oil. It was observed that the weathered oil spread fastest on the concrete and in doing so it came into contact with contaminants and any water that was present on the substratum. On several occasions, the uniform surface of the concrete led to pooling of water while the irregular surface of the stone wall enabled water to drain off. This was a further contributing factor to the percentage gain for the concrete results. Due to the range of data, individual analysis of oil, sorbent, substrata combinations was necessary.

Of the three sorbents used, RecoverIt was the most effective with regard to ease of recovery. The highest percentage loss that RecoverIt had was when it was used to adsorb crude oil on stone wall. This is most likely due to the substratum and oil type as opposed to the sorbent, this is backed up by the result for the 2050 refined motor oil being a 27.7% loss and for the weathered oil a 39.3% loss. The high positive percentage losses are due to the surface area of the stone wall and the negative result is due to the spreading ability of the weathered oil. Klausorb had the highest average percentage loss (23.%), this is not due to its lack of capability as an absorbent but is due to the inherent difficulties of recovering very fine particles mixed with oil off a substratum. The peat's overall negative average is largely due to one result. When crude was spilled on the shingle and recovered with peat by aggravation and washing there was a percentage loss of -91.03%. This is due to the peat's ability to absorb water as rapidly as oil so any of the water that was used to wash the shingle that came into contact with the peat would have been absorbed. This was reflected in the peat's performance as a whole in that seven of the twelve results yielded a negative value.
Two of the three oils used had a positive value; the 2050 refined motor oil had an average loss of 11.89% and the crude 11.31%. The weathered oil had an average loss

of -16.79, this is due to its high water content and ability to spread quickly. Klausorb was the only sorbent to have three positive results for the recovery of the weathered oil. This is due to the sheer number of particles in the Klausorb and their ability to absorb the various oils and water quickly. To put these figures in perspective, the *Exxon Valdez* disaster in Alaska in 1989 saw a total of 9% of the oil on the surface of the sea recovered (White I 1998).

To conclude the work carried out in Southampton for the percentage loss data, the first observation is the high amount of negative results. With regard to the research pathway and the validity of the results it would seem unrealistic to use percentage loss as an indication of success for spills if heavily weathered oils were involved in the field considering how easily the data is corruptible by contaminants. For refined and crude oils that have not undergone extensive weathering this is a feasible option for field based tests. This technique would also be valid in industrial and terrestrial spills where there would potentially be fewer contaminants. This technique could be used as a tool to test the efficacy of products in laboratory conditions.

4.9.4 Carbon and moisture content

The philosophy behind the carbon data collection was to prove quantitatively that there was sufficient carbon in waste oil to be used as fuel. The data was collected in the laboratory prior to Southampton for two reasons. Firstly, to carry out trial and error data collection on the quantities necessary to ensure the methods were representative of the aim and objectives. Secondly, to determine whether or not the amount of carbon in the compounds was sufficiently high to warrant further tests and analysis in Southampton. The data collected in Southampton was designed to determine whether or not there was an adverse impact on the carbon content in field conditions. The environment from which the materials were collected in Southampton may have affected carbon levels due to contaminants in the compound.
Part of the laboratory procedure to measure the carbon content involves calculating the moisture content of the compound. The presence of moisture in a potential source of fuel is a limiting factor. The lower moisture percentage, the less preparation the substance needs prior to incineration.

4.9.4.1 Laboratory results:

Of all the compounds tested, the compounds with weathered oil had the highest moisture content. The presence of moisture in the weathered oil is due to it being collected from the field in the form of a water-in-oil emulsion. There are two considerations that need to be taken into account at this stage. The first is whether the high moisture content in the weathered oil has affected its carbon content and ability to combust. The results show this is not the case as its percentage carbon is 90% compared to an average for all the oils of 92%. The second consideration is that the higher the moisture content of a material that is to be used for fuel, the higher the pre treatment costs are. This may render the weathered oil used in the laboratory and field work unusable as a source of fuel despite its high carbon content. Compounds, despite their individual components that are recovered from substrata or open water are more attractive as a fuel source if they can be recovered before they form an emulsion.

The average moisture content of the weathered oil is 47.6%, the crude 21.3% and the 2050 motor oil 0.2%. The reason the motor oil has such a low moisture content is that is has been refined. The most common technique for refining oil is fractional distillation. Each fraction of crude oil has different sizes, weights and boiling temperatures. The oil is heated and the vapour is pumped into a fractional distillation column. The temperatures in the boiler that boils the crude oil are well in excess of the boiling point of water. This explains the low percentage moisture content in the refined 2050 oil. Crude oil is scientifically speaking a hydrocarbon meaning it is a compound of hydrogen and carbon, it can contain oxygen and sulphur. Statfjord crude was used for the laboratory and field work. The blend of Statfjord used is 16.2% hydrogen and 1ppm (parts per million) of sulphur. The likelihood is that the water found in the samples contaminated the oil at some point during the drilling, extraction or transportation phase http://crudemarketing.chevron.com (1).

The averages for the carbon content tests are as follows, crude 90%, weathered 90% and 2050 motor 94%. As the vast majority of the fuels used to power industry, domestic demands and transportation are carbon based; an average carbon content of 92.1% suggests that oil-sorbent compounds from spill are a feasible fuel source.

4.9.4.2 Southampton results:

The variations between the moisture levels in the laboratory and Southampton results can be explained by two factors. If the data from Southampton is observed, the results for combinations with either weathered oil or shingle as a substratum have elevated moisture levels. A substantive increase was noted in the average moisture levels for the 2050 motor oil. The result that has led to this high average is from the shingle using RecoverIt as the sorbent and recovered by aggravation and washing. It was noted during data collection that the surface area of the shingle held significantly more water than the concrete or stone wall. A percentage of the water that was used to clean the shingle was taken up by the sorbents, a combination of these factors explain the high moisture levels. For the other two oil types, the difference in the average percentage moisture contents between the laboratory and Southampton is low. This suggests that the environmental conditions and the state of the oils affect the moisture levels more than the techniques used to recover the waste.

The carbon levels in the oil-sorbent compounds from Southampton showed an overall increase from the laboratory results. For the weathered oil there are a number of possible explanations for this. It is possible that the variety of oils in the weathered oil could have affected carbon levels in different tests. The more likely explanation for this that applies to all three oils is that contaminants *in situ* at the sample site were partly composed of carbon and this was retrieved along with the oil.

From a perspective of drying and combusting the compounds, observations made during these processes did not note any variations or complications between the two data sets. An option that was discussed as a possible extension to the experimental work was compressing the oil-sorbent compounds into briquettes for use in incinerators. The issue of whether it is feasible to scale these experiments up to an economically viable level is another potential extension of the design.

4.10 Conclusions

In order to critically analyse the success of the laboratory and *ex-situ* field trials it was necessary to discuss the aims and objectives of the study.

> **1) To investigate the efficacy of a range of absorbents in terms of their capability to absorb a given volume of oil spilled on a range of substrata.**
>
> **2) To determine whether a range of compounds of oil and sorbents are suitable for use as fuel.**

4.10.1.1 Review of Aim One

A core theme of the research pathway in the laboratory and field data collection was to ensure the work undertaken was an analysis of a technique as much as a series of results. The results of the data are entirely dependant on the equipment, methodologies and products used. The technique used to quantify their success regardless of the results, has the potential to be used in a diverse range of applications. The notion of analysing colour in polluted and cleaned samples does not take into account the range of biochemical, toxicological or biological tests it is possible to carry out in the event of a spill but it provides strong evidence regarding the success of products used and environmental improvement over time. Of equal importance, it provides a qualitative and quantitative value of the aesthetic value of coastal and marine areas. This technique provides simple, accessible yet vital information regarding the success of operations. The data can be displayed in forms that are visual and accessible for stakeholders. From observations of the data, it is clear that the conditions in Southampton made a substantive difference in the pixel distribution in the polluted and cleaned images. As the pixel analysis has not been used for oil spill response operations, this reinforces the need to validate technology and methodology in laboratory conditions prior to field tests. For each of the pixel values analysed in this chapter, trends and patterns in the data have been highlighted and discussed suggesting that the analysis of pixels is a viable option for judging the effectiveness of sorbents in spill response. This technique could be further developed in testing of new products under lab conditions to determine their effectiveness prior to certification and distribution. The results from the percentage recovery study provided information on the efficacy of the products and the logistics of deployment and recovery in the field. The experimental design tested their behaviour using non aggressive recovery techniques. The following comments can be made regarding the behaviour and efficacy of the sorbents when in contact with varying oils and substrata.

- Increased surface area on the substrata complicates recovery, particularly with fine grained sorbents.
- Fine grain sorbents have the tendency to form 'pastes' with viscous oils which can lead to them becoming persistent on substrata.
- Sorbents that maintain their structure and have a particulate structure sympathetic to recovery yield a higher percentage return.
- From a containment perspective, viscous oils spread with less speed but can be persistent post sorbent application.

As a technique to determine the performance of sorbents, it can be said that percentage recovery is a cost effective simple option. It has potential to be used as an aspect of product testing and review prior to commercial use. Its major limitation as an indicator of success in the field is that presence of contaminants lead to more material being recovered than spilled. In the wake on a spill incident separating all contaminants and oil to determine percentage recovery would not be a feasible option.

4.10.1.2 Review of Aim Two

The most significant aspect of the data for the carbon and moisture content is the differences between the results for the laboratory and Southampton data sets. If the moisture content results are observed, there is a 3.26% difference between the laboratory and field results. This tells us that it is not the location where the oil is recovered from that is responsible for the moisture content, rather the environmental conditions that can influence the composition of the oil. The longer it has been in the environment the higher the likelihood of it becoming emulsified or weathered, this significantly increases the moisture levels and the difficulty of recovering the oil. A positive outcome of the data is that presence of moisture did not affect the compounds ability to burn; this in turn did not skew any of the carbon results.

As a result of this work the carbon tests can be used as effectively in controlled conditions in the laboratory as in the field, and if the oil has reached a certain point of weathering, the circumstances surrounding its collection are immaterial to its ability to be used as a fuel. It would be accurate to say that the less weathered and emulsified the oil the more potential it has as a viable source of renewable fuel.

5 Chapter Five: The role of education and training

5.1 Introduction

This chapter forms a synthesis of the three research areas of the thesis. It evaluates the role of education and training as a functional output of the research pathway and investigates the logistics of designing and delivering Distance Learning (DL) packages. A specific focus on the role of education and training in oil spill response research is demonstrated through the examination of a DLM on oil spill bioremediation developed for the thesis.

It is established that one of the largest gaps between policy statements and real changes on the ground is the challenge of implementation (Vastag G 1996). The targets, aims and objectives may be clearly identified, but how is the transition made from declared ambition to functioning operation? The most progressive governments, industries and companies throughout the world recognize that two of the most cost effective and high impact activities in support of strategic development and implementation are those of education and training (Vastag G 1996).

The core section of the chapter is composed of the development of the DLM for oil spill bioremediation. Bioremediation was selected for this study due to the range of scale and characteristics of marine spills, the dynamics and sensitivity of the environments affected by oils pills, the variety of economic and political influences, and the range of logistic and technological considerations that are taken into account in a clean up operation. The interpretation of bioremediation technology is an effective test bed for the efficacy of education and training initiatives due to the demands of the multi-disciplinary (in both spatial and temporal terms) response approach required. Further to this, as it used infrequently in marine oil spill response operations compared to techniques including booms, skimmers and dispersants; it can be said that the role of education and training has a value added impact in terms of promoting wider use of bioremediation in environments where it can be particularly effective.

In the fields of waste management and oil spill response, education and training strategies are designed to inform and improve the decision making process through dissemination of information and facilitation of communication. The benefits of dissemination of data and education and training are value added in as much that they can:

- Act as a catalyst for further action.
- Raise awareness of key issues.
- Assist continuity of activities and the adoption of best practice.
- Disseminate the importance of concepts, tools and methodologies to a wider audience.
- Encourage the development of local or internal capacity and competence to continue and enhance further objectives of the taught material.
- Demonstrate commitment and progress where evidence of performance is intrinsic to funding and support.
- Recruit support and resources to sustain the activity for the future.
- Maintain ongoing interest and support in projects.

(PROTEKT Handbook 2007, SACODI Handbook 2007)

5.2 Distance learning and oil spill bioremediation

This section of the chapter is designed to demonstrate the structure of a full DLM in oil spill bioremediation education and training. The potential of bioremediation in Vietnamese oil spill response is discussed in chapter four. Its implementation into distance learning was designed as a functional output of the research and to demonstrate an option for further dissemination of oil spill bioremediation research. Milford Haven Port Authority contributed £2000 to the research and development of the DLM. It is designed to be incorporated into a contingency plan or be delivered as a stand alone module.

Two versions of the DLM are presented in this chapter. The first is a streamlined version of the Core Text. This contains a figure of the structure of the package and notes elaborating on each section. References will be made to the larger document. This version is designed to be used prior to the full package for an institution or company who wish to be provided with a brief overview of the package. It can also be utilised as an executive summary and reference document of the Core Text in the

Workshops and Training Courses. The second version consists of the introduction, contents and layout of the full package and one chapter demonstrating the layout, content and assessment processes. This version forms the core reference document for the DLM delivery at educational institutions and is extracted and edited from the project guidelines. The full package is comprised of the following:

- A 'core text' designed for further reading and as a support tool for the user.
- Learning outcomes.
- Assessment exercises.
- Tutors support notes.
- Student support notes.
- Case studies.
- CD ROM's.

The core text is populated with technical material and case studies on:

1) Microbial populations for bioremediation processes
2) Chemistry of bioremediation
3) Decision to use bioremediation
4) Petroleum constituents and susceptibility to breakdown
5) Bioremediation strategies
6) Optimising bioremediation performance
7) Factors affecting bioremediation
8) Advantages and disadvantages of bioremediation
9) Bioremediation in relation to other technologies
10) Limitations
11) Case studies

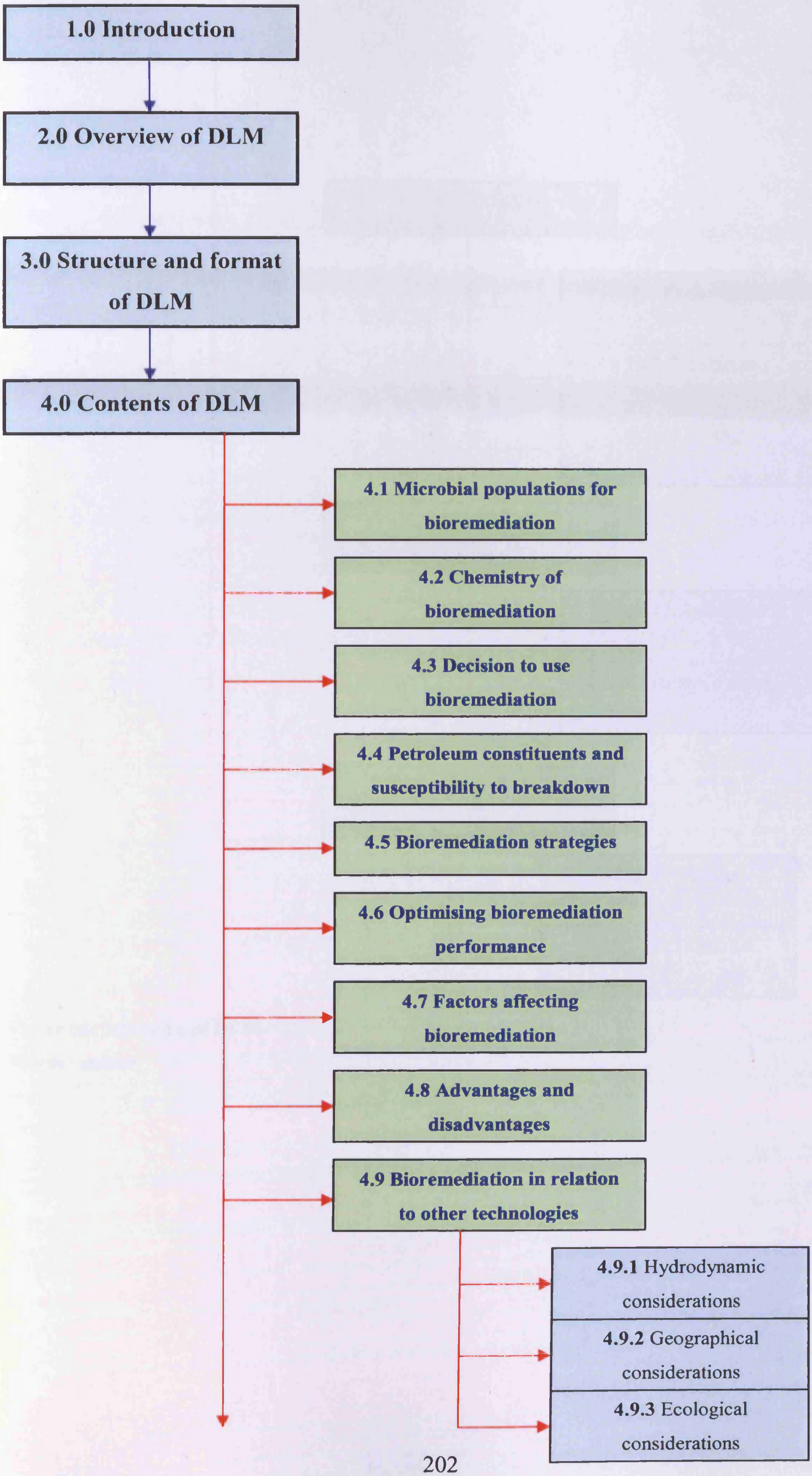
The eleven sections of the core text are dedicated chapters within the DLM. The content for the core text has been extracted from the review of literature and selected scientific reports and case studies (BIOREM Handbook 2006).

The purpose of the core text is to provide a database of information and further links/references to support the taught content. For the sake of this chapter, select aspects and sections of the core text have been extracted and manipulated.

5.2.1 Streamlined DLM

The streamlined DLM provides an overview of its structure without covering the technical detail of the reports.

It can be used as a working example of a distance learning model where the format and methods of assessment could be examined with a view to using them with other material. A figure of the whole package is presented cross referencing with the larger document. Short notes providing the key concepts and working examples are provided on each section and examples of the assessment methods and further reading sources are shown.


1.0 Introduction
2.0 Overview of DLM
3.0 Structure and format of DLM
4.0 Contents of DLM
4.1 Microbial populations for bioremediation
4.2 Chemistry of bioremediation
4.3 Decision to use bioremediation
4.4 Petroleum constituents and susceptibility to breakdown
4.5 Bioremediation strategies
4.6 Optimising bioremediation performance
4.7 Factors affecting bioremediation
4.8 Advantages and disadvantages
4.9 Bioremediation in relation to other technologies
4.9.1 Hydrodynamic considerations
4.9.2 Geographical considerations
4.9.3 Ecological considerations

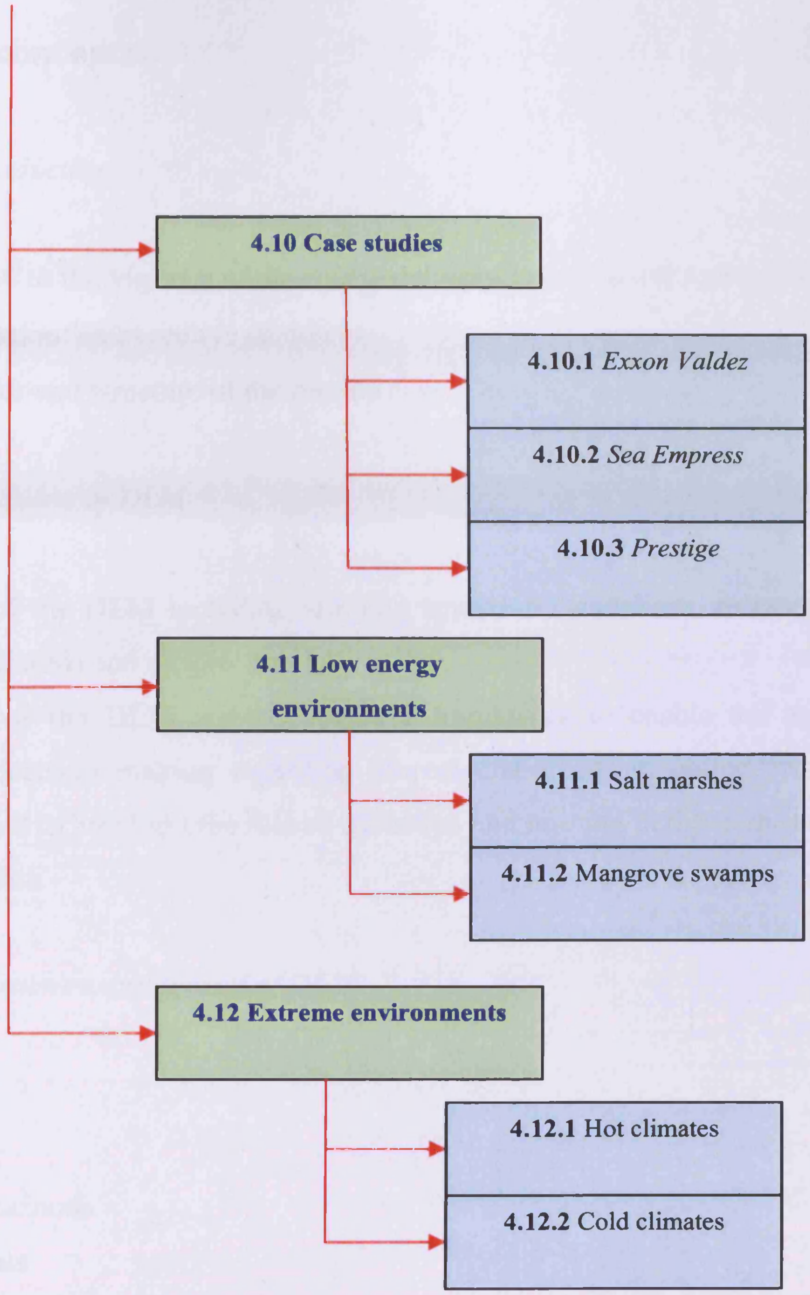


Figure 68: Structure of DLM

Source: author

5.2.1.1 Key concepts:

Chapter One: Introduction

- Introduction to the logistics of the course delivery.
- Bioremediation: an executive summary.
- The logistics and structure of the course.

Chapter Two: Overview of DLM

- Structure of the DLM including teaching approach (guidelines, assessments, support material) and chapter content.
- The aims of the DLM are to provide a framework to enable the user to facilitate decision making regarding bioremediation as an option for spill response and to highlight the role of education and training in dissemination of technical data.

Chapter Three: Structure and format of DLM.

- Structure
- Format
- Delivery methods
- Assessments
- Case studies

Chapter four: Contents of the DLM:

- 4.1 – Microbial populations for bioremediation – outlines the major strains of bacteria that are capable of metabolising oil in the environment.
- 4.2 – Chemistry of bioremediation – outlines the major chemical processes that occur during bioremediation.

- 4.3 – decision to use bioremediation – outlines the main aspects of the decision making process in order to determine whether bioremediation is a feasible option for use.
- 4.4 – Petroleum constituents and susceptibility to breakdown – outlines the major components of petroleum and their respective susceptibility to breakdown by microbial action.
- 4.5 – bioremediation strategies – outlines the processes and principles behind *in –situ* and *ex-situ* bioremediation, and includes case study data for both.
- 4.6 – optimising bioremediation performance – outlines the role of nutrient and oxygen addition to microorganisms that can improve the rate and success rate of bioremediation.
- 4.7 – factors affecting bioremediation – outlines the environmental factors that affect bioremediation and the limitations that the oil type and nature can have on the process.
- 4.8 – advantages and disadvantages of bioremediation – designed to support the decision making process.
- 4.9 – bioremediation in relation to other technologies – outlines the impact of hydrodynamic, geographical and ecological factors on bioremediation and how bioremediation compares with other standard marine oil spill response technologies.
- 4.10 – case studies – provides case study data from three of the major oil spills in the last half century where bioremediation was tested. The response to the *Exxon Valdez, Sea Empress* and *Prestige* incidents are examined.
- 4.11 low energy environments – specialist case studies of low energy highly sensitive environments where bioremediation may be the most effective and least destructive technology available.
- 4.12 – extreme climates – examples of how the technology can work in extremes of temperature. As the process is enzyme based, this is a key consideration when deciding whether to proceed with bioremediation. Both hot and cold climates are detailed.

5.2.2 Extended Version of DLM

One section of the DLM which was delivered as a stand alone module is presented with the associated support material. The section that has been chosen is bioremediation in relation to alternative oil spill response technologies. It was decided to include this chapter as it demonstrates the multi-disciplinary nature of oil spill environmental management, factors affecting bioremediation and a cross analysis of bioremediation and standard oil recovery techniques. This is in contrast to a number of the earlier chapters, which are executive summaries of technical information and options. This section includes the following components:

- One chapter of the full DLM.
- Learning outcomes.
- Assessment exercises.
- Case studies.

5.2.3 Core text - Bioremediation in relation to other technologies.

Learning outcomes:

After reading this chapter, you will be able to:

- **Detail the major limitations of using bioremediation in the field**
- **Discuss the environmental factors that can limit the efficacy of bioremediation in the field**
- **Describe the Microtox® test for toxicity**

Figure 69: Bioremediation in relation to other technologies – learning outcomes

Source: author

This chapter discusses the limitations of bioremediation in the field and provides a cross analysis of bioremediation with standard techniques for oil spill response.

Prior to bioremediation being considered as an effective response tool, it must be deemed effective for the scope and circumstances surrounding the spill incident, taking into account alternative options. Bioremediation has been flagged as an effective technique on beaches and sensitive habitats including saltmarshes (Lee K 2000). It hasn't been tested rigorously as a technique for treating oil in the open ocean. (Bioremediation for marine oil spills background paper 1991). A drawback with this technique is maintaining microbial population levels or nutrients in contact with the oil for a sufficient time to facilitate degradation. Research carried out in Maine showed it was more effective on low energy, sheltered beaches due to reduced dilution rates as opposed to dynamic, high energy environments (Venosa A 2001).

5.2.3.1 Bioremediation Limitations:

This section details the limitations of bioremediation in the field. The impacts of hydrodynamic, geographical and ecological factors on bioremediation efficacy are discussed.

Hydrodynamic factors:

The rate and extent of bioremediation in the field is influenced by the physical, biological and chemical conditions of the contaminated environment. Environmental factors that affect the process include:

- Weathering processes,
- Temperature,
- Availability and concentration of nutrients,
- Concentration of oxygen,
- pH.

(Atlas R 1995)

When oil is introduced into the environment it undergoes a range of physical, biological and chemical changes. These processes affect the behaviour and composition of the oil, and in turn influence the efficacy of response strategies. Types of weathering that affect oil include: spreading, evaporation, dispersion, emulsification, dissolution, oxidation, sedimentation and biodegradation (http://www.itopf.com (6), Vidali M 2001, http://www.itopf.com (9)).

Evaporation of volatile oil compounds benefits microorganisms by removing a range of toxic compounds. However, this can lead to an overall lower biodegradable percentage of oil due to these compounds being degradable (Vidali M 2001).

The characteristics of the oil-water interface are a key factor. Oil degrading bacteria grow at the oil-water interface and formation of water-in-oil emulsions or mousses reduces surface area and biodegradation rates. Tarballs (large accumulations of weathered and unweathered oil) restrict microbial access due to their low surface area (Vidali M 2001).

The formation of oil-in-water emulsions through oil dispersion into the water column increases the surface area of the oil and the potential for biodegradation. An oil-in-water emulsion can be seen in Figure 70 (Vidali M 2001).

Figure 70: Oil in water emulsion
Source: http://www.unis.no (1)

Temperature:

The ambient temperature affects the properties and behaviour of spilled oil and the efficiency of microbial action (Lepo JE 2003). At low temperatures oil viscosity increases while the toxicity of low molecular weight compounds is reduced, this delays the onset of microbial action. Although biodegradation can occur over a wide range of temperatures, it is accepted that microbial action lowers with decreasing temperature (Lepo JE 2003). In marine environments the highest efficient temperature for microbial action is between 15°c and 20°c. The composition of the microbial population also has an effect on the rate of degradation. Organisms that thrive at low temperatures (psychrophilic organisms) have been known to degrade oil at -2°c (Vidali M 2001). It has been observed that during bioremediation trials, the efficiency of bacterial action decreases in winter months (Lee K 1999).

Aerobic conditions:

Aerobic conditions are a factor considered necessary for the degradation of hydrocarbons as the process involves oxygenases (enzyme that catalyze the incorporation of molecular oxygen into a substrate.) (http://dictionary.reference.com/browse/oxygenase). Research has shown that a reduction in the oxygen level leads to reduced biodegradation activity (Swannell R 1996). However this is seldom a limiting factor in the upper layers of the water column or on the surface layer of beach environments. Circumstances where it may become limiting are in subsurface sediments, anoxic zones of water columns, fine grained sediments, freshwater wetlands, mudflats and salt marshes. Due to a lack of oxygen, anaerobic conditions are not widely considered suitable for bioremediation strategies (Swannell R 1996).

Nutrient availability:

Approximately 150mg of nitrogen and 30mg of phosphorous are utilised in the conversion of 1mg of hydrocarbon to cell materials (Swannel R 1996). In the event of a large volume of oil being spilled, phosphorous and nitrogen levels can be compromised and this is a key limiting factor of degradation (Sang-Jin K 2005). Oil degradation has shown to increase with pH with the optimum degradation occurring in slightly alkaline environments. The pH of sea water is stable and marginally alkaline so not thought to be a limiting factor to microbial activity (Swannel R 1996).

Geographical factors:

Collection and analysis of field data is a key aspect of bioremediation research. Recent studies in a range of environments show that bioremediation is affected by the constitution of the contaminated shoreline (Swannell R 1996). The sensitivity of the affected shoreline is a consideration in selecting clean up options. Intrusive mechanical and physical cleanup can adversely affect marine and coastal flora and fauna in the eulittoral and sublittoral zones (Hawkins SJ 1992). The American Institute of Technology have devised a method for determining the sensitivity of a given shoreline with reference to its sensitivity to oil pollution. Four factors are taken into consideration when considering sensitivity.

1) Relative exposure to or shelter from wave and tidal energy,
2) Shoreline slope,
3) Substratum type (grain size, mobility, penetration, ability to support traffic)
4) Biological productivity and sensitivity (Mearns AJ 1997).

Figure 71: High energy exposed rocky shore
Source: http://www.saburchill.com (1)

Figure 72: Low energy sheltered mangrove swamp
Source: http://www.people.cornell.edu (1)

Regarding these factors, it may be said that wave swept rocky shores are less sensitive to clean up actions than a saltmarsh. However, bioremediation would have limited success on a wave exposed rocky shore due to the physical processes controlling the flux of materials and organisms. It is more suited to removing oil in environments including salt marshes and mangroves where techniques such as pressure washing and the addition of chemical dispersants can cause environmental damage (Figures 71 and 72) (Mearns AJ 1997). Wetland environments act as a natural coastal defence and provide support extensive communities of flora and fauna (Whigham DF 1999). However, the fragile nature of a wetland can restrict options for clean up. A significant event in the development of oil spill response in sensitive environments was the reaction to the Bahia las Minas oil spill in Panama. Keller and Jackson (1993) reported a comprehensive range of studies following a major oil spill in tropical coastal habitats. The spill occurred in April 1986 and led to the release of 50,000 barrels of medium weight crude oil being spilled into mangrove forests, seagrass beds and coral reefs to the east of the entrance to the Panama Canal (Burns A 1989). The study of the spill led to a unique opportunity to monitor the effects of oil in tropical ecosystems. One of the major findings was the long term persistence of oil in mangrove mud (Burns K 1999). The sediments became reservoirs of oil that periodically leached out into coastal habitats and affected biota for 6 years (Levings *et al* 1994). As part of the research carried out into the potential for bioremediation in mangroves a series of experiments were carried out to test for the presence of hydrocarbon degrading micro-organisms in representative wetland habitats (Burns K 1999). The biodegradation rates of a number of oils (Gippsland Crude, Arabian Light Crude, Bunker C) that are transported along the Australian coast were also tested. All three oils showed biodegradation of the non-volatile aromatic hydrocarbon fraction, with the Arabian Light oil cultures showed the highest rates of loss. Evaporation was the most significant factor in removing the light alkane and light aromatic hydrocarbons (Burns K 1999).

Field trials:

A potential complication in determining the efficacy of bioremediation in field environments is that oil has to be spilled in order to carry out tests. Tests carried out after spill incidents (including the response to the Bahia las Minas incident) are reliant on the circumstances surrounding the incident being suitable for bioremediation.

The Gulf of Mexico is one of the most intensive petroleum producing areas in the world and it supports 6 million acres of tidal marshes (Alexander SJ 1985). The impacts of petroleum in the environment can persist for years and the marshes are critical in supporting flora, fauna, and coastal defence (Mills MA 2004). Bioremediation has been highlighted as a potential option for oil spill clean up in wetlands. Research by Swannel *et al.* 1996 showed that the addition of nutrients to shoreline environments can stimulate bioremediation but little research has been done in wetland environments (Mills MA 2004). A potential complication with using bioremediation in wetlands is that they are predominantly anoxic and due to the high oxygen demanding sediments, oxygen addition was not considered a feasible strategy (Waite *et al.*, 1999).

An Office of Technology Assessment report to the US congress 1990 and research carried out by Swannell *et al.* in 1996 stressed the need for more scientifically valid controlled studies of petroleum bioremediation (Swannell *et al.* 1996). There have been few statistically sound field trials of bioremediation on shorelines as the majority of field based studies have been opportunistic responses to spills (Lee *et al.*, 2001).

Research was carried out at the San Jacinto Wetland research Facility in Texas. Following a major oil spill in 1984, the site was designated for long term bioremediation research in wetland environments by Texas A and M University and the Texas General Land Office. The first piece of research carried out involved sediment sampling from a contaminated site over an 11 month period to quantify the extent of intrinsic biodegradation in the wetland environment without the addition of external microbial populations. The test area was composed of 21 plots; each $25m^2$ with a minimum of 5m between plots (Mills A 2003).

Figure 73: San Jacinto wetland
Source: http://www.wcb.ca.gov (1)

To ensure data accuracy, one area comprising of six individual plots was selected to analyse the extent of microbial action. The remaining plots were monitored for variable oil dispersion and the heterogeneity of the experimental system. Samples were collected 11 times in the 11 month sample period to determine the temporal changes and spatial distribution of oil in the wetland (Mills A 2003). The results of the study showed that the extent of intrinsic bioremediation reduced the hydrocarbon levels in the control sites by an average of 95% in 150 days (Mills A 2003). This high level is attributed to the fact that the Gulf of Mexico, and in particular the San Jacinto wetlands are exposed to numerous natural oil seeps thus exposing the native microbial population to hydrocarbons. It is further accepted that the study area is nutritionally enriched through regular floods, the San Jacinto watershed is composed predominantly of farm and cattle range land which contribute substantial amounts of nutrients to the system (Mills MA2003). The focus of the research was to quantify the efficacy of intrinsic bioremediation of petroleum contaminated sediments, it was concluded that the wetlands recovered completely with regard to remaining petroleum concentrations. The residues remaining were predominately asphaltic compounds and resins, which due to their composition and lack of bioavailability, posed minimal threat to flora and fauna. It was determined that the bioremediation process was complete within one year of the study commencing thus proposing that intrinsic bioremediation is a feasible option for removing oil from wetland environments. A caution flagged was that although enhanced bioremediation through addition of microorganisms, nitrogen or phosphorous can accelerate microbial degradation rates, care must be taken to ensure that their application does not damage the environment.

Meteorological conditions can affect the decision making process regarding whether to use bioremediation. High wave and tidal energy rapidly removes the oil from a contaminated shoreline, thus reducing the need and often the effectiveness of bioremediation strategies. An example of high seas dispersing oil rapidly can be seen after the *Braer* grounding in 1993 (Edgell N 1994). Successful bioremediation field trials have been carried out on sand, salt marsh, and cobble shorelines (Swannel R 1996). On salt marshes, trials show that low concentrations of oil were treated successfully by nutrient addition (0.3% volume of oil per volume of beach material). At higher oil concentrations, at which the oil had penetrated into the anoxic layer of sediments, oxygen became a limiting factor to the efficiency of bioremediation depletion restricted biodegradation. In such circumstances, oxygen can be added to supplement the microbial population. Low pH in salt marsh sediments may also affect the rate of oil decomposition. As a result of trials taking place in salt marshes, evidence suggests that bioremediation can be used as an option on oil contaminated fine sediments by the addition of nutrient and oxygen. The same applies for shingle beaches in particular to encourage the biodegradation of oil that has entered the subsurface of the shore (Swannel R 1996).

Ecological factors:

Research has focused on the ecological impacts caused by bioremediation agents as opposed to bioremediation being affected by ecological factors (Venosa A 2003). The potential toxicity of bioremediation agents *post*-application is a factor that requires consideration when utilising bacteria. The level of nutrients in the sample site should be maintained at a high enough level to facilitate bacterial action, however excessive levels of nutrients such as ammonia can induce toxic responses in marine organisms (Venosa A 2003). Bioremediation has a range of impacts on the flora and fauna of the treatment area. The standard technique is to determine the potential production of toxic by-products as a result of bioremediation (Zhu X 2001). Two techniques have been devised to assess the impacts of the treatment. Bioassessments are field based analyses characterised by an assessment of the impacts of the contamination and treatment activities on environmental populations. Bioassays are laboratory tests that involve rigorous protocols and controls, both toxicity tests and bioaccumulation studies are classes as bioassays.

Bioassessments have been used extensively in the monitoring of the impact of marine oil spills, the advent of bioremediation as an option in spill response has led to the bioassessments being used to quantify the impacts of clean up operations. (Zhu X 2001). Changes in the balance of benthic communities can be used as a biological marker to quantify the recovery ecosystems when exposed to pollutants (Zhu X 2001). Benthic organisms are used, as contaminants including crude oil bind to sediment particles. Macrobenthic organisms are of particular importance due to their longevity and importance as a food source. Limitations to bioassessment data collection and associated bioremediation include the high amount of unrestricted surface area required for sample collection and analysis of macrobenthic organisms. Further limitations include the issue that sediment-associated contaminants can enter non-benthic communities through processes including resuspension, desorption, ingestion of benthic organisms and ingestion of sediment (Zhu X 2001). Given the range of spatial, temporal and biological interactions that exist between water and sediment, it can be said that to acquire a representative data set of community response to a pollution incident, further bioassessments should be carried out on non-benthic species such as pelagic fish and bacteria (Zhu X 2001).

Bioassessments were further used to analyse the impact of an oil spill in the Gulf War in 1991. The results of the survey showed that along a 45 km stretch of intertidal mangroves and salt-marshes, a range of species were either severely damaged or in the case of *Salicornia europaea,* almost entirely removed. The research cautioned that natural recovery rates for the vegetation would be adversely affected by the presence of the oil and active measures were taken to aid recovery were recommended (Lee K 2001). Due to the fact that contaminants associated with sediment dynamics can affect non-benthic species and that community interactions can lead to contaminant dispersion, alternative options to measure the response of a community to pollution can be used. One such option is to use biomarkers which are a form of bioassay.

Bioassays provide a perspective on the health of an ecosystem as they provide data on the interaction that occurs between the contaminant and the environment. The results are quantitative measures of toxicity (Zhu X 2001). Fish are commonly used as a bioassay organism due to their economic, recreational and aesthetic value. Biological and physiological alterations including structural variations in organs, organelles, and tissues, can occur in fish populations if they are sufficiently exposed to a pollutant. Detection of specific alterations before and after exposure can assess the impact of toxicity. In order to do this, biomarkers are used. Biomarkers are biochemical, physiological or pathological responses measured in organisms on exposure to environmental contaminants (Zhu X 2001). Research was carried out to measure the toxicity of PAH's in fish to evaluate the effectiveness of a wetland bioremediation study (Hodson PV 2001). The results of the study showed that the concentration of PAH's was reduced through sediment dispersion and weathering as opposed to the addition of nutrients. The PAH's were shown to cause deformities and mortality in species of trout and medaka (Hodson PV 2001).

It is also possible to carry out bioassays on benthic organisms. In terms of benthic invertebrates, research has shown that amphipods are the most sensitive and the first to be affected in the presence of pollution. They have been successfully analysed to characterise the impacts of shoreline impacts from oil spill incidents. Gilfallan *et al.* 1995 collected mussels for hydrocarbon tissue analysis to estimate hydrocarbon levels. The oysters were used in a shoreline bioremediation exercise in Delaware Bay to document the loss of oil from the study area and assess the impact of the oil on offshore resources (Gilfallan *et al.* 1995).

The Microtox® test is a commercial bioassay used by regulatory agencies; it is based on the measurement of changes in light emissions from a non-pathogenic bioluminescent marine bacterium upon exposure to test samples. It has been used successfully to test for toxicity in a range of media including sediment, chemicals, effluents and water (Kwan KK 2002). Research by Ho and Quinn (1993) showed strong correlations between the response in the Microtox® test and polycyclic aromatic fractions in sediment samples (Ho *et al.*, 1993). It has also been used to test the effectiveness of recovery from an oil spill in a wetland. Mueller *et al* (1999) monitored the rate of acute toxicity reduction using Microtox®.

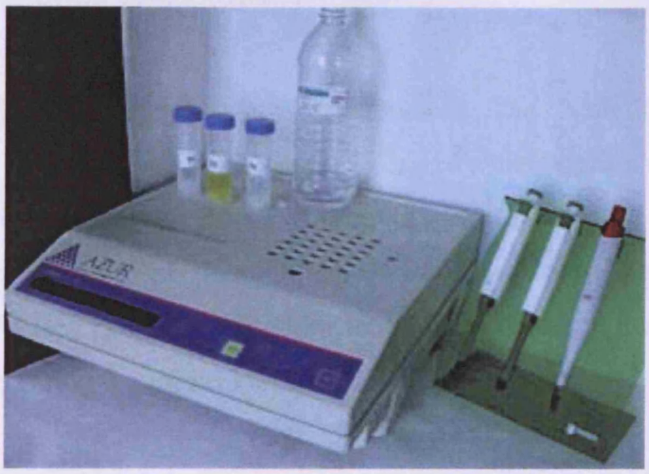


Figure 74: The Microtox® test
Source: http://zimniak.art.pl/34luminesc.jpg

Having discussed the major environmental, geographical and ecological factors that affect bioremediation efficacy, it can be said that there are a range of parameters that affect the efficacy of bioremediation in oil degradation and that the application of bacteria to metabolise oil is environment and oil specific. The hydrodynamic, geographical and ecological conditions at the time of the spill and in the polluted environment affect the efficacy of bioremediation and may render the technology ineffective. This may particularly be the case in anaerobic environments or if a viscous raw crude oil has been spilled. Additional factors to consider when considering the use of bioremediation include, the application of bacteria to an environment can have deleterious impacts on flora and fauna. Monitoring of environmental toxicity and contaminant transfer within communities is critical.

It can be said that the balance between environmental remediation and associated toxicity and ecosystem damage needs to be considered against ecosystem damage from oil presence and mechanical removal. The application of a NEBA or a Time Windows of Response strategy for bioremediation has the potential to balance environmental clean up and environmental sensitivity to response strategies.
In order to analyse the role of bioremediation within the scope of marine oil spill response it is necessary to cross reference it with standard techniques for responding to an oil spill incident.

5.2.3.2 Cross analysis of bioremediation and conventional oil spill response techniques:

This section of the chapter cross references the benefits and cautions of bioremediation technology with the most frequently used options for responding to an oil spill. Cautions and benefits of bioremediation technology are briefly reviewed followed by an analysis of the application of other techniques and their relative advantages and disadvantages. Factors to be considered before making a decision regarding whether to use bioremediation include:

Table 36: Factors affecting bioremediation

Factor	Cautions/considerations
The type and concentration of the spilled oil.	- high oil concentrations are difficult to treat - water-in-oil emulsions are difficult to treat - readily biodegradable oils are amenable to biodegradation
The prevalent climatic conditions	- high wave and tidal energy remove oil from shorelines - degradation decreases in low temperatures - high temperatures can desiccate beach material leading to beach irrigation becoming necessary
The nature of the shore that has been contaminated	- bioremediation has been successful on sand, saltmarsh and cobble shores. - oxygen depleted anoxic sediments inhibit bioremediation - low pH values can reduce oil breakdown
The nutrient and oxygen content of the pore water in the beach	- oxygen depleted anoxic sediments inhibit bioremediation - fine sediments can be treated by supplementing nutrients and oxygen - biosurfactants can be used to wash oil from beaches.

Sources: Swannell R 1996, Blackburn JW 1993, Boopathy R 2000

These factors are an intrinsic aspect of the decision making process in determining which options to use to respond to spilled oil. They provide guidelines and physical and chemical boundaries within which bioremediation is a feasible option, the next stage of the analytical process is to interpret the benefits and cautions of using bioremediation and cross reference them and factors affecting bioremediation with standard response options to oil spills.

Table 37: Bioremediation – benefits and cautions

Benefits	Cautions
- Bioremediation is a natural process, when the pollutant has been metabolised the biodegrative population dies off. - Can be used to completely destroy waste - A range of hazardous substances can be transformed to harmless compounds - Complete destruction reduces pollutant transfer from medium to medium (air:water:land) - Bioremediation carried out on site reduces transport and storage needs. - Cost effective	- The process is limited to compounds that are degradable - Products of bioremediation may be toxic - Strict criteria with regard to environmental variables have to be met for the process to work - Takes longer than conventional clean up operations - Evaluation of bacterial performance can be complicated by changes in environmental variables - Number of hydrocarbon degraders decrease in winter months

Sources: Vidali M 2001, Boopathy R 2000, BIOREM Handbook 2006, Lee K 1999

With reference to Table 37, it can be said that the key benefits of bioremediation are environmental; it is a naturally occurring process that if applied correctly can lead to complete containment destruction. It is particularly applicable to sensitive ecosystems and communities including salt marshes and mangrove swamps where it can be applied with minimal disturbance to the environment. From a logistic perspective, it removes the need to use heavy machinery, extensive manpower and storage facilities for waste oil thus reducing transport and storage requirements. In terms of the disadvantages of the process, they can be considered limitations as opposed to factors that lead to profound negative impacts in affected areas. The process of degradation is fundamentally limited to compounds that are susceptible to microbial action and monitoring the efficacy of a bioremediation product can be complicated by changes in environmental variables. In some cases, the by-products of microbial action can be toxic and further aggravate flora and fauna affected by spilled oil. From a spill response logistics perspective, microbial action can take longer than standard response methods, for this reason, increasing dissemination of information on bioremediation may increase the profile and acceptance of the technology.

There is a critical balance to be achieved when considering the use of bioremediation. Assuming climatic conditions are suitable, the key factors in the decision making process are: whether the technology can provide a net environmental benefit to the polluted environment, the estimated timeframe for the oil to be metabolised and whether the application of bacteria will be cost effective in terms of reducing equipment, transport and storage needs.

In order to cross reference and analyse bioremediation with conventional techniques for spill response, a summary and analysis of standard response options used is required. Table 38 details the major types of conventional treatment, their application, benefits and cautions.

Table 38: Conventional oil spill response techniques – benefits and cautions

Response technique	Method of application	Benefits	Cautions
Chemical Dispersants	• Work boats for small spills • Range of aircraft and helicopters depending on spill size • Vehicles such as tractors • Adapted back packs for shoreline clean up	• Efficient method of cleaning up slicks in open water • Natural process of dispersion is accelerated • No physical interference with the environment	• Potential to be interpreted as adding an additional pollutant to the environment • Potential tainting of fish stocks • Ineffective on oils with a high viscosity • Specialist equipment and logistics needed • 1-2 day functional lifetime after application
Booms	• Towing by one or more vessels • Man handled in shallow water	• Efficient oil containment technique • Foam filled booms are light and inexpensive • Rubber booms have long shelf lives and offer compact storage • They have a high buoyancy to weight ratio and follow wave movements closely	• Limited by weather conditions particularly wave height • Effectiveness depends on the speed that boom is being towed through the water • Light oil spreads quickly, booms need to be applied immediately after a spill • Recovery systems typically have a swath of a few metres, they may not have a significant effect on a large spill • Towing and manoeuvring booms at sea can be difficult
Skimmers	• May be free floating, side mounted on a vessel, built into a vessel, built into the apex of a containment boom, held by a crane or held by hand	• Offer clean up in a wide range of circumstances • Disc skimmers have a high recovery efficiency • Brush skimmers have a wide viscosity range • Efficient in sheltered water	• Prone to difficulties presented by wind, waves and currents • Demand for temporary storage for the collected oil • Debris in the water can cause damage
Sorbents	• Can be applied manually or mechanically using blowers or fans • For use on sea or land	• Useful in clean up operations in inaccessible locations • Inexpensive and usually available in large quantities • Can be used at sea and on land • Synthetic absorbents can absorb up to 70	• Used sorbents present are a toxic waste hazard and need to be disposed of properly • Some absorb water as well as oil and can sink • Some lose particles in the water and are hard to collect after use • Majority of products can only be used once,

		times their own weight in oil	once absorbed, the oil cannot be released • Can be hard to apply in windy conditions
Shoreline clean up	• Manual or mechanical depending on oil type and environment	• Positive political strategy • Aids recovery of amenity beaches and protected areas of shore	• Potential cause of environmental damage • Requires extensive communication and logistics • Inaccessible areas of shore may be impossible to reach • Care must be taken not to remove excessive amounts of substrate • Aggressive techniques such as high pressure water jets and sand blasting harm flora and fauns

Sources: http://www.epa.gov (1), http://oils.gpa.unep.org (1), http://www.itopf.com (5), http://www.cleanupoil.com (1), http://www.oil-spill-web.com (1), http://www.epa.gov/ (2)

Analysis and interpretation

As discussed, a key consideration when using bioremediation is the environmental and climatic window within which to operate. There are environmental considerations with conventional techniques for spill response however the techniques are often used in tandem and a restriction with one may be solved by the use of another. Time Windows of Response are appropriate signposts for the restrictions of a particular spill response technique.

A key benefit that bioremediation has over other technologies is that it has the potential to render the hazardous waste harmless through conversion to cell biomass, water or carbon dioxide and in some cases to destroy the product completely (Croft B 1995, Lee K 2000, NERC 1999). Once the oil has been removed from the environment, the microbial population disperses and dies off thus there is little risk of subsequent pollution (Vidali M 2001). Chemical dispersants and sorbents, both of which are added to the environment can lead to a toxic by-product, may taint fish stocks and in the case of sorbents can be problematic to remove from the environment post-application (Vidali M 2001). With the exception of chemical dispersion, the standard techniques are focused on removal, not destruction of the pollutant. This can cause damage to the environment (particularly in fragile environments or through using heavy machinery), requires extensive logistics to transport and treat the waste and can cause further pollution through landfill and incinerator emissions.

There is potential for more extensive damage to the environment if alternative techniques are inappropriately used or do not behave as expected as demonstrated in the wake of the *Amoco Cadiz* incident (Gilfillan E 1995). An example of field trials where bioremediation was not an effective option for removing spilled oil occurred in the wake of the *Prestige* incident. The tanker ran aground off the north-west coast of Spain in 2002 spilled 63,000 tons of oil onto 1900km of coastline. The chemical composition of the oil that was spilled was not conducive to bioremediation, however laboratory analysis carried out on the oil showed that up to 45% of the TPH (total petroleum hydrocarbons) in the oil had been degraded after seven days (Fernandez-Alverez J 2007). The Beach of

Sorrizo was used as a site for the bioremediation trials. The beach was separated into seven zones and a range of bioremediation products were trialed.
The conclusions of the study showed that neither bioaugmentation nor biostimulation accelerated the degradation of the spilled oil (Fernandez-Alverez J 2007). Degradation of the PAH (polycyclic aromatic hydrocarbon) fraction of the oil was noted but after 18 months, a layer of black heavy oil still coated the beach. It was noted that the mechanical recovery showed a positive success rate for oil removal. This was in part due to the fact that the oil was too thick to penetrate the sand and pebbles on the beach to any depth (Fernandez-Alverez J 2007). As a response to the failure of the bioremediation products, a sunflower biodiesel was used which accelerated the degradation of the aliphatic and aromatic fractions of the residual fuel oil. It was noted that biodiesel could be used as an alternative to methods such as high pressure water hoses that were used on the rocks after *Prestige* (Fernandez-Alverez J 2007). A key recommendation that can be drawn is that in order to minimise environmental damage as a result of a spill and the subsequent clean up strategies, is to decide the most appropriate combination of strategies to deal with the oil having assessed the following:

- Oil type.
- Oil amount.
- Oil state.
- Climatic conditions at the time of the spill.
- Nature of the environment impacted by the oil (sensitivity, accessibility, exposure, ability of the oil to penetrate the shore substrata)

Self assessment questions:

- **Discuss the issues with testing bioremediation products in the field**
- **Discuss THREE environmental, THREE hydrodynamic and THREE geographical factors that affect bioremediation.**
- **Comment on why some environments are more suited to bioremediation than others.**

Figure 75: Bioremediation in relation to other technologies – self assessment questions

5.2.4 Summary and suggestions

Summary:

There are a vast range of environmental variables that affect the behaviour of spilled oil at the coast. Factors including oil type, total amount spilled, time elapsed between spillage and beaching and the range of environmental variables that affect oil behaviour at sea and on land all change the characteristics of a clean up operation. These factors are taken into account when orchestrating and implementing a clean up.

What would you suggest?

Bioremediation has been suggested as a possible option for cleaning a major oil spill of light crude oil. The range of environments affected includes exposed rocky shores, dune ecosystems and sheltered mangroves. How would you go about advising the use of bioremediation in one or a number of these environments?

Summary:

Contingency plans for oil spill response are a multi-disciplinary operation. The range of factors that are considered include: area of application, responsible authority, identification of roles and responsibilities, statutory jurisdiction, plan revision, risk assessment, environmental sensitivities and priorities for protection response, waste disposal operations, training and exercises, health and safety and press and public information.

What would you suggest?

You have been invited as an expert on bioremediation to an oil spill response contingency plan revision session for a regional authority. How would you flag bioremediation as an option for response to a spill and justify its inclusion in the contingency plan?

Summary:

Oil spill response operations and contingency plans are constantly subjected to updates and reviews to facilitate the implementation of best practice. A UK port that handles 10,000 ships per annum of which 70% are tankers is in the process of updating its oil spill response plan. Bioremediation has been flagged as a possible addition to the plan.

What would you suggest?

You have been approached as an expert in bioremediation to detail the advantages and disadvantages of the technology over other technology and whether it is possible to optimise bioremediation performance. Prepare a short report containing advantages, disadvantages and options for optimization.

5.2.5 Tutor marked assessment

With reference to a coastal environment (specific location) with which you are familiar or that you can obtain relevant information for, prepare a 2000 word report to contain the following:

- A brief description of the coastal, marine and climatic conditions.
- A brief overview of the pressures and impacts on the environment (industry, residential, tourism), their magnitude, effects and significance.
- In relation to other oil spill response options detail the potential role of bioremediation of oil spills in the environment you have chosen.
- Detail factors present (refer to coastal, marine and climatic conditions) that may adversely affect the efficacy of bioremediation
- Maps, charts and diagrams and case study data should be used throughout as appropriate.

5.3 Conclusions

This chapter presents a strategic overview of the concept of integrating oil spill research and techniques and education and training initiatives. In an area as environmentally and politically sensitive as oil spill response, the maintenance of knowledge, skills and application is an essential aspect of effective implementation. It can be said that the role of bioremediation in current oil spill response is a minor one, this fact makes it particularly applicable to the development of the education and training material. The structure and content of the DLM in this chapter are designed to demonstrate the structure and delivery of education and training as a cost effective and efficient mechanism to bridge the gap between policy and legislation and implementation. The research in this chapter has not been designed to actively encourage further use of bioremediation in marine oil spill response, rather contribute to the facilitation of increased understanding of the framework within which bioremediation is an option. One emphasis in modern oil spill response science and research is developing and refining the response procedure around long term environmental clean up. The dissemination of information regarding mechanically benign techniques such as bioremediation has the potential for wider exposure of the technology and its increased implementation, where appropriate, in clean up strategies.

In terms of the research pathway of the thesis, the justification of analysing the role of education and training in information dissemination came from two sources. (i), the admission that one of the biggest challenges facing the logistics of environmental management is the gap between legislation and policy (declared ambition), and functional implementation and operation. (ii), the acknowledgement in EU legislation (the IPPC Directive) and in environmental management mechanisms including ISO14001 and EMAS, that education and training is essential to ongoing maintenance of environmental standards. It can be said that there are three core elements in the success of the development and ongoing success of education and training as a tool for information dissemination. For education and training to maintain a factor in communicating policy and legislation, it is critical that the three stages are considered a cyclical process whereby review is fed back into ongoing development. The three stages are:

Table 39: Stages in the success of education and training initiatives

Factor	Considerations
Development	- Resources (including: finances, technical assistance, instructor training, networking, advertising, equipment) - Strategic development of course content - Information sources and research - Identification and demands of target audience
Delivery	- Structure and format of course delivery - Role and scope of assessments - Feedback - Focus on skills, knowledge and communication - Activities focused on development of cognitive skills. - Balance between formal delivery and interactive student participation
Review	- Course evaluation from students, faculties, instructors and academic and

	professional peers - Evaluation of whether course aims and objectives have been met - Course evaluation analysis - Integration of course evaluation into ongoing development - Course accreditation - Review of applicability of course content with legislation and policy

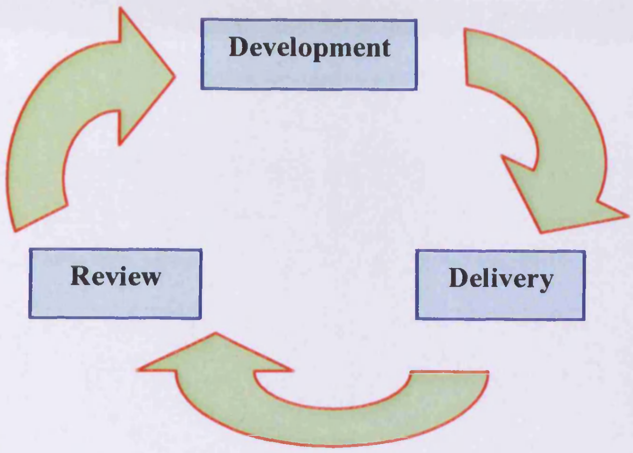


Figure 76: Cyclical development of education and training initiatives

Throughout the three phases, and in any education and training initiative, it can be said that maintenance of communication, partnerships and free dissemination of information are critical. The two factors that are essential for this to be achieved are: (i), internal networking among partners who design, populate and deliver courses and among recipient institution, companies and industries. Partnerships and networks, particularly in education and training, are only as strong as their component parts, especially their weakest link or information source. (ii), a willingness of the recipient community to invest and promote the concepts of education and training and the impacts it can have on industries, businesses and communities. Focus on the strength and maintenance of networks in recipient countries is critical. Taking these factors into consideration, the benefits of education and training as a tool to promote communication, disseminate information, and act as a tool for ongoing maintenance of performance and environmental management include: the cyclical nature of distance learning over time can ensure ongoing compliance with legislation and policy. The versatility, and access and pooling of information that is achieved through working in partnerships in education and training, ensures utmost flexibility in terms of taught content and stated targets. It can be integrated into company targets and business plans as a cost effective technique for employee training. It can be implemented alongside full time employment and run from a remote location. In the current age of global markets and trade, it can be used as a tool to cross political and economic boundaries, reduce costs and share knowledge, skills and experience.

6 Chapter Six: Conclusions

6.1 Introduction

This research has been concerned with the environmental management of the waste stream and energy from waste, with specific reference to marine oil spill incidents. In particular, the thesis has investigated options for deriving energy from marine oil spill waste. Throughout the thesis, the concept of bridging the gap between legislation and policy, and decision making and implementation at operational level was deliberately selected for further research. It formed a functional output of the research pathway through the development of an education and training initiative on bioremediation of oil from marine spill incidents. This chapter is designed to examine the overall context of the research in the wider field and to examine the extent to which the aims and objectives of the research were met. The chronological development and delivery of the research pathway started with a review of the waste management and energy from waste industries, within which marine oil spills were selected as a specialist case study. The research pathway was designed to investigate options for energy from oil spill waste and present functional outputs through two media; the research into energy from oil spill waste through laboratory and *ex-situ* field trials and the development of a distance learning initiatives as an option for training, education and dissemination.

6.2 Core conclusions

The waste industry is expanding in terms of increasing volumes requiring treatment, a more diverse range of products being disposed of and increasingly sophisticated, diverse options for treatment. While these processes are creating a range of issues including: increasing pressure on the logistics of disposal and treatment and increasing pressure on the location and volumes of landfill sites; they are creating opportunities in the energy industry in terms of commercial gain and potential generation of stable, renewable sources of energy (Bulkeley H 2005). The demand for renewable sources of fuel due to increasing political instability in oil-rich states and the demand for reduced reliance on fossil fuels is well documented (http://www.dti.gov.uk (1)). Global concerns over climate change and the necessity to reduce emissions has led to the energy industry entering a phase of transition where reduced reliance on oil and a rapid expansion into renewables is a key priority. It can be said that the key to utilising the potential of existing waste sources as fuel is encompassing the logistic chain of waste management into the wider fields of environmental management and energy generation. It can further be proposed that compliance with policy drives management systems at operational and managerial levels. If this concept is taken one step further, it is reasonable to suggest that if the energy from waste industry is going to be expanded, a key first stage is implementing new legislation and policy that reflects this. Currently, policy at EU level is well established in the fields of renewable energy and waste management and disposal, however, there is no specific piece of legislation focused on energy generation from waste. The Waste Incineration Directive states that is not legally binding to utilise the heat from waste incineration process as fuel, but the heat must be put to as good a use as feasible (http://europa.eu (1)). The EU renewable energy legislation highlights the use of biomass, landfill gas and biogas as options for facilitating member states renewable obligations. Members are obliged by EU law to set targets and develop action plans to increase the use and scope of renewable energy technologies. It can be concluded from this that there is scope for legislative expansion into energy from waste treatment leading to wider operational controls and integration of technologies and expertise, this statement is further supported by the fact that the technology of energy generation from waste is well established and widely used (Kumar S 2000, Umberto D 2003, Ferrer E 2005, Pacey J 1999). The acknowledgement of the potential that energy from waste could have to facilitate further compliance with renewable energy legislation can be a driver to implement further legislation.

Within the scope of energy generation from waste products the research specifically focused on the potential for waste oil from marine spills to be used as a fuel source.

Typically, the waste from oil spills is landfilled, incinerated or treated using one of a number of specialist options including thermal desorption or landfarming (Araruna J 2004, Venosa D 2000, Genouw G 1994). The literature review highlighted the response to the *Volgoneft 248* incident as the sole response operation that used the calorific value of the spilled oil as a factor to quantify the efficacy of the clean up. However, once the oils calorific value had been quantified, it was incinerated with no energy recovery. Based on the statistical evidence from the *Volgoneft 248* investigation and the scope identified for expansion into and integration between renewable energy and waste management, the research investigated the potential for utilising the waste from marine oil spills as fuel. The carbon content of a range of oil-sorbent compounds was determined in the laboratory and statistically analysed. This was done to critically analyse the methods used and to provide a baseline data set in order to determine whether an extension of the study into field conditions was appropriate. An essential aspect of the science of marine oil spill response is to extend laboratory experiments and analysis into the field as the range of biological, physical and chemical factors that the oil and treatment products undergo in the environment can affect the efficacy of a response operation (Swannell R 1996).

The average percentage carbon result from the laboratory was 92.1% and from the *ex-situ* field trials 94.6%. This suggests that despite the moisture content of the compounds being higher in the *ex-situ* data, this did not affect the oils carbon content and associated ability to combust. It is often the case that moisture content is a significant factor in the suitability of a product as fuel, these statistics show that it was not a factor within the investigation into marine oil spill waste. This evidence suggests that in terms of carbon content and ease of combustion there is potential to utilise waste oil-sorbent compounds from marine oil spills as fuel. A theme that emerged in the research into the carbon content of oil-sorbent compounds was the variety in behaviour between oils, sorbents and the substrata they were recovered from. The ease of removing the oil with each combination of oil, sorbent and substrata was recorded and a range of observations and trends were stated from evidence based analysis. Key relationships noted were: the relationship between substrata surface area and sorbent grain size affected the ability to remove the oil-sorbent compound, the finer the sorbent grain, the more likely it was to form a paste that complicated removal, and that the more viscous oils spread less but were more persistent on substrata during removal. As a result of this research it is suggested that a database of the optimum combinations of oil, sorbent and substrata that take into account the physical characteristics of each could be developed. The success of any one combination is based on the percentage recovery of the compound *post*-recovery; this provides evidence of the efficacy of the operation and provides a percentage of the oil, and sorbent product, remaining *in-situ* that may require further response procedures. A key benefit to this process is that analysis can take place solely on knowing the weights of oil spilled and sorbent applied.

If the concept of quantifying and analysing the efficacy of marine oil spill response operations is considered, the use of pixel analysis can be considered a novel application. Image analysis of oil spills was researched in the literature review, it is used to detect and track the trajectory and speed of offshore slicks but no evidence of research was found quantifying the efficacy of the response once oil had grounded was found. As a result of this, the research into the application of Scion Image in quantifying oil and sorbent removal from substrata using pixel distribution in images taken before, during and after the spill was developed. The results were displayed graphically and analysed statistically and the results showed that pixel analysis is an efficient and cost effective technique, in terms of time and resources required, to quantify the success of oil spill clean up operations. This technique is particularly applicable in terms of the visual aesthetics of a spill site and the associated pressure exerted by the public and media in the wake of a spill. It can further be integrated into the concept of optimum combinations of oil, sorbent and substrata and can be used as a data set to graphically and statistically illustrate the variations in shade between substrata *pre*, during and *post* oiling. A further advantage is that regarding processing, displaying and disseminating data, graphical representations of shores during the phases of a clean up are clear and effective visual representatives of progress which can be easily distributed among the media and public. The data can also be statistically analysed and interpreted to build into ongoing analysis of products and logistics.

A key aspect in introducing new and innovative technologies or concepts, and enforcing associated legislation, policy and standards, is ensuring that personnel from senior management to technical staff and operators have sufficient levels of education and training (Barratt R 2006). It has been accepted in academia (Vastag G 1996) and at EU legislation (http://ec.europa.eu (4), DEFRA (3rd ed.), 2004) that education and training are efficient mechanisms to bridge the gap between declared ambition (legislation and policy) and functional implementation and compliance. It can be said that accessibility to, and dissemination of research, are essential to achieve this and to further maintain standards, facilitate development and expansion of the knowledge and technology base and advance management options. Based on these factors an investigation into the pedagogy of education and training initiatives based on distance learning was carried out for the literature review. During the course of the research, the opportunity was taken to contribute to a series of EU funded initiatives based on research activity dedicated to dissemination and promulgation of waste management and oil spill response methodologies. Distance learning modules and interactive workshops and training courses were developed and the knowledge base acquired was utilised to develop the Distance Learning material on the use of bioremediation of marine oil spill waste. The methodologies used were further validated by the diverse nature of participants on the EU funded initiatives which ranged from Government officials to managers, supervisors, foreman, workers, trainees and undergraduates. This highlights the multi and cross-disciplinary demand for training that exists in industry. It further indicates that as a medium for dissemination, education and training courses are applicable at strategic, and local and regional levels.

For education and training to maintain applicability and relevance it is imperative that the process is seen as a cyclical one where advances in technical and legislative practice are incorporated into education initiatives. A further area for cyclical review and revision is integrating feedback from course participants into future work, this is critical to customising material to the target audience and ongoing improvement of delivered material. This cyclical nature of feedback and continual review and revision in the conceptual development of education and training is reflected in the research pathway of the thesis. Case histories of marine oil spill response operations discussed in chapter three of the thesis demonstrate the applicability of this in advancing oil spill response science. The lessons learned from *Torrey Canyon*, *Exxon Valdez* and *Braer* have quantifiably advanced our reaction to, and understanding of, marine oil spills. The focus on oil spills and disseminating new research, such as the use of pixel analysis and utilising oily waste as a fuel source, was addressed through the development of education and training initiatives. It can be said that if policy and legislation are to evolve with supply, demand and available expertise and technology, the last step in the cyclical process of wider environmental management is composed of two core themes. Firstly, to ensure personnel are adequately trained and conversant with the latest legislative and policy related documents, ensuring they are aware of the reasons for legislative change, and secondly, to ensure that the knowledge and expertise of products, technologies, supply and demand that exists at operational level is transferred to those responsible for deriving legislation and policy. The use of education and training initiatives as a tool to facilitate communication and disseminate information can contribute to maintaining the cyclical nature of environmental management at every level from Government and management to foreman and student. It can further facilitate cross boundary discussion in terms of subject area and physical location and as a result, can contribute to further advances in integrating waste management, oil spill response and energy generation

Research into the environmental management of the waste stream, energy from waste and marine oil spills requires a genuinely interdisciplinary approach in order to appreciate the subtleties of the plethora of interrelationships that control the range of aspects and impacts. The derivation of energy from waste material and in particular, the potential of energy generation from marine oil spill waste is likely to be a rewarding study area for future research.

6.3 Future research pathways

The research pathway of the thesis was specifically selected to reflect the requirements of the investigative line. The cut off points in the research were deliberately selected to focus the scope of the research and to validate the stated aims and objectives. During the course of the literature review, research, data collection and analysis, potential future research pathways were identified. The decision was made not to pursue them as this would have extended the scope of the core research beyond the aims and objectives. In terms of future research into the generation of energy from oil spill waste, there is scope for diversifying the range of oils, sorbents and substrata used. The three types of oil used were selected as they are the three major types of oils that have to be managed in spill incidents (refined, crude, weathered), the sorbents all displayed different properties and behaviour when applied, and the substrata were selected as they are typical of the coastline that was oiled after *Sea Empress* ran aground in West Wales in 1996.

A further area of future research is maximising the potential of the waste oil and sorbent in terms of its usability. A series of meetings were held with Paulex, the company that manufacture and supply Klausorb, into the logistics of compressing the waste oil and sorbent into briquettes for use in incinerators. Currently, olive refuse and paper mill waste, waste paper and wheat straw and liquid sewage waste are all compressed and incinerated. (Yaman S 2000, Ayhan D 1998, Slupek S 2000). The feedback from the experts at Paulex was that there was potential for compressing the waste oil and sorbent and manufacturing it commercially as fuel. However, this is not a proposition that could have been aligned with the research pathway and investigative line as the volume of waste required to make it a commercially viable project exceeded the amounts used in the laboratory and *ex-situ* field trials.

There is potential to further integrate the philosophy of the research into environmental management strategies, oil spill response research, energy generation and waste disposal through integrating management of marine oil spill waste with small scale industrial and terrestrial spillages. It is acknowledged in the research that the contribution of large scale marine incidents to global oil spill statistics is small. The research in this thesis is focused on marine spill incidents however the conceptual basis of pollution remediation, environmental clean up and energy generation applies to industry at a global scale irrespective of its marine or terrestrial status. There is potential further research utilising the techniques developed in this thesis to apply them to industries that contribute substantially higher volumes of waste oil to the environment than marine spill incidents.

As discussed in chapter three, an intrinsic aspect of designing and testing products used in marine oil spill response operations is field trials. The decision not to undertake field trials was made for two reasons. In the first instance, UK Environment Agency regulations regarding oil discharge do not include scope for research as there is no guarantee all oil spilled can be recovered. In the second case, had the work been carried out during a response to a spill incident, the comparison with the laboratory analysis would have been skewed due to the environmental variables beyond experimental control in the field. The validity of the *ex-situ* field data was centred on the methodologies and oil, sorbents and substrata used being consistent with that of the laboratory analysis. If the education, training and information dissemination output of the research is considered, it can be said that there is scope to expand the outreach of material through different media and to a wider range of target audiences. This includes the possible addition of workshops and training courses to compliment the formal taught material, utilising the format and delivery of the work carried out in South East Asia on EU funded research initiatives (Green J 2005, Green J 2006, Green J 2006 (1), Green J 2008, BiWaRE Handbook 2005, BIOREM Handbook 2006, SACODI Handbook 2007, http://www.protekt.hs-bremen.de (1)). The media selected were identified as the most appropriate to achieve the goals of the wider research in terms aims and objectives and the nature of the taught material. Its development was funded by Milford Haven Port Authority and it was further validated by peer review from colleagues on the EU funded work who are experts in waste management, energy from waste and oil spill response.

References:

A:

Abu-Quadais M 1996. Fluidized-bed combustion for energy production from olive cake. Journal of Energy. 21 (3), pp173-178.

Acaroglu M, Kocar G, Hepbasli A 2004. The Potential of Biogas Energy. Journal of Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 27 (3), pp251–259.

ACSB 1999. Quality issues in distance learning. Published by: American Assembly of Collegiate Schools of Business (AACSB) St. Louis, MO. (http://www.aacsb.edu)

Adebajo MO, Frost RL, Kloprogge JT, Carmody O, Kodot S 2003. Porous Materials for oil spill clean up: a review of synthesis and absorbing properties. Journal of Porous Materials. 10, pp159-170.

ADEC 1993. Shoreline Treatment Techniques. The *Exxon Valdez* Oil Spill: Final Report, State of Alaska Response. Published by the Alaska Department of Environmental Conservation Chapter 2: Technology, pp61- 87.

Agunwamba JC 1998. Solid Waste Management in Nigeria: Problems and Issues. Journal of Environmental Management. 22 (6), pp849-856.

Alappat BJ, Delebarre A, Pre P, Chandel MK, Delvinquier V, Garabetian JC, Pouxe D, Gonzalez J, Marchand B 2007. Thermal remediation of oil polluted sands from black tides: The fluidized bed option. Journal of Chemical Engineering. 129 (1-3), pp 143-151.

Albaiges J, Morales-Nin B, Vilas F 2006. The Prestige Oil Spill: A scientific response. Marine Pollution Bulletin. 53(5-7) pp205-207.

Alexander SK, Webb Jr., JW 1987. Relationship of *Spartina alterniflora* to sediment oil content following an oil spill. Proceedings of the 1987 Oil Spill Conference. American Petroleum Institute, Washington, D.C. pp445–449.

Allen B, Leeson A 1999. *In situ* bioremediation of petroleum hydrocarbon and other organic compounds. Proceedings from the 5th international *in situ* and on site bioremediation synopsium. April 19-22 San Diego California. pp239-245.

American Petroleum Institute (API) 2001. Effect of Oil and chemically dispersed oil in the environment (Publication No. 4693).

AMSA 2004. Management and disposal of oil spill debris. Canberra: AMSA.

API, NOAA, USCG, USEPA 2001. A Guide for Spill Response Planning in Marine Environments A joint publication of the American Petroleum Institute, National Oceanic and Atmospheric Administration, U.S. Coast Guard, U.S. Environmental Protection Agency Seattle, Washington.

Araruna JT, Portes VLO, Soares APL, Silva MG, Sthel MS, Schramm DU, Tibana S, Hargas H 2004. Oil spills debris clean up by thermal desorption. Journal of Hazardous Materials. 110, pp161-171.

Asifa M, Muneer T 2007. Energy supply, its demand and security issues for developed and emerging economies. Journal of Renewable and Sustainable Energy Reviews. 11 (7), pp1388-1413.

ASTM 1998. Standard test method for tumbler test for coal. Annual Book of ASTM Standards Vol 05.0. Published by the American Society for Testing of Materials, West Conshohochen PA, pp192-194.

Atlas R 1995. Bioremediation of petroleum pollutants. Journal of International Biodeterioration and biodegradation. 31 (4), pp317-327.

Atlas R 1995. Petroleum biodegradation and oil spill bioremediation. Marine Pollution Bulletin. 31 (4), pp178-182.

Ayhan D 1998. Evaluation of biomass residue 1. Briquetting waste paper and wheat straw mixtures. Journal of Fuel Processing Technology. 55 (2), pp175-183.

B:

Baca B, Ward G, Lane CH, Schuler PA 2005. Net Environmental Benefit Analysis of Dispersed Oil on Nearshore Tropical Ecosystems Derived from the 20 year TROPICS Field Study 2005. In proceedings: International Oil Spill Conference, Miami 15th -19th May pp1-4.

Bacella S, Cerichelli G, Chiarani M, Ercole C, Fantauzzi E, Lepedi A, Toro L, Veglio F 2000. Biological Treatment of alkaline industrial waste waters. Journal of Process Biochemistry. 35, pp595-602.

Baker J 1999 Ecological effectiveness of oil spill countermeasures: how clean is clean. Journal of Pure Applied Chemistry. 71 (1), pp135-151.

Banarjee S, Joshi M, Jayaram R 2005. Treatment of oil spills using organo-fly ash. Journal of Desalination. 195, pp32-39.

Barratt RS 2006. Meeting lifelong learning needs by distance teaching – Clean technology. Journal of Cleaner Production. 26 (4), pp585-598.

Bebar L, Stehlik P, Havlen L, Oral J 2005. Analysis of using gasification and incineration for thermal processing of wastes. Journal of Applied Thermal Engineering. 25, pp1045-1055.

Behrens A, Giljum S, Kovanda J, Niza S 2007. The material basis of the global economy: Worldwide patterns of natural resource extraction and their implications for sustainable resource use policies. Journal of Ecological Economics. 64 (2), pp444-453.

Bell S, McGillivray D 2006. Environmental law 6th edition Oxford University Press. Pp145-147.

Bell S, McGillivray D 2006. Environmental law 6th edition. Oxford University Press 2006, pp85-90.

Bernedes E, 2002. Bioenergy and Water—The Implications of Large Scale Bioenergy Production for Water Use and Supply. Journal of Global Environmental Change. 12, pp253–271.

Bidwell Joseph R, Cherry Donald S, Merski, A Thomas 2003. Toxicity Evaluation of a commercial bioremediation agent mixed with crude oil. Journal of Environmental Toxicology and Chemistry. 22 (1), pp84-91.

BIOREM Handbook 2006 (1). The risks and consequences of oil pollution in Vietnam and guidelines on bioremediation of oil spills chapters 2-6. Published by the European Union. Available online at: http://www.bioremediation.hs-bremen.de/. Ref: ASI/B7-301/2598/18-2004/79067

BIOREM Handbook 2006. The risks and consequences of oil pollution in Vietnam and guidelines on bioremediation of oil spills. Published by the European Union. Available online at: http://www.bioremediation.hs-bremen.de/. Ref: ASI/B7-301/2598/18-2004/79067

Birkland TA, Lawrence RG 2002. The Social and Political Meaning of the *Exxon Valdez* Oil Spill. Spill Science and Technology Bulletin. 7 (1-2), pp17-22.

BiWaRE Handbook 2005. Decision Support System for the application renewable energy from biogas and biomass combustion. Report published by the European Union. Ref: ASE/b&/1997/0178-06.

Blackburn JW, Hafker WR 1993. The impact of biochemistry, bioavailability and bioactivity on the selection of bioremediation techniques. Journal of Trends in Biotechnology. 11 (8), pp328-333.

Boopathy R 2000. Factors limiting bioremediation techniques. Journal of Bioresource Technology. 74 (1), pp63-67.

Booth S 1995. The *Braer* Disaster: A Virtuous Crisis? - International Responsibility and Prevention of Incidents at Sea. Journal of Contingencies and Crisis Management. 3 (1), pp38-42.

Bragg JR, Pronce R, Harner E Atlas M 1994. Effectiveness of bioremediation for the Exxon Valdez oil spill. Journal of Nature. 368, pp413-418.

Brekkea C, Solberg A 2005. Oil spill detection by satellite remote sensing. Journal of Remote Sensing of Environment. 95 (1), pp1-13.

Bryan GW, Langston WJ 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Journal of Environmental Pollution. 76, pp89–131.

Bulkeley H, Watson M, Hudson R, Weaver P 2005. Governing Municipal Waste: Towards a New Analytical Framework. Journal of Environmental Policy & Planning. 7 (1), pp1–23.

Burgherr P 2007. In-depth analysis of accidental oil spills from tankers in the context of global spill trends from all sources. Journal of Hazardous Materials. 140 (1-2), pp245-256.

Burns A, Knap A 1989. The Bahia las Minas Oil Spill hydrocarbon uptake by reef building corals. Marine Pollution Bulletin. 20 (8), pp391-398.

Burns K Codi S Swannell R Duke N 1999. Assessing the oil degradation potential of endogenous micro-organisms in tropical marine wetlands. Journal of Mangroves and Saltmarshes. 3, pp67-83.

Burns K, Codi S, Duke N 2000. Gladstone, Australia Field Studies: Weathering and degrading of hydrocarbons in oiled mangrove and salt marsh sediments with and without the application of an experimental bioremediation protocol. Marine Pollution Bulletin. 41 (7-12), pp 392-402.

Burrows P, Rowley C, Owen D 1974. Torrey Canyon: A case Study in accidental pollution. Scottish Journal of Political Ecomony. 21 (3), pp237-258.

C:

Cambre MA 1991. The state of the art in instructional televeision. In GJ Anglin (ed.) Instructional Technology, past, present and future. London: Englewood, pp 267-275.

Carroll J, Boisson F, Fowler SW Teyssie J-L 1997. Radionuclide adsorption to sediments from nuclear waste dumping sites in the Kara Sea. Marine Pollution Bulletin. 35 (7-12), pp296-304.

Chapmana H, Purnella K, Lawb RJ, Kirbyb MF 2007. The use of chemical dispersants to combat oil spills at sea: A review of practice and research needs in Europe. Marine Pollution Bulletin. 54 (7), pp827-838.

chemotaxis. (n.d.). *The American Heritage® Dictionary of the English Language, Fourth Edition*. Accessed March 2008, from http://dictionary.reference.com/browse/chemotaxis.

Chen W Chen C 2001. Combustion characteristics and energy recovery of a small mass burn incinerator. International. Communication of Heat Mass Transfer. 28 (3) pp299-310.

Cheyne I, Purdue M 1995. Fitting definition to purpose: the search for a satisfactory definition of waste. Journal of Environmental Law. 7 (2), pp149-168.

Christensen TH, Kjeldsen P, Albrechtsen HJ, Heron G, Nielsen PH, Bjerg PL, Holm PE 1994. Attenuation of landfill leachate pollutants in aquifers Journal of Critical Reviews in Environmental Science and Technology. 24 (2) pp119-202.

Chu C Lee D 2001. Experimental Analysis of Centrifugal dewatering process of polyelectrolyte flocculated waste activated sludge. Journal of Water Resources. 35 (10), pp2377-2384.

Colin D. Hills A, Pollard SJT 1997. The influence of interference effects on the mechanical, microstructural and fixation characteristics of cement-solidified hazardous waste forms. Journal of Hazardous Materials. 52 (2-3), pp171-191.

Connor P 2003. UK renewable energy policy: a review. Journal of Renewable and Sustainable Energy Reviews. 7, pp65-82.

Cook DA 2007. Web-based learning: pros, cons and controversies. Journal of Clinical Medicine. 7 (1), pp37-42.

Corbet AG 1995. Navigation management: Post Donaldson. Journal of Marine Policy. 19 (6), pp477-486.

Criqui P, Kouvaritakis N 2000. World energy projections to 2030 International Journal of Global Energy Issues. 14 (1-4), pp 116-136.

D:

Dasappa S, Sridhar HV, Sridhar G, Paul G, Mukunda HS 2003. Biomass gasification—a substitute to fossil fuel for heat application. Journal of Biomass and Bioenergy. 25 (6), pp637-649.

DEFRA 2006. A Review of England's Waste Strategy: A Consultation Document. London: DEFRA.

DEFRA 2007. Consultation on the review of the oil spill treatment products approval scheme. London: DEFRA.

Delille D, Basseres A, Desommes A 1998 Effectiveness of bioremediation for oil polluted Antarctic seawater. Polar Biology Vol 19 pp237-241.

Desideri Umberto 2003. Sanitary landfill energetic potential analysis: a real case study. Journal of Energy Conversion and Management. 44, pp1961-1983.

Di Palma L, Ferrantelli P, Merli C, Petrucci E. 2002. Traetment of industrial landfill by means of evaporation and reverse osmosis. Journal of waste Management. 22, pp951-955.

Dijkema GPJ, Reuter MA, Verhoef EV 2000. A new paradigm for waste management. Journal of Waste Management. 20 (8), pp633-638.

Dincer I 2000. Renewable energy policy in the UK a review. Journal of Energy Policy for a Sustainable Energy Future. 32 (17), pp1935-1947.

Duke N, Burns K, Swannell R, Dahlhaus O, Rupp R 2000. Dispersant use and a bioremediation strategy as alternate means of reducing impacts of large oil spills on mangroves: The Gladstone Field Trials. Marine Pollution Bulletin. 41 (7-12), pp403-412.

E:

Edgell N 1994. The Braer Tanker Incident: Some Lessons From the Shetland Islands. Marine Pollution Bulletin. 29 (6-12), pp361-367.

education. (n.d.). *The American Heritage® Dictionary of the English Language, Fourth Edition.* Visited March 2008, from Dictionary.com website: http://dictionary.reference.com/browse/education

Edwards R, White I 1998. The Environmental Impact of the Sea Empress Oil Spill. SEEEC Sea Empress Environmental Evaluation Committee Report. London: The Stationery Office.

Edwards R, White I. 1999. The Sea Empress Oil Spill: Environmental Impact and Recovery. Proceedings of the ITOPF 1999 International Oil Spill Conference 7-12th March 2002 Seattle, Washington.

Efroyumsun R, Nicolette J, Suter II G 2003. A framework for net environmental benefit analysis for remediation or restoration of contaminated sites. Journal of Environmental Management. 34 (3), pp315-331.

El-Fadel M, Findikakis AN, Leckie J 1997. Environmental Impacts of Solid Waste Landfilling. Journal of Environmental Management. 50, pp1-25.

El-Fadel M, Findikakis AN, Leckie JO 1997. Environmental Impacts of Solid Waste Landfilling. Journal of Environmental Management. 50 (1), pp1-25.

Elliott D 2000. Renewable energy and sustainable futures. Journal of Futures Studies. 32 (3-4), pp261-274.

England LS, Lee H, Trevors JT 1993. Bacterial survival in soil – effect of clays and protozoa. Journal of Soil Biology and Biochemistry. 25, pp525–531.

F:

Fernández-Álvarez P, Vila J, Garrido JM, Grifoll M, Feijoo G, Lema JM 2007. Evaluation of biodiesel as bioremediation agent for the treatment of the shore affected by the heavy oil spill of the *Prestige* Journal of Hazardous Materials. 147 (3), pp914-922.

Fernández-Álvarez P, Vila J, Garrido-Fernández JM, Grifoll M, Lema JM 2006. Trials of bioremediation on a beach affected by the heavy oil spill of the *Prestige* Journal of Hazardous Materials. 137 (3), pp1523-1531.

Ferrer E, Aho M, Silvennoinen J, Nurminen RV 2005. Fluidized bed combustion of refuse-derived fuel in presence of protective coal ash. Journal of Fuel Processing Technology. 87 (1), pp33-44.

Ferriera C, Ribeiro A, Ottosen L 2003. Possible applications for solid waste fly ash. Journal of Hazardous Materials. 96, pp201-216.

French D Schuttenberg H 1999. Evaluation of net environmental benefit analysis using fate effects and modelling. In Proceedings of: 1999 International Oil Spill Conference 7-12th March 2002 Seattle, Washington.

G:

Gandy M 1994. Recycling and the Politics of Urban Waste. London: London Earthscan.

Garrett R, Rothenburger S, Prince R 2003. Biodegradation of fuel oil under laboratory conditions and arctic marine conditions. Spill Science and Technology Bulletin. 8 (3) pp297-302.

Gautam AK, Kumar S, Sabumon PC 2007. Preliminary study of physico-chemical treatment options for hospital waste water. Journal of Environmental Management. 83, pp298-306.

Genouw G, de Naeyer F, van Meenen P, van de Werf H, de Nijs W, Verstraete W 1994. Degradation of oil sludge by landfarming — a case-study at the Ghent Harbour. Journal of Biodegradation. 5 (1), pp37-46.

Gilfillan ES, Maher NP, Krejsa CM, Lanphear MF, Ball CD, Meltzer JB, Page DS 1995. Use of remote sensing to document changes in marsh vegetation following the *Amoco Cadiz* oil spill (Brittany, France, 1978) Marine Pollution Bulletin 30 (12), pp780-787.

Goldberg ED 1975 The Mussel Watch — a first step in global marine monitoring, Marine Pollution Bulletin. 6, pp111-114.

Gordon R 1994. Bioremediation and its Application to Exxon Valdez Oil Spill in Alaska. New Hamshire Department of Environmental Sciences unpublished paper.

Gray JM 1997. Environment, policy and municipal waster management in the UK. Transactions of the Institute of British Geographers. 22 (1), pp69-90.

Green C, Soham B, Dilmaghani M 2006. Challenges to a climate stabilising energy future. Journal of Energy Policy. 35, pp616-626.

Green J 2005. BIOREM Distance Learning Model. Available online at http://www.bioremediation.hs-bremen.de/ visited November 2005.

Green J 2006 (1): SACODI tutors notes http://www.tu-dresden.de/wwvwlat/sacodi/documents/SACODI_Training_Scheme_tutors_notes.pdf

Green J 2006 (2) BIOREM Technical Report. Sections 2.6, 2.6, 2.8 Published by the European Union. Available online http://www.bioremediation.hs-bremen.de/

Green J 2006. SACODI Distance Learning Model Core Text: http://www.tu-dresden.de/wwvwlat/sacodi/documents/SACODI_training_module.pdf

Green J 2008. INVENT Distance Learning Model Core Text. Available online at: http://homepages.hs-bremen.de/~office-ikrw/invent/

H:

Hall Jr. LW, Ziegenfuss MC, Anderson RD, Lewis BL 1995. The effect of salinity on the acute toxicity of total and free cadmium to a Chesapeake Bay copepod and fish. Marine Pollution Bulletin. 30, pp376–384.

Hallock JL, Tharakan PJ, Hall CAS, Jefferson M, Wu W 2004. Forecasting the limits to the availability and diversity of global conventional oil supply. Journal of Energy. 29 (11), pp1673-1696.

Hamer G 2003. Solid waste treatment and disposal: effects on public health and environmental safety. Journal of Biotechnology Advances. 22 (1-2), pp71-79.

Hamilton TF, Ballestra S, Baxter MS, Gastaud J, Osvath I, Parsi P, Povinec P, Scott EM 1994. Radiometric investigations of Kara Sea sediments and preliminary radiological assessment related to dumping of radioactive wastes in the Arctic Seas. Journal of Environmental Radioactivity.25 (1-2), pp113-134.

Harayama S, Kasai Y, Hara A 2004. Microbial communities in oil contaminated sea water. Journal of Current Opinion in Biotechnology. 16, pp205-214.

Hare L, Carignan R, Huerta-Diaz MA 1994. A field study of metal toxicity and accumulation by benthic invertebrates; implications for the acid-volatile sulphide (AVS) model, Limnol. Journal of Oceanography. 39, pp1653–1668.

Hawkins SJ, Southward AJ 1992. The Torrey Canyon oil spill: Recovery of rocky shore communities in restoring the nation's marine environment. (Ed. G.W. Thayer). Maryland Sea Grant College. pp 583-632

Head I, Swannell R 1999. Bioremediation of Petroleum Hydrocarbon Contaminants in Marine Habitats. Journal of Current Opinion in Biotechnology. 10, pp234-239.

Ho K, Quinn J 1993. Physical and chemical parameters of sediment extraction and fractionation that influence toxicity, as evaluated by Microtox®. Journal of Environmental Toxicology and Chemistry. 12 (4), pp615-625.

Hodson PV, Zambon S, Ewert A, Ibrahim I, Kiparissis Y, Windle M, Lee K, Venosa AD 2001. Evaluating the efficiency of oil spill countermeasures by monitoring changes in the bioavailability and toxicity to fish of PAH from wetland sediments. . Proceedings of the 24th Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Environment Canada, June 12-14, Edmonton, Alberta (In Press).

Hoffert MI 2003. Response. Journal of Science. 300 pp582–584.

Hoffert MI, Caldeira K, Benford G, Criswell DR, Green C, Herzog H, Jain AK, Kheshgi HS, Lackner KS, Lewis JS, Lightfoot HD, Manheimer W, Mankins JC, Mauel ME, Perkins J, Schlesinger ME, Volk T, Wigley TML 2002. Advanced technology paths to climate stability: energy for a greenhouse plane. Journal of Science. 298, pp981–987.

Hoffert MI, Caldeira K, Jain AK, Haites EF, Harvey LDH, Potter SD, Schlesinger ME, Schneider SH, Watts RG, Wigley TML, Weubbles DJ, 1998. Energy implications of future stabilization of atmospheric CO2 content. Journal of Nature. 395, pp881–884.

Hornung H 1989. Metal levels in some benthic organisms of Haifa Bay, Mediterranean. Journal of Toxicology and Environmental Chemistry. 20–21, pp 255–260.

Hornung H, Krom MD, Cohen Y 1989. Trace metal distribution in sediments and benthic fauna of Haifa Bay, Israel. Journal of Estuary and Coastal Shelf Science. 29, pp43–56.

http://aast.files.wordpress.com (1): http://aast.files.wordpress.com/2007/08/payatas-hillside1.jpg accessed December 2007

http://atdpweb.soe.berkeley.edu (1): http://atdpweb.soe.berkeley.edu /pix/maui/landfill.jpg visited December 2007

http://crudemarketing.chevron.com (1): http://crudemarketing.chevron.com/assay/statfjord_summary.pdf visited Jan 08.

http://darkwing.uoregon.edu (1): http://darkwing.uoregon.edu/~ecotone/es203/envmvmt/valdez.html accessed October 2007

http://ec.europa.eu (1): http://ec.europa.eu/environment/ippc/index.htm accessed June 2007

http://ec.europa.eu (2): http://ec.europa.eu/environment/waste/hazardous/hazardous_consult.htm, accessed May 2007

http://ec.europa.eu (3): http://ec.europa.eu/environment/air/pollutants/stationary/ippc/index.htm accessed March 2008.

http://ec.europa.eu (4): http://ec.europa.eu/environment/ippc/index.htm, accessed May 2007

http://ec.europa.eu (5): http://ec.europa.eu/energy/library/599fi_en.pdf accessed November 2007.

http://eurlex.europa.eu (3): http://eurlex.europa.eu/smartapi/cgi/sga_doc?smartapi!celexplus!prod!DocNumber&lg=en&type_doc=COMfinal&an_doc=2005&nu_doc=628 accessed September 2007

http://eurlex.europa.eu (1): http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32006L0012:EN:NOT accessed August 2007

http://eurlex.europa.eu (2): http://eurlex.europa.eu/smartapi/cgi/sga_doc?smartapi!celexplus!prod!DocNumber&lg=en&type_doc=Directive&an_doc=2001&nu_doc=77 accessed September 2007

http://europa.eu (5): http://europa.eu/scadplus/leg/en/lvb/l27023.htm accessed September 2007

http://europa.eu (1): http://europa.eu/scadplus/leg/en/lvb/l28072.htm accessed May 2007

http://europa.eu (3): http://europa.eu/scadplus/leg/en/lvb/l21197.htm accessed May 2007

http://europa.eu (4): http://europa.eu/scadplus/leg/en/lvb/l27014.htm accessed November 2007

http://europa.eu (6): http://europa.eu/scadplus/leg/en/lvb/l27035.htm accessed September 2007

http://europa.eu (7): http://europa.eu/scadplus/leg/en/lvb/l27065.htm accessed September 2007

http://europa.eu (8): http://europa.eu/scadplus/leg/en/lvb/l28072.htm accessed may 2007 http://ewr.cee.vt.edu (1): http://ewr.cee.vt.edu/environmental/teach/gwprimer/tce/tce.html accessed May 2006

http://greennature.com (1): http://greennature.com/article228.html accessed October 2006

http://greennature.com (1): http://greennature.com/article228.html accessed may 2007

http://gruppen.greenpeace.de (1): http://gruppen.greenpeace.de/aachen/meere-fotos-verschmutzung-braer.jpg accessed October 2007

http://hyperphysics.phy-astr.gsu.edu (1): http://hyperphysics.phy-astr.gsu.edu/Hbase/surten.html accessed May 2008.

http://i6.photobucket.com (1): http://i6.photobucket.com/albums/y250/PhotozOnline/Saint_Johns_Stack_B.jpg accessed August 2007.

http://mnes.nic.in (1): http://mnes.nic.in/annualreport/2006_2007_English/Image/Pic_15_p8.1.jpg accessed July 2006

http://news.bbc.co.uk (1): http://news.bbc.co.uk/olmedia/1420000/images/_1421290_ash300.jpg

http://oceanservice.noaa.gov/: Accessed January 2009

http://oils.gpa.unep.org (1): http://oils.gpa.unep.org/facts/combat-sea.htm accessed April 2007

http://response.restoration.noaa.gov (1): http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=325

&subtopic_id(entry_subtopic_topic)=2&topic_id(entry_subtopic_topic)=1 accessed January 2008.

http://response.restoration.noaa.gov (1): http://response.restoration.noaa.gov/oilaids/monterey/Chapter2.pdf

http://weblog.greenpeace.org (1): http://weblog.greenpeace.org/makingwaves/archives/2006/08/oil_spills.html accessed October 2007

http://whyfiles.org (1): http://whyfiles.org/168oil_spill/images/prestige_rocks.jpg accessed October 2007

http://www.adn.com (1): http://www.adn.com/evos/pgs/photo2.html accessed march 2007

http://www.adn.com (1): http://www.adn.com/evos/pgs/photo2.html accessed may 2007

http://www.amsa.gov.au (1): http://www.amsa.gov.au/Marine_Environment_Protection/National_Plan/Supporting_documents/Management_and_disposal_of_oil_spill_debris.asp accessed March 2007

http://www.axfordsabode.org.uk (1): http://www.axfordsabode.org.uk/images/torreyc9.jpg November 2007

http://www.basel.int (1): http://www.basel.int/pub/basics.html#quest Accessed October 2006.

http://www.basel.int (2): http://www.basel.int/text/con-e-rev.pdf Accessed September 2007

http://www.basel.int (3): http://www.basel.int/pub/basics.html accessed October 2006 http://www.basel.int (4): http://www.basel.int/convention/about.html accessed October 2006

http://www.bioremediation.hs.bremen.de (2): http://www.bioremediation.hs.bremen.de/Download/Kickoff/Pro%20Eco_Meeting%201_Minutes.pdf accessed June 2007

http://www.biware.hs-bremen.de (1): http://homepages.hs-bremen.de/~office-ikrw/biware/ BiWaRE Project Evaluation Report 2005. Compiled by Prof B Szeweitzke.

http://www.carbofil.com (1) http://www.carbofil.com/images/photos/ent_03.jpg accessed December 2007

http://www.ciwem.org (1): http://www.ciwem.org/policy/policies/energy_recovery_from_waste.asp accessed August 2008.

http://www.cleanupoil.com (1): http://www.cleanupoil.com/equipment.htm accessed April 2007

http://www.co.stevens.wa.us (1): http://www.co.stevens.wa.us/publicwrks/Images/Landfill.jpg accessed November 2007

http://www.commondreams.org (1): http://www.commondreams.org/headlines06/images/0227-02.jpg accessed December 2007

http://www.dec.state.ak.us (1): http://www.dec.state.ak.us/spar/perp/response/sum_fy05/041207201/images/orig/041207201_p346.jpg accessed October 2007 http://www.defra.gov.uk (2): http://www.defra.gov.uk/environment/waste/topics/hazwaste/index.htm Accessed November 2006

http://www.defra.gov.uk (3): http://www.defra.gov.uk/environment/waste/topics/landfill-dir/pdf/landfilldir.pdf, accessed May 2007

http://www.defra.gov.uk (6): http://www.defra.gov.uk/environment/ppc/envagency/pubs/pdf/wid-ukreport.pdf accessed October 2007

http://www.defra.gov.uk (1): http://www.defra.gov.uk/Environment/waste/topics/pdf/ecj-definition.pdf accessed June 2007

http://www.defra.gov.uk (4): http://www.defra.gov.uk/environment/waste/wip/newtech/pdf/mht.pdf accessed June 2007

http://www.defra.gov.uk (5): http://www.defra.gov.uk/environment/statistics/coastwaters/cwoil.htm visited March 2008

http://www.defra.gov.uk (7): http://www.defra.gov.uk/environment/climatechange/about/index.htm visited January 2008

http://www.discoverphuquoc.com (1): http://www.discoverphuquoc.com/images/Sao%20Beach.jpg accessed November 2007

http://www.dti.gov.uk (1) http://www.dti.gov.uk/files/file32546.pdf accessed December 2007 http://www.dti.gov.uk (1): http://www.dti.gov.uk/files/file32546.pdf visited Jan 2007

http://www.energie.beratung.at accessed august 2007

http://www.epa.gov (1): http://www.epa.gov/oilspill/pdfs/chap2.pdf accessed April 2007

http://www.epa.gov (2): http://www.epa.gov/oilspill/sorbents.htm accessed April 2007

http://www.epa.gov (3): http://www.epa.gov/earth1r6/6en/xp/lppapp6a.pdf accessed March 2007

http://www.epa.gov (4):

http://www.epa.gov/emergencies/content/learning/oilprops.htm accessed June 2008

http://www.evostc.state.ak.us (1): http://www.evostc.state.ak.us/Gallery/Images/spill/downloadable%20.jpgs/EVOSWEB_022_slick.jpg accessed October 2007

http://www.faolex.fao.org (1):

http://www.faolex.fao.org/docs/texts/aus6388.doc accessed December 2007

http://www.geocities.com (1): http://www.geocities.com/CapeCanaveral/Lab/2094/bioremed.html visited May 2006

http://www.imo.org (1): http://www.imo.org/Conventions/contents.asp?doc_id=678&topic_id=258#1 accessed June 2007.

http://www.imo.org (2): http://www.imo.org/Legal/mainframe.asp?topic_id=358 visited June 2007 http://www.imo.org (3): http://www.imo.org/Conventions/contents.asp?doc_id=678&topic_id=258 accessed December 2007

http://www.imo.org (4): http://www.imo.org/Conventions/contents.asp?doc_id=678&topic_id=258#2 accessed October 08

http://www.imo.org/ http://www.imo.org/ (5) accessed September 2008

http://www.itopf.com (1): http://www.itopf.com/information%2Dservices/data%2Dand%2Dstatistics/case-histories/index.html#exxon-valdez accessed March 2008

http://www.itopf.com (11): http://www.itopf.com/information-services/data-and-statistics/case-histories/#sea-empress accessed September 2007

http://www.itopf.com (10): http://www.itopf.com/information-services/publications/ accessed November 2008.

http://www.itopf.com (2) http://www.itopf.com/casehistories.html accessed March 2007.

http://www.itopf.com (3): http://www.itopf.com/casehistories.html#braer accessed October 2006

http://www.itopf.com (4): http://www.itopf.com/casehistories.html#exxonvaldez accessed August 2006

http://www.itopf.com (5): http://www.itopf.com/dispersa.html accessed April 2007

http://www.itopf.com (6): http://www.itopf.com/fate.html accessed June 2007 http://www.itopf.com (7): http://www.itopf.com/information-services/data-and-statistics/case-histories/#prestige accessed June 2007

http://www.itopf.com (8): http://www.itopf.com/information-services/data-and-statistics/statistics/ accessed March 2008

http://www.itopf.com (9): http://www.itopf.com/marine-spills/fate/weathering-process/documents/tip2.pdf accessed May 2007

http://www.jadedthea.com (1): http://www.jadedthea.com/images/OilSpillBeach.jpg accessed October 2007

http://www.lib.utexas.edu (1): http://www.lib.utexas.edu/maps/middle_east_and_asia/vietnam_rel01.jpg

http://www.livingmemory.org.uk (1): http://www.livingmemory.org.uk/photoarchive/data/browse.php?detail=1&donor=0121&photz=009 visited October 2007

http://www.mcga.gov.uk (1): http://www.mcga.gov.uk/c4mca/chapter_12.pdf accessed June 2007

http://www.oil-spill-web.com (1): http://www.oil-spill-web.com/oilspill/handbook2.htm accessed April 2007

http://www.panda.org (1):

http://www.panda.org/downloads/marine/finalprestige.pdf visited October 2006

http://www.people.cornell.edu (1): http://www.people.cornell.edu/pages/mg254/mangrove.jpg accessed November 2007 http://www.pollutionissues.com (1): http://www.pollutionissues.com/images/paz_01_img0069.jpg accessed Sept 07

http://www.protekt.hs-bremen.de (1): http://www.protekt.hs-bremen.de/Download/Outcome/04%20FG%20Handbook%20EN.pdf

http://www.protekt.hs-bremen.de (2): http://www.protekt.hs-bremen.de/Download/Update/05%20WS%20PT%20EN.pdf accessed September 2007

http://www.radlader.bau.portal.com. Accessed June 2007.

http://www.reisenett.no (1): http://www.reisenett.no/map_collection/middle_east_and_asia/SoutheastAsia.jpg accessed November 2007

http://www.reliefweb.int (1): http://www.reliefweb.int/ochaunep/edr/Pakistan.pdf accessed October 2006

http://www.riverships.ru (1): http://www.riverships.ru/photos/volgoneft_248_0.jpg accessed November 2007

http://www.saburchill.com (1): http://www.saburchill.com/ans02/images/200807002.jpg accessed March 2008

http://www.seacology.org (1): http://www.seacology.org/news/images/JG_dispatch_images/Fishing-Boats.jpg accessed November 2007

http://www.spillcon.com (1): http://www.spillcon.com/2004/papers/BUDD.pdf accessed September 2007 http://www.tu-dresden.de (1): http://www.tudresden.de/wwvwlat/sacodi/documents/Waste%20Handling%20in%20Industries.pdf accessed July 2007

http://www.ukmarinesac.org.uk (1): http://www.ukmarinesac.org.uk/communities/intertidal-reef/ir5_4.htm visited June 2007

http://www.unep.org (1): http://www.unep.org/Documents.Multilingual/Default.asp?DocumentID=52&ArticleID=4415&l=en accessed November 2007

http://www.unesco.org (1): http://www.unesco.org/education/information/nfsunesco/doc/isced_1997.htm accessed June 2007

http://www.unis.no (1): http://www.unis.no/research/technology/images/oil-spill.jpg accessed November 2007

http://www.valdezscience.com (1): http://www.valdezscience.com/dspArticle.cfm?catID=14&artID=1168&artSecID=1165 visited 10th May 2006

http://www.visitpembrokeshire.com (1): http://www.visitpembrokeshire.com/industry/library.asp?ID=3 accessed august 2007

http://www.wcb.ca.gov (1): http://www.wcb.ca.gov/PowerPoint/February%2015,%202007_files/slide0426_image126.jpg accessed January 2008

Hughes B, Duston K Ward C 2002. Engineered bioremediation. Department of Civil and Environmental Engineering, Rice University Houston Texas Published Electronically by the Ground-Water Remediation Analysis Centre.

I:

Ibrahim H, Ilinca A, Perron J 2008. Energy storage systems - Characteristics and comparisons. Journal of Renewable and Sustainable Energy Reviews. 12 (5), pp1221- 1250.

IPIECA Report Series Volume 10. Choosing response options to minimise damage – Net Environmental Benefit Analysis. London: IPIECA

IPIECA Report Series Volume 12. Guidelines for oil spill waste minimisation and management. London: IPIECA.

IPIECA, ITOPF 2002. Industry as a partner for sustainable development: Oil and Gas Technical report. London: IPIECA

ITOPF 1999. VOLGONEFT 248 Oil Pollution, Sea of Mamarra, Turkey 29 December 1999. Oil pollution response operation report London: ITOPF.

J:

Janjua N 2006. Acute health effects of the Tasman Spirit oil spill on residents of Karachi, Pakistan. Journal of BMC Public Health. 6 (84) pp1-11.

Jansen J 2003. Policy Support for Renewable Energy in the European Union, A review of the regulatory framework and suggestions for adjustment. Report commissioned for'Renewable Energy Trends' under ECN project number 7.7448.

Jones W 1998. Practical Applications of Marine Bioremediation. Journal of Current Opinion in Biotechnology. 9, pp300-304.

Jordan A 1998. The implementation of EU environmental policy: a policy problem without a political solution. Journal of Environment and Planning: Government and Policy. Vol 17 pp69-90.

Juanes JA, Puente A, Revilla JA, Alvarez C, Garcia A, Medina R, Castanedo S, Morante L, Gonzalez S, Garcia-Castrillo C 2007. The *Prestige* Oil Spill in Cantabria (Bay of Biscay). Part II. Environmental Assessment and Monitoring of Coastal Ecosystems. Journal of Coastal Research. 23 (4), pp 978–992.

K:

Karam J, Nicell J 1996. Potential applications of enzymes in waste treatment. Journal of Chemical Biotechnology. 69, pp141-153.

Keller BD, Jackson JBC 1993. Long-term Assessment of the Oil Spill at Bahia Las Minas, Panama, US Department of the Interior, Mineral Management Service, Gulf of Mexico OCS Region, New Orleans, LA, Vol. Synthesis Report, Vol I: Executive Summary OCS Study MMS 93-0047 pp.129.

Keranbrun L, Parker H 1998. When should clean up operations be brought to a close – how clean is clean? In Proceedings: '20 years after the Amoco Cadiz symposium' 15-17 October 1998 Brest, France.

Khodijah Chaerun S, Tazaki K, Asada R, Kogure K 2004. Bioremediation of coastal areas 5 years after the *Nakhodka* oil spill in the Sea of Japan: isolation and characterization of hydrocarbon-degrading bacteria. Environment International Journal. 30 (7), pp911-922.

Kim I 2002. Ten years after the enactment of the Oil Pollution Act 1990: a success or a failure? Journal of Marine Policy. 26, pp197-207.

King AM, Burgess SC, Ijomah W, McMahon CA 2005. Reducing waste: repair, recondition, remanufacture or recycle? Journal of Sustainable Development. 14 (4), pp257 – 267.

Kirby MF, Mathiessen P, Rycroft RJ 1996. Procedures for the approval of oil spill treatment products. MAFF Technical Report 102. London: MAFF.

Kirkland LH, Thomson D 1999. Challenges in designing, implementing and operating an environmental management system. Journal of Business Strategy and the Environment. 8, pp128-143.

Kite-Powell H, Hoagland P, Jin D 1998. Policy, law, and public opposition: the prospects for abyssal ocean waste disposal in the United States. Journal of Marine Systems. 14, pp377–396.

Kogevinas M 2001. Human effects of dioxins: cancer, reproductive and endocrine system effects. Journal of Human Reproduction. 7 (3), pp331-339.

Korda A, Santas P, Tenente A, Santas R. 1997. Petroleum hydrocarbon bioremediation: sampling and analytical techniques, in situ treatments and commercial microorganisms currently used. Journal of Applied Microbiology and Biotechnology. 48 (6), pp677-86.

Koumouris GA, Petreniti V, Skanavis C 2005. Public Participation Mechanisms in Environmental Disasters. Journal of Environmental Management. 35 (6), pp821-837.

Kozai K 2003. Satellite derived sea surface height and sea surface wind data fusion for spilled oil tracking. Journal of Advances in Space Research. 32 (11), pp2287-2293.

Kumar S 2000. Technology options for municipal solid waste-to-energy project. Journal of Information Monitoring on Environmental Science. 5 (1), pp1-11.

Kurniawan T, Chan G, Lo W, Babel S 2006. Physico-chemical treatment techniques for wastewater laden with heavy metals. Journal of Chemical Engineering. 118, pp83-98.

Kwan KK, Dutka BJ 1992. Evaluation of toxi-chromotest direct sediment toxicity testing procedure and microtox solid-phase testing procedure. Journal of Environmental Contamination and Toxicology. 49 (5), pp656-662.

L:

Law RJ, Kelly C 2004. The impact of the *Sea Empress* Oil Spill. Journal of Aquatic. Living Resources. 17, pp389–394.

Lawrence A 1998. Energy from municipal solid waste: a comparison with coal combustion technology. Journal of Progressive Energy Combustion Science. 24, pp545-564.

Le Hir M, Hily C 2002. First observations in a high rocky-shore community after the *Erika* oil spill. Marine Pollution Bulletin. 44 (11), pp1243-1252.

Lee JH, Mitchell RJ, Kima BC, Cullen DC, Gu MB 2005. A cell array biosensor for environmental toxicity analysis. Journal of Biosensors and Bioelectronics. 21 (3), pp500-507.

Lee K 1999. *In-situ* bioremediation of oiled shoreline environments. In proceedings: Opportunities for Environmental Applications of Marine Biotechnology: Proceedings of the October 5-6, Washington DC.

Lee K, Doe KG, Lee LEJ, Suidan MT, Venosa AD 2001. Remediation of an oil-contaminated experimental freshwater wetland: Habitat recovery and toxicity reduction. In proceedings: International Oil Spill Conference 2001. American Petroleum Institute, Washington, DC. pp323-328.

Lee K, Levy EM 1989. Enhancement of the natural biodegradation of condensate and crude oil on beaches of Atlantic Canada. In Proceedings: 1989 Oil Spill Conference (Prevention, Behaviour, Control, Cleanup). American Petroleum Institute, Washington, D.C. pp479–486.

Lee K, Merlin F 1999. Bioremediation of oil on shoreline environments: Development of Guidelines and Techniques. Journal of Pure Applied Chemistry. 71 (1), pp161-171.

Lepo JE, Cripe CR, Kavanaugh JL, Zhang S, Norton GP 2003. The Effect of amount of crude oil on extent of its biodegradation in open water and sandy beach- laboratory simulations. Journal of Environmental Technology. 24 (10), pp1291-1302.

Lessard RR, DeMarco G, 2000. The Significance of Oil Spill Dispersants. Spill Science and Technology Bulletin. 6 (1), pp59-68.

Leveille TP 1991. The *Mega Borg* fire and oil spill: a case study, In Proceedings: 1991 International Oil Spill Conference. American Petroleum Institute, Washington, D.C. pp 273–278.

Levings S, Garrity S, Burns KA 1994. The Galeta Oil Spill III. Chronic reoiling and long term toxicity of hydrocarbon residues in the mangrove fringe community. Journal of Estuarine Coastal and Shelf Science. 38, pp365–395.

Li X, Zhao Q, Hao X 1999. Ammonium removal from landfill leachate by chemical precipitation. Journal of Waste Management. 19, pp409-415.

Li Y, Liu H, Zhang O. High-pressure compaction of municipal solid waste to form densified fuel. Journal of Fuel Processing Technology. 74, pp71-81.

Lin SH, Lan WJ 1998. Waste oil/water emulsion treatment by membrane processes. Journal of Hazardous Materials. 59 (2-3), pp189-199.

Longden D, Brammer J, Bastin L, Cooper N 2007. Distributed or centralised energy-from-waste policy? Implications of technology and scale at municipal level. Journal of Energy Policy. 35 (4), pp2622-2634.

Lunel T, Swannell R, Rusin J, Wood P, Bailey N, Halliwell C, Davies L, Sommerville M, Dobie A, Mitchell D, McDonagh M, Lee K 1995. Monitoring the Effectiveness of Response Operations During the *Sea Empress* Incident: a Key Component of the Successful Counter-pollution Response. Spill Science and Technology Bulletin. 2 (2/3), pp 99-112.

Lunel, T. 1998. Sea Empress Spill: Dispersant Operations, Effectiveness and Effectiveness Monitoring In: Trudel, B.K. (ed.). Proceedings of the Conference, "Dispersant Use in Alaska: A Technical Update", Anchorage, Alaska, March 18-19, 1998, Prince William Sound Oil Spill Recovery Institute, Cordova, Alaska.

M:

MAFF 2000. Scientific, Technical and Operational Advice Note – Operational guidelines for the application of bioremediation agents. London: MAFF.

Maila MP, Cloete TE 2004 Bioremediation of petroleum hydrocarbons through landfarming: are simplicity and cost effectiveness the only advantages? Journal of Reviews in Environmental Science and Biotechnology. 3 (4), pp349-360.

Maki H, Utsumi M, Koshikawa H, Hiwatari T, Kohata T, Uchiyama H, Suzuki M, Noguchi T, Yamasaki T, Furuki M, Watanabe M 2003. Intrinsic biodegradation of heavy fuel from *Nakhodka* and the effect of exogenous fertilisation at a coastal area of the Sea of Japan. Journal of Water, Air and Soil pollution. 145 (1-4), pp123-138.

Malkow T 2004. Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. Journal of Waste Management. 24, pp53-79.

Manser AGR, Keeling AA. Practical Handbook of Processing and Recycling Municipal Waste. CRC Press, Boca Raton, 1996.

Marine Pollution Control Unit 1996. The Sea Empress incident. In: A report by the Marine Pollution Control Unit. The Coastguard Agency: Southampton, UK.

Mearns AJ 1997. Cleaning Oiled Shores: Putting Bioremediation to the Test. Spill Science and Technology Bulletin. 4 (4), pp209-217.

Merski A 2000. Cooperative commercialisation: finding alternate oil spill response tools. Spill Science and Technology Bulletin. 6 (5/6), pp289-293.

Metz B, Davidson O, Swart R, Pan J, 2001. International Panel on Climate Change, Third Assessment Report, Working Group III, Climate Change 2001: Mitigation, Cambridge University Press, Cambridge, UK.

Mills MA, Bonner JS, McDonald TJ, Page CA, Autenrieth RL 2003. Intrinsic bioremediation of a petroleum-impacted wetland. Marine Pollution Bulletin. 46 (7), pp887-899.

Mills MA, Bonner JS, Page CA, Autenrieth RL. Evaluation of bioremediation strategies of a controlled oil release in a wetland. Marine Pollution Bulletin. 49, pp425-435.

Mohan R, Spiby J, Leonardi GS, Robins A, Jefferis S 2006. Sustainable Waste Management in the UK: the public health role. Journal of Public Health. 120(10), pp 908-914.

Moller TH 2002 Recovery of sunken oil from the Sea of Mamarra. London: ITOPF.

Moore TG 2008. Global warming: The good, the bad, the ugly and the efficient. European Molecular Biology Organisation Report. 8, pp41–45.

Moretti L 2005 In-situ bioremediation of DNAPL source zones. Washington:USEPA.

Mullin J, Champ A 2003. Introduction/overview of in-situ burning of oil spills. Spill Science and Technology Bulletin. 8 (4), pp323-330.

Mullin J, Champ M 2003. Introduction/Overview to In Situ Burning of Oil Spills. Spill Science & Technology Bulletin. 8 (4), pp323–330.

Murphy JD, McKeogh E, 2006. The benefits of integrated treatment of wastes for the production of energy. Journal of Energy. 31, pp294-310.

N:

Nakamura, S, Kondo Y 2002. Input-output analysis of waste management. Journal of Industrial Ecology. 6 (1), pp 39–64.

Negro-Garcia MC, Villasante CS, Penela AC 2007. Compensating system for damages caused by oil pollution: Background for the *Prestige* assessment damage in Galicia, Spain. Journal of Ocean and Coastal Management. 50, pp57-66.

NERC 1999. A joint research council review of bioremediation research in the United Kingdom. Published by: NERC, BBSRC, EPSRC.

Newton R, Doonga N 2007. Corporate e-learning: Justification for implementation and evaluation of benefits. A study examining the views of training managers and training providers Journal of Education for Information. 25 (2), pp111-130.

Nikitik C, Robinson A 2003. Patterns in Benthic Populations in the Milford Haven Waterway following the Sea Empress Oil Spill with Special Reference to Amphipods. Marine Pollution Bulletin. 46, pp1125-1141.

Nikolopoulou M, Pasadakis N, Kalogerakis N 2007. Enhanced bioremediation of crude oil utilizing lipophilic fertilizers. Journal of Desalination. 211 (1-3), pp286-295.

Nordvik A 1995. The technology windows of opportunity for marine oil spill response as related to oil weathering operations. Spill Science and Technology Bulletin. 2 (1), pp17-46.

Nordvik A 1999. Time window-of-opportunity strategies for oil spill planning and response. Journal of Pure Applied Chemistry. 71 (1), pp5-16.

Nordvik A, Champ M, Bitting K 2003. Estimating time windows for burning oil at sea: processes and factors. Spill Science and Technology Bulletin. 8 (4), pp347-359.

Nordvik A, Simmons JL, Bitting KR, Lewis A, Strøm-Kristiansen T 1996. Oil and water separation in marine oil spill clean-up operations. Spill Science & Technology Bulletin. 3 (3), pp107-122.

O:

O'Sullivan AJ, Richardson AL. 1967. The *Torrey Canyon* disaster and intertidal marine life. Journal of Nature. 214, pp448-451.

Odokuma LO, Dickson AA 2003. Bioremediation of a Crude Oil Polluted Tropical Mangrove Environment. Journal of Applied Sciences & Environmental Management. 7 (2), pp23-29.

Official Journal of the European Communities L 247/1(17.9.2001). Commission recommendation on guidance for the implementation of Regulation (EC) No 761/2001 of the European Parliament and of the Council allowing voluntary participation by organisations in a Community eco-management and audit scheme (EMAS).

Okeke CU, Armour A 2000. Post-landfill siting perceptions of nearby residents: a case study of Halton landfill. Journal of Applied Geography. 20 (2), pp137-154.

Oliveiri R, Robertielllo A, Degen, L 1978. Enhancement of microbial degradation of oil pollutants using lipophilic fertilizers. Marine Pollution Bulletin. 9, pp217–220.

O'Neill BC, Gruebler A, Nakicenovic N, Obersteiner M, Riahi K, Schrattenholzer L, Toth FL 2003. Planning for future energy resources. Journal of Science. 25, pp581-582.

Otay EN, Yenigün O 2000. Volgoneft-248 oil spill in the Marmara Sea. In: 2nd International Conference on Oil Spills in the Mediterranean and Black Sea Regions. October 31st-November 3rd Istanbul, Turkey, pp13–23.

Otoma S, Mori Y, Terazono A, Aso T, Sameshima R 1997. Estimation of energy recovery and reduction of CO2 emissions in municipal solid waste generation. Journal of Resources, Conservation and Recycling. 20, pp95-117.

Oudot J 1984. Rates of microbial degradation of petroleum components as determined by computerised capillary gas chromatography and computerised mass spectrometry. Journal of Marine Environmental Research. 13 (4), pp 277-302.

oxygenase. (n.d.). *The American Heritage® Stedman's Medical Dictionary*. Retrieved March 27, 2008, from Dictionary.com website: http://dictionary.reference.com/browse/oxygenase

P:

P Glen 1995. A European lawyers view of the Governments response to the Donaldson Report. Journal of Marine Policy. 19 (6), pp453-467.

Paine RT, Ruesink JL, Sun A, Soulanille EL, Wonham MJ, Harley DG, Brumbaugh DR, Secord DL 1996. Trouble on Oiled Waters: Lessons from the Exxon Valdez Oil Spill. Annual Review of Ecology and Systematics. 27, pp197–235.

Palfy P, Vircikova E, Molnar L 1999. Processing of arsenic waste by precipitation and solidification. Journal of Waste Management. 19 (1), pp55-59.

Palinkas LA, Russell J, Downs MA, Petterson JS 1992. Ethnic differences in stress, coping, and depressive symptoms after the *Exxon Valdez* oil spill. Journal of Nervous and Mental Disease. 180 (5), pp287-295.

PCNPA 2004. The State of the Park Report. Published by the Pembrokeshire Coast National Park Authority. Pembroke Dock: PCNPA.

pedagogy. (n.d.). *Dictionary.com Unabridged (v 1.1).* Accessed February 2008, from Dictionary.com website: http://dictionary.reference.com/browse/pedagogy

pers.com (1). Personal communication with Michael Golde, April 6 2006 Bremen, Germany.

Peterson C.H., Rice S.D., Short J.W., Esler D., Bodkin J.L., Ballachey B.E., Irons D.B., 2003, Long-term ecosystem response to the "Exxon Valdez" oil spill. Science 302, 2082-2086

Pettorelli N, Vik JO, Mysterud A, Gaillard J-M, Tucker CJ, Stenseth NC 2005. Using the satellite-derived NDVI to assess ecological responses to environmental change Journal of Trends in Ecology & Evolution. 20 (9), pp503-510.

Pham TH, Rabaey K, Aelterman P, Clauwaert P, De Schamphelaire L, Boon L, Verstraete W 2006. Microbial Fuel Cells in Relation to Conventional Anaerobic Digestion. Journal of Technology Engineering in Life Sciences. 6 (3), pp***285 – 292.***

Pimentel D, Herz M, Glickstein M, Zimmerman M, Allen R, Becker K, Evans J, Hussain B, Sarsfeld R, Grosfeld A, Seidel T 2002. Renewable Energy: Current and Potential Issues. Journal of BioScience. 52 (12), pp1111-1120.

Pimentel, D, Patzek, T 2005. Ethanol production using corn, switchgrass and wood: biodiesel production using soybean and sunflower. Journal of Natural Resource Research. 14 (1), pp65–76.

Pit, L, van Kooten C, Love M, Djilal N, 2005. Utility-scale wind power: impact of increased penetration. Proceedings of the International Green Energy Conference, 12–16 June 2005, Waterloo, Ont, Canada, Institute for Integrated Energy Systems, University of Victoria, Victoria, B.C.

Porteous A 2001. Energy from waste incineration — a state of the art emissions review with an emphasis on public acceptability. Journal of Applied Energy. 70, pp157–167.

Porteous A 2005. Why energy from waste incineration is an essential component of environmentally responsible waste management. Journal of Waste Management. 25, pp451-459.

Poznyak T 2007. Decomposition of toxic pollutants in landfill leachate by ozone after coagulation treatment. Journal of Hazardous Materials, doi:10.1016/j.jhazmat.2007.07.098

Prince R 2003. Bioremediation of stranded oil on an Arctic Shoreline. Spill Science and Technology Bulletin. 8 (3), pp303-312.

Prince R, Clark JR, Lee K 2002. Bioremediation effectiveness: removing hydrocarbons while minimising environmental impact. In proceedings: 9th Annual International Petroleum Environmental Conference, Albuquerque, New Mexico, October 22-25.

Pritchard PH, Mueller JG, Rogers JC, Kremer RV, Glaser JA 1992. Oil spill bioremediation: experiences, lessons and results from the Exxon Valdez oil spill in Alaska. Journal of Biodegradation. 3 (2-3), pp315-335.

PROTEKT Handbook 2007. Guidelines for Handling and Treatment of Oil Contaminated Water in Thai Industries and Trades. Brussels: EU and Asia-Invest Programme. Ref: Europeaid/122452/C/G.

R:

Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick, Jr., WJ, Hallett JP, Leak DJ, Liotta CL, Mielenz JR, Murphy R, Templer R, Tschaplinski T 2006. The Path Forward for Biofuels and Biomaterials Science. Journal of Science. 311 (5760), pp484 – 489.

Rainbow PS, Phillips DJH 1993. Cosmopolitan biomonitors of trace metals, Marine Pollution Bulletin. 26, pp593–601.

Rainbow PS, White SL, 1989. Comparative strategies of heavy metal accumulation by crustaceans: zinc, copper and cadmium in a decapod, an amphipod and a barnacle, Journal of Hydrobiologia. 174, pp245–262.

Recorbet G, Steinberg C, Faurie G 1992. Survival in soil of genetically engineered *Escherichia coli* as related to inoculum density, predation and competition. Journal of Microbiology and Ecology. 101, pp251–260.

Ron E, Rosenberg E 2002. Biosurfactants and oil bioremediation. Journal of Current Opinion in Biotechnology. 13, pp249-252.

S:

SACODI DLM Text 2007. http://www.tu-dresden.de/wwvwlat/sacodi/literature.htm Accessed May 2008

SACODI Handbook 2007. Guidelines for Hazardous Waste: Recommendations for environmental politics and administration, Introduction to collection and disposal systems under particular consideration of framework conditions in India and Vietnam. Brussels:

EU and Asia-Invest Programme. http://www.tu-dresden.de/wwvwlat/sacodi/documents/Guidelines_part_I.pdf. Ref: ASIE/2005/102517.

Sadek S, Abou-Ibrahim A, Manasseh C, El-Fadel M 2001. Stability of solid waste sea fills: shear strength determination and sensitivity analysis. International Journal of Environmental Studies. 58, pp217-234.

Salameh MG 2003. Can renewable and unconventional energy sources bridge the global energy gap in the 21st century? Journal of Applied Energy. 75, pp33–42.

Salbu B, Nikitin AI, Strand P, Christensen GC, Chumichev VB, Lind B, Fjelldal H, Bergan TDS, Rudjord AL, Sickel M, Valetova NK, Føyn L 1997. Radioactive contamination from dumped nuclear waste in the Kara Sea — results from the joint Russian-Norwegian expeditions in 1992–1994. Journal of Science of The Total Environment. 202 (1-3), pp185-198.

Sang-Jin K, Dong Hyuk C, Doo S, Young-Sook O 2005. Evaluation of bioremediation effectiveness on crude oil-contaminated sand. Journal of Chemosphere. 59, pp845–852.

Santas R, Santas P 2000. Effects of wave action on the bioremediation of crude oil saturated hydrocarbons. Marine Pollution Bulletin. 40 (5), pp434-439.

Sasikumar C, Papinazath T 2003. Environmental Management: Bioremediation of polluted environment. In proceedings: Third International Conference on Environment and Health India, Chennai, India, 15-17 December.

Scott G 1999. Bioremediation and advanced absorption: new technology in spill response. In proceedings: Canadian National Marine Conference, Halifax (Mari-Tech)

Shailubhai K 1984. Treatment of petroleum industry oil sludge in soil. Journal of Applied Microbiology and Biotechnology. 19 (6), pp437-438.

Shent H, Pugh RJ, Forssberg E 1999. A review of plastics waste recycling and the flotation of plastics. Journal of Resources, Conservation and Recycling. 25 (2), pp85-109.

Shiga H, Shinda K, Hagiwara K, Tsutsumi A, Sakurai M, Yoshida K, Bilgen E 1998. Large-scale hydrogen production from biogas. International Journal of Hydrogen Energy. 23 (8), pp631-640.

Shuhong Y, Leichang H, Olive LY, Ding M, Hu Y, Ding D 2006. Investigation on bioremediation of oil-polluted wetland at Liaodong Bay in Northeast China. Journal of Applied Microbiological Biotechnology. 71, pp543-548.

Slupek S, Buczek A, Kurcz L, Sekula R 2000. Energy Recovery from Liquid Wastes of a Sewage-Treatment Plant. Journal of Energy Sources. 22 (7), pp 641-648.

Sonak S, Sonak M, Giriyan A. 2008. Shipping hazardous waste: Implications for economically developing countries. Journal of International Environmental Agreements: Politics, Law and Economics. 8 (2), pp143-159.

Southward AJ Southward EC 1978. Recolonization of rocky shores in Cornwall after use of toxic dispersants to clean up the Torrey Canyon spill. Presented at: Symposium on Recovery Potential of Oiled Marine Northern Environments; Halifax, Canada. Journal of the Fisheries Research Board Canada. 35, pp682-706.

Spangenberg J 2007. Integrated scenarios for assessing biodiversity risks. Journal of Sustainable Development. 15 (6), pp343 – 356.

Sriram N, Shahidehpour M 2005. Renewable biomass energy Power Engineering Society General Meeting, 2005. IEEE. 1, pp612- 617.

Stephens Jr JS, Hose JE, Love MS 1988. Fish assemblages as indicators of environmental change in nearshore environments. In: D.F. Soule and G.S. Kleppel, (Eds), Marine Organisms as Indicators. Springer: London, pp91–105.

Strange EM, Lipton J, Beltman D, Snyder BD 2002. Scientific and Societal Considerations in Selecting Assessment Endpoints for Environmental Decision Making. The Scientific World Journal. 2 (1), pp12-20.

Stronkhorst J 2003. Environmental impact and recovery at two dumping sites for dredged material in the North Sea. Journal of Environmental Pollution. 124, pp17-31.

Suarez B 2005. Acute health problems among subjects involved in the clean up operation following the *Prestige* oil spill in Asturias and Cantabria (Spain). Journal of Environmental Research. 99, pp413-424.

Swannell R 1995. The effect of bioremediation agents on oil biodegradation in medium fine sand. In proceedings: In Situ and On-site Bioreclamation, Battelle, April 24-27, San Diego.

Swannell R, Lee K, Mc Donaugh M 1996. Field Evaluations of Marine Oil Spill Bioremediation. Journal of Microbiological Reviews. 60 (2), pp342-365.

T:

Tagger S, Bianchi A, Juillard M, LePetit J, Roux B 1983. Effect of microbial seeding of crude oil in sea water in a model system. Journal of Marine Biology. 78, pp13-20.

Tally WK, Jin D, Kite-Powell H, 2004. Post OPA-90 vessel oil spill differentials: transfers versus vessel accidents. Journal of Maritime Policy and Management. 31 (3), pp225-240.

Texas General Land Office 1990. Mega Borg oil spill off the Texas coast: an open water bioremediation test. Texas General Land Office: Texas Water Commission, Austin.

The Waste Strategy for England 2007. London: Crown Copywright. P13

Thiel H 2001 Use and protection of the deep sea - an introduction. Journal of Deep Sea Research Part II: Topical Studies in Oceanography 48 (17-18), pp3427-3431.

Thomson I, Van der Gast C, Ciric L, Singer A 2005. Bioaugmentation for bioremediation: the challenge of strain selection. Journal of Environmental Microbiology. 7 (7), pp909-915.

Thuiller W, Albert C, Araújo M, Berry P, Cabeza M, Guisan A, Hickler T, Midgley G, Paterson J, Schurr M, Sykes M, Zimmermann N 2008. Predicting global change impacts on plant species' distributions: Future challenges. Journal of Perspectives in Plant Ecology, Evolution and Systematics. 9 (3-4), pp137-152.

Tjernström E, Tietenberg T 2008. Do differences in attitudes explain differences in national climate change policies? Journal of Ecological Economics. 65 (2), pp315-324.

Trustee Council, *Exxon Valdez* Oil Spill. 1995. Fiscal Year 1996 Work Plan. *Exxon Valdez* Oil Spill Trustee Council: Anchorage Alaska.

Tsutsumi H, Hirota Y, Hirashima A 2000. Bioremediation on the shore after an oil spill from the *Nakhodka* in the Sea of Japan. Toxicity of a bioremediation agent with microbiological cultures in aquatic organisms. Marine Pollution Bulletin. 40 (4), pp315-319.

Tsutsumi H, Kono M, Takai K, Manabe T, Haraguchi, M, Oppenheimer C 2000. Bioremediation on the shore after an oil spill from the *Nakhodka* in the Sea of Japan:

Field tests of a bioremediation agent with microbiological cultures for the treatment of an oil spill.. Marine Pollution Bulletin. 40 (4), pp320-324.

Tyler PA 2003. Disposal in the deep sea: analogue of nature or *faux ami*? Journal of Environmental Conservation. 30 (1) pp26-39.

U:

U.S. Congress, Office of Technology Assessment, Bioremediation for Marine Oil Spills—Background Paper 1991, OTA-BP-O-70 Washington, DC: U.S. Government Printing Office.

Umbach F 2004. Global Energy Supply and Geopolitical Challenges. In: Francois Godement/Francoise Nicolas/Taizo Yakushiji (eds.), Asia and Europe. Cooperating for Energy Security. A Council for Asia-Europe Cooperation (CAEC)-Task Force Report, Paris: IFRI, S. pp137-168.

Umberto D, Di Maria F, Leonardi D, Proietti S 2003. Sanitary landfill energetic potential analysis: a real case study. Journal of Energy Conservation and Management. 44, pp1969-1981.

UNEP 2002. Draft Strategic Plan for the Implementation of the Basel Convention (2000-2010) Proceedings of the Conference of the parties to the Basel Convention on Control of Trans-Boundary Movement of Hazardous wastes and their Disposal. Sixth meeting Geneva, 9-13 December.

Unnikrishnan S, Hegde DS 2007. Environmental training and cleaner production in Indian industry—A micro-level study. Journal of Resources, Conservation and Recycling. 50(4), pp427-441.

Upreti B, van der Horst D 2004. National renewable energy policy and local opposition in the UK: the failed development of a biomass electricity plant. Journal of Biomass and Bioenergy. 26, pp61 – 69.

US EPA 2007. Emergency Response Program: Oil spill prevention and preparedness report – types of crude oils. Accessed off USEPA website (www.epa.gov) August 2007.

V:

Valentine D 2002. Distance Learning: Promises, Problems and Possibilities. Online Journal of Distance Learning Administration. 5 (3).

Vastag G, Kerekesb S, Rondinelli D 1996. Evaluation of corporate environmental management approaches: A framework and application. International Journal of Production Economics. 43, pp193-211.

Venosa A 2001. NRT Factsheet: Bioremediation in Oil Spill Response. Prepared by US Environmental Protection Agency National Response Team. Washington: USEPA.

Venosa A, Zhy X 2003. Biodegradation of crude oil contaminating marine shorelines and freshwater wetlands. Spill Science and Technology Bulletin. 8 (2), pp163-178.

Ventikos NP, Vergetis E, Psaraftis HN, Triantafyllou G 2004. A high-level synthesis of oil spill response equipment and countermeasures. Journal of Hazardous Materials. 107 (1-2), pp51-58.

Vidali M 2001. Bioremediation – An Overview. Journal of Pure Applied Chemistry. 73 (7), pp1163-1172.

viscosity. (n.d.). The American Heritage® Science Dictionary. Retrieved August 22, 2007, from Dictionary.com website: http://dictionary.reference.com/browse/viscosity

Visvanathan C 1996. Hazardous waste disposal. Journal of Resources Conservation and Recycling. 16, pp201-212.

Voigt D, Brantley S 1996. Chemical fixation of arsenic in contaminated soils. Journal of Applied Geochemistry. 11, pp633-643.

Vrijheid M 2000. Health Effects of Residence near Hazardous Waste Landfill Sites: A Review of Epidemiologic Literature. Journal of Environmental Health Perspectives 108 (1), pp101-112.

W:

Walendziewski J 2002. Engine fuel derived from waste plastics by thermal treatment Journal of Fuel Vol 81, No 4, pp 473-481

Walker AH, Kucklick AH, Michel J 1999. Effectiveness and environmental considerations for non dispersant chemical countermeasures. Journal of Pure Applied Chemistry. 71 (1), pp67-81.

Warren LM, Wallace MW 1994. The Donaldson enquiry and its relevance to particularly sensitive sea areas. The International Journal of Marine and Coastal Law. 9 (4), pp523-534.

Waste Strategy 2000 for England and Wales Part 2. London: Crown Copyright pp7-8

Waste Strategy 2000 for England and Wales Part 2. London: Crown Copyright p32

Waste Strategy 2000 for England and Wales Part 2. London: Crown Copyright p79

Waste Strategy for England 2007: Executive Summary. London: Crown Copyright p7.

Waste Strategy for England 2007: Executive Summary. London: Crown Copyright p1.

Waste Strategy for England and Wales 2000. London: Crown Copyright.

Wayment EC, Wagstaff B 1999. Appropriate technology for oil spill management in developing nations. Journal of Pure Applied Chemistry. 71, pp203-208.

Weber J 1996. The compressed video experience. In proceedings: Summer Conference of the Association of Small Computer Users. North Myrtle Beach, South Carolina. (ERIC Document Reproduction Service No. ED 405 838).

Wee YS, Quazi HA 2005. Development and validation of critical factors of environmental management. Journal of Industrial Management & Data Systems. 105 (1), pp96-114.

Whigham DF 1999. Ecological issues related to wetland preservation, restoration, creation and assessment. Journal of Science of The Total Environment. 240 (1-3), pp31-40.

White I 1998. The Sea Empress Oil Spill in context. In proceedings: International Conference on the Sea Empress Oil Spill 11th-13th, Cardiff Wales.

White Paper, An Energy Policy for the European Union 1995. Commission of the European Communities Brussels, COM(95) 682 final.

Wieczorek A 2004. Pilot scale biofiltration of waste gases containing aliphatic and aromatic hydrocarbons, phenol, cresols and other volatile organic compounds. Journal of Environmental Progress. 24 (1), pp60-66.

Wrenn BA, Suidan MT, Strohmeier KL Eberhart LB, Wilson GJ, Venosa AD, Haines JR, Holder E 1997. Influence of tide and waves on washout of dissolved nutrients from the bioremediation zone of a coarse sand beach: application in oil spill bioremediation. Spill Science and Technology Bulletin. 4 (2), pp99-106.

Wright A, Weaver R, Webb J 1997. Oil bioremediation in salt marsh mesocosms as influenced by N and P fertilisation, flooding and season. Journal of Water, Air and Soil Pollution. 95, pp179-191.

Y:

Yaman S, Sahan M, Haykiri-açma H, Şeşen K, Küçükbayrak S 2000. Production of fuel briquettes from olive refuse and paper mill waste. Journal of Fuel Processing Technology. 68 1, pp23-31.

Z:

Zafar M, Alappat BJ. 2004. Landfill surface runoff and its effect on water quality on river Yamuna. Journal of Environmental Science Health and Toxic Hazardous Substances Environmental Engineering. 39 (2), pp375-84.

Zhu X, Venosa AD, Suidan MT, Lee K 2001. Guidelines for the Bioremediation of Marine Shorelines and Freshwater Wetlands. Spill Science and Technology Bulletin 8 (2), pp163-178.