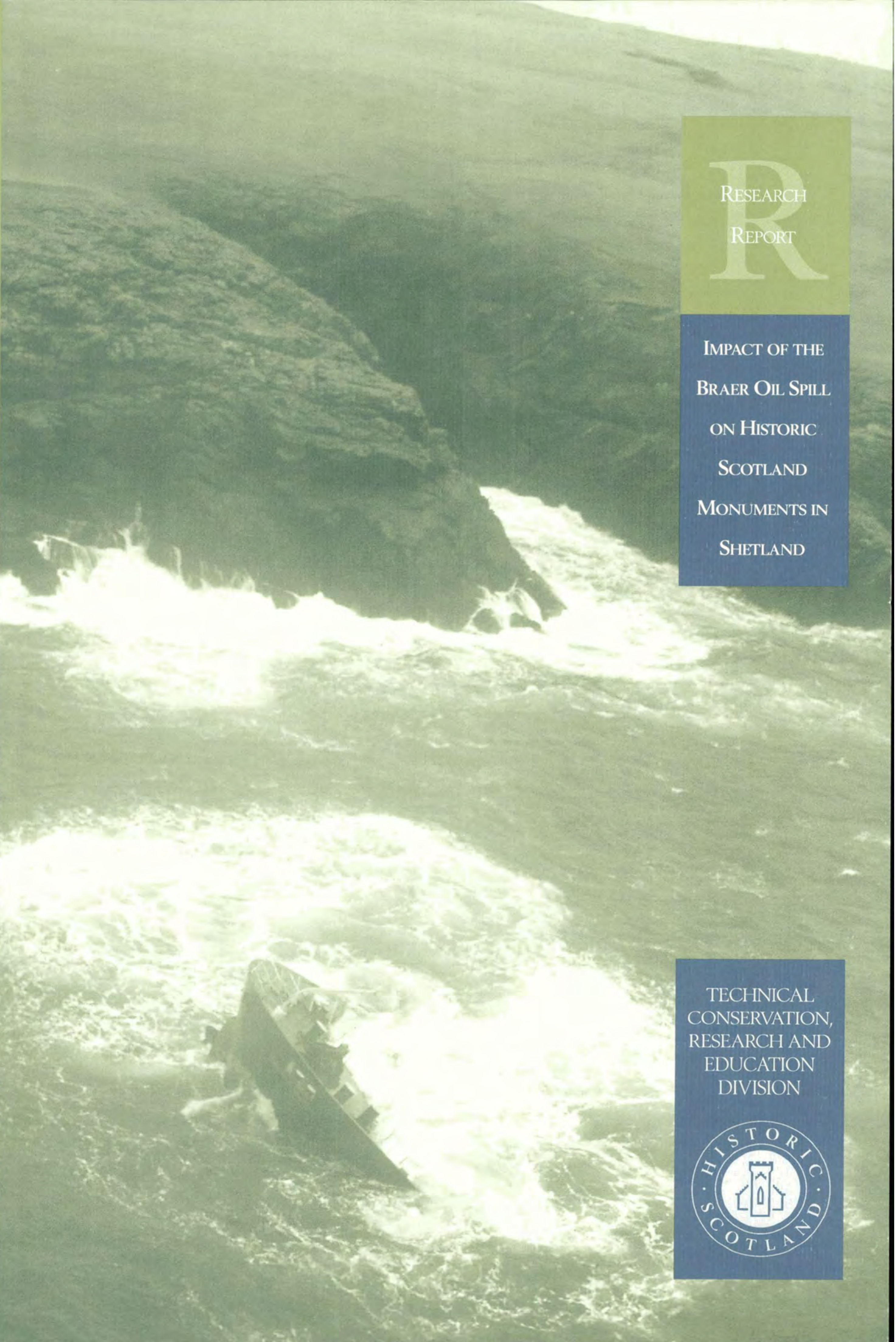

RESEARCH
REPORT

IMPACT OF THE BRAER OIL SPILL ON HISTORIC SCOTLAND MONUMENTS IN SHETLAND

TECHNICAL
CONSERVATION,
RESEARCH AND
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RESEARCH
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IMPACT OF THE BRAER OIL SPILL ON HISTORIC SCOTLAND MONUMENTS IN SHETLAND

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FOREWORD

"Deadly Cargo, worst fears realised as tanker spills....." was the headline of the Shetland Times on Friday 8th January, 1993. Over the next few weeks, 85,000 tons of Gullfaks crude oil escaped from the wreck of the Braer. The spill was the largest ever pollution incident in Scotland and eleventh largest in the world in terms of the quantity of oil released.

In close proximity to the wreck site of the Braer were the Historic Scotland monuments at Jarlsberg and Ness of Burgi. These monuments are amongst the most highly significant of the built remains of the Neolithic peoples that lived on the islands 5000 years ago. A new perspective was therefore brought to bear: while the natural environment has the potential to regenerate, here was a truly non-renewable resource that was potentially threatened by the deposition of oil. A preliminary check revealed that no previous research had been carried out into the impact of an oil spill on the built heritage.

A five year programme of monitoring and associated experiments was therefore initiated. Its aim was to assess the impact of the oil spill on the monuments, and to inform any remediation works that might be necessary to counter any damage caused. In the event, no long-term ill-effects of the deposition of oil on the monuments have been found, although some interesting changes in biological growths colonising the stones of the monuments have been noted.

This research report should be of interest to those who have responsibility for monuments in coastal regions, and to all members of the scientific community that are interested in the long-term impact of oil on the natural as well as the built environment.

Ingval Maxwell
Director
Technical Conservation, Research and
Education Division
Historic Scotland

December 2001

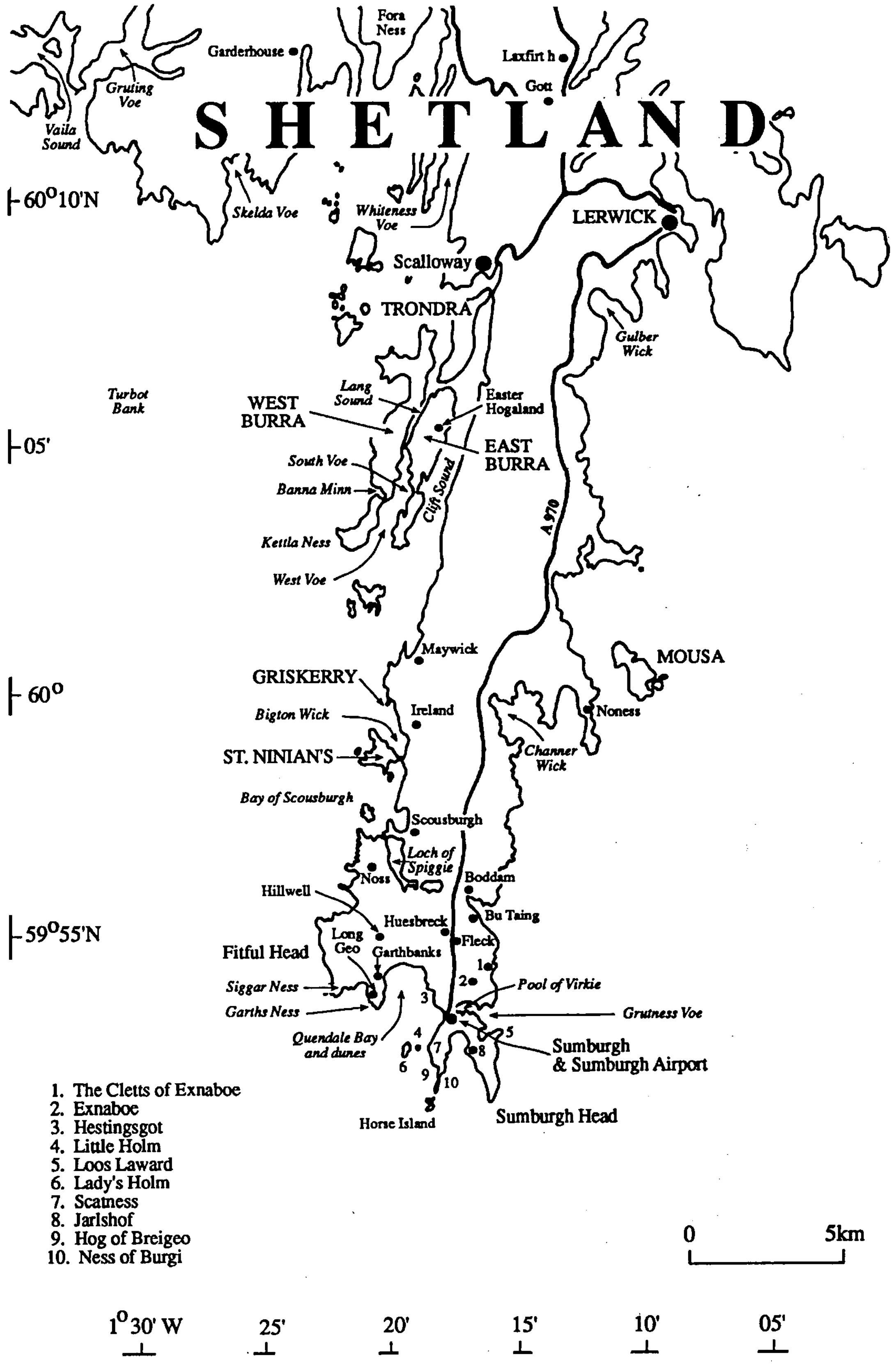


Figure 1. Location of key place names of South Mainland, Shetland (Source: Ritchie & O'Sullivan, 1994)

1 INTRODUCTION

1.1 Introduction

On Tuesday 5 January 1993 1-7, at 11:19Hrs, the MV Braer was confirmed as grounded at Garth's Ness on South Mainland, Shetland (Figure 1). Immediately on the point of impact oil was observed flowing from the vessel into the water. In the days that followed, the Braer discharged its total cargo of Norwegian Gullfaks crude oil which it was carrying (84,700 tonnes) and its bunker oil (300 tonnes) bringing the total release figure to 85,000 tonnes. Although a distinctive "coffee coloured" plume, characteristic of dispersed oil, could be seen some 25km up the western side of Shetland no conventional oil slick formed. The reasons for this being that the Gullfaks crude is a light oil amenable to dispersion, and the stormy weather conditions prevented formation of a conventional oil slick. The properties of the Gullfaks crude are summarised in Table 1.

The area most affected by the oil spill was that coastline in the south west of South Mainland, notably between Scalloway and Sumburgh Head (Figure 2). Small amounts of oil did, however, reach inland in the form of an aerosol of oil droplets and in sea spray due to the severity of the winds. The oil was deposited on grazings, soil and buildings. Situated close to the contaminated coastline is the Jarlshof monument which was contaminated by oil. Despite Historic Scotland, the caretakers of the site, covering areas of exposed stonework shortly after the disaster, areas of masonry were still contaminated by a thin coating of oil. Although significant work has been carried out into the impact of oil spills on marine life, vegetation and soils, very little research has been undertaken into the impact of oil on building stone.

1.2 Scope of Research

This study was commissioned to examine and monitor the impact of the Braer oil spill on Historic Scotland monuments in Shetland, notably the heavily contaminated site of Jarlshof.

The five-year programme was divided into three complementary parts:

- a review of previous investigations into the effects of hydrocarbons on stone buildings and monuments;
- an environmental monitoring programme of the contaminated area with appropriate field control sites;
- experimental studies to investigate the impact of hydrocarbons on the lithologies of the sandstone forming the moument and their physical and microbial decay response properties.

This report addresses each of these sections of the investigation in turn, and presents conclusions and recommendations regarding the appropriate response to any future contamination of a site by crude oil.

As such, the scope of the study has been augmented, and therefore has implications for the conservation of sandstone buildings beyond the direct impacts of the Braer oil spill on Historic Scotland monuments in Shetland.

1.3 Gullfaks crude oil

Gullfaks crude oil is produced from a large field located in block 34110 of the Norwegian sector of the North Sea. Statoil is the operator of the field. Gullfaks is not a typical North Sea crude oil, being more naturally biodegraded than other North Sea crudes. The biodegradation has removed most of the waxy normal paraffins, resulting in a heavier, more naphthenic and aromatic crude. The sulphur and metal contents, in spite of the relatively high density, are still low.

These technical details imply that when Gullfaks crude is spilt onto the sea surface it will float, remain in a liquid form and spread. Additionally, the oil will only very slowly form an emulsion; any emulsion will be relatively unstable (ie it will not form a "chocolate mousse"). Had the weather conditions in Shetland in January 1993 been less violent, mechanical recovery could have been a technical option, since the viscosity of the oil would have remained at a level below that at which skimmers become inoperable.

The oil is readily dispersible (naturally and chemically). However, the extreme dispersibility of this crude cannot be predicted, and may be due to surfactants present in the crude resulting from the unusually high degree of biological degradation of the oil.

For most North Sea crudes one would expect from 40% to 50% to be volatile, but with Gullfaks crude at most only 30% could be expected to evaporate. The extreme dispersibility of the oil and the weather conditions during the spill resulted in the almost complete absence of a surface slick. This will have caused the actual degree of evaporation to have been significantly less than the 30% indicated by its distillation characteristics.

Chemical properties

- Low content of saturates (a naturally biodegraded oil)
- High aromatic and naphthenic content
- Very low wax-content (<2 wt.%)
- Very low asphaltene content (<0.1 wt.%)

Physical properties with increased weathering

- Relatively low evaporative loss (<30% evaporated after 5 days weathering)
- Very low pour-point values (no problem with solidification at sea)
- Relatively high oil density

Water-oil-emulsification properties

- Relatively low water uptake rate (65-80% water content after 5 days weathering)
- Form emulsions with relatively low stability and low vicosity
- Relatively high effectiveness of demulsifiers (breakers and inhibitors)

Effectiveness of dispersant treatment

- Relatively high chemical dispersibility with Finasol OSR-5 (compared with other North Sea crudes)
- High upper viscosity limit for dispersant treatment (4000-7000 cP)
- Relatively large "time window" for dispersant treatment (36 hours to 5 days)

Mechanical recovery

- Due to low water uptake rate it will take 3 hours to 2 days weathering at sea before the w/o-emulsion passes 1000 cP in viscosity

Analytical Results

Density at 15°C	kg/l	0.8798
Specific Gravity at 16°C/15°C	0.9905	
API Gravity at 80/60°F	°API	29.3
Sulphur	mass %	0.42
Total Acid Number	mg KOH/g	0.20
Raid Vapour Pressure (RVP) kPa	28.3	
Pour point	°C	<-45
Viscosity at 20°C	cSt	16.4
Hydrogen Sulphide	Mass %	o ND
Vanadium	mg/kg	1.8
Nickel	mg/kg	1.3

Table 1 Gullfaks crude oil: summary of weathering properties (Source: Ritchie and O'Sullivan (1994))

Salt as NACI	mg/l	8.4
Wax content	mass %	12.9
Flash point	°C	<10
Distillation D-86		
IBP	°C	65
°C 123		
5%		
10%	°C	148
20%	°C	200
30%	°C	249
40%	°C	296
50%	°C	336
60%	°C	360

Table 1 (continued) Gullfaks crude oil: summary of weathering properties (Source: Ritchie and O'Sullivan (1994))

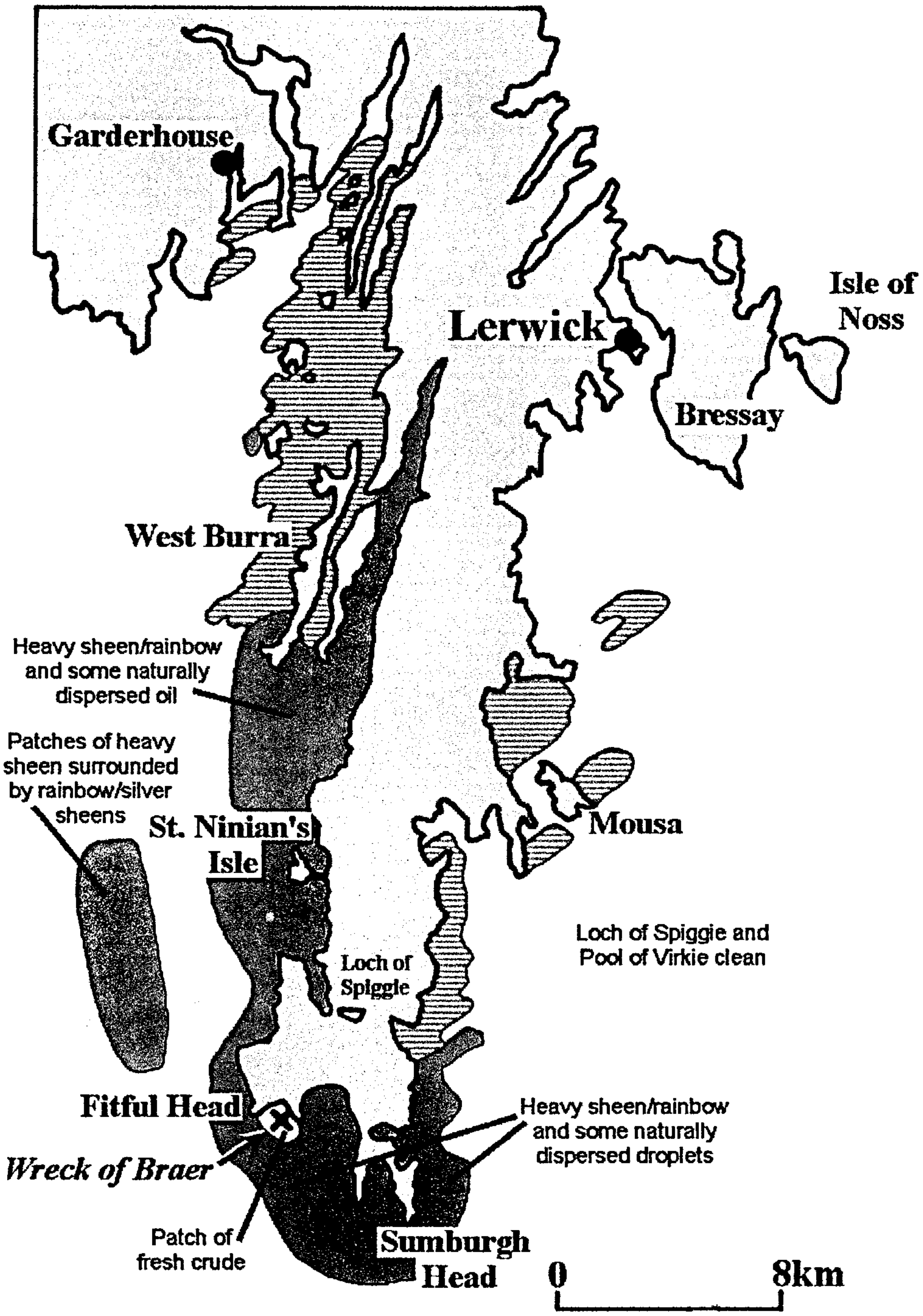


Figure 2 *Extent of oil contamination on January 9th 1993. (Source: Ritchie & O'Sullivan, 1994)*

2 LITERATURE REVIEW

2.1 Introduction

A comprehensive search of the primary, secondary and "grey" literature failed to reveal any investigations that had examined the impact of crude hydrocarbons upon sandstone decay processes. The literature search strategy (detailed in Appendix A) encompassed a wide range of abstracting sources, some of which contained material dating back to the 1950s. While no directly relevant study was found, the review did reveal the potential significance of hydrocarbons to the enhancement or diminution of biological decay processes on stone surfaces. The biogeochemical action of microbial decay is therefore reviewed, prior to an examination of the influence of hydrocarbons on these processes.

2.2 Stone weathering and decay by epilithic communities

The weathering of stone in buildings and monuments is a continuing problem as a result of atmospheric pollution, climatic conditions, edaphic factors, rock type and biological interactions, which until recently were thought to be negligible and are still the subject of some debate (Saiz-Jimenez, 1993). The effects of micro-organisms with regard to their metabolic and mechanical actions is somewhat difficult to quantify and it has still to be established whether such microbial growth is a primary or secondary cause of stone deterioration (Young, 1996). Quantification of microbial biomass and their destructive waste products remain a challenge but is crucial in order to quantify the threat of microbial biodeterioration (Young, 1996). Krumbien has shown that microbial biodeterioration of rock is 100 to 10,000 times faster than chemical biodeterioration (Krumbein, 1992). With the increase of environmental pollution it has now been questioned as to whether this has caused a dramatic increase in biological damage to buildings.

Bacteria, fungi and algae can all be found in mixed communities on decaying stone surfaces (Anderson et al., 1993; Bell et al., 1993; Bock & Sand, 1993; Griffin et al., 1991; Leahy & Colwell, 1990; May &Lewis, 1993; Palmer, 1992; Wainright et al., 1993; Wakefield & Jones, 1998; Winklet 1994). Most frequently the organisms arrive by air in an aerosol or by ground water. These micro-organisms may damage the stone by chemical action through secretion of acids such as nitric, carbonic, sulphuric and other weaker acids.

Microbial biodeterioration can take two forms, firstly there can be chemical action as a result of metabolic waste products being released. Secondly there may be physical damage which can consist of two weathering processes; organic and inorganic acids can be excreted by the organisms as a result of utilising airborne sulphur, nitrogen and organic compounds including hydrocarbons. Such acids leach the binding materials out of rocks and weaken its mineral structure (Sand & Bock, 1991). There may also be water absorbing substances excreted by the organisms which can lead to changes in the porosity and permeability of rocks which result in an eroded surface and one that is more open to water and frost attacks (Morton & Surman, 1994).

The production of nitric and sulphuric acids is associated with a particular group of bacterial species, namely nitrifying and sulphating bacteria. As a result of respiration, carbon dioxide is produced by all organisms which can in turn produce carbonic acid. The most significant type of damage to stone is that caused by organic acids, such as citric and oxalic acids, which are produced by fungi, bacteria and some algae. Physical damage caused by wet-dry cycles and associated mucilage expansion may also be significant in stone decay. Different rock types respond differently to microbes, depending on such characteristics as mineral composition, binding materials, porosity and permeability. Depending on the organism, the damage can be surface deposits, discoloration, pitting and accelerated weathering (Viles, 1995; Young & Wakefield, 1995). Chemoorganotrophic and chemolithotrophic microbes appear to be the biggest threat as they feed on organic and inorganic pollutants including hydrocarbons rather than on phototrophic organisms such as algae and lichens (Krumbein, 1992).

Rock weathering is accelerated by a superficial layer of micro-organisms, called a biofilm. This contains active and dormant micro-organisms and products of their metabolism, such as acids and polymers produced by the microbial cells. The colonisation process begins with autotrophs and progresses to heterotrophic organisms (May et al., 1993). Active biofilms are formed in any location where micro-organisms and moisture are present. All micro-organism are able to attach to surfaces, although the degree and rate of this process and of subsequent microbial growth depend on the type of organism, the nature of the surface and the environmental conditions.

2.3 Bacterial contribution to stone decay

Bacteria are classified by their metabolic activity as autotrophic or heterotrophic, this is a laboratory defined method of classification (Winkler, 1994). Autotrophic bacteria take their energy from the sunlight, chemical oxidation and reduction whereas heterotrophic bacteria take their energy from existing organic substances. A freshly quarried stone has less bacteria on it than a weathered stone surface which may have small clumps of bacteria, or larger colonies along cracks and pores on the stone surface. While the ecology of bacteria in soils has been well studied, bacteria on stone have not been studied to any great extent. What is known is that for any bacteria present on stone their numbers depend on type of stone, the climate and other organisms present.

2.3.1 Autotrophic bacteria

Damage to stone by autotrophic bacteria is rarely in evidence. These bacteria can be further classified by their activity:

(1) nitrogen fixing bacteria

(2) sulphur fixing bacteria

(3) iron bacteria

(4) calcite bacteria

These all have the potential to damage stone by production of various inorganic acids (e.g. sulphuric and nitric acids) and organic acids (oxalic and citric acids). These bacteria also use a carbon source which is usually carbon dioxide. Chemoautotrophic bacteria are rare in nature, but species of Thiobacillus have been isolated from some monuments (Lorenzo & Gomez-Alarcon, 1997).

2.3.2 Heterotrophic bacteria

It is unknown how much damage to stone is caused by heterotrophic bacteria since this has not yet been sufficiently researched, nor has the role of mucilage and organic acid production from these organisms been fully investigated. However, since these bacteria live off available organic matter and require a carbon source, it is possible that oil pollution may increase the amount of bacteria present on a stone surface, since it has been reported that heterotrophic bacteria in soil and marine environments can utilise hydrocarbons leading to degradation of the hydrocarbons (Albaiges et al., 1986; Butt et al., 1986).

Heterotrophic bacteria have been found on decaying building stone and it has been suggested that they are active in the decaying process as a result of mineralising activities (see Table 2), similar to those observed with soil bacteria (Lyalikova & Petushkova, 1991; Sand & Bock, 1991). The activity of these bacteria is governed by the availability of suitable organic matter. It is likely that most rocks contain sufficient organic matter to maintain the growth and activity of micro-organisms.

Heterotrophic bacteria have been shown to be high in numbers in the lower parts of buildings and monuments and at sites protected from rain. Most of the strains isolated from the air samples could also be isolated from the surface of the monument indicating re-inoculation as a possibility (Saiz-Jimenez, 1995). In surface samples of freshly worked building stones 10(3) CFU of heterotrophic bacteria and filamentous fungi per gram of stone was observed after three days exposure (Lewis & May, 1987). Gomezalarcon et al., 1995 have been able to monitor microbial communities activity in the surface layers of stone by looking at the dehydrogenase activity of the micro-organisms. They were able to identify fungi belonging to many genera including Altemaria, Pencillium and Trichoderma and bacteria of the genera Bacillus, Thiobacillus and Micrococcus.

Stassi et al., 1998 have studied the calorimetric behaviour of Bacillus strains, namely, B. cereus, B. subtilis and B. alvei in an attempt to characterise the different phases of these micro-organisms cellular cycles with the hope of being able to monitor their role in biodeterioration of stone. Such micro-organisms are very common with their normal habitat being the soil and can be particularly problematic in biodeterioration as they can produce resistant spores that can survive environmental stress

2.4 Fungal contribution to stone decay

Evidence has been found that fungi extract ions from stone by the production of carbonic, nitric, sulphuric and other weaker acids (Winkler, 1994). Research into the effect of fungi has shown that Ca, K, Mg, Fe, AI and Si are released from stone in that order by nitric and sulphuric acids produced by fungi with Ca recording the greatest loss, Si the least. Fungi are also capable of producing citric and oxalic acids which are believed to be the most active acids in stone decay. It has been reported that hydrocarbons in the environment are biodegraded primarily by bacteria and fungi (Albaiges et al., 1986). Hence on contamination of a stone surface populated by fungi, the growth of which is not inhibited by the presence of oil, the hydrocarbons are likely to be degraded and the population of fungi is likely to increase such that the

Type of metabolism	Type of organism	Energy source	Carbon source	Products
Chemoautotrophy (Chemolithotrophy)	Hydrogen-reducing bacteria	H_2+O_2 (from atmosphere)	CO_2	H_2O+C* (carbon output may support growth of heterotrophs)
	Sulphur-oxidizing bacteria	H_2S+O_2 (from sulphur reducers)		H_2O+S+C (S output supports growth of other S oxidizers)
		$S+O_2+H_2O$ (from sulphur oxidizers)		H_2SO_4+C (acidification of environment
	Iron-oxidizing bacteria	$Fe^{2+}+O_2+H_2O$ (from solution)		$Fe_3^{+}+OH^{-}$ (loss of iron, iron may stain)
	Nitrifying bacteria	NH_3+O_2 (from atmosphere or denitrifying bacteria)		HNO_3+C
Chemoorganotrophs (heterotrophy) anaerobic	Denitrifying bacteria	$H_2+NO_3^{-}$ (H2 from organic carbon, NO_3 from environment or nitrifying bacteria)	CH_2O (Carbohydrate)	NO_2N_2O, N_2, NH_3 (lost into atmosphere or used by nitrifyers
	Sulphur reducing bacteria	$H_2+SO_4^{-}$ (from sulphur oxidizers or degradation of organic compounds containing S such as amino acids)		S or H_2S (used by S oxidizers or sulphation of metals)
Chemoorganotrophy (heterotrophy) aerobic	Bacteria/fungi/ actinomycetes degradaing carbohydrate	$O_2+CH_2O+H_2O$	CH_2O	CO_2+H_2O+C (CO_2 form H_2CO_3 and precipitate CO_3, C represents organic acids mucilage and other chelating agents)
	PAH degrading bacteria	O_2+PAH	PAH	CO_2+H_2O+C (as above, but PAH not completely minerlaized)
Photoautotrophy (aerobic)	Algae and cyanobacteria	CO_2+H_2O+light	CO_2	O_2+C (cellular components like CH_2O,or mucilage, organic acids and other chelating agents)
		$O_2+CH_2O+H_2O$ (dark)	CH_2O	CO_2+H_20+C

*Most C in form of cellular components, slime (mucilage) and possible organic acids and other potential chelating agents.

Table 2 Types of metabolism and products formed from the activities of micro-organisms (Source: Wakefield and Jones, 1998) stone may be damaged further by the increase in fungal activity and production of organic acids.

2.5 Algal contribution to stone decay

Algae are found growing in humid places in a building, where water is retained and evaporation is low, including crevices, holes and cornices (Flores et al., 1997). Algae are often the first organism to colonise stone because their primary requirement is light (Flores et al., 1997). The contribution of phototrophs as direct participants to stone decay has only recently been considered as potentially harmful organisms. Their role in deterioration has traditionally been thought of as largely insignificant and at the most as a supportive role in the nutrition of other micro-organisms. Algae form biofilms to which organic residues and spores can adhere and this may help to support the growth of other micro-organisms (Morton & Surman, 1994; Gaylarde & Morton, 1997).

Algae found in stone are divided into two groups:

(1) green algae (chlorophyta)

(2) blue-green algae (cyanophyta or cyanobacteria)

Stone degradation by algae occurs by mechanical and chemical action. It is known that algae produce metabolic products that are acidic or have a chelating effect which results in mineral dissolution (see Table 2). Biogeochemical damage to stone caused by algae through the production of extra-cellular organic acids, chelating agents and carbonic acid from respiratory carbon dioxide, has been found to cause dissolution of minerals and salt crystallisation (Wakefield & Jones, 1998). Algae also extract ions from stone by the production of nitric and sulphuric acids (Winkler, 1994).

Algae can damage stone by boring into the stone by the action of terminal cells of endolithic (growing in stone) filaments. These filaments can be considerable in mass and large in diameter with thick cell walls which could be particularly destructive to the stone matrix if growth were directed between grains or into cracks and fissures. The presence of mucilage, the creation of new cracks and widening of existing ones would increase the capacity of the material to hold moisture, the presence of which would enhance both chemical and physical decay mechanisms. Endolithic algae actively dissolve carbonates to enable penetration into the substrate. The type of microcavity created is species specific (May & Lewis et al 1993). Many species of algae can colonise buildings for instance 31 taxa were isolated from a granite building in Spain which included Cyanophyta, Chlorophyta and Trentepohlia (Noguero-Seoane et al.,1997).

Some species of cyanobacteria have mucilaginous sheaths around each cell, other species of cyanobacteria and most chlorophyta produce large amounts of amorphous mucilage. Algae is one of the many micro-organisms which resist drought, for example cyanobacteria, by using water retaining sheaths. The expansion and contraction of this sheath and mucilage during wet and dry cycles, can lead to the physical deterioration of stone. Volume changes by wetting and drying can be extreme, for example the average degree of expansion on wetting and by green crusts of cyanobacteria can be as much as 300% (Wakefield et al., 1996). Algae can also contribute to spalling decay by freeze-thaw action (Ortega-Calvo et al., 1993). The force of this expansion and contraction has not been quantified, however, it has been found to be similar in magnitude to the crystallisation force of ice or salts.

2.6 Lichen contribution to stone decay

Lichens are capable of degrading stone substrata through mechanical and/or chemical means. Lichens can undergo freeze-thawing due to being able to retain water with the process being increased as a result of their hyphae penetrating the substratum. With regards to chemical weathering, many chemicals may be excreted, including oxalic acids, lipids and acidic-lichenic substances which have a chelating effect (Seaward, 1997).

2.7 Stone ecosystems

All four types of micro-organisms (bacteria, fungi, algae and lichens) are usually present on stone, more so stone that has been weathered. It is very rarely the case that a particular species of micro-organism will exist in isolation, but rather in interdependence with other micro-organisms particularly at the stone surface where algae communities are the primary producers and produce nitrogen and carbon compounds from photosynthesis, which they secrete into the environment around them. Bacteria and fungi develop in close association with these algae communities and may produce other substances, e.g., vitamins and minerals, that the algae require. Ecosystems are established in cracks, pores and at the stone surface which may experience sporadic bouts of increased activity depending on the factors of climate, moisture availability and nutrient sources. Potentially, the contamination of these communities by the introduction of oil may destroy their structure. This may in turn favour different micro-organisms which are able to degrade the oil and use it as a food source. This may increase their aggressive activity at the stone surface or may efficiently kill off all surface life.

2.8 Sandstone decay by natural weathering

The decay of stone by natural weathering is dependent on a number of agents. Weathering agents include the atmosphere, rising ground moisture (with or without dissolved salts), rainwater, fresh water and salt water. Most of the decay of stone progresses near or at the surface of the ground. Some types of sandstones are known as calcareous sandstone, these sandstones have their particles bound together by a calcium carbonate "cement". Sandstones are porous and if water, usually rainwater, containing carbon dioxide is allowed onto these calcareous sandstones, the calcium carbonate dissolves and the sandstone can break up. Sandstone being a porous stone can be damaged by the freeze/thaw action of water, in the pores, which expands when frozen. This may lead to cracking and ultimately to spalling this is where the stone breaks up. Salts from saline solutions can cause spalling of porous stone by crystallisation in the pores creating stress which can lead to cracking.

2.9 Stone decay and the influence of hydrocarbons

Very little has been written regarding hydrocarbons as a carbon source for stone weathering micro-organisms and in fact the literature is focused in the context of marine oil spill degradation (Atlas, 1995). Although the flora and fauna of these two different environments is somewhat different valuable information may be perhaps gained if a bridge could be made between such areas of research. Hydrocarbon-degrading micro-organisms are ubiquitously distributed in soil and aquatic environments. Populations of hydrocarbon-degraders normally constitute less than 1% of the total microbial communities, but when oil pollutants are present these hydrocarbon-degrading populations increase, typically to 10% of the community (Atlas, 1995).

Petroleum is a natural product resulting from the anaerobic conversion of biomass under high temperature and pressure. Most of its components are subject to biodegradation, but at relatively slow rates (Leahy & Colwell, 1990). Components of crude oil include aromatic, paraffinic and cycloparaffinic structures. Homologues, isomers and combinations result in hundreds of individual hydrocarbon compounds in crude oil. Petroleum is a complex mixture of aliphatic, alicyclic (cycloaliphatic saturated ring structures), and aromatic hydrocarbons and a smaller portion of non-hydrocarbon compounds such as naphthenic acids, phenols, thiols, heterocyclic nitrogen and sulphur compounds as well as metalloporphyrins. There are several hundred individual components in every crude oil, and the composition of each varies with its origin. Susceptibility to biodegradation varies with the type and size of the hydrocarbon molecule. N-alkanes of intermediate chain length (C10-C24) are degraded most rapidly. Short chain alkanes are toxic to many micro-organisms. Very long chain alkanes become increasingly resistant to biodegradation (Saiz-Jimenez, 1997). Alicyclic compounds are frequently unable to serve as the sole carbon source for microbial growth unless they have a sufficiently long aliphatic side chain, but they can be degraded via cometabolism by two or more co-operating microbial strains with complementary metabolic capabilities (Atlas, 1981)

Carbon input from external sources includes environmental pollution in the form of mixed hydrocarbons(kerosene), volatile organic compounds in the atmosphere emitted by various industries (Saiz-Jimenez, 1995). The burning of fossil fuels results in the release of poly-aromatic hydrocarbons (PAHs) into the environment via atmospheric deposition, which can then accumulate in soils and on building stones. The black areas found in zones protected from direct rainfall and from surface run-off are crusts composed of crystals of gypsum mixed with dust and particulates of anthropogenic origin (carbonaceous particles originating from oil and coal combustion, including vehicular emissions, power plants and domestic heating systems). Air pollution provides a source of organic matter to building stone, therefore the deposition of anthropogenic compounds on to stones may affect the colonisation and growth patterns of micro-organisms in stone buildings that are located within a polluted environment (Ortega-Calvo & Saiz-Jimenez, 1997). Ortega-Calvo & Saiz-Jimenez have been able to isolate phenanthrene (PAH) degrading micro-organisms and have suggested that micro-organisms present in building stone may be able to transform atmospheric pollutants that have been deposited on building stone and use them for growth. Although the black gypsum crusts that may be found on buildings within polluted environments are thought to be a result of fossil fuel combustion, Saiz-Jimenez, 1995, reviews the work of others and has suggested that this black coloration may have a biogenic origin and be related to microbial melanins.

The natural decay of stone buildings is intensified by air pollution. As a result, weathering products originate such as water soluble salts, which are considered the most serious ones. In the weathering crusts of some sandstone and limestone samples, sulphates, chlorides, nitrates and dust particles have been detected (Labus, 1997). The action of air pollution with regards to the weathering of historical monuments has been investigated by Moropoulou et al., 1998, and attempts have been made to evaluate the origin of elements and ions in aerosols and total deposition and relate these to possible sources i.e. soil, marine spray, anthropogenic influences and underlying rock using enrichment factors. In a similar study Torfs and Van-Grieken (1997) monitored aerosols and total deposition of a decaying historical building within a highly industrialised area in Greece and recorded high heavy metal and sulphate concentrations. They concluded that aerosols and depositions reflect a relatively small effect of anthropogenic derived elements.

Pollution reduces the diversity of the biological flora but it does not necessarily reduce the total biological cover as often when the micro-climate is favourable organisms that are resistant to pollution, especially cyanobacteria, can grow abundantly even in the most polluted environments (Caneva et al., 1995).

Alkanes, fatty acids, short chain hydrocarbons, kerosene and poly-aromatic hydrocarbons (PAHs) are components of black crusts on the surface of stone in heavily industrialised urban areas (Ortega-Calvo & Saiz-Jimenez, 1996). PAH degraders have been isolated which were also tolerant to benzene and lead, present at normally microbially toxic concentrations at the rock surfaces. The utilisation of complex carbon sources for energy and growth by heterotrophic bacteria can result in the metabolic production of organic acids such as gluconic acid or lactic acid, which can directly interact with the mineral components of stone (Warscheid & Oelting et al., 1991).

The biodegredation processes of PAHs by microbes are aerobic and initiated by oxygenases. Bacteria utilise 2-4-cycle-PAH as growth substrates, leading to their mineralisation. Lignolytic fungi, as well as bacteria, carry out a cometabolic attack on PAH. Studies on bacteria have shown that there are two distinct mechanisms involved; transfer by dissolution in the aqueous phase and direct interfacial uptake. Another important aspect is the fate of PAH in terms of carbon balance during the bacterial degradation of individual PAH and PAH mixtures. High mineralisation can be obtained. In the case of PAH mixtures such high mineralisation levels are obtained using complex micro-flora involving a large participation of cometabolism. In the environment, an important parameter limiting PAH degradation is their accessibility to micro-organisms (Bouchez et al., 1996).

Degradative plasmids can be found in Gram negative bacteria. These plasmid genes can code enzymes necessary for the biodegradation of various xenobiotic compounds. The plasmids may differ in many features such as size, conjugative properties, stability, number and properties of coded enzymic activities. Such degradative plasmids exist for the degradation of n-alkanes, toluene, naphthalene, PAHs etc. (Kostal, 1999).

Bacteria may produce biosurfactants that can facilitate cell-oil contact or assist solubilisation of oil and sorbed phases (Rouse & Sabatini et al 1994) After discharge into the environment, organic compounds will partition into gaseous, aqueous, oil and solid phases. This phase partitioning can have a strong impact on the subsequent bacterial uptake of the organic compound which in turn influences degradability (Mihelcic et al., 1995). Bacteria display variations in the structure, composition and role of the cellular frame that protect them from the environment (Gottschalk, 1986). These barriers not only serve as physical barriers, but also determine the rate and route of substrate penetration into the interior of the cell. Specific uptake mechanisms of oil compounds are necessary if bacterial systems are to degrade oil phase contaminants. Various micro-organisms have developed the ability to overcome some of these difficulties by synthesising surface active agents i.e. biosurfactants. This process allows uptake of utilisation of the hydrophobic compounds (Hommel,1990). They aggregate in micelles or at interfaces between two phases and can either facilitate cell-oil droplet contact or solubilse the oil phase so that it can then be transported into the cell.

The ability of micro-organisms to produce biosurfactants can be extremely important when the degradation of hydrocarbons is crucial for instance as a result of crude oil land contamination. Ivshina et al., 1998 have shown that certain Rhodococcus strains produce biosurfactant during growth on n-alkanes, therefore such micro-organisms may be problematic with respects to stone biodeterioration but we must not forget their importance in other areas (Desai & Banat, 1997).

3 ENVIRONMENTAL MONITORING: FIELD STUDIES

3.1 Introduction

A reconnaissance survey was undertaken in February 1994 to inspect the Historic Scotland monuments contaminated by oil from the Braer wreck, and to identify suitable sites or monuments that could act as control settings for the environmental monitoring programme. The survey was also used to establish the availability of suitable lithological material at both the contaminated and possible control monuments to enable a meaningful monitoring sampling programme to be initiated without degrading the monuments under study. The findings of the survey were used as the basis of the environmental monitoring programme.

3.2 Contaminated monument sites

3.2.1 Jarlshof Grid reference: HU398095

Description: The monument is constructed of red and grey-green sandstone of Old Red Sandstone age. The site suffered heavy hydrocarbon contamination during the Braer wreck as described by Historic Scotland internal reports of inspections made at the time of the accident. At the time of the survey, winter storms had scoured the hydrocarbon contamination off the monument buildings. There was no evidence of colour differences between the areas of the monument that has been heavily contaminated and the remainder of the monument. Traces of hydrocarbon residues were observed on the inner wall and floor of the wheelhouse. Re-deposition of oil remobilized from the sea-bed by winter storms was present.

Evaluation: Sampling and use of the construction lithologies in the environmental monitoring programme was considered inappropriate as it would result in the removal of significant quantities of stone from important areas of the monument.

3.2.2 Ness of Burgi Grid reference: HU387084

Description: Composed of pebbly-gritty reddish sandstone and grey sandstone. No obvious oil contamination in or around the monument. Ample material for sampling same rock types from debris in a defensive ditch and from outcrops along the coast. Unnecessary to extract stones from the monument.

Evaluation: Given the pebbly nature of the construction lithologies there could be some difficulties in collecting a sufficiently large mass of representative rock samples to ensure meaningful, reproducible results on analysis.

3.3 Control Monument Sites

All Historic Scotland monuments on Shetland uncontaminated with hydrocarbons were examined for suitability as a control site. The purpose of a control site is two-fold:

- to provide sampling material for removal and analysis over several years of the monitoring programme
- to provide baseline observations on the weathering behaviour of the construction lithology and thereby provide a basis for comparison with the behaviour of the lithologies comprising the Jarlshof contaminated monument.

To act as a valid control site for the study, prospective sites were required to fulfil a set criteria (Table 3). Each monument was evaluated against this criteria and judged to be suitable or unsuitable as a control site. To be valid as a control monument to the environmental monitoring programme, prospective sites should display the characteristics shown in Table 3:

1. be uncontaminated by hydrocarbons from the Braer wreck
2. the lithologies of the construction materials should be of the same rock type as those of the contaminated monuments
3. construction lithologies should show the same porosity and permeability characteristics as those of the contaminated monuments
4. construction lithologies should be from the same stratigraphic horizon as those of the contaminated monuments
5. there should be ample material for sampling over several years without causing damage to the monument
6. be sited at a rural, coastal location to minimise local climatic exposure variables

Table 3 Evaluation criteria for control monument sites

Criteria 2, 3 and 4 were implemented to establish control lithologies that would display similar physical and chemical characteristics as those which comprise the contaminated monument. Such lithologies would therefore react in a similar manner to the local weathering environment and provide a valid contrast to the behaviour of the construction lithologies of the contaminated monument. Criteria 6 was implemented to ensure comparable weathering conditions at the control sites to those extant at the contaminated monument. This proved to be a valid concern as geographic location and coastal proximity have recently been demonstrated to be important factors that influence the decay and weathering response of building sandstone (Pombo, 1999).

3.3.1 Muness Castle Grid reference: HU629012

Description: The castle is composed of schist, granite and serpentine rock types and is situated on the southern shores of the Isle of Unst in northern Shetland. It is far removed from the coastal zone of hydrocarbon contamination.

Evaluation: Fulfils criteria 1 and 6, but fails as a suitable control site on the basis of the different types of construction lithologies from the Jarlshof contaminated monument.

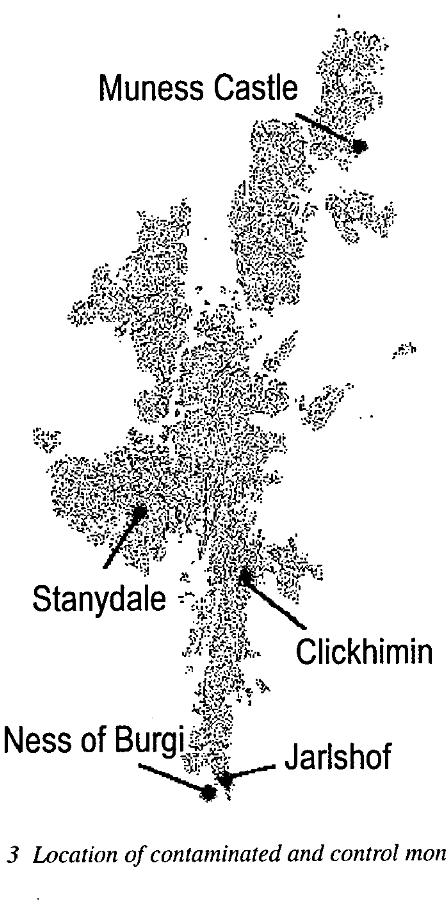


Figure 3 Location of contaminated and control monument sites

3.3.2 Clickhimin Grid reference: HU465408

Description: Situated within the town of Lerwick, the broch is composed of sandstones of Old Red Sandstone age. A small mound of stones close to the monument could supply sampling material for monitoring purposes.

Evaluation: Although composed of sandstone of the same geological age as the construction lithologies of the Jarlshof monument, those of Clickhimin are from a different stratigraphic horizon and show some compositional variations from the Jarlshof sandstone. Of greater concern is the urban setting of this monument which provides a very different weathering environment from the rural-coastal environment of Jarlshof. Fulfils criteria 1, 2 and 5, but fails as a suitable control site on criteria 4 and 6.

3.3.2 Stanydale Grid reference: HU285502

Description: Set in an area of Old Red Sandstone age sediments, far removed from the coastal zone of contamination. Stones scatter the area of the monument which would enable sampling to take place without the need to remove specimens from the monument buildings. However guidance would be required from an Inspector to ensure that proposed sample areas were not of archaeological significance since indiscriminate removal of stone samples could disturb potentially important features.

Evaluation: The site has potential as a control location, since it fulfils criteria 1, 2 and 5. The rural, non-coastal setting means that criterion 6 is failed and as the local sandstone is from a different stratigraphic horizon to that of the Jarlshof lithologies, criterion 4 is also failed.

3.4 Geological rock outcrop survey

Natural geological outcrops of the lithologies which were used to construct the Jarlshof monument would provide valid alternatives to historic monuments for use as control and contaminated sites (although it is recognised that these outcrops will not contain the construction joints seen in stone built monuments). A consideration of the geology of the Shetland Islands is therefore necessary to fulfil two objectives, namely:

- to identify areas of suitable natural outcrops for use as control sites for comparative observations with the Jarlshof monument weathering behaviour and for sampling purposes;
- to locate contaminated natural outcrop sites that are comparable in constituent lithologies to the Jarlshof monument and which would also be suitable for sampling purposes in a lithogeochemical monitoring survey.

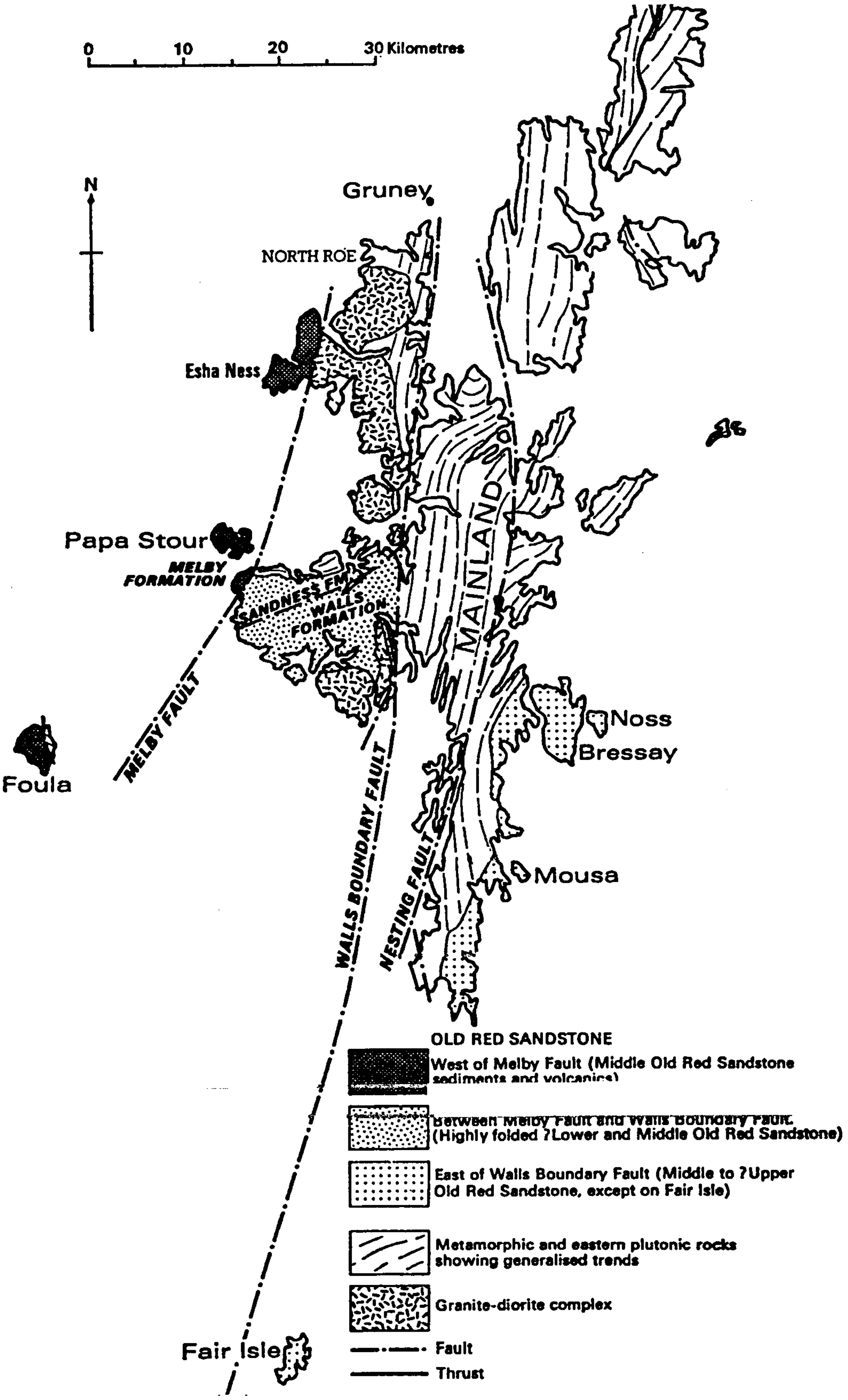


Figure 4 *Shetland Geology (from Mykura 1976)*

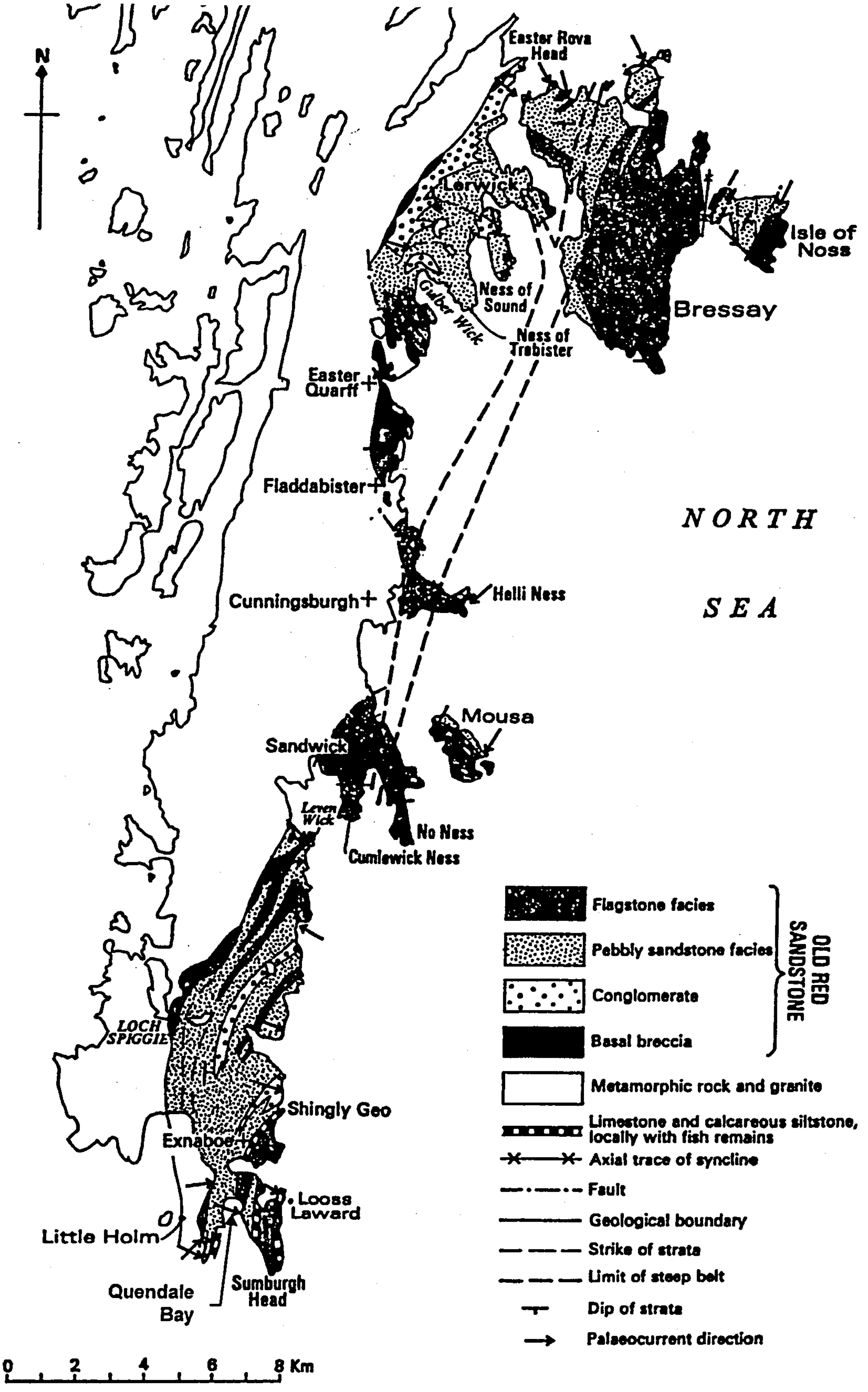


Figure 5 *Old Red Sandstone Geology of South Mainland, Shetland.*

It is therefore essential that the rock types that constitute the contaminated monument are well defined in terms of lithology and stratigraphy.

The structures comprising the Jarlshof monument are composed of sandstone of Old Red Sandstone age ("ORS" – approximately 400 million years old). Sediments of this age are found throughout the Shetland islands (Figure 5). However the geological structure of Shetland, notably the presence of three principal faults, means that the ORS sediments in each section between the faults do not belong to the same stratigraphic formation and cannot be correlated. In practical terms, this means that while they are of the same geological age, the mineralogy, sedimentology and physico-chemical characteristics of each of these groups of sandstones will be different because there were originally laid down in different depositional basins. Despite the wide distribution of ORS rocks in Shetland, only those to the east of the Nesting fault can be considered as suitable equivalents to the monument construction lithologies. Figure 6 illustrates that within this area several sandstone types (or "facies") are found. The Jarlshof monument is constructed of rocks belonging to the pebbly sandstone and the flagstone facies which may be seen to outcrop from Sumburgh Head north to the Lerwick area (Figure 6). However as shown in Figure 6, sandstones of the Lerwick area were deposited in a distinct sub-basin from those of the Sumburgh area and may not belong to the same stratigraphic horizon and are therefore not ideal as control sample locations.

The sandstones of the Sandwick-Mousa area offer a more suitable alternative sampling site for uncontaminated rocks belonging to the flagstone facies, as do the two large quarries located on the Sumburgh Head peninsula. These quarries are exposed to coastal weathering, but the rock faces were not coated with hydrocarbons as occurred at Jarlshof, they were therefore considered to be suitable as additional control site locations. The shoreline that encompasses Quendale Bay to Sumburgh Head (Figures 1 and 5) offers suitable contaminated sites that are comparable in constituent lithologies to the Jarlshof monument and which would be suitable for sampling purposes.

3.5 Identification of lithological control and contaminated monitoring sites

No Historic Scotland monument in Shetland is ideal as a control site for the environmental monitoring programme, though Clickhimin Broch and Stanydale do fulfil several of the required criteria. Natural coastal outcrops and quarries of the Jarlshof construction sandstones are found in the Sumburgh district neighbouring the monument. These provide ample material for sampling purposes and offer greater scope

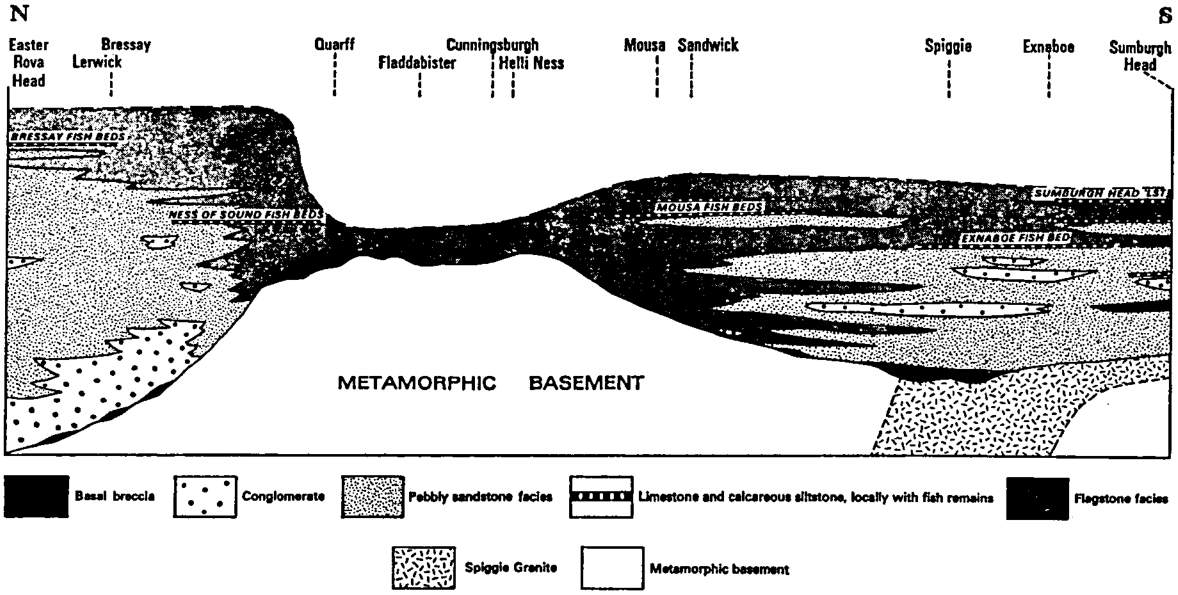


Figure 6 Geological Cross-Section Of South Mainland, Shetland.

and suitability as control and contaminant locations than any of the monuments examined.

Control and contaminated sites that were to be used in the monitoring programme were therefore identified on the basis of several factors:

- this survey of Historic Scotland monuments in Shetland;
- the availability of suitable rock material for sampling;
- the known area of coast subjected to heavy hydrocarbon contamination;
- the geology of Shetland and the lithologies comprising the Jarlshof monument.

3.5.1 Control monitoring sites

The following sites were identified as being of suitable for use as control sites as they are composed of the appropriate lithologies, were uncontaminated by hydrocarbons of the Braer wreck and are located in rural settings exposed to coastal weathering:

- natural shoreline outcrops in the Sandwick - Mousa area
- quarries located on the Sumburgh Head peninsula

Rocks from these localities were used in the weathering experiments developed in parallel with the field environmental monitoring programme, and provided baseline geochemical data for comparison with analysis of the contaminated sites.

3.5.2 Contaminated monitoring sites

Locations in the following area were selected as being suitable for use as contaminated sites to proxy for the Jarlshof monument which could not be subjected to lithological sampling on the scale required for monitoring and experimental purposes. The sites are composed of the appropriate lithologies, were contaminated by hydrocarbons of the Braer wreck to a comparable extent with that of the Jarlshof monument and are located in rural settings exposed to coastal weathering:

- natural shoreline outcrops in the Quendale Bay - Sumburgh Head area;
- the Jarlshof monument site;
- the Ness of Burgi monument site.

Rocks from Quendale Bay/ Sumburgh Head area were used in the weathering experiments developed in parallel with the field environmental monitoring programme, and provided geochemical data for contrast with the control sites.

These sites were used for visual observations for signs of enhanced or diminished physical, chemical or biological stone weathering. These observations were evaluated by comparison with those made on the control sites at each annual inspection.

3.6 Field observations

Throughout the period from February 1994 to July 1998 field visits were made annually to Shetland. In addition to undertaking the geochemical surveys described below, observations were made on the control and contaminated monuments and rock outcrops. These field surveys were carried out to fulfil three objectives:

- to investigate the prospect of redeposition of oil on the monuments;
- to obtain samples of the residual oil from the Braer wreck;
- to compare the behaviour of the oil-contaminated sites, in terms of physical decay and biological growths, with control outcrops.

Attention was particularly paid to the prospect of regular and continuing hydrocarbon redeposition from the reservoir of weathered oil situated on the offshore seabed sediments of southern Shetland.

Figure 7 illustrates the extent of hydrocarbon contamination at Jarlshof in the period January-February 1994. These observations, together with the reported extent of oil pollution over southern Shetland at the time of the wreck (discussed in Chapter 1) were used to delineate the sample sites for the geochemical surveys, and to determine the areas which would be visited annually for visual inspection.

3.6.1 Redeposition of oil

In the February 1994 visit to Jarlshof, the resident archaeologist then employed by Historic Scotland noted that oil re-deposition on the monument area occurred primarily as a consequence of winter storms. This raised the prospect of regular, episodic contamination of the monument.

Each year, the Jarlshof monuments were closely visually examined to identify any oil residues. A x15 hand-lens was used over areas of the sections of the monument known to have been heavily coated during the spill. Moreover, coastal sandstone outcrops previously contaminated were also similarly examined.

No oil residues were found over the five years of the survey. Moreover, annual discussions with the Steward of the Jarlshof site indicated that no redeposition of oil had occurred since the February 1994 visit.

3.6.2 Residual oil

Crude oil sampled by the resident archaeologist from pools at Jarlshof during the pollution event and sealed in a glass vessel was collected in February 1994. This was subsequently used in weathering experiments described in Chapters 5 and 6.

The accessible coastline of South Mainland was walked from Maywick on the west coast to Helli Ness on the east coast. The island of Mousa was also surveyed. This whole area was visited in 1994 and 1995. In subsequent years the only areas along the coast from Garth's Ness to Sandwick were surveyed.

Oil residues were absent over the survey area throughout the five-year monitoring period. The one exception was, however, in the vicinity of the Braer wreck at Garth's Ness. Here in 1994 sticky oil residues were seen to coat patches of beach pebbles, and extensively cover soil and grass in the bay. A distinctive, strong diesel-like odour prevailed in the beach area of the bay. Samples of the oil from the beach pebbles and grass were collected in 1994. In subsequent years the visual appearance of the oil residues diminished as grasses re-colonised the area. However a distinct layer of oil was still present in the soil beneath the grass cover at the time of the final survey in 1998. Residual oil also remained under beach pebbles over this area in 1998.

3.6.3 Sandstone monument and sandstone outcrop survey

To observe any differences in weathering behaviour which may be a consequence of hydrocarbon contamination the following sandstone monuments were inspected annually:

- Jarlshof;
- Ness of Burgi;
- Stanydale;
- Clickhimin.

Mousa Broch was similarly surveyed in 1995 and 1997 when sea conditions permitted.

Attention was particularly paid on these surveys to obvious differences in the extent of biological growths over the monuments compared with Jarlshof.

Similar surveys were also performed on control and contaminated sandstone outcrops in the following areas:

- shoreline outcrops in the Sandwick area;
- quarries located on the Sumburgh Head peninsula;
- previously contaminated shoreline outcrops in the Quendale Bay - Sumburgh Head area.

It was not possible to differentiate between the uncontaminated monuments and outcrops and those which had been coated in hydrocarbons. Each displayed comparable levels of biological growths, which appear to be controlled more by proximity to coastal weathering conditions than any history of oil pollution.

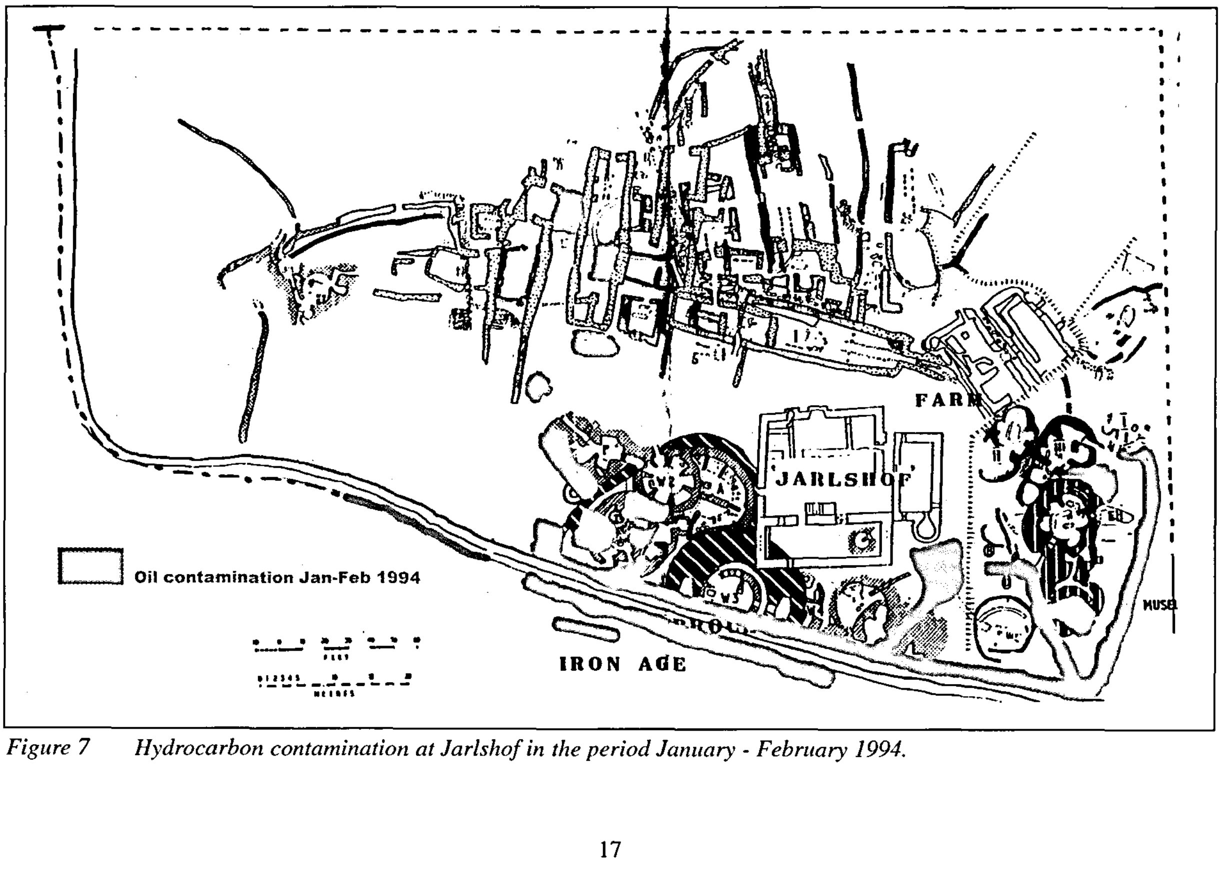
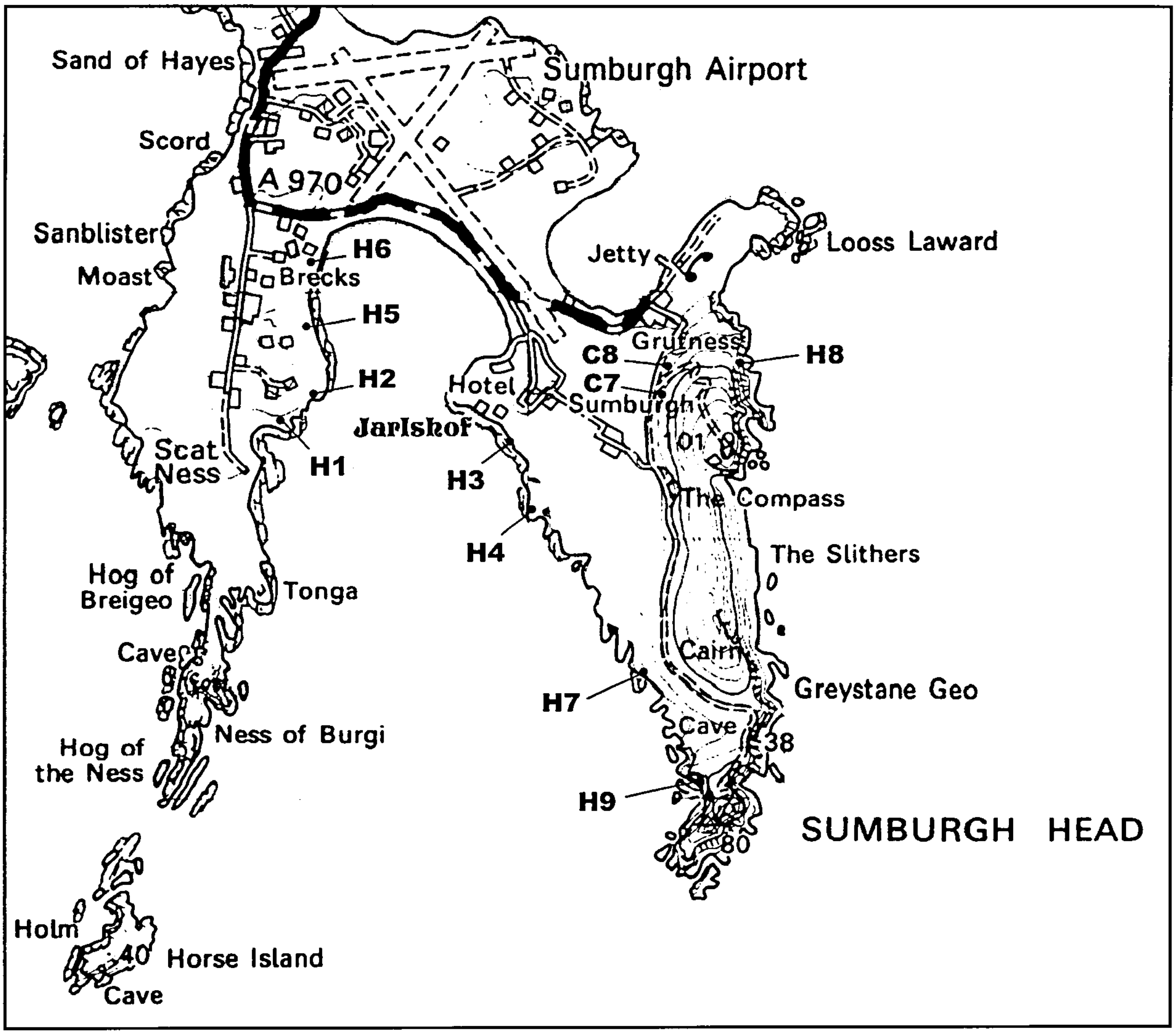


Figure 7 Hydrocarbon contamination at Jarlshof in the period January - February 1994.



KEY

Contaminated site sample station numbers prefaced by 'H'

Control site sample station numbers prefaced by 'C'

Note that sample sites C1 to C6 are located to the north at Sandwick.

Figure 8 Lithogeochemical Survey Sample Sites: Sumburgh area.

4. ENVIRONMENTAL MONITORING: GEOCHEMICAL SURVEYS

4.1 Lithogeochemical survey

Natural geological outcrops of the sandstone lithologies which were used to construct Jarlshof were sampled annually over the period 1994-1996. Samples were collected from contaminated coastal outcrops in the Jarlshof area, and control samples were taken from quarries near Sumburgh Head and coastal outcrops to the north around Sandwick (Figure 8 and Table 4).

Control sites	Lithology
1	pebbly sandstone
2	pebbly sandstone
3	pebbly sandstone
4	pebbly sandstone
5	flagstone
6	flagstone
7	flagstone
8	flagstone

Contaminated sites	Lithology
1	pebbly sandstone
2	pebbly sandstone
3	pebbly sandstone
4	pebbly sandstone
5	flagstone
6	flagstone
7	flagstone
8	flagstone
9	flagstone

Table 4 Lithogeochemical survey sample sites.

In contrast to their low concentrations in sandstones, sulphur, nickel and vanadium can occur at high levels in hydrocarbons (up to c. 5% for sulphur and c.2000 mg/kg for Ni and V) these elements therefore act as a fingerprint for hydrocarbons.

Gullfaks crude oil typically contains 1.8 mg/kg V and 1.3mg/kg Ni in pre-weathered condition. The concentration of these elements may be expected to increase as the volatile constituent mass of the crude oil is lost on weathering, with a concomitant enhancement of residual elements in the heavier fraction. Nickel and vanadium were used as fingerprinting or tracer elements for hydrocarbon contamination in the study area. Sulphur was not used because of the irregular presence of iron sulphide minerals in the sandstone lithologies which would render unreliable any monitoring survey based on this element.

4.1.1 Baseline data

To be effective, any monitoring survey must have reliable baseline or background data for comparison with the survey findings. In the absence of such information, it is not possible to make reliable decisions regarding the degree to which any sample or area has been contaminated.

The Regional Geochemical Atlas of the British Geological Survey provided the necessary baseline data for nickel and vanadium for the sandstones in the study area.

Lithology	Ni	V
pebbly sandstone	4-80	48-448
flagstone	8-32	48-112

Note: data in mg/kg.

Table 5 Baseline sandstone lithogeochemical data (Institute of Geological Sciences, 1978).

4.1.2 Analytical method

Determination of the elements was made by energy-dispersive X-ray fluorescence on sandstone control samples and samples known to have been contaminated by the Gullfaks crude oil.

Each sample was cleaved to ensure the exposed surface and a depth of stone to a maximum of 2cm was subjected to analysis. Sufficient rock was cleaved to provide at least 0.5kg for preparation. This was done to ensure any surface and near-surface contribution to the Ni and V concentration from hydrocarbons was not excessively diluted by a large rock mass. The sample was ground to a fine powder in an agate disk mill, and compressed into a disc under high pressure prior to analysis. Three replicates of each sample were analysed.

4.1.3 Results

Table 6 shows the mean results for each site, for each of the three years of the survey. As can be seen, there is no significant or consistent variation between the concentration of Ni and V in the control samples with those found in the samples from contaminated zones. Furthermore, a comparison with the baseline data range in Table 5 illustrates that all results fall within the background threshold concentration levels. This is shown graphically in Figures 9 and 10. Following these findings the lithogeochemical survey was ceased after the 1996 field season.

4.1.4 Conclusions

The lithogeochemical survey results indicate that no hydrocarbon residues remain from either the initial contamination phase or from any subsequent redeposition of oil from the sea bed sediments.

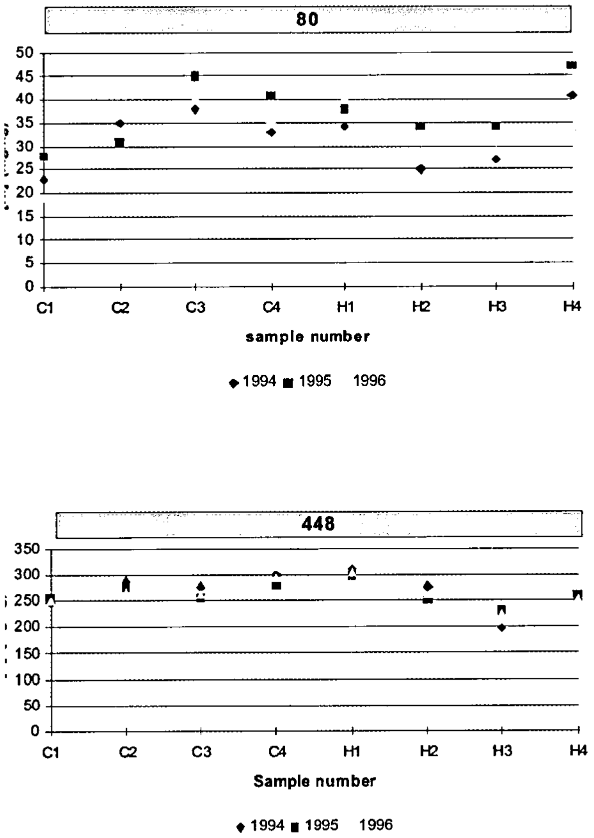
The data confirm visual observations made over the collection period and indicate that the Jarlshof monument may therefore be considered to be clear from any residual hydrocarbon contamination.

4.2 Soil geochemical survey

To complement the lithogeochemical survey, a soil geochemical survey was also implemented. Natural microbial degradation of hydrocarbons in soils is well known, and in some instances an increase in microbial activity following oil contamination has been recorded (Leahy & Colwell 1990). Monitoring the soil hydrocarbon concentration of the Jarlshof site would permit an evaluation of the residence time of such residues and the duration of any potential conservation threat to the monument.

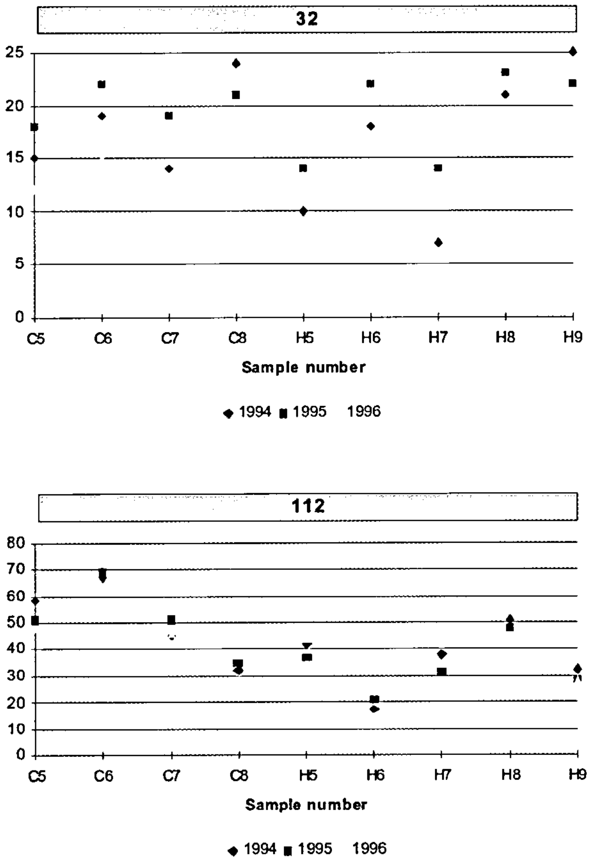
4.2.1 Sampling strategy

Polyaromatic hydrocarbons are pervasive in soils world-wide, and reflect both the distribution of combustion products from the atmosphere and natural occurrences of these compounds. Natural concentrations in a range of unpolluted soil types throughout Europe have been shown to contain hydrocarbon concentrations ranging from 33 - 13,000ppb (Blumer 1961, Vogt et al. 1987; Windsor & Hites 1979, Youngblood & Blumer 1975). In contrast,



▭448 = background threshold concentration
C = control samples, H = contaminated area samples

Figure 9 Ni and V concentrations in pebbly sandstone facies



▭112 = background concentration range
C = control samples, H = contaminated area samples

Figure 10 Ni and V concentrations in flagstone sandstone facies

	1994		1995		1996	
	Ni	V	Ni	V	Ni	V
Control sites						
1 pebbly sandstone	23	247	28	258	19	251
2 pebbly sandstone	35	287	31	276	38	266
3 pebbly sandstone	38	277	45	254	41	262
4 pebbly sandstone	33	301	41	280	36	294
5 flagstone	15	58	18	51	12	48
6 flagstone	19	67	22	69	15	72
7 flagstone	14	45	19	51	17	46
8 flagstone	24	32	21	35	22	28

Means	Ni	V
pebbly sandstone	34	271
flagstone	18	50

	1994		1995		1996	
	Ni	V	Ni	V	Ni	V
Contaminated sites						
1 pebbly sandstone	34	311	38	297	41	304
2 pebbly sandstone	25	277	34	249	29	261
3 pebbly sandstone	27	198	34	231	29	226
4 pebbly sandstone	41	249	47	260	44	253
5 flagstone	10	42	14	37	17	44
6 flagstone	18	17	22	21	21	12
7 flagstone	7	38	14	31	12	35
8 flagstone	21	51	23	48	19	55
9 flagstone	25	32	22	28	19	28

Means	Ni	V
pebbly sandstone	35	260
flagstone	18	35

Note: data in mg/kg

Table 6 Lithogeochemical Survey Results

contaminated soils in urban regions however show hydrocarbon concentrations in the 20,000 - 300,000 ppb range (Blumer et al. 1977, Butler et al. 1984, Jones et al. 1989).

In South Mainland, Shetland local background hydrocarbon concentrations will be enhanced by the deposition of combusted and uncombusted aviation fuel due to the proximity of Sumburgh airport. This loading will have been enhanced by airborne aerosol deposition of oil from the Braer wreck. Hydrocarbon deposition in the Jarlshof area resulting from aircraft activity was present prior to the Braer incident, and is an active, continuing process. This source of contamination was consequently regarded as a background source for the purposes of this monitoring survey which was focused on the consequences of the Braer depositional event.

4.2.2 Soil survey

Baseline soil data

Baseline data were therefore obtained from soils in the Sandwick area. These overly comparable bedrock to the Jarlshof site and provide a valid control comparison. Sample sites are illustrated in Figure 14.

Contaminated soil data

To provide a contrasting comparison, soils from Garth's Ness, close to the wreck site were sampled. Samples were taken from the heavily contaminated bay by the burn, and from the cliff top above the wreck site. Sample sites are illustrated in Figure 13.

Jarlshof monument survey

The Jarlshof monument site was subjected to a survey with samples taken from both exposed sites and others in the lee of monument structures. The sample sites were selected on the basis of a distribution across the site encompassing areas that had been heavily contaminated, and those with minimal hydrocarbon deposition. Sample sites are illustrated in Figure 11.

Ness of Burgi monument survey

The Ness of Burgi monument area was similarly sampled across the site. The highly exposed location of this monument results in heavy leaching of the thin soil by seawater and sea-spray. Sample sites are illustrated in Figure 12.

Sampling procedure

A hollow steel probe, 20mm in diameter was inserted into the soil to a depth of 80-100mm. The resultant soil plug was extracted with a plunger directly into a sample bag which was immediately sealed. Three replicate samples were taken at each site. To prevent cross-contamination of samples, the probe and plunger were cleaned using deionised water and paper towels.

Since, except in the most heavily contaminated areas of Garth's Ness, the hydrocarbon residues remained in the upper 20mm of the soil profile, it was not necessary to take deep core samples for monitoring purposes. Samples were taken from each site annually over the period 1994-1998.

4.2.3 *Analytical method*

A proprietary environmental field test kit was employed to monitor the degradation of hydrocarbon residues in soils. This method has been evaluated and recommended by the United States Environmental Protection Agency (USEPA, 1990). The kit is manufactured by HNU and is based on a catalysed solvent reaction with the soil hydrocarbon residue. This yields a coloured solution which is compared with a standardised colour range to obtain the sample hydrocarbon concentration. The detection limit is 0.5 mg/kg.

To a 10mL ampoule of the extraction solvent, 5g of soil were added. The soil was finely divided with a spatula in order to increase the surface contact between the solvent and the soil and therefore favour maximum extraction of hydrocarbons from the matrix. The solvent is decanted into a test tube and the colour-development catalyst added. The hue and colour intensity that subsequently developed was compared to colour standards to determine the hydrocarbon concentration.

Three replicates were analysed for each soil sample and the results averaged.

4.2.4 *Results*

The results of the five-year survey are shown in Table 7. It is clear from this data, that baseline or background concentration may be taken as 1mg/kg (1,000ppb). This concentration level is within the natural background range for soils, and may be accounted for by the organic-rich, peaty nature of the soils coupled with decades of regular atmospheric deposition as a consequence of heavy aircraft activity over the region.

Figures 15 and 16 show the relative accumulation of hydrocarbons at Garth's Ness and Jarlshof sample sites. The bar charts in these figures illustrate that degradation of the residual hydrocarbons has occurred over the five-year monitoring period. This trend is more clearly illustrated for each of the Jarlshof sample sites in Figure 17.

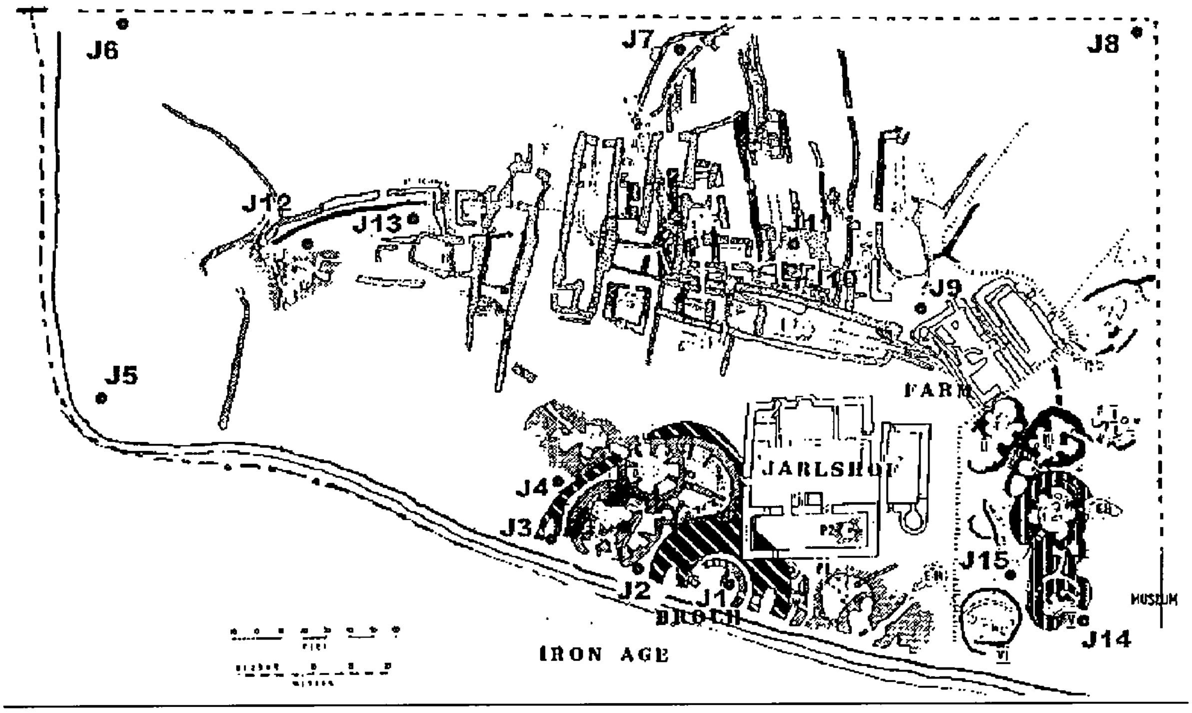


Figure 11 Soil survey sample sites at Jarlshof (hydrocarbon contaminated site).

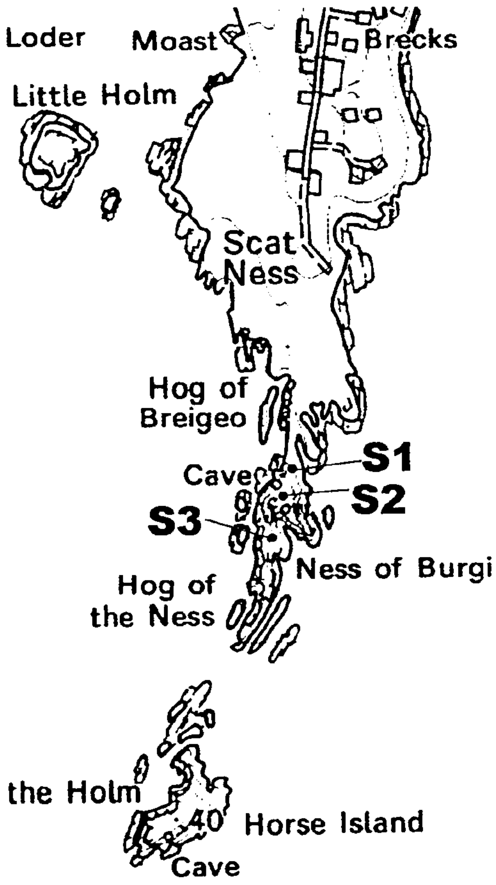


Figure 12 *Soil survey sample site at Ness of Burgi (hydrocarbon contaminated site)*

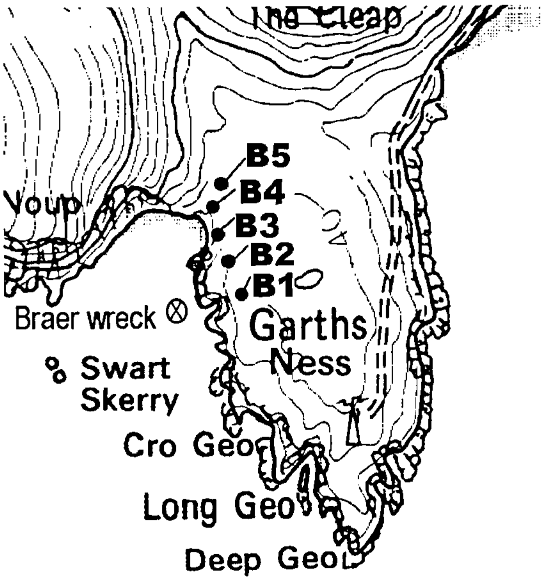


Figure 13 *Soil survey sample site at Garth's Ness (hydrocarbon contaminated site)*

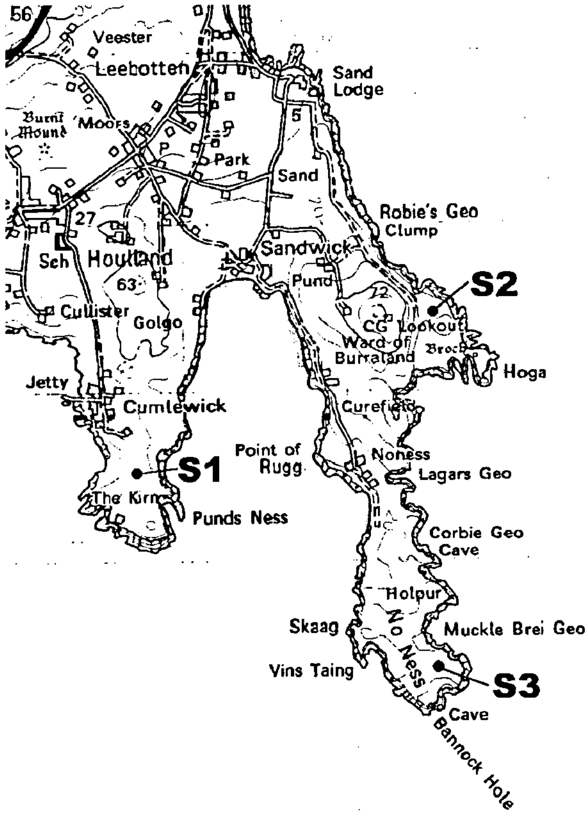


Figure 14 *Soil survey sample site at Sandwick (control site for baseline values)*

Year	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**
Jarlshof						
Station J1	100	70	50	25	5	1
Station J2	50	25	10	5	1	1
Station J3	500	200	100	70	25	1
Station J4	50	30	15	5	1	1
Station J5	50	20	10	5	1	1
Station J6	20	5	5	1	1	1
Station J7	100	50	20	5	1	1
Station J8	25	5	1	1	1	1
Station J9	100	60	25	10	1	1
Station J10	50	20	5	1	1	1
Station J11	25	15	5	1	1	1
Station J12	50	25	15	1	1	1
Station J13	50	25	10	1	1	1
Station J14	300	100	70	30	5	1
Station J15	70	50	20	5	1	1
Ness of Burgi						
Station S1	1	1	1	1	1	1
Station S2	1	1	1	1	1	1
Station S3	1	1	1	1	1	1
Garth's Ness (Contaminated for comparison)						
Station B1	25	15	5	1	1	1
Station B2	50	30	10	5	1	1
Station B3	1000	1000	1000	1000	800	800
Station B4	1000	1000	1000	1000	800	800
Station B5	1000	1000	1000	1000	800	800
Sandwick (Control for comparison)						
Station S1	1	1	1	1	1	1
Station S2	1	1	1	1	1	1
Station S3	1	1	1	1	1	1

Table 7 Hydrocarbon residue concentrations in soils (concentrations in mg/kg)

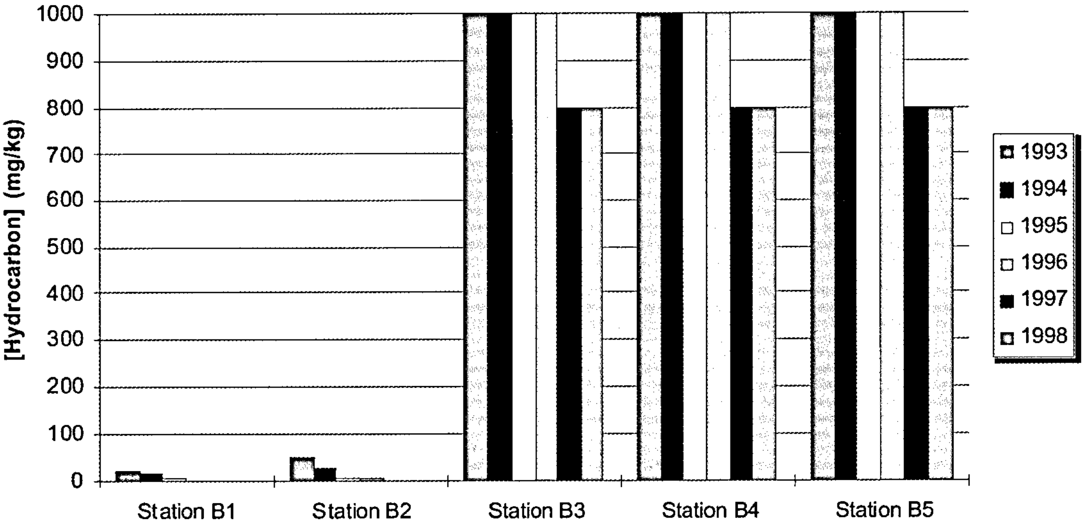


Figure 15 Hydrocarbon contaminant levels in soils from Garth's Ness

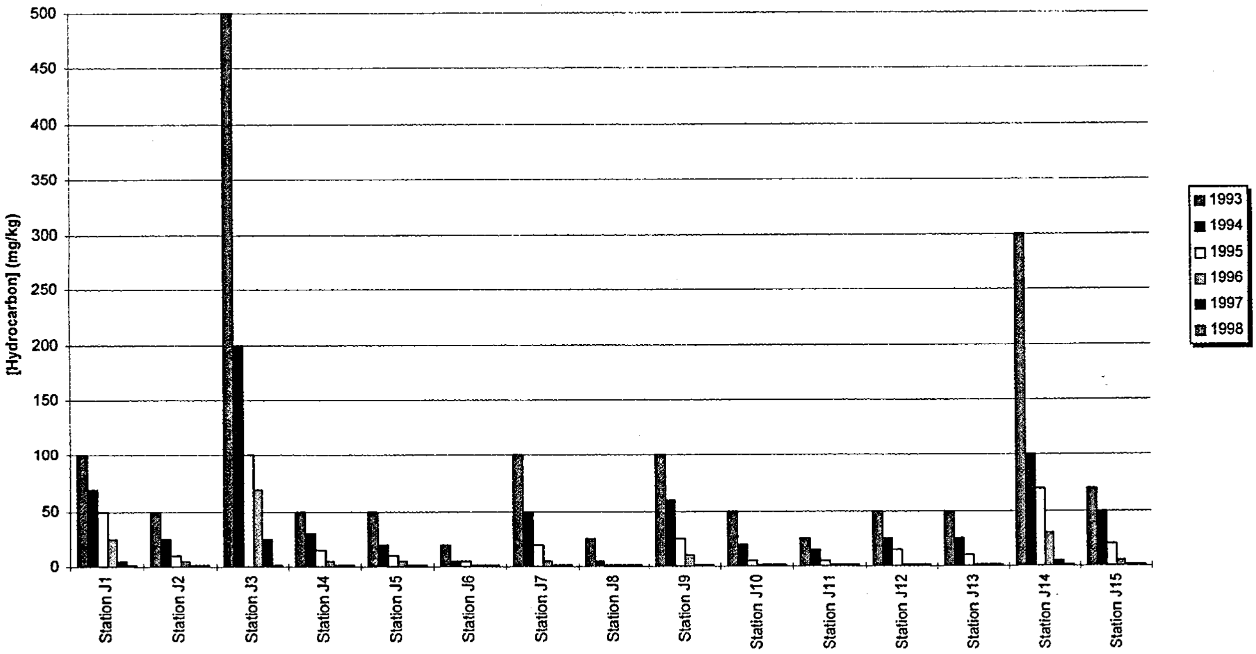


Figure 16 Hydrocarbon contamination levels in soils from Jarlshof.

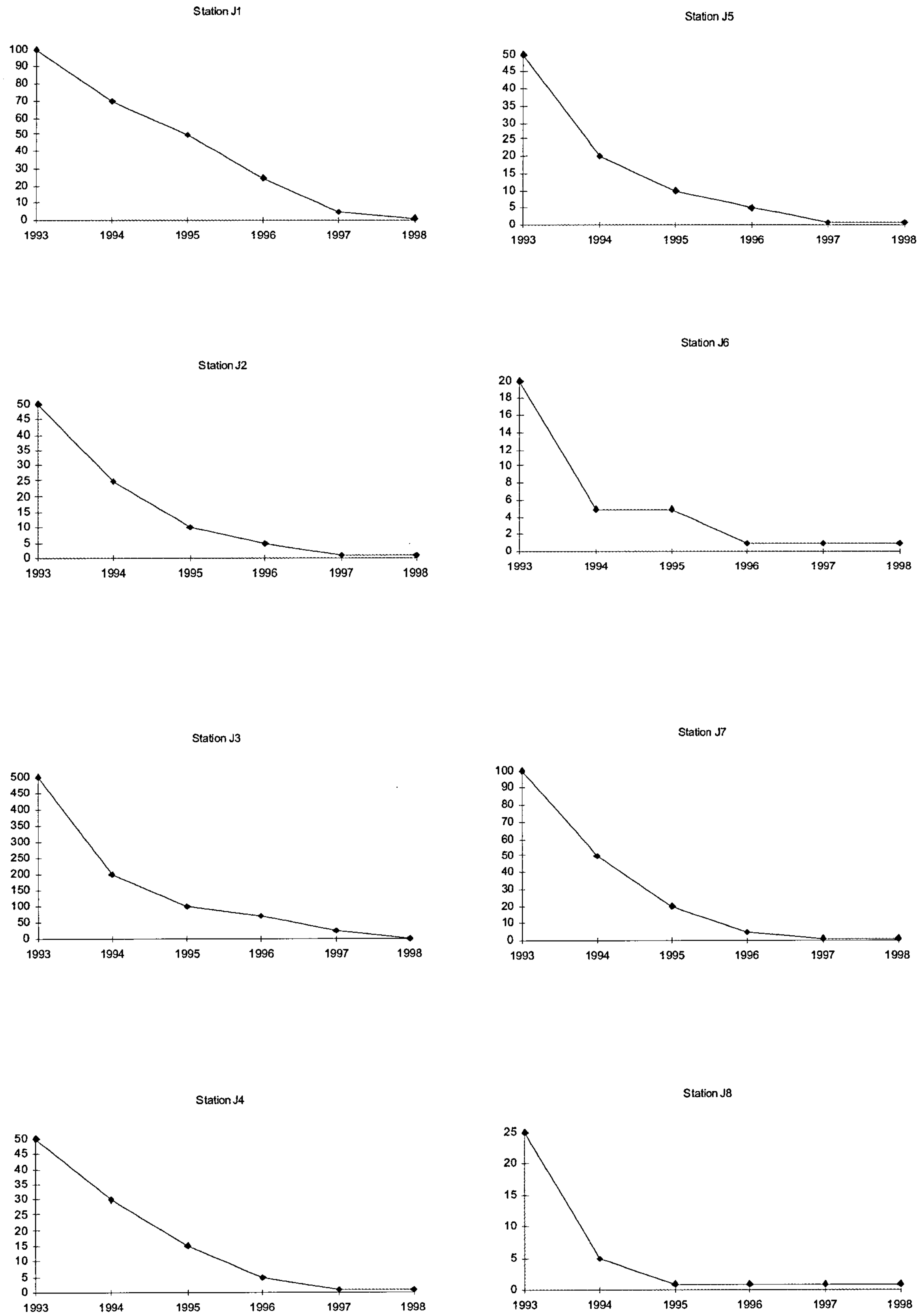


Figure 17 Decline in hydrocarbon concentration with time at Jarlshof sample stations (hydrocarbon concentrations in mg/kg)

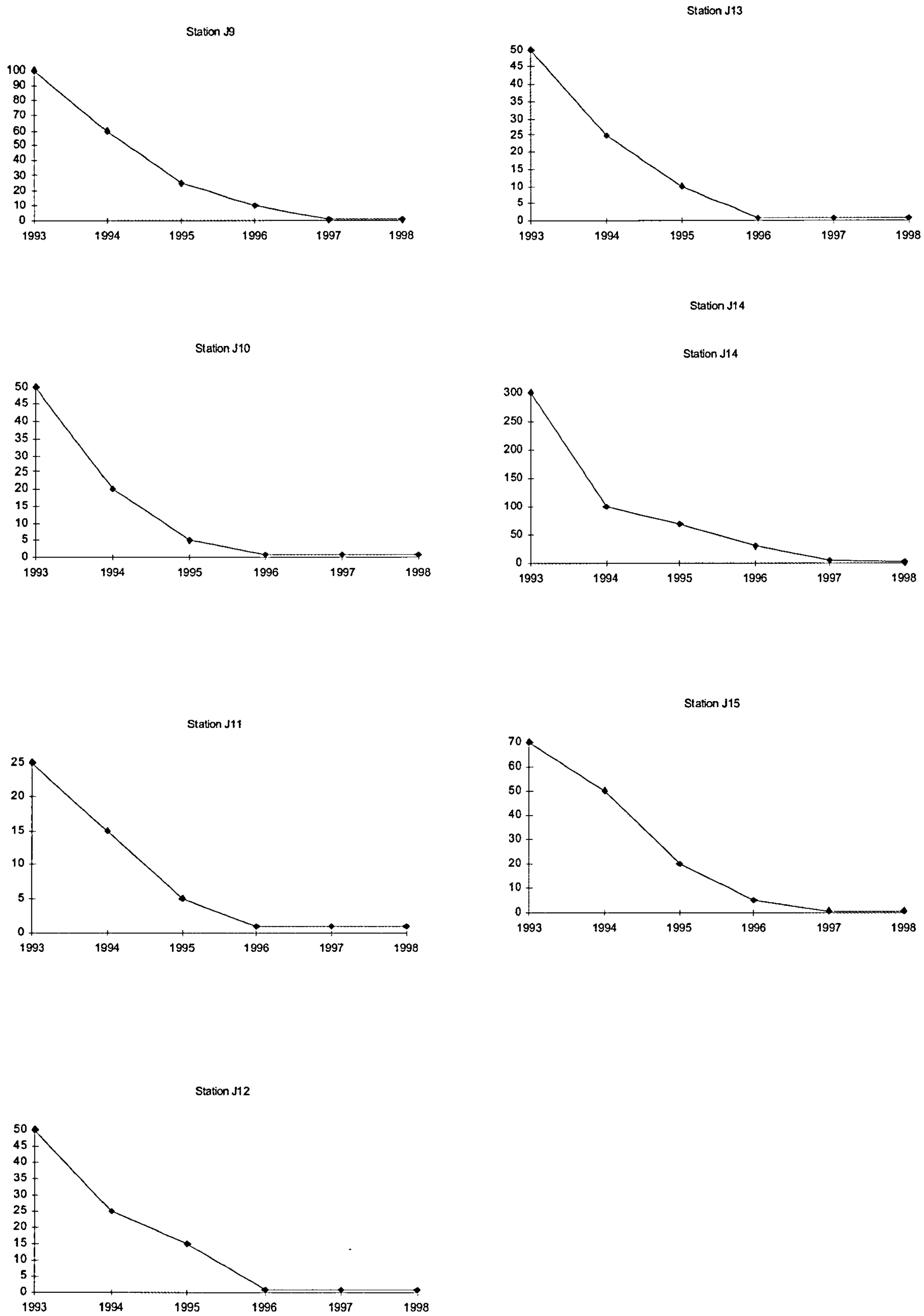


Figure 17 (continued) Decline in hydrocarbon concentration with time at Jarlshof sample stations (hydrocarbon concentrations in mg/kg)

4.2.5 Conclusions

The soil survey data shows that all but the most heavily contaminated sites re-attained the background hydrocarbon concentration level five years after the pollution incident. By the sixth year all survey sites displayed background concentrations, the only exceptions being the sites within the bay at Garth's Ness (samples B3-B5). At these sites a thick coating of waxy oil residue remained within the upper soil profile, a feature not observed elsewhere.

Since at no site did the hydrocarbon concentration rise during the monitoring period, it is evident that redeposition of hydrocarbons from the reservoir in the seabed sediments is not a problem, and the sites are unlikely to experience a recontamination event from the remaining oil of the Braer.

Biodegradation of hydrocarbons in soils is a well-recognised phenomenon (Leahy & Colwell 1990). It is probable that this was the mechanism behind the observed decline in hydrocarbon soil levels over the monitoring period, and it raises the question as to whether such a mechanism might be active on stone surfaces, Of particular interest in this respect is the observation by Leahy & Colwell (1990) that microbial activity can be enhanced by the presence of hydrocarbons. Under such conditions this action would have implications for enhanced biodeterioration of building stone. This prospect is addressed in the Chapters 5 and 6 of this report.

The soil data clearly indicate that hydrocarbon contamination at Jarlshof is no longer present, and the site has returned to its pre-Braer condition. At Ness of Burgi continual and heavy drenching and leaching by seawater had removed any hydrocarbon residues prior to initiation of the survey.

5 EXPERIMENTAL INVESTIGATIONS: PHYSICO-CHEMICAL IMPACTS

5.1 Changes in oil chemistry on weathering

Crude oils vary widely in chemical and physical properties and once exposed to weathering they rapidly undergo degradation due to a number of chemical and physical processes. The most significant initial weathering process is evaporation where the lighter volatile fractions of the oil are lost within the first few hours (this is usually fractions up to C10). Crude oil is also biodegraded by micro-organisms such as bacteria. Since no single microbial species can utilise more than 2 or 3 carbon-types and most preferentially consume the light fractions, it is important to find how crude oil changes by weathering.

5.1.1 Analytical method

There are a wide range of techniques available to the analyst for the analysis of oil, these include gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR) and high performance liquid chromatography (HPLC). The technique chosen for these experiments was GC-MS. It combines the powerful technique of gas chromatography for separating volatile mixtures into individual components, and mass spectrometry which is an extremely sensitive technique for the identification of pure substances. GC-MS has become a major analytical tool for the analysis and identification of all kinds of oil products and crude oils (Butt et al. 1986).

The instrumentation used was a Hewlett-Packard 5890 series 11 gas chromatograph coupled to a Hewlett-Packard 5971A mass spectrometer with a computerised chromatogram library.

Five different samples were analysed:

(1) Gullfaks crude oil taken from the MV Braer.

(2) Shetland grass taken from the area of the disaster about a year after the incident and stored in a paper bag at room temperature.

(3) Uncontaminated Shetland grass as a control, stored in a plastic bag at room temperature for 48 hours prior to extraction.

(4) Sample of sandstone coated with Braer oil and left outdoors for 8 weeks to be weathered, during which time the stone was exposed to heavy rain, snow and high winds.

(5) Sample of sandstone of the same type as above, exposed outside during the same period as a control.

Sandstone samples were stored in a cupboard at room temperature for 4 weeks prior to analysis.

GC-MS operating parameters

Oven Programme

Initial temperature	40°C for 10 minutes
Final temperature	280°C for 5 minutes
Heating rate	15°C per minute
Total run time	31 minutes

Mass Spectrometer

Total ion mode

Mass range of 10-550 amu

Solvent delay 3 minutes

Sample preparation

(1) Braer oil was analysed directly by GC-MS.

(2) Uncontaminated grass was washed with deionised water before extraction procedure to remove any particulate hydrocarbon contamination e.g. from car exhausts, prior to GC-MS analysis.

(3) Shetland grass used as received before extraction and GC-MS analysis.

(4) Both sandstone samples were crushed in a ball mill to powders before extraction and prior to GC-MS analysis.

The GC-MS can only take liquid samples hence the oil had to extracted from the samples of interest so that analysis by GC-MS could be carried out. The sample of Braer oil was analysed directly by GC-MS without dilution in solvent because it was of a low viscosity, volatile and the risk of contamination of the column or damage to the instruments was extremely unlikely.

Extraction procedure

Samples

10g contaminated Shetland grass
10g uncontaminated Shetland grass
30g of oil contaminated stone
30g of uncontaminated stone as a control

Method

(1) Each sample was placed into stoppered conical flasks.

(2) 30ml of n-pentane was added to each sample.

(3) The flasks were placed in an ultrasonic bath at 25°C for 30 minutes to agitate the samples hence releasing the oil and impurities from the oil contaminated samples and the impurities from the control samples.

(4) Solvents were filtered through ordinary filter paper into small beakers and the residues washed with 20ml n-pentane.

(5) Beakers left in warm fume cupboard for solvent to evaporate.

(6) Small amount of n-pentane added to beakers prior to analysis by GC-MS to solubilise the samples for analysis

5.1.2 Results

The mass spectrometry results of the 50 largest peaks of the Gullfaks oil before weathering (Figure 18, Appendix B) shows the constituents of the oil. These range from 7-membered alkanes (i.e. the first peak is most likely 2-methyl-hexane) to very large membered molecules (i.e. the 50th peak is most likely eicosamethylcyclodecasiloxane).

Figure 19 shows the results of the Shetland grass control, this is the baseline for the contaminated grass sample so that the oil peaks would not be confused with the carbon compound peaks of grass.

Figure 20 is the contaminated Shetland grass sample showing how the oil composition has changed after two years of weathering. As can be seen from the chromatogram all the lighter fractions of the oil have evaporated off leaving the heavy tar fractions. No quantitative results could be obtained from the mass spectra of this sample since the oil was at too low a concentration to give an accurate identification of any of the molecules in the oil sample.

Figure 21 shows the results for the sandstone control which provides the baseline for the oil-on-sandstone experiment.

Figure 22 shows the results of the oil-inoculated sandstone sample which was weathered for three weeks. No identification of the individual molecules

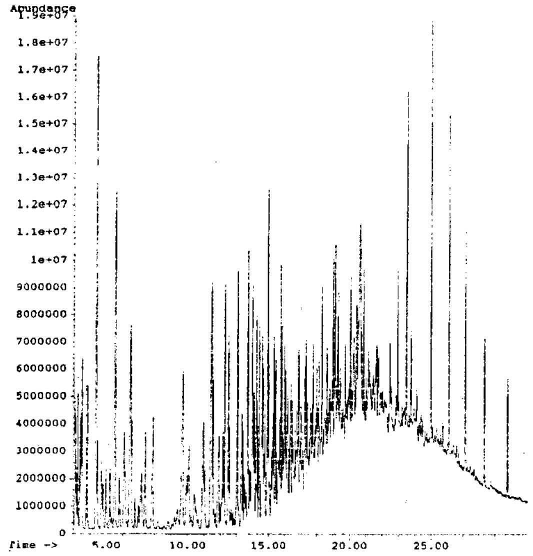


Figure 18 GC-MS chromatogram showing composition of Gullfaks oil before weathering.

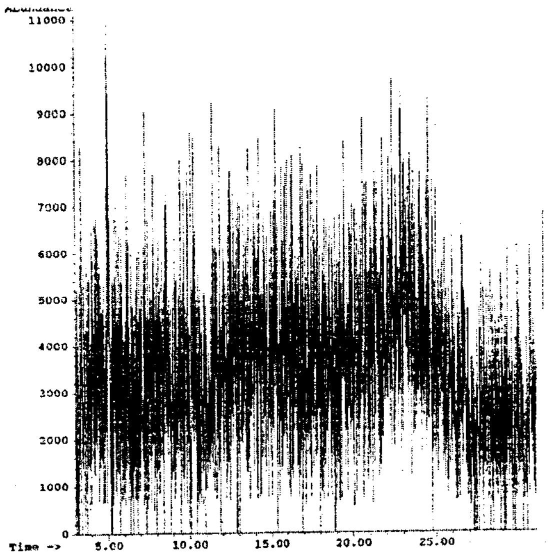


Figure 19 GC-MS chromatogram of Shetland grass control sample.

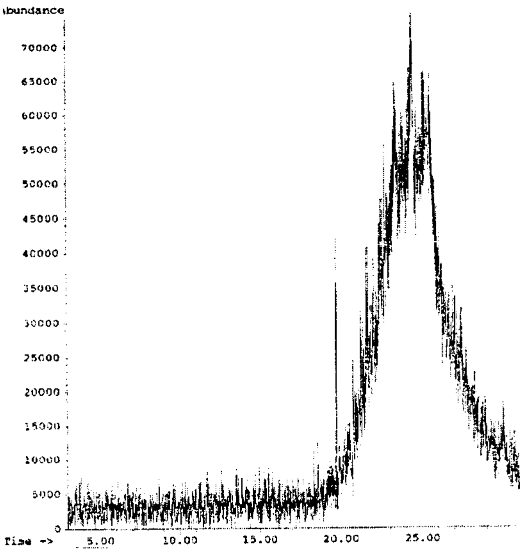


Figure 20 *GC-MS chromatogram of hydrocarbon-contaminated Shetland grass sample after two years of weathering*

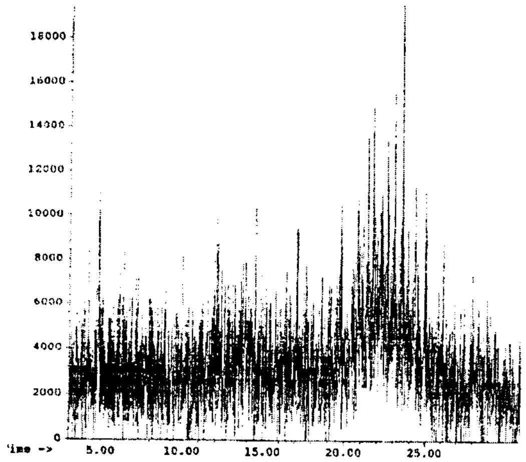


Figure 21 *GC-MS chromatogram for the sandstone control sample*

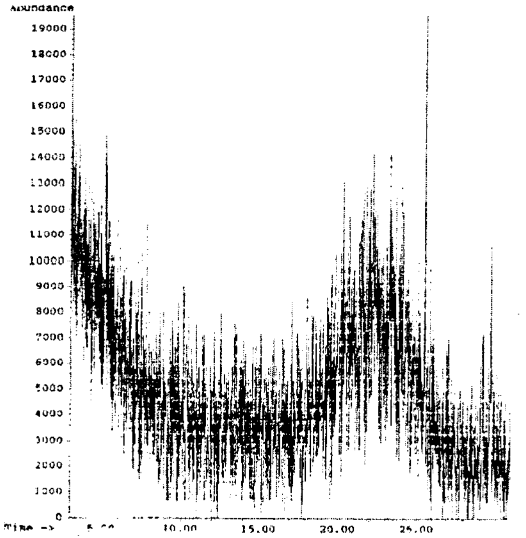


Figure 22 *GC-MS chromatogram of the oil-inoculated sandstone sample, weathered for three weeks*

present could be obtained since the concentrations were too low. However it is possible to observe from the chromatogram that some light fractions of the oil remain on the stone, the medium fractions had mostly been lost and as expected the heavy fractions of the oil were also present. Continued weathering of the oil on sandstone sample for a further five weeks showed all hydrocarbon residues were degraded.

5.1.3 Conclusions

The results of the GC-MS studies show that after initial weathering the oil loses lighter volatile hydrocarbon fractions leaving the heavier tar fractions as residues. Further work would be required to identify the individual molecular components of these residues.

5.2 Impact of oil on the physical weathering of sandstone by freeze-thaw action

Sandstone samples (ORS pebbly sandstone and flagstone facies) were used in a series of experiments to investigate whether a hydrocarbon layer could act as an impermeable hydrophobic barrier. If this were the case then hydrocarbon deposition could enhance sandstone degradation by freeze-thaw action.

5.2.1 Methodology

Each of the sandstone types used in the investigation were cut into a series of 2.5cm cubes. These were used in the following series of experiments.

Experiment series 1

Sample treatments

1. No treatment (control sample).
2. 1ml coating of Braer oil over entire surface.
3. 1ml coating of water over entire surface.
4. One side coated in 1ml Braer oil, other five sides coated in 1ml water.
5. Coated in 1ml oil and left for 2 weeks then 2ml water allowed to soak in.

Procedure

All samples were frozen for 72 hours and then permitted to thaw at room temperature. Observations were made on the samples with a view to identification of any fracture development, grain dislocation and spalling. This cycle was repeated for a period of three weeks to permit simulation of repeated freeze-thaw cycles.

Experiment series 2

Sample treatments

A. Samples placed half immersed in deionised water.

1. No treatment (control sample)
2. 1ml oil coating on upper surface

B. Samples soaked with 2ml deionised water overnight.

1. No treatment (control sample).
2. 2ml oil coating on upper surface.

Procedure

All samples were frozen for a period of three weeks and then permitted to thaw at room temperature. Observations were made on the samples with a view to identification of any fracture development, grain dislocation and spalling. The samples were then frozen again for 72 hours then thawed at room temperature. This freeze-thaw cycle was repeated for a period of 12 weeks.

5.2.2 Results

Experiment series 1

Results from the first series of experiments showed that after three weeks of freeze-thaw cycling no physical change was observed on any of the samples.

Experiment series 2

Results obtained from the second set of experiments showed that after 10 weeks of continuous freeze-thaw cycles the sandstones coated with oil showed no difference in behaviour from the control samples.

5.2.3 Conclusions

Neither type of sandstone used in this investigation showed any change in response behaviour to repeated freeze-thaw cycling when coated with a layer of hydrocarbons.

It would appear therefore that no direct threat from physical weathering on the conservation of historic sandstone monuments can be expected to result from contamination by crude, uncombusted hydrocarbons.

6 EXPERIMENTAL INVESTIGATIONS: BIOLOGICAL IMPACTS

6.1 Effect of oil on the growth of epilithic microbial communities: in agar culture

To investigate whether the presence of hydrocarbons inhibits or promotes the growth of micro-organisms commonly found on stone various epilithic micro-organisms (algae, bacteria and fungi) were selected from existing laboratory cultures and grown under their ideal growth conditions.

Four different strategies were used to see how sensitive the micro-organisms were to oil, both at the surface of the substrate and within the substrate.

- Zone inhibition spread plates with an oil well in the centre to determine whether micro organisms would grow up to the well.
- Zone inhibition pour plates so that it could be more easily observed if the oil promoted or inhibited growth.
- Spread plates with agar oil suspension to bring cultures into direct contact with oil. If oil inhibited growth at the surface this could then be readily observed.
- Pour plates with agar oil suspension so that it could be easily observed if oil inhibited growth at the surface and within agar.

The agar used was specific for the growth of algae, bacteria and fungi, details appear in Table 8.

Micro-organism	Agar type
Algae	Bolds-basal media (BB)
Bacteria	Nutrient agar (NA)
Fungi	Malt extract (ME)

Table 7 Culture media employed

The agar, glassware and Gilson pipette tips used in each experiment were sterilised in an autoclave, ready-sterilised plates were employed and for each inoculation a new sterile tip was used.

6.1.1 Methodology

Zone inhibition spread plates

The following procedure was adopted:

(1) Micro-organisms were extracted from decaying stone samples by shaking in 0.01% TWEEN 80 (a chemical used to dissolve calcium bridges releasing the micro-organisms from stone particles and mucilage present) and 0.05%. peptone (a protein which prevents inhibition of growth caused by the TWEEN 80).

(2) Inoculation (5ml) of BB, NA and ME plates for algae, bacteria and fungi respectively (inoculum was pipetted onto the centre of the agar and spread over the agar surface using a sterile glass spreader).

(3) Wells dug out in centre of each agar plate and 60ml of Braer oil poured in for test plates and sterilised water for control plate (two test plates and one control plate for each agar type).

(4) Each plate was sealed with parafilm to prevent drying out and contamination by micro organisms.

(5) Bacteria and fungi incubated at 23°C in darkness, algae incubated at room temperature under 8W white light to allow photosynthesis.

The micro-organisms on the remaining three types of plates were subcultured from the original zone inhibition spread plates. They were subcultured from the test plates since it was known that these micro-organisms grew in the presence of oil. Six different micro-organisms were selected, one species of algae, 3 species of bacteria and 2 species of fungi. Once taken from the original plates they were placed into separate sterile physiological saline solutions (9ml), shaken and refrigerated for one day until required. This procedure was repeated for the agar oil suspension plates since these saline solutions cannot be kept for more than four days as cultures are not long-lived under these conditions.

Zone inhibition pour plates

The procedure was the same as for the zone inhibition spread plates. However, the agar was inoculated with 0.1ml of the appropriate saline solution containing the isolated micro-organism species when molten at 45°C and shaken by hand prior to pouring onto the plates. Care had to be taken when inoculating the agar since if the temperature was lower than 45°C it set in the sample bottle and if the temperature was higher than 45°C the micro-organisms would have been destroyed.

Agar oil suspension spread plates

The same procedure was followed as for the zone inhibition spread plates, however, 9ml of molten agar had 1ml of Braer oil added. This was shaken in a sterile sample bottle by hand to disperse the oil throughout the agar. The controls had 1ml of sterile water added to them in place of the oil. The agar suspensions were then poured into plates and the surface inoculated with the particular micro-organism in 1ml saline solution.

Agar oil suspension pour plates

Procedure was the same as for the zone inhibition pour plates. 9ml of agar was mixed with 1ml of Braer oil and 1ml of saline solution containing the particular micro-organism, 1ml of sterile water was used in place of the oil for the control plates. Incubation conditions were the same as for the other types of plates, however, the fungi spread and pour agar-oil suspension plates were left in an incubator for three weeks at 12°C to see if the fungi were living off of the oil after initial observations were taken.

6.1.2 Results

Results from these experiments showed how oil contamination affected the growth of the selected micro-organisms.

Zone inhibition spread plates

After three days the fungi and bacteria had grown as discrete colonies over the surface of the agar with no zone of inhibition around the oil in the centre. The fungi grew in discrete colonies with no zone of inhibition around the oil well in the centre, in fact the fungi were observed growing in the oil wells.

The bacteria grew with no zone of inhibition around the oil well. From these plates three different bacteria were subcultured for the later experiments.

The algae were observed growing after 14 days in discrete colonies with no zone of inhibition around the oil well with colonies growing up to the lip of the well.

Zone inhibition pour plates

After three days the fungi were observed growing as discrete colonies with no zone of inhibition around the oil wells. The colonies on the control plate were, in general, larger in size. Growth was also denser on the control plate than the test plates. This suggests that the fungi are inhibited in their growth by the presence of oil.

After eight days it was evident from microscope observations that the bacteria were growing as discrete

Figure 23 Fungal plaques in the agar

Figure 24 Bacterial plaques in the oil-rich suspension

Figure 25 Green fungi test plate after 16 weeks growth

micro-colonies. No zones of inhibition were evident on the plates.

No zone inhibition pour plates for algae were undertaken since the algae had not grown sufficiently to be subcultured when this experiment was initiated.

Agar oil suspension spread plates

Fungi were observed growing after three days. The fungi on the test plates grew mostly as discrete colonies whereas the fungi on the control plates were mostly joined together. After three weeks incubation at 12°C, plaques or zones of clearance appeared in the agar (Figure 23).

After three days the bacteria on the control plates covered the surface of the agar. The bacteria on the test plates appeared as discrete micro-colonies only visible under a microscope. One species of bacteria was observed growing around the oil globules. On these test plates a large number of plaques were present in the suspension suggesting that the bacteria were using the oil as a nutrient source (Figure 24). Attempts to subculture individual bacteria species for further experiments were unsuccessful.

After 25 days, algal growth on the control plates appeared as discrete colonies but no growth was observed on the test plates, suggesting that the algae were not able to propagate in the close proximity of oil. One plate was re-inoculated as a check to see if the algae had been destroyed by the inoculation procedure, after 28 weeks incubation a small colony of algae had grown, however, this died about 21 weeks later suggesting the algae are not able to live for long in an oil-rich environment.

Agar oil suspension pour plates

The fungi isolates had grown mostly as discrete colonies after three days incubation in both the control and test plates, although some colonies appeared to be joined together. The oil present appeared to be much less dense after incubation with plaques present, some fungi also appeared to have soaked up oil giving them a dark appearance (Figure 25).

The growth on the bacteria plates was very dense after three days incubation with a high proportion of plaques present and most of the oil having disappeared.

Algal colonies had grown on the oil free control plates after 25 days, but no growth had occurred on the test plates. This further demonstrates that the algae cannot live in an oil contaminated environment.

6.1.3 Conclusions

It is evident from the results of micro-organisms growth in culture on spread and pour plates, that some fungal and bacterial isolates may be highly tolerant to the presence of oil. These fungal and bacterial isolates grew, in general, as smaller colonies than on the control plates. Initial growth of fungal isolates at the agar surface on the zone inhibition plates was inhibited but recovered fully after 1-2 weeks when growth had advanced into the oil well. On both the fungal and bacterial agar-oil suspension spread and pour plates the appearance of plaques, or zones of clearance, demonstrated for the removal of oil from agar.

The results from the algae inoculated plates showed that although the algae were able to grow relatively close to oil (i.e. in the zone inhibition plates) algae were not able to grow very well - if at all -when the oil was in a greater concentration and dispersed throughout the area (i.e. in the agar-oil suspension plates).

The data imply that any enhancement of biodeterioration of sandstone following hydrocarbon contamination will be due to fungal and bacterial growth mechanisms and not due to algal colonisation.

6.2 Effect of oil on growth of epilithic microbial communities: on sandstone

This series of experiments was undertaken to investigate how oil affects growth of micro-organisms in a natural environment setting, where the micro-organisms take nutrients from the stone substrate and surrounding moisture.

The pebbly sandstone and flagstone sandstone facies were used in the experiment. Two replicate samples of each stone type were used for both controls and tests. The mixed inoculum, containing algae, bacteria and fungi, was of the same composition as that employed in the zone inhibition spread plates, described above.

6.2.1 Methodology

(1) Each sample was coated with 0.5ml Braer oil (test) or 0.5ml sterile water (control) and allowed to soak in prior to inoculation.

(2) The uppermost surfaces of each sample were inoculated with 0.1ml of inoculum.

(3) The test and control samples (in duplicate) were placed into separate petri dishes containing artificial rain.

(4) Samples were sealed with parafilm to prevent drying out and contamination by micro organisms.

Figure 26a Incubation from light to dark conditions. Control sample on the left. Note the brown slime coating the test sample on the right.

Figure 26b Algal growth on flagstone samples. Note the growths on top of the oil contaminated stones.

(5) Incubation (a) under illumination, 8W white light at room temperature for algal growth (b) in darkness at room temperature for bacterial and fungal growth.

6.2.2 Results

Incubation under illumination

After 42 days incubation the control plates of both stone types had algal colonies present on both the stone surfaces and in the water. No algal colonies had developed on any of the test samples which had been treated with oil.

The test samples had, however, developed a brown slime over some sections of the stone surface that were above water level. In addition, the surface of the water was also covered in a cream-coloured film which contrasted with the original dark colour of the oil. On microscopic examination of the brown slime it was revealed to contain many bacterial cells. A sample of the slime was inoculated onto an agar plate and developed into bacterial colonies similar in culture characteristics to the original three bacterial isolates.

Incubation in darkness

Following 42 days incubation the controls of both stone types showed no visible growth. The test samples similarly showed no sign of growth.

To ascertain whether light accelerated the initiation of the brown bacterial slime, samples that had been incubated in the dark were then incubated under illumination and vice versa.

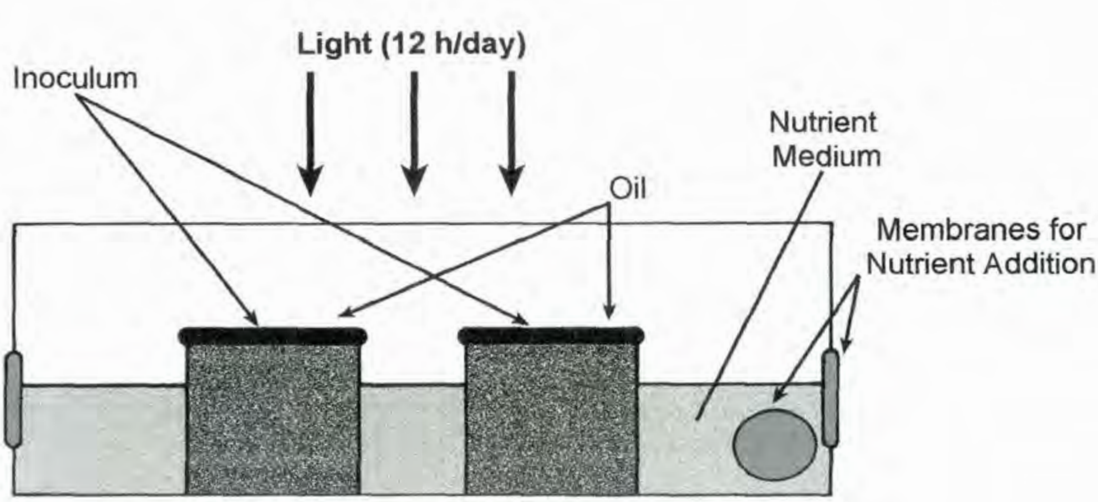


Figure 27 Experimental set-up.

Light to dark incubation

Some of the algal colonies on the controls had died following 63 days incubation in the dark. The test samples containing oil showed that almost all the oil film covering the water surface had become cream-coloured and the brown bacterial slime covered most of the stone surfaces. There appeared to be no oil left in the sample dishes (Figure 26a).

Dark to light incubation

No growth developed on the oil-free pebbly sandstone control incubated under illumination for 63 days. The flagstone control sample however developed large algal colonies. Test samples showed a large increase in the brown bacterial slime and colonisation of the stone surface (Figure 26b).

6.3 Biological growth on contaminated stones

The preliminary experiments described above were expanded into a test series to evaluate the effects of crude oil on microbial communities developing on sandstone.

The colonisation rate of micro-organisms was determined under experimentally controlled conditions by using mixed indigenous inoculum isolated from sandstone buildings. For the purpose of the experiment, sandstone blocks were pre-treated to remove any organic matter.

The following experimental series were established using the experimental set-up illustrated in Figure 27:

- Control: inoculum added on stone (no oil present).
- Oil spread on stone surface and oil-adapted inoculum added subsequently.
- Inoculum added to stone, and oil in indirect contact with the stone surface (only low molecular fractions/volatile components can reach the surface).
- Oil added after 30 days of microbial growth.

In establishing this experimental series it became clear that some method development was necessary to standardise the procedure. Accordingly experiments were set up to fulfil the following objectives:

- Development of a suitable mineral salts solution to optimise microbial growth on sandstone.
- Selection of appropriate nutrient medium to screen and isolate viable bacteria.
- Identification and development of methods to study the overall biomass, and autotrophic biomass (chlorophyll-a).
- Determination of biomass and effect of oil on microbial development.

6.3.1 Results

Mineral Salt Solution

The mineral salt solution used during this experiment was MARSS (Modified Artificial Rain Salt Solution) which contained the following in trace amounts: $MgCl_2x6H_2O$, KCl, Na_2SO_3, NaCl, NH_4NO_3, KH_2PO_4, NH_4Cl, $CaCl_2xH_2O$, $NaHCO_3$, $FeSO_4x7H_2O$, MnCl2, $ZnSO_4x7H_2O$, $(NH_4)(MoO_3)x4H_2O$, $(NH_4)_2SO_4xFeSO_4x6H_2O$.

The stock solution once prepared can be autoclaved and kept for up to 4 months.

Nutrient medium

The current methods used to isolate and further quantify the amount of bacteria in studies concerning biodeterioration of buildings and monuments make use of either high carbon content media (NA, YEA) or diluted version of the above (1/10 strength YEA). However in the literature there is no recommended method for isolation of bacteria from this specific environment. The amount of bacteria present is studied and linked to biological growth on sandstone and therefore knowledge on bacterial population is of vital importance to such studies. Another source of incomparability in such studies are the incubation conditions. Although most authors follow incubation temperature within the range 20 to 25°C, other workers tend to favour higher temperature (37°C). Comparison of existing media will always be an incomplete task due to large number of media that exist and various experimental conditions. Nevertheless, the lack of standardisation in biodeterioration studies can be overcome by comparison of a range of media of different composition. Additionally, the effect of incubation temperature and length of incubation was also evaluated.

Mixed indigenous inoculum isolated from 4 sandstone buildings was used during the media comparison experiments. The inoculum was maintained in MARSS prior to inoculation. Serial dilutions of all media were plated in triplicates, and incubated in parallel at 20, 28 and 37°C. The plates were incubated for 14 days. Colony-forming units (CFU) were determined every 2 days. All plates were kept in plastic bags during the prolonged incubation to prevent dehydration of the

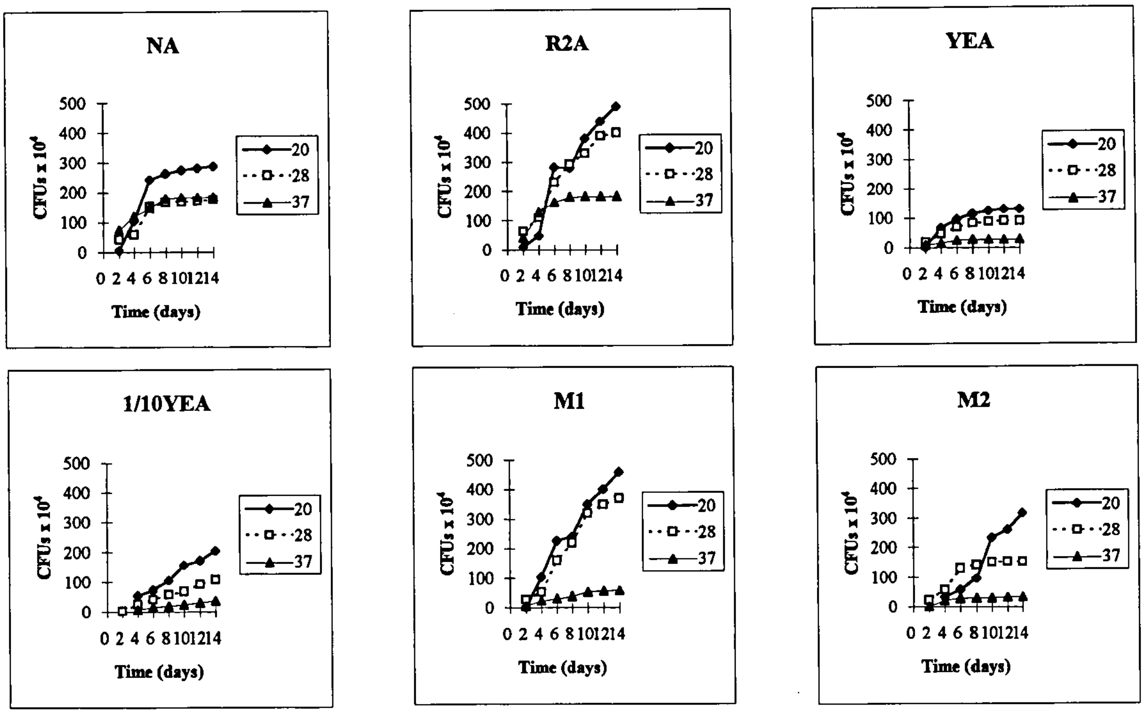


Figure 28 Selection of medium for enumeration of bacteria isolated from sandstone. Figures show average colony-forming units (CFUs) per ml for various media and range of incubation temperatures (20°C, 28°C, 37°C).

plates. The media tested were: NA, YEA, 1/10 strength YEA. In addition, two new media were compared, designated as M1 and M2, with the following composition:

M1

MARSS to dilute to 1L (1.5 strength solution of MARSS was prepared)

Casamino acids (Difco): 0.5 g/L

Yeast extract (Difco): 0.5 g/L

Sodium pyruvate (Sigma): 0.25 g/L

Dextrose: 0.25 g/L

Proteose peptone #3 (Difco): 0.5 g/L

M2

MARSS to dilute to 1L (1.5 strength solution of MARSS was prepared)

Casamino acids (Difco): 0.5 g/L

Yeast extract (Difco): 0.5 g/L

Sodium acetate: 0.25 g/L

Dextrose: 0.25 g/L

Proteose peptone #3 (Difco): 0.5 g/L

All results were obtained by using spread plates. Previous experience had shown that pour plates were unable to recover sufficient number of micro-organisms, and even when they did, they favoured the recovery of particular species, rather than a range of micro-organisms.

Figure 28 shows the average CFUs per ml for various media and range of incubation temperatures tested. At 37°C, the media which supported the highest growth were NA and R2A. During the initial 4-5 days of incubation, both NA and R2A performed equally well when compared to 20 and 28°C, but were rapidly outnumbered by the latter after day 6. In the case with M1, 37°C had 1-log lower recovery than 20 and 28°C. It was obvious that the highest temperature (37°C) showed very poor recovery as compared to 20 and 28°C. The comparison of CFUs of 20 and 28°C, showed that R2A and M1 were superior to all other media tested. Most of the colonies were well established on these two media after day 6. In fact, day 6 growth represented approximately 50% of the final count after 14 days. The colonies that developed after day 6 were small, and as other researchers had shown the number of colonies does not increase significantly

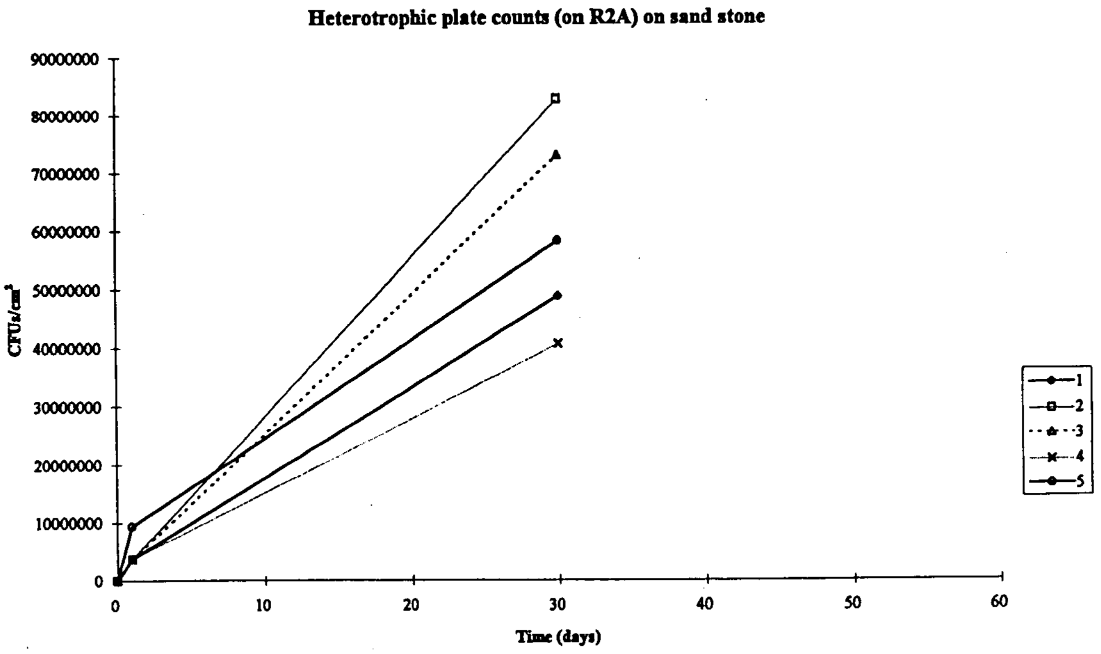


Figure 29 Heterotrophic plate counts (with R2A media) on sandstone. Numbers in key refer to replicate experiments

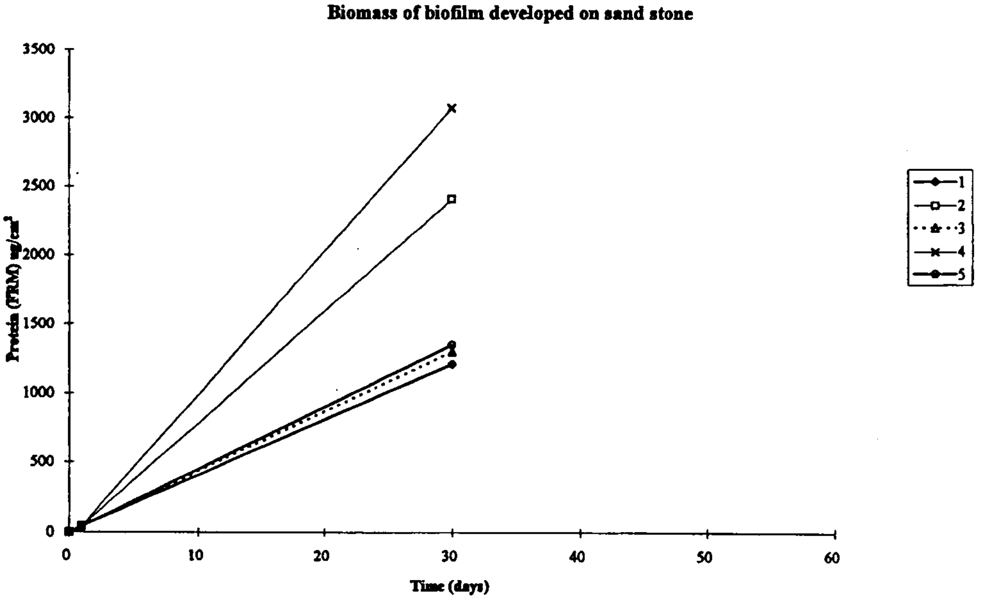


Figure 30 Biomass of biofilm developed on sandstone. Numbers in key refer to replicate experiments

after approximately 10 days. No significant difference was observed between the number of colonies recovered on R2A and M1, however R2A was the preferred medium due to its widespread use and commercial availability. From the range of the incubation temperatures tested, 20°C appeared to be the best. In later comparison, the CFUs were compared in multiple samples after days 8 and 14. Although some differences in the CFUs were found, the day 8 was considered as the final day of the incubation. Further research is pending upon developing M1 as a possible new medium for low carbon requiring (oligocabophilic) bacteria, normally isolated from sandstone or similar environments.

6.4 Development of methods for studying the biomass

The methods which were selected as suitable for the purpose of this study were used for quantification of biofilms growing on the sand particles and were developed by the Environmental Research Group at The Robert Gordon University. The changes in autotrophic biomass are being measured by using hot ethanol extraction of chlorophyll-a, and subsequent determination at 665nm. The number of viable bacteria is being determined as colony forming units (CFUs) on R2A. Measurement of the overall biomass was carried out using cell protein determination.

6.5 Determination of biomass and effect of oil on microbial development

Epilythic microbial biomass was measured during the early colonisation and growth phase of its development. The results show elevated bacterial biomass in an oil-enriched environment (Figures 29 and 30). However algal growths were minimal.

Scanning electron microscopy was used to search for any possible physical changes of the sandstone surface (see SEM photographs, Figures 31 and 32). These illustrate the colonisation of the stone by bacterialogical biomass,

It appears that bacteriological growths are more important than algae in an oil-enhanced environment. Longer-term experiments were performed to test this hypotheses (Figures 33-35).

Bacteriological growth

As shown in Figure 33, the CFUs in the samples treated with hydrocarbons increase almost 20-fold during the experiment and were twice as high as the control samples.

Algal growth

The growth of algae was only observed in the control samples (Figure 34) with little or no growth found on the oil-treated stone surfaces. Microscopic observations reveal the presence of single algal cells only on oil-covered surfaces.

Overall biomass growth

The same trend was observed in both control and oil-coated samples in the initial stages of the experiment. However, over longer incubation periods the control samples attain similar overall biomass to the oil-coated samples (Figure 35). This is a reflection of the predominance of algal biomass in the control samples contrasting with bacteriological biomass in the oil treated samples.

6.6 Conclusions

The experiments on microbial communities growing on sandstone demonstrate that fungal and algal isolates are unable to grow on a stone surface in the presence of oil. The bacteria were able to grow on a stone surface and the proliferation of the bacteria was found to be accelerated by the presence of light.

It is clear from these data that any geomicrobial decay reactions on sandstone in the presence of hydrocarbons would therefore be due to enhanced bacterial activity rather than visible biological growths.

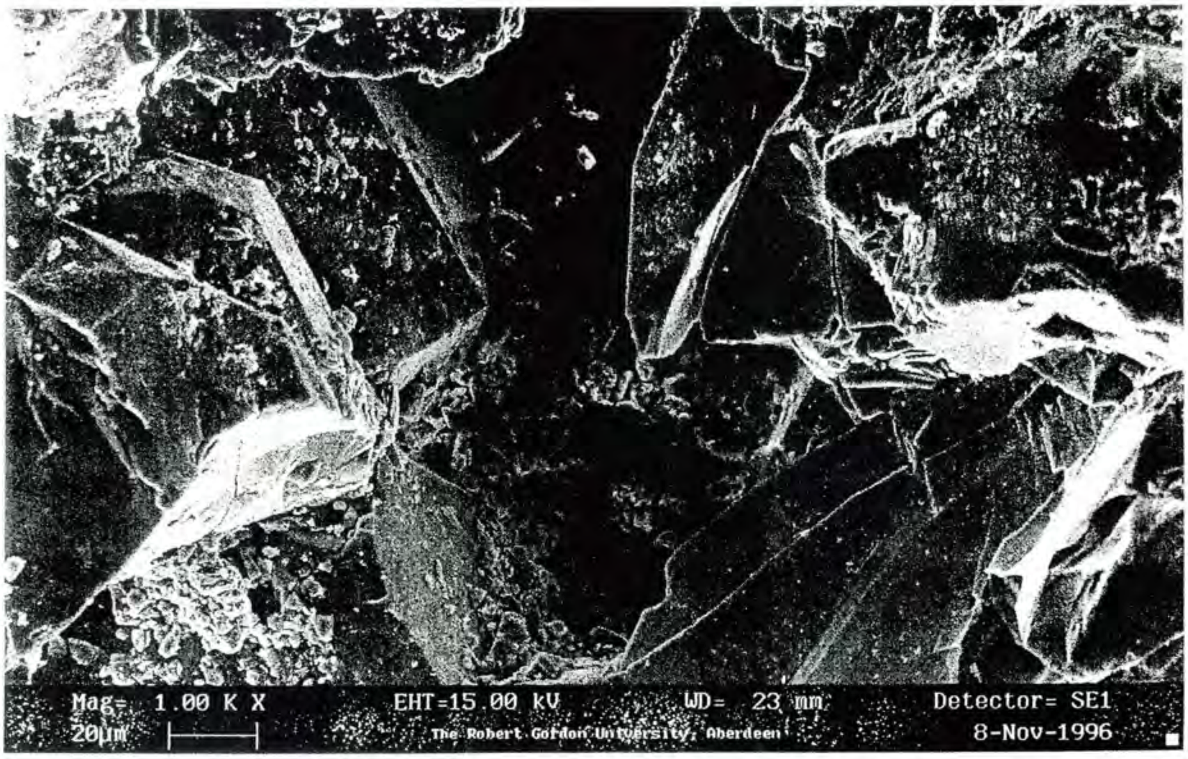


Figure 31 Scanning electron microscope photograph of sandstone prior to inoculation

Figure 32 Scanning electron microscope photograph of sandstone 30 days after inoculation showing colonisation

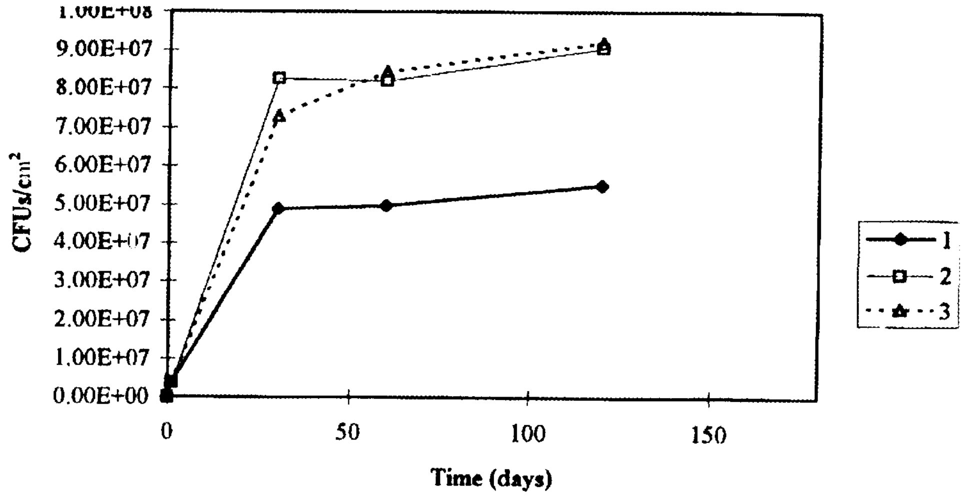


Figure 33 Bacterial biomass (CFUs on R2A media) on sandstone.
Sample 1 represents the control samples, samples 2 and 3 replicate experimental samples.

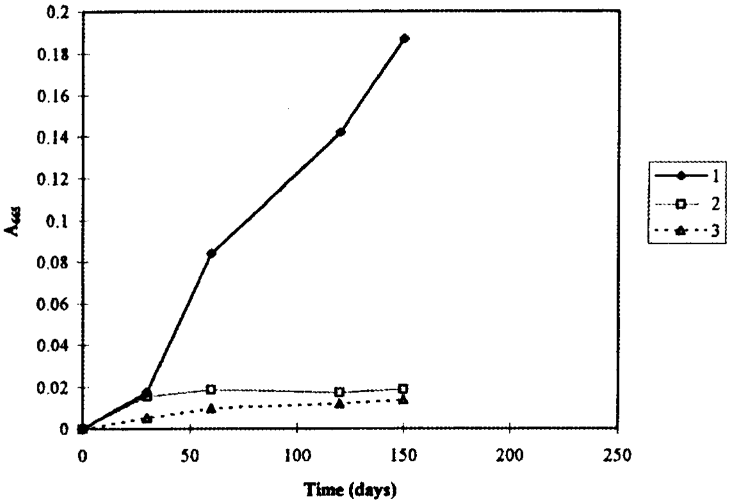


Figure 34 Chlorophyll content on sandstone.
Sample 1 represents the control samples, samples 2 and 3 replicate experimental samples.

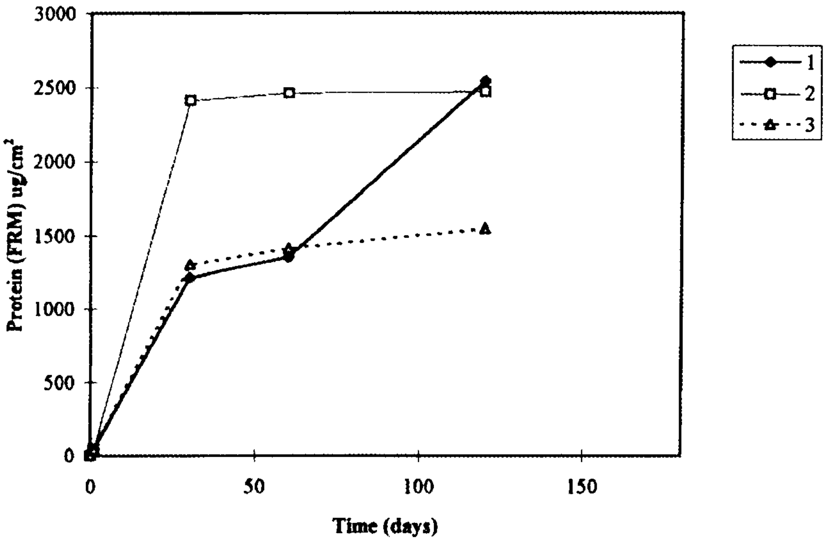


Figure 35 Total biomass on sandstone.
Sample 1 represents the control samples, samples 2 and 3 replicate experimental samples.

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Contamination of the Jarlshof monument with liquid hydrocarbons has highlighted a potential pollution threat to historic sites.

Although very much focused on monitoring the effects of the Braer incident on the Shetland monuments, this work also presents preliminary experimental investigations into the direct and indirect impacts of hydrocarbons on stone buildings and monuments. As such, this Historic Scotland-sponsored programme is the first to focus specifically on hydrocarbon impacts. It represents a pioneering study, the results of which will be of interest world-wide, and which can form the basis of future, more detailed research programmes.

7.1.1 Historic Scotland monuments in Shetland

On the basis of field observations and monitoring of the monuments, inspection and analysis of rock and soil samples from the contaminated monuments and neighbouring areas it may be concluded:

- that soil-retained oil residues have declined to background levels at the Jarlshof monument site
- that any oil residues at Ness of Burgi were rapidly leached within one year of contamination
- that stone-retained oil residues are not present at Jarlshof or Ness of Burgi monuments
- that algal growth is not enhanced by the presence of hydrocarbons
- the oil spillage from the Braer wreck poses no threat to the conservation of the Jarlshof or Ness of Burgi monuments

7.1.2 Impact of hydrocarbons on sandstone monuments

The conclusions arising from the experimental investigations have wider implications. The following comments are not only relevant to the Shetland monuments but are also applicable to sandstone buildings and monuments subjected to contamination by liquid hydrocarbons.

The experimental studies indicate:

- that the presence of hydrocarbons does not interfere with the wetting-drying cycles of the constructional sandstone which is able to "breathe" as usual
- physical freeze-thaw mechanisms leading to stone decay are not promoted by the presence of hydrocarbons
- that algal growth is not enhanced by the presence of hydrocarbons
- that algal growth may be prevented or retarded in the presence of hydrocarbons
- that bacterial growth is enhanced in the presence of hydrocarbons

These latter conclusions are particularly interesting as they imply that certain microbial-biogeochemical sandstone decay mechanisms may be enhanced by the presence of prolonged contact with liquid hydrocarbons, while others are retarded.

7.2 Recommendations

The experience of monitoring the local soil and lithological environment at Ness of Burgi and Jarlshof, coupled with observations on the monuments and the experimental work permits some recommendations to be made on the treatment of sandstone buildings and monuments contaminated by crude, liquid hydrocarbons. These recommendations are based upon the outcome of only one contamination event, one stone type and a series of preliminary experiments. Notwithstanding these limitations, the following suggestions should prove helpful for workers faced with a similar pollution event.

At both Ness of Burgi and Jarlshof the scouring action of seawater proved valuable in removing residual hydrocarbons from both the stonework and surrounding soils. This result is in part due to the nature of the contaminant crude oil (Table 1) but suggests that it may be possible to remove oil contamination through the use of high-pressure water sprays if the surface of the monuments is amenable to such treatment. The use of phosphate-free detergent in such a spray treatment may further aid hydrocarbon dispersal and removal. Any detergents employed should be free of phosphates and non-ionic to prevent the encouragement of colonisation by biological growths.

Physical removal and replacement of surrounding soil and covering protective turf should not be necessary. Only in cases of extreme, or visually obvious, oil coating and contamination should this be necessary, as natural biological action will reduce slight-moderate oil pollution to background levels within 3-4 years. If removal of the soil-turf cover is deemed necessary, professional archaeological advice should be sought first, since removal of soil and turf could be destructive of sensitive archaeological levels and on the case of legally protected sites would require formal permission.

In highly permeable paths or gravel areas, replacement of the filling material may prove necessary as tar-like hydrocarbon residues commonly accumulate sub-surface in such structures and do not readily degrade.

Monitoring surveys following the contamination event should pay particular emphasis on the stimulation and development of biological growths by residual hydrocarbons. If the application of a suitable biocide is deemed necessary, the direct interaction of the biocide with the hydrocarbon residue should be tested on a representative trial stone surface prior to application.

The finding that the presence of hydrocarbons affects some micro-biogeochemical sandstone decay mediums is worthy of further investigation. There are potential implications for the conservation of stone buildings and monuments in environmental settings subjected to the deposition of liquid hydrocarbons and hydrocarbon combustion products. Such situations are not restricted to the urban environment, and are a function of vehicular and air-borne traffic density.

APPENDIX A
SOURCES OF INFORMATION

CD ROM

Catalogue of UK Official Publications (UKOP) 3/1990 - 1/1999

The only single source of bibliographic reformation on publications of organisations in the UK. It lists official documents published either by H.M.S.O or directly by organisations from 1980 onwards. Database contains 160,000 records as of 6/1989 and grows at the rate of approximately 4-5,000 records per quarter.

Community Research and Development (CORDIS) 1/1994 - 1/1999

European Community programme established to stimulate the protection, exploitation and promotion of the results of technological research within the EC. Disseminated information about EC research and technological developments (RTD) programmes and related matters.

Subject coverage includes; energy, environmental matter, information sciences and regional development. The objectives are concentrated on three broad areas covering the range of community research activities.

Society of Petroleum Engineers 1951 - 1995

This is an electronic index to some 20,000 technical papers submitted to the Society of Petroleum Engineers since 1951. The disk contains the first page of each paper. Full text searches can be made on the abstract and the information found on the first page of these papers.

Environmental Abstracts 1975 - 1999

From 1975 until the present, it is a database containing bibliographic records which address the impact of human kind and technology on the environment, with attention to air, water, and noise pollution, solid and toxic wastes, radiological contamination, toxicological effects, control technologies, resource management, population, endangered species and geophysical and climate change. Over 800 journal and periodicals systematically reviewed each month Up-dated quarterly.

Dialog Compendex

This is a general bibliographic database with abstracts. Update frequency every 4 months.

General Science Index 12/1993 - 12/1999

A bibliographic database which is updated monthly. It is available on-line, (up-dated twice weekly) from 1984. The subject coverage includes astronomy, chemistry, earth sciences, biology, conservation and environment. The type of material indexed includes book reviews, proceedings of symposia and conferences.

Science Citation Index 1984 - 1/1999

This is a multidisciplinary index to journal literature in the sciences The SCI cover 3,300 major journals, and indexes 600,000 new items each year.

Comupendex 1989 -1/1999

From 1970 this bibliographic database is updated weekly. It is a version of the Engineering Index providing abstracting information on world engineering and technology. Sample subject coverage; environment, civil engineering, biological engineering and geological engineering.

Coverage 4,500 journals and selected government reports and books.

ONLINE

DATASTAR

Chemical Engineering Abstracts (CEAB)

This database gives full coverage of published information required by practising chemical engineers from 1987. It also incorporates theoretical engineering abstracts. Since 1981 CEAB has been available online, and is updated monthly. Database size: 104,036 documents. The subject content includes chemical engineering and biotechnology abstracts and includes coverage of corrosion and environmental factors. Articles with a significant technical content are selected and documents are assigned to one of the 52 sections with cross references to direct the user from one section to potently relevant abstracts in other sections. Sources include, over 5000 technical journals which are covered. Books, European patents, press releases and technical reports are also extensively covered. Geographic coverage is world-wide and includes full article reviews, technical items and some book reviews.

Science Citation Index (SCISEARCH)

SCISEARCH is a highly current multidisciplinary index to the international literature of science and technology. It corresponds to the science citation index and contains additional material from the current contents series of publications. The database has been online since 1987, is updated weekly and contains over 8 million documents. With weekly updating, SCISEARCH offers extremely fast access to the international literature. SCISEARCH offers versatile retrieval, in addition to more conventional search methods, and citation indexing, which allows identification of current articles using the earlier papers which they have cited. The database has recently been enhanced to offer author keywords. The database indexes articles, reports of meetings, letters, etc. of approx. 4,400 scientific and technical journals published world wide.

Current Contents Search (CCCC)

The online compendium of every Current Contents edition in print. A bibliographic database with coverage from march 1992. The database is updated weekly, simultaneously with the Current Contents print editions: clinical medicine; life sciences; engineering, technology and applied sciences; agriculture, biology and environmental sciences; physical chemical and earth sciences, social and behavioural sciences; arts and humanities. A full bibliographic record with abstract can be retrieved. More than 6,500 research journals in every scientific discipline are indexed for CCCC search.

Chemical Abstracts (CHEM)

Provides comprehensive coverage of all aspects of chemistry interpreted in the widest sense, including reactions, chemical substances, materials, techniques, procedures, apparatus, properties, theories and applications m chemistry and chemical engineering.

Online data from 1967 and updated twice monthly the database contains over 5 million documents on all fields of chemistry, chemical engineering, biochemistry, geochemistry, mineralogy. The database draws citations from 12,000 journals, plus patents, conference proceedings dissertations, technical reports and books. Journal articles account for around 73% of the database. Geographic coverage is world wide and some 500,000 new documents are added to the database each year.

Enviroline (ENVN)

This is a source of information on all areas of the technical, scientific, socio-economic and policy aspects of a wide range of environmental subjects. Online records date from 1971 with monthly updates. The database contains 187,000 documents and provides a broad coverage of scientific, engineering, political and socio-economic aspects of environmental research, resources, issues and awareness. Its interdisciplinary base provides access to more than 5,000 intentional primary and secondary sources. The database corresponds to environmental abstracts. More than 3,500 scientific, technical, business, trade, professional and general periodicals are covered. Further extensive coverage is provided by the inclusion of papers and proceedings of environment-relateded conferences, reports by private and governmental agencies and from congressional hearings environmental project reports and news releases.

Event - (EVNT)

This is a database of international conferences, conventions, symposia, trade fairs, exhibition and major sporting events. Current information to 2000+ and updated monthly, the database contains over 31,000 documents. It contains current and advance information on world wide conferences, exhibitions, trade fans and sporting events. Some workshops and courses are now being included. The events are defined by more than 700 subject classifications.

Toxline (TOXL)

Toxicology information on the effects of drugs, pesticides and other chemicals. The database contains over 1 million documents from 1981 and is updated monthly. Covergae encompasses published material and research in progress in adverse drug reactions, carcinogenesis, mutagenesis, teratogensis, environmental pollution, food contamination and other areas. Most documents include abstracts or indexing terms or CAS registry numbers or a combination of these. Toxline users a wide range of secondary sources, which are included in Toxlines subfiles.

BLAISE - LINE

System for Information on Grey Literature in Europe (SIGLE)

The SIGLE file contains records of "grey" or "nonconventional" literature, i.e. documents that are issued informally in limited numbers and which are not available through normal book-selling channels. Examples of grey literature are scientific and technical reports, theses, proceedings, technical notes, internal reports, private communications, recommendations and official documents. The database is produced by a consortium of European document centres with the help of the Commission of the European Communities. The records in SIGLE are not complete records and do not contain abstracts. SIGLE covers documents which have been made publicly available since 1981. Up until 1983, only the UK centre input documents outside the scientific and technical fields, but from 1983 onwards there is coverage of all subject fields. Records input by the British Centre also appear in British Reports, Translations and Theses (ISSN 0144 7556), published monthly by the British Library Lending Division. The database contains about 250,000 records and is updated monthly.

European Association for Grey Literature Exploration (EAGLE)

SIGLE is managed by EAGLE, an international committee consisting of representatives of those EU countries whose national centres provide information on all types of grey literature produced m their countries. The field and subject coverage contains the following areas; aeronautics, agriculture, plant and veterinary sciences, astronomy and astrophysics, atmospheric sciences, humanities, psychology and social sciences, biological and medical sciences, electronics and electrical engineering, computer scieuce, energy and power, materials, mathematical, industrial and civil marine engineering, methods and equipment, military sciences, missile technology, navigation, communication, detection and counter measure, nuclear science and technology, ordnance, physics, propulsion and fields and space technology.

H.M.S.O.

Once the sole Official UK Government Publisher, producing some 9,000 new items each year across a broad range of subject areas. The database is the direct equivalent of the daily, monthly and annual catalogues published since 1976. The database is updated monthly and approximately 9,000 HMSO imprints plus 3,000 agency records are added per year

DIALOG - DIALINDEX

National - Technical Information service (file 6 ntis)

This file consists of summaries of U.S. Government sponsored research, development and engineering plus analyses prepared by federal agencies and their contractors. The subject coverage includes: administration and management, aeronautics and aerodynamics, agriculture and food, astronomy and astrophysics, atmospheric sciences, biomedical technology and engineering, building technology, chemistry, chemical engineering, communication, computers, control and information theory, electron technology, energy, environmental pollution and control, health planning, industrial and mechanical engineering, library and information sciences, military sciences, navigation, guidance and control, nuclear engineering, photography and recording devices, physics, propulsion and fuels and urban and regional technology. The database contains records from 1964 with over 1.8 million records and is updated monthly.

ABI/inform (file 15)

This file includes details on every aspect of business, including company histories, competitive intelligence and new product development. Subject coverage includes: accounting, banking, computers, economics, engineering management, communications, finance, health care, human resources, insurance, information trends, law management, marketing, public administration, real estate, taxation, telecommunications and transportation. The database is updated weekly, which adds apporximately 1,200 records per update, and contains over 6 million documents dating from 1971.

PTS PROMPT (file 16)

Predicates an Overview of Markets and Technology (PROMT). This is a multiple industry database that provides broad, international coverage of companies products, markets and applied technologies for all industries. Subject coverage of the file includes: new products and technologies, research and development, new and expanded facilities. PTS is a multi-industry database and offers comprehensive coverage of more than 60 manufacturing and service industries including: biotechnology, chemicals, construction, fabricates metal production, petroleum and energy products. The file dates from 1972, is updated daily with approx. 2,500 per update. The file size is now in excess of 3 million records.

Enviroline (file 40)

This covers the worlds environmental related information. It provides indexing and abstracting coverage of more dm 1,000 international primary and secondary publications reporting on all aspects of the environment. Subject coverage includes: air pollution, environmental design and urban ecology, land use and pollution, toxicology and environmental safety, transportation, water pollution, weather modification and geophysical change. The database contains over 250,000 records dating from 1971, and is updated each with approx. 1,200 records per update.

CAB Abstracts (file 50)

This was formally the Commonwealth Agricultural Bureaux. CAB has long been recognised as a leading scientific information service in agriculture and related sciences. Coverage includes: animal science and production, veterinary medicine and parasites, crop science and production, forestry, economics, development and sociology, machinery and buildings and biotechnology. Over 500,000 records date from 1984, with a monthly update of approx. 12,000 documents.

Geoarchive (file 58)

A comprehensive database covering all types of information sources in geoscience. Subject coverage includes: energy sources, engineering geology, geochronology, historical geology, palaeontology, petrology, sedimentology and tectonics. The database contains 1 million records from 1972 with a monthly update of approx. 5,000 records per update.

EMBASE (file 73 Excerpta Medica)

This is a comprehensive index of world literature on human medicine and related disciplines. Subject coverage includes, biochemistry, bioengineering, pollution control, toxicology and virology. The file holds over 9 million records from 1974 with a weekly update of approx. 12,000 documents.

PTS Aerospace Defence Markets and Technology (file 80)

This provides full text articles and abstracts covering all aspects of the world-wide aerospace industry. A sample subject coverage includes: products and systems, production, shipments, plant processes and government. The file dates from 1982 with approx. 4,000 records added per month. Current file size is over 675,000 records.

Fluid Engineering Abstracts (file 96 Fluidex)

This is a specialised data base produced by Elsevier Science publishers. It provides a comprehensive source of information on all aspects of fluid engineering and fluid behaviour. A sample subject coverage includes: coastal and inland fluid engineering, works offshore technology, multiphase flow, oil hydraulics, material properties and corrosion. The file conta8ins in excess of 500,000 records dating from 1974 and is updated monthly with 1,500 records per update.

Water Resources Abstracts (file 117)

This provides comprehensive coverage of a range of water-related topics in the life, physical and social sciences, as well as the engineering and legal aspects of the conservation, control, use and management of water. A sample subject coverage includes: nature and properties of water, water supply, augmentation and conservation, engineering works and hydraulics. The file dates from 1968 onwards, is updated monthly with approx. 1,000 records and holds 300,000 records.

Toxline (file 156)

This database covers the toxicological, pharmacological biochemical and physiological effects of drugs and other chemicals. Coverage includes: air pollution, environmental pollution, pesticides and herbicides and waste disposal. The file holds over 2.5 million records from 1965 with a monthly update of approx. 10,000 documents.

Insurance Periodicals Index (file 169)

This file indexes and abstracts 35 of the most widely read insurance industry journals and magazines. Coverage encompasses catastrophes, health insurance, legislation, pollution and products liability. Records date from 1984 and are updated weekly with approx. 300 records per update. The file currently holds in excess of 150,000 records.

Zoological Record Online (file 185)

This file provides extensive coverage of the world zoological literature with emphasis on systematic taxonomic information. Coverage includes: biochemistry, ecology, histology, palaeontology, zoogeography. The file contains 150,000 records from 1978 and is updated monthly with approx. 7,000 records.

Paperchem (file 240)

This is a comprehensive database covering all patent and journal literature related to pulp and paper technology. The file includes related topics such as engineering and process control, corrosion, pollution and water. The file dates from 1967, is updated monthly apart from the month of June with approx. 1,200 records per update. The file contains over 350,000 records.

Petroleum/Energy Business News Index - (file 257 APIBIZ)

The file indexes 25 primary publications which cover a broad of current political, social and economic news. Subject coverage includes: exploration and drilling, refining and marketing, government publications, environmental issues, and transport and storage.

The file holds over one million records from 1975 with a weekly update of 650+ documents.

CA Search (file 399)

CA Search combines the condensed version of chemical abstracts with controlled vocabulary. Subject coverage includes, the literature of chemistry and its applications, is divided into the following principle areas: applied chemistry, biochemistry and biology, chemical engineering, chemistry of substances, macromolecular chemistry, organic and inorganic chemistry, physical and analytical chemistry and properties and reactions. The sources are derived from journals, patents, reviews, technical reports, monographs, conference and symposium proceedings, dissertations and books. The file holds from 1967, which is updated weekly. The file size is over10 million records.

Infomat International Business (file 583)

This file provides a world-wide coverage of companies, products and industries with a focus on Europe. The major strength of the database is its broad coverage of industry and business publications. Subject coverage contains information on competitor activities, joint venture and license agreements, company news, new and emerging technologies, economic forecasts, legislation. Infomat covers a broad range industries including biotechnology, chemicals, computers, construction and civil engineering, energy, food and beverages, media marketing and advertising, packages and paper, printing and publishing and telecommunications. Infomat international Business covers over 600 sources published in more than 20 countries. The file contain information from 1986 onwards, which is updated weekly with approx. 30,000 records. The file size stands at over 1 million records.

Reuters (file 611)

This file contains the complete text of the Reuter Library Service and the Reuter Business Report. The file provides access to current (updated continuously around the clock) information on business and international news. Subject coverage includes: international news, regional news for Africa, Asia and Latin America, sports, small businesses, stocks, commodities, high technology, personal finance and energy. Reuters draws on a network of over 1,000 Reuter journalists and photographers working in over 1000 bureaux world wide. The file dates from 1987 onwards, and is continuously updated with approx. 550 records. The file size is approx. 2.5 million records.

PR Newswire (file 613)

Contains the complete text of news releases prepared by U.S. and Canadian companies, public relations agencies, trade associations, city state U.S. federal and non-U.S. Government agencies and other sources covering the entire spectrum of the news. the subject coverage includes new products, new scientific discoveries, government agency announcements, medicine and science, politics, travel and transportation, demographics and environment. The file dates from 1987and is updated continuously with approximately 500 records per day. The file size stands at over 10 million records.

McGraw-Hill Publications (file 624)

This file contains the complete text of over 30 magazines and newsletters owned and published by McGraw-Hill. Subject coverage includes: companies, economy, government, industries, labour, management and technology. Sources consist of a continually growing collection of over 30 of the premier publications for numerous industries. The file data commences at 1985, and is updated weekly with approx. 1,800 records. The file size is approx. 1.4 million records.

Business Date Line (file 635)

Contains the full text of major news feature stories from 350 regional business publications from throughout the U.S and Canada Subject coverage includes: industry regulation, major industry coverage and new product development. The file contains articles from over 350 business publications and newspapers, dates from 1985, is updated weekly and contains 700,000 records.

Trade and Industry ASAP (file 648)

This file provides the complete text and indexing for major articles for more than 90 trade-specific and general business publications. Subject coverage includes: aerospace and aviation, agriculture , forestry, commodities, business and economics, computers and electronics, construction, design and manufacturing, real estate, industrial engineering, oil and gas, public utilities, taxation and transportation. The file is updated monthly with approx. 10,000 records per update. It dates from 1983 and holds over 1 million records.

EUROPEAN SPACE AGENCY

Pascal (file 14)

The main subject area is a multidisciplinary file, covering the core of the worlds scientific and technical literature. It is the online version of the print publication "Bibliographic Internationale". Subject coverage includes: physics, chemistry, life sciences, (biology, medicine, psychology), applied sciences and technology, information sciences and documentation, energy, metallurgy, civil engineering, building and public works, earth sciences, biotechnology, zoology, agricultural sciences and tropical medicine. sources include journal articles, thesis, conference proceedings, technical reports, books, patents, and biotechnology. Over 8,500 journals are scanned with source material published in multiple languages: English 63%, French 12%, Russian loo/o, German 8%, other Languages 7%. The file runs from 1973 with approx. 10 million references which are updated with approx. 40,000 references monthly.

Oceanic (file 17)

This is a bibliographic file that deals with all aspects of the oceanic crust to the water surface. Over 2000 source publications (journals, conference proceedings and books) are scanned for the inclusion of about 10,000 references annually. The subject coverage includes: marine biology, biological oceanography, physical and chemical oceanography, meteorology, geology, geophysics and geochemistry, marine pollution, living and non-living marine resources, ships and shipping, engineering, materials, government and law. The file dates from 1964 with approx. 220,00 references which are up dated monthly.

Aquatic Sciences and Fisheries Abstracts (file 52 ASFA)

This is a major data source of information about world-wide literature and reports on science and technology of the marine and freshwater environments. The ASFA file corresponds to the printed titles, Aquatic Sciences and Fisheries Abstracts. Subject coverage includes: aquaculture, aquatic biology, biological oceanography, chemical oceanography, coastal zone management, commerce trade and economics, diving, ecology and ecosystems, environmental studies, fisheries, geologic oceanography, law of the sea, limnology, marine biology, marine policy, pollution and technology, meteorology, ocean engineering, ocean resources, off-shore activities, physical oceanography, underwater acoustics and optics, underwater vessels and buoys. Over 5,000 primary source journals are continuously scanned for items for inclusion in the file. As well as journal articles, which form about 60% of the sources, technical reports, conference papers, books, maps and other documents are covered. The file dates from 1982, with approx. 260,000 references with monthly updates of approx. 3000 references.

Eaudoc (file 73)

This is a comprehensive small database devoted to water resources, which are written in French.

Brix/Flair (file 74)

This is produced by the Fire Research Station Library. It is a bibliographic file, containing references and abstracts to books, conference proceedings, journal articles and research reports. Subject coverage includes: properties, performance and use of materials in buildings, structural design, integrity and performance. Effects of indoor and outdoor environment on building services, construction practice and economics. Sources: 300 scientific journals and newspapers (120 for Flair). The file contains information from 1969, with 125,000 records which are updated monthly at the rate of 500 references.

PRINTED JOURNALS & ABSTRACTS

Petroleum Abstracts

These describe publications relating to the exploration and production of petroleum world-wide. First published in 1973.

British Reports, Theses And Translations

BRIT lists publications described as grey literature which is frequently difficult to identify and locate. The source material includes: papers, reports, pamphlets and translations from government, universities and learned institutions and doctoral theses from 1970. Also listed are some official reports and translations from the Republic of Ireland. BRIT is a major contributor to SIGLE. Subject coverage includes: aeronautics, environmental pollution, protection and control, biological and medical sciences, methods and equipment, propulsion and fuels.

Petroleum Engineer International

Coverage includes: off-shore technology, oil technology trends and drilling exploration.

Petroleum Review

Coverage includes: hydrotreating, technology news, legal frameworks.

International Petroleum Abstracts incorporating Offshore Abstracts

This journal provides an extensive review of the onshore-offshore oil and gas industry, exploration and development. Coverage includes: geology, geophysics, drilling, production, transport, refinery processes, analysis and testing gas oil and bitumen. Source material relating specifically to all those involved in, or manufacturing for, the off-shore oil and gas industry are represented. World-wide coverage of scientific and technical journals, conference papers, research reports, trade literature, standards and patents.

Petroleum Times

This is a monthly journal covering the hydrocarbon industry. Coverage includes: exploration and production, transportation and storage, refining and processing and technical reports.

APPENDIX B

GC-MS PEAK IDENTIFICATION OF THE 50 LARGEST PEAKS OF THE BRAER OIL

Pk#	RT	Area%	Library/ID
1	3.14	1.09	C:\DATABASE\wiley.1 Hexane, 2-methyl- Pentane, 2,4-dimethyl- Pentane, 2,4-dimethyl-
2	3.30	1.29	C:\DATABASE\wiley.1 Hexane, 3-methyl- Hexane, 3-methyl- Heptane, 4-methyl-
3	3.43	1.00	C:\DATABASE\wiley.1 Cyclopentane, 1,3-dimethyl-, cis- Cyclopentane, 1,3-dimethyl-, cis- Cyclopentane,1,3-dimethyl-, trans
4	3.49	1.16	C:\DATABASE\wiley.1 Cyclopentane,1,3-dimethyl-, trans Cyclopentane, 1,3-dimethyl-, cis- Cyclobutanone, 2,2-dimethyl-
5	3.54	1.57	C:\DATABASE\wiley.1 Cyclopentane, 1,3-dimethyl-,cis- Cyclopentane, 1,2-dimethyl-,cis- Cyclopentane, 1,3-dimethyl-,trans
6	3.83	1.46	C:\DATABASE\wiley.1 Heptane Heptane Heptane
7	4.38	7.13	C:\DATABASE\wiley.1 Cyclohexane, methyl- Cyclohexane, methyl- Cyclopropane,1,1,2,3-tetramethyl
8	4.69	1.07	C:\DATABASE\wiley.1 Cyclopentane, ethyl- Cyclopentane, ethyl- Cyclopentane, ethyl-
9	5.54	5.45	C:\DATABASE\wiley.1 Benzene, methyl- Benzene, methyl- SPIRO[2.4]HEPTA-2,6-DIENE

10	6.07	1.57	C:\DATABASE\wiley.1 Heptane, 2-methyl- Heptane, 2-methyl- Heptane, 2,3,4-trimethyl-
11	6.46	4.15	C:\DATABASE\wiley.1 Cyclohexane, 1,3-dimethyl-, trans- Cyclohexane, 1,3-dimethyl-, cis- 2-Pentene, 2,4,4-trimethyl-
12	7.14	1.09	C:\DATABASE\wiley.1 CYCLOPENTANE,1-ETHYL-2-METHYL- Cyclopentane, 1-ethyl-2-methyl-, c Cyclopentane, 1-ethyl-3-methyl-, t
13	7.38	1.50	C:\DATABASE\wiley.1 Cyclohexane, 1,2-dimethyl-, trans- Cyclohexane, 1,4-dimethyl-, cis- CYCLOHEXANE, 1,2-DIMETHYL-
14	7.87	2.66	C:\DATABASE\wiley.1 Octane Heptane, 2,4-dimethyl- Octane
15	9.70	3.93	C:\DATABASE\wiley.1 Cyclohexane, ethyl- Cyclohexane, ethyl- Cyclohexane, ethyl-
16	9.96	1.08	C:\DATABASE\wiley.1 Heptane, 2,6-dimethyl- Heptane, 2,6-dimethyl- Octane, 2,6-dimethyl-
17	10.92	2.42	C:\DATABASE\wiley.1 Benzene, ethyl- Benzene, 1,4-dimethyl- Benzene, 1,3-dimethyl-
18	11.43	6.04	C:\DATABASE\wiley.1 Benzene, 1,3-dimethyl- Benzene, 1,4-dimethyl- XYLENE
19	11.51	1.26	C:\DATABASE\wiley.1 Heptane, 2,3-dimethyl- Heptane, 2,3-dimethyl- Decane, 5,6-dimethyl-
20	12.27	2.82	C:\DATABASE\wiley.1 XYLENE Benzene, 1,3-dimethyl- Benzene, 1,3-dimethyl-

21	12.50	2.49	C:\DATABASE\wiley.1 Cyclohexane, 1-ethyl-4-methyl-, tr Cyclohexane, l-ethyl-4-methyl-, tr 2-Pentene, 3-ethyl-4,4-dimethyl-
22	13.07	3.18	C:\DATABASE\wiley.1 1-Eicosene 2-Hexene, 3,4,4-trimethyl- Cyclohexane, 1-ethyl-4-methyl-, tr
23	13.71	2.40	C:\DATABASE\wiley.1 Cyclohexane, propyl- Cyclohexane, propyl- Cyclohexane, octyl-
24	13.98	2.04	C:\DATABASE\wiley.1 Octane, 2,6-dimethyl- Octane, 2,6-dimethyl- Nonane, 3-methyl-
25	14.05	1.12	C:\DATABASE\wiley.1 Benzene, propyl- Benzene, propyl- Phenethylamine, N-benzyl-p-chloro-
26	14.13	1.17	C:\DATABASE\wiley.1 1-Decene, 2,4-dimethyl- Heptane, 2,3,6-trimethyl- Decane, 2,5,6-trimethyl-
27	14.24	1.95	C:\DATABASE\wiley.1 Benzene, 1-ethyl-2-methyl- Benzene, 1-ethyl-4-methyl- Benzene, 1-ethyl-3-methyl-
28	14.41	1.99	C:\DATABASE\wiley.1 Benzene, 1,2,3-trimethyl- Benzene, 1,3,5-trimethyl- Benzene, 1,2,4-trimethyl-
29	14.58	2.21	C:\DATABASE\wiley.1 Benzene, 1-ethyl-2-methyl- Decane Decane
30	14.77	1.09	C:\DATABASE\wiley.1 3-Octene, 2,6-dimethyl- Octane, 2,6-dimethyl- DIHYDRO-CITRONELLAL
31	14.93	3.63	C:\DATABASE\wiley.1 Benzene, 1,3,5-trimethyl- Benzene, 1,3,5-trinethyl- Benzene, 1,2,3-trimethyl-

32	14.97	0.99	C:\DATABASE\wiley.1 Benzene, 1,3,5-trimethyl- Benzene, 1,3,5-trimethyl- Cyclohexane, 1,1-dimethyl-
33	15.31	1.16	C:\DATABASE\wiley.1 Decane Decane Decane
34	15.42	1.15	C:\DATABASE\wiley.1 Benzene, 1,2,4-trimethyl- Benzene, 1,2,3-trimethyl-- Benzene, 1,2,3-trimethyl-
35	15.73	1.61	C:\DATABASE\wiley.1 Decane, 4-methyl- Decane, 4-methyl- Decane, 4-methyl-
36	15.80	1.31	C:\DATABASE\wiley.1 Cyclohexane, butyl- Cyclohexane, 1,11-(1,5-pentanediyl Cyclohexane, pentyl-
37	15.96	1.09	C:\DATABASE\wiley.1 Benzene, 1-methyl-3-propyl- Benzene, (1-methylpropyl)- Benzene, 1-methyl-2-propyl-
38	16.46	1.10	C:\DATABASE\wiley.1 Benzene, 4-ethyl-1,2-dimethyl- Benzene, 1,2,3,4-tetramethyl- Benzene, 1-ethyl-3,5-dimethyl-
39	17.24	1.44	C:\DATABASE\wiley.1 Naphthalene, decahydro-2-methyl- Dihydrocarvone Naphthalene, decahydro-2-methyl-
40	18.31	1.27	C:\DATABASE\wiley.1 Heptadecane, 2,6,10,14-tetramethyl Undecane, 2,6-dimethyl- Nonane, 3-methyl-
41	18.98	1.18	C:\DATABASE\wiley.1 Heptane, 3-ethyl-5-methyl- Tridecane, 7-methyl- Tetracosane, 2,6,10,15,19,23-hexam
42	11	1.65	C:\DATABASE\wiley.1 Naphthalene, 1-methyl- Naphthalene, 1-methyl- Naphthalene, 2-methyl-

43	19.29	1.00	C:\DATABASE\wiley.1 Naphthalene, 1-methyl- Naphthalene, 2-methyl- Naphthalene, 2-methyl-
44	20.05	1.00	C:\DATABASE\wiley.1 Nonane, 3,7-dimethyl- Pentadecane, 2,6,10,14-tetramethyl Decane, 5-propyl-
45	23.52	3.05	C:\DATABASE\wiley.1 OCTADECAMETHYLCYCLONONASILOXAN MORPHINE GLUCURONIDE-PENTATHS 2H-1,4-Benzodiazepin-2-one, 7-chlo
46	24.98	2.25	C:\DATABASE\wiley.1 EICOSAMETHYLCYCLODECASILOXANE TETRADECAMETHYLCYCLOHEPTASILOXAN OCTADECAMETHYLCYCLONONASILOXANE
47	26.10	1.85	C:\DATABASE\wiley.1 Benzeneacetic acid, alpha.,3,4-tr Benzeneacetic acid, alpha.,3,4-tr TETRACOSAMETHYLCYCLODODECASILOXA
48	27.14	1.66	C:\DATABASE\wiley.1 Benzoic acid, 2,4-bis[(trimethylsi BISTRINETHYLSILYL N-ACETYL EICOSAS 2,6-DIHYDROXYBENZOIC ACID 3TMS
49	28.32	1.14	C:\DATABASE\wiley.1 OCTADECAMETHYLCYCLONONASILOXANE EICOSAMETHYLCYCLODECASILOXANE BISTRIMETHYLSILYL N-ACETYL EICOSAS
50	29.78	1.07	C:\DATABASE\wiley.1 EICOSAMETHYLCYCLODECASILOXANE TETRACOSAMETHYLCYCLODODECASILOXANE Trisiloxane, 1,1,1,5,5,5-hexamethy

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