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A Review of the Contaminant Status of the Irish Sea

CEFAS Contract report C2436

TITLE: Contaminant Status of the Irish Sea

REPORT REF: C2436/01

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CONTRACT REF: C2436

REPORT STATUS: FINAL REPORT

DATE OF ISSUE: 15th March 2005

CLENT: Geotek Ltd

DISTRIBUTION:

This document was produced as part of the UK Department of Trade and Industry's offshore energy Strategic Environmental Assessment programme. The SEA programme is funded and managed by the DTI and coordinated on their behalf by Geotek Ltd and Hartley Anderson Ltd.

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EXECUTIVE SUMMARY

This report forms part of a number of technical publications that contribute to the overall Strategic Environmental Assessment (SEA) process. The scope of this report is to consider the major sources of contamination to the Irish Sea (SEA 6 area), from offshore energy installations, and to put these into the context of other sources of contamination to the Irish Sea. In this respect information and data specific to contamination of the Irish Sea marine environment by the activities of the offshore energy industry and associated activities is particularly relevant. However, the report also considers contamination of the wider environment, in the form of monitoring programme data and specific studies, within the Irish Sea. In both sections described, the report covers contamination in terms of measured values, where available, in different matrices (water, sediment and biota) and their associated biological effects. The report also details the presence and effects of radiation in the Irish Sea. The observed levels of contamination their spatial coverage and temporal trends (where available) are discussed.

The following summary conclusions have been drawn from the available data on sources and levels of contamination.

Inputs to the Irish Sea

Inputs of natural and anthropogenic contaminants to the Irish Sea are largely from riverine discharges. Studies that have measured riverine inputs vs. direct discharge of metals to the Irish Sea show that riverine inputs contribute >80% of most measured concentrations of metals. An exception to this is mercury where the value is closer to 50% (OSPAR, 2004).

Offshore energy installation contamination

The oil and gas industry in the Irish Sea is small by comparison to that of the North Sea but bears comparison to that of the Southern North Sea which is dominated by gas production and for which many of the platforms are in relatively shallow water.

Chemicals are used for a variety of functions in the extraction and production of oil and gas. The discharge of production and drilling chemicals, residual oil and compounds derived from the formation water produced with the oil or gas during extraction and production can contribute to the contaminant concentration in sediments and water. Chemical use offshore is regulated to reduce the quantities used and to ensure the use of those that are least harmful: The new offshore chemicals regulations (OCR, 2002) require operators to source alternative products to avoid the use of those which contain chemicals that are very persistent, bioaccumulative or toxic or have a combination of these properties.

The drilling fluids used in Liverpool Bay and Morecambe Bay are either water-based or consist of an organic phase (either mineral oil or synthetic). However, the majority of compounds making up the drilling mud system are inorganic salts which disperse relatively rapidly and are of very low toxicity. There is some evidence of metal contamination in the sediment in the vicinity of some of the platforms in Liverpool Bay and the co-occurrence of the weighting chemical barium suggests that this may be related to drilling activity. Although some of the metal concentrations measured fall within the OSPAR environmental assessment criteria (EAC) range for metals in sediments and therefore indicate some potential for biological effects, none were apparent as evidenced by the lack of disturbance in the

associated benthic communities. Unlike the Northern North Sea there is no indication of build up of large cuttings piles around the platforms in both Liverpool Bay and Morecambe Bay and therefore the impacts associated with cuttings piles are also likely to be limited.

A wide range of chemicals is used in the production of oil and gas, although generally fewer in the production of gas. In general, the most toxic chemicals are used in very small quantities and dilution of produced water to below the level at which acute toxic effects are observed usually occurs within 50-1000 metres of the discharge point. The data on which these toxic thresholds are based is frequently derived from continuous exposure of organisms for periods up to several days, a situation that is unlikely to occur in the environment. Therefore the predicted distance for dilution of produced water to below the level at which acute effects may occur is probably conservative. However, in a recent study (Biological Effects of Contaminants in Pelagic Ecosystems; BECPELAG) a variety of sub-lethal biological effects have been demonstrated in caged organisms deployed in the vicinity of offshore platforms. The results of these recent work programmes monitoring the effects of produced water on pelagic ecosystems need to be fully evaluated before firm conclusions on the likelihood of wider field effects can be made.

Chemical use and remobilisation of contaminated sediments may also occur during the development of offshore wind farms. The North Hoyle offshore wind farm, off the North Coast of Wales, was completed in 2003 and further licences have been issued, in the Irish Sea (e.g. Rhyl Flats, Burbo Bank and Barrow). Their construction and operation is subject to government legislation including the Food and Environment Protection Act 1985 (FEPA), Electricity Act 1989 and incorporates certain requirements detailed in the Offshore Chemicals Regulations (OCR) 2000. In terms of potential sources of contamination the Environmental Impact Assessments (EIA) for each development cover scenarios of remobilisation of contaminants during construction. To date there have been no offshore wind farms built in areas of significant contaminant loading. Once commissioned all chemical use and storage areas in the offshore facility are required to be fully bunded (i.e. capacity to retain waste has to be >10% of the volume stored). In addition, all chemicals used in lubrication, maintenance etc. are subject to the OCR process, or through a process of testing to the standard of the OCR.

Environmental monitoring programmes, chemical status and effects data and information

Due to the hydrophobic nature of many organic compounds and the partitioning of metals to suspended particles, the concentrations of dissolved contaminants in seawater samples are often low or below detection limits. Of those contaminants that were measured, in water within the SEA 6 area, highest concentrations were generally found at estuarine and coastal sites that are subject to high industrial input such as the Mersey estuary. Environmental quality standards were exceeded for mercury and zinc at the Mersey and Ribble estuary sites, suggesting a dominant riverine input rather than offshore discharges as the contaminant source. High mercury and zinc concentrations could be attributed to industrial and wastewater discharges into these estuaries. Metal concentrations were generally found to fall significantly in water samples taken further offshore. Highest concentrations were found from the Morecambe Bay samples but concentrations were below the limits of detection in samples from the three offshore sites sampled.

In Irish Sea samples contaminant concentrations in sediments were generally higher than those found in seawater. Concentrations of polycyclic aromatic hydrocarbons (PAH) and polycholorinated biphenyls (PCB) were significantly higher in inshore areas where there was either riverine input and/or direct industry discharges. Offshore negative correlations were found in the Western Irish Sea between PAH concentration and grain size of sediments. Positive correlations were found to be present between metal distribution and percentage silt and clay. Concentrations of alkyl phenols (AP) were below the limit of detection.

Due to the lipophilic properties of many organic contaminants, relatively high concentrations can be found in biological tissues. Importantly, the lower molecular weight PAH (e.g. 2 to 3 ring group of PAH such as naphthalene, fluorene, phenanthrene, and anthracene) have significant acute toxicity to aquatic organisms. Whereas, the high molecular weight PAH (202 and above), 4 to 7 ring (from chrysenes to coronenes), whilst not acutely toxic are known to exhibit carcinogenic effects. Metals are also often found in higher concentrations in animal tissues compared to that found in water. Concentrations of contaminants in biota are varied and sometimes difficult to predict based upon exposure. In the SEA 6 area the highest concentrations of contaminants were generally found in organisms sampled in areas of high sediment contaminant loading which are generally correlated with areas of high riverine input.

Highest concentrations of PAH, CB compounds and all metals (other than mercury or silver) were measured in mussels from the Mersey estuary, which correlates well with sediment concentrations. However, elevated levels were also found in mussels in the vicinity of Milford Haven after the Sea Empress oil spill. Highest concentrations of CB in fish were found in Liverpool Bay. Similarly high concentrations were found east of Anglesey and offshore in Morecambe Bay. High concentrations of mercury were found in fish from the Mersey estuary, Liverpool and Morecambe Bays with lead showing a similar distribution. Interestingly, lead and cadmium concentrations were highest in fish collected from Cardigan Bay. It is likely that the source of this particular contamination is from historic lead mining, the run off reaching the bay via the Ystwyth and Reidol rivers.

From the Irish Sea dataset marine mammals appear to bioaccumulate compounds such as PCB and other dioxin like substances because; such substances are stored in blubber and the animals tend to have long exposure times (due to their natural longevity and their presence at the top of their food webs). Jepson et al., 1999, have studied the relationship between the concentrations of PCB and infectious disease prevalence in harbour porpoises. From UK data, combined blubber concentrations of 25 chlorobiphenyl (CB) congeners in healthy harbour porpoises that died of acute physical trauma (mainly as a result of net damage) were compared with the total concentration of 25CB in animals that died of infectious disease (n=82). The group with infectious diseases had significantly higher total CB blubber concentrations than the group with physical traumas.

Biological effects measure the response of an organism to contaminants, rather than the levels of the contaminants themselves and thus attempt to provide the link between the contaminants present and the health and quality of the marine environment. In the SEA 6 area biological effects measures showed that the largest impacts generally occurred in areas with the highest contaminant concentrations. For instance, fish sampled in Morecambe and Liverpool Bay, Burbo Bight and off the Cumbrian coast had elevated levels of the enzymes that are responsible for detoxification of compounds found in oil relative to fish sampled from other sites. Similarly high values for the metabolic products of these compounds were found. Significantly, metabolism of PAH may result in the production of genotoxic metabolites with potentially mutagenic and carcinogenic properties. Measurement of these, by way of DNA adducts analysis, shows highest values in samples from Burbo Bight (Liverpool Bay area). Fish diseases and pathological changes in the liver have long been used as indicators of environmental stress on fish populations. Within the Irish Sea, liver nodules in dab are most common at sites in Liverpool Bay and Cardigan Bay. They are also present in most other regions at lower levels. Due to the lack of long term data sets trends cannot be clearly determined. However, the incidence of liver pathologies appears to be declining at Rye Bay (reference site) since 2001 and increasing in Liverpool Bay and Cardigan Bay sites since 2000 and 1995 respectively.

Radioactivity

Inputs of artificial radionuclides around the UK are dominated by discharges from Sellafield, on the Cumbrian coast. However, discharges of radionuclides from Sellafield have decreased significantly since the 1970s, as a result of various measures. In most cases current discharges are at least 100 times lower than peak discharges. Discharges of technetium-99 from Sellafield rose significantly in 1994, following the installation of the Enhanced Actinide Removal Plant (EARP), but have recently declined significantly concomitant with the introduction of new abatement technology.

Remobilisation from sediments contaminated by historical discharges is now the predominant source of ^{137}Cs, $^{239+240}$ Pu and ^{241}Am to the water column and appears to be largely governed by natural sediment mixing and re-suspension processes. Artificial radionuclide activities in fish and shellfish are also a result of remobilisation from contaminated sediments and are responsible for dose to the local critical group. Anthropogenic activities involving sediment disturbance such as trawling, installation of wind turbines and oil/gas pipelines are likely to increase re-dissolution from the reservoir of contaminated sediment residing on the seabed. Their impact warrants further study. Information concerning radionuclide releases into the Irish Sea directly associated with oil and gas production is not available.

Gaps in our understanding and future risks

The Water Framework Directive aims to protect the physical and biological integrity of aquatic systems. The overall objective is good status to be achieved by December 2015. The main focus of the directive is groundwater and surface water quality out to 1 nm from the coast. However the UK government’s vision for management of our marine resources supports an integrated approach to the management of estuaries, the coastal zone and associated coastal waters. In this context the quality and status of the marine environment associated with offshore oil and gas installations is important.

The limited amount of near field (within a few kilometres of the installations) data available on contaminant concentrations make it difficult to determine any clear trends and to fully assess the importance of offshore oil and gas industry chemical inputs to Liverpool Bay and Morecambe Bay. In particular, the concentration of the compounds commonly detected in produced water should be characterised for both Morecambe Bay and Liverpool Bay in order to enable the accurate calculation of the contribution of the offshore industry to chemical loads. This may increase in importance as land based discharges come under greater control and produced water discharges increase.

A range of biological and chemical techniques are now available that could be deployed to allow a more sensitive and focussed assessment of potential chronic toxicity associated with the discharge of chemicals in offshore oil and gas production. The UK NMMP does not include specific monitoring of offshore energy installations. This has lead to a lack of data specific to the Irish Sea installations. Additional studies that address this gap would provide a more complete picture of the biological impacts of installations.

A range of natural physical and biological processes influence sediment remobilisation. However, the influence of offshore energy installations upon sediment remobilisation and hence to associated radionuclide availability in the water column should be quantified. For example, the Scroby Sands windfarm development (North Sea) is currently being studied to assess the change to sediment transport processes (Contract: Development of Generic Guidance for Sediment Transport Monitoring Programmes in Response to Construction of Offshore Windfarms).

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1. INTRODUCTION

The Strategic Environmental Assessment (SEA) process has been defined as 'the formal, systematic and comprehensive process of evaluating the effects of a proposed policy, plan or programme or its alternatives, including the written report on the findings of that evaluation, and using the findings in publicly accountable decision making'. This report forms part of a number of technical publications that contribute to the overall assessment. The scope of this report is to consider the major sources of contamination to the Irish Sea (SEA 6 area) from offshore energy installations. In addition the report considers other land-based sources to assess the relative impact these installations are having. The report evaluates the environmental concentrations of chemicals against background levels and provides spatial and temporal assessments where possible. Evidence of biological effects is discussed in relation to the observed types and associated levels of contamination. Finally, the report discusses radioactivity in the Irish Sea resulting from natural and anthropogenic sources.

2. DATA SOURCES AND APPROACH

The report is broken down into three sections. The first (Section 3; Assessment of near field data around offshore energy installations) identifies data and information that is specific to the oil and gas industry for the SEA6 area. However, supporting data that may be of relevance or where gaps in the literature exist (not necessarily directly related to the Irish Sea) has also been included. The data for this first section has been gathered from Environmental Impact Assessments for oil and gas developments in the Irish Sea, pre and post development surveys of oil and gas production facilities in Liverpool Bay (2002), the Environmental Emissions Monitoring System Detailed Emissions Reports (EEMs, 1999-2003) and CEFAS/Dti Offshore Chemicals Notification Scheme data.

The following section (Section 4; Monitoring programmes, survey and research based data and information) deals with data collected from monitoring programmes and studies in the Irish Sea that fall within the SEA 6 area. Of particular importance in this section is the data gathered as part of the United Kingdom National Marine Monitoring Programme (UK NMMP). Data for the NMMP is presented in a number of publications that include the CEFAS Aquatic Environment Monitoring Reports (AEMR) (1998, 1999-2000 and 2000-2001), Quality Status report - Region III Celtic Seas (QSR 2000), UK NMMP second report (1999-2001) and the Charting progress: An Integrated Assessment of the State of the UK Seas report (2005).

Section 5 is concerned with radioactivity in the marine environment. Publications of importance include the Radiation in Food and the Environment (RIFE) report, the MARINA II study (Betti *et al*., 2004) and the data published in the CEFAS AEMRs.

3. ASSESSMENT OF NEAR FIELD DATA AROUND OFFSHORE ENERGY INSTALLATIONS

3.1 INTRODUCTION

Few specific data exist for the Irish Sea in terms of contamination from offshore energy installations, namely, the oil and gas industry. This is likely to be due to the size of operations in this sea area compared to those in the North Sea, where attention and research interest is focussed. However, data that is available has been presented in this section, therefore representing information that is strictly focussed on the oil and gas industry, associated activities and direct effects. Section 4 follows on to describe effects upon the wider environment.

3.2 THE DEVELOPMENT OF THE OIL AND GAS INDUSTRY IN THE IRISH SEA

There are six fields in production in the Irish Sea, of these four are gas producing fields. Of the others one delivers a combination of oil and gas and one produces oil only. The first discovery was Morecambe South in 1974.

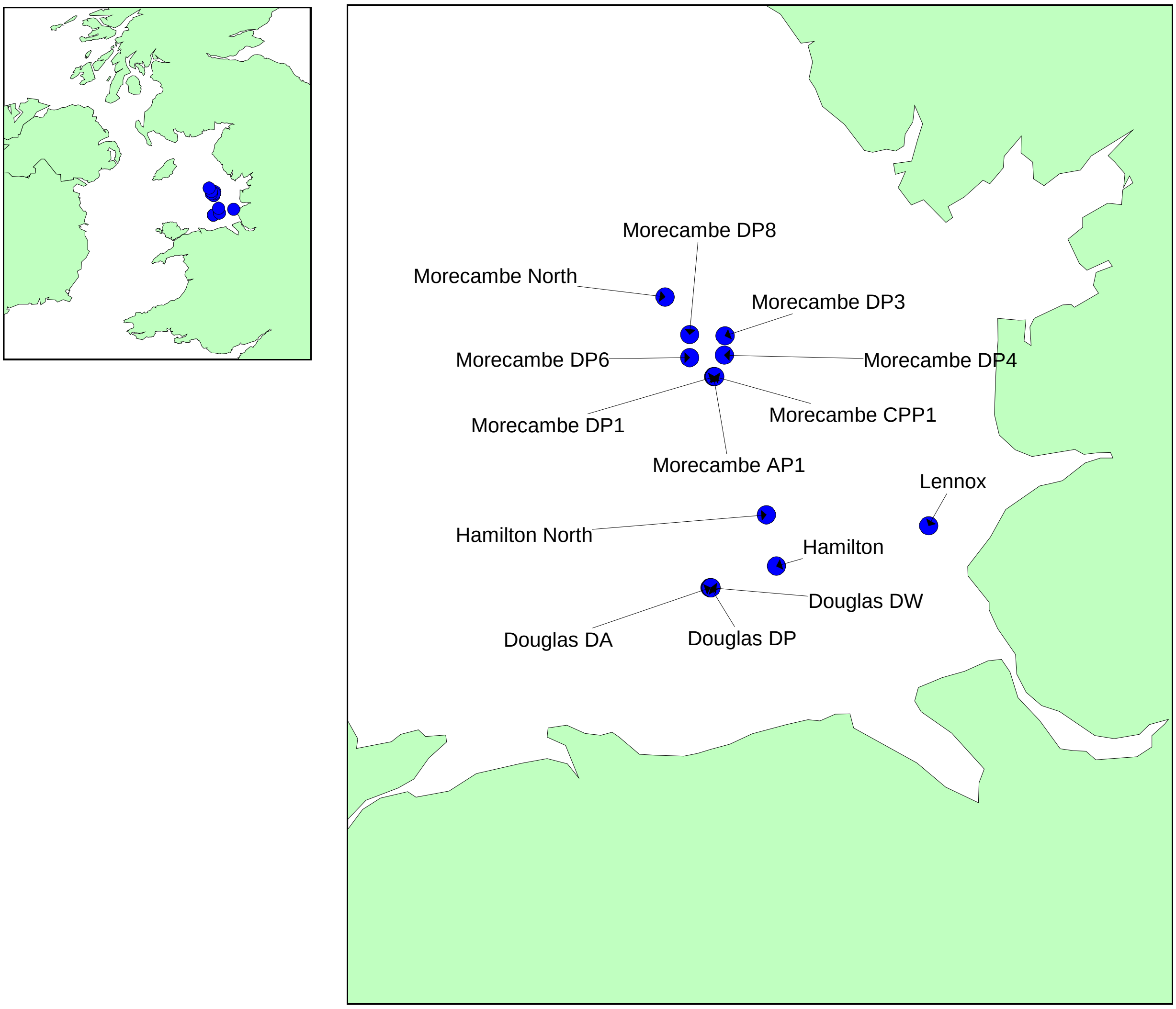

Figure 1. Locations of oil and gas installations in the Irish Sea.

3.2.1 Liverpool Bay

Beginning in 1988 a period of survey and exploration in Irish Sea blocks 110/13 and 110/15 led to the development of five major oil and gas installations in Liverpool Bay. These installations came into service from the early 1990s (Table 1). The Liverpool Bay development represented the first oil production off the west coast of Britain. It consists of: The Douglas production platform, producing oil and gas, three smaller production platforms (Hamilton, Hamilton North and Lennox) a major oil storage and offloading installation (OSI) and additionally an onshore gas processing Terminal at Point of Ayr. During the summer of 2000 a subsea installation (Hamilton East) was also developed inshore of Hamilton.

Table 1. Dates of discovery and first production of Oil and Gas in Liverpool Bay (million tonnes and billion (US) cubic metres)

Installation	Discovered	Production started	Hydrocarbon	Estimated original recoverable reserves
Douglas	1990	Jan. 1996	Oil	11.3 mt
Hamilton	1990	Feb. 1996	Gas	14.6 bm^3
Hamilton North	1991	Dec. 1995	Gas	6.7 bm^3
Lennox	1992	Mar. 1996	Oil/Gas	7.6 mt

3.2.2 Morecambe Bay

The South Morecambe field, which covers an area of 11 square miles, is one of the UK's largest gas fields. It was commissioned in January 1984, starting first production in early 1985. It consists of a central processing complex and four drilling/wellhead platforms. Each drilling/wellhead platform produces gas, gas condensate and produced water. The North Morecambe platform, which extracts gas from the smaller North Morecambe field and can be controlled remotely from South Morecambe, was installed in the middle of 1992 and commissioned in October 1994 (Table 2).

Table 2. Dates of discovery and first production of Gas in Morecambe Bay (billion (US) cubic metres)

Installation	Discovered	Production started	Hydrocarbon	Estimated original recoverable reserves
DPPA (Morecambe North)	Feb 1976	Oct. 1994	Gas	27.4 bm^3
Morecambe South	Sep 1974	Jan. 1985	Gas	136.3 bm^3

3.3 THE DEVELOPMENT OF OFFSHORE WIND FARMS

The North Hoyle offshore wind farm off the North Coast of Wales was completed in 2003 and further licences have been issued, in the Irish Sea (e.g. Rhyl Flats, Burbo Bank and Barrow). Their construction and operation is subject to government legislation including the Food and Environment Protection Act 1985 (FEPA), Electricity Act 1989 and incorporates certain requirements detailed in the Offshore Chemicals Regulations (OCR) 2000. In terms of potential sources of contamination the Environmental Impact Assessments (EIA) for each development cover scenarios of remobilisation of contaminants during construction. To date there have been no offshore wind farms built in areas of significant contaminant loading. Once commissioned all chemical use and storage areas in the offshore facility are required to be fully bunded (i.e. capacity to retain waste has to be >10% of the volume stored). In addition, all chemicals used in lubrication, maintenance etc. are subject to the OCR process, or through a process of testing to the standard of the OCR.

3.4 REGULATORY CONTROLS ON CHEMICAL USE AND DISCHARGE

Chemicals used by the offshore oil and gas industry for hydrocarbon exploitation and production on the UK continental shelf (UKCS) were classified based on hazard criteria into ‘Categories or Groups’ under the original voluntary Offshore Chemical Notification Scheme (“old” OCNS) (1979-1993) and the “revised” Notification Scheme (1993-1996). In this classification, chemicals were classified on the basis of potential biodegradation, bioavailability and toxicity to three taxonomic groups of organisms (fish, crustacea and algae).

In the “revised” OCNS scheme (active until the end 2001), the initial Group-classification was determined using Table 3. All submitted toxicity data for the product were compared to these categories and the value giving the worst case ‘Initial Grouping’ (i.e. the test giving the most toxic response) was used as the initial Group for the product.

Table 3. Initial OCNS group classification guidelines values based on exposure toxicity results (ppm) in laboratory tests

	High (A) to Low (E) Hazard				
Initial Grouping	**A**	**B**	**C**	**D**	**E**
Result from aquatic Toxicity test	<1	>1-10	>10-100	>100-1,000	>1,000
Result from sediment Toxicity test	<10	>10-100	>100-1,000	>1,000-10,000	>10,000

This initial Group could be adjusted up or down, by one or two groups, depending on the biodegradation and bioaccumulation potential of the components in the preparation. The 'final' Group assigned was therefore based upon the overall environmental hazard posed by the product with group ‘A’ representing the highest and group ‘E’ the lowest. A further category, ‘Z’ is used for chemicals used in sealed systems and not normally intended for discharge.

The Harmonised Mandatory Control System for the Use and Reduction of Offshore Chemicals replaced this scheme (OSPAR decision 2000/2). Under the new approach Offshore Chemicals are ranked according to their hazard quotient (predicted discharge concentration relative to the measured no effect concentration). The hazard quotient is calculated using the Chemical Hazard and Risk Model (Karman, 1996). However for this discussion the 'old' OCNS categories will be used for all products so that comparisons may be more easily made between years.

3.5 CHEMICAL USE AND DISCHARGE

In comparison to the North Sea, the offshore oil and gas industry in the Irish Sea is considerably smaller in size of operation. The majority of the platforms in the Irish Sea produce gas rather than oil. The extraction and production of gas generally uses a smaller range of chemicals although some of these, such as gas hydrate inhibitors may still be discharged in relatively large quantities compared to chemicals used for other purposes.

Chemicals are used for a variety of functions in the extraction and production of oil and gas. Many chemicals used are mixtures of two or more compounds although single compounds such as methanol and monoethylene glycol are also commonly used.

3.5.1 Drilling Chemicals

Wells are drilled through the sub-sea strata in order to evaluate the potential for oil and gas extraction, to appraise the potential of any hydrocarbon reservoirs found and to extract oil and gas for use. During the exploration phase a number of wells may be drilled before a suitable well is developed for production; though advances in seismic surveying technology have considerably reduced the number of unsuccessful exploration wells. Drilling fluids are used to lubricate the drill bit and drilling assembly and to facilitate removal of rock fragments (cuttings). Drilling fluids also maintain well pressure (preventing uncontrolled blowouts or ‘kicks’ of formation fluids up to the wellhead) and the stability of the formation (preventing hole enlargement by erosion of the formation). The total tonnage of chemicals discharged in drilling operations in Morecambe Bay and Liverpool Bay varies considerably from year to year. Figure 2 shows that no drilling activity associated with the Liverpool Bay installations occurred during 2001 and that with the exception of 2003 drilling discharges associated with the Morecambe Bay installations have been consistently higher.

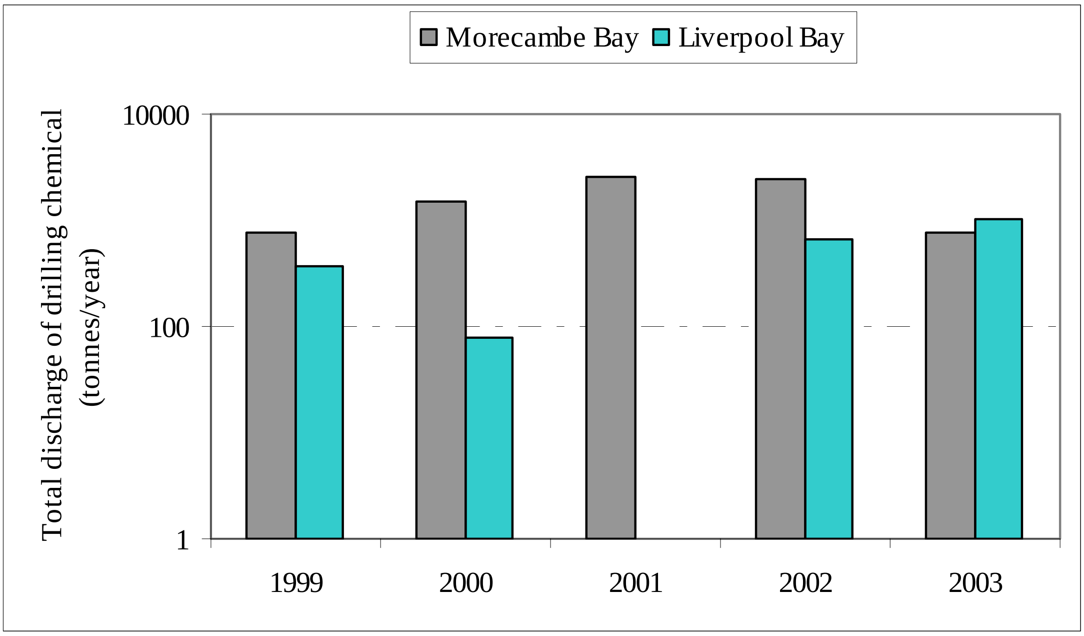

Figure 2. Total drilling chemical discharges (tonnes, shown on a logarithmic scale) in Morecambe Bay and Liverpool Bay between 2000 and 2003

The drilling fluid systems in current use are mostly water-based. Organic phase fluids, (either mineral oil-based or synthetic) are used for drilling through reactive shales to prevent the loss of aqueous fluids into the formation; their discharge is however restricted to 1% by weight on cuttings by OSPAR Decision 2000/3. Each type of fluid contains a wide range of other chemicals to modify its properties to suit the formation being drilled. Table 4a and 4b show the different functions of drilling chemicals and some of the more common additives in use.

Table 4a. Main chemical functions and types of additives used in drilling operations

Chemical Function Group	Function	Typical Composition
Acidity Control Chemical	Control pH, reducing corrosion and also activating some emulsifiers.	Lime (Ca $(OH)^2$) is with OBM/SBM. Caustic soda, and other inorganic compounds including NaOH, KOH, $Ca(OH)^2$, K_2CO_3 in WBMs.
Biocide	Prevent the growth of bacteria within a drilling fluid	Gluteraldehyde, Tetrakishydroxymethyl phosphonium sulphate
Brine (Completion fluid)	Clear heavy weight brines used when drilling into reservoir formations to avoid blocking pores with solids from conventional drilling mud thus impeding the flow of oil or gas.	Bromides, carbonates, formates and chlorides of potassium, calcium, sodium and zinc. Caesium formate
Cement/or cement additive	Cement and additives used to control the setting time of cement when pumping; to add flexibility; to improve adhesion the well bore etc.	Various synthetic polymers
Corrosion inhibitor	Used to prevent corrosion when using acidic completion and stimulation chemicals.	Phosphate ester salts
Defoamer (Drilling)	Reduces or eliminates foaming by controlling surface tension	Stearates and fatty acid derivatives
Dispersant	Separates particles within a fluid to increase the viscosity	Organophillic lignite
Drilling lubricant(s)	Additives used to enhance the lubricity of water-based mud	Vegetable oils, esters, graphite
Emulsifier(s)	Stabilise water in oil Emulsions in an OPF.	Fatty acids (and derivatives), rosin acid (and derivatives) prepared from sodium soaps from the paper industry and fatty imidazoline derivatives. Secondary emulsifiers include amines, amides, sulfonic acids, lignosulfonates, alcohols and related co-polymers.
Fluid loss additive	Reduces the loss of fluid from mud into drilled formation and controls the thickness of mud solids (filter cake) on the inside of the well bore	Bentonite clay, lignite and polymers: carboxymethyl cellulose (CMC), polyanionic cellulose (PAC) and modified starch.
Hydrogen sulphide scavenger	Used to prevent corrosion and occupational health problems caused by build-up of H_2S	Iron (III) oxide (ironite sponge), zinc oxide, triazines etc.
Lost Circulation Material	Block pores and fractures to prevent the loss of whole mud into the formation.	Crushed nut shell, shredded vegetable fibre, mica flakes, calcium carbonate, shredded cellophane:

Table 4b. Main chemical functions and types of additives used in drilling operations continued

Chemical Function Group	Function	Typical Composition
OPF Additive	Concentrated inorganic salt solutions prevent interactions of drilling fluid with reactive clays and soluble salts.	$CaCl_2$, (NaCl). Typical use concentrations are 20% $CaCl_2$ brine, added by 20-40% to the mud.
OPF base Oils	Mineral oil used as the continuous phase of an Organic Phase Drilling Fluid.	
OPF Oil based Drilling Fluid	An emulsion of water and other additives in which the continuous phase is mineral oil	
OPF synthetic-based Drilling Fluid	An emulsion of water and other additives in which the continuous phase is a water-immiscible organic fluid of animal or mineral or vegetable origin.	
OPF base Synthetics	The continuous phase of a Synthetic-based OPF	Poly alpha-olefins, linear alpha-olefins, esters
Pipe release Chemicals	Used to free drill pipe which as become stuck in the well bore	Ethylene glycol monobutyl ether
Oxygen scavenger	Prevent corrosion caused by bacteria	Ammonium bisulphite, sodium bisulphite
Shale inhibitor/Encapsulator	Prevent the loss of drilling fluid into shale	Silicates, acrylamides, lignite
Tracer chemicals		Various fluorinated or deuterated compounds
Viscosifiers	Build viscosity through complex interactions with the emulsions.	Bentonite clay in the majority of most water-based muds. Organic polymers derived from cellulose, starch, xanthan and guar gums.
Water based mud drilling fluid additives	Concentrated inorganic salt solutions prevent interactions of drilling fluid with reactive clays and soluble salts.	For WBMs: KCl, NaCl. For completion fluids NaCl, $CaCl_2$, $ZnCl_2$, $CaBr_2$ and $ZnBr_2$.
Weighting chemicals	Increase weight of mud, to balance well pressure.	Most commonly barium sulphate (barite), which may contain traces of heavy metals. Also calcium carbonate, dolomite, hematite & manganese tetraoxide
Well stimulation chemicals	Used to initiate the flow of oil or gas from a newly completed well	
Well bore clean-up chemicals	Used to remove mud solids and filter cake during completion	

The quantity and types of chemicals used in any drilling operation is dependent upon the nature of the formation drilled and the difficulties which are encountered during the process. Figures 3 and 4 show the quantities of chemicals discharged in 2003 from drilling operations in Liverpool Bay and Morecambe Bay.

The largest quantities of chemicals discharged during drilling operations are water-based drilling fluid additives and weighting chemicals. With reference to Tables 4a and 4b these chemicals are mostly calcium or sodium chlorides and bicarbonates, which are unlikely to have a negative impact upon marine organisms after dilution by dispersion. The weighting chemicals also include barite ($BaSO_4$) for which there is some laboratory (Farestveit *et al.*, 1994) and field (Gordan, *et al.*, 1992) data that indicate the potential for toxic effects. However the robustness of the findings of some of the studies on barium toxicity has been questioned.

Although the solubility of barite is low and is likely to be considerably reduced as a result of the high sulphate concentrations associated with cuttings piles, there may also be a number of other metals present as impurities of barite (e.g. lead and copper). These other metals are toxic in their own right and have been shown to be present at elevated concentrations in the vicinity of drilling operations. However, use of slim hole design for drilling wells minimises cuttings production. Remote vehicle surveys of the seabed in the vicinity of the Lennox platform immediately after completion of drilling operations has not indicated cuttings accumulation. A similar situation is indicated for drilling operations in Morecambe Bay.

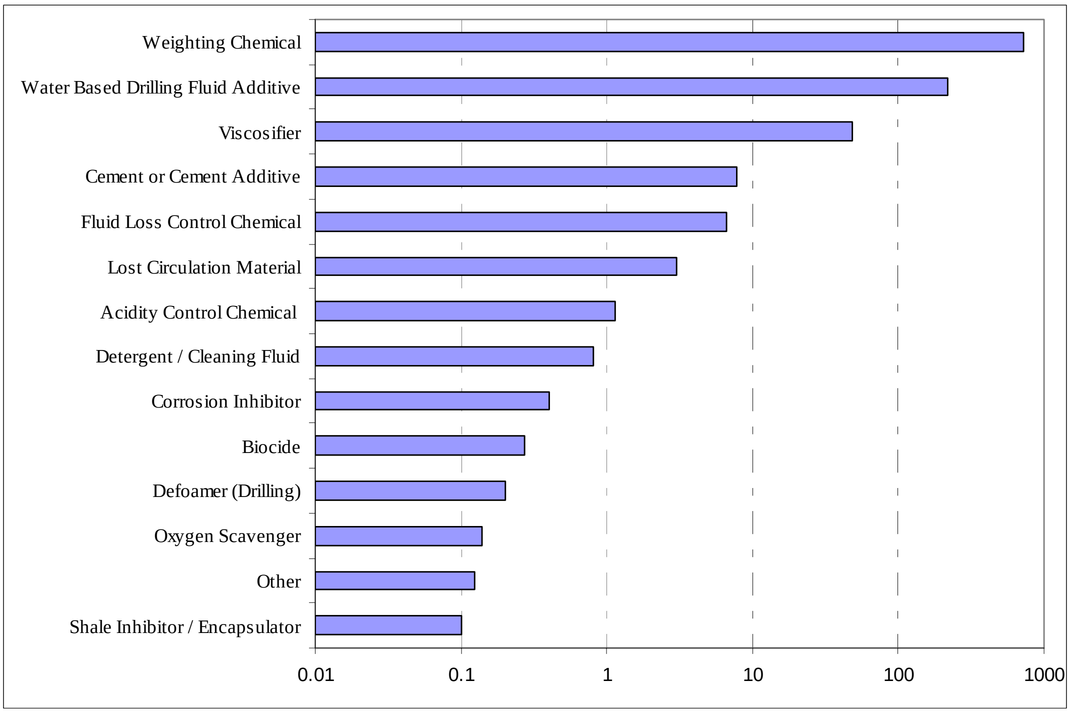

Figure 3. Drilling chemical discharges (tonnes, on a logarithmic scale) by function in Liverpool Bay in 2003

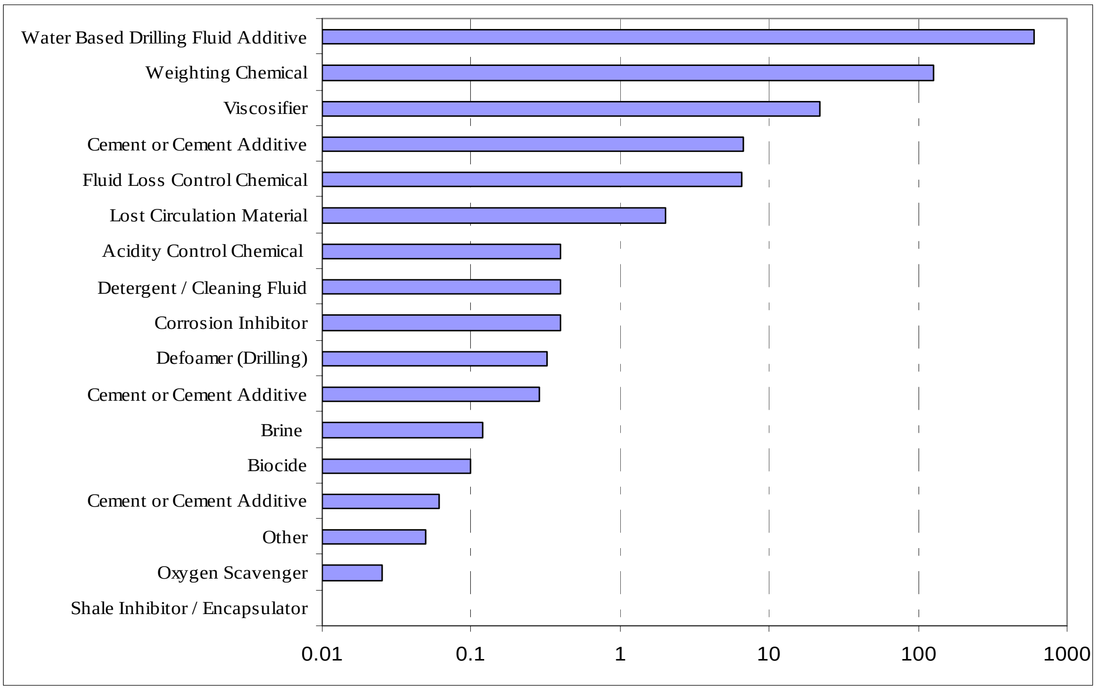

Figure 4. Drilling chemical discharges (tonnes, shown on a logarithmic scale) by function in Morecambe Bay in 2003

Drilling fluids frequently have a wide range of components, many of which are of very low toxicity (Table 5). Although some components such as detergents have a higher toxicity than other additives this is usually offset by the lower quantities used.

Table 5. Acute toxicity of major constituents of drilling fluids mg/l (based on, Terzaghi *et al.*, 1998)

Product Type	**Algae**	**Brine shrimp (*Artemia salina*)**	**Maximum concentration in drilling fluids**
Lignosulphonate	356	3953	23000
Modified starch	ND	10000	17000
Soltex asphalt	216	>10000	17000
XC-polymer	>400	291	6000
Mor-rex maltodextrin	ND	>10000	15000
Carboxymethyl cellulose (CMC)	>10000	>10000	9000
Polyanionic cellulose (PAC)	>10000	>10000	14000
Wetting agent/detergent	65.4	341	800
Defoamer alcohol	9.15	5.41	1500

Figure 5 shows the Offshore Chemical Notification Scheme hazard groups and tonnages discharged for drilling chemicals in Liverpool Bay. However, the major tonnage of chemicals discharged fell in categories D and E (sediment toxicity>1,000-10,000 mg/kg).

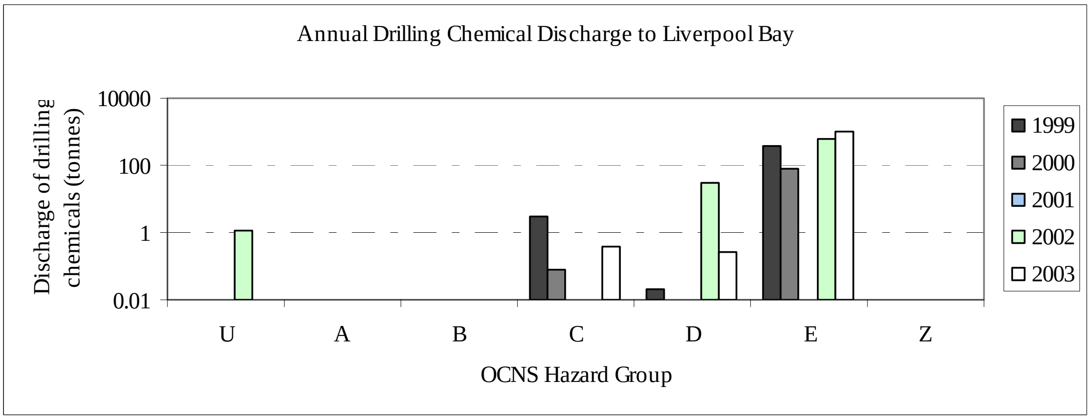

Figure 5. Tonnage of chemicals (shown on a logarithmic scale) in different OCNS hazard groups used during drilling operations in Liverpool Bay between 1999 and 2003

Figure 6 shows the Offshore Chemical Notification Scheme (OCNS) hazard groups and tonnage discharged for drilling chemicals in Morecambe Bay between 1999 and 2003. During 2002 less than 1 tonne of drilling chemicals discharged were in hazard group A (sediment toxicity <10 mg/kg). The majority of chemicals discharged during this period (99.9%, 7967 tonnes) fall into hazard groups D and E (sediment toxicity >1,000-10,000 or >10,000 mg/kg).

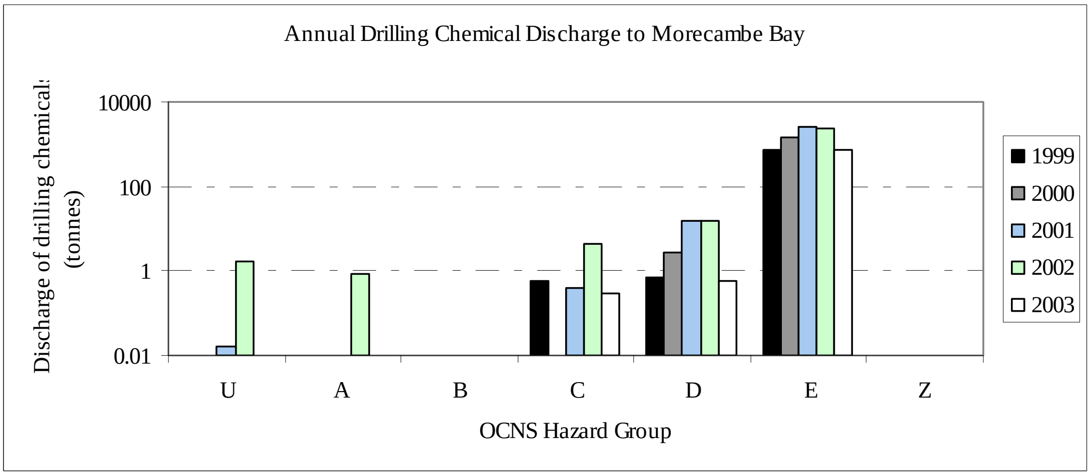

Figure 6. Tonnage of chemicals (shown on a logarithmic scale) in different OCNS hazard groups used during drilling operations in Morecambe Bay between 1999 and 2003

3.5.2 Biological impacts of drilling activity:

The main impacts reported from drilling activity derive from studies conducted in the Northern North Sea. Due to the use of organic phase fluids in drilling operations conducted up to 1997 in the deep waters of this area, drill cuttings have accumulated in piles underneath platforms where there is minimal disturbance from storms or the relatively weak residual currents. The toxicity of many of these cuttings piles is primarily related to the level of oil contamination. The depth of cuttings and their oil content have been shown to determine the level of initial impact upon the benthic fauna and the rate at which it recovers in areas associated with drilling activity e.g. cuttings depths >10mm (Bakke *et al*., 1986) and oil on cuttings concentrations >400µg/g (Hird and Tibbetts, 1996) are likely to limit oil degradation and hence faunal recolonisation.

Due to the shallow water depth in Liverpool Bay and Morecambe Bay and the close proximity to shore of many of the installations, only water based mud (WBM) has been allowed to be discharged during drilling operations since the beginning of oil and gas activities in the Irish Sea. Water based muds are of low toxicity (LC50 > 50000 ppm in sediment, Daan *et al*., 1994) and most of their components are of high solubility which contributes to more rapid and greater dilution. These properties contribute to the fact that no impacts upon the benthic community are observed to within 25 metres of drilling sites in studies using WBM (Daan *et al*., 1994) and the impacts observed appear to be mostly related to physical effects (Davies and Kingston, 1992). Drilling sites from around a North Sea oil platform with a history of using oil-based mud by contrast show acute toxicity to the amphipod *Corophium volutator* as far as 600 m from the platform (Briggs and Grant, 2002). Toxicity of sediments to *C. volutator* was closely correlated with their hydrocarbon content whilst polar organics, sulphide, ammonia and other water soluble substances were of much lower significance.

Modelling of cuttings deposition in Morecambe Bay indicates cuttings distributed ~400 metres in each direction along an east west axis from well sites with the bulk of cuttings within 50 metres of the well location and cuttings depths of less than 15 millimetres over approximately 93 percent of the deposition area (Burlington Resources Environment Statement, Rivers Fields Development, 2002; Crosby exploration well 110/14-F; and Greeba exploration well 110/12-5). A similar situation is likely to exist for dispersal of drill cuttings in Liverpool Bay. Measurements of sediment barium concentration (a weighting agent used in drilling muds) indicate widespread low levels of barium up to 5 kilometres from each of the main installations (Holt and Shalla, 2001).

Analysis of the biota in the vicinity of each of the installations in Liverpool Bay in 2001 showed no major detrimental changes within sites as a result of developments since 1994 (Holt and Shalla, 2001). Similar data collected for the central complex of the Morecambe Field did not indicate an impact of the development upon the diversity of benthic organisms (Rees, 1994)

3.5.3 Production Chemicals

Oil and gas removed from sub-sea strata may be associated with formation water and sometimes with water injected to maintain reservoir pressure. Following physical and chemical treatment to separate the majority of oil, the remaining water is usually discharged to sea. This production water contains residual oil and a wide range of chemicals including phenols, organic acids and other chemicals derived from the formation water as well as chemicals used to facilitate oil separation and other processes on the platform. Figure 7 and Figure 8 show the amount of the main production chemicals discharged in Liverpool Bay and Morecambe Bay in 2003.

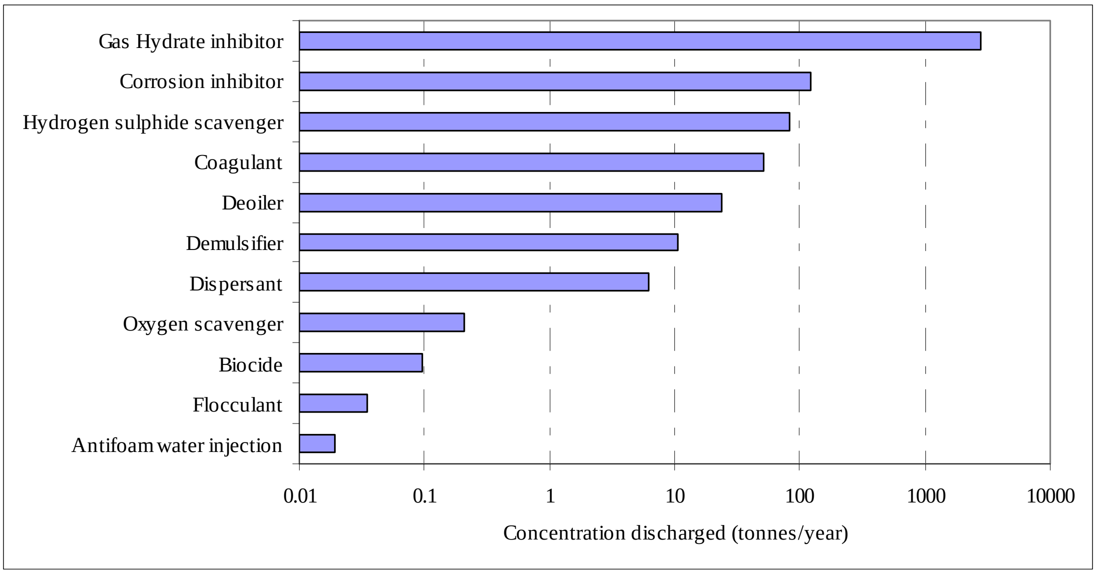

Figure 7. Production chemical discharges (tonnes, shown on a logarithmic scale) by function in Liverpool Bay in 2003

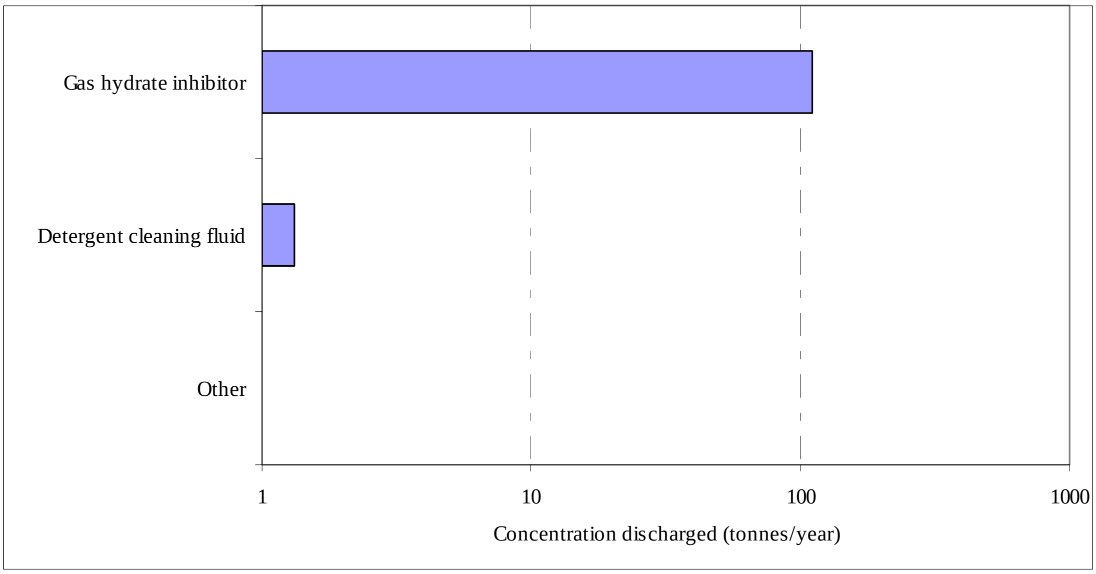

Figure 8. Production chemical discharges (tonnes, shown on a logarithmic scale) by function in Morecambe Bay in 2003

No chemical discharges were recorded for Liverpool Bay in 1999 and 2000 (Figure 9). This was because there were difficulties with oil separation to achieve the consented 40ppm oil in water discharge at the Douglas platform after production started at its Lennox satellite. Produced water was stockpiled in the Offshore Storage and Offloading Installation (OSI) and then taken to a specialist bio-remediation plant in Milford Haven for treatment and disposal. Subsequently, the use of a new demulsifier and addition of extra plant on the OSI achieved the acceptable oil in water discharge limit.

Gas production generally uses fewer chemicals than oil production. From 2001 onwards the discharge of production chemicals in Liverpool Bay is between 10 and 100 times that of

Morecambe Bay. Table 6 lists the main chemicals and their functions that are used in production of oil and gas.

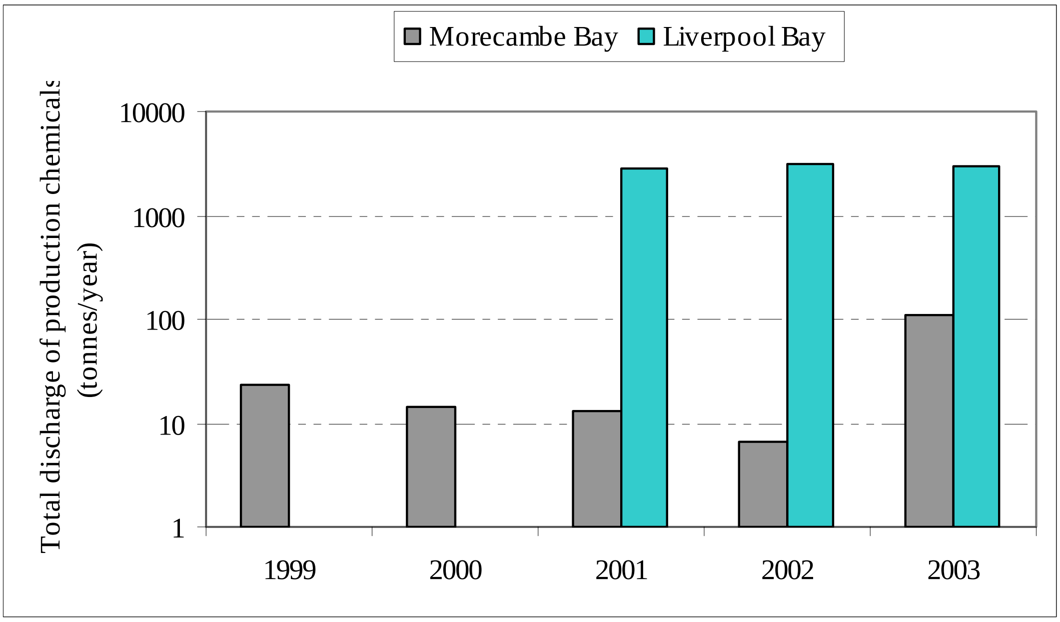

Figure 9. Total Production chemical discharges (tonnes, shown on a logarithmic scale) in Morecambe Bay and Liverpool Bay between 1999 and 2003

Table 6 shows that production chemicals are used in a wide range of processes and a variety of different chemistries are required to meet these demands. Not all chemicals used will be discharged in produced water, as some will partition with the produced oil or gas and so be exported to the refinery. Figure 10 and Figure 11 show the estimated quantity of chemicals discharged in relation to hazard classification of production chemicals from installations in Liverpool Bay and Morecambe Bay between 1999 and 2003.

Although thirty different chemical products are used to treat oil on the Douglas platform, those used in the greatest quantities are gas hydrate inhibitors (generally methanol) and corrosion inhibitors. Biocides are also used in relatively small quantities to prevent the growth of marine organisms and bacteria in the pipe work and reservoir. Although 25-30 kg discharged per year falls into group A for which the toxicity is <10 mg/l the majority of the chemical discharge falls in OCNS hazard groups with toxicity >1-10 mg/l (Figure 10).

Table 6. Main chemical functions used in production of oil and gas

Chemical Function Group	Function	Typical Composition
Antifoam (hydrocarbons)	Crude oil is a mixture of hydrocarbons ranging from methane to high molecular weight paraffins and asphalts. The mixture behaves as a single liquid phase in the reservoir but turns to foam with the reduction of pressure in the well and separation plant. Such foaming causes significant problems in oil and water separators.	Polyglycol esters or silicones
Antifoam (water injection)	Used to prevent the formation of foam in deaeration towers for injection water.	Polyglycol esters
Biocides	Prevents biological growth in the seawater intake and injection systems and within pipework and vessels.	Sodium hypochlorite and various organic biocides quaternary amine salts, amine acetates, formaldehyde and gluteraldehyde.
Carrier Solvent		Ethylene glycol monobutyl ether, monoethylene glycol, polyethylene glycol
Coolant or additive	Anti-freeze and corrosion inhibitor additives in closed circulation heat exchangers, pumps and pipework	Monoethylene glycol, sodium nitrite
Corrosion inhibitor	Corrosive gases in produced water (oxygen, hydrogen sulphide, carbon dioxide) and seawater itself, can cause corrosion in pipework and tubulars.	Products generally comprise complex mixtures: amides, amines, amine salts, imadazolines, quaternary ammonium salts.
Demulsifier	Oil is produced in association with natural formation water or mixed formation & injection waters. The water to oil ratio increases with time to the extent that a mature reservoir produces more water than oil. Passage through pipework and valves turns the mixture in to an emulsion.so most installations use demulsifiers to accelerate separation.	These include: oxalkylated resins (alkylphenol/formaldehyde reaction products), polyglycol esters, alkyl aryl sulphonates.
Deoiler	Used after primary separation with demulsifiers to remove residual oil from produced water before discharge	Polyaluminium chloride
Dye	Fluorescent dyes used for leak detection in subsea pipework and hydraulic systems. Visible in seawater at very low concentrations.	Fluorescein; Rhodamine B
Emulsifier	Oil left in produced water following primary separation is removed to <40 ppm,	Positively charged polyamines or polyamine quaternary compounds added to cause the negatively charged oil droplets to aggregate.
Flocculant	Small suspended solids are removed with chemicals. Coagulants, similar to cationic polymers are used for reverse emulsion breaking.	Flocculants are generally high molecular weight polymers, although aluminium or iron chlorides and sulphates are also used.
Gas hydrate inhibitor	Hydrates are ice-like solids, which can form above 0°C in gas wells and pipelines	Freeze-ups can be prevented by the addition of methanol or monoethylene glycol.
Hydraulic fluid	Used to operate blow out preventers andsubsea valves. Hydraulic fluids used in cranes, winches and other machinery are exempt.	Mostly based on monoethylene glycol with the addition of corrosion inhibitors and dye.
Hydrogen sulphide scavenger	Acid gases (H_2S and CO_2) are of a corrosive nature and toxic to humans.	Iron (III) oxide (ironite sponge), zinc oxide, triazines etc.
Oxygen Scavenger	Prevent the growth of bacteria in injection water, pipelines etc.	Sodium bisulphite, ammonium bisulphite
Scale dissolver	Used to remove scale from the inside of well tubulars.	Hydrochloric acid, citric acid, formic acid, EDTA
Scale inhibitor	Scaling from water-borne minerals, salts and corrosion products can occur within pores of the formation itself as reservoir pressures reduce and within well tubulars. Scale inhibitors inhibit crystal growth	Most are based on phosphonates, phosphate esters or acrylic acid copolymers.
Thinner	Added to particularly viscous oils to make them easier to pump and reduce drag in pipelines.	Xylene, aromatic naphtha
Tracer	Sometimes injected into wells to investigate possible interconnection between reservoirs	Fluorinated and deuterated compounds
Water clarifier	Seawater is used to maintain pressure by displacing oil through the reservoir. Suspended solids and micro-organisms must be removed before injection.	Polyacrylamides, ferric sulphate
Wax dissolver	Solid hydrocarbon waxes build up dissolved	low-cut aromatic solvents.
Wax inhibitor	Solid hydrocarbon waxes deposition may be inhibited	vinyl polymers, sulphonate salts or mixtures of alkyl and aryl polyethers;

Production chemical discharges in Morecambe Bay between 1999 and 2002 were between 7 and 24 tonnes, increasing to 111 tonnes in 2003. These values are considerably smaller than those for Liverpool Bay. Most of the chemicals discharged into Morecambe Bay are of low toxicity. Lethal concentration to 50% of the organisms (LC_{50})>100-1,000 mg/l with 75% or more in OCNS group D and E (LC_{50} >1,000-10,000) (Figure 10).

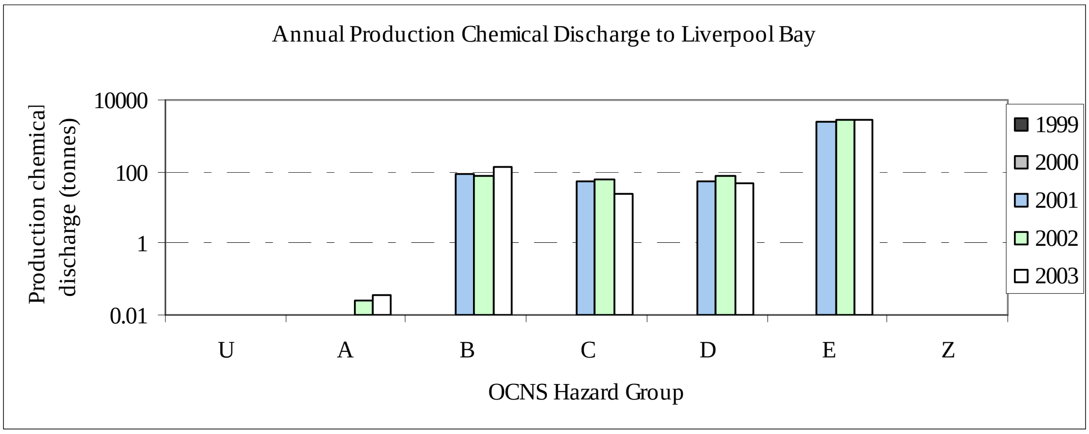

Figure 10. Tonnage of chemicals (shown on a logarithmic scale) in different OCNS hazard groups used in oil and gas production in Liverpool Bay between 1999 and 2003

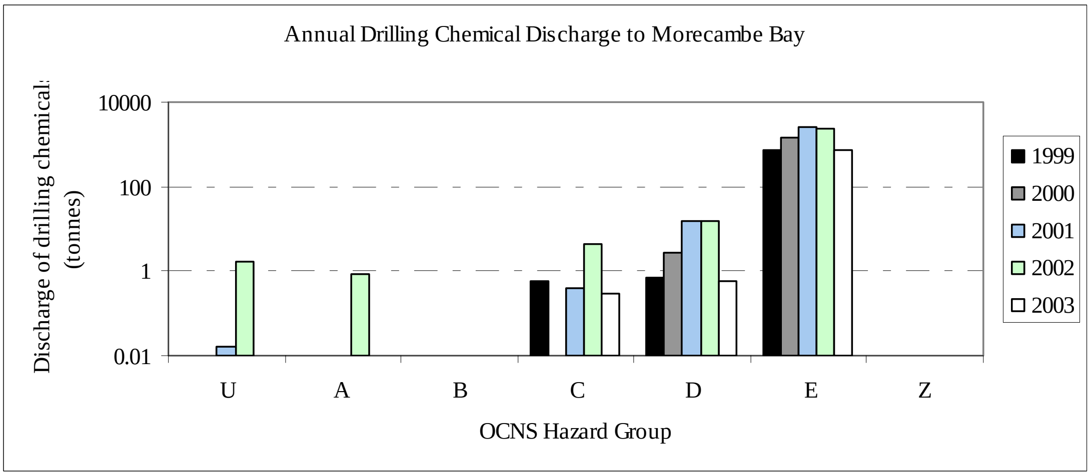

Figure 11. Tonnage of chemicals (shown on a logarithmic scale) in different OCNS hazard groups used in gas production in Morecambe Bay between 1999 and 2003

3.5.4 Acute toxicity of chemicals in produced water

The toxicities of a range of chemicals used in the production process are shown in Table 7. Chemicals of higher toxicity such as biocides are generally used and discharged in relatively smaller quantities (several hundred kilograms per year). Corrosion inhibitors, some of which may have high toxicity, particularly to algae, may be used in larger quantities (around 1 tonne per year). Laboratory studies indicate that the partitioning of different corrosion inhibitors between the oil and produced water phase, and hence their contribution to produced water toxicity, may be highly variable (Henderson *et al*., 1999).

Table 7. Acute toxicity of some of the chemical types used in oil and gas production (EC_{50} mg/l) (Based on data from Holdway, 2002)

Chemical Type	**Algae *(Skeletonema costatum)***	**Brine shrimp (48-hour) (*Artemia salina*)**	**Microtox (minutes) *(Vibrio fischeri)***
Corrosion inhibitior	0.2-2	>20-25	15-50 (15)
Scale inhibitor	60	1000	>1000 (15)
Demulsifier	20	30	20 (15)
Flocculant	>1000	>15000	>15000 (15)
Biocide (glutaraldehyde)	-	19.03^a	9.06 (30)
Biocide			20.2-33.7 (15)
Antifoam	120	150	9 (15)
Surfactant (sodium dodecyl sulphonate)	-	29.21	0.276 (15)

In addition to production chemicals, their reaction products and residual oil, produced water contains a variety of organic and inorganic compounds. The concentration of compounds derived from the formation water such as carboxylic acids is dependent upon the nature of the field being exploited.

Organic acids are one of the components of produced water that are present in the highest concentration in North Sea fields, up to 1g/l total organic acids (Somerville *et al.*, 1987; Utvik, 1999). However salts of the acids identified are of low toxicological concern. The concentrations of other components commonly measured in produced water are shown for both oil and gas fields in Table 8.

Table 8. Concentration range of compounds (mg/l) measured in production water from oil and gas fields on the Dutch Continental Shelf (Cofino *et al.*, 1993).

Compound	**Oil platforms Range**	**Gas platforms Range**
Oil -IR	<0.1-3	<.1-156
Oil -GCMS	0.7-2	1-170
Benzene	0.4-5	0.3-440
Toluene	0.01-2	4-145
Xylenes	0.1-7	0.8-84
Naphthalene	0.07	<0.1-1.2
Aceitic acid	<1-200	27-74
Propionic acid	<1-7	4-17
Sr	94-386	3-231
Zn	0.01-0.09	0.02-72
Pb	<.1	<.001-11
Cu	0.02-0.03	0.007-0.055
As	1-12	<1-210
Cd	<2	<2-210
Cr	4-11	4-27
Ni	20-95	10-110

Based on data from the Dutch Continental Shelf (Table AH) and toxicity data from literature, residual oil contributes the most to the toxicity of produced water (Slager *et al.*, 1992). However benzene and zinc also make a relatively high contribution to the toxicity of produced water from gas platforms. The toxicity of undiluted produced water, to a number of aquatic species, from North Sea platforms is shown in Table 9.

Table 9. Acute toxicity of undiluted produced water to a range of aquatic species from North Sea platforms (based on data from E&P forum 1994; Stromgren *et al*., 1995)

Type of organism	Endpoint	Time days	EC/LC_{50} (%) dilution	NOEC (%) dilution	Type of platform
Algae					
Phaeodactylum tricornutum	Growth	4	0.09-3.6	0.03-0.18	Gas
Skeletonema costatum	Growth	2	4.5-67.6		Oil
Skeletonema costatum	Growth	3	2.3-30		Oil
Bivalves					
Crassostera gigas (larvae)	Mortality	2	5		Oil
Crassostera giga (embryos)	Mortality	2	0.5-24.8		Oil
Mytilus edulis	Growth	5	0.2-1.9		Oil
Abra alba	Faecal pellet production	5	1.1-4		Oil
Copepods					
Acartia tonsa	Immobility	1	5		Oil
Amphipods					
Chaetogammarus	Mortality	4	0.18-3.2		Gas
Shrimp					
Artemia salina	Mortality	1	160-180		Oil
Crangon crangon	Mortality	1	20		Oil
Fish (adult)					
Poecilia reticulate	Mortality	4	0.75-42.3	0.056-32	Gas
Salmo gardineri	Mortality	2	10		Oil

The test data in Table 9 is based on exposure periods of one to several days. Organisms living in the waters around offshore platforms are unlikely to remain within the produced water plume for sufficient time to suffer mortality or other acute effects (since they are free drifting). Dispersion and dilution of produced water will vary with location and will be influenced by the produced water density, the discharge rate, the depth at which it is discharged and local current velocity and state of tide. Liverpool Bay is shallow, 29 meters in the vicinity of the Douglas platform. Very much more water is co-produced with oil than with gas. Thus, the produced water volume from the Douglas platform discharged in Liverpool Bay ranges between 5,000-10,000 m^3/day whereas the same volume of water would be discharged from the Morecambe South platform over one year. Dye tracer studies and the results of modeling for North Sea platforms with similar produced water discharge rates and residual current velocities to those of Douglas, indicate that dilutions of 1:100 may be achieved within 50m of the discharge point and 1:2800 at 1,000m (Somerville, 1987). Assuming that the above dilution of produced water is achieved at Douglas and that the toxicity is of the same order of magnitude to that described in Table 9 then the maximum dilution achieved at 2,800m would be sufficient to dilute the produced water concentration in seawater to below the no observed effect concentration (based on continuous exposure) for the most sensitive species in Table 9. In addition to dispersion mixing and dilution, the concentration of compounds present in produced water will also be progressively reduced as a result of biodegradation.

3.5.5 Produced water- other toxic effects - oestrogen receptor agonists

Of particular concern are those compounds, which can disrupt the normal functioning of the endocrine system and various techniques have been developed to detect and quantify the presence of such compounds. One such technique uses yeast cells that incorporate the human oestrogen receptor and which produce a measurable response in the presence of compounds that can bind to the receptor and mimic natural estrogens. A study for the Oslo and Paris (OSPAR) Commission (Lye, 2000) concluded that alkylphenols (C8 and C9) from the degradation of alkylphenol ethoxylates (APnEO), added as production chemicals to certain offshore procedures, and certain polycyclic aromatic hydrocarbons (PAH) were the principal estrogenic compounds found in offshore discharges. The in vitro estrogen receptor (ER) agonist potency of a number of alkylphenols has been investigated using the in vitro yeast estrogen screen (YES) assay (Routledge and Sumpter, 1996). Their estrogenic potency varies and is dependent on a number of structural properties. The total estrogenic activity is, therefore, dependent on which compounds are present and in what quantities. Although the use of APnEO has now been phased out in the offshore industry, produced waters still contain in vitro estrogen receptor (ER) agonists in the form of short-chain (C1 to C5) and long chain (C9) alkylphenols (Thomas *et al*., 2004). Short-chain (C1 toC7) alkylphenols are natural components of crude oil that are suitably hydrophilic (indicated by KOW data) to partition into the aqueous phase during oil–water separation and are consequently found in produced water discharges (Dale *et al*., 1995, Taylor *et al*, 1997).

The ER agonist potency and C1 to C9 alkyl substituted phenol content of offshore produced water effluents have been determined at one Irish Sea installation (Douglas - oil) and N. Sea installations. The in vitro reporter gene assay was used to determine ER agonist potency, whilst gas chromatography coupled to mass spectrometry (GC-MS) was used to quantify the concentration of alkylphenols. The cytotoxicity observed as yeast growth inhibition in samples from the Douglas platform is shown in Table 10. The data are presented in the form of concentration factor LOECs (lowest observed effect concentration). The lower the concentration factors of observed effect, the more toxic the effluent sample. For comparison, other oil platforms in the North Sea had ER agonist activity that ranged from the LOD (Limit of detection) to 91 ng E2 equivalents l^{-1}. In previous studies effluents collected from the UK sector had an ER agonist potency of between 3 and 5 ng E2 l^{-1}, whilst effluents collected from the Statfjord C platform in the Norwegian sector had an activity of between 23 and 28 ng E2/l.

Table 10. ER agonist potency and summary C1 to C5 alkylphenol concentrations in produced water from the Douglas platform, Irish Sea (from Thomas *et al*., 2004).

	Produced water	**ER agonist activity**				**Alkylphenol concentration**					
Platform	number Volume discharge/ m^3 yr^{-1}	ng E2 l^{-1}	Std Dev	Yeast growth Inhibition (Conc. Factor LOEC)	g E2 yr^{-}	Sum C1	Sum C2	Sum C3	Sum C4	Sum C5	Total
Douglas	2,505,040	<0.1	0.3	>625	-	110	143	71	40	<LOD	365

3.5.6 Biological effects in pelagic ecosystems programme (BECPELAG)

The evidence suggests that produced water discharges are not acutely toxic except within the immediate vicinity of the discharge point and generally when there is more than 1% produced water present. Over the last 20 years there has been a greater focus on compounds that are persistent and toxic and might biomagnify in the foodchain. Few studies to date consider chronic toxicity of compounds discharged in produced water but potential effects may be more widely spread as they commonly occur at lower exposure concentrations.

The ICES Biological Effects Monitoring in Pelagic Ecosystems workshop (BECPELAG) was a multi-national, multi-discipline study looking at techniques suitable for monitoring the medium to longer term effects of contaminants on pelagic (open water, or offshore) ecosystems. A major part of the study involved deployment of large cages of Cod (*Gadus morhua*) and Blue mussels (*Mytilus edulis*) in a transect moving away from an oil platform in the Statfjord oil field (North Sea). Different components of the pelagic ecosystem, from bacteria and microzooplankton through zooplankton and fish were included in the study. In addition to the field-collected organisms, caged cod and blue mussels, passive samplers; diffuse gradient thin films (DGT's) and semi-permeable membrane devices (SPMD's) were deployed at 8 locations. The caged organisms and passive samplers were analysed using a wide range of biomarkers and bioassays for chemical, molecular, cellular and physiological changes. e.g. toxicity bioassays, enzymatic induction (EROD), lysosomal damage, Scope for Growth (SFG), genotoxicity, endocrine disruption effects, metallothionein induction, PAH metabolites, acetylcholinesterase inhibition, bacterial diversity. Although the programme was focussed on North Sea platforms it is of value in this context since the monitoring techniques deployed provided valuable information on their variability of responses, usefulness and ability to detect trends along pollution gradients. In summary, the early data from the study appears to show that, as proximity to the oil platform increases.

- Hydrocarbon concentrations in the water increase (Macintosh *et al*., 2002).
- PAH concentrations in fish and zooplankton increase (Ruus and Klungsøyr, 2002).
- CYP1A (detoxification enzyme) levels in herring show a possible rise as the hydrocarbon content of the water increases (Hylland and McIntosh, 2002).
- PAH derived bile metabolites increase in fish (Aas, Jonsson, *et al*., 2002).
- DNA adduct levels rise in fish (Liewenborg *et al*., 2002; Aas, Regoli, *et al*., 2002).
- Detectable histological changes to both cod (Feist *et al*., 2002), and mussels (Feist *et al*., 2002, Bilbao *et al*., 2002).
- Increased levels of glutathione-s-transferase activity in cod (Danischewski, 2002)
- Some estrogenic activity in all extracts. No androgenic activity (*in vitro* tests) (Thomas *et al*., 2002).
- AhR agonist activity found in almost all surface water sample extracts (Thomas *et al*., 2002).
- Blue mussels show cell and tissue biomarker responses (Bilbao *et al*., 2002).

The study also found:

- Produced water caused detectable genotoxic effects using both the Mutatox assay (Åkerman *et al*., 2002) and the Comet assay (Danischewski *et al*., 2002).
- Toxic effects of oil tested in the laboratory may be enhanced (photoactivation) or decreased (photodegradation) in the presence of increased UV light at normal environmental levels e.g daylight. (Lyons *et al*., 2002).

Some methods which were used in the BECPELAG study, showed no response change corresponding to oil platform proximity:

- No EROD response in Cod (Förlin and Hylland, 2002).
- No rise in acetylcholinesterase in Cod (Danischewski, 2002).
- No observed effects to metallothionein concentrations in mussel tissue (Erk and Raspor, 2002).
- *Tisbe battagliai* and *Skeletonema costatum* assays were mostly unaffected by extracts of surface waters from near oil platforms (Thomas *et al*., 2002).

All BECPELAG references are available online at:
http://www.iis.niva.no/PELAGIC/web/participants_only/wrap-up%20conference/overview.htm

3.5.7 Near field chemical contamination - Liverpool Bay

3.5.7.1 Metals

Five metals (zinc, nickel, chromium, cadmium and lead) were measured in the water column immediately downstream of the main installations (Hamilton, Hamilton North, Lennox and the Douglas OSI) in Liverpool Bay in 1993, 1994 and 2001. The mean concentration is below the UK environmental quality standard value for seawater for each of the metals measured over all three years (Figure 12). Zinc concentrations at Hamilton and Douglas were elevated in 2001 compared to 1993 and 1994 and were high when compared to coastal waters in general. The highest zinc levels were measured at Lennox (13µg/l). Lead levels were also raised and are high (0.7-0.85µg/l) by comparison to those of coastal waters (NMMP, 1999 and 2002).

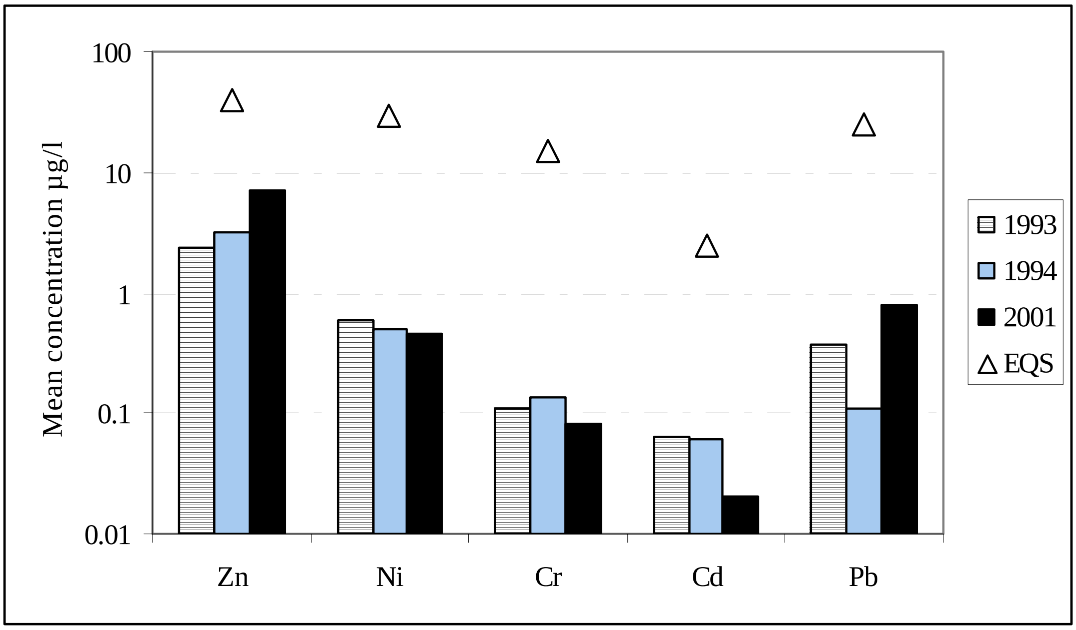

Figure 12. Mean concentration (shown on a logarithmic scale) for five metals measured in the surface of the water column downstream of the main installations in Liverpool Bay in 1993 (hatched bar), 1994 (light bar) and 2001(dark bar). The triangles denote UK Environmental Quality Standards (EQS') for seawater expressed as annual average dissolved concentration (Cole *et al.*, 1999)

The concentration of selected metals in pooled sediment samples collected from locations within 5 kilometres of each of the main installations in Liverpool Bay in 1994 and 2001 is shown in Figure 13. Metal concentrations vary between sites and sample dates. Barium concentration increases in sediment samples between 1994 and 2001. For the other metals sampled, with the exception of zinc at Hamilton North and Lennox, the mean concentrations are generally lower in 2001 compared to those measured in 1994. Cadmium was below the limit of detection in all samples. Although barium concentration was elevated in the sediment in 2001 there was no clear concentration trend in this or other metals measured in sediment samples with distances from each of the installations. Ecotoxicological assessment criteria for metals in sediment were developed by OSPAR (1997). The sediment metal concentrations for copper, lead and zinc, all overlap their respective EAC ranges 5-50, 5-50 and 50-500µg/kg dw. This overlap suggests that there is a potential for biological effects as a result of sediment metal exposure to benthic organisms. Sediment concentrations of chromium are mostly below the EAC range for chromium in 2001, 10-100µg/kg dw.

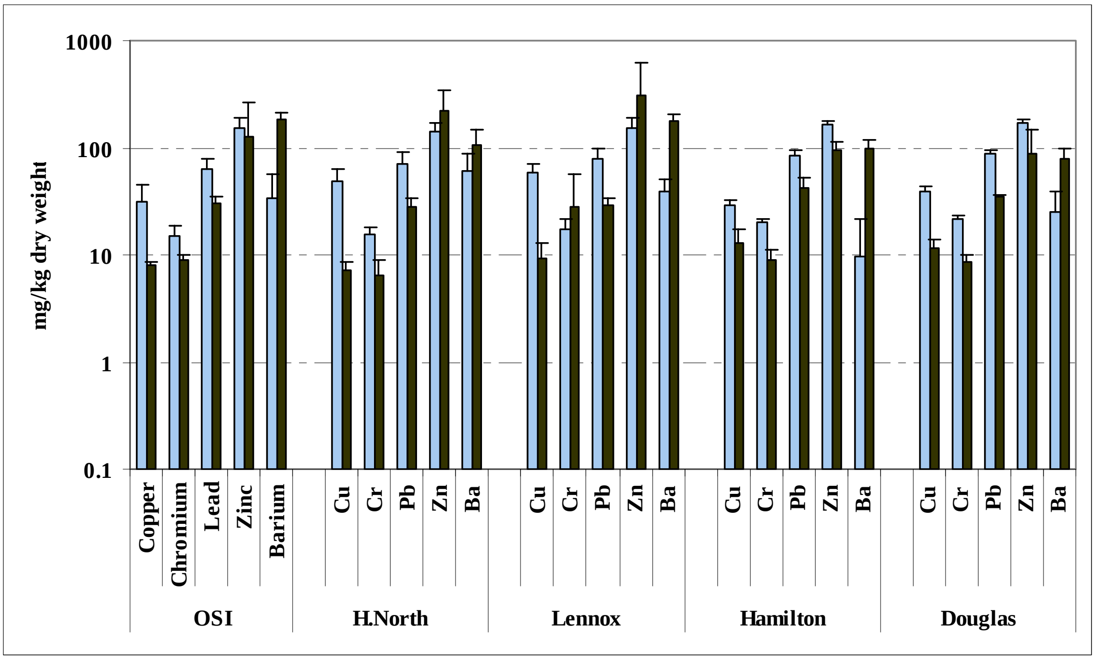

Figure 13. Mean and standard deviation for metal concentrations measured in the <63µm fraction of sediment sampled around the installations in Liverpool Bay in 1994 (light bar) and 2001(dark bar)

3.5.7.2 Polycyclic aromatic hydrocarbons

In the same study in which sediment samples were analysed for metals, samples were analysed for total polycyclic aromatic hydrocarbons (PAH). The results of the analysis for total PAH are shown in Figure 14. PAH may be derived from pyrogenic sources as well as from spills or discharge of oil.

The distribution of individual PAH was also measured in sediment samples from each site. Individual PAH concentrations were higher in 2001 than 1994 in all samples. However, due to the large variation in PAH concentration between sediment samples the concentration increase between 1994 and 2001 was significantly different only at Hamilton and Douglas ($p<0.05$). The ratio of different PAH indicates that the increased PAH concentrations at the OSI, Hamilton and Douglas are from pyrogenic sources while those at Lennox are from pyrogenic and petrogenic sources. However, it is noted that oil that has been in the sediment for some time, and has therefore partially degraded, may have similar ratios of PAH to those found in hydrocarbons from pyrogenic sources.

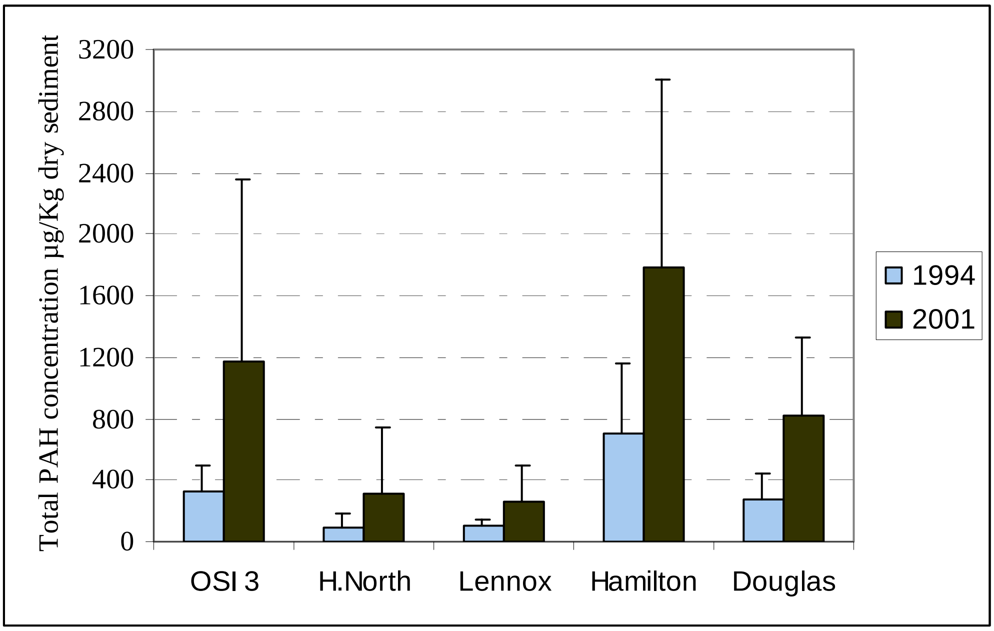

Figure 14. Mean and standard deviation total PAH concentration measured in the <63µm fraction of sediment sampled around the installations in Liverpool Bay in 1994 and 2001

The concentration of seven PAH are shown in Figure 15 together with sediment ecotoxicological assessment criteria (EAC) which indicate a concentration range below which no harm to the marine environment would be expected (OSPAR, 1997).

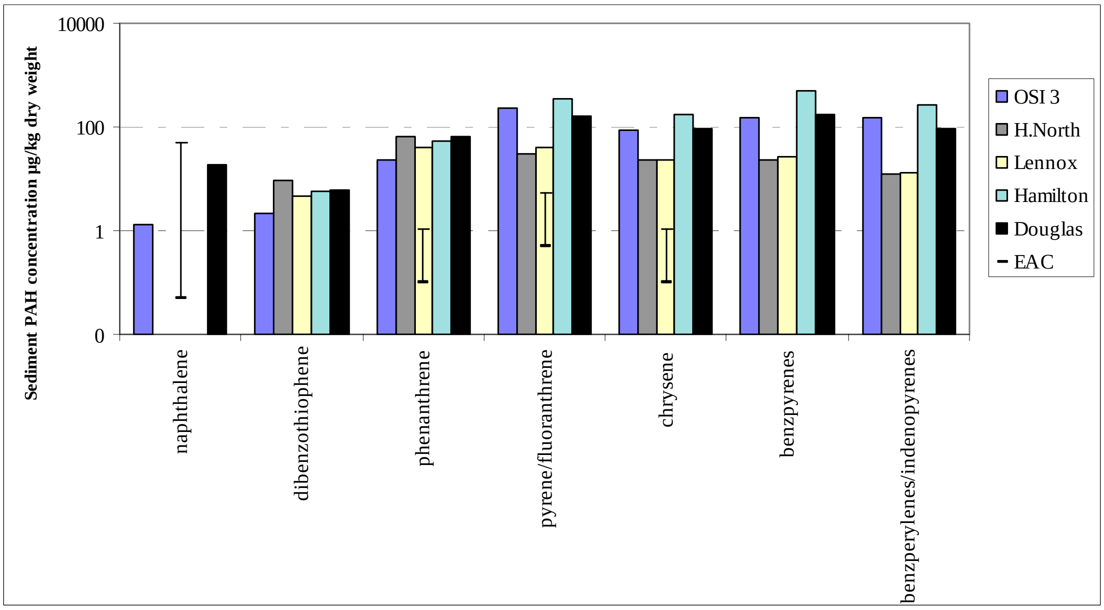

Figure 15. Mean concentration of seven PAH and Ecotoxicological Assessment Criteria (EAC) (OSPAR, 1997) in the <63µm fraction of sediment sampled around the installations in Liverpool Bay in 2001

3.5.7.3 Corrosion inhibitors, scale inhibitors and gas treating chemicals

Chemicals used in the offshore production process include demulsifiers, biocides, corrosion inhibitors, scale inhibitors and gas treatment chemicals. Studies of corrosion inhibitors indicate that many of them partition predominantly to the aqueous phase, while demulsifiers partition to the oil phase of produced water (Grigson *et al*., 2000). The corrosion inhibitor, benzalkonium quaternary ammonium salts have been found in low concentrations (0.74–10.84 ng/g) in the sediments near two North Sea oil platforms. There have been few research studies reported on this common group of chemicals so relatively little is known about their fate, behaviour and effects.

3.5.8 Near field chemical contamination - Morecambe Bay

No survey data comparable to Liverpool Bay was available for the Morecambe Bay installations. If drilling activity was responsible for the metal concentrations around installations in Liverpool Bay then concentrations around installations in Morecambe Bay are likely to be similar or higher as a larger amount of drilling activity took place between 2000 and 2002.

Lower total amounts of oil were discharged from Morecambe Bay installations between 2000 and 2003 (0.06-0.55 tonnes/yr) compared to Liverpool Bay (119-150 tonnes/yr). The equivalent levels of contamination in Morecambe Bay would be expected to be much lower if PAH contamination of sediments near installations in Liverpool Bay is primarily from this source.

3.6 Summary

The oil and gas industry in the Irish Sea is small by comparison to that of the North Sea but bears comparison to that of the Southern North Sea which is dominated by gas production and where many of the platforms are in relatively shallow water.

Chemicals are used for a variety of functions in the extraction and production of oil and gas. The discharge of production and drilling chemicals, residual oil and compounds derived from the formation water produced with the oil or gas during oil and gas extraction and production can contribute to the contaminant concentration in sediments and water. Chemical use offshore is regulated to reduce the quantities used and to ensure the use of those that are least harmful: The new offshore chemicals regulations (OCR, 2002) require operators to source alternative products to avoid the use of those which contain chemicals that are persistent, bioaccumulative or toxic or have a combination of these properties.

The majority of drilling fluids used in Liverpool and Morecambe Bays are water-based, though organic phase fluids (either mineral oil or synthetic-based) may be used for some well sections, with the cuttings taken to shore for cleaning and disposal. The majority of compounds making up the drilling mud system are inorganic salts and clays, which disperse relatively rapidly and are of low toxicity. There is some evidence of metal contamination in the sediment in the vicinity of some of the platforms in Liverpool Bay and the co-occurrence of the weighting chemical barium suggests that this may be related to drilling activity. Although some of the metal concentrations measured fall within the OSPAR EAC range for metals in sediments and therefore indicate some likelihood of biological effects, none were apparent as evidenced by the lack of disturbance in the associated benthic communities. Unlike the Northern North Sea there is no indication of build up of large cuttings piles around the platforms in both Liverpool and Morecambe Bays and therefore the impacts associated with these are also likely to be limited.

A wide range of chemicals is used in the production of oil and gas, generally fewer in the production of gas. The most toxic chemicals are used in very small quantities and dilution of produced water usually occurs within 50-1000 meters of the discharge point to concentrations below the level at which acute toxic effects are observed. The data on which these observations are based is frequently derived from continuous exposure of organisms for periods up to several days, which is a situation unlikely to occur in the environment. Therefore the predicted distance for dilution of produced water to concentrations below the level at which acute effects may occur is probably conservative. However a variety of sub lethal biological effects have been demonstrated in caged organisms deployed in the vicinity of offshore platforms. The results of recent work programmes monitoring the effects of produced water on pelagic ecosystems will therefore need to be fully evaluated before firm conclusions can be made on the likelihood of wider field effects.

4. MONITORING PROGRAMMES, SURVEY AND RESEARCH BASED DATA AND INFORMATION

4.1 INPUTS TO THE SEA 6 AREA

The Irish Sea is a semi-enclosed region, highly influenced by fresh water discharges, resulting in the Irish Sea being less saline than the North Sea or English Channel. A large proportion of the land on the coastal area of the Irish Sea is used for agricultural purposes and therefore the industry that does exist is concentrated in certain areas. The major industrial locations within the region are found in Merseyside and Lancashire. Small areas of industrial development are found in Cumbria and on Deeside in Clwyd. On the western side of the Irish Sea the main industrial areas include Belfast and Dublin. All of these industrial areas are likely to contribute to the contaminant input to the Irish Sea.

Inputs of oil to the marine environment arise from a wide variety of sources. Although large spillage's following tanker accidents tend to have a high public profile, the majority of petroleum hydrocarbons enter the sea from; shipping, oil and gas exploration and production, natural oil seeps, sewage discharges, storm water run-off and road drainage, riverine inputs, atmospheric fall-out due to fossil fuel combustion and discharges from terminals and refineries. Some hydrocarbons are biosynthesised by phytoplankton, specific PAH such as perylene are produced during early diagenesis in shallow sediments. No recent estimates of the relative magnitude of inputs from these various sources have been made for the Irish Sea.

Input data for metals and organic compounds measured from dredge material dumped in to the Irish Sea are displayed in Table 11. Over the last ten years highest metal inputs were found for Pb, Zn and As. Inputs from Pb, Cu, Ni and Cd from dredge dumping have remained relatively stable between 1993 and 2003. Inputs from Zn and Cr were relatively high between 1993 and 1997 (average 376 and 111.68 t/y respectively), since then (1998-2003) inputs from dredge material for both Zn and Cr have reduced markedly (average 131.2 and 20.11 t/y respectively). The opposite pattern was observed for As and Hg with low input reported between 1993-1997 (average 4.7 and 1.5 t/y respectively), with increased inputs from 1998 to 2003 (average 381.2 and 144.1 t/y).

Organic contaminant concentrations in dredge material are only available from 2002. A marked increase in the concentrations of DBT, TBT and PCB (ICES 7) were reported between 2002 and 2003. However, this apparent increase represents an increase in the data reported for these substances. Oil inputs in 2003 from dredged material amounted to 371.55 t/y.

Table 11. Concentrations of metals and organic contaminants measured in dredge material dumped in to the Irish Sea between 1993 and 2003 (all estimated values in tonnes unless indicated).

Year	Dumped (t)	Solids (t)	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As	DBT (kg)	TBT (kg)	PCBs ICES7 (kg)
1993	5,580,120	3,120,386	1.55	104.45	78.02	2.02	63.99	132.05	412.44	0.14			
1994	4,457,906	2,984,388	0.54	100.90	55.42	1.25	40.20	192.75	329.95	0.04			
1995	4,809,423	3,150,288	0.67	125.01	67.73	1.40	45.76	253.67	380.89	0.07			
1996	5,935,712	4,117,335	0.79	117.11	66.92	1.42	44.80	254.89	384.35	3.88			
1997	4,113,204	2,547,446	1.00	110.93	61.85	1.20	43.37	151.90	372.36	19.49			
1998	4,462,013	2,740,476	1.36	1.12	18.33	102.51	56.08	112.93	53.14	319.35			
1999	6,775,521	3,338,293	1.67	134.43	81.16	1.77	161.85	63.08	436.44	25.64			
2000	4,387,531	2,562,587	1.14	140.22	67.24	1.42	134.85	56.64	368.77	30.38			
2001	8,986,875	6,199,685	2.23	398.86	134.98	2.20	227.65	139.43	778.25	62.23			
2002	5,626,500	3,691,223	1.21	113.19	67.26	1.08	54.42	120.88	430.78	35.34	0.02	0.085	0.00
2003	5,157,916	3,753,532	2.17	0.94	31.32	87.43	62.20	108.54	44.26	348.93	51.20	436.30	2.90

Table 12. Sources of metals and organic contaminants in to the Irish Sea from direct discharge and river inputs (OSPAR Commission, 2004).

		Cd	Hg	Cu	Pb	Zn	γ-HCH	PCB	SPM(2)
		[t]	[t]	[t]	[t]	[t]	[kg]	[kg]	[kt]
Direct discharge	Low Est	0.36	0.3	17.5	26.3	98	0.2	0	74.1
	Up Est	0.66	0.4	17.5	27.3	98	6.3	0.6	74.1
Riverine inputs	Low Est	2.4	0.3	122	115	717	10	4	591
	Up Est	3.5	0.5	123	120	723	81	425	597
Total	Low Est	2.76	0.6	139.5	141.3	815	10.2	4	665.1
	Up Est	4.16	0.9	140.5	147.3	821	87.3	425.6	671.1
Riverine Inputs	Low Est	87.0	50.0	87.5	81.4	88.0	98.0	100.0	88.9
as % of total	Up Est	84.1	55.6	87.5	81.5	88.1	92.8	99.9	89.0

(γ-HCH, hexachlorocyclohexane; SPM, suspended particulate matter; Low/Up Est, low/ upper estimate).

A comprehensive study was carried out between 2000 and 2002 to determine the inputs of a number of organic and metal contaminants in to the surrounding waters of Northern Europe, including the Irish Sea (OSPAR Commission, 2004). Data from this study for the Irish Sea has been summarised in Table 12. With the exception of Hg, where direct discharge and river inputs were approximately equal, riverine inputs contributed to greater than 80% of the total contaminant concentration. For the organic contaminants γ-HCH and PCB river inputs contributed up to 95% and 99.9% respectively.

4.2 SAMPLING PROGRAMMES AND LOCATION MAPS

The majority of data has been obtained from the UK National Marine Monitoring Program (UK NMMP) during the last five years. The sites are those from where physical, biological and chemical data have been collected in support of the UK's mandatory monitoring requirements under the OSPAR Joint Assessment and Monitoring Programme (JAMP) (Figure 16). Locations of sampling sites where specific data were taken including sediment, fish, shellfish and locations of mammal strandings are illustrated in Figure 17. In addition to the UK NMMP, data has been included from other recent peer reviewed papers and technical reports where appropriate.

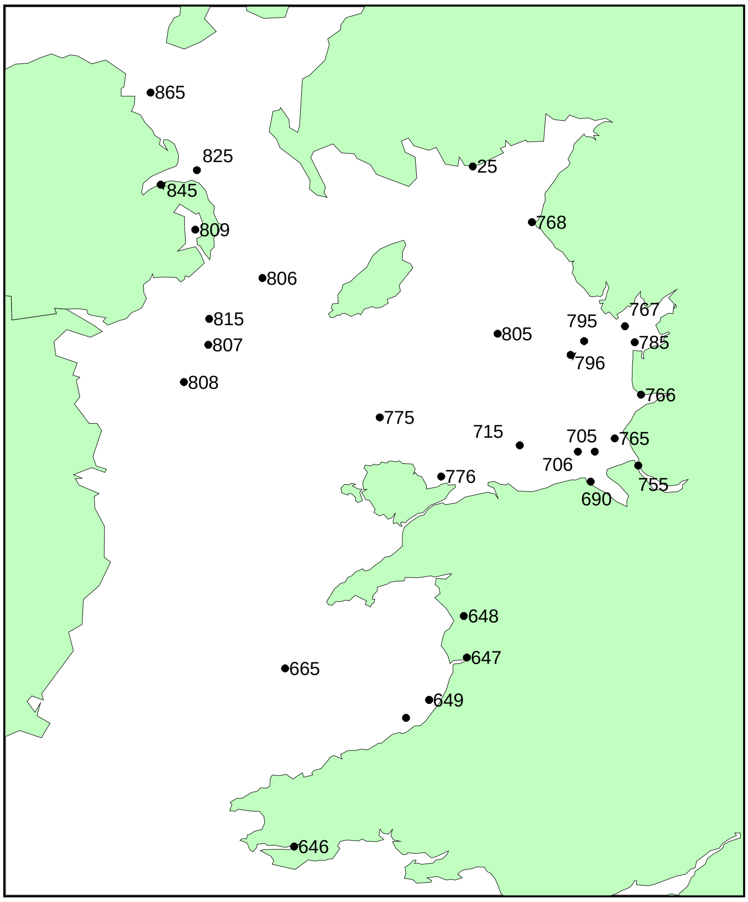

Figure 16. Map of SEA 6 survey area showing the locations of the UK NMMP sampling sites for which data is reported.

Figure 17. Map of SEA 6 survey area showing the locations of the selected sampling sites where specific data has been reported. Sites include sediment, shellfish and mussel sampling sites and locations of mammal strandings.

4.3 CHEMICALS IN THE ENVIRONMENT

4.3.1 Introduction

This section is a review of the types and concentrations of chemicals present in the Irish Sea due to the variety of inputs already described. The determinands have been reviewed according to the principal matrix of origin, namely; water, sediment and biota. Compounds discharged by the oil and gas industry include types of hydrocarbons such as *n*-alkanes, branched alkanes, cycloalkanes, and polycyclic aromatic hydrocarbons (PAH). Other compounds of importance include chlorinated biphenyls (CB) and metals. Concentrations of these chemicals in the Irish Sea are reviewed in the following sections.

4.3.2 Water

4.3.2.1 Total Hydrocarbons (THC)

Crude oil is a mixture of tens of thousands of compounds. Although these can be measured individually it is often useful to analyse samples by total hydrocarbons. The total input of petroleum hydrocarbons into the marine environment, as a whole, has been estimated as 3.2 million tonnes per year (McElroy *et al*., 1989).

Survey data carried out between 1982-3 in Morecambe Bay prior to the development of the Morecambe Bay Gas Field reported seawater concentrations of THC ranging from 1.3 to 40 µg/l with most concentrations towards the lower end of this range (Law *et al*., 1988). These values were comparable with THC data collected from the North Sea (Law *et al*., 1994).

4.3.2.2 Polycyclic aromatic hydrocarbons (PAH)

Although many PAH arise naturally from sources such as volcanoes, oil seeps and forest fires, it is strongly suggested that anthropogenic sources of PAH are the major input to the environment (McElroy *et al*., 1989). Due to their high octanol-water (K_{ow}) and organic carbon adsorption (K_{oc}) partition coefficients PAH have a tendency to adsorb to suspended particles deposited to the sediments, and the potential to bioaccumulate in marine organisms. Consequently, PAH concentrations are often low or below the limit of detection in the water column.

The concentrations of 15 PAH in water samples from the UK NMMP are shown in Table 13. Six of the 15 PAH analysed for were below the limit of detection at all stations in the Sea 6 area. Of those PAH detected, concentrations of fluoranthene and pyrene were highest.

The maximum fluoranthene concentration of 6 ng/l at NMMP sites 785 and 705 was less than the maximum allowable concentration (MAC) of 10 ng/l (Defra, 2003). Toxicity data for pyrene is not available for a MAC to be calculated. Total PAH concentrations were undetected at three of the offshore stations (805, 775 & 665). Highest concentrations were found within the Morecambe Bay area (station 785), this also corresponded with the highest suspended particulate matter (SPM) load found at this station.

Table 13. Concentration of PAH in water samples collected during 1999-2001 from the UK NMMP stations in the Irish Sea (ng/l).

NMMP site	Naph	Acen	Fluor	Phen	Anth	Fluoranth	Pyr	BaA	Chrys	BeP	BbF	BkF	BaP	DBahA	BghiP	ΣPAH	SPM
25	<50	<3	<1	<8	<1	5	4	<2	<2	<1	1	1	2	1	2	15	NR
805	<6	<1	<2	<3	<1	<2	<1	<6	<4	<2	<2	<4	<4	<12	<17	ND	0.9
795	<50	<3	<1	<8	<1	3	2	<2	<2	<1	1	<1	1	<1	<1	6	1.6
785	<50	<1	<1	<8	<1	6	4	3	2	<1	2	1	3	1	3	24	5
775	<6	<1	<2	<3	<1	<2	<1	<6	<4	<2	<2	<4	<4	<12	<17	ND	NR
715	<50	<3	<1	<8	<1	1	<1	<2	<2	<1	<1	<1	<1	<1	<1	1	1.1
705	<6	<1	<2	<3	<1	6	3	<6	<4	<2	2	<4	<4	<12	<17	11	NR
665	<50	<3	<1	<8	<1	<1	<1	<2	<2	<1	<1	<1	<1	<1	<1	ND	0.7
655	<50	<3	<1	<8	<1	<1	1	<2	<2	<1	<1	<1	<1	<1	<1	1	1.6

(Naph, naphthalene; Acen, acenaphthene; Fluor, fluorine; Phen: phenanthrene; Anth, anthracene; Fluoranth, fluoranthene; Pyr, pyrene; BaA, benz[*a*]anthracene; Chrys, chrysene; BeP, benzo[*e*]pyrene; BbF, benzo[*b*]fluoranthene; BkF, benzo[*k*]fluoranthene; BaP, benzo[*a*]pyrene; DBahA, dibenz[*a,h*]anthracene; BghiP, benzo[*ghi*]perylene. ND, no PAH compound detected; NR, no results; ΣPAH, sum of 15 PAH concentrations, SPM, concentration of suspended particulate matter). The less than symbol (<) indicates the limit of detection for a particular compound.

4.3.2.3 Chlorinated Biphenyls (CB)

The determination of chlorinated biphenyls (CB) in seawater is not undertaken within the UK NMMP as their determination at the very low concentrations present in the dissolved phase presents a major sampling and analytical challenge. They can be monitored more effectively in other matrices such as sediments and biological tissues.

4.3.2.4 Metals

Cadmium loads in to the Irish and North seas have fallen by about 75% between 1990 and 2001. Cadmium in discharges from the non-ferrous metals and fertiliser industries have been reduced and further action on cadmium in waste, phosphate fertilisers and releases from metal industries have been recommended (OSPAR Commission, 2002). The fall in cadmium load to the Irish Sea is thought to be mainly due to reductions in inputs from an industrial source at Whitehaven, which was closed in the mid 1990s (Swift, 1995). This overall reduction in cadmium discharges to the coastal waters is reflected in the concentrations in seawater samples taken from NMMP stations in the Irish Sea (Table 14). Maximum cadmium concentrations were found in samples taken from the mouth of the Ribble estuary (0.07 µg/l), however this is significantly lower than the Environmental Quality Standard (EQS) of cadmium in marine waters (2.5 µg/l, SEPA, 2004).

Similar to that described for cadmium, there was a reduction of about 70% in the mercury load during 1990-2001. This was due to controls on discharges from chlor-alkali plants and other industries. However, despite this apparent reduction in discharge, dissolved mercury concentrations exceeded the EQS of 0.3 µg/l at five of the seven NMMP stations measured. Particularly high mercury concentrations were found in both the Mersey (16.1 and 22.5 µg/l) and the Ribble (19.25 µg/l) estuaries, identifying sources of large riverine inputs.

Copper loads in to estuarine and coastal waters have been reported to be fluctuating during the 1990s with an overall downward trend. Copper concentrations were highest in water samples taken from the mouth of the Ribble estuary (3.88 µg/l). However, this concentration did not exceed the seawater copper EQS of 5 µg/l.

The UK input of lead reduced significantly during 1985 to 1990 caused by the phasing out of lead in petrol. Due to the high particle reactivity of lead, estuarine suspended solids and near-shore sediments act as efficient traps for this metal. As a result, dissolved concentrations of lead in seawater are often low. Measured concentrations of dissolved lead within the Irish Sea were significantly lower than the EQS for this metal in seawater (25 µg/l).

Nickel concentrations ranged between 0.31 and 1.73 µg/l, with maximum concentrations found in the Mersey estuary. These concentrations did not exceed the EQS of 15 µg/l.

As described for copper, zinc loads to estuarine and coastal waters have fluctuated during the 1990s with an overall downward trend. However, despite this reduction, dissolved zinc concentrations exceeded the EQS of 10 µg/l in the Mersey (12.77 µg/l) and the Ribble (11.25 µg/l). These high concentrations were likely to result from a mixture of industrial and domestic wastewater discharges into these estuaries.

Table 14. Median metal concentrations measured in seawater samples from NMMP sites in the Irish Sea between 1999 and 2002 (µg/l)

NMMP site		Cd	Hg	Cu	Pb	Ni	Zn
755	Mersey	0.05	16.06	3.01	0.23	1.73	12.77
765	Outer Mersey	0.05	22.5	1.71	0.14	0.74	7.14
766	Ribble	0.07	19.25	3.88	0.4	1.14	11.25
767	Morecambe Bay	0.04	10	1.02	0.08	0.31	1.94
768	Cumbria Coast	0.04	10	2.79	0.18	0.57	5.57
845	Belfast Lough	0.04	0.05	1.61	0.5	1.16	5.07

4.3.2.5 Alkylphenols

Alkylphenol polyethoxylates (APEOs) have previously been used in the oil and gas industries as rig washes and cuttings cleaners where they were discharged directly into the sea without treatment (Blackburn *et al*., 1999). However, following a voluntary agreement between government and suppliers of offshore Exploration and Production chemicals (E & P) to phase out products containing known endocrine disruptors, there are now no products containing alkylphenols or alkylphenol ethoxylates on the UK list of notified chemicals (Environmental Data Services Report, 1999).

The EQS steering group, on the basis of a quantitative structure-activity relationship (QSAR), has set discharge limits for APEOs. Maximum allowable concentration (MAC) for nonylphenol (NP) and octylphenol (OP) was set at 2.5 µg/l. This limit was exceeded for NP at two adjacent stations; SE Isle of Man (805), and off Morecambe Bay (795), (Table 15). In contrast, the 2.5 µg/l limit for OP was not exceeded at any of the stations in the Irish Sea during the 1999 survey.

Table 15. Concentration of alkylphenol ethoxylates in seawater samples taken from NMMP sites in the Irish Sea (µg/l, CEFAS, 2001).

	NMMP Site	Nonylphenol		Ethoxylates		Octylphenol	
		Total	Dissolved	Total	Dissolved	Total	Dissolved
655	Cardigan Bay	1.5	0.21	0.97	0.55	<0.01	<0.01
665	Offshore Cardigan Bay	0.31	0.34	1.7	3.7	<0.01	<0.01
705	Liverpool Bay	0.49	0.28	1.1	0.8	0.11	0.04
715	Offshore Liverpool Bay	0.92	0.23	2.8	0.47	0.12	0.48
776	Red Wharf Bay Anglesey	0.91	0.25	0.45	0.78	0.1	0.22
795	Off Morecambe Bay	2.2	4.2	0.41	2.9	<0.01	<0.01
805	SE Isle of Man	5.2	2.9	1.7	0.22	<0.01	<0.01
815	Dundrum Bay	2	1.7	0.34	0.19	0.14	<0.01

4.3.3 Sediment

The extent to which trace metals and trace organic compounds discharged to the marine environment are deposited into sediments depends on their solubility. Trace organic compounds in particular are not generally soluble in water and are more likely to be detected in sediments. Metals have a tendency to partition to suspended particulate matter within the water column, which are subsequently deposited to sediments. Therefore, sediment contaminant concentrations are usually significantly greater than those found in the water column.

4.3.3.1 Polycyclic aromatic hydrocarbons (PAH)

The median concentrations of 10 PAH compounds in sediment samples collected from UK NMMP sites in the Irish Sea during 1999 and 2002 can be seen in Table 16. Sediment PAH concentrations were significantly greater than the PAH concentrations of corresponding seawater samples. This is to be expected due to the known low solubilities and high partitioning of PAH compounds to suspended particulates.

The most common PAH compounds detected in the sediment samples from the Irish Sea were fluoranthene, benzo[*ghi*]perylene, phenanthrene & pyrene. These four PAH made up approximately 55% of the total PAH concentration.

Table 16. Median concentrations of 10 PAH in sediment samples collected during 1999-2002 from NMMP stations in the SEA 6 area (µg/kg dw).

NMMP site		Anth	BaA	BaP	BghiP	Chr+Tri	Fluo	IcdP	Naph	Pa	Pyr	ΣPAH
25	Solway	5.33	21.3	21.7	23.92	26.31	38.45	25.7	18.4	34	30.72	245.84
646	Milford Haven	39.4	131	157	148.5	182.6	248.9	169.1	281	0	217.8	1574.84
647	Dovey	11.1	33.3	14.4	33.24	56.5	80.22	36.12	112	71.1	57.44	565.8
648	Mawddach	15.1	41.9	38.3	34.17	58.23	96.66	35.16	119	37.7	71.46	547.31
655	Cardigan Bay	11.5	44.6	40.6	35.6	41.52	98.8	29.4	23	60	66.4	536.5
690	Dee	10	3.63	4.2	19.68	4.805	9.205	15.1	27.8	14.1	8.23	96.3
715	Liverpool Bay	0.6	2.55	2.98	2.06	2.015	3.055	2.17	2.56	3.3	2.58	23.7
755	Mersey	420	880	1441	1283	1001	3164	919.2		1533	3355	13996.8
765	Mersey	14.7	43.7	69	47.67	46.67	64.67	38.67		47.7	85.67	458.4
766	Ribble	65	117	142	105.6	139.9	462.4	85.44		321	413.3	1851.71
767	Morecambe Bay	0.1	0.98	1.91	7.3	1.99	9.18	7.16		3.08	24.51	56.21
768	Cumbria Coast	196	588	801	882	670.2	1684	830.2		889	1546	8085.8
805	SE Isle of Man	4.71	18.7	30.3	31.96	26	45.34	35.72	11.5	34.2	40.46	278.83
806	NE Irish Sea	17.1	68.1	79.4	122.5	101.3	120.3	0	44.6	90.4	93.38	737.03
807	NE Irish Sea	16.2	63.3	71.7	135.3	107	111	0	54.8	86.4	77.7	723.4
808	Irish Sea Buoy	13.7	50.7	59.5	107.8	83.7	89.5	0	40.3	72	61.7	578.9
809	Strangford Lough	11.4	48.9	56.3	90.25	59.85	79.7		25.1	50.5	67.58	489.53
815	Dundrum Bay	14	61.3	76.3	133.6	87.7	109	0	37.5	74.1	81.8	675.3
825	Belfast Lough	0.58	2.34	2.5	5.78	3.5	4.58	4.58	2.08	5.44	4.13	35.28
845	Belfast Lough	20	46.4	72.6	122.6	73.46	91.5	116.6	40.5	86	89.2	752.82
865	North Channel	1.23	3.28	4.33	7.475	4.72	5.08	0	3.37	5.32	4.405	39.19

(Anth, anthracene; BaA, benz[*a*]anthracene; BaP, benzo[*a*]pyrene; BghiP, benzo[*ghi*]perylene; Chr+Tri, chrysene + triphenylene; Fluo, fluoranthene; IcdP, indenol[1,2,3-cd]pyrene; Naph, naphthalene; Pa, phenanthrene; Pyr, pyrene).

The distribution of total PAH in sediment samples of the Irish Sea is illustrated in Figure 18. Significantly higher PAH concentrations were recorded at inshore sites particularly the Mersey estuary and the Cumbria coast where PAH concentrations were 14 and 8 mg/kg dw respectively.

Elevated concentrations were analysed in samples from the inshore sites of Milford Haven and the Ribble compared to those from offshore sites. In general PAH concentrations in offshore sites dropped off significantly compared to sediment sites inshore. For example, total PAH concentrations reduced markedly between the Mersey estuary the outer Mersey and the Liverpool Bay site (NMMP 715), changing from 14 to 0.5 to 0.02 mg/kg dw respectively. Dilution of the river input by the Irish Sea, enhanced by the low solubility of PAH compounds may have caused this reduction in PAH with increased distance from the Mersey estuary.

Further investigations into PAH contamination of the western Irish Sea has been studied. The sum of PAH concentrations in sediments ranged between 83 and 2300 ng/g (Guinan *et al.*, 2001). In a more recent study, concentrations of the sum of 15 PAH in 22 surficial sediment samples ranged from below 100 µg/kg to 1422 µg/kg dw (Charlesworth *et al.*, 2002). These values were comparable with the data from the UK NMMP sites (Table 16).

These concentrations are typical of coastal shelf sediments, but greater than those observed for marine sediments remote from anthropogenic sources (Charlesworth *et al*., 2002).

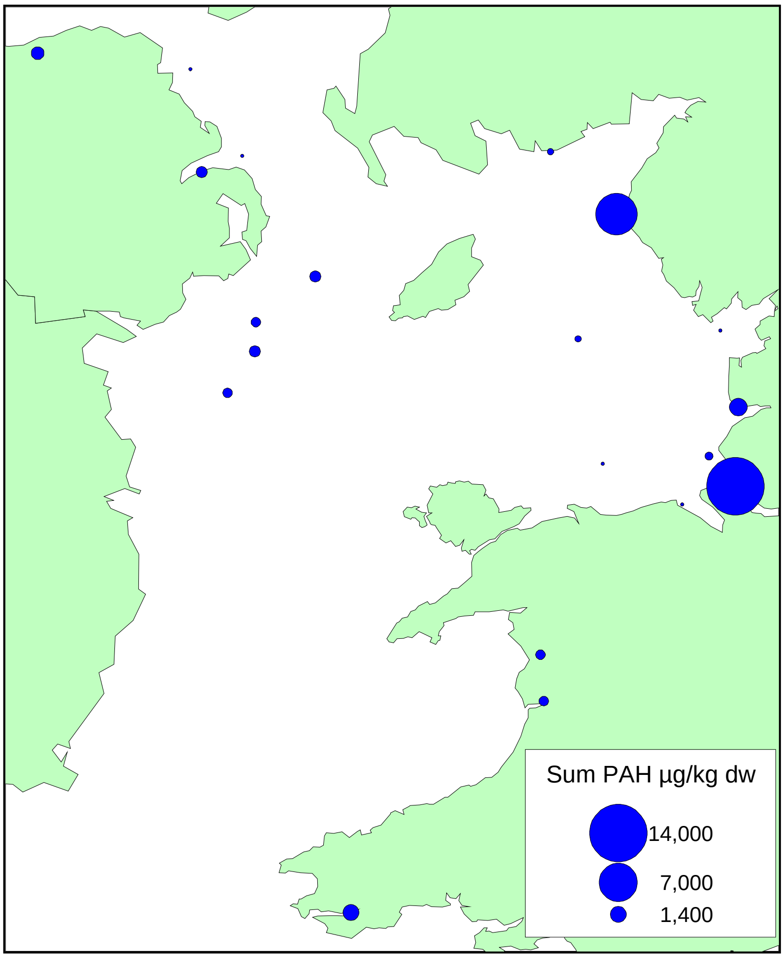

Figure 18. Concentrations of total PAH (µg/kg dry weight) in sediment samples taken from NMMP sites in the Irish Sea.

The presence of organic matter in sediments is believed to be important in terms of PAH distribution. Gravels and coarse sands have little capacity to take up hydrocarbons, whereas silts and muds with a high organic matter content have a high capacity for uptake. This was found in the western Irish Sea were higher PAH concentrations were found in muddy sediments compared to sandy sediments (Charlesworth *et al*., 2002).

From the profile of PAH and through diagnostic ratios, it was concluded by Charlesworth *et al*., (2002) that PAH in the sediments of the western Irish Sea were dominated by combustion sources, although the significant concentrations of alkylated PAH suggested that a petrogenic source was more significant in the north-west Irish Sea.

4.3.3.2 Chlorinated biphenyls (CB)

The distribution of the sum of ten chlorinated biphenyls (CB) in sediment samples in the Irish Sea is illustrated in Figure 19. Total CB concentrations ranged from 0.7 to 63.8 µg/kg dw. As previously described for sediment PAH (Figure 18), highest concentrations of CB were found in the mouth of Mersey estuary (63.8 µg/kg dw), with elevated concentrations found in other inshore sites at Cumbria coast (16 µg/kg dw), Milford Haven (7.3 µg/kg dw) and Belfast Lough (5 µg/kg dw). At all offshore sites measured CB sediment concentrations were less than 3 µg/kg dw.

Following the Piper Alpha incident in 1988, Wells *et al*., (1989) defined a series of (arbitrary) concentration guidelines (on a dry weight basis) for categorisation of concentrations of CB in sediments:

<0.2 µg/kg contamination not detectable
0.20 to 20 µg/kg slightly contaminated
21 to 100 µg/kg contaminated
>100 µg/kg heavily contaminated

Using this guideline, only one site, the Mersey estuary would be classed as contaminated. All of the other sediment sites would be classified as slightly contaminated. From monitoring of CB in sediment samples of Morecambe Bay (CEFAS, 1997), with the exception of one site situated at the river entrance at Aberystwyth, all sites within the Morecambe Bay area were categorised as either not contaminated or slightly contaminated. These ranged from < 0.2 to 7 µg/kg dw for the ICES 7 CB. The exceptionally high concentration of CB reported in sediments at the entrance of the river Ystwyth at Aberystwyth was believed to be due to disturbance by water flows resulting from excavation works in the harbour area prior to sampling (CEFAS, 1997).

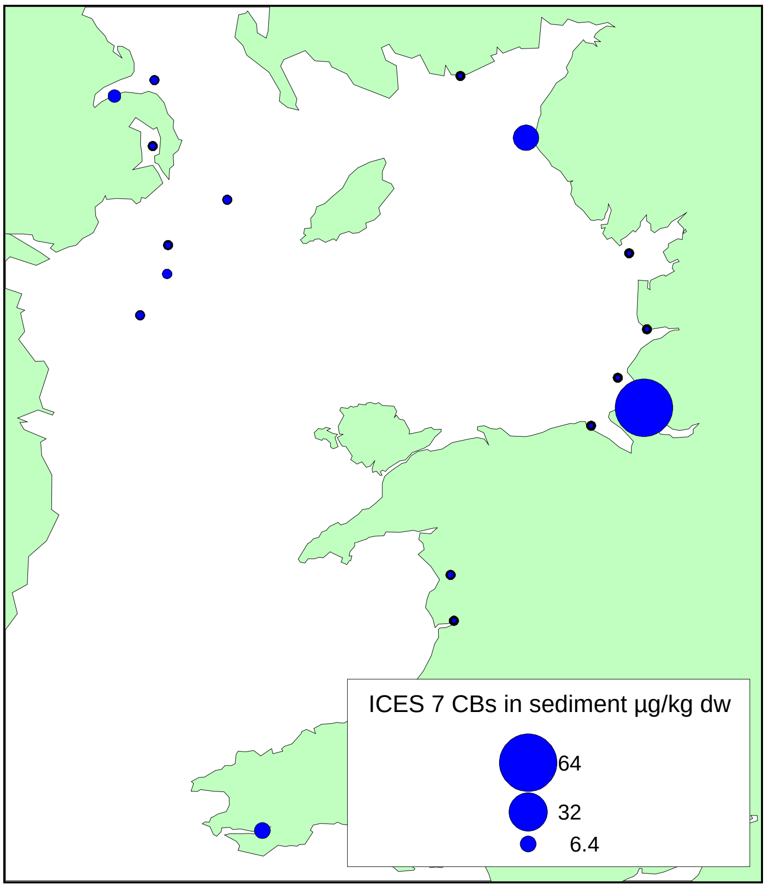

Figure 19. Concentrations of total CB (µg/kg dry weight) in sediment samples taken from NMMP sites within the Irish Sea. ICES 7: the seven congeners of the ICES primary list

4.3.3.3 Metals

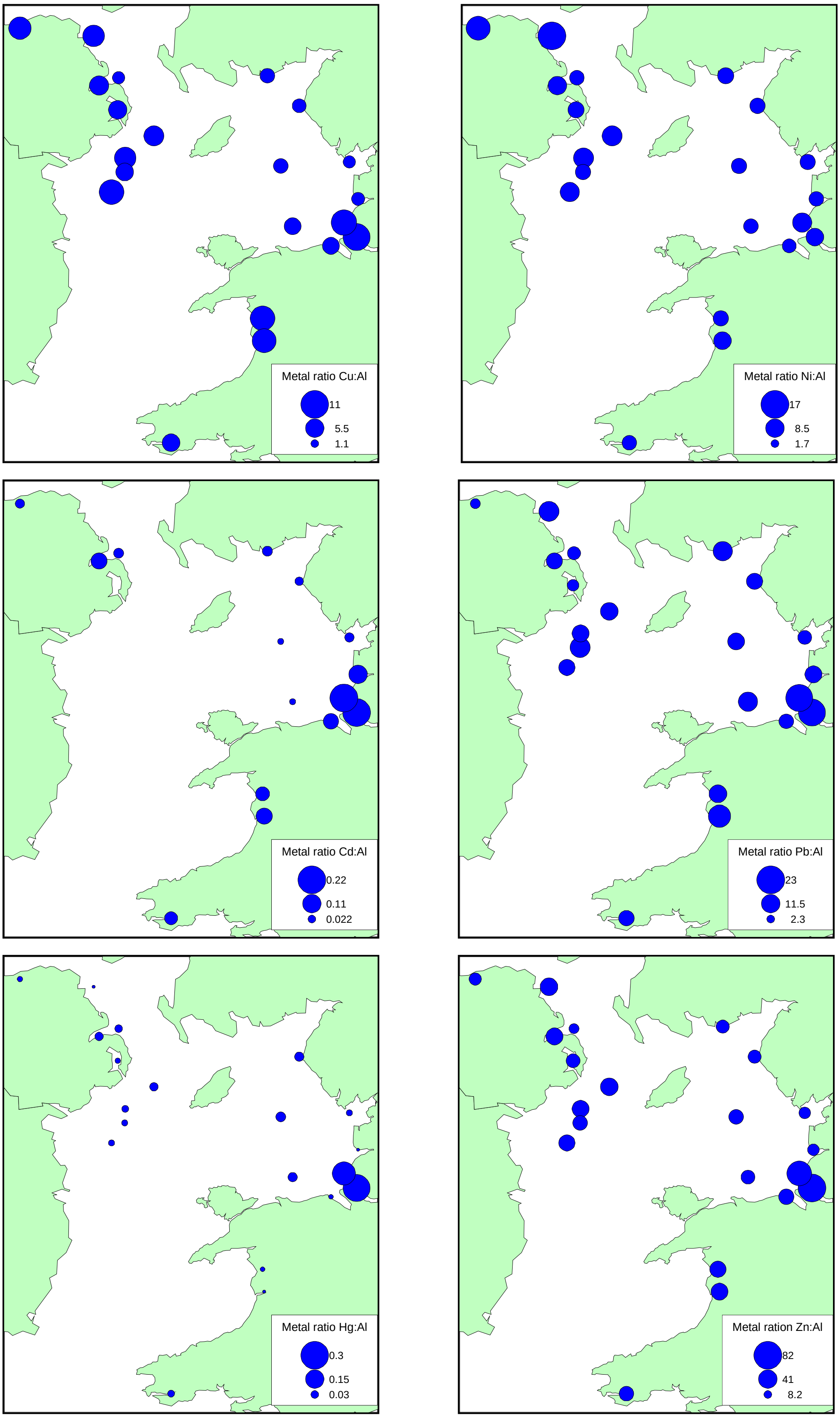

Figure 20. Metal distributions in the Irish Sea. Metals normalised with aluminium to compensate for the granulometric and mineralogical differences (NMMP 1999-2001).

Strong correlations exist in the Irish Sea between metal concentrations and % silt/clay (Charlesworth *et al*., 1999). No statistically significant correlation exists between organic carbon and trace metals, inferring that the concentrations of metals are predominantly determined by grain size. To compensate for the effects of these granulometric and mineralogical differences, and to identify areas of the anthropogenic inputs, the data was normalised to aluminum ratios (Figure 20).

With the exception of nickel, all metal aluminium ratios were highest within the area of the Mersey estuary. This may be attributed to the large degree of manufacturing and industrial activity within this area. This is consistent with that reported by Rowlatt and Lovell (1994), which showed elevated levels of metals in the north-east Irish Sea, attributed to inputs from the industrial areas of north-west England.

Charlesworth *et al*. (1999) reported metal concentrations in sediments from the north-west Irish Sea. From this study they found that all metals (Fe, Ni, Zn, Mn, Pb, Cr, Cu) showed highest metal: Al ratios in the vicinity of the North Channel disposal ground (NW Irish Sea). From the data in the UK NMMP survey (Figure 20), metal:Al ratios in North Channel of the Irish Sea were elevated for Ni and Cu and slightly elevated for Zn and Pb.

4.3.3.4 Alkylphenol ethoxylates

At all stations in the Irish Sea concentrations of NP and ethoxylates were below the limit of detection (0.2 and 1 µg/g respectively, Table 17). Only low concentrations (0.05 µg/g) of OP were detected at five of the seven sites.

Table 17. Concentration of alkylphenol ethoxylates in sediment samples taken from UK NMMP sites in the Irish Sea (µg/g, CEFAS, 2001).

NMMP Site		Nonylphenol	Ethoxylates	Octylphenol
665	Cardigan Bay	<0.19	<1.00	0.01
655	Offshore Cardigan Bay	<0.19	<1.00	<0.01
776	Liverpool Bay	<0.19	<1.00	0.01
715	Offshore Liverpool Bay	<0.19	<1.00	<0.01
705	Red Wharf Bay, Anglesey	<0.19	<1.00	<0.01
795	Off Morecambe Bay	<0.19	<1.00	0.02
805	SE Isle of Man	<0.19	<1.00	0.01
815	Dundrum Bay	<0.19	<1.00	0.05

4.3.4 Biota

Due to the lipophilic properties of many organic contaminants, relatively high concentrations can be found in biological tissues. Metals are also often found in higher concentrations in animal tissues compared to that found in water. The following section will focus on the concentration of contaminants within selected species collected as part of the UK NMMP. Additional data is included were appropriate from other programmes and studies.

4.3.4.1 Total Hydrocarbons (THC)

No specific data is available for the Irish Sea, however, Stagg (1994) found that dab exposed to oil-based drill cuttings accumulate base oil and aromatics hydrocarbons in a concentration dependent manner. The overall concentrations reached in the liver and muscle of the fish are low and yet exposure regimes are typically high, particularly in close proximity (500-1,000m) to oil platforms in the northern North Sea.

4.3.4.2 Polycyclic aromatic hydrocarbons (PAH)

Physical and chemical characteristics such as solubility and reduction potential of PAH varies with molecular weight. As a result, PAH differ in their behaviour, distribution in the environment, and their effects on biological systems. The lower molecular weight PAH (e.g. 2 to 3 ring group of PAH such as naphthalene, fluorene, phenanthrene, and anthracene) have significant acute toxicity to aquatic organisms. Whereas the high molecular weight PAH (202 and above), 4 to 7 ring (from chrysenes to coronenes), whilst not acutely toxic are known to exhibit carcinogenic effects.

Median concentrations of 9 PAH compounds measured in the tissues of mussels, *Mytilus edulis* are shown in Table 17. Overall, pyrene was the most abundant PAH compound in the tissues of the mussel, followed by fluorene and chrysene + triphenylene. Total PAH concentrations ranged from 26 to 148 µg/kg ww, with highest PAH concentrations found in the tissues of mussels collected in the outer Mersey estuary. This coincides with maximum PAH in sediment samples taken from the Mersey estuary (Table 17).

Table 17. Median PAH concentrations in mussels collected from NMMP stations in the Irish Sea during 1999-2001 (µg/kg wet weight).

NMMP site		Pa	Anth	Flu	Pyr	BaA	Chr+Tri	BaP	BghiP	IcdP	ΣPAH
690	Dee	12.55	-	10.56	7.35	-	9.8	-	5.15	-	45.41
755	Mersey	6.12	0.5	15.4	28.4	6.19	14.9	4.19	5.5	0.5	81.7
765	Outer Mersey	1.52	0.8	18.4	45.63	15	26.32	14.29	15.25	10.47	147.68
766	Ribble	0.71	0.5	26.62	54.2	1.53	17.98	1.23	2.2	1.58	106.55
767	Morecambe Bay	1.07	0.5	6.2	7.84	1.95	4.67	0.98	1.72	0.72	25.65
768	Cumbria Coast	0.81	0.5	6.44	7.27	2.4	4.77	1.38	1.73	0.5	25.8

(Pa, phenanthrene; Anth, anthracene; Flu, fluorene; Pyr, pyrene; BaA, benz[*a*]anthracene; Chr+Tri, chrysene + triphenylene; BaP, benzo[*a*]pyrene; BghiP, benzo[*ghi*]perylene; IcdP, indenol[*1,2,3-cd*]pyrene.).

Widdows *et al*. (2003) reported further analysis of chemical contaminants in the tissues of mussels sampled from sites around the Irish Sea between 1996 and 1997 (2002). The concentrations of 2- and 3-ring PAH were highest in mussels from St. Ishmaels, Milford Haven (22.5 µg/g dw), 6 months after the Sea Empress oil spill. This PAH concentration was significantly higher than any other recorded in the Irish Sea, although elevated levels of 2- and 3-ring PAH were reported on the Lancashire coast at New Brighton (4.47 µg/g dw). Repeated sampling the following year (1997) found a reduction in the PAH concentration of mussels from St. Ishmaels, Milford Haven (7.87 µg/g dw), approximately 33% of values recorded the previous year.

4.3.4.3 Chlorinated Biphenyls (CB)

The median concentration of 7 CB in mussels collected from inshore areas of the Irish Sea ranged from 2.7 to 15.68 µg/kg ww, with maximum concentrations reported in mussels from the outer Mersey (Table 18). This corresponds to maximum CB concentrations reported in the sediments of the Mersey (Figure 19). These high concentrations reflect the degree of urbanisation/industrialisation of the area.

Table 18. Median concentrations of CB in mussels collected from UK NMMP sites in the Irish Sea during 1999-2002 (µg/kg wet weight).

NMMP site		**cb28**	**cb52**	**cb101**	**cb118**	**cb138**	**cb153**	**cb180**	**Σ7 CB**
690	Dee	0.24	0.38	0.95	0.74	1.55	2.34	0.14	6.35
755	Mersey	0.43	0.95	2.22	1.85	3.31	4.09	0.18	13.02
765	Outer Mersey	0.39	1.47	2.73	2.21	3.86	4.60	0.41	15.68
766	Ribble	0.10	0.21	1.40	1.14	2.07	2.63	0.14	7.69
767	Morecambe Bay	0.10	0.17	0.53	0.48	1.10	1.32	0.10	3.80
768	Cumbria Coast	0.10	0.11	0.43	0.29	0.70	0.95	0.12	2.70
809	Strangford Lough	0.84	0.78	0.78	0.58	0.59	0.61	0.78	4.95
845	Belfast Lough	0.83	0.91	1.03	1.89	1.89	2.38	0.61	9.54

In a previous study, the total CB concentration of 21 CB congeners in mussels collected from the Irish Sea were reported in the range 3 to 162 µg/kg dw (Thompson *et al*., 1996). Maximum CB concentrations were reported in mussels collected from New Brighton on the Lancashire coast, with elevated concentrations recorded in mussels collected off the coasts of Belfast (123 µg/kg dw) and Holyhead (92 µg/kg dw).

The median concentrations of CB in the liver of fish collected at UK NMMP sites in the Irish Sea are illustrated in Figure 21. Total CB concentrations ranged from 132 to 3186 µg/kg wet weight (ww), with highest concentrations found in the Liverpool Bay. Significantly elevated concentrations of CB were also found in the liver of fish collected from Red Wharf Bay, near Anglesey (2753 µg/kg ww), The Mersey (2727 µg/kg ww), offshore Morecambe Bay (2565 µg/kg ww) and offshore Cardigan Bay (1612/µg kg ww).

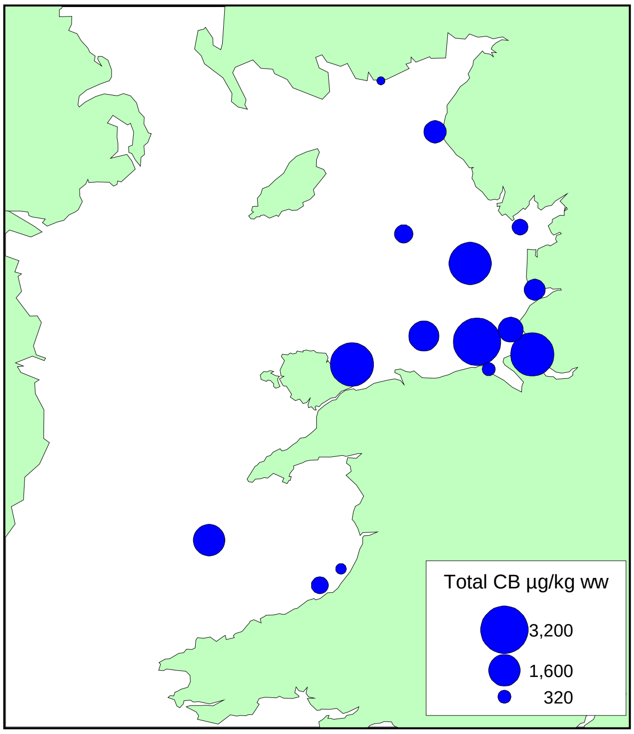

Figure 21. Concentrations of CB in fish liver collected at UK NMMP sites in the Irish Sea (µg/kg wet weight) (1999-2001).

Concentrations of CB in blubber samples from strandings of the common porpoise, (*Phocoena phocoena*) on the coast of the Irish Sea between 2001 and 2002 have been determined (Table 19). The sum of 25 CB concentrations ranged between 3.55 to 34.97 mg/kg ww, with no significant gender differences. The sum of ICES 7 congeners (28, 52, 101, 118, 138, 153 and 180) accounted for between 60 and 70% of the total 25CB concentrations in all analyses.

Overall, the concentration of PCB found in the blubber of stranded porpoises was markedly greater than that found in other matrices (i.e. water and sediment). This is expected due to the lipophilic properties of CB as well as their bioaccumulation within a top predator. However, due to the wide geographical movements of the common porpoise care should be taken in relating these concentrations to that of a local area and the Irish Sea in general.

Table 19. Concentrations of PCB's measured in blubber of the common porpoise, (*Phocoena phocoena*) from UK strandings during 2001-2002 in the SEA 6 area (mg/kg wet weight).

year	sex	ΣICES7	Σ25CB
2002	F	16.33	26.39
2002	M	6.01	9.23
2002	F	12.52	20.12
2002	M	2.9	4.48
2002	M	21.91	34.97
2002	F	3.39	5.12
2002	M	7.95	12.23
2001	M	7.6	11.52
2001	M	12.74	19.52
2001	F	8.8	12.71
2001	M	5.7	8.40
2001	F	2.49	3.55
2001	M	4.41	6.48
2001	F	5.43	7.92
2001	M	10.79	16.33

ΣICES7 = sum of ICES 7 congeners 28, 52, 101, 118, 138, 153 and 180)

4.3.4.4 Metals

Median concentrations of metals in mussels from inshore sites of the Irish Sea were analysed in samples collected between 1999 and 2001 (Table 20). Cadmium concentrations ranged from 208.85 to 465.29 µg/kg ww, with the highest concentrations found in mussels from the Mersey estuary. Copper concentrations were also elevated in mussels from the Mersey estuary, although maximum concentrations were found in mussels from Belfast Lough (1987 µg/kg ww).

Lead concentrations ranged from 353 to 1669 µg/kg ww with highest concentrations found in mussels from the Mersey estuary. A similar pattern was also reported for Zn with highest concentrations in the Mersey estuary (37.5 mg/kg ww). Mercury concentrations were highest in mussels from Morecambe Bay (77.7 µg/kg ww). This is in agreement with Widdows *et al*. (2002) who reported elevated Hg concentrations in mussels collected along the Lancashire coast. Silver concentrations in mussels ranged from 50 to 260.7 µg/kg ww, with all concentrations on the west coast of England <59 µg/kg ww. The elevated concentrations found in mussels off the east-coast of Ireland agree with similar elevated concentrations in Dublin Bay reported by Widdows *et al*. (2002). Inputs from the photographic industry were suggested as a possible reason for these high Ag concentrations (Widdows *et al*., 2002).

Table 20. Median concentrations of metals measured in mussels collected during 1999-2001 from NMMP stations in the Irish Sea (µg/kg wet weight).

NMMP site		Cd	Cu	Pb	Zn	Hg	Ag
690	Dee	212.13	923.04	1550.32	23784.66	30.82	
755	Mersey	345	1310	1160	27200	54.3	50
765	Outer Mersey	465.69	1544.34	1668.92	37527.72	54.38	50
766	Ribble	208.85	1663.25	723.46	18730.72	36.75	58.57
767	Morecambe Bay	272.33	961.8	980.17	14334.75	70.73	50
768	Cumbria Coast	227.41	1094.9	652.05	12673.66	37.15	50
809	Strangford Lough	248.19	1377.77	352.75	14707.46	25.93	123.07
845	Belfast Lough	227.43	1987.21	507.23	25050.96	18.59	260.66

Mercury concentrations in fish muscle collected from the Irish Sea ranged from 69 to 338 µg/kg ww, with maximum Hg concentrations found in the Mersey (Figure 22). Elevated Hg concentrations were also found in fish muscle collected from two sites within Liverpool Bay (230 and 199 µg/kg ww) and offshore Morecambe Bay. This is likely to be as a result of historical discharges of mercury from the chlor-alkali industry within this area. Lead concentrations in fish livers showed a similar pattern to that observed for Hg with higher concentrations reported in the Mersey estuary area. However, the highest Pb liver concentrations were found in fish collected inshore at Cardigan Bay (576 and 520 µg/kg ww). Elevated concentrations of Pb were found in the livers of fish collected from Morecambe Bay (440 µg/kg ww) and offshore in the north -west Irish Sea in Dundrum Bay (500 µg/kg ww).

Similar to that described for Pb, Cd concentrations were highest in livers of fish collected from Cardigan Bay (335 µg/kg ww), with elevated concentrations in fish livers offshore in the north -west Irish Sea in Dundrum Bay (170 µg/kg ww).

Arsenic concentrations in fish muscle collected from the Irish Sea ranged from 2.3 to 10.1 mg/kg ww, with maximum concentrations found in fish collected from Solway in the north-east Irish Sea.

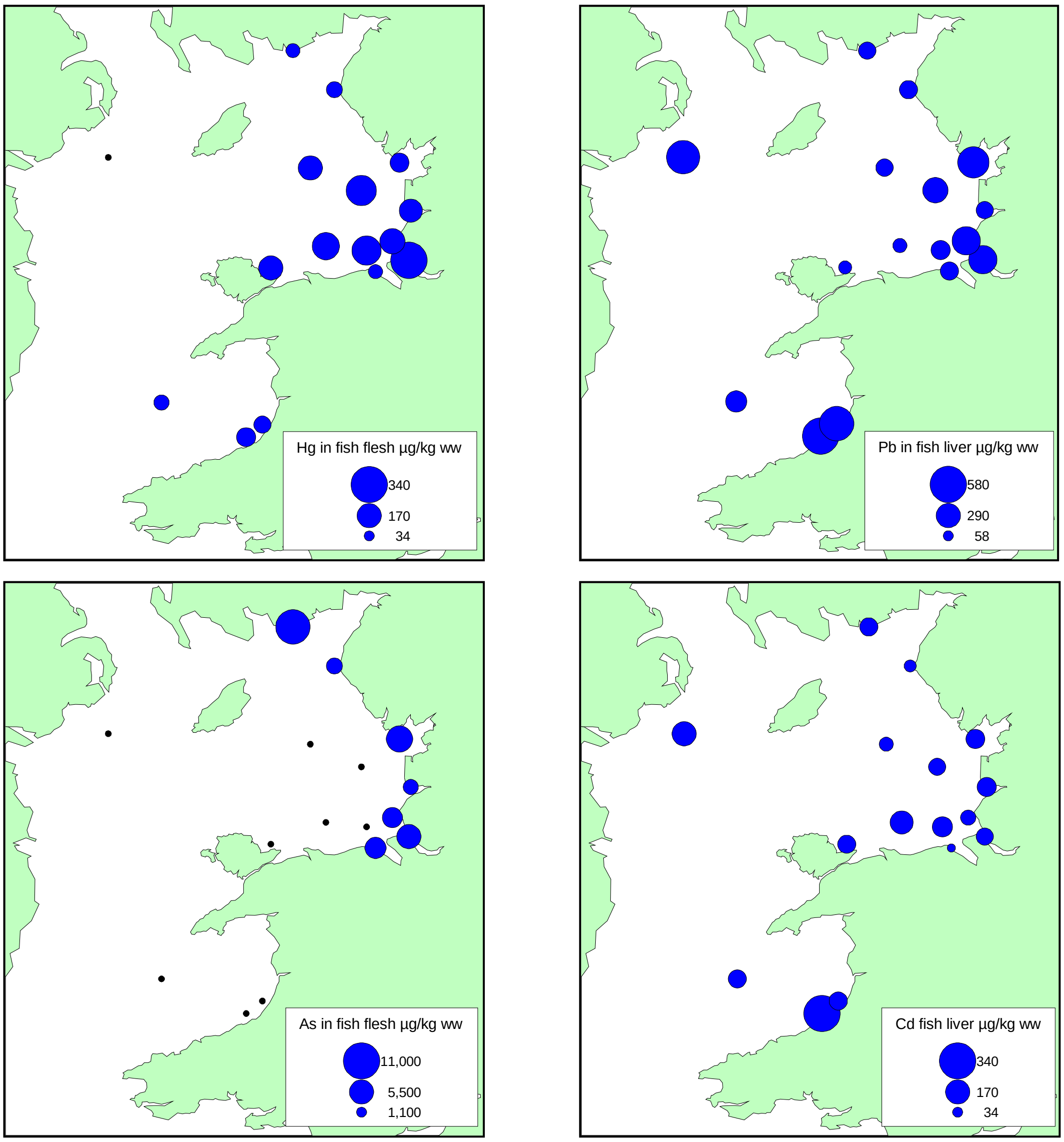

Figure 22. The median concentrations of metals measured in fish liver collected during 1999-2001 from NMMP stations in the Irish Sea (µg/kg ww).

Concentrations of metals in blubber samples from strandings of the common porpoise, (*Phocoena phocoena*) in samples collected from the Irish Sea between 2001 and 2002 have been determined (Table 21). All metal concentrations exhibited little variation between individual porpoises with no visible difference between genders. Concentrations of Cr, Ni, Cd and Pb were often low or undetected in blubber samples. The most abundant metal was Fe with concentrations ranging from 161 to 504 mg/kg ww, followed by Zn (20 -159 mg/kg ww) and Cu (5.8-43 mg/kg ww). Due to bioaccumulation processes the metal concentrations were significantly higher than those reported in fish tissues described above.

Table 21. Concentrations of metals measured in blubber of the common porpoise, *Phocoena phocoena* from UK strandings during 2001-2002 in the SEA 6 area (mg/kg ww).

Year	Sex	TS%	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Ag	Cd	Hg	Pb	Hg:Se
2002	F	24.9	< 0.09	6.3	407	< 0.09	9.2	89	0.27	4.0	1.7	< 0.05	13	0.08	1.28
2002	M	27.4	< 0.09	5.4	132	< 0.09	11	34	0.43	0.63	0.15	< 0.05	0.83	< 0.03	0.52
2002	F	25.7	< 0.09	7.0	348	< 0.09	9.8	159	0.38	2.0	0.56	< 0.05	5.3	< 0.03	1.04
2002	M	27.0	0.18	5.9	215	0.25	9.9	35	0.78	1.5	0.5	< 0.05	2.7	< 0.03	0.71
2002	M	26.8	< 0.09	6.2	269	0.17	5.8	54	0.61	3.7	0.73	< 0.05	10	< 0.04	1.06
2002	F	25.7	0.3	5.7	274	0.12	12	29	1.2	9.0	2.3	0.1	13	< 0.04	0.57
2002	M	25.8	0.35	6.2	479	0.16	15	87	0.23	4.2	0.97	0.09	9.1	< 0.03	0.85
2001	M	25.7	0.1	9.6	177	< 0.04	25	95	0.26	0.46	0.35	< 0.02	0.57	< 0.02	0.49
2001	M	27.8	0.09	5.9	341	< 0.05	7.6	31	0.42	4.7	2.0	0.22	10	< 0.02	0.84
2001	F	28.2	0.09	6.4	349	< 0.04	9.7	34	0.29	1.4	0.99	0.14	2.6	< 0.02	0.73
2001	M	29.3	< 0.1	6.4	161	< 0.1	16	44	0.4	4.5	16	0.08	10	< 0.04	0.87
2001	F	30.2	< 0.04	6.8	504	< 0.04	16	37	0.41	1.9	0.73	0.03	4.4	< 0.02	0.91
2001	M	30.9	0.07	7.5	420	< 0.03	43	55	0.79	2.9	0.9	0.05	4.0	0.03	0.54
2001	F	55.9	< 0.07	2.9	214	0.51	20	20	0.77	0.56	0.13	< 0.04	0.93	< 0.03	0.65
2001	M	30.0	0.17	6.3	284	0.21	13	39	0.35	3.8	0.99	0.2	10	0.02	1.04

4.3.4.5 Butyl tin (BT)

From work carried out by Widdows *et al*. (2002), the concentration of organotin compounds were generally low in mussels collected from sites around the Irish Sea. On the UK mainland coast, the sum of Butyl tins (ΣBT) ranged from 'not detected' to 0.49 µg/kg dw, with highest values occurring in mussels from St. Ishmaels, Milford Haven in the vicinity of the oil terminal and loading jetties. Elevated concentrations were also reported in mussels collected near ports/ harbours (e.g. Fishguard, Mersey, Heysham). The ΣBT were generally lower on the east coast of Ireland ranging from 0.06 to 0.66 µg/kg dw (Widdows *et al*., 2002).

Concentrations of tributyltin (TBT) dibutyltin (DBT) and monobutyltin (MBT) have been reported in the blubber of stranded common porpoises (*Phocoena phocoena*) (Table 22). The sum of these concentrations ranged from 0.08 to 247 µg/kg ww. Markedly higher concentrations of butyl tins in porpoise blubber were reported in strandings from 2000 & 2001 than that found in 2002. With the exception of one sample taken in 2001, DBT was the most abundant BT making up, on average, 70% of the total BT concentration. This proportion of DBT is comparable to concentrations found in the livers of stranded porpoises and grey seals reported by Law *et al*., (1998), as well as that found in liver samples of other pelagic mammals (CEFAS, 2001).

Table 22. Concentrations of butyl tins measured in blubber of the common porpoise (*Phocoena phocoena*) from UK strandings located in the SEA 6 area during 2000-2002 (µg/kg ww).

Year	TBT	DBT	MBT	ΣBT	DBT/ΣBT
2000	8	24	< 1	32	0.750
2000	36	169	12	217	0.779
2000	17	114	6	137	0.832
2000	7	39	6	52	0.750
2001	25	99	8	132	0.750
2001	41	195	11	247	0.789
2001	< 6	< 4	10	10	0.000
2001	< 5	41	10	51	0.804
2001	0.095	0.63	0.028	0.753	0.837
2001	0.048	0.035	< 0.005	0.083	0.422
2001	0.033	0.071	< 0.005	0.104	0.683
2002	0.029	0.056	< 0.005	0.085	0.659
2002	0.024	0.052	< 0.005	0.076	0.684
2002	0.04	0.08	0.036	0.156	0.513
2002	0.041	0.092	0.039	0.172	0.535

4.3.4.6 Organochlorines

Concentrations of Dichlorodiphenyltrichloroethane (DDT) and its main metabolite dichlorodiethylene (DDE) have been reported in the blubber of stranded common porpoises (*Phocoena phocoena*)(Table 23). The sum of DDT concentrations ranged from 0.52 to 7.06 µg/kg ww. The proportion of the main metabolite DDE with respect to ΣDDT ranged between 43-61%. There was no apparent difference in ΣDDT concentrations of porpoise blubber between the years 2000, 2001 and 2002.

Table 23. Concentrations of organochlorines measured in blubber of the harbour porpoise (*Phocoena phocoena*) from UK strandings located in the SEA 6 area during 2000-2002 (µg/kg ww).

Year	%HEL	ΣDDT	DDE/ΣDDT
2000	88	1.97	0.609
2000	89	3.02	0.464
2000	92	2.27	0.485
2000	92	1.48	0.500
2001	93	0.52	0.519
2001	91	0.91	0.484
2001	90	1	0.570
2001	92	2.5	0.520
2001	84	7.06	0.425
2001	89	1.87	0.588
2001	92	2.88	0.486
2002	92	2.11	0.521
2002	92	4.43	0.542
2002	92	0.81	0.605
2002	90	1.9	0.579

4.3.5 Other compounds

4.3.5.1 Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) include Benzene, Toluene, Ethyl-benzene and Xylene (BTEX). Concentrations of these VOCs are generally found to decrease with increased salinity to levels below the limit of detection in samples taken from the near coastal sites and offshore stations (Dawes & Waldock, 1994).

4.3.5.2 Brominated Flame Retardants (BFRs)

BFRs are of particular interest due to the large quantities that are used commercially, and because some members of this group have been detected at increasingly high concentrations as environmental contaminants and in animal tissues. It should be noted that BFRs are not directly related to the offshore energy industry, but have been included in this report due to their importance as environmental contaminants.

Polybrominated diphenyl ethers (PBDEs) are one of the main groups of BFRs extensively used as flame retardant additives in polymeric materials such as acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS). Consequently, they find many applications in both domestic and commercial situations (Gutzman, *et al*., 1999).

PBDEs can be considered to be environmentally stable and persistent compounds, being resistant to acids, bases, reducing and oxidising compounds. They are hydrophobic, lipophilic contaminants that have a tendency to accumulate in animal tissues. The concentration of BDEs determined from the liver samples of dab, (*Limanda limanda*) collected offshore Anglesey can be seen in Table 24. The most abundant BDE congeners were BDE47 and BDE119. When the lipid content in the samples were relatively high (4.9-7.7%), BDE47 was the dominant congener making up between 70 and 78% of the Σ 7BDEs. In samples were lipid content was less than 0.5% BDE119 was by far the most abundant congener amounting to 88-92% of the Σ 7BDEs. BDE119 was almost undetected in samples with raised lipid content. There was a large variation in the Σ 7BDEs between the samples ranging from 6.9 to 357.5 µg/kg ww.

Concentrations of BDEs have been reported in the blubber of stranded common porpoises *Phocoena phocoena* (Table 25). The sum of ten BDE concentrations ranged from 0.33 to 1.755 µg/kg ww. Overall, as described for the dab liver over, BDE47 was the most abundant BDE congener, although its proportion varied between 8.4 and 70.2% of the total BDEs. There was no apparent difference in Σ10 BDE concentrations of porpoise blubber between the years 2000-2002.

Table 24. Concentration of BDEs in the liver of dab, *Limanda limanda* collected off the coast of Anglesey, 1999-2001 (µg/kg ww).

Lipid %	BDE28	BDE75	BDE71	BDE47	BDE66	BDE77	BDE100	BDE119	Σ 7BDEs
7.7	0.62	0.17	4	89	1.6	<0.5	23	0.24	118.63
4.9	3.4	0.23	17	241	3.5	0.57	42	0.57	308.27
7.1	<0.5	<0.5	1.9	54	1.1	<0.5	17	<0.5	74
5.6	<0.5	<0.5	3.2	100	1.9	<0.5	25	<0.5	130.1
5.7	<0.5	<0.5	<0.5	4.8	<0.5	<0.5	2.1	<0.5	6.9
<0.5	1.3	<0.5	8.7	1.2	<0.5	<0.5	<0.5	129.8	141
<0.5	2.7	<0.5	19	2.9	<0.5	<0.5	<0.5	332.9	357.5
<0.5	0.9	<0.5	8.6	1	<0.5	<0.5	<0.5	84.5	95
<0.5	<0.5	<0.5	10	1.8	<0.5	<0.5	<0.5	141.9	153.7
<0.5	<0.5	<0.5	0.68	<0.5	<0.5	<0.5	<0.5	7.6	8.28

Table 25. Concentrations of Brominated diphenyl ethers (BDE) measured in blubber of the harbour porpoise (*Phocoena phocoena*) from UK strandings located in the SEA 6 area during 2000-2002 (mg/kg ww).

Year	Σ10 BDEs	BDE47/ΣBDEs
2000	1.221	0.622
2000	0.642	0.084
2000	0.518	0.425
2000	0.815	0.515
2001	0.357	0.644
2001	0.681	0.543
2001	0.627	0.702
2001	0.632	0.206
2001	1.755	0.114
2001	0.532	0.395
2001	0.676	0.237
2002	0.677	0.532
2002	0.566	0.247
2002	0.33	0.515
2002	0.718	0.404

4.3.6 Summary

Due to the hydrophobic nature of many organic compounds PAH, PCB and THC and the partitioning of metals to suspended particles, the concentrations of dissolved contaminants in seawater samples were often low or undetected. Of those contaminants that were measured, highest concentrations were generally found in seawater samples collected from estuarine and coastal sites that are subject to high industrial input such as the Mersey estuary. Environmental quality standards (EQS') were exceeded for mercury and zinc at the Mersey and Ribble estuaries, suggesting a dominant riverine input rather than offshore discharges as the contaminant source. High mercury and zinc concentrations could be attributed to industrial and waste water discharges into these estuaries. Metal concentrations were generally found to fall significantly in water samples taken further offshore. Although only low concentrations of PAH were detected, highest concentrations were found within the Morecambe Bay area and undetected in the three offshore sites.

In contrast to those chemicals described above, alkylphenols are more soluble in water and are less likely to partition to suspended particulates to be deposited in sediments. Maximum levels of nonylphenol (NP) and octylphenol (OP) were found in samples from Morecambe Bay.

Concentrations of PAH and CB were significantly higher in inshore areas where there was either riverine input and/or industry. In addition, PAH concentrations in sediments in the western Irish Sea are negatively correlated with grain size. Correlations in the Irish Sea are also present between metal distribution and percentage silt and clay. Concentrations of APs were below the limit of detection.

Concentrations of contaminants in biota are dependent on concentrations in the environment, their bioavailability, their structure and activity and the metabolic processes of the species studied. Complex interactions between these processes need to be understood to understand the relevance of concentrations of contaminants. In general the highest concentrations of contaminants were found in organisms sampled in areas of high sediment contaminant loading which are generally correlated with areas of high riverine/run off input.

Marine mammals appear to be susceptible to bioaccumulation of compounds such as PCB due to their high trophic level, long life span and limited ability for metabolism and excretion.

4.4 BIOLOGICAL EVIDENCE OF CONTAMINATION

4.4.1 Introduction

There are two main sources of potential biological effects upon marine organisms that are associated with oil and gas production activities; those caused by production discharges i.e. produced water and those associated with drilling activities. Both of these discharges are likely to be chronic in their nature, although biological effects may be acute. Accidental spillages and aerial emissions are also routes of deposition of contaminants to the environment. Oil spills may lead to local ecological changes, which may be dramatic for a period but are usually within the normal range of fluctuations in marine environments, except perhaps for species with a low rate of reproduction or in sensitive areas.

The contaminants in produced water plumes, and from drilling, may have direct effects on populations of pelagic invertebrates and vertebrates in the vicinity (especially those that are sessile) and indirect effects via bioconcentration and bioaccumulation of contaminants. Drilling activities primarily have effects on the benthic infauna directly underneath and some distance from a platform, but they also potentially have impacts on fish species that live in the sediment and feed upon invertebrate populations that may be contaminated.

Contaminant exposure may occur via passive diffusion or active uptake processes. Exposure may be via ingestion or absorption processes. Biological effects of petroleum hydrocarbons on marine organisms are dependent on their bioavailability and persistence, the ability of an organism to accumulate and metabolise compounds and the ability of hydrocarbons to interfere with normal metabolic pathways that may alter an organisms chances of survival to reproduction (Capuzzo, 1987). Polycyclic aromatic hydrocarbons (PAH) are ubiquitous contaminants of UK estuarine, coastal and marine waters. They originate mainly from incomplete combustion processes and from the petrochemical industry (NRC, 1983). PAH are hydrophobic molecules that have the ability to become associated with sediments once released to the marine environment.

The effects of contaminants upon biological systems may manifest themselves from the molecular to the population level. From biochemical effects to community level changes, the complexity of systems, the number of compensatory mechanisms and lag time from exposure to effect increase exponentially. Predictive ability therefore decreases ascending the levels. The ability to detect biological effects at higher levels is limited by the absence of reliable tests (population, community and ecosystem). Where such laboratory and field tests have been carried out that pertain to possible contaminant discharges from oil and gas activities they are discussed.

The measurement of the biological effects of contaminants has been carried out as part of the UK National Marine Monitoring Programme (UK NMMP) in support of the OSPAR Joint Assessment and Monitoring Programme (JAMP). In addition several other monitoring programmes have contributed data to the SEA 6 area. Biological effects measure the response of an organism to contaminants, rather than the levels of the contaminants themselves. Biological effects monitoring therefore attempts to provide the link between the contaminants present and the health and quality of the marine environment.

4.4.2 Biomarkers of Contaminant Exposure in Fish

4.4.2.1 EROD Induction

Some of the most biologically significant groups of contaminants in the benthic marine environment are the polycyclic hydrocarbons (PAH), the planar polychlorinated biphenyls (PCB), the dibenzo-furans and the dioxins. These compounds are extremely hydrophobic and lipophilic, tending to become associated with fine sediments.

Fish detoxify a number of these organic contaminants, specifically polycyclic aromatic hydrocarbons (PAH) and some polychlorinated biphenyls (PCB), by a metabolic pathway - the mixed function oxygenase (MFO) system. The MFO system metabolises ingested compounds to those that are more readily excretable. However, certain PAH are metabolised, via the MFO system, into active metabolites that may exert mutagenic, toxic and carcinogenic effects. The activity of the MFO system can be measured by the catalytic activity of the enzymes in this system. This is termed the ethoxyresorufin-O-deethylase (EROD) assay in fish liver (expressed as pM/ min/mg protein). Parent PAH are generally not measured in fish tissues (such as muscle) since they are often found to be very low even in highly contaminated areas (Varansi *et al.*, 1989). This is because, once ingested, these compounds are readily metabolised (by such mechanisms as the MFO system) in the liver and excreted into the gall bladder.

High levels of EROD activity were found in male dab (*Limanda limanda*) off Morecambe, St Bees Head and Outer Cardigan Bay (927, 809 and 787 pM/min/mg protein respectively) in 1999. High values were also found in females at the Liverpool Bay and Irish Sea stations, (low in North Sea females at the same time).

In 2000, dab were sampled at 19 sites (Table 26). The data were similar for both sexes, reflecting the reproductive state of the fish at the time, so were combined. Highest values on the west coast were at near-shore sites in Liverpool Bay (Off Morecambe and Burbo Bight) and Dundrum Bay, east coast of Ireland. Dab were again sampled from 7 Irish Sea sites in 2001. The data showed, overall, slightly reduced EROD values. Low values were again recorded in samples from Cardigan Bay. 2002 saw relatively higher values across the Irish Sea, although Cardigan Bay again had the lowest EROD activity. The current data sets are not currently comprehensive enough, temporally, to undertake trend analysis.

Table 26. Mean EROD values (pM/min/mg protein) for dab (*Limanda limanda*) caught at UK NMMP stations in the Irish Sea. EROD activity was analysed by the method of Burke and Mayer (1974) as described by Stagg *et al.*, (1995).

NMMP site		2000	2001	2002
768	St Bees			596
805	SE Isle of Man	214	139	564
767	Morecambe Bay	370	255	872
705	Burbo Bight	403		604
715	Liverpool Bay	167	132	654
776	Red Wharf Bay	152	82	377
	North Cardigan Bay			100
656	Inner Cardigan Bay	175	32	213
665	Outer Cardigan Bay	125	102	253
815	Dundrum Bay	405	429	

4.4.2.2 Bile Metabolites

Synchronous fluorescence spectroscopy is a screening method based on a method by Ariese *et al.*, (1993) and adapted by D. Barbe (unpublished) for analysing bile for PAH metabolites. 1-Hydroxy pyrene(1-OH pyrene), the main metabolite of pyrene, accounts for a large percentage of the total PAH metabolites in the bile of fish exposed to PAH (Krahn *et al.*, 1987). The use of 1-OH pyrene as a standard allows a basic measure of PAH exposure to be made.

Bile samples to be screened in this manner have been collected from dab samples sampled at UK NMMP stations during research cruises since 1998 (Table 27). In 2002 highest levels were found at Burbo Bight and Morecambe Bay.

Table 27. Mean bile metabolites (1-OH pyrene equivalents) for dab (*Limanda limanda*) caught at NMMP stations in the Irish Sea (µg/l).

NMMP station		1998	1999	2000	2001	2002
805	S E Isle of Man				158	247
815	Dundrum Bay	162		77	156	
768	St Bees Head		235			311
656	Inner Cardigan Bay	186	170	115	209	160
665	Outer Cardigan Bay		111	125	180	158
776	Red Wharfe Bay	162	202	147	238	243
705	Liverpool Bay	316		129	307	
715	Liverpool Bay				173	180
705	Burbo Bight		346	213		402
767	Morecambe Bay	274	357	325	314	392

4.4.2.3 DNA Adducts in the Irish Sea

Parent PAH are extensively metabolised in fish, therefore body burden analysis by standard analytical methods does not provide an adequate assessment of exposure. Significantly, metabolism of PAH may result in the production of genotoxic metabolites with potentially mutagenic and carcinogenic properties. The DNA adducts formed by the interaction of these reactive PAH metabolites with DNA are the precursors of DNA mutation and as such are mechanistically linked to the initiation and progression of cancer. An association between elevated sediment PAH contamination, DNA adduct formation and liver pathology in benthic fish species has previously been found (Myers *et al.*, 1990). Analysis of DNA adducts in liver provides a sensitive biomarker of PAH exposure. Between 1996-2000 DNA adducts were assessed in the liver of the flatfish dab, *Limanda limanda*, collected as part of the NMMP programme from Cardigan Bay, Red Wharf Bay, Burbo Bight and Liverpool Bay. DNA adducts were detected in fish analysed from each site and, in the majority of cases, the DNA adduct profiles detected were indicative of exposure to a complex mixture of genotoxins. However, DNA adduct level varied spatially and temporally within the sample sets analysed. For example, dab sampled from outer Cardigan Bay between 1996 and 1998 did not display any DNA adducts detectable under current assay conditions (see Figure 23). This is in agreement with the view that outer Cardigan Bay is a suitable offshore reference site with minimal anthropogenic contamination (∑15PAH 26 µg/kg sediment; Woodhead *et al.*, 1999).

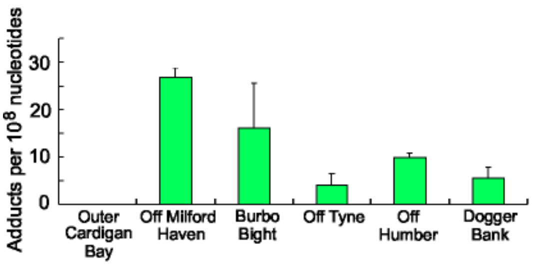

Figure 23. Liver DNA levels collected from Dab (*Limanda limanda*) from offshore locations around the UK. Note that no adducts were found in Outer Cardigan Bay in 1998.

In contrast, those dab caught at outer Cardigan Bay during 1999 and 2000 contained DNA adduct profiles characteristic of exposure to complex mixtures of carcinogenic metabolites (Table 28).

Table 28. Levels of hepatic DNA adducts (DNA adducts per 10^8 undamaged nucleotides) in dab from UK waters.

Date	Station	NMMP	DNA adducts per 10^8 undamaged nucleotides
6/2000[a]	Outer Cardigan Bay	665	6 ±1.39[b](10)
6/1999	Outer Cardigan Bay	665	10 ±1.9 (9)
6/1998	Outer Cardigan Bay	665	0 (5)*
6/1996	Outer Cardigan Bay	665	0 (5)*
6/2000	Burbo Bight	705	2.3 ±1.3 (10)
6/1999	Burbo Bight	705	6.1 ±1.4 (10)
6/1998	Burbo Bight	705	5.6 ±2.2 (10)
6/1996	Burbo Bight	705	16.2 ±9.4 (4)*
6/2000	Liverpool Bay	715	7.5 ±1.2 (10)
6/2000	Red Wharf Bay	776	8.2 ±1.9 (10)
6/1999	Red Wharf Bay	776	12.7 ±2.2 (10)

[a] *sample date*
[b] *numbers in parentheses represent number of individual liver samples analysed*
**Number in parentheses represents number of pooled samples analysed (3 fish per pool)*

4.4.2.4 Disease Induction

Fish diseases and pathological changes in the liver have long been used as indicators of environmental stress on fish populations. The International Council for the Exploration of the Sea (ICES) has contributed to standardised methodologies for their assessment. Externally, conditions used for monitoring include acute and healing ulcerations, lymphocystis, epidermal hyperplasia/papilloma and hyperpigmentation. Internally, liver lesions comprising nodules and larger, more developed tumours have become routine for the monitoring of health in offshore fish species, such as the dab *(Limanda limanda)*. Although the aetiology of certain diseases is known, for example an iridovirus is known to cause lymphocystis, that of others remains uncertain. However, measurement of these diverse conditions in individual fish assists with providing a monitor on the overall health of fish within a given population. Sampling and disease reporting protocols follow quality assurance guidelines established internationally (Bucke *et al.*, 1996; Feist *et al.*, 2004; BEQUALM).

Within the Irish Sea liver nodules, in dab, are most prevalent at sites in Liverpool Bay and Inner Cardigan Bay. They are also present in most other regions at lower prevalence levels. Due to the lack of long term data sets trends in prevalence cannot be clearly determined. However, the incidence of liver pathologies appears to be declining at Rye Bay since 2001 and increasing in Liverpool Bay and Cardigan Bay sites since 2000 and 1995 respectively.

Table 29. External disease and liver nodule prevalence in dab (*Limanda limanda*) caught at UK NMMP stations (values reported as %).

Sampling site	Year	Nearest NMMP site	No. Fish Examined	Lymph.*	Ulc.*	Epi.*	Hyp.*	Liver nodules
Inner Cardigan Bay	2000	656	231	2.6	9.1	1.3	8.2	25.0
	2001		112	0.0	6.3	1.8	2.7	25.0
Red Wharf Bay	1999	776	265	1.9	9.8	1.1	0.4	0.6
	2000		223	0.0	9.9	0.9	0.9	4.0
	2001		294	0.0	13.9	0.3	0.0	0.5
Inner Liverpool Bay	2000	706	206	3.9	14.0	0.5	1.5	3.5
Liverpool Bay	1999	715	290	1.0	16.9	1.0	0.3	5.3
	2000		291	1.4	28.2	2.1	1.4	4.2
	2001		259	0.0	18.1	0.8	0.4	5.0
Morecambe Bay	2000	795	263	1.1	14.1	0.8	0.4	0.0
	2001		271	0.0	11.8	1.1	0.0	0.6
St. Bees	1999	768	253	2.0	7.1	2.8	0.0	4.0
	2000		147	8.2	4.8	1.4	4.8	0.0
Burbo Bight	1999	705	355	1.7	9.9	2.8	0.3	4.6
	2000		234	2.1	17.9	1.7	0.4	1.5
	2001		225	0.0	20.0	0.9	0.0	4.9
SE Isle of Man	2001	805	158	2.5	14.6	0.6	0.0	0.0

Lymph=Lymphocystis, Ulc=Ulceration, Epi=Epidermal papilloma, Hyp=Hyperpigmentation.

A range of pre-neoplastic and neoplastic pathology is present in dab from all sites where macroscopic nodules are recorded (Table 29). These lesions are still detected, but at lower levels in the livers of dab sampled from locations where macroscopic nodules are less prevalent. Although the range of possible lesions in flatfish is large, the categories here have been restricted to those that are indicative of contaminant exposure:

Grade 1 indicates ‘no abnormalities detected’
Grade 2 ‘foci of cellular alteration (FCA)’
Grade 3 ‘benign tumours’ (e.g. adenoma, cholangioma, hemangioma)
Grade 4 ‘malignant tumours’ (e.g. carcinoma)

The proportion of dab sampled from the Burbo Bight sites exhibiting Grade 4 pathology (Figure 24) was considerably higher than at the control site (Rye Bay, English Channel). At the Cardigan Bay sites, the prevalence of hyperpigmentation increased during the 1990s (CEFAS, 1998 and 2000), the proportion of fish displaying Grade 2 liver pathologies remained fairly consistent but there was an increase in the prevalence of Grade 3 liver pathologies (Figure 25). Hyperpigmentation was a prominent condition in dab from several areas but had low prevalence in the Irish Sea.

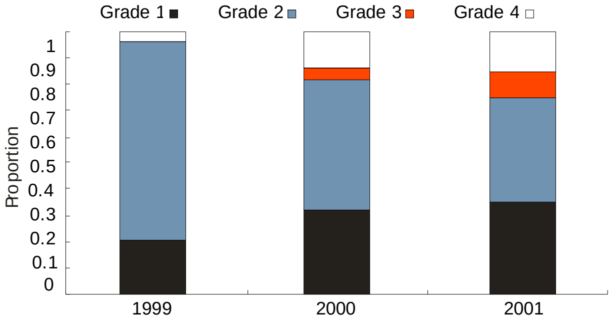

Figure 24. Chart showing the proportion of grades of liver pathology in dab sampled from Burbo Bight (Inner Liverpool Bay) 1999-2001

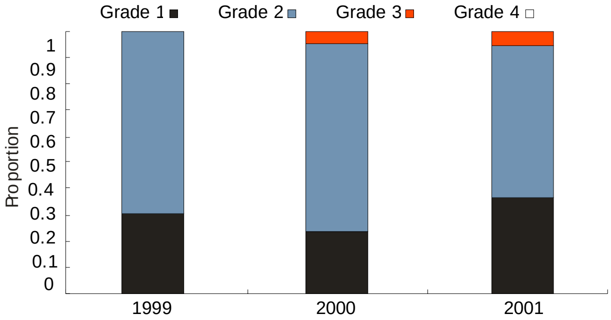

Figure 25. Chart showing the proportion of grades of liver pathology in dab (*Limanda limanda*) sampled from Cardigan Bay 1999-2001

4.4.3 Biomarkers of Contaminant Exposure in Mussels

4.4.3.1 Scope for Growth

Scope for Growth (SFG) measurements provide a measure of physiological stress response in marine mussels. Between 1996 and 1997 a study that investigated SFG and chemical contaminants in the tissues of mussels, at 38 coastal sites, around the Irish Sea was carried out (Widdows *et al*., 2002). On the UK mainland coast Widdows *et al*. (2002) found that SFG showed a general, negative, trend with a significant decline in water quality in the Liverpool and Morecambe Bay region. High water quality was measured along the west coast of Wales. The decline in SFG of mussels was associated with a general increase in contaminant levels. Elevated concentrations of PAH, TBT, DDT, Dieldrin, gamma-HCH, PCB and a few metals (Cd, Se, Ag and Pb) were measured. A quantitative toxicological interpretation (QTI) of the combined tissue residue chemistry and SFG measurements indicated that at a majority of coastal sites c. 50 to >80% of the observed decline in SFG was due to PAH as a result of fossil fuel combustion and oil spills. Sewage was also noted as being an important contributor to reduce SFG.

4.4.4 Endocrine Disruption

Endocrine disruption embraces a multitude of mechanisms of action, including effects on growth, behaviour, reproduction and immune function. The best known form of endocrine disruption involves substances which mimic or block the action of hormones at their receptor molecules. It is also possible for xenobiotic chemicals to affect the receptor protein synthesis itself affecting metabolism, transport or excretion of hormones, to interfere with the feedback mechanisms operating through the hypothalamus and pituitary gland or to damage endocrine organs directly. The concern is that many of the substances that cause endocrine disruption have the potential to act at very low concentrations and can be particularly effective during embryonic or larval development.

The earliest known example of endocrine disruption in the UK is the ‘imposex’ effect on dogwhelks caused by exposure to the antifoulant, tributyltin (TBT). This interferes with testosterone metabolism in female whelks, causing them to develop male sexual organs.

Other well documented examples of endocrine disruption have been the oestrogenic effects of treated sewage effluents on fish (e.g Harries *et al.*, 1997). This can cause the production of vitellogenin (VTG) in male fish. VTG is a protein precurser to egg yolk, usually only found in females and formed by the liver in response to oestrogens. This feminisation of male fish can also be shown in the histology of ‘intersex’ fish, where testicular tissue contains eggs in various stages of development (Figure 26).

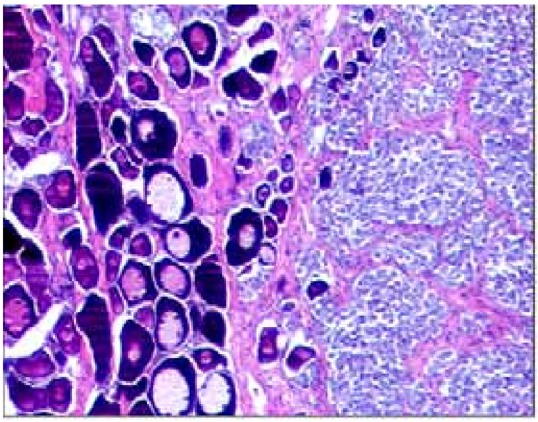

Figure 26. Testis histology from an intersex male flounder showing developing oocytes in the testicular tissue.

A variety of substances have been found to have oestrogenic properties including APE’s, APEO’s and various excreted synthetic oestrogens from humans and farmed animals. The effects of these are usually diluted on the way down rivers and estuaries and are often undetectable in the open sea. For this reason most surveys to date have focussed on estuaries and rivers to look for this effect. Available survey data on dab from the Irish Sea suggests that Liverpool Bay is contaminated enough to cause detectable VTG induction, with open water fish caught at the Liverpool Bay site and the Red Wharf Bay site having high levels of VTG in the plasma of male fish (Figure 27)(Allen, 1999).

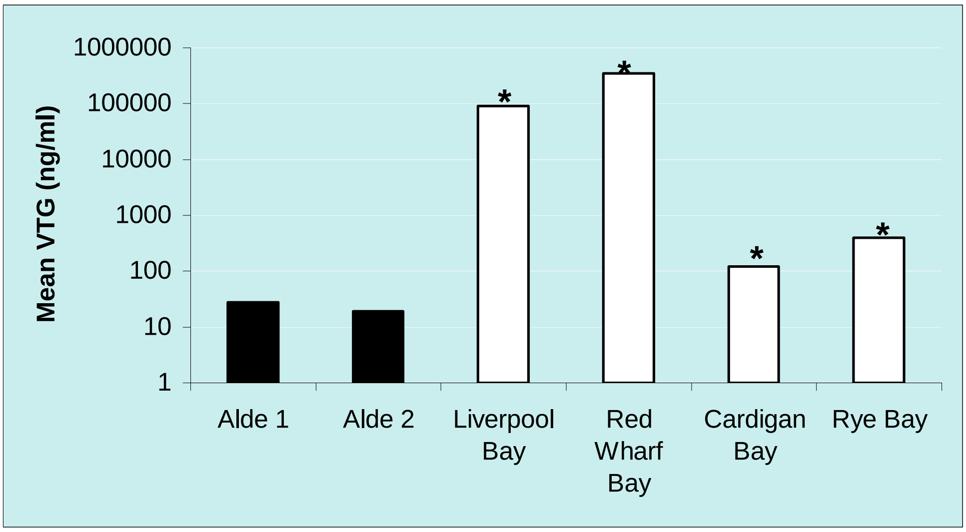

Figure 27. Mean plasma VTG (shown on a logarithmic scale) in male flounder from Irish Sea sites. Alde sites 1 and 2 are reference sites. Rye Bay site is a south coast reference site. (After Allen 1999).

Recent research has found that VTG induction is found in several species of openwater fish (Cho *et al*., 2003 (Japan gizzard shad), De Metrio *et al*., 2003 (Mediterannean swordfish), Fossi *et al*., 2002 (Mediterannean swordfish, tuna), Hara *et al*., 2001 (Japan grey mullet)) including large cod. Samples of small, male, cod which make up the entire data set for the Irish Sea have not shown signs of VTG induction, other than in farmed fish and at one coastal site. Larger fish, caught around the oil fields of the North Sea have had raised levels of VTG in the plasma of male fish. The aetiology is presently unknown but circumstantial evidence favours the hypothesis that cod pick up estrogenic endocrine disrupters via their diet, which changes as they grow.

4.4.5 Impact of Oil spills

The environmental impact of accidental oil spillage will depend not just on the quantity of oil released, but on a complex set of factors including the composition of the oil, toxicity, size (surface area and depth) of the spill, location, hydrography (tides, currents etc.) and weather conditions.

4.4.5.1 The Sea Empress oil spill

On 15 February 1996 the *Sea Empress*, bringing crude oil to Milford Haven in south-west Wales, ran aground and over the following week released 72,000 tonnes of crude oil and 480 tonnes of fuel oil into the sea. Despite a rapid and effective clean-up response at sea, oil came ashore along 200 km of coastline – much of it in a National Park – in an area of international importance for its wildlife and natural beauty. A ban was imposed on commercial and recreational fishing in the region and there was concern that tourism, important to the local economy, would be badly affected by the heavily oiled beaches. Several thousand oiled birds washed ashore, leading to a major cleaning and rehabilitation operation (SEEC, 1998).

The oil spill itself impacted areas of coastline within and immediately adjacent to the SEA 6 area. The conclusions of the Sea Empress spill were that effects on fisheries were less severe than could be expected. There were no reports of mortalities of commercially exploited crustaceans or fish. However, higher tissue concentrations of PAH were found in bivalve molluscs within and outside the haven. The use of dispersants has been cited as significantly reducing the impact of the oil spill on fisheries by reducing the amount of oil that reached the shoreline.

4.4.6 Summary

Biological effects measure the response of an organism to contaminants, rather than the levels of the contaminants themselves. Biological effects monitoring therefore attempts to provide the link between the contaminants present and the health and quality of the marine environment. In the SEA 6 area biological effects measures showed that impacts were generally greatest in areas where contaminant levels were at their highest concentrations. For instance, measures of the enzymes, in fish, that are responsible for detoxification of compounds found in oil were elevated in Morecambe and Liverpool Bays, Burbo Bight and off the Cumbrian coast relative to other sites. Similarly high values for the metabolic products of these compounds were found. Significantly, metabolism of PAH may result in the production of genotoxic metabolites with potentially mutagenic and carcinogenic properties. Measurement of these, by way of DNA adducts analysis, shows highest values in samples from Burbo Bight (Liverpool Bay area). Fish diseases and pathological changes in the liver have long been used as indicators of environmental stress on fish populations. Within the Irish Sea liver nodules, in dab, are most prevalent at sites in Liverpool Bay and Cardigan Bay. They are also present in most other regions at lower prevalence levels. Due to the lack of long term data sets trends in prevalence cannot be clearly determined. However, the incidence of liver pathologies appears to be declining at Rye Bay (reference site) since 2001 and increasing in Liverpool Bay and Cardigan Bay sites since 2000 and 1995 respectively.

Biological effects measures showed that effects were generally greatest in areas of higher measured contamination. However, there are many problems arising from using a mobile species, such as dab in biomonitoring programmes, not least the fact that determining previous exposure history is difficult. There is a paucity of data detailing the migrational movements of dab; the few studies conducted have suggested that populations of dab tend to be a temporary aggregation of fish originating from a larger area (Rijnsdorp *et al.*, 1992). Therefore, the results of a biological effect monitoring program using dab or other migratory species can only be interpreted in general terms, especially when the endpoints measured (such as DNA adducts) are slowly induced and are persistent once induced.

Marine mammals appear to be susceptible to bioaccumulation of compounds such as PCB due to their high trophic level, long life span and limited ability for metabolism and excretion. The relationship between the levels of PCB and infectious disease prevalence in harbour porpoises has been studied by Jepson *et al.*, 1999. Summed blubber concentrations of 25 chlorobiphenyl congeners in healthy harbour porpoises that died of acute physical trauma (mainly by catch) were compared with Σ25CB values in animals that died of infectious disease (n=82). The infectious disease group had a significantly greater Σ25CB values than the physical trauma group. This association was independent of other confounding variables (Jepson *et al*., 2005).

5. RADIOACTIVITY

5.1 INTRODUCTION

Over sixty radionuclides can be found in the environment, and they can be placed in three general categories:

1. Primordial - been around since the creation of the Earth
2. Cosmogenic - formed as a result of cosmic ray interactions
3. Human produced - enhanced or formed due to human actions

Primordial radionuclides are those left over from when the world and the universe were created. They are typically long lived, with half-lives often on the order of hundreds of millions of years. Consequently ^{238}U and ^{232}Th and their daughter products are present in both the water column and seabed sediments of the Irish Sea.

Cosmogenic radionuclides such as ^{3}H and ^{14}C are continuously produced in the upper atmosphere as a result of cosmic ray induced spallation and particle interactions. They can have long half-lives, but the majority have shorter half-lives than the primordial nuclides. They are transported into seawater via the hydrologic cycle.

Humans have used radioactivity for one hundred years and, through its use, added to the natural inventories. This is particularly true of the Irish Sea. The status of the Irish Sea, with respect to radioactivity, has been the subject of a number of major reviews of published material (Kershaw *et al*., 1992; Mitchell *et al*., 1996), which should be consulted for a more comprehensive treatment. In addition, a compilation of papers on all aspects of the behaviour of plutonium, and the other actinide elements, in the Irish Sea has been published in a special issue of the Journal of Environmental Radioactivity (Woodhead, 1999).

5.2 SOURCES OF RADIOACTIVITY

5.2.1 Natural radioactivity

An assessment of radionuclide input into seas in the OSPAR area as a result of oil and gas production was carried out for the MARINA II study (Betti *et al*., 2004). They concluded that, although information concerning production rates is readily available, (see UK Oil and Gas Energy Reports, 1998–2001, "The Brown Book"), there are much less data on the volume of co-produced water and on radionuclide concentrations. It is well known that the produced waters and solid sludge contain elevated levels of natural radioactivity (NORM), mainly ^{226}Ra, ^{228}Ra and their daughter products and that the activity of wastes from individual platforms' oil and gas production wells varies widely. Consequently, although the authors of the MARINA II report were able to derive estimates of radionuclide releases into the North Sea associated with oil and gas production, comparable information for the Irish Sea is lacking.

Anthropogenic, inputs of naturally occurring radionuclides are also associated with industrial processes (Betti *et al*., 2004). The most significant was the former Marchon phosphate-processing plant near Whitehaven, with an estimated annual discharge, in the 1980s, of about 35 tonnes U, and an unquantified input of daughter-products. This resulted in elevated concentrations of ^{226}Ra in seawater (~ factor of 3), ^{210}Po in biota, and of ^{230}Th and ^{210}Pb in sediments (Poole *et al*., 1995). The treatment of phosphate ore ceased in 1992 and both the discharges and environmental concentrations fell substantially. This activity also took place on a local scale in Ireland, and discharges were discontinued in the early 1980s (Ryan *et al*., 1997).

An average of 4 tonnes per annum U has been released from Sellafield, but without an equivalent loading of daughter products, and the impact has been negligible. Relatively high concentrations of ^{234}Th, and its daughter ^{234m}Pa (e.g. 75 kBq/kg), can occur in sediments from the Ribble estuary as a result of discharges from the fuel fabrication plant at Springfields (Assinder *et al*., 1997). It is not clear whether this influence extends significantly beyond the estuary, but is likely to be limited due to the short half-life of ^{234}Th (24 days).

5.2.2 Artificial radioactivity

For the last fifty years, inputs of artificial radionuclides to Irish Sea have been dominated by discharges from the nuclear reprocessing facilities at Sellafield (formerly Windscale) on the Cumbrian coast. The magnitude of these releases, made under the authorisation of the UK Government, has tended to mask contributions of radionuclides from other sources such as the 1986 Chernobyl accident, the effects of which are largely terrestrial, and residues from atmospheric weapons testing.

The main activities that produce waste at Sellafield are the reprocessing of irradiated fuel and the conditioning and storage of nuclear materials and wastes. Discharges began in 1952 (Gray *et al*., 1995) for which annual discharge the operator publishes figures in the RIFE report series (Environment Agency *et al*., 2004). The authorised discharge limits are reviewed periodically. The quantities of radionuclides discharged has changed markedly since releases began in 1952, as a result of changes in throughput, storage and waste treatment processes.

Discharges from Sellafield peaked in the early 1970s (Figure 28). A number of counter-measures were introduced, including the Site Ion Exchange Effluent Plant (SIXEP, in 1986), which controlled Cs discharges, and the Enhanced Actinide Removal Plant (EARP, in 1994). EARP allowed the treatment of medium-active, stored liquors, which also contained ^{99}Tc - not treated by EARP- and consequently these discharges (which are of limited radiological significance) rose in the mid-1990s. Discharges of ^{129}I, ^{90}Sr, ^{14}C, ^{60}Co, and ^{3}H also increased as a result of operational changes at the site, including the starting up of the Thermal Oxide Reprocessing Plant (THORP) in 1995. During 2003, discharges of ^{99}Tc were reduced due to a successful trial of new abatement technology.

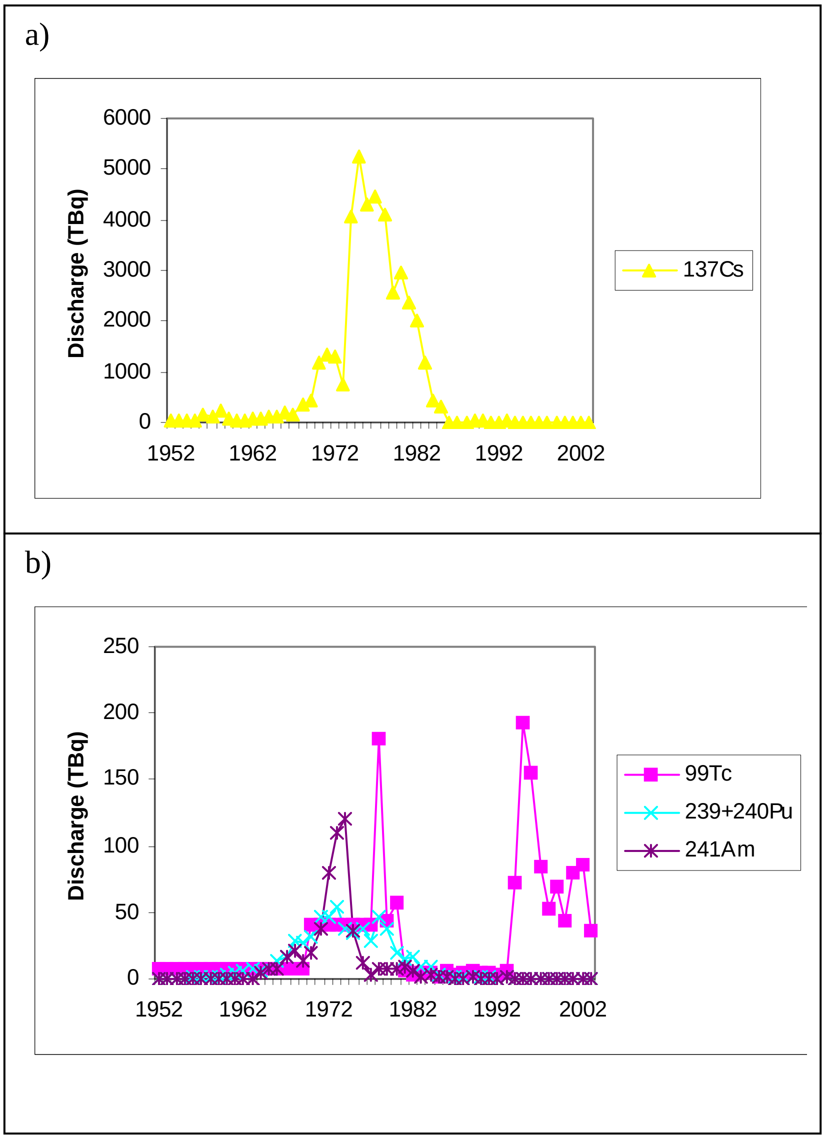

Figure 28. Annual discharges of liquid wastes to sea from Sellafield of: (a) ^{137}Cs, (b) ^{99}Tc, $^{239+240}$ Pu and ^{241}Am.

In addition to Sellafield, a number of establishments on the west coast of Great Britain are also authorised to release small amounts of radioactivity. The activities concerned include power generation, nuclear fuel production, manufacturing of medical supplies and military/naval operations. Their discharges and the adjacent environments are subject to regular monitoring. In all cases the resulting public radiation exposures are very low and difficult to distinguish from radiation due to Sellafield and nuclear fallout.

There are no ‘nuclear sites’ under the terms of the Radioactive Substance Acts 1993 in Northern Ireland, or for that matter in Eire. There are of course minor radioactivity discharges from hospitals, universities, etc. that do not fall within the surveillance remit.

5.3 RADIONUCLIDE DISTRIBUTION

5.3.1 In seawater

Those radionuclides that are relatively soluble in seawater (e.g. ^{3}H, ^{90}Sr, ^{99}Tc, Cs, ^{129}I) tend to be dispersed throughout the eastern Irish Sea before being advected through the North Channel (Figure 29(a)). A much smaller proportion enters the western Irish Sea and passes along the coast to the south and exits via the St George's Channel. Sellafield-derived radionuclides are still detectable on the western Irish seaboard, but are close to background levels attributable to global atmospheric fallout (Pollard *et al.*, 1996). The activities of most radionuclides in water exiting the North Channel during the 1990s are lower than previously, due to reductions in the discharges. A slow steady decline in the concentration of ^{137}Cs has also been observed in waters in the vicinity of the Sellafield pipeline (Figure 29(b)), although there is evidence that level are being maintained at higher levels by remobilisation from the seabed sediment (McCubbin *et al.*, 2002a).

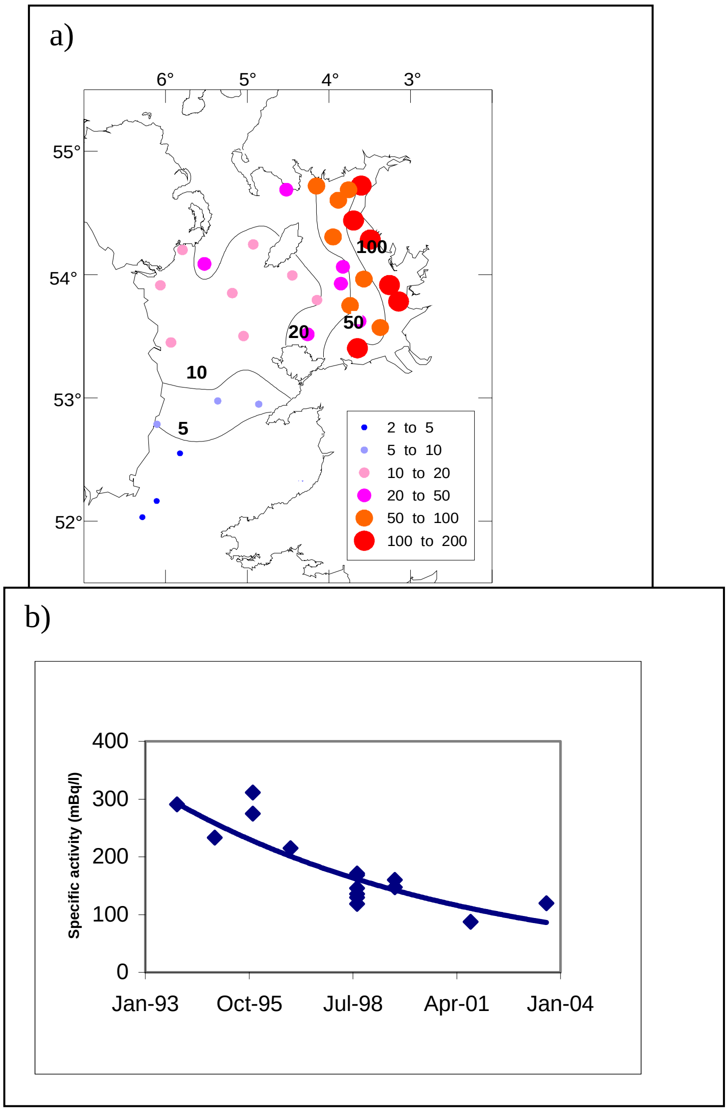

Figure 29. Activity of dissolved ^{137}Cs (mBq/l) in the Irish Sea, a) Spatial distribution in September 2003, b) Temporal variation off the Sellafield pipeline.

The increase in the ^{99}Tc discharges from 1994, which peaked in 1995, provided a readily measurable increase in water concentrations. The apparent transit time of <3 months in 1994, from Sellafield to the North Channel, was much faster than had previously been estimated, based on Cs distributions (Leonard *et al*., 1997). Increases in concentrations were also detected in the western Irish Sea (Pollard *et al*., 1996). The time- and space- evolution of the ^{99}Tc signal is the subject of continuing studies

Plutonium isotopes and ^{241}Am also occur in the water column, in dissolved, colloidal and adsorbed forms, although the total quantity in seawater is a much smaller fraction than that associated with seabed sediments (Leonard *et al*., 1999). Plutonium in the water column follows a similar dispersion route as caesium, although concentrations are lower by several orders of magnitude. The estimated inventory in the water column has remained constant between the mid 1980s and the last survey undertaken in 1994, despite the significant decrease in the discharge rate throughout the 1980s and the 1990s (Leonard *et al*., 1999). The ratio of ^{238}Pu/^{239,240}Pu in the water column was similar to that of the surface sediments and markedly different from the ratio recorded in contemporaneous discharge (Figure 30).

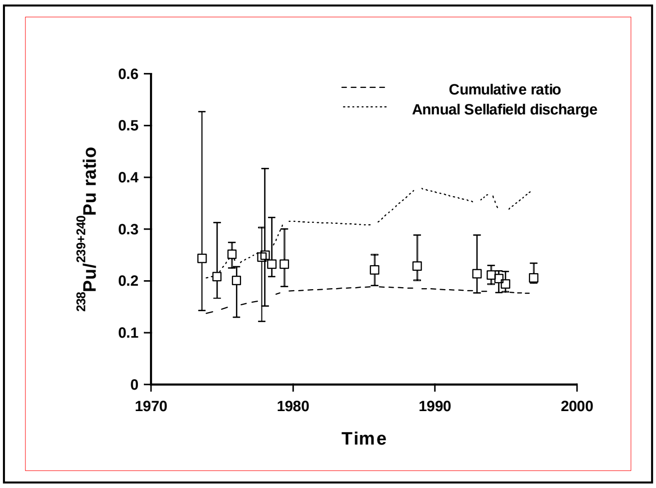

Figure 30. Mean ^{238}Pu/$^{239+240}$Pu ratios in surface seawater of the Irish Sea, 1973-1996. Bars indicate minimum and maximum values. Dotted and dashed lines indicate ratios in annual and cumulative Sellafield discharges, respectively.

Although a new survey is clearly required, the available information, together with data from laboratory studies (McCubbin *et al*., 2002b), indicates that remobilisation of Pu is taking place and that this process will continue for a considerable time (in the order of 10^2 years).

5.3.2 In sediment

The last survey to assess the inventory of artificial radionuclides in the Irish Sea was carried out more than a decade ago (Poole *et al*., 1995; Kershaw *et al*., 1999). These studies showed that the sub-tidal sediments of the Irish Sea contain a very substantial repository of Cs, Pu and Am radionuclides. The highest concentrations in surface sediments are associated with the outfall and a zone of muddy sediments running parallel to the English coast (Figure 31). A second area of fine-grained sediments between the Irish coast and the Isle of Man also has elevated concentrations.

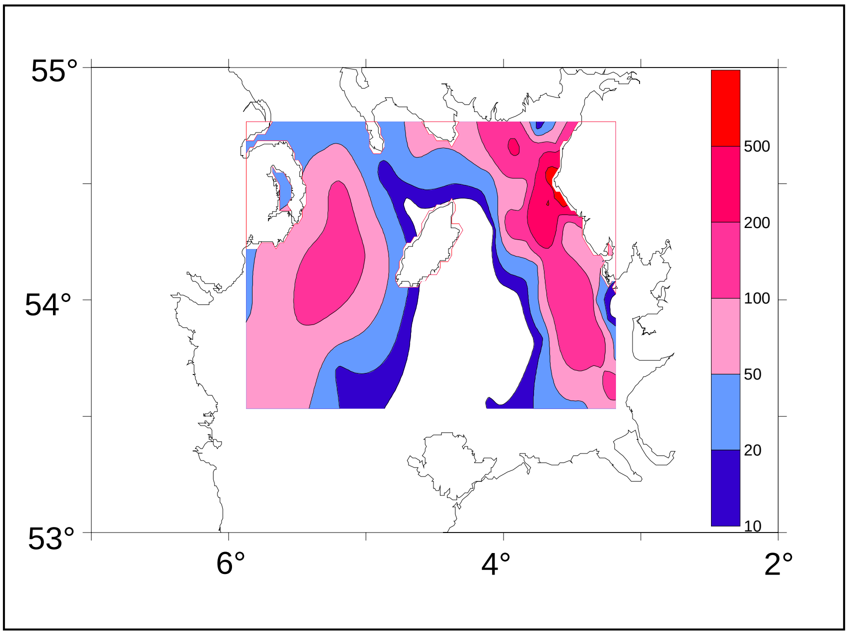

Figure 31. Distribution of ^{137}Cs (Bq/kg) in surficial subtidal sediments in 1995.

Mixing of the surface sediments by tidal currents and wave activity is widespread in the Irish Sea, and results in a corresponding mixing and dispersion of the radioactive signal. Contaminated sediment is transported north to the south coast of Scotland and into the estuaries along the Scottish and English coasts (MacKenzie *et al*., 1994). The distribution of radionuclides within the seabed is markedly heterogeneous, as a result of incomplete or episodic mixing processes. The subtidal sediments are subject to tidal resuspension, waves, fishing disturbance and mixing by benthic organisms (bioturbation). Overall sediment accumulation rates are thought to be low in the eastern Irish Sea but contamination by Sellafield radionuclides has been detected at depths of 1.5 m. The degree of heterogeneity tends to increase with depth. All these processes serve to disperse and dilute radioactive contamination.

Sediments in estuarine systems can be subject to physical disturbance on time-scales of weeks to decades. Marginal areas, especially saltmarsh/merse, have provided opportunities to observe a record of Sellafield discharges, preserved in sediments undisturbed by physical or biological processes. The contaminated sediment laid down in a particular year tends to reflect the integrated signal of previous discharges (MacKenzie *et al*., 1994) because of sediment reworking and mixing en-route. In contrast, exposed beaches tend to be well-mixed to the base of wave action and, being sandy, have low radionuclide concentrations. Areas of saltmarsh, and adjacent low-lying ground, are subject to tidal inundation, with consequent radionuclide contamination. Hovercraft-based studies by the British Geological Survey in the intertidal areas of SW Scotland, the Solway Firth, and the Cumbrian and Fylde coast have revealed the current, fine-scale distribution of radionuclides (Jones *et al*., 1999). Substantial changes in the distribution of the main channels in the Solway were evident, by comparison with earlier surveys, implying the reworking of massive quantities of sediment and hence large-scale redistribution of radionuclides. Highest concentrations were still located predominantly in regions of fine sediment deposition, near the shoreline and along the margins of creeks, for example. Saltmarsh can be eroded rapidly but generally it tends to be stable over periods of decades. At such sites the inventory of long-lived radionuclides is still increasing.

5.3.3 In biota

Large numbers of environmental samples are collected and analysed as part of monitoring and surveillance programmes managed by the Environment Agency (EA), Food Standards Agency (FSA) and the Scottish Environment Protection Agency (SEPA); these data are collated and jointly published in the RIFE report series (Environment Agency *et al*., 2004). Selected data are provided in Figure 32 for concentrations of ^{239,240}Pu in winkles collected from Nethertown on the Cumbria coast close to Sellafield. Despite large decreases in discharges of ^{239},^{240}Pu, there is only a small reduction in concentrations, with a small increase in 2001 – 2002 in both discharges and concentrations. A similar pattern is apparent for ^{241}Am except for the lack of discharge increases (Smith *et al*., 2004). The observations are consistent with remobilisation from contaminated seabed sediments providing the predominant source term. Concentrations of ^{241}Am are also influenced by ingrowth from past discharges of ^{241}Pu.

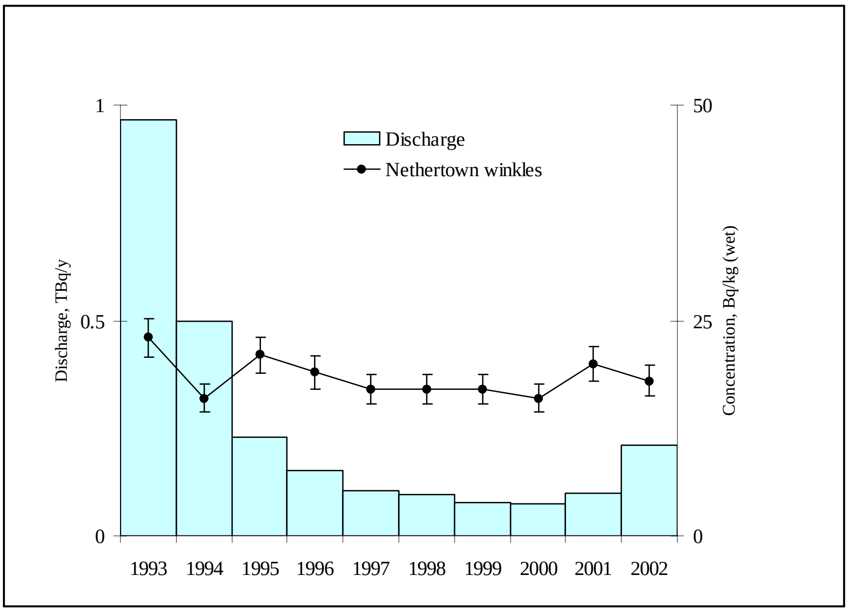

Figure 32. Activity of ^{239,240}Pu in Cumbrian winkles in comparison to Sellafield discharges.

5.4 ENVIRONMENTAL IMPACT

5.4.1 Effects on humans

To assess the impact on the public, habits surveys are carried out to identify potential exposure pathways and critical groups of the public – i.e. those individuals, or groups of individuals, receiving the highest radiation doses. Radiation doses to the most exposed people are assessed by combining the data on the habits of the critical group with the environmental monitoring results.

Doses to high rate seafood consumers in Cumbria as a result of discharges from Sellafield were assessed to be 0.21 mSv/a in 2003 (Environment Agency *et al.*, 2004). The principal radionuclides were ^{239,240}Pu and ^{241}Am, resulting from remobilisation from contaminated seabed sediments. A review of past critical group doses due to Sellafield (Hunt, 1995) concluded that the highest exposures were around 1.9 mSv/a in 1975 and primarily due to radiocaesium in fish. The reductions in doses since then have been due to reduced discharges from Sellafield as a result of improved waste treatment processes.

5.4.2 Effects on the environment

The absorbed radiation dose rates received by organisms living in the N.E. Irish Sea were summarised in the UNSCEAR report (1996). Estimates based on a 1988 survey (Woodhead, unpublished data) indicated a maximum dose rate to plaice gonad of 0.59 µGy/h compared with a maximum of 18 µGy/h estimated from the earlier data. Reviews of available data on radiation effects on aquatic organisms have concluded that chronic radiation exposure at dose rates less than 1 mGy/h are unlikely to produce effects on fish gonads and there would not be any adverse effect at the population level at dose rates <400 µGy/h. All estimated dose rates to aquatic organisms in the NE Irish Sea are well below these values, even those based on historical data which are likely to be an order of magnitude or so greater than those occurring at the present time.

5.5 CONCLUSIONS

- Inputs of artificial radionuclides around the UK are dominated by discharges from Sellafield, on the Cumbrian coast.

- Discharges of radionuclides from Sellafield have decreased significantly since the 1970s, as a result of various measures. In most cases current discharges are at least 100 times lower than peak discharges.

- Discharges of technetium-99 from Sellafield rose significantly in 1994, following the installation of the Enhanced Actinide removal Plant (EARP), but have recently declined significantly concomitant with the introduction of new abatement technology.

- Information concerning radionuclide releases into the Irish Sea associated with oil and gas production is missing.

- Remobilisation from sediments contaminated by historical discharges is now the predominant source of ^{137}Cs, $^{239+240}$ Pu and ^{241}Am to the water column and appears to be largely governed by sediment mixing and resuspension processes.

- Artificial radionuclide activities in fish and shellfish are also a result of remobilisation from contaminated sediments and are responsible for dose to the local critical group.

- Anthropogenic activities involving sediment disturbance such as trawling, installation of wind turbines and oil/gas pipelines likely to increase redissolution from the reservoir of contaminated sediment residing on the seabed. Their impact warrants further study.

6. GENERAL DISCUSSION AND CONCLUSIONS

6.1 Inputs (Pressures)

In Liverpool Bay and Morecambe Bay the riverine inputs of major groups of organic contaminants and metals are several orders of magnitude greater than those from the Offshore Oil and Gas industry. Based on metal concentration data from the UKOOA produced water survey (2003) and the produced water volume discharged from the Douglas platform in Liverpool Bay (2003), the inputs of cadmium, copper lead and mercury are estimated to be <0.15, 0.06, 0.27 and 0.008 tonnes/yr. By contrast, riverine inputs of cadmium, copper lead and mercury are 4.16,1405,1473 and 0.9 tonnes/yr, respectively (based on upper estuary values). With the exception of mercury, dredge material based inputs are lower than the riverine inputs but are nevertheless several orders of magnitude higher than those from the oil and gas industry (Table A). Although the offshore oil and gas industry will contribute most of the load of specific offshore chemicals the load of other contaminants e.g. pesticides, PCBs and brominated flame retardants will almost exclusively be derived from land-based sources. Reference to the figures showing contaminant concentration emphasise the contribution of riverine sources to the overall contaminant load in SEA region 6.

6.2 CONCENTRATIONS IN THE ENVIRONMENT (STATE)

The concentration of metals (zinc, nickel, chromium, cadmium and lead) in the water column in the vicinity of the main installations in Liverpool Bay was broadly comparable to the values measured in the Mersey estuary.

The concentration of some metals was elevated in the sediment in close proximity to platforms in Liverpool Bay. However, the sediment metal concentration is higher in the Mersey estuary. The total PAH concentration in sediments shows a similar pattern to that of sediment metals with concentrations approximately ten times higher in the Mersey estuary by comparison to samples taken near to the Douglas platform. However in intermediate areas sediment metal concentrations are low.

6.3 EFFECTS ON BIOTA (IMPACTS)

Offshore oil and gas activities are strictly controlled under EC and national legislation. Oil based drilling fluids have not been extensively used for wells drilled in the SEA 6 area and once operational, production facilities are subject to national authority controls which, in common with those applied to drilling operations, accord with OSPAR guidelines. Adverse effects on biota assessed at the point of discharge are often localised and acute. For instance, toxicology tests on produced waters from several North Sea platforms to species of marine organism have demonstrated acute toxicity, even with high levels of dilution. Similarly, effects on the benthic communities, by either smothering or direct toxicity, have been shown to be localised in their extent. Dilution and dispersion effects are key factors responsible for the lack of observable acute toxicological effects at distance from platforms.

Despite the effects of dilution and dispersion concentrations of contaminants are present in the wider marine environment that can cause, measurable, chronic effects in biota. Links between exposures to oil, and its derivatives, and adverse effects in fish species have been demonstrated in laboratory studies. Biological effects techniques have been developed that act as generic screens for compounds often associated with oil and gas activities. Several of those techniques that have appropriate quality assurance associated with them are routinely measured under the UK National Marine Monitoring Programme (NMMP). The current NMMP data sets are not comprehensive enough to undertake trend analysis, however, areas of high contamination can be identified. In particular Liverpool Bay and Morecambe Bay both had high values for biological effects that are likely to be induced by hydrocarbon contamination. Interestingly, the incidence of liver pathologies appears to also be rising in Liverpool Bay (and Cardigan Bay). However, it is seldom possible to attribute measured effects to one source of contamination. The data from the techniques used demonstrates the complexity of the environment and the understanding and time long series of data necessary to interpret results and place them in an environmental context.

Oil as a pollutant of the marine environment arises from two main sources, accidental spillages and illegal operational discharges from ships. The SEA Empress oil spill is the most recent, notable spill. Although the dispersed oil did not accumulate in offshore sediments there was extensive oiling of seabirds and heavy, localised mortalities of benthic fauna. There were also reductions in the abundance of subtidal crustaceans locally. However, further afield effects were not apparent, part of which is attributed to the use of dispersants which prevented further ecological damage. In summary, despite the images of widespread destruction and mortality of marine species large spills generally only have a transient effect on most impacted species.

7. GAPS IN OUR UNDERSTANDING AND FUTURE RISKS

The Water Framework Directive aims to protect the physical and biological integrity of aquatic systems. The overall objective is good status to be achieved by December 2015. The main focus of the directive is groundwater and surface water quality out to 1 nm from the coast. However the UK government's vision for management of our marine resources supports an integrated approach to the management of estuaries, the coastal zone and associated coastal waters. In this context the quality and status of the marine environment associated with offshore oil and gas installations is important.

The limited amount of near field (within a few kilometres of the installations) data available on contaminant concentrations make it difficult to determine any clear trends and to fully assess the importance of offshore Oil and Gas industry chemical inputs to Liverpool Bay and Morecambe Bay. In particular, the concentration of the compounds commonly detected in produced water should be characterised for both Morecambe Bay and Liverpool Bay in order to enable the accurate calculation of the contribution of the offshore industry to chemical loads. This may increase in importance as land based discharges come under greater control and produced water discharges increase.

A range of biological and chemical techniques are now available and should be deployed to allow a more sensitive and focussed assessment of potential chronic toxicity associated with the discharge of chemicals in offshore oil and gas production.

Available data indicate that drill cuttings are relatively widely dispersed. Some more robust data to support this hypothesis is required.

A range of natural physical and biological processes influence sediment remobilisation. However the influence of oil and gas activities upon sediment remobilisation and hence to associated radionuclide availability in the water column should be quantified.

8. REFERENCES

Allen, Y. T., Scott, A. P., Matthiessen, P., Haworth, S., Thain, J. E. and Feist, S. W., 1999. Survey of estrogenic activity in United Kingdom estuarine and coastal waters and its effects on gonadal development of the flounder *Platichthys flesus*. *Environmental Toxicology and Chemistry* **18**: 1791–1800.

Annual survey of reported discharges attributed to vessels and offshore oil and gas installations operating in the United Kingdom pollution control zone 2003. *Advisory Committee on Protection of the Sea, Annual Report*, March 2004.

Assinder, D. J., Mudge, S. M. and Bourne, G. S., 1997. Radiological assessment of the Ribble Estuary. I. Distribution of radionuclides in surface sediments. Journal of Environmental Radioactivity, **36**: 1-19.

Bakke, T., Green, N. W., Naes, K., and Pedersen, A., 1986. Drill cuttings on the sea bed. Phase 1 and 2. Field experiments on the benthic recolonization and chemical changes in response to various types and amounts of cuttings. In: *Oil based drilling fluids. Cleaning and environmental effects of oil contaminated drill cuttings. Proceedings*. Norsk Petroleumsforbund, Trondheim, pp17-31.

Baumard, P., Budzinski, H., Garrigues, P., Dizer, H. and Hansen, P. D., 1999. Polycyclic aromatic hydrocarbons in recent sediments and mussels (Mytilus edulis) from the Western Baltic Sea: occurrence, bioavailability and seasonal variations. *Marine Environmental Research* **47**: 17–47.

BECPELAG references available online at BECPELAG Website. Abstracts

Betti , M., Aldave de las Heras, L., Janssens, A., Henrich, E., Hunter, G., Gerchikov, M., Dutton, M., van Weers, A. W. Nielsen, S., Simmonds, J., Bexon, A. and Sazykina, T., 2004. Results of the European Commission Marina II Study Part II—

effects of discharges of naturally occurring radioactive material. *Journal of Environmental Radioactivity*, **74**: 255-277.

Blackburn, M. A., Kirkby, S. J. and Waldock, M. J., 1999. Concentrations of Alkylphenol polyethoxylates entering UK estuaries. *Marine Pollution Bulletin*, **32** (2): 109-118.

Briggs, A. D. and Grant, A., 2002. Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts? *Marine Environmental Research*, **53** (1): 95-116.

Bucke, D., Vethaal, A. D., Lang, T. and Mellergaard, S., 1996. Common diseases and parasites in the North Atlantic: Training guide for identification. *ICES Techniques in Marine Environmental Science,* No. **19**: 27pp.

Capuzzo, 1987. Biological effects of petroleum hydrocarbons: assessments from experimental results. In: *Long-term environmental effects of offshore oil and gas development*. Eds: Boesch, D. F., Rabalais, N. N., Elsevier, UK. pp 343-410.

CEFAS, 1997. Monitoring and surveillance of nonradioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1994. Science Series *Aquatic Environment Monitoring Report*, CEFAS, Lowestoft, **47**: 59pp.

CEFAS, 1998. Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1995 and 1996. Science Series *Aquatic Environment Monitoring Report*, CEFAS, Lowestoft, **51**: 116pp.

CEFAS, 2000. Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1997. Science Series *Aquatic Environment Monitoring Report*, CEFAS, Lowestoft, **52**: 92pp.

CEFAS, 2001. Monitoring and surveillance of nonradioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1998. Science Series *Aquatic Environment Monitoring Report*, CEFAS, Lowestoft, **53**: 75pp.

Charlesworth, M., Service, M., Mitchell, S. H. and Oliver, W. T., 1999. Metals in surficial sediments of the North-West Irish Sea. *Bulletin of Environmental Contamination and Toxicology*. **62**: 40-47.

Charlesworth, M., Service, M. and Gibson, C. E., 2002. PAH contamination of western Irish Sea sediments. *Marine Pollution Bulletin*. **44**: 1421-1434.

Charting progress: An Integrated Assessment of the State of the UK Seas, 2005. Defra. http://www.defra.gov.uk/environment/water/marine/uk/stateofsea/

Cho S.-M., Kurihara, R., Strussmann, C. A., Uozumi M., Yamakawa, H., Yamasaki, T., Soyano, K., Shiraishi, H., Morita, M., Hashimoto, S., 2003. Histological abnormalities in the gonads of konoshiro gizzard shad (*Konosirus punctatus*) from coastal areas of Japan. *Environmental Science*, **10**(1): 25-36.

Cofino, W. P., Slager, L. K. and van Hattum, B., 1993. *Environmental aspects of produced water discharges from oil and gas production on the Dutch Continental Shelf.* Part I Overview of surveys on the composition of produced waters conducted on the Dutch Continental Shelf. Commissioned by The Netherlands Oil and Gas Exploration and Producing Association (NOGEPA). ISBN 90-5383-218-1.

Currie, D. R., Isaacs, L. R., 2005. Impact of exploratory offshore drilling on benthic communities in the Minerva gas field, Port Campbell, Australia. *Marine Environmental Research* **59** (3): 217-233.

Daan, R. K., Mulder, M., Leewen, A., 1994. Differential sensitivity of macrozoobenthic species to discharges of oil-contaminated drill cuttings in the North Sea. *Netherlands Journal of Sea Research*, **33**(1), 113-127.

Dale, J. D., Larter, S., Aplin A. C., and MacLeod, G., 1995. In: *Organic Geochemistry: Developments and applications to energy, climate, environment and human history*. Eds: Grimalt, J. O. and Dorronsorro, C. AIGOA, San Sebastian, Spain, pp. 396–398.

Davies, J. M. and Kingston, P. F., 1992. Sources of environmental disturbance associated with offshore oil and gas developments. Cairns, W.F., Editor. In: *North Sea oil and the environment. Developing oil and gas resources, environmental impact and responses*, Elsevier, Amsterdam, pp. 417–439.

Dawes, V. J. and Waldock, M. J., 1994. Measurement of volatile organic compounds at UK national monitoring plan stations. *Marine Pollution Bulletin*, **28** (5): 291-298.

DEFRA, 2003. Derivation of Aquatic Quality Standards for Priority List Substances not Covered by Existing UK Regulations. Final Report to the Department for Environment, Food and Rural Affairs.

Environmental Data Services Report (ENDS), 1999. Chemical firms ‘buying time’ on APES phase out’ **289**: 6.

E&P Forum, 1994. North Sea Produced Water: Fate and Effects in the Marine Environment. Report No. 2. 62/204.

De Metrio, G., Corriero, A., Desantis, S., Zubani, D., Cirillo, F., Deflorio, M., Bridges, C. R., Eicker, J., Serna, J. M. S., Megalofonou, P., Kime, D. E., 2003. Evidence of a high percentage of intersex in the Mediterranean swordfish (*Xiphias gladius* L.). *Marine Pollution Bulletin*, **46**: 358-361.

Environment Agency, Environment and Heritage Service, Food Standards Agency and Scottish Environment Protection Agency, 2004. Radioactivity in Food and the Environment, 2003. RIFE-9. Environment Agency, EHS, Food Standards Agency and SEPA, Bristol, Belfast, London and Stirling.

Farestveit, R., Hylland, K. and Haaland, H., 1994. Bioavailability of metals in weight materials for drilling muds. In: *Biologisk tilgjengelighet av tungmetaller I baritt og ilmenitt*. Eds: Schaanning, M., Ruus, A., Bakke, T., Hylland, K., Olsgard, F., Norwegian Institute for Water Research, Trondheim, Statoil. Report No. O-21337. pp. 1-36.

Feist, S. W., Lang, T., Stentiford, G. D. and Köhler, A., 2004. The use of liver pathology of the European flatfish, dab *(Limanda limanda* L.) and flounder *(Platichthys flesus* L.) for monitoring biological effects of contaminants. *ICES Techniques in Marine Environmental Science,* No. **38**: 42pp.

Fossi, M. C., Casini, S., Marsili, L., Neri, G., Mori, G., Ancora, S., Moscatelli, A., Ausili, A., Notarbartolo-Di-Sciara, G., 2002. Biomarkers for endocrine disruptors in three species of Mediterranean large pelagic fish *Marine Environmental Research*; **35**, pp. 667-671.

Gesteira, J. L. G. and Dauvin, J. C., 2000. Amphipods are good bioindicators of the impact of oil spills on soft-bottom macrobenthic communities. *Marine Pollution Bulletin,* **40** (11): 1017-1027.

Gray, J., Jones, S. R. and Smith, A. D., 1995. Discharges to the environment from the Sellafield site, 1951-1992. *Journal Radiological Protection*, **15**: 99-131.

Grigson, S. J., Wilkinson, A., Johnson, P., Moffat, C.F. and McIntosh, A. D., 2000. Measurement of oilfield chemical residues in produced water discharges and marine sediments. *Rapid Communications In Mass Spectrometry*: **14**, (23): 2210-2219.

Guinan, J., Charlesworth, M., Service, M., and Oliver, T., 2001. Sources and Geochemical Constraints of Polycyclic Aromatic Hydrocarbons (PAH) in Sediments and Mussels of two Northern Irish Sea-loughs. *Marine Pollution Bulletin,* **42**, (11): 1073-1081.

Gordan Jr., D. C., Cranford, P. J., Muschenheim, D. K., Loder, J. W., Keizer, P.D., Kranck, K., 1992. Managing the Environmental Impact of Offshore Oil Production. Ed: Ryan, P. M. In: *Proceedings of the 32nd Annual Meeting of the Canadian Society of Environmental Biologists,* St. John’s, Newfoundland, Canada, pp.139-147.

Grigson, S. J., Wilkinson, A., Johnson, P., Moffat, C.F. and McIntosh, A. D., 2000. Measurement of oilfield chemical residues in produced water discharges and marine sediments. *Rapid Communications In Mass Spectrometry*: **14**, (23): 2210-2219.

Gutzman, D., Chénier, R., Pasternak, J., Suffredine, L. and Taylor, K., 1999. Environmental Risk Assessment of Brominated Flame Retardants under the Canadian Environmental Protection Act, 1999. In: *Assessments of Chemical Substances Conducted Under the Canadian Environmental Protection Act, 1999 (CEPA 1999),* Environment Canada, Environmental Protection Service.

Hara, A., Matsubara, H., Soyano, K., 2001. Endocrine and sexual disruption in wild grey mullet. In: *UK-Japan Research Cooperation on Endocrine Disrupting Chemicals* Eds: (Overseas Environmental Cooperative Center Japan). Tokyo, Ministry of the Environment of Japan**,** 42-46.

Harries, J. E., Sheahan, D. A., Jobling, S., 1997. Estrogenic activity in five UK rivers detected by measurement of vitellogenesis in caged male trout. *Environmental Toxicology and Chemistry*; **16**: 534-542.

Henderson, S. B., Grigson, S. J. W., Johnson, P. and Roddie, B. D., 1999. Potential impact of production chemicals on the toxicity of produced water discharges from North Sea oil platforms. *Marine Pollution Bulletin,* **38**, (12): 1141-1151.

Hird, S. J. and Tibbetts, P. J. C., 1995. An examination of biodegradation of aliphatic hydrocarbons from oil-based drilling muds. In: *The Physical and Biological Effects of Processed Oily Drill Cuttings*. Metocean Report No.2.61/202 to the E&P Forum, 104-114.

HMSO, 1989. Statutory Instrument 1989. The Surface Waters (Dangerous Substances) (Classification). In: *Water, England and Wales*. No. 2286.

Holdway, D.A., 2002. The acute and chronic effects of wastes associated with offshore oil and gas production on temperate and tropical marine ecological processes. *Marine Pollution Bulletin,* **44**: 185-203.

Holt, T. J., and Shalla, S. H. A., 2001. Baseline survey in support of the development of hydrocarbon production at BHP's Hamilton East site, Liverpool Bay. A report to BHP Petroleum Ltd. C2581/11-01 v1.

Hunt, G. J., 1995. Radiation Doses to Critical Groups since the early 1950s due to Discharges of Liquid Radioactive Waste from Sellafield. In: *International Symposium on Environmental Impact of Radioactive Releases* (IAEA), Vienna, IAEA-Sm-339/16.

Jepson, P. D., Bennett, P. M., Allchin, C. R., Law, R. J., Kuiken, T., Baker, J. R., Rogan, E. and Kirkwood. J. K., 1999. Investigating potential associations between chronic exposure to polychlorinated biphenyls and infectious disease mortality in harbour porpoises from England and Wales, *The Science of the Total Environment,* **243-244**: 339-348.

Jones, D. G., Roberts, P. D., Strutt, M. H., Higgo, J. J. and Davis, J. R., 1999. Distribution of ^{137}Cs and inventories of ^{238}Pu, $^{239/240}$Pu, ^{241}Am and ^{137}Cs in Irish Sea intertidal sediments. *Journal of Environmental Radioactivity,* **44**: 159-189.

Karman C.C., Vik, E.A., Schobben, H.P>M., Ofjord, G.D. and Dokkum, H.P., 1996. CHARM III. Main report. TNO-report R96/355

Kershaw, P. J., Denoon, D. C. and Woodhead, D. S., 1999. Temporal trends in plutonium and americium concentrations and inventories in Irish Sea sediments. *Journal of Environmental Radioactivity,* **44**: 191-221.

Kershaw, P. J., Pentreath, R. J., Woodhead, D. S. and Hunt, G. J., 1992. A review of radioactivity in the Irish Sea. *Aquatic Environment Monitoring Report*, MAFF Directorate of Fisheries Research, Lowestoft., **32**: 1-65.

Krahn, M. M., Burrows, D. G., MacLeod, W. D. Jr. and Malins, D. C., 1987. Determination of individual metabolites of aromatic compounds in hydrolyzed bile of English sole (*Parophrys vetulus*) from polluted sites in Puget Sound, Washington. *Archives of Environmental Contamination and Toxicology*, **16** (5): 511-522.

Law, R. J., Blake, S. J., Jones, B. R. and Rogan, E., 1998. Organotin compounds in liver tissue of harbour porpoises (*Phocoena phocoena*) and grey seals (*Halichoerus grypus*) from the coastal waters of England and Wales. *Marine Pollution Bulletin*, **36**, (3): 241-247.

Law, R. J., Waldock, M. J., Allchin, C. R., Laslett, R. E. and Bailey, K. J., 1994. Contaminants in seawater around England and Wales: Results from monitoring surveys, 1990-1992. *Marine Pollution Bulletin*, **28**: 668-675.

Law, R. J., Fileman, T. W., Fileman, C. F. and Limpenny, D. S., 1988. The distribution of hydrocarbons and metals in the north-eastern Irish Sea prior to development of Morecambe Bay gas field. *Oil and Chemical Pollution*, **5**: 285-320.

Leonard, K. S., McCubbin, D., Brown, J., Bonfield, R. A. and Brooks, T., 1997. Distribution of Technetium-99 in UK coastal waters. *Marine Pollution Bulletin*, **34** (8): 628-636.

Leonard, K. S., McCubbin, D., Blowers, P. and Taylor, B. R., 1999. Dissolved plutonium and americium in surface waters of the Irish Sea, 1973-1996. *Journal of Environmental Radioactivity*, **44**: 129-158.

Lye, C. M., 2000. Impact of oestrogenic substances from oil production at sea. Toxicology Letters. **112–113**: 265-272.

MacKenzie, A. B., Scott, R. D., Allan, R. L., Ben Shaban, Y. A., Cook, G. T. and Pulford, I. D., 1994. Sediment radionuclide profiles: implications for mechanisms of Sellafield waste dispersal in the Irish Sea. *Journal of Environmental Radioactivity*, **23**: 36-69.

McCubbin, D., Leonard, K. S., Brown, J., Kershaw, P. J., Bonfield, R. A. and Peak, T., 2002a. Further studies of the distribution of 99Tc and 137Cs in UK and European coastal waters. *Continental Shelf Research*, **22** (10): 1417-1445.

McCubbin, D., Leonard, K. S. and Emerson, H. S., 2002b. Influence of thermal and photochemical reactions upon the redox cycling of Pu between solid and solution phases in seawater. *Marine Chemistry*, **80** (1): 61-77.

McElroy, A. E. Farrington, J. W., Teal, J. M., 1989. Bioavailability of polycyclic aromatic hydrocarbons in the aquatic environment. Ed: Varanasi, U. In: *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*, CRC Press, Boca Raton, pp. 1-42.

Mitchell, P. I., Kershaw, P. J. and Leon Vintro, L., 1996. Radioactivity in the Irish Sea: past practices, present status and future perspectives. In: *Radionuclides in the Oceans, Inputs and Inventories, les editions de physique*. Eds: Guegueniat, P., Germain, P. and Metivier, H. pp. 155-175.

Myers, M. S., Landahl, J. T., Krahn, M. N., Johnson, L. L. and McCain, B. B., 1990. Overview of studies on liver carcinogenesis in English sole from Puget Sound; evidence for a xenobiotic chemical etiology. Pathology and epizootiology. *Science of the Total Environment,* **94**: 33-50.

National Research Council (NRC), 1983. Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects. National Academy Press, Washington, D.C. p. I-3 to D-26.

OSPAR 1999, OSPAR/ICES. Workshop on the overall evaluation and update of background/reference concentrations of nutrients and for contaminants in sea water, biota, sediments. OSPARCommission, meeting document NoASMO97/4/Info.1.60pp.

OSPAR Commission, 2002. Cadmium**.** Hazardous Substances Series. OSPAR Commission.

OSPAR Commission, 2004. Overview of the results of the Comprehensive Study on Riverine Inputs and Direct Discharges (RID) from 2000 to 2002. Monitoring and Assessment Series No. 218.

Pollard, D., Long, S., Hayden, E., Smith, V., Ryan, T. P., Dowdall, A., McGarry, A. and Cunningham, J. D., 1996. Radioactivity monitoring of the Irish marine environment 1993-1995. Radiological Protection Institute of Ireland, RPII - 96/5, 41 pp.

Poole, A. J. Allington, D. J., and Denoon, D. C., 1995. Temporal and spatial survey of dissolved ^{226}Ra in coastal waters of the eastern Irish Sea. *Science of the Total Environment,* **168** (3): 233-247.

Poole, A. J., Denoon, D. C. and Woodhead, D.S., 1996. The distribution and inventory of ^{137}Cs in sub-tidal sediments of the Irish Sea. Eds: Germain, P, Guary, J. C., Guegueniat, P. and Metivier, H. In: *Radionuclides in the oceans RADOC 96–97*. Proceedings Part 1: inventories, behaviour and processes. Radioprotection-Colloques, 32(C2), 263–270.

Rees, E. I. S., 1994. Drilling and Pipelines the effect on the Benthic Environment. In: Irish Sea Forum, Seminar on oil and gas exploitation Manx Museum, Douglas, 20/21 January, 1994.

Routledge, E. J. and Sumpter, J. P., 1996. Oestrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. *Environmental Toxicology and Chemistry,* **15**: 241-249.

Rijinsdorp, A. D., Vethaak, A. D. and van Leeuwem P. I., 1992. Population biology of dab *Limanda limanda* in the South Eastern North Sea. *Marine Ecology Progress Series,* **91** (1-3): 19-35.

Rowlatt, S. M. and Lovell, D. R., 1994. Lead, zinc and chromium in sediment around England and Wales. *Marine Pollution Bulletin*. **28**: 828-830.

Ryan, T. P., Germain, P., Dowdall, A. M., Leclerc, G. and Pollard, D., 1997. A Comparison of ^{210}Po in *Mytilus edulis* and *Fucus vesiculosus* in French and Irish Coastal Waters. Eds: Germain, P, Guary, J. C., Gueguениat, P. and Metivier, H. In: *Radionuclides in the oceans RADOC 96–97*. Proceedings Part 1: inventories, behaviour and processes Radioprotection Colloques, 32(C2): 345-352.

SEEEC (Sea Empress Environmental Evaluation Committee), 1998. The environmental impact of the Sea Empress oil spill. Final Report of the Sea Empress Environmental Evaluation Committee. London, The Stationery Office.

SEPA, 2004. Environmental Quality Standards (EQSs) list, Issue No. 1. Technical guidance manual for licensing discharges to water, Annex G.

Slager, L. K., van Hattum, B., Tromp Meesters, M., Scholten, M. C. Th., Kaag, N. H. B. M., Cofino, W. P., Feenstra, J. F., 1992. Environmental aspects of produced water discharges on the Dutch Continental Shelf. Part III. Environmental effects. ISBN 90-5192-021-0.

Smith, B. D., Hunt, G. J. and Camplin, W. C., 2004. The impact of liquid radioactive waste discharges from Sellafield to the Irish Sea in recent years. In: Proceedings of the 11th International Congress of the International Radiation Protection Association, Madrid, 23-28 May 2004.

Soclo, H. H., Garrigues, P. H., and Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Marine Pollution Bulletin,* **40**: 387–396.

Somerville, H. J., Bennett, D., Davenport, J. N., Holt, M. S., Lynes, A., Mahieu, A., McCourt, B., Parker, J. G., Stephenson, R. R., Watkinsn, R. J., and Wilkinson, T. G., 1987. Environmental Effect of Produced Water from North Sea Oil Operations. *Marine Pollution Bulletin,* **18** (10): 549-558.

Stagg, R. M., 1994. The effects of drill cuttings and on the dab *Limanda limanda*. E & P Forum Report.

Stromgren, T., Sorstrom, S. E., Schou, L. Kaarstad, I., Aunaas, T., Brakstad, O. G., Johansen, O., 1995. Acute toxic effects of produced water in relation to chemical composition and dispersion. *Marine Environmental Research,* **40** (2): 147-169.

Swift, D. J., Smith, D. L., Allington, D. J. and Winpenny K., 1995. A laboratory and field study of ^{210}Po depuration by edible winkles (*Littorina littorea* L.) from the

Cumbrian Coast (north-eastern Irish Sea). *Journal of Environmental Radioactivity*, **26** (2): 119-133.

Taylor, P., Larter, S., Jones, M., Dale, J. and Horstad, I., Geochim., 1997. The effect of oil-water-rock partitioning on the occurrence of alkylphenols in petroleum systems. *Geochimica et Cosmochimica Acta*, **61** (9), 1899-1910.

Terzaghi, C., Buffagni, M., Cantelli, D., Bonfanti, P., Camatini, M., 1998. Physical-chemical and ecotoxicological evaluation of water based drilling fluids used in Italian off-shore. *Chemosphere*, **37** (14/15): 2859-2871.

Thomas, K. V., Balaam, J., Hurst, M, R. and Thain, J. E., 2004. Bio-analytical and chemical characterisation of offshore produced water effluents for estrogen receptor (ER) agonists. *Journal of Environmental Monitoring*, **6**: 593-598.

Thompson, A., Allen, J. R., Dodoo, D., Hunters, J., Hawkins, S. J., Wolff, G. A., 1996. Distributions of chlorinated Biphenyls in mussels and sediments from Great Britain and the Irish Sea coast. *Marine Pollution Bulletin*, **32** (2): 232-237.

UK Oil and Gas Energy Reports, 1998–2001. ("The Brown Book"). http://www.dbd-data.co.uk/brownbook/index.htm.

United Nations Scientific Committee on the Effects of Atomic Radiation, 1996. Effects of radiation on the environment.

Wells, D. E., Kelly, A., Findlayson, D. M., Eaton, S., Robson, J. and Campbell, L., 1989. Report of the survey for PCB contamination following the Piper Alpha incident. SOAFD Marine Laboratory, Aberdeen.

Widdows, J., Donkin, P., Staff, F. J., Matthiessen, P., Law, R. J., Allen, Y. T., Thain, J. E., Allchin, C. R., Jones, B. R., 2002. Measurement of stress effects (scope for growth) and contaminant levels in mussels (*Mytilus edulis*) collected from the Irish Sea. *Marine Environmental Research*. **53**: 327-356.

Woodhead, D. S., 1999. Actinides in the Irish Sea. *Journal of Environmental Radioactivity*, **44**: 127–128.

Woodhead, R. J., Law, R. J. and Matthiessen, P., 1999. Polycyclic Aromatic Hydrocarbons (PAH) in surface sediments around England and Wales, and their possible biological significance. *Marine Pollution Bulletin*, **38**, 773-79.

9. ACRONYMS

AP	Alkylphenols
BEQUALM	Biological Effects Quality Assurance in Monitoring Programmes
CEFAS	Centre for Environment, Fisheries and Aquaculture Science
CEMP	Co-ordinated Environment Monitoring Programme
CYP1A	Cytochrome P450 1A – detoxification enzyme measured in fish
EAC	Ecotoxicological Assessment Criteria
EARP	Enhanced Actinide Removal Plant
EROD	Ethoxyresorufin-o-deethylase
ICES	International Council for the Exploration of the Seas
JAMP	Joint Assessment and Monitoring Programme
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated biphenyls
UKCS	United Kingdom Continental Shelf
UK NMMP	United Kingdom National Marine Monitoring Programme
OBM	Oil Based Mud
OCNS	Offshore Chemical Notification Scheme
OCR	Offshore Chemicals Regulations
OSPAR	Oslo and Paris Comission
SEA	Strategic Environmental Assessment
SIXEP	Site Ion Exchange Effluent Plant
VTG	Vitellogenin (egg yolk protein)
WBM	Water Based Mud