



# **A Review of the Contaminant Status of SEA 8 covering the Western Approaches, Celtic Sea and English Channel**

**for  
Geotek Ltd**

**Cefas Contract report C3006**

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TITLE: A Review of the Contaminant Status of SEA 8 covering the Western Approaches, Celtic Sea and English Channel

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## **EXECUTIVE SUMMARY**

This report considers the major sources of contamination to the Bristol Channel, Celtic Sea, South Western Approaches and English Channel, here collectively termed Strategic Environment Assessment Area 8 (SEA8). The Department of Trade and Industry (DTI) established, in 1999, the SEA process for the marine environment of the UK to enable the economic benefits of offshore energy developments to be weighed against the need for environmental protection. The SEA8 area, in contrast to other SEA areas, does not at this time include any offshore oil and gas assets. However, the largest onshore oilfield in Western Europe, Wytch Farm is located on the Devon coast, and from shore-based wells exploits the oil reservoir extending under Poole harbour. As a result of the absence of major offshore development, this report focuses on an assessment of major contaminant inputs and the resulting contamination of the wider environment in terms of chemical contaminants, biological effects and radioactivity identified by monitoring programme data and specific studies. The observed levels of contamination, their spatial coverage and temporal trends are discussed.

### **Inputs to SEA8**

Riverine inputs represent the major contribution to contaminants in the SEA8 area. This reflects the importance of diffuse sources such as runoff from agricultural land and urban runoff via surface drains and storm overflows. The SEA8 area also lacks offshore oil and gas development activity, which is a potential source of particular contaminant groups in SEA2 and SEA6. Other relatively less significant contaminant inputs include small marine incidents that result in chemical spills. Although there have been three more major marine incidents in the SEA8 area, these did not result in prolonged or widespread contamination.

### **Environmental monitoring programmes, chemical status and effects data and information**

The concentrations of dissolved contaminants in the offshore seawater samples of the SEA8 area were either low or below the level of detection for current analytical tools. This was mainly due to the characteristics of the individual compounds (i.e. low solubility/ or partitioning to suspended particles), which have a tendency to collect in either sediment and /or biological tissues. Of those contaminants that were detected, highest concentrations were generally found in seawater samples collected from coastal waters in close proximity to industrial inputs such as the Severn estuary. Environmental quality standards (EQSs) for metals and maximum allowable concentrations (MACs) for alkylphenolic chemicals were not exceeded at any of the monitoring stations within the SEA8 area. In contrast, many polycyclic aromatic hydrocarbon (PAH) concentrations exceeded their MACs at Southampton, Tamar and at the mouth of the River Severn. However, significant PAH concentrations were not detected in seawater samples taken further offshore.

As sediments adsorb many groups of contaminants it is not surprising that most sediment contaminant concentrations were at least 3 orders of magnitude higher than those measured in seawater samples. With the exception of alkylphenols, which were not detected in any of the sediment samples, highest concentrations of all contaminants measured in sediment samples were consistently found at the mouth of the River Severn/ Bristol channel. The proximity of this area to industrialised centres (e.g. Bristol, Cardiff, Swansea) was likely to be responsible for the higher concentrations of contaminants. Elevated concentrations of metals were also

found at the mouth of the River Tamar. Historical mining activity is thought to be the major contributor to the high sediment metal loads within this area.

Contaminant concentrations in biological tissues are dependent on a variety of factors such as contaminant characteristics, bioaccumulation factors, tissue type and detoxifying mechanisms of the organisms, to name just a few. Comparison of the contaminant data between sediments and biota revealed a good relationship with highest concentrations of contaminants found in species collected from areas of high sediment contamination (e.g. Severn estuary). This was the case for tissue samples from the mussels and the dab, a marine flatfish species. The bodies of marine mammals recovered from shore areas within SEA8 had significantly higher contaminant concentrations than either fish or mussels. This is compounded by their high trophic level, long life span and limited ability for detoxification and excretion.

Overall, contaminant concentrations irrespective of sample type were lower in the SEA8 area compared to the other coastal waters of the UK such as the Irish Sea (SEA6) and North Sea (SEA2). This may be partly due to the comparatively larger riverine components of the North and Irish Seas, which transport higher concentrations of contaminants as a result of land runoff and the increased proximity to industrialised areas. In addition the stronger influence of the North Atlantic waters in the English Channel are likely to lead to increased water flux and dilution. The absence of offshore oil and gas activities within the SEA8 also means that localised higher areas of contamination are absent from this source at this time.

Biological effects data were not available in species collected from the mouth of the River Severn, the site of relatively high contaminant concentrations. Therefore, comparisons between elevated contaminant concentrations and biomarker response for this area were not possible. However, in other SEA8 sample areas, with the exception of the higher level of imposex in dogwhelks (indicative of tributyltin exposure), the generally low contaminant concentrations present are reflected in reduced biological effects. Although data for many of the biological effects measured in dab populations were often sparse, the level of biological effect activity measured indicates low contaminant exposure by comparison to samples from other SEA areas. The same was also true for mussel populations for which measures of stress for many of the groups sampled were also indicative of low levels of exposure to contaminants.

## **Radioactivity**

Inputs of artificial radionuclides in the Bristol Channel are dominated by discharges from Cardiff, Oldbury and Hinkley Point, although new abatement technology at Cardiff should significantly reduce future discharges of tritium and carbon-14.

Discharges of organic tritium from Cardiff have been found to bioaccumulate in local fish populations. This is believed to form the major contributing consumption pathway to critical group dose in the Bristol Channel. Concentrations in the English Channel were low and can be attributed to other sources such as Chernobyl, weapon test fallout and discharges from other establishments.

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 Bristol Channel and English Channel directly associated with oil and gas production is not available.

### **Gaps in our understanding and future risks**

This report has highlighted that there are fewer datasets available for chemical and particularly biological effects data in the SEA8 area for which environmental status was evaluated. There are also fewer UK CSEMP sites within the SEA8 from which data could be obtained. The relatively fewer industrial riverine inputs into the English Channel as well as the lack of offshore oil and gas installations within the area may make this area less of a focus than some of the more northerly industrialised locations. With the potential variations in rainfall frequency and intensity, temperature and sea level that are forecast as a result of climate change it will be important to establish good baseline datasets in areas such as SEA8. Particularly as climate change factors may influence contaminant mobilisation and bioavailability and hence impact good ecological status of many locations within the SEA8 area. Monitoring programs should therefore address this gap in information. With the overall objective of good status in all River Basins to be achieved by December 2015 under the Water Framework Directive the integration of biological effects data with chemical status information will also become increasingly important.

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## **1. INTRODUCTION**

The Department of Trade and Industry (DTI) established, in 1999, the Strategic Environmental Assessment (SEA) of the marine environment of the UK to enable the economic benefits of offshore energy developments to be weighed against the need for environmental protection. 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 SEA 8 area, which includes the Bristol Channel, Celtic Sea, South Western Approaches and English Channel. The assessment takes into account the major inputs of contaminants to this area, which include riverine and point source inputs as identified under OSPAR, contaminants associated with dredged material and those contaminants that may enter the marine environment as a result of accidental discharges or spills. 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 resulting from natural and anthropogenic sources although these are not significant for installations and operations in this area.

## **2. DATA SOURCES AND APPROACH**

The report is broken down into three main sections the first two cover contaminant status and biological effects measurements of the SEA 8 area dealing with data collected from monitoring programmes and studies in the area. Of particular importance in this section is the data gathered as part of the United Kingdom National Marine Monitoring Programme (UK NMMP) and more recently from its successor the Clean and Safe Seas Environmental Monitoring Programme (CSEMP). Data for the NMMP is presented in a number of publications that include the Cefas Aquatic Environment Monitoring Reports (AEMR) (1998, 1999-2000, 2000-2001, 2002-2003 and 2003-2004), 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 3 is concerned with radioactivity in the marine environment. Publications of importance include the Radiation in Food and the Environment (RIFE) report, and the data published in the Cefas AEMRs.

### **3. MONITORING PROGRAMMES, SURVEY AND RESEARCH BASED DATA AND INFORMATION**

#### **3.1 INPUTS TO THE SEA 8 AREA**

The Severn Estuary and Bristol Channel is a well-mixed and energetic macrotidal estuary. There is considerable industrial activity along both the northern and the southern shores that includes the Milford Haven oil refinery. Urban development associated with the cities of Bristol, Gloucester, Newport, Cardiff and Swansea have industrial areas and large populations which are both sources of direct and indirect contaminant input to the SEA 8 area. The English Channel is part of the Atlantic Ocean that separates Great Britain from France and joins the North Sea to the Atlantic. It is one of the busiest sea routes in the world, with the major ports of Southampton and Le Havre on English and French sides respectively. Highest populations are present in Portsmouth, Southampton and Bournemouth.

Produced Water discharges and drill cuttings arising from offshore oil and gas activities have contributed to contaminant inputs in other SEA areas but the primarily onshore exploitation and development of oil and gas reserves in SEA8 means that contamination does not occur from these sources.

The onshore Wytch Farm oilfield southwest of Poole was discovered in 1973. The first stage of development at Wytch Farm began in the late 1970s. In 1993 land-based, extended reach drilling operation (which can reach more than 10 kilometres horizontally from the wellhead) has been used to exploit the reservoir beneath Poole Bay.

Contaminant inputs to the marine environment arise from a wide variety of other sources. Although large spillages following tanker accidents tend to have a high public profile, the majority of petroleum hydrocarbons, for example, enter the sea from; shipping, 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. Many of these sources are also the dominant ones for metals and organics.

##### **3.1.1 Contaminant inputs associated with dredged sediment dumping**

Contaminant inputs to the marine environment from dredged material disposal operations are likely to be much lower than the total contaminant loads reported due to the continual return of sediments from disposal sites to dredging sites by natural currents. In addition, the bulk of dredged material disposed will not add new contaminants from anthropogenic sources to the sea, provided all input paths, such as direct discharge, riverine and atmospheric inputs or diffuse sources are taken into account in the overall estimation of contaminant inputs to the sea. It must also be recognised that loads of naturally occurring contaminants include a substantial proportion derived from the background content of the contaminants in the mineral matrices. For these reasons, contaminant inputs associated with dredged sediment and concentration trends over time must be interpreted with caution. Input data for metals and organic compounds measured from dredge material dumped to the SEA8 area in 2005 are shown in Tables 1-3.

**Table 1. Concentrations of metals measured in dredge material dumped in different sea areas adjacent to the SEA8 area in 2005 (all estimated values in tonnes unless indicated).**

Location	Dumped tonnes	Solids tonnes	Cd	Hg	As	Cr	Cu	Pb	Ni	Zn
Lundy	4682868	2010596	1.25	0.66	50.71	111.42	122.96	177.53	94.59	597.06
Portland	24269	20094.73	0.00	0.00	0.33	0.72	0.32	0.93	0.82	3.79
Plymouth	192948	97925.46	0.03	0.06	5.21	3.56	15.00	11.93	3.02	29.00
Wight	1911341	1085132	0.16	0.15	13.21	30.25	23.61	24.49	16.25	71.37
Dover	614573	341868.9	0.02	0.02	2.43	7.04	1.75	4.26	3.36	11.97

The highest loads of a selection of metals were measured in the Lundy and Wight sea areas. The Lundy area receives inputs from the Bristol Channel, which includes contributions from a number of major industrial sites; the same is true but to a lesser extent to inputs to Wight which include Southampton Water. A similar pattern is apparent for PAHs, organometallics and chlorinated biphenyls.

**Table 2. Concentrations of Hydrocarbons, pesticides and organometallics in dredge material dumped in different sea areas adjacent to the SEA8 area in 2005 (all estimated values in tonnes unless indicated).**

Location	Oil	$\Sigma$ 9 PAHs	$\Sigma$ PAHs	HCB*	g-HCH*	DDT*	TBT*	DBT*
Lundy	709.03	9.35	18.48	0.00	0.00	0.00	185.22	29.76
Portland	0.11	0.00	0.00	0.00	0.00	0.00	0.24	0.02
Plymouth	9.22	0.29	0.41	0.00	0.00	0.00	3.55	1.52
Wight	130.42	0.55	1.05	0.00	0.00	0.00	111.91	17.33
Dover	0.44	0.00	0.01	0.00	0.00	0.00	4.46	1.88

\*Values in kilograms

**Table 3. Concentrations of chlorinated biphenyls in dredge material dumped in different sea areas adjacent to the SEA8 area in 2005 (all estimated values in kilograms).**

Location	CB#28	CB#52	CB#101	CB#118	CB#138	CB#153	CB#180	$\Sigma$ ICES7
Lundy	1.90	0.64	0.64	0.64	1.27	1.27	1.27	55.04
Portland	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Plymouth	0.08	0.27	0.50	0.51	0.64	0.51	0.27	0.29
Wight	0.02	0.02	0.04	0.04	0.04	0.03	0.02	0.04
Dover	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00

### 3.1.2 Contaminant inputs associated with direct discharges and riverine inputs

A comprehensive study was carried out in 2004 to determine the inputs of a number of organic and metal contaminants into the surrounding waters of Northern Europe, including the SEA8 area (OSPAR Commission, 2004). Data from this study for the SEA8 area has been summarised in Tables 4 and 5. With the exception of PCBs for which measured concentrations were highly variable, riverine contributions for metals and selected organics were mostly greater than 57%. Riverine contributions also dominated for nitrogen species, whereas for phosphates direct inputs were more broadly comparable. Dominant riverine inputs of particular contaminants reflect the importance of diffuse sources such as runoff from agricultural land and urban runoff via surface drains and storm overflow.

**Table 4. Sources and load of metals and selected organics (tonnes unless indicated) to the SEA8 area from direct discharge and river inputs (OSPAR Commission, 2004).**

Discharge Type	Estimate	Cd	Hg	Cu	Pb	Zn	g-HCH * <sup>1</sup>	PCBs *
Sewage	Lower	0.03	0.02	6.77	1.94	31.25	0.18	0.00
	Upper	0.04	0.02	6.81	2.24	31.25	3.78	5.26
Industrial	Lower	0.02	0.00	0.71	1.20	67.81	0.00	2.16
	Upper	0.02	0.00	0.63	1.21	67.82	0.13	4.01
Riverine	Lower	0.68	0.20	73.07	38.97	330.18	0.24	0.00
	Upper	1.73	0.31	74.06	59.09	337.11	21.03	16.83
Riverine as % of total	Lower	93.15	90.91	90.71	92.54	76.92	57.14	0.00
Riverine as % of total	Upper	96.65	93.94	90.87	94.48	77.29	84.32	64.48

\* in kilograms, <sup>1</sup>(γ-HCH, hexachlorocyclohexane)

**Table 5. Sources and load of nutrients (kilotonnes ) to the SEA8 area from direct discharge and river inputs (OSPAR Commission, 2004).**

Discharge Type	Estimate	NH4-N	NO3-N	PO4-P	Total N	Total P	SPM
Sewage	Lower	9.31	2.90	1.65	11.76	1.65	19.06
	Upper	9.36	3.01	1.68	12.30	1.68	19.09
Industrial	Lower	0.15	0.01	0.00	0.03	0.00	2.60
	Upper	0.16	0.02	0.01	0.03	0.01	3.60
Riverine	Lower	0.89	48.33	1.41	45.92	1.41	411.45
	Upper	0.95	48.33	1.42	67.10	1.42	414.94
Riverine as % of total	Lower	8.60	94.32	46.08	79.57	46.08	95.00
Riverine as % of total	Upper	9.07	94.10	45.66	84.48	45.66	94.82

SPM, suspended particulate matter

### 3.1.3 Contaminant inputs associated with marine incidents

Wide ranges of shore-based and maritime activities have the potential to contaminate the marine environment. The Maritime and Coastguard Agency (MCA) has statutory responsibility for taking action when oil or other hazardous substances are discharged or spilt from shipping or other maritime activities. The Advisory Committee on Protection of the Sea (ACOPS), reports incidents that occur each year on behalf of MCA in an annual survey. Table 6 shows the source and type of pollution reported in the SEA8 area during 2005.



**Table 6. Source, number and type of pollution from accidental discharges/spills reported in SEA8 during 2005 (ACOPS, 2006).**

Enumeration area	Vessel/ offshore pollution source		Pollution type					
	Identified	Suspected	1	2	3	4	5	6
Southern England	13	14		11	3		3	
South-west England	9	11	1	18		1		
Bristol Channel & South Wales	17(1)	2		14	1	3		1

1. crude oil
2. bunker, diesel, fuel and gas oils
3. lubrication and hydraulic oils
4. Other oil types
5. Unidentified oil
6. other chemical substances

Spills of bunker, diesel and fuel oils are the dominant type of contaminant input to SEA8 with generally higher numbers of reported incidents in the Southwest and Bristol Channel probably reflecting greater difficulty in attributing sources of pollution to busy shipping areas in the English Channel.

In addition to accidental spills and discharges that occur on a small scale annually, there have been a number of more major incidents in the SEA8 area. The *levoli Sun*, an Italian chemical product tanker sank in October 2000, 11 miles Northwest of Alderney in the English Channel. The vessel carried a mixed cargo comprising 4000 tonnes of styrene, and 1000 tonnes each of methyl ethyl ketone and *iso*-propyl alcohol. Fortunately each of these chemicals is of low toxicity, persistence and bioaccumulation potential. Around 1000 tonnes of the relatively insoluble styrene were lost through evaporation at the sea surface. There were no major risks to human health or environmental impact as a result of the spill.

The 'Sea Empress' oil tanker grounded outside Milford Haven (UK) in February 1996, spilling approximately 72 000 t of crude oil into Milford Haven Harbour in south Wales, and contaminating nearly 200 km of coastline. Studies of specific enzyme activities in fish that are associated with exposure to PAHs, indicated effects up to 3 months after the incident in fish sampled from sites close to the main area of the spill (Kirby et al, 1999).

In 1989 the vessel MV Perintis sank 35 miles south east of Brixham in the English Channel. Amongst the cargo were a number of pesticides: 0.6 t of cypermethrin, 1.0 t of permethrin, and 5.8t of lindane ( $\gamma$ -hexachlorocyclohexane, HCH). None of the lindane containers were recovered although 80% of the permethrin and all of the cypermethrin containers were recovered. An extensive monitoring programme followed this event with samples collected during research cruises between 1989 and 1993. Although the data from the English Channel showed some variability, all the concentrations reported were low, with few  $>1\text{ng l}^{-1}$  and the maximum of  $1.8\text{ng l}^{-1}$ . In general the higher concentrations were found inshore and were considered to represent inputs from land.

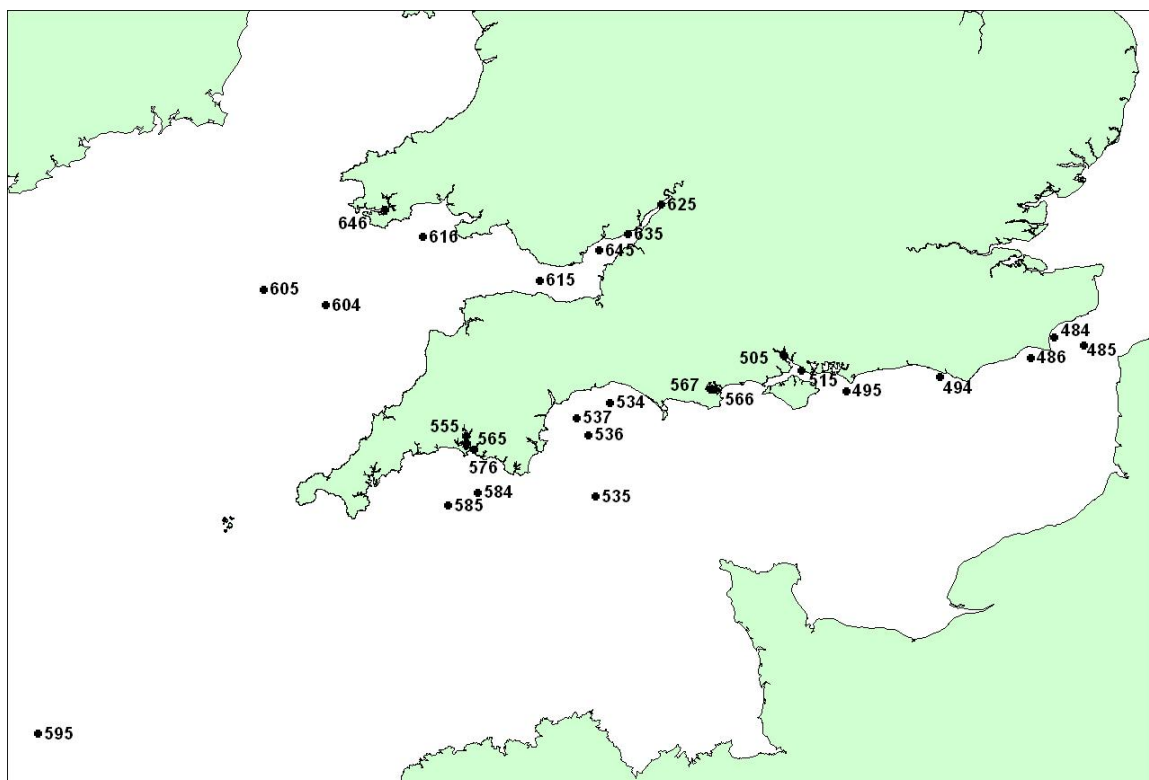
Of the major incidents described the Sea Empress had the potential for the longest remaining impact within the SEA8 area. A more recent retrospective review of the incident concludes that the fact it was possible for extensive dispersant operations to be carried out at the time meant that the impact of the spill was considerably reduced (Law and Kelly, 2004). Levels of hydrocarbons remained low in all finfish (total PAHs including 19 groups was  $186\ \mu\text{g kg}^{-1}$

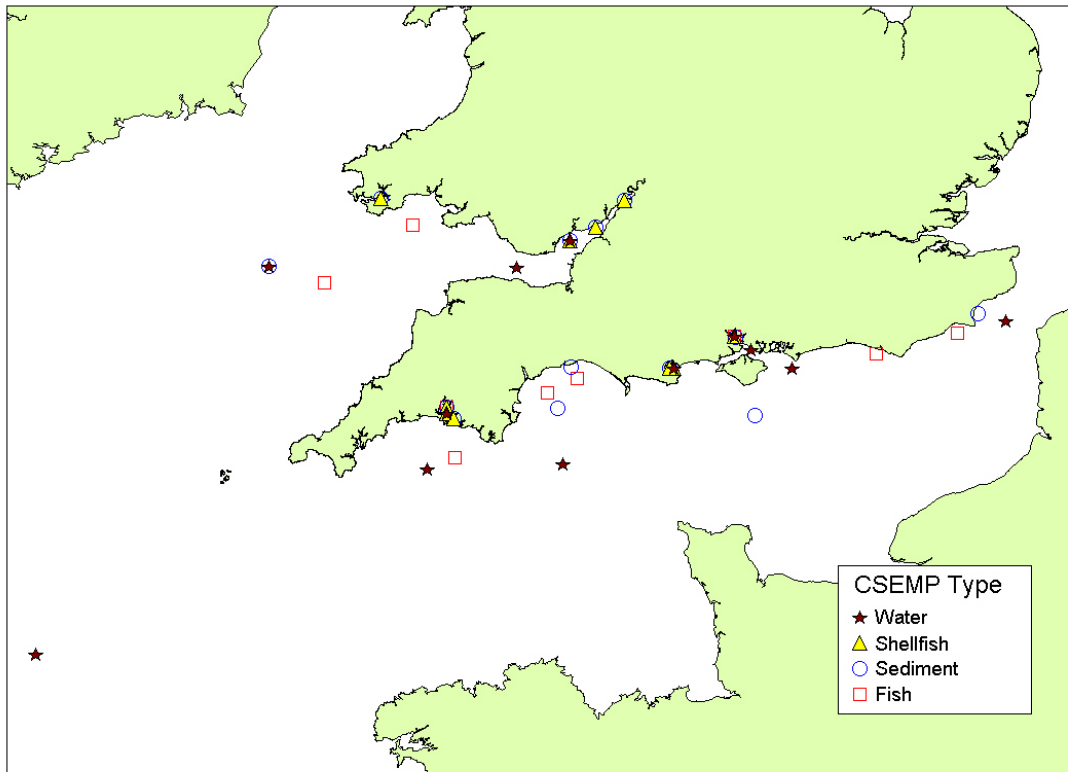
wet weight). Other than in Milford Haven itself, hydrocarbon concentrations also remained low in crustacea. Despite some early high tissue concentrations measured in whelks in a localised area around Carmarthen Bay other samples of whelks taken across the whole area yielded much lower hydrocarbon values. For bivalve molluscs hydrocarbon contamination rose rapidly immediately during and after the incident and then declined steadily over the next four months. In some areas of the south Pembrokeshire coast oil persisted subtidally to the end of 1996.

### 3.2 SAMPLING PROGRAMMES AND LOCATION MAPS

The majority of data has been obtained from the United Kingdom Clean and Safe seas Environmental Monitoring Program (UK CSEMP, formerly UK NMMP) during the last five years. Where earlier datasets may provide further insight into contaminant trends these have also been included. 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 1). Locations of sampling sites where specific data were taken including water, sediment, fish and shellfish are illustrated in Figure 2. In addition to the UK CSEMP, other Cefas survey data from individual surveys has also been included together with data from other recent peer reviewed papers and technical reports where appropriate.

**Figure 1. Map of SEA 8 survey area showing the locations of the UK CSEMP sampling stations for which data are reported.**





**Figure 2. Map of SEA 8 survey area showing the locations of the selected UK CSEMP sampling stations where specific data has been reported. Stations include water, sediments, shellfish and fish sampling sites.**

### 3.3 CHEMICALS IN THE ENVIRONMENT

#### 3.3.1 Introduction

This section is a review of the types and concentrations of chemicals present in the SEA8 area 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.

#### 3.3.2 Water

##### 3.3.2.1 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 for 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). Specific data on recent THC concentrations in the SEA8 area are not currently available. Values measured in the English Channel in 1992 ranged were between  $<0.1$  and  $0.3\mu\text{g l}^{-1}$  Ekofisk crude oil equivalents. Samples in 1993 included some sites on the Tamar (Tamar, Hamoaze) for which a higher concentration of  $5.8\mu\text{g l}^{-1}$  Ekofisk crude oil equivalents, was recorded.

### 3.3.2.2 Polycyclic aromatic hydrocarbons (PAHs)

Natural sources of PAHs occur through volcanic activity, oil seeps and forest fires. However, anthropogenic sources of PAHs are the major input to the marine environment (McElroy *et al.*, 1989). PAHs are characterised with a high octanol water ( $K_{ow}$ ) and organic carbon adsorption ( $K_{oc}$ ) partition coefficient. This results in them adsorbing to suspended particles and becoming deposited to the sediments and having the potential to bioaccumulate in the tissues of marine organisms. Consequently, PAH concentrations are often low or below the limit of analytical detection in the water column.

The concentrations of 10 PAHs measured in water samples collected from the UK CSEMP stations in the SEA8 between 1993-1994 are shown in Table 7. PAH were not detected at 7 of the 13 CSEMP stations. Higher concentrations of PAHs were found closer to the coast with highest concentrations measured in water samples from Southampton and Tamar. Of the 10 PAHs measured, naphthalene, fluoranthene and pyrene were the most abundant at all sites. These are derived from a petroleum rather than a pyrogenic source. The maximum allowable concentration (MAC) of 10 ng/l (Defra, 2003) for many of the PAH compounds was exceeded at the coastal sites.

**Table 7. Concentration of PAH in water samples collected from the UK CSEMP stations in the SEA8 area (1993-1994, ng/l).**

Station	CSEMP No.	Year	Naph	PA	Anth	Flu	Pyr	BaA	Chrys	BeP	BaP	BghiP	SumPAH
South Varne	485	1993	<15	<8	<1	<1	<1	<2	<2	<1	<1	<1	nd
		1994	<6	<3	<1	<2	<1	<6	<4	<2	<4	<17	nd
Selsey Bill	495	1993	<15	<8	<1	<1	<1	<2	<2	<1	<1	<1	nd
		1994	<6	<3	<1	<2	<1	<6	<4	<2	<4	<17	nd
So'ton - Dock head	505	1993	<15	<8	<1	10	11	6	3	1	2	3	36
So'ton - Brambles Buoy	515	1993	<15	24	3	45	48	34	22	9	21	19	255
So'ton - Hook Buoy	525	1993	<15	32	6	75	80	49	37	6	38	32	356
Central Channel	535	1993	<15	<8	<1	<1	<1	<2	<2	<1	<1	<1	nd
		1994	<6	<3	<1	<2	<1	<6	<4	<2	<4	<17	nd
R. Tamar - Warren Point	555	1993	27	25	1	18	20	11	9	5	11	13	140
		1994	31	<3	<1	6	4	<6	<4	<2	<4	<17	41
		1994	8	<3	<1	2	2	<6	<4	<2	<4	<17	12
R. Tamar - Hamoaze	565	1993	<15	<8	<1	<1	10	6	4	1	4	5	29
		1994	272	20	<1	27	25	9	10	<2	12	<17	376
		1994	<6	<3	<1	<2	2	<6	<4	<2	<4	<17	2
Off Tamar	575	1994	<6	<3	<1	<2	<1	<6	<4	<2	<4	<17	nd
Off Plymouth Sound	585	1993	<15	<8	<1	<1	<1	<2	<2	<1	<1	<1	nd
		1994	<6	<3	<1	<2	<1	<6	<4	<2	<4	<17	nd
Western Approaches	595	1993	<15	<8	<1	<1	<1	<2	<2	<1	<1	<1	nd
		1994	<6	<3	<1	<2	<1	<6	<4	<2	<4	<17	nd
Celtic Deep	605	1993	<15	<8	<1	<1	<1	<2	<2	<1	<1	<1	nd
		1994	<6	<3	<1	<2	<1	<6	<4	<2	<4	<17	nd
R. Seven - Nash Point	615	1993	<15	17	3	27	25	13	15	7	15	14	138
		1994	6	<3	3	30	18	5	9	6	11	<17	88

(Naph, naphthalene; PA: phenanthrene; Anth, anthracene; Flu, fluoranthene; Pyr, pyrene; BaA, benz[*a*]anthracene; Chrys, chrysene; BeP, benzo[*e*]pyrene; BaP, benzo[*a*]pyrene; BghiP, benzo[*ghi*]perylene. nd, no PAH compound detected; ΣPAH, sum of 10 PAH concentrations. The less than symbol (<) indicates the limit of detection for a particular compound.

### 3.3.2.3 Chlorinated Biphenyls (CBs)

The determination of chlorinated biphenyls (CBs) in seawater is not undertaken within the UK CSEMP as their determination at the very low concentrations 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.

### 3.3.2.4 Metals

Metal concentrations in seawater samples collected from UK CSEMP sites within the SEA8 area are shown in Table 8. Arsenic, cadmium and chromium concentrations at all sites were significantly below the Environmental Quality standard (EQS) of 25, 2.5 and 30 µg/l respectively. Fluctuating copper loads were reported in estuarine and coastal waters during the 1990s with an overall downward trend. Copper concentrations were highest in water samples taken from the Milford Haven (1.47 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 as a result of the phasing out of added 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 SEA8 area were significantly lower than the EQS for this metal in seawater (25 µg/l).

Dissolved mercury concentrations exceeded the EQS of 0.3 µg/l at all CSEMP stations measured, with all median mercury concentrations measured as 10 µg/l. The concentration of nickel in Southampton waters was 3 µg/l. This was significantly less than the EQS of 15 µg/l for this metal.

As described for copper, zinc loads to estuarine and coastal waters have fluctuated during the 1990s with an overall downward trend. Maximum dissolved zinc concentrations were found at Milford Haven (6.06 µg/l), although this concentration did not exceed the EQS of 10 µg/l Zn.

**Table 8. Median metal concentrations measured in seawater samples from UK CSEMP stations in the SEA8 area between 1999 and 2005 (µg/l).**

Station	CSEMP	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Zn
Southampton Water	505	1.05	0.25	0.50	1.30	3.00	2.50	10.00	3.00	4.20
Southampton Water	515	1.20	0.25	0.50	0.89		2.50	10.00	3.00	4.00
Tamar	565		0.25					10.00		
Poole Harbour	566		0.25					10.00		
Milford Haven	646	1.11	0.04	0.29	1.47	3.60	0.08	10.00		6.06

### 3.3.2.5 Alkylphenols

Alkylphenol polyethoxylates (APEOs) are decomposition products from non-ionic surfactants, and are also present in some pesticide formulations, paints and other commercial products. Despite voluntary bans by detergent manufacturers, alkylphenols are still present in sewage effluent discharges. Alkylphenols were also used by 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 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).

**Table 9. Concentration of alkylphenol ethoxylates in seawater samples taken from UK CSEMP stations in the SEA8 area ( $\mu\text{g/l}$ , Cefas, 2001).**

Station	CSEMP Site	Nonylphenol		Ethoxylates		Octylphenol	
		Total	Dissolved	Total	Dissolved	Total	Dissolved
Lyme Bay	537	0.29	0.24	0.46	0.12	0.06	0.10
Lyme Bay	536	0.13	<0.01	0.14	0.46	<0.01	<0.01
Off Plymouth	585	0.19	0.74	0.36	0.43	0.02	0.03
Western Approaches	595	0.27	0.26	0.40	1.30	0.04	0.06
Celtic Deep	605	0.37	0.33	0.48	1.00	0.06	0.10

Maximum allowable concentrations (MACs) for nonylphenol (NP) and octylphenol (OP) were set at  $2.5 \mu\text{g/l}$ . This limit was not exceeded at any of the CSEMP sampling sites within the SEA8 area during the 1999 survey (Table 9).

### 3.3.3 Sediment

The extent to which trace metals and organic contaminants are deposited into sediments is partially dependent on their solubility. Many non-polar, trace organic compounds are not very 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.

#### 3.3.3.1 Polycyclic aromatic hydrocarbons (PAHs)

The mean concentrations of 10 PAH compounds in sediment samples collected from UK CSEMP sites in the SEA8 area during 1999 to 2005 can be seen in Table 10. 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.

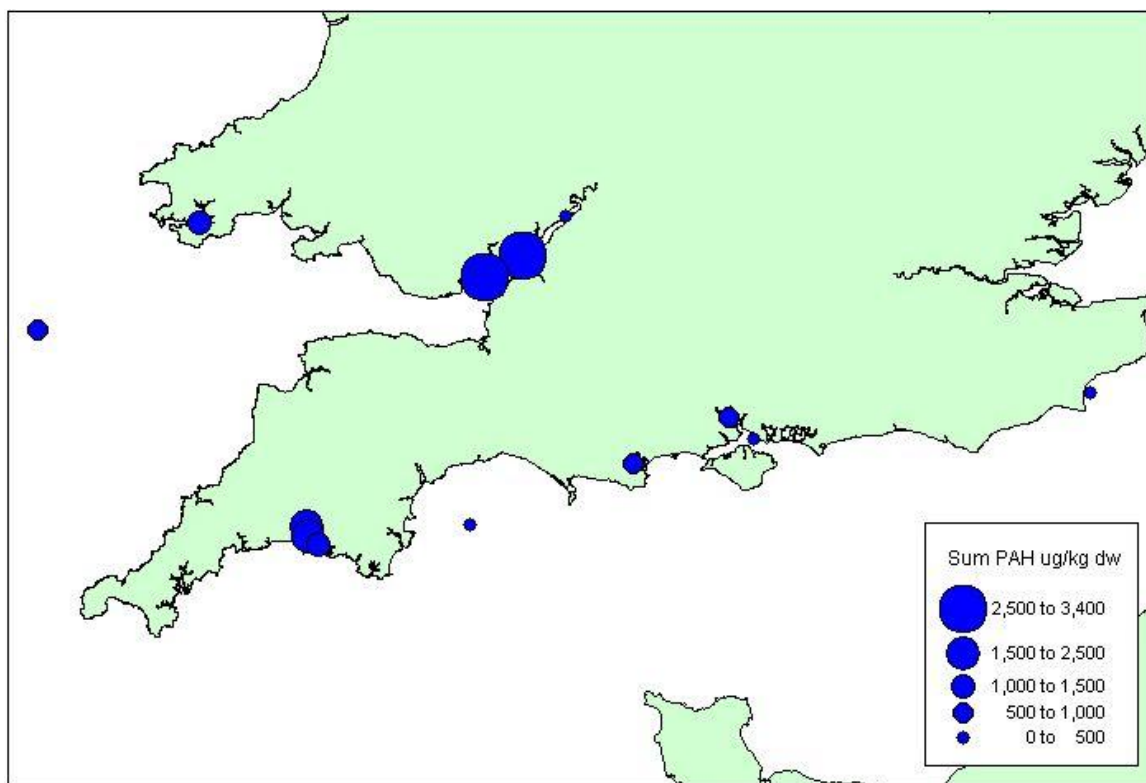
The most common PAH compounds detected in the sediment samples from the SEA8 were fluoranthene, pyrene, chrysene + triphenylene and benzo[*a*]pyrene. These four PAHs made up approximately 60% of the total PAH concentration.

**Table 10. Mean concentration of 10 PAHs in sediment samples collected during 1999-2005 from UK CSEMP stations in the SEA8 area ( $\mu\text{g}/\text{kg}$  dry weight).**

Station	CSEMP NO.	Naph	PA	Anth	Flu	Pyr	BaA	Chr+Tri	BaP	BghiP	Icdp	Sum PAHs
Dungeness	484	9.2	29.8	5.1	69.6	51.8	28.8	39.2	35.8	28.6	32.6	331
Southampton Water	505	77.0	36.8	16.4	92.5	125.8	46.8	62.1	67.8	64.9	85.2	675
Southampton Water	515	28.6	23.7	10.0	33.7	30.6	15.1	13.6	13.3	10.6		179
Lyme Bay	536	1.3	3.8	2.2	12.8	9.8	6.2	7.3	5.3	4.4	6.1	59
Tamar	555		88.6	32.0	249.8	296.2	171.2	200.2	239.0	171.6	181.8	1,630
Tamar (Hamoaze)	565		97.7	35.1	264.0	268.0	155.2	191.2	219.2	162.4	155.6	1,548
Poole Harbour	566		31.0	10.0	58.7	48.2	30.6	38.1	31.2	31.2	32.5	312
Poole Harbour	567		42.7	10.0	97.9	88.7	52.4	65.9	56.4	51.9	49.3	515
Off Tamar	576		98.6	38.1	208.8	217.6	131.8	150.4	186.0	129.0	123.8	1,284
Celtic Deep	605	26.4	78.6	23.4	145.8	94.0	57.0	82.4	53.8	56.0	52.0	669
Severn (Purton)	625	24.8	29.2	10.7	28.8	25.0	14.6	18.2	11.9	10.9	10.8	185
Severn (Bedwin)	635	417.6	390.0	100.1	417.9	316.0	207.8	687.5	224.3	218.0	321.6	3,301
Severn (Peterstone)	645	428.4	414.5	107.3	456.1	348.9	230.9	308.7	257.3	239.4	396.4	3,188
Milford Haven	646	230.4	137.6	37.2	219.3	190.1	113.6	166.4	130.5	122.4	142.4	1,490

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

The distributions of total PAHs in sediment samples of the SEA8 are illustrated in Figure 3. The highest concentrations of PAHs were found at the two stations at the mouth of the River Severn (CSEMP 635, 645), where the sum of 10 PAHs was 3,301 and 3,188  $\mu\text{g}/\text{kg}$  (d.w.) respectively. These elevated concentrations of PAHs are typical of inshore industrial areas. Overall, lower concentrations of PAHs were found at CSEMP stations further offshore. The greater contribution to PAH load was derived from petroleum rather than a pyrogenic source.



**Figure 3. Concentrations of total PAHs in sediment samples taken from CSEMP stations in the SEA 8 area ( $\mu\text{g}/\text{kg}$  dry weight).**

### 3.3.3.2 Chlorinated biphenyls (CBs)

The mean concentrations of the ICES 7 chlorinated biphenyls (CBs) in sediment samples collected from UK CSEMP sites in the SEA8 area during 1999 to 2005 can be seen in Table 11. Total CB concentrations ranged from 0.94 to 32.59  $\mu\text{g}/\text{kg}$  (d.w.), with highest and lowest concentrations found at CSEMP stations near the mouth of the River Severn. The distribution of the Sum of ICES 7 CBs in the SEA8 area can be seen in figure 4.

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 CBs in sediments:

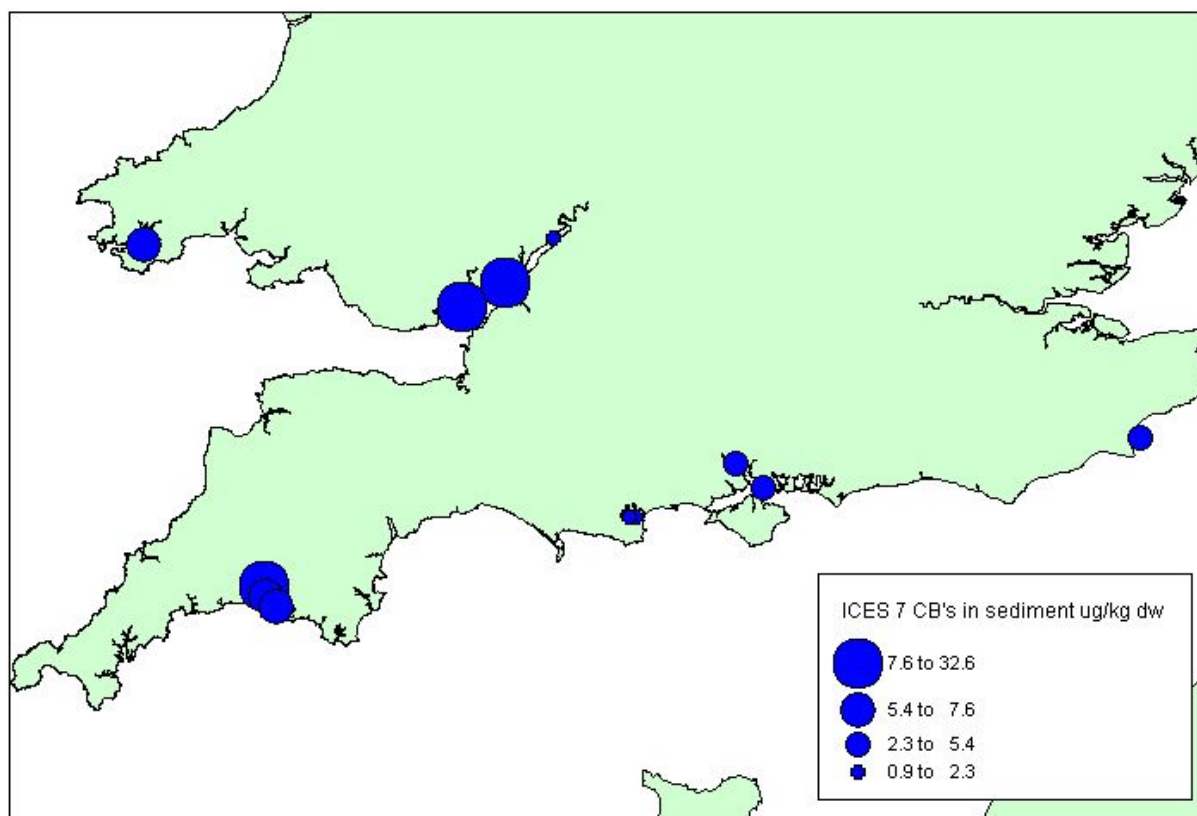
- <0.2  $\mu\text{g}/\text{kg}$  contamination not detectable
- 0.20 to 20  $\mu\text{g}/\text{kg}$  slightly contaminated
- 21 to 100  $\mu\text{g}/\text{kg}$  contaminated
- >100  $\mu\text{g}/\text{kg}$  heavily contaminated

Using this guideline, the two Severn stations (CSEMP 635, 645) would be classed as contaminated. All of the other sediment stations would be classified as slightly contaminated.



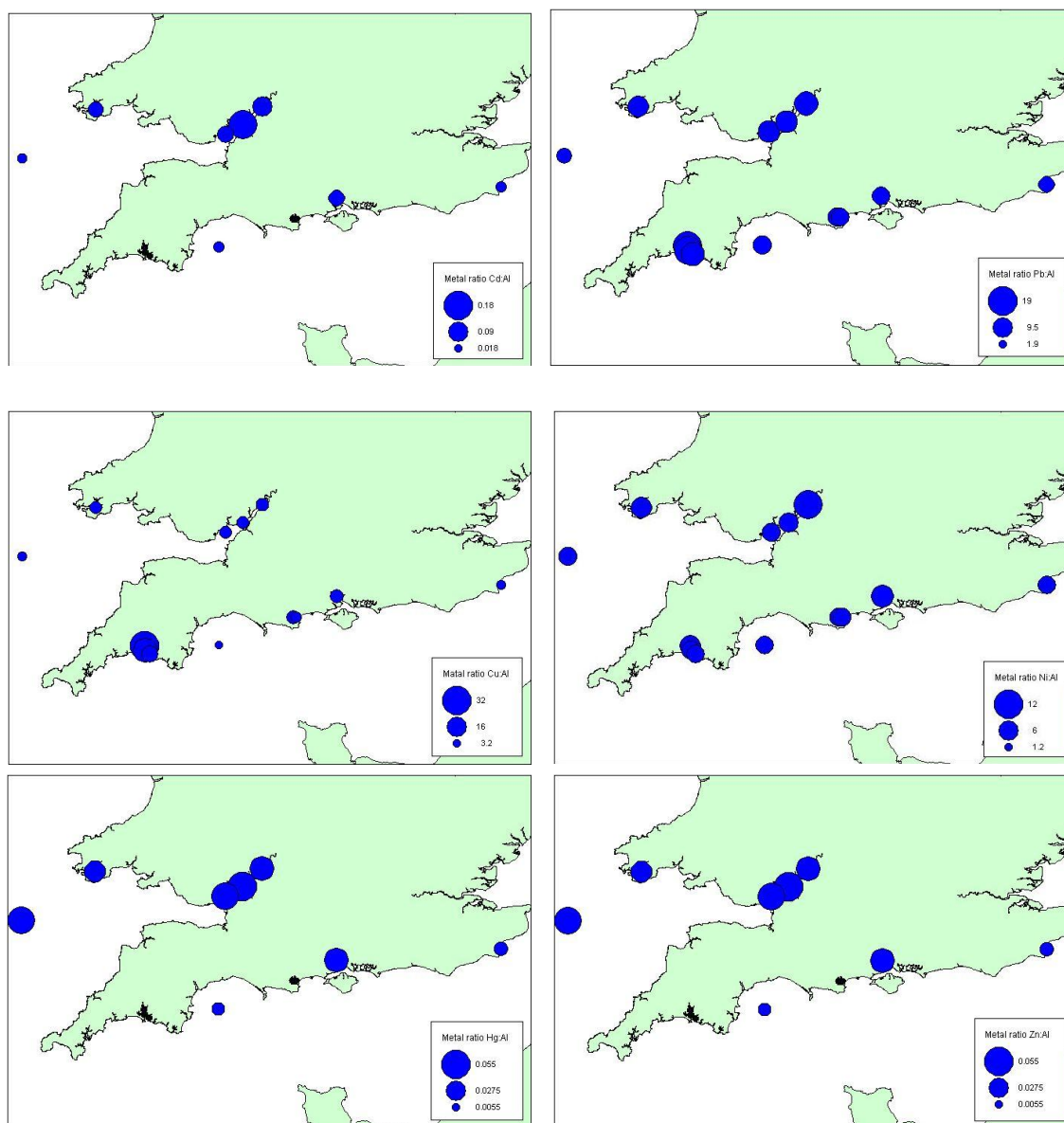
**Table 11. Mean concentration of chlorinated biphenyls (CBs) in sediment samples collected during 1999-2005 from UK CSEMP stations in the SEA8 area ( $\mu\text{g}/\text{kg}$  dry weight).**

Station	CSEMP No.	CB28	CB52	CB101	CB118	CB138	CB153	CB180	SUM ICES7
Dungeness	484	0.33	0.22	0.72	0.84	1.04	1.15	0.84	5.15
Southampton Water	505	0.33	0.22	0.72	0.84	1.04	1.15	0.84	5.15
Southampton Water	515	0.10	0.16	0.24	0.17	0.46	0.65	0.54	2.32
Tamar (Warren Point)	555	0.26	0.52	0.80	1.37	1.89	2.19	0.59	7.60
Tamar (Hamoaze)	565	0.31	0.53	0.93	1.58	1.77	1.70	0.70	7.52
Poole Harbour (Upper south)	566	0.10	0.32	0.11	0.22	0.26	0.27	0.12	1.41
Poole Harbour (Wytch)	567	0.10	0.36	0.15	0.34	0.37	0.38	0.13	1.83
Off Tamar	576	0.17	0.36	0.67	1.14	1.28	1.27	0.55	5.44
Severn (Purton)	625	0.18	0.11	0.10	0.10	0.18	0.14	0.13	0.94
Severn (Bedwin)	635	7.94	2.94	2.49	3.69	5.65	5.18	4.69	32.59
Severn (Peterstone)	645	7.40	2.64	2.40	3.60	5.20	5.29	5.10	31.62
Milford Haven	646	1.30	0.93	0.62	1.13	1.06	1.00	0.58	6.61



**Figure 4. Concentrations of ICES 7 CB congeners in sediment samples taken from UK CSEMP stations within the SEA8 area. ICES 7: the seven congeners of the ICES primary list ( $\mu\text{g}/\text{kg}$  dry weight).**

### 3.3.3.3 Metals



**Figure 5. Metal distributions in the SEA8. Metal concentrations are normalised to aluminium concentrations in each sample in order to compensate for the granulometric and mineralogical differences (UK CSEMP 1999-2005).**

To compensate for the effects of granulometric and mineralogical differences, and to identify areas of the anthropogenic inputs, the metal data collected between 1999 and 2005 was normalised with respect to aluminum (Figure 5).

Copper: Aluminum ratios were highest in sediments taken from the mouth of the Tamar. Historical mining activity in this area as well as high levels of boating activity may have contributed to this elevated Cu: Al ratio. Elevated Pb: Al ratios were also found at the Tamar CSEMP stations. For all other metals (i.e. Ni, Cd, Hg and Zn), highest Al ratios were found at the CSEMP stations at the mouth of the River Severn. These elevated metal concentrations are likely to derive from increased land run-off with proximity to industrialised areas.

Selected metal concentrations in sediments collected from sites within the Severn estuary and Bristol Channel were recently reported (Duquesne et al., 2006). Metal concentrations (in mg/kg dw) ranged as follows for Cd (0.1-1.4), Cr (10-90), Cu (1-47), Ni (4-45), Pb (5-92) and Zn (20-340). Comparisons between these results and those previously reported (Butterworth et al., 1972; Chester & Stoner, 1975) showed a significant decline in metal sediment concentrations over the last 30 years. The apparent decline in metal sediment concentrations within this area was attributed, by the authors, to be a result of a reduced industrial activity as well as improvements in the environmental control on emissions.

### 3.3.3.4 Alkylphenol ethoxylates

At all CSEMP stations in the SEA8 area, concentrations of nonylphenol and ethoxylates were below the limit of detection (<0.19 and <0.01 µg/g respectively, Table 12). Octylphenols were detected at very low concentrations at four of the six stations, with a maximum concentration of 0.03 µg/g.

**Table 12. Concentration of alkylphenol ethoxylates in sediment samples taken from UK CSEMP stations in the SEA8 area (µg/g, Cefas, 2001).**

Station	CSEMP No.	Nonylphenol	Ethoxylates	Octylphenol
South Varne	485	<0.19	<0.01	0.01
Rye Bay	486	<0.19	<0.01	<0.01
Selsey Bill	495	<0.19	<0.01	0.01
Lyme Bay	536	<0.19	<0.01	<0.01
Off Plymouth	585	<0.19	<0.01	0.02
Celtic Deep	605	<0.19	<0.01	0.03

### 3.3.4 Biota

Due to the lipophilic properties of many non-polar 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 CSEMP.

#### 3.3.4.1 Total Hydrocarbons (THC)

No specific data are available for the SEA8 area. Data for the North Sea shows elevated concentrations of aromatic hydrocarbons in Dab exposed to oil-based drill cuttings (Stagg, 1994). However, the absence of offshore oil platforms in the SEA8 area minimises exposure to hydrocarbons except in near shore areas associated with harbours and ports.

#### 3.3.4.2 Polycyclic aromatic hydrocarbons (PAHs)

Physical and chemical characteristics such as solubility and reduction potential of PAHs varies with molecular weight. As a result, PAHs differ in their behaviour,

distribution in the environment, and their effects on biological systems. The lower molecular weight PAHs (e.g. 2 to 3 rings such as naphthalene, fluorene, phenanthrene, and anthracene) have significant acute toxicity to aquatic organisms, whereas the high molecular weight PAHs ( $\geq 202$ , 4 to 7 rings from chrysenes to coronenes), although not acutely toxic, are known to exhibit carcinogenic effects.

Median concentrations of 10 PAH compounds measured in the tissues of mussels, *Mytilus edulis* are shown in Table 13. Overall, naphthalene and fluoranthene were the most abundant PAH compounds in the tissues of the mussels. Total PAH concentrations ranged from 68.80 to 407.12  $\mu\text{g}/\text{kg}$  ww, with highest PAH concentrations found in the tissues of mussels collected at the mouth of the Severn (Peterstone, CSEMP 645). This coincides with the maximum PAH concentrations in sediment samples taken from the mouth of the Severn (Table 10).

**Table 13. Mean PAH concentrations in mussels collected from UK CSEMP stations in the SEA8 area during 1999-2005 ( $\mu\text{g}/\text{kg}$  wet weight).**

Station	CSEMP NO.	Naph	PA	Anth	Flu	Pyr	BaA	Chr+Tri	BaP	BghiP	Icdp	Sum PAHs
Tamar (Warren Point)	555	85.29	13.91	2.64	16.95	25.29	18.07	19.34	9.54	5.93	6.31	203.25
Tamar (Hamoaze)	565	12	13.1	1.9	8	10.7	6.4	9.4	2.8	3	1.5	68.8
Poole Harbour (Wytch)	567	50.65	8.1	1.34	14.72	14.23	4.56	10.42	0.98	2.07	1.26	108.34
Off Tamar Severn	576	26.5	15.3	1.9	8.9	9	6.2	9.4	2.8	2.3	1.7	84
(Peterstone)	645	36.3	23.76	16.33	82.51	58.21	50.96	52.37	35.74	17.38	33.58	407.12

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

In addition to the CSEMP data, Widdows et al., (2002) reported high concentrations of 2- and 3-ring PAHs in mussels collected from Milford Haven (22.5  $\mu\text{g}/\text{g}$  dw), 6 months after the Sea Empress oil spill (Feb 1996). Repeated sampling the following year found a reduction in the PAH concentration of mussels from Milford Haven (7.87  $\mu\text{g}/\text{g}$  dw), approximately 33% of values recorded the previous year.

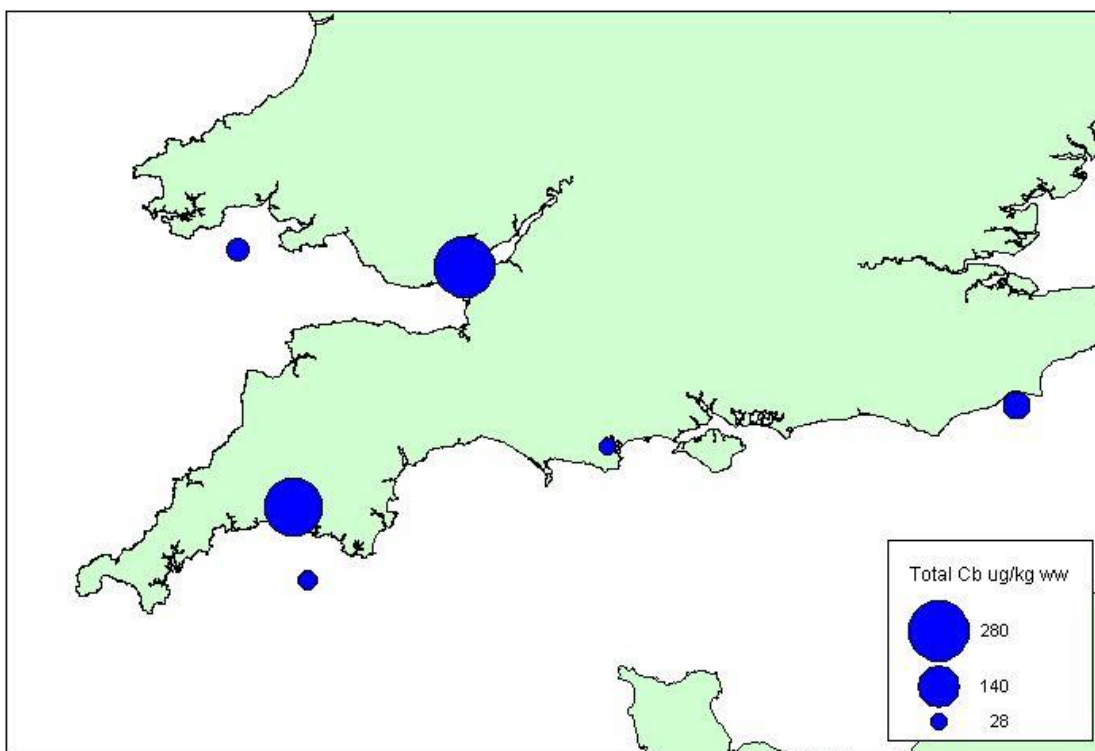
### 3.3.4.3 Chlorinated Biphenyls (CBs)

The mean concentration of the ICES 7 CB congeners (28, 52, 101, 118, 138, 153 and 180) in mussels collected from inshore areas of the SEA8 area ranged from 3.0 to 10.2  $\mu\text{g}/\text{kg}$  ww, with maximum concentrations reported in mussels from the Severn (Peterstone, Table 14). This corresponds to maximum CB concentrations reported in the sediments of the Severn (Table 7, Figure 4). The CB congeners 138 and 153 were the most abundant, contributing between 58 and 77% of the overall Sum of ICES 7 CBs for all stations.

The mean concentrations of the sum of ICES 7 CBs in the liver of dab, *Limanda limanda* collected at UK CSEMP stations in the SEA8 are illustrated in Figure 6. Total CB concentrations ranged from 30.13 to 277.97  $\mu\text{g}/\text{kg}$  (ww), with highest concentrations found at the mouth of the River Severn. Slightly elevated concentrations of total CBs were also found in the fish livers collected from the Tamar (278  $\mu\text{g}/\text{kg}$  ww).

**Table 14. Mean concentrations of CBs in mussels collected from UK CSEMP stations in the SEA 8 area during 1999-2005 ( $\mu\text{g}/\text{kg}$  wet weight).**

Station	CSEMP No.	CB28	CB52	CB101	CB118	CB138	CB153	CB180	Sum ICES 7
Tamar (Warren Point)	555	0.11	0.25	1.23	1.69	2.19	2.93	0.15	8.5
Tamar (Hamoaze)	565	0.25	0.42	1.28	1.85	2.36	3.17	0.16	9.5
Poole Harbour (Wytch)	567	0.11	0.18	0.39	0.49	0.67	1.08	0.13	3.0
Off Tamar	576	0.13	0.20	1.04	1.57	2.35	3.23	0.19	8.7
Severn (Peterstone)	645	0.10	0.28	0.69	0.59	3.13	4.76	0.65	10.2



**Figure 6. Concentrations of ICES 7 CB congeners in fish liver collected at UK CSEMP stations in the SEA8 area ( $\mu\text{g}/\text{kg}$  wet weight) (1999-2005).**

Concentrations of CB in blubber samples from marine mammal strandings, principally the common porpoise, (*Phocoena phocoena*) on the coast of the SEA8 between 1996 and 2005 are presented in Table 15. The sum of 25 CB concentrations ranged between 2.31 to 48.38 mg/kg ww (equivalent to an approximate range of concentrations of 4.6 to 96 mg/kg ww as the Aroclor 1254 product). The sum of ICES 7 congeners accounted for between 60 and 70% of the total 25CB concentrations in all analyses.

The limited data available for the Bottlenose dolphin (*Tursiops truncatus*) and the Sowerby's beaked whale (*Mesoplodon bidens*) prevent any interspecies comparisons being made. Overall, the concentration of CBs found in the blubber of stranded mammals were markedly greater than those found in other matrices (i.e. water and sediment) and other biota. This is expected due to the lipophilic properties of CBs 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 SEA8 in general.

**Table 15. Concentrations of CBs measured in blubber of the common porpoise, (*Phocoena phocoena*) from UK strandings in the SEA 8 area (mg/kg wet weight).**

Species	Year	Location	SICES7	S25CBs
Common porpoise <i>Phocoena phocoena</i>	1996	Falmouth, Cornwall	30.78	46.55
	2000	Woolacombe Sands, Devon	4.77	7.25
	2001	Kingsbridge estuary, Devon	5.58	9.02
	2001	Crow Point, Devon	1.47	2.31
	2001	Westcombe Beach, Devon	31.83	48.38
	2001	Puttsborough, Devon	2.99	4.8
	2001	South Milton Sands, Devon	2.88	4.74
	2001	Sandwich Bay, Kent	8.08	12.44
	2001	Freshwater East, Pembrokeshire	28.76	43.09
	2001	Swansea Beach, Swansea	6.595	10.96
	2001	Pembrey, Carmarthenshire	2.21	3.382
	2002	Swansea Beach, Swansea	3.738	6.178
	2003	Pembrey, Carmarthenshire	8.727	13.91
	2004	Clevedon Bay, Somerset	18.9	28.68
	2004	Eastbourne, East Sussex	2.5	3.828
	2004	Rye Harbour, East Sussex	2.08	3.432
	2004	Swansea Beach, Swansea	15.54	25.33
	2004	Watchet, Somerset	3.345	5.101
	2004	East Prawle, Devon	8.428	13.33
Bottlenose dolphin <i>Tursiops truncatus</i>	2004	Gwithian, Cornwall	22.60	35.52
	2005	Penzance Harbour, Cornwall	91.70	138.43
Sowerby's beaked whale <i>Mesoplodon bidens</i>	2002	Praa Sands, Cornwall	1.498	2.097

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

### 3.3.4.4 Metals

Mean concentrations of metals in mussels from inshore sites of the SEA8 were analysed in samples collected between 1999 and 2005 (Table 16). Arsenic concentrations ranged from 1688 to 2622 µg/kg ww, with highest concentrations found at the mouth of the River Severn. Cadmium and chromium concentrations were also found to be highest at the Severn site (1684 µg/kg Cd ww; 1108 µg/kg Cr ww). Copper concentrations ranged from 1232 to 12810, with maximum concentrations at the Southampton water site. This maybe related to the high level of boating activity within this area.

**Table 16. Mean concentrations of metals measured in mussels (*Mytilus sp.*) collected between 1999-2005 from UK CSEMP stations in the SEA8 area (µg/kg wet weight).**

Station	CSEMP No.	As	Cd	Cr	Cu	Pb	Hg	Zn
Southampton Water	505	2481	143	215	12810	656	19	13354
Tamar (Warren Point)	555	1688	247	264	2321	1892	15	38458
Tamar (Hamoaze)	565	2500	256	500	2890	4440	38	75100
Poole Harbour (Wytch)	567	1709	112	193	1232	2132	16	16473
Off Tamar	576	2520	156	540	2580	3740	55	53700
Severn (Peterstone)	645	2622	1684	1108	1546	1073	52	20280

Lead concentrations ranged from 656 to 4440  $\mu\text{g}/\text{kg}$  ww with highest concentrations found in mussels from the Tamar (Hamoaze). Similarly, highest concentrations of zinc were found at this Tamar site (75  $\text{mg}/\text{kg}$  ww). Mercury concentrations ranged from 15 to 55  $\mu\text{g}/\text{kg}$  ww with highest concentrations in mussels from Off Tamar.

Arsenic concentrations in fish muscle collected from the SEA8 ranged from 0.9 to 8.1  $\text{mg}/\text{kg}$  ww, with maximum concentrations found in fish collected from the mouth of the River Severn (Figure 7). Mercury concentrations in fish muscle ranged from 46 to 107  $\mu\text{g}/\text{kg}$  ww, with highest Hg concentrations found in fish collected from the mouth of the River Severn.

Lead and cadmium concentrations in fish livers showed a similar pattern to that observed for mercury and arsenic with highest concentrations found in fish collected from the mouth of the River Severn. Lead and cadmium concentrations ranged from 30 to 245 and 34 to 312  $\mu\text{g}/\text{kg}$  ww respectively.



**Figure 7. The mean concentrations of metals measured in fish muscle/ liver collected during 1999-2005 from UK CSEMP stations in the SEA8 area ( $\mu\text{g}/\text{kg}$  ww).**

In addition, metal concentrations have been reported in five shark species collected from the Celtic sea during 2000 (Domi et al., 2005). Kidney and muscle samples were analysed for metals with highest concentrations found in kidney samples (Zn - 46-62  $\text{mg}/\text{kg}$  dw, Cd - 0.16-1.4  $\text{mg}/\text{kg}$  dw, Fe - 167-302  $\text{mg}/\text{kg}$  dw, Cu - 5.6-6.3  $\text{mg}/\text{kg}$  dw, Se - 4.5-33  $\text{mg}/\text{kg}$  dw). These concentrations were higher than those reported in the dab samples, which is likely to be due to increased bioaccumulation in the shark which is a higher predator species.

Metal concentrations of metals measured in blubber samples of three marine mammal species collected from UK strandings in the SEA8 area during 1996-2005 have been determined (Table 17). The most abundant metal in the blubber of mammalian strandings was Fe with concentrations ranging from 77 to 766 mg/kg ww, followed by Zn (25-97 mg/kg ww) and Cu (2.5-81 mg/kg ww). Metal concentrations were ranked Fe > Zn > Cu > Hg > Se > Mn > Ni > Cr > Ag > As > Cd > Pb, with concentrations of Ni, Cr, Ag, As, Cd and Pb either low or undetected in the blubber samples. Concentrations of copper and zinc are homeostatically controlled in marine mammals (and other animals) and fall within a relatively narrow range, suggested to be 3 – 30 mg/kg ww for copper and 20 to 100 mg/kg ww for zinc in adults (Law, 1996).

**Table 17. Concentrations of metals measured in blubber samples of three marine mammal species collected from UK strandings in the SEA8 area during 1996-2005 (mg/kg ww).**

Species	Year	Location	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Ag	Cd	Hg	Pb	Hg:Se
Common porpoise <i>Phocoena phocoena</i>	1996	Falmouth, Cornwall	0.06	3.7	222	< 0.04	4.8	25	0.5	9.8	0.9	0.29	23	0.05	0.92
	2000	Woolacombe Sands, Devon	< 0.04	3.7	281	< 0.04	2.5	97	0.4	4.9	0.7	0.09	18	< 0.02	1.45
		Kingsbridge estuary, Devon	0.09	4.4	409	0.04	9.9	44	0.4	1.1	0.4	< 0.02	0.7	< 0.01	0.26
	2001	Crow Point, Devon	< 0.05	4.5	120	< 0.05	6.4	42	1.1	25	1.4	0.3	80	0.04	1.26
	2001	Westcombe Beach, Devon	0.05	7.4	221	< 0.04	3.4	85	0.2	1.9	0.4	0.04	3.6	< 0.02	0.75
		Puttsborough, Devon	0.06	4.9	199	< 0.04	7.6	76	0.2	0.7	0.5	< 0.02	1	< 0.02	0.57
	2001	South Milton Sands, Devon	0.1	3.6	77	0.04	5.5	42	0.7	11	2.5	0.25	17	0.02	0.61
		Sandwich Bay, Kent	0.08	5.6	336	< 0.05	5.9	55	0.2	1.6	1	0.03	1.9	< 0.02	0.47
	2001	Freshwater East, Pembrokeshire	0.17	6	286	0.11	5.7	73	0.2	4.1	0.6	0.18	14	< 0.02	1.34
		Swansea Beach, Swansea	< 0.1	5.0	145	< 0.1	8.4	34	0.8	1.8	0.8	< 0.06	1.5	< 0.04	0.33
	2001	Pembrey, Carmarthenshire	< 0.09	3.0	115	0.1	81	54	0.3	3.0	0.8	< 0.05	2.3	< 0.04	0.30
		Swansea Beach, Swansea	6.2	6.4	124	7.7	34	35	0.6	1.0	0.7	< 0.05	1	< 0.03	0.38
	2003	Pembrey, Carmarthenshire	< 0.07	6.1	277	< 0.07	10	39	0.3	3.5	0.5	0.08	4.4	< 0.03	0.49
		Clevedon Bay, Somerset	< 0.08	5.5	100	< 0.08	7.3	71	0.5	33	0.4	0.45	67	< 0.03	0.80
	2004	Eastbourne, East Sussex	< 0.08	6.5	484	< 0.08	14	40	0.1	1.8	0.4	0.06	1.3	< 0.03	0.28
		Rye Harbour, East Sussex	< 0.09	6.5	472	< 0.09	13	35	0.5	2.9	0.7	0.05	1.0	< 0.04	0.14
2004	Swansea Beach, Swansea	< 0.08	6.8	594	< 0.08	13	32	0.4	6.1	0.4	0.04	3.4	0.06	0.22	
	Watchet, Somerset	< 0.06	7.8	766	< 0.06	29	88	0.3	1	0.3	< 0.02	0.6	0.03	0.24	
2004	East Prawle, Devon	< 0.06	5.9	104	< 0.06	8.9	43	0.5	4.4	0.3	0.08	7.7	0.03	0.69	
Bottlenose dolphin <i>Tursiops truncatus</i>	2004	Gwithian, Cornwall	< 0.08	4.5	674	0.14	9.8	83	0.5	8.9	0.5	0.21	17	< 0.03	0.75
	2005	Penzance Harbour, Cornwall	< 0.07	2	474	< 0.07	3.5	53	0.3	33	0.3	0.39	86	0.03	1.03
Sowerby's beaked whale <i>Mesoplodon bidens</i>	2002	Praa Sands, Cornwall	0.41	4.0	259	0.15	9.6	39	0.5	3.8	0.3	2.9	6.9	< 0.03	0.71



Due to the limited number of *T. truncates* and *M. bidens* strandings, interspecies comparisons cannot be made. However, the metal concentrations in the mammalian samples were markedly greater than that found in other matrices (i.e. water and sediment). In addition, due to bioaccumulation processes, the metal concentrations were higher than those reported in fish and mussel tissues described above.

### 3.3.4.5 Butyl tin (BT)

On the UK mainland coast, the sum of Butyl tins ( $\Sigma$ BT) in mussels have been reported to range from 'undetected' to 0.49  $\mu\text{g}/\text{kg dw}$ , with highest values occurring in mussels from Milford Haven (Widdows et al., 2002.) The elevated  $\Sigma$ BT concentrations in Milford Haven were suggested to be due to the oil activities and commercial vessels in the local area.

Concentrations of tributyltin (TBT) dibutyltin (DBT) and monobutyltin (MBT) have been reported in the blubber of stranded marine mammals (Table 18). The sum of these three compounds ranged from 38 to 797  $\mu\text{g}/\text{kg ww}$ . DBT was the most abundant BT making up between 58 to 100% 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 18. Concentrations of butyl tins measured in blubber samples of three marine mammal species collected from UK strandings in the SEA8 area during 1996-2005 ( $\mu\text{g}/\text{kg ww}$ ).**

Species	Year	Location	TBT	DBT	MBT	SumBT	DBT/SumBT
Common porpoise <i>Phocoena phocoena</i>	1996	Falmouth, Cornwall	36	147	10	193	0.76
	2000	Woolacombe Sands, Devon	8	22	8	38	0.58
	2001	Kingsbridge estuary, Devon	29	65	6	100	0.65
	2001	Crow Point, Devon	22	67	11	100	0.67
	2001	Westcombe Beach, Devon	43	155	18	216	0.72
	2001	Puttsborough, Devon	16	44	6	66	0.67
	2001	South Milton Sands, Devon	121	193	21	335	0.58
	2001	Sandwich Bay, Kent	106	630	61	797	0.79
	2001	Freshwater East, Pembrokeshire	33	242	12	287	0.84
	2001	Swansea Beach, Swansea	32	73	<5	105	0.70
	2001	Pembrey, Carmarthenshire	23	36	<5	59	0.61
	2002	Swansea Beach, Swansea	20	119	<5	139	0.86
	2003	Pembrey, Carmarthenshire	16	84	10	110	0.76
	2004	Clevedon Bay, Somerset	30	112	24	166	0.67
	2004	Eastbourne, East Sussex	35	94	10	139	0.68
	2004	Rye Harbour, East Sussex	37	63	<3	100	0.63
	2004	Swansea Beach, Swansea	20	84	17	121	0.69
	2004	Watchet, Somerset	<4	17	<3	17	1.00
	2004	East Prawle, Devon	16	51	<3	67	0.76
Bottlenose dolphin <i>Tursiops truncatus</i>	2004	Gwithian, Cornwall	< 5	46	12	58	0.79
	2005	Penzance Harbour, Cornwall	< 5	92	30	122	0.75
Sowerby's beaked whale <i>Mesoplodon bidens</i>	2002	Praa Sands, Cornwall	36	89	36	161	0.55

### 3.3.4.6 Organochlorines

Concentrations of Dichlorodiphenyltrichloroethane (DDT) and its main metabolite dichlorodiethylene (DDE) have been reported in the blubber of three stranded marine mammal species (Table 19). The sum of DDT concentrations ranged from 0.15 to 33.51 µg/kg ww. The proportion of the main metabolite DDE with respect to the sum of DDT ranged between 46-95%. The highest sum of DDT concentrations were found in the two *T. truncatus* samples. However, the limited number of stranded animals of this species prevents any firm inter-comparisons to be made. The high values of the ratio of the DDT breakdown product DDE to total DDT indicates historic rather than recent inputs.

**Table 19. Concentrations of organochlorines measured in blubber samples of three marine mammal species collected from UK strandings located in the SEA8 area during 1996-2005 (µg/kg ww).**

Species	Year	Location	%HEL	SumDDT	DDE/SumDDT
Common porpoise <i>Phocoena phocoena</i>	1996	Falmouth, Cornwall	94	3.87	0.52
	2000	Woolacombe Sands, Devon	88	2.20	0.59
	2001	Kingsbridge estuary, Devon	86	0.56	0.77
	2001	Crow Point, Devon	87	0.15	0.66
	2001	Westcombe Beach, Devon	90	2.03	0.54
	2001	Puttsborough, Devon	95	0.43	0.56
	2001	South Milton Sands, Devon	92	0.38	0.47
	2001	Sandwich Bay, Kent	90	1.81	0.77
	2001	Freshwater East, Pembrokeshire	75	2.24	0.63
	2001	Swansea Beach, Swansea	93	1.30	0.56
	2001	Pembrey, Carmarthenshire	76	3.73	0.46
	2002	Swansea Beach, Swansea	95	1.79	0.73
	2003	Pembrey, Carmarthenshire	94	1.50	0.73
	2004	Clevedon Bay, Somerset	89	2.05	0.63
	2004	Eastbourne, East Sussex	92	0.78	0.68
	2004	Rye Harbour, East Sussex	93	1.50	0.73
	2004	Swansea Beach, Swansea	88	1.09	0.57
2004	Watchet, Somerset	76	0.42	0.54	
2004	East Prawle, Devon	88	0.59	0.61	
Bottlenose dolphin <i>Tursiops truncatus</i>	2004	Gwithian, Cornwall	78	6.13	0.77
	2005	Penzance Harbour, Cornwall	31	33.51	0.95
Sowerby's beaked whale <i>Mesoplodon bidens</i>	2002	Praa Sands, Cornwall	81	1.72	0.64

### 3.3.5 Other compounds

#### 3.3.5.1 Antifouling paint booster biocides

Booster biocides are compounds that are added to antifouling paints to enhance their performance in preventing the colonisation of boat hulls by algae and seaweeds. The concentrations of eight organic booster biocides were measured in Southampton waters, Plymouth Sound and offshore sites during 1998. The eight booster biocides were: Irgarol 1051; diuron; zinc pyrithione (ZPT); dichlofluanid; thiocyanomethylthiobenzothiazole (TCMTB); tetrachloromethylsulfonol (TCMS) pyridine; Kathon 5287 and zineb. Of these eight, only two booster biocides (Irgarol and diuron) were present at detectable concentrations these are listed in Table 20.

The highest concentrations of irgarol and diuron were found in the Hythe Marina (208 and 632 ng/L respectively). As might be expected elevated concentrations of irgarol and diuron were found in inland water samples collected close to marinas and harbours with high boating activity and low water exchange. Lowest concentrations were found in offshore samples with low or undetected concentrations. Diuron concentrations were found at markedly higher concentrations than Irgarol in all seawater samples collected.

**Table 20. Concentrations of two booster biocides, Irgarol and Diuron from inshore and offshore seawater samples collected during 1998 from the SEA8 area (ng/L).**

Sample Station	Location	Irgarol 1051	Diuron	Sample Station	Location	Irgarol 1051	Diuron
Southampton waters	Beaulieu - Penerley Farm	<1	<1	Sutton Harbour, Plymouth	Melampus	1	8
	Beaulieu - Buckers Hard	22	106		Mallard Beacon	1	8
	Beaulieu - Exbury River	9	32		Sutton Harbour Berth 1	16	137
	Calshot	4	9		Sutton Harbour Berth 2	14	115
	Hythe Marina	208	632		Queen Ann's Battery	3	26
	Cracknore Hard	4	25		Sutton Harbour by Lock	16	93
	Fawley refinery	4	24		Offshore	Celtic Deep	<1
	Upper docks	3	21	Western Approaches		<1	<1
	Lower docks	5	21	Off Plymouth		<1	1
	Ocean village (marina)	13	82	Lyme Bay		<1	<1
	Itchen mouth	8	32	Solent 1		<1	3
	Netley Abbey Castle	6	30	Solent 2		1	7
	Hamble - Port Hamble Marina	27	150	Solent 3		1	9
	Hamble - Mercury Yacht Harbour	33	162	Solent 4 (Calshot)		2	11
	Hamble - Swanwick Marina	39	117	Solent 5 (Hamble mouth)		6	29
	Hamble mouth	13	52	Solent 6		1	8
	Outer water	2	14	Solent 7		1	4
	Hill head	3	13	Rye Bay		<1	1
	Upper Hamble	31	101	South Varne		<1	<1

Sediment concentrations of booster biocides determined in marine sediments collected from Southampton waters were low (Table 21). Irgarol was detected at concentrations between 0.3 and 3.5 µg/ kg and diuron between 0.4 and 6.2 µg/ kg. These concentrations were within the ranges previously reported (Thomas et al., 2002).

**Table 21. Concentrations of selected booster biocides in sediment samples collected from Southampton waters during 1999.**

Location	Irgarol 1051 (µg/L)	Diuron (µg/L)
Fawley Refinery	0.4	0.4
Cracknore Hard	0.6	1.4
Power Station	0.3	0.8
Docks (upper)	0.3	0.7
Docks (Lower)	0.4	0.9
Ocean Village (Marina)	0.6	1.4
Hamble - Swanick Marina	1.1	2.3
Hamble - Mercury Yacht Harbour	1.2	1.7
Hamble - Port Hamble Marina	0.4	1.3
Hythe Marina	3.5	6.2

### 3.3.6 Summary

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 were often low or below levels of detection. Of those contaminants that were measured, highest concentrations were generally found in seawater samples collected from estuarine and coastal sites that were more influenced by industrial inputs such as the Severn estuary. Environmental quality standards (EQS) for all metals were not exceeded at any of the CSEMP sites within the SEA8. In contrast, many of the PAH concentrations in the seawater were found to exceed their maximum allowable concentrations (MACs) at Southampton, Tamar and Severn CSEMP stations. PAHs were not detected in the seawater from offshore stations. Alkylphenols were often low or undetectable in the water samples and did not exceed their MACs at any of the CSEMP sampling stations within the SEA8 area.

Sediment concentrations of PAHs and CBs were higher in inshore areas where there was either riverine input and/or industrial activity. Highest concentrations were found at the mouth of the River Severn. Sediment metal concentrations were also found to be higher at the mouth of the River Severn, with elevated concentrations also found at the mouth of the River Tamar. Concentrations of alkylphenols in sediments were below the limit of detection.

The concentration of contaminants in biological tissues is dependent on the environmental concentration, their bioavailability, their structure and activity, and the metabolic processes of the species studied. Overall, the highest concentrations of contaminants were found in animals sampled in areas of high sediment contaminant loading, which were generally associated with areas of high riverine inputs and increased proximity to industrialised areas.

Highest PAH, CB and metal concentrations were found in mussels collected from the mouth of the River Severn. This corresponded with the maximum PAH, CB and metal concentrations in sediment from this area. The mouth of the River Severn was also the site of the highest concentration of CBs in the dab liver samples and highest metal concentrations in fish liver and muscle samples.

Marine mammals appeared to be susceptible to bioaccumulation of compounds with significantly higher concentrations of all contaminants found in the blubber of marine mammals compared to other matrices (i.e. water and sediment) and other biota (mussels and fish). This may not be surprising due to their high trophic level, long life span and limited ability for metabolism and excretion.

Irgarol and diuron were the only two of eight booster biocides detected in the inland waters of Southampton. Elevated concentrations of irgarol and diuron were found in inland water samples collected close to marinas and harbours with high boating activity and low water exchange. They were low or undetected in offshore water samples.

### **3.4 BIOLOGICAL EVIDENCE OF CONTAMINATION**

#### **3.4.1 Introduction**

The measurement of the biological effects of contaminants has been carried out as part of the Clean Safe Seas Environmental Monitoring Programme (CSEMP) in support of the OSPAR Joint Assessment and Monitoring Programme (JAMP). In addition several other monitoring programmes have contributed data to the SEA8 area. Biological effects measure the response of an organism to contaminant exposure, rather than the levels of the contaminants themselves. The effects of contaminants upon biological systems may manifest themselves from the molecular to the population level. With increasing complexity of the system studied the number of compensatory mechanisms and lag time from exposure to effect increase, which reduces certainty in prediction. Nevertheless biological effects monitoring provides the link between the contaminants present and the health and quality of the marine environment. Used alongside chemical analysis biological techniques are able to integrate the effects of multiple exposures to chemicals and respond to the bioavailable fraction of chemicals and hence more accurately reflect the potential for environmental impact.

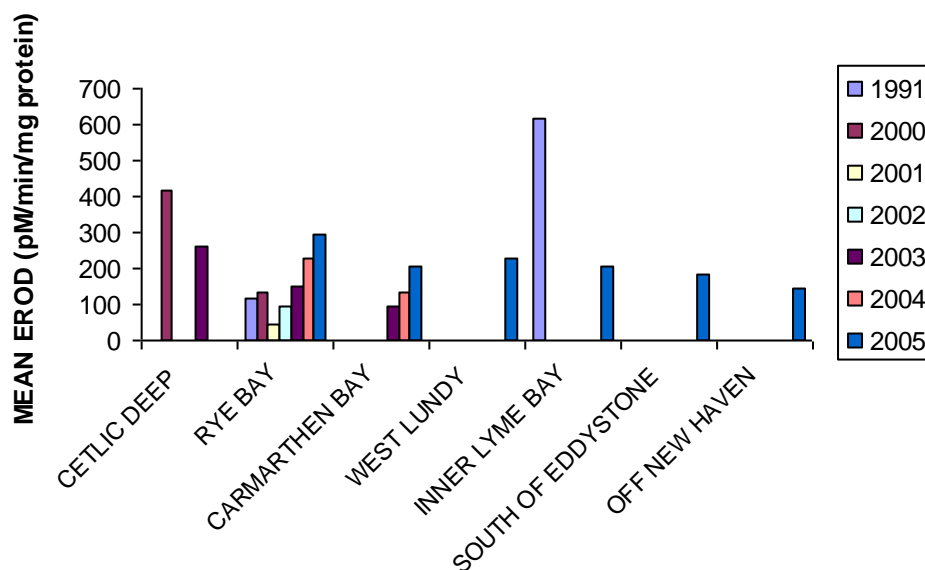
#### **3.4.2 Biomarkers of Contaminant Exposure in Fish**

##### ***3.4.2.1 EROD Induction***

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

Fish detoxify a number of these organic contaminants, specifically PAHs and some PCBs, 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 PAHs 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 PAHs are generally not measured in fish tissues (such as muscle) since the concentrations 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 via the gall bladder.



**Figure 8. Chart showing mean Hepatic EROD values (pM/min/mg protein) for dab (*Limanda limanda*) caught at UK CSEMP stations in SEA 8. EROD activity was analysed by the method of Burke and Mayer (1974) as described by Stagg *et al.*, (1995).**

Dab were sampled at seven sites between 1991 and 2005 (Figure 8). The data were similar for both sexes, reflecting the reproductive state of the fish at the time, so were combined. All sites were not sampled each year and the only site where comprehensive data was available is Rye Bay. EROD values are seen to generally increase over the years at this site indicating an increase in PAH and/or PCB concentrations. However, the highest value of 295 pM/min/mg protein recorded in 2005 is still considered relatively low in comparison to possible values of 1000 or more. The highest value recorded for all the sites over the years was 619 pM/min/mg protein at Inner Lyme Bay in 1991. This high level was possibly due to an entirely natural phenomenon linked to the breeding cycle in which an effect is caused by temperature changes and steroid metabolism. The EROD value had decreased at this site by 2005 to concentrations similar to the other areas in SEA8. The data sets are not currently comprehensive enough, to undertake trend analysis.

In response to the *SEA EMPRESS* oil spill (15<sup>th</sup> February 1996) the EROD assay was deployed for two separate sampling occasions. The first survey conducted did not catch the target species of dab and plaice in abundant quantities, however the second survey

produced a more extensive set of data. This is shown in Table 22. Although the levels are generally high, this may be due to natural spawning activity; therefore the data set may not be entirely reliable. Despite this, it is perhaps noteworthy that the highest levels in this data set were seen at the two sites closest to the oil spill - Turbot Bank and Freshwater West. Although these values were significantly higher than the other sampled stations it is not possible to conclude that this was an effect of the oil spill due to the spawning condition of the fish.

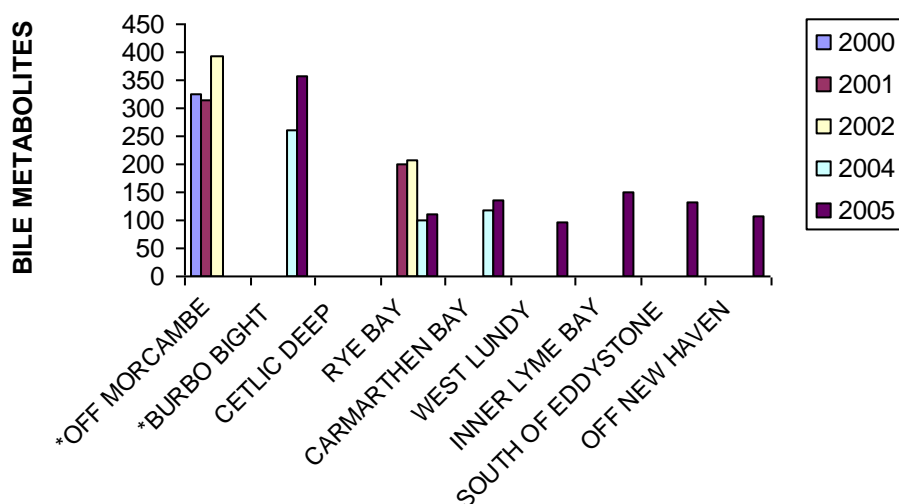
**Table 22. Hepatic EROD activity levels (pM/min/mg protein) in dab and plaice sampled after the SEA EMPRESS oil spill (May 1996 - PROVIDER).**

<b>SITE</b>	<b>Dab</b>	<b>Plaice</b>
St Brides Bay	1496	404
St Brides Bay - Off		
Skomer	1624	418
Saundersfoot/Amroth	-	714
Tenby	2122	812
Off Manorbier	2860	768
Offshore Caldey	2634	738
Offshore Carmarthen	3619	1032
Rhossili Bay	3062	672
Off Pembrey	3551	632
Central Carmarthen	2915	982
Turbot Bank	4909	785
Freshwater West	3918	840
Offshore Milford		
(Reference)	3888	-
Carmarthen Bay	3799	-

### **3.4.2.2 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. The main metabolite of pyrene, 1-Hydroxy pyrene (1-OH pyrene), accounts for a large percentage of the total PAH metabolites in the bile of fish exposed to PAHs (Krahn *et al.*, 1987). The use of 1-OH pyrene as a standard allows a basic measure of PAH exposure to be made.

Figure 9 shows Bile Metabolite data from fish sampled at CSEMP sites from 2000 to 2005. Only 2005 has a comprehensive data set from several stations from SEA8. In previous years, Rye Bay was regularly sampled as this is often used as a reference site and only two other sites (Celtic Deep and Carmarthen) were sampled on one occasion each. As this is the case, it is not possible to determine any trends for an extensive area. However, looking at Rye Bay alone there is a decrease in bile metabolites for the last two years sampled, and therefore, a possible decrease in PAH concentration in this area. For the purposes of comparison, the sites with the highest value for each respective year (Morecambe Bay and Burbo Bight) have been included in the chart. From this we it can be seen that concentrations of Bile Metabolites and therefore PAH exposure concentrations in this SEA8 area are generally low.



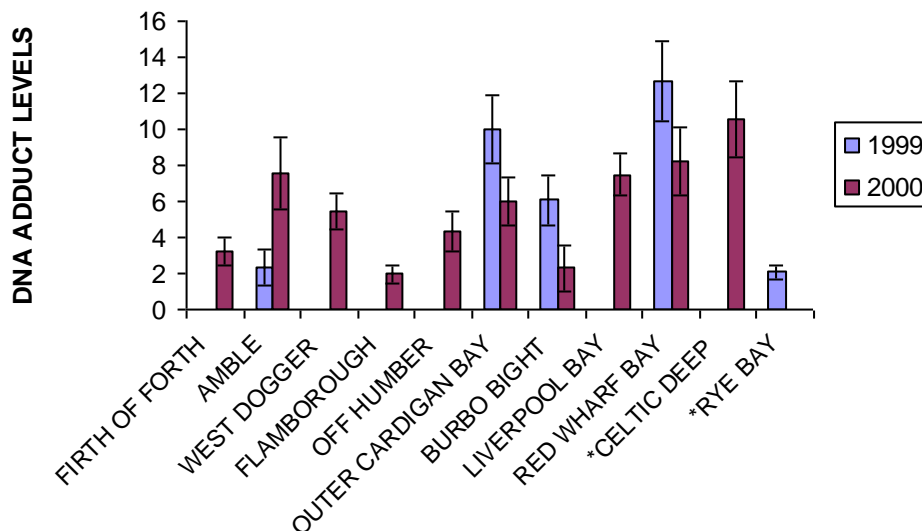
**Figure 9. Chart showing mean Bile Metabolites values (ppb 1-OH Pyrene) for dab (*Limanda limanda*) caught at UK CSEMP stations in SEA 8. \* Indicates sites with the highest values for that year.**

### 3.4.2.3 DNA Adducts

Parent PAHs are extensively metabolised in fish, therefore body burden analysis by standard analytical methods does not provide an adequate assessment of exposure. Significantly, metabolism of PAHs 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 that is also relatively persistent.

Very few data are available for DNA adducts within the SEA8 area. Figure 10 shows the two sites – Celtic Deep and Rye Bay - where sampling occurred in 1999 and 2000 respectively. For comparison purposes, the entire data set for all the stations in 1999 and 2000 are also shown on the chart. It can be seen from this that Rye Bay in 1999 had a particularly low occurrence of DNA adducts ( $2.1 \pm 0.4$  (10 fish sampled) per  $10^8$  undamaged nucleotides) whereas Celtic Deep in 2000 had a particularly high occurrence ( $10.6 \pm 2.1$  (10 fish sampled) per  $10^8$  undamaged nucleotides) for that year. This indicates that dab from this area may have been exposed to a complex mixture of carcinogenic metabolites. However, it cannot be ruled out that these high levels may be indicative of migratory fish and the source of contamination may be some distance from the sampling site. As multiple year data is not available for this area, it is not possible to determine if this elevated value is a persistent problem for the Celtic Deep area or a one off occurrence. However, contaminant concentrations at this offshore station are often low or below detection (see previous section) and thus unlikely to pose a threat to marine life.



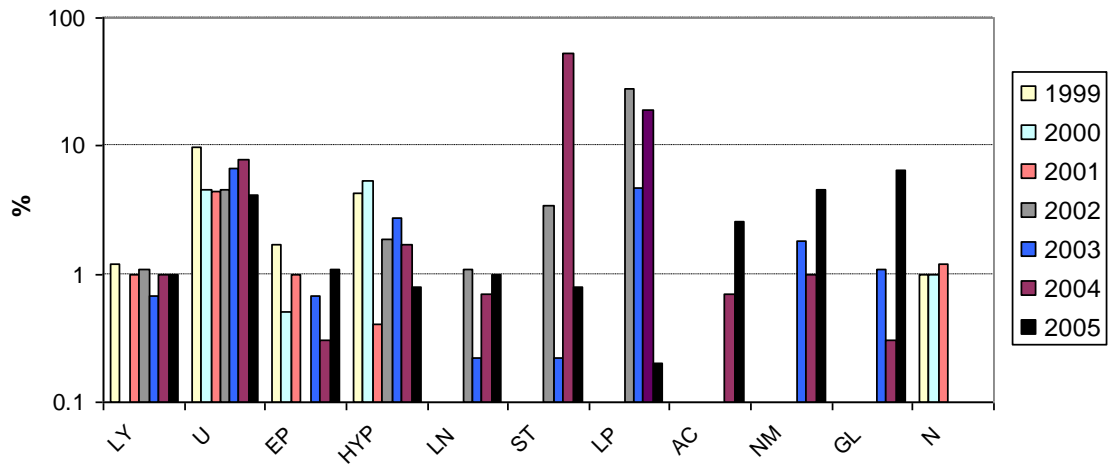


**Figure 10. Chart showing levels of Hepatic DNA adducts (DNA adducts per 10<sup>8</sup> undamaged nucleotides) in dab (*Limanda limanda*) from UK coastal waters. \* indicates sampling sites within the SEA8 area.**

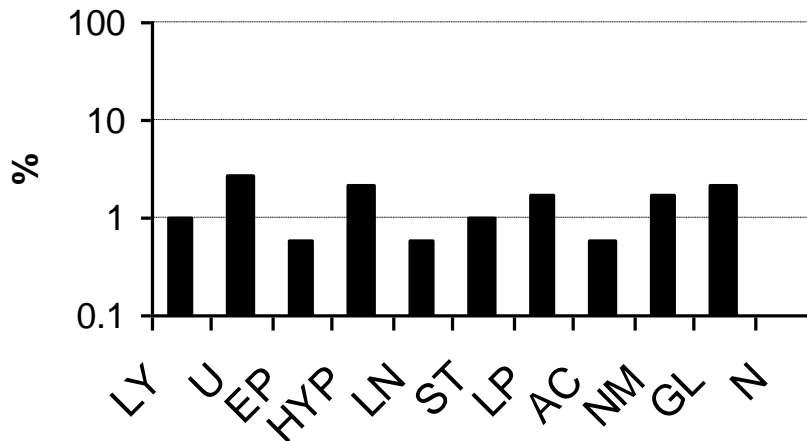
#### 3.4.2.4 Disease Induction

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. External conditions used for monitoring include acute and healing ulcerations, lymphocystis, epidermal hyperplasia/papilloma and hyperpigmentation. Internal pathologies include 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). Details of disease and pathological changes spanning seven years of sampling at Rye bay are presented in Figure 11. A wider range of disease categories were diagnosed from 2002 onwards hence the apparent increase in disease status. Four disease categories recorded in 1999, Lymphocystis, Ulceration,

Epidermal papilloma and Hyperpigmentation generally decreased or stayed at similar levels. In 2002 and 2004 levels of *Lepeophthierius* were somewhat elevated and in 2004 *Stephanostomum* was seen to be particularly high. The reason for this is unclear.



**Figure 11. Chart showing the occurrence of external disease and liver nodule prevalence (on a logarithmic scale) in dab (*Limanda limanda*) caught at UK CSEMP station Rye Bay from 1999 to 2005 (values reported as % of total fish sampled).**

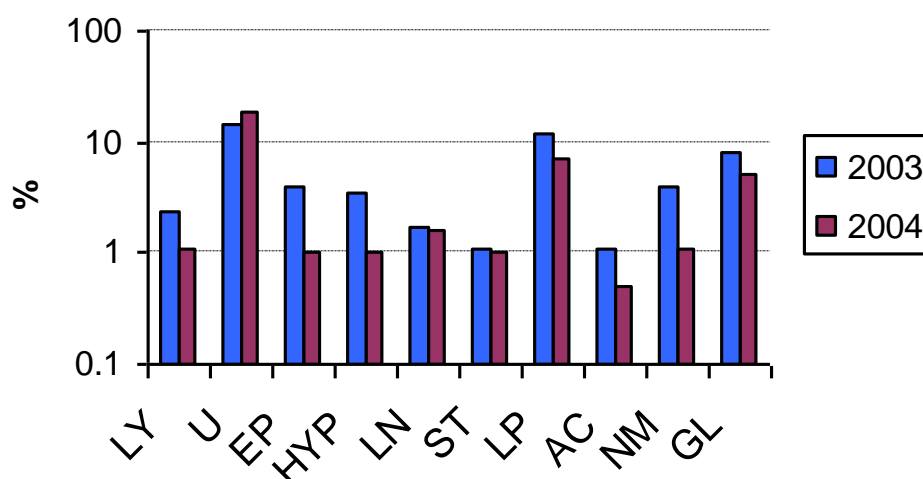


**Figure 12. Chart showing the occurrence of external disease and liver nodule prevalence (on a logarithmic scale) in dab (*Limanda limanda*) caught at Lyme Bay UK CSEMP stations in 2005.**

Ly=Lymphocystis, U=Ulceration, Ep=Epidermal papilloma, Hyp=Hyperpigmentation, LN=Macroscopic Liver Lesion, ST=Stephanostomum, LP=Lepeophthierius, AC=Acanthochochondria, NM=Nematodes, GL=Glugea, N=Liver Nodules

In 2005 dab sampled from Lyme Bay were assessed for disease status (Figure 12). By comparison to Rye Bay (Figure 10) during 2005 fish from Lyme Bay showed a

slightly lower occurrence of disease. Figure 13 shows disease status for dab sampled from Carmarthen Bay for 2003 and 2004. In both 2003 and 2004 levels of disease were broadly comparable and appear to be higher across more categories than was the case for Lyme Bay or Rye Bay. Incidents of lymphocystis, ulceration and glugea were higher in both years in Carmarthen Bay than for any other disease.



**Figure 13. Chart showing the occurrence of external disease and liver nodule prevalence (on a logarithmic scale) in dab (*Limanda limanda*) caught at Carmarthen Bay UK CSEMP stations in 2003 and 2004. (values reported as % of total fish sampled).**

### 3.4.3 Biomarkers of Contaminant Exposure in Mussels

#### 3.4.3.1 Scope for Growth

Scope for Growth (SFG) provides a measure of the physiological stress response in marine mussels. Results from this assay are grouped into three categories according to the energy usage calculated for mussels from different sites or test groups in experimental studies:

- >15 J g h<sup>-1</sup> = High growth potential/low stress;
- 5-15 J g h<sup>-1</sup> = Moderate growth potential/moderate stress;
- < 5 J g h<sup>-1</sup> = Low growth potential/high stress.

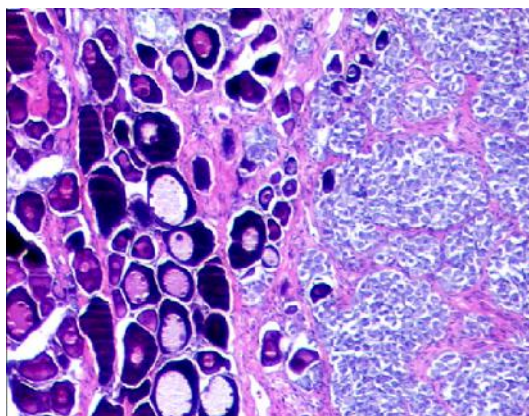
Between 1996 and 1997 mussels collected from 38 coastal sites around the Irish Sea were assessed for tissue concentrations of various chemical contaminant and SFG, (Widdows *et al.*, 2002). Two of the sites in this survey– Port Quinn and Zennor are included in the SEA8 area. Both of these sites had SFG values indicative of good water quality (>15 J g h<sup>-1</sup>) and low stress.

### 3.4.4 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 include the oestrogenic effects of treated sewage effluents on fish (e.g Harries *et al.*, 1997). This can cause the liver to produce vitellogenin (VTG) a female specific egg yolk precursor protein in male fish. 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 14).



**Figure 14. 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 alkylphenol ethoxylates and various natural and synthetic oestrogens excreted by humans and livestock. The effects of these chemicals 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. Recent research has found that VTG induction is found in several species of marine fish (Cho *et al.*, 2003 (Japan gizzard shad), De Metrio *et al.*, 2003 (Mediterranean swordfish), Fossi *et al.*, 2002 (Mediterranean 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 in the North Sea had raised

levels of vitellogenin in the plasma of male fish. The aetiology is presently unknown but circumstantial evidence favours the hypothesis that cod accumulate estrogenic endocrine disrupters via their diet, which changes as they grow.

#### 3.4.4.1 Imposex in Dogwhelks

Imposex is the development of male sexual organs in female whelks and periwinkles and has been found to be a very sensitive indicator of TBT exposure. In severe cases of imposex it can lead to sterility in females and detrimental reproductive effects on individuals and populations

Shoreline populations of toothed adult *N. lapillus* were sampled by hand between spring low water and mid tide levels at sites used in earlier surveys in 1992 and 1998. 40-50 individuals were taken for analysis. The shell length of each animal was measured, and individuals were classified by their shell length according to observations by Moore (1936), i.e. juveniles (10–15 mm shell length), sub-adults (15–21 mm), and un-toothed adults (21–26 mm and 26–35 mm). At each of the juvenile and sub-adult survey sites, an attempt was made to obtain 20 individuals from each of the above size classes (and 40 toothed adults). *N. lapillus* were sexed and dissected to expose the reproductive organs and allow determination of imposex. The degree of imposex as measured by Vas Deferens Sequence Index (VDSI – Table 23), was determined using international standard techniques (OSPAR, 2002).

**Table 23. Oslo And Paris Commission Biological effects assessment criteria for imposex in *N. lapillus*, based on VDSI (OSPAR, 2002)**

Assessment class	<i>N. lapillus</i> VDSI	Effects and impacts
A	VDSI = <0.3	The level of imposex in the more sensitive gastropod species is close to zero (0 - ~30% of females have imposex) indicating exposure to TBT concentrations close to zero, which is the objective in the OSPAR strategy of hazardous substances.
B	VDSI = 0.3 - <2.0	0 The level of imposex in the more sensitive gastropod species (~30 – ~100 % of the females have imposex) indicates exposure to TBT concentrations below the EAC derived for TBT. e.g. adverse effects in the more sensitive taxa of the ecosystem caused by long term exposure to TBT are predicted to be unlikely to occur.
C	VDSI = 2.0 - <4.0	The level of imposex in the more sensitive gastropod species indicates exposure to TBT concentrations higher than the EAC derived for TBT. e.g. there is a risk of adverse effects, such as reduced growth and recruitment, in the more sensitive taxa of the ecosystem caused by long-term exposure to TBT.
D	VDSI = 4.0 - 5.0	The reproductive capacity in the populations of the more sensitive gastropod species, such as <i>N. lapillus</i> , is affected as a result of the presence of sterile females, but some reproductively capable females remain. e.g. there is evidence of adverse effects, which can be directly associated with the exposure to TBT.
E	VDSI = > 5.0	Populations of the more sensitive gastropod species, such as <i>N. lapillus</i> , are unable to reproduce. The majority, if not all females within the population have been sterilized
F	VDSI = -	The populations of the more sensitive gastropod species, such as <i>N. lapillus</i> and <i>Ocenebrina aciculata</i> , are absent/expired.

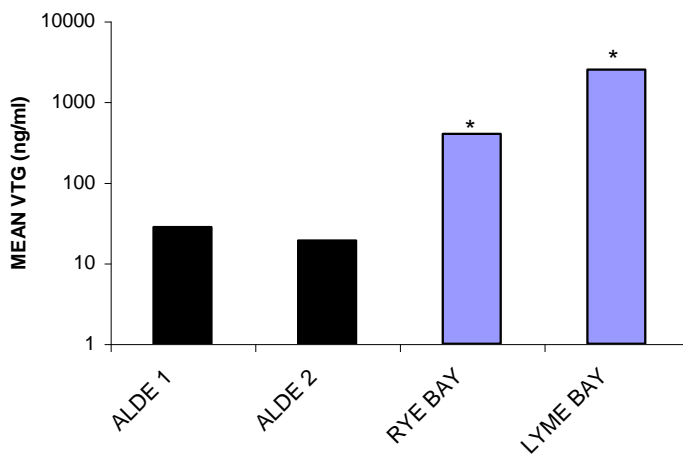


**Figure 15. Map showing the assessment of 2004 VDSI data from adult dog whelks (*N. lapillus*) sampled in the vicinity of SEA8. Data are presented in accordance with OSPAR assessment classes A-D (See Table 23).**

The results of the 2004 dog-whelk imposex study for SEA8 can be seen in Figure 15. The majority of sites in this area fall into the OSPAR category ‘c’ indicating exposure to TBT concentrations higher than the EQS (2 ng/L). Generally high levels of imposex are associated with areas of high shipping activity and the lower values were found at the greatest distance away from TBT inputs. However, water and sediment samples analysed for the presence of TBT from SEA8 were mostly below the level of detection. These samples were however taken from sites that were slightly further offshore to those in the dog-whelk survey. One exception to this was in the area off Milford Haven where the highest levels of TBT in tissues of mussels were reported. This coincides with particularly high shipping activities in this area of SEA8.

#### **3.4.4.2 Vitellogenin induction in male Flounder**

Data from male flounder in Rye Bay and Lyme Bay (Figure 16) suggest that contamination in these areas is high enough to produce a significant elevation in vitellogenin concentration in male fish. However, the level of contamination is likely to be moderate as levels of vitellogenin induction from other coastal areas (such as Liverpool Bay and Red Wharf Bay) are far higher, indicating higher levels of contamination probably mostly associated with the input of the final effluents of sewage treatment works.



**Figure 16. Mean plasma VTG (shown on a logarithmic scale) in male flounder from English Channel sites. Alde sites 1 and 2 are reference sites.(After Allen 1999). \* denotes significantly different from control (Alde).**

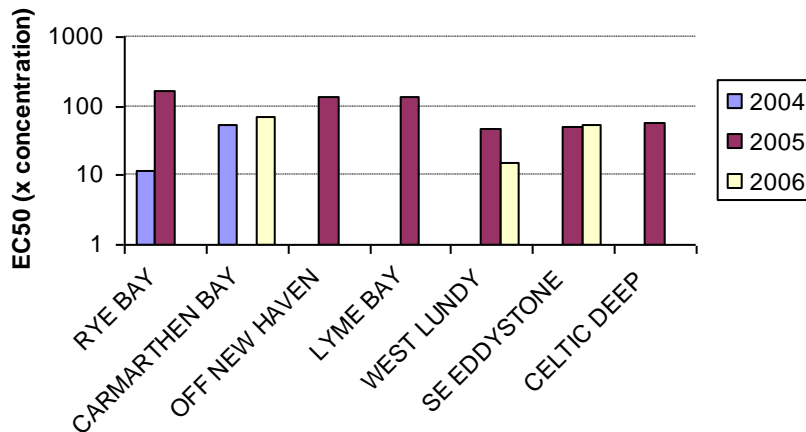
### 3.4.5 Water Column Toxicity Bioassays

To enable trends in contaminant levels in coastal and offshore waters to be assessed large sample volumes of water can be extracted and tested in standard toxicity test protocols. Samples of water were collected from around the UK in 2004, 2005 and 2006. 60 L of water was collected at each site by submerging a stainless steel churn to a depth of 1m using a weighted churn sampler. 50L of water was immediately placed into a 50 L pressure vessel and extracted using solid-phase columns of media capable of adsorbing polar organic contaminants. Test solutions were prepared as a logarithmic dilution series. Several toxicity assays were conducted on each extract the results are presented as a median effect concentration (EC50) in order for comparisons to be made.

#### 3.4.5.1 Oyster Embryo Bioassay (OEB)

The methodology for the oyster embryo bioassay was taken from the Cefas Standard Operating Procedure (SOP 1579, 2006) prepared in accordance with the Environment Agency's published SCA (Standard Committee of Analysts) method, 'The direct toxicity assessment of aqueous environmental samples using the oyster (*Crassostrea gigas*) embryo-larval development test (2006). Briefly, oysters (*Crassostrea gigas*) were manually stripped of gametes. Gamete quality was assessed microscopically and the sexes of individuals identified. Gametes were collected using wide bore pasteur pipettes and placed into beakers of reference seawater at 16°C for fertilisation and development to 16-32 cell stage. Embryo suspensions were then adjusted to the required density and transferred in set volumes to the test solutions. Embryo suspensions were added to the test solutions to achieve densities of approximately 50 embryos ml<sup>-1</sup>. Raw data were analysed using the Toxcalc statistical package (Tidepool Scientific, USA).

The results for this assay are shown in Figure 17. The most comprehensive data set is from 2005 for which the greatest toxicity was measured in a sample from West Lundy (the EC50 was equivalent to a concentration factor of approximately 48x) and the lowest toxicity was recorded for a sample from Rye Bay (for which a concentration factor of 172x was required to produce the EC50). This result for Rye Bay contrasts to the previous years result, for which toxicity was approximately 15 times higher.



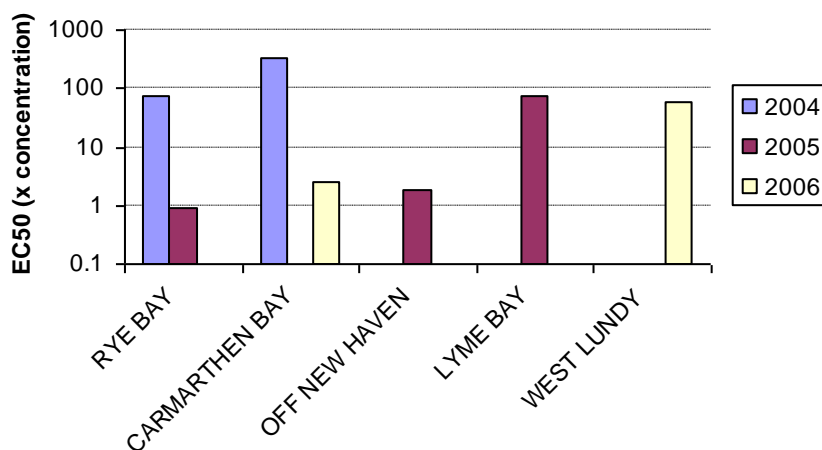
**Figure 17. Chart showing the EC50 values (on a logarithmic scale) of water samples taken from sites within SEA 8 in 2004, 2005 and 2006 using the Oyster Embryo Bioassay.**

#### 3.4.5.2 Marine Algae Bioassay

The methodology for the marine algae (*Skeletonema costatum*) bioassay was taken from the Cefas Standard Operating Procedure (SOP 1574, 2006) as recommended by the Environment Agency. Briefly, the *S. costatum* assay was conducted in 96-well microplates. Each sample was run as a dilution series in 2 microplates with a control of clean seawater (Cefas, UK). Each plate was incubated in continuous light (2000 Lux) at 21°C whilst being shaken at 100 RPM on an orbital shaker. Algal growth was measured by fluorescence (excitation 430 nm, emission 670 nm) at 0 h, 24 h, 48 h and 72 h. A positive control, using ZnSO<sub>4</sub>, was run concurrently with each batch of samples to check that the sensitivity of each batch did not vary significantly. Raw data were analysed using the Toxcalc statistical package (Tidepool Scientific, USA).

The results for this assay are shown in Figure 18. Water samples from Carmarthen Bay shows a large increase in toxicity between 2004 and 2006. In 2005 seawater samples from Rye Bay only required a concentration factor of 0.92x to produce an EC50 for *S. costatum*. This also represents an increase in toxicity from samples taken at this location in 2004.





**Figure 18. Chart showing the EC50 values (on a logarithmic scale) of water samples taken from sites within SEA8 in 2004, 2005 and 2006 using the Marine Algae (*Skeletonema costatum*) Bioassay.**

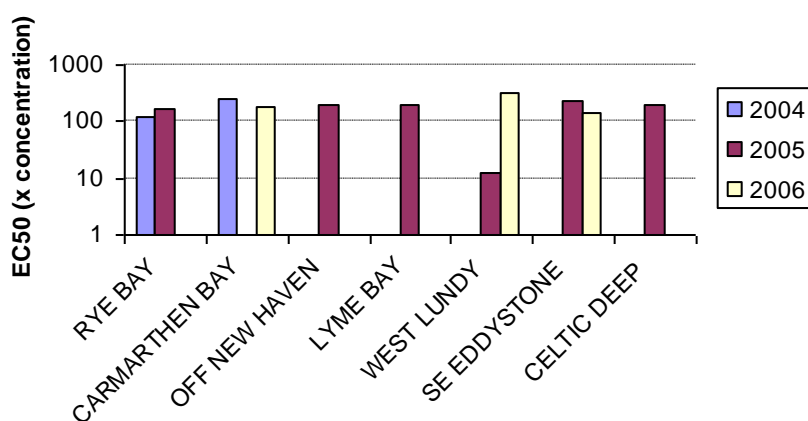
#### 3.4.5.3 *Tisbe battagliai* Bioassay

The methodology for the *Tisbe battagliai* (marine hapacticoid copepod) bioassay was taken from the Cefas Standard Operating Procedure (SOP 1575, 2006) prepared in accordance with the Environment Agency's published SCA (Standard Committee of Analysts) method, 'The direct toxicity assessment of aqueous environmental samples using the marine copepod *Tisbe battagliai* lethality test (2005).

Dilutions of sample extracts were made using aged seawater filtered to 0.2 µm. Solutions were made up on the day of the test to prevent any degradation of the extracts in seawater before the test began.

Tests were conducted in 12 cell well plates. Each well contained 5 mls of test solution, 4 replicates were used for each concentration. At the start of the test 5 *T. battagliai* were introduced to each well. Mortality was recorded at 24 h and 48 h. The raw data from these *T. battagliai* assays were analysed using the Toxcalc statistical package (Tidepool Scientific, USA). Samples were run in batches, each batch included a zinc control run alongside to confirm the sensitivity of the test species to enable comparison between test batches.

The results for this assay are shown in Figure 19. Most samples for all three years show relatively low toxicity. Slightly higher toxicity was present in the West Lundy sample in 2005 compared to that from other sites in this year.



**Figure 19. Chart showing the EC50 values (on a logarithmic scale) of water samples taken from sites within SEA 8 in 2004, 2005 and 2006 using the Marine Copepod (*Tisbe battagliai*) Bioassay.**

#### 3.4.5.4 Summary of Water Column Bioassay Results

There are considerable discrepancies in the majority of the toxicity data from 2004, 2005 and 2006 with regards to the oyster, marine algae and marine copepod assays. It is therefore difficult to draw any definitive conclusions as to the degree of contamination in these areas from these results. However, West Lundy seawater extracts show high toxicity in the *Tisbe* assay in 2005 and Oyster Embryo assay in 2005/2006. Toxicity for this area is also high for *Skeletonema* in 2006. The toxicity of extracts from Rye Bay samples is variable over the three bioassays and years, however in 2004 both the oyster embryo and Marine algae tests showed similarly high levels of toxicity. In 2005 and 2006, sample extracts from samples taken Off New Haven and Carmarthen Bay respectively showed high toxicity to the algae that was not reflected in the other tests possibly indicating the presence of compounds such as biocides that have greater phytotoxicity.

#### 3.4.6 Sediment Toxicity Bioassays

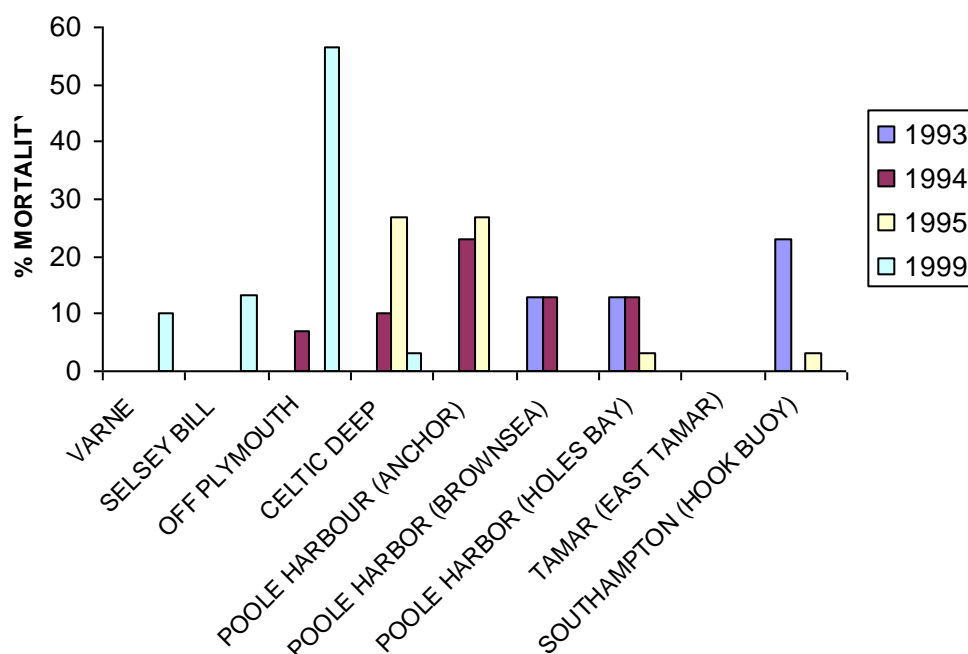
Two whole sediment bioassays, using the polychaete *Arenicola marina* and the crustacean amphipod *Corophium volutator* have been developed, which are now routinely used in the CSEMP. *Arenicola marina*, commonly known as the lugworm, is a surface deposit feeding polychaete, which inhabits intertidal and subtidal areas, whereas *C. volutator* is a marine amphipod, which can be found on the foreshore of most unpolluted estuaries in the UK. Since 1996, sediment samples have been taken and stored onboard research vessels, before being transported back to the laboratory and bioassayed.

Intermediate and offshore sediments are collected using a Reineck Box corer. From each undisturbed core the top 10cm layer of sediment is removed and homogenised, from which a sample is taken for bioassay. A Day grab is sometimes used during periods of inclement weather or where the sediments are not suitable for coring. In estuaries, sediment samples are usually collected using a hand-held van Veen grab.

Reference sediment was collected from Shoeburyness, Essex (a relatively uncontaminated coastal site with few local contaminant inputs) and was used as a negative control.

### 3.4.6.1 *Corophium volutator*

Animals were collected from a nearby muddy shore on the river Crouch estuary. Sediment samples were homogenised before placing into 1-litre glass beakers. The beakers were filled with 2cm depth of sediment (about 300g dry weight) and for each field and control sample, three replicates were set up. Filtered seawater (10µm) was added 24 hours later to the 850ml mark and aeration supplied. The beakers were then left for a further 24hrs, ten adult *Corophium* (4-6 mm in length) were then added to each test beaker. After 10 days the content of each beaker was sieved and the number of surviving *Corophium* recorded. The results are expressed as percentage mortality after 10 days.



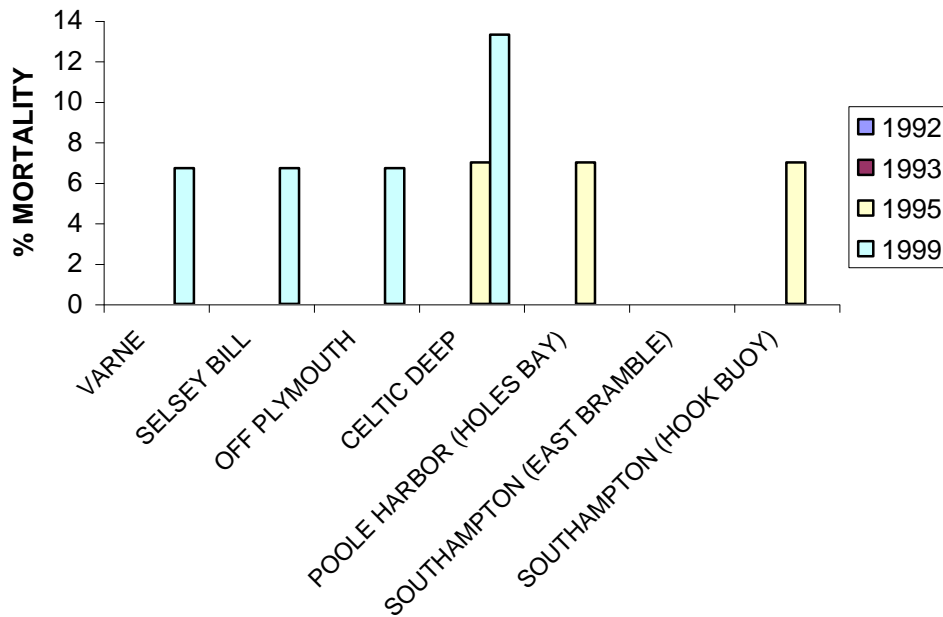
**Figure 20. Chart showing the % mortality of *Corophium volutator* to sediment samples taken from CSEMP sites in SEA8 from 1993 to 1999.**

The results for the *C. volutator* assays can be seen in Figure 30. Only one site in one year (Off Plymouth in 1999) shows significant mortality of 56.6%.

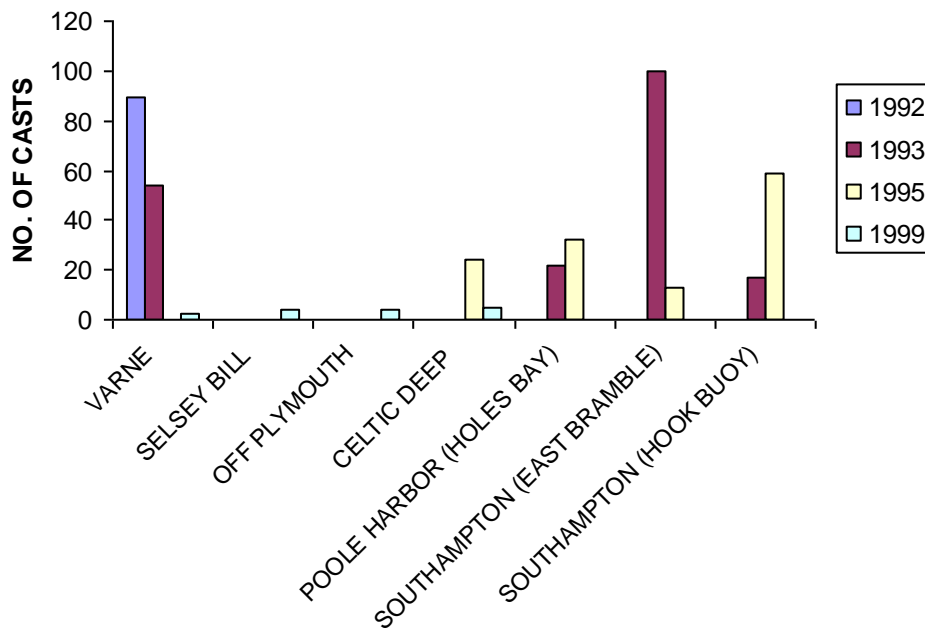
### 3.4.6.2 *Arenicola marina*

Animals were obtained from a local bait supplier and either used in the test on the same day or kept in a clean layer of reference sediment, running seawater and aeration, until ready for use. When the sediment samples had been thoroughly defrosted and homogenised they were placed into polythene boxes. The boxes were filled with a 4cm depth of sediment and for each field and control sample, three replicates were set up. Filtered seawater (10µm) was added 24 hours later to give a 3-

4 cm layer on top of the sediment. Aeration was then added. The tanks were then left for another 24 hours. If the animals were in a holding tank beforehand, they were first gently sieved from the tank and then added to the test sediment. Five animals of approximately 1 g were placed into each test container. After 10 days the contents of each test container were sieved and the number of surviving worms recorded. The number of casts produced on the surface of the sediment was also counted daily during the exposure period to obtain the measure of the feeding rate of the animals. This was used as a measure of the sublethal effects. The casts were smoothed over after each count. The survival results are expressed as mean daily number of casts. The control mortality must not exceed 10 percent for the test to be considered valid.



**Figure 21. Chart showing the % mortality of *Arenicola marina* to sediment samples taken from CSEMP sites in SEA8 from 1993 to 1999.**



**Figure 22. Chart showing the number of casts made by *Arenicola marina* each day in sediment samples taken from CSEMP sites in SEA 8 from 1993 to 1999.**

The mortality results for the *A. marina* assay can be seen in Figure 21. No significant mortality was seen at any of the sites for any of the years. Figure 22 shows the number of casts produced by the animals over the testing period. These results indicate that feeding rate was significantly reduced in 4 sites in 1999 and moderately reduced in 3 sites in 1995. This shows that the sediment in these sample locations is moderately contaminated.

#### 3.4.6.3 Summary of sediment Assays

The sediment test results highlight the importance of using a battery of tests when assessing sediment quality, as the one incident of toxicity to *C. volutator* was not seen with *A. marina*. This shows the differing susceptibility of the two species. The cast data for *A. marina* can also give a useful indication of the chronic effects of the contamination in the sediment as it is likely that the locations where cast numbers were low would eventually show higher mortality than a control.

#### 3.4.7 Acetylcholinesterase Activity

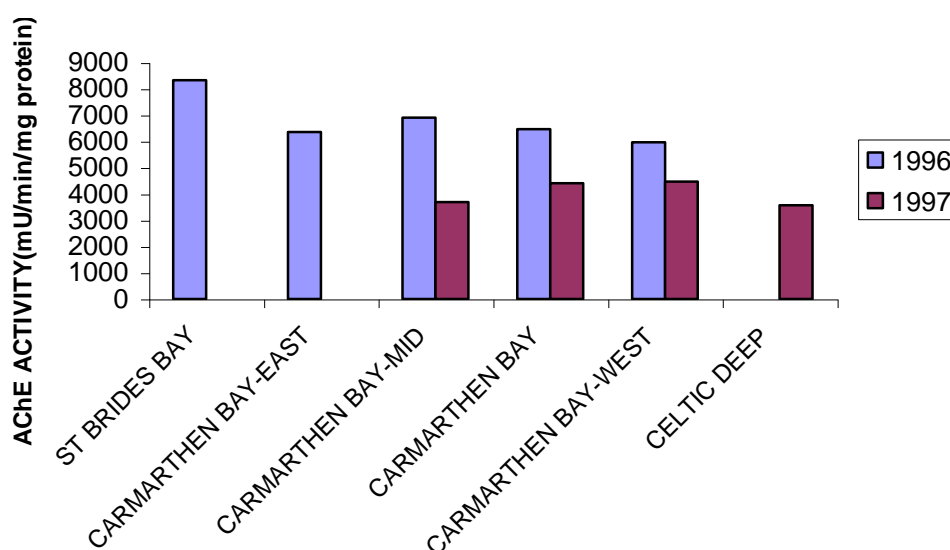
Acetylcholine (ACh) is the primary neurotransmitter in the sensory and neuromuscular systems in a range of organisms including fish. As such, the activity of this system is vital to normal behaviour in this group (Payne *et al.*, 1996) and it represents a prime target on which toxicants can act to cause a detrimental effect. For normal neurotransmitter functioning the levels of ACh at a neuro-junction must be carefully regulated and this is done by the activity of the enzyme acetylcholinesterase (AChE), which degrades the ACh into the inactive products choline and acetic acid, which are reabsorbed and used as raw materials for the continued production of ACh.

Inhibition of the AChE enzyme results in the build up of ACh causing a continuous and excessive stimulation of the nerve/muscle fibres, which results in tetany and eventual paralysis and death. Some of the most potent inhibitors are the organophosphate and carbamate pesticides and it is primarily with the environmental monitoring of these chemicals that this technique is applied.

The data presented in this report represents that obtained during annual CSEMP surveys carried out in 1996 and 1997. The ChE activity levels were measured in dab that were killed and dissected within 1 hour of capture. A strip of muscle was collected and placed in liquid nitrogen for storage and then transported back to the laboratory for analysis.

After no more than four months storage, samples were homogenised then centrifuged to produce a supernatant that was used as a ChE source. Tests were performed in quadruplicate in 96-well microplates. Measurements of AChE activity were normalised to protein content and expressed as  $\text{mUmin}^{-1} \text{mg}^{-1}$  ( $1\text{U} = 1\text{mOD unit}$ ). Protein analyses were carried out on the same muscle homogenate as the AChE activity measurements.

The results for this assay are shown in Figure 23. Although it looks as if the activity for 1997 was lower than that of 1996, this may not be significant as all the values for all the sites sampled were lower for this year (ranging from 2491 to 5263, whereas values for 1996 ranged from 4643 to 9107). For each year the values for SEA8 were generally average to high indicating no significant contamination with organophosphates and carbamate pesticides in this area.

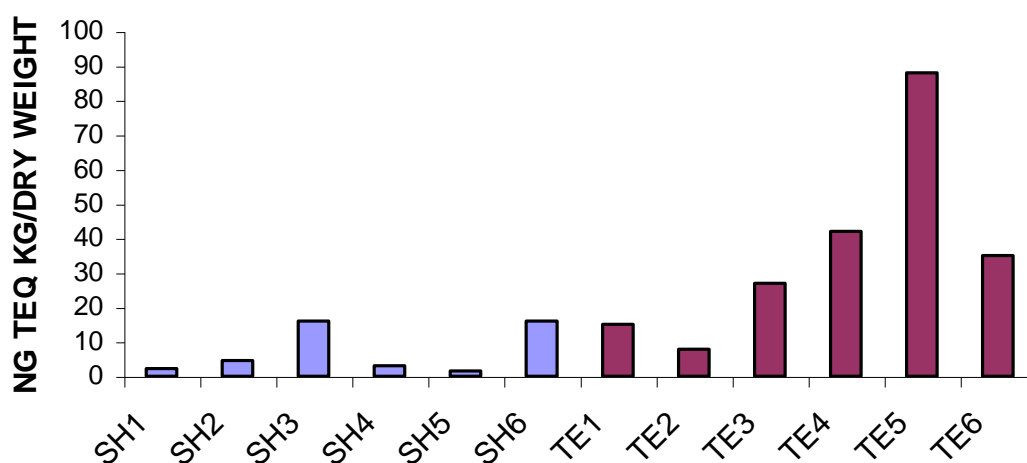


**Figure 23. Chart showing the mean AChE activity in dab muscle tissue sampled on the CIROLANA in 1996 and 1997.**

### 3.4.8 DR-CALUX Bioassay for the detection of Dioxins

Sediments from a number of UK estuaries including Southampton water have been tested for the presence of dioxins and dioxin-like compounds using a bio-analytical assay, DR-CALUX. The dioxin responsive-chemically activated *luciferase* expression assay uses a coupled receptor-reporter gene system and responds specifically to compounds, which interact with the aryl hydrocarbon receptor. This includes dioxins and furans and other compounds with a similar mode of action. Increasing concentrations of dioxins and dioxin-like compounds cause an increase in the luminescence produced in the assay, which can be calibrated to yield a toxic equivalent (TEQ) value relative to the most active dioxin compound (2, 3, 7, 8-tetrachlorodibenzo- *p* -dioxin; TCDD). Whole surface sediment samples were collected using a stainless steel van Veen grab, transferred to hexane rinsed glass jars and stored frozen until analysed (Hurst *et al.*, 2004).

Values from Southampton water were amongst the lowest values for all the estuaries sampled and are shown alongside values for the Tees, which has some of the highest values and is shown for comparison (Figure 24).



**Figure 24. Chart showing TEQ Values for sediment samples produced using DR-CALUX assay. SH1 to SH6 are Southampton water sites whereas TE1 to TE6 are Tees sites.**

### 3.4.9 Summary

The biological evidence of contamination for SEA8 shows that contamination is generally low in this area. Specifically, where biological data were available, there were definite indications that levels of PAHs, PCBs, organophosphates and carbamate pesticides were low. Several of the biological indicators showed that general contamination was not prevalent in most of the sites sampled.

There were however several areas where possible evidence of localised contamination was seen. There was possible PAH and PCB contamination within the vicinity of the SEA EMPRESS oil spill in 1996 although this was not entirely conclusive and could perhaps be explained by other factors. There is almost certainly TBT contamination in

very localised coastal areas of SEA8 as indicated by dog-whelk imposex studies in 2004. This contamination seems to coincide with areas of high shipping and marina activity.

The results from sediment and water column bioassays indicate some moderate contamination in several areas. However the data set is not yet comprehensive enough to draw any firm conclusions from these studies.



## 4 RADIOACTIVITY

### 4.1 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  $^{238}\text{U}$  and  $^{232}\text{Th}$  and their daughter products are present in both the water column and seabed sediments.

Cosmogenic radionuclides such as  $^3\text{H}$  and  $^{14}\text{C}$  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 use radioactivity for a variety of purposes and a number of sites and industries therefore can contribute to the natural inventories. Some of the wastes are released into the air or discharged to water, the radioactivity can then enter the environment and from there, the food chain. Monitoring programmes to ensure that human exposures from food and the environment are within legal limits are conducted on behalf of the UK Environment Agencies and the Food Standards Agency. Different matrices (seawater, sediment and biota) are sampled for analysis from the marine environment and are reported below in the context of sites that are potential sources of radioactivity in the SEA8 area. The data presented here include a subset of those reported in annual Radioactivity in Food and the Environment Reports (RIFE 11, 2006) and data from Cefas Annual Environmental Monitoring Reports (AEMR 57, 2002).

#### 4.1.1 Seawater surveys

A programme of surveillance into the distribution of key radionuclides is maintained using research vessels and other means of sampling. The seawater surveys reported here also support international studies concerned with the quality status of coastal seas (e.g. OSPAR, 2000) and provide information that can be used to distinguish different sources of manmade radioactivity (e.g. Kershaw and Baxter, 1995).

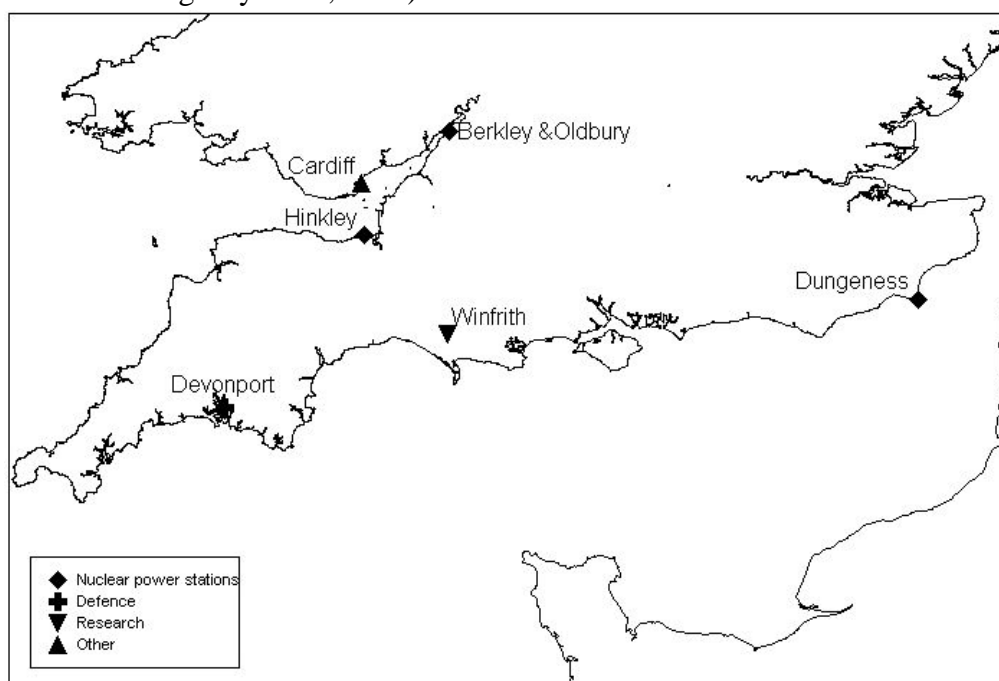
#### 4.1.2 Sediment surveys

The last survey to assess the inventory of artificial radionuclides was carried out more than a decade ago (Poole *et al.*, 1995; Kershaw *et al.*, 1999). Mixing of the surface sediments by tidal currents and wave activity is widespread and results in a corresponding mixing and dispersion of the radioactive signal. The subtidal sediments are subject to tidal resuspension, waves, fishing disturbance and mixing by benthic organisms (bioturbation). 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 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. Saltmarsh can be eroded rapidly but generally it tends to be stable over periods of decades.

### 4.1.3 Biota Surveys

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).



**Figure 25. Principal areas of radioactive waste disposal in the vicinity of coastal and estuarine sites associated with the SEA8 area.**

## 4.2 SURVEY LOCATIONS

### 4.2.1 Research Establishments

Winfrith, Dorset

Discharges of radioactive wastes from this site continued in 2005, at the low rates typical of recent years. Liquid wastes are disposed of under authorisation to deep water in Weymouth Bay. Concentrations of radionuclides in the marine environment largely continued at the low levels found in recent years.

**Table 24, part A. Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Winfrith, 2005.**

Material	Location	No of samp. obs	<sup>14</sup> C	<sup>60</sup> Co	<sup>65</sup> Zn	<sup>99</sup> Tc	<sup>137</sup> Cs	<sup>238</sup> Pu	<sup>239</sup> Pu+ <sup>240</sup> Pu	<sup>241</sup> Am	<sup>242</sup> Cm	<sup>243</sup> Cm+ <sup>244</sup> Cm	Total alpha	Total beta
Plaice	Weymouth Bay	2		<0.04	<0.12		0.09			<0.12				
Bass	Weymouth Bay	2		<0.05	<0.19		0.23			<0.19				
Crabs	Chapmans Pool	1		0.15	<0.13		<0.05	8.6E-05	0.0004	0.001	*	1.7E-05		
Crabs	Lulworth Banks	1	32	<0.07	<0.15		<0.05	0.00015	0.0008	0.0013	*	5.2E-05		
Pacific Oysters	Poole	1		<0.12	<0.33		<0.09			<0.19				
Cockles	Poole	1		0.25	<0.13		<0.04			<0.05				
Whelks	Poole Bay	1		0.16	<0.12		<0.04	0.00051	0.0026	0.0003	*	2.5E-05		
Whelks	Lyme Regis	1		<0.07	<0.24		<0.06	0.00022	0.0017	0.0017	*	2.6E-05		
Scallops	Lulworth Ledges	1		<0.05	<0.13		<0.05	0.00031	0.0024	0.0005	*	*		
Clams	Portland Harbour	1		0.18	<0.28		0.08			<0.07				
Fucus serratus	Kimmeridge	2		0.33	<0.23	0.3	<0.07			<0.28				
Fucus Serratus	Bognor Rock	2		0.12	<20	0.6	<0.06			<0.06				
Seaweed	Lulworth Cove	2		<2.1		<1.0	<1.7			<2.5				
Seaweed	Lulworth Cove	2		<0.32			<0.25			<0.45			<2.8	15

\* Not detected by the method used

#### 4.2.2 Nuclear Power Stations

This section considers the effects of discharges from nuclear power stations during 2005. There are a total of 19 nuclear power stations at 14 locations in the UK, of which four are in areas that have a potential influence on the SEA8 area (Berkeley, Oldbury, Dungeness and Hinkley Point).

Berkeley and Oldbury are both Magnox power stations. Berkeley Power Station ceased electricity generation in March 1989, but radioactive wastes have been and are still being generated by decommissioning operations. In addition, there is a component of the discharge from the operation of the adjoining Berkeley Centre. Berkeley Centre acts as the headquarters for the generating Magnox stations and provides support functions including radiochemical laboratories used for analysis of liquid effluents and environmental samples. The Oldbury Power Station has continued operation and because the effects of both sites are on the same area, Berkeley and Oldbury are considered together for the purposes of environmental monitoring. Liquid radioactive wastes are discharged to the Severn estuary.

Data for 2005 are presented in Table 25. Where comparisons can be drawn, gamma dose rates and concentrations in the aquatic environment were generally similar to those in recent years. Most of the artificial radioactivity detected was due to tritium and radiocaesium. Concentrations of radiocaesium represent the combined effect of discharges from the sites, other nuclear establishments discharging into the Bristol Channel and weapons testing, and possibly a small Sellafield-derived component. Caesium-137 concentrations in sediment have remained the same for the last decade. Relatively high concentrations of tritium were detected in fish and shellfish and these were likely to be mainly due to discharges from GE Healthcare, Cardiff. Very small concentrations of other radionuclides were detected but, taken together, were of low radiological significance.

**Table 25 Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Berkeley and Oldbury nuclear power stations, 2005.**

Material	Location	No of samp. obs	<sup>14</sup> C	<sup>60</sup> Co	<sup>65</sup> Zn	<sup>99</sup> Tc	<sup>137</sup> Cs	<sup>238</sup> Pu	<sup>239</sup> Pu+ <sup>240</sup> Pu	<sup>241</sup> Am	<sup>242</sup> Cm	<sup>243</sup> Cm+ <sup>244</sup> Cm	Total alpha	Total beta
Plaice	Weymouth Bay	2		<0.04	<0.12		0.09			<0.12				
Bass	Weymouth Bay	2		<0.05	<0.19		0.23			<0.19				
Crabs	Chapmans Pool	1		0.15	<0.13		<0.05	8.6E-05	0.0004	0.001	*	1.7E-05		
Crabs	Lulworth Banks	1	32	<0.07	<0.15		<0.05	0.00015	0.0008	0.0013	*	5.2E-05		
Pacific Oysters	Poole	1		<0.12	<0.33		<0.09			<0.19				
Cockles	Poole	1		0.25	<0.13		<0.04			<0.05				
Whelks	Poole Bay	1		0.16	<0.12		<0.04	0.00051	0.0026	0.0003	*	2.5E-05		
Whelks	Lyme Regis	1		<0.07	<0.24		<0.06	0.00022	0.0017	0.0017	*	2.6E-05		
Scallops	Lulworth Ledges	1		<0.05	<0.13		<0.05	0.00031	0.0024	0.0005	*	*		
Clams	Portland Harbour	1		0.18	<0.28		0.08			<0.07				
<i>Fucus serratus</i>	Kimmeridge	2		0.33	<0.23	0.3	<0.07			<0.28				
<i>Fucus Serratus</i>	Bognor Rock	2		0.12	<20	0.6	<0.06			<0.06				
Seaweed	Lulworth Cove	2		<2.1		<1.0	<1.7			<2.5				
Seaweed	Lulworth Cove	2		<0.32			<0.25			<0.45			<2.8	15

## Hinkley

At this establishment, there are two separate 'A' and 'B' nuclear power Stations. Authorised discharges of radioactive liquid effluent from both power stations are made via a common cooling water outlet to the Bristol Channel. Analyses of seafood and marine indicator materials and measurements of external radiation over intertidal areas were carried out. The environmental results for 2005 are presented in Tables 26 (a) and (b). Where results can be compared, the concentrations observed in seafood and other materials from the Bristol Channel were generally similar to those in 2004

(see also Figure 26). Concentrations of tritium in cod and shrimps were similar to their levels in 2004. Concentrations of other radionuclides in the aquatic environment represent the combined effect of releases from these stations, plus other establishments that discharge into the Bristol Channel. Other contributors are Sellafield, GE Healthcare at Cardiff, weapons tests and Chernobyl fallout. Apportionment is generally difficult at the low levels detected. However, the majority of tritium and carbon-14 in seafood was likely to have been due to disposals from GE Healthcare, Cardiff. The concentrations of transuranic nuclides in seafoods were of negligible radiological significance. Gamma radiation dose rates over intertidal sediment, measured using portable instruments, were similar to those for 2004.

**Table 26, part A. Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Hinkley nuclear power station, 2005.**

Material	Location	No of samp. obs.	Organic <sup>3</sup> H	<sup>3</sup> H	<sup>14</sup> C	<sup>54</sup> Mn	<sup>60</sup> Co	<sup>90</sup> Sr	<sup>99</sup> Tc	<sup>125</sup> Sb	<sup>134</sup> Cs	<sup>137</sup> Cs	<sup>144</sup> Ce	<sup>155</sup> Eu
Cod	Stolford	2	320	330	30	<0.11	<0.11			<0.22	<0.11	<0.61	<0.38	<0.16
Shrimps	Stolford	2	240	260	44	<0.10	<0.10			<0.22	<0.11	<0.58	<0.39	<0.16
Whelks	Stolford	1		2300	67	<0.12	<0.12			<0.27	<0.12	<0.43	<0.51	<0.19
Seaweed	Pipeline	2					<2.2	<0.50	22	<0.10	<1.8	<1.9	<5.6	
Sediment	1.6 km East pipeline	2					<1.8	<0.13				<0.25		
Sediment	Pipeline	2					<0.78	<1.6				7.1		
Sediment	0.8 km west pipeline	2					<0.59	<1.4				4.1		
Sediment	Stolford	2					<0.73	<1.7				7.2		
Sediment	Stearr flats	2					<0.69	<1.7				16		
Sediment	River Parrett	2					<1.8	<1.6				38		
Seawater	Pipeline	2					<0.33	<0.020			<0.30	<0.24	<1.2	

**Table 26, part B. Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Hinkley nuclear power station, 2005 continued.**

Material	Location	No of samp. obs.	<sup>238</sup> Pu	<sup>239</sup> Pu + <sup>240</sup> Pu	<sup>241</sup> Am	<sup>242</sup> Cm	<sup>243</sup> Cm + <sup>244</sup> Cm	Total alpha	Total beta
Cod	Stolford	2			<0.09				
Shrimps	Stolford	2	0.0001	0.0005	0.0007	*	2E-05		
Whelks	Stolford	1			<0.09				
Seaweed	Pipeline	2			<2.4				
Sediment	1.6 km East pipeline	2			<2.4				
Sediment	Pipeline	2			<1.1				
Sediment	0.8 km west pipeline	2			<0.87				
Sediment	Stolford	2			<1.0				
Sediment	Stearf flats	2			<1.1				
Sediment	River Parrett	2			<2.4				
Seawater	Pipeline	2			<0.63			<2.4	14

\* not detected by the method used

## Dungeness

There are two separate nuclear power stations on the Dungeness site. Discharges are made via separate but adjacent outfalls and stacks, and for the purposes of environmental monitoring these are considered together. Marine monitoring included analysis of seafood and sediments. The results of monitoring for 2005 are given in Tables 27(a) and (b). Concentrations of radiocaesium in marine materials are attributable to discharges from the stations and to weapon test fallout with a long distance contribution from Sellafield. Apportionment is difficult at these low levels. The small concentrations of transuranics in whelks and sediment were typical of levels expected at sites remote from Sellafield. No tritium was detected in seafood.

**Table 27. Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Dungeness nuclear power station, 2005.**

Material	Location	No of samp. obs.	Organic <sup>3</sup> H	<sup>3</sup> H	<sup>14</sup> C	<sup>60</sup> Co	<sup>99</sup> Tc	<sup>242</sup> Cm	<sup>238</sup> Pu	<sup>239</sup> Pu + <sup>240</sup> Pu	<sup>231</sup> Am	<sup>243</sup> Cm + <sup>244</sup> Cm	Total alpha	Total beta
Plaice	Pipeline	2	<25	<25		<0.10					<0.17			
Cod	Pipeline	1		<25		<0.05					<0.12			
Whiting	Pipeline	1		<25		<0.07					<0.07			
Bass	Pipeline	1		<25		<0.05					<0.13			
Crabs	Hastings	1				<0.04					<0.19			
Shrimps	Pipeline	2	<25	<25	34	<0.13					<0.11			
Whelks	Pipeline	2				<0.11		*	0.0007	0.0031	0.005	0.0002		
Cuttlefish	Hastings	1				<0.19					<0.13			
Seaweed	Copt Point	2				<1.4	<2.5				<1.7			
Mud and sand	Rye Harbour	2				<0.67		*	0.051	0.26	0.23	0.011		
Sediment	Rye Harbour1	2				<0.79					<1.2			350
Sediment	Rye Harbour 2	2				<0.90					<1.3			170
Sediment	Chamber Sands	2				<0.56					<0.79			
Seawater	Pipeline	2		47										
Seawater	Dungeness South	2				<0.37					<0.47		<2.8	15

### Radiochemical Production

GE Healthcare manufactures radioactively labelled materials for use in medicine, research and industry. The company's principal establishment is located in Amersham, Buckinghamshire although it also operates from Cardiff. The Cardiff laboratory produces radiolabelled compounds used in research and diagnostic kits used in medicine. Liquid wastes are discharged into public sewers, which after passing through a new wastewater treatment works discharges into the Severn estuary near Orchard Ledges.

The results of routine monitoring in 2005 are presented in Table28. The main effect of liquid discharges is seen in enhanced tritium and carbon-14 activities in samples above background levels.

**Table 28. Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Cardiff, 2005.**

Material	Location	No. of samp. obs.	Organic <sup>3</sup> H	<sup>3</sup> H	<sup>14</sup> C	<sup>99</sup> Tc	<sup>125</sup> I	<sup>131</sup> I	<sup>134</sup> Cs	<sup>137</sup> Cs	<sup>155</sup> Eu
Cod	East new pipeline	1		510	30			*	<0.16	0.72	<0.22
Flounder	East new pipeline	3	9700	11000	120			*	<0.09	0.55	<0.16
Sole	East new pipeline	2		6500	130			*	<0.17	0.35	<0.23
Mullet	East new pipeline	1		83	44			*	<0.08	0.41	<0.19
Lesser spotted dogfish	Off Orchard ledges	2	1100	1200	51			*	<0.14	0.6	<0.30
Skates Rays	Off Orchard ledges	2	1600	1800	82			*	<0.10	1.1	<0.18
Mussels	Orchard ledges	2	3000	3300	60			*	<0.13	0.58	<0.27
Fucus vesiculosus	Orchard ledges	2	67	81	23			*	<0.08	0.62	<0.17
Seaweed	Orchard ledges	2		64	<25	<7.6	<1.6				
Mud	Orchard Ledges East	2	68	87				<6.8	1.8	28	<2.3
Sediment	East new pipeline	2		130	<25		<0.74			13	
Sediment	West new pipeline	2		85	<25		<0.74			13	
Seawater	Orchard Ledges East	2		10							
Seawater	Orchard Ledges	2		12	<4.0			<0.25			

The results of sample analyses show that virtually all of the total tritium in marine samples was associated with organic matter. The tritium is strongly bound to organic matter and has the potential to transfer through the marine foodchain from small organisms to accumulate in fish. Since early 2004, limits were reduced for all the radionuclides and the management conditions were improved. Future arisings of carbon 14 and tritium will be treated where possible to reduce and recycle the radionuclides. Provided the treatment plant is successful this should significantly reduce the discharges of tritium and carbon-14 in the future.

Discharges of organic tritium in 2005 were similar to those in 2004. The current levels of discharge are likely to be maintained until the plant becomes fully operational. Data indicate that a significant proportion of the tritium present in water is associated with organic matter. Concentrations of other radionuclides in aquatic samples were low and can largely be explained by other sources such as Chernobyl, weapon test fallout and discharges from other establishments.



#### 4.2.4 Defence Establishments

##### Devonport, Devon

Devonport consists of two parts: the Naval Base, which is owned and operated by the MoD, and Devonport Royal Dockyard, which is owned and operated by Devonport Royal Dockyard Limited (DRDL). DRDL refits, refuels, repairs and maintains the Royal Navy's nuclear powered submarines and has an authorisation granted by the Environment Agency to discharge liquid wastes to the Hamoaze, which is part of the Tamar Estuary and to the local sewer and gases, mists and dusts to atmosphere. The MoD Naval Base is permitted to discharge liquid wastes to the sewer under an administrative agreement with the Environment Agency. The routine monitoring programme in 2005 consisted of measurements of gamma dose rate and analysis of fish, shellfish, fruit, grass and sediments. The results given in Tables 29(a) and (b) were similar to those in 2004 where comparisons can be drawn. Trace quantities of caesium-137, technetium-99 and americium-241 were found in the marine environment. These were most likely to have originated from Chernobyl and from spent fuel reprocessing elsewhere. Activation products were below LoDs.

**Table 29, part A. Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Devonport, 2005.**

Material	Location	No sampling Observations	Organic <sup>3</sup> H	<sup>3</sup> H	<sup>14</sup> C	<sup>54</sup> Mn	<sup>60</sup> Co	<sup>65</sup> Zn
Ballan Wrasse	Plymouth Sound	2				<0.12	<0.09	<0.35
Crabs	Plymouth Sound	1			18	<0.13	<0.11	<0.31
Shrimps/prawns	Lynher Estuary	1			39	<0.18	<0.15	<0.45
Winkles	Torpoint (South)	1				<0.23	<0.19	<0.58
Cockles	Southdown	1				<0.17	<0.18	<0.40
Mussels	R Lynher	2	<25	<25		<0.08	<0.08	<0.22
Fucus vesiculosus	Kinterbury	2				<0.08	<0.09	<0.23
Mud	Kinterbury	2				<0.75	<0.68	<1.8
Sediment	Torpoint (South)	2		<25			<1.3	
Sediment	Loowell	2		<25			<1.4	
Seawater	Torpoint (South)	2		<4.0	<4.0		<0.31	

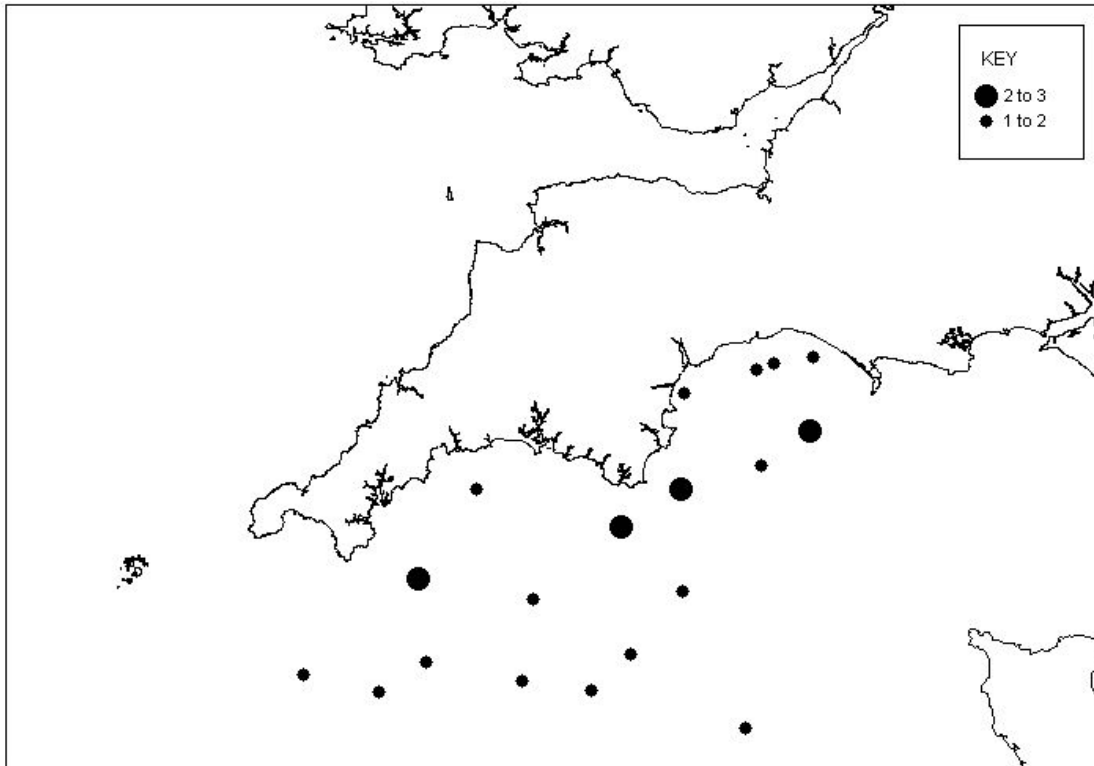
**Table 29, part B. Mean radioactivity concentration (wet), Bq kg<sup>-1</sup> in marine organisms sampled in the vicinity of Devonport, 2005.**

Material	Location	No sampling Observations	<sup>125</sup> Sb	<sup>131</sup> I	<sup>134</sup> Cs	<sup>137</sup> Cs	<sup>155</sup> Eu	<sup>241</sup> Am
Ballan Wrasse	Plymouth Sound	2	<0.20	*	<0.10	0.18	<0.15	<0.07
Crabs	Plymouth Sound	1	<0.23	*	<0.11	0.09	<0.16	<0.08
Shrimps/prawns	Lynher Estuary	1	<0.40	*	<0.17	0.14	<0.35	<0.32
Winkles	Torpoint (South)	1	<0.44	*	<0.20	0.17	<0.28	<0.13
Cockles	Southdown	1	<0.37	*	<0.18	0.15	<0.25	<0.13
Mussels	R Lynher	2	<0.19	*	<0.08	0.10	<0.16	<0.12
Fucus vesiculosus	Kinterbury	2	<0.16	*	<0.09	0.16	<0.16	<0.12
Mud	Kinterbury	2	<1.7	<5.4	<1.2	3.3	<2.3	0.12
Sediment	Torpoint (South)	2				<1.4		
Sediment	Lopwell	2				<3.3		
Seawater	Torpoint (South)	2						

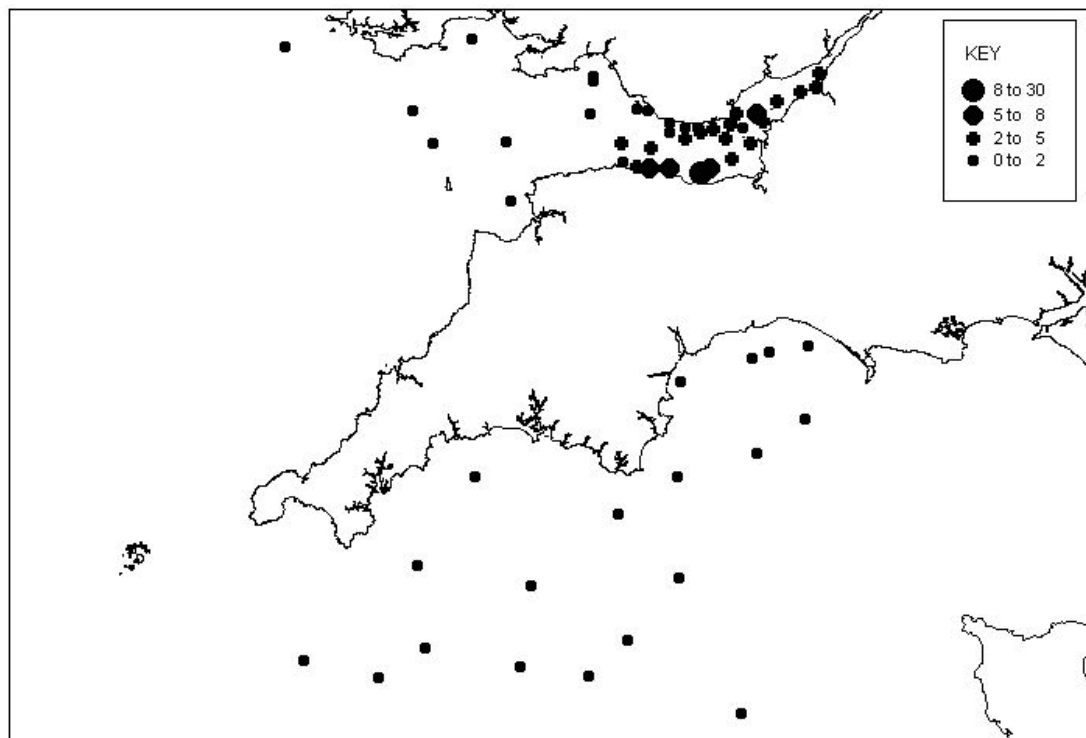
#### 4.2.5 Wider radionuclide distribution

##### 4.2.5.1 In seawater

The research vessel programme on radionuclide distribution includes Annual surveys of the Bristol Channel/western English Channel. The results of the 2002 cruises are presented in Figures 26 and 27. Those radionuclides that are relatively soluble in seawater (e.g. <sup>3</sup>H, <sup>90</sup>Sr, <sup>99</sup>Tc, Cs, <sup>129</sup>I) tend to be dispersed. Concentrations of caesium-137 in the western English Channel ranged from 0.001-0.003 Bq l<sup>-1</sup> with an average concentration of 0.0017 Bq l<sup>-1</sup> (Figure 26). Slightly enhanced levels apparent along some of the European coastline were likely to be the result of discharges from La Hague (France) nuclear reprocessing plant. Detectable <sup>3</sup>H concentrations were observed in the Severn estuary near the points of release from the Amersham plc radiopharmaceutical plant at Cardiff and the Hinkley Point nuclear power station (Figure 27). The greatest concentrations (up to ~30 Bq l<sup>-1</sup>) were observed on the English side in the vicinity of the Hinkley Point nuclear power station, compared with <5Bq l<sup>-1</sup> in the vicinity of Amersham facility at Cardiff. Outside of the typical tidal excursion downstream of the points of discharge <sup>3</sup>H concentrations decrease rapidly.



**Figure 26. Concentration of  $^{137}\text{Cs}$  (mBq kg $^{-1}$ ) and  $^3\text{H}$  (mBq kg $^{-1}$ ) in surface seawater in the Bristol Channel (September 2001).**



**Figure 27. Concentration of  $^{137}\text{Cs}$  (mBq kg $^{-1}$ ) and  $^3\text{H}$  (mBq kg $^{-1}$ ) in surface seawater in the English Channel (September 2001).**

### **4.3 CONCLUSIONS**

- Most of the artificial radioactivity detected in the SEA8 area was due to tritium and radiocaesium. Concentrations of radiocaesium represent the combined effect of discharges from the sites, other nuclear establishment discharges, particularly in the Bristol Channel, and weapons testing, and possibly a small Sellafield-derived component.
- For the Bristol Channel for which the highest tritium and carbon-14 levels were recorded for the SEA8 area, source apportionment is generally difficult at the low levels detected. However; the majority of tritium and carbon-14 in seafood was likely to have been due to disposals from GE Healthcare, Cardiff.
- In each of the sample categories, the effects were localised and were not observed further a field in the water or indeed in seafood.
- Abatement technology is being introduced at Cardiff. Future arisings of carbon 14 and tritium will be treated where possible to reduce and recycle the radionuclides. Provided the treatment plant is successful this should significantly reduce the discharges of tritium and carbon-14 in the future.
- Slightly enhanced levels of caesium-137 apparent along some of the European coastline were likely to be the result of discharges from La Haque (France) nuclear reprocessing plant.

## **5 GENERAL DISCUSSION AND CONCLUSIONS**

### **5.1 INPUTS (PRESSURES)**

With the exception of phosphates for which sewage inputs make a comparable level of contribution, riverine inputs are the dominant source of contaminants to the SEA8 area. This reflects the importance of diffuse sources such as runoff from agricultural land and urban runoff via surface drains and storm overflows. The SEA8 area also lacks offshore oil and gas development activity, which is a potential source of particular contaminant groups in SEA2 and SEA6. Other relatively less significant contaminant inputs include small marine incidents that result in chemical spills. Although there have been three more major marine incidents in the SEA8 area these did not result in prolonged or widespread contamination.

### **5.2 CONCENTRATIONS IN THE ENVIRONMENT (STATE)**

The concentrations of dissolved contaminants in the seawater samples of the SEA8 area were either low or below detection limits with current analytical tools. This was mainly due to the characteristics of the individual compounds (i.e. hydrophobic and/or partitioning to suspended particles), which have a tendency to collect in either sediment and /or biological tissues. Of those contaminants that were detected, highest concentrations were generally found in seawater samples collected from coastal waters in close proximity to industrial inputs such as the Severn estuary. Metal EQSs and alkylphenol MACs were not exceeded at any of the CSEMP stations within the SEA8 area. In contrast, many PAH concentrations exceeded their MACs at

Southampton, Tamar and at the mouth of the River Severn. However, PAH concentrations were not detected in seawater samples taken further offshore.

As might be expected, most sediment contaminant concentrations were at least 3 orders of magnitude higher than those measured in seawater samples. With the exception of alkylphenols, which were undetected in all sediment samples, highest concentrations of all contaminants measured in sediment samples were consistently found at the mouth of the River Severn/ Bristol channel. The proximity of this area to industrialised centres (e.g. Bristol, Cardiff, Swansea) was likely to be responsible for the higher concentrations of contaminants. Elevated concentrations of metals were also found at the mouth of the River Tamar. Historical mining activity was thought to be the major contributor to the high sediment metal loads within this area.

Contaminant concentrations in biological tissues are dependent on a variety of factors such as contaminant characteristics, bioaccumulation factors, tissue type and detoxifying mechanisms of the organisms concerned. Comparison of the contaminant data between sediments and biota revealed a good relationship with highest concentrations of contaminants found in species collected from areas of high sediment contamination (e.g. Severn estuary). This was the case for mussel and dab samples. Bioaccumulation of contaminants in marine mammals appeared to be responsible for the significantly higher contaminant concentrations measured. This is compounded by their high trophic level, long life span and limited ability for detoxification and excretion.

Overall contaminant concentrations irrespective of sample matrix were lower in the SEA8 area compared to the other coastal waters of the UK such as the Irish Sea (SEA6) and North Sea (SEA2). This may be partly due to the larger riverine component of the North and Irish Seas, and the stronger influence of North Atlantic water in the English Channel, creating increased water flux and dilution. The lack of offshore oil activity within the SEA8 may also be a factor in the relatively low contaminant concentrations in the area.

Oil and natural gas deposits are associated with solids and formation water, which contain naturally radioactive salts. These salts are frequently released in produced water at activity concentrations of less than  $0.1\text{Bq g}^{-1}$  to  $1000\text{ Bq g}^{-1}$ . The radioactivity from oil and gas production is associated with different compounds and isotopes to those typically measured in estuarine and coastal areas and that arise from industrial sources. Radioactivity from oil and gas production is also generally low by comparison to the specific activity associated with many man-made radioactive sources. The disposal of radioactive scales from offshore structures can however present some environmental concerns as this represents a concentrated input source. In the SEA8 area the absence of offshore exploitation of oil and gas deposits means that radioactivity measured in this area originates from other sources. The highest inputs recorded here are those for  $^3\text{H}$  in fish (mean wet concentration  $11\text{ Bq g}^{-1}$ ) sampled in the vicinity of Cardiff. However in the vicinity of a coastal power station such as Dungeness equivalent levels of activity measured in fish are  $<0.025\text{ Bq g}^{-1}$ .

### **5.3 EFFECTS ON BIOTA (IMPACTS)**

With the exception of the elevated levels of imposex in dog whelks (indicative of tributyl tin exposure), collected in selected coastal sites with the SEA8, the low

contaminant concentrations measured were reflected in the biological effects data. Although data for many of the biological effects measured in dab populations were often sparse, the level of biological effect activity measured, indicates low contaminant exposure by comparison to samples from other SEA areas. The same was also true for mussel populations for which measures of stress for many of the groups sampled were also indicative of low levels of exposure to contaminants. Overall, from chemical and biological effects data, the SEA8 was considered as a relatively clean area.

## **6. GAPS IN OUR UNDERSTANDING AND FUTURE RISKS**

This report has highlighted that there are fewer datasets available for chemical and particularly biological effects data in the SEA8 area for which environmental status was evaluated. There are also less UK CSEMP sites within the SEA8 from which data could be obtained. The relatively fewer industrial riverine inputs into the English Channel as well as the lack of offshore oil and gas installations within the area may make this area less of a focus than some of the more northerly industrialised locations. With the potential variations in rainfall frequency and intensity, temperature and sea level that are forecast as a result of climate change it will be important to establish good baseline datasets in areas such as SEA8. Particularly as climate change factors may influence contaminant mobilisation and bioavailability and hence impact good ecological status of many locations within the SEA8 area. Monitoring programs should therefore address this gap in information.

With the overall objective of good status in all River Basins to be achieved by December 2015 under the Water Framework Directive the integration of biological effects data with chemical status information will also become increasingly important.

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## 8. GLOSSARY

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