Science Series
Aquatic Environment Monitoring Report no. 63

Monitoring of the quality of the marine environment, 2008–2010

Cefas

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Foreword

Aquatic Environment Monitoring Report No. 63 collects together work carried out in 2008–2010 by Cefas scientists in support of our monitoring and surveillance duties (see Background to the Work). The information presented covers both environmental surveillance at offshore and coastal sites and site-specific work carried out in support of risk assessments and regulatory procedures. Some of the science reported here forms a part of wider efforts to integrate data from Departments and Agencies in the UK, including those of the Devolved Administrations, to provide a comprehensive picture of the quality of the marine environment within the UK's nationally co-ordinated marine monitoring programme. Other components are unique to Cefas due to our requirement to understand ecosystem response resulting from potential pressures from deposit, extraction, discharge and construction activities. The strategy for the national monitoring programme is set within the UK Marine Monitoring and Assessment Strategy (UKMMAS). The overall aim of the UKMMAS is to shape the UK's capability, within national and international waters, to provide the evidence required for sustainable development within a clean, healthy, safe, productive and biologically diverse marine ecosystem and, within one generation, to make a real difference. The programme manual, known as the Green Book, is available in downloadable format from http://cefas.defra.gov.uk/publications/scientific-series/green-book.aspx accessed 27 June 2012.

The programme seeks to develop time trend data for a number of sites around the UK and this work is augmented by special surveys of compounds likely to pose specific risks, or for which few data exist.

The Defra report Safeguarding our Seas (Defra, 2002) set out a vision for 'clean, healthy, safe, productive and biologically diverse seas '. It started a process which has changed the UK's approach to monitoring and assessment of our seas. The next stage in this process was the preparation of the first integrated assessment of our seas, Charting Progress (Defra, 2005). This provided a baseline for the state of our marine environment at that time, and much was learnt from the process of its preparation. Charting Progress proposed a number of action, including the development of the UKMMAS. Within this strategy, four evidence groups have been established to collate data on the themes of:

- Clean and Safe Seas
- Healthy and Biologically Diverse Seas
- Productive Seas
- Ocean processes

So as to make explicit the links between the topics covered in this report and the aims of the UKMMAS, topics have been grouped under the first three of these headings. The process has recently been taken further, with the preparation of a second integrated assessment report, Charting Progress 2, which was published in 2010 (Defra, 2010). An OSPAR Quality Status Report for the NE Atlantic region was also published in 2010 (OSPAR, 2010).

This report, earlier reports in the AEMR series and other publications are also available in downloadable format from the Cefas website: http://www.cefas.defra.gov.uk/

Robin Law
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Background to the work

As an Executive Agency of the Department for Environment, Food and Rural Affairs (Defra), Cefas carries out work in support of Defra's strategic priorities, all of which underpin the overarching aim of ensuring that everyone can live within their environmental means.

Within this framework, environmental work at Cefas is directed at research, monitoring and assessment of the impact of potentially harmful substances or activities on the quality of the marine, coastal and estuarine environments. We are involved directly in advising on UK and international legislation and in developing policy relating to management of the aquatic environment. We provide advice to Governments, enforcement agencies and policymakers throughout the world on the development and implementation of monitoring and assessment programmes and control measures.

An important component of our work is to provide advice to Ministers in Defra and other government departments on all aspects of non-radioactive contamination of the aquatic environment.

For the year 2010, the deposit of substances and articles in the sea, principally the disposal of dredged material (as opposed to discharge into the sea via pipelines) and the use of material during marine construction (eg windfarms and port developments) and coastal defence works, was controlled by a system of licences issued under Part II of the Food and Environment Protection Act 1985 (as amended) (FEPA) (Great Britain Parliament, 1985a). Certain operations (eg the deposit of scientific equipment or navigation aids) were exempt from licensing under the Deposit in the Sea (Exemptions) Order 1985 SI 1985 No. 1699 (Great Britain Parliament, 1985b). The marine licensing provisions of the Marine and Coastal Access Act 2009 that came into force on 1st April 2011 have now taken over from Part II of FEPA for the licensing function in England, Wales and Northern Ireland (Great Britain Parliament, 2009) . In Scotland, the marine licensing provisions of the Marine (Scotland) Act 2010 took over the licensing function from FEPA on the same date. Following devolution in 1999, Defra (then MAFF) continued to license deposits in the sea around the Welsh coast on behalf of the Welsh Assembly Government. On 1st April 2007 the responsibility for the licensing function in England and Wales transferred from Defra to the Marine and Fisheries Agency (MFA). Subsequently, the Marine Management Organisation (MMO) took over this responsibility in England from 1st April 2010 and the Welsh Assembly Government took over this responsibility in Wales at the same time. During 2010, the licensing function in Scotland was the responsibility of Marine Scotland and in Northern Ireland it was the responsibility of the Northern Ireland Environment Agency. Disposal at sea is also regulated by OSPAR, and our work enables the UK to fulfill its obligations as a Contracting Party to the Convention.

The Cefas Regulatory Advice Team evaluates scientific and technical aspects of licence applications and makes regular visits to licence holders to ensure that any stipulated conditions are being met. Conducting monitoring programmes in support of risk assessments enables Defra to ensure the effectiveness of the assessment process and provides a basis for decisions on future policy for the management of marine resources. Cefas scientists monitor the environmental conditions at marine disposal sites (see, for example, Bolam *et al.* 2011) and compare the results with those obtained during more general monitoring studies, allowing action to be taken if unexpected impacts should occur. This also provides a feedback loop which ensures that risk assessments undertaken within the licensing process incorporate the most recent research findings.

Under the Water Resources Act (1991) (Great Britain Parliament, 1991), Defra is a statutory consultee for all controlled discharges to controlled (tidal) waters. Cefas scientists assess the fishery implications of applications for consent to discharge permits. Consideration is given to resources in the area, the toxicity of the effluent, local hydrographic conditions and any standards set out in national policy or EU Directives.

Under the requirements of the EU Marine Strategy Framework Directive (MSFD) (EU, 2008), member states are required to assess their waters with respect to demonstrating, or moving towards, 'Good Environmental Status' (GES). Cefas is working with Defra and the Joint Nature Conservation Committee to establish criteria by which GES might be assessed for each of the 11 descriptors established under MSFD, and also contributes to the Evidence Groups established under UKMMAS which will provide the necessary data for the initial and subsequent assessments.

We also provide advice to the Department of Energy and Climate Change (DECC) and other departments concerning the control of pollution in other areas affecting the marine environment, including the offshore extraction of oil and gas and marine aggregates. The statutory Offshore Chemical Notification Scheme and the Environmental Impact Assessment and Natural Habitats (Extraction of Minerals by Marine Dredging) (England and Northern Ireland) Regulations on the winning of aggregates, respectively, control these activities.

On Defra's behalf, Cefas is responsible for monitoring intermediate and offshore stations around England and Wales within the UK Clean Seas Environment Monitoring programme (CSEMP), which seeks to integrate national and international monitoring programmes for all relevant UK government agencies. The data gathered are assessed by the Clean and Safe Seas Evidence Group (CSSEG) within UKMMAS. Each year, we collect samples of seawater, sediment and biota for chemical analysis and deploy a number of biological effects techniques, including water and sediment bioassays and fish disease surveys. An integrated process for gathering and assessing chemical and biological effects data is currently under development within ICES/OSPAR, with Cefas input. The current phase of the monitoring programme is focussed on the detection of long-term temporal trends in contaminant concentrations and the development and deployment of a wider range of validated biological effects techniques at a variety of cellular and subcellular levels. Some of the data derived from these studies are summarised in this report. The CSEMP allows us to ascertain the effectiveness of regulatory measures takne to reduce the inputs of hazardous substances to UK seas. In addition, it contributes to the UK's international monitoring obligations to demonstrate compliance with various EU Directives; Dangerous Substances Directive (76/464/EEC); Shellfish Hygiene Directive (79/923/EEC); Fishery Products Directive (91/493/EEC); the Commission Decision 93/351/EEC concerning maximum mercury limits in fishery products, and similar requirements under OSPAR. Currently, a group led from within Cefas is working to redesign our component of the CSEMP so as to ensure that it meets current requirements (under MSFD, for example) and, as far as possible, dovetails with monitoring undertaken within 1 nautical mile of the coast around England and Wales (as well as in rivers and estuaries) by the Environment Agency under the EU Water Framework Directive (2000/60/EC).

In order to ensure that the advice provided to Defra and other regulators is always based on the most up-to-date knowledge and techniques, Cefas carries out a wide range of applied research and development to provide for the future needs of monitoring and surveillance programmes. For example, we have made a number of significant contributions to environmental protection and, as a consequence of our work, have established a worldwide reputation in the field of aquatic environmental research.

More information on our research programmes is available on the Cefas website: www.cefas.defra.gov.uk

Glossary of terms

AQC	Analytical Quality Control
BAC	Background Assessment Concentration (under OSPAR)
BDE	Brominated diphenyl ether (a PBDE congener)
BDE209	Decabromodiphenyl ether
BEQUALM	Biological Effects Quality Assurance in Monitoring Programmes
BN	Benign neoplasms
CB	Chlorobiphenyl (a PCB congener)
Cefas	The Centre for Environment, Fisheries and Aquaculture Science
CEMP	Co-ordinated Environmental Monitoring Programme (of OSPAR)
CSEMP	Clean Seas Environment Monitoring Programme
CSIP	Cetacean Strandings Investigation Programme
CSSEG	Clean and Safe Seas Evidence Group
CYP1A	Cytochrome P450 1A
DECC	Department for Energy and Climate Change
Defra	Department for Environment, Food and Rural Affairs
DNA	Deoxyribonucleic acid
EA	Environment Agency
EAC	Environmental Assessment Criteria (under OSPAR)
EC	European Community
ECNI	Electron capture negative ionisation MS mode
ENTL	Early non-neoplastic toxicoplastic lesions
EQS	Environmental Quality Standard
ERL	Effects Range Low
ERM	Effects Range Median
EROD	7-ethoxyresorufin-*O*-deethylase (an enzyme)
EU	European Union
FCA	Foci of cellular alteration
FEPA	Food and Environment Protection Act 1985
GC-MS	Coupled gas chromatography-mass spectrometry
GES	Good Environmental Status (under the MSFD)
HMW PAH	High molecular weight polycyclic aromatic hydrocarbons
IBTS	International bottom trawl survey
ICES	International Council for the Exploration of the Sea
ICP-AES	Inductively-coupled plasma-atomic emission spectrometry
ICP-MS	Inductively-coupled plasma-mass spectrometry

IMO	International Maritime Organisation
JAMP	Joint Assessment and Monitoring Programme (of OSPAR)
JRC	Joint Research Centre (of the EU)
LMW PAH	Low molecular weight polycyclic aromatic hydrocarbons
LSD	Fisher's least significant difference
MAFF	Ministry of Agriculture, Fisheries and Food (forerunner of Defra)
MERMAN	Marine Environment Monitoring and Assessment National database
MFA	Marine and Fisheries Agency (forerunner of the MMO)
MMO	Marine Management Organisation
MN	Malignant neoplasms
MPMMG	Marine Pollution Monitoring Management Group
MPN	Most probable number
MS	Mass spectrometry
MSFD	Marine Strategy Framework Directive (of the EU)
NIEA	Northern Ireland Environment Agency
NMMP	National Marine Monitoring Programme
NOAA	National Oceanic and Atmospheric Administration (of the USA)
NSIL	Non-specific and inflammatory lesions
OSPAR	Commission for the Protection of the North-east Atlantic
PAH	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diphenyl ether flame retardants
PCBs	Polychlorinated biphenyls
PHH	Planar halogenated hydrocarbons
PSA	Particle Size Analysis
PSD	Particle Size Distribution
QUASIMEME	Quality Assurance of Information for Marine Monitoring in Europe
RPSI	Relative Penis Size Index
SEPA	Scottish Environment Protection Agency
SHS	Shellfish hygiene system database
SIXEP	Site Ion Exchange Effluent Plant (at BNFL Sellafield)
SQG	Sediment quality guidelines
TBT	Tributyltin
UKMMAS	UK Marine Monitoring and Assessment Strategy
VDSI	Vas deferens Sequence Index
WFD	Water Framework Directive (of the EU)

Highlights

- Concentrations of caesium-137 in the Irish Sea have declined since the previous survey undertaken in 2007 (Chapter 1).
- The influence of sediment type and organic carbon content on concentrations of contaminants in sediments around England and Wales has been assessed (Chapter 2).
- Elevated concentrations of mercury and lead were observed in sediments from the Irish Sea (CSEMP 715 and CSEMP 805) and of lead also off the Tyne/Tees area of NE England (Chapter 3).
- The highest levels of polycyclic aromatic hydrocarbons in sediments were observed off NE England (CSEMP 245) as a result of historical contamination of local estuaries (Chapter 4).
- Concentrations of brominated diphenyl ethers (BDEs – flame retardant compounds) in sediments were dominated by BDE209, contributing 75–100% of the total (Chapter 5).
- Of three areas in which sediments were analysed, the highest concentrations of chlorobiphenyls (CBs) were found in the Bristol Channel/Celtic Sea area and of BDEs in the Tyne/Tees area. In the English Channel, concentrations were generally low for both (Chapter 6).
- Concentrations of CBs in dab liver are not showing significant downwards trends despite regulation having been in force for *ca.* 30 years, suggesting that they will remain elevated for many years to come (Chapter 7).
- Concentrations of mercury (in dab muscle), cadmium and lead (in dab liver) were elevated in some areas adjacent to industrialised estuaries. A positive temporal trend was observed for cadmium and lead off the Tyne, which nonetheless showed concentrations well below the EC food limit values (Chapter 8).
- During the period 2003–2010, concentrations of BDEs in dab liver have been declining steeply at the majority of sampling sites (Chapter 9).
- There has been an overall increase in shellfish waters classified as class B and a decrease in those classified as class C, indicating a general decrease in faecal contamination of harvesting areas (eg, from sewage discharges) (Chapter 10).
- An initial assessment of offshore seabed litter has been made, indicating higher levels of litter off the west coast of England and Wales than in the North Sea (Chapter 11).
- Following controls on the use of PBDEs within the EU, concentrations of BDEs in porpoise blubber have decreased by approximately two-thirds, but falls in CB concentrations have stalled and are likely to remain high for decades (Chapter 12).
- An approach to the age-corrected measurement of liver disease in dab which could be employed as part of an assessment of good environmental status for Descriptor 8 (contaminants are not at levels giving rise to pollution effects) under the Marine Strategy Framework Directive has been developed (Chapter 13).
- An approach to the integrated assessment of chemical and biological effects monitoring for polycyclic aromatic hydrocarbons has been described (Chapter 14).
- Sediment bioassays have been applied to toxicity assessment at a dredged material disposal site in Tees Bay (Chapter 15).
- The incidence and severity of imposex (the imposition of male sexual characteristics on female dogwhelks) has continued to decline following a ban on the use of tributyltin in antifouling paints applied to ships (Chapter 16).
- Information is provided on advice which Cefas gives in relation to fishery implications of pipeline discharges and the licensing of deposits in the sea (Chapters 17 and 18).

Clean and Safe Seas

1. Radioactivity in UK coastal waters

Authors: Kins Leonard and Paul Smedley

1.1 Topic and background

Radioactivity in the environment comes from several sources, including permitted radioactive discharges from both nuclear and non-nuclear sites, residues from the Chernobyl accident and atmospheric testing, plus natural radiation. The UK Government is committed to preventing pollution of the marine environment from ionising radiation, with the ultimate aim of reducing concentrations in the environment to near background values for naturally occurring radioactive substances, and close to zero for artificial radioactive substances (Department of Energy and Climate Change, Department of the Environment, Northern Ireland,The Scottish Government and Welsh Assembly Government, 2009).

Results from the distribution of concentrations of key radionuclides in UK coastal waters provide evidence of progress towards achievement of the Government's vision. These results also support International studies concerned with the quality status of coastal seas (eg OSPAR, 2010). The programme of radiological surveillance provides the source data and therefore the means to monitor and make an assessment of progress in line with the UK's commitments towards OSPAR's 1998 Strategy for Radioactive Substances target for 2020.

1.2 Sampling undertaken in previous years

The research vessel programme used to determine radionuclide distributions comprises of biennial surveys of the Irish Sea and the North Sea, together with smaller annual surveys of the Bristol Channel and the western English Channel. Surface seawater samples were collected to determine caesium-137 and tritium concentrations.

1.3 Summary of results obtained

The 2008 caesium-137 data for the North Sea (Figure 1.1) show very low activities (< 0.01 Bq l^{-1}) throughout the majority of the survey area, In 2008, typically high activities were observed at two stations close to the Norwegian Coast, due to the input of Chernobyl-derived caesium-137 from the Baltic, via the Skagerrak. The 2008 survey also indicates a few anomalous results of slightly elevated caesium-137 in the southern North Sea. These are likely to be outliers, or the outcome of complex water circulation from an unknown source (possibly Chernobyl-derived).

The 2009 caesium-137 data for the Irish Sea (Figure 1.2) show a band of higher concentrations along the coast to the north and south of Sellafield, with levels decreasing with distance from the coast. Slightly raised levels are evident to the southeast of the Isle of Man, possibly an indication of re-dissolution of caesium-137 from the eastern Irish Sea mud patch.

As expected, the tritium concentrations observed in the Irish Sea in 2009 (Figure 1.3) are higher than those observed in the North Sea in 2008 (Figure 1.4), due to the influences from Sellafield and other nuclear sites. The majority of samples to the south and west of the Isle of Man contained tritium concentrations below the limit of detection.

In the Bristol Channel, the combined effect of tritium discharges from Cardiff, Berkeley, Oldbury and Hinkley Point nuclear sites remains evident in samples from points close to these installations (Figure 1.5). However, the general level is low (~ 3 Bq l^{-1}) and many samples were below the limits of detection in both 2008 and 2009.

Caesium and tritium concentrations in the western English Channel were low (~ 0.002 Bq l^{-1} and ~ 2 Bq l^{-1}, respectively) in both 2008 and 2009.

1.4 Length of time series available

For the purpose of OSPAR evaluations, Cefas has radionuclide data from these specific locations in the North and Irish Seas (given in the figures) since 1995. Additionally, Cefas has data sets for concentrations of radionuclides in UK coastal waters over a much longer period.

1.5 Summary of trend observed/not

Caesium-137 concentrations in the North Sea are only slightly above the global fallout levels in surface waters (~0.00012–0.0028 Bq l^{-1}, Povinec *et al.*, 2005). The overall distribution in the North Sea is characteristic of that observed in the previous 5 years. In the previous three decades the impact of discharges from the reprocessing plants at Sellafield and La Hague has been readily apparent, carried by the prevailing residual currents from the Irish Sea and the English Channel, respectively (Povinec *et al.*, 2003). The activity of caesium-137 in the North Sea has tended to follow the temporal trends of the discharges, albeit with a time lag.

Overall caesium-137 concentrations in the Irish Sea have decreased since the last Irish Sea survey in 2007 (Environment Agency, Food Standards Agency, Northern Ireland Environment Agency and Scottish Protection Agency, 2008), when levels above 0.1 Bq l^{-1} were observed, and are a fraction of their 1970s peak of up to 30 Bq l^{-1}.

The predominant source of caesium-137 to the Irish Sea is now considered to be remobilisation into the water column from activity associated with seabed sediment. Discharges from Sellafield have decreased substantially since the commissioning of the SIXEP waste treatment process in the mid 1980s, and this has been reflected in a near exponential decrease in shoreline seawater concentrations at St Bees (Figure 1.6).

The effect of reduced tritium discharges over the last decade, particularly from Cardiff, has resulted in much lower tritium concentrations in the Bristol Channel.

1.6 Graphics and illustrations

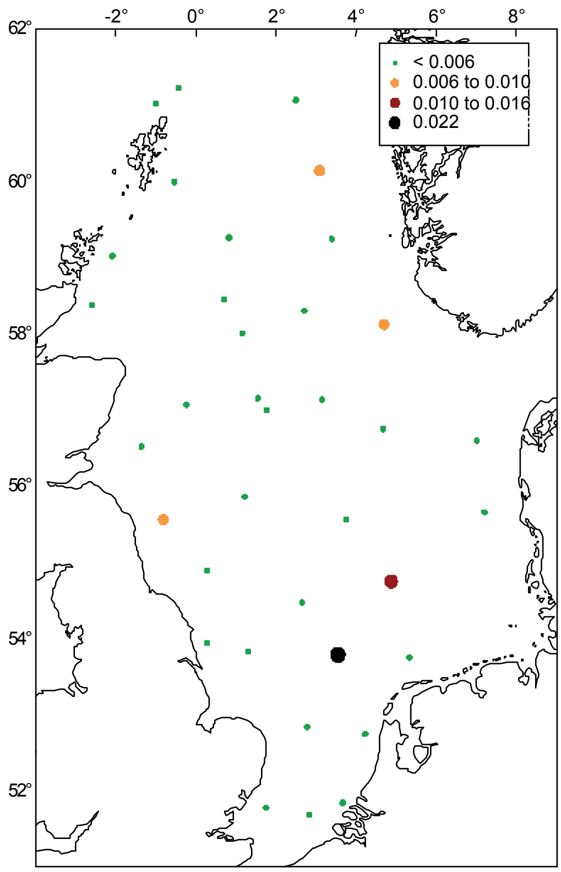


Figure 1.1. Concentrations (Bq l^{-1}) of caesium-137 in filtered seawater from the North Sea, August–September 2008.

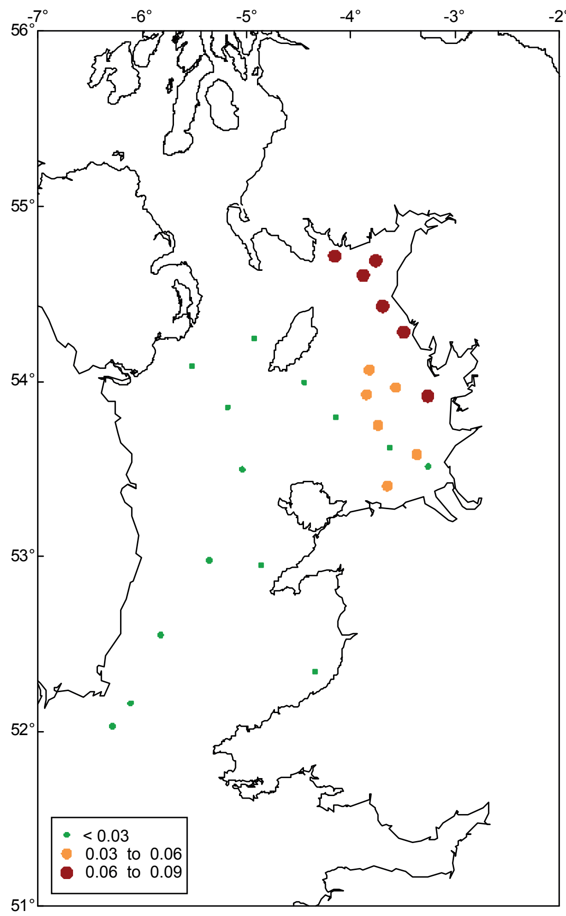


Figure 1.2. Concentrations (Bq l^{-1}) of caesium-137 in filtered surface water from the Irish Sea, July 2009.

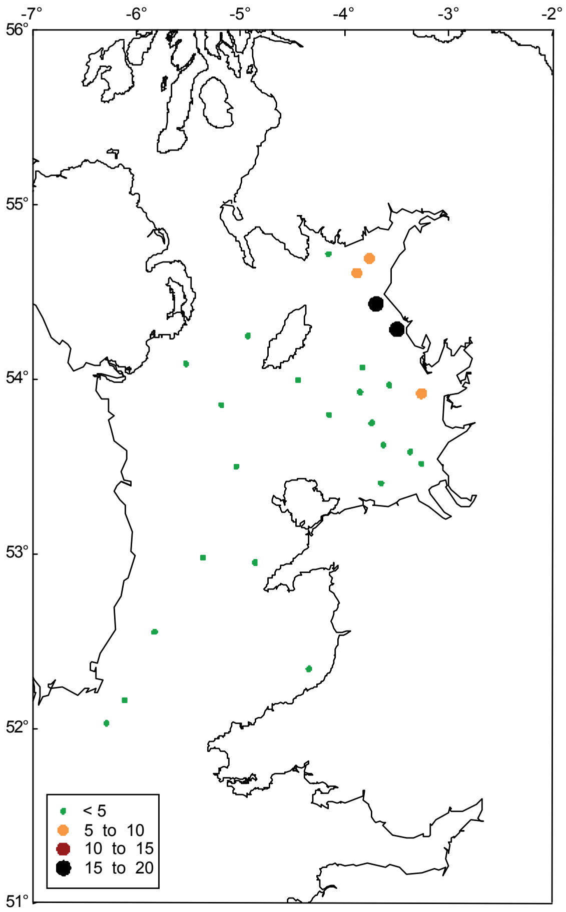


Figure 1.3. Concentrations (Bq l^{-1}) of tritium in surface water from the Irish Sea, July 2009.

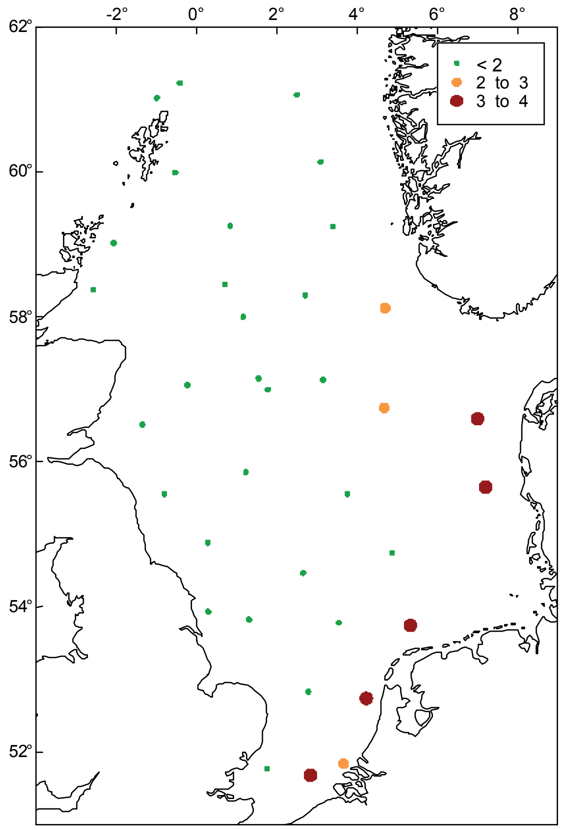
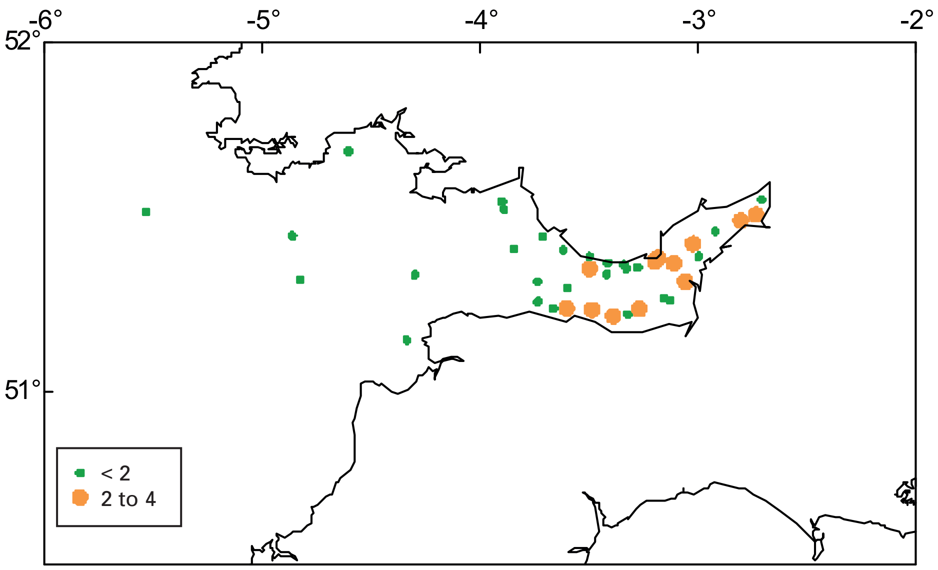


Figure 1.4. Concentrations (Bq l^{-1}) of tritium in surface water from the North Sea, August–September 2008.

Figure 1.5. Concentrations (Bq l^{-1}) of tritium in surface water from the Bristol Channel, September 2009.



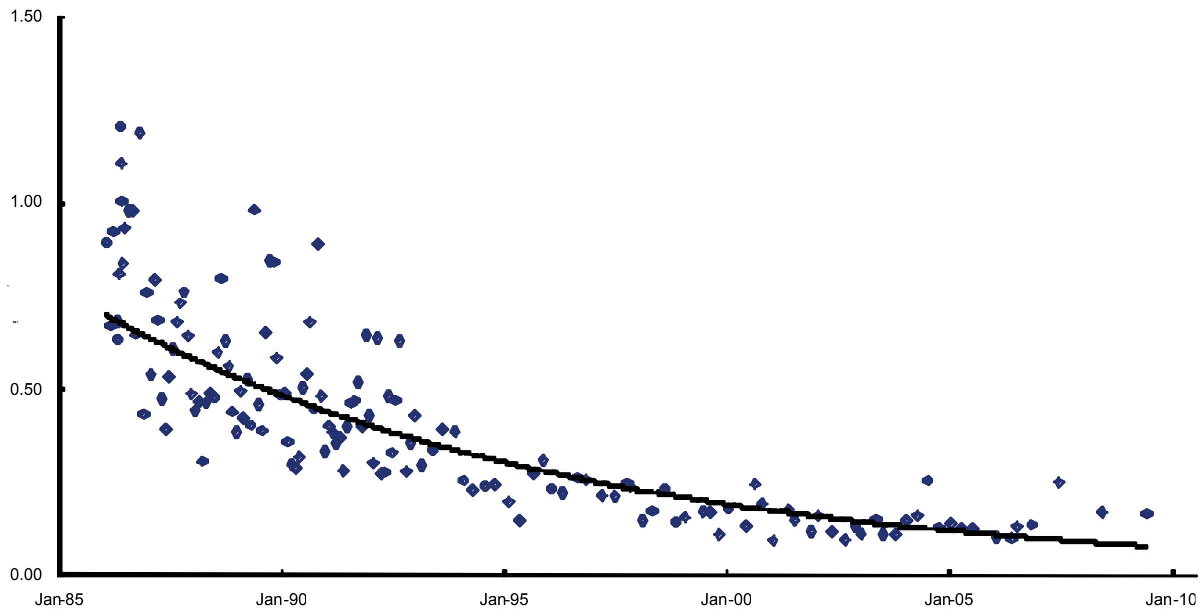


Figure 1.6. Temporal variation in concentrations of caesium-137 in shoreline seawater close to Sellafield (at St Bees), 1986–2009.

2. Trends in sediment type and organic carbon at CSEMP sites

Author: Claire Mason

2.1 Sediment characterisation trends for CSEMP sites between 1999 and 2010

2.1.1 Introduction

Marine sediments vary in grain size, in relation to varying availability of source sediments, different hydrodynamic regimes, and varying environmental conditions such as seasonal changes. CSEMP sites are chosen to reflect changes in the environment, aiming to show trends in contaminants in relation to anthropogenic changes in response to reduction in such anthropogenic contaminant inputs into the marine environment. Therefore, these sites need to be accumulating, that is, not dispersive. Accumulating areas are areas of low energy where recent finer sediments entering the environment are likely to be deposited and remain in this area, acting as sediment sinks. In addition, the sediment that accumulates gives a best indication of changes if it is fine (< 63µm) as many contaminants are closely associated with such finer sediment. Fine sediment containing clays, made up of clay minerals, which are charged, are able to adsorb contaminants, such as metals. In addition they are small, and have a relatively high surface area to mass ratio. This relatively high surface area gives more surface for contaminants to adhere to.

There are 15 CSEMP sites in the inshore/offshore marine environment around England and Wales that are monitored by Cefas as part of the CSEMP programme. Particle size analysis (PSA) has been completed for sediments from 11 of the 15 sites to determine temporal trends in sediment type. It is expected there will not be changes in sediment type at these sites over time, and that any changes in contaminant concentrations observed are not caused by change in sediment type, but as a result of anthropogenic changes such as reduced concentrations in response to reduced anthropogenic inputs into the marine environment.

2.1.2 Methods

PSA is completed on sediment samples using sieve and laser methods. PSA was completed on each sample by wet sieving at 63 µm. The > 63 µm fraction was dry sieved at ½ phi intervals down to 4 phi (63 µm). The < 63 µm fraction was freeze-dried and analysed using laser diffraction. Sieve and laser diffraction data were merged to form a complete particle size distribution (PSD) for each sample.

Sediments PSDs are compared and temporal trends identified from data where available from 1999 to 2010 for CSEMP sites 245, 285, 295, 345, 475, 484, 536, 605, 655, 715 and 805. Replicates were averaged to produce a PSD for each site for each year. These were grouped using Entropy, a non-hierarchal clustering method that groups sediments based on their full distribution. EntropyMax is a Windows-based software that groups large matrices of PSD data sets into a finite number of groups. It is described in more detail by Stewart *et al.* (2009). The sediments were divided into 12 groups (sediment groups 1–11 with 11 being made of 2 groups a and b). PSD histograms for each sediment group (Figure A.1), and sediment descriptions and summary statistics produced using Gradistat (Blott and Pye, 2001) (Table A.1.) are given in Annex A1.

2.1.3 Results

The sediments at CSEMP sites are mainly muddy sands and sands (Table 2.1a and b). Table 2.2 shows the sediment group for each CSEMP site for each year. It is clear that for most of the sites considered there are minimal changes in the sediment distribution and at most CSEMP sites the sediment group is the same for each year, except at CSEMP 484, CSEMP 475 and CSEMP 805. In 2003, CSEMP 484 was more mixed than in other years. Two of the replicates contained some gravel, but the mode of 215 µm for the sand is the same as for other years. In 2006 and 2009, CSEMP 475 is more gravelly than in other years. The mode of sediment (427.5 µm) in these years is consistent with other years. At CSEMP 805, sediments are in sediment group 4 in 2000, 2003, 2004, 2005 and 2007 and in sediment group 8 in 1999, 2006, 2008, 2009 and 2010. These groups are different and it is unclear why this pattern is observed. Positional data was queried for this site in 2007 and it is possible that for some years sampling has occurred at a slightly different position to other years as indicated in Figure 2.1.

When considering trends in contaminant concentrations it is important to understand the differences in silt/clay(%) content as contaminants tend to be associated with smaller particles as indicated in the introduction. Figure 2.1 shows silt/clay content at CSEMP sites over this time period. There is variability in the silt/clay content between sites and it is important to understand this when comparing contaminant concentrations between CSEMP sites. The variability of silt/clay(%) between years, as shown by 95% confidence limits in graph (inset in Figure 2.1), is small (all <+/- 2% except at CSEMP 484 with 5% which had one year with a different sediment group that other years). At CSEMP 655, the 95% confidence limits are +/- 17%. While this is higher than at the other sites, there are only results for 2 years here, and when considering the overall PSD both sediments fall in sediment group 2.

Table 2.1a. Sediment descriptions for each group, based on the average PSD for each group, including summary statistics produced in Gradistat (Blott and Pye, 2001).

Sediment group	Sediment description	Number of samples	Mode 1 (µm)	Mode 2 (µm)
1	Muddy sand (very fine), bimodal	13	76.5	37.75
2	Muddy sand (very fine), unimodal	12	76.5	
3	Muddy sand, unimodal	9	152.5	
4	Muddy sand, bimodal	7	152.5	302.5
5	Slightly gravelly sand (fine, mode 152.5µm))	10	152.5	
6	Muddy sand (fine, mode 215µm)	8	215	
7	Sand (fine, mode 215µm)	12	215	
8	Sand	5	215	
9	Sand (medium)	9	427.5	
10	Gravelly muddy sand	1	215	19200
11a	Gravelly sand (mode 427.5µm)	5	427.5	
11b	Gravelly sand (mode 302.5µm)	9	302.5	

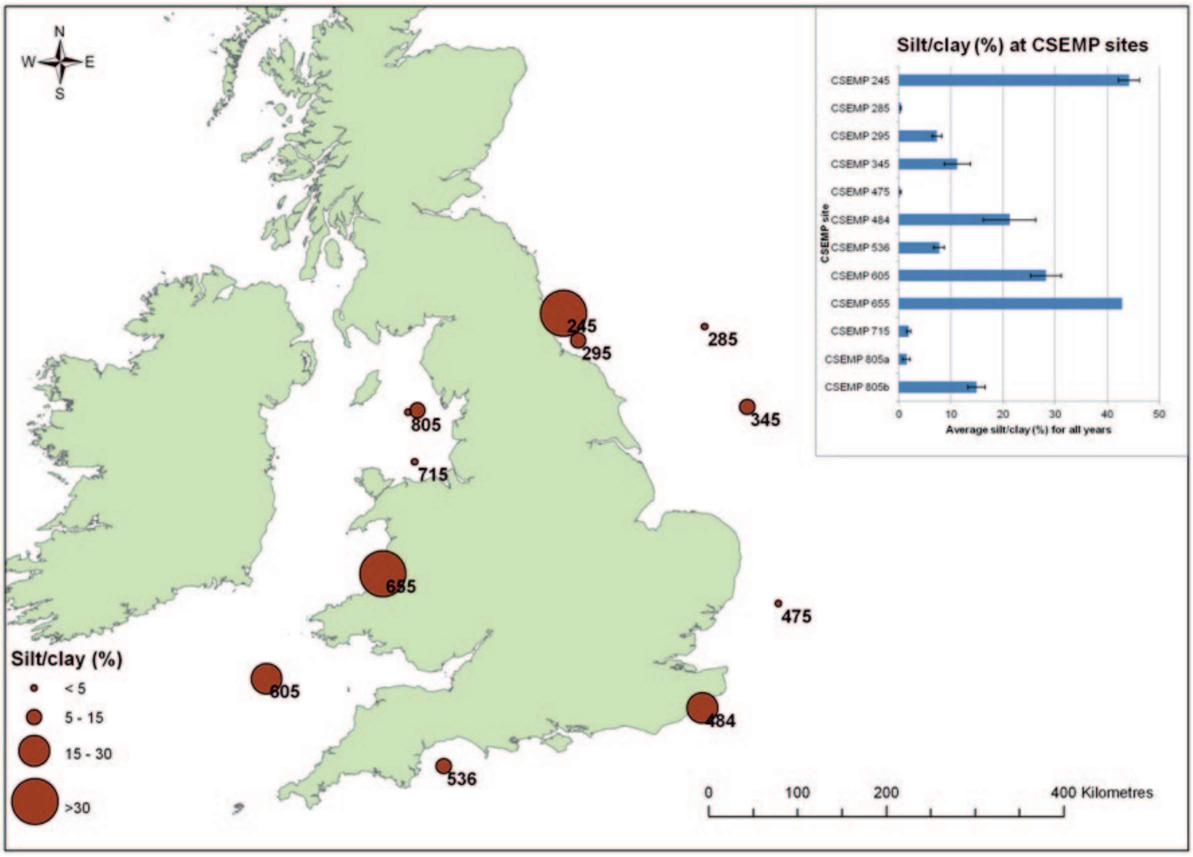
Table 2.1b. Average percentage of main sediment classes in each sediment group produced in Gradistat (Blott and Pye, 2001).

Sediment group	Gravel (%)	Very coarse sand (%)	Coarse sand (%)	Medium sand (%)	Fine sand (%)	Very fine sand (%)	Silt/clay (%)
1	0.11	0.34	0.33	1.03	4.04	48.30	45.85
2	0.12	0.14	0.33	0.69	6.72	62.52	29.47
3	0.03	0.07	0.10	0.28	53.90	34.39	11.23
4	0.16	0.12	0.93	11.82	48.89	25.36	12.73
5	1.88	0.26	2.60	6.67	79.86	8.36	0.37
6	0.85	0.68	1.26	13.07	46.54	16.53	21.06
7	0.52	0.26	1.62	13.19	64.31	12.39	7.72
8	0.09	0.13	1.16	22.64	72.60	1.91	1.46
9	0.42	0.34	9.59	87.74	1.66	0.07	0.17
10	18.61	0.55	0.95	8.57	47.85	11.59	11.87
11a	6.90	1.03	3.70	80.70	6.46	0.30	0.92
11b	7.14	0.91	1.93	73.21	13.78	0.98	2.05

CSEMP Station code	CSEMP 245	CSEMP 285	CSEMP 295	CSEMP 345	CSEMP 475	CSEMP 484	CSEMP 536	CSEMP 605	CSEMP 655	CSEMP 715	CSEMP 805
Station Name	Off Tyne	Off Tyne/Tees	Off Tees	Off Humber/Wash	Thames (Gabbard)	Channel	Lyme Bay	Celtic Deep	Cardigan Bay	Liverpool Bay	SE Isle of Man
1999	1	n	4	3	n	n	7	2	n	11a	8
2000	1	n	n	n	9	n	7	2	n	11b	4
2001	1	5	n	n	9	n	7	2	2	11b	n
2002	1	5	n	n	9	6	7	2	n	11b	n
2003	1	5	n	3	9	10	7	2	n	11b	4
2004	1	5	n	3	9	6	7	2	n	11b	4
2005	1	5	n	3	9	6	7	2	n	11b	4
2006	1	5	n	3	11a	n	7	2	n	11b	8
2007	1	5	n	3	9	6	7	2	n	11b	4
2008	1	5	n	3	9	6	7	2	n	11a	8
2009	1	5	n	3	11a	6	7	2	n	11a	8
2010	1	5	4	3	9	6	7	2	2	11b	8

Table 2.2. Sediment groups for each CSEMP site for each year.

Figure 2.1. Map showing average silt/clay (%) for each CSEMP site, with a bar chart inset in top right hand corner showing average with 95% confidence limits to give an indication of variability across the years measured. Correct position for CSEMP 805 is indicated by label. For some years sediments may have been collected from a location to west indicated by second circle. CSEMP 805a in the graph is the correct position, and CSEMP 805b shows results from location to west. Refer to main text.



2.1.4 Conclusions

- There has not been much change in sediment type at each of the CSEMP sites considered.
- There are differences in silt/clay (%) between sites that need to be considered when interpreting contaminant concentrations, if comparing relative enrichment between CSEMP sites.

2.2 Organic carbon trends at CSEMP sites between 2007 and 2010

2.2.1 Introduction

Variation in organic matter content, measured as organic carbon (m/m %), can also be responsible for variations in contaminant concentrations in marine sediments. Sediments with higher organic carbon content have more potential to adsorb contaminants than sediments with lower organic carbon content. Therefore organic carbon is measured to assist interpretations of temporal trends of contaminant concentrations. Organic carbon (m/m %) is measured on two fractions of sediment, the whole sediment fraction (< 2 mm), to help with organic contaminant concentration interpretation, and the fine sediment fraction (< 63 µm), to help with metal contaminant concentration interpretation. Organic contaminants are measured in the whole sediment fraction (< 2 mm) and metal contaminants are measured in the fine sediment fraction (< 63 µm). It is expected that there will be higher organic carbon (m/m %) in the fine sediment fraction (< 63 µm) than in the whole sediment fraction (< 2 mm). However, in some regions around England and Wales, such as the Tyne and Tees in the north-east, relatively high organic carbon (m/m %) is found in the whole sediment fraction (< 2 mm) due to the presence of coal.

Figure 2. Organic carbon (m/m %) for (a) < 2 mm fraction and (b) < 63 µm fraction at CSEMP sites between 2007 and 2010. There are fewer sites which have organic carbon content determined for the < 63 µm fraction than for the < 2 mm fraction. The bar chart inset in the right hand corner of each map shows the average organic carbon (m/m %) at each CSEMP site. Error bars show standard deviation indicating variability between years.

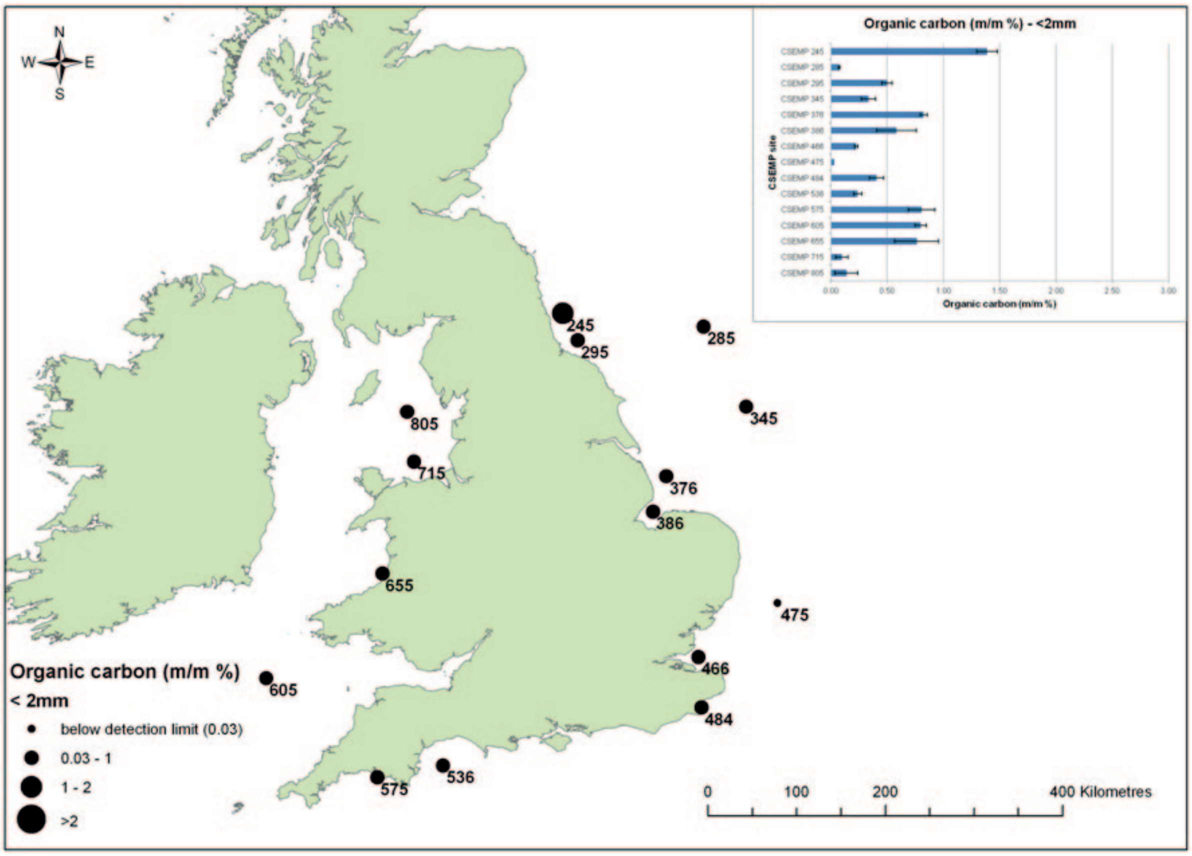


Figure 2.2a.

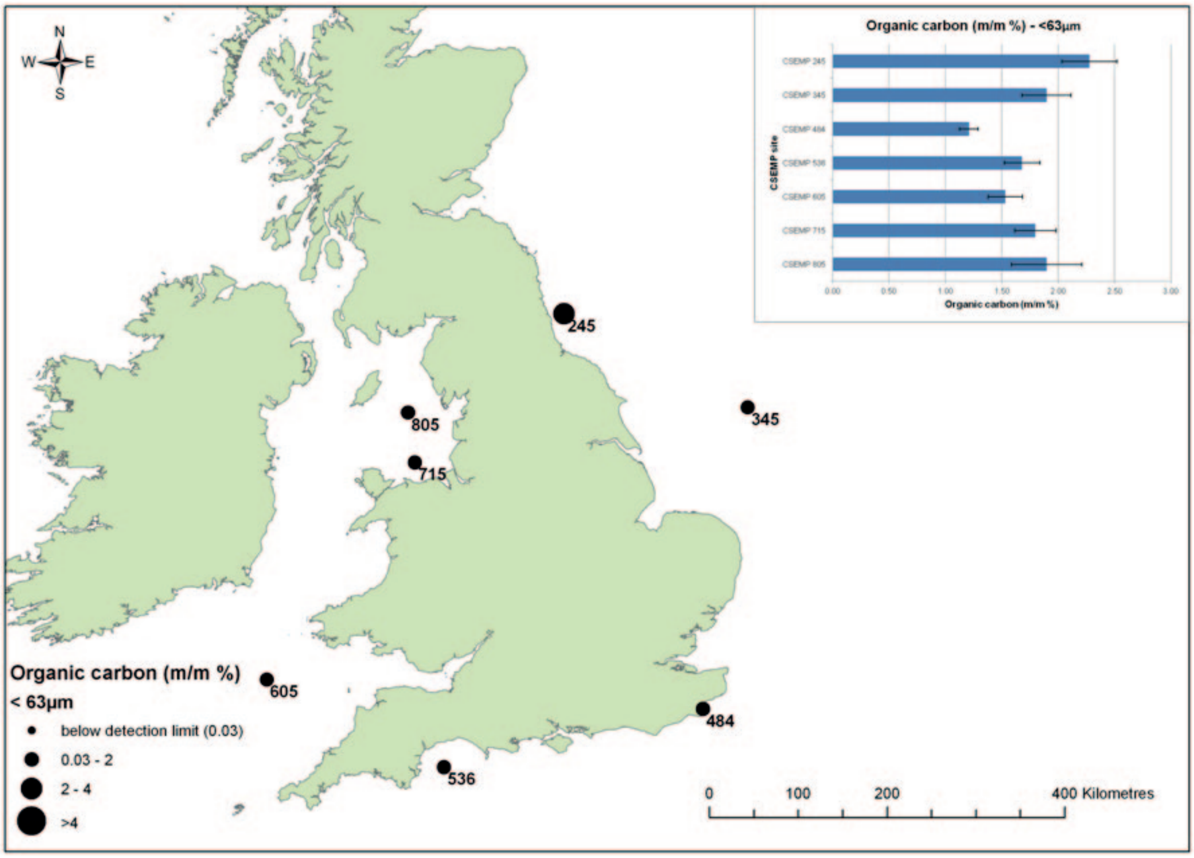


Figure 2.2b.

2.2.2 Methods

Organic carbon is measured on both the < 63 µm fraction and < 2 mm fraction of sediment. The < 2 mm sediment fraction is ground. Inorganic carbon is removed using sulphurous acid, and then organic carbon content is determined using a Leeman CE440 elemental analyser.

Organic carbon content (m/m %) is compared and temporal trends identified from data, where available, from 2007 to 2010 for the whole sediment fraction for CSEMP sites 245, 345, 376, 386, 475, 484, 536, 605, 655, 715 and 805, and for the fine sediment fraction (< 63 µm) for CSEMP sites 245, 345, 376, 484, 536, 715 and 805. Replicates were averaged to produce a mean organic carbon content (m/m %) for each site for each year.

2.2.3 Results

Organic carbon content (m/m %) is similar for each site for each year measured at CSEMP sites. Maximum standard deviation measured is +/- 0.20 m/m %, as indicated in bar charts inset in maps (Figure 2.2). There is variation in organic carbon (m/m %) between CSEMP sites, as shown in Figure 2.2, which is more distinct in the whole sediment fraction (< 2 mm) than the fine sediment fraction (< 63 µm).

2.2.4 Conclusions

- Organic carbon content (m/m %) is similar for each site for each year measured at CSEMP sites.
- Organic carbon content (m/m %) differs between CSEMP sites.
- This difference is more distinct in the whole sediment fraction (< 2 mm) than the fine sediment fraction (< 63 µm).

Annex A1. Supporting data for CSEMP sediment PSD temporal trends

Figure A.1. Sediment groups used for CSEMP PSD temporal assessment. Each averaged PSD for each site for each year is represented in histogram, one histogram for each defined sediment group.

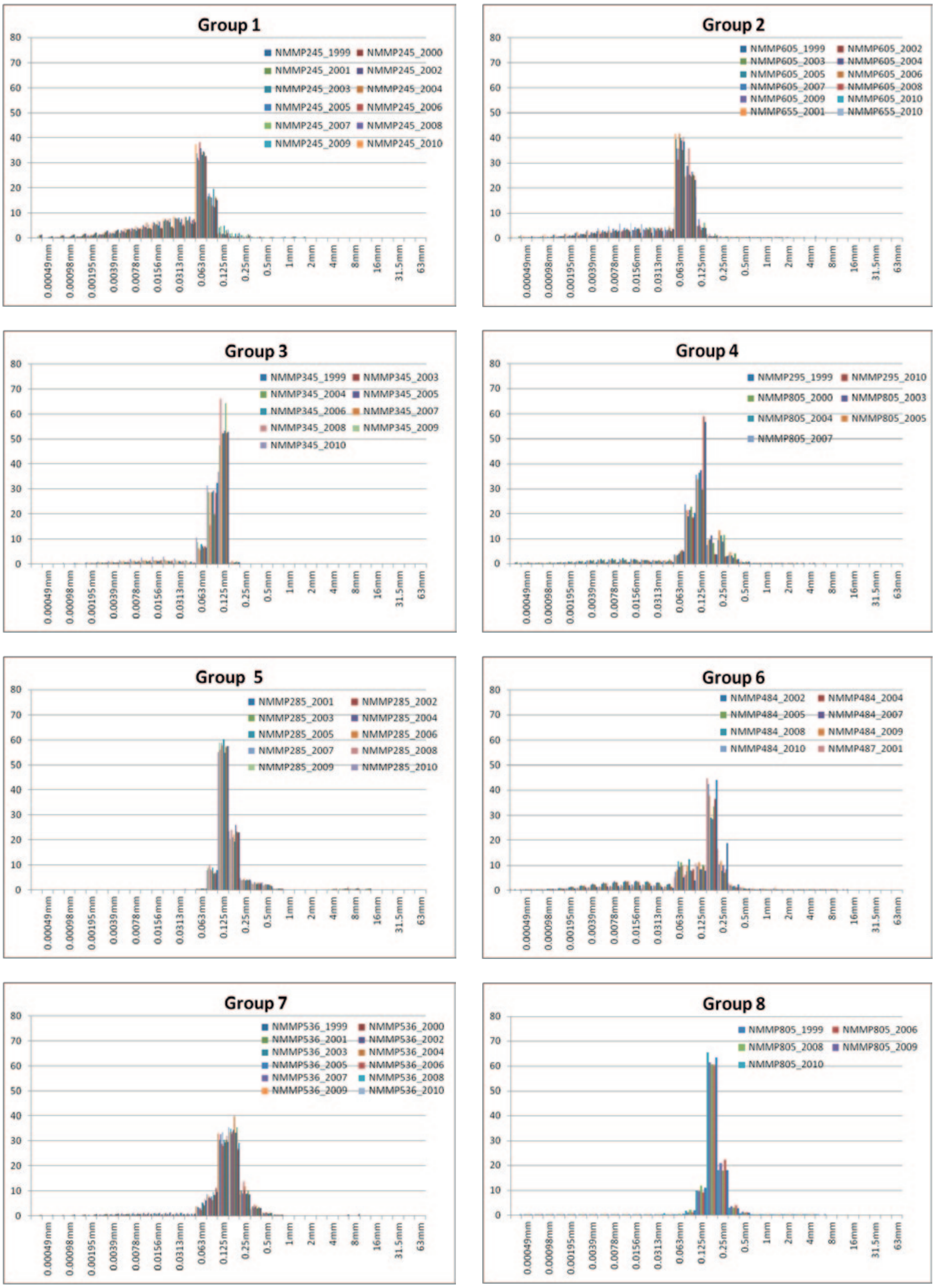


Figure A.1. continued Sediment groups used for CSEMP PSD temporal assessment. Each averaged PSD for each site for each year is represented in histogram, one histogram for each defined sediment group.

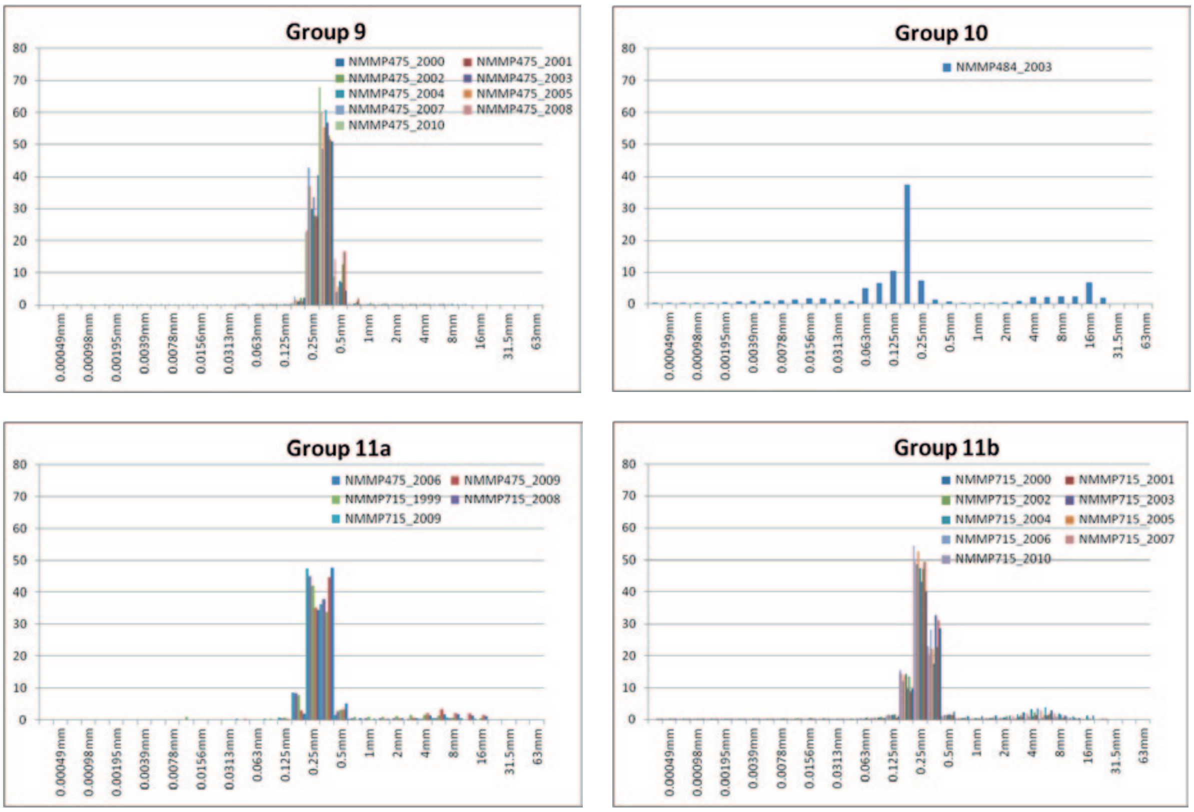


Table A.1. Sediment descriptions and summary statistics for each averaged PSD for each site for each year, produced using Gradistat (Blott and Pye, 2001).

Group	CSEMP site_year	Sample type	Textural group	Mode 1 (µm)	Mode 2 (µm)	Mode 3 (µm)	Gravel (%)	Sand (%)	Silt/clay (%)	Very coarse sand (%)	Coarse sand (%)	Medium sand (%)	Fine sand (%)	Very fine sand (%)
1	NMMP245_1999	Unimodal, Very Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.30	56.52	43.19	1.09	0.61	1.62	5.23	47.96
1	NMMP245_2000	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.19	53.86	45.95	0.46	0.51	1.41	2.75	48.73
1	NMMP245_2001	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.27	58.87	40.86	0.71	0.60	2.04	4.75	50.77
1	NMMP245_2002	Bimodal, Poorly Sorted	Slightly Gravelly Sandy Mud	76.50	26.70		0.07	49.57	50.36	0.10	0.13	0.42	1.79	47.14
1	NMMP245_2003	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50	37.75		0.16	60.89	38.95	0.10	0.22	1.30	6.48	52.79
1	NMMP245_2004	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50	26.70		0.07	50.25	49.68	0.07	0.11	0.28	2.23	47.55
1	NMMP245_2005	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.05	55.18	44.77	0.10	0.26	0.44	2.31	52.06
1	NMMP245_2006	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50	37.75		0.04	57.41	42.55	0.11	0.16	0.36	1.99	54.80
1	NMMP245_2007	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50	37.75		0.07	56.62	43.31	0.14	0.50	1.64	6.75	47.60
1	NMMP245_2008	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50	37.75		0.02	53.54	46.44	0.41	0.21	0.34	2.87	49.71
1	NMMP245_2009	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50	37.75		0.15	59.82	40.03	0.96	0.85	1.81	5.78	50.42
1	NMMP245_2010	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50	37.75		0.01	55.85	44.14	0.01	0.01	0.56	2.22	53.04
5	NMMP285_2001	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			1.77	97.77	0.46	0.23	2.05	6.76	80.36	8.37
5	NMMP285_2002	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			3.23	96.32	0.45	0.27	2.33	6.23	80.29	7.20
5	NMMP285_2003	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			2.70	96.88	0.42	0.33	2.59	6.38	80.32	7.27
5	NMMP285_2004	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			2.29	97.32	0.39	0.26	2.70	6.63	80.77	6.96
5	NMMP285_2005	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			1.68	98.06	0.26	0.27	2.65	6.03	79.69	9.41
5	NMMP285_2006	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			1.67	97.96	0.37	0.26	2.62	7.03	79.87	8.18
5	NMMP285_2007	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			1.52	98.15	0.33	0.27	2.91	6.99	79.63	8.35
5	NMMP285_2008	Unimodal, Well Sorted	Slightly Gravelly Sand	152.5			0.98	98.82	0.20	0.19	2.22	6.18	79.94	10.30
5	NMMP285_2009	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			2.11	97.52	0.37	0.28	2.46	6.39	79.21	9.19
5	NMMP285_2010	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			0.88	98.63	0.49	0.28	3.47	8.05	78.47	8.35
4	NMMP295_1999	Unimodal, Moderately Sorted	Slightly Gravelly Sand	152.5			0.21	92.01	7.77	0.30	1.21	5.07	60.24	25.20
4	NMMP295_2010	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	152.5			0.72	92.46	6.82	0.15	0.92	4.42	62.81	24.17

Table A.1. continued Sediment descriptions and summary statistics for each averaged PSD for each site for each year, produced using Gradistat (Blott and Pye, 2001).

Group	CSEMP site_year	Sample type	Textural group	Mode 1 (µm)	Mode 2 (µm)	Mode 3 (µm)	Gravel (%)	Sand (%)	Silt/clay (%)	Very coarse sand (%)	Coarse sand (%)	Medium sand (%)	Fine sand (%)	Very fine sand (%)
3	NMMP345_1999	Unimodal, Moderately Sorted	Slightly Gravelly Sand	152.5			0.03	93.03	6.94	0.05	0.13	0.29	53.65	38.91
3	NMMP345_2003	Unimodal, Moderately Sorted	Slightly Gravelly Muddy Sand	152.5			0.01	88.99	11.00	0.01	0.03	0.24	53.34	35.37
3	NMMP345_2004	Unimodal, Moderately Sorted	Slightly Gravelly Sand	152.5			0.01	91.47	8.52	0.02	0.08	0.22	65.09	26.05
3	NMMP345_2005	Unimodal, Moderately Sorted	Slightly Gravelly Sand	152.5			0.01	90.88	9.12	0.02	0.07	0.34	54.00	36.45
3	NMMP345_2006	Unimodal, Moderately Sorted	Slightly Gravelly Muddy Sand	152.5			0.02	89.88	10.10	0.02	0.03	0.18	52.80	36.85
3	NMMP345_2007	Unimodal, Moderately Sorted	Slightly Gravelly Muddy Sand	152.5			0.00	87.87	12.13	0.01	0.09	0.38	53.01	34.38
3	NMMP345_2008	Unimodal, Moderately Sorted	Slightly Gravelly Sand	152.5			0.17	89.95	9.88	0.28	0.24	0.36	67.26	21.82
3	NMMP345_2009	Unimodal, Moderately Sorted	Slightly Gravelly Muddy Sand	152.5			0.00	86.79	13.21	0.23	0.23	0.27	48.40	37.66
3	NMMP345_2010	Unimodal, Poorly Sorted	Muddy Sand	152.5			0.00	79.82	20.18	0.01	0.01	0.22	37.55	42.03
9	NMMP475_2000	Unimodal, Very Well Sorted	Slightly Gravelly Sand	427.5			0.88	99.08	0.04	0.28	4.83	91.41	2.51	0.04
9	NMMP475_2001	Unimodal, Well Sorted	Slightly Gravelly Sand	427.5			0.12	99.79	0.09	0.35	18.77	79.17	1.44	0.06
9	NMMP475_2002	Unimodal, Well Sorted	Slightly Gravelly Sand	427.5			0.67	98.40	0.94	1.03	13.79	80.58	2.64	0.36
9	NMMP475_2003	Unimodal, Well Sorted	Slightly Gravelly Sand	427.5			0.54	99.41	0.05	0.27	7.26	90.39	1.46	0.03
9	NMMP475_2004	Unimodal, Very Well Sorted	Slightly Gravelly Sand	427.5			0.28	99.64	0.08	0.17	7.64	90.71	1.09	0.04
9	NMMP475_2005	Unimodal, Very Well Sorted	Slightly Gravelly Sand	427.5			0.09	99.87	0.04	0.13	5.87	92.35	1.51	0.02
11a	NMMP475_2006	Unimodal, Moderately Sorted	Gravelly Sand	427.5			8.73	90.60	0.67	0.87	5.66	81.68	2.31	0.08
9	NMMP475_2007	Unimodal, Very Well Sorted	Slightly Gravelly Sand	427.5			0.65	99.12	0.23	0.31	4.50	91.31	2.91	0.09
9	NMMP475_2008	Unimodal, Well Sorted	Slightly Gravelly Sand	427.5			0.60	99.37	0.03	0.54	14.76	83.34	0.72	0.01
11a	NMMP475_2009	Unimodal, Poorly Sorted	Gravelly Sand	427.5			12.57	87.16	0.27	0.59	3.42	79.85	3.14	0.16
9	NMMP475_2010	Unimodal, Very Well Sorted	Slightly Gravelly Sand	427.5			0.00	99.96	0.04	0.03	8.93	90.32	0.65	0.02
6	NMMP484_2002	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0			0.92	83.55	15.52	0.45	1.17	20.92	51.89	9.13
10	NMMP484_2003	Bimodal, Very Poorly Sorted	Gravelly Muddy Sand	215.0	19200.0		18.62	69.49	11.89	0.55	0.94	8.57	47.84	11.59
6	NMMP484_2004	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0	76.50		0.35	74.57	25.08	0.21	0.73	9.45	46.02	18.16
6	NMMP484_2005	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0	76.50		0.34	71.59	28.06	0.32	0.85	8.15	43.54	18.73
6	NMMP484_2007	Bimodal, Very Poorly Sorted	Slightly Gravelly Muddy Sand	215.0	76.50		1.56	67.68	30.76	0.50	1.13	11.77	36.79	17.49
6	NMMP484_2008	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0	107.5		0.58	72.18	27.24	0.48	0.92	9.14	37.47	24.17
6	NMMP484_2009	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0			1.08	84.42	14.49	1.44	1.82	13.79	49.05	18.33
6	NMMP484_2010	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0			1.04	81.90	17.06	1.20	1.45	12.21	52.11	14.93

Table A.1. continued Sediment descriptions and summary statistics for each averaged PSD for each site for each year, produced using Gradistat (Blott and Pye, 2001).

Group	CSEMP site_year	Sample type	Textural group	Mode 1 (μm)	Mode 2 (μm)	Mode 3 (μm)	Gravel (%)	Sand (%)	Silt/clay (%)	Very coarse sand (%)	Coarse sand (%)	Medium sand (%)	Fine sand (%)	Very fine sand (%)
7	NMMP536_1999	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0			1.98	87.93	10.10	0.24	1.66	11.67	58.67	15.68
7	NMMP536_2000	Unimodal, Poorly Sorted	Slightly Gravelly Sand	152.5			1.07	90.00	8.93	0.28	1.78	11.46	58.73	17.74
7	NMMP536_2001	Unimodal, Poorly Sorted	Slightly Gravelly Sand	215.0			0.50	93.11	6.40	0.25	1.54	13.29	65.71	12.30
7	NMMP536_2002	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0			0.34	89.49	10.17	0.18	1.38	12.06	62.65	13.21
7	NMMP536_2003	Unimodal, Moderately Sorted	Slightly Gravelly Sand	215.0			0.48	91.57	7.95	0.22	1.40	11.68	63.48	14.79
7	NMMP536_2004	Unimodal, Moderately Sorted	Slightly Gravelly Sand	215.0			0.35	94.30	5.35	0.25	1.98	15.81	67.56	8.69
7	NMMP536_2005	Unimodal, Moderately Sorted	Slightly Gravelly Sand	215.0			0.30	94.20	5.50	0.24	1.71	13.81	67.80	10.64
7	NMMP536_2006	Unimodal, Moderately Sorted	Slightly Gravelly Sand	215.0			0.21	92.71	7.07	0.25	1.88	18.24	62.32	10.01
7	NMMP536_2007	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	215.0			0.18	89.51	10.31	0.22	1.40	11.94	65.07	10.86
7	NMMP536_2008	Unimodal, Moderately Sorted	Slightly Gravelly Sand	215.0			0.38	91.79	7.83	0.38	1.80	13.78	65.15	10.66
7	NMMP536_2009	Unimodal, Moderately Sorted	Slightly Gravelly Sand	215.0			0.37	93.45	6.18	0.32	1.70	13.30	66.46	11.68
7	NMMP536_2010	Unimodal, Moderately Sorted	Slightly Gravelly Sand	215.0			0.02	93.14	6.84	0.24	1.21	11.18	68.07	12.43
2	NMMP605_1999	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.09	68.44	31.47	0.15	0.75	0.96	4.99	61.60
2	NMMP605_2002	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.00	71.22	28.78	0.03	0.17	0.49	5.02	65.51
2	NMMP605_2003	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.00	70.01	29.99	0.06	0.35	1.05	7.86	60.70
2	NMMP605_2004	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.02	71.00	28.97	0.09	0.18	0.41	4.68	65.65
2	NMMP605_2005	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.00	69.97	30.03	0.02	0.14	0.43	4.79	64.59
2	NMMP605_2006	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.02	71.18	28.80	0.03	0.10	0.35	3.80	66.90
2	NMMP605_2007	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.02	66.88	33.10	0.03	0.13	0.41	5.11	61.20
2	NMMP605_2008	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	107.5			0.02	74.15	25.82	0.20	0.21	0.56	5.99	67.20
2	NMMP605_2009	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.03	76.20	23.77	0.66	0.48	1.31	9.19	64.56
2	NMMP605_2010	Unimodal, Poorly Sorted	Muddy Sand	76.50			0.00	74.95	25.05	0.01	0.26	0.58	5.40	68.70
2	NMMP655_2001	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	76.50			0.08	74.89	25.03	0.26	0.69	1.27	6.03	66.64
2	NMMP655_2010	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	107.5	18.85		1.17	55.97	42.86	0.18	0.55	0.50	17.75	36.99

Table A.1. continued Sediment descriptions and summary statistics for each averaged PSD for each site for each year, produced using Gradistat (Blott and Pye, 2001).

Group	CSEMP site_year	Sample type	Textural group	Mode 1 (µm)	Mode 2 (µm)	Mode 3 (µm)	Gravel (%)	Sand (%)	Silt/clay (%)	Very coarse sand (%)	Coarse sand (%)	Medium sand (%)	Fine sand (%)	Very fine sand (%)
11a	NMMP715_1999	Unimodal, Moderately Sorted	Gravelly Sand	302.5			7.36	90.78	1.86	1.91	4.05	75.81	8.52	0.50
11b	NMMP715_2000	Unimodal, Poorly Sorted	Gravelly Sand	302.5			12.68	85.91	1.42	2.35	3.47	68.72	10.72	0.65
11b	NMMP715_2001	Unimodal, Moderately Sorted	Gravelly Sand	302.5			5.52	93.21	1.27	0.44	1.70	80.77	9.70	0.60
11b	NMMP715_2002	Unimodal, Moderately Sorted	Gravelly Sand	302.5			6.84	90.12	3.03	1.14	1.99	70.02	15.34	1.64
11b	NMMP715_2003	Unimodal, Moderately Sorted	Gravelly Sand	302.5			6.12	91.13	2.75	0.75	2.03	75.84	11.19	1.32
11b	NMMP715_2004	Unimodal, Poorly Sorted	Gravelly Sand	302.5			13.50	84.63	1.87	0.90	1.97	64.89	15.84	1.02
11b	NMMP715_2005	Unimodal, Moderately Sorted	Slightly Gravelly Sand	302.5			4.88	93.31	1.81	0.78	1.82	74.61	15.33	0.77
11b	NMMP715_2006	Unimodal, Moderately Well Sorted	Slightly Gravelly Sand	302.5			3.98	93.49	2.53	0.74	1.73	76.60	13.46	0.97
11b	NMMP715_2007	Unimodal, Poorly Sorted	Gravelly Sand	302.5			8.66	88.96	2.37	0.65	1.28	70.01	15.85	1.17
11a	NMMP715_2008	Unimodal, Well Sorted	Slightly Gravelly Sand	302.5			2.63	96.54	0.83	1.23	3.36	82.62	9.02	0.31
11a	NMMP715_2009	Unimodal, Well Sorted	Slightly Gravelly Sand	302.5			3.21	95.84	0.95	0.53	2.02	83.50	9.33	0.45
11b	NMMP715_2010	Unimodal, Well Sorted	Slightly Gravelly Sand	302.5			2.08	96.45	1.47	0.45	1.43	77.32	16.55	0.70
8	NMMP805_1999	Unimodal, Well Sorted	Slightly Gravelly Sand	215.0			0.07	98.75	1.18	0.08	1.01	20.77	74.65	2.24
4	NMMP805_2000	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	152.5	302.5		0.01	82.73	17.26	0.08	1.06	15.69	38.04	27.85
4	NMMP805_2003	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	152.5			0.03	86.66	13.31	0.09	0.59	11.54	48.74	25.71
4	NMMP805_2004	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	152.5	302.5		0.01	84.04	15.95	0.07	0.84	14.73	46.06	22.34
4	NMMP805_2005	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	152.5	302.5		0.07	87.29	12.64	0.08	1.12	18.15	43.21	24.73
8	NMMP805_2006	Unimodal, Well Sorted	Slightly Gravelly Sand	215.0			0.18	98.63	1.19	0.14	1.33	26.14	69.73	1.29
4	NMMP805_2007	Bimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	152.5	302.5		0.04	84.65	15.31	0.07	0.83	13.13	43.10	27.52
8	NMMP805_2008	Unimodal, Well Sorted	Slightly Gravelly Sand	215.0			0.04	97.06	2.89	0.09	1.05	20.80	72.42	2.71
8	NMMP805_2009	Unimodal, Well Sorted	Slightly Gravelly Sand	215.0			0.07	98.54	1.39	0.28	1.52	24.43	70.85	1.46
8	NMMP805_2010	Unimodal, Well Sorted	Slightly Gravelly Sand	215.0			0.09	99.27	0.64	0.07	0.91	21.04	75.38	1.87

3. Levels and trends of metals in sediments, 2006–2010

Authors: Thi Bolam and Jon Barry

3.1 Introduction

Trace metals of natural origin are found in the environment and therefore the concentration in, and input to, the North Sea contains a natural and an anthropogenic component, both of which may vary over time.

In this section, metals concentrations in surficial sediments around the coasts of England and Wales collected under the Clean Seas Environment Monitoring Programme (CSEMP) are assessed against the Background Assessment Concentrations (BACs) established by OSPAR and Effects Range Low/Effects Range Median (ERL and ERM) concentrations developed for the US EPA, which is founded on a large database of sediment toxicity and benthic community information (Long *et al.*, 1998). The ERL/ERM methodology derives Sediment Quality Guidelines (SQGs) representing, respectively, the 10th and 50th percentiles of the effects dataset. This approach is a reasonably conservative one, and has been partially validated using North American field data. By collecting samples at around 45 fixed stations in intermediate and open sea areas around England and Wales, the aim of this programme is to investigate possible long-term trends in concentrations of metals, spatial variability and metals enrichment in the environment around England and Wales.

3.2 Methods

Sediment samples were collected using a 0.1m^2 modified Day grab, with 5 replicates being taken at each of the sampling sites.

Analysis was carried out by total sediment digestion (using hydrofluoric acid) on the fine sediment fraction (< 63 µm). Quantification was performed using inductively-coupled plasma-mass spectrometry (ICP-MS) and inductively-coupled plasma-atomic emission spectrometry (ICP-AES) for the determination of concentrations of Al, As, Cd, Cr, Cu, Hg, Li, Mn, Ni, Pb, Rb, V and Zn.

A 5-years-time series (2006–2010) was available within this study for the investigation of possible time-trends.

The possible temporal trends were investigated by calculating the mean of observations for each sampling station and year, and by fitting a linear regression model to these means.

The upper 95% confidence limit based on the mean levels from 2006-2010 (this is equivalent to fitting a model with zero slope to the mean levels) was also compared with the OSPAR BAC, ERL and ERM limit values for Cd, Hg and Pb (Table 3.1).

Table 3.1. BACs, ERL and ERM Limit values for metals in sediment as µg kg^{-1} dry weight

Assessment criteria for trace metals (µg kg^{-1} dry weight, BAC normalised to 5% Al content)

Assessment	BAC	ERL	ERM
Hg	70	150	710
Cd	310	1,200	9,600
Pb	38,000	47,000	218,000

3.3 Results

The variability (%RSD) of the 5 replicates is summarised in Tables 3.2, 3.3 and 3.4 for Cd, Hg and Pb, respectively, for each sampling year and each station.

The relative standard deviation (%RSD) ranges from 3.3% to 64.5% for Cd, from 6.1% to 54.4% for Hg and from 3.4% to 52% for Pb.

Overall, Pb variability is noticeably smaller than those for Cd and Hg due to the readily detectable levels of Pb present in the 5 replicates. The high variability (or not determined %RSD) of Cd and Hg was mainly due to concentrations being below the limit of detection.

Table 3.2. %RSD of cadmium in sediments.

Station	2006	2007	2008	2009	2010
CSEMP475	nd	nd	45.3 (n=4)	nd	nd
CSEMP484	7.0 (n=3)	36.1 (n=5)	3.3(n=5)	nd	18.8(n=5)
CSEMP536	52.3 (n=2)	17.4(n=5)	9.2(n=5)	nd	19.8(n=5)
CSEMP285	16.8(n=5)	8.8(n=2)	27.7(n=5)	nd	38.2(n=5)
CSEMP345	13.5(n=5)	56.8(n=5)	nd	nd	9.8(n=4)
CSEMP715	nd	7.8(n=5)	17.2(n=3)	18.1(n=5)	18.7(n=5)
CSEMP805	22.9(n=3)	64.5(n=5)	14.8(n=2)	12.0(n=5)	5.0(n=5)
CSEMP245	15.5(n=4)	28.8(n=5)	nd	nd	13.5(n=5)
CSEMP605	10.9(n=5)	29.6(n=5)	nd	38.5(n=5)	5.9(n=3)

nd= not determined due to 1 single sample analysed or <LOD value

Table 3.3. %RSD of mercury in sediments.

Station	2006	2007	2008	2009	2010
CSEMP475	nd	nd	nd	nd	nd
CSEMP484	16.5(n=5)	nd	27.1(n=5)	54.4(n=3)	10.8(n=2)
CSEMP536	nd	nd	34.3(n=3)	nd	8.8(n=2)
CSEMP285	18.2(n=4)	7.0(n=2)	nd	nd	28.2(n=2)
CSEMP345	nd	16.4(n=3)	nd	nd	18.8(n=3)
CSEMP715	26.1(n=2)	15.4(n=5)	46.6(n=2)	13.2(n=4)	18.1(n=5)
CSEMP805	20.7(n=5)	43.7(n=5)	42.4(n=4)	18.4(n=4)	20.9(n=5)
CSEMP245	6.1(n=2)	nd	13.6(n=5)	nd	11.0(n=5)
CSEMP605	8.6(n=4)	52.0(n=3)	nd	nd	37.7(n=3)

nd= not determined due to 1 single sample analysed or <LOD value

Table 3.4. %RSD of lead in sediments.

Station	2006	2007	2008	2009	2010
CSEMP475	nd	nd	51.2 (n=4)	5.2 (n=2)	9.9 (n=2)
CSEMP484	5.4(n=5)	3.4(n=5)	9.2(n=5)	10.3(n=5)	21.6(n=5)
CSEMP536	4.3(n=5)	17.7(n=5)	10.7(n=5)	12.7(n=5)	16.8(n=5)
CSEMP285	31.2(n=5)	21.1(n=2)	26.9(n=5)	44.5(n=5)	23.1(n=5)
CSEMP345	4.0(n=5)	29.6(n=5)	9.1(n=5)	16.5(n=5)	9.4(n=5)
CSEMP715	42.3(n=3)	20.1(n=5)	43.2(n=5)	43.1(n=5)	30.3(n=5)
CSEMP805	29.9(n=5)	15.6(n=5)	38.6(n=5)	52.0(n=5)	33.0(n=5)
CSEMP245	4.2(n=5)	26.0(n=5)	10.1(n=5)	11.4(n=5)	11.6(n=5)
CSEMP605	3.9(n=5)	18.6(n=5)	8.4(n=5)	9.4(n=5)	26.0(n=5)

nd= not determined due to 1 single sample analysed or <LOD value

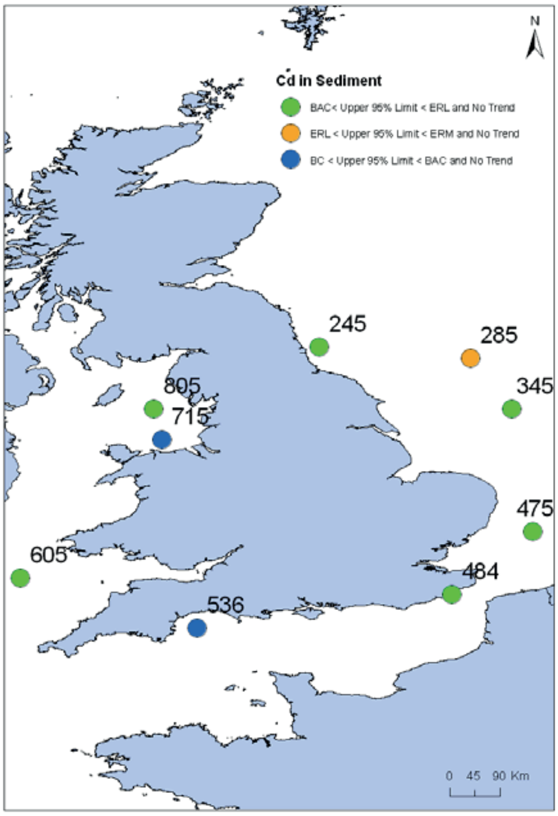


Figure 3.1. Cadmium in sediment at CSEMP stations in relation to assessment criteria.

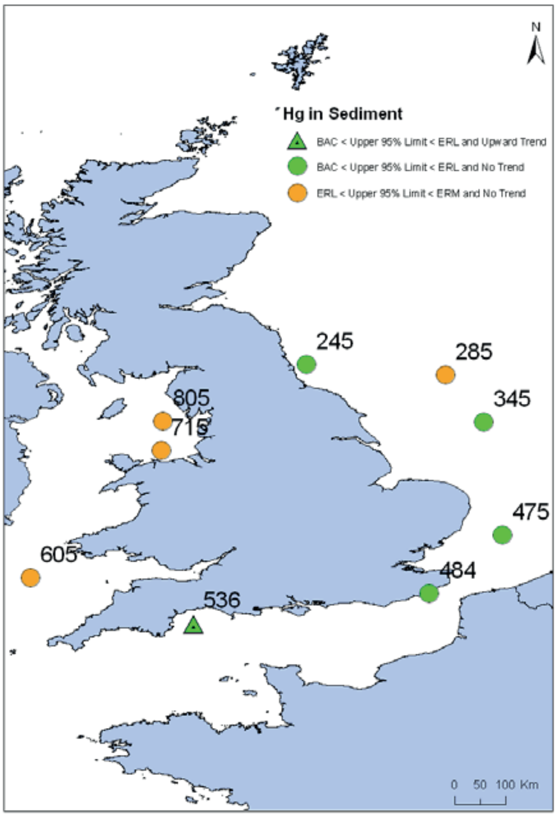


Figure 3.2. Mercury in sediment at CSEMP stations in relation to assessment criteria.

3.3.1 Cadmium in sediment

The upper 95% confidence limit concentrations for 2006–2010 were in the range of 265–1335 µg kg^{-1} dry weight, with concentrations at most sites just above the BAC and well below the ERL and ERM limit values. The upper 95% confidence limit concentrations were found to be below the BAC in the Western Channel and in the Irish Sea (CSEMP 536 and CSEMP 715) at 275 and 265 µg kg^{-1} dry weight of sediment, respectively (Figure 3.1).

One station in the central North Sea recorded an upper 95% confidence limit concentration of 1,335µg kg^{-1} dry weight of sediment (CSEMP 285), which is above the ERL limit value but below the ERM limit value.

No significant temporal trend was observed for Cd concentrations in sediment over the studied period.

The concentrations of cadmium in sediment were found to be more elevated in some sea areas offshore from historically industrialised estuaries (eg, CSEMP 245), although toxicological effects are unlikely and many sites have concentrations close to background.

Monitoring should be maintained in areas where elevated concentrations occur that are potentially of concern, especially off the Tyne/Tees area.

3.3.2 Mercury in sediment

The upper 95% confidence limit concentrations for 2006–2010 were in the range of 81–401 µg kg^{-1}dry weight of sediment, with levels above the ERL but below the ERM limit value for stations located in the eastern Irish Sea (CSEMP 715 and CSEMP 805). Stations in the Celtic Deep (CSEMP 605) and off Tyne/Tees (CSEMP 285) also showed concentrations above the ERL limit value, but to a lesser extent. Elsewhere, mercury concentrations were below the BAC but above the BC (Figure 3.2).

A significant increasing temporal trend was observed for Hg in sediment over the studied period at the Western Channel station (CSEMP 536), Figure 3.3, however the upper 95% confidence limit concentration for 2006–2010 at this station was below the BAC limit value, therefore toxicological effects are unlikely.

Since most stations exhibited mercury concentrations above the ERL limit value, monitoring should be maintained in areas where elevated concentrations that are potentially of concern have been shown to occur.

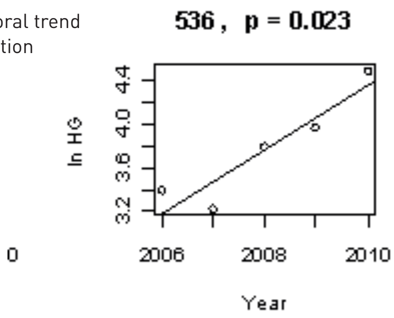


Figure 3.3. Temporal trend for mercury at station CSEMP 536.

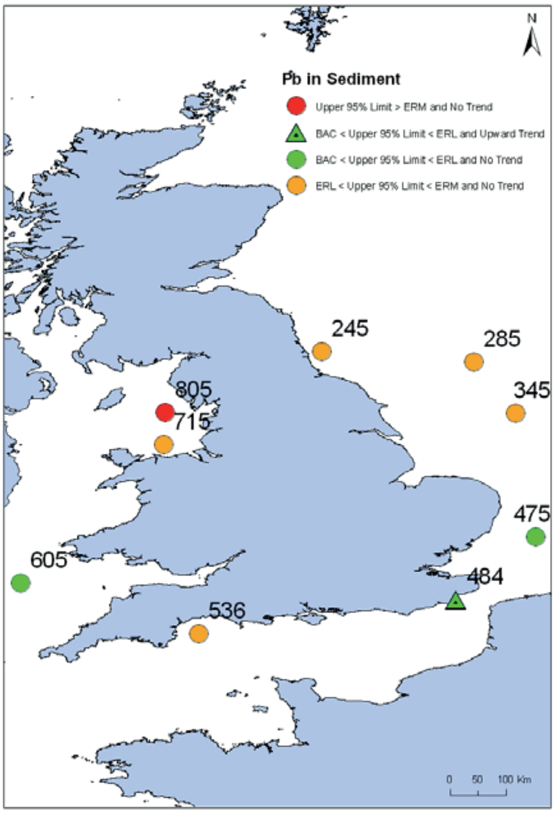


Figure 3.4. Lead in sediment at CSEMP stations in relation to assessment criteria.

3.3.3 Lead in sediment

The upper 95% confidence limit concentrations for 2006–2010 were in the range of 32,000–1,259,000 µg kg^{-1} dry weight of sediment, with levels at most sites above the ERL but below the ERM limit values (Figure 3.4).

Stations CSEMP 605 (Celtic Deep), CSEMP 484 in the Eastern Channel, and CSEMP 475 off the Thames estuary showed values close to background, whereas station CSEMP 805 in the Irish Sea area exhibited lead concentration 6 times higher than the ERM limit value.

A significant increasing temporal trend was observed for Pb in sediment over the studied period at the Eastern Channel (station CSEMP 484), Figure 3.5, but the upper 95% confidence limit concentration in 2010 at this station was below the BAC limit value, therefore toxicological effects are unlikely.

Since most stations depicted lead concentrations above the ERL limit value, monitoring should be maintained in areas, especially where elevated concentrations occur that are potentially of concern. Despite exhibiting a 'green' status at station CSEMP 484, the significant increasing trend showed that the lead level could rise above the BAC value in the future so monitoring should also be maintained at this station.

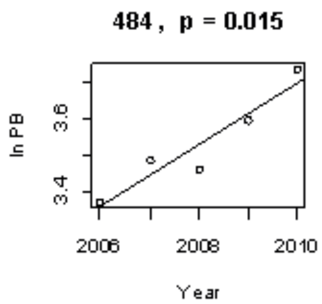


Figure 3.5. Temporal trend for lead at station 484.

3.3.4 Other metals in sediment

Temporal trends were also studied for arsenic (As), copper (Cu), chromium (Cr), nickel (Ni) and zinc (Zn).

Positive significant trends were observed for Cu and Ni at station CSEMP 245 (Tyne/Tees area), for Ni at station CSEMP 805 (Irish Sea area), for Cr at station CSEMP 605 (Celtic Deep) and for Zn at station CSEMP 484 (Humber area). The upward time trends may be related to the industrialised nature of the estuaries adjoining these areas.

Interestingly, only As exhibited decreasing trends, at 3 stations in the Humber, Eastern Channel and Irish Sea areas (stations CSEMP 285, CSEMP 536 and CSEMP 805, respectively). This may reflect decreases in As input to these regions over the last 5 years (Figure 3.6).

Since no statistical comparison to the BAC/ERL/ERM limits values was carried out for these metals, it is difficult to assess their potential toxicological effects.

3.4 Overall conclusion

The BAC values, which are derived to cover a wide geographical area, are used to assess the status of each OSPAR region, for instance, in Quality Status Reports. However, trace metal concentrations vary naturally at much smaller spatial scales due to local geochemical differences, so applying a single OSPAR BAC set of values for assessment might not be the most suitable approach to use. There is, therefore a need to derive sets of regional metal baselines that could be more representative of the areas to be assessed. A separate study on regional metal baselines has been carried out, and more detailed information is provided in Cefas (2011).

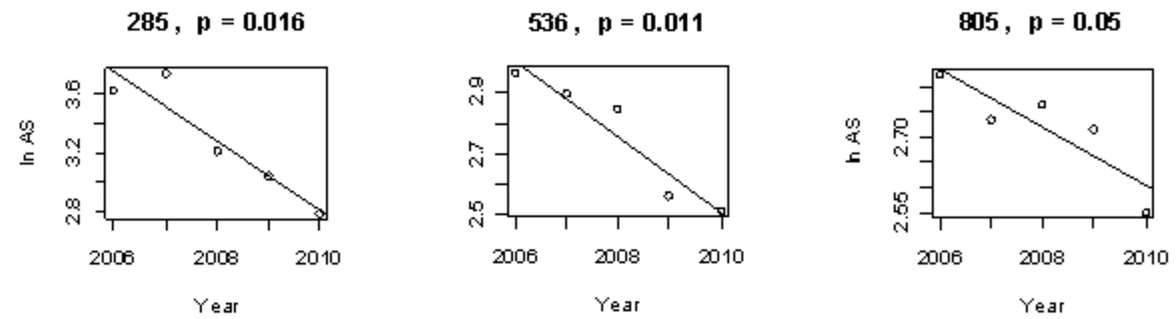


Figure 3.6. Temporal trend for arsenic at stations CSEMP 285, CSEMP 536 and CSEMP 805.

4. Polycyclic aromatic hydrocarbons (PAH) in sediments collected within the Clean Seas Environment Monitoring Programme (CSEMP), 2000–2010

Authors: Heather S. Rumney, Jon Barry and Robin J. Law

4.1 Introduction

In 1998, the first phase of the UK National Marine Monitoring programme (NMMP) was completed. Amongst other aims, this targeted an assessment of spatial variability in sediment PAH concentrations. The ending of the first phase was marked by the publication of the first NMMP report (MPMMG, 1998). Following this, the programme was switched to the investigation of temporal trends at 15 UK sites, beginning in 2000. These were sampled by Cefas following the procedural guidelines given within the Clean Seas Environment Monitoring Programme (CSEMP) Green Book. This requires the collection of 5 replicate sediment samples randomly within a 50 m radius at each sampling site, so giving an indication of the small-scale variability of concentrations in PAHs found at each sampling location.

4.2 Methods

Sediment samples, collected using grab samplers and stored in glass jars, were frozen immediately after collection and not defrosted until required for analysis. Each homogenised wet sediment sample was extracted using alkaline saponification followed by liquid/liquid solvent extraction. A separate subsample of sediment was also taken for a total solids determination as all results are reported on a dry weight basis as, when sediments are collected, the water content is often dependent on the type of sampler used. The sample extract was then passed through an alumina chromatography column in order to remove polar compounds (mainly pigments as lipids are destroyed during saponification), concentrated to 1 ml and sealed in an autosampler vial. A suite of 22 parent PAH and groups of alkylated PAH were then determined using coupled gas chromatography-mass spectrometry (GC-MS) in electron impact ionization mode. Quantification was by reference to known amounts of deuterated PAH internal standards added prior to digestion, with analytical quality control samples being run within each sample batch (Full details can be found in Kelly *et al.*, 2000).

The limit of detection in sediment is set at 0.1 μg kg^{-1} dry weight for each PAH compound or group.

Quality assurance is guaranteed by Cefas participation in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) laboratory proficiency scheme, which involves analysis of sediment samples twice per year as an external quality check (Law et al., 2000). QUASIMEME requires that, for data to be considered valid, the percentage of satisfactory result (z scores < ± 2) should be > 70%. This requirement was met in these studies.

All samples are run under an analytical quality control (AQC) protocol, which involves the analysis of procedural blanks and certified or laboratory (in-house characterised) reference materials within each sample batch. The reference material currently used is a marine sediment certified reference material (NIST 1944) produced by the National Institute of Standards and Technology in the USA.

4.3 Data interpretation and guidance

Table 4.1: Mean ΣPAH22 (μg kg^{-1} dry weight) and range of concentrations found in sediments from 15 CSEMP sites (2000-2010).

		2000		2001		2002		2003		2004		2005		2006		2007		2008		2009		2010	
Station	**Location**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**
CSEMP 245	Off Tyne	4110	3640-4570	5000	4300-5700	5160	4800-5520	3480	3240-3730	4520	4250-4790	4490	4230-4740	5110	4750-5470	5090	4610-5570	4640	4770-5110	4540	3750-5320	4190	3690-4690
CSEMP 285	Off Tyne/Tees			37.2	20.3-54.1	55.3	30.4-80.1	71.2	35-107	24.0	20.7-27.3	21.6	16.4-26.7	37.2	22.1-52.2	26.7	23.1-30.4	53.4	46.4-60.5	53.8	21.4-86.2	23.5	14.8-32.2
CSEMP 295	Off Tees											3600	3160-4030	3370	2610-4120	3480	1780-5180	3690	3370-4010	3280	2890-3670	2460	2140-2780
CSEMP 345	Off Humber/ Wash	519	395-640	378	328-429	503	445-561	498	375-620	360	303-418	394	329-460	396	364-428	467	412-523	417	315-518	549	487-610	535	440-630
CSEMP 376	Off Wash	2820	2420-3220	2060	1470-2650	2500	2150-2860	3050	2600-3500	3210	2870-3550	2790	1930-3640	3130	2650-3620	3640	2620-4660	2970	2610-3330	2990	2250-3730	2050	972-3130
CSEMP 386	Wash			1520	498-2537	1080	686-1480	1440	1240-1640	970	550-1390	1060	648-1480	1190	303-2080	1560	778-2350	3410	0-8470	978	713-1240	1690	637-2740
CSEMP 466	Thames	462	349-575	260	199-322	631	367-894	253	107-399	325	161-490	195	111-278	252	65.4-439	239	182-296	335	186-484	311	82.6-539		
CSEMP 475	Outer Gabbard	19.0	0-38.4	1.0	0.6-1.5	0.3	0-0.6	4.3	3.9-4.8	4.8	4.3-5.4	10.3	6.1-14.6	10.8	5.5-16.2	0.0	0.0	26.3	18.3-34.4	5.8	1.7-10	1.5	0.6-2.3
CSEMP 484	Dungeness			178	134-222	246	189-303	209	171-247	380	280-480	671	439-902	657	588-726	508	423-594	488	251-725	339	276-402		
CSEMP 536	Lyme Bay	110	38.5-181	81	48-114	109	24.6-192	137	109-164	67.7	51.3-84.1	96.3	42.7-150	63.4	37.2-89.5	155	3.5-306	99	87.6-110	108	18.6-198	50.5	35.9-65.1
CSEMP 575	Off Tamar											1220	891-1550	5850	0-12800	3630	2400-4850			2360	1590-3130	1010	793-1220
CSEMP 605	Celtic Deep			896	752-1040	1310	997-1630	1540	737-2340	1000	750-1260	1270	926-1610	789	695-883	1250	776-1730	1130	936-1320	1290	1080-1490	932	637-1230
CSEMP 655	Cardigan Bay			1430	1370-1500	1340	1170-1510	1240	1080-1410	1160	1090-1230	1060	1010-1110	995	871-1120	1240	1110-1370	979	880-1080	916	746-1080	815	697-933
CSEMP 715	Liverpool Bay	114	0-237	54.2	10-98	142	23.2-260	102	14.1-190	155	64.7-245	180	48.4-310	122	20.7-224	1470	0-4420	175	35.8-315	53.1	0-111	109	52.6-165
CSEMP 805	SE Isle of Man			691	535-848	530	502-559	519	440-594	496	331-660	481	468-493	84.8	57.9-112	630	531-730	160	55-264	117	3.2-231	103	86.8-120

From the data presented in Table 4.1, we find that the highest concentration of summed PAHs is consistently found at CSEMP 245 (off Tyne) off the north-east coast of England, with concentrations in muddy sands consistently between 4,000–5,000 µg kg^{-1} dry weight over the 10 year period. The broadest range was found in 2002: 4,800–5,520 µg kg^{-1} dry weight. The sole exception to this was in 2006, when samples from CSEMP 575 (off Tamar) in the south-west of England, where sampling only commenced in 2005, yielded an average of 5,850 µg kg^{-1} dry weight, with a maximum concentration of 12,800 µg kg^{-1} dry weight. The levels at the off Tamar site then steadily decreased over the following years, to an average of approximately 1,000 µg kg^{-1} dry weight in 2010. The sampling programme was extended in 2005 to include another site; CSEMP 295 (off Tees), where summed PAH concentrations were found to be in the range 2,000–4,000 µg kg^{-1} dry weight. Similar summed PAH concentrationswere also found at CSEMP 376 (off Wash), with a maximum of 3,600 µg kg-1 dry weight in 2007. Concentrations of summed PAHs in the range of 2,000–3,000 µg kg^{-1} dry weight are found in at CSEMP 386 (the Wash). Concentrations of summed PAHs in the range of 1,000–2,000 µg kg^{-1} were found at CSEMP 605 in the Celtic Deep and at CSEMP 655 in Cardigan Bay, both off the coast of Wales. Concentrations of summed PAHs in the range of 300–1,000 µg kg^{-1} dry weight are typically found in the south-east corner of the country, at CSEMP 466 in the Thames and at CSEMP 484 (Dungeness), on the west coast off the South-east Isle of Man (CSEMP 805), and offshore from the Humber /Wash area (CSEMP 345). Concentrations < 300 µg kg^{-1} dry weight are generally found in sandier sediments in Liverpool Bay(CSEMP 715), though in 2007 one outlier was found within the replicate data. It appeared to contain a much higher concentration, thus skewing the data for this site. This is likely to be due to additional PAH from a specific source contained within that one replicate sample. At Lyme Bay (CSEMP 536) on the South Coast we also found concentrations typically < 300 µg kg^{-1}dry weight. The lowest concentrations were always found at CSEMP 475 in the Outer Gabbard region of the southern North Sea where the concentration is typically < 100 µg kg^{-1} and the sediment composition is clean sand.

Table 4.2. Sediment description and overall mean ΣPAH_{22} µg kg^{-1} found in sediments from 15 CSEMP sites (2000–2010).

Station/ Location	Sediment description	overall mean ΣPAH_{22} µg kg^{-1} 2000–2010
CSEMP 245 (off Tyne)	Muddy sand (very fine)	4,194
CSEMP 285 (off Tyne/Tees)	Slightly gravelly sand (fine, mode 152.5 µm)	37
CSEMP 295 (off Tees)	sandy mud (mode 152.5 µm)	2,840
CSEMP 345 (off Humber/Wash)	Muddy sand (mode 152.5 µm)	418
CSEMP 376 (off Wash)	Muddy sand	2,601
CSEMP 386 (Wash)	Muddy sand	1,354
CSEMP 466 (Thames)	Muddy sand	297
CSEMP 475 (Outer Gabbard)	Sand (medium)*	7
CSEMP 484 (Dungeness)	Muddy sand (fine, mode 152.5 µm)**	368
CSEMP 536 (Lyme Bay)	Slightly gravelly muddy sand (fine, mode 215 µm	90
CSEMP 575 (off Tamar)	Gravelly sand	2,345
CSEMP 605 (Celtic Deep)	Muddy sand (fine)	1,037
CSEMP 655 (Cardigan Bay)	Muddy sand (fine)	1,016
CSEMP 715 (Liverpool Bay)	Gravelly sand	223
CSEMP 805 (SE Isle of Man)	sand (mode 215 µm)	347

* except 2006 and 2009 where was gravelly sand
** except in 2003 where was gravelly muddy sand

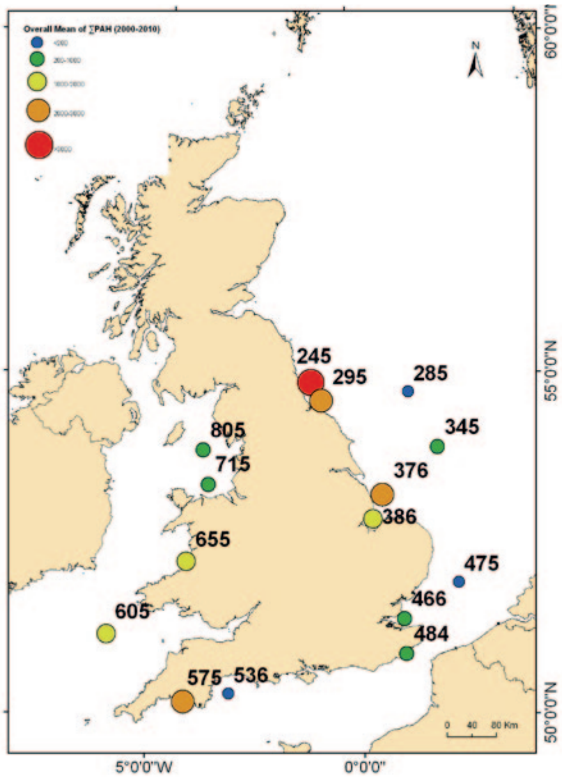


Figure 4.1. CSEMP sites in England and Wales showing overall mean ΣPAH (2000–2010).

From the data in Table 4.2 and the map in Figure 4.1 showing the distribution of overall means of summed PAHs, we can see that the greatest concentration is found in the north-east of England off the Tyne at CSEMP 245 where the sediment type is more muddy, compared to the cleaner sands found offshore at CSEMP 285. High concentrations off the north-east of the Tyne/Tees area reflects the high levels of PAH contamination previously observed in these estuaries as a result of historical contamination from industry (Woodhead *et al.*, 1999). Those sites where the sediment type is a mixture of mud and sand yield intermediate concentration of PAHs, ranging from 297 µg kg^{-1} dry weight at CSEMP 466 in the Thames to 135 µg kg^{-1} dry weight at CSEMP 386 in the Wash. But, generally, concentrations are found to be lower on the west coast than on the east coast, with some additional spatial variability according to sediment type.

In order to make an assessment of PAH trends at CSEMP stations we analysed statistically the summed PAH concentration data for the 15 CSEMP sites. Generally, the data are for the period 2000 or 2001 to 2010. However, two of the time series start from 2005 (CSEMP 295 and CSEMP 575). There are usually 5 replicates from each CSEMP station in each year. Because of the two short time series and recognising that any trends present seem to be linear, the potential time trends were assessed using linear regression. The mean of observations for each station and year were taken and the linear regression model fitted to these means. All data were transformed to natural logarithms prior to analysis in order to take account of a few zero observations (Figure 4.1). This is to make the distribution of PAH reasonably Gaussian and so that the variance is not dependent on the magnitude of the PAH concentrations.

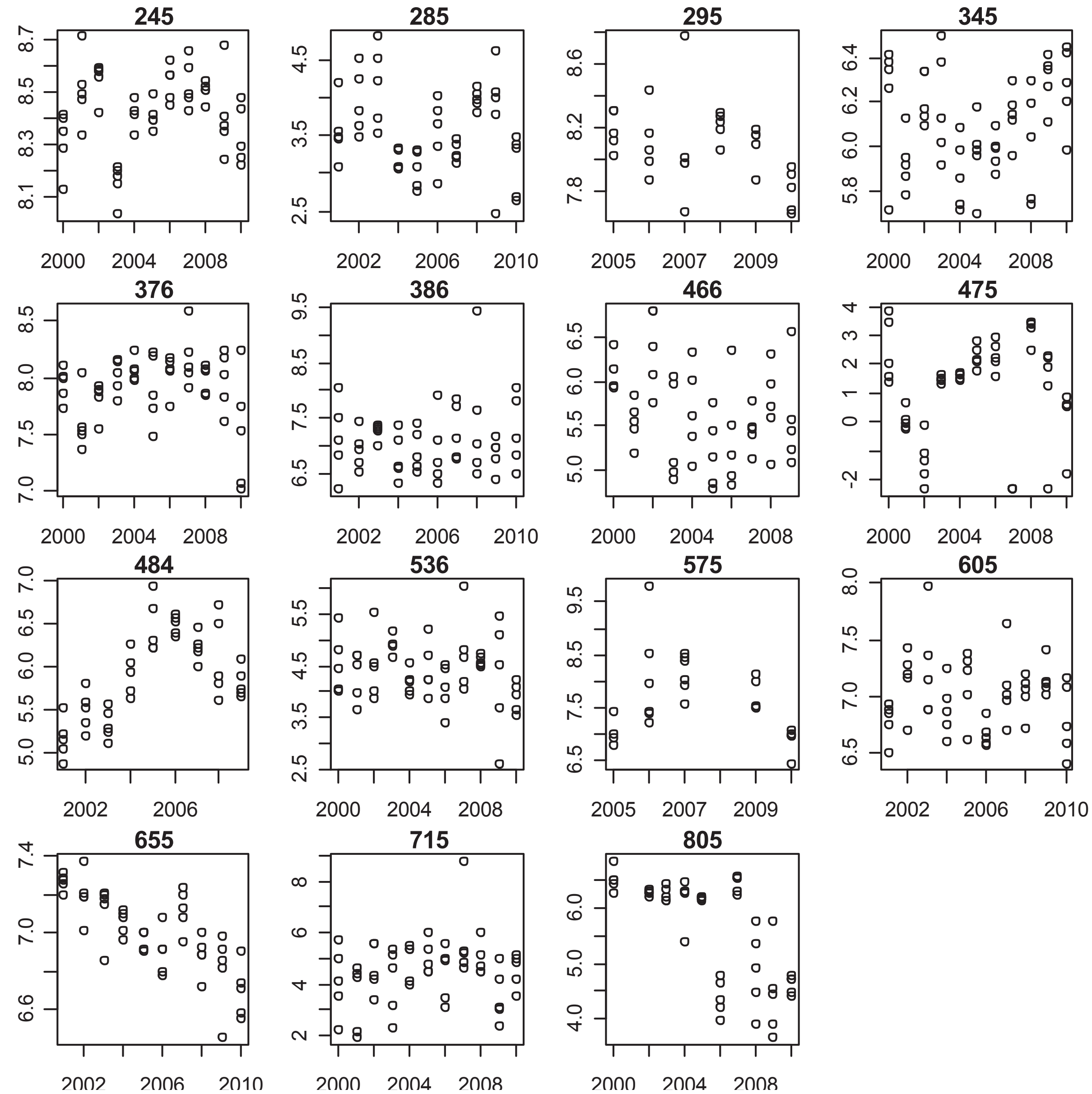


Figure 4.2. Plots of summed PAH concentrations natural log-transformed for each CSEMP site.

Figure 4.2 shows plots of the raw log data for each station, in which CSEMP 805 and CSEMP 655 seem to be showing the clearest linear trends. Figure 4.3 shows the mean of the log-transformed values for each site plus linear trend lines fitted to these mean values. The p-value for the statistical significance of the slope of each trend is shown in the title of each plot. The only two stations with p-values below 0.05 (and so statistically significant) are CSEMP 805 (SE Isle of Man ($p = 0.011$)) and CSEMP 655 (Cardigan Bay ($p < 0.001$)). These both exhibit downward trends. The trend for CSEMP 484 ($p = 0.06$) is close to statistical significance at the 5% level, with an apparently increasing trend. In general, however, there is a high degree of variability and not much apparent evidence of trends for the other CSEMP stations.

At present there is no UK legislation regarding the acceptability of levels of PAHs found in marine sediments. Cefas currently has action level limits for contaminants such as trace elements and PCBs in dredged material for possible disposal to sea, but none currently for PAHs. Reviews of the approaches taken in other countries to the development of sediment quality guidelines (SQGs) has indicated that the most promising of the currently available co-occurrence methods is the Effects Range Low/Effects Range Median (ERL/ERM) methodology, which is founded on a large database of sediment toxicity and benthic com-

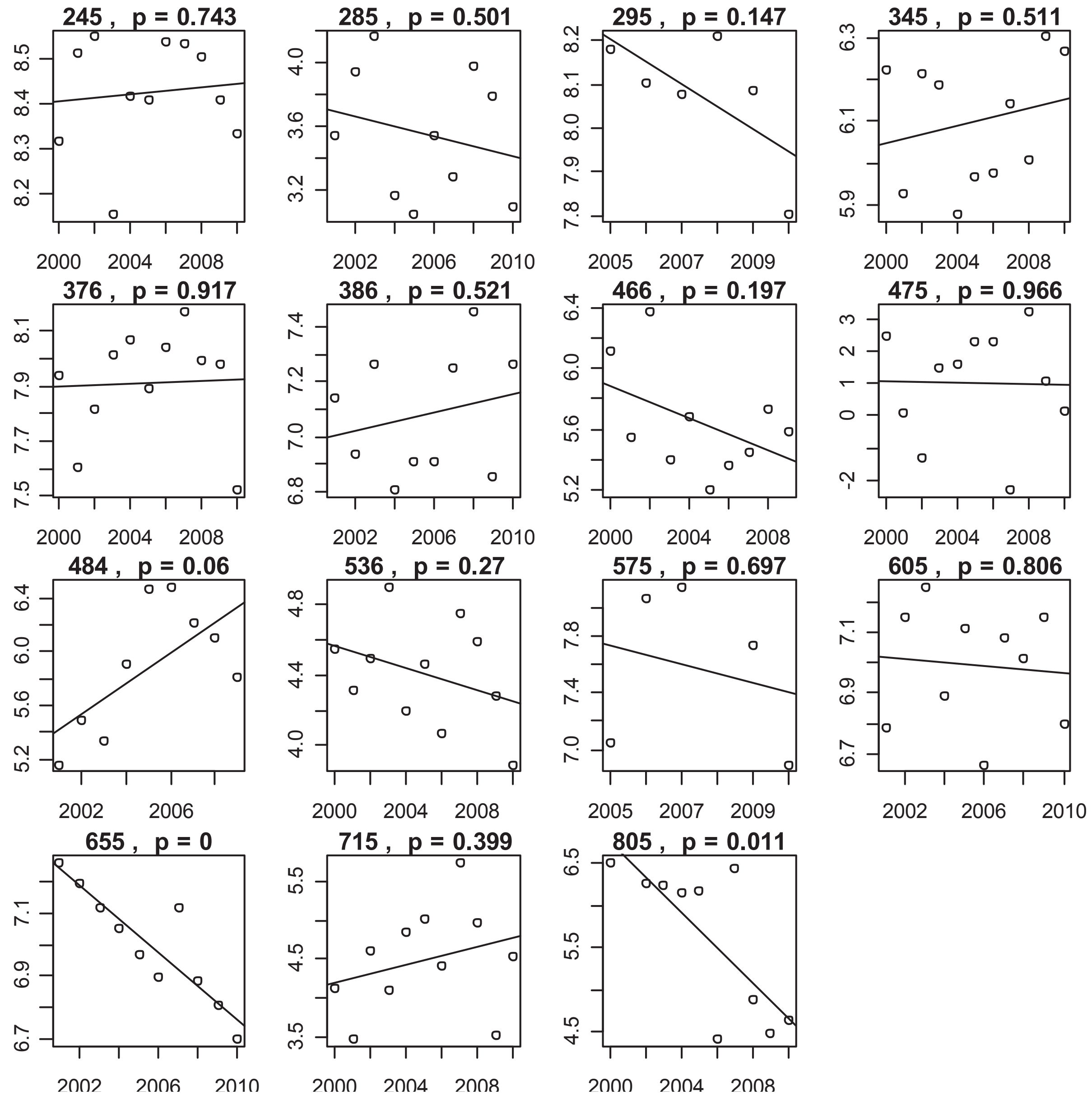


Figure 4.3. Plots of mean log-transformed summed PAH concentration data by year, fitted linear regression lines, and p-values for statistical significance of the regression slope for each station.

munity information (Long *et al.*, 1998; Rowlatt *et al.*, 2002).

The ERL/ERM methodology derives SQGs representing, respectively, the 10th and 50th percentiles of the effects dataset, and these are usually derived for individual parent PAH compounds. In a regulatory context, where SQGs are to be used as informal (non-regulatory) benchmarks to aid in the interpretation of sediment chemistry (Long *et al.*, 1998), this becomes complicated when a large number of individual PAH compounds are determined, as is usually the case and was also in this study.

This has led to separate ERL/ERM derived SQGs being set for 'Low molecular weight PAHs' and 'High molecular weight PAHs' (Gorham-Test, 1998). In this context, LMW PAH includes the 2- and 3-ring PAH compounds naphthalene, monomethyl naphthalenes, acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene, primarily oil-derived compounds; HMW PAH includes the 4- and 5-ring PAH compounds fluoranthene, pyrene, benz[a]anthracene chrysene, benzo[a]pyrene and dibenz[a,h]anthracene, primarily combustion-derived compounds. Although a wider suite of PAH is determined routinely for both licensing and monitoring purposes, these subsets can be considered as toxicity markers for the PAH as a whole. The ERL and ERM concentrations for low molecular weight PAHs (LMW PAH) and high molecular weight PAHs (HMW PAH) applied to this assessment are given in Table 4.2.

Table 4.2. ERL and ERM concentrations for LMW and HMW PAHs in sediments (μg kg^{-1} dry weight) (from Gorham-Test, 1998).

PAH compounds	ERL	ERM
LMW PAH	552	3,160
HMW PAH	1,700	9,600

The ERL and ERM values for LMW PAH are lower than those for HMW PAH as they exhibit a higher level of acute toxicity.

Table 4.3. ERL and ERM values for LMW and HMW PAHs found at CSEMP sites, 2000–2010.

Station	Number of samples	LMW > ERL	LMW > ERM	HMW > ERL	HMW > ERM
CSEMP 245	54	53	0	0	0
CSEMP 285	50	0	0	0	0
CSEMP 295	30	27	0	0	0
CSEMP 345	55	0	0	0	0
CSEMP 376	55	38	0	0	0
CSEMP 386	50	3	0	0	0
CSEMP 466	50	0	0	0	0
CSEMP 475	55	0	0	0	0
CSEMP 484	45	0	0	0	0
CSEMP 536	54	0	0	0	0
CSEMP 575	26	7	0	5	0
CSEMP 605	50	0	0	0	0
CSEMP 655	50	0	0	0	0
CSEMP 715	55	1	0	0	0
CSEMP 805	50	0	0	0	0

From Table 4.3 it is apparent that, at CSEMP 245 (off Tyne), the ERL for LMW PAHs is breached in 53 of 54 samples. Also, at CSEMP 295 (off Tees), 27 of 30 samples similarly breach the ERL for LMW PAHs. The ERL for LMW PAHs was exceeded in 38 of 55 samples from CSEMP 376 (off Wash), in only 7 of 26 samples from CSEMP 575 (off Tamar), and in 3 of 50 samples from CSEMP 386 (The Wash). Only 1 sample out of 50 exceeded the ERL for LMW PAHs at CSEMP 715 (Liverpool Bay). No sites breached the ERM for LMW PAHs. The ERL for HMW PAHs was breached at CSEMP 575 (off Tamar), but no sites breached the ERM for HMW PAHs.

The ERLs for LMW PAHs have been breached mainly off the East Coast of England, particularly close to the heavily contaminated estuaries of NE England. We could assume, therefore, that there are some correlations to regional distributions around the UK. In order to advise on the action limits for PAH contaminants in the UK, it may be suitable to use the ERL/ERM methodology to develop regional action limits. There is though a need for some understanding of the role played by organic carbon (and particularly black carbon) in binding PAH and reducing their toxicity before these action limits can be set with confidence. These are studies we intend to undertake in the near future.

5. Polybrominated diphenyl ethers (PBDEs) in sediments: spatial and temporal trends

Authors: Jon Barber, Philippe Bersuder and Thi Bolam

5.1 Introduction

The main programme for monitoring the status of contaminants in UK waters is the Clean Seas Environment Monitoring Programme (CSEMP). Within the CSEMP, the concentrations of a range of specific chemicals which are persistent, toxic and have the ability to accumulate in food chains are determined. Polybrominated diphenyl ethers (PBDEs) are additive flame retardant compounds that have been used extensively in textiles, thermoplastics, polyurethane foams, and electronic products. Three PBDE formulations were marketed, the penta-, octa- and deca-mix products, which differ by the average level of bromination in the mixture. The BDE congeners BDE47 and BDE99 typically made up > 70% of the penta-mix products, BDE183 > 40% of the octa-mix products and BDE209 (the fully brominated congener, decabromodiphenyl ether) > 97% of the deca-mix products. The penta- and octa-mix technical products are no longer in use, having been banned in the EU since 2004. The deca-PBDE technical mixture has been in use more recently than the other formulations, although its use has been restricted in the EU since 2008. In this section, BDE congener concentrations in surface sediments sampled around the coasts of England and Wales under the CSEMP are assessed. By collecting and analysing samples from 15 fixed stations in intermediate and open sea areas around England and Wales, the aim of this programme is to detect spatial variability and eventually long-term time trends in BDE congener concentrations in surficial sediments taken at those sites.

5.2 Sampling sites

In 2010, 14 fixed stations were visited by the RV *Cefas Endeavour*. Sediment samples were collected using a 0.1 m^2 modified Day grab at each of the sampling sites. This requires the collection of 5 replicate sediment samples, randomly within a 50m radius at each site, giving an indication of the small-scale variability of concentrations of BDE congeners at each site. Sediment samples were stored in glass jars, frozen immediately after collection and not defrosted until required for analysis. Sampling was also performed in 2009 at the same 14 stations, plus an additional one.

5.3 Methods

BDE congener concentrations were determined in the sediment samples and are reported on a dry weight basis. Sediment samples were air dried and sieved (< 2 mm) in a controlled environment. 10 g of dried sediment were mixed with sodium sulphate, transferred to a glass *Soxhlet* thimble and topped with 1 cm of sodium sulphate. ^{13}C-labelled BDE209 was added as internal standard to all samples prior to the extraction step. Samples were extracted over a 6 h period using 50:50 hexane:acetone, with an average of 9–10 cycles h^{-1}. An aliquot of the *Soxhlet* extract was cleaned up and fractionated using alumina (5% deactivated) and silica (3% deactivated) chromatography columns, respectively. The silica column fractionation results in two fractions, the first fraction containing BDE209 and the second fraction containing the other BDE congeners. After addition of internal standard CB200, BDE concentrations were determined using an Agilent 6890 GC with 5973 MS in electron capture negative ionisation (ECNI) mode. For BDE209, separation was performed on a 15 m x 250 µm, 0.1 µm film thickness DB-1 capillary column (J&W). The separation of the other BDEs was performed on a 50 m × 250 µm, 0.25 µm film thickness DB-5 capillary column (J&W). Quantitation of BDE209 was performed using an internal standard and 7 calibration levels (range 0.5–500 ng/ml). Quantitation of the other BDEs was performed using internal standards and 8 calibration levels (range 0.1–50 ng/ml). The identification of BDE congeners was based on the retention time of individual standards in the calibration mixtures. Full details of the analytical methodology are given in de Boer *et al.* (2001). Twelve BDE congeners were determined (BDE17, BDE28, BDE47, BDE66, BDE85, BDE99, BDE100, BDE138, BDE153, BDE154, BDE183 and BDE209, and the sum of all measured BDEs (∑12 BDEs) was calculated for each sample. All samples were run under an analytical quality control (AQC) protocol, which involved analysing blanks and either certified or laboratory reference materials within each sample batch. The reference material currently used is marine sediment certified reference material NIST 1944 produced by the National Institute of Standards and Technology in the USA. Quality assurance is also guaranteed with participation in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) laboratory proficiency scheme.

5.4 Results

BDEs were detected in sediments from 13 of the 14 stations sampled in 2010 (see Table 5.1). ∑12 BDEs concentrations ranged from < 0.32 µg kg^{-1} dry weight (dw) at the Thames Gabbard site to 16 µg kg^{-1} dw in Liverpool Bay. BDE209 was the dominant BDE congener present, making up 75–100% of ∑12 BDEs, and was detected at more stations than the other BDE congeners, which were detected in samples from only 9 of the 14 stations. Of the remaining 11 BDE congeners, BDE47 was the major congener present, making up 30–100 % of the ∑11 BDEs, or 0.1–13% of ∑12 BDEs. BDE99, another representative of the penta-mix PBDE technical product, was detected in sediments from 7 of the 14 stations, making up 23–100% of the ∑11 BDEs. It was at a higher abundance than BDE47 at three CSEMP stations: CSEMP 245 (off Tyne), CSEMP 295 (off Tees) and CSEMP 376 (Humber). BDE183, indicative of the octa- or deca-PBDE technical mixtures, was only detected at one station in 2010, CSEMP 245 (off Tyne).

The results from 2010 have been plotted on maps in Figure 5.1. The highest concentrations of BDE209 were found at CSEMP 715 (Liverpool Bay) (16 µg kg^{-1} dw) with the next highest at CSEMP 245 (off Tyne) (7.1 µg kg^{-1} dw) and at CSEMP 655 (Cardigan Bay) (5.3 µg kg^{-1} dw). For the other 11 BDEs, the distribution was slightly different, with none being detected in sediments from Liverpool Bay. Highest concentrations of their representative BDE, BDE47, were found in the North East, with mean concentrations of 0.31, 0.19, 0.16 and 0.10 µg kg^{-1} dw at CSEMP 245 (off Tyne), CSEMP 376 (Humber), CSEMP 295 (off Tees) and CSEMP 386 (The Wash), respectively. Concentrations were below LODs for the 11 BDEs (excluding BDE209) in sediment samples from several offshore stations in the North Sea and Irish Sea, and in samples from inshore stations in the western English Channel. In contrast, BDE209 was only below the LOD at CSEMP 475 (Thames Gabbard) in the southern North Sea, which has a clean sand substrate.

Table 5.1. Concentrations of BDEs in sediments collected from CSEMP stations in 2010.

		Sediment concentration (in µg kg^{-1} dry weight)						%BDE209		BDEs detected (in order of abundance)[a]
		BDE47		BDE209		∑12 BDEs				
Location	CSEMP Station	Mean	Range	Mean	Range	Mean	Range	Mean	Range	
Off Tyne	245	0.31	0.23-3.8	7.1	2.0-13	8.2	2.9-14	82	70-93	BDE209, BDE99, BDE47, BDE153, BDE154, BDE183, BDE100
Off Tyne/Tees	285	<0.02	<0.02	0.064	<0.1-0.32	0.064	<0.32-0.32	100	100	(BDE209)
Off Tees	295	0.16	0.14-0.16	1.5	0.82-2.5	1.9	1.2-3.0	75	69-86	BDE209, BDE99, BDE47, BDE153, BDE100, BDE154
Off Humber /Wash	345	0.024	<0.02-0.034	0.14	0.10-0.23	0.19	0.12-0.29	77	68-84	BDE209, BDE47, BDE99
Humber	376	0.19	0.13-0.27	3.3	2.3-5.4	3.8	2.6-6.2	86	80-90	BDE209, BDE99, BDE47, BDE66 (BDE153, BDE28, BDE100)
Wash	386	0.10	0.02-0.18	1.2	0.57-2.1	1.4	0.67-2.3	85	70-90	BDE209, BDE47, BDE99 (BDE66)
Thames	466	N/A		N/A		N/A		N/A		N/A
Thames (Gabbard)	475	<0.02	<0.02	<0.1	<0.1	<0.32	<0.32			
Channel	484	0.028	<0.02-0.060	1.9	1.4-2.6	1.9	1.4-2.6	98	97-100	BDE209, BDE47
Lyme Bay	536	<0.02	<0.02	0.13	0.10-0.18	0.13	0.10-0.18	100	100	BDE209
Off Tamar	575	<0.02	<0.02	1.9	0.65-3.8	1.9	0.65-3.8	100	100	BDE209
Celtic Deep	605	0.040	<0.02-0.070	0.51	0.38-0.67	0.57	0.38-0.77	91	78-100	BDE209, BDE47, BDE99
Cardigan Bay	655	0.048	<0.02-0.090	5.3	2.3-16	5.4	2.4-16	97	96-100	BDE209, BDE47, BDE99
Liverpool Bay	715	0.020	<0.02-0.040	16	4.2-25	16	4.2-25	100	100	BDE209, BDE47
SE Isle of Man	805	<0.02	<0.02	2.7	1.6-3.9	2.7	1.6-3.9	100	100	BDE209

N/A: Not analysed in 2010

[a] congeners in parentheses were detected in less than half of the replicate samples

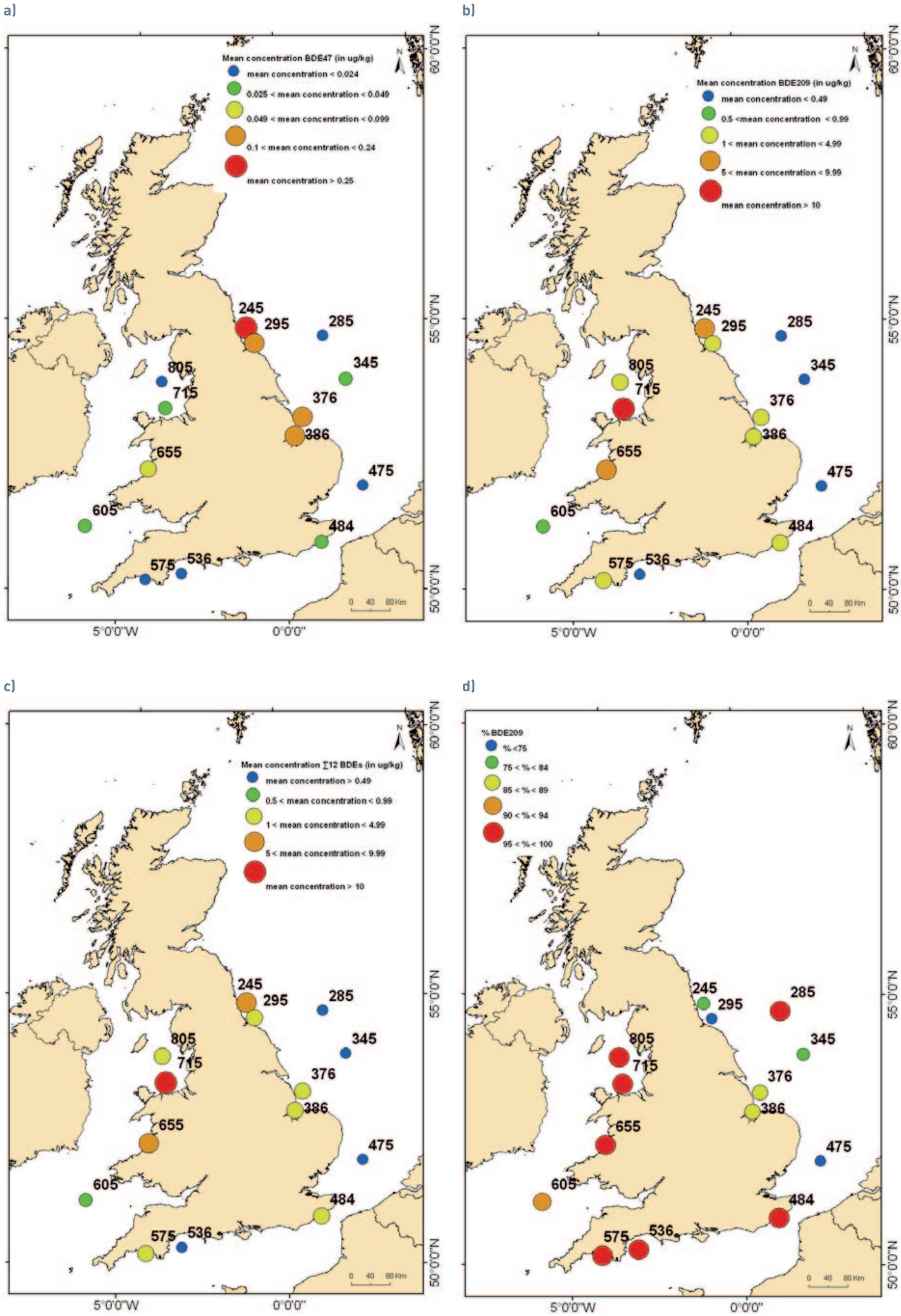


Figure 5.1. Sampling locations for sediments analysed in 2010, colour-coded for BDE concentration, showing a) BDE47, b) BDE209, c) ∑12 BDEs and d) proportion of ∑12 BDEs made up by BDE209. Note the different scales on the different maps.

Monitoring of sediment samples at CSEMP stations only began in 2009, so there are insufficient data available to investigate temporal trends. Results in 2009 were similar to those in 2010 (see Table 5.2). One additional station in the Thames was analysed in this earlier sampling year, and BDEs were detected in sediments from 13 of the 15 stations sampled. ∑12 BDEs concentrations ranged from < 0.32 µg kg^{-1} dw in sediments from CSEMP 475 (Thames Gabbard) and CSEMP 285 (off Tyne/Tees), to 9.8 µg kg^{-1} dw in Liverpool Bay. BDE209 was the main BDE congener present, making up 72–100% of ∑12 BDEs. Of the remaining 11 BDEs, BDE47 was the major congener present, making up 22–100% of the ∑11 BDEs, or 0–63% of ∑12 BDEs. BDE99 was detected in sediments from 7 of the 14 stations, and making up 27–51% of the ∑11 BDEs. BDE183 was detected at 2 additional stations in 2009, CSEMP 285 (off Tyne/Tees) and CSEMP 376 (Humber), in addition to CSEMP 245 (off Tyne).

Table 5.2. Concentrations of BDEs in sediments collected from CSEMP stations in 2009.

		Sediment concentration (in µg kg^{-1} dry						%BDE209	
		BDE47		BDE209		∑12 BDEs			
Location	CSEMP Station	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Off Tyne	245	0.41	0.37-0.50	3.6	3.1-4.1	5.0	4.6-5.6	72	68-75
Off Tyne/Tees	285	<0.02	<0.02	<0.1	<0.1	<0.32	<0.32		
Off Tees	295	0.24	0.23-0.25	2.2	1.7-3.1	3.0	2.4-3.9	73	69-79
Off Humber /Wash	345	0.037	0.031-0.045	<0.1	<0.1	0.065	0.058-0.072	0	0
Humber	376	0.36	0.26-0.43	5.5	3.2-8.0	6.5	3.9-8.9	84	80-89
Wash	386	0.12	0.10-0.14	1.4	0.84-2.3	1.7	1.1-2.6	84	80-89
Thames	466	0.035	0.030-0.040	2.1	1.4-2.6	2.1	1.5-2.6	96	94-97
Thames (Gabbard)	475	<0.02	<0.02	<0.1	<0.1	<0.32	<0.32		
Channel	484	0.022	<0.02-0.028	2.3	1.4-3.4	2.3	1.4-3.5	98	97-100
Lyme Bay	536	0.019	<0.02-0.027	0.23	0.14-0.38	0.25	0.16-0.40	92	88-100
Off Tamar	575	0.045	0.02-0.061	2.3	1.5-3.7	2.4	1.6-3.8	98	97-99
Celtic Deep	605	0.054	0.044-0.064	0.92	0.72-1.0	1.0	0.86-1.1	90	84-92
Cardigan Bay	655	0.059	0.047-0.066	3.4	2.8-4.3	3.6	2.9-4.4	97	96-98
Liverpool Bay	715	0.010	<0.02-0.031	9.8	2.5-17	9.8	2.5-17	100	99-100
SE Isle of Man	805	0.024	<0.02-0.034	1.8	<0.1-3.9	1.8	<0.32-3.9	98	96-99

5.5 Discussion

BDEs have been detected in sediments from most stations with the exception of some offshore stations in the North Sea. Currently there are no FEPA action levels for BDEs in sediments (used in dredged material disposal licensing), no Water Framework Directive/Marine Strategy Framework Directive (WFD/MSFD) Environmental Quality Standards (EQS) for sediment, and no OSPAR assessment concentrations with which to compare these results. Based on abundance, BDE209 is the most important BDE congener to monitor, although it is bioaccumulated to only a limited extent (Leslie *et al.*, 2011). In addition to possible direct toxic effects, there is concern over the ability of BDE209 to debrominate in the environment, yielding lower brominated congeners which may be more mobile, more bioaccumulative and more toxic (Hutchinson *et al.*, submitted). BDE209 and the other BDE congeners currently have a geographical different distribution pattern, which probably reflects their different uses and sources of release into the environment. BDE209 has a wider distribution, being present in all geographical areas, with the highest concentrations found in Liverpool Bay. The other 11 BDEs have a more limited distribution, having the highest concentrations in the Tyne/ Tees area, and being below LOQs in the Western Channel. Not enough data is currently available to investigate temporal trends of BDEs in sediments.

6. Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in sediments: spatial distribution in selected areas of the North Sea, English Channel and Celtic Sea

Authors: Jon Barber, Philippe Bersuder and Thi Bolam

6.1 Introduction

The main programme for monitoring the status of contaminants in UK waters is the Clean Seas Environment Monitoring Programme (CSEMP). Within the CSEMP, the concentrations of a range of specific chemicals which are persistent, toxic and have the ability to accumulate in food chains are determined. Polychlorinated biphenyls (PCBs) are present in the environment as a result of widespread historical use of these products, mainly in electrical transformers. Although the ban on new uses of PCBs was put in place in 1981, these compounds are very persistent in the environment and significant falls in environmental concentrations may take decades. Polybrominated diphenyl ethers (PBDEs) are additive flame retardant compounds that have been used extensively in textiles, thermoplastics, polyurethane foams, and electronic products. Three PBDE formulations were marketed, the penta-, octa- and, deca-mix products, which differ in the average degree of bromination in congeners present in the mixture. BDE47 and BDE99 typically made up > 70% of the penta-mix products, and BDE183 > 40% of the octa-mix products. Penta- and octa-mix technical mixtures are no longer in use, having been banned in the EU since 2004. In this section, PCB and PBDE concentrations in surface sediments sampled in 4 areas around the coasts of England and Wales, in order to provide evidence for use in a redesign of the CSEMP, are assessed.

6.2 Sampling sites

In 2008, 32 stations were sampled in the Bristol Channel area of the Irish Sea and 32 stations were sampled in the Tyne/Tees area of the North Sea from onboard the RV *Cefas Endeavour*. In 2009, 24 stations were sampled in the Western and Eastern areas of the English Channel, also from onboard the RV *Cefas Endeavour*. Sediment samples were collected using a 0.1 m^2 modified Day grab. Sediment samples were stored in glass jars, frozen immediately after collection and not defrosted until required for analysis.

6.3 Methods

PBDE and PCB concentrations were determined in the sediment samples and are reported on a dry weight basis. Sediment samples were air dried and sieved (< 2mm) in a controlled environment. 10 g of dried sediment were mixed with sodium sulphate, transferred to a glass Soxhlet thimble and topped with 1 cm of sodium sulphate. Samples were extracted over a 6 h period using 50:50 hexane:acetone, with an average of 9–10 cycles h^{-1}. An aliquot of the Soxhlet extract was cleaned up and fractionated using alumina (5% deactivated) and silica (3% deactivated) columns, respectively. The silica column fractionation results in two fractions, the first fraction containing CBs and the second fraction containing BDEs. After addition of internal standard CB53, CB concentrations were determined with an Agilent 6890 GC with µECD. The separation of analytes was performed on a 50.0 m × 200 µm, 0.33-µm-film-thickness DB-5 capillary column (J&W). The identification of CB congeners was based on the retention time of individual standard compounds in the calibration mixtures. Quantification was performed using internal standards and 7 calibration levels (range 0.5–100 ng/ml). Full details of the analytical methodology are given in Allchin *et al.* (1989). 25 CB congeners were determined, and the ∑ICES 7 CBs (CB28, CB52, CB101, CB118, CB138, CB153, CB180), and the sum of all 25 measured CBs (∑CBs) were calculated. After addition of internal standard CB200, BDE congener concentrations were determined with an Agilent 6890 GC with 5973 MS in electron capture negative ionisation (ECNI) mode. The separation of the BDE congeners was performed on a 50.0 m × 250 µm, 0.25-µm-film-thickness DB-5 capillary column (J&W). Quantification of BDE congeners was performed using internal standards and 8 calibration levels (range 0.1–50 ng/ml). The identification of BDEs congener was based on the retention time of individual standard compounds in the calibration mixtures. Full details of the analytical methodology are given in de Boer *et al.* (2001). 11 PBDE congeners were analysed (BDE17, BDE28, BDE47, BDE66, BDE85, BDE99, BDE100, BDE138, BDE153, BDE154 and BDE183, and the sum of all measured BDEs (∑11 BDEs) were calculated. All samples are run under an analytical quality control (AQC) protocol, which involved analysing blanks and reference materials within each sample batch. The reference material currently used is marine sediment certified material NIST 1944 certified by the National Institute of Standards and Technology in the USA. Quality assurance is also guaranteed with participation in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) laboratory proficiency scheme.

6.4 Results

6.4.1 Bristol Channel and the Celtic Sea

PCBs were at quantifiable concentrations in sediment samples from 13 of the 32 stations in this area, with ∑ 25 CBs concentrations ranging by a factor of 14 between 0.68 and 9.4 µg kg^{-1} dry weight (dw) (see Figure 6.1a). BDEs were at quantifiable concentrations in samples from 30 of the 32 stations, with ∑ 11 BDEs concentrations ranging by a factor of 11 from 0.032 to 0.35 µg kg^{-1} dw (see Figure 6.1b). However, it is important to note that method LOQs for BDEs are better than for CBs, which will affect the proportion of non-detects. BDE47 dominated the ∑ 11 BDEs, making up > 50% of the sum at 27 of the 32 stations (range 32–100%). BDE99 was the only other widely detected congener, being present in samples from 19 of the 32 stations, and making up 19–50% of ∑ 11 BDEs, when present. There was considerable spatial variability in measured concentrations for both CBs and BDEs, with stations with elevated concentrations of both contaminants being co-located at the same locations. Most of the stations were some distance from land and any local sources, so these 'hotspots' were most likely a function of different sediment type, with higher organic matter sediments accumulating higher levels of contaminants than lower organic matter sediments. Due to their frequency of detection and measured concentrations, both CBs and BDEs are of interest in this area.

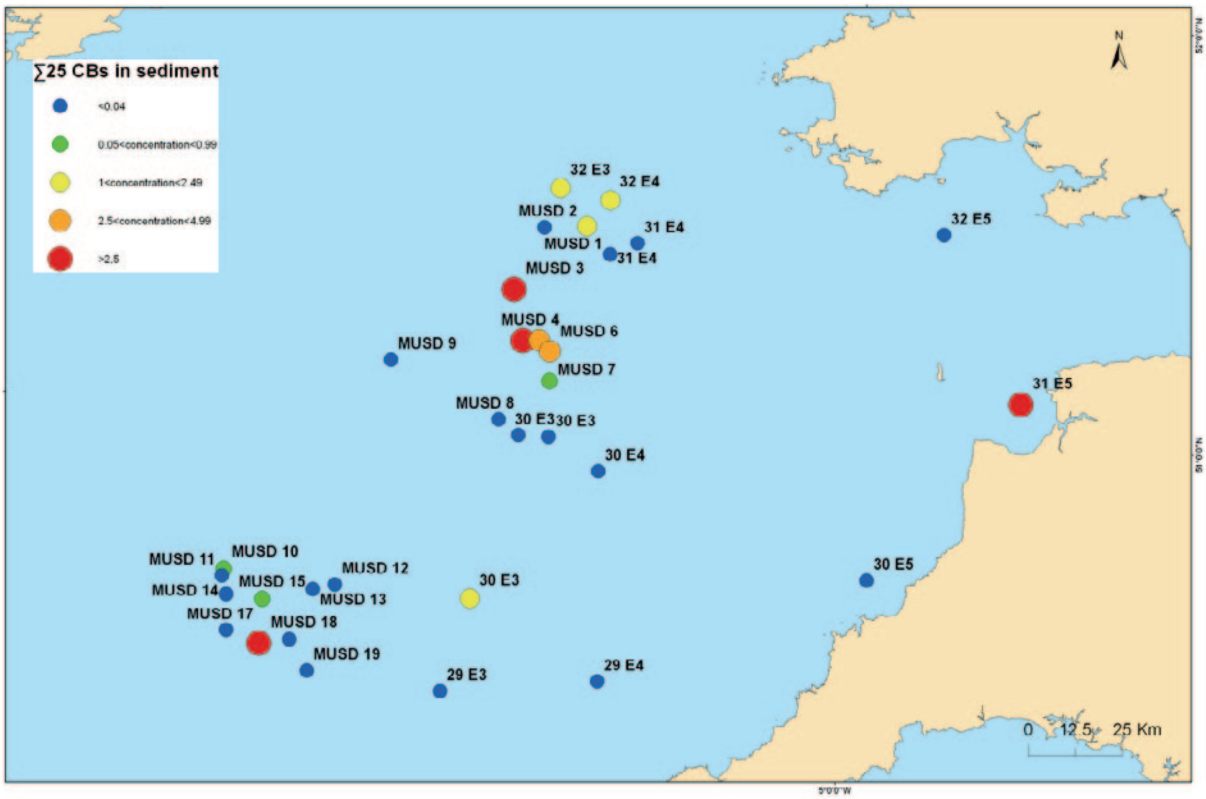
6.4.2 Tyne/Tees area of the North Sea

CBs were at quantifiable concentrations in sediment samples from 5 of the 32 stations in this area, with ∑ 25 CBs concentrations ranging by a factor of 17 between 0.1 and 1.7 µg kg^{-1} dw (see Figure 6.2a). BDEs were at quantifiable concentrations in samples from 31 of the 32 stations, with ∑ 11 BDEs concentrations ranging by a factor of 70 from 0.028 and 2.0 µg kg^{-1} dw (see Figure 6.2b). Highest concentrations of both contaminants were found in sediments from the 4 stations closest to the mouths of the rivers Tyne and Tees. At these stations, up to 9 of the 11 BDEs were detected, whereas stations further offshore were dominated by BDE47 and, to a lesser extent, BDE99. Considering the low frequency of detection of CBs, it is not worth carrying out widespread sediment analysis for these contaminants in this area, although analysis of them in the closest to shore stations may be of interest.

6.4.3 Western and Eastern areas of the English Channel

CBs were at quantifiable concentrations in sediment from only 1 of the 24 stations in this area, where the ∑ 25 CBs concentration was 0.21 µg kg^{-1} dw. BDEs were detected in sediment samples from 14 of the 24 stations, with ∑ 11 BDEs concentrations ranging by a factor of ~3 from 0.025 to 0.064 µg kg^{-1} dw (see Figure 6.3), although only BDE 47 was detected in samples from this area. Highest concentrations were detected at stations close to shore, with sediment concentrations from offshore stations in the Channel being below LODs. Levels were also elevated in some offshore stations in the Celtic Sea. Considering the very low frequency of detection of CBs, it is not worth carrying out widespread sediment analysis for these contaminants in this area.

a)



b)

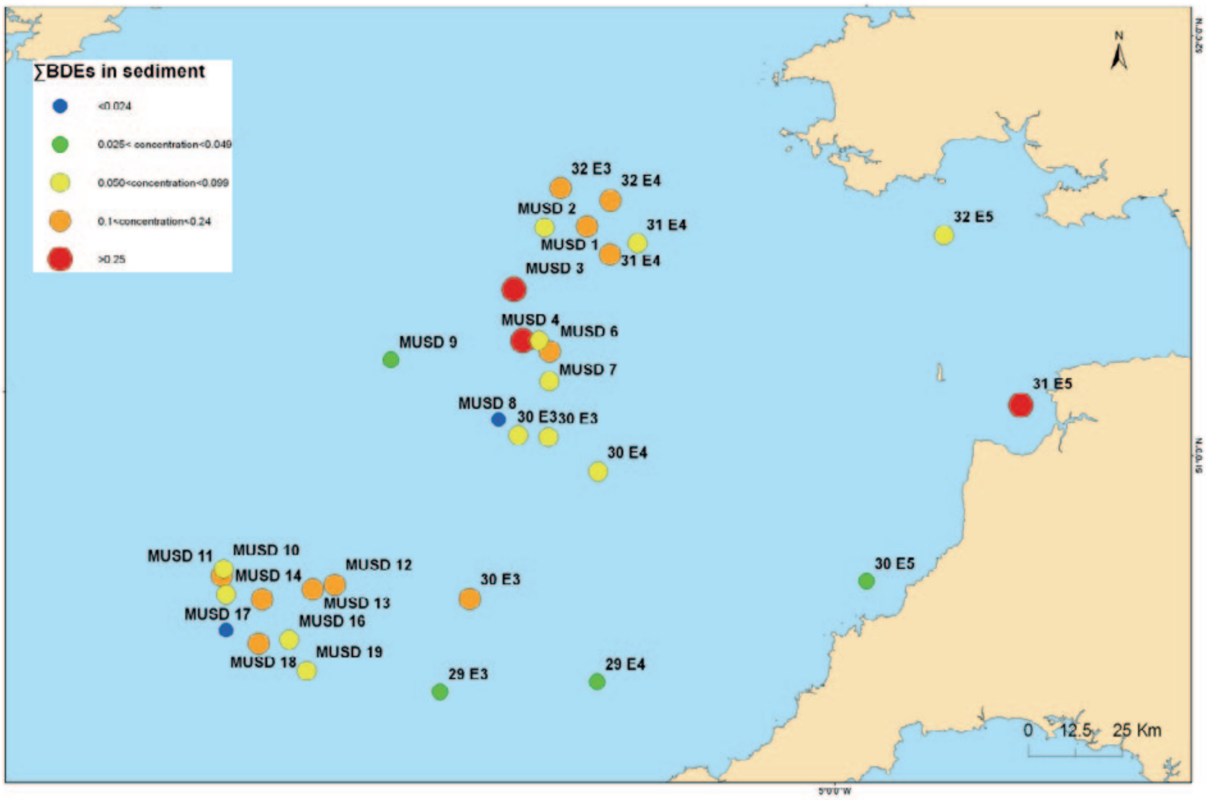
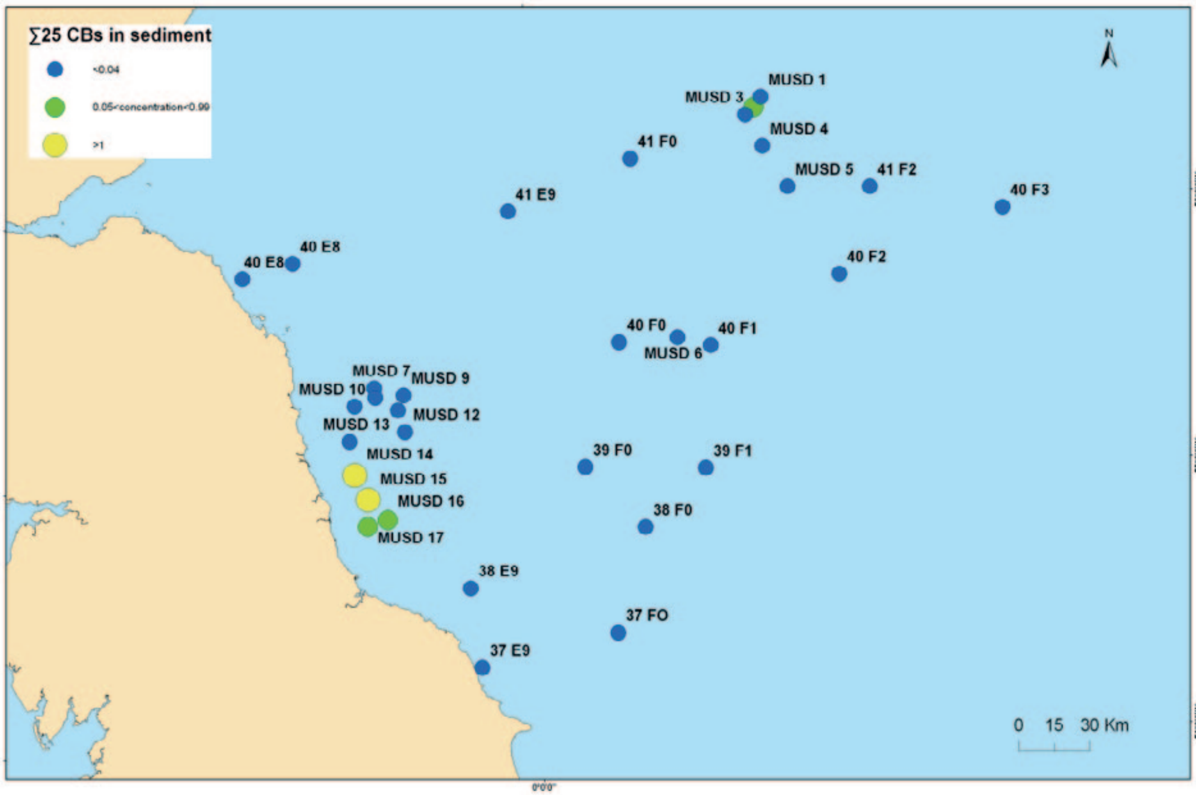


Figure 6.1. Sampling locations for sediments analysed in the Bristol Channel and Celtic Sea area of the Irish Sea in 2008, colour-coded for contaminant concentration, showing a) ∑25 PCBs and b) ∑11 BDEs. Note the different scales on these maps.

a)



b)

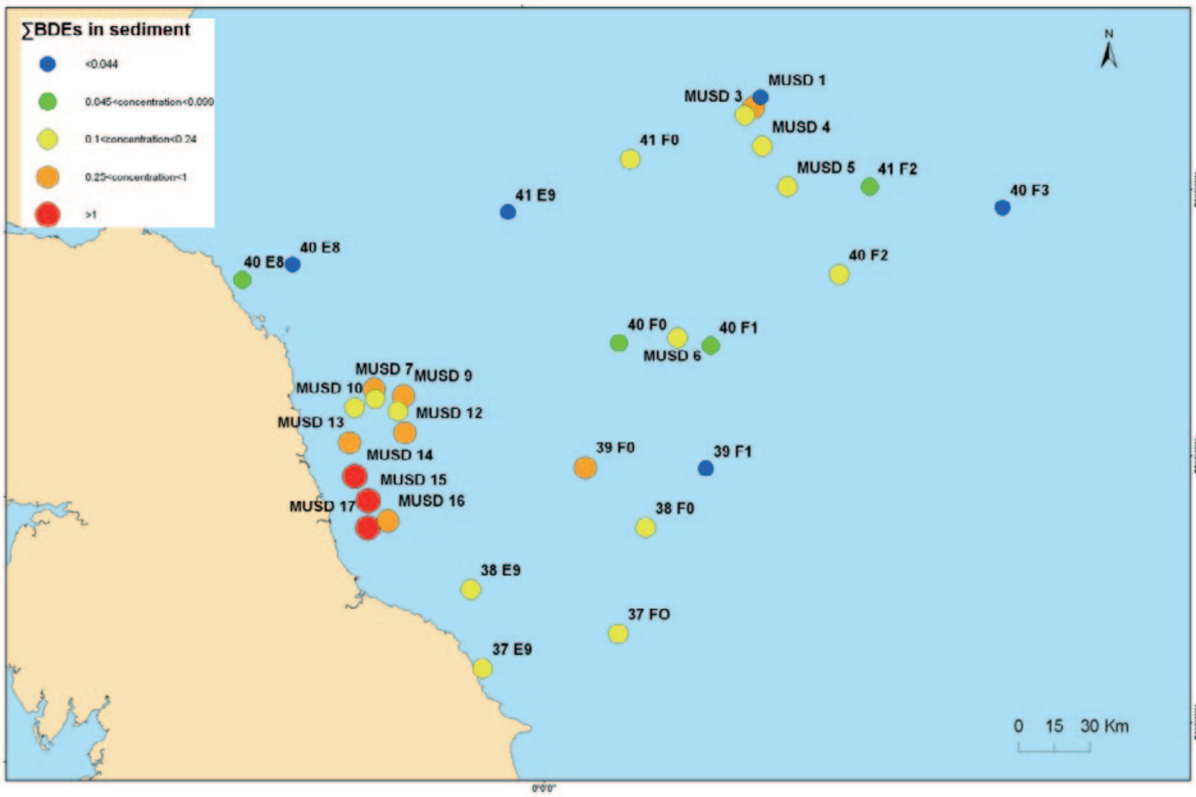


Figure 6.2. Sampling locations for sediments analysed in the Tyne/Tees area of the North Sea in 2008, colour-coded for contaminant concentration, showing a) ∑25 PCBs and b) ∑11 BDEs. Note the different scales on these maps.

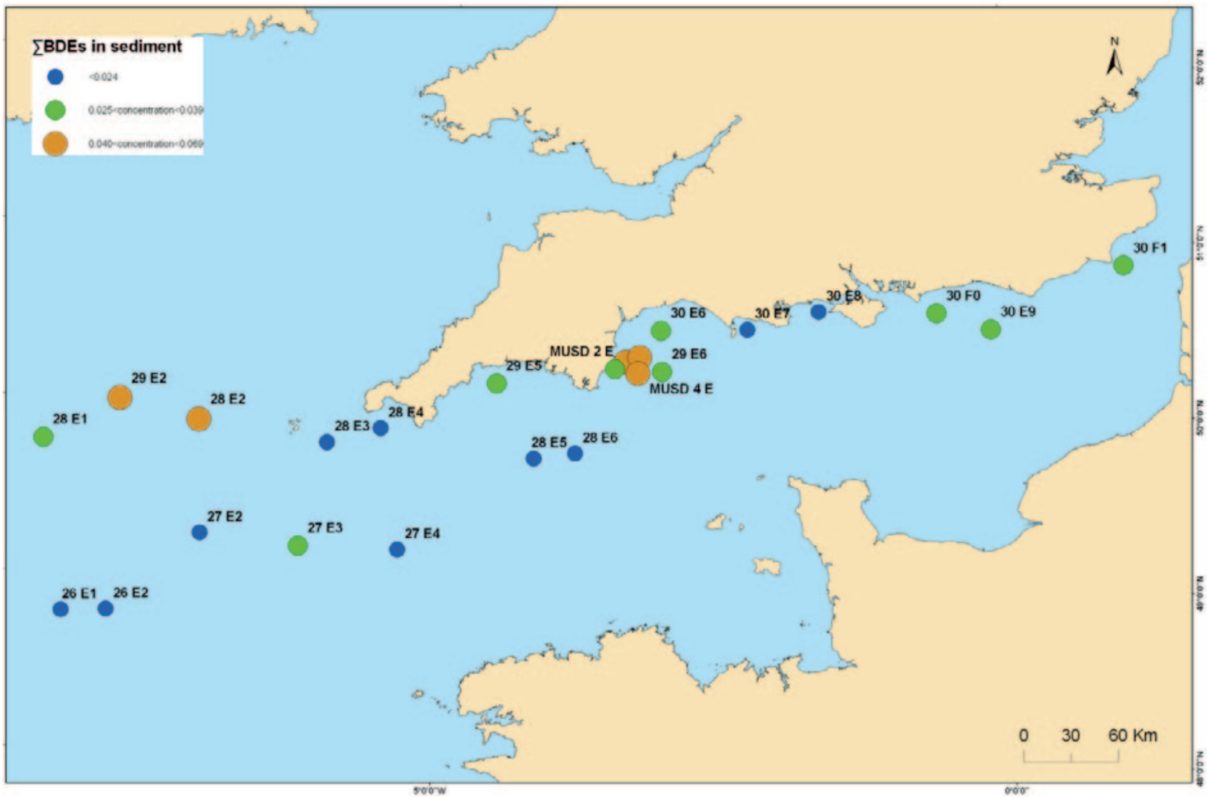


Figure 6.3. Sampling locations for sediments analysed in the Western and Eastern English Channel in 2009, colour-coded for contaminant concentration, showing ∑11 BDEs. CBs were also determined but were below limits of detection in all samples but one.

6.5 Discussion

Of the three areas studied, sediments in the Bristol Channel and Celtic Sea area contained the highest CBs concentrations, the Tyne/Tees area contained the highest BDEs concentrations, and the Western and Eastern Channel was generally low for both sets of contaminants. Contamination of the Rivers Skerne and Tees by PBDEs downstream of a manufacturing facility, extending into the adjacent areas of the North Sea, has been documented previously (Allchin *et al.*, 1999; Boon *et al.*, 2002). Within a geographical area there can be considerable variation in contamination levels, which may be related to the type of sediment present and its organic content. For monitoring purposes, it is recommended that samples from different stations within an area are collected rather than multiple replicates from the same stations. However, it is important to continue monitoring at the stations for several years more to gain information about possible temporal trends in concentrations.

7. Polychlorinated biphenyls (PCBs) in fishes: spatial and temporal trends

Authors: Philippe Bersuder, Jon Barber, Thi Bolam and Jon Barry

7.1 Introduction

The main programme for monitoring the status of contaminants in UK waters is the Clean Seas Environment Monitoring Programme (CSEMP). CSEMP measures the concentrations of a number of specific chemicals which are persistent, toxic and have the ability to accumulate in food chains. PCBs are present in the environment as a result of widespread historical use of these products, mainly in electrical transformers. Although the ban on new uses of PCBs was put in place in 1981, these compounds are very persistent in the environment and significant falls in environmental concentrations may take decades. In this section, PCB concentrations in dab (*Limanda limanda*) tissues sampled around the coasts of England and Wales under CSEMP are assessed against the OSPAR Background Assessment Concentrations (BACs) and EC limit values established in order to protect the health of human consumers. By collecting samples at around 45 fixed stations in intermediate and open sea areas around England and Wales, the aim of this programme is also to detect any contaminant long-term trends, spatial variability and contaminant enrichment in fish tissues at those sites.

7.2 Sampling undertaken in 2010

In 2010, 18 fixed stations were visited by the RV *Cefas Endeavour*, together with additional stations in Dublin Bay and Dundrum Bay. A pool of 25 fish was collected at each site. Five individual liver tissue samples were bulked, giving 5 pooled replicates for each of the sampling sites.

7.3 Methods

PCB concentrations were determined in dab livers and are reported on a wet weight basis. 5 g of homogenised fish liver were mixed with sodium sulphate and left to dry overnight. Sulphated samples were transferred to a glass *Soxhlet* thimble and topped with 1 cm of sodium sulphate. Samples were extracted over a 6 h period using 50:50 hexane:acetone, with an average of 9–10 cycles h^{-1}. Following extraction, an aliquot of sample was tested for extractable lipid content gravimetrically by drying the aliquot. Subsequently, another aliquot of the *Soxhlet* extract was cleaned up and fractionated using alumina (5% deactivated) and silica (3% deactivated) columns, respectively. After addition of internal standard CB53, a congener not found in environmental samples, CB congener concentrations were determined using an Agilent 6890 GC with µECD. The separation of analytes was performed on a 50 m × 200 µm, 0.33-µm-film-thickness DB-5 capillary column (J&W). The identification of CB congeners was based on the retention time of individual standard compounds in the calibration mixtures. Quantification was performed using internal standards and 7 calibration levels (range 0.5–100 ng/ml). Full details of the analytical methodology are given in Allchin *et al.* (1989). 25 PCB congeners were analysed, and the ∑ICES 7 CBs (CB28, CB52, CB101, CB118, CB138, CB153, CB180), and the sum of all 25 measured CBs (∑CBs) were calculated. All samples were run under an analytical quality control (AQC) protocol, which involved analysing blanks and certified or laboratory reference materials within each sample batch. The certified reference material currently used is the cod liver oil BCR 349 produced by the European Commission Joint Research Council (JRC) Institute for Reference Materials and Measurements. Quality assurance is also guaranteed with participation in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) laboratory proficiency scheme.

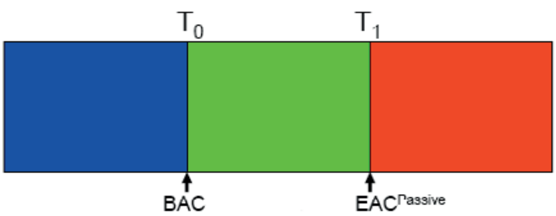
The assessment methodology applied here was the ‘traffic light’ system used by OSPAR to assess Co-ordinated Environmental Monitoring Programme (CEMP) data for the QSR2010 (OSPAR, 2009a), using Background Assessment Concentrations (BACs) and Environmental Assessment Criteria (EACs) for the ICES7 CBs in fish (see Table 7.1). Concentrations are expressed in µg kg^{-1} wet weight then normalised to lipid weight. EACs for CBs in shellfish or fish are not recommended for use in assessments as they are below BACs. Therefore, EACs for CBs in sediment were used to calculate concentrations of CBs in mussel tissue in equilibrium with sediment containing CB concentrations equal to the EACs in sediment and it was proposed that these calculated values (termed EAC^{passive}) be used as the green/red transition (T1) (Figure 7.1) for CBs in mussels and fish liver. Concentrations below BACs would be considered to have high environmental status. Concentrations significantly below EAC^{passive} could be considered to have good environmental status and those above, bad environmental status. The station is deemed to have 'bad' environmental status if 'bad' status occurs for more than one ICES7 CB congener. The 95% bound upper confidence bound concentrations observed in 2010 were compared to the green/red transition (EAC^{passive}) for CBs in fish liver.

Table 7.1. OSPAR assessment criteria for CBs in fish from Charting Progress 2.

Assessment criteria for CBs in fish (μg kg^{-1} lipid weight)

Compound	BAC	EAC^{passive}
CB28	0.22	64
CB52	0.12	108
CB101	0.14	120
CB118	0.17	24
CB138	0.15	316
CB153	0.19	1600
CB180	0.10	480

Figure 7.1. Transition points for CBs in biota (OSPAR 2009b).



Temporal trends were investigated at sites with 4 or more years data (total of 26 sites) for Σ25 CBs, ΣICES7 CBs and CB118. Temporal trends were obtained by calculating the mean of observations for the same station and year, and by fitting a linear regression model to these means, which has the advantage of removing any spatial correlation between observations.

7.4 Results

In 2010, CBs levels in dab livers were reported for 20 stations, and the sum of ICES7 CBs is summarised in Table 7.2. The highest mean ΣICES7 concentration was found for the Inner Liverpool Bay site (1,270 μg kg^{-1} lipid weight) followed by Morecambe Bay (804 μg kg^{-1} lipid weight) and Liverpool Bay (729 μg kg^{-1} lipid weight), while the lowest was for South Eddystone (74 μg kg^{-1} lipid weight).

The 95% bound upper confidence concentrations were compared to the blue/green transition (BAC) and green/red transitions (EAC^{passive}) on an individual congener basis for the ICES7 CBs (Figure 7.2). Concentrations exceeded the EAC^{passive} for 3 congeners, namely CB118 (85% of stations), CB101 (10% of stations) and CB138 (5% of stations) and these were therefore classified as having poor environmental status (ie, red within the traffic light scheme). The high proportion of stations with a 'red' status for CB118 is a result of CB118 being the most toxic of the ICES7 CBs as it is the only one of the seven which can attain a planar configuration and so elicit 'dioxin-like' toxicity. CB118 therefore has the lowest EAC^{passive} (24 μg kg^{-1} lipid weight) of all ICES7 congeners (Table 7.1). Only two stations had two or more congeners with concentrations above the EAC^{passive}, and these were the Inner Liverpool Bay (CSEMP 706) and Liverpool Bay (CSEMP 715). South Eddystone (CSEMP 584), the North Cardigan Bay (CSEMP 649) and Dublin Bay were the only stations where none of the ICES 7 CBs exceeded the green/red transition.

Charting Progress 2 (Defra, 2010) and the associated CSSEG feeder report (http://chartingprogress.defra.gov.uk/clean-and-safe-seas-feeder-report accessed 27 June 2012) provide an assessment of CBs in fish liver in the UK, based on the same assessment criteria, but on time series over several years. While the assessment for CB118 is very similar across the UK, that of the other ICES7 congeners generally shows a better status for the 2010 data.

Figure 7.2. Sampling locations and assessment for individual ICES7 CB congeners for fish liver analysed in 2010, colour-coded for CB concentration.

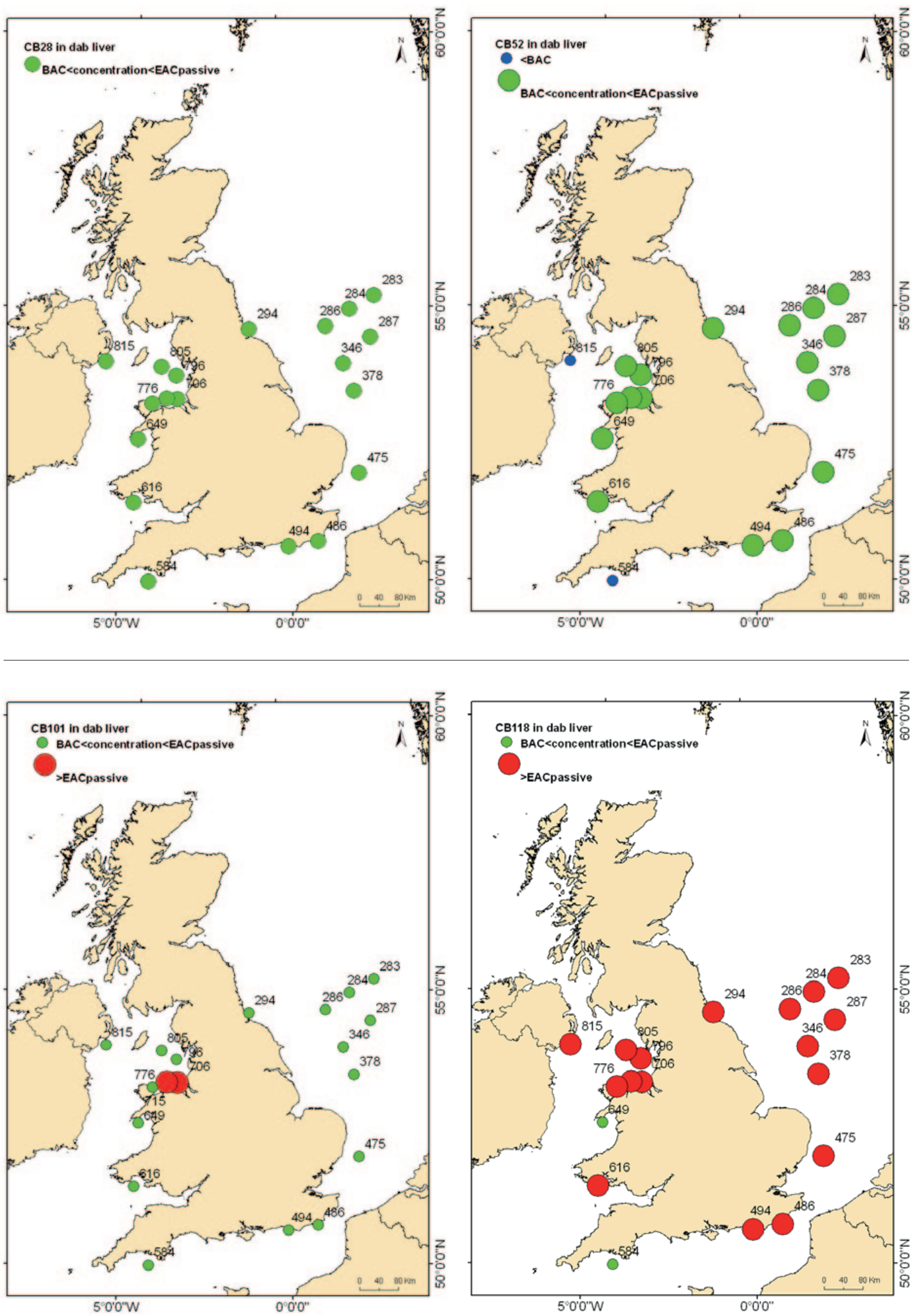


Figure 7.2. continued Sampling locations and assessment for individual ICES7 CB congeners for fish liver analysed in 2010, colour-coded for CB concentration.

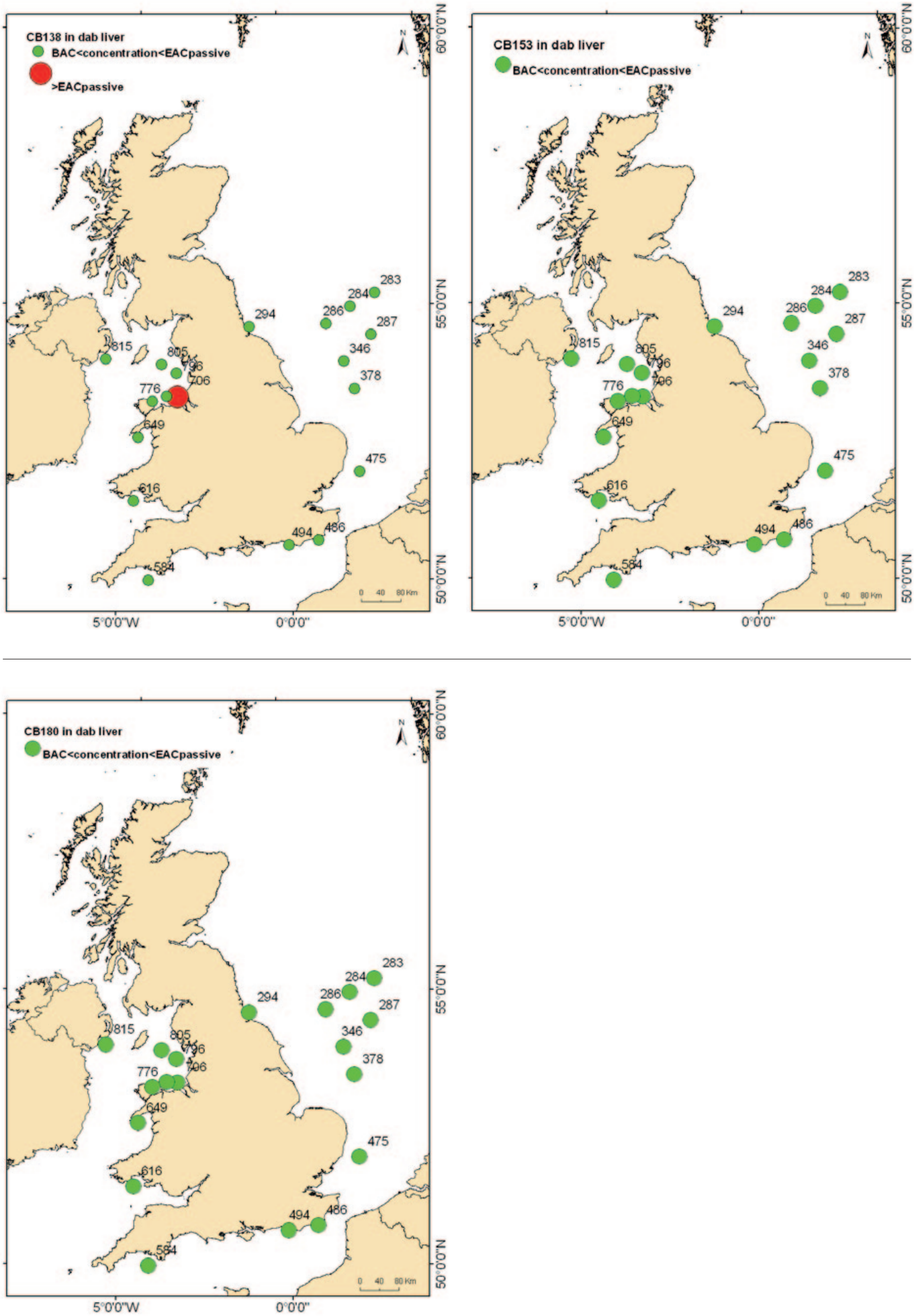


Table 7.2. Mean concentrations and range of CB118, ΣICES7 CBs and ΣCBs (25 congeners) for dab liver samples collected in 2010 at 19 CSEMP stations and Dublin Bay (mg kg^{-1} lipid weight).

Location	CSEMP station	Latitude	Longitude	Dab liver concentration (in mg kg^{-1} lipid weight)					
				Sum of 25 CBs		Sum ICES7 CBs		CB118	
				Mean	Range	Mean	Range	Mean	Range
North Dogger 1	283	55.289	2.904	0.45	0.13-0.61	0.32	0.19-0.82	0.048	0.024-0.089
North Dogger 2	284	55.065	2.082	0.25	0.11-0.23	0.18	0.16-0.32	0.029	0.018-0.040
West Dogger	286	54.777	1.295	0.51	0.20-0.59	0.37	0.30-0.79	0.047	0.033-0.055
Dogger Central	287	54.527	2.699	0.22	0.10-0.23	0.16	0.14-0.32	0.025	0.017-0.036
Tees Bay	294	54.756	-1.136	0.41	0.21-0.55	0.31	0.29-0.71	0.037	0.025-0.060
Off Humber	346	54.071	1.797	0.40	0.17-0.57	0.30	0.21-0.75	0.041	0.025-0.078
Indefatigable Bank	378	53.563	2.083	0.41	0.13-0.45	0.27	0.22-0.70	0.034	0.016-0.055
Thames (Gabbard)	475	52.048	2.098	0.49	0.13-0.73	0.33	0.19-1.1	0.047	0.020-0.11
Rye Bay	486	50.825	0.798	0.64	0.30-0.55	0.43	0.44-0.79	0.068	0.051-0.083
Off Newhaven	494	50.756	-0.056	0.38	0.15-0.26	0.26	0.22-0.39	0.040	0.024-0.039
South Eddystone	584	50.107	-4.101	0.11	0.067-0.081	0.074	0.10-0.13	0.010	0.0095-0.011
Carmarthen Bay	616	51.548	-4.605	0.52	0.22-0.42	0.30	0.38-0.71	0.031	0.022-0.040
North Cardigan Bay	649	52.708	-4.524	0.19	0.061-0.21	0.12	0.10-0.30	0.014	0.0071-0.017
Inner Liverpool Bay	706	53.471	-3.358	2.0	1.1-1.4	1.3	1.7-2.2	0.21	0.16-0.25
Liverpool Bay	715	53.472	-3.699	1.2	0.53-1.1	0.73	0.87-1.86	0.097	0.066-0.15
Red Wharf	776	53.375	-4.13	0.45	0.22-0.39	0.26	0.36-0.68	0.034	0.027-0.054
Morecambe Bay	796	53.905	-3.41	1.3	0.63-1.0	0.80	0.99-1.6	0.11	0.088-0.14
SE Isle of Man	805	54.056	-3.875	0.88	0.32-0.77	0.51	0.55-1.3	0.059	0.042-0.089
Dundrum Bay	815	54.116	-5.619	0.64	0.33-0.64	0.46	0.42-0.90	0.054	0.041-0.071
Dublin Bay		53.24	-5.949	0.17	0.089-0.13	0.11	0.14-0.21	0.016	0.014-0.019

Temporal trends were investigated at 26 sites with 4 or more years of data for the total of 25 CBs (ΣCBs), the ΣICES7 CBs and CB118 (Table 7.3). The patterns for ΣCBs and ICES7 CBs was identical in that concentrations in samples from most stations showed no significant upward or downward trend. However, at three stations (Amble (CSEMP 244), North Cardigan Bay (CSEMP 649), Inner Cardigan Bay (CSEMP 656)) significant downward trends were observed. None of the sites showed a statistically significant upward trend for either ΣCBs or the ΣICES7 congeners. For CB118, significant downwards trends were observed again for the Amble and Inner Cardigan Bay samples but also in the Inner Liverpool Bay (CSEMP 706) samples. A significant upwards trend was observed in samples from Tees Bay (CSEMP 294), and this is of concern even though ΣCBs and ICES7 CBs showed only a non-significant upwards trend.

The general pattern of just a few trends being detected in various stations supports similar finding reported in Charting Progress 2 (Defra 2010), although the model used was different. Interestingly, the increasing trend for CB118 in Tees Bay was also reported under Charting Progress 2, which indicates that there is possibly an input (either ongoing or historic) of PCBs in this area.

Overall, the lack of significant downwards trend in CB levels in fish liver combined with a large proportion of samples with congeners occurring at levels well above EACs (ie, CB118), and therefore possibly causing adverse effects in the environment, indicates that CB levels in the marine environment will remain of concern for many years to come.

Table 7.3. Temporal trends for ΣCBs, ICES7 CBs and CB118 (trends: ↓ significant downwards; ↑ significant upward; ↔ no significant trend; ↘ non-significant downward; ↗ non-significant upward)

Location	CSEMP station	Latitude	Longitude	Sampling period	No of years	Total 25 CBs	ICES7CBs	CB118
Amble	244	55.495	-1.127	1999-2009	10	↓	↓	↓
North Dogger 1	283	55.289	2.904	2003-10	8	↔	↔	↔
North Dogger 2	284	55.065	2.082	2001-10	9	↔	↔	↔
West Dogger	286	54.777	1.295	1998-2010	12	↘	↘	↘
Dogger Central	287	54.527	2.699	2000-10	11	↘	↘	↔
Tees Bay	294	54.756	-1.136	2001-10	9	↗	↗	↑
Flamborough	344	54.245	0.499	1999-2009	11	↘	↘	↘
Off Humber	346	54.071	1.797	1998-2010	11	↔	↔	↘
Outer Humber	377	53.323	0.425	1998-2008	7	↔	↔	↔
Indefatigable Bank	378	53.563	2.083	2003-10	8	↘	↔	↘
Thames (Gabbard)	475	52.048	2.098	2000-09	7	↔	↔	↔
Rye Bay	486	50.825	0.798	1999-2009	11	↔	↔	↔
Off Newhaven	494	50.756	-0.056	2005-10	1	↘	↘	↘
Inner Lyme Bay	534	50.614	-2.93	2005-09	4	↔	↔	↔
South Eddystone	584	50.107	-4.101	2005-10	6	↔	↔	↔
Carmarthen Bay	616	51.548	-4.605	2003-10	8	↔	↔	↔
North Cardigan Bay	649	52.708	-4.524	2002-10	6	↓	↓	↘
South Cardigan Bay	654	52.191	-4.494	2003-07	4	↔	↔	↔
Inner Cardigan Bay	656	52.298	-4.273	1997-2007	9	↓	↓	↓
Off Cardigan Bay	665	52.396	-4.895	1999-2004	4	↘	↘	↘
Inner Liverpool Bay	706	53.471	-3.358	1998-2010	13	↘	↘	↓
Liverpool Bay	715	53.472	-3.699	2000-10	10	↘	↘	↘
St Bees Head	769	54.512	-3.794	2003-09	7	↔	↘	↔
Red Wharf	776	53.375	-4.13	1998-2010	13	↔	↔	↔
Morecambe Bay	796	53.905	-3.41	1998-2010	13	↘	↘	↘
SE Isle of Man	805	54.056	-3.875	2000-2009	9	↔	↔	↔

8. Levels and trends of metals in fish, 2006–2010

Authors: Thi Bolam and Jon Barry

8.1 Introduction

Trace metals of natural origin are found in the environment and therefore the concentration in, and input to, the North Sea contains a natural and an anthropogenic component, both of which may vary over time. These can pose threats to aquatic organisms because of their bioaccumulation potential, persistence and (in some cases) toxicity. Fish are considered as good indicator species because they may accumulate high concentrations of some metals from water and from their diet. Different metals may accumulate preferentially in different organs of the fish.

In this section, concentrations of a suite of metals in tissues of the flatfish dab (*Limanda limanda*) sampled around the coasts of England and Wales under the Clean Seas Environment Monitoring Programme (CSEMP) are assessed against the Background Assessment Concentrations (BACs) and EC limit values set for the protection of the health of human consumers. By collecting samples at around 45 fixed stations in intermediate and open sea areas around England and Wales, the aim of this programme is to investigate possible long-term trends in concentrations of metals, spatial variability and metals enrichment in the environment around England and Wales.

8.2 Methods

A pool of 25 fish is collected at each site by trawling. Samples of muscle and liver tissue from five individual fish are bulked, yielding 5 replicates for each of the sampling sites.

Analysis was carried out using acid microwave digestion of dab muscle and liver samples. Quantification was performed by inductively-coupled plasma-mass spectrometry (ICP-MS) and inductively-coupled plasma-atomic emission spectrometry (ICP-AES) for the determination of concentrations of Cu, Hg and Zn in muscle tissue, and Cd, Cu, Hg, Pb and Zn in liver tissue.

A 5-years-time series (2006–2010) was available within this study for the investigation of possible time-trends.

The possible temporal trends were investigated by calculating the mean of observations for each sampling station and year, and by fitting a linear regression model to these means.

The upper 95% confidence limit based on the mean levels from 2006–2010 (this is equivalent to fitting a model with zero slope to the mean levels) was also compared with the OSPAR BAC and EC maximum food limit values in order to assess the data (Table 8.1).

Table 8.1. Background Assessment Concentrations and EC food limit values for metals in fish (μg kg^{-1} wet weight).
* BC – OSPAR Background Concentrations have not been defined as yet for metals in fish.

Trace metal concentrations (μg kg^{-1} wet weight)

Assessment	BC	Blue < BAC (T_0)	Amber < EC maximum food level (T_1)
Hg (muscle)	*	35	500
Cd (liver)	*	26	1000 (bivalve tissue)
Pb (liver)	*	26	1500 (bivalve tissue)

8.3 Results

The relative standard deviation (%RSD) of the 5 replicates, indicating variability in concentrations at each sampling location, is summarised in Tables 8.2, 8.3 and 8.4 for Hg in muscle, Cd and Pb in liver, for each sampling year and each station.

The %RSD ranges from 5.0% to 73.9% for Hg, from 8.5% to 85.8% for Cd and from 0% to 89.9% for Pb.

Overall, Hg variability in muscle is noticeably less than that observed for Cd and Pb in liver. This is probably due to the fact that sample size for muscle tissue is significantly larger than for liver tissue, thus giving a more homogeneous sample and so a lower variability in determined concentrations.

Table 8.2. Relative standard deviations (%RSD) of concentrations of mercury in dab muscle.

Station	2006	2007	2008	2009	2010
CSEMP475	10.3(n=4)	46.2(n=5)	43.8(n=5)	69.9(n=5)	10.1(n=5)
CSEMP649	25.5(n=5)	27.1(n=5)	nd	16.5(n=5)	56.2(n=5)
CSEMP656	15.7(n=5)	nc	nc	19.2(n=5)	36.3(n=5)
CSEMP486	18.0(n=5)	9.3(n=5)	35.3(n=5)	61.6(n=5)	27.4(n=5)
CSEMP494	35.2(n=5)	26.0(n=5)	45.9(n=5)	17.8(n=5)	34.3(n=5)
CSEMP534	21.0(n=5)	34.4(n=5)	35.2(n=5)	34.6(n=5)	nc
CSEMP283	14.4(n=5)	20.3(n=5)	28.6(n=5)	13.2(n=5)	17.4(n=5)
CSEMP284	34.2(n=5)	19.9(n=5)	60.8(n=5)	20.1(n=5)	32.9(n=5)
CSEMP286	22.0(n=5)	29.3(n=5)	31.9(n=5)	24.5(n=5)	34.9(n=5)
CSEMP287	39.5(n=5)	8.6(n=5)	30.4(n=5)	5.0(n=5)	21.8(n=5)
CSEMP346	23.5(n=5)	28.7(n=5)	45.6(n=5)	35.1(n=5)	59.0(n=5)
CSEMP378	14.1(n=5)	23.4(n=5)	22.9(n=5)	8.5(n=4)	20.0(n=5)
CSEMP706	10.6(n=5)	27.7(n=5)	46.5(n=5)	47.6(n=5)	22.9(n=5)
CSEMP715	22.3(n=5)	22.6(n=5)	17.0(n=5)	22.6(n=5)	24.6(n=5)
CSEMP769	8.4(n=5)	36.7(n=5)	37.4(n=5)	22.6(n=5)	nc
CSEMP776	21.1(n=5)	20.2(n=5)	44.2(n=5)	14.7(n=5)	30.5(n=5)
CSEMP796	16.1(n=5)	31.2(n=5)	14.4(n=5)	13.3(n=5)	13.6(n=5)
CSEMP805	22.9(n=5)	17.4(n=5)	24.2(n=5)	16.2(n=5)	30.9(n=5)
CSEMP616	23.5(n=2)	13.3(n=5)	37.4(n=5)	57.9(n=5)	19.4(n=5)
CSEMP243	25.5(n=5)	14.7(n=5)	49.2(n=5)	15.2(n=5)	nc
CSEMP244	14.0(n=5)	38.6(n=5)	22.5(n=5)	25.5(n=4)	nc
CSEMP294	46.7(n=5)	20.3(n=5)	34.8(n=5)	56.3(n=5)	16.7(n=5)
CSEMP344	73.9(n=5)	24.7(n=5)	48.7(n=5)	22.3(n=5)	nc
CSEMP584	16.1(n=5)	21.1(n=5)	28.6(n=5)	26.3(n=5)	34.2(n=5)

nd= not determined due to 1 single sample analysed or <LOD value

nc: samples not collected

Table 8.3. Relative standard deviations (%RSD) of concentrations of cadmium in dab liver.

Station	2006	2007	2008	2009	2010
CSEMP475	29.6(n=4)	23.9(n=5)	32.9(n=4)	51.3(n=5)	43.7(n=5)
CSEMP649	41.8(n=5)	31.4(n=5)	30(n=3)	77.0(n=5)	70.3(n=5)
CSEMP656	26.1(n=5)	54.2(n=5)	22.4(n=3)	nc	19.3(n=5)
CSEMP486	15.4(n=5)	nd	22.5(n=5)	28.0(n=5)	33.9(n=5)
CSEMP494	40.1(n=5)	nd	33.0(n=5)	29.8(n=5)	37.2(n=5)
CSEMP534	19.9(n=5)	42.4(n=2)	24.9(n=4)	37.3(n=5)	nc
CSEMP283	26.2(n=5)	17.1(n=5)	24.7(n=5)	21.5(n=5)	21.8(n=5)
CSEMP284	22.6(n=5)	49.4(n=5)	33.5(n=5)	24.0(n=5)	27.5(n=5)
CSEMP286	51.9(n=5)	48.1(n=5)	24.9(n=5)	61.7(n=5)	23.5(n=5)
CSEMP287	37.4(n=5)	19.3(n=5)	26.1(n=5)	37.1(n=5)	24.9(n=5)
CSEMP346	59.5(n=5)	34.5(n=5)	55.5(n=5)	45.0(n=5)	18.8(n=4)
CSEMP378	52.5(n=5)	54.3(n=5)	65.1(n=4)	85.8(n=4)	41.7(n=4)
CSEMP706	30.4(n=5)	43.9(n=5)	27.8(n=5)	50.4(n=5)	26.1(n=5)
CSEMP715	35.7(n=5)	27.8(n=5)	27.7(n=5)	14.4(n=5)	63.5(n=5)
CSEMP769	27.1(n=5)	35.4(n=5)	14.3(n=5)	25.1(n=5)	nc
CSEMP776	28.3(n=5)	19.5(n=5)	26.5(n=5)	32.9(n=5)	15.3(n=5)
CSEMP796	31.0(n=5)	28.1(n=5)	23.3(n=5)	18.3(n=5)	30.9(n=5)
CSEMP805	nd	20.1(n=5)	25.0(n=5)	35.7(n=5)	58.3(n=5)
CSEMP616	19.1(n=5)	8.5(n=5)	19.7(n=5)	16.1(n=5)	49.5(n=5)
CSEMP243	26.2(n=4)	29.9(n=5)	12.3(n=5)	78.1(n=5)	nc
CSEMP244	32.6(n=5)	20.0(n=5)	42.6(n=5)	15.4(n=5)	nc
CSEMP294	47.6(n=5)	23.3(n=5)	66.5(n=5)	24.4(n=5)	86.4(n=5)
CSEMP344	17.6(n=5)	78.1(n=5)	40.5(n=5)	75.2(n=5)	nc
CSEMP584	40(n=5)	nd	nd	nd	45.7(n=5)

nd= not determined due to 1 single sample analysed or <LOD value

nc: samples not collected

Table 8.4. Relative standard deviations (%RSD) of concentrations of lead in dab liver.

Station	2006	2007	2008	2009	2010
CSEMP475	0(n=4)	nd	nd	39.5(n=5)	56.3(n=5)
CSEMP649	20.3(n=5)	26.6(n=5)	47.2(n=3)	75.1(n=5)	37.7(n=5)
CSEMP656	44.8(n=5)	35.2(n=5)	32.7(n=3)	nc	41.8(n=5)
CSEMP486	10.5(n=4)	nd	nd	11.7(n=5)	54.7(n=5)
CSEMP494	16.1(n=4)	nd	nd	18.1(n=4)	46.4(n=5)
CSEMP534	21.1(n=5)	33.4(n=5)	34.2(n=5)	72.3(n=5)	nc
CSEMP283	39.1(n=5)	nd	22.8(n=5)	nd	56.4(n=5)
CSEMP284	47.1(n=2)	20.3(n=5)	20.2(n=4)	nd	nd
CSEMP286	nd	35.3(n=4)	29.4(n=5)	30.3(n=5)	66.8(n=5)
CSEMP287	54.9(n=4)	nd	22.8(n=5)	68.7(n=5)	nd
CSEMP346	42.9(n=5)	18.7(n=5)	89.9(n=4)	51.7(n=5)	27.7(n=5)
CSEMP378	33.3(n=4)	31.8(n=5)	17.3(n=5)	20.9(n=5)	24.1(n=5)
CSEMP706	57.8(n=5)	61.5(n=4)	24.6(n=5)	43.6(n=5)	19.4(n=5)
CSEMP715	48.2(n=5)	11.1(n=3)	41.5(n=5)	23.3(n=5)	21.8(n=5)
CSEMP769	55.5(n=5)	33.1(n=5)	38.6(n=5)	44.1(n=5)	nc
CSEMP776	69.0(n=4)	17.8(n=5)	26.2(n=5)	25(n=3)	17.8(n=5)
CSEMP796	57.5(n=5)	47.8(n=5)	17.8(n=5)	51.1(n=5)	49.1(n=5)
CSEMP805	29.7(n=5)	38.5(n=2)	47.2(n=5)	36.5(n=5)	71.3(n=5)
CSEMP616	32.8(n=5)	32.0(n=5)	7.8(n=5)	63.8(n=5)	25.3(n=5)
CSEMP243	39.5(n=4)	30.4(n=5)	24.9(n=5)	46.9(n=5)	nc
CSEMP244	17.7(n=5)	25.9(n=5)	31.1(n=5)	34.7(n=5)	nc
CSEMP294	20.8(n=5)	50.9(n=5)	19.9(n=5)	31.3(n=5)	40.5(n=4)
CSEMP344	17.8(n=5)	44.5(n=5)	26.5(n=5)	26.6(n=5)	nc
CSEMP584	85.7(n=5)	34.9(n=5)	13.9(n=5)	12.3(n=5)	17.2(n=5)

nd= not determined due to 1 single sample analysed or <LOD value

nc: samples not collected

8.3.1 Mercury in fish muscle

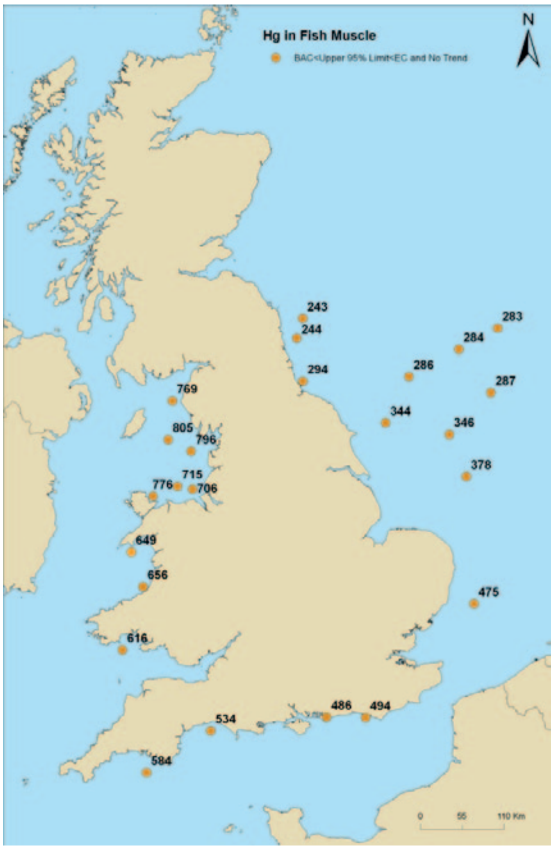


Figure 8.1. Mercury in fish muscle assessment.

The upper 95% confidence limit concentrations for 2006–2010 were in the range of 52–305 µg kg^{-1} wet weight, with levels at all sites above the BAC but below the EC food limit value. Slightly elevated concentrations were found in the Eastern and Western Channel, whereas more elevated concentrations were recorded in the Tyne, Humber, Cardigan Bay and Irish Sea areas (Figure 8.1).

No temporal trend was observed for Hg in fish muscle over the studied period.

The concentrations of mercury in fish muscle are found to be more elevated in waters adjacent to some industrialised estuaries.

Monitoring should be maintained in areas where elevated concentrations have been found, especially in the Irish Sea area, which was historically contaminated with mercury.

8.3.2 Cadmium in fish liver

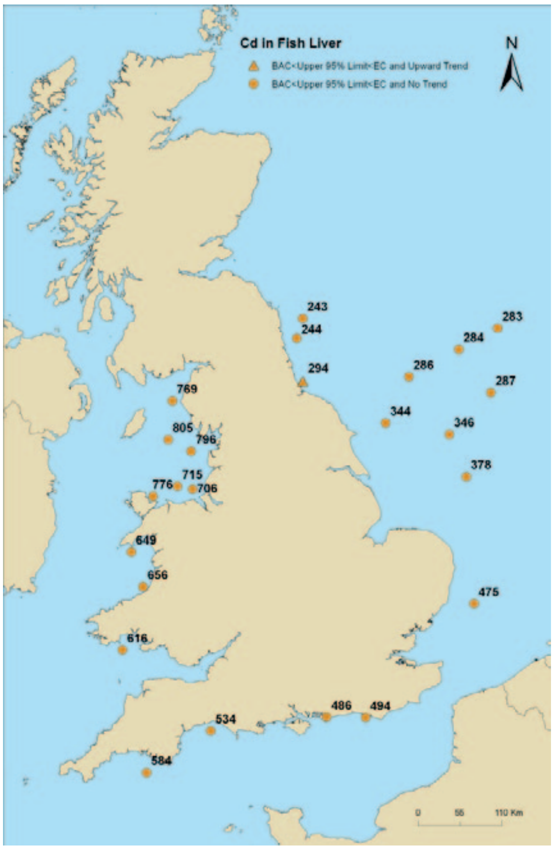


Figure 8.2. Cadmium in fish liver assessment.

The upper 95% confidence limit cadmium concentrations for 2006–2010 were in the range of 63–554 µg kg^{-1}, with levels at all sites above the BAC and below the EC food limit value. As for mercury in fish muscle, slightly elevated concentrations were found in the Eastern and Western Channel, whereas more elevated concentrations were recorded in the Irish Sea, Tyne and Humber areas (Figure 8.2).

A positive trend was observed at the Tyne area (CSEMP 294) (Figure 8.3). However, the upper 95% limit concentration for 2006–2010 was 325 µg kg^{-1}, which is well below the EC food limit value.

The concentrations of cadmium in fish liver are found to be more elevated in waters adjacent to some industrialised estuaries.

Monitoring should be maintained in areas where elevated concentrations have been found, in particular in the Tyne area (CSEMP 294) where a positive trend was observed over the last 5 years.

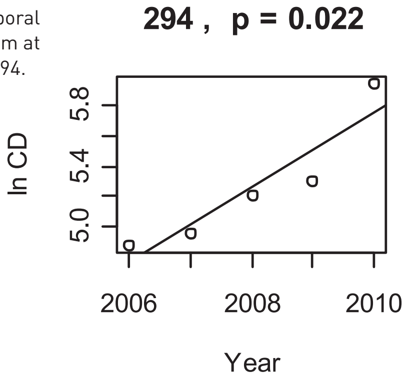


Figure 8.3. Temporal trend for cadmium at station CSEMP 294.

Interestingly, a downward trend was observed for lead from 2006 to 2010, at stations CSEMP 346 and CSEMP 494, which also showed concentrations below the EC limit values.

The concentrations of lead in fish liver are found to be more elevated in waters adjacent to some industrialised estuaries and coastal areas. The very high levels of contamination were found at individual sites within each area and not at every site within these areas, and for this reason and because fish flesh in which levels are lower is consumed rather than fish liver, are not likely to raise concerns regarding human consumers.

Monitoring should be maintained in areas where elevated concentrations have been found, in particular in the areas where positive trend was observed over the last 5 years.

8.3.3 Lead in fish liver

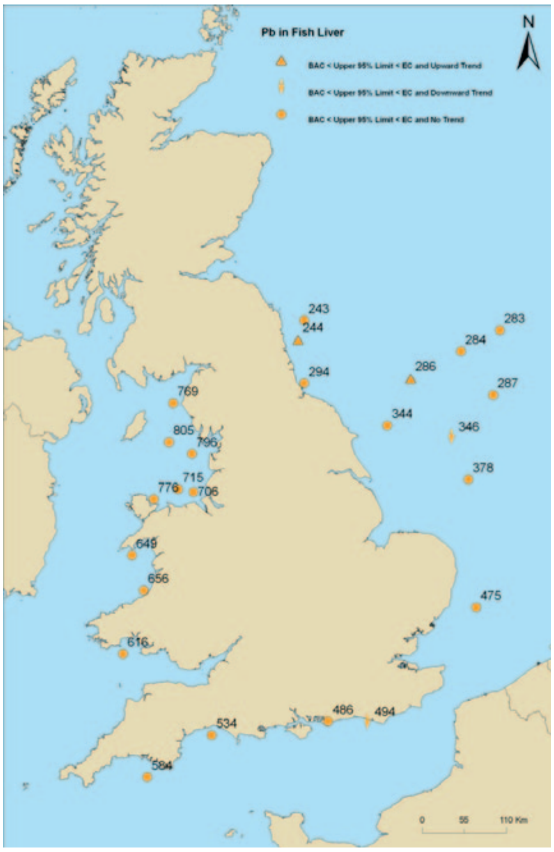


Figure 8.4. Lead in fish liver assessment.

All stations surveyed in 2006–2010 recorded upper 95% confidence limit concentrations for lead above the BAC but below the EC food limit value. Elevated Pb values were found around the Tyne, Humber, Anglia and Irish Sea areas. Slightly less elevated Pb concentrations can be seen elsewhere (Figure 8.4).

An upwards trend was observed at stations located at the Tyne (CSEMP 244) and Humber (CSEMP 386) stations (Figure 5). However, the upper 95% confidence limit concentrations for 2006–2010 were at 152 and 248 µg kg^{-1}, respectively, which are still well below the EC limit value.

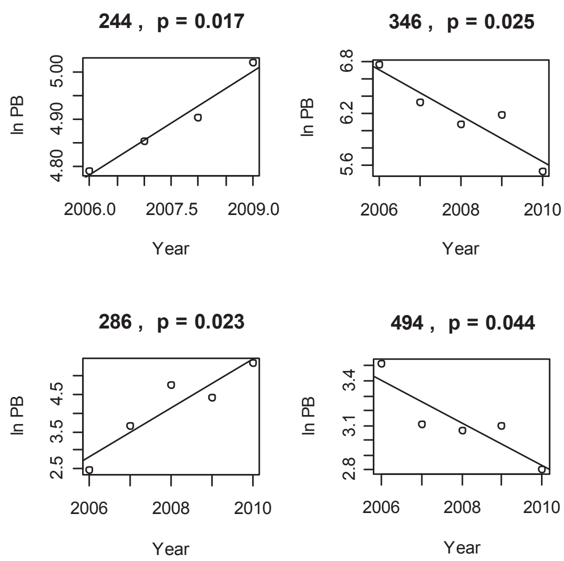


Figure 8.5. Temporal trends for lead

8.3.4 Other metals in fish muscle and liver

In addition to the above metals, copper and zinc were also determined in both fish tissues. Only temporal trends can be derived since there were no BAC/EC limit values available for copper and zinc in fish muscle and liver on which to base an assessment.

For fish muscle, copper at stations CSEMP 715 and CSEMP 776, both in the Irish Sea area, exhibited an upward trend, whereas zinc seems to be decreasing over the 5 year period at stations CSEMP 294 (Tyne/Tees areas) and CSEMP 616 (Severn area).

For fish liver, mercury showed a downward trend at station CSEMP 715 whereas copper seems to be increasing at the same station. Zinc exhibited a negative trend at station CSEMP 475 (Anglia) and at station CSEMP 534 (Eastern English Channel).

9. Polybrominated diphenyl ethers (PBDEs) in fishes: spatial and temporal trends

Authors: Jon Barber, Philippe Bersuder, Jon Barry and Thi Bolam

9.1 Introduction

The main programme for monitoring the status of contaminants in UK waters is the Clean Seas Environment Monitoring Programme (CSEMP). CSEMP measures the concentrations of specific chemicals which are persistent, toxic and have the ability to accumulate in food chains. Polybrominated diphenyl ethers (PBDEs) are additive flame retardant compounds that have been used extensively in textiles, thermoplastics, polyurethane foams, and electronic products. Three PBDE formulations were marketed, the penta-, octa- and, deca-mix products, which differ in the average level of bromination in the mixture. BDE47 and BDE99 typically made up > 70% of the penta-mix products, BDE183 > 40% of the octa-mix products and BDE209 > 97% of the deca-mix products. Penta- and octa-mix technical products are no longer in use, having been banned in the EU since 2004. The deca-mix PBDE formulation has been in use more recently than the other technical mixtures, although its use has been restricted in the EU since 2008. In this section, BDE congener concentrations in dab (*Limanda limanda*) tissues sampled around the coasts of England and Wales under CSEMP are assessed. By collecting samples at around 26 fixed stations in intermediate and open sea areas around England and Wales, the aim of this programme is to detect any contaminant long-term time trends, spatial variability and contaminant enrichment in fish tissues at those sites. Samples have been collected and analysed for BDEs since 2003. Analysis of BDE209 in samples has not been carried out, since BDE209 is only weakly bioaccumulated.

9.2 Sampling undertaken in 2010

In 2010, 18 fixed stations were visited by the RV *Cefas Endeavour*. A pool of 25 fish was collected at each site. Samples were stored in glass jars, frozen immediately after collection and not defrosted until required for sample preparation. Five individual liver tissue samples were bulked, yielding 5 pooled replicates for each of the sampling sites.

9.3 Methods

BDE congener concentrations were determined in the dab liver samples and are reported on a wet weight basis. 5 g of homogenised fish liver were mixed with sodium sulphate and left to dry overnight. Sulphated samples were transferred to a glass Soxhlet thimble and topped with 1 cm of sodium sulphate. Samples were extracted over a 6 h period using 50:50 hexane:acetone, with an average of 9–10 cycles h^{-1}. Following extraction, an aliquot of sample was tested for extractable lipid content gravimetrically after drying the aliquot. Subsequently, another aliquot of the Soxhlet extract was cleaned up and fractionated using alumina (5% deactivated) and silica (3% deactivated) chromatography columns, respectively. After addition of internal standard CB200, BDE congener concentrations were determined with an Agilent 6890 GC with 5973 MS in electron capture negative ionisation (ECNI) mode. The separation of analytes was performed on a 50 m × 250 µm, 0.25-µm-film-thickness DB-5 capillary column (J&W). The identification of BDE congeners was based on the retention time of individual standards in the calibration mixtures. Quantification was performed using internal standards and 8 calibration levels (range 0.1–50 $ngml^{-1}$). Full details of the analytical methodology are given in de Boer *et al.* (2001). 11 BDE congeners were analysed (BDE17, BDE28, BDE47, BDE66, BDE85, BDE99, BDE100, BDE138, BDE153, BDE154 and BDE183), and the sums of all measured BDEs (∑11 BDEs) were calculated. All samples are run under an analytical quality control (AQC) protocol, which involved analysing blanks and certified or laboratory reference materials within each sample batch. The certified reference material currently used is the cod liver oil BCR 349 produced by the European Commission Joint Research Council (JRC) Institute for Reference Materials and Measurements. Quality assurance is also guaranteed with participation in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) laboratory proficiency scheme. Temporal trends for all stations with a minimum of 4 years data were obtained by calculating the mean of observations in the same station and year, and by fitting a linear regression model to these means.

9.4 Results

BDEs were detected at all of the 18 stations analysed in 2010 (see Table 9.1). ∑11 BDEs concentrations ranged from 0.00061 mg kg^{-1} wet weight (ww) in a fish from CSEMP 584 (South Eddystone) to 0.020 mg kg^{-1} ww in a fish from CSEMP 494 (off Newhaven). BDE47 was usually the major congener present, making up 32–100% of the ∑11 BDE concentrations. Only two stations had BDE47 < 50% of the ∑11 BDEs, CSEMP 776 (Red Wharf Bay) and CSEMP 805 (SE Isle of Man), where BDE154 was the predominant congener. BDE100 was usually the second most abundant congener apart from at these 2 stations and CSEMP 796 (Morecambe Bay). In contrast to sediments, BDE99 was not found in high abundance, and was only detected in fish from the stations in the Irish Sea. BDE99 may be debrominated to BDE47, explaining the dominance of BDE100 compared with BDE99 and the relatively high trophic magnification of BDE47 in the marine food web (Wan *et al.*, 2008). BDE183, indicative of the octa-PBDE technical mixture, was detected at four stations in the Irish Sea in 2010, generally at locations where BDE154 was in high abundance and a wider range of congeners was detected.

Table 9.1. Concentrations of BDEs in livers of dab (*Limanda limanda*) collected from CSEMP stations in 2010 (mg kg^{-1} wet weight).

Location	CSEMP station	Latitude	Longitude	Dab liver concentration (in mg kg^{-1} ww)				BDEs detected (in order of abundance)[a]
				BDE47		Total11BDEs		
				Mean	Range	Mean	Range	
North Dogger 1	283	55.289	2.904	0.0040	0.0019-0.0082	0.0050	0.0024-0.010	BDE47, BDE100
North Dogger 2	284	55.065	2.082	0.0028	0.0013-0.0046	0.0032	0.0013-0.0053	BDE47, BDE100
West Dogger	286	54.777	1.295	0.0044	0.0035-0.0064	0.0053	0.0042-0.00 76	BDE47, BDE100
Dogger Central	287	54.527	2.699	0.0027	0.0021-0.0036	0.0032	0.0025-0.0044	BDE47, BDE100
Tees Bay	294	54.756	-1.136	0.0027	0.0014-0.0058	0.0036	0.0017-0.0071	BDE47, BDE100, BDE153, BDE154
Off Humber	346	54.071	1.797	0.0016	0.00047-0.0037	0.0019	0.00047-0.0042	BDE47, BDE100
Indefatigable Bank	378	53.563	2.083	0.0037	0.0024-0.0049	0.0047	0.0030-0.0068	BDE47, BDE100 (BDE154)
Thames (Gabbard)	475	52.048	2.098	0.0027	0.0015-0.0039	0.0035	0.0019-0.0052	BDE47, BDE100 (BDE154)
Rye Bay	486	50.825	0.798	0.0025	0.0020-0.0029	0.0031	0.0025-0.0036	BDE47, BDE100
Off Newhaven	494	50.756	-0.056	0.0032	0.0028-0.0033	0.020	0.0039-0.065	BDE47, BDE100 (BDE153, BDE154)
South Eddystone	584	50.107	-4.101	0.00061	0.0003-0.00094	0.00061	0.0003-0.00094	BDE47
Carmarthen Bay	616	51.548	-4.605	0.0016	0.0011-0.0022	0.0023	0.0016-0.0036	BDE47, BDE100 (BDE154)
North Cardigan Bay	649	52.708	-4.524	0.00096	0.00075-0.0012	0.0014	0.00078-0.0017	BDE47, BDE100 (BDE153)
Inner Liverpool Bay	706	53.471	-3.358	0.010	0.0087-0.015	0.018	0.014-0.026	BDE47, BDE100, BDE154, BDE153, BDE99 (BDE183, BDE28)
Liverpool Bay	715	53.472	-3.699	0.0070	0.0050-0.0093	0.013	0.0096-0.0179	BDE47, BDE100, BDE154 (BDE99, BDE28)
Red Wharf Bay	776	53.375	-4.13	0.0047	0.0031-0.0057	0.015	0.011-0.0183	BDE154, BDE47, BDE100, BDE153, BDE183 (BDE99, BDE28)
Morecambe Bay	796	53.905	-3.41	0.0077	0.0061-0.0091	0.018	0.014-0.020	BDE47, BDE154, BDE100, BDE153, BDE183, BDE99 (BDE28)
SE Isle of Man	805	54.056	-3.875	0.0029	0.00077-0.0048	0.0092	0.0020-0.015	BDE154, BDE47, BDE100, BDE153, (BDE183, BDE99)

[a] congeners in parentheses were detected in less than half of the replicate samples

The data for 2010 have been plotted on maps as shown in Figure 9.1. The highest concentration of ∑11 BDEs was found at CSEMP 494 (off Newhaven) in the Eastern English Channel. The next 4 highest concentrations of ∑11 BDEs, together with the 4 highest concentrations of BDE47, BDE154, BDE100, BDE183 and BDE99 were found at stations CSEMP 706 (inner Liverpool Bay), CSEMP 796 (Morecambe Bay), CSEMP 715 (Liverpool Bay) and CSEMP 706 (Red Wharf Bay) in the Irish Sea. This distribution pattern is very different to that found in sediments, with highest ∑11 BDE concentrations found at stations in the northeast of England, and with low concentrations detected in Liverpool Bay. BDE209, however, was detected at high concentrations in sediments in this area, so it is possible that the BDEs detected in the fish might originate from the debromination of BDE209. Alternatively, it is possible that the sediment stations are not representative of the general area and a wider range of locations need to be sampled in future in order to gain a true representation of the spatial variability.

Up to 7 years of data exists for levels of BDEs in dab livers, and the plots in Figures 9.2 and 9.3 show for ∑11 BDEs and BDE47, respectively, the *p*-values and trends for each of the 26 stations that are regularly visited under the CSEMP monitoring program.

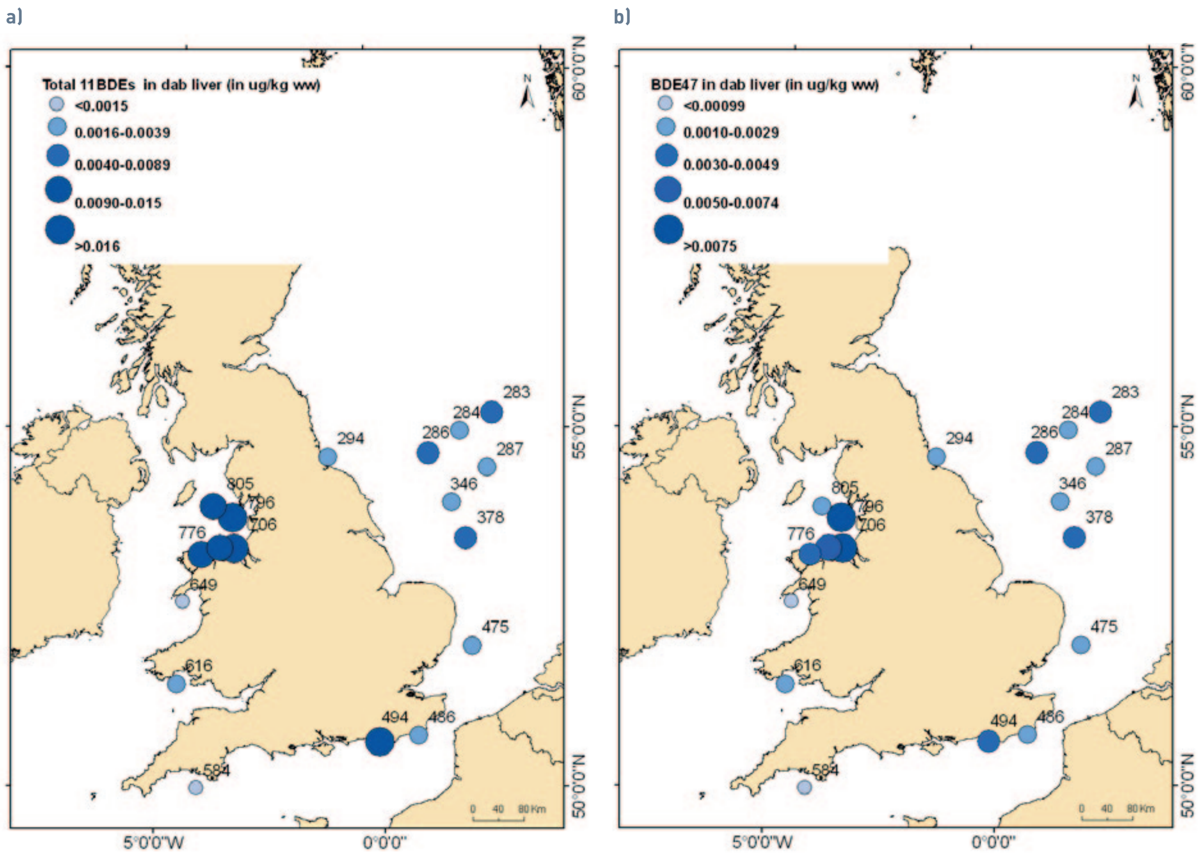


Figure 9.1. Sampling locations for dab livers analysed in 2010, colour-coded for BDE concentration, showing a) ∑11 BDEs, and b) BDE47. Note the different scales on the different maps.

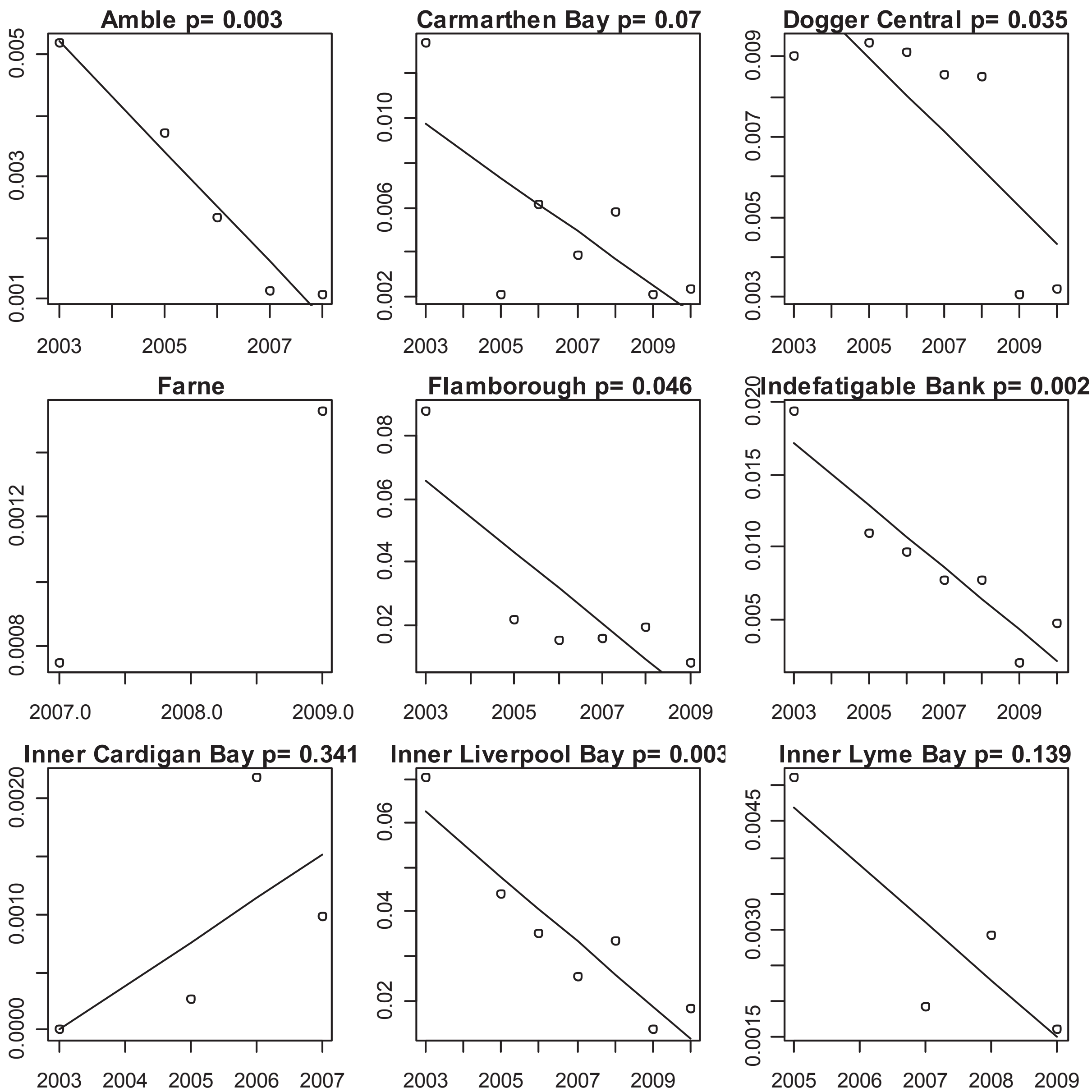


Figure 9.2a. Temporal trends of mean ∑11 BDE concentrations in dab liver from 2003–2010 at different stations.

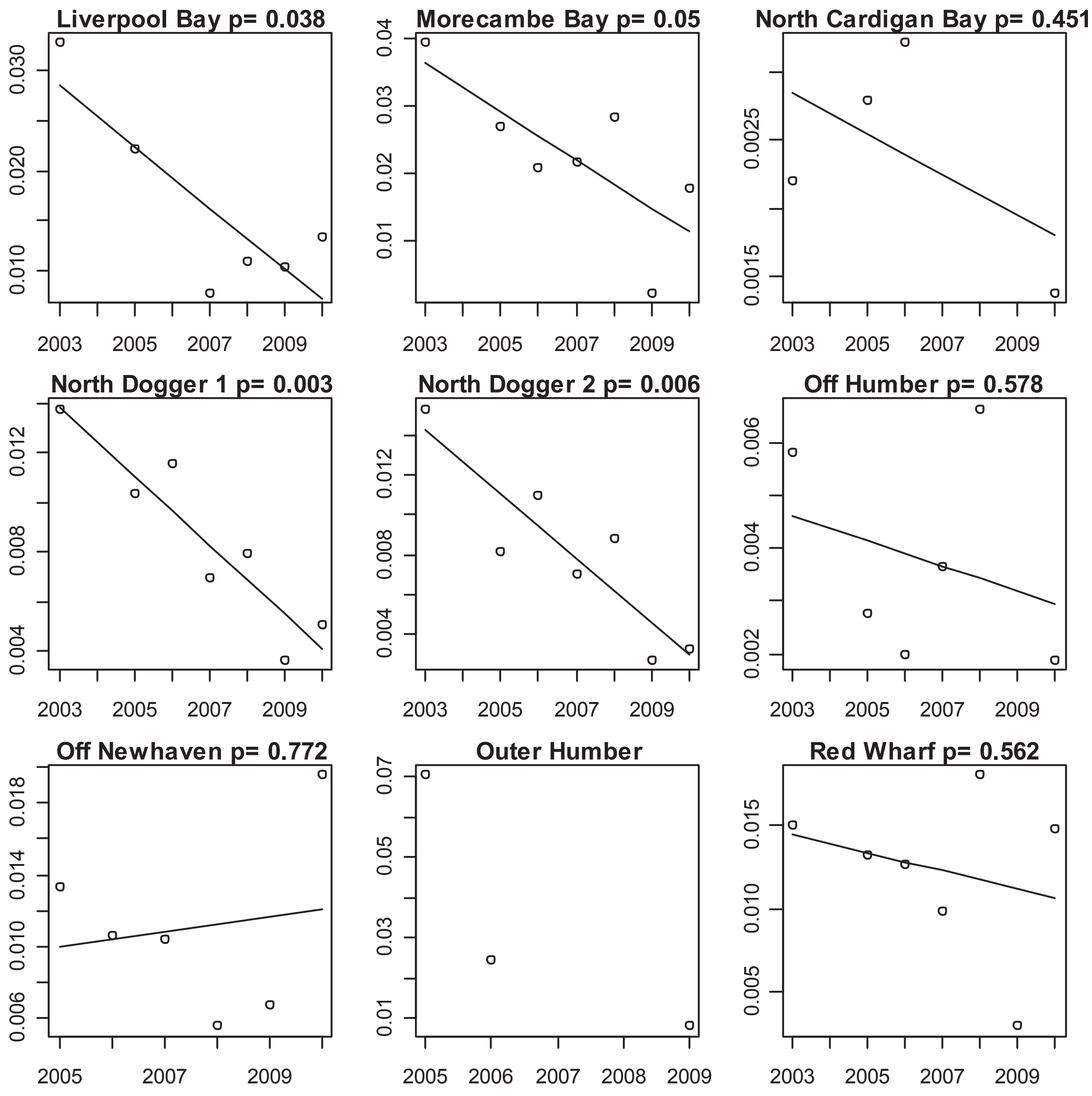


Figure 9.2b. Temporal trends of mean ∑11 BDE concentrations in dab liver from 2003–2010 at different stations.

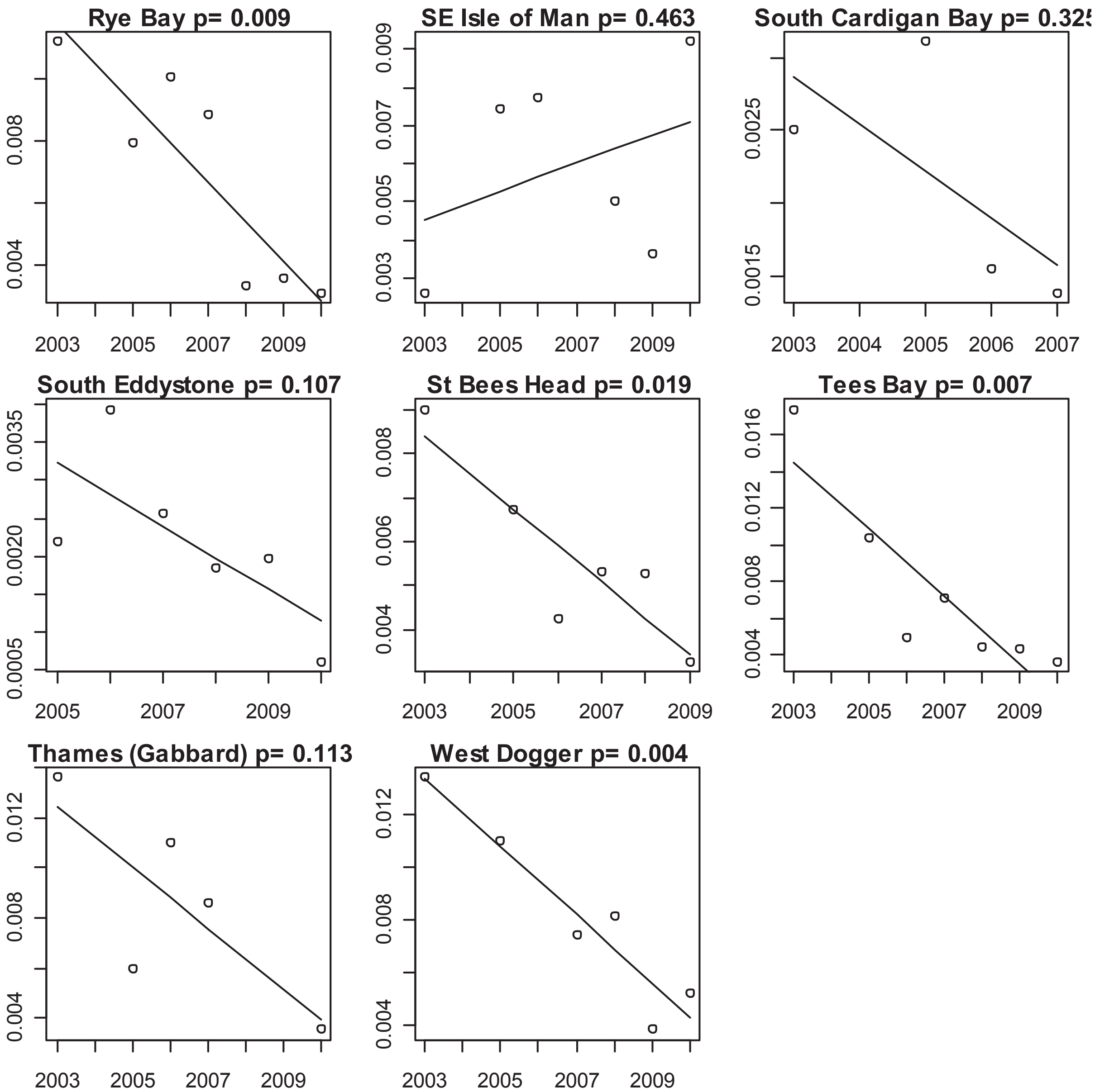


Figure 9.2c. Temporal trends of mean ∑11 BDE concentrations in dab liver from 2003–2010 at different stations.

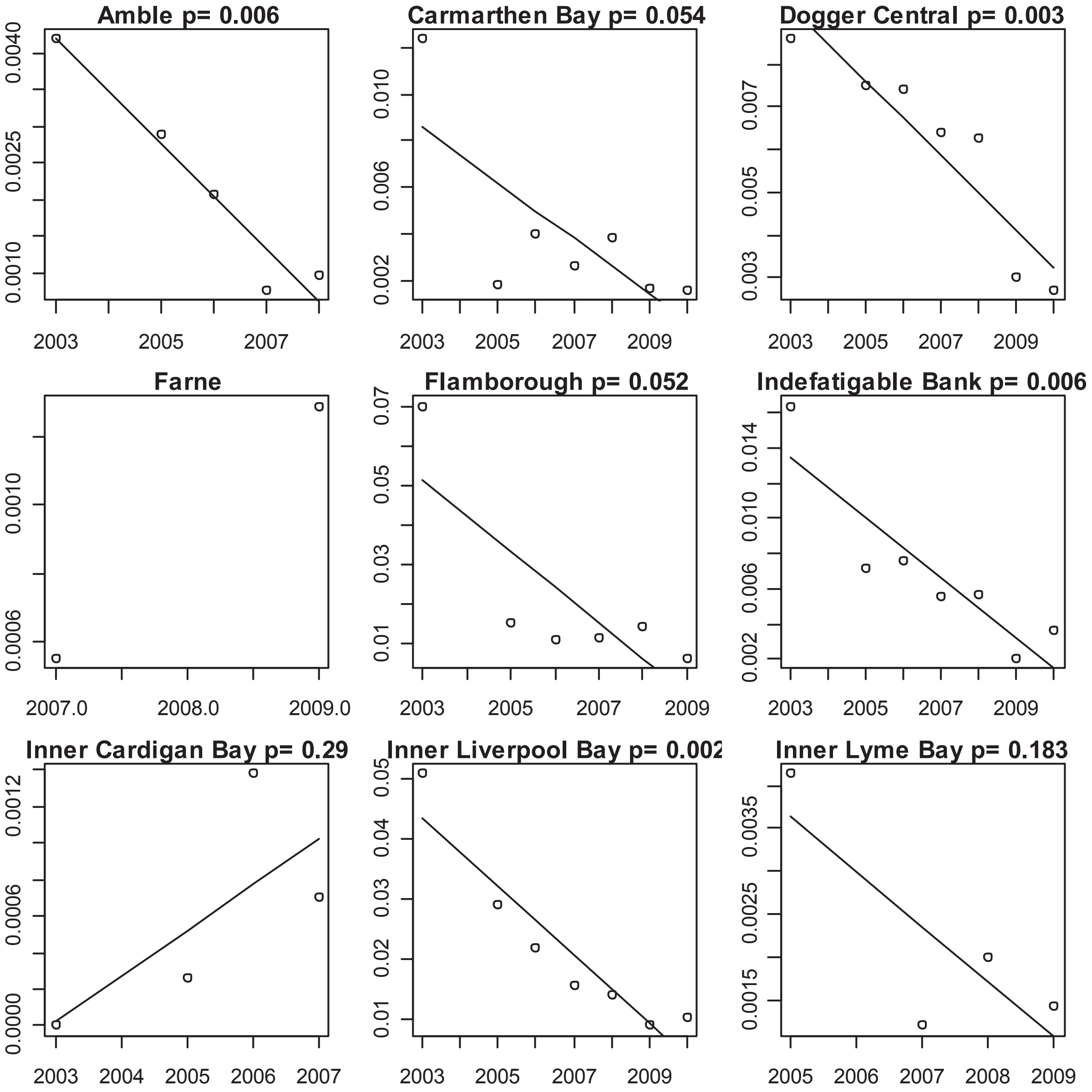


Figure 9.3a. Temporal trends of mean BDE47 concentrations in dab liver from 2003–2010 at different stations.

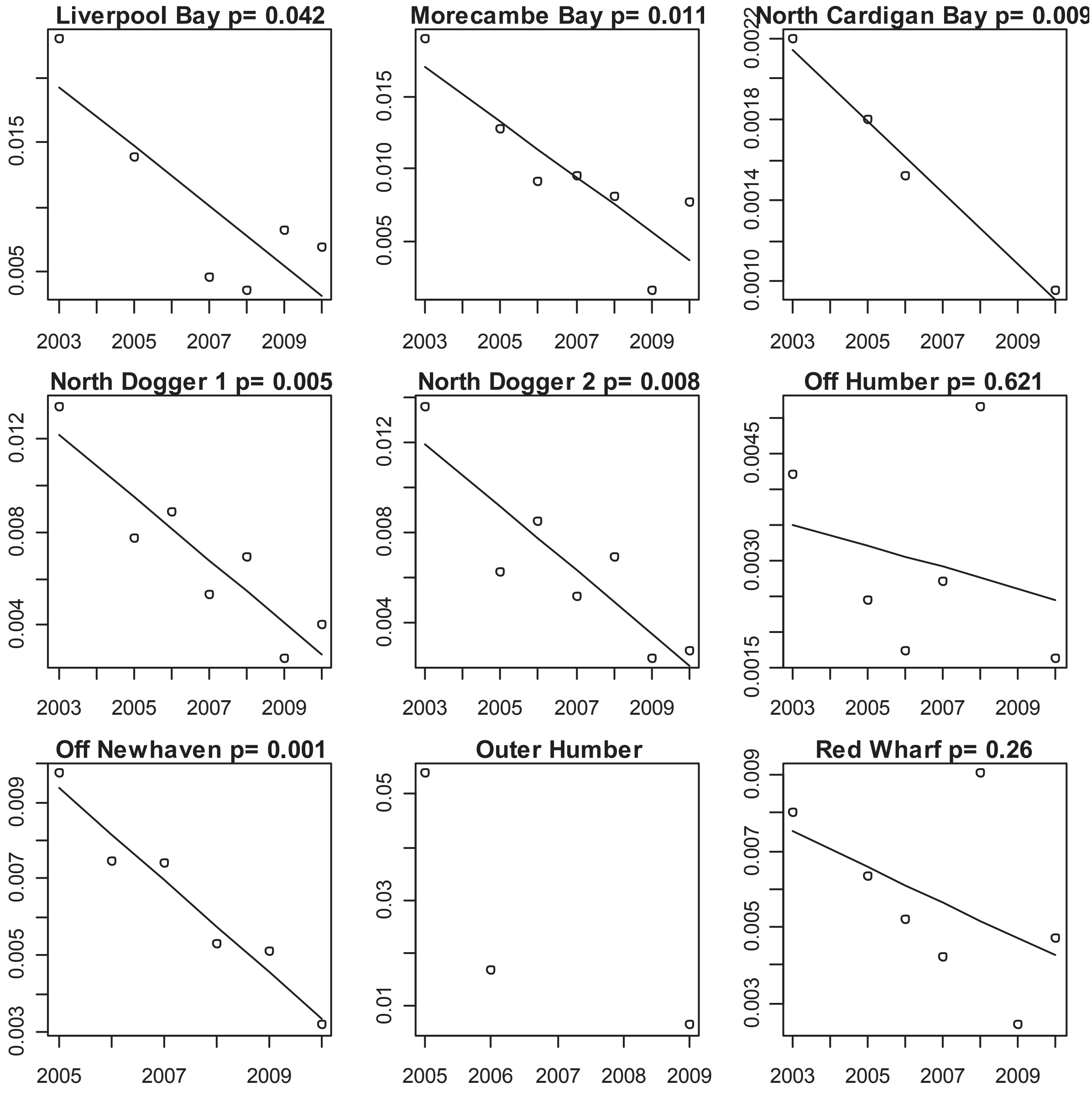


Figure 9.3b. Temporal trends of mean BDE47 concentrations in dab liver from 2003–2010 at different stations.

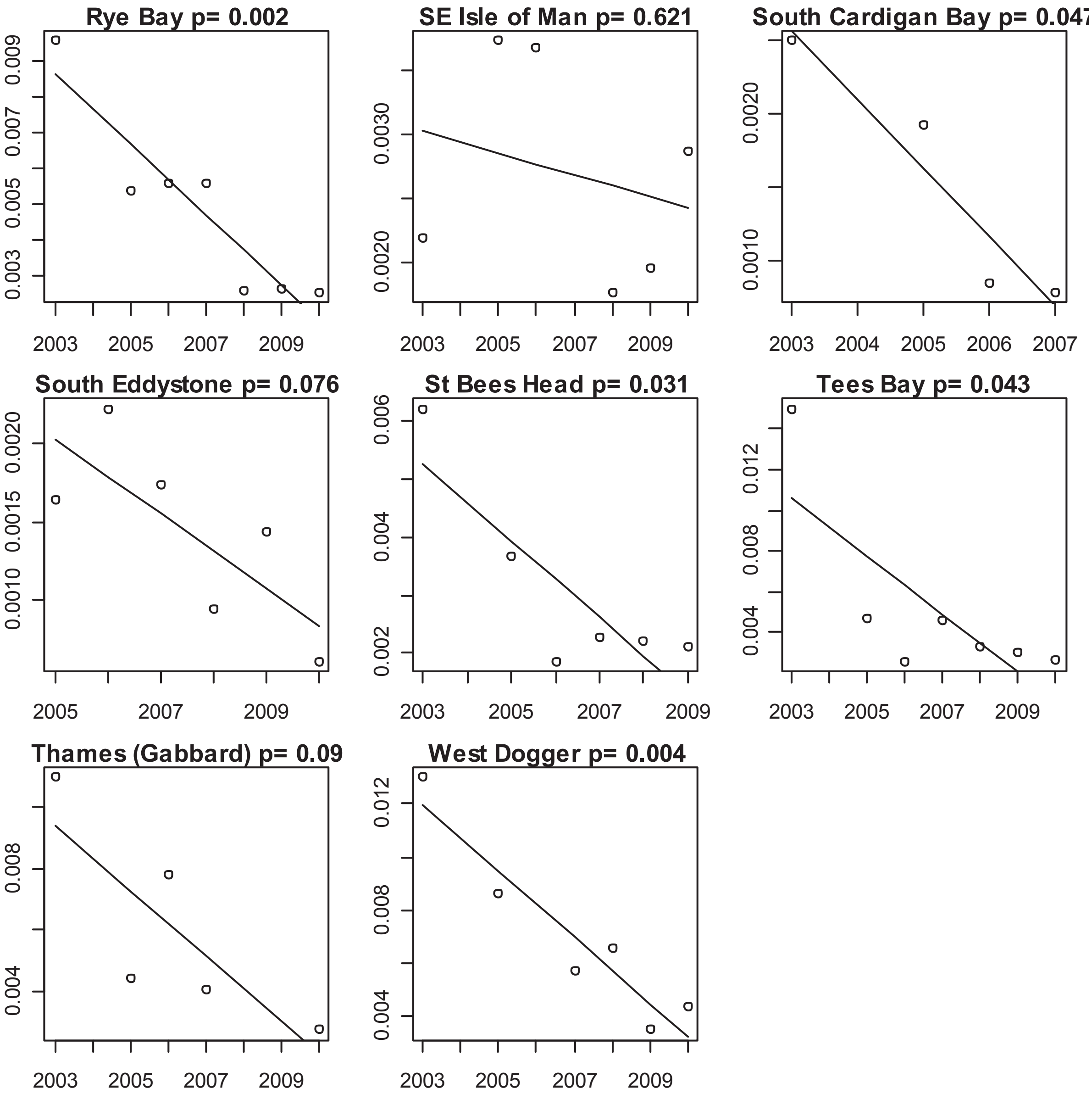


Figure 9.3c. Temporal trends of mean BDE47 concentrations in dab liver from 2003–2010 at different stations.

The trend results for the different CSEMP stations are summarised in Table 9.2 and plotted geographically in Figure 9.4. Statistically significant trends with $p < 0.05$ are shown as vertically upwards or downwards pointing arrows at the sampling locations. Non significant trends in concentrations upwards or downwards are shown as angled upwards and downwards arrows, and no apparent trend is shown by horizontal arrows. Fish from 13 out of 26 stations showed significant decreases at 95% confidence interval for ∑11 BDEs, and fish from 15 out of 26 stations showed significant decrease at 95% confidence interval for BDE47. With such short time series, the decline would need to be quite large to result in a statistically significant trend (ie, $p < 0.05$). It is thus surprising that such a lot of the series are statistically significant, and demonstrates that BDE concentrations in dab livers are declining rapidly at many locations. These trends match those found in UK harbour porpoises (Law *et al.*, 2010a) and demonstrate the effectiveness of the EU ban on use of the penta- and octa-mix PBDE technical products. Significant declines were found at widespread geographical locations in the North Sea, Irish Sea and English Channel.

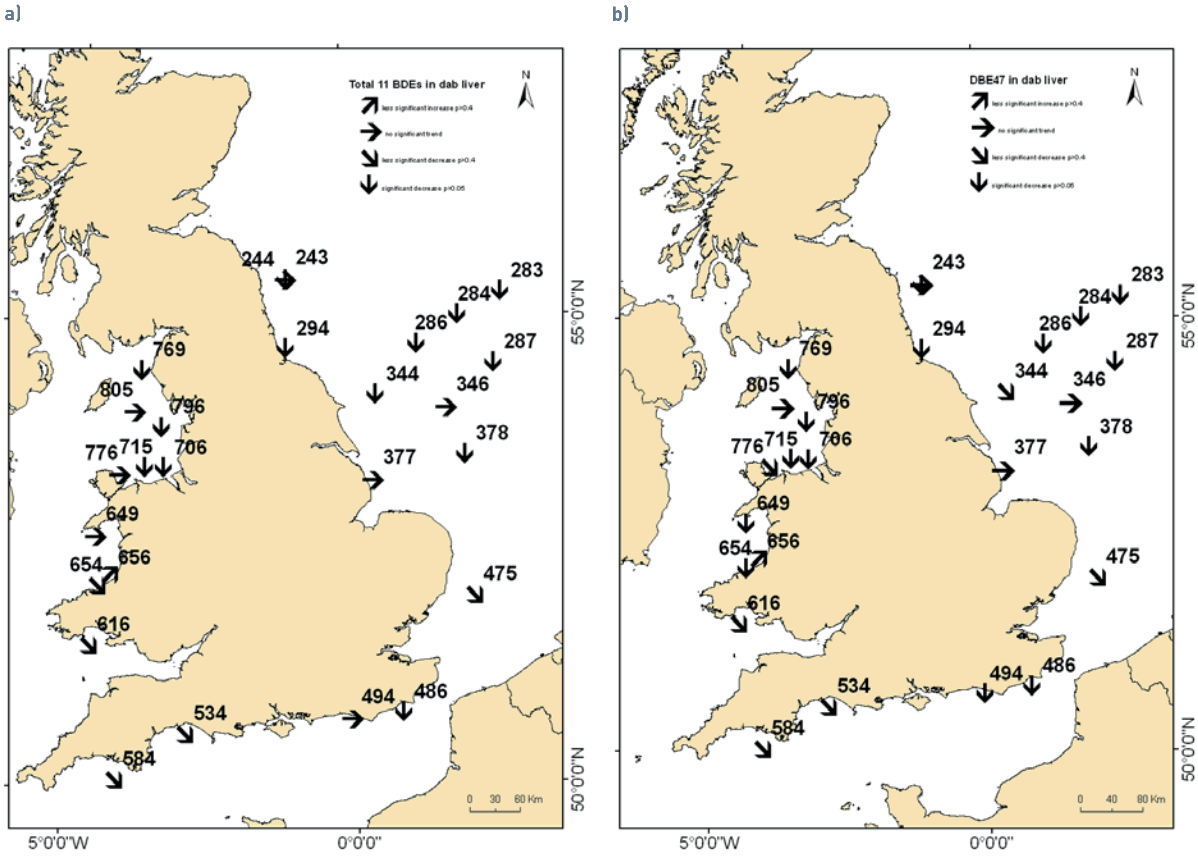


Figure 9.4. Map of sampling locations for dab livers analysed between 2003 and 2010, with arrows showing temporal trends, as described in the text, for a) ∑11 BDEs, and b) BDE47.

Table 9.2. Temporal trends of BDE concentrations in livers of dab (*Limanda limanda*) collected from CSEMP stations between 2003 and 2010.

Location	CSEMP station	Latitude	Longitude	Sampling period	No. of years	Total11BDEs		BDE47	
						Trend	p-value	Trend	p-value
Farne	243	55.488	-1.114	2007-09	2	↔		↔	
Amble	244	55.495	-1.127	2003-08	5	↓	0.003	↓	0.006
North Dogger 1	283	55.289	2.904	2003-10	7	↓	0.003	↓	0.005
North Dogger 2	284	55.065	2.082	2003-10	7	↓	0.006	↓	0.008
West Dogger	286	54.777	1.295	2003-10	6	↓	0.004	↓	0.004
Dogger Central	287	54.527	2.699	2003-10	7	↓	0.035	↓	0.003
Tees Bay	294	54.756	-1.136	2003-10	7	↓	0.007	↓	0.043
Flamborough	344	54.245	0.499	2003-09	6	↓	0.046	↘	0.052
Off Humber	346	54.071	1.797	2003-10	6	↔	0.578	↔	0.621
Outer Humber	377	53.323	0.425	2005-09	3	↔		↔	
Indefatigable Bank	378	53.563	2.083	2003-10	7	↓	0.002	↓	0.006
Thames (Gabbard)	475	52.048	2.098	2003-10	5	↘	0.113	↘	0.09
Rye Bay	486	50.825	0.798	2003-10	7	↓	0.009	↓	0.002
Off Newhaven	494	50.756	-0.056	2005-10	6	↔	0.772	↓	0.001
Inner Lyme Bay	534	50.614	-2.93	2005-09	4	↘	0.139	↘	0.183
South Eddystone	584	50.107	-4.101	2005-10	6	↘	0.107	↘	0.076
Camarthen Bay	616	51.548	-4.605	2003-10	7	↘	0.07	↘	0.054
North Cardigan Bay	649	52.708	-4.524	2003-10	4	↔	0.451	↓	0.009
South Cardigan Bay	654	52.191	-4.494	2003-07	4	↘	0.325	↓	0.047
Inner Cardigan Bay	656	52.298	-4.273	2003-07	4	↗	0.341	↗	0.29
Inner Liverpool Bay	706	53.471	-3.358	2003-10	7	↓	0.003	↓	0.002
Liverpool Bay	715	53.472	-3.699	2003-10	6	↓	0.038	↓	0.042
St Bees Head	769	54.512	-3.794	2003-09	6	↓	0.019	↓	0.031
Red Wharf Bay	776	53.375	-4.13	2003-10	7	↔	0.562	↘	0.26
Morecambe Bay	796	53.905	-3.41	2003-10	7	↓	0.05	↓	0.011
SE Isle of Man	805	54.056	-3.875	2003-10	6	↔	0.463	↔	0.621

9.5 Discussion

BDEs have been detected in dab livers at all 26 stations monitored under the CSEMP. Levels have declined at significant rates in samples from many of the stations since monitoring began in 2003. Currently, there are no OSPAR assessment criteria with which to compare the concentrations found currently, but the proposed Environmental Quality Standard (EQS) for BDEs in biota under the Water Framework Directive (WFD) is 0.0085 μg kg^{-1} wet weight for the sum of the 6 congeners BDE28, BDE47, BDE99, BDE100, BDE153 and BDE154. $\sum$6 BDEs at the stations found to have the lowest and highest BDE contamination in 2010 were 0.61 and 19 μg kg^{-1} wet weight at South Eddystone (CSEMP 584) and off Newhaven (CSEMP 494), respectively. These concentrations are 71 times and more than 2000 times higher than this new proposed EQS concentration. Even if levels continue to decrease at current rates, it will be many years before levels of BDEs in dab fall below the proposed EQS value. The difference in spatial distributions for BDEs in sediment and fish is marked, and it may be worth investigating levels of BDE209 in fish in the Irish Sea, as recent studies show that it can be detected in fish (eg, Shaw *et al.*, 2009).

10. Shellfish microbiology

Author: Ron Lee

10.1 Topic and background

Faecal contamination of the marine environment may originate from continuous and intermittent sewage outfalls, diffuse pollution from wild and farm animals, as well as pollution from any of these sources carried to the sea by rivers and streams. Bivalve molluscan shellfish concentrate bacteria and viruses present in contaminated seawater and these can cause illness in consumers: controls are applied on commercial shellfisheries under EU regulations to reduce the risk. The extent of the contamination within harvesting areas is determined by monitoring for faecal indicator bacteria in the shellfish: faecal coliforms for the Shellfish Waters Directive (from the environmental perspective) and *Escherichia coli* for the Food Hygiene Regulations. The monitoring is exclusively targeted at commercial harvesting areas. For further detail on the Shellfish Waters Directive see: Defra. Shellfish Waters Directive. http://www.defra.gov.uk/environment/quality/water/water-quality/shellfish-directive/ accessed 7 June 2012. For other relevant legislation see European Communities (2004, 2006).

10.2 Sampling undertaken in previous year

In England and Wales, Cefas manages the shellfish waters monitoring programme on behalf of the Environment Agency and the shellfish hygiene monitoring programme on behalf of the Food Standards Agency. Samples are mainly taken by local authority environmental health departments and tested at local or regional laboratories: Health Protection Agency (for England) and Public Health Wales. A small number of shellfish waters sites are sampled by Environment Agency staff and tested at the EA National Laboratory. The number of sites sampled has varied over time, but around 500 locations are sampled monthly for food hygiene purposes and 142 are sampled quarterly for shellfish waters purposes. In general, the shellfish waters sampling points represent a subset of the shellfish hygiene sites.

10.3 Summary of results obtained

Under the Shellfish Waters Directive, a guideline value of 300 faecal coliforms per 100 g of shellfish should be met in at least 75% of samples.

For the food hygiene legislation, harvesting areas are classified as A, B or C according to increasing concentrations of *E. coli* in a time series of data. Those areas that do not even meet the requirements for class C are termed prohibited. For further detail see: Cefas. Classifying shellfish harvesting. http://www.cefas.defra.gov.uk/our-science/animal-health-and-food-safety/food-safety/classifying-shellfish-harvesting.aspx accessed 7 June 2012 and: Food Standards Agency. Classification of shellfish harvesting areas:http://www.food.gov.uk/foodindustry/farmingfood/shellfish/shellharvestareas/ accessed 7 June 2012.

10.4 Length of time series available

Some shellfish waters have been sampled since the early 1980s but, as many were designated more recently, sampling has been undertaken since the date of designation: the number of locations sampled for this purpose has increased markedly over time. Cefas has been involved in the programme management since 2008. Harvesting areas have been sampled for food hygiene purposes since 1992.

10.5 Summary of trend observed/not

There has been an increase over time in the proportion of shellfish waters meeting the guideline value. This would imply a decrease in faecal contamination at the monitoring points and may well be associated with initiatives aimed at decreasing pollution from both point and diffuse sources. However, there have been changes in the number of designated waters over time, as well as changes in the sampling strategy, and this may also have influenced the proportion of waters meeting the guideline value.

There has been an overall increase in the proportion of areas classified as B with time with an associated decrease in the proportion of areas classified as C. This also indicates a general decrease in faecal contamination of harvesting areas. However, there are year-to-year fluctuations superimposed on this general trend.

10.6 Graphics and illustrations

Figure 10.1 shows the locations of commercial shellfish harvesting areas in England and Wales.

Figure 10.2 shows the percentage of designated shellfish waters in England and Wales meeting the guideline standard under the shellfish waters directive from 2002 to 2010. Figure 10.3 shows the percentage of commercial shellfish harvesting areas in England and Wales falling into each shellfish hygiene classification category over the same period.

Figure 10.1. Location of classified commercial shellfish production areas in England and Wales.

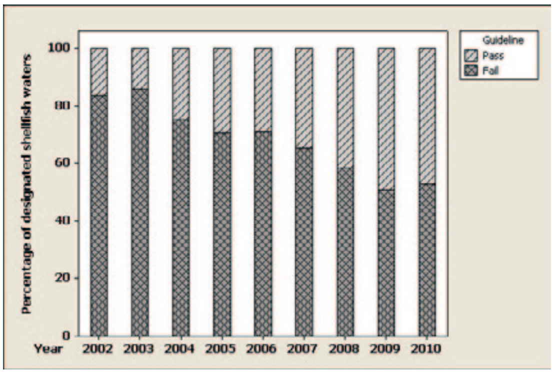


Figure 10.2. Percentage of designated shellfish waters passing the guideline value.

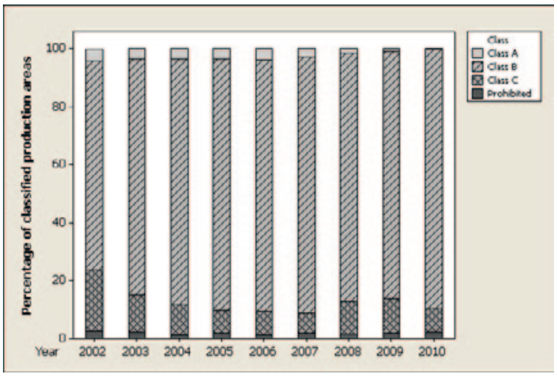


Figure 10.3. Percentage of production areas in each class, 2002–2010.

11. Marine litter

Author: Thomas Maes

11.1 Topic and background

Litter enters the marine environment and is deposited on beaches and in the marine environment from a variety of sources, including direct littering by beach visitors, discarded or lost fishing gear from fishing vessels, illegal dumping by ships and small marine craft, sewage discharges, fly-tipping and so on. Litter is also carried by rivers and streams into coastal waters, so littering in urban areas can make a significant contribution to marine litter. Litter may be transported over long distances by currents and wind.

11.2 Sampling undertaken in previous years

Cefas collects offshore seabed litter from around 100 different sites as part of the International Bottom Trawl Survey (IBTS) and CSEMP cruises. During these cruises, different techniques have been developed to collect and categorize marine litter which have been used to develop a new marine litter record sheet, showing different litter categories, like plastic, paper and rope. Sampling locations are shown in Figure 11.1.

11.3 Summary of results obtained

Collecting marine litter during the IBTS and CSEMP cruises has shown that a wide variety of items are routinely collected from the UK inshore and offshore seabed. Plastic made up 48% of marine litter found during IBTS and CSEMP cruises. Synthetic rope, natural rope and twine accounted for over 23% of litter found during the IBTS and CSEMP cruises. The results of a litter category study suggest that plastic is the most abundant litter type, and a spatial distribution analysis has shown litter hotspots in the Celtic Deep and Carmarthen Bay.

11.4 Length of time series available

Cefas has data available from 1992–2008. During the 16 years of sampling, 3593 items of litter were collected, including over 1400 plastic bags and almost 800 pieces of synthetic rope. The distribution of marine benthic litter by litter category and over time is shown in Figure 11.2.

11.5 Spatial coverage

Large amounts of litter were found on the west coast and especially in Morecambe Bay (CSEMP 767), Cardigan Bay (CSEMP 649, CSEMP 655 and CSEMP 656), Carmarthen Bay (CSEMP 616) and Celtic Deep (CSEMP 605). Smaller quantities of litter were observed in the North Sea, but not concentrated within any single region.

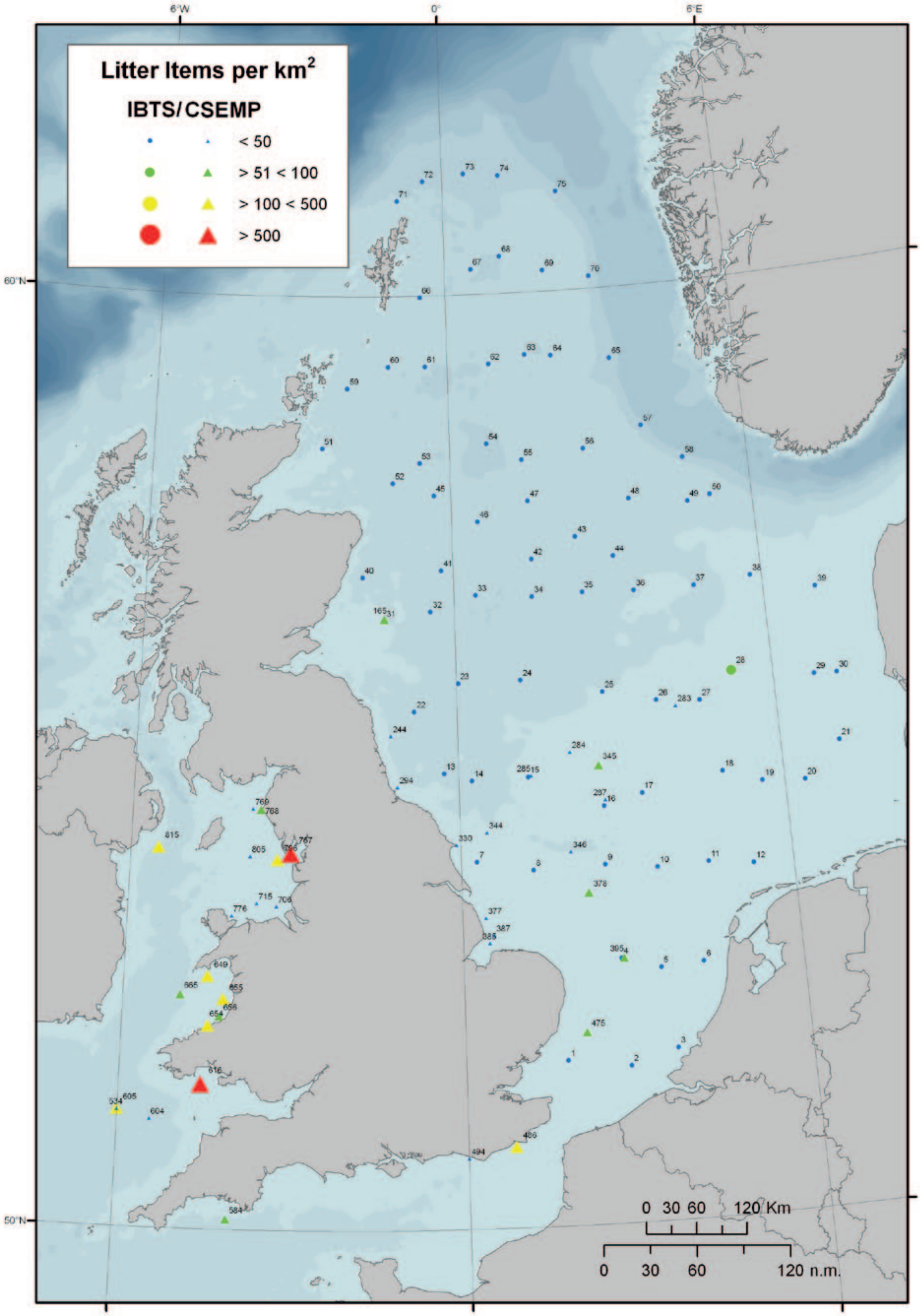


Figure 11.1. Locations and quantities of litter collected on cruises during the time period 1992–2008.

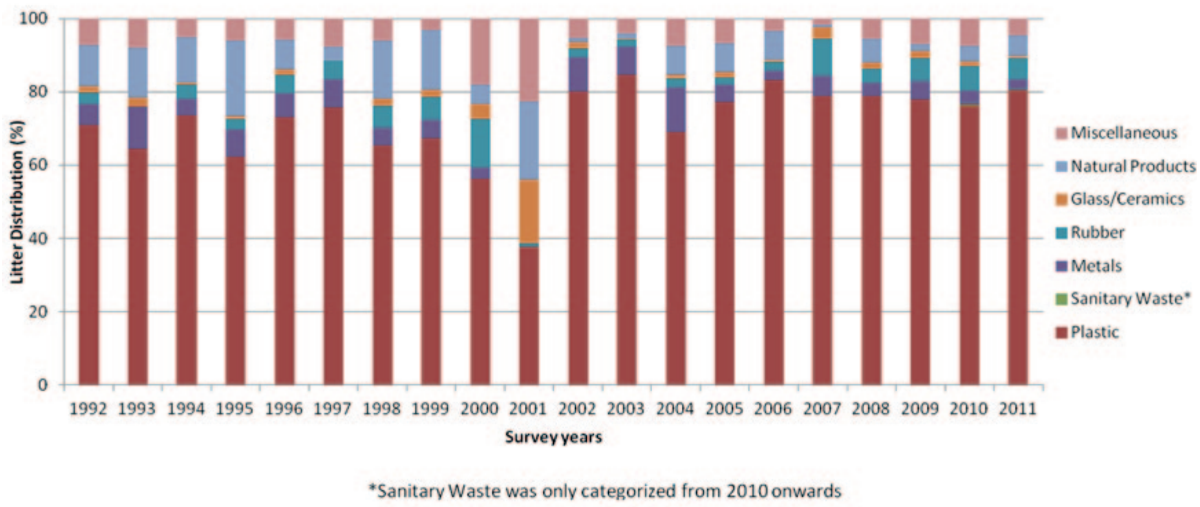


Figure 11.2. Marine benthic litter distribution from 1992–2011, as a percentage.

11.6 Summary of trend observed/not

During the CSEMP cruises a slight increase of average litter abundances were observed between 2000 and 2008, but litter items per km^2 decreased between 2004 and 2008. During the IBTS cruises, litter concentrations also increased between 1992 and 2008. A decrease of litter concentrations were observed between 1993 and 1998. High levels of litter at similar levels to 1995 were again observed in 2005 and 2008.

Analysing data for Carmarthen Bay, where we found the highest average concentration of marine litter, shows that there are strong yearly fluctuations in litter concentrations. Therefore, each station was examined separately to identify yearly changes. It showed that there is high inter-annual variability at individual stations, especially at CSEMP compared to IBTS stations. Quantities of litter showed a slight increase during 2003 and 2004 in the CSEMP compared to other years.

Healthy and Biologically Diverse Seas

12. Contaminants in marine mammals

Authors: Robin Law and Jon Barry

12.1 Topic and background

The UK government has funded the Cetacean Strandings Investigation Programme since 1990. Cetaceans stranded or bycaught around UK coasts are subjected to post-mortem investigation in order to establish cause of death. In a selection of these animals, particularly porpoises as they are distributed around the entire UK coastline, contaminant analyses are also undertaken in order to study possible associations between contaminant burdens and death due to infectious disease. As cetaceans are top predators in the marine environment, they are particularly at risk from lipophilic contaminants which bioaccumulate through their foodchain and can reach high concentrations in their blubber. This makes them suitable species in which to study temporal trends in concentration.

12.2 Brominated diphenyl ethers

12.2.1 Sampling undertaken in previous year

Brominated diphenyl ethers were determined in nine harbour porpoise blubber samples taken in 2008.

12.2.2 Summary of results obtained

Σ9BDE concentrations (the sum of the 9 congeners determined: BDE28, BDE47, BDE66, BDE85, BDE99, BDE100, BDE138, BDE153 and BDE154) ranged from 0.1 to 1.3 mg kg^{-1} lipid weight.

12.2.3 Length of time series available

In UK porpoises, Σ9BDE concentrations are available for 415 individual animals collected from 1992–2008.

12.2.4 Spatial coverage

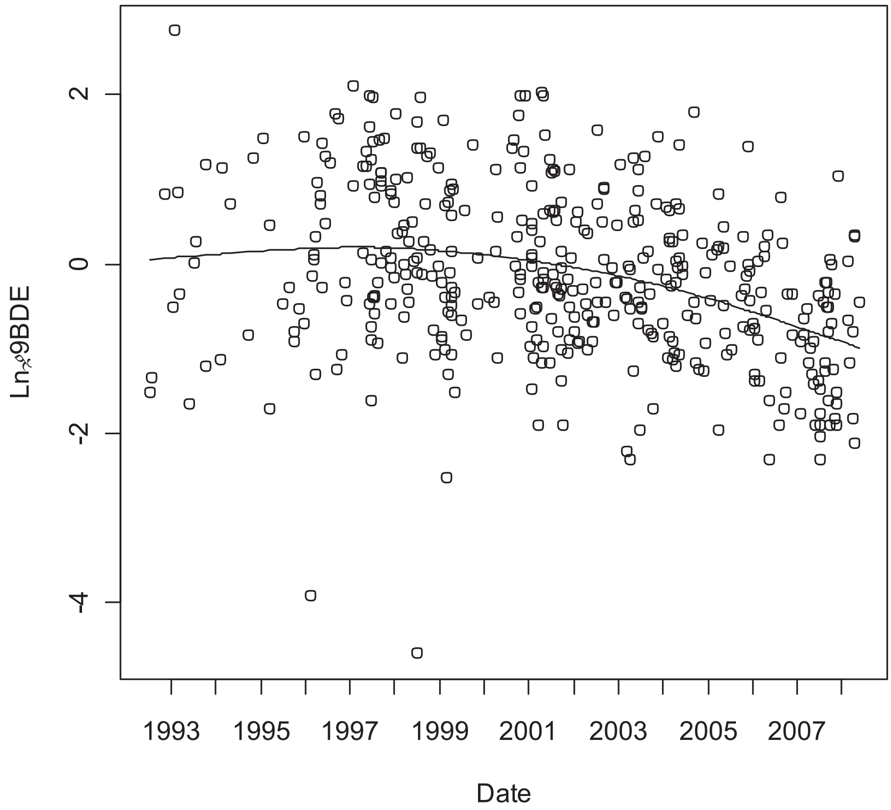
The locations from which porpoises were taken for post-mortem study and BDE analysis are shown in Figure 12.1.

Figure 12.1. The locations from which the porpoises were sampled in order to study temporal trends over the whole period.

12.2.5 Summary of trend observed/not

Over the whole time period, Σ9BDE concentrations ranged from not detected in a 15 year old male porpoise from Eastern England sampled in 1998 (reference number SW1998/115) to 15.7 mg kg^{-1} lipid weight in a juvenile female porpoise from the Shetland Islands sampled in 1993 (SW1993/10b). Possible temporal trends were studied using non-parametric statistics (see Law *et al.*, 2008). Our analysis indicates that, overall, median Σ9BDE concentrations peaked around 1998, and have since reduced by between 54.5% and 76.1% to 2008. Our best point estimate is that the reduction has been 65.5%. This decline was highly statistically significant ($p < 0.001$) and was not confounded by a range of other factors which were also considered (area, season, nutritional status, stranded/bycaught and age class). The detail is presented in Law *et al.* (2010a), and the data and trend are illustrated in Figure 12.2.

Figure 12.2. Ln Σ9BDE concentrations in porpoise blubber on a lipid basis by year. The continuous line represents the smoothed values from a Generalized Additive Model fitted to the data.



12.3 Chlorobiphenyls

12.3.1 Sampling undertaken in previous year

Analysis of chlorobiphenyls in blubber of harbour porpoises stranded or bycaught during 2008–2010 has not been conducted.

12.3.2 Summary of results obtained

No new data available.

12.3.3 Length of time series available

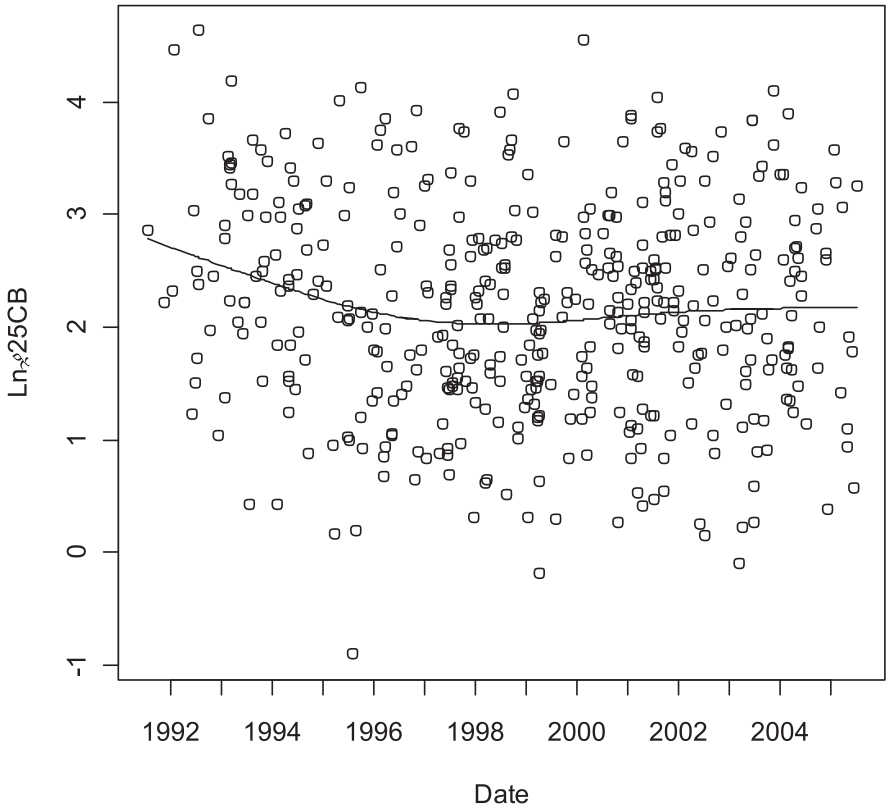
Although no new data were available, we have undertaken time-trend analysis of all available data for Σ25CBs (Law *et al.*, 2010b). In UK porpoises, Σ25CB data are available for 440 porpoises stranded during 1991–2005. Sampling locations are shown in Figure 12.3. Concentrations ranged from 1.0 to 160 mg kg^{-1} lipid weight overall, with the highest concentration in a newborn porpoise which died of starvation and was found at Aberystwyth in Ceredigion, West Wales, in 1995 (reference number SW1995/102). The full dataset is available in the electronic supplementary information submitted alongside Law *et al.* (2010b) and available on the Elsevier website for Marine Pollution Bulletin. Further information on the testing for confounding factors and subregional trends can be found in Law *et al.* (2010b).

12.3.4 Spatial coverage

See Figure 12.3.

Figure 12.3. The locations from which the porpoises were sampled in order to study temporal trends in CB concentrations over the whole period.

Figure 12.4. Ln Σ25CB concentrations in porpoise blubber on a lipid basis by year. The continuous line represents the smoothed values from a Generalized Additive Model fitted to the data.



12.3.5 Summary of trend observed/not

Median Σ25CB levels by year ranged from 5.8 to 13.34 mg kg^{-1} lipid weight. Overall, Σ25CB levels seemed to decline in the mid-1990s, maybe in response to the original ban implemented from the 1980s onwards, but then seemed to plateau out (Figure 12.4). This trend was not confounded by a range of other factors which were also considered (area, season, nutritional status, stranded/bycaught and age class).

From the data presented here, it is clear that chlorobiphenyl concentrations have declined in UK harbour porpoises as a result of bans on the use of PCBs enacted in the UK beginning more than two decades ago, in line with other findings. The plateauing of the current trend suggests that diffuse inputs are now sufficient to maintain current levels. This contrasts with steep declines observed for organochlorine pesticides in birds and marine mammals (Henny *et al.*, 2009 a & b; Leonel *et al.*, 2010; Vorkamp *et al.*, 2008, 2009). Increased susceptibility to infectious disease mortality in the most PCB-contaminated individuals looks likely to continue for some time yet, and further efforts to limit or eliminate PCB discharges to the marine environment are needed. In Norway, Sweden and Switzerland, such activities have begun. Many buildings built from the late 1940s to the early 1980s contain significant quantities of PCBs in building materials and coatings (particularly joint sealants). Programmes to identify and remove and collect such materials for secure disposal are underway (Asplund *et al.*, 2010; Funcke, 2010; Lilliehorn, P., 2010; Lundkvist, 2010; Ottesen *et al.*, 2010; Wagner, 2010a & b).

13. Contaminant induced flatfish liver pathology as an MSFD assessment tool

Authors: John P. Bignell, Stephen W. Feist and Grant D. Stentiford

13.1 Introduction

The presence of liver tumours has been classified as a direct indicator of historic contaminant exposure, particularly to chemicals that initiate and promote their formation (Myers *et al.*, 1990, 1991, 1992, 1994; Reichert *et al.*, 1998; Schiewe *et al*. 1991). In the UK, the Clean Seas Environment Monitoring Programme (CSEMP) monitors the proportion (prevalence) of the flatfish dab (*Limanda limanda*) with liver tumours at offshore sites, and flounder (*Platichthys flesus*) at inshore and estuarine sites according to procedures of the OSPAR Co-ordinated Environmental Monitoring Programme (CEMP) (OSPAR 1998a, b).

At some offshore sites in the North Sea, liver tumour prevalence in dab has exceeded 10 % in recent years (Feist *et al.*, 2004) while prevalence in estuarine species can be higher (Stentiford *et al.*, 2003; Koehler, 2004). These figures are significantly elevated over those observed in other wildlife populations (eg, Fowler, 1987; Harshbarger, 2004). In addition to the assessment of grossly visible tumours, histopathological assessment of liver samples allows for the diagnosis of microscopic tumours and pre-tumours not visible during whole fish assessments. Recording these pathologies, which are thought to precede the development of grossly visible benign and malignant tumours give an early warning of detrimental health effects. Pathologies preceding the formation of benign and malignant tumours include so-called foci of cellular alteration (FCA), non-neoplastic toxicopathic lesions (such as nuclear and cellular polymorphism) and other lesions associated with cell death, inflammation and regeneration. Currently, there are 32 liver pathologies in flatfish classified under the international Biological Effects Quality Assurance in Monitoring Programmes (BEQUALM) initiative (Feist *et al.*, 2004). Cefas is the reference laboratory for this aspect of BEQUALM.

Tumour formation is a multi-step, gradual process for which the underpinning molecular steps, and the role of environmental exposure, are rarely known. Most human cancers (tumours) appear later in life, with one explanation for this pattern proposing that cancer is fundamentally linked to ageing. Studies of lifespan in a taxonomically diverse range of animals (including fish) have however, suggested that, although cancer prevalence may be higher in older animals, in laboratory exposure trials using a model carcinogen, animal groups with a lifespan of between 3 and 50 years developed tumours at a similar rate, with latent periods of approximately 1 year between exposure and presence of tumours. In this context, the time dependence for tumour development appeared more related to the cumulative dose of carcinogen than to either lifespan of the host or to the rate of ageing (Lijinsky, 1993).

Recent studies undertaken at Cefas (Stentiford *et al,* 2009; 2010) have classified marine sites based on their disease profile by applying a simple 'harm score' which considers the sum of diseases observed in individuals and subsamples of the population. For utilisation in the recent Defra Charting Progress II report (http://chartingprogress.defra.gov.uk), the harm score was categorised into three levels (Type A, B and C) which classifies the disease severity and prevalence observed in fish from distinct locations. This approach showed that site specific disease profiles (harm scores) are generally consistent in multi-year studies (Stentiford *et al*. 2009). Further detailed work on flatfish populations captured at different offshore sites demonstrated the effect of age on the overall 'harm' score, and specifically on the onset of liver pathologies associated with cancer (Stentiford *et al*. 2010). However, despite the expected age effect (tumour prevalence increases with age), a relative acceleration of this effect occurred in fish populations from certain regions; with the onset of pre-cancers and cancer occurring approximately 2 years earlier in fish sampled from the North Sea (Dogger Bank) compared to those from the English Channel (Rye Bay) and Irish Sea (Liverpool Bay). Specifically, liver tumour and pre-tumour prevalence and severity increases in fish of 3 or 4 years of age at the Dogger sites and at approximately 5 to 6 years old in those from the Irish Sea. This demonstrates that despite age being an important factor in the prevalence of tumours in flatfish, other exogenous factors are responsible for this premature onset of tumours in dab at particular sites routinely sampled under the CSEMP (Stentiford *et al.*, 2010).

In the course of this work, it was observed that the total length of individual flatfish sampled in monitoring programmes is not a reliable surrogate for the age of that fish. Some populations of fish were older when compared to fish of the same size from a different population. Consequently, given the aforementioned importance of age in disease onset, a redesign of methodology utilised for the sampling of flatfish for disease monitoring was implemented during 2010 and 2011. This redesign ensures an accurate assessment of contaminant-induced liver pathology, specifically liver tumours and pre-tumours, in flatfish sampled during the UK CSEMP. These changes are timely, provide efficiency savings for monitoring and improve the delivery of our science.

This case study reported here describes the prevalence and apparent age at onset for diseases of dab collected for a regional assessment of the English Dogger Bank. We have applied a recently developed assessment tool which utilises liver disease to calculate a 'harm score' in wild flatfish populations (Stentiford *et al.*, 2009), to age-verified samples collected during the 2010 UK CSEMP programme. The application of the assessment tool in this manner removes the confounding factor of age from disease assessment and allows for an assessment of harm in younger age classes of fish (ie, prior to the onset of known age-related effects). Assessment of harm in specific age classes of dab allows for a true site-site and year to year comparison of health in UK flatfish populations and thereby provides a robust tool which could be used within the assessment of Good Environmental Status (GES) under Descriptor 8 (contaminants are not at levels giving rise to pollution effects) of the Marine Strategy Framework Directive (MSFD) (Lyons *et al.* 2010).

13.2 Materials and Methods

13.2.1 Sampling

Despite the utility of liver pathology (including cancer) as a top level marker of contaminant exposure in marine and estuarine fish, sampling strategies recommended by ICES and utilised previously in the UK CSEMP have been demonstrated to be unable to discount the effects of age on the development of liver pathology in sentinel species (Stentiford *et al.* 2010). During the 2010 UK CSEMP programme, harm score data (associated specifically with liver disease) was collected alongside chemistry and biomarker data (reported elsewhere) from the dab as part of a regional assessment of the Dogger Bank. Dab were collected from 4 sites across the North, West, Central and South Dogger Bank region. In contrast to previous studies of this type, and in light of data presented by Stentiford *et al.* (2009), dab sampled from these sites were considered as a meta-population representing the region, rather than specific sites. The sampling programme also considered the following pertinent points raised by Stentiford *et al.* (2010):

1. The presence of fish between 1 and 4 years old at all sites currently sampled under the UK CSEMP.
2. The increase in harm score (associated with liver diseases) in fish aged 4 years old and above.
3. The presence of sufficient numbers of 3 and 4 year old fish to accurately undertake age-corrected site-to-site comparisons of harm.

In total, 519 dab were sampled from across the English Dogger Bank region in June 2010 onboard RV *Cefas Endeavour* by use of 30-minute tows of a Granton trawl. Upon landing, live dab were immediately removed from the catch, and sorted into flow-through tanks containing aerated seawater. Fish were segregated into size classes of 10–14 cm, 15–19 cm, 20–24 cm, and 25 cm and above. Size classes represented the likely range of sizes retained by the trawl and, accordingly, the likely spread of age classes present at the target sites (+1 year and above).

Fish were euthanised and upon opening of the body cavity, the liver was assessed for the presence of visible liver tumours (Figure 13.1) according to the guidelines set out by Feist *et al.* (2004). Samples of liver from all fish (including those containing tumours) were removed and fixed for 24 hr in 10 % neutral buffered formalin before transfer to 70 % industrial methylated spirit for subsequent histological assessment. In order to prevent the appearance of *post mortem* artefacts, only live fish were sampled. Fixed liver samples were processed to paraffin wax in a vacuum infiltration processor by using standard protocols (Feist *et al.*, 2004). Blocks were cut at 3–5 µm on a rotary microtome and resulting tissue sections mounted onto glass slides before staining with haematoxylin and eosin (H & E). Stained sections were analysed by light microscopy (Eclipse E800, Nikon, UK) and diagnosis of liver pathology types followed the guidelines set out by Feist *et al.* (2004) (Table 13.1). Digital images of pathological features were obtained by use of the Lucia™ Screen Measurement System (Nikon, UK).

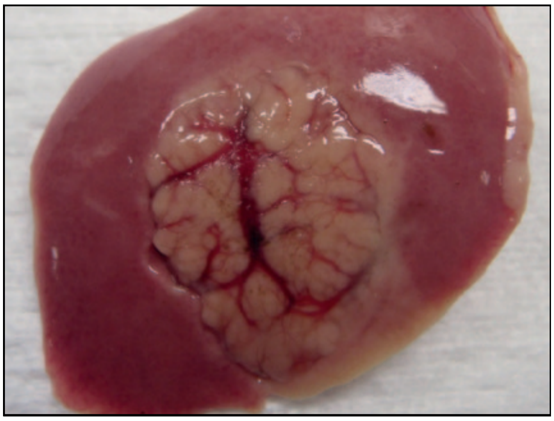


Figure 13.1. Liver tumour from a dab sampled during 2010 showing a typical pronounced network of blood vessels permeating throughout the tumour mass.

For ageing, otoliths were removed from individual fish and stored in separate vials for subsequent processing in the laboratory. Preparation, mounting, cutting, staining and reading of otoliths followed the methods of Easey and Millner (2008) and age data (in years) was generated for each fish assessed for disease.

13.3 Data analysis

Previous work by Stentiford *et al.* (2009, 2010) developed a 'harm score' index for dab populations sampled using the quality assurance procedures for disease diagnosis as detailed by Feist *et al.* (2004). The harm score is based on a cumulative assessment of the prevalence of specific liver diseases (including cancer) measured in dab populations from marine sites. It is based upon empirical observations of liver diseases in over 5000 individual fish sampled over a five year period. It assigns a score (0–3) to the 5 BEQUALM liver pathology categories (Table 13.2); the cumulative score (maximum 15) leading to an overall 'harm score' that depicts the relative departure of those populations from an empirical baseline. The harm score is further divided into 3 'site types' (A, B, C) that have been proposed as an assessment tool for classifying UK marine sites based upon the liver diseases observed in fish from those sites (Table 13.3).

In this report, we have extended this principle to calculate the harm score in dab collected from the English Dogger Bank region. Following histological assessment of liver diseases in dab, percentage prevalence data was summarised by BEQUALM categories and pooled by age according to Stentiford *et al.* (2010). This was used to determine the overall harm score for each age class of dab sampled from the English Dogger Bank region.

Table 13.1. Liver disease categories established under BEQUALM Fish Disease Measurement programme (Feist *et al.*, 2004). Five disease categories exist, each containing several specific pathological types.

(1) Non-specific and inflammatory lesions (NSIL)

Coagulative necrosis
Apoptosis
Macrovesicular Steatosis
Microsvesicular Steatosis
Hemosiderosis
Variable glycogen content
Melanomacrophage centres
Lymphocytic/monocytic infiltration
Granuloma
Fibrosis
Regeneration

(2) Early non-neoplastic toxicopathic lesions (ENTL)

Phospholipidosis
Fibrillar inclusions
Hepatocellular/nuclear polymorphism
Hydropic degeneration
Spongiosis hepatis

(3) Foci of cellular alteration (FCA)

Clear cell
Vacuolated
Eosinophilic
Basophilic
Mixed

(4) Benign neoplasms (BN)

Hepatocellular adenoma
Cholangioma
Hemangioma
Pancreatic acinar cell adenoma

(5) Malignant neoplasms (MN)

Hepatocellular carcinoma
Cholangiocarcinoma
Pancreatic acinar cell carcinoma
Mixed hepatobiliary carcinoma
Hemangiosarcoma
Hemangiopericytic sarcoma

Table 13.2. Prevalence (%) ranges for five BEQUALM liver disease categories measured during 5 years of historical liver disease monitoring (Stentiford et al, 2009, 2010). The prevalence range of each disease over the period has been divided into quartiles and a score assigned to each quartile (0 to 3). A zero score is taken to represent the 5-year baseline prevalence for each disease. Higher scores depict higher prevalences. Scores assigned to the prevalence of each disease at each site in each year allow an overall 'harm score' to be assigned.
KEY: *ENTL= Early non-neoplastic toxicopathic lesions, FCA= Foci of Cellular Alteration, BN= Benign neoplasm, MN= Malignant neoplasm, NSIL= Non-specific and inflammatory lesions*

	LOW	HIGH	RANGE	BASELINE	LOW-MID	HIGH-MID	HIGH
NSIL	42	100	58	0 TO 56.5	56.6 TO 71	71.1 TO 85.5	ABOVE 85.5
ENTL	0	26	26	0 TO 6.5	6.6 TO 13	13.1 TO 19.5	ABOVE 19.5
FCA	2	58	56	0 TO 16	16.1 TO 30	30.1 TO 44	ABOVE 44
BN	0	24	24	0 TO 6	6.1 TO 12	12.1 TO 18	ABOVE 18
MN	0	8	8	0 TO 2	2.1 TO 4	4.1 TO 6	ABOVE 6
			HARM SCORE	**0**	**1**	**2**	**3**

Table 13.3. Site typing based upon harm scores for liver pathology according to Stentiford *et al*. (2009, 2010).

TYPE A (Baseline)	TYPE B (Elevated)	TYPE C (High)
Up to 50% of fish with no indication of BEQUALM liver pathology categories (NAD)	Less than 30% of fish with no indication of BEQUALM liver pathology categories (NAD)	Less than 20% of fish with no indication of BEQUALM liver pathology categories (NAD)
Low prevalence (<5%) of fish with NNT liver lesions and approximately 50 % prevalence of NSI liver lesions	Low prevalence (<10%) of fish with NNT liver lesions but an elevated prevalence of NSI liver lesions (up to 90%)	Similar prevalence of NNT liver lesions to Type B sites but a consistently high prevalence (up to 100%) of NSI liver lesions
Low prevalence of fish with liver FCA (<10%) and BN liver tumours (<5%). MN liver tumours very rare or absent.	Prevalence of FCA can exceed 15%. BN liver tumour prevalence around 10%. MN liver tumours more common than in Type A (up to 6%)	High prevalence (up to 50%) of FCA with BN liver tumour prevalence often exceeding 15%. MN liver tumours still comparatively rare though generally comprise a larger proportion of observed liver tumours than Type B (up to 8%).
Cumulative liver pathology harm score ≤5	Cumulative liver pathology harm score >5 and ≤10	Cumulative liver pathology harm score >10

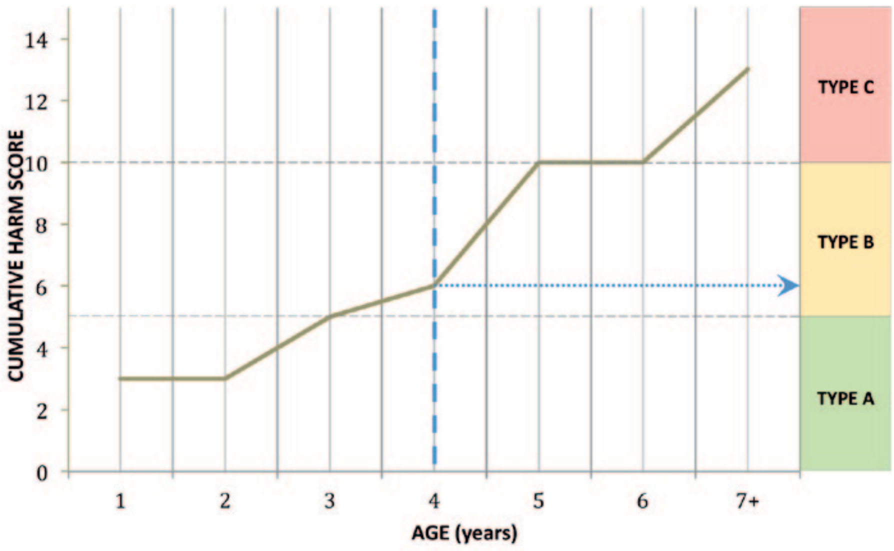
13.4 Results

A summary of liver disease prevalence data by BEQUALM category and age class is presented in Table 13.4. This data was used in combination with prevalence range data from previous studies (Table 13.2) to calculate the overall harm score for individual age classes. When harm scores (or specific prevalence categories) are considered against the specific site types of Stentiford *et al.* (2009, 2010) (see Table 13.4), the age-related harm curve shows a familiar elevation at ages above 4 years old. Specifically, fish of above 4 years of age show a significant increase in the prevalence of FCA (15.4% at 4 years, 44.2% at 5 years) and of the tumour category HCA (2.6% at 4 years, 9.2% at 5 years). Previous work of this type, utilising data from other UK locations in the English Channel and the Irish Sea also depict an age-related pattern in fish of above 4 years of age, albeit at a lower magnitude (Stentiford *et al.* 2010). In this context, the 4 year old fish population at the English Dogger Bank have a similar harm score to the 6 year old fish population from the Irish Sea (Stentiford *et al.* 2010). Assessment of harm in fish of 4 years old and below therefore provides an age-corrected assessment of contaminant-induced liver pathology in dab and also depicts an elevated harm in fish of this age category from the English Dogger Bank Region; Type B in this assessment (Figure 13.2).

Table 13.4. Summary of liver disease data from 519 dab (*Limanda limanda*) sampled from the English Dogger Bank in 2010. (a) Disease prevalence (%) by BEQUALM liver pathology category and age class. (b) Harm score by BEQUALM liver pathology category and age class.
KEY: *ENTL = Early non-neoplastic toxicopathic lesions, FCA = Foci of Cellular Alteration, BN = Benign neoplasm, MN = Malignant neoplasm, NSIL = Non-specific, inflammatory lesions.*

		(a) Prevalence (%)					(b) Harm					Overall Harm
Age	n=	NSIL	ENTL	FCA	BN	MN	NSIL	ENTL	FCA	BN	MN	
1	121	76.0	9.9	5.8	0.0	0.0	2.0	1.0	0.0	0.0	0.0	3.0
2	39	92.3	5.1	5.1	2.6	0.0	3.0	0.0	0.0	0.0	0.0	3.0
3	60	98.3	11.7	18.3	3.3	0.0	3.0	1.0	1.0	0.0	0.0	5.0
4	39	97.4	25.6	15.4	2.6	0.0	3.0	3.0	0.0	0.0	0.0	6.0
5	120	100.0	15.8	44.2	9.2	2.5	3.0	2.0	3.0	1.0	1.0	10.0
6	102	97.1	17.6	46.1	9.8	2.9	3.0	2.0	3.0	1.0	1.0	10.0
7+	38	100.0	21.1	42.1	26.3	5.3	3.0	3.0	2.0	3.0	2.0	13.0

Figure 13.2. Liver pathology harm score according to age for dab sampled from the English Dogger Bank region in 2010.



13.5 Conclusions

We describe a fit for purpose approach to the age-corrected measurement of liver disease in dab sampled as part of the UK CSEMP. This has been achieved by pooling of samples from across a distinct CSEMP region (English Dogger Bank) and by incorporating age assessment into harm score calculation according to the published findings of Stentiford *et al.* (2009, 2010). Specifically, harm is assessed in with the rational that accelerated harm (ie, cancer and precancerous conditions of the liver in younger fish) rather than overall harm per se, is the usable assessment tool for measuring adverse biological effects in marine flatfish. By pooling of samples of fish from across defined offshore regions (identified under Defra Charting Progress II) and by assessing harm at a previously identified critical time period for disease development (3–4 years) (Stentiford *et al.* 2010), we are able to accurately assess health in younger age classes of fish, between multiple regions in multiple years. Our findings indicate that dab from the English Dogger Bank region continue to demonstrate an elevated level of disease, including pre-neoplastic liver pathologies and benign or malignant cancers.

The refined approach to sampling has been incorporated into the UK CSEMP programme and now offers a fit for purpose assessment tool that could be applied under Descriptor 8 of the Marine Strategy Framework Directive for the assessment of Good Environmental Status in UK waters.

As such:

- Achievement of efficiency savings by undertaking scientific cruises on RV *Cefas Endeavour* as a two year rolling programme. This approach permits the sampling of (1) the North Sea and East English Channel region and (2) the Irish Sea and West English Channel regions, during alternating years.
- Assessment of harm (associated with disease) will be undertaken at a regional level. These regional areas are stipulated within the MERMAN national database as follows: Tyne/Tees, Humber/Wash, Anglia, East English Channel, West English Channel, Severn, Cardigan Bay and Liverpool Bay.
- Fish will be pooled from designated CSEMP sampling stations within these CSEMP regions, specifically by sampling fish from defined size ranges (10–14 cm, 15–19 cm, 20–24 cm, and 25 cm+) to ensure sufficient numbers of all age classes are sampled. All fish will be processed for histological examination and age assessment. The pooling of data at the regional level will offer enhanced sensitivity without increased effort. The assessment of age is a critical prerequisite for assessment of harm in dab and should therefore be incorporated into monitoring programmes which utilise fish health for assessment of GES under Descriptor 8 of the MSFD.
- Following histological assessment and otolith examination, site type classification (Type A, B or C) will be made according to the generated liver disease harm scores in fish of 4 years of age or below (Type A, B, C).
- *Accelerated* harm (ie, in younger age classes of fish), rather than harm *per se* (in unclassified ages of fish) is considered as the assessment tool than can be utilised across sites and years under Descriptor 8 of the MSFD.
- The sampling regime adopted will also provide data under MSFD descriptor 8 for evidence of direct effects of endocrine disruption by allowing for the recording of intersex (particularly ovotestis) in external male fish by the histological assessment of gonads taken together with liver samples at post mortem. A similar approach to liver pathology and intersex measurement is envisaged for flounder collected from specific estuarine locations and may also be extended to other flatfish (eg, plaice) given appropriate collection of empirical data for background levels of harm in these species.

14. Levels of contaminant related biological effect in fish collected from offshore locations

Authors: Brett Lyons, Mark Kirby and John Thain

14.1 Topic and background

The induction of cytochrome P450 enzymes (CYP1A induction as measured by EROD [7-ethoxyresorufin-*O*-deethylase] activity) is an important step in the metabolism of many pollutants, such as certain planar halogenated hydrocarbons (PHHs) and polycyclic aromatic hydrocarbons (PAHs) and other structurally similar compounds. As such, the measurement of EROD activity in the liver of fish is useful for biomonitoring purposes because its expression and activity can increase upon the exposure of fish to contaminants such as dioxins, planar PCBs and PAHs (eg, benzo[*a*]pyrene). The induction of CYP1A can lead to the production of genotoxic metabolites (particularly those formed after the biotransformation of PAHs) and, as a consequence, it can be used as an indicator that adverse effects may be occurring in exposed animals. In support of this there is a considerable amount of field evidence correlating CYP1A induction with DNA damage, chemical carcinogenesis and other pathological conditions in marine organisms (OSPAR, 2010). The measurement of PAH metabolites in fish bile has also been widely used as a biomarker of PAH exposure since the early 1980s. When a fish is exposed to PAHs, its liver (through the induction of enzyme systems such as CYP1A) will detoxify and eliminate these contaminants. The presence of PAH-metabolites in bile is the final stage of the biotransformation process whereby lipophilic PAHs are transformed to a more soluble form and then passed from the organism in bile or urine, which can then be quantified using standard analytical approaches (eg, HPLC or synchronous fluorescence spectrometry).

Both EROD and PAH metabolite analysis techniques are internationally accepted in marine monitoring programmes and were amongst the first biomarker techniques to be incorporated into the OSPAR Joint Assessment and Monitoring Programme in 2000. In this respect they are designated as techniques to assess exposure to contaminants (eg, PAH) and will be used to address the question posed by both OSPAR and the Marine Strategy Framework Directive (MSFD) Good Environmental Status (GES) descriptor 8 *'...are contaminants present in the marine environment at levels giving rise to adverse biological effects?'*

14.2 Studies undertaken during 2008–2010

The data presented here was collected during 2008–2010 (June/July) from up to twenty four sites sampled as part of the Clean Seas Environment Monitoring Programme (CSEMP). The target species was the benthic flatfish dab (*Limanda limanda*) and liver and bile were sampled concomitantly from up to 20 fish per location (see Tables 14.1 and 14.2).

14.3 Methods and data assessment

The methods used for both EROD and bile measurements follow standard published in the ICES Techniques in Marine Environmental Sciences series (http://www.ices.dk/products/techniques.asp). EROD activity was determined using a fluorescent assay (Stagg & McIntosh, 1998) whereas bile metabolite data was generated using direct fluorescence and reported as 1-hydroxypyrene equivalents (Ariese *et al.*, 2005).

Species specific assessment criteria for EROD activity and bile metabolites have been developed over recent years and details of which can be found in the OSPAR background documents supporting each biological effect technique (Lyons *et al.*, 2010; ICES, 2011). The framework for developing assessment criteria for biological effects measurements are based on Background Assessment Concentrations (BACs), which is the level of biological response at a 'pristine' or 'remote' site based on contemporary or historical data and, where available, Environmental Assessment Criteria (EACs) which represent the biological effects measurement below which no chronic effects are expected to occur in marine species, including the most sensitive species (ICES, 2011). EROD and bile metabolite data was assessed against predefined ICES assessment criteria by estimating the 90^{th} percentile of lognormal distribution based on sample mean and standard deviation and comparing this with the Background Assessment Criteria or Environmental Assessment Criteria (if appropriate).

14.4 Exposure assessment criteria: EROD activity

Background assessment criteria for EROD activity have been developed using the 90th percentiles of values from reference sites and can be used to distinguish between ‘background’ and ‘elevated’ levels of contaminant exposure (ICES, 2010). At present, EAC assessment criteria for EROD are not available and the transition point for detecting whether ‘exposure’ to contaminants has occurred is deemed to be > 147 (for male fish) and > 178 (for female fish) pmol/min/mg protein (see Figure 14.1).

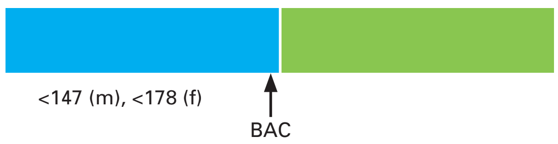


Figure 14.1. Assessment criteria for male (m) and female (f) dab (*L. limanda*) hepatic EROD activity expressed as pmol/min/mg protein (ICES, 2010; 2011)

14.5 Effect assessment criteria: bile metabolite data

ICES have produced both BAC and EAC transitions for the presence of 1-hydroxypyrene equivalents in the bile of dab (ICES, 2010; 2011).The BAC (150 ppb 1-hydroxypyrene equivalents) has been derived from reference sites while the EAC (22,000 ppb 1-hydroxypyrene equivalents) has been derived from toxicological experiment data (Figure 14.2).

Figure 14.2. Assessment criteria for bile metabolite data (pyrene-type ppb; synchronous scan fluorescence 341/383 nm) in dab. For additional information see ICES, 2010; 2011.

14.6 Summary of findings

A total of 24 sites were sampled for dab and analysed for EROD activity and bile metabolite concentrations determined. For EROD and bile, 14 and 13 sites, respectively, were sampled across all years between 2008 and 2010 (Tables 14.1 and 14.2). The results have been assessed using the latest ICES assessment criteria, as recommended by Study Group on Integrated Monitoring of Contaminants and Biological Effects (ICES, 2011). Accordingly, EROD and bile metabolite measurements have been grouped into different categories depending on whether EAC-equivalent assessment criterion have been set or not (see Figures 14.1 and 14.2). These two categories have been termed ‘exposure indicators’ (where an EAC has not been set, as is the case for EROD) and ‘effects indicators’ where an EAC (equivalent to significant pollution effect, as is the case for bile metabolites) has been set for the measurement.

The data generated indicated that EROD activity was only consistently considered to be at or around background levels at 3 out of the 24 sites investigated between 2008 and 2010. All 3 sites (New Haven, Lyme Bay and South Eddystone) were situated in the English Channel and have previously been shown to be at or close to background (http://chartingprogress.defra.gov.uk). West Dogger Bank and Inner Liverpool Bay were the only 2 sites to consistently displayed elevated levels of EROD activity across all 3-years of monitoring. The induction of EROD activity indicative of exposure to chemical contaminants is consistent with the finding that levels of persistent, bioaccumulative and toxic chemicals (such as PCBs) are still being detected within their tissues (see chapters 8 and 9 of this report)

The assessment of bile metabolite data indicated that all bar one site (West Dogger Bank, 2009) displayed evidence that fish were being exposed to polycyclic aromatic hydrocarbons above background levels. However, according to the assessment criteria deployed the level of exposure, while above background, is below a level at which long term effects (eg, reproduction and carcinogenic) in marine species would occur.

The data for EROD and bile metabolites presented here provide evidence of exposure and effect and it is important that the two biomarker responses reported here are used in an integrated assessment with chemical contaminant concentration in sediment and biota and with other higher biological effect responses, as recommended by the Study Group on Integrated Monitoring of Contaminants and Biological Effects (ICES 2011). Once complete the assessment framework outlined by ICES (2011) will be well suited to determine whether Good Environmental Status is being achieved for Descriptor 8 of MSFD (concentrations of contaminants are at levels not giving rise to pollution effects).

Table 14.1. Assessment of EROD levels in liver of dab. EROD data was assessed against predefined ICES assessment criteria by estimating the 90th percentile of lognormal distribution based on sample mean and standard deviation and comparing this with the Background Assessment Concentration.

Common name	Region	2008 Assessment status EROD		2009 Assessment status EROD		2010 Assessment status EROD	
		Male	Female	Male	Female	Male	Female
Amble	Tyne Tees	311 ± 203	344 ± 275	231 ± 156	219 ± 219	NS	NS
Farne	Tyne Tees	153 ± 99	96 ± 51	NS	NS	NS	NS
Tees Bay	Tyne Tees	131 ± 69	84 ± 52	294 ± 170	414 ± 234	146 ± 88	182 ± 128
Flamborough	Tyne Tees	96 ± 102	69 ± 56	148 ± 130	122 ± 90	NS	NS
North East Dogger	Humber Wash	211 ± 127	260 ± 314	101 ± 120	65 ± 65	110 ± 82	59 ± 58
North Dogger	Humber Wash	87 ± 68	146 ± 151	85 ± 51	44 ± 30	77 ± 55	80 ± 66
West Dogger	Humber Wash	170 ± 165	170 ± 158	206 ± 172	185 ± 146	272 ± 185	301 ± 247
Central Dogger	Humber Wash	84 ± 71	168 ± 213	94 ± 75	64 ± 37	62 ± 43	59 ± 29
Off Humber	Humber Wash	176 ± 173	245 ± 132	NS	NS	330 ± 165	291 ± 117
Indefatigable Bank	Humber Wash	32 ± 39	53 ± 48	78 ± 73	35 ± 12	177 ± 166	154 ± 78
Gabbard	Anglia	63 ± 28	84 ± 54	NS	NS	70 ± 51	75 ± 67
Rye Bay	Eastern Channel	31 ± 26	26 ± 11	82 ± 34	51 ± 23	98 ± 54	179 ± 158
Newhaven	Eastern Channel	14 ± 9	21 ± 26	68 ± 27	86 ± 47	28 ± 17	49 ± 20
Lyme Bay	Eastern Channel	44 ± 43	62 ± 33	49 ± 25	54 ± 26	32 ± 14	68 ± 49
South Eddystone	Western Channel	30 ± 14	41 ± 36	58 ± 21	66 ± 39	44 ± 14	55 ± 24
West Lundy	Severn	74 ± 91	216 ± 183	NS	NS	NS	NS
Carmarthen Bay	Severn	78 ± 81	69 ± 36	67 ± 41	61 ± 37	24 ± 25	37 ± 28
South Cardigan Bay	Cardigan Bay	NS	NS	19 ± 26	13 ± 13	NS	NS
North Cardigan Bay	Cardigan Bay	125 ± 103	207 ± 88	19 ± 9	12 ± 6	NS	NS
Red Wharf Bay	Irish Sea	68 ± 61	60 ± 54	49 ± 40	72 ± 48	53 ± 78	18 ± 13
Inner Liverpool Bay	Irish Sea	128 ± 99	196 ± 133	62 ± 73	205 ± 328	167 ± 148	178 ± 194
Liverpool Bay	Irish Sea	200 ± 197	73 ± 72	35 ± 17	51 ± 74	28 ± 24	106 ± 124
St Bee's Head	Irish Sea	73 ± 53	80 ± 68	123 ± 76	283 ± 263	NS	NS
Morecambe Bay	Irish Sea	226 ± 183	507 ± 778	192 ± 75	261 ± 162	NS	NS

NS = no sample

Table 14.2. Assessment of bile metabolite levels in liver of dab. Bile metabolite data was assessed against predefined ICES assessment criteria by estimating the 90th percentile of lognormal distribution based on sample mean and standard deviation and comparing this with the Background Assessment Criteria or Environmental Assessment Criteria.

Common name	Region	2008 Assessment status bile Male + Female	2009 Assessment status bile Male + Female	2010 Assessment status bile Male + Female
Amble	Tyne Tees	245 ± 74	141 ± 39	NS
Farne	Tyne Tees	258 ± 143	NS	NS
Tees Bay	Tyne Tees	325 ± 45	224 ± 60	255 ± 68
Flamborough	Tyne Tees	287 ± 120	143 ± 48	NS
North East Dogger	Humber Wash	190 ± 48	114 ± 58	167 ± 67
North Dogger	Humber Wash	140 ± 88	110 ± 37	124 ± 52
West Dogger	Humber Wash	219 ± 80	112 ± 22	165 ± 53
Central Dogger	Humber Wash	131 ± 65	130 ± 58	165 ± 57
Off Humber	Humber Wash	222 ± 554	NS	159 ± 55
Indefatigable Bank	Humber Wash	285 ± 77	162 ± 44	121 ± 39
Gabbard	Anglia	336 ± 68	NS	229 ± 58
Rye Bay	Eastern Channel	253 ± 55	237 ± 78	203 ± 63
Newhaven	Eastern Channel	212 ± 93	145 ± 40	231 ± 57
Lyme Bay	Eastern Channel	276 ± 97	187 ± 88	214 ± 79
South Eddystone	Western Channel	196 ± 65	270 ± 35	167 ± 42
West Lundy	Severn	197 ± 64	NS	NS
Carmarthen bay	Severn	NS	249 ± 276	189 ± 37
South Cardigan Bay	Cardigan Bay	216 ± 75	173 ± 55	NS
North Cardigan Bay	Cardigan Bay	311 ±103	179 ± 70	NS
Red Wharf Bay	Irish Sea	256 ± 75	243 ± 96	221 ± 53
Inner Liverpool Bay	Irish Sea	555 ± 259	445 ± 516	243 ± 131
Liverpool Bay	Irish Sea	213 ± 69	225 ± 180	188 ± 55
St Bee's Head	Irish Sea	350 ± 159	511 ± 754	NS
Morecambe Bay	Irish Sea	433 ± 206	253 ± 42	NS

NS = no sample

15. Bioassay assessment of sediment toxicity at a selected dredge disposal site – comparison of laboratory and field-based data

Authors: Dave Sheahan, Tom Fisher and Andy Smith

15.1 Topic and background

Approximately 40 million tonnes of dredged material may be disposed of in one year at up to 150 sites in estuaries and coastal sites around the UK (Bolam *et al.*, 2006). In the UK, Cefas, on behalf of MMO, provides an ongoing evaluation of dredged material disposal sites in support of licensing activities, in terms of the contaminant burden associated with the original dredged material and the biological diversity and quality of the benthic organisms in the vicinity of the disposal site. The sediment bioassays used provide data allowing a comparison of the sediments from the original dredge locations and chosen disposal sites. The results show that they can aid the interpretation of benthic species diversity data particularly where the changing nature of the sediments may be a confounding factor.

15.2 Sampling undertaken in previous year(s)

July 2009: Sediment samples were taken at three stations in the vicinity of the inner Tees Bay dredged material disposal site (Figure 15.1). Two marine species, the polychaete worm *Arenicola marina* and the amphipod crustacean *Corophium volutator* were chosen as test organisms for the whole sediment phase. July 2010: Sediment samples were taken from the same three stations as the previous year with one addition (IND5) at the outer edge of the dredge site (Figure 15.1). The test species were the polychaete worm *A. marina* and the amphipod *C. volutator*.

15.3 Summary of results obtained

This study indicated that whole sediment bioassays using the polychaete worm *Arenicola marina* and the amphipod crustacean *Corophium volutator* offered several options for the assessment of sublethal test endpoints.

The chemical contaminants measured in the sediments at the disposal site do not show an obvious relationship to either the biological community data or to the toxicity test results (Table 15.1). To provide an indication of status of the sediment trace metal contamination, reference is made to the Effects Range Low (ERL) concentrations based on the 10th percentile of the distribution of contaminant concentrations associated with adverse biological effects and the Effects Range Median (ERM) based on the 50^{th} percentile. The sediment quality guidelines derived by the National Oceanic and Atmospheric Administration (NOAA) under the US National Status and Trends Program follow this approach (Long *et al.*,1998; Rowlatt *et al.*, 2002).

Whilst sediment characteristics are important in determining effects, the varied and complex nature of potential contaminant sources means that there may be other unmeasured contaminants present at this site which may also be contributing to the observed results. The bioavailability of contaminants is also strongly controlled by sediment conditions and this is not necessarily apparent from direct measures of contaminant levels alone particularly where sediment analysis methods include extraction techniques that do not necessarily reflect just the bioavailable fraction of selected contaminants. The results correlated well with benthic community analysis conducted at the same sampling sites but did not show a clear correlation with a range of chemical contaminant data for the samples. This suggests that the inclusion of bioassays allows for assessment of the bioavailability of both known and unknown contaminants adding to the weight of evidence in dredged material assessment.

15.4 Length of time series available

The focus of previous sediment toxicity studies was on harbours and transects along estuaries so only these data for 2009 and 2010 exist for the Tees disposal site.

15.5 Summary of trend observed/not

Trend analysis is not possible.

15.6 Graphics and illustrations

Figure 15.1. The locations of three sampling stations from 2009 (IT1, IT4, IND2) and the additional site sampled in 2010 (IND5).

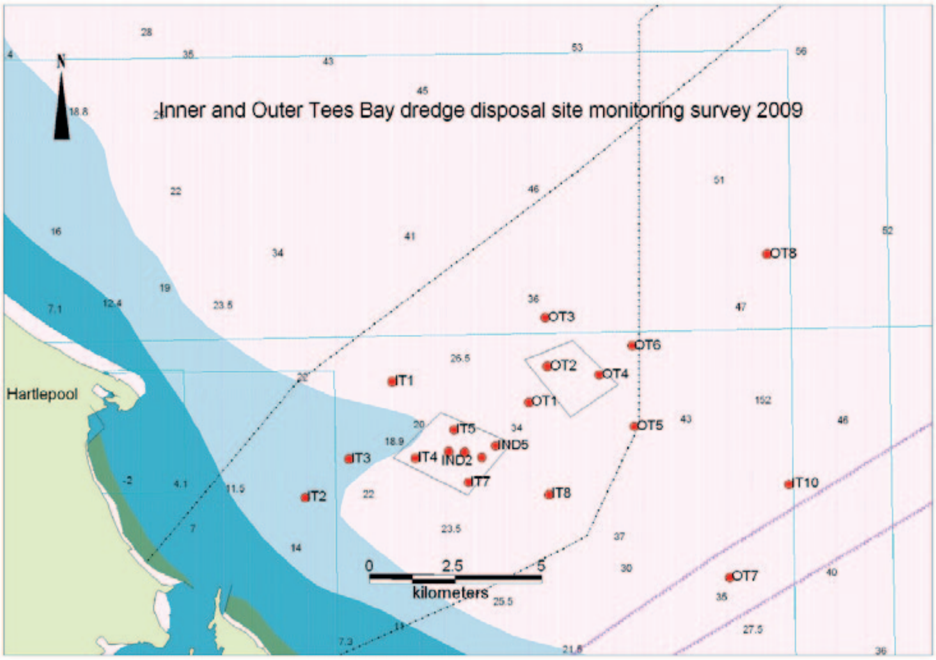


Table 15.1. Summary of contaminant data, macrofaunal survey data and sediment toxicity data (this study) for sediments sampled from locations inside and outside the inner Tees disposal site.

	Metals	THC	PAH	Macrofauna	*Corophium* Survival	*Arenicola* Survival	*Arenicola*[1] Cast No.
2009							
IT1	**Cr**, Cu, Ni, Pb, Zn[2]	2[3]	2	3			
IT4	As, **Cr**, Cu, **Ni,** Pb, Zn	1	1	1.5	Low		
IND2	Cr, **Ni**	3	3	1.5	Low	Low	Low
2010							
IT1	**Cr,** Cu, Ni, Pb, Zn	3	3	4			3
IT4	Cr, Cu, Hg, Ni, Pb, Zn	1	1	1.5			2
IND2	Cr, Cu, Hg, Ni, **Pb**, Zn	2	2	1.5	Low	Low	1
IND5	Cr, Hg, Ni, Pb	4	4	3			4

[1] Sites which had a significantly lower cast number than the control are marked. Sites in 2010 are marked in order of cast number, highest (4) and lowest (1), but significant differences between sites could not be confirmed.

[2] Those metals exceeding ERL values are shown and those which are highest for a given metal are underlined and those exceeding ERM values are in bold. Cr (chromium); Cu (copper); Hg (mercury); Ni (nickel); Pb (lead); Zn (zinc)

[3] Scale from 1 to 4. Number '1' indicates highest contaminant levels, and lowest macrofauna numbers, species and biomass. 'Low' indicates those sites for which there was statistically lower survival for all species tested.

16. Imposex in the dogwhelk (*Nucella lapillus*): monitoring around England and Wales, 2004–2010

Authors: E.E. Manuel Nicolaus, John Thain, Eva Garnacho, David Stephens and Thomas Maes

16.1 Topic and background

Imposex is the imposition of male sexual characteristics on female gastropods which have been found to be one of the most sensitive indicators of tributyltin oxide (TBT) exposure (Huet et al, 2004). The incidence of imposex was found to be caused by TBT when used as a biocide in marine antifouling paints for yachts and large ships in the mid 1980s. In *Nucella lapillus*, the effect is dose related and severe imposex can lead to sterility in females which has detrimental reproductive effects on both individuals and populations. The process and characterisation of imposex has been well documented by Gibbs *et al* (1987), Oehlmann *et al*. (1991), and Santos *et al* (2002), for example.

Over the last two decades legislation has been introduced, firstly to control the use of TBT-based antifouling paints on yachts and more recently the use and then the prohibition of these biocides on large ships. Previous imposex (in *Nucella lapillus*) surveys in 1992 and 1997 were conducted to establish data to support and justify UK, EU legislation on the use of organotin compounds. Between 2003 and 2008, legislation introduced by the International Maritime Organisation (IMO) banning the use of organotin on all ships became effective. This will, in the long term, clearly have an important influence in reducing TBT concentrations in the marine environment and in reducing levels and severity of imposex in gastropods. The 2004, 2007 and 2010 surveys conducted fulfilled the UK obligation under OSPAR to report on the incidence of imposex in UK waters on a regular basis (OSPAR, 2008).

16.2 Sampling undertaken in previous year

The aim of the 2010 survey was to collect dogwhelks from each of the sampling locations used in the 2007 survey. The 2010 sampling locations are shown in Figure 16.1, and include areas close to ports eg, Dover, Southampton Water and Milford Haven, areas close to shipping lanes (traffic separation zones), eg, Dover Straits, Isle of Wight and Holyhead, and areas away from the influence of shipping, including 'background reference' sites.

16.3 Summary of results obtained

In this survey 76 of the 86 2007 sites were re-sampled successfully and had enough females present to carry out an assessment.

Figure 16.1 shows all the stations where sufficient females were found to carry out an assessment and gives a geographical overview of the imposex stage found at a particular site. The seven sites investigated at which no adult female dogwhelks could be found were Herne Bay, New Quay, Maryport, Moelfre, Polzeath, St. Davids and Whitesands.

A summary of the data, including the VDSI values and the associated OSPAR assessment class is given in Table 16.1 for the 2010/11 data, including the sample sites and whether juveniles or eggs were observed or not. In 2010/11, 8 of the 76 sites showed level C or higher incidence of imposex. These eight sites still show higher TBT concentrations than the Ecotoxicological Assessment Criteria (EAC) derived for TBT, which could cause adverse effects on growth and recruitment. Nonetheless, juveniles were present at the sites, indicating a good level of recovery. It is noteworthy that at St. Mawes (Falmouth) and Parsons Rock (North Sunderland) the Vas deferens Sequence Index (VDSI) increased from 2.59 to 3.72 and 3.55 to 4, respectively, from 2007 to 2010/11, indicating that adverse effects can be directly associated with the exposure to TBT.

Overall, the assessment shows that, of the 76 sites, 64 recorded either a decrease in VDSI or remained at the same value, and 12 sites showed an increase in the VDSI. Of these 12 sites, nine of them stayed in the same assessment class, with the exception of Hartlepool, Parsons Rock (North Sunderland) and Tenby which showed a change in class, from B to C, C to D, and B to C, respectively. No eggs were observed at the two Tyne and Tees sites, but juveniles were present indicating a recovery in population. Generally, the coastal areas of the south coast and the north east coast had higher VDSI values, ie, more B and C than A OSPAR class sites.

16.4 Length of time series available

Imposex in *Nucella lapillus* has been monitored between 1992 and 2010/11.

16.5 Summary of trend observed/not

18 years of imposex monitoring around England and Wales showed a strong recovery of *Nucella lapillus* and a decrease in the impact of TBT since 1992.

In 1992 not one site in the UK was at background imposex level, class A on the OSPAR assessment scale, whereas 100% of sites were at classes C or D. In contrast, in 2010/2011 42% of the sites were observed to be at class A. In the intervening surveys 1997/1998, 2004 and 2007 there was a gradual improvement in the level of imposex in each class recorded as shown by the changes in the proportion of imposex within each class; this is shown in Table 16.1a and presented graphically in Figure 16.2. Table 16.1 gives a summary of the imposex development in England and Wales between 1992 and 2010/11. It can be seen that there is an increase in class A organisms over time. Table 16.1b presents the VDSI and Relative Penis Size Index (RPSI) mean values and standard deviations for each year. The RPSI shows greater improvements over time compared to the VDSI index, as the VDSI index is more sensitive to lower TBT concentrations. A multiple comparison of variance (ANOVA) for VDSI between the different years and within years shows that there are statistically significant differences with a 95% confidence level ($p<0.05$) between 1992, 2004, 2007 and 2010 VDSI means. Figure 3 shows the different means with the intervals based on Fisher's least significant difference (LSD).

16.6 Graphics and illustrations

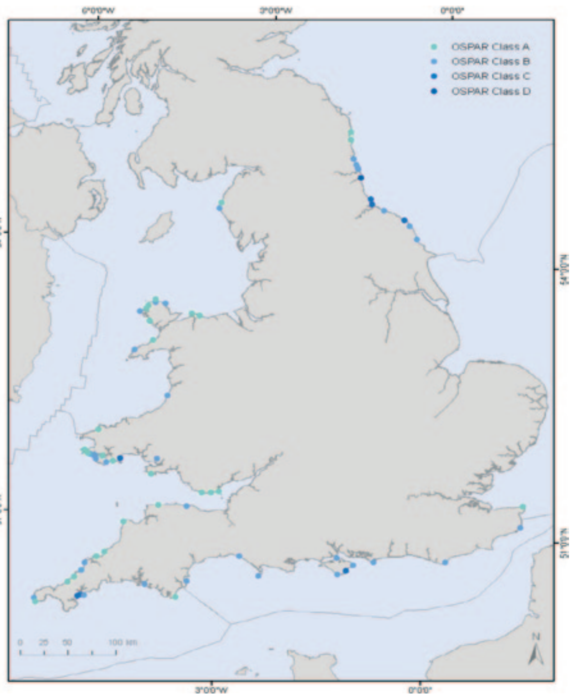


Figure 16.1. OSPAR classification of dogwhelks from 2010/11 England and Wales sampling sites; OSPAR classifications go from A (background incidence of imposex) to F (populations of the more sensitive gastropod species are absent/expired).

Table 16.1. Summary statistics for the assessed imposex monitoring surveys since 1992.

16.1a. Number of sites in each OSPAR assessment class for imposex for each reporting year between 1992 and 2010/11 in England and Wales.

	Number of sites in each OSPAR Assessment class						
Sampling Year	N	F	E	D	C	B	A
1992	14			8	6		
1997	73	1		13	38	21	
2004	47				31	13	3
2007	86				28	46	12
2010/11	76			1	7	36	32

16.1b. Mean and standard deviation for VDSI and RPSI values showing a decrease in TBT influenced imposex occurrence over time

Sample Year	1992	1997	2004	2007	2010/11
Mean VDSI ± St. Dev.	3.95 ± 0.58	2.74 ± 1.05	2.25 ± 1.08	1.44 ± 1.06	0.72 ± 0.86
Mean RPSI ± St. Dev.	16.81± 10.20	5.56± 8.15	2.79 ± 4.19	0.68 ± 1.29	0.38 ± 2.18

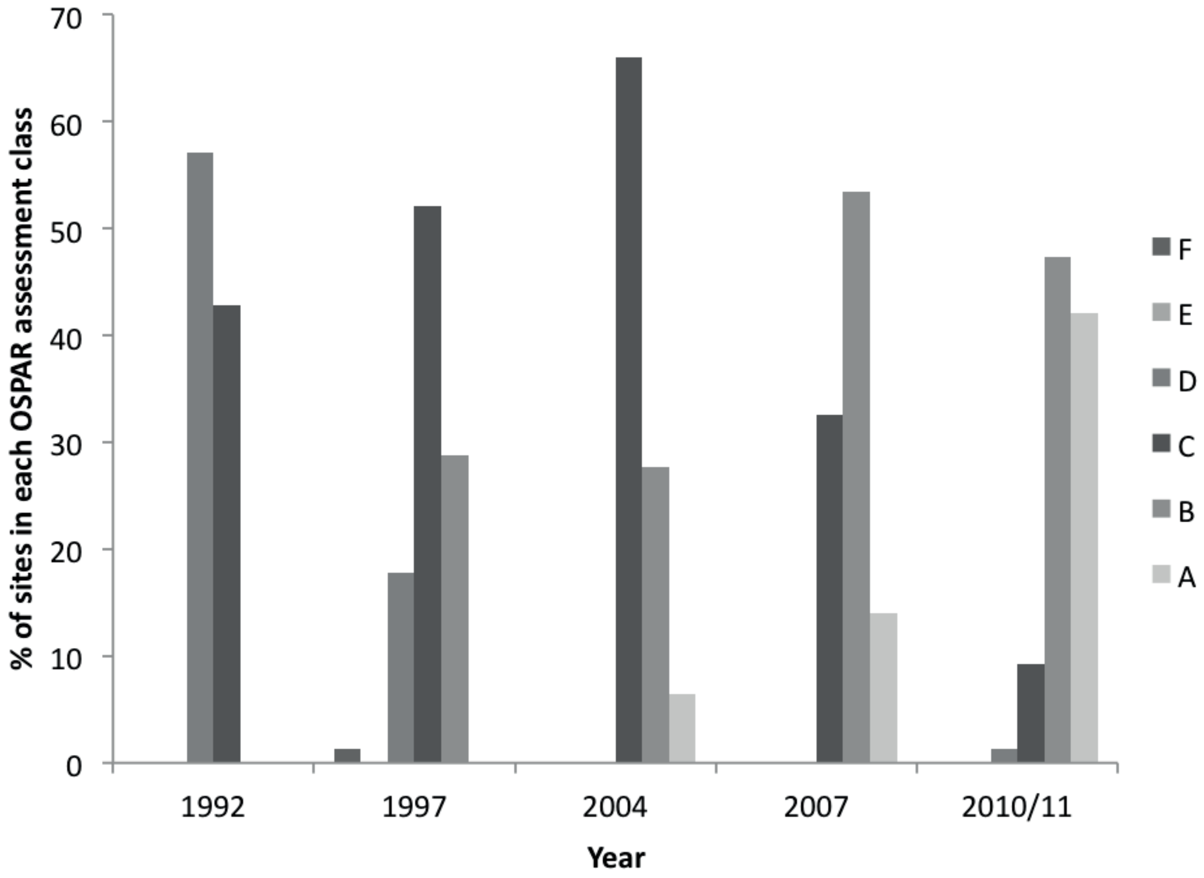


Figure 16.2. Percentage of sites in each OSPAR assessment class for imposex for each reporting year between 1992 and 2010 in England and Wales. A–F indicating the Assessment criteria

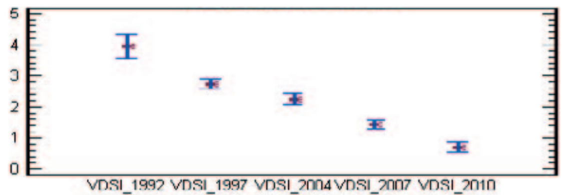


Figure 16.3. 1992, 1997, 2004, 2007, 2010 VDSI Mean values with intervals based on Fisher's least significant difference (LSD) procedure and at 95% confidence level

Productive Seas

17. Advice on fishery implications of pipeline discharges

Authors: Simon Kershaw, Carlos Campos and Nicola Mitchard

17.1 Topic and background

This section gives a brief summary of activities carried out during 2008–10 in connection with the provision of advice on fishery implications of pipeline discharges given by Cefas to the Environment Agency on behalf of Defra and Welsh Government. This advisory work takes into consideration fishery resources in designated shellfish waters and areas classified for the commercial production of shellfish, toxicity of the effluent, circulation of pollutants and compliance with standards laid down in the legislation. This includes, among others, consideration of shellfishery issues with respect to sewage improvement schemes, advice on water quality requirements to meet shellfish flesh standards, investigations of water quality in shellfisheries, guidance and advice to the industry and maintenance of mapping and IT tools to enable these assessments.

17.2 Summary of pipeline discharge applications

During 2008–2010 Cefas assessed 307 individual discharge applications, of these a total of 197 (64%) were assessed for their potential to impact on shellfish waters and/or production areas. Shellfish hygiene issues therefore continued to be the most common concerns addressed. The majority of applications received were for discharges consisting of domestic sewage effluent from both individual dwellings and water-company owned assets.

Table 17.1. Numbers of applications assessed during the period 2008–10.

	2008		2009		2010	
Type of application	**Total**	**Shellfish related**	**Total**	**Shellfish related**	**Total**	**Shellfish related**
Continuous						
Primary	9	0	4	4	3	1
Secondary	21	12	69	46	45	36
Tertiary	2	2	2	2	7	5
Intermittent						
Storm	9	4	21	12	16	8
Emergency	6	3	16	9	12	5
Trade	6	4	29	18	17	14
Other	5	2	6	4	8	6
TOTAL	52	27	147	95	108	75

The majority of applications received in each year were for continuous discharges of secondary (biologically treated) effluent. Of these, 70% were thought to potentially impact upon nearby shellfish production areas. The tertiary treated discharge applications received were for UV disinfection or membrane filtration processes aimed at enhancing the reduction of microbiological contamination beyond that conferred by secondary (biological) treatment alone. In 2010 two thirds of applications for tertiary treated discharges were of benefit to shellfish areas in terms of reducing bacteriological loading. Applications for primary treated effluent constituted a minor percentage (5.2%) of the total number of applications during the three-year period.

Storm overflow discharges pose a significant risk to shellfisheries. Applications for 46 storm discharges (approximately 15% of the total number of applications received) were received in 2008–10, of which 52% were identified as potentially impacting on shellfisheries. Where water company discharge improvements are identified to benefit shellfish waters, the Environment Agency (EA) policy requirements restrict overflow operation to a maximum of ten spills per annum (in aggregation with other impacting storm discharges averaged over a ten year period). Where discharges are applied for without funding targeting shellfish waters specifically, Cefas has advised restrictions on overflow operation with the intention of protecting public health.

Emergency overflows come into operation when there is a major process or infrastructure failure at the waste water treatment works or sewerage pumping station. Discharges from emergency overflows may cause severe contamination of shellfisheries. Applications for 34 emergency discharge applications were received. In advising on such applications, Cefas requests urgent notification of emergency events to local authorities responsible for sampling and enforcement of shellfish harvesting areas so that appropriate action can be taken to protect public health.

Trade discharges were assessed for impacts of any chemicals, suspended solids or other inorganic components on shellfisheries and the marine environment in general. 52 applications to discharge trade effluent were received from 2008 to 2010 which represents 17% of all applications received during this three year period. Approximately 70% of all trade applications received were thought to have a potential adverse impact on nearby shellfisheries.

17.3 General shellfish water quality advice

Cefas has requested that the water companies provide an annual report of spills from storm and combined sewer overflows and, where necessary, has asked for clarification that discharges had been considered in aggregation with others impacting on the same fishery. The review of annual spill reports is of paramount importance in identifying problem discharges that require further improvement. Cefas has also highlighted the (sometimes large) discrepancies between predicted and actual sewage spill frequencies.

Cefas has maintained regular liaison meetings with EA shellfish contact officers, both regionallly (1–3 per annum) and national (annually) in which local discharge permitting issues, national technical issues and policies have been identified and discussed. This has proved effective in championing the consideration of the marine environment and fisheries interests and influencing scheme outcomes, prior to any formal discharge consent application.

On request, advice was given to the shellfish industry regarding the potential impacts of individual discharges on their activities.

17.4 Shellfish Hygiene System (SHS) maintenance

Details of all applications, consents and authorisations have been entered onto SHS, a geographically referenced database and mapping tool that integrates information on over 18,000 records of current and historic sewage discharges to saline waters in England and Wales. This provides unique intelligence and is a strategic tool used alongside other Cefas tools to underpin impact assessments and policy decisions in the marine environment.

17.5 Trends in the hygiene status of shellfisheries

The Government has set a target for all shellfish harvesting areas in England and Wales to achieve a microbiological classification of, at least, class B as categorised under Regulation (EC) No 854/2004. The percentage of class B shellfish production areas has shown an increasing trend since 1992 (Figure 1). The most significant increase was achieved resulting from delivery of improvements under the third water company assessment management plan (AMP3), 2000–2005. This was the first water company investment period in which shellfish water quality acted as a specific driver for sewage infrastructure improvement.

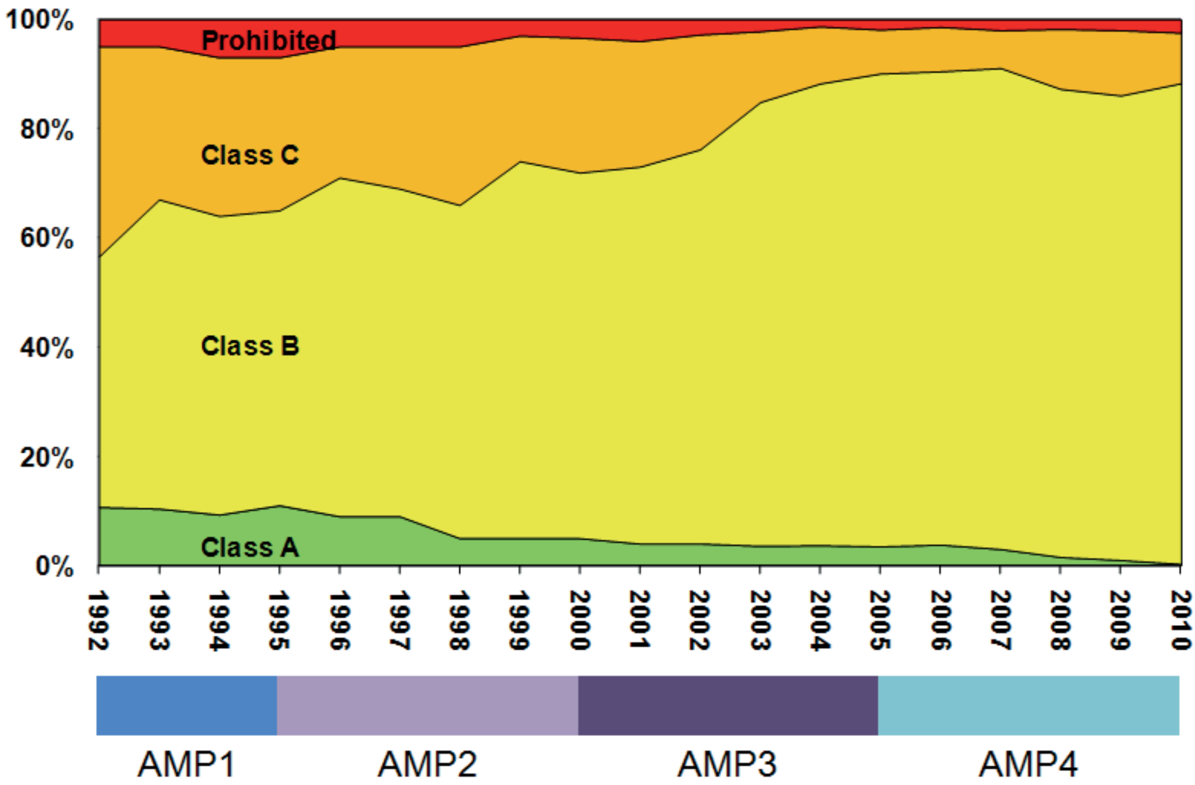


Figure 17.1. Percentage of shellfish production areas in each hygiene classification category since the implementation of statutory public health controls in England and Wales and corresponding water company investment (asset management) plans.

Notes: class A (Most Probable Number of *E. coli* ≤ 230 $100g^{-1}$ flesh); class B (MPN of *E. coli* ≤ 4,600 $100g^{-1}$ flesh in 90% of the samples); class C (MPN of *E. coli* ≤ 46,000 $100g^{-1}$ flesh); prohibited (MPN of *E. coli* > 46,000 $100g^{-1}$ flesh).

Less than 1% of shellfish production areas in England and Wales currently achieve class A standard.This standard would correspond to very low levels of microbial contamination in the water which would allow marketing of shellfish direct for human consumption without any further processing. Additional discharge improvements and/or measures to tackle diffuse pollution would be required to increase the number of class A shellfisheries in the future.

18. Licensing of deposits in the sea

Authors: Chris Vivian and Sara Pacitto

18.1 Introduction

This section gives information about the licensing of deposits in the sea around the coasts of England and Wales in the period 2008–2010 under Part II of the Food and Environment Protection Act 1985 (as amended) (FEPA) (Great Britain Parliament, 1985). In order to provide a complete picture for the UK as a whole, licensing statistics for Scotland and Northern Ireland are also included in this section.

18.2 Legislation and licensing authorities

For the year 2010, the deposit of substances and articles in the sea, principally the disposal of dredged material (as opposed to discharge into the sea via pipelines) and the use of material during marine construction and coastal defence works, was controlled by a system of licences issued under Part II of FEPA. Certain operations (eg, the deposit of scientific equipment or navigation aids) were exempt from licensing under the Deposit in the Sea (Exemptions) Order 1985 SI 1985 No. 1699.

Note that the marine licensing provisions of the Marine and Coastal Access Act 2009 that came into force on 1st April 2011 have now taken over from Part II of FEPA for the licensing function in England, Wales and Northern Ireland. In Scotland, the marine licensing provisions of the Marine (Scotland) Act 2010 took over the licensing function from FEPA on the same date.

Following devolution in 1999, Defra (then MAFF) continued to license deposits in the sea around the Welsh coast on behalf of the Welsh Assembly Government. On 1st April 2007 the responsibility for the licensing function in England and Wales transferred from Defra to the Marine and Fisheries Agency (MFA). Subsequently, the Marine Management Organisation (MMO) took over this responsibility in England from 1st April 2010 and the Welsh Assembly Government took over this responsibility in Wales at the same time.

During 2010, the licensing function in Scotland was the responsibility of Marine Scotland and in Northern Ireland it was the responsibility of the Northern Ireland Environment Agency.

18.3 Enforcement

Officers of the MFA up until April 2010 and the MMO from that date, enforced the provisions of FEPA (Part II) and undertake regular inspections from a network of port offices in England and Wales. In Scotland, authorised staff of Marine Scotland also hold such enforcement powers, as do staff of the Northern Ireland Environment Agency. Officers of the Welsh Assembly Government commenced enforcement activities from April 2010. Details of enforcement activity in all parts of the UK in 2008, 2009 and 2010 are given in Table 18.1a.

Table 18.1a. Enforcement activity in the UK during 2008–2010.

Year	Country	Inspections	Warning/advisory letters
2008	England & Wales*	134	5
	Scotland	11	0
	Northern Ireland	28	5
2009	England & Wales*	72	5
	Scotland	6	0
	Northern Ireland	55	1
2010	England*	72	16
	Wales**	55	2
	Scotland	15	5
	Northern Ireland	33	0

* Includes Isle of Man, Jersey and Guernsey
** The Welsh government began licensing in April 2010

In England and Wales there were 2, 0 and 1 successful prosecutions for illegal marine works in 2008, 2009 and 2010 respectively. There was also 1 unsuccessful prosecution in 2009.

Scientists from the Cefas Regulatory Assessment Team have the powers to make site visits and to support enforcement officers from the MFA, and now the MMO, in any enforcement visits. Visits are made to construction sites and disposal vessels. Samples are taken and records, including logbooks, are checked. Cefas Regulatory Assessment Team staff carried out 20 site visits in 2008, 10 site visits in 2009 and 0 site visits in 2010.

Table 18.1b. Inspection activity in England and Wales by the MFA during 2008–2010.

District	2008			2009			2010		
	No. of inspections		No. of infringements	No. of inspections		No. of infringements	No. of inspections		No. of infringements
	Construction	Disposal		Construction	Disposal		Construction	Disposal	
Humber	11	7	0	15	3	3	4	1	0
Eastern	12	2	0	7	0	2	24	3	3
London	0	0	0	2	0	0	0	0	0
Merseyside & Fylde	1	1	0	7	1	1	2	2	1
Northern	25	1	2	25	7	2	2	1	0
South eastern	13	6	1	10	4	1	16	4	3
South western	8	3	1	7	0	0	6	0	0
Wales	27	2	0	35	7	2	**	**	**
Western	11	0	0	2	0	0	5	2	2
Total	108	22	4	110	22	11	59	13	9

* The MMO took over inspections from the MFA in April 2010.
** The Welsh government took over licensing in Wales from the MMO in April 2010. Figures for 2010 and subsequent years are reported separately.

18.4 Licensing of dredged material disposal

Table 18.2 gives details for the period 2006 to 2010 of the number of sea disposal licences issued, the quantity of waste licensed and the quantity actually deposited, together with information on those contaminants in the wastes which the UK is required to report internationally to meet obligations under the OSPAR and London Conventions. A proportion of the trace metals in this dredged material is natural, but the mineral structure is such that it will not be available to marine organisms.

Figures 18.1 to 18.3 show the main disposal sites used in 2008, 2009 and 2010 and the quantities deposited at each site. Although applications for licences are required to show evidence that they have considered alternative disposal options including beneficial use, the problems of having silty materials for disposal, and matching the timing of dredging campaigns and the demand for sediments, have meant that most of the finer materials, in particular, are deposited at sea.

Table 18.2. Summary of dredged material licensed and disposed of to sea during 2006–2010.

Country	Year	Licenses Issued	Licensed Quantity (Tonnes)	Wet Tonnage Deposited	Dry Tonnage Deposited	Quantities of metals in wastes deposited (tonnes)						
						Cd	Cr	Cu	Hg	Ni	Pb	Zn
ENGLAND AND WALES	2006	65	21,468,725	26,833,340	13,989,803	4	622	422	4	362	914	2,085
	2007	76	47,458,635	30,617,428	15,882,324	5	713	498	4	408	1,053	2,364
	2008	67	73,358,021	27,945,417	13,875,959	5	682	498	4	407	1,008	2,306
	2009	88	55,502,041	27,522,965	15,289,685	4	580	443	4	378	867	1,925
	2010*	82	46,230,050	20,778,721	11,047,382	4	447	307	3	267	665	1,443
SCOTLAND	2006	24	4,566,531	1,701,046	850,523	0	58	36	1	29	62	124
	2007	22	3,006,279	2,018,862	1,032,455	0	41	21	0	25	34	73
	2008	22	4,151,451	3,025,429	1,805,141	0	63	33	1	40	50	114
	2009	18	3,058,200	3,245,813	1,814,498	0	38	20	0	21	36	74
	2010	25	10,715,247	3,235,975	1,646,595	1	123	67	0	15	69	187
NORTHERN IRELAND	2006	3	176,999	833,426	507,942	1	68	49	0	42	59	209
	2007	3	454,000	429,285	265,074	0	21	8	0	13	9	34
	2008	5	732,999	258,485	132,642	0	15	14	0	11	16	33
	2009	5	1,446,000	968,446	527,825	1	69	52	1	46	66	199
	2010	4	650,900	78,748	43,976	0	5	3	0	3	3	12
WALES	2010	7	10,547,822	4,703,680	2,441,549	0	70	41	0	59	87	347
U.K. TOTAL	2006	92	26,212,255	29,367,812	15,348,268	6	748	508	5	433	1,034	2,418
	2007	101	50,918,914	33,065,575	17,179,852	5	775	527	4	446	1,096	2,471
	2008	94	78,242,471	31,229,331	15,813,742	5	760	545	5	458	1,074	2,453
	2009	111	60,006,241	31,737,224	17,632,008	5	688	515	5	445	970	2,197
	2010	118	68,144,019	28,797,124	15,179,501	5	646	418	4	345	824	1,989

Notes. Tonnages deposited relate to quantities in the calendar year concerned, which may be covered by two or more licences, including one or more issued in previous years.
*England only.

18.5 Other licensed activity

Under Part II of FEPA, licences are also required for certain other activities or deposits made below the mean high water springs mark for construction purposes. Each licence application is carefully considered, in particular, to assess the impact on the tidal and intertidal habitat, hydrological effects, potential interference to other users of the sea and risk to human health. Details of these licences issued in 2008, 2009 and 2010 are shown in Table 18.3.

Further activities involve the use of tracers, the application of biocides, and burial at sea. Generally, the anticipated environmental impact from these deposits is minimal and little or no monitoring is required. Details of these licences issued in 2008 to 2010 are also shown in Table 18.3 respectively.

Licences have also authorised the disposal of a small amount of fish waste, details are given in Tables 18.4 a & b.

Table 18.3. Other categories of licences issued during 2008–2010.

Year	Country	Construction (new and renewal)	Tracers, biocides etc	Burial at sea
2008	England & Wales*	188	11	11
	Scotland	84	1	0
	Northern Ireland	17	0	0
2009	England & Wales*	179	10	11
	Scotland	93	0	0
	Northern Ireland	19	0	0
2010	England*	182	12	13
	Wales**	38	1	0
	Scotland	126	74	0
	Northern Ireland	12	0	0

* Includes Isle of Man, Jersey and Guernsey
** The Welsh government began licensing in April 2010

Table 18.4a. Fish waste licensed for disposal at sea in 2010

Country	Licensed quantity (tonnes)	Company and source of waste	Disposal sites	Quantity deposited (wet tonnes)	Quantity deposited (dry tonnes)
England and Wales	0	Quay Fresh & Frozen Foods Ltd, New Quay	New Quay	1,708	1,708

Note. No fish wastes were licensed or disposed of in Scotland or Northern Ireland during the period covered by this report.

For information on licensed quantities and tonnages deposited see footnote to Table 18.2.

Table 18.4b. Summary of fish waste licensed and disposed of to sea during 2006–2010.

Country	Year	Licenses Issued	Licensed Quantity (Tonnes)	Wet Tonnage Deposited	Dry Tonnage Deposited
ENGLAND AND WALES	2006	0	0	1,203	1,203
	2007	0	0	1,469	1,469
	2008	0	0	1,837	1,837
	2009	1	2,000	1,887	1,887
	2010	0	0	1,708	1,708
SCOTLAND	2006	0	0	0	0
	2007	0	0	0	0
	2008	0	0	0	0
	2009	0	0	0	0
	2010	0	0	0	0
NORTHERN IRELAND	2006	0	0	0	0
	2007	0	0	0	0
	2008	0	0	0	0
	2009	0	0	0	0
	2010	0	0	0	0
U.K. TOTAL	2006	0	0	1,203	1,203
	2007	0	0	1,469	1,469
	2008	0	0	1,837	1,837
	2009	1	2,000	1,887	1,887
	2010	0	0	1,708	1,708

Note. For information on licensed quantities and tonnages deposited see footnote to Table 18.2.

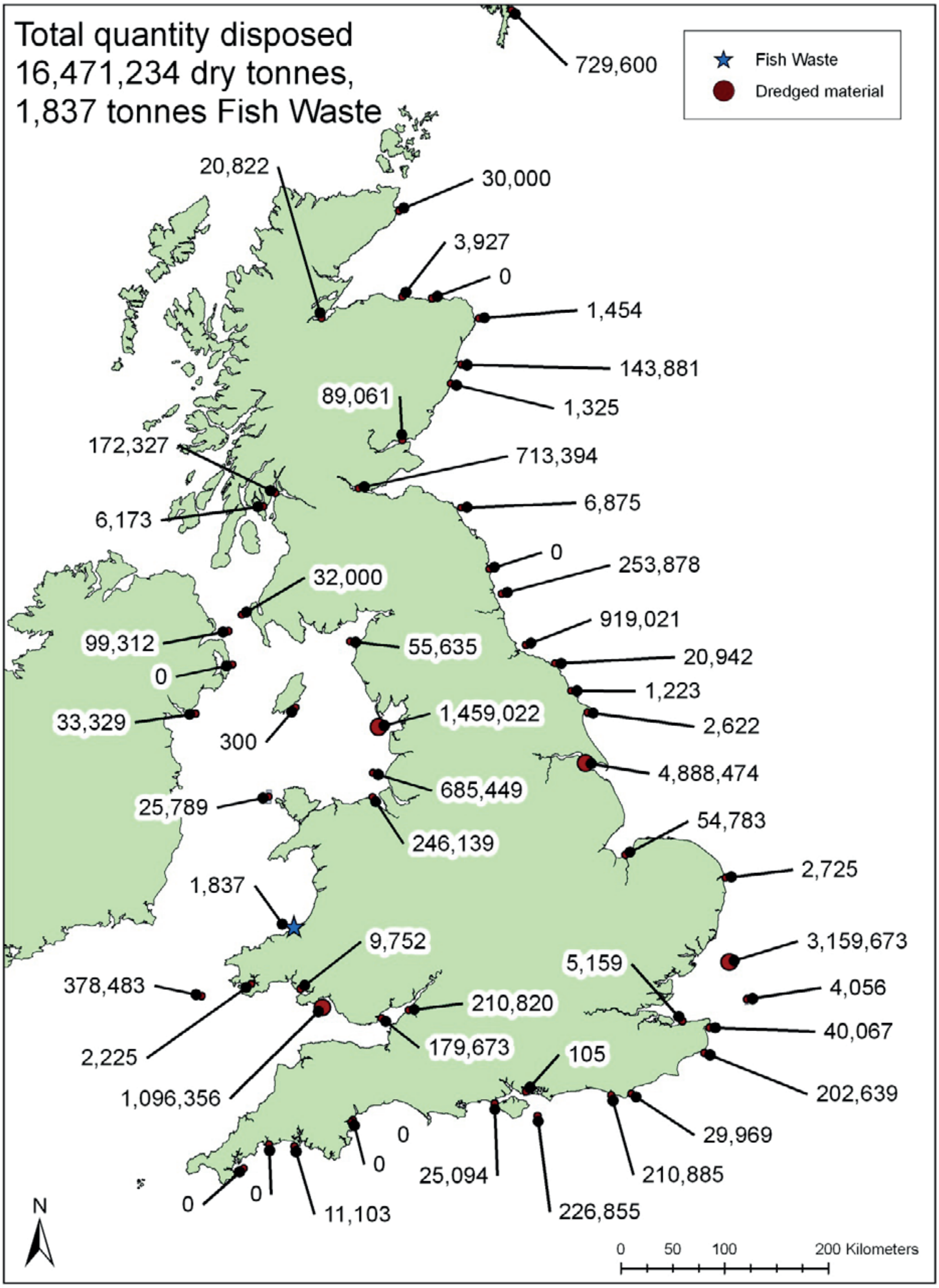


Figure 18.1. Amount of dredged material disposed of to sea in 2008.

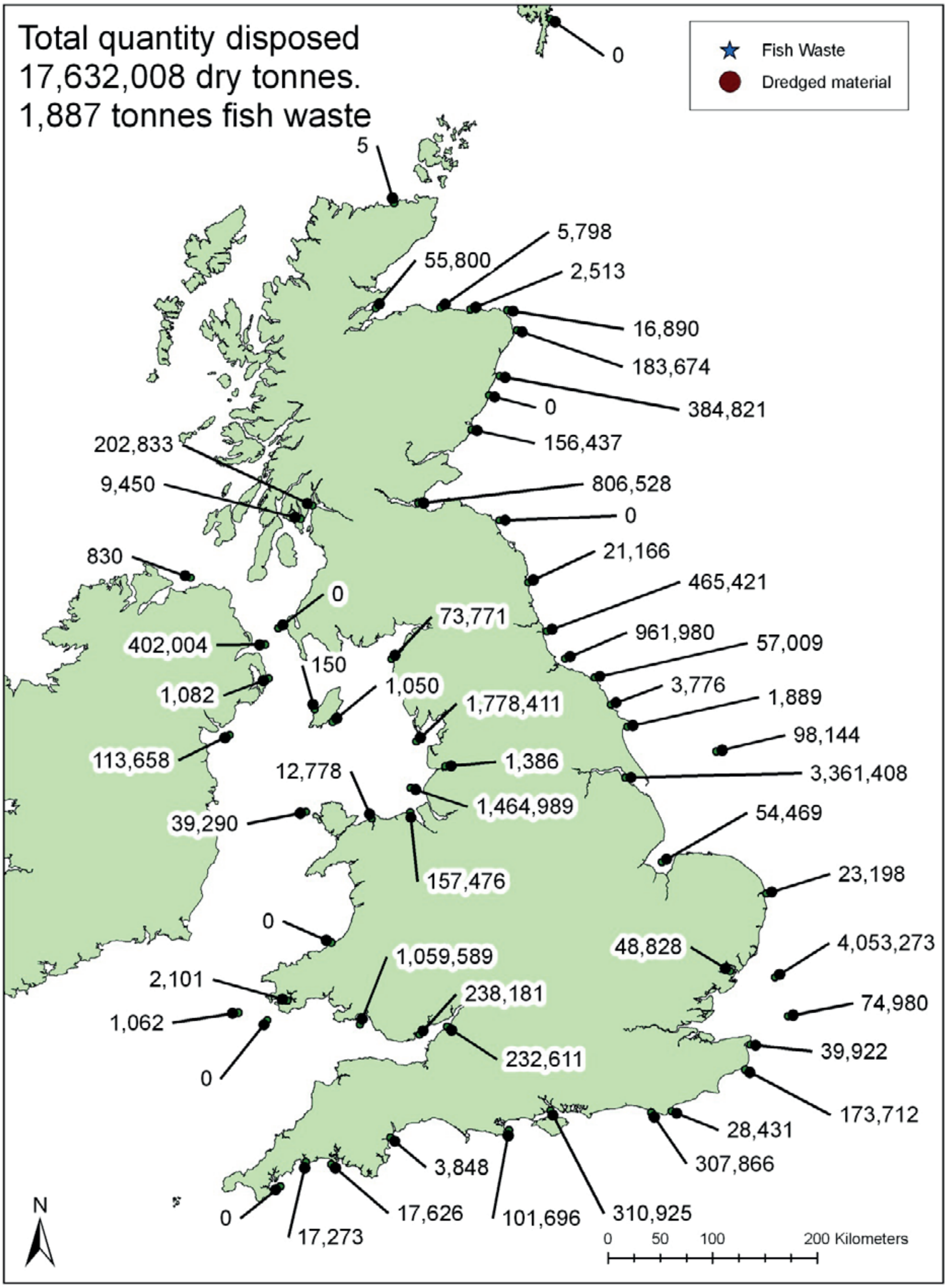


Figure 18.2. Amount of dredged material disposed of to sea in 2009.

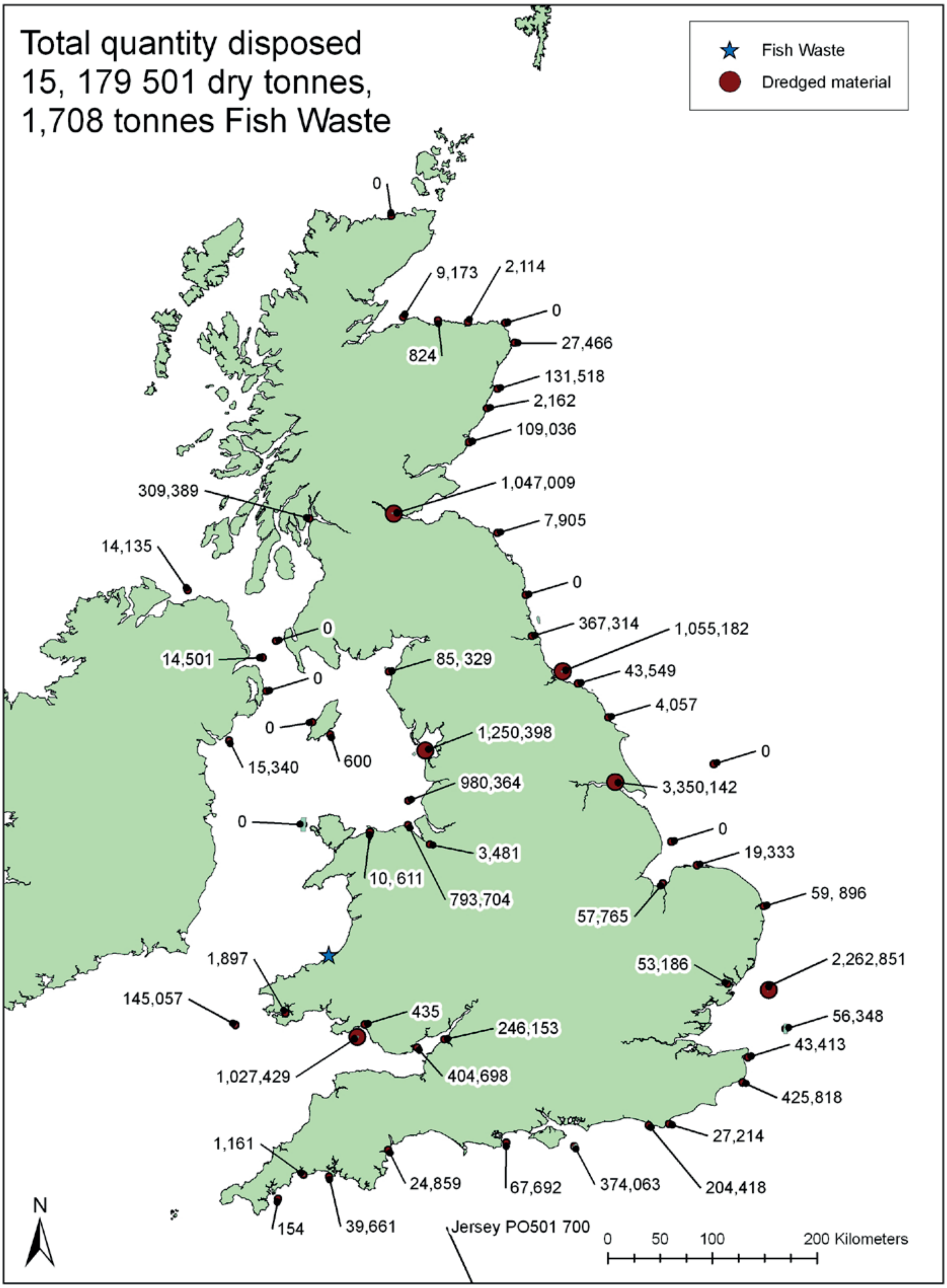


Figure 18.3. Amount of dredged material disposed of to sea in 2010.

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