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CONTAMINANT STATUS OF THE NORTH SEA

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CONTAMINANT STATUS OF THE NORTH SEA

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Chemicals used offshore

The main contaminants associated with the oil and gas industry in the North Sea come from produced water and drill cuttings. Produced water is now the main source, having overtaken drill cuttings since the change from oil based muds (OBMs) to other, less harmful alternatives and since the maturity of the production fields.

Cuttings Piles

There is a wide range of metals in cuttings piles. However, in most cases the reported concentrations of the "Red List" metals are low. The average concentration range for a number of metals, at different depths in cuttings piles, was determined following a study of eleven cuttings piles in the North Sea (CORDAH, 1999). The highest average concentration for depths of 1-10 cm for all eleven piles was 8 µg g^{-1} Cd, 33 µg g^{-1} Hg, 173 µg g^{-1} Pb and 40,000 µg g^{-1} Fe. For barium, which is a major component of drilling muds, the highest average concentration was 86,000 µg $g^{-1.}$

Concentrations of metals and hydrocarbons in cuttings piles

Metal	**Concentration µg g^{-1}**	**Hydrocarbon sampled**	**Concentration mg kg^{-1}**
Cadmium	0.1 – 8 [1]	Naphthalene	75[1]
Copper	110 [2]	Phenanthrene	3[3]
Mercury	0.1-33 [1]	Anthracene	12[2]
Nickel	1-49 [2]	Fluoranthene	0.1[3]
Lead	16-173 [1]	Pyrene	0.5[3]
Zinc	2-435 [2]	Chrysene	0.3[3]
Iron	40,000	Benzo[*a*]anthracene	0.1[3]
Barium	86,000	Benzo[*a*]pyrene	0.007[2]

1. Law and Fileman, 1985.
2. Data from Davies *et al.,* 1989, for the Beryl A cuttings pile.
3. Data for the Fulmar cuttings pile.

Produced Water

The hydrocarbon-producing areas of the North Sea can be divided into three regions. The northern and central areas produce both oil and gas while the southern North Sea predominantly produces gas with some fields also producing condensate. Higher quantities of corrosion inhibitors, gas treatment products and scale inhibitors are discharged into the North Sea than chemicals of any other functional group.

Peak annual values (tonnes) of chemicals discharged by functional group between 1992 and 1998 (Value in parenthesis is year observed)

	Tonnes Year^{-1}		
Chemical category	**Northern North Sea**	**Central North Sea**	**Southern North Sea**
Biocides	127 (94)	98 (95)	55 (93)
Corrosion inhibitors	1770 (96)	215 (97)	74 (96)
Gas treatment	1916 (94)	1810 (97)	2437 (94)
Scale inhibitors	2677 (93)	3030 (97)	-

Chemicals in the environment

With regard to the wider environment of the North Sea and levels of contaminants in different matrices the following conclusions are drawn:

Water

Water samples with the highest levels of chemical contamination are found at inshore estuary and coastal sites subject to high industrial usage. Where, for example, concentrations of total hydrocarbons (THCs) are found to be high offshore, these are in the immediate vicinity of installations with concentrations generally falling to background levels within a very short distance from discharge.

Summary of contaminant levels typically found in surface waters of the North Sea

Location	THC (µg l^{-1})	PAH (µg l^{-1})	PCB (ng l^{-1})	Ni (µg l^{-1})	Cu (µg l^{-1})	Zn (µg l^{-1})	Cd (ng l^{-1})	Hg (ng l^{-1})
Oil & Gas Installations	1–30[1]	-	-	-	-	-	-	-
Estuaries	12-15[2,3]	>1	30[2]	-	-	-	-	-
Coast	2	0.02–0.1	1 – 10[4]	0.2-0.9[2,3]	0.3-0.7	0.5-2.2	10-32	0.25-41
Offshore	0.5-0.7[2,3]	Below det.	-	0.2-0.6	0.3-0.6	0.5-1.4	10-51	1.6-69

[1] Law and Hudson, 1986

[2] OSPAR Commission, 2000

[3] Law *et al*., 1994

[4] SOAEFD, 1996

Sediments

Trends in the concentration and distribution of contaminants in sediments, particularly hydrocarbons (HCs), are similar as those described for surface water contamination. There are, however, some notable exceptions. For example, the levels of certain metals appear higher in the southern North Sea compared to the northern North Sea (Pb, V, Cu and Fe). Recent work on seasonal current circulation patterns within the southern North Sea suggests that this may be due to coastal contamination transported offshore without being widely dispersed.

Summary of contaminant levels typically found in surface sediments from the North Sea

Location	THC (µg g^{-1})	PAH (µg g^{-1})	PCB (µg kg^{-1})	Ni (µg g^{-1})	Cu (µg g^{-1})	Zn (µg g^{-1})	Cd (µg g^{-1})	Hg (µg g^{-1})
Oil & Gas Installations	10-450[1]	0.02-74.7[2]	1,917[6]	17.79[7]	17.45	129.74	0.85	0.36
Estuaries	-	0.2-28[5]	6.8-19.1	-	-	-	-	-
Coast	-	-	2	-	-	-	-	-
Offshore	17-120[2]	0.2-2.7[3,4]	<1[4]	9.5	3.96	20.87	0.43	0.16

[1] Dann *et al.*, 1992
[2] Law and Fileman, 1985
[3] Klamer and Fomsgaard, 1993
[4] OSPAR Commission, 2000
[5] CEFAS, 1998
[6] Wells *et al.,* 1988
[7] UKOOA, in press

Biota

There are two main sources of potential biological effect upon marine organisms that are associated with oil and gas production activities: those caused by production discharges, i.e. produced water, and those associated with drilling activities. Operational aerial emissions may also give rise to deposition of contaminants (in particular the lower molecular weight compounds such as naphthalene and pyrene) on the sea surface.

Exposure of marine organisms to contaminants occurs by two routes, either through passive diffusion or active uptake processes via surface membranes, or through absorption from the gut in association with fatty materials. Organisms spending the majority of their life-cycle in the water column are therefore likely to receive the highest exposure to contaminants that remain in solution. Contaminants that are/or become readily associated with suspended particles are likely to become associated with the sediments. The main exposure route for particle bound contaminants will be through direct ingestion by various benthic species or indirectly when these same species are consumed by other organisms. In addition, those organisms living in close association with the sediments may also absorb contaminants from interstitial water.

Evidence of biological effects

The biological effects of platform activities are wide-ranging. The contaminants in produced water plumes may have direct effects on populations of both pelagic invertebrate and vertebrate species in the vicinity of the discharge and also indirect effects via bioaccumulation and bioconcentration of contaminants through the food chain. Drilling activities primarily have effects on the benthic fauna directly underneath and some distance from a platform, but they also potentially have impacts on fish species that live in close association with the sediment and feed upon invertebrate populations that may be contaminated.

The effects of contaminants upon biological systems can be manifested at a number of different levels of organisation ranging from the cellular and organ level through to changes in the sizes of populations and ultimately to altered diversity and functioning within the community of interacting populations. Changes that occur at the cellular and organ level may provide an ‘early warning system’ of more dramatic and possibly irreversible effects upon populations or communities. The occurrence of various biological effects following exposure to contaminants that are predominantly associated with oil and gas exploration and production activities are discussed in relation to data from laboratory studies and from monitoring programmes.

Gaps in our understanding

Within the framework of OSPAR and the North Sea Conferences, the UK is working with other contracting parties to develop marine management and monitoring strategies. Clearly the offshore activities of the oil and gas industry are being taken into account in this process, but further work is required, especially:

1. To further identify and determine current and potential inputs of chemicals in produced water, field concentrations, chemical fate and biological effects of such substances, in particular the potential for long-term impacts.
2. To define the likely zone of influence of contaminants released upon disturbance of cutting piles, and the implications for wider-field contamination levels in the North Sea.
3. To overcome the present lack of ecotoxicological assessment criteria and/or background/reference concentrations for oil.
4. To close the gaps in knowledge in respect of temporal trends and spatial distribution. Monitoring efforts should be optimised within the Joint Assessment Monitoring Programme (JAMP).
5. To develop tools for the assessment of substances and effects of concern. It is essential that a structured approach is taken and that it fully integrates biological techniques and chemical monitoring. Further development of biomarker techniques according to widely accepted protocols and more efficient data management and dissemination are also strongly recommended.
6. To develop an ecosystem approach, which has been a major recommendation of the 1997 International Ministerial Meeting, for protecting the environment according to OSPAR's Annex V. An important aspect of this approach is improved integration between the different sectors operating in the sea, but also between scientists, policy makers and other stakeholders. Through concerted action these parties should progress towards effective use of the resource whilst protecting and conserving the ecosystems and biological diversity of the North Sea.

Regulatory controls

The UK as with other States in the Northeast Atlantic is responsible for regulating pollution from seabed installations within the Exclusive Economic Zone (EEZ), an area up to 200 nm offshore. International conventions and regulations, such as the International Convention for the Prevention of Pollution from Ships (MARPOL) and the London Convention, apply both within and outside the EEZ. In addition, developments at the European level have a significant bearing on how the industry is regulated. The most important of these, particularly with regard to activities in the coastal zone, is the publication of the EC Water Framework Directive in the EC Official Journal on 22 December 2000.

The potential problem of increased chemical discharges has been handled on one front by adoption in 1996 of OSPAR Decision 96/3 on a Harmonised Mandatory Control System for the Use and Reduction of the Discharge of Offshore Chemicals. The new approach came into force in June 2000 after a trial period and effectively supersedes previous OSPAR measures with respect to offshore chemicals. Included in the new approach is a procedure to assess chemicals according to their hazard ranking and to promote the principle of substitution when less hazardous alternatives to chemicals in current use are available.

Future risks

In most cases, the high concentrations of some contaminants in sediments within 500 m of producing platforms are probably due to cuttings discharge. The effects on benthic communities can be observed out to 3-5 km, though the zone of impact decreases following cessation of cuttings discharges. There is also the potential for redistribution of contaminants if cuttings piles are removed at decommissioning, therefore best practice is presently being determined through pilot studies.

Another issue of concern is the potential for cumulative impacts in areas where a number of platform ‘footprints’ overlap, and further fingerprinting of HCs and other contaminants, together with suitable numerical modelling should be investigated. Although significant quantities of chemicals are being discharged in the produced water, their effects are mitigated through their rapid dilution and dispersion. Nevertheless, HCs, polycyclic aromatic hydrocarbons and other chemicals can be detected at elevated levels (relative to background) close to the source of discharge. Subtle biochemical signals can be detected much further away, but their significance at the individual and population level is largely unknown. Future R&D must assess the significance of the offshore discharges relative to larger discharges from coasts (including atmospheric deposition) and their relative impacts in intermediate and offshore waters.

1. INTRODUCTION

The DTI is conducting a Strategic Environmental Assessment prior to further licensing in the region of the mature oil and gas provinces in the North Sea. A series of technical reports have been commissioned to contribute to the overall assessment. This report considers the major potential sources of chemical contamination of the North Sea from oil and gas exploration and production activities in northern, central and southern production field areas of the North Sea. These are then evaluated against background levels and trends throughout the North Sea where they have been sampled, particularly as a result of the 1993 North Sea Task Force (NSTF) surveys and more recently OSPAR (combined Oslo and Paris Commissions) and NMMP (National Marine Monitoring Programme). Finally, the report considers evidence of biological effects resulting from chemical inputs derived from the offshore activities of the oil and gas industry. This report was compiled in consultation with Fisheries Research Services, Marine Laboratory Aberdeen.

2. DATA SOURCES AND APPROACH

Data, such as those collated to support evaluations of the quality status of the North Sea (1987, 1990, 1993, 2000) and the UK NMMP reports are presented in a variety of publications, including CEFAS Aquatic Environmental Monitoring Reports (AEMRs) and reports from UKOOA (United Kingdom Offshore Operators Association). Of particular relevance is a study recently commissioned by UKOOA (in press), which has transferred historical environmental survey data around oil and gas platforms from paper reports into a database, enabling a comprehensive analysis to be undertaken. Information from a draft of this report has been included where relevant. In addition, literature searches were undertaken so as to identify other studies on the sources and effects of contamination relevant to the oil and gas activities in the North Sea.

In 1995 the OSPAR Commission (combined Oslo and Paris Commissions) adopted a Joint Assessment and Monitoring Programme (JAMP), intended to build on the experience gained through its former Joint Monitoring Programme (JMP) and the Monitoring Master Plan of the North Sea Task Force (NSTF). Monitoring work undertaken to satisfy the Convention requirements has recently been reported (OSPAR Commission, 2000) which presents an assessment of marine environmental conditions and, where possible, describes the temporal changes that have been observed in the Greater North Sea, since the 1993 Quality Status Report (QSR).

In 1987/88, the Marine Pollution Monitoring Management Group (MPMMG) reviewed the monitoring carried out in UK estuaries and coastal waters and concluded that there would be considerable merit in the regular sampling of a network of coastal monitoring stations. This network was to include offshore stations as reference stations, as recommended by OSPAR at the NSTF meeting in 1989. The first phase of spatial surveys (National Monitoring Programme (NMP)), allowed an evaluation of environmental marine quality around the UK (MPMMG, 1998). The second phase (NMMP) began in 1999 with the emphasis on the detection of longer-term temporal trends.

The structure of the present report reflects the approach taken in reviewing the available data, namely:

Section 3:	The identification and quantification of functional types of chemicals used at sea by the industry (data taken from the OCNS-HMCS and UKOOA);
Section 4:	An overview of chemicals in the environment (OSPAR-QSR and NMMP);
Section 5:	Evidence of biological effects caused by the release of contaminants associated with the operations of the oil and gas industry;
Section 6:	Gaps in our understanding;
Section 7:	Regulatory controls;
Section 8:	Future risks to the environment.

3. CHEMICALS USED OFFSHORE

3.1 Introduction

Hydrocarbons have been produced from the North Sea for over 30 years. On the UK continental shelf some 280 platforms and 300 subsea completions are currently producing approximately 2.3 million barrels per day of oil and 100 million m^3 per day of gas. This effort involves the use of approximately 2000 chemical products (CEFAS, in press).

The original voluntary Offshore Chemical Notification Scheme (“old” OCNS) (1979-1993) and the “revised” Notification Scheme (1993-1996) classified exploration and production (E&P) products used on the UK continental shelf (UKCS) into ‘Categories or Groups’ based on hazard criteria. In this classification, chemicals were (and still are) classified on the basis of their potential biodegradation, bioavailability and toxicity to a range of taxonomic groups, using protocols and test species approved by the Oslo and Paris Commissions. These classifications assist operators in taking environmental factors into account when selecting products for use offshore. The OCNS applies to all products used in the drilling, completion, stimulation and operation of a well and products used to treat all fluids produced from a well (including rig washes, drilling lubricants and hydraulic fluids used to control sub-sea wellheads).

In the “revised” OCNS scheme (active until the end 2001), the initial Group-classification is determined using Table 1. All submitted toxicity data for the product are compared to these categories and the value giving the worst case ‘Initial Grouping’ (i.e. the test giving the most toxic response) is used as the initial Group for the product. All values are presented in parts per million.

Table 1 Initial group classification guidelines values

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

This initial Group can be adjusted up or down, by one or two groups, depending on the biodegradation and bioaccumulation potential of the components in the preparation. The 'final' Group assigned is therefore based upon the overall environmental hazard posed by the product.

In the new scheme the assessment and regulation of offshore chemicals has been reviewed by OSPAR and the implementation of the Harmonised Mandatory Control Scheme (HMCS) will result in a revision to the current classification procedure in the UK. The basis for these new regulations will be an assessment by generic risk using a comparison of Predicted Effect Concentration (PEC) and Predicted No Effect Concentration (PNEC), followed by site specific risk assessments for all chemicals used offshore.

The objective of these harmonised controls is to prevent pollution which might result from routine discharges or accidental losses of E&P products from offshore operations. The UK has agreed to introduce a mandatory chemicals control scheme in line with the OSPAR HMCS for the use and reduction of the discharge of offshore chemicals (in accordance with PARCOM Decision 2000/2) by the end of 2001.

According to 1999 industry returns to the UKOOA Environmental Emissions Monitoring System (EEMS) database an estimated 180,000 tonnes of chemicals are discharged annually into the UK sector of the North Sea. These discharges fall into two categories:

1. Drilling fluids (or ‘muds’) which adhere to rock cuttings that are disposed of into the sea at any site where a well is being drilled.

2. Production chemicals added to the hydrocarbon-water mixture pumped up from the reservoir. A proportion of these are then discharged to sea in the ‘produced’ water from 110 installations where hydrocarbons are separated from water before export, either by pipeline or by tanker. In many cases these installations process fluids from a number of satellite platforms or subsea wellheads.

3.2 Drilling Chemicals

In the early days of North Sea development, all wells were drilled with water-based muds (WBM) using the experience of US companies operating in the Gulf of Mexico. WBMs are formulated either with fresh water, seawater or with a brine (e.g. KCl). The salinity ranges from 0 to approximately 900 kg/m^3, depending on the salt type and desired density of the mud (OLF, 1998). The environmental impact of drilling with WBMs was found to be very small. Later, diesel oil began to be added to water-muds to combat problems encountered when drilling through strata containing shales, claystones and salts which softened, swelled or dissolved on contact with WBMs causing the drill string to stick or, even worse, the well to collapse. The move into progressively deeper water in the late 1970s also increased the need for directional drilling, which required the greater lubrication and temperature tolerance of oil-based muds (or OBMs). The formulation and use of diesel-based muds became routine in the late 1970s and early 1980s.

Drilling operations accordingly became a significant source of oil being discharged to the sea during the 1980s and early 1990s. Between the late 1960s and 1994 some 200,000 tonnes of oil associated with cuttings were discharged into the North Sea. Diesel was used as a base oil until 1983, when more refined low-toxicity OBMs (mostly based on de-aromatised kerosenes) came into use. Diesel was finally banned in 1984 from OBMs. There have also been increasingly stringent requirements for the cleaning of oiled cuttings prior to their discharge.

Table 2 Major chemical functions and types of additives used in drilling muds

Chemical Function Group	Function	Composition
Weighting Materials	• Increase weight of mud, which maintains well pressure. • Major component of mud system.	• Most commonly barite, which may contain traces of heavy metals.
Viscosifiers	• Build viscosity through complex interactions with the emulsions.	• Bentonite clay in the majority of most water-based muds. • Organic polymers derived from cellulose and natural biopolymers also used.
Fluid loss control agents	• Serve to reduce the loss of fluid from mud into drilled formation.	• Bentonite clay, lignite and polymers: carboxymethyl cellulose (CMC), polyanionic cellulose (PAC) and modified starch.
Emulsifiers	• Stabilise oil-in-water emulsions.	• Fatty acids (and derivatives), rosin acid (and derivatives) prepared from sodium soaps from the paper industry and fatty imidazoline derivatives. • Secondary emulsifiers include amines, amides, sulfonic acids, lignosulfonates, alcohols and related co-polymers.
Brines	• Concentrated inorganic salt solutions balance the interactions of drilling fluid with clay and soluble salts.	• For WBMs: KCl, NaCl. • For completion fluids NaCl, $CaCl_2$, $ZnCl_2$, $CaBr_2$ and $ZnBr_2$. • For OBM/SBMs, $CaCl_2$, (NaCl). Typical use concentrations are 20% $CaCl_2$ brine, added by 20-40% to the mud.
Alkaline chemicals	• Control pH, reducing corrosion and also activating some emulsifiers.	• Lime ($Ca\ (OH)^2$) is with OBM/SBM. • Caustic soda, and other inorganic compounds including NaOH, KOH, $Ca(OH)^2$, K_2CO_3 in WBMs.
Lost circulation materials	• Block pores and fractures.	• Crushed nut shell, shredded vegetable fibre, mica flakes, calcium carbonate, shredded cellophane: concentrations used varies widely.
Shale control additives	• Prevent fluid loss in dry reactive shales and prevent the swelling of shale and possibility of stuck pipes	• Most commonly KCl, also polyglycols and polyglycerols, polyacrylamides (with high molecular weight), aluminium sulfate, inorganic silicates, sulfonated asphalts and synthetic cationic polyamines.
Lubricants and detergents	• Enhance the rate of penetration of drill string	• Most common lubricants are modified natural esters, fatty acids or glycol esters. • Most popular detergent used is ethoxylated alcohols.

Drilling activity in the North Sea has therefore left a legacy of accumulated drill cuttings beneath offshore installations, most of which are contaminated with the residues from oil-based drilling muds. In June 1998, UKOOA launched an initiative to identify the best available techniques and best environmental practice for dealing with these cuttings piles. As part of this programme, the physical characteristics of cuttings piles were determined for a representative sample and a model was derived to allow estimates of the size and dimensions of the remaining piles (CORDAH, 1999). Using the derived equations and mapped pile volumes received from operators it was estimated that there are approximately 787,500 m^3 of *in situ* cuttings in the central North Sea and about 503,218m^3 of *in situ* cuttings in the northern North Sea.

The types and amounts of chemical additives included in the mud formulation vary according to the physical characteristics of the mud required. Drill cuttings with associated drilling muds may therefore contain a range of contaminants, e.g. certain heavy metals which may present an environmental risk if they are present at elevated concentrations and in a toxic state. Barite may be contaminated with variable amounts of heavy metals depending on the source of the mineral, and since it is used in large quantities in muds, it is the main source of heavy metals contamination in cuttings piles.

The major chemical functions and types of additives used in the various drilling muds are illustrated in Table 2.

In addition to those chemicals listed in Table 2, biocides and corrosion inhibitors are also added to formulated drilling muds. It should however be noted that for many applications, mud mixes may consist of relatively few chemicals and often these are classified by OSPAR as Presenting Little Or No Risk (PLONOR).

In general, studies on drill cuttings from oil and gas platforms have concluded that OBMs have impacted on the marine environment. Studies indicate that biological changes can be detected in benthic communities up to 5 km from some drilling sites (Gray *et al*., 1990). However, the effects are most noticeable in a zone that generally extends to a maximum of between 500-1,000 m from the drilling site . The more recent use of alternative products such as synthetic based muds (SBMs) and WBMs has reduced environmental impacts. The change of products has also been supplemented by an improvement in methods used to separate the mud from the cuttings. In a number of cases, drill cuttings can now be reduced to a fine slurry to be re-injected. Alternatively, cuttings may be treated and disposed of on shore (Kroncke *et al*., 1992).

However, Davies *et al.* (1989), showed that quantities of oil in cuttings discharges varied considerably between individual sites and may be minimal in cases where WBMs are employed. In the early 1980s, when diesel based muds were extensively used, cuttings were discharged with between 6-17% diesel adhering to them. However, between 1981 and 1985 the use of diesel muds was phased out in favour of low aromatic base oils. Toxicity tests on the new base-oil and on muds formulated with them confirm that they have greatly reduced toxicity compared to the diesel oils (Blackman *et al.*, 1982). Nevertheless, the discharge of oily cuttings peaked first in 1985, with similarly high levels attained in 1988. An additional factor influencing the overall level of impact is that less stringent cleaning was required when using low aromatic base oil compared to the diesel oils. During this period an average of 1,000-1,500 tonnes of cuttings were discharged per well, consisting of approx. 150-250 tonnes of oil and approx. 10 tonnes of chemicals which reached the seabed. The initial switch from diesel to alternative base muds made little difference on impact to the environment, giving rise to the assertion that the base oil may not be the critical factor determining the toxicity of a particular drilling mud formulation. However, discharges of oil-based mud ceased at the end of 1996.

All drilling on the UKCS since 1997 has used WBMs with organic-phase fluids (OPFs) (which are usually low-toxicity mineral oils) being used only for those well sections where they are necessarily required. Cuttings from well sections drilled with OPFs are usually shipped to shore for cleaning, or sometimes re-injected if a suitable well exists at the drilling location, whereas cuttings from WBM sections are discharged to sea. In 1999, 157,253 tonnes of water-based drilling chemicals and additives were reported as being discharged to the UKCS. Of these, some 54,000 tonnes were weighting agents, predominantly barite.

3.2.3 Quantifying Drilling Chemical Inputs

There is a wide range of metals in cuttings piles. In most cases however the reported concentrations of the "Red List" metals are low. The average concentration range for a number of metals, at different depths in cuttings piles (Table 3) was determined following a study of eleven cuttings piles in the North Sea (CORDAH, 1999). The highest average concentration for depths of 1-10cm for all eleven piles were 8 µg g^{-1} Cd, 33 µg g^{-1} Hg, 173 µg g^{-1} Pb and 40000 µg g^{-1} Fe. For barium which is a major component of drilling muds, the highest average concentration was 86000 µg $g^{-1.}$

Table 3 Concentrations of metal in cuttings piles

Metal	**Cuttings pile concentration µg g^{-1}**
Cadmium	0.1 – 8 [1]
Copper	110 [2]
Mercury	0.1-33 [1]
Nickel	1-49 [2]
Lead	16-173 [1]
Zinc	2-435 [2]

1. Average concentration range sampled in the upper 10 cm of eleven cuttings piles (CORDAH, 1999)
2. Lowest and highest total concentration for North West Hutton cuttings pile (Gerrard *et al*., 1998)

The hydrocarbon concentrations in cuttings piles are indicated in Table 4. The values shown are derived from samples collected from two cuttings piles.

Table 4 The highest concentration of a range of hydrocarbons measured in samples from two cuttings piles

Hydrocarbon sampled	**Concentration mg kg^{-1}**
Naphthalene	75 [1]
Phenanthrene	3[3]
Anthracene	12 [2]
Fluoranthene	0.1[3]
Pyrene	0.5[3]
Chrysene	0.3[3]
Benzo[*a*]anthracene	0.1[3]
Benzo[*a*]pyrene	0.007 [2]

1. Law and Fileman, 1985.
2. Data from Davies *et al*., 1981, for the Beryl A cuttings pile.
3. Data for the Fulmar cuttings pile.

Data for the North West Hutton cuttings pile (Gerrard *et al*., 1998) also indicates the presence of nonylphenol at concentrations of 0.28-0.33 mg kg^{-1} dry weight (dw).

A wide range of contaminants may be present in cuttings piles, however, the information currently available is limited. The rate at which contaminants are released from a pile will be strongly influenced by the physical nature of the pile and the potential degree of disturbance it will undergo during different sea conditions.

3.3 Production Chemicals

Production treating chemicals are used on oil and gas platforms for a number of functions including prevention of corrosion and scale formation, to aid the free flow of oil or gas and to separate oil from formation water. To meet the functional demands of the offshore environment a wide range of chemicals are required. The main chemical functions are described in Tables 5 and 6 respectively. Most production chemicals are made up of a number of individual chemical components although there may be common chemical groups for products with similar functions. The Offshore Chemicals Database (CEFAS, in press) currently lists over 2000 products that have full, temporary or provisional classification for use in oil and gas production on the UK Continental shelf. There are on average three chemical components per product, although the number of chemical components ranges between 1-16. Although a potentially wide range of products may be used for a variety of functions offshore, in practice, chemicals utilised at offshore installations during any given year may be relatively few. Of those products used, not all will be subject to discharge and will either be used within closed circulation systems or, due to their physicochemical characteristics, will partition to the process stream.

Table 5 Description and function of chemicals used in oil and gas production

Product Function	Function description
Corrosion inhibitors	Corrosive gases in produced water (oxygen, hydrogen sulphide, carbon dioxide) and seawater itself, can cause corrosion in pipework and tubulars. Products generally comprise complex mixtures: amides, amines, amine salts, imadazolines, quaternary ammonium salts.
Scale inhibitors	Scaling can occur within pores of the formation itself as reservoir pressures reduce and within well tubulars. Scale inhibitors inhibit crystal growth. Most are based on phosphonates, phosphate esters or acrylic acid copolymers.
Emulsion breakers	Water is dispersed in oil or as wells age, a reverse emulsion is produced, with oil suspended in water. Most installations use demulsifiers to accelerate separation. These include: oxalkylated resins (alkylphenol/formaldehyde reaction products), polyglycol esters, alkyl aryl sulphonates.
Reverse emulsion breakers	Oil left in produced water following primary separation is removed to <40 ppm, using positively charged polyamines or polyamine quaternary compounds added to cause the negatively charged oil droplets to aggregate.
Antifoam chemicals	Hydrocarbon foaming causes significant problems in oil and water separators. Polyglycol esters or silicones can reduce these.
Paraffin treatment and dewaxing chemicals	Solid hydrocarbon waxes build up in tubing, vessels and flowlines. Deposition may be inhibited by vinyl polymers, sulphonate salts or mixtures of alkyl and aryl polyethers; also by pushing scrapers or pigs through flowlines and pipelines often in combination with low-cut aromatic solvents.
Water treatment chemicals	Seawater is used to maintain pressure by displacing oil through the reservoir. Suspended solids and micro-organisms must be removed before injection. It is also used to cool process vessels and in fire fighting systems.
Biocides	Sodium hypochlorite prevents biological growth in the seawater intake and injection systems. Typically 0.2 to 0.5 ppm hypochlorite is discharged. Organic biocides are also added to prevent growth of sulphate-reducing bacteria which cause damage to the pumps and tubing and H_2S within pressure piping. Typical biocides include quaternary amine salts, amine acetates, formaldehyde and gluteraldehyde.
Flocculants and coagulants	Suspended solids are removed with mechanical strainers, while smaller particles are removed by chemicals. Coagulants, similar to cationic polymers are used for reverse emulsion breaking. Flocculants are generally high molecular weight polymers, although aluminium or iron chlorides and sulphates are also used.
Hydrate inhibition	Hydrates are ice-like solids, which can form above 0°C in gas wells and pipelines. Freeze-ups can be prevented by the addition of methanol or monoethylene glycol. Treatment may be required when extra wells are started from cold and also before shutdowns. Subsea completions usually require continuous treatment.
Gas dehydration	Monoethanol glycol or triethanol glycol are used to adsorb water from the gas. Glycols, whether for hydrate inhibition or dehydration, are recycled. Where produced water is very saline, re-distillation is impossible and large quantities can be discharged.
Gas sweetening	Acid gases (H_2S and CO_2) are of a corrosive nature and toxic to humans. Biocides are often added to produced fluids to prevent sulphide corrosion within pipework and vessels.

Table 6 Description and function of chemicals used in the stimulation and workover procedures

Product Function	Function description
Stimulation and workover chemicals	Stimulation and workover treatments are performed to improve the productivity or injectivity of wells, although careful attention to cleanliness during completion and injection can reduce the need for such work.
Acids	Used to open up lumen at the bottom of wells in limestone reservoirs. A mixture of hydrochloric and hydrofluoric acids, known as 'mud acid' can dissolve sand and also clays, which may have entered the formation from drilling mud. Organic acids such as acetic, formic and citric acids may also be used to prevent chloride corrosion of tubulars. Citric acid or EDTA can be used to remove scale deposits.
Hydraulic fracturing	Requires large volumes of fluid containing proppants and other additives to be pumped under high pressure into the formation. The most common proppants are graded sands and alumina which has a greater crushing strength. These materials may be coated with phenolic or epoxy resins, which harden at elevated temperatures in the formation and lock the proppant into place. Oil soluble resins can be added to increase the fracture lengths attainable with given pumping capacity.
Brines	Range in density from concentrated sodium chloride through calcium chloride to bromides of which zinc bromide is the heaviest. Caesium formate is increasingly used as a safer alternative to zinc bromide.
Viscosifiers	Typical viscosifiers: celluloses, guar gum and starches or sugars although synthetic polymers may be needed in high temperature wells.

Pipeline commissioning chemicals

A variety of chemicals may be required in the preparation of pipelines for use. Corrosion inhibitors, biocides, fluorescein dye and ammonium bisulphite oxygen scavengers are added to seawater in newly laid pipelines, either individually or as a cocktail. The contents are discharged to sea after pressure testing. The pipelines are then dried with methanol, which is also discharged to sea, before being put into service.

3.4 Quantifying Production Chemical Inputs

The hydrocarbon-producing areas of the North Sea can be divided into three regions. The northern and central areas produce both oil and gas while the southern North Sea predominantly produces gas with some fields also producing condensate.

3.4.1 Northern North Sea

It can be seen from Figure 1 that higher quantities of corrosion inhibitors, gas treatment products and scale inhibitors are discharged in this area than chemicals of any other function group. Gas treatment products and scale inhibitors are discussed further in relation to their discharges in the central North Sea. Given the similarities in water depth and volumes discharged, similar conclusions may be drawn in relation to the northern North Sea.

Corrosion Inhibitors

The wide variation in the formulation of corrosion inhibitors does not lend itself to the development of techniques for routine monitoring, or to generalisations of their partitioning or biodegradation. However these chemicals are worth further consideration due to their moderate to high toxicity. The CEFAS Offshore Chemicals Database lists 287 current, proposed or withdrawn formulations which could, potentially, have been in use between 1992 to 1998. The toxicity categories for these products are represented in Figure 2. The highest toxic response produced by the majority of these (81%) is less than 10 ppm. In every case the pelagic species *Acartia tonsa* or *Skeletonema costatum*, are the most sensitive. This in part may be due to the high water solubility of many of these products. However, the function of corrosion inhibitors is to sequester corrosion causing radicals from seawater. It is therefore also possible that the ‘toxicity’ to *Skeletonema costatum* may, in part, be due to the sequestering of nutrients from the test solution during the toxicity test. Since the introduction of the HOCNF in 1996 there has been a noticeable drive towards the use of less toxic and more biodegradable chemicals. It should also be noted that some of these more toxic chemicals may have been used in situations in which no discharges were made.

In cases in which chemical use and discharge does take place it should be remembered that toxicity testing is carried out on the formulated product as supplied and that this may bear little resemblance to the substances discharged. Most of these products include a surface active component in the formulation to maximise the interaction of the active ingredients with the surface requiring protection. Once dosed, the active ingredients are intended to remain on internal surfaces of pipes and other equipment in contact with the process stream for a period of time, while the carrier solvents, reaction products and any overdose of formulated product are discharged. Consequently the toxicity shown by the formulated products may not be reflected in the proportion discharged to the environment.

3.4.2 Central North Sea

It is interesting to note that discharges of corrosion inhibitor to the northern North Sea are far higher than in the central North Sea (Figure 3) although operating conditions might be expected to be similar. Reasons for this have not been fully ascertained, though possible explanations include the following:

- There may be a greater number of mature fields in the area which inject seawater to maintain reservoir pressures. These, therefore, may require a higher proportion of corrosion inhibitors.

- There may be other operational conditions unique to this area.

- The majority of discharges in this area have been reported by a single operator whose procedures might result in an increased use and discharge of products of a particular chemistry, in comparison to other operators.

The larger chemical discharges above 1000 tonnes are limited to only a few discrete categories of chemicals for each of the North Sea regions. Other chemical functional groups used are limited to less than about 250 tonnes per annum in each case. In the case of the CNS this may total an additional discharge of around 2000 tonnes of total chemicals. Again chemical discharge is based on the quantity of chemicals ‘as dosed’ and it will not follow that the same proportions of specific chemical components of a formulation will be discharged, due to differences in physico-chemical properties and partitioning. Many of the formulations will comprise large proportions of biodegradable organic solvents or hydrocarbon based solvents which will be returned to the refinery via the oily water separators. Most active ingredients which are released exhibit some biodegradation, and, even where this is combined with moderate to high toxicity, it is likely that far field effects would be minimal although some local effects may be found close to installations.

Polymers are usually highly persistent, although because they exhibit low toxicity due to their lack of water solubility they would appear to present a low risk to the marine environment. However, OSPAR has identified the persistence of polymers as a concern. Many polymers are used by the industry due to their effectiveness in providing a substrate on which to split oil in water mixtures (demulsifiers). It is possible that quantities of demulsifier may be discharged to the sea. Given the concerns of OSPAR and the wide scale and necessary use by the industry of this group of chemicals it may be relevant to investigate their wider scale impact.

The greatest quantities of chemical discharges to the central North Sea are of scale inhibitors and gas treatment products.

Scale Inhibitors

As the majority of these chemicals are required to be water soluble, the most toxic response is therefore usually shown by pelagic species for which moderate to low toxicity is exhibited. The chemistry of these products is largely based on amine salts, phosphonates and polymers, some formulations also having a proportion of added surfactant. Either water or water soluble organics such as monoethylene glycol are typically used as solvents in these products. The polymers used are frequently based on organic acids, such as maleic acids and they exhibit low to moderate biodegradation combined with low potential for bioconcentration. These characteristics result in products of low risk which accordingly attract Revised OCNS groups D and E. However, it should be remembered that these groupings only describe hazard and in view of the large quantities used on a regular basis by the industry, it is possible that a more formal assessment of their cumulative risk is called for. Risk assessments of these discharges need to consider the reaction products as well as any possible residual un-reacted product. A few scale inhibitors are based on hydrocarbon solvents, probably for use in dual-phase systems. These tend to exhibit much greater toxicity, and the solvents also show higher potential for bioconcentration though this is often coupled with good biodegradation. These are clearly higher hazard products (also reflected in their OCNS groups), however they may not pose any additional risk since many hydrocarbon based solvents used offshore are exported with the product-stream to the refinery. Again, this may represent a situation that warrants further investigation.

Gas treatment products

Most gas treatment products are based on glycols and amines in an aqueous base. These products tend to exhibit low toxicity to pelagic taxa and show moderate to good biodegradation with little tendency to bioaccumulate. Accordingly most of these products attract Revised OCNS groups D and E. Some of the amine-based products also contain a quantity of polymer, probably to provide a substrate on which the reactions take place. These polymers do not exhibit ready biodegradation, but when viewed against the generally low toxicity of this group of products, this would not appear to present a great risk.

3.4.3 Southern North Sea

The discharge of various chemical groups in the southern North Sea is shown in Figure 4. As might be expected for an area high in natural gas deposits, the major group of chemicals used are those involved in gas treatment (the characteristics of which have already been discussed in relation to the central North Sea). As discussed elsewhere, no hydrosulphate scavengers are used in the North Sea, so all gas treatment chemicals used here are for hydrate suppression or dehydration.

The marked increase in the discharge of gas treatment products during 1994 is difficult to explain. Some installations have had problems with saline produced water that has prevented the usual recycling of gas dehydration products. When this happens, significant quantities of glycol may be discharged and while these chemicals are relatively non-hazardous, the installations concerned are situated in comparatively shallow water. Therefore, site specific risk assessments are required in view of the large quantities which can be discharged.

Discharges of the other function groups in the southern Gas fields are minimal, and it can be seen that the range of products required for gas production is considerably smaller than that required for oil production.

Produced Water

Produced water is mainly derived from the oil/gas-bearing formation but may also be comprised of seawater injected to maintain reservoir pressure. This water is normally discharged offshore by those installations where it is separated from oil and gas. Oil production water is different to gas production water in a number of ways, as outlined in Table 7. Upon discharge the produced water contains dispersed oil, other organic compounds including dissolved hydrocarbons, organic acids, phenols and traces of production chemicals. Among the constituents of some produced waters is naturally occurring radioactive material (NORM). In addition to radionuclides dissolved in produced water, radioactivity may be associated with insoluble low specific activity (LSA) scale which builds up in pipework and various equipment.

Produced water is now a major source of chemical contamination generated by the oil and gas industry, e.g. 24,286 tonnes of chemicals were reported as discharged to the UKCS in produced water in 1999. The quantity of oil production water is greater than the gas production water, but this is dependent on the age of the installation (Gillibrand *et al*., 1995). However, although the produced water from gas installations is lower in quantity, it often contains higher concentrations of oil and other hydrocarbon compounds as well as trace metals and other production chemicals.

The chemical composition of produced water is very field dependent. However, Table 7 to 12 compare the ranges for some of the more major chemical components present in discharges from oil and gas platforms. The general differences between the discharges from oil and gas platforms are also summarised in Table 12.

Table 7 Trace metal concentrations for samples of produced water from a number of North Sea oil and gas platforms compared with trace metal concentrations in seawater

Metal	Gas Platform [1] Concentration range (µg l^{-1})	Oil Platform [2] Concentration range (µg l^{-1})	Seawater range,[2] North sea (µg l^{-1})
Barium	1790 (390-12500)	87 (200-228000)	<22-80
Cadmium	50 (5-210)	2 (0.4-5)	0.004-0.028
Copper	25 (19-80)	10 (2-82)	0.0005-0.4
Iron	Na	4 (100-15000)	2
Mercury	4 (0.1-22)	0.002 (0.0001-0.03)	0.03
Chromium	50(15-50)	8 (5-10)[1]	
Lead	50 (35-6400)	700 (400-8300)	0.02-0.1
Nickel	45 (21-85)	75 (45-87)[1]	
Arsenic	1.5 (1-10)	2.8 (0.8-8)[1]	
Zinc	14000 (1300-66000)	700 (500-1300)	<5-823

[1] (Cofino *et al*., 1993); [2] (OLF, 1998).
Na – Not available

Table 8 Volatile Aromatic Hydrocarbon concentrations for samples of produced water from a number of North Sea oil and gas platforms

Component	Gas platform [1] Concentration range (mg l^{-1})	Oil Platform[2] Concentration range (mg l^{-1})
Benzene	0.3-440	0.8-4.6
Toluene	0.01-2	1.0-3.5
Ethylbenzene	Na	0.3-0.6
Xylene	0.1-7	0.2-0.7

[1](Cofino *et al*., 1993); [2] (Rϕe, 1999).

Table 9 Polycyclic Aromatic Hydrocarbon concentrations for samples of produced water from a number of North Sea oil and gas platforms

Component	Gas platform[1] Median concentration and (range) (µg l^{-1})	Oil Platform[2] Median concentration and (range) (µg l^{-1})
Naphthalenes	300 (57-1100)	860-1230
Phenanthrenes	7(3-19)	50.9-99.8
Dibenzothiophenes	Na	17.5-37.8
Acenaphtylene	59 (4-173)	Nd
Acenaphthene	63 (39-168)	0.3-1.8
Fluorene	7(3-17)	2.7-16.2
Fluoranthene	Na	0.4-7.8
Pyrene	1 (0.1-2)	0.7-8.6
Chrysene	<0.1	0.1-0.5
Benz[a]anthracene	<0.1	0.6-2.4
Benzo[a]pyrene	<0.1	<0.1-0.2
Benzo[ghi]perylene	<1	0.1-0.6
Benzo[k]fluoranthene	<0.1	0.2-0.8

[1] (Cofino *et al*., 1993); [2] (Rφe, 1999).
Na – not available
Nd – not detected

Table 10 Phenol and organic acid concentrations for samples of produced water from a number of North Sea oil and gas platforms

Component	Gas platform[1] Concentration range (mg l^{-1})	Oil Platform[2] Concentration range (mg l^{-1})
Phenols	1.13-14.1	0.1-29.5
Organic acids (<C6)	Na	757-1135

[1] (Cofino *et al*., 1993); [2] (Flynn *et al*., 1996).
Na – not available

Table 11 Radioactivity ranges for samples of produced water from a number of North Sea oil platforms

Component	Concentration range [1] (Bql l^{-1})
214 Pb	6-9
214 Bi	6-8
228 Ac	<2-17
226 Ra	6-9

[1] (Rφe, 1999).

Table 12 General differences between produced water from oil and gas installations (adapted from NSTF, 1993a & b, and van Zwol (OSPAR Commission, 2000))

	Oil	**Gas**
General composition	Pure water, formed from condensation of the hot gases, or mixture of condensed water and saline formation water. May be mixed with injected water.	Moderately saline formation water.
Injected water	May be mixed with injected water.	No water injected.
Change in salinity	Salinity increases.	Salinity remains similar.
Quantity	Higher for oil installation (2,400 - 40,000 m^3 day^{-1}). Dependant on maturity of installation <1% at the beginning of production, and up to 95% of the total discharge at the end of the field reserve.	Lower for gas installation (1.6 - 30 m^3 day^{-1}). Dependant on maturity of installation.
Particle size of oil droplets	>50 microns.	<20 microns.
Oil and aromatic concentration	Lower levels of oil and aromatic compounds.	Higher oil and aromatic compounds.
Monoaromatic concentration	Lower levels of monoaromatic hydrocarbons.	Benzene, toluene, xylene contribute main component. Can be present in high concentrations.
Polyaromatic hydrocarbon concentration	Lower levels of polyaromatic hydrocarbons.	Low molecular weight compounds above detection limit. Naphthalene occurred most, biphenyl next.
Trace metal concentration	Lower trace metals (depends ratio formation water/injected water. Injected water much lower trace metal concentrations)	Higher levels of trace metals.
Production chemicals Glycols and alcohols (Coffino et al., 1993)	Lower levels of methanol and glycols.	Higher levels of methanol and glycols.

3.5 Summary

The main contaminants associated with the oil and gas industry in the North Sea come from produced water and drill cuttings. Produced water is now the main source, having overtaken drill cuttings since the change from Diesel Based Muds (DBMs) to other, less harmful, alternatives.

Produced water and drill cuttings contain a wide range of organic and inorganic chemicals that may all have an impact on the environment if discharged in sufficient quantities. Nevertheless, the majority of the chemical discharges are organic in nature and are therefore prone to significant alteration in their properties (including toxic effects) once they enter the marine environment, although in the anoxic conditions that exist in many cuttings piles, the degradation rate for many chemicals may be slow.

Many of the complex polymers used by the industry to separate oil in water mixtures and to stimulate well production have been identified by OSPAR as compounds of concern due to their persistence in the environment. Given their widespread and necessary use by the industry it may be relevant to investigate their wider scale impact on the marine environment.

4. CHEMICALS IN THE ENVIRONMENT

4.1 Introduction

The preceding section reviewed the types and quantities of chemicals discharged by the industry operating in the North Sea. This information has been used to identify relevant substances sampled and analysed as part of wider spatial scale monitoring programmes such as the NMMP (Figure 5) and OSPAR. The determinands have been reviewed below according to the principal matrix of origin, namely water, sediment and biota.

4.2 Water

4.2.1 Total Hydrocarbons (THCs)

Crude oil is a complex mixture of tens of thousands of compounds. Most are types of hydrocarbons in the classes *n*-alkanes, branched alkanes, cycloalkanes, triterpanes and aromatics such as PAHs (polyaromatic hydrocarbons). These groups can be determined individually, but they may also be analysed as total hydrocarbons, usually by measurement of one function (absorption of infra-red radiation or emission of fluorescence at specific wavelengths, for example) and extrapolation to equivalents of an oil standard.

Total hydrocarbon values of 1-5 $\mu g\ l^{-1}$ have been reported in water in the vicinity of oil platforms and in areas of intensive shipping. In the German Bight, the Elbe plume mainly influences the distribution of total hydrocarbons. Concentrations range from 15 $\mu g\ l^{-1}$ in the mouth of the Elbe estuary to 2 $\mu g\ l^{-1}$ along the Frisian coast, which highlights the relatively high quantities of THCs being discharged into estuaries (OSPAR Commission, 2000) compared to the offshore zone.

In addition, Law *et al*. (1994) showed that in general, very low hydrocarbon concentrations are found offshore compared to levels found in some estuaries. For example, the highest values observed offshore were 2.5 $\mu g\ l^{-1}$, from 1990-92, compared to about 64 $\mu g\ l^{-1}$ for certain estuarine samples (Table 13).

Table 13 Concentrations of THC (µg l^{-1} Ekofisk crude oil equivalents) in sub-surface seawater from offshore locations, 1990-1992 (Law et al., 1994)

			THC		
Location	**Site**	**Coastal/Estuarine**	**1990**	**1991**	**1992**
Off Tyne	NMP 245	Coastal	0.3	0.6	0.4
Off Tyne/Tees	NMP 285	Coastal	1.9		
Off Tees	NMP 295	Coastal	2	<0.3	5
Off Humber/Wash	NMP 345	Coastal	0.4	na	na
Humber	NMP 375	Coastal	0.6	<0.3	2.5
Wash	NMP 385	Coastal	1.2		1.5
Outer Thames	NMP 465	Coastal	1.2	1.2	1.1
Outer Gabbard	NMP 475	Coastal	0.3		0.8
South Varne	NMP 485	Coastal	0.4		0.2
Tyne	Jarrow Slake	Estuarine	17	31	8.2
Tees	No. 15 buoy	Estuarine	35	19	64
Wear	Wearmouth Bridge	Estuarine	16	13	7.4
Humber	No. 10 buoy	Estuarine	nd	6.7	12

nd = not detected
na = not applicable

By contrast, surveys of hydrocarbon levels around 5 North Sea oil production platforms in 1981 showed the highest THC in water to be 30 µg l^{-1}. These findings from the early 1980s are supported by Law and Hudson (1986), whose data showed concentrations not exceeding 43 µg l^{-1} in the immediate vicinity of the Auk platform.

Stagg *et al.* (1996), measured concentrations of oil in water along two North-South transects between 57°N and 62°N (1°E and 1.5°E), within the northern North Sea. Results show a distinct north-south gradient in the hydrocarbon concentration, peaking around installations associated with oil and gas exploration and production. The report shows a progressive increase in hydrocarbon concentration from values of around 0.5 µg l^{-1} in pristine areas in the north and west, ranging up to 3 and 4 µg l^{-1} in areas of most intense exploration and production. At sites with higher levels of contamination there is a distinct depth profile of hydrocarbons with a minimum value occurring between 10-50 m in depth. Modelling using known amounts of produced water discharge did not predict the high oil in water measured so it is unclear what the precise source of the hydrocarbon contamination is.

4.2.2 Polyaromatic Hydrocarbons (PAHs)

Like THCs, the PAHs exhibit similar trends. For example, higher concentrations were generally found in coastal and estuarine samples compared to offshore waters, with total PAH concentrations exceeding 1 µg l^{-1} found in the Tees, Humber, Great Ouse and Thames estuaries. In the German Bight, the concentration of PAH was found to be between 0.018 and 0.09 µg l^{-1} (OSPAR Commission, 2000).

Table 14 Background concentrations of some PAHs, adapted from OSPAR Commission, 2000.

PAHs	**Water (ng l^{-1})**	
	Northern North Sea	**Central and Southern North Sea**
Benzo[*a*]pyrene	0.002 - 0.005	0.002 - 0.004
Fluoranthene	0.073 - 0.285	0.104 - 0.264
Benzo[*b*+*k*] fluoranthene	-	-
Benzo[*b*] fluoranthene	0.004 - 0.017	0.003 - 0.009
Indeno[1,2,3]pyrene	0.004 - 0.017	0.006 - 0.012

Generally PAH concentrations at offshore sites are low or undetectable (Table 14). However, Rowlatt and Davies (1995), points out that there are pronounced levels of PAHs in the open sea, especially in the area around 55.5°N and 0°E, near the Dogger Bank. However, the limited distribution of sampling stations in this case does not allow for an adequate assessment of the wider North Sea for PAHs (Figure 6).

4.2.3 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls have never been used as chemical additives in the North Sea, but they have been used in transformer oils in electrical plants on platforms. Due to changes in legislation they should now be confined to the older fields.

Due to their low solubility, PCB concentrations in water are usually extremely low and hence difficult to detect. From a 1990 survey of Scottish waters (SOAEFD, 1996), it was concluded that values in the majority of areas were less than 1 ng l^{-1} for the sum of all the congeners. However, in the Elbe plume, CB 153 concentrations were found up to 30 ng l^{-1}, whereas at other locations in the German Bight, concentrations were below 10 ng l^{-1} (OSPAR Commission, 2000).

Wells *et al.* (1988) reported on PCB contamination immediately after the Piper Alpha disaster of 1988. It was estimated that following the disaster that 760 kg of chlorinated biphenyls (CBs) reached the sediment, but those water samples collected did not contain any detectable concentrations of CBs.

4.2.4 Metals

Law *et al*. (1994) reported that offshore, trace metal concentrations of Ni, Cu, Zn, Cd and Pb are generally higher in the North Sea compared to the English Channel (Figure 7). There was also little variation in the concentrations of trace metals across both sea areas from samples collected in 1991 and 1992. The highest offshore concentrations of Pb were seen in the North Sea, probably as a result of atmospheric inputs (see Table 15).

Table 15 Concentrations of dissolved trace metals in sub-surface seawater from offshore locations, 1991-1992 (μg l^{-1}: except Cd, total Hg and Pb; ng l^{-1})

	Ni		Cu		Zn		Cd		Pb		Hg	
Site	**1991**	**1992**	**1991**	**1992**	**1991**	**1992**	**1991**	**1992**	**1991**	**1992**	**1991**	**1992**
NMP 245	0.49	0.22	0.32	0.41	0.66	0.5	11	10		36	4.6	36
NMP 285	0.5	0.24	0.56	0.33	0.53	0.55	12	51	81	69	3.9	69
NMP 295	0.38	0.26	0.24	0.23	0.35	0.25	10	12	70	71		71
NMP 345	0.41	0.28	0.31	0.32	0.27	0.37	10	17	34	49	1.6	49
NMP 375	0.26	0.29	0.71	0.44	2.2	0.5	22	16	21	45	2.3	45
NMP 385	1	0.28	0.74	0.61	1	0.61	27	10	190	40	0.25	40
NMP 395	0.42	0.38	0.31	0.57	0.45	0.59	15	22	49	35	1.7	35
NMP 465	0.9	0.64	0.83	0.45	0.92	0.75	32	23	73	41	5	41
NMP 475	0.59	0.36	0.49	0.43	1.4	0.64	18	4	29	29	1.6	29
NMP 485	0.44	0.43	0.29	0.43	0.22	0.65	14	19	24	41	0.13	41

Relative to metal concentrations in estuaries, those observed at intermediate and offshore sites were low. Many of the metals included in the survey show higher metal concentrations in the southern North Sea than in the northern North Sea with the exception of Pb (see below). This is attributed to the generally lower salinity in the southern North Sea, a consequence of the greater fresh water input from major rivers.

The North Sea can be considered as a mixing zone between runoff from land-based sources and the relatively ‘clean’ North Atlantic water entering from the north of Scotland and west via the English Channel. The location of several major rivers and water circulation patterns explain why riverine runoff from eastern Britain is mainly discharged and confined to the southern North Sea. For this reason, most dissolved metals are more concentrated in the southern North Sea, the exception being Pb. Dissolved Pb is quickly removed onto the surfaces of suspended particulate matter (SPM) which is relatively high in this sea area (Figure 8). It is not transported in dissolved phase to the southern North Sea by coastal circulation patterns. Since Pb from estuarine sources tends to be trapped in nearshore areas, atmospheric inputs of Pb become increasingly important away from the coast. Concentration variations between the offshore northern North Sea and southern North Sea regions can be explained by differing removal rates of dissolved Pb from the water column. These, in turn, depend on the SPM loadings in each region. The lower dissolved Pb concentrations in the southern North Sea are therefore a consequence of the greater SPM loadings in this region (CEFAS, 1998). However, relatively high, dissolved Pb concentrations in the vicinity of Dogger Bank may be attributed to the comparatively clear waters of this area, where there is little removal onto particlulate matter (MPMMG, 1998).

4.2.5 Alkylphenol

Alkylphenol polyethoxylates have previously been used in the oil and gas industries as rig washes and cuttings cleaners, where they are discharged directly into the sea without treatment (Blackburn *et al.,* 1999). Following a voluntary agreement between Government and suppliers of offshore E & P chemicals to phase out products containing known endocrine disrupters, there are now no products containing alkylphenols or alkylphenol ethoxylates on the UK list of Notified Chemicals. Their use is also being phased out in other industries and ten major manufacturers of polyacrylamide emulsion compounds have agreed a Europe-wide exclusion of APEOs by the year 2001 (ENDS Report, 1999). Water sampling for alkylphenol polyethoxylates, using NMMP guidelines, was conducted at a total of 52 sites during two research vessel cruises, *RV CIROLANA* 3a/98 and 3b/98. Of these, 19 were from NMMP stations. Samples were taken at offshore, intermediate and estuarine sites. The majority of the highly contaminated samples in this study were found in coastal or estuarine sources, in areas of high industrial activity (DEFRA, in press).

4.3.7 Summary

Water samples with the highest levels of chemical contamination are found at inshore estuary and coastal sites subject to high industrial usage (see Table 16). Where, for example, concentrations of THCs are found to be high offshore, it is in the immediate vicinity of installations with concentrations falling to background levels within a very short distance from discharge.

Table 16 Summary of contaminant levels typically found in surface waters of the North Sea

Location	THC (μg l^{-1})	PAH (μg l^{-1})	PCB (ng l^{-1})	Ni (μg l^{-1})	Cu (μg l^{-1})	Zn (μg l^{-1})	Cd (ng l^{-1})	Hg (ng l^{-1})
Oil & Gas Installations	1–30[1]	-	-	-	-	-	-	-
Estuaries	12-15[2,3]	>1	30[2]	-	-	-	-	-
Coast	2	0.02–0.1	1 – 10[4]	0.2-0.9[2,3]	0.3-0.7	0.5-2.2	10-32	0.25-41
Offshore	0.5-0.7[2,3]	Below det.	-	0.2-0.6	0.3-0.6	0.5-1.4	10-51	1.6-69

[1] Law and Hudson, 1986

[2] OSPAR Commission, 2000

[3] Law *et al*., 1994

[4] SOAEFD, 1996

4.3 Sediment

4.3.1 Total Hydrocarbons

The quantity of total hydrocarbons in sediments tends to show an increase from the southern North Sea to the northern North Sea. This trend, however, is closely linked to the spatial distribution of sediment type. Background hydrocarbon concentrations are generally higher in fine sediments (muds and silts) than in coarser sediments (sands and gravels) due to their greater surface area and adsorptive capacity, so may not accurately reflect the actual amount of oil discharged by the industry.

Nevertheless, it is noteworthy that drilling activity has been considerably more intensive in the northern and central sectors compared to the southern sector. Consequently the input of oil derived contaminants would be expected to be greater in the northern part of the North Sea. The effects of this will be exacerbated by the much lower rates of dispersal in the muddy deep water areas in the north as opposed to the mobile coarse sediments of the shallow southern sector. Relatively recent high resolution chemical detection techniques (fingerprinting) of hydrocarbon residues will go a long way to identifying the source of contamination, for example, some preliminary analysis has been able to distinguish residues from two or more different phases of drilling which used different OBMs.

Comparison of the contaminant levels in sediment in the central sector of the North Sea illustrates the importance of sediment type in determining the overall levels of contamination found. Data from analysis of UK offshore oil and gas environment surveys 1975-1995 (UKOOA, in press) highlights a clear trend of increased levels of contaminants in fine, muddy sediments in the northern North Sea compared to the coarser sandy sediments of the southern North Sea.

The analysis of sediment samples taken in the mid to late 1980s reveal elevated levels of THCs compared to the present day, and this is probably related to the concurrent period of intensive oil field developments and the heavy use of OBMs [see comment above].

In general, sediment contamination tends to be very localised, for example within an area of about 500 m around most platforms the sediments are typically contaminated by hydrocarbons and a range of other compounds, and this is true for all sectors where there is production activity. This is due to the rapid fall-out of discharged drill cuttings to the seabed, leading to the formation of large, discrete, piles of cuttings below platforms. However, there is a high degree of variance in the data indicating that individual platforms do vary widely in the quantity and areal extent of their contamination of sediments.

Where samples have been collected at distances in excess of 5000 m from the source of discharge, and the levels of THCs in the sediment are high, it is thought that these may be due to other sources of contamination, for example, from the shipment of Middle East crude oil owing to the high levels of certain hydrocarbons which are typical of this type of oil (UKOOA, in press). However, there are at present few observations, as detailed analysis of far field sediment samples has rarely been carried out. Phenanthrenes and dibenzothiopenes show a significant reduction in the central and northern sectors in latter years, perhaps reflecting the change from diesel based drilling muds to other types of fluids (UKOOA, in press).

Law and Fileman (1985) showed that THCs of sediment samples collected from sites in the North Sea, English Channel, Irish Sea and a number of estuarine areas ranged from 0.27-340 $\mu g\ g^{-1}$ (dw) of Ekofisk crude oil equivalents. The highest THC found in offshore samples was 120 $\mu g\ g^{-1}$ in the gas field area off north Norfolk. High THCs were also found in the central and northern part of the North Sea, 33$\mu g\ g^{-1}$ and 17$\mu g\ g^{-1}$, respectively. There were no operational hydrocarbon discharges near the sampling site for the central North Sea, but the northern sampling site was in an area of oil production, close to the many fields around the Ekofisk complex.

Between 1 and 1.5×10^6 t of drill cuttings are currently estimated to lie on the sea floor of the North Sea (USEIA, 1998). Considerable amounts of oil adhering to drill cuttings have contaminated the seabed locally. In a study of 12 well sites on the Dutch continental shelf where OBM cuttings have been discharged during the 1980s and early 1990s, the chemical analysis revealed elevated oil concentrations at five of the locations, and traces of oil visually observed at another two locations (Dann and Mulder, 1996). Maximum concentrations, measured over the upper 10 cm layer were generally in the order of 10-50 $\mu g\ g^{-1}$, but at one location a concentration of 200 $\mu g\ g^{-1}$ was found. Elevated oil concentrations only occurred within the first 100–250 m from the platforms and it is suggested that the zone where persistent biological effects may be expected on the benthic community generally, extends to a maximum radius of 200 m from OBM discharge sites. In the Norwegian sector, a survey of 14 fields showed that hydrocarbon contaminated sediments could in some cases extend to 2-8 km from the fields (Bakke *et al*., 1996; OSPAR Commission, 2000).

By contrast, studies on the *Leman* and *Thames* Gas Fields in 1987, revealed that in this area of the North Sea, turbulence and unstable mobile sediments quickly disperse discharged drilling materials away from the platforms. Furthermore, relatively few wells are drilled at each site compared to drilling for oil in the northern North Sea. It seems probable however, that in such high energy areas any anthropogenic influences may be subsidiary to the effects of natural processes on the benthos, other than on a very local scale (MAFF, 1990).

THCs around the Ravenspurn gas field development were found to be generally low, with a tendency for slightly higher values at stations closest to the field. For example, in an area to the north of Ravenspurn, concentrations of THC ranged from 5.8-18 μg g^{-1} dry mass Ekofisk crude oil equivalents, which were marginally higher than those previously recorded for the same area prior to production (1.0-11 μg g^{-1}; Law and Fileman, 1985). In addition elevated values of 25-44 μg g^{-1} THCs were noted to occur in sediments located in the direction of the tidal ellipse. It was also noted that the degree of weathering increases with distance from the platform. The increased levels of THCs in sediments in the immediate vicinity of the Ravenspurn platform is in line with that seen at many other installations (Davies *et al.*, 1984a and 1989). In the case of the Ravenspurn platform values of more than 1000 times the background levels of THC were measured within 500 m of the platform, with background concentrations not being re-established until some 3,000 m downstream of the discharge.

Stagg *et al.* (1995) highlights the significant levels of sediment contamination by base oil, composed of unresolved mixtures of aliphatics and n-alkane compounds in the immediate vicinity of several platforms studied in the northern North Sea.

Dann *et al.* (1992), analysed sediments along a transect aligned with the tidal ellipse one year after drill cutting discharges had ceased. The analysis revealed a clear gradient in contamination levels, with oil concentrations ranging from 250-450 μg g^{-1} dry sediment within 250 m of the source and gradually decreasing to <20 μg.g^{-1} beyond about 750 m. Barium concentrations showed a similar pattern of response.

4.3.2 PAH

Offshore, the most common type of PAHs are naphthalene, phenanthrene, chrysene and benzo[*a*]pyrene with total PAH concentrations generally found to vary between 0.028 and 0.2 mg kg^{-1} (OSPAR Commission, 2000). There is some evidence to suggest that the levels in sediments in the northern North Sea are higher than in the southern North Sea (Table 17). However most studies determine only parent PAHs and in oils generally, alkyl substituted PAH predominate over the parent compound. Furthermore, the number of parent PAHs determined is usually limited.

Table 17 Background concentrations of some PAHs, adapted from OSPAR Commission, 2000.

PAH	Sediments (ng g^{-1} dw)	
	Northern North Sea	Southern North Sea
Benzo[*a*]pyrene	8.8 – 112	<0.2 - 51
Fluoranthene	14 – 160	0.72 - 97
Benzo[*b*+*k*] fluoranthene	46 – 434	1.1 - 142
Benzo[*b*] fluoranthene	-	-
Indeno[1,2,3-*cd*]pyrene	43 – 212	<0.2 - 70

Klamer and Fomsgaard (1993) analysed offshore surface sediments for total PAH in the <63 micron sediment fraction and found values to vary between 0.7-2.7 mg kg^{-1}. At other sites concentrations of PAHs are low or undetectable (MPMMG, 1998; CEFAS, 1998).

Low molecular weight PAHs such as naphthalenes, phenanthrenes and dibenzothiophenes show trends of increasing levels towards inshore/coastal areas of the North Sea (Figure 9). These compounds and their alkylated derivatives are usually associated with diesel contamination, and so are more likely to be related primarily to shipping and land-based sources rather than offshore oil and gas production. General shipping traffic in the southern sector is likely to be denser than in the open sea further to the north. For example, the main lanes run from the German Bight via Europort and down through the Dover Strait, and from the German Bight to the NE ports and Felixstowe in the North Sea. Other metal contaminants in central and southern sectors also display a longitudinal trend of increased levels towards the west (closer inshore), providing further evidence that some of these contaminants may be derived from coastal discharges, runoff, rivers and estuaries. Some PAHs and other hydrocarbon compounds show a temporal trend of reducing background levels with the northern and central sectors. This trend might be related to the discontinuation of the use of diesel based drilling muds in the mid 1980s (UKOOA, in press).

Naphthalene concentrations around 5 North Sea oil production platforms in 1981, can be seen rising from 21 to 811 ng g^{-1} (dw) at distances from 5 to 0.5 nm from Thistle and from 31 to 74,700 ng g^{-1} at distance 5 to 0.5 nm from Beryl (Law and Fileman, 1985).

4.3.3 PCB

Data on CBs in sediments generally show the same distribution as observed for metals in sediments, with higher concentrations tending to be found in areas where fine-grained sediments are deposited, such as in estuaries, fjords and certain coastal areas (Andersen *et al*., 1993).

Individual CB congeners are commonly detected in sediments but levels are generally low in the western North Sea (less than 2 µg kg^{-1}), with the highest levels measured in the Forth estuary (ΣPCB_7 6.8-11.3 µg kg^{-1}), but values are much greater in the eastern parts of the North Sea (Table 18). Concentrations in the open sea are generally less than 1 µg kg^{-1} (OSPAR Commission, 2000).

Table 18 PCB background/reference concentrations in surface sediments (OSPAR Commission, 2000)

PCB	Sediments (µg kg^{-1} dw)	
	South Norway/Skagerrak	**German Bight**
PCB-2831	-	680
PCB-5232	-	260
PCB-101	62	730
PCB-153 (Figure 10)	90	1650
PCB-138	116	1200
PCB-180	60	600

Klamer and Fomsgaard (1993), analysed surface sediments in the <63 µm fraction off the Humber and recorded total CB values in the order of 2.92-19.07 µg kg^{-1}.

Wells *et al.* (1988), reported on PCB contamination immediately after the Piper Alpha disaster of 1988. A total of 75 seabed sediment samples were taken from the seabed surrounding Piper Alpha which revealed that the level of CBs were significantly above baseline concentration (>5µg kg^{-1}) in all but 10 of the samples. Indeed, 14 samples had levels >100 µg kg^{-1} with the max concentration of 1,917 µg kg^{-1} found relatively close to the original site of the platform.

4.3.4 Metals

Concentrations of all metals at offshore sites were relatively low compared with those of estuaries. (MPMMG, 1998 - Figures 11-17). For mercury, riverine inputs are clearly the dominant source, which is reflected by elevated mercury concentrations in the sediments of some Norwegian fjords, along the Swedish west coast and in some English estuaries. In contrast, except for the area north of the Dogger Bank, the central parts of the North Sea have sediments containing mercury concentrations falling within typical values.

Higher concentrations of lead in sediments were found in the Scheldt Estuary, the Baie de Seine, on the north-east coast of England and in the Norwegian Trench.

It may be deduced from these observations that the coast in general, and rivers in particular, are sources of trace metals. In addition to natural sources, sediments may be contaminated by shore-based industry, especially around large conurbations. Coastal areas of particular note for relatively high sediment metal concentrations are the German Bight and the area off north-east England. Both areas reflect the effects of industry and to some degree, mineralisation in the catchment areas.

The Dogger Bank is an offshore area where cadmium concentrations are relatively high. The fact that the sediments between the nearest industrial or mineralised source (north-east England) and the Bank do not show elevations, together with consideration of the water circulation in the North Sea suggest that the metals found on the Bank are not derived directly from the coast. However, some recent work under taken by CEFAS (J. Brown, *pers. comm.*), shows jet flows associated with summer stratification moving from the UK coast near Flamborough Head, directly to the Dogger Bank, which may provide the direct transport pathway for contamination derived from the UK east coast. This combined with the fixation of metal in sediments by sedimenting phyto-plankton after the spring bloom could give rise to the elevated levels at this specific location.

Kingston *et al*. (UKOOA, in press), comments that measurements of barium show a trend of increasing levels from the southern North Sea to the northern North Sea. This trend, like that of THCs, is closely linked to the spatial distribution of sediment types. However, certain metals, (Pb, V, Cu and Fe, in particular) show trends of increasing levels in the southern part of the North Sea, but it is considered that these contaminants are mainly derived from terrestrial and shore based sources.

In nearly all cases, gross contamination by metals extends no further than 500 m downstream from production platforms (Table 19). In the northern and central sectors the level of contamination and the variety of metals which contribute to this contamination are much greater than in the southern sector. Barium, however, shows evidence of elevated levels in the area within 500 to 1,000 m of the platforms.

Table 19 Mean levels of metals at selected distance increments from active platforms in ppm (from UKOOA, in press)

Metal	**0-500m**	**501-1000m**	**1001-1500m**	**1501-2000m**	**2001-3000m**	**3001-4000m**	**4001-5000m**	**>5000 m**
Barium - bioavailable	1754.74	724.6	443.18	392.46	294.08	385.7	232.41	238.67
Barium - total	33562.12	1116.67	1192.36	955.24	532.02	631.75	434.06	320.26
Cadmium - bioavailable	0.38	0.05	0.35	0.04	0.05	0.08	0.05	0.05
Cadmium - total	0.85	1.26	5.56	1	0.95	0.2	0.56	0.43
Chromium - bioavailable	13.36	7.62	8.18	8.02	6.91	8.24	8.32	6.71
Chromium - total	34.68	27.55	30.49	30.47	26.66	18.85	19.73	17.73
Copper - bioavailable	13.65	2.78	2.65	2.91	2.53	3.24	2.47	2.2
Copper - total	17.45	8.25	7.25	7.15	7.34	8.96	4.78	3.96
Nickel - bioavailable	9.79	6.16	6.51	4.47	5.14	4.5	5.26	5.71
Nickel - total	17.79	14.36	15.36	16.64	13.72	9.18	9.81	9.5
Lead - bioavailable	63.62	11.05	8.28	7.94	7.33	8.03	6.72	5.34
Lead - total	57.52	18.86	16.34	13.68	13.08	11.7	12.14	12.12
Vanadium - bioavailable	16.08	12.24	10.86	10.81	10.24	11.32	11.99	11.48
Vanadium - total	32.61	25.39	27.22	22.85	20.94	16.22	19.17	20.15
Zinc - bioavailable	94.28	17.45	13.49	13.31	12.1	14.91	13.16	12.58
Zinc - total	129.74	33.82	38.5	27.3	35.83	21.43	26.15	20.87
Iron - bioavailable	8842.86	5526.97	4820.21	5149.24	4280.44	5022.03	5480.61	4162.04
Iron - total	14096.14	12822.08	11484.38	14505.79	9665.61	8793.78	7637.47	7052.83
Mercury - bioavailable	0.15	0.05	0.03	0.05	0.05	0.04	0.04	0.04
Mercury - total	0.36	0.24	0.22	0.26	0.25	0.33	0.18	0.16

4.3.5 Alkylphenols

Although there is some concentration data for alkylphenolic chemicals in sediments in UK estuaries (Blackburn *et al*., 1999) there is a lack of data for alkylphenols from offshore sediments. High levels of octylphenol and nonylphenol ethoxylates (OPE and NPE, cleaning agents with an endocrine disruption capacity) were found in sediments in the River Scheldt, at 20 $\mu g\ kg^{-1}$ and 300 $\mu g\ kg^{-1}$ respectively, and in the Elbe at 5.6 $\mu g\ kg^{-1}$ and 107 $\mu g\ kg^{-1}$ respectively. In the UK, the OPE levels varied between less than 0.1 $\mu g\ kg^{-1}$ and 15 $\mu g\ kg^{-1}$ and the NPE levels between 23 and 44 $\mu g\ kg^{-1}$ (OSPAR Commission, 2000).

4.3.6 Summary

Trends in the concentration and distribution of contaminants in sediments, particularly hydrocarbons (HCs), are similar to those described for surface water contamination (Table 20). There are, however, some notable exceptions. For example the levels of certain metals appear higher in the southern North Sea compared to the northern North Sea (Pb, V, Cu and Fe). Recent work on seasonal current circulation patterns within the southern North Sea provides a possible explanation for the source of the contaminants being of coastal origin.

Table 20 Summary of contaminant levels typically found in surface sediments from the North Sea

Location	**THC (µg g^{-1})**	**PAH (µg g^{-1})**	**PCB (µg kg^{-1})**	**Ni (µg g^{-1})**	**Cu (µg g^{-1})**	**Zn (µg g^{-1})**	**Cd (µg g^{-1})**	**Hg (µg g^{-1})**
Oil & Gas Installations	10-450[1]	0.02-74.7[2]	1,917[6]	17.79	17.45	129.74	0.85	0.36
Estuaries	-	0.2-28[5]	6.8-19.1	-	-	-	-	-
Coast	-	-	2	-	-	-	-	-
Offshore	17-120[2]	0.2-2.7[3,4]	<1[4]	9.5	3.96	20.87	0.43	0.16

[1] Dann *et al.*, 1992, [2] Law and Fileman, 1985, [3] Klamer and Fomsgaard, 1993,
[4] OSPAR Commission, 2000, [5] CEFAS, 1998, [6] Wells *et al.,* 1988, [7] UKOOA, in press

4.4 Biota

4.4.1 THC

Stagg (1994) highlighted that dab exposed to oil-based drill cuttings accumulate base oil and aromatics in a concentration dependent manner. The overall concentrations reached in the liver and muscle of the fish are low and yet exposure regimes are typically high, particularly in close proximity (500-1,000m) to oil platforms in the northern North Sea. McIntosh *et al*. (1990) analysed samples of commercial fish (152 cod, 16 plaice and 23 dab were collected), from as many ICES squares as possible in the northern North Sea. None of the fish which were analysed were considered to be tainted. However, an oily taint was found in plaice caught within 5 km of platforms that form a cluster of between 9 and 18 drilled wells in any one area.

Johnsen *et al.* (1996), were unable to detect a significant increase in hydrocarbon levels in fish caught in the vicinity of oil and gas production fields compared to remote reference areas on the Norwegian continental shelf. A slight elevation in concentration of THCs was observed in haddock from the northern North Sea but further interpretation of the results showed that sources of hydrocarbon contamination varied within the total sampling area. This observation suggests that local discharge sources in areas with high petroleum production are most likely to be the source of hydrocarbon contamination in fish in this area.

Moe *et al.* (1994) obtained samples of a number of fish species at different North Sea oil-field sites. Petrogenic contamination of different origin was observed in almost all samples, though tainting (assessed by organoleptic testing of cod), was not found.

Stagg and McIntosh (1996), measured the concentration of oil in water and the associated effects on fish larvae, along two North-South transects between 57°N and 62°N at longitude 1°E and 1.5°E, within the northern North sea. Results show a distinct north-south gradient in the hydrocarbon concentration peaking around installations associated with oil and gas exploration and production. Depth averaged data show that the mean concentration in the top 50 m was between 3-4 µg l^{-1} at latitudes 56°N and 59°N, falling to values of 0.2-0.5 µg l^{-1} in the more pristine waters to the north and west. The results suggest a significant elevation of hydrocarbons in a large area of the northern North Sea (5-10 times higher than background levels) which, at these concentrations, would have deleterious effects on fish larvae.

4.4.2 PAH

Moffat *et al.* (1998), studied PAH concentrations after an oil spill at the Captain field. The PAH concentrations in haddock muscle from reference sites were generally <15 ng g^{-1}. There were no significant differences between the impacted zone and reference site samples for haddock PAH.

Recent field experiments in the Tampen area on the Norwegian shelf have shown significantly increased levels of PAHs in caged mussels and passive samplers up to 10 km away from the nearest produced water discharge sites. The levels in mussels ranged from 2.5-140 times the local background concentrations, depending on their distance from the site of discharge (OSPAR Commission, 2000).

The concentrations of both aliphatic and aromatic hydrocarbons in the liver showed a significant negative regression to distance from the platform. It was concluded that the source of PAH accumulation in the fish was unlikely to be sediment. Elevated concentrations of hydrocarbons were measured in mussels deployed in cages at 5 m depth and up to 10 km from the Brent oil platform in the North Sea. These data suggest that there are bioavailable hydrocarbons in seawater at considerable distances from platforms in the North Sea. Furthermore, hydrocarbons in water are the main route of uptake for fish following oil spills (see for instance Law & Hellou, 1999). An alternative source of contamination is uptake from the diet; however, few measurements of PAHs in invertebrates have been made in the North Sea, particularly those known to be consumed by fish as food (Somerville *et al.*, 1987).

Solé *et al.* (1998), stated that whole body total PAHs were likely to be 57-206% higher in *M. edulis* from the Skagerrak, Norwegian and Swedish sites (up to 62 ng g^{-1}) compared with the Faroe Islands.

Toril and Ståle, (1999) used semi-permeable membrane devices (SPMDs, lipid filled membranes used for sampling organic compounds from seawater) and blue mussels (*Mytilus edulis*) to determine the bioavailable fraction of PAHs from oil produced water in the North Sea. The SPMDs reflect the water-soluble fraction of the PAHs, which is probably the most important route of exposure for organisms living in the water column and presumably the only fraction available for uptake by a respiratory route. Residues in the mussels represent both water soluble and particle-bound fractions and give information about bioavailability of PAHs for organisms at higher trophic levels. In both SPMDs and mussels, the concentration of PAHs increased significantly towards the discharge point, with the strongest contribution from the lower molecular weight compounds (naphthalene, phenanthrene, dibenzothiophene, and their C_1-C_3 homologues).

4.4.3 PCB

For fish and shellfish, the general pattern shows higher CB concentrations in samples taken from the southern North Sea compared to those collected in the northern North Sea. Figure 18 shows concentrations of seven individual chlorobiphenyl congeners in cod liver from three areas of the North Sea (1979 - 87), and a clear gradient in concentration from north to south, towards the area of greatest inputs (Source: de Boer, 1988; Andersen et al., 1993).

Concentration of PCBs in dab liver off UK coasts were found to be less than 0.1 µg kg^{-1}, except in the Thames estuary (ΣPCB_7: 0.19 µg kg^{-1}) and the Forth estuary (ΣPCB_7: 0.355 µg kg^{-1}) where these were the highest values recorded for the western North Sea.

For blue mussel samples collected along the coast of Norway, mean concentrations were generally about twice the background levels. The mean concentrations of the CB153 congener in blue mussel tissue from the coasts of Germany and Belgium are on average about 12 times greater than background levels. The ΣPCB_7 levels off the German coast vary from 1.5-15 times the background levels. Along the coast of Norway, the mean concentrations of CB153 were about twice as high as the background levels for blue mussels, in all but a few sites (OSPAR Commission, 2000).

A spatial trend for PCBs in fish liver was observed in the North Sea, with the highest values being found off the Thames. There was a general decrease northwards towards the Dogger Bank area where concentrations were all in the lower JAMP categories but, for whiting, 'medium' category values were generally obtained in the area between Thames and the Outer Silver Pit. In previous years, concentrations have been higher in samples from this area (Figure 19) (see MAFF, 1990; MAFF, 1992). No values above 0.1 mg kg^{-1} for the ICES sum of seven CB congeners (Σ7CBS) were recorded in the North Sea area (Figure 20).

Wells et al. (1988) reported on PCB contamination immediately after the Piper Alpha disaster of 1988. Fish did not contain CBs in the filleted edible tissue above the normal range found in other North Sea fish, 402 - 862 µg kg^{-1} (de Boer, 1988), and pink shrimps also obtained close to Piper Alpha did not contain any measurable level of CBs. Samples of pink shrimp from the Fladen Ground contained 54 µg kg^{-1} (not above baseline) in the exoskeleton, and none was detected in the abdomen. Mussels obtained from the platform legs contained concentrations of CBs of 10.8 µg kg^{-1} whereas typical baseline values obtained from mussels around the Scottish coastline also contain between 10-100 µg kg^{-1} of CBs. Generally, all the concentrations of CBs measured in fish and shellfish between July 1988 and February 1989 were within baseline values found elsewhere in the northern North Sea and other relatively uncontaminated waters.

Wells et al. (1991) reported again on Piper Alpha in 1991 and this indicated that PCB concentrations found in fish and shellfish were still low. All but one fell into the lowest contamination level category in respect of the guidelines adopted for the JMP of OSPAR - <10 µg kg^{-1} of PCB in non-fatty fish muscle and shellfish, <2,000 µg kg^{-1} in round fish liver, and <500 µg kg^{-1} in flatfish liver. Comparable studies of fish in the North Sea have generally found levels higher than these. Dab, rough dab and plaice from north of 56ºN have concentrations of PCB in the liver of between 180-18,250 µg kg^{-1} with a mean value of 660 µg kg^{-1} (Knickmeyer and Steinhart, 1990), compared to 369 µg kg^{-1} found in the liver of the 'witch' fish near Piper Alpha. Cod livers from north of 57ºN were found to have a mean concentration of 844 µg kg^{-1} PCB (de Boer, 1988), compared to 396 µg kg^{-1} found off Piper Alpha. Fish taken from the southern North Sea have substantially higher levels of PCB than fish found further north. For example, whiting off the Dutch coast contain between 63-

12,473 µg kg^{-1} PCB with a mean of 4,530 µg kg^{-1} (Westerhagen et al., 1989). The mean concentration of PCB in whiting liver off Piper Alpha was 238 µg kg^{-1}.

4.4.4 Metals

The mean concentration of Hg, from samples around the UK coast, was between 0.3-0.11 mg kg^{-1} (ww), similar to that (0.05-0.12 mg kg^{-1}) found in dab samples collected in 1989-91 (MPMMG, 1998).

Concentrations of Hg are generally low, with virtually all values in or near the lower JAMP category for both fish and mussels. In an earlier study of dab from the southern North Sea, Claussen (1988) noted a clear decrease in Hg levels from the coast to the open sea. There was little evidence of such an obvious spatial trend in the work of Claussen, though some relatively high concentrations were found in fish samples from the Thames up to a mean of 0.14 mg kg^{-1} (ww) in whiting. Earlier work by MAFF (1990) indicates that concentrations of mercury in dab from the Humber estuary - 0.22 mg kg^{-1} (ww), are considerably higher than reported here (Figure 21).

Concentrations of Hg in dab collected in 1994 were generally low at or near the JMG 'lower' level category - <0.1 mg kg^{-1} (ww) in most areas (CEFAS, 1998) (Figure 22).

Levels of Cu in fish muscle were generally less than 0.3 mg kg^{-1} (ww) (i.e. in the lower half of the expected ranges). Concentrations in the fish liver were much higher than those in muscle (by a factor of 10 or more), but there appeared to be no clear spatial pattern in the results. Although differences between samples were not great, the highest concentration in mussels -1.8 mg kg^{-1} (ww), occurred in the Humber area (Bull Fort and Cleethorpes). These stocks are not known to be commercially exploited, but even here the Cu values were considerably less than the Food Standards Committees' recommended limit (MAFF, 1992).

The picture for Zn in fish was similar to that for Cu, with concentrations in muscle being within the expected range - up to 6.0 mg kg^{-1} (ww). Values in the liver, though generally about ten times higher, showed no obvious spatial pattern. As in earlier work (MAFF, 1990), highest levels in mussels occurred in the Tyne area - 49 mg kg^{-1} (ww). Concentrations in all samples, including those from stocks which are not commercially exploited (such as the Tyne) were therefore less than the Food Standards Committees' guideline value of 50 mg kg^{-1} (ww) (MAFF, 1992).

Claussen (1988) reported relatively higher Cd levels in the livers of dab taken from the Dogger Bank when compared with adjacent areas off the coasts of Britain and Germany. In the present study, results were variable but some relatively high values - >0.4 mg kg^{-1} (ww), were recorded in both whiting and dab livers from stations on the Dogger Bank (Figure 23). The highest concentration found, apart from Dogger Bank, in the liver was 0.60 mg kg^{-1} (ww). Cd is normally present in very low levels in fish muscle and for those fish found to have relatively high Cd in the liver, concentrations in muscle samples were only ~0.005 mg kg^{-1} (ww). As in previous years, the maximum concentration of cadmium in mussels taken from the east coast of England occurred in the Humber.

The maximum value for Cd in fish liver, found in the earlier North Sea survey, was 0.96 mg kg^{-1} (ww) with a median of 0.18 mg kg^{-1} (Figure 24) (MPMMG, 1998). Concentrations of Cd in dab liver, were generally below 0.2 mg kg^{-1} (ww), except in the area offshore of the Tyne-Humber previously identified as a hot-spot (Figure 22).

Levels of Pb in fish liver were all below the limit of detection for the analytical method used. Concentrations in mussels showed a spatial pattern, which was similar to earlier work, with the highest values being found along the north-east coast.

0.03 mg kg^{-1} (ww) was recorded in the Moray Firth (MPMMG, 1998). Concentrations of lead in dab liver above 0.2 mg kg^{-1} were found only off the Tees and Humber (Figure 25).

4.5 Other Production Chemicals

4.5.1 Volatile aromatic hydrocarbons

Concentrations of volatiles were generally found to decrease with increasing salinity to levels below the limits of detection in samples taken from the near coastal sites and offshore stations (Dawes and Waldock, 1994).

Aromatic hydrocarbon residues, from produced water, are dominated by mono-aromatic (BTEX and phenols) and lower molecular weight PAHs. These are considered to be the most acutely toxic components of the organic contaminants in produced water (Slager *et al.,* 1992), although heavy metals and high concentrations of naturally-occurring organic acids from the formation may also contribute to the observed toxicity (Slager *et al.,* 1992).

4.5.2 Corrosion inhibitors, scale inhibitors, gas treating chemicals

Grigson *et al*. (2000), stated that corrosion inhibitors partition primarily to the aqueous phase, while demulsifiers partition primarily to the oil phase of produced water. Scale inhibitors were found to be discharged in the produced water at the concentrations they were dosed. Marine sediments in the proximity of two North Sea oil platforms contained low levels of benzalkonium quaternary ammonium salts (0.74-10.84 ng g^{-1}), typical corrosion inhibitor chemicals.

4.5.3 Summary

In most, if not all cases the high concentrations of some contaminants in sediments within 500 m of producing platforms are due to cuttings discharge. The effects on benthic communities can be observed out to 3 - 5 km, though this reduces rapidly following cessation of discharges. Although significant quantities of chemicals are being discharged in the produced water the rapid dilution and dispersion of them mitigates for their effect. Hydrocarbons (HCs), polycyclic aromatic hydrocarbons (PAHs) and chemicals can be detected at elevated (relative to background) levels close to the source of discharge, however, subtle biochemical signals can be seen much further away, but their significance at the individual and population level is largely unknown.

In relation to concentrations of relevant determinants sampled throughout the sea area as a whole it is noteworthy that water samples with the highest levels of chemical contamination are found at inshore estuary and coastal sites subject to high industrial usage. Where, for example, concentrations of THCs are found to be high offshore, it is in the immediate vicinity of installations with concentrations falling to background levels within a very short distance from the discharge. Trends in the concentration and distribution of contaminants in fish, particularly hydrocarbons, are similar to those described for surface water contamination. There are, however, some notable exceptions. For example, the levels of certain metals in fish appear higher in certain parts of the southern North Sea, particularly in the vicinity of the

Dogger Bank, compared to the northern North Sea (e.g. Pb, V, Cu and Fe). As already stated, recent work investigating seasonal current circulation patterns within the southern North Sea may offer an explanation for a mechanism (pathway) by which coastal contaminants move offshore without being widely dispersed.

5. BIOLOGICAL EVIDENCE OF INDUSTRY CONTAMINATION

5.1 Introduction

There are essentially two main sources of potential biological effect upon marine organisms that are associated with oil and gas production activities; those caused by production discharges i.e. produced water and those associated with drilling activities. Aerial emissions may also give rise to deposition of contaminants (in particular the lower molecular weight compounds such as naphthalene and pyrene) on the sea surface. These may become bioavailable to aquatic organisms but are not considered further in this section because of the relatively small contribution to the contaminant load in the marine environment.

Exposure of marine organisms to contaminants occurs by two routes, either through passive diffusion or active uptake processes via surface membranes, or through absorption from the gut in association with fatty materials. Organisms spending the majority of their life-cycle in the water column are therefore likely to receive the highest exposure to contaminants that remain in solution. Contaminants that are/or become readily associated with suspended particles are likely to become associated with the sediments. The main exposure route for particle bound contaminants will be through direct ingestion by various benthic species or indirectly when these same species are consumed by other organisms. In addition those organisms living in close association with the sediments may also absorb contaminants from interstitial water.

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

The effects of contaminants upon biological systems can be manifested at a number of different levels of organisation. Effects may occur at the cellular or organ level (where various biochemical or histopathological changes may be measured), to changes in behaviour or viability of individual organisms, through to changes in the size of populations and ultimately to altered diversity and functioning within the community of interacting populations. Changes that occur at the cellular and organ level may provide an ‘early warning system’ of more dramatic and possibly irreversible effects upon populations or communities. The occurrence of various biological effects following exposure to contaminants that are predominantly associated with oil and gas exploration and production activities are discussed in relation to data from laboratory studies and from monitoring programmes.

5.2 Biomarkers of contaminant exposure

Changes that occur at the biochemical, cellular or organ level in an organism as a result of contaminant exposure could aid the identification of the responsible contaminants and their source. Any changes of this kind which, respond in a consistent and measurable way to a chemical or class of chemicals can potentially be used in biomonitoring of the presence and effects of significant pollutants.

A range of biomarkers that can identify exposure to PAHs and other contaminants that may be associated with offshore exploration and production activities are now available. Some of the more commonly used biomarkers are described below:

5.2.1 EROD Induction

The mixed function oxygen (MFO) system of vertebrates is a group of enzymes that catalyse the conversion of endogenous or exogenous lipophilic substrates to more polar products. They occur in the smooth endoplasmic reticulum, require oxygen NADPH and a cytochrome P450 monooxygenase isoenzyme, and they are inducible. Under normal conditions their activity is relatively low but if the organism is exposed to certain compounds, the MFO activity increases, apparently to enhance the detoxification of the inducer.

The induction of the cytochrome P450 component of the system can be readily assessed through the *in vitro* measurement of 7-ethoxyresorufin-O-deethylase (EROD) activity. For pollution monitoring, its measurement is largely confined to mammals and fish since it is expressed at very low or undetectable levels in invertebrates. MFO metabolism is particularly important when dealing with the effects of PAH, since its activity on this group of compounds can create the production of genotoxic intermediates which can damage DNA and lead to neoplasia (see below). It has been suggested (Kruner *et al.*, 1996) that, in general, EROD activities above 0.8 nmol min^{-1} mg^{-1} protein are indicative of a strong pollution influence. However, it must be borne in mind that baseline levels can vary substantially depending on the species and hence what level is deemed significantly elevated can also vary. EROD has been induced in the laboratory at sedimentary PAH concentrations as low as 1000-1300 µg kg^{-1} (dw) (Payne *et al.*, 1988; van Veld *et al.*, 1990). The OSPAR NOEC for oil in sediment around oil and gas installations is 10 µg g^{-1} dry mass or 2-3 times above background levels. Very high sedimentary concentrations of PAH can be lethal to fish (81000-322000 µg kg^{-1} (dw) ΣPAH; Roberts *et al.*, 1989) but the major concern with respect to these compounds is the carcinogenicity of some congeners e.g. benz[a]anthracene, chrysene, and benzo[a]pyrene.

Many studies have measured EROD induction in a variety of fish species in the marine and estuarine environments, as part of national and international monitoring programmes (e.g. CEFAS, 1998; CEFAS, 2000; Kirby *et al*, 2000; MPMMG, 1998). Relatively few of these have focussed on monitoring effects specifically associated with oil and gas production platforms. However, there is some evidence to suggest that monoxygenase activity is elevated in those areas impacted by the oil industry, and these are reviewed below.

In a series of laboratory experiments, Stagg (1994) exposed dab (*Limanda limanda*), a bottom living flatfish, to drill cuttings for 30 days in order to investigate the accumulation of hydrocarbons and associated biological effects. Concentrations tested reflected those found in sediments within 500-1000m of oil platforms in the northern North Sea. Although the fish accumulated base oil and aromatics derived from the oil in a dose-dependent manner, concentrations were low. EROD was not induced and there were no histopathological effects attributable to cuttings exposure. The lack of EROD induction was attributed to several factors, including the low level of aromatics in the drilling fluid. The fact that the aromatics present were 2-3 ring as opposed to 4-6 ring which are the most important inducers, and the possibility that the base oil contained an EROD inhibitor were also considered to be important contributing factors.

Dab caught at various distances from a group of oil platforms in the northern North Sea had elevated hepatic EROD and eECOD activity in both male and female fish caught close to the platforms. The increases in EROD level were more marked in females (10-20 fold increase) compared with males which exhibited a four-fold increase for both EROD and eECOD. Elevation of another biomarker, aryl-hydrocarbon hydrolase (AHH - analogous to EROD) which was attributed to hydrocarbon contamination, was also recorded in cod and whiting caught around several North Sea installations compared to those caught at more distant locations (Davies *et al.*, 1984b). Lange *et al.* (1992) found EROD activity to be higher at some locations in the northern North Sea which was tentatively ascribed to effects from oil platforms. Stagg *et al.* (1995) caught dab at various distances from a group of oil platforms in the North Sea and measured hepatic EROD activity. Fish caught within 20 km of the platforms had significantly elevated activity. A comparison of PAH levels in fish livers and sediment indicated that there was little relationship between the two, implying that the source of PAH accumulation was unlikely to be sediment. It was postulated that bioavailable hydrocarbons in water and/or hydrocarbons in invertebrates that the fish feed upon were the possible routes of exposure for the fish studied in this work.

The North Sea Task Force (NSTF,1993a) reported that elevated EROD in dab liver at a single station in Subregion 1 were possibly due to the station's proximity to oil platforms in the region. However, since only one station was sampled, there was no gradient of response, making it difficult to interpret the result. Samples of liver from cod caught in the vicinity of oil platforms also contained elevated EROD compared to other stations sampled.

Aas and Klungsøyr (1998) investigated the effects of PAH contamination from offshore oil platforms in the Norwegian sector of the North Sea, in terms of EROD activity in cod (*Gadus morhua*), haddock (*Melanogrammus aeglefinus*) and long rough dab (*Hippoglossoides platessoides*). They found no elevated levels of this biomarker compared to the reference site and concluded that fish populations in the vicinity of the platforms were not affected by contamination from 2-5 ring PAH compounds.

Renton and Addison (1992) measured EROD in dab (*Limanda limanda*) from stations along the German Bight transect in the southern North Sea (a pollution gradient from the Elbe estuary), and at an abandoned drilling site, as part of the ICES/IOC Bremerhaven Workshop (see Stebbing and Dethlefsen, 1992, for details). EROD declined with increasing distance offshore. Fish from the drilling site had EROD levels similar to fish from offshore stations, suggesting that the surface sediments had recovered from any impact of past oil exploration activity.

Another more recent study, again on the German Bight, showed that EROD activity in dab and flounder (*Platichthys flesus*) was significantly correlated with PAH levels in muscle tissues (Westerhagen *et al.*, 1989).

Stagg and McIntosh (1996) measured EROD in sandeel and gadoid fish larvae on two transects in the North Sea that passed through areas of intense oil exploration, development and production activity into pristine waters in the north and west. Although EROD activity in the larvae was highly variable (attributed to net damage), samples taken from the southern end of the transect, where measured hydrocarbons in the water were highest, showed elevated EROD levels indicating that bioavailable PAHs were present in the water column at biologically significant concentrations. Additional work is necessary to determine if such exposure is associated with deleterious effects. Furthermore, the significance of the risk to fish larvae and the threat to fisheries from exposure to water-column PAHs needs to be established, particularly to link PAH exposure with EROD, DNA damage and growth and survival of fish larvae.

5.2.2 Bile Metabolites

PAHs in fish tissues are difficult and impractical to measure since they are rapidly metabolised and excreted in bile. However, analysis of bile for the presence of PAHs and/or their metabolites is a useful tool in aquatic biomonitoring (Britvic *et al*, 1993). Although this biomarker has seldom been used as an indicator of contamination from the oil and gas industry, Kirby *et al.* (2000) showed that laboratory exposure of flounder to 20 mg kg^{-1} benzo[a]pyrene led to clear increases in the levels of bile metabolites, up to an order of magnitude higher than controls. In the same study, wild-caught dab and flounder from Liverpool Bay and the Tyne estuary had significantly elevated bile metabolites compared to fish caught in the reference control estuary.

5.2.3 DNA adducts

DNA adducts are covalently bound addition products formed when electrophilic chemical species attack the nucleophilic sites in DNA. The levels of genotoxin-DNA complexes in bioindicator species can be used as biomarkers of environmental contamination (Lyons *et al.*, 1999). Furthermore, laboratory studies have shown that they play a role in the initiation of chemical carcinogenesis (Miller and Miller, 1981).

Aas *et al.* (2000) performed a laboratory experiment to ascertain threshold effects levels for oil contamination using cod. They measured EROD induction, PAH metabolites in bile and DNA adduct formation after 30 days exposure to 0.06, 0.25 and 1 ppm crude North Sea oil. Exposure-dependent responses were observed for all three biomarkers. The lowest nominal concentration corresponded to a measured PAH concentration of 0.3 ppb. At this concentration EROD activity was slightly elevated compared to controls and PAH metabolites and DNA adducts were also increased. At 1 ppm the level of DNA adducts increased throughout the exposure period and only slightly decreased after the fish were transferred to clean water for 7 days. This information, the authors conclude, provides a useful contribution to environmental risk assessments with regard to oil pollution. The concentrations of oil applied in this study are comparable with levels found under oil slicks (Neff and Stubblefield, 1995). The lowest concentration used is one order of magnitude less than oil concentrations in seawater in the vicinity of platforms in the North Sea - 1-5 ppb (Stagg and McIntosh, 1996). On a related note, pacific herring and pink salmon embryos had increased mortalities after exposure to weathered crude oil at concentrations as low as 0.7 and 1 ppb, and sublethal effects were apparent at 0.4 ppb (Carls *et al.*, 1999; Heintz *et al.*, 1999).

Lyons *et al.* (1999) measured elevated DNA adduct formation and correspondingly high PAH metabolite concentrations in flounder collected from the Tyne estuary, indicating that a proportion of the bioavailable PAH was converted to genotoxic metabolites.

5.2.4 Lysosomal membrane damage

Lysosomes are subcellular organelles present in large numbers in the cells of eukaryotic organisms and have a wide range of functions including digestion, reproduction, membrane repair, developmental processes and protein turnover (Livingstone *et al.*, 2000). Lysosomes can accumulate toxic chemicals, including PCBs and PAHs which are damaging to cells, as well as the normal cellular molecules and pathogens. Uptake of toxic substances leads to breakdown of their membranes and leakage of the contents into the cytosol, resulting in cellular dysfunction or death. Lysosomal damage, expressed as an increase in the permeability of the membrane, is well established as a biomarker of contaminant-induced stress in a variety of marine invertebrates and vertebrates (Moore, 1990).

To date, there have been no specific studies conducted to assess the effects of oil and gas platform discharges (produced water or drill cuttings) on lysosomal membrane permeability in fish or invertebrates (but see section 'ICES/IOC Pelagic Workshop' below). However, laboratory studies of exposure to PAHs and monitoring for general chemical contamination have been performed.

Lysosomal damage has been investigated in mussel (*Mytilus edulis*) digestive gland cells and blood cells following *in vivo* exposure to the PAHs fluoranthene, phenanthrene and anthracene. Either the 'neutral red' technique, where the capacity of the lysosomes to retain the dye, neutral red, is measured (Lowe and Pipe, 1994; Lowe *et al.,* 1995) or a reduction in lysosomal latency (Moore and Farrar, 1985) has been used as a measure of damage. All PAHs adversely affected lysosome membranes. Widdows *et al.* (1982) measured lysosomal latency in mussel digestive cells exposed to low concentrations (6-78 µg l^{-1}) of the water-accommodated fraction of North Sea oil for 4 weeks or 5 months. Long-term exposure to 30 µg l^{-1} significantly reduced the lysosomal latency in experimental mussels, and after 100 days exposure the lysosomal latency was zero, suggesting severe physiological disturbance in the lysosomes.

Environmental monitoring programmes have employed the mussel lysosomal membrane biomarker (e.g., Lowe and Fossato, 2000; Wedderburn *et al.*, 2000; Moore *et al.*, 1999), but not, as is known, in the North Sea. The neutral red technique has been deployed with dab hepatocyte lysosomes as part of the ICES/IOC Bremerhaven Workshop, however (Lowe *et al.*, 1992). Lysosomal membrane integrity was most severely impaired following contaminant exposure at nearshore sites and there was a general improvement in the condition of exposed hepatocytes in samples taken further offshore.

5.2.5 Immune response impairment

Another less commonly used but, nevertheless, important biomarker-type measurement of contaminant effects is upon the immune response. Several different endpoints can be measured; these include lymphocyte counts, lysozyme levels and numbers of kidney antibody secreting cells. Zelikoff (1994) describe in detail the subject of fish immunotoxicology and Livingstone *et al.* (2000) review immunological studies with mussels.

One study pertinent to this evaluation is that of Tahir *et al.* (1993) who investigated the effects of short-term exposure to sediments containing oil-based drilling mud on the immune response of dab. A four-week exposure to 4, 8,12 and 16% w/w affected the various parameters measured, either in an inhibitory or stimulatory manner. The authors concluded that further experiments are required to investigate the *in vivo* consequences of this immune modulation, the effects of longer-term exposure and the potential for return to normal immune responsiveness following transfer to clean water.

5.2.6 Disease induction

Hepatic lesions and a variety of other disease conditions have been detected in marine bottom dwelling fish from contaminated environments (Myers *et al*., 1990). These lesions resemble those induced experimentally in fish (Moore and Myers, 1994) by chronic exposure to PAH-contaminated sediments and diet (Vogelbein *et al*., 1998). Many field studies have now also established the existence of a strong link between the occurrence of these lesions and exposure to contaminants, in particular PAHs (Malins *et al*., 1987). Studies conducted around drilling platforms in the Gulf of Mexico have shown the high prevalence of a range of disease conditions in several species of fish, by comparison to fish from areas distant from the drill site. There are several examples that indicate the existence of a relationship between contamination and disease in the North Sea, however, these are associated with coastal areas with distinct sources of pollution (Vethaak and Rheinhalt, 1992).

5.3 Scope for Growth

Scope for Growth (SFG) is a measure of the energy that is available to an organism for growth and gamete production. Of the food consumed by an animal, part of it is absorbed while the remainder is excreted. From the total energy absorbed, a major portion is used for respiration and a small amount is lost in excretion. The remainder is termed Scope for Growth. Din and Abu (1993) investigated the sublethal effects of three produced waters from oil terminals in Malaysia on the clam *Donax faba*. They found that SFG was reduced from 7-10 J g^{-1} dry tissue h^{-1} in the controls to -9 J g^{-1} dry tissue h^{-1} in produced water concentrations equivalent to their LC_{40}.

Widdows *et al.* (1987) measured SFG and tissue hydrocarbon concentrations in the blue mussel *Mytilus edulis* at sites in the vicinity of the Sullom Voe oil terminal (Shetland) in the North Sea. They found a negative relationship between SFG and the concentration of aromatic hydrocarbons in the tissue. Mussels living in the vicinity of the oil terminal had consistently high hydrocarbon levels (an order of magnitude greater than background) over the 4 year study period, and there was a concomitant decline in SFG at these sites. An order of magnitude increase in the tissue concentrations of 2 and 3-ringed PAHs resulted in a 50% reduction in the growth potential of this species. SFG in mussels was used to monitor changes in environmental quality in the North Sea (Widdows *et al*, 1995). A general trend of decreasing SFG from north to south was observed, reflecting both the major inflow of clean water from the North Atlantic and the overall increase in environmental contamination, with increasing urbanisation and industrialisation towards the south. Specific effects of offshore oil and gas installations were not monitored, although at the majority of sites a large contribution to the decline in SFG was due to PAHs. The proportion of these that derived from oil and gas activities is uncertain.

5.4 Produced Water Toxicity

Van Zwol (1996) summarised available information on the composition of produced water and evaluated potential environmental impacts. Produced water discharges contain a complex mixture of oil dispersed as fine droplets, deposited scale and corrosion products, gas drying agent residues and/or production chemicals. The relative importance of produced water emission has increased due to the reduction in oil contamination from drill cuttings.

There are large differences in the chemical composition of produced waters, each being unique to each production system. Aliphatic oil, monoaromatics and heavy metals account for most of the toxicity observed in produced water on the Dutch continental shelf (Slager *et al.*, 1992). Results show that the aromatic hydrocarbon residues are dominated by monoaromatic (benzene, toluene, xylene and phenols) and lighter polyaromatic residues. These are considered to be the most acutely toxic components of the organic contaminants in produced water, although heavy metals may also contribute to the observed toxicity (Slager *et al*., 1992). However, lack of toxicity data for some chemicals such as PAHs, xylenols, cresols and production chemicals precluded accurate estimation of the acute effects of these components.

The toxicity of produced water may vary greatly e.g. produced water from three oilfields in the Norwegian sector showed large differences in chemical composition and toxicity towards four test organisms (Stromgren *et al*., 1995). The EC_{50} values for these organisms ranged from 0.2 to ca 30% of produced water in the test medium. However biodegradation of the produced water changed the chemical composition and reduced the toxicity. Comparable to this, acute toxicity may vary over three orders of magnitude depending on the test species and produced water tested. The acute toxic effects of produced water to marine species has been widely reported (Somerville *et al.*, 1987; Girling and Streatfield, 1988; Girling ,1989; Brandehaug *et al.*, 1992; Brown *et al.*, 1992; Stromgren *et al.*, 1995; Stagg and McIntosh., 1996). Test species have included bacteria (*Photobacterium phosphoreum*), algae (e.g. *Skeletonema costatum*), bivalves *Mytilus edulis*, *Abra alba* and *Crassostrea gigas*, crustaceans *Artemia salina*, *Acartia tonsa*, *Tisbe battagliai and Mysidopsis bahia* and fish (e.g. rainbow trout (*Oncorhynchus mykiss*)). Zooplankton species tend to be the most sensitive to produced water (Davies and Kingston, 1992), while fish larvae and phytoplankton tend to be more robust (Gamble *et al.*, 1987). Zooplankton appears to be affected at the egg or very early naupliar stages of development. The mechanism suggested for this toxicity is that the hydrocarbons accumulated in the lipid-rich eggs of copepod zooplankton are released internally at the pre-feeding stage when the lipids become exhausted (Davies and Kingston, 1992).

Toxicity in seawaters adjacent to and at a distance from platforms differs depending on specific location. For example, Stagg *et al.* (1996) found that the acute toxicity observed in neat produced water disappeared in water samples taken from around the study platform. Stromgren *et al.* (1995) combined model data for produced water dispersion (diluted to 1-4% at discharge point and to 0.1% 3-4km from platform) and toxicity data, and concluded that acute toxicity was only to be expected in the immediate vicinity of outlets. At a distance of >2km, toxic effects were predicted to be negligible. Davies and Kingston (1992) concluded in their review, that the evidence from experiments suggested that the produced water being discharged into the North Sea would not have a direct toxic effect beyond the immediate vicinity of the platform. This, of course, may change if the chemicals used in the oil extraction process and hence found in the produced water change e.g., increased use of surfactant chemicals for enhanced oil recovery.

Other studies have assessed the effects of produced water on settlement of gastropod mollusc larvae, early life stages of a sea urchin and sublethal effects on a clam species. Raimondi and Schmitt (1992) found that larvae of the gastropod mollusc *Haliotis rufescens* exposed to produced water plumes in the field had a significantly reduced probability of completing the transition to adulthood, and that this effect was directly related to distance from the source and exposure duration. Acute effects of produced water on sea urchin gametes were absent, but sublethal effects were apparent (Krause *et al.*, 1992; Krause, 1994).

5.4.1 Bioconcentration

Recent field experiments in the Tampen area on the Norwegian shelf have shown that caged mussels had significantly increased levels (2.5-140 times normal background concentrations) of PAHs, even up to 10 km away from the nearest produced water discharge sites (OSPAR Commission, 2000). Similarly, Utvik and Johnsen (1999) measured increased PAH concentrations in mussels with decreasing distance from a produced water discharge point. These concentrations were higher than obtained from semi-permeable membrane devices (SPMDs) consisting of polyethylene tubing filled with neutral lipid, because they represented both the water-soluble and particle-bound fraction of PAHs.

However, chemical contaminants originating in produced water discharges were also observed in mussels and SPMDs within 1 km of discharge from Ekofisk 2/4K installation (Durrell *et al*., 2000). The contaminant concentrations decreased rapidly with distance from the platform as was evident from samples collected 5 km, and further, from the discharge. Background contaminant concentrations were reached about 10 km from the Ekofisk area. Barium was the only metal with clearly elevated concentrations in mussels deployed closer to Ekofisk 2/4K, than away from this location. All the approaches used to assess ecological risks of produced water discharges in the Ekofisk region are consistent in showing that because of relatively low toxicity and rapid dilution in the receiving water environment, produced water is likely to pose a very low risk to marine organisms.

5.5 Drill Cuttings Toxicity

Until 1985, the well-drilling process used OBMs and the discharged drill cuttings were therefore heavily loaded with hydrocarbons. Since then, low-aromatic base oils or water-based drilling fluids (WBM) which have lower toxicity have been used. These alternatives, coupled with the ban on sea-discharge of drill cuttings by some countries (not the UK) have led to a reduction in this source of oil contamination. Nevertheless a wide range of other chemicals, metals, surfactants, biocides may be present in different cuttings piles.

The environmental impact of drill cuttings discharges at offshore installations has been extensively studied in most North Sea areas where exploration and exploitation activities have been concentrated i.e. in the British, Dutch and Norwegian sectors. Field surveys in all sectors have generally focused on the effects on macrobenthic infauna communities, and there is no doubt that contamination from oil-based drilling muds has consequences for these communities around production platforms. The arguments have centred upon the distance from a platform that the effects can be found. The primary effect of drill cuttings is physical smothering at the drilling site and toxicological effects on the benthos, including reduction in numbers of sensitive species, increase in abundance of opportunistic species, increased mortality and reduction in diversity. The OSPAR Quality Status Report (2000) briefly summarises current knowledge of biological impacts due to offshore oil and gas activities. It cites a recent review by Gray *et al.* (1999) who conclude that biological changes in benthic communities can be detected up to 5 km from the drilling site, but usually not further than 3 km. The major changes occur up to a maximum of 500-1000 m from the drilling source. These changes are due mainly to the discharge of drill cuttings.

In a survey of effects around the Leman and Thames gas fields in 1987, MAFF concluded that there was no evidence of effects on the benthos, i.e. as indicated by no reduction in diversity or proliferation of pollution indicator species close to the platforms. However, it was recommended that a more intensive survey was required to delineate any gradients and investigate localised effects (MAFF, 1990).

A similar survey of the Ravenspurn gas field was conducted in 1988 and 1989. Total PAH concentration was >3000 µg kg^{-1} 200 m from the platform and rapidly declined with distance from the platform. This finding agrees with data produced in studies conducted by Davies *et al* (1984a, 1989) which showed that PAH concentrations in the sediments were greater than 1000 times background levels within 500 m of a discharging platform, and concentrations returned to background levels approximately 3000 m downstream in the direction of the major current. They also indicated that effects on the benthos from platforms using oil-based drilling fluids were generally confined to within 2 km of the platform, and serious effects (i.e. as impoverished community and/or no fauna beneath or close to the platform) are found only within 500m.

In the North Sea Task Force Assessment report for Subregion 1 of the North Sea (NSTF, 1993a), effects on the macrobenthic community were found up to 5000 m from the discharge site (Statfjord C, Valhall), and were reported to be related to the amount of oil-based drill cuttings. It was concluded that the change from diesel to low-aromatic base oil did not seem to have led to any improvement in the benthic communities. In Subregion 4, benthic macrofauna abundance and species richness were affected up to 100-750 m distant, depending on the location. Sensitive species densities were affected up to 1-2 km away (NSTF, 1993b). It was reported that laboratory experiments had confirmed that the effects were caused by oil in the sediment. Studies of recolonisation after cessation of drilling activities showed that the affected area is reduced to within 500 m of the platform within 4 years. This recolonisation could have been due to a decrease in toxicity of oil due to weathering/biodegradation, a decrease in bioavailability, redistribution of the contaminants or a combination of these.

The toxicity of drill cuttings from the North West Hutton platform in the North Sea was assessed using a luminescent bacterium (*Photobacterium phosphoreum*) test (Microtox™). A reduction in luminescence occurred but was attributed to additives in the drill mud adhering to the cuttings rather than the base oil itself (Neustadt *et al.*, 1995).

Dann *et al.* (1992) assessed the effects of oil-contaminated drill-cuttings discharges at an abandoned site in the Dutch sector of the North Sea. One year after drilling ceased, there was still a clear gradient in contamination levels, with total hydrocarbon concentrations ranging from <20 mg kg^{-1} dry sediment beyond 750 m from the platform to 250-450 mg kg^{-1} dry sediment within 250 m. Subtle effects on benthic community structure were evident as far away as 2 km from the platform, as indicated by the absence of the sensitive species *Montacuta ferruginosa*, *Harpinia antennaria* and *Callianassa subterranea*. Within 750 m, dominant species abundance decreased and typical opportunistic species were more frequent within a 250 m radius. In another study, Dann *et al.* (1994) monitored effects on macrozoobenthos around 11 drilling locations that used oil-based drilling muds and 4 that used water-based muds. Species that were abundant by nature at most locations were found to have a reduced abundance at OBM sites but not at WBM sites, and were considered useful indicators of OBM stress. In addition, the opportunistic polychaete *Capitella capitata* consistently occurred in increased numbers only at the OBM sites.

In laboratory experiments, the deposit-feeding bivalve *Abra alba*, an important sediment reworker species in European waters, had significantly reduced faecal pellet production (i.e. a reduced feeding rate) when exposed to diesel oil and oil-based drilling muds (Strømgren *et al*, 1993). Five-day EC_{50}s ranged from 57 to 1087 mg kg^{-1}. A significant correlation between EC_{50}s and the naphthenic content was found. Since the faecal pellet production returned to normal after animals had been transferred to clean sediment for 4-6 days, the authors concluded that the hydrocarbons affected ingestion behaviour rather than indicating toxic effects on physiological processes within the organism. A reduction in feeding activity of *A. alba* may slow down the bioturbation of sediments, thus affecting the sediment dynamics and abundance and distribution of bottom fauna.

5.5.1 Endocrine Disruption

Three major sources of potential endocrine disrupting (ED) substances have been identified as being in use on or produced from oil and gas production platforms - alkylphenols, bisphenol-A and PAHs. As yet, no specific studies have been carried out to assess the long-term effects of these inputs to the offshore marine environment, in terms of endocrine disruption in fish or invertebrates, but the potential is certainly there. The alkylphenols have been gradually phased out since 1998, and are no longer used in oil and gas operations on the UKCS. However the degradation products of alkylphenols are relatively persistent, particularly in the anoxic conditions that may exist in many cuttings piles. The bioavailability of these compounds is therefore uncertain. The same is true for bisphenol A and the PAHs that are associated with the cuttings. Further information regarding the prevailing concentrations of these chemicals in waters and sediments around platforms is needed in order to make judgements about potential impacts. The evidence for endocrine disruption of these three chemicals is briefly described below.

Alkylphenols

Alkylphenol polyethoxylates are nonionic surfactants, used for a variety of functions including industrial detergents. Their alkylphenol and lower ethoxylate degradation products have been shown to be weakly oestrogenic both *in vitro* and *in vivo* (see Servos, 1999 for a review). *In vivo* effects (vitellogenin production by male trout) of nonylphenol and octylphenol were apparent at 20 and 4.8 µg l^{-1} respectively (Harries *et al.*, 1995). Higher ethoxylates are not oestrogenic. Concentrations of total extractable alkylphenols in surface waters in the Mersey and Tees estuaries have been reported to be 11 and 76 µg l^{-1} respectively (Blackburn *et al.*, 1999). Concentrations of nonylphenol in Tees estuary sediments reached 9 µg g^{-1}, while in fish tissues levels ranged from 30-180 g g^{-1} (ww) (Lye *et al.*, 1999). There is currently very little data for measured concentrations in the vicinity of oil and gas platforms. However, some data for total extractable alkylphenols in drill cuttings at the West Hutton platform (J. Balaam, *pers. comm.*) indicated that nonylphenol concentrations were 48 µg g^{-1} 100 m from the platform.

Bisphenol-A

Bisphenol-A is a precursor compound for some component of drilling fluids and may be discharged to the environment via the drill cuttings either as a breakdown product or as an impurity. It has been shown to be weakly oestrogenic both *in vitro* and *in vivo* (Krishnan *et al.*, 1993; Kloas *et al.*, 1999). Lindholst *et al.* (2000) have recently demonstrated that water concentrations between 40-70 µg l^{-1} caused vitellogenin induction in rainbow trout. Environmental data is limited, but concentrations between 80 to >4000 µg l^{-1} in effluents have been reported (EA, 1998), and at the West Hutton platform, concentrations in sediment 100 m from the platform reached 7 µg g^{-1} (J. Balaam, *pers. comm*.)

PAHs

The endocrine disrupting effects of PAHs have been studied using fish species, but effects on invertebrates have not been described, although the potential is there. The effects of PAHs on the process of vitellogenesis in fish has been reviewed by Nicolas (1999); although PAHs can have deleterious effects, this varies between species, populations and even between individuals, making general conclusions difficult. Possible mechanisms of action have yet to be identified. Oestrogenic and anti-oestrogenic effects have been reported (Andersen *et al*., 1996 a and b).

5.6 ICES/IOC Pelagic Workshop

A very recent study (taking place February to September 2001) that will be of interest is the ICES/IOC practical workshop for biological effects of contaminants in pelagic ecosystems (Hylland, 2000). The objective of this workshop is to assess the ability of selected methods to detect biological effects of contaminants in pelagic ecosystems under uniform and standardised conditions. The methods will be assessed for their applicability in future monitoring programmes. The practical work has focussed on two areas in the North Sea that has inputs of contaminants into the pelagic ecosystem: a coastal area (German Bight) and an area in the vicinity of an oil platform (Statfjord). Each area has four sampling locations, three within a contamination gradient and a fourth outside the affected area (reference site). At each of the sites, sampling for water and pelagic organisms will take place on multiple occasions in 2001. In addition, cages with blue mussels, fish (Atlantic cod, 3-spined stickleback) and fish eggs (herring) were deployed at each of the eight sites in April and were sampled in June. A wide range of biomarkers and bioassays have been/will be conducted with either whole organisms or tissue samples e.g. toxicity, EROD, lysosomal damage, Scope for Growth, genotoxicity, endocrine disruption effects, metallothionein induction, embryonic development, PAH metabolites, acetylcholinesterase inhibition, to name a few. The results of this large exercise will be published in due course, but more information can be found on the web site www.niva/no/pelagic/web.

6. GAPS IN OUR UNDERSTANDING

Within the framework of OSPAR and the North Sea Conferences, the UK is working with other contracting parties to develop a management strategy for the seas based upon an ecosystem approach. An integral part of developing this strategy is a review of marine monitoring programmes and how best they can be integrated in support of the Governments on-going commitment to protect the marine environment. This is required for two reasons; i. to ensure that there is an adequate balance of effort between the sampling programmes, and ii. the fact that OSPAR (the 5 new strategies) and the EC Directives (Water Framework and Habitat Directives in particular) increasingly require countries to take a holistic view in protecting and managing their marine environments (essentially habitats).

This change has also been recognised in ICES with the Council having recently established an additional advisory committee, the Advisory Committee on Ecosystems (ACE) to handle the provision of ecosystem related advice as described in the new Rules of Procedure (Rule 26). A driving force behind this organisational change is the need to offer a framework for an ecosystem approach to the management of marine ecosystems which can deliver "sustainable use of ecosystem goods and services and conservation of ecosystem integrity.

Clearly the offshore activities of the oil and gas industry have to be taken into account when developing existing monitoring programmes to deliver a comprehensive and coherent marine environmental monitoring network for the UK.

To facilitate this process R&D in the following areas is required:

1. To further identify and determine current and potential inputs of chemicals in produced water, field concentrations, chemical fate and biological effects of such substances. In particular the potential for long-term impacts.

2. To determine the likely zone of influence of contaminants released upon disturbance of cutting piles; and the implications for wider-field contamination levels in the North Sea.

3. To overcome the present lack of ecotoxicological assessment criteria and/or background/reference concentrations for oil.

4. To close the gaps in knowledge in respect of temporal trends and spatial surveys, monitoring efforts should be optimised within the JAMP.

5. To develop tools for the assessment of substances and effects of concern. It is essential that a structured approach is taken and that it fully integrates biological techniques and chemical monitoring. Further development of biomarker techniques according to widely accepted protocols and more efficient data management and dissemination are also strongly recommended.

6. To develop an ecosystem approach, which has been a major recommendation of the 1997 International Ministerial Meeting, for protecting the environment according to OSPAR's Annex V. An important aspect of this approach is improved integration between the different sectors operating in the sea, but also between scientists, policy makers and other stakeholders. Through concerted action these parties should progress towards effective use of the resource whilst protecting and conserving the ecosystems and biological diversity of the North Sea.

7. REGULATORY CONTROLS

In the wider context of sustainable development, there are a number of developments at the international level which may have a bearing on how the industry is regulated within UK coastal waters. The most important of these being the publication of the EC Water Framework Directive in the EC Official Journal on 22 December 2001. In addition, closer links are being established between the European Environment Agency (EEA) and the Marine Conventions, including OSPAR through the Inter Regional Forum. The EEA are particularly keen to use environmental data from all available sources, to aggregate information and produce indicator based reports on all aspects of environmental quality.

In practice, sustainable development is defined as meeting four key objectives - 'social progress, effective environmental protection, prudent use of natural resources and the maintenance of acceptable living standards'. Although these objectives are broad, the development of indicators focuses on specific issues to monitor progress towards objectives and to communicate the effectiveness of environmental protection policy to managers, policy makers and the general public.

Measurement of the quality of waters, sediment and biota is essential for several reasons, firstly to trace contaminants through the ecosystem, secondly to assess which media or species may be at risk, and thirdly, to assess the effectiveness of pollution control measures. A comparison of measured levels to background concentrations (BACs) indicates the degree to which the environment is enriched in the particular contaminant. A comparison of measured levels to Ecological Assessment Criteria (EAC) indicates whether environmental quality objectives are being met, such as to protect marine life.

These standards (BACs and EACs) have been adopted by OSPAR (although they are not statutorily enforceable – OSPAR 97/15/1, Annex 5) as assessment tools for the QSR. Although some of the values can be applied throughout the maritime area, some can only be applied on a regional basis. It is important to note that background values do not represent target values and they should not be used as such.

The UK as with other States in the Northeast Atlantic is responsible for regulating pollution from seabed installations within the EEZ an area up to 200 nm offshore. International conventions and regulations, such as the International Convention for the Prevention of Pollution from Ships (MARPOL) and the London Convention, apply both within and outside the EEZ.

In the UK sector the major developments of the offshore oil industry have been in the northern and central North Sea. The major gas fields are situated mainly in the shallower southern regions. Between 1990 and 1998 the number of offshore oil production platforms in the UK sector increased from 46 to 263 (OGP, 2001)

Offshore installations are significant sources for the input of oil to the UK maritime area. However, overall, inputs of oil have decreased from a maximum of about 16500 t in 1990 to about 9000 t in 1998 (56%). The reduction of oil discharges on cuttings has made the major contribution to this reduction. During the period 1990 to 1998, the discharge of oil with production water increased from about 4400 t to about 8200 t even though the OSPAR target standard of 40 mg l^{-1} was met by 90% of the installations in 1997. As oilfields mature, it is anticipated that the discharges of produced water and associated oil will continue to increase. In the case of the relatively small discharges of produced water from gas platforms, the discharge of aromatic compounds may exceed the discharge of dispersed oil. This rise is due to the increased number of installations and increasing amounts of production water associated with progressive exploitation of the oil fields.

Produced water contains considerable amounts of dissolved substances, including monocyclic aromatic hydrocarbons (i.e. BTEX), polycyclic aromatic hydrocarbons (PAHs) and phenols. There may also be (as yet) unidentified organic compounds, heavy metals and production chemicals. The lack of information on the partitioning of oil field chemicals and their reaction products is too limited at present to make an assessment of impacts on environmental quality and ecosystem effects. Increasing oil production and ageing of the oil fields are reasons for growing concern. This is because quantities of produced water will increase and associated discharges of hazardous substances are expected to increase further.

The DTI introduced a voluntary Offshore Chemical Notification Scheme (OCNS) in 1979, which placed chemicals used by the UK offshore industry into 'categories' dependant on their toxicity.

To address the potential problem of increased chemical discharges, In 1990 OSPAR began working towards harmonising testing requirements for oilfield chemicals throughout the NE Atlantic sector. In anticipation of this, the UK Government introduced a Revised OCNS in 1993. This scheme classified chemicals into ‘Groups’ based on the potential hazard they presented to the marine environment. Classification was dependant on the chemicals’ biodegradation and bioavailability characteristics together with their toxicity to a broader range of taxonomic groups using species and test protocols approved by OSPAR. The dataset was modified in detail in 1996 to suit the new Harmonised Offshore Chemical Notification Format data set introduced with OSPAR Decision 96/3.

OSPAR Decision 96/3 introduced the Harmonised Mandatory Control System for the Use and Reduction of the Discharge of Offshore Chemicals. The new approach came into force in June 2000 after a trial period and effectively supersedes previous OSPAR and national measures with respect to offshore chemicals. Included in the new approach is a procedure to assess chemicals according to their hazard ranking and to promote the principle of substitution when less hazardous alternatives to chemicals in current use are available.

Ministers at the Fourth International Conference on the Protection of the North Sea invited OSPAR to ban (with certain exceptions) the discharge of oil contaminated cuttings by 1997. As some synthetic fluids were found to possess properties that could result in adverse impacts on benthic communities, the UK industry undertook a voluntary agreement to phase them out by 2000. Following a review within OSPAR of measures relating to cuttings contaminated with organic-phase drilling fluids, a new comprehensive Decision was adopted in June 2000 (OSPAR Decision 2000/2), which rules out discharges of such cuttings except, in exceptional circumstances, those contaminated with synthetic fluids.

8. FUTURE RISKS

8.1 Cuttings Piles

The two major sources of contamination from the oil and gas industry offshore are the drill cuttings piles accumulated under installations, mainly in the central and northern North Sea and the produced water discharges that are increasing as a larger number of fields reach the end of their life.

One of the main concerns is the fate of cuttings piles upon decommissioning of installations. However the major issues are being tackled by the UK Offshore Operators Association (UKOOA) in a Drill Cuttings Initiative launched in June 1998. The key objectives of the program are to identify best environmental practice and best available techniques for dealing with drill cuttings piles in the North Sea. (Further information on the UKOOA Drill Cutting Initiative can be found at http://www.ukooa.co.uk/issues/).

Contaminants associated with the drill cuttings may separate into solution as the cuttings are deposited on the seabed. Those contaminants that remain adsorbed are likely to remain in the piles for considerable periods providing the pile remains undisturbed. There is a wide range of contaminants in cuttings piles. Estimates suggest that, where oil-based muds have been used, between 1 and 1.5 tonnes of formulated mud may have been discharged per well drilled. Approximately 0.1-0.25 tonnes of this total may be oil, with other chemicals making up the balance (Davies and Kingston, 1992).

A laboratory investigation into the leaching of metals and hydrocarbons from drill cuttings conducted by Delvigne (1995) as part of the E & P Forum Joint Study concluded that the rate of leaching of metals was too slow to be detected within the 21-day period of the experiment. Although there is likely to be some release of contaminants from undisturbed piles, dilution will occur rapidly and biological effects as a result of leached contaminants are likely to be restricted to the immediate vicinity of the pile. However erosion and dispersal of cuttings material may result in an increase in the zone of impact around a pile.

Data from several studies including the use of models indicate that cuttings piles in the central North Sea are likely to be dispersed over a wider area than those in the northern North Sea (Brandsma, 1996; BMT, 1999). This is due to the higher current activity and possibly also the greater influence of waves in the relatively shallower southern North Sea. A model of natural pile dispersion indicated that the interaction between constant erosion and degradation of the piles will probably result in a slow, controlled erosion rate (BMT, 1999). However it was stressed that there is a need to verify this in field and/or laboratory studies. Available data suggest that both the depth of deposited cuttings as well as the concentration of associated oil will determine the rate at which faunal recovery occurs. Cuttings depths >10mm (Bakke *et al.*, 1985) and oil concentrations >400 µg g^{-1} (Hird and Tibbetts, 1996) are likely to limit oil degradation and hence faunal colonisation. Measurable biological effects (mainly reduction in species diversity) around cuttings piles may extend up to 5 km but generally are not greater than 3km (Gray *et al*., 1999). If it is assumed that the zone of effect around an oil platform is a circle of 3 km radius, then the total area of effect is ~28 km^2. If the major factor contributing to the observed biological effects is oil-based cuttings and in particular diesel oil, this was phased out in 1997 when there were 79 oil installations that may potentially have used diesel oil based muds. If it is assumed there are 79 cuttings piles with worst-case zones of effect of ~28 km^2 then the total area of the UK sector of the North Sea that may show some biological impact is ~2212 km^2.

As a consequence of their hydrophobic nature, PAHs in aquatic environments become associated with particulates. Sediments therefore represent the most important reservoir of PAHs in the marine environment. The concentration range for specific hydrocarbons in a number of cuttings piles is shown in Figure 26. The ecotoxicological assessment criterion (EAC) (OSPAR Commission, 2000) is also shown. EAC values are based on the concentrations of specific substances (in this case, specific polycyclic aromatic hydrocarbons) in the marine environment below which no harm to either the environment or to biota is expected. Only the concentrations of anthracene, phenanthrene and naphthalene exceed the EAC values. Anthracene and phenanthrene are present at comparable concentrations to those in the sediments of UK estuaries such as the Tees that are associated with industrial regions in the UK (Woodhead *et al*., 1999). The naphthalene concentration is an order of magnitude higher than those found in industrialised estuaries in the UK.

PAHs associated with cuttings piles under anoxic conditions may be very persistent. Upon disturbance and redistribution of the cuttings they have the potential for causing biological effects. Phenanthrene and naphthalene are both moderately toxic, concentrations of 680 and 11000 µg l^{-1} result in 50% mortality of brine shrimp after 48 hours exposure (Abernethy *et al*., 1986). Both compounds are also moderately bioconcentrated (Grimwood, 1996). Both phenanthrene and naphthalene exert their toxic effect through non-specific mechanisms (narcosis) effecting the function of biological membranes and hence processes such as osmoregulation and neurotransmission (see review by Van Wezel and Opperhuizen, (1995)). Anthracene is by contrast more toxic, a concentration of 32 µg l^{-1} results in 50% mortality of brine shrimp after 48 hours exposure and it is also bioconcentrated to a greater extent (Grimwood, 1996).

The main problem in assessing the significance of these compounds and the other PAHs in sediments upon redistribution of the cuttings material is their bioavailability. Benthic invertebrates (Baumard *et al*., 1998) and fish (Hellou *et al*., 1994) will take up sediment-associated PAH. The high mass weight PAH are more strongly adsorbed leading to their uptake by non-selective deposit feeding organisms.

The ability of organisms to metabolise PAHs will also influence the ultimate level of bioaccumulation. Some invertebrate species are able to metabolise PAHs but in many the necessary enzyme activity is weak or not present at all (e.g. Eertman *et al*., 1995). In contrast, many fish species are able to do this (Livingstone, 1993). Outside of the risk to the health status of organisms resulting from the bioaccumulation and toxicity of PAHs, is an added concern due to the presence of carcinogenic PAHs.

There is sufficient consistency in some laboratory datasets to indicate that elevated response are generally associated with hydrocarbon concentrations in excess of approximately 100 mg kg^{-1} (ERT, 1999). Assuming an approximate average oil-on-cuttings concentration of 10%, this would correspond to a cuttings-in-sediment concentration of 0.1%.

In addition to hydrocarbons there are likely to be a wide range of metals present in cuttings piles. These represent trace contaminants associated with the barium used as a weighting agent in drilling muds or in the case of chromium may derive from the chrome lignosulphonates used for a variety of functions before its use was phased out.

Barium is a major component of drilling muds and data recorded from 10 of 15 cuttings piles where core samples had been taken indicated a wide range in barium concentrations (250µg g^{-1} to >110,000 µg g^{-1}, CORDAH, 1999). The data for other metals indicate that they are present at much lower concentrations than barium. Figure 27 shows metal concentrations in several cuttings piles compared with the EAC value derived for each metal. It can be seen that lead, mercury and copper exceed the EAC limits by the largest margin. The potential for toxic effects may be limited in the proximity of the cuttings pile due to the relatively protected conditions persisting within pile, land the resultant low exchange rates of metals with overlying seawater. The bioavailability of metals associated with the cuttings piles may also be limited particularly in anoxic conditions since they may form metal mono- and disulphides (Shimmield *et al.*, 1999). However there is some potential for increased metal fluxes and metal release to occur upon oxidation of metal mono- and disulphides if the cuttings pile is substantially disturbed. In some circumstances however, oxygenation can reduce metal availability by promoting co-precipitation with iron and manganese hydroxides (Krantzberg ,1994). The potential for direct toxic effects of the metals within cuttings piles is therefore uncertain, however the bioavailability and potential bioaccumulation of metals warrant further consideration.

Historically, nonylphenol ethoxylates (NPEs) (a group of industrial chemicals with surfactant properties) were commonly used as emulsifiers in drilling fluids, and as cuttings cleaners and rig washes. The use of NPEs was phased out since one of the major breakdown products of NPEs, nonylphenol, was shown to have a range of harmful effects to aquatic organisms (Servos, 1999). Nonylphenol becomes strongly associated with sediments and may only be partially degraded over a period of several months particularly in anoxic conditions (Ekelund *et al*., 1993). There is little data on nonylphenol concentrations in cuttings piles however Gerrard *et al*., (1998) reported a value of 0.28 mg kg^{-1} nonylphenol in a cuttings pile sampled 100m from the platform. Comparable concentrations of nonylphenol have been measured in freshwater sediments downstream of 30 wastewater discharges in a study conducted in the USA (range <0.0029 to 2.96 mg kg^{-1}, Naylor *et al.* 1992). Nonylphenol is moderately bioaccumulated by marine invertebrates (McCleese *et al*., 1980) and fish (Granmo and Kollberg, 1976) however elimination of nonylphenol also occurs relatively rapidly. The main concern with nonylphenol is its endocrine disrupting properties as reviewed in Staples *et al*. (1998). However these effects are relatively weak by comparison to natural estrogens.

Surfactant chemicals present in cuttings pile or discharged in produced water may also have an important secondary effect upon the bioavailability of other chemicals e.g. PAHs (Saumyen *et al*., 1998). Contaminants may be solubilized in the micellar phase of some nonionic surfactants which enables them to be transferred directly from the micelle to the cell without needing to make contact with the intervening water.

In summary the main effect of concern in relation to cuttings piles is the potential toxicity upon redistribution after disturbance. More soluble compounds are likely to be released from the cuttings prior to settlement or immediately following subsequent disturbance. In most cases the more soluble contaminants are likely to have a lower potential for bioconcentration and exposure will be transient as the released material is diluted in the residual or tidal currents. Contaminants associated with the settled cuttings have potential for bioconcentration particularly by sediment dwelling organisms. However there is uncertainty regarding the bioavailability of metals, PAHs and nonylphenol that may be associated with the cuttings.

A comprehensive review of contaminants in cuttings piles suggests that the hydrocarbon concentration can be considered a ‘marker’ for approximate toxicity in cuttings piles: major toxic effects are observed in the concentration range 50-200 mg kg^{-1}; the threshold for chronic effects might lie in the region of 10 mg kg^{-1}, and the no-effect concentration falls in the range of 1-10 mg kg^{-1}.

8.2 Produced Water

Most studies on produced water from oil and gas platforms have concluded that it is diluted and dispersed very quickly once discharged, and that there are unlikely to be any acute effects, except within the immediate vicinity of the platform. The initial dilution of the produced water can be very rapid, typically reducing the initial concentration by a minimum factor of between 300 and 3000 within 100m of the discharge (Murray-Smith *et al*., 1996). Tidal movements may also facilitate greater mixing and rapid dilution to levels which are not acutely toxic (Stagg *et al.*, 1996). At distances in excess of 100m, the physical dilution is less rapid but other removal processes such as biodegradation may become important. At 1 km from the discharge point, the predicated range of dilutions is between 1000 and 16000. Aliphatic oil, monoaromatics and heavy metals account for most of the toxicity observed in produced water on the Dutch continental shelf (Slager *et al*., 1992). Results show that the aromatic hydrocarbon residues are dominated by monoaromatic (Benzene, Toluene, Xylene and phenols) and lighter polyaromatic residues. These are considered to be the most acutely toxic components of the organic contaminants in produced water, although heavy metals may also contribute to the observed toxicity (Slager *et al.*, 1992). Figure 28 shows the concentration of eight metals measured in produced water compared to the OSPAR EAC values for the same metals. Figure 29 shows a comparison of the concentration of 6 hydrocarbons with the relevant EAC values. The concentration of metals and hydrocarbons shown in Figure 28 and 29 with the exception of anthracene all fall below the respective EAC values.

The major concerns in relation to produced water are the potential presence of persistent and bioaccumulative chemicals. Bioaccumulation in the food-chain may in fact be significant in marine planktonic organisms due to their high surface to volume ratio (OLF, 1998). It is therefore important that monitoring programmes continue to address this issue. PAHs, metals and phenolic chemicals have been detected and monitored in produced water discharges however there is a need to quantify the contributions to toxicity and identify other chemicals or reaction products that may have significant biological effects, e.g. corrosion inhibitors (Grigson *et al*., 2000).

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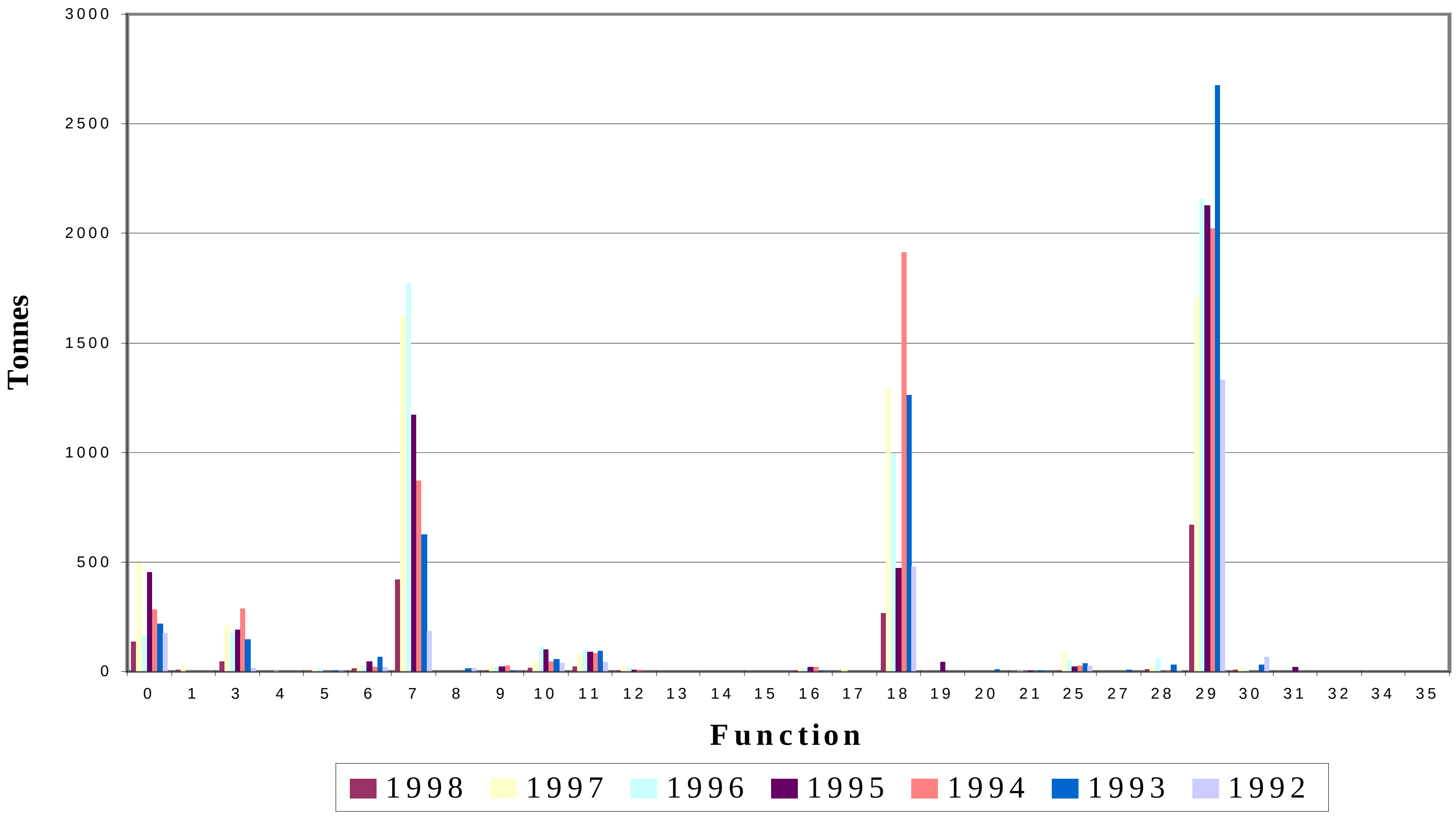


0 Missing Value
1 Antifoaming (Hydrocarbons)
2 Asphalts and Asphalt Based Products
3 Biocides
4 Carrier Solvent
5 Cement and cement additives
6 Coagulant/Deoiler
7 Corrosion Inhibitor
8 Cuttings Wash Fluids
9 Defoamers
10 Demulsifiers
11 Detergent/cleaning fluids
12 Dispersant
13 Drilling Lubricants
14 Dye
15 Emulsifier
16 Flocculant (Water Injection)
17 Fluid Loss control
18 Gas Treatment
19 Gel
20 Inorganic Chemicals
21 Laboratory Chemicals
24 Oil Based Mud and Additives
25 Oxygen Scavengers
27 Polymeric Viscosifier
28 Scale Dissolver
29 Scale Inhibitor
30 Shale Inhibitor/Encapsulator
31 Thinner
32 Viscosifier
33 Water Based Mud and Additives
34 Weighting Agents and Inorganic
35 Synthetic Based Mud and Additives

Figure 1 Annual discharges (1992-1998, in tonnes) of chemicals in various function groups, from installations in the northern North Sea - (where no value is shown these chemicals may be restricted to use without discharge)

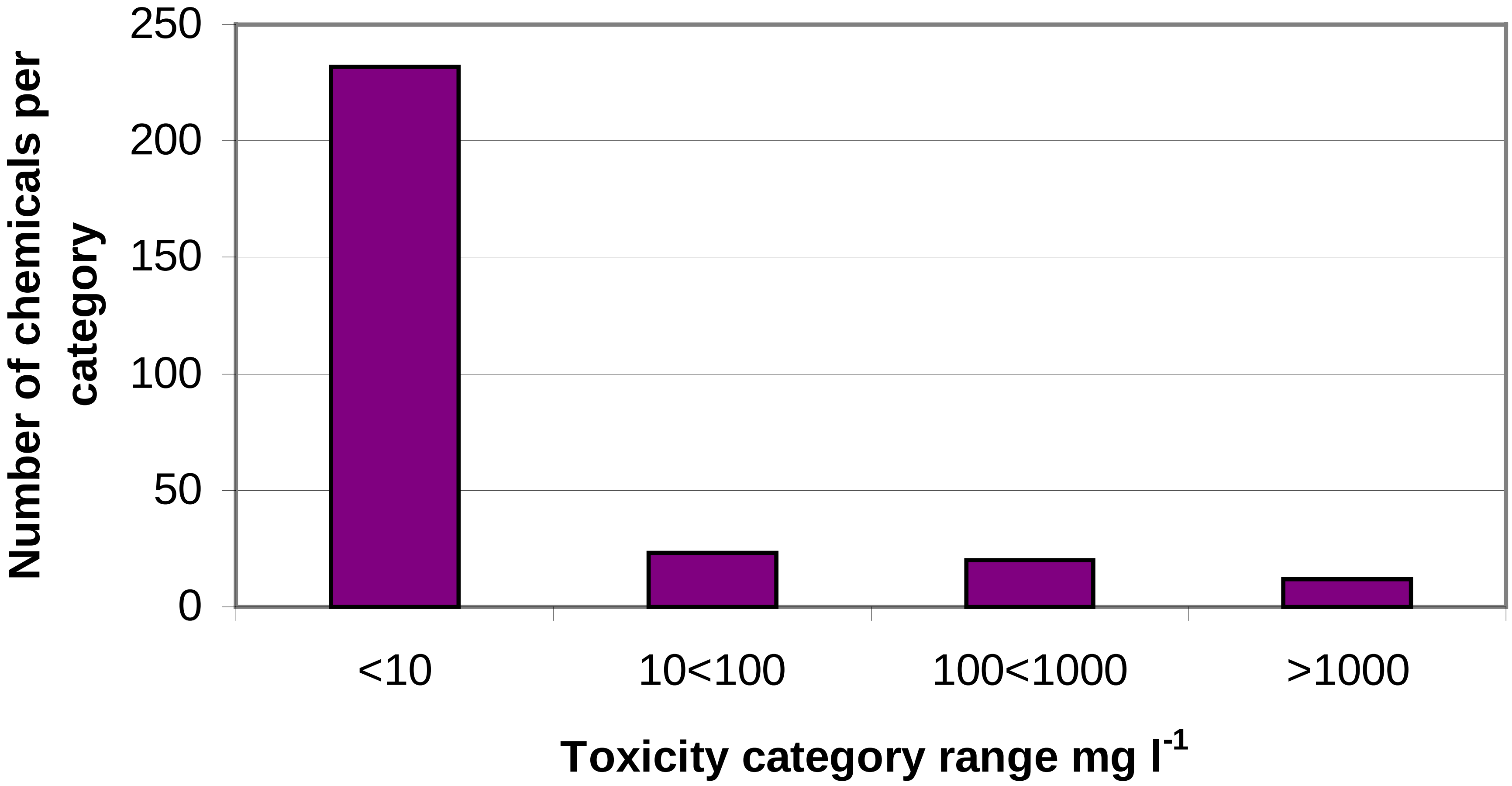
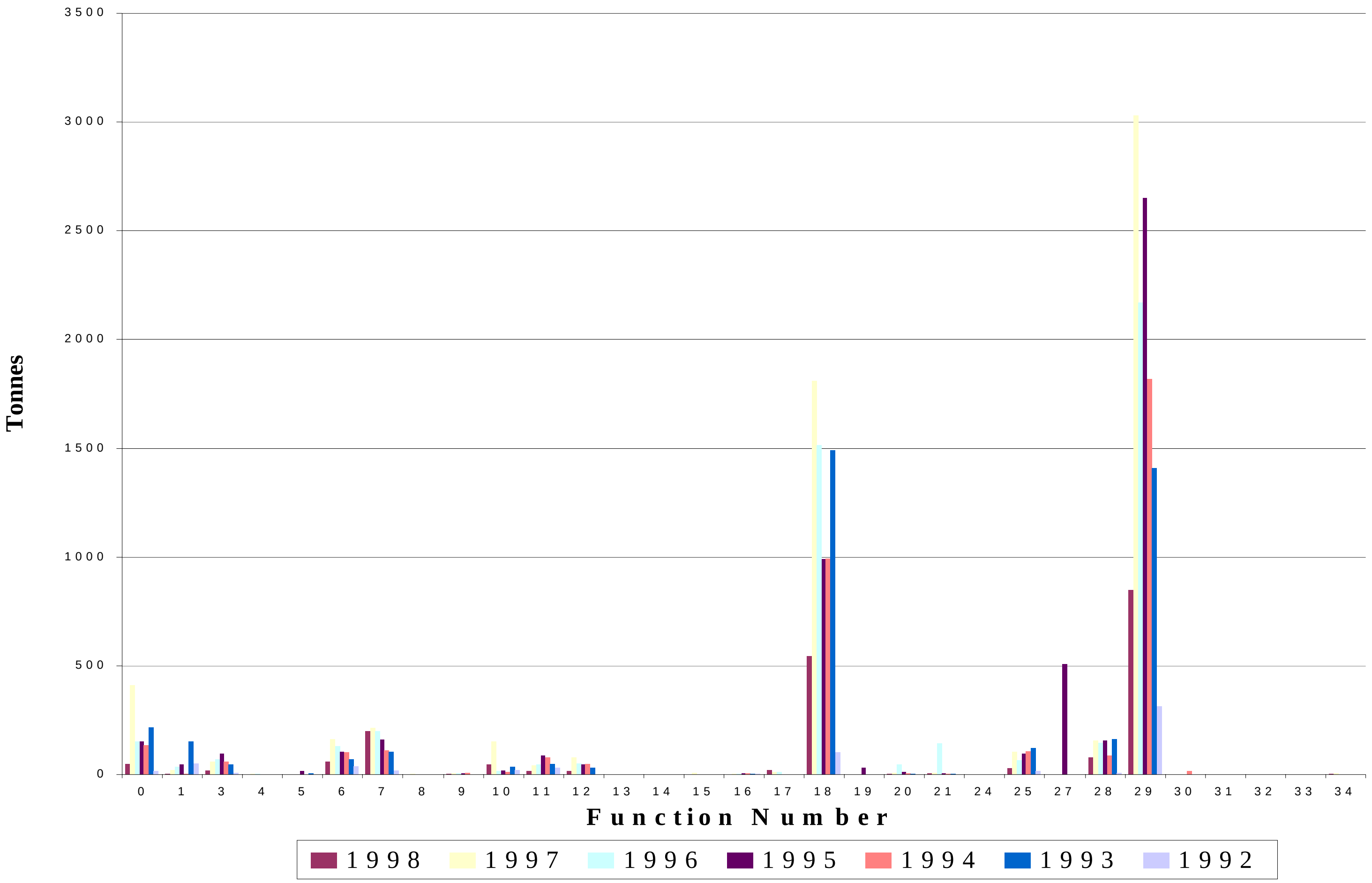


Figure 2 Number of corrosion inhibitors used by the industry (not necessarily discharged) between 1992-1998 - classified in terms of their toxicity



0 Missing Value
1 Antifoaming (Hydrocarbons)
2 Asphalts and Asphalt Based Products
3 Biocides
4 Carrier Solvent
5 Cement and cement additives
6 Coagulant/Deoiler
7 Corrosion Inhibitor
8 Cuttings Wash Fluids
9 Defoamers
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12 Dispersant
13 Drilling Lubricants
14 Dye
15 Emulsifier
16 Flocculant (Water Injection)
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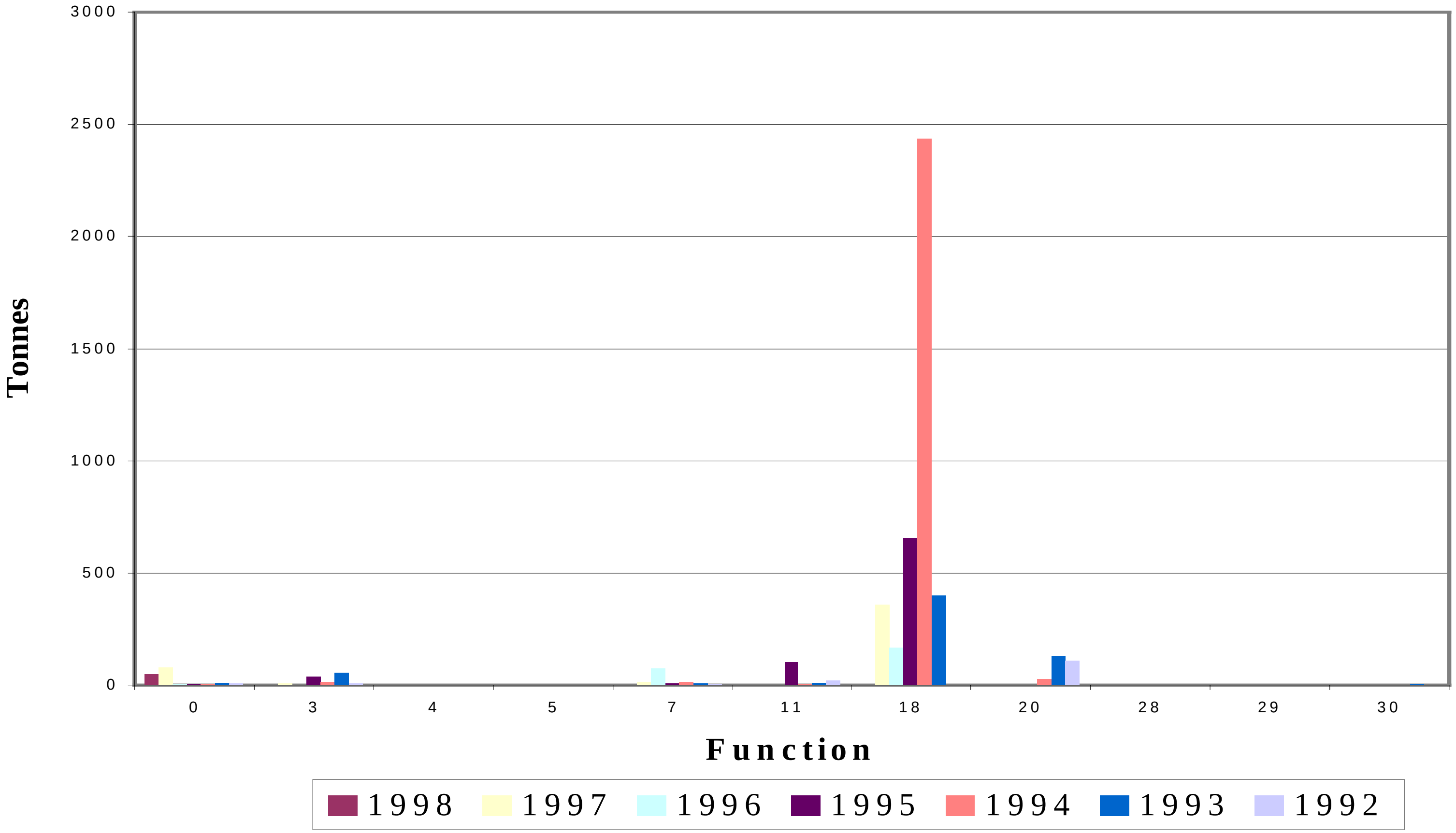
20 Inorganic Chemicals
21 Laboratory Chemicals
24 Oil Based Mud and Additives
25 Oxygen Scavengers
27 Polymeric Viscosifier
28 Scale Dissolver
29 Scale Inhibitor
30 Shale Inhibitor/Encapsulator
31 Thinner
32 Viscosifier
33 Water Based Mud and Additives
34 Weighting Agents and Inorganic
35 Synthetic Based Mud and Additives

Figure 3 Annual discharges (1992-1998, in tonnes) of chemicals in various function groups, from installations in the central North Sea - (where no value is shown these chemicals may be restricted to use without discharge)



0 Missing Value
1 Antifoaming (Hydrocarbons)
2 Asphalts and Asphalt Based Products
3 Biocides
4 Carrier Solvent
5 Cement and cement additives
6 Coagulant/Deoiler
7 Corrosion Inhibitor
8 Cuttings Wash Fluids
9 Defoamers
10 Demulsifiers
11 Detergent/cleaning fluids
12 Dispersant
13 Drilling Lubricants
14 Dye
15 Emulsifier
16 Flocculant (Water Injection)
17 Fluid Loss control
18 Gas Treatment
19 Gel
20 Inorganic Chemicals
21 Laboratory Chemicals
24 Oil Based Mud and Additives
25 Oxygen Scavengers
27 Polymeric Viscosifier
28 Scale Dissolver
29 Scale Inhibitor
30 Shale Inhibitor/Encapsulator
31 Thinner
32 Viscosifier
33 Water Based Mud and Additives
34 Weighting Agents and Inorganic
35 Synthetic Based Mud and Additives

Figure 4 Annual discharges (1992-1998, in tonnes) of chemicals in various function groups, from installations in the southern North Sea - (where no value is shown these chemicals may be restricted to use without discharge)

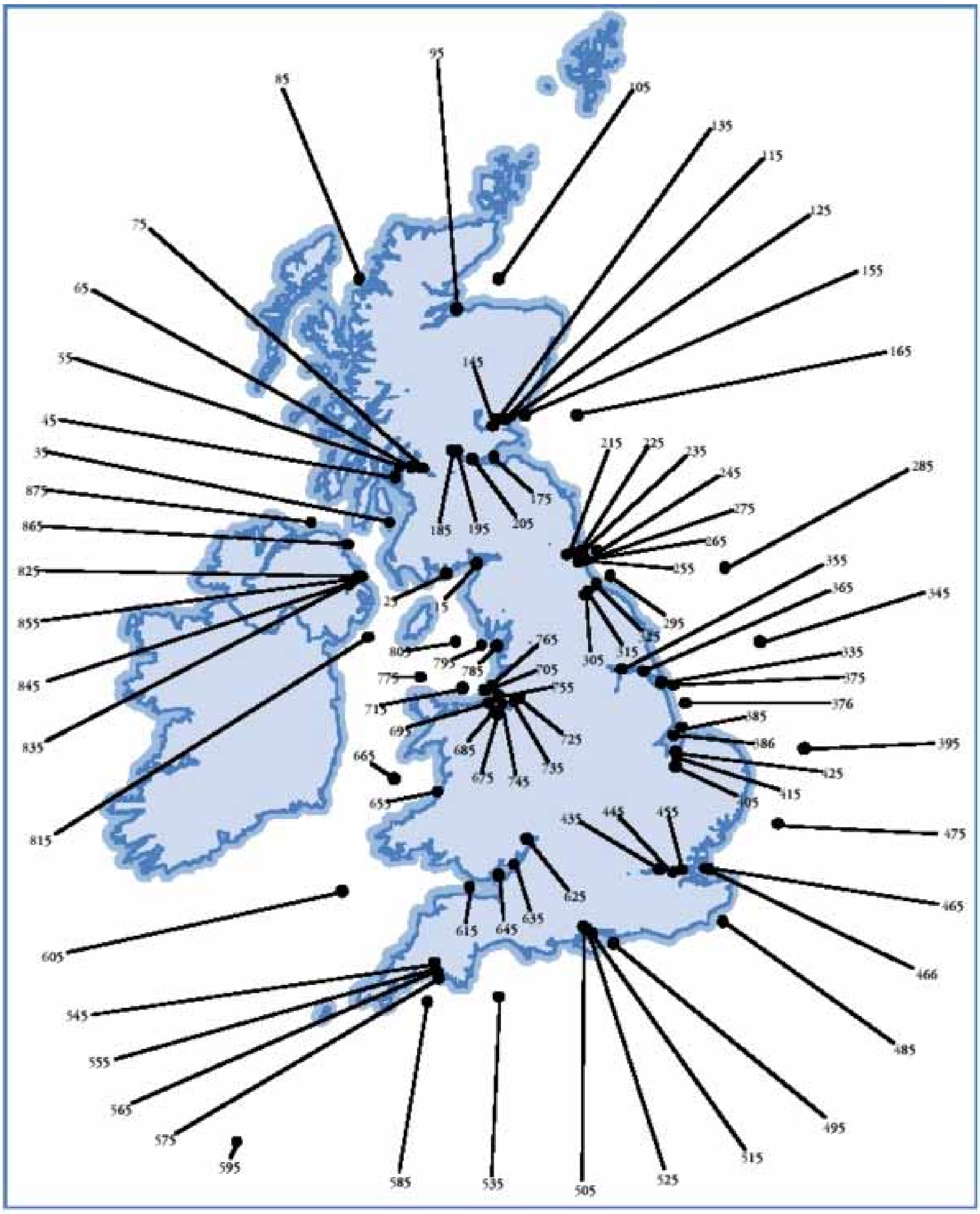


Figure 5 Locations of NMP stations (MPMMG, 1998)

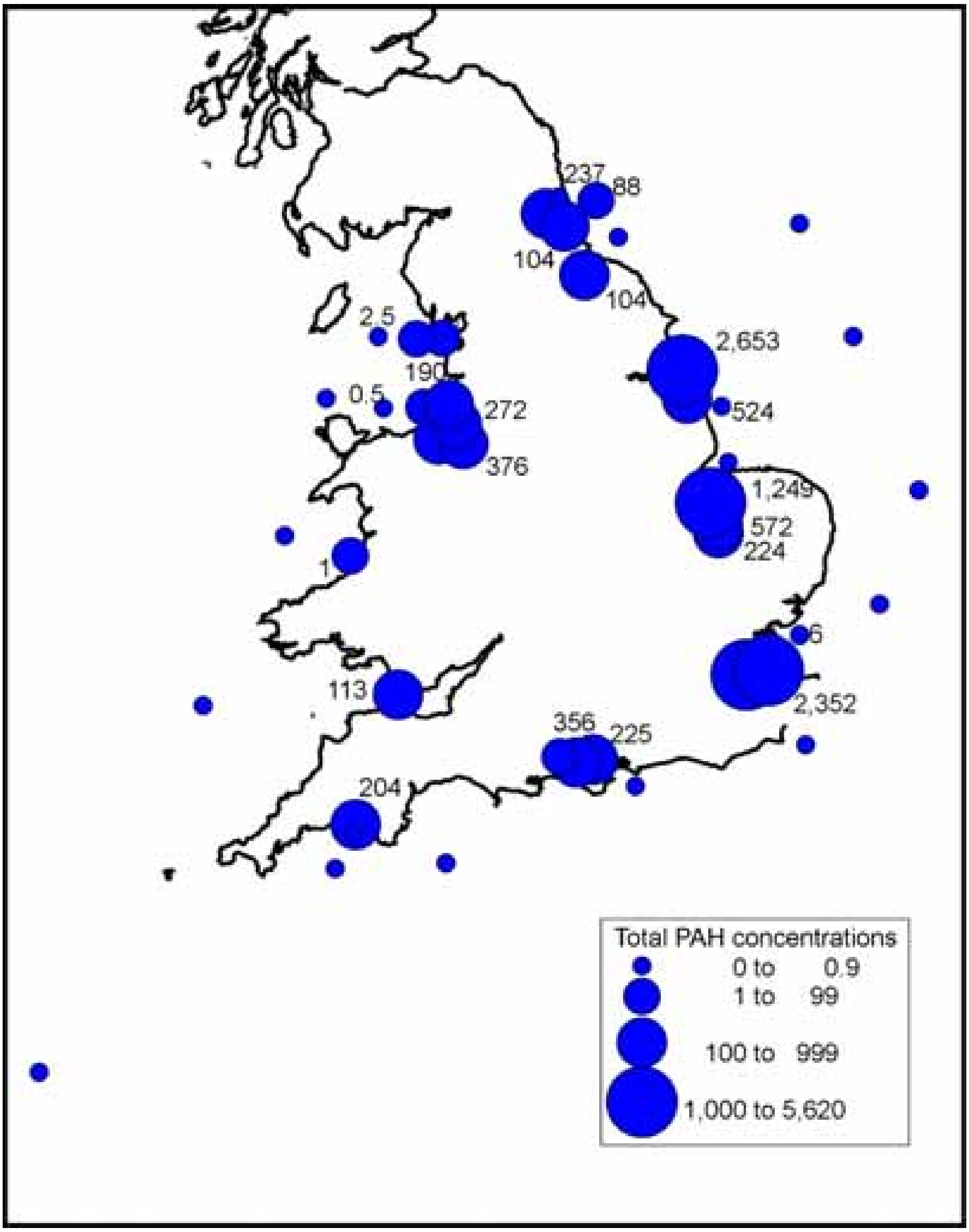


Figure 6 Total polycyclic aromatic hydrocarbons (PAH) concentrations (ng l^{-1}) in unfiltered sea water (MAFF, 1998)

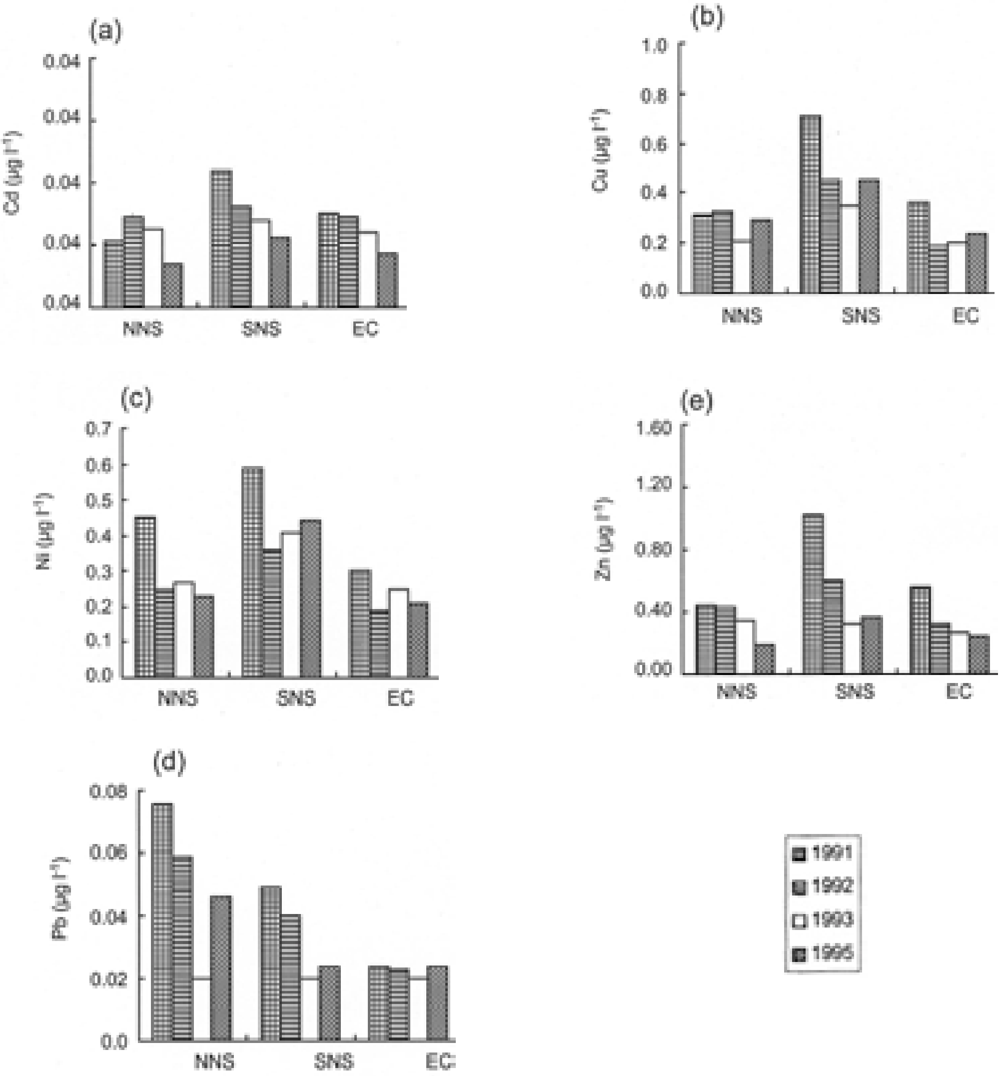


Figure 7 Histograms of median metal concentrations (μg l^{-1}) in each geographical area – northern North Sea; southern North Sea; English Channel (a) Cd, (b) Cu, (c) Ni, (d) Pb, (e) Zn (MAFF, 1998)

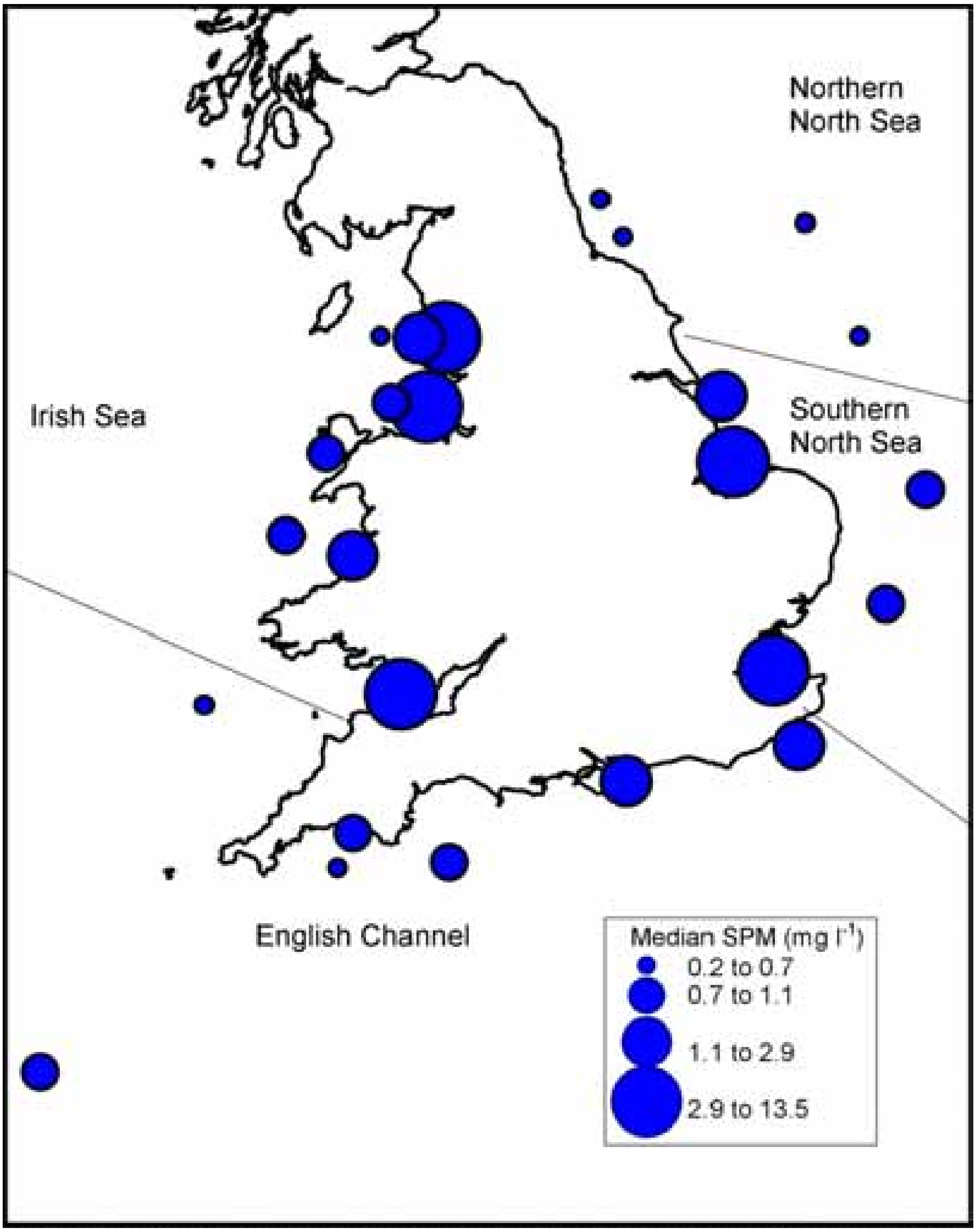


Figure 8 Map showing the divisions of NMP sites for geographical comparison, together with median suspended particulate matter (SPM) concentrations (mg l^{-1}) at each site for the five years sampled (MAFF, 1998)

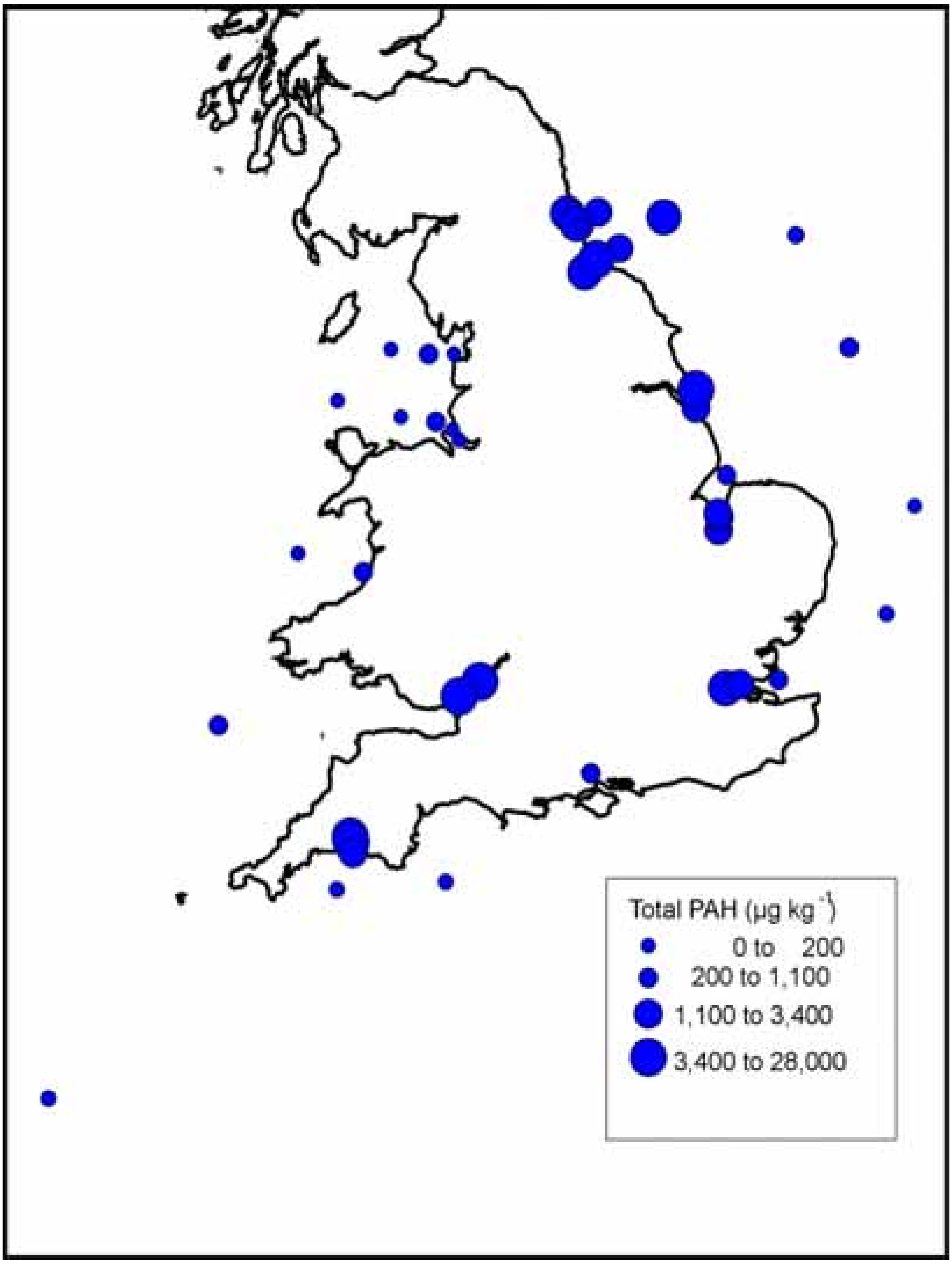


Figure 9a **Concentrations (µg kg^{-1}) of PAH (sum of 10 individual PAH compounds) in sediments from NMP stations (MAFF, 1998)**

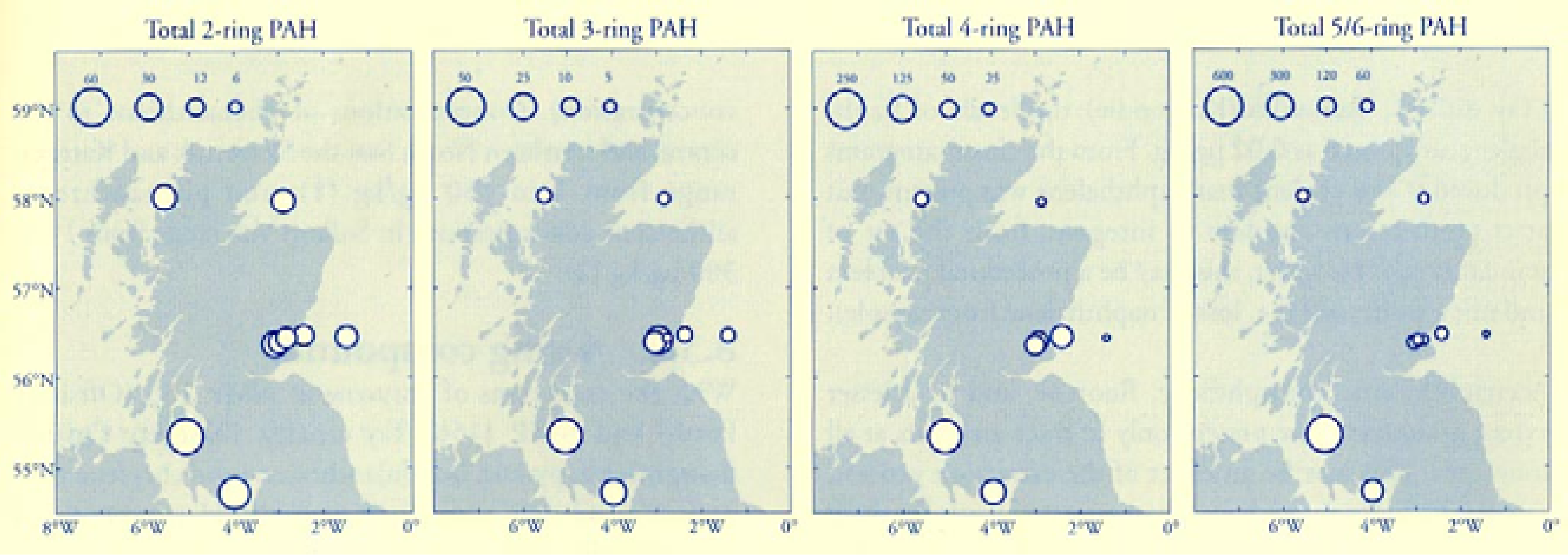


Figure 9b Total concentrations (µg kg^{-1}) of 2-, 3-, 4- and 5-ring PAH compounds in sediments from NMP sites for Scotland (NMP, 1998)

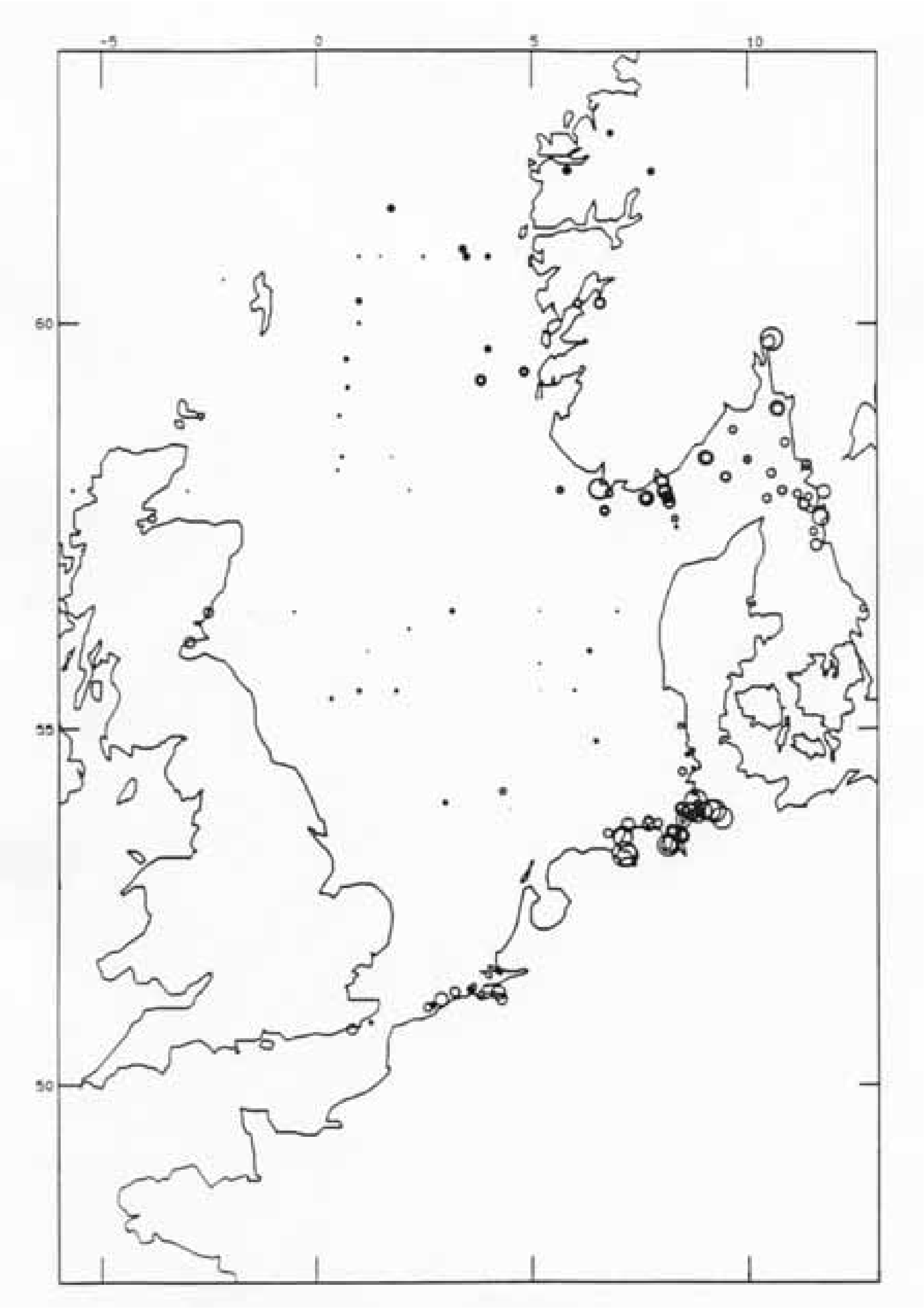


Figure 10 Distribution of CB153 concentrations in North Sea sediments <2000 µm. The circle area is proportional to the value; the maximum shown is 3µg kg^{-1} (Rowlatt *et al.*, 1995)

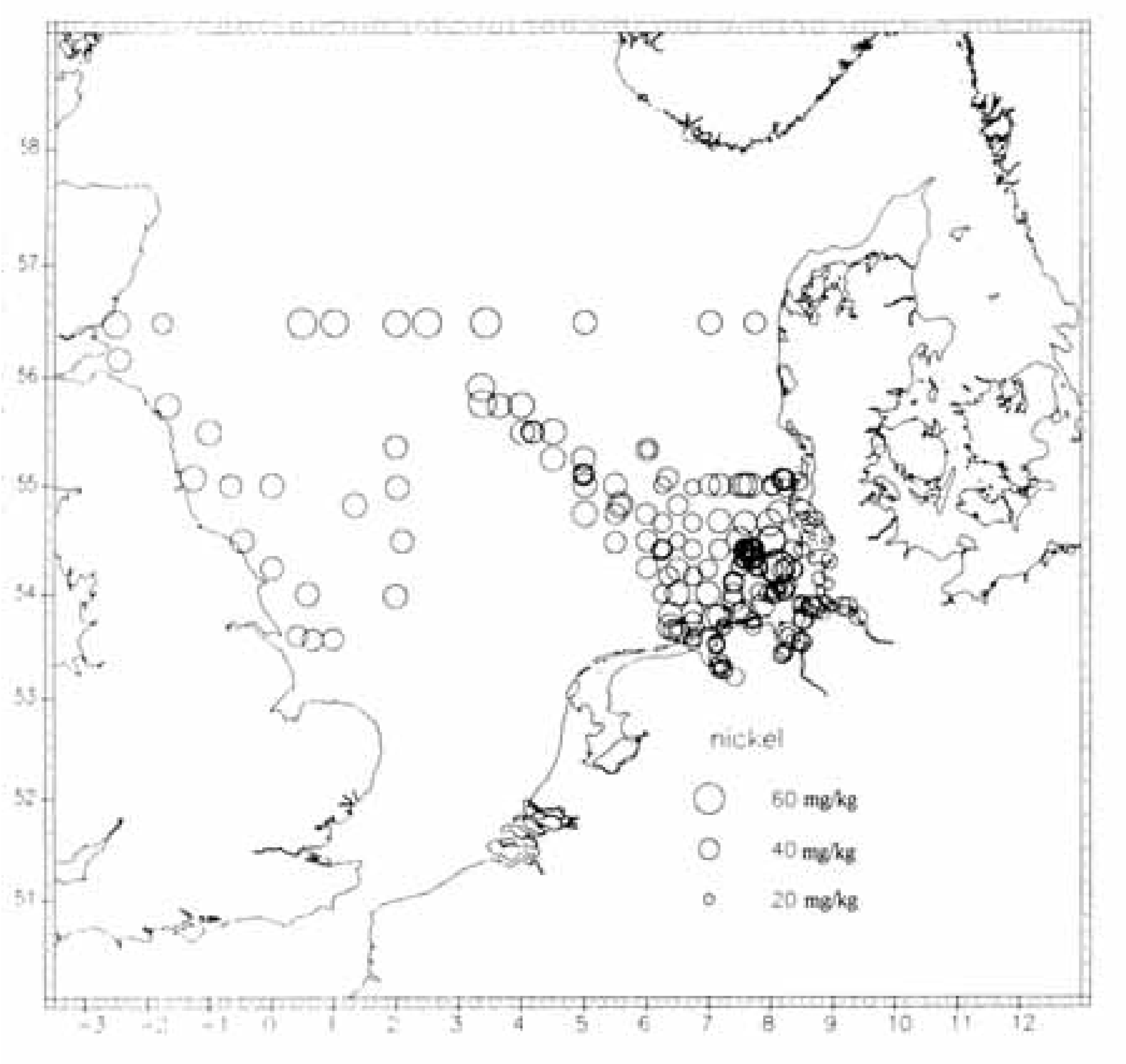


Figure 11 Distribution of nickel concentrations in North Sea sediment fines < 20 µm (Rowlatt *et al*., 1995)

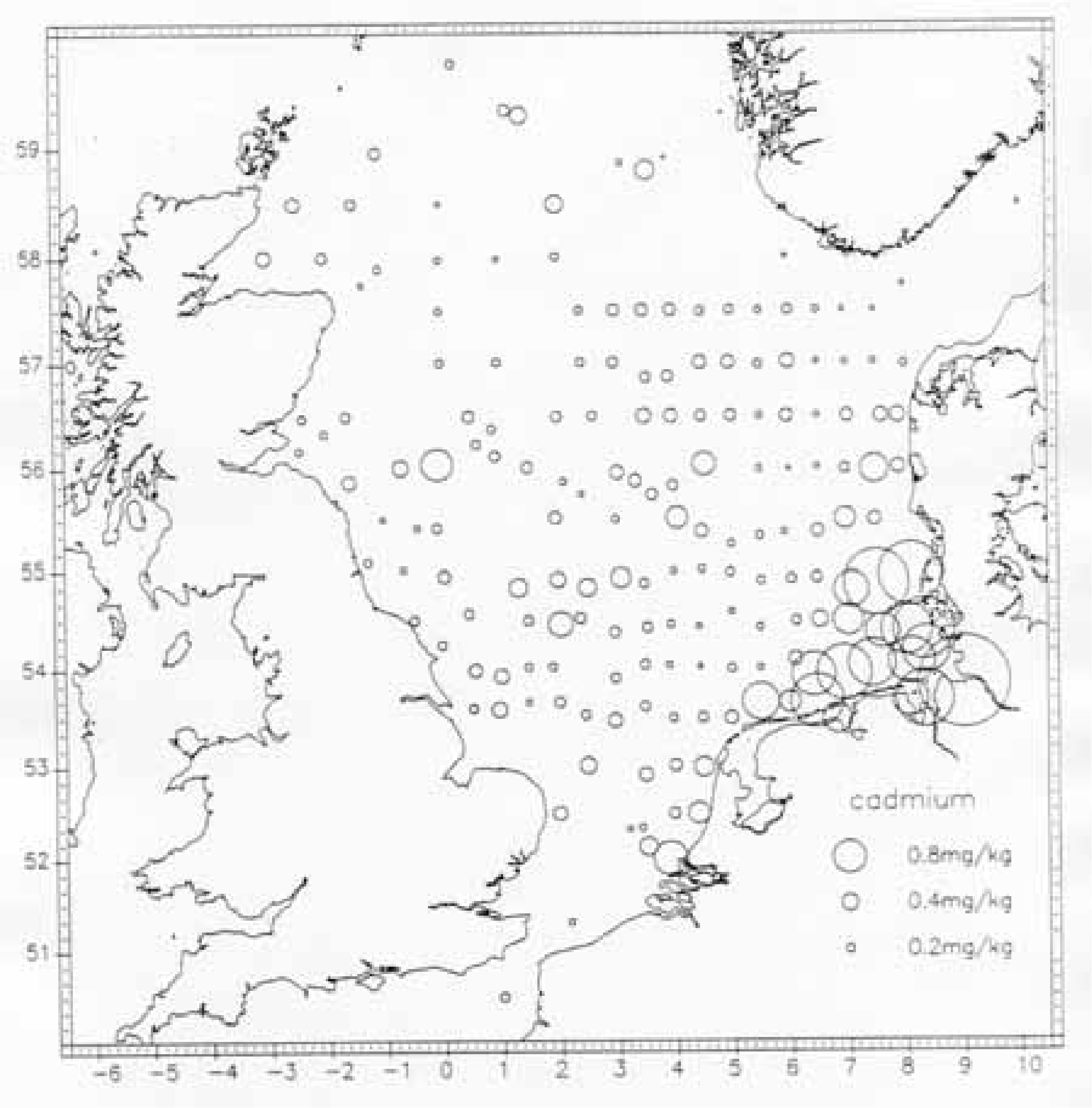


Figure 12 The distribution of cadmium concentrations in North Sea sediment fines <20 µm (BHSG data) (Rowlatt *et al.*, 1995)

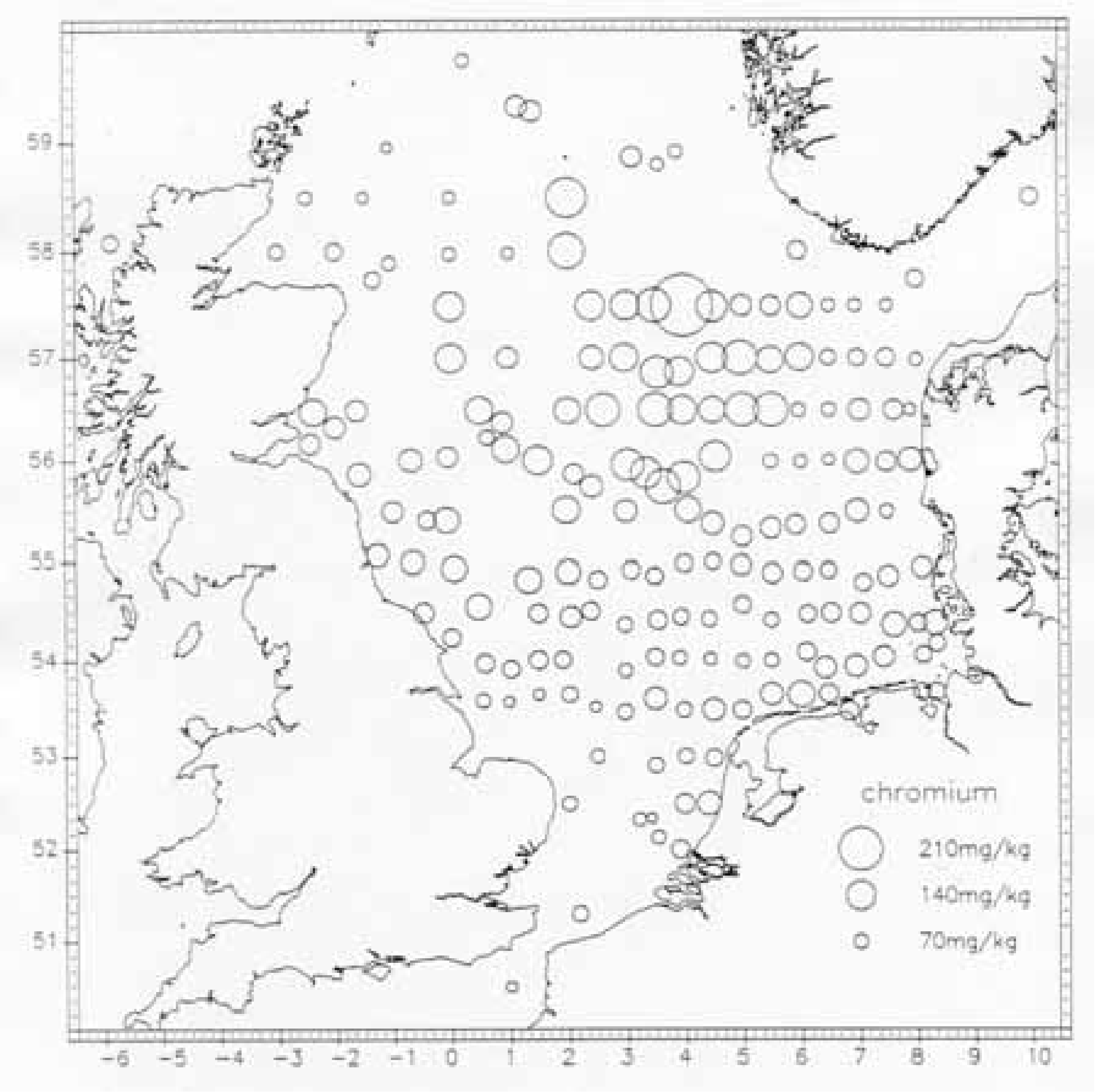


Figure 13 Distribution of chromium concentrations in North Sea sediment fines <20 μm (Rowlatt *et al.*, 1995)

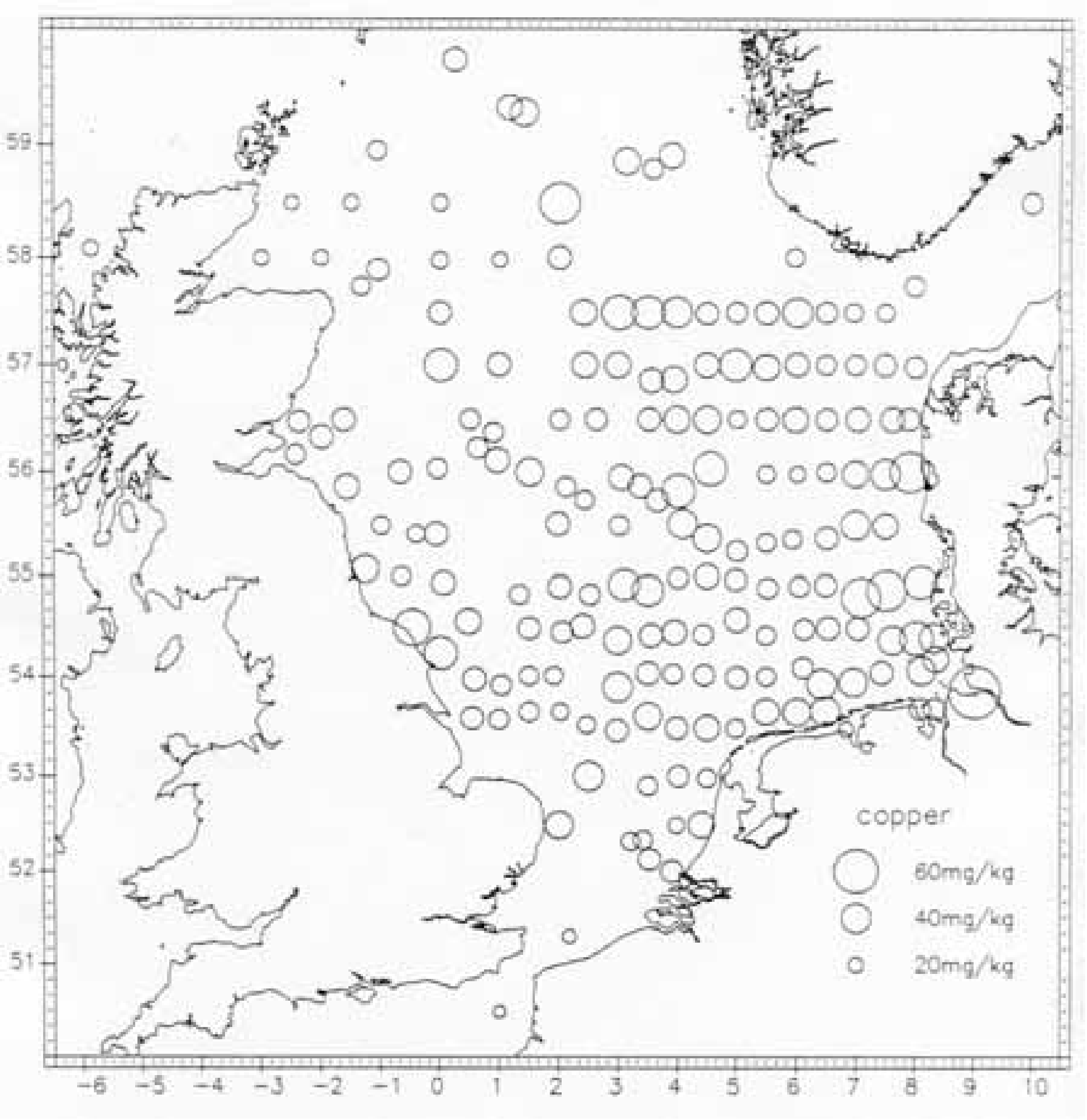


Figure 14 Distribution of copper concentrations in North Sea sediment fines <20 µm (Rowlatt *et al*., 1995)

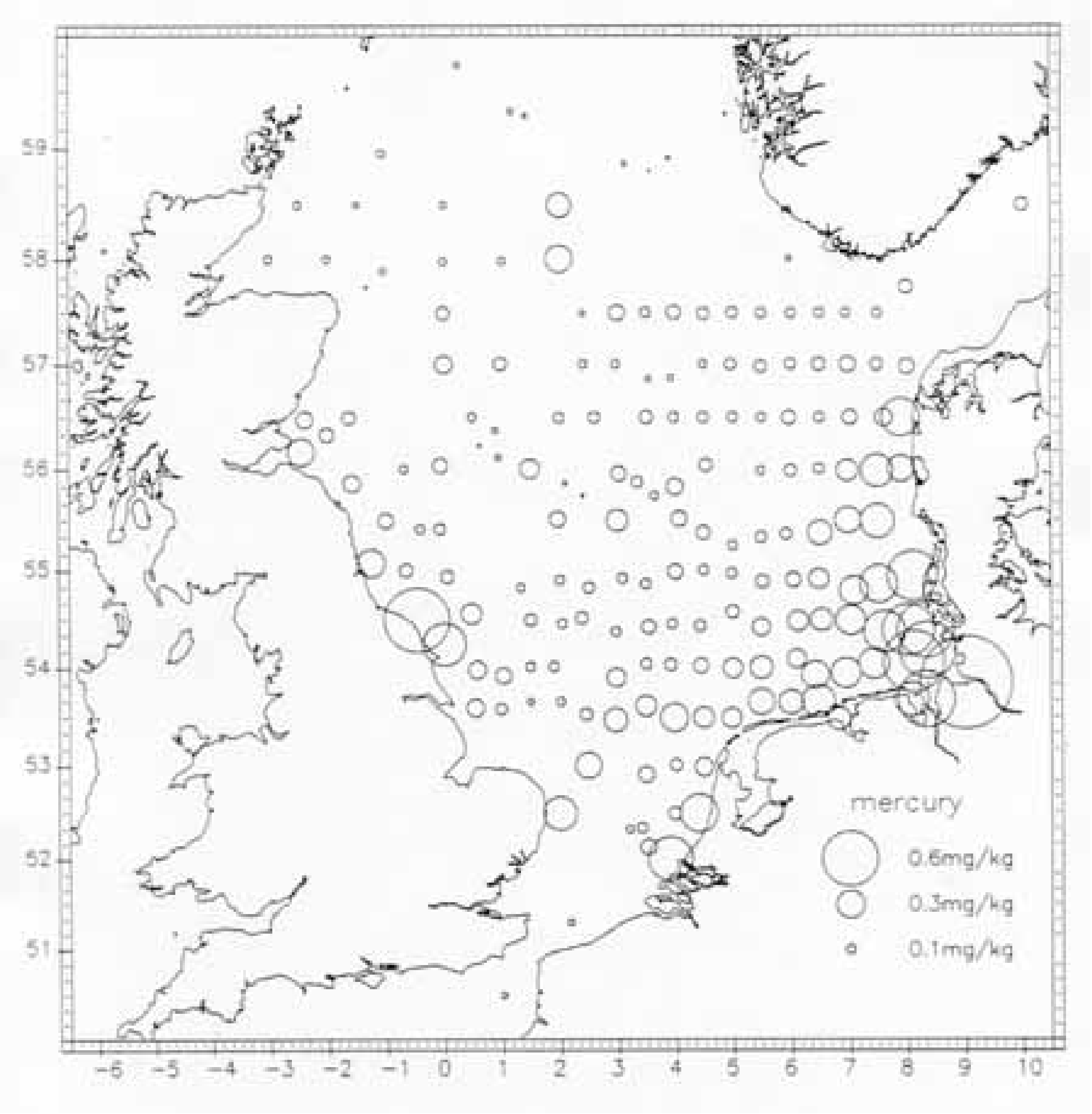


Figure 15 Distribution of mercury concentrations in North Sea sediment fines <20 μm (Rowlatt *et al*., 1995)

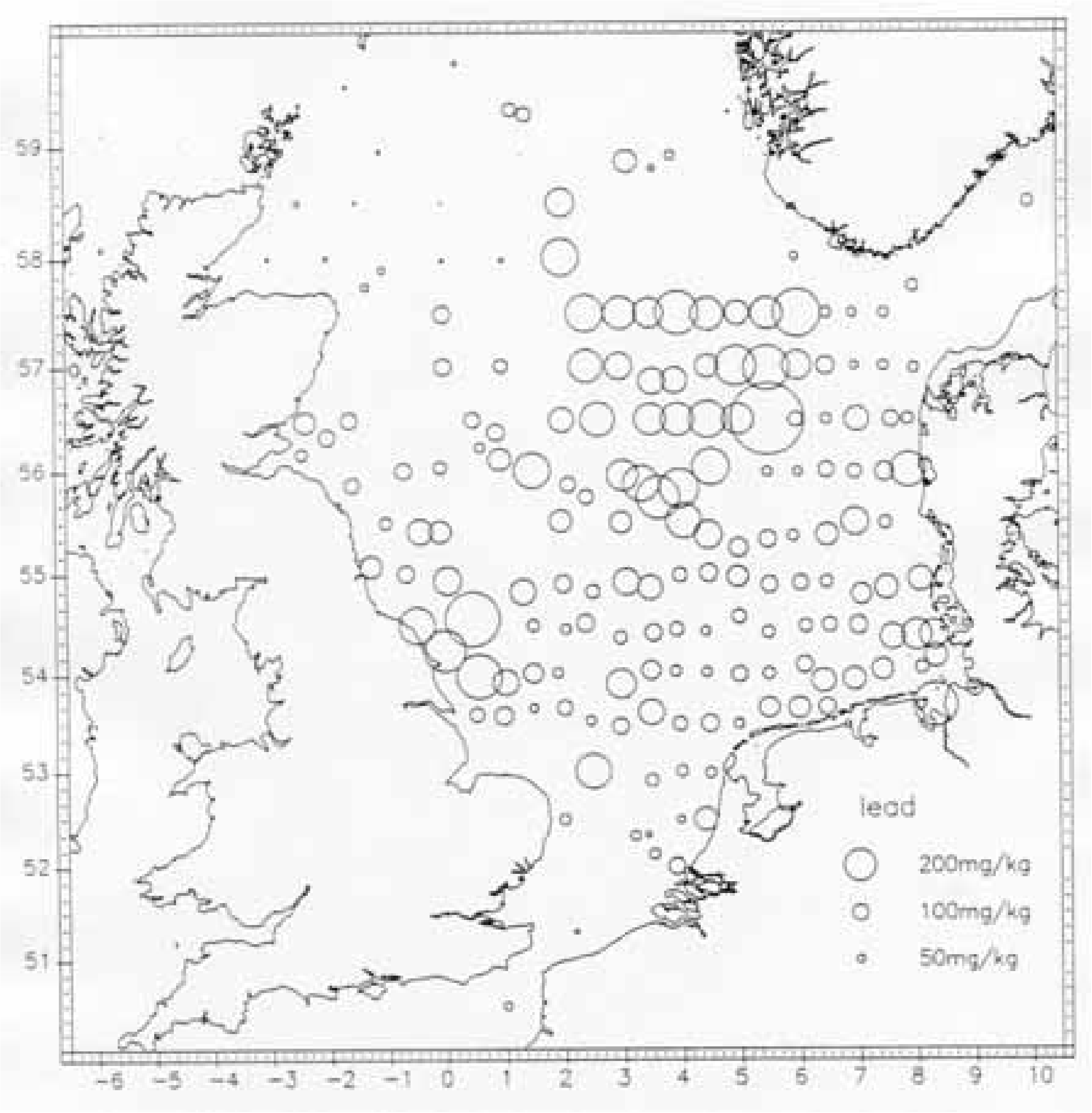


Figure 16 Distribution of lead concentrations in North Sea sediment fines <20 µm (Rowlatt *et al*., 1995)

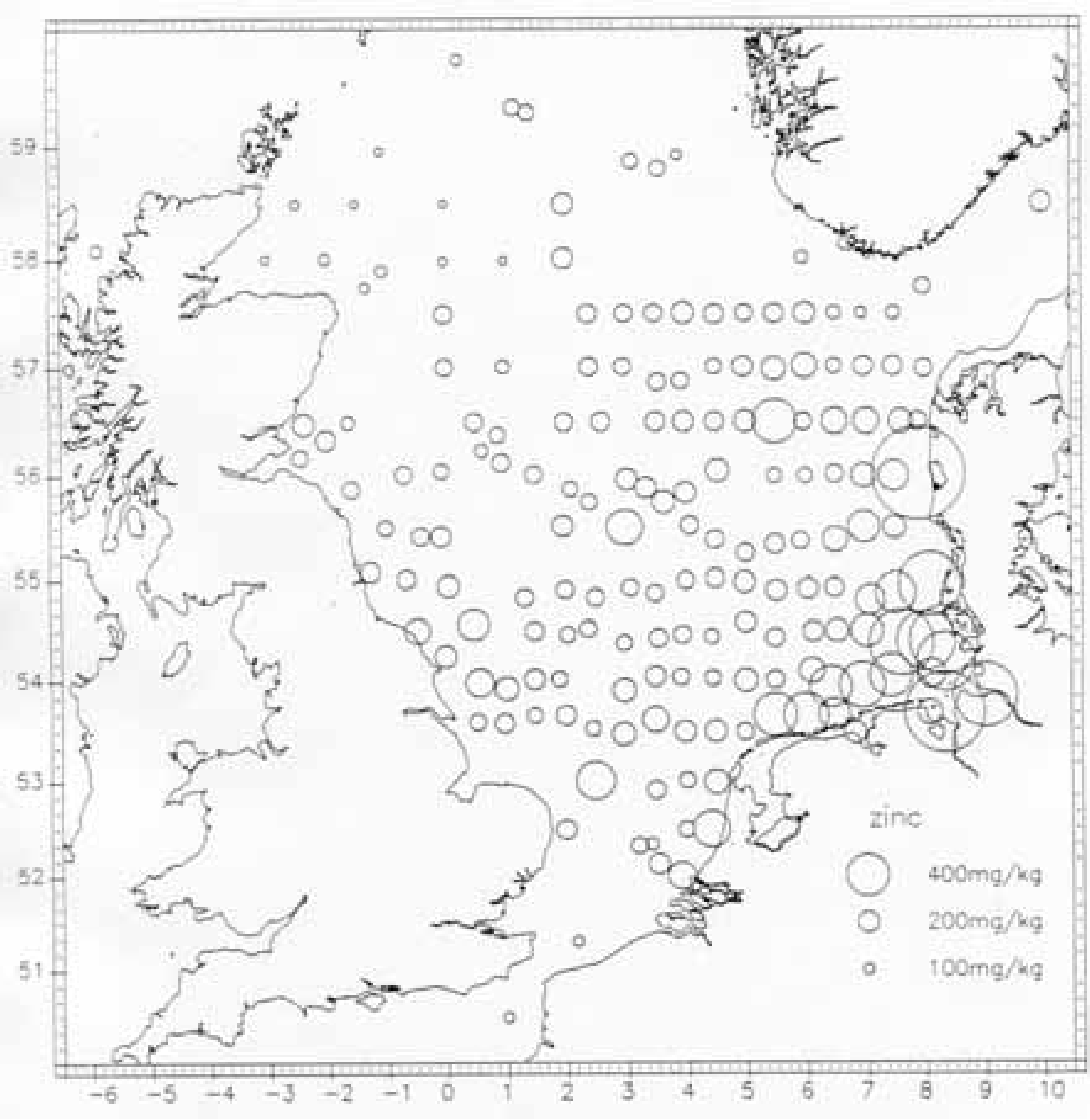


Figure 17 Distribution of zinc concentrations in North Sea sediment fines < 20 µm (Rowlatt *et al*., 1995)

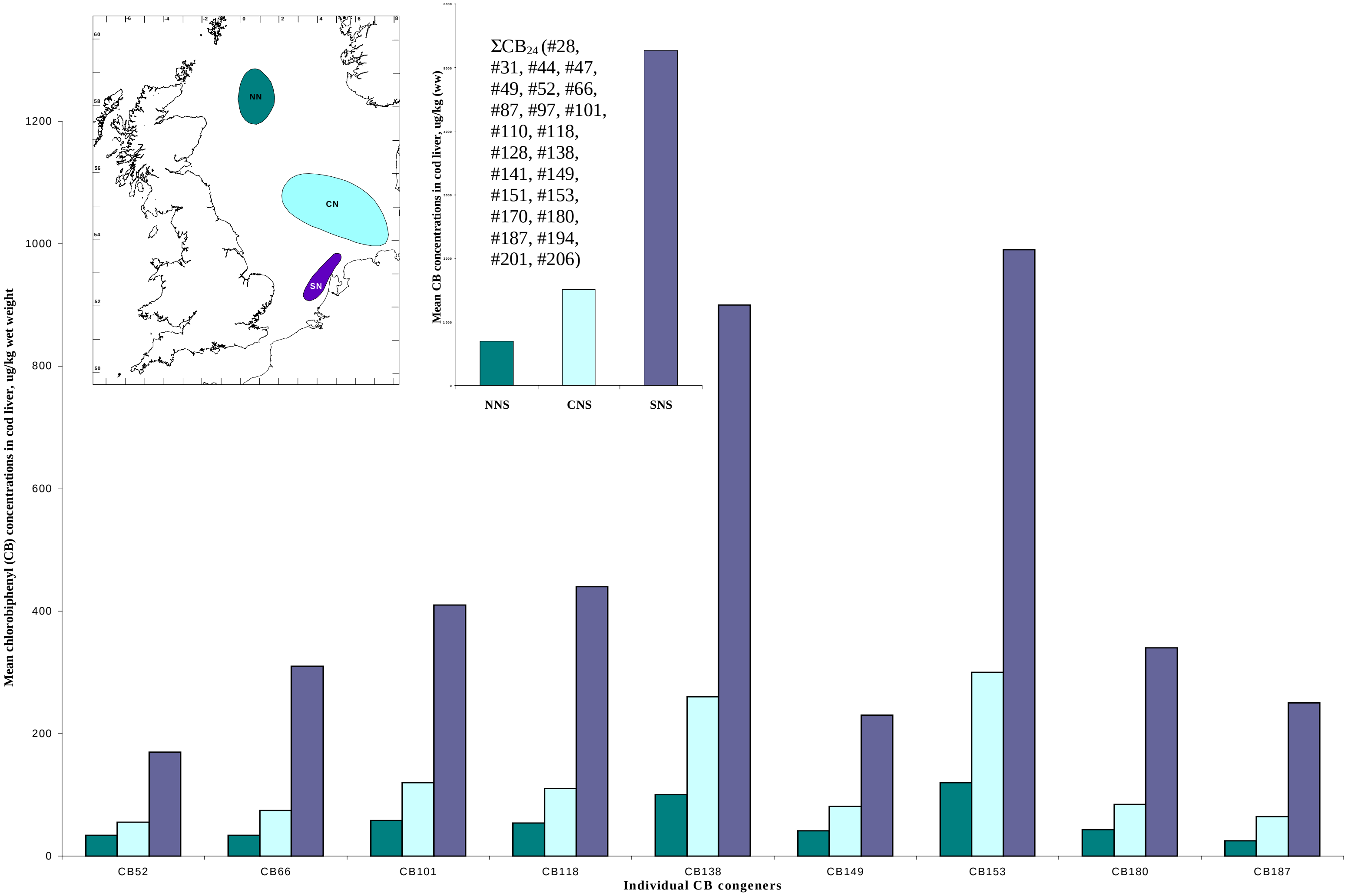


Figure 18 Concentrations of CB congeners in cod liver from three areas of the North Sea (1979-1987) (de Boer, 1988)

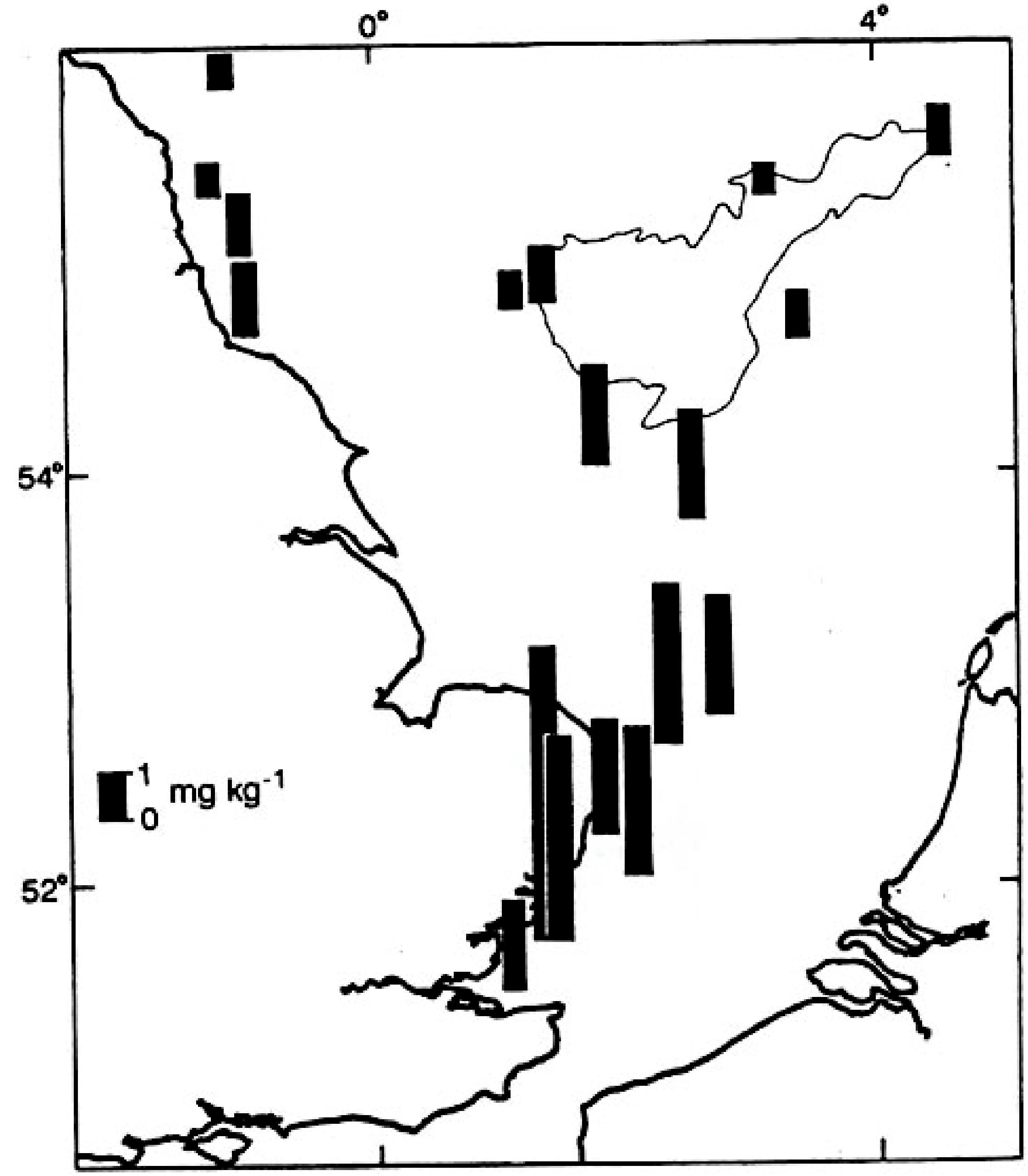


Figure 19 Concentrations of PCBs (mg kg^{-1}) in whiting liver (MAFF, 1992)

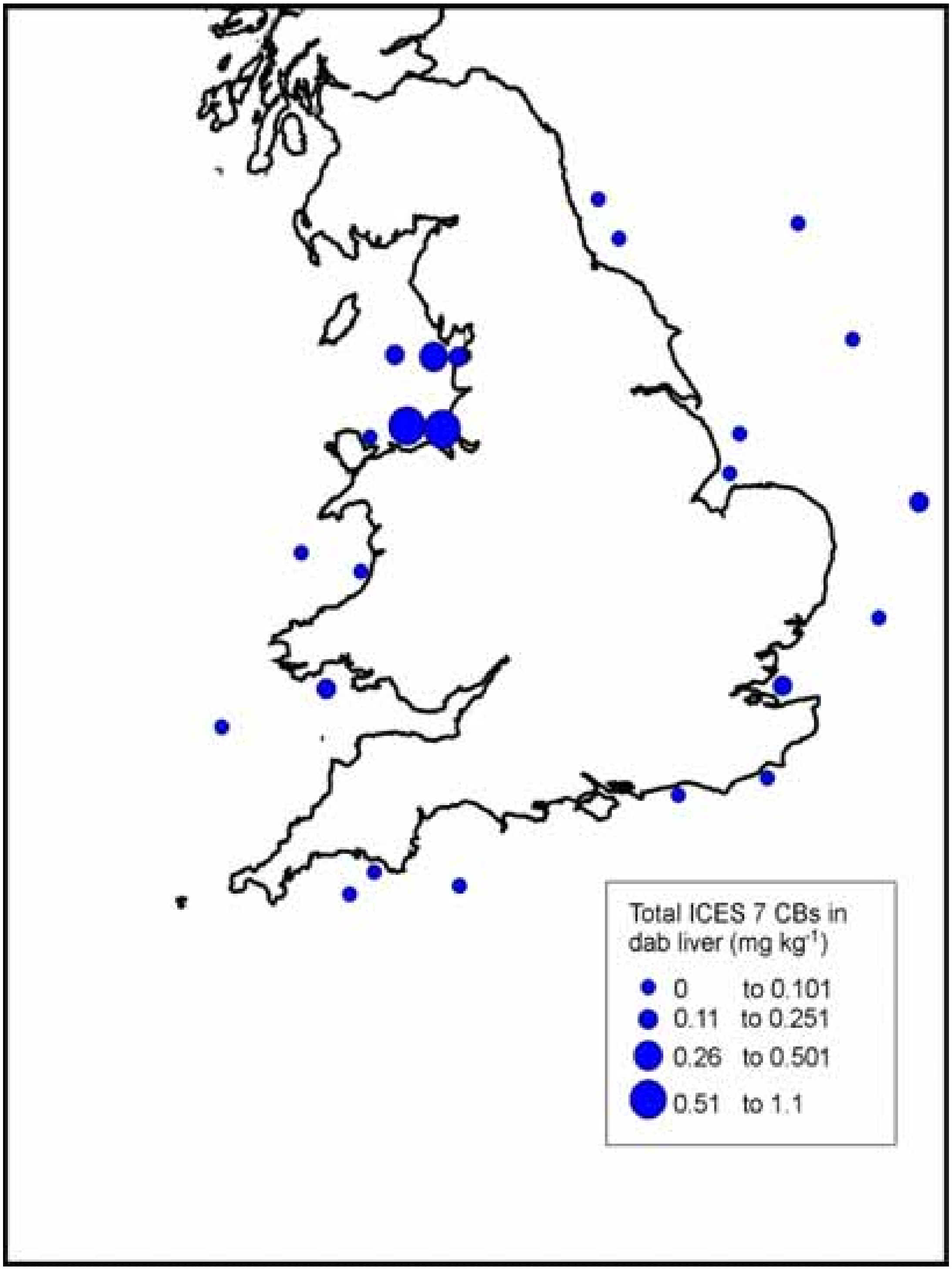


Figure 20a Concentrations of total ICES 7 CBs (mg kg^{-1} wet weight) in fish liver (MAFF, 1998)

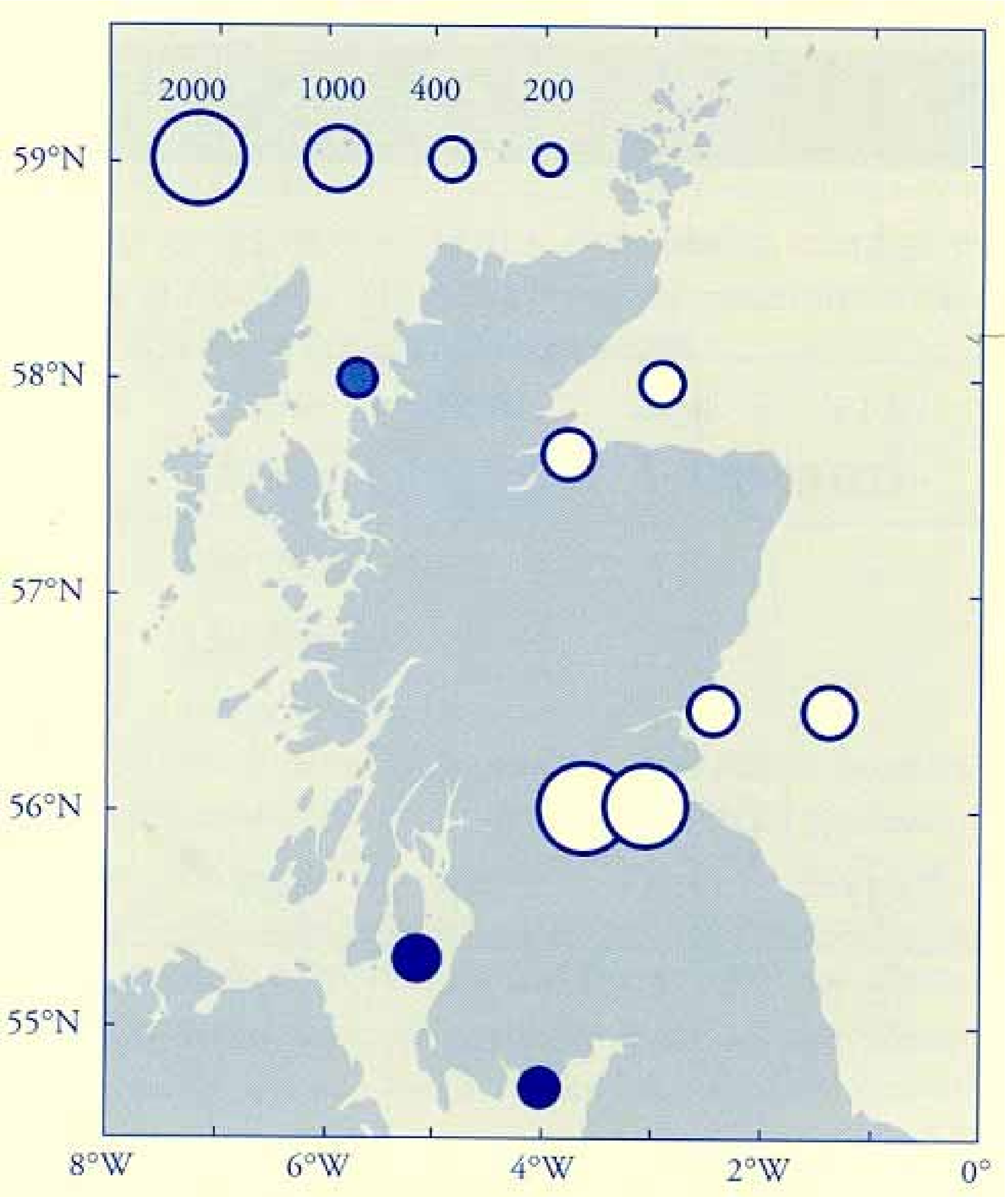


Figure 20b ΣPCBs ICES $_7$ (mg kg^{-1})in fish liver sampled off Scotland (NMP, 1998)

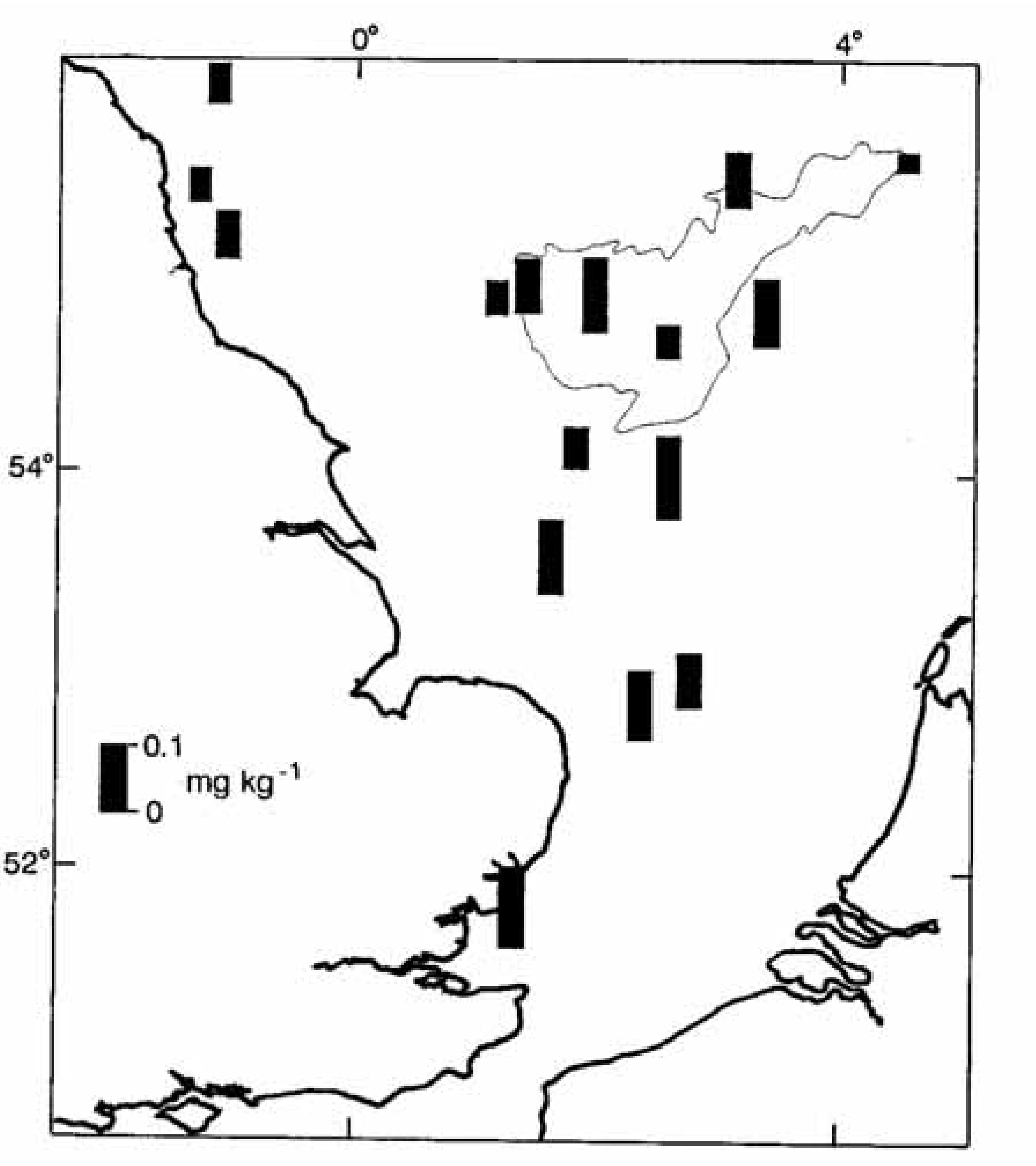


Figure 21 Concentrations of mercury (mg kg^{-1}) in dab muscle (MAFF, 1992)

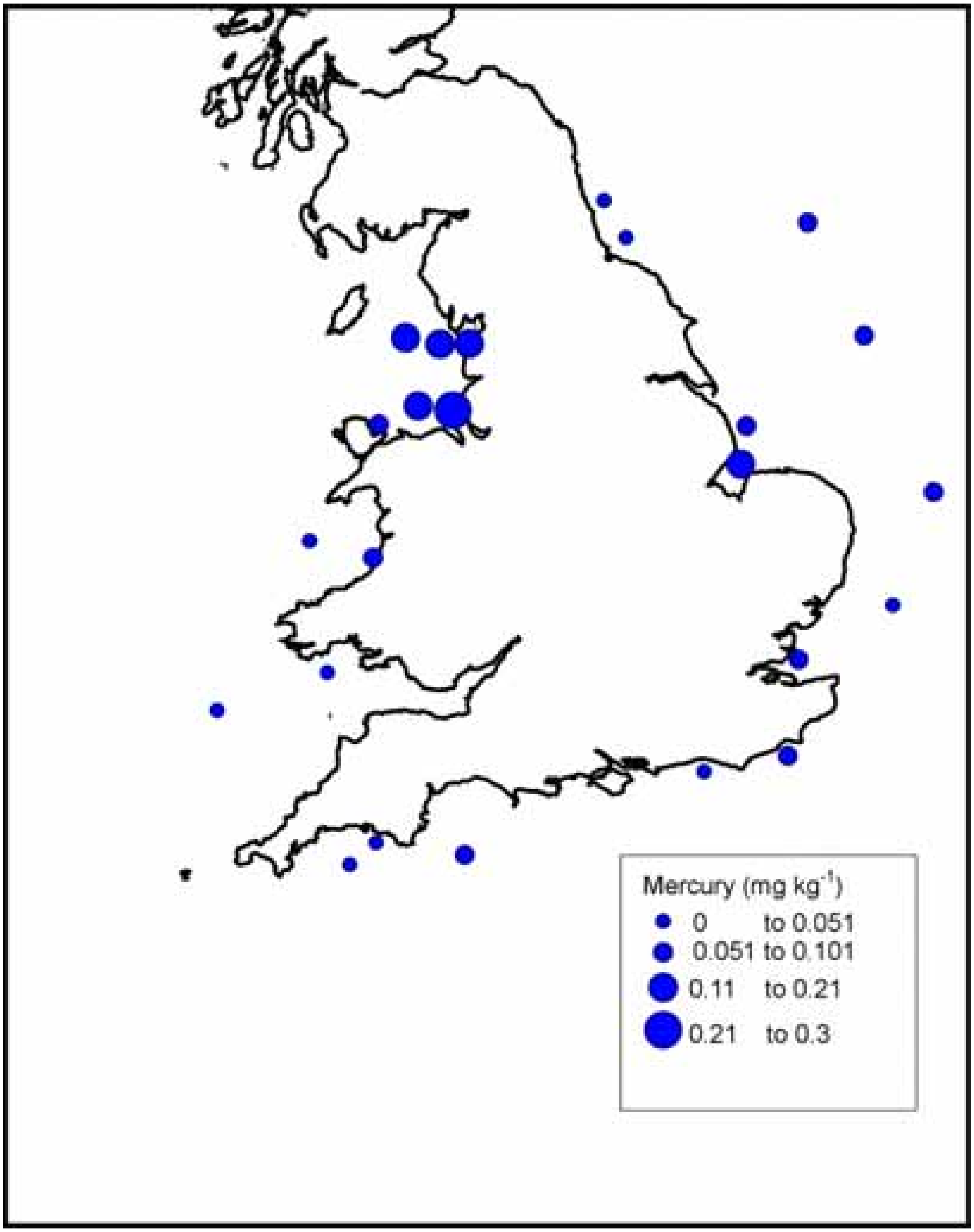


Figure 22a Concentrations of mercury (mg kg^{-1} wet weight) in dab muscle (MAFF, 1998)

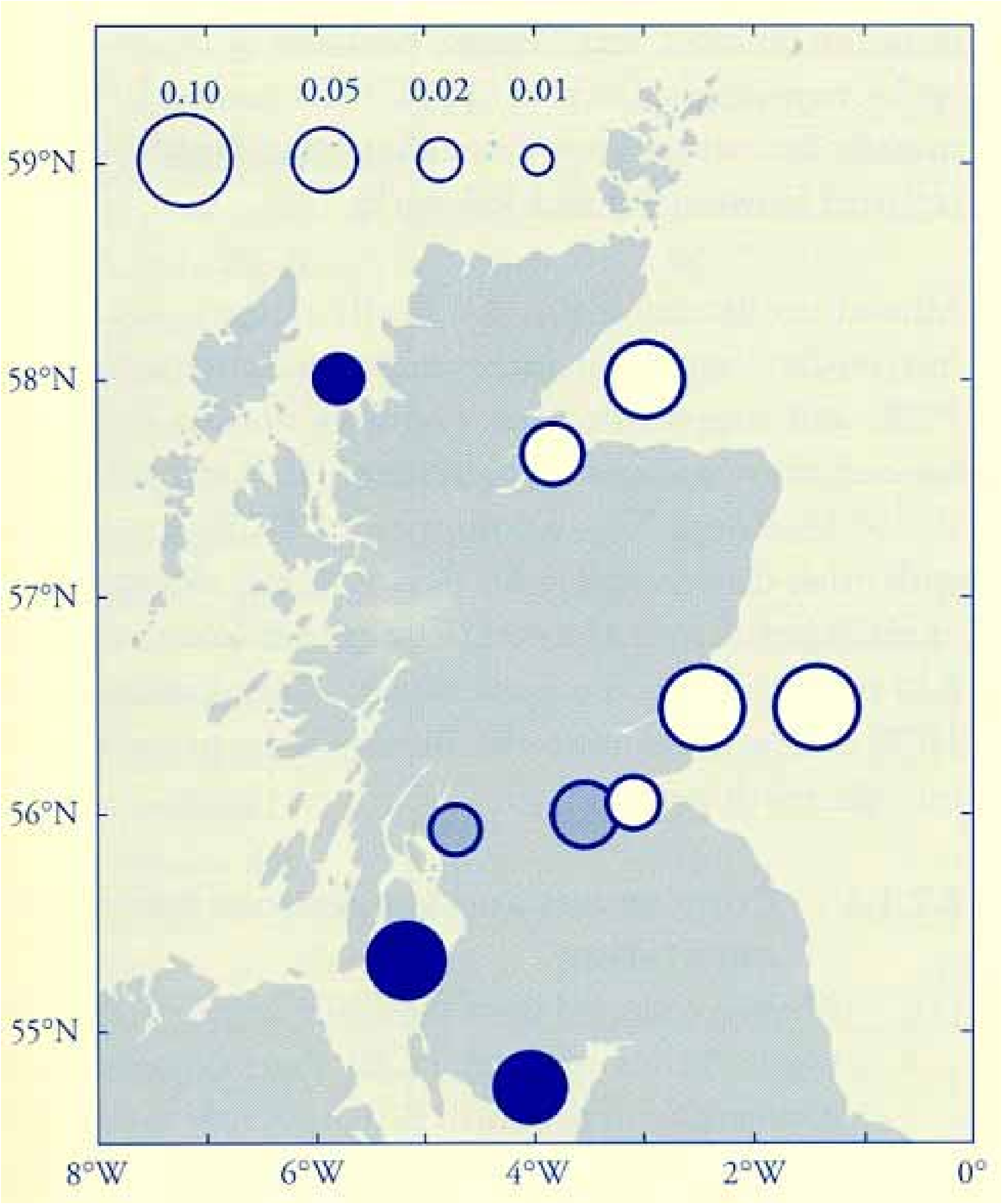


Figure 22b Concentrations of mercury in fish muscle (mg kg^{-1} wet weight) around Scotland (NMP, 1998)

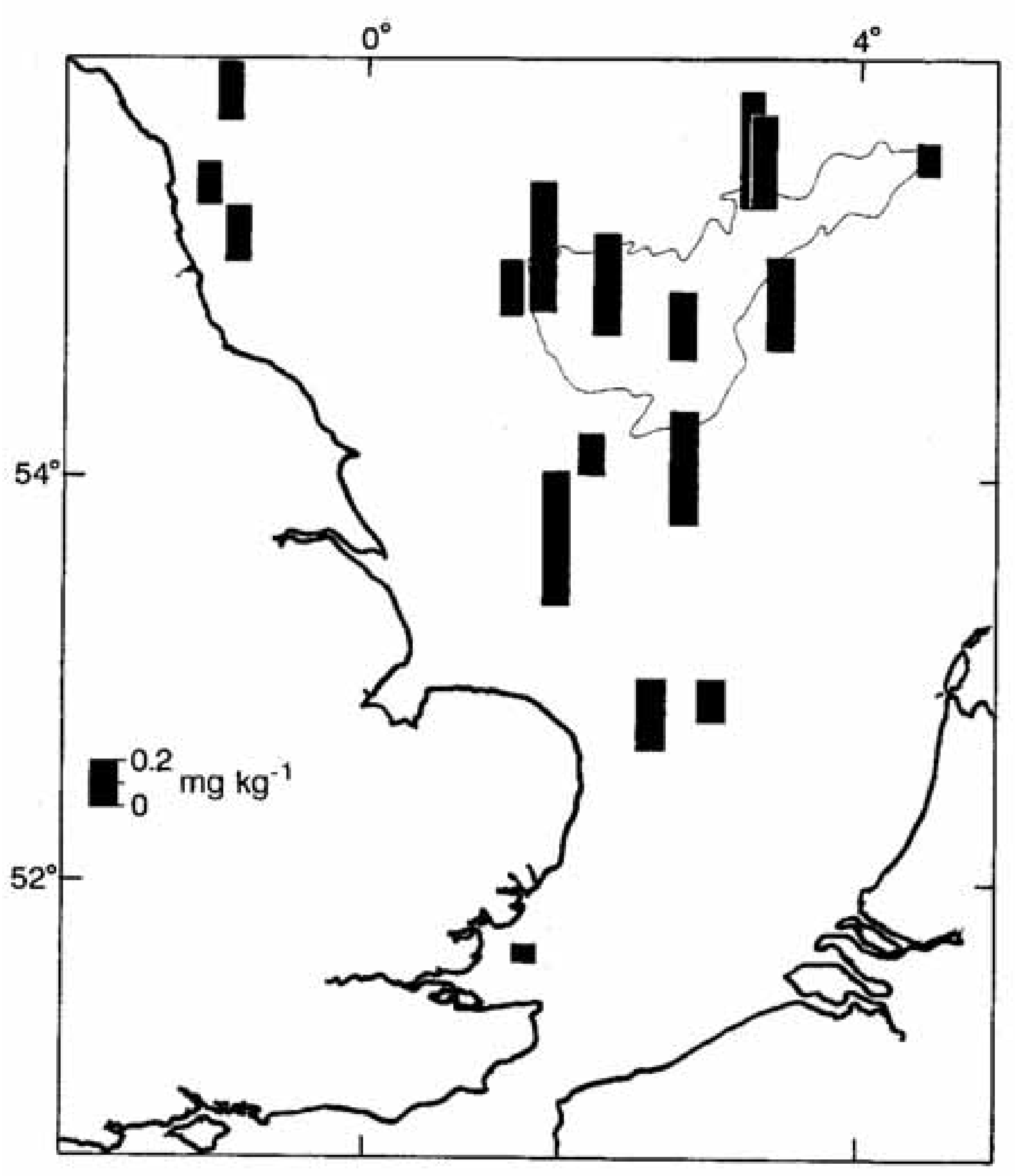


Figure 23 Concentration of cadmium (mg kg^{-1}) in dab liver (MAFF, 1992)

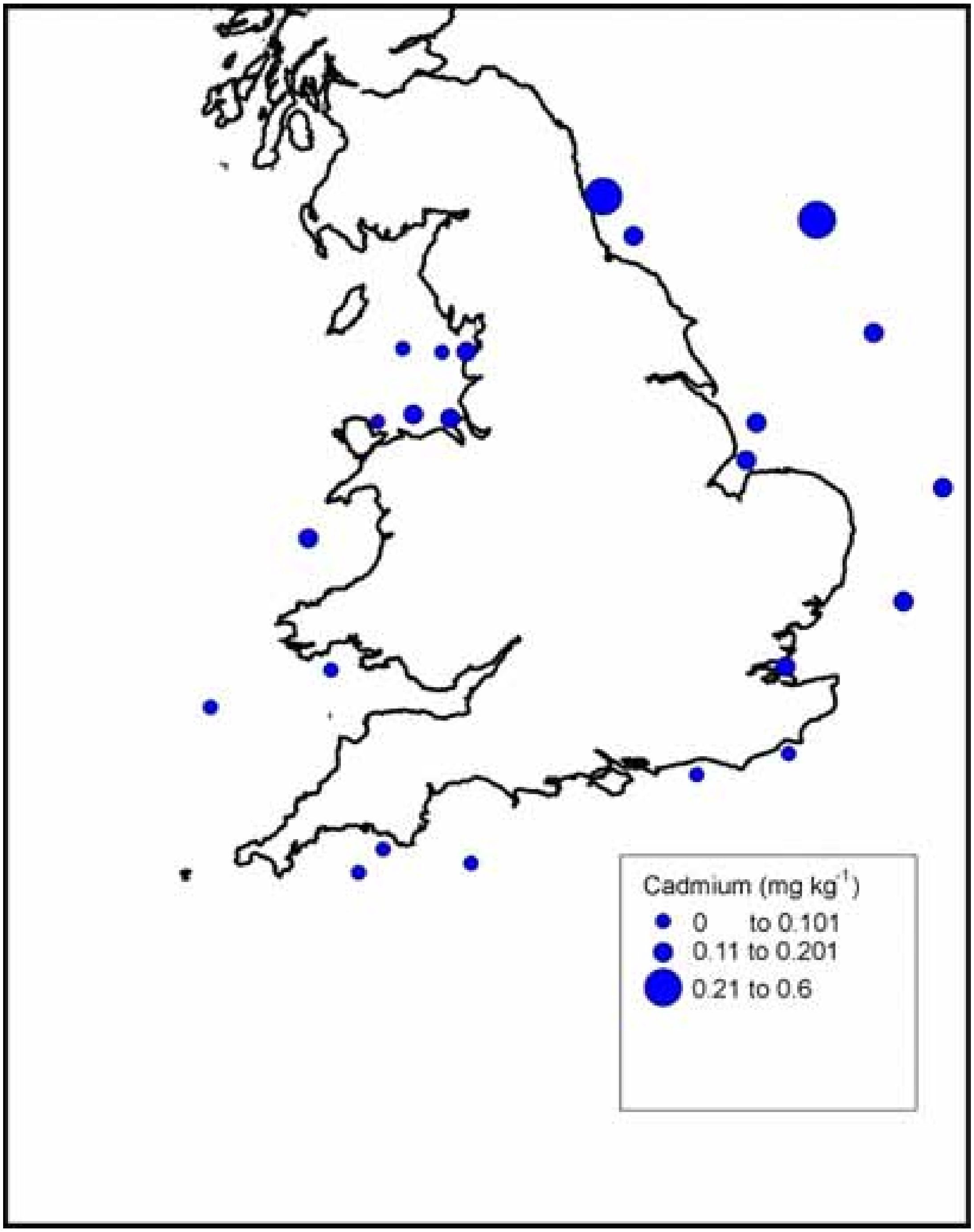


Figure 24a Concentrations of cadmium (mg kg^{-1} wet weight) in dab liver (MAFF, 1998)

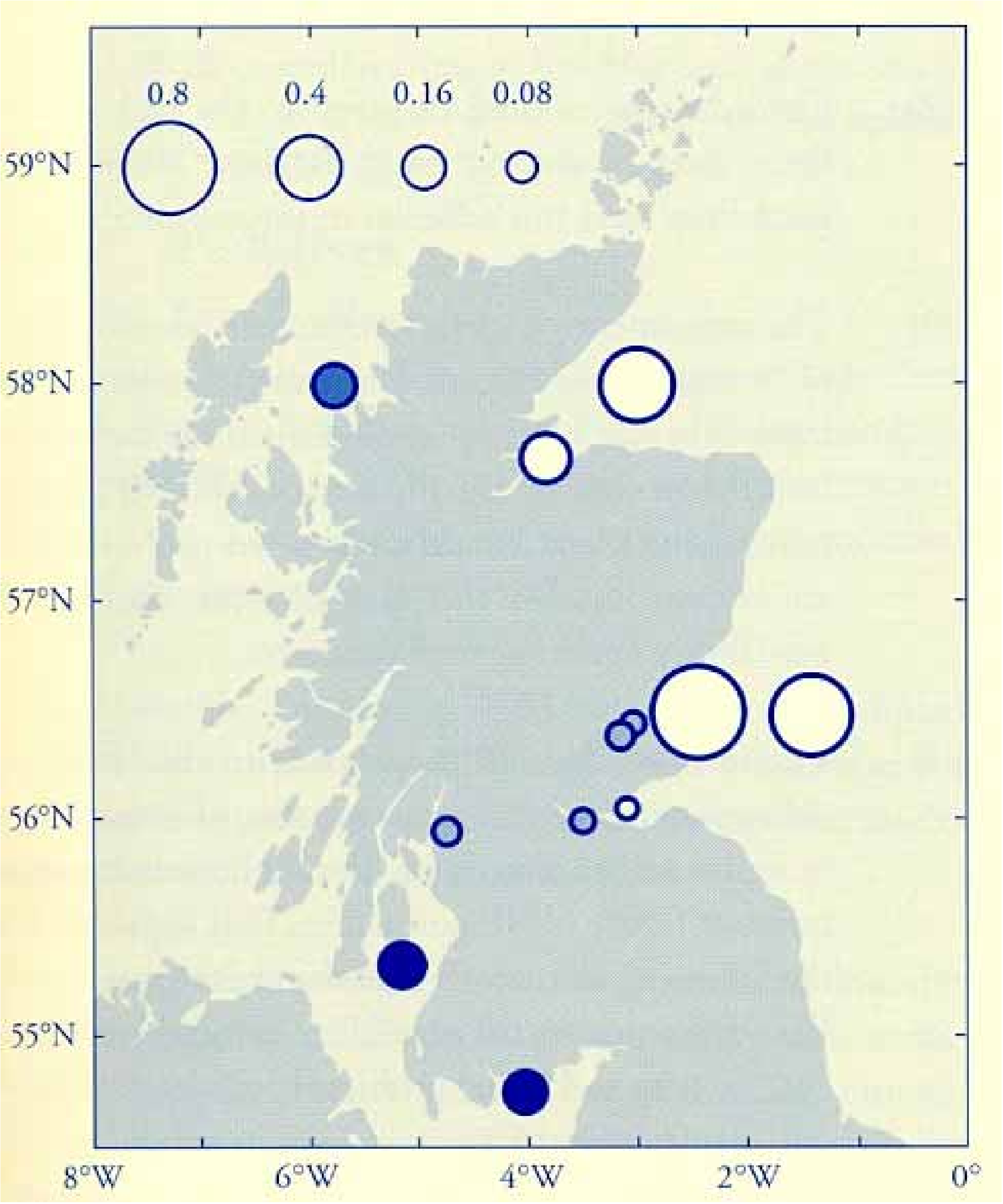


Figure 24b Cadmium concentrations (mg kg^{-1} wet weight) in fish liver sampled off Scotland (NMP, 1998)

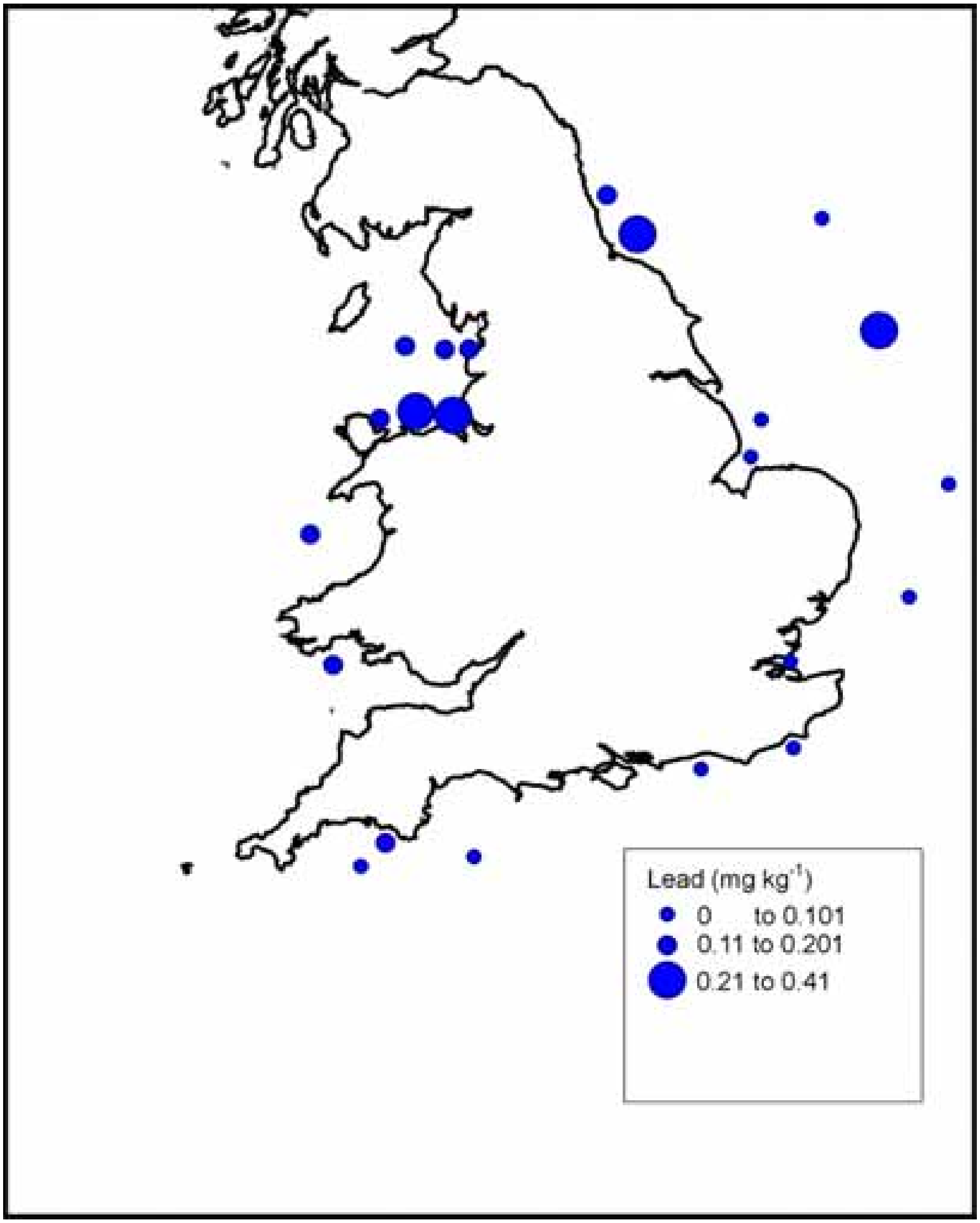


Figure 25a Concentrations of lead (mg kg^{-1} wet weight) in dab liver (MAFF, 1998)

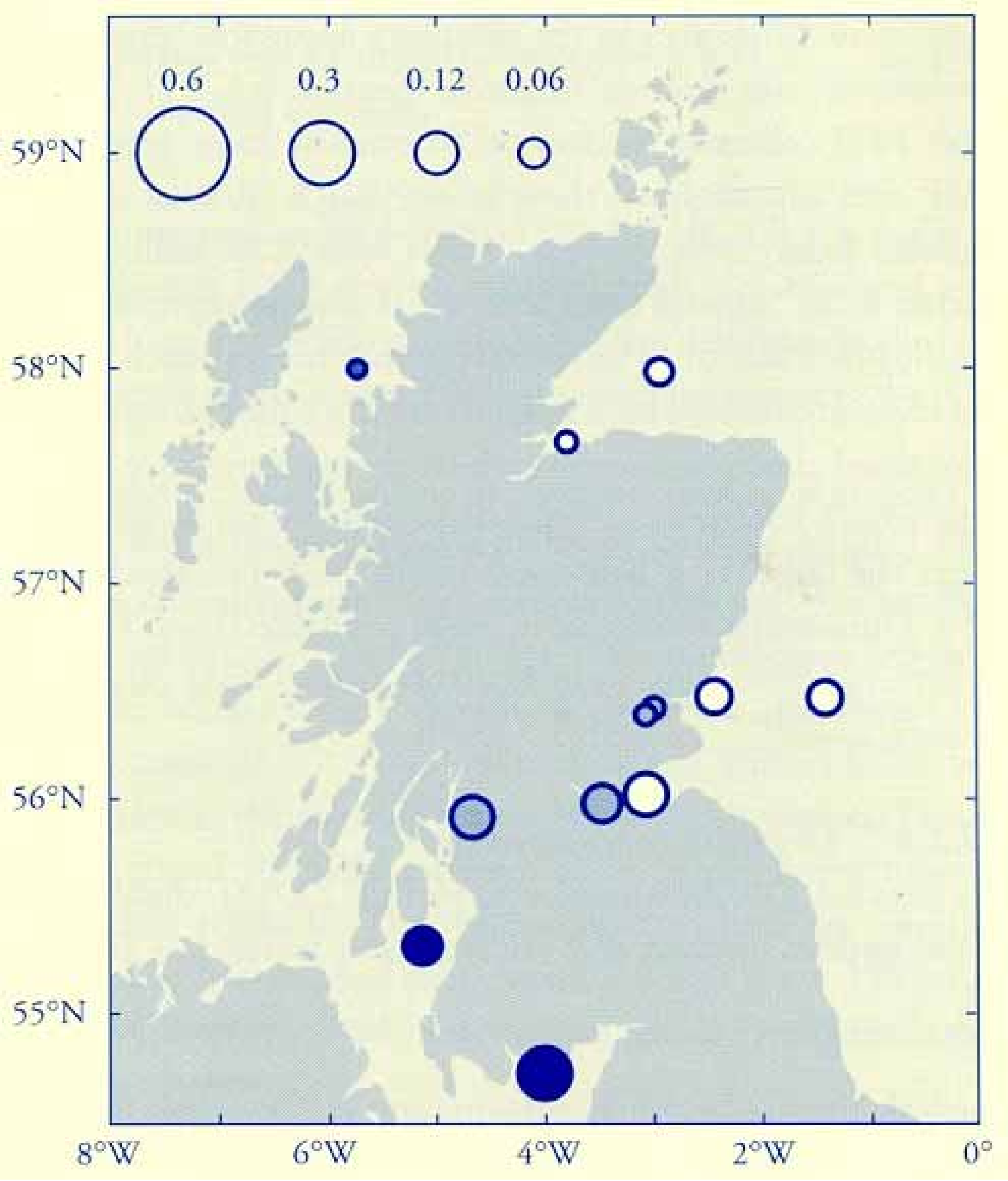


Figure 25b Concentrations of lead (mg kg^{-1} wet weight) in fish liver sampled off Scotland (NMP, 1998)

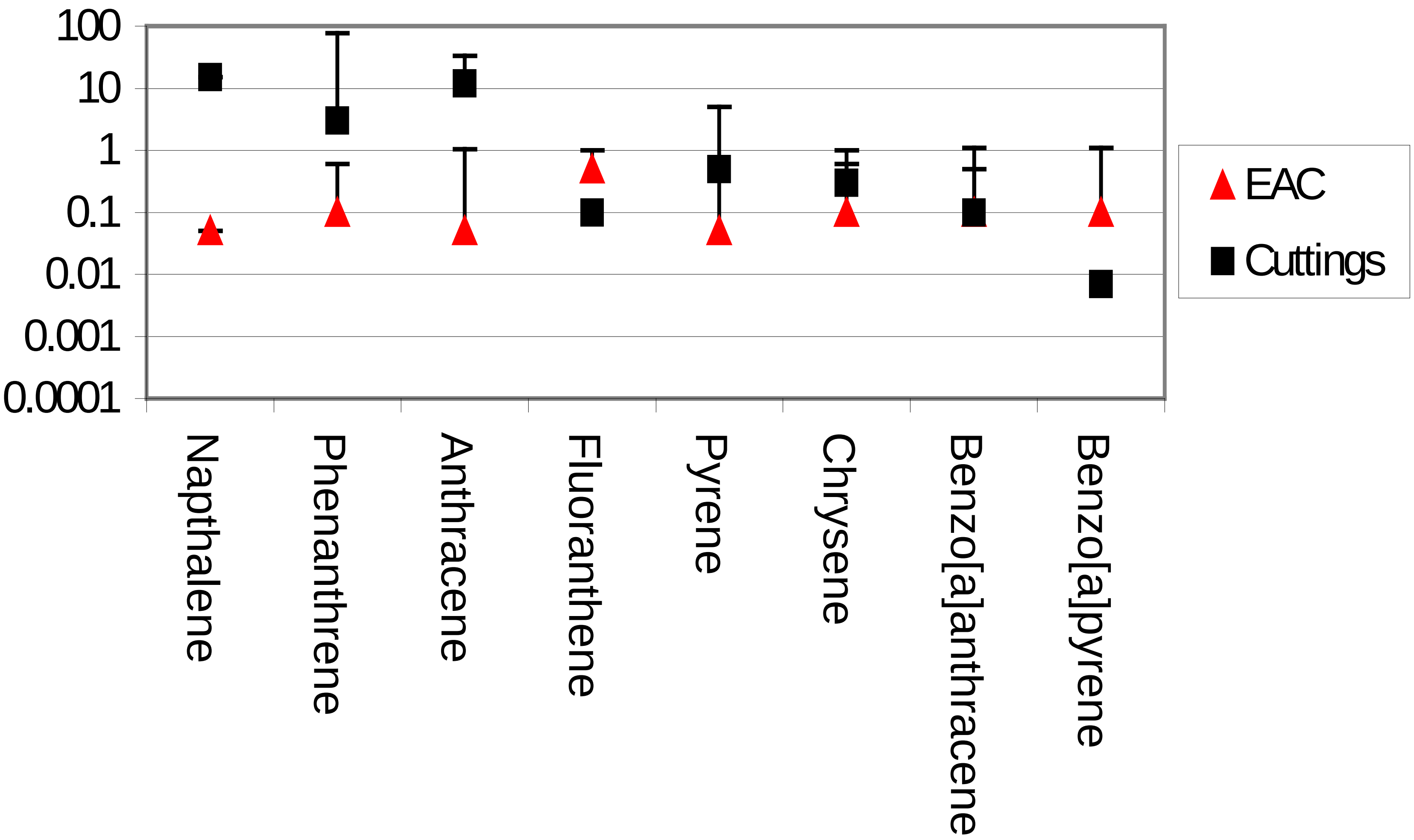


Figure 26 Concentration ranges (mg kg^{-1}) for 8 hydrocarbons measured in cuttings piles (based on data from CORDAH, 1999 and Gerrard *et al.*, 1998). The triangles show the ecotoxicological assessment criteria (OSPAR 2000)

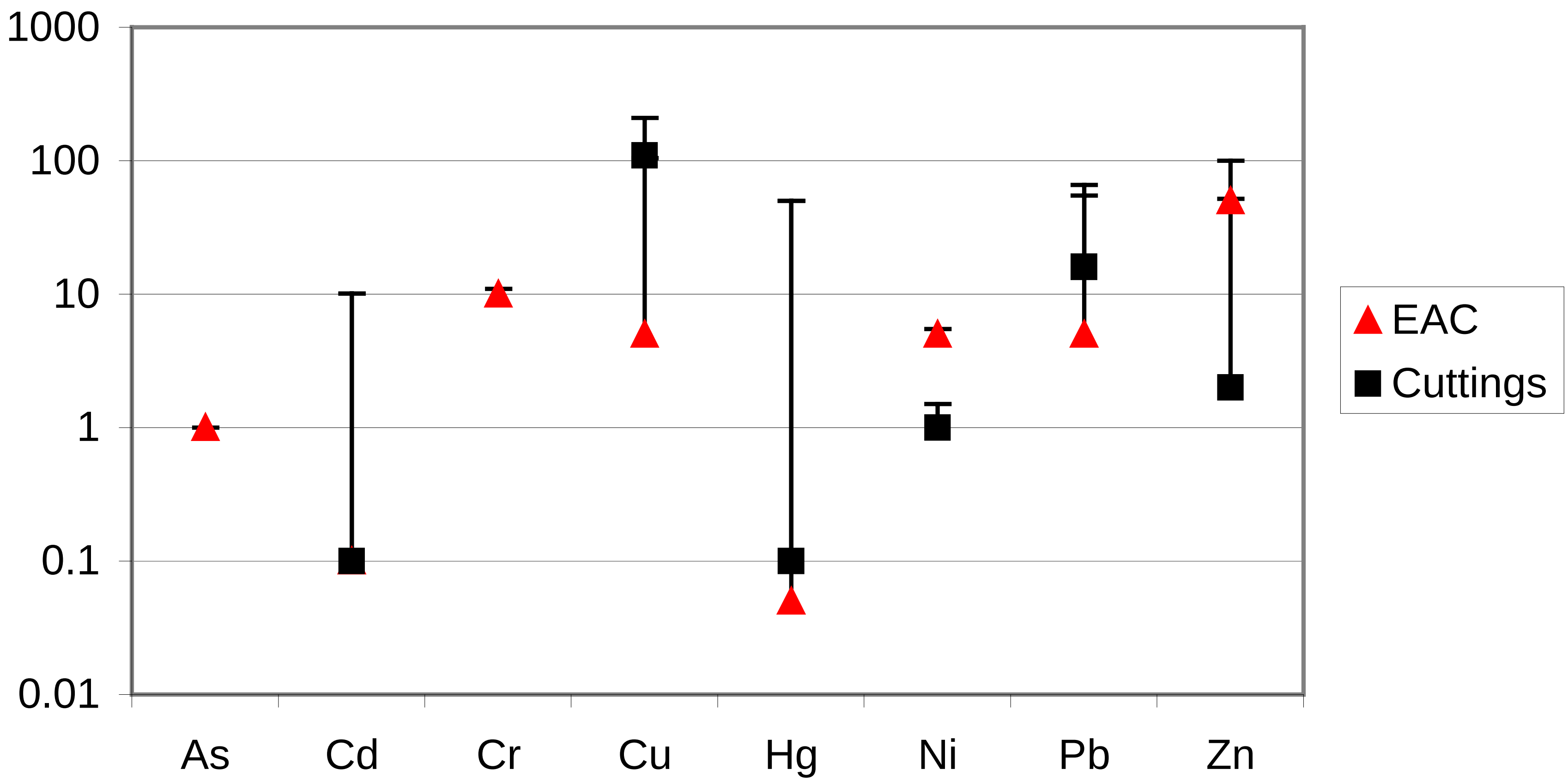


Figure 27 Concentration ranges (mg kg^{-1}) for 8 metals measured in cuttings piles (based on data from CORDAH, 1999 and Gerrard *et al*., 1998)

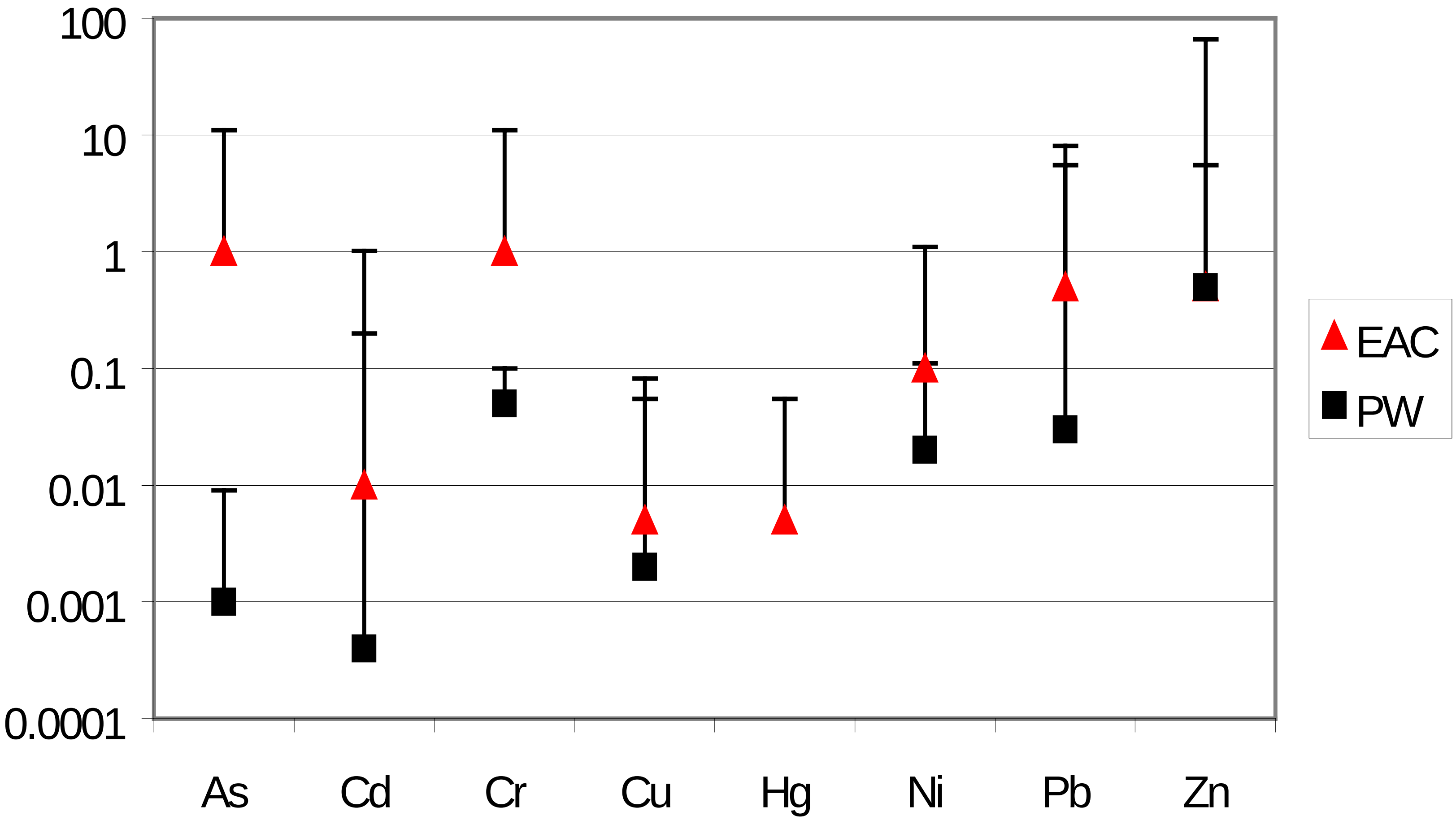


Figure 28 Concentration ranges (µg l^{-1}) for 8 metals measured in produced water (PW) (based on data from Davies, 1987 and Roe, 1999)

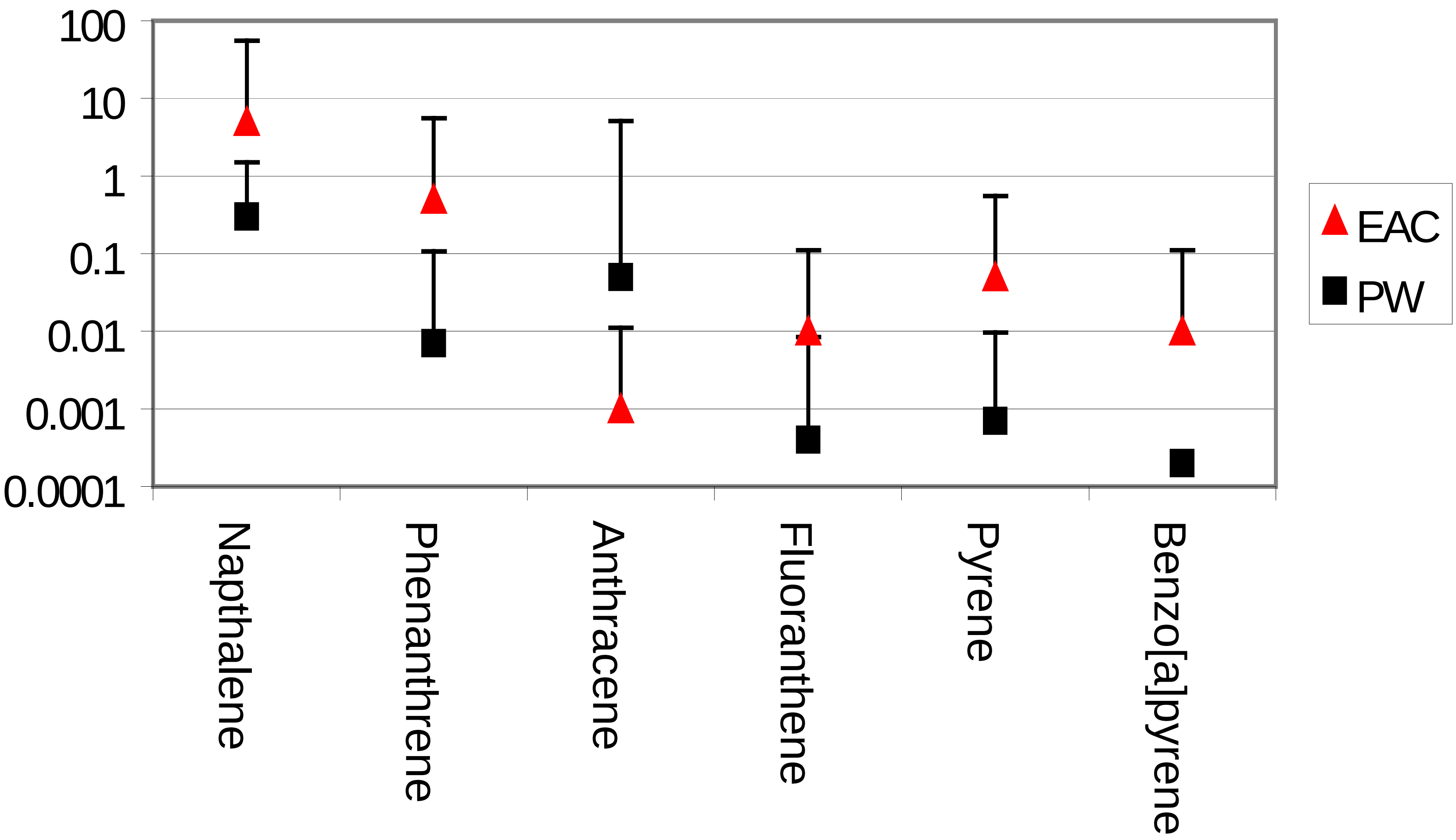


Figure 29 Concentration ranges (µg l^{-1}) for 6 hydrocarbons measured in produced water (based on data from Davies, 1987 and Re, 1999)