POLYCHLORINATED BIPHENYLS IN MARINE SEDIMENTS AND DREDGED MATERIAL AROUND ENGLAND AND WALES

Jacqueline Reed

Coastal and Estuarine Research Unit,
Department of Geography,
University College London.

December 2000

Submitted for
examination of Ph.D.
at the University of London.

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ABSTRACT

This study provides the first comprehensive investigation of polychlorinated biphenyl (PCB) contamination of marine sediments and dredged material in England and Wales. A geographically extensive analysis of data acquired through national monitoring programmes since 1990 is used to define 'typical' concentrations for coastal and offshore sediments. Spatial variation is investigated on a regional basis and temporal trends in PCB loadings are examined where sufficient repeat sampling has been undertaken. The nature of within-site spatial and chemical variation in contaminant loadings are investigated through an intensive case study of a known PCB 'hotspot' in the Port of Swansea.

Offshore sediments around England and Wales are found to be largely uncontaminated by PCBs. Concentrations in estuarine sediments are much higher, with particular 'hotspots' being evident in the River Blyth and in Cardiff Bay. PCB concentrations in dredged material are typically an order of magnitude above those found in marine sediments, with several areas of concern being identified in North East England, South Wales and North West England. PCB concentrations in a third of all dredged material samples analysed since 1990 exceed current Sediment Quality Guidelines. Many of the most contaminated samples have been obtained from commercial dockyards in South Wales (principally Cardiff, Newport and Swansea).

Multivariate and geostatistical methods are used to investigate more fully the spatial and chemical structure of PCB concentrations within King's Dock, Swansea. Principal component analysis shows that variation in PCB homologue profiles is consistent with historical contamination from the more chlorinated commercial Aroclor® mixtures.

Spatial variation of the less chlorinated PCB congeners appears to be more structured than the more chlorinated CBs. This high spatial dependence of the less chlorinated PCBs is attributed to properties such as volatility and solubility. Total organic carbon influences the concentration of the more chlorinated CBs, since it encourages adsorption to sediments. Ordinary kriging is conducted to estimate PCB concentrations throughout King's Dock. The resulting inventories show that, in this case, conventional monitoring significantly over-estimates the total PCB inventory.

Geostatistically-based sampling and analysis is appropriate for the intensive monitoring of known PCB 'hotspots', and lessons from the Swansea case study are integrated into a new protocol for sampling and for assessment of dredging licence applications.

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ABBREVIATIONS

Ah	Aryl hydrocarbon receptor
ABP	Associated British Ports
BP	British Petroleum
CBs	Chlorinated biphenyls
CCME	Canadian Council of Ministers of the Environment
CEFAS	Centre for Environment, Fisheries and Aquaculture Science
CIRIA	Construction Industry Research and Information Association
COPA	Control of Pollution Act
DANI	Department of Agriculture of Northern Ireland
DETR	Department of Environment, Transport and the Regions
DGPS	Differential Global Positioning System
DOE	Department of Environment
DNA	Deoxyribose nucleic acid
EA	Environment Agency
EDA	Exploratory data analysis
EEA	European Environment Agency
EFD	Environment & Fisheries Department
EHS	Environment & Heritage Service
EPA	Environmental Protection Act
EQO	Environmental Quality Objective
EQS	Environmental Quality Standard
ERL	Effects range low
ERM	Effects range median
EU	European Union
FEPA	Food & Environment Protection Act (1985)
GCSDM	Group Coordinating Sea Disposal Monitoring
GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Pollution
GC-ECD	Gas chromatography with electron capture detector
HP	Hewlett Packard
IADC	International Association of Dredging Companies
ICE	Institution of Civil Engineers
ICES	International Council for Exploration of the Seas
IMO	International Maritime Organisation

ABBREVIATIONS (Contd.)

IOC	Intergovernmental Oceanographic Commission
IUPAC	International Union Pure and Applied Chemists
JAMP	Joint Assessment and Monitoring Programme
JMP	Joint Monitoring Group of the Oslo & Paris Convention
JONUS	Joint Nutrient Study
LDC	London Dredging Convention
MAFF	Ministry of Agriculture, Fisheries and Food
MPMMG	Marine Pollution Monitoring Management Group
NMMP	National Marine Monitoring Programme
NOAA	National Oceanographic & Atmospheric Administration
NR	National Reference
NSCDs	North Sea Conference Declarations
OMC	Organic matter content
OSPAR	Oslo and Paris Commission
PAHs	Polycyclic aromatic hydrocarbons
PARCOM	Paris Commission
PC	Principle component
PCA	Principle component analysis
PCBs	Polychlorinated biphenyls
PIANC	Permanent International Association of Navigation Congress
POPs	Persistent organic pollutants
QC	Quality Control
QUASIMEME	Quality Assurance of Information in Marine Environmental Monitoring in Europe
SEPA	Scottish Environmental Protection Agency
SERAD	Scottish Executive Rural Affairs Department
SOAEFD	Scottish Office for Agriculture, Environment & Fisheries Department
SPM	Suspended particulate matter
TIE	Toxicity identification & evaluation
TBT	Tributyltin
TOC	Total organic carbon
UK	United Kingdom
UN	United Nations

ABBREVIATIONS (Contd.)

UNCED	United Nations Conference on Environment & Development
UNEP	United Nations Environment Programme
US	United States
USACE	United States Army Corps Engineers
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
Σ_7CBs	Total of 7 CBs (CB#28, CB#52, CB#101, CB#118, CB#138, CB#153, CB#180)
Σ_{25}CBs	Total of 25 CBs (CB#18, CB#28, CB#31, CB#44, CB#47, CB#49, CB#52, CB#66, CB#101, CB#105, CB#110, CB#118, CB#128, CB#138, CB#141, CB#149, CB#151, CB#153, CB#156, CB#158, CB#170, CB#180, CB#183, CB#187, CB#194)

Papers prepared and submitted during completion of thesis

Reed, J., Morris, S., French, J.R. & Allchin, C.R. 2001. Distribution of PCBs in marine sediments and dredged material in England and Wales. *Marine Pollution Bulletin.* In prep.

Reed, J., Morris, S., French, J.R. & Allchin, C.R. 2001. Patterns and profiles of Polychlorinated biphenyls in marine sediments and dredged material from offshore, estuarine and industrialised areas in England and Wales from 1990 to 1999. *Environmental Pollution.* In prep.

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ACKNOWLEDGEMENTS

I am grateful to the Jackson Environment Institute at University College London for the part-time award for a postgraduate studentship.

I would like to thank my supervisor Jon French for the opportunity to undertake this study and for his advice and guidance throughout this period of research. I would particularly like to thank Steve Morris for his advice, invaluable support and continuous encouragement. I would like to acknowledge Steve Rowlatt's efforts in proof reading my work. I would also like to extend thanks to Adrian Chappell who has provided many hours of supervision and support. I am grateful to Margaret Oliver for her discussions on geostatistics and advice on sampling design. Similarly, I would also like to thank Richard Webster for his advice.

I am grateful to Dave and Sarah Limpenny and Kevin Thomas for their help and assistance with the field sampling. I would also like to thank many other colleagues at CEFAS for their support and encouragement, and would like to particularly thank John Portmann, Mike Waldock, Lindsay Murray, Colin Allchin and Jacqueline Lavender.

I would particularly like to thank Keith Cooper for his daily encouragement and support. His kindness has provided me with the strength to complete this research.

I would like to thank Sarah Smith, Claire Desbrow, Alex Khaldi, Natasha Pullum, Matthew Dunn and Brett Lyons for their friendship and comfort. I would like to especially thank my parents and sisters for their kind support and wonderful belief in my ability.

CHAPTER ONE

Introduction

This chapter provides an overview of the nature of PCBs as environmentally persistent, and potentially highly toxic, organic compounds. The history of PCB production and use is briefly reviewed, together with the international and national legislatory frameworks governing their phased prohibition and disposal. The legacy of PCBs in the aquatic environment is explored, with particular reference to sediment contamination in UK shallow coastal and estuarine waters. These environments include industrialised areas, in particular dockyards, which are dredged for navigation or expansion, and their sediments often contain elevated concentrations of PCBs. It is argued that PCBs continue to present a pollution hazard, the extent of which is only partly indicated by existing monitoring programmes. Within this context, the present study aims to evaluate the effectiveness of these programmes, to investigate the nature of within-site PCB variability, and explore the feasibility of more scientifically-informed monitoring in support of dredging licence applications.

1 Introduction

Many industrial processes and uses of commercial products have produced contamination in environmental systems around the world. Contamination, in this sense, is defined as the release of a by-product of human activity, chemical or physical, sometimes, although not necessarily, causing harm to human health and/or the natural environment (Calow, 1998). In contrast, marine pollution is defined as the introduction of substances or energy into the environment resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities, impairment of quality for use of seawater and reduction of amenities (GESAMP, 1993). The major distinction between these terms is that pollution actually causes harm whilst contamination can be present but does not cause deleterious effects. The control of chemical pollution is thus a priority for governments and their executive agencies. Of the chemicals present in the environment, it is the more persistent, bioaccumulative and toxic pollutants that are of most concern to countries worldwide (OSPAR Commission, 1996).

Many contaminants enter the aquatic environment, including metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), tributyltin (TBT), radionuclides, nitroaromatics, steroids, booster biocides, pharmaceuticals and organophosphates (De Flora *et al.*, 1991; Thomas *et al.*, 1999). Particular classes of artificial compounds give rise to major pollution concerns: these include PCBs, mercury, dioxins and TBT. Despite restrictions over the production and use of hazardous substances and the increasing scope of environmental legislation, there are increasing concerns over the risks posed by these chemicals to human health and aquatic life.

Coastal and estuarine environments are particularly at risk as these are focal points for riverine deposition and for anthropogenic discharges (such as industrial and domestic effluent). There is particular concern over the marine environment (especially shallow seas) given its long-term function as a repository for industrial discharges (OSPAR, 2000; Szefer, 2000). The main sources of pollutant discharge include primary industries, such as metal and petroleum refineries, smaller manufacturing plants producing plastics and pharmaceuticals and sewage discharges (Houk, 1992). In the UK, a recent review estimated the annual industrial and commercial waste production to be between 70 and

100 million tonnes, of which 70% is from industry (DETR, 1999). The amount of hazardous (or 'special') waste generated annually in the UK in 1997/98 was estimated to be 5.58 million tonnes (DETR, 1999).

To protect the environment from the harmful effects of industrial chemicals, levels of specific compounds are routinely monitored in the air, water, sediments and biota. Sampling conducted by government and other organisations aims to monitor environmental loadings, and detect changes to these distributions as contaminants are continuously disturbed by natural redistribution through erosional adjustments and by anthropogenic activities such as dredging (Kennish, 1994; Calmano & Förstner, 1996). Many compounds are not permanently sorbed to sediments and can be remobilised by physico-chemical conditional changes induced by natural and anthropogenic activity.

The accumulation of Polychlorinated biphenyls (PCBs) in the marine environment is of particular concern. These compounds are persistent, toxic, often poorly metabolised and can bioaccumulate along food chains (World Health Organisation, 1993; OSPAR, 2000). They are considered to be one of the most mutagenic and teratogenic (i.e. causing reproductive impairment) group of compounds in the environment (Fishelson *et al.*, 1994). Although the manufacture of PCBs ceased in the EU in 1978 and new uses have been progressively banned since 1980, there was a long period of use and hence a strong historical legacy of environmental contamination. PCBs continue to enter the environment from diffuse and point sources (CEFAS, 1997a). The purpose of the research summarised in this thesis is to present and analyse all available sediment PCB data collected under monitoring programmes in England and Wales since 1990, and to investigate regional and within-site variability in PCB concentrations with a view to improving our understanding of the processes controlling their distribution and fate in coastal and estuarine sediments. This work also provides a scientific basis for the development of more representative and statistically robust sampling procedures for the assessment of sediment PCBs in support of dredging and disposal licensing.

1.1 Chemical and physical properties of PCBs

The basic structure of PCBs is the biphenyl molecule. The benzene ring, which is typically planar, can have either a single bond (as in Figure 1.1) or a double bond. PCBs exist as different numbers of chlorine atoms substituted in the biphenyl ring with differing configuration of congeners (Blanchard *et al.*, 1997). The chlorobiphenyl isomers are compounds that have the same number of chlorine atoms but have different structural arrangements. The degree of chlorination and the number of chlorine atoms to the biphenyl molecule is shown in Table 1.1. This numbering of CBs is proposed by the International Union of Pure and Applied Chemists and is known as the IUPAC numbering system (Ballschmitter & Zell, 1980). By convention, the chemical names of PCBs include the number of positions of the chlorine atoms on the biphenyl ring. For example, a hexachorobiphenyl which is 2,2',4,4',5,5' chlorobiphenyl is denoted as CB#153, as shown in Figure 1.2. Substitution of chlorine atoms for hydrogen atoms can occur in ten positions and so it is possible to have a total of 209 distinct chlorobiphenyl (CB) congeners (Bolgar *et al.*, 1995; see Appendix 1).

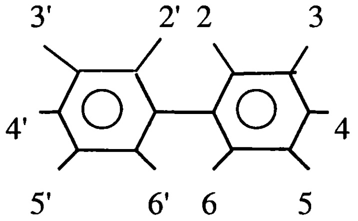


Figure 1.1: The basic biphenyl molecule and possible configurations (Ballschmitter & Zell, 1980; Jones *et al.*, 1991). The positions on the biphenyl ring are also referred to as the *ortho* (2,2',6,6'), *meta* (3,3',5,5') and *para* (4,4') positions of the CB molecule.

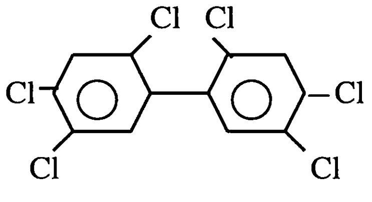


Figure 1.2: Configuration of 2,2',4,4',5,5' chlorobiphenyl or CB#153.

The structural characteristics of CBs (such as their planarity) are especially important in determining their stability and persistence in the environment and thus their potential for uptake and retention in aquatic organisms. Planar PCBs are considered to be the most critical toxicants: they have been associated with body weight loss, reduced fecundity, hepatic damage, dermal disorders, thymic atrophy, immunotoxicity, endocrine disruption and reproductive toxicity (Landers & Bunce, 1991; deVoogt, 1996; Hylland *et al.*, 1996; Knights, 1997).

Table 1.1: Number of isomers and congeners of PCBs *(de Voogt, 1996).*

Isomer Group	mono	di	tri	tetra	penta	hexa	hepta	octa	nona	deca
No. of isomers & congeners	3	12	24	42	46	42	24	12	3	1
Molecular Formula	$C_{12}H_9$ Cl	$C_{12}H_8$ Cl_2	$C_{12}H_7$ Cl_3	$C_{12}H_6$ Cl_4	$C_{12}H_5$ Cl_5	$C_{12}H_4$ Cl_6	$C_{12}H_3$ Cl_7	$C_{12}H_2$ Cl_8	$C_{12}H$ Cl_9	C_{12} Cl_{10}

The molecular structure of PCBs is similar to the natural hormone chemical oestrogen, or 17β-oestradiol. These chemicals have thus been re-classified as endocrine disrupting chemicals because they mimic oestrogen, causing the artificial stimulation of the liver to produce vitellogenin (eggyolk) and other proteins that are used to form eggshell (Hyllner *et al.*, 1991). These chemicals may influence protein and lipid deposition, growth and can influence the sex of embryos and eggs particularly in lower invertebrates (Bye & Lincoln, 1986; Sumpter *et al.*, 1996). There are now increasing concerns about PCBs in light of new research on endocrine distrupors in the environment (Sumpter *et al.*, 1996; CEFAS, 1999).

The physical properties of PCBs, as determined by their past industrial applications, can also influence their behaviour and fate once introduced into the natural environment. Commercial PCBs were produced to physical, rather than chemical specifications, and thus contain a mixture of isomers (Clark, 1989). Consequently, PCBs exhibit a wide range of melting points, vapour pressures, total molecular surface areas, solubilities, viscosities, specific gravity and molecular weights (Niimi, 1996). The individual CBs present in commercial mixtures have very different physico-chemical properties. In general, however, the commercial formulations are characterised by low reactivity, low degradability, low vapour pressure, low water solubility and high dielectric constants (Clark, 1989).

1.2 Production and use of PCBs

Although PCBs were first synthesised in Germany in the late 1880s (Jones *et al.*, 1991; Swackhamer, 1996), the first commercial mixtures were manufactured in the US, by Monsanto, in 1929. From the 1930s through to the 1970s, a number of commercial PCB products were used extensively throughout the world. Specific uses were determined by the various characteristics of the commercial mixtures. PCB formulations found wide application in industry, primarily in electrical equipment, and in the manufacture of paints, plastics, adhesives, coating compounds and pressure-sensitive copying paper (Swackhamer, 1996). Three distinct areas of application can be identified. First, in controlled closed systems, such as transformers and capacitors. Second, in partially closed systems using hydraulic fluids, lubricants, and oils. And third, in open-ended applications including adhesives, plasticisers, pesticide extenders and surface coatings (Kimborough, 1980; Jones *et al.*, 1991). Controlled closed systems typically contain large volumes of PCBs (for example, as dielectric fluids in transformers) and so the effective disposal or recycling of these systems is of paramount importance (Jones *et al.*, 1991). Partially closed systems are comprised, in general, of small sealed units although such systems are known to leak PCBs (Morris, 1995). PCBs in open-ended applications are almost impossible to recover.

An estimated 1.2 million tonnes of PCBs have been produced worldwide and over 30% of this total is estimated to have been released into the environment through accidental spillages and disposal to landfills (Bletchley, 1984; Knights, 1997). PCBs are present at significant concentrations in some waste tips and landfill sites (Morris, 1995). Some 31% of the total PCB inventory is estimated to be mobile within the environment and only 4% is estimated as having been destroyed (Tanabe, 1988). In the UK, total production is estimated to have been 66,748 tonnes with approximately 60% being used in the domestic sector (Morris, 1995; Alcock *et al.*, 1996). Approximately 8,000 tonnes of PCBs are still in use in the UK in over 8,000 transformers and 45,000 large capacitors (Knights, 1997).

1.2.1 Commercial manufacture of PCBs

PCB compounds consist of mixtures of aromatic chemicals manufactured by the direct chlorination of biphenyl in the presence of a catalyst, such as ferric chloride to produce crude PCBs (World Health Organisation, 1993). Trade names for commercial mixtures of PCBs included Aroclor® (manufactured in the United States by Monsanto, and the most important of the compounds used in the UK), Clophen (Germany), Phenoclor (Italy), Kanechlor (Japan), Pyralene (France), and Sovol (Russia) (Bolgar *et al.*, 1995). These products contain different numbers and quantities of congeners (see below) and are used in a variety of applications. Product names often indicate the degree of chlorination. For example, Aroclor® 1260 has a 60% weight-percentage of chlorine. Mixtures range from 21% - 68% chlorine by weight and the most common mixtures used in the UK were Aroclor® 1242, 1248, 1254 and 1260 (Morris, 1995). Monsanto voluntarily ceased the manufacture of Aroclor® in the UK in the late 1970s.

Several analyses of commercial mixtures have been undertaken to determine exact congener quantities (Duinker & Hillebrand, 1983; Hess *et al.*, 1995; Frame *et al.*, 1996; Safe, 1996). By way of exemplification, some characteristics of different mixtures of Aroclors are shown in Table 1.2. Of particular importance here are the very different water solubilities resulting from differences in chlorination. High solubilities and high volatility will enable greatest mobility amongst CBs, these are often associated with the less chlorinated CBs. This relationship is related to molecular weight. Thus the fate of PCBs in the environment is related to molecular size, weight, configuration, composition and environmental stability (i.e. susceptibility to degradation and/or transformation). In essence, this is represented by the half-life of individual CBs.

Table 1.2: Principal isomers in commercial mixtures of Aroclors (*Morris, 1995).*

Aroclor®	Form	Volatility *	Solubility in water **	Principal isomers	Reported number of congeners
1242	clear, mobile oil	338	240	Cl_2 - Cl_4	27 - 74
1248	clear, mobile oil	152	52	Cl_3 - Cl_5	43 - 63
1254	yellow, viscous oil	53	12	Cl_4 - Cl_6	27 - 116
1260	yellow, sticky resin	13	3	Cl_5 - Cl_7	35 - 124

* @ 250°C [(g cm^{-2} h^{-1}) x 10^{6}]
** @ 25°C (μg l^{-1})

The quantification of PCBs in commercial formulations has been used to identify congeners in environmental samples (such as, sediments, water, fish and biota) in order to ascertain their behaviour and fate within specific environmental compartments. Congener patterns in environmental samples are usually different from commercial mixtures due to physico-chemical processes operating in the environment which causes PCB profile modification. Some of these processes include diffusion, evaporation, adsorption and uptake, biotransformation and degradation of PCBs (Hess *et al.*, 1995). Environmental concentrations are often highly variable and CB profiles in environmental samples are typically different to profiles in commercial mixtures or known sources (Jiménez *et al.*, 1996; Safe, 1996). Vanier *et al.* (1996) suggest that, although congeners are altered by environmental processes, more accurate PCB quantification is possible if samples are based on a large number of congeners.

1.3 Environmental behaviour and fate of PCBs

There are many reviews and studies concerning the fate of pollutants in the environment (Sheehan *et al.*, 1985; Samiullah, 1990; Iwata *et al.*, 1994; Van Leeuwen & Hermens, 1995; Champ & Seligman, 1996; Harrad, 1996; Connell *et al.*, 1998; Lun *et al.*, 1998; Davis, 1999). The movement of highly mobile chemicals such as persistent organic pollutants (POPs) is also well documented (Mackay, 1991; Iwata *et al.*, 1994; Wania & Mackay, 1996; Jones & de Voogt, 1999; Wania & Mackay, 1999).

PCBs, in particular, are relatively stable and have been found in different phases in the atmosphere, water column, sediments and biota. In the atmosphere, PCBs may be present in the vapour phase as a result of volatilisation from landfills containing PCB wastes, sewage sludge, oil spills and dredged material (SOAEFD, 1997). In water, PCBs are preferentially adsorbed on to organic suspended particulate matter (SPM) and are present in smaller concentrations in the water column in the dissolved phase (Abarnou *et al.*, 1987). The more chlorinated PCBs (i.e. those CBs with a high Cl component) have a greater tendency to adsorb on to sediments and these are retained in the longer term (Safe, 1996). Sediments play an important part in the marine environment, often being both a source of organic contaminants to aquatic organisms at different trophic levels and also a sink for particular contaminants. Although the sorption of PCBs can immobilise them for relatively long periods in the aquatic environment, desorption can occur into the water column via both abiotic and biotic routes (Lieu *et al.*, 1996). This is an important issue when sediments are subjected to reworking in the aquatic environment.

The movement, accumulation rate and eventual distribution of PCBs in the environment thus depends on a number of factors, including sediment properties (organic matter content (OMC), particle size, particulates and mineralogy); characteristics of biota (% lipids, age, sex and trophic level); the duration and level of exposure; and the different chemical and physical properties of individual chlorobiphenyls present (see below). These factors, together with the level of chlorination, affect the rate of degradation of PCBs in the environment (Dexter & Field, 1989; Harrad, 1996; Niimi, 1996; Hellou *et al.*, 1997). Many exogenous (environment-related) and endogenous (organism-related) variables influence the movement and distribution of PCBs in the marine environment. These variables can determine the long term fate and effects of PCBs (Hellou *et al.*, 1997).

The abundance of PCBs in the environment is attributed to their redistribution, transportation and deposition in various environmental compartments. Concentrations of PCBs in general have shown a slow, progressive decline over the last two decades (Jones *et al.*, 1991; Morris, 1995; Laane *et al.*, 1999). However, the overall decline in PCB loads has not been seen in some areas. This can be attributed to continuing discharges to the aquatic environment, uncontrolled disposal and incineration of municipal wastes, remobilisation and redistribution in sediments/air and water, and bioaccumulation in biota. Understanding the behaviour of PCBs in different phases in the environment is crucial to determining the eventual fate and loadings of these pollutants.

The environmental behaviour of a substance involves a variety of complex and interacting processes, mechanisms and properties. The main input, output and redistribution processes involved with the movement of PCBs are summarised in Table 1.3. The most important processes are transportation between and within media, abiotic and biotic transformation, degradation (including mineralisation), partitioning and bio-accumulation (Sheehan *et al.*, 1985; Samiullah, 1990; Van Leeuwen & Hermens, 1995).

A schematic representation of the most important pathways for an organic chemical in the environment is presented in Figure 1.3. The interchanging of a chemical between environmental compartments takes place through exchanges between gases in the troposphere, adsorption as aerosols in the atmosphere, as hydrols in the water column and adsorption onto aquatic sediments (Samiullah, 1990). In the environment, some PCB congeners are more abundant than others. This may be due to the nature of the source (i.e. the congeners present within the original commercial product), their variable persistence and their differential mobility and transportability.

Table 1.3: Summary of the main processes determining the fate of PCBs (Morris, 1995).

Input Processes	Output Processes	Redistribution Processes
Atmosphere and atmospheric deposition	Volatilisation	Partitioning between dissolved and particulate phases
Gas absorption	Sedimentation	Transfer up the foodweb by bioaccumulation & biomagnification
Tributary loadings	Surface water outflows	Metabolism in biota
Sediment resuspension	Exchange with groundwater	Desorption in soils
Diffusion	Degradation and deposition	Adsorption in soils
Direct discharges	Photolysis	
	Biotic depuration	
	Reductive dechlorination	

The movement of PCBs occurs via an interchange between the atmosphere, hydrosphere, soils, sediments and biota. Several processes transform congeners by changing their chemistry and physical structure. For example, in hydrolysis, oxidation and conjugation reactions, molecules are changed by the introduction of polar groups (-OH, $-NH_2$, -COOH) (Van Leeuwen & Hermens, 1995). These processes allow the excretion of contaminants from biological systems.

PCBs are continuously redistributed within and between the environmental compartments shown in Figure 1.3 but eventually find an efficient sink in either the deep sea and/or the stratosphere (Samiullah, 1990). A sink is defined here as an environmental compartment or phase in which a chemical ultimately accumulates (Samiullah, 1990). The nature of the sink depends on the environmental mobility of the chemical. In order to provide a background understanding of the fate of PCBs in and between different media, various processes and factors influencing their movement are discussed below.

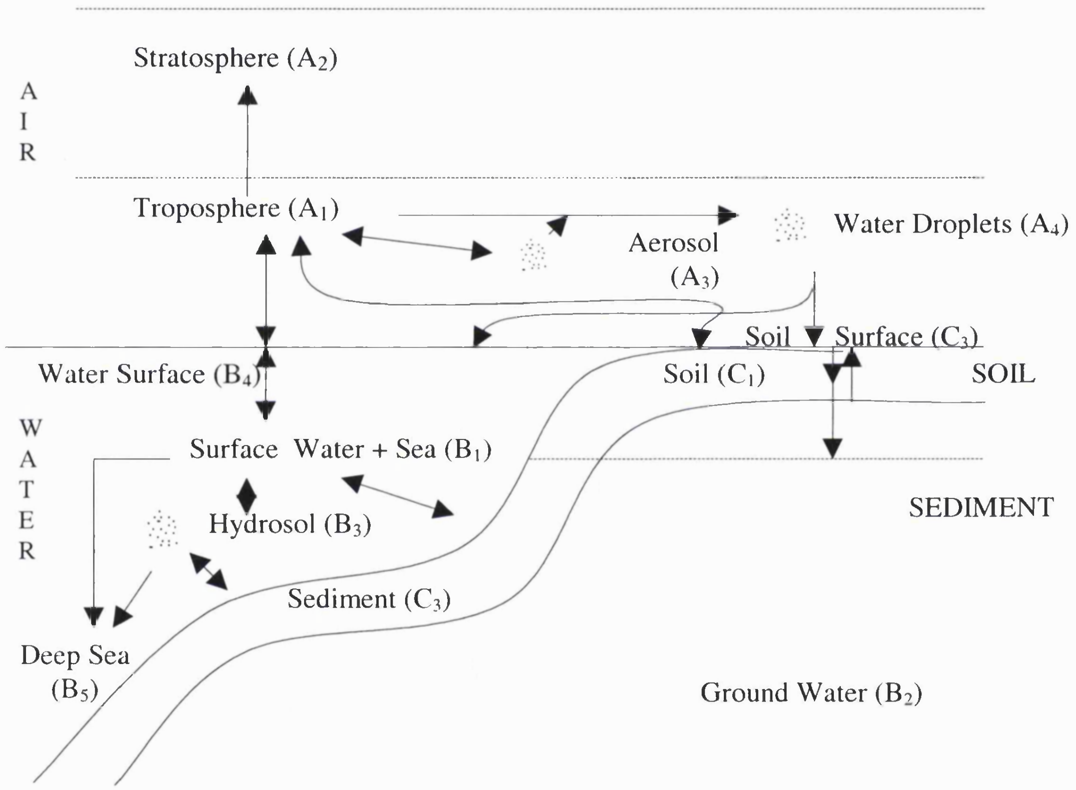


Figure 1.3: Important pathways for organic chemicals in the environment (*Samiullah, 1990*).

1.3.1 Movement of PCBs in the atmosphere

In the atmosphere, PCBs are present in several forms: vapour, particulate and in the dissolved phase. PCBs migrate through the atmosphere as gases and are transported at different velocities over long and short distances (Wania & Mackay, 1996). Congeners that have a tendency to volatilise are continuously evaporated and deposited in air, water and soil and the rate of evaporation is determined by changes in temperature (Table 1.4; Wania & Mackay, 1996). The degree of chlorination is, therefore, particularly important in the volatilisation and redistribution of PCBs by atmospheric physical and chemical processes. The main processes governing the movement of PCBs in the atmosphere are wet and dry deposition (Vale & Harrison, 1994).

One measure of the tendency of a compound to volatilise is the octanol-air partition coefficient (K_{oa}). This is the ratio of the concentration of a substance in octanol and air at equilibrium (Wania & Mackay, 1996). PCBs characteristically have a wide range of mobility due to the physical and chemical structure of each congener. The partitioning of a compound at equilibrium between the vapour and aqueous phase is represented by the Henry's Law Constant (K_H). This constant is a term used to estimate a congener's tendency to volatilise. There is a tendency for the more semi-volatile organic compounds to be present in the atmosphere, and these are deposited at different rates depending on the partitioning of the individual congeners between the gaseous and aqueous phases (Atkinson, 1996). CBs with greater than six chlorines are typically associated with the particle-phase and these may remain in the atmosphere for in the region of 5 to 30 days (Atkinson, 1996).

Table 1.4: Mobility of polychlorinated biphenyls in the atmosphere *(Wania & Mackay, 1996).*

Global transport behaviour	**Low Mobility** (rapid deposition and retention at source)	**Relatively Low Mobility** (preferential deposition and accumulation in mid-latitudes)	**Relatively High Mobility** (preferential deposition and accumulation in polar latitudes)	**High Mobility** (worldwide atmospheric dispersion, no deposition)
PCBs	**8 - 9 Cl**	**4 - 8 Cl**	**1 - 4 Cl**	**0 - 1 Cl**
Log octanol-air partition coefficient (K_{oa})	10		8	6
Log P_l	-4		-2	0
Temperature of condensation (T_c)	+30°C		-10°C	-50°C

Log P_l = Log vapour pressure of subcooled liquid

1.3.2 Movement of PCBs in water

The majority of PCBs tend to have low solubilities, are generally non-polar and are hydrophobic. These characteristics dictate the partitioning of PCBs within an aqueous system and generally govern their subsequent transport, movement and fate. The octanol-water partition coefficient (K_{ow}) is used to estimate the partitioning of a compound between aqueous and organic phases (Karickhoff *et al.*, 1979). K_{ow} is defined as the ratio of a compound's concentration in the octanol phase to its concentration in the aqueous phase, where octanol is a surrogate for organic matter (either in soils and sediments or lipids in biota and in lipids in the oceanic microlayer; Strachan, 1988).

The behaviour and eventual fate of congeners in water are determined by their log K_{ow} value which provides an expression of their solubility in water (Dannenberger & Lerz, 1996). In general, the log K_{ow} values for PCBs are high due to their hydrophobic nature. Congeners that have log $K_{ow} < 4$ are more effectively taken up through the water column (i.e. in the dissolved phase) and congeners that have log $K_{ow} > 5$ tend to bind more strongly to lipids. The individual liposolubility properties of the congeners are especially important because some congeners can preferentially penetrate the body wall of target organisms. PCBs can also enter across the gills of some organisms and are generally taken up by food. This can lead to increased body burdens of specific congeners. Congeners binding strongly to lipids (Log K_{ow} >5) are preferentially biotransferred through the food chain (Hellou *et al.*, 1997; Knights, 1997). Biomagnification can also occur between successive trophic levels (Peterman *et al.*, 1996; Knights, 1997). Biomagnification is the process whereby the concentration of a chemical in the tissues of organisms increases as the chemical moves up the food chain (Calow, 1998).

The range of aqueous solubility for PCBs is 0.016 - 640 $\mu g\ l^{-1}$ (Morris, 1995). The lowest solubilities are associated with those congeners with the highest level of chlorination (Mackay *et al.*, 1983). Table 1.5 summarises the solubilities and associated properties of a selected number of PCBs.

Concentrations of PCBs in seawater are influenced by source inputs, affinity to suspended particulate matter (SPM) and the solubility, persistence and stability of individual congeners. PCBs tend to be associated with organic matter and sediment particles via sorption, and are removed from the aqueous phase via deposition to the sediment bottom or are taken up by aquatic organisms (such as micro-organisms) via mechanisms of feeding (Clark, 1989; Koelmans *et al.*, 1997). However, the majority of PCBs in the marine environment are associated with the particulate phase and are found in interstitial waters between colloidal and dissolved phases as a function of their solubilities and degree of chlorination (Burgess *et al.*, 1996). The ability of PCBs to partition between aqueous and solid phases is measured by the adsorption coefficient (K_{oc}). This is the ratio of the amount of chemical adsorbed (per unit weight of organic matter) to the concentration in the aqueous phase at equilibrium (Lyman *et al.*, 1982). Some typical values for Log K_{oc} are given in Table 1.5.

Table 1.5: Physico-chemical properties of PCBs *(Eisenreich, 1987).*

Congener #	Structure	Solubility^{+}	Octanol-water partition coeff. [Log (K_{ow})]	Adsorption coefficient [Log (K_{oc})]	Vapour pressure $^{++}$	Henry's Law Constant (H)$^{+++}$
28	2,4,4'	-	5.69	4.61	-	9.6
52	2,2',5,5'	360	6.09	4.67	190	-
101	2,2',4,5,5'	110	7.07	4.89	35	12.9
118	2,3',4,4',5	100	7.12	6.08	9.5	3.5
153	2,2',4,4',5,5'	37	7.75	-	6.5	6.6
138	2,2',3,4,4',5	4.4	7.44	-	48	4.1
180	2,2',3,4,4',5,5'	17	-	-	5.0	11.1

+ (mol m^{-3}) x 10^{-6} - no available data
++ (atm.) x 10^{-9}
+++ (@ 15°C; Pa m^{3} mol^{-1}) (Baker & Eisenreich, 1990)

1.3.3 Movement of PCBs in sediments

There are several sources and pathways by which PCBs can enter sediments. The rate of movement of these compounds depends on the sediment type, moisture content, temperature, organic matter content and other factors/processes affecting partitioning. There are several different phases in sediments including the solid phase (sediment), liquid phase (interstitial/elutriate/pore water) and the gaseous phase (sediment air). In the case of PCBs, less chlorinated CBs tend to be relatively mobile and move through these phases more readily than the more chlorinated congeners due to their higher vapour pressures and solubilities. Some compounds move vertically through sediments in the liquid phase but this is dependent on the organic matter content of the soluble phase. The more chlorinated congeners tend to be associated with the organic fraction of the sediment, partitioning into lipids and waxes in the sediment (Hess *et al.*, 1995). CBs have also been associated with sediment particulates and minerals (for example, silica) in sediments which are useful sites for bonding (Morris, 1995). Another important factor is particle size and a number of studies (for example, Ab Razak & Christensen, 1996) have found PCBs to be associated with clay.

The total organic carbon (TOC) content of sediments is associated with the finer fractions and the Oslo and Paris Commission (OSPAR, 1993) stipulate that this be calculated for the particle size <63 μm fraction. The Wentworth scale defines the 63 μm size as the sand/silt boundary (Folk, 1980), and sediment particles <63 μm include clays and very fine to coarse silts. Clays and silts provide particularly good sites for the surficial retention of contaminants (Sheehan *et al.*, 1985; Dyer, 1986). The association of PCBs with this finer fraction is one route for filter-feeding species to be exposed to environmental chemicals (Piérard *et al.*, 1996). The rate at which PCBs are associated with sediments is dependent on the physical structure and chemistry of congeners, local environmental conditions and the nature of the sediment or soil system (Lyman *et al.*, 1982).

The degree of sorption of PCBs to sediments is dependent not only on the organic matter content and surface area of the sediment but also on the chlorination level of the constituent CBs. The degree of sorption tends to increase as the chlorine content of the chlorobiphenyl and the total organic carbon content of the sorbent increases (Karichoff *et al.*, 1979; Horzempa & Di Toro, 1983; Sheehan *et al.*, 1985; Samiullah, 1990). PCBs with a high K_{oc} value have a tendency to bind strongly to organic matter, with more chlorinated biphenyls being preferentially adsorbed. The low aqueous solubilities and the hydrophobic nature of PCBs result in high K_{oc} values. The sorption of PCBs to sediments has been reported to be in the order of hexa- > tetra- > di-CBs (Morris, 1995). More chlorinated biphenyls are adsorbed in greater quantities and are retained more effectively on the sorbent surface. The rate of adsorption depends also on the absence of *ortho*-substitution of the chlorobiphenyl molecule (Morris, 1995). No *ortho*-substitution or a low degree of substitution favours adsorption. However, as the degree of chlorination increases, this effect becomes less important.

The desorption and remobilisation of PCBs from sediments into the aqueous phase is an important process, especially when the dredging and disposal of sediments is being considered (Sheehan *et al.*, 1985; DiGiano *et al.*, 1993; Lieu *et al*, 1996; Meier *et al*, 1997). The degree of desorption is dependent on the compound's polarity, the pH, available organic matter content and the percentage of silt and clay fractions in the sediment (Morris, 1995).

1.3.4 PCB concentrations in coastal sediments

Several studies have been conducted in the UK to determine PCB concentrations in marine sediments. Some of these studies are indicated in Table 1.6. The term 'concentrations' is hereafter used to refer to total CBs. Concentrations reported to date in the UK are measured between the limit of detection (nd) and 3040 μg kg^{-1}. Not surprisingly, the highest concentrations are associated with coastal areas close to industrial activities.

It is important to consider these levels in a wider context, particularly in relation to those reported for other European countries. In so doing, it should be realised that the wide variety of analytical protocols, definitions of total CBs and sampling methodologies makes direct comparisons difficult. These values should be interpreted as indicators of PCB concentrations due to the poor comparability between analytical methods. PCB concentrations in Europe and worldwide are provided in Table 1.7 and 1.8.

In continental Europe, the range of concentrations (1 - 1248 μg kg^{-1}) is generally comparable to that reported for the UK. However, in the UK, there are clearly some very contaminated sites, notably the River Blyth, in North East England. Concentrations reported for countries worldwide vary significantly. The overview of studies given in Table 1.8 illustrates that in the US and Japan, there are much higher maximum concentrations in sediments: in some localised cases these are an order of magnitude higher than maximum European levels. These instances can be largely attributed to past use of PCBs, that is in the manufacture of electronic capacitors (Brown *et al.*, 1985), accidental spillages, discharges from concentrations of factories and paper mills, effluents from large urban areas (Ohsaki *et al.*, 1997) and unregulated and illegal disposal (Achman *et al.*, 1996).

Table 1.6: UK concentrations of $\sum$CBs in coastal sediments (μg kg^{-1}) as determined by selected recent studies.

Location	$\sum$CB	Reference
Southern North Sea	nd – 4.7	Boon *et al.* (1985) △
North Sea (including Fladen Ground, Kattegat/Skagerrak /Norwegian Channel and inner German Bight)	0.10 – 4.40	Knickmeyer & Steinhart (1989)▽
Southern North Sea	0.01 – 6.8	Lohse (1991)▽▽
Skagerrak	0.5 – 28	
Northern North Sea	1.05 – 2.26	
North Sea and German Bight	0.10 – 9.18	Landgraff *et al.* (1992)▽
Irish Sea	0.2 - 42	Thompson *et al.* (1996)
Burbo Bight, R. Mersey	13	Camacho-Ibar & McEvoy (1996)
North Wales coast	0.35	Camacho-Ibar & McEvoy (1996)
Humber Estuary	nd - 84	Tyler & Millward (1996)
Essex Coast (salt marsh)	<1 - 242	Scrimshaw *et al.* (1996)
Tees Estuary	nd - 204	Proudfoot (1995)
Blyth Estuary	nd – 3039.9	Proudfoot (1995)
South West England	25 – 46.9	EA (1995)
North Sea	13 – 1023 (TOC)	Marencic *et al.* (1993)
Newport, South Wales	<10	EA (1992)
Liverpool Bay	0.08 - 38	Camacho-Ibar (1991)

nd = not detected
TOC = results normalised to total organic carbon
$\sum$CB = summation of individual CBs
△ = *based on a synthetic mixture containing 85 individual PCB components*
▽ = *based on a synthetic mixture containing 24 individual PCB components*
▽▽ = *based on the sum of three CBs (CB#138, CB#153 & CB#180)*

Table 1.7: Concentrations of ∑CBs determined in selected studies of European coastal sediments (μg kg^{-1}).

Location	∑CBs	Reference
German Bight	66.9 – 193.1	Hühnerfuss *et al.* (1997)
River Seine	81 – 364.5	Teil *et al.* (1996)
Wadden Sea	743.3 – 1247.3	Marencic *et al.* (1993)
Lake Garda, Italy	89	Bossi *et al.* (1992)
Mediterranean Coast	1.2 - 401	Mangani *et al.* (1991)
Scheldt Estuary	217 - 1068	van Zoest & van Eck (1990)
North Greenland	6 – 65	Kjølholt & Hansen (1986)
Venice Gulf	1 - 185	Donazzolo *et al.* (1983)
Turkey Coast	208.6	Bastürk *et al.* (1980)

∑CB = summation of individual CBs

Table 1.8: Worldwide concentrations of ∑CBs in coastal sediments (μg kg^{-1}).

Location	∑CBs	Reference
Tokyo	0.00031 – 0.13	Ohsaki *et al.* (1997)
Fiji Islands	<0.05 – 29.68	Morrison *et al.* (1996)
Gulf of Bothnia	~1600 - 8500	van Bavel *et al.* (1995)
Australia	0.5 - 790	Iwata *et al.* (1994)
India	5 - 1000	Iwata *et al.* (1994)
Japan	63 – 240	Iwata *et al.* (1994)
Taiwan	2 - 230	Iwata *et al.* (1994)
Vietnam	0.2 - 140	Iwata *et al.* (1994)
California	2 - 1782	Rice *et al.* (1993)
Lake Shinji, Japan	30,000 - 10^5	Sugiura (1992)
South Carolina Estuaries	<10 - 622	Marcus & Renfrow (1990)
Hudson River, New York	~10^6	Bopp *et al.* (1981)

Recent studies of PCBs (for example, Morris, 1995; Van Der Poel & Ros, 1995; Laane *et al.*, 1999) have indicated that over the last two decades, average concentrations in the environment have declined following a peak in the 1970s and 80s. However, in some localities, for example in South Wales, UK, these downward trends have not been observed (Reed & Waldock, 1998). Limited data availability, particularly for the marine environment, remains a fundamental obstacle to the confirmation of temporal trends in PCB levels.

1.4 Monitoring programmes

Monitoring as defined here is the repeated observation or measurement "of the quality of emissions or effluents, or sources that lead to these, or specific places in the environment possibly subjected to them....of which the latter can involve both chemical and biological assessment" (Calow, 1998). The purpose of pollution monitoring programmes is to provide information on rates of release of pollutants into the environment, degree and changes of environmental contamination and biological effects (Moriarty, 1988). Monitoring is also conducted for compliance, and in terms of UK government monitoring programmes (see below) this is typically directed towards legislative commitments, for example, compliance to agreed quality standards or emission controls. A well designed monitoring scheme can detect changes in the environmental parameter(s) of interest with an appropriate degree of statistical significance (Segar & Stamman, 1986).

Many government monitoring programmes are a product of legislative enforcement measures or initiatives for compliance monitoring of substances to ensure specific target levels or standards are not exceeded. These target or standards are set by a variety of legislative frameworks both nationally and internationally. Monitoring is, therefore, conducted to ensure that discharges do not exceed an acceptable limit. This is achieved by measuring the amount and distribution of a contaminant in the environment.

In the UK, the Marine Pollution Monitoring Management Group (MPMMG) was set up in 1974 by the DOE, now Department of Environment, Fisheries and Rural Affairs (DEFRA) and is responsible for the co-ordination of government monitoring strategies in the UK. The aim of the MPMMG is to ensure that UK pollution monitoring is based on sound science and is appropriately targeted so as to obtain the most from the necessarily limited resources. The membership of the MPMMG includes scientists from the Centre for Environment, Fisheries and Aquaculture Science (CEFAS), Environment Agency (EA), Department of Environment, Fisheries and Rural Affairs (DEFRA), Scottish Office Agriculture, and Fisheries Department (SOAEFD), Department of Agriculture for Northern Ireland (DANI) and the Scottish Environment Protection Agency (SEPA). A recent finding of this group is the urgent need to review existing monitoring programmes. Such a review would help determine the current state of the environment by utilising information and data collected from contemporary programmes to provide baseline data to augment future monitoring strategies. Indeed, little attention has been paid to the accuracy and ability of monitoring schemes to identify changes over time and space.

1.4.1 Legislative frameworks

The principal organisations concerned with the formulation and implementation of environmental legislation in the UK are shown in Figure 1.4. UK legislation is increasingly influenced by wider European Union (EU) directives. For example, in 1972 the UK Government, in common with most other European Governments, signed the London Convention for the Prevention of Marine Pollution by dumping of wastes and other matter (Bray *et al.*, 1997). In response to increasing levels of riverine and atmospheric pollution, the Paris Commission (PARCOM) and the North Sea Conference Declarations (NSCDs) were initiated in 1974. The UK also became a contracting party of the Oslo Convention (OSCON) and later the OSPAR Convention which oversees dumping in the North Atlantic and North Sea areas. The aim here was to encourage member states to voluntarily manage their pollutant discharges and environmental loadings. PARCOM and OSCON were replaced by the Oslo and Paris Convention (OSPAR) in 1992. The OSPAR Convention plays a more central role in the regulation of industrial discharges and the disposal of waste chemicals.

The primary concerns of the OSPAR Convention are to prevent pollution of the maritime environment by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the environment which are near background values for naturally occurring substances and close to zero for man-made synthetic substances (OSPAR Commission, 1998). The ultimate aim will be to achieve the target of a cessation of discharges, emissions and losses of hazardous substances by the year 2020 (OSPAR Commission, 1998). Programmes and measures for their reduction must be prepared by signatory governments by 2003.

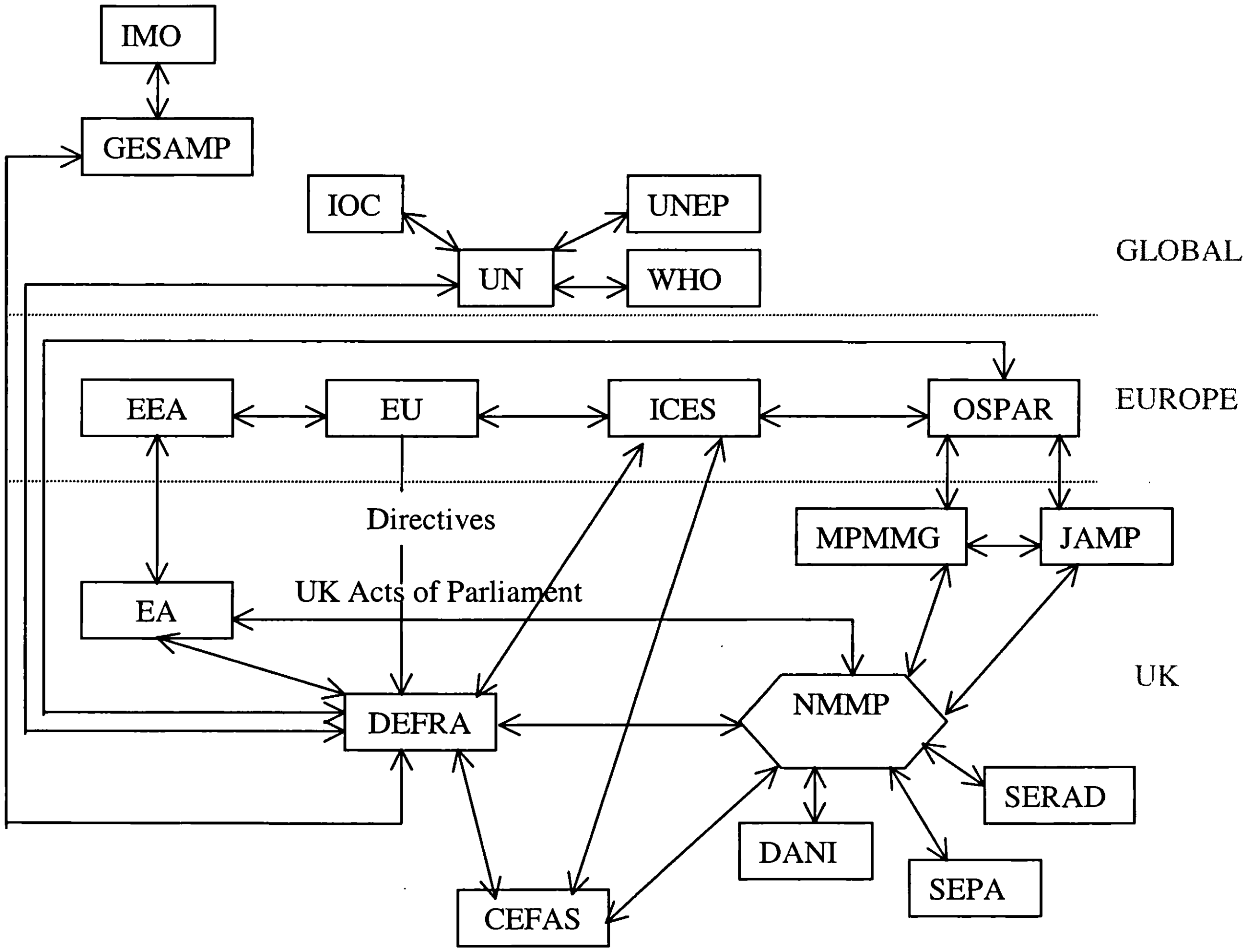


Figure 1.4: Organisations involved with legislative controls and monitoring in UK.

The OSPAR Convention has classified PCBs as hazardous substances which are "substances that are toxic, persistent and liable to bioaccumulate" (OSPAR Commission, 1998). PCBs are on the OSPAR List 1 (Black List) which requires priority action through the Dangerous Substances Directive (76/464/EEC). There is also a Red List of chemicals requiring action and a strategy to manage hazardous substances. Other European legislation (Council Directive 76/403/EC) prohibits the uncontrolled discharge, dumping and tipping of PCBs (or equipment containing PCBs).

In the UK, the Department of Environment, Fisheries and Rural Affairs (DEFRA) co-ordinates recommendations and legislative measures proposed by the OSPAR Convention and develops national policies and regulations concerning the control of these hazardous substances. The DEFRA have also compiled a list of priority chemicals which are applicable to the UK environment and these are based on the OSPAR Convention black list. PCBs are included on the UK list (UK Red List) of environmental pollutants (Agg & Zabel, 1990; Johnston *et al.*, 1996).

The UK legislative framework includes the Control of Pollution Act (COPA) of 1974, the Food and Environment Protection Act (FEPA) of 1985, and the Environmental Protection Act (EPA) of 1990. The Control of Pollution (Supply and Use of Injurious Substances): Regulation of 1980 (SI 1980 No. 638) restricts the sale and use of PCBs as instructed under the Control of Pollution Act (1974). The Control of Pollution (Supply and Use of Injurious Substances): Regulation of 1986 (SI 1986 No.902) bans the production of new equipment containing PCBs and the sale of second hand equipment containing PCBs under the same Act.

The control of PCBs has taken a significant step forward in the late 1990s. In the UK, DEFRA estimated in 1994 that all PCBs used in UK open-ended applications had already been destroyed or disposed via incineration or landfill (Department of Environment, 1994). Since then, DEFRA has agreed to implement the OSPAR Commission initiative to regulate the destruction of stocks of PCBs and control their current use by 1995 and at the latest by 1999. In 1996, a Council Directive (96/59/EC) was passed which required the member states to organise the controlled collection and destruction of remaining stocks and sources of PCBs (and any hazardous substitutes) by 1999. The recent action taken by DEFRA to destroy stocks of PCBs should provide an incentive to further limit their use and promote a reduction of levels in the environment in the coming decades.

National government bodies and agencies (e.g. DEFRA, EA and CEFAS) are now provided with clearly defined targets, protocols and objectives for the monitoring of specific environmental contaminants (OSPAR Commission, 1998). National targets set by the OSPAR Convention include controls on discharges to achieve designated Environmental Quality Standards (EQSs) and the staged restrictions on the use and eventual prohibition of particular compounds.

At present, however, there are no environmental quality standards (EQSs) for PCBs in the UK (Elliott, 1996; Rowlatt *et al.*, 2000). Many government organisations are in the process of reviewing methodologies and developing field validation of proposed standards, but have yet not decided on the most appropriate method for the UK (Rowlatt *et al.*, 2000). The Group Co-ordinating Sea Disposal Monitoring (GCSDM), a sub-group of the MPMMG has been set up to define a set of sediment quality criteria which could be employed as guidelines on 'safe' levels of organic contaminants in sediment (CEFAS, 1997b). This review is now complete and a proposed sediment quality standard for some CBs is defined for the UK (see Table 1.9) and a summary is provided in CEFAS (1997b). There is also an Environmental Quality Standards Steering Group that meets regularly to discuss implementing standards for regulatory purposes and discusses approaches deemed suitable for the UK (Matthiessen, pers. com. 2000).

The proposed sediment quality target values for PCBs in European countries (Shea, 1988; Di Toro *et al.*, 1991; MAFF, 1993; OSPAR, 1994; CEFAS, 1997b; OSPAR, 1999), USA (Barrick *et al.*, 1988; Long & Morgan, 1990; Long, 1992; MacDonald, 1993; Long *et al.*, 1994; Long *et al.*, 1995; USEPA, 1996; USEPA, 1999; NOAA, 1999), Canada (CCME, 1995; Smith *et al.*, 1996a; Smith *et al.*, 1996b), Hong Kong (Ankley *et al.*, 1996), Australia and New Zealand (Batley, 1997; ANZECC, 1999; Batley & Maher, 1999) are listed in Table 1.9. Sediment quality values are derived by numerous methods incorporating theoretical calculations (Equilibrium Partitioning), laboratory testing (Spiked Sediment Toxicity Testing) and samples collected from a variety of areas (Effects Range-Low, Effects Range-Median, Threshold Effects Level, Probable Effects Level) and a mixture of some or all of these methods (Sediment Quality Triad).

The International Council for the Exploration of the Sea (ICES) proposed that an exceedance of the ICES guidelines (Table 1.9) may indicate restrictions of inputs to a site or more detailed investigations at specific sites. In addition to these levels, a 'no measurable-change' clause is required to ensure contamination does not increase.

In 1988, after a major source of PCBs entered the UK marine environment via an explosion on the Piper-Alpha oil rig in the North Sea, sediment quality guidelines for total PCBs (the sum of 25 or $\sum_{25}$CBs) were proposed in the UK. These guidelines are used by DEFRA to assess contamination levels in marine sediments (MAFF, 1993). The

Σ_{25}CBs are classified into four tiers (Table 1.10), and the associated guidelines are used to assess risks and hazards to the UK marine environment.

The OSPAR Commission, which administers the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, recommends quality guidelines are used for assessing chemical monitoring data in order to identify potential areas of concern, and to indicate which substances could be considered a priority. This has not been achieved, to date, in the UK. Quality guidelines are not recommended by OSPAR as firm standards or as triggers for remedial action, but rather as indicators of the need for more detailed chemical and biological monitoring.

Table 1.9: Sediment Quality Guidelines proposed for PCBs in selected countries worldwide.

CB #	Sediment quality target value	Country of origin (units used to define EQS)
Σ_7CBs$^{\triangle}$	0.02	Dutch (mg kg^{-1} d/w normalised to 10% OC and 25% clay ($<2\mu$m)) (Shea, 1988)
Σ_7CBs$^{\triangle}$	0.001-0.01^{P}	OSPAR (mg kg^{-1} d/w. 1% organic carbon) (OSPAR, 1999)
Σ_7CBs$^{\triangle}$	0.023	Hong Kong (mg kg^{-1} d/w. whole sediment) (Ankley *et al.*, 1996)
Σ_7CBs$^{\triangle}$	0.023	Australian and New Zealand (mg kg^{-1} d/w. 1% organic carbon) (ANZECC, 1999)
Σ_7CBs$^{\triangle}$	2.31*	Europe (-oc is the normalisation to organic carbon). (Di Toro *et al.*, 1991)
Total PCBs	0.0227 – 0.180	US ERL and ERM (mg kg^{-1} d/w) (Long *et al.*, 1995)
Total PCBs	1.0 – 3.1	US AET-L and AET-M values (mg kg^{-1} d/w) (USEPA, 1999)
Total PCBs	0.0216 – 0.189	Canada threshold effect levels (TELs) and probable effect levels (PELs) (μg kg^{-1}) (CCME, 1995)
Total PCBs	0.10 – 0.20	CEFAS Action Level 1 & 2 for dredged material licensing (mg kg^{-1} d/w)

$^{\triangle}$= sum of CB#28, CB#52, CB#101, CB#118, CB#138, CB#153, and CB#180
^{P} = provisional, awaiting more data
* = provisional ICES guidelines calculated on a percentage basis in terms of their maximum concentration in any Aroclor® mixture. These sediment action levels have been devised using the Equilibrium Partitioning (EP) approach.

Table 1.10: Sediment Quality Guidelines based on criteria from Wells *et al.* (1989).

Category	PCB Concentration ($\mu g\ kg^{-1}$)	Classification
Tier 1	< 0.2	Contamination not detectable
Tier 2	0.2 - 20	Slightly contaminated
Tier 3	21 - 100	Contaminated
Tier 4	> 100	Heavily contaminated

The environmental quality objective (EQO), defined as acceptable amount of substances in the environment (Mance, 1987), is essential for the protection of the marine environment in terms of ecosystem maintenance and the preservation of the environment (CEFAS, 1997b). In Europe, the UK has adopted environmental quality objectives (EQOs) whilst other member states have introduced emission standards. Emission standards are defined as acceptable amounts of chemicals in discharges to the environment (Moriarty, 1988). Both approaches require compliance monitoring to ensure that discharges do not exceed a specified regulatory limit and that contaminants in the environment do not accumulate to unacceptable levels.

Even with the control of PCB wastes and stocks, such persistent chemicals remain a problem in the environment. An environmental inventory of PCB concentrations, at this point in time, would usefully identify those areas requiring additional monitoring, risk assessment and remediation. Such a review of PCB loadings in the environment would assist OSPAR in establishing the extent of the problem and help the planning of programmes and measures for their reduction (OSPAR Commission, 1998). The present study makes a contribution towards this effort, by critically examining the existing UK sediment PCB database and identifying gaps in our understanding that might be addressed through better monitoring. This is a crucial part of the planning and eventual reduction of man-made synthetic substances by 2020.

1.4.2 National monitoring programmes

Monitoring of PCBs in England and Wales before 1990 was, in the majority of cases, concerned with measuring concentrations in fish and shellfish. This was in response to various legislative commitments at the time requiring monitoring of certain food sources (the Food and Environment Protection Act, 1985; the 3rd International Conference on North Sea Protection in the Hague, March 1990 (Lohse, 1991) and as a result of the United Nations World Commission on Environment and Development (Brundtland Report, 1987)). Much of the subsequent monitoring in the environment has been conducted under the Environmental Protection Act (1990) and is a result of the UK government's increasing commitment to environmental protection. Such initiatives as 'This Common Inheritance' (DOE, 1990) and the agreement to improve environmental conditions as a result of the United Nations Intergovernmental Panel on Climate Change, 1990 (Leggett, 1990); the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro, June 1992 and the United Nations conference in Kyoto, Japan, in 1998 illustrate changing environmental concerns globally.

ICES is responsible for the organisation of monitoring programmes and the collation of environmental data on pollution compounds and their potential impacts. In the UK, the largest monitoring programme is the UK National Marine Monitoring Programme (NMMP). This programme was devised under the MPMMG in 1987/88 and is managed by CEFAS, DEFRA, EA, Environment and Heritage Service (EHS), Fisheries Research Services Marine Laboratory, Scottish Environment Protection Agency (SEPA), Scottish Office Agriculture (SOA), Environment and Fisheries Department (EFD) and Department of Agriculture for Northern Ireland (DANI). These organisations have statutory obligations to protect and monitor the marine environment. The NMMP was designed to provide monitoring that is co-ordinated, cost effective and consistent with national and international legislative requirements (MPMMG, 1998). A key objective of the NMMP is to establish the spatial distribution of contaminants, identify their biological impact, detect trends in contaminant concentrations and to measure long-term natural variability in physical, biological and chemical parameters at selected sites (MPMMG, 1994; MPMMG, 1998). Monitoring of natural long-term behaviour will help disaggregate unnatural fluctuations due to specific pollution events and natural variability (for example, due to algal blooms, El Niño and storm surges).

The network of UK monitoring sites is classified into: inshore sites; intermediate sites, defined as areas where there is a salinity gradient in the sites from major estuaries, through the interface between the estuarine plume and open sea water and out to the offshore sites (for example, Western Approaches) (MPMMG, 1994); and offshore sites within the North Sea and the English Channel selected by the North Sea Task Force Group.

Other programmes which consider PCBs include the monitoring of sea disposal activities including pipeline discharges, sewage sludge (ceased in 1998) and dredged material disposal. These national monitoring schemes are designed to assess: impacts on biological ecosystems; hindrance to navigational uses from settled material or during disposal operations; sediment quality; and impacts on fishing activities amongst others. Also, monitoring of radioactivity in the Irish Sea (from the Sellafield nuclear processing plant), nutrient studies, biological habitat surveys and surveys of marine fish farms have been incorporated into the programmes, all of which are co-ordinated by MPMMG. The MPMMG have set common guidelines and standards for monitoring in these areas (MPMMG, 1998).

1.4.3 Monitoring and licensing of dredged material for disposal

Dredging is defined as the removal of sediment from the bottom of water bodies by machine (Calow, 1998) and inevitably disturbs the environment in which it is conducted. Dredging is essential for maintaining access to ports, improving or maintaining discharges or flows of rivers, waterways or channels, provide construction material (aggregates), mining and beach nourishment (IADC, 1997). The dredging process consists of three phases: excavation; transport; and placement or use of the material dredged. The excavation and disposal phases of the operation have the potential to affect all forms of marine life through both physical impact and the release of possible contaminants (ICE, 1995). Contaminants released into solution during dredging or remaining on suspended particulate material can contaminate or induce mortality in aquatic animals. This could have a serious impact on the economy, for example, by causing deleterious effects on fishing, causing a decline in fish stocks, and shellfish harvesting (ICE, 1995). The redistribution of substances by dredging constitutes a real environmental hazard especially where polluted material is concerned. The redistribution and accumulation of contaminants is becoming an increasing concern amongst environmentalists, governments and international organisations (DiGiano *et al.*, 1993; ICE, 1995; Van den Hurk *et al.*, 1997). Adverse environmental impacts from dredging can occur at both the site of dredging and at the disposal ground (Reed & Waldock, 2000). The type and magnitude of those effects depends on a number of factors; the chemical and physical nature of the dredged material, location of dredging and disposal sites and the dredging equipment employed to remove the material.

At present, the UK government has not adequately addressed the issue of disposing of contaminated material (Murray, 1995). In the case of PCBs, concentrations in UK coastal sediments have been reported to be elevated in some areas as a result of contamination from past production and from use in various industrial activities (Proudfoot, 1995; Camacho-Ibar & McEvoy, 1996; Klungsøyr *et al.*, 1996; Scrimshaw *et al.*, 1996; Thompson *et al.*, 1996; Leah *et al.*, 1997). Dredging activity in harbours and estuaries around the UK has the potential to significantly alter the spatial distribution of these contaminants. The remobilisation of sediments into suspension can cause partitioning between different environmental compartments (Section 1.3) and redistribute PCBs over short and long distances (Kennish, 1994; Wania & Mackay, 1999). The risk of widespread contamination from PCBs, via their redistribution by dredging, is a possibility where sediments are licensed for disposal to sea.

In 1972, the UK government, in common with many other European governments, signed the Oslo Convention for the Prevention of Pollution by Dumping from Ships and Aircraft and the London Dumping Convention for the Prevention of Marine Pollution by Dumping of Wastes and other Matter (de Silva & Thomas, 1994; Bray *et al.*, 1997). This legislation provided a power of enforcement first proposed under the Dumping at Sea (1974) Act. These powers have since been revised under the Food and Environment Protection Act (FEPA) (1985). The main provisions of this last Act are designed to prevent the pollution of the sea by substances that are liable to create hazards to human health, to harm living resources and marine life, to damage amenities or to interfere with other legitimate uses of the sea. The Food and Environment Protection Act, Part II (1985) states that the Licensing Authority can permit a licence for disposal at sea but must aim to:

1) protect the marine environment, the living resources which it supports and human health;
2) prevent interference with legitimate uses of the sea; and
3) consider other alternative methods of dealing with substances or articles.

To date, the FEPA assessment of dredged material prior to disposal involves chemical analysis of OSPAR priority list chemicals only, that is to say, no biological tests/bioassays are conducted. The suite of chemicals measured are used as indicators of environmental conditions at a site. An alternative to disposal is the beneficial use of dredged material for environmental restoration programmes. The term beneficial covers..."all productive and positive uses of dredged material ranging from fish and wildlife habitat development, to human recreation, to industrial/commercial uses" (USACE, 1986). Beneficial use of dredged material will become increasing important in the future as new methods for managing environmental problems are effectively introduced. In the UK, these include the mitigation of estuarine salt marsh and foreshore erosion (e.g. Harwich; French *et al.*, 2000) and beach replenishment (e.g. South Wales; PIANC, 1990; Paipai, 1995). Since 1992, all applicants requiring sea disposal licences for dredged material from England and Wales are required to consider the potential for beneficial use of the material in addition to methods for its disposal. If alternative methods of dredged material disposal, such as estuarine foreshore recharge (French *et al.*, 1999), coastal protection (Environment Action, 1996), salt marsh feeding (Murray, 1994; Paipai, 1995) or beach nourishment (de Silva & Thomas, 1994; Bray *et al.*, 1997) are to be encouraged, it is crucial to accurately measure contaminant loadings in dredged material.

In the meantime, sea disposal of dredged material remains, to a large extent, the most cost-effective means of disposal. In the UK, the Department of Environment, Fisheries and Rural Affairs (DEFRA) are the licensing authority for the disposal of material to sea in England and Wales. The Centre of Environment, Fisheries and Aquaculture Science (CEFAS) provides advice to DEFRA on each licence application and conducts chemical analyses of sediments in support of these licences. CEFAS currently deals with approximately 150 applications each year to deposit material to sea. The total quantity of material licensed annually is around 40 million m^3 (Burt, 1995) of which 1 – 9 million m^3 are derived from capital dredgings and 13 – 33 million m^3 are from maintenance dredging. This material is disposed of at designated offshore sites, of which there are approximately 100 around the UK coast (Campbell, 1991). By way of comparison, approximately 20 million m^3 of sediments are dredged annually from the river Rhine/Meuse (Rotterdam harbour) and a further 10 million m^3 are dredged from the Rivers Scheldt (Antwerp), Weser (Bremerhaven) and Elbe (Hamburg) (Calmano &

Förstner, 1996). An important consideration before licensing the disposal of such material to sea is the level of both organic and inorganic contaminants in the dredged material.

Some of the material considered for sea disposal includes dredged material and fish wastes (Waldock, M., pers. comm., 2001). Dredged material is classified as either capital or maintenance and this classification is divided into material type depending on the geological origin, hydrological cycling, sedimentation patterns, contamination and frequency of channel or harbour clearance requirements (Campbell, 1991; CIRIA, 1995; ICE, 1995; UNEP, 1996). Capital dredged material is previously undisturbed sediment (clay, chalk, boulder and rocks) and is not usually affected by chemicals from anthropogenic activities. Maintenance dredged material is typically fine-grained silts, which are routinely removed from approach channels to harbours, docks and marinas and at locations within these areas. Such fine sediments are often sinks for pollutants such as metals, petroleum hydrocarbons or persistent organochlorine compounds such as PCBs (CEFAS, 1997a).

The impacts of disposing of material to the marine environment include the partitioning of chemicals between different phases and, therefore, the possible release of pollutants with the potential to cause adverse biological effects (Campbell, 1991). Remobilisation and resuspension of sediments through storm events and dredging activities are important processes together with bioturbation for re-mobilising PCBs (Calmano & Förstner, 1996). The resuspended sediments are typically very fine and provide an important pathway for the transportation and dispersion of PCBs, which may then become available to filter-feeders and organisms that live and feed on or in contaminated sediments (DiPinto & Coull, 1997). For example, Smith *et al.* (1996c) suggested that sediments mixed with as little as 5% dredged material could have an effect on immune capability in the common shrimp (*Crangon crangon*). This finding was based on short-term exposure of organisms under laboratory conditions to increasing percentages of contaminated dredged material.

Before a licence to dredge sediments from the coastal zone and dispose of the material to sea is granted, the OSPAR Commission and the London Dredging Convention (LDC) recommends the analysis of 2-5 samples from the proposed dredging zone to characterise the PCB loading of the material in support of the licence application. Also, other information is considered before a licence is granted, in a weight of evidence approach, including: tonnage; location and nature of disposal sites; sediment composition (particle size); location of Special Protection Areas (SPAs), Special Areas of Concern (SACs) and Special Sites of Scientific Interest (SSSIs); and the potential use of dredged material for beneficial use schemes. The OSPAR Commission guidelines suggest that each actively dredged area is re-sampled every 3 to 5 years. Sampling is sometimes requested from the whole dredged area to ensure that samples are 'representative'. More frequently in the UK, sample locations are selected by CEFAS to reflect areas where sediments are fine enough to retain contaminants. The sampling sites are thus not typical of average background levels of contaminants but, rather, represent areas with elevated contamination levels (chiefly past or present heavily industrialised or urban areas). In the UK, a total of 25 separate chlorobiphenyl congeners (Σ_{25}CBs) are routinely determined in dredged material prior to licensing a disposal. The set of congeners includes: CB#18, #28, #31, #44, #47, #49, #52, #66, #101, #105, #110, #118, #128, #138, #141, #149, #151, #153, #156, #158, #170, #180, #183, #187 and #194.

The OSPAR Commission guidelines emphasise the need for alternative methods of disposal but have not considered a more effective sampling design for assessing the spatial distribution and spatial variability of contaminants. The ability of existing sampling programmes to determine local contamination levels is questionable (Krumgalz *et al.*, 1989; Einax *et al.*, 1992; Kelly *et al.*, 1994; Wagner, 1995; Johnston *et al.*, 1996; Ambrose, 1997).

1.6 The PCB problem

Of the contaminants giving rise to significant pollution concerns, PCBs are regarded as especially hazardous, due to their toxicity, persistence and ability to bioaccumulate. The historical use, manufacture and uncontrolled and accidental disposals of PCBs continue to present pollution hazards today. Despite the increasing scope of regulatory controls, levels of PCBs in sediments are not declining as expected, especially in South Wales and North East England (CEFAS, 1997c). The hazards associated with such compounds are real and an appropriate risk assessment of sediments is required to manage localised pollution. The OSPAR Commission will encourage European governments to reduce anthropogenic chemicals in the environment to near background (for natural chemicals) or zero levels (for man-made substances) by 2020 (OSPAR Commission, 1998). This will require a more comprehensive sampling programme in order to co-ordinate resources to remediate particularly polluted areas. The scientific basis for such a programme is not yet in place.

One of the major shortcomings of the present statutory regulations is the limited scope of sampling strategies employed to assess the chemical concentrations in marine and estuarine sediments and dredged material. Present sampling programmes have a limited spatial resolution. The lack of contaminant information makes it difficult to understand the processes operating in the vicinity of a site and hinders the identification of source areas where contamination has occurred. A more comprehensive sampling strategy could help explain the mechanisms and processes controlling the spread of a substance so that misclassification of contaminated material does not lead to disposal at sea or beneficial use, but to appropriate remediation.

At present, the sampling strategies employed to estimate chemical concentrations in sediments and dredged material are inadequate to determine contaminant concentrations locally as shown in a recent survey by Associated British Ports (ABP 1996). The limitation of such an approach is a consequence of both the analysis, that is limited to specific congeners of which the most toxic congeners are not included (mostly due to costs), and in terms of sampling (ad hoc coverage and limited sample numbers). There are difficulties with not only obtaining a truly ‘representative’ sample, but also deciding how many samples to take to optimally estimate an area to be dredged and these are issues that need to be addressed.

Contamination of estuarine and coastal marine sediments both as a consequence of historical and present day inputs presents a continuing problem for the management of sediments and dredged material. In order to reduce chemicals in the environment by 2020, research is required in the identification of unsampled sites, known polluted sites, possible sources (both diffuse or point sources), level reduction and prevention of further contamination of sediments through studies of processes operating in the environment. The persistence and toxicity of PCBs will continue to cause a hazard in the marine environment even though their production has been banned and their current use has been restricted in the UK.

1.7 The present study: aims and objectives

The preceding review has highlighted the need for an improved understanding of both the distribution and behaviour of residual PCB contamination. This is especially true of the UK, where past industrial uses have resulted in complex contamination histories within coastal and estuarine sediments. Within this context, the aims of the present study are two-fold:

First, to analyse information within current databases and to evaluate the effectiveness of existing monitoring programmes as a basis for detecting spatial variations (and any temporal trends) in PCB concentrations within marine, coastal and estuarine sediments and dredged material in England and Wales. This study critically examines the results of sediment PCB monitoring since 1990 in order to identify and account for any areas with elevated concentrations of PCBs, and to determine whether concentrations have declined over the last decade.

Second, to investigate the nature of within-site variability in PCB concentrations in dock sediments as these sites are potentially subject to disturbance and redistribution through dredging activity.

Within these broad aims, a number of specific objectives are identified:

1. to establish an inventory of PCBs in English and Welsh coastal and estuarine sediments by statistically analysing the geographically extensive data acquired under the UK NMMP between 1990 and 1999;
2. to establish the extent and magnitude of PCB concentrations in dredged material sampled under the FEPA programme in England and Wales between 1990 and 1999;
3. to determine any spatial patterns or trends in sediment PCB concentrations at the national scale over the last decade;
4. to determine the nature of local spatial variability in PCB concentration and chemical composition using an intensive case study of a known site of contamination in King's Docks, Swansea; and
5. to incorporate findings from the intensive study into an improved sampling protocol for the evaluation of licence applications for dredged material disposal.

CHAPTER TWO

Research Design

This chapter outlines the distinctive features of the study design, most notably the integration of a geographically extensive investigation of existing monitoring data with an intensive case study of a site known to have elevated PCB loadings. The extensive study examines the spatial distribution of PCB concentrations in marine sediments (the NMMP data set) and dredged material (the FEPA data set) recorded in England and Wales over the last decade. The intensive study assesses within-site variability of PCB concentrations in the bottom sediments of a dock prior to dredging.

2 Introduction

The aim of many sampling programmes is to evaluate the environmental impacts of one or more contaminants within one or more environmental compartments (e.g. water, sediment or biota). In order to achieve this, an assessment or estimation of the spatial distribution and the spatial correlation of the contaminant(s) is necessary (Wang & Qi, 1998). The measurement of contaminants in the field is usually limited by financial resources. Consequently, only a few samples are taken to provide a 'snapshot' of concentrations locally. Due to these financial constraints, extensive monitoring programmes often produce data that are not truly 'representative' of the area and generally provide limited information concerning the spatial distribution of the contaminants involved. The spatial variability of contaminants is often high, especially in sediments due to their heterogeneous nature, and therefore the reliability of the estimated inventories becomes questionable (Stoeppler, 1997).

Our present understanding of PCB concentrations in marine sediments and dredged material in England and Wales is extremely limited. This is to a large extent due to a lack of available field data for estuarine and coastal environments and a lack of interpretation of the data that has been collected. If PCB concentrations are to be reduced by 2020, as specified by the OSPAR Commission, then the extent of the PCB problem (i.e. the magnitude of sediment PCB levels and their spatial and temporal distribution) in England and Wales requires a much more thorough investigation than has hitherto been attempted. There is thus both a scientific and an applied rationale for this kind of study. The combined approach adopted in this study therefore attempts to (i) scientifically evaluate the current NMMP and FEPA monitoring programmes, utilising PCB concentrations, so that the variability of concentrations in space and time from sediments around England and Wales are evaluated; and (ii) apply the knowledge attained above to lead into an investigation of the within-site variability of concentrations in dock dredged material, which subsequently forms part of the risk management of dredging licence applications. The present study appropriately uses two different approaches: an 'extensive' and an 'intensive' research design.

The most common approach to the monitoring of contaminants in the field utilises an extensive research design (Sayer, 1992). Such an approach is concerned with the elucidation of the more common and general patterns of a contaminant as a whole.

Although individual observations or sites may be similar, they may not actually connect or interact. To investigate any connections between such sites, it may be necessary to separate contaminant concentrations into geographical areas to increase similarities between individual sites. The advantages of adopting an extensive research design is that it provides background descriptive information to the research and forms general patterns or structures of phenomenon. The disadvantage is that it is not possible to attribute causality.

In contrast, an intensive study aims to investigate the causal processes operating in a particular case or limited number of cases. This approach focuses on how sites or areas share similar attributes. Sites, therefore, have either similar or different properties but are related to each other structurally or causally (Sayer, 1992). What distinguishes the scientific approach adopted in this study from previous approaches to the study of PCBs in sediments is the combination of the extensive and intensive approaches in order to examine the general patterns of PCB concentrations in sediments, and to achieve at least a preliminary investigation of the mechanisms or processes governing their distribution and redistribution. The results from such studies can subsequently provide an input to the wider area of research concerned with the transportation of PCBs in different environmental compartments and the environmental processes which influence the presence of PCBs at a variety of spatial scales. Furthermore, this work will provide the basis for improved risk assessment of hazardous substances, such as PCBs, in dredged material and will inform the future monitoring of marine sediments.

The organisation of this thesis reflects the research design described above. The first stage of the research introduces the problems associated with PCBs and briefly summaries the current understanding of research undertaken to date in England and Wales (Chapter 1). Chapter 2 outlines the research design applied to the analysis of the 'extensive data set' (from NMMP and FEPA monitoring programmes in England and Wales) and a local case study (the 'intensive data set').

Chapter 3 presents an assessment of the spatial distribution and variability of PCB concentrations in the coastal zone of England and Wales since 1990. The purpose of this assessment is to determine the overall level and geographical distribution of PCB contamination, and examine the application and appropriateness of existing monitoring programmes.

Chapter 4 introduces a detailed ('intensive') case study of the local environmental variability of PCB concentrations in dredged material. King's Dock, Swansea is selected as the case study because concentrations are known to be higher here than at other docks in England and Wales. The 'representativeness' of the existing sampling design and techniques are assessed and a new sampling strategy is evaluated.

In Chapter 5, geostatistical techniques are used to identify spatial patterns and structures of individual congeners, Σ_{25}CBs, total organic carbon (TOC) and particle size within the King's Dock data. The scientific and risk assessment implications of the results obtained in this study are discussed more fully in Chapter 6. The results from the intensive study (Chapter 4 and 5) are used to develop an improved sampling protocol for assessing licensing applications for the disposal of dredged material to sea. The main findings and recommendations for future research are summarised in Chapter 7.

2.1 Structure of existing monitoring programmes in England and Wales

In the UK, the DEFRA, EA and CEFAS are responsible for the monitoring of hazardous substances in the environment. Aside from specifically-funded research projects, routine monitoring is carried out under the UK National Marine Monitoring Programme (NMMP), concentrating on the estuarine and marine environment, and the monitoring of hazardous substances in dredged material under the Food and Environment Protection Act (FEPA), 1985.

The most comprehensive monitoring programme is the UK NMMP. This began in the late 1980s and was initiated to co-ordinate marine monitoring in the UK. Sampling sites are located in major estuaries in the UK as well as at offshore locations. The aim of NMMP is to provide a clear overall picture of the spatial distribution of major contaminants (and their biological effects) with a view to selecting key sites for future trend monitoring. Specific objectives of NMMP are:

- to establish, as precisely as practicable, the spatial distribution of contaminants in different areas of UK waters and to define their current biological status, thus identifying any areas of specific concern;
- to detect, with appropriate accuracy, trends in both contaminant concentrations and biological quality in those areas identified as being of concern; and

- to measure long-term natural trends in physical, biological and chemical parameters at selected sites (MPMMG, 1998).

The NMMP encompasses 91 locations around the UK and sampling consists of sediments, fish, shellfish, benthos and water for chemical and biological analyses. The sample design for monitoring sediments under NMMP initially included some limited provision for assessing the variability of measured chemicals, either from natural sources or from the sampling techniques employed. Each of the 91 NMMP sites selected by the MPMMG board are initially assessed by sampling sediments on a nine point grid (MPMMG, 1998). At each site, sediments are collected by either a tightly closing 0.1 m^2 grab sampler or by means of a suitable corer (MPMMG, 1994). For PCB analysis, CEFAS only collect one sediment sample at each NMMP site due to limited funding by government bodies.

2.1.1 Spatial structure of the NMMP data set

A survey of 87 of the NMMP sites (representing 16 estuaries, 18 intermediate and 21 offshore sites) was carried out between 1990 and 1997 (MPMMG, 1998). Marine sediments sampled under this programme in addition to other sites sampled under other smaller monitoring programmes (e.g. monitoring of sediments at dredged disposal grounds) are located in the North Sea (Figure 2.1), English Channel (Figure 2.2), Celtic Sea (2.3), Bristol Channel (Figure 2.4) and the Irish Sea (Figure 2.5). Appendix 2 contains site location numbers. The network of monitoring sites operated under NMMP include a combination of Joint Monitoring Group stations, North Sea Task Force stations and sites where salinity changes markedly in major estuaries (Section 1.4.2). The JMG and NSTF schemes were organised prior to organisation of the NMMP and these schemes have subsequently been replaced by sampling conducted under NMMP. The NMMP sites include upper, middle and lower estuarine locations and offshore areas. A range of contamination gradients are incorporated, as sampling encompasses industrialised/agricultural areas, and offshore sites which serve as reference stations for comparison with more heavily contaminated estuaries and coastal areas.

Under the NMMP, sediment samples are normally analysed for a suite of 11 CBs which includes the ICES seven (Σ_7CBs) congeners (CB#28, #52, #101, #105, #118, #128, #138, #153, #156, #170 and #180). These congeners have been selected because of their

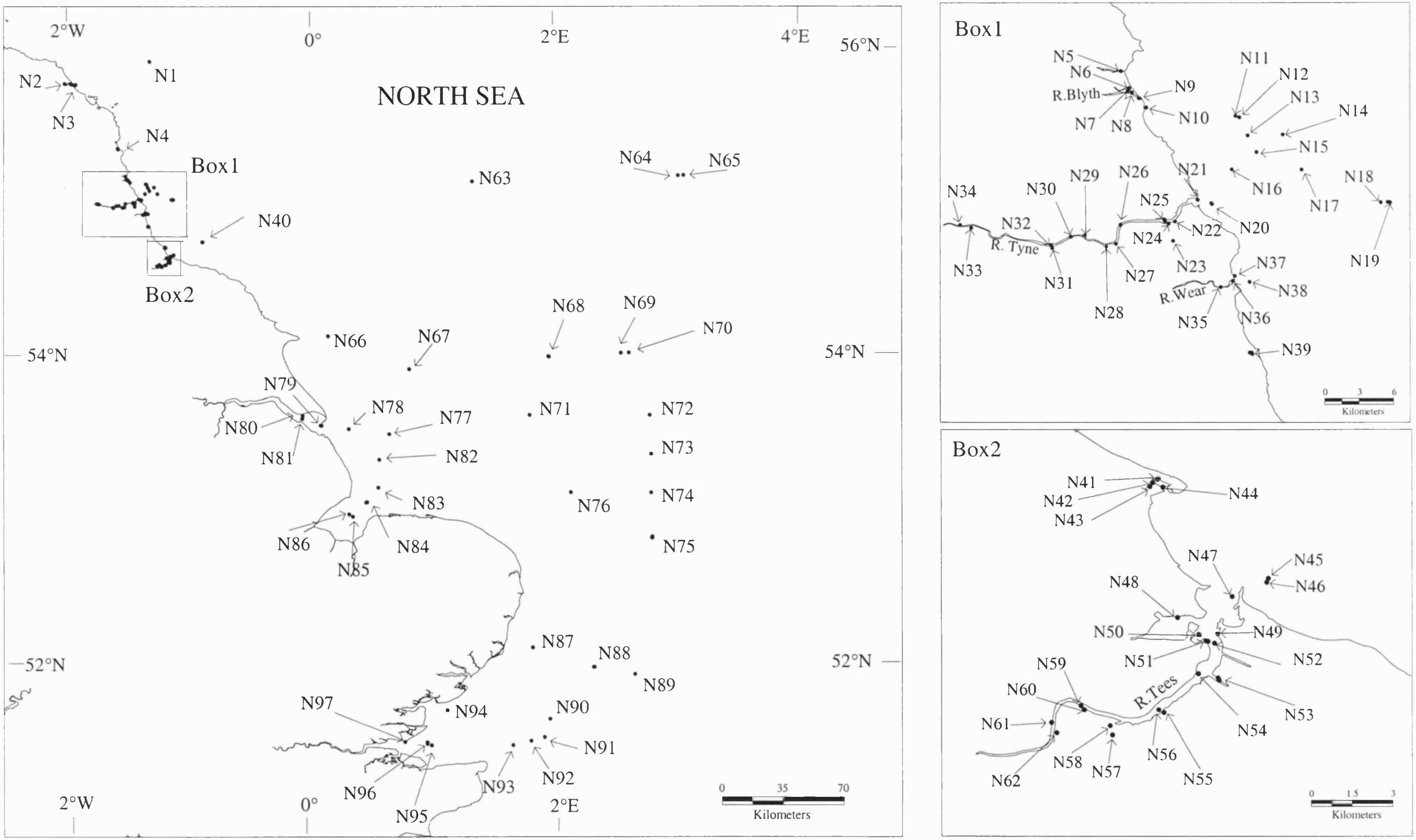


Figure 2.1: Location of sites sampled under the NMMP and other smaller programmes since 1990 in the North Sea *(N=North Sea)*

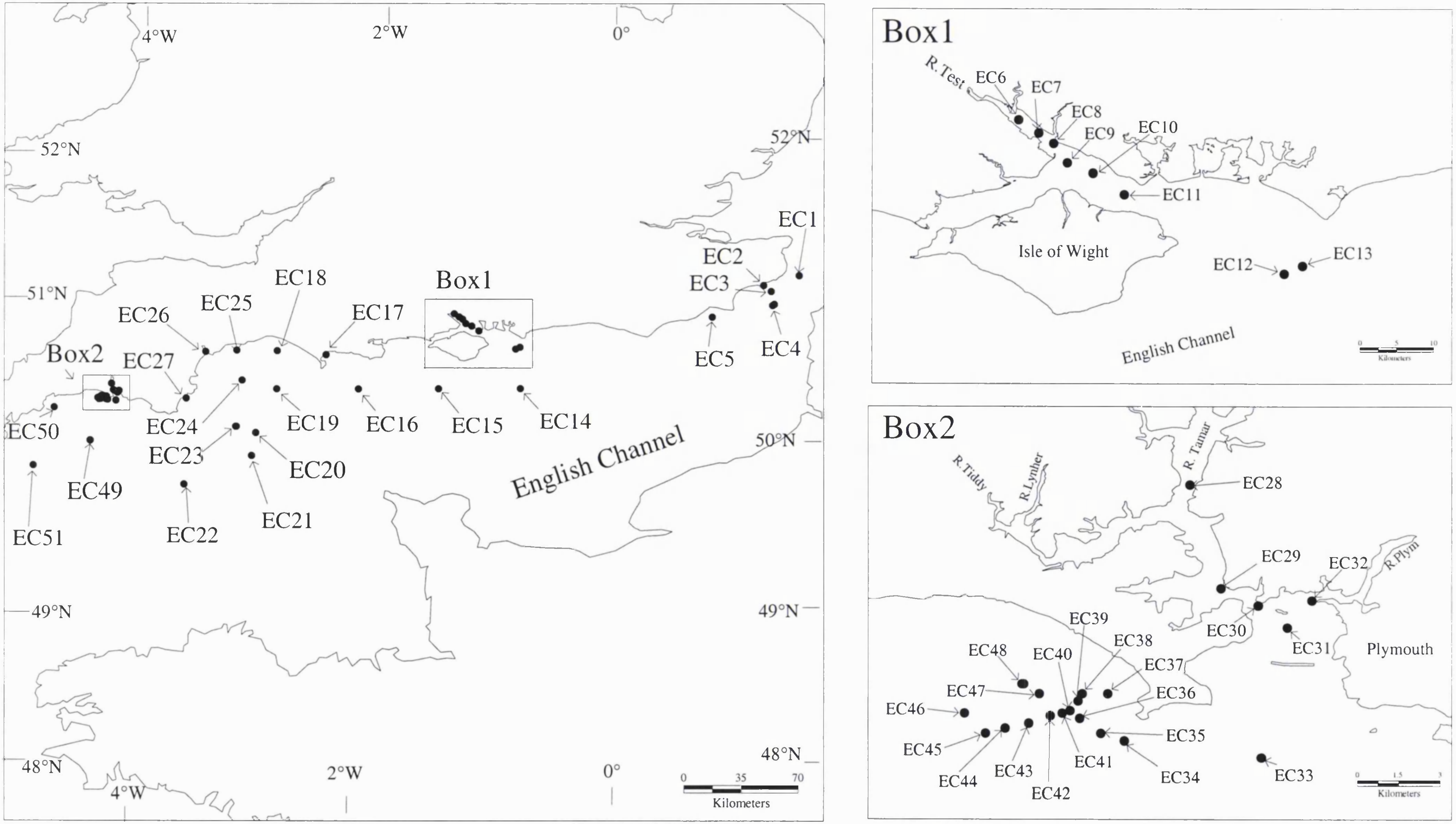


Figure 2.2: Location of sites sampled under the NMMP and other smaller programmes since 1990 in the English Channel
(EC = English Cnannel)

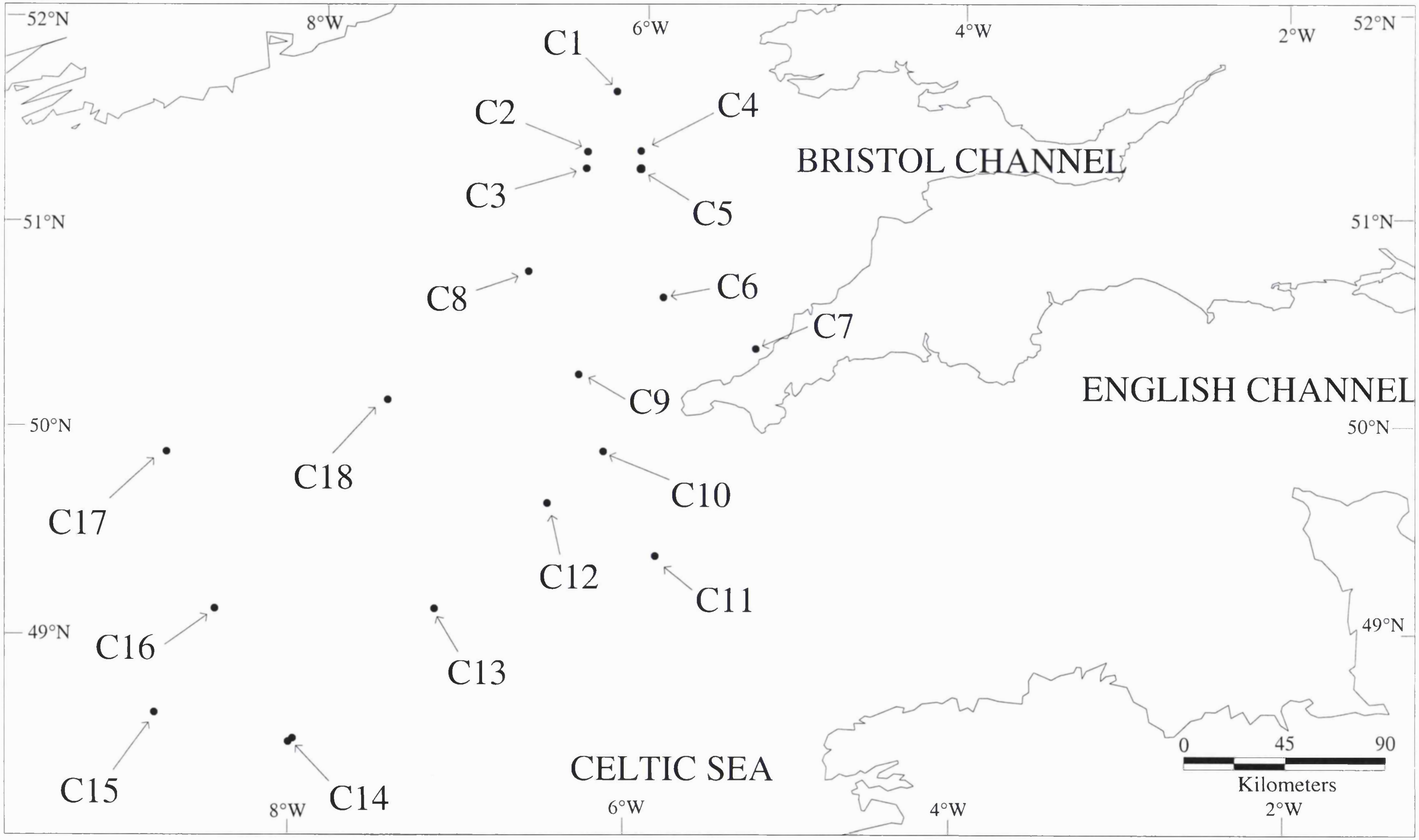


Figure 2.3: Location of sites sampled under the NMMP and other smaller programmes since 1990 in the Celtic Sea

(C = Celtic Sea)

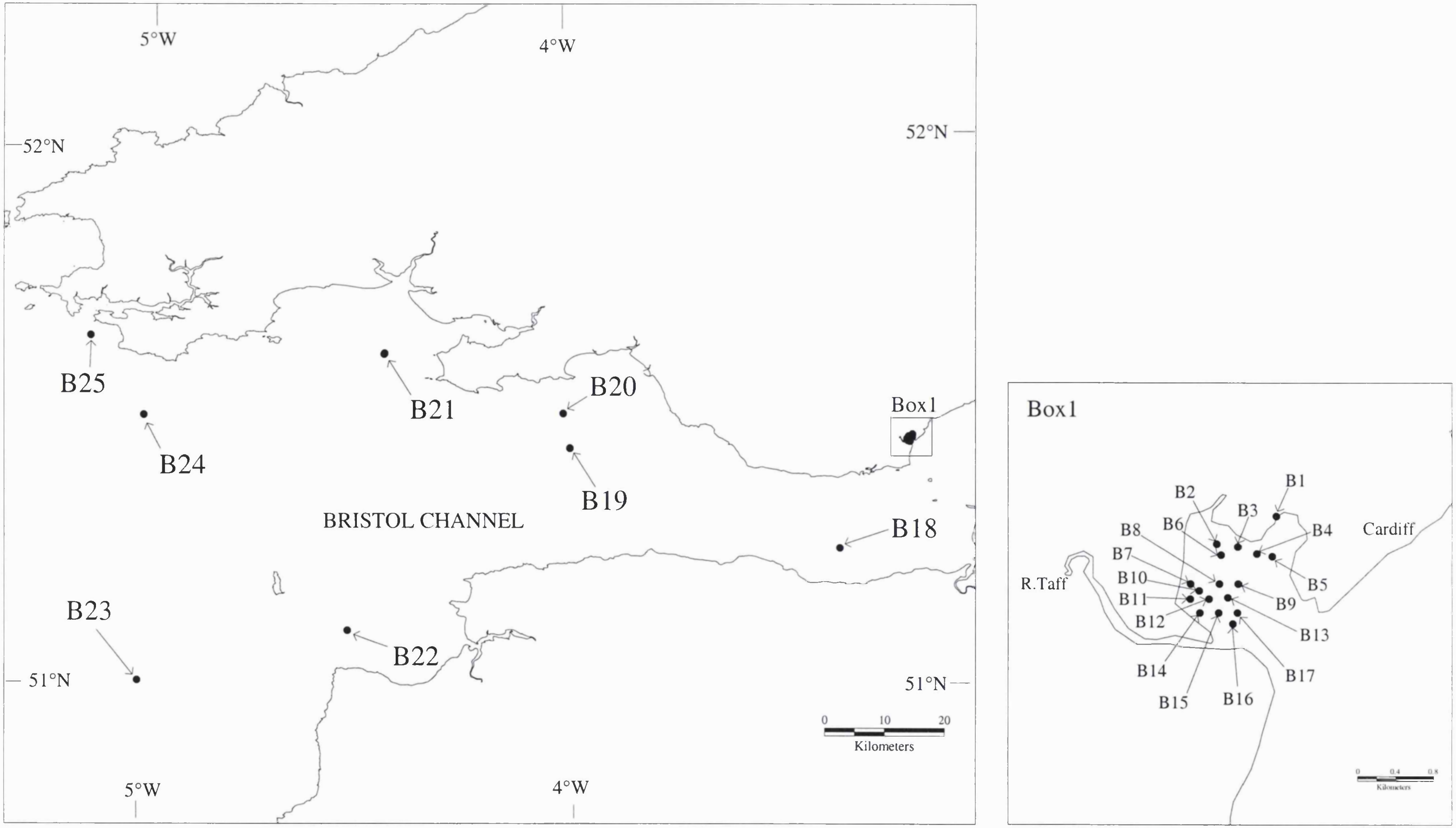


Figure 2.4: Location of sites sampled under the NMMP and other smaller programmes since 1990 in the Bristol Channel
(B= Bristol Channel)

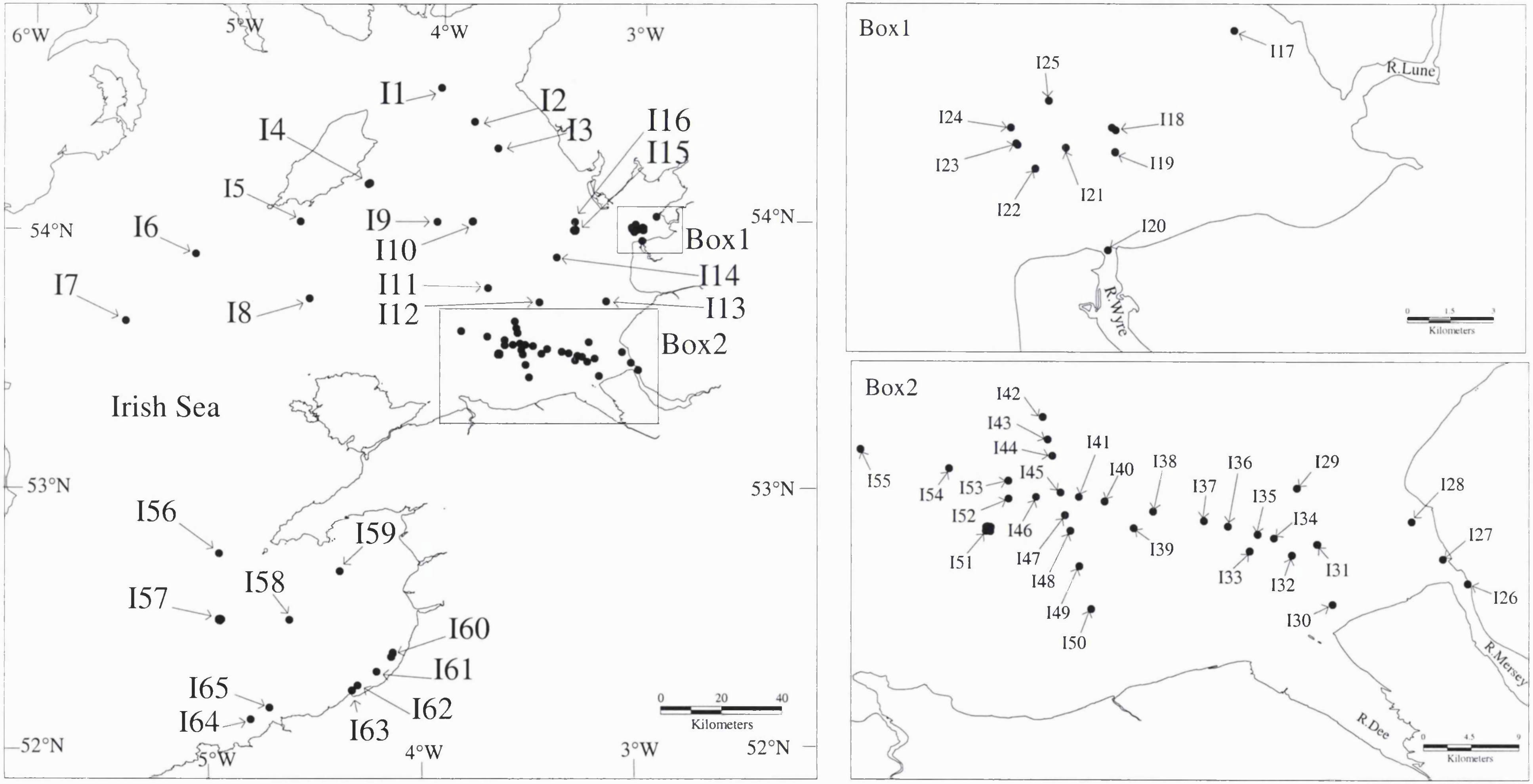


Figure 2.5: Location of sites sampled under the NMMP and other programmes since 1990 in the Irish Sea
(I = Irish Sea)

occurrence and abundance in source materials, toxicity, molecular structure and degradability. Many government institutes and other organisations only monitor the ICES Σ_7CBs, so that collaborative and comparative studies are possible. However, CEFAS routinely analyses sediments for Σ_{25}CBs (which also includes ICES 7) because this represents a broader spectrum of chlorination. A limitation of even this approach is that many highly toxic congeners (for example, the dioxin-like CBs such as CB#77, CB#126 & CB#169) are not recorded in routine analyses (McFarland & Clarke, 1989).

As a result of the NMMP, there is now a considerable volume of data pertaining to PCB contamination in offshore waters and industrialised estuaries in England and Wales. The data have not been critically evaluated to date. The physical-chemical characteristics of PCBs dictate that these contaminants preferentially adsorb onto sediments particularly where these are fine grained and/or contain a high proportion of organic carbon (OC). Estuaries with high percentages of fine grained sediments and high OC content generally have higher levels of contaminants. Ideally, the concentrations should be normalised to particle size or organics (Koelmans *et al.*, 1997). Unfortunately, detailed particle size and OC of sediments are unavailable for this study.

2.1.2 Spatial structure of the FEPA data set

In addition to the NMMP sampling, sediment surveys are also conducted in support of licence applications to dredge harbours, docks, estuaries or any marine environment and dispose of material to the aquatic environment under FEPA (1985). The UK government (via CEFAS) is required to take 'representative' samples from proposed dredging areas to determine a variety of contaminant concentrations (e.g., metals, PAHs, organotins and PCBs). Sediments are acquired using a hand held grab and surface material (1 cm depth) sampled for PCB analysis. OSPAR recommends the analysis of 2-5 sediment samples from proposed dredging sites (Oslo Commission, 1993). Since 1990, PCBs have been measured in dredged material (Section 1.4.3). If sediments have concentrations higher than suggested CEFAS Action Levels 1 and 2 (100 and 200 μg kg^{-1}, respectively), these areas are further sampled to establish the spatial extent of contamination locally (CEFAS, 1997b). However, due to financial constraints and limited resources, this additional sampling does not, at times, permit a full assessment of site contamination.

The locations of FEPA sites in North East England, East England, South England, South Wales and North West England are indicated in Figures 2.6 – 2.10, respectively. Due to the recent expansion of UK port and harbour facilities (Kennish, 1994; IADC, 1997; French *et al.*, 1999), there have been a large number of areas requiring dredging licences and subsequently a large number of sediments have been sampled for PCBs. Other areas in docks, ports, harbours and mid channels have required dredging licences to improve navigation and access for larger ships. This increase in dredging has become a particular problem in the UK and one that is growing (Murray, 1995; Murray, 2000). If concentrations of PCBs and other chemicals are to be reduced to zero or near zero levels by 2020 (OSPAR Commission, 1998), the disposal of a range of hazardous substances from land-based sources and dredged material must be restricted.

An accurate assessment of the local spatial variability in concentration is therefore essential to prevent the unnecessary distribution of PCBs into offshore environments (Kennish, 1994). However, there are problems associated with measuring the spatial variability of PCBs at the local scale. Sampling and chemical analysis are expensive and it is therefore difficult to estimate the extent of contaminated areas. Regulators are conscious that operators have limited financial resources to pay for sampling and conflicts arise between sample numbers and the need to determine local scale variations in PCB concentrations. To improve our understanding of local variability, a case study is carried out to assess concentrations in dredged material at a local spatial scale. These results are used to estimate concentrations at unsampled locations within the case study, and to examine the implications for licensing of different degrees of sampling effort.

2.1.3 Analysis of the 'extensive' data sets (NMMP and FEPA)

The NMMP and FEPA data sets are presented and analysed in Chapter 3. The data sets are separated into regions so that estuaries in industrialised areas can be assessed separately from offshore marine sites. The magnitude of concentrations and their variability in marine sediments and dredged material are established and the principal patterns or trends identified. A number of estuaries are investigated in more detail to identify any similarities in their sediment 'PCB profiles' that might provide insights into the potential sources of contamination. A PCB profile is a graphic representation of the degree of chlorination exhibited in various sediments at a site.

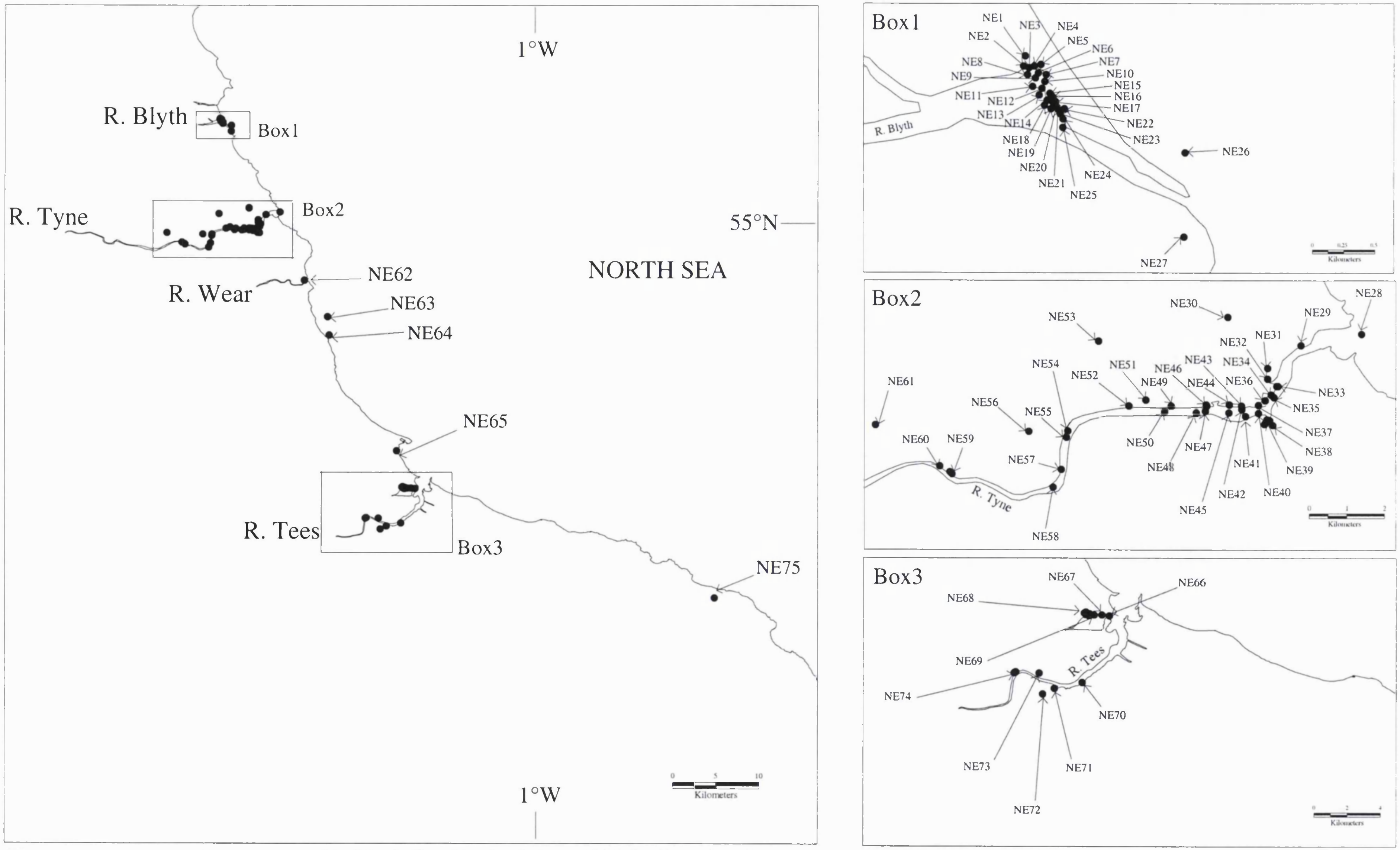


Figure 2.6: Location of sites sampled in North East England since 1990 for licensing disposal of dredged material
(NE = North East England)

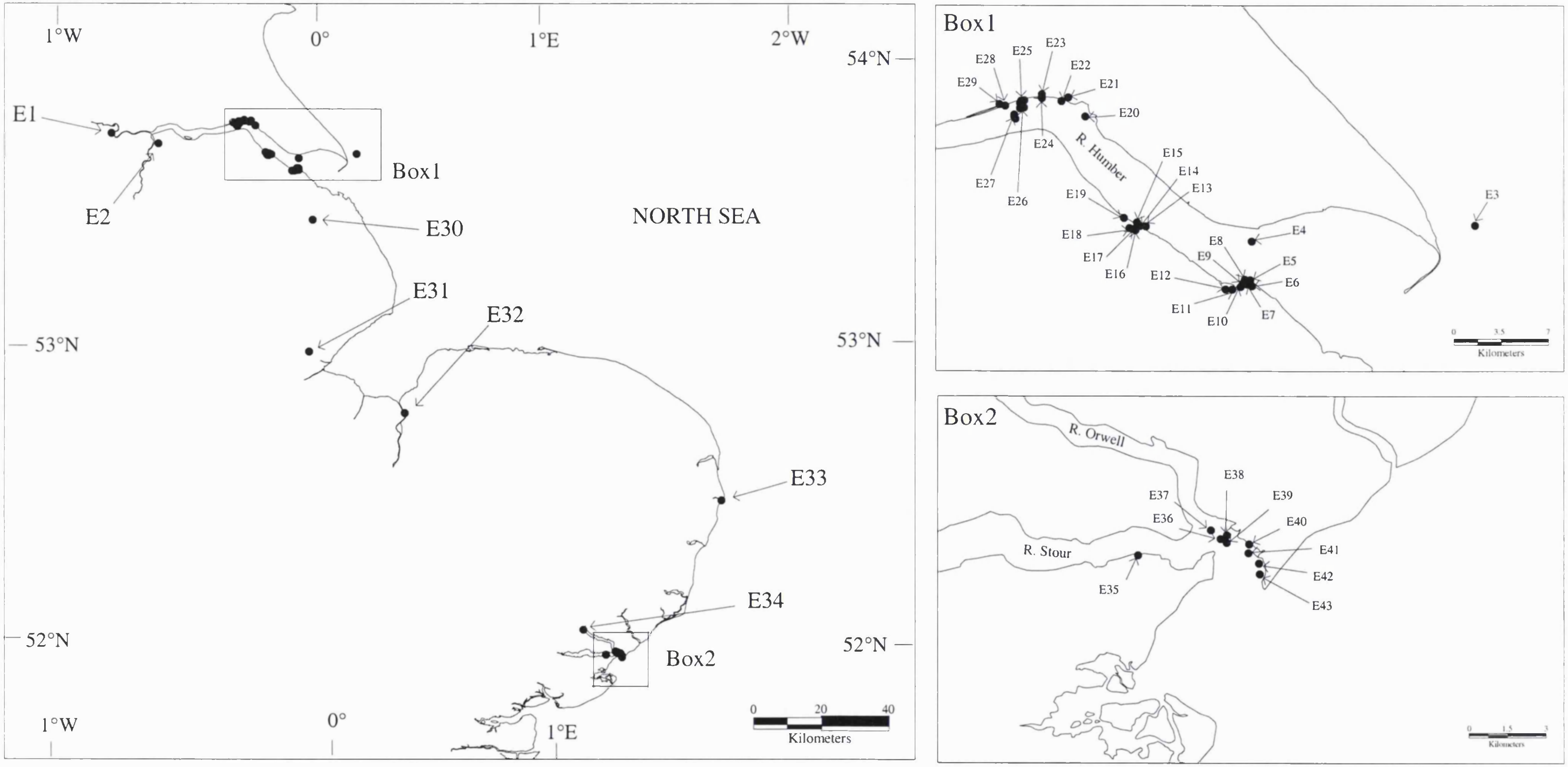


Figure 2.7: Location of sites sampled in East England since 1990 for licensing disposal of dredged material

(E = East England)

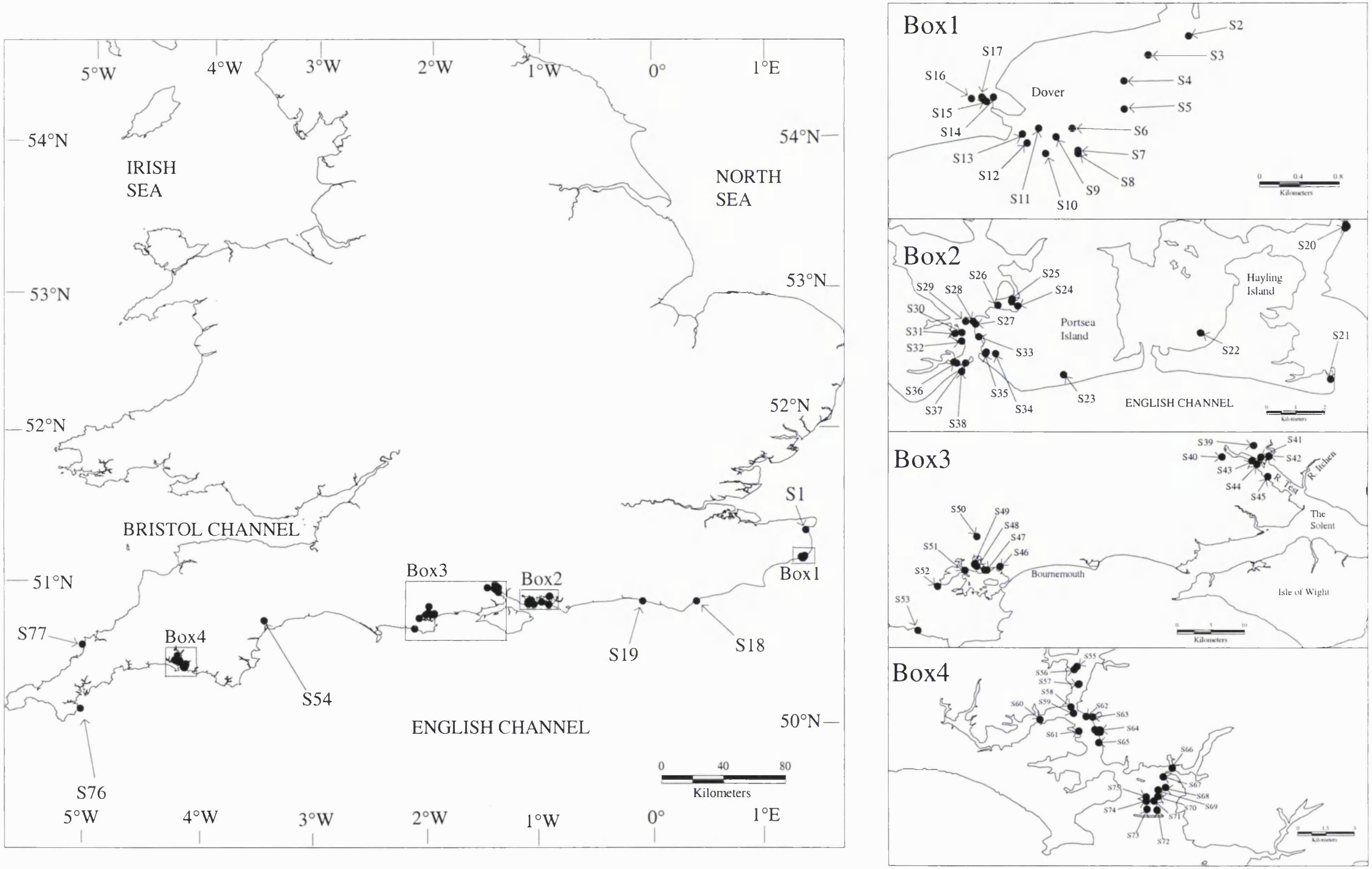


Figure 2.8: Locations of sites sampled in South England since 1990 for licensing disposal of dredged material
(S = South England)

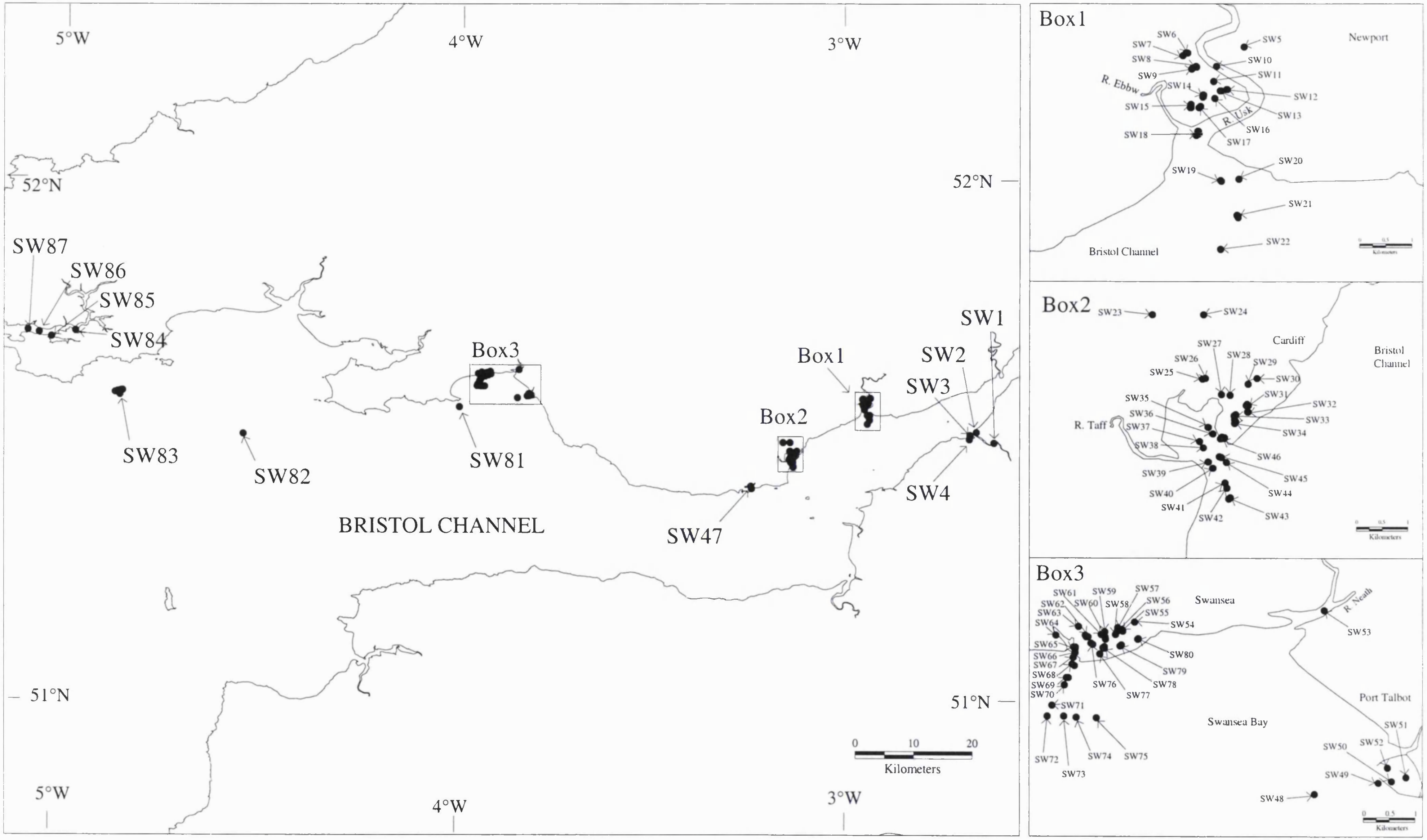


Figure 2.9: Location of sites sampled in South Wales and South West England since 1990 for licensing the disposal of dredged material.
(SW = South Wales)

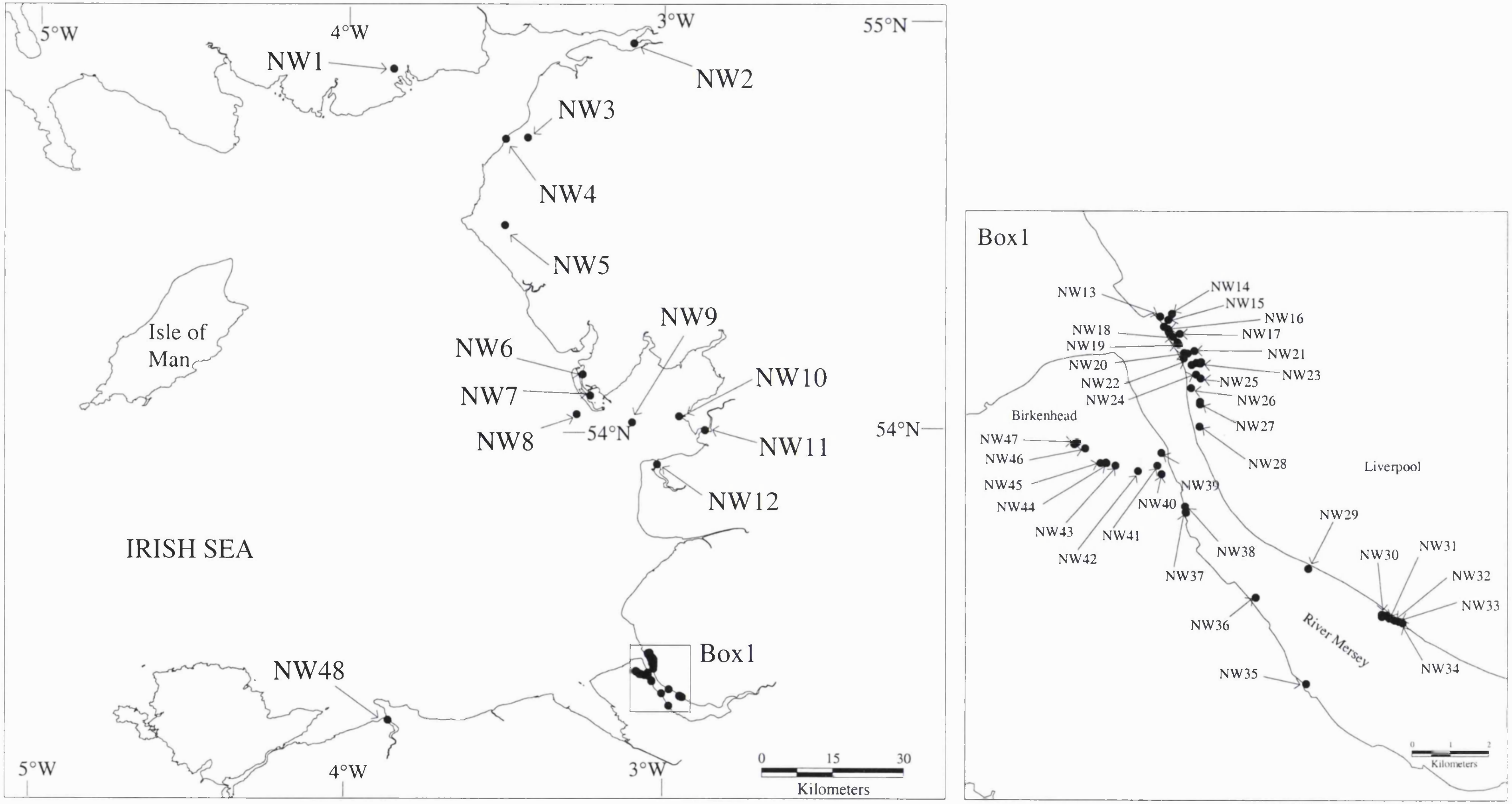


Figure 2.10: Location of sites sampled in North West England and North Wales since 1990 for licensing disposal of dredged material

(NW = North West England/North Wales)

2.2 Case study design

To improve our understanding of the local spatial variability of PCBs, a case study of an active commercial dock within the Port of Swansea, South Wales, is conducted. This intensive study investigates the spatial distribution and environmental variability of PCBs in sediments in a single locality. Particle size and total organic content of the sediment are measured for normalisation of PCB concentrations. The nature of the spatial sampling design and the density of sampling in the case study ultimately enabled the use of spatial statistical analysis (i.e. geostatistics) to quantify the spatial structure and evaluate the representativeness of the sampling scheme (see Chapter 5).

2.2.1 Swansea Docks

The Port of Swansea consists of the Prince of Wales Dock, King's Dock and Queen's Dock (Figure 2.11). The River Tawe runs along the western boundary of the docks, and the docks are separated from the river by a system of lock gates. All three docks are inter-connected and King's Dock has a dry docking facility on the south-west border.

Swansea Docks are owned by Associated British Ports (ABP) and all three docks are currently operational (although Prince of Wales Dock is only used to transport fish to the quayside market). In Queen's Dock, there is a BP terminal and large cargo ships enter the terminals to distribute oil and petroleum through large pipelines. Other activities within the dock complex include: general cargo handling; maintenance of vessels along the quayside; dry docking for tankers, ferries and cargo vessels and lay-by facilities for the numerous tugs operating from the port (ABP, pers. comm., 1996). King's Dock was selected as the case study location because it is known to be contaminated with PCBs (Reed & Waldock, 1998), has recently been refused licences to dredge sediments and appears to have a spatial distribution of sediment PCBs which is difficult to characterise under the current CEFAS sampling scheme. The main difficulties have been few sample numbers, patchy distributions, no clear trends, no identification of point sources nor an idea of potential diffuse sources. To date, no firm conclusions have been reached as to the source of PCB contamination in the dock. The EA suspect that mishandling of PCB waste material, destined for the RECHEM site, has accidentally entered the dock in 1992 from a visiting Swedish vessel (Hutchings, D., 1999).

2.2.2 King's Dock

King's Dock is located between Prince of Wales and Queen's Docks (Figure 2.11) and is 1.5 km x 0.5 km in size. There are 4 - 5 active berths (within the main dock) plus 2 dry docks (204 x 28 m and 171 x 23 m) for vessel repair, vessel decommission, tank cleaning and repairs, hull cleaning, repainting and pressure jetting. King's Dock is currently used to transport and store coal, cement and oil.

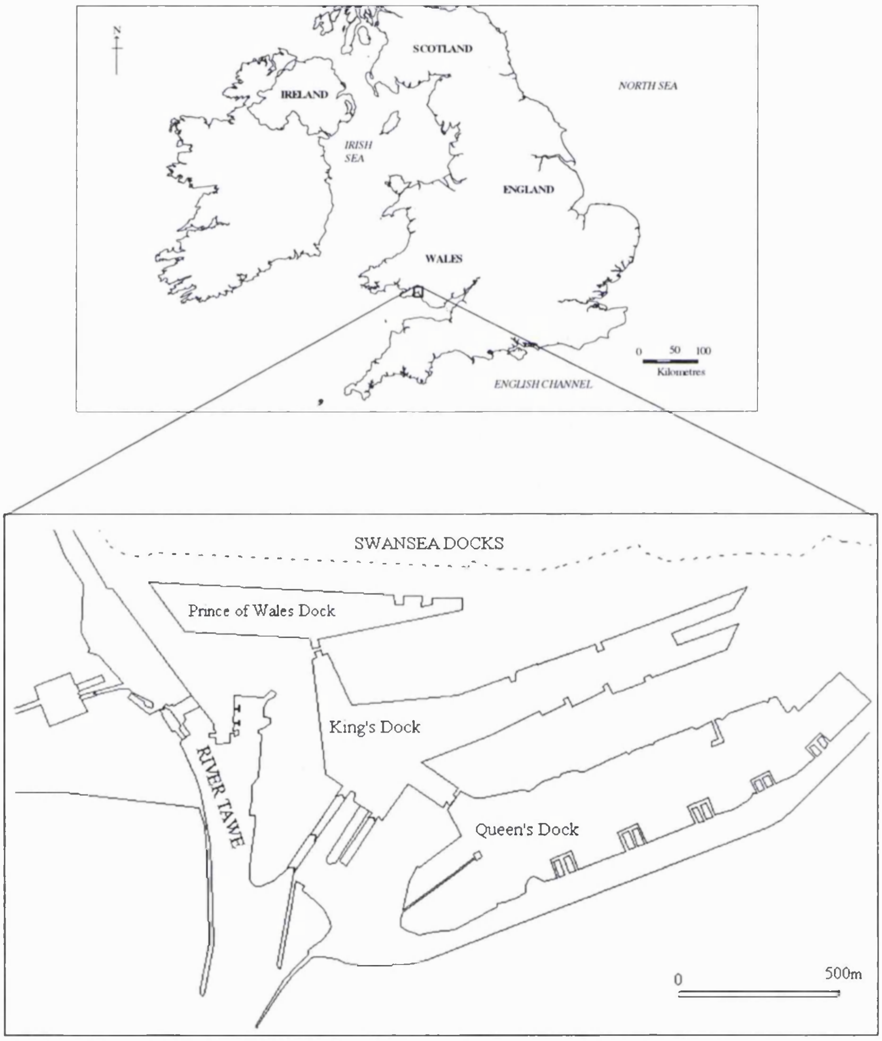


Figure 2.11: Location of the Port of Swansea (*ABP, 1996*).

ABP have recently requested permission to dredge King's Dock and sampling in support of their licence application has already been conducted by CEFAS to determine PCB concentrations in the bottom sediments (ABP, 1996). During 1994 – 1996, high concentrations were measured at a few locations in King's Dock. Unfortunately, under the current CEFAS sampling programme, the spatial distribution of PCBs has proven to be difficult to determine due to the ‘patchiness’ of the concentrations.

In response to the elevated concentrations reported by CEFAS, ABP Research and Consultancy Ltd conducted a more intensive sampling of all three docks in an effort to better establish the extent of PCB contamination (Figure 2.12). In 1996, 12 sediments samples were collected in King’s Dock. The aim of this sampling was to take samples close to possible sources of contamination. ABP concluded from this survey that the PCBs present in King’s Dock were likely to be from a historical source and suggested that there were no contemporary sources of PCB contamination in the docks. The spatial distribution of PCBs in the dock sediments remained unclear, however, owing to the high degree of spatial variability, which is poorly represented even by the more intensive sampling commissioned by ABP.

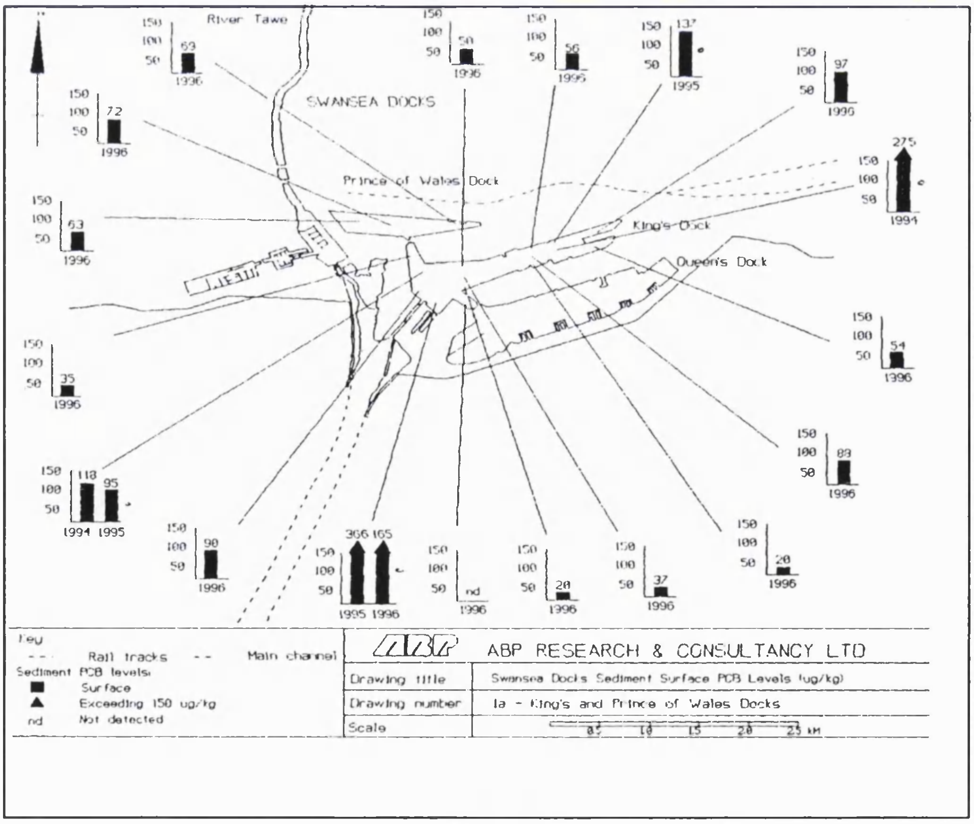


Figure 2.12: Σ_{25}CB concentrations in Prince of Wales Dock and King’s Dock: 1994 - 1996 (*ABP, 1996*).

2.2.3 Aspects of sampling design

Sampling strategies used in environmental monitoring are concerned with estimating, as accurately as possible, the variation of the phenomenon under investigation. Spatial variability can be a product of random events or long-term processes occurring over short or long distances and at different magnitudes (Goderya, 1998). The objectives of many pollution monitoring programmes are to determine the concentration, source, fate and behaviour of the compound and to make a risk assessment of its effects (Yost *et al.*, 1982). It is unrealistic to monitor the whole expanse of a sampling area, and so a number of samples are taken which are representative of the study area. In many cases, this requires sophisticated sampling strategies.

Most measurements or sampling procedures for environmental media are conducted at discrete points and these are expected to be 'representative' of the study area (Yost *et al.*, 1982). The results from these points are then extrapolated to the non-sampled areas but it is infrequently determined whether the data really represent the area as a whole. In the past, the calculation of the mean or median value (and variation around the mean) has been used to describe an extended area not sampled within the survey (Quevauviller, 1995). The spatial heterogeneity of the area and the variability of the data both remain unknown (Quevauviller, 1995). Sources of variability in data include those within a site (subsamples), between sites, temporal sampling and laboratory analysis (i.e. quality control). These factors have implications for sediment sampling since contaminated sediments are typically heterogeneous in their structure and chemical composition (Stoeppler, 1997).

A particular problem with the above approach is caused by the occurrence of 'hotspots' and extreme values in the data set. These isolated elevated values may reflect an exceptional event (e.g. a chemical leaking from a container) rather than the long term trend or spatial pattern in the study area (Stoeppler, 1997). In some sampling programmes, the identification of these 'hotspots' may be more important than characterisation of spatial average values.

Studies of spatial variability and the modelling of spatial data began in the early 1900s by Student (1907) and a review of the early work in this field can be found in Cressie (1991). Sampling strategies for environmental monitoring can be classified according to their spatial design (Table 2.1). A recent study of lead levels in one area of contaminated land by Ramsey & Argyraki (1997) highlighted some of the problems associated with choosing the most appropriate sampling design and identified the measurement of uncertainty when classifying land as contaminated. Ramsey & Argyraki (1997) questioned the 'representativeness' of samples taken in the field and suggested that sampling uncertainty on an estimated mean concentration of a chemical could be as large as 55%. This can have severe implications where land is classified as contaminated or, in this case, where dredged material is acceptable for disposal to sea. Several studies of soils, rainfall and chemical inventories have tried to improve the representativeness of sampling by dividing their sampling area into sub-regions so that more accurate descriptions of the spatial patterns or gradients are obtained (Webster & Burgess, 1984; Isaaks & Srivastava, 1989; McBratney *et al.*, 1991; Quevauviller, 1995).

Table 2.1: Sampling strategies for environmental monitoring (*Quevauviller, 1995*).

Spatial design	Typical use
Passive monitoring: sampling by chance	Monitoring of accidental effects of unknown origin
Selected sampling	Research, long-term observation, background monitoring, reference stations
Transect/gradient sampling	Reach of source-related pollution
Grid sampling	Large-scale surveys/inventories/screenings
Random sampling	Small-scale surveys of randomly distributed phenomena
Stratified random sampling	Spatial distribution of pollutants in populations
Active or experimental monitoring: exposition of sampling devices, bio-indicators or artificial habitats	Source-related pollutant impact assessment

Some of the most widely used sampling techniques are the systematic, classical random or stratified random sampling (Keith, 1988). These methods have been adopted for sampling in many environmental media including streams, soils, sediments, municipal wastes and dredged material (Yost *et al.*, 1982; Burgess & Webster, 1984; Pitard, 1988; Keith, 1988; Webster & Oliver, 1990; Webster & Boag, 1992; Ramsey & Argyraki, 1997). The random sampling design is defined so that each member of the population has an equal chance of being selected at every draw (Snedecor & Cochran, 1980). This design is unbiased because each site has the same chance of being sampled (Stoeppler, 1997). The disadvantages are that it is not possible to use any available information of the study area (i.e. if information was utilised, the sampling would become biased), nor information about the structure of the population, it is not reproducible and spatial patterns or gradients may not be clearly established because of uneven density of sampling points (Snedecor & Cochran, 1980; Quevauviller, 1995; Stoeppler, 1997). Consequently, a combination of random and non-random sampling design has been recognised as being more efficient than simple and stratified random sampling (Olea, 1974) and many variations on this theme have been proposed (e.g. Oliver, 1984; Oliver & Webster, 1986a; Cressie, 1991; Oliver & Badr, 1995; Chappell *et al.*, 1996; Hunt, 1996; Wang & Qi, 1998).

The systematic sampling design is also widely used and is generally preferred when spatial structures or patterns of a compound have to be determined, such as in the estimation of the total inventory of a chemical within an area (Quevauviller, 1995). An example of this design is a transect following a known gradient, such as, the distance from a point source. Other designs are based around regular, rectangular, triangular, hexagonal, W-shape and circular grids (Quevauviller, 1995; Stoeppler, 1997; Chang *et al.*, 1998; Wang & Qi, 1998). Circular grids have been employed in monitoring point source and unknown spreading of pollution (Stoeppler, 1997). Triangular grids are reported in the literature as being more effective and efficient than square grid designs for detecting directed structures in soils (Stoeppler, 1997). The advantage of systematic sampling is that it is simple to employ. The disadvantage is that results may be biased when the sampling intervals coincides with regular fluctuations in the environmental phenomenon of interest (Cressie, 1991).

To understand environmental processes and determine a contaminant's distribution in the environment, it is important to study the relationship between variables. Geostatistics can be used to estimate and characterise a contaminant and is also used to investigate a contaminant's continuity at different spatial scales (Isaaks & Srivastava, 1989; Oliver & Badr, 1995). A geostatistical approach utilises information on statistical correlation and the spatial continuity characteristics of environmental variables, and is therefore particularly suited as a tool to estimate concentrations of PCBs in sediments at previously unsampled locations based on the pattern or trend over different spatial scales.

The most important part of the sampling strategy, for geostatistical analysis, is the provision of reliable data for the estimation of the variogram (see Chapter 5). Reliable data are required so that the spatial structure of the sample variogram is modelled at different distances. Warrick & Myers (1987) suggest that if the sampling plan includes a combination of a coarse fixed grid and random sampling points, it can provide reliable data at various spatial scales. An unbalanced nested strategy that can be adapted to include few or many stages, depending on resources, is able to provide data at different distances at small and large intervals. As this approach is a hierarchy of sampling sites separated by different distances, it is effective in describing spatial variation (Chappell, 1995). Oliver (1984) used a 5-stage unbalanced hierarchical nested sampling design to measure the scale of spatial variation in soils of the Wyre Forest (see Figure 2.13). An unbalanced hierarchical nested sampling design is developed so that repeated samples are attained at short and long distances but repetition is minimised over the shortest distances because random variables are expected to be closely related at this range. It is possible, however, that even over the shortest distances, there can be some unresolved variance, that is spatial variability that has not been encapsulated by the shortest sampling distance (Webster & Oliver, 1990).

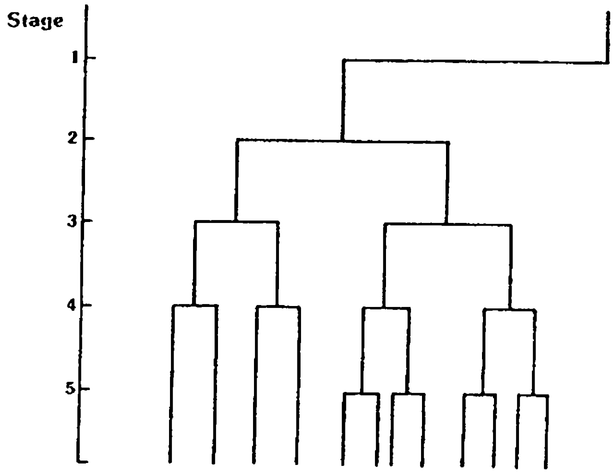


Figure 2.13: An example of an unbalanced hierarchical sampling scheme (*Webster & Oliver, 1990*).

For example, the estimation of a contaminant, Z, in different stages is:

$$Z_{ijk....m} = \mu + A_i + B_{ij} + C_{ijk} + ... + \varepsilon_{ijk....m} \qquad [2.1]$$

where, $Z_{ijk\cdots m}$ = the value of the $_m$th unit in....the $_k$th class at stage 3, in the $_j$th class at stage 2, and in the $_i$th class at stage 1 and μ = general mean (Webster & Oliver, 1990).

At each stage, the contaminant is assumed to be an independent random variable. The stages are designed so that small classes are subdivided within larger classes. This aims to encapsulate the small scale variability. This approach was first used in the late 1930s (Youden & Mehlich, 1937) and has proven to be an efficient method of sampling (Oliver & Webster, 1986a; Webster & Oliver, 1990; Jackson & Caldwell, 1993; Pettitt & McBratney, 1993; Hunt, 1996). Significantly, an unbalanced nested scheme not only achieves a high spatial resolution but can also determine the main source of variation at the scale of the investigation without the need to replicate samples at all locations (Webster & Boag, 1992; Chappell *et al.*, 1996). The advantage of the unbalanced nested sampling approach is that it can economically determine the spatial structure, pattern of variation and scale of variance in the phenomena under investigation at several orders of magnitude (Oliver, 1984; Webster & Oliver, 1990; Oliver & Webster, 1991; Oliver & Badr, 1995).

The nested sampling design has not previously been applied to the sampling of marine sediments although it has proven to be effective in sampling spatial variability in soil variables in a variety of land based studies (Oliver, 1984; Oliver & Webster, 1986b; Chappell *et al.*, 1996). The aim of the sampling in King's Dock is to determine the local spatial variability of PCBs in the bottom sediments. This is achieved by employing an unbalanced hierarchical sampling design over various stages and distances.

2.2.4 Sample design adopted at King's Dock, Swansea

Sampling conducted in King's Dock consisted of a five stage unbalanced nested sampling design (Oliver & Webster, 1986a; Webster & Oliver, 1990) with separating distances at: 405, 135, 45, 15 and 5 m (Figure 2.14). The increase in distances from 5 m to 405 m is geometric (Oliver & Badr, 1995).

This scheme is implemented as follows. First, the Dock is initially divided into a grid of 5 x 2 sampling stations. These ten stations represent the first sampling stage. At each of the main ten stations, two replicate samples are collected at ~zero distance. The purpose of taking these replicate samples (i.e. repeated sampling at the same site) is to determine the variance within the sample (ie.e to determine the inherent heterogenity of sediments, quality of laboratory analysis, sampling error and PCB distributions over small distances) (see Chapter 4) and to estimate the nugget variance (see Chapter 5). In this study, the shortest distance, 5 m, is dictated by the size of the sampling boat and the accuracy of positioning. At specific sites, sub-samples are also taken to establish within-sample variance. The latter will assist the determination of sampling design accuracy, the quality of analytical methods and PCB concentrations within a specific sediment size.

Second, at each of the ten main stations, samples are taken at distances described above along a random bearing using a random number table or calculator (Oliver & Badr, 1995). If the bearing encounters land or an obstacle, another random bearing is taken. A plan view of the sampling sites produced by the application of this approach to King's Dock is shown in Figure 2.15.

The measurement of sample position is also a source of error. In this study, all samples were located using a Differential Global Positioning System (DGPS), with the antenna mounted in the stern of the boat as close as possible to the grab-sampler operator. To control for the error in position-fixing, positions were also obtained from a shore-based electronic theodolite (ETS) tracking a prism held adjacent to the DGPS antenna. The correspondence between the two sets of co-ordinates was excellent, with a root mean square 'error' of 2.3 m. This is close to the estimated accuracy of the DGPS when operated (as here) with a remote baseline beacon.

All sediment sampling was conducted using a Van Veen grab (Rumohr, 2000). The current methodology for collecting sediments adopted by CEFAS requires the top 1-2 cm of sediment for analysis (MPMMG, 1994). For baseline monitoring, Marcus & Renfrow (1990) recommended sampling the top 0.3 cm of the sediment for PCB analysis. Armstrong *et al.* (1993) collected samples of surface sediments in Lake Michigan at 30 sites and calculated that 55 - 80% of all sedimentary PCB burden was contained in the surface layer (at an average depth of 1.16 cm). For the sampling programme at King's Dock, the top 2 cm of sediment were collected for analysis. All samples were acquired during a four day sampling campaign in 1996.

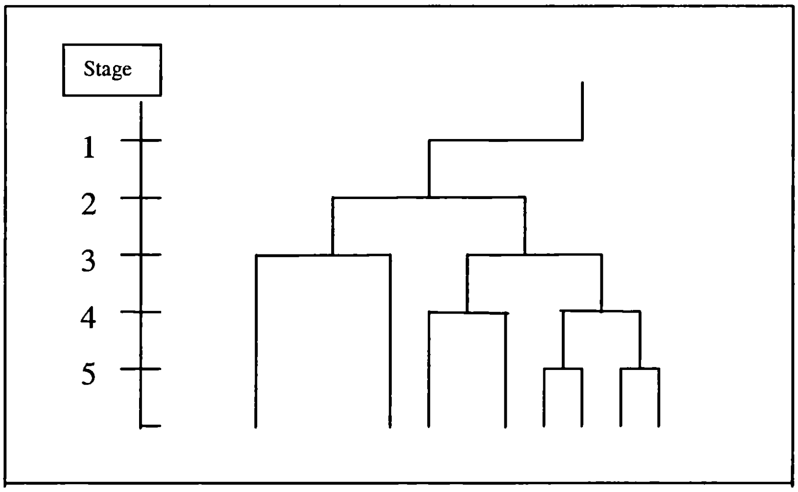


Figure 2.14: Hierarchy of stages for unbalanced nested sampling design for one of the ten stations in King's Dock.

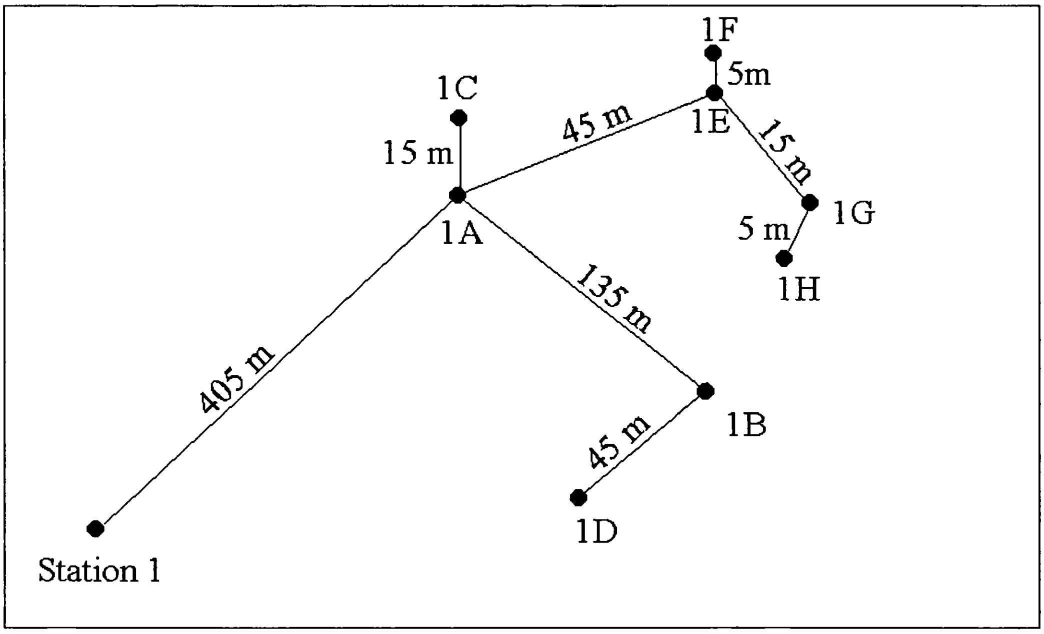


Figure 2.15: Plan view of sampling points for one of the main stations.

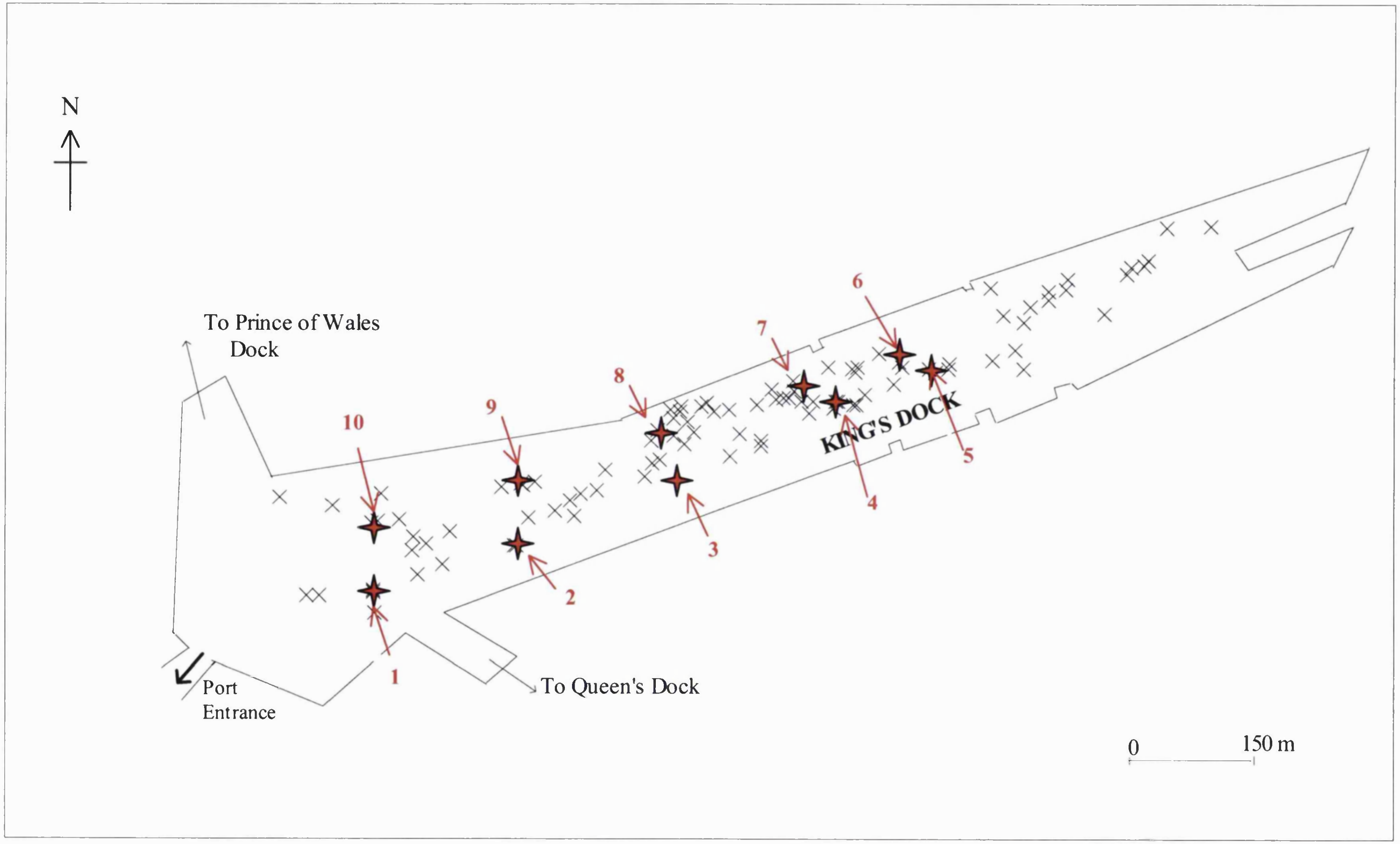


Figure 2.16: Location of sites sampled in King's Dock, Swansea (n=101). Numbers in red symbolise the 10 main sampling stations.

A metal spoon was used to transfer the sediment from the Van Veen grab into a hexane-rinsed 500 g glass jar. Hexane-rinsed foil was placed on top of the jars which were stored in crates and frozen at -19°C. Oliver & Webster (1991) recommended a minimum sample number of 100 samples for the calculation of the sample variogram. In this study, 101 sediment samples were analysed for $\sum_{25}$CBs (see Figure 2.16 for locations); these include subsamples and repeated samples at a site so that small scale spatial variability is considered in the data analysis.

2.2.5 Analytical procedures

The analytical procedures employed in this study include the extraction and analysis of PCBs, determination of sediment particle size and the estimation of the total organic content of the sediments. These procedures are summarised briefly below.

Several techniques for the extraction, clean up (removal of particles and other interfering compounds) and analysis of sediments for environmental PCBs are well documented (see, for example, Smedes & de Boer, 1998; Donnelly *et al.*, 1996; Gardinali *et al.*, 1996). The method used here (and described in detail in Appendix 3) has proven reproducibility and is known to achieve excellent recoveries (Allchin *et al.*, 1989). It has been developed, and tested in inter-laboratory tests, as part of QUASIMEME, an EU Standards, Measurements and Testing initiative, to improve the measurement of chlorobiphenyls in marine sediments (Cofino & Wells, 1994; Megginson *et al.*, 1994; de Boer & Wells, 1996; de Boer *et al.*, 1997; de Boer & Wells, 1997). Significantly, this methodology has been used for all routine sediment PCB analyses undertaken in England and Wales since 1990. It is, therefore, the most appropriate for a study such as this which seeks not to develop new analytical techniques, but to improve the sampling basis of existing monitoring protocols.

A graphical summary of the sample preparation, extraction and analysis is given in Figure 2.17. Prior to analysis, sediment samples were homogenised and dried, and a 10 g subsample was added to 25 g anhydrous sodium sulphate. The sediment was placed in a Soxhlet extraction apparatus and 60 ml acetone and hexane (1:1) was added. The sediment was extracted for 6½ hours and a 100 ml extract was retained and concentrated to 1 ml. A clean-up method using gravimetric column chromotography with alumina was performed on the extract and the first fraction retained. A further clean-up procedure using gravimetric column chromatography with silica gel was performed and again the first fraction was retained. The extract was concentrated and transferred to a gas chromatography – electron capture detector (GC-ECD) for analysis.

Particle size is an important supporting parameter in contaminant studies since the size of particles (especially the silt and clay sized fractions) determines the number of binding sites for chemicals (Turki, 1998). This can significantly influence the degree of sorption, and can be a major factor causing non-uniform distributions of sorbed pollutants within sediments (Ab Razak & Christensen, 1996). Particle size was determined for all the King's Dock samples using standard wet and dry sieving procedures (CEFAS, 1996). Sediments were initially wet sieved and the < >63 μm fractions retained. Each fraction was subsequently oven dried and dry sieved to determine the percentage of sediments retained in each fraction. The most useful summary measure derived from these procedures is the percentage of particles < 63 μm. This sand-silt boundary is important because sediments containing the largest fractions of grains < 63 μm are typically associated with the highest contaminant concentrations (Boon *et al.*, 1985).

Total organic content (TOC) is used here as an indicator of sediment organic matter content. The latter can also strongly influence the concentration of contaminants associated with the sediment. Karickhoff *et al.* (1979), for example, observed a high correlation between levels of organic pesticides and the organic matter content in soil samples. Standardising PCB concentrations to TOC or particle size is common, and is routinely used in the studies of marine sediments (see, for example, Knickmeyer & Steinhart, 1989; Lohse, 1991).

TOC was determined for the King's Dock samples by a standard loss on ignition technique (Gross, 1971). This utilised subsamples of sediment (100 g w/w) which were allowed to air dry at room temperature. The sample was then ground and passed through a 200 μm sieve. After sieving, a 20 g subsample was dried at 110°C for 8 hours to removal interstitial moisture. Subsequently, a subsample (10 g) was placed into a muffle furnace and heated at 550 °C for 4 hours. After cooling to room temperature, weight loss was calculated as a percentage of initial sample weight. This is a crude technique (Gross, 1971) and is employed here because financial resources were limited. Another method, such as titration, is preferable (Van Iperen & Helder, 1985). The laboratory analysis of all variables (PCBs, TOC and particle size analysis) for 100 sediment samples is very labour intensive and expensive, both in staff time and in the equipment/consumables required to conduct the analysis.

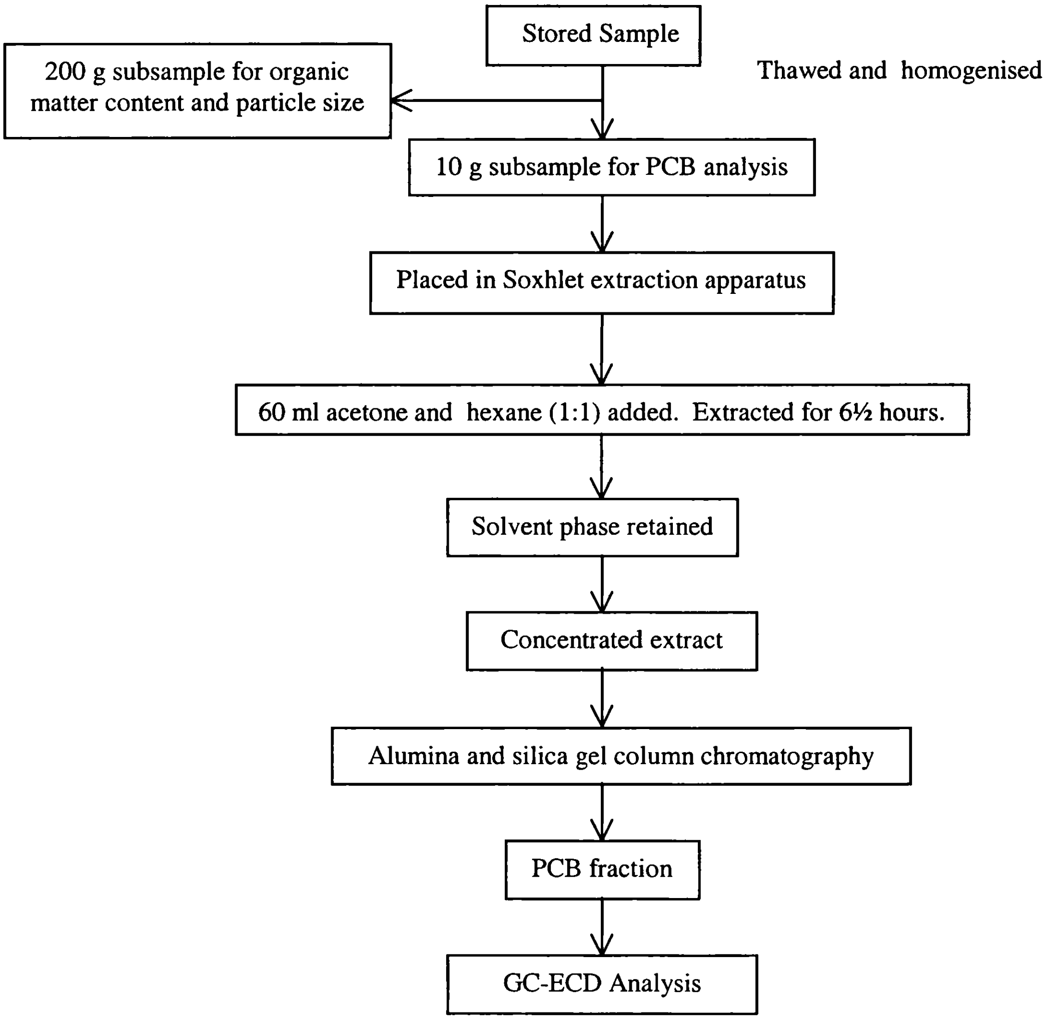


Figure 2.17: Flow diagram of sediment PCB analysis.

The PCB method has been adopted in the extensive sampling approaches and all methods have been used in the intensive study. The extensive approach is aimed at critically evaluating existing sediment PCB information collected under the UK NMMP, and examines a number of issues concerning the robustness of the underlying sampling and measurement procedures. The extensive study is used to identify regional geographical patterns in sediment PCB levels and to identify systematic differences in both concentration and chemical composition between selected depositional environments and locations. The more intensive approach is used to identify important scales of within-site variability in sediment PCBs, as a means of inferring the controls on their dynamics and fate, and also to provide a basis for improving current sampling procedures. Importantly, both datasets are comparable because the method used to determine the PCB content of sediments and dredged material has remained unchanged since 1990.

CHAPTER THREE

Evaluation of PCB Concentrations in Marine Sediments and Dredged Material around England and Wales between 1990 and 1999

The spatial distribution and temporal patterns of PCBs in marine sediments, sampled under the National Marine Monitoring Programme, and in dredged material under the Food and Environment Protection Act (1985), have been established at various sites around England and Wales. This geographically extensive study shows that PCB concentrations in offshore marine sediments are low, with the exception of some sites close to disposal grounds or near to known point sources. Estuarine sediments exhibit low concentrations of PCBs, but there are a number of localities where concentrations are high and seem to have increased in recent years. In particular, sediments sampled in some dockyards, subject to dredging, are grossly contaminated.

3 Introduction

Although PCBs were banned in the UK over two decades ago and their subsequent use restricted, their persistence and potential toxicity means that they can still remain a hazard in the marine environment. Indeed, redistribution of PCBs by natural and anthropogenic processes has caused these compounds to become a widespread pollution problem (Kennish, 1994). There is, therefore, a clear need for further research to determine the nature and extent of this problem in the seas and estuaries around England and Wales. The extensive data acquired through monitoring by CEFAS are here collated and evaluated in order to determine the distribution of PCBs in offshore and estuarine environments.

In this chapter, data describing the contemporary concentrations, environmental and spatial distribution and temporal patterns of PCBs in marine sediments and dredged material in England and Wales are analysed both qualitatively and quantitatively. The analysis covers the period from 1990 to 1999. Specific components of these analyses, for both surficial marine sediments and dredged material include the:

1. estimation of average concentrations to establish whether a typical background concentration can be defined for comparison with other published work;
2. determination of any change in PCB concentrations since 1990;
3. characterisation of the magnitude, spatial distribution and environmental variability of PCB concentrations; and
4. comparison of congener profiles in sediments and dredged material with those found in commercial Aroclor® mixtures.

Due to the large amount of samples involved (n = 1,361), the data have been organised into a number of geographic regions. Within each region, the data are further separated into type sites: offshore marine sediments; estuarine sediments; and inner and outer dredged material sites. Selected sites are presented to determine any similarities between locations. The later stages of the analysis (3 and 4 above) use principal component analysis (Flury & Riedwyl, 1988; Manly, 1995) and require the regional marine sediment and dredged material data sets to be combined. The total sum of 25 CBs is denoted either by Σ_{25}CBs or by the term 'concentrations'.

3.1 PCB concentrations in marine & estuarine sediments: 1990 - 1999

Since 1990, monitoring of estuarine and marine sediments in England and Wales has been conducted under the NMMP. Sediments have been sampled over several years, although not necessarily at the same sites or over consecutive years. Monitoring sites are located offshore and at the mouth of major estuaries (Figure 3.1). The whole data set includes a total of 439 samples collected between 1990 and 1999. For the present analysis, the location of sites sampled under NMMP has been subdivided into regions around England and Wales. These regions are defined as follows: North Sea, English Channel, Celtic Sea, Bristol Channel and Irish Sea. Within each region, the data have been further separated into two site types: offshore sediments (blue sample sites) and estuarine sediments (red sample sites). Separation of data into regions may aid the identification of general spatial patterns and temporal trends (Sayer, 1992) and may help link some of the estuarine sites with their potential sources of contamination.

From this extensive data set (n=439), a space-time average concentration can be calculated for all estuarine and marine sediments. This value is 18 ± 73 μg kg^{-1} (±1 standard deviation). If, however, the data set is dissaggregated into offshore marine sites and inshore estuarine sites, the average concentration in offshore sediments (n=307) is 2.02 ± 6.2 μg kg^{-1} and in estuarine sediments (n=132) is 53.6 ± 126 μg kg^{-1}. This indicates that estuarine sites have higher but also more variable PCB levels. Sampling issues are thus likely to be particularly important in these areas.

Median concentrations and a measure of the variability around this value (half of the difference between the 25th and 75th percentiles) over time in offshore and estuarine surface sediments within each region are presented in Table A4.1 (see Appendix 4) and Figure 3.2 and 3.3. Presented in this way, it is evident that the mean PCB concentration in offshore sediments is influenced by one or two sites containing high concentrations. A more representative concentration typically found in offshore sediments is 0.32 μg kg^{-1} (the median value). Median values are accepted as being more representative than the arithmetic mean due to the high PCB values which skew the data. Summary statistics at this stage are best shown as frequency charts (see Figures 3.2 and 3.3) rather than box and whisker plots because additional information, such as the national mean and median of estuarine and offshore sediments, are presented. In estuarine sediments, there are a number of sites which exhibit elevated levels offshore (e.g. the Tyne and Cardiff Bay). Again, high levels at some sites in the coastal zone produce a skewed distribution and the median of 12 μg kg^{-1} better represents the space-time average concentration in estuarine sediments.

Where repeat sampling was undertaken at a site, the change (%) in concentrations over time is presented in Table A4.1 (see Appendix 4). Over the period of NMMP (1990-1999), not all the monitoring programmes have been coordinated or consistent in terms of the spatial information they provide. Although concentrations of some contaminants are high, as will be shown, it is particularly difficult to establish changes over time. As several of these sites are not sampled exactly at the same location, it is possible that these profiles do not represent changes in time but within-site variability. Due to the limited repeat sampling, and errors associated with this, these changes may not reveal any additional information at this stage. These examples illustrate that spatial variability at a site may be very important thus supporting the need for further local scale investigations (see Chapters 4 and 5).

The spatial distribution and variability of PCBs in all regions around England and Wales has thus been determined. In offshore sediments, for example, concentrations appear to have remained low (< 10 μg kg^{-1}) and are often < 2 μg kg^{-1} (Figure 3.2). This is not unexpected, since these sites are located far from industrial and other sources of contamination. Two sites located in the North Sea (near the offshore Tyne Dock dredged material disposal ground) exhibit concentrations which are over an order of magnitude higher (93 and 22 μg kg^{-1}, respectively) than expected in this environment.

In estuarine sediments, concentrations are generally higher than those measured immediately offshore (Figure 3.3) (Table A4.2, Appendix 4). Concentrations in estuarine and offshore sediments sampled under the NMMP have been collated for each individual year to illustrate the intensity of sampling in each year (Figure 3.4). Due to the lack of sediment quality standards in the UK, the concentrations are categorised using the classification defined by Wells *et al.* (1989). These categories are separated into four tiers based on Σ_{25}CBs: Tier 1 is <0.2 ; Tier 2 is 0.2 – 20; Tier 3 is 21 – 100; and Tier 4 is >100 μg kg^{-1} (see Chapter 1). Geographical patterns of concentrations between 1990-1997 are presented in Figure 3.4. No sediments were analysed in 1998 and 1999.

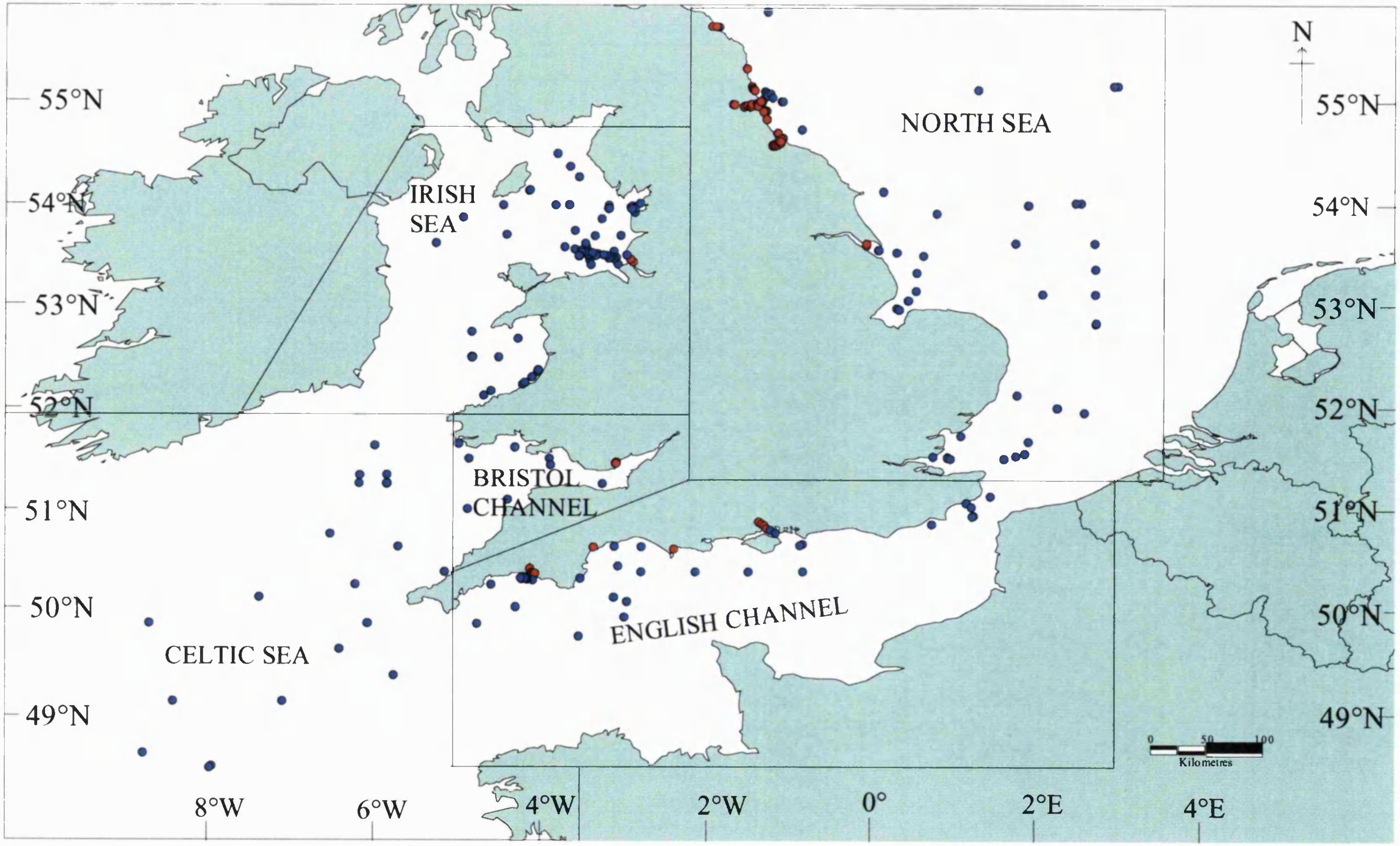
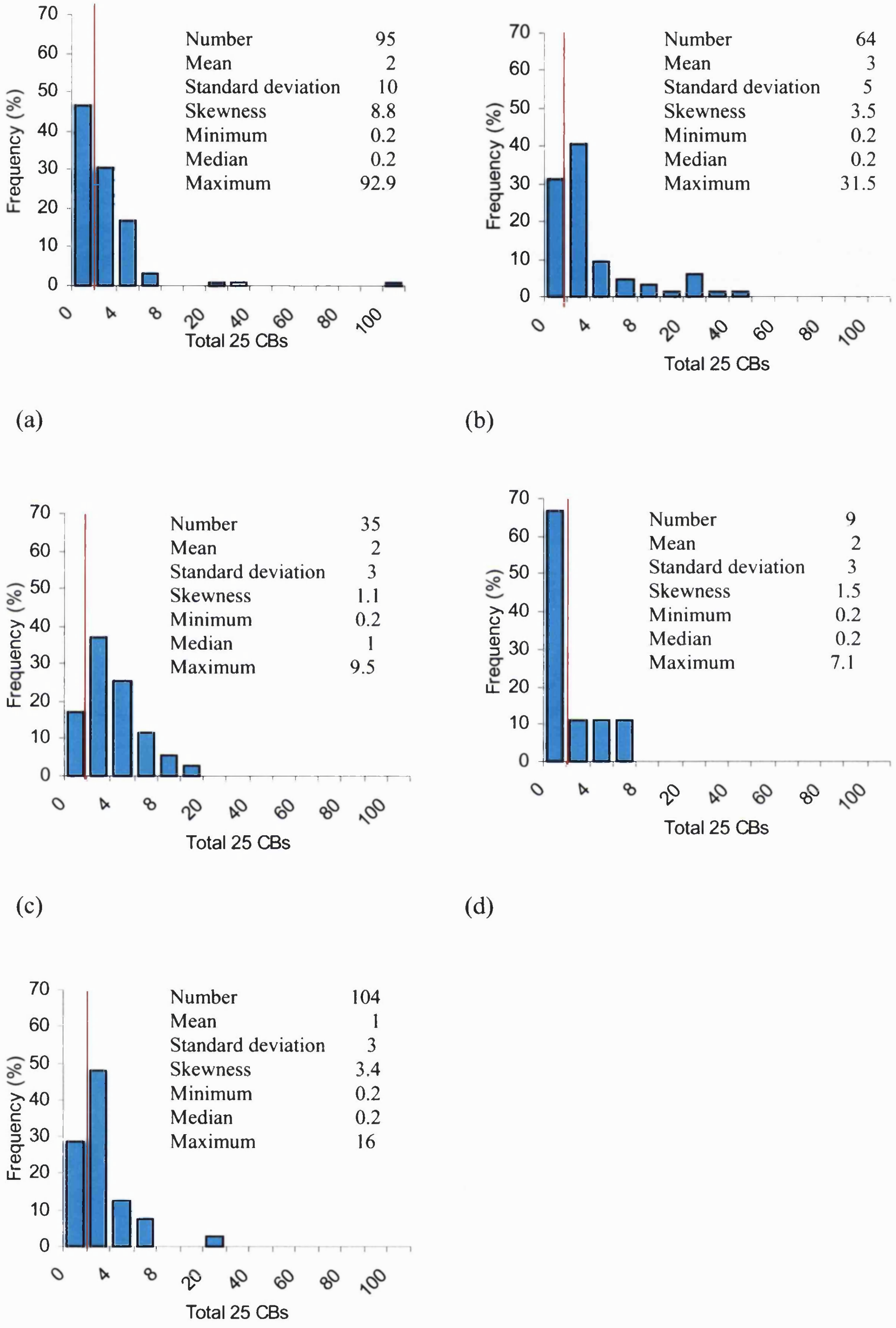


Figure 3.1: Regions in England and Wales sampled under NMMP between 1990 and 1999. Red points are estuarine sediments; blue points are offshore sites.



(a) (b)

(c) (d)

(e)

Figure 3.2: Summary statistics of Σ_{25}CBs (μg kg^{-1}) in offshore sediments between 1990 and 1997 in the: (a) North Sea; (b) English Channel; (c) Celtic Sea; (d) Bristol Channel; and (e) Irish Sea. (Red line represents the national mean of 2 μg kg^{-1}).

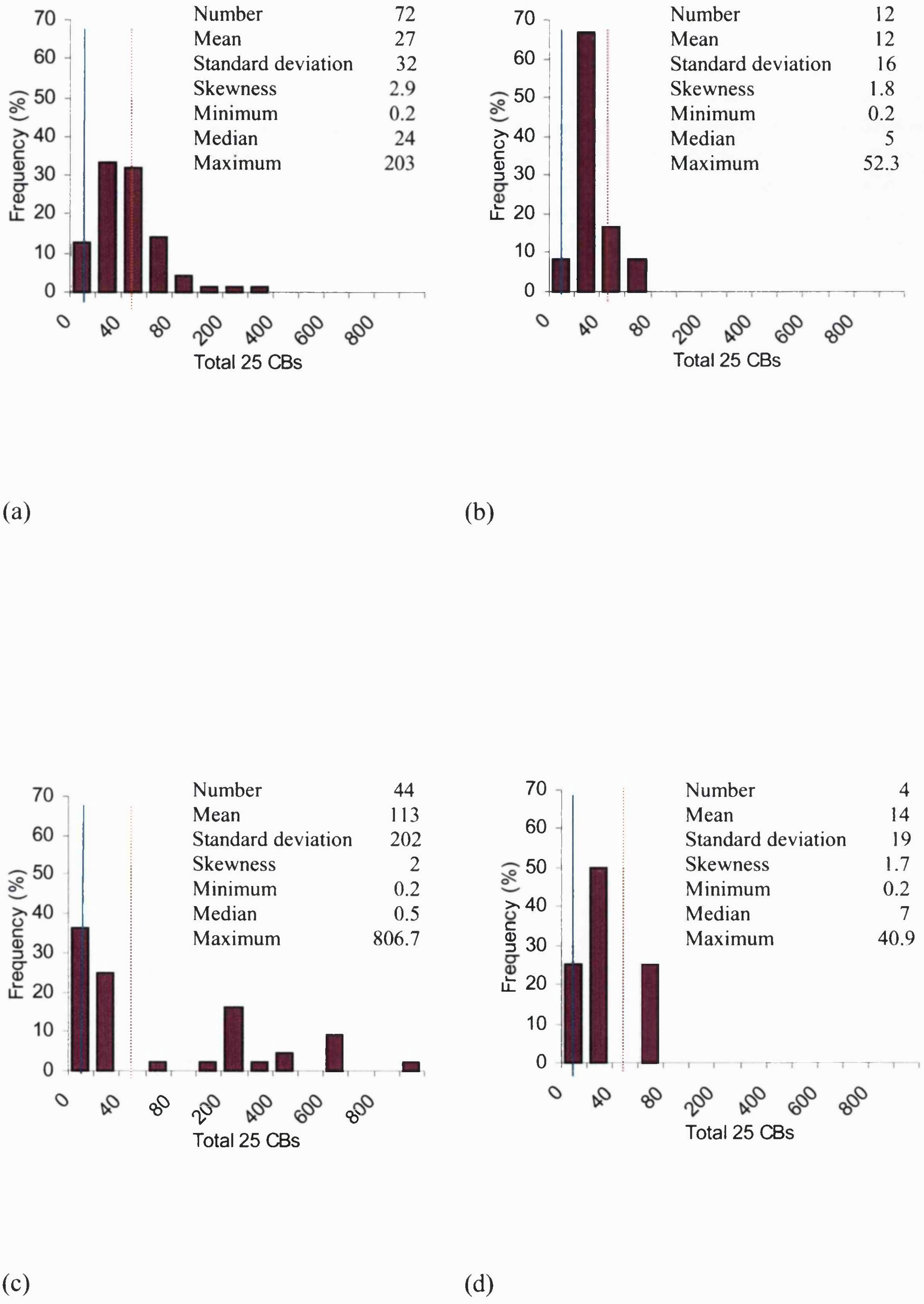


Figure 3.3: Summary statistics of Σ_{25}CBs (μg kg^{-1}) in estuarine sediments between 1990 and 1997 in the: (a) North Sea; (b) English Channel; (c) Bristol Channel; and (d) Irish Sea. (Blue line represents national median of 12 μg kg^{-1}; red dotted line represents the national mean of 54 μg kg^{-1}).

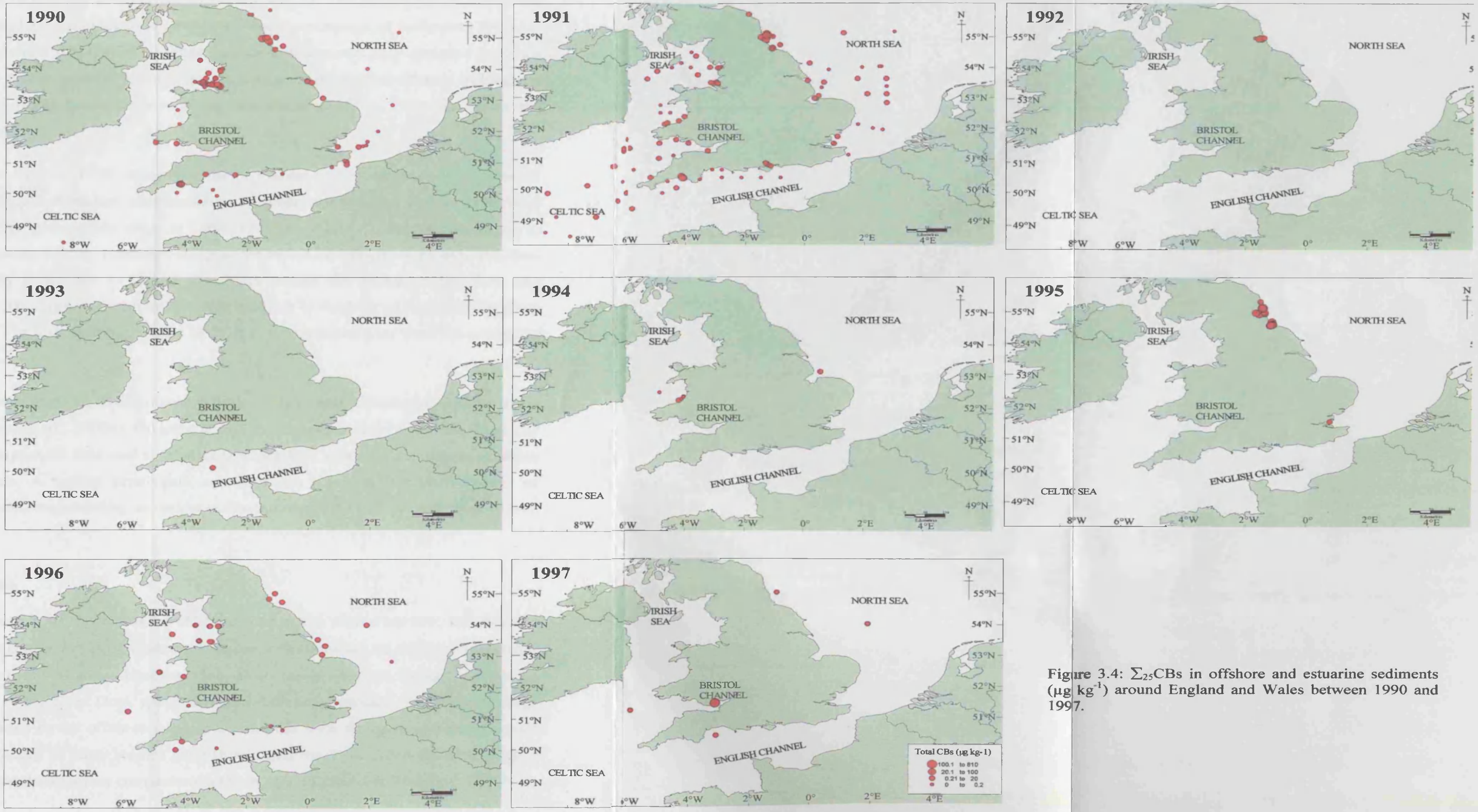


Figure 3.4: Σ_{25}CBs in offshore and estuarine sediments (μg kg^{-1}) around England and Wales between 1990 and 1997.

In general, sediments in offshore and estuarine sites (86%) can be classified as uncontaminated or slightly contaminated (Tiers 1 and 2). The percentage of sediments regarded as contaminated (Tier 3) is 11% and a small percentage of sediments (3%) are heavily contaminated (Tier 4). The latter represent sediments only sampled between 1995 and 1997. Not surprisingly, the large percentage of offshore sediments in England and Wales contain low concentrations or are uncontaminated (i.e. PCBs are below the limit of detection).

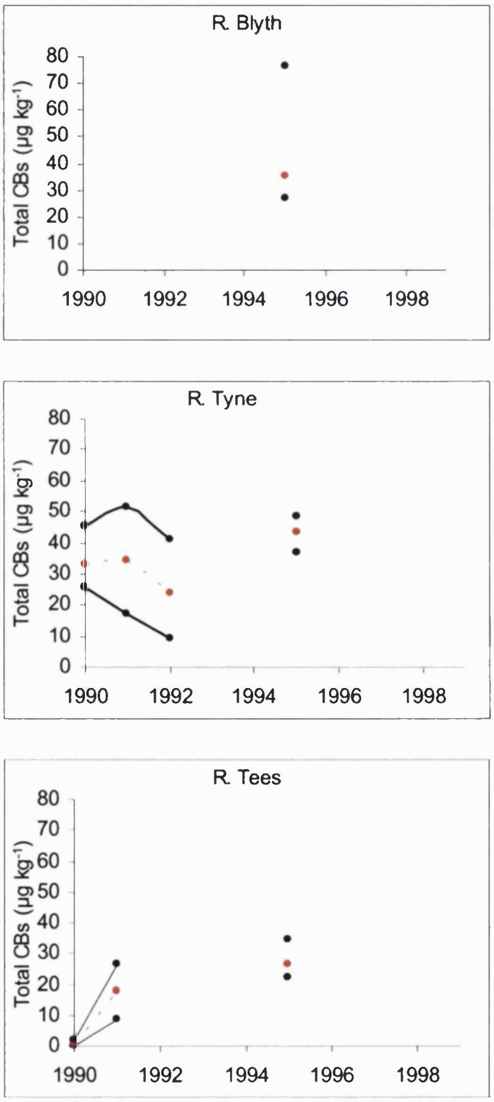
Temporal trends of total PCB concentrations in marine and estuarine sediments at all sites are investigated. Absolute concentrations between sample sites vary considerably as indicated by the interquartile range in Table A4.1 (Appendix 4). This is also shown in selected case studies below. There are no apparent trends and fluctuations over the time period are likely to be due to spatial variability within the estuary rather than any change in time. The biggest problem with this analysis is the lack of repeated sampling year after year. For this reason, changes in PCB concentrations over time are presented in the appendix.

The range of concentrations in sediments in both offshore and estuarine sediments is 0 – 807 μg kg^{-1} (Reed *et al.*, 2000a). Concentrations in offshore sediments do not show any appreciable change over time and a value of 0.32 μg kg^{-1} generally represents offshore marine sediments. A typical benchmark concentration (i.e. concentrations typical of type environments) representing estuarine sediments around England and Wales is 12 μg kg^{-1}.

3.1.1 North Sea

Sediment concentrations at most of the offshore sites in this region are low, between 0 – 6 μg kg^{-1}. There are, however, two sites where concentrations are an order of magnitude higher than the mean offshore concentration. Both these sites are located within the dispersion zone of the Tyne Dock dredged material disposal ground. Such isolated high PCB concentrations so far offshore suggest a link here with dredged material disposal operations, especially as other studies have shown that the Tyne Dock disposal ground is currently accumulating other contaminants (such as TBT; Reed & Waldock, 2000).

To further investigate the spatial distributions of CBs, a number of case studies (Rivers Blyth, Tyne and Tees) are used to establish whether there are any similarities between sites. Fluctuations over time at each site are shown in Figure 3.5. Due to a lack of repeat sampling and low power of sampling effort, changes over time cannot be quantified but may instead suggest spatial variability is high. The analysis of these sites is based upon the identification of homologue profiles. Homologues are chemicals having a similar structure. In the case of PCBs, there are six such homologue groups; tri-, tetra-, penta-, hexa-, hepta- and octa-CBs (World Health Organisation, 1993). Individual CB concentrations are normalised to that of $\sum_{25}$CBs and expressed in terms of percentage abundance. The individual CBs are then summarised as homologue groups. The mean homologue profile (plus one s.d.) for each estuary is presented in Figure 3.6a-c. These profiles attempt to show disparities between site types and regions.



(a)

(b)

(c)

Figure 3.5: Temporal changes in estuaries in North Sea sampled under NMMP between 1990 and 1997; a) Blyth, b) Tyne, c) Tees.

As shown in Figure 3.6, the general sediment profile in the River Blyth has the highest contribution (~40%) from the tri-CBs (mostly CB#31). The profiles in the River Tyne and Tees are different to the Blyth having greater abundance of tetra- and hexa-CBs. A comparison of the cumulative frequencies of homologue groups at specific sampled sites in each of these estuaries is presented in Figure 3.7a-c. This novel approach is effective in that any obvious deviations from the generalised shape and slope of the sediment profiles are easily identified. The NMMP PCB data have never been scrutinised in such a way before. Importantly, additional information far beyond that obtained through conventional compliance monitoring, can be elicited. This may help establish changes to or identify similar sediment profiles at/between sites in response to single or multiple source(s) of contamination and environmental or anthropogenic processes. The contributions and abundance of specific CBs from this analysis may provide evidence of the fate and behaviour of PCBs in coastal and offshore environments.

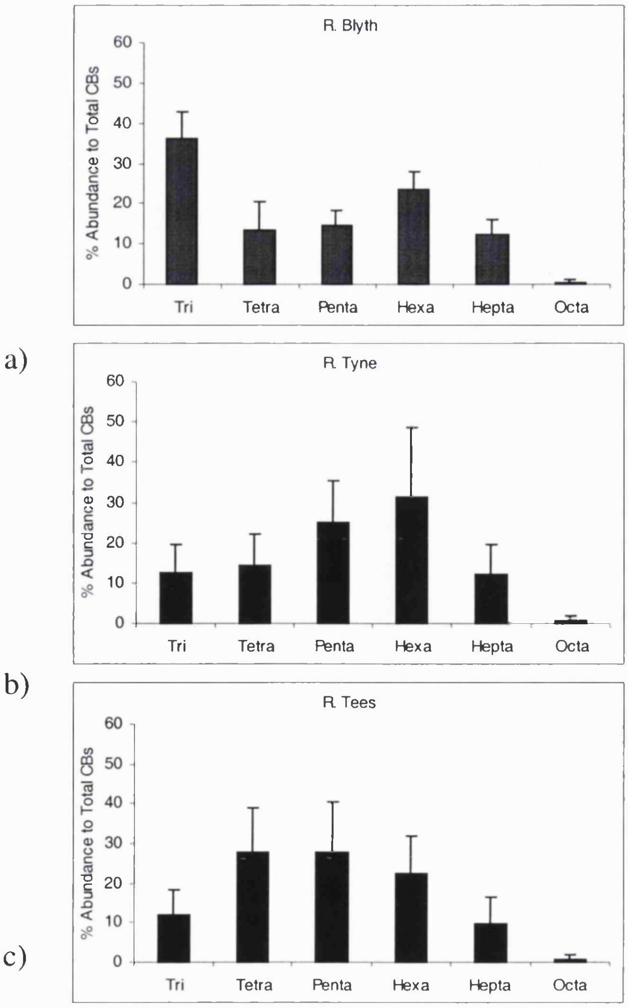
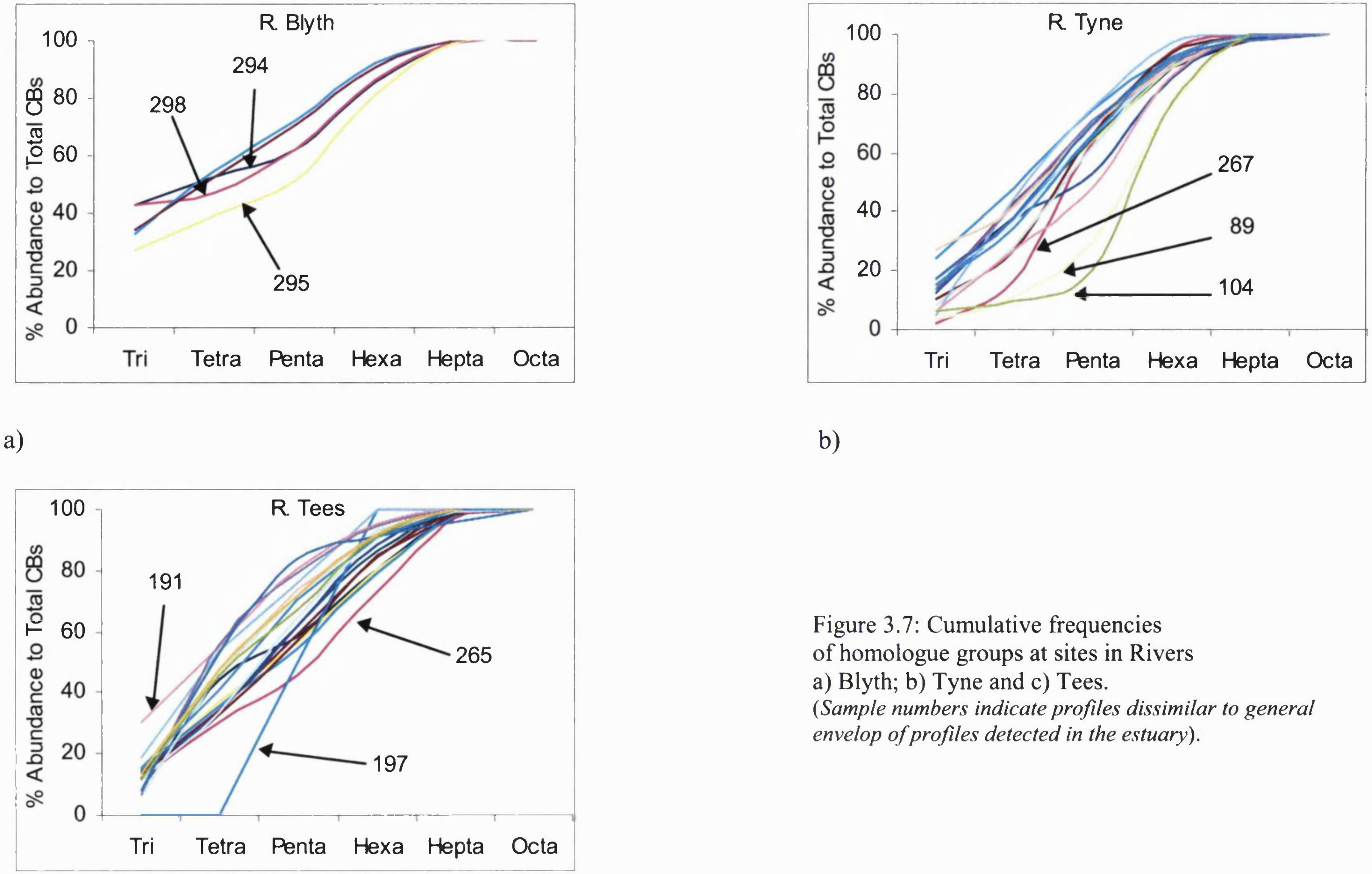


Figure 3.6: Mean homologue profiles (as % of $\sum_{25}$CBs) (± 1 std. dev.) in estuaries in North Sea sampled under NMMP between 1990 and 1997; a) Blyth, b) Tyne, c) Tees.



a)

b)

c)

Figure 3.7: Cumulative frequencies of homologue groups at sites in Rivers a) Blyth; b) Tyne and c) Tees.
(*Sample numbers indicate profiles dissimilar to general envelop of profiles detected in the estuary*).

For example, the cumulative frequencies in Figure 3.7a, are separated into two distinctive profile shapes; those sites located in the inner Blyth estuary (294, 295 and 298) and other sites located in the outer estuary. The inner estuary sites are probably located close to a source, especially as the tri-CBs are generally higher. The outer estuary sediments have reduced tri-CBs possibly due to their greater solubility and shorter half-life in the environment. Also, the contributions from both penta- and hexa-CBs are higher in these offshore sediments and this is probably a consequence of their greater persistence and resistance to degradation compared to the less chlorinated CBs.

In Figures 3.7b, the distribution of profiles at sites in the River Tyne are generally similar, in terms of their overall shape (highest contribution from CB#110), although there are some individual sites that do not fit this pattern. This is also the case in the River Tees. In Figures 3.7c, the River Tees homologue profiles are generally similar to those from the Tyne. Sites where profiles are particularly different are indicated. Sediments located at the mouth of the Tees estuary (Site 191) contain the highest contribution of tri-CBs. As tri-CBs are less resistant to degradation and are generally found at lower concentrations in the outer estuary sites, this site may be a point source.

3.1.2 English Channel

NMMP sediment sampling in the English Channel included sites at Dover, Southampton Water, Isle of Wight, River Hamble, Lyme Bay, Weymouth, River Exe, Plymouth Sound and River Tamar. In general, concentrations are consistently < 2 μg kg^{-1}, although estuarine sediments in Southampton Water and the River Tamar contain higher concentrations (in the range 12 - 54 μg kg^{-1}). Temporal changes since 1990 at sites in the English Channel are shown in Figure 3.8.

In comparison with the North Sea, sampling in this region has been limited. This is particularly evident in the temporal coverage, where many sites have only been sampled once between 1990 and 1999. Due to this extremely infrequent sampling, no temporal trends can be reliably identified in this region. However, it is possible to investigate the spatial distribution and patterns of PCBs in the River Tamar (Figure 3.9a -b).

In general, sediments within the estuary exhibit similar homologue profiles although one site (146) shows particularly different variability in the penta-, hexa- and hepta-CBs. The sediment PCB profile at this site is different in both its shape and overall concentration. Concentrations at this site are lower than other sites in the Tamar.

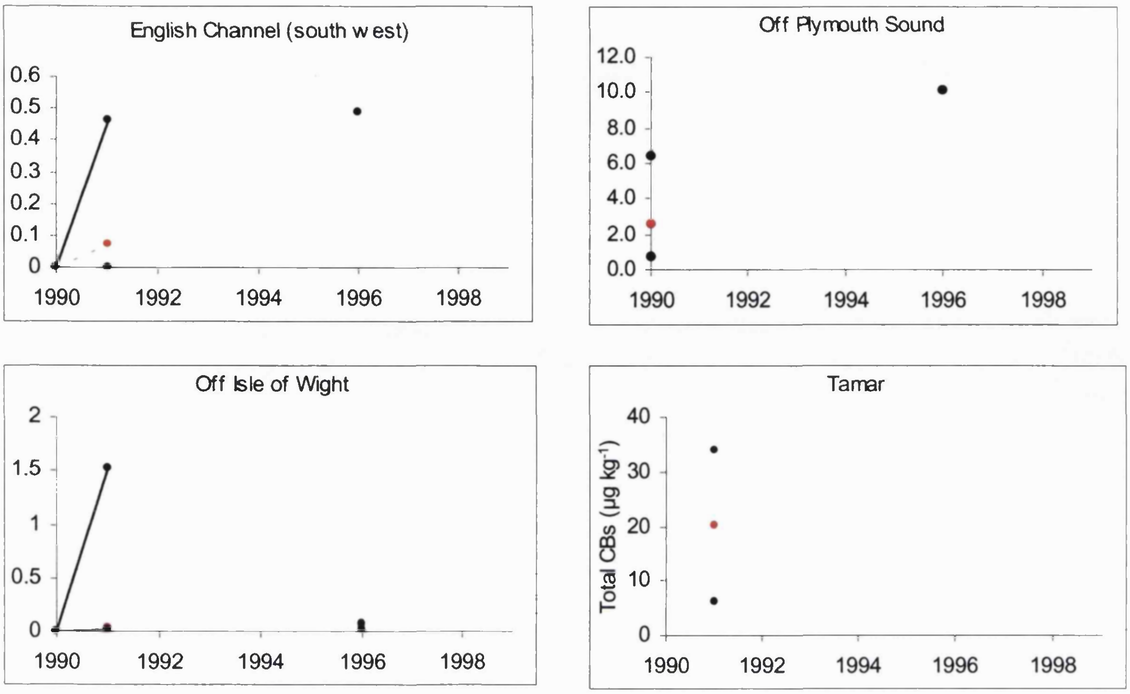
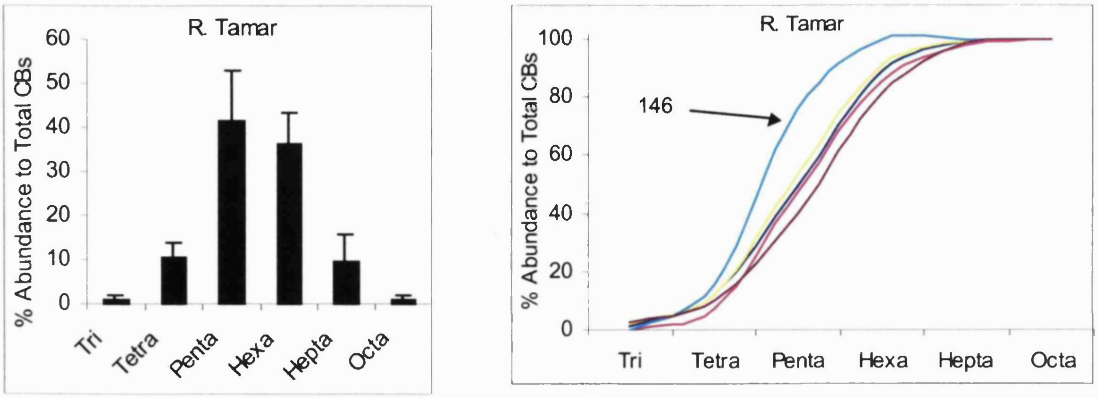


Figure 3.8: Temporal changes in estuaries in English Channel sampled under NMMP between 1990 and 1997.

This site is located furthest offshore, suggesting that sediment PCB profiles are altered by environmental processes as material is moved from the estuary to distances offshore.



a)

b)

Figure 3.9: a) Mean homologue profile (as % of Σ_{25}CBs) in sediments sampled in the River Tamar in 1991. (*Error bars represent 1 standard deviation*); b) Cumulative frequencies of homologue groups in the same sediments.

3.1.3 Celtic Sea

NMMP sampling in offshore sediments has been conducted in the Celtic Sea and Western Approaches between 1990 and 1991 and in the north of the Celtic Sea in 1991, 1996 and 1997. Σ_{25}CB concentrations are < 10 µg kg^{-1} at all sites. The highest concentrations in this region were detected in sediments sampled in the outer Bristol Channel and in the southern area of the Irish Sea. Due to very low concentrations (often close to the detection limit), no further analysis of the homologue groups is possible for this region.

3.1.4 Bristol Channel

Concentrations in offshore sediments in this region are generally < 8 µg kg^{-1}. In 1997, concentrations at a large number of sites in Cardiff Bay were >100 µg kg^{-1} (mean = 113 ± 202 µg kg^{-1}, n = 44). Temporal variations since 1990 in Cardiff Bay are shown in Figure 3.10. Unfortunately, due to the high spatial variability throughout the Bay it is not possible to establish any spatial pattern due to high variability in sediment profiles.

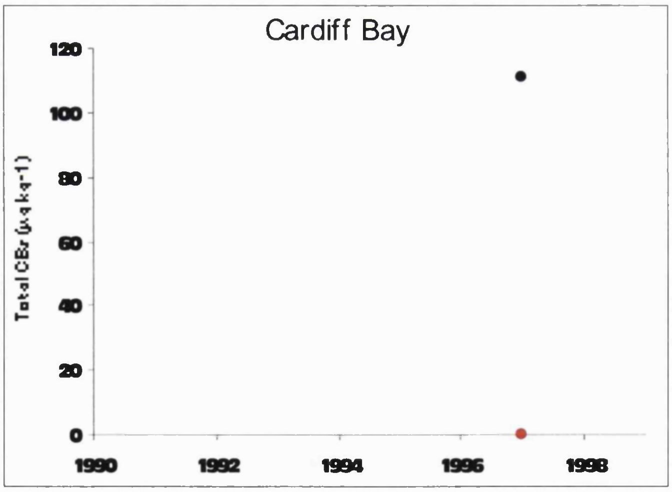


Figure 3.10: Temporal changes in estuaries in Cardiff Bay sampled under NMMP between 1990 and 1997.

Sampling, at this time, was conducted not by NMMP but by the Cardiff Bay Barrage Development Group to investigate contaminant concentrations within the Bay prior to the construction of the Cardiff Bay barrage. The range of concentrations was 0 – 800 µg kg^{-1}. These sediments represented some of the highest concentrations found in bay sediments around England and Wales over the last decade. Such high PCB concentrations were not only measured in surficial sediments, but were also detected in sediments down to a depth of 1m. It is likely that localised mixing of sediments has continued to contaminate sediments in the area.

3.1.5 Irish Sea

Sediments have been sampled in Liverpool Bay, Cardigan Bay and south of the Isle of Man. Sediments sampled offshore contained concentrations < 17 µg kg^{-1} except near Seacombe Ferry in the River Mersey (40 µg kg^{-1}). Temporal changes of PCB concentrations in River Mersey are shown in Figure 3.11. Sampling has been linited throughout the site both temporally and spatially. To investigate any spatial patterns of concentrations in this region, mean homologue profiles from the River Mersey are presented in Figure 3.12.

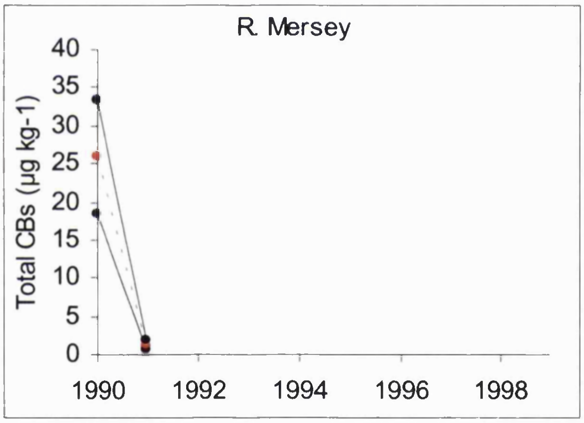


Figure 3.11: Temporal changes in estuaries in River Mersey sampled under NMMP between 1990 and 1997.

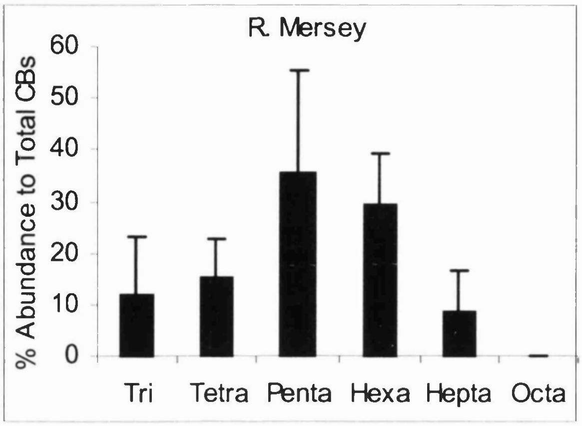


Figure 3.12: Mean homologue groups (as % of Σ_{25}CBs) in sediments sampled in River Mersey. (*Error bars represent 1 standard deviation*).

In this example, the high standard deviation around the mean in each group suggests that there is particularly high spatial variability within the estuary. This may be due to the limited number of samples (*n* = 3) collected under NMMP which may not be representative of the site. There are not enough samples to compare homologue profiles adequately, although it is significant that there are a number of homologue groups (tri-, hepta- and octa-CBs) that are not present in offshore sediments. Tri-CBs have previously been shown to be less abundant offshore, possibly due to their solubility and greater bioavailability to biota. Several sites have shown similar patterns offshore.

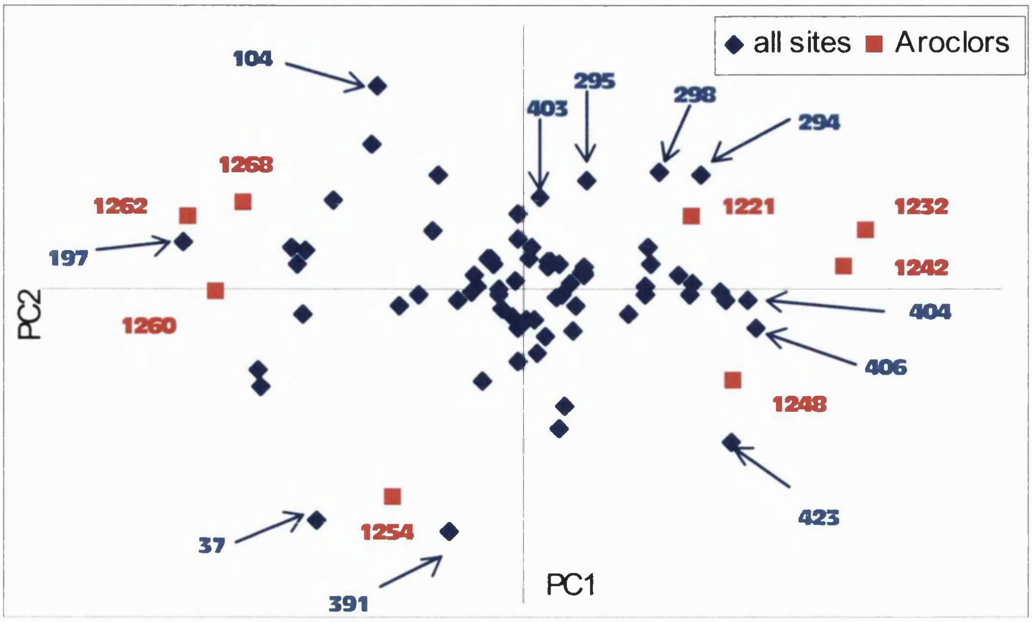
3.1.6 Comparison of sediment CB profiles under NMMP

So far in this analysis, it has been possible to establish broad geographical and spatial patterns of PCBs at sites around England and Wales. The high spatial variability identified within estuaries is a problem and one which requires further investigation. To this end, the homologue profiles in sediments at all sites described above are analysed to determine any similarities between homologue profiles in sediments. This analysis includes a comparison of sediment profiles with those of commercial Aroclor® mixtures (that is, Aroclor® 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268). In the past, PCBs were compared with commercial mixtures as a means of measuring concentrations in environmental samples (MAFF, 1987; Borlakoglu *et al.*, 1990). Although there are difficulties with such a comparison, similarities between congeners in environmental samples can be identified and can prove to be informative, identifying possible point source(s) of contamination (Brown *et al.*, 1987; Brown & Wagner, 1990; Butcher & Garvey, 1999). Similarities between homologue profiles in sediments and homologue profiles of a specific Aroclor® mixture is here conducted by principal component analysis (Manly, 1995).

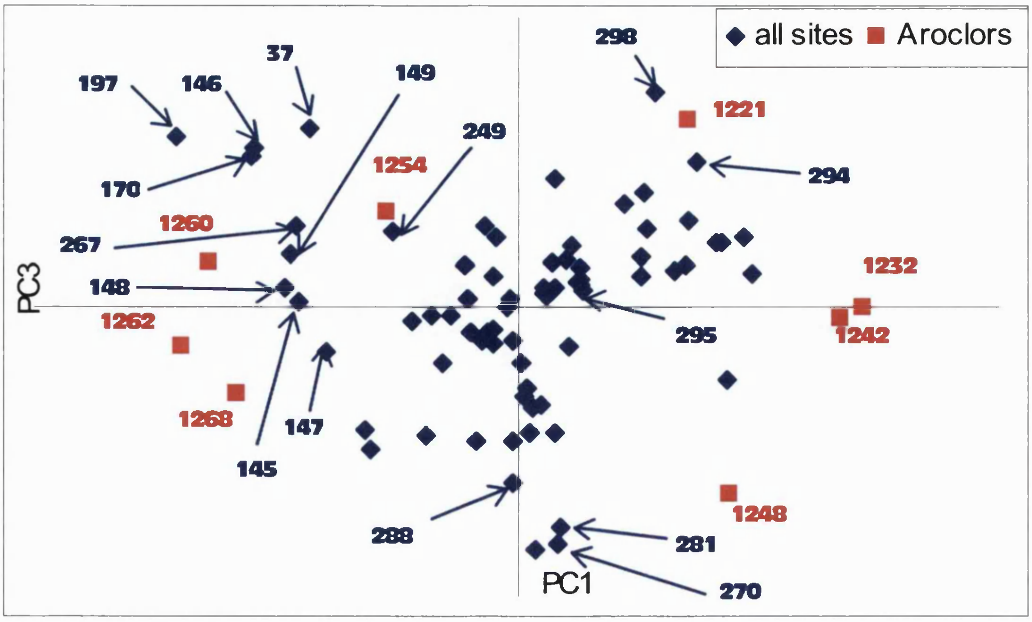
Principal component analysis reduces the number of variables being considered to a small number of indices (known as the principal components) that are linear combinations of the original variables. This technique has been proven to be effective in environmental studies of this nature (Zitko, 1994). The first two or three principal components provide a good summary of all the original variables. All data, that is the full 25 congeners, were used in the analysis and the principal component analysis was conducted using Genstat® 5 software package (Genstat 1997). In this case, the principal components, PC 1 and 2 account for 80% of the variation in the sediment homologue profiles ($n = 74$). Plots of PC1 against PC2 and PC1 against PC3 are presented in Figure 3.13 a-b. Most of the variation in PC1 is explained by tri- and penta- CBs. In the case of PC2, most of the variation is explained by hexa- and tetra-CBs, whilst in PC3, the variation is explained by tri-, tetra- and penta-CBs.

In Figure 3.13a and b, the majority of sites are distributed around the origin. There are, however, a few sites that are separated due to various differences in their homologue profiles. The Blyth estuary, for example, is clearly separated by PC1 owing to the high percentage contribution from the tri-CBs. Profiles from sediments in the River Tamar are also separated because these have higher contributions from the more chlorinated CBs. Several sites located in more industrialised estuaries, such as, the River Tees (Figure 3.13a) and the River Tyne (Figure 3.13b) are separated from other sites because of their site specific contaminant histories. The majority of other sites cannot be closely associated with other sites or to a particular Aroclor® mixture or homologue group. Most sites appear to contain a mixture of PCBs from Aroclors 1248, 1254 and 1260, and these mixtures were widely used in England and Wales (Morris, 1995).

To investigate the extent and variability of PCB contamination in the coastal zone, particularly in harbours, docks and marinas, concentrations in dredged material are collated and discussed below.



a)



b)

Figure 3.13: PCA of homologue profiles in marine sediments at selected sites around England and Wales; a) PC1 and PC2; b) PC1 and PC3. N.B. Site numbers are shown in Appendix 2.

3.2 PCB concentrations in dredged material: 1990 - 1999

In industrial areas, harbours, ports, docks, marinas, river channels, estuaries and at other sites along the coastline where dredging is required for navigation and construction, dredged material is routinely sampled and analysed for Σ_{25}CBs before being licensed for sea disposal. Since 1990, dredged material has been sampled under the Food and Environment Protection Act (FEPA) (1985) Part II (see Chapter 2) using specific sampling protocols as specified by the Oslo Commission (Oslo Commission, 1993). As with the NMMP, not every site is sampled annually or in the same location and sampling is often spatially limited (CEFAS, 1997a). The aim of sampling under FEPA is not to determine temporal changes but, rather, to define representative samples over the proposed dredged material site. As such, only the spatial distribution and patterns of concentrations in inner estuaries, marinas, docks, harbours, ports and other industrialised areas along the coastline are investigated.

Since 1990, a total of 922 measured Σ_{25}CBs concentrations have been obtained for dredged material at various sites around England and Wales. For the present analysis, samples taken under FEPA (1985) have been subdivided into regions around England and Wales. These regions include North East England, East England, South England, South Wales and North West England and these are presented in Figure 3.14. Within each region, the data are separated into two areas; outer estuary (light blue circles) and inner estuary (dark blue circles). The inner estuary sites include docks, harbours, marinas, port and river channels. The outer estuary sites include approach channels to docks, sites in the mouth of estuaries and disposal grounds. The purpose for separating the data set is to investigate whether general patterns or trends can be identified in these discrete areas (cf. Sayer, 1992).

Median concentrations and a measure of the variability around this value (half of the difference between the 25th and 75th percentiles) over time in dredged material within each region are presented in Table A4.2 (Appendix 4). Where sampling occurred more than once at a site, the change (%) in concentrations is calculated and is also presented in Table A4.2. Again, this change is attributed to high spatial variability rather than any increase or decrease in concentration over time. Investigations at all sites showed that concentrations have tended to fluctuate showing no significant overall increasing or decreasing trend. The lack of temporal trends and high level of fluctuations in PCB concentration are shown in each case study below. Some sites have consistently elevated median annual total PCB concentrations (such as dockyards in Cardiff, Newport and Swansea and in the outer Usk estuary near Newport). In most cases, the local spatial variability is very high and the spatial resolution limited. The median concentration of 34 $\mu g\ kg^{-1}$ represents typical concentrations in dredged material in England and Wales. The median is used in preference to the mean (85 ± 237 $\mu g\ kg^{-1}$) because of the skewed distribution of concentrations. The range of concentrations in dredged material in the 1990s is 0 – 3500 $\mu g\ kg^{-1}$.

The distribution of $\sum_{25}$CBs in dredged material in outer and inner estuaries of England and Wales is summarised in Figure 3.15 and Figure 3.16. High concentrations at some sites gives cause for concern, especially at sites where dredged material contain concentrations > 100 $\mu g\ kg^{-1}$. Concentrations above this level are regarded as heavily contaminated (Wells *et al.*, 1989) causing harm to benthic communities (MacDonald *et al.*, 2000). Since 1995, the number of sites in this range has increased significantly and they now account for approximately one third of total sites sampled since 1990. Such continuously high concentrations in dredged material over long periods of time is consistent with similar research undertaken in the Firth of Clyde, UK (Kelly & Ball, 1995; Kelly & Campbell, 1995). Elevated concentrations at some sites in England and Wales do not reflect general declining trends found in other countries (Bossi *et al.*, 1992; Laane *et al.*, 1999). This may be due to the different approaches to compliance monitoring, regulation of dredged material disposal and controls on PCB use and destruction adopted by various countries.

Dredged material exhibiting the highest concentrations are measured at sites in the Blyth, Tees, Tyne, Mersey, Orwell, Humber, Swansea, Barry, Cardiff, Newport and Avonmouth. The geographical distributions of Σ_{25}CBs in dredged material between 1990 - 99 are presented in Figure 3.17 a-j. There are a wide range of concentrations both at sites within a region and between regions. The highest concentrations are consistently found in the North East, South Wales and North West. These areas were highly industrialised in the past and have a legacy of contamination spanning many years and in some cases several decades. Today, a large number of dockyards are still operational and, although PCBs have been banned and their use restricted, these areas are still hotspots of contamination due to historical processes, application, use and disposal of PCBs (Proudfoot, pers. comm., 1998). More detailed analyses of concentrations in dredged material at various sites within each region are presented below.

3.2.1 North East England

Sampling has been conducted at sites in dockyards in the estuaries of the Blyth, Tyne and Tees. Temporal changes at each site are shown in Figure 3.18. Although sampling is limited, an analysis of concentrations over spatial scales is conducted to establish any general patterns or trends at these locations.

In the River Blyth, sampling was conducted in support of dredging in the approach channel to the dockyards. Concentrations in dredged material were typically 35 – 98 μg kg^{-1} except at one site. Here, concentrations were extremely high (512 - 3523 μg kg^{-1}, n = 6). Overall, concentrations are highly variable and the majority of dredged material (~74%) are contaminated whilst just over a quarter of sites are heavily contaminated (> 100 μg kg^{-1}). Highest concentrations were found in the docks but elevated concentrations were also found in the outer Blyth estuary during 1992 and 1995. The wide range of concentrations at sites in both the inner and outer estuaries demonstrate the high variability of concentrations in dredged material. Such concentrations offshore suggest localised contamination in the estuary.

To further investigate the spatial distributions of Σ_{25}CBs, the same approach is adopted here as in Section 3.1 above. Individual CB concentrations are normalised to Σ_{25}CBs and expressed as a percentage abundance. The individual CBs are then summarised into

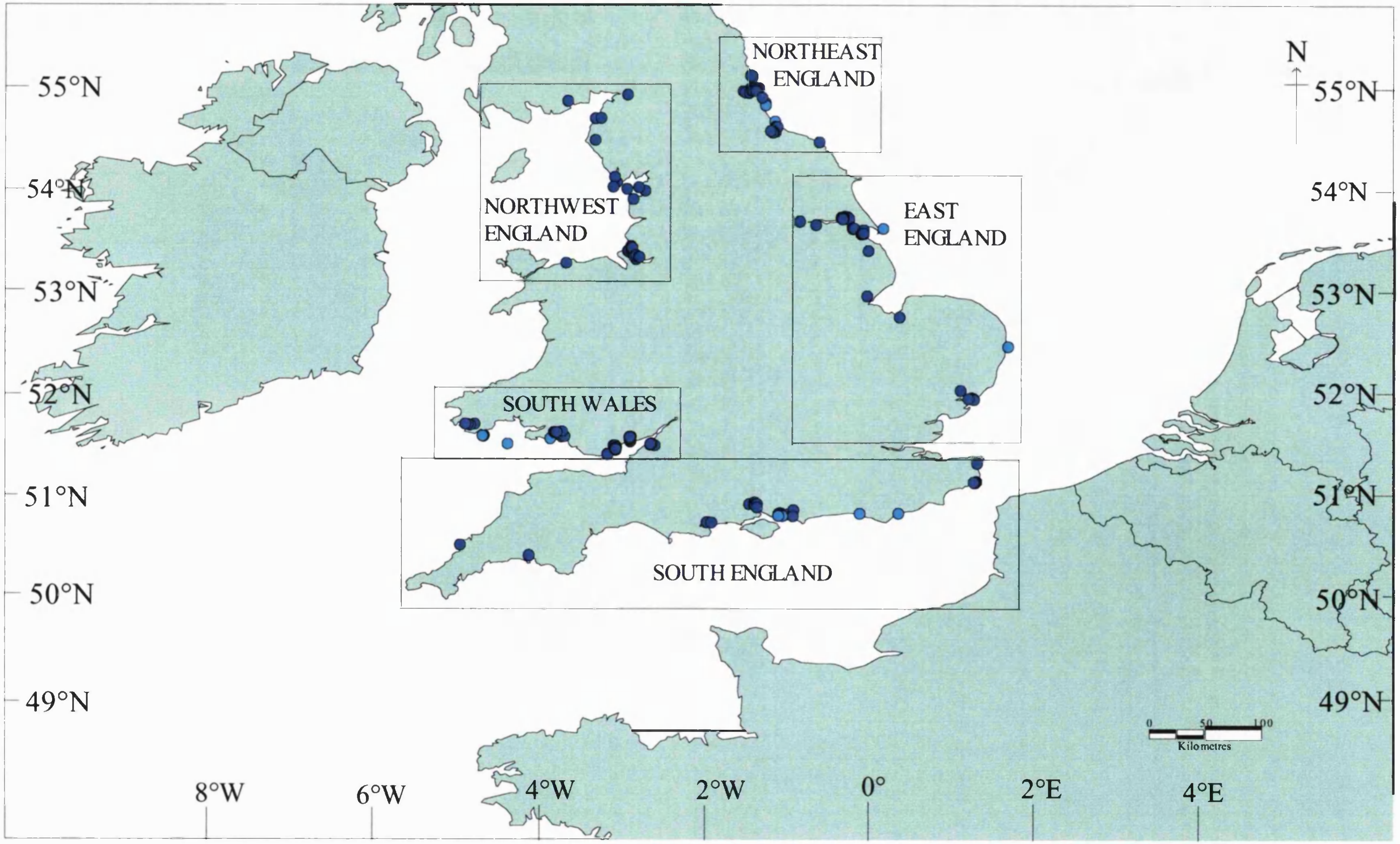


Figure 3.14: Location of regions where dredged material has been sampled around England and Wales under FEPA between 1990 and 1999 (dark blue circles are inner estuary sites; light blue circles are outer estuary sites).

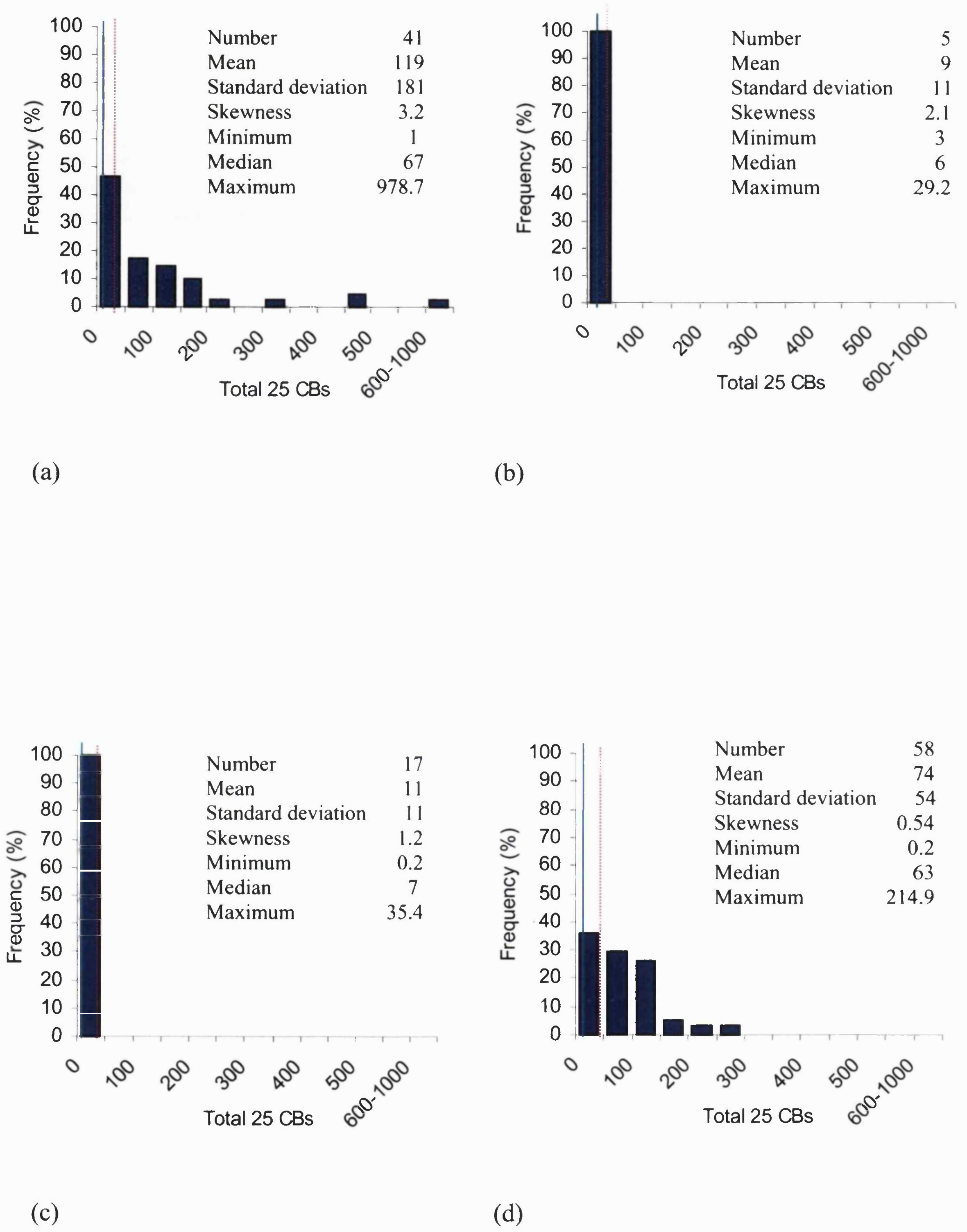


Figure 3.15: Summary statistics of Σ_{25}CBs (µg kg^{-1}) in dredged material between 1990 and 1999 at outer estuary sites in the: (a) North East; (b) East; (c) South; and (d) South Wales. (Blue line represents national median of 34 µg kg^{-1}; red dotted line represents the national mean of 85 µg kg^{-1}).

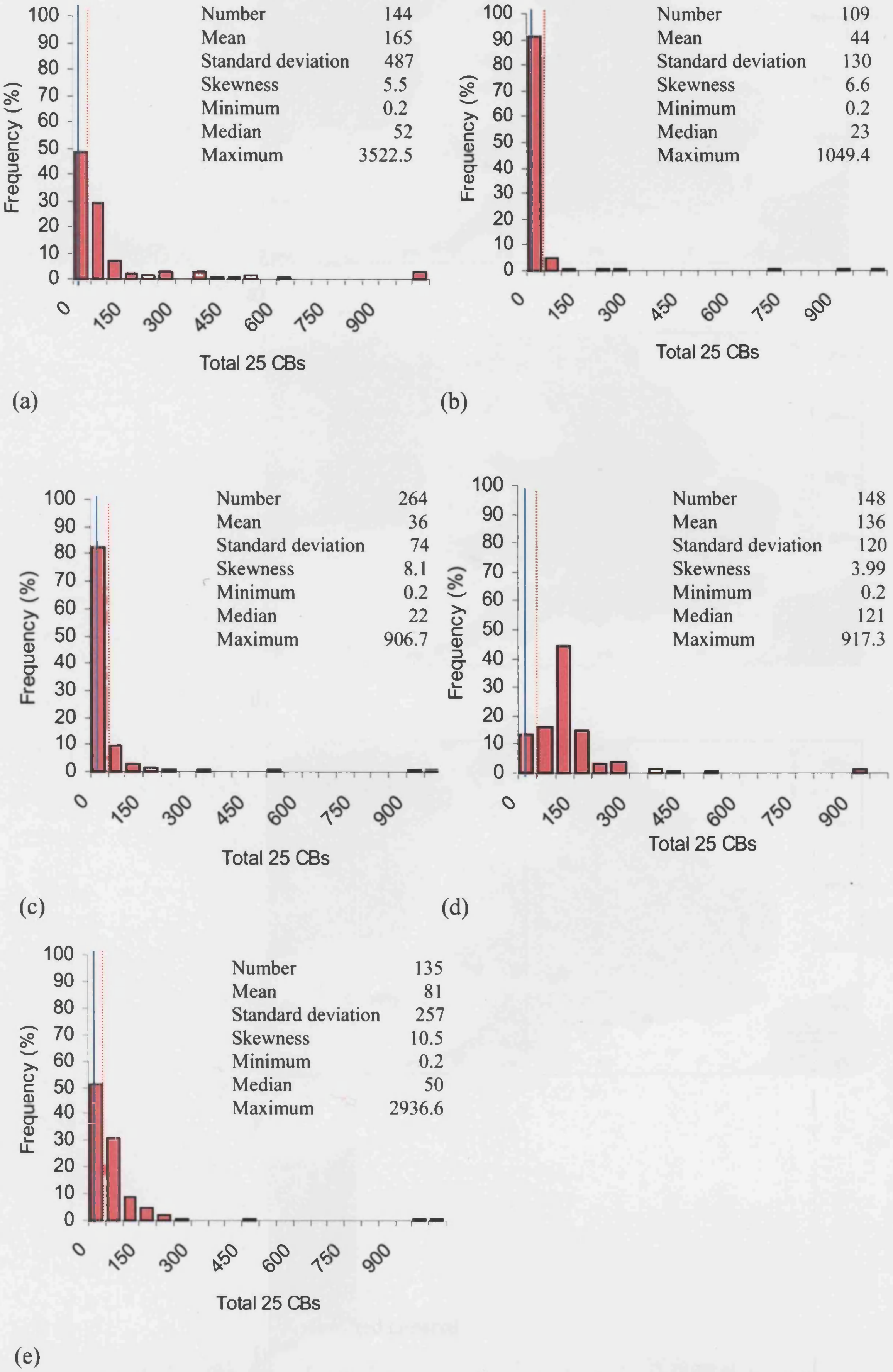
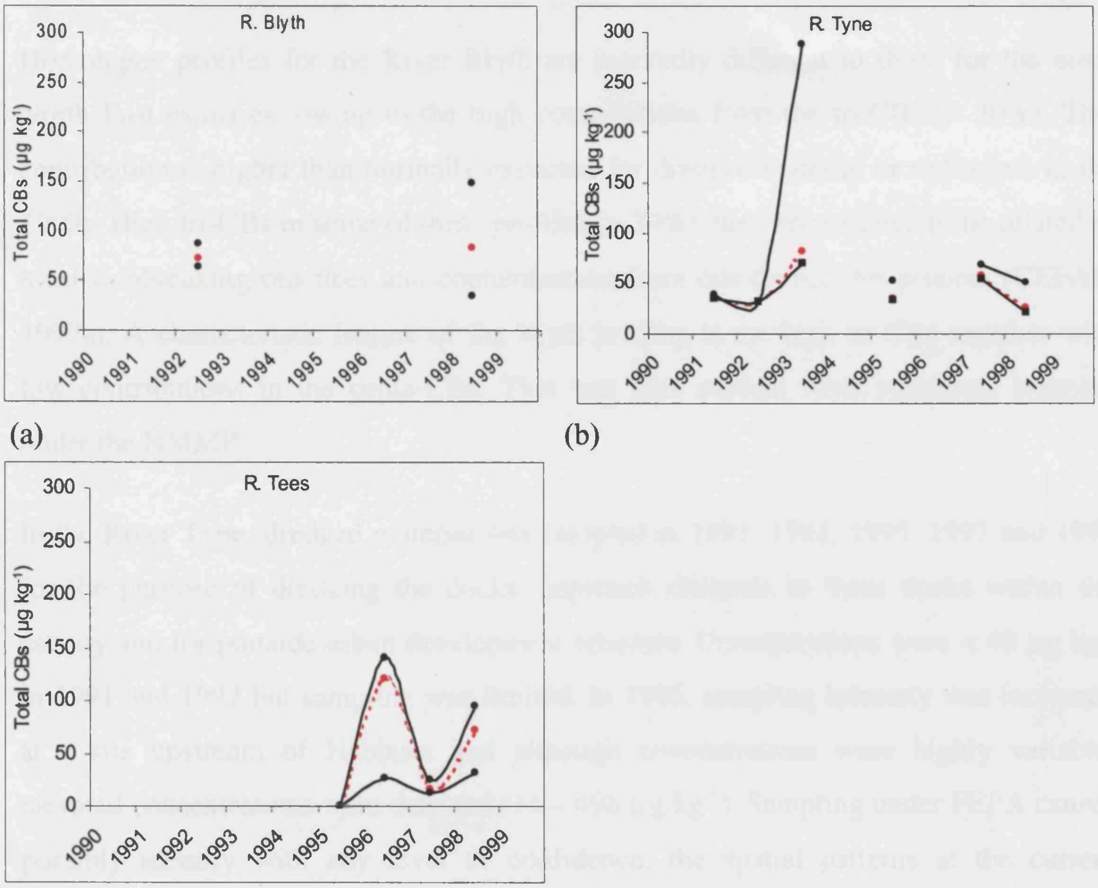


Figure 3.16: Summary statistics of Σ_{25}CBs (µg kg^{-1}) in dredged material between 1990 and 1999 at inner estuary sites in the: (a) North East; (b) East; (c) South; (d) South Wales; and (e) North West England. (Blue line represents national median of 34 µg kg^{-1}; red dotted line represents the national mean of 85 µg kg^{-1}).

Figure 3.17: Geographical and temporal distribution of $\sum_{25}$CBs in dredged material around England and Wales between 1990 and 1999.



(a) (b)

(c)

Figure 3.18: Temporal changes in docks in (a) Blyth, (b) Tyne and (c) Tees sampled under FEPA.

homologue groups (tri-, tetra-, penta-, hexa-, hepta- and octa-CBs) and these are presented in Figure 3.19.

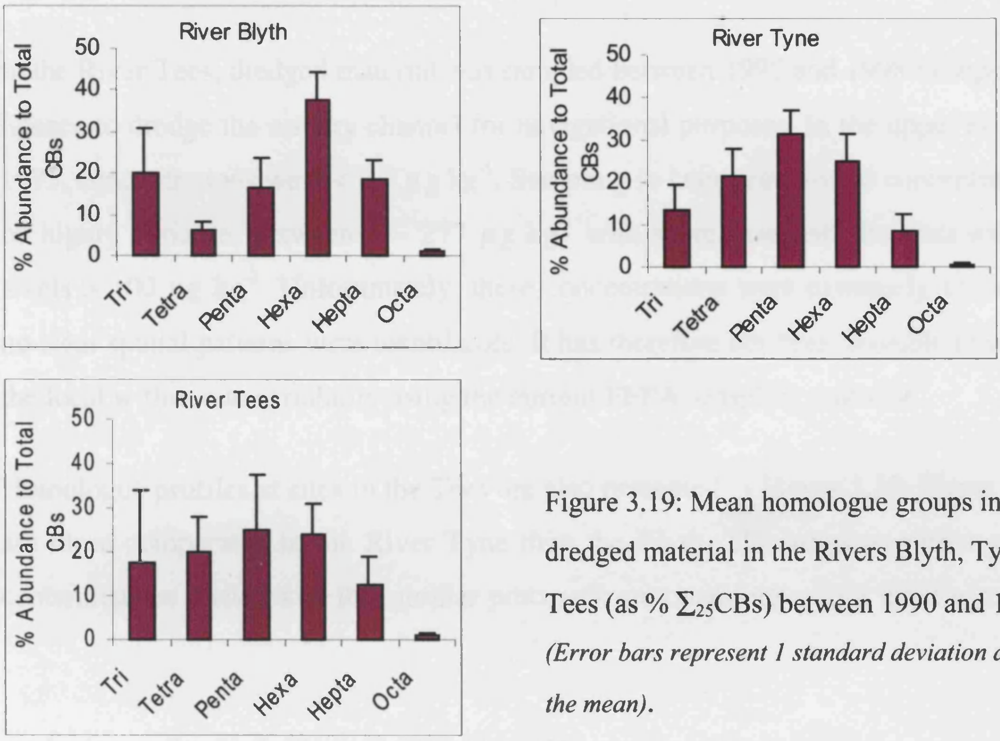


Figure 3.19: Mean homologue groups in dredged material in the Rivers Blyth, Tyne and Tees (as % Σ_{25}CBs) between 1990 and 1999.
(Error bars represent 1 standard deviation around the mean).

Homologue profiles for the River Blyth are markedly different to those for the other North East estuaries, owing to the high contributions from the tri-CBs (> 30%). This contribution is higher than normally expected for dredged material or sediments in the 1990s. High tri-CBs in some of these profiles (> 30%) have been shown to be related to local shipbreaking practices and contamination from oils during this process (CEFAS, 1997a). A characteristic feature of the Blyth profiles is the high tri-CBs together with low contributions in the penta-CBs. This was also evident from sediments sampled under the NMMP.

In the River Tyne, dredged material was sampled in 1991, 1992, 1995, 1997 and 1998 for the purpose of dredging the docks, approach channels to these docks within the estuary and for portside urban development schemes. Concentrations were < 40 μg kg^{-1} in 1991 and 1992 but sampling was limited. In 1995, sampling intensity was increased at a site upstream of Hebburn and although concentrations were highly variable, elevated concentrations were detected (14 – 498 μg kg^{-1}). Sampling under FEPA cannot possibly identify with any level of confidence, the spatial patterns at the current intensity of sampling due to the low power of the current sampling approaches undertaken. FEPA is therefore *under sampling* contaminants at all locations.

Mean homologue profiles in the River Tyne are dissimilar to the River Blyth profiles due to lower contributions from the tri-CBs and higher contributions from the tetra- and penta-CBs. The River Tyne dredged material profiles appear to be similar to the River Tyne profiles sampled under NMMP. This is further investigated in Section 3.4.

In the River Tees, dredged material was sampled between 1995 and 1998 in support of a licence to dredge the estuary channel for navigational purposes. In the upper estuary, in 1995, concentrations were < 0.2 μg kg^{-1}. Sampling in later years found concentrations to be highly variable, between 1 – 277 μg kg^{-1} with more than half the sites exhibiting levels > 100 μg kg^{-1}. Unfortunately, these concentrations were extremely variable and no clear spatial patterns were identifiable. It has therefore not been possible to establish the local within-site variability using the current FEPA sampling protocol.

Homologue profiles at sites in the Tees are also presented in Figure 3.19. These profiles are more comparable to the River Tyne than the Blyth. This suggests either common contamination histories or that similar processes are operating within these estuaries. It has not been possible to identify the source within the estuary or establish local within-site variability.

3.2.2 East England

Dredged material was sampled in the Rivers Humber, Orwell, Stour, Waveney, the Wash and Spurn Head. Sites in the Wash, River Stour and outer estuaries exhibited concentrations averaging 34 ± 20 µg kg^{-1}. More extensive surveys were conducted in the Humber and Orwell and these sites are selected as case studies for this region.

In the River Humber, dredged material was sampled in 1990, 1992-1995 and 1998 in support of dredging required for navigational purposes. Temporal changes of PCB concentrations here are shown in Figure 3.20. In most instances, concentrations are consistently at or below the national median dredged material concentration. However, sampling conducted at a site in the upper estuary sites indicated elevated concentrations (299 µg kg^{-1}) whilst towards the mouth of the Humber, concentrations were lower (0.7 – 45 µg kg^{-1}, *n* = 12). Evidence suggests that sampling to date has also established high spatial variability within the estuary. FEPA sampling has not established the spatial distribution locally or determined possible sources of contamination in the upper estuary.

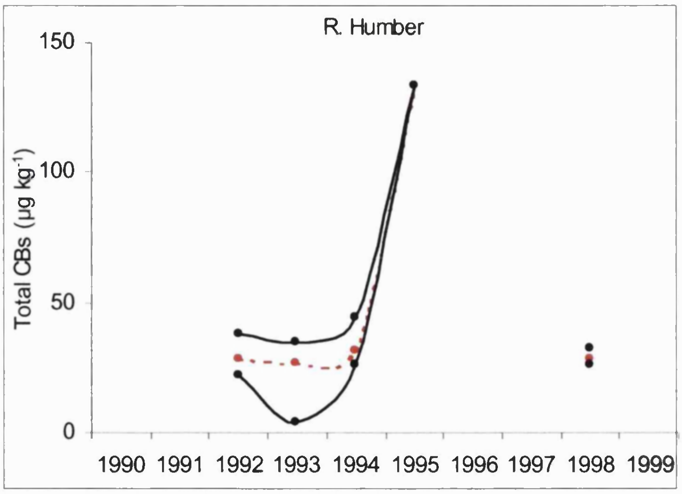


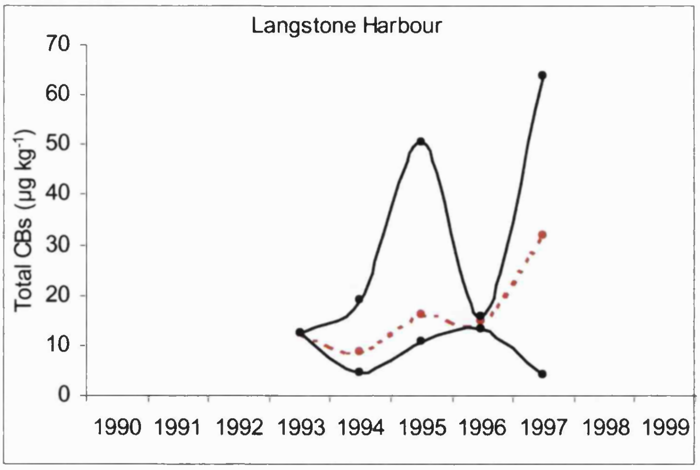
Figure 3.20: Temporal changes in PCB concentrations in River Humber sampled under FEPA.

In the River Orwell, in 1993, dredged material was sampled in the inner estuary in support of a licence to dredge a marina for further development and expansion. Concentrations were highly variable (0 – 1,049 µg kg^{-1}) and further sampling was necessary to established the specific contaminated area. Sampling was conducted at 22 sites making it possible to designate an exclusion zone containing elevated concentrations. These sediments were considered unsuitable for sea disposal and were subsequently transported to landfill. This site is a good example where FEPA, by increasing the sampling intensity, can provide not only representative samples but also establish the local spatial distribution of a contaminant.

3.2.3 South England

Sampling was conducted within the harbour wall at Dover, in the River Stour (Kent), Newhaven, Eastbourne, Chichester harbour, Langstone harbour, the River Hamble, Southampton Water, Solent, Poole, the River Exe, the River Tamar, Gosport, Newquay, Holesbay and at a site off the Manacles. The purpose of dredging here was a combination of dock and harbour developments, deepening approach channels to docks and deepening river channels to improve navigation for large ships. In Dover, the River Stour, Newhaven, Eastbourne, Chichester Harbour, the River Exe, Solent and the inner estuary of the Hamble, concentrations were slightly contaminated (34 ± 14 $\mu g\ kg^{-1}$). However, at sites in the middle Hamble estuary, Southampton Water, Holesbay, Newquay and Gosport, concentrations were slightly higher (13 – 62 $\mu g\ kg^{-1}$). There were several sites exhibiting elevated concentrations and these include, Kimmeridge (34 – 140 $\mu g\ kg^{-1}$), Manacles (124 – 223 $\mu g\ kg^{-1}$) and Poole (0 - 907 $\mu g\ kg^{-1}$). Absolute concentrations within each site varied considerably and spatial variability within the estuary was often high. Concentrations in Langstone Harbour were highly variable and local scale variability is therefore a particular problem. For example, concentrations can be as low as < 15 $\mu g\ kg^{-1}$ at one site whilst at other sites, concentrations can be as high as 183 $\mu g\ kg^{-1}$. Temporal changes in PCB concentrations at various sites in this area are shown in Figure 3.21.

Mean homologue profiles at sites in Langstone Harbour, Poole, Plymouth, Southampton Water, and the Solent are presented in Figure 3.22. These profiles typically have high penta- and hexa-CBs and low tri-, tetra-, hepta- and octa-CBs. This suggests that a similar commercial mixture of PCBs was used historically in this region.



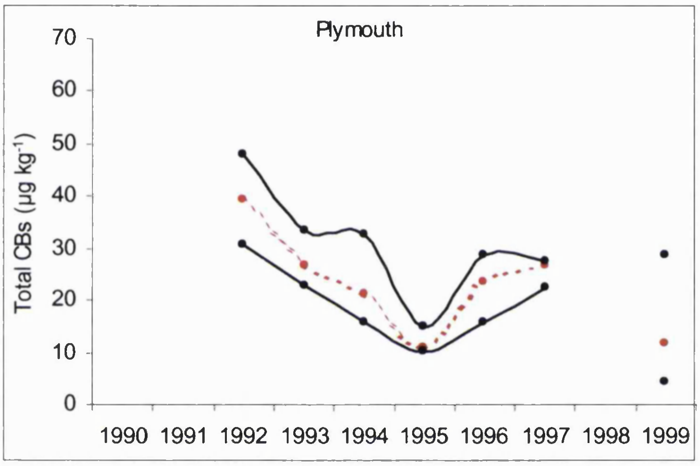


Figure 3.21: Temporal changes in PCB concentrations at various sites in South England sampled under FEPA.

Sampling conducted in the River Tamar between 1992 and 1997 and in 1999 was in support of a licence to deepen the estuary channel for improved navigation. Concentrations in the inner estuary were between 0 – 63 µg kg^{-1}, but were more elevated in the outer estuary (12 – 100 µg kg^{-1}). The spatial variability within the estuary is clearly high and representative sampling has not been ascertained. Further sampling at the local site scale is recommended so that within-site variability is determined. This would provide important information of contaminant loadings within the estuary and possible processes influencing spatial distribution of contaminants. This cannot be achieved under the current FEPA sampling protocol.

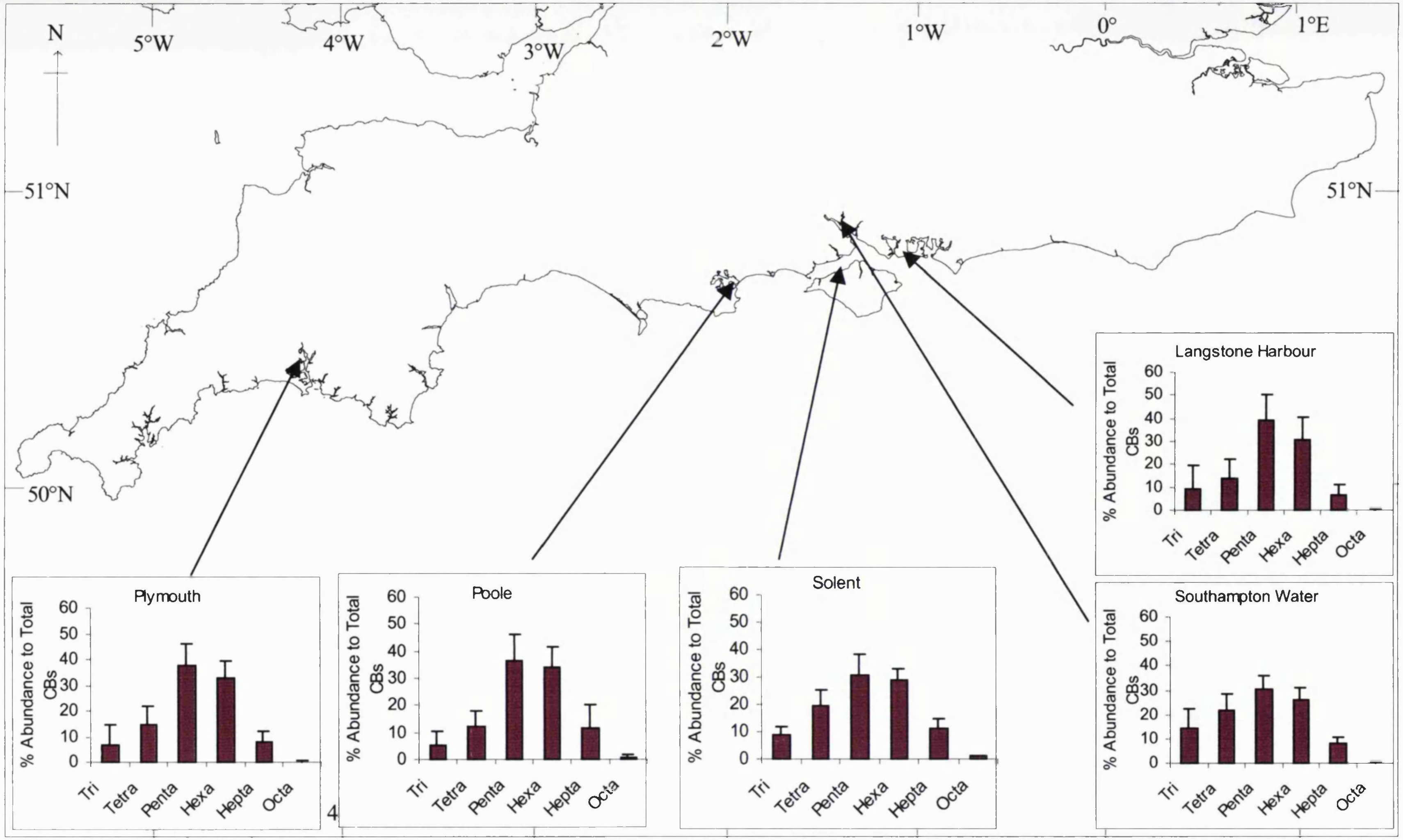


Figure 3.22: Mean homologue groups in dredged material at sites sampled in estuaries in South England (as % of Σ_{25}CBs) between 1990 and 1999. (*Error bars represent 1 standard deviation*).

3.2.4 South Wales and South West England

Dredged material was sampled in Newport, Cardiff, Barry, Port Talbot, Swansea, Carmarthen Bay, Pembrokeshire Coast, Neath, Milford Haven and Avonmouth. Sampling in this area was in support of licences to dredge an area within dock systems and approach channels to maintain shipping access. In this region, dredged material sampled in Neath, Milford Haven and Avonmouth exhibited low concentrations. However, concentrations were spatially quite variable (18 – 190 μg kg^{-1}) off Pembrokeshire coast and Carmarthen Bay. Median concentrations in the docks of Newport, Cardiff, Barry, Swansea, and in the outer River Usk estuary and Swansea Approach Channel over different sampling intervals are presented in Table A4.2 (Appendix 4) and temporal changes are shown in Figure 3.23. Sites in Swansea Docks, Cardiff Docks and Newport Docks exhibit consistently elevated concentrations (> 100 μg kg^{-1}). In the outer River Usk estuary, concentrations are also at or above 100 μg kg^{-1}, which is exceptionally high for an estuary site in England and Wales.

Although there is high spatial variability in sediment PCB concentrations at many sites within South Wales, further investigations at specific sites (i.e. in docks and outer estuary sites) may assist with the determination of similar spatial patterns of PCB profiles (i.e. homologue groups) between such sites. Homologue profiles at these sites are thus presented in Figure 3.24 a-b and the cumulative frequencies are presented in Figure 3.25 a-g. These figures are referred to in the case studies presented below.

Newport Docks and River Usk

In the River Usk, both in the inner and outer estuary, concentrations were highly variable (97 – 215 μg kg^{-1}). Concentrations are particularly high offshore, possibly due to discharges from the outfall of the Monsanto chemical plant which historically discharged PCBs into the Channel. Although this plant does not manufacture PCBs today, it still has a consent to discharge PCBs into the Bristol Channel from residual deposits at the site (Reed & Waldock, 1998).

Concentrations in Newport Docks are also highly variable. For example, many locations exhibit concentrations that are consistently high (> 120 μg kg^{-1}), but sites within the north (405 μg kg^{-1}), south (109–223 μg kg^{-1}) and centre of the dock (215–917 μg kg^{-1}) have particularly elevated concentrations. To further elucidate their spatial variability,

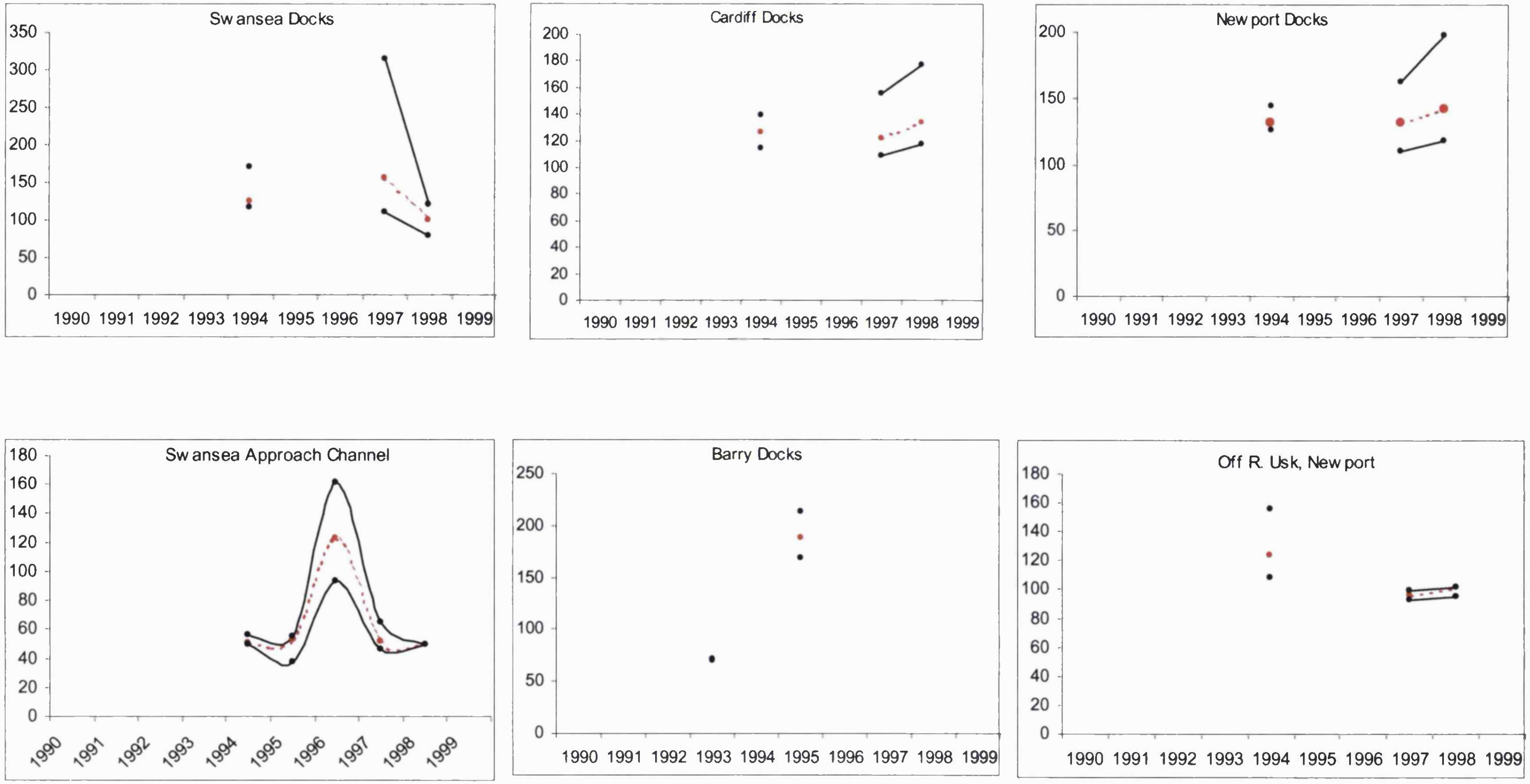


Figure 3.23: Temporal changes in PCB concentrations in South Wales sampled under FEPA.

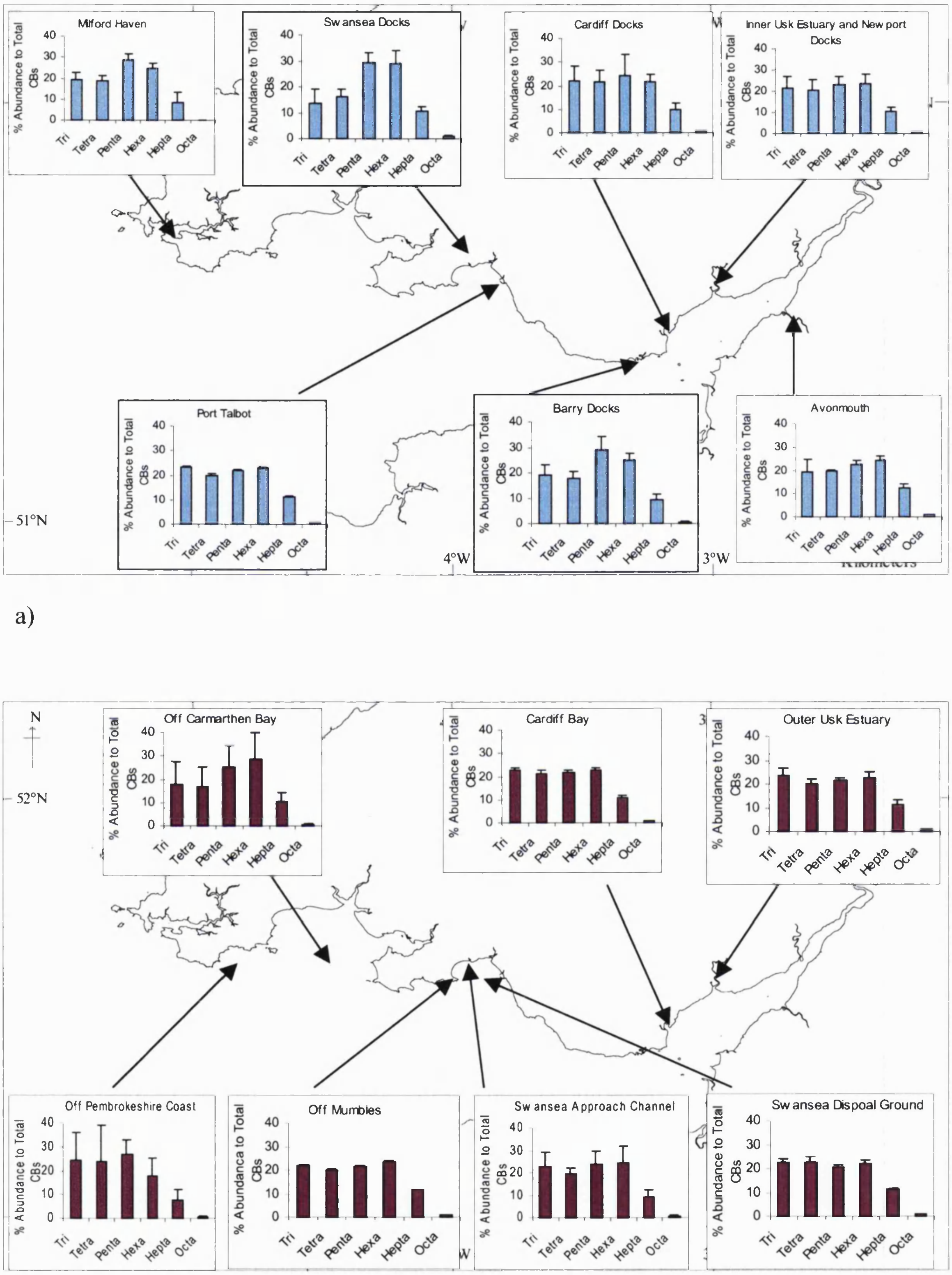
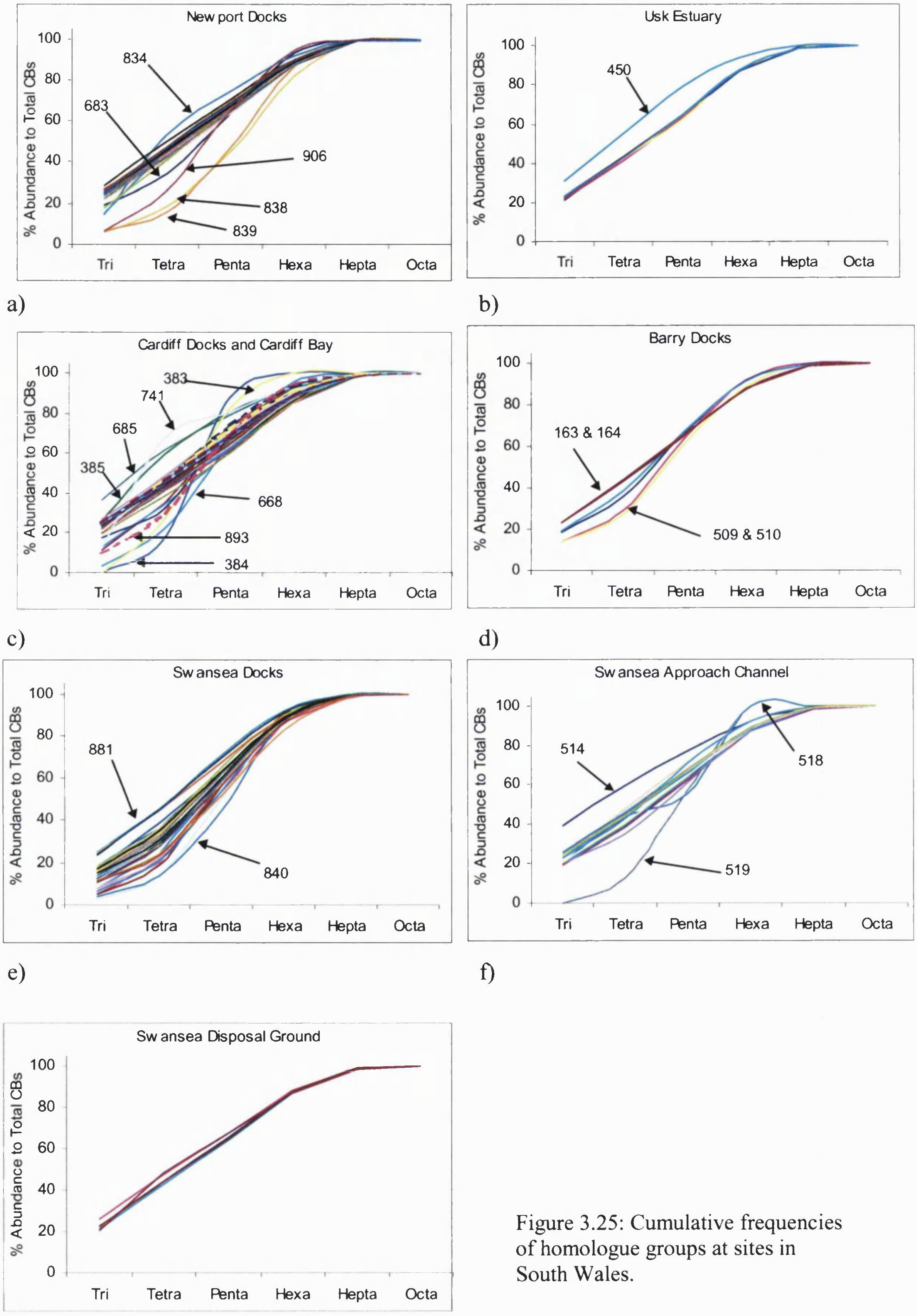


Figure 3.24: Mean homologue groups in dredged material at sites sampled in South Wales (as % of $\sum_{25}$CBs) between 1990 and 1999; a) inner estuaries (docks and highly industrialised areas); b) outer estuaries and disposal grounds. (*Error bars represent 1 standard deviation*).



a)

b)

c)

d)

e)

f)

g)

Figure 3.25: Cumulative frequencies of homologue groups at sites in South Wales.

mean homologue profiles at sites in the dock and in the River Usk are presented in Figure 3.24 a-b. These homologue profiles are generally similar although sites in the outer Usk estuary contain higher concentrations of tri-CBs than those in Newport Docks. The most distinctive profile in the River Usk, site 450, is located closest to the Monsanto plant discharge. Cumulative frequencies of homologue profiles are presented in Figure 3.25 a-b. The majority of profiles in Newport Docks are similar except as indicated. The latter profiles are located at sites in the north of Newport Docks and their profiles suggest contamination histories are complex.

Cardiff Docks and Cardiff Bay

In Cardiff docks, in 1994 and 1997, concentrations are also highly variable (1 - 289 μg kg^{-1}). Concentrations were consistently > 100 μg kg^{-1} and are often elevated at particular sites (500 μg kg^{-1}). Outside the docks, in the north east of Cardiff Bay, concentrations are also elevated (108 – 122 μg kg^{-1}). This may be from contaminated sediments washed outside of the dock by ship movements. In the bay entrance, concentrations are particularly high (2 – 289 μg kg^{-1}). However, some of the sediments were sampled at depth (1 metre) and as high concentrations were measured throughout the sediment core, it is likely that sediment deposition rates and migration of contaminants by physical, chemical and biological means causes localised mixing of sediments which has subsequently continued to contaminate surface sediments in the area. The sediments at this site therefore represent a historical record of PCB deposition from historic use.

Homologue profiles for sites in Cardiff Docks and Cardiff Bay are presented in Figure 3.24 a-b. Profiles in Cardiff Bay are generally comparable to those in Cardiff Docks and those observed in the Usk estuary, Newport Docks, Port Talbot, Avonmouth, Swansea disposal ground, Swansea approach channel and the Mumbles. However, there is some variability in these profiles in Cardiff Docks.

Barry Docks

Concentrations in dredged material are spatially variable, but are typically <100 μg kg^{-1}. Cumulative frequencies of profiles presented in Figure 3.25d show different profile distributions suggesting within-site variability is a problem. Sampling under FEPA has not established this variability nor determined representative samples within the site.

Profiles are a mixture of those typically detected in Cardiff, Newport and Swansea Docks. This again implies that the spatial variability within the site is high.

Port Talbot

At Port Talbot, dredged material has been sampled at sites located within the harbour wall and in the approach channel to the dock. Concentrations were less variable here than at other sites in this region (48 – 67 μg kg^{-1}). Mean homologue profiles at these sites are presented in Figure 3.24a and profiles are comparable with those identified in Cardiff and Newport. Sampling under FEPA has been limited ($n = 5$) and therefore it is unclear whether these results accurately represent PCB concentrations in dredged material at this site.

Swansea Docks, Approach Channel, Disposal Ground and the Mumbles

Concentrations in the approach channel to Swansea Docks are < 2 – 84 μg kg^{-1} and the highest concentrations are located at sites nearest the dock gates. At the outer Swansea Bay dredged material disposal ground, offshore PCB concentrations are relatively high (45 – 123 μg kg^{-1}). In the west of the Bay (near Mumbles), concentrations are also high (99 – 107 μg kg^{-1}) possibly due to the circulatory patterns in Swansea Bay causing the redistribution of contaminated material.

In Swansea docks, sampling was conducted in Queen's Dock and King's Dock in 1994, 1997 and 1998. In King's Dock, concentrations are typically > 100 μg kg^{-1}, although highest concentrations (911 μg kg^{-1}) are restricted to the west of the dock, close to the dock gates and loading bays. In Queen's Dock, concentrations are also generally >100 μg kg^{-1} but maximum concentrations are lower.

Mean homologue profiles from Swansea docks, the approach channel and the offshore disposal ground are presented in Figure 3.24. Offshore sites exhibit similar profiles and are comparable to profiles from Cardiff Bay, outer Usk estuary, Mumbles, Cardiff Docks, Newport Docks, Port Talbot and Avonmouth. In contrast, homologue profiles from Swansea docks are dissimilar (having higher contributions of penta and hexa-CBs) to the majority of other docks in South Wales, except at Barry Docks and Milford Haven. This suggests either similar contamination histories or that similar environmental processes are influencing PCB patterns at the sites in Cardiff Bay, outer Usk estuary, Mumbles, Cardiff Docks, Newport Docks, Port Talbot and Avonmouth.

Cumulative frequencies of homologue groups in Swansea Docks are presented in Figure 3.25e. Profiles are broadly similar in shape although there is high variability of tri-CBs (4 - 24%). Similarly, cumulative frequencies of homologue groups in the Swansea Approach Channel generally have the same distribution except as indicated. Sites containing higher than average contribution from the tri-CBs may represent a point source, especially as these sites have elevated concentrations and are located near to the dock gates.

3.2.5 North West England and North Wales

In North West England, sampling was conducted in the River Mersey, the River Wyre, the River Lune, and at Heysham, Barrow-in-Furness, St. Bees Head and Maryport. The only site sampled in North Wales was located at Conwy. Dredged material at all sites except the River Mersey were regarded as slightly contaminated (see Appendix 4.2).

In the River Mersey, sampling was conducted between 1990 – 92, 1994 – 95 and 1997 - 1999. Temporal changes of PCB concentrations since 1990 are shown in Figure 3.26. The majority of sites are located in dockyards on the north and south of the river but additional sampling was conducted offshore at the disposal ground. The aim of sampling at the disposal ground was to investigate any elevation changes to the sea bed and accumulation of contaminants in sediments causing the disposal ground to reach its capacity to accommodate increasing quantities of dredged material (MAFF, 1993; MAFF, 1994; CEFAS, 1997a).

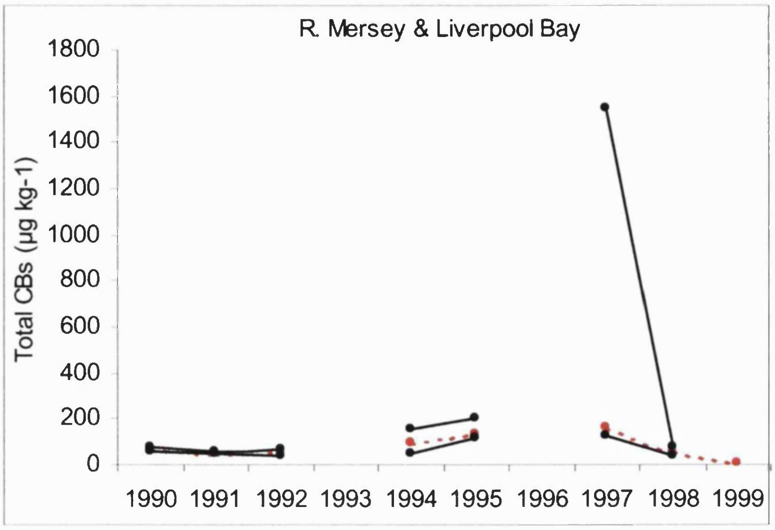


Figure 3.26: Temporal changes in PCB concentrations in River Mersey sampled under FEPA.

Concentrations in dredged material in the dockyards vary considerably. For example, in the northern dockyards, concentrations are low (<30 μg kg^{-1}) but concentrations are also found to be >100 μg kg^{-1}. Indeed, concentrations not only remain high but are, in extreme cases, particularly elevated at some sites (96 - 2,937 μg kg^{-1}). Even close to the mouth of the river, concentrations are found in the range of 57 – 486 μg kg^{-1}. Such a wide range of concentrations at the local scale suggest that sampling under FEPA is inadequate and cannot establish: within-site variability; the distribution of contaminants locally; identify hotspots or suggest possible sources of contamination within the estuary or dock.

3.3 Comparison of dredged material homologue profiles under FEPA

To determine whether homologue profiles in dredged material are similar at sites around England and Wales, and if sites are similar to commercial Aroclors® mixtures, principal component analysis (PCA) (Manly, 1995) was conducted. This approach aims to identify docks, marinas, harbours and ports with comparable site histories and identify sites giving cause for particular concern. It may also be possible to identify sites that are possible point sources. The cumulative homologue profiles of Aroclor® 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268 are used in this analysis. Specific attention is given to Aroclors 1248, 1254 and 1260 as these are known to have been used historically in the UK (Morris, 1995).

PCA was conducted using Genstat® 5 software package (Genstat, 1997). Principal components PC1 and PC2 account for 78% of the variation in the homologue profiles in dredged material (n=712). Data used in this analysis were only those sites containing PCB concentrations > 0.2 μg kg^{-1} (i.e. above the minimum detection level). Analysis was focused on these sites because increasing concentrations > 0.2 μg kg^{-1} are classified at different degrees of contamination (see Table 1.10). The importance of PC1 and PC2 is that these orthogonal planes explain over three quarters of the variation in the data set. The summation of PC1 to PC3 accounts for 96% of all variation. Plots of PC1 against PC2 and of PC1 against PC3 for all sites and for Aroclor® mixtures are presented in Figure 3.27 a-b. Most of the variation in PC1 is explained by tri- and penta-CBs. In PC2, the variation is mostly explained by tetra- and tri-CBs.

In general, the majority of sites plot close to the origin in Figures 3.27 a and b, and it is not possible to identify specific patterns or trends. However, several sites are different suggesting similar local spatial distributions. For example, in Plymouth, Langstone

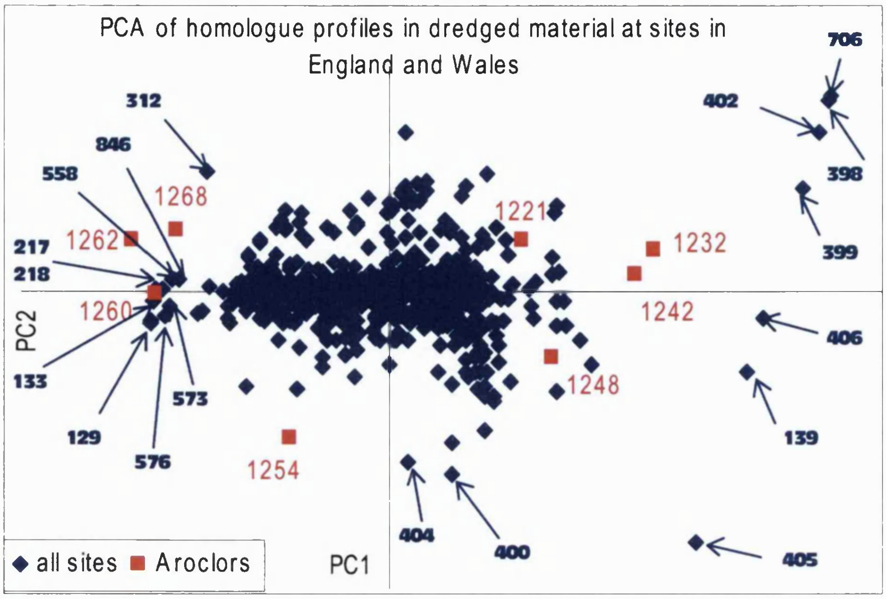
Harbour, Tees and Poole (sites 129, 133, 217, 218, 558, 573, 576 and 846) sites are separated on account of higher contributions from the hexa-CBs and less, if any, tri-CBs. Sites in the River Blyth are separated on the high positive PC1 axis because of high levels of tri-CBs. This was also evident under NMMP sampling. The majority of sites in the Rivers Tyne and Tees plot close to the origin, suggesting once again, similar contaminant histories or processes operate in the docks.

In South Wales, the majority of sites in Cardiff Docks, Newport Docks, Avonmouth, Swansea Approach Channel and off the River Usk are similar and separate along the positive PC1 and positive PC2 axes. Within this region, these sites may have been subject to similar sources or environmental processes affecting local distributions. The sites in Swansea Docks and Barry Docks plot separately from the other sites due to lower contributions from the tri- and tetra-CBs and a large contribution from the hexa-CBs. These sites have clearly been influenced by different sources of PCBs to other sites in this region (Proudfoot, pers. comm., 2000).

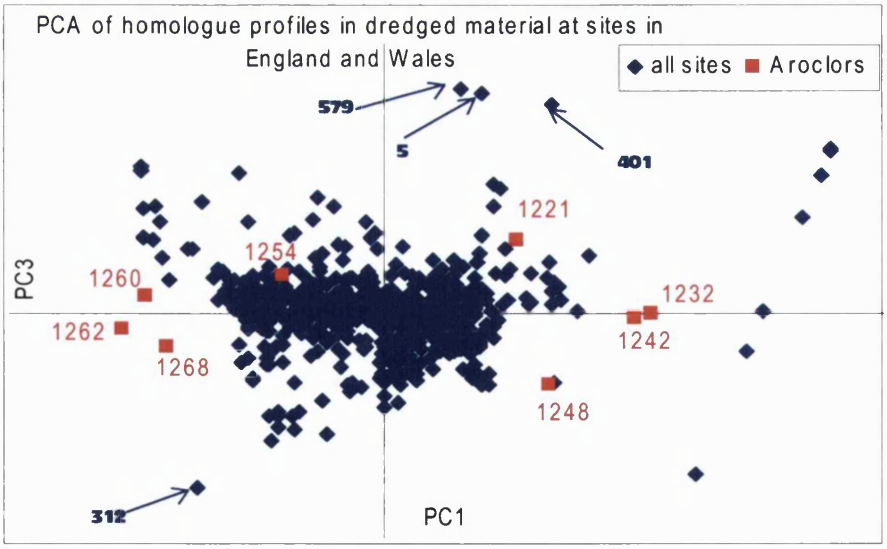
In essence, therefore, it has been difficult to establish patterns or trends in the majority of dredged material (96%) sampled to date. However, dredged material in the Rivers Blyth, Orwell, Humber, Tees, Mersey and in Cardiff exhibit elevated contributions from the less chlorinated CBs and these represent 4% of all dredged material sites sampled under FEPA between 1990 and 1999. These contributions are higher than expected and are areas of concern. Similarities have been suggested between PCB profiles in marine sediments sampled under NMMP and dredged material sampled under FEPA. This is further investigated below.

3.4 Comparison of marine sediments and dredged material homologue profiles

To investigate any similarities between sites inshore and offshore in England and Wales, the two extensive data sets (NMMP and FEPA) are combined and principal component analysis is performed on all sites initially and results from this analysis are presented individually for selected rivers, bays and docks (see Figure 3.28). PC1 and PC2 account for 78% of the variation. The homologue groups explaining most of the variation in PC1 are the tri-, penta- and hexa-CBs. In PC2, these groups are the tetra- and tri-CBs. To determine whether offshore and inshore sites have similar profiles, specific estuaries are presented in Figures 3.28 a-e.

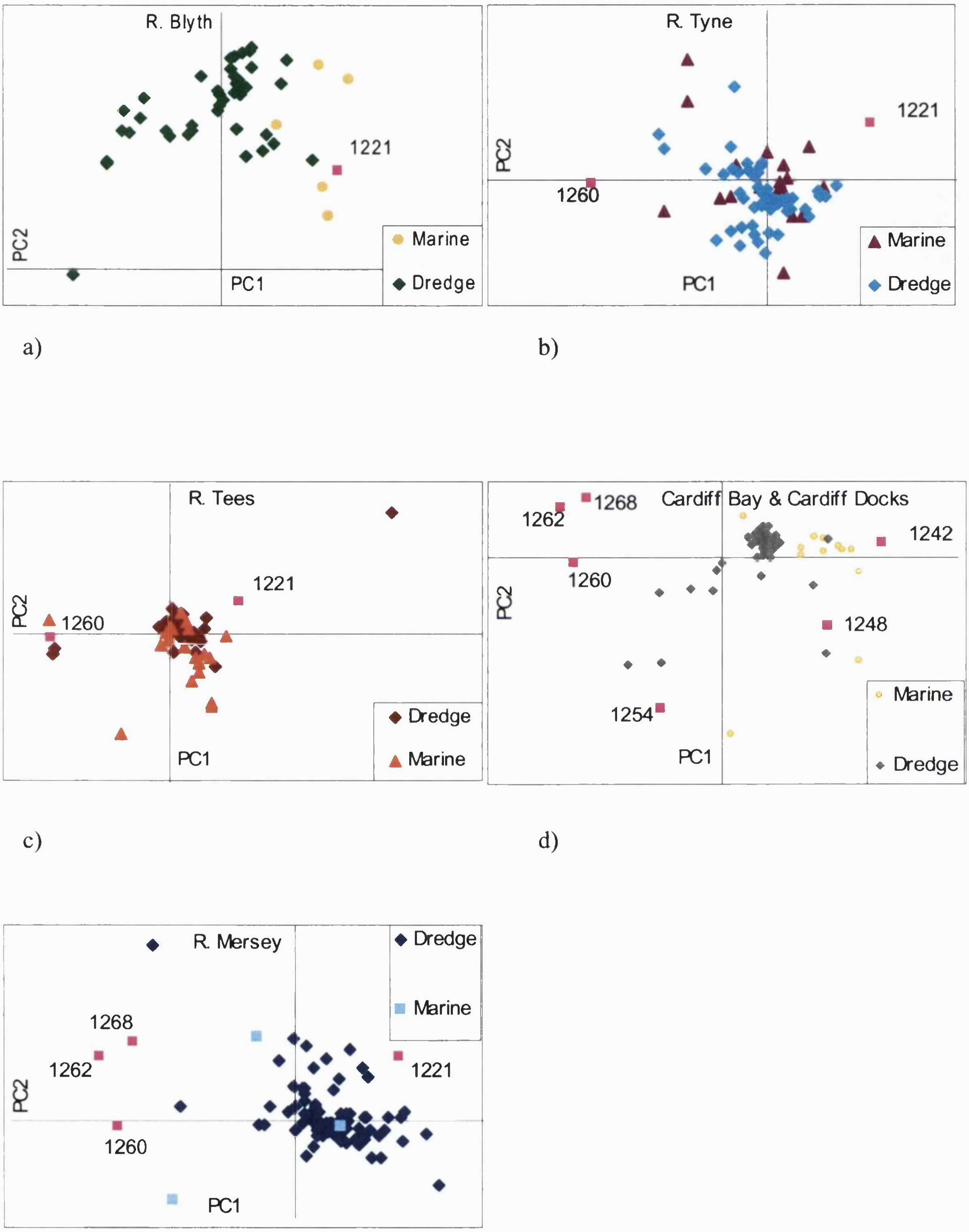


a)



b)

Figure 3.27: PCA of dredged material in regions around England and Wales: (a) PC1 and PC2; (b) PC1 and PC3. N.B. Site numbers are shown in Appendix 2.



a) b)

c) d)

e)

Figure 3.28: PCA of marine sediments and dredged material in: a) River Blyth; b) River Tyne; c) River Tees; d) Cardiff Bay & Cardiff Docks; and e) River Mersey.

In the River Blyth, marine sediments are separated from dredged material along the PC1 axis mainly due to contributions from the tri-CBs (Figure 3.28a). It is possible that PCB contamination here may have originated from the same source, but concentrations from the tri- and tetra-CBs are much lower offshore. The less chlorinated CBs are more soluble and are less persistent in the environment. In the River Tyne, both dredged material and marine sediments have similar distributions of PCBs (Figure 3.28b). This is also the case in the River Tees (Figure 3.28c). Here, the majority of sites plot close to the origin. A few sites plot separately from the main group and this is attributed to high tri-CBs on the positive PC1 axis and penta-CBs on the negative PC1 axis.

Marine sediments in Cardiff Bay and dredged material in Cardiff Docks generally separate into two groups (see Figure 3.28d). In Cardiff Docks, the largest group of sites plot close to the origin and are similar to some of the marine sediments distributions in Cardiff Bay. There is another group of sites in the docks which plots along the negative PC1 and negative PC2 axis and these sites exhibit different distributions to other sites. These are markedly different to all other profiles suggesting either a different source or their distributions have been affected by environmental processes.

In North West England, sites in the River Mersey generally plot along the positive PC2 axis and positive PC1 axis close to the origin due to contributions in the tri- and tetra-CBs (see Figure 3.28e). The marine sediment data are limited (n=3) and it is therefore not possible to conclude whether these sites are similar to dredged material. Further sampling is required to establish any similarities between sites in the River Mersey.

3.5 Summary

The analysis presented in this chapter represents the most thorough treatment of PCBs in sediments in England and Wales undertaken to date. It has provided a first step towards understanding the magnitude, spatial distribution and variability of PCB concentrations in sediments in England and Wales. For the first time, 'typical' concentrations representing offshore and estuarine sediments and dredged material in inner and outer estuaries have been calculated. A more general comparison of sediment and dredged material homologue profiles at several sites in estuaries and docks has been performed and some general similarities are inferred from available data.

There are, however, several important limitations to the data analysed in this chapter. At a national scale, data coverage is both spatially uneven and temporally inconsistent: many areas have either not been sampled or else have been sampled only infrequently in the last decade. The current NMMP sampling is spatially limited and there is insufficient repeat monitoring at key sites over long timescales. At a regional scale, the spatial resolution of data is particularly limited. The spatial variability and the spatio-temporal structure of the data in many areas make it difficult to establish patterns or trends due to the small number of sample sites. Similarly, it is difficult to determine whether sediment PCBs have become progressively dechlorinated or have increased in chlorination over time. Further investigations of environmental processes, for example, adsorption, sedimentation, transfer into the foodchain and metabolism in marine biota, should be conducted to establish those processes which may ultimately govern sediment profile changes within the coastal zone (see Section 1.3).

Current sampling conducted for licensing dredged material for sea disposal is also inadequate. The variable PCB concentrations and differences in homologue profiles emphasise this problem which is especially evident in dockyards in North East and North West England and South Wales. At present, only 2-5 samples are requested before a licence is granted to dredge sediments for sea disposal. The preceding analysis has shown that PCB concentrations in dredged material, especially within dock systems, and in sediments at some other coastal sites give serious cause for concern and that several sites exhibit concentrations consistently above current CEFAS 'Action Levels' (> 200 $\mu g\ kg^{-1}$).

Current monitoring programmes have not, in most cases, established confident spatail distributions of PCB concentrations in coastal and estuarine sediments, determined temporal changes in concentration over longer timescales (an original objective of NMMP, see Section 2.1), established spatial variability of PCBs at the local scale or attempted to trace sources of PCB contamination where there is evidence of elevated concentrations or consistently high or apparently increasing concentrations at specific sites. One of the objectives under FEPA is to protect the marine environment, living resources which it supports and human health (see Section 1.4.3). The identification and management of PCB sources can increase the protection of these resources and prevent future concerns regarding harm to marine ecosystems. Also, the lack of other sediment characteristic information, such as particle size and total organic carbon data has hindered the interpretation of PCB levels at specific sites.

The limitations of existing monitoring programmes are becoming an increasing problem for three reasons. First, the UK government is encouraging the use of dredged material for alternative uses, such as beneficial use, instead of licensing it for sea disposal. Second, an offshore dredged disposal site (e.g. at Tyne Dock) has started to accumulate contaminants (e.g. TBT) potentially exposing marine flora and fauna to higher than expected levels of some contaminants (Reed & Waldock, 2000). Third, OSPAR are encouraging member states to reduce hazardous substances to zero or near zero levels by 2020 (OSPAR Commission, 1998). Current monitoring of marine sediments and assessments of dredged material have clearly failed to achieve their aims (see section 2.1) at some sites and improvements to monitoring and risk assessment procedures are crucial at this time. Further research is therefore required to improve our knowledge of the magnitude, spatial variability and spatial structure of PCB concentrations in sediments at the local (site) scale. The next phase of the present study investigates these issues and attempts to improve the procedures used for the estimation and characterisation of CBs in dredged material.

CHAPTER FOUR

Environmental Variability of PCBs in Sediments in King's Dock, Swansea

This chapter presents the results of an intensive study of the sediments of King's Dock, Swansea. Bottom sediment samples are analysed for PCB concentrations, total organic carbon (TOC) and particle size (% <63 μm). Exploratory data analysis is used to characterise the distribution of sediment PCBs and investigate any relationships with associated environmental parameters. Multivariate statistics, including principal component analysis and cluster analysis, are employed to further explore the variability in the PCB data set. To further investigate the robustness of the sampling protocol, within-grab sample variability and analytical replicates are evaluated.

4 Introduction

The preceding analysis of PCB concentrations and differences in homologue profiles throughout dockyards in North East and North West England and in South Wales emphasises the problems of spatial variability and lack of characterisation of PCB concentrations at the local scale. Moreover, although several sites in England and Wales clearly exhibit PCB concentrations consistently above current 'Action Levels' (> 200 μg kg^{-1}), the extent of contamination is not well defined. Existing assessments of contaminant concentrations in sediments, both in terms of temporal and spatial monitoring undertaken to date and sampling prior to dredge licence approval, has been shown in the preceding chapter to be clearly inadequate.

The purpose of this 'intensive' case study is to characterise the spatial distribution of sediment PCB concentrations in King's Dock, Swansea, and to assess sources of spatial variability. The specific objectives of this intensive investigation are as follows:

1. to establish the overall magnitude, environmental variability and spatial distribution of sediment PCB concentrations in the dock;
2. to investigate possible point sources in King's Dock sediments; and
3. to estimate the components or sources of spatial variability within the study site.

4.1 Exploratory data analysis

The analysis of PCB concentrations in King's Dock sediments uses both descriptive univariate and multivariate statistical techniques. First, exploratory data analysis (EDA) is conducted so that summary statistics of the distributions of PCB concentrations, TOC and particle size (% < 63μm) are established. The employment of histograms, regression plots, scattergrams and other means of illustrating relationships is essential to establish fundamental patterns in these data sets (Isaaks & Scrivastava, 1989; Rossi *et al.*, 1992). Second, multivariate statistical techniques, such as principal component analysis and cluster analysis, are also used to explore trends and patterns in the data (Zitko, 1994).

4.1.1 Distribution of Polychlorinated biphenyls in sediments

UK regulation of the dredging of sediments is presently based upon an assessment of contaminants measured in sediments prior to licensing disposal to sea (see Chapter 1). To place the King's Dock samples in an appropriate regulatory context, the distribution of total PCB concentrations is plotted against national average concentrations and CEFAS Action Levels in Figure 4.1.

Concentrations range from 16 to 3018 μg kg^{-1} with a mean of 201 ± 347 μg kg^{-1} (one s.d.), with of coefficence of variance of 173% and a median of 121 μg kg^{-1} (*n*=101). The mean is distorted by several extreme values (i.e. 3018, 1717 and 808 μg kg^{-1}). This distribution is not only comparable to the range measured throughout England and Wales (see Chapter 3) but has comparable variability. Such a wide concentration span at this local scale exemplifies the problem with identifying sites that not only are representative of an area, but include concentrations that are elevated and/or represent a broad magnitude of scales. King's Dock therefore represents a site that has as much spatial variation as the whole of England and Wales.

The histogram and summary statistics of total CB concentrations are presented in Figure 4.2. The important feature of Figure 4.2 is the positive skewness in the distribution. In general, the highest (> 200 μg kg^{-1}) and lowest (< 50 μg kg^{-1}) concentrations occur with the smallest frequency. Over half the sites sampled exhibit concentrations between 100 – 150 μg kg^{-1}. Concentrations are above the CEFAS Action Level 1 (> 100 μg kg^{-1}) and therefore further investigation would be required prior to the licensing of sediments for disposal (Waldock, R. pers. comm., 2000). Such an investigation would include, for instance, a calculation of total loadings within the dock, a requirement which is addressed more fully in Section 5.4.3.

Clearly, concentrations are consistently high (> 100 μg kg^{-1}) and this is reflected in the median value which is approximately three times higher than the value (34 μg kg^{-1}) for England and Wales. Such high average concentrations have not been reported previously in the UK environment. However, studies of UK terrestrial soils and research undertaken by Morris (1995) demonstrate that total PCB concentrations in soils in the vicinity of the site of former PCB manufacture were around 300 μg kg^{-1}. The average concentration measured in sediments in King's Dock is not as high as this value, but isolated 'hotspots' within the dock exhibit concentrations as high or higher than those measured in soils on-site at the Solutia plant, Newport (Morris, 1995).

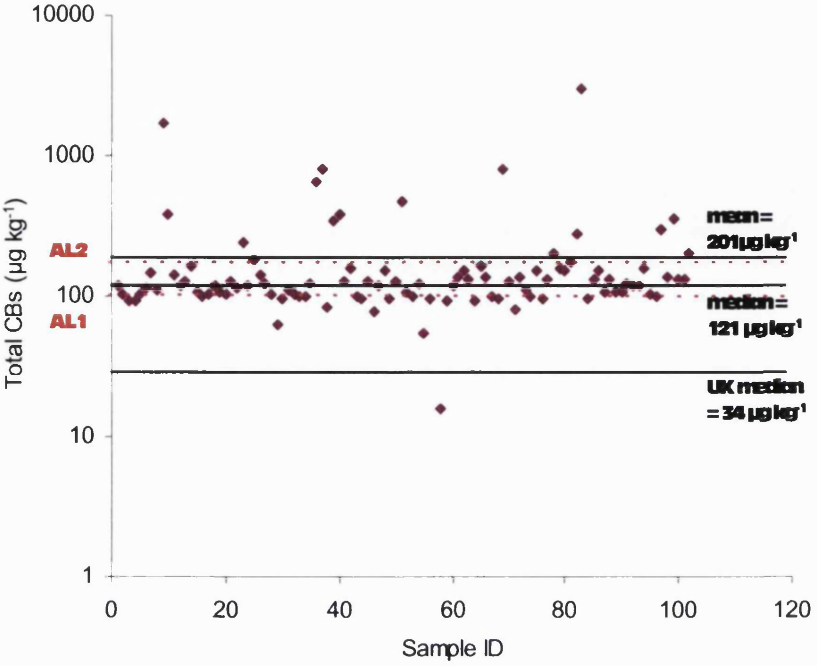


Figure 4.1: Σ_{25}CBs (µg kg^{-1}) in sediments in King's Dock. (Action Level (AL) 1 (100 µg kg^{-1}) and Action Level (AL) 2 (200 µg kg^{-1})).

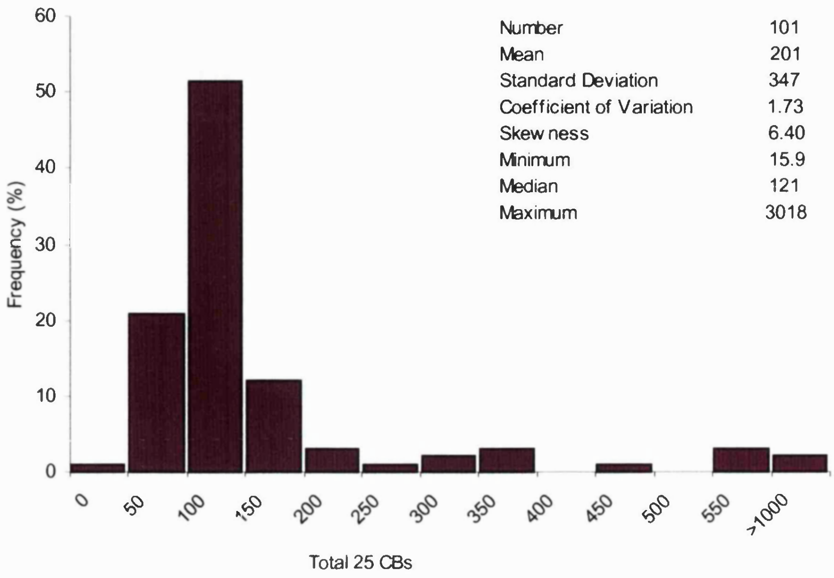


Figure 4.2: Frequency histogram and some summary statistics of Σ_{25}CBs in sediments, King's Dock.

The contour maps presented in Figure 4.3 provide an initial insight into some of the spatial features and trends of total PCB concentrations in King's Dock sediments. These contour maps have been produced using the default mapping methods available in the SURFER software package. Highest concentrations are estimated to be in the west of the dock and large areas exhibit concentrations > 200 $\mu g\ kg^{-1}$. At this stage, the models selected to map concentrations in the dock are chosen without any knowledge of the sample patterns or possible spatial structure (see Section 5.2). These contouring methods are typically available in most contour mapping software packages. The concentrations in each example show similar interpolated patterns but differ in detail. Without an understanding of the variogram structure and form, it is difficult to determine which of these kriged maps (Figure 4.3 a-b) are the most representative of the estimated spatial distribution PCBs. A contour map produced from model parameters obtained from the actual sample variogram is presented in Section 5.3.2 (Fig. 5.9). The analysis undertaken here using different default mapping methods in SURFER is used to highlight the potential misuse of software packages which are available 'of the shelf'. Often, these packages are used without prior knowledge of the methods being used to generate contour maps and such data analysis and interpretation are dangerous especially where government bodies are using these for decision making purposes and/or are incorporated in risk assessment management plans.

The extreme values responsible for the skewness are more clearly identified in Figure 4.4 a - d. In this example, concentrations of total PCBs at the lowest 10% (10 percentile) (Fig. 4.4 a), <50% (50 percentile or median value) (Fig. 4.4 b), >50% (Fig. 4.4 c) and highest 10% (90 percentile) (Fig. 4.4 d) are located in the dock. Figure 4.4 d shows a tendency for the highest concentrations to be located in the west half of the dock. However, in Figure 4.4 a, the lowest concentrations are located both as a cluster in the east half of the dock and at another site located in the middle section of the dock. There is also one site located in the west of the dock, in close proximity to the highest concentrations. In Figures 4.4 b and c, concentrations are more or less uniformly distributed throughout the sampling area.

Previous sampling in Swansea docks, in 1994, 1997 and 1998 (ABP, 1996; CEFAS, 2001) also identified elevated concentrations in the west of the dock, close to the dock gates and loading bays. Moreover, in the east of the dock, concentrations were lower than other sites (~80 $\mu g\ kg^{-1}$). In general, concentrations are typically > 100 $\mu g\ kg^{-1}$ and have been since 1994 suggesting that sediment-bound PCBs remain in the environment

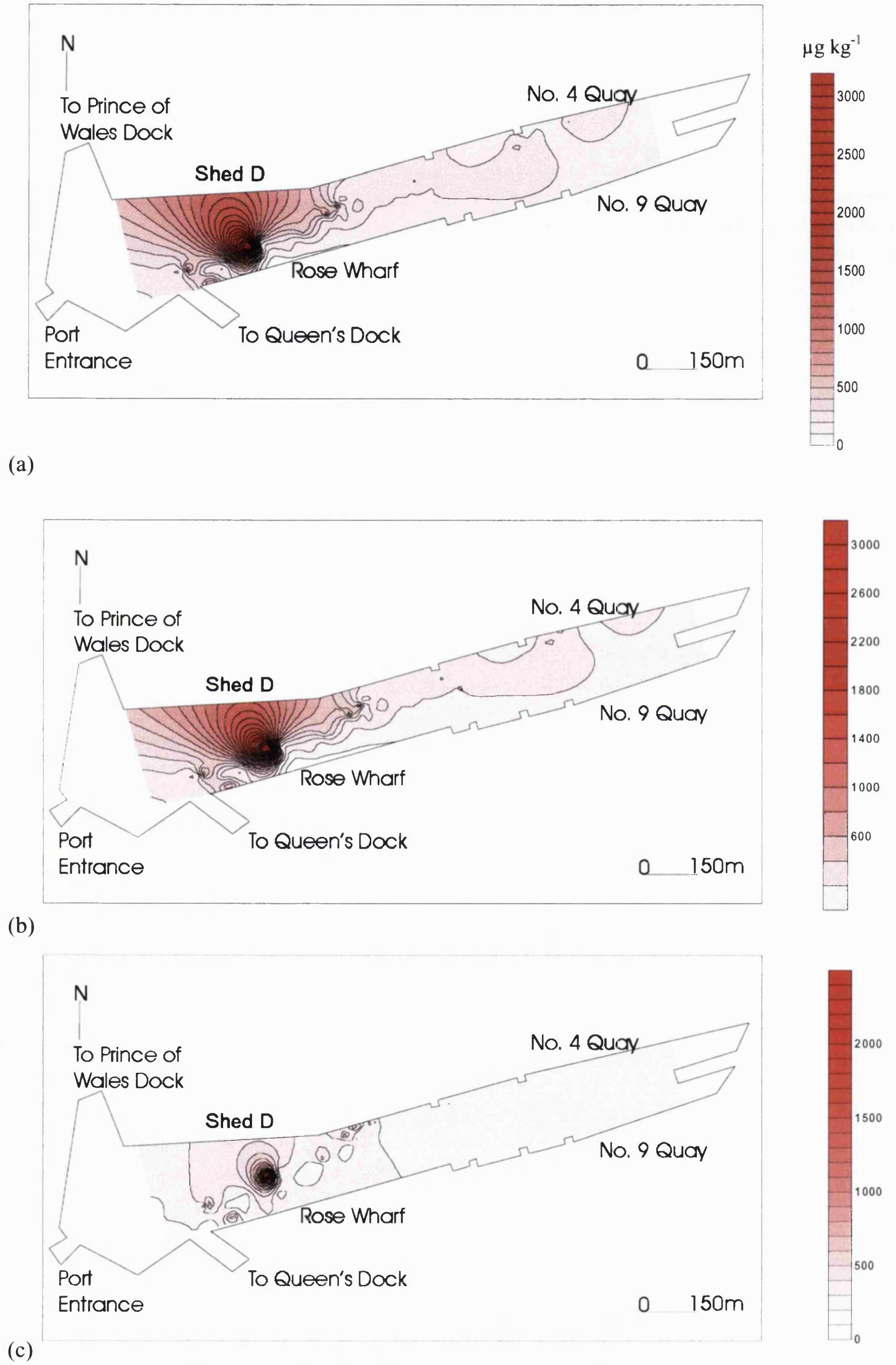


Figure 4.3: Contour map of Σ_{25}CB concentrations in sediments in King's Dock, Swansea using: (a) kriging with a linear model; (b) kriging with a spherical model; & (c) inverse distance weighting.

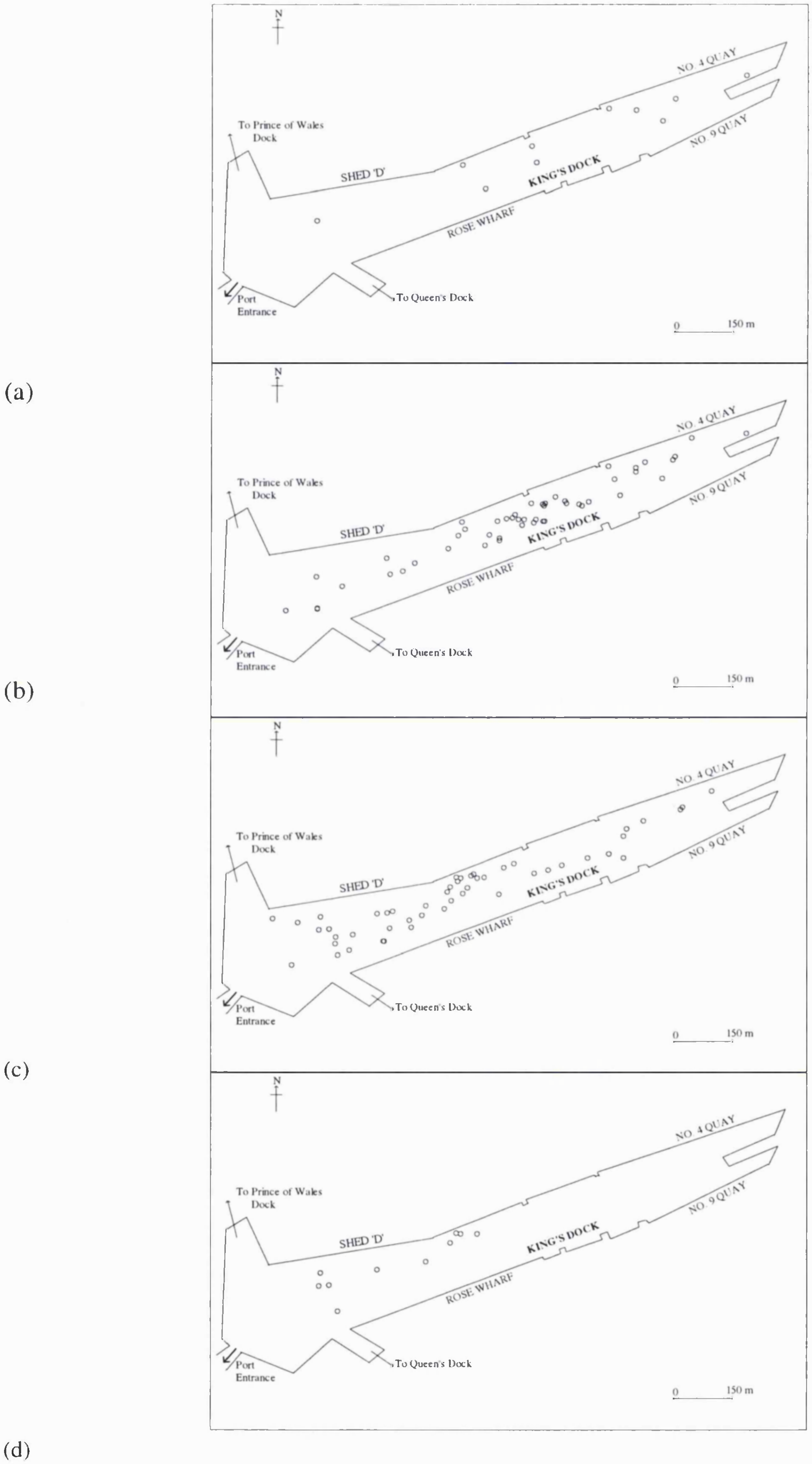


Figure 4.4: Distribution of sampling sites within dock: lowest 10% (a); < 50% (b); > 50% (c) and highest 10% (d) concentrations of $\sum_{25}$CBs.

over relatively long time periods. Sinkkonen & Paasivirta (1998) believe the biodegradation life of POPs in the environment to be as long as several years to tens of years.

The composition or relative abundance of homologue groups in sediments, in terms of the actual measured concentration standardised to total PCB concentrations, is given in Figure 4.5. The profile shape is comparable to previous sampling, as shown in Figure 3.16a. Similarly, highest contributions are from the penta- and hexa-CBs (>50% of the total). Qualitative observations of chromatograms and relative abundance graphs reveal that the homologue profile is comparable to Aroclor® 1254, although the profile is likely to comprise of other mixtures of Aroclors (Reed & Nicholson, 2000).

A typical GC-ECD chromatogram of PCBs in a sediment sample is shown in Figure 4.6. At this stage, due to the presence of individual CBs of both high and low degrees of chlorination, it is difficult to establish any relationship to the composition of specific Aroclor® mixtures. Further investigations of this kind are conducted in Section 4.2.

The cumulative frequencies of homologue groups are shown in Figure 4.7. This approach identifies those sites that do not fit the general envelope of profiles. The majority of identified sites in Figure 4.7 are in the highest 10% of total PCB concentrations. Further investigations of these profiles are shown in Figure 4.8. The location of these sample points are shown in Figure 4.8.

There are two clearly distinct divisions within the profiles in Figure 4.8. A group of samples (7e, 8g and 10c) have penta- and hexa-CBs that are seen to be enriched compared to other sites. The high relative abundance of these compounds is correspondingly a consequence of the source (Morris, 1995) and/or relationship with other environmental parameters (Steen *et al.*, 1978). The other group is a mixture of samples located at sites 1g, 4d, 6d and 6e. In the latter group, the former site is seen to be different from all others due to the enrichment of octa-CBs: this sample is located near Shed D in the west of the dock. Sample 4d is a mixture of homologue groups which may be attributed to its location within the dock (i.e. close to the dock entrance and turning area for ships entering and leaving the dock). Resuspension of sediments within this turbid zone may influence the adsorption of PCBs to sediments (Pavlou & Dexter, 1979) and therefore change the original PCB signature. The samples at 6d and 6e thus have higher tri- and tetra-CBs compared with other samples presented in Figure

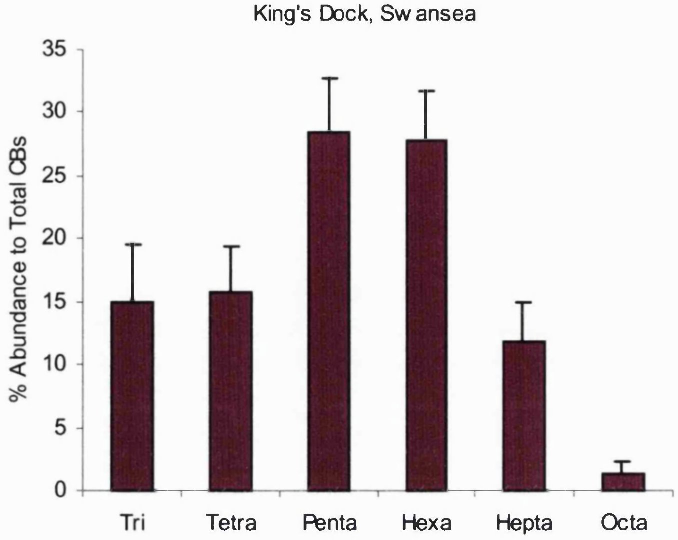


Figure 4.5: Percentage contribution of homologue groups relative to Σ_{25}CBs in sediments in King's Dock.

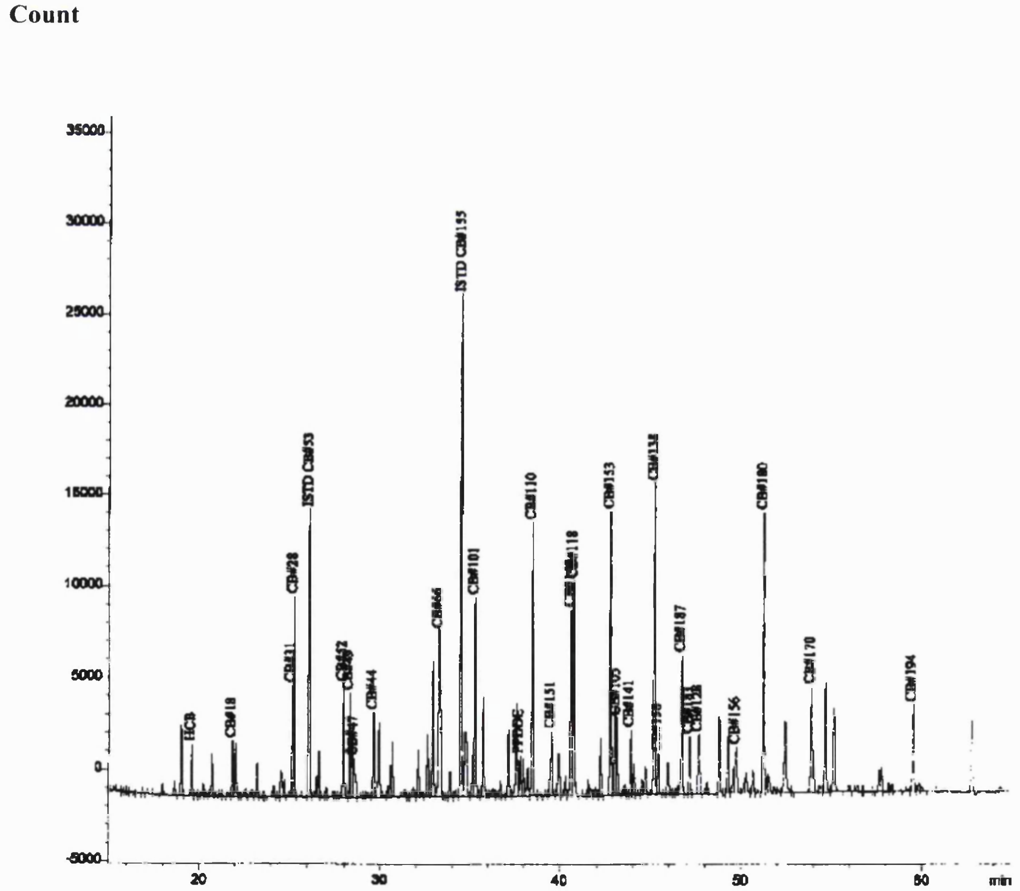
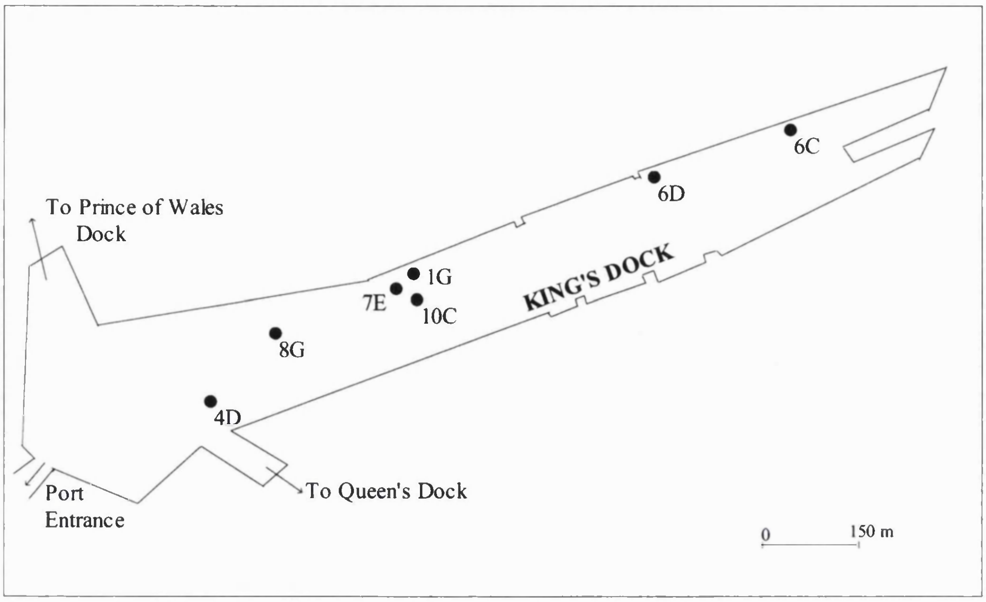


Figure 4.6: Chromatogram of a sediment sample taken from King's Dock.



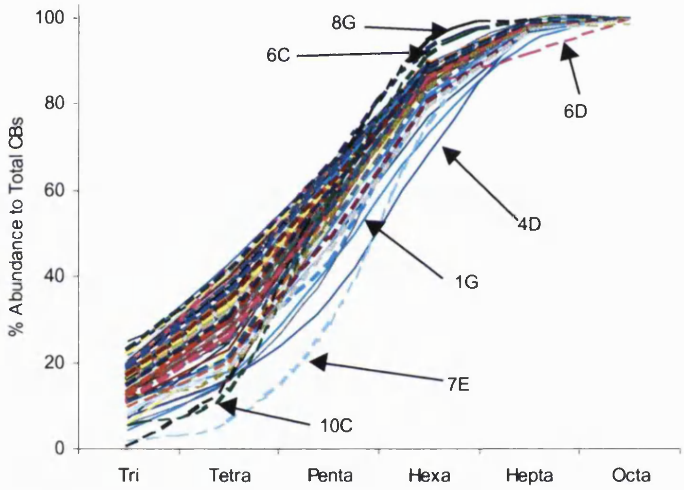


Figure 4.7: Cumulative frequencies of homologue groups in sediments in King's Dock.

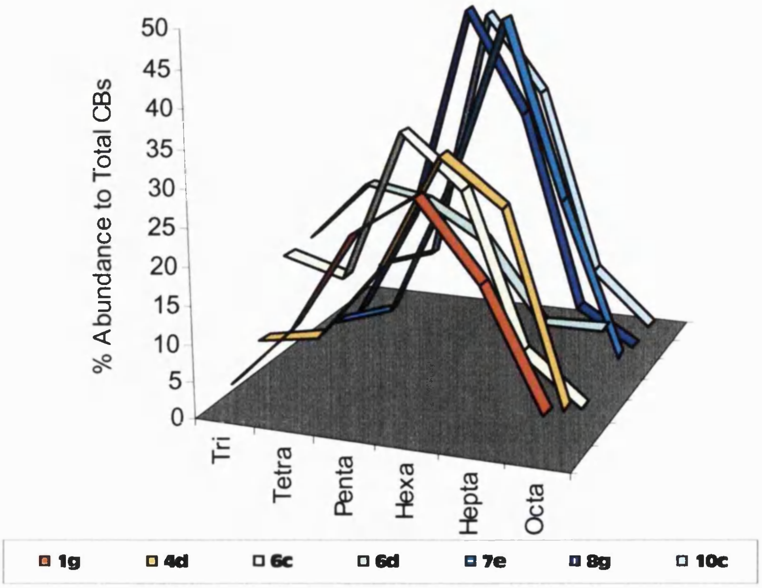


Figure 4.8: Percentage contributions of homologue groups relative to $\sum_{25}$CBs at selected sediment samples (1g, 4d, 6c, 6d, 7e, 8g and 10c).

4.8. Sample 6d exhibits low total PCB concentrations (<10% of all sites) but is heavily enriched with octa-CBs. This combination of both low and high degrees of chlorination makes it difficult to establish the potential mixture of Aroclors contributing to these profiles.

It is important to determine whether the distribution of concentrations is a result of environmental factors such as the organic content of the sediments or their particle size (and therefore clay, silt or sand composition). The following section investigates the relationship between total CB concentrations and TOC and particle size. The ultimate aim here is to determine whether there should be procedural changes to the assessment of contaminants (such as normalisation to environmental parameters) prior to licensing and disposal of sediments to sea.

4.1.2 PCBs and their relationship with TOC and particle size in sediments

Total organic content (TOC) of sediments is here defined by loss-on-ignition (LOI) (550 °C) of oven dried sediment samples (*n*=99). Possible correlations with PCB concentrations are sought. However, no discernible relationship between TOC and Σ_{25}CBs is found in the King's Dock sediments (Figure 4.9). The lack of any relationship with Σ_{25}CB concentrations and TOC may be due to the technique used to define TOC (Gross, 1971). As mentioned in Chapter 2, this is a low cost and simple technique, and the estimation of organic carbon could be improved by other more sophisticated approaches.

The plot in Figure 4.9 is biased by several anomalous points of data, identified as sites 1g, 3g, 4d, 4e, 7e, 8g and 10Rep1. Furthermore, the percentage of particles <63 μm is also not identifiably related to concentrations of Σ_{25}CBs (Figure 4.10). This is again attributed to anomalous data points, some of which correspond to those shown in Figure 4.9. Larsen *et al.* (1985) similarly found no relationships with these environmental parameters at Wilkinson Basin, Gulf of Maine, US. However, several authors have found particle size and TOC to be important factors determining the partitioning extent of PCB isomers (i.e. homologue groups) (Steen *et al.*, 1978; Chiou *et al.*, 1979; Karickhoff *et al.*, 1979; Lohse, 1991; Rutherford *et al.*, 1992; Ab Razak & Christensen, 1996; Girvin & Scott, 1997; Koelmans *et al.*, 1997; Brannon *et al.*, 1998).

Although there is no evidence of a correlation between total PCB concentrations and TOC or particle size here (including an analysis to assess the consequence of removing

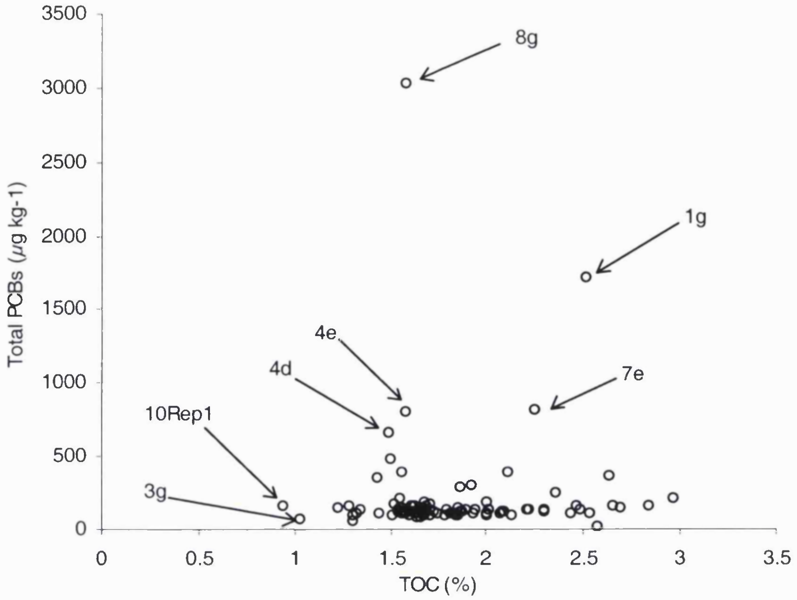


Figure 4.9: Scatter plot of total PCB concentrations and TOC (%) in sediments in King's Dock. (*Arrows indicate outlying values referred to in text*).

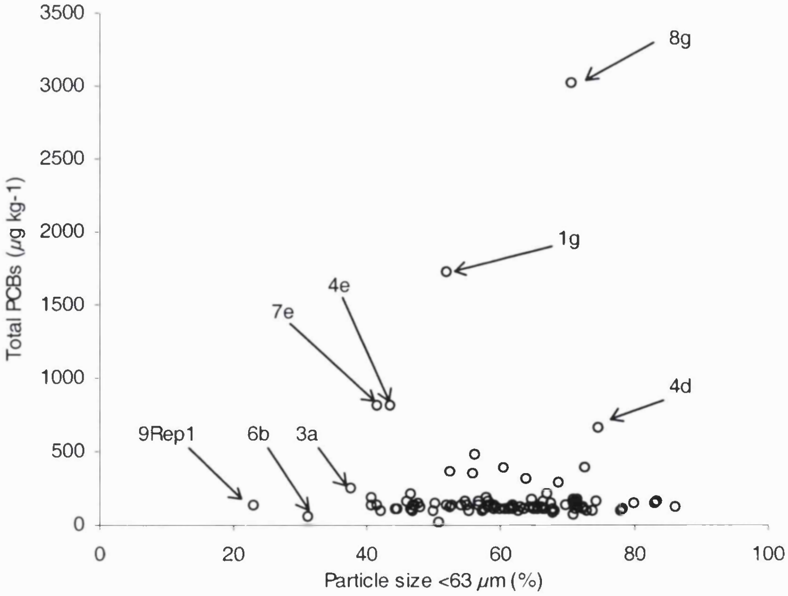


Figure 4.10: Scatter plot of total PCB concentrations and particle size (% <63 μm) in sediments in King's Dock. (*Arrows indicate outlying values referred to in text*).

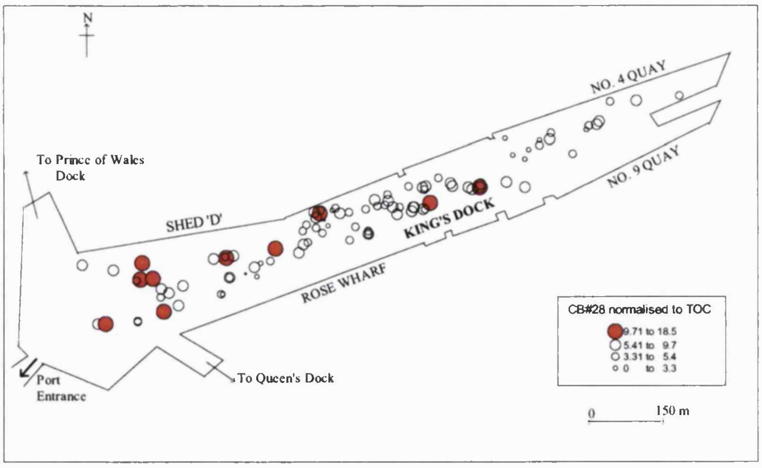
outliers to determine any underlying trend), further investigations are conducted into possible relationships with individual CBs. A selection of individual CBs (chosen to represent different degrees of chlorination) are normalised to TOC (Figure 4.11) and particle size (Figure 4.12).

The normalisation of individual CBs to both TOC and particle size <63 μm clearly identifies a relationship between high concentrations of the more chlorinated congeners (penta-, hexa-, hepta- and octa-CBs (i.e. CB#110, #153, #180 and #194)) and high percentages of TOC and particle size (% <63 μm) (in Figures 4.11 and 4.12), although the latter is less well defined. This relationship is a function of the physico-chemical properties of these congeners. Research by Burgess *et al.* (1996) suggests that di- and tri-CBs are approximately 40% and 65% colloidally bound, respectively, whilst tetra-, penta-, hexa-, hepta- and octa-CBs are about 80% colloidally bound.

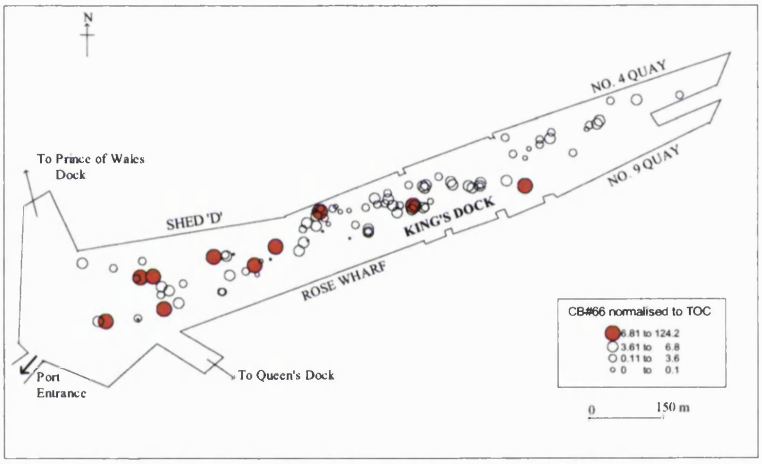
Other authors have demonstrated that the relationship of PCBs with environmental parameters is complicated by a number of factors, including delayed sorption; steric hindrance (Brownawell & Farrington, 1986); colloidal stability (Burgess *et al.*, 1996); and the presence of elemental carbon or small coal particles (Achman *et al.*, 1996). All of these can disguise the relationship between TOC and PCB concentrations. In King's Dock, there were contributions of elemental carbon or small coal particles in some sediment samples, which is not surprising since the dock has active coal handling facilities at No. 4 quay and Rose Wharf. This may have prevented the expected statistically significant correlation between total PCBs and TOC. Similar results were found by Achman *et al.* (1996) in the lower Hudson Estuary, New York.

In summary, sediment concentrations in King's Dock are highly variable and extend over a wide range (16 – 3018 μg kg^{-1}). The average concentration is high in a national context (201 μg kg^{-1}) and sediments exhibit elevated levels at a number of locations within the dock. The highest concentrations are clustered in the western part of the dock and lower concentrations are located in the eastern part of the dock (Figure 4.4). The spatial distribution of concentrations with measured environmental parameters, such as TOC and particle size, has been well characterised and only the more chlorinated CBs were typically associated with TOC (Figure 4.11) and particle size (Figure 4.12).

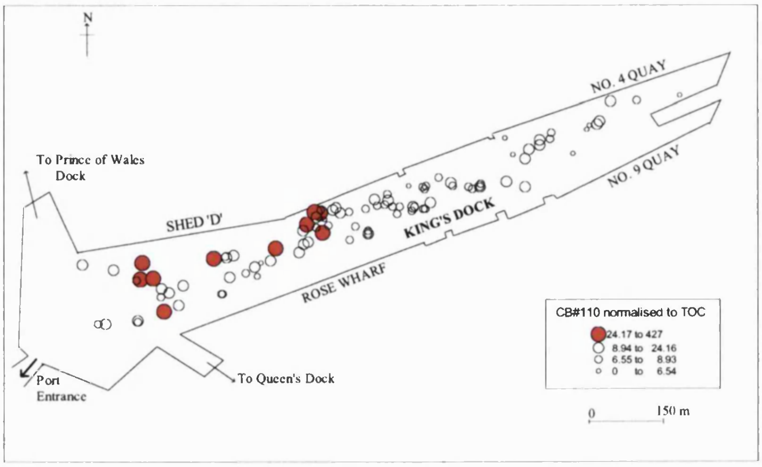
The purpose of the following sections is to establish any similarities between observed congener profiles and those found in commercial Aroclor® mixtures in order to


N
NO. 4 QUAY
To Prince of Wales Dock
NO. 9 QUAY
SHED 'D'
KING'S DOCK
ROSE WHARF
CB#28 normalised to TOC
9.71 to 18.5
5.41 to 9.7
3.31 to 5.4
0 to 3.3
Port Entrance
To Queen's Dock
0
150 m

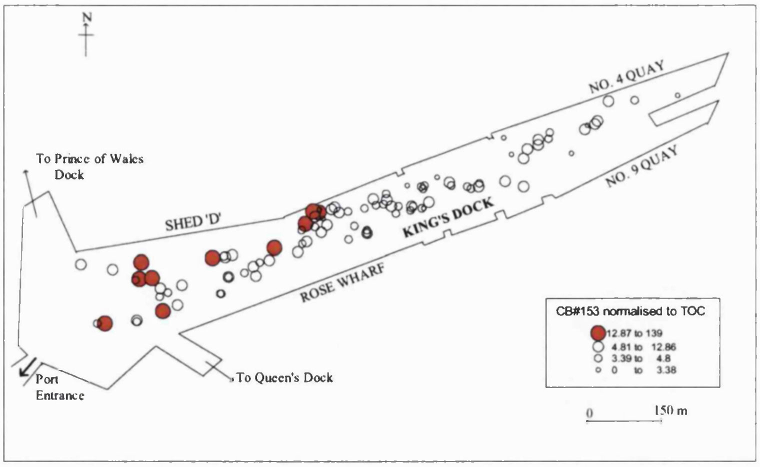
(a)


N
NO. 4 QUAY
To Prince of Wales Dock
NO. 9 QUAY
SHED 'D'
KING'S DOCK
ROSE WHARF
CB#66 normalised to TOC
6.81 to 124.2
3.61 to 6.8
0.11 to 3.6
0 to 0.1
Port Entrance
To Queen's Dock
0
150 m

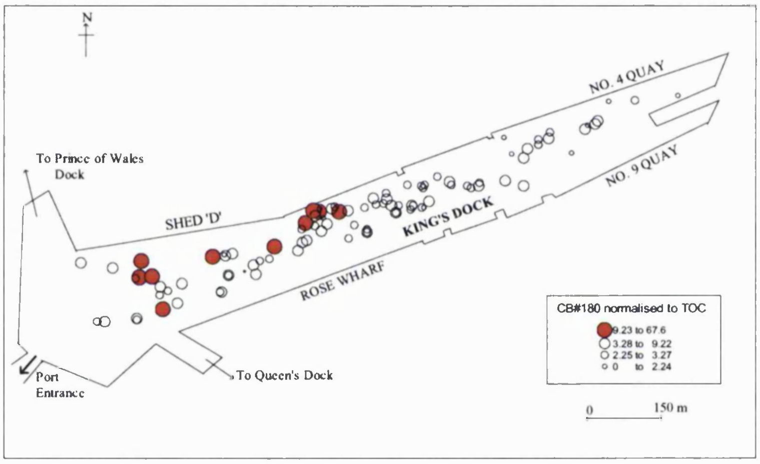
(b)


N
NO. 4 QUAY
To Prince of Wales Dock
NO. 9 QUAY
SHED 'D'
KING'S DOCK
ROSE WHARF
CB#110 normalised to TOC
24.17 to 427
8.94 to 24.16
6.55 to 8.93
0 to 6.54
Port Entrance
To Queen's Dock
0
150 m

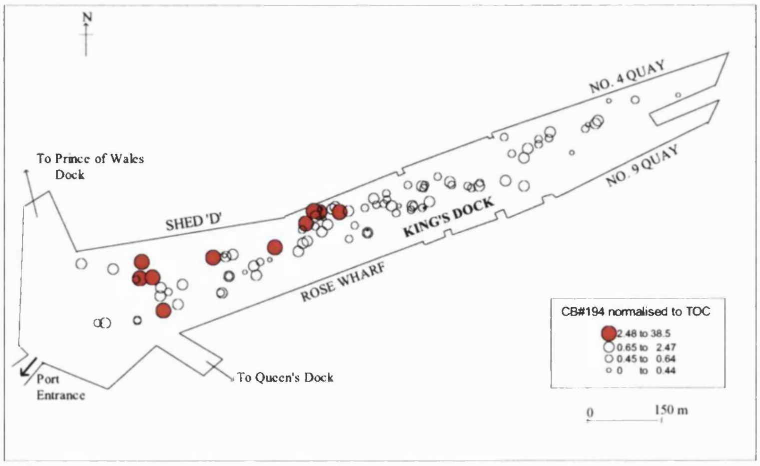
(c)



(d)

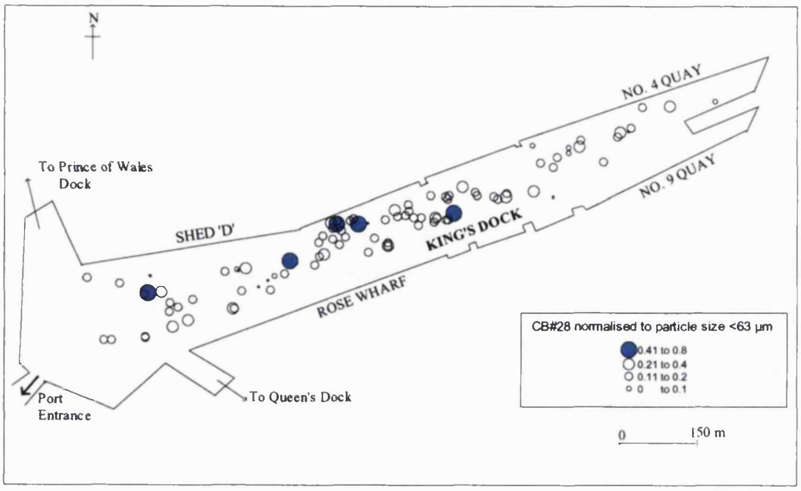


(e)

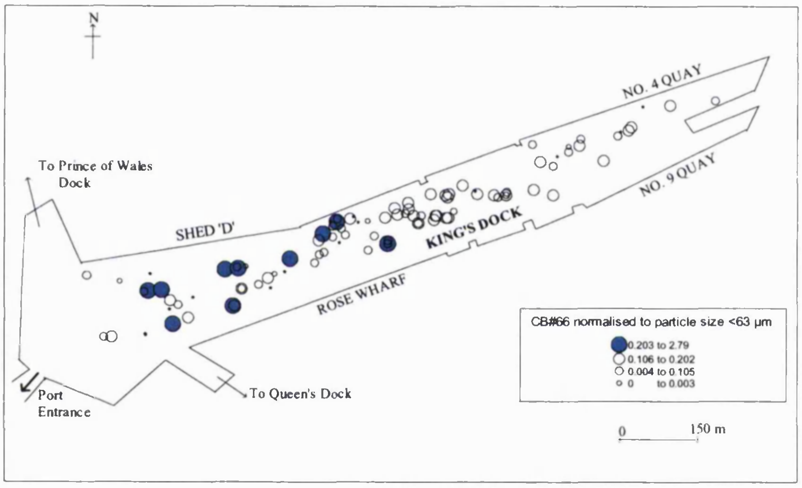


(f)

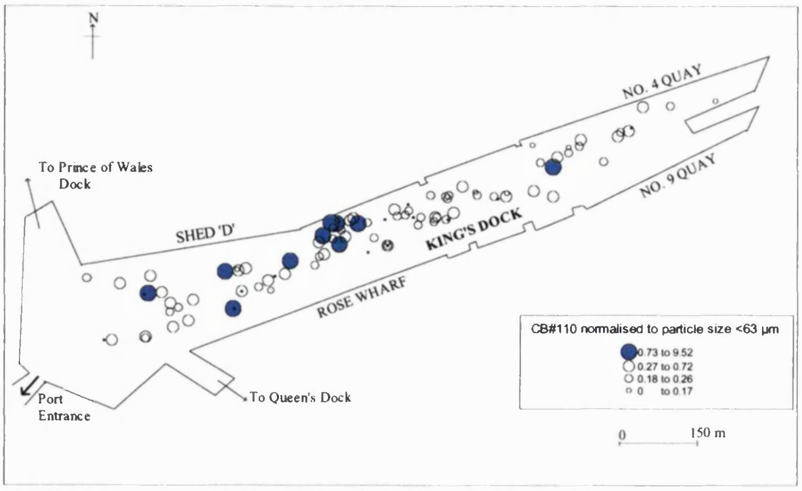
Figure 4.11: Distribution of selected CBs normalised to TOC across King's Dock: CB#28 (a); CB#66 (b); CB#110 (c); CB#153 (d); CB#180 (e) and CB#194 (f).


N
NO. 4 QUAY
NO. 9 QUAY
To Prince of Wales Dock
SHED 'D'
KING'S DOCK
ROSE WHARF
Port Entrance
To Queen's Dock
CB#28 normalised to particle size <63 µm
0.41 to 0.8
0.21 to 0.4
0.11 to 0.2
0 to 0.1
0
150 m

(a)


N
NO. 4 QUAY
NO. 9 QUAY
To Prince of Wales Dock
SHED 'D'
KING'S DOCK
ROSE WHARF
Port Entrance
To Queen's Dock
CB#66 normalised to particle size <63 µm
0.203 to 2.79
0.106 to 0.202
0.004 to 0.105
0 to 0.003
0
150 m

(b)


N
NO. 4 QUAY
NO. 9 QUAY
To Prince of Wales Dock
SHED 'D'
KING'S DOCK
ROSE WHARF
Port Entrance
To Queen's Dock
CB#110 normalised to particle size <63 µm
0.73 to 9.52
0.27 to 0.72
0.18 to 0.26
0 to 0.17
0
150 m

(c)

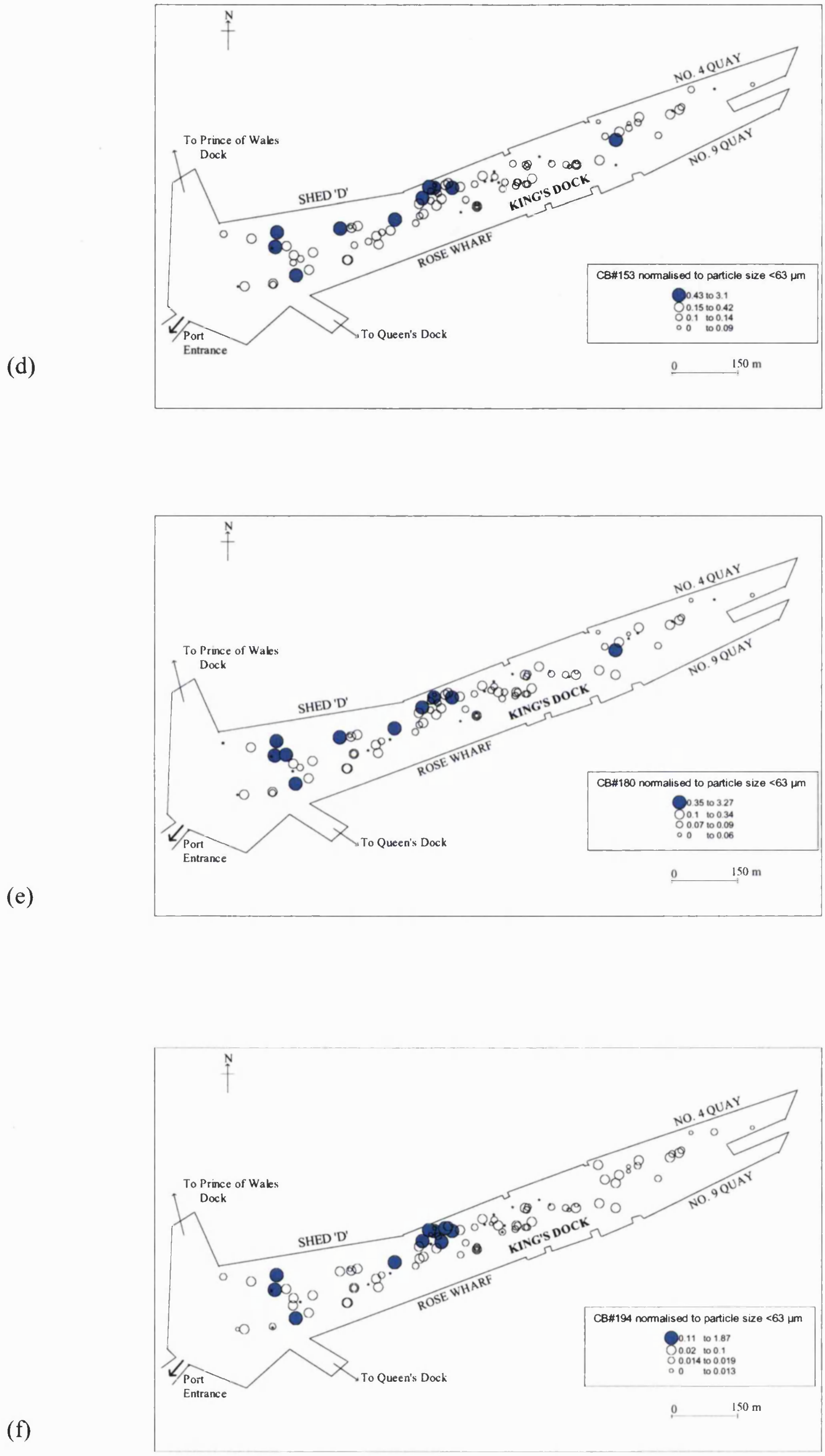


Figure 4.12: Distribution of selected CBs normalised to particle size across King's Dock: CB#28 (a); CB#66 (b); CB#110 (c); CB#153 (d); CB#180 (e) and CB#194 (f).

determine possible point sources within the dock (Section 4.2) and to estimate the components or sources of spatial variability within the study site (Section 4.3).

4.2 Multivariate classification

Multivariate classification techniques involve the analysis of several related random variables simultaneously, each one considered equally important at the start of the analysis (Manly, 1995). The application of multivariate statistical methods such as Principal Component Analysis (PCA) and Cluster Analysis (CA) has been adopted by several authors who believe this integrated approach is the most appropriate for the examination of large environmental databases (Einax *et al.*, 1992; Zitko, 1994; Ausili *et al.*, 1997). Moreover, a multivariate analysis approach can be used successfully for the identification and assessment of sources of contamination and for the characterisation of various geochemical and chemical processes related to anthropogenic activities (DelValls *et al.*, 1998). These techniques aim to detect similarities, differences and/or relationships among samples (Zitko, 1994). King's Dock sediment PCB concentrations are therefore examined using PCA and CA techniques to determine any clusters of similarity between samples and to identify potential mixtures of Aroclors® responsible for the PCB sediment distribution in the dock.

4.2.1 Principal Component Analysis (PCA)

Principal component analysis is a technique that reduces the number of variables being considered to a small number of indices, known as principal components, that are linear combinations of the original variables (Manly, 1995). The principal components are orthogonal planes that are fitted to the data and which account, sequentially, for decreasing amounts of variance. This is a parametric technique which assumes that the data has a normal distribution. Accordingly, data should be log transformed if necessary and/or standardised if different units or scales are involved (Chappell, 1995). The advantage of this technique is that the variation in the data can be accounted for more concisely than univariate statistics. In this case, PCA is employed to identify the main congeners producing the greatest variation in the data.

In this study, PCA is performed on the correlation matrix, i.e. upon variables that are auto-scaled (standardised). All analyses are performed using the principal component option in the Genstat® software package (Genstat, 1997). As shown in the preceding sections, the PCB data are highly skewed and as PCA is a technique sensitive to outliers, samples were removed until the skew of all individual CBs and total CBs was considerably reduced (<1). The data used in the analysis (see Appendix 5) were subsequently untransformed (*n*=88). The 13 samples removed from the PCA analysis are regarded as 'hotspots' on the basis that their total PCB concentration is $> 200\ \mu g\ kg^{-1}$.

The application of PCA to the 25 variables indicates that these can be represented by five principal components, which together account for 95.4% of the total variance (Table 4.1). Most of the variance (85%) is explained by the first three principal components. This suggests a large amount of inter-correlation between congeners which explain the majority of the variance.

The component loadings for each congener are shown in Table 4.2. The highlighted dominant loadings may be used for the interpretation of the first two principal components (Figure 4.13). The first principal component is dominated by CB#110, #138, #118 and #153 in decreasing order of importance. This component accounts for ~60% of the variance and has positive loadings on the concentrations of CBs. The second principal component is dominated by CB#66, #28, #31 and #101. Examination of a plot of principal component scores in the first two principal components (Figure 4.14) reveals the variation in the congeners that load heavily on the principal components.

An examination of the loading plot (Figure 4.13) indicates that much of the spread in the composition of the sediments is caused by three groups of CBs. First, there is CB#110. Second, there are CB#28, #31 and #66. Third, there are CB#101, #118, #138 and 153. In Figure 4.14, the first and second groups of CBs causes sediments to be separated in the top right quadrant when concentrations are high. The reverse is true when concentrations are low.

The third group of CBs causes sediments to separate in the bottom right quadrant, again this is when concentrations are high. The sediment samples located furthest in the right quadrant particularly resemble the profile of Aroclor® 1254 and 1260 because of the high abundance of hexa- and hepta-CBs. Principal component 1 describes the potential sources of commercial Aroclor® mixtures responsible for the sediment homologue profiles. This is because CBs that dominate principal component 1 also contribute a high percent abundance to specific mixtures. The most likely potential Aroclor® mixtures contributing to PCB loadings in King's Dock are therefore 1254 and 1260/62.

The second principal component represents sediments that have high concentrations of less chlorinated tri- and tetra-CBs and lower concentration of the penta- and hexa-CBs compared to those separated along PC1. The separation of these sediments suggests that principal component 2 describes possible processes influencing those congeners that are found to be present. Such processes may include, dechlorination (van Zoest & van Eck, 1990), adsorption (DelValls *et al.*, 1998) and anthropogenic activities (such as ship movements and dredging) causing turbation of sediments (Achman *et al.*, 1996; DelValls *et al.*, 1998). Specific mechanisms to explain the enrichment of less chlorinated congeners in marine particulates are reported by van Zoest & van Eck (1990). They suggest three mechanisms are responsible including atmospheric deposition, degradation of more chlorinated congeners and discharges of PCB mixtures enriched in these congeners.

The outcome from the multivariate analysis remains somewhat speculative, and other interpretations may be possible. However, the principal component scores provide an insight into the structure of the data and its interpretation in terms of the commercial Aroclor® mixtures which are most likely to be responsible for sediment homologue profiles observed.

4.2.2 Cluster Analysis (CA)

Cluster analysis is another multivariate technique used to identify a number of groups containing similar properties (Manly, 1995). The optimum number of groups required to best describe a multivariate data set is defined by using the Wilk's criterion (Webster & Oliver, 1989). The technique is non-hierarchical clustering using the sum of squares criterion. This technique identifies the number of groups required to fit all of the similarities in the data. The aim in this section is to identify any similarities between sediments sampled throughout King's Dock and to investigate the specific mechanisms/processes that may be operating between clusters of samples.

Table 4.1: Principal component eigenvalues of multiple congeners in sediments obtained at sites throughout King's Dock.

Principal Components	Latent Roots	% Variance	% Cumulative Variance
1	5022	58.9	58.9
2	1515	17.8	76.7
3	715	8.4	85.1
4	575	6.7	91.8
5	305	3.6	95.4

Table 4.2: Principal component loadings of multiple congeners in sediments obtained at sites throughout King's Dock.

Principal components	1	2	3
CB#18	0.04543	0.14273	0.06556
CB#28	0.18429	**0.58887**	0.01081
CB#31	0.0883	**0.29464**	0.04702
CB#44	0.09236	0.0487	-0.00374
CB#47	0.02694	0.02683	0.02436
CB#49	0.0766	0.01504	-0.01027
CB#52	0.16638	-0.0441	-0.03596
CB#66	0.01415	**0.61394**	**0.4317**
CB#101	0.25763	**-0.21025**	0.1021
CB#105	0.13192	0.02594	0.00067
CB#110	**0.59169**	0.16067	**-0.67957**
CB#118	**0.31585**	-0.08643	0.13862
CB#128	0.06565	-0.02123	0.0401
CB#138	**0.3411**	-0.10969	0.22463
CB#141	0.06649	-0.02563	0.04425
CB#149	0.22381	-0.13653	0.15663
CB#151	0.06607	-0.03103	0.04715
CB#153	**0.31075**	-0.1475	0.23256
CB#156	0.06108	-0.00669	0.02951
CB#158	0.0402	-0.01246	0.01877
CB#170	0.11423	-0.02001	0.09677
CB#180	0.23659	-0.07325	0.28068
CB#183	0.05131	-0.01434	0.0566
CB#187	0.14891	-0.13672	0.25976
CB#194	0.06528	-0.07959	0.13652

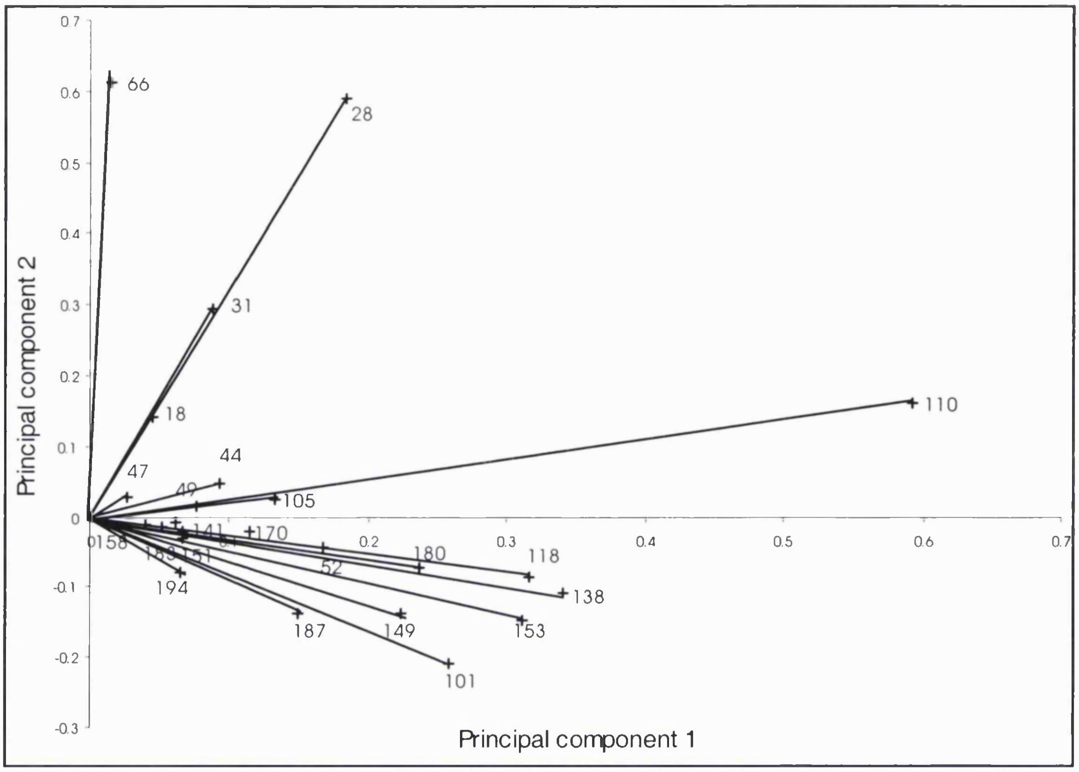


Figure 4.13: Individual CB eigenvalues plotted in the plane of the first two principal components.

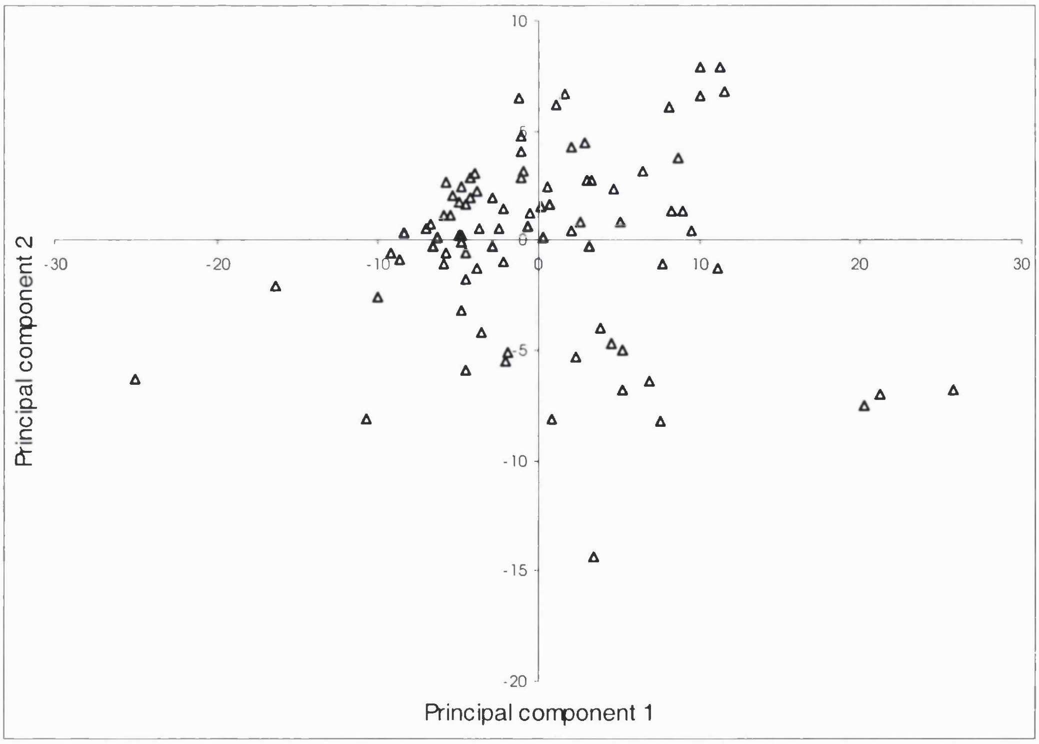
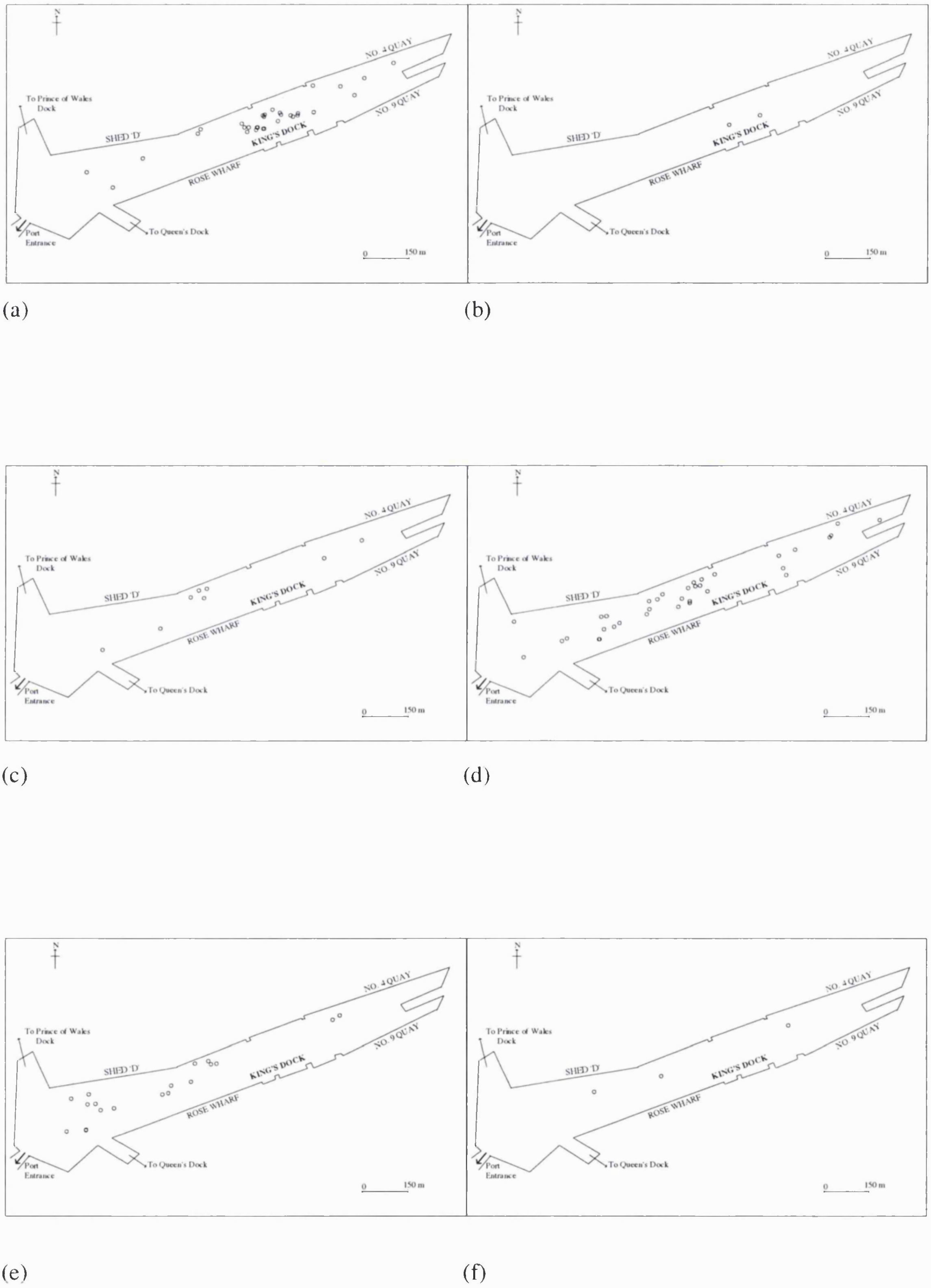


Figure 4.14: Principal component scores plotted in the plane of the two first principal components.



(a) (b)

(c) (d)

(e) (f)

Figure 4.15: Distribution of sampling sites within King's dock: cluster 1 (a); cluster 2 (b); cluster 3 (c); cluster 4 (d); cluster 5 (e) and cluster 6 (f).

In this analysis, sediment samples (*n*=88) are clustered into six groups using Genstat® software (Genstat, 1997) and each group is plotted using Mapinfo® software (Figure 4.15). This approach provides an easy way of visualising the spatial distribution of similar clusters of samples.

Sediments in cluster group 1 have homologue profiles comparable to those found in the Severn Estuary (Section 3.2.4). These profiles are characterised by equal contributions (~20%) from tri- and tetra-CBs, higher contributions (~25%) from penta- and hexa-CBs and a 'step-like' progression of decreasing contributions from hepta- and octa-CBs. These sediments are located towards the middle and east side of the dock between Rose Wharf and No. 9 Quay.

In cluster group 2, there are only two sites and these are located close to Shed D and at the entrance to King's Dock. These sediments exhibit very high concentrations of tri-CBs and low concentrations, on average, of hexa-CBs. Conversely, sediments in cluster group 3 have lower tri- and tetra-CBs and high contributions from the hexa- and hepta-CBs. In cluster group 4, sediments are located throughout the dock and are similar to cluster group 1 except these sediments have slightly less contributions from tri-CBs. This group and cluster group 1 are similar to sediments in cluster group 5 except this group contains sediments exhibiting less tri-CBs and higher contributions from penta- and hexa-CBs. These sediments are clustered at sites close to the entrance to all three docks, opposite Shed D and opposite No. 4 Quay. Finally, sediments in cluster group 6 have low contributions of tri-CBs and high contributions of penta-CBs. These sites are distributed, separately, opposite Shed D, Rose Wharf and No. 4 Quay.

The separation of the six cluster groups is mostly associated with the relative contributions of two groups of homologues. First, the tri-CBs and second, the penta-, hexa- and hepta-CBs. Sediments are separated by contributions of specific homologue groups and this has also been shown in Figure 4.14. Similar sites have been identified using both techniques, for example, sediments containing high concentrations of the less chlorinated CBs (identified as cluster group 2) are also identified in the top right quadrant of Figure 4.14. Cluster groups 1, 4 and 5 have similar features and these sediments are located in Figure 4.14 close to the origin of PC1 and PC2 providing corroborative evidence of mixed Aroclor® sources. Sediments in Cluster group 3 have higher contributions of the hexa-CBs (CB#138 and CB#153) and, as such, plot in the bottom right quadrant of Figure 4.14. Sediments in cluster group 6 plot similarly in this quadrant due to high contributions of the penta-CBs (CB#101 and #118). Both these techniques have established a number of sites within the dock that have similar properties. The contributions of specific homologue groups to sediment profiles have established sites that could be potential source points and principal component analysis has identified sites that contain a mixture of specific commercial mixtures (Aroclor® 1254 and 1260). Cluster analysis also established sites containing average PCB concentrations suggesting that these sites are contaminated away from the point source, probably as a consequence of sediment resuspension and therefore the dispersion of PCBs by shipping activities within the dock.

4.3 Sediment sampling for sources of spatial variability

During the survey of King's Dock, samples were taken to estimate the magnitude of spatial variability at three levels of replication (i.e. *sites*, *grabs* and *subsamples*) within the sampling area. During sampling, nine *sites* were selected for replicate grab samples or *sites*, and for three individual *grabs*, the sediment was sampled to provide replicate *subsamples* within a *grab*. The components of variance in total PCBs are estimated between *sites*, between repeat *grabs* taken at a *site*, and between replicate *subsamples* of a sediment within a *grab*. This statistical technique is described in Zar (1984).

Figure 4.16 shows the spatial distribution within the dock of the replicate *sites* (i.e. those sites where repeat *grabs* and *subsamples* were taken). The spatial distribution of *All Sites* is shown previously in Figure 2.15. The estimation of the components of variance for Total PCBs, the ICES 7 CBs, individual ICES 7 CBs and two additional CBs which, on average, account for more than 5% of the Total PCB concentrations (Σ_{25}CBs) is presented in Table 4.3.

The left-hand section of Table 4.3 shows the means and estimated components of variance for Total PCBs, ICES7 and nine individual CBs at replicate *sites* (i.e. *Replicate Sites*). The total standard deviation is the square root of the sum of the squares of the between *subsample*, between *grab* and between *site* standard deviations. The right-hand section of Table 4.3 shows the mean, total standard deviation from *All Sites* and the estimated between *site* standard deviation. The latter is obtained by subtracting the squares of the between *subsamples* and between *grab* standard deviations estimated from *Replicate Sites* (as above) from the square of the total standard deviation from *All Sites*.

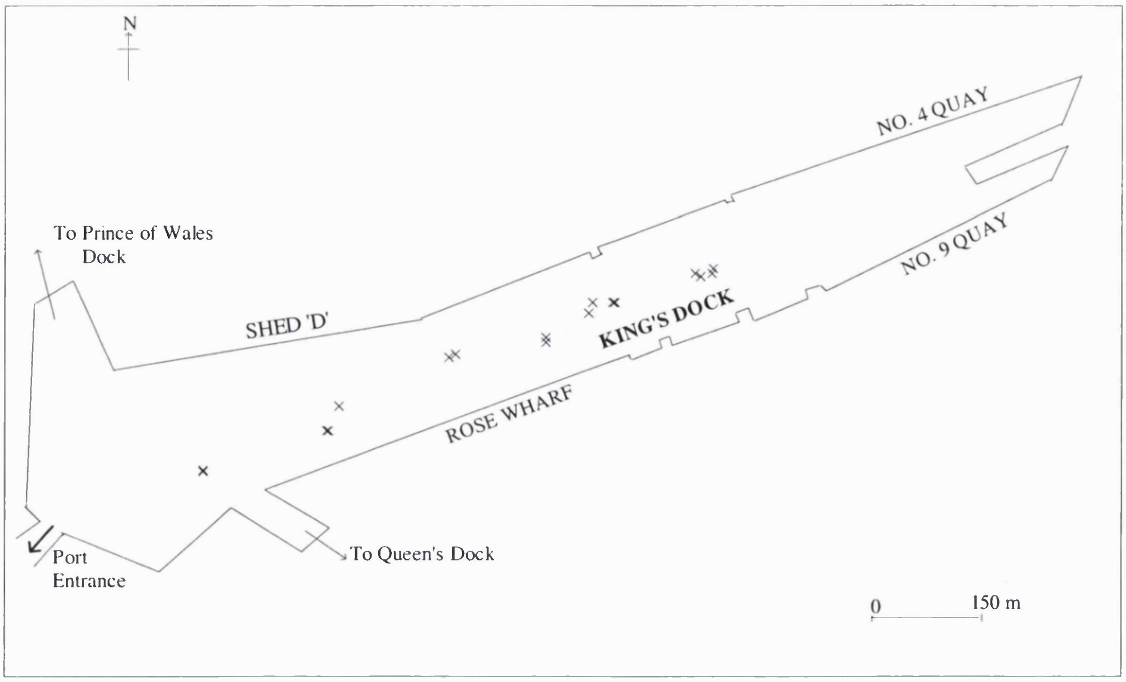


Figure 4.16: Distribution of sampling sites within King's Dock at replicate *sites*.

On closer examination of the data from *All Sites*, there appear to be two samples (with extremely high concentrations for most CBs, i.e. samples 8g and 1g) largely responsible for the very high total standard deviations. The analysis of the *All Sites* data was thus repeated but with these two samples excluded. The final three columns show the resultant lower *total* standard deviations.

The variability shown in Table 4.3 can be attributed to a combination of sampling error, precision of analytical measurement and the inherent variability of the sample population (Kelly *et al.*, 1994). To determine the effects of variance from chemical analysis, data were obtained from CEFAS regarding analytical quality (Allchin, pers. comm., 2000). Table 4.4 shows the current relative standard deviations obtained from repeated chemical analyses of replicate samples for individual ICES 7 CBs together with the corresponding standard deviations expressed relative to the mean concentrations of *Replicate Sites* and *All Sites*.

The most prominent feature of Tables 4.3 and 4.4 is the large difference between the *total* standard deviations estimated from the *Replicate Sites* (22% of *All Sites*) and those estimated from *All Sites* (100%). There is no evidence of any between *site* variability at

Replicate Sites for Total CB and ICES 7 CB concentrations. This suggests that *Replicate Sites* sampling considerably under-estimates the true variability in the dock. This may be due to the narrow range of the *Replicate Sites* data (i.e. the small sample size). The sampling distance between *sites* was ~150 m and similar scales of variability was found by Rice *et al.* (1993) and Brown & Fish (1999).

Research conducted by Rice *et al.* (1993) in Moss Landing sediments (California, USA) found that the major sources of variability of ∑PCBs were between sites and random effects. Similarly to the results described above for King's Dock, they also found that subsites within each site contributed little variability. These results suggest that over large spatial scales, sediments are generally heterogeneous, with local 'hot spots' of very high concentrations. Indeed, a small proportion (2%) of samples in King's Dock have extremely high concentrations. Conversely, sediments are more homogeneous over small spatial scales. It is likely that the major source of variance in King's Dock sediment PCB levels is attributed to spatial variability. This agrees with the findings of other researchers (Boehm & Farrington, 1984; Galassi & Migliavacca, 1986; Rice *et al.*, 1993).

The contribution of the variance associated with the appropriate analytical procedure, for some CBs, appears to be a large element of the between *subsample* component of variability. This provides corroborative evidence supporting the belief that PCB concentrations in sediments are homogeneous over small scales.

Table 4.3: Summary of means and components of variance.

	Replicate Sites					*All Sites*					
						(All data)			(2 extreme samples excluded)		
	Mean	*Between sub samples*	*Between grabs*	*Between sites*	*Total*	*Mean*	*Between sites*	*Total*	*Mean*	*Between sites*	*Total*
CB#28	10.4	5.9	0.0	0.9	6.0	11.2	5.7	5.7	10.9	4.9	4.9
CB#52	5.0	0.1	0.5	0.6	0.8	7.8	3.3	16.7	5.9	3.3	3.3
CB#101	6.3	0.3	0.8	1.1	1.4	12.4	7.3	32.1	8.6	7.3	7.3
CB#110	16.2	3.8	0.0	0.8	3.9	28.2	13.8	68.3	20.2	13.8	14.3
CB#118	7.6	2.8	0.0	0.0	2.8	15.9	12.2	34.1	11.5	12.2	12.5
CB#138	9.2	0.7	1.6	0.5	1.8	17.8	14.1	34.7	13.4	14.1	14.2
CB#149	6.6	0.8	0.5	0.9	1.3	11.3	8.8	22.9	8.7	8.8	8.8
CB#153	8.2	0.3	1.4	0.7	1.6	15.6	13.3	28.5	12.0	13.3	13.4
CB#180	5.9	0.2	1.4	0.0	1.4	11.5	13.5	21.5	9.4	13.5	13.6
ICES 7 CBs	52.1	9.3	5.8	0.0	10.9	91.6	62.7	160.7	71.3	62.7	63.6
Total CBs	118.9	12.2	15.7	0.0	19.9	200.8	127.2	347.1	157.0	127.2	128.7

ICES 7 CBs include CB#28, #52, #101, #118, #138, #153 and #180.

Table 4.4: Components of variance as % relative standard deviations.

	Replicate Sites					*All Sites*			
						(All data)		(2 extreme samples deleted)	
	AQC[*]	*Between sub samples*	*Between grabs*	*Between sites*	*Total*	*Between sites*	*Total*	*Between sites*	*Total*
CB#28	9.9	56.9	0.0	8.9	57.6	50.9	50.9	45.0	45.4
CB#52	8.7	2.8	9.3	12.8	16.0	41.6	213.6	54.7	55.3
CB#101	8.2	4.0	12.6	18.0	22.3	58.5	258.9	83.8	84.4
CB#110	-	23.4	0.0	5.0	23.9	48.9	242.2	68.4	70.9
CB#118	9.7	36.7	0.0	0.0	36.7	76.7	214.5	105.6	108.3
CB#138	8.9	7.1	17.3	5.0	19.3	79.2	194.9	105.0	105.8
CB#149	-	12.0	7.5	13.2	19.3	77.4	202.7	100.7	101.3
CB#153	8.5	3.7	17.2	8.6	19.6	85.4	182.7	110.6	111.3
CB#180	11	3.8	24.1	0.0	24.4	117.7	186.5	143.7	144.5
ICES 7 CBs	-	17.8	11.1	0.0	21.0	68.4	175.4	87.8	89.2
Total CBs	-	10.2	13.2	0.0	16.7	63.3	172.9	81.0	82.0

[*] *Analytical Quality Control*

4.3.1 Comparisons of distributions of *Replicate Sites* and *All Sites*

A comparison between *Replicate Sites* and *All Sites* was conducted to determine any differences in spatial variability and representativeness of data collected at *All Sites*. The distribution of Total CB concentrations at *Replicate Sites* (Figure 4.17) is in contrast to the *All Sites* distribution shown in Figure 4.2 above. Although the shape of the distributions below 300 $\mu g\ kg^{-1}$ are very similar, there is an additional spread of high concentrations for *All Sites* that is not evident in the *Replicate Sites*. As mentioned previously, there is a tendency for sampling positions for *All Sites* corresponding to concentrations above 300 $\mu g\ kg^{-1}$ (the highest 10%) to be located in the western half of the dock. However, comparisons with Figure 4.16 shows that although some sampling positions for the *Replicate Sites* also fall in this western half, concentrations here are not as elevated (Figure 4.18).

The relationship between CB concentrations and TOC and particle size in sediments at *Replicate Sites* is investigated. A similar relationship found at *All Sites* was also found at *Replicate Sites*. In other words, there is no discernible relationship between TOC or particle size and Total PCBs. Conversely, research undertaken by Rice *et al.* (1993) found a significant difference between subsites based on sediment TOC concentrations. Rice *et al.* (1993) suggested that depositional factors may be responsible for these subsite differences. As shown previously, such differences are not found in King's Dock.

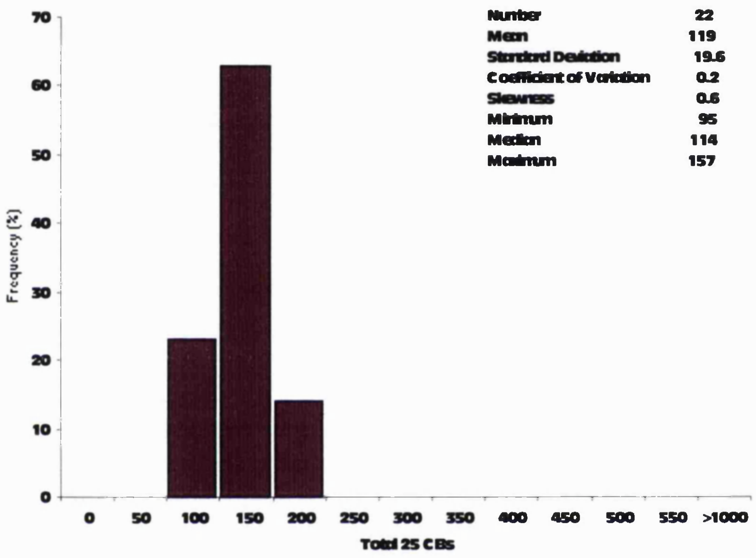


Figure 4.17: Frequency histogram and some summary statistics of $\sum_{25}$CBs in sediments at *Replicate Sites* in King's Dock.

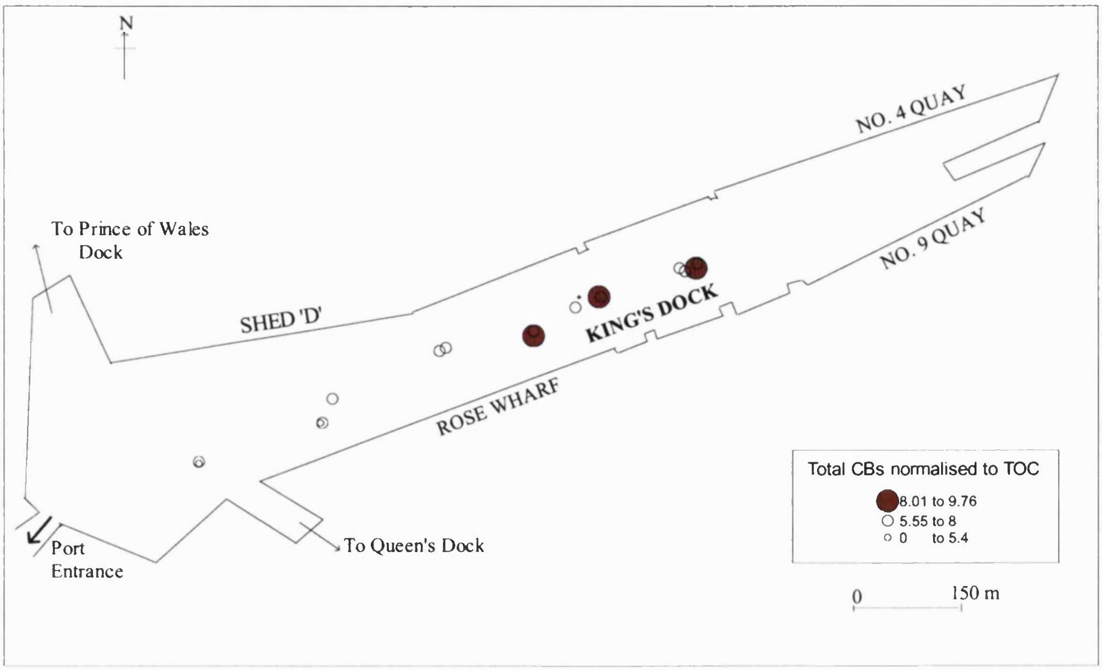


Figure 4.18: Distribution of Total PCB concentrations (µg kg^{-1}) at *Replicate Sites* in King's Dock.

4.3.2 Conclusions and implications for survey design

The assessment of dredged material aims to establish the distribution of measured contaminants focusing on both the overall magnitude and the identification of elevated concentrations or 'hotspots'. This study of spatial variability has found two important features. First, the between *site* and *total* standard deviations estimated from the *Replicate Sites* sampling points considerably *under-estimate* the true variability in the dock. This suggests that it would be necessary to identify many sampling points to obtain a reasonable estimate of the mean, and especially of the spatial distribution. That is to say, the power of sampling should be increased in the future to address the issues of under estimation. This is discussed further in Section 6.3. Second, the variability of the within-grab *subsamples* is attributed to the analytical variance suggesting that at a very small spatial scale, PCB concentrations are homogeneous.

In this case study, it may be beneficial to stratify the dock, for example by dividing it into eastern and western areas prior to sampling. This would enable the identification of sites exhibiting elevated concentrations generally identified in the west. In the eastern region, sampling could be directed at establishing lower concentrations (i.e. to represent the overall magnitude of their distribution) but sampling intensity could be reduced here. However, to determine the spatial distribution of PCBs, a large number of sediments should be sampled overall to minimise 'field variance'. The uncertainty of estimated mean concentrations of contaminants can be between 20 to 50 % depending on the location and properties of the site (Krumgalz *et al.*, 1989; Kelly *et al.*, 1994; Ramsey & Argyraki, 1997). The costs associated with analysing large numbers of sediment samples for PCBs and other contaminants are high and in terms of government regulatory budgets, unrealistic. However, the issues highlighted by various legislative frameworks suggests that the protection of the marine environment is of the utmost concern. European initiatives, such as the reduction of hazardous substances by 2020, provides a promising first step but requires financial commitment to be completely successful.

4.4 Summary

In this case study, more intensive sampling has established the spatial distribution and magnitude of PCB concentrations in sediments in King's Dock. Moreover, multivariate techniques have estimated structures in the PCB data and have proven successful in the identification of potential sources, in terms of commercial Aroclor® mixtures. These techniques also provide insights into environmental mechanisms and processes operating in the dock. Sampling at very small scales has established sources of spatial variability and assisted with the interpretation of PCB distributions over larger scales.

Cost-effective monitoring requires optimum numbers of samples to assess the distributions of sediment PCB concentrations. Several studies have considered optimal surveys for repeated sampling over time (Rice *et al.*, 1993; Kelly *et al.*, 1994). An increasingly important issue today is the limited financial resources available for environmental monitoring. To address this, modelling of contaminant concentrations is one method that can be effective. However, estimation techniques are only as good as the models fitted to the data and the quality and quantity of field data. The estimation of PCB concentrations at unsampled locations, for example, could provide better inventories of contaminants. The next stage, therefore, considers modelling the spatial structure and pattern of PCBs, to use the models to estimate concentrations at unsampled locations, assess the sampling effort required to perform the statistical computations and to calculate total PCB loadings in sediments prior to licensing dredged material to sea.

CHAPTER FIVE

Geostatistical Analysis of Sediment PCBs in King's Dock, Swansea

This chapter uses geostatistical methods to investigate the spatial structures and patterns of individual CBs, total CBs and the supporting environmental parameters, total organic carbon (TOC) (%) and particle size (% <63 μm), in the sediment of King's Dock. Sample variograms are estimated and modelled in order to characterise the spatial variation of individual congeners. Ordinary kriging is then employed to estimate CB inventories for the dock. The computation of variograms using less sampling effort is attempted and the implications of different sampling intensities for the subsequent estimation of total loadings using ordinary kriging are discussed.

5 Introduction

A problem with current risk assessment protocols for PCBs in dredged material is that unrepresentative sampling may lead to the misclassification of contaminated material. This in turn may lead to the unintended redistribution of these compounds into the marine environment. A more scientifically-informed approach, one which aims to understand and take account of the spatial variability in PCB contamination, might significantly improve the accuracy of such risk assessments and improve the quantification of the risks posed by PCBs.

Many studies have shown that the geographical distribution of contaminants can be autocorrelated in space and time (Oliver & Webster, 1986a; Oliver & Webster, 1989; Quevauviller, 1995). Autocorrelation can be defined as the pattern and spatial interrelationship of phenomena (Oliver & Webster, 1986a). One of the most effective tools for determining spatial scales, patterns of variation and to improve sampling efficiency is a variogram (Burgess & Webster, 1984; Webster & Oliver, 1990; Cressie, 1991; Hunt, 1996; van Tooren & Mosselman, 1996; Stoeppler, 1997; Wang & Qi, 1998). The variogram is a graph which has a distance (lag distance) plotted against the mean value of the squared difference between samples at a distance (h) apart ($\gamma(h)$). It represents the continuity of a random variable. As the $\gamma(h)$ increases, there is less similarity between samples. The nature of this increase is important and can inform something about the nature of the continuity of the random variable. Also, spatial structures can be determined from the variogram and this is generally dependent on the behaviour of the variable in the range (Matheron 1963). It is possible to use variograms to determine the spatial continuity at short and long distances (Pitard, 1988) and to identify potential underlying processes responsible for the variation and spatial structure (Oliver, 1987; Chappell *et al.*, 1996). The variogram can be used to estimate the optimum number of samples required for future sampling campaigns and can be used to determine the variation in other areas (Burgess & Webster, 1984; Russo, 1984; van Groenigen & Stein, 1998).

Defining the variogram is the first important task and this approach has been adopted in King's Dock to investigate spatial dependence, structure and patterns of CBs over a variety of spatial scales.

The objectives of the geostatistical analysis carried out here are as follows:

1. to use the variogram to investigate the spatial structure and patterns of individual CBs, total CBs and related environmental parameters (TOC (%) and particle size (% $< 63\ \mu$m));

2. to infer, from the variogram, possible mechanisms governing the spatial distribution of individual CBs in sediments;

3. to achieve a more precise estimation of sediment PCB loadings prior to the evaluation of a dredging licence application for the dock; and

4. to assess the minimum sampling effort required for future sampling of PCBs in dock sediments.

5.1 Regionalised variable theory

Geostatistics has been developing since the early 1900s (Mercer & Hall, 1911; Youden & Mehlich, 1937) but it was not until the 1960s that its application was fully demonstrated. Matheron (1971) applied geostatistical techniques to improve the estimation of ore grade in mining. Here, the important concept of geostatistics, that is the regionalised variable, was realised. A regionalised variable is a random variable. It is defined by a function which describes the geographical distribution of natural phenomena. The theory is that the variation in an attribute Z may be defined by a stochastic component and a constant (Oliver *et al.*, 1989a), such that:

$$Z_{(x)} = \mu_v + \varepsilon_{(x)} \qquad [5.1]$$

where x represent the spatial co-ordinates, μ_v is the mean in an area, v, and $\varepsilon_{(x)}$ is the spatially dependent random variable. The latter has a mean of zero and a variance which is given by:

$$\mathrm{var}[\varepsilon(x) - \varepsilon(x+h)] = E\left[\{\varepsilon(x) - \varepsilon(x+h)\}^2\right] = 2\gamma\,(h) \qquad [5.2]$$

where h is a vector, the lag, that separates the two sites x and x + h in both the direction and distance. It is the separation, not the position of h itself, that determines the variance of $\varepsilon(x)$. The mean and the variance of the differences are assumed to be stationary, supporting the intrinsic hypothesis (Matheron, 1971). However, if there is local drift or trend present, the intrinsic hypothesis does not hold. In this case, the trend in the property is removed and a variogram is estimated using the residuals (Oliver, 1987; Chappell, 1995).

A regionalised variable is spatially continuous, and geostatistical techniques estimate its rate and manner of change along a specific plane or orientation in one, two or three dimensions. The degree of spatial dependence between samples is measured by the semivariance, which expresses the rate of change of a regionalised variable (Davis, 1986). The semivariances, $\gamma(h)$, or variogram, is half the expected squared difference between two values separated by a lag, h. The sum of the squared differences between the pairs of points separated by the distance interval is calculated. These semivariances are plotted against the lag distance to form a variogram.

The theory of regionalised variables has been reviewed by many including Matheron (1971), Isaaks & Srivastava (1989) and Webster & Oliver (1990). Central to this theory is the notion that phenomena are spatially dependent but have geographical distributions that cannot be adequately defined by deterministic functions. Geostatistics applies the theory of regionalised variables to determine the random and structured nature of spatial variables and the variable's spatial distribution. This structured component is related to the spatial dependence of variables (Oliver, 1987).

5.2 Variogram estimation and modelling

A variogram is defined as 'a function that characterises the second-order dependence properties of a stochastic process defined on the *m*-dimensional Euclidean space' (Encyclopedia of Statistical Sciences, 1988). The variogram is typically a measure of the similarity, on average, between points a given distance, h, apart (Burgess & Webster, 1984). Other measures can be used, such as the median (see Cressie, 1991). The equation for calculating the variogram is:

$$\gamma(h) = \frac{1}{2M(h)} \sum_{i=1}^{M(h)} \{z(x_i) - z(x_i + h)\}^2 \qquad [5.3]$$

where M(h) is the number of comparisons at a given lag (h), and $z(x_i)$ and $z(x_i + h)$ are the observed values of a property Z at x_i and x_i+h, respectively. By changing the lag (h) an ordered set of values is obtained, which is the experimental or sample variogram.

The form of the variogram is typically either bounded by a *sill*, where semivariances calculated from different separation distances reach a level where the values do not increase, or do not have a sill and are unbounded (Figure 5.1). The *range* or span of the variogram is the distance at which the semivariance approaches the sample variance (or sill) and this defines a neighbourhood within which all locations are related to one another. The range thus defines the limit of spatial dependence. The samples within this neighbourhood can be used to estimate the regionalised variable (Diamond & Armstrong, 1984). The shape and form of the initial slope of the variogram, within the range, can indicate the rate of change in the property. If there is no range, the variogram is described as pure nugget (i.e. its variance remains the same at increasing lags).

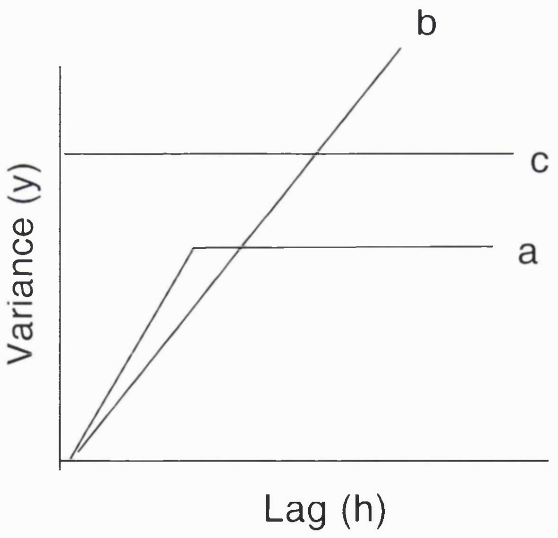


Figure 5.1: Bounded (a), unbounded (b) and pure nugget (c) variogram models (adapted from *Oliver & Webster, 1991*).

The semivariances are generally modelled to estimate the underlying sample variogram. There are different methods of modelling the variogram. The model fit is especially important in the first few lags as this affects kriging variances (see Section 5.3 below). The model parameters are used in kriging, a method that, in this case study, allows the estimation of individual CBs, total CBs and environmental parameters in the dock sediment. The models used to fit sample variograms in this study include the circular, spherical, exponential and linear model (Figure 5.2). The model that best explains the percentage variance is selected as the 'best fit'. The equations for each of these models are as following:

linear model (*Isaaks & Srivastava, 1989*);

$$\gamma(h) = |h| \qquad [5.4]$$

spherical (*Webster & Oliver, 1990*);

$$\left\{ \gamma(h) = \mathrm{c} \left\{ \frac{3h}{2a} - \frac{1}{2}\left(\frac{h}{a}\right)^3 \right\} \text{for } h \leq a \right. \qquad [5.5]$$

circular (*Webster & Oliver, 1990*);

$$\left\{ \gamma(h) = \mathrm{c} \left\{ 1 - \frac{2}{\pi}\cos^{-1}\frac{h}{a} + \frac{2h}{\pi a}\sqrt{\left(1 - h^2/a^2\right)} \right\} \text{for } h \leq a \right. \qquad [5.6]$$

exponential (*Isaaks & Srivastava, 1989*).

$$\gamma(h) = 1 - \exp\left(-\frac{3h}{a}\right) \qquad [5.7]$$

where a is the range of the model (which marks the limit of spatial dependence), h is the lag and c is the sill variance.

As shown in Figure 5.2, the linear model does not reach a sill but continues to increase as the lag (h) increases. The spherical model behaves linearly over the smaller lags nearest the origin but flattens out, reaching the sill at larger distances. The sill is reached at approximately two thirds of the range. The circular model is similar to the linear model at smallest lags but curves markedly as h approaches the sill. The exponential model is also linear at very short distances near to the origin, but rises less steeply before reaching the sill. This model reaches its sill asymptotically. The effective range of spatial dependence is expressed as 3 times that of the value provided by the model. The sill is approximately one fifth of the range (Webster & Oliver, 1990).

The accuracy of the variogram is determined by the number of samples and of inter-site comparisons at different lags. Webster & Oliver (1992) have shown that the latter affects the magnitude of semivariance error. Subsequently, research has shown that a variogram should be reliable at 225 sample sites and that approximately 100 sites is recommended as a minimum. The number of samples will affect the quantity of comparisons that determine the variogram and therefore affect the accuracy of the model fit and subsequent estimation. The sampling design, that is the sample location and spacing over short and long distances, is also a contributing factor to the variogram reliability.

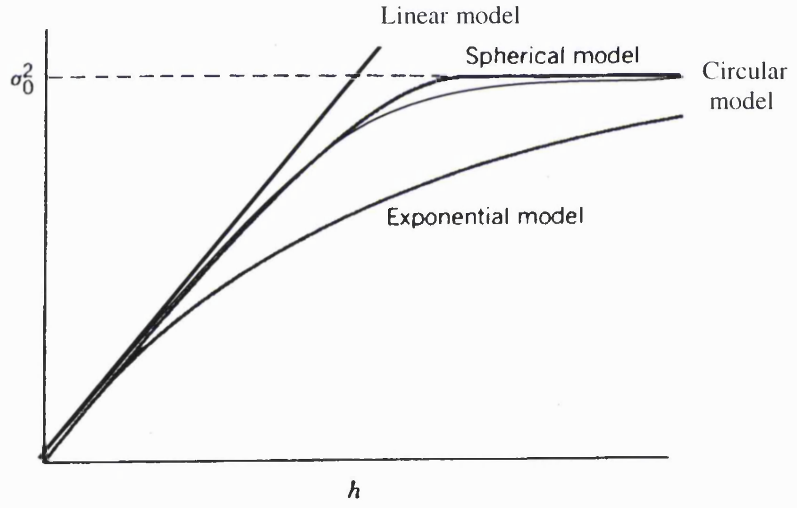


Figure 5.2: Linear, spherical, circular and exponential models (*Isaaks & Srivastava, 1989; Webster & Oliver, 1990*).

In the present study, summary statistics of the variables and their histograms were computed to identify any outliers in the data and to determine the extent of any departure from a normal distribution (Journel, 1983; Rossi *et al.*, 1992; Miller, 1993). To ensure the variogram was reliable, a variogram was produced using untransformed King's Dock data (n=101) and their log normalised values (using two techniques: natural logarithm and base-10 logarithm). The data were so highly skewed that the variograms of both the transformed and non-transformed data behaved erratically. In Chapter 4, the skew of total CBs was shown to be 6.4, which is characteristic of occasional outliers. The estimation of the variogram in light of non-normal data is an identified problem (Cressie & Hawkins, 1980). Several authors have attempted to address the problem of nonnormal data (Cressie & Hawkins, 1980; Cressie, 1991). In this case study, outliers were identified up to an order of magnitude higher than the average PCB concentration and were thus identified as specific 'hotspots'. The removal of these outliers or 'hotspots' would thus allow the modelling of those PCB concentrations typically being exhibited in sediments in King's Dock. The subsequent removal of the outliers thus considerably reduced the skew of total CBs to 0.14 and allowed the estimation of a reliable variogram. The skew of the individual CBs were also examined and were deemed to be acceptable if the skew was < + or – 2 (Oliver, M.A., pers comm., 1998).

Both the supporting environmental properties and CB concentrations (n = 88) were found to be approximately normally distributed and did not require transformation prior to the variogram analysis. Initially, variograms were computed for total CBs, individual CBs and other environmental parameters in four different directions (0, 45, 90 and 135°) to determine the spatial variation and patterns in these planes. Unfortunately, there were too few data to describe any anisotropy accurately. It is therefore assumed there is no anisotropy and omnidirectional variograms form the basis of the analysis presented here for individual congeners, total PCBs, particle size (% < 63 μm) and TOC (%) using equation 5.3. Mathematical models (Figure 5.2) are fitted to the experimental values using least squares approximation (Genstat, 1997). Best-fit models are selected using a combination of the sum of squares error and the standard error, and the model parameters then used to solve ordinary kriging equations for estimation at unsampled locations.

5.2.1 Variograms of principal component scores

Since there are 25 congeners, principal component analysis has been conducted to investigate whether some of these might explain more of the variation than others (see Chapter 4). This ordination technique enables the variation in many properties to be described by a few new leading principal axes. This can help to reduce the number of congeners examined for geostatistical analyses and experimental variograms can therefore be computed using the scores of a principal component analysis. Oliver &

Webster (1989), Chappell *et al.* (1996) Einax & Soldt (1998) and Einax & Soldt (1999) found that variograms of the leading principal components explained most of the spatially dependent variation because both techniques enabled the investigation of similarities in the data set, examined relationships between several variables and determined spatial structures or relations between sampling points.

As demonstrated in Chapter 4, the first two principal components account for almost 80% of the variation. The congeners that explain most of the variation on PC1 are CB#110, CB#118 (penta-CBs) and CB#153 (a hexa-CB) which are intermediate in the spectrum from less to more chlorinated CBs. For PC2, it is the less chlorinated congeners, CB#28 (a tri-CB) and CB#66 (a tetra-CB) that explain most of the variation.

Sample variograms of PC1 and 2 are presented in Figure 5.3 and the model type and parameters are presented in Table 5.1. The variogram of PC1 is best modelled by an exponential function with a range or spatial dependence of 153 m. This variogram appears to show some periodic variation which may be due either to the contributing CBs in this plane (see Section 5.2.2) or to the nature of the sampling scheme. Similar variogram periodicity has also been found in several other studies including, for example, the topography of the Bland Plain in New South Wales (Webster & Oliver, 1986b) and the concentration of caesium-137 in soils in South-west Niger (Chappell, 1995).

The variogram of PC2 has a range of 215 m and is modelled by the circular model. In this component, individual CBs responsible for this variation have similar variogram forms. The break in this sample variogram is possibly evidence of two regions within the dock (i.e. different concentrations and patterns in the west and east). As variograms are based on difference between average similarities, this difference may be more extreme in two distinctive areas within the dock and as a result produce two distinct semivariances (see McBratney *et al.*, 1991).

The individual CBs influencing PC1 include some penta- and hexa-CBs (CB#110, #118, and #153) and these are the most abundant PCBs in the commercial mixture Aroclor® 1254, a suspected source for the PCB contamination in King's Dock (see Chapter 4). Conversely, PC2 is fitted with a circular model, and individual CBs explaining the variation not only have similar fitted models but have similar spatial dependence. Individual CBs explaining the variation in the PC2 plane include the tri-and tetra-CBs (CB#28, #31, and #66). Sample variograms and fitted models for these CBs show the highest spatial dependence. Spatial variation in this component may be due to both chemical and physical processes operating within the dock system. Also, anthropogenic activities, such as ship movements, may be influencing the individual patterns of CBs, as seen in some sample variograms, by mixing and resuspending sediments. For example, movement of large ships and tugs can create bathymetric changes and therefore effect the redistribution of PCBs within the sediments.

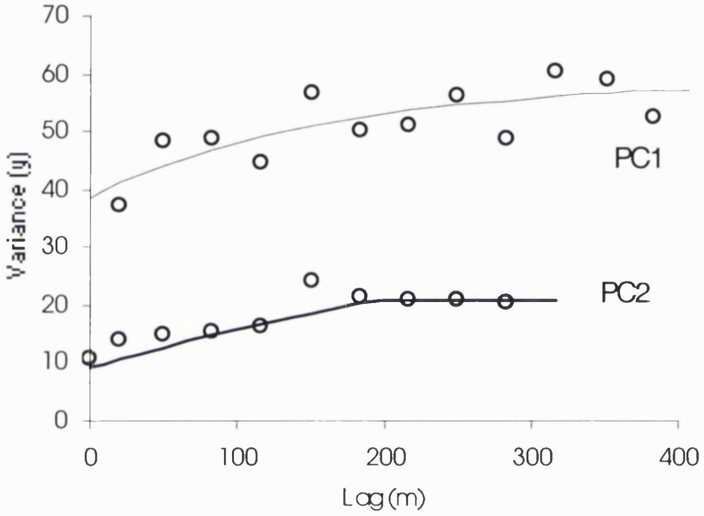


Figure 5.3: Sample variograms of principal component 1 and 2.

5.2.2 Variograms of individual CBs, total CBs and sediment properties

Sample variograms of individual CBs (Figure 5.4 a-f), total CBs (Figure 5.5), TOC (Figure 5.6) and particle size (Figure 5.7) are also computed. Table 5.1 displays the parameters of the variogram models. The circular model provides the best fit for the less congeners, whilst the spherical and circular models provide the best fit for the penta-CBs. The hexa- and some hepta-CBs are best fitted by a linear model whilst other hepta- and octa-CBs are fitted with either a spherical or circular model. A linear model provides the best fit for total CBs and is also the best fit for particle size. In contrast, the sample variogram for TOC is best fitted by an exponential model.

The range of spatial dependence for those individual CBs not fitted by linear models is between 117 – 279 m whilst the range for particle size is 321 m. Several congeners have sample variograms with similar spatial structures. For example, the model variograms for the tri-, tetra-, and penta-CBs show essentially that semivariances continue to increase until reaching a sill at between 150 - 250 m. Again, some variograms show slight periodicity at this distance. Periodicity occurs where there is some regularity in the spatial distribution. This periodic nature has, in the past, been modelled using periodic functions (Chappell, 1995). Importantly, periodic structures which do not have discrete boundaries can be estimated by geostatistics. In this instance, the sampled area is ideally divided into separate 'common' subregions and variograms computed for each of these subregions. Unfortunately, the regional variograms are likely to be unreliable because there are too few samples. The average range of spatial dependence for other congeners defined by their models is approximately 220m.

There are several CBs (including: CB#44, #47, #49, #105, #128, #141, #151, #156, #158 and #183) that are best fitted with a nugget effect model (Figures 5.4 b-e). This model does not provide an estimation of spatial correlation (Isaaks & Srivastava, 1989), suggesting sediment samples at any particular location in the dock are dissimilar to nearby sediment samples. These variograms show no clear spatial structure, suggesting that the minimum sampling distance was too large to establish short scale variability. Other studies have also found pure nugget effects in variograms of soil properties (Oliver, 1984; Oliver & Webster, 1986a; Oliver, 1987). These studies showed that although the spatial variation was not determined with the sampling strategies first employed, it was possible to estimate the form of the autocorrelation by sampling again at closer distances.

Several variograms are fitted with an unbounded linear model (see Table 5.1). This model is not a transition model because it does not reach a sill. As the semivariances increase linearly as the lag (h) increases, there is evidence of some spatial continuity of the regionalised variable. This is not uncommon and several studies have used linear variograms to describe soil properties (Webster & Burgess, 1984; Oliver & Webster, 1986a). Indeed, this type of model is sometimes fitted where there is a trend or drift in these values (Webster & Oliver, 1990). In these cases, the trend or drift can be removed and the residuals used to compute the variogram (Chappell *et al.*, 1996). This is especially true where there is a convex-upward form at the origin of the model. This is evident in the variograms of CB#138, #149 and #153 (Figure 5.4 d).

Examination of individual CB concentrations in sediments from King's Dock, using geostatistical techniques, has identified spatial patterns and structures within their distribution that might provide insight into the ways in which they behave within dock sediments. The variograms suggest that the spatial variation in the less chlorinated CBs (i.e. tri-, tetra-, and penta-CBs) is more patchy and structured (Figures 5.4 a-c) than that for the more chlorinated ones (i.e. hexa- and some hepta-CBs) which have unbounded variograms (Figures 5.4 d-e). This may be related to their different patterns of relative susceptibility to various physico-chemical and biological processes. For example, the less chlorinated CBs, which are more volatile, are present in the water column in the dissolved phase and are characteristically more mobile than the more chlorinated CBs. The spatial dependence of the less CBs is attributed to their relative levels of volatility and solubility.

Conversely, the more chlorinated CBs have a greater tendency to adsorb on to sediments and these are retained in the longer term. They are generally restricted and immobile due to their low solubilities and high K_{ow} values. Spatial dependence of the more chlorinated CBs is possibly a response to rapid immobilisation by their association with the sediment organic fraction, and partitioning into lipids and waxes in the sediments (Hess *et al.*, 1995). Sediments rich in organic compounds adsorb the lipophilic PCB compounds to a higher degree than minerogenic sediments (Karickhoff *et al.*, 1979). The more chlorinated CBs distribution is probably also affected by microbial degradation within sediments and interface transfer from the sediments to the water. This can occur by elution from the surface in colloidal bound form (i.e., the form that predominates in the sediment pore water) and dispersal of PCB bearing particles from the surface (Brown & Wagner, 1990).

The magnitude of spatial variation determined in this study is similar to that found by Brown & Fish (1999) who identified local spatial variabilities and overall regional trends of PCBs in the Lower Hudson river. They established spatial variation in both PCB level and composition over a 200 m scale and attributed this to local releases rather than to a dominant upstream source. Similarly, in this case study, sample variograms of individual congeners and total CBs suggest a comparable scale of spatial dependence and therefore suggest that possible local accumulation sites exist: these are located in the west and south of the dock. Indeed, some sample variograms and their models can be used to infer some of the environmental mechanisms governing the distribution of PCB concentration within the dock system.

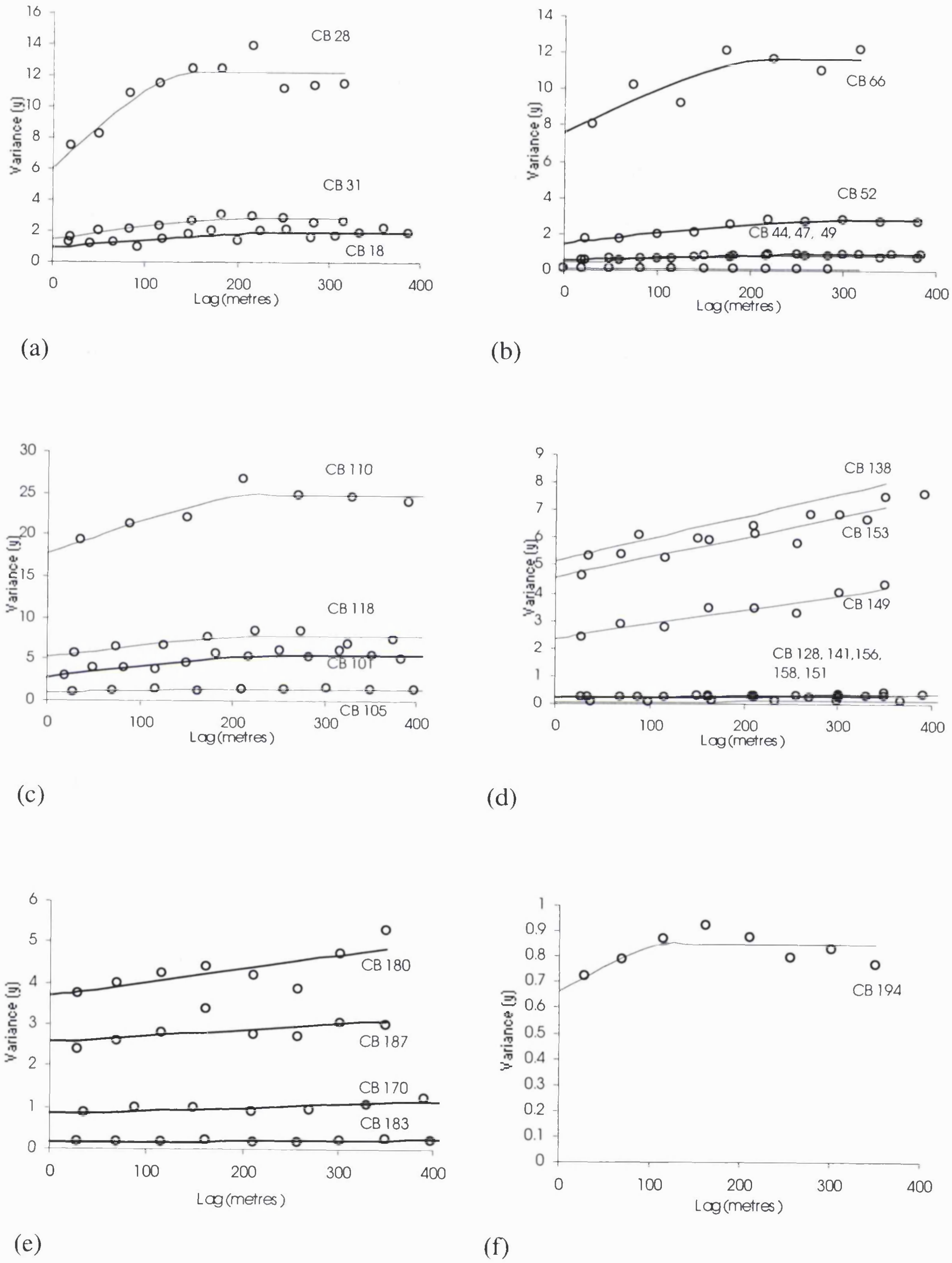


Figure 5.4: Sample variograms of the homologue groups: a) Tri-CBs; b) Tetra-CBs; c) Penta-CBs; d) Hexa-CBs; e) Hepta-CBs and f) Octa-CBs.

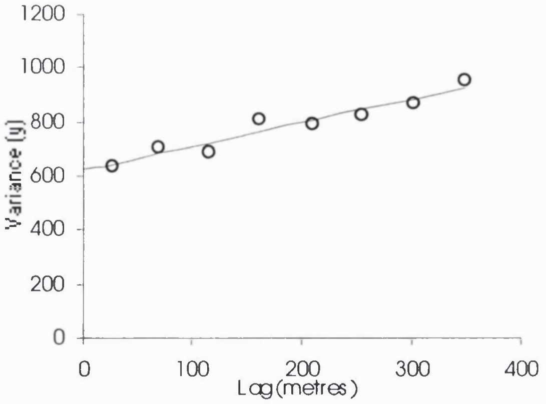


Figure 5.5: Sample variogram of Total CBs (μg kg^{-1}).

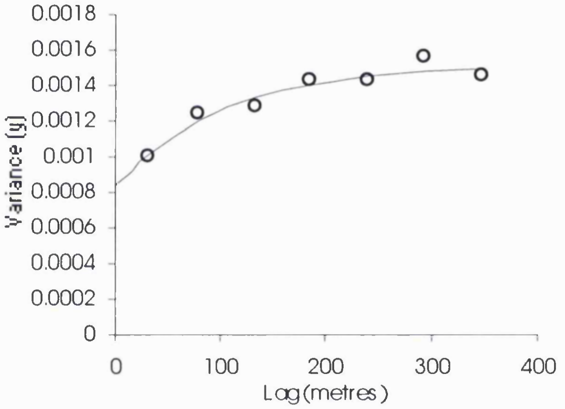


Figure 5.6: Sample variogram of TOC (%).

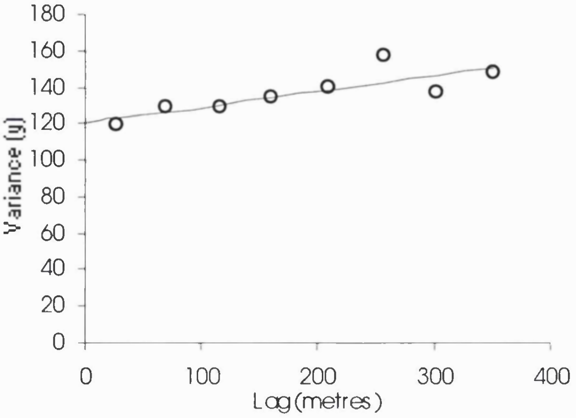


Figure 5.7: Sample variogram of particle size (% < 63 μm).

Table 5.1: Model type and parameters for the sample variograms.

CB#	Model Type	% fit	Range (m)	C	Gradient	Nugget Variance	Sill	Std Error
18	C	54	255	0.98		0.91	1.89	1145
28	C	79	142	6.14		6.02	12.16	428
31	S	85	208	1.40		1.40	2.80	
44	C	93	279	0.36		0.52	0.88	440
47	S	85	249	0.04		0.05	0.08	
49	C	84	238	0.38		0.43	0.81	654
52	C	94	270	1.32		1.44	2.76	449
66	C	60	207	4.04		7.57	11.61	1157
101	C	82	258	2.76		2.79	5.55	641
105	C	81	273	0.41		0.98	1.40	1309
110	S	76	224	7.15		17.65	24.80	1049
118	C	62	227	2.54		5.24	7.78	1073
128	L	96			0.0003	0.21		0.11
138	L	87			0.0081	5.16		6.3
141	L	78			0.0030	0.22		0.42
149	L	84			0.0052	2.36		4.51
151	L	79			0.0004	0.21		0.43
153	L	85			0.0073	4.56		6.06
156	L	80			0.0002	0.21		0.22
158	L	90			0.0002	0.06		0.01
170	L	54			0.0008	0.85		1.79
183	L	61			0.0002	0.15		0.40
180	L	51			0.003	3.69		0.23
187	S	38	170	0.84		2.14	2.98	1372
194	C	32	117	0.18		0.66	0.85	1050
Total CBs	L	90			0.87	622		22.6
Total organic carbon (%)	E	91	321*	0.0006		0.0008	0.0015	636
Particle size (% <63μm)	L	61			0.085	120.41		4.96
PC1	E	55	153	19.76		38.66	58.42	1753
PC2	C	77	218	11.80		9.27	21.05	732

Model Type: C = Circular, S = Spherical, E = Exponential, L = Linear.
* = Effective range was multiplied by 3; PC = Principal Component.

N.B. Nugget variance is often attributed to a number of sources of variation (e.g. measurement and sampling errors) (Oliver, 1984).

In summary, variograms provide a clear description of the spatial structure of individual CBs and total PCBs. The variograms of TOC and particle size provides a means of interpolating the environmental variation of PCBs over an area. To estimate the individual CB concentrations, total CBs, TOC and particle size at unsampled locations, kriging can be performed using the fitted model parameters (Table 5.1). Kriging may prove to be a useful technique for estimating contaminant loads (by initially interpreting between sampling sites and loads calculated from estimated concentrations across an area, see Section 5.4.3) and may be able to provide information on PCB concentrations within an area based on the spatial structure and patterns of the local distribution of PCBs. This is an innovative approach which can be applied to be the regulatory assessment of dredged material and for the determination of concentrations above zero or near background levels as defined by the OSPAR Commission (1998).

5.3 Kriging

Geostatistical modelling of individual CBs and their associated environmental parameters provides a means of estimation at unsampled locations. Kriging, defined as a minimum-mean-squared-error method of spatial prediction (Cressie, 1991), provides an estimate of values with minimum and known variance (Burgess & Webster, 1980; Burgess & Webster, 1984; Voltz & Webster, 1990). Cressie (1991) has suggested that variogram-model fitting and kriging are effective techniques for spatial prediction and are valuable tools in spatial sampling design. In fact, kriging is recognised as a particularly powerful estimation process in intensive surveys (Burgess & Webster, 1984).

Certain studies have discussed weaknesses in the kriging technique and the consequences these may have on estimations (for review, see de Kwaadsteniet, 1990). In some cases, particular assumptions of spatial behaviour and structure can affect kriging results. However, geostatistical methods have been used to better understand the underlying processes influencing the variation of particular phenomenon (Yost *et al.*, 1982; Clark, 1987; Oliver & Webster, 1990; Rossi *et al.*, 1992; Jackson & Caldwell, 1993; Chappell *et al.*, 1996; Colin *et al.*, 1996; Fernandes & Simmonds, 1996; Garcia & Froidevaux, 1996; Pebesma & de Kwaadsteniet, 1996; Ball *et al.*, 1998; Goderya, 1998; Singh *et al.*, 1998; Wang & Qi, 1998).

5.3.1 Theory

Kriging aims to provide estimations with minimal variance and errors. Kriging is a method of weighted averaging of observed values of a property within a neighbourhood. If an average value of z is to be determined in an area, B, then its estimate is a weighted average of the observed data $z(x_1)$, $z(x_2)$.....$z(x_n)$ which can be inside or outside the area, such that:

$$z(B) = \sum_{i=1}^{n} \lambda_i \, z(x_i). \qquad [5.8]$$

where λ are the weights assigned to the sampling points. These weights have a total of 1 to ensure they are unbiased (Webster & Oliver, 1990).

There are many different kriging methods, for example, simple, ordinary (Webster & Oliver, 1990), punctual (Sminchak *et al.*, 1996) and block kriging (McBratney *et al.*, 1991). Ordinary kriging is a method that aims to provide a linear unbiased estimation of the data. This method also aims to minimise the error variance (see Isaaks & Srivastava, 1989). Block kriging, however, involves the estimation of the mean value of a spatial variable within a prescribed local area: this is only effective if the variogram and the fitted models are accurate (Isaaks & Srivastava, 1989; Chappell *et al.*, 1996; Colin *et al.*, 1996). The main intention here is to use the sample variogram to estimate PCB concentrations in sediments. This can best be achieved by ordinary kriging because this method retains small scale variability which is lost if block kriging is performed. The pros and cons of these methods are discussed in Isaaks & Srivastava (1989).

5.3.2 Ordinary kriging of individual CBs and total CBs

Kriging maps of selected individual congeners and total CBs are shown in Figure 5.8 a-i and 5.9, respectively. Individual congeners show discrete patches of elevated concentrations in specific areas. The less chlorinated CBs tend to be most elevated towards Shed D (CB#18 and #28) whilst elevated concentrations of the more chlorinated CBs are located towards Rose Wharf.

In Figure 5.8 a (CB#18) and b (CB#28), there is a distinct accumulation site in the west area of the dock. Elevated concentrations are found at 200 – 250 m from the western dock boundary. These concentrations are very localised and have probably been dispersed rapidly from a point source, possibly into the water column. Moreover, there is an additional area exhibiting elevated concentrations and this is located at 600 – 700 m from the western dock boundary. This again may be another local accumulation site due to the presence of high CB#28 concentrations.

In Figure 5.8 c (CB#66), there are marked areas of high and low concentrations of CB#66. The spatial distribution and pattern of CB#66 appears to be well defined and exhibits good spatial structure. This chlorobiphenyl is also responsible for much of the variations observed in PC2. The distribution of this congener is aligned in a north east – south west direction. This spatial pattern may be attributed either to a local accumulation site (these explain the highest concentrations), spatial pattern and structure of TOC (Figure 5.11 a) or particle size (%< 63 μm) (Figure 5.11 b). Unlike other groups before, the distribution of these tetra-CBs is beginning to be influenced by sediment characteristics, as these CBs are retained in the particle-phase more efficiently.

The spatial pattern of all penta-CBs, except CB#110 (Figure 5.8 e), is almost identical to CB#101 (Figure 5.8 d) and CB#118 (Figure 5.8 f). The most elevated concentrations are located at 200 - 250 m which is located further south than the tri-CB concentrations. This is attributed to the high percentage of TOC within sediments located in this area (Figure 5.11 a). Again, these CBs are preferentially fixed to sediments and are typically associated with the presence of TOC within sediments. This is because of their physico-chemical properties (i.e. high log K_{ow}; Mackay, 1991).

In contrast, CB#110 has a very different spatial pattern and structure. The sample variogram is indicative of high spatial dependence within the range (224 m), but this congener is the only one (compared to other CBs in this homologue group) to exhibit low concentrations in the south west. There are, however, elevated concentrations further north of this area which is comparable to the tri-CBs. This congener is one of the most abundant CBs in the commercial mixture Aroclor® 1254 and it is possible that elevated concentrations are highest closest to an accumulation site in this area.

The pattern and structure of the hexa- and hepta-CBs are typified by CB#153 (Figure 5.8 g) and CB#180 (Figure 5.8 h). The kriged maps of CB#153 and CB#180 show there is a more continuous distribution over the area. The variograms of CB#153 and CB#180 are fitted with a linear model with a convex-upward form at the origin suggesting local drift or trend (Figure 5.4 d and e). The continuity and regularity of the regionalised variable can be described by the shape of the variogram and its behaviour near the origin. If the variogram takes a parabolic form near the origin, this is interpreted as local drift (Webster & Oliver, 1990; Chappell *et al.*, 1996). The concave upward shape is due to the rate of change in concentration. These results suggest that the concentrations of the more chlorinated CBs gradually change over distance, perhaps in association with other environmental parameters not measured or in response to long term environmental processes, such as dechlorination.

In Figure 5.8 i, the spatial structure and pattern of CB#194 is different to other congener distributions. There are two distinct areas where concentrations are elevated. These are located at 250 m in the south west area of the dock. Although the sample variogram of CB#194 demonstrated spatial dependence within the range (117 m) (Figure 5.3 f), there is a 'hole-effect' at 250 m. The term 'hole-effect' is used to describe samples that are similar at larger distances that those at smaller distances (Isaaks & Srivastava, 1989). In this case, this suggests that concentrations at a 250m distance are similar to those at smaller distances. This is evident from Figure 5.8 e. The localised concentration of this congener is attributed to specific accumulation sites and its immobility is due to the high K_{oc}, low solubility and low vapour pressure.

The pattern of total CB concentrations in Figure 5.9 is generally comparable to the TOC pattern in Figure 5.11 a. In this study area, total CBs are predominantly composed of the more chlorinated CBs. The pattern of total CBs therefore strongly reflects the partitioning behaviour of penta-, hexa- and hepta-CBs which are preferentially adsorbed to TOC. Evidence of this latter relationship was presented in Chapter 4. The distribution of CB#118 (Figure 5.8 f) clearly demonstrates the close relationship between more chlorinated congeners and TOC within sediments. The distribution of these congeners is subsequently restricted by strong binding to the organic phase. In fact, sediments rich in organic compounds adsorbs the lipophilic PCB compounds to a higher degree than minerogenic sediments (Karickhoff *et al.*, 1979). The adsorption of PCBs to sediments has been reported to be in the order of hexa > tetra > di-CBs (Morris, 1995). More chlorinated biphenyls are adsorbed in greater quantities and are retained more effectively on the sorbent surface.

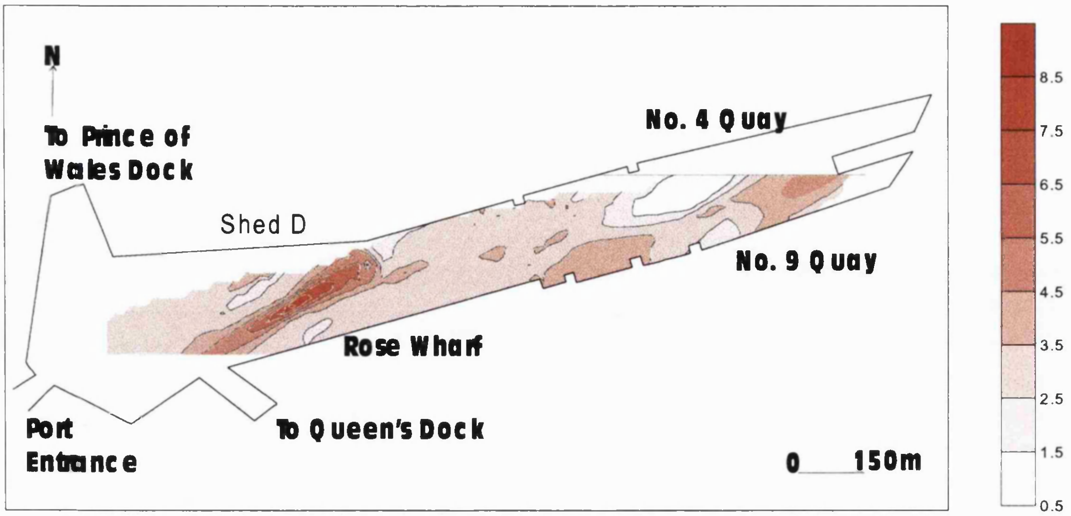


Figure 5.8 a: Kriged map of CB#18.

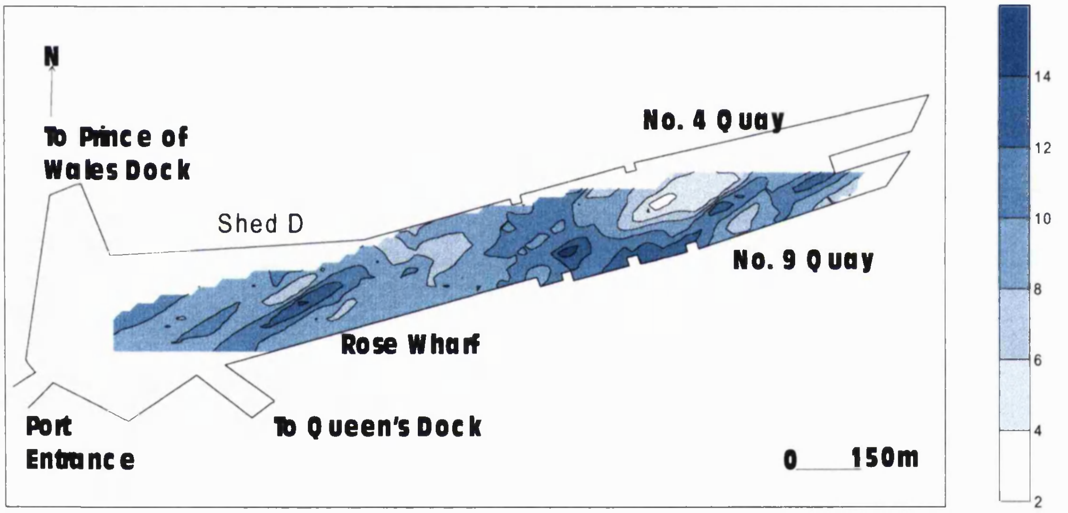


Figure 5.8 b: Kriged map of CB#28.

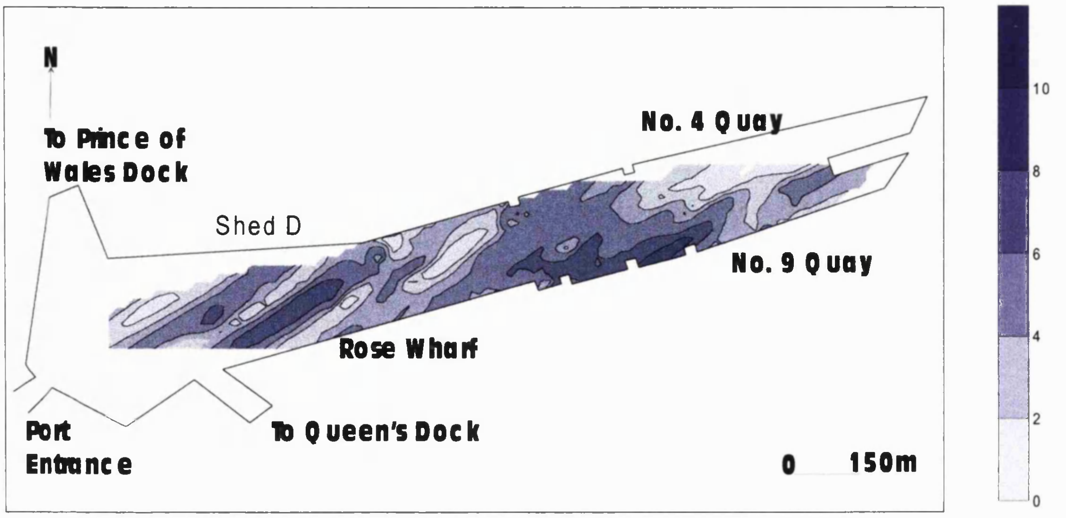


Figure 5.8 c: Kriged map of CB#66.

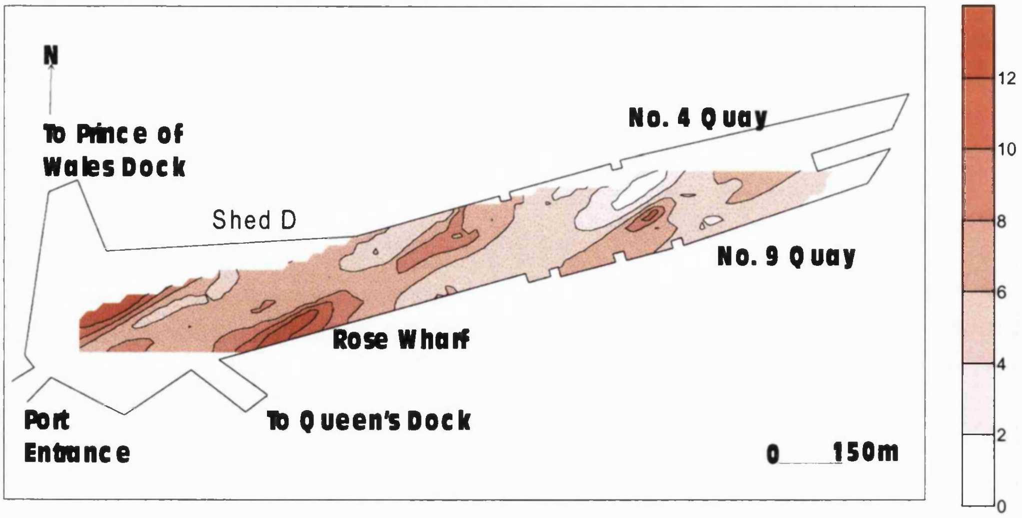


Figure 5.8 d: Kriged map of CB#101.

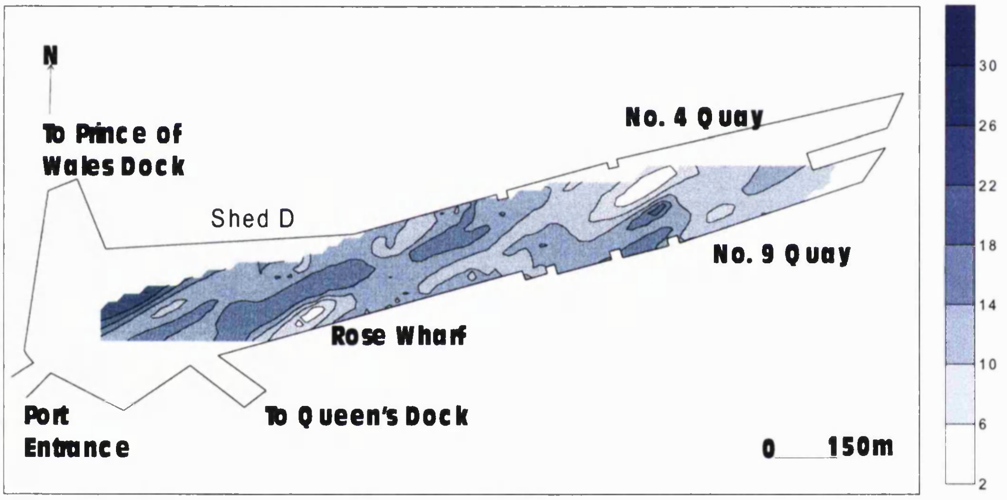


Figure 5.8 e: Kriged map of CB#110.

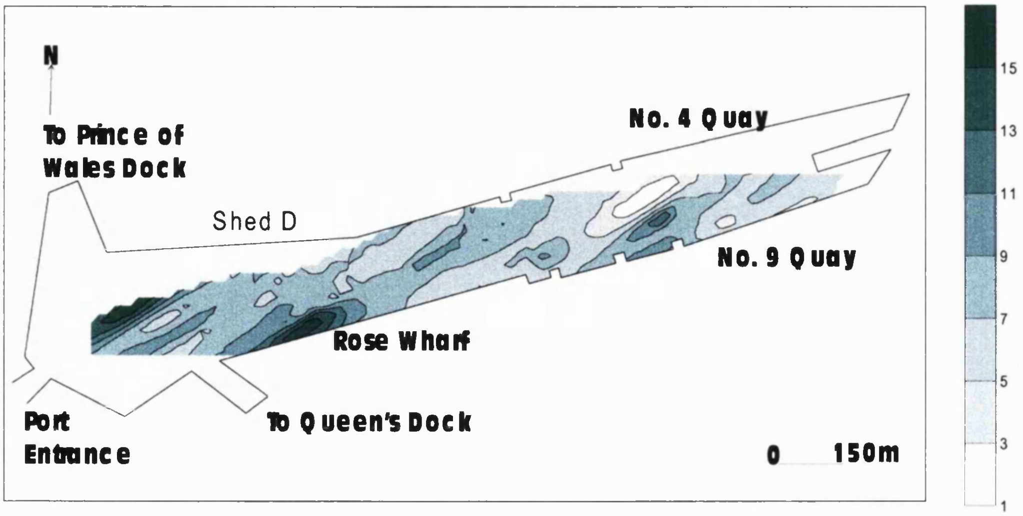


Figure 5.8 f: Kriged map of CB#118.

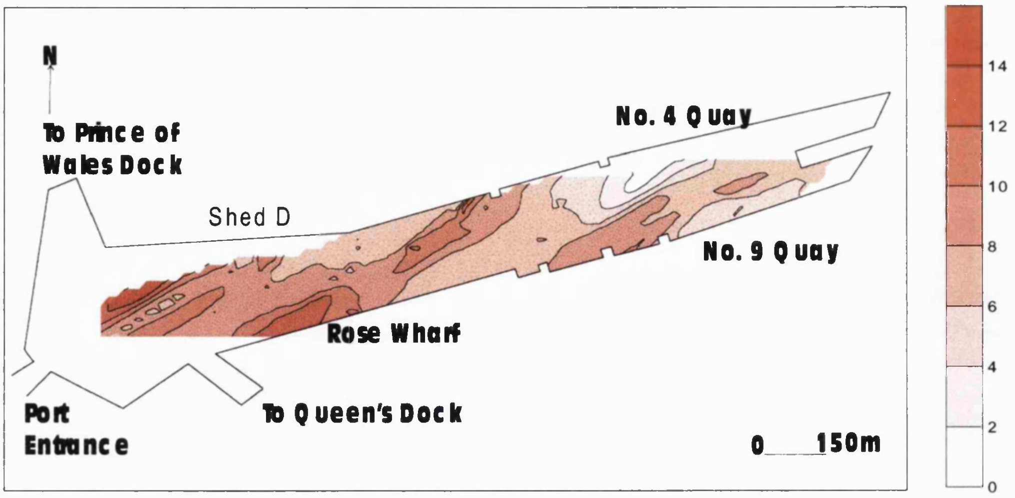


Figure 5.8 g: Kriged map of CB#153.

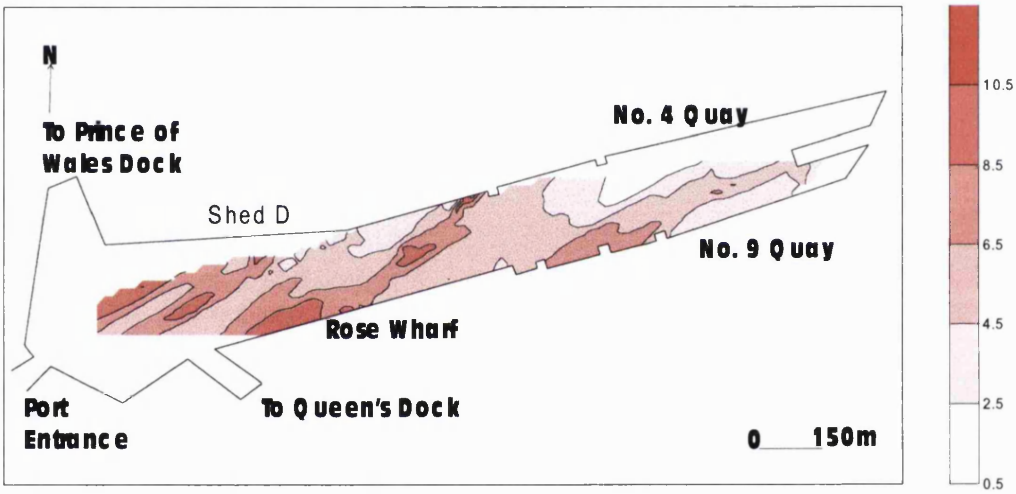


Figure 5.8 h: Kriged map of CB#180.

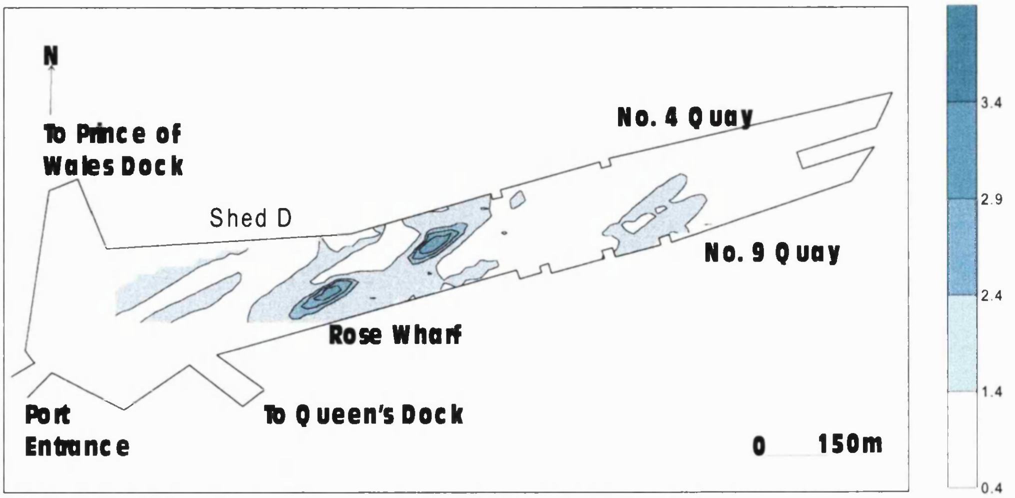


Figure 5.8 i: Kriged map CB#194.

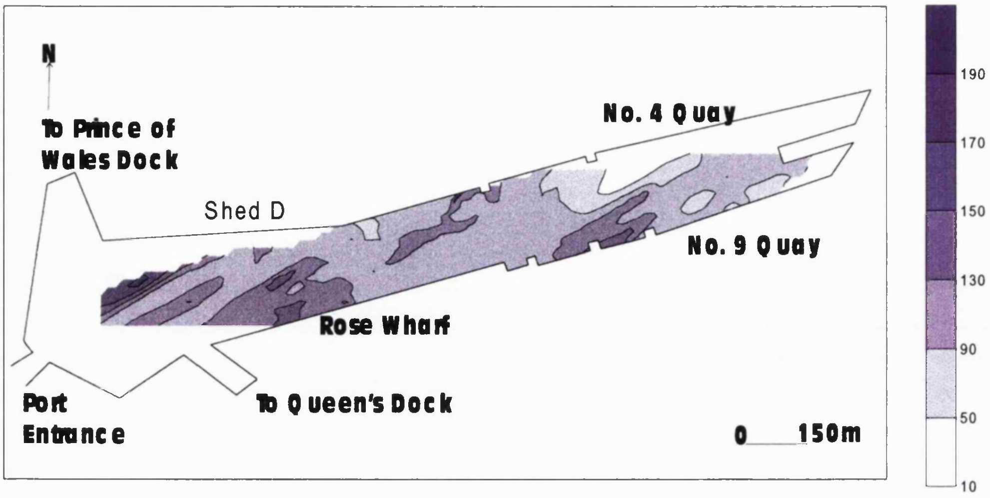


Figure 5.9: Kriged map of Total CBs.

The kriging estimation standard errors are calculated for each parameter and an example (using CB#28) is displayed as a perspective diagram (Figure 5.10). The kriging error is the difference between the estimated value and the true value at that same location. The average error of a set of *k* estimates is defined by Isaaks & Srivastava (1989) as:

$$\text{Average Error} = mr = \frac{1}{k}\sum_{i=1}^{k} ri = \frac{1}{k}\sum_{i=1}^{k} \bar{v}i - vi$$

[Eq. 5.9]

where v is the variable at a location and r is the error.

In Figure 5.10, the smaller errors, and more reliable estimations, are found in the centre of the dock where the ten sampling nests are located. Higher errors are associated with unsampled areas that are typically located close to the edge of the dock: these were inaccessible due to moored vessels. Within the sampling area, errors were generally <1, but were on occasion higher. Some congeners, for example CB#153 and CB#180, had high estimation errors. These errors could be associated with sampling and/or measurement errors.

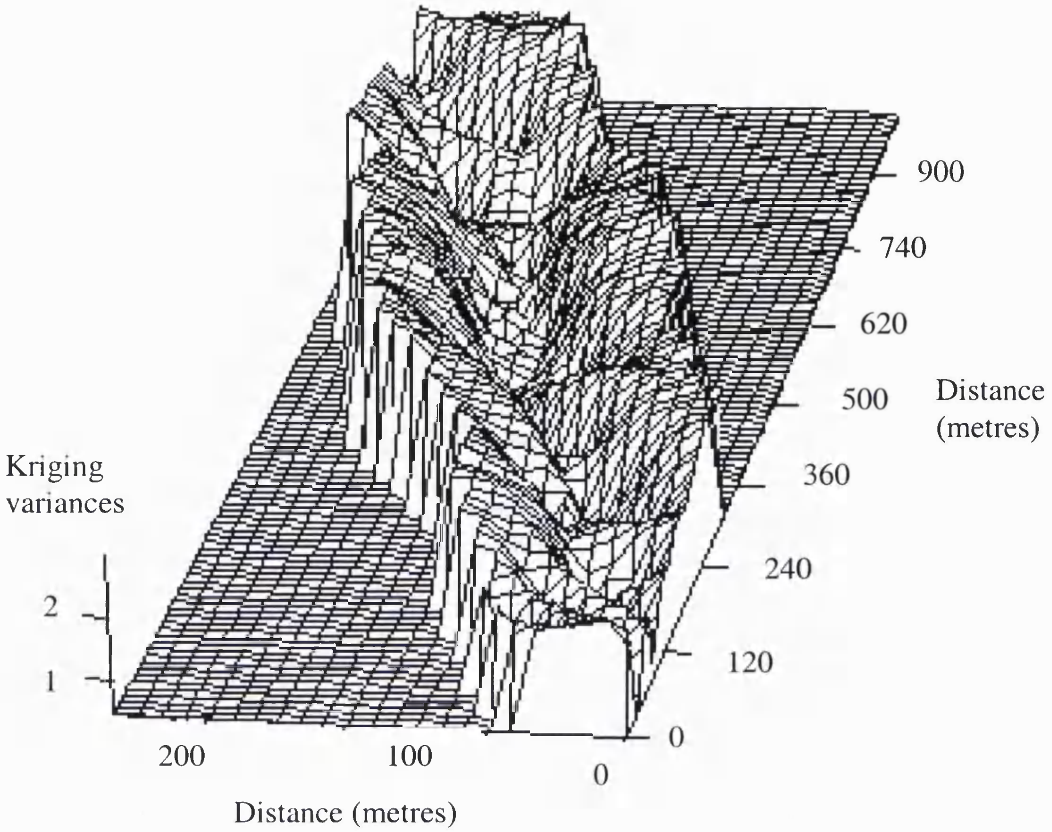


Figure 5.10: Example of kriging standard errors using CB#28.

5.3.3 Ordinary kriging of environmental parameters

Kriging maps of TOC (%) and particle size (% <63 μm) are shown in Figure 5.11 a and b, respectively. The distribution of particle size is more homogeneous than that for TOC. There are specifically defined areas where TOC is particularly high. In general, sediments towards the west side of the dock have a higher percentage of particles < 63 μm. This distribution may reflect the settlement of fine particles from outside the dock gates.

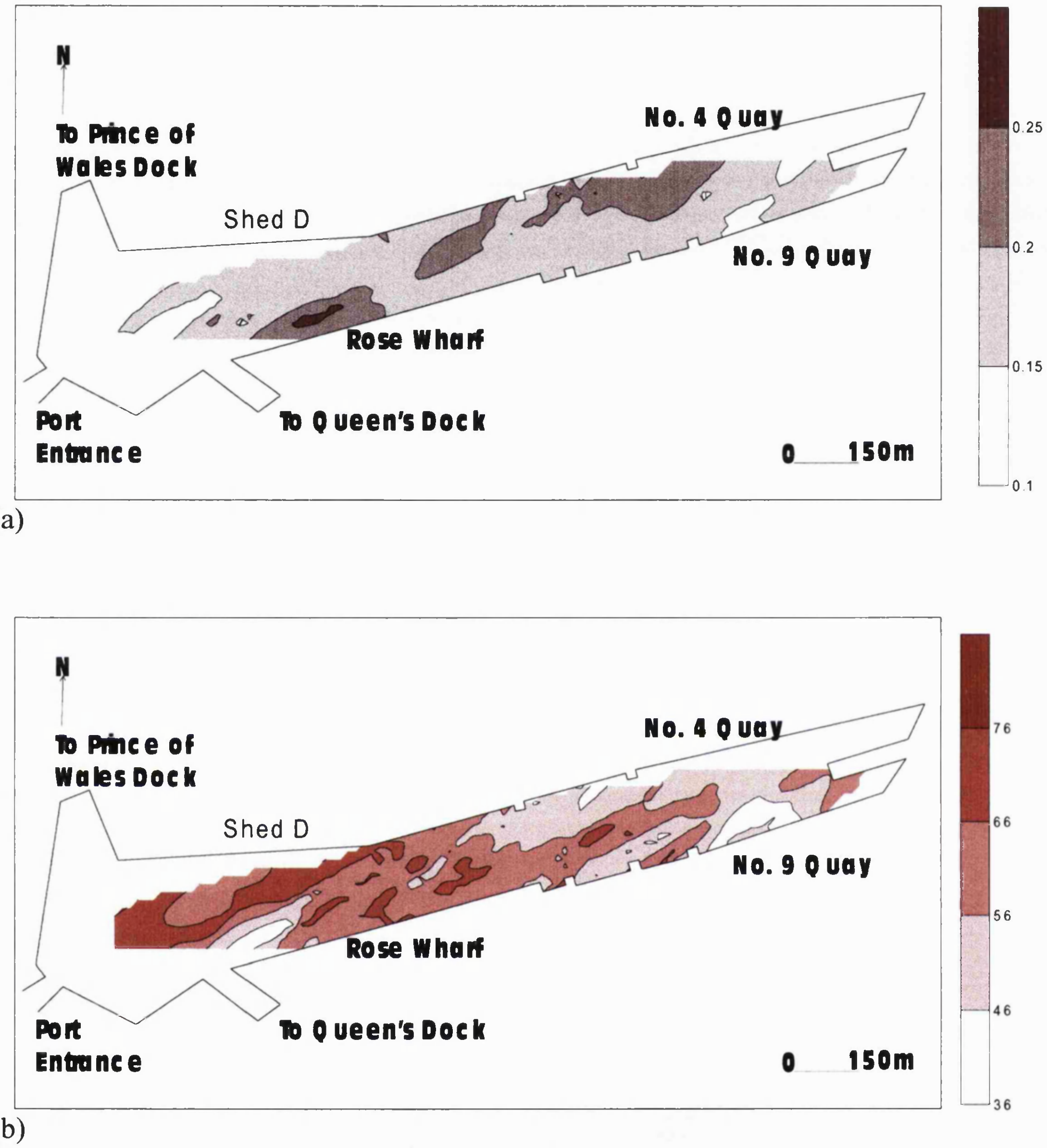


Figure 5.11: Kriged map of (a) TOC (%) and (b) particle size (% < 63 μm).

The kriging maps of the sediment properties can suggest mechanisms by which CBs are distributed within the dock system. For example, high concentrations of total CBs (Figure 5.9) are found in discrete isolated patches towards the south west and the south east of the dock where the percentage of TOC within the sediment is high. The distribution of the less chlorinated CBs in Figure 5.8 a-c is restricted because of their relatively high volatility and high solubility. In contrast, the distribution of more chlorinated CBs in Figure 5.8 d-i is restricted to discrete areas possibly in response to rapid immobilisation by their association with TOC and partitioning into lipids and waxes in the sediments (Clark, 1989; Hess *et al.*, 1995; Koelmans *et al.*, 1997). The more chlorinated CBs preferentially adsorb to TOC and this is suggested as the reason for their similar spatial scales of variation. The variograms and kriged maps of individual CBs not only illustrate possible environmental processes operating within the dock system, but demonstrate close links with environmental parameters such as TOC. The distribution of individual CBs is therefore caused by movement of PCBs from local accumulation sites. The overall distribution is governed by individual physico-chemical parameters of CBs.

5.4 Assessment of the sampling approach using geostatistical methods

The most important part of the sampling strategy, for geostatistical analysis, is the provision of reliable data for calculating the variogram. The number of samples involved in the calculation of the variogram is an important consideration even at the early stages of sampling design. Too few samples will provide inadequate information of the spatial patterns and structures producing less reliable estimations (Wang & Qi, 1998). Early research did not adequately recognise the importance and influence that sample numbers have on the reliability of the variogram. Indeed, the sampling plan is an important influencing factor as it can provide reliable data at different spatial scales (Oliver, 1987; Warrick & Myers, 1987). Samples required to compute the variogram vary between studies and can range from 25 sample pairs (Lin & Roesler, 1988), 28 (Chang *et al.*, 1998), 30 pairs (Warwick & Myers, 1987), 35 individual samples (Pitard, 1988) to 100 samples as a minimum requirement (Oliver & Webster, 1991).

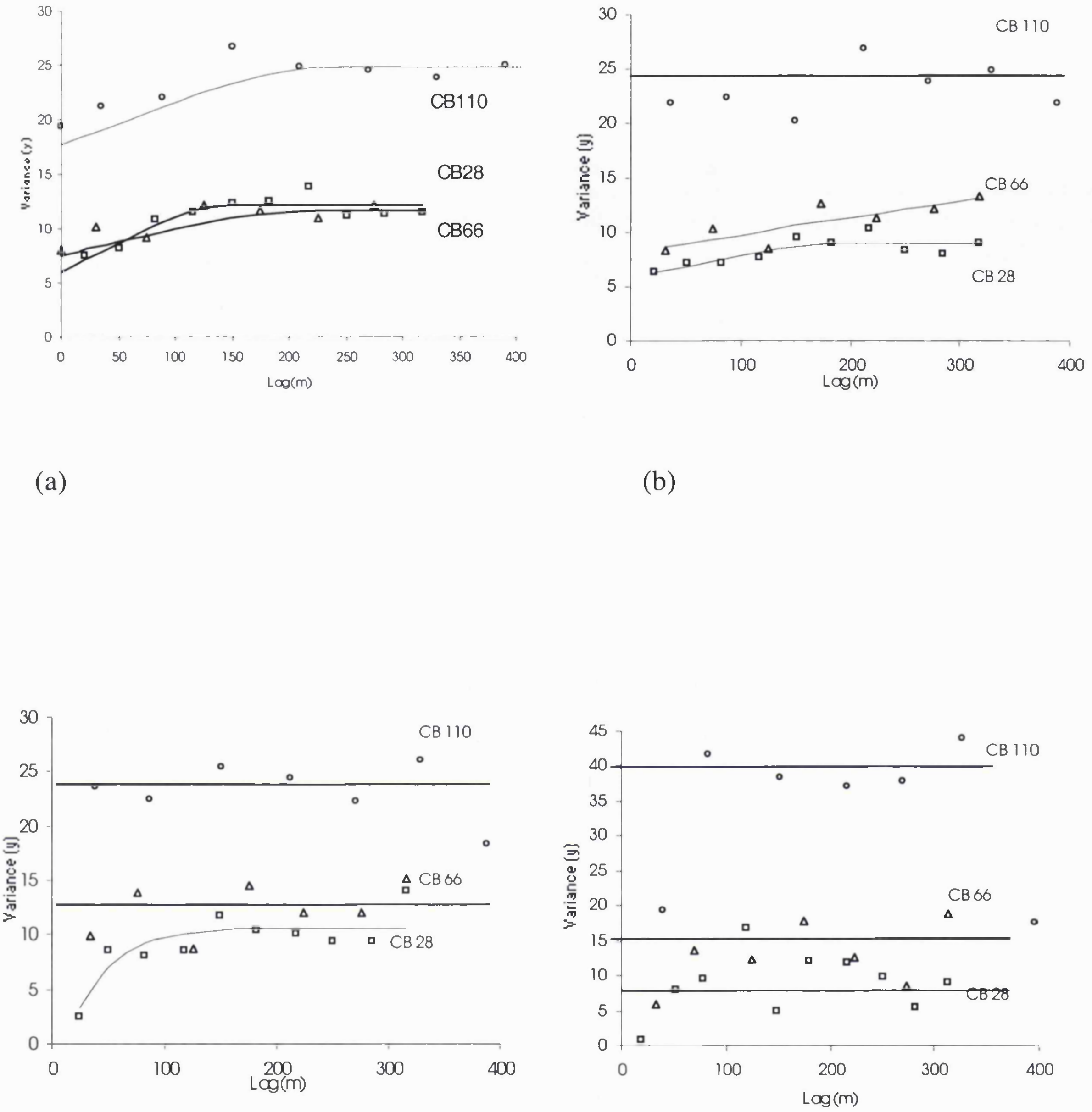
There are few studies investigating the numbers of samples required to compute a reliable variogram (Webster & Oliver, 1992; Chang *et al.*, 1998). At present, the proposed minimum number of samples to compute the variogram is 100 (Webster & Oliver, 1992). The costs involved with sampling sediments, dredged material and other environmental matrices and analysing these samples for PCBs and other mixtures of contaminants (e.g. TBT, PAHs, pesticides and metals) are high. The practicalities and costs of assessing dredged material before licensing material for disposal at sea is an important consideration if geostatistical methods are to be used in any regulatory decision-making framework. This issue is addressed in the following sections. The aims here are first, to assess the effects of the removal of samples on the experimental variograms and kriged maps of selected CBs and total CBs; and second, to assess total PCBs loadings in sediments calculated by two different methodologies.

5.4.1 Removal of samples and consequences for variogram computation

To investigate whether the number of samples affect the structure and form of the sample variogram, the sampling effort in King's Dock was reduced to 75% (*n*=66), 50% (*n*=44) and 25% (*n*=22). The dock was initially dividing into sections. Equal samples were randomly selected and removed from each section. This approach provided the closest simulation of likely sampling outcomes under less intensive monitoring scenarios. At each reduced sampling effort, the sample variograms of selected CBs (CB#28, #66 and #110) (Figure 5.12 a-d) and total CBs (Figure 5.13a-d) were computed using Genstat® (Genstat, 1997). The model type and parameters for the separate sampling efforts are presented in Table 5.2.

The effects of reducing sampling effort on the variogram structure and form are dramatic. For example, the model fitted to the 75% sampling effort variogram of CB#28 has a more gentle slope that reaches the sill at a lower variance, and this is achieved over a larger range (189 m). This change in shape suggests that there is less spatial dependence within the range. This implies that samples are likely to be more similar between 0 – 189 m. The fitted model has therefore *over-estimated* the range, indicating limits where there may not be any real spatial continuity.

In general, the effects of reducing sampling effort include: a higher nugget variance; more erratic behaviour especially over small distances; no defined range or sill due to limited spatial structure at the shortest lags and nugget variograms where no models could be fitted to the sample variograms. As soon as the sampling effort is reduced, variograms have a more generalised form showing continuous changes over distance. The spatial structure has therefore not been adequately captured here showing that the structure and form of the variogram is lost by reducing the sampling effort.



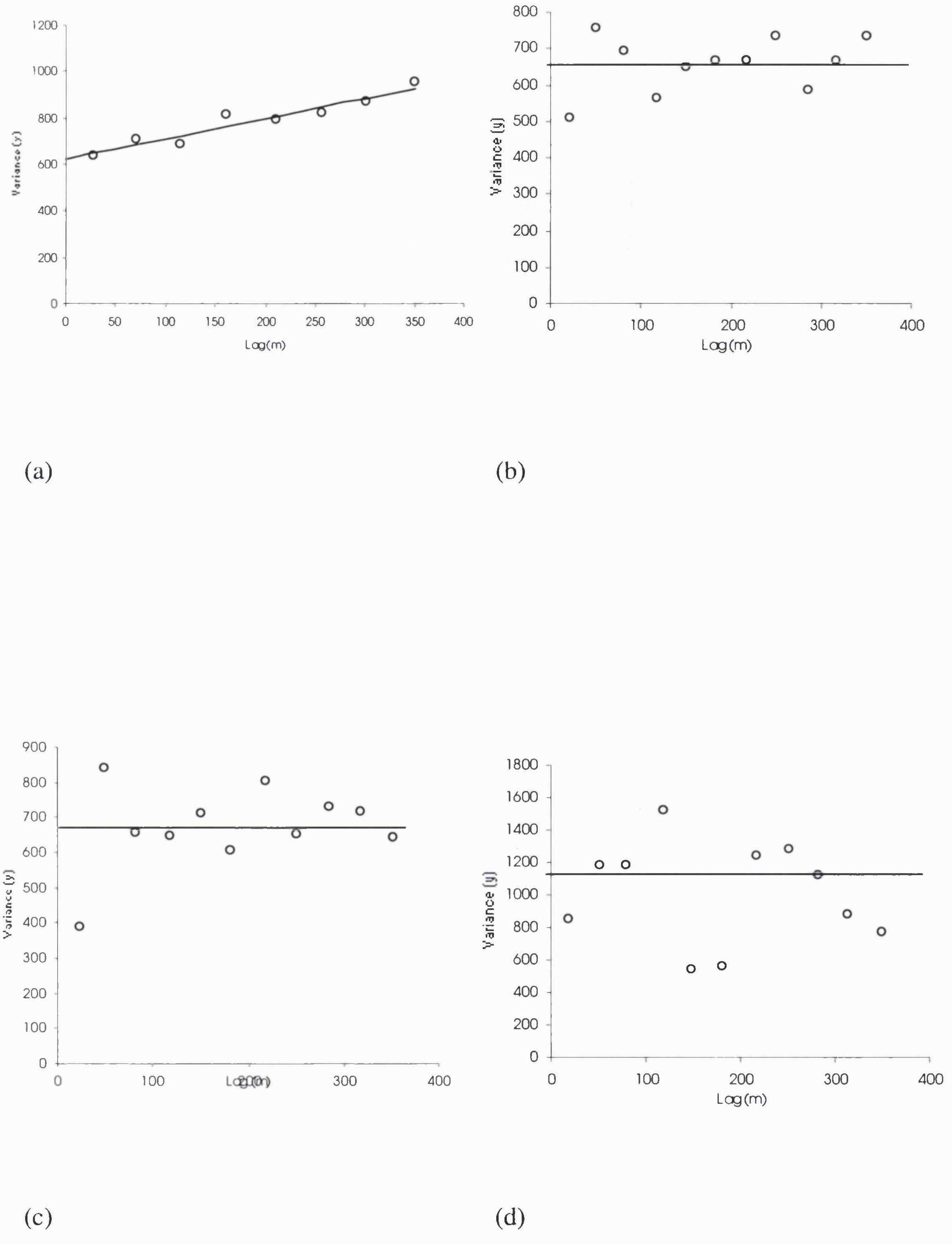
(a)

(b)

(c)

(d)

Figure 5.12: Sample variograms of CB#28, #66 and #110 employing 100% sampling effort (a), 75% sampling effort (b), 50% sampling effort (c) and 25% sampling effort (d).



(a) (b)

(c) (d)

Figure 5.13: Sample variograms of Total CBs employing 100% sampling effort (a), 75% sampling effort (b), 50% sampling effort (c) and 25% sampling effort (d).

Table 5.2: Model type and parameters for sample variograms at reduced sampling effort.

CB#	Sampling effort (%)	Model type	% fit	Range (m)	C	Nugget variance	Gradient	Sill	Std error
28	25	*							
	50	E	52	105	14.71	-4.15		10.56	313
	75	C	57	189	3.213	5.829		9.04	956
66	25	*							
	50	*							
	75	L	58	N/A	N/A	8.249	0.016	N/A	0.945
110	25	*							
	50	*							
	75	*							
Total CBs	25	*							
	50	*							
	75	*							

* = nugget model fitted

5.4.2 Removal of samples and consequences for kriging

Ordinary kriging was performed using the model parameters in Table 5.2. The same search criteria was adopted as before so that kriging maps of CBs could be compared to estimations from the 100% sampling effort. The distribution of CB#28 (Figure 5.14 a-b) and CB#66 (Figure 5.15) shows the consequences of the model fit at 75% and 50% sampling effort.

Although the distributions are more generalised, it is possible to identify some similar patterns and structures with those produced from the 100% sampling effort (see Figures 5.8 b and c). It has, however, proven difficult to accurately identify areas within the dock that may constitute possible sources of PCBs. In Figure 5.14 a and b, the overall area of the dock (where CB concentrations are estimated) is reduced and concentrations over small scales are more variable. This is evident from the sample variograms and is described by the form of the fitted model (i.e. no range and high nugget variance).

In Figure 5.15, the spatial pattern of CB#66 is less effectively described by the model parameters fitted from the 75% sampling effort. Again, the estimated area is reduced and the distributions are more continuous over the sample area. There are less well defined areas of high and low concentrations of CB#66, and the alignment of CB#66 concentrations in a north east – south west direction is less well characterised. The reduced sampling effort has not established CB distributions over small scales and not identified possible local accumulation sites. Again, this analysis confirms the need for a high sampling effort to reliably represent spatial variation in sediment PCBs.

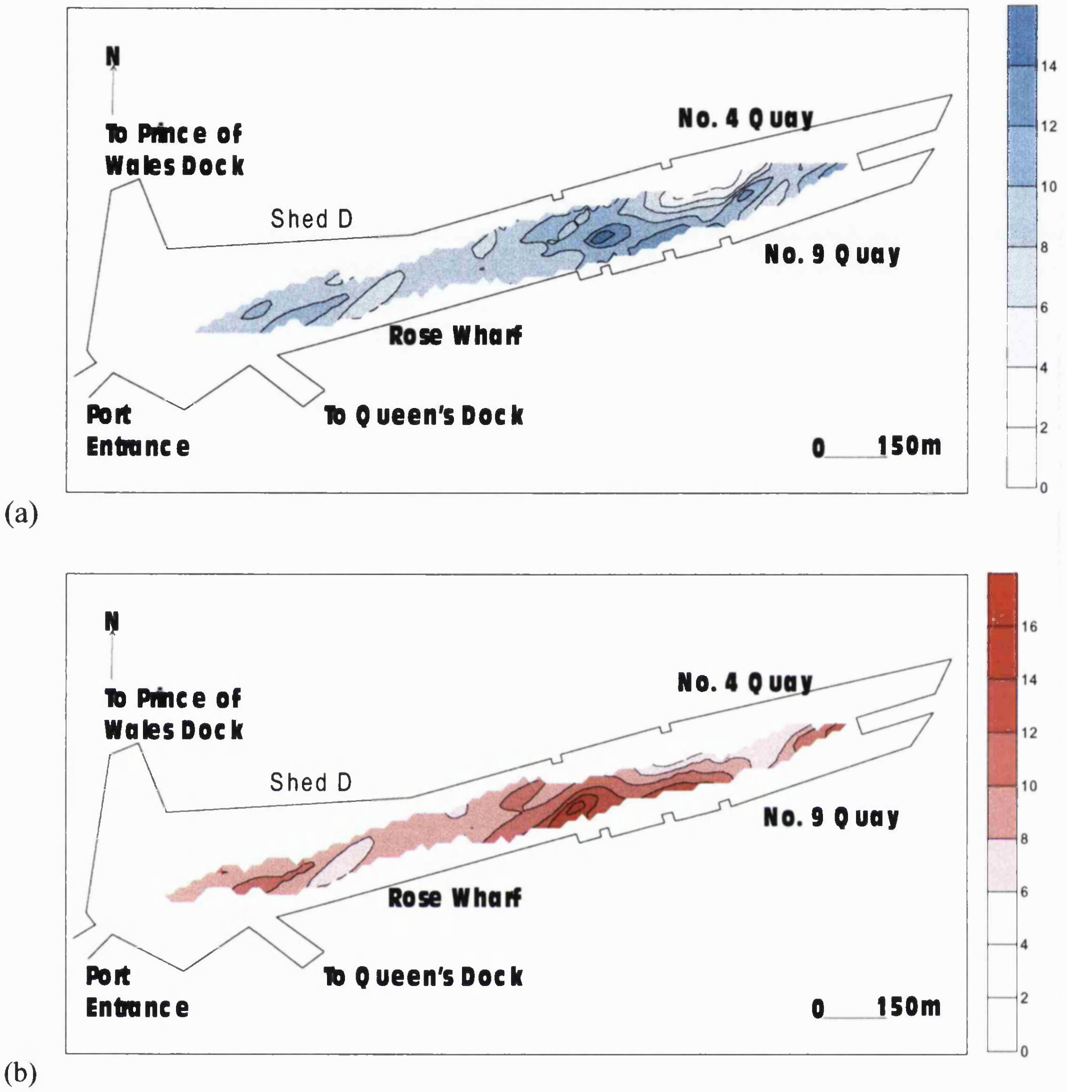


Figure 5.14: Kriged map of CB#28 employing 75% (a) & 50% sampling effort (b).

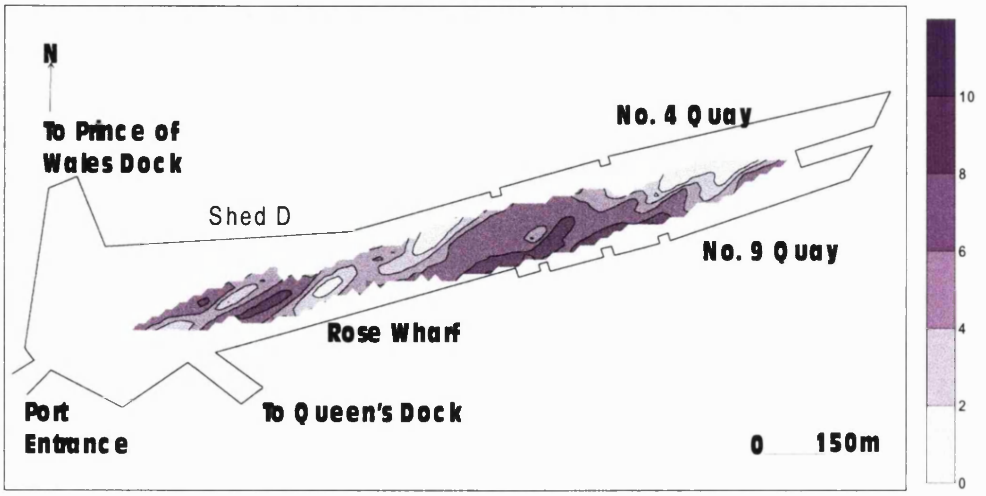


Figure 5.15: Kriged map of CB#66 employing 75% sampling effort.

5.4.3 Total CB loading estimates in dredged material prior to sea disposal

In England and Wales, the regulatory authority (CEFAS) currently determines the loadings of contaminants in sediments prior to the acceptance of a licence to dredge an area and disposal of material at sea. The method adopted for this assessment includes the calculation of chemical concentrations and loadings from areas within the proposed dredging zone. A number of sediment samples are requested (typically 2-5 samples) and a suite of contaminants are analysed. Loadings are calculated within the proposed dredging zone if concentrations are above a particular Action Level. If concentrations are higher than these Action Levels, the zone is divided into areas based on sediment concentrations. Within each designated area, the mean value is calculated. If concentrations are similar throughout the proposed dredging zone, the mean value is determined for the entire site. To calculate the total loading for the site, the quantity of sediment to be dredged (tonnes or m³) is multiplied by the concentration. This is either calculated for each individually defined area and a total figure derived (Equation 5.10), or is simply calculated once for the whole site.

$$\mathbf{L} = \sum \left((\mu_i \, . \, x_i) + (\mu_j \, . \, x_j) + (\mu_k \, . \, x_k) + (\mu_{ijk \cdots m} \, . \, x_{ijk \cdots m}) \right) \qquad [5.10]$$

where **L** is the total loading, μ is the mean chemical concentration of the individual area $_{i,\, j,\, k \cdots m}$, and x is the quantity of sediment to be dredged in the area $_{i,\, j,\, k \cdots m}$.

The total PCB loadings for King's dock have been calculated using the above method. PCB concentrations from sampling conducted by CEFAS in 1994 (n=2) and 1995 (n=3) are initially used in the calculation and these figures are compared to sampling conducted in the intensive case study (n=101) (Table 5.3).

In 1994, a licence was submitted to dredge 1,300,000 tonnes (or approximately 1,000,000 m³) of sediments from the dock. Sampling was conducted in two locations (n=2). Total CB concentrations were above Action Level 1 in the west of the dock and above Action Level 2 in the north east. Total loadings are presented in Table 5.3.

In 1995, another licence to dredge a similar quantity of material was submitted and sampling was again conducted but in three locations (n=3). Total CB concentrations were above Action Level 1 at two locations in the centre of the dock and above Action Level 2 at one location in the west (see Table 5.3).

Table 5.3: Total loadings in King's Dock, Swansea.

Year	n	L_1	L_2	L_3	L_4	L_5	L_6	Total Loading of $\sum_{25}$CBs (g)
Method 1: Action Levels								
1994	2	76.7	178.8	n/a	n/a	n/a	n/a	255
1995	3	91.0	158.6	n/a	n/a	n/a	n/a	250
1996*	101	129.3	132.6	n/a	n/a	n/a	n/a	262
Method 2: Kriging								
1996*	101	7.4	79.7	8.0	36.5	0.4	8.2	140

* Identical sampling campaign
L1 – L6 = Different locations within the dock and relative loadings of PCBs in each location.

Although sampling conducted for the present case study was not in support of a licence application, the total CB concentrations are used to calculate loadings for a similar quantity of sediment as above. The aim here is to determine the extent to which sampling density affects the total loading calculation. (The case study sampling in 1996 is the major sampling campaign to date). A large number of sediments exhibited total CB concentrations above Action Level 1 (n=86) and these were generally located in the centre and east of the dock. Sediments exhibiting concentrations above Action Level 2 (n=15) were located in the west of the dock (see Table 5.3).

In this example, the method used to calculate total loadings of sediment PCBs in King's Dock (Method 1 only) has provided consistent results independent of sample size. This is attributed to the identification of elevated PCB concentrations at all sampling events. The probability of sampling a 'hotspot' with only 2 or 3 samples is questionable. In this case, it was fortunate that these areas were sampled.

A different method was subsequently adopted to confirm the loading calculations above. The kriged map of total CBs (Figure 5.9) was used to determine concentrations within specific areas and loadings were calculated as a percentage of the total area. This is calculated using Image-Pro Plus software. A similar quantity of sediment (1,300,000 tonnes) was used to calculate the total loading. King's Dock was separated into 6 regions (L1 – L6) based on the kriging contours and hotspots. Total loadings are presented in Table 5.3.

Based on these two methods, the estimation of loadings using method 2 (i.e. the designation of kriged contours within the dock area) provides an improved estimation of the total PCB loading because these estimates are based on local patterns and spatial structures of PCBs as described by the sample variograms and fitted models. The first method is based on fewer samples which ultimately limits the overall estimation of PCB loads. As such, the calculations of PCB concentrations within areas exceeding specific Action Levels (Method 1) appears to *over-estimate* the total PCB loadings. The different approaches have distinct advantages and disadvantages depending on the overall aim of the sampling and destination of dredged material. For instance, if financial resources are limited, and dredged material is disposed at sea, a crude calculation may provide a good first step in the investigation of contaminant levels; although this is dependent on the identification of hotspots (Reed & Nicholson, 2000). However, if the dredged material is to be identified for beneficial use projects or remediation, which is costly, a more accurate assessment of chemical loadings would be required. The designation of multiple regions from a kriged map (which uses model parameters fitted to the sample variogram) is appropriate, especially where more accurate loads are required.

5.5 Summary

The need to develop more effective risk assessments of dredged material has provided an opportunity to develop a sampling scheme to identify the scale, magnitude and extent of spatial variation of PCBs in the sediments of an active commercial dock. Geostatistical methods have been used here to model individual CBs and environmental parameters over a known extent and to better understand the underlying processes influencing their variation. It has been possible to establish the spatial dependence of the less chlorinated CBs, suggesting that their solubility and volatility influence their spatial distribution. In contrast, the distribution of the more chlorinated CBs has been shown to be less structured (i.e. more continuous) reflecting their affinity to TOC in sediments. It has also been possible to identify areas within the dock that are the most likely sources of contamination. The estimation of all these environmental parameters has shown that by investigating spatial structures and relationships, it is possible to provide a more accurate assessment of contaminant loads and identify potential contaminant sources. Reliable estimates are achievable and can lead to more effective and improved risk assessment of dredged material prior to disposal.

CHAPTER SIX

Discussion

This chapter provides a discussion of the distribution of PCBs in estuarine, coastal and marine sediments and dredged material in England and Wales since 1990. The extent of PCB contamination and sources of within-site variability of sediment PCB concentrations at one locality are discussed. The sampling strategy agreed by the OSPAR Commission is critically reviewed together with the sampling regime adopted by CEFAS in support of a licence application procedure for dredging disposal at sea. An improved sampling protocol for evaluating such licensing applications is presented.

6 Discussion

6.1 Evaluation of PCB concentrations in sediments and dredged material monitored under NMMP & FEPA since 1990 in England and Wales

In England and Wales, concentrations of PCBs in sediments are measured routinely as a result of legislative commitments including UK Acts of Parliament and EU directives. The collation of existing data on PCB concentrations in marine and estuarine sediments and in dredged material has enabled the first critical assessment of the monitoring approaches currently in use. By taking a holistic approach, it is possible to identify generalised patterns and hint at underlying trends, both spatially and, to a more limited extent, temporally. The holistic approach can also identify gaps in knowledge which can be prioritised in more intensive studies.

Although the monitoring programmes undertaken between 1990 and 1999 have not achieved a high spatial resolution, some general statement can be made concerning national average sediment PCB concentrations within the various type environments. For example, low and often undetectable PCB concentrations (< 0.2 μg kg^{-1}) are typically found in offshore sediments throughout this period. A mean of 2 ± 6 μg kg^{-1} is appropriate to describe this environment. The higher than anticipated variability around this mean value is a consequence of specific conditions at two sites: Cardiff Bay and the Bristol Channel.

The Bristol Channel area has historically been a repository for PCBs entering the environment via wastewater discharged from the Monsanto plant at Newport (Solutia, 1998). Inputs from past activities in this vicinity have undoubtedly contributed to the elevated offshore sediment PCB burdens in the Bristol Channel. Previous studies have also revealed localised PCB 'hotspots' in other offshore or estuarine locations, for example, along the US coast (e.g. Florida) (Kostas *et al.*, 1994), in South Carolina estuaries (Marcus & Renfrow, 1990), California (Rice *et al.*, 1993), Australia, India, Japan and Taiwan (Iwata *et al.*, 1994). Future monitoring of sediment PCBs in offshore environments is necessary, but should be focused upon such known problem areas.

The situation within estuaries is more complex than that for offshore environments. The national average PCB concentration within estuarine sediments is significantly higher than that for offshore environments at 53.6 ± 126 μg kg^{-1}. Limited sampling makes it difficult to establish localised distributions, pollution gradients and areas of concern.

The average value can, however, typically describe PCB concentrations found in estuaries around England and Wales. Similar average concentrations are also reported elsewhere in Europe, notably in the Scheldt estuary (van Zoest & van Eck, 1990), the German Bight (Hühnerfuss *et al.*, 1997), the Venice Gulf (Donazzolo *et al.*, 1983), the Mediterranean coast (Mangani *et al.*, 1991) and the River Seine (Teil *et al.*, 1996).

The difficulties in interpreting the highly variable PCB concentrations in estuarine sediments are further exacerbated when dredged material is also considered. In docks, ports, harbours, marinas, river channels and other industrialised areas around the coastline of England and Wales, a wide range of concentrations (0 – 3,500 μg kg^{-1}) are found. Other countries have also recorded similar concentrations, for example, New York (Bopp *et al.*, 1981) and the Gulf of Bothnia (van Bavel *et al.*, 1995). A typical average (arithmetic mean) value in sediments at dredging sites is 85 ± 237 μg kg^{-1}. However, due to the high skewness, a median value of 34 μg kg^{-1} is perhaps more typical of concentrations in dredged material around England and Wales.

These findings are significant and should inform government of the potential loading of PCBs in estuarine sediments and dredged material in England and Wales. Previous studies of PCB budgets and inventories (Harrad, 1996; Tanabe, 1988) suggested that terrestrial soils are the largest sink of PCBs. In a recent study conducted by the University of East Anglia (1993), an average concentration of PCBs in UK terrestrial soils was calculated at 30 μg kg^{-1} which is similar to concentrations in estuarine and industrialised sediments described above. In the present study, dredged material, and to some extent estuarine sediments, are also shown to be a significant sink (they may also therefore be a potential future source). The extensive data set can therefore prove useful for future budget and loading calculations.

All sites sampled under NMMP and FEPA have been assessed using worldwide sediment quality guidelines to see if sediment contamination is likely to cause toxic effects to benthic communities. In general, concentrations at offshore sites and up to 86% of the estuarine sites lie below these guidelines. Such sites can thus be considered effectively uncontaminated. However, concentrations at 11% of total sites are above the guidelines set by several countries (e.g. Netherlands, Australia, New Zealand, Hong Kong and > the effects range low or ERL value). The ERL value is intended to represent concentrations below which adverse effects are not frequently expected (Long, 2000a). At those sites exhibiting concentrations above the ERL value, adverse effects are expected, although further investigations would be required to establish regional variability (Long *et al.*, 2000). A small percentage of total sites (3%) exceed the effects range median or ERM value (Long *et al.*, 1995) and are of particular concern. The ERM value is intended to represent concentrations above which adverse effects are more frequently expected (Long *et al.*, 2000).

Although approximately a third of all dredged material samples analysed since 1990 (37%) contain PCB concentrations below these guidelines, a large proportion of sites (55%; $n = 510$) exceed guidelines set by Netherlands, Australia, New Zealand and Hong Kong, and are above the ERL value. A small percentage of sites (8%; $n = 71$) exceeds the ERM value (Long *et al.*, 1995). A recent study by MacDonald *et al.* (2000) of consensus-based sediment effect concentrations for total PCBs suggested that chronic effects on sediment-dwelling organisms are likely to occur at concentrations in excess of 70 $\mu g\ kg^{-1}$ d/w. Where comparing these thresholds with the concentrations reported in this study, it is likely that over two thirds of dredged material sampled in docks, harbours, ports, marinas and other industrialised areas could potentially cause chronic effects on sediment-dwelling organisms. Indeed, a number of these sites with concentrations in the range 780 - 25,100 $\mu g\ kg^{-1}$ may impose acute effects on benthic organisms (cf MacDonald *et al.*, 2000). Importantly, and of paramount concern, is the apparent increase in PCB concentrations seen at some sites (for example, in the Rivers Tees and Tyne). This implies that sediments at a wide range of sites may exceed current guidelines in the near future. Further evidence is required in UK to determine sediment quality and effects on benthos. One approach that could be utilised is the Sediment Quality Triad (Chapman, 1992).

From a temporal perspective, sediment PCB concentrations in England and Wales do not exhibit any clear systematic decline over the last decade around England and Wales. By combining all of the above types of environments, it is apparent that PCBs are stable over many years, even decades. The overall spatial mean in estuarine sediments and dredged material is higher than expected, and its variation in time is similarly elevated, perhaps reflecting local spatial variability rather than any trends over time. The temporal average values tend to fluctuate and the standard deviations around this value are high, and in some cases higher than the average value.

At a number of sites around England and Wales, concentrations have remained elevated for many years. For instance, sites including: Newport Docks; Cardiff Docks; Swansea

Docks; the outer Usk estuary near Newport; the River Tyne; the River Tees; and Avonmouth contain elevated concentrations over consistently long time periods. Similar elevated concentrations have been recorded elsewhere in the UK, for example, in Scottish sewage sludge disposal grounds (Kelly & Ball, 1995; Kelly & Campbell, 1995) and in the River Tees (Proudfoot, 1995).

Other areas appear to show an overall increase in mean PCB concentration over time. These areas include: the River Blyth; the River Humber; Langstone Harbour; Poole; the Solent; Southampton Water; Avonmouth; Barry Docks; Cardiff Docks; Newport Docks; Milford Haven; Barrow-in-Furness and Heysham. Some of these sites have increasing but still relatively low concentrations (e.g. Langstone Harbour, the Solent, Southampton Water, Milford Haven, Barrow-in-Furness and Heysham) and, as such, are unlikely to be of concern. At other sites a temporal increase in average PCB concentrations maybe more apparent than real. For example, this may arise as a consequence of the high spatial variability in PCB concentrations, coupled with the temporal sparseness of the repeat sampling. In such areas, particularly docks, ports and harbours, where PCB contamination may be spatially uneven, more sophisticated sampling schemes are required to unambiguously identify real temporal trends in contamination.

Conversely, at some locations, concentrations have been effectively reduced through direct intervention, such as, effective emission controls. For example, in offshore sediments in the Bristol Channel and in the outer Taff and Usk estuaries. These areas have received a gradual reduction of PCB discharges due to the cessation of PCB manufacture, a reduction in emissions and through strict controls on discharge consents brought about by legislation introduced in the late 1980s and early 1990s. Wastewater discharge facilities introduced at the Monsanto site in Newport have greatly reduced PCB inputs into the Severn Estuary (Morris, 1995). A recent study reported by Laane *et al.* (1999) also demonstrates a decline in PCB loads in Dutch offshore sediments due to similar legislative commitments in the form of strict discharge controls. In the latter case, the relocation of a dredged material disposal ground to a more dispersive site may have additionally contributed to the reduced accumulation of contaminated sediments in later years (Stronghurst, pers. comm., 2000). This illustrates the important role of government in the enforcement and control of pollutants and the potential effectiveness of measures to manage their loads and burdens in the marine environment.

In estuarine environments, government action has also been effective in reducing PCB burdens. For example, sampling in the River Blyth found estuarine sediments contaminated with PCBs. These sediments are known to have been contaminated during the decommissioning of a submarine in the mid-1990s (CEFAS, 1997a). This specific pollution event has been attributed to a lack of good management practices at the dock, including contamination from waste oils, and action has since been taken to improve the removal of on-site waste. In the River Mersey, sediment concentrations clearly exhibit a decline due to the cessation of sewage sludge disposal in the late 1990s (Rees, pers. comm., 2000). Concentrations have declined in other areas after sampling had been conducted under FEPA (1985). In the Rivers Orwell, Tyne and Mersey, a reduction of PCB burdens has been directly related to the removal of contaminated riverine sediments to landfill. In Cardiff Bay, high concentrations were found at up to 1 m in depth. Due to the Cardiff Bay Barrage development (Murray, L.A., pers. comm., 2000), these sediments have been removed and transported to landfill.

At the regional scale, it is possible to propose areas of concern requiring priority action and additional monitoring. Areas of concern are defined here as either sites exhibiting consistently elevated concentrations above current CEFAS 'Action Level 2' (> 200 μg kg^{-1}) or sites which are elevated above typical concentrations found in the surrounding type environment (e.g. estuaries, the marine environment, the offshore environment or dredged material inner or outer estuary sites).

Within the marine environment, one area located in the North Sea, close to the offshore Tyne dredged material disposal ground, is of particular concern. Here, sediments exhibit PCB concentrations at an order of magnitude higher than typical average concentrations for this environment. Evidence presented by Reed & Waldock (2000) shows the Tyne dredged disposal ground to have recently accumulated TBT both in surficial sediments and in sediments at depth (to 0.5 m). The present study confirms that sediments dredged from the River Tyne are the most likely source of PCB contamination here. Similarly, in Swansea Bay, sources of PCBs in offshore sediments include dredged material disposed at the designated disposal ground. Further investigations should be conducted on sediments sampled at these sites.

In estuaries, areas of concern are identified in the River Tamar and the Usk estuary. Here, contaminated sediments are located in the outer estuary where PCB concentrations are typically > 100 μg kg^{-1}. This is exceptionally high for estuarine sediments and these higher than average concentrations may be due to localised inputs, flocculation (coagulation of suspended particulate matter at fresh/saltwater interfaces (Carter, 1991)), tributary loadings and/or adsorption to sediments. A comparison of homologue profiles between sites in the outer Usk estuary and Newport Dock illustrates that sites further offshore contain higher tri-CBs than those inshore. This is unexpected as sites offshore are further from terrestrial inputs and historic use. The offshore sediments exhibiting high concentrations of tri-CBs are located at sites sampled closest to the Monsanto plant discharge, suggesting that the Monsanto discharge may be a contributing source of PCBs to these localised elevated tri-CBs. However, recent monitoring has provided evidence that PCB concentrations have started to decline in this area (Reed & Waldock, 1998), although further monitoring is required to provide further confirmation of this trend. Other studies not conducted under NMMP have also reported sediments containing elevated concentrations, for example, along the Essex Coast (Scrimshaw *et al.*, 1996). This site would also be an area of concern.

Docks and marinas in South Wales are currently being further investigated as a priority (Reed & Waldock, 1998; Bird, P., pers. comm., 2000). However, high spatial variability evident in other estuaries and docks (e.g. in the River Tyne, especially upstream of Hebburn and near Scotswood Bridge, and in the River Tees, near Victoria Bridge) have not been effectively investigated. In the River Tees, sampling to date suggests that contamination is generally concentrated in the upper sections of this estuary. Further sampling in both estuaries is proposed here, in order that potential sources of contamination may be clearly identified and local sediment PCB burdens established. A more intensive sampling is suggested as a way forward to determine within-site variability.

Interestingly, the PCB reductions in Swansea Docks, which is evident from the analysis in Chapter 3, is not evident in subsequent sampling undertaken in the intensive study (Chapters 4 and 5). The number of sites with elevated concentrations (> 200 - 3,000 μg kg^{-1}) measured in King's Dock confirms that the FEPA sampling strategy provides only limited insights into true PCB inventories at the proposed dredge sites. Such evidence suggests that sampling using FEPA guidelines does not provide accurate estimates of sediment PCB concentrations.

Within the scope of the holistic analysis, it has been possible to indicate sites which may be a potential point source or accumulation site in an estuary or dock. The identification of sites is tentative due to limited spatial resolution locally. It is a first attempt at directing future investigations to those areas deemed to be influencing conditions at sites so that target levels are reduced to background levels by 2020. These sites have been identified by detailed investigations of homologue profiles.

The identification of comparable homologue profiles between NMMP and FEPA dredged material sites has confirmed that profiles in dredged material are similar to sediments sampled under NMMP. This is seen in the Rivers Blyth, Tyne and Tees, although marine sediments contained lower percentages of the less chlorinated CBs and higher contributions from the more chlorinated CBs in the outer Blyth estuary. This is likely to be a consequence of their physico-chemical properties (i.e. greater solubility of the tri-CBs and greater persistence of the penta- and hexa-CBs) and degradation or transport by environmental processes, such as diffusion, adsorption and transfer into the foodchain. Initial studies using the extensive data set provide direct evidence that dredged sediments are a source of contamination to the offshore environment.

In some instances, however, offshore sediments have distinctively different homologue profiles compared to those within the estuary. This is seen in the Rivers Tamar and Mersey. Few sites sampled under the NMMP and FEPA schemes provide enough information to suggest possible reasons for changing PCB patterns. Such changes may be due to either inputs from complex mixtures of PCBs, disturbance from natural events or anthropogenic activities locally and/or other environmental processes, including: sedimentation; adsorption; desorption; diffusion; dechlorination; bioturbation and partitioning between air/water/sediment and biota (Safe, 1996; Vanier *et al.*, 1996; Jiménez *et al.*, 1996; Lamoureux & Brownawell, 1997, see Section 1.3). Further investigations under NMMP could provide additional information on possible processes changing PCB signatures and PCB sediment burdens in estuarine environments. Further investment in sampling should be considered.

Also, changing homologue profiles at the above site types over time appear to be very inconsistent and clear trends are complicated by large standard deviations. The large variances are attributed to local spatial variabilities rather than to changes over time. PCBs remain relatively stable for decades (Sinkkonen & Paasivirta, 1998). Due to limited repeat sampling and errors associated with this (i.e., large variances, sampling error, analytical error and exact site identification), it is not possible to reveal any additional useful information from the extensive data set. It is therefore proposed that a new sampling strategy be designed and incorporated in to the NMMP.

The data generated from this study provide a useful baseline record of sediment PCB concentrations in the estuarine, coastal and marine environment in England and Wales where, previously, such data have been limited or non-existent. The NMMP results have made available preliminary information on the amounts of these compounds in marine and estuarine sediments and findings may contribute to the design of future sampling strategies with the view to monitoring their attenuation over longer timescales. Indeed, the aims of the NMMP is to determine the spatial extent of PCB contamination in estuaries and changes to these levels over time, and although there has been a large sampling effort, there have been few sampling sites that have provided enough information to determine such changes or patterns. It is also not possible to identify some of the processes redistributing these chemicals in sediments or their persistence within UK sediments. The limitations of the NMMP are clearly evident and future sampling under this programme must address these issues.

Neither FEPA and NMMP sampling have established confident PCB concentrations in sediments in areas along the coastline, established within-site variability, determined local scale variation, identified temporal trends or defined possible sources of PCB contamination at specific sites. Local spatial variability is a problem in interpreting results at sites in Langstone Harbour, the River Tyne, the River Mersey, Swansea Docks, Newport Docks and other sites in South Wales. The sites in the River Mersey and South Wales are areas of concern requiring significant financial commitment and monitoring to identify sources and contamination extent within docks and estuaries. In the River Mersey, contaminated sediments are identified towards the inner estuary close to industrialised areas but further sampling is required to establish local scales of variability.

However, despite this, results obtained from FEPA sampling and NMMP monitoring have provided the following information: average concentrations typically expected in estuarine, marine and dredged sediments; location of areas of concern; identification of offshore contaminated sites; location of possible local sources (although further investigations are required here); identification of possible hotspots; general trends in homologue profiles in specific locations (e.g. Severn Estuary); comparabilities between dredged material and marine sediments and areas where high spatial variabilities exist.

6.2 Nature of local spatial variability of PCB concentrations in dredged sediments in King's Dock, Swansea – the intensive study

The intensive study, in King's Dock, Swansea, has provided a unique opportunity to explore PCB concentrations in dredged material at a very local scale. The environmental variability and spatial distribution of PCBs are consequently investigated using univariate and multivariate statistics as well as geostatistics. By using geostatistical methods it has been possible to assess both patterns and structures in the data and thus develop a method that estimates concentrations at unsampled locations. The adopted sampling scheme, utilising a combined grid and nested sampling approach, has been able to address the problems of local spatial variability providing suggestions as to the scale and sources of PCB variability.

The most important issue to address in the intensive study is the problem of spatial variability. This is one of the biggest limitations identified in the extensive study above. A better representation of spatial variability is achieved by increasing sample numbers and by incorporating sampling at a range of short and long distances. Although increasing sampling intensity has provided a better estimation of the mean, the variability around the mean is actually very high. The mean total PCB value of 201 ± 347 μg kg^{-1} and the median value of 121 μg kg^{-1} are considerably higher than values calculated in dredged material in England and Wales. This is attributed to the positive skew of the distribution which is greater in the case study than in the distribution calculated for England and Wales. This is due to several elevated PCB concentrations found within the site. The overall range of concentrations in King's Dock is, however, similar to those found at other sites sampled in England and Wales (e.g. the River Blyth, the River Orwell, Newport Docks and the River Mersey).

Highest concentrations are found in the west of the dock suggesting that accumulation sites are located near to loading bays at Shed D and Rose Wharf Bay. The lowest concentrations are found in the east side of the dock furthest from the contaminated area. Near uniform concentrations (~100 μg kg^{-1}) are distributed throughout the middle section of the dock. These levels are either indicative of a diffuse source(s) located within the site or represent concentrations redistributed as a consequence of shipping activities which move or mix the sediment. Importantly, the distribution of some CBs is dependent on specific environmental parameters, such as TOC (Achman *et al.*, 1996), colloidal matter (Burgess *et al.*, 1996) and particle size (Smedes, pers. comm., 2000) and these too influence their distribution within dock sediments.

The normalisation of individual CBs to TOC and particle size is an important stage in the assessment of PCBs within dock sediments. To date, these parameters are not routinely measured and are not included in the FEPA regulatory assessment. In King's Dock, it is clear that the distributions of several individual CBs are affected by the content of organic matter in sediments. The adsorption of PCBs to sediments has been reported by Morris (1995) to be in the order of hexa- > tetra- > di-CBs and this is consistent with the findings of this study. Accordingly, it is proposed that these parameters are included routinely, both in national monitoring and in the regulatory assessment of dredged material.

Possible sources of spatial variability within the case study have been also been addressed in the intensive study. Concentrations measured in sediments at *Sites*, in *Grabs* and in *Subsamples* are statistically analysed and results show that sampling at *Sites* does not estimate the true variability of concentrations in the dock. This is possibly due to the limited sample size at *Sites* (n = 10). Spatial variability therefore exists between *Sites*, i.e. at ~150 m. Similar environmental variability of PCBs was found by Rice *et al.* (1993). Further evidence provided by geostatistical analysis in this study suggest individual CB variograms have limits of spatial dependence or environmental variability at similar distances (117 - 280 m). Small scale variability (*Subsamples* taken within a *Grab*, and between *Grabs*) is attributed to analytical errors suggesting that sediments are homogeneous over this scale.

The high nugget variance in the sample variograms of all CBs and environmental parameters suggests that there is some unresolved variance or small scale heterogeneity. The measurement of the sampling positioning error and analytical error will contribute a small amount to the nugget variance but cannot explain it all. Soares (pers. comm., 2000) suggested that the sample size was likely to be the greatest contributor to the nugget. Although Armstrong *et al.* (1993) suggested sampling surficial sediments at an average depth of 1.16 cm, Soares (pers. comm., 2000) found that by sampling at greater depth (~50 cm), it was possible to reduce the nugget effect considerably. Perhaps regional contamination histories influence chemical variation at the local scale and, therefore, sampling surficial sediments or sediments at depth should be site specific.

The magnitude of spatial variation determined in this study is comparable to other studies in the US (Achman *et al.*, 1996; Brown & Fish, 1999). The nature of this environmental variability was attributed to local releases of PCBs rather than a dominant source. In the case study here, it is proposed that two local accumulation sites have produced the overall spatial distribution of sediment PCBs in King's Dock; these are located in the south west and south east. This is significant as previous sampling by CEFAS and ABP was unable to establish spatial variation locally or identify point sources or accumulation sites within the dock. As ABP have been refused a licence to dredge King's Dock, this information will assist them in their management of PCB contaminated sediments, enabling them to identify areas (i.e. in the west) that can either be removed to landfill, capped or remediated, or other areas (i.e. in the east) that may be deemed suitable for sea disposal (under the current CEFAS assessment procedure).

Several individual CBs are responsible for producing most of the variation and spatial structure in the King's Dock data set. Results from the principal component analysis conducted in Chapter 4 show CB#110, #138, #118 and #153 as heavily loading PC1 and CB#66, #28, #31 and #101 loading PC2. The spatial structure found in PC1 is attributed to the local PCB source, that is, to various different Aroclor® mixtures. In contrast, the spatial structure of PC2 is attributed to environmental and anthropogenic processes operating within or near the sediments causing changes to sediment PCB signatures. Further investigations including measurements of colloidal matter, full particle size range and more detailed organic matter analysis are required to facilitate a greater understanding of the potential factors governing sediment PCB distributions within a site.

Experimental variograms of individual congeners, total PCBs, particle size, TOC and their principal components have provided a clear description of the spatial structure of these parameters as well as insights into the possible mechanisms affecting their distribution. The variograms of the less chlorinated CBs (i.e. tri-, tetra- and penta-CBs) suggest that spatial variation is more patchy and structured compared with the more chlorinated ones (i.e. hexa- and some hepta-CBs) which have unbounded models. This particular feature may be related to their different patterns of relative susceptibility to various physico-chemical and biological processes. Indeed, high spatial dependence of the less chlorinated CBs is attributed to high volatility and high solubility and their movement influenced by their behaviour in the dissolved phase.

Spatial dependence of the more chlorinated CBs is possibly a response to rapid immobilisation by their association with the sediment organic fraction, partitioning into lipids and waxes in the sediment (Hess *et al.*, 1995) and accelerated fixation to sediments, a characteristic of their low solubilities, hydrophobicity and lipophilic nature (high K_{ow} and K_{oc} values). These congeners are adsorbed to sediments in greater quantities than the less chlorinated CBs and are often bound more strongly. It is their environmental behaviour that governs the spatial patterns and structures identified by the sample variogram.

Variogram models and kriging maps have clearly identified two areas within the dock that have elevated PCBs and these are believed to be likely sources of past contamination. Such 'hotspots' have, in the past, been of major concern and regulatory action has been focused at such sites. However, average concentrations (~100 μg kg^{-1}) typically exhibited in dredged material in docks in South Wales, for example, are of increasing concern. For example, 93% of all sites sampled in this study contain concentrations > 70 μg kg^{-1}. MacDonald *et al.* (2000) suggest that at this concentration, sediments could cause chronic toxic effects to sediment-dwelling organisms. At the other 6% of sites, sediment-dwelling organisms could potentially experience acute toxic effects. Unpublished results, by Reed (2000) show acute toxicity in King's Dock sediments sampled at sites in close proximity to Shed D, No. 4 quay, No. 9 quay, Rose Wharf, Shed A and Shed B. Using a 10 day whole sediment bioassay, the survival of the annelid polychaete, the common lugworm *(Arenicola marina)* was reduced by 44%. An increase in mortality to 75% was observed during a 100 day whole sediment bioassay using the same method. The mortality could not be attributed to PCB concentrations alone, but is likely to result from the effects of other chemicals or as a consequence of additive, synergistic or antagonistic effects of contaminant mixtures.

Investigations of sampling effort required to reliably compute a variogram for kriging have shown that a reduction in sampling effort dramatically affects the structure and form of the sample variograms. A reduction of 25% sampling effort has, in the case of CB#28, over-estimated the range. The effects on the variogram form by further reducing the sampling effort to 50% were: higher nugget variances; more erratic behaviour, especially over shorter distances; no defined range or sill; and a higher incidence of nugget variograms. By reducing the sampling effort, the structure and form of the variogram is lost. The number of samples and the sampling plan are considered to be important influencing factors in the calculation of a reliable variogram. Early stages of sampling design should thus consider the number of samples required to calculate the variograms. Several other studies have considered the issues of sample numbers and the sampling plan design (Chang *et al.*, 1998; Wang & Qi, 1998; Frogbrook & Oliver (2000) and similarly found them to have influencing effects on the variograms.

The determination of total PCB loads in sediments prior to accepting a licence to dispose of dredged material at sea was assessed by two different methods (Table 5.3). The current method adopted by CEFAS utilises often limited sample numbers to estimate loads above or below current CEFAS 'Action Levels'. The CEFAS method appeared to *over-estimate* the PCB load when compared to the kriging method. The implications for such over-estimations is the outright refusal of a dredging licence, partial refusal of a licence designating an area that can be dredged and other areas designated to landfill. The economic costs, both in terms of landfill prices or loss of business due to inaccessibility to the docks (i.e. through silting of dock gates as in Swansea Docks or the main estuary channel as in the River Tyne), is significant. The kriging method is a more accurate method of estimation than that adopted by CEFAS because it is not only based on a larger number of samples (i.e. less uncertainty) but the variogram models are fitted to the field collected sample data and therefore represent the spatial patterns and structures at the local scale.

6.3 Towards an improved sampling protocol for PCB sampling in support of dredge licensing

Improvement of the basis for estimating PCB concentrations in dredged material using the above approach has enabled a more accurate means of assessing a contaminant's distribution, loading and variability in the environment. Consequently, this approach can assist with the legislative requirement under FEPA (1985) which aims to prevent pollution of the seas by substances liable to create hazards to human health and/or harm living resources. This is particularly important where dredged material is assessed for beneficial use projects and where large volumes of dredged material (and therefore potentially elevated contaminant loads) are re-distributed into potentially sensitive intertidal environments. This approach may also improve the ability of pollution monitoring programmes to identify sources and spatial patterns of chemicals with the ultimate aim of realistically and effectively reducing levels by 2020 (OSPAR, 2000).

Unfortunately, in order to adequately assess the magnitude and environmental variability of sediment PCB concentrations at the local scale, it is necessary to take a reasonable number of samples for analysis. Costs of chemical analysis are high, but it is not just financial resources that are the problem. Costs of *under sampling* can be high as well. Consequences of under sampling, for example, could mean ineffective compliance monitoring and a reduction in the quality of our environment. To date, monitoring and sampling in England and Wales have been shown to be limited by financial resources and this has led to a lack of spatial coverage, representativeness, sparse repeat sampling and possible misclassification of sites. In order to better assess sediment contaminant levels, sampling strategies need to be urgently revised and the cost-effectiveness of different approaches evaluated. A new approach to dredged material assessment is presented. It is intended that this approach be included with other improved risk assessment strategies of dredged material including biological effects and benthic community structure analysis and monitoring (Porebski & Osborne, 1998; Allen *et al.*, 1999; Porebski *et al.*, 1999; Reed *et al.*, 1999; Rowlatt *et al.*, 2000; Matthiessen, pers. comm. 2000).

In designing a sampling programme, it is often necessary to define optimum numbers of samples. There are various statistical techniques including chemometrics (Keith, 1988; del Castilho & Breder, 1997) and geostatistics (Russo, 1984; Isaaks & Srivastava, 1989; Webster & Oliver, 1990; Oliver & Webster, 1991; Chang *et al.*, 1998) that can help determine this optimum number. Various minimum sample numbers and sampling designs have been proposed for geostatistical analysis (Russo, 1984; Webster & Oliver, 1992; Chang *et al.*, 1998; Wang & Qi, 1998; Frogbrook & Oliver, 2000). In most cases, the optimum number will often relate to the size of study area to be sampled and the extent and degree of contamination. In some cases, there may be benefits to stratifying areas prior to sampling so that sites are more homogeneous (Wagner, 1995). For specific techniques such as kriging, there is some debate concerning the minimum number of samples required. Published minimum sample sizes range from: 25 (Lin & Roester, 1988), 28 (Chang *et al.*, 1998), ≥ 30 (Russo, 1984) to 100 (Oliver & Webster, 1991; Frogbrook & Oliver, 2000). Importantly, these studies suggest that sampling should be well designed to incorporate small scale variability: this is especially important for kriging estimations. Also, sample numbers should be increased if more information is required on a population's distribution and if the behaviour of the variogram is important at greater distances. The assessment of contaminants in dredged material is conducted over both small and large distances (often kilometers). At larger distances, more intensive sampling is recommended to better estimate a reliable sample variogram, one which encapsulate the spatial structure and patterns at these distances. The increased intensity of sampling is required to generate a greater number of comparisons at larger lags.

The success of any improved sampling protocol is ultimately dependent on the objectives of the sampling and the precision in which information is obtained (Osberghaus & Helmers, 1997). Acceptable levels of confidence should be defined at the outset as this, together with financial constraints, can determine practical sample numbers. This is particularly important for the acceptance or rejection of licensing applications as the misclassification of dredged material could potentially lead to either offshore contamination (Reed & Waldock, 2000) or economic problems for maritime operators. It is appropriate, therefore, to provide an assessment of confidence levels and, in particular, the standard errors associated with current sampling schemes including FEPA and OSPAR.

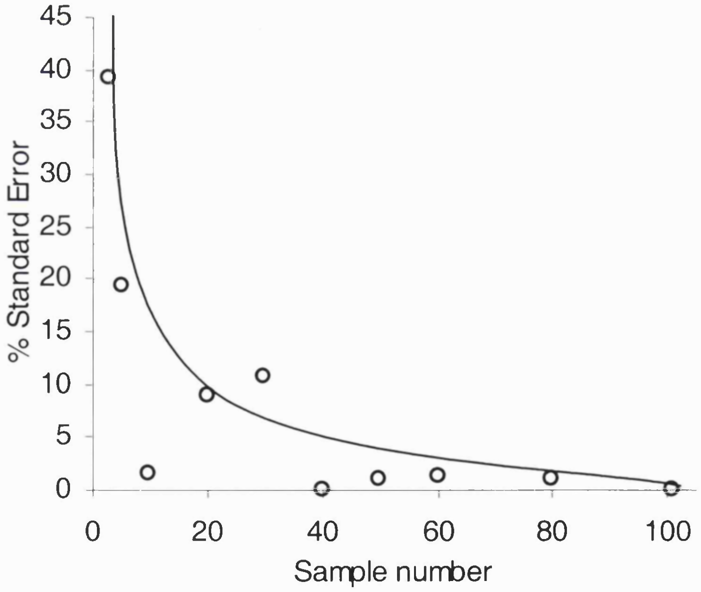


Figure 6.1: Percent standard error against sample size for average total PCB concentration in sediments in King's Dock.

In King's Dock, an estimate of the standard error (%) of the average $\sum_{25}$CBs associated with measuring concentrations at 3, 5, 10, 20, 30, 40, 50, 60, 80 and 100 locations is calculated. Figure 6.1 shows that at very sparse sampling, there is a large standard error, as would be expected. This error is reduced to 3 - 12 % if sampling is increased to between 10 - 30 samples and the uncertainty is more slowly reduced at > 40 samples. A recent study by Osberghaus & Helmers (1997) indicated that representative samples of wastes (e.g. sewage sludge) could be obtained if a ± 25 % variation of the average value (based on acceptable statistical certainty) was accepted. Sampling of <25 sites in an area suggests that there is less return for increasing effort. It is worthwhile increasing the sampling effort to determine a more accurate estimation of contaminant loads, establish local spatial distributions and identification of sources. Regulatory assessment of dredged material, using the FEPA sampling scheme of between 3 - 5 sediment samples, could *misclassify sediments* for sea disposal. At King's Dock, the standard error for concentrations of average $\sum_{25}$CBs in sediments was between 20 and 40%. This may explain why CEFAS and ABP could not determine spatial patterns or provide accurate estimations on PCB concentrations in sediments locally. A cost benefit analysis is possible by selecting an example cost of analytical services, e.g. £200 per sample analysed.

The cost of PCB analysis at various sampling intensities are shown in Table 6.1. Current practices under FEPA (using Method 1 in 5.4.3) costs approximately £400-600. Although this is relatively inexpensive, the possibility of over estimating the actual contaminant load is high and therefore may have knock on costs for disposal. For example, the cost for disposal of uncontaminated dredged material to sea is ~£10 per tonne. The average amount of material to be dredged in King's Dock is 1,300,000 tonnes. The cost of disposal of this volume of material to sea is £13,000,000. However, if this material is identified as contaminated (>200 μg kg^{-1}) or if calculated estimated loads are high, which is possible if Method 1 is adopted, then costs to transport sediments to landfill increases to £100 per tonne. If this scenario was to occur, costs to move this material to landfill would be £130,000,000. If a better method is available to identify PCB distribution and load (i.e. Method 2), costs could be saved by investing in more intensive sampling (£5,000- 20,000). Increased sampling and more accurate estimations of PCBs can produce more confident load calculations and potentially reduce disposal costs by identifying sediments that may require landfill disposal or increase the volume of sediments that can be disposed to sea.

Table 6.1: An example of cost for PCB analysis in sediments at various sampling intensities.

Sampling Intensity (*n*)	Cost of PCB Analysis (£)
2-3	400-600
10	2,000
25	5,000
50	10,000
100	20,000

Various approaches to sampling have been discussed in the literature (Keith, 1988; Webster & Oliver, 1990; Kelly *et al.*, 1994). In general, the sampling plan attempts to estimate some of the following: regional means; variances and trends; differences in means and variances between areas; spatial correlation functions; probability of detecting an extreme value; confidence level on various sampled variables; and detailed contour maps on selected variables. Also, it may be important to identify sources or environmental processes operating at a site to determine the extent of localised pollution (CEFAS, 1997a; Reed & Waldock, 2000). To improve the assessment of PCBs in dredged material at the local scale, an innovative sampling protocol is developed.

To improve the quality of these assessments, standardised procedures for sampling, storage and analysis should be incorporated into the proposed sampling protocol to reduce overall estimation errors (Wagner, 1995). Furthermore, an estimation of the measurement uncertainty from field sampling is especially important as this can be between 10 and 55 %, suggesting heterogeneity is a limiting factor (Krumgalz *et al.*, 1989; Wells *et al.*, 1994; Ramsey & Argyraki, 1997). Often, measurement uncertainty from field sampling can be reduced by normalising chemicals to TOC or to other environmental variables (i.e. major metals (such as aluminium), alumino-silicates from fine particles (such as clays) and particle size) (Morris, 1995; Brewers *et al.*, 1998; Smedes, pers. comm., 2000). The reduction of this uncertainty will provide a better assessment of chemical concentrations in sediments and therefore lower the risk of mismanaging dredged material. As suggested previously, it is proposed that TOC and particle size analysis are concomitantly analysed.

It is therefore appropriate to design a sampling protocol that provides adequate sampling for compliance monitoring rather than designing a scheme that provides intensive sampling for other scientific purposes. The proposed sampling protocol aims to provide various improved steps in the risk assessment of dredged material quality prior to disposal. A tiered approach is proposed in Figure 6.2. This type of approach (i.e. a tiered structure) has already been proven to be effective in assessing sediment quality (Porebski & Osborne, 1998; Chapman *et al.*, 1999; Porebski *et al.*, 1999; Stronghurst, pers. comm., 1999). The main difference between previous work and the approach proposed in Figure 6.2 is the incorporation of different sampling options in Tier 1. The approach also attempts to improve on past sampling designs by addressing issues such as field variance, confidence limits and loading calculations.

In Tier 1, as soon as a dredge licence application is received, any historic data should be collated prior to sampling. If there are no data or sediments sampled previously at the same site are expected to be historically uncontaminated, sampling is prioritised into areas where there are fine sediments or, for example, sediments containing a high percentage of TOC. As shown in the intensive study, these areas are those which typically contain elevated concentrations of PCBs. Given the high cost of laboratory detection of PCBs, prioritising sites at this stage is economically cost-effective. (It should be noted that it is recommended that other areas are incorporated so that sampling is representative and not biased to either high or low concentrations, and that loading calculations are thus representative of an area (Snedecor & Cochran, 1980; del Castilho & Breder, 1997)). It is desirable, therefore, to stratify a location into areas so that sampling can cover a range of sediment characteristics and therefore the full range of contaminant concentrations. Areas selected for sampling and chemical screening can only be undertaken if the secondary environmental variables described above are initially assessed using geostatistical techniques. Sample numbers here are based on requirements for variogram modelling. The analysis of such sediment characteristics are less expensive than chemical analysis and can help prioritise or stratify areas before chemical screening in Tier 2 (Wagner, 1995). Sampling for chemical analysis requires a minimum of 10 but should include between 10 - 40 samples depending on specific site characteristics. This number is based on agreed confidence limits and percentage standard error (see Figure 6.1).

Conversely, if sediments have been identified as contaminated, a more intensive sampling strategy is immediately implemented in order to assess the contamination extent and source, and possibly to provide an insight into processes affecting the contaminant's distribution. At this stage, site selection should incorporate geostatistical analysis of chemical concentrations. Sample numbers depend on acceptable kriging estimate variances and reliability of the variogram model. Consequently, as most assessments of contaminant levels are required over large distances, a nested sampling scheme similar to the scheme conducted in King's Dock could prove the most cost-effective.

The second Tier provides full chemical screening including normalising sediment PCB concentrations to TOC, particle size or other parameters so that field variance is better understood. This is an important step in the assessment of contaminants (Keith, 1988) and may help to reduce the total percentage error as shown in Figure 6.1. An assessment of sediment chemical levels to CEFAS Action Levels provides specific management options in the next Tier. Further research is being conducted to update these Action Levels in view of recent studies undertaken in the US and Europe (Reed *et al.*, 2000d).

Tier 3 determines whether sediments can be disposed at sea. If contaminant levels are below Action Level 1, sediments are acceptable for sea disposal. If, however, contaminant levels are between Action Levels 1 and 2, load calculations should be determined and if the load is below a specific threshold, sediments are accepted for sea disposal. If the loading exceeds this threshold, further sampling is required. In light of recent work by MacDonald *et al.* (2000), this threshold could provisionally be set at 70 $\mu g\ kg^{-1}$. This figure should be continuously reviewed to include not only chronic toxic effects but also the bioaccumulation potential of PCBs and other information on population level effects. If, however, contaminant levels are above Action Level 2, the first option is to conduct further sampling and analysis using geostatistical techniques. If sediment contaminant levels continue to exceed this level, sediments should be either contained, remediated or removed and transported to landfill. Improved procedures, such as those proposed above, are essential for effective management of PCBs, even though this may increase the proportion of dredged material that is unacceptable for sea disposal (O'Connor, 1999).

This type of approach has been suggested by Wakeman & Suszkowski (1999) as an effective strategy for managing contaminated dredged material. Various reduction scenarios, using modelling programs and loading calculations, are currently being conducted by the US Army Corps of Engineers (Wakeman & Suszkowski, 1999). It is here proposed that a similar management approach be considered in the UK.

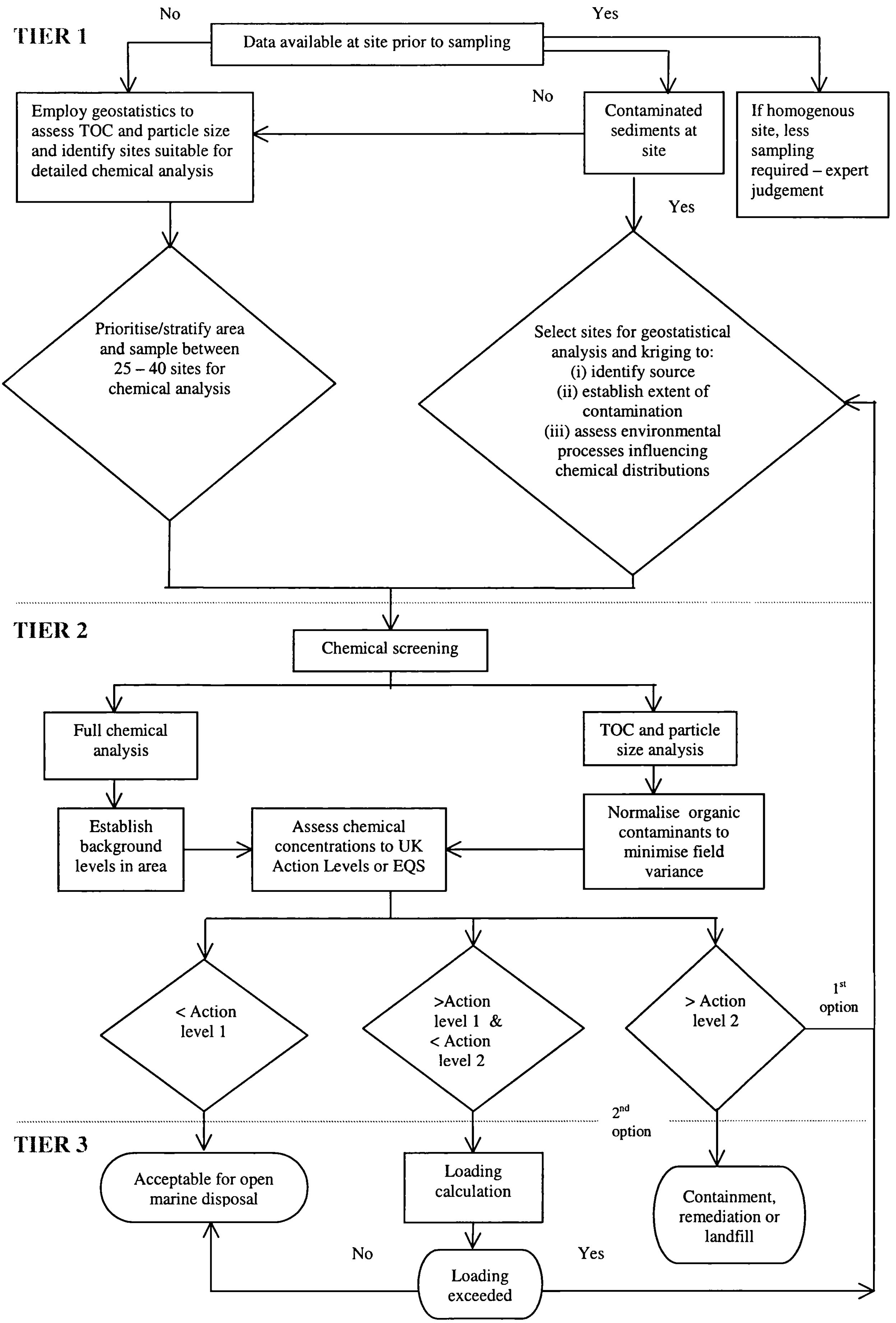


Figure 6.2: Tiered sampling protocol proposed for the evaluation of chemical concentrations in dredged material.
(Total PCB CEFAS Action Level 1 = 100 $\mu g\ kg^{-1}$ and Level 2 = 200 $\mu g\ kg^{-1}$).

In order for government organisations to effectively reduce contaminant levels by the 2020 deadline (OSPAR, 2000), it is essential that an integrated approach to the management of sediments is adopted. The underlying monitoring must always be cost-effective but should also be focused on producing high quality, accurate and appropriate information. In terms of reducing chemical concentrations (currently <100 μg kg^{-1}), information concerning the contaminant's spatial distribution is crucial to the identification of sites requiring remediation or other action. The number of samples required to achieve this should be > 25 (as suggested in Figure 6.1). Kriging in King's Dock has also been shown to be effective in the areal estimation and classification of sediment PCB concentrations and loads. This statistical technique can be used where an assessment of many chemicals is required and where it is necessary to establish pollutant patterns (Yost *et al.*, 1982; Zitko, 1994; Chappell, 1995; Snodgrass & Kitanidis, 1997; DelValls *et al.*, 1998). As a first step, it is proposed that dredged material located at heavily contaminated sites around England and Wales be assessed using these techniques.

New sampling schemes to assess concentrations of contaminants in the environment should be in place by 2003 so that targets set by OSPAR to reduce levels of hazardous substances to zero or near zero (i.e. background) levels can be met by 2020 (OSPAR, 2000). At the most heavily contaminated sites, such as those in industrialised areas and ones typically requiring dredging, there is an urgent need to determine point sources, spatial patterns and environmental distribution of chemicals. Effective designation of sites can accelerate the removal, remediation (physical separation or biological degradation) and/or containment (i.e. immobilisation) of contaminated material. A cost-benefit analysis of this approach should now be undertaken as this is beyond the scope of this study. Establishing the true costs and benefits of environmental protection and enhancement in the aquatic environment is imperative (Gaterell & Lester, 2000). The measurement and effective estimation of persistent organic pollutants, such as PCBs, can assist the management and eventual attenuation of contaminated sediments in the future.

CHAPTER SEVEN

Conclusions and Recommendations

The important findings of the 'extensive' study of the spatial distribution of PCBs in marine and estuarine sediments, and dredged material in England and Wales are given. The characterisation of PCB concentrations, in terms of the spatial structure, in the 'intensive' study, King's Dock, is summarised. The sampling scheme adopted for King's Dock has implications for other sampling strategies applied to similar areas. The proposed sampling protocol is reviewed and presented.

7 Conclusions and recommendations

7.1 Conclusions

PCB concentrations in offshore marine sediments around England and Wales are generally low, often close to or below the limits of detection. Most of these sites can thus be considered unpolluted. In estuarine sediments, however, the situation is very different and elevated concentrations are generally found in estuaries and enclosed bays. The overall magnitude of PCBs in both marine, estuarine and dredged material sites is highly variable. In the marine environment, concentrations are found between 0 – 800 $\mu g\ kg^{-1}$. In dredged material, concentrations are much higher, between 0 – 3500 $\mu g\ kg^{-1}$. Average concentration values are calculated for marine sediments (0.32 $\mu g\ kg^{-1}$), estuarine sediments (12 $\mu g\ kg^{-1}$) and dredged material (34 $\mu g\ kg^{-1}$). These levels are comparable to other European and worldwide investigations.

A broad statement of sediment quality, with regards to PCB contamination, around England and Wales has identified sites within North East England, North West England and in South Wales that are classified as heavily contaminated, and in some cases, grossly contaminated. These areas were heavily industrialised and this pollution is a consequence of historic PCB production and use. In the marine environment, 3% of sediments sampled to date are found to be heavily contaminated and 14% of marine sediments exceed current worldwide sediment quality guidelines (SQGs). In contrast, approximately 30% of dredged material is found to be heavily contaminated and 63% of dredged material sites exceed current SQGs.

This investigation has led to the identification of several areas of particular concern. These areas include: the Tyne dredged material disposal ground; the Bristol Channel; Cardiff Bay; the Rivers Blyth, Tyne, Tees and Mersey; Swansea Docks; Newport Docks; Cardiff Docks and Barry Docks. For some of these sites, possible sources of PCBs can be identified. In the Tyne and Tees, for example, dredged material disposal is implicated in the contamination of the outer estuary and offshore environment.

A more intensive case study of King's Dock, Swansea, has highlighted the local scale spatial variability of PCBs in dock sediments. The sampling scheme enabled areas of highest concentrations (> 200 $\mu g\ kg^{-1}$), located towards the west of the dock, and lowest concentrations, towards the east, to be established where previous sampling schemes have not identified such spatial patterns. In the dock, over half the sediments exhibit concentrations between 100 – 150 μg kg^{-1}, in excess of the current CEFAS Action Level 1. Such PCB concentrations in sediments could induce chronic effects to benthic communities. To date, no benthic analysis of sediments has been incorporated in the routine analysis of dredged material licensing, although this will change as from 2002 (Murray, L.A., pers. comm., 2000). The case study also demonstrated the benefits of normalising the more chlorinated CBs to TOC a consequence of the fact that these CBs have an affinity for organic matter.

The spatial structure of individual CBs in King's Dock sediments has been described by combining both multivariate and geostatistical techniques. Models fitted to sample variograms of individual CBs, total CBs, principal components 1 and 2, TOC and particle size are used to characterise the spatial variation of each variable. The average scale of spatial variation (i.e. range) of individual CBs is 220 m. Spatial variation is more structured in the less chlorinated CBs whilst the more chlorinated CBs are best fitted with unbounded models suggesting little spatial dependence. This behaviour is attributed to the different susceptibility of these individual CBs to various physico-chemical and biological processes. For example, less chlorinated CBs have higher solubilities and are therefore more mobile in the environment. More chlorinated CBs are hydrophobic, less soluble, and generally adsorb to sediments much more effectively, thereby reducing their environmental mobility.

Estimates of the sampling effort required to compute reliable variograms indicate that by reducing sampling effort by >25 % percent relative to this 'intensive' (n=101) study, sample variograms become predominantly nugget (i.e. no spatial structure or form). Model fitting becomes generally unreliable. Nugget variance is often attributed to sampling errors or laboratory quality controls. In King's Dock, the potential contribution from the sampling error was determined by the analysis of replicate samples. The greatest source of spatial variability in the King's Dock samples was identified between *sites* at a scale of approximately 150 m. This distance is comparable to previously published studies of PCBs in estuarine sediments (Rice *et al.*, 1993; Brown & Fish, 1999). At smaller scales (i.e. *subsamples* within a *grab*), PCB concentrations are typically homogeneous. The small scale variation is attributed to the analytical procedure. The nugget variance is thus a combination of sampling intensity (i.e. number of samples), sampling design, support (i.e. size) of samples and possible the volume of sediment (i.e. depth) (Soares, A., pers comm., 2000).

Based on the results of the Swansea case study, a 3-tiered sampling protocol has been designed to improve upon the current FEPA sampling. Regulatory assessment of dredged material requires the calculation of contaminant loadings and the case study results show that these calculations can be grossly inaccurate in areas of high but variable contamination. The 3-tiered sampling approach incorporates a number of stages and investigative steps within these stages:

- incorporate geostatistical techniques including kriging estimations of chemicals;
- improve field variance;
- normalise contaminants to sediment characteristics;
- consider an assessment of contamination extent;
- investigate possible sources of contamination and processes affecting its distribution;
- revise chemical action levels and compare these with existing SQGs; and
- produce management options prior to sea disposal.

It is important to update and change current PCB monitoring procedures in light of this and other recent research. The existing NMMP and FEPA sampling schemes are shown to be inadequate. The protocol proposed here provides, not only a more thorough assessment of contaminants in dredged material, but also, more stringent controls on the disposal of contaminated material. Improving the quality of our environment must be the ultimate goal and this type of scientifically informed approach will help reduce levels of contaminants - an aim which the UK government, under OSPAR, are committed to achieving by 2020.

7.2 Recommendations for future research

Based on the findings of this study, further research should usefully be directed towards three key areas.

1. Cost-benefit analysis of a wider range of sampling protocols is necessary to improve not only the risk assessment of contaminants in dredged material, but also to contribute to the determination of chemical concentrations for compliance monitoring. It may be important, for example, to investigate the use of disjunctive kriging or simulations (i.e. conditional simulations), to assess the probability of values exceeding certain thresholds.

2. The development of biological tests to assess chronic toxicity and bioaccumulation of PCBs is another area of research that has not been fully explored in UK, although this has been evaluated in the derivation of sediment guidelines and action levels in other countries. This type of research would provide a means of establishing contaminant-specific effects on benthic populations, and provide a basis for critical re-evaluation of existing threshold values (such as the CEFAS Action Levels and SQGs).

3. As the OSPAR deadline for reducing contaminant concentrations to near zero or background levels approaches, it will be necessary to investigate possible large-scale or in-situ remediation techniques for reducing PCB concentrations in sediments. This would be particularly beneficial in the case of grossly contaminated dredged material. These techniques should be both practical and cost-effective.

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APPENDIX 1

Table A1.1: Total number of Polychlorinated biphenyls *(World Health Organisation, 1993).*

No.	Structure	No.	Structure	No.	Structure
Mono-CBs		Tetra-CBs		Penta-CBs	
1	2	40	2,2',3,3'	82	2,2',3,3',4
2	3	41	2,2',3,4	83	2,2',3,3',5
3	4	42	2,2',3,4'	84	2,2',3,3',6
		43	2,2',3,5	85	2,2',3,4,4'
Di-CBs		44	2,2',3,5'	86	2,2',3,4,5
4	2,2'	45	2,2',3,6	87	2,2',3,4,5'
5	2,3	46	2,2',3,6	88	2,2',3,4,6
6	2,3'	47	2,2',4,4'	89	2,2',3,4,6'
7	2,4	48	2,2',4,5	90	2,2',3,4',5
8	2,4'	49	2,2',4,5'	91	2,2',3,4',6
9	2,5	50	2,2',4,6	92	2,2',3,5,5'
10	2,6	51	2,2',4,6'	93	2,2',3,5,6
11	3,3'	52	2,2',5,5'	94	2,2',3,5,6'
12	3'4	53	2,2',5,6'	95	2,2',3,5',6
13	3,4'	54	2,2',6,6'	96	2,2',3,6,6'
15	4,4'	55	2,3,3',4	97	2,2',3',4,5
		56	2,3,3',4'	98	2,2',3',4,6
Tri-CBs		57	2,3,3',5	99	2,2',4,4',5
16	2,2',3	58	2,3,3',5'	100	2,2',4,4',6
17	2,2',4	59	2,3,3',6	101	2,2',4,5,5'
18	2,2',5	60	2,3,4,4'	102	2,2',4,5,6'
19	2,2',6	61	2,3,4,5	103	2,2',4,5',6
20	2,3,3'	62	2,3,4,6	104	2,2',4,6,6'
21	2,3,4	63	2,3,4',5	105	2,3,3',4,4'
22	2,3,4'	64	2,3,4',6	106	2,3,3',4,5
23	2,3,5	65	2,3,5,6	107	2,3,3',4',5
24	2,3,6	66	2,3',4,4'	108	2,3,3',4,5'
25	2,3',4	67	2,3',4,5	109	2,3,3',4,6
26	2,3',5	68	2,3',4,5'	110	2,3,3',4',6
27	2,3',6	69	2,3',4,6	111	2,3,3',5,5'
28	2,4,4'	70	2,3',4',5	112	2,3,3',5,6
29	2,4,5	71	2,3',4',6	113	2,3,3',5',6
30	2,4,6	72	2,3',5,5'	114	2,3,4,4',5
31	2,4',5	73	2,3',5',6	115	2,3,4,4',6
32	2,4',6	74	2,4,4',5	116	2,3,4,5,6
33	2',3,4	75	2,4,4',6	117	2,3,4',5,6
34	2',3,5	76	2',3,4,5	118	2,3',4,4',5
35	3,3',4	77	3,3',4,4'	119	2,3',4,4',6
36	3,3',5	78	3,3',4,5	120	2,3',4,5,5'
37	3,4,4'	79	3,3',4,5'	121	2,3',4,5',6
38	3,4,5'	80	3,3'5,5'	122	2,3,3',4,5
39	3,4',5	81	3,4,4',5	123	2',3,4,4',5

Table A1.1: Total number of Polychlorinated biphenyls *(World Health Organisation, 1993) contd.*

No.	Structure	No.	Structure	No.	Structure
Penta-CBs		Hepta-CBs		Deca-CBs	
124	2',3,4,5,5'	170	2,2',3,3',4,4',5	209	2,2',3,3',4,4',5,5',6,6'
125	2',3,4,5,6'	171	2,2',3,3',4,4',6		
126	3,3',4,4',5	172	2,2',3,3',4,5,5'		
127	3,3',4,5,5'	173	2,2',3,3',4,5,6		
		174	2,2',3,3',4,5,6'		
Hexa-CBs		175	2,2',3,3',4,5',6		
128	2,2',3,3',4,4'	176	2,2',3,3',4,6,6'		
129	2,2',3,3',4,5	177	2,2',3,3',4',5,6		
130	2,2',3,3',4,5'	178	2,2',3,3',5,5',6		
131	2,2',3,3',4,6	179	2,2',3,3',5,6,6'		
132	2,2',3,3',4,6'	180	2,2',3,4,4',5,5'		
133	2,2',3,3',5,5'	181	2,2',3,4,4',5,6		
134	2,2',3,3',5,6	182	2,2',3,4,4',5,6'		
135	2,2',3,3',5,6'	183	2,2',3,4,4',5',6		
136	2,2',3,3',6,6'	184	2,2'3,4,4',6,6'		
137	2,2',3,4,4',5	185	2,2',3,4,5,5',6		
138	2,2',3,4,4',5'	186	2,2',3,4,5,6,6'		
139	2,2'3,4,4',6	187	2,2',3,4',5,5',6		
140	2,2',3,4,4',6'	188	2,2',3,4',5,6,6'		
141	2,2',3,4,5,5'	189	2,3,3',4,4',5,5'		
142	2,2',3,4,5,6	190	2,3,3',4,4',5,6		
143	2,2',3,4,5,6'	191	2,3,3',4,4',5',6		
144	2,2',3,4,5',6	192	2,3,3',4,5,5',6		
145	2,2',3,4,6,6'	193	2,3,3',4',5,5',6		
146	2,2'3,4'5,5'				
147	2,2'3,4',5,6	Octa-CBs			
148	2,2',3,4',5,6'	194	2,2',3,3',4,4',5,5'		
149	2,2',3,4',5',6	195	2,2',3,3',4,4',5,6		
150	2,2',3,4',6,6'	196	2,2',3,3',4,4',5,6'		
151	2,2',3,5,5',6	197	2,2',3,3',4,4',6,6'		
152	2,2',3,5,6,6'	198	2,2',3,3',4,5,5',6		
153	2,2',4,4',5,5'	199	2,2',3,3',4,5,6,6'		
154	2,2',4,4',5,6'	200	2,2',3,3',4,5',6,6'		
155	2,2',4,4',6,6'	201	2,2',3,3',4,5,5',6'		
156	2,3,3',4,4',5	202	2,2',3,3',5,5',6,6'		
157	2,3,3',4,4',5'	203	2,2',3,4,4',5,5',6		
158	2,3,3',4,4',6	204	2,2',3,4,4',5,6,6'		
159	2,3,3',4,5,5'	205	2,3,3',4,4',5,5',6		
160	2,3,3',4,5,6				
161	2,3,3',4,5',6	Nona-CBs			
162	2,3,3',4'5,5'	206	2,2',3,3',4,4',5,5',6		
163	2,3,3',4',5,6	207	2,2',3,3',4,4',5,6,6'		
164	2,3,3',4',5',6	208	2,2',3,3',4,5,5',6,6'		
165	2,3,3',5,5',6				
166	2,3,4,4',5,6				
167	2,3',4,4',5,5'				
168	2,3',4,4',5,6				
169	3,3',4,4',5,5'				

APPENDIX 2

Table A2.1: Sample numbers of sites sampled under the NMMP and other sampling programmes in the North Sea.

Site	Sample Number
N1	106
N2	105
N3	107, 108, 198-200
N4	291-3
N5	299
N6	294
N7	298
N8	295
N9	296
N10	297
N11	235
N12	232
N13	231
N14	230
N15	229
N16	234
N17	228
N18	187
N19	93, 359, 431-9
N20	103, 195
N21	104
N22	276
N23	266
N24	253
N25	92, 277
N26	89, 186
N27	245
N28	246
N29	247
N30	90, 185
N31	248-52
N32	267
N33	268
N34	244
N35	102, 194
N36	193
N37	101
N38	192
N39	94, 95, 188, 358
N40	96, 189, 360
N41	271, 275
N42	272
N43	274
N44	273
N45	91
N46	196
N47	97, 98, 190

Table A2.1 (contd.) Site	**Sample Number**
N48	280, 282
N49	279
N50	278
N51	281, 283
N52	99, 100, 191
N53	284, 288
N54	197
N55	289
N56	285
N57	269
N58	286
N59	287
N60	290
N61	265
N62	270
N63	233
N64	5, 6
N65	132
N66	222
N67	152
N68	7, 8, 136, 310, 369-77
N69	135
N70	134
N71	216
N72	215
N73	223
N74	178, 224
N75	79, 80, 179, 355
N76	225
N77	221
N78	317
N79	39, 40, 150
N80	35, 36
N81	37, 38
N82	151, 318
N83	259-62
N84	41, 42, 154, 316
N85	155
N86	153
N87	226
N88	86, 183
N89	177
N90	85
N91	83
N92	82
N93	81
N94	184, 242
N95	182
N96	84, 241, 357
N97	264

Table A2.2: Sample numbers of sites sampled under the NMMP and other sampling programmes in the English Channel.

Site	**Sample Number**
EC1	227
EC2	88
EC3	87
EC4	11, 114
EC5	116
EC6	141
EC7	142
EC8	139
EC9	140
EC10	313
EC11	138
EC12	115
EC13	312
EC14	217
EC15	218
EC16	219
EC17	110, 111
EC18	209
EC19	211
EC20	311
EC21	9
EC22	10
EC23	112, 254
EC24	378-86
EC25	210
EC26	113
EC27	137
EC28	145
EC29	148
EC30	149
EC31	146
EC32	147
EC33	315
EC34	34
EC35	33
EC36	32
EC37	30, 31
EC38	24, 25
EC39	28, 29
EC40	26, 27
EC41	119
EC42	18, 19
EC43	16, 17
EC44	14, 15
EC45	12, 13
EC46	120
EC47	20, 21
EC48	22, 23, 118
EC49	117, 220, 239, 314

Table A2.2 (contd.) Site	**Sample Number**
EC50	212
EC51	213

Table A2.3: Sample numbers of sites sampled under the NMMP and other sampling programmes in the Celtic Sea.

Site	**Sample Number**
C1	128
C2	237
C3	131
C4	238
C5	301-9, 361-8
C6	144
C7	130
C8	129
C9	204
C10	201
C11	143
C12	202
C13	207
C14	109, 243
C15	206
C16	208
C17	205
C18	203

Table A2.4: Sample numbers of sites sampled under the NMMP and other sampling programmes in the Bristol Channel.

Site	**Sample Number**
B1	387-92
B2	400-402
B3	397-99
B4	395, 396
B5	393, 394
B6	403, 404
B7	405-7
B8	408, 409
B9	410, 411
B10	412-4
B11	415-7
B12	418, 419
B13	420, 421
B14	422-4
B15	425, 426
B16	427, 428
B17	429, 430
B18	181
B19	356

Table A2.4 (contd.) Site	**Sample Number**
B20	180
B21	1, 236
B22	123
B23	121
B24	122
B25	4

Table A2.5: Sample numbers of sites sampled under the NMMP and other sampling programmes in the Irish Sea

Site	**Sample Number**
I1	175
I2	176
I3	77-78
I4	214, 133
I5	162
I6	157
I7	156
I8	324
I9	164
I10	334, 354
I11	165
I12	43
I13	76
I14	44
I15	351-3, 329-333, 346
I16	163
I17	73, 172
I18	171, 174
I19	72
I20	74-75
I21	347
I22	348
I23	349-50
I24	173
I25	71
I26	68, 168
I27	69, 170
I28	70, 169
I29	46
I30	167
I31	49
I32	341
I33	340
I34	166
I35	50
I36	47
I37	51
I38	52
I39	48

Table A2.5 (contd.) **Site**	**Sample Number**
I40	54
I41	55
I42	60
I43	61
I44	62
I45	56
I46	57
I47	63-64
I48	65
I49	66
I50	67
I51	335-9, 342-45,
I52	53
I53	58
I54	59
I55	45
I56	158
I57	161, 263, 319-23, 325-28
I58	160
I59	2
I60	127, 257, 258, 300
I61	256
I62	255
I63	3, 124-126
I64	159
I65	240

Table A2.6: Sample numbers of sites sampled in dredged material in North East England.

Site	**Sample Number**
NE1	94
NE2	63
NE3	65
NE4	64
NE5	66
NE6	71
NE7	72
NE8	67-70
NE9	73
NE10	75
NE11	74
NE12	76-81
NE13	83
NE14	84
NE15	82
NE16	85
NE17	86, 737, 865, 866
NE18	87
NE19	735, 736
NE20	864

Table A2.6 (contd.) Site	**Sample Number**
NE21	863
NE22	88-93
NE23	862
NE24	734
NE25	733
NE26	95-99
NE27	541-50, 580-94
NE28	777
NE29	782
NE30	701-3
NE31	189, 190
NE32	191-9
NE33	789, 531
NE34	791
NE35	778
NE36	792, 530
NE37	795
NE38	867
NE39	783, 868-71
NE40	796
NE41	797
NE42	779
NE43	784
NE44	785
NE45	798
NE46	532, 786
NE47	533
NE48	534
NE49	793
NE50	799, 800
NE51	17
NE52	794
NE53	62
NE54	528
NE55	527
NE56	16
NE57	790
NE58	781
NE59	787, 529
NE60	788
NE61	780
NE62	200-205
NE63	206-8
NE64	713-716
NE65	185-88
NE66	709
NE67	708
NE68	704-6, 710, 711
NE69	707
NE70	572-9

Table A2.6 (contd.) Site	**Sample Number**
NE71	712
NE72	748-55
NE73	535-540, 756-9
NE74	872-6
NE75	147, 148

Table A2.7: Sample numbers of sites sampled in dredged material in East England.

Site	**Sample Number**
E1	134-7
E2	36
E3	1, 2
E4	293
E5	287
E6	292
E7	138-146
E8	286
E9	288
E10	289
E11	290
E12	291
E13	303
E14	305
E15	306
E16	301
E17	302
E18	304
E19	34, 37-46
E20	294
E21	296
E22	295
E23	298
E24	297
E25	35, 809-811
E26	812-14
E27	815-17
E28	299
E29	300
E30	502
E31	280-5
E32	149-151
E33	160-162
E34	165, 184
E35	395-409
E36	390
E37	389
E38	387
E39	388
E40	391

Table A2.7 (contd.) Site	**Sample Number**
E41	392
E42	393
E43	394

Table A2.8: Sample numbers of sites sampled in dredged material in South England.

Site	**Sample Number**
S1	61
S2	526
S3	525
S4	524
S5	410
S6	523
S7	412
S8	411
S9	414
S10	416
S11	415
S12	417
S13	522
S14	419
S15	420
S16	520
S17	418, 521
S18	489-94
S19	109, 110
S20	829-832
S21	912-915
S22	212
S23	25-30
S24	555, 556
S25	557, 558
S26	854, 855
S27	421-43, 481-88
S28	850, 851
S29	852, 853
S30	219-222
S31	553, 554
S32	105
S33	216-218
S34	916-920
S35	618-629
S36	742, 743, 746, 747
S37	744, 745
S38	213-215, 801-808
S39	223
S40	211
S41	31, 224-8
S42	108
S43	229-234

Table A2.8 (contd.) **Site**	**Sample Number**
S44	630-631
S45	106-107
S46	859-861
S47	605-609
S48	610-614
S49	845-49
S50	104
S51	615-617
S52	552
S53	474-480
S54	209-210
S55	32-33
S56	497
S57	195-496
S58	910-911
S59	908-909
S60	562
S61	111-133
S62	559
S63	239-269
S64	561, 632-646
S65	560
S66	563
S67	279
S68	278
S69	277
S70	275
S71	274
S72	271-2
S73	270
S74	273
S75	276
S76	235-238
S77	727-732

Table A2.9: Sample numbers of sites sampled in dredged material in South Wales.

Site	**Sample Number**
SW1	60
SW2	504
SW3	505-506
SW4	507
SW5	856-8
SW6	838-9
SW7	836
SW8	683, 906
SW9	834-5
SW10	907
SW11	681-2, 905

Table A2.9 (contd.) Site	**Sample Number**
SW12	679-80, 904
SW13	360, 454
SW14	678, 903
SW15	676, 901, 359, 453
SW16	684
SW17	677, 902
SW18	358, 452, 675, 900
SW19	451, 899
SW20	674
SW21	356, 450, 673, 898
SW22	357
SW23	361-3
SW24	738-41
SW25	351-5
SW26	667-8
SW27	670
SW28	665, 892
SW29	666, 893
SW30	894
SW31	663-4, 348, 891
SW32	445-6, 662, 890
SW33	661, 889
SW34	447, 349, 660, 888
SW35	672
SW36	671
SW37	685
SW38	659
SW39	658
SW40	657
SW41	347
SW42	444
SW43	656, 897
SW44	374-386
SW45	346, 896
SW46	449, 669, 448, 350, 895
SW47	163-4, 508-511
SW48	364
SW49	366
SW50	367
SW51	368
SW52	369
SW53	691
SW54	841
SW55	456, 697, 881
SW56	370
SW57	844
SW58	842
SW59	840
SW60	837, 843, 460
SW61	696

Table A2.9 (contd.) **Site**	**Sample Number**
SW62	455, 698, 371
SW63	883
SW64	880
SW65	878, 514-5
SW66	516
SW67	693
SW68	372, 517
SW69	373, 518-9
SW70	692, 877
SW71	512-3
SW72	365
SW73	686
SW74	604
SW75	569-571
SW76	694-5, 879
SW77	699, 885
SW78	457, 882, 884
SW79	459, 886
SW80	458, 700, 887
SW81	687-690
SW82	21-24, 100-101
SW83	595-603, 464-68
SW84	102-103
SW85	461-3
SW86	469-473
SW87	551

Table A2.10: Sample numbers of sites sampled in dredged material in North West England.

Site	**Sample Number**
NW1	822
NW2	818
NW3	339-44
NW4	345
NW5	564-568
NW6	820
NW7	333-338
NW8	819
NW9	821
NW10	156-9, 823
NW11	155
NW12	152-154
NW13	772
NW14	18-20
NW15	775
NW16	320-2, 498-500, 767, 774,
NW17	317
NW18	318
NW19	319, 773

Table A2.10 (contd.) **Site**	**Sample Number**
NW20	766, 771
NW21	765
NW22	770
NW23	763-4, 824-28
NW24	761-2
NW25	307-316
NW26	760
NW27	653-55
NW28	47-52
NW29	53-59
NW30	717-722
NW31	723
NW32	724
NW33	725
NW34	726
NW35	323
NW36	324-5
NW37	327-8
NW38	326
NW39	921-2
NW40	3-15
NW41	768
NW42	769
NW43	332
NW44	331, 776
NW45	330
NW46	329
NW47	501, 503
NW48	647-52

APPENDIX 3 -Analytical procedures used in sediment PCB determination

Reagents and solvents

The reagents and solvents used in the analysis of PCBs are shown in Table A3.1.

Table A3.1: Reagents and solvents.

Reagents and Solvents	Manufacturer
Silica Gel 60	Merck
Alumina	BDH Chemicals Ltd., Poole, England.
Sodium sulphate (anhydrous)	BDH Chemicals Ltd., Poole, England.
Analar	
Copper Turnings	Aldrich
n-Hexane glass distilled grade	Rathburn Chemicals Ltd., Walkerburn, Scotland
Acetone glass distilled grade	Rathburn Chemicals Ltd., Walkerburn, Scotland
2,2,4-Trimethylpentane (TMP)	Rathburn Chemicals Ltd., Walkerburn, Scotland

To minimise the possibility and extent of contamination, all reagents were cleaned and tested before use (cf de Boer & Wells, 1996). In the case of solvents, purity was checked using GC-ECD.

Preparation of glassware

Glassware was soaked overnight in pyroneg and, after rinsing with water, was placed in 10% acid for a minimum of 4 hours (Oslo & Paris Commission, 1996). Prior to use, all glassware was rinsed with acetone and *n*-hexane.

Preparation of sediment for PCB extraction

Sediment samples were stored frozen. Prior to analysis, each sediment sample was homogenised and a subsample (50 g) air dried to a constant weight in a fume-cupboard. Dry sediment was ground using a pestle and mortar and passed through a 2 mm sieve. A subsample of 10 g was measured into a 60 ml beatson jar. Anhydrous sodium sulphate (25 g) was mixed into the sample to absorb moisture remaining in the sediment. Samples were stored at 5°C overnight to ensure complete dehydration. Smedes & de Boer (1997) observed that sodium sulphate can cause some analytes to be irreversibly adsorbed but suggested that reference materials prepared under the same conditions can be used to check recoveries. There was always a possibility of contamination or loss of samples during the drying, sieving and grinding processes therefore blanks, reference materials and replicate sampling were included to check recoveries (Quevauviller, 1995; Chiarenzelli *et al.*, 1997). Similar precautions were taken here. These and other analytical problems concerning PCB analysis are more fully discussed by Quevauviller (1995).

Soxhlet extraction of sediment

Anti-bumping granules and 30 g of copper turnings were added to a flat bottom flask (copper turnings serve to remove elemental sulphur from the sediment). Marine sediments typically have sulphur in the sample matrix and this interferes with the identification of CBs on the GC chromatogram (Folch *et al.*, 1996). Acetone and *n*-hexane (1:1; 60 ml) were subsequently added. The sediment sample was transferred to a glass extraction thimble using a large diameter glass filter funnel. The thimble was loaded into a Soxhlet apparatus. Temperature settings on the mantles were set so that the solvent cycles did not exceed ~20 cycles per hour. The extraction period for sediments was 6½ hours, although where sediments consisted of very small particle sizes, the extraction time was extended to 24 hours to ensure complete recovery of all PCB residues. These residues are known to bond more tightly to smaller-sized particles (Allchin *et al.*, 1989). After the sample was exhaustively extracted, it was quantitatively transferred to a 100 ml volumetric flask.

Several other extraction methods are available including saponification, ultrasonic and supercritical fluid extraction (SFE) (Langenfeld *et al.*, 1993; Bøwadt & Johansson, 1994; Bøwadt *et al.*, 1995; Sterzenbach *et al.*, 1997). Soxhlet extraction is often considered to be the most appropriate method for the determination of combined congeners and chlorinated pesticides (Quevauviller, 1995). This thesis does not attempt to improve upon this method. Rather, it utilises it as a proven approach which ensures compatibility with previous UK work, including the NMMP surveys.

Clean up of extracted sediment

Clean up was required to remove any interfering compounds with the characterisation of CBs on the chromatogram and involved a two-stage procedure. First, gravimetric column chromatography was performed using alumina as an absorbent. This removed any particles from the extracted sediment sample, leaving a clean solvent extract. Second, gravimetric column chromatography was performed with silica gel. This procedures removed interfering compounds.

Alumina fractionation clean up

A 50 ml aliquot of sample extract was evaporated to 1 ml under a constant stream of oxygen-free nitrogen. Borosilicate glass chromatography columns (150 mm x 6 mm i.d.) were loaded with a plug of *n*-hexane rinsed cotton wool and 3 g of 5% deactivated alumina. The 1 ml extracted sample was quantitatively transferred to the top of the alumina column using a Pasteur pipette. The sample was absorbed gravimetrically onto the alumina and, after rinsing the sample extract residues from the centrifuge tube, 20 mls of *n*-hexane was added to the solvent reservoirs. The first 2½ mls of *n*-hexane from the column were collected for CB analysis. (Other organochlorine pesticides were analysed but only the CB results are presented in this thesis). The eluants from the CB fraction were evaporated down to 1 ml under a constant stream of oxygen-free nitrogen.

Silica gel fractionation

The borosilicate glass chromatography columns (300 mm x 6 mm i.d.) were initially plugged with *n*-hexane rinsed cotton wool and packed with 3 g of 3% deactivated silica gel. The alumina fraction was quantitatively transferred to the top of the silica column using a Pasteur pipette. The aliquot was absorbed on to the silica and the solvent topped up with 10 mls of *n*-hexane in the solvent reservoirs. The first 8 mls were collected for CB analysis. This fraction was evaporated to 0.1 ml and 1 ml of 2,2,4-Trimethylpentane was added to the sample. This was subsequently evaporated down to 0.5 ml and 100μl of internal standard was added. The sample was made up to a final volume of 1 ml using 2,2,4-Trimethylpentane. The sample was transferred into 1 ml GC vials and placed in the GC autosampler ready for analysis by gas chromatography – electron capture detector (GC-ECD).

Gas Chromatography - Electron Capture Detector (GC-ECD)

The GC used in this study was a Hewlett Packard Model HP5890 equipped with a HP7673A autosampler. Autosampling and data acquisition was controlled using HP3365 HPChem Station software. A 50 m x 0.2 mm HP-5 ID x 0.33 μm capillary column was used for high-resolution analysis of individual CBs (Allchin *et al.*, 1989; Quevauviller, 1995). Operating conditions and temperature programme employed were designed to optimise CB recovery. Injection port temperatures were held at 270°C. The inlet purge valve was splitless and was opened 2 minutes into the run. The injection volume for each sample was 1 μl using a 10 μl syringe. The process ran for 90 minutes with an initial temperature setting of 90°C for the first 2 minutes. Subsequent temperatures were raised in two stages. First, it was raised to 165°C at a rate of 15°C min^{-1}, and second, it was raised to 285°C at a rate of 2°C min^{-1}. The detector gas was 5% methane in argon used at a flow rate of 50-60 ml min^{-1}. The electron capture detector was set at 300°C. The carrier gas is high-purity hydrogen.

To enable multilevel calibration, seven CB standards were prepared in 2,2,4-Trimethylpentane and 1 µl of stock injected onto the column. The chromatograms were integrated and CB concentration measured in relation to the internal standard (CB#53) and individual CB peak height. All results were expressed in pg μl^{-1} or $\mu g\ kg^{-1}$. The minimum detection limit for CBs in sediments was 0.2 $\mu g\ kg^{-1}$.

Quality control

Two reference samples were analysed with each batch of sediment samples. These comprised of standard Canadian sediment reference material HS-1 and HS-2. These reference sediments originated from Nova Scotian harbours and are natural marine sediment materials used for the determination of PCBs after spiking with the commercial PCB mixture Aroclor® 1254 (Sim *et al.*, 1988). To check the analytical quality, two subsamples of HS-2 were analysed with every batch. The recovery of congeners was checked using standard quality control (QC) charts. An example of such a QC chart for CB#153 is shown in Figure A3.1.

The mean and standard deviation (upper control level (UCL) and lower control level (LCL)) of congeners were calculated to indicate QC in the laboratory. In Figure A3.1, the determinands lie within the confidence limits. All of the sediment samples were checked using the above approach.

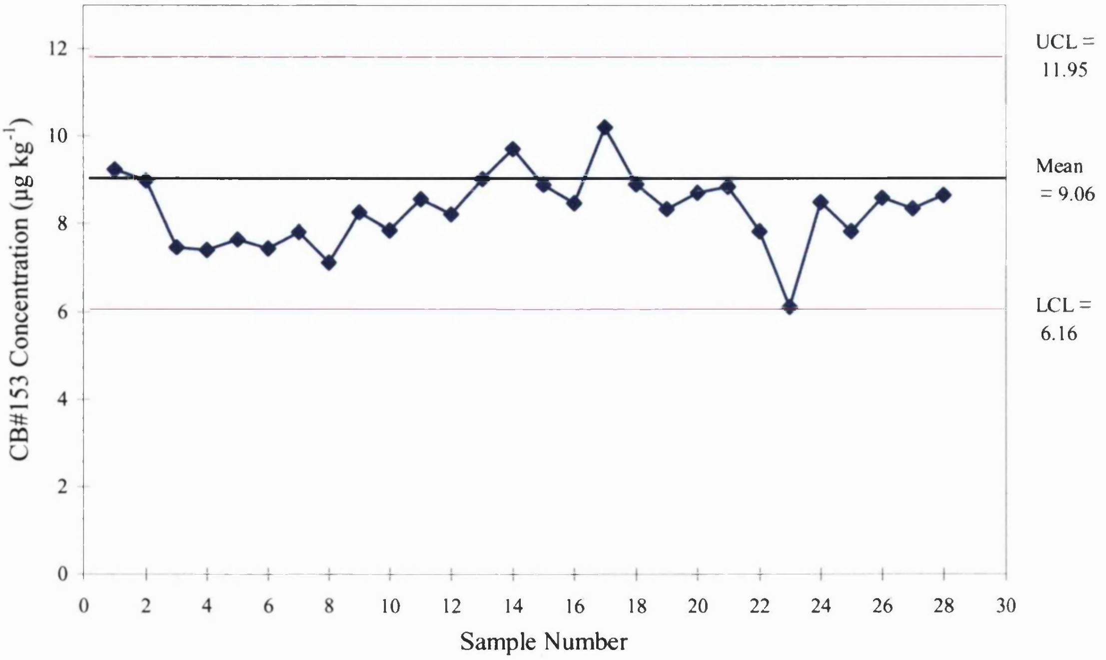

Figure A3.1: Quality control chart for CB#153 in reference material HS-2.

APPENDIX 4

Table A4.1: Median PCB concentrations ($\mu g\ kg^{-1}$) and standard deviations (half of the difference between the 25 and 75 percentiles) in surface sediments sampled in offshore and estuarine areas under NMMP between 1990-1999

Region	1990	1991	1992	1993	1994	1995	1996	1997	% Reduction
NORTH SEA									
Offshore Sediments									
North sea (central)	0 ± 0 (2)	0.4 ± 0.1 (7)					0 ± 0 (1)		I
North Sea (north)	0 ± 0 (4)	0.2 ± 0.3 (7)					2.8 ± 0 (1)	0 ± 0 (9)	I
North Sea (south)	0 ± 0 (5)	0 ± 1.1 (5)							*
Offshore River Humber	1.8 ± 0.6 (2)	0.3 ± 0 (1)					0.4 ± 0 (1)		78
Offshore River Tees	0.3 ± 0.1 (2)	0 ± 0.2 (3)					4.6 ± 0 (1)		I
Offshore River Thames	1.7 ± 0 (1)	1.7 ± 0.8 (2)				10.8 ± 0 (1)	0 ± 0 (1)		100
Offshore River Tweed	0 ± 0 (2)	0 ± 0 (1)							*
Offshore River Tyne	0.4 ± 0.2 (2)	2.3 ± 0.2 (9)					2.8 ± 0 (1)	0 ± 0 (9)	100
Offshore River Wear	0 ± 0 (1)	1.9 ± 0 (1)							I
The Wash	0.4 ± 0.1 (2)	1.0 ± 0.2 (5)			2.7 ± 1.0 (4)		2.1 ± 0 (2)		I
Estuarine Sediments									
Hartlepool Bay						31.2 ± 6.4 (5)			-
River Blyth						35.4 ± 24.9 (5)			-
River Coquet						0.8 ± 1.0 (3)			-
River Humber	3.9 ± 1.9 (4)								-
River Tees	0.5 ± 1.0 (4)	17.7 ± 8.8 (2)				26.4 ± 6.3 (16)			I
River Tweed	0.0 ± 0 (2)	1.8 ± 0.9 (2)							I
River Tyne	32.9 ± 9.9 (4)	34.1 ± 17 (2)	23.8 ± 15.9 (10)			43.2 ± 5.7 (5)			I
River Wansbeck						44.3 ± 0 (1)			-
River Wear	32.9 ± 0 (2)	32.0 ± 15.8 (2)							3
Seaham	0.3 ± 0.2 (2)	0.0 ± 0 (1)					0.3 ± 0 (1)		0
ENGLISH CHANNEL									
Offshore Sediments									
English Channel (south west)	0 ± 0 (1)	0.1 ± 0.2 (4)					0.5 ± 0 (1)		I
Lyme Bay	0 ± 0 (3)	0.02 ± 0.01 (4)		0.52 ± 0 (1)			0.11 ± 0 (1)	0.29 ± 0.18 (9)	I
Off Dover Coast	0 ± 0.42 (5)	0.04 ± 0 (1)							I
Off Isle of Wight	0 ± 0 (1)	0.03 ± 0.75 (3)					0.05 ± 0.03 (2)		I

Table A4.1 (contd.) *Region*	1990	1991	1992	1993	1994	1995	1996	1997	% Reduction
ENGLISH CHANNEL contd.									
Off Plymouth Sound	2.6 ± 2.8 (26)						10.2 ± 0 (1)		I
Start Bay		0 ± 0 (1)							-
Estuarine Sediments									
River Exe	4.0 ± 0 (1)								-
River Tamar		20.3 ± 13.9 (5)							-
Southampton Water		4.0 ± 2.8 (4)							-
Weymouth	3.0 ± 0.3 (2)								-
CELTIC SEA									
Offshore Sediments									
Celtic Sea (north)		1.8 ± 1.2 (6)					3.8 ± 1.0 (9)	2.0 ± 2.1 (8)	I
Celtic Sea/Western Approaches	0 ± 0 (1)	0.3 ± 0.0 (10)							I
Off Perranporth		0.4 ± 0 (1)							-
BRISTOL CHANNEL									
Offshore Sediments									
Bridgwater Bay		0.4 ± 0 (1)							-
Off Bideford Bay		0.2 ± 0.04 (2)							-
Off Carmarthen Bay	2.7 ± 0 (1)	4.7 ± 0 (1)							I
Off Milford Haven	0.3 ± 0 (1)								-
Off Swansea Bay		7.1 ± 0 (1)					0 ± 0 (1)		100
Pembrokeshire Coast		0.6 ± 0 (1)							-
Estuarine Sediments									
Cardiff Bay								0.5 ± 55.3 (44)	-
IRISH SEA									
Offshore Sediments									
Irish Sea (north)	0.4 ± 0.2 (2)	1.0 ± 0.4 (2)							I
Irish Sea (Off Isle of Man)		0.2 ± 0.7 (6)					0.3 ± 0.1 (3)		I
Off Cardigan Bay	0 ± 0 (2)	0.9 ± 0.6 (9)			0 ± 0 (5)		1.2 ± 0.9 (10)		I
Off Liverpool Bay	0.3 ± 0.5 (27)	0.4 ± 0.2 (4)					0.5 ± 0.5 (11)		I
Off Morecambe Bay	0 ± 0.4 (5)	0 ± 0.3 (5)					2.0 ± 0.7 (13)		I
Estuarine Sediments									
River Mersey	25.9 ± 7.5 (2)	1.2 ± 0.6 (2)							95

Table A4.2: Median PCB concentrations ($\mu g\ kg^{-1}$) and standard deviations (half of the difference between the 25 and 75 percentiles) in surface dredged material sampled in outer and inner estuaries under FEPA (1985) between 1990-1999

Region	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	% Reduction
NORTHEAST ENGLAND											
Outer Estuary											
Hartlepool				11.7 ± 3 (4)							-
Off Blyth			80.9 ± 21 (5)			52.7 ± 37 (10)	159.2 ± 106 (15)				I
Off Seaham				73.4 ± 40 (3)					8.7 ± 6 (4)		88
Inner Estuary											
River Blyth			71.7 ± 12 (32)						83.7 ± 57 (10)		I
River Esk, Whitby				10.3 ± 2 (2)							-
River Tees						0 ± 0 (6)	121.7 ± 57 (8)	15.2 ± 5 (9)	71.2 ± 32 (17)		I
River Tyne		36 ± 2 (2)	31.2 ± 0 (1)	81.7 ± 110 (11)		34.9 ± 6 (8)		58.3 ± 8 (3)	25.9 ± 16 (29)		29
River Wear				18.3 ± 3 (6)							-
EAST ENGLAND											
Outer Estuary											
Off Lowestoft (R. Waveney)				3.1 ± 7 (3)							-
Off River Humber	6 ± 0 (2)										-
Inner Estuary											
King's Lynn, Great Ouse (The Wash)				10.1 ± 9 (3)							-
River Humber			28.3 ± 8 (13)	26.5 ± 15 (13)	31.2 ± 9 (21)	133.6 ± 0 (1)			28.4 ± 3 (9)		I
River Orwell				28.4 ± 9 (20)	1.7 ± 1 (23)						94
The Haven, Boston (The Wash)					3.8 ± 1 (6)						-
SOUTH ENGLAND											
Outer Estuary											
Off Eastbourne						2.7 ± 2 (6)					-
Off Langstone Harbour			11.8 ± 5 (6)		25.3 ± 5 (3)						I
Off Newhaven				0.4 ± 0.2 (2)							-

Table A4.2 (contd.)*Region*	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	% Reduction
Inner Estuary											
Chichester Harbour					7.23 ± 0 (1)						-
Dover (Harbour)					0.3 ± 1 (10)	1.85 ± 1 (7)					I
Emsworth Yacht Harbour, Chichester									34.5 ± 1.6 (5)		-
Exmouth					34.5 ± 7 (2)						-
Gosport									25.03 ± 20 (16)		-
Holesbay									46.30 ± 10 (3)		-
Langstone Harbour				12.6 ± 0 (1)	8.5 ± 7 (30)	16.3 ± 20 (8)	14.8 ± 1.2 (6)	32.0 ± 30 (12)			I
Newquay									48.3 ± 26.2 (6)		-
Plymouth			39.2 ± 9 (2)	26.7 ± 5 (23)	21.2 ± 8 (41)	13.3 ± 3 (4)	26.2 ± 4.1 (4)	26.8 ± 3 (15)		11.9 ± 12 (4)	70
Poole								10.9 ± 8 (10)	345.4 ± 229.4 (5)		I
Port Solent Marina										8.1 ± 1 (4)	
R. Stour				11.7 ± 0 (1)							-
River Stour, Kent (Nr. Sandwich)			3.6 ± 0 (1)								-
Solent									5.2 ± 2 (4)	27.2 ± 5 (5)	I
Southampton Water			12.8 ± 0 (1)	30 ± 1 (3)	31.7 ± 10 (13)			13.2 ± 2 (2)			I
The Manacles					188.4 ± 32 (4)						-
Tyneham						63.9 ± 34 (7)					-
Wareham							26.6 ± 0 (1)	6.4 ± 2 (3)			76
SOUTH WALES											
Outer Estuary											
Off Carmarthen Bay			105.5 ± 34 (6)								-
Off Mumbles								103.9 ± 2 (4)			-
Off Pembrokeshire Coast						76.4 ± 81 (5)		0 ± 0.3 (9)			100
Off River Taff, Outer Cardiff Bay					111.4 ± 0.1 (2)			97.5 ± 0 (1)	109.4 ± 0 (1)		2
Off River Usk, Newport					123.6 ± 24(4)			96.3 ± 3 (2)	101.6 ± 4 (3)		18
Port Talbot Approach Channel					53.7 ± 3 (2)						-

Table A4.2 (contd.)*Region*	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	% Reduction
Swansea Approach Channel					50.8 ± 3 (3)	53.2 ± 9 (8)	123 ± 34 (3)	51.9 ± 9 (4)	48.9 ± 0 (1)		4
Inner Estuary											
Avonmouth			54.6 ± 0 (1)			77.2 ± 5 (4)					I
Barry Docks				70.1 ± 1 (2)		187.8 ± 22 (4)					I
Cardiff Docks					126.1 ± 13 (30)			122.1 ± 23 (17)	133.4 ± 30 (13)		I
Milford Haven				3.5 ± 2 (2)		0 ± 9 (8)	12.7 ± 0 (1)				I
Neath								1.3 ± 0 (1)			-
Newport Docks					131.2 ± 9 (6)			131.5 ± 26 (10)	141.4 ± 40 (15)		I
Port Talbot					57.7 ± 5 (3)						-
Swansea Docks					125.4 ± 27 (8)			156.8 ± 102 (7)	100.6 ± 25 (16)		20
NORTHWEST ENGLAND											
Inner Estuary											
Barrow-in-Furness					0.6 ± 4 (6)				5.5 ± 0.4 (2)		I
Conwy								10.8 ± 3 (6)			-
Heysham				1.3 ± 1.5 (4)					8.1 ± 0 (1)		I
Maryport					4.0 ± 2 (7)						-
Off Heysham									5.6 ± 0 (1)		-
River Lune				2.3 ± 0 (1)							-
River Mersey	69.0 ± 14 (13)	50.1 ± 2 (3)	56.1 ± 17 (13)		93.1 ± 53 (26)	139.8 ± 42 (5)		164.0 ± 710 (3)	54.8 ± 22 (32)	5.3 ± 1 (2)	92
River Wyre				0 ± 3 (3)							-
Solway									9.5 ± 1 (2)		-
St. Bees Head							12.8 ± 5 (5)				-

- = Only one observation
I = % Increase
* = No change over time
In brackets, number of samples analysed.

APPENDIX 5

Table A5.1: PCB Concentrations in King's Dock, Swansea.

Site	#18	#28	#31	#44	#47	#49	#52	#66	#101	#105	#110	#118	#128	#138	#141	#149	#151	#153	#156	#158	#170	#183	#187	#180	#194	Total CBS
1 REP 1	3.32	8.36	4.84	3.62	1.21	3.53	5.76	0.2	8.24	2.89	17.51	7.53	1.86	10.69	2.15	8.53	2.42	9.74	1.27	1.19	2.81	1.72	3.82	6.26	0.96	120.23
1 REP 2	3.12	7.4	4.38	3.51	1.05	3.31	5.27	0.2	6.78	2.63	15.33	6.58	1.6	9.12	1.76	7	1.93	8.06	1.13	1.01	2.35	1.38	3.23	5.2	0.9	104.03
1A	2.9	8.09	4.64	3.01	1.1	2.89	4.01	6.05	4.85	2.8	11.91	6.08	1.48	7.02	1.38	5.09	1.44	6.32	1.19	0.86	2.19	1.17	2.78	4.55	0.99	94.79
1B	2.64	8.84	4.83	2.65	1.05	2.63	3.51	6.37	4.49	3.07	11.47	6.43	1.48	7.07	1.31	4.7	1.33	6.09	1.2	0.85	2.14	1.11	2.66	4.62	0.92	93.46
1C	3.22	7.77	4.48	3.09	1.09	3.23	4.56	5.56	5.91	2.38	13.94	6.1	1.45	8.26	1.52	6.13	1.73	7.55	1	0.86	2.18	1.29	3.43	4.95	1.06	102.74
1D	3.66	9.96	5.61	3.32	1.27	3.23	4.7	6.52	5.78	2.41	13.77	6.11	1.5	8.62	1.64	6.45	1.85	7.84	1.01	0.9	2.53	1.62	4.5	6.61	1.97	113.38
1E	3.28	7.85	4.68	3.57	1.47	3.94	5.94	0.2	8.54	3.15	18.18	9.23	2.21	11.95	2.22	9.62	2.84	12.5	1.74	1.22	3.82	2.35	11.88	10.65	5.32	148.15
1F	2.91	8.06	4.56	3.33	1.28	3.5	5.57	6.15	6.8	2.42	15.11	6.67	1.46	8.19	1.65	6.75	1.93	7.97	0.97	0.9	2.26	1.37	3.43	5.2	0.93	109.37
1G	12.68	40.53	20.66	18.26	0.2	17.43	33.52	144.9	83.13	0.2	181.5	176.3	40.11	181.1	35.87	67.92	20.49	161.0	0.2	25.04	92.82	26.18	70.17	170.2	97.0	1716.87
1H	4.2	17.7	9.77	9.68	2.8	10.02	17.25	0.2	27.68	16.45	61.82	36.18	7.73	35.03	6.53	23.44	6.19	29.93	6.76	4.47	9.16	4.93	14.06	20.83	7.01	389.62
2REP1	2.66	11.02	5.96	3.69	1.37	4.02	5.54	9.75	7.26	4.67	21.75	10.35	2.14	11.05	2.15	7.13	2.07	9.42	1.99	1.31	3.59	1.69	3.92	7.09	1.51	143.1
2REP2	3.47	8.53	4.96	3.57	1.25	3.83	5.15	6.94	6.72	3.37	17.25	7.66	1.87	9.2	1.84	6.55	1.9	8.21	1.47	1.15	2.8	1.49	3.43	5.78	1.1	119.49
2A	3.47	13.93	7.25	3.67	1.42	3.49	4.41	10.36	5.51	4.14	16.53	8.44	1.94	9.58	1.77	5.93	1.69	8.06	1.69	1.06	3.13	1.49	3.36	6.37	1.27	129.96
2B	3.33	14.5	7.94	4.1	1.67	4.59	6.53	11.72	8.09	5.27	22.87	11.66	2.21	12.07	2.27	7.29	2.19	10.25	2.26	1.39	3.63	1.8	4.55	7.88	2.26	162.32
2C	4.02	10.61	5.91	3.67	1.29	3.66	4.32	7.26	4.87	3.01	13.98	6.33	1.58	7.31	1.42	5.06	1.44	6.43	1.2	0.89	2.26	1.18	2.75	4.67	0.92	106.04
2D	2.93	7.81	4.34	2.97	1.01	3.16	4.38	5.98	5.41	3.06	14	6.71	1.63	7.42	1.42	5.05	1.45	6.78	1.21	0.89	2.19	1.23	3.09	5.09	1.3	100.51
2E	3.41	9.66	5.34	3.12	1.18	3.34	4.15	6.99	5.06	2.98	13.61	6.44	1.51	7.41	1.45	5.24	1.53	6.67	1.12	0.88	2.2	1.22	2.89	4.78	0.92	103.1
2F	3.79	11.23	6.16	3.54	1.33	3.76	4.42	7.97	5.58	3.43	15.24	7.49	1.72	8.66	1.71	5.81	1.65	7.71	1.56	1.11	2.85	1.47	3.68	6.08	1.58	119.53
2G	3.7	10.1	5.62	3.32	1.24	3.27	4.27	7.23	5.1	3.09	14.4	6.66	1.57	7.41	1.42	5.2	1.51	6.67	1.17	0.91	2.17	1.21	2.93	4.72	0.91	105.8
2H	3.61	10.45	5.71	3.21	1.23	3.03	3.98	7.2	4.83	2.93	13.42	6.33	1.5	7.23	1.43	5	1.45	6.62	1.12	0.88	2.19	1.19	2.92	4.77	0.96	103.19
3REP1	2.77	8.92	5.11	3.89	1.22	4.79	5.91	0.2	8.15	4.15	19.43	9.59	2.44	10.56	2.27	7.65	2.12	9.48	1.99	1.45	3.48	1.77	4.1	6.51	1.59	129.34
3REP2	2.56	9.57	5.58	2.79	1.29	3.61	5.14	7.41	6.4	2.8	15.51	7.28	1.54	9.15	1.71	6.6	1.79	8.16	1.22	0.96	2.62	1.53	4.15	6.09	1.74	117.2
3A	2	7.39	4.81	5.83	1.85	6.58	10.25	0.2	18.97	0.2	29.64	13.57	3.69	26.17	7.11	24.72	8.56	29.94	4.12	3.13	7.23	4.12	8.24	14.39	1.97	244.28
3B	2.88	12.42	6.74	2.91	1.42	3.58	4.63	9.11	5.69	2.91	14.58	7.26	1.58	9.06	1.71	6.36	1.77	7.99	1.29	0.97	2.86	1.55	3.61	5.99	1.14	120.01
3C	2.18	6.63	3.89	7.12	1.62	8.27	13.92	0.2	14.93	7.25	32.57	17.07	2.8	12.88	2.31	9.18	2.43	11.76	2.36	1.6	3.36	1.5	4.8	6.75	2.3	179.48
3D	3.06	19.61	8.54	3.56	1.42	4.22	4.66	0	5.97	5.46	22.81	12.63	2.11	11.24	1.71	5.72	1.6	9.07	2.11	1.19	3.22	1.41	3.32	7.19	1.52	143.35
3E	3.78	15.71	8.36	3.72	1.36	4.41	4.89	8.54	5.15	3.58	13.24	8.54	1.56	8.99	1.65	5.07	1.47	7.7	1.78	1.02	2.87	1.24	2.5	5.86	1.04	124.03
3F	1.42	7.67	4.25	2.12	0.96	3.26	5.42	0.2	7.04	2.67	14.82	7.65	1.34	9.12	1.79	6.51	1.68	7.96	1.37	1.03	2.65	1.34	3.11	5.42	1.2	101.8

Site	#18	#28	#31	#44	#47	#49	#52	#66	#101	#105	#110	#118	#128	#138	#141	#149	#151	#153	#156	#158	#170	#183	#187	#180	#194	Total CBS
3G	0.56	2.78	1.51	0.89	0.34	1.69	2.09	0.2	4.94	2.2	10.15	6.18	1.3	7.31	1.23	4.55	1.02	5.8	1.15	0.78	1.51	0.67	1.51	2.9	0.52	63.58
3H	2.44	6.23	3.6	3.04	1.15	2.88	4.57	4.37	6.15	2.54	13.68	6.01	1.73	7.92	1.68	6.09	1.74	7.54	1.06	1	2.16	1.25	2.76	4.2	0.73	96.52
4REP1	2.71	10.52	5.77	2.77	1.25	3.42	4.29	7.71	5.55	2.79	13.65	6.93	1.5	8.63	1.7	6.18	1.72	7.63	1.2	0.95	2.59	1.41	3.19	5.38	0.94	110.38
4REP2	3.76	10.25	5.61	3.3	1.24	3.55	4.24	6.57	5.02	2.36	12.97	5.74	1.48	7.54	1.41	5.46	1.54	6.81	0.92	0.82	2.17	1.27	2.96	4.72	0.89	102.6
4REP3	3.62	9.49	5.6	3.15	1.26	3.76	4.07	6.02	4.9	2.48	13.21	5.62	1.53	6.93	1.47	5.37	1.6	6.48	0.89	0.87	2.17	1.25	2.97	4.41	0.8	99.92
4A	3.17	8.52	4.8	3.05	1.08	2.77	4.01	6.16	5.21	2.55	14.08	5.75	1.5	7.53	1.43	5.76	1.6	6.85	1	0.82	2.17	1.28	2.91	4.66	0.85	99.51
4C	3.49	8.64	5.05	3.85	1.24	3.53	5.9	0.2	7.56	3.31	21.03	7.87	1.95	10.06	1.99	7.83	2.23	9.15	1.41	1.12	2.86	1.59	3.46	5.92	1.14	122.18
4D	7.11	27.43	13.76	7.38	2.91	9.7	10.3	27.73	19.92	0.2	51.39	49.52	9.96	62.02	14.64	27.94	9.03	60.45	32.14	7.61	45.22	13.81	29.15	97.51	20.57	657.2
4E	7.53	27.29	14.28	12.28	4.34	16.13	25.23	77.66	44.42	0.2	100.14	83.25	14.67	77.74	13.97	34.75	9.48	70.36	27.86	11.14	36.75	9.17	15.39	58.74	9.15	801.72
4F	2.93	7.48	4.16	2.68	0.91	2.57	3.49	5.34	4.35	2.2	11.06	4.92	1.32	6.46	1.2	4.78	1.34	5.77	0.9	0.69	1.89	1.1	2.56	4.15	0.87	85.12
4G	5.7	22.62	11.77	5.6	2.15	5.56	8.22	0.2	15.48	19.14	39.88	38.94	8.11	34.96	5.86	11.92	3.29	27.67	13.31	5.23	16.4	3.76	6.99	26.15	7.41	346.12
4H	5.58	26.22	12.29	5.65	2.15	8.54	8.32	21.26	15.19	25.27	45.6	49.2	8.21	35.91	5.73	11.96	3.04	27.64	13.01	5.09	14.21	3.53	6.49	25.44	5.36	390.89
5REP1	4.58	11.66	6.51	3.66	1.37	4.25	4.58	7.25	6.11	2.58	14.3	6.3	1.81	10.59	2.21	7.78	2.23	9.84	1.29	1.15	3.98	2.03	4.17	8.17	1.35	129.75
5REP2	3.37	26.07	10.04	3.83	1.57	4.55	4.67	0	5.75	5.68	23.47	13.05	2.13	11.84	1.78	5.95	1.66	9.64	2.2	1.23	3.62	1.54	3.52	8.19	1.74	157.09
5REP3	4.01	10.71	5.84	3.47	1.27	3.94	4.2	6.68	4.75	2.5	13.1	5.51	1.45	6.95	1.25	5.04	1.39	5.88	0.87	0.76	1.96	1.08	2.5	4.11	0.78	100
5A	3.32	9.15	5.04	3.02	1.06	2.93	3.96	6.32	4.87	2.52	13.43	5.66	1.41	6.91	1.25	4.95	1.42	6.18	0.96	0.75	1.95	1.07	2.6	4.05	0.82	95.6
5B	3.39	9.57	5.43	3.83	1.38	3.97	5.68	7.21	7.45	2.92	17.74	7.68	1.77	10.07	1.89	7.53	2.12	9.1	1.23	1.13	2.93	1.63	3.84	6.13	1.16	126.78
5C	2.7	5.71	3.5	2.39	0.87	3.13	3.87	4.39	4.75	1.74	10.54	4.73	1.03	5.77	1.08	4.58	1.24	5.45	0.72	0.65	1.58	0.9	2.18	3.39	0.65	77.54
5D	3.32	10.14	5.46	3.42	1.25	3.61	4.65	7.35	6.23	3.04	17.19	7.05	1.74	9.19	1.75	6.83	1.94	8.27	1.2	1.01	2.59	1.46	3.47	5.5	1.03	118.69
5E	2.23	7.11	3.92	3.99	1.81	5.21	7.86	0.2	14.95	5.83	0	19.27	3.22	15.4	2.35	10.4	2.59	13.87	2.35	1.6	3.08	1.99	9.23	9.87	4.87	153
5F	2.76	6.29	3.7	2.68	0.99	3.86	4.51	0.2	5.99	2.13	13.27	6.04	1.4	8.31	1.67	6.29	1.75	7.79	1.05	0.95	2.6	1.42	3.26	5.29	1.07	95.07
5G	3.06	7.88	4.74	4.02	1.37	4.29	6.76	0.2	9.52	3.6	21.97	8.84	1.96	9.85	2	8.4	2.3	9.74	1.27	1.22	2.15	1.52	3.64	5.07	0.76	125.93
5H	5.24	24.78	11.78	6.02	2.39	9.59	9.66	23.5	16.96	30.88	52.65	56.45	9.3	42.12	7.17	13.62	3.69	32.64	16.24	5.68	21.63	4.85	12.12	42.34	17.7	479
6REP1	4.21	11.33	6.53	3.87	1.4	3.57	4.83	6.83	5.21	2.31	13.44	5.62	1.44	7.5	1.4	5.56	1.56	6.84	0.86	0.83	2.18	1.25	2.94	4.72	0.83	107.06
6REP2	3.73	10.59	5.88	3.53	1.3	3.35	4.49	6.34	5.05	2.24	12.98	5.43	1.41	7.15	1.34	5.46	1.45	6.48	0.85	0.8	2.05	1.18	2.8	4.39	0.78	101.05
6A	5.94	13.93	8.53	5.14	1.74	5.25	6.06	6.8	5.88	2.63	14.1	6.33	1.66	8.75	1.72	6.37	1.79	7.75	1.1	0.98	2.53	1.37	2.98	5.11	0.9	125.34
6B	2.12	5.98	3.52	1.99	0.68	2.06	2.47	3.47	2.58	1.57	6.22	3.35	0.77	3.69	0.73	2.6	0.71	3.29	0.67	0.45	1.14	0.58	1.35	2.33	0.53	54.85
6C	3.91	7.05	4.74	3.6	0.96	3.37	5.45	0.2	7.4	2.74	15.61	7.18	1.6	7.89	1.38	5.57	1.39	6.48	0.98	0.98	1.4	0.8	1.62	2.77	0.46	95.33
6D	0.64	1.33	0.71	0.45	0.16	1.74	0.69	0.9	0.69	0.31	1.92	0.79	0.2	0.87	0.18	0.54	0.12	0.87	0.12	0.08	0.27	0.13	0.32	0.57	1.3	15.9
6E	4.91	9.4	6.04	3.45	1.11	4.09	4.35	4.46	4.57	1.82	9.85	4.61	1.2	6.6	1.31	4.92	1.36	6.07	0.93	0.76	2.13	1.01	2.29	3.96	0.73	91.93
6F	2.77	6.58	3.89	2.92	0.85	3.48	4.05	0.2	6.83	0.2	13.35	6.22	1.92	12.69	2.88	9.51	2.73	12.09	1.59	1.45	5.01	2.42	4.4	9.38	1.26	118.27

	#18	#28	#31	#44	#47	#49	#52	#66	#101	#105	#110	#118	#128	#138	#141	#149	#151	#153	#156	#158	#170	#183	#187	#180	#194	
6G	3.89	11.87	6.49	4.76	1.56	4.47	5.77	7.72	7.98	3.42	19.02	8.33	2.15	11.19	2.06	8.31	2.39	9.26	1.38	1.26	3.1	1.66	3.91	6.2	1.21	139.36
6H	4.13	11.75	6.62	4.38	1.55	4.59	6.07	8.28	9.02	3.83	19.55	10.02	2.51	13.09	2.48	9.36	2.7	11.97	1.65	1.48	3.64	2.05	4.7	7.89	1.59	154.9
7REP1	3.55	14.12	7.38	3.67	1.45	4	4.56	10.76	5.61	4.22	17.03	8.85	1.9	9.46	1.8	6.01	1.74	7.99	1.61	1.08	3.09	1.45	3.22	6.06	1.21	131.82
7REP2	3.57	9.02	5.05	3.11	1.1	3.39	3.8	6.07	4.52	2.31	12.17	5.26	1.41	6.94	1.28	5.09	1.39	6.28	0.86	0.76	1.99	1.15	2.76	4.43	0.9	94.61
7A	3.7	13.55	7.34	4.48	1.69	4.55	6.32	12.55	8.45	5.35	25.61	11.68	2.43	12.01	2.22	7.81	2.3	10.58	2.16	1.41	3.7	1.75	4.05	7.48	1.68	164.85
7B	4.21	11.47	6.45	3.88	1.36	3.44	4.86	8.44	6.4	3.27	18.36	7.41	2.04	10.51	2.04	7.5	2.18	9.73	1.61	1.14	3.43	1.84	4.42	7.52	1.82	135.33
7C	3.32	6.84	4.23	3.19	1.12	5.21	4.96	5.46	6.02	2.35	13.59	6.32	1.35	7.7	1.42	5.78	1.62	7.19	0.96	0.85	2.13	1.2	3.1	4.65	0.91	101.47
7D	2.82	7.89	4.44	2.88	1.01	2.97	3.98	6.06	5.21	3.17	12.28	6.72	1.56	7.66	1.45	5.25	1.45	6.51	1.37	0.94	2.33	1.17	2.61	4.54	0.92	97.19
7E	2.66	7.63	4.63	6.15	1.69	5.66	14.27	8.75	48.93	28.14	74.18	30.38	15.56	101.7	28.68	80.55	25.6	102.5	12.96	11.72	40.94	20.51	45.15	76.28	13.07	808.27
7F	3.78	9.88	5.56	4.01	1.44	3.99	6	7.19	7.92	3.03	18.39	8.3	1.78	9.63	1.84	7.33	2.08	8.81	1.21	1.09	2.67	1.55	4	5.89	1.24	128.61
7G	2.61	7.69	4.19	2.4	0.88	3.54	3.17	5.31	4.24	2.04	10.93	5.13	1.15	6.14	1.07	4.42	1.19	5.45	0.75	0.64	1.63	0.92	2.27	3.48	0.68	81.92
7H	6.06	12.94	7.67	5.1	1.52	3.96	6.17	8.27	6.95	3.21	17.69	7.83	1.88	10.08	1.85	6.99	1.91	8.93	1.23	1.15	2.82	1.57	3.58	6.17	1.08	136.61
8REP1	3.47	10.04	5.63	3.56	1.31	3.6	4.88	6.74	6	2.63	15.28	6.64	1.51	8.22	1.55	6.36	1.74	7.34	1	0.91	2.35	1.32	3.14	4.98	0.91	111.11
8REP2	3.3	8.4	4.83	3.19	1.13	2.96	4.6	5.94	5.5	2.27	13.98	5.83	1.46	7.42	1.39	5.76	1.52	6.71	0.85	0.82	2.03	1.2	2.94	4.54	0.97	99.54
8REP3	3.6	13.75	7.1	3.93	1.5	3.95	5.32	11.26	7.27	5.01	22.19	10.77	2.54	12.08	2.14	7.26	2.13	9.95	2.22	1.37	3.62	1.68	3.79	6.91	1.37	152.71
8REP4	2.18	8.7	4.78	2.55	1.04	2.88	3.77	6.46	4.91	2.92	11.73	6.71	1.34	7.09	1.34	5.01	1.38	6.47	1.25	0.87	2.24	1.13	2.82	4.67	1.11	95.35
8A	5.4	11.36	6.62	4.63	1.45	3.88	6.04	7.86	7.62	3.19	18.24	8.15	1.92	10.45	1.95	7.42	1.94	8.89	1.31	1.17	2.64	1.45	3.32	5.58	0.96	133.44
8B	3.17	11	5.79	5.51	1.71	5.15	9.36	0.2	14.69	7.11	31.51	16.75	3.63	19.11	3.74	12.71	3.67	17.04	3.37	2.36	5.84	2.74	6.13	11.2	2.24	205.53
8C	2.8	10.51	5.54	3.31	1.15	3.41	4.44	9.1	6.91	5.06	19.79	10.61	2.95	15.19	3.12	8.63	2.51	12.63	3.18	1.92	6.44	2.79	4.95	10.92	1.75	159.61
8D	3.38	10.63	5.82	4.1	1.32	3.48	5.79	8.74	8.78	5.45	21.67	11.75	2.61	12.81	2.36	8.29	2.34	11.06	2.31	1.55	3.76	1.84	3.97	7.53	1.46	152.8
8E	12.14	16.39	11.75	6.44	2.02	5.81	9.78	9.18	9.29	3.61	20.5	9.24	2.03	11.48	2.26	8.92	2.52	10.42	1.36	1.26	3.38	1.99	4.86	7.85	1.68	176.16
8F	16.25	16.65	12.15	9.8	2.85	9.42	15.42	0.2	17.61	0.2	38.55	20.33	4.53	22.57	4.64	16.74	4.67	21.02	4.39	2.89	7.11	3.79	9.27	14.86	4.22	279.73
8G	4.35	12.68	7.9	55.25	9.38	39.67	168.6	196.1	314.9	119.4	673.6	286.4	74.38	286.6	52.4	214.1	40.1	218.9	44.9	41.01	41.88	18.79	30.84	58.71	6.81	3017.69
8H	3.69	7.36	4.51	3.23	1.03	3.76	4.62	5.36	5.71	2.25	12.84	5.8	1.39	7.27	1.36	5.5	1.51	6.61	0.89	0.82	1.89	1.09	2.55	4	0.69	95.73
9REP1	3.15	8.78	4.99	3.67	1.32	3.68	5.75	7.66	8.05	3.67	18.16	8.85	2.05	10.55	1.98	7.7	2.12	9.47	1.58	1.24	2.8	1.6	4.05	6.24	1.45	130.56
9REP2	3.1	8.74	5.04	4.24	1.48	4.16	6.75	8.46	9.13	3.8	19.5	9.59	2.21	12.22	2.52	9.32	2.74	11.7	1.9	1.46	4.54	2.29	5.22	9.43	1.83	151.37
9A	3.52	11.34	6.44	3.55	1.38	3.52	4.72	7.54	5.18	2.96	13.12	6.55	1.48	7.83	1.45	5.49	1.56	6.89	1.14	0.88	2.3	1.24	3.01	4.91	0.98	108.98
9B	4.27	13.41	7.53	4.4	1.65	4.24	5.93	8.38	6.85	3.68	16.33	8.43	1.84	9.85	1.88	6.72	1.99	8.68	1.45	1.16	2.8	1.53	3.73	6.05	1.31	134.09
9C	3.53	10.31	5.71	3.25	1.23	3.24	4.15	7.2	5.13	2.95	12.99	6.63	1.53	7.97	1.43	5.45	1.54	6.9	1.17	0.89	2.27	1.26	2.98	5.07	1	105.78
9D	1.98	7.2	3.99	2.84	0.9	2.8	4.63	8.36	6.38	3.44	14.72	8.44	1.53	8.06	1.5	5.43	1.53	7.35	1.41	0.98	2.27	1.17	3.28	4.95	1.55	106.69
9E	3.66	11.33	6.24	3.52	1.42	3.8	5.29	7.95	6.75	3.47	15.89	8.22	1.76	9.58	1.78	6.76	1.87	8.47	1.42	1.12	2.64	1.5	3.43	5.73	1.13	124.73

	#18	#28	#31	#44	#47	#49	#52	#66	#101	#105	#110	#118	#128	#138	#141	#149	#151	#153	#156	#158	#170	#183	#187	#180	#194	
9F	3.95	11.89	6.63	3.83	1.46	3.68	5.11	7.91	6.11	3.36	14.86	7.53	1.7	8.8	1.75	6.37	1.81	7.94	1.27	1.03	2.5	1.42	3.34	5.35	1.01	120.61
9H	3.66	10.37	5.92	3.51	1.32	3.88	4.83	7.13	6.16	3.35	14.98	7.71	1.95	9.66	1.72	6.48	1.76	8.62	1.48	1.06	2.7	1.41	3.45	5.84	1.12	120.07
10REP1	2.24	9.64	5.4	3.99	1.42	4.09	7.38	8.19	10.46	4.27	21.88	11.12	2.43	14	2.78	10.24	2.84	12.74	1.79	1.62	3.8	2.22	5.62	8.62	2.01	160.79
10A	3.42	9.11	5.16	3.41	1.18	3.25	4.81	6.47	5.88	2.41	14.22	6.12	1.51	7.56	1.46	5.98	1.64	7.35	0.93	0.86	2.16	1.27	3.16	4.81	0.91	105.04
10B	3.36	8.69	4.76	3.35	1.09	3.03	4.44	5.85	4.84	2.31	14.06	5.22	1.4	7.3	1.39	5.89	1.63	6.21	0.84	0.77	2.39	1.3	3.17	5.07	0.88	99.24
10C	2.19	9.19	5.06	5.09	1.47	4.8	12.66	0.2	32.8	13.68	56.65	30.75	7.12	31.9	5.37	19.24	4.3	23.28	5.76	4.07	5.83	2.41	5.77	10.19	2.36	301.94
10D	3.52	10.66	5.99	3.87	1.34	3.62	6.23	7.49	8.51	3.4	19.03	8.62	2.12	11.43	2.31	8.51	2.31	10.22	1.42	1.33	3.07	1.74	3.87	6.61	1.04	138.26
10E	8.5	23.7	11.54	5.43	2.25	5.52	8.38	0.2	15.27	22.68	41.74	47.67	8.09	34.02	5.17	10.13	2.8	27.59	13.87	4.77	14.01	3.2	7.76	24.79	10	358.88
10F	3.2	7.86	4.52	3.19	1.13	3.36	5.32	0.2	7.59	3.41	17.82	8.21	2.3	12.61	2.41	8.62	2.44	10.9	1.79	1.29	4.84	1.96	6.11	10.08	3.56	134.52
10G	2.97	7.62	4.3	3.33	1.19	3.36	5.46	0.2	9.64	3.94	21.11	10.15	2.56	12.58	2.17	8.79	2.16	11.06	1.56	1.44	2.79	1.59	4.54	6.33	1.54	132.18
10H	5.15	7.04	4.05	4.58	1.41	3.7	6.05	5.91	12.02	4.65	27.06	11.23	3.57	17.77	4.02	13.82	4.21	18.37	2.55	1.95	7.23	3.25	11.11	15.22	5.35	201.27