The Distribution and Reactivity of Organochlorines in Estuaries

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The Distribution and Reactivity of Organochlorines in Estuaries

by

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Dedication

This thesis is dedicated to my wife Emma whom I met in the course of these studies. Over the years it has taken me to complete this work she has provided me with four beautiful children and taken more than her fair share of the effort in their upbringing whilst I have struggled in selfish pursuit of my academic goals.

The Distribution and Reactivity of Organochlorines in Estuaries

Andrew O. Tyler

Abstract

In February 1997, the Governing Council of the United Nations Environment Programme initiated a protocol to reduce the risks to human health and the environment arising from persistent organic pollutants. The initial list of 12 families of organochlorine pollutants included polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) selected for their persistence, bioaccumulation capacity and toxicity. The aim of this work was to further understanding of the behaviour of these organochlorines (OCs) in estuarine systems.

Field surveys were conducted at UK estuarine (Humber, Clyde and Dee) and coastal locations. Sediments were analysed for OCs and a range of chemical and physicochemical properties (trace metals, organic carbon content, specific surface area). Hydrographic measurements were also made to assist in defining the estuarine environment. Concentrations of PCDD/DF on a dry weight basis ranged from non-detectable (n.d.) to 11100 pg g^{-1} and PCB from n.d. to 3000 ng g^{-1}. Estuarine OC contamination was generally elevated above coastal waters concentrations.

The distribution of OCs was studied to determine the extent of source, compound physicochemical, and particulate geochemical influences. In the Clyde estuary some source-related effects were observed but in the Humber estuary, characterised by highly dynamic conditions, these were masked by mixing of sediments. The characteristics of the sorbent were found to be of key importance with the content and nature of particulate organic carbon being the major control.

To further understand the sorption behaviour of OCs, partitioning experiments were conducted with ^{14}C analogues of the compounds under realistic estuarine gradient conditions (K_d range from 2.4×10^4 to 49.4×10^4 for TCB and 23.1×10^4 to 313×10^4 for TCDD). Particle concentration was found to be of key importance and it was concluded that this effect was transferable to environmental situations. Salinity was found to be a minor influence on partitioning behaviour.

Development of sorption sub-models and their incorporation into an integrated estuarine contaminant transport model was demonstrated. A particle interaction-based sorption model was shown to only partially account for the observed partitioning behaviour; inclusion of an irreversibly adsorbed fraction may more adequately represent estuarine partitioning. Riverine and outfall discharges were simulated in the integrated contaminant transport model to demonstrate the influence of tidal hydrodynamics, sediment dynamics and variable partitioning applied to the Humber estuary.

Declarations

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award.

This study was financed under the Department of Trade and Industry's 'Wealth from the Oceans' programme under contract number MTD/MO/9/118. Significant support in the form of release from company duties, expenses and payment of fees was provided by British Maritime Technology.

These studies were undertaken on a part-time basis from 1991 to 1999. Fieldwork, sample preparation and analyses and the laboratory experiments were carried out as part of the DTI project entitled 'Geochemical Cycling of Contaminants in Estuaries' which was managed by the author. Chemical analyses of organochlorines was carried out by staff at Rechem Environmental Services, as part of the project. Supporting analyses of trace metals and specific surface areas were carried out jointly between the author and project co-workers. All other sampling, analysis and experiments were carried out by the author. There was close involvement with the encoding of the coupled hydrodynamic-chemistry modelling system, PISCES, including specification, integration of chemical concepts and calibration/validation of the modelling.

From 1991 to 1994, numerous extended periods (typically 2 weeks) were spent engaged in fieldwork or at the University of Plymouth working in the laboratory. Throughout the study period, a programme of advanced study was undertaken which included guided reading in topics related to environmental and estuarine organic geochemistry. A two week full-time EU Advanced Science course on 'Biogeochemical Processes in Estuaries and Shelf Seas' was attended. Instruction was provided on laboratory techniques for lipid extraction, safe handling and use of ^{14}C radiotracers using scintillation counting. Introductory instruction was also given in a range of analytical methodologies including multi-point BET nitrogen gas adsorption, flame atomic absorption spectrophotometry, gas chromatography and high resolution mass spectrometry.

Relevant scientific seminars and conferences were regularly attended at which work was often presented; external institutions were visited for consultation purposes and scientific papers were prepared for publication.

Publications

Tyler, A.O. 1992 Organic micropollutant contamination in the coastal boundary zone. BMT Technical Report No. 46514. Wealth from the Oceans Programme. Department of Trade & Industry. Contract No. MTD/MO/9/118. 85 pp.

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Presentations and Conferences Attended

Estuarine and Coastal Sciences Association Conference 21, Gent, Belgium, 9 - 14th September 1991.

Marine Chemistry Society Meeting, Southampton University, 16/17th December 1991.

Dioxin '92 Conference, Tampere, Finland, 24 - 28th August 1992. Oral paper presented (see list above).

DTI Wealth from the Oceans Project Meeting, Rechem Environmental Services, 16th October 1992. Presentation on the progress of the 'Geochemical Cycling of Contaminants in Estuaries'.

Organohalogen Compounds, 1 Day Meeting, Warren Spring Laboratory, 17th November 1992.

Marine Chemistry Workshop, Torquay, 18/19th May 1993, Oral presentation on 'Sources, transport and fate of dioxins and PCBs in marine systems'.

9th Bi-annual Meeting on Dioxins and PCBs, Beaulieu, 30th June 1993.

Dioxin '93 Conference, Vienna, Austria, September 1993, Oral paper presented (see list above).

Estuarine and Coastal Sciences Association Conference 23, Groningen, The Netherlands, September 1993. Poster on 'Dioxins in sediments of the Clyde Estuary, UK' presented *in absentia*.

Inland and Coastal Water Quality '93. Measurement and Modelling, Environmental Physics Group, Institute of Physics, Stevenage, 29th September 1993. Co-authored presentation by Dr. A. Turner on 'Modelling Trace Metals in Estuaries using the K_D Concept'.

International Symposium on PCDDs, PCDFs, PCBs and PAHs, Lancaster University, 5/6th January 1994. Poster presentation on 'Dioxins in sediments of the Clyde Estuary'.

North Sea Task Force, UK Liaison Group Meeting, London, 17th January 1994.

NERC LOIS Programme Modelling Workshop, Proudman Oceanographic Laboratory, Bidston, 27/28th April 1994.

Irish Sea Group Meeting, Plymouth Marine Laboratory, 13th December 1995. Presentation on modelling organic contaminants in estuaries.

Tyler, A.O. 1996. Where does it all end up? The transport and fate of chlorinated organics in aquatic environments. Presented at the Second International Symposium on Dioxins and Related Compounds: Sources, Environmental Significance and Effects. Netherwood Hotel, Grange-over-Sands, Cumbria, 24/25 April 1996.

Courses and External Meetings

Numerous visits to and meetings with Rechem Environmental Services to discuss dioxin and PCB analyses, deliver samples, receive instruction on analytical methodologies and collect data.

Regular meetings with the Clyde River Purification Board (now SEPA).

Meeting with Prof. Roger Falconer to discuss model development. 27th November 1992 and 27th November 1995

Visit to Coalite Chemicals, Bolsover, to discuss dioxins in discharges to the River Doe Lea, 21st December 1992.

Visit to Dr. Chris Wright at MAFF Food Science Laboratory, Norwich, to collect ^{14}C standards and discuss matters relating to use of the standards, 23rd July 1993.

Biogeochemical Processes in Estuaries and Shelf Seas, MAST Advanced Science Course, Plymouth, 2 weeks, August 1993.

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Chapter 1. Introduction

1. Introduction

1.1 Pollution in Estuaries and Coastal Waters

By virtue of their geography and dynamic environment, estuaries and coastal waters have long been repositories for industrial pollution (Olausson & Cato, 1980). Widespread use of organic chemicals in agriculture has resulted in land runoff and river-borne discharge into estuaries. Industry, attracted to estuary sites by the proximity of sea transportation, urban settlements, and cooling water, has used estuaries and coastal waters as a site for direct discharge of effluent. Terrestrial and coastal combustion sources have combined through river runoff and direct deposition to load estuaries and coastal waters with combustion related contaminants.

Although estuaries form an interface between rivers and the receiving waters of the adjacent shelf sea, they tend to act as a filter and sink for pollution received through riverine, atmospheric and direct pathways (Schubel & Carter, 1984). Many contaminants of concern tend to associate with sediment particles which can be retained in estuaries over decadal timescales only being dispersed by a gradual remobilisation of bed sediments into coastal waters.

In recent years, there has been particular concern over the widespread occurrence of persistent chlorinated organic compounds in the marine environment. This largely man-made class of organic compounds has been used extensively in agricultural and industrial applications since the 1900's. Until fairly recently the accumulation of these compounds in environmental media and their low level toxicity was not appreciated and scientific investigation was hampered by analytical problems associated with identification and quantification of these compounds at concentrations typically found in marine environments.

In February 1997, the Governing Council of the United Nations Environment Programme initiated a global legally binding instrument to reduce the risks to human health and the environment arising from the release of twelve classes of Persistent Organic Pollutants (POPs); aldrin, dieldrin, DDT, endrin, chlordane, hexachlorobenzene, mirex, toxaphene, heptachlor, PCBs, dioxins and furans. This unprecedented international action was taken in response to the wide acceptance that these POPs posed a risk to human health and to the environment, and were subject to long-range transport to regions where they had never been previously used, thus posing a global threat (UNEP, 1999). This thesis focuses on polychlorinated dibenzo-para-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), three members of this high priority group of POPs.

1.2 Hydrography of Estuaries and Coastal Waters

1.2.1 Estuarine Classification

A working definition of an estuary is provided by Cameron & Pritchard (1963):- “a semi-enclosed coastal body of water having a free connection to the open sea and within which the sea-water is measurably diluted with fresh water deriving from land drainage”. Estuaries are sometimes classified on the basis of shape with the ‘coastal plain’ estuary usually a result of land sinkage or a flooded river valley, the ‘deep basin’ such as the Norwegian fjord, and the ‘bar-built’ estuary consisting of a bar enclosing a channel.

An alternative and more geochemically significant classification is on the basis of salinity stratification. The four classifications are: vertically mixed, slightly stratified, highly stratified and salt wedge. Vertically mixed estuaries tend to be shallow, often with large tidal ranges (up to 15 m), low river flows and occasionally wave environments. The salt wedge estuary at the other extreme exhibits a saline intrusion beneath the high outflow of fresh water. The resulting salt wedge migrates up and down the estuary under the influence of tide and river flow.

1.2.2 Estuarine Hydraulics

By virtue of its geology and geographical position an estuary exhibits a complex interplay between river flow and tidal influx, which causes an interaction between marine and terrestrial sediments. The complexity of estuarine environments is further compounded by the various timescales over which these processes occur. Most estuaries experience strong tidal influences producing semi-diurnal or diurnal influxes of seawater and the spring and neap variations arising from the lunar cycle. This influx interacts with river discharges within the estuary varying on seasonal cycles but also strongly influenced by random events such as river spates and storm surges induced by extremes of weather. Superimposed on these variations are the longer timescale variations in geomorphology and climate.

1.2.3 Estuarine Sediment Dynamics

The hydraulics of an estuary imply a dynamic sediment transport regime which is further complicated by the mixing between seaward fluxing lithogenic sediment from land runoff and riverbed sources, and calciferous material from marine origins (Postma, 1980). A wide spectrum of sediment type may be encountered within an estuary and may vary from non-cohesive, sand, gravel and shell fragments to fine clay and silt material, which is often rich in organic matter and highly cohesive.

Sediment transport is strongly influenced by tidal and seasonal changes. Tidal hydrodynamics dominate the resuspension and deposition of sediments and strong flows often lead to the development of a geochemically reactive ‘turbidity maximum’ in the upper reaches of an estuary. The seasonal cycle plays an important part in the retention of sediments within an estuary. During low river flow conditions, tidal asymmetry leads to a landward transport of sediment known as 'tidal pumping' (Uncles *et al.*, 1985). This process is reversed when high river flows flush sediments down-estuary. The result of this process is sediment retention times measured in years compared with water flushing timescales of days (Bale *et al.*, 1985; Uncles *et al.*, 1983).

The interplay between estuarine hydrography and sediment type produces a complex distribution of sediment. A general upstream increase in finer, lithogenic, organic rich sediment is usually observed. This is combined with hydraulic influences which tend to deposit finer sediments in embayments and on the inside of bends in the estuary often leaving extensive inter-tidal mudflats and scouring all except the coarse sand/gravel fractions in the main flow channels. In many estuaries this natural distribution is further influenced by capital and maintenance dredging and artificial obstructions to current flows.

1.3 Biogeochemistry of Estuaries and Coastal Waters

1.3.1 Biogeochemical Transport

The biogeochemistry of estuaries and coastal waters is strongly dependent on the hydrography, sediment regime, and geochemistry of water and sediment. Trace contaminants are transported either dissolved in the water column or adsorbed to sediments. In some cases, temporary biological compartments may also play a role in contaminant transport. Dissolved phase contaminants are diluted and dispersed through mixing in the estuary and flushing into the receiving coastal waters. Sediment bound contaminants follow more complex transport pathways and represent the major contaminant burden in an estuary often over decadal timescales (Van Zoest & Van Eck, 1993a; Wade *et al.*, 1994).

Although transport is dominated by physical processes in an estuary, it is the biogeochemistry of sediments and water, and the physicochemical properties of the contaminant which often determine preferred transport pathways. Many compounds of concern are hydrophobic, and sorb onto and into sediment particles. This leads to their long retention in an estuary which, combined with their toxicity, resistance to degradation and liability to bioaccumulate, results in their status as high priority contaminants.

1.3.2 Sediment-water Partitioning

The extent and reversibility of contaminant partitioning onto sediments is subject largely to geochemical influences. Most sediment bound contaminants are found to prefer sediments with a high surface area indicating more active sites for adsorption (Turner *et al.*, 1991). Trace metals are often found preferentially bound to ferrous or humic coatings on particles. For organic contaminants, the nature of the organic fraction of the particle is seen to be more influential (Broman *et al.*, 1991). Within an estuary, the salinity gradient is seen to strongly influence metal partitioning behaviour although there is considerable variation between metals. For organic contaminants, salinity seems influential and partitioning is dominated by the estuarine gradient in particle characteristics.

1.3.3 Role of Biota

Biota may play a part in the partitioning and subsequent transport of contaminants although estuaries are not always particularly fertile due to their turbidity-reduced light penetration. Estuaries are usually subject to a single plankton bloom in the summer which may be exposed to contaminants in the water column (Delbeke *et al.*, 1990). However, the main exposure of biota to estuarine contaminants is through bed-dwelling species which filter-feed on sediments resulting in accumulation of lipophilic compounds in lipid tissues and leached metals in digestive systems. Although there is a carcinogenic risk to biota from toxic trace contaminants, by far the main threat to biota within an estuary is deoxygenation caused by domestic sewage discharge and organic 'oxygen demanding' wastes from industry. Several estuaries declared dead have revived once oxygen balances have been restored even though bed sediments still remain repositories for toxic trace contaminants.

1.4 Structure, Nomenclature & Physical Properties of PCDD/PCDF/PCBs

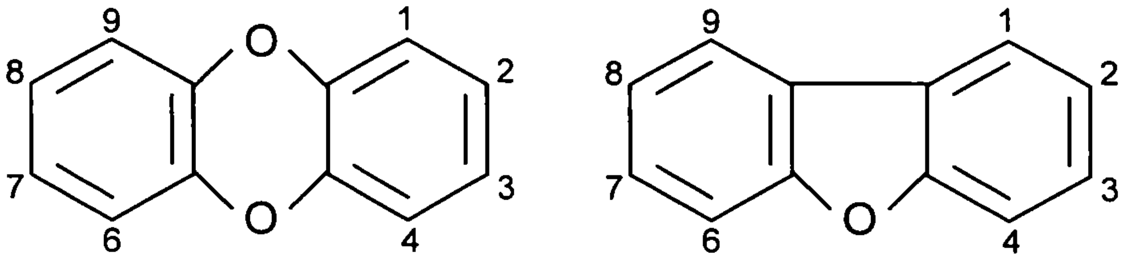
1.4.1 Chlorinated Organic Compounds

Organochlorine compounds (OCs) are hydrocarbon compounds containing one or more carbon-chlorine bonds. The classes of OC compounds are extensive, ranging from lower molecular weight aliphatic compounds to the high molecular weight aromatic compounds.

OCs can originate from both natural and anthropogenic sources. Large quantities of OCs are biogenically derived, mainly from marine algae. Much of this is in the form of multi-chlorinated methane and ethane compounds (EuroChlor, 1994). PCDDs and PCDFs have a significant number of natural combustion sources which include volcanoes, forest fires etc. Evidence from Japanese sediment cores dated back ~8,000 years clearly show the presence of dioxins (Hashimoto *et al.*, 1990). However, the general increase in environmental concentrations over the last century has been largely due to industrial sources (Alcock *et al.*, 1993; Halsall *et al.*, 1997) and certain OCs such as PCBs are entirely anthropogenically derived and were produced for many years until environmental concerns led to a halt in manufacture and restriction on usage and disposal (Tanabe, 1988).

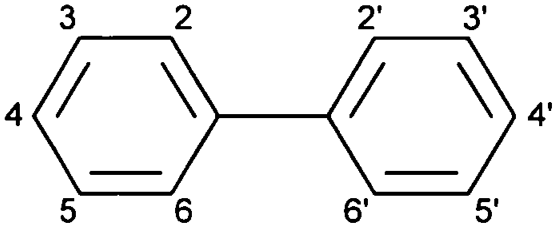
1.4.2 Chemical Structures and Nomenclature

The structure of high molecular weight OCs implies a class of compounds which tend to be less flammable, more stable, more hydrophobic, and consequently more cause for environmental concern. Figure 1.1 shows the structure of the PCDD, PCDF and PCB families of compounds;



Dibenzodioxin

Dibenzofuran



Biphenyl

Figure 1.1. Chemical Structures of Dibenzodioxin, Dibenzofuran and Biphenyl (Numbers Indicate Chlorine Positions for PCDD, PCDF and PCB)

Tradenames & Acronyms

PCDDs, PCDFs and PCBs are referred to by a number of acronyms and, in the case of commercially produced PCBs, several tradenames. Table 1.1 gives some of the common names by which these compounds are known;

Compound	**Tradenames & Acronyms**
Polychlorinated dibenzodioxins	Often refered to as PCDDs or dioxins, a name that is also sometimes used to refer to both PCDDs and PCDFs
Polychlorinated dibenzofurans	Often refered to as PCDFs or furans
Polychlorinated biphenyls	Refered to collectively as PCBs. Several tradenames including Aroclor®, Clophen®, Phenoclor®, Kaneclor®, Santotherm®, Fenclor®

Table 1.1. Tradenames and acronyms for PCDDs, PCDFs & PCBs.

1.4.3 Physical and Chemical Properties

The physical and chemical properties of OCs are of primary importance in determining the behaviour of these compounds in the marine environment.

The systematic change in physicochemical properties within a family of compounds also helps to simplify the otherwise complex problems of predicting behaviour for a wide range of individual congeners. The following physical and chemical properties contribute to the environmental properties of these compounds (Howard, 1989; Verschuren, 1983).

Molecular Weight

Molecular weight gives a first approximation of the behaviour of an individual compound. As molecular weight increases, the solubility of the compound decreases as well as its tendency to volatilise.

Water Solubility

Water solubility is a primary property in the consideration of OC behaviour in aquatic systems and as such provides a good estimation of a compounds tendency to partition into the aqueous phase. It is also used in the estimation of likely volatilisation of the compound from water.

Vapour Pressure

Vapour pressure is a key property required for estimation of the volatilisation of OCs from water or sediment. Using vapour pressure and solubility, Henry's Law Constants can be calculated for estimation of water-air exchange of OCs.

Octanol-water Partition Coefficient

The octanol-water partition coefficient, K_{ow} is a measure of the polarity of the compound and is therefore essential in determining the partitioning behaviour of an OC between environmental compartments. The K_{ow} of a chemical is defined as the ratio of concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system.

$$K_{ow} = \frac{\text{concentration in octanol phase}}{\text{concentration in aqueous phase}} \qquad 1.1$$

Congener Specific Properties

Although OCs tend to be high molecular weight, low solubility, low vapour pressure, high K_{ow} compounds, there is a significant range of physical and chemical properties encountered within a specific family of compounds. The changes in physical and chemical properties generally reflect the degree of chlorination; solubility and vapour pressure fall, and K_{ow} rises as chlorination increases. The chlorine substitution arrangement is also influential in determining physical and chemical properties. The general trend in properties is helpful in estimating the behaviour of families of OCs once the behaviour of a few congeners are established. The following tables (Table 1.2 & 1.3) summarise some of the properties of PCDDs and PCBs and illustrate the range of physical and chemical properties.

Compound	**Vapour Pressure (Pa)**	**Solubility (μg/l @ 20°C)**	**log K_{ow}**
2,3,7,8-TCDD	6.2×10^{-7}	0.019	6.0 - 7.0
1,2,3,4,7-PeCDD	8.8×10^{-8}	0.118	7.4
1,2,3,4,7,8-HxCDD	5.1×10^{-10}	0.004	7.8
1,2,3,4,6,7,8-HpCDD	7.5×10^{-10}	0.002	8.0
OCDD	1.1×10^{-10}	0.000074	8.2

Table 1.2. Physical and chemical properties PCDD congeners (DoE, 1989)

Compound [IUPAC]	**Vapour Pressure (mm Hg)$^{+}$**	**Solubility (mg/l)***	**log K_{ow}^{+}**
2,4-DiCB [7]	1.8×10^{-3}	1.4	5.15
2',3,4-TCB [33]	7.7×10^{-5}	0.078	6.1
2,2',5,5'-TeCB [52]	3.7×10^{-5}	0.046	6.26
2,2',3,4,5'-PeCB [87]	1.6×10^{-5}	0.022	6.85
2,2'4,4',5,5'-HxCB [153]	5.2×10^{-6}	0.0088	7.44
2,2'3,3'4,4'5,5'-OCB [194]	-	0.0070	8.68
Decachlorobiphenyl	-	0.015	9.60

Table 1.3. Physical and chemical properties of PCB congeners ($^{+}$Erickson, 1986, *Hutzinger et al., 1974)

1.5 Environmental Properties of PCDD/PCDF/PCBs

By virtue of their physical and chemical properties, OCs have distinctive environmental properties which dominate their biogeochemical behaviour and result in their persistence and bioavailability. These properties have been used by UNEP to select the priority OCs for preparation of the POPs Protocol. The POPs Protocol sets criteria which include atmospheric half life ≥ 2 days, persistence in water with half life ≥ 2 months, persistence in soil and sediments with half life ≥ 6 months, and bio-accumulation factors of > 5,000 or log $K_{ow} > 5$ (UNEP, 1998). There are a range of physical and chemical properties associated with different families of compounds and individual congeners within these families. This leads to a wide variation in the environmental properties observed for OCs.

1.5.1 Hydrophobicity

The hydrophobicity of OCs is one of their most characteristic and important properties giving rise to their tendency to preferentially adsorb onto sediment in marine environments. This has significant implications for their transport in the marine environment and their ability to disperse. This is discussed in detail later in this chapter.

Quantification of hydrophobicity can be implied from a number of measurements. A simple estimation may be obtained from the solubility of the compound in water, but the common measure used widely by environmental chemists is the K_{ow} (Lyman, 1982).

The K_{ow} parameter does have limitations in its use for environmental studies due to the fact that it does not consider the geochemistry of the partitioning phases as they would occur in a natural marine system. However, its relationship to sediment/water partition coefficients (Mackay, 1991) and bioconcentration factors for aquatic life (Gobas *et al.*, 1991) make it a useful starting point for investigations of OC behaviour. Later in this chapter, the sediment/water partition coefficient, K_d, will be introduced; this takes better account of both the properties of the compound and the partitioning phases.

1.5.2 Lipophilicity

The apolarity of OCs gives rise to another important environmental property closely related to hydrophobicity, that of lipophilicity. This expresses the preference of the compound to partition into lipid or fat phases. As with hydrophobicity, K_{ow} is a useful parameter with which to assess lipophilicity. It must be noted that the definition of lipid is somewhat loose as the term covers a large number of diverse chemicals present in natural environments (Harvey & Boran, 1985). Operationally, lipid may be defined as that which partitions into the apolar phase of a two phase apolar-polar system. By definition it therefore excludes some 'lipid' components such as the phospholipids. This is not considered a limitation as, on the principle of 'like dissolves like', OCs will always favour an apolar phase.

1.5.3 Volatility

Although not a property usually associated with high molecular weight compounds, the volatility of certain OCs can be an important consideration in their long term transport and fate (Atlas *et al.*, 1986; Halsall *et al.*, 1999). Methods for estimating the volatility of organic compounds generally rely on the value of the Henry's law constant, H as an indicator of susceptibility to volatilisation. From the tables given above, Henry's Law Constant can approximated thus (Lyman, 1982);

$$H = \frac{P_{vap}}{S} \text{ (atm m}^3\text{ mol}^{-1}\text{)} \qquad 1.2$$

where P_{vap} is the vapour pressure in atmospheres (atm) and S is the solubility in mol m^{-3}. P_{vap} and S must be applied for the compound in the same physical state.

As the value of H falls the compound is essentially less volatile. In the range $10^{-7}<H<10^{-5}$, volatilisation is slow and at a rate determined by H. Below about 2×10^{-5}, the compound tends to partition into water and transfer is gas phase controlled. Between 10^{-3} and 10^{-5} liquid phase and gas phase resistances are both important and volatilisation can be a significant transfer mechanism (Lyman, 1982). Theoretically therefore, for a compound such as 2,2',5,5'-tetrachlorobiphenyl with a Henry's law constant of 3.05×10^{-4}, volatilisation may be expected to be important. It must be borne in mind that this calculation does not account for the dynamics of the marine environment which will be a major influence on actual volatilisation rates.

1.6 Sources of PCDD/PCDF/PCBs to the Marine Environment

Chlorinated organic compounds have been manufactured for many years for agricultural and industrial applications and are now considered ubiquitous in the environment (Berry *et al.*, 1993). Unlike PCDD/PCDFs, PCBs are entirely man-made and have been placed on government priority lists following discovery of their widespread occurrence in the environment. The use of PCBs has been banned and their disposal is strictly regulated.

1.6.1 Usage and Manufacture

Polychlorinated biphenyls

Probably the most notorious OC deliberately produced by man, PCBs were manufactured from 1929 until 1976 when their production was effectively halted by the US Toxic Substances Control Act 1976. World production figures of between 1.2×10^9 and 1.53×10^9 kg have been estimated (Russian production figures are not known) of which approximately 30% is now resident in the environment (Tanabe, 1988).

The thermal stability and inertness of PCBs as well as their excellent dielectric properties have made them ideal for use as fluids in electrical transformers and capacitors and as hydraulic fluids. They have also found use in a range of other applications including fire retardants, heat transfer applications, and plasticizers. PCBs were manufactured under a range of brandnames (e.g. Aroclor®, Clophen® and Kanechlor®) each containing a unique mixture of congeners (Erickson, 1986).

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans

PCDDs and PCDFs have no commercial uses and are produced entirely as un-wanted by-products of industrial production. Although largely produced from incineration/combustion processes, industrial production has been a significant source in the past. PCDD/PCDFs have been found in paper pulp mill sludge where chlorine bleaching is in use (Champoux, 1996; Clement, 1989; Kähkönen et al., 1998; Wade *et al.*, 1997), manufacture of chlorinated phenols such as PCP (Hagenmaier *et al.*, 1986; Turkstra & Pols, 1989), PCBs (Erickson, 1986, Tanabe, 1988), herbicides (Rappe, 1992a), and chloroalkali (Kannan *et al.*, 1999). The occurrence of PCDD/PCDFs as co-contaminants in PCB mixtures has been suggested as contributing to the toxic effects of these mixtures (Tanabe, 1988). Dioxin exposure of Vietnam forces and citizens was found to be due to PCDD/PCDF co-contamination of 2,4,5-T used as a defoliant (Gough, 1991).

1.6.2 Sources

Sources of PCDD/PCDFs and PCBs to the marine environment arise from three principal sources; manufacture, industry and combustion;

Manufacture

Manufacture of either the compound itself or another product of which the OC is a precursor or formation product is an obvious source of OCs. Several of the largest incidents of OC contamination for example, have arisen as a direct result of deliberate discharges or accidents at chemical plants. The ICMESA TCP production plant at Seveso, Italy was responsible for a major dioxin release following an accident in 1976 (Bertazzi, 1991) and the herbicide plant at Newark on the Passaic River, USA caused severe contamination by dioxins which were formed as a by-product of the manufacture of 2,4,5-trichlorophenoxy acetic acid (Rubinstein *et al.*, 1990). More recently, severe environmental contamination by OCs has been reported in Russian plants formerly used for the manufacture of chemical weapons (Federov *et al.*, 1993).

Industrial

PCBs have been widely used in industrial applications where they are distributed widely in small quantities which are extremely difficult to regulate. Although there have been some major contamination incidents from industrial use of PCBs such as the General Electric capacitor manufacturing plant on the Hudson River, USA which caused significant releases of contamination over many years (1950-1976) (Bopp *et al.*, 1981), most releases of PCBs from industrial sources are small. These emissions are often caused by failure to identify the substance, breaking of old equipment (e.g. transformers, capacitors) or illegal dumping to avoid the high costs of professional disposal services.

Combustion

Combustion sources are identified as the major source of dioxins (Abad *et al.*, 1997; Alcock *et al.*, 1999; Rappe, 1992b). Combustion processes resulting in the possible formation of dioxins include chemical, hospital and municipal incinerators as well as domestic fires, vehicle exhausts, power stations and accidental fires (DoE, 1989; Meharg *et al.*, 1997). Although the chemistry of dioxin formation in combustion is not fully understood (Iino *et al.*, 1999), it is known that temperature and residence time in incinerators are critical to dioxin formation and destruction (Bumb *et al.* 1980; Tuppurainen *et al.*, 1998). As a result, the polluting incinerators tend to be those with a large throughput where control of these parameters is difficult, or those which are not in continuous use such as hospital incinerators which also incinerate considerable quantities of plastic material. Toxic chemical incinerators have received much attention as potential sources of dioxins although it is these incinerators which use the most advanced technology to ensure optimum combustion conditions.

1.7 Toxicity of PCDD/PCDF/PCB to Marine Biota

Ecotoxicological research presents the greatest challenges associated with understanding the impact of chlorinated organic compounds in the marine environment. Importantly, it is also vital to the determination of 'priority compounds' for hazard assessment. As with their physicochemical properties, chlorinated organic compounds have a wide range of toxic effects, mechanisms of toxicity and degrees of toxicity. Furthermore, toxicity varies considerably between target species.

1.7.1 Assessment of Toxicity

Of all the OCs, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) has probably attracted the most attention in toxicity studies. Although not typical in its toxicity, it has been described as "the most potent carcinogen known to man" (Culliton, 1991). This compound provides an illustration of the complexities associated with assessing the toxicity of OC compounds in the marine environment. Attention on dioxins was renewed by a re-assessment of dioxin toxicity by the US Government which again promoted their extreme toxicity (USEPA, 1994a, b, c).

1.7.2 Toxic Mechanisms

The exact mechanisms of OC toxicity, in common with most environmental pollutants, are not completely understood. Dioxins are known to have a high binding affinity to hepatic cytosolic receptor protein (A*h* receptor) eliciting a range of toxic responses including body weight loss (many laboratory animals die of a wasting syndrome), thymic atrophy, dermal disorders, hepatic damage, teratogenicity, reproductive toxicity and immunotoxicity (Vos *et al.*, 1988). The mechanisms of toxicity of other OCs (e.g. PCBs) are known to have similarities to that of dioxins. Of crucial importance in determining the toxicity of an individual congener is the substitution position of the chlorine atoms (Miyata *et al.*, 1989). For dioxins, substitution at the 2, 3, 7 and 8 positions illicits the greatest toxic response. For PCBs, those that achieve isostereomerism with dioxins by having four or more chlorine atoms in *para* and *meta* positions and no chlorines in *ortho* positions (coplanarity), induce similar toxic responses. Bearing in mind the dependence of physical and environmental properties on the degree and position of the chlorine atoms, there are important implications for toxicity arising from geochemical transport and fate.

1.7.3 2,3,7,8-TCDD Toxicity

Most of the research associated with 2,3,7,8-TCDD toxicity has been conducted on terrestrial species with the objective of determining the likely toxicity to humans and safe levels for human intake. Research has taken two paths; epidemiological investigations in humans exposed to the compound following industrial accidents, and toxicological studies involving laboratory animals.

There have been several well publicised cases of dioxin contamination of humans. These include the 1976 Seveso accident where 35,000 humans were exposed following a chemical plant explosion (Bertazzi, 1991) and the exposure of Vietnamese civilians and US troops serving in Vietnam following application of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) as a defoliant. Despite several reported toxic effects including chloroacne, no human has ever died as a direct result of dioxin exposure (Gough, 1991). Epidemiological studies continue on exposed populations but these, by their nature, take many years to produce results and so far have been inconclusive.

Laboratory toxicological studies have highlighted a fundamental problem in assessing the priority of 2,3,7,8-TCDD as a pollutant and assigning a 'safe maximum human intake'. This problem is the extreme variance in sensitivity to 2,3,7,8-TCDD between various species. Doses <1 $\mu g\ kg^{-1}$ are lethal to guinea pigs, whereas hamsters tolerate doses of milligrams per kilogram (Poland & Knutson, 1982). This contrast has fuelled scientific debate and subsequent legislation for several years with no sign of a conclusive statement. In the marine environment the problem is even greater with a fundamental lack of data on which to base risk assessments.

1.7.4 Toxicity in the Marine Environment

The capacity for biomagnification discussed later in this chapter results in concentrations of OCs in target species high enough to elicit a toxic response. Outward signs of toxic defects have been found throughout the marine foodchain. In phytoplankton, Biggs *et al.* (1978) reported significant inhibition of growth in estuarine species exposed to Aroclor 1254 with a consequent shifting of the community structure towards smaller forms, At the top of the foodchain, fish and marine mammals have been reported with a range of toxic responses supposed to result from environmental pollution including lymphocystic infection of flatfish and fin erosion and skin ulcer disease in various species (McCain *et al.*, 1992, Vos *et al.*, 1988).

Immunotoxic effects have been reported where direct suppression of the immune system caused by exposure to OCs leaves the target species vulnerable to other viruses and infections. It was this type of response that was highlighted as a possible explanation for the deaths of 18,000 common seals (*Phoca vitulina*) in the North Sea during 1988. The seal epidemic was caused by an outbreak of phocine distemper virus which in itself was not a result of the suspected PCB contamination. It was thought however, that the scale of the mortality could be explained by immunosuppression by PCB toxic effects. The results of a detailed study of dead and live seals following the epidemic did not lead to conclusive evidence of PCB implication in the deaths (Hall *et al.*, 1992; Skarre *et al.*, 1990).

In recent years a further chronic toxic effect has been widely reported arising from exposure of animals and fish to a range of contaminants. This so-called estrogenic activity results from chemicals inadvertently mimicking the behaviour of the hormone estrogen (Colborn *et al.*, 1993). This produces disruption of the sexual development of male species with consequent reductions in sperm count, fertility and structural abnormalities in reproductive organs (Cotton, 1994; The Lancet, 1995). PCBs, PCDDs and PCDFs have been reported as estrogenic compounds by a number of authors (Routledge & Sumpter, 1996; Sumpter & Jobling, 1995). Sumpter & Jobling (1995) report estrogenic activity in male rainbow trout arising from concentrations of Aroclor 1221 at concentrations as low as 1μM.

1.7.5 Management of Toxicity

The issue of toxicity and hazard assessment of OCs presents managers and scientists with a problem. On the one hand, the issue of toxicity is central to the study of a compound of potential environmental concern. On the other hand, the wide range of toxic effects and species dependency, together with the mass of contradictory data result in a confused picture not conducive to management and regulatory decisions.

The toxic equivalent system developed for dioxins and furans is an attempt to provide a simple expression of toxicity as it relates to a family of compounds. The system is based on normalisation of the toxicity of the various toxic congeners against the toxicity of 2,3,7,8-TCDD, the most toxic congener (Kutz *et al.*, 1988). Of the 210 dioxin/furan congeners, only the 17 2,3,7,8-substituted congeners are seen as having significant toxic potential. As the reference congener, 2,3,7,8-TCDD is given unit value. All the other 2,3,7,8-substituted congeners are then assigned a multiplier ranging from 0.5 (1,2,3,7,8-PeCDD) to 0.001 (OCDD, OCDF) based on their relative toxicity. Although the multipliers assigned are still subject to debate, the International Toxic Equivalent Factor (TEQ) system has proved successful in presenting dioxin/furan data in a meaningful and comparable format. It is worth noting that the system has no geochemical significance and is irrelevant when considering the transport and fate of the compound in the aquatic environment.

Although there have been attempts to extend the TEQ system to include some of the co-planar PCB congeners due to their synergistic toxic effects, the system is reliant on large data sets of congener specific toxicity which exist for very few families of OCs.

1.8 Biogeochemical Behaviour of PCDD/PCDF/PCBs in Estuaries and Coastal Waters

The behaviour of chlorinated organic compounds in the marine environment is the major focus of this thesis. In this chapter a brief overview of the partitioning into the various compartments of the marine system (water, sediment, air, biota) is provided together with a summary of removal mechanisms (biodegradation, photodegradation and volatilisation) significant in determining behaviour in estuarine systems. Subsequent chapters provide a more detailed discussion of the partitioning behaviour of OCs.

1.8.1 Sediment-Water Partitioning

The partitioning of OCs between water and sediment is a major influence on their transport and fate in marine environments. The environmental properties of OCs, in particular their hydrophobicity, result in a strong affinity with the solid phase. Unlike dissolved phase components which disperse rapidly in estuarine and coastal environments, the transport and fate of sediment-bound OCs is dominated by the complex dynamics of sediment transport.

The processes which dominate the mechanisms of sorption appear to be complex. Scientific knowledge in this area is limited to a basic understanding of the controlling parameters for OC sorption and virtually non-existent for quantification of sorption kinetics and reaction rates. Data available from field and laboratory studies shows the sorption of OCs to marine sediment to be dependent on a number of general factors; the physicochemistry of the compound, the geochemistry of the solid phase and the nature of the dissolved phase.

The physicochemistry of OCs dictates their basic sorption tendencies to any sorbing phase (e.g. sediment, biota). The geochemistry of the dissolved and solid phases, on the other hand, are dependent on a large number of parameters all of which are highly variable in estuarine and coastal environments.

1.8.2 Sediment/water-Biota Partitioning

The partitioning of OCs into biota is important as it is primarily through this pathway that ultimately human exposure to OCs may be achieved. Some of the highest OC levels in human breastmilk in the world are found amongst the Inuit people living in the Arctic (Oehme, 1991). This high exposure is due to the global transport of OCs to higher latitudes (discussed in Section 1.9.1) and the largely fish/seal-based diet of the Inuit. The properties of toxicity, persistence and liability to bioaccumulate have resulted in widespread accumulation throughout ecosystems and the marine environment, often serving as the ultimate repository for contaminants of terrestrial origin, has therefore suffered acutely from accumulation of these contaminants (Hashimoto *et al.*, 1998).

Bioaccumulation, biouptake/depuration rates, biomagnification and biodegradation are all complex processes dependent not only on the environmental properties of individual compounds but also to a large extent, on the biology of the target species. Experiments on marine biota have been carried out on a small number of plants and species allowing conclusions to be drawn on the basic behaviour of OCs in biota (Axelman *et al.*, 1997). Extrapolation of observations to other species is not easy and results may only be generalised with caution.

Bioaccumulation and Biomagnification

The lipophilicity and persistence of OCs promotes an extraordinary degree of bioaccumulation coupled with an unusual capacity amongst marine ecosystems to amplify contaminant concentrations despite comparatively low water/sediment concentrations (Wade *et al.*, 1997). Marine mammals inhabiting pristine oceans show considerably higher PCB body burdens than their terrestrial counterparts living in close proximity to pollution sources (Tanabe, 1988).

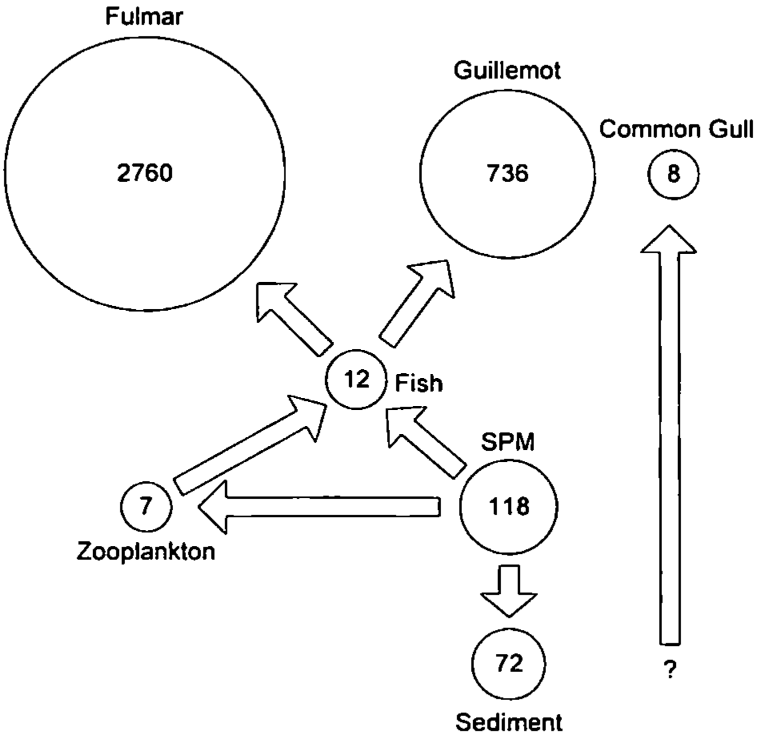


Figure 1.2. PCB levels in different compartments of the coastal zone of the Southern Bight of the North Sea. Concentrations in $\mu g\ g^{-1}$ lipid. (after Delbeke & Joiris, 1988)

Within a marine ecosystem, biomagnification through the foodchain is well illustrated by the processes shown in Figure 1.2 where analysis of PCBs (expressed on a lipid weight basis) in a number of species is shown in a foodweb. Clearly, species at the top of the foodchain receive a significantly enhanced dose of PCBs through predation (Champoux, 1996; Delbeke & Joiris, 1988; Kannan *et al.*, 1999).

Nowhere is biomagnification more in evidence than in top predators such as marine mammals (seals, whales, dolphins, porpoises). These species have thick subcutaneous fat (blubber) deposits forming a significant proportion of their bodyweight into which the lipophilic OCs partition and are retained. In addition, a significant transfer of OCs occurs during lactation. Striped dolphins for example may transfer 60% of PCB residues in the mother to the new-born through lipid-laden milk (Tanabe *et al.* 1994). Obviously exposure of young to such concentrated doses of OCs raises serious concerns over potential toxic impacts.

1.8.3 Bio-uptake and Depuration

There have been limited process studies on the uptake of OCs into marine plants and biota. The only reliable data has been obtained under controlled conditions in laboratory experiments or implied from analysis of levels in biota from natural waters and it is from these data that the mechanisms behind bioaccumulation processes must be deduced.

Uptake of OCs into plants is a significant pathway to accumulation in grazing biota within marine systems. Certain plants have a significant capacity to sorb organic substances and thus act as a reservoir and even a transport mechanism for OCs in aquatic systems (Gobas *et al.*, 1991).

Aside from predation, the pathways by which OCs are taken up by benthic species are not well understood. It is likely that, given the sediment-bound nature of OCs, ingested sediments must form an important source of OC contaminants. Accumulation mechanisms in this case could either be through direct ingestion or filtering of contaminated particles, or uptake directly from pore waters. Mesocosm studies involving dioxins have underlined the importance of the foodchain pathway for biomagnification from contaminated sediments to higher benthos (e.g. fish; Muir *et al.*, 1992).

As with geochemical relationships, there is evidence that depuration mechanisms are dependent on the structural details of the compound. Accumulation experiments with ragworm (*Nereis diversicolor*), showed significant differences in extent and kinetics of depuration between the six PCB congeners studied (IUPAC Nos. 52, 44, 95, 101, 87, 153). Slow elimination and the significant presence of some pentachlorobiphenyls, as well as low occurrence of biphenyls highly chlorinated in one ring, were observed in the ragworm population (Goerke & Weber, 1990).

It is believed that the nature of the bioconcentration process for OCs in plants such as the macrophytes and in fish are similar, resulting largely from lipid-water partitioning. However, differences are observed, particularly when considering the nature of certain OCs with very high K_{ow}. Whilst for plants, the plant-water partition coefficient, K_{pw} - K_{ow} relationship is linear for all K_{ow} values (Gobas *et al.*, 1991), in fish (e.g. rainbow trout, *Salmo gairdneri*) the relationship breaks down for K_{ow} values above ~ 6 (Servos *et al.*, 1989). For marine mammals on the other hand, analysis of species in Lake Baikal, Siberia (Kucklick *et al.*, 1994) showed good correlation between log BCF (Bio-Concentration Factor) and log K_{ow} for OCs (PCB, HCH, heptachlor and toxaphene).

1.8.4 Removal Processes

There are a number of removal processes which are vital to describing the overall transport and fate of OCs in the marine environment. The first two are degradation processes (biodegradation, photodegradation) which are most important for removal or transformation of the compounds and potentially important for the remediation of seriously contaminated areas. The third process is volatilisation which although not usually associated with high molecular weight compounds, has been shown to be a significant removal process for certain compounds.

Biodegradation

OCs are generally regarded as highly resistant to biodegradation. However, considerable research has been carried both under controlled conditions in the laboratory and in field studies demonstrating that biodegradation is possible and makes a contribution, albeit small, to removal of OCs from marine environments (Kobayashi & Rittmann, 1982; Reichardt *et al.*, 1981). Interest in biodegradation as a possible remedial measure for OC contaminated sediments or effluents is attractive given the existing use of enhanced microbial biodegradation in sewage treatment. The use of carefully selected populations of microbes, and maintenance of conducive environmental conditions may significantly improve the biological treatment of these wastes.

In the natural environment, the significance of biodegradation as a removal process is highly variable (Lake *et al.*, 1992). Within a typical estuary a range of degrading environments will be encountered, some with a high potential for degrading certain OCs and some with little or no potential. Evidence from studies of PCB degradation even suggest that for complete mineralization of a higher chlorinated biphenyl an anaerobic environment might be required followed by an aerobic environment to complete the degradation (Abramowicz *et al.*, 1993).

Unlike natural compounds, anthropogenic OCs are resistant to biodegradation often because the enzymes necessary to effect the necessary transformations for removal through common metabolic pathways are missing (Kobayashi & Rittmann, 1982). With OCs, the persistence of the compounds is thought to arise from the chlorine content and substitutions in the *meta*-position on the benzene ring as well as the size of the compounds. These characteristics suggest that the location of the chlorine atom, the halogen involved and the extent of chlorination are the important considerations in determining the potential for degradation (Abramowicz *et al.*, 1993; Rhee *et al.*, 1993).

Degradation Mechanisms

The principal degradation mechanism for OCs is successive dechlorination (Abrahamsson & Klick, 1991; Ballerstedt *et al.*, 1997). In PCBs, for example, stepwise dechlorination of 2,3,4,3',4'-pentachlorobiphenyl results in a mono-biphenyl transformation product which would be easily metabolised by aerobic bacteria (Abramowicz *et al.*, 1993).

The mechanisms by which dechlorination may be achieved are not well understood. Both aerobic and anaerobic dechlorination of OCs has been demonstrated but the efficiency of these methods is highly variable. Aerobic bacterial biodegradation of PCBs is well studied but seems to be limited to the lower chlorinated congeners. Anaerobic degradation on the other hand has been shown to be capable of dechlorinating even highly chlorinated OCs although interestingly, under these anaerobic conditions, the lower chlorinated transformation products are more recalcitrant (Abramowicz *et al.*, 1993).

Photodegradation

Limited photodegradation of OCs has also been reported (Choudhry *et al.*, 1985; Friesen *et al.*, 1993; Mackay, 1991) although in comparison with other organic chemicals it cannot be considered a major removal mechanism.

The radiation most likely to initiate photodegradation is from high energy short wavelength photons at the blue and near UV end of the spectrum (approximately, 390 nm) (Mackay, 1991). In estuarine and coastal waters there is a high degree of light attenuation by water and suspended particulate matter (SPM) reducing the exposure of OCs to photolysis except for the small concentrations in the dissolved phase and sediments suspended in the water column.

Photolysis is highly dependent on the structure of the OC. Although dioxins are not readily degraded under biological and chemical conditions, there is some evidence for PCDD/PCDF photodegradation in aquatic environments. Laboratory experiments using lake water demonstrated, by analysis of photoproducts, that the degradation mechanism involved a rapid dechlorination, ring opening with C-O bond cleavage, and hydroxylation, possibly by reaction with hydroxy radicals (Friesen *et al.*, 1993).

Air-Sea Exchange

Earlier in this chapter the volatility of OCs was introduced as a potentially significant transfer mechanism. In fact it appears that their volatility has been largely responsible for the global transport of these compounds to polar regions and that the atmosphere acts as a major source of OCs to the ocean (Wania & Mackay, 1993). Atlas *et al.* (1986) estimated that up to 98% of PCBs entering the ocean came from atmospheric transfer (*c.* 1,700 t year^{-1}).

The mechanisms of air-sea transfer of OCs are complex. OCs will exist in the atmosphere in either the vapour phase or bound to particles (Welsch-Pausch & McLachlan, 1998). It has been suggested that by far the larger amount of OCs in the atmosphere exists in the vapour phase (Harner *et al.*, 1998) although in coastal regions closer to potential sources, higher concentrations may be found in the particulate phase (Atlas & Giam, 1986). There are several ways in which atmospherically transported OCs may be deposited. Dry deposition of particle-bound OCs would occur under gravitational settling or impact with the sea surface. Wet deposition is regarded as the major transfer process with scavenging from both vapour and particulate phases.

From current knowledge we may expect estuarine and coastal zones to exhibit a complex coupling with the atmosphere so that areas of contamination may act as sources whereas pristine areas will remain as sinks for OCs. In this way the historical legacy of OC pollution will remain in flux for many decades to come.

1.9 Reported Concentrations of PCDD/PCDF/PCBs in Estuaries and Coastal Waters

From our understanding of the behaviour of OCs, the importance of marine environments as a reservoir for these contaminants should not be underestimated. Concentration of industrial developments in the vicinity of estuaries and coastal waters, runoff from agricultural land into rivers and hence the sea, and the environmental properties of OCs all point to coastal environments as a sink for OCs from many sources.

Environment	PCB load (tonnes)	Percentage of PCB load	% of world production
Terrestrial & coastal			
Air	500	0.13	
River and lake water	3,500	0.94	
Seawater	2,400	0.64	
Soil	2,400	0.64	
Sediment	130,000	35	
Biota	4,300	1.1	
Total (A)	143,000	39	
Open Ocean			
Air	790	0.21	
Seawater	230,000	61	
Sediment	110	0.03	
Biota	270	0.07	
Total (B)	231,000	61	
Total load in the environment (A + B)	374,000	100	31
Degraded and incinerated	43,000		4
Land-stocked	783,000		65
World production	1,200,000		100

Table 1.4. Estimated PCB loads in the environment (Tanabe, 1988)

Table 1.4 provides an analysis of global PCB loads emphasising the importance of the marine environment and particularly the coastal regions as an OC reservoir. The marine environment in total represents over 90% of the PCB load in the environment of which over 50% is present in the coastal zone.

1.9.1 Global Concentrations

Although research described in this thesis concentrates predominantly on concentrations of OCs in estuarine and coastal environments, it is impossible to ignore the global consequences of the transport of OCs from terrestrial and coastal areas to the world's most remote places. The following section summarises oceanic and shelf sea concentrations; estuarine concentrations are discussed in Chapter 3.

A comprehensive global sampling exercise carried out by Iwata *et al.* (1993) analysed PCBs in air and seawater. PCB concentrations showed a remarkable homogeneity in the oceans and sea sampled. In previous surveys during the 1980's a clear peak in concentration of PCB in mid latitudes was observed. As contamination in developed nations has decreased, levels have fallen but an expansion of PCB usage in tropical regions has tended to compensate in lower latitudes. The occurrence in high latitudes has been caused by latitudinal transport so that the overall picture is of similar concentrations in all the world's oceans. Further analysis carried out by the authors examining the congener patterns also showed an increase in the ratio between lower chlorinated and higher chlorinated congeners as the latitude increased. This is consistent with the transport model developed which would preferentially transport the lower chlorinated, higher volatility congeners.

OC concentrations in open ocean marine mammals provide a good indication of the extent of OC contamination as well as illustrating the biomagnification of these compounds in top predators. The geographical distribution of PCBs in these samples taken in the early 1980's show a strong peak in PCB levels in the mid-latitudes coinciding with high levels in marine mammals (Tanabe, 1988). In dolphins from the Pacific, concentrations up to 40 $\mu g\ g^{-1}$ wet blubber have been recorded. Is it also evident that from seawater concentrations in the pg g^{-1} range, the top predators have accumulated body burdens of ng g^{-1} (wet blubber).

1.9.2 Background Concentrations

To understand the significance of OC concentrations reported for the marine environment, it is necessary to put them in the context of the typical background concentrations for the environment sampled. The global levels of PCBs reported by Iwata *et al.* (1993) indicate that for PCBs in water this background figure is well above the limits of analytical detection (8.3 pg l^{-1} for Σ PCBs).

In estuaries and coastal waters, the determination of 'background' concentrations becomes more difficult as proximity to sources becomes a significant influence. Dioxin studies in Japan revealed PCDDs at significant concentrations (~ 2-8 ng g^{-1}) in core samples dating back approximately 8000 years. In coastal areas however, concentrations of 10-100 pg g^{-1} have been regarded as 'background' (Turkstra & Pols, 1989). In practice, typical background concentrations should be determined for each environment by sampling a number of what may be regarded as 'relatively clean reference sites' for comparison purposes. It is clear that what constitutes 'clean' for a pristine ocean could not be applied to an industrialised estuary.

1.9.3 Shelf Seas

The dynamics of shelf seas are inextricably linked to coastal and estuarine systems resulting in continuous exchanges of water masses, sediment and biota. In European waters there have been several surveys of OC levels in the North Sea and the Baltic Sea both of which receive a considerable contaminant load from their coastal waters.

Concentrations of OCs in seawater and suspended sediment have been reported by several authors. Schulz-Bull *et al.* (1991) in a survey of the North Sea and English Channel reported dissolved total PCBs (sum of 31 congeners) ranging from 13 to 415 pg l^{-1}. In the Baltic Sea, average PCDF/PCDF dissolved concentrations of 0.12 pg l^{-1} were reported set against suspended particulate concentrations averaging 0.23 pg l^{-1} (Broman *et al.*, 1992).

In bed sediments a considerable variation in concentration of OCs throughout the North Sea has been observed, with the southern North Sea and Skagerrak exhibiting the highest burdens. High concentrations (up to 28 ng g^{-1} dry weight) were found either in areas receiving direct sources of contamination (e.g. estuary plumes, offshore incineration area) or in sinks for fine organic rich sediments. Of the latter, the Skagerrak is an example of a relatively source-free region which receives a pre-contaminated sediment load from the counter-clockwise circulation in the southern North Sea (Lohse, 1991).

The pattern of dioxin contamination in North Sea bed sediments was studied by Evers *et al.* (1993). In the central North Sea, away from coastal pollution sources, total PCDD/PCDF concentrations of 657 pg g^{-1} (dry weight) were encountered whereas estuary plumes showed elevated concentrations as high as 10557 pg g^{-1}. This evidence strongly suggests that estuaries make a major contribution to the shelf sea concentrations of OCs.

OC concentrations in shelf sea biota have been the focus of some study. Delbeke *et al.* (1990) found PCB concentrations in net plankton (>50μm) in the North Sea varying from non detectable (n.d.) to 3 μg g^{-1} dry weight which showed a strong increase in lower latitudes when expressed on a μg l^{-1} basis. In zooplankton on the same survey, concentrations ranged from n.d. to 3 μg g^{-1}.

As discussed earlier in this chapter, recent studies of biota in the North Sea have focused on marine mammals following an outbreak of phocine distemper epizootic in the North Sea common seal (*Phoca vitulina*) in 1988 which was thought at the time to be connected to high concentrations of PCBs in these top predators. A comprehensive survey at the time showed PCB concentrations in blubber (expressed as Aroclor 1254 equivalent) ranging from 0.7 - 99 μg g^{-1} wet weight (Hall *et al.*, 1992). In a similar study of the same species in Norwegian waters, concentrations of PCBs in blubber varied from 0.4 - 38 $\mu g\ g^{-1}$.

1.10 Gaps in Knowledge

A thorough review of published and on-going research at the outset of these studies identified clear gaps in knowledge of the occurrence of chlorinated organics in estuaries and coastal waters and the geochemical processes that dictate their transport and fate. Specifically, the following gaps in knowledge were highlighted as issues towards which this these studies could make a contribution;

1. Significant lack of data on dioxin levels and distribution in marine environments. Virtually no data available for the UK marine environment.

2. Little information available on sources of dioxins and PCBs to the marine environment.

3. Limited knowledge of the sorption preferences of chlorinated organics in estuary and coastal environments. Few attempts to quantify the sorption behaviour of dioxins and PCBs.
4. Very little information quantifying water-sediment partitioning coefficients in marine environments. No investigations of the dependence of partitioning coefficient on master estuary and coastal variables.

5. No attempts to model dioxin and PCB behaviour on a mechanistic basis in marine environments.

1.11 Aims of the Study

Based on the perceived gaps in knowledge, studies have focused on elucidation of the partitioning behaviour of chlorinated organics through detailed analysis of their occurrence in the marine environment and by studying their partitioning under laboratory conditions. Specific aims of this thesis were therefore;

1. To present a comprehensive review of literature on dioxin and PCB sources, toxicity, sampling, analysis, environmental concentrations and behaviour in marine systems.

2. To establish sampling methodologies and analytical protocols for the measurement of environmental concentrations of dioxins, PCBs and supporting variables.

3. To conduct field surveys in a number of contrasting estuary and coastal sites aimed at establishing distributional patterns, elucidating sources of dioxins/PCBs, and determining the variation with sample geochemistry.

4. To quantify the dependence of sorption behaviour on the geochemistry of the particulate phase.

5. To study the sediment-water partitioning behaviour of dioxins and PCBs under laboratory conditions.

6. To bring together field and laboratory data in a sediment-water exchange model describing the sorption behaviour of dioxins and PCBs in marine systems and to demonstrate the integration of such a model in an integrated estuarine contaminant transport model.

Chapter 2. Field Sampling and Analysis

2. Field Sampling and Analysis

2.1 Surveys

From Spring 1991 through to Autumn 1993 a programme of field surveys was conducted. Where possible these surveys were timed to coincide with other on-going studies and monitoring programmes to maximise the amount and type of data collected. A range of vessels were used on these surveys varying from the Natural Environment Research Council (NERC) vessel *RRS Challenger* to chartered fishing vessels. The Scottish Environment Protection Agency (SEPA) vessel *Endrick II* was used for the Clyde work and the Environment Agency vessel *Sea Vigil* was used for the Humber survey. A number of additional short excursions were made to a number of study sites to collect samples for laboratory experiments (Humber, Clyde, Dee, Beaulieu, Dart). All the surveys conducted involved the sampling of sediment and water. Some of the estuarine surveys also included measurements of primary hydrographic variables (current flow, SPM concentration, salinity etc.). Study sites are shown in Figure 2.1 and Table 2.1 summarises the main surveys conducted.

Survey Site	**Date**	**Measurements**	
		Hydrographic	**Chemical**
Morecambe Bay	Spring 1991		✓
UK Coastal Waters	Summer 1991		✓
Clyde Estuary	Summer 1991		✓
Dee Estuary	Autumn 1991	✓	✓
Clyde Estuary	Summer 1992	✓	✓
Clyde Estuary	Summer 1993		✓
Humber Estuary	Autumn 1993	✓	✓

Table 2.1. Survey Programme

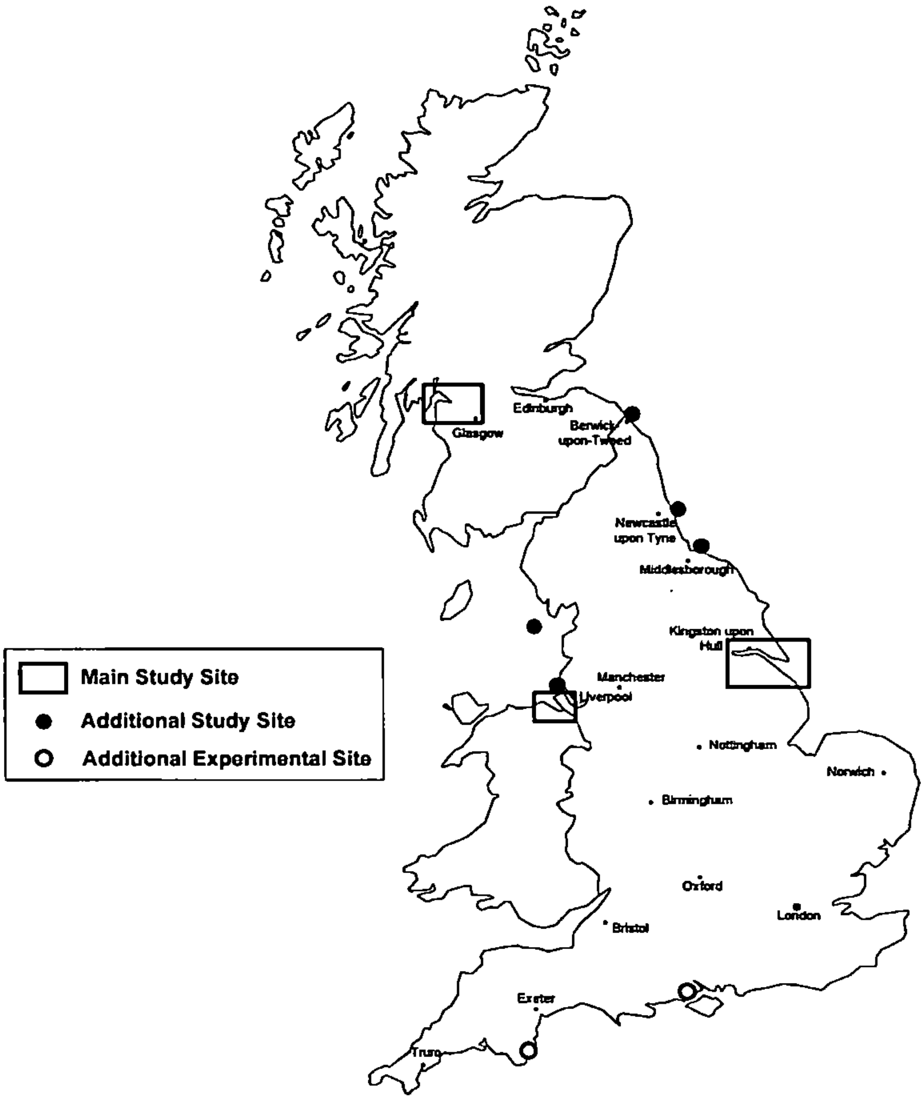


Figure 2.1. Study Sites

2.2 Sampling Strategy

Each of the surveys conducted during the study involved the sampling of sediment for analysis and on some surveys, the collection of SPM. Sampling methodologies were determined at the start of the study based on previous experience and other work (Delbeke *et al.*, 1990; Turner *et al.*, 1991). These methods were kept consistent throughout the study.

2.2.1 Bed Sediments

Bed sediments were collected using a variety of methods depending on sample site location (sub- or inter- tidal) and the nature of substrate. Typically, at least 500 g of sample was taken to provide sufficient material for the suite of analyses undertaken. Sub-tidal samples were collected using Shipek grab, Day grab or piston corer. In upper estuary regions where consolidated cohesive sediment was found, the piston corer was used where possible with the advantage of maintaining good sample integrity and providing a short core. In areas of non-cohesive sediment (Dee, Humber and lower Clyde estuaries) the Shipek grab was used. Offshore (Morecambe Bay) a box corer was used and sub-cores were retrieved for analysis. At all times, care was taken in abstracting the sample from the sampling device to avoid any possible contamination from the device or from previous samples. In inter-tidal areas samples were collected by hand using hexane washed spatulas.

Samples for organic analysis were stored in 500 g hexane-washed glass jars. Jar caps were lined with hexane-washed aluminium foil. Separate samples were taken for inorganic analyses and stored in acid-washed plastic pots. All samples were frozen at -20°C as soon as practically possible and kept frozen in the dark until required for analysis.

2.2.2 Suspended Particulate Matter

SPM was collected separately for organic and inorganic analysis. For organic analysis an all-glass filtration apparatus was used. Typically, 1000 ml of seawater was filtered through hexane-washed glass fibre filters under vacuum. Filters were stored frozen in hexane-washed aluminium foil wraps prior to analysis. SPM for inorganic analysis was collected by similar methods but using a bulk filtration system capable of filtering approximately 10 l of water through 142 mm diameter Millipore filters (0.45 μm poresize).

2.3 Sample Analysis

The analysis of OCs is not straightforward due to the low concentrations encountered in environmental samples and the difficulties in isolating, identifying and quantifying them. Laboratory methodologies involve extensive sample clean-up procedures prior to analysis and quality assurance is required to ensure reproducible and comparable analyses.

2.3.1 Selection of Compounds for Analysis

The first step in analysis of OCs such as dioxins and PCBs is to determine the specific compounds which are to be the target of the analysis. For these studies specific families of compounds were to be investigated. With PCBs comprising 209 congeners and dioxins and furans, 135 and 75 congeners respectively, analysis and quantification of all congeners was impractical and for the purposes of this study, unnecessary. What was required for this study was a range of representative congeners allowing congener-specific geochemical variability to be investigated (Duinker *et al.*, 1988).

Currently, the selection criteria that have been used to choose OC compounds for analysis are not consistent. Much PCB analysis has been conducted on a 'total PCB' basis with samples of technical mixtures used as external quantification standards. This method suffers from differences between samples and commercial mixtures which distort the results obtained by this method of quantification. A refinement of this has been the selection by the International Committee on Exploitation of the Sea (ICES) of seven congeners representing PCBs with chlorination extents from tri-chlorinated to heptachlorinated (IUPAC Nos. 28, 52, 101, 118, 153, 138 and 180). The basis of selection for the 'ICES 7' is largely on the prevalence in technical mixtures and the fact that these congeners are relatively easy to analyse accurately. The selection is not on the basis of ecological significance (e.g. no focus on toxic coplanar congeners) and supplementary lists of congeners for analysis are appearing such as the extended 29 congener list used by the UK Ministry of Agriculture, Fisheries and Food (MAFF) which includes some of the more toxicologically significant congeners. It was decided that the 'ICES 7' list would be adequate for this study bearing in mind the range of chlorinities represented and the availability of other datasets for inter-comparison. To further aid inter-comparison, 'total' PCB was also analysed.

In contrast with the PCBs, dioxin congener selection criteria have been based on toxicological studies for some time and a 'standard' analysis is almost always undertaken comprising the 17 toxicologically significant 2,3,7,8 substituted dibenzo-*p*-dioxin and dibenzofuran congeners. As with the PCB list, this 'standard' analysis spans a wide range of chlorinities and was therefore accepted for this study.

The overall sampling, storage and analytical procedure determined at the outset of the studies in summarised in Figure 2.2.

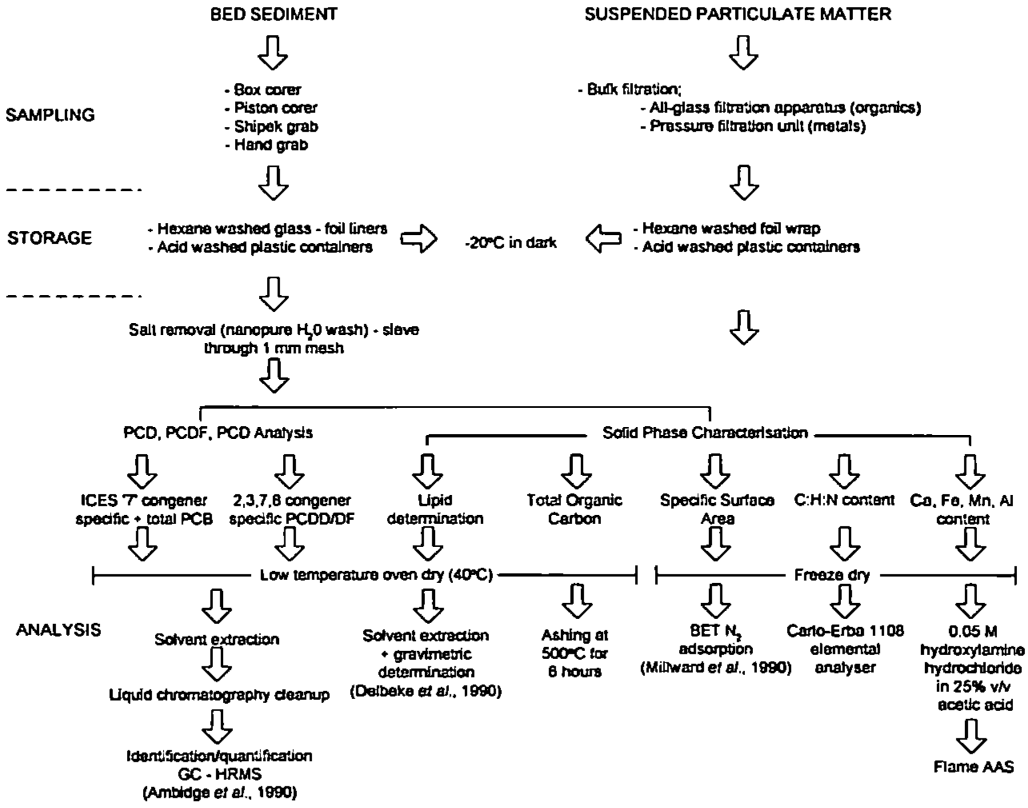


Figure 2.2. Summary of Sample Collection, Storage and Analytical Protocols

It should be noted that all samples analyses were carried out on a dry weight basis and are reported as dry weight unless explicitly stated otherwise.

2.3.2 Sample Preparation, Extraction and Cleanup

Samples for analysis were analysed immediately where possible, or defrosted from frozen samples. Prior to analysis, samples were sieved through a 1 mm mesh and oven-dried at 40°C. The dried sample was weighed (approx. 50 g), spiked with sixteen ^{13}C dioxin and furan internal standards, and soxhlet extracted with toluene (Mallinckrodt-Nanograde) for 12 h. The resultant extract was reduced to a volume of about 0.5 ml by freeze-drying, prior to liquid chromatography.

The solvent extracts were subjected to liquid chromatography on a two-stage silica (Merck, 70-230 mesh)/florisil (BDH, 60-100 mesh) column. The sample was eluted initially with hexane (Mallinckrodt-Nanograde) whereby the total PCB fraction was eluted through the entire column and the PCDD/PCDFs transferred to the top of the florisil column.

2.3.3 Detection and Quantification of PCDD/PCDF

PCDD and PCDF sample analysis was carried out according to an established method (Pettit *et al.*, 1990). Following liquid chromatography, the upper silica column was discarded and 2% methylene chloride (Mallinckrodt-Nanograde) in hexane was passed through the lower florisil column prior to eluting the PCDD/PCDF fraction with 100% methylene chloride. The collected PCDD/PCDF fraction was reduced to a suitable volume by freeze-drying, solvent exchanged with nonane (Mallinckrodt-Nanograde), and transferred to septum cap vials for autosampler chromatographic injection.

For the analysis of dioxins and furans, the sample was injected onto a 60m x 0.25mm i.d. DB5 column at an initial temperature of 130°C, held for 2 min, then programmed to 270°C at 20°C min^{-1}, held at 270°C for 10 min, then programmed to a final temperature of 286°C at 1°C min^{-1}. The column was directly interfaced to a VG 70S magnetic sector mass spectrometer operating at 28eV, 10,000 x resolving power in the selected ion monitoring mode. The instrument monitored three of the most intense molecular isotope peaks for each of the dioxins and furans. Confirmation of the presence of each compound was made by reference to the EPA Draft Proposals QAL 152 1/1/87, resting on a correlation of retention times (± 3s), and the verification that the relative intensity of the isotope peaks was within ± 15% of the theoretical value.

In addition to the quantification of all 17 2,3,7,8-substituted dioxin and furan congeners, total homolog concentration was quantified for all homologs (tetra, penta, hexa, hepta, and octa). This was achieved by injecting a 'window defining' mixture containing ^{13}C standards of the first and last eluting congeners in each homolog group. All peaks between these marker congeners were assumed to be congeners within the same homolog group provided that they met the criteria specified above. The number of peaks were also checked against the theoretical number of congeners in the homolog group.

2.3.4 Detection and Quantification of PCB

Following cleanup the sample was evaporated to dryness in a freeze-drier and reconstituted with 1 ml toluene. A VG 70S magnetic sector GC-MS interfaced to an HP 5890GC with DB5 capillary column was used for the analysis. The instrument was configured to operate in selected ion mode with maximum sensitivity at 1000 resolution. Mass calibration was checked to ensure that reference peaks had correct centroids. PCB standards were run in order of ascending concentration followed by a blank. Samples were run in batch mode ensuring that the signal-noise ratio was greater than 2:1 and response was maximised within ± 5 seconds of reference retention time.

2.3.5 Analysis Quality Assurance

Quality assurance of the sample analysis was a considered of paramount importance, particularly considering the acknowledged difficulties in the analysis. The laboratory had participated in the development of acceptance criteria for analytical data and these guidelines were followed rigorously throughout (Ambidge *et al.*, 1990). Specifically these guidelines state that the ion responses for the three ions must maximise within ± 1 scan, with a signal to noise ratio > 2:1 for all relevant channels. This protocol gives routine detection limits down to 1 pg l^{-1} of PCDD and PCDF injected. Prior to sample analysis, a standard mixture of dioxins was analysed, and the instrument was tested for the above criteria, and the calibration verified. The analysis was then performed including blank runs to accommodate for any carry-over through use of an autosampler on the GC-MS instrument. Recoveries of the ^{13}C spikes were in the range 75-80% and the reproducibility was ± 10%. Every three months, the full method and instrumentation are validated by the analysis of a standard reference material; a spiked soil sample provided by Cambridge Isotope Laboratories. Typical results are provided in Appendix I. In addition, full procedural blanks submitted for analysis under this project were all found to be below the limits of detection which are given in Table 2.2.

External quality assurance was performed via submission of blind replicates for analysis. Two sets of samples (4 replicates) were submitted and the results of the analysis are given in Table 2.2. From this it can be seen that the reproducibility was fair with percentage standard deviation generally below 20%. Higher standard deviations tend to coincide with lower concentrations highlighting the difficulties of analysis at such low concentrations.

Homolog	Sample HI13 (pg g^{-1})			Sample HI6 (pg g^{-1})			Detection Limit (pg g^{-1})
	Mean	Std Dev	% Std Dev	Mean	Std Dev	% Std Dev	
2378-TCDD	7	3	43	2	1	41	1
TCDD	370	54	15	237	51	21	10
PeCDD	212	26	12	149	17	11	20
HxCDD	110	16	14	77	12	16	40
HpCDD	302	47	16	219	47	21	10
OCDD	1775	64	3	1231	148	12	50
TCDF	137	14	10	99	21	21	10
PeCDF	277	35	13	182	53	29	20
HxCDF	114	13	12	79	10	13	40
HpCDF	97	25	25	75	10	14	20
OCDF	427	12	3	303	49	16	50
PCDD	2777	104	4	1915	210	11	
PCDF	1054	67	6	738	65	9	
PCDD/PCDF	3831	163	4	2654	255	10	
TEQ	24	5	19	14	2	11	
Total PCB	72	13	17	53	7	13	

Table 2.2. Replicate Sample Analysis Results (n = 4) and Detection Limits for Chlorinated Organic Analyses

As can be seen from the above table, there is a variability in the detection limits for different homologs as well as error margins in replicate samples. Analytical results were reported by the laboratory with varying precisions depending on the achievable quantification of the congener or homolog. Throughout this work it has been necessary to sum homologs to present Total PCDD, Total PCDF and Total PCDD/PCDF. In doing so, the figures reported by the laboratory have been used for consistency and to maintain an audit trail to the original reported data. This often results in the total values being reported to an unrealistic number of significant figures. It should be stressed therefore that this reporting convention does not imply that the results for summations of homologs are precise to this number of significant figures. In general, totals for PCDD and PCDF should be considered to a precision of two significant figures.

2.4 Sediment Characterisation

Geochemical investigation of hydrophobic contaminants in aquatic environments necessitates a characterisation of the solid phase. Specifically, information is required on the geochemical composition of the particles and an indication of their geological origin i.e. whether marine-derived or of fluvial origin. The characterisation of sediments for this study followed a protocol to ensure that all analysed samples could be described in terms of their geochemical characteristics.

2.4.1 Specific Surface Area

Specific surface area (SSA) gives an important measure of the availability of particle surface sites for adsorption. SSA was determined using gravimetric multi-point BET N_2 adsorption (Brunauer *et al.*, 1938). Sample pre-treatment concentrated on preservation of the original particle structure prior to analysis using freeze drying with subsequent storage under vacuum desiccation to prevent loss of surface area by water vapour adsorption. Between 100 and 300 mg of sample was accurately weighed into an aluminium bucket and out-gassed in the apparatus (full description: Carter, 1983) using a vacuum pump with cold trap until constant weight was achieved (~ 10 hr). The sample was cooled to 77°K using liquid nitrogen and the uptake of successive doses of N_2 gas (at 40 mm Hg intervals, taking approximately 25 minutes to equilibrate) was monitored by a CI Electronics microbalance. SSA was then calculated using the BET equation (Brunauer *et al.*, 1938) assuming monolayer coverage of the particles by nitrogen gas which has a known specific surface area.

2.4.2 Carbon Content

The carbon fraction of the solid phase presents a geochemically significant fraction when considering the behaviour of chlorinated organic compounds in estuarine and coastal waters (Broman *et al.*, 1991; Delbeke *et al.*, 1990). Total carbon consists of inorganic and organic fractions and it is the organic fraction which may control the sorption behaviour of organic compounds.

Recent studies of hydrophobic organic compound behaviour have focused on a further sub-phase of the total organic carbon fraction, namely the lipid content (Preston & Raymundo, 1993).

The term 'lipid' covers a wide range of substances generally referred to as 'fats' and comprising a large number of mainly natural compounds in aquatic systems. Chlorinated organic compounds are apolar which requires the definition of lipid to be further refined into apolar and polar fractions. Although natural lipids are largely apolar, there are some more polar fractions such as the phospholipids, which are not thought to be significant in controlling chlorinated organic compound reactivity (Schneider, 1982).

Determination of Total Organic Carbon Content

Total organic carbon content determination was carried out by loss on ignition following high temperature ashing. A pre-weighed sample (1-2 g) was dried at 40°C, ground and placed in a crucible in a high temperature oven for 6 hours at 500°C. Following ashing, the sample was re-weighed to determine the loss on ignition.

Determination of Apolar Lipid Content

Time was spent developing a reliable method for the determination of apolar lipid content. Initially, a modified method based on that of Dole and Meinhertz (1960) was used. This method used a binary mixture of hexane and propan-2-ol (1:4 v:v) to extract a sediment sample in an ultrasonic bath. The binary mixture was then decanted into a separation funnel and water added. The phases were separated using the separation funnel and the hexane fraction was evaporated to give a dry mass of lipid material. This method was found to have poor reproducibility at the concentrations being analysed. Heterogeneity in extraction efficiency, difficulties in accurately separating the phases, and inadvertent transfer of sediment to the separation funnel were believed to contribute to the poor results.

A method was therefore adopted which avoided liquid-liquid phase separation and provided a more rigorous extraction of the lipid material from the sediment sample. The method of Delbeke *et al.* (1990) was chosen as an established method for determination of lipid content in marine sediments. Sediments were dried at low temperature (40°C), homogenised with a pestle and mortar and placed in a soxhlet thimble. The sediments were then extracted for 5 hours with a 150 ml mixture of 10% acetone, 90% *n*-hexane. Following extraction the extracts were evaporated to dryness, weighed, and the apolar lipid fraction resolubilized with successive 2 ml hexane washes and carefully decanted. The resultant extract was evaporated to dryness again and weighed. Subtraction of the two weight determinations yielded the total apolar lipid content. Table 2.3 shows the reproducibility of this method on a number of replicate sediment samples;

Batch	**n**	**Mean ($mg\ g^{-1}$)**	**Std. Dev.**	**% Std. Dev.**
1	6	10.55	0.7	6.6
2	4	1.54	0.12	7.8
3	5	1.36	0.12	8.8
4	4	5.32	0.38	7.1
5	4	31.27	1.23	3.9

Table 2.3. Reproducibility of Apolar Lipid Determinations.

2.4.3 Trace Metals (Fe, Mn, Ca, Al) Analysis

Trace metals (Fe, Mn, Ca, Al) were analysed for certain samples to give an indication of sediment geochemistry and reactivity. Iron:manganese ratios gauge the relative importance of each oxide phase to the particle surface properties (Turner, 1990) and have been used to distinguish different particle populations on a geographical basis (Duinker & Nolting, 1976). Calcium content of sediments is used as an indicator of particles of marine origin and can be used as a tracer of marine-derived material (Loring *et al.*, 1983; Turner *et al.*, 1992). The Ca:Al ratio is also used as a normalising parameter for grain size and mineralogical effects. It may also be of value when discriminating between particle populations (Turner *et al.*, 1994).

Trace metal determinations were carried out by flame atomic absorption spectrophotometry (AAS) using the flame mode following a partial leaching to extract the 'available' metals i.e. those associated with the hydrous Fe and Mn coatings and available for participation in geochemical reactions. Approximately 250 mg of sample was sieved and extracted using 0.05 M hydroxylamine-hydrochloride in 25% v/v acetic acid (BDH AristaR) for 16 h at room temperature (Turner *et al.*, 1991). Samples were analysed using an Instrumentation Laboratory 151 atomic absorption spectrophotometer in the flame mode. Table 2.4 summarises the detection limits and relative standard deviations for the metals determined;

Metal	**Detection Limit (μg ml^{-1})**	**Relative Std. Dev. (%)**
Fe	0.03	9.2
Mn	0.03	8.8
Ca	0.15	7.5
Al	0.5	12.6

Table 2.4. Detection limits and relative standard deviations for metal analyses.

Chapter 3. Distribution of Organochlorines in Estuarine and Coastal Waters

3. Distribution of Organochlorines in Estuarine and Coastal Waters

This chapter presents the primary data sets obtained from samples collected at the project survey sites. These include the various hydrographic supporting datasets, and the analytical results from the sampling surveys. Analytical results have been presented as spatial and axial distributions for the estuary study sites. Concentrations of analytes in cores have been presented as vertical profiles. Despite the general lack of data for chlorinated organic studies in the UK, intercomparisons have been made with existing UK and international studies.

Throughout this chapter a common nomenclature has been adopted for sampling station identification. The survey stations are numbered with a prefix as follows; C - Clyde survey, H - Humber survey, D - Dee Survey. The type of sampling station is indicated by a second letter; S - Sub-tidal station, I - Inter-tidal station, C - Core sample station, T - Tidal station.

3.1 Study Sites

The literature review (Chapter 1) identified a lack of data on dioxins in estuaries and coastal waters and a scarcity of data on PCB concentrations. It was decided therefore that an initial survey was necessary to establish a general picture of contaminant concentrations and distributions and to assist in the selection of sites for detailed investigation. A number of criteria were assessed when considering study sites;

- Existing contaminant concentrations (from initial survey);
- Previous studies of the sites;
- Accessibility and operational constraints;
- Classification of site i.e. typical, abnormal etc.;
- Offers of fieldwork collaboration;
- Compatibility with related research programmes e.g. North Sea programme, Sediment Resuspension Study (SERE), and Land Ocean Interaction Study (LOIS).

In addition, consideration was given to estuaries with contrasting hydrodynamics, sediment regimes and geochemical characteristics. Figure 3.13 shows a map of the UK with all study sites indicated. The samples analysed and key analytes/determinants are given in Table 3.1. All analyses are reported on a dry weight basis unless otherwise stated.

Date	**Location**	**Samples Analysed**	**Key Analytes & Determinants**
Spring 1991	Morecambe Bay	1 bed 1 core	PCDD, PCDF, PCB
Summer 1991	Tweed, Tees, Tyne, Humber, Mersey, Clyde	8 bed	PCDD, PCDF, PCB, SSA, C, OrgC, Lipid, Fe, Ca, Mn
Summer 1991	Humber	5 bed	PCDD, PCB, SSA, Fe, Mn
Summer 1991	Clyde	5 bed	PCDD, PCDF, PCB, SSA, C, OrgC, Fe, Ca, Mn
Autumn 1991	Dee*	9 bed	PCDD, PCDF, PCB, SSA, C, OrgC, Fe, Ca, Mn
Summer 1992	Clyde*	36 bed 3 SPM	PCDD, PCDF, PCB, SSA, C, OrgC, Lipid, Fe, Ca, Mn
Summer 1993	Clyde*	13 bed 8 SPM 3 core	PCDD, PCDF, PCB, SSA, C, OrgC, Lipid, Fe, Ca, Mn
Autumn 1993	Humber*	22 bed 9 SPM	PCDD, PCDF, PCB, SSA, C, OrgC, Lipid, Fe, Ca, Mn

*NOTE: C - Carbon, OrgC - Organic Carbon, SSA - Specific Surface Area, *hydrographic measurements made (salinity, temperature, pH, dissolved oxygen, current speed/direction)*

Table 3.1 Summary of Field Sampling Programme

3.1.1 UK Coastal Waters

The survey of UK marine sediments was carried out as part of a broad assessment of OC concentrations. The sites chosen were mainly at the mouths of large industrialised estuaries and a 'pristine' estuary (Tweed). Two surveys were carried out; one as part of the NERC SERE programme in Morecambe Bay and the second as part of the MAFF CIROLANA '91 cruise of coastal monitoring stations. A total of 8 bed sediment samples were analysed from coastal and estuarine plume sites. A sediment core sample was analysed from Morecambe Bay.

3.1.2 Dee Estuary, Wales

Site Description

The Dee Estuary is a macrotidal estuary situated in Liverpool Bay on the west coast of England and Wales (see Figure 3.1). The estuary receives its main freshwater input (36.8 cumecs average fluvial input) from the River Dee. The estuary extends as far as the weir at Chester with the seaward boundary 35 km downstream discharging into Liverpool Bay. The estuary is funnel shaped, dividing into two distinct zones; the upper zone extending 15 km downstream from the weir with a 100 m wide canalised channel contained between flood-banks, and a lower estuary, approximately 5 km wide and roughly rectangular (Shell, 1987).

The Dee estuary is a relatively uncontaminated estuary receiving water from a largely rural catchment, although Law *et al.* (1991) reported a source of PCBs from a contaminated industrial site. The estuary receives inputs of domestic sewage and relatively small amounts of industrial effluent. The estuary supports an important salmon fishery and has a large population of grey seals (*Halichoeris grypus*). The entire estuary is designated as a Site of Special Scientific Interest (SSSI).

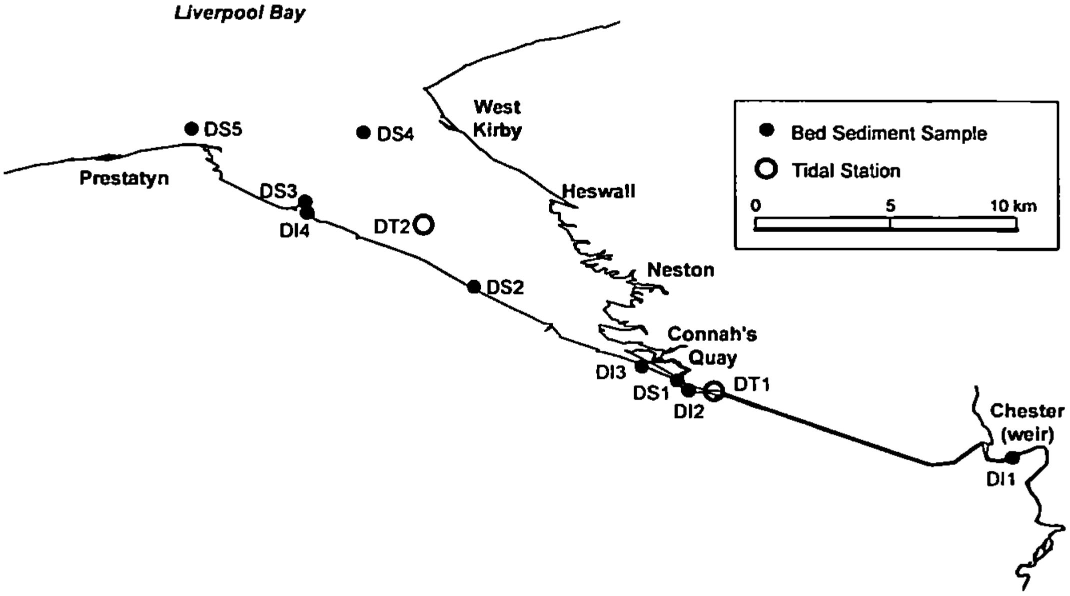


Figure 3.1. Dee Estuary Location Map

Hydrography and Sediment Regime

A programme of hydrographic measurements was carried out over a three day period in December 1991. Neap tidal conditions prevailed and river flow was below average (12.9 ± 4.4 $m^3 s^{-1}$ regulated flow for the previous 5 days). Axial transects of the estuary were conducted and two tidal stations were occupied (Turner *et al.*, 1994).

The Dee Estuary is subject to strong tidal influences with a mean spring tidal range at the mouth of 7.7 m. The tidal wave is asymmetric within the estuary such that at Connah's Quay the ebb tide lasts ~10 h followed by a ~2 h flood tide. Tidal currents in the estuary reach 1.5 m s^{-1} during spring tides. Currents measured as part of this study at a mid-estuary tidal station (DT2) indicate maximum currents up to 1 m s^{-1} (Figure 3.2).

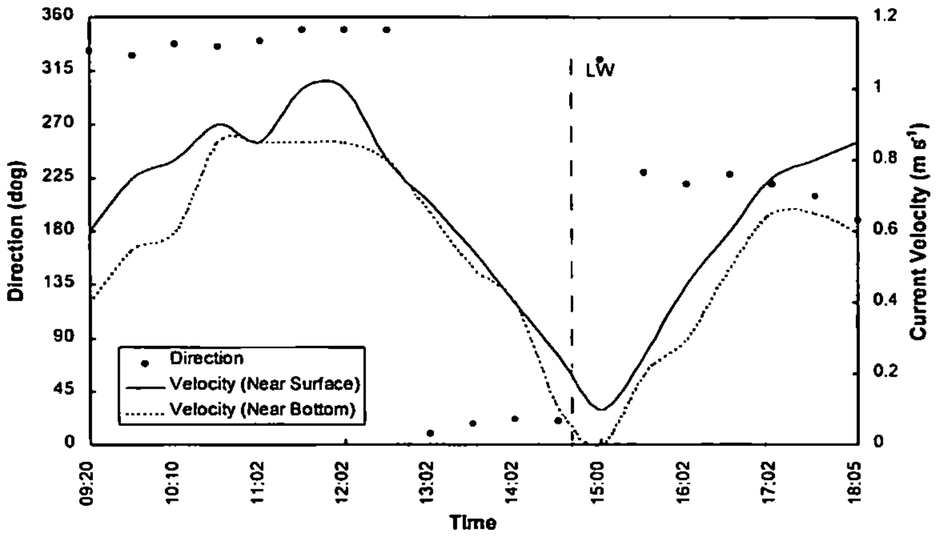


Figure 3.2. Mid-Estuary Current Flow Measurements - Station DT2

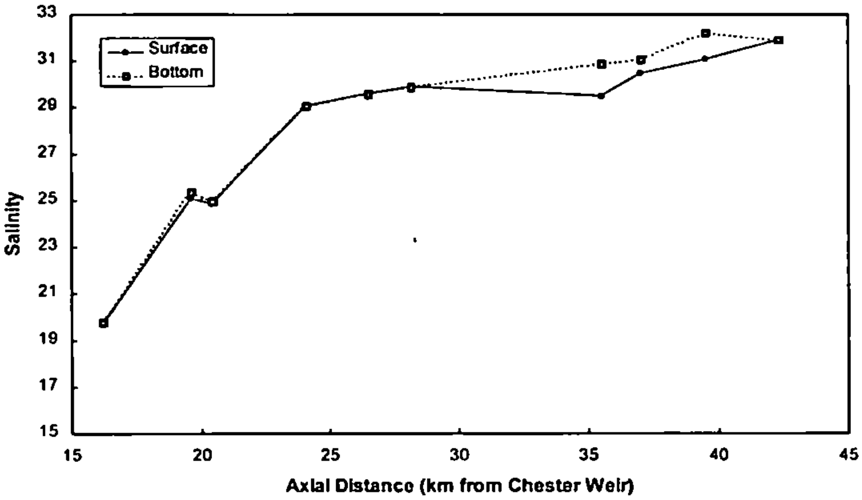


Figure 3.3. Axial Salinity Profile

Measurements of salinity distribution on an ebb tide axial transect show some limited salinity stratification at the mouth of the estuary (Figure 3.3). Tidal cycle salinity distributions reflect the tidal wave modification. Figures 3.4 a & b show measurements of salinity at the lower (DT2) and upper estuary (DT1) tidal stations shown in Figure 3.1. The upper estuary station shows the effect of the long ebb tide with a period of 4 hours of riverine flow followed by an extremely rapid rise in salinity with the flood tide. At the lower estuary station, the salinity profile follows the semi-diurnal tidal pattern.

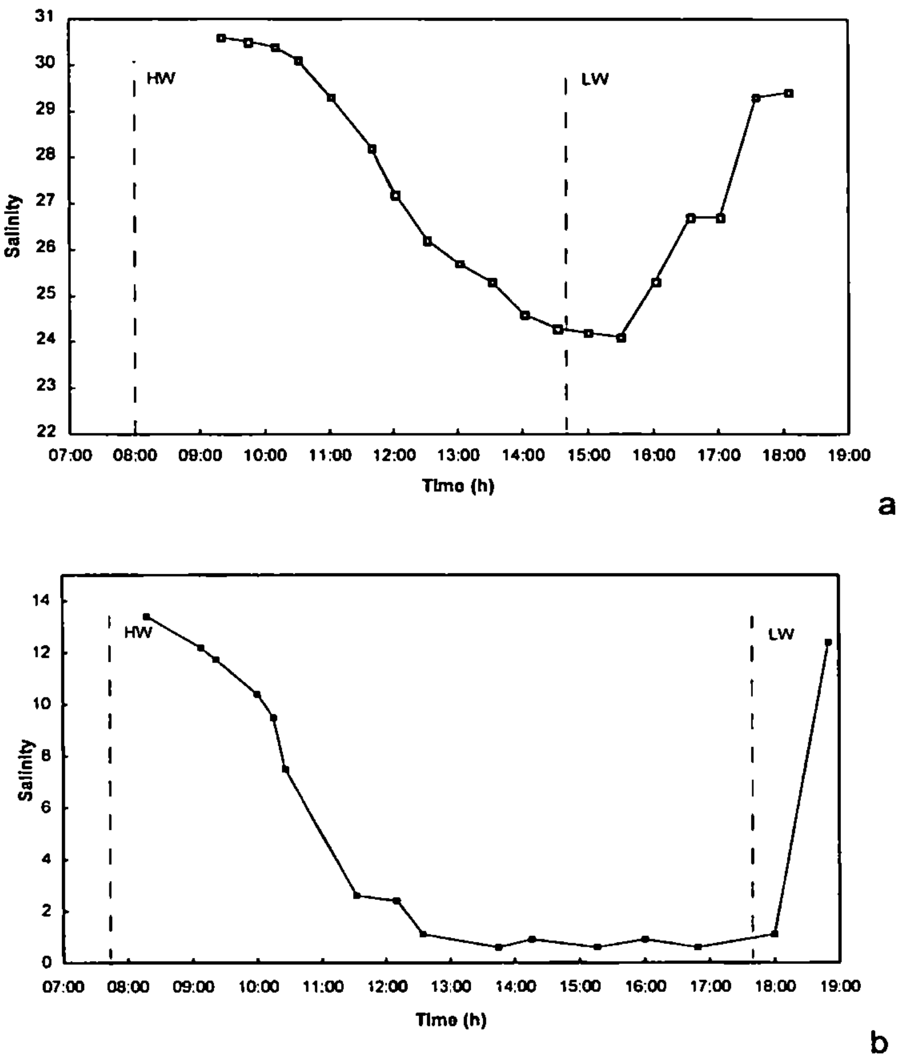


Figure 3.4. Tidal Cycle Salinity Profile, (a) Lower Estuary (DT2), (b) Upper Estuary (DT1)

The Dee Estuary is characterised by the significant accretion of sediments in the estuary over a period of many years. In 1732 salt marsh encroachment and siltation resulted in canalisation to keep the navigable channel open to Chester which was then Britain's second port (BMT, 1990).

Suspended sediment concentrations in the estuary were determined from the dried mass retained on pre-weighed Whatman GF/C filters (pore size 1.2 μm) after vacuum filtration of ~1000 ml water. Suspended sediment concentrations were generally less than 60 mg l^{-1}, considerably lower than other macrotidal estuaries in the UK (Morris *et al.*, 1987; Turner *et al.*, 1991). The <63 μm fraction of peripheral inter-tidal sediments was 44 ± 21%

although the estuary has a predominately sandy bed and extensive sandbanks. The estuary receives sediment from offshore and the adjacent north Wales coast (BMT, 1990; Turner *et al.*, 1994).

Particle Characteristics

The origin of sediments in the estuary has been confirmed by geochemical characterisation using Ca:Al ratios. The Ca content of estuarine sediment is principally of marine origin and may be used as an indicator of marine origin. Using the Ca:Al ratio allowed normalisation for grain size and mineralogical effects thus discriminating between particle populations. Ca:Al ratios for sediments within the estuary compared well with ratios for Irish Sea sediments (~120), which could be considered as the marine end-member of the sediment mixing series. However the riverine end-member sediments above the weir at Chester had ratios which indicated significant fluvial origins (Ca:Al = 7.8). This ratio corresponded with a similar value (Ca:Al = 6.4) for permanently suspended particulate matter found in the estuary.

Both SSA and lipid measured in the estuary were low in comparison with the other major study sites. SSA values ranged from 2.2 $m^2 g^{-1}$ in the river to 5.6 ± 3.0 $m^2 g^{-1}$ in the outer estuary. Lipid content was generally low in estuary sediments, ranging from non-detectable to 4.4 mg g^{-1}.

3.1.3 Clyde Estuary

Site Description

The Clyde Estuary is a partially stratified, meso-tidal estuary situated on the west coast of Scotland (Figure 3.5). The Clyde system consists of an estuary, an inner Firth and an outer Firth, together referred to as the Firth of Clyde. The estuary phase, the focus for this study, is taken as extending from a tidal weir at the city of Glasgow to a line drawn between Gourock and Kilcreggan. The Clyde Estuary is an industrialised estuary with direct pollutant inputs from

Glasgow via industrial/domestic sewage outfalls and atmospheric deposition from incinerator and other diffuse sources (SEPA, pers comms).

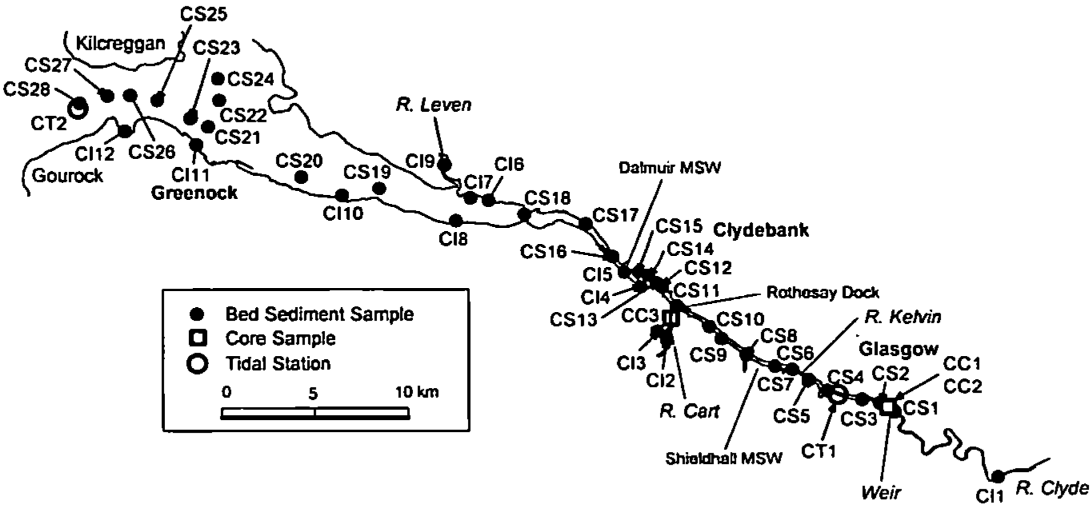


Figure 3.5. Clyde Estuary Location Map

Hydrography & Sediment Regime

During the 1992 Clyde survey a programme of hydrographic measurements was carried out to define the hydrographic regime within the estuary. Current flow measurements were made at two tidal stations in conjunction with salinity, temperature and turbidity measurements. River discharge during the field measurements was 152 m^3 s^{-1}.

Tidal range in the estuary varies between 1.9 m (neaps) and 3.0 m (springs). Current speeds measured during this survey at the lower estuary station, CT2 are illustrated in Figure 3.6. A maximum current of 0.5 m s^{-1} was recorded on the surface with bottom current velocities not exceeding 0.15 m s^{-1}.

Salinity distribution was measured during the August 1992 survey (see Figures 3.7 a and b). In the upper estuary a significant salt gradient is observed becoming less pronounced with downstream distance. This compares well with similar profiles measured by Mackay & Leatherland (1976).

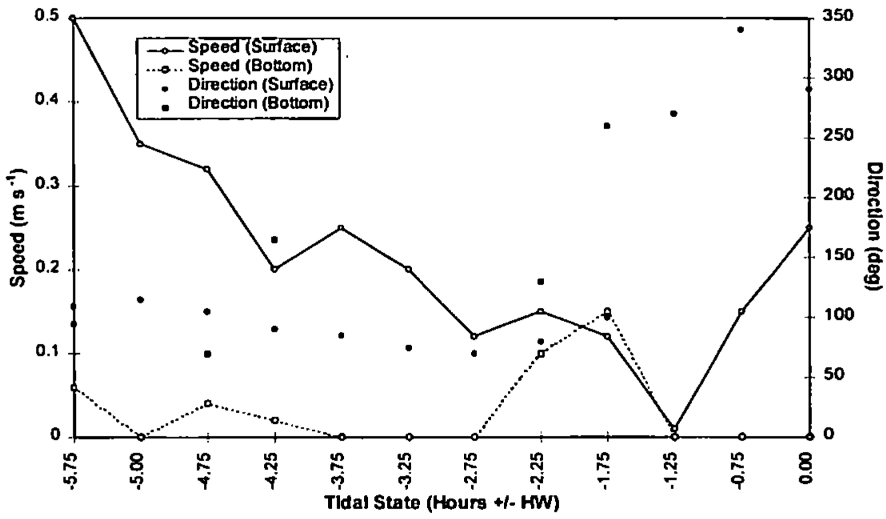


Figure 3.6. Current Speed and Direction (Surface & Bottom) at Lower Estuary Station (CT2)

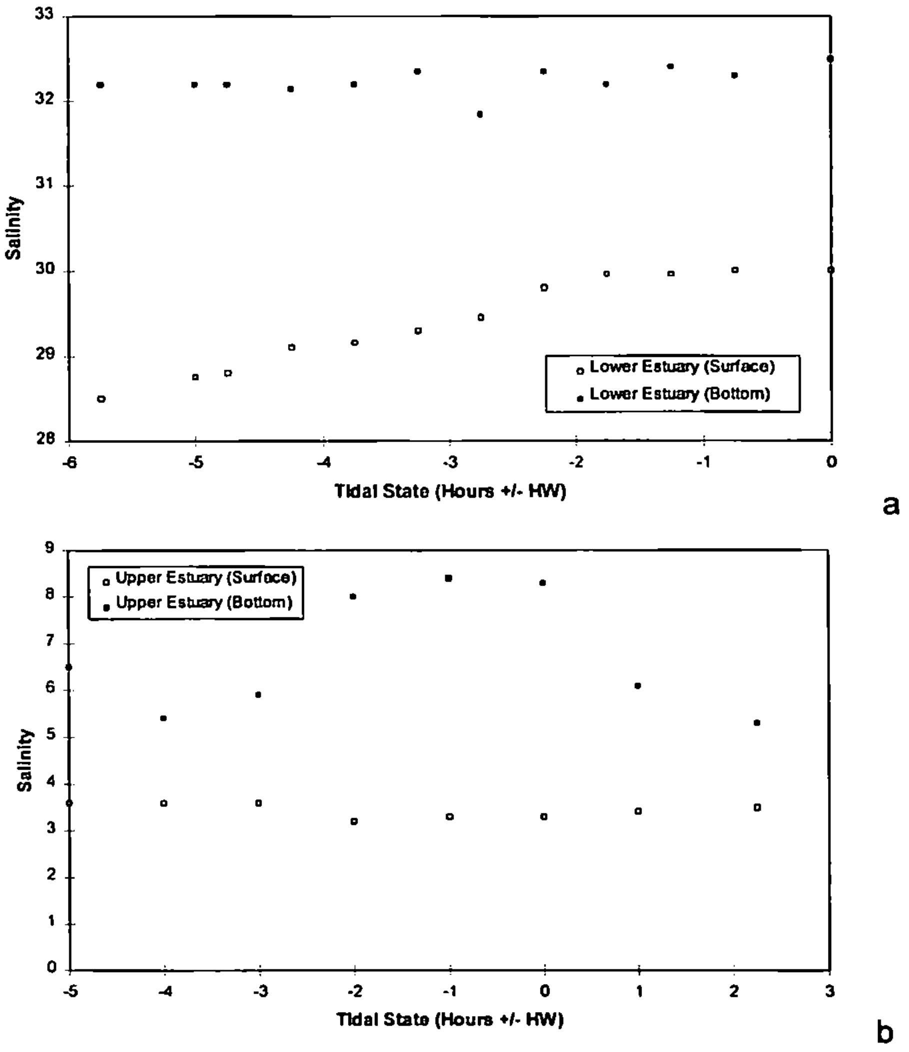


Figure 3.7. Tidal Cycle Salinity Profile at Upper (CT1) and Lower (CT2) Estuary Stations

The Clyde has a high biological oxygen demand from sewage discharges in the upper estuary (Scottish Environmental Protection Agency and Scottish Office Agriculture, Environment and Fisheries Department). Sediments sampled in the upper estuary were observed to be anoxic, particularly in sub-surface sediments. Measurements made during this study showed evidence of some oxygen depletion at the bottom of the water column at the lower estuary station, CT1 (see Figure 3.8).

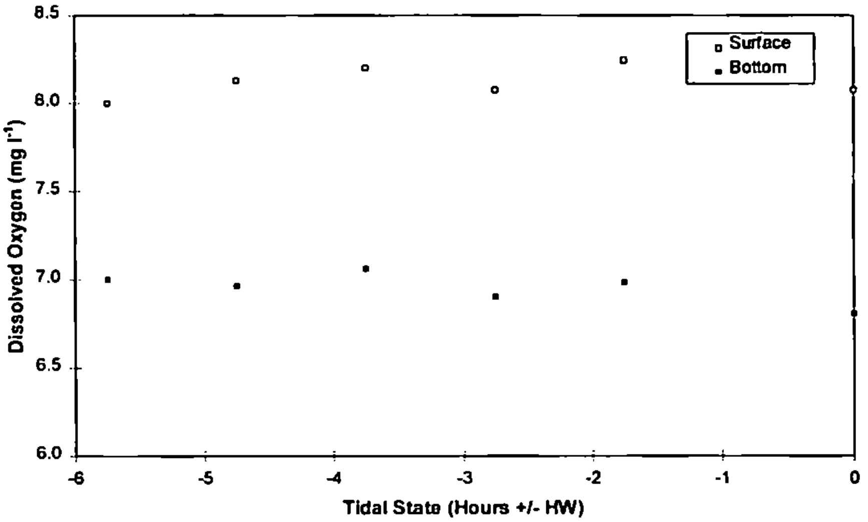


Figure 3.8. Dissolved Oxygen at Lower Estuary Station

The sediments in the estuary are mainly fine silt and clays. Concentrations of SPM in the estuary are relatively low and invariant (Balls, 1988; Curran, 1986). Mackay & Leatherland (1976) estimated that 100,000 tonnes of suspended sediment enter the Clyde Estuary annually. Of this, nearly 8,000 tonnes is derived from the Municipal Sewage Works (MSW) at Shieldhall and Dalmuir (Scottish Environmental Protection Agency, 1996). Until the early 1980s the estuary was dredged upstream to within approximately 2 km of the weir. Since then the estuary has been dredged up to the confluence with the River Kelvin with most dredging focused between Clydebank and Rothesay Dock (Douglas Hoad, Clyde Ports, pers comms).

Particle Characteristics

Ca:Al ratios ranging from 1.0 to 25.8 with an average of 7.0 ± 5.7 indicate that the majority of sediments in the estuary are of fluvial origin. Of the three main estuaries under study, the Clyde Estuary has the highest organic carbon content in bed sediments with average lipid content of 4.2 ± 3.8 mg g^{-1}. Specific surface areas are comparatively low 4.7 ± 3.8 $m^2 g^{-1}$ probably due to sediment pore blocking by organic material.

3.1.4 Humber Estuary

Site Description

The Humber Estuary is one of the UK's major industrialised estuaries, situated on the north east coast of the UK (Figure 3.9). The estuary, stretching 62 km from Trent Falls (confluence of the River Trent and River Ouse) to Spurn Point, is a macro-tidal estuary with a characteristic flare in width from 0.5 km in the tributary rivers to approximately 8 km at Spurn Point. Tidal influence extends beyond Trent Falls a further 72 km up the River Trent and 62 km up the River Ouse. Water depths in the estuary are generally shallow with the main channel maintained for shipping by dredging (Denman, 1979; Justice & Arnett, 1990; Woodward & Fair, 1993).

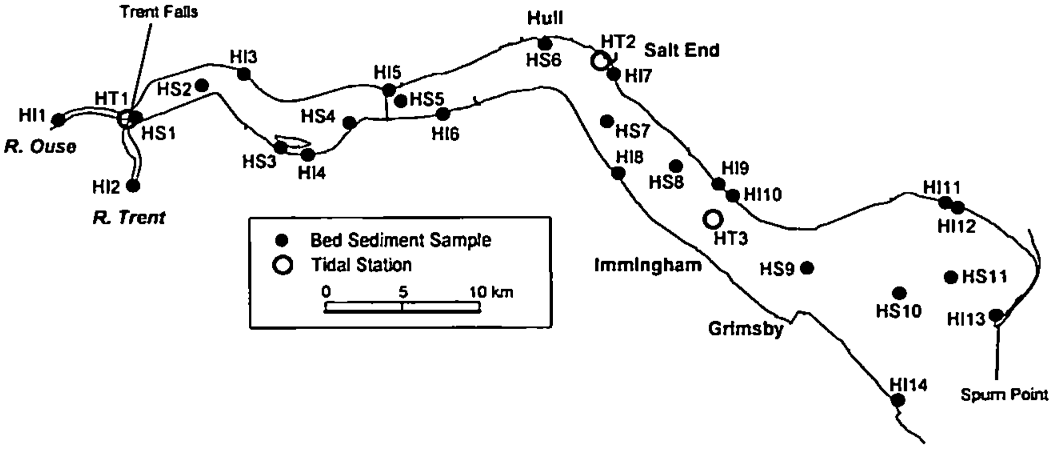


Figure 3.9. Humber Estuary Location Map

Hydrography and Sediment Regime

Although the Humber Estuary is a well studied estuary (Humber Estuary Committee), some limited hydrographic measurements were made concurrently with sampling. These measurements included salinity, SPM and current flow. River discharge during the field measurements was 234 m^3 s^{-1}.

Maximum tidal range at Saltend on spring tides is 7.4 m and 3.9 m on neap tides. River input varies from approximately 200 m^3 s^{-1} to 1550 m^3 s^{-1} during flood conditions. The combination of morphology and large tidal ranges result in a highly dynamic well mixed estuary. Current velocities measured during this study recorded velocities up to 3 m s^{-1} at Trent Falls, 1.5 m s^{-1} at Saltend and 2 m s^{-1} at Immingham. These are consistent with literature values (Woodward & Fair, 1993).

The well mixed characteristics of the estuary result in a relatively uniform vertical salinity distribution although stratification, covering 5 salinity units, may be present at near the mouth. Measurements of salinity variation at tidal stations HT1, HT2 and HT3 are shown in Figure 3.10.

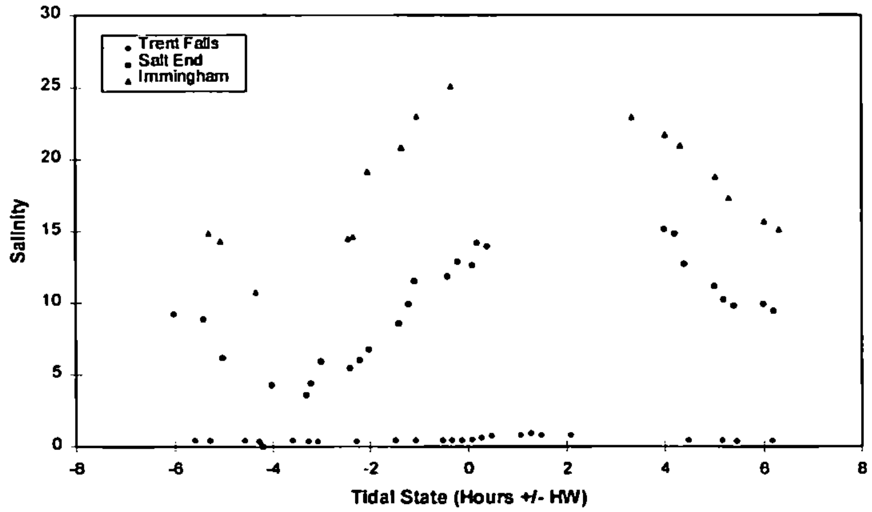
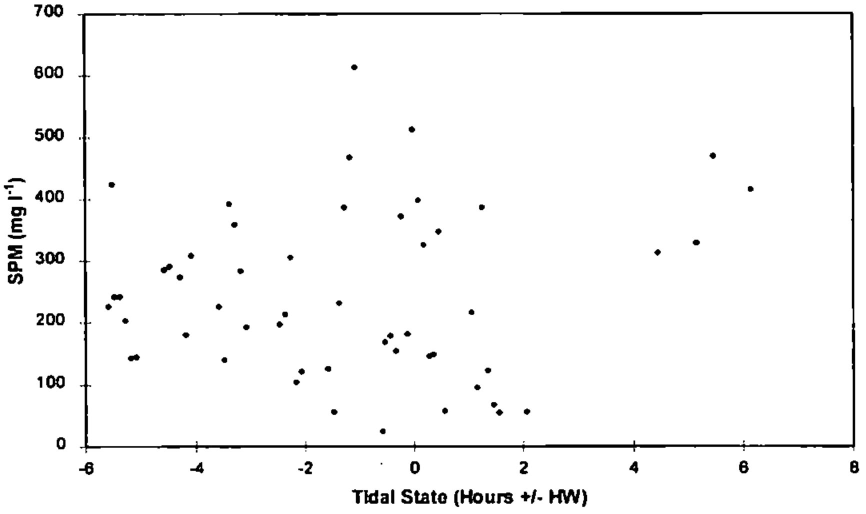


Figure 3.10. Salinity Measurements at Trent Falls (HT1), Salt End (HT2) and Immingham (HT3)

Humber sediment is predominately of marine origin with an estimated 60000 tonnes of sediment deposited in the estuary annually (Pethick, 1988). The erosion of adjacent coastlines (~1.4 x 10^6 tonnes per year) provides the source for much of this material (McCave, 1987). Approximately 200000 tonnes of fluvial material passes directly through the estuary due to the dynamic conditions maintaining suspension of this predominately fine sediment (Pethick, 1988). Sediment residence time in the Humber is estimated at approximately 40 years (Turner *et al.*, 1991).

Suspended sediment concentrations are elevated in the estuary with characteristic turbid swirls known locally as 'warps'. A range of SPM concentration from 200 mg l^{-1} at the mouth to over 1,000 mg l^{-1} at Saltend is typical (Freestone *et al.*, 1987). Measurements made during this survey (Figure 3.11 a, b, c) recorded SPM concentrations in the proximity of Immingham (HT3), Salt End (HT2) and Trent Falls (HT1).



a

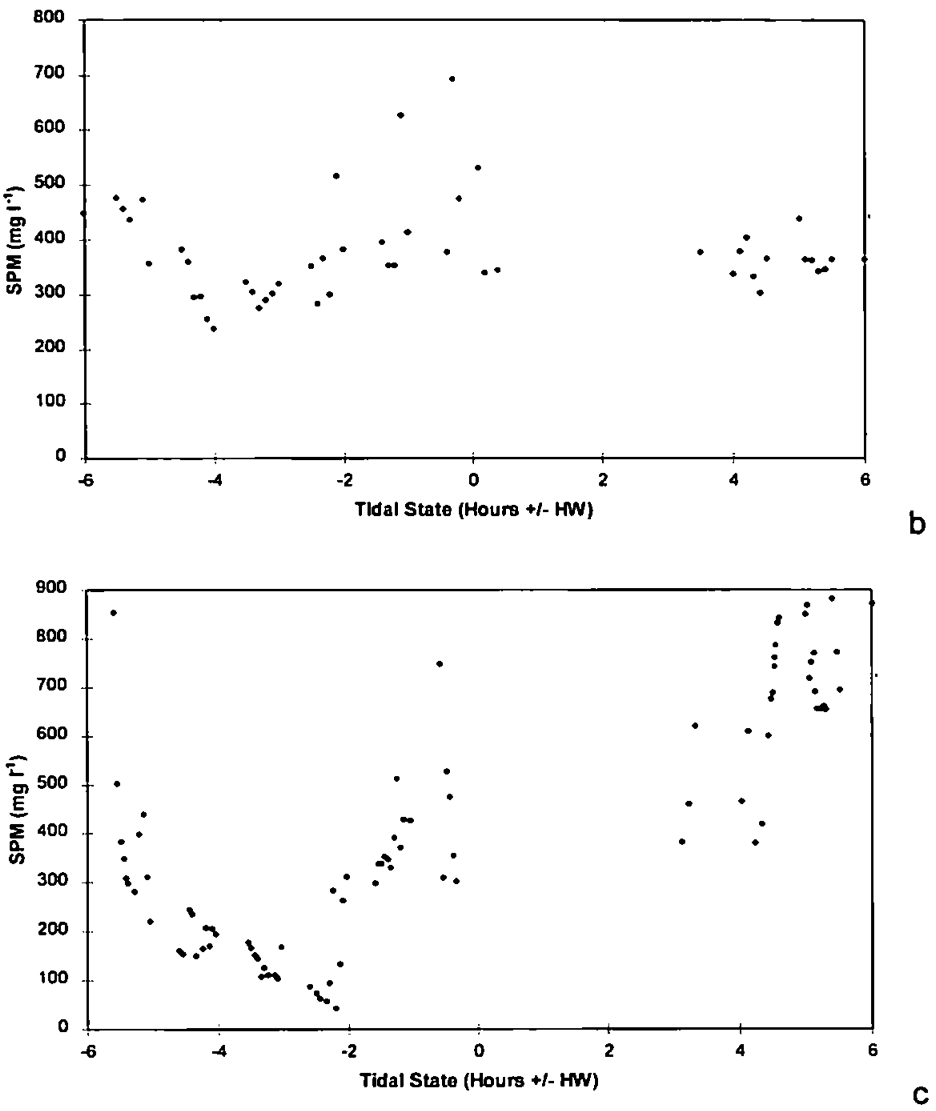


Figure 3.11. Measurement of Suspended Particulate Matter Concentration at (a) Trent Falls (HT1), (b) Salt End (HT2), (c) Immingham (HT3)

In the upper estuary, at Trent Falls, SPM concentrations are seen as variable with no distinct pattern. Typically 200-300 mg l^{-1} is in permanent suspension. At Salt End in the middle estuary (30 km from Trent Falls), some tidal variation is noted with permanently suspended concentrations of approximately 400 mg l^{-1}. It should be noted that this mid-estuary station was situated close to a tidal mud flat which provided a localised source of mobile sediment. At the Immingham outer estuary station (43 km from Trent Falls), significant tidal influence is observed with concentrations varying between 100 and 900 mg l^{-1}.

Particle Characteristics

The dynamic physical environment of the Humber results in bottom sediments in the main channels of the Estuary dominated by coarse sediments of marine origin. Inter-tidal areas hold finer sediments in the clay/silt fraction (Justice & Arnett, 1990). Average Ca:Al ratios from main channel samples taken during these studies were 105 ± 22 indicating the marine origin of these deposits.

The Humber has been characterised by sediments of high specific surface area. Turner *et al* (1991) measured SSA of suspended sediments in the estuary averaging approximately 25 m^2 g^{-1}. Measurements of bed sediments made during this study confirmed this data with an average SSA of 18 ± 5.8 m^2 g^{-1}. The higher value for suspended sediments would be expected with finer sediments held in suspension. In contrast with the Clyde, the Humber has low lipid content with less potential for pore blocking by organic material (Glegg *et al.*, 1987; Titley *et al.*, 1987). Additionally, the Humber contains major anthropogenic sources of amorphous Fe derived from acid-iron waste discharges on the south bank of the Estuary (Millward & Glegg, 1997; Newell *et al.*, 1984). Adsorption of 'fresh' Fe on particle surfaces increases particle surface area and reactivity (Turner, 1990).

3.1.5 Summary of Sediment Characteristics

The characteristics of sediment in the estuaries under study are key to understanding the sorption preferences of OCs. Bed sediment physicochemical characteristics are presented in Table 3.2. Dee and Humber Estuary sediments are seen to be dominated by sediment of marine origin. Lipid content is low in both estuaries. The Clyde Estuary is dominated by lithogenic sediments with higher lipid content indicating the organic-rich nature of the sediment. Surface area is low in the Dee and Clyde estuaries. In the Dee estuary this is probably due to the coarser sediments whereas, in the Clyde, this is more likely due to pore blocking by organic matter. In the

Humber Estuary, the SSA is much higher and this is attributed to surface active anthropogenic Fe coatings on the sediments. The importance of these contrasting sediment characteristics in determining chlorinated organic contaminant distributions will be discussed in the next chapter.

Estuary	SSA ($m^2 g^{-1}$)	Lipid (mg g^{-1})	Ca:Al Ratio
Dee	4.1 ± 3.6	1.0 ± 1.6	131.9 ± 98.4
Humber	17.9 ± 5.8	1.4 ± 2.9	105.8 ± 22.4
Clyde	4.7 ± 2.8	4.2 ± 3.8	7.0 ± 5.7

Table 3.2. Summary of Physicochemical Characteristics in the Humber, Dee and Clyde Estuaries

3.2 Occurrence of PCDD/PCDF & PCBs

The following section discusses the distribution of chlorinated organics at the coastal and estuarine study sites described above. Distributional data is presented spatially on maps with data plotted in quantified bands. Where survey stations were occupied during more than one year's survey, the concentrations have been averaged (residence times in the estuary are sufficiently long that temporal comparisons between surveys only 1-2 years apart are not realistic). The same data has also been plotted axially with estuary features marked where relevant. A full summary of the analytical data is presented in Appendix II.

Under this study, apolar lipid content has been employed as a normalising measurement. The specific relevance of apolar lipid content as the chosen normalising parameter is discussed in detail in the next chapter. The spatial distribution maps have lipid normalised data co-plotted with raw data for comparison. Where lipid content falls below 0.5 mg g^{-1}, data has not been plotted. Such low content is close to the limit of detection and has the potential effect of distorting normalised values. A full discussion of these data is presented in the Chapter 4.

3.2.1 UK Coastal Waters Survey

Figure 3.12 shows the sampling locations occupied in the UK and a summary of the data from the UK coastal waters survey is given in Table 3.3.

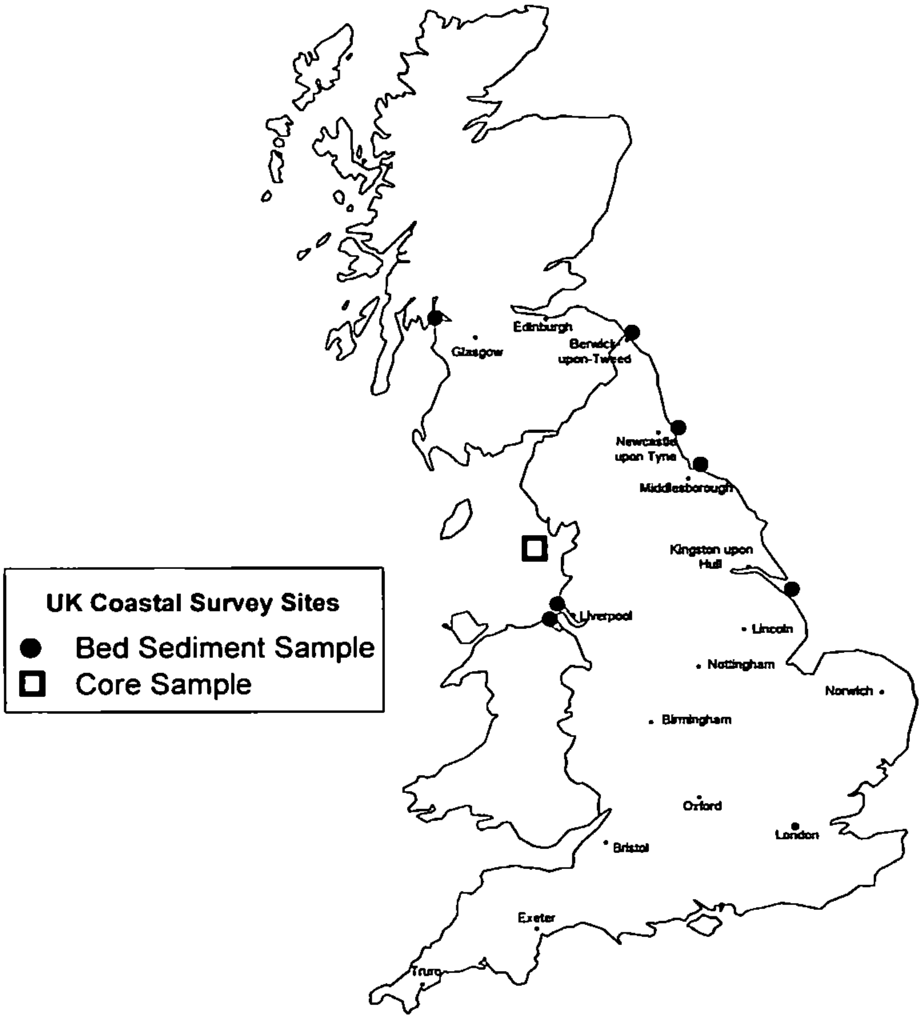


Figure 3.12. UK Coastal Survey Sites

Congener/ homolog	Tyne	Mersey	Tees	Humber	Tweed	M'cambe Bay	Clyde (lower estuary)	Dee (lower estuary)
2,3,7,8 TCDD	n.d.	0.3	0.1	n.d.	0.8	<0.3	3.5	3
TCDD	1	3	1	2	4	6	17	20
PeCDD	<1	<9	<1	<13	<12	<0.6	47	50
HxCDD	3	<7	3	4	11	10	34	60
HpCDD	3	9	2	5	24	40	79	120
OCDD	13	36	3	10	89	150	110	500
2,3,7,8 TCDF	1	2	n.d.	2	2	2	4	10
TCDF	4	11	2	9	16	21	16	60
PeCDF	3	4	2	5	10	16	15	40
HxCDF	6	9	3	7	15	35	28	70
HpCDF	9	8	14	6	13	22	35	110
OCDF	59	13	3	6	16	22	6	110
Total PCDD	21	65	8	35	128	206	287	750
Total PCDF	81	46	23	32	69	116	99	390

Table 3.3. Concentrations (pg g^{-1}) of PCDD and PCDF from the UK Coastal Survey

With the exception of the Clyde sample (taken in the Inner Clyde Estuary), all samples were taken at the mouths of each estuary, and with the exception of the Morecambe Bay core, all samples were representative of surface sediments. From Table 3.3, total PCDD can be seen to vary from 8 - 750 pg g^{-1} and PCDF from 23 - 390 pg g^{-1}. This compares with PCDD concentrations in the range 256 - 445 pg g^{-1} and PCDF varying from 354 - 673 pg g^{-1} reported by Evers *et al.* (1993) in the coastal Wadden Sea and southern North Sea.

To put these data in context and bearing in mind the ubiquity of their occurrence, it is desirable to establish a benchmark or 'background' concentration. The general paucity of data for marine sediments makes this difficult. Laane (1992) suggests that until natural production of these compounds has been proved, background should be taken as zero. On this basis, with the reported ubiquity of these compounds (Tanabe *et al.*, 1994), most estuarine and coastal sediments would be considered as elevated above background. Turkstra & Pols (1989) regarded PCDD/PCDF sediment concentrations of between 10 and 100 pg g^{-1} on a TEQ basis (see Chapter 1, section 1.7.5) as 'background' in their study of estuaries in the Netherlands.

Norwood *et al.* (1989) in a study of Narragansett Bay obtained values of < 0.93 and 15 pg g^{-1} for 2,3,7,8 TCDD and TCDF, respectively, at their 'relatively clean reference site'. Oehme *et al.* (1993) considered 47 pg g^{-1} total PCDD/PCDF as a background concentration in studies of the Barents Sea.

Although the Tyne, Mersey, Tees, Humber, Dee and Clyde are estuaries receiving pollutant inputs from large conurbations and industrial activities, only the Dee and the Clyde have PCDD/PCDF concentrations exceeding the 'background' values above. In general, set against the 'background' values suggested by Turkstra & Pols (1989) and Norwood *et al.* (1989), surface sediments from coastal locations around the UK show no conclusive evidence of significantly elevated PCDD/PCDF concentrations.

Morecambe Bay Core Sample

A core sample was taken from a box core in Morecambe Bay. The core was sectioned and sampled at the surface, 14cm and 28cm depth. The resulting profile of PCDD, PCDF and PCB is shown in Figure 3.13.

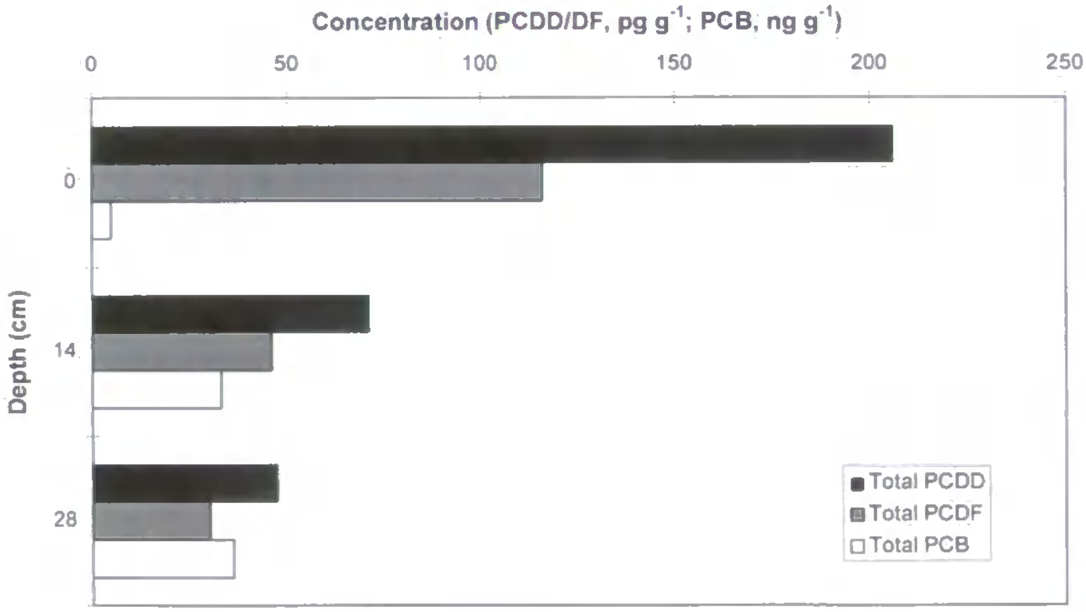


Figure 3.13. Profile of PCDD, PCDF and PCB in Morecambe Bay Core Sample

Concentrations in the core are relatively low compared with other shelf sea samples collected in the southern North Sea (Evers *et al.*, 1993). The concentrations of both PCDD and PCDF fall rapidly with depth. At 28 cm, concentrations for several homologs are below detection. Conversely, PCB concentrations increase in depth; an observation often reported from PCB core analyses (Van Zoest & Van Eck, 1993b; Alcock *et al.*, 1993). Although no dating of the core was attempted the decline in PCB concentrations is often dated from the mid-1970s when PCB production and usage declined. This would tentatively suggest sedimentation of approximately 1 cm yr^{-1} if the 14 cm sample represented a pre-decline maximum. The elevated surface concentrations for PCDD/PCDF seem to indicate recent anthropogenic inputs possibly derived from atmospheric deposition, increased estuarine inputs or dumping of contaminated material in the region. More detailed segmentation of the core and accurate dating would be required to strengthen any conclusions.

3.2.2 Dee Estuary

General Concentrations and Comparison with Other Studies

Nine stations were sampled in the Dee estuary; 5 sub-tidal stations and 4 inter-tidal stations (see Appendix II for full data summary). Concentrations of PCDD ranged from 530 - 1880 pg g^{-1} and PCDF from 340 - 710 pg g^{-1}. Total PCBs in the range non-detectable to 20 ng g^{-1} were found. There is very little other data on chlorinated organics in the Dee estuary for comparison. A survey by Law *et al.* (1991) reported one sample with a concentration of 45 $\mu g\ g^{-1}$ (dry mass expressed as Arochlor 1254). This sample was taken several kilometres upstream of Chester. Within the estuary, most samples analysed were below detection. Only a single sample in fine sediments at West Kirby indicated a measurable concentration of 0.09 $\mu g\ g^{-1}$ (dry mass expressed as Arochlor 1254).

Spatial and Axial Distributions

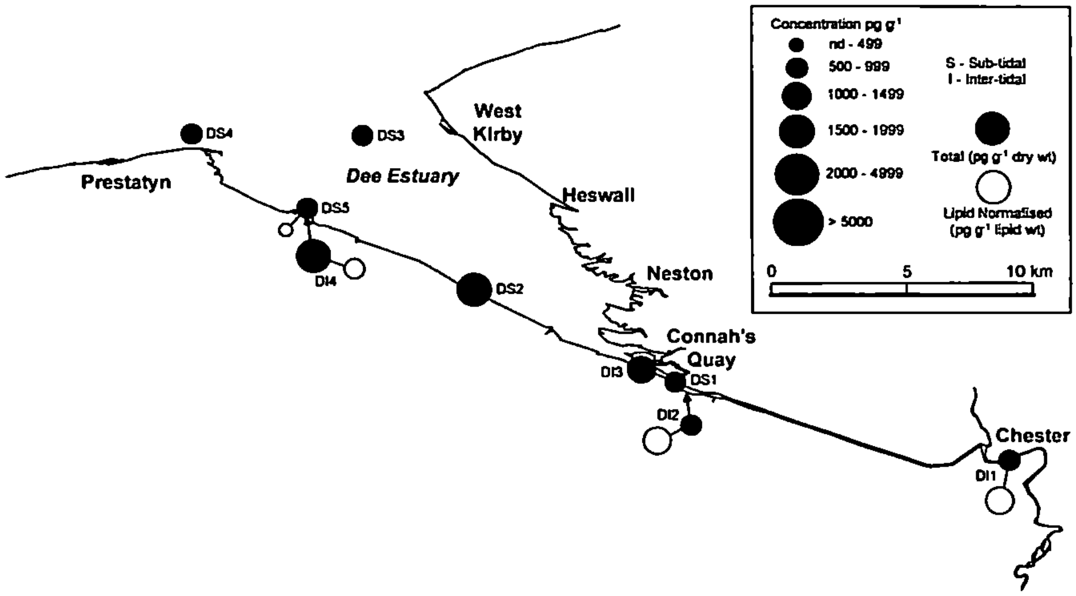


Figure 3.14. Spatial Distribution of PCDD in the Dee Estuary

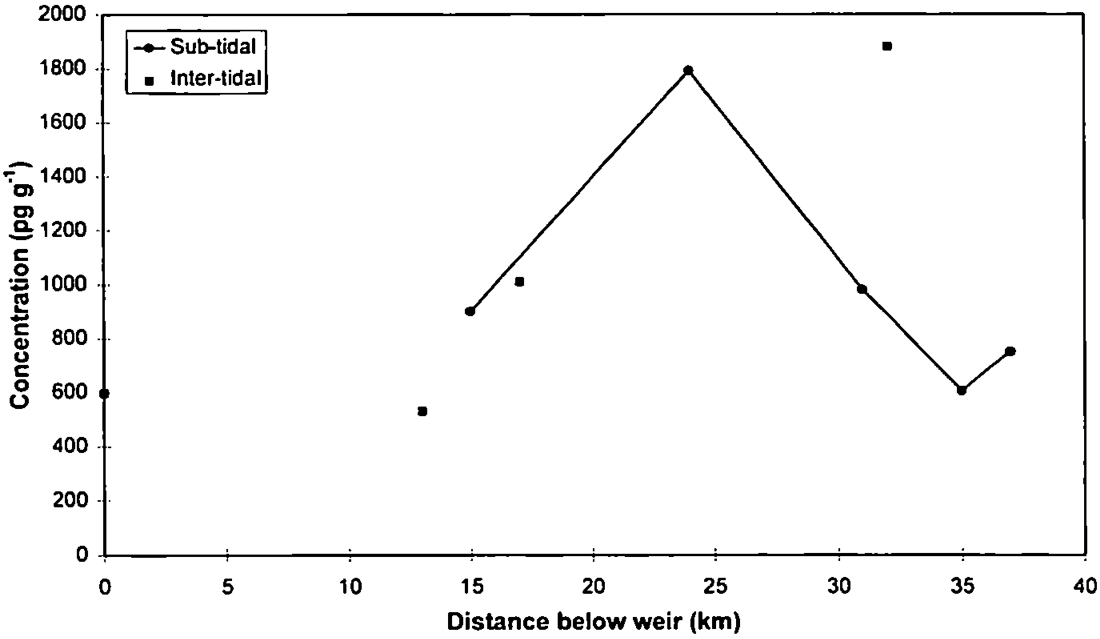


Figure 3.15. Axial Distribution of PCDD in the Dee Estuary

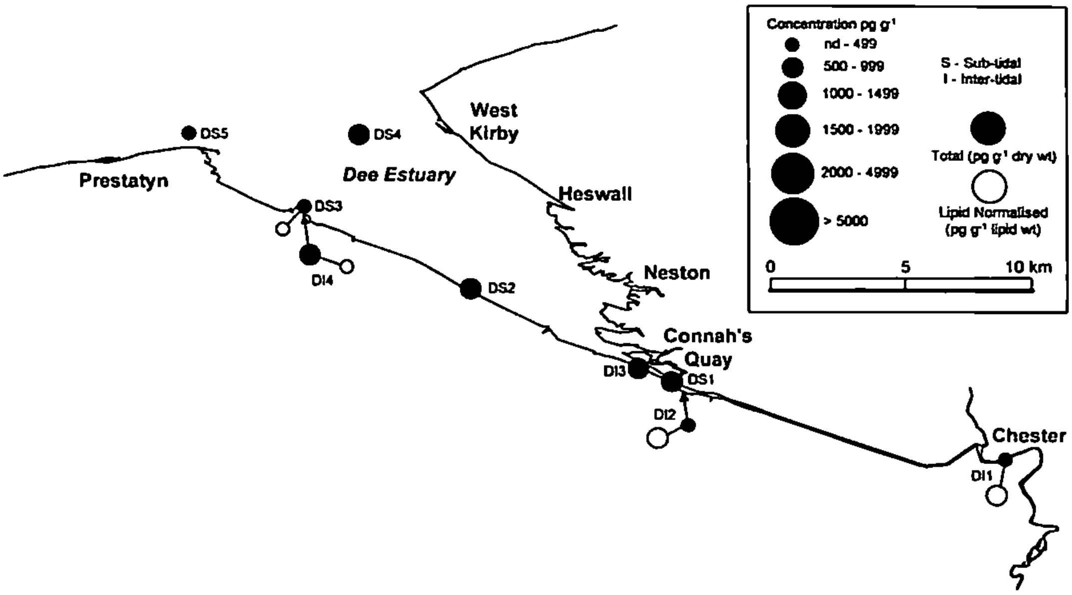


Figure 3.16. Spatial Distribution of PCDF in the Dee Estuary

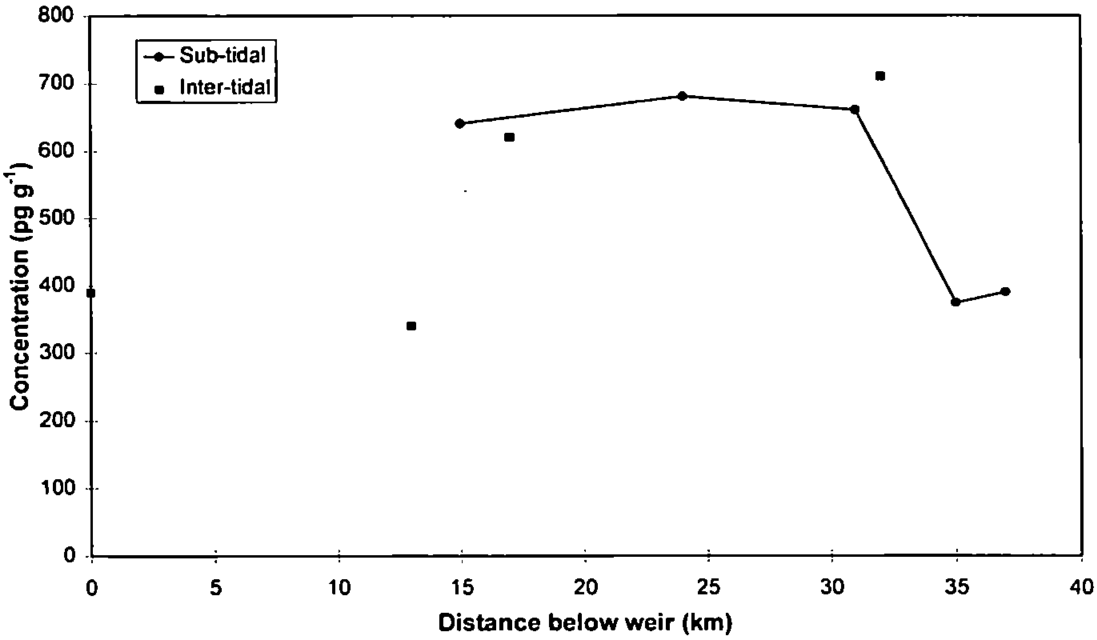


Figure 3.17. Axial Distribution of PCDF in the Dee Estuary

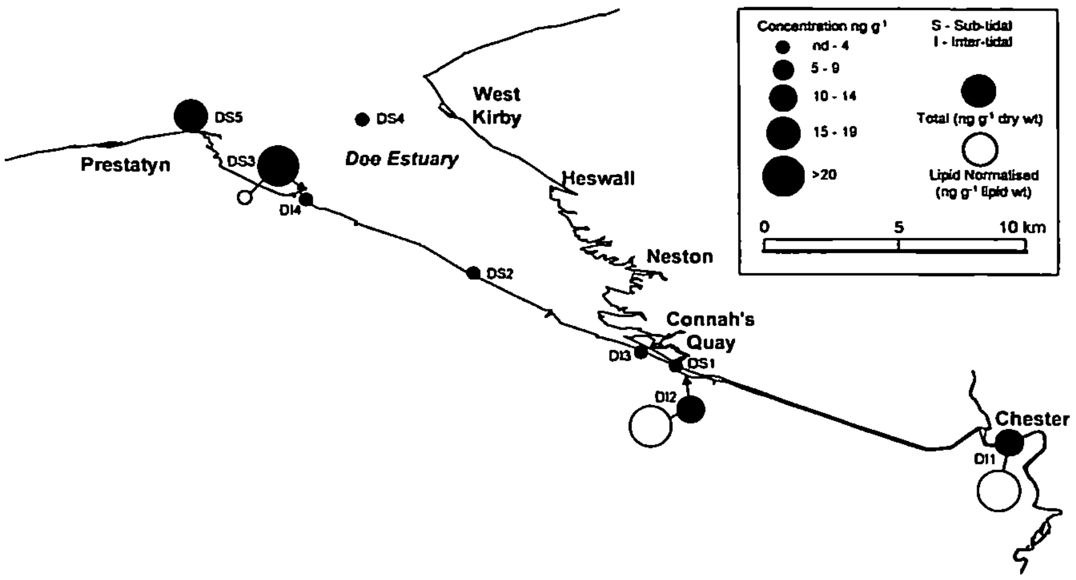


Figure 3.18. Spatial Distribution of PCB in the Dee Estuary

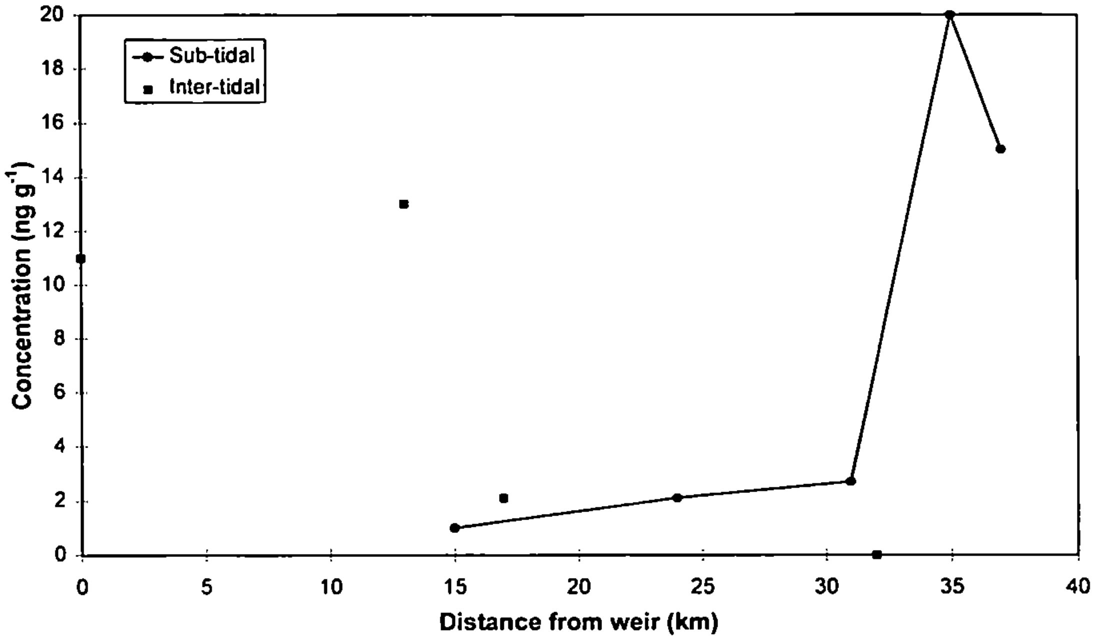


Figure 3.19. Axial Distribution of PCB in the Dee Estuary

Figures 3.14 - 3.19 show the spatial and axial distributions of PCDD, PCDF and PCB in the Dee Estuary. PCDD and PCDF concentrations are relatively homogenous in the estuary. There is little variation between inter-tidal and sub-tidal samples, reflecting the well mixed sediment conditions in the estuary. PCB concentrations are more variable with the highest concentrations found in two sub-tidal samples close to (DS3) and at the mouth (DS5) of the estuary. Consistent with the PCDD/PCDF measurements, there is little difference between inter-tidal and sub-tidal samples taken in close proximity.

3.2.3 Clyde Estuary

General Concentrations

In total, 42 km of the Clyde Estuary was sampled from the weir to the Inner Firth with surveys conducted in 1991, 1992 and 1993. Concentrations of total PCDD, PCDF and PCB varied considerably within the estuary but were generally the highest measured at the three principal study sites. Maximum values for total PCDD and PCDF were 11100 and 2891 pg g^{-1} respectively. In addition to surface samples, sub-surface and core samples were also taken and are discussed below. A full tabulation of analytical data is provided in Appendix II.

Comparison with Other Studies

There has been no known sampling and analysis of PCDD and PCDF in the Clyde Estuary to compare with the analyses made during this study. However, there are some samples from the Clyde Estuary analysed for PCBs by the Scottish Environmental Protection Agency (SEPA). A limited number of samples are reported in the UK National Monitoring Programme Scottish Regional Report (SEPA & SOAEFD). This report gives PCB concentrations as a sum of the 'ICES 7' congeners (Nos. 28, 53, 101, 118, 138, 153, 180). Values reported in the estuary include 7.2 ng g^{-1} at Erskine and 12 ng g^{-1} at Port Glasgow. These values compare with those measured during this survey which range from non-detectable to 108 ng g^{-1}.

Other data has been provided by Mr. D. Pirie at SEPA who reports PCB (sum ICES 7) concentrations ranging from 17 to 47 ng g^{-1} and total PCB concentrations ranging from 43 to 111 ng g^{-1} in the upper estuary (from the weir to 0.5km downstream of Dalmuir). This compares with concentrations (sum ICES 7) measured during this study in the upper estuary ranging from non-detectable to 132 ng g^{-1}.

A comprehensive survey of the sewage sludge dumpsite located in the outer Firth of Clyde also sampled a bed sediment in close proximity to the most seaward samples taken on this study (Kelly and Campbell, 1995). A concentration of 45 ng g^{-1} for Σ ICES 7 congeners was reported. This compares closely with concentrations of 22 and 44 ng g^{-1} Σ ICES 7 at the two seaward end member stations (CS27 and CS28). Concentrations up to 500 ng g^{-1} were measured at the former dumpsite in the outer Firth.

Spatial and Axial Distributions

Figures 3.21 - 3.26 show the spatial and axial distributions of PCDD, PCDF and PCB in surface samples.

The same general pattern of distribution is evident for PCDD, PCDF and PCB in the estuary. Determining whether such co-distribution is due to common sources or preferential accumulation at particular sites requires further investigation (see Chapter 4). At the weir, concentrations are low but immediately downstream at Station CS2 (0.8 km below the weir) there is a marked peak in concentration which includes the highest PCB concentration (3000 ng g^{-1}) measured during these studies. Between 0.8 km and approximately 4.0 km from the weir concentrations are relatively low but start to increase from this point to an upstream maximum at 15 km from the weir, in the vicinity of the Dalmuir MSW and the confluence of the Clyde and Cart tributary. In the middle estuary concentrations are generally low until, at approximately 35 km from the weir there is another significant peak in all analytes in the vicinity of the Ironotter Point long outfall.

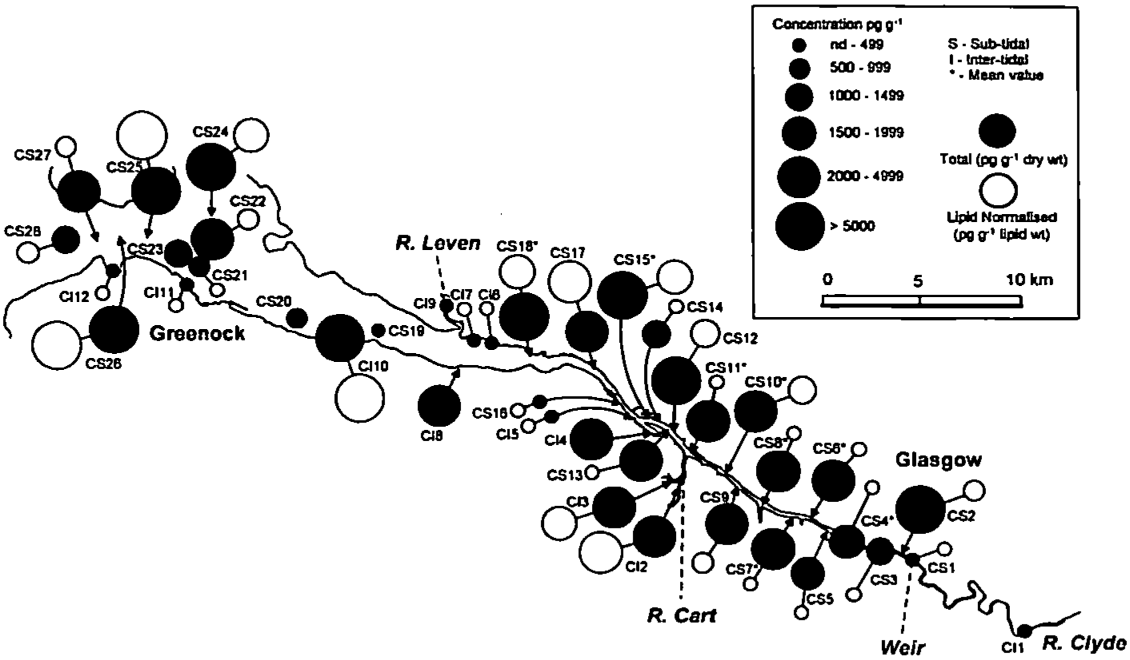


*Figure 3.20. Spatial Distribution of PCDD in the Clyde Estuary 1991-1993 (*Mean for Two or Three Years)*

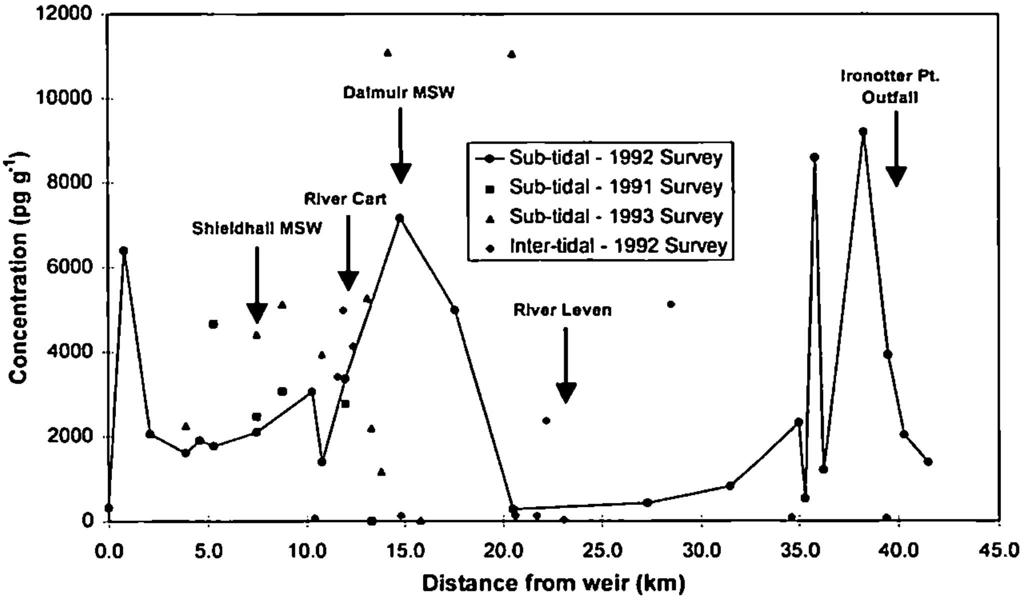


Figure 3.21. Axial Distribution of PCDD in the Clyde Estuary

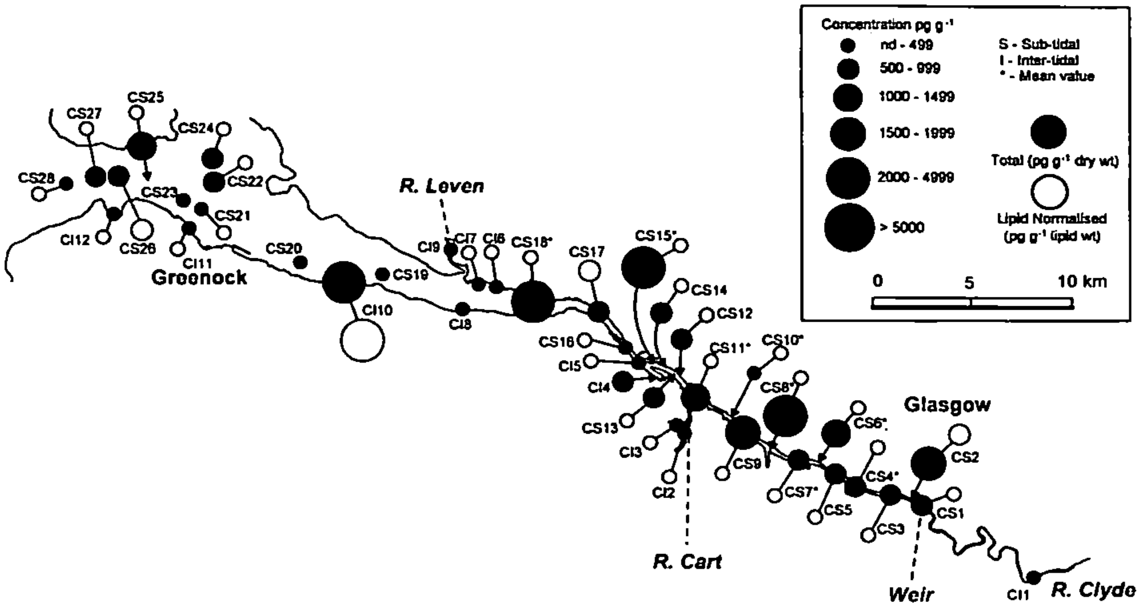


*Figure 3.22. Spatial Distribution of PCDF in the Clyde Estuary 1991-1993 (*Mean for Two or Three Years)*

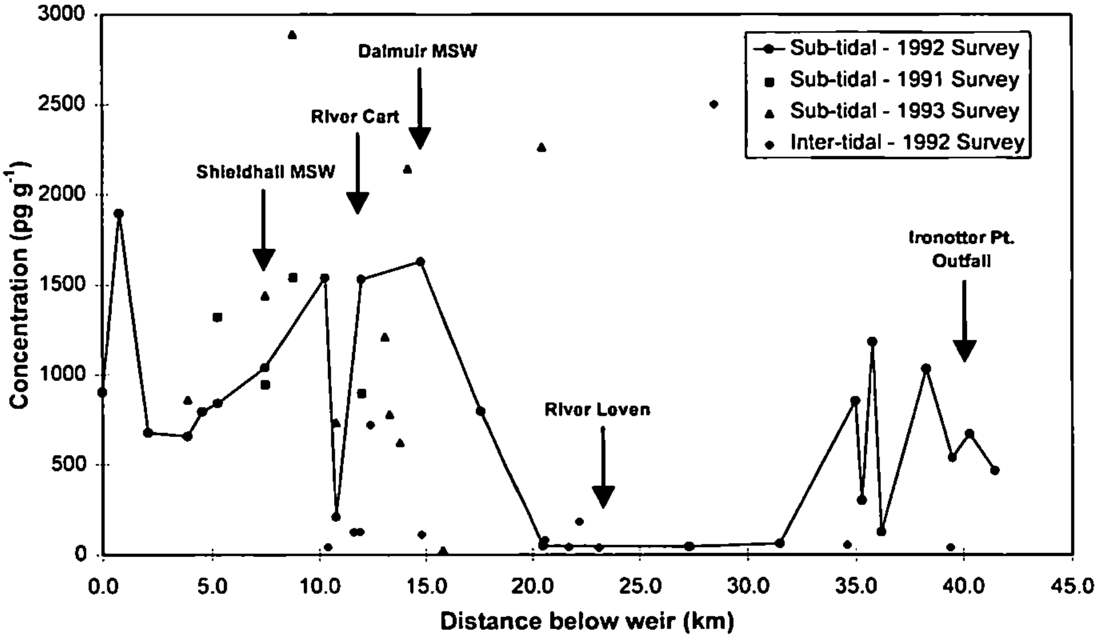


Figure 3.23. Axial Distribution of PCDF in the Clyde Estuary

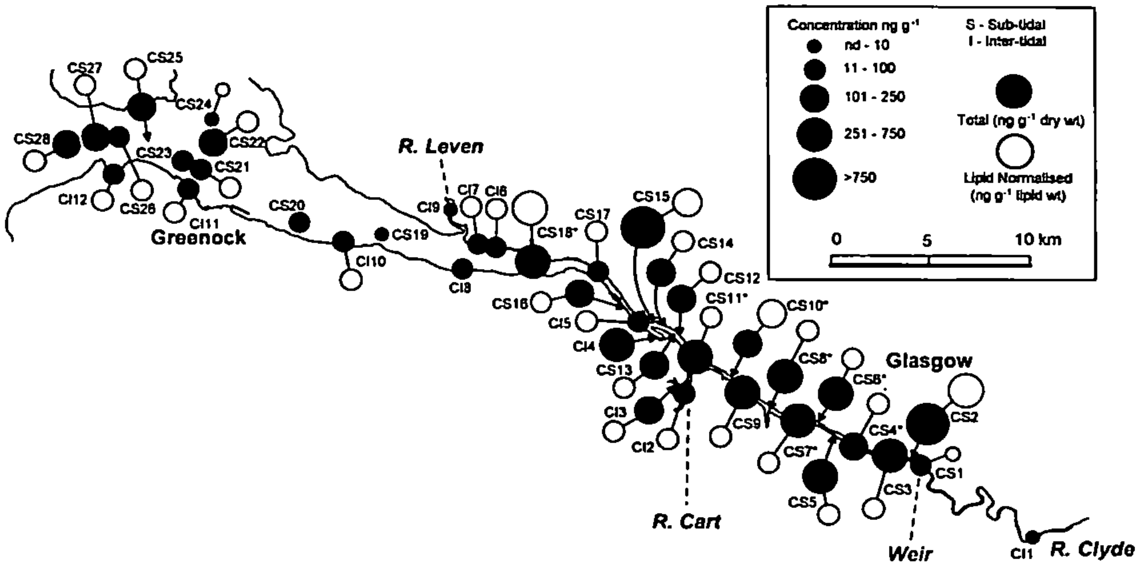


Figure 3.24. Spatial Distribution of PCB in the Clyde Estuary 1991-1993 (*Mean for Two or Three Years)

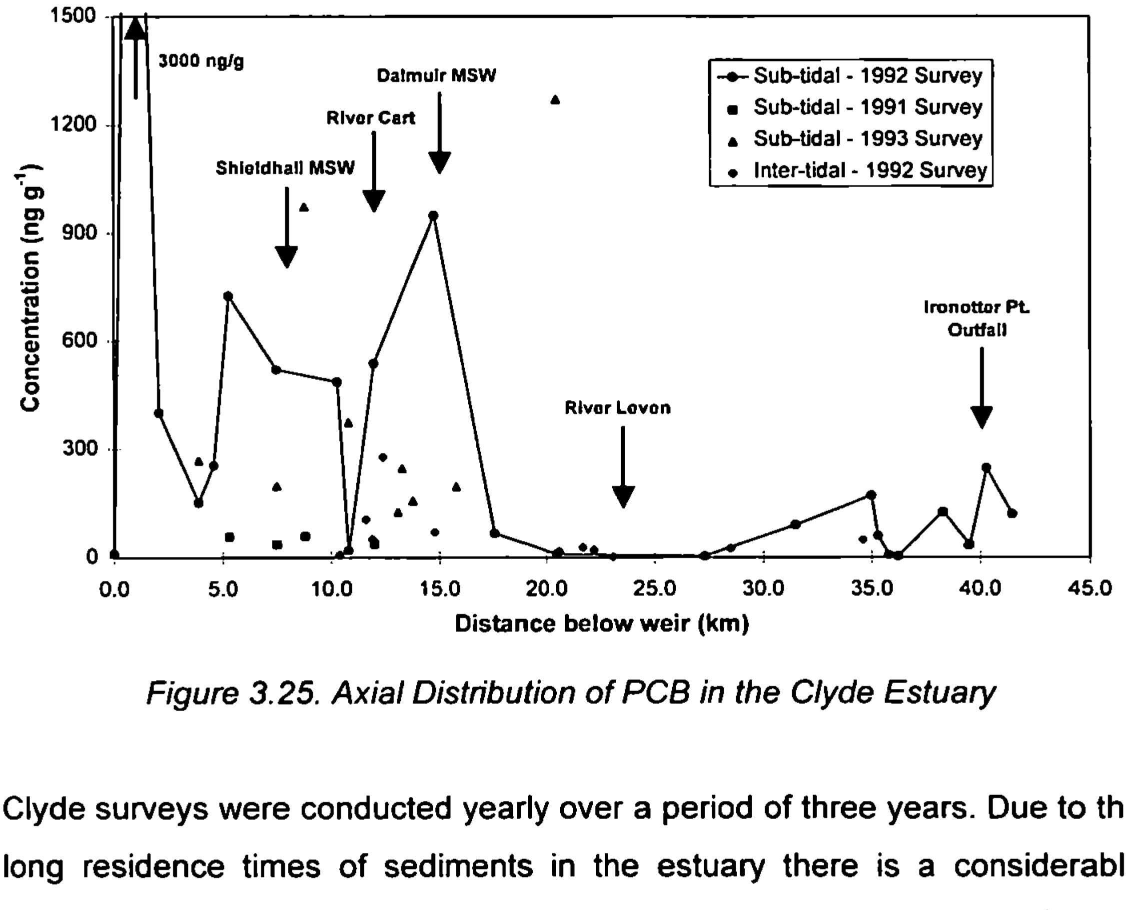


Figure 3.25. Axial Distribution of PCB in the Clyde Estuary

Clyde surveys were conducted yearly over a period of three years. Due to the long residence times of sediments in the estuary there is a considerable 'inertia' in the system when examining time-dependent trends of such persistent compounds. There is considerable variability noted between samples taken at the same stations in consecutive years. In the upper estuary samples taken during different surveys record similar concentrations but in the middle estuary there is significant variability. Such variability underlines the problems inherent in sampling discrete locations particularly in an environment where the characteristics of the sampling media are likely to vary considerably. This emphasises the importance of considering the nature of the sample media when interpreting the results.

Sub-surface and Core Samples

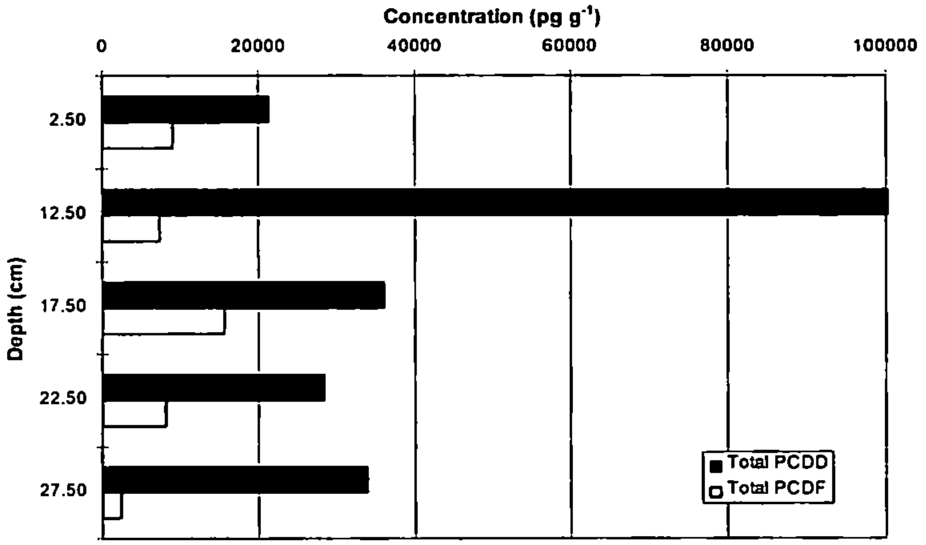
During the 1993 Clyde survey the opportunity was taken to sample three of the upper estuary stations at two depths (surface and 10 cm). In addition, three core samples were analysed to depths of 30 cm. The results from the two-depth samples in the upper estuary are summarised in the following table;

Station (depth)	**Total PCDD ($pg\ g^{-1}$)**	**Total PCDF ($pg\ g^{-1}$)**	**Total PCB ($ng\ g^{-1}$)**
CS1 (0cm)	2260	862	268
CS1 (10cm)	2190	740	307
CS3 (0cm)	5125	2891	974
CS3 (10cm)	8015	1415	-
CS4 (0cm)	4410	1440	198
CS4 (10cm)	5120	1520	221

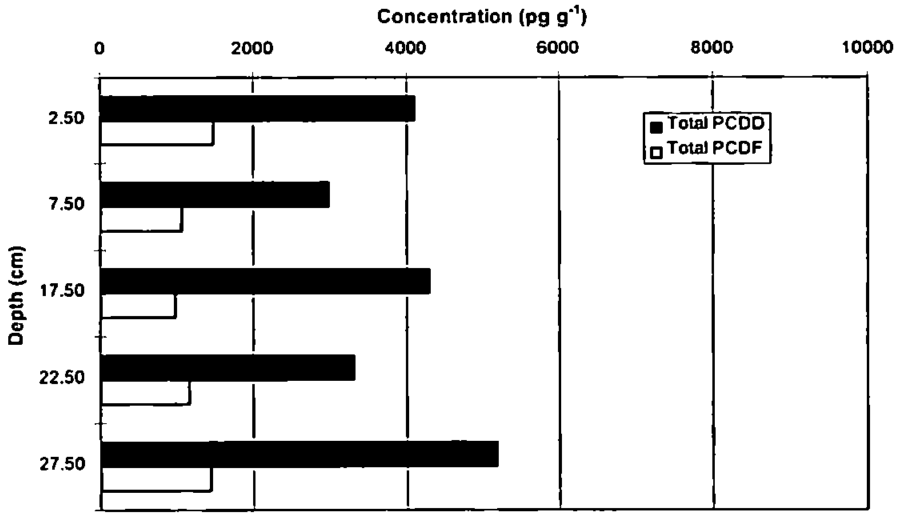
Table 3.4. Total PCDD, PCDF and PCB Concentrations at 0 cm and 10 cm depth at Upper Estuary Stations

Table 3.4 shows a strong homogeneity in the top 10 cm of the bed sediment for all analytes. The percentage standard deviation ranged from 2% to 48% with an average of 15%. This observed homogeneity indicates that either the bed sediments have been fairly well mixed (e.g. through natural or external disturbance), or that the flux of pollutant input in recent times has been fairly constant. The estuary is subject to dredging operations which disturb sediments. However at Stations CS1 and CS3 no dredging has been carried out, and at CS4 no dredging would have taken place since the mid-1980s. It may be speculated that the observations are caused partly by a constancy in the flux of source material and partly through natural re-working of sediments in the estuary.

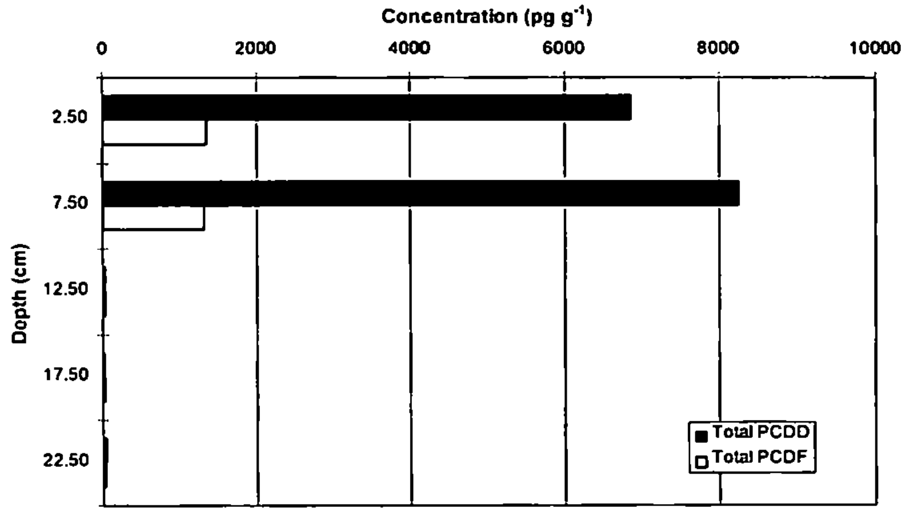
Three core samples were taken in the estuary to a depth of 25 cm. Two cores were taken in close proximity in the upper estuary approximately 150 - 300 m below the weir. A third core was taken in the River Cart. The PCDD and PCDF concentrations for the three cores are shown in Figures 3.26 a-c.



a



b



c

Figure 3.26. Clyde Estuary Core Sample PCDD/PCDF Concentration Profiles, (a) CC1, (b) CC2, (c) CC3

Station CC1 shows a relatively homogenous profile except for one sample at 12.5 cm depth which indicates concentrations of PCDD rising to 100000 pg g^{-1}. This profile could be explained by a historical peak in inputs which has subsequently become buried in less contaminated sediments but the nearby core at Station CC2 shows no evidence of a peak in concentration at depth with generally lower concentrations homogeneously distributed throughout the profile. Alternatively, a localised organic rich layer may explain the accumulation at this one depth (organic carbon analyses were not, unfortunately, carried out for these cores). At the second location, CC3 in the River Cart, the profile shows a distinct surface layer peak in concentration down to 7.5 cm. Below this depth, no detectable PCDD/PCDF could be found.

Figure 3.27 shows the PCB concentration profile in the three core samples. The higher concentrations in cores CC1 and CC2 are consistent with PCDD/PCDF concentrations in the same cores. Both CC1 and CC2 show elevated concentrations in the 12.5 - 17.5 cm layers. CC3 shows the same dramatic reduction in concentration beneath this level observed for PCDD/PCDF. Without core dating and a knowledge of likely disturbances in the past, it is difficult to relate the observed depth profiles to specific sources or events. However, in a study of a salt marsh sediment core, Van Zoest &

Van Eck (1993b) found a significant peak in PCB concentration at approximately 15 cm depth which was dated to approximately 1965. Alcock *et al.* (1993) in a study of PCBs in UK soils dating from 1940 to 1992, also observed a sharp increase in soil PCB content between 1940 and the early 1960s with a maximum during the late 1960s / early 1970s. This was followed by a dramatic reduction in concentrations. Although relating the observed core profiles to the rise and peak in PCB inputs may be unsustainable, the reduction in concentration in the surface layer may reflect reduced inputs in recent years.

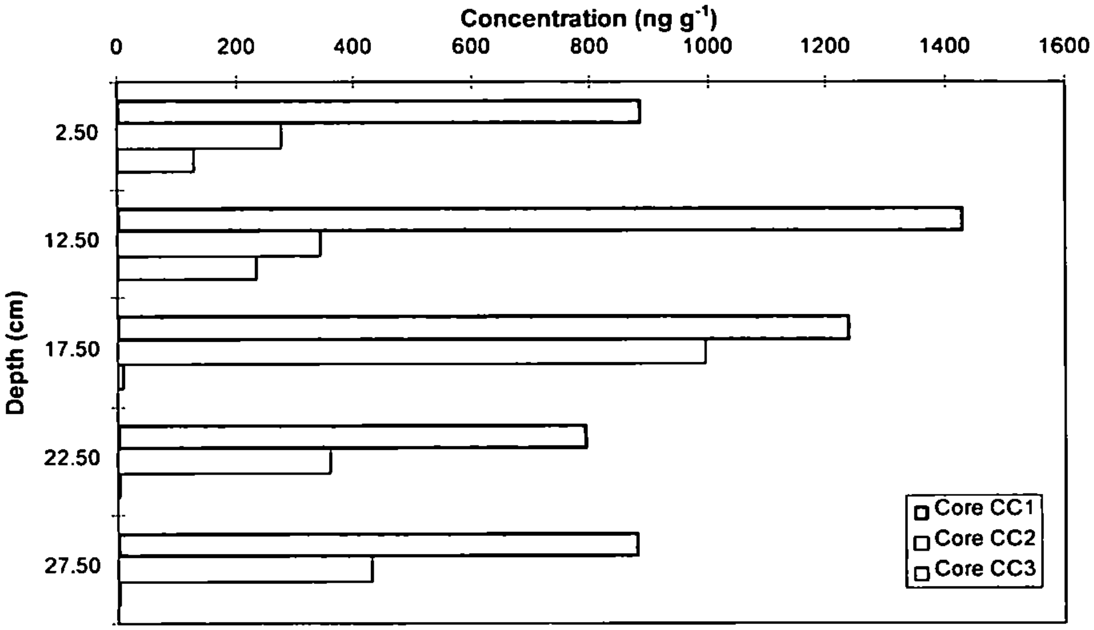


Figure 3.27. Clyde Estuary Core Sample PCB Concentration Profiles

3.2.4 Humber Estuary

The detailed Humber survey was carried out in October 1993 with a limited number of samples collected earlier in 1991. A full summary of the analytical data is presented in Appendix II. Total PCDD/PCDF concentrations in the estuary were in the range non-detectable to 3827 pg g^{-1}. These concentrations are elevated with respect to 'background' concentrations reported in the literature (Oehme *et al.* 1993; Turkstra & Pols, 1989). Evers *et al.* (1993) reported PCDD/PCDF values in North Sea estuaries from 1006 to

4736 pg g^{-1} including two samples taken at a station at the mouth of the Humber Estuary with total PCDD/PCDF values of 1846 pg g^{-1} (surface, <63 μm) and 10557 pg g^{-1} (15 cm, <63 μm). No samples analysed as part of this survey reached concentrations as high as that of the 15 cm depth samples analysed by Evers *et al.* (1993), although surface sample concentrations were similar to these data.

Total PCB concentrations ranged from non-detectable to 84 ng g^{-1}. Klamer & Fomsgaard (1993) reported ΣCB concentrations (summation of 12 congeners) ranging from ~3 - 20 ng g^{-1} in the Humber plume. The only station in the same vicinity as this study recorded a ΣCB concentration of approximately 17 ng g^{-1} compared to concentration of between 9.8 and 51.6 ng g^{-1} (summation of 7 congeners) at stations close to the estuary mouth (HI14, HS10, HS11).

Spatial and Axial Distributions

The spatial and axial distribution of total PCDD, PCDF and PCB in the estuary is shown in Figures 3.28 - 3.33. The spatial and axial plots of PCDD, PCDF and PCB indicate relatively homogenous distributions with few clear patterns of concentration, in contrast with the Clyde Estuary distributions. Generally, concentrations are higher in the finer accumulated inter-tidal sediments than the coarser sub-tidal bed sediments. In the upper estuary sub-tidal PCDD and PCDF concentrations are low and show a general downstream increase. Inter-tidal sediment concentrations in the upper estuary are relatively high but in the middle estuary, approximately 25 to 40 km from Trent Falls, fall noticeably except for one sample at Salt End near to Hull. Concentrations rise again in the lower estuary possibly indicating additional anthropogenic inputs in this region known to receive significant inputs from chemical industries situated on the south bank of the estuary.

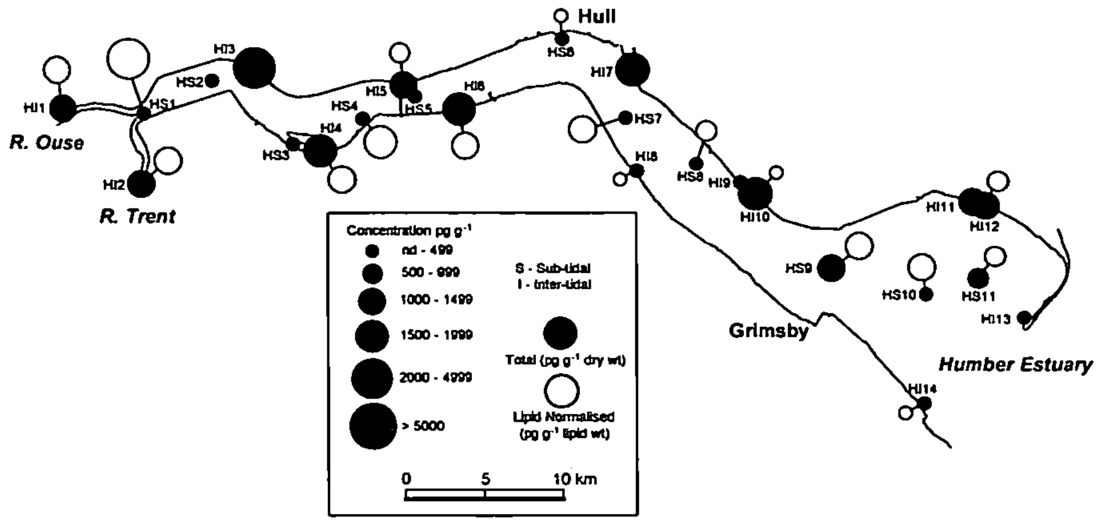


Figure 3.28. Spatial Distribution of PCDD in the Humber Estuary.

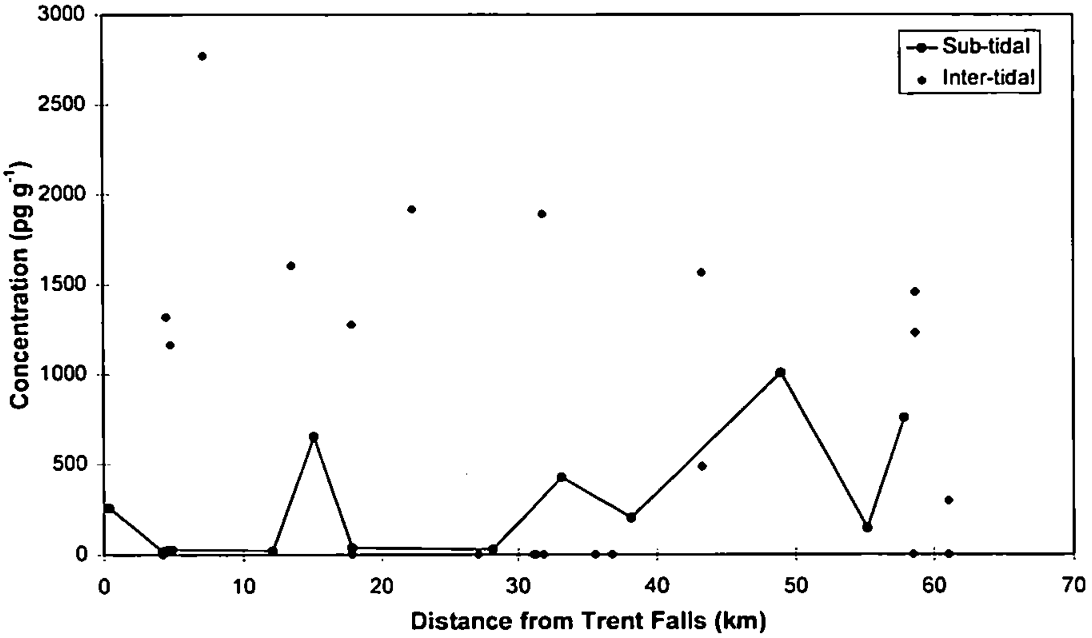


Figure 3.29. Axial Distribution of PCDD in the Humber Estuary

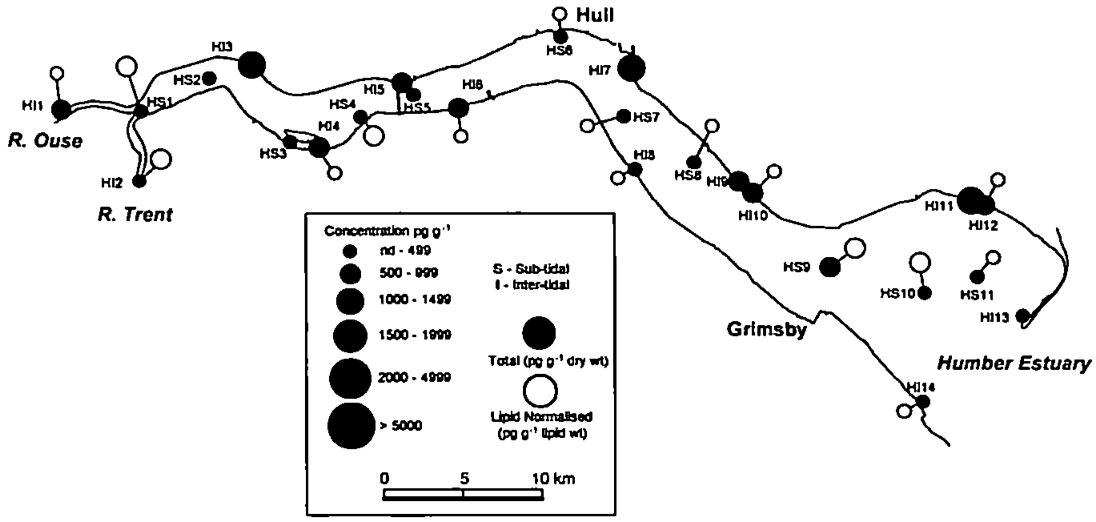


Figure 3.30. Spatial Distribution of PCDF in the Humber Estuary.

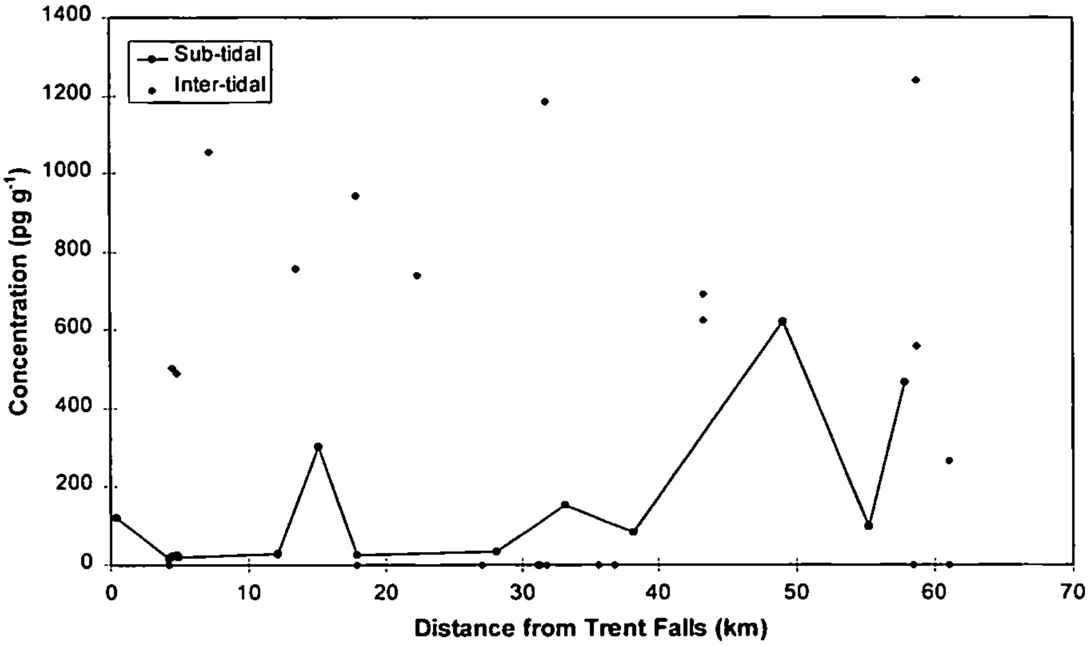


Figure 3.31. Axial Distribution of PCDF in the Humber Estuary

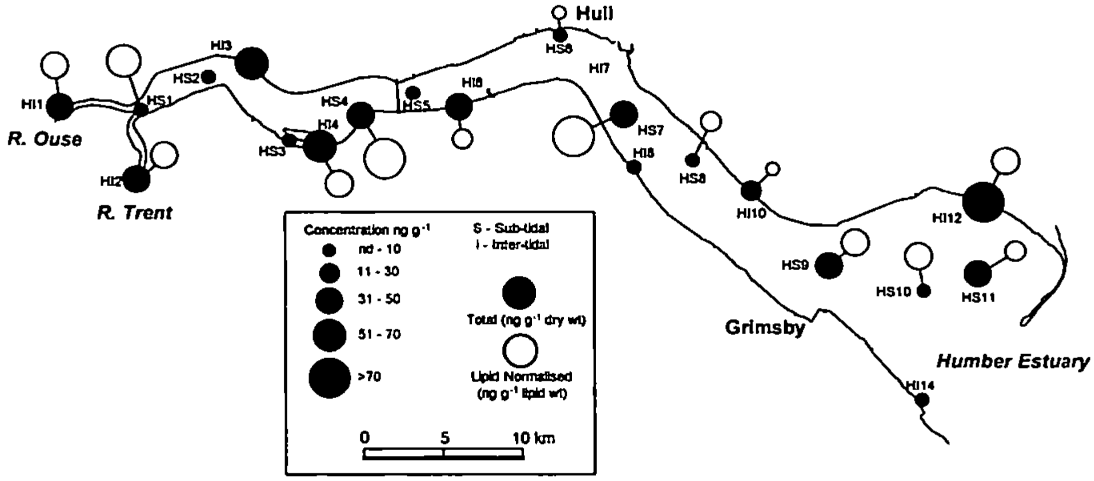


Figure 3.32. Spatial Distribution of PCB in the Humber Estuary

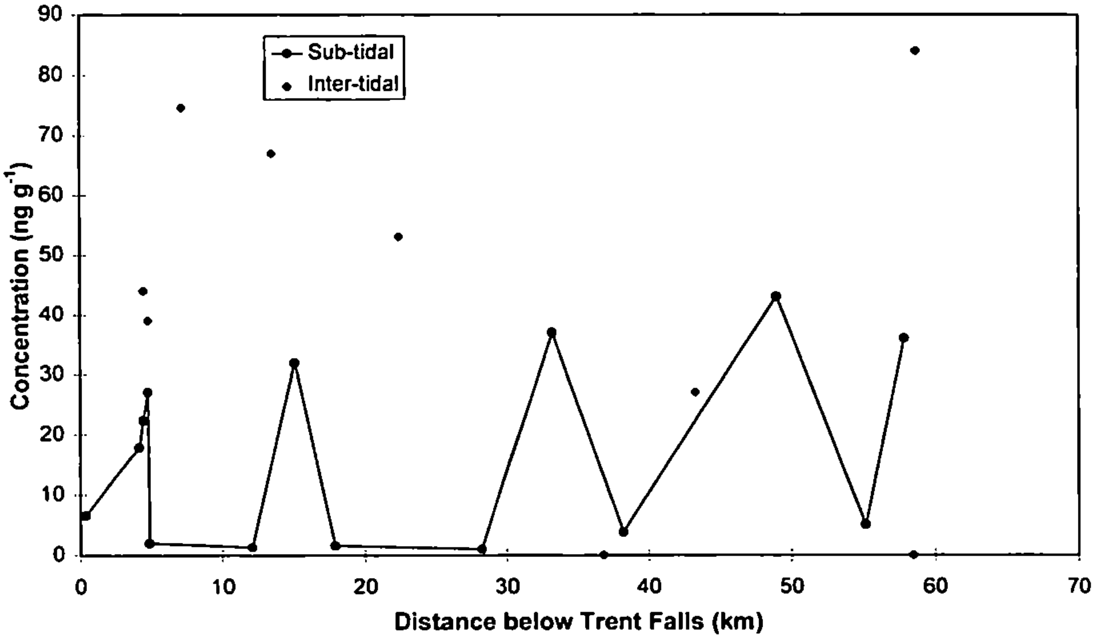


Figure 3.33. Axial Distribution of PCB in the Humber Estuary

Suspended Sediment Samples

In addition to bed samples, suspended sediment samples were analysed for PCDDs, PCDFs and PCBs. Suspended sediment represents a major transport pathway for such hydrophobic contaminants and is an important determinant in transport studies. Considerable problems are apparent in collecting sufficient suspended sediment for analysis whilst avoiding gross contamination. Difficulty was encountered in achieving analytical detection limits. From 9 samples analysed, PCDD/PCDF congeners could only be quantified in 4 samples. In these samples only 2,3,7,8 TCDD (3 - 4 pg g^{-1}) and 1,2,3,4,6,7,8 HpCDD (14 - 20 pg g^{-1}) were detected. These concentrations are similar to bed sediment concentrations and although the data should be treated with caution, there is an indication that the suspended sediment adsorbed dioxin is probably derived from resuspended bed sediment. Further work in this important area is required using suitable bulk filtration techniques to obtain more material for accurate quantification of all major congeners.

3.2.5 Covariation Between PCDD, PCDF and PCB

The covariation between PCDD and PCDF, and PCDD/PCDF and PCB has been examined. Some covariation might be expected between PCDD and PCDF as most sources of dioxin contain both dioxin and furan congeners. A correlation between PCDD/PCDF and PCB may also be expected where there is a commonality in sources, for example a mixed waste effluent or PCBs which are co-contaminated with PCDD/PCDF (Tanabe, 1988).

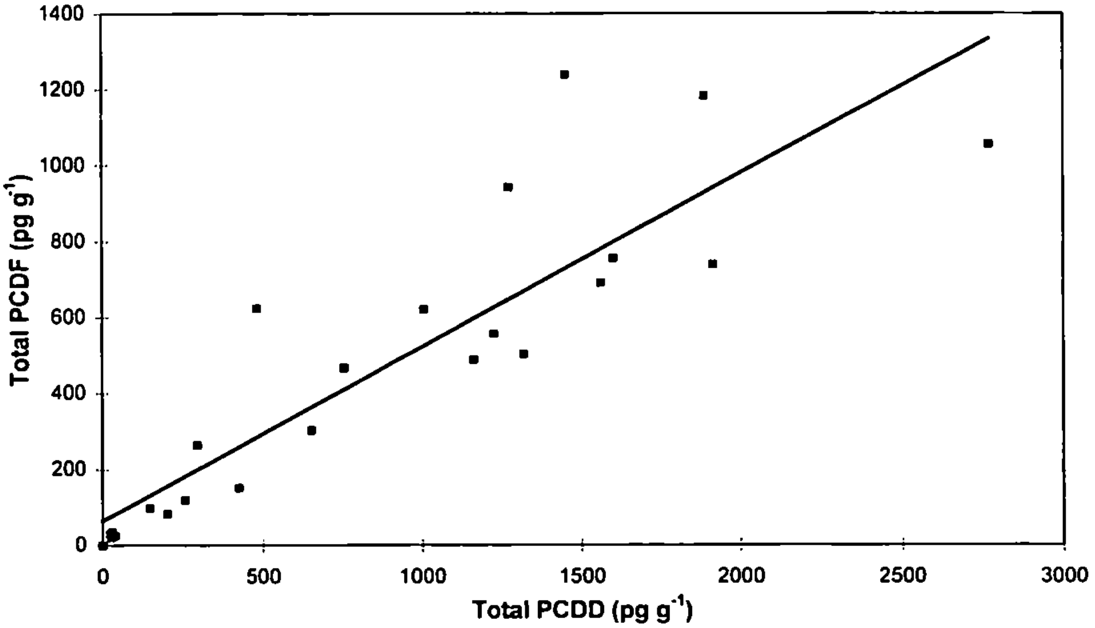


Figure 3.34. Correlation between Total PCDD and Total PCDF in the Humber Estuary (r^2 = 0.79)

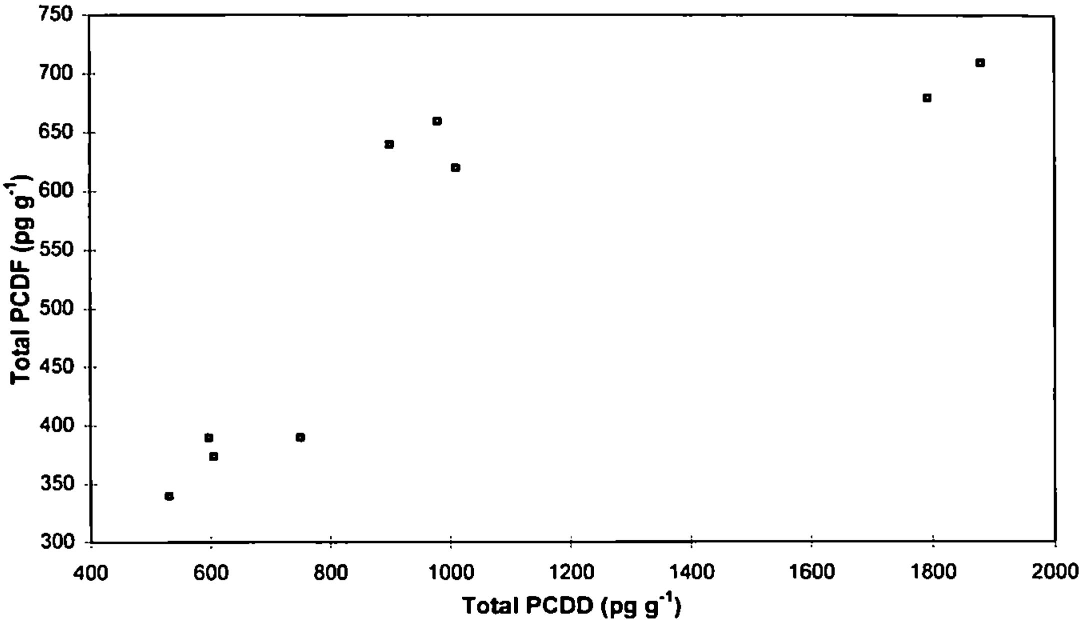


Figure 3.35. Correlation between Total PCDD and Total PCDF in the Dee Estuary

A positive linear correlation (r^2 = 0.79) was found between Total PCDD and Total PCDF in the Humber Estuary (Figure 3.34). In the Dee Estuary there was also a positive correlation with some non-linearity in the relationship (Figure 3.35). The Clyde Estuary showed no significant correlation between Total PCDD and Total PCDF.

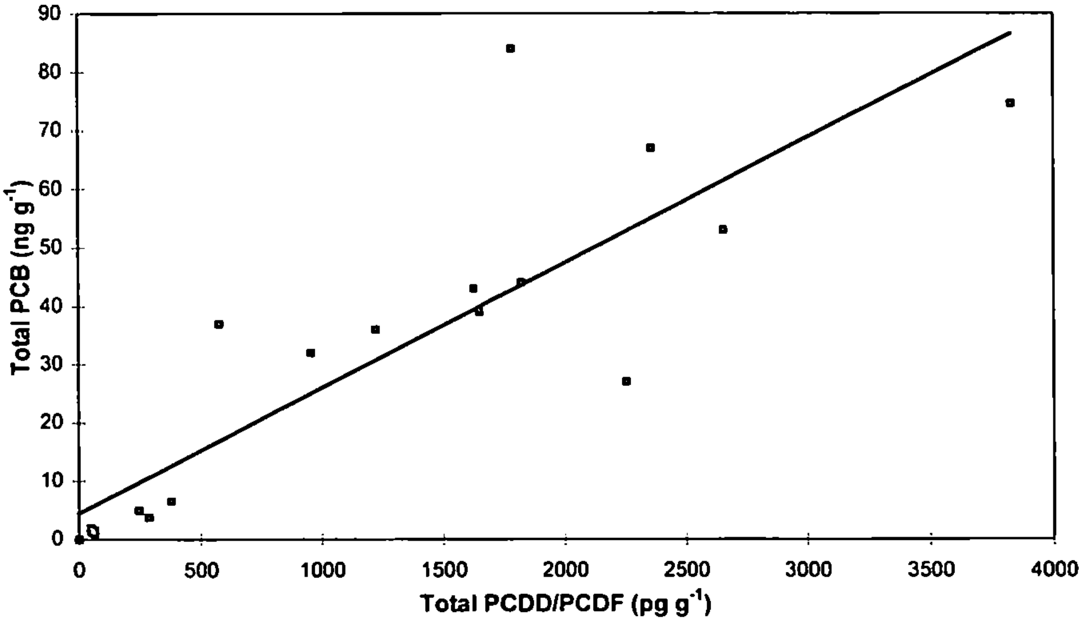


Figure 3.36 Correlation between Total PCDD/PCDF and Total PCB in the Humber Estuary (r^2 = 0.76)

A positive correlation (r^2 - 0.76) between Total PCDD/PCDF and Total PCB was found in the Humber (Figure 3.36) but again there was no significant correlation in the Clyde Estuary. In the Dee Estuary some non-linear correlation is observed but negatively correlated (Figure 3.37).

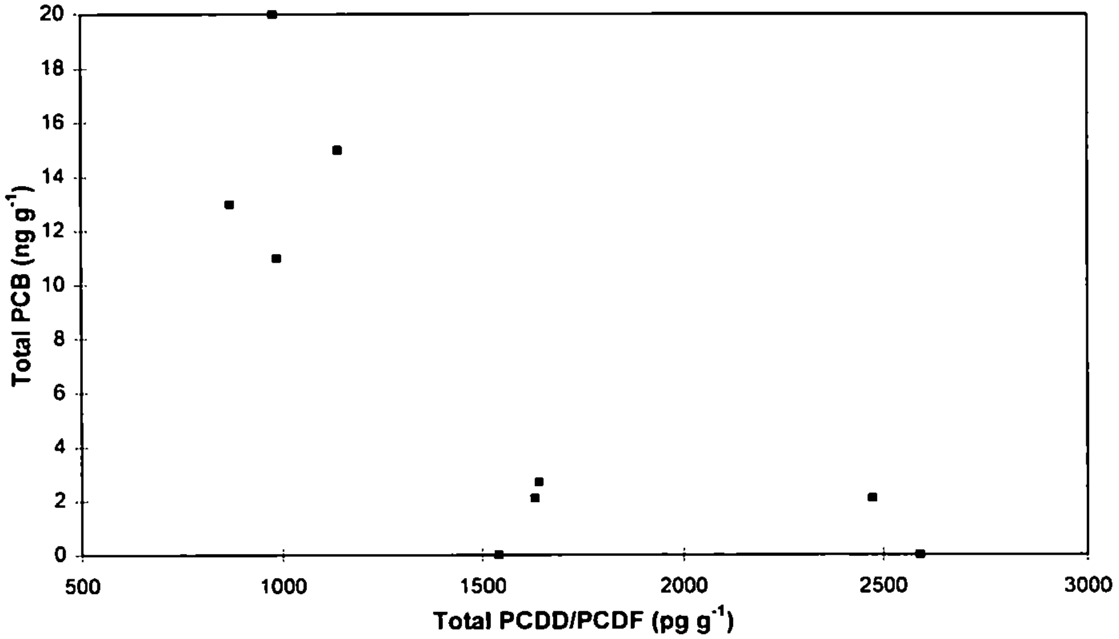


Figure 3.37. Correlation between Total PCDD/PCDF and Total PCB in the Dee Estuary

The cases where positive correlation has been found probably suggest that the dominant source(s) contain both PCDD and PCDF in a relatively constant ratio. This is further examined in Chapter 4 where PCDD:PCDF ratios are examined. In the Clyde Estuary, the ratios vary significantly possibly indicating multiple sources contributing to the contamination. The correlation between PCDD/PCDF and PCB in the Humber may be indicative of PCB co-contamination with PCDD/PCDF but is more likely due to the sorption properties of sediments which would preferentially adsorb both PCB and PCDD/PCDF. This is discussed in detail in Chapter 4. The inverse correlation observed between PCB and PCDD/PCDF in the Dee indicates independent sources for these contaminants. It should be noted however, that the number of samples is probably too small to draw firm conclusions.

3.3 Summary

Table 3.5 summarises the concentrations of OCs measured in estuary and coastal sediments. A summary of reported concentrations from other reported work for the same sites is also presented together with results from other comparative surveys in estuaries and shelf seas in Europe and the USA. The general summary from this comparison is that UK estuaries and coastal waters are not heavily contaminated with PCBs, PCDDs and PCDFs. The concentrations in estuaries are above those recorded for shelf seas and are somewhat higher than values established as 'background' for coastal waters. However, the contamination of estuary sites falls well below that recorded for estuaries such as the Hudson River and coastal regions such as Chesapeake Bay.

Compound	Estuary/coastal Environment	Concentration	Reference
Total PCDD/PCDF	Barents Sea	23 - 103 pg g^{-1}	Oehme *et al.*, 1993
PCDD/PCDF TEQ	Barents Sea	0.31 - 1.1 pg g^{-1}	Oehme *et al.*, 1993
2,3,7,8-TCDD	Hudson River, USA	n.d. - 21000 pg g^{-1}	Bopp *et al.*, 1991
2,3,7,8-TCDD	Hudson River, USA[1]	120 - 260 pg g^{-1}	Bopp *et al.*, 1991
Total PCDD/PCDF	N.E. USA estuaries	~2000 - ~30000 pg g^{-1}	Norwood *et al.*, 1989
Total PCDD/PCDF	Rhine estuary	0.2 - 18 ng g^{-1}	Evers *et al.*, 1988
Total PCDD/PCDF	Rhine estuary[2]	2350 - 4736 pg g^{-1}	Evers *et al.*, 1993
Total PCDD/PCDF	Wester Scheldt[2]	1146 - 1541 pg g^{-1}	Evers *et al.*, 1993
PCDD/PCDF TEQ	Netherlands estuaries	10 - 5180 pg g^{-1}	Turkstra & Pols, 1989
Mean PCDD	Fukuoka, Japan	11000 pg g^{-1} (rivers) 7600 pg g^{-1} (offshore)	Ohsaki *et al.*, 1997
Mean PCDF	Fukuoka, Japan	1300 pg g^{-1} (rivers) 980 pg g^{-1} (offshore)	Ohsaki *et al.*, 1997
Total PCDD/PCDF	N. North Sea	443 - 1406 pg g^{-1}	Oehme *et al.*, 1993
PCDD/DF TEQ	N. North Sea	5.5 - 17.2 pg g^{-1}	Oehme *et al.*, 1993
Total PCDD/PCDF	Humber estuary[2]	1846 - 10557 pg g^{-1}	Evers *et al.*, 1993
Total PCDD/PCDF	UK coastal sites	31 - 1140 pg g^{-1}	This work
Total PCDD/PCDF	Humber estuary	< n.d. - 3827 pg g^{-1}	This work
2,3,7,8-TCDD	Humber estuary	< 0.2 - 20.2 pg g^{-1}	This work
PCDD/DF TEQ	Humber Estuary	1 - 38.9 pg g^{-1}	This work
Total PCDD/PCDF	Clyde estuary	< 48 - 13324 pg g^{-1}	This work
2,3,7,8-TCDD	Clyde estuary	< 0.5 - 28 pg g^{-1}	This work
PCDD/DF TEQ	Clyde estuary	< 1.6 - 60 pg g^{-1}	This work
Total PCDD/PCDF	Dee estuary, Wales	870 - 2590 pg g^{-1}	This work
2,3,7,8-TCDD	Dee estuary, Wales	2 - 4 pg g^{-1}	This work
PCDD/PCDF TEQ	Dee estuary, Wales	10 - 23 pg g^{-1}	This work
Total PCB	Hudson River, USA	~10 μg g^{-1}, Aroclor 1254	Bopp *et al.*, 1982
Total PCB	Mohawk River, USA[2]	380 ng g^{-1}, Aroclor 1254	Bopp *et al.*, 1982
Total PCB	Chesapeake Bay, USA[3]	70 ng g^{-1}, Aroclor 1254	Bopp *et al.*, 1982
Total PCB	San Francisco Bay, USA[4]	30 ng g^{-1}, Aroclor 1254	Bopp *et al.*, 1982
PCBs	W. Mediterranean[1,5]	1.7 - 16.6 pg l^{-1}	Dachs *et al.*, 1997
PCBs	Humber Plume[5]	2.92 - 19.07 ng g^{-1}	Klamer & Fomsgaard, 1993
Total PCB	Clyde estuary	< 1 - 3000 ng g^{-1}	This work
Total PCB	Humber estuary	< 1 - 84 ng g^{-1}	This work
Total PCB	Dee estuary, Wales	< 1 - 20 ng g^{-1}	This work
Total PCB	Dee estuary, Wales	< 1 - 45000 ng g^{-1}	Law *et al.*, 1991

Table 3.5. Reported OC concentrations in estuaries and coastal plumes.(Surficial Bed Sediments except [1]SPM, [2]<63μm fraction, [3]0-5 cm, [4]0-10 cm, [5]Sum of 12 congeners)

Chapter 4. Controls on Estuarine Distribution of Organochlorines

4. Controls on Estuarine Distribution of Organochlorines

Based on the OC distributional data reported in Chapter 3, this chapter examines the data in the context of the controlling factors which influence occurrence. The 'fingerprint' of samples is compared between sites and against standard samples as an indication of source. The behaviour of individual compounds is examined to determine how the physicochemistry of the compound may influence patterns of distribution. Sediment characteristics determined during the sample analysis are then presented and a detailed examination of the relationship between adsorbed OCs and the solid phase is conducted. The result of this detailed examination provides the basis for a geochemical interpretation of environmental occurrence at the study sites as well as forming the basis for distributional modelling.

4.1 Controls of Distribution

In Chapter 1 there was a detailed review of factors which are influential in determining distribution. These may be summarised as three major controls on the distribution of chlorinated organics in the environment;

4.1.1 Sources

The sources of OCs are an obvious control on distribution. Chlorinated organic compounds enter the environment via both direct e.g. chemical manufacturing, accidental spillage (Clement *et al.*, 1989; Hagenmaier *et al.*, 1986; Turkstra & Pols, 1989) and diffuse sources e.g. atmospheric deposition, terrestrial run-off (Bumb *et al.*, 1980; Halsall *et al.*, 1993). PCBs have not been manufactured in the UK since 1976 so direct sources tend to be limited to accidental spillage e.g. during decommissioning of industrial equipment using PCBs. PCDD/PCDFs are unwanted by-products of manufacturing and combustion processes and as such, often enter the environment via diffuse sources such as road run-off and atmospheric deposition. Overall, atmospheric deposition is the primary diffuse source to the marine environment (Rappe 1992b). Although PCDD/PCDFs are not manufactured, their formation through different reaction pathways result in distinctive patterns in their homolog groups and congener profiles. These patterns can be used to identify potential sources (Swerev and Ballschmiter, 1989).

4.1.2 Compound Chemistry

The physical chemistry of organic compounds is a fundamental determinant of their behaviour once released into the marine environment. The families of PCB and PCDD/PCDF compounds span a wide range of physicochemical properties. For example, the polarities of PCBs expressed as log K_{ow} values range from 5.15 (2,4-DiCB) to 9.6 (decachlorobiphenyl) (Erickson, 1986). Although PCBs and PCDD/PCDFs are typically presented as summations of their individual compounds or even on a toxicity normalised basis (Kutz *et al.*, 1988), when in the environment they behave as individual compounds. With long environmental residence times in marine sediments this can become an important factor in understanding their distribution.

4.1.3 Sorbent Physicochemistry

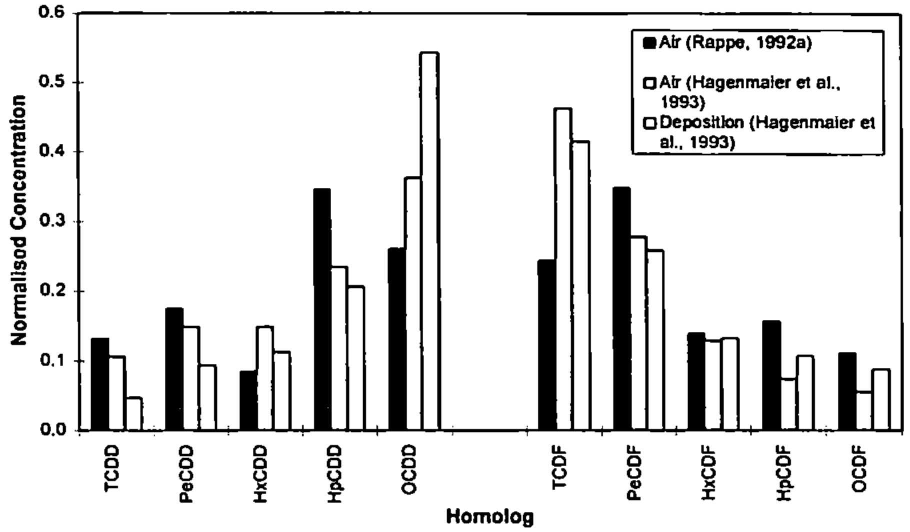
Numerous studies of contaminant reactivity in the marine environment have stressed the importance of sorbent physiochemistry in determining sorption preferences (Broman *et al.*, 1991; Delbeke *et al.*, 1990; Duinker, 1986; Grathwohl, 1990; Murphy *et al.*, 1994; Preston & Al-Omran, 1989). Although theoretical sediment-water partition coefficients can be established from basic compound physicochemistry it is found in practice that these can be significantly modified by the nature of the sorbent. Estuarine systems commonly contain a wide range of sediments varying from coarse mineral particles, usually of marine origin to fine organic rich particles from fluvial origins. In industrialised estuaries, natural particles may be modified by anthropogenic inputs, such as high organic loads from domestic sewage works and acid-iron wastes from metal processing plants.

4.2 Source Related Distribution

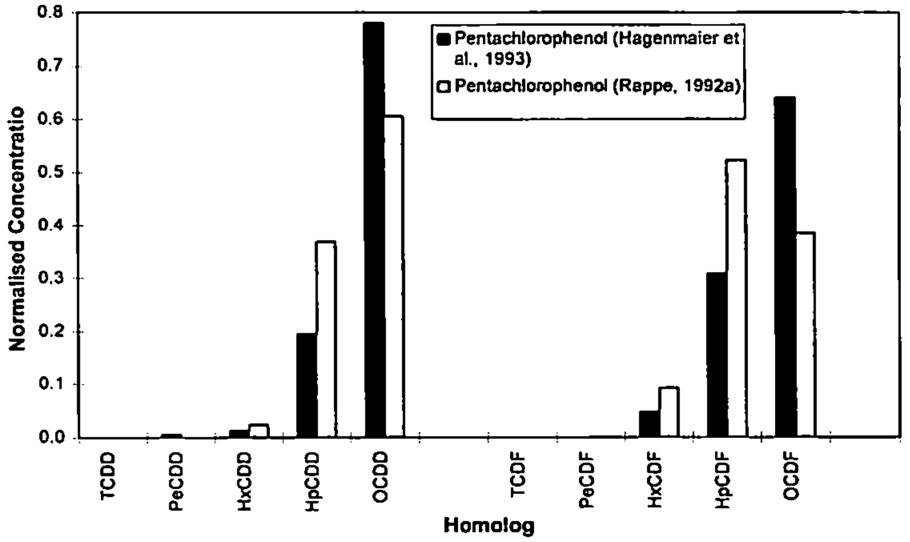
PCDDs and PCDFs arise from a number of well characterised sources including incineration, domestic fires, vehicle exhausts, chemical manufacturing processes involving use of chlorine, and sewage sludge. Under certain conditions it is possible to elucidate the source of dioxins found in environmental samples by comparing their homolog profiles or congener patterns with characteristic source 'fingerprints' (Fattore *et al.*, 1997; Näf *et al.*, 1992; Swerev & Ballschmiter, 1989). There are a number of indicators which can be used in assessing sources;

- The profile of the homologs
- The PCDD:PCDF ratio
- The isomer-specific distribution of compounds of the same degree of chlorination
- The patterns of the 2,3,7,8 substituted congeners
- The general pattern of the congeners

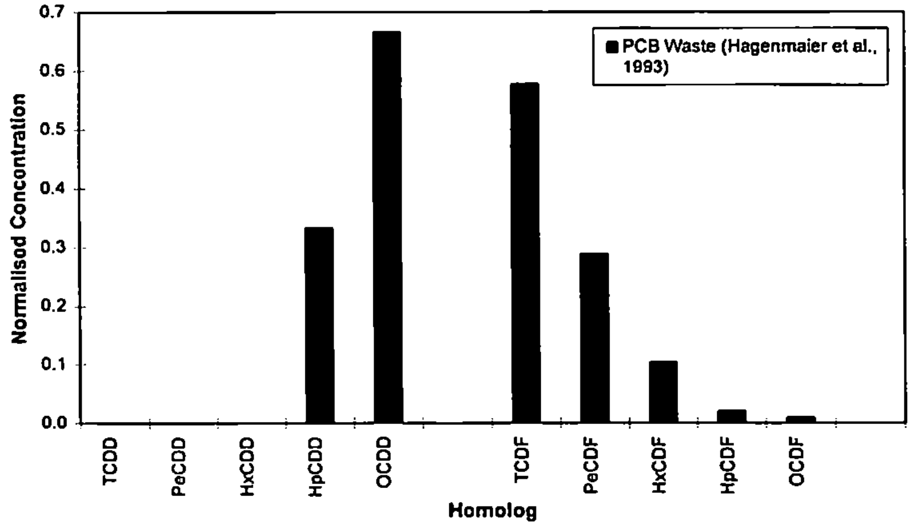
In this study homolog profiles, PCDD:PCDF ratios and 2,3,7,8 substituted congener patterns have been used for inter-comparison with published source data. PCDD and PCDF analyses have been summarised in homolog profile and congener pattern format in an attempt to determine potential sources. Concentrations of each homolog or congener have been expressed on a normalised basis by expressing as a fraction of the total PCDD or PCDF for the sample. This facilitates intercomparison between samples of differing PCDD/PCDF concentrations. It should be noted that it is not possible to inter-compare the 2,3,7,8 substituted congener patterns with the homolog profiles as the latter contain the total number of congeners in each homolog group.


Normalised Concentration
0.0
0.1
0.2
0.3
0.4
0.5
0.6
■ Air (Rappe, 1992a)
□ Air (Hagenmaier et al., 1993)
□ Deposition (Hagenmaier et al., 1993)
TCDD
PeCDD
HxCDD
HpCDD
OCDD
TCDF
PeCDF
HxCDF
HpCDF
OCDF
Homolog

a


Normalised Concentratio
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
■ Pentachlorophenol (Hagenmaier et al., 1993)
□ Pentachlorophenol (Rappe, 1992a)
TCDD
PeCDD
HxCDD
HpCDD
OCDD
TCDF
PeCDF
HxCDF
HpCDF
OCDF
Homolog

b


Normalised Concentration
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
■ PCB Waste (Hagenmaier et al., 1993)
TCDD
PeCDD
HxCDD
HpCDD
OCDD
TCDF
PeCDF
HxCDF
HpCDF
OCDF
Homolog

c

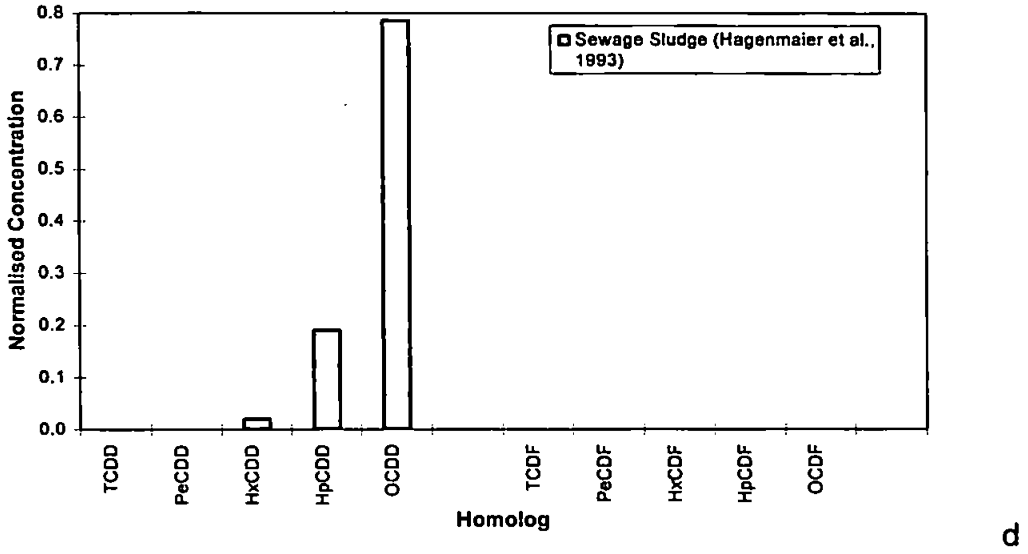


Figure 4.1 a-d. Typical PCDD/PCDF homolog profiles for a range of sources (Hagenmaier et al., 1993; Rappe, 1992a)

Figure 4.1 a-d shows homolog profiles for samples of manufacturing and combustion sources taken from published literature (Hagenmaier et al., 1993; Rappe, 1992a). Figure 4.1a shows homologs for two atmospheric air samples and an atmospheric deposition sample. Although some variation is noted, there are clear similarities between the air samples from two different sources and between the air and deposition profile. There are also similarities between the pentachlorophenol (PCP) source profiles derived from two different samples (Figure 4.1b). This observed consistency in the character of these source profiles forms the basis of the source-occurrence matching approach. Profiles derived from municipal sewage sludge and PCB waste are also presented in Figure 4.1c and d respectively.

The source-occurrence techniques cannot be applied in the same way to PCBs as these are manufactured as a mixture of congeners which give particular products a signature of PCB congeners. Theoretically this might allow individual product use to be identified but the similarity between different products and the modification of these signatures through degradation and differential environmental behaviour makes such identification impractical.

4.2.1 Atmospheric Sources

Atmospheric sources (incineration, domestic fires, vehicle exhaust) are the largest diffuse source of dioxins to the environment (Rappe, 1992b). In a comprehensive study of PCDDs and PCDFs in UK freshwater lakes and reservoirs, Rose & McKay (1996) reported atmospheric inputs as the predominant source to sediments based on homolog profile and congener pattern analysis. It is important therefore to determine the contribution of atmospheric deposition to the occurrence of chlorinated organics in the estuaries under study. This assessment has been carried out using homolog profile and congener pattern analysis comparing profiles and patterns in the samples from the study estuaries with patterns/profiles from atmospheric studies.

In an independent study conducted by the Warren Spring Laboratory (WSL) (Clayton *et al.*, 1992; Coleman *et al.*, 1997) detailed analyses were carried out on air samples collected over a 12 month period at air sampling stations at Cardiff, London, Manchester and Stevenage. Samples of both ambient air and deposited atmospheric particulates were analysed. 2,3,7,8 substituted congeners from the WSL survey have been summarised to provide a congener pattern representative of UK atmospheric samples. Initially a comparison was carried out between samples from the four sampled cities. This comparison is summarised in Figure 4.2 and shows a close similarity between each site. For the purposes of this assessment it is assumed therefore that these sites are typical for the UK and that atmospheric profiles and patterns at the estuary study sites would be similar.

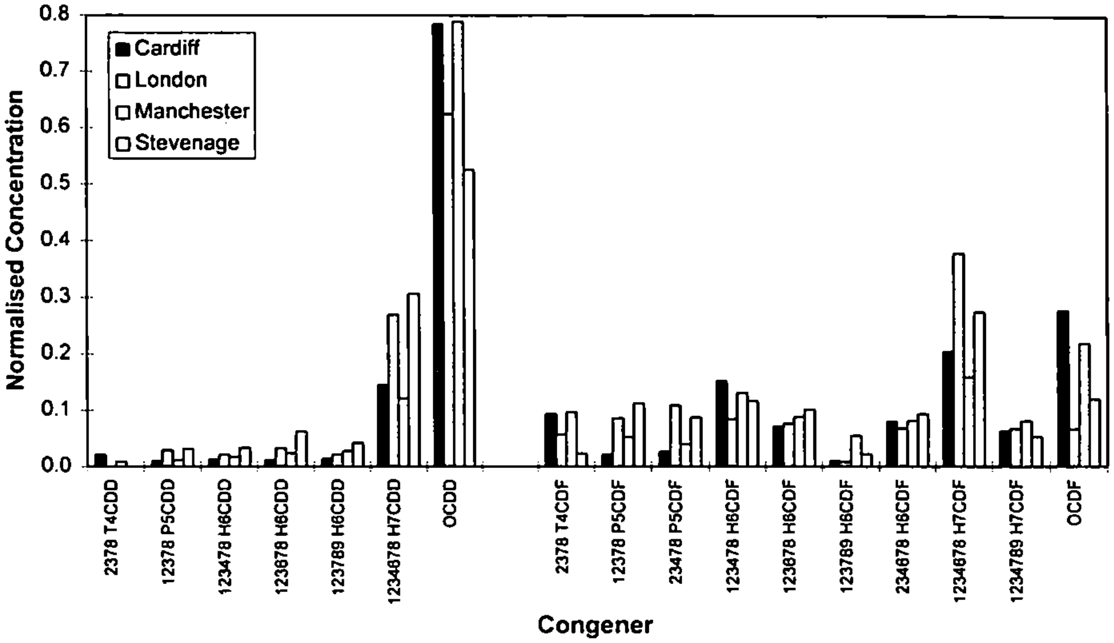


Figure 4.2 Atmospheric Sample Congener Patterns for Four UK Cities

To confirm that the patterns in atmospherically deposited particulates (a pathway for estuarine input) are similar to those in ambient air samples, a comparison between atmospheric concentrations and deposition concentrations is summarised in Figure 4.3, confirming the similar pattern of 2,3,7,8- substituted congeners in deposited and atmospheric samples.

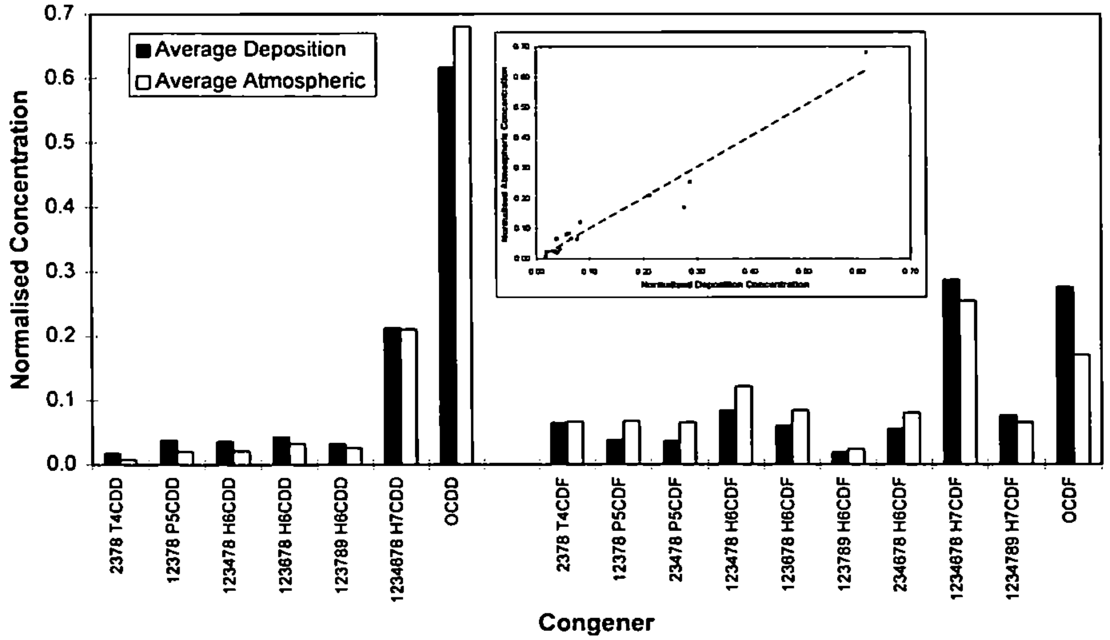


Figure 4.3. Atmospheric and Deposition Concentrations (R^2 = 0.95, p < 0.001)

On the basis of these comparisons it has been assumed that the congener patterns from the WSL survey are representative of general UK atmospheric deposition and can be reasonably compared with estuary samples collected during this study.

4.2.2 Other Sources

The other principal sources considered under this project are municipal sewage waste which is known to be discharged at some of the estuary study sites (Figure 4.1d), and the chemical manufacture or use of pentachlorophenol (Figure 4.1b) which is also carried out at one known location within the study sites. PCDD/PCDF co-contamination with PCB waste has been previously documented (Erickson, 1986; Tanabe, 1988) and a comparison profile is presented (Figure 4.1c).

4.2.3 Clyde Estuary

The Clyde Estuary showed notable variation in homolog profiles implying heterogeneity in source inputs to the estuary. The source-occurrence studies of the Clyde Estuary have concentrated on two regions where distribution studies indicate possible variations in sources. The first of these is the upper estuary region where the River Cart joins the Clyde Estuary and sewage discharges are present (see Figure 4.4). The industrial history of the Clyde estuary has resulted in a number of possible PCB and PCDD/PCDF sources in the past. A locomotive plant located 6 miles upstream of the weir at Hamilton and the Babcock dock in the River Cart both used PCBs. There are a number of historical pentachlorophenol (PCP) sources in the estuary including the Paisley sewage works and a Ministry of Defence factory located just above the weir at Dulmarnock (SEPA, pers comms). The second region of interest is in the lower estuary where a considerable increase in PCDD/PCDF concentration is observed (see Figure 4.5) in the vicinity of the Ironotter Point outfall.

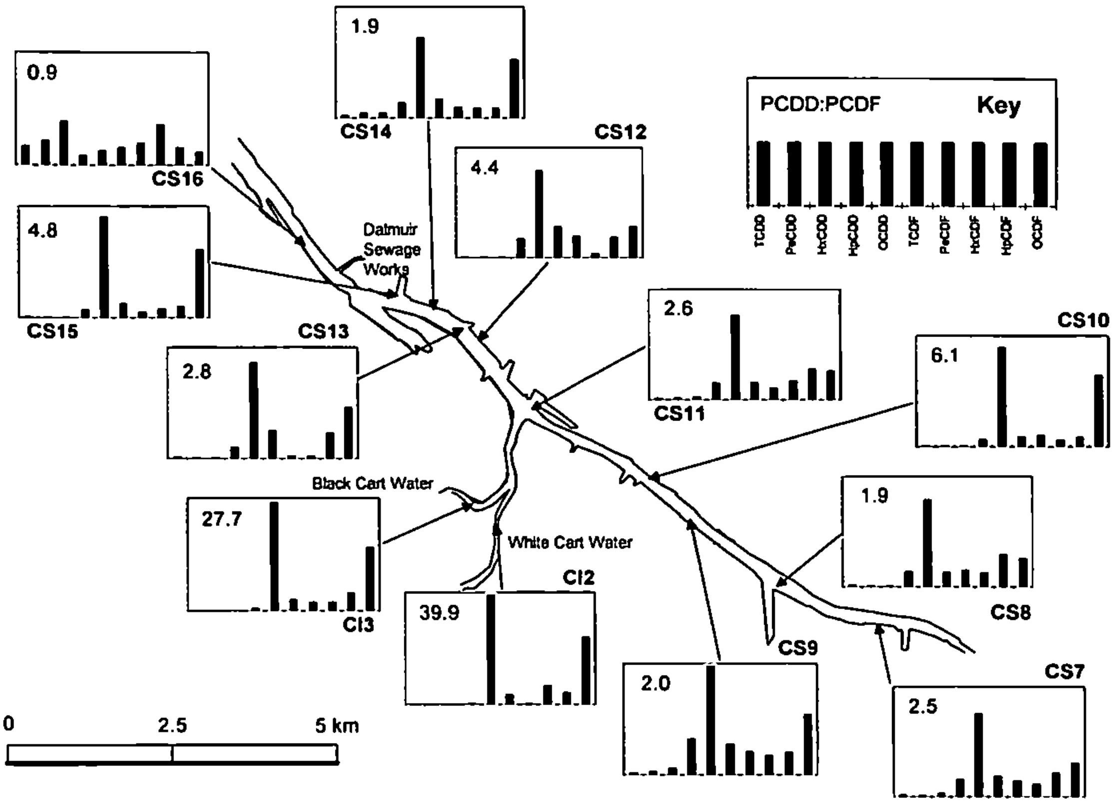


Figure 4.4. Homolog Profiles and PCDD:PCDF Ratios in the Upper Clyde Estuary

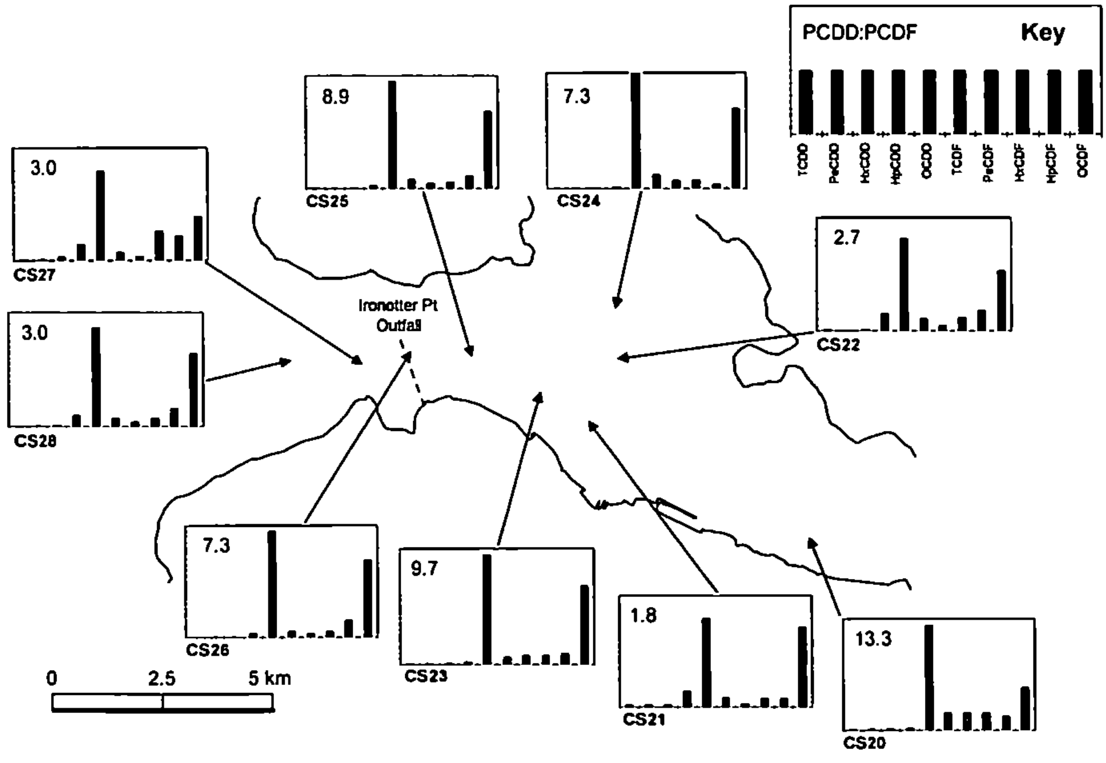


Figure 4.5. Homolog Profiles and PCDD:PCDF Ratios in the Lower Clyde Estuary

Figures 4.4 and 4.5 show homolog profiles and PCDD:PCDF ratios in the Clyde Estuary. There is a remarkable variation in PCDD:PCDF ratio in the whole estuary from 0.36 to 39.9 with an average of 5.15. This compares with a range of 0.13 - 7.71 (mean = 1.93) in the Rhine estuary where 45 samples were collected in 1984 and 1985 (Evers *et al.*, 1988), and a range of 0.42 to 2.43 (mean = 0.8) reported by Evers *et al.* (1993) for a number of estuary mouth and shelf sea locations (Wadden Sea, Ems-Dollard, Rhine, Wester Scheldt, North Sea, Humber). Compared with these other studies the profiles in the Clyde show a general dominance of higher chlorinated homologs, with dibenzodioxin concentrations usually greater than dibenzofuran concentrations. From the source signature profiles shown in Figures 4.1 a-d, this would be indicative of PCP-derived sources where hepta- and octo-homologs are dominant and municipal sewage sludge sources where dibenzofuran concentrations are relatively low and heptachlorinated dibenzodioxin and octochlorinated dibenzodioxin homologs are abundant.

Upper Clyde Estuary

In the upper estuary, shown in Figure 4.4, the variation of homolog profiles in the vicinity of the River Cart confluence is presented. Upstream of the confluence with the River Cart, homolog profiles at stations CS7 to CS11 show a general dominance of HpCDD and OCDD for the dibenzodioxins but a relatively flat profile for dibenzofurans. These profiles have similarities to the atmospheric profile in Figure 4.1a. To further confirm atmospheric sources as a major contributor to these sites, a typical Clyde estuary congener pattern has been compared to the congener patterns established as typical of UK atmospheric deposition (Figure 4.3).

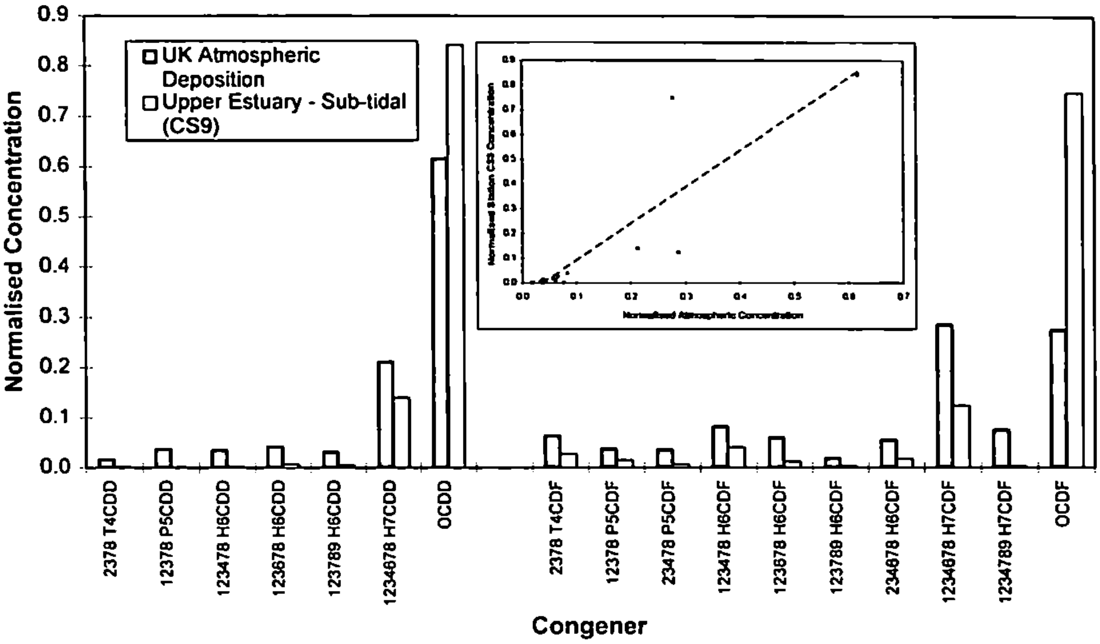


Figure 4.6. Congener Pattern in Clyde Estuary Compared With Average UK Atmospheric Deposition ($R^2 = 0.78$, $p < 0.001$)

The congener pattern in Figure 4.6 compares reasonably with the atmospheric deposition congener pattern (Figure 4.3) although OCDF is enhanced in the estuarine sample possibly indicating the interference of other sources or the relative reduction of other lower chlorinated compounds due to degradation and loss from the system (see detailed discussion later in this Chapter).

Downstream from these sites, within the White Cart Water and Black Cart Water there is a large increase in the PCDD:PCDF ratio indicating a significant increase in PCDD input in this area. Similar observations in the Rhine suggested that PCP derived inputs were responsible (Hagenmaier *et al.*, 1986). Downstream of the confluence there is some evidence, although not entirely conclusive, that homolog profiles have been modified by this input. Stations CS13 - CS15 show considerable similarity to the River Cart profiles. These observations support the previously discussed increase in concentration in this region shown in Figure 3.22 and 3.24.

Lower Clyde Estuary

There is a known sewage source in the lower Clyde Estuary at the Ironotter Point outfall which discharges into the centre of the estuary. All the homolog profiles in this region show a strong dominance of OCDD and OCDF. Several of the stations have high PCDD:PCDF ratios which may indicate additional PCDD inputs in the area. This may imply a source of municipal sewage-derived dibenzodioxins which have relatively high OCDD concentrations (see Figure 4.1d).

The signature profile of combustion-derived atmospheric inputs is not particularly strong compared with the profile in Figure 4.1a which shows a dominance of higher chlorinated dibenzodioxins and lower chlorinated dibenzofurans. In a comprehensive study of historical PCB levels in UK soils, Alcock *et al.* (1993) observed a gradual shift in the relative proportion of individual congeners with time. In the most recent samples, a greater proportion of higher molecular weight homolog groups was observed. Czuczwa & Hites (1986) also noted that environmental samples show a bias towards the OCDD congener whereas combustion sources are generally more evenly distributed. Rappe (1992a) suggested that photochemical degradation of lower chlorinated species and photochemical formation of higher chlorinated dioxins may enhance HpCDD and OCDD in the atmosphere thus altering atmospherically deposited profiles.

The modification of homolog profiles may be explained by two factors. Chlorinated organic compounds do not all have the same degradation potential or degradation pathways. Higher chlorinated congeners are less susceptible to oxidative transformation (Adriaens *et al.*, 1995). However, reductive chlorination is an identified pathway that has been observed for chlorinated organics which would tend to remove higher chlorinated compounds (Abramowicz *et al.*, 1993; Adriaens *et al.*, 1995). The pathway and extent of degradation will be dependent on the presence of the microbial population (Kobayashi & Rittmann, 1982) which is likely to be highly variable in an estuary where both aerobic and anaerobic conditions exist. The modification of homolog profiles of environmental samples over time is highly likely. Prediction of exactly how profiles will change with time is difficult and is likely to vary spatially within an estuary.

The second factor, differential transport, is more complex and is discussed in greater detail later. The homologs represent a wide range of chemical compound properties with the lower chlorinated, more polar compounds, having lower solubilities, binding preference and a higher volatilisation potential. Loss of lower chlorinated compounds from bed sediments by dissolution and volatilisation will therefore alter the profiles.

The long residence time of sediments within estuary systems inevitably leads to significant biogeochemical modification of the signature profiles. It is likely that only samples taken in close proximity to major point sources would provide enough evidence to allow unequivocal identification of a specific source.

4.2.4 Dee Estuary

Figure 4.7 presents the homolog profiles for the Dee estuary. The most striking observation is that the homolog profiles are almost identical. Furthermore, PCDD:PCDF ratios only vary from 1.4 - 2.6 with a mean of 1.8 ± 0.48. These ratios are similar to those reported by Evers *et al.* (1988) in the Rhine estuary, 1.93 ± 1.66.

The homogeneity in the profiles may be explained by the relatively dynamic conditions in the Dee estuary which result in sediment re-working and mixing of sediments of different origins (BMT, 1990; Turner & Millward, 1994). It may also indicate that the sources to the estuary are predominately diffuse and relatively uniform over the entire system. This would imply atmospheric deposition as the major source to the estuary.

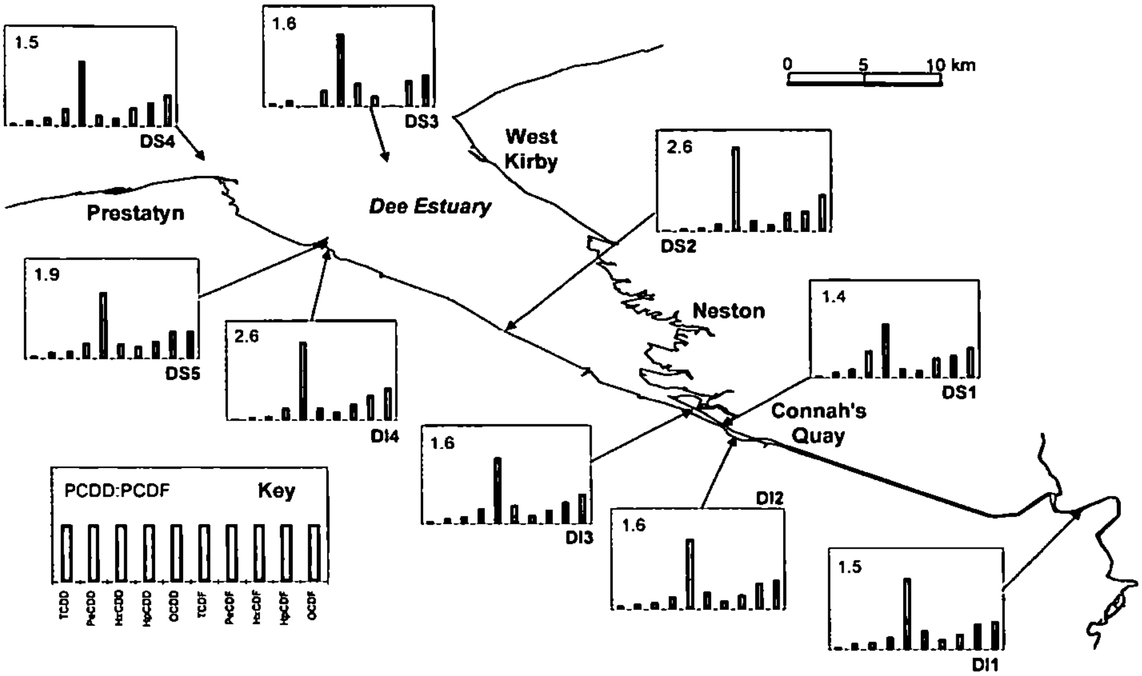


Figure 4.7. Homolog Profiles and PCDD:PCDF Ratios for the Dee Estuary

It is difficult to form any firm conclusions on the source of PCDD and PCDF to the estuary. The profiles are flatter than those observed in the Clyde possibly indicating an atmospheric source. However, the lower chlorinated dibenzofurans characteristic of atmospheric aerosols are not present in the profiles. This may well be due to aquatic degradation and transportation processes selectively removing the lower chlorinated compounds. There is no evidence of any PCB derived sources (reported in Law *et al.*, 1991) but this is unsurprising given that the industrial source was located well upstream in the river and the sediment re-working evident in the estuary.

4.2.5 Humber Estuary

The homolog profiles for the Humber Estuary are plotted in Figure 4.8. PCDD:PCDF ratios range from 0.73 to 2.8 with an average of 1.86 comparing closely with ratios in the Dee estuary. The homogeneity in PCDD:PCDF ratios is also consistent with the Dee and in contrast with the Clyde. There are less discernible trends in the homolog profiles than in the Clyde. Most show dominance of higher chlorinated dioxin homologs with a more even distribution of furan homologs.

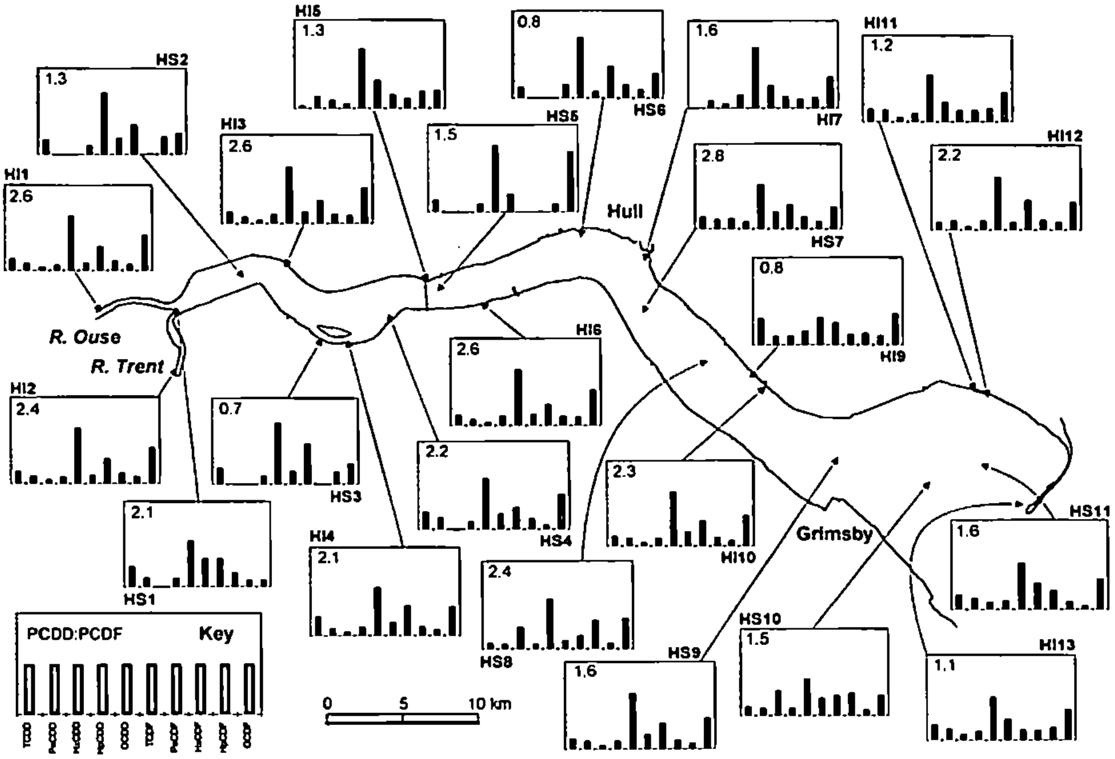


Figure 4.8. Homolog Profiles and PCDD:PCDF Ratios for the Humber Estuary

Although there is significant industry located on the Humber Estuary, there are no established significant OC sources to the estuary. The only exception is a well publicised source of dioxins well upstream of the estuary reported in the Public Register which indicated PCDD/PCDF concentrations up to 64000 pg g^{-1} TEQ in sediments of a tributary of the River Rother sampled in October 1991. In 1993 the concentrations in these sediments close to the Coalite Chemicals chlorophenol facility at Bolsover ranged from 5144 to 45311 pg g^{-1} TEQ. None of the profiles in Figure 4.8 corresponds with the characteristic PCP homolog profile shown in Figure 4.1b. A detailed study of the sediments of the River Doe Lea (which received the PCP plant discharge) was carried out under this study. Source-occurrence pattern matching to source samples was conducted as well as geochemical investigations. The results of this work remain *sub judice* and unfortunately cannot therefore be reported.

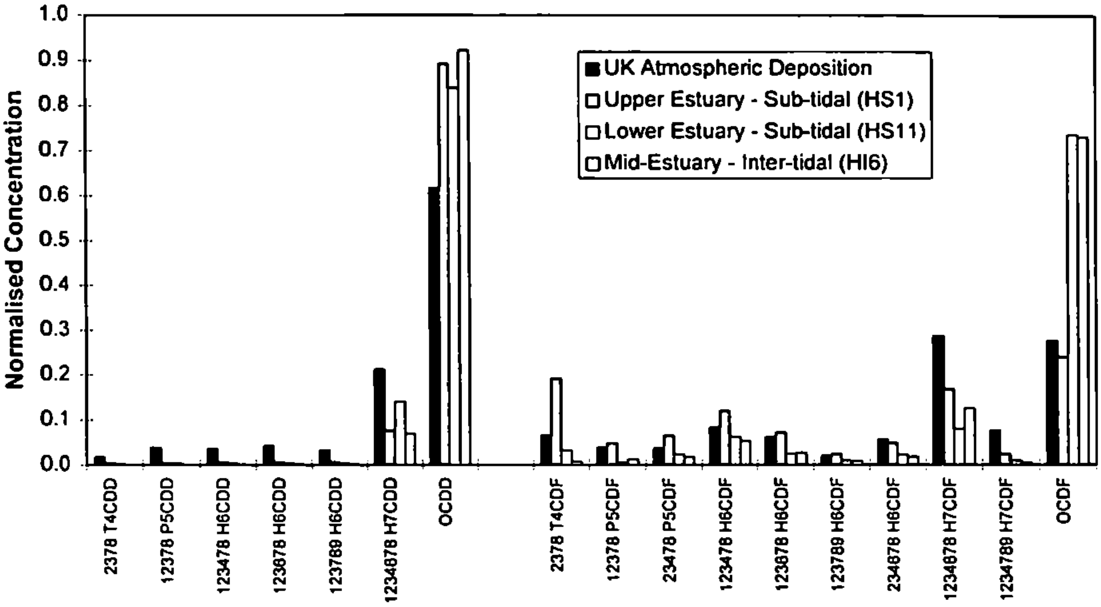


Figure 4.9. Congener Patterns in Humber Estuary Compared With Average UK Atmospheric Deposition

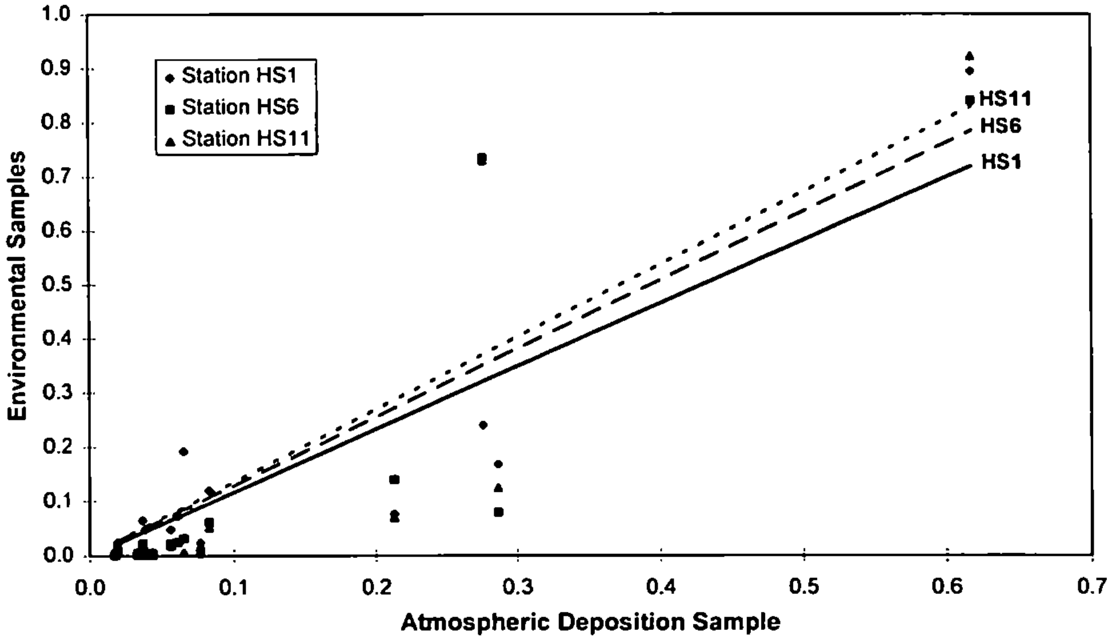


Figure 4.10. Correlation Between the Normalised Concentrations of Environmental Samples and Average UK Atmospheric Deposition Sample (R^2 Range = 0.73 - 0.83, p = <0.001)

Overall it is possible that the Humber PCDD/PCDF load is predominately atmospherically derived. It is likely that point sources do exist but these are readily masked by the dynamic mixing conditions within the estuary. Further confirmation is provided by congener pattern analysis of samples at various locations within the estuary and shown in Figure 4.9 and 4.10.

The predominance of atmospheric deposition as the major source of PCDD and PCDF to the Humber Estuary is understandable when considering the extent of urbanisation in the region and the large number of emitting industrial sources.

4.2.6 Use of Source-Occurrence Matching in Estuaries

This study has permitted an analysis of homolog profiles and congener patterns for environmental samples and comparison with source-derived profiles/patterns. The profiles in the Humber and Dee estuaries indicate the homogeneity that can exist in a dynamic estuary where source-related effects are rapidly masked by the redistribution of impacted sediments. In the Clyde, under more quiescent conditions, some indication of point sources can still be elucidated although not unequivocally. The long retention time for estuarine sediments allows degradation and other loss mechanisms (e.g. volatilisation, dissolution) to selectively remove compounds on the basis of their physicochemical properties.

It is suggested that the application of these largely qualitative source-occurrence techniques must be used with caution in estuarine environments. Where a strong point source exists, environmental samples taken in the near vicinity may permit the source to be relatively unambiguously identified (Jonsson *et al.*, 1993). Further from the source, or in dynamic mixing conditions, it is unlikely that such identification would be possible. The application of more sophisticated quantitative multivariate techniques (Näf *et al.*, 1992) is not considered justifiable in these circumstances where multiple, predominately diffuse sources are likely, and samples represent a significant time history of inputs.

4.3 Compound Chemistry

The physical chemistry of organic compounds is a fundamental control on their behaviour in the environment (Duinker, 1986; Larsson, 1983; Mackay, 1991). In considering the controls on particulate sorbed hydrophobic organic compounds, the K_{ow} provides an excellent 'catch-all' property which is universally used in the study of organic compound behaviour (Lyman, 1982). The relationship between K_{ow} and chemical structures is more complex but in general terms, high molecular mass compounds (e.g. PCBs, dioxins, furans) will have a high aromaticity, high apolarity, low solubility, small Henry's Law constant (therefore low volatility) and high lipophilicity. In the environment this translates to a high binding potential to particles, high biouptake and bioaccumulation potential and probably a resistance to degradation.

Although they may all be classed as high molecular mass compounds, within the families of PCB, PCDD and PCDF compounds there is a wide range of K_{ow} values. These are summarised in Tables 1.1 and 1.2. Solubilities, for example, range from 0.019 mg l^{-1} for 2,3,7,8-TCDD to 0.00074 mg l^{-1} for OCDD. For the PCBs, solubilities range from 1.4 mg l^{-1} for 2,4-DiCB to 0.007 mg l^{-1} for 2,2',3,3',4,4',5,5'-OCB. Within these families, the degree of chlorination is the major determinant of aromaticity. The other significant influence is the position of the chlorines on the benzene rings.

4.3.1 Implications for Behaviour in an Estuary

Both PCBs and PCDD/PCDFs enter the environment as a mixture of compounds. In the case of PCBs, this is usually in the form of a manufacturer prepared technical mixture which has been specifically engineered for an application. For dioxins and furans, as seen in the previous section, the source will tend to produce a characteristic mixture of compounds. Once in the environment, these compounds will behave independently of one another and their environmental transport and fate will reflect their individual compound properties. Although this is well understood in many contaminant studies, the focus in studies of chlorinated organics is often on the family as a whole (e.g. analysis conducted and reported against a reference technical mixture in the case of PCBs).

A number of observations might be expected in an estuary based on the range of physical chemistry encountered in these groups of compounds. The lower chlorinated congeners would be expected to volatilise more readily and to solubilise more easily. They would therefore be expected to disperse more readily in the environment. The higher chlorinated compounds would be expected to bind more efficiently to sediments and be more resistant to degradation and therefore persist longer. The net effect would be a shift in the relative pattern of congeners from lower chlorinated to higher chlorinated compounds over a period of time. This is demonstrated by Götz *et al.* (1994) comparing homolog profiles between dissolved and SPM samples. The dissolved sample profiles showed a higher proportion of the lower chlorinated, more soluble homologs. The pattern analyses performed in the previous section for sediment samples are, in almost all cases, skewed towards higher chlorinated congeners when compared with unaltered patterns from characterised sources.

Demonstrating the hypothesised effects is more difficult. In the Clyde Estuary, the mixing of sediments is limited and a gradient is formed. Sediments contaminated in the upper estuary will move gradually down the estuary over protracted periods of time. By plotting the ratio between the lowest chlorinated homolog (TCDD/F) and the highest chlorinated homolog (OCDD/F) for PCDDs and PCDFs against distance downstream, some pattern might be evident suggesting that downstream sediments contained reduced proportions of lower chlorinated compounds i.e. the TCDD/F:OCDD/F ratio would be lower.

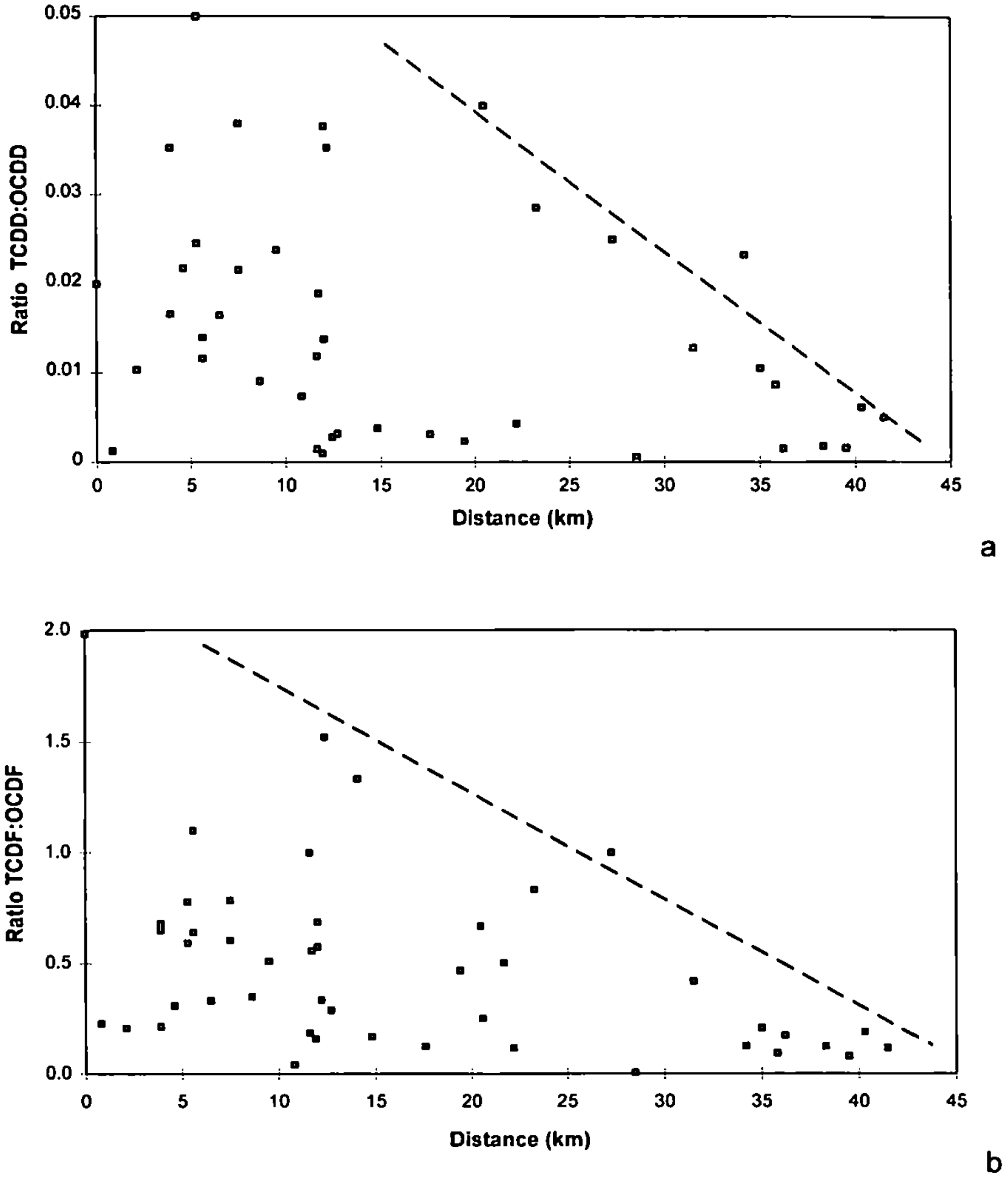


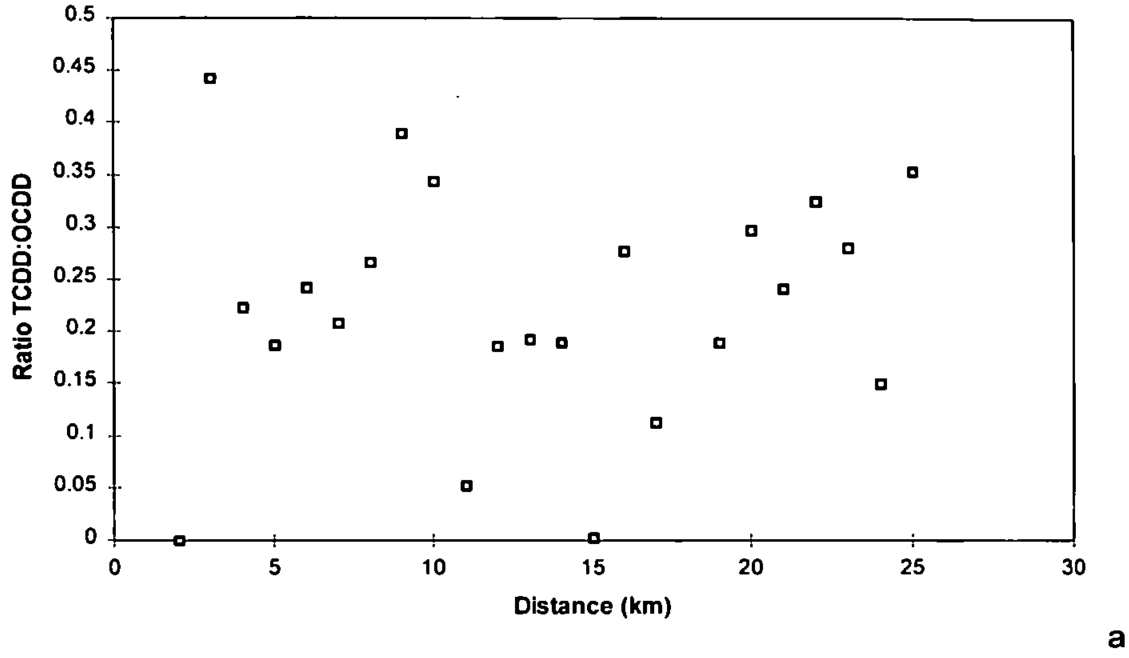
Figure 4.11. Ratio of (a) TCDD:OCDD and (b) TCDF:OCDF Concentration with Axial Distance in the Clyde Estuary (- - - - Arbitrarily Defined to Highlight Change in Ratio)

Figure 4.11 a and b show the tetra:octa-chlorinated ratios in the Clyde Estuary (there are some outlying data points for both graphs which have not been plotted and the line is hand-drawn to highlight the change in ratio with downstream distance). In the upper estuary the ratios are highly variable but in the lower estuary there is some evidence of a general reduction in ratio indicating a higher proportion of higher chlorinated compounds in this region.

Interpretation of this data is not straightforward as there are several factors which may lead to these observations. However separation of these factors based on the data analysed is not possible.

The first cause of changes in homolog ratios is the interference of individual sources. In the Clyde this has already been demonstrated where some regions, including the lower estuary, show evidence of direct source related patterns. Trying to remove these effects by normalisation against source characterised profiles might be possible in extremely well defined situations e.g. in close proximity to a known high concentration source, but in the mixed environment of an estuary the source signature is not strong enough. Degradation is another effect which will lead to an apparent change in homolog ratios (Kobayashi & Rittmann, 1982; Rappe, 1992b; Reichardt *et al.*, 1981). This is extremely complex and the degradation pathways are not well understood. Dechlorination has been shown to be a likely degradation pathway which might have the effect of removing lower chlorinated compounds but at the same time forming lower chlorinated compounds from higher chlorinated precursors (Adriaens *et al.*, 1995; Abramowicz *et al.*, 1993; Hutzinger *et al*, 1974; Rhee *et al.*, 1993). The dependence of degradation extent and pathway on a complex range of conditions including the bacterial populations in abundance prevent any form of normalisation to remove the effects of this factor (Lake *et al.*, 1992).

Demonstration of the hypothesis that differential transportation of compounds occurs in the estuary cannot be concluded from analysis of the homolog ratios. It is however interesting to compare the situation in the Humber Estuary where the sediments are highly mixed by the dynamic environment (Falconer & Owens, 1990). Figure 4.12 a and b show the ratios plotted for the Humber Estuary (excluding some outlying points). The notable differences between the pattern of TCDD:OCDD ratios in the Clyde and Humber is accounted for by the predominance of OCDD previously noted in the Clyde and attributed to source related inputs.



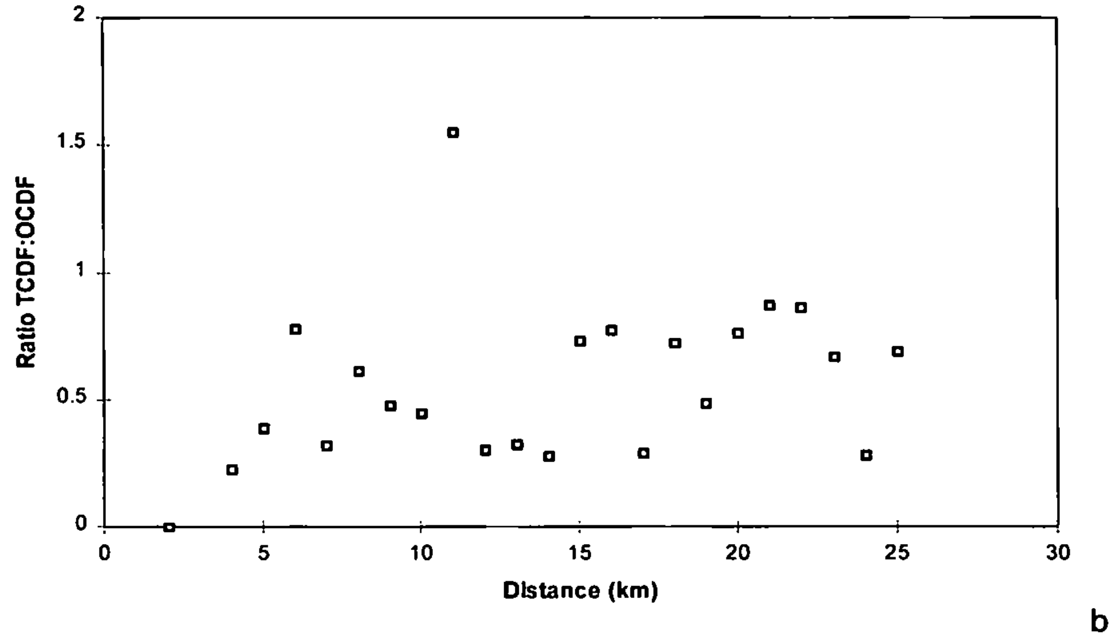


Figure 4.12. Ratio of (a) TCDD:OCDD and (b) TCDF:OCDF Concentration with Axial Distance in the Humber Estuary

No discernible patterns are evident in the Humber Estuary ratios. As well as effectively masking any source related effects that may exist, the mixing conditions in the Humber prejudice any attempts to determine geochemically related changes. The Humber is subject to significant internal cycling of sediments where tidal pumping and seasonally variable river flows combine to give particle residence time of approximately 18 years (Grant & Middleton, 1993). One of the consequences of this dynamic sediment regime is that indiscriminate mixing completely masks the emergence of distinct source related homolog profiles.

4.4 Sorbent Physicochemistry

The importance of the sorbent in determining the sorption behaviour of PCBs and dioxins is very widely reported (Broman *et al.*, 1991; Delbeke *et al*, 1990; Duursma *et al.*, 1989; Hiraizumi *et al.*, 1979; Jonsson *et al.*, 1993; Klamer *et al.*, 1990; Lohse, 1991; Means *et al*, 1980; Pierard *et al.*, 1996; Steen *et al.*, 1978). The relationship between the sorbent and the sorbate is not straightforward however. Three key factors are generally considered; the concentration of sorbent material, the physical structure of the sorbent material, and the geochemical composition of the sorbent material (Murphy *et al.*, 1990). The relative importance of these controls appear to depend considerably on the environment under study.

Sediments analysed in the study estuaries have been quantitatively characterised in terms of their physical and geochemical composition. Surface area has been used as a measure of the physical characteristics of particles and the sites available for surface adsorption (Glegg *et al.*, 1987; Hiraizumi *et al.*, 1979). Organic carbon content has been measured to indicate geochemical composition (Delbeke *et al.*, 1990). The cumulative importance of sorbent physical and geochemical characteristics was demonstrated by Zhou *et al.* (1995a) in experiments with the high molecular weight pyrethroid, tefluthrin which has a similar log K_{ow} (6.5) to 2,3,7,8-TCDD (6.8). In initial experiments, Zhou *et al.* examined the variation of partition coefficient with different 'pure' mineral particles and demonstrated that surface area was the key determinant for sorptive capacity. The next experiments dosed the pure mineral particle with humic acid to produce a range of mass fraction organic carbon (f_{oc}) contents. This demonstrated the importance of organic carbon content, with partitioning coefficient increasing with increasing f_{oc}. Finally, various different humic coatings were applied to demonstrate the importance of organic carbon composition in determining sorption preference.

While the solid-solution partitioning of a hydrophobic organic compound between pure water and a homogenous mineral particle or single characterised organic carbon coating may be a relatively unambiguous relationship, the modification of both the solution and solid phases in a natural estuarine system significantly complicates the sorption behaviour. Although the literature reaches a clear consensus that physical and geochemical sorbent characteristics determine sorption behaviour, there is significant disagreement on the relative importance of the major controls. In particular, studies investigating total organic carbon as a sorption control have sometimes identified TOC as a major control (Karickhoff *et al.*, 1979; Lohse, 1991; Means *et al.*, 1980; Paviou & Dexter, 1979; Preston & Raymundo, 1993; Steen *et al.*, 1978) but a similar number have observed no significant correlation between TOC and hydrophobic organic compound sorption (Broman *et al.*, 1991; Duursma *et al.*, 1989; Klamer *et al.*, 1990; Piérard *et al.*, 1996). The most likely explanation for this apparent contradiction in observation is that the composition of organic matter is also of key importance (Grathwohl, 1990; Maruya *et al.*, 1996; Murphy *et al.*, 1994; Zhou *et al.*, 1995b).

To develop the simple sediment-water phase model further, a number of additional phases have been defined. These are shown diagramatically in Figure 4.13. Three compartments have been identified; particulate, dissolved and colloidal. Operational definitions of the size range for each compartment are taken from Sigleo & Means (1990). It is common for the colloidal compartment to be ignored in sediment-water partitioning models but the properties of material in this compartment are often highly preferential for sorption of hydrophobic organic compounds (Baker *et al.*, 1986; Burgess *et* *al.*, 1996; Sigleo & Means, 1990; Wijayaratne & Means, 1984) and are discussed in detail in Chapter 5.

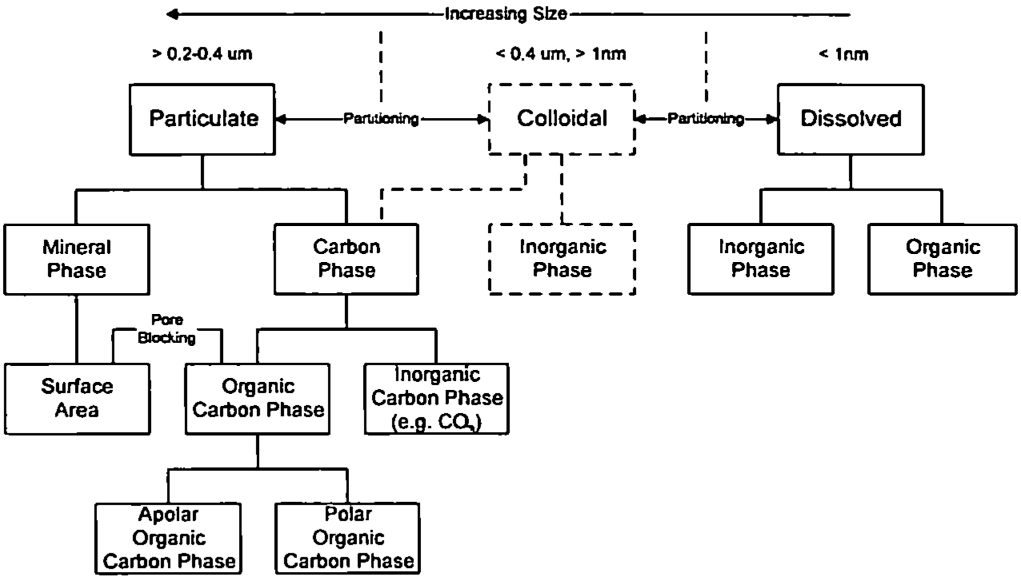


Figure 4.13. Sediment-Water Partitioning Sorbent Phases (operational sizes from Sigleo & Means, 1990)

This section focuses on the solid phase where the particulate compartment has been divided into two main phases; a base mineral particle phase, and an associated carbon phase. These phases have been characterised in terms of SSA, total carbon, organic carbon and apolar lipid content. The covariance between these physicochemical descriptors and concentrations of total PCDD, PCDF and PCB in the Clyde and Humber estuaries is summarised in Tables 4.1 and 4.2 and discussed in detail in the following sections.

Correlation Matrix - Linear Fit R^2 Values							
	PCDD	PCDF	PCB	Total C	Org. C	Lipid	SSA
PCDD	1.00						
PCDF	-	1.00					
PCB	-	-	1.00				
Total C	0.35*	0.52	0.54	1.00			
Org. C	0.30*	0.52	0.57	-	1.00		
Lipid	0.21*	0.53	0.64	-	-	1.00	
SSA	0.04*	0.01*	0.02*	-	-	-	1.00

Table 4.1. Correlation Between PCDD, PCDF and PCB, and Sediment Characteristics in the Clyde Estuary (- not significant, p > 0.1)*

Correlation Matrix - Linear Fit R^2 Values						
	PCDD	PCDF	PCB	Total C	Org. C	Lipid
PCDD	1.00					
PCDF	-	1.00				
PCB	-	-	1.00			
Total C	0.68*	0.65*	0.12*	1.00		
Org. C	0.67*	0.61*	0.04*	-	1.00	
Lipid	0.82	0.86	0.83	-	-	1.00

Table 4.2. Correlation Between PCDD, PCDF and PCB, and Sediment Characteristics in the Humber Estuary (- not significant, $p > 0.1$)*

4.4.1 Mineral Phase

Surface area has been determined for sediments in each of the main study estuaries. The mineral base phase of the particle is subject to modification by absorbed and adsorbed coatings. Particles in the Humber may contain fresh iron coatings (Turner *et al.*, 1991) which augment the specific surface area (17.9 ± 5.8 m^2 g^{-1}) of the underlying matrix. Organic carbon is likely to reduce surface area by blocking the pore structure of the particle (Karickhoff, 1984, Glegg *et al.*,1987). This latter effect introduces a complication in considering the sorptive capacity of estuarine sediments where particles may have their surface area, and therefore their adsorptive capacity, reduced by organic carbon coatings which in turn increase absorbtion potential by providing apolar absorption sites.

Some evidence of possible organic carbon pore blocking action in the Clyde Estuary is shown in Figure 4.14 where high surface areas are only seen for particles of relatively low lipid content. No significant correlations were found for any compounds with SSA. Figure 4.15 is illustrative of the relationships found (R^2 values ranging from 0.01 to 0.04, $p > 0.1$).

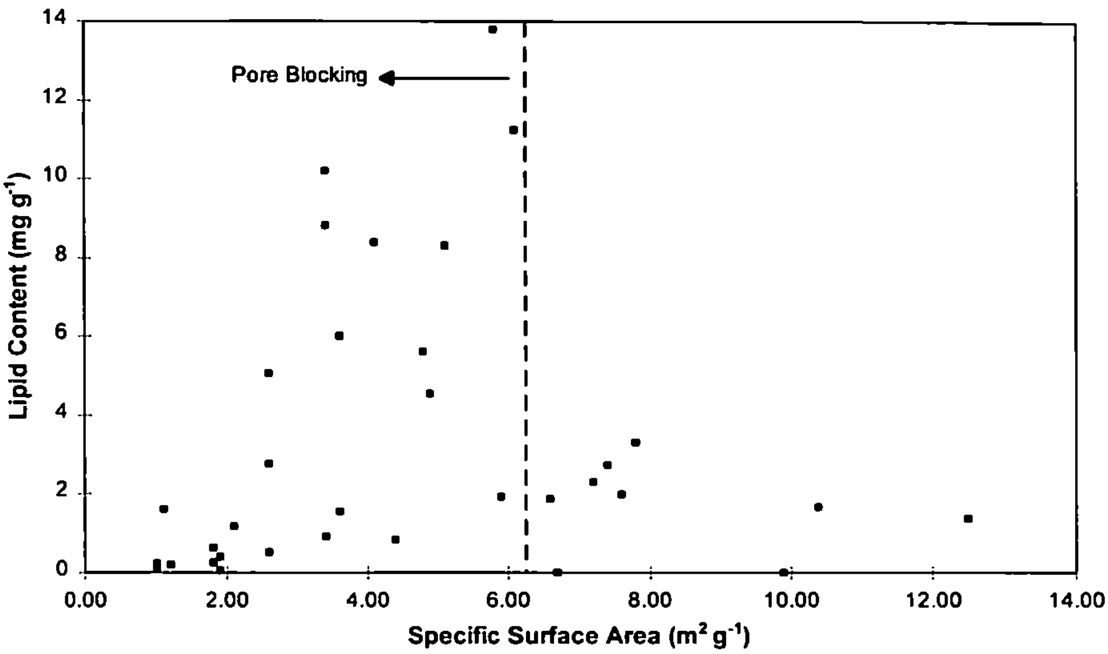


Figure 4.14. Relationship between Lipid Content and Specific Surface Area in the Clyde Estuary (- - - Arbitrarily Defined to Indicate Possible Pore Blocking)

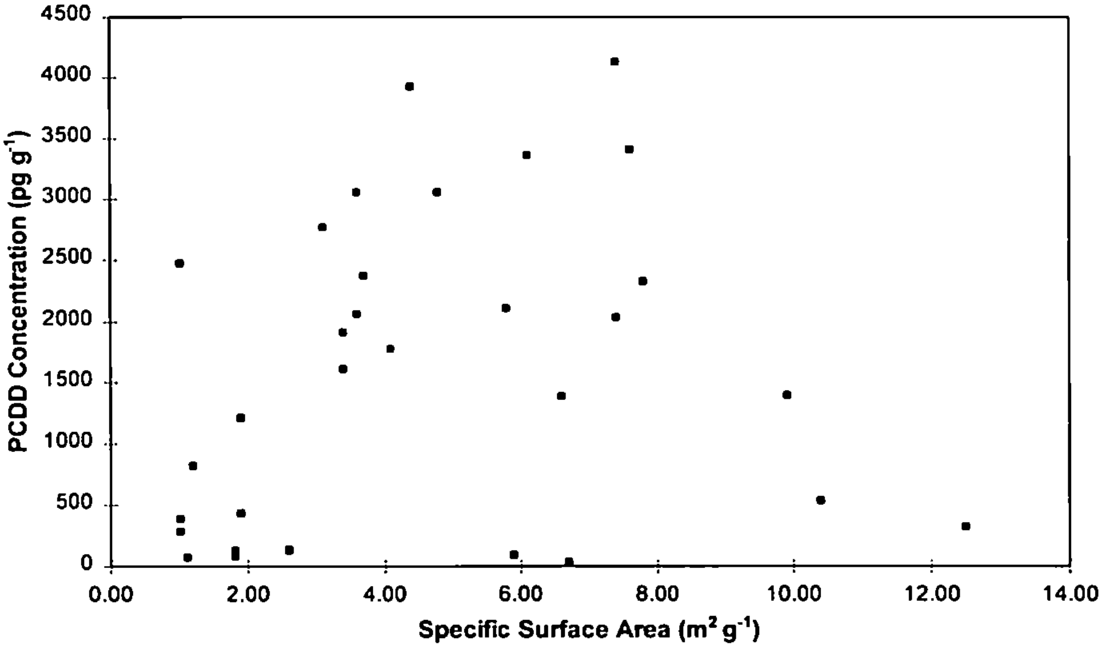


Figure 4.15. Relationship between PCDD and Specific Surface Area in the Clyde Estuary

Although the importance of surface area has been demonstrated in laboratory studies using pure mineral particles, it seems that the physical structure is of only minor importance in natural estuarine sediments where geochemical composition dominates. Based on the sorption model developed by Karickhoff

(1984), Curtis *et al.* (1986) determined that mineral effects would become important at organic carbon content < 0.02% and compound log $K_{ow} < 4$. On this basis, it is unlikely that any SSA relationships would be noted for organochlorine compounds and estuarine sediments (no samples analysed were < 0.02 % organic carbon content). This is exemplified by one specific sample in the Clyde Estuary at Station CS10. As Figure 4.16 shows, at this station the SSA was one of the highest recorded in the estuary (9.9 $m^2 g^{-1}$) but the lipid content was below detection limits. Visually, the sample consisted of a fine grey coloured clay which was possibly representative of substrate sediments uncovered following localised dredging. At this station, as shown in Figures 3.21-3.26, the concentration of PCBs and PCDD/PCDFs was very low compared with surrounding sediments indicating that the physicochemistry of the sediment at this station was not a preferential sorbent for chlorinated organics.

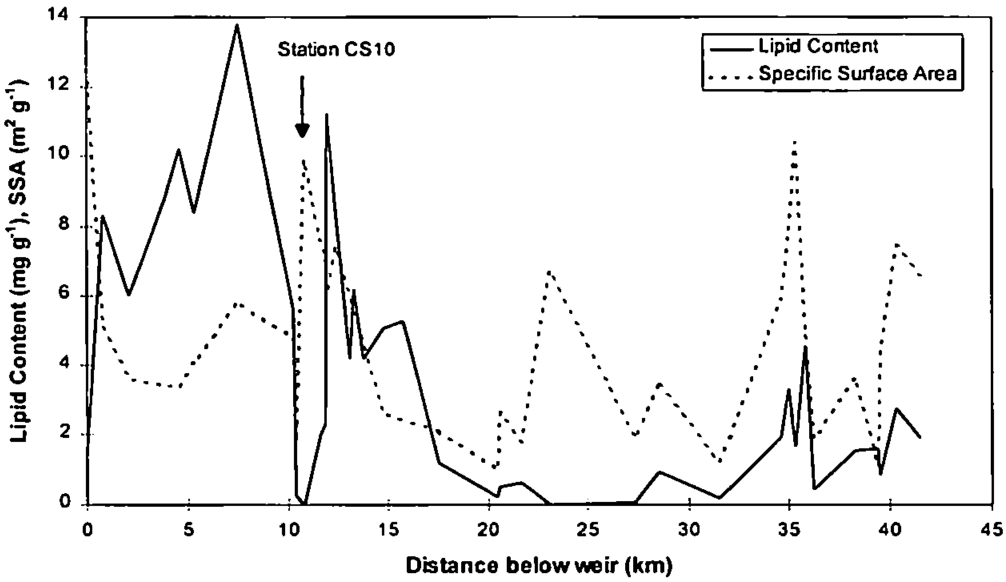


Figure 4.16. Axial Profile of Lipid Content and SSA in the Clyde Estuary

A number of studies have noted correlation between size fractions in bed sediments and hydrophobic organic compound concentrations (Delbeke *et al.*, 1990; Klamer *et al.*, 1990; Paviou & Dexter, 1979; Preston & Al-Omran, 1989). However, it has been variously observed in natural systems that there is often a strong correlation between particle size fraction and the organic carbon composition (Delbeke *et al.*, 1990; Lohse, 1991; Paviou & Dexter, 1979) which again points to geochemical composition dominating over physical structure in estuarine and coastal environments.

4.4.2 Geochemical Composition

The carbon phase consists of two sub-phases; organic carbon, and inorganic carbon. In an estuary the inorganic carbon phase may be derived from marine sources e.g. marine carbonates, whereas the organic phase is likely to be derived from lithogenic or anthropogenic sources (Preston & Prodduturu, 1992). The organic carbon geochemistry of natural sediments is extremely complex due to the huge number of organic carbon compounds, both anthropogenically and lithogenically derived, which contribute to the geochemical matrix (Karickhoff *et al.*, 1979; Maruya *et al.*, 1996; Preston and Al-Omran, 1989; Zhou *et al.*, 1995a, b). In an estuary, long sediment residence times permit significant modification of organic matter during sedimentation and burial. Such changes in organic matter during burial are summarised in Figure 4.17.

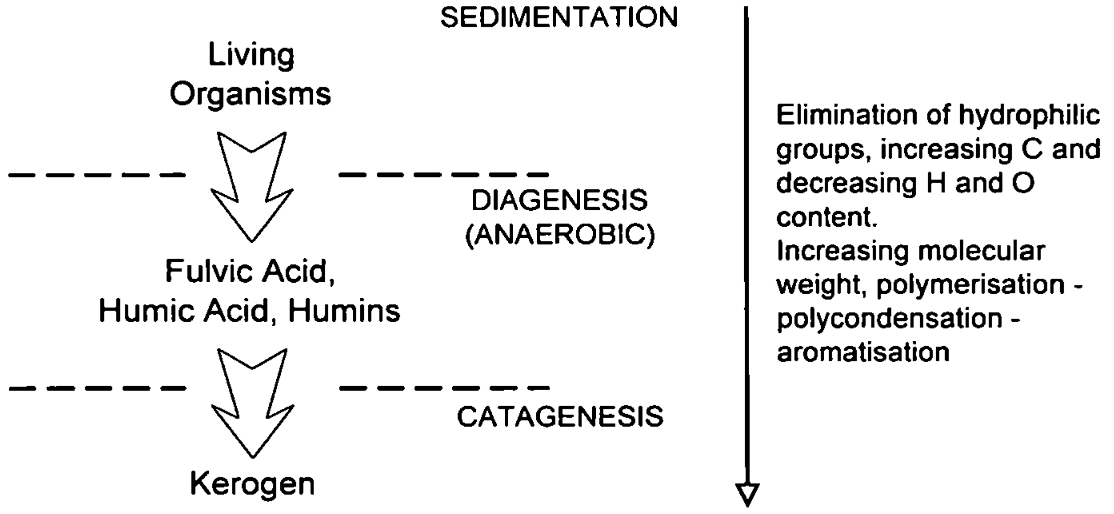


Figure 4.17. Change of the Organic Matter During Burial (after Grathwohl, 1990)

Grathwohl (1990) examined K_{oc}s for a number of chlorinated aliphatic compounds on sediments with widely ranging natural organic carbon contents arising from different stages of diagenesis and weathering. It was observed that the relative amount of oxygen-containing functional groups increased or decreased with burial and weathering. High oxygen-containing functional groups resulted in an increase in the overall polarity of organic polymers in the organic matter with consequent reductions in sorption capacity. Although no detailed analysis of organic matter has been performed, it is hypothesised that organic material sedimenting in an estuary such as the Clyde may be significantly transformed over long time periods with consequent variations in its polarity and sorption capacity.

In practice, these transformations would be extremely difficult to parameterise and predict. A simple two-compartmentalisation has been adopted between apolar organic carbon and polar organic carbon. On the broad principle that 'like dissolves like', extremely lipophilic chlorinated organic compounds would be expected to have an affinity for apolar sorption sites and this is a consistently reported observation for hydrophobic organic compounds (Al-Omran & Preston, 1987; Broman *et al.*, 1991; Delbeke *et al.*, 1990; Delbeke & Joiris, 1988; Preston & Al-Omran, 1989; Preston & Raymundo, 1993). This apolar organic phase is referred to operationally as the apolar lipid phase. The apolar lipid phase contains a complex cocktail of components including free sterols, fatty alcohols, free fatty acids, triacylglycerols, wax and sterol esters and hydrocarbons (Galois *et al.*, 1996).

Polar material in the solid phase may also be important for the sorption of hydrophobic organic compounds, in particular the presence of humic material which is a major feature of estuarine particles (Murphy *et al.*, 1990; Murphy *et al.*, 1994; Zhou *et al.*, 1994). The definition of humic material is difficult due to the extreme heterogeneity in its composition (Gauthier *et al.*, 1987). Harvey & Boran (1985) described marine humic substances as "a macromolecule composed of amino acid-carbohydrate condensation products with some fatty acids attached through ester linkages along with a little bit of everything else in the sea" !

One point of note, particularly in the light of the apolar lipid extractions performed under this study, is that humic substances would not generally be considered solvent extractable. In fact, the molecular structure of humic material will often consist of a hydrophilic molecule with apolar functional groups. This permits the material to act as a bridge between apolar organic compounds and the aqueous phase and underlines its potential importance in partitioning behaviour (Chiou *et al.*, 1986; Gauthier *et al.*, 1987; McCarthy & Jimenez, 1985; Zhou *et al.*, 1995a). The formation of humic acids is not well understood but work carried out by Harvey and co-workers and summarised in Harvey & Boran (1985) proposes a marine lipid as a precursor to a marine fulvic acid which is in turn a precursor to a marine humic acid. In an estuary system, lipid material may degrade to humic material and in doing so, change the sorption potential for hydrophobic organic compounds.

Carbon Geochemistry in the Humber and Clyde Estuaries

Under this study, the nature of the carbon phase has been analysed to characterise the particles in the study estuaries and identify the impact on sorptive capacity. As far as possible, samples analysed for chlorinated organic compounds were also analysed for total carbon, total organic carbon and apolar lipid content.

Examination of the relationship between the carbon phases shows marked differences between the particulate carbon chemistry of the two main study estuaries. Figure 4.18 shows an extremely strong correlation ($R^2 = 0.999$, $p < 0.001$) between total carbon and total organic carbon in the Clyde Estuary. From these analyses, it appears that almost all (98 ± 6%) of the carbon in Clyde Estuary sediments sampled during this study is of organic origin. In contrast, the organic component of carbon in Humber sediments is only 52 ± 25 %. A similar analysis performed for a sediment sample from the Mersey estuary indicated that organic carbon content represented 54% of the total carbon content (Al-Omran & Preston, 1987).

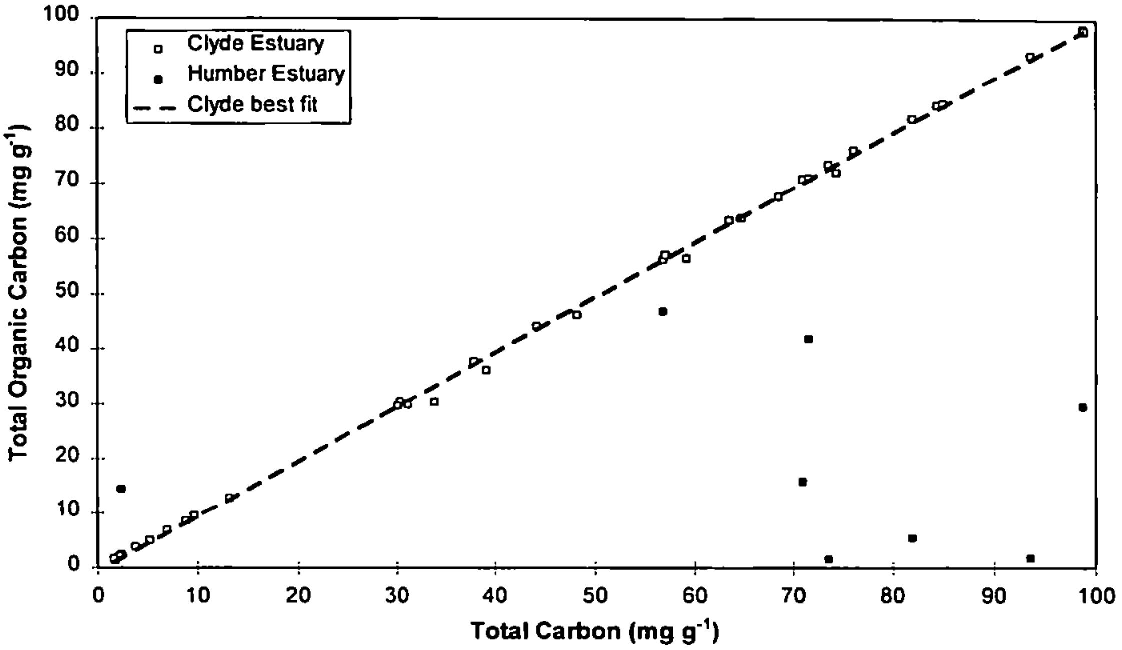


Figure 4.18. Relationship between Total Carbon and Total Organic Carbon in Clyde and Humber Estuary Sediments

Figure 4.19 shows the relationship between apolar lipid content and total organic carbon in the study estuaries. No correlation between organic carbon and apolar lipid content is observed in the Humber. In the Clyde there is some correlation with an indication that sediments with a high total organic carbon content have a disproportionately high apolar lipid content. The mean lipid content of total organic carbon is 7.7 ± 7.5% in the Clyde and 9.88 ± 10.23 % in the Humber. This compares with 15% lipid in TOC for a Mersey sediment sample (Al-Omran & Preston, 1987) and 26 ± 23 % in nine Baltic Sea samples (Broman *et al.*, 1991). Galois *et al.* (1996) in a comprehensive analysis of lipid biomarkers in the Marennes-Oléron Bay, France, found that on average over a year, 10.5% of particulate organic carbon in SPM consisted of lipid material. Of this, 43 % on average consisted of apolar lipid content.

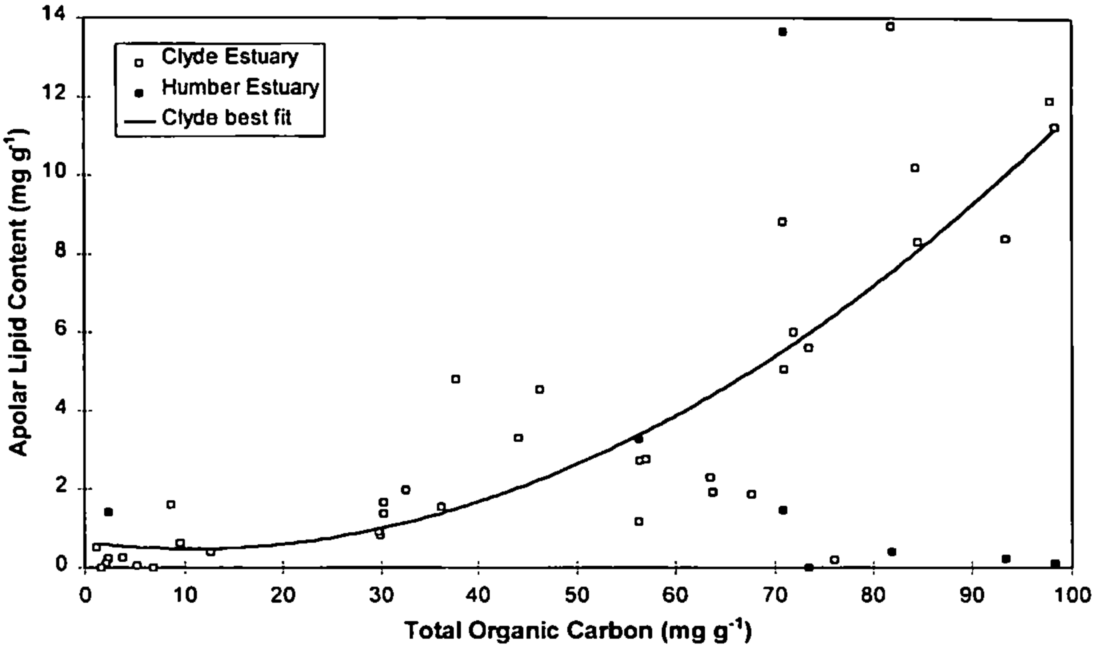
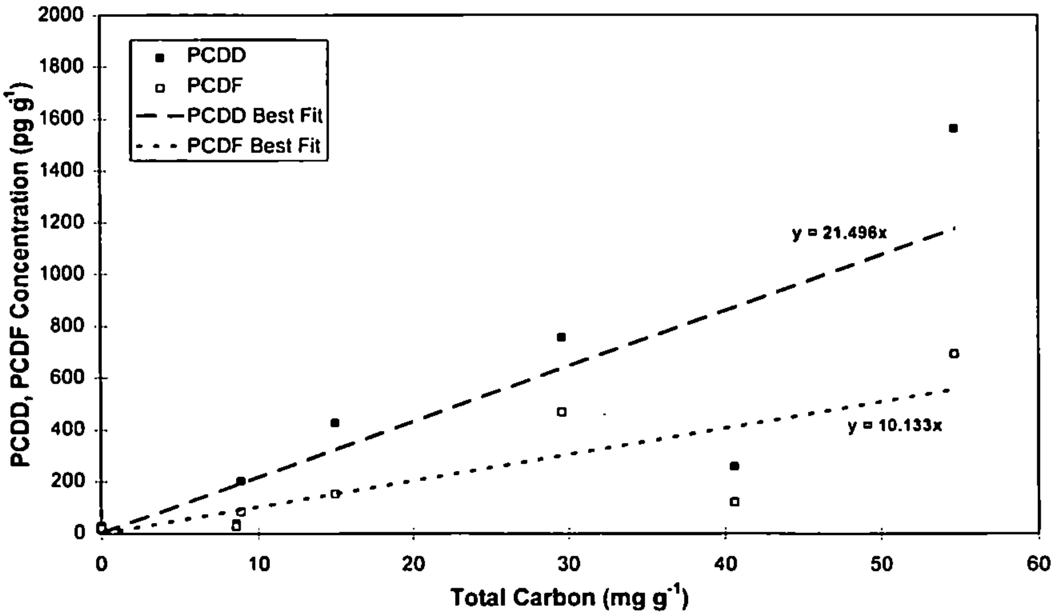


Figure 4.19. Relationship between Total Organic Carbon and Apolar Lipid Content in Clyde and Humber Estuary Sediments

PCDD and PCDF Covariance with Organic Carbon

Total PCDD and PCDF covariation with each defined carbon compartment (total carbon, total organic carbon and apolar lipid content) has been plotted for the Humber Estuary in Figure 4.20 a-c.



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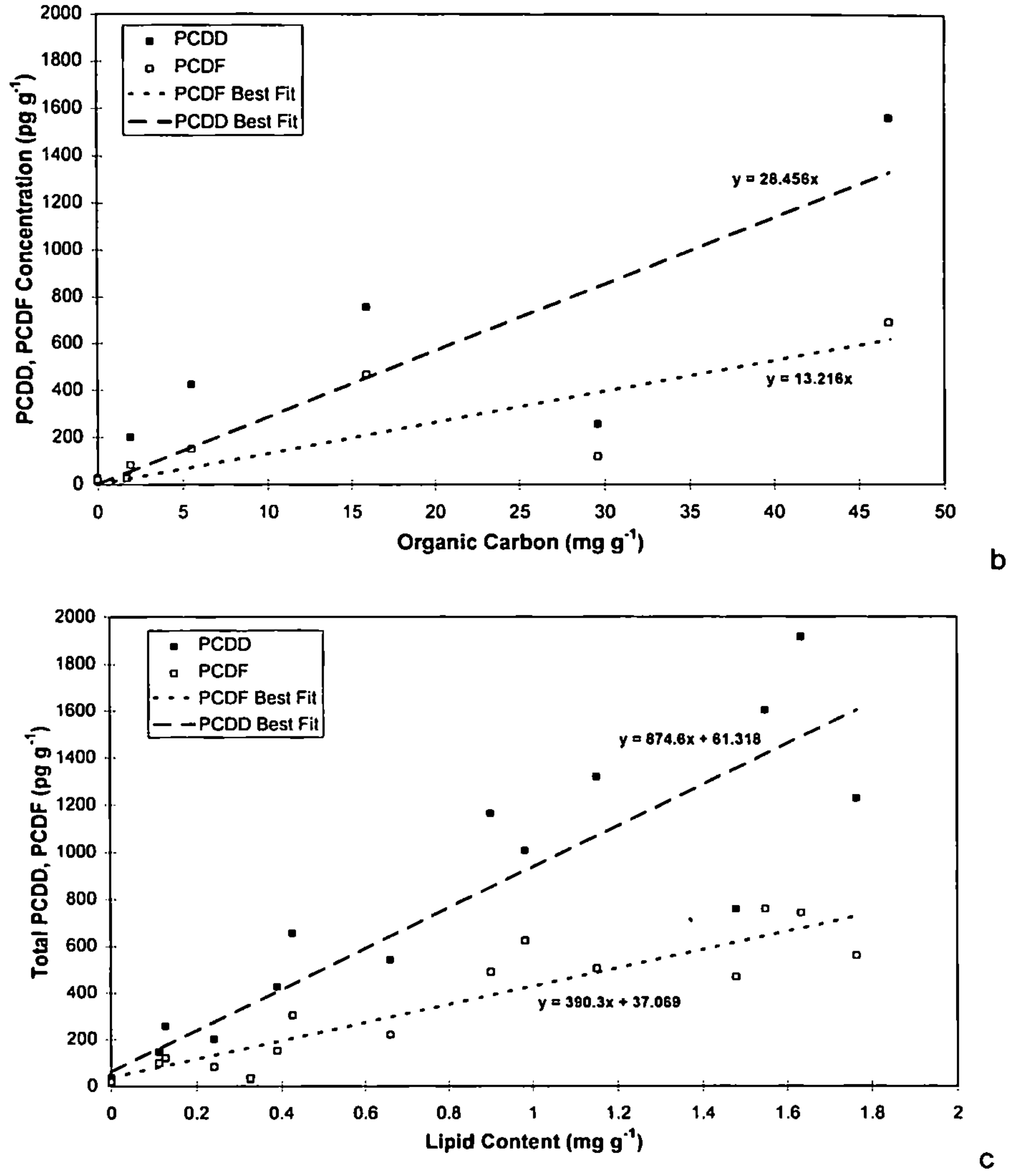


Figure 4.20. Covariation of total PCDD and PCDF with (a) Total Carbon, (b) Total Organic Carbon, and (c) Apolar Lipid Content in the Humber Estuary

Correlations between total PCDD/PCDF and total carbon and total organic carbon are similar but not significant (R^2 = 0.68, PCDD; 0.65, PCDF, $p > 0.1$ for total carbon and R^2 = 0.67, PCDD; 0.61, PCDF, $p > 0.1$, for total organic carbon). However, significant correlations ($p < 0.001$) were found for apolar lipid content (R^2 = 0.82, PCDD; 0.86, PCDF) indicating that an adequate description of organochlorine sorption preference in this estuary requires a distinction between polar and apolar particulate organic carbon phases. This has been further tested by co-plotting total TCDD and OCDD against apolar lipid content. From the discussion in section 4.3, a weaker correlation might be expected for lower chlorinated homologs and this is borne out in Figure 4.21 although the difference in correlation coefficients does not merit a significant conclusion to be drawn.

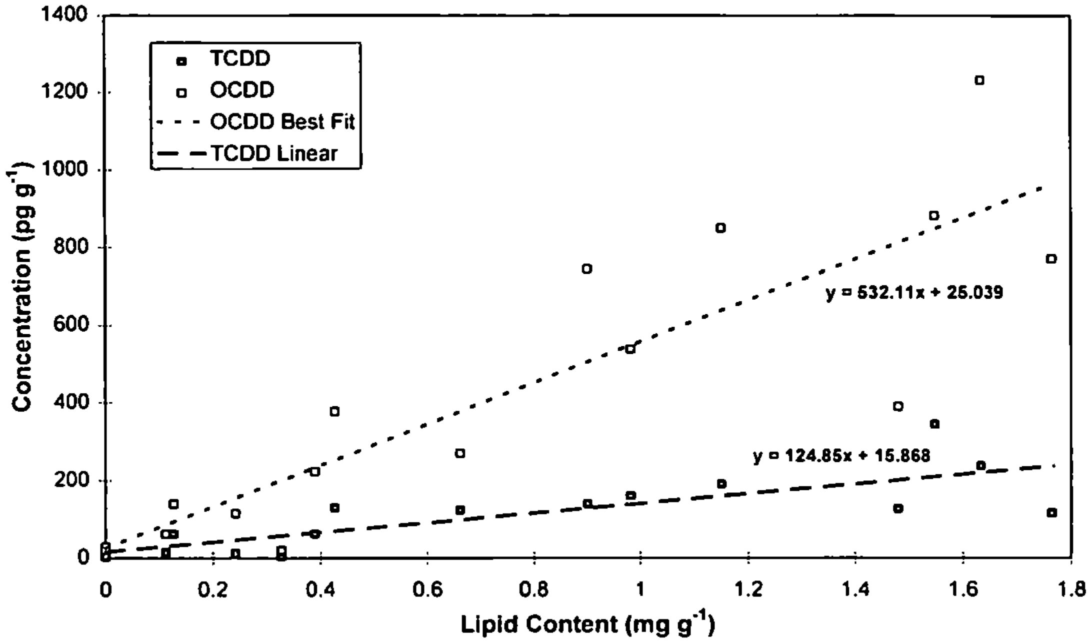


Figure 4.21. Covariance between Apolar Lipid Content and TCDD (R^2 = 0.66, $p < 0.001$), OCDD (R^2 = 0.78, $p < 0.001$) in the Humber Estuary

In the Clyde Estuary similar analyses of the covariance between PCDD and PCDF and particulate carbon phases show weak correlations (R^2 varying from 0.21 - 0.53), particularly for PCDD. This is exemplified in Figure 4.22 which shows a plot of all samples analysed for total PCDF in the Clyde Estuary but no significant correlation. Zhou *et al.* (1998) observed that organic carbon covariance with PAHs was enhanced when samples were grouped according to degree of contamination. Figure 4.23 shows the covariance between total PCDF and TOC for samples with PCDF concentrations < 1600 pg g^{-1}.

The Clyde Estuary is characterised by higher lipid content (4.2 ± 3.8 mg g^{-1}) compared with the Humber Estuary (1.4 ± 2.9 mg g^{-1}). It is hypothesised that particulate matter in the Humber Estuary is lipid-limited so that apolar organic compounds must seek limited preferable sorption sites for long term adsorption. Organochlorine compounds will tend to cycle in the estuary system until securing permanent sorption sites. In the Clyde by contrast, there is an abundance of lipid material which may irreversibly absorb highly lipophilic compounds soon after they enter the system. This would imply that preferential sorption sites are identified by geographical proximity to sources and that there is less cycling of compounds in the system.

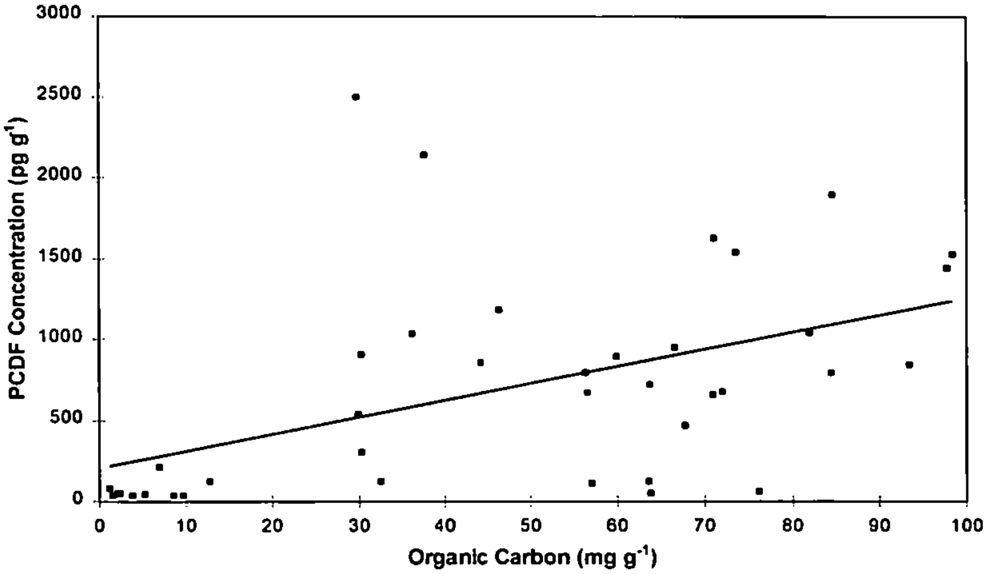


Figure 4.22. Total PCDF Covariance with Total Organic Carbon ($R^2=0.24$, $p > 0.1$). All Samples in the Clyde Estuary

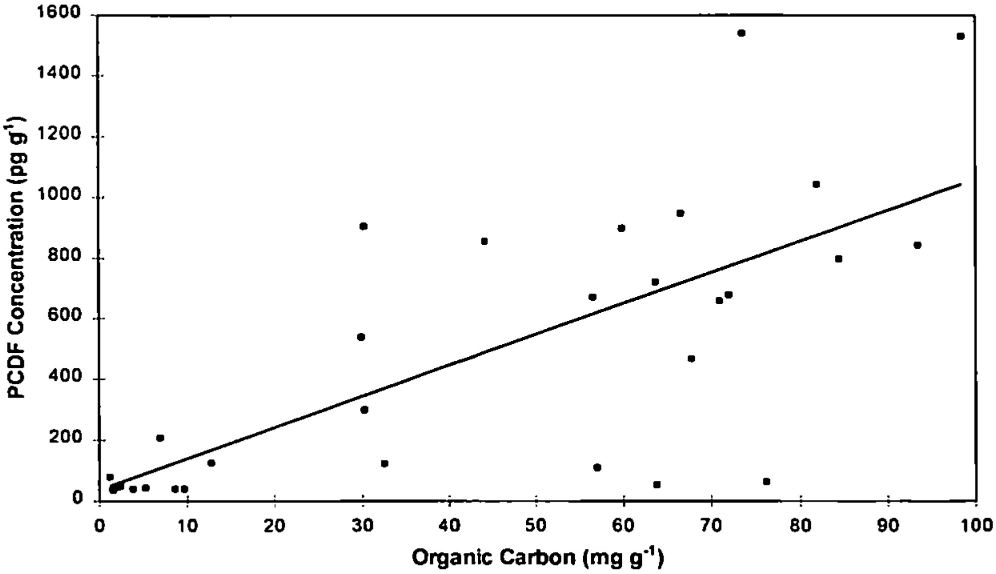
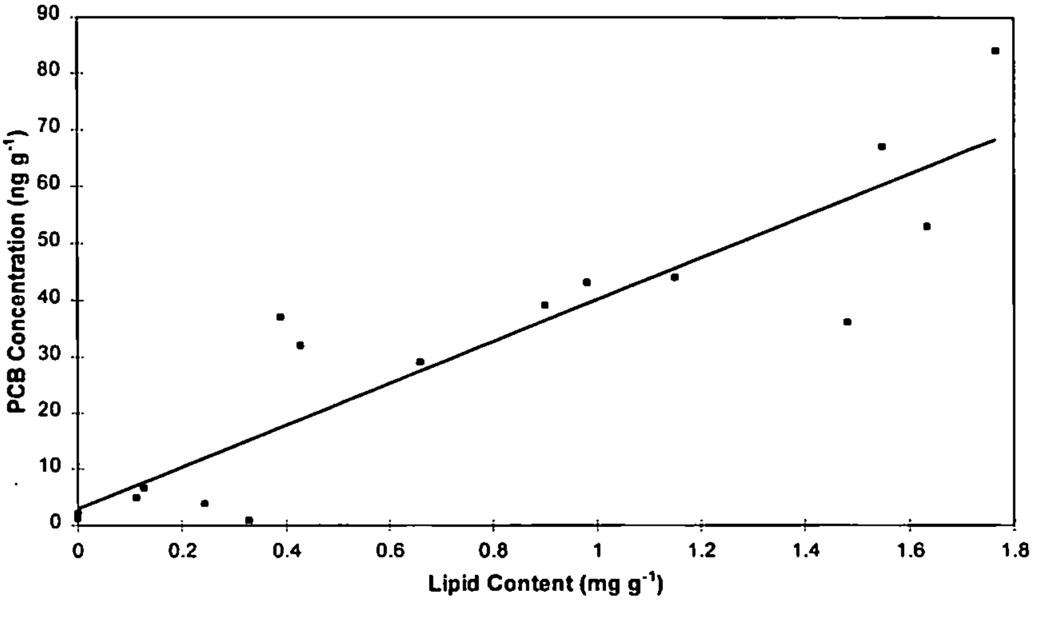


Figure 4.23. Total PCDF Covariance with Total Organic Carbon ($R^2=0.52$, $p < 0.01$). Samples with total PCDF < 1600 pg g^{-1} in the Clyde Estuary

PCB Covariance with Organic Carbon

In the Humber Estuary there is no significant correlation between total PCB and either total carbon ($R^2 = 0.12$, $p > 0.1$) or total organic carbon ($R^2 = 0.04$, $p > 0.1$). However, there is strong correlation with apolar lipid content shown in Figure 4.24a. This underlines the importance of apolar lipid as the key organic carbon phase in understanding the sorption behaviour of these OCs.



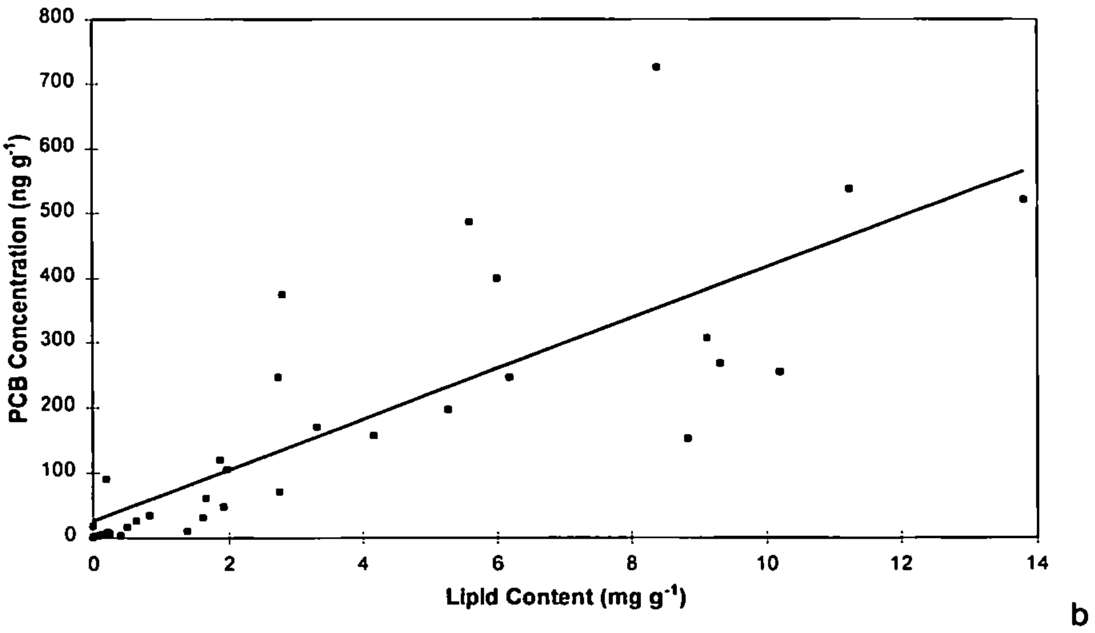


Figure 4.24. Covariance between Total PCB and Apolar Lipid Content in the (a) Humber Estuary ($R^2 = 0.83$, $p < 0.001$) and (b) Clyde Estuary ($R^2 = 0.63$, $p < 0.001$)

In the Clyde Estuary correlations between PCB and total carbon, total organic carbon and apolar lipid content are similar (R^2 = 0.54, 0.57 and 0.64 respectively with $p < 0.001$) but increasing in correlation with the apolarity of the carbon phase (Figure 4.24b). The association of PCB with lipid content was stronger than PCDD and PCDF in the Clyde Estuary.

4.4.3 Particle Association Models

A number of workers have proposed sorption models to describe the natural partitioning behaviour of hydrophobic compounds (Adriaens *et al.*, 1995; Di Toro & Horzempa, 1982; Di Toro *et al.*, 1986; Karickhoff, 1984; Preston & Raymundo, 1993; Wu & Gschwend, 1986). These models describe the association of hydrophobic compounds into various particle phases over different timescales.

Preston & Raymundo (1993) in studies of Linear Alkyl Benzene (LAB) association with estuarine sediments discriminated between contaminant incorporated within the bulk of the particle (particle volume related) and therefore possibly derived directly from the source, and contaminant associated with the particle surface (surface area related) and more likely to have adsorbed to particles within the wider environment. By relating these processes to geometrical parameters, two relationships were established;

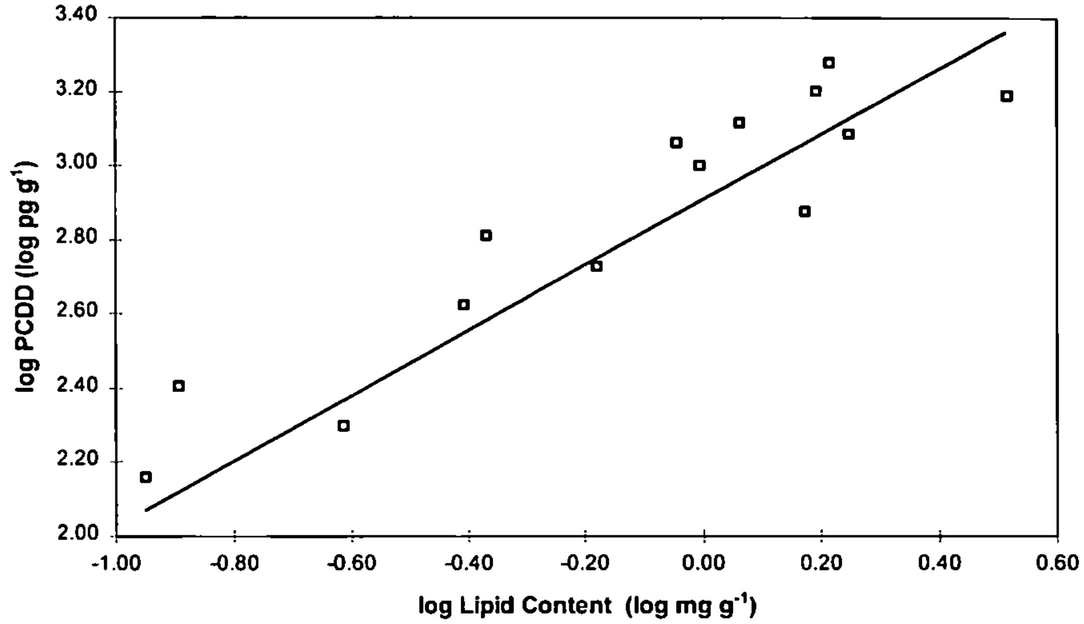
For bulk association,

$$[\text{Particulate Contaminant}] \propto [\text{Lipid}]$$

For surface adsorption,

$$\log\,[\text{Particulate Contaminant}] \propto \log\,[\text{Lipid}]$$

This model has been tested by comparing linear particulate contaminant-lipid, and log-log particulate contaminant-lipid relationships. Figure 4.25 a-c show example log-log relationships for the Humber Estuary. These can be compared with Figure 4.20c and 4.24 which show the linear relationships. Table 4.3 compares R^2 values for the linear and log-log relationships, and provides the gradient and intercept for the significant log-log relationships.



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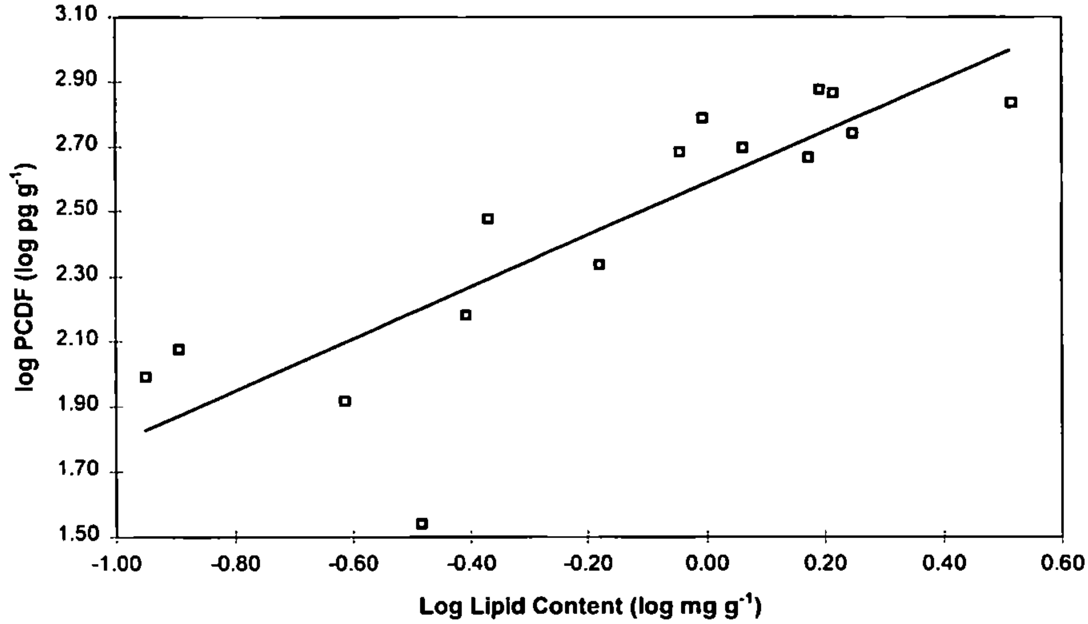

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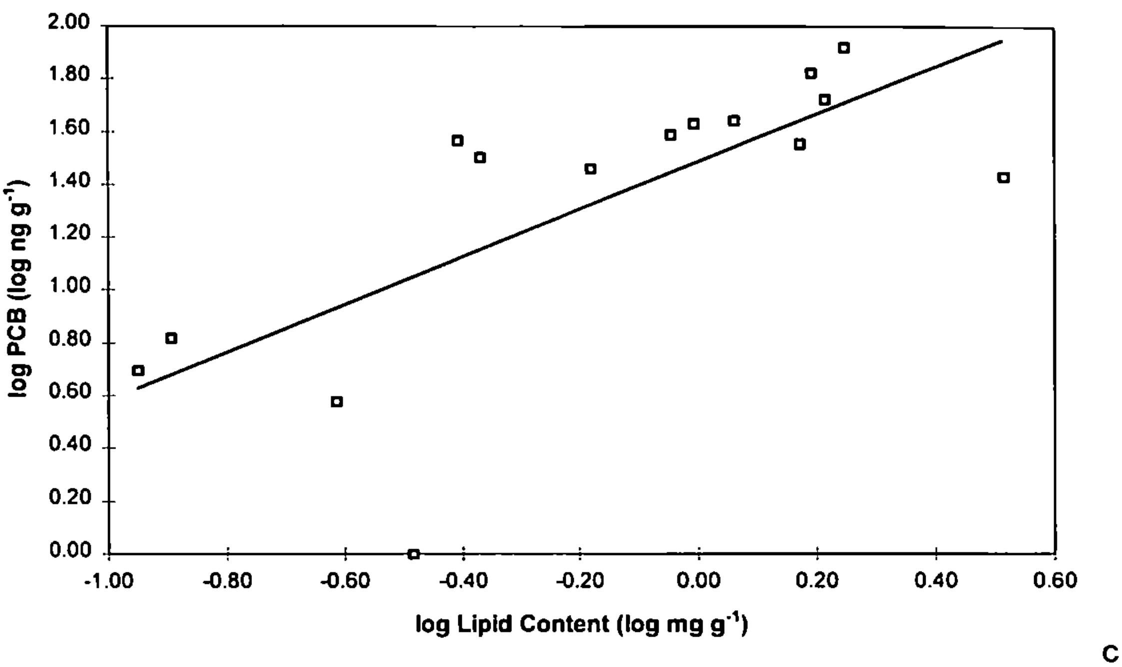


Figure 4.25. Log. Lipid Content vs (a) log. PCDD, (b) log. PCDF, (c) log. PCB in the Humber Estuary

Estuary	Compound	log P - log Lipid				linear P - Lipid	
		R^2	p	a	b	R^2	p
Humber	PCDF	0.70	< 0.01	0.80	2.58	0.86	< 0.001
	PCDD	0.60	< 0.02	0.88	2.91	0.82	< 0.001
	PCB	0.52	< 0.05	0.90	1.48	0.83	< 0.001
Clyde	PCDF	0.53	< 0.01	0.67	2.21	0.53	< 0.01
	PCDD	0.18	ns	0.42	2.77	0.21	ns
	PCB	0.78	< 0.001	0.98	1.61	0.64	< 0.001

Table 4.3. Correlation Comparison for Linear and Log-log. Relationships between Lipid and Contaminant Concentration (P). ns - not significant.

Significant correlations are found between PCDD, PCDF, PCB and lipid content in both estuaries for both relationships with the exception of PCDD in the Clyde Estuary. In the Humber Estuary the linear relationship provided a better fit than the log-log relationship whereas there was little difference in the Clyde. The implication, at least for the Humber Estuary, is that chlorinated organic compounds in the estuary may be associated with source derived particulate matter where the contaminant is inherently bound into the particle interstices or particle-associated organic matter. This is consistent with the homolog profile analysis that indicated atmospheric deposition as the predominant source to the Humber. One further point of note is that the gradient (a) and intercept (b) for the log-log relationships are similar and the gradient is close to that obtained by Preston & Raymundo (1993) for LABs and with the theoretical gradient of 2/3 predicted by the surface association model.

The surface association model described by Preston & Raymundo (1993) is often presented as a two-stage adsorption process. The first stage consists of a physical adsorption to the particle which is a function of the available sorption sites on the particle surface. Adsorption rates and extents are likely to be related to the physical properties of the particles (i.e. specific surface area) and the availability of suitable particles (i.e. concentration of particles in the solute - see Chapter 5), and exist in a relatively reversible state of sorption. In the second stage, over longer timescales, the hydrophobic organic compound is adsorbed into lipophilic material within the particle matrix where it remains in a relatively irreversibly sorbed state. The extent and kinetics of this stage are a function of the polarity of the particle matrix and the resistance of the apolar sites to subsequent modification (e.g. degradation).

The kinetics of the sorption process has been described as a two-stage process with a rapid initial adsorption within minutes, followed by a slower absorption over a period of hours → days (Di Toro & Horzempa, 1982). This was summarised by Karickhoff (1984) by defining two components; a rapidly adsorbed 'labile' fraction (P_1), and a 'non-labile' fraction (P_{n1}). The labile component is assumed as equilibrium (K_1) with the non-labile fraction treated as a mass transfer coefficient (K_2);

$$C \xleftrightarrow{K_1} P_l \xleftrightarrow{K_2} P_{nl} \tag{4.1}$$

There are problems in reconciling such sorption models with the observations of bed sediment adsorbed OCs in natural systems. The first obstacle is that, in contrast to marine metal chemistry, there are no analytical methods established to discriminate between the labile and non-labile components. The second issue relates to timescale. The adsorption kinetics of stage 1 and 2 are not coincident with sediment residence timescales within an estuarine system (years → decades) or the timescales for removal of high molecular weight compounds from the system (years → decades depending on compound, Adriaens *et al.*, 1995). In sampling bed sediments for high molecular weight compounds a temporally integrated sample is analysed where, although some exchange processes including surface adsorption of 'new' contaminant and migration into the particle matrix may be in progress, a high proportion of the sorbate consists of absorbed contaminant highly resistant to desorption processes. This quasi-steady state accounts for the dominance of physical estuary processes in distributing hydrophobic contaminants in an estuary and explains the homogeneity in distribution observed for the Humber with dynamic mixing conditions, compared with the heterogeneity of distribution in the Clyde resulting from the selective deposition of sediments of differing geochemical characteristics on a geographical basis.

Although physical processes are assumed to dominate the distribution of chlorinated organics in estuaries, some release of compounds may be expected. As already discussed, solubilisation and volatilisation may account for some desorption of the more polar compounds. Other compounds may rely on the breakdown of the sorbent to promote a search for more preferential sorption sites. This has been reported by Delbeke *et al.* (1990) and Delbeke & Joiris (1988) who highlighted the temporary role of the biota as a compartment for hydrophobic contaminant sorption. The lipid material within particle matrices identified as the primary sorption site for apolar compounds can also be considered as a temporary compartment as there are established degradation pathways for this material (Harvey & Boran, 1985). It can be hypothesised that chlorinated organic compounds would be released during breakdown of the apolar matrix. This would provide a continually cycling proportion of the chlorinated organic load within the estuary. However, in comparison with the reservoir of chlorinated organic compounds held in sedimentary repository this would only represent a relatively small fraction and would be unlikely to significantly influence the observed associations with bed sediments.

4.4.4 Normalised Distributions

The preceding analysis has established apolar lipid content as the primary control on chlorinated organic compound distribution. On this basis, apolar lipid content has been selected as an appropriate normalisation parameter to assist in removing sedimentary variability from distribution analysis of OC occurrence. Lipid normalised PCDD, PCDF and PCB spatial and axial distributions have been plotted. Where lipid content falls below 0.5 mg g^{-1}, data has not been plotted. Such low content is close to the limit of detection and has the potential effect of distorting normalised values.

Spatial distributions of raw and lipid normalised bed sediment concentrations are shown in Figures 3.20, 3.22 and 3.24 (Clyde Estuary) and 3.28, 3.30 and 3.32 (Humber Estuary). Axial profiles of OC concentration for sub-tidal sediments on a lipid normalised basis are shown in Figures 4.26 and 4.27 (Clyde Estuary) and 4.28 and 4.29 (Humber Estuary). The Clyde Estuary distributions can be compared with raw distributions in Figures 3.21, 3.23 and 3.25.

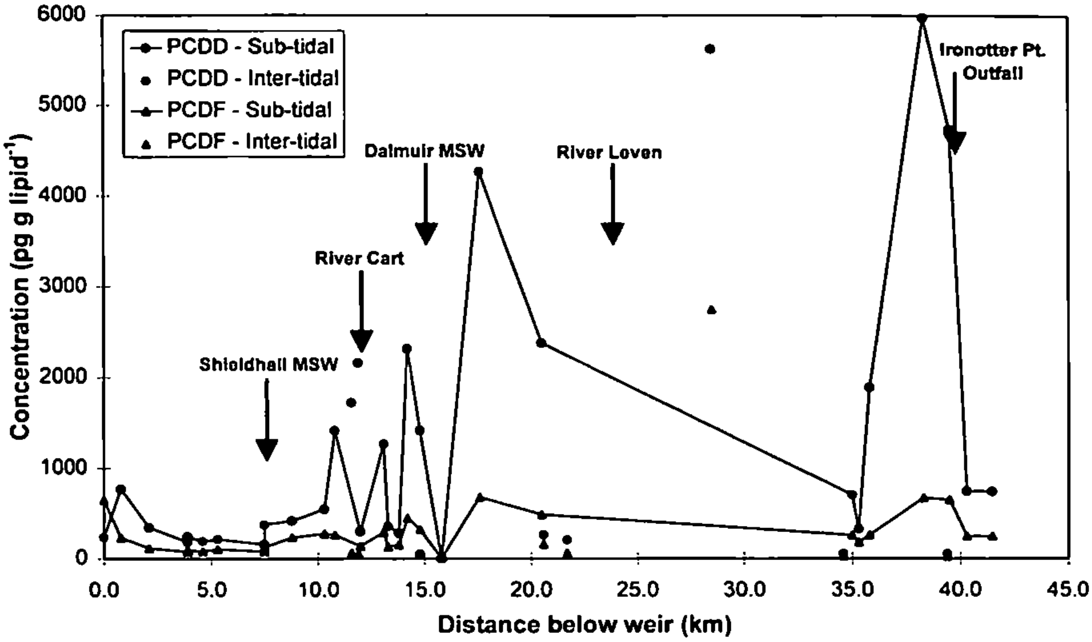


Figure 4.26. Axial Distribution of Lipid Normalised PCDD and PCDF in the Clyde Estuary

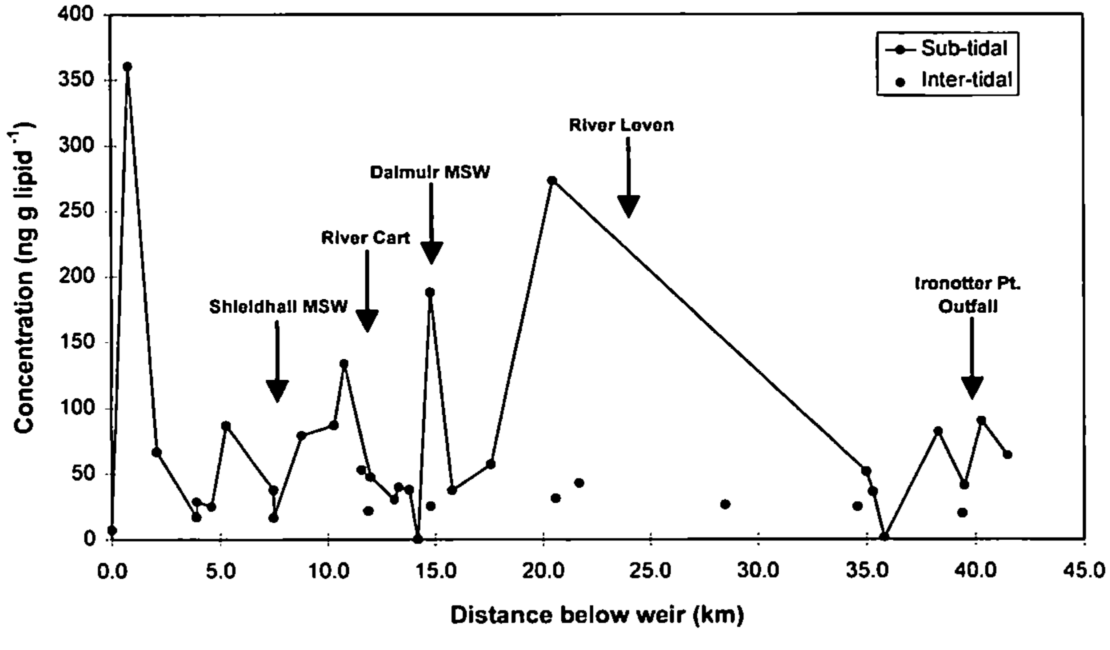


Figure 4.27. Axial Distribution of Lipid Normalised PCB in the Clyde Estuary

In the Clyde Estuary, the normalised distribution shows significant differences to the raw distribution. PCDD and PCDF distributions both indicate low concentrations from the weir to 10km in contrast to the peak immediately below the weir and the generally rising concentrations in the raw data. This implies that the concentrations measured in this upper estuary region are a function of the sediment type rather than significant sources in the vicinity. Elevated concentrations are still evident at between 10 and 20 km from the weir indicating that this is probably an area where sources exist, possibly attributable to the MSW in this area. The peaks in concentration in the vicinity of the Ironotter outfall are also evident in the normalised profile indicating sources present in this area.

The lipid normalised PCB distribution is more complex. A single high concentration sample is still evident immediately below the weir. There is no evidence of elevated normalised PCDD/PCDF concentrations at this site which indicates that a specific point source of PCBs may be responsible for this occurrence. Concentrations in the middle and lower estuary are fairly homogeneous with the exception of a number of isolated elevated concentrations. These locations have little coincidence with stations showing elevated PCDD/PCDF concentrations. Similarly, there is no evidence of elevated concentrations of PCB in the vicinity of the Ironotter Point outfall where PCDD/PCDF concentrations are high. One further point of note is that the normalised inter-tidal samples are generally very low, particularly for PCBs. Inter-tidal areas, located at the periphery of the main flow channels and subject to lower current flows, are often regions of accretion of fine sediments. From this analysis it seems that sediment type is the major determinant of OC content in these sediments rather than sources directly to these regions. These sediments may have originated close to a point source and then been selectively distributed into these areas by physical transport processes.

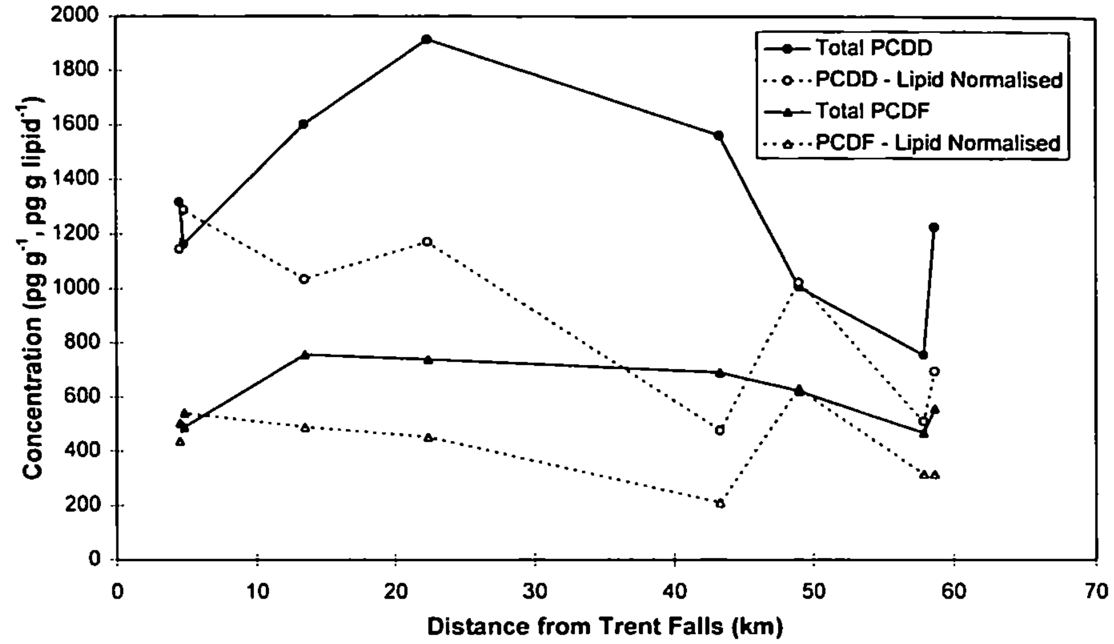


Figure 4.28. Axial Distribution of Lipid Normalised PCDD/PCDF in the Humber Estuary

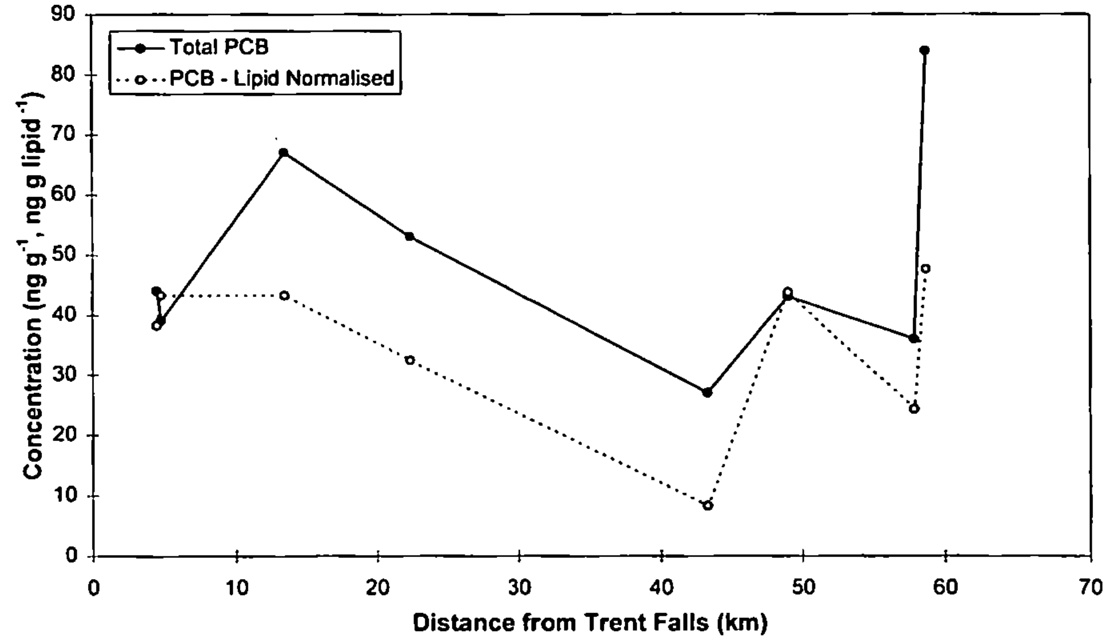


Figure 4.29. Axial Distribution of Lipid Normalised PCB in the Humber Estuary

In the Humber Estuary, the effect of lipid normalisation is to reduce the spatial variation in PCDD, PCDF and PCB concentrations in sediments. Figures 3.28, 3.30 and 3.32 clearly show the effect of normalisation in comparison with raw values where the fairly even distribution is further homogenised by the normalisation. It has already been concluded from the homolog analysis that the dynamic mixing conditions in the Humber have resulted in an even distribution of compounds in the estuary. Similar effects have been observed in studies of trace metal distribution in the Humber Estuary. Grant & Middleton (1993) studied metals distribution which, following normalisation, were found to be uniform despite the presence of a number of significant point sources within the estuary. This led to the conclusion that the sediments in the Humber Estuary represented a 'single well mixed pool'.

4.5 Summary

This Chapter has considered the three major controls on OC distribution in estuaries; source, compound physicochemistry and sorbent geochemistry. Neither of the study estuaries has received major known sources of OCs in the past and although some evidence of point sources exist in the Clyde Estuary, the main source to the Clyde, Humber and Dee estuaries appears to be atmospheric deposition. The influence of compound physicochemistry, although fundamentally of key importance, cannot be easily separated from the other controls in particular the geochemistry of the sorbent. Physical characteristics of the sorbent were found to be of little importance but the organic carbon fraction, in particular the apolar lipid content, was found to be of major significance in determining sorption preference. Although determination of the preferred sediments for sorption was a function of sediment characteristics, the geographical occurrence has been found to be strongly dominated by the mixing characteristics of the estuary. The dynamics of the Humber Estuary resulted in extensive mixing of sediments and a consequent homogenous distribution of contaminants within the estuary whereas the Clyde Estuary's relatively quiescent environment tends to selectively distribute sediment-bound OCs within geographically distinct zones.

Dynamic sorption models are not generally effective in describing the observed bed sediment associated partitioning due mainly to the inconsistency between dynamic sorption timescales and the residence times of estuarine sediments and persistency of adsorbed OCs. However, although deposited sediments hold the vast majority of the estuarine inventory of OCs, there remains a key requirement to understand and model the dynamic sorption behaviour of these compounds to suspended particulate matter. This compartment represents a major pathway for exposure to biota and release into the wider environment and is therefore of management concern. The next Chapter seeks, through laboratory experiments, to further understanding of the key processes influencing sorption behaviour and to parameterise this behaviour in sorption models.

Chapter 5. Laboratory Investigation of Sorption Behaviour

5. Laboratory Investigation of Sorption Behaviour

Chapter 4 discussed the key controls on chlorinated organic compound sorption in the selected estuaries based on analysis of bed sediments. This was achieved by determining the covariance of solid phase sorption with sediment properties. The transport mechanism for hydrophobic organic compounds in an estuary is predominately by advection and cycling of SPM. In order to better understand the solid-solution partitioning process in estuaries it is necessary to study the partitioning behaviour between natural suspended sediments and waters. This chapter presents the results from laboratory experiments designed to evaluate the sorption behaviour of PCBs and dioxins onto natural estuarine sediments.

5.1 Radioisotope Sorption Studies

The use of radioisotopes in environmental science is widespread (Caron *et al.*, 1985; Goulding, 1986; Horzempa & Di Toro, 1983; Larsson, 1983; Voice *et al.*, 1983; Rawling *et al.*, 1998). These studies generally involve the introduction of a radiolabelled analog of the compound under study to a reactor maintained under carefully controlled laboratory conditions. For the type of compounds under study in this project, this label would usually be ^{14}C. The environmental conditions in the microcosm can be controlled and monitored to study the behaviour of the compound under these synthetic conditions. In such laboratory experiments, use of radiolabelled compounds have a number of key advantages;

- Chromatographic or spectrometry techniques are unnecessary, resulting in reduced processing of samples and allowing large numbers of samples to be analysed for each experiment.

- Detection limits are low, limited only by the background activity count detected by the scintillation counter.
- Possibilities for contamination are greatly reduced.

There are also disadvantages which must be taken into account when designing and executing experiments;

- It is not possible to monitor degradation during the experiment as the ^{14}C label will be counted whether it is still associated with the precursor compound or with some degradation by-product. In this study the relatively short timescales for experiments and the high molecular weight compounds used mitigate against this problem.
- Although impurities in the ^{14}C-labelled compound are small; if these impurities have different properties to the target compound (e.g. much higher solubility) they can significantly affect the apparent partitioning (Gu *et al.*, 1995).

With these factors in mind, the development of an experimental protocol was undertaken.

5.2 Experimental Development

5.2.1 Objectives

Following the study of sorption preferences for compounds in bed sediments, the following objectives were established for the sorption experiments;

- Estimation of compound solubility in natural and pure water.
- Study of the effect of particle characteristics on partitioning coefficient.
- Study of the variation of partition coefficient with a natural estuarine salinity, SPM concentration and particle type gradient.

Experimental development was conducted over a 4 month period to refine the method and ensure its suitability for the planned study. A thorough review was conducted initially to examine the approaches already in use. Active use of radiolabelled compounds in laboratory environmental sorption experiments started in the early 1980s (Horzempa & Di Toro, 1983; Larsson, 1983; Voice *et al.*, 1983). The general experimental methodology was to add a spike of a radiolabelled stock compound to a multi-phase (sediment-water, sediment-water-air) system usually held in a small receptacle such as a centrifuge tube. The sample was equilibrated for a fixed period of time and then separated. Separation was usually achieved by centrifugation and the resulting phases either added directly to a scintillant for counting on a scintillation counter or, in the case of particulate matter, filtered and added to a scintillation cocktail. Compound adsorbed to the glass walls of the receptacle was also extracted with hexane and added to scintillant for counting. Following counting, the counts for each phase were converted to mass via the specific activity of the compound which then allowed calculation of the partition coefficient (Voice *et al.*, 1983). Other techniques have involved variations on this basic design including use of dialysis membranes for solid-water separation to avoid centrifugation (Brunk *et al.*, 1997; Landrum *et al.*, 1984).

5.2.2 Experimental Method

The method chosen for development follows closely the methods of Caron *et al.* (1985), Means (1995), and Zhou & Rowland (1995). It has subsequently been further developed by co-workers continuing the studies in this field (Rawling *et al.*, 1998). The initial objectives in the development of a robust technique were assurance that the mass balance of partitioning between water, sediment, and the reactor was quantified, and that the experiments produced readily repeatable results.

Initially the method was developed using 9-methylanthracene which was readily available prior to delivery of the organochlorine compounds. 9-

methylanthracene is a compound of higher solubility than most organochlorine compounds, so although its use allowed the development of the basic experimental design, it did not assist in addressing one of the fundamental problems associated with such experiments conducted with highly hydrophobic compounds, namely adsorption to the walls of the glass reactor. This additional phase is a major consideration in the experimental design and two approaches were tested to assess the optimum method for determining the sediment-water partition coefficient.

Test Substances

Two compounds were selected for use in the experiments; ^{14}C-[UL]-2,2',5,5'-tetrachlorobiphenyl (2,2',5,5'-TCB - IUPAC 52), and ^{14}C-[UL]-2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). These compounds were selected for a number of reasons;

- Contrasting K_{ow} and solubility values (see Table 5.1 below)
- Analysed as part of the bed sediment study
- Most widely studied of the polychlorinated biphenyl and dioxin compounds permitting maximum inter-comparability with other studies

	2,2',5,5'-TCB	**2,3,7,8-TCDD**
Manufacturer	Sigma Chemical Co.	Radian Corporation
Specific Activity	13.32 mCi mmol^{-1}	33 mCi mmol^{-1}
Purity	>98%	>99%
Concentration	21.9 μg l^{-1}	18.5 μg l^{-1}
Molecular Mass	292	320
log octanol-water partition coefficient	5.84[a]	6.80[c]
Solubility @ 25°C	25.4 μg l^{-1} [b]	0.019 μg l^{-1} [c]

[a]Hawker & Connell (1988), [b]Rapaport & Eisenrich (1984), [c]Shui *et al.* (1988)

Table 5.1. Properties of ^{14}C-labelled Compounds Used in Sorption Studies

The stock of 2,3,7,8-TCDD was obtained from the MAFF CSL Food Science Laboratory in Norwich. The 2,2',5,5'-TCB was obtained directly from Sigma

Chemical Co. The purity of both compounds was checked by the supplier prior to despatch. Both compounds were supplied in toluene and upon receipt, diluted stock solutions of both compounds were made up in hexane. The activity of the stock solution was regularly checked by injection of a stock spike into liquid scintillant and counting on the scintillation counter.

At all times stock solutions were kept refrigerated in the dark to minimise the potential for bacterial and photodegradation (Marple *et al.*, 1986). All the experiments were conducted over a 9 month period from first obtaining the radiolabelled compounds.

Spiking and Equilibration

In previous and subsequent work the preparation of the reactor has been seen to be important in minimising adsorption of highly hydrophobic compounds to the glassware (Hunter *et al.*, 1996; Rawling *et al.*, 1998). Hunter *et al.* (1996) found that up to 80% of 2,2',5,5'-TCB could be lost to glassware if cleaning methods were not adequate. For these studies, new centrifuge tubes were used. Before each set of experiments these were soaked in a Decon 90 solution, rinsed with deionized water, dried in a constant temperature oven at 200°C for at least 4 hours and then hexane rinsed prior to use.

The introduction of the radiolabelled spike is another important consideration in initiating experiments. The general approach taken usually involves the addition of the spike in solvent which is then evaporated prior to addition of the sorbent matrix (Means, 1995; Walters & Guiseppi-Elle, 1988; Zhou *et al.*, 1995a). In this study a 25 μl spike containing 0.02 μCi of compound was placed on the wall of an empty tube by microsyringe. The hexane carrier solvent was then evaporated under a laminar flow hood.

Once the spike was successfully transferred to the centrifuge tube, a 20 ml aliquot of the suspended sediment-water sample was added to the tube. The top of the tube was sealed with a hexane-washed glass stopper. The tubes were then placed on a shaker for 12 hours during which the SPM was maintained in suspension. After reference to the literature, 12 hours was considered a reasonable time for such hydrophobic compounds to reach an apparent equilibrium state (Cornelissen *et al.*, 1997). Karickhoff (1984) reported sorption of polynuclear aromatic hydrocarbons reaching apparent equilibrium within a 'few hours'. Di Toro & Horzempa (1982) report sorption of a hexachlorobiphenyl to various sorbents, including sediments, within 'minutes to hours' and a number of radiochemical sorption studies have adopted incubation times of ≤ 24 hours (Means *et al.*, 1980; Rawling *et al.*, 1998; Voice *et al.*, 1983).

Phase Separation

The separation of the phases following incubation is of major importance in determining the sediment-water partition coefficient. The operational definition of the phase separation process and its relevance to actual environmental conditions are discussed below. Two general approaches to phase separation have been employed previously; direct counting of sediments, and calculation of adsorbed mass by mass balance following determination of the glass-adsorbed and solute mass.

Direct counting of sediments follows two general approaches. The less common approach was adopted by Voice *et al.* (1983) who filtered solids following centrifugation to remove a sample of supernatant, and added the filter paper directly to the scintillation vial. Hegeman *et al.* (1995) centrifuged samples, withdrew the supernatant and added the particles to MeOH for direct extraction. Hunter *et al.* (1996) followed a similar approach by extracting PCB directly from sediments with acetone at the end of the equilibration. The alternative calculation of the mass balance to determine solid phase concentrations has been used widely (Means, 1995; Murphy *et al.*, 1994; Rawling *et al.*, 1998; Walters & Guiseppi-Elle, 1988).

During the experimental development, a method of direct extraction of sediments was attempted initially. Following centrifugation the supernatant sample was taken (4 ml), followed by removal and disposal of the remainder of the supernatant. Hexane was then added to the tube which was placed in a shaker for 12 hours to extract both the sediments and the glass wall adsorbed compound. Separately the glass wall adsorbed mass was determined in experiments conducted in the absence of particles, and subtracted from the solid + glass wall mass to provide the solid phase adsorbed mass of compound. Although this technique seemed to work well with the experiments conducted with 9-methyl anthracene (mean K_d = 1938, n=8) where reproducibility was excellent (standard deviation ranging from 1.1 to 2.8 %), once applied to the highly hydrophobic 2,3,7,8-TCDD replicate percentage standard deviations rose to between 20 and 114 %. There are probably several reasons for this;

- The glass wall adsorbed fraction was taken as a mean from the experiments in the absence of particles. There was significant variation in the measurement of this fraction (63 % standard deviation for n=3).
- The glass wall adsorption experiments were conducted in the absence of particles which would result in modified thermodynamic equilibrium conditions.
- It was extremely difficult experimentally to avoid take-up of particles in the pipette when decanting the supernatant from the centrifuge tubes. With the high solubility 9-methyl anthracene this made significantly less difference than with the low solubility 2,3,7,8-TCDD.

As a result of the unsatisfactory results from this approach the method was modified. Thus, following removal of the supernatant sample, the particles were discarded and the glass wall was extracted with 4 ml of hexane with the centrifuge tube placed back on the shaker for a further 12 hours to ensure that the wall-adsorbed compound was solubilized by the hexane. A 2 ml sample of the hexane was then added to liquid scintillant for counting. Table 5.2 shows comparative percentage standard deviations for the two methods applied to the same set of samples. The values for 2,3,7,8-TCDD are still fairly high (31 - 59 %) but this is attributed to the general difficulties in working with this very low solubility compound. Percentage standard deviations for experiments using 2,2',5,5'-TCB were routinely < 20 %. It was decided at an early stage, based on these method development results, that all samples would be analysed at least in triplicate for all experiments.

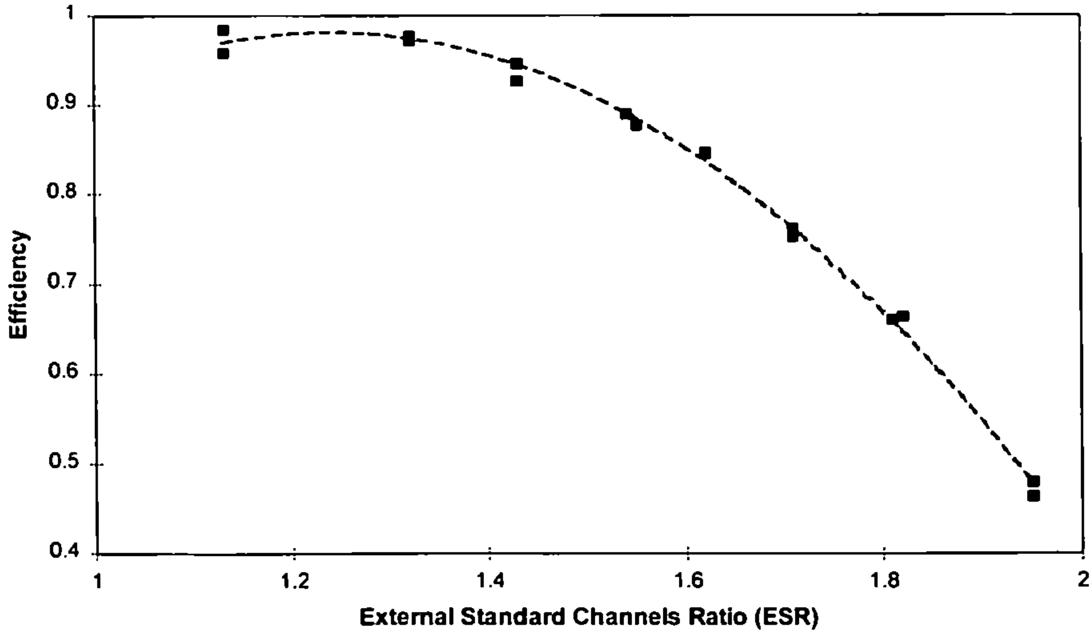
Sample No.	% Standard Deviation	
	Direct Particle Extraction (n=2)	Glass Wall Extraction (n=4)
1	105	31
2	20	59
3	47	17
4	98	52
5	114	42

Table 5.2. Comparison between Standard Deviations for 2,3,7,8-TCDD K_d obtained from Alternative Extraction Methods

The centrifugation of samples was also carefully considered. Servos & Muir (1989) and Gschwend & Wu (1985) both observed little difference in K_d values obtained from different centrifugation speeds and times, particularly at low suspended sediment concentrations (< 10 mg l^{-1}). Suspended sediment concentrations used in this study were well below this concentration. In this study therefore the samples were centrifuged for 30 minutes at 3,000 rpm. The centrifuge tube was loosely covered with a hexane washed foil cap to prevent entry of extraneous material and reduce any evaporative loss. To what extent this centrifugation process removes so-called 'Non-Settling Particles' cannot be determined and the implications of this are discussed later.

Mass Determination and Partition Coefficient Calculation

Following phase separation, each pair of solute and glass-wall extracted samples were added to a counting vial containing 10 ml of Ultima Gold scintillation cocktail (Canberra Packard). This was then counted on a Philips 4700 scintillation counter. Prior to commencement of the experiments, quench curves had been prepared for both compounds for hexane and water. These were prepared by adding a known concentration spike of the target compound to a counting vial containing the scintillation cocktail. A quenching agent (carbon tetrachloride, CCl_4) was then added to each vial at different concentrations to provide a range of quenching standards which were then counted on the scintillation counter. The resulting counting efficiency was calculated by first subtracting the background count, and then expressing the counts per minute (CPM) as a fraction of the known disintegrations per minute (DPM) of the reference spike. The quench curves were prepared by plotting the counting efficiency against the External Standard Channels Ratio (ESR) used by the instrument. From the ESR value, the quench curve was used to determine the counting efficiency. Example quench curves for 2,2,5,5-TCB in hexane and water are shown in Figure 5.1 a and b.



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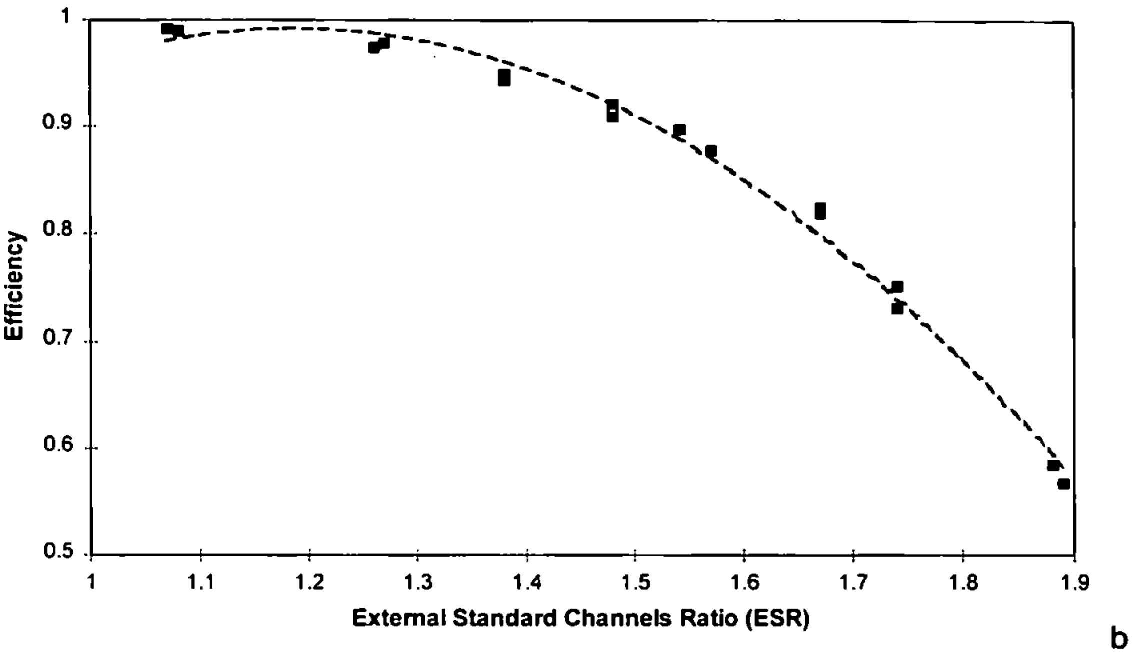


Figure 5.1. Quench Curves for 2,2',5,5'-TCB in (a) Water Matrix, and (b) Hexane Matrix

Samples were counted for 20 minutes or until two standard deviations from the mean count was less than 1%. Following counting, the CPM recorded by the scintillation counter were converted to DPM using the quench curves to provide an efficiency and applying the efficiency factor as follows;

$$\text{DPM} = \text{CPM. Efficiency} \qquad 5.1$$

The absolute DPM was then calculated by subtracting the background DPM from the DPM. Finally, the K_d was calculated as follows;

$$K_d = \frac{P}{C} = \frac{(A_s - (A_c + A_w)}{A_c} \cdot \frac{V}{m} \qquad 5.2$$

where P is the particulate concentration, C is the dissolved concentration, A_s, A_c, and A_w are the activities of the original spike, supernatant and wall adsorbtion respectively, V is the dissolved phase volume (ml) and m is the particulate mass (mg). Experiments were conducted to measure recovery of the ^{14}C spike with recoveries measured at 78 ± 15% based on 10 samples.

It should be noted that this study determined single point K_d values rather than repeating each point on the mixing gradient for a range of added spikes masses to produce a sorption isotherm. The assumption inherent in this approach is that the empirical Freundlich equation (Equation 5.3) widely used to describe the sediment-water partitioning, has a value of n = 1;

$$P = K_d . C^{1/n} \qquad 5.3$$

such that,

$$P = K_d . C \qquad 5.4$$

A wide range of sorption experiments using hydrophobic organic compounds has shown this to be a reasonable assumption (Horzempa & Di Toro, 1983; Means & Wijayratne, 1982; Rawling *et al.*, 1998; Voice *et al.*, 1983; Walters & Guiseppi-Elle, 1988) and where non-linear isotherms have been noted, this has arisen in experiments where sorbate concentrations far higher than those normally encountered in environmental media have been used (Grathwohl, 1990; Karickhoff *et al.*, 1979). Assuming linear isotherms permitted a far larger number of samples to be processed than would have been possible if sorption isotherms were produced for each sample.

5.2.3 Study Sites, Sample Collection and Mixing

Four study sites were chosen for sorption experiments. Two of these, the Humber and Clyde estuaries, were chosen as they were the primary sites for the distribution studies. Two others, the Dart and Beaulieu estuaries were chosen as sites of a convenient size and proximity to the laboratory to permit rapid processing of samples after collection. The Dart Estuary is a small estuary located in South Devon with its source on Dartmoor, draining moorland and agricultural land. The Beaulieu Estuary is another small estuary, situated in Hampshire and draining the heath and marshland of the New Forest. It is reported to contain relatively high concentrations of DOC

(Hunter & Liss, 1982) and Fe (Holliday & Liss, 1976). There is no knowledge of any studies of OCs in either estuary.

Immediately prior to each batch of experiments (usually less than 48 hours), the estuary was visited and two large volume samples taken (typically 20 litres) from the River End Member (REM) and the Marine End Member (MEM). Depending on the location, these were either taken from the bank/shore, a bridge, or from a vessel and stored in a plastic carboy. A portable salinometer was used to check the salinity before sampling to ensure the maximum range of salinities possible. Upon return to the laboratory, a sub-sample was filtered to obtain an accurate measure of the SPM concentration and the salinity was re-checked. During the duration of the study, the following sampling surveys were conducted;

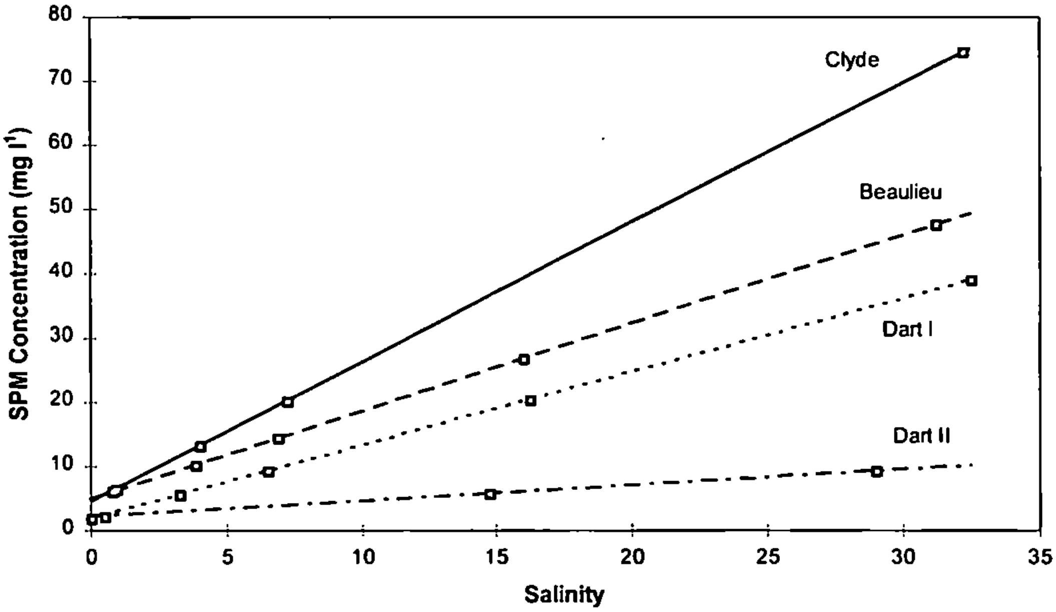
Date	Estuary
September 1993	Tamar*
January 1994	Clyde
February 1994	Humber
	Clyde
March 1994	Humber
	Beaulieu
March 1994	Dart x 2
April 1994	Clyde

*Only used during method development

Table 5.3. Sorption Experiment Sampling Surveys

Most of the experiments conducted involved the admixing of the two end member samples taken from the study estuaries. The sample volume used in the incubations was kept constant at 20 ml so aliquots from each end member sample was used in varying proportions to simulate the estuarine gradient. One key consideration in the use of this method is that a gradient is simultaneously simulated for a suite of variables including particle composition, SPM concentration, salinity and pH. As such it represents the field environment as closely as possible but has the disadvantage of permitting less diagnosis of specific controlling variables. To investigate the influence of salinity independent of particle composition, one experiment was conducted where the MEM was pre-filtered before use. This permitted a simulation of the salinity gradient while maintaining homogeneity in the composition (but not the concentration) of the SPM.

Figure 5.2 shows the mixing gradients created for the four study estuaries. End member SPM and salinities are summarised in Table 5.4 and 5.5. The Clyde, Beaulieu and Dart estuaries have SPM concentrations within a similar range (< 80 mg l^{-1}). In all cases, the REM sample was taken in the river where the SPM concentration was relatively low. Samples in the MEM contained significantly higher SPM concentrations. In the Humber Estuary the SPM concentrations in the end members were similar (250 and 300 mg l^{-1}) resulting in a relatively homogenous distribution decreasing seawards.



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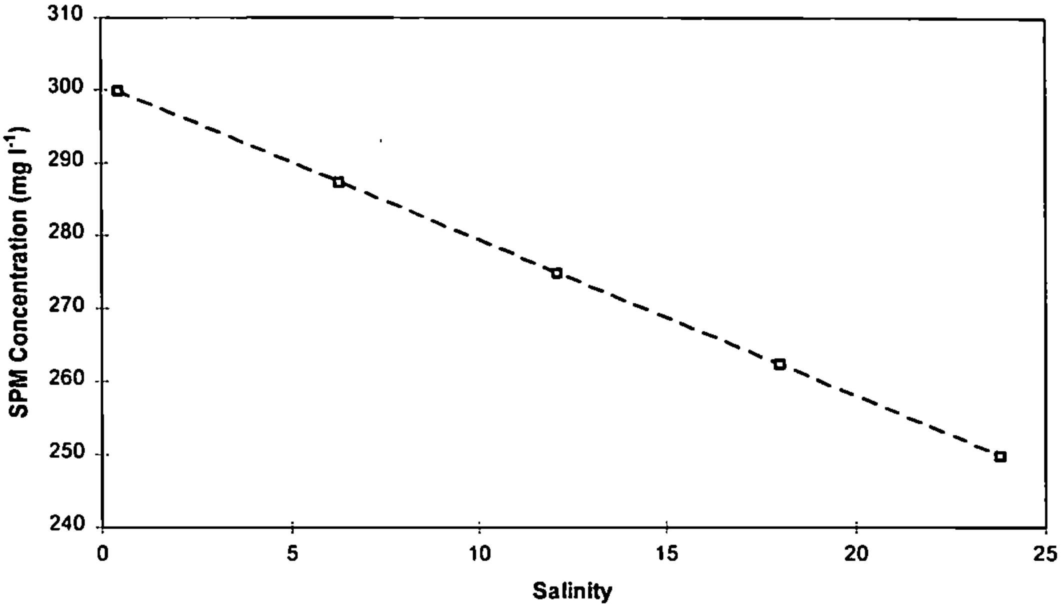


b

Figure 5.2 Mixing Gradients (SPM v Salinity) for (a) Clyde, Beaulieu, Dart and (b) Humber Estuaries

5.3 Experimental Results

Table 5.4 and 5.5 summarises the K_d values measured during the experiments in the end member samples. The percentage in the dissolved phase has been calculated from the K_d using following equation;

$$\%\text{Dissolved} = \frac{100}{(1 + K_d . SPM . 10^{-6})} \qquad 5.5$$

In all cases the K_ds for 2,3,7,8-TCDD were substantially higher (usually at least one order of magnitude higher) than 2,2',5,5'-TCB as would be expected from the solubility and K_{ow} data. In the Clyde, Dart and Beaulieu estuaries there was large decrease in K_d at the MEM but in the Humber Estuary the difference in REM and MEM K_ds was less, with a rise in K_d at the MEM. The K_d gradient is discussed in more detail below.

Estuary	Salinity	SPM (mg l^{-1})	TCB K_d	% Dissolved	TCDD K_d	% Dissolved
Humber	0.4	300	5.6 x 10^4	6	23.1 x 10^4	1
Clyde	0.9	6.5	18.0 x 10^4	46	313.1 x 10^4	5
Beaulieu	0.8	6.0	49.4 x 10^4	25	-	-
Dart I	0	1.8	32.7 x 10^4	63	-	-
Dart II	0.5	2.3	26.7 x 10^4	62	-	-

Table 5.4. K_d, Salinity and SPM for REM Samples (n=4)

Estuary	Salinity	SPM (mg l^{-1})	TCB K_d	% Dissolved	TCDD K_d	% Dissolved
Humber	23.8	250	10.7 x 10^4	4	32.2 x 10^4	1
Clyde	32.2	74.5	3.3 x 10^4	29	78.9 x 10^4	2
Beaulieu	31.2	47.6	12.9 x 10^4	14	-	-
Dart I	32.5	39	2.4 x 10^4	52	-	-
Dart II	29.0	9.4	11.1 x 10^4	49	-	-

Table 5.5. K_d, Salinity and SPM for MEM Samples (n=4)

Direct comparison of K_ds from this study and other work is difficult as the simulated environment differs significantly between studies. An average K_d for 2,2',5,5'-TCB of 5.2 x 10^4 in 5 estuaries (Scheldt, Rhine, Ems, Weser and Elbe) was measured by Duinker (1986). Van Zoest & Van Eck (1993b) found 50% of 2,2',5,5'-TCB in the Scheldt Estuary bound to particulates. Nau-Ritter & Wurster (1983) reported K_ds for ^{14}C-Aroclor 1254 onto pure mineral particles (illite and chlorite) of between 1 x 10^4 and 1.4 x 10^4. In laboratory studies conducted using natural samples, Rawling *et al.* (1998) measured K_ds of typically 12 x 10^4 -15 x 10^4 at similar solids concentrations. For 2,3,7,8-TCDD, Broman *et al.* (1991) reported an average K_d of 400 x 10^4 for nine stations in the Baltic Sea. Abarnou *et al.* (1987) found 80% adsorption of hexachlorobiphenyl (slightly more apolar than 2,2',5,5'-TCB) to SPM. The K_ds reported from the literature are all consistent with those determined during these experiments.

5.3.1 Solubility

A set of initial experiments were conducted to determine an indicative solubility of 2,2',5,5'-TCB in both filtered river water and MilliQ deionized water and 2,3,7,8-TCDD in filtered river water. This was achieved by adding a spike of known activity to a volume of water, equilibrating and counting the activity in the dissolved phase. The experiments using 2,3,7,8-TCDD were conducted during the method development and gave elevated values (solubility of ~ 0.3 μg l^{-1}) compared with a published solubility of 0.019 μg l^{-1} (Shui *et al.*, 1988). This may have been due to the high concentration of 2,3,7,8-TCDD (18.5 μg l^{-1}) required to achieve a reasonable DPM, or the presence of DOM in the river water. Rawling *et al.* (1998) found that at concentrations above the published solubility at saturation there was a dramatic increase in solubility and highly variable results. The 2,3,7,8-TCDD experiments were also conducted using the initial methods where the glass wall fraction was not determined directly and this may have also adversely affected repeatability.

The solubility of 2,2',5,5'-TCB was found to be 12.3 ± 0.7 μg l^{-1} (n=4) in MilliQ deionized water which compares favourably with the published solubility of 25.4 μg l^{-1} (Mackay *et al.*, 1980) and a solubility of 15 μg l^{-1} reported by Rawling *et al.* (1998) using a similar radiochemical method. In filtered river water there was a small increase in solubility to 16.8 ± 2.4 μg l^{-1} (n=4). This increase in solubility in river water may be explained by the presence of dissolved organic matter in the river water which has been widely reported to increase apparent solubility (Chiou *et al*, 1987; Hassett & Anderson, 1979; Gauthier *et al.*, 1987; Hunchak-Kariouk *et al.*, 1997).

5.3.2 Solids Concentration Effect

Environmental sorption science has introduced a significant level of complexity in understanding and interpreting the data generated from field measurements, laboratory experiments and model predictions by the use of operational definitions of various system phases. This is brought about by the need to compartmentalise the environment into manageable phases which don't necessarily align exactly with the physicochemical nature of the environment under study. In consideration of the notional solid-water partitioning of organic compounds, at a simple level two phases are defined; particulate (P) and dissolved (C) with a partition coefficient K_d defined as;

$$K_d = \frac{P}{C} \qquad 5.6$$

Many workers have, however, found this two-phase system to be over-simplistic when considering the mechanisms of organic compound sorption in the marine environment (Baker *et al.*, 1986; Burgess *et al.*, 1996; Eadie *et al.*, 1990; Hassett & Millicic, 1985; Hinton *et al.*, 1993; Pankow & McKenzie, 1991; Sigleo & Means, 1990; Wijayaratne & Means, 1984). This is due to the complexity of the composition of the dissolved, quasi-dissolved and particulate phases. Of relevance to organic compound sorption is truly dissolved organic matter (may include dissolved humics), colloid-bound apolar material (e.g. lipid), colloidal-bound humic material and both inorganic and organic phases of the particulate phase as discussed in Chapter 4.

The possibilities for hydrophobic organic compound sorption are summarised diagramatically in Figure 5.3. The operational separation between 'dissolved' and 'solid' phases has been typically set at approximately 0.4 μm (Sigleo & Means, 1990). However, this cut-off includes colloidal material (typically in the size range > 1nm to < 0.4 μm) in the dissolved fraction. This colloidal material has a complex composition but is widely reported to contain both polar and apolar organic matter.

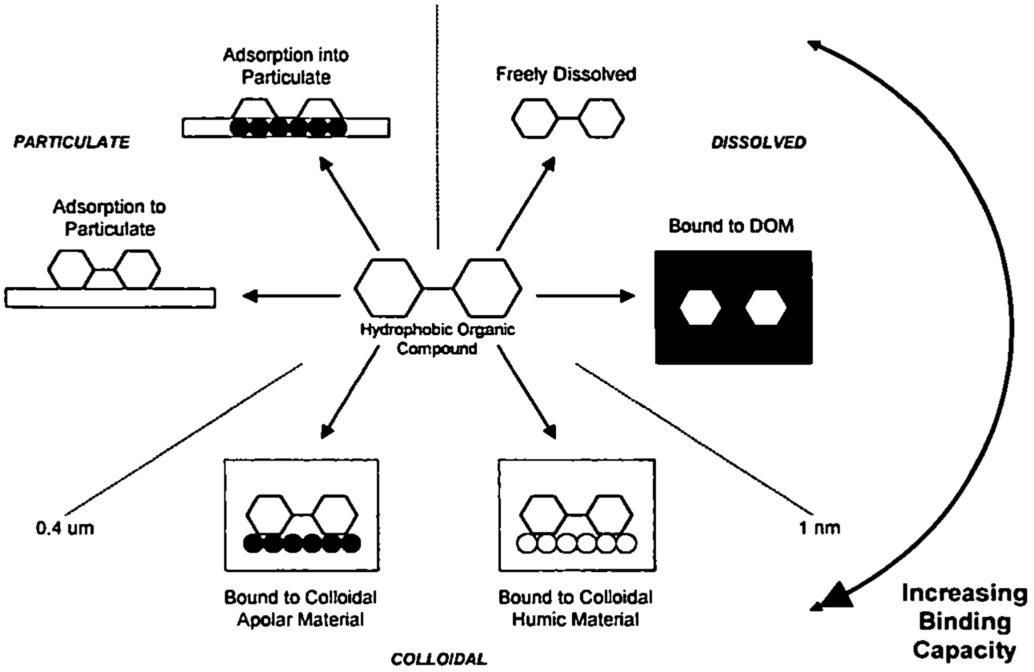


Figure 5.3. Possible Phases for Hydrophobic Organic Compound Sorption

Of particular interest in both the dissolved and colloidal fractions, is the presence of humic material which contributes significantly to the high sorptive capacity reported for colloidal material. No experiments have been designed under this study to examine the interaction of PCBs and dioxins with colloidal phases or, more specifically, the humic substances which may be present. It is not proposed therefore to engage in a lengthy discussion on the role of these sub-phases, although the presence of the colloidal phase is an important consideration in the solids concentration effect discussed below.

In a practical sense during this study, the definition of the various phases are considered more simply. Although there may be implications for sorption kinetics and reversibility in the transfer of hydrophobic organic compounds between the phases outlined above, in an estuarine system there are only two primary transport pathways; advection and dispersion in the water, and dispersion according to the sediment dynamics. On this basis, the solid phase can be defined as that which is dominated by sediment transport and therefore would include all suspended and bed sediment material found in the estuary, and the dissolved phase can be taken to include colloidal phases which would be largely transported within the water column. We can understand the sediment-water partition coefficient to be a 'transport pathway partition coefficient'. For integrated estuarine modelling purposes, such as described in Chapter 6, this two-phase description is quite sufficient.

The solids concentration effect is a very widely reported observation in sorption studies (Gschwend & Wu, 1985; Lodge & Cook, 1989; O'Connor & Connolly, 1980; Voice *et al.* 1983). There has been an on-going debate for many years over the occurrence of the effect and its realism to actual environmental conditions. The first observations of an apparent decrease in sediment-water partition coefficient with increasing suspended solids concentration was first reported by O'Connor & Connolly (1980). Apart from conceding that there was no fundamental basis for the correlation - which appears on face value not to observe the laws of thermodynamic equilibrium - they presented comprehensive data for many compounds illustrating the effect.

Data from this study has been analysed to show the relationship between the K_d obtained and the SPM concentration in the sample. Figure 5.4 a and b shows the relationships derived for the four study estuaries. These are consistent with other studies which also established relationships of the form;

$$\log K_d = -b. \log SPM + a \qquad 5.7$$

A summary of regression constants together with those from other studies on the sorption behaviour of 2,2'5,5'-TCB are presented in Table 5.6. The Clyde, Dart and Beaulieu estuaries all show a significant apparent solids concentration. The linear regression gradients for these estuaries are similar and compare very closely with a number of other studies summarised in Table 5.6. The overall magnitude of the K_d differentiates between the sites which compares with other investigations using different sorbents (Voice *et* *al.*, 1983). The Humber also shows a correlation albeit weaker which may be explained by the relatively homogenous SPM concentration distribution used in the experiments. When considering this data it must be remembered that, unlike most studies specifically examining the solids concentration effect, these simulated gradients also embody the changes in particle composition, salinity etc. However, the solids concentration effect is evident for both the Humber and the other estuaries even though the slope of the SPM concentration gradients are opposed (see Figure 5.2).

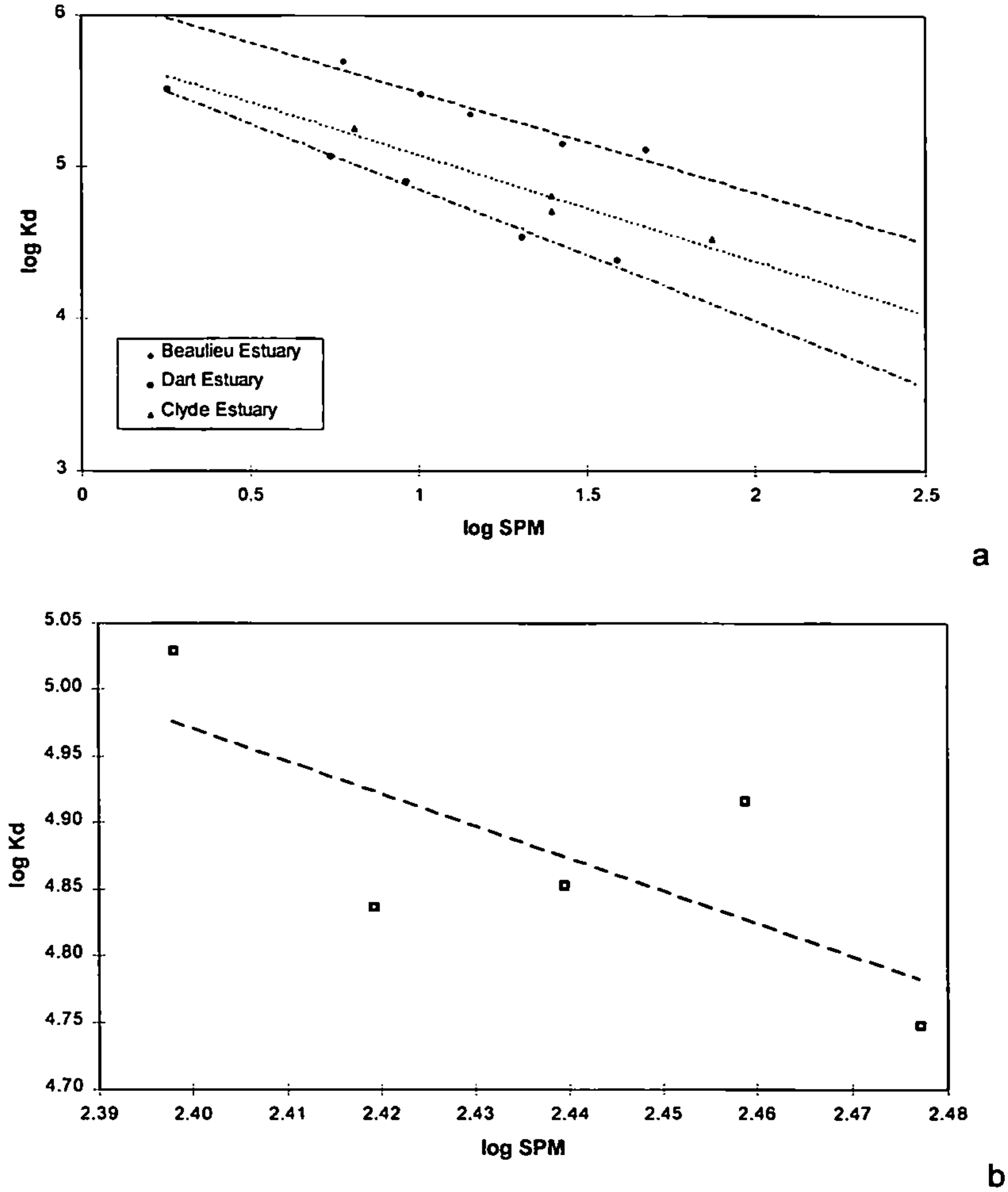


Figure 5.4. 2,2',5,5'-TCB K_d as a Function of SPM for the Study Estuaries (a) Beaulieu, ($R^2 = 0.94$, $p < 0.02$); Dart, ($R^2 = 0.99$, $p < 0.001$); Clyde, ($R^2 = 0.95$, $p < 0.05$); (b) Humber, ($R^2 = 0.54$, not significant)

Sample	SPM Range (mg. l^{-1})	Regression Constants		Reference
		a	b	
Unfiltered Lake Michigan water	0.3-1.9	0.75	5.00	Eadie *et al.* (1990)
Unfiltered Lake Superior water	0.2-8	1.08	5.30	Baker *et al.* (1986)
Unfiltered North Sea coastal water	1-150	-0.94	6.20	Duinker (1986)
Filtered R. Plym	~10-1000	0.61	4.50	Rawling *et al.* (1998)
Filtered English Channel water	~10-1000	0.50	4.00	Rawling *et al.* (1998)
Dart estuary	1.8-39	-0.86	5.72	This work
Beaulieu estuary	6.0-47.6	-0.66	6.16	This work
Clyde Estuary	6.5-74.5	-0.68	5.78	This work
Humber Estuary	300-250	-2.45	10.86	This work

Table 5.6. Comparison between Regression Constants for log K_d = -b. log SPM + a Obtained from Various Studies of 2,2'5,5'-TCB Sorption

To attempt to isolate the solids concentration effect, the REM with its natural SPM from the Dart estuary was admixed with filtered Dart estuary MEM water thus maintaining the same particle composition but varying the solids concentration. The salinity gradient was still simulated simultaneously. Using the same unfiltered MEM and REM samples, a standard gradient was also simulated for comparison. Figure 5.5 shows the log SPM vs log K_d for both filtered MEM and unfiltered cases.

The use of the filtered MEM maintained solids concentrations at the lower end of the scale. However, there was overlap in SPM concentration with the unfiltered samples at approximately 2 mg l^{-1}. Both experimental results show an equally strong linear correlation between log K_d and log SPM. In addition, the gradient of the linear regression is almost identical. The implication from these observations is that the solids concentration effect is an important effect in these experiments, and possibly more influential than other parameters such as salinity.

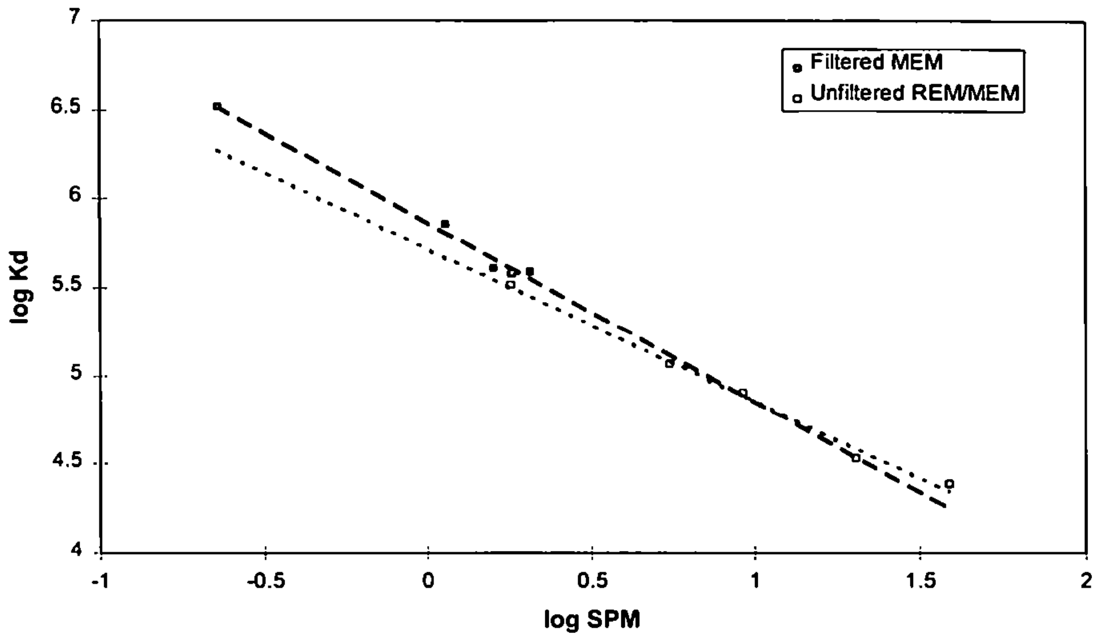


Figure 5.5. K_d vs SPM for the Filtered and Unfiltered MEM in the Dart Estuary (Unfiltered, $R^2 = 0.99$, $p < 0.001$, n=3; Filtered MEM, $R^2 = 0.99$, $p < 0.01$, n=3)

It was not the intention of these studies to further contribute to the debate on the solids concentration effect. From a practical standpoint, it is important to distinguish between a laboratory artefact, a real phenomena but which only exists in the laboratory experiment, and a real phenomena measured experimentally and transferable to the real environment (e.g. particle interaction effects). A number of explanations have been put forward over the past 20 years to explain the solids concentration effect. Central to many of these explanations is the presence of the 'third phase', the colloidal or Non-Settling Particulate (NSP) phase.

The early work by O'Connor & Connolly (1980) was conducted on a wide range of inorganic metals and organic chemicals implying that the solids concentration effect is not chemically promoted but may be due to physical interactions. Voice *et al.* (1983) surmised that the solids concentration effect was due to the presence of a NSP phase which was derived from the solid phase but counted in the dissolved phase following separation and that the effect would be likely to occur in the environment. This investigation was followed by the work of Gschwend & Wu (1985) where increasing NSP concentrations with solids concentration were demonstrated. By pre-washing sediments to reduce the availability of material likely to form NSPs, partition coefficients were shown to be linear with solids concentration (Walters *et al.*, 1989). An alternative explanation was proffered by Di Toro *et al.* (1986) using an experimental design that explicitly excluded variations in NSP concentrations. It was suggested that increased higher solids concentrations may be responsible for increasing particle interaction induced desorption which would lower K_d values. Mackay & Powers (1987) continued the development of the model proposed by Di Toro *et al.* and added to the explanation by proposing a sorption process consisting of a 'loose surface accumulation' of apolar organic compounds which can be disrupted by particle collisions. As the solids concentration rises, the potential for particle interaction-induced desorption increases. The relationship between K_d and SPM concentration was summarised in the following equation which is discussed in detail in the next chapter;

$$K_d = \frac{f_{oc}.K_{oc}}{(1 + 0.7.f_{oc}.K_{oc}.SPM)} \qquad 5.8$$

where f_{oc} is the fraction of organic carbon, K_{oc} is the organic carbon partition coefficient, and SPM is the solids concentration. This is referred to in this study as the Di Toro & Mackay Model. Using values of $K_{oc} = 0.41.K_{ow}$ (Karickhoff, 1984), $f_{oc} = 0.15$, and a range of solids concentrations covering those measured during this study (extended from 1 mg l^{-1} to 1,000 mg l^{-1}), the relationship in Figure 5.6 was derived.

The main point of note from this model is that the realistic natural solids concentrations used in these studies are on the upper flatter part of the curve and may be approximated as a straight line ($R^2 = 0.96$, $p < 0.01$). This is consistent with the observations from this study. Mackay & Powers (1987) define a breakpoint in the curve when there is sufficient concentration of sorbent to sorb half the compound. At higher sorbent concentrations it is not possible to sorb more than half because collision-induced desorption rates are rapid. The application of this model is discussed in further detail in Chapter 6.

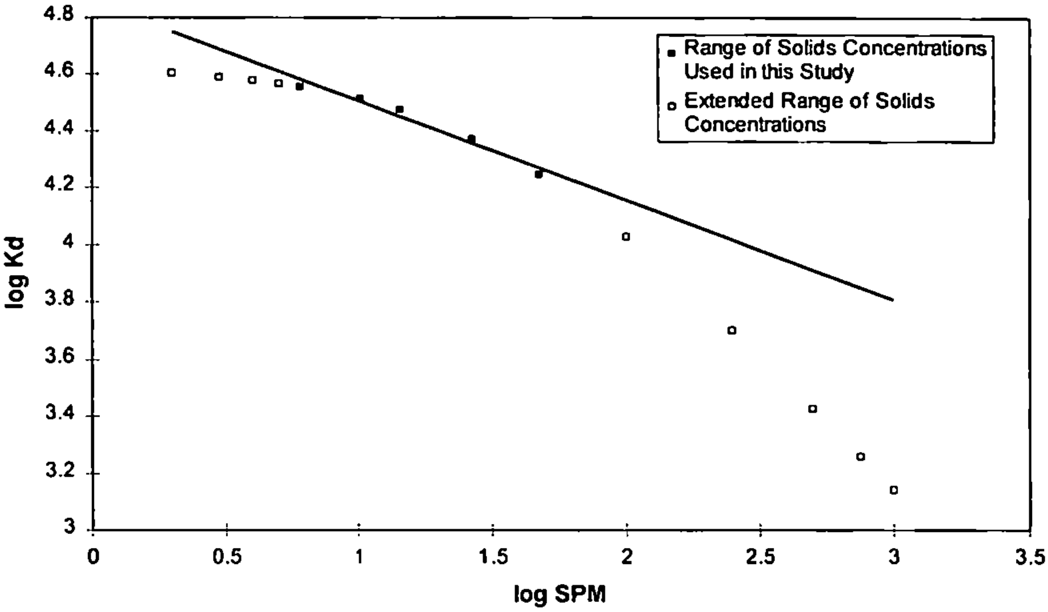


Figure 5.6. log K_d vs log SPM using the Di Toro and Mackay Model

Work over the past few years has continued to investigate the effect (Jepsen *et al.*, 1995; Rawling *et al.*, 1998; Zhao & Lang, 1996) much of which has focused on investigation of the NSP explanation. Servos & Muir (1989) found experimental determination of NSP concentration to explain a significant part of the effect but indicated that particle interactions or some similar hypothesis was required to fully explain the observations. Rawling *et al.* (1998) on work using natural samples, observed that no additional NSP effect was seen in highly turbid samples (~500 mg l^{-1}). This implied that NSP material released *in situ* via SPM was of limited importance. This conflicts with previous experimental observations (e.g. Gschwend & Wu, 1985; Servos & Muir, 1989) where either particle populations still contained significant pore water colloids, or pure water was used as a solute which would not have been in equilibrium with the SPM and promoted material transfer.

In summary, there still remains uncertainty in the causes of the particle concentration effect but there is no doubt that it is a feature of all typical sorption experiments and is likely to increase in importance with higher K_{ow} compounds (Booij, 1993). There is corroborating field evidence that the solids concentration effect may be observed under actual environmental conditions. Baker *et al.* (1986) measured solids concentration effects with PCB congeners at SPM concentrations of ~ 0.2 - 6 mg l^{-1} and Bergen *et al.* (1993) reported similar results at concentrations of ~ 0 - 30 mg l^{-1}. Of particular relevance, Zhou *et al.* (1998) showed a correlation between SPM concentration and PAH concentrations in Humber Estuary.

In deriving suitable partitioning descriptors for use in integrated contaminant transport models, an established relationship between K_d and SPM concentration is straightforward to implement. Provided that extrapolation of the laboratory measured relationship to the field is reasonable which may be assumed given the efforts spent in eliminating laboratory artefact, then whether the effect is caused by NSPs or particle interactions is largely hypothetical. The release of NSPs from particles and their subsequent transport within the water body would be encompassed by an operationally defined 'transport pathway partition coefficient' and particle interaction effects could be assumed to be directly represented by laboratory conditions. The inclusion of solids concentration effects via a sorption sub-model in an integrated estuary model is discussed in Chapter 6.

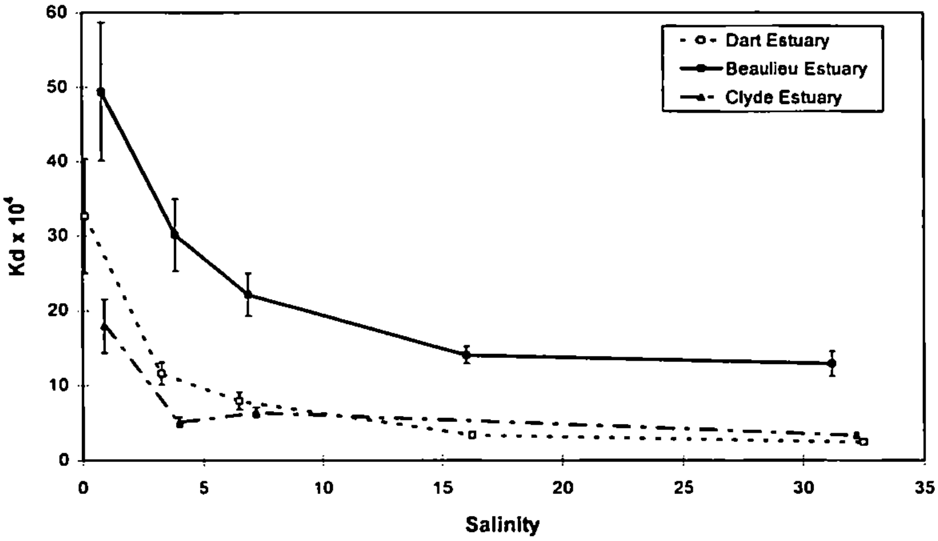
5.3.3 Characterised Sediments

An attempt was made to study the sorption of 2,3,7,8-TCDD onto sediments for which sorption characteristics were known (SSA and apolar lipid content). A range of lipid content were chosen ranging from n.d. to 10.7 mg g^{-1} and with a range of SSA values from 3.4 to 9.9 m^2 g^{-1}. It should be noted that these particle characteristics were determined on whole sediments whereas a <63μm fraction was used in the experiments. The experiments yielded no meaningful correlations. The K_d values for all populations were of similar magnitude and subject to percentage standard deviations of between 17 and

58%. The lack of correlation may have been simply due to the mis-match between characteristics measured in whole sediments and those in the <63μm fraction used in the experiments. However, it was observed that, with the exception of one sample, the lipid content and SSA were inversely correlated. This may have resulted in a some levelling of the sorption competitiveness between the different particle populations resulting in the observed homogeneity in partition coefficients derived.

5.3.4 Estuarine Salinity Gradient

As already discussed, the estuarine gradient simulated for these experiments implicitly includes gradients in salinity, particle composition and SPM concentration. The variation of 2,2',5,5'-TCB K_d with salinity (representing conservative mixing) has been plotted for the 4 study estuaries (Figures 5.7 a and b). Standard deviations on all samples were usually better than 20%.



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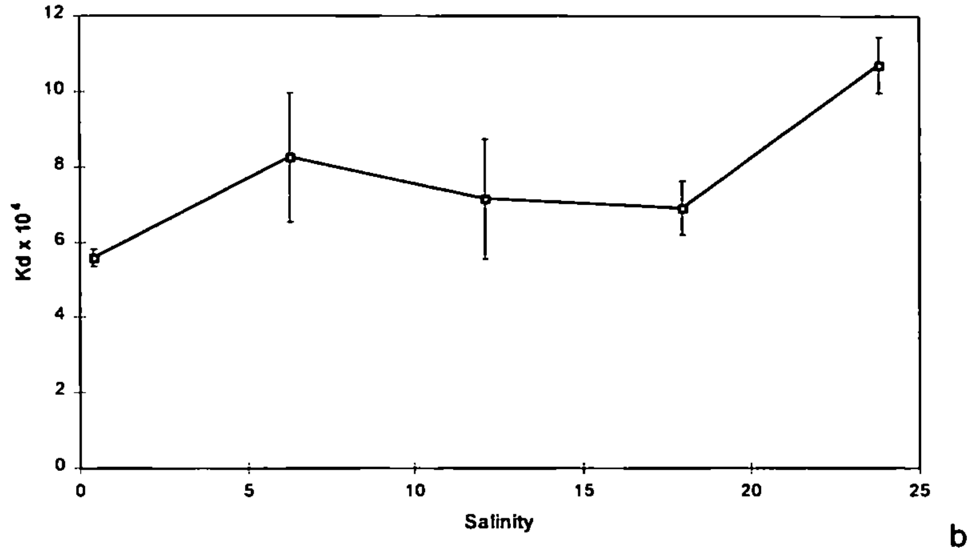


Figure 5.7. Comparison of 2,2',5,5'-TCB K_d vs Salinity in the (a) Dart (n=4), Beaulieu (n=4) and Clyde (n=3) Estuaries, and (b) Humber Estuary (n=4)

The Dart, Beaulieu and Clyde estuaries are seen to exhibit a very similar behaviour with high K_d values at the REM, falling rapidly within the low salinity zone (salinity, 0 - 5) to a MEM K_d of < 25% of the REM value. The Humber exhibits a contrasting behaviour with a relatively even distribution increasing slightly with salinity. K_d values in the Humber are of a similar magnitude to those in the lower Dart, Clyde and Beaulieu estuaries.

From the sediment analyses reported in Chapter 4, the Humber and Clyde estuaries were seen to have contrasting characteristics. Sediments in the Humber were more homogenous with a lower apolar lipid content compared with Clyde sediments. Although the homogeneity in SPM concentration sampled in the Humber for the experiments was more of a function of the timing and precise location of sampling, the homogeneity in SPM composition is expected and would be expected to give rise to relatively uniform partitioning within the estuary. This observation is also borne out by analyses of SPM for PAH conducted by Zhou *et al.* (1998) which show a general homogeneity with the salinity gradient in the Humber Estuary and partitioning experiments conducted using ^{14}C permethrin and bis (2-ethylhexyl) phthalate both of which showed very similar trends to those found for both 2,2'5,5'-TCB and 2,3,7,8-TCDD (see below) in the Humber Estuary (Zhou & Rowland, 1997). The Clyde, alternatively, has a heterogeneous suspended sediment population which would be likely to give rise to variable partition coefficients. In the upper estuary fine, organic rich sediments would tend to provide strong binding surfaces whereas, in the lower estuary, dilution of this material with lipid depleted sediments probably of marine origin would provide less competitive sites for sorption.

Figure 5.8 shows the variation of the K_d for 2,3,7,8-TCDD with salinity in the Clyde and Humber estuaries. Standard deviations were high (averaging just over 50%) for these experiments reflecting the difficulty of working with this extremely hydrophobic compound. Despite this, trends were established consistent with the observations made for 2,2',5,5'-TCB. Partition coefficients for 2,3,7,8-TCDD were 3-4 times higher than 2,2',5,5'-TCB in the Humber, and 17-24 times higher in the Clyde. In the Clyde, where a reservoir of apolar organic material on particles is established, this increase in K_d is consistent with the increase in K_{oc} values derived from the K_{ow} values in Table 5.1 using the relationship K_{oc} = 0.41 K_{ow} (Karickhoff, 1981) which yields a 2,3,7,8-TCDD K_d of 11 times the 2,2'5,5'-TCB value. It also suggests that the Humber SPM may represent a depleted source of suitable sorption sites.

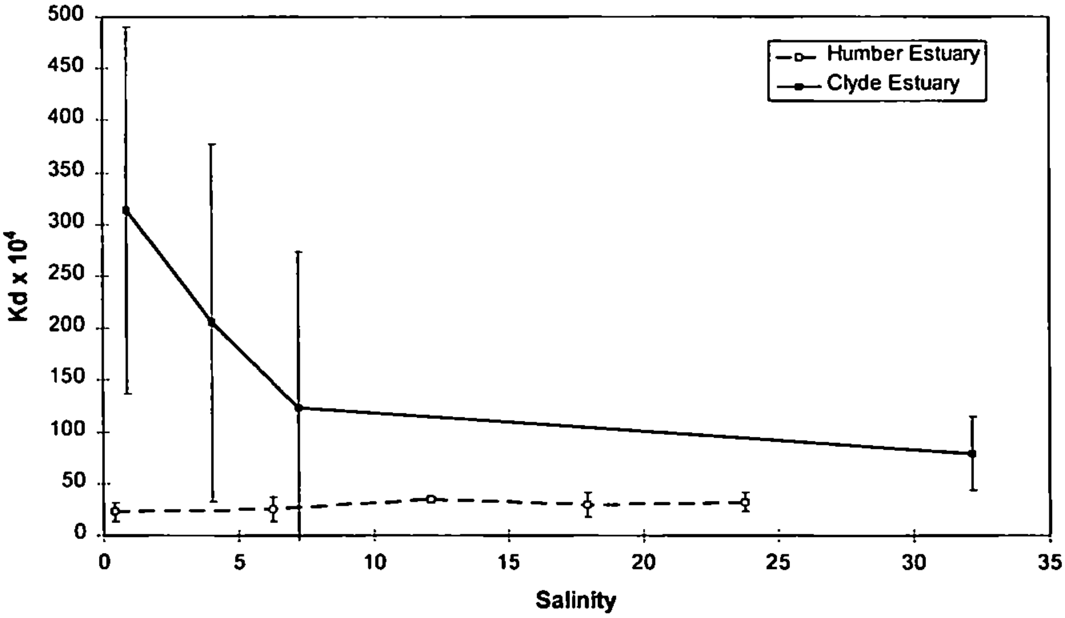


Figure 5.8. Variation of 2,3,7,8-TCDD K_d with Salinity in the Clyde and Humber Estuaries (n=4)

Salting Out

In the Clyde Estuary, the K_d for 2,3,7,8-TCDD showed a rapid decrease in the low salinity region. By contrast, in the Humber the K_d was relatively constant with some slight increase towards the MEM in an assumed relatively homogenous particle population. The observation was further corroborated by an experiment conducted using samples from the Dart estuary using 2,2',5,5'-TCB where a comparison was made between the natural estuarine gradient, and a gradient where the effects of change in SPM composition were removed by filtering the MEM. The results are shown in Figure 5.9.

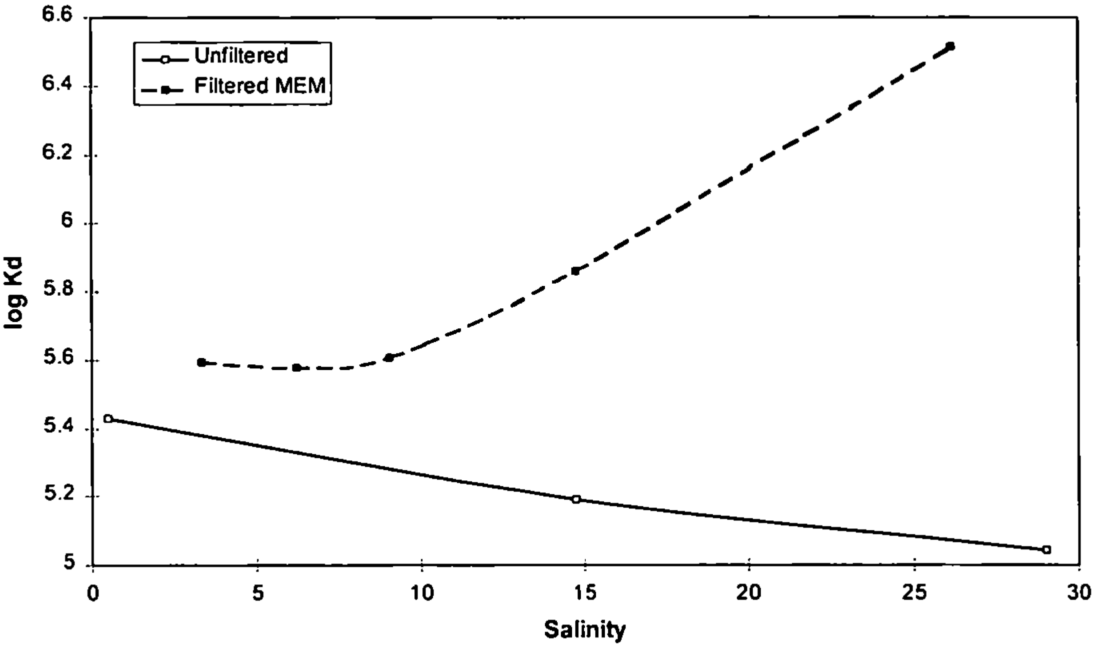


Figure 5.9. Comparison between K_d vs Salinity for Filtered and Unfiltered Marine End Members (MEM)

Increased K_d values overall for the filtered MEM samples were observed as would be expected where the highly sorptive particle population from the REM was present throughout the gradient and not diluted with marine origin particles. The more remarkable feature is the significant increase in K_d towards the MEM (the MEM value itself should be treated with caution as the mass of particles was so small (0.23 mg l^{-1}) that in such a small test sample (20 ml), possibilities for large errors were present in computing the particulate concentration).

The 'salting out' effect is a widely reported observation for hydrophobic organic compound solubility in a salinity gradient (Brunk *et al.*, 1997; Karickhoff, 1984; Means, 1995; Rawling *et al.*, 1998; Rossi & Thomas, 1981; Zhou & Rowland, 1997). Other authors have reported constancy in partition coefficient with salinity changes for some PAHs (Hegeman *et al.*, 1995), and Means & Wijayaratne (1982) reported a decrease in K_{oc} for atrazine which was explained in terms of colloidal changes.

Means (1995) hypothesised that increasing electrolytes as the salinity increases alter the structure of water and its interactions with non-electroytes. In addition, compression of the electrostatic double-layer assists sorption potential. The effect of 'salting out' is expressed by the Setchenow relationship;

$$\log\left(\frac{C_r^{rw}}{C_r^{sw}}\right) = \sigma M \tag{5.9}$$

where, C_r^{rw} and C_r^{sw} are the relative solubilities in river water and seawater respectively, σ_r is the Setchenow constant. By plotting the total molar salt concentration, M against log K_d^s/K_d^0 (where K_d^s and K_d^0 are the partition coefficients at some salinity S and in unsaline water), it is possible to deduce the Setchenow coefficient σ_r (Means, 1995). This was carried out for the filtered MEM Dart estuary experiment, excluding the MEM data point (Figure 5.10).

Although the dataset is extremely limited (the other datasets have a gradient of particle composition and therefore cannot be treated in this way), a linear fit may be appropriate. The gradient provides a measure of the Setchenow coefficient which in this case is σ_r = 2.6. This value is somewhat higher than those reported by Means (1995) for pyrene in a number of environments (0.273 - 0.846). Means suggests that if the slope was equal to a value of ~0.3 (typical Setchenow constants for a range of PAHs measured in solution and referenced to Whitehouse, 1984), then salting out may be taken to be solely responsible for the decrease in solubility. Above this value other factors such as changes associated with the organic phase of the sorbent are likely to be important. In this case, salting out is probably only a small influence and this is substantiated by Karickhoff (1984) who provides a factor of 1.2 for changes in partition coefficient in a freshwater-seawater saline gradient. For the Dart experiment, the factor is approximately 1.8 so we can conclude that salinity changes *per se* are not a major control on sorption behaviour.

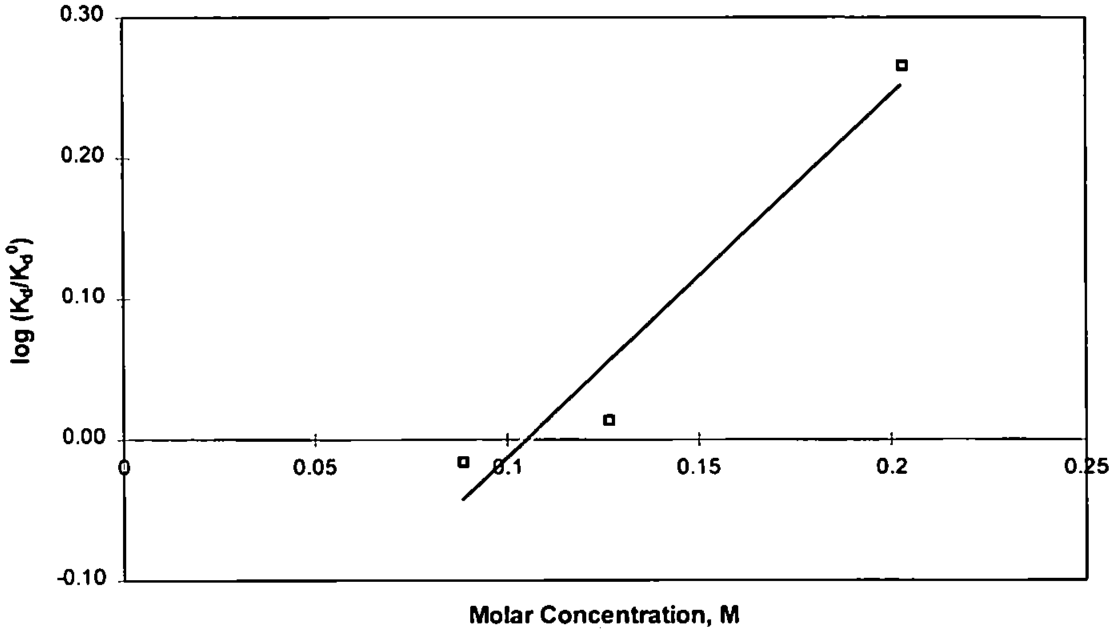


Figure 5.10. Plot of log (K_d/Kd_0) vs Molar Concentration for 2,2'5,5'-TCB in the Dart Estuary with Filtered MEM used to Simulate Salinity Gradient

5.3.5 Summary

The experiments conducted have permitted the relative importance of salinity, particle concentration and particle composition on the partitioning of TCB and TCDD to be determined. Particle concentration is found to be a significant influence in determining the extent of sorption. Although there is still discussion on the mechanisms leading to this effect, the balance of opinion would describe the effect in terms of NSP material with a high sorptive capacity acting as a third phase, and increasing particle interactions with higher solids concentration contributing to desorption. In both cases, these effects can be reasonably extrapolated for real environmental conditions and this is substantiated by findings from field studies. The effect of salinity on sorption behaviour, whilst measurable, is not a major consideration. Particle composition is likely to be a major control on sorption behaviour. Experiments conducted under this study were not conclusive and future studies should try and better investigate the relationship between SPM geochemical properties and K_d. Chapter 6 will concentrate on the approaches to incorporating these findings in models of contaminant transport.

Chapter 6. Modelling Organochlorine Behaviour in Estuaries

6. Modelling Sorption Behaviour

In previous chapters, the controls on the adsorption of OCs onto particles have been identified and quantified. The objective of this chapter is to develop a partitioning sub-model, together with associated algorithms, for OCs. The sub-model is designed to be integrated within an estuarine model capable of predicting water and sediment transport under varying conditions of river flow and tidal hydrodynamics. This Chapter shows the application of this coupled chemistry-hydrodynamic model to the transport of OCs in the Humber Estuary.

6.1 Sorption Sub-model Development

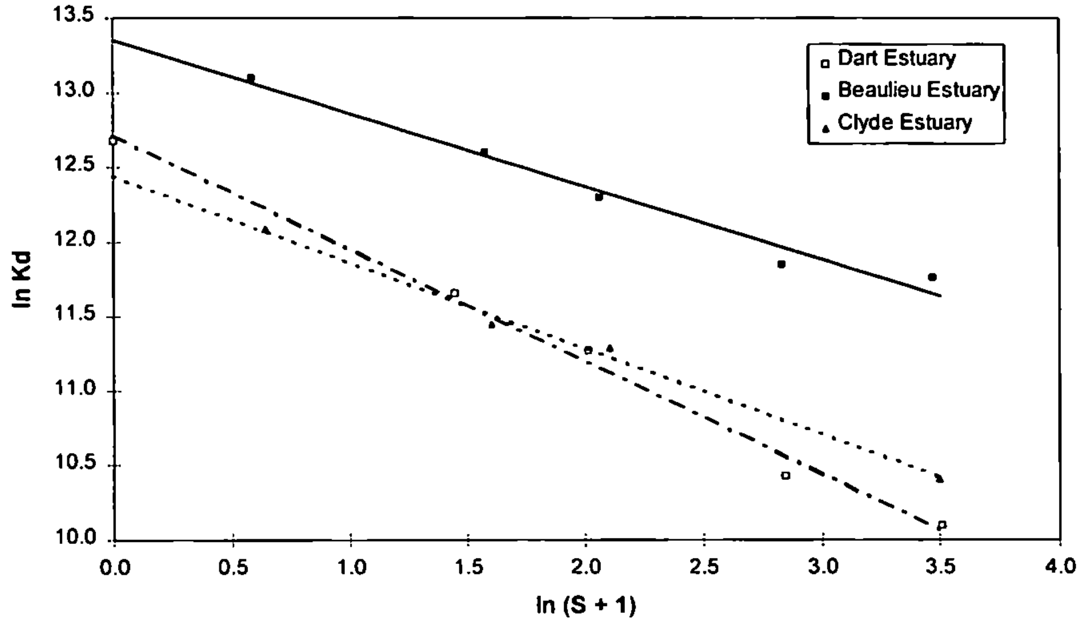
6.1.1 K_d - Salinity Relationships

Incorporation of sorption relationships in models of contaminant transport requires the ability to encapsulate the sorption behaviour of compounds in a relationship related to the major estuarine variables (e.g. salinity, SPM concentration) which are readily predictable (Endicott & Cook, 1994). In studies of metal behaviour in several estuaries an exponential K_d - salinity relationship has been found to define the reactivity of trace constituents (Turner & Millward, 1994; Turner & Tyler, 1995) and has been adopted in estuarine contaminant transport models such as ECOS (Liu *et al.*, 1998; Plymsolve, 1991) and PISCES (Ng *et al.* 1996) in the form;

$$\ln K_d = b. \ln (S + 1) - \ln K_d^0 \qquad 6.1$$

where K_d^0 is the partition coefficient in freshwater and b is a contaminant and estuary specific constant.

In the sorption studies salinity has been used as the reference variable for the simulated estuarine gradients. As shown in Figure 5.2, SPM concentration in the mixing experiments is linear with salinity and particle compositional parameters will also hold a linear relationship with salinity. It has been possible to apply the K_d - salinity model to the estuarine gradients simulated in the experiments by plotting ln K_d against ln (S + 1) (Figure 6.1);



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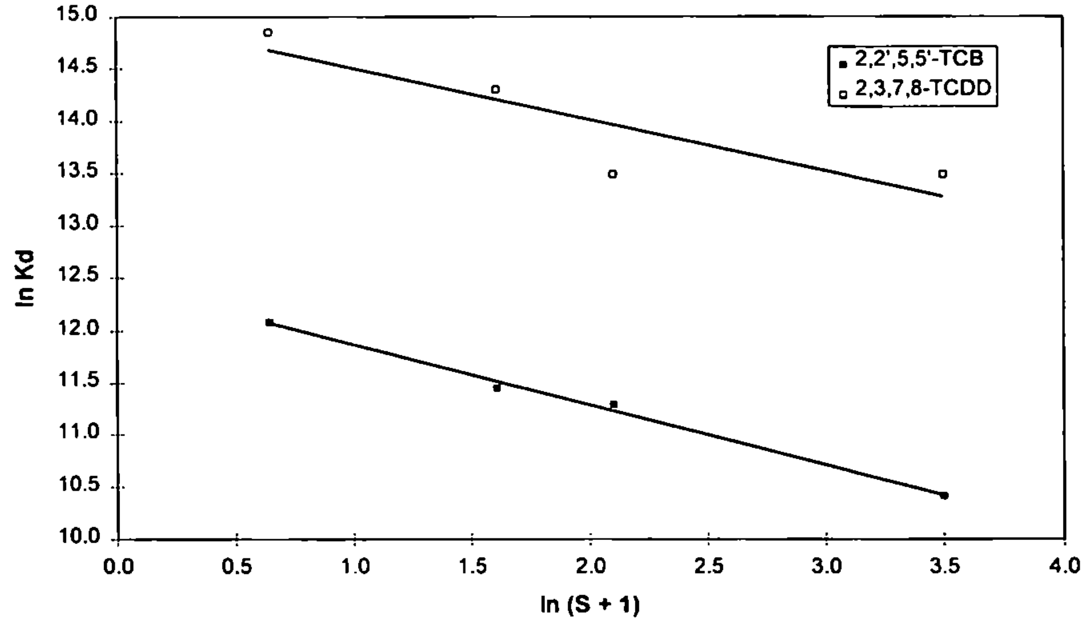

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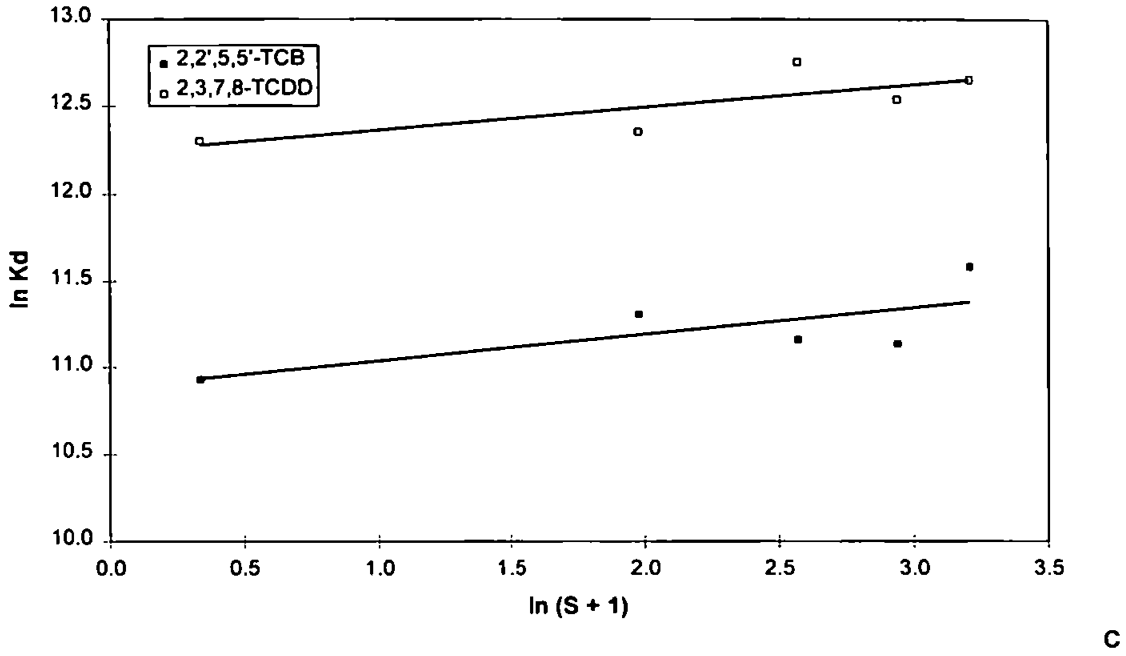


Figure 6.1. ln (S + 1) vs ln (K_d) Relationship for (a) 2,2',5,5'-TCB in the Dart, Beaulieu, and Clyde Estuaries, (b) 2,2',5,5'-TCB and 2,3,7,8-TCDD in the Clyde Estuary, and (c) 2,2',5,5'-TCB and 2,3,7,8-TCDD in the Humber Estuary

Estuary	Compound	R^2	p	b	ln K_d^0
Dart	2,2',5,5'-TCB	0.99	< 0.001	-0.76	12.7
Beaulieu	2,2',5,5'-TCB	0.98	< 0.01	-0.49	13.3
Clyde	2,2',5,5'-TCB	0.99	< 0.01	-0.58	12.4
Humber	2,2',5,5'-TCB	0.52	> 0.1	0.15	10.9
Clyde	2,3,7,8-TCDD	0.77	> 0.1	-0.49	15.0
Humber	2,3,7,8-TCDD	0.60	> 0.1	0.13	12.2

Table 6.1. ln (S + 1) vs ln (K_d) Relationship R^2, p and Values for b and K_d^0

A linear relationship with significant correlations is established for 2,2',5,5'-TCB in the Clyde, Dart and Beaulieu estuaries (see Table 6.1). The values for b and ln K_d^0 are similar in these three estuaries, which are characterised by steep axial gradients in particle composition. The Humber, with it's axially well mixed conditions and uniform particle composition does not show a significant correlation with either 2,2'5,5'-TCB or 2,3,7,8-TCDD. A non-significant correlation is also found in the Clyde Estuary for 2,3,7,8-TCDD but this is probably due to the high standard deviations obtained in the sorption experiments.

In trace metal studies, salinity has a major physicochemical importance (Turner & Millward, 1994). Certain metals (e.g. Cd and Zn) exhibit lower K_ds as salinity increases due to chloride-complexation of sorbable metal ions (Bourg, 1987). Others (e.g. Cs) may face increasing competition for sorption sites from seawater cations (Mg^{++}, Ca^{++}) (Olsen *et al.*, 1981). The K_d - salinity relationship therefore has a causative link to the controlling parameters for metal sorption behaviour. For chlorinated organic compounds, it has already been established that salinity *per se* is not a major influence and that the concentration and composition of particulate matter is the primary control. The linearity observed is a function of the relationship between salinity and SPM concentration/composition as simulated in the experiments and has no reasonable relationship to the known physicochemical controls on chlorinated organic sorption. Notwithstanding these comments, these established relationships are still a useful way to represent sorption on a wholly empirical basis with salinity acting as a surrogate for processes which are either not fully understood or not quantifiable.

6.1.2 Chlorinated Organic Sorption Model

The development of a sorption model capable of predicting K_d from known physicochemical controls on chlorinated organic sorption has therefore been investigated. In Chapter 5, the model developed by Di Toro *et al.* (1986) and expanded upon by Mackay & Powers (1987) was introduced in the context of the solids concentration effect. Under this study the model has been assessed and applied to the experimental datasets. The performance of the model applied to an estuarine gradient has been compared with the laboratory data for each of the study estuaries.

Di Toro & Mackay Model

The Di Toro & Mackay particle interaction model was developed originally by Di Toro to model the reversible sorption of trace metals to pure clay substrates. Three sorption processes were defined;

surface reversible adsorption

$$C_w + SPM \Rightarrow k_{ads} \Rightarrow C_w{=}SPM \tag{6.2}$$

where C_w is the dissolved phase contaminant concentration, k_{ads} is the adsorption rate constant and SPM is the SPM concentration.

spontaneous desorption

$$C_w{=}SPM \Rightarrow k_{s\text{-}d} \Rightarrow C_w + SPM \tag{6.3}$$

where $k_{s\text{-}d}$ is the spontaneous desorption rate constant.

particle interaction induced desorption

$$C_w{=}SPM + SPM \Rightarrow k_{p\text{-}d} \Rightarrow C_w + 2.SPM \tag{6.4}$$

where $k_{p\text{-}d}$ is the particle interaction induced desorption

At equilibrium, the reversible partition coefficient $K_{d[r]}$ is;

$$K_{d[r]} = \frac{k_{ads}}{(k_{s-d} + SPM.k_{p-d})} \tag{6.5}$$

It should be emphasised that this relationship has been defined for exchangeable surface bound OCs. The 'true' partition coefficient K_d, can defined as;

$$K_d = K_{d[r]} + K_{d[p]} \tag{6.6}$$

where $K_{d[p]}$ is the partition coefficient for OCs which are permanently adsorbed within strong binding sites on the particles, as described by Kan *et al.* (1997).

Defining the reversible partition coefficient, excluding particle interaction effects, as $K_{d[x]}$ where;

$$K_{d[x]} = \frac{k_{ads}}{k_{s-d}} \qquad 6.7$$

then,

$$K_{d[r]} = \frac{K_{d[x]}}{1 + \left(\frac{SPM.K_{d[x]}}{\upsilon} \right)} \qquad 6.8$$

where $\upsilon = k_{ads}/k_{p\text{-}d}$ and is defined by Mackay & Powers (1987) as a collision efficiency term. By relating $K_{d[x]} = K_{oc}.\ f_{oc}$, Mackay & Powers extended the model to incorporate the role of particulate organic carbon in the sorption process as follows;

$$K_{d[r]} = \frac{K_{oc}.\ f_{oc}}{1 + \left(\frac{SPM.K_{oc}.f_{oc}}{\upsilon} \right)} \qquad 6.9$$

Mackay and Powers (1987) gave $1/\upsilon$ a value of 0.7 based on experimental mean values for the slope of the $K_{d[r]}$ vs SPM graph (Di Toro *et al.*, 1986). Values for the study estuaries have been obtained (see Figure 5.4) and tabulated in Table 6.2;

Estuary	Compound	$1/\upsilon$
Dart	2,2'5,5'-TCB	0.87
Beaulieu	2,2'5,5'-TCB	0.66
Clyde	2,2'5,5'-TCB	0.68
Clyde	2,3,7,8-TCDD	0.57
Humber	2,2'5,5'-TCB	2.45
Humber	2,3,7,8-TCDD	1.81

Table 6.2. Value for Collision Efficiency, $1/\upsilon$ for Study Estuaries and Compounds

Values of $1/\upsilon$ are similar to the mean values determined by Di Toro *et al.* (1986) in all estuaries except for the Humber estuary. The values obtained for different compounds (2,2',5,5'-TCB and 2,3,7,8-TCDD) in the Clyde are similar. The experimentally determined values of 1/υ (Table 6.1) have been used in the application of the Di Toro and Mackay model rather than the mean value provided by Mackay & Powers. Applying the Di Toro & Mackay Model initially to varying K_{oc} and SPM values, but assuming a constant f_{oc} (= 0.2), the predicted behaviour of the OCs is shown in Figure 6.2.

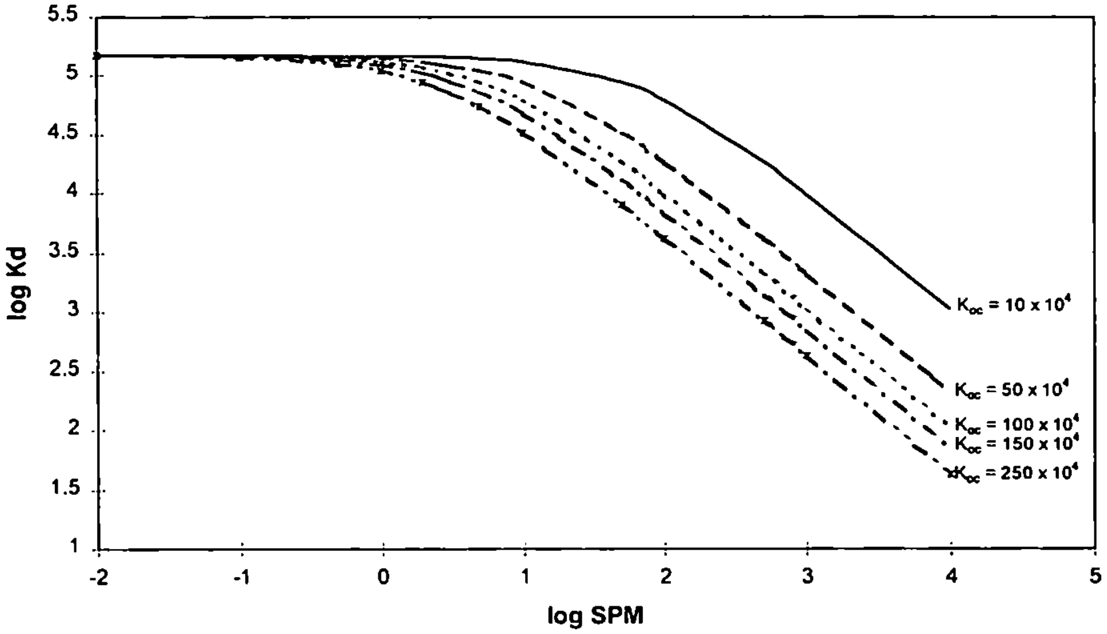


Figure 6.2. Predicted K_ds Using the Di Toro & Mackay Model with Varying SPM Concentration and K_{oc} (f_{oc} = 0.2, 1/υ = 0.7)

The model has been applied over a wide range of sediment concentrations from 0.01 - 10,000 mg l^{-1} and for a range of K_{oc} values consistent with high molecular weight compounds. At relatively low SPM concentrations there is no solids concentration effect and the K_d is directly related to $K_{oc}.f_{oc}$. However, within the range of SPM concentrations typically encountered in an estuarine system (10 - 1000 mg l^{-1}) a solids concentration effect is applicable at all relevant K_{oc} values. There is little significant difference in the SPM concentration range over which the solids concentration effect is noted and by 100 mg l^{-1}, the relationship is linear for all values of K_{oc}. This emphasises the basis of the model as predicting the physical sorption of exchangeable surface bound OCs rather than the physicochemical adsorption of the resistant component.

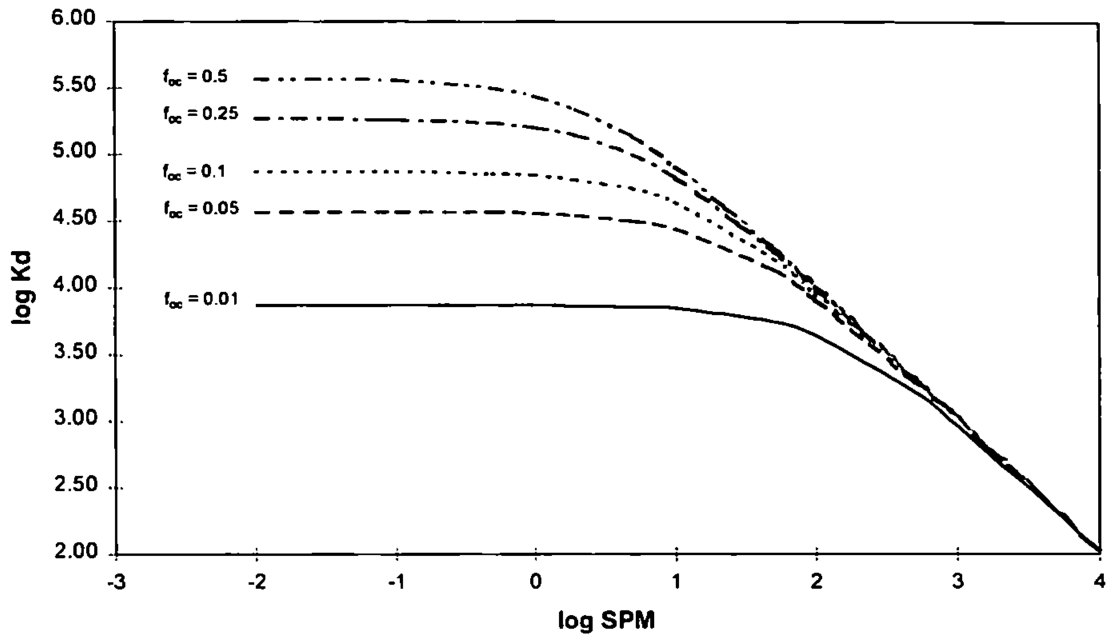


Figure 6.3. Behaviour of Di Toro & Mackay Model with Varying SPM Concentration and f_{oc} (K_{oc} = 1 x 10^6, 1/υ = 0.7)

Figure 6.3 shows the behaviour of the model with a fixed K_{oc} of 1 x 10^6 and f_{oc} varying from 0.01 to 0.5. At low SPM concentrations f_{oc} has a strong influence on K_d, but at higher SPM concentrations, the relationship between K_d and SPM becomes independent of f_{oc}. The range of typical estuarine SPM concentrations falls within the transition zone and therefore will be of significance. It is suspected that the model becomes unrealistic at this point because of its reliance on a purely physical process that is reversible and does not consider the physicochemical potential to irreversibly adsorb into the particle matrix. Mackay & Powers (1987) also state that the model predicts a lower extent of sorption than is observed, perhaps because collisions are less than 100% efficient.

Sorption Sub-model Model Performance

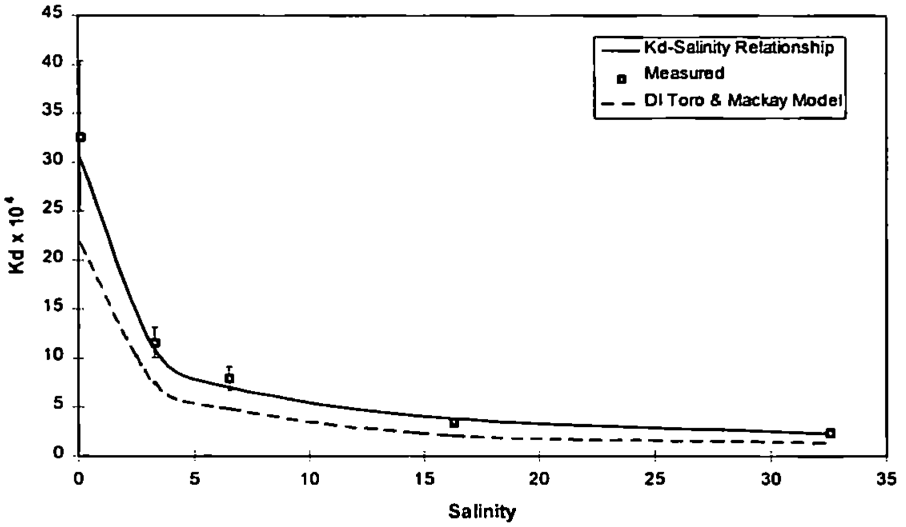
To assess the performance of the K_d - salinity relationship (Equation 6.1) and the Di Toro and Mackay model (Equation 6.9), both have been applied to the sorption study datasets and inter-compared. In the application of the Di Toro and Mackay model, the values of K_{oc} has been derived from the K_{ow} value for the compound according to Karickhoff (1981);

$$K_{oc} = 0.41.\ K_{ow}\ \text{(Karickhoff, 1981)} \qquad 6.10$$

Unfortunately, f_{oc} values were not obtained for samples used in the sorption experiments. These have been calculated from the observed K_d and the K_{oc} values using Equation 6.11. Van Zoest & Van Eck (1991) validated this relationship with a number of PCB congeners measured in the marine environment. The values obtained for f_{oc} are also in reasonable agreement with general organic carbon levels obtained from analysis of bed sediments in the various estuaries.

$$f_{oc} = \frac{K_d}{K_{oc}} \qquad 6.11$$

The values of 1/υ are taken from the experimentally derived values in Table 6.2 and the SPM concentrations are from the experimental gradients given in Tables 5.4 and 5.5 and shown in Figure 5.2.



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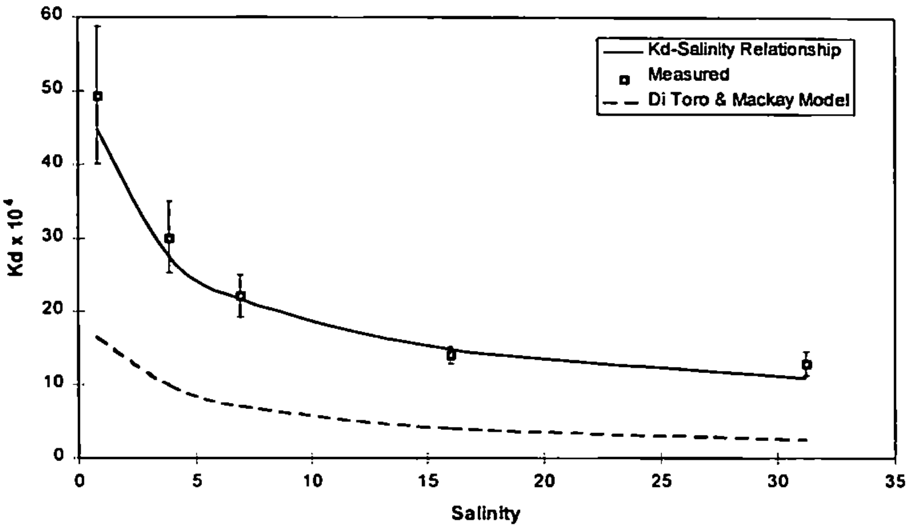
Kd-Salinity Relationship
Measured
Di Toro & Mackay Model
60
50
40
30
20
10
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Kd x 10⁴
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5
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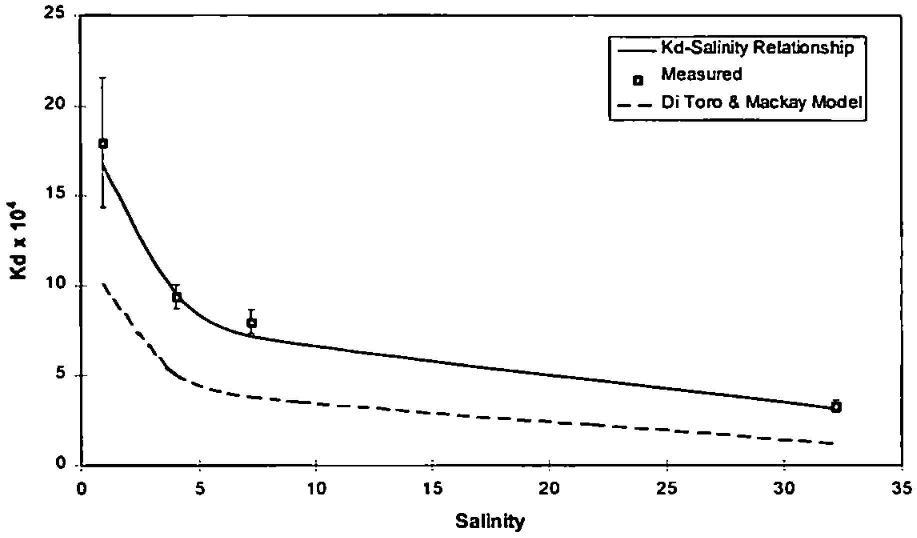
25
30
35
Salinity

b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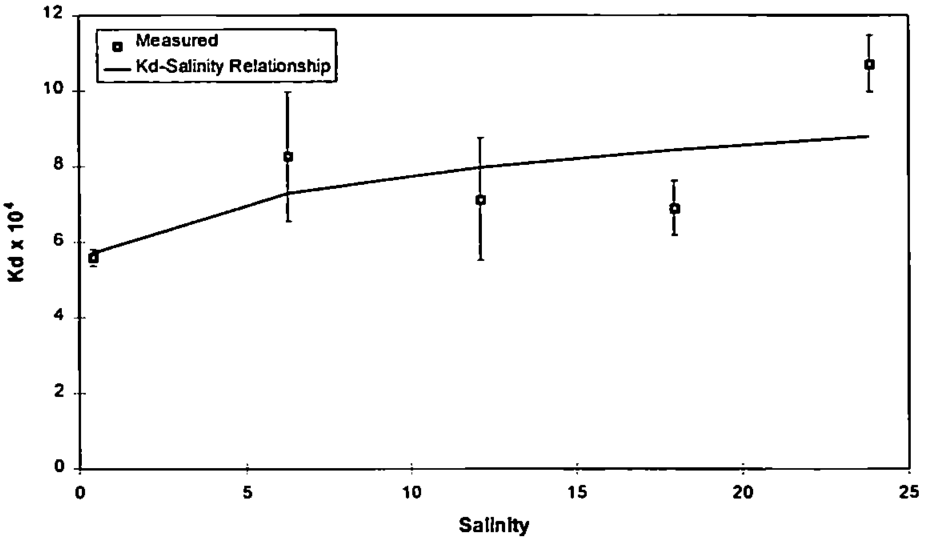
Salinity

c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Kd-Salinity Relationship
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25
Salinity

d

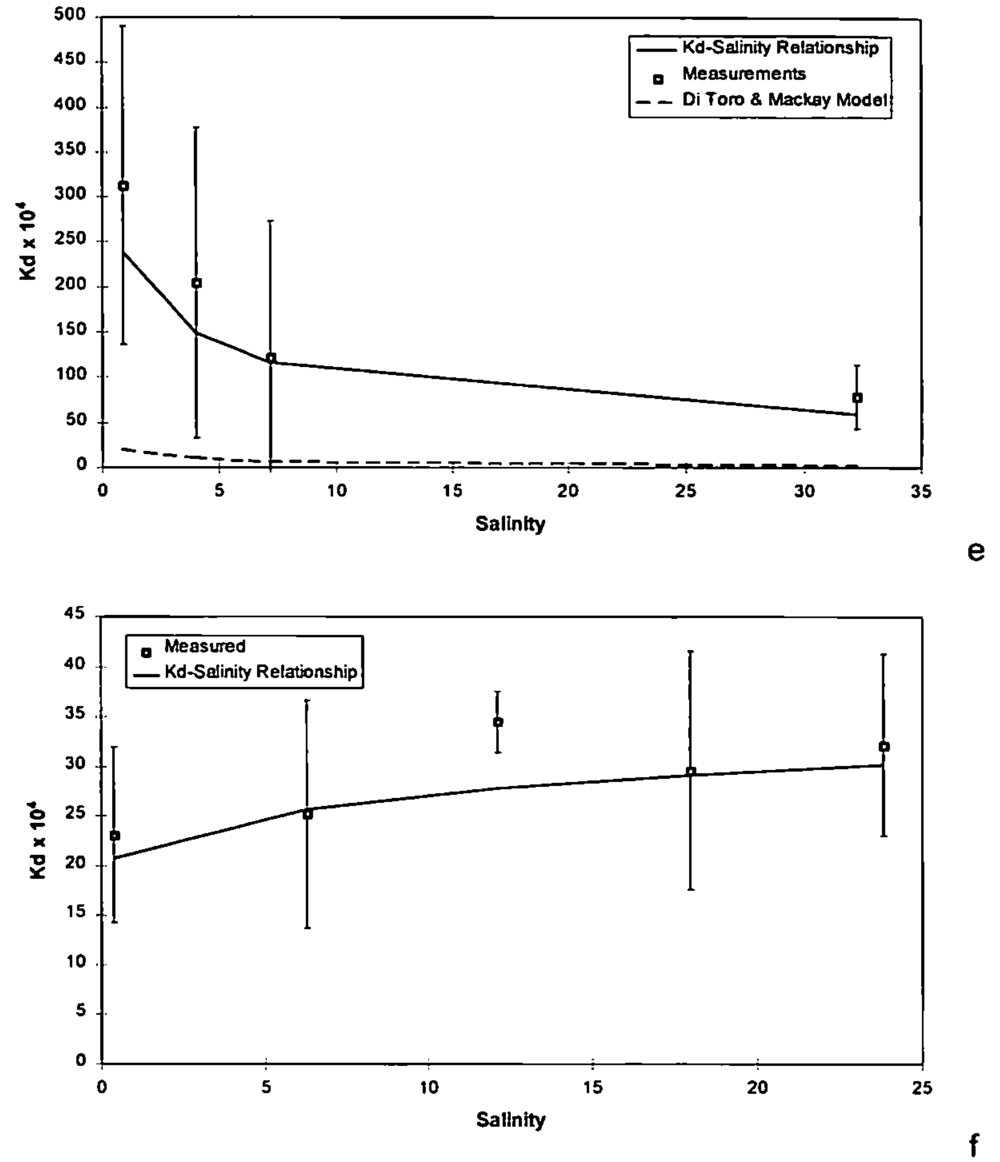


Figure 6.4. Comparison between Di Toro & Mackay Model and K_d-Salinity Relationship, and K_d Values measured in the Sorption Experiments for 2,2',5,5'-TCB in (a) Dart Estuary, (b) Beaulieu Estuary, (c) Clyde Estuary, (d) Humber Estuary and (d) 2,3,7,8-TCDD in the (e) Clyde Estuary, and (f) Humber Estuary

The application of the Di Toro and Mackay model and the K_d - salinity relationship for the Clyde, Beaulieu, Dart and Humber estuaries is shown in Figure 6.4. Results for the application of the Di Toro and Mackay model to the Humber are not shown as the model failed to make any reasonable prediction of the measured K_d gradient.

The K_d-salinity relationship provides a good description of the measured data from which it has been derived, particularly in the Dart, Clyde and Beaulieu estuaries which are characterised by a significant axial variation in particle composition. The empirical basis of the relationship requires site specific constants for K_d^0 and b to be determined experimentally and therefore no generic estuary application can be envisaged.

The Di Toro and Mackay model potentially offers a generally applicable relationship for all estuary systems. In the Clyde, Dart and Beaulieu estuaries the model performs well in predicting the trend of axial variation of K_d. There is tendency in all estuaries for the model to underestimate the high partition coefficient in the very low salinity zone. In Figure 6.2 the Di Toro & Mackay model predicts a solids concentration effect at the very low SPM concentrations present at the REM (1.8 mg l^{-1}). This may not happen in reality due to low collision frequencies in such a disperse particle population.

A major factor in the underestimation of the REM partition coefficient is likely to arise because the Di Toro & Mackay model is predicting the reversible K_d taking no account of the likely permanent binding that will take place. The reversibility of chlorinated organic sorption and the identification of a irreversibly sorbed fraction has been studied by a number of workers (Di Toro & Horzempa, 1982; Horzempa & Di Toro, 1983; Karickhoff, 1984; Wu & Gschwend, 1986). A two-phase sorption model can be proposed where initial sorption to the particle surface is followed by a slower incorporation in the particle matrix. This secondary process results in a much tighter binding which is more resistant to desorption. For highly hydrophobic compounds such as PCBs and PCDD/Fs, adsorption into the particle matrix may occur fairly readily, particularly if the particle has organic carbon coatings which are preferential for adsorption. If this were occurring during the mixing experiments (Di Toro & Horzempa found an adsorbed PCB fraction strongly resistant to desorption after only 3 hours of equilibration), then the solids concentration effect would be lessened and K_d values would be higher. This would not be accounted for in the Di Toro & Mackay Model.

To provide an estimate of the irreversibly adsorbed fraction, the percentage of reversibly adsorbed OC predicted by the Di Toro and Mackay model has been subtracted from the measured percentage of particulate adsorbed OC. This of course assumes that the failures in the Mackay and Di Toro model to fully represent the observations is wholly due to omission of the permanently bound fraction. Table 6.3 summarises the percentage of particulate bound OC and the estimate of irreversibly bound OC. The latter has also been plotted in Figure 6.5.

Estuary	**Compound**	**Total % Adsorbed (Range)**	**% Irreversibly Adsorbed**	
			Mean	**Standard Deviation**
Dart	2,2',5,5'-TCB	39 - 49	12	2
Beaulieu	2,2',5,5'-TCB	75 - 86	27	3
Clyde	2,2',5,5'-TCB	54 - 71	18	4
Clyde	2,3,7,8-TCDD	95 - 98	39	1

Table 6.3. Range of Particulate Adsorbed OC and Estimated Irreversibly Adsorbed Fraction for the Study Estuaries

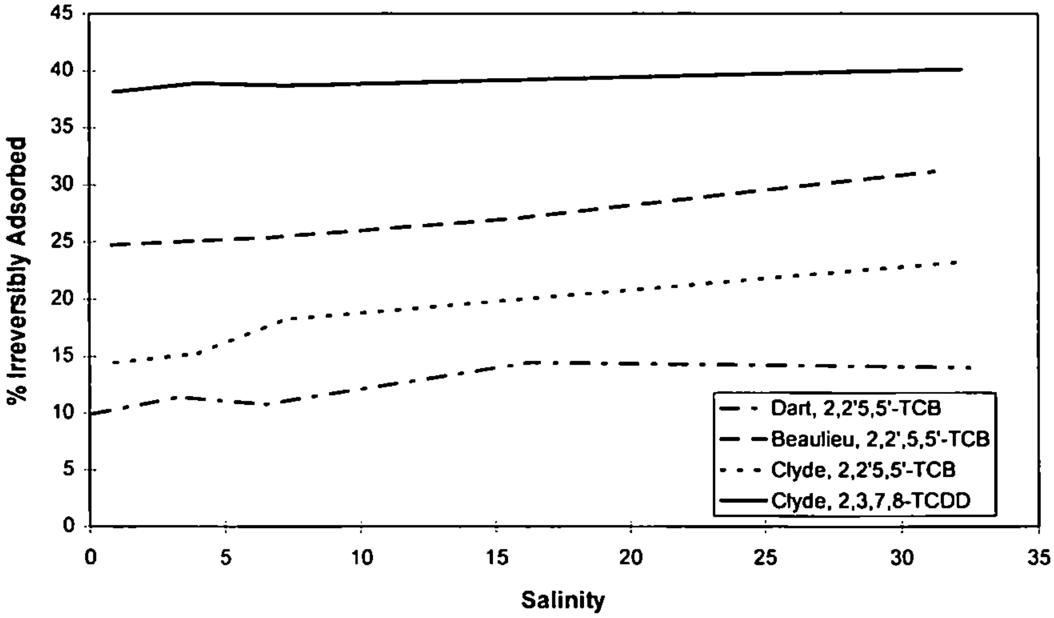


Figure 6.5. Axial Variation of Estimated Irreversibly Adsorbed OC Fraction

There is a notable constancy (standard deviations range from 1 - 4 %) in the irreversible fraction estimated for each of the estuaries. The magnitude of this fraction varies from 12 % in the Dart Estuary for 2,2',5,5'-TCB to 39 % in the Clyde Estuary for 2,3,7,8-TCDD, and correlates with the general magnitude of partition coefficient in the estuary and the polarity of the compound (2,3,7,8-TCDD has an estimated irreversible fraction of twice that of 2,2'5,5'-TCB in the Clyde Estuary). These observations provide a potential means to extend the Di Toro and Mackay model to determine $K_{d[p]}$ (see Equation 6.6) parameterised on the basis of particulate organic carbon content and the compound's K_{ow}. Further experiments would be required to develop a suitable algorithm but the linearity observed in the irreversibly adsorbed fraction implies that this relationship would probably be simple.

The Di Toro and Mackay model fails to satisfactorily reproduce the axial K_d variation for 2,3,7,8-TCDD in both the Clyde (see Figure 6.4e) and Humber estuaries. It may be speculated that this highly hydrophobic compound exhibits a reduced desorption potential (as illustrated by its estimated 40% irreversibly adsorbed fraction, Table 6.3) and therefore cannot be described accurately by a model which predicts particle interaction-induced desorption. The reasons for the inability of either relationship to predict the sorption behaviour of 2,3,7,8-TCDD or 2,2',5,5'-TCB in the Humber estuary are not entirely clear. In all aspects of this work the Humber estuary has contrasted sharply with the other study estuaries and the sorption behaviour appears to be no exception. The SPM concentrations in the experiments (250-300 mg l^{-1}) were the highest amongst the estuaries studied and the lack of a discernible SPM concentration gradient was also unique although not untypical for the Humber Estuary (REM = 302 mg l^{-1}, MEM = 254 mg l^{-1}, Zhou & Rowland, 1997). At these SPM concentrations, the Di Toro & Mackay model predicts high particle-induced desorption rates which may not be occurring if a significant fraction of OC is being permanently absorbed.

The organic carbon content of the particulate phase is an important input to the Di Toro and Mackay model as illustrated in Figure 6.3. For this application, derived f_{oc} values have been used whereas actual values would have been preferable. The values do however seem reasonable, and compare well with measured values. For example, in the Humber estuary derived f_{oc} values are in the range 0.08 - 0.14 which compares with measured values of 0.0571 - 0.0981 (Zhou & Rowland, 1997). In Chapter 4, it was shown that apolar lipid content is a more precise indicator of chlorinated organic compound sorption preferences. The importance of the nature of particulate organic matter as well as its fractional content has been well demonstrated for hydrophobic compound sorption (Murphy *et al.*, 1990; Zhou *et al.* 1995a). This is further underlined by Mackay & Powers (1987) where the potential sensitivity of the K_{oc} - K_{ow} relationship to the 'condition' of the organic carbon is identified. As the organic carbon fraction becomes more 'open and fluffy' the value for K_{oc} will approach that of the K_{ow}. The semi-empirical model is sensitive to the values obtained for K_{oc} which might explain the underestimation of K_d in the REM of some estuaries as this zone would be characterised by organic material with high sorptive capacity. Overall, the use of f_{oc} as a quantitative descriptor of sorption preference is probably too crude and future models will need to develop a more rigorous parameterisation of the controls on sorption.

6.2 Integrated Contaminant Transport Modelling

Ever increasing regulation of discharges of contaminants to estuarine and coastal waters present challenges to industry and the regulator in determining acceptable levels of consent for discharge, and then monitoring highly complex waste stream discharges and estuarine water quality to determine compliance and maintenance of Environmental Quality Standards. As a result there has been an increasing adoption of numerical models to assist in evaluating individual discharges and the combined effects of multiple discharges into the same receiving waters (GESAMP, 1991).

Although water quality models for parameters such as dissolved oxygen are well established and reliable, models for trace contaminants are still at a developmental stage. There are some key challenges which still exist in modelling trace organic contaminants within integrated estuarine and coastal models and these are discussed in this Chapter. Notwithstanding these limitations, results from the sorption studies and modelling have been implemented in an integrated estuary model of the Humber Estuary to demonstrate how such models can contribute to management decision making.

6.2.1 PISCES Estuarine Contaminant Transport Model

The PISCES estuarine contaminant transport model was developed as a component of this research programme. The objective was to build upon established models of estuarine physics and develop geochemical sub-routines that could describe the behaviour of trace metal and organic contaminants. The author was actively involved in the development of the model throughout the programme. This included a significant input to the specifications and extensive testing and validation of the model code. Under this study the author prepared all the relevant input data, performed the model runs and processed/presented all of the resulting model data.

The overall function of the model is described in Figure 6.6. PISCES is based on the established DIVAST model which provides numerical code to predict hydrodynamics, sediment and solute transport (Falconer, 1993; Falconer & Chen, 1991; Falconer & Owens, 1990). The model predicts the hydrodynamic flow within the estuary from bathymetric depths and the tidal wave propagation in the estuary interacting with riverine flows. The sediment transport is based on the size distribution of the bed sediment and the bed stress calculated from the hydrodynamics to predict erosion and deposition. The salinity gradient is also modelled as a conservative dissolved constituent.

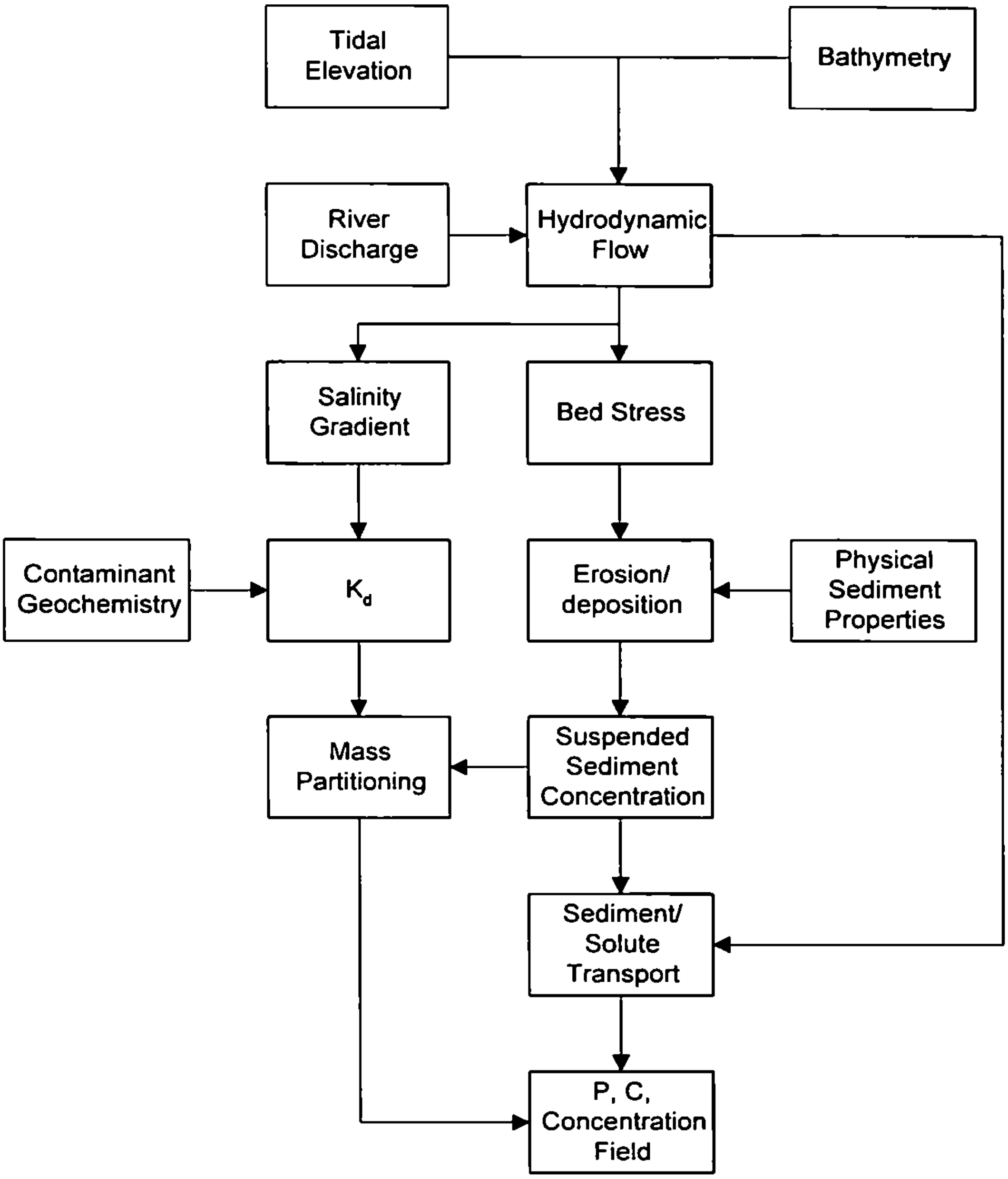


Figure 6.6. Functional Outline of the PISCES Contaminant Transport Model

Basis of Numerical Model

The PISCES model defines two transport pathways for contaminants in the estuary; dissolved transport, or adsorbed to suspended particulate matter. The distribution of contaminants between the two phases is described by the K_d which is related to salinity either by explicit tabulation of K_d against salinity, or by the relationship defined in Equation 6.1. The transport of the contaminant in the dissolved phase is defined by an integrated transport and mass balance equation containing the following terms;

Advection	-	Dispersion/Diffusion	-	Mass Transformation
f (C, u, v)		f (C, D)		f (S_o, S_d, S_k)

where C is the dissolved phase concentration, u and v are velocity components in the x and y directions, D is dispersion and diffusion coefficients, and S_o, S_d, S_k are source/sink, volatilisation, and degradation terms respectively.

Transport in the solid phase is modelled using the van Rijn formulation (van Rijn, 1984a; van Rijn, 1984b) which describes the advection, diffusion, erosion and deposition of sediments based on sediment diameter to determine critical erosion and settling velocities. A modification was made to the formulation so that cohesive sediments (diameter <40μm) were modelled as a permanently suspended 'wash load'. This is shown in diagrammatic form in Figure 6.7.

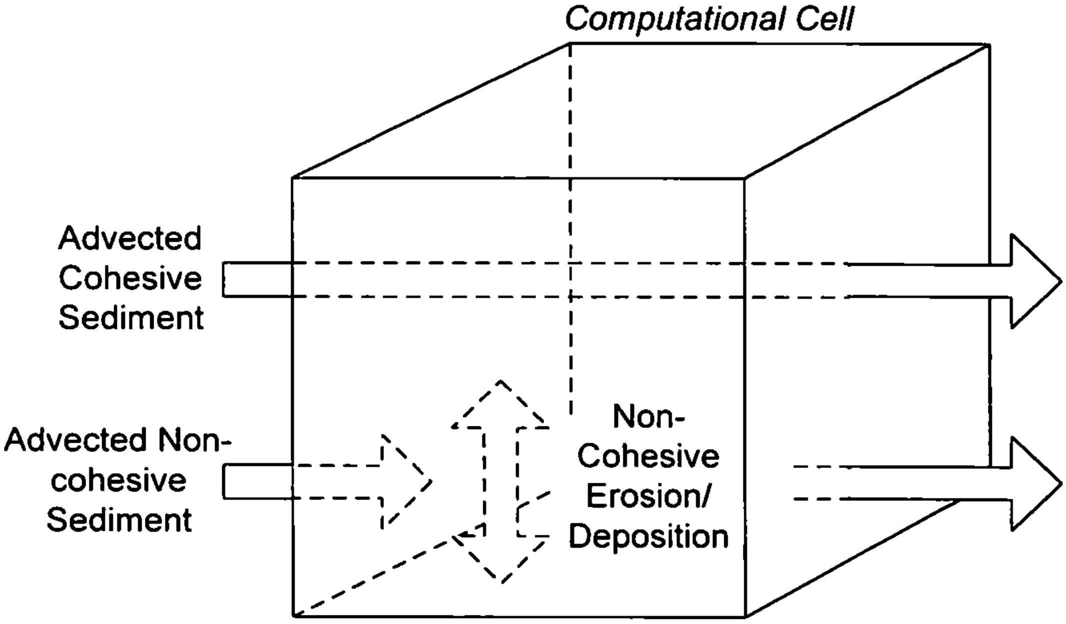


Figure 6.7. Sediment Transport in the PISCES Model

At each timestep of the model, the predicted salinity in each computational cell is used to determine the K_d. Based on the concentrations in the cell at the previous timestep, the new K_d is used to re-partition the contaminant into the dissolved and solid phases followed by application of the transport equations described above.

6.2.2 Model Configuration

The model was configured for the Humber Estuary from Trent Falls to the estuary mouth (Figure 6.8). A 300 x 300 m computational grid size was selected with a timestep of 60s. The calibration and validation of the hydrodynamics, sediment transport and salinity gradient is described in Ng *et al.* (1996) in Appendix II.

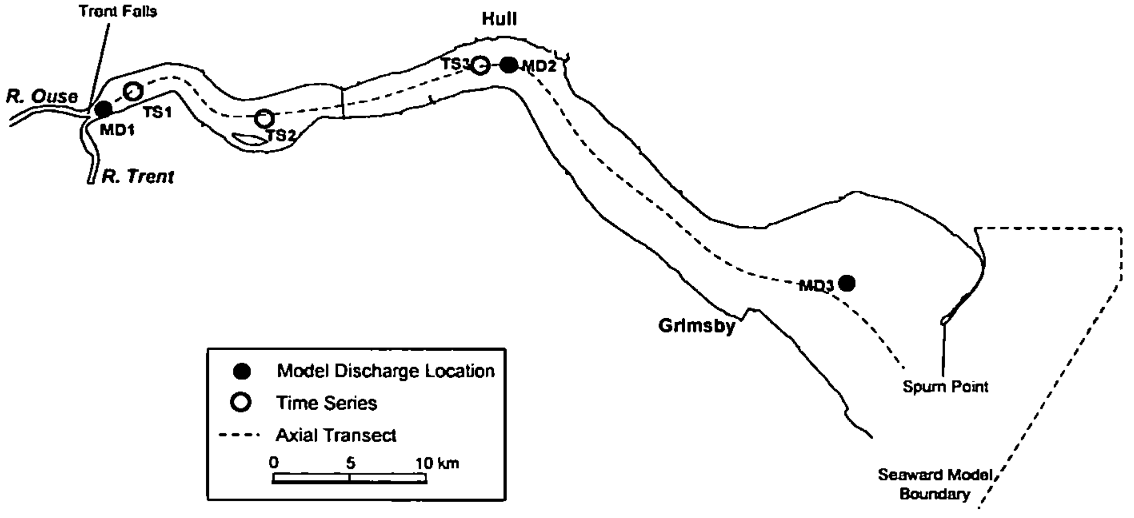


Figure 6.8. Humber Model Configuration Showing Discharge Locations, Axial Transect and Timeseries Stations

It would be highly desirable to implement the sorption relationships described in this Chapter within the modelling framework. These relationships describe partitioning as a function of K_{oc}, SPM, f_{oc} and some empirical constants. There is however a fundamental problem with such an implementation. The modelling of sediment transport is based on physical sediment characteristics which determine the settling and erosion velocities. The grain size of sediments does not have a direct or straightforward relationship to the geochemical characteristics e.g. f_{oc}. This 'missing link' prevents a direct prediction of K_d from master estuarine variables estimated by the model. For the purposes of this demonstration therefore, the empirically determined K_d -

salinity gradient for 2,2,5,5'-TCB has been used with salinity as the conservative master estuarine variable predicted by the model. Two K_d gradient scenarios have been defined and are shown in Figure 6.9. Scenario 1 is the empirically derived K_d - salinity relationship for the Humber. Scenario 2 is the relationship derived for the Beaulieu. These have been selected to represent contrasting sorption behaviour.

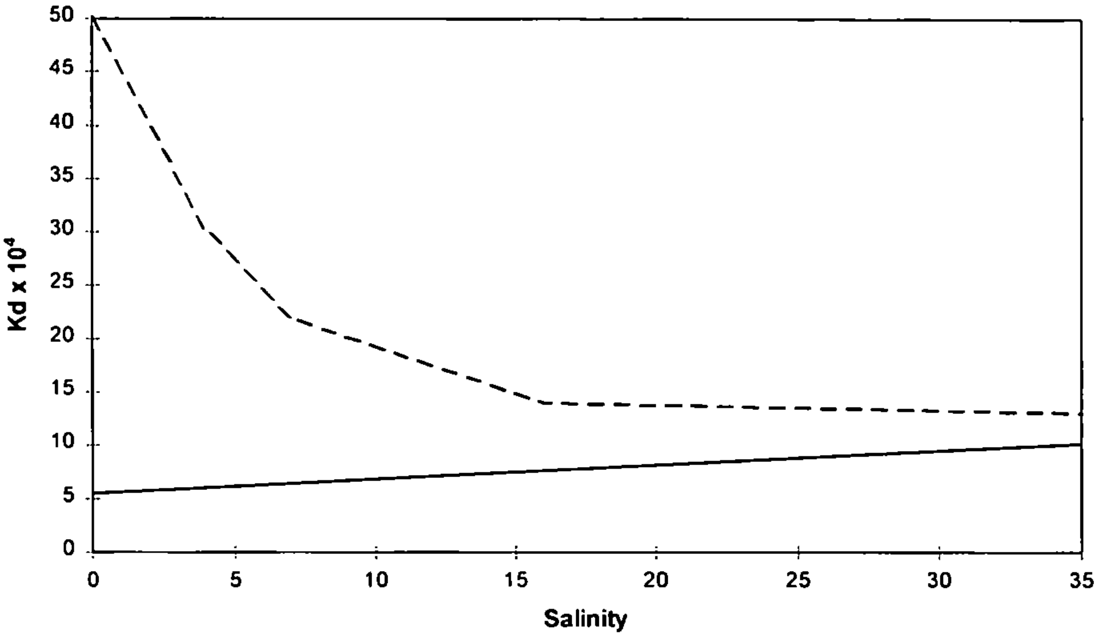


Figure 6.9. K_d - Salinity Relationships Used in the Modelling (——Scenario 1 - Humber, - - - - Scenario 2 - Beaulieu)

Three contaminant discharge scenarios have been defined. Two of these are configured to represent point discharges at the middle and mouth of the estuary that might be representative of an outfall discharge (MD2, MD3). The third scenario, located at the REM represents a riverine discharge (MD1). The model has been run for 10 tidal cycles (120 hours). This has allowed the model to establish a reasonable equilibrium. It does not, however, extend to the full flushing time of the estuary which is approximately 40 days (Turner *et al.*, 1991). Table 6.4 summarises the discharge scenarios with the locations shown in Figure 6.8.

Location	Reference (Figure 6.9)	Discharge Concentration ($\mu g\ l^{-1}$)	Discharge ($m^3\ s^{-1}$)	River Discharge ($m^3\ s^{-1}$)	K_d Scenario
River	MD1	1.0	250	250	1
River	MD1	1.0	250	250	2
Mid-estuary	MD2	10.0	0.5	250	1
Lower estuary	MD3	10.0	0.5	250	1

Table 6.4. Model Run Scenarios

It should be stressed that the objective of the modelling has been to demonstrate the integration of dynamic sorption in an estuary model and to show the influence of partition coefficient in determining estuarine distribution, rather than provide a wholly realistic simulation of PCBs in the Humber Estuary.

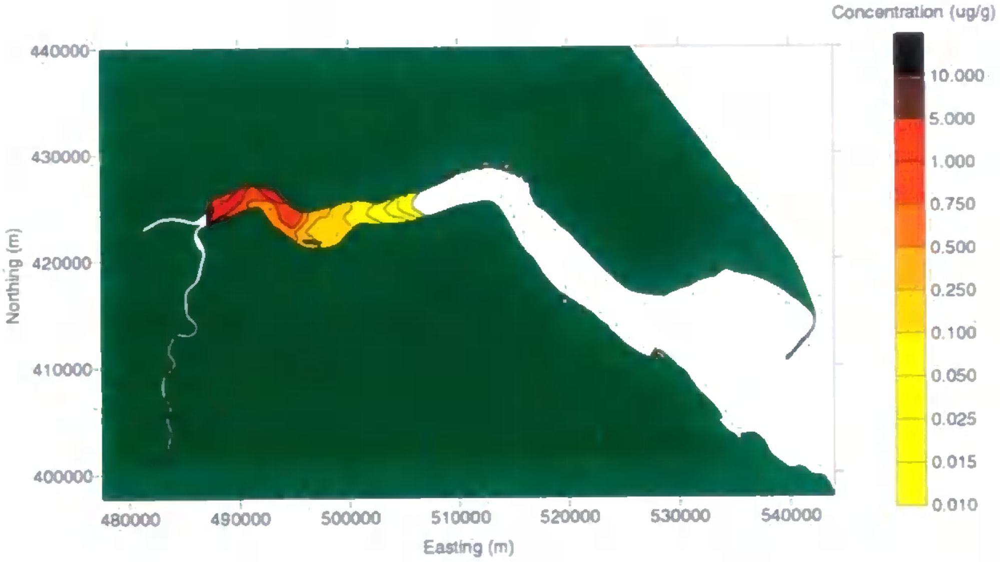
6.2.3 Model Predictions

Predictions from the model have been output at hourly intervals and referenced to High Water (HW). From this data, axial profiles have been extracted along the transect shown in Figure 6.8 and timeseries plots have been obtained at three locations, TS1, TS2 and TS3 also shown in Figure 6.8.

Riverine Discharge Scenarios

The tidal dynamics of dissolved and particulate phase PCB is shown in Figures 6.10 and 6.12. Generally concentrations are in the range 0 - 5 $\mu g\ g^{-1}$ (particulate phase) and 0 - 0.1 $\mu g\ l^{-1}$ (dissolved phase) which is high but reflects the relatively high concentration set for the river discharge (1 $\mu g\ l^{-1}$, compared with 0.1 - 2800 $\mu g\ l^{-1}$ for the contaminated Hudson River, USA, Paviou & Dexter, 1979). The predicted environmental concentrations are not however unrealistic of industrialised estuary sites. In a study of New Bedford Harbour, USA, Brownawell & Farrington (1985) reported dissolved phase concentrations in the range 0.0036 - 0.329 $\mu g\ l^{-1}$ with concentrations in pore waters up to 20.1 μg l^{-1}. Duursma *et al.* (1989) reported SPM concentrations up to 0.4 μg g^{-1} and Paviou & Dexter (1979), concentrations up to 1.77 μg g^{-1}.

Figure 6.10 shows the spatial distribution of suspended particulate PCB at four tidal states; HW - 3 (maximum flood), HW (slack water), HW + 3 (maximum ebb) and Low Water (LW - slack water). In Figure 6.10a the flood tide is transporting material up-estuary. This material has been previously contaminated and therefore there is a high concentration of contaminated material is maintained in the upper estuary. At HW (Figure 6.10b) most of the contaminated material has been transported into the river and downstream penetration is limited. As the ebb tide reaches its maximum (Figure 6.10c) much of the contaminated SPM is moved downstream so that by LW (Figure 6.10d) the distribution extends halfway down the estuary. The axial profile shown in Figure 6.11 also illustrates this dynamic tidal behaviour. There is a rapid reduction in concentration with axial distance which is caused primarily by dilution through mixing with uncontaminated MEM waters and SPM. Within 15 km of the riverine discharge, concentrations have fallen to trace quantities.



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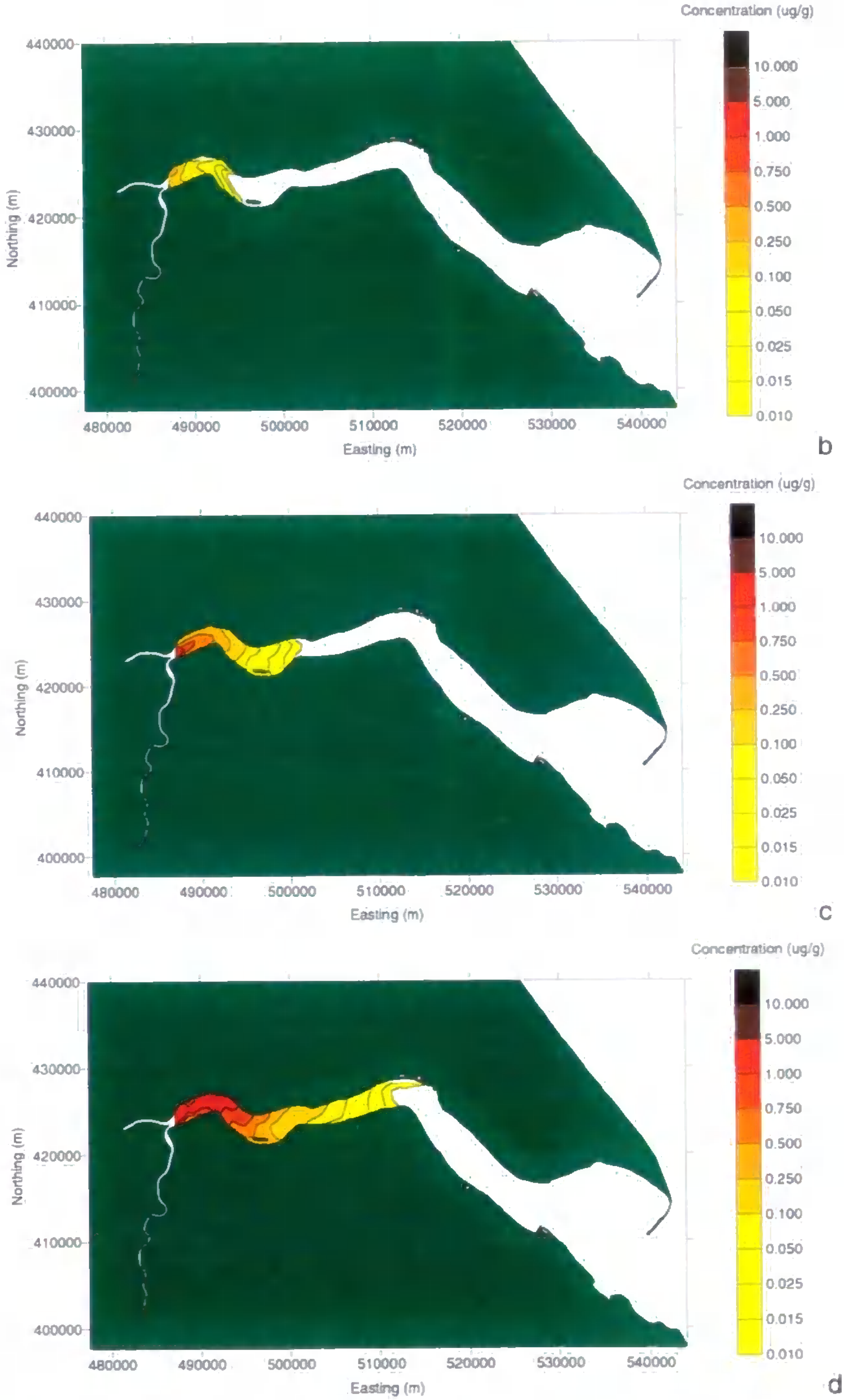


Figure 6.10. Suspended Particulate Phase PCB Concentration Distribution at (a) HW - 3, (b) HW, (c) HW + 3, (d) LW (River Discharge, K_d Scenario 1)

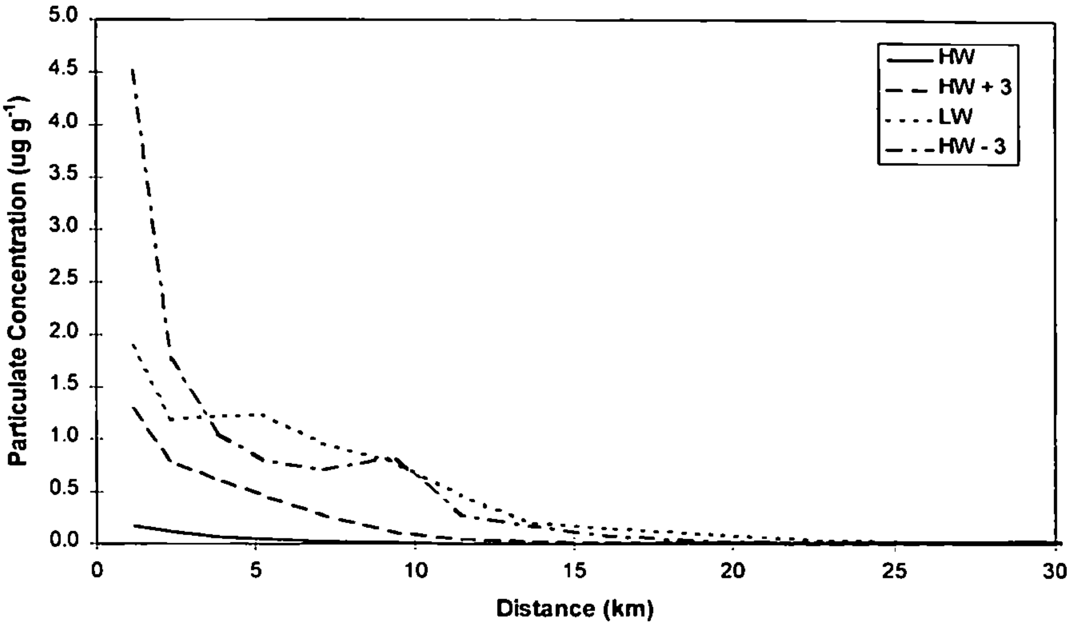


Figure 6.11. Axial Profile of Suspended Particulate PCB Concentration (River Discharge, K_d Scenario 1)

Figure 6.12 shows the dissolved phase PCB concentration for two tidal states (HW - 3, LW) corresponding to the SPM distributions shown in Figure 6.10. Figure 6.13 shows clearly the strong correlation between dissolved and particulate concentrations (compared with Figure 6.11) which is to be expected with the model's assumption of instantaneous and fully reversible kinetics. The tidal timeseries of PCB concentration in SPM and water also highlights this correlation and is shown in Figure 6.14. At TS1, approximately 3km from the river discharge input, the tidal cycle can be clearly seen with highest concentrations at LW when the current speed is very low and lowest concentrations at HW when the location is under the influence of relatively clean water brought upstream by the flood tide. At station TS2 the concentrations have fallen by an order of magnitude due to dilution. By TS3, there is no significant dissolved phase concentration and only peaks of SPM-associated concentration either side of LW.

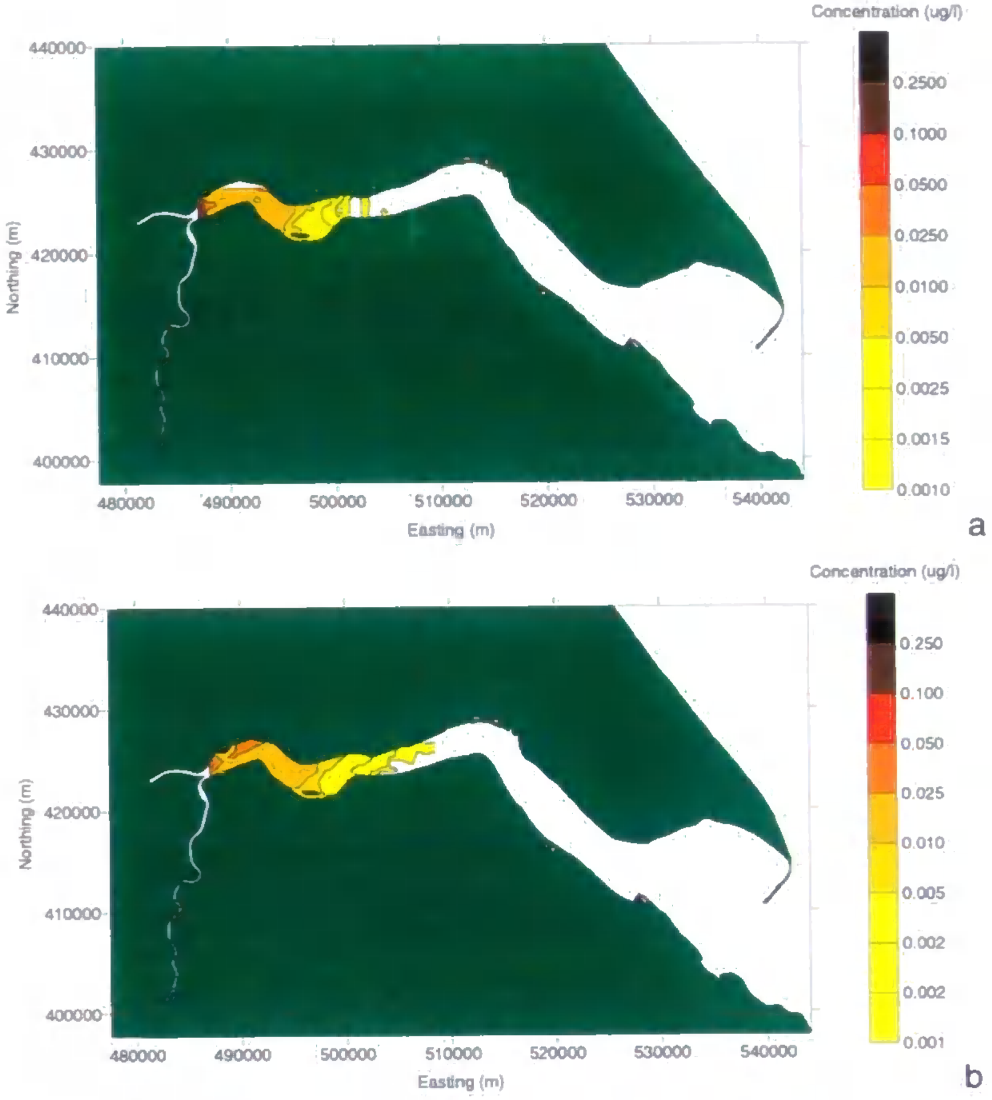


Figure 6.12. Dissolved Phase PCB Concentration Distribution at (a) HW - 3, (b) LW (River Discharge, K_d Scenario 1)

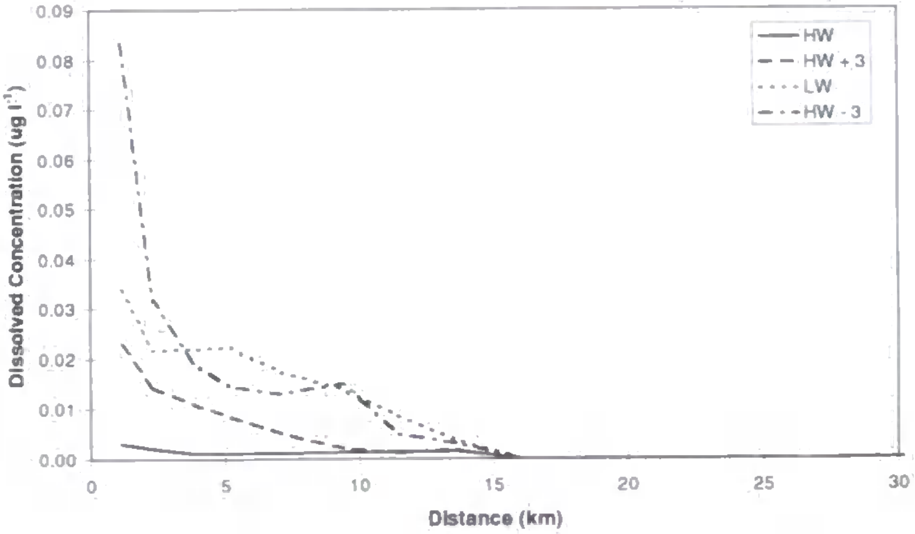


Figure 6.13. Axial Profile of Dissolved PCB Concentration (River Discharge, K_d Scenario 1)

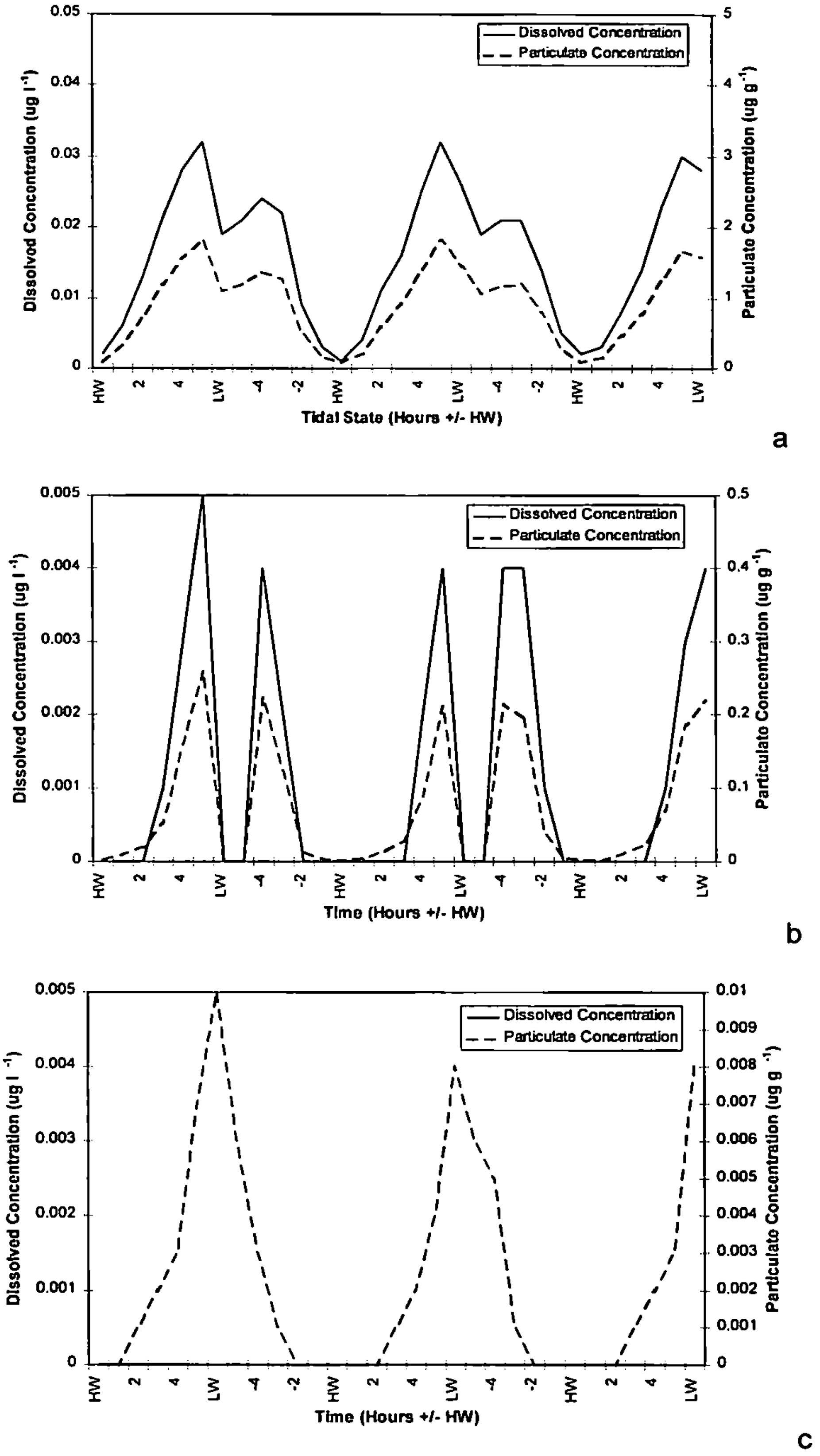
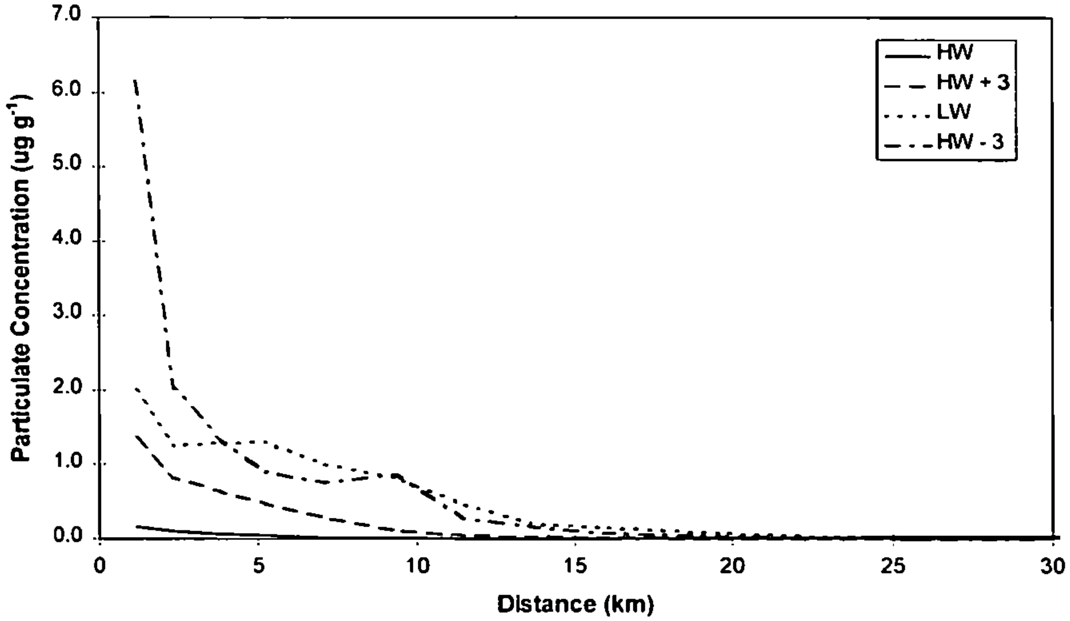


Figure 6.14. Suspended Particulate and Dissolved Phase Concentration Timeseries at (a) TS1, (b) TS2, (c) TS3 (River Discharge, K_d Scenario 1)

The significance of the change in K_d in the estuary has been demonstrated by comparing the relationship between K_d and salinity derived for the Humber with that for the Beaulieu, both applied within the Humber model. Figure 6.15 shows the axial transects for PCB concentration in SPM and water using the Beaulieu K_d - salinity relationship. The most significant observation is that although the PCB concentration associated with SPM is almost the same (slightly higher at LW), the dissolved concentration is approximately an order of magnitude lower with the Scenario 2 K_d - salinity relationship. The broad implication of these predictions is that assuming an unlimited capacity for sorption to sediments, the particulate phase concentration is dependent on the concentration of contaminant input to the system. Dissolved phase concentrations by contrast, are determined by the partition coefficient.



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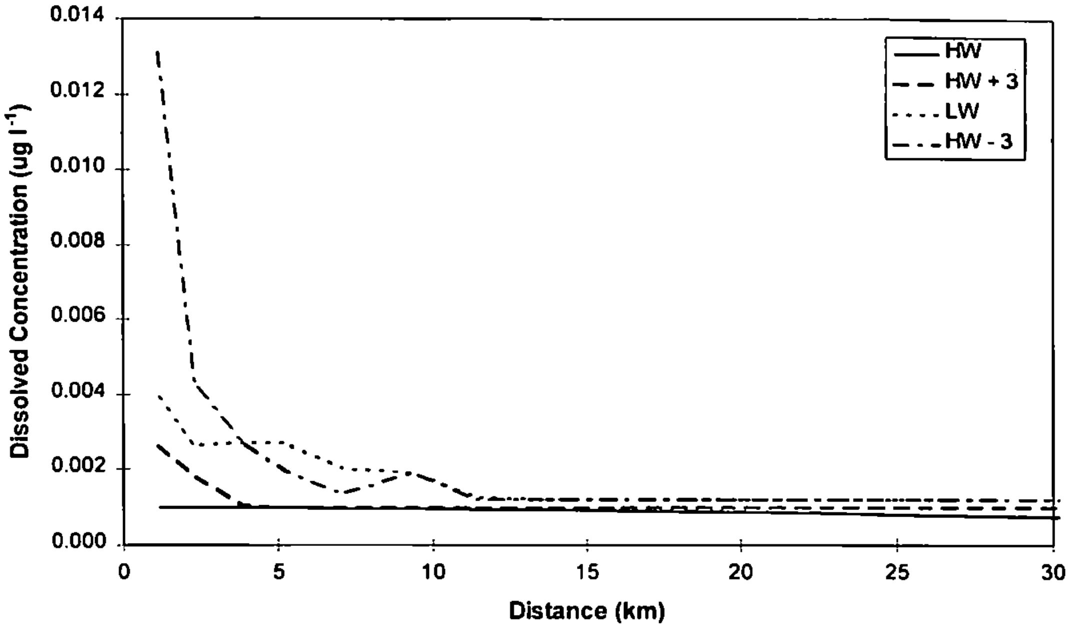


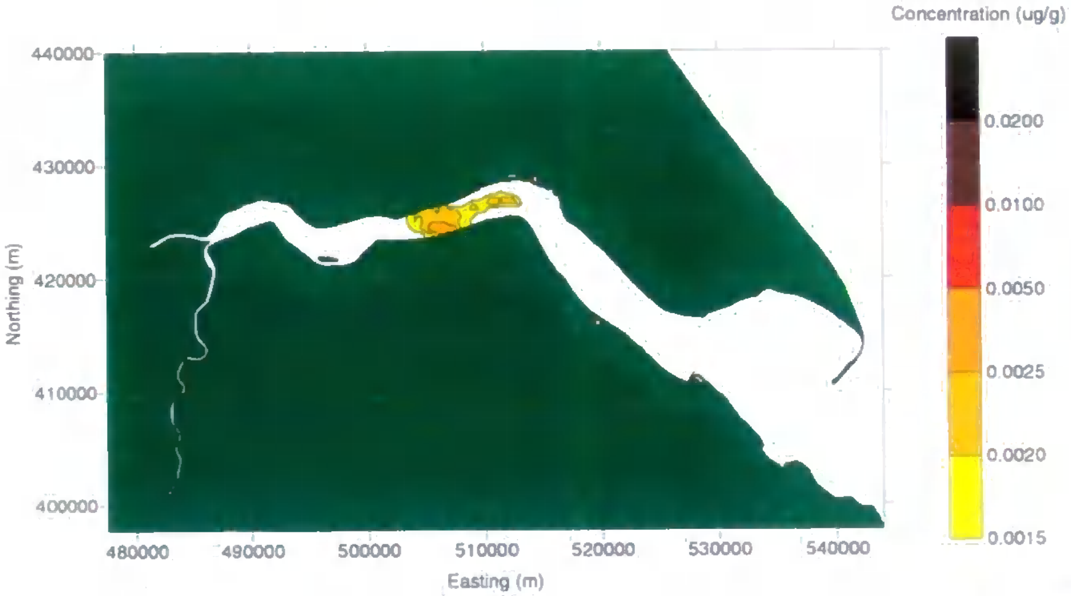
b

Figure 6.15. Axial Profile of Dissolved PCB Concentration in (a) SPM, and (b) Water (River Discharge, K_d Scenario 2)

Outfall Scenarios

The two outfall discharge scenarios demonstrate the effect of mid- and lower estuary inputs typical of an industrial outfall discharging to the estuary. Figures 6.16 and 6.17 show the PCB concentration in SPM at the mid-estuary (MD2) and lower estuary (MD3) stations respectively (see Figure 6.8). The concentrations in SPM are low, typically less than 0.05 ug g^{-1}. As expected therefore, dissolved phase concentrations were insignificant and have not been plotted.

Tidal dynamics dominate the dispersion of PCB from the simulated outfall discharges. Although the discharge is high, the influence of the discharge is fairly limited (within 10 km of the discharge location). During slack water (HW and LW) the discharged material 'pools' in the vicinity of the discharge creating elevated concentrations. These pools then disperse as the current speed increases. Figure 6.17c shows material from the lower estuary discharge advecting outside the estuary on the ebb tidal flow.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Easting (m)

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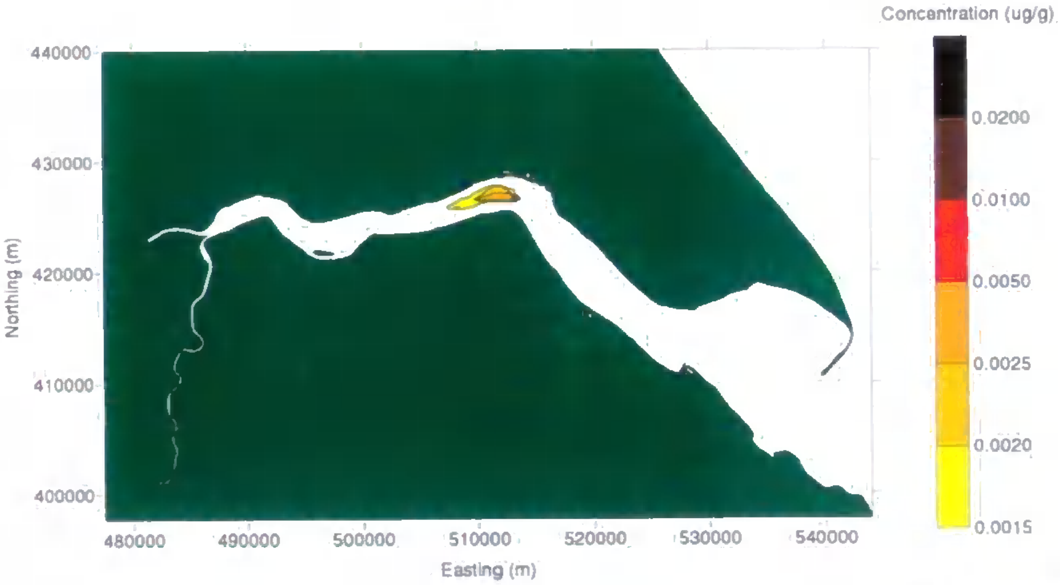
Concentration (ug/g)
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Easting (m)

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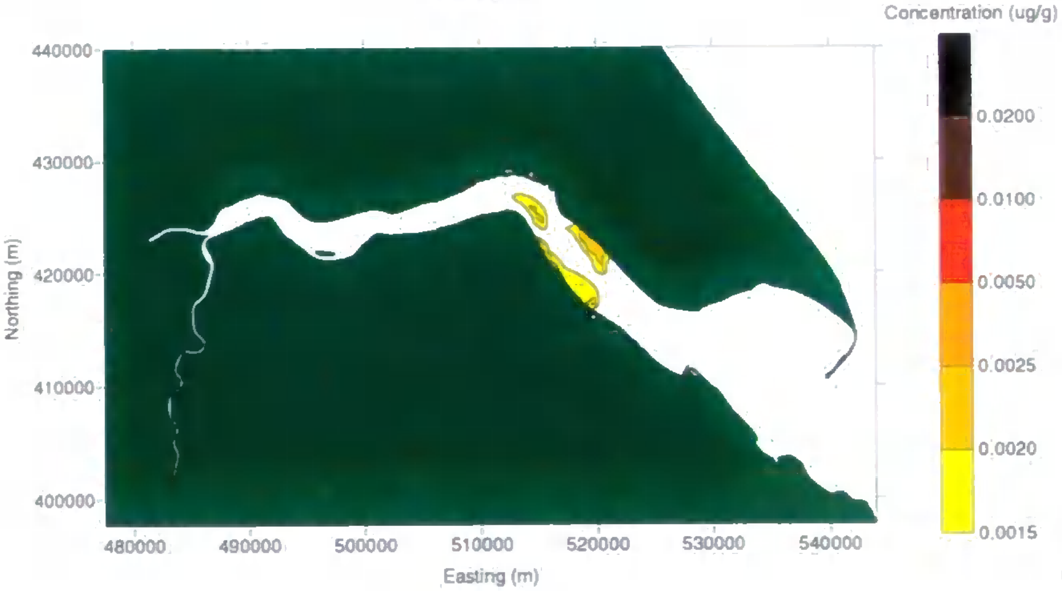
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400000
Northing (m)
480000
490000
500000
510000
520000
530000
540000
Easting (m)

c

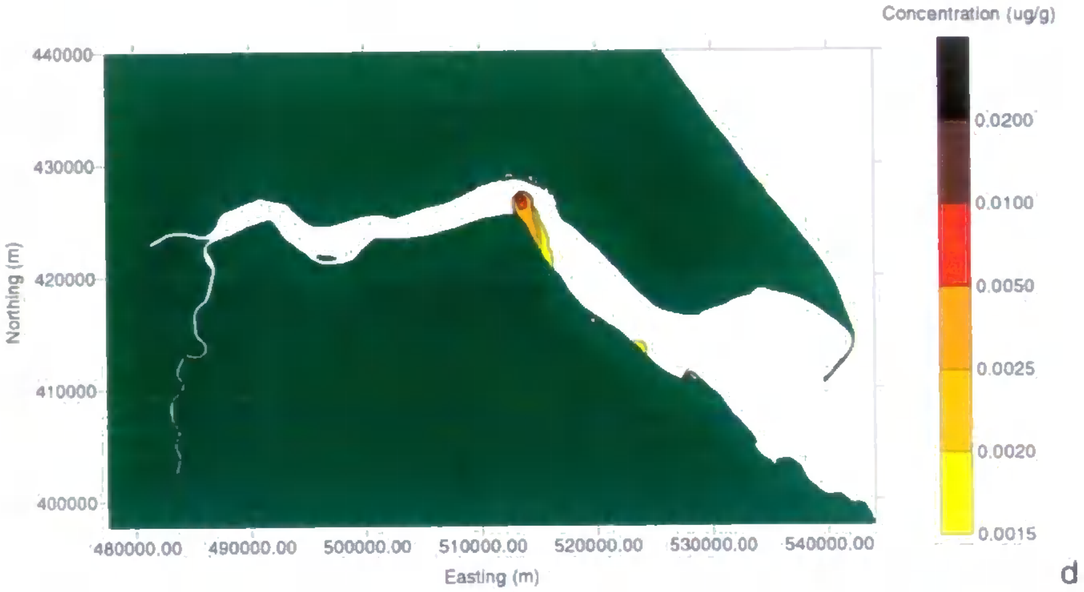
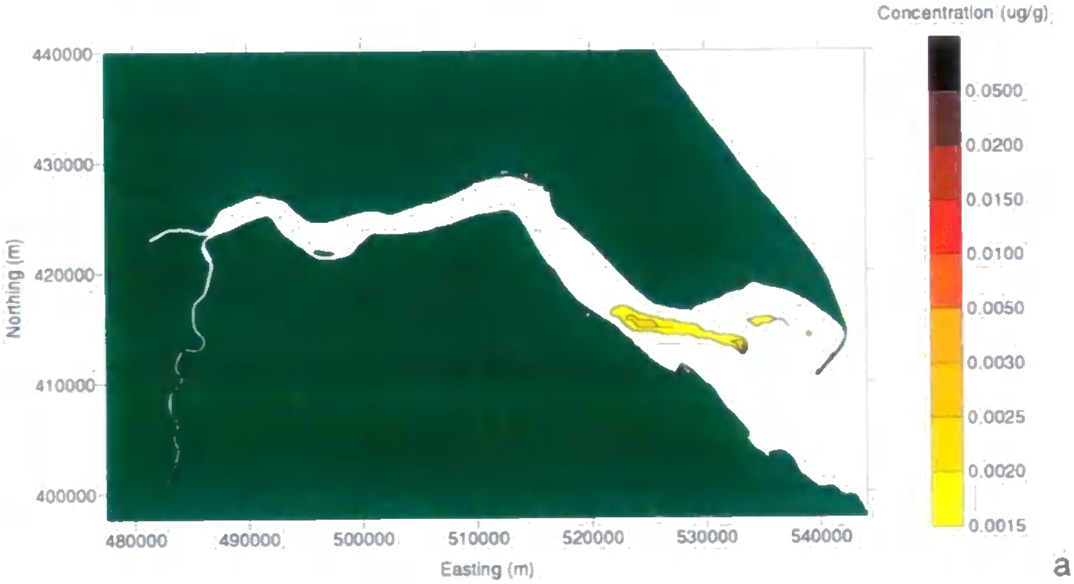


Figure 6.16. Suspended Particulate Phase PCB Concentration Distribution at (a) HW - 3, (b) HW, (c) HW + 3, (d) LW (Mid-estuary Discharge)



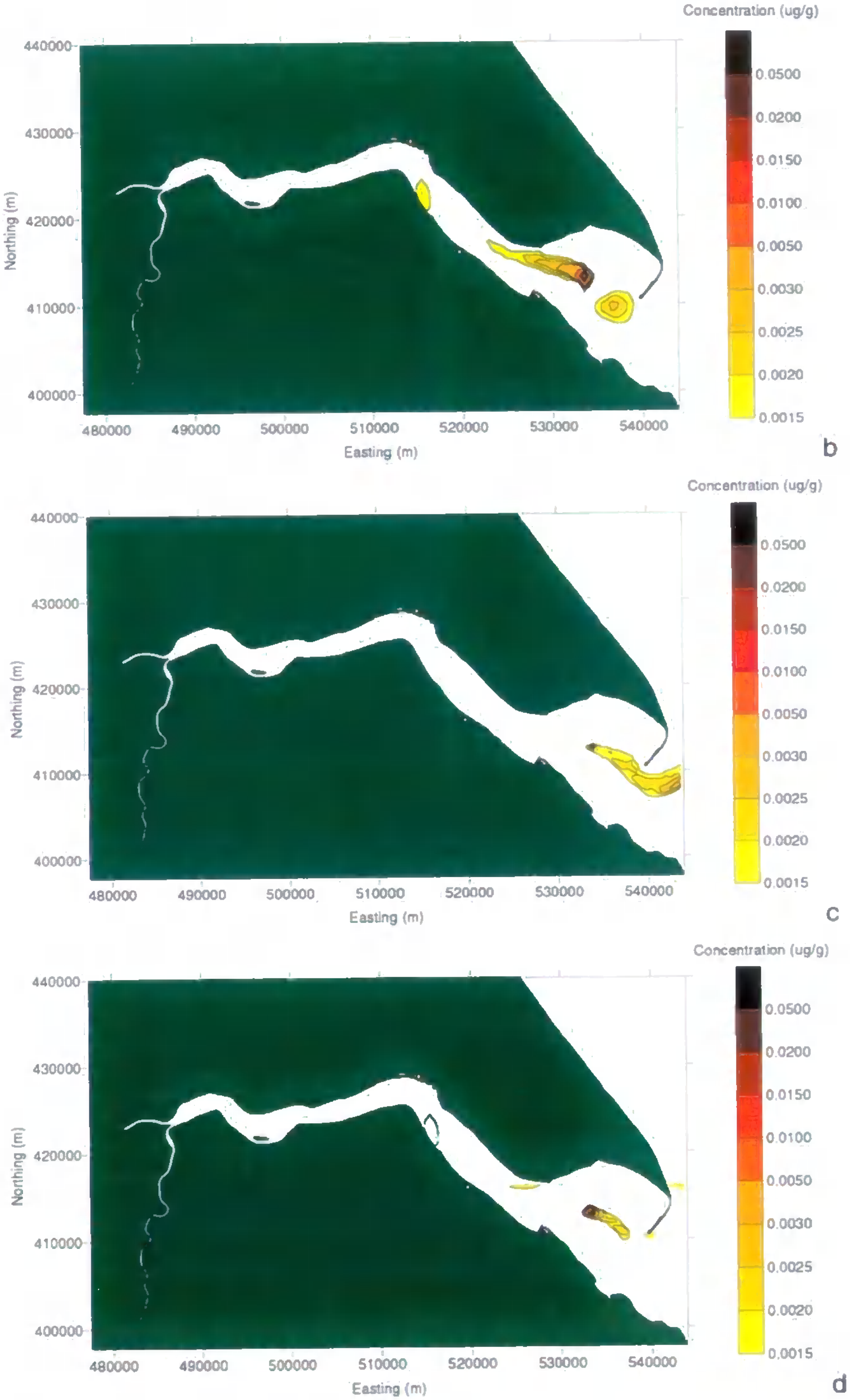


Figure 6.17. Suspended Particulate Phase PCB Concentration Distribution at (a) HW - 3, (b) HW, (c) HW + 3, (d) LW (Mid-estuary Discharge)

There are areas, illustrated well in Figure 6.17b, where there are elevated concentrations away from the discharge location. The area southeast of the discharge location was identified by Falconer & Owens (1990) as an area of high net deposition based on DIVAST model runs (used as the physics modelling basis for the PISCES model). Such areas will tend to act as sinks for sediment associated contaminants and may therefore be of management importance.

6.2.4 Summary

This Chapter has demonstrated the possibilities for incorporating sorption relationships within an integrated contaminant transport model applied to a dynamic estuary. However, there remain enormous challenges to developing integrated contaminant transport models capable of representing organic contaminant behaviour in an estuary. As already highlighted, there is currently a 'missing link' between the physical sediment characteristics which the physics models use to represent sediment dynamics, and the geochemical characteristics which have been shown to be key in determining OC sorption behaviour. It may be that a reasonable parameterisation of the relationship between physical and geochemical characteristics can be derived. This might be expected given that finer sediments have a tendency towards a high surface area and high apolar lipid content whereas coarser sediments, often from marine origin, tend to be lipid depleted with lower surface areas. If a relationship can be defined, it is likely to be estuary-specific and would need to be empirically determined.

The reversibility of sorption and kinetics of sorption reactions are not considered in the current model. This is a major failing but one which is extremely difficult to address without methods to distinguish between irreversibly sorbed chemical and the fraction available for desorption. Incorporation of kinetics is somewhat easier as these can be determined experimentally and new models are being developed to incorporate reaction kinetics. It must also be remembered that the modelling of sediment dynamics is also at a rudimentary stage, particularly for cohesive sediments and this is likely to hamper accurate modelling of hydrophobic compound behaviour for the foreseeable future.

There are several other factors which must also be considered in developing integrated models for organic compound behaviour. Dissolved organic carbon is seen to be an important influence in determining partitioning. There has been very little attempt made to model the complex dynamics of DOC in estuaries. Organic compounds have a number of complex removal processes which must also be represented. Of these, volatilisation is perhaps the most simple and can be incorporated as a half life or derived using a formulation which considers the mixing conditions more rigorously (Lyman, 1982). Degradation is extremely complex and realistic modelling is not achievable at present. In most cases the degradation pathways are poorly understood. The pathways and particularly the rates are highly dependent on the type and quantity of degrading microbes which themselves are likely to have highly variant populations within an estuary. As the compounds degrade (e.g. dechlorinate in the case of organochlorines) the degradation by-products will have a different geochemical behaviour. For example, through dechlorination, OC degradation products will tend to have lower polarity, more likelihood of volatilisation, and a lower partition coefficient.

Finally, timescale is a major consideration in organic contaminant modelling. The persistence of these compounds requires that models are able to represent the dynamics over long periods of time. This is not practical with the approach demonstrated in this Chapter, which is more suited to studying the short term impact of specific anthropogenic inputs. The algorithms required to fully represent the estuarine tidal dynamics are numerically expensive with model run times that are impractical for long term studies. Fugacity models have shown some success in representing a multi-phase system over long times scales (Mackay, 1991) but there is a considerable way still to go in fully representing all the known significant controlling influences.

Chapter 7. Summary and Future Work

7. Summary and Future Work

7.1 Summary of Studies Conducted

7.1.1 Distribution of OCs in the UK Marine Environment

This work provides the first comprehensive survey of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran distribution in UK estuaries and coastal waters. It also significantly supplements the data on polychlorinated biphenyl occurrence. This contribution to knowledge is vital given the recent international priority status given to these compounds through the UNEP Persistent Organic Pollutant Protocol.

In the UK estuaries studied, although there was evidence of elevated concentrations of OCs, these were not considered of undue concern when compared to other reported studies of estuarine environments in Europe and the USA.

7.1.2 Factors Influencing OC Distribution

The factors contributing to the observed distributions formed a major focus of this work. Three principal factors were considered; the source of OCs, the physicochemical properties of the OC compounds, and the geochemical composition of the particulate sorbent. The homolog profiles and congener patterns for the samples were compared against reference profiles and patterns for characterised sources. This led to the overall conclusion that atmospherically derived diffuse sources were a significant input to estuaries with samples comparing with atmospheric deposition patterns from a survey of dioxins and furans in UK urban air. Elucidation of specific point sources was found to be difficult due to the mixing of sediments in the estuary combined with the long residence times of OCs. However, there was some evidence that the Clyde estuary may have been contaminated with point sources of pentachlorophenol and possibly sewage sludge. Overall it was considered that source-occurrence matching techniques are likely to be of limited use in an environmental system where the dynamic conditions effectively mix the sample material on such a wide geographical basis, except possibly where there is a significant source and samples are collected relatively close to the emission.

The physicochemical properties of OCs vary widely and imply a significant range of environmental properties. In practice it is very difficult to separate distributional effects arising from the property of the compound, from other influences. Tentative evidence was found in the Clyde Estuary, with its' fairly distinct down-estuary gradient of sediment type, that ratios between lower chlorinated and higher chlorinated homologs changed with downstream distance implying that material contaminated in the upper estuary may be selectively transported down-estuary. In the Humber estuary, with its' highly dynamic mixing conditions, no pattern was observable.

The role of particulate sorbent properties in determining sorption preferences was studied in detail. The physical structure of the particles, measured by determining their specific surface area, was found to be of little importance. On the other hand the composition of the particle, in particular the content and type of organic carbon, was found to be a major controlling factor. Determination of apolar lipid content was undertaken as this represents the most apolar phase of the organic carbon phase of the particle. This was found in both estuaries, but particularly the Humber Estuary, to have the strongest correlation with adsorbed OC. The relative abundance of lipid material in the Clyde estuary was thought to weaken the lipid-OC relationship as OCs may readily locate preferential sorption sites at or close to the point of input to the system. In the Humber estuary, OCs may cycle within the system seeking sorption sites on the relatively lipid depleted particles.

A particle association model was applied to the data to try and determine whether sorbed OC was associated with the bulk of the particle or more loosely associated with the particle surface. The implication from the model is that OCs may tend to be inherently bound into the particles interstices or particle-associated organic matter and may even remain associated with source-derived particulates. Further confirmation of the adsorbed state of OCs to estuarine particles is considered difficult as the residence times of sediments in an estuary infer that at any time, whilst some OC may be in exchange (either partitioning into another environmental compartment, or migrating within the particle itself), the bulk of the adsorbed OC will be semi-permanently incorporated in the particle. This relatively steady state condition explains the predominance of physical processes in distributing OCs within an estuary.

OC concentrations were normalised against lipid content to highlight the distribution with the variation in sorbent characteristics substantially removed. In the Clyde Estuary this was useful in assisting identification of possible sources to the estuary. In the Humber the effect was predominately to further reduce the spatial variation in OC concentration which underlined the characteristics of the Humber as a single well mixed pool of sediment.

7.1.3 Sorption Studies

To further study the sorption behaviour of OCs under realistic estuarine conditions, sorption experiments were designed where a ^{14}C-labelled OC compound was introduced into a simulated estuarine gradient of salinity, particle composition and particle concentration. K_d values were found to vary significantly with the polarity of the compound and the estuarine environment (K_d range from 2.4×10^4 - 49.4×10^4 for TCB and 23.1×10^4 - 313×10^4 for TCDD). The influence of salinity on OC sorption was examined and although some evidence of 'salting out' was seen, it was concluded that salinity *per se* was a relatively minor influence.

Consistent with a large number of other studies, the concentration of particulate matter was found to be a major control in determining K_d. Explanation of this solids concentration effect include inter-particle collision-induced desorption, and the presence of colloidal material which cannot be easily separated during the experiments. In the latter case, for practical application in models of estuarine contaminant transport where there are two transport pathways (dissolved/colloidal transport in the water column, and sediment-bound transport), it is considered that the distinction between colloidal and dissolved OC is not significant.

7.1.4 Sorption Modelling

The physical explanation for the solids concentration caused by inter-particle collision-induced desorption was studied by applying a model developed by Di Toro *et al.* (1986) and expanded by Mackay & Powers (1987). This model reproduced the trend in axial variation of K_d in the study estuaries (except the Humber Estuary) reasonably well although there was a significant fixed error. This was attributed to the model's assumption of readily reversible sorption which takes no account of the significant irreversibly sorbed OC fraction identified in the estuarine distribution studies. However, the model did provide a good basis for prediction of OC sorption based on the K_{oc} of the compound, f_{oc} of the sorbent and the SPM concentration.

7.1.5 Integrated Contaminant Transport Modelling

The application of sorption models within an integrated estuarine transport model was demonstrated. However, it was necessary to use a relationship between salinity and compound K_d to predict the variation of K_d with the estuarine gradient. This was due to an inability to relate the physical parameters which define the sediment dynamics within the model (e.g. median particle diameter) to geochemically significant parameters such as f_{oc}. This shortcoming currently hampers integrated estuarine contaminant transport modelling and requires work to establish an operational relationship between physical and geochemical properties.

The model was configured with time-varying hydrodynamics and sediment dynamics for the Humber Estuary. Model scenarios were selected to simulate a riverine input and point source discharges. The model predicted the dispersion of OC under tidally varying conditions. The partitioning between dissolved and solid phases was modelled for two contrasting K_d-salinity relationships taken from the experimental sorption studies. These suggested that the particulate phase concentration is regulated by the source input of OC (assuming an unlimited sorption capacity). Dissolved phase concentrations were highly dependent on the K_d and changed by over an order of magnitude for the relationships tested.

The simulation of hypothetical discharge scenarios demonstrated the use of the model in determining the dispersive capacity of receiving waters and the consequent environmental concentrations of OC. The model was also able to identify sink areas for particulate bound OC.

7.2 Future Work

The following areas have been identified as priorities for future investigation;

1. The recent inclusion of PCDD, PCDFs and PCBs on the UNEP international priority list should be responded to by a UK-wide survey to establish the distribution of these contaminants in all UK marine environments in the proximity of urban areas.

2. Analysis of SPM for OCs is vital to understanding their transport in estuaries. Collection of sufficient material without contamination is a major challenge and will require the construction of special apparatus to bulk filter sufficient volumes of water. As well as OC analysis, the SPM samples need to be characterised in terms of lipid content, surface area etc.

3. More attention is needed to study the composition, origins and geochemical modification of apolar lipid material. Specifically, the

degradation of this material and subsequent release of sediment-bound OCs needs to be studied.

4. Methods need to be developed to discriminate between labile and non-labile fractions of adsorbed OC. This is important in the derivation and validation of suitable sorption sub-models.

5. Sorption sub-models need to be extended to incorporate both reversibly and irreversibly sorbed OC.

6. To further the integrated modelling of OCs in estuarine environments, it is essential to derive the relationship between the characteristics of sediments which determine their physical transport, and those properties that determine their geochemical behaviour. This will permit prediction of the major processes which influence the transport and fate of OCs in estuaries.

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Appendix I
PCDD and PCDF Analysis of Standard Reference Material

Lot - MAR - 2198585A

INTERLABORATORY CONSENSUS VALUES AND TOLERANCE LIMITS

ANALYTE	TARGET VALUE[a] (ng/g)	CONSENSUS VALUE[b] (ng/g)	RANGE OF EXPECTED VALUES[c]	
			Lower	Upper
Dioxins				
2,3,7,8-TCDD	0.5	0.46 ± 0.03	0.26	0.67
1,2,3,7,8-PCDD	1.0	0.96 ± 0.06	0.56	1.37
1,2,3,4,7,8-HxCDD	1.0	0.90 ± 0.06	0.50	1.29
1,2,3,6,7,8-HxCDD	1.0	0.87 ± 0.05	0.52	1.21
1,2,3,7,8,9-HxCDD	1.0	0.90 ± 0.06	0.46	1.33
1,2,3,4,6,7,8-HpCDD	1.5	1.39 ± 0.10	0.71	2.07
OCDD	3.5[d]	3.51 ± 0.22	1.98	5.03
Furans				
2,3,7,8-TCDF	0.5	0.45 ± 0.03	0.26	0.64
1,2,3,7,8-PCDF	1.0	0.87 ± 0.04	0.59	1.15
2,3,4,7,8-PCDF	1.0	0.86 ± 0.06	0.41	1.31
1,2,3,4,7,8-HxCDF	1.0	0.88 ± 0.05	0.53	1.23
1,2,3,6,7,8-HxCDF	1.0	0.95 ± 0.09	0.34	1.56
1,2,3,7,8,9-HxCDF	1.0	0.82 ± 0.06	0.39	1.26
2,3,4,6,7,8-HxCDF	1.0	0.91 ± 0.06	0.48	1.35
1,2,3,4,6,7,8-HpCDF	1.5	1.27 ± 0.11	0.52	2.01
1,2,3,4,7,8,9-HpCDF	1.5	1.12 ± 0.12	0.25	1.98
OCDF	2.5	2.25 ± 0.15	1.17	3.33

[a] The target value represents the amount of each analyte that was initially added to the soil. The difference between these values and the consensus values should be a good indication of the expected percent recovery of the analytical procedure.

[b] Refers to mean value and confidence limit (at the 95% confidence level) of interlaboratory study based on triplicate analyses by 10 laboratories.

[c] These values represent the upper and lower 95% tolerance limits which indicate the range of results that 95% of the laboratories should obtain 95% of the time for a single sample analysis.

[d] Includes average value of 1.0 ng/g present in native soil before fortification.

Test Certificate No:

Name of Laboratory : Rechem Environmental Research
Address : Rechem International
Charleston Rd Hythe Southampton SO45 3NX

Name of Client : Rechem
Address : Fawley

Sample Identifier : Reference Soil for December 1995
Sample No: 15075/D

Date of Receipt :
Date of Analysis : 15/12/95
Date of Report : 19/12/95

Instrument : VG 70S
GC Column : DB5
Calibration File : 151295

Test Method : 1122
Blank : S8

expressed as ng / g

Congener	Conc	TEFs	TEQ	DL	Rec %
2,3,7,8-TCDF	0.34	0.100	0.0338	0.0400	73
1,2,3,7,8-PeCDF	0.90	0.050	0.0451	0.0700	56
2,3,4,7,8-PeCDF	0.95	0.500	0.4735	0.0700	56
1,2,3,4,7,8-HxCDF	0.86	0.100	0.0863	0.0500	65
1,2,3,6,7,8-HxCDF	0.90	0.100	0.0900	0.0500	70
2,3,4,6,7,8-HxCDF	0.85	0.100	0.0849	0.0500	66
1,2,3,7,8,9-HxCDF	0.88	0.100	0.0879	0.0800	60
1,2,3,4,6,7,8-HpCDF	1.24	0.010	0.0124	0.0600	70
1,2,3,4,7,8,9-HpCDF	1.29	0.010	0.0129	0.0900	63
OCDF	2.29	0.001	0.0023	0.0800	
2,3,7,8-TCDD	0.40	1.000	0.3980	0.0700	62
1,2,3,7,8-PeCDD	0.76	0.500	0.3815	0.0800	68
1,2,3,4,7,8-HxCDD	0.84	0.100	0.0836	0.1200	65
1,2,3,6,7,8-HxCDD	0.85	0.100	0.0847	0.1100	68
1,2,3,7,8,9-HxCDD	0.80	0.100	0.0799	0.1000	
1,2,3,4,6,7,8-HpCDD	1.36	0.010	0.0136	0.0600	67
OCDD	3.43	0.001	0.0034	0.0500	55
TEQ			1.9738		

*	Isomer Not detected
TEQ	Toxic Equivalent Value
TEF	Toxic Equivalent Factor
Conc	Concentration
DL	Detection Value

Name of Analyst : K Pettit

Signature of Analyst :

Test Certificate No:

Name of Laboratory : Rechem Environmental Research
Address : Rechem International
Charleston Rd Hythe Southampton SO45 3NX

Name of Client : Rechem
Address : Fawley

Sample Identifier : Reference Soil for November
Sample No: 15043/D

Date of Receipt : 28/11/95
Date of Analysis : 05/12/95
Date of Report : 06/12/95

Instrument : VG 70S
GC Column : DB5
Calibration File : 51295

Test Method : 1122
Blank : s8

expressed as ng / g

Congener	Conc	TEFs	TEQ	DL	Rec %
2,3,7,8-TCDF	0.45	0.100	0.0449	0.0401	66
1,2,3,7,8-PeCDF	1.11	0.050	0.0554	0.0501	58
2,3,4,7,8-PeCDF	0.65	0.500	0.3231	0.0401	58
1,2,3,4,7,8-HxCDF	1.01	0.100	0.1014	0.0200	64
1,2,3,6,7,8-HxCDF	1.14	0.100	0.1137	0.0301	63
2,3,4,6,7,8-HxCDF	1.05	0.100	0.1050	0.0200	65
1,2,3,7,8,9-HxCDF	0.89	0.100	0.0895	0.0301	63
1,2,3,4,6,7,8-HpCDF	1.53	0.010	0.0153	0.0401	61
1,2,3,4,7,8,9-HpCDF	1.52	0.010	0.0152	0.0501	55
OCDF	2.74	0.001	0.0027	0.0501	
2,3,7,8-TCDD	0.54	1.000	0.5371	0.0401	66
1,2,3,7,8-PeCDD	0.98	0.500	0.4890	0.0200	66
1,2,3,4,7,8-HxCDD	1.01	0.100	0.1009	0.0501	63
1,2,3,6,7,8-HxCDD	1.05	0.100	0.1052	0.0501	64
1,2,3,7,8,9-HxCDD	1.00	0.100	0.1000	0.0501	
1,2,3,4,6,7,8-HpCDD	1.56	0.010	0.0156	0.0401	60
OCDD	4.54	0.001	0.0045	0.0601	52
TEQ			**2.2186**		

*	Isomer Not detected
TEQ	Toxic Equivalent Value
TEF	Toxic Equivalent Factor
Conc	Concentration
DL	Detection Value

Name of Analyst : K Pettit

Signature of Analyst :

Appendix II
Summary of Sample Analyses

Station Number	Year Sampled	Sample	TEQ (pg g^{-1})	PCDD/F (pg g^{-1})	PCDD (pg g^{-1})	PCDF (pg g^{-1})	2378TCDD (pg g^{-1})	TCDD (pg g^{-1})	PeCDD (pg g^{-1})	HxCDD (pg g^{-1})	HpCDD (pg g^{-1})	OCDD (pg g^{-1})	TCDF (pg g^{-1})	PeCDF (pg g^{-1})	HxCDF (pg g^{-1})	HpCDF (pg g^{-1})	OCDF (pg g^{-1})
Mersey	1991	Sub-tidal	1.6	111	65	46	0.3	3	<9	<7	9	36	11	4	9	8	13
Tyne	1991	Sub-tidal	1.5	102	21	81	n.d.	1	<1	3	3	13	4	3	6	9	59
Humber	1991	Sub-tidal	1.7	67	35	32	n.d.	2	<13	4	5	10	9	5	7	6	6
Tees	1991	Sub-tidal	0.6	31	8	23	0.1	1	<1	3	2	3	2	2	3	14	3
Tweed	1991	Sub-tidal	2.8	197	128	69	0.8	4	<12	11	24	89	16	10	15	13	16
Clyde	1991	Sub-tidal	7.6	384	285	99	3.5	17	47	34	79	110	16	15	28	35	6
Dee	1991	Sub-tidal	15.0	1140	750	390	3.0	20	50	60	120	500	60	40	70	110	110
Morecambe Bay	1991	Core (1cm)	3.7	322	206	116	<0.3	6	<0.6	10	40	150	21	16	35	22	22
Morecambe Bay	1991	Core (14 cm)	1.7	117	71	46	0.3	3	<5	<5	18	50	15	6	<5	10	15
Morecambe Bay	1991	Core (28 cm)	1.2	78	48	30	0.3	3	<3	<5	10	35	8	<3	<5	9	13

Table A.1. PCDD and PCDF Analyses for UK Coastal Sites

Station Number	Year Sampled	Sample	Total PCB ng g^{-1}
Clyde	1991	Sub-tidal	7
Dee	1991	Sub-tidal	15
Morecambe Bay	1991	Core (1cm)	5
Morecambe Bay	1991	Core (14 cm)	33
Morecambe Bay	1991	Core (28 cm)	36

Table A.2. PCB Analyses for UK Coastal Sites

Station Number	Year Sampled	Sample	SSA ($m^2 g^{-1}$)	Fe ($mg g^{-1}$)	Mn ($mg g^{-1}$)	Al ($mg g^{-1}$)	Ca ($mg g^{-1}$)
Mersey	1991	Sub-tidal	<1	0.71	0.17	0.075	14.4
Tyne	1991	Sub-tidal	<1	0.97	-	-	14.5
Tees	1991	Sub-tidal	<1	0.45	0.12	0.053	35.5
Tweed	1991	Sub-tidal	2.6	1.43	0.08	0.2	18.1
Clyde	1991	Sub-tidal	<1	1.08	0.042	0.19	1.46
Dee	1991	Sub-tidal	-	1.86	0.57	0.29	37.30
Morecambe Bay	1991	Core (1cm)	1.9	0.97	0.2	0.081	16.2
Morecambe Bay	1991	Core (14 cm)	2.7	0.9	0.1	0.073	14.6
Morecambe Bay	1991	Core (28 cm)	2.1	0.62	0.17	0.1	25.7

Table A.3. Geochemical Sediment Characteristics for UK Coastal Sites

Station Number	Year Sampled	Sample	Distance (km)	TEQ (pg g^{-1})	PCDD/F (pg g^{-1})	PCDD (pg g^{-1})	PCDF (pg g^{-1})	2378TCDD (pg g^{-1})	TCDD (pg g^{-1})	PeCDD (pg g^{-1})	HxCDD (pg g^{-1})	HpCDD (pg g^{-1})	OCDD (pg g^{-1})	TCDF (pg g^{-1})	PeCDF (pg g^{-1})	HxCDF (pg g^{-1})	HpCDF (pg g^{-1})	OCDF (pg g^{-1})
CS1	1992	Sub-tidal	0.0	52.9	1228	325	903	0.5	5	15	20	35	250	248	175	210	145	125
CS2	1992	Sub-tidal	0.8	35.2	8299	6401	1898	0.6	6	10	285	1500	4600	148	80	250	770	650
CS3	1992	Sub-tidal	2.1	11.4	2736	2058	678	0.5	16	30	92	380	1540	58	15	95	230	280
CS4	1992	Sub-tidal	3.9	11.5	2270	1612	658	0.5	20	27	50	315	1200	60	17	101	200	280
CS4(U)	1993	Sub-tidal	3.9	19.1	3122	2260	862	3.0	110	30	60	400	1660	195	90	112	165	300
CS4(L)	1993	Sub-tidal	3.9	17.4	2930	2190	740	3.0	60	40	40	350	1700	170	70	110	140	250
CS5	1992	Sub-tidal	4.6	17.6	2706	1911	795	0.5	32	24	60	325	1470	100	90	105	175	325
CS6	1991	Sub-tidal	5.3	57.0	5986	4666	1320	28.0	86	180	100	800	3500	210	170	320	350	270
CS6	1992	Sub-tidal	5.3	16.6	2615	1774	841	1.0	65	60	74	275	1300	148	210	115	118	250
CS7	1991	Sub-tidal	7.5	36.0	3418	2472	946	17.0	40	87	85	405	1855	106	135	310	260	135
CS7	1992	Sub-tidal	7.5	23.4	3150	2110	1040	1.0	57	53	105	395	1500	175	190	175	210	290
CS7(U)	1993	Sub-tidal	7.5	27.3	5850	4410	1440	5.0	50	50	100	640	3570	320	170	100	350	500
CS7(L)	1993	Sub-tidal	7.5	25.9	6640	5120	1520	5.0	50	50	100	640	4280	550	240	100	130	500
CS8	1991	Sub-tidal	8.8	60.0	4600	3060	1540	20.0	110	120	100	550	2180	230	240	420	460	190
CS8	1993	Sub-tidal	8.8	15.5	8016	5125	2891	0.9	74	4	4	565	4478	387	460	4	870	1170
CS9	1992	Sub-tidal	10.3	27.9	4600	3060	1540	5.0	50	75	135	700	2100	300	230	195	225	590
CI1	1992	Inter-tidal	10.4	3.2	120	80	40	1.0	10	10	10	10	40	10	10	12	5	3
CS10	1992	Sub-tidal	10.8	4.5	1605	1398	207	1.0	10	10	10	18	1350	7	10	10	5	175
CS10	1993	Sub-tidal	10.8	21.2	4685	3950	735	3.0	30	60	60	500	3300	115	120	60	110	330
CI3	1992	Inter-tidal	11.6	6.5	3532	3409	123	0.5	5	10	10	84	3300	13	10	10	20	70
CI2	1992	Inter-tidal	11.9	8.2	5114	4989	125	0.5	5	10	10	64	4900	12	1	22	14	76
CS11	1991	Sub-tidal	12.0	37.6	3666	2770	896	17.0	75	104	73	528	1990	96	100	210	350	140
CS11	1992	Sub-tidal	12.0	27.3	4898	3368	1530	6.0	38	20	135	425	2750	330	170	180	275	575
CI4	1992	Inter-tidal	12.4	18.6	4850	4130	720	1.0	10	10	10	600	3500	175	10	140	280	115
CS12	1993	Sub-tidal	13.1	27.5	6480	5270	1210	5.0	50	50	50	920	4200	345	240	50	230	345
CS13	1993	Sub-tidal	13.3	11.1	2986	2206	780	2.0	36	20	20	230	1900	200	20	20	180	360
CS14	1993	Sub-tidal	13.8	16.2	1794	1170	624	3.0	30	60	60	170	850	110	64	60	60	330
CS15	1993	Sub-tidal	14.2	40.4	13245	11100	2145	3.0	30	60	60	1650	9300	325	140	250	300	1130
CS15	1992	Sub-tidal	14.8	21.6	8790	7163	1627	4.0	27	10	45	31	7050	194	80	88	115	1150
CI5	1992	Inter-tidal	14.8	4.3	242	132	110	1.0	10	10	10	100	2	43	10	10	45	2
CS16	1993	Sub-tidal	15.8	1.6	48	23	25	0.4	4	5	9	2	3	4	5	9	4	3
CS17	1992	Sub-tidal	17.6	12.1	5790	4994	796	1.0	15	20	34	175	4750	70	45	48	68	565
CS18	1992	Sub-tidal	20.5	3.2	334	285	49	1.0	10	10	10	5	250	10	10	10	4	15
CS18	1993	Sub-tidal	20.5	31.7	13324	11060	2264	2.0	20	20	20	2600	8400	470	20	24	740	1010
CI6	1992	Inter-tidal	20.6	3.0	213	134	79	0.5	5	10	10	13	96	5	10	14	30	20
CI7	1992	Inter-tidal	21.7	2.3	169	129	40	0.5	5	5	10	21	88	5	5	10	10	10

Station Number	Year Sampled	Sample	Distance (km)	TEQ (pg g^{-1})	PCDD/F (pg g^{-1})	PCDD (pg g^{-1})	PCDF (pg g^{-1})	2378TCDD (pg g^{-1})	TCDD (pg g^{-1})	PeCDD (pg g^{-1})	HxCDD (pg g^{-1})	HpCDD (pg g^{-1})	OCDD (pg g^{-1})	TCDF (pg g^{-1})	PeCDF (pg g^{-1})	HxCDF (pg g^{-1})	HpCDF (pg g^{-1})	OCDF (pg g^{-1})
CI8	1992	Inter-tidal	22.2	6.1	2555	2373	182	1.0	10	10	10	43	2300	15	10	12	16	129
CI9	1992	Inter-tidal	23.1	2.9	73	37	36	1.0	10	10	10	2	5	10	10	10	4	2
CS19	1992	Sub-tidal	27.3	3.3	478	434	44	1.0	10	10	10	4	400	10	10	10	4	10
CI10	1992	Inter-tidal	28.5	17.9	7619	5119	2500	1.2	3	10	8	98	5000	15	20	85	180	2200
CS20	1992	Sub-tidal	31.5	3.8	888	826	62	1.0	10	10	10	16	780	10	10	10	8	24
CI11	1992	Inter-tidal	34.6	3.6	149	97	52	1.0	12	10	10	15	50	20	10	10	8	4
CS22	1992	Sub-tidal	35.0	13.0	3184	2330	854	1.5	20	10	35	365	1900	94	45	105	155	455
CS21	1992	Sub-tidal	35.3	5.0	838	538	300	1.0	10	10	10	78	430	27	10	24	24	215
CS24	1992	Sub-tidal	35.8	23.5	9777	8595	1182	1.5	13	10	17	55	8500	142	85	90	45	820
CS23	1992	Sub-tidal	36.2	4.3	1335	1210	125	1.0	10	10	10	30	1150	8	10	10	12	85
CS25	1992	Sub-tidal	38.3	20.6	10237	9205	1032	1.0	16	18	86	285	8800	88	50	64	120	710
CI12	1992	Inter-tidal	39.4	3.2	116	77	39	1.0	10	10	10	7	40	10	10	10	6	3
CS26	1992	Sub-tidal	39.5	9.5	4470	3931	539	1.0	6	10	10	155	3750	30	20	30	84	375
CS27	1992	Sub-tidal	40.3	19.0	2708	2037	671	1.0	10	22	75	300	1630	50	26	180	150	265
CS28	1992	Sub-tidal	41.5	6.8	1855	1389	466	1.0	6	13	20	140	1210	35	20	36	75	300
CC1	1993	Core (2.5 cm)	-	52.7	30338	21313	9025	<4	<40	<40	123	2190	19000	115	<40	350	960	7600
CC1	1993	Core (12.5 cm)	-	156.8	107300	100000	7300	<5	<50	<50	<100	12000	88000	100	<50	<100	800	6400
CC1	1993	Core (17.5 cm)	-	82.0	51487	35857	15630	<7	<70	<70	<70	1857	34000	110	<70	400	1120	14000
CC1	1993	Core (22.5 cm)	-	58.7	36405	28275	8130	<5	<50	<50	<70	1275	27000	190	<50	270	870	6800
CC1	1993	Core (27.5 cm)	-	64.9	36185	33845	2340	<4	<40	<50	145	2700	31000	130	<50	300	1010	900
CC2	1993	Core (2.5 cm)	-	42.6	5540	4060	1480	<5	50	<50	870	440	2700	310	220	280	170	500
CC2	1993	Core (7.5 cm)	-	35.3	3915	2840	1075	<5	<50	<50	<50	340	2500	240	185	230	20	400
CC2	1993	Core (17.5 cm)	-	13.7	5250	4290	960	<1	60	<10	<20	630	3600	260	<10	<20	300	400
CC2	1993	Core (22.5 cm)	-	33.2	4336	3170	1166	<5	<50	<50	<50	470	2700	156	100	270	230	410
CC2	1993	Core (27.5 cm)	-	36.0	6489	5040	1449	<5	<50	<50	<50	1540	3500	370	160	79	170	670
CC3	1993	Core (2.5 cm)	-	23.9	8214	6852	1362	<2	34	<20	58	260	6500	210	90	187	175	700
CC3	1993	Core (7.5 cm)	-	18.8	9490	8200	1290	<2	<20	<20	<20	1000	7200	220	<20	<20	170	900
CC3	1993	Core (12.5 cm)	-	2.4	0	0	0	<0.6	<6	<9	<10	<4	<5	<6	<9	<10	<8	<5
CC3	1993	Core (17.5 cm)	-	1.9	0	0	0	<0.4	<4	<7	<10	<4	<5	<4	<7	<10	<8	<5
CC3	1993	Core (22.5 cm)	-	2.8	0	0	0	<0.6	<6	<10	<20	<6	<5	<6	<10	<10	<8	<5

Table A.4. PCDD and PCDF Analyses for the Clyde Estuary. Distance from weir (km). U - Upper, L - Lower (10 cm).

Station Number	Year Sampled	Sample	Distance (km)	Total PCB (ng g^{-1})	PCB (ng g^{-1}) 28	52	101	118	138	153	180	Sum ICES 7
CS1	1992	Sub-tidal	0.0	10	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.07
CS2	1992	Sub-tidal	0.8	3000	11	14	14.9	6.1	18.6	15.5	27.8	107.9
CS3	1992	Sub-tidal	2.1	400	0.8	0.8	1.2	1.1	1.7	1.4	1.2	8.2
CS4	1992	Sub-tidal	3.9	152	2.8	7.7	9.4	6.6	6.5	6.1	4.5	43.6
CS4(U)	1993	Sub-tidal	3.9	268	-	-	-	-	-	-	-	-
CS4(L)	1993	Sub-tidal	3.9	307	-	-	-	-	-	-	-	-
CS5	1992	Sub-tidal	4.6	254	2.6	2.5	2.9	2.8	2.8	1.9	<0.01	15.51
CS6	1991	Sub-tidal	5.3	57	-	-	-	-	-	-	-	-
CS6	1992	Sub-tidal	5.3	726	12	14	15.4	9.5	9.7	6.5	7.1	74.2
CS7	1991	Sub-tidal	7.5	36	-	-	-	-	-	-	-	-
CS7	1992	Sub-tidal	7.5	520	9.5	1.4	1.6	1.5	4.1	3.1	<0.01	21.21
CS7(U)	1993	Sub-tidal	7.5	198	-	-	-	-	-	-	-	-
CS7(L)	1993	Sub-tidal	7.5	221	-	-	-	-	-	-	-	-
CS8	1991	Sub-tidal	8.8	59	-	-	-	-	-	-	-	-
CS8	1993	Sub-tidal	8.8	974	-	-	-	-	-	-	-	-
CS9	1992	Sub-tidal	10.3	486	12	19	20	17	22	7	35	132
CI1	1992	Inter-tidal	10.4	7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.07
CS10	1992	Sub-tidal	10.8	18	1.9	2	2.4	2.1	0.9	0.8	<0.01	10.11
CS10	1993	Sub-tidal	10.8	374	-	-	-	-	-	-	-	-
CI3	1992	Inter-tidal	11.6	105	3.1	4.7	5.2	5.1	7.2	6.7	9.2	41.2
CI2	1992	Inter-tidal	11.9	50	1.7	1.9	1.2	1.3	1.1	0.9	0.9	9
CS11	1991	Sub-tidal	12.0	37	-	-	-	-	-	-	-	-
CS11	1992	Sub-tidal	12.0	537	3	0.1	0.2	0.3	2	2.1	<0.01	7.71
CI4	1992	Inter-tidal	12.4	277	6.2	9.1	10.1	9.4	11.2	10.6	5.2	61.8
CS12	1993	Sub-tidal	13.1	126	-	-	-	-	-	-	-	-
CS13	1993	Sub-tidal	13.3	247	-	-	-	-	-	-	-	-
CS14	1993	Sub-tidal	13.8	157	-	-	-	-	-	-	-	-
CS15	1992	Sub-tidal	14.8	950	10	15	11	10	12	17.3	4.7	80
CI5	1992	Inter-tidal	14.8	70	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.07
CS16	1993	Sub-tidal	15.8	197	-	-	-	-	-	-	-	-
CS17	1992	Sub-tidal	17.6	67	2.3	4	2.7	2.8	2.5	2.3	1.4	18
CS18	1992	Sub-tidal	20.5	9	0.5	0.5	0.4	0.4	0.6	0.45	0.01	2.86
CS18	1993	Sub-tidal	20.5	1270	-	-	-	-	-	-	-	-
CI6	1992	Inter-tidal	20.6	16	0.2	<0.01	<0.01	<0.01	0.1	0.1	<0.01	0.44
CI7	1992	Inter-tidal	21.7	27	0.2	0.6	1.1	1.4	0.9	<0.01	<0.01	4.22
CI8	1992	Inter-tidal	22.2	20	1.7	1.9	2.4	2.1	1.7	1.5	1.1	12.4

Station Number	Year Sampled	Sample	Distance (km)	Total PCB (ng g^{-1})	PCB (ng g^{-1})							Sum ICES 7
					28	52	101	118	138	153	180	
CI9	1992	Inter-tidal	23.1	1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.07
CS19	1992	Sub-tidal	27.3	3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.07
CI10	1992	Inter-tidal	28.5	24	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.07
CS20	1992	Sub-tidal	31.5	90	1	6.8	7	4.8	5.7	5.9	3.3	34.5
CI11	1992	Inter-tidal	34.6	48	2.6	2.4	2.6	2.5	2.6	3.1	3.2	19
CS22	1992	Sub-tidal	35.0	171	2.8	9	7	6.7	6.3	9	0.01	40.81
CS21	1992	Sub-tidal	35.3	60	0.8	2.8	2.9	3	1.7	1.9	1	14.1
CS24	1992	Sub-tidal	35.8	7	0.4	1.3	1.4	1.2	0.7	0.7	0.1	5.8
CS23	1992	Sub-tidal	36.2	4	0.5	0.2	<0.01	<0.01	<0.01	<0.01	<0.01	0.75
CS25	1992	Sub-tidal	38.3	126	0.1	0.6	0.7	0.6	1	1.2	<0.01	4.21
CI12	1992	Inter-tidal	39.4	32	1.1	1.5	1.6	1.4	0.9	0.7	<0.01	7.21
CS26	1992	Sub-tidal	39.5	34	0.3	0.34	0.6	0.9	1	1.1	1	5.24
CS27	1992	Sub-tidal	40.3	247	2	2.6	3.1	3.2	4.7	4.6	2.1	22.3
CS28	1992	Sub-tidal	41.5	120	3.2	5.6	5.8	4.4	8.1	7.7	9.7	44.5
C1	1993	Core (2.5 cm)	-	887	-	-	-	-	-	-	-	-
C1	1993	Core (12.5 cm)	-	1430	-	-	-	-	-	-	-	-
C1	1993	Core (17.5 cm)	-	1240	-	-	-	-	-	-	-	-
C1	1993	Core (22.5 cm)	-	794	-	-	-	-	-	-	-	-
C1	1993	Core (27.5 cm)	-	881	-	-	-	-	-	-	-	-
C2	1993	Core (2.5 cm)	-	277	-	-	-	-	-	-	-	-
C2	1993	Core (7.5 cm)	-	343	-	-	-	-	-	-	-	-
C2	1993	Core (17.5 cm)	-	995	-	-	-	-	-	-	-	-
C2	1993	Core (22.5 cm)	-	359	-	-	-	-	-	-	-	-
C2	1993	Core (27.5 cm)	-	430	-	-	-	-	-	-	-	-
C3	1993	Core (2.5 cm)	-	130	-	-	-	-	-	-	-	-
C3	1993	Core (7.5 cm)	-	234	-	-	-	-	-	-	-	-
C3	1993	Core (12.5 cm)	-	9	-	-	-	-	-	-	-	-
C3	1993	Core (17.5 cm)	-	3	-	-	-	-	-	-	-	-
C3	1993	Core (22.5 cm)	-	4	-	-	-	-	-	-	-	-

*Table A.5. PCB Analyses for the Clyde Estuary. Distance from weir (km).
U - Upper, L - Lower (10 cm).*

Station Number	Year Sampled	Sample	Sample	Distance (km)	Total C (mg g^{-1})	Org C (mg g^{-1})	Lipid Cont. (mg g^{-1})	SSA (m^2 g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})	Al (mg g^{-1})	Ca (mg g^{-1})
CS1	1992	Sub-tidal	SUB	0.0	30.4	30.3	1.39	12.5	2.87	2.02	1.10	1.09
CS2	1992	Sub-tidal	SUB	0.8	85	84.6	8.32	5.1	10.80	1.09	1.40	4.99
CS3	1992	Sub-tidal	SUB	2.1	74.3	72	6.01	3.6	6.40	0.45	1.20	7.67
CS4	1992	Sub-tidal	SUB	3.9	70.9	70.9	8.83	3.4	11.7	0.58	1.5	4.14
CS4(U)	1993	Sub-tidal	SUB	3.9	-	-	9.319	-	21.7	14.7	-	-
CS4(L)	1993	Sub-tidal	SUB	3.9	-	-	9.12	-	22.2	13.5	-	-
CS5	1992	Sub-tidal	SUB	4.6	84.4	84.4	10.2	3.4	7.95	0.29	1.40	3.52
CS6	1991	Sub-tidal	SUB	5.3	-	-	-	2.2	12.6	0.447	0.63	4.02
CS6	1992	Sub-tidal	SUB	5.3	93.5	93.5	8.39	4.1	6.42	0.42	0.95	3.28
CS7	1991	Sub-tidal	SUB	7.5	66.8	66.5	-	<1	6.9	0.32	0.38	5.05
CS7	1992	Sub-tidal	SUB	7.5	81.9	81.9	13.8	5.8	10.50	0.37	1.30	5.05
CS7(U)	1993	Sub-tidal	SUB	7.5	98.8	97.9	11.89	-	23	1.35	-	-
CS7(L)	1993	Sub-tidal	SUB	7.5	-	-	6.27	-	16.4	0.38	-	-
CS8	1991	Sub-tidal	SUB	8.8	-	-	-	3.6	14.3	0.449	1.1	5.13
CS8	1993	Sub-tidal	SUB	8.8	-	-	12.34	-	-	-	-	-
CS9	1992	Sub-tidal	SUB	10.3	73.5	73.5	5.6	4.8	6.88	0.29	1.10	4.46
CI1	1992	Inter-tidal	IT	10.4	3.8	3.8	0.25	1.8	1.36	0.09	0.20	0.98
CS10	1992	Sub-tidal	SUB	10.8	6.9	6.9	n.d.	9.9	2.62	0.33	0.51	5.39
CS10	1993	Sub-tidal	SUB	10.8	-	-	2.8	-	-	-	-	-
CI3	1992	Inter-tidal	IT	11.6	-	32.6	1.98	7.6	2.33	0.06	0.63	1.78
CI2	1992	Inter-tidal	IT	11.9	63.5	63.5	2.31	7.2	6.70	0.19	1.40	4.94
CS11	1991	Sub-tidal	SUB	12.0	59.9	59.9	-	3.1	8.2	0.158	0.83	3.82
CS11	1992	Sub-tidal	SUB	12.0	98.7	98.4	11.23	6.1	8.54	0.40	1.03	4.26
CI4	1992	Inter-tidal	IT	12.4	63.9	63.7	-	7.4	3.74	0.07	1.00	2.31
CS12	1993	Sub-tidal	SUB	13.1	-	-	4.16	-	9.14	0.27	-	-
CS13	1993	Sub-tidal	SUB	13.3	-	-	6.19	-	16.3	0.67	-	-
CS14	1993	Sub-tidal	SUB	13.8	-	-	4.16	-	-	-	-	-
CS15	1993	Sub-tidal	SUB	14.2	37.9	37.7	4.79	-	-	-	-	-
CS15	1992	Sub-tidal	SUB	14.8	71.5	71	5.06	2.6	3.39	0.23	0.84	2.25
CI5	1992	Inter-tidal	IT	14.8	57.1	57	2.75	2.6	1.53	0.02	0.46	1.10
CS16	1993	Sub-tidal	SUB	15.8	-	-	5.267	-	-	-	-	-
CS17	1992	Sub-tidal	SUB	17.6	56.8	56.3	1.17	2.1	1.21	0.07	0.42	0.91
CS18	1992	Sub-tidal	SUB	20.5	2.4	2.4	0.22	1	0.94	0.11	0.19	0.78
CS18	1993	Sub-tidal	SUB	20.5	-	-	4.65	-	12.1	0.47	-	-
CI6	1992	Inter-tidal	IT	20.6	1.8	1.2	0.51	2.6	1.48	0.06	0.26	1.74
CI7	1992	Inter-tidal	IT	21.7	9.6	9.6	0.63	1.8	0.83	0.06	0.19	0.56

Station Number	Year Sampled	Sample	Sample	Distance (km)	Total C (mg g^{-1})	Org C (mg g^{-1})	Lipid Cont. (mg g^{-1})	SSA (m^2 g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})	Al (mg g^{-1})	Ca (mg g^{-1})
CI8	1992	Inter-tidal	IT	22.2	-	-	-	3.7	1.93	0.19	0.40	1.40
CI9	1992	Inter-tidal	IT	23.1	1.6	1.6	n.d.	6.7	0.87	0.03	0.09	0.16
CS19	1992	Sub-tidal	SUB	27.3	5.2	5.2	0.07	1.9	1.20	0.29	0.16	1.09
CI10	1992	Inter-tidal	IT	28.5	30.1	29.8	0.91	3.4	1.40	0.10	0.35	4.89
CS20	1992	Sub-tidal	SUB	31.5	76.1	76.1	0.19	1.2	1.67	0.14	0.17	4.38
CI11	1992	Inter-tidal	IT	34.6	64.7	63.8	1.93	5.9	2.29	0.04	0.38	2.00
CS22	1992	Sub-tidal	SUB	35.0	44.2	44.2	3.31	7.8	7.70	0.36	0.98	7.20
CS21	1992	Sub-tidal	SUB	35.3	33.9	30.3	1.66	10.4	3.08	0.12	0.38	9.32
CS24	1992	Sub-tidal	SUB	35.8	48.3	46.3	4.55	4.9	10.40	0.34	1.00	4.88
CS23	1992	Sub-tidal	SUB	36.2	13.1	12.7	0.41	1.9	1.42	0.10	0.29	1.16
CS25	1992	Sub-tidal	SUB	38.3	39.1	36.2	1.54	3.6	3.46	0.18	0.48	3.60
CI12	1992	Inter-tidal	IT	39.4	8.8	8.6	1.61	1.1	0.89	0.06	0.26	4.70
CS26	1992	Sub-tidal	SUB	39.5	31.2	29.9	0.83	4.4	2.72	0.29	0.36	3.44
CS27	1992	Sub-tidal	SUB	40.3	59.2	56.5	2.74	7.4	6.56	0.28	0.79	6.99
CS28	1992	Sub-tidal	SUB	41.5	68.5	67.7	1.88	6.6	4.33	0.20	0.61	7.03

Table A.6. Geochemical Sediment Characteristics for the Clyde Estuary. Distance from weir (km). U - Upper, L - Lower (10 cm).

Station Number	Year Sampled	Sample	Distance (km)	TEQ (pg g^{-1})	PCDD/F (pg g^{-1})	PCDD (pg g^{-1})	PCDF (pg g^{-1})	2378TCDD (pg g^{-1})	TCDD (pg g^{-1})	PeCDD (pg g^{-1})	HxCDD (pg g^{-1})	HpCDD (pg g^{-1})	OCDD (pg g^{-1})	TCDF (pg g^{-1})	PeCDF (pg g^{-1})	HxCDF (pg g^{-1})	HpCDF (pg g^{-1})	OCDF (pg g^{-1})
HS1	1993	Sub-tidal	0.4	5.2	377	257	120	0.8	62	28	<10	27	140	40	40	20	10	10
HI1	1993	Inter-tidal	4.5	12.3	1821	1318	503	4.0	190	120	61	97	850	48	144	61	40	210
HI2	1993	Inter-tidal	4.8	13.9	1651	1163	488	3.5	140	110	52	116	745	67	160	56	33	172
HS2	1993	Sub-tidal	4.9	1.0	47	27	20	<.2	5	<4	<4	3	19	4	7	<4	4	5
HI3	1993	Inter-tidal	7.2	24.1	3827	2771	1056	7.0	370	213	110	303	1775	138	278	114	98	428
HS3	1993	Sub-tidal	12.1	1.0	50	21	29	<.2	4	<4	<4	2	15	4	14	<4	4	7
HI4	1993	Inter-tidal	13.5	16.2	2358	1602	756	2.6	344	138	79	159	882	118	256	79	56	247
HS4	1993	Sub-tidal	15.1	7.6	956	653	303	2.8	130	87	<5	58	378	54	76	37	16	120
HI5	1991	Inter-tidal	17.9	38.9	2216	1273	943	20.2	45	176	123	71	858	304	148	110	185	196
HS5	1993	Sub-tidal	17.9	1.2	64	38	26	<.2	5	<5	<5	4	29	5	<5	<5	3	18
HI6	1993	Inter-tidal	22.4	14.7	2654	1915	739	2.0	237	149	77	220	1232	99	182	80	75	303
HS6	1993	Sub-tidal	28.2	1.4	64	28	35	<0.2	4	<5	<5	5	20	3	13	6	4	10
HI7	1991	Inter-tidal	31.9	24.2	3072	1888	1184	0.6	5	170	100	293	1320	314	164	128	149	429
HS7	1993	Sub-tidal	33.2	6.2	577	425	152	1.3	62	50	52	38	223	31	44	23	14	40
HI8	1993	Inter-tidal	36.8	1.4	n.d.	n.d.	n.d.	<0.2	<2	<4	<10	<2	<5	<2	<4	<10	<4	<5
HS8	1993	Sub-tidal	38.2	5.7	284	201	83	0.4	13	12	50	12	115	9	13	27	6	29
HI9	1991	Inter-tidal	43.3	23.6	1107	483	624	15.0	148	49	52	80	154	163	81	86	68	226
HI10	1993	Inter-tidal	43.3	16.3	2253	1562	691	5.0	190	150	72	150	1000	120	205	72	47	247
HS9	1993	Sub-tidal	49.0	11.6	1626	1005	621	1.7	160	130	67	110	538	164	136	72	33	216
HS10	1993	Sub-tidal	55.2	4.0	244	145	99	0.5	15	13	42	13	62	20	23	26	7	23
HS11	1993	Sub-tidal	57.9	9.9	1222	755	467	1.3	127	97	65	76	390	140	102	43	20	162
HI14	1993	Inter-tidal	58.5	1.4	n.d.	n.d.	n.d.	<0.2	<2	<4	<10	<2	<5	<2	<4	<10	<4	<5
HI11	1991	Inter-tidal	58.7	30.9	2693	1453	1240	9.9	222	206	83	151	791	284	167	170	195	424
HI12	1993	Inter-tidal	58.7	13.4	1783	1226	557	3.5	116	144	56	140	770	52	198	67	56	184
HI13	1991	Inter-tidal	61.1	9.3	559	295	264	4.8	53	40	21	31	150	66	32	32	39	96

Table A.7. PCDD and PCDF Analyses for the Humber Estuary. Distance from Trent Falls (km)

Station Number	Year Sampled	Sample	Distance (km)	Total PCB (ng g^{-1})				PCB (ng g^{-1})				Sum ICES 7
					28	52	101	118	138	153	180	
HS1	1993	Sub-tidal	0.4	7	0.5	0.7	0.9	1.4	0.7	0.9	<0.5	5.1
HI1	1993	Inter-tidal	4.5	44	2.4	3.4	7	9.3	<0.5	5	<0.5	27.1
HI2	1993	Inter-tidal	4.8	39	3	5.6	8.4	10.7	2.1	1.2	<0.5	31
HS2	1993	Sub-tidal	4.9	2	1	0.8	<0.2	<0.5	<0.5	1.6	<0.5	3.4
HI3	1993	Inter-tidal	7.2	75	6.8	6	15	12	2.4	1.9	<0.5	44.1
HS3	1993	Sub-tidal	12.1	1	0.5	<0.2	<0.2	<0.5	<0.5	<0.5	<0.5	0.5
HI4	1993	Inter-tidal	13.5	67	4.4	7.5	12	16.9	1.9	2.7	1	46.4
HS4	1993	Sub-tidal	15.1	32	4.7	9.6	14.4	15.6	3.7	4.6	1.4	54
HI5	1991	Inter-tidal	17.9	-	-	-	-	-	-	-	-	-
HS5	1993	Sub-tidal	17.9	2	0.9	1.1	<0.2	<0.5	<0.5	<0.5	<0.5	2
HI6	1993	Inter-tidal	22.4	53	2.8	4.7	7.7	10.2	1.2	2.3	<0.5	28.9
HS6	1993	Sub-tidal	28.2	1	<0.2	<0.2	<0.2	<0.5	<0.5	<0.5	<0.5	n.d.
HI7	1991	Inter-tidal	31.9	-	-	-	-	-	-	-	-	-
HS7	1993	Sub-tidal	33.2	37	3.1	10.4	16.4	17.9	4.6	7.4	2.1	61.9
HI8	1993	Inter-tidal	36.8	<1	<0.5	<0.5	<0.2	<0.5	<0.5	<0.5	<0.5	0
HS8	1993	Sub-tidal	38.2	4	0.3	1.1	1.7	1.4	0.6	0.9	<0.5	6
HI9	1991	Inter-tidal	43.3	-	-	-	-	-	-	-	-	-
HI10	1993	Inter-tidal	43.3	27	3.6	4.7	9	11.4	1.2	1.4	<0.5	31.3
HS9	1993	Sub-tidal	49.0	43	2.5	3.5	6.9	8.9	<0.5	1.2	<0.5	23
HS10	1993	Sub-tidal	55.2	5	0.4	1.6	2	1.7	1.9	1.2	1	9.8
HS11	1993	Sub-tidal	57.9	36	2.9	8.7	14.6	21.4	2.4	0.9	0.7	51.6
HI14	1993	Inter-tidal	58.5	<1	<0.2	<0.2	<0.2	<0.5	<0.5	<0.5	<0.5	n.d.
HI11	1991	Inter-tidal	58.7	-	-	-	-	-	-	-	-	-
HI12	1993	Inter-tidal	58.7	84	5.5	5.7	9	10.4	1.5	1	<0.5	33.1
HI13	1991	Inter-tidal	61.1	-	-	-	-	-	-	-	-	-

Table A.8. PCB Analyses for the Humber Estuary. Distance from Trent Falls (km).

Station Number	Year Sampled	Sample	Distance (km)	Total C (mg g^{-1})	Org C (mg g^{-1})	Lipid Cont. (mg g^{-1})	SSA (m^2 g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})	Al (mg g^{-1})	Ca (mg g^{-1})
HS1	1993	Sub-tidal	0.4	40.6	29.6	0.127	-	-	-	-	-
HI1	1993	Inter-tidal	4.5	-	-	1.151	-	-	-	-	-
HI2	1993	Inter-tidal	4.8	-	-	0.902	-	-	-	-	-
HS2	1993	Sub-tidal	4.9	n.d.	n.d.	n.d.	-	-	-	-	-
HI3	1993	Inter-tidal	7.2	-	-	n.d.	-	-	-	-	-
HS3	1993	Sub-tidal	12.1	-	-	n.d.	-	-	-	-	-
HI4	1993	Inter-tidal	13.5	-	-	1.549	-	-	-	-	-
HS4	1993	Sub-tidal	15.1	-	-	0.427	-	-	-	-	-
HI5	1991	Inter-tidal	17.9	-	-	-	22.3	8.5	1	0.41	36.4
HS5	1993	Sub-tidal	17.9	8.6	1.7	n.d.	-	-	-	-	-
HI6	1993	Inter-tidal	22.4	-	-	1.634	-	-	-	-	-
HS6	1993	Sub-tidal	28.2	-	-	0.327	-	-	-	-	-
HI7	1991	Inter-tidal	31.9	-	-	-	8	3.81	0.5	0.16	23.2
HS7	1993	Sub-tidal	33.2	15	5.5	0.39	-	-	-	-	-
HI8	1993	Inter-tidal	36.8	27.1	14.4	1.409	-	-	-	-	-
HS8	1993	Sub-tidal	38.2	8.9	1.9	0.242	-	-	-	-	-
HI9	1991	Inter-tidal	43.3	-	-	-	21.3	8.51	0.82	0.42	40.6
HI10	1993	Inter-tidal	43.3	54.7	46.8	3.28	-	-	-	-	-
HS9	1993	Sub-tidal	49.0	-	-	0.983	-	-	-	-	-
HS10	1993	Sub-tidal	55.2	-	-	0.112	-	-	-	-	-
HS11	1993	Sub-tidal	57.9	29.6	15.9	1.48	-	-	-	-	-
HI14	1993	Inter-tidal	58.5	-	-	0.085	-	-	-	-	-
HI11	1991	Inter-tidal	58.7	-	-	-	18.2	7.28	0.66	0.34	34.2
HI12	1993	Inter-tidal	58.7	-	-	1.765	-	-	-	-	-
HI13	1991	Inter-tidal	61.1	-	-	-	19.9	7.71	0.9	0.36	35.2

Table A.9. Geochemical Sediment Characteristics for the Humber Estuary. Distance from Trent Falls (km)

Station Number	Year Sampled	Sample	Distance (km)	TEQ (pg g^{-1})	PCDD/F (pg g^{-1})	PCDD (pg g^{-1})	PCDF (pg g^{-1})	2378TCDD (pg g^{-1})	TCDD (pg g^{-1})	PeCDD (pg g^{-1})	HxCDD (pg g^{-1})	HpCDD (pg g^{-1})	OCDD (pg g^{-1})	TCDF (pg g^{-1})	PeCDF (pg g^{-1})	HxCDF (pg g^{-1})	HpCDF (pg g^{-1})	OCDF (pg g^{-1})
DI1	1991	Inter-tidal	0.0	15.0	987	597	390	4.0	17	40	45	75	420	75	45	60	100	110
DI2	1991	Inter-tidal	13.0	10.0	870	530	340	2.0	20	30	40	70	370	60	40	50	90	100
DS1	1991	Sub-tidal	15.0	19.0	1540	900	640	3.0	20	50	80	250	500	60	100	130	150	200
DI3	1991	Inter-tidal	17.0	23.0	1630	1010	620	3.0	30	60	80	160	680	120	80	90	140	190
DS2	1991	Sub-tidal	24.0	22.0	2472	1792	680	4.0	27	50	75	140	1500	75	85	130	140	250
DS4	1991	Sub-tidal	31.0	18.0	1640	980	660	2.0	25	55	85	175	640	75	90	125	160	210
DI4	1991	Inter-tidal	32.0	22.0	2590	1880	710	4.0	30	60	80	230	1480	90	90	120	180	230
DS3	1991	Sub-tidal	35.0	21.0	979	605	374	4.0	20	40	5	100	440	90	60	4	100	120
DS5	1991	Sub-tidal	37.0	15.0	1140	750	390	3.0	20	50	60	120	500	60	40	70	110	110

Table A.10. PCDD and PCDF Analyses for the Dee Estuary. Distance from Chester weir (km)

Station Number	Year Sampled	Sample	Distance (km)	Total PCB ng g^{-1}
DI1	1991	Inter-tidal	0.0	11
DI2	1991	Inter-tidal	13.0	13
DS1	1991	Sub-tidal	15.0	<1
DI3	1991	Inter-tidal	17.0	2
DS2	1991	Sub-tidal	24.0	2
DS4	1991	Sub-tidal	31.0	3
DI4	1991	Inter-tidal	32.0	<1
DS3	1991	Sub-tidal	35.0	20
DS5	1991	Sub-tidal	37.0	15

*Table A.11. PCB Analyses for the Dee Estuary.
Distance from Chester weir (km).*

Station Number	Year Sampled	Sample	Distance (km)	Lipid Cont. (mg g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})	Al (mg g^{-1})	Ca (mg g^{-1})
DI1	1991	Inter-tidal	0.0	0.42	0.73	0.14	0.45	5.7
DI2	1991	Inter-tidal	13.0	0.44	1.60	0.49	0.27	34.5
DS1	1991	Sub-tidal	15.0	n.d.	0.49	0.10	0.09	17.0
DI3	1991	Inter-tidal	17.0	n.d.	2.68	1.10	0.53	42.8
DS2	1991	Sub-tidal	24.0	n.d.	0.29	0.09	0.04	16.2
DS4	1991	Sub-tidal	31.0	n.d.	0.35	0.10	0.07	14.1
DI4	1991	Inter-tidal	32.0	2.61	5.35	1.06	0.71	37.7
DS3	1991	Sub-tidal	35.0	4.4	4.06	0.47	0.42	34.6
DS5	1991	Sub-tidal	37.0	-	1.86	0.57	0.29	37.3

Table A.12. Geochemical Sediment Characteristics for the Dee Estuary. Distance from Chester weir (km).

Appendix III
Published Work

DIOXIN '92

12th International Symposium on Dioxins and Related Compounds

24 - 28 August 1992
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Organohalogen compounds, Volume 9

SOURCES OF EXPOSURE

Finnish Institute of Occupational Health
Helsinki 1992

Dioxins in UK Estuaries

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Introduction

Estuaries receive waste from a number of diffuse and direct sources including outfalls, dump sites[1], landfill sites[2], and by atmospheric deposition[3]. The hydrodynamics of estuaries and coastal waters ensure that hydrophobic pollutants are widely distributed. Waters around the United Kingdom are significantly polluted with hydrophobic organic pollutants and it is suggested that such contamination may be adversely affecting marine life.

The problems associated with the analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs) at the trace concentrations found in environmental samples have resulted in little comprehensive research on the behaviour of PCDDs and PCDFs in estuaries and coastal waters. Quantitative information on partitioning behaviour and sorption reaction kinetics is not yet available; much of which is required as a precursor to modelling PCDD/PCDF transport and fate in complex marine systems.

Approach and Methodology

The first objective of the current three year study has been to establish a primary database of estuarine data for general reference and calibration of future model developments. Such datasets are currently not available for UK estuarine and coastal waters. Over a period of 1 year, sediments samples have been taken using grab and core samplers from a number of key coastal locations around the UK including the Mersey, Tees, Tyne, Tweed, core samples from the Irish Sea and axial surveys of the Dee, Clyde and Humber.

Sample analysis has been carried out using methods adapted from analysis of soil samples. Samples were solvent extracted and the extractant concentrated. Liquid chromatography was then used to elute the extractant and the PCDD/PCDF collected, concentrated to a suitable volume. The PCDD/PCDF analysis was carried out by passing the sample through a gas chromatogram directly interfaced to a high resolution mass spectrometer (VG 70S) operating in the selected ion monitoring mode (SIM). Homolog groups and specific congeners were identified and quantified by reference to ^{13}C PCDD/PCDF IQSs.[4]

To supplement the PCDD/PCDF data, all samples were analysed for particulate CHN using a combustiometric technique, lipid content using the Dole & Meinhurtz solvent extraction method and specific surface areas (SSA) established using BET N_2 adsorption[5].

Results and Discussion

Homolog	Sediment Samples PCDD/DF (ppt dry weight)							
	Clyde Estuary Stations (Distance from Glasgow, km)					Morcambe Bay (Core Sample)		
	1 (3km)	2 (4km)	3 (5km)	4 (10km)	5 (22km)	0 cm	14cm	28cm
2,3,7,8 TCDD	16	7	19	9	1.5	6	0.3	0.3
TCDD	86	40	110	75	17	6	3	2.5
PeCDD	180	87	120	104	47	<0.6	<5.0	<3.0
HxCDD	100	85	100	73	34	10	<5.0	<5.0
HpCDD	800	405	550	528	79	40	18	10
OCDD	3500	1855	2180	1990	108	150	50	35
2,3,7,8 TCDF	28	17	20	17	3.5	2	3.0	0.5
TCDF	210	106	230	96	15.9	21	15	8
PeCDF	170	135	240	100	14.5	16	6	<3.0
HxCDF	320	310	420	210	28	35	<5.0	<5.0
HpCDF	350	260	460	350	35	22	10	9.0
OCDF	270	135	190	140	5.9	22	15	13
Total PCDD	4666	2472	3060	2770	285	206.6	81	55.5
Total PCDF	1320	946	1540	896	99.3	116	51	38
Nato/CCMS Equivalent	57	36	60	37.6	7.6	3.7	1.7	1.2

Table 1. PCDD/PCDF Concentrations in Morcambe Bay and Clyde Estuary Sediments.

Table 1 summarises results from analyses carried out on core samples from Morcambe Bay and the axial survey of the Clyde. The samples from Morcambe Bay are representative of a UK coastal shelf sea environment receiving waste from a number of industrialised estuaries (Clyde, Mersey, Dee, Severn). The Clyde is an industrialised estuary with direct pollutant inputs from the City of Glasgow via industrial/domestic sewage outfalls.

Due to their ubiquity in the marine environment, it is difficult to determine 'background' concentrations of PCDD/DF in the marine environment. Turkstra and Pols (1989) regarded total PCDD/PCDF sediment concentrations of between 10 and 100 ppt as background levels in their study of the Noordzeekanaal in the Netherlands. Norwood et al (1989) in a study of Narragansett Bay obtained a value of < 0.93 ppt 2,3,7,8 TCDD at their "relatively clean reference site". Set against these assessments, the levels of PCDDs and PCDFs found in Clyde sediments may be regarded as elevated and those in Morcambe Bay as background. PCDDs and PCDFs were, however, concentrated in the surface sediments in Morcambe Bay whereas PCB concentrations increased with depth.

The source of PCDD/PCDFs to the Clyde estuary is not clear. Sample homolog profiles from local incineration sources and direct sewage inputs may help in the future to elucidate the source. From the axial distribution of PCDDs and PCDFs (discussed below) however, it would seem likely that a direct source(s) to the estuary is present.

Due to their hydrophobicity, the transport and axial distribution of PCDDs and PCDFs in estuaries is dominated by the physicochemical characteristics and transport mechanisms of estuarine sediments. Generally, organic micropollutants are expected to favour fine sediments with high surface areas, high organic carbon content and high lipid content. Clyde sediments in the lower estuary tend to be of marine origin with high grain size and low organic content compared with the upper estuary's finer, organic rich sediments. An expected general decrease in total PCDD and PCDF concentration was therefore observed down the estuary.

An initial examination concludes that the dispersive hydrodynamics of the estuary and the effectiveness of an estuary as a filter for fine grained sediments received from it's tributary rivers, is probably responsible for the observed dilution. In this case however, the homolog profiles have been examined more closely to see the way in which individual chlorohomolog groups, with their varying toxic significance, are affected by estuarine transport.

Homolog	Clyde Estuary Stations				
	1 (3km)	2 (4km)	3 (5 km)	4 (10 km)	5 (22km)
TCDD	1.8	1.6	3.6	2.7	6.0
PeCDD	3.9	3.5	3.9	3.7	16.5
HxCDD	2.1	3.5	3.3	2.6	12.0
HpCDD	17.2	16.4	18.0	19.2	27.7
OCDD	75.0	75.0	71.2	71.8	37.8
TCDF	15.9	11.2	14.9	10.7	16.0
PeCDF	12.9	14.3	15.6	11.2	14.6
HxCDF	24.2	32.6	27.3	23.4	28.2
HpCDF	26.5	27.5	29.9	39.1	35.2
OCDF	20.4	14.3	12.3	15.6	5.9

Table 2. Homolog concentrations as a percentage of total PCDD/PCDF

Table 2 shows individual homolog concentrations as a percentage of the total PCDD/PCDF concentration. In the upper estuary (sites 1,2), octachlorinated congeners dominate the dibenzodioxin pattern. Downstream at sites 3 and 4, a reduction in relative OCDD concentration is noted, compensated by an relative increase in HpCDD concentrations. At the outer estuary site 5, a significant decrease in OCDD is compensated by relative increases in all the lower chlorinated homologs. The pattern for PCDF homologs is less clear but a downstream decrease in OCDD concentration relative to the other homologs is also obvious. In the Humber, a similar pattern is observed from sediments taken axially down the estuary with OCDD relative concentrations decreasing from 69.9 % to 50.8 % and TCDD increasing from 0.2 % to 18 %.

Two possible explanations of these observations can be made. Several studies of PCB behaviour indicate that metabolic biodegradation of a PCB can occur[8], a first stage of which is often dechlorination[9]. This would result in a coupled relative increase in lower chlorinated congeners and decrease in lower chlorinated congeners as a function of the pollutant's residence time in the estuary. Bearing in mind the widely reported persistence of PCDDs and PCDFs[10], the extent of the apparent 'dechlorination' may be unlikely.

An alternative explanation is based on the observed dependence of geochemical behaviour on the basic physicochemical properties of the compound and in particular the octanol-water partition coefficient[11] (often used to express the hydrophobicity of the compound). Variations in the partitioning behaviour of individual congeners on the basis of their chlorinity would infer differential transport within the estuary system resulting in changes in the relative homolog concentrations as observed in Clyde and Humber sediments.

Initial studies of PCDD and PCDF contamination in UK estuaries have therefore concluded that PCDD and PCDF transport and distribution is significantly affected by the hydrodynamics of the estuary and the physicochemical characteristics of sediment within the estuary. Axial variations in the relative concentrations of individual chlorohomologs suggests that dechlorination or differential geochemical transport may be important mechanisms in the behaviour of PCDDs and PCDFs in estuarine environments.

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DIOXIN '93

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Source and Fate of Polychlorinated Dibenzo-p-dioxins, Polychlorinated Dibenzofurans and Polychlorinated Biphenyls in Estuary Systems; A Major UK Estuary Study

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Introduction

The impact of tighter regulation of European water quality is resulting in an increased awareness of the iunfluence of trace organic contaminants in marine ecosystems. In many cases however, limited scientific knowledge of the mechanisms and kinetics dominating contaminant behaviour in estuary systems is hampering model development and the effective implementation of new legislation.

Ongoing research has demonstrated the complexity of chlorinated organic pollutant geochemistry in aquatic environments. The importance of congener specific physicochemical properties is well established[1], but only recently has the geochemistry of the solid phase sorbant been shown to be significant[2]. Strong variations in such controlling variables are commonplace in dynamic estuarine systems.

Approach and Methodology

This paper presents the second report of a current three year research programme studying the transport and fate of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in aquatic systems. In 1991 a pilot survey of the Clyde estuary in Scotland was carried out[3]. This was followed in the summer of 1992, by a major survey where over 40 samples of bed sediment, inter-tidal sediment and suspended particulate matter (SPM) were collected and analysed.

Sediment samples were collected using grab and corer techniques. Bulk water samples were filtered in all-glass apparatus for SPM collection. All samples were analysed for

PCDDs, PCDFs (2,3,7,8-substituted congeners) and PCBs (total and ICES 7 congeners). The analytical methodology, carried out to an established protocol[4], is given in a previous paper[3]. In addition to the organic micropollutant analyses, determinations of carbon content (combustiometric technique), specific surface area (SSA) (BET N_2 adsorption) and lipid content (solvent extraction) were also made.

Results and Discussion

The Clyde estuary is situated on the west coast of Scotland and is an industrialised estuary with direct pollutant inputs from the city of Glasgow via industrial/domestic sewage outfalls and atmospheric deposition from incinerator and other diffuse combustion sources.

In total, 42 km of the estuary was sampled from the weir to the inner firth. Concentrations of total PCDD, PCDF and PCB varied considerably within the estuary. Maximum values for total PCDD and PCDF were 9200 and 2500 ppt respectively compared with 4700 and 1500 ppt in the 1991 survey. Total PCB concentrations varied from 1 to 3000 ppb. Significant changes in other variables were also observed; lipid content ranged from below detection (0.3 mg/g approx) to 13.8 mg/g, SSA varied from < 1 to 12.5 m²/g.

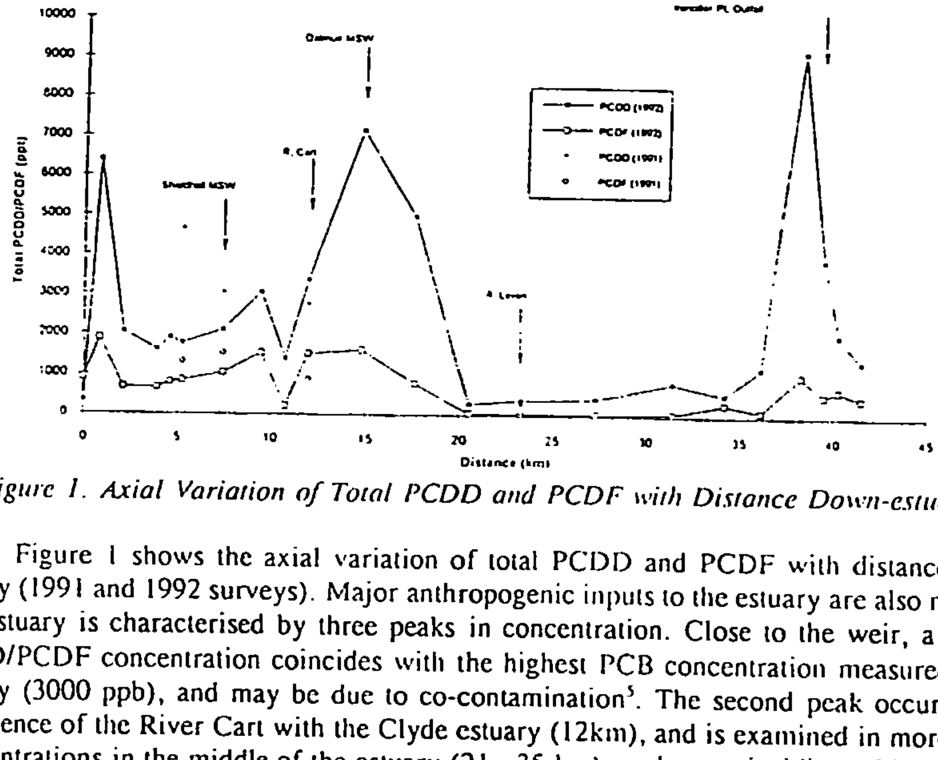

Figure 1. Axial Variation of Total PCDD and PCDF with Distance Down-estuary.

Figure 1 shows the axial variation of total PCDD and PCDF with distance down-estuary (1991 and 1992 surveys). Major anthropogenic inputs to the estuary are also marked. The estuary is characterised by three peaks in concentration. Close to the weir, a peak in PCDD/PCDF concentration coincides with the highest PCB concentration measured in the estuary (3000 ppb), and may be due to co-contamination[5]. The second peak occurs at the confluence of the River Cart with the Clyde estuary (12km), and is examined in more detail. Concentrations in the middle of the estuary (21 - 35 km) are low, coinciding with sediments of low lipid content (< 1.5 mg/g) and SSA (< 2 m²/g). The third PCDD/PCDF peak occurs in the inner firth in the vicinity of a long outfall at Ironotter Point.

Although the 1992 survey generally confirms observations of a systematic variation in PCDD:PCDF ratio in the 1991 survey (approx 2), there is significant change in PCDD:PCDF ratio in the vicinity of the River Cart confluence coinciding with a peak in total PCDD/PCDF concentration. In the upper estuary (0 - 12 km) PCDD:PCDF ratios range from 0.4 to 2.4 (avg. 2.2). In the mid-estuary region (12 - 35 km) PCDD:PCDF ratios vary from 4.4 to 9.7 (avg. 6.3). Samples taken in the River Cart at the interface between the upper and mid estuary regions have PCDD:PCDF ratios of 27.7 and 39.9. Two major factors appear to influence the distribution of PCDD/PCDF within the estuary; solid phase sorbant characteristics and pollutant input sources.

Generally, the estuary may be classified into regions of fine sediment with high surface areas and lipid content favourable for the adsorption of lipophilic contaminants[2] and areas of coarse sediment of marine origin with low lipid content. The upper estuary and inner firth have high SSA and lipid content compared with the middle estuary. Broadly, this pattern is reflected in the PCDD/PCDF distribution.

If the PCDD and PCDF concentrations are normalised for lipid and SSA, the peak concentrations occur in the middle estuary. Assuming that the PCDD and PCDF is bound in the lipid fraction of the sediment, these mid-estuary sediments hold a far greater contaminant load that those of the more lipid rich upper estuary sediments. Dilution effects may in part explain these observations; PCDD/PCDF inputs in the upper estuary bound to lipid-rich sediments are transported down-estuary and diluted by coarser lipid depleted sediments in the mid-estuary region.

The Clyde estuary is subject to a multiplicity of potential sources of PCDD/PCDF/PCB. The estuary is known to receive direct waste input from the iron/steel industry, PCB dump leachate and PCP as well as other diffuse combustion sources. The profile of homolog groups in environmental samples is well established as a signature of PCDD/PCDF source[6].

In this study concentrations of each homolog group, tetra- through octa-, have been normalised against total PCDD and total PCDF to produce homolog profiles. From the distribution of relative homolog concentrations, the upper estuary was identified as a region of significant homolog profile variation. This has been investigated in detail by mapping sample homolog profiles. Results for an up-estuary area (5 - 18 km) are shown in Figure 2.

Homolog profiles at stations 7 and 8, although biased to the octa- homolog show significant concentrations in all other homolog groups similar to that expected in combustion source profiles. The River Cart joins the Clyde estuary 12 km from the weir. Sample I11 in the White Cart Water and I12 in the Black Cart Water have completely different homolog profiles dominated by the octa- homolog group. The White Cart Water receives waste from an outfall known to discharge PCP waste. PCP homolog profiles also exhibit the dominance of the octa- homolog group.

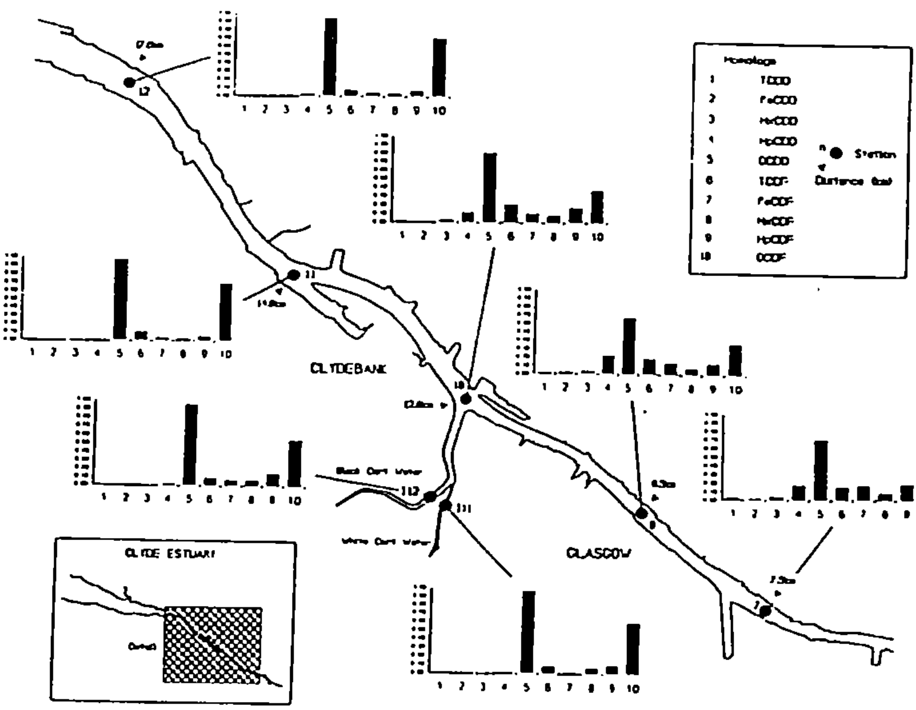

Figure 2. Homolog Profiles for Samples in the Clyde Estuary (5 - 18 km)

Downstream of the River Cart confluence, the homolog pattern in the estuary also changes significantly, showing the same octa- homolog dominance as the River Cart samples. The change in homolog profiles also coincides with a variation in PCDD:PCDF ratio and a peak in PCDD and PCDF concentration. The conclusion from these observations is that the River Cart tributary is making a significant estuary input of PCP derived PCDD/PCDF which dominates the downstream PCDD/PCDF distribution.

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Polychlorinated Dibenzo-para-dioxins and Polychlorinated Dibenzofurans in Sediments from U.K. Estuaries

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Concentrations of polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been determined in sediments from U.K. coastal locations adjacent to the estuaries of the Dee, Humber, Mersey, Tees, Tweed and Tyne and from an offshore site in Morecambe Bay. The sediments had total PCDD/DF concentrations of <100 pg g^{-1}, except for the Dee and Morecambe Bay which had total PCDD (total PCDF) concentrations of 750 (390) and 207 pg g^{-1} (116 pg g^{-1}), respectively. However, estuarine sediments collected during axial transects of Dee, Humber and Clyde Estuaries had total PCDD (total PCDF) concentrations in the range 530–1880 (340–710), 300–1890 (260–1240) and 290–4670 pg g^{-1} (100–1540 pg g^{-1}), respectively. Examination of the homologue groups showed that about 70% of PCDDs were in the octa-chlorinated form in the Dee and Clyde, whereas for PCDFs the hepta- and hexa-chlorinated forms were relatively more important. The association of PCDD/DFs with particle surfaces was interpreted using data on sediment characteristics and a two-stage adsorption model. The conclusions from this study have implications for the estuarine transport of PCDD and PCDF and their uptake by benthic organisms.

Introduction

According to Kjeller *et al.* (1991) the concentrations of polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans (denoted as PCDD/DFs) in soils have been increasing since 1900 because of a growth in atmospheric deposition. These observations support the contention that PCDD/DFs have penetrated many environmental reservoirs, including estuaries (Department of the Environment, 1989). Thus, atmospheric inputs of halogenated hydrocarbons, as the products of incineration and power generation (Brown *et al.*, 1990; Atkinson, 1991), contribute to estuarine contamination. However, influxes also come from sewage disposal (Weerasinghe *et al.*, 1985;

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Hagenmaier *et al.*, 1986) and leachates from landfills and redundant industry (Commoner *et al.*, 1987; Bopp *et al.*, 1991) and potentially from offshore dumping activities (Law *et al.*, 1991).

Studies of the partitioning behaviour of organic micropollutants in the marine environment suggest that the physicochemical properties of suspended particulate matter (SPM) and sediments can determine the fraction in the particulate phase. Studies on PCBs in the Scheldt Estuary show that the sediment PCB concentration is dependent on the organic carbon content, specifically the lipid fraction (Delbeke *et al.*, 1990). Similarly, the concentrations of linear alkyl benzenes (LABs) in River Mersey sediments are linked to the particle properties, although contaminant–grain size relationships were obscured by a stronger correlation between the contaminants and organic carbon content and lipid concentrations (Preston & Raymundo, 1993). Furthermore, laboratory uptake experiments of hydrophobic organic compounds (e.g. anthracene) onto mineral phases doped with various concentrations of humic material showed that the removal of the organics was augmented by higher concentrations of adsorbed humics (Murphy *et al.*, 1990). However, in a study of PCDD/DFs in River Rhine sediments there were no strong statistical correlations between the concentrations of the contaminants and either the <16 µm grain size fraction or the percentage of organic carbon (Evers *et al.*, 1988).

The association of chlorinated organics with particles is also complicated by the fact that they can undergo degradation (Kobayashi & Rittmann, 1982). Halogenated phenols undergo progressive dehalogenation in anoxic marine sediments and at temperatures up to 30 °C (Abrahamsson & Klick, 1991). PCBs have also been observed to undergo dechlorination, which was specific to the chlorination pattern of the congeners (Rhee *et al.*, 1993). This process is clearly important and must be considered, along with the role of grain size and particulate organic matter, in the interpretation of the sedimentary distribution of chlorinated organics.

Despite the toxicological importance of these compounds (Poland & Knutson, 1982) there is no information on their distribution and behaviour in U.K. estuaries and coastal waters, mainly due to the constraints imposed by the complex analytical methodology (HMIP, 1989). Nevertheless, information is vitally needed especially since chlorinated compounds may be implicated in adverse affects on marine life (Reijnders, 1986). In this paper we report, for the first time, determinations of the concentrations of PCDD/DFs in sediments from U.K. estuaries. Particular attention was given to the Dee, Humber and Clyde Estuaries, each of which have a contrasting geochemistry. This study provides an essential database for the development of conceptual models for the transport and fate of PCDD/DFs in estuaries and coastal waters.

Methods

Sample collection

Sediments were collected using grab and core samplers from strategic coastal locations around the U.K. (see Figure 1), including estuarine plume regions of the Mersey, Tees, Tyne and Tweed, core samples from the Irish Sea, and during axial estuarine surveys of the Dee, Humber and Clyde. Sediment samples were coned and quartered, to obtain representative aliquots, and then stored in hexane-washed glass containers at − 20 °C.

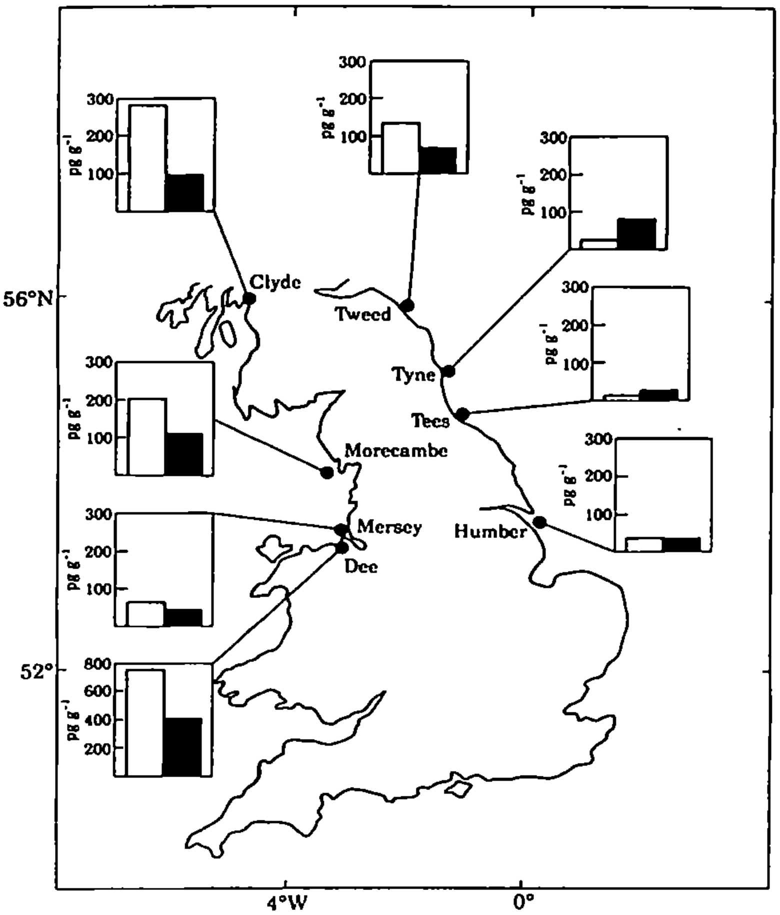

Figure 1. Location of sampling sites and total PCDDs (□) and PCDFs (■) in coastal surface sediments.

Analysis of PCDDs and PCDFs

PCDD and PCDF analyses were carried out by an established GC-MS method (Pettit *et al.*, 1990). This laboratory has participated in the development of acceptance criteria for analytical data and during this study it has applied the agreed quality controls for analyses of PCDD/DFs (Ambidge *et al.*, 1990). Prior to analysis, samples were sieved through a 1 mm mesh and oven-dried at 40 °C. The dried sample was weighed (about 50 g), spiked with sixteen ^{13}C dioxin and furan internal standards, and soxhlet extracted with toluene (Mallinckrodt-Nanograde) for 12 h. The resultant extract was reduced to a volume of about 0·5 ml by freeze-drying, prior to liquid chromatography.

The solvent extracts were subjected to liquid chromatography on a two-stage silica (Merck, 70–230 mesh)/florisil (BDH, 60–100 mesh) column. The sample was eluted initially with hexane (Mallinckrodt-Nanograde) whereby the total PCB fraction was eluted through the entire column and the PCDD/DFs transferred to the top of the florisil column. The upper silica column was discarded and 2% methylene chloride (Mallinckrodt-Nanograde) in hexane was passed through the lower florisil column prior to eluting the PCDD/DF fraction with 100% methylene chloride. The collected

PCDD/DF fraction was reduced to a suitable volume by freeze-drying, solvent exchanged with nonane (Mallinckrodt-Nanograde), and transferred to septum cap vials for autosampler chromatographic injection.

For the analysis of dioxins and furans, the sample was injected onto a 60 m × 0·25 id. DB5 column at an initial temperature of 130 °C, held for 2 min, then programmed to 270 °C at 20 °C min^{-1}, held at 270 °C for 10 min, then programmed to a final temperature of 286 °C at 1 °C min^{-1}. It was directly interfaced to a VG 70S magnetic sector mass spectrometer operating at 28 eV, 10 000 × resolving power in the selected ion monitoring mode. The instrument monitored three of the most intense molecular isotope peaks for each of the dioxins and furans. To optimize sensitivity, the homologue groups (tetra- through octa-CDD/DFs) were monitored in turn, with due regard for their known chromatographic retention times. Confirmation of the presence of each compound was made by reference to the EPA Draft Proposals QAL 152 1/1/87, resting on a correlation of retention times (± 3 s), and the verification that the relative intensity of the isotope peaks is within ± 15% of the theoretical value. In addition, the ion responses for the three ions must maximize within ± 1 scan, with a signal to noise ratio of 2·5. This protocol gives routine detection limits down to 1 pg l^{-1} of PCDD and PCDF injected. Prior to any analysis, a standard mixture of dioxins was analysed, and the instrument was tested for the above criteria, and the calibration verified. The analysis was then performed including blank runs to accommodate for any carry over through use of an autosampler on the GC-MS instrument. Recoveries of the ^{13}C spikes were in the range 75–80%, the reproducibility was ± 10% and the blanks were dependent on the degree of chlorination but were <10 pg g^{-1} (assuming a 50 g sample).

Determination of other sedimentary variables

Freeze-dried aliquots of the samples were analysed for total particulate carbon using a Carlo-Erba 1108 elemental analyser and specific surface area (SSA) using BET N_2 adsorption (Millward *et al.*, 1990). Apolar lipid content was determined gravimetrically following solvent extraction (Delbeke *et al.*, 1990). Concentrations of particulate calcium and iron were determined by conventional flame AAS following extraction by 0·05 M hydroxylamine hydrochloride in 25% v/v acetic acid.

Results and discussion

Distribution of total PCDD/DFs in coastal sediments

Figure 1 shows the locations of the sediment samples from the mouths of estuaries, together with histograms of total PCDD/DF concentrations (dry weight of the <1 mm grain size fraction). Table 1 gives the concentrations of 2, 3, 7, 8-TCDD/DF congeners in these sediments and the concentrations of each homologue group tetra- through octa-CDD/DF. Currently, it is not possible to ascertain whether a sample contains elevated PCDDs and/or PCDFs because it has been suggested that background concentrations of halogenated organic compounds should be taken as zero until their natural production has been proved (Laane, 1992). However, Turkstra and Pols (1989) regarded total PCDD/DF sediment concentrations of between 10 and 100 pg g^{-1} as ' background ' in their study of the Noordzeekanaal in The Netherlands. Norwood *et al.* (1989) in a study of Narragansett Bay obtained values of <0·93 and 15 pg g^{-1} for 2, 3, 7, 8-TCDD and TCDF, respectively, at their ' relatively clean reference site '.

Although the Tyne, Mersey, Tees, Humber, Dee and Clyde (n.b. the Clyde sample is located in the inner estuary) are estuaries receiving pollutant inputs from large

TABLE 1. PCDD and PCDF concentrations (pg g^{-1}) in U.K. coastal surface sediments

Congener/ homologue	Tyne	Mersey	Tees	Humber	Tweed	Morecambe Bay (offshore)	Clyde (lower estuary)	Dee (lower estuary)
2, 3, 7, 8-TCDD	ND	0·3	ND	ND	1	6	2	3
TCDD	1	3	1	2	4	6	17	20
PeCDD	<1	<9	<1	<13	<12	<0·6	47	50
HxCDD	3	<7	3	4	11	10	34	60
HpCDD	3	9	2	5	24	40	79	120
OCDD	13	36	3	10	89	150	110	500
2, 3, 7, 8-TCDF	1	2	ND	2	2	2	4	10
TCDF	4	11	2	9	16	21	16	60
PeCDF	3	4	2	5	10	16	15	40
HxCDF	6	9	3	7	15	35	28	70
HpCDF	9	8	14	6	13	22	35	110
OCDF	59	13	3	6	16	22	6	110
Total PCDD	21	65	10	35	140	207	287	750
Total PCDF	81	46	23	32	69	116	100	390
Nato/CCMS equivalent	1·46	1·56	0·58	1·69	2·83	3·7	7·6	15

ND, Not detectable.

TABLE 2. PCDD/DF concentrations (pg g^{-1}) in a sediment core from Morecambe Bay in the Irish Sea

Homologue group	Core profile		
	Surface (0 cm)	Middle (14 cm)	Bottom (28 cm)
TCDD	6	3	3
PeCDD	<0·6	<5	<3
HxCDD	10	<5	<5
HpCDD	40	18	10
OCDD	150	50	35
TCDF	21	15	8
PeCDF	16	6	<3
HxCDF	35	<5	<5
HpCDF	22	10	9
OCDF	22	15	13

conurbations and industrial activity, only the Dee and the Clyde have PCDD/DF concentrations higher than the ' background ' values given above. The Tweed is thought to be non-industrialized but the PCDD/DF concentrations in Table 1 are comparable with the industrialized estuaries. The concentrations of PCDD/DFs in the surface sediment from Morecambe Bay are marginally above the ' background ' values (see Table 2) and the core profile shows evidence of temporal changes in the input of chlorinated hydrocarbons. The concentrations of PCDD/DF are higher in the surface layer than at depth, which could arise either because of the increase in atmospheric deposition of the compounds as suggested by Kjeller *et al.* (1991) or because of increased estuarine inputs or dumping of contaminated material in this region. However, set

Table 3. Geochemical characteristics of sediments in U.K. estuaries. Mean ± SD given for the Dee, Humber and Clyde

Estuary	SSA ($m^2 g^{-1}$)	Carbon (%)	Lipid ($mg g^{-1}$)	Iron ($\mu g g^{-1}$)	Calcium ($\mu g g^{-1}$)	PCDD ($pg g^{-1}$)	PCDF ($pg g^{-1}$)
Dee	4·1 ± 3·6	1·7 ± 1·2	—	1930 ± 1800	26 700 ± 12 560	1017 ± 509	540 ± 148
Humber	18 ± 5·8	4·0 ± 1·0	1·6 ± 0·7	7100 ± 1900	33 540 ± 6000	1098 ± 680	851 ± 408
Clyde	2·2 ± 1·2	4·5 ± 2·9	6·5 ± 5·0	8620 ± 5200	3900 ± 1480	2449 ± 1660	1052 ± 497
Tweed	2·6	1·3	—	1430	18 100	140	69
Tees	<1·0	1·2	—	450	35 500	9	23
Tyne	<1·0	0·7	—	970	14 500	22	81
Mersey	<1·0	0·8	—	710	14 400	81	46

against the ' background ' values suggested by Turkstra and Pols (1989) and Norwood *et al.* (1989), surface sediments from coastal locations around the U.K. show no conclusive evidence of elevated PCDD/DF concentrations.

One reason for the observed differences in sediment PCDD/DF concentrations between the coastal locations could be due to variability in sediment characteristics. Table 3 summarizes geochemical parameters of the coastal and estuarine sediments along with their PCDD/DF concentrations. Sediments at the mouth of the Dee consisted of fine material with a relatively high SSA of 8·5 $m^2 g^{-1}$ and total carbon content of 1·8%. Both these sediment characteristics contribute to the sorption of PCDDs and PCDFs (Evers *et al.*, 1988), which, for the Dee, had total concentrations of 750 and 390 pg g^{-1}, respectively. Similarly, the sediment at the mouth of the Humber had an SSA of 7·9 $m^2 g^{-1}$, mainly caused by the influence of iron precipitates, and a total carbon content of 2·4%, together with total PCDD/DF concentrations of 295 and 264 pg g^{-1}, respectively. On the other hand, sediments from the Tees, Tyne and Mersey had PCDD/DF concentrations of <100 pg g^{-1}, possibly because the sediments consisted of coarser material of marine origin, as evidenced by high calcium contents, SSAs of <1 $m^2 g^{-1}$ and lower total carbon concentrations.

The relatively low concentrations of PCDD/DFs determined in sediments at the estuary mouths could be a result of long residence times for sediments within estuarine systems. Recycling of sediment within an estuary ensures retention; for example, a sediment residence time of 20 years has been estimated for the Humber Estuary (Turner *et al.*, 1991). It may be concluded, therefore, that estuaries are important reservoirs for PCDD/DFs released into the aquatic environment via rivers, industrial discharge and dumping. Particle-bound PCDD/DFs may be slowly fluxing into adjacent shelf seas but continual dilution by marine sediments is sufficient to prevent elevated PCDD/DF concentrations being detected, except in localized coastal areas where fine, organic-rich materials of fluvial origin are depositing.

Inter-estuarine comparison: Dee, Humber and Clyde Estuaries

Axial concentrations of total PCDD/DFs. Table 4 summarizes the results from analysis of surface sediments collected along the axes of the Dee, Humber and Clyde Estuaries. Within each estuary, the concentrations of total PCDD/DFs are substantially above those obtained at the estuary mouths and those previously described as ' background ' values. Figure 2 shows axial concentrations of total PCDD/DFs determined in sediments

Table 4. PCDD/DF concentrations (pg g^{-1}) in Dee, Humber and Clyde Estuary sediments

Congener/ homologue group	Dee Estuary (distance below weir in km)									Humber Estuary (distance below bridge in km)					Clyde Estuary (distance below Glasgow in km)				
	0	13	15	17	24	31	32	35	37	0	14	24	37	43	3	4	5	10	22
2, 3, 7, 8-TCDD	4	2	3	3	4	4	4	2	3	20	<1	15	10	5	16	19	7	9	2
TCDD	17	20	20	30	27	20	30	25	20	45	5	150	220	53	90	110	40	75	17
PeCDD	40	30	50	60	50	40	60	55	50	180	170	49	210	40	180	120	87	104	47
HxCDD	45	40	80	80	75	50	80	85	60	120	100	52	83	21	100	100	85	73	34
HpCDD	75	70	250	160	200	100	230	175	120	170	290	80	150	31	800	550	410	528	79
OCDD	420	370	500	680	1500	440	1480	640	500	860	1320	150	790	150	3500	2180	1860	1990	110
2, 3, 7, 8-TCDF	20	10	10	30	15	20	20	15	10	27	29	11	25	5	28	20	17	17	4
TCDF	75	60	60	120	75	90	90	75	60	300	310	160	280	66	210	230	110	96	16
PeCDF	45	40	100	80	85	60	90	90	40	150	160	81	170	32	170	240	140	100	15
HxCDF	60	50	130	90	130	60	120	125	70	110	130	86	170	32	320	420	310	210	28
HpCDF	100	90	150	140	140	100	180	160	110	190	150	68	200	39	350	460	260	350	35
OCDF	110	100	200	190	250	120	230	210	110	200	430	230	420	96	270	190	140	140	6
Total PCDD	597	530	900	1010	1852	650	1880	980	750	1375	1885	481	1453	295	4670	3060	2482	2770	287
Total PCDF	390	340	640	620	680	430	710	660	390	950	1180	625	1240	264	1320	1540	960	896	100
Nato/CCMS equivalent	15	10	19	23	22	21	22	18	15	39	24	24	31	9	57	60	36	38	8

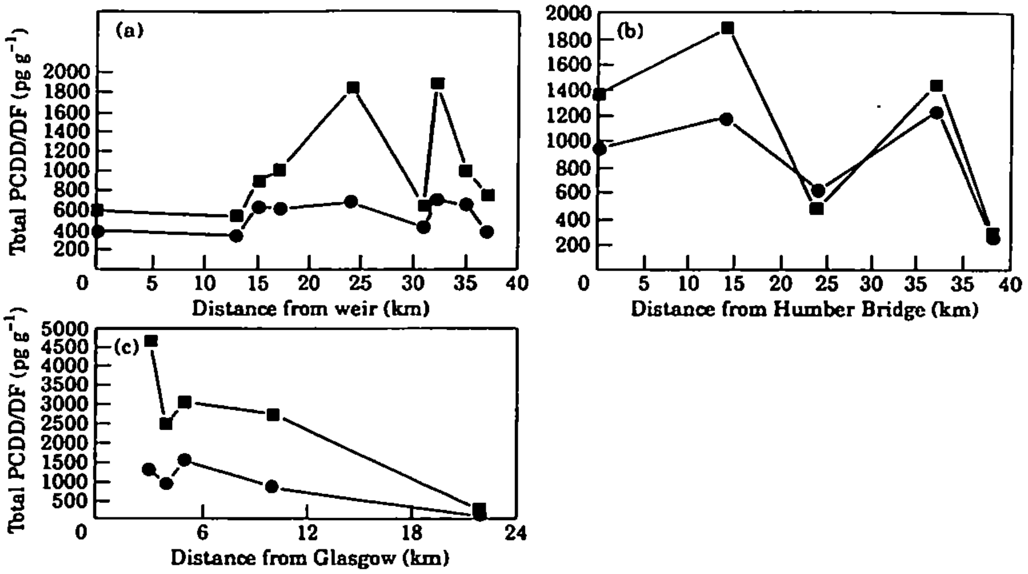

Figure 2. Axial variation in total PCDDs (■—■) and PCDFs (●—●) in the (a) Dee Estuary, (b) Humber Estuary and (c) Clyde Estuary.

of the Dee, Humber and Clyde Estuaries. Overall, the concentrations of total PCDD/DFs in the Clyde are about double those for the Dee and Humber. Although a down-estuary decrease in the concentration of total PCDD/DFs is observed for the Clyde and Humber, there are differences in the trends of PCDD/DFs between the two estuaries. In the Humber, sediments have a mean PCDD:PCDF ratio of 1·2, with approximately equal total PCDD/DF concentrations in the lower estuary whereas in the Clyde there is considerably more total PCDD than total PCDF throughout the estuary, with a mean PCDD:PCDF ratio of 2·8. The pattern in the Dee Estuary is more complex and mid-estuarine maxima in total PCDD/DF concentrations were detected and the PCDD:PCDF ratio (mean 1·8) was more variable. The different estuarine PCDD:PCDF ratios could be either source-related or a consequence of biogeochemical processes.

Group homologue profiles. The homologue groups from the axial surveys of the Dee, Humber and Clyde Estuaries have been estimated as a percentage of total PCDD and PCDF, so that the relative contribution of each homologue group can be examined independent of the local PCDD/DF concentration. The results are plotted against distance down-estuary for the Dee [Figure 3(a,b)] and the Clyde [Figure 3(c,d)]. In the Dee Estuary the PCDDs show little down-estuary variation, with the octa-CDD (OCDD) homologues being about 70% of the total, hepta-CDD (HpCCD) about 15% and the tetra-, penta- and hexa-CDDs (TCDD, PeCDD and HxCDD) each contributing <10%. For the PCDFs, OCDF represents about 30% of the total, followed by a 25% contribution from HpCDF and TCDF, and PeCDF and HxCDF contributing 15–20% each. All, however, are constant with distance down-estuary. This indicates that in the Dee a uniform trend of PCDD/DF homologue groups is maintained throughout the estuary regardless of their concentration and sediment type.

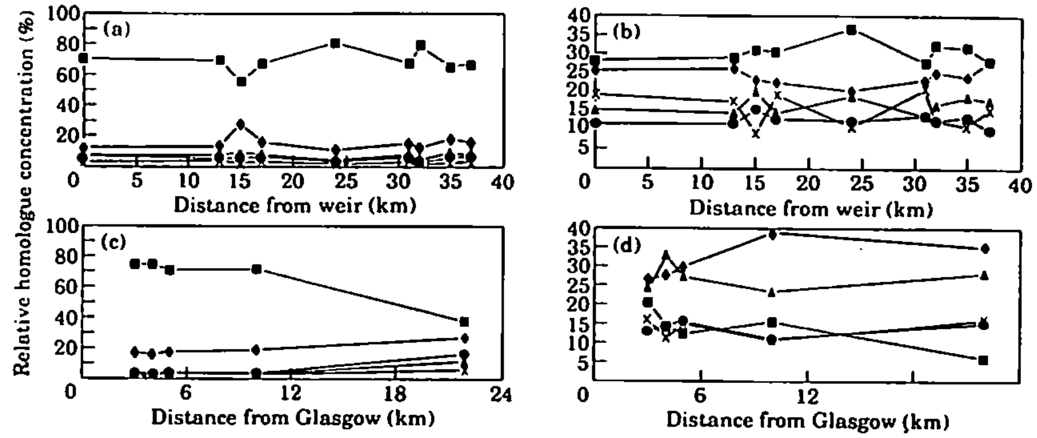

Figure 3. Axial distribution of percentage of homologue groups: (a) PCDDs in the Dee Estuary, (b) PCDFs in the Dee Estuary, (c) PCDDs in the Clyde Estuary and (d) PCDFs in the Clyde Estuary. In (a) and (c): (×—×) TCDD; (●—●) PeCDD; (▲—▲) HxCDD; (◆—◆) HpCDD; (■—■) OCDD. In (b) and (d): (×—×) TCDF; (●—●) PeCDF; (▲—▲) HxCDF; (◆—◆) HpCDF; (■—■) OCDF.

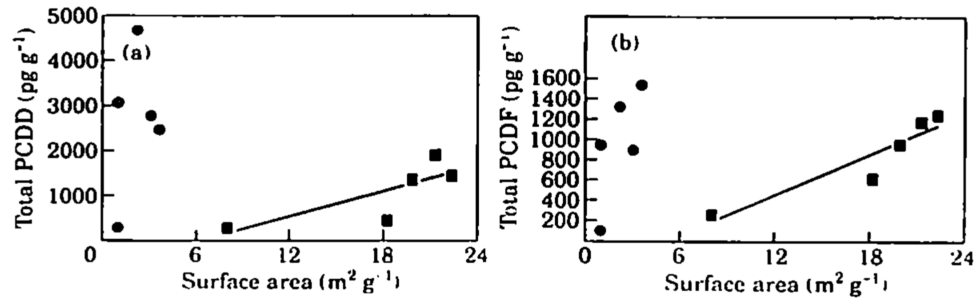

Figure 4. Relationship between specific surface area and PCDD/DFs: (a) PCDDs in the Clyde Estuary (●) and the Humber Estuary (■); (b) PCDFs in the Clyde Estuary (●) and the Humber Estuary (■).

In the Clyde Estuary [Figure 3(c,d)] the OCDD homologue group dominates throughout the estuary, being in excess of 70% in the upper 12 km. At 22 km the relative amount of the OCDD homologue group decreases to 40% but is compensated for by increases in the lower chlorinated homologues, which are thought to be more toxic. For the furans, HpCDF (about 30%) is the most prevalent homologue group, followed by HxCDF at 25% and then OCDF whose contribution decreases from about 20 to 5% in the down-estuary direction. On one hand, this analysis confirms the fact that the higher chlorinated species are the most particle-reactive (Ernst *et al.*, 1988; Lodge & Cook, 1989). However, exceptions occur in the Clyde, such as the decrease in the proportion of OCDD and the lack of a systematic trend in the proportions of PCDF homologues. Possible reasons for these observations follow. (1) The PCDD/DF homologue groups could originate from local man-made sources, which need to be identified and linked to the sediment composition using source–occurrence matching (Swerev & Ballschmiter, 1989). (2) The biodegradation of specific homologues could be occurring. Studies of PCB behaviour indicate that metabolic biodegradation can occur (Goerke & Ernst,

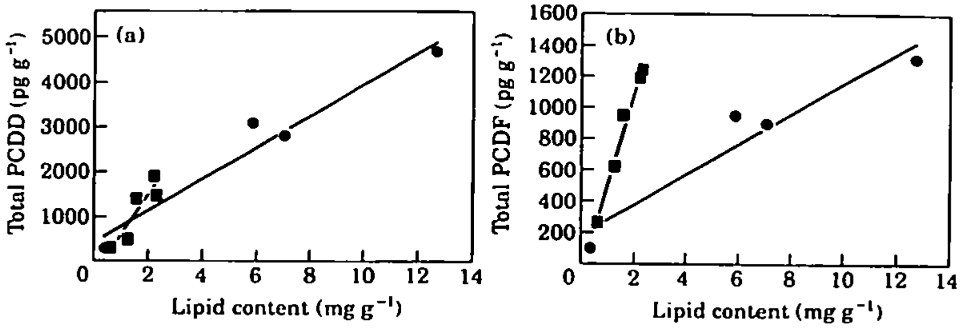

Figure 5. Relationship between lipid content and PCDD/DFs: (a) PCDDs in the Clyde Estuary (●) and the Humber Estuary (■); (b) PCDFs in the Clyde Estuary (●) and Humber Estuary (■).

1986; Rhee *et al.*, 1993), an initial stage of which is dechlorination (Kobayashi & Rittman, 1982). The loss of chlorine atoms by higher chlorinated congeners, during a long particle residence time in the Clyde Estuary, could enhance the contributions of lower chlorinated homologue groups. Despite the fact that this process has been identified for PCBs, more work is required to confirm the existence of a biologically driven dechlorination mechanism for PCDD/DFs. (3) Differential sorption behaviour is taking place. Each congener possesses a physicochemical character which uniquely defines its hydrophobicity, lipophilicity and sorption behaviour.

The data presented here are not in sufficient detail to unravel the relative importance of each of these processes and further work is required.

Relationships of total PCDD/DFs to sediment characteristics. Attempts have been made to interpret variations in PCDD/DF sediment concentrations in terms of grain size effects and the concentration and type of particulate carbon (Evers *et al.*, 1988; Servos *et al.*, 1989; Broman *et al.*, 1991). In this study, SSA was taken as the measure of grain size and both total carbon and lipid content were determined in selected sediments.

Particles in the Humber Estuary are conditioned by a large anthropogenic source of iron which yields sediments with relatively high SSAs (Turner *et al.*, 1991) because particles become coated with fresh iron precipitates. Although the total carbon content is similar for the Humber and the Clyde, the high calcium concentration of Humber sediments (see Table 3) suggests that much of the carbon is in the form of calcium carbonate. In contrast, the Clyde sediments have much less calcium and a larger fraction of the carbon is as lipids. Given the relatively high concentration of iron in Clyde sediments one might have expected the sediments to have high SSAs. However, the particulate iron is not in a freshly deposited form and sediment-bound organic molecules can depress the SSA by blocking some of the internal pore structure of the particles (Millward *et al.*, 1990).

The relationships between SSA and total PCDD/DF are shown in Figure 4(a,b) for the Clyde and Humber Estuaries. The variables are only weakly correlated, with the Clyde sediments having higher PCDD/DF concentrations per m^2 of particle surface, compared with the Humber. The PCDD/DF concentrations of sediments from the Dee Estuary are not correlated with SSA and the highest pollutant concentrations were identified with sediments of low SSA. However, the association of organic micropollutants with particulate organic carbon is also important (Delbeke *et al.*, 1990; Broman *et al.*, 1991; Tanabe *et al.*, 1991; Preston & Raymundo, 1993) and Figure 5(a,b) shows the relationship between lipid content and total PCDD/DF concentrations in the Clyde and Humber estuaries. Notwithstanding the fact that there are only five data points, correlations between lipid content and the Humber PCDD and PCDF concentrations are $r=0{\cdot}88$ (significant at 95%) and $r=0{\cdot}99$ (significant at 99%), respectively.

Studies of the association of LABs in River Mersey Estuary sediments has led to the suggestion that their particle–water interaction involves two processes (Preston & Raymundo, 1993). The first one entails LAB association with the bulk particle and its internal pores; a reaction which is assumed to occur at or near to the source. The second process occurs away from the source and involves LAB adsorption onto surface sites connected with lipids. This two-stage sorption model could also be valid for PCDD/DFs because of their apparent association with organic phases (Servos *et al.*, 1989). The small number of samples in this work mitigate against providing definitive statistical evidence for this hypothesis. However, the relationship between SSA and total PCDD/DF indicates that the reticules of the sediment particles offer sites whereby the first of the two mechanisms may be satisfied. The stronger relationship between lipid concentration and the total PCDD/DF concentration suggests that the surface adsorption process could be occurring and that surface-bound lipids could scavenge PCDD/DFs from the water column. In order to test this possibility the lipid and PCDD data from the Clyde and Humber were combined and log[PCDD] was regressed against log[lipid] as Preston and Raymundo (1993) have suggested. The regression yields a correlation coefficient of 0·92 for nine samples, which is significant at the 99% level. Furthermore, the slope of the regression line is 0·76, which compares with their values of 0·79 for LABs and 0·66 for the theoretical slope. Although the number of samples here is small there is circumstantial evidence that PCDD/DFs exist on sediment particles at two different locations, viz one located within the particle microstructure and one located on the particle surface.

Conclusions

The results presented here form the first benchmark survey of PCDDs and PCDFs in surface sediments from U.K. estuaries and coastal waters. The survey shows that sediments at the mouths of industrialized estuaries (Humber, Mersey, Tees and Tyne), in Morecambe Bay and a non-industrialized estuary (Tweed) are not significantly contaminated with PCDDs or PCDFs, only the Clyde and the Dee have concentrations above assumed ‘ background ’ values. Inter-site variability of PCDD/DF concentrations could largely be due to differences in sediment characteristics.

Sediment mobility within an estuary is strongly influenced by variability in grain size parameters and the chemical factors governing cohesiveness. Differential transport of PCDD and PCDF homologue groups within an estuary can be anticipated, especially where homologue groups with greater lipophilic tendencies preferentially adsorb onto fine, organic-rich particulate matter. Such particles (which could include biogenic and lithogenic materials) could follow a transport pathway dictated by the interplay between settling and advection. However, cohesive lithogenic particles, once deposited, may remain sedimented for a considerable period. Other less lipophilic homologues, on the other hand, may be bound to particles with physicochemical characteristics favouring different transport pathways. The long retention times for particles in estuaries also suggests that biodegradation of PCDD/DFs is possibly occurring and that dechlorination reactions need further investigation.

The concentrations of PCDD/DF sediments from the inner estuaries of the Dee, Clyde and Humber were much higher than those at their mouths. Sediment characteristics played an important role in determining the concentrations of total PCDD/DF obtained. Although the main influence was the presence of organic carbon in the form of lipids, the specific surface area and microstructure of the particle was also thought to play a role. The interpretation of the limited dataset suggests that the PCDD/DFs may be associated with two different types of adsorption site; those situated on the internal surfaces of the sediment particles and the others situated on the external surfaces. It is important to identify precisely how labile the PCDD/DFs are at these particle locations, because this will influence their ability to repartition between particles should more favourable adsorption sites become available, for example during spring blooms when the organic-rich surfaces of phytoplankton are present. Furthermore, these findings raise a question as to the bioavailability of PCDD/DFs to those filter-feeding organisms using sediments as a source of food—as these organisms digest sediments, are both the surface-bound and matrix-bound fractions of sedimentary PCDD/DFs removed from the particles during the feeding process? Clearly, this question can only be answered when more information is available on the sorption behaviour of these toxins. In order to model the behaviour and transport of PCDD/DF in an estuary, more information is required on the extent of uptake, susceptibility to preferential sorption and possible re-partitioning onto more suitable solid phases, including competition from phytoplankton. Experiments involving ^{14}C-labelled dioxins would seem to have the best potential in revealing their reactivity with sediment particles.

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The Distribution and Chemical Composition of Particles in a Macrotidal Estuary

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Spatial and short-term temporal measurements of hydrographic parameters [salinity and concentration of suspended particulate matter (SPM)] and sediment characteristics (specific surface area, major and trace metals, C and N, ^{137}Cs and ^{241}Am) have been undertaken in a rapidly accreting macrotidal estuary (Dee Estuary, north-east Wales). The composition of the sediment indicates a dominance of marine material in the estuary and that fine SPM is fluvial in origin, admixing in the water column with coarse, tidally suspended bed material. The time-variable composition of SPM in the upper estuary, where tidal energy converges, was tested against a particle mixing model incorporating the compositions of permanently suspended and temporarily suspended populations operationally fractionated according to settling velocities. Agreement with the model was reasonable but suggested additional processes such as selective resuspension and/or advection of particle types. The behaviour and characteristics of different sediment populations are discussed in the context of the cycling and fluxes of particle-bound constituents and sorptive removal of dissolved constituents, and a flux model for the accumulation of ^{137}Cs in the estuary is developed.

Introduction

Although rivers are major contributors of continental sediment to the world ocean it has been shown that estuaries, encompassing the river–ocean interface, often act as net traps for sediment derived from coastal erosion (Kirby, 1987; Mulholland & Olsen, 1992). On a finer scale, estuarine sediment dynamics embrace particle-selective resuspension, mudflat processes, particle interactions such as flocculation, and differential settling and transport of grains. These processes are driven by river flow and tidal energy and are, therefore, spatially and temporally variable, and tend to be accentuated in macrotidal environments (Bale *et al.*, 1985, 1989; van Leussen, 1988; Dyer, 1989; Eisma *et al.*, 1990). From a chemical viewpoint, it is of fundamental importance to understand the nature and

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mobility of estuarine particles in order to accurately determine the land–ocean fluxes of sediment-bound constitients (Buckley & Winters, 1983; Windom *et al.*, 1989; Huang *et al.*, 1992) and quantify the exchange of constituents between solid and solution (Turner *et al.*, 1993; Turner & Millward, 1994).

Studies on estuarine particle dynamics have often involved geochemical tracers, i.e. particle populations are distinguished and/or traced according to characteristics of their geochemical composition. Such tracer characteristics that have been adopted include major element contents normalized with respect to aluminium (Gobeil *et al.*, 1981), carbon isotope ratios (Lucotte, 1989), C:N ratios (Matson & Brinson, 1990) and artificial radionuclides (Brydsten & Jansson, 1989); other potential tracers include lignin (Reeves & Preston, 1991) and stable lead isotope ratios (Kersten *et al.*, 1993). To this end we have conducted a geochemical study of particles [whole sediment; sieved sediment; suspended particulate matter (SPM), and its components as distinguished by settling velocities] from the Dee Estuary, north-east Wales, a macrotidal estuary subject to continual accretion from offshore sediment sources. The main objective was the development of flux models for particles and particle-bound constituents that are generally applicable to energetic, macrotidal environments.

Study site

The Dee Estuary (Figure 1) drains 1816 km^2 of rural north-west England and north-east Wales. The axial distance from the weir (Chester) to the mouth (Liverpool Bay, Irish Sea) is 35 km. Progressive siltation of the estuary led to canalization through saltmarsh in the 18th century and the estuary can now be divided into two distinct zones: for 15 km downestuary of the weir the channel is about 100 m wide and contained between floodbanks, hereafter termed the upper estuary; the remainder of the estuary is approximately 5 km wide and roughly rectangular, hereafter termed the lower estuary. The average freshwater runoff of the Dee is 36·8 m^3 s^{-1}, natural flow variability is regulated according to daily and seasonal abstraction requirements, and the freshwater input to Liverpool Bay is augmented by a further 40 m^3 s^{-1} from the Mersey Estuary (Taylor, 1986). Spring and neap tidal ranges at the mouth are 7·7 and 4·1 m, respectively, and mean spring tidal currents are about 1·5 m s^{-1} (BMT, 1990).

Sampling and methods

Field measurements

Master variable measurements were undertaken in December 1991 at a time of low river discharge (12·9 ± 4·4 m^3 s^{-1} regulated flow for the previous 5 days) both spatially, during two axial transects of the lower estuary from a fishing vessel (flood and ebb tides), and temporally during two tidal cycles (one in the lower estuary from an anchored fishing vessel, and one in the upper estuary from an inflatable craft). Salinity and temperature were determined *in situ* using an MC-5 T-S bridge; at low salinities (<3 psu) 500 ml samples were returned to the laboratory in Plymouth and the salinity was more accurately determined using a WTW conductivity probe calibrated against standard seawater diluted accordingly. The concentration of SPM was determined from the dried mass retained on pre-weighed Whatman GF/C filters (pore size 1·2 μm) after vacuum filtration of up to 1000 ml water.

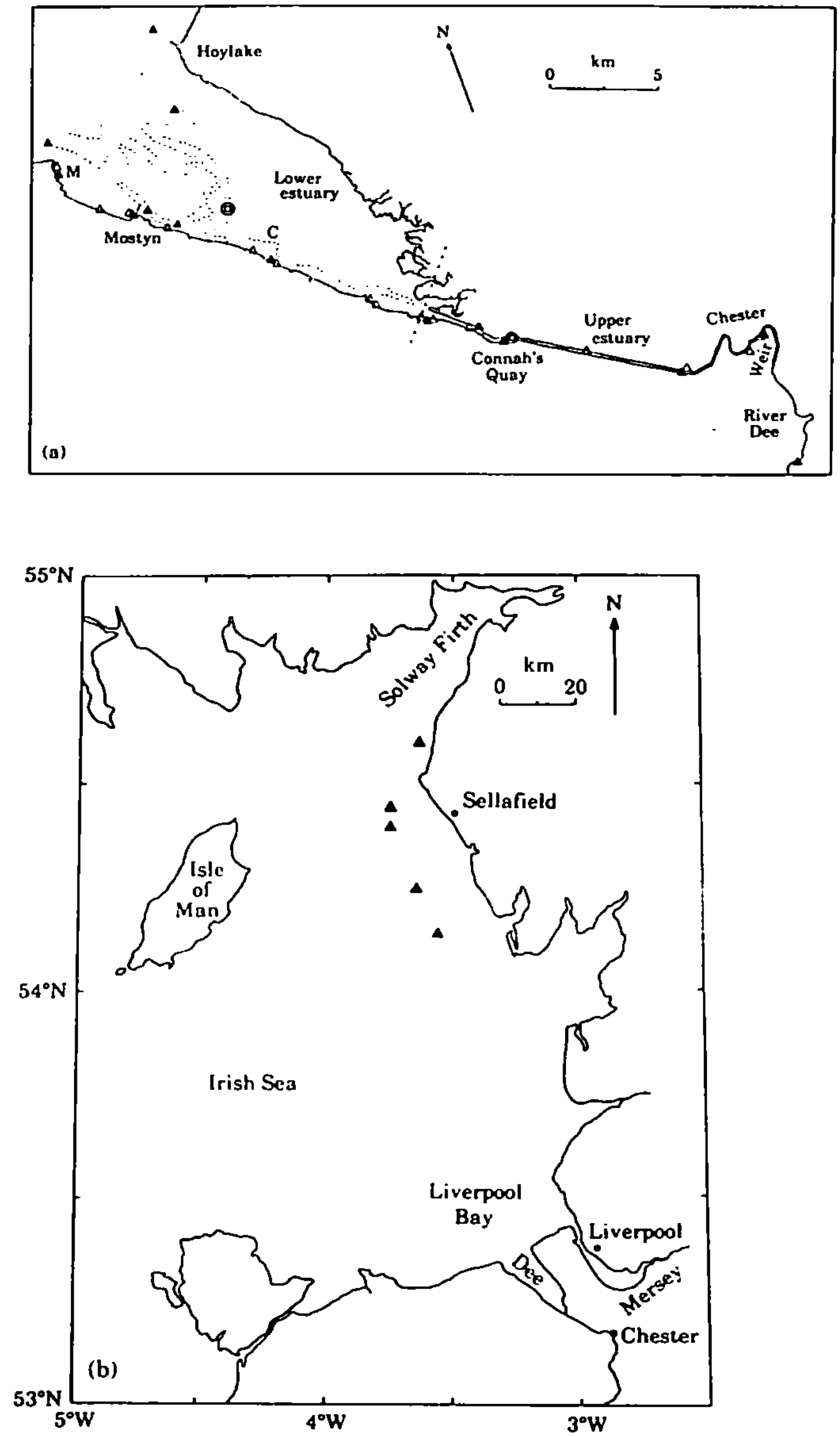

Figure 1. Sampling locations for sediment (▲, whole samples; △, <63 µm samples), SPM (◎, tidal stations) and organisms (C, cockles; M, mussels) in the (a) Dee Estuary and (b) Irish Sea.

Sediment collection

The locations of sediment sampling sites in the Dee Estuary and Irish Sea are shown in Figure 1. Intertidal sediment samples for size fractionation and chemical analyses were collected along the west bank of the estuary during October 1991. Intertidal sediments for whole analysis, and cockles and mussels were taken along the same bank during December 1991; subtidal sediments for whole analysis were collected using a Shipek Grab deployed from the fishing vessel during the axial transects of the lower estuary. For the collection of SPM for chemical characterization, surface samples of about 10 l were taken at the tidal stations in acid-cleaned carboys and filtered through 142 mm diameter Millipore filters (pore size 0·45 μm) in a perspex assemblage under *c.* 2 atm nitrogen pressure. During low slack water at the upper station the bed was agitated using the oar of the inflatable craft and 20 l of the turbidized water was sampled in a carboy for SPM fractionation by settling.

Additional marine sediment samples for whole analysis were taken by Day Grab in the Irish Sea during NERC *Challenger* Cruise 88a (February 1992).

Sediment preparation

Sediment samples for silt fractionation were wet sieved through 63 μm nylon mesh using *c.* 20 ml dispersant (2% w/w sodium hexametaphosphate, BDH AnalaR) and *c.* 500 ml distilled water. A 20 ml aliquot of the sieved suspension was vacuum filtered through a pre-weighed 47 mm diameter Millipore filter (pore size 0·45 μm), rinsed with *c.* 10 ml distilled water and freeze-dried. Sediment samples for whole analysis, after sieving through 1 mm nylon mesh, SPM samples retained on 142 mm filters and the soft tissue of organisms were rinsed with *c.* 10 ml distilled water and freeze-dried.

In the laboratory, the 20 l turbidized sample was shaken thoroughly before being allowed to settle. After 30 min, about 10 l containing fine suspended material was siphoned into a smaller vessel, leaving a residual suspension dominated (w/w) by relatively dense settlable material. This time-scale is considered representative of the time available for grain settling around slack water, and, therefore, yields an operational, yet realistic separation of permanently suspended (PS; settling velocity $<0{\cdot}01$ cm s^{-1}, grain diameter about 5 μm) and temporarily suspended (TS; settling velocity $>0{\cdot}01$ cm s^{-1}) estuarine sediment fractions. About 500 ml from each suspension were vacuum filtered through pre-weighed Millipore filters (0·45 μm pore size) and the residues were washed with distilled water and freeze-dried.

Chemical analysis

The specific surface area (SSA) of freeze-dried sediment and SPM samples was determined by a BET nitrogen gas adsorption technique (Millward *et al.*, 1990); at least 100 mg sample are required for this method which limited the number of SPM analyses. Total contents of C and N were determined using a Carlo-Erba 1108 Elemental Analyser calibrated with sulfanilamide standards.

Available metals, or more specifically metals associated with hydrous Fe and Mn oxide coatings, were operationally determined following extraction from *c.* 50 mg SPM samples and *c.* 250 mg sieved and whole sediment samples by 0·05 M hydroxylamine-hydrochloride in 25% v/v acetic acid (BDH AristaR) for 16 h at room temperature (Turner *et al.*, 1991). A comparison of metals extracted from a variety of estuarine SPM samples by the acetic acid leach and HF (or HNO_3) digestions have shown that the leach removes between *c.* 1·5% (Al) and *c.* 85% (Ca and Mn) of the total metal, and that this fraction for a given metal is relatively invariant (Loring *et al.*, 1983; Turner, 1990; Turner *et al.*, 1992*a*). About 500 mg freeze-dried cockle and mussel tissue were microwave digested in PTFE bombs using 5 ml of a 3:2 mixture of HNO_3 and H_2O_2 (BDH, AristaR). Analysis of Al, Ca, Fe, Mn, Cu, Pb and Zn was performed using an Instrumentation Laboratory 151 atomic absorption spectrophotometer in the flame mode and analysis of Cd and Cr was performed using a Perkin Elmer 4100 ZL Graphite furnace atomic absorption spectrophotometer with Zeeman splitting background correction. The detection limits of these analyses ($\mu g\ ml^{-1}$) were as follows: Al, 0·50; Ca, 0·15; Fe, 0·03; Mn, 0·03; Cd, 0·002; Cr, 0·003; Cu, 0·02; Pb, 0·075; Zn, 0·12; and analysis of five replicates of a sieved sediment sample gave the following relative standard deviations (%): Al, 12·6; Ca, 7·5; Fe, 9·2; Mn, 8·8; Cd, 18·8; Cr, 31·9; Cu, 15·6; Pb, 8·1; Zn, 9·3. The relatively poor reproducibility obtained for Cd, Cr and Cu was due to working close to the detection limits for this sample.

The radionuclides ^{241}Am and ^{137}Cs were determined on freeze-dried sediment and organism samples using a high purity Ge detector encased in a lead chamber. Between 15 and 50 g freeze-dried samples were counted for between 2 and 15 h and the spectra were analysed using a 4K channel Canberra Series 80 multi-channel analyser calibrated against uncontaminated sediments spiked with Amersham International standards.

Results and discussion

Sediment dynamics

Figure 2 shows the spatial and tidal distributions of salinity and SPM concentration. Slight stratification (up to 0·7 psu per m) is evident towards the mouth of the estuary but the water column is well-mixed upstream due to convergence of tidal energy. The tidal wave is essentially symmetrical in the lower estuary but is severely distorted in the upper estuary. SPM concentrations are low compared with other U.K. macrotidal estuaries (Morris *et al.*, 1987; Turner *et al.*, 1991) and there is no evidence of a turbidity maximum. The $<63\ \mu m$ fraction of sediment was $44 \pm 21\%$, although intertidal samples were selected for their muddy quality and a dominance of sandy material was observed throughout the estuary. A summary of all metal and radionuclide concentrations, SSAs and C and N contents is given in Tables 2–4.

As a result of the residual currents in the eastern Irish Sea the Dee receives sediment from offshore and the adjacent north Wales coast (BMT, 1990). The rate of sediment accretion in the Dee is compared with the Mersey and Humber, two other U.K. estuaries experiencing large-scale siltation from offshore sources, in Table 1. Also given is the supply of fluvial material calculated according to an empirically derived prediction equation relating catchment area (x, km^2) to fluvial sediment influx (y, $t\ a^{-1}$) as follows (Wilmot & Collins, 1981):

$$y = 60x^{0\cdot78} \qquad (1)$$

These estimates indicate that fluvial material comprises only a minor fraction (*c.* 0·5%) of the total sediment supply to the Dee Estuary. This is also affirmed from geochemical characterization of the sediment. The Ca content of estuarine sediment is principally of marine origin and this parameter serves as a tracer of marine derived material (Loring *et al.*, 1983; Nolting *et al.*, 1989; Turner *et al.*, 1992*a*). Adopting a Ca:Al ratio as a means of normalizing for grain size and mineralogical effects was found to provide a parameter which more clearly discriminates particle populations (Table 2).

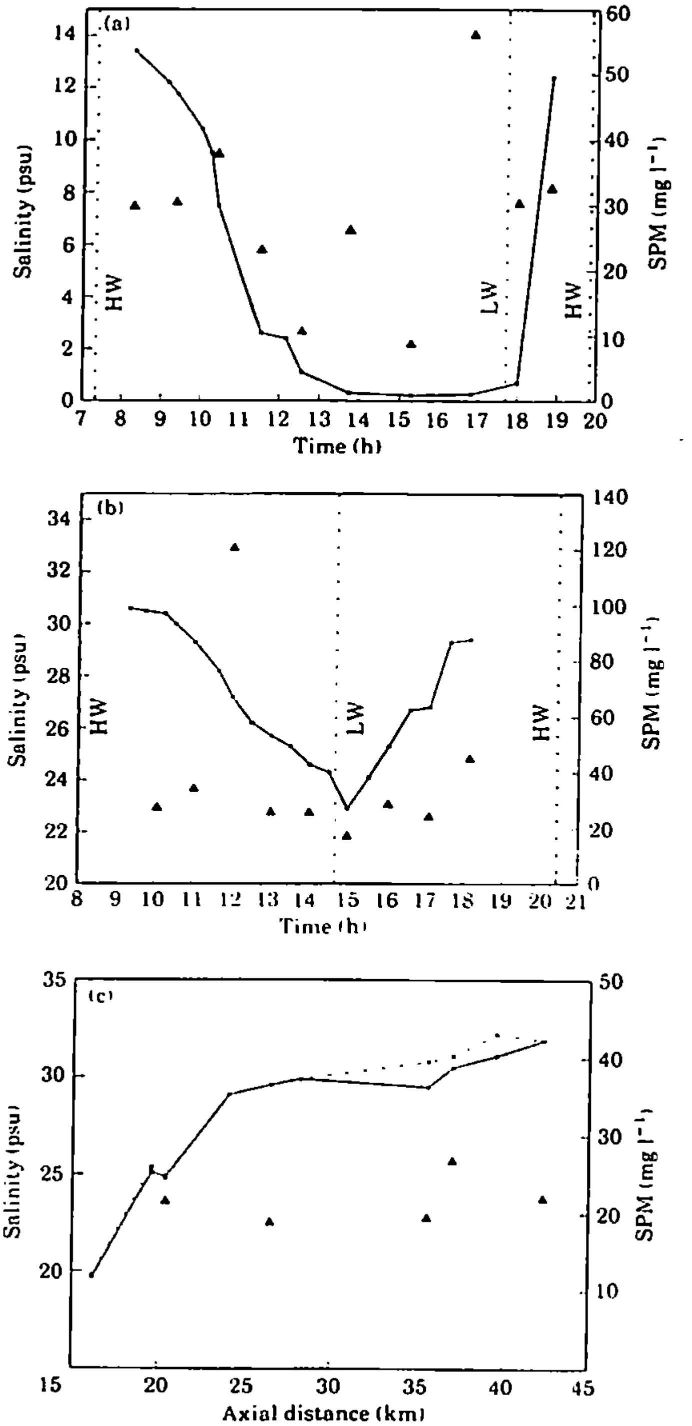

Figure 2. The distributions of salinity near surface (———), near bottom (– – –), and SPM concentrations (▲, near surface), in the Dee Estuary measured at the (a) upper estuary tidal station, (b) lower estuary tidal station and (c) ebb tide axial transect. HW, High water; LW, low water.

TABLE 1. A comparison of the accretion and fluvial input of sediment to three macrotidal estuaries

	Net accretion			Fluvial sediment supply[b]		
	($mm\ a^{-1}$)	($10^6\ m^3\ a^{-1}$)	($10^6\ t\ a^{-1}$)[a]	x (km^2)	y ($10^6\ t\ a^{-1}$)	(% total)
Dee (BMT, 1990; this work)	18	2·3	4·6	1816	0·021	0·46
Mersey (Taylor, 1986; O'Connor, 1987)	16	1·3	2·6	4535	0·043	1·7
Humber (O'Connor, 1987; Turner *et al.*, 1991)	12–15	2·5–3·0	5·0–6·0	27 000	0·17	3·1

[a]Assuming 1 $m^3 = 2$ t. [b]Calculated according to equation (1).

The pathways of sediment and SPM in the Dee as inferred from Ca:Al ratios are shown in Figure 3 and discussed below. The ratio in Irish Sea sediment is 120 and throughout the sediment of the estuary is of the same order indicating effective upestuary transport and dispersion of marine-derived material by strong tidal currents. In the riverine section of the Dee above the weir, which is breached only during spring tides, this ratio in the sediment is an order of magnitude lower (Ca:Al = 7·8) but similar to that of the PS material (Ca:Al = 6·4). The SPM of the upper estuary has a ratio which varies temporally between the values of the PS material and the bed sediment. This suggests that the PS material is principally fluvial in origin, and is admixed in the water column of the upper estuary with a proportion of resuspendible marine material which varies according to tidal stress on the bed. Assuming that the PS material behaves conservatively, combining its SPM concentration of 7·2 mg l^{-1} (as determined by filtration) with the annual average river discharge yields a net land–sea flux of PS material of 8400 t a^{-1}, or 40% of the total fluvial sediment input to the Dee Estuary according to equation (1) (see Table 1). In the lower estuary the SPM is characterized by a higher Ca:Al ratio than SPM in the upper estuary due to the admixture of advected PS material with fine marine particles enriched in Ca. Neglecting the possible influence of resuspension on particle distributions in the lower estuary, the Ca:Al ratio of marine end-member SPM may be calculated from the mixing of fluvial PS and marine SPM end-members, assuming that these populations behave conservatively. Thus, a representative SPM concentration of 35 mg l^{-1} and mean Ca:Al ratio of 47 for lower estuary particles, and an SPM concentration of 7·2 mg l^{-1} and Ca:Al ration of 6·4 for PS particles yield a Ca:Al ratio of 58 for marine material. In practice, however, it is difficult to precisely parametrize the chemical composition of the marine end-member as it comprises spatially and temporally variable sub-populations derived from a variety of lithogeneous and biogenic sources (Turner *et al.*, 1992*b*).

Fluxes of ^{137}Cs and ^{241}Am

The radionuclides ^{137}Cs and ^{241}Am, like Ca, are marine-derived constituents (from a remote source at Sellafield some 120 km to the north of the estuary; Hunt, 1988). Their distributions in the Dee are uniform below the weir after Al or SSA normalization, hence a significant ($P = 0·02$) linear correlation exists between Ca and ^{137}Cs. The concentrations of ^{137}Cs and ^{241}Am in Dee sediments below the weir represent *c.* 40 and 15%, respectively, of

TABLE 2. Acetic acid-extractable major element concentrations of Dee Estuary and Irish Sea samples

		Al (mg g⁻¹)	Ca (mg g⁻¹)	Fe (mg g⁻¹)	Mn (mg g⁻¹)	Ca:Al ratio
Dee whole sediment						
Lower estuary	$x \pm s$	0·32 ± 0·20	34·7 ± 10·2	2·38 ± 1·66	0·57 ± 0·31	140 ± 54
	n	8	8	8	8	8
	R	0·07–0·71	14·1–46·0	0·35–5·35	0·099–1·06	53–220
Upper estuary	$x \pm s$	0·34 ± 0·20	31·8 ± 10·8	1·49 ± 0·92	0·50 ± 0·43	120 ± 54
	n	4	4	4	4	4
	R	0·09–0·53	17·0–4·28	0·49–2·68	0·10–1·10	73–190
River	$(n=2)$	0·58	3·9	1·33	0·44	7·8
Dee < 63 μm sediment						
Lower estuary	$x \pm s$	0·53 ± 0·11	52·9 ± 23·2	2·61 ± 0·47	0·98 ± 0·38	100 ± 42
	n	10	10	10	10	10
	R	0·40–0·69	34·5–104	1·64–3·36	0·47–1·47	57–180
Upper estuary	$x \pm s$	0·64 ± 0·18	37·4 ± 4·6	2·31 ± 0·49	0·92 ± 0·33	65 ± 30
	n	4	4	4	4	4
	R	0·38–0·78	31·2–41·2	1·59–2·67	0·66–1·41	42–107
River	$(n=1)$	0·38	14·9	1·06	0·16	39
Dee SPM						
Lower estuary	$x \pm s$	0·95 ± 0·18	43·2 ± 2·7	4·18 ± 0·65	1·39 ± 0·16	44 ± 11
	n	7	7	7	7	7
	R	0·72–1·24	38·7–45·9	3·34–5·21	1·22–1·60	32–63
Upper estuary	$x \pm s$	1·29 ± 1·04	28·8 ± 5·4	4·53 ± 3·48	0·57 ± 0·32	38 ± 24
	n	7	7	7	7	7
	R	0·26–2·78	18·8–35·7	0·95–10·7	0·18–1·07	11–72
PS[a]	$(n=1)$	3·46	22·2	17·2	3·98	6·4
TS[b]	$(n=1)$	0·16	20·8	1·10	0·23	130
Dee organisms[c]						
Cockle tissue	$(n=1)$	na	11·7	0·55	0·031	na
Mussel tissue	$(n=1)$	na	3·69	0·43	0·024	na
Irish Sea whole sediment	$x \pm s$	0·23 ± 0·06	26·6 ± 5·5	1·38 ± 0·25	0·28 ± 0·25	120 ± 22
	n	5	5	5	5	5
	R	0·12–0·27	18·1–32·1	1·07–1·66	0·25–0·30	98–150

[a] Permanently suspended material, [b] temporarily suspended material, [c] dry weight. na, Not analysed.

the concentrations in Irish Sea sediments near to the discharge at Sellafield indicating a significant yet complex southerly transport of radionuclide contaminated sediment in the eastern Irish Sea. The ratio of ^{137}Cs to ^{241}Am in the estuary (4·6 ± 0·92) is significantly higher than in the Irish Sea nearer the source (1·3 ± 0·60) indicating a relative enrichment of ^{137}Cs in the estuary. This cannot be related to the differential decay of ^{137}Cs (half-life = 30 years) and ^{241}Am (half-life = 435 years), and was not matched by an equivalent increase in the isotopic ratio of ^{137}Cs to ^{241}Am in the Sellafield discharge over decadel time-scales (McColl *et al.*, 1990). Ratios calculated from data given by Camplin (1993) in the source region are about 1·0 and 1·3 for sand and mud, respectively; in Liverpool Bay the ratios are about 3·9 for both sand and mud. These values compare favourably with

TABLE 3. Acetic acid-extractable trace metal concentrations of Dee Estuary and Irish Sea samples

		Cd ($\mu g\,g^{-1}$)	Cr ($\mu g\,g^{-1}$)	Cu ($\mu g\,g^{-1}$)	Pb ($\mu g\,g^{-1}$)	Zn ($\mu g\,g^{-1}$)
Dee whole sediment						
Lower estuary	$x \pm s$	0·28±0·10	3·3±4·5	13±19	42±20	110±48
	n	8	7	7	7	7
	R	0·17–0·43	0·13–13·2	1·6–56	8·8–69	66–180
Upper estuary	$x \pm s$	0·38	1·3±0·93	5·4±4·2	28±20	110±57
	n	2	4	3	4	4
	R	0·26–0·49	0·43–2·6	1·8–10	4·0–52	44–180
River	($n=2$)	1·1	0·9	2·9	49	120
Dee <63 μm sediment						
Lower estuary	$x \pm s$	1·0±0·75	1·7±0·75	13±16	52±13	250±110
	n	9	10	10	10	10
	R	0·13–2·3	0·26–2·7	4·4–56	33–73	130–430
Upper estuary	$x \pm s$	0·95±0·89	1·9±0·72	5·2±3·4	64±11	300±43
	n	4	4	4	4	4
	R	0·03–1·9	1·0–2·7	2·3–10	50–77	240–340
River	($n=1$)	1·5	1·5	19	36	120
Dee SPM						
Lower estuary	$x \pm s$	2·9±1·6	1·9±0·58	22±4·8	93±13	390±200
	n	7	6	7	7	7
	R	1·1–4·8	0·78–2·3	18–31	82–120	230–810
Upper estuary	$x \pm s$	2·8±3·2	2·7±1·1	12±11	48±25	270±190
	n	7	5	7	7	7
	R	0·55–9·3	1·1–4·0	1·4–34	17–79	71–530
PS[a]	($n=1$)	8·1	19·3	42	100	830
TS[b]	($n=1$)	0·38	0·47	2·0	13	89
Dee organisms[c]						
Cockle tissue	($n=1$)	0·42	1·0	5·4	5·5	79
Mussel tissue	($n=1$)	1·1	0·91	11	8·5	130
Irish Sea whole sediment	$x \pm s$	0·31±0·19	1·1±0·52	2·3±0·43	21±6·7	18±6·6
	n	5	5	5	5	5
	R	0·16–0·63	0·50–1·9	1·6–2·8	11–27	6·7–23

[a]Permanently suspended material, [b]temporarily suspended material, [c]dry weight.

those reported herein but also indicate that the ratio is independent of sediment texture. The question arises, therefore, what mechanism is responsible for the relative enrichment of ^{137}Cs in Dee Estuary sediment?

In order to assess the transport pathways of ^{137}Cs and ^{241}Am in the Irish Sea and Dee Estuary distribution coefficients, K_Ds, have been derived. Analysis of SPM and water in the Irish Sea indicates a K_D of 5×10^5 l kg^{-1} for ^{241}Am (Mitchell *et al.*, 1990), and laboratory incubations using Irish Sea water labelled with ^{137}Cs indicate a K_D of $2{\cdot}5 \times 10^2$ l kg^{-1} (Turner & Millward, 1994). Thus, ^{137}Cs (as Cs$^+$) has a relatively high solubility in seawater whereas ^{241}Am (which forms insoluble hydroxides; Aston & Stanners, 1982) has a high particle affinity. For a representative SPM concentration in coastal seawater of 5 mg l^{-1} these K_Ds indicate that 1% ^{137}Cs and 70% ^{241}Am are transported with the SPM. Thus, the ^{241}Am in the Dee Estuary sediments reflects the deposition of coastal SPM and

TABLE 4. Carbon and nitrogen contents, specific surface areas (SSAs) and radionuclide concentrations of Dee Estuary and Irish Sea samples

		C (%)	C:N ratio	SSA ($m^2 g^{-1}$)	^{241}Am ($mBq\ g^{-1}$)	^{137}Cs ($mBq\ g^{-1}$)
Dee whole sediment						
Lower estuary	$x \pm s$	2·5±1·2	12·9±2·2	5·6±3·0	74±14	270±180
	n	7	7	8	6	8
	R	0·41–4·0	8·7–15·0	0·5–8·5	52–93	22–580
Upper estuary	$x \pm s$	2·3±1·2	12·5±2·2	4·6±2·8	45±30	160±130
	n	4	4	4	3	4
	R	0·71–3·5	9·2–14·1	0·5–6·9	24–80	47–350
River	($n=2$)	1·5	12·1	2·2	nd	38
Dee <63 µm sediment						
Lower estuary	$x \pm s$	5·1±1·4	10·4±3·0	10·4±1·6	160	740
	n	10	10	10	1	1
	R	3·9–8·4	6·3–15·6	7·1–12·1	—	—
Upper estuary	$x \pm s$	4·9±0·61	9·2±2·9	9·2±1·3	na	na
	n	4	4	4		
	R	4·1–5·5	6·5–13·0	7·7–10·7		
River	($n=1$)	1·9	6·6	2·5	na	na
Dee SPM						
Lower estuary	$x \pm s$	5·6±0·49	8·4±0·85	8·3±1·7	na	na
	n	7	7	3		
	R	4·8–6·1	7·4–10·0	6·4–9·5		
Upper estuary	$x \pm s$	5·6±4·1	7·0±2·1	4·4±4·1	na	na
	n	6	6	4		
	R	1·4–10·7	5·2–10·8	0·5–9·3		
PS[a]	($n=1$)	14·0	5·8	na	na	na
TS[b]	($n=1$)	1·3	11·8	na	na	na
Dee organisms[c]						
Cockle tissue	($n=1$)	na	na	na	nd	32
Mussel tissue	($n=1$)	na	na	na	nd	49
Irish Sea whole sediment	$x \pm s$	3·0±2·7	12·2±0·82	5·5±2·6	460±360	500±310
	n	5	5	5	5	5
	R	0·91–7·8	11·2–13·0	2·2–8·1	170–990	210–1010

[a] Permanently suspended material, [b] temporarily suspended material, [c] dry weight. na, Not analysed; nd, not detected.

the influx and dispersion of contaminated bed load material. Combining the flux of marine sediment to the Dee (Table 1) with concentrations of ^{241}Am and ^{137}Cs in sediment from the mouth of the estuary yields respective influxes of 0·1 and 0·5 TBq a^{-1}. Additionally, for ^{137}Cs a significant fraction enters the estuary in dissolved form and on encountering waters of lower ionic strength, hence lower concentration of competing sorbable ions (e.g. Ca^{2+}, Mg^{2+}), in the upper estuary is able to sorb onto resuspendible sediment according to its equilibrium K_D in Dee low salinity water (3×10^3 l kg^{-1}; Turner & Millward, 1994). Tidally averaged salinity data in the upper estuary and the average freshwater discharge to the estuary, yield an average flux of *c.* 10 $m^3 s^{-1}$ seawater to the upper estuary. Given the concentration of dissolved ^{137}Cs in Irish Sea water close to the mouth of the Dee is

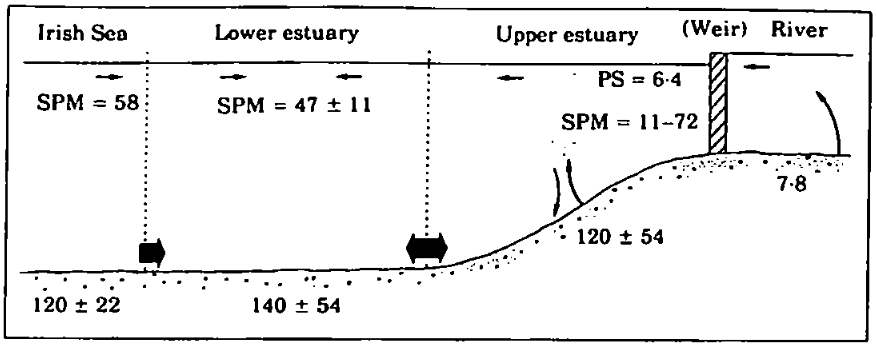

Figure 3. Ratios of acetic acid-extractable Ca:Al in whole sediment and SPM and hypothesized particle transport in the Dee Estuary. Ca:Al ratio for Irish Sea SPM has been derived from end-member particle mixing considerations. Thin arrows denote SPM transport, including bed exchange, and thick arrows denote bed load transport. PS, Permanently suspended material.

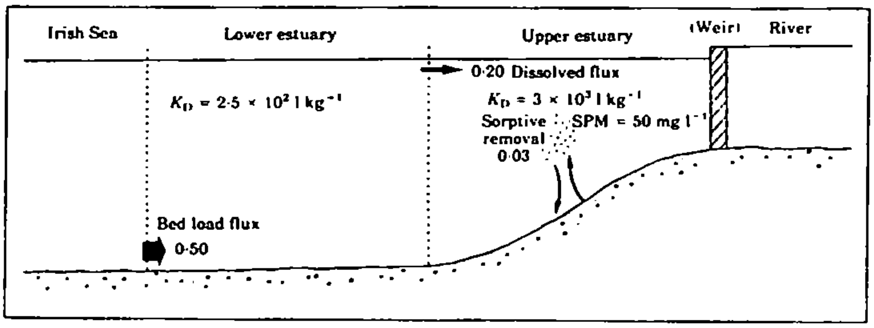

Figure 4. The cycling and fluxes (TBq a^{-1}) of ^{137}Cs in the Dee Estuary.

TABLE 5. Removal of ^{241}Am and ^{137}Cs from sediment samples by the acetic acid leach

	^{241}Am (%)	^{137}Cs (%)
Dee whole sediment ($n = 3$)	45	0
Irish Sea whole sediment ($n = 3$)	58	0

0·5 Bq l^{-1} (Hunt, 1988) this results in a net flux of soluble ^{137}Cs to the upper estuary of 0·2 TBq a^{-1}. The instantaneous addition of 50 mg l^{-1} (or about 0·25 m^2 l^{-1} for a representative SSA of 5 m^2 g^{-1}) resuspendible bed sediment into the water column then yields a sorptive removal rate of ^{137}Cs of 0·03 TBq a^{-1} according to the low salinity K_D, which amounts to about 4% of the total supply and 15% of the dissolved supply of ^{137}Cs to the estuary. These fluxes of ^{137}Cs in the Dee Estuary are depicted in Figure 4.

Treatment of selected samples with the acetic acid leach failed to remove any adsorbed ^{137}Cs ions (Table 5) indicating an irreversible reaction which results in its gradual accumulation in the sedimentary reservoir. Full BET N_2 adsorption–desorption isotherms undertaken on selected sediment and SPM samples from throughout the estuary

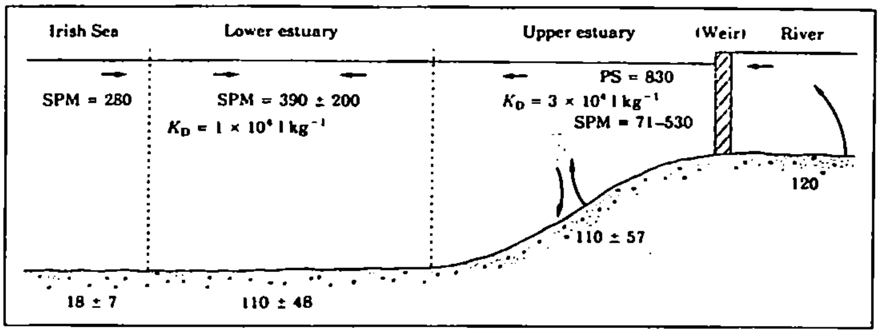

Figure 5. The concentrations of acetic acid-extractable Zn in Dee Estuary whole sediment and SPM. Zn in Irish Sea SPM has been derived from particle mixing considerations. PS, Permanently suspended material.

exhibited hysteresis typical of estuarine sediments from other environments (Millward *et al.*, 1989, 1990) indicating slit-shaped pores with most of the volume contained within pores of diameters 5–7 nm, thus able to accommodate irreversible fixation of ^{137}Cs to internal sites (Evans *et al.*, 1983). Consequently, concentrations of ^{137}Cs in cockles and mussels from the estuary are significantly lower than in the sediment (Table 4) because the bioavailable fraction of ^{137}Cs to detritus-feeding organisms is negligible.

There is potential for accumulation in the estuary of other toxic trace elements which have a higher K_D in the low salinity zone than in seawater via uptake onto resuspendible particles of the upper estuary. These include Cd and Zn (Turner *et al.*, 1993; Turner & Millward, 1994) and their origin may be either riverine (through catchment sources) or marine (Liverpool Bay, which is strongly influenced by anthropogenic sources in the Mersey Estuary). Removal of a significant fraction of ^{137}Cs in the Dee Estuary, and reported estuarine removal of other oceanic trace constituents such as ^{210}Pb and Pu (Olsen *et al.*, 1989) and U (Maeda & Windom, 1982; van den Berg *et al.*, 1991), has important implications concerning the fate of pollutants discharged into the marine environment.

It is apparent from the ^{137}Cs flux calculations above that this mechanism alone cannot account for a 3-fold enrichment of ^{137}Cs/^{241}Am in the estuary. Moreover, a similar enrichment is evident in the coastal (i.e. saline) environment of Liverpool Bay (Camplin, 1993). Thus, an additional possibility exists of a kinetically slow (of the order of months to years) secondary sorption reaction of ^{137}Cs occurring within the particle lattice (Evans, 1983) during transport of particles from the source.

The cycling and fluxes of particulate trace metals

The distribution and transport of particulate trace metals in the Dee is exemplified for Zn in Figure 5; K_D values have been derived from radiotracer incubation experiments using low salinity Dee water and Irish Sea water (Turner & Millward, 1994). Concentrations of Zn, as with all trace metals and C and N, are highest in the most mobile, PS material due to a large particle surface area:volume ratio. The retention of these particles in the estuary is likely to be limited to a time-scale similar to that of the freshwater replacement time, probably of the order of 10 days (BMT, 1990). Combining trace metal concentrations of the PS fraction with the flux of this material through the estuary (8400 t a^{-1}) yields the following fluxes of acetic acid-extractable particulate metals (kg a^{-1}) to Liverpool Bay: Fe, $1{\cdot}4 \times 10^5$; Mn, $3{\cdot}3 \times 10^4$; Cd, 68; Cr, 160; Cu, 350; Pb, 840 and Zn, $7{\cdot}0 \times 10^3$.

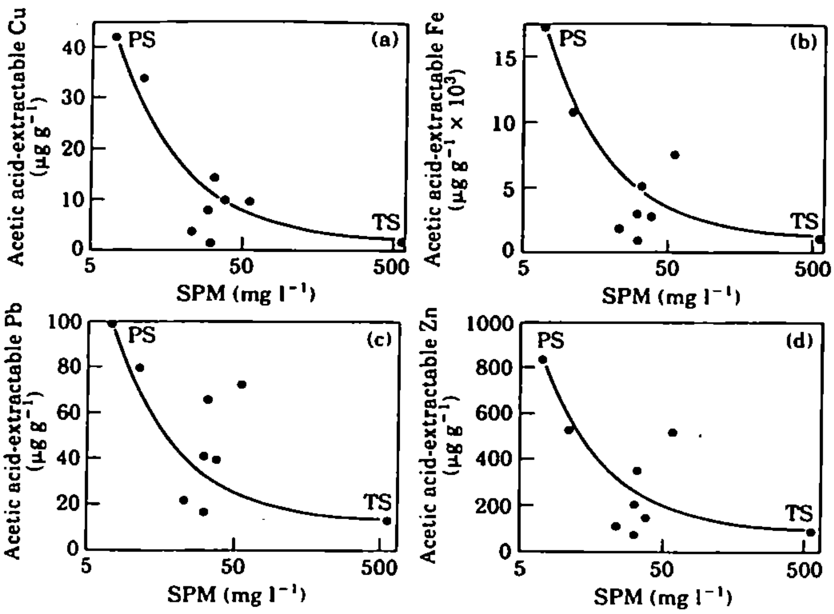

Figure 6. A comparison of observed (●) with predicted [(———); calculated according to equation (2)] acetic acid-extractable trace metal composition [(a) Cu, (b) Fe, (c) Pb and (d) Zn] of resuspendible particles in the upper Dee Estuary as a function of concentration of resuspending particles, SPM. PS, Permanently suspended material; TS, temporarily suspended material.

The range in metal and C and N concentrations of SPM of the upper estuary tidal station was encompassed by the PS and TS (or bed sediment) fractions suggesting that local resuspension controls the temporal distribution of SPM composition, hence particulate metal concentrations, in this region of the estuary. The metal contents of SPM in the lower estuary are more uniform and are intermediate between the TS and PS fractions of the upper estuary suggesting that resuspension is of less importance in controlling the temporal distribution of SPM in the broader, less energetic region of the lower estuary. The composition of marine (Liverpool Bay) end-member material can be predicted from the relative proportions of PS material and lower estuary SPM as explained above, and is as follows: Fe, 0·81 mg g^{-1}; Mn, 0·72 mg g^{-1}; Cd, 1·6 µg g^{-1}; Cr, <1 µg g^{-1}; Cu, 17 µg g^{-1}; Pb, 91 µg g^{-1}; Zn, 280 µg g^{-1}; C, 3·4%, and C:N, 9·1.

A particle mixing model

The time-variable particulate metal concentration of SPM in the upper estuary, *Me*(*t*), due to changes in the proportion of TS material via changing tidal stress on the bed, can be predicted from the following equation incorporating the composition of the PS and TS materials:

$$Me(t) = \frac{(SPM - SPM^{PS})Me^{TS} + SPM^{PS}Me^{PS}}{SPM} \tag{2}$$

where:

$$SPM = SPM^{TS} + SPM^{PS} \tag{3}$$

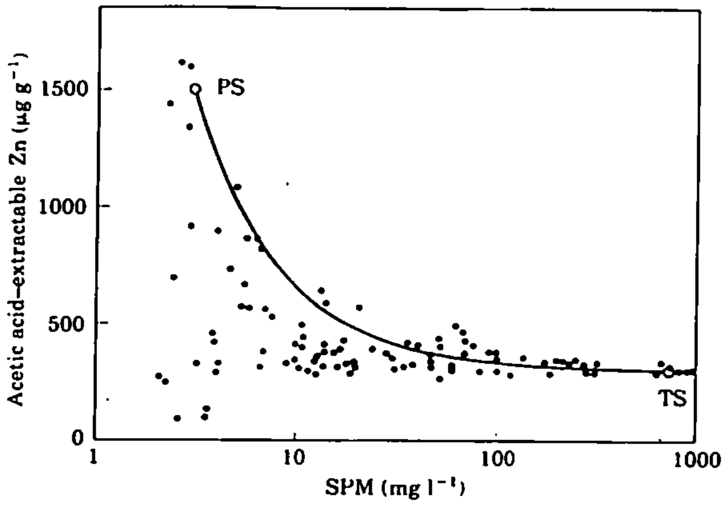

Figure 7. Acetic acid-extractable Zn concentration of SPM versus SPM concentration for the Tamar Estuary (redrawn from Ackroyd, 1983). (———), Predicted according to equation (2) using the following values: $SPM^{PS} = 3$ mg l^{-1}; $SPM^{TS} = 750$ mg l^{-1}; $Zn^{PS} = 1500$ μg g^{-1}; $ZN^{TS} = 300$ μg g^{-1}.

and where SPM^{PS} is the concentration of PS material (7·2 mg l^{-1}), of particulate metal concentration Me^{PS}, SPM is the observed concentration of suspended particles, and SPM^{TS} is the variable concentration of resuspending particles of particulate metal concentration Me^{TS}. Although it has been suggested that resuspension of particles engenders removal of dissolved constituents such as ^{137}Cs and Zn, the model assumes that solid-solution interactions are ineffectual to the bulk composition of particles (Mantoura & Morris, 1983; Turner *et al.*, 1991). Model predictions and measured values for Cu, Pb, Fe and Zn are shown in Figure 6 against the concentration of SPM. Although the model has only been tested for a small range of SPM, agreement is only reasonable indicating additional effects such as advective fluxes of particle populations, selective resuspension of particle types and particle–particle interactions. Moreover, the implication of a coarse-grained bed, low SPM concentrations and the absence of a turbidity maximum is that resuspension events are relatively short-lived in the upper Dee Estuary.

Figure 7 shows the concentration of acetic-leachable Zn in Tamar Estuary suspended particles as a function of SPM concentration (Ackroyd, 1983). Representative end-member values selected for the model prediction were as follows: $SPM^{PS} = 3$ mg l^{-1}; $SPM^{TS} = 750$ mg l^{-1}; $Zn^{PS} = 1500$ μg g^{-1}; $Zn^{TS} = 300$ μg g^{-1}; although a better fit could be attained (by eye) by either reducing Zn^{PS} to 1000 μg g^{-1} or halving SPM^{PS}. It is surprising that these data conform well with an inverse relationship predicted by a two end-member particle mixing model as *in situ* investigations have shown that Tamar particles exhibit interactive behaviour (aggregation/disaggregation) and a complex distribution of size, density and settling velocities (Bale *et al.*, 1985, 1989; West *et al.*, 1990). The end-members can be identified as particles of fluvial origin (the advecting population, PS; $SPM < 5$ mg l^{-1}) and particles resuspended from the bed (the resuspending population, TS; $SPM > 500$ mg l^{-1}); the particle population which does not conform with the relationship (i.e. $SPM < 5$ mg l^{-1} and $Zn < 500$ μg g^{-1}) can be identified as being of marine origin (Ackroyd, 1983) and is likely to represent an additional advecting population.

The implication of these observations is the general applicability of a particle mixing model for defining and predicting the spatial and temporal distributions of particle-bound constituents in energetic, macrotidal environments such as estuaries and coastal seas. To this end the model provides an important component in the development of a pollution management tool for particle reactive contaminants.

Conclusions

Chemical characterization of sediment and SPM from the Dee Estuary has enabled the origin and transport of particles to be determined. The sedimentary reservoir of the estuary is dominated by coarse-grained material supplied by coastal and sea-bed erosion and transported upestuary by tidal asymmetry. The SPM comprises two distinct populations: fine, organic-rich fluvial material, which is the major carrier of trace constituents (w/w), is spatially and temporally admixed with coarse suspendible bed material in accordance with tidal stress on the bed, providing the potential for sorptive removal of dissolved constituents such as ^{137}Cs, Cd and Zn. Calculations based on sediment flux data and radiochemical laboratory experiments indicate that about 15% of dissolved ^{137}Cs entering the upper estuary is removed by this process. The time-variable composition of SPM in the upper estuary was predicted using a simple resuspension model based on the compositions of operationally fractionated PS and TS particles; agreement with field data was only partially successful, however, suggesting additional processes such as selective resuspension and/or advection of particle types.

An important implication of these observations and model calculations is their potential significance to the more accurate prediction of land–ocean fluxes and internal cycling of pollutants in accreting, macrotidal environments.

Acknowledgements

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Biogeochemistry of intertidal sediments

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Modelling adsorption and desorption processes in estuaries

A. Turner and A.O. Tyler

3.1 Introduction

Many inorganic and organic pollutants are of great concern to water quality managers owing to their persistence, toxicity and liability to bioaccumulate (Tanabe, 1988; Robards & Worsfold, 1991; Bryan & Langston, 1992; McCain *et al.*, 1992; Förstner, 1993). The major temporary or ultimate sink for such pollutants in estuaries is the sedimentary reservoir, including intertidal deposits (Hanson, Evans & Colby, 1993; van Zoest & van Eck, 1993; Kennicutt *et al.*, 1994), and definition of the biogeochemical mechanisms by which they absorb onto, desorb from and repartition amongst natural, heterogeneous particle populations is essential in order to assess their environmental fate. In estuaries, prediction of the distribution of pollutants is further compounded by intense temporal and spatial gradients of the reaction controlling variables such as salinity, dissolved oxygen concentration and particle composition, occurring both within the sediment and in the water column during particle suspension.

This chapter focuses on an empirical technique to study the sorptive behaviour of trace metals and trace organic compounds in estuaries. Thus, the partitioning of constituents between particles and solution is determined experimentally, without identifying the inherent reaction mechanisms or reactant speciation, under controlled laboratory conditions using natural samples spiked with radiotracer analogues of the constituent of interest (Turner *et al.*, 1993). Adsorption and desorption processes may be modelled as a function of particle concentration, and the controlled variables of salinity and dissolved oxygen concentration, by incorporating empirically derived results into simple mass balance equations. This approach is exemplified herein using site-specific results from two contrasting estuarine environments, namely the Clyde and Humber, and the calculated results are discussed in the context of their agreement with field measurements of trace constituents in these estuaries. Although the arguments and discussion are presented explicitly for sorption processes occurring in the water column they may be extrapolated to the intertidal environment where chemical reactivity is also promoted by changes in dissolved oxygen concentration (Kerner & Wallmann, 1992) and salinity (Carroll *et al.*, 1993).

3.1.1 The Clyde and Humber Estuaries

The physical characteristics of the Clyde and Humber Estuaries are listed in Table 3.1, and typical axial distributions of salinity, concentration of suspended particulate matter (SPM) and dissolved oxygen concentration are shown in Figure 3.1. The Clyde is a partially stratified, mesotidal estuary. Irregularities in its axial salinity distribution arise from a multiplicity of fresh water sources along the tidal estuary. The SPM concentrations are low and relatively invariant and an occasional, weak turbidity maximum results from trapping of fine sediment by convergent subsurface flows (Curran, 1986). The high biochemical oxygen demand of sewage discharges combined with the poor exchange between subsurface and surface waters results in an extensive area of oxygen depletion in the upper estuary (Curran, 1986). In contrast, the Humber is a well-mixed, macrotidal estuary, and a turbidity maximum generated by tidal resuspension of bed sediment is a regular feature of the low salinity zone (Turner, Millward & Morris, 1991).

3.2 Determination of distribution coefficients

The distribution coefficient, or partition coefficient, K_D (v/w), parameterises the ratio of adsorbed particulate concentration, P (w/w), to dissolved concentration, C (w/v), of a constituent, and may be determined empirically

Table 3.1 Physical characteristics of the Clyde and Humber Estuaries

	Clyde[a]	Humber[b]
Axial length (km)	40	62
Mean river flow ($m^3\ s^{-1}$)	44 (+ 63[c])	246
Tidal range at mouth, neaps/spring (m)	1.9/3.0	3.5/6.2
Residence time (days)	10–20	–40
Riverine sediment discharge ($t\ a^{-1}$)	83 000	170 000

[a] Mackay & Leatherland (1976); Curran (1986)
[b] Turner *et al.* (1991)
[c] contribution from tributaries to the tidal estuary

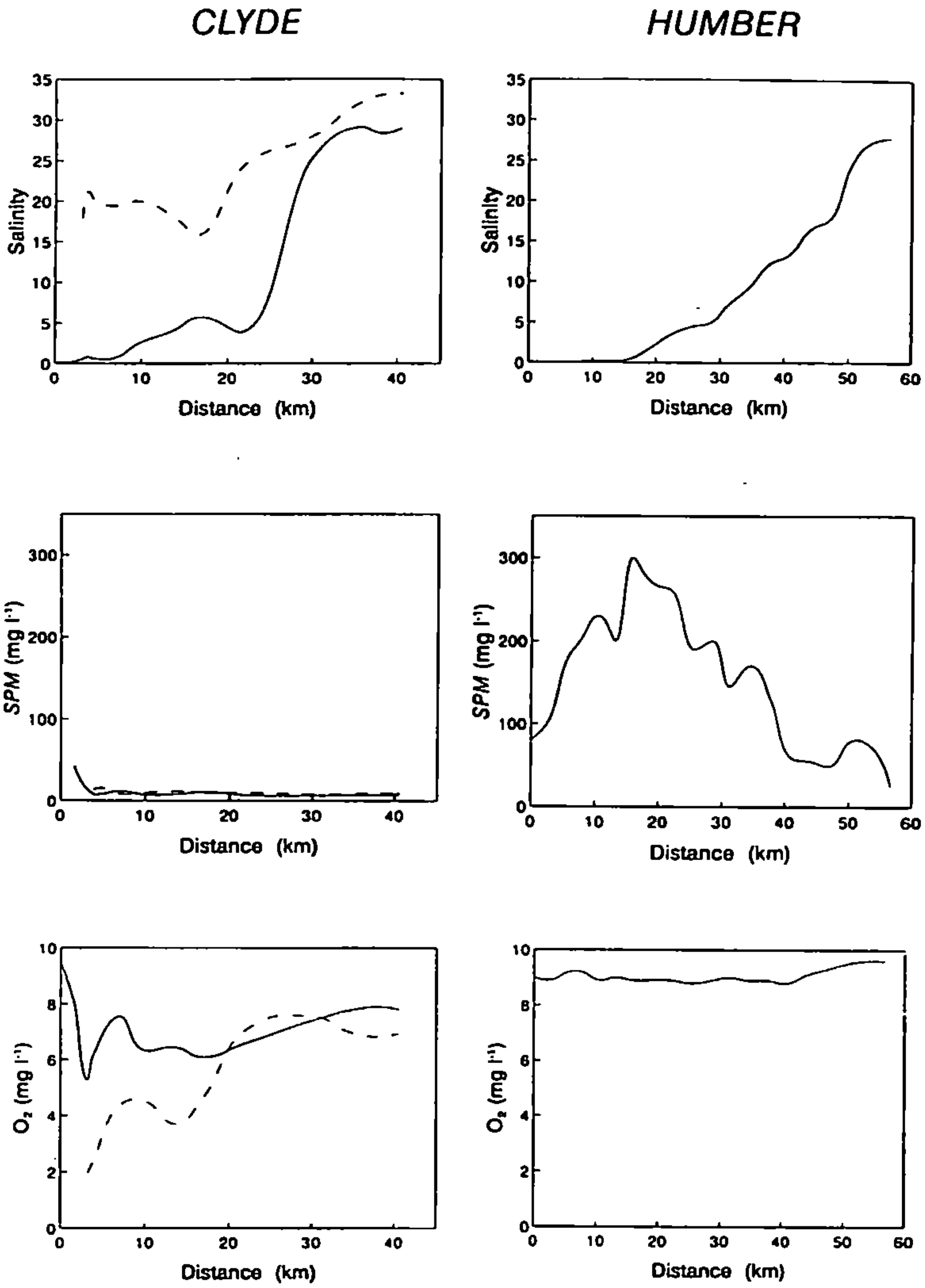


Figure 3.1 Distributions of salinity, suspended particulate matter (SPM) and dissolved oxygen determined during axial samplings of the Clyde (8/92; ebb tide, river flow including tributary inputs = 152 m^3 s^{-1}) and Humber (1/88; flood tide, river flow = 234 m^3 s^{-1}). Solid lines denote near surface measurements and broken lines denote near bottom measurements. Distance is measured from the weir at Glasgow on the Clyde and from Trent Falls on the Humber.

by doping natural samples with radiotracer analogues and analysing the adsorbed and dissolved reactant concentrations by a suitable radiochemical method.

Water samples used for the experimental studies of trace metals and chlorinated organic compounds were collected from the shore near to the river and marine end-members of the Humber and Clyde Estuaries and stored cool and in the dark before being used. Trace metal studies using Humber samples were undertaken onboard Royal Research Ship *Challenger* within 48 hours of collection and are described in detail elsewhere (Turner *et al.*, 1993); the remaining experiments were undertaken in the laboratory in Plymouth within one week of sample collection. The simulation of estuarine mixing was achieved by mixing aliquots of unfiltered end-member samples in different proportions. For the trace metal studies mixed samples of 50 or 100 ml were contained within acid-cleaned 150 ml polyethylene vessels and spiked with 50 or 100 μl of a cocktail consisting of sub-nanomolar concentrations of ^{109}Cd and ^{137}Cs (Amersham International) in dilute HCl. This resulted in a small reduction in pH in the Humber experiments which was neutralised by the addition of a spike of ammonia solution diluted accordingly. The samples were equilibrated for 120 hours and filtered through pre-weighed 0.45 μm pore size Millipore cellulose acetate filters mounted in a Millipore filtration unit. The filtrates and filters were stored in unused 150 ml polyethylene vessels and 50 mm diameter petri dishes, respectively, and their activities were determined using a high purity Ge detector connected to a Canberra Series 80 Multichannel Analyser. Disintegrations were counted for 1000 seconds and this gave statistical counting errors ($\pm 0.5\sigma$) of $< 5\%$. The distribution coefficient, K_D (ml g^{-1}), is then given as follows:

$$K_D = \frac{P}{C} = \frac{A_p . V}{A_c \, m f} \tag{3.1}$$

where A_p and A_c are the activities on the particles and in solution, respectively, m is the mass of particles on the filter (g), V is the volume of filtrate (ml), and f is a geometry factor which corrects for the differential sensitivity of the detector towards filter and filtrate samples. Replicate experiments using estuarine samples have indicated that K_Ds determined by this technique are generally reproducible within 10% (Turner & Millward, 1994).

The effect of oxygen depletion on the partitioning was investigated by bubbling nitrogen through a Clyde river end-member sample for 12 hours prior to spiking and thereafter throughout the incubation. This achieved a dissolved oxygen concentration of 1.5 mg l^{-1} compared with 8.0–8.5 mg l^{-1} under ambient, aerated laboratory conditions, and thus approximates the observed range in concentrations of the upper reaches of the estuary (Figure 3.1).

Two ^{14}C-labelled chlorinated organic compounds were selected for investigation: 2,3,7,8-TCDD (Chemsyn), the most toxic of the dioxin congeners; and 22′55′-TCB, IUPAC 52 (Sigma Chemicals), an abundant PCB congener. A 25 µl spike of 0.02 µCi compound in hexane was placed on the side of a hexane-washed 50 ml glass centrifuge tube using a glass microsyringe; the hexane was then evaporated under a laminar flow hood and a sample of 20 ml was added (Zhou, Rowland & Mantoura, 1995; Zhou & Rowland, 1997). After shaking the stoppered tube for 12 hours, the contents were centrifuged at 3000 rpm for 30 minutes to separate the particulate and dissolved phases. A 2 ml aliquot of supernatant was pipetted into a glass vial containing 10 ml Ultima Gold Liquid Scintillation Cocktail, taking care not to disturb particles at the bottom of the centrifuge tube. The particles were then discarded along with the remaining water and the residual compound adsorbed to the centrifuge walls was extracted in 4 ml hexane for 12 hours on a shaker. A 2 ml aliquot of the extract was then pipetted into a glass vial containing 10 ml scintillation cocktail. All sample vials were counted on a Philips 4700 scintillation counter and calibrated against matrix-matched standards quenched using CCl_4. The K_D (ml g^{-1}) was derived from mass balance as follows:

$$K_D = \frac{P}{C} = \frac{A_s - (A_c + A_w)}{A_c} \cdot \frac{V}{m} \tag{3.2}$$

where A_s, A_c and A_w are the respective activities of the original spike, the supernatant and that adsorbed onto the walls of the centrifuge tube, V is the volume of supernatant (ml) and m is the mass of particles (g) in the original suspension derived from subsample filtration through pre-weighed Whatman GF/F filters. Experiments were performed in triplicate or quadruplicate and the reproducibility of the resulting K_Ds was generally better than 10% for 22′55′-TCB, and up to about 40% for 2,3,7,8-TCDD due to its poor solubility and consequent low activity in solution.

3.3 Results and model calculations

3.3.1 Fraction of constituent in solution

The K_Ds for the trace metals and chlorinated organic compounds are shown against salinity in Figure 3.2. End-member K_Ds have been combined with representative end-member SPM concentrations (*SPM*) (Figure 3.1) in order to calculate the fraction of constituent in solution, ζ, as follows:

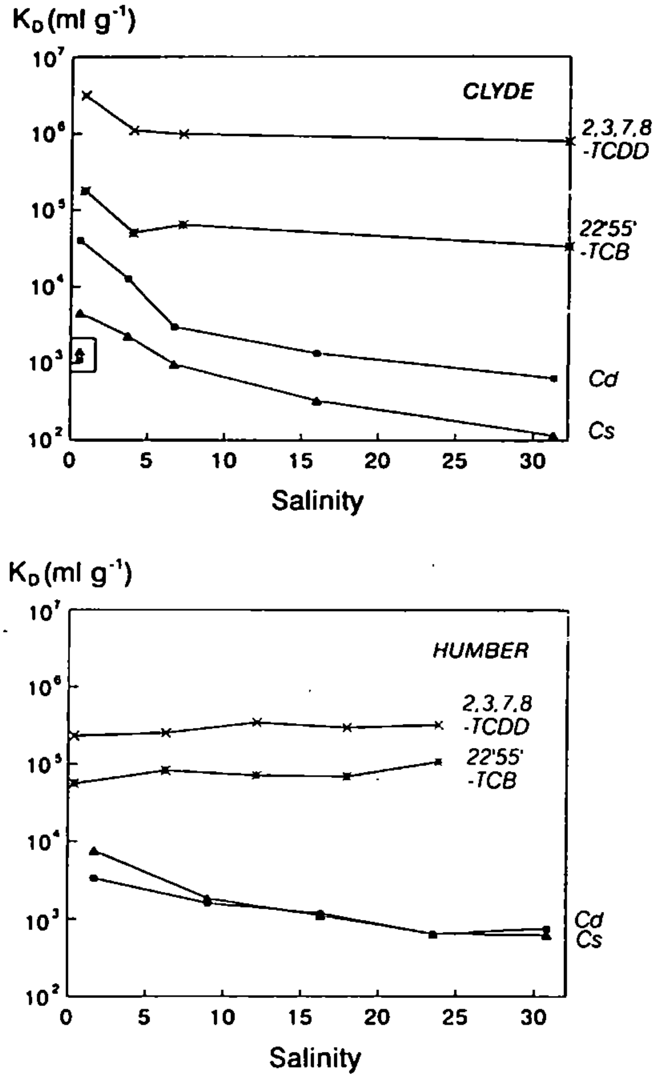


Figure 3.2 Distribution coefficients, K_Ds, against salinity for the Clyde and Humber mixed samples. Boxed data points denote K_Ds determined using the sample incubated under de-oxygenated conditions.

$$\zeta = \frac{C}{C + P \cdot SPM} = \frac{1}{1 + K_D \cdot SPM} \qquad (3.3)$$

The magnitude of this fraction (Table 3.2), which has important implications concerning the bioavailability, transport and fate of these constituents (Balls, 1989; Pankow & MacKenzie, 1991; Webster & Ridgway, 1994) varies from more than 90% for Cd and Cs in sea water and oxygen depleted waters of the Clyde, to less than 5% for 2,3,7,8-TCDD in the Humber Estuary and the low salinity zone of the Clyde.

3.3.2 Salinity and particle character dependence of partitioning

All constituents in the Clyde exhibit a reduction in K_D with increasing salinity; in the Humber, K_Ds for Cd and Cs decrease with increasing salinity whereas K_Ds for 22′55′-TCB and 2,3,7,8-TCDD are relatively invariant. Regarding trace metals, although inter-estuarine variability of end-member K_Ds arises through differences in end-member particle and water composition, the distribution of K_Ds induced by mixing of end-members is controlled principally by salinity and not changes in net particle character (Turner *et al.*, 1993). Thus, a reduction in K_D with increasing salinity, S, which is characteristic of many metals (Li, Burkhardt & Teraoka, 1984), results from an increase in the proportion of the sorbable species being complexed by sea water anions (Cl^- and SO_4^{2-}) and an increasing occupation of particle sorption sites by sea water

Table 3.2 The percentage of trace metals and chlorinated organic compounds in solution, calculated according to Equation (3.3) using end-member K_Ds and representative concentrations of suspended particulate matter (SPM). REM and MEM denote river and marine end-members, respectively

	SPM (mg l^{-1})	Cd	Cs	22′55′-TCB	2,3,7,8-TCDD
Humber					
REM	100	75.1	57.0	15.2	4.2
MEM	100	93.0	94.2	8.5	3.0
Clyde					
REM	10	71.5	95.7	35.8	3.1
REM*	10	98.8	98.7	—	—
MEM	10	99.4	99.9	75.0	11.2

*De-oxygenated river end-member sample

cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), and may be defined by the following general relationship (Bale, 1987; Turner & Millward, 1994):

$$\ln K_D = b \cdot \ln(S + 1) + \ln K_D^0 \qquad (3.4)$$

where K_D^0, the partitioning in fresh water, and b are constants. Values of these constants for Cd and Cs in the Clyde and Humber have been derived from regressions of $\ln K_D$ versus $\ln (S + 1)$ and are given in Table 3.3. The parameterisation of the sorptive behaviour of constituents in the form of such generic relationships is extremely useful for the refinement of chemical codings in contaminant transport models (Plymsolve, 1991; Ng *et al.*, 1996).

Regarding chlorinated organic compounds, the information presented herein and elsewhere (Tyler *et al.*, 1994) suggests that particle character rather than salinity exerts the key influence on their estuarine distributions. The chemical characteristics of typical Clyde and Humber end-member particles are given in Table 3.4. Thus, Humber river and marine end-member particles have similar chemical characteristics engendering a relatively uniform distribution of K_D, whereas in the Clyde, riverine particles have a higher content of Fe–Mn hydroxides and carbon for the sorption of compounds and a reduction in K_D is observed as the proportion of riverine particles in the admixture decreases. More specifically, recent studies suggest that adsorption of trace organic compounds onto natural particles is controlled dominantly by the apolar lipid content (Preston & Raymundo, 1993; Tyler *et al.*, 1994). Higher absolute K_Ds in the Clyde than in the Humber are, therefore, reflected by inter-estuarine differences in particulate lipid content (Clyde sediment = 6.5 ± 5.0 mg g^{-1} cf. Humber sediment 1.6 ± 0.7 mg g^{-1}; Tyler *et al.*, 1994).

Table 3.3 Regression analyses of $\ln K_D$ versus $\ln(S+1)$ ($n = 5$) for Cd and Cs (see Equation (3.4))

Estuary		Slope, b	Intercept, K_D^0 (ml g^{-1})	r^2 (%)	p
Clyde	Cd	− 1.42	80 800	96.5	0.002
	Cs	− 1.25	11 000	95.8	0.002
Humber	Cd	− 0.653	6 000	92.8	0.005
	Cs	− 1.05	21 000	99.0	< 0.001

3.3.3 Desorption modelling

The foregoing discussion suggests that the estuarine distributions of trace organic compounds are determined largely by natural particle mixing processes and the rates at which sorbed compounds redistribute amongst different particle types. In contrast, the partitioning of trace metals in estuaries is controlled principally by salinity (Equation (3.4)) and their distributions will be determined to some extent by desorption from seaward fluxing particles. Assuming no loss or gain of seaward fluxing particles, and neglecting possible additional sources of trace metals such as pore-water infusion, this effect may be quantified from mass balance of constituent as follows (Li *et al.*, 1984):

$$C^{S1} + P^{S1} \cdot SPM^{f} = C^{S2} + P^{S2} \cdot SPM^{f} \tag{3.5}$$

where SPM^{f} is the concentration of seaward fluxing particles traversing an axial or vertical salinity gradient, S1–S2. Assuming that the sorption reaction is fully reversible, the relative changes in adsorbed particulate and dissolved concentrations along this salinity gradient are given as follows:

$$\frac{P^{S2}}{P^{S1}} = \frac{SPM^{f} + 1/K_{D}^{S1}}{SPM^{f} + 1/K_{D}^{S2}} \tag{3.6}$$

and:

$$\frac{C^{S2}}{C^{S1}} = \frac{P^{S2}}{P^{S1}} \cdot \frac{K_{D}^{S1}}{K_{D}^{S2}} \tag{3.7}$$

Table 3.4 The composition of typical end-member particles from the Clyde and Humber. Fe and Mn were determined following extraction by hydroxylamine hydrochloride–acetic acid. Carbon and nitrogen were determined using an elemental analyser. Specific surface area (SSA) was determined using a BET nitrogen adsorption technique (nd = not determined). REM and MEM denote river and marine end-members, respectively.

	Fe (mg g^{-1})	Mn (mg g^{-1})	Carbon (%)	Carbon/ Nitrogen	SSA (m^2 g^{-1})
Clyde					
REM	8.40	1.02	9.9	9.2	7.1
MEM	3.52	0.29	9.3	10.3	nd
Humber[a]					
REM	10.1	1.32	4.9	15.8	31.4
MEM	11.2	1.05	5.2	13.9	20.6

[a] Turner *et al.* (1993)

Note that these equations are also valid for trace organic compounds if the seaward fluxing particle population is chemically modified *in situ* through, for example, precipitation or dissolution of Fe–Mn oxides and/or organic coatings.

The relative change in dissolved or adsorbed concentration of trace metals due to the flux of particles along a dissolved oxygen gradient, O2–O1, may be calculated likewise using K_Ds determined under different oxygen conditions. Thus:

$$\frac{P^{O2}}{P^{O1}} = \frac{SPM^f + 1/K_D^{O1}}{SPM^f + 1/K_D^{O2}} \tag{3.8}$$

and:

$$\frac{C^{O2}}{C^{O1}} = \frac{P^{O2}}{P^{O1}} \cdot \frac{K_D^{O1}}{K_D^{O2}} \tag{3.9}$$

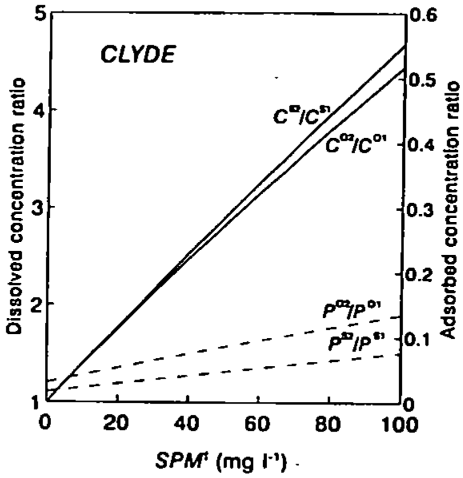
Figure 3.3 shows dissolved and adsorbed particulate concentration ratios for Cd as a function of seaward fluxing particle concentration, SPM^f, calculated according to Equations (3.6) and (3.7) using end-member K_Ds for the Humber and Clyde, and according to Equations (3.8) and (3.9) using K_Ds determined under extreme dissolved oxygen concentrations in the Clyde. Although for a given concentration, SPM^f, the relative change in dissolved concentration in the Clyde effected by variations in both salinity and dissolved oxygen is greater than the relative change in dissolved concentration in the Humber effected by variations in salinity, the magnitude of the advecting particle population is considerably smaller in the Clyde. Thus, for a representative concentration of SPM^f in the Clyde of ~ 10 mg l^{-1} (Figure 3.1), $C^{S2}/C^{S1} = C^{O2}/C^{O1} \sim 1.4$, $P^{S2}/P^{S1} \sim 0.02$ and $P^{O2}/P^{O1} \sim 0.04$. Particle fluxes in dynamic macrotidal estuaries are spatially and temporally variable (Morris *et al.*, 1986), but a hypothetical particle population of concentration 250 mg l^{-1} traversing the full salinity range of the Humber Estuary yields the following concentration ratios: $C^{S2}/C^{S1} = 1.5$, and $P^{S2}/P^{S1} = 0.35$. According to these calculations the largest relative change in Cd concentration occurs in Clyde suspended particles and results in a 25- to 50-fold reduction of the adsorbed particulate fraction.

3.3.4 Adsorption modelling

Sorptive removal of dissolved constituents is engendered by the addition of sorption sites. In estuaries this is achieved through tidally induced resuspension of bed particles that are depleted of the adsorbed constituent relative to equilibrium. This effect may be quantified by the following equation derived from mass balance (Morris, 1986):

$$\frac{C}{C^0} = \frac{1 + K_D \cdot SPM^0}{1 + K_D \cdot SPM^0 + K_D \cdot SPM^a(1 - \alpha)} \tag{3.10}$$

where C/C^0 is the ratio of dissolved constituent concentration in turbidised water to that in ambient water (i.e. fractional removal), SPM^a is the concentration of added or resuspended particles, SPM^0 is the concentration of ambient suspended particles, and α defines the depletion



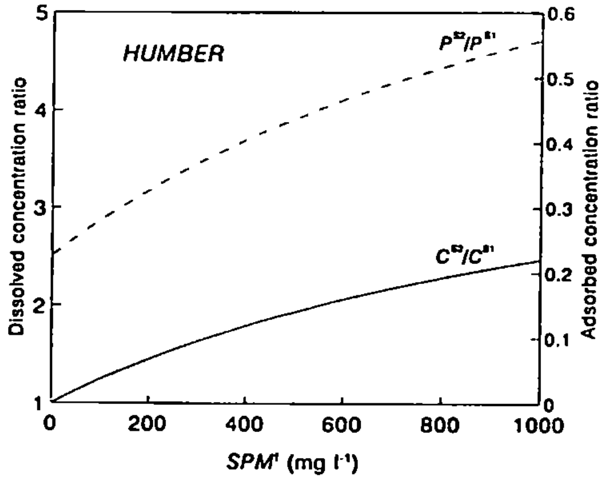


Figure 3.3 Dissolved and adsorbed particulate concentration ratios as a function of fluxing particle concentration (SPM^f) for Cd in the Clyde and Humber, calculated according to Equations (3.6)–(3.9).

of adsorbed constituent on the added particles relative to equilibrium in the turbidised water (i.e. P^a/P). Such constituent-depleted particles are derived from the marine reaches of an estuary where anthropogenic inputs are generally less significant and particle sorption sites are occupied by sea water cations, and are transported up-estuary by asymmetric tidal currents. The calculated sorptive removal of constituents is shown for the Humber Estuary in Figure 3.4 within an added particle concentration range of 0–1000 mg l^{-1}, using river end-member K_Ds and an ambient particle concentration of 5 mg l^{-1}; the value of α of 0.50 is based on empirical estimates given by Morris (1986). Under these conditions 50% removal of dissolved constituent is achieved at the following approximate added particle concentrations: Cd, 700 mg l^{-1}; Cs, 250 mg l^{-1}; 22'55'-TCB, 50 mg l^{-1}; 2,3,7,8-TCDD, 20 mg l^{-1}. Application of the sorption model to the Clyde Estuary is not appropriate for the following reasons. Firstly, although localised disturbance of the bed occurs during dredging operations, there is no evidence of extensive resuspension from axial and vertical SPM distributions (Figure 3.1). Moreover, bottom current speeds are lower than the critical erosion velocity for representative grain diameters (Curran, 1986). Secondly, there is little potential for up-estuary transport of marine particles due to slow subsurface currents and deep basins in the outer estuary which act as

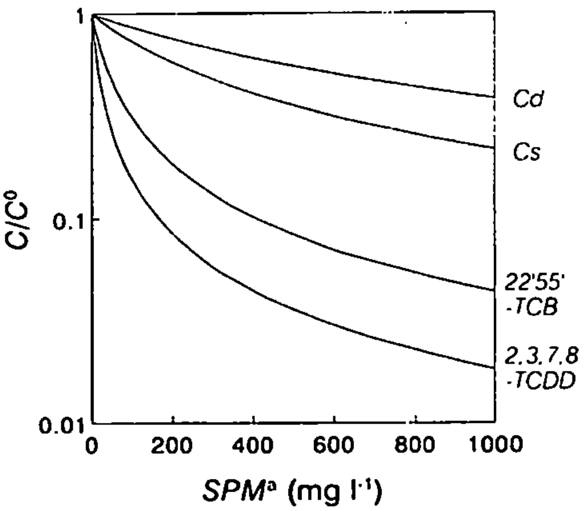


Figure 3.4 The removal of dissolved trace metals and chlorinated organic compounds as a function of added particle concentration (SPM^a) in the river end-member of the Humber Estuary, calculated according to Equation (3.10) for $SPM^0 = 5$ mg l^{-1} and $\alpha = 0.50$.

sediment traps (Mackay & Leatherland, 1976). It is conceivable, however, that removal of certain trace metals (including Cd) may be achieved via the precipitation of insoluble sulphide species (Zwolsman & van Eck, 1993). A continual source of sulphide (namely, the reducing bottom sediments) is not accounted for in the laboratory simulations and this serves to exemplify potential limitations with our attempts to replicate multiple, interactive environmental processes in laboratory enclosures.

3.4 Discussion

Although chemical parameters such as distribution coefficients are fundamental to understanding the geochemical reactivity of trace

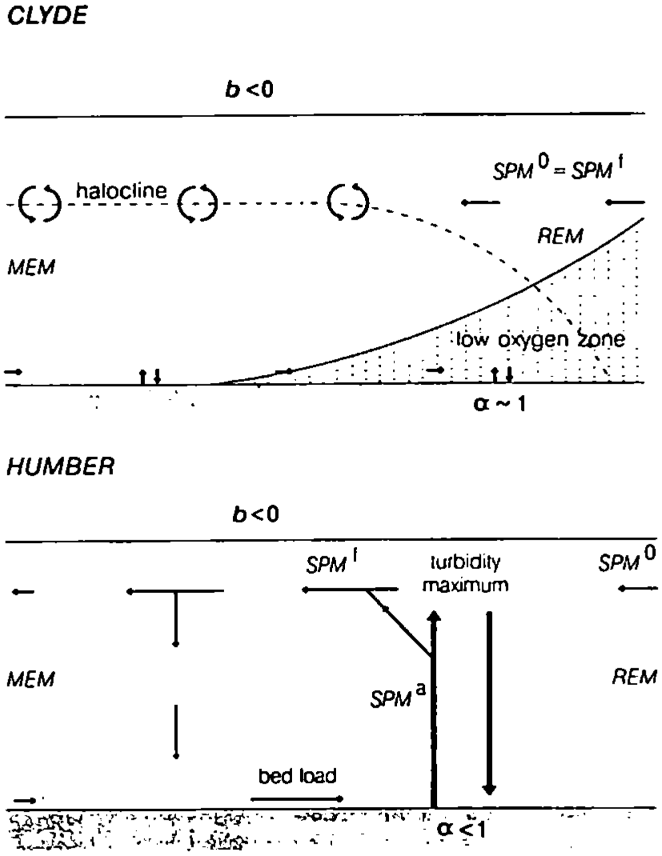


Figure 3.5 Schematic illustration of particle fluxes in the Clyde and Humber Estuaries. Arrow size denotes relative magnitude of the flux. The broken line represents the boundary of the saline intrusion and the river. REM and MEM denote river and marine end-members, respectively. All terms are defined in the text.

constituents in estuaries, the foregoing calculations have emphasised the important role of sediment dynamics on chemical distributions. In the Humber Estuary sorption reactions are promoted by substantial resuspending and advecting particle fluxes, as conceptualised in Figure 3.5, and the suspended particle populations are in a dynamic state of exchange with subtidal and intertidal material. In highly energetic, macrotidal estuaries a proportion of riverine suspended particles are transported into the turbidity maximum, where the magnitude of the seaward advecting population is augmented by particles resuspended by tidal currents (Morris *et al.*, 1986). Trace metals are desorbed from these particles downestuary in accordance with the magnitude of b, the rate of change of K_D with salinity, until they are deposited as the current speeds are reduced. An admixture of this sediment and marine derived material is then transported up-estuary as bedload by asymmetric tidal currents to the null zone where it is resuspended into the turbidity maximum engendering sorptive removal of dissolved constituent in accordance with the value of α, the extent of depletion (relative to equilibrium) of adsorbed constituent on the particles. Field investigations of various dissolved trace metals (diagnosed as constituent–salinity plots) in the Humber Estuary have demonstrated conservativeness (Balls, 1985; Kitts *et al.*, 1994) as well as a variety of reactive distributions (Gardiner, 1982; Edwards, Freestone & Urquhart, 1987; Coffey & Jickells, 1995). Differential behaviour amongst constituents reflects differences in chemical parameters such as end-member K_Ds, α, and the reversibility of sorption, whereas intra-constituent variability arises from temporal variability of component sediment fluxes.

Chemical reactivity in the Clyde is governed by the flux of particles through lateral and vertical gradients of salinity or dissolved oxygen and there is little exchange of particles between the water column and the bed (Figure 3.5). Because of the low and invariant concentrations of suspended particles, calculations predict that sorptive reactivity in the water column will result in a significant modification of the trace metal composition of suspended particles. Seasonal measurements of trace metals on suspended particles available to 1M NH_4OAc (an operational measure of an exchangeable particulate fraction) indicate a persistent reduction from the upper estuary to the lower estuary (Muller, Tranter & Balls, 1994); for Cd, an exchangeable particulate concentration ratio, X^{S2}/X^{S1}, is about 0.20. Although an order of magnitude greater than the adsorbed particulate ratio calculated (Equation (3.6)), reflecting analytical difficulties associated with the determination of an exchangeable fraction and the assumption in the calculations that the adsorbed metal is completely exchangeable (Equations (3.6)–(3.9)), these field measurements demonstrate a distinct seaward modification of the Cd content of the suspended particle population. Calculations also predict that accompanying changes in the dissolved phase are likely to be difficult to detect. Thus, conservative distributions of dissolved trace metals are generally observed (Mackay & Leatherland, 1976; Muller, Tranter & Balls, 1994), deviations from the theoretical dilution line being accounted for by multiple straight line segments resulting from a variety of tributary inputs of different compositions (Mackay & Leatherland, 1976), and direct anthropogenic inputs to the tidal estuary (Muller Tranter & Balls, 1994).

Although the arguments and calculations presented herein are qualitatively compatible with field observations from two contrasting estuaries, accurate quantitative predictions will rely on a better definition of chemical parameters such as α and sorption time constants, and a greater understanding of estuarine sediment dynamics including the interaction between suspended populations and subtidal/intertidal deposits. Nevertheless, the partitioning data and sorption models are particularly useful *per se* in providing a general understanding of the likely environmental transport and fate of constituents about which relatively little is known, such as PCBs and dioxins.

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MODELLING CONTAMINANT GEOCHEMISTRY IN ESTUARIES

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Abstract—A numerical model predicting the transport and fate of contaminants in estuaries has been developed and tested. The modelling framework allows for (1) advection and diffusion of contaminants in the dissolved phase, (2) partitioning of contaminants between the dissolved and adsorbed phases, (3) input of adsorbed contaminants to the water column due to the resuspension of bed sediment, (4) accumulation of contaminants in the bed sediment due to deposition of suspended sediment and (5) in the case of organic contaminants, losses due to volatilization and biodegradation. Particle-water interactions throughout the estuary are encoded using relationships between empirically-derived partition coefficients and salinity, which have been coupled to an established two-dimensional depth integrated hydrodynamic and sediment model configured for the Humber Estuary, England, to simulate the distributions and transport of cadmium and zinc. The model has been run for a range of tidal and river flow conditions, and has been calibrated against field measurements of hydrodynamic parameters, salinity, suspended sediment concentrations and dissolved trace metal conentrations, and validated using independent dissolved trace metal data sets. The application of the model is discussed to a wide range of estuaries where the fate of trace metal contaminants is of immediate concern.

Key words—modelling, trace metal contaminants, estuaries, partitioning, water quality, geochemistry

NOMENCLATURE

t = time
x and y = horizontal orthogonal co-ordinates
U = depth averaged velocity component in the x direction
V = depth averaged velocity component in the y direction
H = total depth of water column
C = dissolved contaminant concentration (w/v)
$D_{xx}, D_{xy}, D_{yx}, D_{yy}$ = depth averaged longitudinal dispersion and turbulent diffusion coefficients in the x and y directions
S_0 = source or sink of dissolved contaminant
S_d = first-order decay rate or growth rate of dissolved contaminant
S_k = total kinetic transformation rate
K_D = partition coefficient (v/w)
P = adsorbed concentration of contaminant (w/w)
S = salinity
b = gradient of $\ln K_D^0$ vs $\ln (S + 1)$
K_D^0 = partition coefficient in fresh water ($S = 0$)
Δt = time step
Δx = size of computational grid in the x and y direction
DMS = change in mass of adsorbed contaminants due to advection and diffusion of suspended sediments
Q_A = depth integrated velocity component in the x direction at face A
SPM = concentration of suspended sediment (cohesive and non-cohesive)
SPM_A = SPM at boundary A (see Fig. 1)
P_{A1} = concentration of adsorbed contaminant in cell $i - 1, j$ at time $n\Delta t$ if flow is moving from cell $i - 1, j$ to cell i, j, or in cell i, j at time $n\Delta t$ if flow is from cell i, j to cell $i - 1, j$
$(D_{xx})_A$ = D_{xx} at boundary A (see Fig. 1)
P_{A2} = concentration of adsorbed contaminant in cell i, j at time $n\Delta t$ if derivative of SPM with respect to x at boundary A is out of cell i, j, or in cell $i - 1, j$ at time $n\Delta t$ if derivative of SPM with respect to x at boundary A is into cell i, j
G = change in concentration of contaminant in water column due to deposition of suspended sediment and resuspension of bed sediment
SPM^* = change in mass of SPM due to resuspension or deposition
P^* = concentration of adsorbed contaminant in bed sediment if resuspension occurs, or in suspended sediment if deposition occurs

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C' = concentration of dissolved contaminant due to advection and diffusion of the fluid

P_b = concentration of adsorbed contaminant in bed sediment

F = rate constant, positive for sediment deposition and negative for sediment erosion.

INTRODUCTION

With increasing public awareness of the environmental impact of pollutant discharges and the implementation of more stringent legislation relating to industrial emissions (e.g. the Integrated Pollution Control and the EC Integrated Pollution Prevention and Control Directive; Commission of the European Communities, 1993), pollution managers have sought accurate models to predict the transport and fate of trace metals and organic contaminants. Estuaries are favourable sites for industrial and urban development but are physically and chemically highly complex environments. In the water column contaminants may be transported either in solution, or associated with suspended particles. The partitioning between these two phases is dependent on estuarine controlling variables, including salinity, pH, availability of complexing species and the physical and chemical characteristics of suspended particles and is, therefore, difficult to predict from theoretical considerations.

The parameterization of estuarine particle–water interactions of pollutants may, however, be achieved empirically by examining the time-dependent behaviour of a contaminant with its radioactive counterpart added to natural samples maintained under carefully controlled laboratory conditions (Turner *et al.*, 1993; Turner and Millward, 1994). This approach yields particle–water interaction functions relevant to reaction conditions encountered in estuaries, together with the quantification of adsorption kinetics through the derivation of reaction time constants. In this work, the application of site-specific, empirically-derived partition coefficients to the modelling of estuarine contaminants is demonstrated using a two-dimensional (2-D) depth integrated hydrodynamic and transport model of the Humber Estuary, England (Falconer and Chen, 1991; Falconer and Owens, 1990), incorporating experimentally-derived partition coefficients for Cd and Zn.

DESCRIPTION OF THE NUMERICAL MODEL

The tidal and riverine water flows are calculated using a 2-D, depth-integrated, numerical hydrodynamic algorithm (Falconer and Owens, 1990). The advection and diffusion of dissolved contaminants due to the water flows, the potential increase in concentration from anthropogenic and atmospheric sources, and the kinetic transformation of chemical species are defined by the following equation:

$$\underset{\text{(i)}}{\frac{\partial CH}{\partial t}} + \underset{\text{(ii)}}{\left(\frac{\partial CUH}{\partial x} + \frac{\partial CVH}{\partial y}\right)}$$

$$- \underset{\text{(iii)}}{\frac{\partial}{\partial x}\left(HD_{xx}\frac{\partial C}{\partial x} + HD_{xy}\frac{\partial C}{\partial y}\right)}$$

$$- \underset{\text{(iii)}}{\frac{\partial}{\partial y}\left(HD_{yx}\frac{\partial C}{\partial x} + HD_{yy}\frac{\partial C}{\partial y}\right)}$$

$$- \underset{\text{(iv)}}{H(S_0 + S_d + S_k)} = 0 \qquad (1)$$

The terms S_d and S_k are the potential for volatization and/or degradation of organic compounds and the kinetic transformation rate, respectively, but these aspects of the model are not explored here. The term S_0 is either a source or sink of dissolved contaminants. The terms in equation (1) represent the change in concentration of the dissolved contaminant due to: (i) local effects; (ii) transport by advection; (iii) longitudinal dispersion and turbulent diffusion; and (iv) source or sink, decay or growth and kinetic transformation effects.

The distribution of contaminants between the dissolved and adsorbed particulate phases is defined by an empirically-derived equilibrium partition coefficient, K_D, as follows:

$$K_D = \frac{P}{C} \qquad (2)$$

where P and C are concentrations of contaminant adsorbed on suspended particles and in solution, respectively. The K_Ds employed represent quasi-equilibrium attained over 5 days but kinetic effects may be incorporated by defining the time-dependence of K_D as determined experimentally. K_D is varied as a function of salinity (S) in either one of the following two ways:

(i) using the relationship (Millward and Turner, 1995; Turner and Millward, 1994):

$$\ln K_D = b \ln (S + 1) + \ln K_D^0 \qquad (3)$$

where b and K_D^0 are constants;

(ii) using explicit tabulations of measured values of K_D as a function of salinity.

Fine cohesive sediments ($< 2\ \mu$m) are modelled as permanently suspended particles (wash load) using equation (1) with S_0, S_d and S_k set to zero. Flocculation, consolidation and erosion/deposition are not accounted for owing to their poor definition. The advection, diffusion and erosion/deposition of coarser non-cohesive sediments are modelled using the formulation developed by van Rijn (1984a, b).

The change in mass of adsorbed contaminant in a computational cell i, j due to the advection and diffusion of the suspended sediment during the time interval $n\Delta t$ to $(n + 0.5)\Delta t$, is calculated from:

$$\mathrm{DMS} = M_A - M_B + M_D - M_C \qquad (4)$$

where M_A, M_B, M_C and M_D are the masses of adsorbed contaminants carried across the cell boundaries A, B, C and D, respectively (Fig. 1). M_A is evaluated using:

$$M_A = \frac{\Delta t \Delta x}{2}\left[Q_A \mathrm{SPM}_A P_{A1} - H_A (D_{xx})_A \left.\frac{\partial \mathrm{SPM}}{\partial x}\right|_A P_{A2}\right] \qquad (5)$$

where Δx is the size of the computational grid in the x and y direction, Q_A is the depth integrated velocity component in the x direction at boundary A and SPM_A is the concentration of suspended sediment (cohesive and non-cohesive) at boundary A. P_{A1} is the concentration of adsorbed contaminant in cell $i - 1, j$ at time $n\Delta t$ if the flow is moving from cell $i - 1, j$ to cell i, j, or concentration of adsorbed contaminant in cell i, j at time $n\Delta t$ if the flow is from cell i, j to cell $i - 1, j$. P_{A2} is the concentration of adsorbed contaminant in cell i, j at time $n\Delta t$ if the derivative of SPM with respect to x at boundary A is out of the cell i, j, or concentration of adsorbed contaminant in cell $i - 1, j$ at time $n\Delta t$ if the derivative of SPM with respect to x at boundary A is into the cell i, j. The mathematical quantities M_B, M_C and M_D are defined similarly.

It is assumed that the bed sediment is a single well-mixed layer and that input of contaminant to the water column by resuspension is spontaneous. Changes in concentration of contaminant in the water column due to the deposition or resuspension of sediment are calculated using:

$$G = \mathrm{SPM}^* P^* \qquad (6)$$

where SPM^* is the change in mass of the suspended sediment concentration due to resuspension or deposition, P^* is the concentration of adsorbed contaminant in the bed sediment if resuspension occurs, or concentration of adsorbed contaminant of the suspended sediment if deposition occurs.

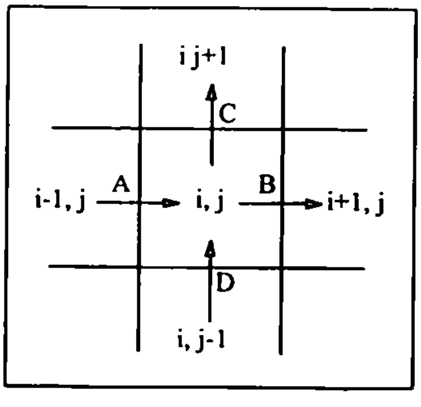

Fig. 1. Advection and diffusion of suspended sediments into the computational cell i, j from its four neighbours across boundaries A, B, C and D.

At time $(n + 0.5)\Delta t$ and in computational cell i, j, the concentrations of dissolved $(C^{n+1/2})$ and adsorbed $(P^{n+1/2})$ contaminants are determined from the mass balance:

$$C^{n+1/2} + \mathrm{SPM}^{n+1/2} P^{n+1/2} = C^n + \frac{P^* \mathrm{SPM}^n H^n (\Delta x)^2 + \mathrm{DMS}}{H^{n+1/2} (\Delta x)^2} + G \qquad (7)$$

where

$$P^{n+1/2} = (K_D)^{n+1/2} C^{n+1/2} \qquad (8)$$

The concentration of adsorbed contaminant in the bed material, P_b, in the cases of deposition and erosion, respectively, is calculated from:

$$\frac{dP_b}{dt} = FP \qquad (9)$$

and

$$\frac{dP_b}{dt} = FP_b \qquad (10)$$

where F is a rate constant which is positive in equation (9) and negative in equation (10).

HUMBER ESTUARY APPLICATION

Model set-up

The numerical model described above has been used to study the spatial and temporal distribution of dissolved and suspended particulate trace metals in the Humber Estuary [Fig. 2(a)]. The estuary is well-mixed (Gameson, 1982) allowing the use of a 2-D depth integrated formulation. The differential equations were solved using an implicit alternating direction finite difference scheme. A 2-D computational square grid, with a cell size of 300 × 300 m, covers the entire estuary [Fig. 2(b)] and a time step of 60 s is employed. The fresh water discharge from the Rivers Trent and Ouse is modelled as a numerical pipeline (two computational cells wide) feeding into the estuary at Trent Falls. The length of the pipeline and the depths of its cells are chosen such that (i) the tidal volume is the same as that of the two rivers and their tributaries combined and (ii) the cells at the upstream extent of the pipeline are not subject to tidal influences. At the seaward end, a tidal elevation boundary [line AB shown in Fig. 2(b)] is used to drive the hydrodynamic module. A no-flow free streamline boundary [line BC shown in Fig. 2(b)] is placed along a drogue observed streamline (British Transport Docks Board, 1974). The depth of the domains used in the calculations were determined from the recent bathymetric data supplied by Associated British Ports (ABP).

A well-tested hydrodynamic module (Falconer, 1993) is employed to calculate time and spatially

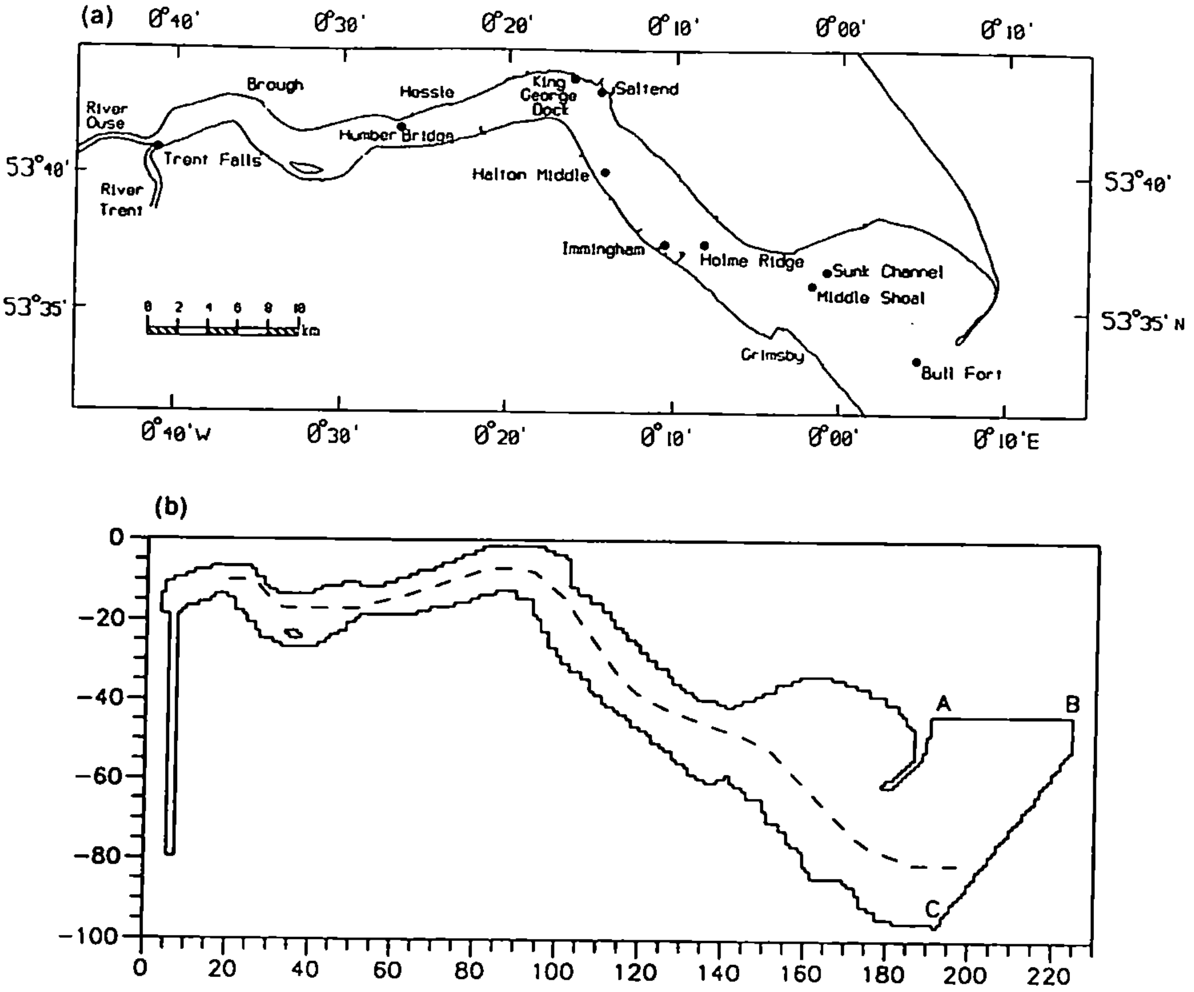

Fig. 2. (a) The study area. (b) The modelling grid. AB represents the water elevation boundary and BC represents the no-flow boundary. The dotted line represents the track along which model results of dissolved contaminants and salinity are plotted in Figs 6 and 8. Labellings on the x and y axes are the model co-ordinates.

varying water elevations and water velocities. Two tides (24.8 h) of water elevation data are used to provide the driving forces at the seaward boundary. The salinity and fine sediment distributions are calculated using equation (1), with the term (iv) set to zero. The transport of coarse (non-cohesive) sediments is evaluated utilizing a recently developed sediment transport module (Owens, 1987; Lin and Falconer, 1995) and the size composition of coarse sediments in the Humber Estuary is taken from Owens (1987). Flooding and drying of intertidal zones are also allowed for using the algorithms developed by Falconer and Chen (1991).

Calibration and validation of hydrodynamic, sediment transport and salinity modules

The physical data for calibration and validation of the hydrodynamic, sediment transport and salinity modules were obtained from (i) published information (Lowry *et al.*, 1992), (ii) hydrographic measurements undertaken during axial and anchor station surveys in the Humber Estuary from the National Rivers Authority (NRA) vessel *Sea Vigil* during October 1993 and (iii) measurements undertaken by the NRA and ABP.

The hydrodynamic module was calibrated against water elevation data obtained by ABP on 18 October 1993 at the Humber Bridge, King George Dock and Immingham. Water elevation data measured at Bull Fort during the same period were used to drive the model at the seaward boundary. River discharges were estimated from the daily mean flow data supplied by the NRA. The model was also run under various tidal conditions and was found to simulate accurately published velocity data (British Transport Docks Board, 1974; Hydraulic Research Station, 1970) at 12 stations distributed throughout the estuary for neap and spring tides.

The coarse sediment transport module was calibrated against suspended sediment (> 40 μm) concentrations measured in September 1979, under a spring tide and with a low river discharge (76 $m^3\ s^{-1}$), at Middle Shoal, Sunk Channel and Halton Middle (British Transport Docks Board, 1980). The model was run under similar conditions and the results are shown in Fig. 3 with high water (HW) times referenced

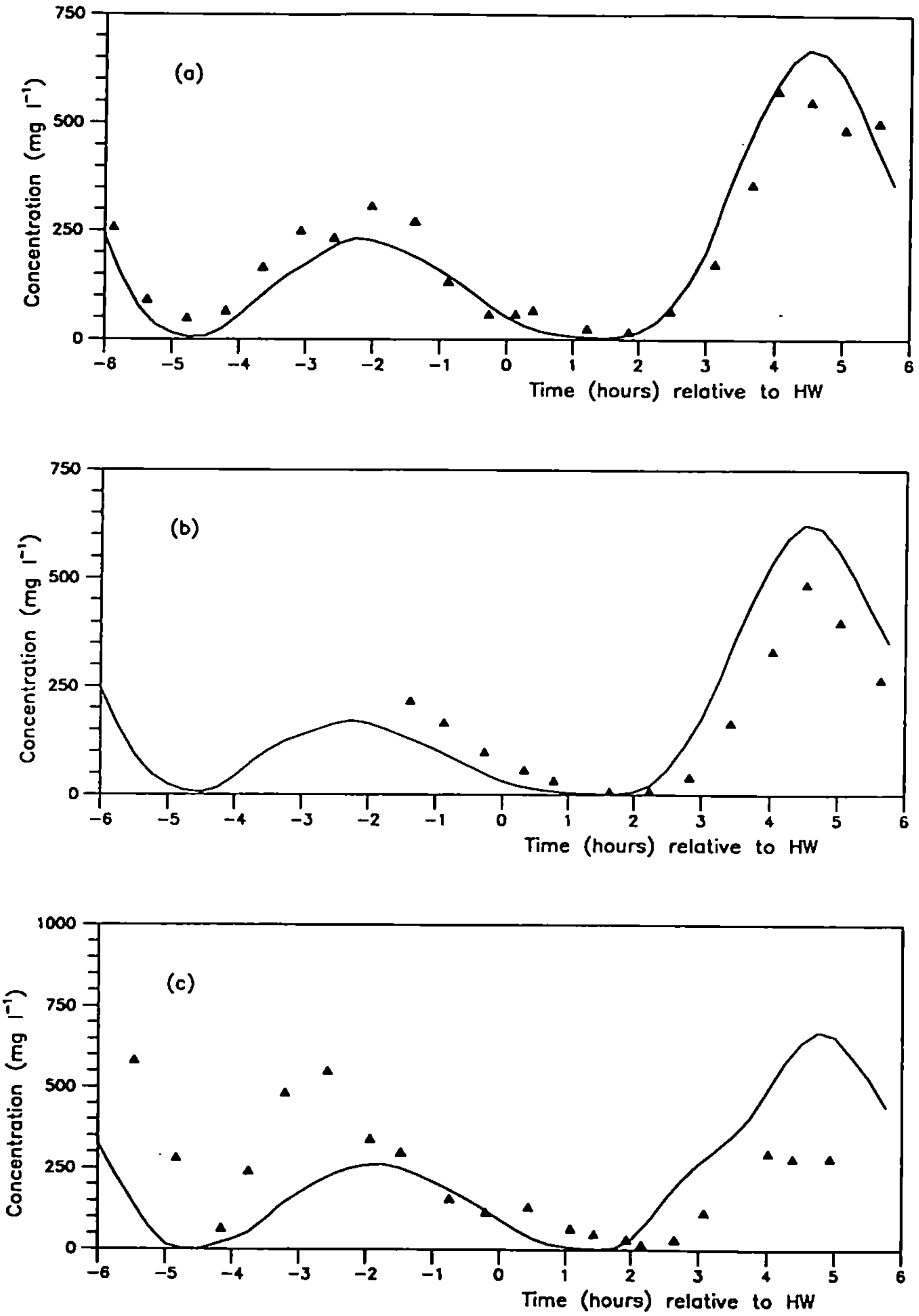

Fig. 3. Measured (▲) and modelled (—) distributions of coarse suspended sediment concentrations for: (a) Middle Shoal; (b) Sunk Channel; and (c) Halton Middle. High Water (HW) is referenced to Immingham.

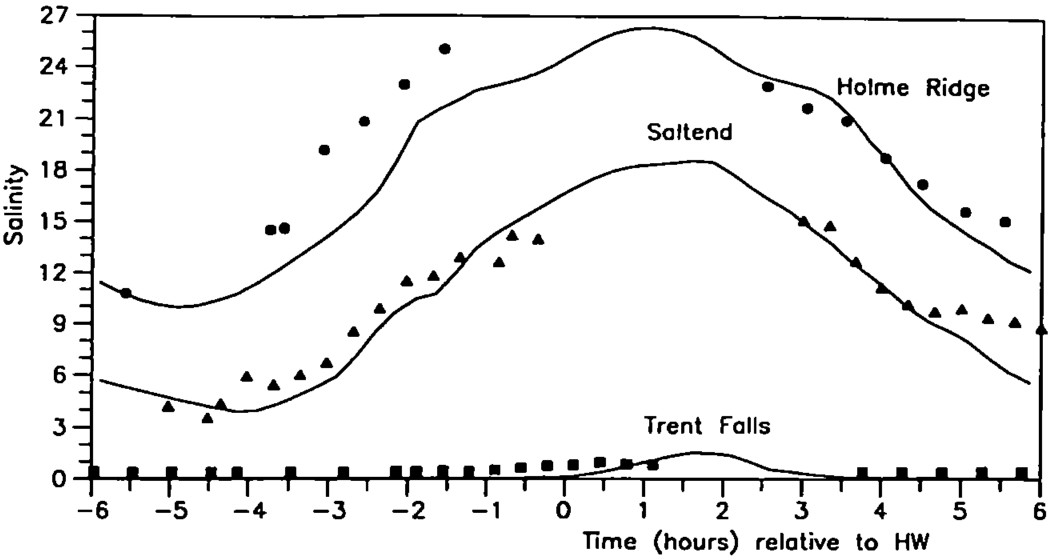

Fig. 4. Measured (■, ▲, ●) and modelled (—) distributions of salinity at Trent Falls, Saltend and Holme Ridge. High Water (HW) is referenced to Immingham.

to Immingham. Although good agreement was obtained with field data at Middle Shoal and Sunk Channel, 3-D effects on the flood plain near Halton Middle result in less satisfactory agreement here.

The model was run under a spring tide to calibrate the salinity transport module against salinity data collected at Saltend and Holme Ridge during 14 and 15 October 1993. The average river discharge into the modelled area was estimated at 454.6 $m^3 s^{-1}$. The initial distribution of salinity over the entire estuary was determined from published values (Gameson, 1982). After calibration, model results were consistent with observations at Saltend, Holme Ridge and Trent Falls (Fig. 4).

Diagnostic modelling of trace metals

The performance of the contaminant transport and accumulation module was assessed by running the model for the following partitioning scenarios under a typical spring tide and a high river discharge of 454.6 m^3 s^{-1}: (1) no partitioning of contaminants between the dissolved and adsorbed phases, i.e. $K_D = 0$; (2) no salinity dependence of K_D (i.e. setting the value of b in Table 1 to zero); (3) salinity dependence of K_D based on empirically-derived partitioning results for Cd (see Table 1); and (4) increasing the salinity dependence of K_D (increasing b to -1.5). The boundary values of permanently suspended fine sediment (wash load) were set at 450 and 50 mg l^{-1} at the river and seaward ends, respectively (Gameson, 1982). The boundary values of the dissolved contaminant concentration were based on observations of dissolved Cd and were 0.5 μg l^{-1} at the freshwater gauging station on the River Ouse and 0.06 μg l^{-1} at the seaward end (Edwards *et al.*, 1987; Table 1). The rate constant F in equations (9) and (10) was kept at zero. The freshwater Cd concentration and total river flow yield a Cd flux to the estuary of 19 kg day^{-1}, which is higher than the mean river input observed in 1990 (7.1 kg day^{-1}) and the combined input of 3.0 kg day^{-1} from sewage and industrial effluents (PARCOM, 1991).

Dissolved contaminant concentrations derived from a 2-D modelling system are not a single-valued function of salinity (Wood and Baptista, 1993), as is evident from the spatial distributions of salinity and dissolved constituent at HW calculated using partitioning data for scenario 3 (Fig. 5). Thus, in order to diagnose the geochemical reactivity simulated by the model in terms of dissolved contaminant–salinity plots (Millward and Turner, 1995) the concentrations of dissolved contaminant at HW along the axial track given in Fig. 2(b) were plotted as a function of salinity for the four partitioning scenarios. Initial and resulting (after 5 tidal cycles) distributions of dissolved contaminant are shown in Fig. 6. The axial distributions of permanently suspended fine sediment (wash load) and coarse suspended sediment are shown in Fig. 7 and

Table 1. End-member dissolved metal concentrations (Edwards *et al.*, 1987) and empirically-derived partitioning functions [calculated according to equation (3) using empirically-derived K_Ds; Turner *et al.*, 1993] for the Humber Estuary

Metal	Freshwater end member (μg l^{-1})	Seaward end member (μg l^{-1})	K_D^0 (ml g^{-1})	b
Zn	15.0	3.0	6400	+0.034
Cd	0.5	0.06	6600	−0.653

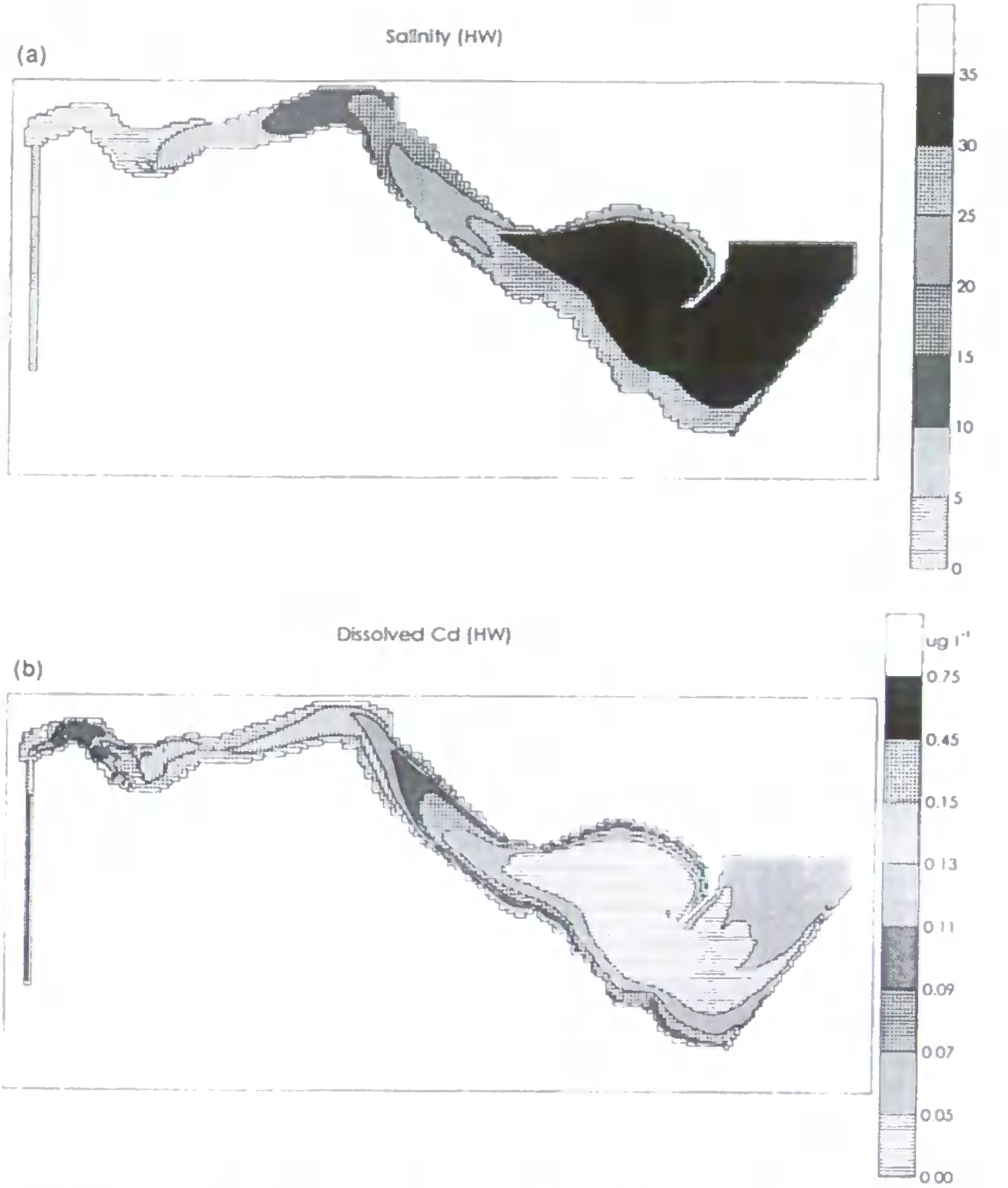

Fig. 5. The modelled spatial distributions (after 5 tidal cycles) of (a) salinity and (b) dissolved Cd at HW (Immingham) under spring tide conditions and for a river discharge of 454.6 m^3 s^{-1}. $K_D^0 = 6600$ ml g^{-1} and $b = -0.653$.

reproduce the turbidity maximum which is a regular feature of the low salinity reaches of the estuary (Turner *et al.*, 1991). With no partitioning (scenario 1), the dissolved metal concentration varies linearly with salinity as expected from conservative behaviour, based on dilution only. When particle–water interactions are incorporated into the code (scenario 2), the dissolved concentration–salinity plot exhibits negative deviation from the theoretical dilution line representing removal of dissolved contaminant through sorption onto suspended particle surfaces. As the partitioning decreases exponentially with salinity (scenarios 3 and 4), sorptive removal is more than counterbalanced by desorption from seaward advecting suspended particles as they encounter a reduction in partitioning with increasing salinity and a broad peak in the contaminant–salinity plots is produced; this peaking effect is enhanced and shifted down-estuary as the magnitude of the parameter *b* is increased.

The results for scenario 3, incorporating partitioning data for Cd (Turner *et al.*, 1993), are shown in more detail in Fig. 8. Here, values of dissolved contaminant concentration and salinity were calculated over a tidal cycle along the axial track shown in Fig. 2(b), and, for a given salinity, an averaged value of dissolved contaminant concentration was plotted together with its standard deviation. Also given is a composite plot of dissolved Cd under various tidal conditions and river discharges, based on published values (Edwards *et al.*, 1987) and measurements undertaken on samples collected during October 1993. The mid-estuarine maximum, which is a general characteristic of estuarine dissolved Cd distributions (Elbaz-Poulichet *et al.*, 1987; Bewers and Yeats, 1989), is evident from the field data. Although a better fit with observed distributions could be achieved by increasing the magnitude of b, it is suspected that dissolved Cd concentrations in the Humber are augmented by additional inputs which have not been accounted for in the simulation. Including a single substantial mid-estuarine point source of dissolved metal (i.e.

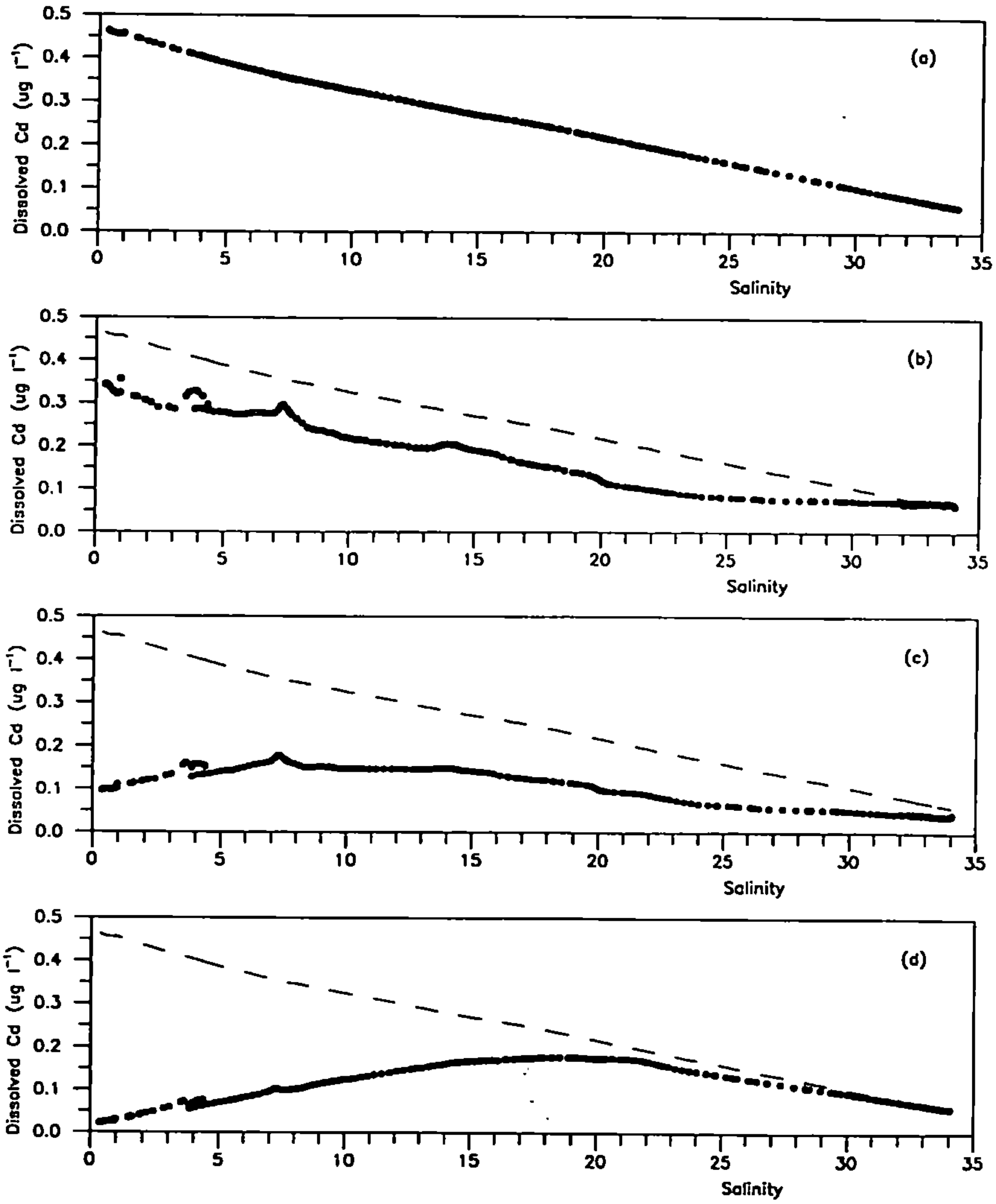

Fig. 6. Initial (– – –) and resulting (after 5 tidal cycles; · · ·) distributions of dissolved Cd at HW (Immingham) along the axial track shown in Fig. 2(b). (a) $K_D = 0$; (b) $K_D^0 = 6600$ ml g^{-1} and $b = 0$; (c) $K_D^0 = 6600$ ml g^{-1} and $b = -0.653$; (d) $K_D^0 = 6600$ ml g^{-1} and $b = -1.5$.

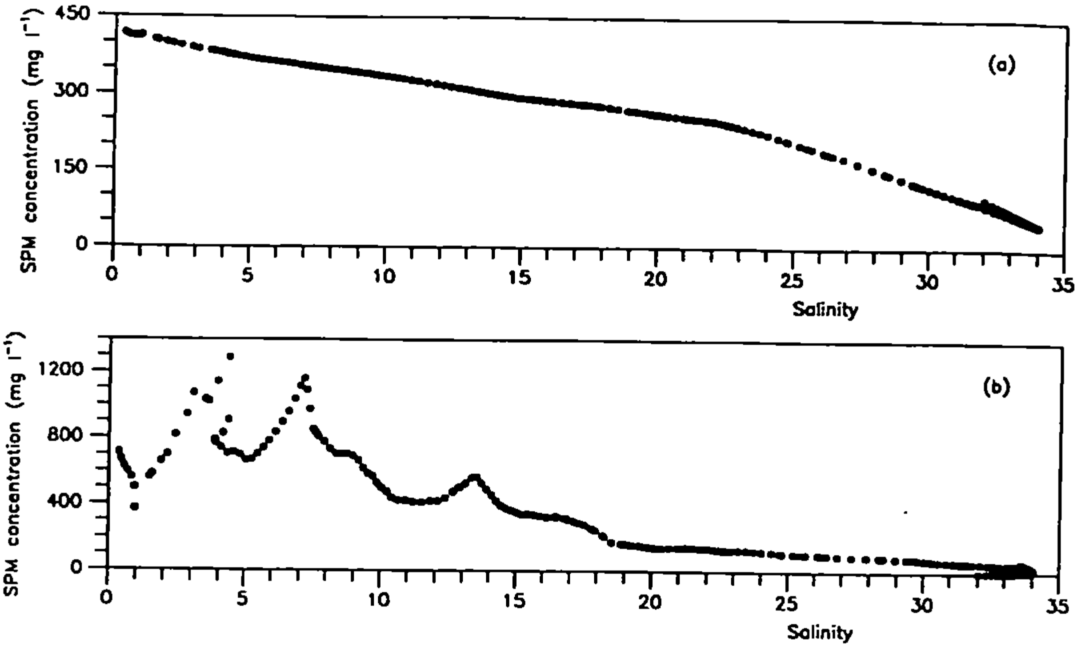

Fig. 7. Resulting distributions of suspended sediment concentration (after 5 tidal cycles) along the axial track shown in Fig. 2(b). (a) Permanently suspended sediment (wash load) and (b) coarse suspended sediment.

inclusion of S_0) 0.012 m^3 s^{-1} and Cd = 10,000 μg l^{-1} (equivalent to 10 kg Cd day^{-1}) did not make a significant difference to the computed Cd distribution. The lack of agreement between observed and calculated Cd distributions may be due to (i) the presence of inputs considerably in excess of 10 kg day^{-1}, possibly via porewater infusion, and/or (ii) analytical uncertainties in the dissolved Cd determinations. Clearly, further axial distributions of dissolved Cd are required, together with a better definition of sediment porewater processes.

Calibration and validation of the contaminant transport and accumulation module

The contaminant transport and accumulation module was calibrated against dissolved and particulate trace metal data measured at Bull Fort (near the mouth of the Humber Estuary), as remote as possible from anthropogenic inputs. Samples were collected during Challenger Cruise CH42 of the NERC North Sea Project on 27 December 1988 under mid-tide conditions and with an estimated river discharge of

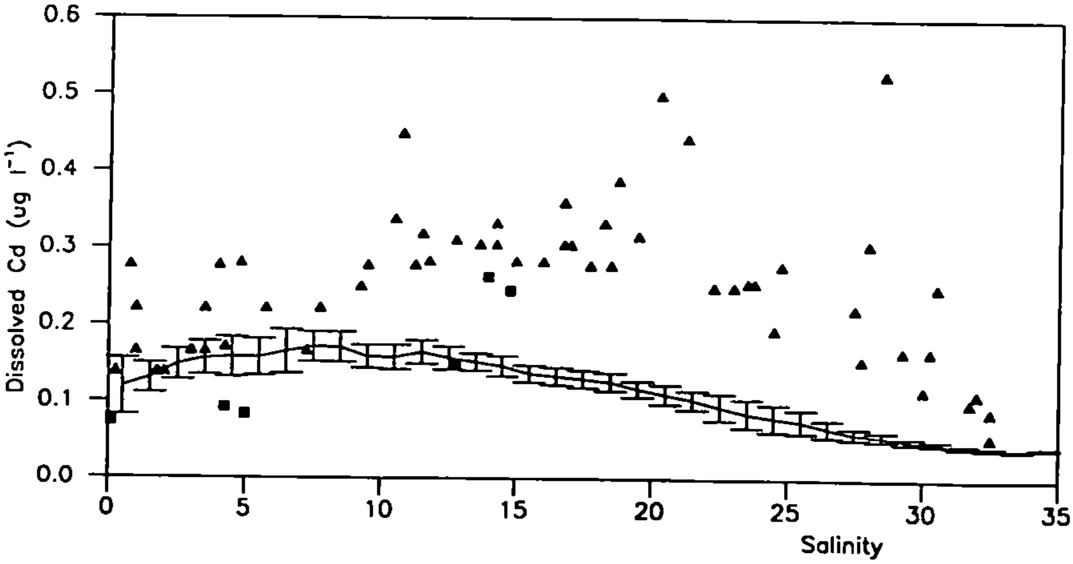

Fig. 8. Dissolved Cd as a function of salinity. The continuous line with error bars represents model results obtained as described in the text. Triangles represent field data from Edwards *et al.* (1987); squares represent field data collected during the *Sea Vigil* survey in October 1993.

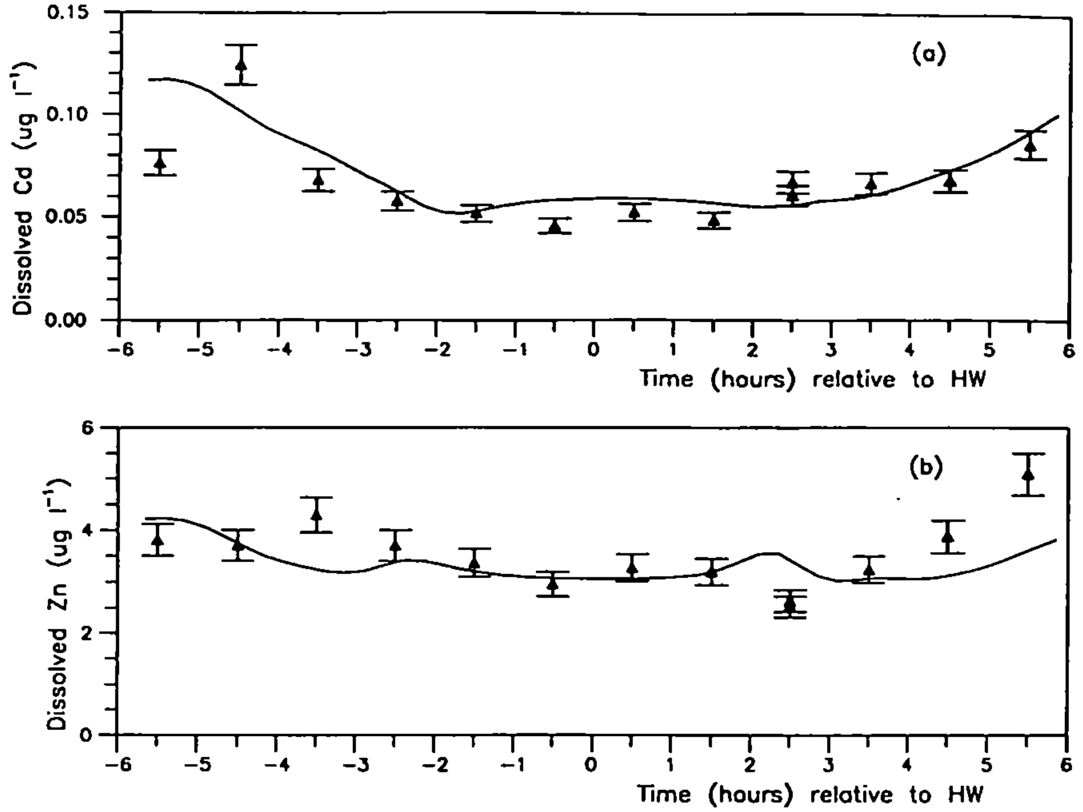

Fig. 9. Modelled (—) and measured (▲, 27 December 1988) distributions of dissolved (a) Cd and (b) Zn concentrations as a function of time at Bull Fort. Error bars encompass the analytical uncertainty of the dissolved metal analysis. HW is referenced to Immingham.

405 $m^3\ s^{-1}$ (Lowry *et al.*, 1992). Cadmium and zinc were selected because their partitioning characteristics have been defined (Turner *et al.*, 1993). The boundary values of dissolved metal concentrations and the empirically-derived partitioning parameters are shown in Table 1.

The model results and observed data (including error bars defining the analytical uncertainties; Althaus, 1992) are plotted in Figs 9 and 10. Observed distributions of dissolved Cd and Zn are reasonably well reproduced by the model; however, observed and modelled concentrations of particulate Cd and Zn differ by an order of magnitude (see Fig. 10). This discrepancy is the result of the difference between the particulate metal associations that are modelled and measured. By definition of the partition coefficient [equation (2)] the model determines the adsorbed fraction of particulate metal, whereas the analysis of particulate metals entails digestion of suspended sediment samples in 1 M HCl which non-selectively dissolves a greater fraction of particulate metals. This laboratory analysis includes those particulate metals occluded within oxides and more refractory minerals which are unable to participate in short-term biogeochemical reactions.

The model was run for a neap tide and with a river discharge of 107 $m^3\ s^{-1}$ to validate it against a second trace metal data set, determined from samples collected at Bull Fort during the NERC North Sea Project Challenger Cruise CH69 on 2 August 1990. Distributions of dissolved Cd and Zn are reasonably well reproduced by the model.

CONCLUSIONS

A geochemical module based on empirically-derived partition coefficients, coupled to a two-dimensional depth integrated hydrodynamic model of the Humber Estuary, has formed the basis of a geochemical contaminant transport model. The model simulates reasonably accurately the axial and tidal distributions of dissolved Cd and Zn in the estuary, although the particulate adsorbed distributions are difficult to verify owing to a lack of analytical techniques capable of determining an adsorbed component of particulate metals. Because the chemical driving variables are empirically derived, the simulation of other metals and trace organic contaminants will rely on further experimental studies using site-specific samples. The model has potential for the more general diagnosis and prediction of contaminant cycling in natural environments and further refinements will provide a valuable tool for the solution of practical problems encountered in water quality management.

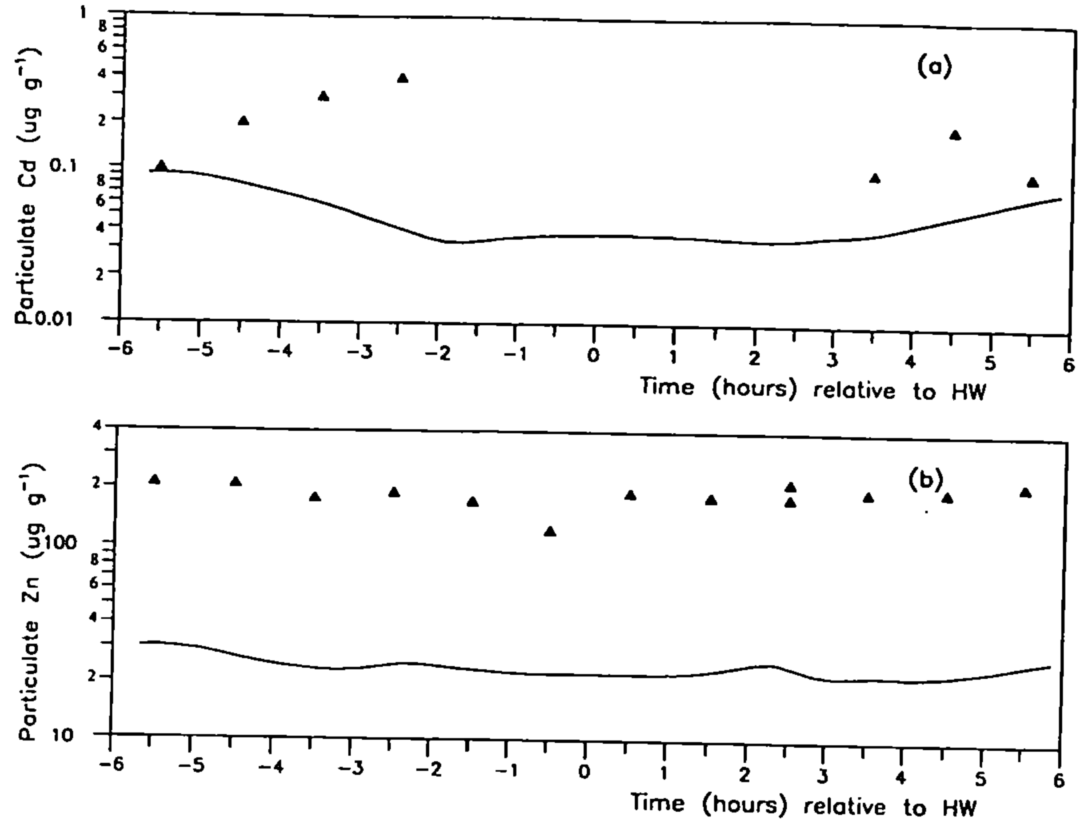

Fig. 10. Modelled (—) and measured (▲, 27 December 1988) distributions of particulate (a) Cd and (b) Zn concentrations as a function of time at Bull Fort.

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Distribution and Partitioning of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans and Polychlorinated Biphenyls in the Humber Estuary, UK

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The distribution and concentration of polychlorinated dibenzo-para-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in Humber Estuary bed sediment and in suspended particulate matter were extensively studied. Dioxin concentrations in sediments ranged from below detection to 3830 pg g^{-1} and PCB concentrations were from non-detectable to 84 ng g^{-1}. These concentrations were low in comparison to other estuaries. The concentrations of chlorinated organics were found to be correlated with sediment lipid content, which is a significant factor in determining the contaminant distribution in the Humber Estuary. Laboratory experiments were carried out using ^{14}C-radiolabelled compounds to determine partition coefficients (K_D). A K_D of 2.5×10^5 was determined for 2,3,7,8-TCDD and that of 6.4×10^4 for 2,2′,5,5′-TCB; these did not vary significantly with salinity. There was no evidence in either the concentration data or the homolog profiles that contamination from tributaries to the Humber Estuary had penetrated the estuary in significant quantities. Copyright © 1996 Elsevier Science Ltd

The occurrence of chlorinated organic compounds in the marine environment is of international concern due to their persistence, toxicity and bioaccumulation in the lipid tissues of marine biota (Delbeke & Joiris, 1988; Gribble, 1994; Tanabe *et al.*, 1994). Chlorinated organic compounds include dioxins comprising polychlorinated dibenzo-para-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs). These compounds have not been well studied in the marine environment, but are again coming under closer scrutiny following the publication of a recent US EPA review of the toxicity of dioxins (US EPA, 1994a–c). The Humber Estuary, north-east UK, is considered to be an important source of pollutants to the North Sea (North Sea Task Force, 1993). Although high concentrations of dioxins have been detected in bed sediments at the mouth of the Estuary (Evers *et al.*, 1993), Tyler *et al.* (1994) found little evidence of contamination in the lower Humber Estuary and other coastal sites around the UK. However, there are many possible sources of the chlorinated organics in the marine environment and concern has been expressed by the National Rivers Authority (NRA) over significant concentrations of dioxins in sediments in the vicinity of a chlorophenol plant located on a tributary to the River Rother (NRA, 1994), approximately 70 km south-east of the River Trent (Fig. 1a). The mechanisms by which dioxins may be transported from sources within estuaries is largely unknown, but the hydrophobic nature of these compounds suggests that particle-water interactions involving suspended particulate matter (SPM) could be significant (Murphy *et al.*, 1994; Hegeman *et al.*, 1995).

This paper presents the results of the first comprehensive survey of PCDDs, PCDFs and PCBs in bed sediments and SPM of the Humber Estuary and study of partitioning behaviour using ^{14}C-labelled dioxin and PCB compounds.

Materials and Methods

Sampling

Samples were collected during two surveys of the Humber estuary; a limited inter-tidal sampling survey carried out in summer 1991 by the Ministry of Agriculture, Fisheries and Food (MAFF) as part of the CIROLANA 1991 cruise, and an extensive estuary survey in October 1993. Sediment samples were collected using a Shipek grab for sub-tidal samples and by hand for inter-tidal samples. All samples were stored in hexane-washed glass jars with foil cap liners. Suspended particulate matter was collected by bulk filtration (~750–1000 ml) through 0.7 μm hexane-

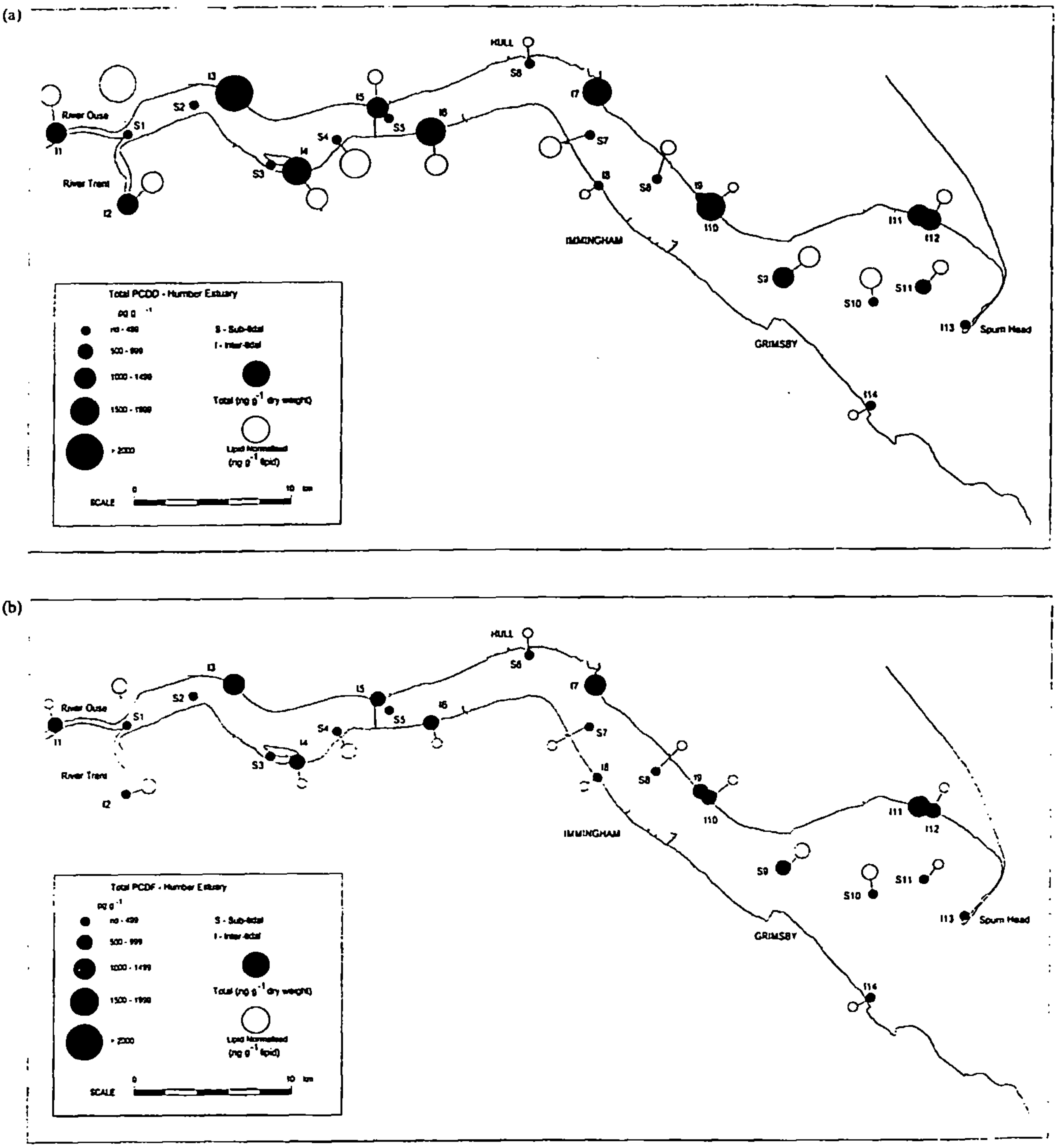

Fig. 1 (a) PCDD distribution in the Humber Estuary expressed on a pg g^{-1} and pg g^{-1} lipid basis. (b) PCDF distribution in the Humber Estuary expressed on a pg g^{-1} and pg g^{-1} lipid basis.

washed Whatman GF/F filters using an all glass apparatus. Between 100 and 290 mg was collected by this method. Filters were stored in hexane-washed foil wraps. All samples were stored in the dark at −20°C prior to analysis.

Analysis

Chlorinated organic compound analysis was carried out using established GC-MS methods (Pettit *et al.*, 1990) in accordance with agreed acceptance criteria and quality controls for PCDD/DF analysis (Ambidge *et al.*, 1990). Sediments were sieved through a 1 mm mesh and oven-dried at 40°C prior to analysis. Full analytical methodologies can be found in Tyler *et al.* (1994). All 17 2,3,7,8-substituted PCDD and PCDF congeners were quantified together with the homolog totals (tetra- to octa-). Total PCB concentration and the ICES 7 congeners (IUPAC numbers 28, 52, 101, 118, 153, 138 and 180) were also resolved. Two full procedural 'blind' analyses were also submitted for analysis. These are

TABLE 1
Mean and standard deviations for two samples analysed in quadruplicate.

	Sample 13 (pg g^{-1})			Sample 16 (pg g^{-1})		
Homologue	Mean	SD	%SD	Mean	SD	%SD
2378-TCDD	7	3	43	2	1	41
TCDD	370	54	15	237	51	21
PeCDD	212	26	12	149	17	11
HxCDD	110	16	14	77	12	16
HpCDD	302	47	16	219	47	21
OCDD	1775	64	3	1231	148	12
TCDF	137	14	10	99	21	21
PeCDF	277	35	13	182	53	29
HxCDF	114	13	12	79	10	13
HpCDF	97	25	25	75	10	14
OCDF	427	12	3	303	49	16
PCDD	2777	104	4	1915	210	11
PCDF	1054	67	6	738	65	9
PCDD/DF	3831	163	4	2654	255	10
TEQ	24	5	19	14	2	11
Total PCB	72	13	17	53	7	13

reported as a mean and standard deviation (four replicates) in Table 1.

Apolar lipid content, defined operationally as the fraction partitioning into a two phase acetone–hexane system, was determined on all sediments collected on the 1993 survey following an established method (Delbeke *et al.*, 1990). Sediments were washed with Milli-Q water to remove salt and dried at low temperature. Samples were then extracted for 5 h in 10% acetone *n*-hexane. Lipid content was determined gravimetrically following removal of the polar extract. Reproducibility on replicate samples was found to be better than 9% on five sample runs.

Laboratory experiments

To investigate the partitioning behaviour of dioxins and PCBs in the Humber Estuary, a series of mixing experiments were conducted using ^{14}C-labelled compounds (Turner & Tyler, 1995). Such experiments allow partitioning behaviour to be studied under carefully controlled conditions without the difficulties encountered in determining concentrations analytically.

The experiments were conducted using river and marine end member samples containing SPM taken from the River Ouse and Humber Estuary. A simulated estuarine gradient was obtained by admixing the two end member samples. Radiolabelled 2,2′,5,5′-tetrachlorobiphenyl-UL-^{14}C (Sigma Chemical Co.), with specific activity of 13.32 mCi mmol^{-1}, or 2,3,7,8 tetrachlorinated dibenzo-*p*-dioxin-UL-^{14}C (Radian Corporation), with specific activity of 33 mCi mmol^{-1}, was used in the experiments. For each experiment 0.02 μCi of the radiolabelled compound was added in solvent to a 50 ml centrifuge tube. Following evaporation of the solvent, a 20 ml sample of natural water was added and the tube was shaken for 12 h. The tube was then centrifuged for 30 min at 3000 rpm to separate the suspended sediment. A 4 ml sample of the dissolved phase was removed and added to 10 ml of Ultima Gold scintillation cocktail (Canberra Packard). The particles were resuspended and flushed from the tube. The tube was then shaken with 4 ml hexane to remove the glass-adsorped ^{14}C compound. Two millilitres of the hexane was then added to the scintillant and all samples were counted on a Philips 4700 scintillation counter. Each experiment was carried out in triplicate or quadruplicate and the partition coefficient, K_D, calculated by mass balance from determination of the dissolved phase counts (CPM) and loss to the glass. The recovery of the ^{14}C spike using this method was typically >80%.

Results and Discussion

Concentrations and distribution

A summary of the analytical results are given in Table 2 with sample sites referenced in Fig. 1a. PCDD/DF analyses were summarized using the NATO/CCMS (or International) toxic equivalent factor (TEF) which sums the 17 2,3,7,8-substituted congeners on the basis of their toxic equivalence to 2,3,7,8-TCDD.

Total PCDD/DF concentrations in the Estuary ranged from non-detectable to 3826 pg g^{-1} (24.1 pg g^{-1} TEQ). Generally, these concentrations are elevated with respect to 'background' concentrations reported in the literature (e.g. total PCDD/DF between 10 and 100 pg g^{-1}; Turkstra & Pols, 1989). Oehme *et al.* (1993) reported concentrations in the range 440–1400 pg g^{-1} (5.5–17.2 pg g^{-1} TEQ; Nordic model) in northern North Sea waters. Previous work by these authors (Tyler *et al.*, 1994) reported PCDD/DF concentrations in coastal North Sea sediments of 43–209 pg g^{-1} (0.6–2.8 pg g^{-1} TEQ). Evers *et al.* (1993) reported PCDD/DF values in North Sea estuaries from 1006–4736 pg g^{-1}, with two samples taken at a station at the mouth of the Humber Estuary with total PCDD/DF values of 1846 pg g^{-1} (surface, <63 μm) and 10 557 pg g^{-1} (15 cm, <63 μm). No samples analysed as part of this survey reached concentrations as high as that of the 15 cm depth samples analysed by Evers *et al.* (1993), although surface samples concentrations were comparable with these data.

The distribution of total PCDD and total PCDF in the Estuary is shown in Figs 1a and 1b. Generally, PCDD/PCDF concentrations are higher in the finer accumu-

TABLE 2

Summary of PCDD, PCDF and PCB analyses and lipid determinations for all samples. Sample sites are indicated in Fig. 1a.

Homolog	Sample concentration (pg g^{-1})*																								
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	I1	I2	I3	I4	I5†	I6	I7†	I8	I9†	I10	I11†	I12	I13†	I14
2378-TCDD	0.8	<0.2	<0.2	2.8	<0.2	<0.2	1.3	0.4	1.7	0.5	1.3	4	3.5	7	2.6	20.2	2	0.6	<0.2	15	5	9.9	3.5	4.8	<0.2
TCDD	62	4.6	4	130	5.4	3.8	62	13	160	15	127	190	140	370	344	45.1	237	4.6	<2	148	190	222	116	53	<2
PeCDD	28	<4	<4	87	<5	<5	50	11.5	130	13	97	120	110	213	138	176	149	170	<4	49	150	206	144	40	<4
HxCDD	<10	<4	<4	<5	<5	<5	52	50	67	42	65	50	52	110	74	123	77	100	<10	52	69	83	56	21	<10
HpCDD	27	2.9	2	58	3.6	4.6	38	11.5	110	13	76	97	116	303	159	171	220	293	<2	80	150	151	140	31	<2
OCDD	140	19	15	378	29	20	223	115	538	62	390	850	745	1775	882	858	1232	1320	<5	154	1000	791	770	150	<5
TCDF	40	3.9	4.3	54	5.4	2.8	31	8.5	164	20	140	48	67	138	118	304	99	314	<2	163	120	284	52	66	<2
PeCDF	77	7	13.6	76	<5	13	44	12.7	136	23	102	144	160	278	256	148	182	164	<4	81	205	167	198	32	<4
HxCDF	20	<4	<4	37	<5	5.8	23	27	72	26	43	61	56	114	79	110	80	128	<10	86	72	170	67	32	<10
HpCDF	10	4.2	4	15.6	2.5	3.5	14	5.8	33	6.8	20	40	33	98	56	185	75	149	<4	68	47	194	56	39	<4
OCDF	10	5	7	120	17.8	10	40	29	216	23	162	210	172	428	247	196	303	429	<5	226	247	424	184	96	<5
PCDD	<267	<34.5	<29	<658	<48	<38.4	425	201	216	145	755	1307	1163	2777	1597	1373	1915	1888	<23	483	1559	1453	1226	295	<23
PCDF	157	<24.1	<32.9	302.6	<35.7	35.1	152	83	1005	98.8	467	503	488	1054	756	943	739	1184	<25	624	691	1240	557	264	<25
PCDD/DF	<424	<58.6	<61.9	960.6	<83.7	<73.5	577	284	621	244	1222	1810	1651	3831	2353	2316	2654	3072	<48	1107	2250	2693	1784	559	<48
TEQ	5.2	<1	<1	7.6	<1.2	<1.4	6.2	5.7	11.6	4	9.9	12.3	13.9	24.1	16.2	38.9	14.7	24.2	<1.4	23.6	16.3	30.9	13.4	9.3	<1.4
Total PCB (ng g^{-1})	6.6	2	1.3	32	1.6	1	37	3.8	43	5	36	44	39	72	67	-	53	-	-	-	27	-	84	-	-
Lipid (mg g^{-1})	0.13	nd	nd	0.43	nd	0.33	0.39	0.24	0.98	0.11	1.48	1.15	0.9	nd	1.55	-	1.63	-	1.41	-	3.28	-	1.77	-	0.09

*Sample concentration: S, Sub-tidal; I, inter-tidal.
†Collected on CIROLANA '91 cruise.
nd, not detected.

d inter-tidal sediments than the coarser sub-tidal bed iments. There appear to be higher concentrations in e inter-tidal sediments of the lower Estuary perhaps ggesting some anthropogenic input. The distribution f total PCBs is shown in Fig. 2 and shows similar atterns to the dioxin distribution, with concentrations ranging from non-detectable to 72 ng g^{-1}.

Source identification and homolog profile analysis

PCDDs and PCDFs arise from a numbr of well characterized sources including incineration, domestic fires, vehicle exhausts and chemical manufacturing processes involving the use of chlorine and sewage sludge. Under certain conditions it is possible to elucidate the source of dioxins found in environmental samples by comparing their homolog profiles or congener patterns with characteristic source 'fingerprints' (Swerev & Ballschmiter, 1989).

From the data in Table 2, no consistent pattern was observed between homolog profiles throughout the Estuary although many exhibited characteristics of combustion source profiles. It is likely in an industrialized estuary such as the Humber with several conurbations on its banks, that a multiplicity of diffuse and low concentration direct sources may exist. This will tend to confuse any potential source-occurrence matches between homolog profiles. Furthermore, the dynamic tidal environment of the Humber Estuary infers a reworking of sediments within the Estuary which could promote chlorination dependent differential transport masking source-occurrence related effects (Tyler *et al.*, 1994).

The NRA public register (NRA, 1994) indicated TEQ concentrations up to 64 000 pg g^{-1} in sediments of a tributary of the River Rother sampled in October 1991. In 1993, the concentrations in these sediments close to the chlorophenol facility ranged from 5144 to 45 311 pg g^{-1} TEQ. Although the industrial source is some distance from the Humber Estuary, there remains some concern over possible long-term transport from this site into the Estuary. Concentrations measured during this survey, particularly those samples taken in the River Ouse and River Trent, showed no evidence of any abnormal dioxin loads entering the Estuary. Furthermore a homolog profile analyis showed no obvious similarity between samples from sites near the chlorophenol plant and those from the Humber Estuary.

Suspended sediment sample concentrations

In addition to bed samples, suspended sediment samples were analysed for PCDDs, PCDFs and PCBs. Suspended sediment represents a major transport pathway for such hydrophobic contaminants and is an important determinant in transport studies. Considerable problems are apparent in collecting sufficient suspended sediment for analysis whilst avoiding gross contamination. Difficulty was encountered in achieving analytical detection limits. From nine samples analysed, PCDD/DF congeners could only be quantified in four samples. In these samples only 2,3,7,8 TCDD (3–4 pg g^{-1}) and 1,2,3,4,6,7,8 HpCDD (14–20 pg g^{-1}) were detected. These concentrations are comparable with bed sediment concentrations and although the data should be treated with caution, there is an indication that the suspended sediment adsorbed dioxin is probably derived from resuspended bed sediment. Further work in this important area is required using bulk filtration techniques to obtain more material for accurate quantification of all major congeners.

Lipid association

Examination of chlorinated organic compound distributions for source attribution without considera-

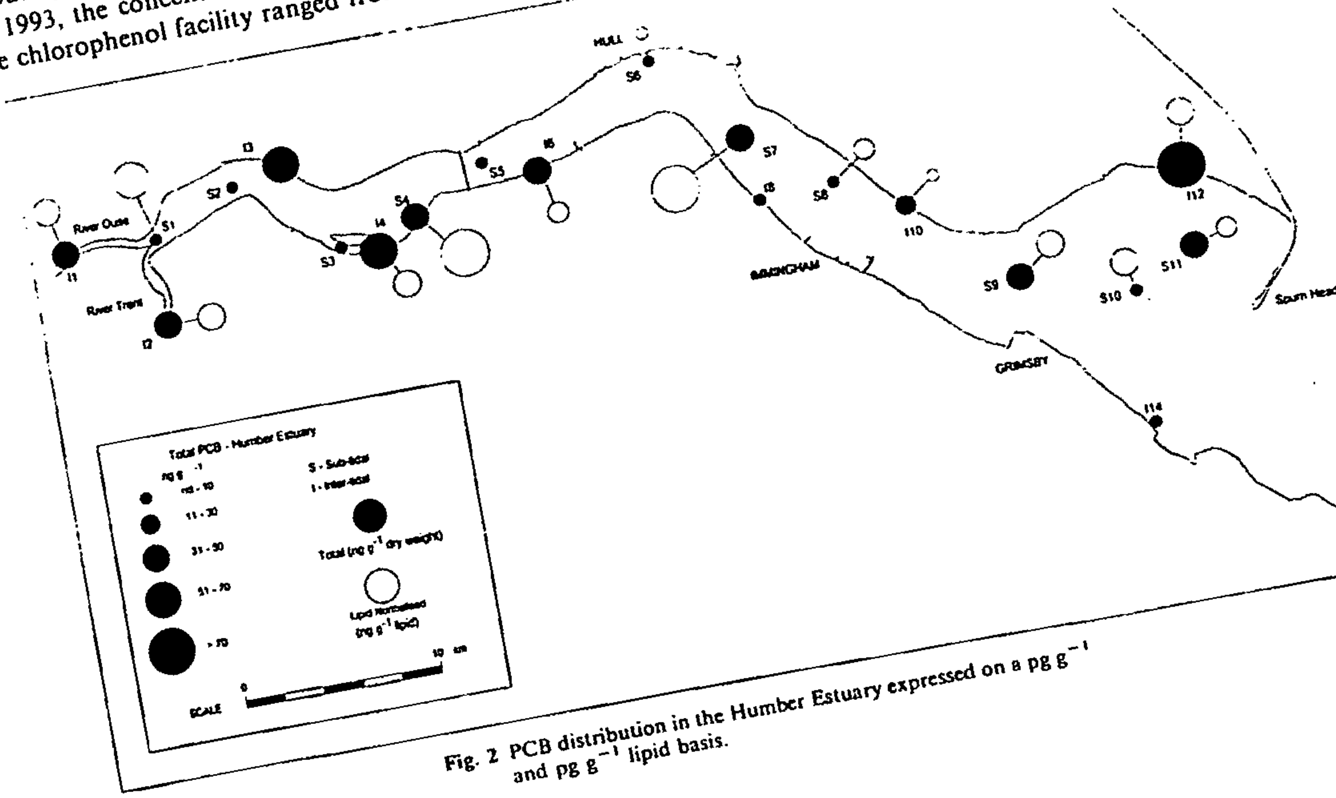

Fig. 2 PCB distribution in the Humber Estuary expressed on a pg g^{-1} and pg g^{-1} lipid basis.

tion of solid phase physicochemistry can be misleading. PCDD/DFs and PCBs are highly apolar compounds with a strong affinity for apolar lipid material. Estuarine particles may be coated with lithogenic humics (Murphy *et al.*, 1994) or be contaminated with anthropogenically derived oil or fatty (e.g. sewage) deposits which render them preferential for contaminant adsorption. Previous work (Delbeke *et al.*, 1990; Preston *et al.*, 1993; Tyler *et al.*, 1994) has demonstrated an association between hydrophobic organic compounds and apolar lipid content. This association is a key factor in determining the behaviour, transport and subsequent distribution of such compounds and as such apolar lipid content represents an ideal normalizing parameter for distribution studies.

Samples analysed on this survey have been correlated with sediment lipid content. Figure 3 shows a significant non-linear correlation between lipid content and total PCDD and PCDF and Fig. 4 shows the correlation with total PCB. A significant fit is found in all cases for a logarithmic relationship. Lipid content of sediments within the Estuary was generally low (non-detectable to 3.28 mg g^{-1}) compared with other estuaries studied (e.g. Clyde, non-detectable to 12.3 mg g^{-1}). However, there was still considerable variation of lipid content within the Humber Estuary which appears to contribute significantly to the distribution of PCDDs, PCDFs and PCBs.

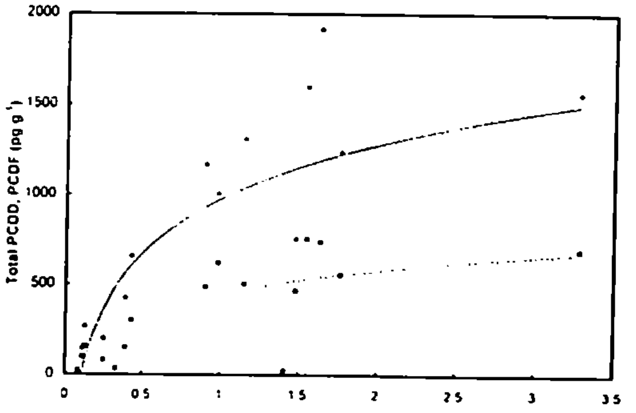

Fig. 3 Relationship between PCDF, PCDD and lipid content for Humber Estuary sediments; ●, total PCDD (pg g^{-1}); ■, total PCDF (pg g^{-1}); - - - - - log PCDF ($r = 0.77$, $p < 0.01$); ———— log PCDD ($r = 0.76$, $p < 0.01$).

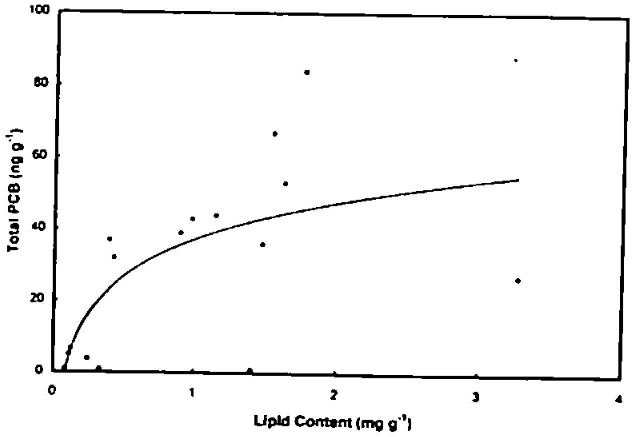

Fig. 4 Relationship between PCB and lipid content for Humber Estuary sediments; ●, total PCB (ng g^{-1}); ———— log PCB ($r = 0.66$, $p < 0.01$).

To establish a more representative picture of the distribution of PCDDs, PCDFs and PCBs in the Estuary, concentrations were normalized against lipid content. The resultant distributions are shown in Figs 1a, 1b and 2. The effect of lipid normalization is to considerably reduce the spatial variation in PCDD, PCDF and PCB concentrations in sediments. The resulting distribution is remarkably homogenous. The hypothesis put forward for the observed homogeneity is two-fold.

It has already been concluded from homolog profile analysis that considerable reworking of sediments within the Estuary may be masking source-related variations in concentration. Once sorption preference related effects have been removed (by lipid normalization) one would equally expect the observed homogeneity in distribution. To further support this hypothesis, the partitioning behaviour of dioxins and PCBs has been investigated with labortory experiments.

Particle–water interaction studies

Relatively few determinations of the partition coefficients for chlorinated organics exist in the literature, despite the fact that this function is an important component of the modelling of contaminant transport (Ng *et al.*, in press). The partition coefficient is defined as:

$$K_D = C_p / C_s,$$

where C_p is the concentration on the particles and C_s is the concentration in solution. The values of C_p and C_s were determined from the mass balance of the ^{14}C compounds used in the mixing experiments. The results are plotted in Fig. 5 as a function of salinity. The partition coefficients for 2,3,7,8-TCDD are about an order of magnitude higher than those for 2,2′,5,5′-TCB, reflecting the lower solubility of the former compound. In general these K_Ds are relatively low due to the lower apolar lipid content of particulate matter in the Humber. In addition, the partitioning of these organic compounds shows little variation as a function of salinity, as Hegeman *et al.* (1995) found for cosolvent partition coefficients for phenanthrene. Thus, the partitioning appears to buffer concentrations of the dioxins and PCBs and may be a factor contributing to the observed homogeneity in bed sediment concentrations. Furthermore, the mean residence time of particles

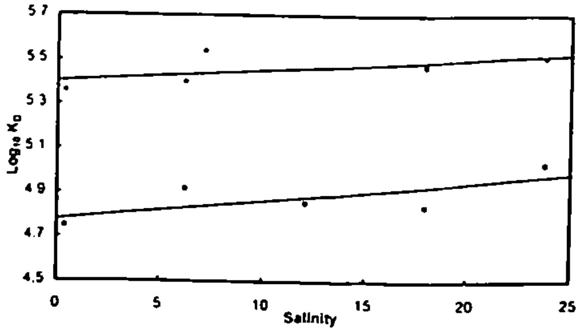

Fig. 5 Experimentally determined K_D values for 2,2′,5,5′-TCB and 2,3,7,8-TCDD in the Humber Estuary; ●, 2,3,7,8-TCDD; ■, 2,2′,5,5′-TCB.

within the Humber has been estimated to be of the order of 18 years (Turner *et al.*, 1991), which in combination with the elevated partition coefficients suggests that estuarine retention of chlorinated organics from anthropogenic sources could be occurring. The fact there is little evidence of major contamination of the bed sediments suggests that the anthropogenic source strength is weak.

Conclusions

Concentrations of dioxins and PCBs in the Humber Estuary whilst elevated above 'background' concentrations are comparatively low and below previously reported levels. There is no evidence of penetration to the Humber Estuary from sources of dioxins reported in the contaminated tributary, in either measured concentrations or homolog profile analysis.

Dioxin and PCB concentrations show a strong dependence on the apolar lipid content of the solid phase as reported in a number of other studies. Once the effects of bed sediment geochemistry are removed by lipid normalization, a homogeneity in dioxin and PCB distribution is observed. It is suggested that this is the result of sediment reworking and mixing within the Estuary. Further evidence supporting this hypothesis, derived from laboratory studies of partitioning behaviour, shows dioxin and PCB partition coefficients are independent of salinity in the Humber Estuary.

This work demonstrates the importance of solid phase geochemistry and the dynamics of estuarine sediment regimes in determining the distribution of organochlorine contaminants in estuarine environments.

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