AN INVESTIGATION OF METAL PARTITIONING AND ORGANIC POLLUTION IN SURFACE SEDIMENTS FROM TEES BAY AND THE TEES ESTUARY, UK.

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Declaration

I hereby certify that this is my own work, except where otherwise acknowledge, and that it has not been submitted previously for a degree at this, or any other university.

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Abstract

Concern about the possible contamination by metals, hydrocarbons and PCBs of Tees Bay and the Tees estuary, and potential sources of such materials has led to this study of surficial sediments. Surface sediment samples were collected from the Tees estuary and Tees Bay and were analysed for grain size, organic carbon content, metals, hydrocarbons (aliphatic and polyaromatic) and polychlorinated biphenyls (PCBs).

The Tees estuary sediments are largely organic-rich clayey-silts, while the Bay sediments are organic-poor sands. All of the metals measured (Cd, Co, Cr, Cu, Ni, Pb and Zn) have significantly higher concentrations in the sediments of the Tees estuary than in those of Tees Bay ($P<0.01$), and the mean averages decrease in the order Zn > Pb > Cr > Cu > Ni > Co > Cd. These significantly higher concentrations remain apparent when the data are normalized to remove the effect of grain size variation, suggesting that the sediments of the Tees estuary are enriched in metals in comparison with the sediments of Tees Bay and that these differences are not the result of the different grain size distributions. Metal partitioning was determined by sequential extraction, using the scheme of Tessier *et al.* (1979) as recently modified by Ajayi and Van Loon (1989), in order to assess the likely behaviour of metals in the sediments studied. The results of the sequential extraction showed that the partitioning patterns of Cd, Cr, Cu and Zn differed between the marine and estuarine sediments. In the Tees Bay sediments the residual fraction hosted >50% of all of the metals, except Cd and Pb. In the Tees estuary, however, this fraction only accounted for >50% of the Cd, Co and Ni. Significant portions of Cd are contained in fractions 1 and 2 in both the Tees estuary sediments and those from Tees Bay. Because of the toxicity and availability of Cd this may pose a serious problem to the ecosystem. The total Pb in the sediments is also quite high, particularly in the Tees estuary, and even the small proportion in fraction 2 could cause deleterious effects. High concentrations of Cd and Pd, in Tees Bay and the Tees estuary sediments, and Cr and Zn, in Tees estuary sediments, were associated with fraction 3. Concern is directed to heavy metals associated with fraction 3 because changing environmental conditions can transfer these elements from the sediments into the aqueous phase. Cu was the only metal significantly associated with fraction 4. This fraction is likely to have an important role as a sink for trace metals, particularly for Cu and to a lesser extent Cr and Zn.

Petroleum hydrocarbons, both aliphatic and polyaromatic (PAHs), were detected and quantified in all samples. The distributions of the n-alkanes, acyclic isoprenoids (especially pristane from coal), triterpanes and steranes, in most sediments from both areas, were indicative of pollution by fossil fuels. On the other hand, a few sediments from the estuary contain hydrocarbons from both biogenic and anthropogenic sources. Polyaromatic hydrocarbon assemblages observed in the samples were relatively rich in hydrocarbons having petrogenic origins. However, the presence of pyrolytic derived components was also indicated by several characteristic component composition ratios. Single PCB congeners were determined in the sediments studied. The PCB profile is fairly constant in sediments from both areas and similar to that of Aroclor 1260 and 1254. The similarity to the commercial mixtures, with only a slight enrichment of the lighter congeners, indicates that sources responsible for PCB pollution are located in the Tees area.

The sediments of the Tees estuary tend to be more highly polluted, by metals, hydrocarbons and PCBs, than those of the Bay, particularly in the middle section of the estuary. However, there is a general decrease in the concentrations of these compounds from the middle to the mouth of the estuary, while within the Bay area offshore sites showed higher concentrations. Distributions of inorganic and organic constituents in the Tees Bay were significantly influenced by the organic carbon content and particle size of sediments.

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Chapter One

Introduction

1.0 Introduction

1.1 General

Pollution may be defined as: "An event or continuing circumstances whereby there are introduced into the environments of air, land or water substances that may adversely affect the balance of nature and human well-being" (Olson and Burgess, 1967). Pollution of the environment can therefore have wide reaching consequences. Pollution can be classified according to the environment it affects (or at least into which it is initially discharged), *i.e.* air, land, fresh-water, marine; according to the nature of pollutant, *i.e.,* radioactive materials, hydrocarbons, or according to its effects, *i.e.* lethal, chronic, mutagenic. These classifications obviously inter-relate or overlap. In particular, materials which are persistent or discharged in bulk tend to end up in the sea wherever they were first discharged. Marine pollution is a specific problem at the present time. The internationally accepted definition of marine pollution is that used by the United Nations Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) which reads:-

> " Introduction by man of substances or energy to the marine environment resulting in such deleterious effects as harm to living resources or marine life, hazards to human health, hindrance to marine activities, including fishing, impairment of quality for use of seawater and reduction of amenities " (Cole, 1979).

In this, the concept linking pollution with harm is made evident and the principal areas in which harm may be experienced are clearly stated.

Disposal of pollutants often results in a degradation of environmental quality (Prohic and Kniewald, 1987). Moreover, rivers and other surface waters (e.g. from municipal and industrial wastes and surface run-off) are by far the most important mechanism for the transport of inorganic and organic matters to the sea. Estuaries are, thus, an important stage in the global sedimentary cycle (Salomons and Forstner, 1984). Inorganic and organic matter entering an estuary may be composed of not only natural compounds but also varying levels of anthropogenic compounds, such as metals, aliphatic hydrocarbons, polyaromatic hydrocarbons and chlorinated organics, depending on proximity to areas of urban development. Changes in the dynamic properties of river water in the estuarine environment result in the accumulation of fine-grained sediment with a high organic matter content, which can, through adsorption processes, play an important role in the transport of trace metals and hydrophobic compounds to the sea (Pelletier *et al.*, 1991). For this reason, sediments have been widely used to identify sources of pollution, to evaluate its extent and to diagnose the environmental quality of aquatic system (Forstner, 1989).

1.2 The area under investigation

1.2.1 Geography of the Tees catchment

The Tees, rises on the south-eastern slopes of Cross Fell, in the north Pennines, some 893 m above sea level (Brady *et al.*, 1983; Archer, 1992), and is one of the largest rivers discharging into the North Sea from the United Kingdom (Fig. 1.1), the others being the Tyne and the Humber. The river is 160 km long and has a catchment area of 2400 km^2 (Environment Agency, 1997; Fig. 1.2).

The River Tees enters the North Sea through a long winding estuary flowing in a general north-easterly direction across a flat agricultural plain, bounded by the Cleveland Hills to the south and the hills of Durham to the north (Carter, 1980). This lower part of the estuary receives discharges of industrial wastes and untreated sewage from the Teesside conurbation (Carter, 1980).

Teesside is an area of about 579 km^2 situated on either side of the estuary of the river Tees, and extending upstream for a distance of about 27 km from the sea. Along the river Tees lie the six towns that make up the core of Teesside (Billingham, Stockton-on-Tees, Thornaby-on-Tees, Middlesbrough, Eston and Redcar). In addition, small towns and villages of Cleveland, the suburban villages south of Middlesbrough, the rural areas around Teesside and on the small part of the Durham coalfield also lie within this area (Wilson and Womersley, 1969). This brings the total population of a Teesside to 850 000 (Environment Agency, 1997).

The only other towns close to Teesside are Hartlepool, to the northeast, and Darlington, to the west. Hartlepool is 8 km, and Darlington16 km, from the nearest urban parts of Teesside. To the south lie the North York Moors and the farmlands of the North Riding in which the largest towns are Northallerton, and Whitby (29 and 40 km from Teesside, respectively).

There is variety of natural landscape within the Teesside area, but changes from one distinctive area to another are often almost imperceptible. According to House and Fullerton (1960) the topography of the lower Tees may be divided into

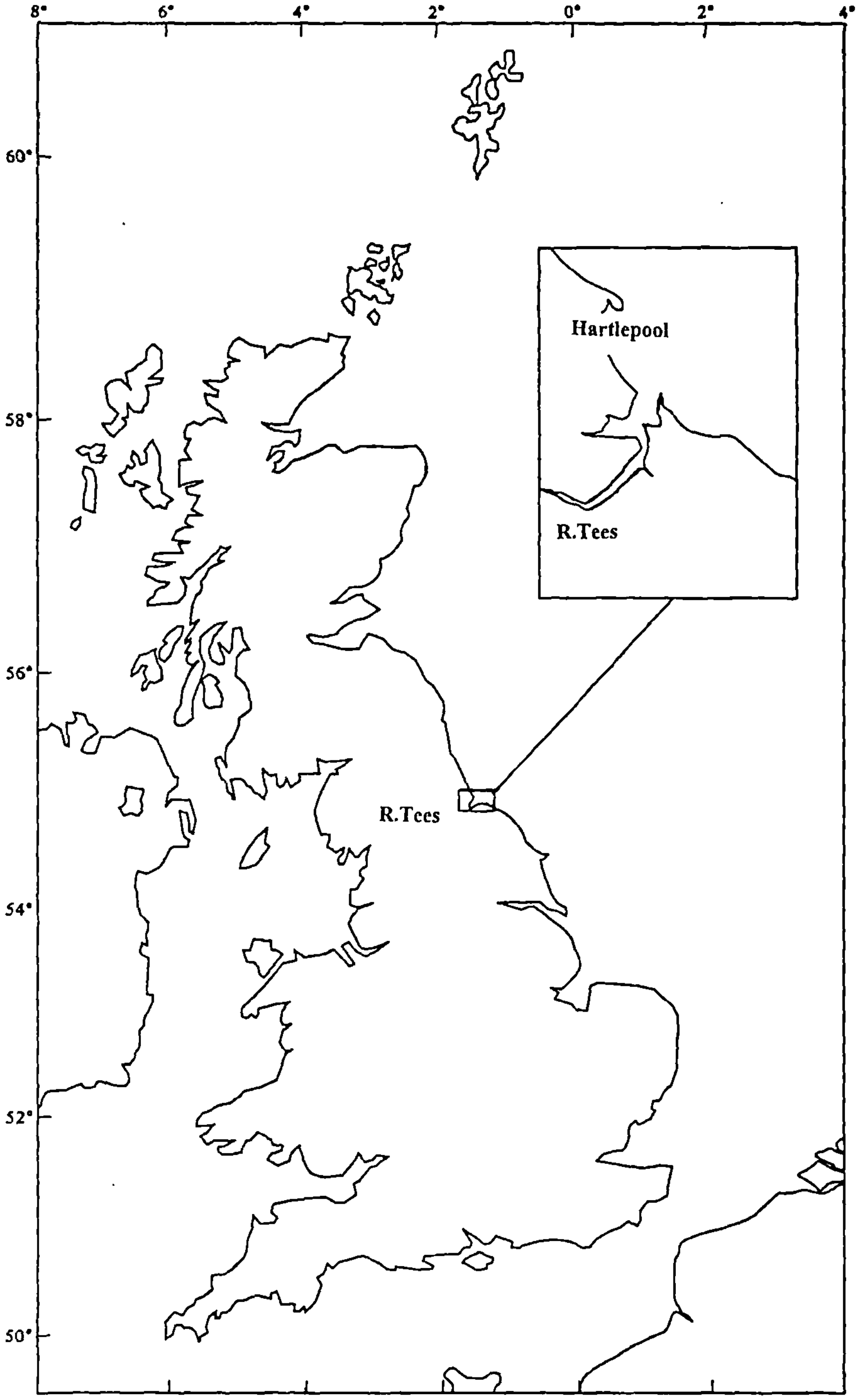


Figure 1.1. Map showing the study area (in set) and its location in North East England (main map).

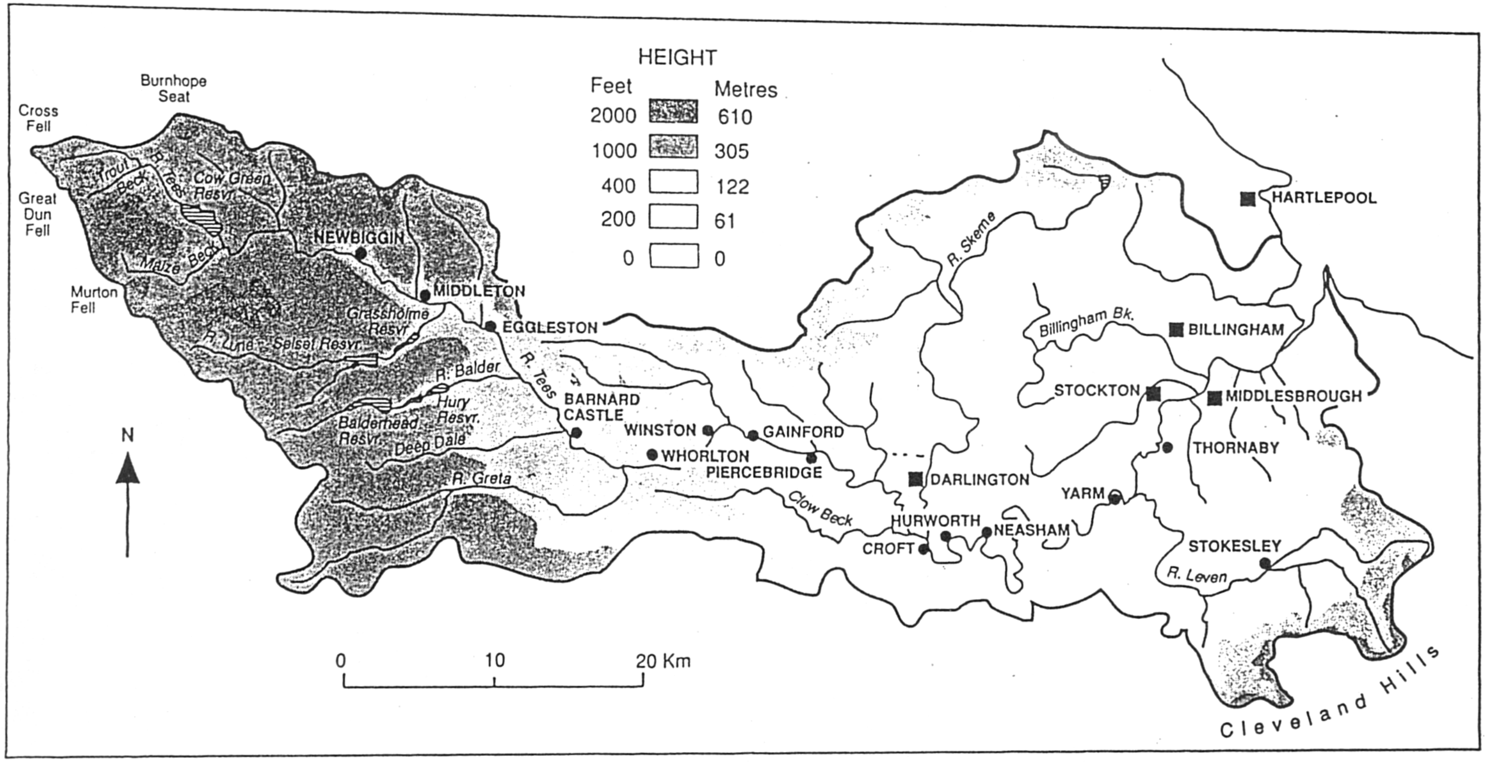


Figure 1.2. The river Tees and its catchment, (from Archer, 1992).

three major units: the estuarine flood plain, the glacial drift low land and the Cleveland hills.

The estuarine flood plain is a triangular lowland opening north-eastwards from an apex near Stockton and enclosing the Tees estuary. Within this land area of some 81 km^2 lies much of the built-up area of Middlesbrough, the south bank towns and parts of Stockton and West Hartlepool, together with the majority of the larger industrial plants and facilities of lower Teesside.

The Glacial Drift Lowland (see section 1.2.3 and Fig. 1.3) is a region around the estuarine flood plain and extends northwards onto the dip-slope of the Magnesian limestone plateau and southwards into the valleys and up the flanks of the Cleveland hills. It extends westwards beyond Darlington. There is a greater variety of soil parent material in the clays, sands, gravels and alluvium of this tract and the land forms and slopes are more pronounced than in the estuarine plain. The town of Darlington together with much of Stockton and West Hartlepool, lies on the drift lowland, which is also the most fertile farmland in the region. The Cleveland Hills lie along the southern boundary of Teesside, and are underlain by Jurassic sediments.

The limit of the tidal influence is at high at Worsall some 40 km from the sea. From High Worsall, past Yarm and Preston towards Stockton and Thornaby, the Tees flows between steep natural banks through what is still predominantly agricultural land. The River Leven, the principal tributary of the tidal Tees, enters from the south about 6 km downstream of Yarm. At Stockton the river valley opens out onto the estuarine flood plain. The section from Stockton downstream to Cargo Fleet is the older industrial area and until the early 1970s the great majority of effluent outlets were concentrated here. The banks are mainly slag or mud slopes, with numerous wharves, many of which are now disused. Billingham Beck enters from the north, separating the built-up areas of Stockton and BIllingham. The river channel in this middle reach of the estuary is artificial, the bottom having been dredged, the course straightened and the banks reinforced. Formerly much of the land close to the river was marshy; the Ironmasters District of Middlesbrough is on the site of Newport Marshes. At Cargo Fleet, the Tees opens out again into a wide, shallow basin of tidal mud and sand flats, with a single dredged channel to the sea, which replaced a division of the river which had previously encircled the sand banks to the main channel and which are known as Seal Sands (Porter 1973; Rowley and Beavis, 1979).

As shown in section 1.2.4., the Tees estuary is surrounded by the largest concentration of chemical industries in Europe and it is one of the largest ports in the UK in term of volume of trade. The most seaward section of the estuary, from Middlesbrough's Newport Bridge to the river mouth, is highly industrial and consists of a dredged channel bounded on both sides by port and storage facilities and industrial installations (e.g. North, 1975; Davies *et al.*, 1991; Beynon *et al.*, 1994; Environment Agency, 1997).

There are numerous small, parallel stream-courses; of these only the Stainby beck, in the west has created a noticeable valley, joining the old course of the river Tees, to the south-east of Stockton (House and Fullerton, 1960).

1.2.2 Hydrology of the Tees catchment

The total discharge of the river Tees amounts to approximately 17 m^3s^{-1} (Gibbons, 1988; Davies *et al.*, 1991). The river Tees, dominates the catchment; as of its four significant tributaries, the Lune, Balder, Skerne and Leven, none is comparable to the main river in size or flow. In its upper course the Tees is one of the fastest flowing rivers in England, but in its lower reaches it is slow and sluggish, meandering over a level or slightly undulating plain, before emptying into the sea through a wide bell-shaped estuary (House and Fullerton, 1960).

The Moors around Cross Fell, where the river sourced, have the highest and most persistent rainfall in the Pennines, with annual totals of more than 2000 millimeters (mm). Most of this rain reaches the river within minutes because there is little chance for the water to soak into already saturated peat or impermeable rock. Rainfall in the lower part of the catchment (e.g. average annual rainfall at Stockton is 750 mm) is much less than on the hills (Archer, 1992).

The principal man-made changes in the river have been designed to solve problems of navigation and water supply but these measures have gradually alleviated flooding as much as those designed primarily for flood protection. Work in the lower reaches of the estuary was aimed primarily at the improvement of navigation between Stockton and the sea. At higher elevations a series of reservoirs has been built to meet the needs of a growing population and the rapidly developing industrial demand for water. Reservoired sub-catchments now cover a far greater proportion of the total Tees catchment than in any other major north eastern river. They have been built in the wettest areas which normally contribute the most to floods.

The effect of the reservoirs on flooding is twofold. When they are drawn down, as they commonly are during the summer months, they absorb the flood water and hence reduce the flood volume downstream. Even when they are full they delay the flood wave and reduce the peak, roughly in proportion to the reservoir surface area (Archer, 1992).

The first Pennine reservoir to be constructed was at Hury in 1894 and the last at Cow Green in 1970. The reservoirs have gradually reduced the flood potential of the Tees over the last hundred years. The sequence of reservoir construction, their capacities and catchment areas are shown in Table 1.1.

Table 1.1. Details of Teesdale Reservoirs (after Archer, 1992).

Name	**Year of completion**	**Dam height meters**	**Capacity million cubic meters**	**Reservoir area km^2**	**Catchment area km^2**
Hurry	1894	30	3.90	0.51	43.1
Blackton	1896	24	2.11	0.27	-
Grassholme	1915	33	6.06	0.57	78.7
Selset	1960	39	15.32	1.11	-
Balderhead	1965	48	19.67	1.17	-
Cow Green	1970	25	40.92	3.12	58.9

The Tees estuary extends for 40 km to the tip of the North Gare and South Gare breakwaters (Carter, 1980). The whole body of water in the estuary moves up and down with each flood and ebb tide. Superimposed on this movement the fresh water entering the estuary from the upper river flows mainly to the sea in the surface layer, picking up and carrying with it the salt water from the beneath. To replace the latter there is a movement of salt water from the sea up the estuary in the bottom layers. As a result water in the middle stretch of the estuary is highly stratified, the salinity increasing from the surface to the bottom. Matter suspended or dissolved in the surface layers moves further seaward on the ebb than upstream on the flood and thus passes gradually out to the sea. On the other hand, matter suspended or dissolved in the bottom layers moves gradually further upstream. Water entering tidal reaches moves only slowly seawards, especially if the volume of fresh water coming in from the upper river is small (Carter, 1980).

1.2.3 Geology of the Tees catchment

In general, the Tees catchment is dominated by a succession of sedimentary rocks from Carboniferous to Jurassic, with Carboniferous igneous intrusions (Fig 1.3).

The Carboniferous rocks dip steadily eastwards from Cross Fell (NY 687344) to the coast, across the Alston Block. The northern, western and southern limits of the block are marked by major faults, whilst to the south-east the Coal Measures are overlain by rocks of Permian and Triassic (Johnson, 1995).

Of the igneous rocks of this age, the Whin Sill is responsible for the most impressive topographical features, outcropping near the headwaters of the River Tees, to provide the rapid of Cauldron Snout (NY 814287) and the magnificent fall at High Force, near Middleton-in-Teesdale (Johnson, 1995).

In the extreme east the Magnesian Limestone, of Permian age, forms a persistent west-facing scarp and undulating plateau from Hartlepool towards Darlington, passing south of that town and thence towards Richmond and Ripon. Surface outcrops of the limestone are rare in this area, though represented in Hartlepool headland and a pronounced ridge to the south-west of Darlington (House and Fullerton, 1960).

The Triassic deposits (sandstone, mudstones), which contain important deposits of salt and anhydrite, are relatively soft and are almost wholly submerged beneath a cover of glacial drift and post-glacial sediments (clay, peat, alluvium, river gravels and blown sands). Outcrops occur at the Scars at West Hartlepool and also where meanders of the Tees and Leven have cut through the overlying drift. (House and Fullerton, 1960).

Jurassic sediments outcrop in the south eastern portion of the Tees catchment only, and form the strong escarpment of the Cleveland halls from which the Tees tributary the river Leven flows.

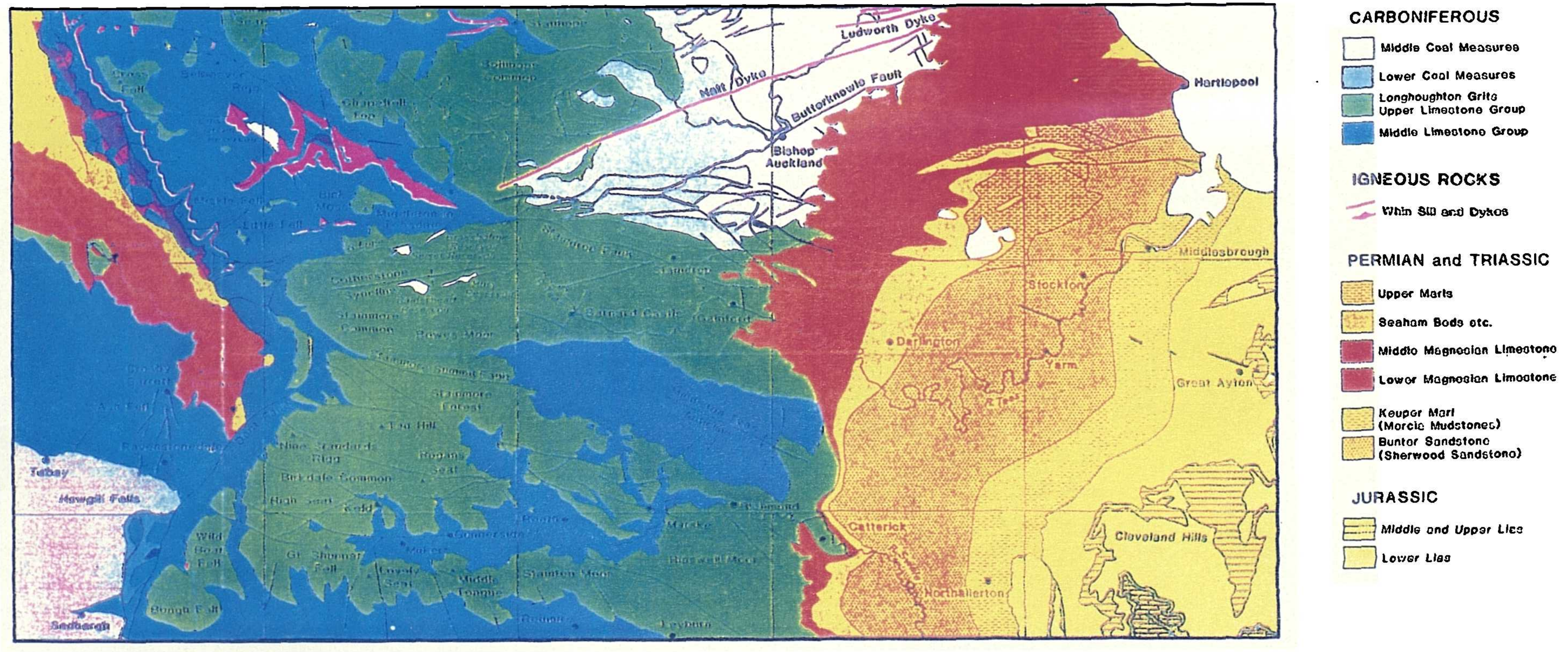


Figure 1.3. The main geological regions of Tees basin, north-east England, (from Johnson, 1995).

The Tees River also drains part of the northern Pennine orefield, which has for centuries played a major role in the history of settlement and economic evolution of these uplands (Raistrick, 1934). Mineralization in the north Pennines occurs as veins and replacement bodies (Dunham, 1948). The vein orebodies occupy tension cavities, formed on fault planes, which in some instances have been enlarged by solution of wall-rocks, although this must be of secondary importance since similar veins occur in sandstones, limestones and silicified shales. The flats are replacements, or disseminations of ore minerals, and filling of solution cavities, in wall rocks and these tend to increase the width of ore-zone (Johnson, 1995).

The principal base metal minerals are galena (PbS) and sphalerite (ZnS). Both contain significant concentrations of trace metals including Cd, Cu and Ag (Young *et al.*, 1987). Pb and Zn ores are associated with Fe/Mn oxides and Fe sulphides, as well as the economically important minerals such as baryte ($BaSo_4$), witherite ($BaCo_3$) and fluorite (CaF_2) (Macklin and Dowsett, 1989).

Pb and Ag have been mined in the northern Pennine since Roman times (Raistrick and Jennings, 1965) though up to the early part of the seventeenth century metal ores were worked by isolated and small-scale exploration. After 1650, with the introduction of new techniques of dressing smelting and the use of short drainage levels in deeper underground workings, the northern Pennines were established as Britain's leading Pb and Zn producer (Schnellmann and Scott, 1970). Pb production in the region peaked during the middle decades of the nineteenth century while the heyday of Zn mining was somewhat later, between 1880 and 1920 (Dunham, 1944).

A long history of metal mining in the northern Pennines has left a legacy of heavy metal pollution in many north east England river systems (Macklin and Rose, 1986). Although large-scale mining in the north Pennine Orefield ceased shortly before World War II (Dunham, 1948) under flood conditions significant quantities of sediment-borne metals still enter local rivers; some directly from the erosion of mine tailings (Aspinall and Macklin, 1985) but the majority through reworking of metal contaminated mining-age alluvium by contemporary river channels (Lewin *et al.*, 1988). Released metalliferous fines may be deposited on adjacent floodplains causing long-term contamination of riparian agricultural land (Lewin and Macklin, 1987), or temporarily stored in the interstices between gravel-sized sediment within river channels there potentially endangering both fisheries and water quality (Macklin and Dowsett, 1989).

1.2.4 The industrialization of the Tees Estuary

The River Tees has been a focal point for trade since the 12th century, but large scale industrialization commenced only after the development of the coal trade in the 19th century (Brady *et al.*, 1983; RCHME, 1993). One of the first of these new industries to be established, was iron and steel making which began in 1841, when Bolckow and Vaughan opened a rolling mill at Middlesbrough (North, 1975; Beynon *et al.*, 1994). Together with associated shipbuilding and engineering industries, the iron and steel industry has been important in the industrial life of the area ever since (Le Guillou, 1978; Shillabeer and Tapp, 1989; North East of England Regional Development Group, 1993; RCHME, 1993). The chemicals industry was established some years later and has become of increasingly important to the area's economy, especially from 1918 onwards as the natural advantages of a coastal location, the availability of large areas of suitable land and the possibility of constructing wholly new labour forces proved to be decisive locational attractions. (Beynon *et al.*, 1994). Chemicals and petrochemicals gradually replaced iron and steel as the most significant industry on the Tees estuary between 1931 and 1961. Since 1961, these industries have continued to expand their output. The three ICI sites at Billingham, Wilton and North Tees form the largest chemical/petrochemical complex outside the US (Rowley and Beavis, 1979).

The major expansion of Billingham, on the north bank of the Tees was a direct consequence of the merger, in 1926, of Brunner-Mond with three other British companies to form Imperial Chemical Industries (ICI). ICI attempted to emulate the integrated complexes of the German chemical industry, selling to the vast market offered by the British Empire various chemical products, such as fertilizers (Reader, 1970). The formation of ICI led to a tripling of ammonia capacity at Billingham. This was accompanied by a diversification of production (although still largely of inorganic chemicals) into the manufacture of cement and sulphuric acid (the latter was based on anhydrite deposits, extraction of which began in 1928), as well as the first compound fertilizers based on nitrogen and phosphate. During the 1930s output was somewhat reduced at Billingham as demand fell, but one response to this was a search for new products and further diversification of production into a plant to hydrogenate coal and creosote to petrol. The Second World War and the demands of the wartime economy led to both and increased demand for existing products from Billingham as well as the further development of new ones (for example, isooctane and victane for aviation fuel). Thus, new production levels were attained in the war years (Beynon *et al.*, 1994).

At Wilton, where production commenced in 1950, chemicals are derived from crude oil, with plants covering ethylene, propylene and other materials onto such forms as glycols, polythene and terylene. The nylon works at Wilton, established in 1958, has since expanded capacity four-fold. The smaller 340-acre site at North Tees commenced production in the 1960s with the establishment of aromatic plants and an ethylene liquefaction plant (Rowley and Beavis, 1979).

The development of the large ICI complexes, together with the natural advantages of the estuary, undoubtedly encouraged the location on Teesside of other independent chemical companies. In 1934, British Titan Products (now BTP Tioxide) commenced production of titanium dioxide pigments at Billingham. Titanium dioxide is used in a wide range of products such as paints, plastics, fibers and paper. Organic compounds of titanium and other metals were produced by another subsidiary, Titanium Intermediate Ltd., which was also based at Billingham. These chemicals had a wide range of industrial application including catalysts, retexturing agents, adhesion promoters, paint thixotropy controllers, heat resistant paint media, resin ingredients and glass container improvers (North, 1975).

By 1945 ICI had developed a diverse and complex web of both national and international connections (Fig. 1.4) and within this, Billingham was the largest single chemicals productions complex in the world, producing a wide range of products based on sulphuric acid, nitrate, petroleum (from creosote) and calor gas. (Beynon *et al.*, 1994).

The large development of chemicals and steel on Teesside proved to be sufficiently attractive in 1957 for British Oxygen to set up a plant to produce oxygen and nitrogen. Since then several additional plants were established and the total capacity in 1972 of 2,700 tonnes a day made Teesside the largest single gas producing

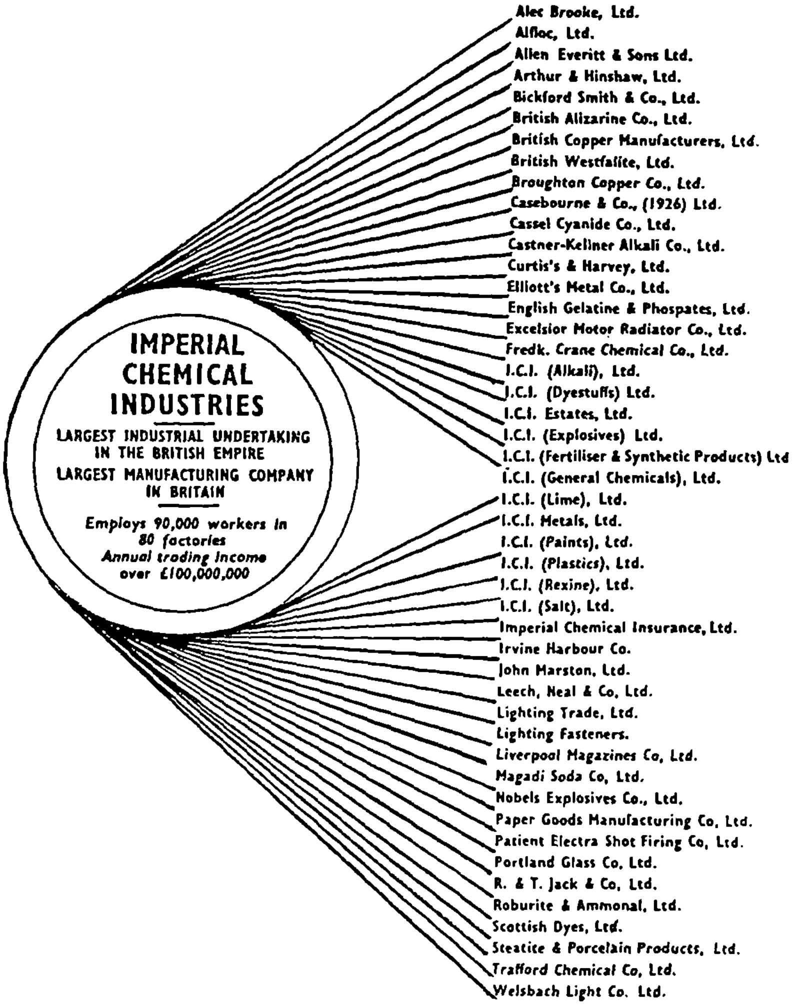


Figure 1.4. ICI's national connection, 1945. (from Beynon et al., 1994).

centre in Europe. Many firms were supplied by a pipeline which crossed the River via the framework of the Transporter Bridge. British Oxygen also operated its largest distribution in the North East from its site at Teesport (North, 1975).

The increasing demand for petroleum fractions as feedstock induced ICI and Phillips to construct a refinery on the north bank of the River and this was opened in 1966. This was quickly followed by Shell U.K. Ltd. which constructed a refinery on the south bank close to Teesport (opened in 1968 and closed in 1984, Beynon *et al.*, 1994). Demand was growing particularly in the North East and it was a logical step to assess the potential sites in that region for the new refinery.

The River Tees which was steadily being deepened to take large vessels was the most suitable and was fringed by large areas of tidal mudflats suitable for reclamation. Large tracts of flat land, mainly reclaimed, close to deep water were two reasons for the continued development of capital intensive industries such as petrochemicals. In particular some, 1,700 acres at Seal Sands on the north bank of the estuary is being steadily reclaimed (Fig. 1.5). The reclamation is achieved by building an embankment around part of the land area to be reclaimed and then pumping sand and mud from the river bed into it as part of the deepening operation (Porter, 1973; North, 1975; Cleeves, 1990; Hardy *et al.*, 1993; Beynon *et al.*, 1994). Suitable materials such as slag are then tipped on top. Based upon the scheduled dredging operations the Tees and Hartlepool Port Authority were reclaiming land at the rate of 200 acres a year by the late 1960's (North, 1975).

The refinery of Phillips-Imperial occupied land on the southern side of Seal Sands. In 1970 Monsanto Textile opened a plant (closed in 1985, Beynon *et al.*, 1994) with a capacity of 90,000 tonnes a year for the manufacture of acrylonitrile used for making Acrilan fiber and certain plastics. Rohm and Haas opened a plant in 1972 (closed in 1981, Beynon *et al.*, 1994) to produce methyl methacrylate and other acrylic monomers. Such developments created a need for specialist chemical storage facilities. By 1972 this has led to the establishment, by Tees Storage Co. Ltd., of a new tank farm at Seal Sands (North, 1975).

With the development of North Sea gas and oil Teesside is in a very favourable position to become an even more important petrochemical storage distribution and processing centre. Both Phillips and Shell had by 1972 discovered oil

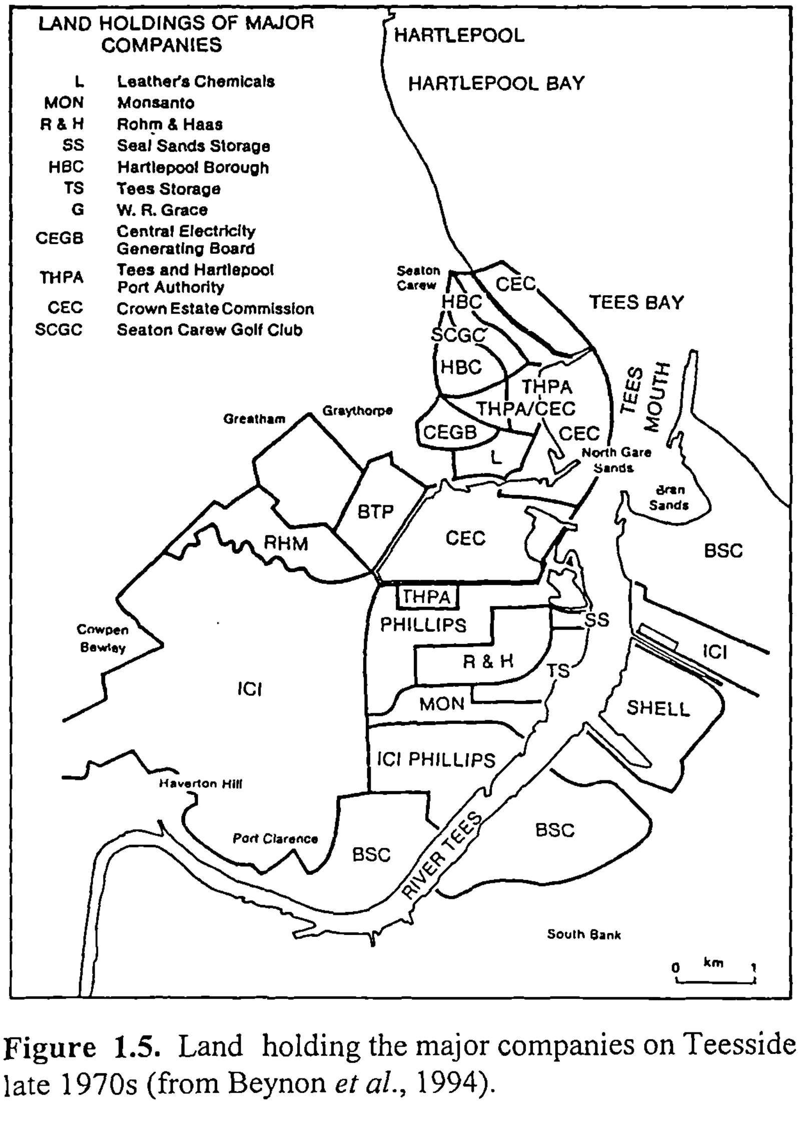


Figure 1.5. Land holding the major companies on Teesside, late 1970s (from Beynon *et al.*, 1994).

fields in the North sea and possessed bases on Teesside for expanding capacity. Land was also available for other firms. In 1973, the Norwegian Government gave permission for Phillips to pipe oil from Ekofisk Field in Norwegian Sector of the North Sea to Teesside, a distance of some 322 km (North, 1975; Beynon *et al.*, 1994).

In addition to the chemical industry on Teesside, steelmaking has also undergone massive expansion. The iron and steelmaking industry is the largest single employer on the south bank of the Tees, a position it has held for century. In 1973 British Steel Company (BSC) embarked on a major new ironmaking development at Redcar, the largest in the UK (Rowley and Beavis, 1979; Frid *et al.*, 1991).

1.2.5 Previous Studies on the Tees Estuary

The Tees Estuary is beginning to recover from the chronic pollution which started in the 1920s as a consequence of the development of iron, steel and chemical industry (Environment Agency, 1997). Together with the industrial use of the Tees the river is also used for the disposal of domestic sewage. Until the completion of the Portrack sewage works in 1985, which provides primary treatment for sewage draining from both sides of the river, the untreated sewage of more than 400 000 people was discharged to the tidal River Tees (Porter, 1973; Brady *et al.*, 1983; Shillabeer and Tapp, 1989). Water quality was probably at its worst in the early 1970s, with over 500 tonnes of Biological Oxygen Demand (BOD) load discharged daily from chemical, petrochemical and steel making industries, and from untreated domestic sewage (Environment Agency, 1997). The main problem in the Tees estuary was industrial waste; it received 137×10^4 m^3 of chemical pollutants and 11×10^4 m^3 of sewage per day (Hardy *et al.*, 1993). Since 1970 the river has made a dramatic improvement in quality with daily BOD less than 100 tonnes per day (Shillabeer and Tapp, 1989; Hardy *et al.*, 1993; Environment Agency, 1997). However, the river remains subject to discharges from a number of chemical and petrochemical works, plus the domestic sewage from the adjacent urban populations (Shillabeer and Tapp, 1990). Johnston *et al.* (1991) state that some 0.5×10^6 m^3 of industrial effluents were being discharged daily, with three quarters of the total issuing from just three sites (1-3 in Fig. 3.2). The compositions of the discharged effluents are complex, and the estuary remains one of the most contaminated in the UK for a variety of pollutant classes (Porter, 1973; Gray, 1976; Murray and Norton, 1979; Davies *et al.*, 1991; Hardy *et al.*, 1993; Laslett, 1995).

To the author's knowledge, only a few studies on trace metals have focused on sediments from Tees estuary and Tees Bay, and no data are available on metal speciation, hydrocarbons (aliphatic and polyaromatic) and polychlorinated biphenyls in this important part of the UK.

The most comprehensive study of trace metals on the Tees estuary sediments is that of Davies *et al.* (1991) who sampled the estuary at 31 sites between Newport Bridge and the river mouth. Total metal concentrations were found to be comparable with other industrialized rivers and average metal concentrations decreased in the order Zn > Pb > Cu > Cr > Ni > Cd. These authors also reviewed the limited earlier data on metal concentrations in the Tees estuary sediments (Murray and Norton, 1979; Delo and Burt, 1988) and concluded that average Cr, Cu and Zn concentrations had decreased significantly over time, and that Cd, Pb and Ni had decreased slightly.

Taylor (1979) is the only published study of trace metals on the Tees Bay. Six of the metals studied (Cd, Co, Cr, Hg, Ni and Pb) were generally found at similar levels to those of an uncontaminated area and only Cu, Mn and Zn were found at elevated levels. This author concluded that the geology of the area can be a more important factor than the industrial input in deciding the metal content of marine sediments.

Published data are also available, from a few studies, on waters from the Tees. The distribution of heavy metals in the surface water of the Tees estuary has been studied by Taylor (1982). The results of this study indicate that the chemistry of the estuarine waters is complicated, both by the number of effluent inputs and by the variation in the total to soluble metal ratios, but the average concentration of the soluble metals are with limits proposed by US Environmental Protection Agency (EPA) as being satisfactory for the maintenance of marine life. Law *et al.* (1997) have investigated the level of PAHs in water from the Tees, as well as from other estuaries and coastal waters around England and Wales. They found that the highest concentrations of PAH, particularly 2- and 3-ring PAH, were detected in the Tees estuary, at sites close to a steel manufacturing plant.

1.3 *Aims of the Study*

The aims of this project are:

1) to assess both the concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn in the sediments of Tees Bay and the Tees estuary, and the chemical forms in which they occur. In addition total metal concentrations in the sediments studied from both areas will be compared with those found in the sediment samples from a number of different geographical areas;
2) to survey the aliphatic hydrocarbons in sediments from Tees Bay and the Tees estuary and to establish the importance of parameters derived from these hydrocarbons for the estimation of aquatic environmental pollution;
3) to assess the occurrence and distribution of PAHs in sediments of the Tees Bay and Tees estuary, and compare concentrations in this area with those found in the sediment samples from a number of different geographical areas. In addition possible relationships between PAHs and sediment characteristics will be evaluated and potential origins identified;
4) to determine distribution patterns of PCB congeners and compares concentrations in the area with those found in sediment samples from a number of different geographical areas. In addition, total PCB concentrations are reported as Aroclor-equivalent concentrations, based on the concentrations of isomers and congeners of a particular degree of chlorination which are resolved and summed to provide a total PCB concentration.

Chapter Two

Literature Review

2.0 Literature Review

2.1 Sources and fate of pollutants in estuarine and coastal environments:

2.1.1 Trace metals

The most important aspects of the pollution of the marine environment are the hazards to human beings caused by consuming polluted fish and shellfish and the damage inflicted on marine organisms and ecosystems. The reduction of marine amenities and the possible interference with marine activities are of secondary importance (Bernhard and Zattera, 1975).

It has been well established that many metals that enter the aquatic environment accumulate eventually in bottom sediments (Dickson *et al.*, 1987; NRC, 1989; Burton, 1992). Moreover, it is known that sediment-bound metals are released to interstitial water at rates sufficient to exert adverse effects on resident biota (Birge *et al.*, 1987; Burgess and Scott, 1992). Although naturally present in estuarine and marine environments, heavy metals such as Cd, Hg, and Pb are biologically non-essential and demonstrably toxic even at relatively low concentrations (NRC, 1989; Baudo *et al.*, 1990). Other metals, including As, Cu, Mn, Fe, Ni and Zn are biologically essential at trace levels, but can be toxic when present in excess amounts (NOAA, 1991).

The accumulation of metals in sediments is substantial in coastal estuaries located within highly urbanized and industrialized areas (Wilber and Hunter, 1979). Metal accumulation in sediments has been linked to specific local sources such as discharges from smelters (Cu, Pb and Ni), metal-based industries (e.g. Zn, Cr and Cd from electroplating), paint and dye formulators (Cd, Co, Cr, Cu, Pb, Hg, Se and Zn), petroleum refineries (As and Pb), as well as effluents from chemical manufacturing plants (Williams *et al.*, 1978; Forstner, 1990).

Table 2.1 presents a list of these metals deemed to pose the greatest risk to the aquatic environment. Mercury is generally considered to be the most harmful both to human beings and to marine organisms, followed by zinc and copper which are important pollutants only to marine organisms.

There has been concern about metals in the aquatic environment for a long time, but it took the tragic events in Minamata Bay, Japan, to really draw attention to the severity of the problem. Between 1953 and 1960, more than 100 persons in Minamata were killed or disabled through eating fish and shellfish contaminated with methyl mercury (Irukayama, 1966). The mercury had come from industrial discharges into the bay. This tragedy was soon followed by another in Japan when many more people were poisoned by eating fish contaminated with cadmium, from mine wastes (Yamagata and Shigematsu, 1970). These tragedies have drawn attention to the hazards of Hg and Cd to man and also illustrates how problems of contamination from industries can arise from metals other than those being specifically sought.

Table 2.1 Importance of metals as marine pollutants (From Bernhard and Zattera, 1975).

Metal	Route to the ocean*	Average concentration in seawater mg/l	Safe concentration mg/l ^{c}	Relative importance	
				To marine organisms	To human beings
Hg	A, R	0.1	0.1	Important	Important
Zn	A, R	2	20	Significant	Negligible
Cu	D, R	1	10	Significant	Uncertain
Pb	A, R	0.02	10	Slight	Slight
Cd	A, R	0.02	0.2	Slight	Slight
As	D	2	10	Slight	Negligible
Cr	D, R	0.04	10	Slight	Uncertain
Ti	A	2	-	Slight	Negligible

*A =through atmosphere, D =dumping, R = through rivers or pipelines.

^{C} Equal to concentrations considered to pose minimal risk of deleterious effects.

2.1.1.1 Fluxes of metals through the hydrocycle

The hydrosphere covers the larger part of the earth's surface, and is made up of a number of, in most cases, relatively homogenous parts (e.g. rivers, lakes, oceans, atmospheric water, ground water). Metals in the hydrosphere occur in three main phases: as dissolved metal, as metal bound in some form to particulate material suspended in the water, and as metal fixed within the deposited sediments (Fergusson, 1990). Much of the metal mobilized during natural crustal weathering and by anthropogenic activities is dispersed by water, which transports the metal towards the land/sea margins. In this sense, waters may be regarded as the carrier of a wide variety of chemicals, especially metals, to the aquatic environments.

An understanding of the processes by which metals enter the environment and the mechanisms that control their transport and distribution is essential if the ultimate fate of the metal is to be understood. Metals enter natural waters by the weathering of rocks and soils, from the atmosphere, and by anthropogenic input. These mechanisms can introduce the metal into surface waters in either a dissolved or particulate phase, where they are subject to a number of physical, chemical and biological reactions that distribute them throughout the hydrosphere. Figure 2.1 shows a schematic of the hydrocycle and the way that the various sources and sinks of metals are inter-related. The outer ring represents particle transport, where the sediment and suspended particles in rivers, estuaries and oceans are major sources and sinks for metals. The inner ring represents natural waters and their effect on the transport of metals to the various sinks. It can also be seen from Figure 2.1 that the outer and the inner rings represents the interchange between river water and fluvial sediments and between estuarine water and estuarine sediments. Finally, the centre represents the atmosphere and its influence on all parts of the hydrocycle.

Trace metals are introduced directly in each compartment (Fig. 2.1) and are transported from one compartment to another. Sediments in rivers, estuaries and the seas are important material as they are the main location of the trace metals in the hydrosphere. They have been classified in a variety of ways according to different criteria such as their source, the particle size and their composition. Some of the more important sources are listed in Table 2.2 (Davies and Gorsline, 1976; Kranck, 1980).

Table 2.2 Classification of sediments according to source (from Fergusson, 1990).

Source	**Comments**
Terrigenous	From weathering of terrestrial rocks, main source of inorganic sediments, ~ 206×10^{14} g y^{-1} of solid material.
Biogenous	From living material in water systems, the sediments arise from biological skeletal material and main components are SiO_2 and $CaCO_3$.
Organic	From the plant and animal material, i.e. soft tissue.
Volcanic	From volcanism on sea floor.
Authigenic	Chemical processes and precipitation in the ocean sediments.

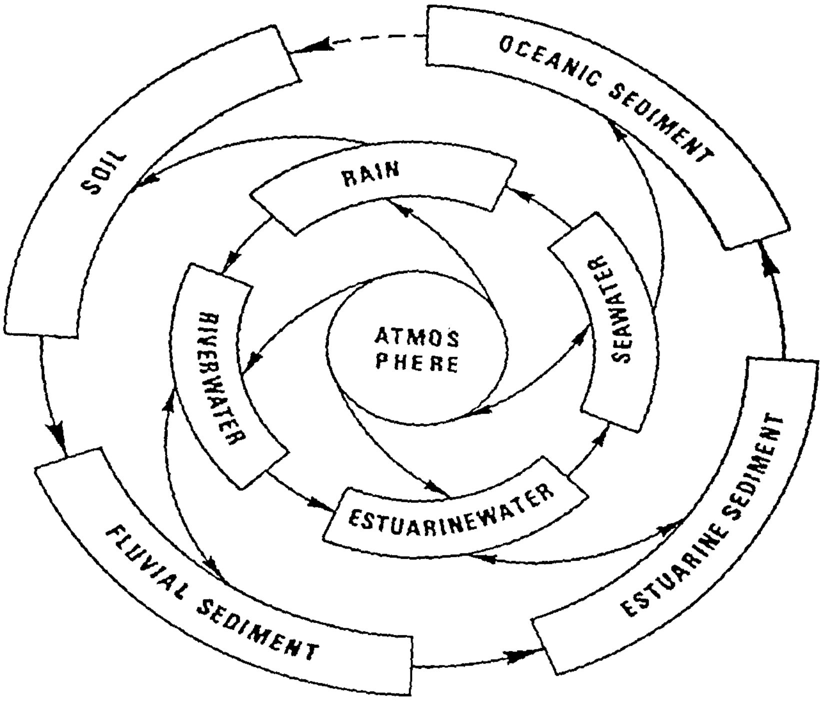


Figure 2.1. Movement of metals through the hydrocycle (from Salomons and Forstner, 1984)

2.1.1.2 Sources of trace metals

2.1.1.2.1 Natural sources

Unlike many contaminants, trace metals are normal constituents of natural waters and traces at least are always found in the organisms inhabiting them (Clark, 1992). Metals enter these environments through weathering of the earth's crust, and steady-state background concentrations of metals occur in seawater (Bishop, 1983). Natural materials enter the hydrosphere from water run-off and the atmosphere. Materials from the atmosphere include windblown silicate dust, volcanic emissions, sea spray, forest fires and biological emissions (Baut Menard and Chesselet, 1979; Ng and Patterson, 1981; Zoller, 1984). The material that enters by run-off comes from the weathering of geological materials, which eventually gets into the aquatic environments (Forstner, 1986; Smith, 1985). The composition of river water includes the products of mechanical and chemical weathering of rocks, either in solution or as particles, and components which are washed from the atmosphere in rainfall and may originally have been contained in salt particles of marine origin or dust particles from the land. It seems probable that continental weathering plays a major part in determining the heavy metal composition of large rivers (Turekian, 1971).

2.1.1.2.2 Anthropogenic inputs

In addition to the mainly natural processes that have been mentioned above, the input of pollutants can exert a significant influence on the trace metal compositions of some aquatic waters, especially those located within highly urbanized and industrialized areas (Chester, 1990).

Human activities have introduced large quantities of metals to localized areas of the sea. Some of the anthropogenic sources of the trace metals to the hydrosphere are: industrial, such as mining and smelting, urban run-off, sewage effluents, production and use of compounds and materials containing the heavy elements, shipping, waste dumping, agriculture run-off, burning of fossil fuels and leaching of waste dumps (Murozumi *et al.*, 1969; Mueller *et al.*, 1976; Christensen *et al.*, 1978; Rickard and Nriagu, 1978; Baut Menard and Chesselet, 1979; Hazen and Kaneip, 1980; Forstner, 1980,1986,1987; Heit *et al.*, 1981; Ng and Patterson, 1981; Moore and

Ramamoorthy, 1984; Smith, 1985, 1986). All of these wastes may reach the ocean from rivers, ocean out-fall discharges, or direct dumping (Bishop, 1983).

Another major route of metals to the aquatic environment, particularly near the coasts of the industrialized countries, is through the atmosphere. Lead from automobile exhaust, mercury from the production of cement, and zinc and other metals emitted during the combustion of fossil fuels may all reach the aquatic environments through the atmosphere. Atmospheric processes are still poorly understood and estimates of inputs of metals to the sea by this route vary quite widely, but all estimates suggest that this input is considerable (Clark, 1992).

For large water systems (estuaries and seas), there has been debate over the relative strengths of riverine (fluvial) and atmospheric inputs. The source strengths are controlled by a number of complex, often interrelated, environmental factors which operate in an individual river basin; these factors include rock lithology, relief, climate, the extent of vegetation cover and the magnitude of pollutant inputs (Chester, 1990). However, the atmosphere is considered to be the major source of the trace metals to the oceans (Baut Menard and Chesselet, 1979; Lum and Edgar, 1983). Table 2.3 shows the estimated inputs (in 1987) of four metals to the North Sea by various routes (Clark, 1992). The atmosphere is a more significant route for lead than it is for other metals.

Table 2.3 Input of four metals to the North Sea (t yr^{-1})(from Clark, 1992).

Source	Copper	Mercury	Lead	Zinc
Rivers	1290-1330	20-21	920-980	7360-7370
Dredging	1000	17	170	8000
Atmosphere	400-1600	10-30	2600-2700	4900-11000
Direct Discharge	315	5	170	1170
Industrial dumping	160	0.2	200	450
Sewage sludge	100	0.6	100	220
Incineration	3	-	2	12

Similarly, the atmosphere is considered by Buat Menard (1984) to be the major source of the lead to the hydrosphere. Estimates of atmospheric fluxes to the sea surface are given in Table 2.4, together with the ratio of the dissolved riverine flux. A ratio of >1 suggests that the atmospheric input is the more significant, however, particulate material in the rivers was not included, and if included might reduce the ratio to less than 1. In the case of Pb it appears that because of the high ratio, atmospheric input is the main route to the hydrosphere. A comparison of atmospheric inputs with the upwelling from the deeper ocean to the surface layer, indicates that 90% of the Pb, and 50% of the Cd comes from the atmosphere.

Table 2.4 Atmospheric fluxes of heavy metals to the sea surface (from Buat Mernard, 1984).

	South Atlantic Bight		**North Sea**		**West Mediterranean**	
Element	**Flux***	**Ratio****	**Flux**	**Ratio**	**Flux**	**Ratio**
As	45	2.1	28	1.7	54	
Se			22	1.1	48	
Cd	9	2.7	43		13	
Sb			58		48	
Hg	24	2.2		2.1	5	0.8
Pb	660	9.5	2650	6.8	1050	6.2

* ng cm^{-2} y^{-1}, ** Ratio = {atmospheric flux/riverine flux (soluble)}.

2.1.1.3 Removal and sinks for metals

Once the metals enter waters, by the various inputs, many processes occur which have an effect on the fate of the metals (Fig. 2.2).

In surface waters the metals, held within particulate mineral forms and those adsorbed onto suspended matter, are ultimately removed to the sediments by gravitational settling (Lal, 1977). Precipitation of dissolved metals, and the removal of metals associated with clay minerals or organic material by flocculation and sedimentation are also important removal mechanisms (Sholkovitz, 1976; Evans *et al*, 1977; Boyle *et al*, 1977; Van Olphen, 1977). This also provides particle surfaces for further adsorption of metals. These removal mechanisms are particularly important for the removal of metals in estuaries, for example high concentrations of trace metals have been reported in the sediments of the Rhine and Elbe and Tokyo Bay estuaries (Muller and Forstner, 1975; Duinker and Nolting, 1976; Fukushima *et al.*, 1992).

Metals can also be incorporated into biomass by ingestion or adsorption, and can be removed from the water body by sedimentation once the organism dies. (Bostrom *et al.*, 1974; Chester and Aston, 1976; Baudo, 1982).

Sedimentation of metal bearing material does not however mean that the metal is removed from the hydrocycle, since metals can still be interactive with the water column. Klinkammer *et al.* (1982) reported the diffusion of Cu, Mn, Ni, and Cd from

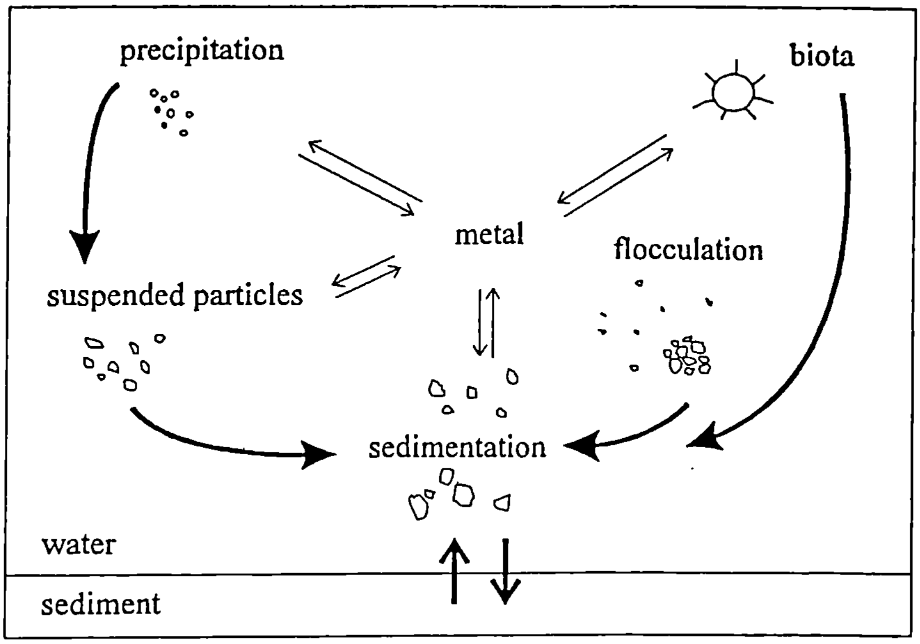


Figure 2.2. Schematic of removal processes in water bodies (from Hill, 1996).

marine sediments. Diffusion into the water column is also linked to the redox conditions of the sediment, for example the reduction of Mn(IV) to the more soluble Mn(II) makes it more likely to diffuse out of the sediment (Evans *et al.*, 1977). However, the ultimate fate of metals that reach the ocean is to be irreversibly incorporated into sediments, where they undergo diagenesis and tectonic uplift before being weathered and once again entering the hydrocycle.

2.1.1.4 Estuary and coastal waters and sediments

Estuaries and coastal zones are the sites which commonly receive anthropogenic waste either directly, by deposition from the atmosphere, or as part of the dissolved or particulate load of rivers. The concentrations of the trace metals in estuarine and coastal waters and sediments vary considerably from one place to another, depending on the inputs. Data presented in Tables 2.5-2.7 for water and sediments indicate the wide range of levels, especially for cadmium, lead, zinc and copper. Concentrations of the metals are usually higher in areas closer to the land, and in confined water bodies such as harbours estuaries and channels, closed to urbanized areas, because of additional sources of metals such as industrial and urban inputs.

Trace metals undergo, during their transport, numerous changes as the result of dissolution, precipitation and sorption phenomena, discussed in section 2.1.3. The distribution patterns of trace metals among the various parts of the estuaries have been found to be very complicated as a result of a great number of simultaneous and independent physical, chemical and biological processes involved (Salomons and Forstner, 1984; Bilinski *et al.,* 1991).

Figure 2.3 shows a simplified schematic of the modification of the riverine flux in the estuarine environment. Metals transported by the river water in association with particles of sufficient size will settle out of the water column and be deposited in the sediment. However, metals sorbed to particles are also in equilibrium with the dissolved phase, such that the particles may act as a source of dissolved metals, by releasing them into solution, or as a sink of dissolved metals by removing them via various physical, chemical, and biological processes.

The low salinity zone is the region where river water first comes into contact with sea water. This region is where the largest changes in pH and speciation occur, as

Table 2.5 Mean concentrations (ug/l) of dissolved trace metals in estuarine and marine waters.

Location	Cr	Cu	Co	Cd	Zn	Pb	Ni	Ref.
Estuarine Waters								
Upper Loch Linnhe, Scotland		0.28		0.04	0.48	0.05	0.26	1
The Indian River Lagoon, Florida	0.15	1.10	0.03	0.01	0.80	0.03	0.35	2
Marine Waters								
English Channel		0.31		0.02	0.47	0.02	0.27	3
North sea		0.44		0.02	0.60	0.05	0.42	3
N. North Sea		0.20		0.02		0.06		4
N. North Sea		0.14		0.02		0.03		5
Irish Sea		0.74		0.04	1.10	0.06	0.49	3
Liverpool Bay		1.45		0.27	11.86	1.74		6
Gulf of Gera, Greece		0.95		0.02	0.34	0.48	0.65	7
Euripos Straits, Greece		4.50			1.60	19.40	1.79	8
Narragansett Bay, USA		2.30		4.50	5.10	0.14	4.50	9
Atlantic water		0.07		0.01		0.03		10

References:

1- Hall *et al.* (1996).
2- Trocine and Trefry (1996)
3- Laslett (1995).
4- Brugmann *et al.* (1981)
5- Ball (1985).
6- Abdullah *et al.* (1972).
7- Doukakis *et al.* (1993).
8- Dassenakis and Kloukiniotou (1994).
9- Huizenga (1981).
10- Owens (1984)

Table 2.6 Range values (ug/l) of dissolved trace metals observed in near-shore UK waters.

Location	Cd	Cu	Ni	Pb	Zn	Reference
Humber	0.001-0.11 0.05-0.22	0.18-1.10 0.75-2.80	0.02-2.50 0.90-6.30	0.006-0.16 0.02-0.42	0.06-2.3 5.1-13.0	Hall *et al.* (1996) Laslett (1995)
Tyne	0.01-0.13	0.30-1.60	0.36-2.80	0.09-1.10	0.6-21.90	Laslett (1995)
Wear	0.01-0.02	0.33-1.00	0.51-2.90	0.07-0.41	0.50-6.10	Laslett (1995)
Tweed	0.008-0.01	0.58-4.70	0.48-0.80	0.09-0.17	0.60-1.90	Laslett (1995)
Mersey	0.01-0.05	1.40-3.30	0.80-9.40	0.03-0.46	1.50-16.00	Laslett (1995)
Severn	0.31-1.48	2.20-4.20	1.90-3.60	1.50-4.10	11.00-22.00	Owens (1984)
Morecambe Bay	0.10-0.043	1.80-1.90	0.82-1.40	0.03-0.17	1.50-7.40	Laslett (1995)
East Coast of UK	0.004-0.026	0.10-0.70	0.14-0.70	0.02-0.18	0.30-1.40	North Sea Task Force (1993)

Table 2.7 Mean concentrations (ug g^{-1}, dry weight) of trace metals in estuarine and marine sediments.

Location	**Cd**	**Co**	**Cu**	**Cr**	**Ni**	**Pb**	**Zn**	**Ref.**
Estuarine Sediments								
Humber Estuary, UK	0.4		43.0		30.0	68.0	203.0	1
	0.5	16.0	54.0	77.0	39.0	113.0	252.0	2
Mersey Estuary, UK	1.2	13.0	84.0	84.0	29.0	124.0	379.0	2
Restronguet Creek, UK	1.5	21.0	2398	32.0	58.0	341.0	2821.0	2
Severn Estuary, UK		7.0	38.0		36.0	119.0	280.0	3
	0.6	15.0	38.0	55.0	33.0	89.0	259.0	2
Tamar Estuary, UK	1.0	21.0	330.0	47.0	44.0	235.0	452.0	2
Tyne Estuary, UK	2.2	11.0	92.0	46.0	34.0	187.0	421.0	2
Firth of Clyde	3.4		37.0		50.0	86.0	165.0	
Clyde Estuary	7.0		225.0		69.0	528.0	1680.0	
Solway Firth	<1.0		10.0		38.0	37.0	63.0	4
Rhine River, France	28	35.0	397.0	397.0	167.0	333.0	1096.0	5
Bidasoa Estuary, France	1.1	10.8	100.0	56.0	35.0	150.0	410.0	6
The Indian River Lagoon, Florida	0.2	2.3	24	28.0	6.3	7.1	54.0	7
Huanghe Estuary, China			22.0	63.74	46.5	21.6	71.3	8
Marine Sediments								
Southern Atlantic coast of Spain	9.0		221.0	67	46	116	1000	9
Baltic Sea		22.0	78.0		43	25	110	10
Wadden Sea	0.5		22.0	84	37	37	103	11
Mid-Coast Mine, USA	0.4		20.3	34.9	19.9	21.7	66.8	12
Coastal southern Californian baseline	0.3		8.3	22	9.7	6.1	43	13
Grand Desert Beach	0.2	4.3	8.7	10.2	7.5	5.4	41.5	
Dalhousie Harbour	1.0	8.7	17.7	24.6	23.4	29.3	519.5	
Belledune Harbour, Canada	43.6	12.3	269	41.6	22.5	1638	6285.5	14
South east coast of India	2.4		17.0	138		53	62	15
Tokyo Bay, Japan	1.0		49.7	71.1	30.5	47.0	275.7	16
Sydney shelf, Australia			48.0		53	38	115	17
North-western coast of Arabian Gulf	0.3	2.0	2.6		10.1	3.6	13.7	18

References:

1- Gardiner (1982).
2- Bryan and Langston (1992).
3- Chester and Stoner (1975).
4- Mackay *et al.* (1972).
5- Forstner and Wittmann, (1981).
6- Saiz-Salinaz, *et al.* (1996).
7- Trocine and Trefry (1996).
8- Zhang *et al.* (1988).
9- Izquierdo *et al.* (1997).
10- Manheim (1961).
11- Laane (1992).
12- Larsen and Gaudette (1995).
13- Word and Mearns (1979).
14- Samant *et al.* (1990).
15- Subramanian and Mohanachandran (1990).
16- Fukushima *et al.* (1992).
17- Birch and Davey (1995).
18- Al-Hashimi and Salam (1985).

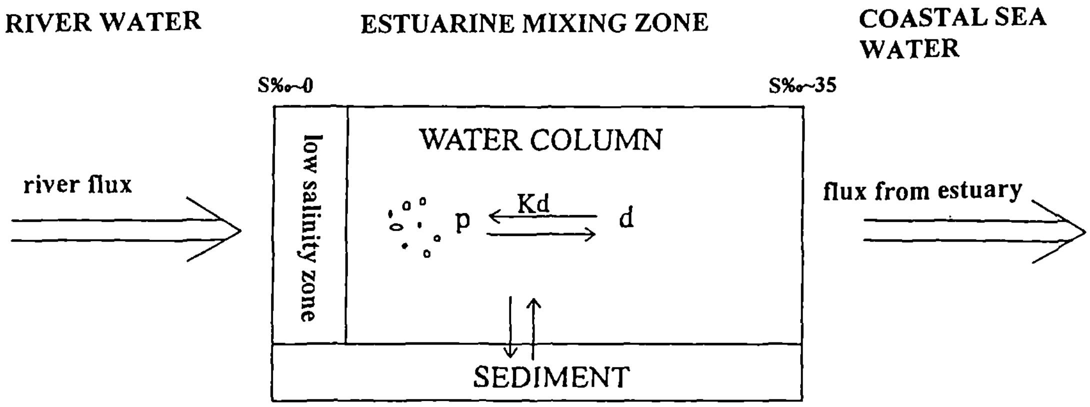


Figure 2.3. Schematic of fluxes within the estuarine environment. $p \overset{Kd}{\rightleftarrows} d$ indicates particulates-dissolved reactivity associated with physical, chemical and biological processes in the estuarine mixing zone. ↑↓ indicates two-way exchange of components between the water and sediment phases (from Chester, 1990).

well as where rapid flocculation of clays and organic material occurs (Boyle *et al.*, 1977; Mantoura, 1987; Yan *et al*, 1992). It is also the most turbid region where much of the exchange between particulate and dissolved material occurs. These processes have the potential to play a very important role in determining the fate of metals in the estuarine environment.

In the absence of any reactivity across the salinity gradient, the physical mixing of the river and the sea water end member components would lead to a theoretical dilution line on the mixing graph shown in Figure 2.4. A component which falls on this line will have its concentration determined purely by the mixing processes of the estuary, either with a concentration higher in sea water end-member (Fig. 2.4 i), or higher in the river water end-member (Fig. 2.4 ii). The component is said to be conservative (or non-reactive) under these circumstances. In contrast, the behaviour of a component that is added to, or is removed from the estuary during mixing is termed non-conservative (or reactive). This results on deviations from the theoretical dilution lines on the mixing graph.

Conservative mixing has been observed for Mn and Zn in the Bealieu Estuary (Holliday and Liss, 1976), and for dissolved organic carbon (DOC) in the Severn estuary (Mantoura and Woodward, 1983). Non-conservative behaviour has been widely reported for a number of component during estuarine mixing. Large removal of Fe has been reported from many estuaries (Holliday and Liss, 1976; Moore *et al.*, 1979). Trace metals have also been reported to be removed from solution during estuarine mixing (Turekian, 1977; Duinker and Nolting, 1976; Morris, 1986; Fukushima *et al.*, 1992), whereas the addition of Cu at low and at high salinities of the same estuary has also been reported (Windom *et al.*, 1983). The addition of metals to the water column from particles which may result from the increase of ionic strength, whereby sea water cations compete for binding sites on particulate material, and released metals are complexed by the high concentrations of sea water anions.

The release of metals from sediments can result in an important flux of redox sensitive elements such as Mn, which can be sedimented as the insoluble Mn (IV) phase but in reducing sediments can be remobilized as the soluble Mn (II) phase (Lynn and Bonatti, 1965).

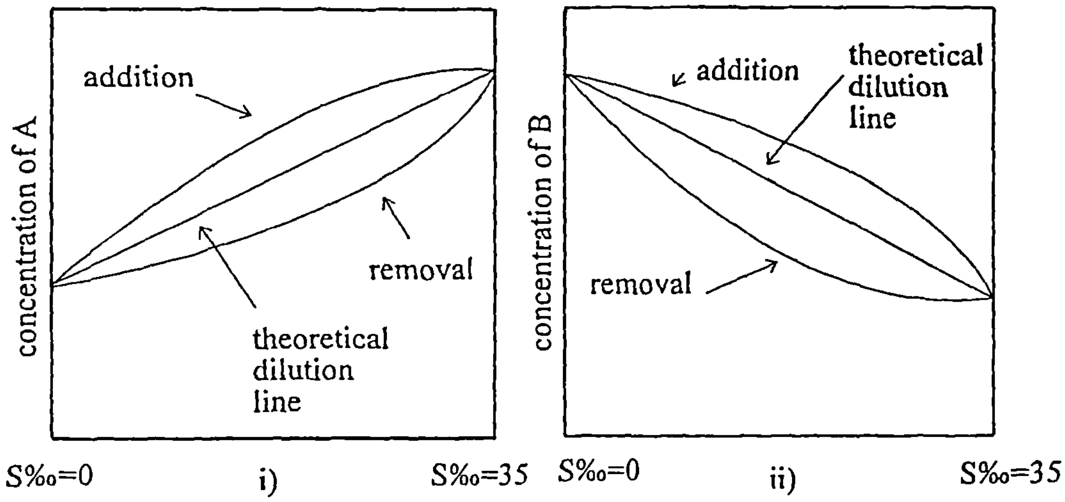


Figure 2.4. Schematic estuarine mixing diagrams, where i) the concentration of the sea water end-member is a higher, and ii) where the concentration of the river water end-member is a higher.

Sediments can act as a reservoir and changing environmental conditions, such as physical disturbance (Boughriet *et al.*, 1994) or diagenesis (Petersen *et al.*, 1995), may cause a remobilization of the accumulated metals, and the sediments may therefore persist as a source of pollutants long after the cessation of direct discharge. To assess the environmental impact of polluted sediments, information on total concentrations alone is not sufficient because heavy metals are present in different chemical forms in sediments (metal carbonates, oxides, sulfides, organometallic compounds, etc.). Only part of the metals present can be easily remobilized. Thus, the chemical form of the metals in the sediment is of great significance in determining behaviour in the environment and their remobilization potential (Rauret *et al.*, 1988).

Several methods for determining the different forms of metals in sediments are described in scientific literature (Kersten and Forstner, 1990). The most widely used methods are based on sequential extraction procedures, whereby several reagents are used consecutively to extract operationally-defined phases from the sediment in a set sequence (Lopez-Sanchez *et al.*, 1993). The various chemical leaching schemes as well as the reagents employed are considered in section 2.2.

2.1.2 Hydrocarbons

Of all aquatic pollutants, hydrocarbons, the principal components of petroleum, have received the greatest attention internationally, politically, and scientifically. Initially, this overwhelming concern was due primarily to the highly visible effects of oil pollution soiling of beaches, the presence of oil films and tar balls on surface waters, and the lethal effects of oil and petroleum hydrocarbons on aquatic organisms (Preston, 1989; Laws, 1993). Oil pollution is much more evident than other forms of marine pollution, and therefore, it is easier to get public support to combat it. Recently, more insidious long term effects of oil pollution have become apparent, and these have intensified the drive to minimize oil discharges into the world's oceans. The emphasis in this section on marine oil pollution is not mean to imply, however, that oil pollution of fresh water systems is not a serious problem. However, some of the issues associated with marine oil pollution, such as offshore drilling and the use of supertankers to transport oil, are peculiar to the marine environment. Many of the other issues are equally relevant to freshwater and marine systems. In other words, a study of marine oil pollution encompasses most, if not all, of the problem relevant to freshwater oil pollution as well (Laws, 1993).

The presence of oil in marine waters can have adverse impacts on both natural and human-manufactured resources (Bishop, 1983). Among the effects on natural systems are the following:

1): damage to the marine ecosystem by eliminating or decreasing populations of certain species;
2): hazard to humans from ingesting contaminated food;
3): damage to fisheries, seaweed, birds, marine mammals, and other wildlife; and
4): modification of habitats, delaying or preventing recolonization.

The study of marine oil pollution is an extremely complex one because of the myriad sources of petroleum materials entering the oceans, because oil is composed of thousands of different compounds, and because the fate of these materials is governed by many separate physical, chemical, and biological factors. The following sections will address the origin, the sources, the fate, and the significance of hydrocarbons in the aquatic environment.

2.1.2.1 Origin of hydrocarbons in the environment

Life on this planet is dependent on the trapping of solar energy by photosynthetic organisms. In this process, the energy is utilized to convert carbon dioxide into organic molecules. Eventually living organisms release the energy as heat, and carbon dioxide is returned to the atmosphere. However, it is now known that micro-organisms are the principal agent for the recycling of carbon in nature. The metabolic capabilities of this group of organisms have evolved throughout geological time and it is probably true to say that all organic compounds produced by living organisms are subject to biodegradation by micro-organisms (Gibson, 1977).

Figure 2.5 illustrates the natural carbon cycle in the nature with particular reference to hydrocarbon molecules. It is well known that linear and branched alkanes are produced by living organisms (Streitwieser and Heathcock, 1985). These compounds are also found in petroleum (Butt *et al.*, 1985).

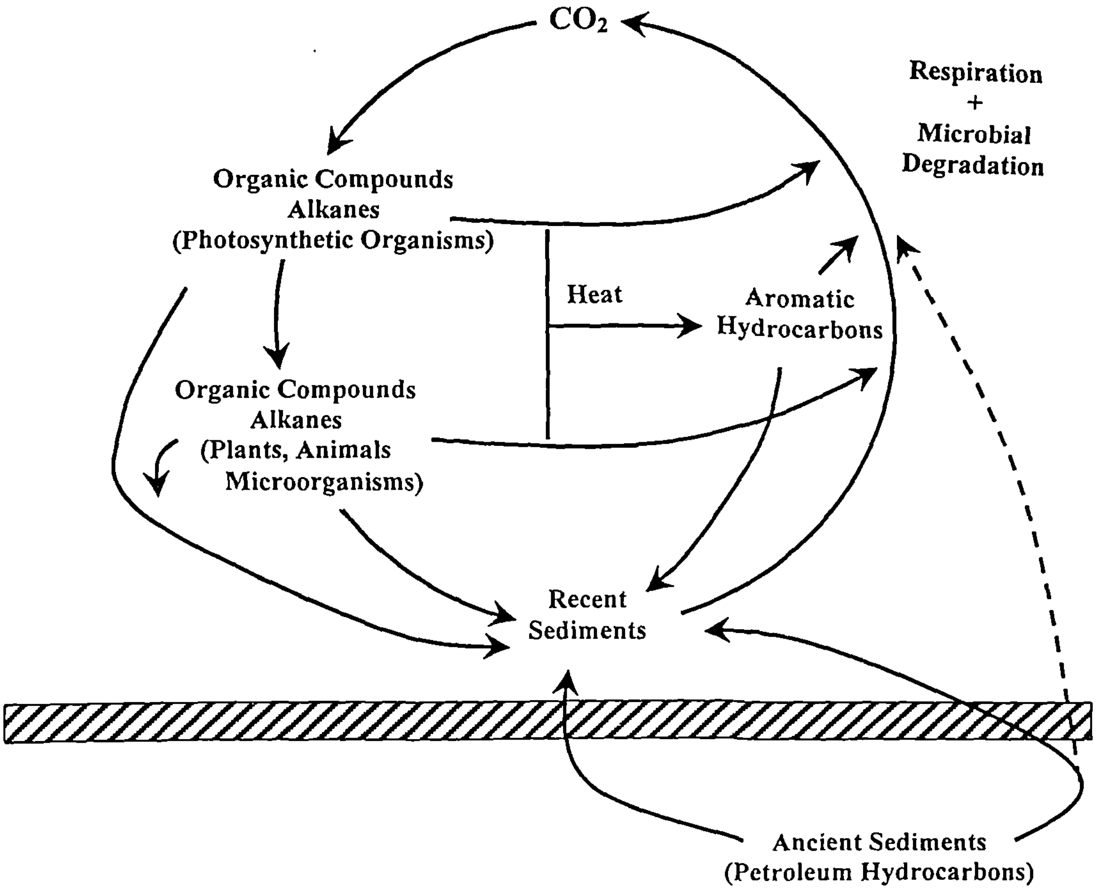


Figure 2.5. Cycle of hydrocarbons in the environment (from Gibson, 1977).

2.1.2.2 Sources of hydrocarbons

Marine oil pollution is not just a local problem. Petroleum hydrocarbons are introduced into the marine environment by a variety of pathways including natural and anthropogenic inputs. Accidental oil spills may be the most visible source, but they are far from the most important from the standpoint of total input (Bertrand, 1979), as discussed in section 2.1.2.2.2.

2.1.2.2.1 Natural sources

Long before human beings began using petroleum products, there was oil pollution in the oceans. Throughout the oceans there are places where oil naturally migrates, from geological reservoirs, to the sedimentary surface beneath the sea and enters the overlying water (Cowell, 1976). This oil has been entering marine waters, from submarine seeps, for millions of years. However, these seeps now make up a very small percentage of the total oil entering the marine environment. Over 6 million tonnes of oils enter the ocean every years of which only about 600,000 tonnes is from natural seeps (Anon, 1975).

Oily substances are also produced from the natural decay of marine plants and animals. There are major problems associated with estimating the annual production of biological hydrocarbon input because of a lack of data. One estimate is that these inputs may amount to as much as 6 million tonnes per year (m t y^{-1})(Koons and Monaghan, 1976). This estimated quantity (6 m t y^{-1}) of biological hydrocarbons produced by these organisms approximates to the amount of hydrocarbons resulting from all nonplanktonic oil inputs combined. Most of this naturally occurring oil is biodegraded by marine bacteria (Clark, 1992), so that the impact on the environment is minimal.

A third natural input of oily substance to the sea is from the sediments erosion. Estimates of the input of petroleum due to the erosion of continental rocks are based on indirect calculations, since there are only a few places where erosional inputs can by studied in detail. The calculation of the NRC (1985) are based on estimates of the amount of organic carbon transported to the ocean by rivers and the percentage of that carbon accounted for by petroleum. Fluvial inputs of organic carbon are estimated to be 400 m t y^{-1}. Based on the analysis of this carbon and of the carbon in ancient sedimentary rocks, petroleum is estimated to account for about 0.0125% of this figure, or 0.05 m t y^{-1}.

2.1.2.2.2 Anthropogenic inputs of hydrocarbons

Since about 100 years ago, with the coming of the "age of oil", the world production of oil has increased dramatically (Table 2.8), and half of it is transported by sea. As a result, oil pollution of the marine environment has drastically increased and become more objectionable.

Table 2.8 World oil production, 1938-1978 (from Bertrand, 1979).

Year	Total production 10^6 tonnes $year^{-1}$
1938	272
1946	375
1950	525
1955	770
1960	978
1965	1504
1970	2335
1975	2709
1978	3055

Oil enters the marine environment through numerous anthropogenic sources. The most conspicuous source of oil pollution is, of course, accidental oil spills from tankers or from offshore drilling or production platforms. However, these spills actually make up a very small percentage of the total oil entering the marine environment. Over 6 million tonnes of oil enters the oceans each year, of which only about 500,000 tonnes is from shipping accidents (Bertrand, 1979).

The anthropogenic inputs of petroleum hydrocarbon into the sea may be summarized as follows :

1- Offshore drilling and oil production,

2- Shipping operations, including deballasting, bilge cleaning and tanker operations,

3- Tanker accidents,

4- Coastal refineries and petrochemical plants,

5- Coastal municipal wastes,

6- Coastal industrial wastes,

7- Urban runoff,
8- River runoff,
9- Recreational boating,
10- Atmospheric fallout.

More difficult to assess is the input of petroleum hydrocarbons resulting from each of these sources individually. Consequently, the total quantity of such compounds entering the oceans annually has been variously estimated as 2 million tonnes (MIT, 1970), 0.7-3 million tonnes (Butler *et al.*, 1973), 3.81 million tonnes (USCG, 1973), and 6.1 million tonnes (NAS, 1975; Table 2.9). Recent estimates vary between 1.3 and 8.8 m t yr^{-1} (Preston, 1989).

According to NAS (1975; see Table 2.9), approximately one-third of the total petroleum entering the sea is introduced through transportation activities (i.e. tanker operation, tanker accidents, dry docking, bilge and fuel oil, non-tanker accidents). The share attributable to tanker accidents, the most newsworthy source, is only a small part (about 200,000 tonnes per year; NAS, 1975) of the total oil entering the marine environment. Rivers and urban run-off account for another third. Coastal facilities, such as municipal sewage plants, oil refineries and industrial plants, contribute 13%. Some petroleum hydrocarbons initially go into the atmosphere and then are carried down by precipitation into the oceans. This source accounts for about 10% of the total.

Table 2.9 Estimated world input of total petroleum hydrocarbons annually entering the sea (m t yr^{-1}) (from NAS, 1975).

Source	**Total amount**
Marine transportation	2.13
Offshore oil production	0.08
Coastal oil refineries	0.2
Industrial wastes	0.3
Municipal wastes	0.3
Urban runoff	0.3
River runoff	1.6
Atmospheric fallout	0.6
Natural seeps	0.6
Estimated total world marine oil production	6.11

2.1.2.3 Fate of pollution by petroleum hydrocarbons in the marine environment

In order to develop reasonable methods of controlling oil spills and long-term, low-level discharges, it is necessary to understand the processes acting on the oil at any given time following its release into the environment. When a spill occurs, many physical, chemical and biological processes, known collectively as ''weathering processes'', going on naturally in the ocean act on the spilt oil. Some of the processes are most important immediately after the spill occurs, others become increasingly important as time goes on. The exact details of these processes depend on many factors including the nature of the oil, but for a typical crude oil the weathering scheme outlined in Figure 2.6 is appropriate. Figure 2.6 relates the time following discharge of a crude oil into the sea to various processes of movement and degradation. Line length represents the probable time span of any process, while the line width indicates the intensity of the process through time and in relation to other concurrent processes.

Spreading is a rapid and dominant process at the time of a spill, waning steadily until it more or less stops within a week to ten days. The spreading process is controlled by the physical and chemical properties of the oil and the environment into which it is released (Clark, 1992). In rough seas, wind and wave action play an important role in the break-up of the oil slick, into small patches and windows. Oil spilled into very cold waters may spread at a lower rate, especially if it has a high viscosity as does heavy waxy oil. Other processes, such as evaporation, dissolution, dispersion and emulsification, are enhanced by spreading (Preston, 1989).

The drifting process results from the action of currents, winds and tides upon slicks. The drifting process is always active, from the moment a spill commences until the slick disappears from the surface of the sea. The significance of drift is dependent upon the proximity of the slick to beaches and fishing grounds or other biological resources (Exxon Corporation, 1978).

Evaporation is the primary initial process involved in the removal of oil from the sea. It is simply the process of transformation of oil components from the liquid phase to the vapour phase. Rates of evaporation of oil at sea are determined by wind velocity, water and air temperature, intensity of the sun's rays, roughness of the sea and the physical properties of the oil (Bishop, 1983). Through evaporation, an oil slick

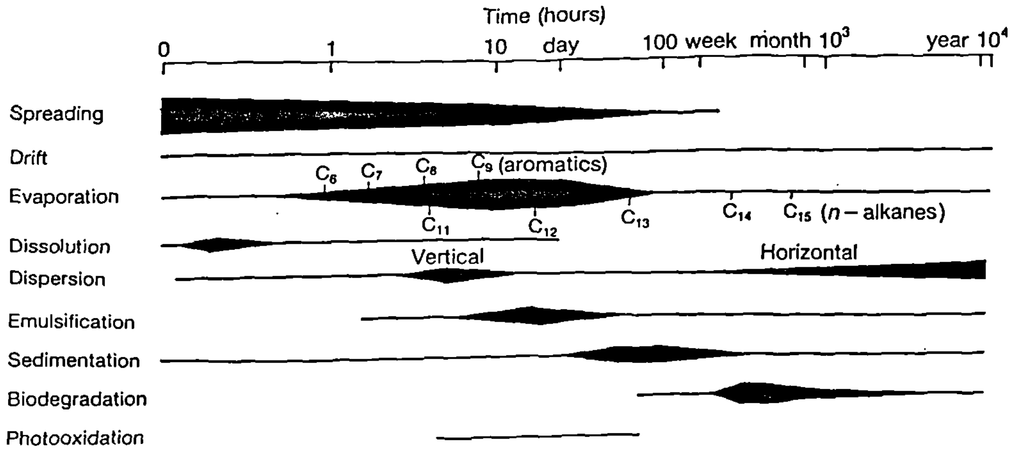


Figure 2.6. Time-course of factors affecting oil spilled on the sea (from Clark, 1992).

composed of light, low-boiling components will be rapidly depleted. Some of these low-boiling components, such as benzene and toluene, are among the most toxic hydrocarbons in oil. Thus, their rapid removal from the slick tends to reduce the toxicity of the slick.

Dissolution is another initial process acting on any spilled oil. This process involves the dissolving in the sea-water of certain components in the oil. Most components of oil have only a limited solubility in water; solubility becomes negligible above about C_{10} (Bishop, 1983). However, a few compounds, notably the lighter, low boiling point aromatic hydrocarbons and those containing polar groups such as sulfur, nitrogen, and oxygen, are sufficiently soluble to be dissolved fairly rapidly by seawater (Macko *et al.*, 1982). These compounds are the same hydrocarbons which are susceptible to evaporate processes. Environmental factors, such as water turbulence, can significantly increase the rate of the dissolution process. High temperature also has the indirect effect of deoxygenating the water and increasing the metabolic activity of its inhabitants, thus enhancing the effects of other pollutants (Nelson-Smith, 1972). The evidence, however, is that dissolution is less important than evaporation (Preston, 1989).

The process of dispersion results in a mixture of oil with water. Extremely small droplets of oil are incorporated into water in the form of a dilute oil-in-water suspension. The process reaches a maximum rate only a few hours (4-10) following a spill but continues for some time. The condition of the sea is probably the single most important controlling factor but temperature, oil composition, viscosity and specific gravity are also significant. Commercially available dispersants can help remove oil from the water surface by this means but necessarily result in elevated concentrations of hydrocarbons in the water (Preston, 1989). In open seas, these concentrations are rapidly reduced to very low levels. Many toxic components will have already evaporated prior to dispersion.

Water-in-oil (as distinct from oil-in-water) emulsions may also form. As with dispersion, sea conditions are probably the single most important factor in creating an emulsion, but the chemical composition, viscosity and specific gravity of the oil, and the water temperature, are also important. The rougher the seas, the more active the process. Water-in-oil emulsions form floating semi-solid lumps, often described as

Chocolate Mousse (Preston, 1989; Clark, 1992). Most water-in-oil emulsification will occur from a few hours to several days after the spill. Depending on its stability, a water-in-oil emulsion may persist and age to form tar balls or lumps, or it may fragment and disperse as extremely small particles. Tar balls can persist for many years.

Sedimentation occurs if the specific gravity of the oil becomes greater than that of water or if the churning action of the waves drives the oil into the bottom. Evaporation and dissolution of lighter components may leave a residue of smaller, denser oil particles which can adhere to inorganic sediment. This process is most significant in areas near shores, bays and estuaries where the suspended inorganic sediment load is high. Fine-grained clay materials may absorb large quantities of dissolved hydrocarbons from the water. Sedimentation may occur throughout the lifetime of a spill. Once on the bottom, oily materials may move laterally great distances. It has been reported that in deep water depositional areas the sediments can be regarded as a sink for hydrocarbons, but in a shallower and more dynamic environments significant remobilization could occur (Law and Biscaya, 1994).

Biodegradation is an important later process in degrading oil in the sea. Processes such as evaporation and, to a much lesser extent, dissolution remove the volatile components of the oil spill, leaving a residue. This residue may exist at the air-sea interface, in mid-water or in the underlying sediments. Petroleum-utilizing microbes (bacteria, yeasts, moulds) are found in all the waters and sediments of the world. Rates of biodegradation are controlled by the availability of microbes, oil composition, temperature, and of supplies such as nitrogen, phosphorus and oxygen (Preston, 1989). The lighter or lower molecular weight components are degraded faster than the heavier, high molecular weight ones. In general, higher temperatures increase the degradation activities of microbes.

Photochemical oxidation is another process that degrades the oil on the sea's surface. The effectiveness of this process is dependent on the intensity of sunlight, temperature, chemical composition and the physical state of the oil on the water surface (Bishop, 1983). Under these conditions a variety of photo-oxidation reactions may occur. A number of the oxidation products (which are largely high molecular weight materials; Preston, 1989) are insoluble in water and remain with the body of slick. In contrast, water soluble photo-oxidation products (which are largely aliphatic and aromatic acids, alcohols, ethers and dialkyl peroxides; McAuliffe, 1977; Malins, 1980) tend to be carried away from the slick and diluted naturally, with water. The formation of tar lumps virtually precludes further photochemical oxidation because of their low surface area: volume ratios and because light cannot be transmitted beyond the highly degraded, tarry surface (Exxon Corporation, 1978).

2.1.2.4 Significance of pollution by petroleum hydrocarbons in the aquatic environment

Interest in the organic chemistry of the marine environment has increased considerably in the past two decades, due to advances in analytical techniques such as gas chromatography/mass spectrometry (GC/MS) enabling identification of compounds present at very low concentrations and to the development of new concepts. The organic matter present in seawater and sediments shows one constant characteristic: its complexity. Because of the accelerated demand for energy during the past half century, pollution of the marine environment by petroleum and petroleum hydrocarbons has been increased. With the great increase in worldwide transportation of petroleum and petroleum products (refined oil, solvent, and plastic), significant progress in determining the sources, fates and effects of petroleum compounds in the marine environment has resulted in the last two decades.

Before 1968, investigations focused mainly on visible slicks, the aesthetic problem of tar on beaches, and the acute effects of oil spills on birds. By the early 1970's, it was recognized that the lack of a visible slick did not mean that the problem of oil pollution has been removed from the environment (NRC, 1975). After slicks had visibly disappeared, measurable amounts of oil in water, biota and sediments of coastal ecosystems could persist for periods ranging from days to years. Pathways of anthropogenic hydrocarbons into water bodies are diverse. In addition to oil spills, coastal areas and estuaries receive chronic inputs from a variety of sources including industrial discharge, marinas, urban-runoff, and atmospheric fallout (Bidleman *et al.*, 1990). Hence a number of works have been published recently concerning the determination of concentrations of hydrocarbons in marine waters and sediments (Tables 2.10 and 2.11). The data presented in Tables 2.10 and 2.11 show the

Table 2.10 Reported concentrations (mean or range if mean are not reported) of *n*-alkanes in estuarine and marine waters (ug/l) and sediments (ug/g).

Location	Concentration	References
Water		
Narragansett Bay, Rhode Island	0.85	Duce *et al.* (1972)
Magnetic Island Antarctica	0.09-0.17	Green *et al.* (1992)
Sediments		
Mersey estuary	10.76	Readman *et al.* (1986)
Dee estuary	1.83	
Tamar estuary	12.60	
Forth estuary (Tancerd Bank)	21.7	Ajayi and Poxton (1987)
Forth estuary (Longament)	7.7	
Forth estuary (Port Edgar)	21.9	
St. Lawrence Estuary, Canada (site 1)	2.83	Pelletier *et al.* (1991)
Lake of Washington.	7.7	Wakeham and Carpenter (1976)
Beaufort Sea, Alaska	1.4-5	Venkatesan and Kaplan (1982)
San Pedro, the southern California Bight	7.6	Venkatesan *et al.* (1980).
Nearshore Atlantic	1.96	Snedaker *et al.* (1995)
Bay region, Atlantic	3.44	
Venezuelan coast	1.5-14	Jaffe *et al.* (1995)
Inside the Harbour of Alexandria, Egypt	42	Aboul-Kassim and Simoneit (1995)
Arabian Gulf	8.92-10.92	Al-Saad and Al-Timari (1993)
Kuwait coastal zone	0.74-1.70	Mille *et al.* (1992)
Bahrain coastal zone	0.56-2.10	
Oman coastal zone	0.49-5.20	
Innershore of Makassar Strait, Indonesia	0.3	Noor *et al.* (1987)
Tama river sediments (Tokyo area)	52	Matsumoto (1983)
Chichi-jima Island, Japan	12	

Table 2.11 Reported concentrations (mean or range if mean are not reported) of PAHs in estuarine and marine waters (ng/g) and sediments (ng/g).

Location	**Concentration**	**References**
Water		
River Tyne (South Ferry Landing))	1323	Law *et al.* (1997)
River Tyne (Tyne Bridge)	336	
River Humber (Spurn Head)	5	
River Humber (North Killingholme)	83	
River Thames (West Thurrock)	390	
Southampton water (Dock Head)	39	
River Tamar (Warren Point)	50	
Liverpool Bay	9	
Rive Mersey (Quuen Channel)	112	
Admiralty Bay, Antarctica	80	Bicego *et al.* (1996)
Baltic Sea	6.88	Witt (1995)
North Sea	2.25	
Cedar Greek, Sarasota Bay	1721	Sherblom *et al.* (1995)
Caples Hall, Sarasota Bay	355	
Blackburn Bay, Florida	56	
Sediments		
Severn estuary	9000	Thompson and Eglinton (1978)
Rhone delta, France	1225-2427	Lipiatou and Saliot (1991b)
Coastal area of Barcelona and Valencia	1396-2313	Grimalt *et al.* (1984)
Ligurian sea of Monaco	599-723	Burns and Villeneuve (1983)
Baltic Sea	223.30-1179.53	Witt (1995)
Adriatic Sea	12-174	Marcomini *et al.* (1986)
Gulf of Lions	182-763	Lipiatou and Saliot (1991b)
St. Lawrence estuary, Canada, (site 1)	238	Pelletier *et al.* (1991)
Beaufort Sea, Alaska	200-300	Venkatesan and Kaplan (1982).
Gulf of Mexico	9.800	Nishimura and Baker (1986)
Castle Harbour, Bermuda	209	Burns *et al.* (1990)
Coast of Montevideo, Uruguay	170-4940	Moyano *et al.* (1993)
Sullivans creek catchment, Australia	609	Leeming and Maher (1992)
Brisbane River Estuary, Australia	3940-16110	Kayal and Connell (1989)
New Zealand Offshore	0.255-6.582	Kennicutt and Brooks (1990)
Magnetic Island, Antarctica	7	Green *et al.* (1992)

concentrations of *n*-alkanes and PAHs in estuary and marine waters and sediments. It can be seen from these two tables that the concentrations of hydrocarbons vary considerably from one area to another and that sediments are commonly used for the assessment of the extent of petroleum pollution. This approach arises from the concept that they act as pollutant sink and provide an integrated picture of the events taking place in the water column (Ramos *et al.*, 1989). It is difficult, however, to relate the concentration of hydrocarbons directly to environmental pollution. It should always be taken into account that such compounds may be produced in nature, while equally, quantities of aliphatic and aromatic hydrocarbons found in the marine environment are influenced by a number of secondary factors. The most important factors next to synthesis of hydrocarbons by marine organisms themselves are biodegradation, photochemical oxidation, evaporation and dissolution in water (Herbes *et al.*, 1980; Lamparczyk *et al.*, 1988).

The description of a given suite of hydrocarbons in a specific sample as natural or pollutant is a matter of judgement in interpreting the meaning of objective chemical analysis. The judgement is not difficult to make in cases where substantial levels of certain hydrocarbons are encountered. Therefore, for example, with a full suite of aliphatic and high levels of aromatic hydrocarbons, it is easy to make an accurate judgement whereas, for example with very low levels, a clear decision is difficult. In general, in unpolluted areas, hydrocarbons associated with marine sediment are often a mixture of algal or other marine remains, and terrigenous plants. The distributions of hydrocarbons in aquatic sediment, especially the top 0-20 cm, generally have identifiable sources. The predominance of low molecular weight (smaller than C_{23}) *n*-alkanes in gas chromatograms are indicative of organic matter derived mainly from algae and partially from zooplankton, bacteria and fungi (Al-Saad and Al-Timari, 1993). However, a predominance of high molecular weight hydrocarbons (larger than C_{23}) is generally considered to be indicative of organic matter originating from land and aquatic plants. Fossil hydrocarbons can enter the aquatic environment through natural and anthropogenic sources (Jeng, 1981).

Since hydrocarbon concentrations, in recent aquatic sediments, alone cannot be treated as a direct indication of marine environmental pollution, several additional parameters have been suggested as indicators, of which the best known are the distribution of normal (e.g. the odd to even carbon atom ratios) and acyclic isoprenoid alkanes (e.g. Pr/C_{17}, Ph/C_{18}), steranes and triterpanes (e.g. Blumer and Sass, 1972; Dastillung and Albrecht, 1976; Brassell *et al.*, 1978; Albaiges and Albrecht, 1979; Herbes *et al.*, 1980; Wise *et al.*, 1980; Douglas *et al.*, 1981; Jones *et al.*, 1983). These compound classes do occur in petroleum with sufficiently characteristic distributions that enables them to be distinguished from naturally occurring hydrocarbons in recent sediments. Also, they can be determined with relative ease in sedimentary lipid mixtures, and further, the steranes and triterpanes remain relatively unaffected by processes such as evaporation, dissolution and chemical or microbial attack (Jones *et al.*, 1986).

In contrast, PAHs make up only a small fraction of the total hydrocarbons, compared to the *n*-alkane fraction, that enter the aquatic environment but are of concern as many have been found to be carcinogenic and/or mutagenic (NAS, 1972). However, by examining the relative abundance of PAH and their alkylated homologues, it is possible to identify sources of PAH and broadly determine the relative contribution of each sources (Leemin and Maher, 1992).

2.1.3 Polychlorinated biphenyls (PCBs)

PCBs are chlorinated hydrocarbons but are not used as pesticides. Instead, they are widely used as plasticizers, fire-retardant paint ingredients, hydraulic fluids, heat exchange fluids, and insulating fluids in electrical capacitors and transformers. They were first synthesized by Schmidt and Schulz (1881) before the turn of the century and were first manufactured industrially in 1929, in the United States. Of the 209 possible isomers and congeners, more than 150 are found in commercial mixtures, *e.g.* Aroclor, Clophens, etc. (Duinker *et al.*, 1988; Bossi *et al.*, 1992). In the United States, the only large producer of PCBs was the Monsanto Chemical Company, which sold them from 1929 to 1975 under the Aroclor trademark. Not all PCBs are Aroclors, but most Aroclors are mixtures of PCBs. The name Aroclor is frequently used interchangeably with PCB. The very characteristics that made Aroclors desirable commercial products cause the persistent problems with PCBs.

Since 1930, in particular after 1945, and until the early 1980s, the total world production of polychlorinated biphenyls (PCBs) has been $\sim 1.2 \times 10^6$ t (Tanabe, 1988), mainly for use in transformer liquids. From the latter half of the 1950s, production of PCBs in Europe increased drastically, peaking at the end of the 1960s (De Voogt and Brinkman, 1989). After the discovery of the presence of PCBs throughout the environment PCB production reduced, and by 1970 it had decreased to 10% of the peak values. Significant quantities are still in use, however, mainly in older electrical equipment. The principal manufacturers have restricted the sale of PCBs in an attempt to minimize the hazard to the environment. However, some companies have retained stocks of these compounds, and discharges to the environment may be expected to continue for some time.

Polychlorinated biphenyls (PCBs) have been recognized as a major group of environmental pollutants since the late 1960s (US EPA, 1976; Hutzinger *et al.,* 1980). Because of excellent flame resistance, electrical properties, and chemical stability, PCBs found application in a wide variety of industrial uses including heat-transfer fluids, hydraulic fluids, solvent extender, plasticizers, flame retardants, organic diluents, and dielectric fluids (Christensen and Lo, 1986). The application of PCBs has mainly occurred in the industrially developed world of the Northern Hemisphere. Hence, the major releases to the environment have occurred in these regions. However, residues of chlorinated organic microcontaminants are also reported in environmental media from all geographical latitudes, because of their large production and worldwide use, and thus show a global occurrence: from more remote areas, such as Antarctica (Risebrough *et al.*, 1976), sub-Antarctic regions (De Boer and Wester, 1991) and the Arctic (e.g. Muir *et al.*, 1988; Norstorm *et al.,* 1988; Gregor and Gummer, 1989), to exposed tropical marine and estuarine ecosystems (e.g. Boon *et al.*, 1989; Hungspreugs *et al.*, 1989; Everaarts *et al.*, 1991; Siriwong *et al.*, 1991). In summary, they are "semivolatile, persistent, lipophilic, organochlorine compounds", and over 100 congeners have been reported to occur in environmental samples (Alcock *et al.*, 1994).

2.1.3.1 Sources and fate of PCBs in the environment

Chlorinated hydrocarbons differ from petroleum hydrocarbons because they are not readily degraded by chemical oxidation or bacterial action. Like metals, they are essentially permanent additions to the environment but, unlike metals, these compounds are man-made and do not occur naturally.

PCBs are released to the environment, from the products and devices containing them, in various ways. Water discharges (spills, dumps, accidents and waste streams) to the aquatic environment are an important direct route for these substances into the marine environment. On the other hand, as PCBs are somewhat volatile it is believed that they would tend to transport to the aquatic environment indirectly by the atmosphere, depending on the wind and precipitation conditions (Harvey and Steinhauer, 1976; McClure and Lagrange, 1977; Alcock *et al.*, 1994). The characteristic that makes PCBs such a problem is their stability and, therefore, persistence in the environment. The occurrence of PCBs or the individual congeners and many other halogenated organic compounds in environmental compartments is well documented (e.g. Tatem, 1986; Preston, 1989).

PCBs are extremely insoluble in water, but they adsorb strongly on to particles which causes them to settle to the sediments. Their concentrations in water, therefore, is much lower than sediments (Table 2.12). Estuarine and coastal marine sediments can act as long or short term reservoirs of PCBs in the aquatic ecosystem as a whole, because of the strong hydrophobic (lipophilic) character of PCBs. (Lee *et al.*, 1979; Wakeham and Farrington, 1980; Brownawell and Farrington, 1986; Colomobo *et al.*, 1990). Such sediments can preserve a historical record of their deposition, and their analysis may thus reveal the historical record of such contaminants (Martin and Hartman, 1985). Therefore, sediment analysis has been widely used to detect sources of PCB pollution and to assess the ecological risk.

Sorption reactions involving interstitial waters and sediments particles control the rates and mechanisms of transport of PCBs within in and out of sediments, and also affect the bioavailability of these compounds. Other diagenetic processes such as biological and chemical transformation reactions, diffusion, advection, and mixing and resuspension of the sediment bed, will also affect the distribution of these hydrophobic compounds in sediments and pore waters (Berner, 1980). The relative importance of each of these processes depends on the molecular structure, biological activity and physical chemical properties of PCBs, as well as properties of the sedimentary environment (Brownawell and Farrington, 1986). The accumulation of

Table 2.12 Reported concentrations (mean or range if mean are not reported) of PCBs in estuarine and marine waters (ng/l) and sediments (ng/g).

Location	**Total PCBs**	**Reference**
Water		
Coastal waters of the English Channel and the North Sea	1.4-29	Marchand and Caprais (1985)
Seine Bay	3	
Loire Upstream Estuary	18	
India	0.34-48	Iwata *et al.* (1994)
Thailand	<0.24-4.40	
Vietnam	0.45-8.00	
Indonesia	0.38-2.10	
Solomon Island	<0.05-1.10	
Japan	0.32-0.74	
Taiwan	0.09-2.10	
Australia	<0.05-2.20	
Sediments		
Essex Coast, UK	0.3-34.2	Scrimshaw *et al.* (1994)
Humber Bay	3-19	Klamer and Fomsgaard (1993)
Humber Estuary, UK	1-84	Tyler and Millward (1996)
Irish Sea	0.2-42	Thompson *et al.* (1996)
Liverpool Bay	30	Thompson *et al.* (1996)
Belfast	8	
Dublin	6	
Firth of Clyde (Carroch Head)	5.51	Kelly (1995)
Firth of Clyde (Pladda)	3.5	
Firth of Forth (St. Abbs Head)	1.1-26	Borewell *et al.* (1986)
Firth of Forth (Bell Rock)	1.1-26	
North North Sea	0.7	SOAFD (1986)
Coastal waters of Venice, Italy	5-744	Van Vleet *et al.* (1988)
The Lagoon of Venice	0.003-0.020	Raccanelli *et al.* (1989)
Scheldt estuary	217-1068	Van Zoest and Van Eck (1990)
Axios River, Greece	4-24	Larsen and Fytianos (1989)
Aliakmon River, Greece	1-7	Larsen and Fytianos (1989)
Thermaikos Gulf, Greece	5-39	Larsen and Fytianos (1989)
California	2-1728	Rice *et al.* (1993)

Table 2.12 Continued.

Location	Total PCBs	Reference
Sediments		
Castle Harbour, Bermuda	1.5	Burns *et al.* (1990)
San Francisco Bay	1.2-1400	Phillips and Spies (1988)
Rio de La Plata, Argentina	2-998	Colombo *et al.* (1990)
Gulf of Mexico, 1986	<0.1-190	
Gulf of Mexico, 1987	<0.1-3730	Sericano *et al.* (1990)
Hong Kong Bay	1155	Kannan *et al.* (1989)
River of Fukuoka Prefectture, Japan	0.00064 - 2.200	
offshore of Fukuoka Prefectture	0.00031- 0.31	Ohsaki *et al.* (1997)
Manukau Harbour, New Zealand	0.5-14.2	Fox *et al.* (1988)
India	5-1000	
Thailand	11-250	
Vietnam	0.2-140	
Indonesia	6-220	
Papua New Guinea	3-54	
Solomon Island	1-5	
Japan	63-240	
Taiwan	2-230	
Australia	0.5-790	Iwata *et al.* (1994)

PCBs in estuarine and marine environments has been studied in several parts of the world. This has provided information on the historical input and on post-depositional mobility and reactivity of these compounds (e.g. Pavoni *et al.*, 1987; Oliver *et al.*, 1989). Most studies have shown that post-depositional mobility and reactivity are not very important. Thus, in most cases some information is obtained about the historical input. Van Zoest and Van Eck (1993), for example, found that PCBs are mobilized after deposition.

2.2 A review of selective leaching technique

2.2.1 Introduction

Selective leaching techniques had not been used in this department before, and consequently some effort was put into making sure that the methods were implemented correctly.

The chemistry of contaminated sediments is of a complex nature since their metal concentrations vary significantly (Chester and Hughes, 1967; Rapin *et al.*, 1983). Sediments are not homogenous (Guy *et al.*, 1978) but are heterogeneous mixtures of components of different origin and chemical behaviour (Martin *et al.*, 1987). According to Tessier and Campbell (1988) these components, which act as traps for heavy metals introduced into the aquatic environment from both natural (lithogenic) and anthropogenic sources, exist as aggregate particles and includes: residues of weathering and erosion (such as clays and other aluminosilicates, iron and manganese oxyhydroxides), substances produced by biological activity, such as organic matter (living organisms and biological detritus, humic substances), inorganic products (carbonates, phosphates and silica), and diagenetic products (e.g. the iron and manganese oxyhydroxide formed in the upper layer of the sediment and the sulphides in the deeper strata). Goldberg (1954) has classified these components, according to their origin, into five categories: lithogenous, hydrogenous, biogenous, cosmogenous and atmogenous.

The total metal concentration provides important information about the pollution level only if the background or geochemical composition is known. However, metal origin, whether natural or anthropogenic, is difficult to determine. To assess the environmental impact of polluted sediments the determination of total content of heavy metals is not enough (Salomons and Forstner, 1980); it is essential to know the chemical forms of the metal in the sediment in order to determine their behaviour in environmental processes.

The principal objective of a metal partitioning study is to quantify and identify the chemical forms of a targeted metal in aquatic particles in order to evaluate its impact in environmental/biological systems. However, the direct measurement of trace metals associated with a given sediment is seldom feasible, due mainly to the great number of phases present and the low concentrations of trace metals. Therefore, indirect methods must be used. In this context, partial extractants, often called selective extractants, have been used to gain information about the association of trace metals in sediment. Methods involving single or multiple chemical extraction steps with a series of extractants chosen in order of increasing strength have been developed for separating trace metals present in the sediment broad geochemical classes but it is generally recognized that the partitioning of trace metals, into specific fractions (or phases), obtained by such methods is operationally defined by the sequence of extractants used.

2.2.2 Development of chemical leaching techniques in sediments analysis:

Several investigators have attempted, during the last two decades, to develop chemical leaching techniques for the determination of the quantities of metals associated with different phases of sediments (e.g. Gibbs, 1973; Gupta and Chen, 1975; Brannon *et al.*, 1976; Tessier *et al.*, 1979; Forstner *et al.*, 1981). These sequential extraction procedures give an indication of the available fraction of the total metal that may undergo changes due to alteration in the physico-chemical and biological characteristics of the environment (Salomons and Forstner, 1984), despite their often poor selectivity (Chao, 1972; Engler *et al.*, 1977; Reuther *et al.*, 1981). Such procedures utilize a series of 'selective' reagents to remove metals from various component fractions. The methods are operationally defined by the sequence of the extractants used.

Earlier studies on heavy metals in sediments were confined to the partitioning of metals into detrital and non-detrital fractions (Hirst and Nicholls,1958; Gad and LeRiche, 1966). The metal associated with the detrital (lithogenous) fraction can be regarded as that bound into the internal structure of aluminosilcate and other detrital minerals. Metals associated with the non-detrital (non-lithogenous) fraction may have been fixed in a number of ways, some of which may bind them more strongly than the other. Attempts have been made by many authors to devise a chemical extraction procedure for the separation of metals associated with the non-detrital fraction. The various chemical leaching techniques and the regents employed are considered in subsequent sections.

2.2.2.1 Separation of residual from non-residual forms:

Earlier studies on the distribution of heavy metals attempted to differentiate detrital and non-detrital metal fractions in marine sediments. Such chemical partitioning of metals allows deductions to be made as to the site of the metals and the pathway by which they have entered the sediments. The non-detrital fraction, transported in solution or colloidal form and incorporated into the sediment from solution in a variety of ways such as adsorption, precipitation, or extraction by living organisms, has the potential to be environmentally mobile and so to take part in the biogeochemical cycle (Loring, 1976a). In contrast, the heavy metals in the detrital fraction, transported in solid form, are locked up in the lattices of their host minerals (Loring, 1976a) and are relatively unreactive in the low temperature diagenetic environment. The proportions of these two fractions can be determined by direct analysis of the two fractions, or indirectly, by reference to another element such as Al or Li which are believed to record the proportion of detrital input (Chester, 1990).

Different reagents, such as weak acids, reducing agents combined with acid or chelating agents, have been used in order to isolate the elements associated with the detrital and the non-detrital fractions. As early as 1958, Goldberg and Arrhenius used EDTA (ethylenediaminetetra acetate) to examine the partitioning of metals into detrital and authogenic (non-detrital) fractions in deep-sea sediments. Hirst and Nicholls (1958) described a chemical method to isolate detrital from the more reactive non-detrital forms of carbonate sedimentary rocks by using dilute acetic acid (25% ,v/v). This method was used by Chester (1965), in a series of reef and non-reef carbonates, to study trace metal partitioning. Lynn and Bonatti (1965) used hydroxylamine hydrochloride in a study of manganese distribution in Pacific pelagic sediments. In order to determine the same phases Chester and Hughes (1967) introduced a reducing agent of 1 *M* hydroxylamine hydrochloride coupled with a weak acetic acid for the separation of the metals associated with ferromanganese nodules, carbonate minerals and adsorbed trace elements from pelagic sediments. The authors found that this technique will act on inorganically bound non-residual trace metals, and will not affect those of organic phases.

Of the above mentioned techniques, it has been found that both the acetic acid and the hydroxylamine acetic acid techniques are not suitable for differentiation between detrital and non-detrital fractions in coastal and estuarine sediments, which often contain appreciable amount of organic matter, because these two leaching solutions do not liberate trace metals that form strong complexes with organic matter (Agemian and Chau, 1976 and 1977; Salomons and Forstner, 1980).

Further studies, have been carried out (e.g. Loring, 1976 a,b; Malo, 1977) with the aim of identifying a single reagent to totally dissolve the non-residual fractions (e.g. weak and dilute acids such as 0.5 N HCl, CH_3 COOH and 0.3 N HCl, respectively), and to differentiate the inorganic from the organic ones. These one-step extraction methods, which are rapid and simple to apply, have been widely used in environmental studies since they: clearly show the contrast between background and abnormal concentrations of different metals (Bradshaw *et al.*, 1974); differentiate background (Loring, 1976 a,b) from anthropogenic levels of different contaminants (Skei and Paus, 1979); and can also be used as a preliminary trace metal pollution tool prior to sequential extraction (Chester *et al.*, 1985). Despite their advantages for environmental studies, these techniques suffer from certain disadvantages which can be summarised as follows: 1) There is a problem involving readsorption which can occur at neutral pH (Malo, 1977; Rendell *et al.*, 1980), which means that metals liberated with a given solution may be readsorbed onto the remaining solid phase; 2) The difficulty of finding a single reagent capable in dissolving all the organic and inorganic labile forms (non-residual) without also attacking the detrital ones (Tessier *et al.*, 1979; Martin *et al.*, 1987); and 3) The fraction of the total metal extracted by any single reagent method will depended upon the type of sample used (Chester and Hughes, 1967; Agemian and Chau, 1977).

2.2.2.2 Sequential leaching techniques

The various methods described above in section 2.2.2.1. employ a single reagent to separate all the non-detrital fractions (phases), and to differentiate organic from inorganic ones. However, more sophisticated techniques, such as those employed by soil scientists, sequentially extract a number of non-detrital fractions, and to allow a more detailed insight into the distribution of metals within the sediment. These sequential extraction procedures are based on the successive use of a series of leaching reagents which are believed to remove phase specific forms of sediment-bound metals, each successive treatment being more drastic in chemical action or a different nature than the previous one.

Gibbs (1973) described a method in which the association of metals in sediments divided into four binding fractions: 1) adsorptive, 2) coprecipitated by hydrous Fe and Mn oxides, 3) complexed by organic matter, and 4) incorporated into crystalline solids. The first three fractions in this classification are associated with the non-detrital fraction where the latter is associated with the detrital fraction. This classification, of Gibbs (1973), lead to the existence of five or six metal bound fractions, by using sequential extraction procedures, (Tessier *et al.*, 1979; Salomons and Forstner, 1980): 1) exchangeable, 2) carbonates, 3) Fe - Mn oxides ; in Salomons and Forstner (1980) scheme this stage was treated as a) easily reducible, and b) moderately reducible, 4) organic and sulfides, and 5) residual.

Many such sequential extraction procedures have been described in the literature and used for speciation of heavy metals in sediments, *e.g.* :-

- differentiation of trace metals into a reducible, an oxidizable and a resistant fraction (Presley *et al.*, 1972; Bruland *et al.*, 1974);
- distinction between exchangeable metals, metals present in metal hydroxide coatings, organic solids, and the crystal phase (Gibbs, 1973, 1977); and
- determination of metal contents in interstitial water and in exchangeable, easily reducible, moderately reducible, organic and residual fractions (Gupta, and Chen, 1975; Brannon *et al.*, 1976).

However, the most widely used scheme in the literature is the one proposed by Tessier *et al.* (1979). This five-step sequential extraction scheme has been applied to a wide variety of sediment samples in various environments (e.g. lake, estuarine, coastal and deep sea sediments) and enables the distinction of exchangeable, carbonate, Fe-Mn oxides, organic and sulfide, and residual fractions.

A summary of the reagents that have been proposed in the literature, and the phases upon which they are believed to act, is given in Table 2.13. It should be noted that there are many difficulties associated with the choice of the extraction reagents used to bring a particular phase into solution, and in the sequence of the reagent addition. This topic is discussed in the subsequent section.

Table 2.13 Common reagents used for the extraction of metals associated with different chemical phases in sediments.

Geochemical Phase	**Reagent**	**Reference**
Water soluble	1- H_2O	Gupta and Chen (1975)
Exchangeable	1- NH_4OAC	Brannon *et al.* (1976)
	2- $MgCl_2$	Gibbs (1973)
	3- $BaCl_2$	Meguellati *et al.* (1983)
Carbonate	1- HOAc	Gupta and Chen (1975)
	2- CO_2 treatment	Forstner and Patchineelam (1976)
	3- NaOAc/HOAc	Tessier *et al.* (1979)
	4- Acidic cation exchange	Deurer *et al.* (1978)
Easily reducible	1- NH_2OH. HCL	Brannon *et al.* (1976)
	2- NH_2OH. HCl/HNO_3	Chao (1972)
Fe-Mn oxides	1- NH_2OH. HCl/HOAc	Tessier *et al.* (1979)
Moderately reducible	1- NH_2OH. HCl/HOAc	Chester and Hughes (1967)
	2- NH_2OH. HCl/HCl	Chao and Liyi (1983)
	3- NH_2OH. HCl/Na citrate	Robbins *et al.* (1984)
	4- $(NH_4)_2C_2O_2/H_2C_2O_4$	Forstner *et al.* (1981)
	5- $(NH_4)_2C_2O_2/H_2C_2O_4$/tin chloride	Shuman (1982)
	6- $(NH_4)_2C_2O_2/H_2C_2O_4$/ascorbic acid	Shuman (1982)
	7- $Na_2S_2O_4$ + Na citrate	Brannon *et al.* (1976)
	8- a) $Na_2S_2O_4$ Na citrate	
	b) NH_2OH. HCl/HOAc	Gupta and Chin (1975)
Organic and sulphide	1- H_2O_2/HNO_3	Presley *et al.* (1972)
	2- H_2O_2/NH_4OAc	Gupta and Chen (1975)
	3- NAOCl	Gibbs (1973)
Residual	1- $LiBO_2$ fusion	Gibbs (1973)
	2- $HF/HClO_4/HNO_3$	Gupta and Chen (1975)
	3- HF/HNO_3	Brannon *et al.* (1976)
	4- $HF/HClO_4$	Tessier *et al.* (1979)
	5- HNO_3	Forstner *et al.* (1981)

2.2.2.3 Choice of reagents

The primary problem in devising a sequential extraction scheme for trace metals is the choice of a reagent, for each step of the scheme, which will dissolve one phase of the sediment, without solublization of any other. Among the many problems which have been identified with the use of these sequential extractions schemes (e.g. Calmano and Forstner, 1983; Salomons and Forstner, 1984; Martin *et al.*, 1987; Kersten and Forstner,1990) are:

1): Reactions are influenced by the experimental factors such as the ratio of the extracting reagent to the solid matter, the length time of the extractions, the extraction sequence and the temperature. Some of the extractants are more specific than others as is demonstrated by Heath and Dymond (1977). A high solid contents together with an increased buffer capacity may cause the system to overload, such an effect is reflected by changing the pH values in time dependent test with hydroxylamine hydrochloride (initial pH = 2) and oxalate/oxalic acid (pH = 3) buffer solutions (Forstner *et al.*, 1981).

2): Sample pre-treatment is more important for anoxic samples than for oxic (see e.g. Rapin *et al.*, 1986), and incorrect sample handling may cause significant changes in speciation.

3): The differentiation of organic and sulphidic metal forms, both contributing to the oxidizable fraction, is not as yet possible (Papp *et al.*, 1991).

4): Some extractants used in the reducing steps (e.g. dithionite/citrate in Tessier *et al.*, 1979; Shuman, 1982) result in the formation of insoluble precipitates, contamination by metals in the reagent, decomposition of the reagent and formation of sulfides, and clogging of the burner during atomic absorption analysis.

5): Readsorption of metals, and occasionally precipitation may occur (Rendell *et al.*, 1980).

6): The absence of standardized conditions for sampling, sample preservation, fractionation schemes (e.g. the choice of reagents for the various extraction, and the sequence of the reagent addition), and analytical techniques makes it difficult to compare experimental data derived from studies in which such parameters differ significantly or even not listed, although during recent years researchers have tended to use similar extraction sequences. The sequence of reagent addition, may vary considerably. As shown in Table 2.14, Meguellati *et al.* (1983) recommended the extraction of the oxidizable fraction before the Fe-Mn oxides (reducible) fraction despite earlier results showing that, in acidic conditions, hydrogen peroxide causes manganese oxide dissolution rather than organic matter oxidation (Jenne and Luoma, 1977). Thus, this extraction scheme is not suitable for use with sediments which contains appreciable amounts of manganese oxide. An alternative procedure is to insert the oxidation step between the two reduction steps (Brannon *et al.*, 1976). This extraction procedure does not necessarily destroy the carbonate phase before the following steps are performed, so the sample keep its buffering capacity (Forstner *et al.*, 1981).

7): Selectivity: The basic assumption of sequential extraction procedures is that the extractants used are able to selectively remove one phase without any solublization of the others. However, it is generally recognized in the literature that the partitioning of elements obtained by the various extraction procedures with reagents of various strength is not as selective as sometimes stated, therefore, operationally defined element reactivity is generally used rather than attempts to individually characterize each sedimentary phase (Van Valin and Morse, 1982). This lack in the selectivity is generally attributed to readsorption of the released trace metals onto the solids remaining after the extractions (Tessier and Campbell, 1988).

Several possible approaches for the evaluation of extraction efficiency and selectivity exist, and many have been carried out as shown in Table 2.15. Rapin and Forstner (1983) tested the selectivity of different leaching steps in the Tessier *et al.* (1979) scheme on pure samples of known geochemical phases such as Ca, Mn, Cd and Pb carbonates, Fe/Mn oxides nodules, amorphous iron sulfide and crystalline lead sulphide (galena), and crystalline Fe oxides (goethite and hematite). After each extraction step the leachate was analysed, and the residual sediment remaining after extractions was studied by scanning electron microscopy with energy dispersive X-ray (EDAX). The selectivity proved to be sufficient for the carbonate phase extracted by sodium acetate (pH 5), acceptable for most metals associated with Fe/Mn oxides except for Pb, Cd, Zn, and Cr extracted with hydroxylamine hydrochloride, poorly

Table 2.14 Sequential leaching procedures used in the literature.

Method	Geochemical phase							
	Soluble	Exchangeable	Carbonate	Easily reducible	Fe-Mn oxide	Moderatelyreducible	Organic/sulphide	Residual
1	H_2O_2	NH_4OAc		$NH_2OH.\ HCl$		$Na_2S_2O_4$ + Na citrate[5]	H_2o_2/NH_4OAc[4]	$HF/HClO_4$
2	H_2O_2	NH_4OAc	HOAc	$NH_2OH.\ HCl/HNO_3$		a) $Na_2S_2O_4$ + Na citrate b) $NH_2OH.\ HCl/HOAc$	H_2o_2/NH_4OAc[5]	$HF/HNO_3/HCLO_4$
3			HOAc	$NH_2OH.\ HCl$, pH2		$NH_2OH.\ HCl/HOAc$	H_2o_2/NH_4OAc[3]	$HF/HNO_3/\ HClO_4$
4		$MgCl_2$	NaOAc*, pH5		$NH_2OH.\ HCl/HOAc$		H_2o_2/NH_4OAc	$HF/HClO_4$
5		$BaCl_2$	NAOAc , pH5[3]			$NH_2OH.\ HCl/HOAc$	H_2o_2/NH_4OAc[2]	$HF/HNO_3/HClO_4$
6		$MgNO_3$		$NH_2OH.HCl$,pH2[3]		$(NH_4)_2C_2O_4/H_2C_2O_4$	NaOCl[2]	$HF/HNO_3/HCl$
7		$MgCl_2$			$Na_2S_2O_4$+Na citrate		NaOCl	$LiBO_2$ fusion
8			NAOAc, pH5			$NH_2OH.\ HCl/$ Na citrate	$NaDS/NaHCO_3$[2]	HF/HNO_3
9		NH_4OAc	NAOAc, pH5			$(NH_4)_2C_2O_4/H_2C_2O_4$	H_2o_2/NH_4OAc	HNO_3
10		$MgCl_2$			$Na_2S_2O_4$+Na citrate		$NaOCl/Na_2S_2O_4$ +Na citrate	$LiBO_2$ fusion
11		$MgCl_2$	NaOAc, pH5		$NH_2OH.\ HCl/HOAc$		H_2O_2/NH_4OAc	$HF/HClO_4/HNO_3$

* OAC= Acetate; DS = Dodecyl sulfate.

Method :-

1- Brannon *et al.* (1976).
2- Gupta and Chen (1975).
3- Filipek and Owen (1978)
4- Tessier *et al.* (1979).
5- Meguellati *et al.* (1983).
6- Shuman (1983)
7- Gibbs (1973).
8- Robbins *et al.* (1984).
9- Forstner *et al.* (1981)
10- Gibbs (1977).
11- Lee and Kittrik (1984).

Table 2.15 A number of possible approaches for the evaluation of extraction selectivity, (after Campbell and Tessier, 1987; Kersten and Forstner, 1990).

- Use of pure phases (with and without spiking of trace elements)
  - Alone
  - In model sediment
  - Spiked into natural sediments
- Analysis of extracts and/or residual sediment for various ‘complementary’ parameters
  - Major elements such as Al, Si, Mg, K, etc.
  - Organic carbon
  - Inorganic carbon
  - Total sulfur
  - Acid volatile sulfide
- Successive extraction with the same reagent
- Comparison with results obtained from other techniques such as direct instrumental analysis or chemical modeling

satisfactory for those metals present in amorphous and crystalline sulfides extracted by acidified hydrogen peroxide where appreciable amounts of Fe, Mn and Ca were liberated in the various fractions before applying the oxidation step which was designed to remove those metal sulfides. However, it has been suggested by Kersten and Forstner (1990) that the poor selectivity of the above sequential leaching scheme for the sulfide samples is probably caused by partial oxidation, since the experiments were not conducted under oxygen free conditions. Rapin and Forstner (1983), also tested the selectivity of the sequential extraction procedure on sediment samples from marine and freshwater environments, and found that selectivity was sufficient for organic carbon in both sediment samples, with almost all of the organic carbon remaining intact until the oxidation step, and for sulfur in the reduced marine sediment. Poor selectivity for sulfur was found in the anoxic freshwater sediment where appreciable amounts were extracted in the various fractions before the oxidation step, probably due to the presence of less stable iron monosulphides minerals rather than pyrite (Salomons and Forstner, 1984).

Despite these problems, leaching techniques still represent one of the few tools available for examining trace metals speciation in sediments. Section 2.2.3 will focus on the suitability and selectivity of the most commonly used extractants.

2.2.2.4 Sample storage and preparation

The discussion in the previous section has shown that the partitioning data obtained by any sequential extraction procedure are influenced by many factors, such as the choice of reagents used for the various extractions, the extraction sequence, the length of each extraction step, the ratio of extractant to sediment and by inherent analytical problems such as incomplete selectivity and readsorption. In addition to these problems, there is also the difficulty of preserving sample integrity between the times of the sample collection and extraction. Problems with sample handling procedures have been recognized (LaFleur, 1976), but often, methods of sediment storage before extraction are not reported despite the fact that inappropriate sample storage may result in changes in the composition of the collected sediments.

For oxic sediments Thomson *et al.* (1980) have tested various storage methods, such as wet storage, freezing and oven drying. They stressed that extractions should be conducted as soon as possible after sample collection as none of the above mentioned methods preserved the initial partitioning of the sediments.

With regard to anoxic sediments, Engler *et al.* (1977) stressed that "the anaerobic integrity of the samples must be maintained throughout manipulation and extraction". Recently, the effects of the various preservation techniques (wet storage, freezing, freeze and oven drying) on metal speciation in anoxic sediment samples has been reported by Kersten and Forstner (1986, 1987) and Rapin *et al.* (1986). They found that the metal speciation data from sequential leaching procedures, can be affected by:

1) the techniques used to preserve the sediments before analysis, and
2) the presence or absence of atmospheric oxygen during the extraction procedures.

Their effects have been most strongly demonstrated for anoxic sediments which have been brought into contact with oxygen during the sampling, drying and extraction procedures and can result in artifact-induced interstage metal mobility. For example, Kersten and Forstner (1986, 1987) showed that when anoxic sediments, from Hamburg harbour, were extracted by a sequential extraction procedure as received, and under controlled oxygen-free conditions, within a glove box at room temperature, the fractionation patterns were different from those obtained when the same sediments were either freeze dried or oven dried under normal atmospheric conditions. They attributed these changes as mainly due to the contact of the anoxic sediments with air. Furthermore, Rapin *et al.* (1986) reported that speciation changes can also occur when oxic sediments are air and freeze dried, but to a lesser extent than those involving anoxic sediments.

2.2.3 Assessment of suitability of different chemical leaching techniques :

2.2.3.1 Exchangeable and adsorbed phase extractants

Exchangeable, or 'loosely held' is the least well defined fraction, and normally constitutes only a small portion of the total metals in a sediment. This fraction includes those metals which are weakly attached to the surface of clays, hydrous oxides, organic coating and fine grained carbonate. The addition of a neutral (pH 7) salt solution, usually a high concentration (1 *M)*, monovalent or divalent cation chloride, acetate or nitrate, is commonly used to promote displacement of metal ions physically bound by electrostatic attraction to negative sites on particle surface (Pickering, 1986; Kersten and Forstner, 1990).

The most extensively used reagents in the literature, which have been employed to liberate exchangeable metals, are magnesium chloride ($MgCl_2$) and ammonium acetate (NH_4OAc). According to Pickering (1986) in his review on solid speciation, magnesium chloride sediment leachates contained only low levels of Al, Si and organic carbon, which indicates that this reagent does not affect silicates, sulphides or organic matter. Fe concentrations were also found to be very low, consistent with the low solubility of Fe/Mn at neutral pH values. Slight dissolution of carbonates (2-3%) was observed. The major objection to the use of magnesium chloride for the determination of exchangeable metals is the possibility of formation of dissolved metal-chloro complexes (Forstner and Wittmann, 1981). For this reason, Shuman (1985) used magnesium nitrate, however, this reagent causes matrix effects during the analytical determination of some elements by atomic absorption spectrometry (Thomas, 1987).

Ammonium acetate has been criticised due to its tendency to attack carbonates (Tessier *et al.*, 1979; Rapin and Forstner, 1983; Towner, 1984). In addition, ammonium acetate also causes partial dissolution of $CaSO_4$ (Rhoades and Krueger, 1968), $BaSO_4$ (Okazaki *et al.*, 1962), Mn oxyhydroxides (Jenne, 1968) and metal oxide coating (Gibbs, 1973).

Recently, workers have used barium chloride triethanolamine (Forstner and Patchineelam, 1980), and barium chloride (Meguellati *et al.*, 1983), however the concomitant increase in the pH is a drawback (Forstner, 1985). Furthermore, there is a tendency for barium salts to crystallise out of solution after sediment treatment and there is also a matrix effect during atomic absorption measurement (Towner, 1984).

In spite of their disadvantageous dissolving and complexing properties both neutral 1 *M* ammonium acetate and magnesium chloride remain the most widely used and acceptable reagents for the evaluation of exchangeable trace metal concentrations.

2.2.3.2 Carbonate phase extractants

Carbonate in sediments exist as cements and coatings coprecipitated with trace metals. Reaction with sodium acetate (NaOAc), adjusted to pH 5 with acetic acid

(HOAc), is complete and effective at selectively dissolving the carbonate minerals with their associated trace elements, without dissolving significant organic matter, aluminosilicate minerals, or Fe/Mn oxides (Tessier *et al.*, 1979; Rapin and Forstner, 1983; Lyle *et al.*, 1984). It has been confirmed (Rapin and Forstner, 1983) that at pH 5, CH_3 COONa recovers most of the metal present in carbonate minerals (e.g. Ca, Mn, Cd, Pb) and the reagent has been used in nearly all sequential schemes (e.g. Tessier *et al.*, 1979; Forestner *et al.*, 1981; Hickey and Kittrick, 1984).

Alternative carbonate dissolution techniques involve acidic cation exchange resins (Deurer *et al.*, 1978), or introduction of CO_2 gas into a bottle containing a suspension of the sample material (Forstner and Patchineelam, 1976). However, with the cation exchange resin some sediment particles may be entrapped by the resin. Such particles would then be leached by the HCl which is used for stripping the resin of metals adsorbed during the sediment treatment. This could give rise to considerable increase in the resin extracted metals, although to overcome this draw-back the resin may be scrubbed by a short ultrasonication and wet sieving (Kersten and Forstner, 1990). On the other hand, with the carbonate dissolution method the generation of the CO_2 and the formation of the carbonic acid during the reaction can lead to considerable change in the pH value. The CO_2 extraction method is extremely laborious and time consuming. Furthermore, under oxygenated conditions reprecipitation occurs following CO_2 treatment.

Therefore, sodium acetate, adjusted to pH 5 with acetic acid was chosen as the extractant for the carbonate fraction.

2.2.3.3 Reducible phase extractants

Iron (Fe III) and manganese (Mn IV) are important constituents of soils and sediments, and occur in varying physical form as coatings on detrital particles, cement between particles, matrix component, and as concretions (the so-called ferromanganese nodules). Such oxides have a high capacity for metal adsorption and are excellent scavengers of trace metals. The association of trace elements with these precipitated oxides ranges from exchangeable (loosely adsorbed) forms, through moderately fixed (e.g. with amorphous oxides) to relatively strongly bound (e.g. occluded in goethite and other oxide minerals). The metals in this fraction are more strongly bound than the exchangeable or carbonate fraction and are unlikely to have any immediate biological impact. Crystalline oxides are more resistant to attack than the non-crystalline oxyhydrates of Fe and Mn. Amorphous ferromanganese oxyhydrate with their associated elements can be dissolved under the effect of redox gradient, in sediments, leading to a marked increase in trace metals in interstitial water (Kersten and Forstner, 1990). A selective dissolution technique for these materials should be to differentiate between amorphous and crystalline iron oxides in order to be useful for environmental studies.

Extraction procedures with emphasis on easily reducible phases best reflect the processes involved in the diagenetic remobilization of various elements from these oxides in sediments and methods for the differentiation of reducible forms in sediments have been applied to pelagic deposits since the early days of manganese nodules research. However, in some sequential extraction procedures the reducible fraction is differentiated into easily and moderately reducible phases.

The easily reducible phase consists mainly of manganese oxyhydroxides together with some amorphous iron hydroxides. This fraction is usually leached with a combined solution of acid-reducing agent. The concentrations, volumes and pH need to be carefully selected so that little iron oxide is dissolved. The moderately reducible phase consists mostly of the resistant manganese oxide and crystalline iron oxides and is also leached with a combined solution of acid-reducing agent.

Several extractants have been proposed. Acidified hydroxylamine hydrochloride, dissolved in acetic or nitric acid (Chester and Hughes, 1967; Presley *et al.*, 1972; Agemian and Chau, 1976), is one of the most widely reagents to separate the authigenic 'non-detrital' fraction from pelagic deposits (Chester and Hughes, 1967), or as a part of several sequential leaching schemes as an extractant for the reducible fraction (Burrows and Hulbert, 1975; Tessier *et al.*, 1979). With acetic acid present (25%), increasing hydroxylamine hydrochloride (NH_2 OH. HCl) concentration from 0.1 *M* to 1.0 *M* results in higher extracted Fe level (Chester and Hughes, 1967; Chao, 1972; Frampton and Reisenauer, 1978) and using hot (96°C) 0.04 *M* NH_2 OH. HCl (Tessier *et al.*, 1979), extraction was mostly complete after 6 h. The organic carbon content of the extracted sediments was not reduced by this treatment, indicating that there was little attack on organic matter, and as the extract contained low levels of Si and Al, attack on major silicate mineral was also slight (Tessier *et al.*, 1979). A good extractant for Fe Should have both a reducing agent and an acid or complexing agent to ensure that Fe will not reprecipitate as it is released into solution (Kersten and Forstner, 1990). The low pH value of this acid-reducing extractant contributes to the release of Al and Si from river sediments (Tessier *et al.*, 1979) as well as from opal (Chester and Hughes, 1967). Despite these disadvantages, this extraction couple has been widely applied as part of sequential extraction schemes.

Another type of a combined acid-reducing agent consists of 0.1 *M* nitric acid and hydroxylamine hydrochloride, and is used for extracting manganese oxides (i.e. easily reducible phase) (Chao, 1972). This reagent should perform well if put in a sequence before an amorphous iron oxides leachate since it will solublize the manganese and very little iron (Chao, 1972; Shuman, 1982). Towner (1984) proposed the use of 0.25 *M* hydroxylamine hydrochloride in 1.0 *M* Na-acetate. This reagent dissolved a very large proportion of manganese in the sediment and only a small amount of iron, with minimal attack on organic matter and clay minerals.

Robbins *et al.* (1984) decided to use hydroxylamine hydrochloride buffered to pH 5 by the addition of sodium citrate. It was considered that sodium citrate should minimize readsorption of released metals and enhance dissolution of any amorphous and poorly crystalline iron oxyhydroxides and the use of this solution, buffered to pH 5, minimizes attack on aluminosilicates, and formation of insoluble precipitates which may characterise oxalate. Although this method minimized the readsorption of metals released it enhanced the dissolution of amorphous and poorly crystalline iron oxide. Thus, the differentiation between manganese and iron oxides was not possible.

Another useful reagent for extraction of amorphous iron oxides is 0.1 *M* oxalic acid, buffered to pH 3 with ammonium acetate, commonly known as Tamm's reagent. This reagent treatment has been used in soil and sediment studies as an extractant to dissolve amorphous iron oxides in darkness. When performed in the dark, the reagent is believed to dissolve only amorphous Fe and Al oxides, with attack on silicates or crystalline goethite being minimal (Landa and Gast, 1973). In a recent study (Chao and Liyi, 1983) a combined reagent of 0.25 *M* hydroxylamine hydrochloride and 0.25 *M* hydrochloric acid, which is similar in selectivity to the acidified ammonium oxalate reagent, has been introduced.

Another popular reducing reagent is dithionate-citrate buffer (DCB). This reagent, which contains sodium citrate, sodium dithionate and sodium bicarbonate, has been shown to be capable of dissolving both amorphous and crystalline oxyhydroxide present in soils and sediment (Gibbs, 1973; Jenne *et al.*, 1974; Gupta and Chen, 1975). However, according to Coffin (1963), this mixture is not recommended for use with pelagic sediments because it also attacks iron-rich silicates. A reagent containing 0.3 *M* $Na_2S_2O_4$, 0.175 *M* Na citrate and 0.025 *M* H citrate, initially used by Anderson and Jenne (1970), was later adopted by Tessier *et al.* (1979) as one stage of sequential extraction scheme for sediment samples. Several problems are encountered with use of this reagent as reported by Tessier *et al.* (1979) and Shuman (1982). According to these authors dithionate-citrate couple is highly contaminated with metals (e.g. Zn) and its purification is difficult. Furthermore, it cause frequent clogging of the burner during analysis of the extracted solution by AAS.

Shuman (1982) introduced an ascorbic acid-ammonium oxalate extraction, as a suitable substitute for Na-dithionate. According to Shuman (1982), this acid-reducing and complexing couple is an easily analyzed solution, well-defined chemically and without the contamination problems of dithionite.

2.2.3.4 Organic/sulphide phase extractants

Trace metals become bound to various forms of organic matter including living organisms, detritus, coatings on mineral particles etc. In sediments and soils, the organic content consists of complex polymeric material known as fulvic and humic acids (with high metal adsorptive capacity) and non-humic substances such as carbohydrates, proteins, peptides, amino acids, fats, waxes and resin (Pickering, 1986).

A number of chemical extractants have been used in the literature for the removal of the organic matter fraction together with its associated elements either by oxidative destruction or dissolution in alkaline solutions. Some of those chemical reagents are considered below.

The earliest reported reagent used for extracting organic matter is sodium hydroxide. This reagent is considered as a successful reagents for extracting the labile organic (humic and fulvic acids) but may remobilize metals from phosphates and silicates (Forstner and Patchineelam, 1980; Morrison, 1986).

Sodium pyrophosphate ($Na_4P_2O_7$), with or without added NaOH, has been widely used for extracting metal bound to organic matter from soils and sediments (Bremer and Lees, 1949; Evans, 1959; McKeague and Day, 1966; Thomson *et al.*, 1980; Shuman, 1982). These chemical solutions are reasonably efficient in extracting the fulvic and humic acid fractions of organic matter, but not the refractory organic matter in samples (Kersten and Forstner, 1990). The most important factor in determining the efficiency of the solution is the pH, which is commonly between 7 and 10. At a lower pH the extraction of the organic matter in the solution decreases and the dissolution of amorphous iron oxyhydroxides increase. Towner (1984) and Kersten and Forstner (1990) reported that treatment with 0.1 *M* $Na_4P_2O_7$, buffered to pH 10, does not dissolve iron oxyhydroxides. This solution treatment has been inserted by Towner (1984) and Chester and Hughes (1967) in an early stage of the sequential extraction scheme, between the easily and moderately reducible fractions, for extracting metal associated with humic and fulvic organics.

Sodium hypochlorite (NaOCl) buffered to pH 9.5 has been used by several investigators (Lavkulich and Wiens, 1970; Gibbs, 1973; Hoffman and Fletcher, 1981; Shuman, 1983; Papp *et al.*, 1991). This reagent generally removes more organic carbon than does the stronger oxidant H_2O_2, due to the solubilization of organic matter such as humic acid in alkaline medium, with minimal removal of silicon, manganese, iron and aluminium (Pickering, 1986; Kersten and Forstner, 1990).

Sodium dodecyl sulfate (SDS), 1% w/v, buffered to pH 8.3 with 0.2 *M* $NaHCO_3$ was introduced by Robbins *et al.* (1984). This buffer solution was used for the separation of metals in association with the easily extractable organic fraction in sediments and may slightly attack clay minerals.

The most widely used oxidizing agent is acidified hydrogen peroxide (H_2O_2). The oxidation process is promoted by heating, either at 85°C for several hours (Gupta and Chen, 1975; Tessier *et al.*, 1979) or by evaporating to dryness (Shuman, 1979). The use of an acidic solution (usually adjusted to pH 2 with HNO_3) prevents scavenging of metal ions by any Fe (III) hydroxide precipitates formed at higher pH (Pickering, 1986; Kersten and Forstner, 1990). The choice of boiling 30% H_2O_2

represents a compromise between complete oxidation and alteration of aluminosilicate minerals (Tessier *et al.*, 1979). However, since organically associated metal released during hydrogen peroxide digestion procedure is readily adsorbed on clays it is important to extract the residue immediately after heating (Morrison, 1986; Kersten and Forstner, 1990).

The use of the hydrogen peroxide/acidified ammonium acetate couple has been widely adopted for the organic and sulfide extraction in anoxic and oxic sediments because the adsorbed cations may be exchanged more effectively with ammonium ions. Gupta and Chen (1975) reported that treatment with hydrogen peroxide-ammonium acetate couple removes a larger fraction of the metals than does acidified hydrogen peroxide. The application of the peroxide reagent after the oxide reducing reagent in a sequential extraction scheme is preferred, avoiding problems which may occur from the formation of oxalate as a result of hydrogen peroxide treatment and oxide dissolution.

2.2.3.5 Residual phase extractants

After the removal of the above non-detrital (or non-lithogenous) components from the sediment sample, the residue consists of detrital or lithogenous materials (such as silicate and other resistant components). The elements associated with these residual materials are not environmentally significant because they are mainly located in the lattice-position in lithogenous minerals. The determination of this residual fraction has been considered useful at least as a control for comparing the sum of all individual leachate steps to the result for the bulk analysis of the respective element (Kersten and Forstner, 1990).

Strong acid treatments similar to those adopted for total digestion, where the dissolution can be achieved by hydrofluoric acid in combination with other oxidizing mineral acids such as nitric, perchloric, or hydrochloric acid, can be used to decompose the residual sediment materials.

2.2.4 Sequential extraction scheme used in the present investigation

The sequential extraction scheme employed in the study is described below in terms of the various operationally defined partitioning fractions involved, and the experimental details are described in Chapter 3. This fractionation scheme, which was developed by Tessier *et al.* (1979) and recently modified by Ajayi and Van Loon (1989), was chosen because it defines a wide variety of geochemical fractions and avoids overemphasis of any given fraction, such as fraction 3 (e.g. extracted by hydroxylamine hydrochloride and containing the reducible phase). The principal operationally defined host components associated with each fraction in the fractionation scheme, and the reagents used to act on the sediment in a specific manner, in order to effect the stage separations, are summarized below, in the order in which they were used, in the following five fractions:

Fraction 1: This fraction is obtained by extracting the sediment with 1 *M* magnesium chloride ($MgCl_2$; pH 7). Trace metals released in this stage are classified as weakly held, or exchangeable.

Fraction 2: The extractants for this fraction is 1 *M* sodium acetate (NaOAc) adjusted to pH 5.0 with acetic acid (HOAc). This reagent brings into solution trace metals associated with carbonate phase.

Fraction 3: This fraction is composed of trace metals extracted when the residue from fraction 2 is treated with 0.04 *M* hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% (v/v) acetic acid (HOAc). Reducible components of the sediment, including hydrous oxides of iron (III) and manganese (IV), are attacked by this extractant.

Fraction 4: This fraction is obtained by treated the residue from fraction 3 with the following reagents: 0.02 *M* nitric acid, 30% hydrogen peroxide (H_2O_2) adjusted to pH 2.0 with nitric acid, and 3.2 *M* ammonium acetate (NH_4OAc) in 20% (v/v) nitric acid. Organic matter and sulphides are the principal oxidizable phases brought into solution by this reagent.

Fraction 5: This fraction is the residual fraction obtained by complete dissolution of the residue from fraction 4 of the fractionation scheme by treatment with a nitric/hydrofluoric/perchloric ($HNO_3/HF/HClO_4$) acid mixture. Elements released at this fraction are also classified as being detrital, in character, and are mainly located in the lattice-held positions in lithogenous minerals.

Chapter Three

Experimental Procedure

3.0 Experimental Procedure

3.1 Sampling and sample preparation

Sediment samples were collected aboard the University of Newcastle Upon Tyne research vessel '*Bernicia*' on the 7th, 8th and 9th of May 1991 at 37 stations in Tees bay and River Tees estuary, North-East England (Figs. 3.1 and 3.2). With the exception of sites 35 and 42, in the Tees estuary, and sites 3, 4, 6, 7, 12, 13, 17, 20, 22, 24, 25, 26 and 29, in Tees Bay, all samples were taken using a Haps corer. Sub-samples for analysis were taken from the centres of each core immediately the corer was recovered, using PVC tubes 32 mm in diameter. These tubes were immediately sealed to prevent ingress of air. Once in the laboratory the cores were extruded using a PTFE piston, divided into 5 cm thick slices, homogenized, and stored in polythene vials at -5°C until required for analysis. These operation were carried out as far as possible in a glove box under a nitrogen atmosphere, in order to prevent post-sampling oxidation influencing speciation. Sites 35, 42, 3, 4, 6, 7, 12, 13, 17, 20, 22, 24, 25, 26 and 29, were sampled by van Veen grab, with sub-samples for analysis being taken from the centre of the grab using a polythene spoon, to avoid contamination by metallic parts of the grab. The grab samples were placed in sealed glass jars for transport to the laboratory where they were homogenized under nitrogen, and stored at -5°C until analysed. The 0-5 cm depth samples from cores, and the material collected by grab sampler were used for the purpose of this study.

3.1.1 Sampling strategy

The study area is located at 0°59′-1°15′ W and 54°34′-54°44′ N (see Fig. 1.1) and encompasses the Tees Bay, together with the estuary of the river Tees. Tees Bay (Fig. 3.1) was sampled in a series of seven transects running approximately perpendicular to the coastline. One transect (sites 1-4) was located north of the Bay, and one transect (sites 25 and 26) was located south of the Bay. Five transects (sites 5-24) were made close to the Bay, between Hartlepool and Redcar. Three sites (27-29) close to the mouth of the estuary were also sampled, in order to study any changed and the estuary/Bay interface.

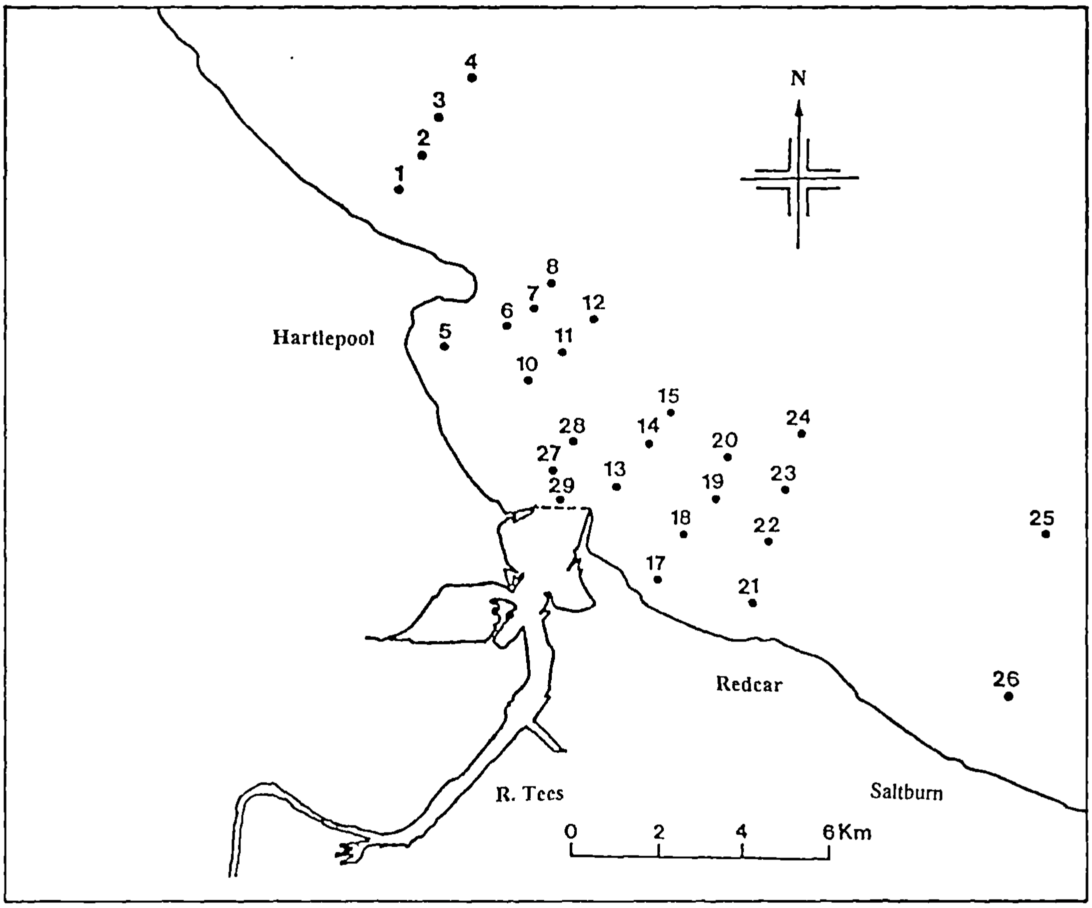


Figure 3.1. Tees Bay map showing sampling sites.

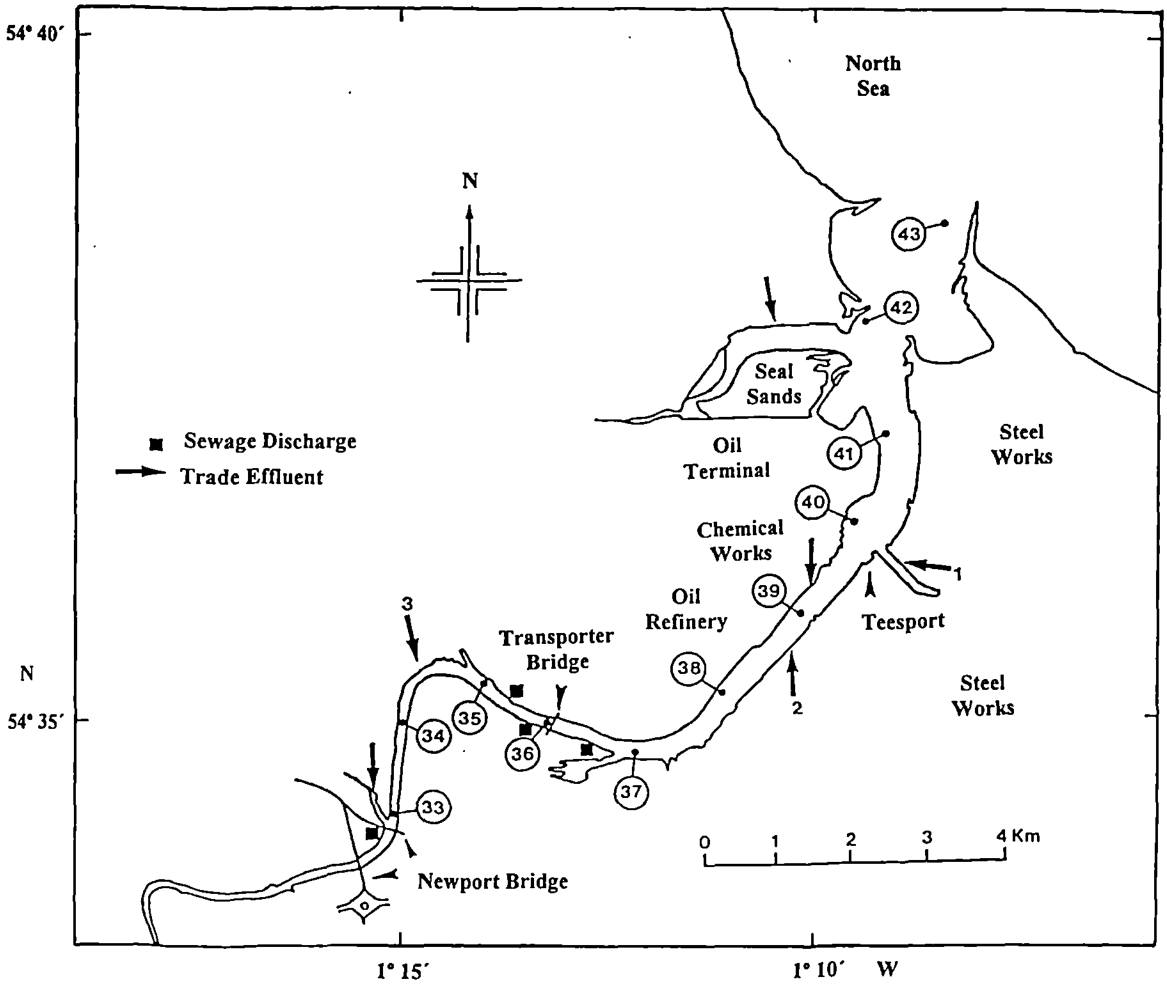


Figure 3.2. Tees Estuary map showing sampling sites and main effluent inputs.

The Tees estuary (Fig. 3.2) was sampled in a systematic fashion, from Newport Bridge to its mouth, the sample points being located at ~ 1 km intervals between sites 33-36, and at ~ 1.5 km intervals between sites 36-43. At some sites sampling locations were migrated up to 200 m upstream or downstream to reflect sediment conditions, as a result of river traffic. For descriptive purposes the sampling area has been divided into three specific regions called the upper reaches of the estuary (sites 33 and 34), the middle reaches of the estuary (sites 35-41) and the lower reaches of the estuary (sites 42 and 43).

3.2 Bulk sediment analysis

3.2.1 Carbon analysis

Samples were analysed for total carbon and total organic carbon (TOC). Carbonate carbon was calculated by difference between these two measurement.

3.2.1.1 Total carbon analysis

~ 100 mg aliquots of each sample were weighed into ceramic crucibles. The samples were analysed for carbon using the Leco WR12 analyser (section 3.2.1.3).

3.2.1.2 Total organic carbon (TOC)

~ 100 mg aliquots of each sample were weighed into porous ceramic crucibles. Carbonate carbon was removed by two additions of hot 18% hydrochloric acid, which was added in a drop-wise manner until effervescence ceased. Then the acid was rinsed from each crucible four times with deionised water. The crucibles was left until the water drained off, before they were transferred into an oven and left overnight to reach complete dryness. The samples were then analysed for carbon using the Leco WR12 analyser (section 3.2.1.3).

3.2.1.3 Operating the Leco WR12 Analyzer

All carbon analysis were performed using a Leco WR12 carbon analyser. This was calibrated using metal rings of 1 gm weight, each containing 0.671%C. Each ring was ignited in a separate crucible, together with copper and iron accelerants, and the raw carbon content determined by the instrument was recorded. The average of three analyses was taken and the difference between the average analysis and the theoretical analysis (0.671%C) was calculated. The machine was then readjusted to read 0.671. A fourth ring was used to check the accuracy of the calibration. Cu and Fe accelerants were added to each sample and these were then analysed on the instrument. Since the machine was calibrated on 1 g standards, the total carbon and the total organic carbon can be calculated by using the following equation:

$$(1000/W) \times \text{raw carbon content} = C\ \%$$

Where: W = original weight of sample in mg; C = T.O.C or Total Carbon.

3.2.2 Sulphur analysis

Approximately 100 mg of the powdered sample was placed in a pre-ignited ceramic boat and covered with *ca.* 1 g of tin to augment the combustion temperature. This was heated in a furnace at a temperature of 1400°C in an oxygen atmosphere. The evolved sulphur dioxide (SO_2) was bubbled through an acidified solution of potassium iodide (KI) which was subsequently titrated against a solution of potassium iodate (KIO_3) using a starch indicator. Sulphur contents were calculated taking blanks into account and calibrating to a sulphur standard (14.34%).

3.2.3 Particle size analysis

approximately 1-2 g aliquots of the sediment samples were weighed into beakers, to which 10 ml distilled water were added. The beakers were sonicated overnight and the grain size distribution of the sediment fraction was determined by laser beam scattering (Coulter Counter, Model LS100). After analysis the sediments were classified according to their sand-silt-clay ratio.

3.3 Inorganic analysis

3.3.1 Total metal analysis

Prior to total metal analysis the sediments were thawed, homogenised, dried at 105°C (for 18-24 h) and ground, with a pestle and mortar, to a powder. The 1 g aliquots of the dry samples were weighed into PTFE beakers, to which 2 ml nitric acid (BDH AnalaR; 65%), 6 ml hydrofluoric acid (BDH AnalaR; 40%) and 2 ml perchloric (Merck Spectrosol; 70%) were added. The beakers were heated gently on a hotplate for about three hours (80°C), for digestion to occur, following with the temperature was increased (180°C) and the acids evaporated to near dryness. After cooling a further 2 ml of perchloric acid was added to the sample and the contents were evaporated once more to near dryness. Hydrochloric acid (5 ml) and enough deionised water to half fill the beaker were then added and the sample was heated gently for about 1 hour to dissolve any salts. Finally, the solution was transferred to a small Pyrex conical beaker, and heated until any remaining salts had dissolved. the volume was then made up to 100 ml with deionised water. The solution were analysed for Cd, Co, Cr, Cu, Ni, Pd and Zn by flame atomic absorption spectrophotometry (section 3.3.3)

3.3.2 Sequential extraction procedure

The detailed experimental procedure for the five leaching stages is summarised in Table 3.1.

Following initial dewatering by centrifugation subsamples of homogenised wet sediment equivalent to 1 g dry weight (dry weight determined on a separate sample) were analysed, into clean dry centrifuge tubes. The first reagent in the leaching scheme was added, the mixture was shaken on a mechanical orbital shaker for the appropriate time (Table 3.1) and the centrifuge tube was then transferred to a centrifuge and spin at 3000 r.p.m for 20 minutes. The resulting supernatant was decanted into a volumetric flask and made up to the final volume with the reagent used in the extraction. The residue was washed with 8 ml deionised water and re-centrifuged. The solid residue remaining after each extraction stage was then treated with the next reagent in the scheme. The residue remaining after the stage 4 extraction, was transferred from the centrifuge tube to a pre-cleaned PTFE beaker, dried and digested with a HNO_3-HF-$HClO_4$ mixture following to the procedure described above for total metal analysis.

The sequence of fractionation operations was carried out without delay once started and any necessary storage (e.g. overnight) during the analyses was at 4°C (Ajayi and Van Loon, 1989). Sample handling and all stages in the magnesium chloride, sodium acetate buffer, and the hydroxylamine hydrochloride extractions were conducted within the glove box at room temperature. All these chemical

Table 3.1 Time of mechanical agitation and temperature at which the sequential extraction was performed.

Geochemical phase	**Extraction reagent**	**Extraction condition**	**Final volume**
Fraction 1 (F1; e.g. Exchangeable)	1 *M* $MgCl_2$ (pH 7)	shake at room temperature for 1 h.	10
Fraction 2 (F2; e.g. Carbonate)	1 *M* NaOAc adjusted to pH 5 with HOAc	shake at room temperature for 5 h.	20
Fraction 3 (F3; e.g. Reducible)	0.04 *M* $NH_2OH.HCl$ in 25% (v/v) HOAc	shake at 96°C for 6 h.	20
Fraction 4 (F5; e.g. Oxidizable))	0.02 *M* HNO_3 + 30% H_2O_2 (pH 2 with HNO_3). On cooling add 3.2 *M* NH_4Oac in 20% (v/v) HNO_3	shaken occasionally at 85°C for 5 h then shaken on addition of NH_4Oac for a further 0.5 h (see note 1 below)	20
Fraction 5 (F5; e.g. Residual)	NHO_3-HF-$HClO_4$	see note 2 below	100

Note 1. To the residue (from F3) 3 ml of HNO_3 and 2 ml of H_2O_2 were added, and the mixture was allowed to stand at room temperature until the initial reaction subsided. The remaining 3 ml of H_2O_2 was added to the sample, to make up the first 5 ml H_2O_2 recommended in the method, and the mixture was heated at 85°C for 2 hours with occasional agitation. A second 3 ml was then added and the sample was heated again to 85°C for 3 hours with intermittent agitation. After cooling, 5 ml of HN_4 OAc was added and the sample was diluted to 20 ml and agitated continuously for 30 minutes.

Note 2. Residual fraction: The residue (from F4) was digested as described in section 3.3.

extractants were deaerated with oxygen free N_2 prior to contact with the samples and the centrifuge tubes were closed to ensure the integrity of the sample solution outside the glove box during the mechanical shaking and centrifuging procedures (Kersten and Forstner, 1986). The solutions resulting from each leaching stage were analysed by flame atomic absorption spectrophotometry (section 3.3.3).

3.3.3 Atomic absorption spectrophotometry (AAS)

All solutions resulting from the total metal dissolutions, and the selective leaching procedure were analysed for Cd, Co, Cr, Cu, Ni, Pb and Zn by atomic absorption spectrophotometry (AAS). This is by far the most commonly used method for the analysis of trace metals in environmental samples. The technique involves the absorption of light of a specific wavelength by atomic species of the element which are produced by a flame or other thermal device. The amount of light absorbed by the atomic species is proportional to the concentration of the ground state atoms of the element present. The light source used is a hollow cathode lamp, with the cathode constructed of the same element as that under analysis, or an electrodeless discharge lamp which contains a small quantity of the element to be determined. The latter type is of longer life and produce a better signal-to-noise ratio, especially for the more volatile metals, although it needs a special power supply and their conditioning time is longer.

Various atomization techniques may be used, including aspiration of aqueous solutions into a controlled flame, carbon rods, graphite furnaces and hydride generation, but in the present work all metals were measured in the sample solutions using a Varian Spectra AA-300 Atomic Absorption Spectrophotometer in the appropriate flame mode (air/acetylene or nitrous oxide/acetylene). The operating conditions, for each metal studied, were as indicated in Table 3.2.

A multi-element stock standard solution was prepared from 1000 ug/ml single element standard (BDH, Spectrosol) and this was used for the preparation of secondary standard solutions. The working standards were prepared in a matrix matching as closely as possible those of the analyte solutions.

Blanks were run concurrently with samples to check any possible reagent, or other operationally associated contamination. The mean absorbance of the reagent blanks was subtracted from the absorbance of the sample to obtain the true absorbance of the sample.

Table 3.2 Instrumental parameters for a Varian AA-300 Flame Atomic Absorption Spectrophotometer.

Element	Lamp current (mA)	Slit Width (nm)	Wave length (nm)	Flame	Background correction
Cd	4	0.5	228.8	air/acetylene	on
Co	7	0.2	240.7	air/acetylene	on
Cr	7	0.2	357.9	N_2O/acetylene	off
Cu	4	0.5	324.8	air/acetylene	off
Ni	4	0.2	232.0	air/acetylene	on
Pb	5	1	217.0	air/acetylene	on
Zn	5	1	213.9	air/acetylene	on

To assess the accuracy and the precision of the analyses of trace metals, the in-house standard reference material BOB1 (Ocean-floor Basalt; Birmingham University), with accepted values for Co, Cr, Cu, Ni, Pb and Zn (Table 3.3), was analysed along with the samples; checks were carried out after every 5 samples and Nanopure water was aspirated between samples in order to continuously monitor base line drift. The mean, standard divination, average recovery, and relative standard deviation (Sr) values, for duplicate analyses of the reference material, are summarized in Table 3.3.

Table 3.3. Results of the analysis of BOB1 (this work) compared with the accepted values.

Metal	Recommended values (ug/g)	This study mean values (ug/g)	S.D.[a] of values	Average recovery %	Sr[b] of mean values %
Co	55	51	1.4	92.7	2.7
Cr	267	257	1.4	96.3	0.5
Cu	62	62	0.4	100.4	0.6
Ni	105	101	1.4	96.2	1.4
Pb	4.0	3	0.4	81.3	13.3
Zn	67	67	1.2	99.6	1.8

S.D.[a] = Standard deviation.
Sr[b] = Relative standard deviation ($S_r = (S/X) \times 100$, where S = standard deviation, X = mean).

As far as the partitioning of trace metals is concerned, the lack of standard reference materials containing known trace element phase distributions made it impossible to determine the accuracy and, consequently, the selectivity of the extraction procedures (Giani *et al.*, 1994). This aspect probably represents one of the critical problems of these methods (Giordano *et al.*, 1992; Giani *et al.*, 1994; Li *et al.*, 1995). The sequential procedure used was chosen because it has been widely investigated (Tessier *et al.*, 1982; Van Valin and Morse, 1982) and the limits of this approach have been clearly identified (Kheboian and Bauer, 1987; Martin *et al.*, 1987). In addition, the results of selective leaching procedures mentioned in Chapter 4 (Table 4.7; section 4.3) shows that in the majority of cases the sums of the extracted fractions agree, to within ± 20%, with the independently determined total metal concentrations, supporting the overall accuracy of the extraction procedure. Similar checks on accuracy have been performed by other studies of selective leaching procedures (Li *et al.*, 1995).

3.4 Organic analysis

Within this section are the practical details of the various procedures utilised to extract, purify and fractionate aliphatic, aromatic and polychlorinated biphenyl hydrocarbons isolated from sediment samples.

3.4.1 Glassware

Glassware was generally cleaned by allowing it to stand overnight in a Decon 90 solution, followed by rinsing with tap water, doubly distilled water and finally methanol. Glassware was then dried overnight at 150°C, and prior to use was rinsed with the appropriate solvent. It is necessary to avoid rinsing with any solvent that can interfere in the chemical analysis for which the glassware is to be used, i.e., caution must be taken with DCM when PCB analysis was carried out. Solvent rinsed aluminium foil was used to exclude dust during storage. Pipettes and syringes were also cleaned with solvent before use.

3.4.2 Solvents and reagents

All solvents (such as methanol, MeOH; dichloromethane, DCM; petroleum ether, PE; BP 40-60°C) were redistilled and subjected to GC analysis to ensure purity. Distilled water was always doubly distilled in a Milli-Q^{50} apparatus. Anhydrous sodium sulphate (BDH Chemical Ltd., England) was dried in a clean glass beaker for five hours at 150°C and cooled, after removal from the oven, in a clean desiccator which had no grease on its ground glass surfaces. Silica, alumina, cellulose thimbles, cotton wool and copper turnings were prextracted before use. The extracted silica and alumina were kept activated in an oven at 110°C until required. Evaporation of large amounts of solvent was carried out with a Büchi rotary evaporator under water pump vacuum and at 40°C. Small residual solvent quantities were removed by evaporation under a gentle stream of dry N_2.

3.4.3 Extraction of soluble organic matter from sediments

A known weight of freeze-dried sediment, estimated from the TOC result, was placed in a pre-weighed and pre-extracted cellulose soxhlet thimble and covered with a plug of cotton wool. The samples were then extracted in a soxhlet apparatus using

400 ml of an azeotropic mixture of dichloromethane (DCM) and methanol (93:7 v/v), and a few anti-bumping granules, for 48 h. Before extraction commenced, an internal standard (1- eicosene) was added to the sediment for the quantitation of saturated hydrocarbons. Copper turnings (activated in hydrochloric acid) were added to the flask (approximately 5, but variable depending on the sample matrix) to remove any elemental sulphur present in the extracts. It must be noted that if the copper turns completely black during the extraction period, the process can be halted and more copper should be added when the solvent has cooled.

The resulting extract was rotary evaporated using a Büchi evaporator to near dryness (*ca.* 2 ml of solvent remaining), to give the total soluble organic matter of the sample. This reduced extract was quantitatively transferred with DCM washings to a volumetric flask (25 ml). A known volume of the final extract (*ca.* 5 ml) was then transferred to a preweighed vial, where it was blown to dryness under a gentle stream of nitrogen until a constant weight of organic matter was recorded. The remaining extract (approximately 20 ml in the 25 ml volumetric flask) was then ready for separation by thin-layer chromatography (for aliphatic and aromatic hydrocarbons) and column chromatography (for chlorinated hydrocarbon).

3.4.4 Separation of aliphatic and aromatic fractions

Approximately 20 mg of the soluble organic matter of each sample was fractionated by TLC. Glass plates (20 x 20 cm) were cleaned overnight in chromic acid, scrubbed with detergent, rinsed with distilled water, and oven dried. The cleaned plates were coated with Kieselgel 60 (silica gel) in a slurry with deionized water (1 part silica to 2 parts water). The plates were spread to a uniform thickness of 0.5 mm and then left to air dry before drying in an oven at 120°C for not less than three hours. After drying, the plates were cleaned of impurities by development in distilled ethyl acetate, followed by reactivation in an oven at 110°C (24 hours).

After preparation of the TLC plate, the top 1 cm of silica was removed from the upper edge of the plate (where the contaminants had been concentrated by the ethyl acetate). In addition, two lines were scored into the silica approximately 3 cm from the right-hand edge of the plate to create an isolated strip of silica on which to run retention time standards (n-C_{18}, n-butyl benzene and phenanthrene). The sample (up to 20 mg) was spotted in a straight line, approximately 1cm above the bottom of the plate, in the main area of the plate, using a drawn out capillary tube. A mixture of *n*-C_{18}, *n*-butyl benzene and polyaromatic phenanthrene standards (which represents aliphatic, monoaromatic and polyaromatic hydrocarbons, respectively) was eluted in the same plate, alongside the sample band, to act as a guide in removing hydrocarbon fractions. The plate was developed with petroleum ether in a clean TLC tank, ensuring that the level of the solvent was below the level of the loaded sample and standards. Identification of the resulting compounds band was assisted by spraying the plate with Rhodamine 6G (in methanol), and visualizing briefly under UV light. Distinction between the bands was aided by the retention standards, and the R_f values noted. The bands were scraped off the plate onto separate pieces of pre-cleaned aluminium foil, and then into short columns (plugged with cotton wool). The columns were washed through with 50 ml of petroleum ether/DCM (45:5 v/v) for the aliphatic fraction (F1), petroleum ether/DCM (25:25 v/v) for the monoaromatic hydrocarbon fraction or DCM for the polyaromatic fraction. The resulting fractions were collected in round-bottomed flasks and rotary evaporated to near dryness. Finally, the aliphatic fraction was transferred to a pre-weigh vial, using a minimum amount of solvent, and blown dry under nitrogen until a constant weighed was recorded. In this study , we are primarily concerned with saturated hydrocarbons in fraction 1 and PAH in fraction 3.

3.4.5 Separation of polychlorinated hydrocarbons from sediments

A known volume (equivalent to 60 mg) of the soluble organic matter of each sample (section 3.4.1), was transferred to a preweighed vial, and blown dry under nitrogen until a constant weight was record. The sample extract was redissolved in 1 ml petroleum ether, adsorbed onto a small amount of deactivated alumina, dried on top of a glassware drying oven and used for the separation of polychlorinated hydrocarbons from the sediment. The clean-up and fractionation procedures were carried out, in two steps, by column chromatography on alumina and silica, because some methods of analysis, such as gas chromatography, require the removal of polar lipids and other materials, as described below. Again, great care must be taken not to introduce contamination during any steps of the analysis.

3.4.5.1 Alumina clean-up

Approximately 40 mg of soluble organic matter adsorbed onto activated alumina was quantitatively transferred to the top of alumina column. The alumina used was a neutral aluminium oxide (Merck 1077 70-120 mesh) and was prepared for use by cleaning in a soxhlet apparatus with hexane for 24 hours and firing in a muffle furnace in a quartz dish at 800°C for 4 h, to remove any lightweight organic compounds which may interfere with the analysis at a later stage; this also serves to completely activate the alumina. The activated alumina was transferred to a desiccator and allowed to come to room temperature. Before use in analyses, the activated alumina was deactivated to the 5% level by adding, with pasteur pipette, 5 g of double distilled water extracted with an equal volume of hexane to 95 g of the activated alumina, which was weighed into a round-bottomed flask. The flask was then stored in air-tight containers, shaken on a laboratory shaker for 30 minutes, and used within seven days.

The column, borosilicate glass chromatography column (150 mm x 6 mm i.d.) with solvent reservoir, was prepared immediately prior to use. The column was plugged with petroleum ether-washed cotton wool, using a clean glass rod, then packed dry with 3 g of 5% deactivated alumina. The alumina was topped with a small quantity of anhydrous sodium sulphate, to ensure that the sample is completely dry and to maintain the correct level of deactivation of alumina.

After preparation of the column, the sample (adsorbed onto alumina) was carefully packed on the top of the alumina column, allowed to drain into the adsorbent bed. Solvents was added to the solvent reservoir and the sample was separated into three fractions, taking care never to allowed the liquid to fall below the upper surface since air would be entrapped, which would disturb the column. The three fractions, collected in measuring cylinders, were nominated as AF1, AF2 and AF3 and made up of 2ml petroleum ether, 10 ml petroleum ether and 6 ml of 20% diethyl ether in hexane, respectively. After the collection of AF2, any petroleum ether remaining in the solvent reservoir was removed with the aid of pasteur pipette and replaced with 20% diethyl ether in hexane. Fraction 1 was evaporated back to 1 ml of petroleum ether solution in a vial, for further fractionation on silica gel. Fraction 2 was retained to be combined with a silica fraction (SF2) and fraction 3 was reduced to near dryness and then taken back in hexane to a final volume of 1 ml.

3.4.5.2 Silica column fractionation

The 1 ml sample of extract from the alumina column (AF1) was carefully transferred to the top of silica column (300 mm x 6 mm i.d.) and allowed to drain into the bed of the column and eluted into a 10ml measuring cylinder. The silica gel used (3 g; Merck 7734 70-230 ASTM) had been activated to 3% in a similar fashion to the alumina after firing at 600°C. The vial was rinsed three times with 0.5 ml pet. ether and added to the top of the column, as soon as the liquid reached the top of the column, the rest of the 7 ml pet. ether was carefully added without disturbing the upper surface of the column during each addition. The eluted 7 ml pet. ether is referred to as fraction 1 (SF1) and contains chlorobiphenyls, chlorobenzene and DDE. When the liquid had again just reached the top of the column, 16 ml of pet. ether was added carefully and the collecting measuring cylinder was replaced with a second one. The 16 ml eluate is referred to as fraction 2 (SF2) and contains DDT (Chlorinated pesticides). SF1 was reduced to 1 ml; SF2 and AF2 were combined then reduced to 1 ml. In this study , we are primarily concerned with chlorobiphenyls in fraction 1 (SF1).

3.4.6 Gas chromatography

The aliphatic hydrocarbon fractions were analysed using a Carlo Erba 5160 Mega Series Gas Chromatograph. The sample in dichloromethane (ca. 1 ul) was injected and separation performed on a flexible silica capillary column (25 m x 0.32 mm i.d.) coated with a 0.17 um HP-5 phase. A temperature programme of 50-300 at 4 °C min^{-1} was employed, holding the upper temperature for 20 minutes. Cold on-column injection was used, with a hydrogen carrier gas (flow 2 ml/min; pressure 50KPa). A flame ionization detector (FID) was used, maintained at 310°C. Identification of the *n*-alkanes was made by comparison of relative retention times with a co-injected standard (1- eicosene). Quantitation of each compound was obtained by measurement of the peak area of the GC response, compared to the that of a known standard (1- eicosene).

The PAH fractions were analysed using a Carlo Erba 5360 Mega Series gas chromatograph, using on-column injection. The sample in DCM was spiked, before injection, with a known amount of 1,1 binaphthyl which used as an internal standard. All chromatographic conditions were the same as for the aliphatic fraction. Preliminary identification of the PAHs was made by comparison of retention times with authentic standards. The PAH standard, used in the present study, was a mixture of 16 compounds; i. e. naphthalene (N), 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), 2,6-dimethylnaphthalene (2,6-DMN), biphenyl (Bi), fluorene (F), phenanthrene(P), fluoranthene (Fl), pyrene(Pyr), chrysene (Chr), perylene (Per) and 1,1 binaphthyl. Confirmation of these identifications was obtained using GC/MS (section 3.4.7).

The polychlorinated biphenyl fractions were analysed using a Carlo Erba 5360 Mega Series gas chromatogram fitted with an ECD detector and a column (30 m x 0.25mm i.d.) coated with a 0.25 um HP-5 phase. A temperature programme of 60-150 °C at 30°C min^{-1} and 150-285°C at 2.5°C was employed, holding the upper temperature for 5 minutes. The PCBs were tentatively assigned using comparison with Aroclors 1260 and 1254 standards and ICES standards (Figs. 8.2, 8.3 and 8.4) for the seven individual congeners studied (IUPAC Nos: PCB-28, PCB-52, PCB-101, PCB-153, PCB-138 and PCB-180). Quantification was based on peak area measurement and comparison to response of reference standards (see Chapter 8; Figs. 8.2-8.4). Quantitation was carried out by the external standard method.

Data for all fractions were acquired using a VG Multichrom data system.

3.4.7 Gas chromatography/mass spectrometry (GC/MS)

The aliphatic and PAH fractions were subsequently analysed by GC/MS using a Hewlett-Packard 5890 GC (with split / splitless injection) interfaced to a Hewlett-Packard 5970B quadrupole mass selective detector (ionizing voltage 70 eV; filament current 200ua; source temperature 200°C; multiplier voltage 2600V). The acquisition was controlled by a HP series 900 (216) computer in Full Scan Mode for identification purpose and in Selective Ion Mode (SIM) for greater sensitivity. The gas chromatograph was fitted with an HP-1 (ultra) fused silica capillary column (25 m x 0.25 mm i.d.; 0.11um film thickness) and the injection solvent was dichloromethane.

The oven was temperature programmed at 40-300°C/min, and the final temperature held for 20 minutes. Helium was employed as the carrier gas (flow rate 1 ml/min; pressure 50 Kpa). Compounds were identified by comparing relative retention times and mass fragmentogram response with standards and literature data. Individual PAHs were quantified by using the response factor of corresponding standards relative to each internal injection standard. The response factors were determined from a GC/MS run of the standards.

Chapter Four

Results of Trace Metals

4.0 Results of Trace Metals

4.1 Sediment composition

The analytical results for the textural character of Tees Bay and the Tees estuary sediments as well as their content of organic carbon, carbonate carbon and sulphur are summarized in the following subsections

4.1.1 Textural character

Results of grain size analysis of sediments from Tees Bay and the Tees estuary, and their textural classification, are presented in Tables 4.1 and 4.2. The textural characteristics of sediments, from both areas, have been defined using Shepard's (1954) triangular diagram (Fig. 4.1), and are shown in Figures 4.2 and 4.3. It is clear, from Table 4.1 and Fig. 4.2, that the surface sediments at all Tees Bay sites, with the exception of sites 4, 23 and 25, are composed predominantly of sand with minor proportions of clay and silt and that size distributions show relatively little variability with location. Site 23 differs slightly, and is characterized by sediment containing a predominance of silty sand. The two most seaward sites in the last line at the southern and northern ends of the Tees bay (sites 4 and 25), however, differ more significantly. Both sites have similar textures to the Tees estuary sites and are composed mainly of clayey-silt particles, with low contents of sand. Contour maps of sand, clay and silt contents in the surface sediments from Tees Bay (Figs. 4.4-4.6) were drawn based on the results in Table 4.1. Figure 4.4 shows the sand distribution at all Tees Bay sites. It shows clearly that the grain size of the surface sediment decreases on going from the shoreface, where there are much higher sand contents (84-95%), to the offshore part of the bay where the sand content decreases sharply to about 20% (in sites 4 and 25). This decrease is correlated well with an increase in the content of fine fractions (clay and silt), as shown in Figures 4.5 and 4.6. The clay and silt contents are about 1-7% and 2-8%, respectively, in the nearshore and increases to about 20% and 50% in the offshore (sites 4 and 25).

In the Tees estuary, surface sediments have a variable composition, from silty-sand, at sites 33, 38, to sandy-silt, at site 42, sand-silt-clay, at site 43, and clayey-silt at sites 35, 36, 37, 39, 40 and 41 (Table 4.2 and Fig. 4.3).

Table 4.1 Results of grain size analyses of Tees Bay sediments, and their textural classification (Shepard, 1954).

Sample No.	Sand %	Silt %	Clay %	Textural Classification
1	84	8	8	sand
2	76	13	11	sand
3	78	16	6	sand
4	24	59	17	clayey silt
5	90	8	2	sand
6	94	5	1	sand
7	96	3	1	sand
8	91	5	4	sand
10	90	5	4	sand
11	95	4	1	sand
12	93	5	2	sand
13	97	2	1	sand
14	96	3	1	sand
17	100	0	0	sand
18	86	9	5	sand
19	86	9	5	sand
20	94	4	2	sand
21	97	2	1	sand
22	89	8	3	sand
23	70	22	8	silty sand
24	83	12	5	sand
25	16	59	25	clayey silt
26	95	2	3	sand
27	94	5	1	sand
28	96	3	1	sand
29	100	0	0	sand
Mean	85.1	10.4	4.5	
Median	92.0	5.0	2.5	
Min.	16.0	0.0	0.0	
Max.	100.0	59.0	25.0	
Std. Dev.	20.55	15.15	5.69	

Table 4.2 Results of grain size analyses of Tees estuary sediments, and their textural classification (Shepard, 1954).

Sample No.	Sand %	Silt %	Clay %	Textural Classification
33	27	55	18	silty sand
34	17	65	18	clayey silt
35	15	63	22	clayey silt
36	7	66	27	clayey silt
37	15	58	27	clayey silt
38	26	59	15	silty sand
39	11	65	24	clayey silt
40	8	68	24	clayey silt
41	8	62	30	clayey silt
42	69	21	10	sandy silt
43	20	55	25	sand-silt-clay
Mean	20.3	57.9	21.8	
Median	15.0	62.0	24.0	
Min.	7.0	21.0	10.0	
Max.	69.0	68.0	30.0	
Std. Dev.	33.94	13.00	5.96	

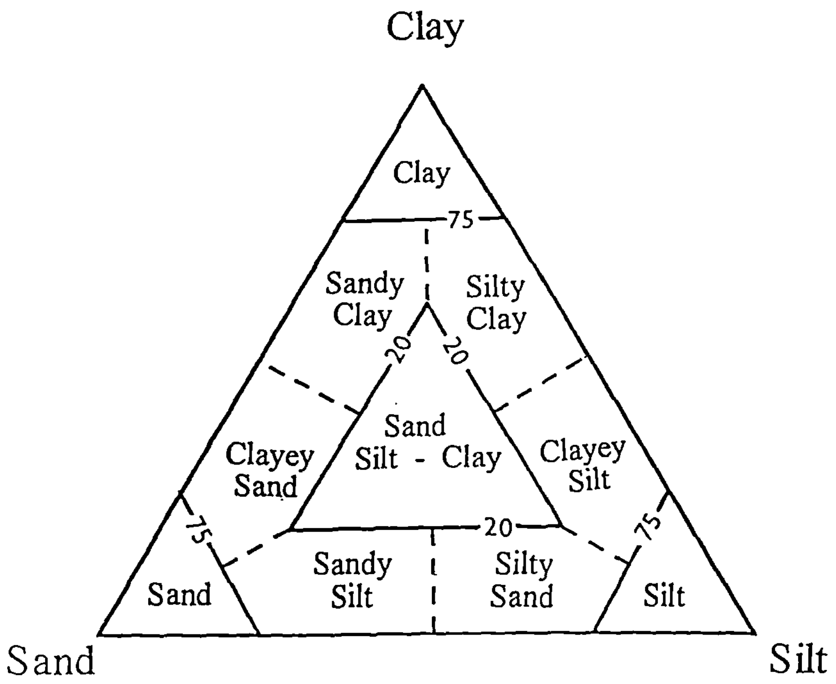


Figure 4.1. Sediments classification according to Shepard (1954).

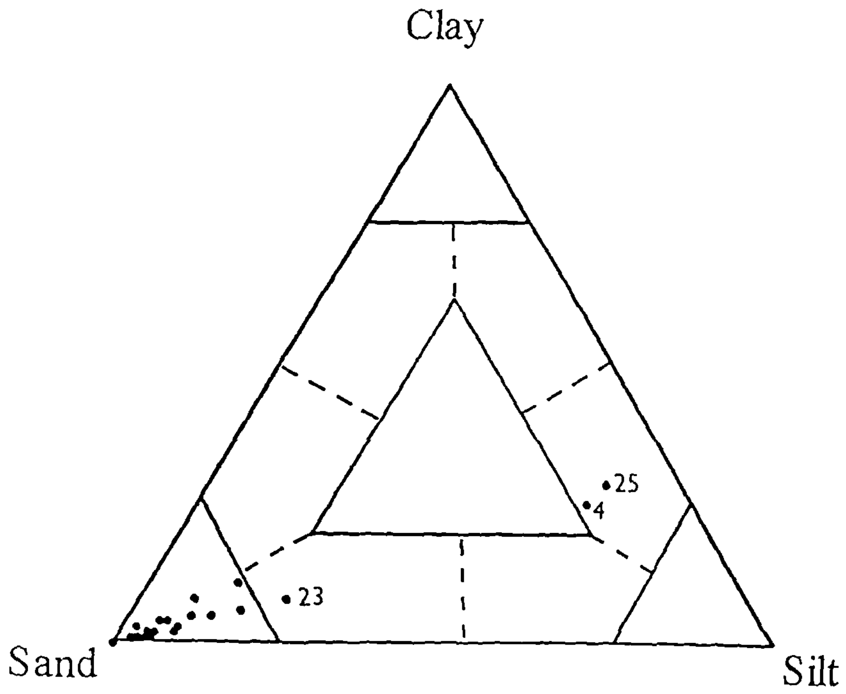


Figure 4.2. Grain size distributions of sediments from Tees Bay according to Shepard (1954).

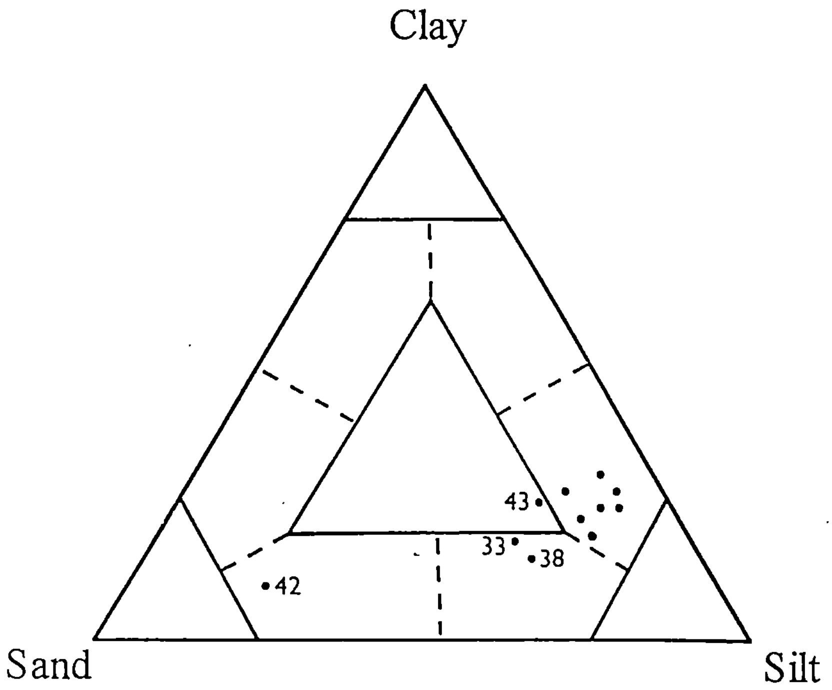


Figure 4.3. Grain size distributions of sediments from the Tees Estuary according to Shepard (1954).

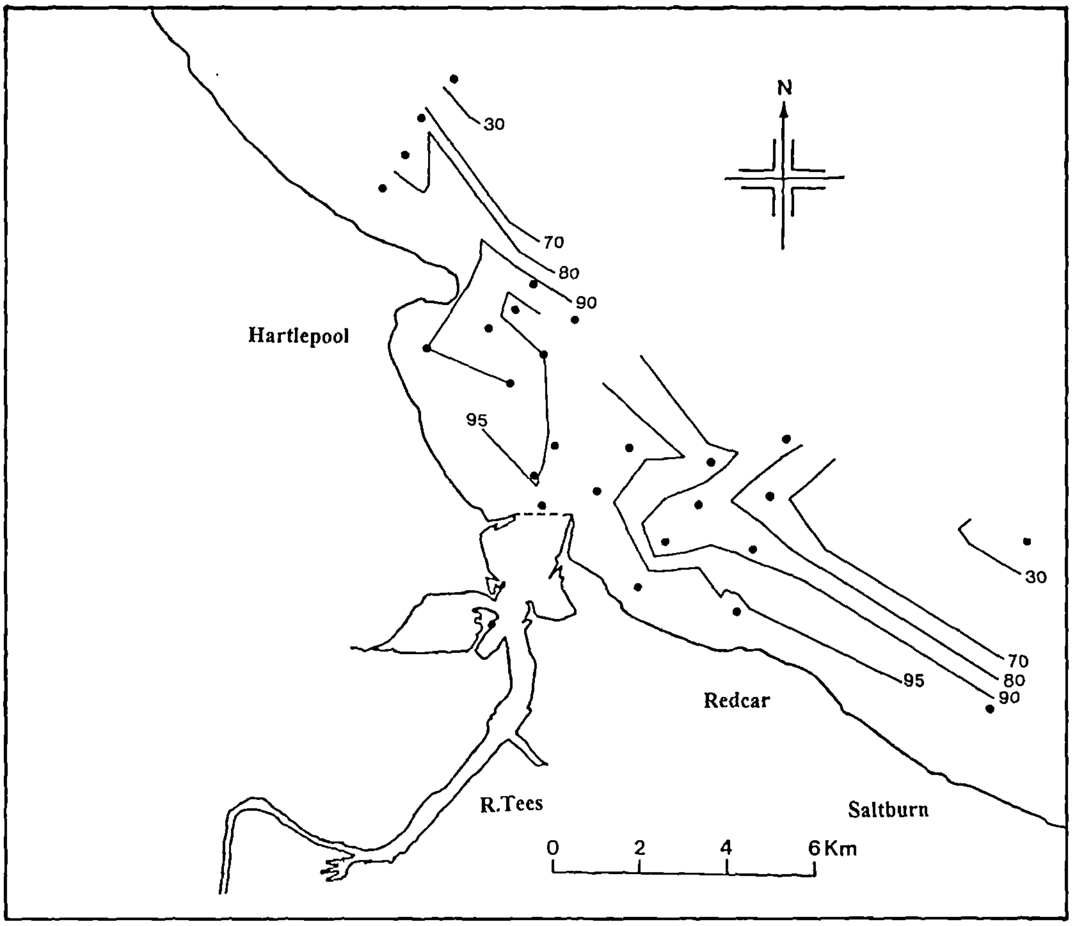


Figure 4.4. Map showing the distribution of sand (%) in Tees Bay sediments.

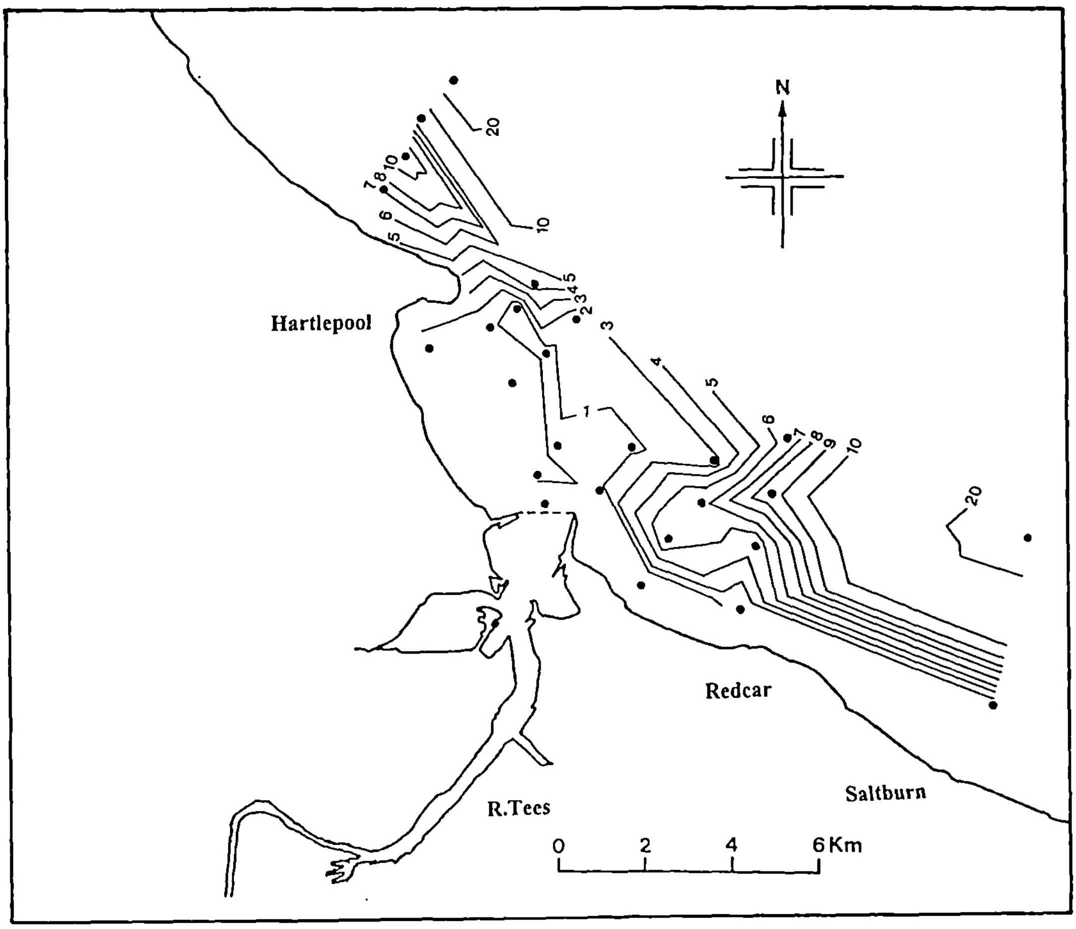


Figure 4.5. Map showing the distribution of clay (%) in Tees Bay sediments.

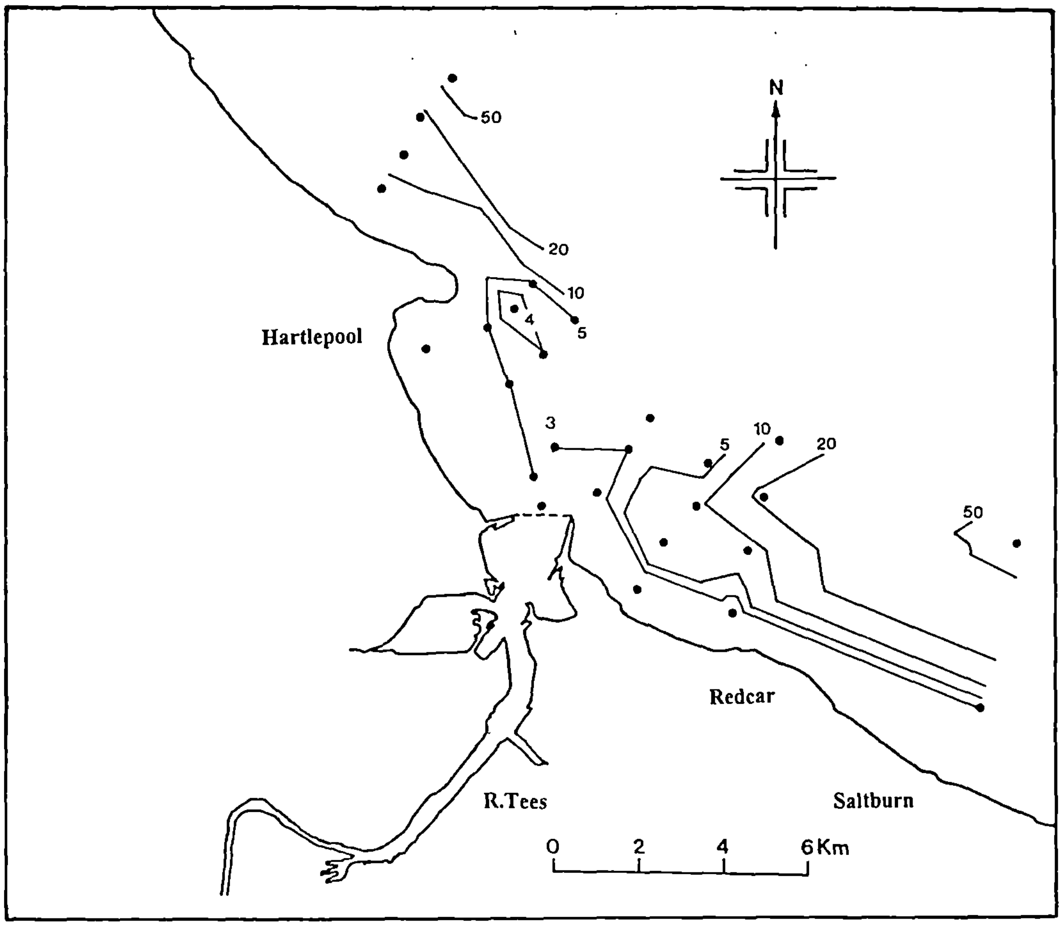


Figure 4.6. Map showing the distribution of silt (%) in Tees Bay sediments.

4.1.2 Total organic carbon (TOC), carbonate carbon and sulphur

In Tables 4.3 and 4.4, the results of the TOC, carbonate carbon and sulphur analyses of the surface sediments from Tees Bay and the Tees estuary, are shown.

In the surface sediments of Tees Bay (Fig. 4.7), the highest TOC value was found at site 4 (8%), with another peak value measured in sediment from site 25 (6%). Low values are typical of the sandy sediments where site 29 yielded a minimum of 0.22% TOC.

For the Tees estuary, all surface samples show high contents of TOC, which vary between 3.96% and 12.41% with the majority of the samples being over 5% TOC. Surprisingly, a high TOC content (12.41%) is found in the sandy sediment sampled near the mouth of the estuary.

The samples, from both areas, were low in carbonate carbon, but generally the samples taken from Tees Bay are higher in carbonate carbon compared to the Tees estuary (Tables 4.3 and 4.4). The highest carbonate carbon were shown by samples 11, 28, 13, 20 and 3 (which contains 8.34, 8.26, 6.48, 6.26 and 6.23 % carbonate carbon, respectively). The sulphur values were also low for all samples (between 0.75-0.03% and 0.57-0.15% sulphur in Tees Bay and the Tees estuary, respectively).

4.2 Total metal concentrations

Metal concentrations in the surface sediments (0-5 cm depth) from Tees Bay and the Tees estuary are shown in Table 4.5 and 4.6, respectively. It can be seen from the data in Table 4.5 that the concentrations of the seven metals in Tees Bay vary in the range: Cd, 5.2-1.3 ug g^{-1}; Co, 37.4-5.9 ug g^{-1}; Cr, 141.2-5.8 ug g^{-1}; Cu, 70.5-2.7 ug g^{-1}; Ni, 38.7-2.3 ug g^{-1}; Pb, 100-11.8 ug g^{-1}; Zn, 159.8-18.8 ug g^{-1}. The distributions of the metals in Tees Bay are illustrated in Figures 4.8-4.14. These maps show that most of the metals (except Cd) are distributed in a similar manner. The higher metal concentrations are located along the offshore sites and there is a gradient of decreasing metal concentrations towards the nearshore sites. This gradient take place across sediment of similar texture and composition. Amongst the offshore sites, site 4 (the most seaward site at the northern end of the bay) and site 25 (the most seaward site at the southern end of the bay), both clayey-silts (Table 4.1 and Fig. 4.2) with high TOC contents (Fig. 4.7), have relatively high metal concentrations. The highest

Table 4.3 Carbonate Carbon, TOC and Sulphur in sediments from Tees Bay.

Sample No.	Carbonate Carbon %	TOC %	Sulphur %
1	1.34	2.33	0.75
2	2.27	2.31	0.32
3	6.23	0.76	0.13
4	1.65	8.00	0.49
5	4.11	3.62	0.38
6	1.29	2.25	0.19
7	1.17	1.09	0.32
8	1.31	1.58	0.15
10	3.81	0.73	0.19
11	8.34	0.39	0.26
12	1.32	0.50	0.13
13	6.48	0.27	0.08
14	0.92	0.28	0.03
17	4.80	0.26	0.08
18	1.13	0.54	0.22
19	1.24	0.54	0.14
20	6.26	0.34	0.26
21	1.74	0.26	0.08
22	0.63	0.84	0.13
23	4.33	0.71	0.19
24	1.08	1.36	0.09
25	1.77	5.95	0.30
26	1.26	0.31	0.29
27	1.60	0.46	0.12
28	8.26	0.36	0.13
29	1.49	0.22	0.09
Mean	2.91	1.39	0.21
Min.	0.63	0.22	0.03
Max.	8.34	8.00	0.75
Std. Dev.	2.40	1.87	0.15

Table 4.4 Carbonate Carbon, TOC and Sulphur in sediments from the Tees estuary.

Sample No.	**Carbonate Carbon %**	**TOC %**	**Sulphur %**
33	1.49	3.96	0.39
34	1.39	5.32	0.27
35	1.36	4.88	0.34
36	1.86	5.36	0.39
37	1.59	5.26	0.56
38	1.29	3.95	0.15
39	1.71	7.06	0.50
40	1.65	6.94	0.44
41	1.21	8.12	0.45
42	0.99	12.41	0.32
43	1.61	7.01	0.57
Mean	1.45	6.39	0.40
Min.	0.99	3.95	0.15
Max.	1.86	12.41	0.57
Std. Dev.	0.25	2.41	0.13

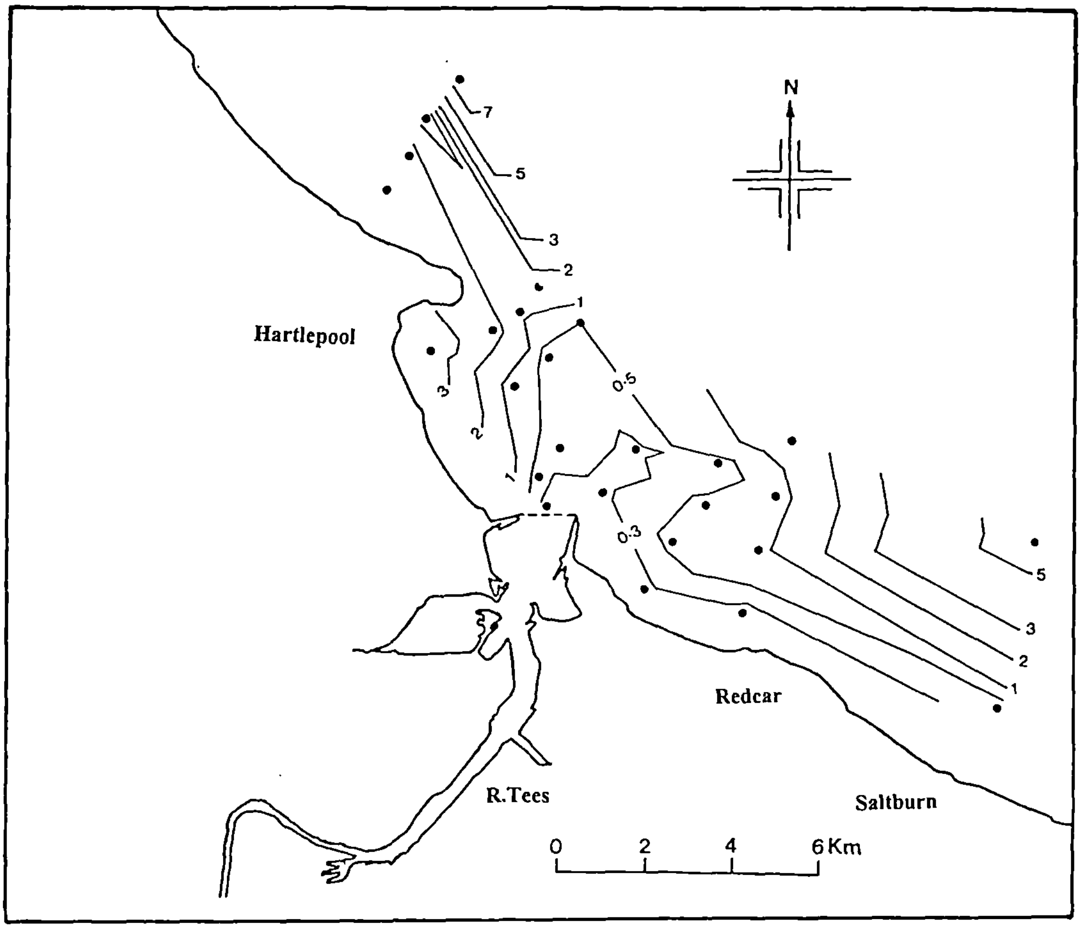


Figure 4.7. Map showing the distribution of TOC (%) in Tees Bay sediments.

Table 4.5 Metal concentrations in surface sediments from Tees Bay.

Sample No.	Cd ug/g	Co ug/g	Cr ug/g	Cu ug/g	Ni ug/g	Pb ug/g	Zn ug/g	Al %
1	3.2	16.9	44.1	31.3	13.8	39.1	110.3	13.5
2	5.0	18.0	71.2	21.7	18.1	45.4	83.9	14.9
3	2.6	20.8	37.6	16.0	11.1	45.8	91.1	13.4
4	5.2	37.4	141.2	70.5	38.7	100.0	159.8	15.4
5	2.5	14.7	45.4	23.1	14.0	27.8	89.8	11.8
6	2.7	13.3	30.7	15.5	12.5	36.5	78.4	12.6
7	3.0	18.2	32.0	14.4	12.6	38.4	83.8	12.3
8	2.4	9.0	22.9	7.9	21.1	30.7	66.3	11.4
10	2.6	11.5	29.3	9.5	7.9	20.3	59.7	11.3
11	3.5	12.4	28.2	11.6	8.4	20.3	60.3	11.8
12	2.9	14.5	34.4	7.6	9.4	35.4	61.8	11.6
13	3.1	10.1	25.4	4.0	6.8	12.4	43.9	10.6
14	2.3	7.7	25.4	4.8	6.6	20.9	42.1	10.0
17	1.3	5.9	7.9	2.7	2.3	13.0	29.9	8.7
18	2.4	11.2	33.1	11.5	6.0	20.1	50.6	12.6
19	2.6	9.9	36.1	8.0	8.2	30.1	64.4	11.8
20	3.6	15.1	19.8	8.9	7.6	32.0	71.1	11.7
21	1.9	8.8	8.0	3.7	2.9	13.4	29.2	10.4
22	2.7	15.6	45.3	10.6	10.0	25.9	61.0	12.6
23	3.8	16.3	41.3	18.7	15.1	40.8	68.6	13.2
24	2.8	16.3	51.5	11.9	11.0	50.1	110.0	13.1
25	4.6	30.2	103.6	44.1	35.7	75.8	122.1	15.8
26	2.0	14.6	17.2	5.3	5.2	17.8	48.9	11.7
27	1.8	9.2	26.0	8.1	9.3	13.2	45.4	10.2
28	2.4	14.6	46.7	8.9	7.6	20.8	67.5	10.3
29	2.8	14.0	5.8	3.1	4.2	11.8	18.4	11.1
Mean	2.9	14.9	38.9	14.7	11.8	32.6	69.9	12.1
Min.	1.3	5.9	5.8	2.7	2.3	11.8	18.4	8.74
Max.	5.2	37.4	141.2	70.5	38.7	100	159.8	15.8
Std. Dev.	0.93	6.71	29.02	14.72	8.69	20.03	31.32	1.67

Table 4.6 Metal concentrations in surface sediments from the Tees Estuary.

Sample No.	Cd ug/g	Co ug/g	Cr ug/g	Cu ug/g	Ni ug/g	Pb ug/g	Zn ug/g	Al %
33	4.6	27.3	166.7	52.1	31.1	357.9	326.8	15.6
34	5.8	31.4	223.6	82.9	38.4	477.6	394.3	16.7
35	6.8	30.1	275.6	101.6	39.3	565.3	490.3	16.6
36	6.6	35.6	316.0	131.9	45.4	537.8	538.9	17.2
37	8.7	33.6	576.8	240.6	45.8	679.5	721.2	18.2
38	5.9	30.2	313.5	124.3	37.9	219.9	392.1	16.0
39	9.8	55.6	319.8	262.1	46.7	316.6	777.4	15.8
40	6.2	51.2	218.8	150.0	49.1	161.1	387.9	17.3
41	5.2	47.5	166.7	102.6	47.2	102.5	208.3	17.5
42	2.6	16.2	36.2	24.9	20.8	36.5	65.2	13.8
43	5.2	35.0	154.3	82.4	40.5	93.9	180.0	16.8
Mean	6.1	35.8	251.6	123.2	40.2	322.6	407.5	16.5
Min.	2.6	16.2	36.2	24.9	20.8	36.5	65.2	13.8
Max.	9.8	55.6	576.8	240.6	49.1	679.5	777.4	18.2
Std. Dev.	1.93	11.45	138.24	72.64	8.35	218.43	218.01	1.19

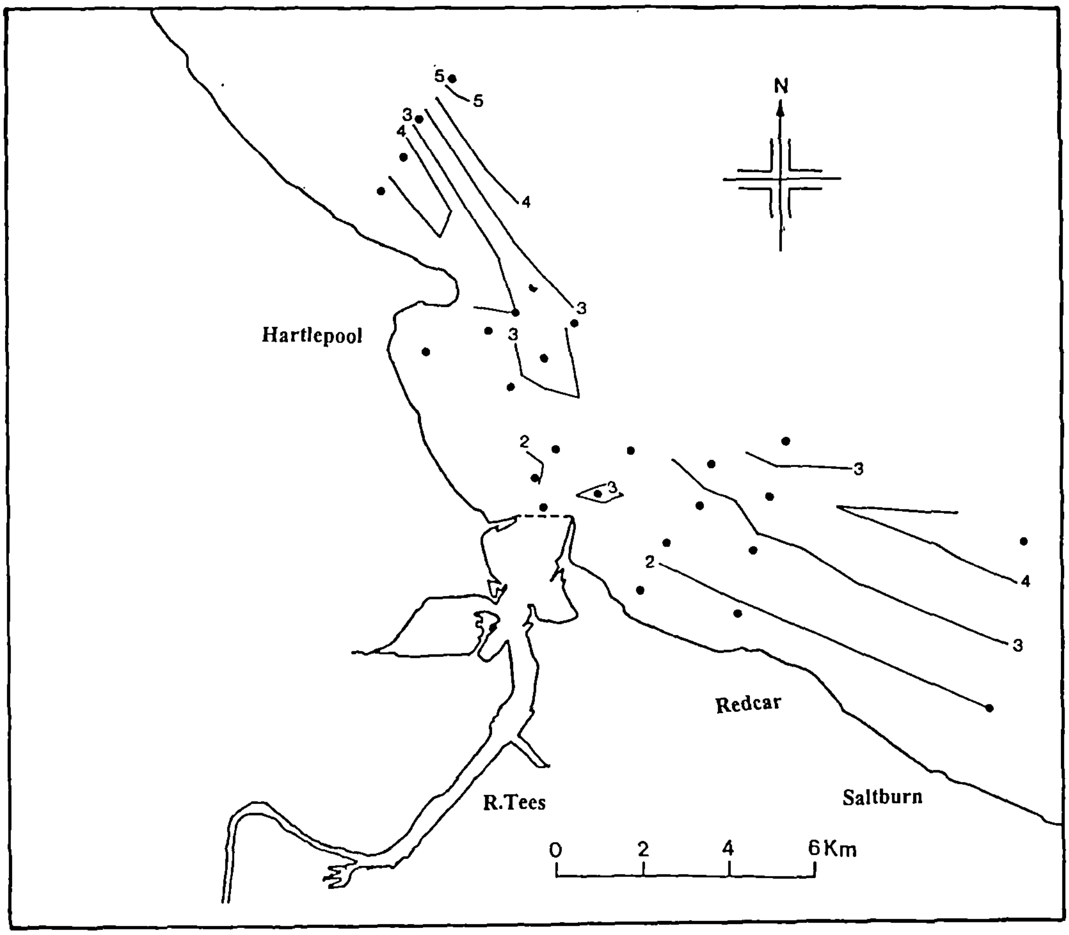


Figure 4.8. Map showing the distribution of Cd (ug g^{-1}) in Tees Bay sediments.

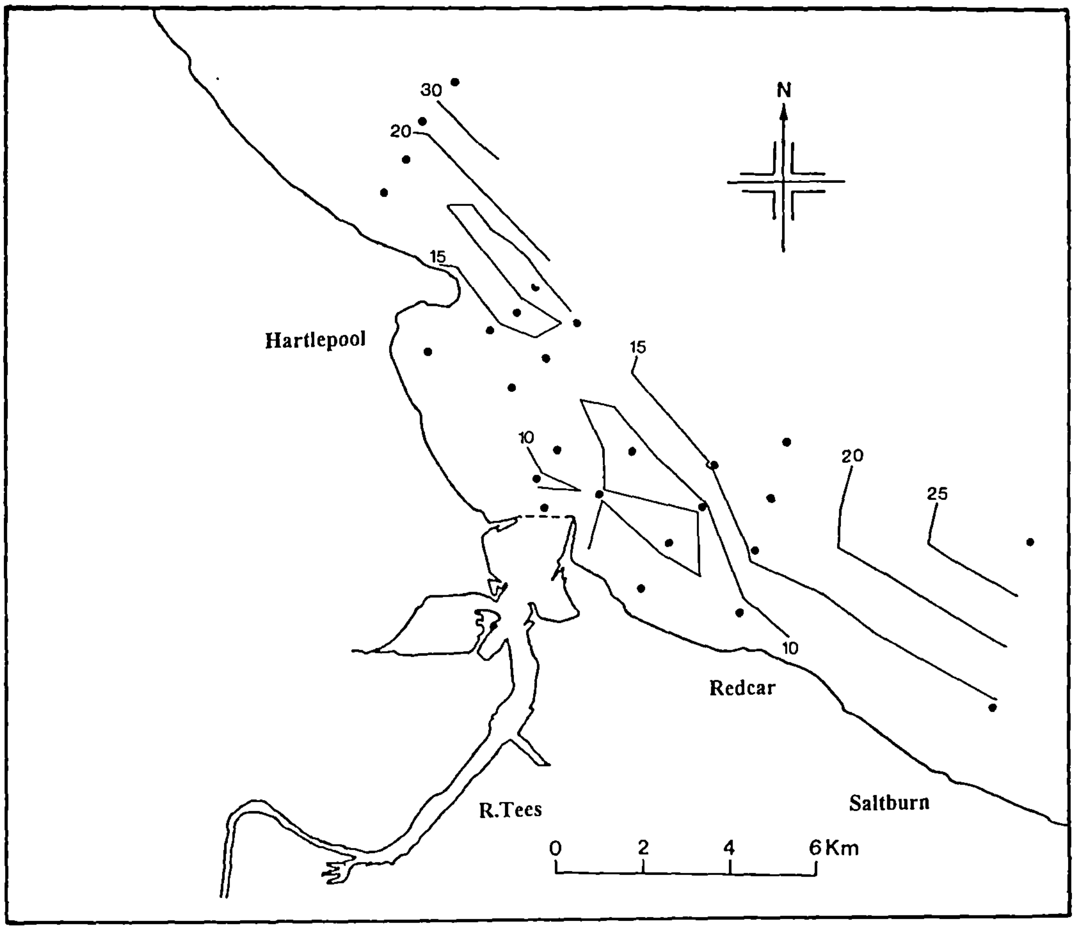


Figure 4.9. Map showing the distribution of Co (ug g^{-1}) in Tees Bay sediments.

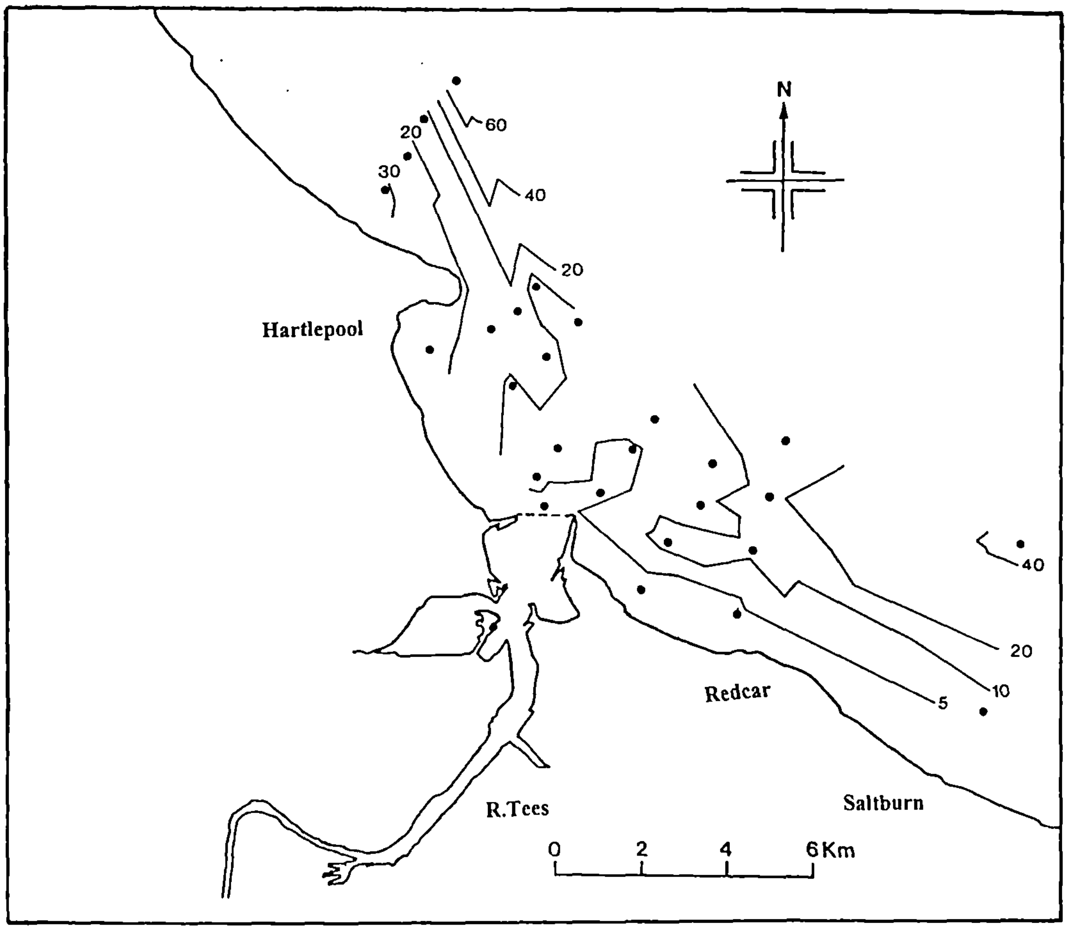


Figure 4.10. Map showing the distribution of Cu (ug g^{-1}) in Tees Bay sediments.

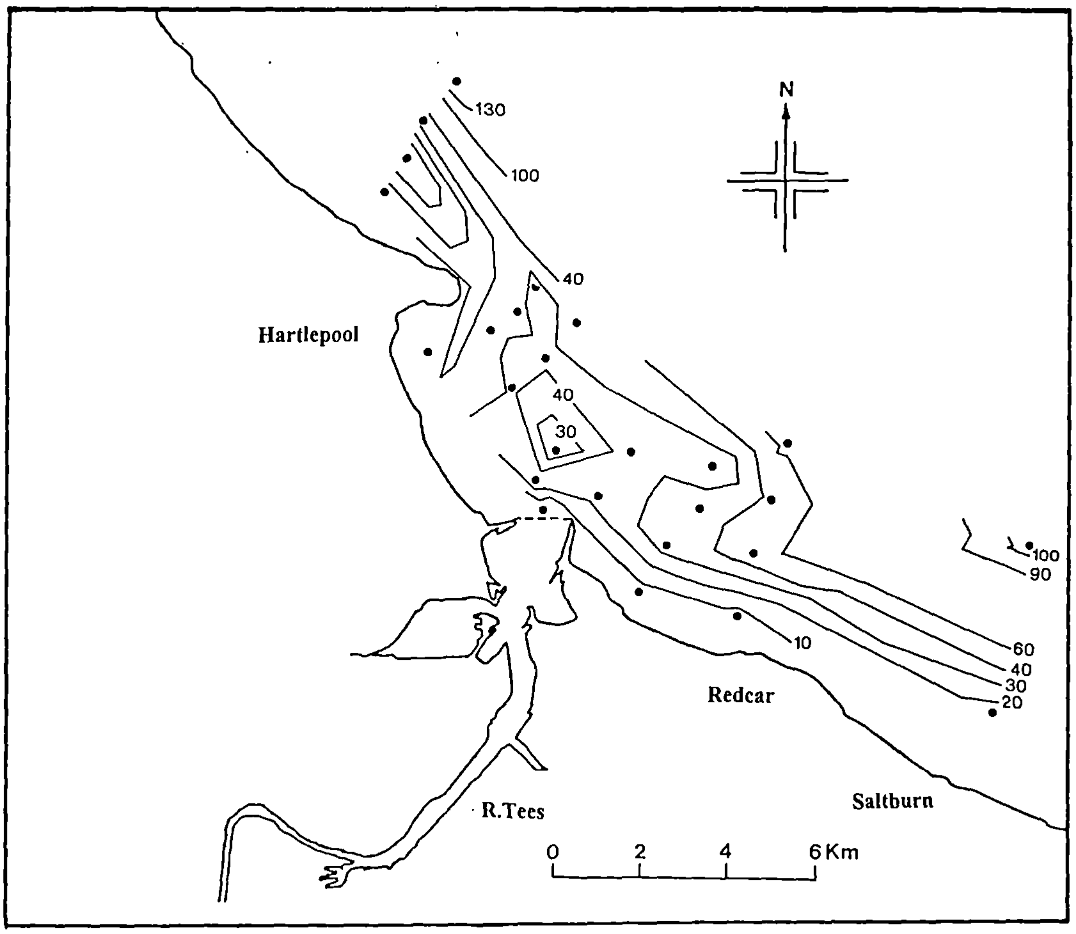


Figure 4.11. Map showing the distribution of Cr (ug g^{-1}) in Tees Bay sediments.

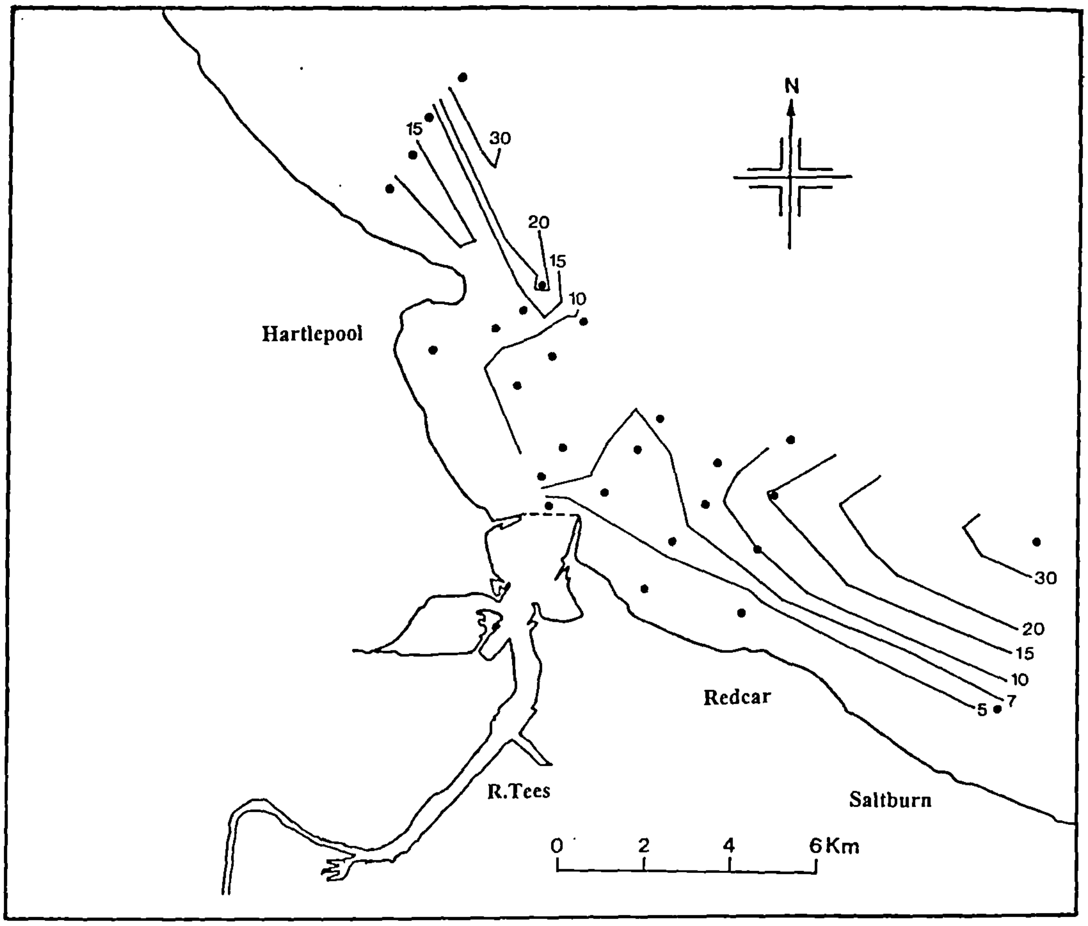


Figure 4.12. Map showing the distribution of Ni (ug g^{-1}) in Tees Bay sediments.

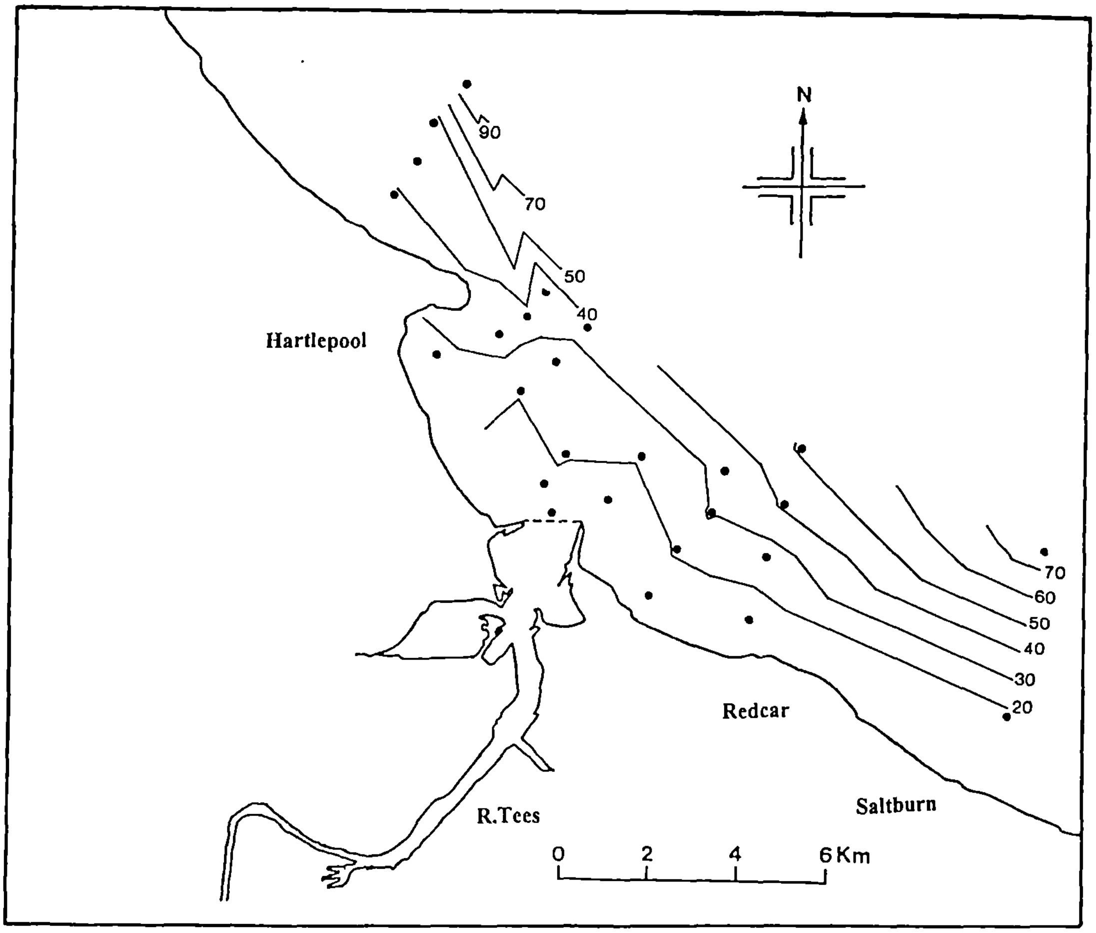


Figure 4.13. Map showing the distribution of Pb (ug g^{-1}) in Tees Bay sediments.

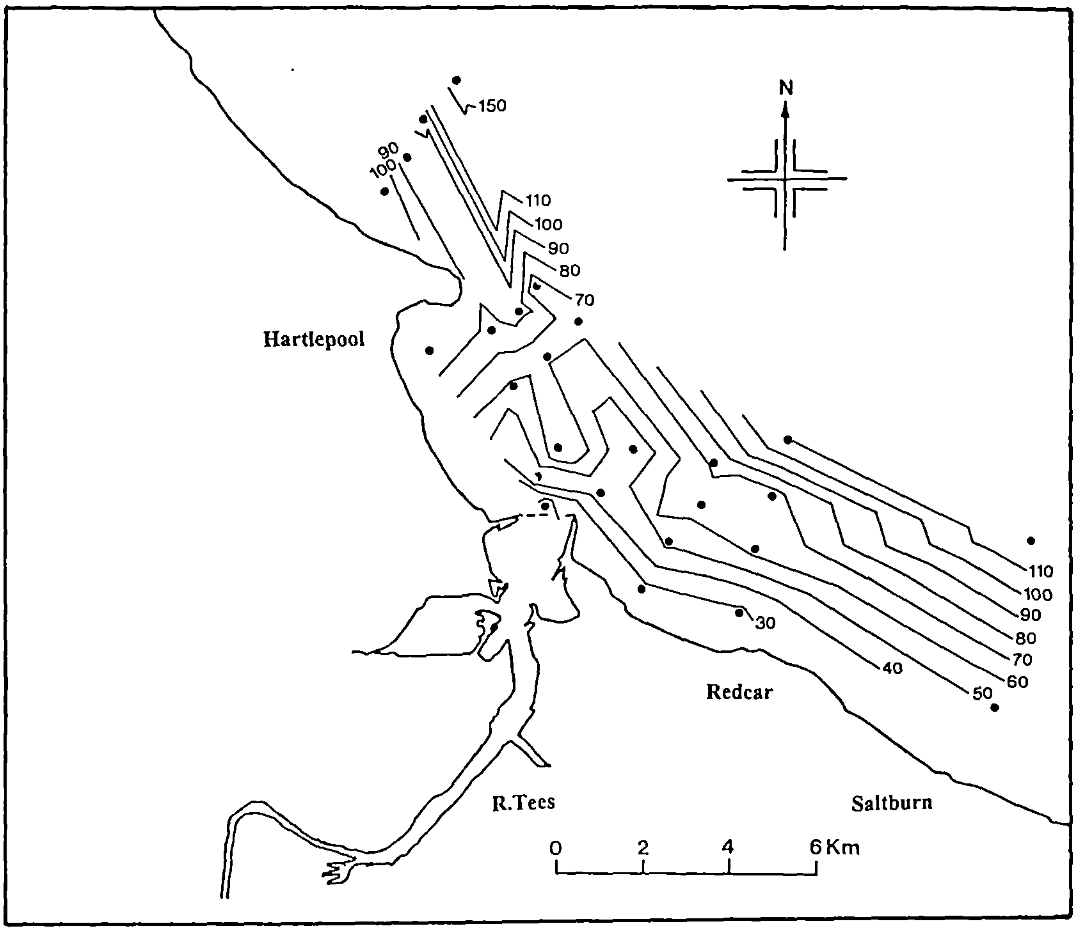


Figure 4.14. Map showing the distribution of Zn (ug g^{-1}) in Tees Bay sediments.

concentrations of all seven metals were found at site 4 (159.8, 141.2, 100, 70.5, 38.7, 37.4, and 5.2 ug g^{-1} for Zn, Cr, Pb, Cu, Ni, Co, and Cd, respectively). The lowest metal concentrations are observed at the sites which have a high sand content (e.g. sites 17 and 29). Sediment collected at the mouth of the estuary (site 29), which might have been expected to give intermediate values between the estuary and bay sediments, contained smaller concentrations of all metals, except Cd, than either the inner or outer bay sediments (in average: 18.4, 5.8, 11.8, 3.1, 4.2, 14, and 2, for Zn, Cr, Pb, Cu, Ni, and Co, respectively). It appears, therefore, that the metal levels increase from nearshore to open sea, with the exception of Cd which is distributed irregularly.

In comparison with the Tees Bay sediments, the trace metal concentrations in the surface sediments collected from the Tees estuary (Fig. 4.15 and Table 4.6), varied greatly. The metal concentrations fall in the ranges: Cd, 9.8-2.6 ug g^{-1}; Co, 55.6-16.2 ug g^{-1}; Cr, 576.8-36.2 ug g^{-1}; Cu, 262.1-24.9 ug g^{-1}; Ni, 49.1-20.8 ug g^{-1}; Pb, 679.5-36.5 ug g^{-1}; Zn, 777.4-65.2 ug g^{-1}. In order to understand the metal distribution better, the sampling area is divided into three specific regions called the upper reach of the estuary (sites 33 and 34), the middle reach of the estuary (sites 35 to 41) and the lower reach of the estuary (sites 42 and 43), as mentioned in Chapter 3 (section 3.1.1). Generally, the measured trace elements show fairly similar distributional patterns with the higher concentrations, for all seven metals, typically occurring in the middle reaches of the estuary (between locations 35-41, i.e. 10.4 km and 2.9 km from the mouth of the estuary; Fig. 4.15). Zn, for example, has a concentration of 327.8 ug g^{-1} in the upper reaches of the estuary, near Newport Bridge (site 33, i.e. 13.9 km from the river entrance), increasing to 777.4 ug g^{-1} in the middle reaches (site 39, i.e. 6.1 km from the river entrance), whereas the concentration near the mouth of the estuary (site 43) is 180 ug g^{-1} (Fig. 4.15a). Pb and Cr exceed 100 and 155 ug g^{-1}, respectively, between sample sites 33-41 but beyond this point gave lower concentrations (Fig. 4.15a). Cu lies between 101.6-262.1 ug g^{-1} in the middle reach, whilst not exceeding 82.9 ug g^{-1} in the upper or lower reaches of the estuary (Fig. 4.15a). Cd, Co, and Ni are also concentrated in the middle region of the estuary but the concentrations of these three metals in the upper reaches (site 33), were lower than sample site 43, near

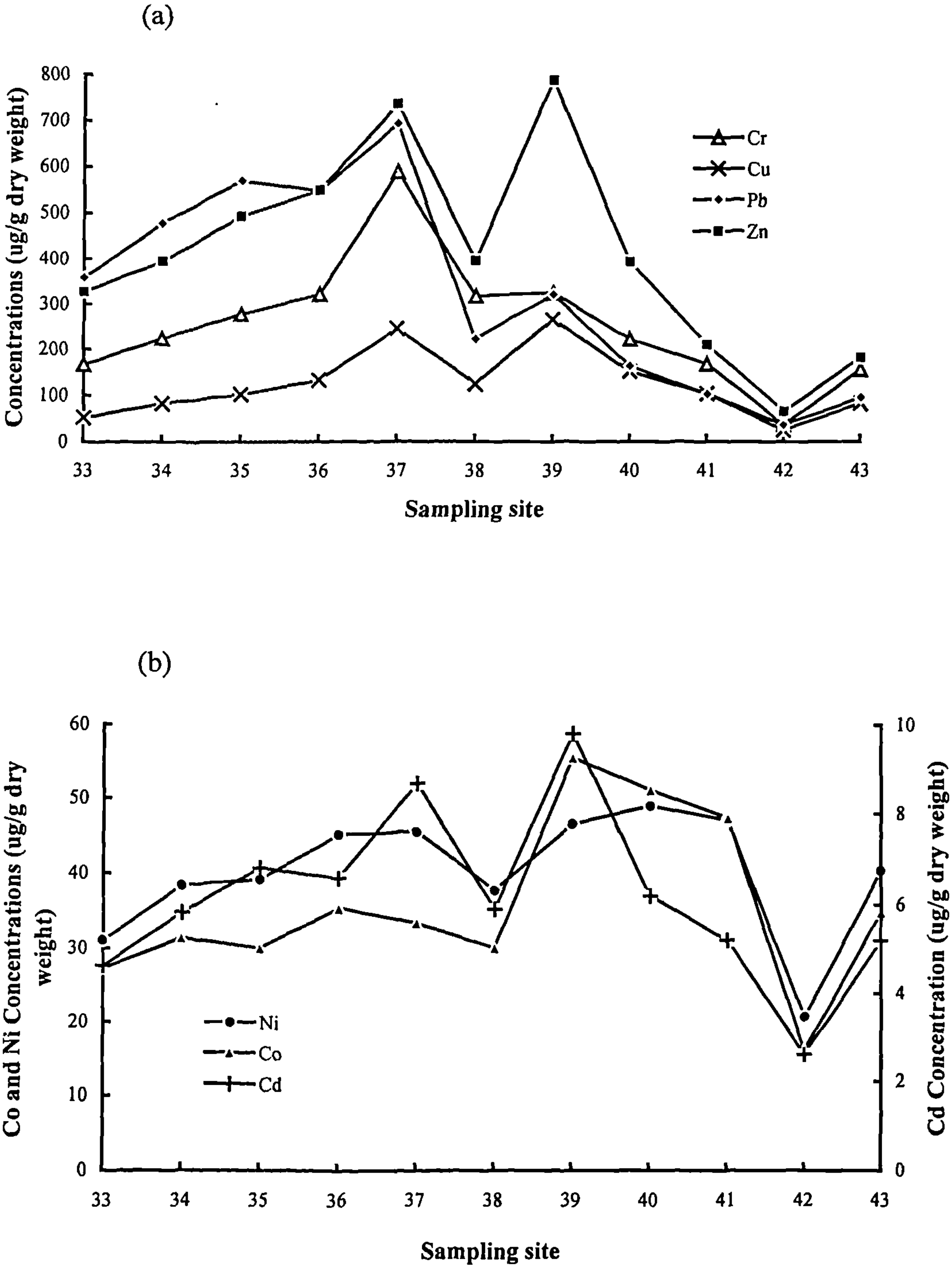


Figure 4.15. Total concentrations of (a) Cr, Cu, Pb and Zn, and (b) Cd, Co and Ni in surface sediments from the Tees Estuary.

the mouth of the estuary (Fig. 4.15b). The lowest concentrations of all seven metals occurred at station 42, near the mouth of the estuary.

4.3 Geochemical partitioning

The sediment samples, from Tees Bay and the Tees estuary, were subjected to the five stages sequential leaching technique as described in Chapter 3, and the data obtained are given in the Appendix as: 1) concentration of elements in each of the individual fractions together with the sum of the five fractions and their recoveries, and 2) the percentage of the total concentration of the elements in each sequential leaching fraction. The individual fractions themselves are identified by the suffixes F1 to F5; e.g. F3 refers to the stage 3 that extracted by hydroxylamine hydrochloride (e.g. reducible).

The mean, range and standard deviation of the total metal concentration, the sum of their partitioning between the various fractions, and their recoveries, in the surface sediments from Tees Bay and the Tees estuary, are summarized in Table 4.7. The percentage recoveries, reported in Table 4.7, for the five fractions, fall in the ranges: Cd, 80.0-115.4%; Co, 79.5-119.8%; Cr, 80.7-115.9%; Cu, 79.5-119.6%; Ni, 80.6-108.0%; Pb, 80.1-116.2%; Zn, 80.3-105.3%. The results of the percentage recoveries of Cu, Ni, Pb and Zn determined in the present study agree well with those reported by Li *et al.* (1995) using similar technique.

The partitioning characteristics of each metal in all stations, from both the Tees estuary and Tees Bay, are outlined individually below on an element by element basis. To aid interpretation of the data the average partitioning of the metals, in the surface sediment samples from the Tees Bay and the Tees estuary, together with the ranges and the standard deviation values are summarized, in terms of concentration (ug/g) and percentage (%) contribution, in Tables 4.8 and 4.9, are plotted in Figures 4.16-4.29.

4.3.1 Cd

Cadmium is the only one of the seven metals analysed for which fraction 1, i.e. that extracted by magnesium chloride (e.g. exchangeable), was found at most stations, in relatively high proportions (0.4-9.2 and 0.4-8.3% in the Tees estuary and Bay

Table 4.7 Independent total metal concentrations and sum of the chemical partition fractions (mean, range and standard deviation values) in the surface sediments from Tees Bay and the Tees Estuary.

		Total concentration ug/g			Sum of metal in the five fractions ug/g			Recovery %		
Metal	Location	Mean	Range	S.D	Mean	Range	S.D	Mean	Range	S.D
Cd	Tees Bay	2.9	1.3-5.2	0.93	2.8	1.2-5.2	0.93	97.3	80.0-120.0	13.67
	Tees Estuary	6.1	2.6-9.8	1.93	5.9	3.0-8.9	1.77	98.1	88.1-115.4	8.83
Co	Tees Bay	14.9	5.9-37.4	6.71	13.5	5.3-35.3	7.08	89.5	79.5-113.4	8.40
	Tees Estuary	35.8	16.2-55.6	11.45	39.4	14.0-60.0	12.46	109.5	86.4-119.8	10.50
Cr	Tees Bay	38.9	5.8-141.2	29.02	34.9	6.4-118.8	27.21	90.9	97.0-114.7	10.27
	Tees Estuary	251.6	36.2-576.8	138.24	247.9	29.2-599.9	145.64	96.7	80.7-115.9	10.56
Cu	Tees Bay	14.7	2.7-70.5	14.72	14.2	2.3-56.1	13.74	96.2	79.5-116.9	11.26
	Tees Estuary	123.2	24.9-240.6	72.64	132.6	25.9-272.2	77.64	107.1	100.4-119.6	6.20
Ni	Tees Bay	11.8	2.3-38.7	8.69	10.7	2.3-38.2	8.95	87.8	80.6-107.0	7.14
	Tees Estuary	40.2	20.8-49.1	8.35	38.7	21.4-47.4	7.09	97.0	87.1-108.0	6.26
Pb	Tees Bay	32.6	11.8-100.0	20.03	30.5	8.9-86.0	19.81	92.4	82.8-116.2	11.54
	Tees Estuary	322.6	36.5-679.5	218.43	310.9	41.1-549.6	191.77	100.7	80.1-112.6	8.81
Zn	Tees Bay	69.9	18.4-159.8	31.32	65.4	15.2-140.2	30.69	92.7	80.3-114.8	9.00
	Tees Estuary	407.5	65.2-777.4	218.01	382.1	53.3-682.6	187.79	94.4	81.8-105.3	7.59

Table 4.8 Summary of mean, range and standard deviation values of trace metal fractions (ug/g) in the surface sediments of Tees Bay and the Tees Estuary. (N.B. *n* = 26 in the sediment samples of Tees Bay, and 11 in the Tees Estuary).

		Sequential Leaching Stage														
		F1			F2			F3			F4			F5		
Metal	**Location**	**Mean**	**Range**	**SD**	**Mean**	**Range**	**SD**	**Mean**	**Range**	**SD**	**Mean**	**Range**	**SD**	**Mean**	**Range**	**SD**
Cd	Tees Bay	0.07	0.01-0.20	0.05	0.39	0.20-1.10	0.20	1.01	0.20-2.00	0.42	0.00	0.00	0.00	1.35	0.40-3.50	0.73
	Tees Estuary	0.34	0.02-0.80	0.25	0.49	0.10-1.00	0.26	1.75	0.30-3.50	1.04	0.40	0.10-1.00	0.31	2.96	1.40-4.20	0.72
Co	Tees Bay	0.12	0.00-0.40	0.13	1.17	0.50-1.70	0.42	3.38	1.70-7.00	1.43	0.54	0.00-3.30	0.74	8.30	2.80-24.30	5.10
	Tees Estuary	0.34	0.10-0.80	0.26	2.00	0.60-3.70	0.90	5.89	3.20-14.50	3.56	3.58	0.90-6.90	1.88	27.54	7.90-39.20	8.30
Cr	Tees Bay	0.00	0.00	0.00	0.25	0.02-1.00	0.24	4.26	1.10-19.30	4.54	1.16	0.00-6.00	1.48	29.20	4.70-94.20	21.47
	Tees Estuary	0.00	0.00	0.00	5.62	0.90-25.70	6.94	95.25	6.50-275.80	72.18	60.63	1.50-156.10	43.30	86.43	19.80-142.80	31.76
Cu	Tees Bay	0.00	0.00	0.00	0.46	0.00-1.20	0.32	0.50	0.10-1.10	0.25	5.33	0.00-29.40	7.20	7.93	1.90-25.80	6.64
	Tees Estuary	0.00	0.00	0.00	0.25	0.00-1.00	0.41	2.62	1.10-4.50	1.16	95.25	7.00-221.10	66.43	34.47	17.00-53.80	12.04
Ni	Tees Bay	0.00	0.00	0.00	0.32	0.02-2.00	0.36	0.73	0.10-2.30	0.52	1.47	0.20-5.30	1.33	8.13	1.60-30.70	7.06
	Tees Estuary	0.00	0.00	0.00	0.75	0.30-1.40	0.38	4.30	1.70-6.60	1.37	5.74	4.20-6.80	0.86	27.88	15.00-36.20	6.14
Pb	Tees Bay	0.01	0.00-0.20	0.04	4.90	1.40-10.80	2.40	15.96	3.80-49.90	12.07	0.92	0.00-3.40	0.83	8.73	2.30-25.80	5.81
	Tees Estuary	0.28	0.00-0.70	0.25	29.16	7.00-74.00	21.22	164.98	21.40-334.60	109.56	37.82	2.20-84.20	27.98	78.68	10.50-138.00	43.01
Zn	Tees Bay	0.00	0.00	0.00	4.01	0.70-8.60	2.18	19.26	4.60-41.70	8.88	4.81	1.10-14.70	3.13	37.34	8.80-80.70	18.98
	Tees Estuary	0.21	0.00-0.90	0.27	22.99	4.20-53.70	15.41	160.30	14.70-226.40	74.44	86.25	4.60-218.10	61.32	112.32	29.80-193.70	48.99

Table 4.9 Summary of mean, range and standard deviation values of trace metal fractions (%) in the surface sediments of Tees Bay and the Tees Estuary. (N.B. $n = 26$ in the sediment samples of Tees Bay, and 11 in the Tees Estuary).

		Sequential Leaching Stage (%)														
		F1			F2			F3			F4			F5		
Metal	Location	Mean	Range	SD	Mean	Range	SD	Mean	Range	SD	Mean	Range	SD	Mean	Range	SD
Cd	Tees Bay	2.55	0.38-8.33	2.10	15.26	3.85-41.18	8.84	35.58	11.76-63.24	11.20	0.00	0.00	0.00	46.61	15.81-67.13	13.20
	Tees Estuary	5.68	0.38-9.23	3.33	9.58	2.38-33.33	8.66	27.56	8.93-39.33	11.50	6.27	1.82-14.29	4.00	50.91	38.20-61.82	7.62
Co	Tees Bay	0.79	0.00-3.01	0.88	10.14	2.99-24.15	5..03	26.00	18.52-38.24	5.28	3.10	0.00-9.35	2.43	59.97	49.72-73.64	6.36
	Tees Estuary	0.97	0.24-2.86	0.88	5.05	2.31-6.62	1.31	15.21	8.49-30.00	7.20	8.68	4.30-12.38	2.33	70.09	52.38-79.84	8.73
Cr	Tees Bay	0.00	0.00	0.00	0.89	0.08-4.26	0.87	12.10	5.63-21.33	4.56	3.33	0.00-9.33	2.28	83.68	68.00-92.58	6.85
	Tees Estuary	0.00	0.00	0.00	2.23	0.44-4.79	1.43	35.30	22.26-47.55	8.45	22.44	5.14-37.03	9.69	40.03	23.72-67.81	11.31
Cu	Tees Bay	0.00	0.00	0.00	5.28	0.00-14.29	4.19	5.37	0.55-17.86	3.66	29.01	0.00-52.41	12.70	60.34	45.99-82.61	9.87
	Tees Estuary	0.00	0.00	0.00	0.38	0.00-2.32	0.72	2.53	0.66-5.35	1.51	65.81	27.03-81.23	14.61	31.28	18.11-65.64	13.00
Ni	Tees Bay	0.00	0.00	0.00	3.32	0.52-8.70	1.80	7.72	1.76-14.13	3.24	13.40	5.29-21.80	4.07	75.56	66.67-94.76	6.02
	Tees Estuary	0.00	0.00	0.00	2.04	0.66-4.17	1.08	11.14	6.88-17.28	3.29	15.07	12.78-19.63	2.07	71.75	64.14-78.12	4.55
Pb	Tees Bay	0.06	0.00-1.54	0.30	18.42	7.89-42.86	7.98	49.56	28.79-66.90	10.08	3.06	0.00-10.61	2.05	28.90	16.37-45.45	6.84
	Tees Estuary	0.13	0.00-0.66	0.19	10.95	3.13-20.55	5.17	51.30	40.46-60.88	5.59	10.96	5.35-15.32	2.99	26.66	20.56-32.64	4.13
Zn	Tees Bay	0.01	0.00-0.18	0.04	6.31	2.41-11.53	2.74	30.24	16.43-38.50	5.58	7.00	5.42-11.27	1.38	56.44	50.57-68.25	4.48
	Tees Estuary	0.04	0.00-0.17	0.05	6.43	2.49-13.85	3.20	40.91	27.58-51.34	8.43	20.51	8.63-31.95	6.07	32.11	25.93-55.91	8.49

sediments, respectively, Figs. 4.16 and 4.17). This contrasts with Ni, Cr, Cu, and to a lesser extent with Pb, Zn, and Co where the proportion of metal associated with fraction 1 was very low. The partitioning of Cd in other fractions is similar to Cr, Pb and Zn being dominated by fractions 5 (38.2-61.8%), i.e. that extracted by a nitric/hydrofluoric/perchloric acids mixture (e.g. residual), and 3 (24.6-39.3%), i.e. that extracted by hydroxylamine hydrochloride (e.g. reducible), with minor amounts of fraction 4, i.e. that extracted by hydrogen peroxide and ammonium acetate (e.g. oxidizable) and fraction 2, i.e. that extracted by sodium acetate (e.g. carbonate). Fraction 3 clearly declines in significance beyond site 40, whereas fraction 2 becomes more important near the mouth of the estuary (sites 41, 42 and 43; Fig. 4.16).

For Tees Bay sediments (Fig. 4.17), the highest percentage of the total Cd is associated with fraction 5 (15.8-67.3%) or fraction 3 (11.8-63.2%), and there is no detectable metal in fraction 4. The percentage of Cd held in fractions 1 and 2 (2.55 and 15.26%, respectively) is very low in comparison with fractions 3 and 5 (35.58 and 46.61%, respectively), except in sample site 27 in which the percentage of Cd held in fraction 2 (41.2 %) is much higher than fraction 3.

4.3.2 Co

Cobalt is found in all five phases at all sites in the Tees estuary (Fig. 4.18). The partitioning of Co at all sites except 39 and 42 suggests that a major proportion is held in fraction 5 (71.5-79.8%) with moderate amounts associated with fractions 3 (8.5-16.7%) and 4 (4.3-11.5%); the contributions of Co associated with fractions 2 (2.3-6.6%) and 1 (0.2-2.9%) being much lower. The relative proportions of these fractions remains more or less unchanged between sites, with the exception of sites 39 and 42 where Co in fraction 3 is of increased importance (27.6 and 30.0%, respectively).

The Tees Bay region again exhibits very strong association of Co with fraction 5 (Fig. 4.19). The content of this fraction is extremely high (50.0-70.6%). Levels found in fraction 3 are also high (18.5-38.2%), whereas the contributions of the remaining fractions are low: fraction 1 (0-3.0%); fraction 2 (3.0-24.1%); fraction 3 (0.0-9.3%).

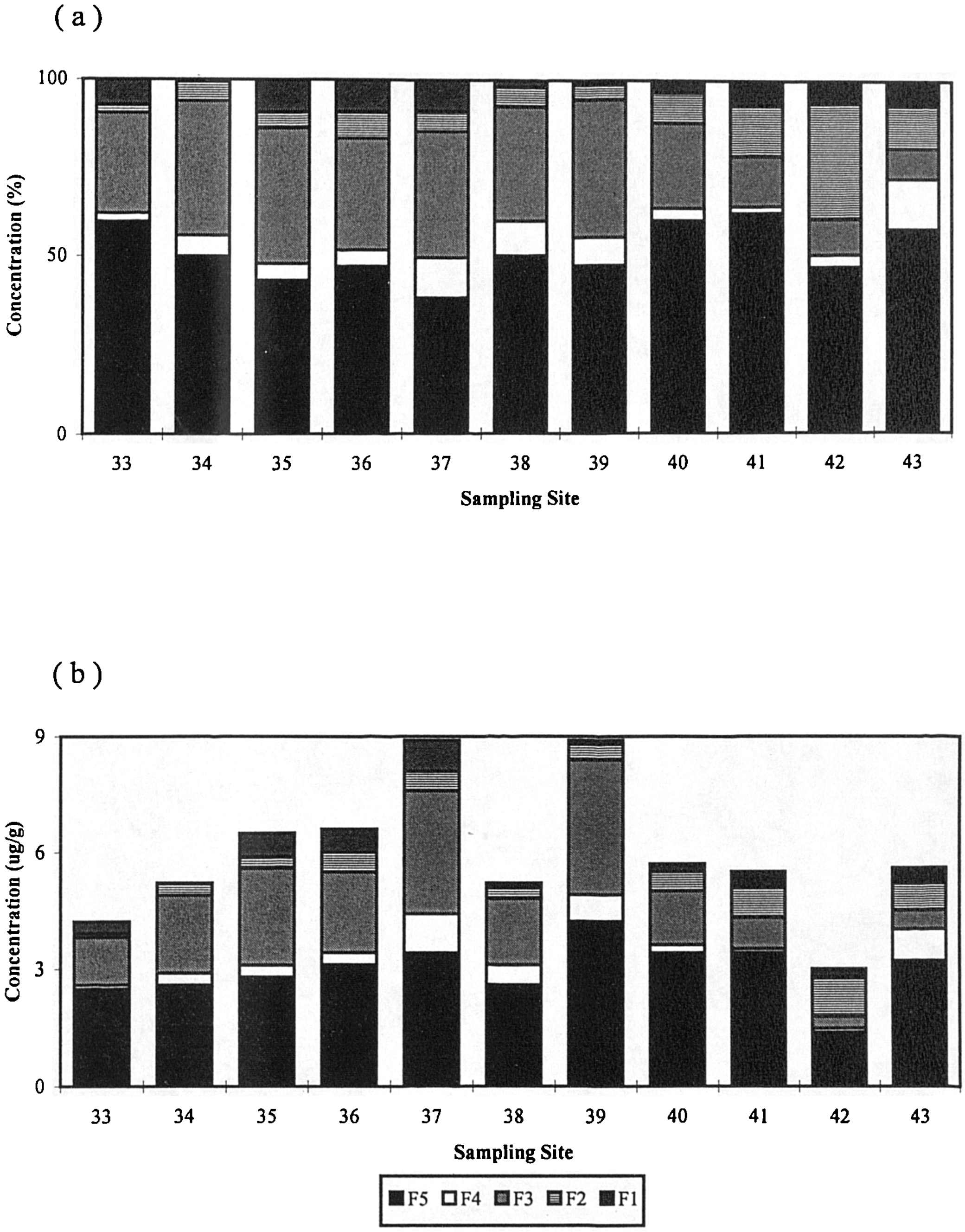


Figure 4.16 Percentage distribution (a) and absolute concentration (b) of Cd in the five geochemical phases in the surface sediments from the Tees Estuary. F1 = Extractable with 1 *M* magnesium chloride (pH 7); F2 = Extractable by 1 *M* sodium acetate adjusted to pH 5 with acetic acid; F3 = Extractable with 0.04 *M* hydroxylamine hydrochloride in 0.1 *M* nitric acid; F4 = Extractable with 30% hydrogen peroxide, adjusted to pH 2 with nitric acid, and 3.2 *M* ammonium acetate in 20% nitric acid; and F5 = $HNO_3/HF/HClO_4$-Extractable.

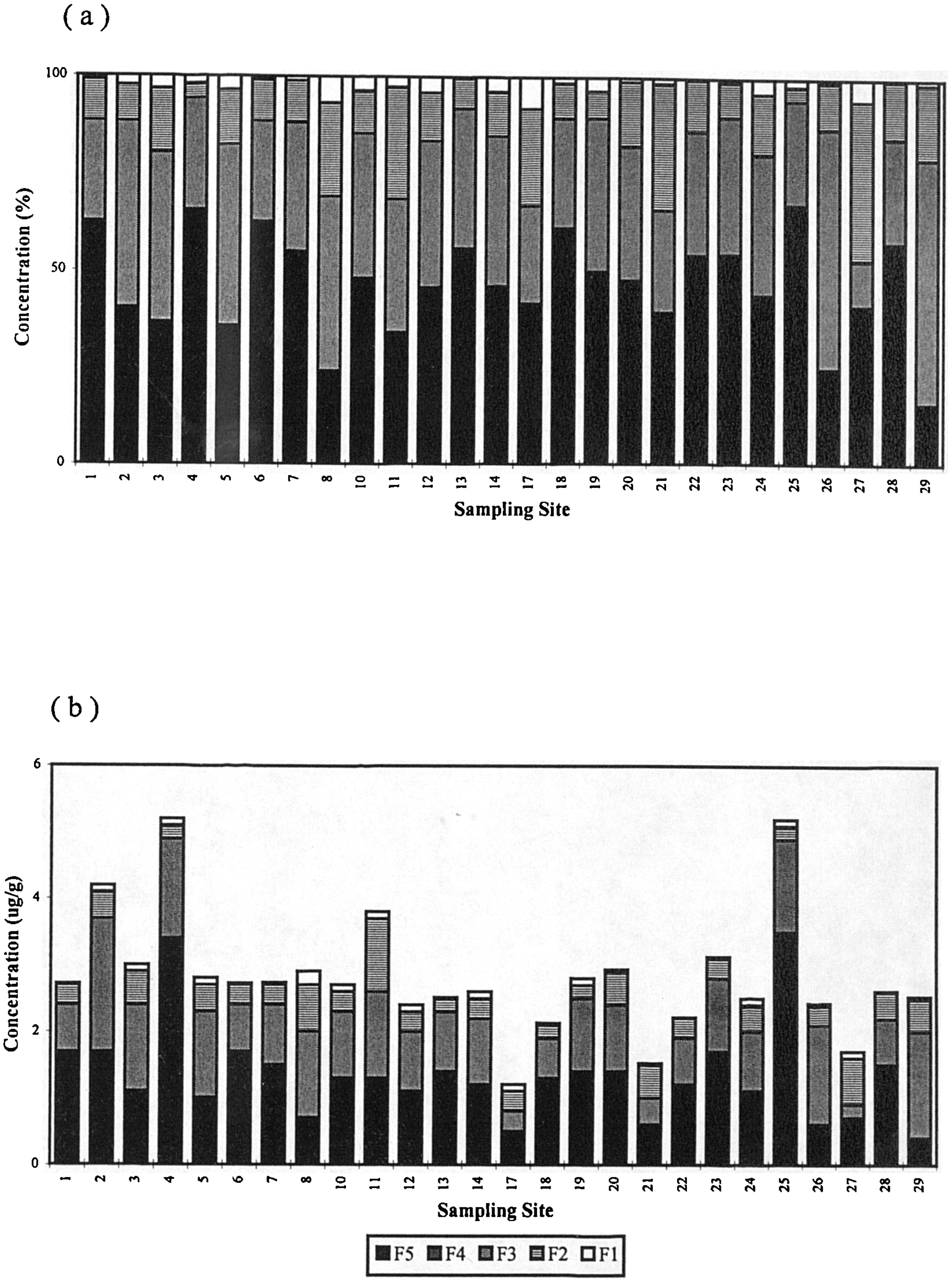


Figure 4.17 Percentage distribution (a) and absolute concentration (b) of Cd in the five geochemical phases in the surface sediments from Tees Bay. F1 - F5 as for Fig. 4.16.

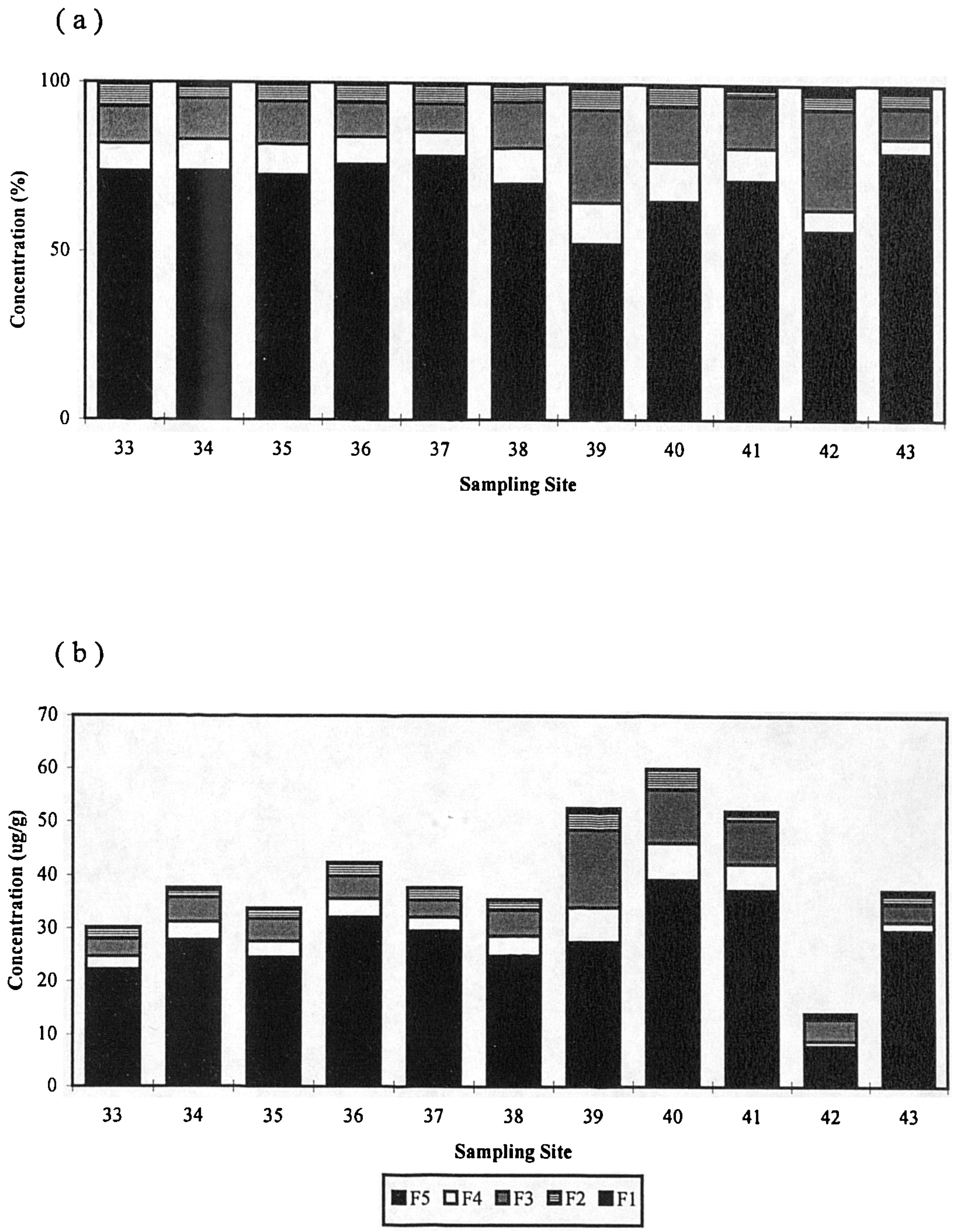


Figure 4.18 Percentage distribution (a) and absolute concentration (b) of Co in the five geochemical phases in the surface sediments from the Tees Estuary. F1 - F5 as for Fig. 4.16.

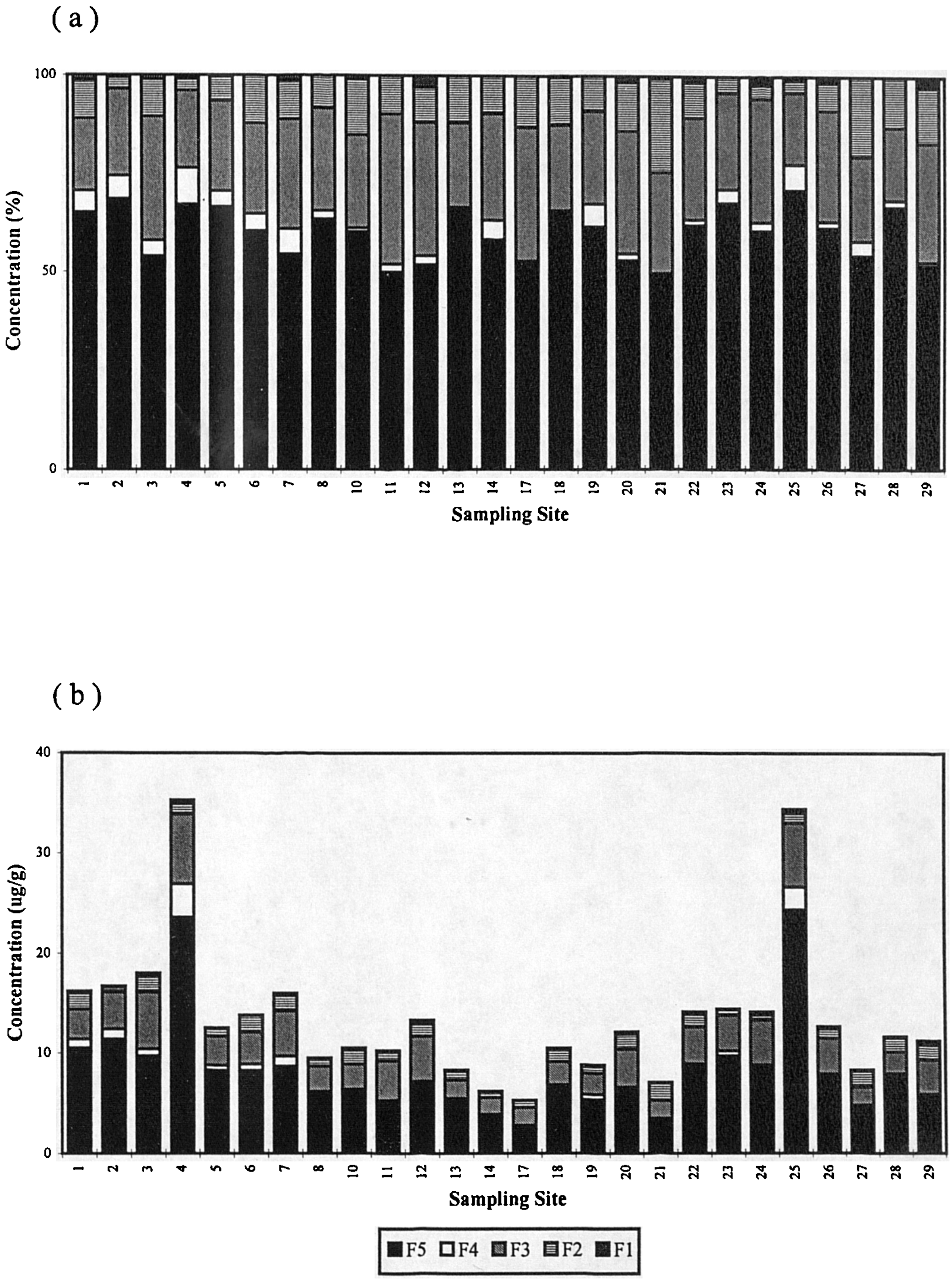


Figure 4.19 Percentage distribution (a) and absolute concentration (b) of Co in the five geochemical phases in the surface sediments from Tees Bay. F1 - F5 as for Fig. 4.16.

4.3.3 Cr

Figures 4.20 and 4.21 depict the distribution of Cr species in the surface sediments of the Tees estuary and Tees Bay. As mentioned above (see section 4.2) Cr concentrations vary from 5.9 to 576.8 ug g^{-1} (see Tables 4.5 and 4.6) and are higher in the Tees estuary sediments than those from the Bay (see Table 6.5b; Chapter 5). Cr was not detected in fraction 1 in either area. The partitioning of Cr in the Tees estuarine sediments (Fig. 4.20) is characterized by the importance of fractions 3 (22.3-47.5%), 4 (5.1-37.0%) and 5 (23.7-67.8%). A low contribution is made by fraction 2 (0.4-4.8%). It is also appears from the partitioning of Cr in the Tees estuary that the relative proportions of the three dominant fractions are irregular for all samples. The data for the middle region of the estuary show a tendency of Cr to occur mainly in fraction 3 (34.8-47.5%) and to a lesser extent in fractions 5 (23.7-46.2%) and 4 (14.3-30.6%). In the upper reaches of the estuary (sites 33 and 34) Cr is still held in fractions 3., 4 and 5, but, for these sediments, fractions 4 (34.7 and 37.0%) and 5 (37.1 and 38.8%) become relatively more important than fraction 3 (26.9 and 23.8%). At site 42 (in the lower reaches of the estuary), which is composed mainly of sand, fraction 5 shows the unusually high value of 67.8%.

As for Zn, a significant change in the partitioning of Cr is noted in the samples from Tees Bay (Fig. 4.21). At these sites, the partitioning of Cr continues again the trend indicated by site 42 in that fraction 5 becomes the principle host, containing 71.8-92.6%. Moderate percentages of the total Cr are found in fraction 3 (5.6-20.7%), whereas much lower percentages are found in fractions 4 (0.0-9.3%) and 2 (0.1-4.3%).

4.3.4 Cu

Cu concentrations in the upper 5 cm of sediments at all estuarine sites, except site 42, exceed those for uncontaminated sediments (45 ug g^{-1}) reported by Turekian and Wedepohl (1961). As illustrated in Figure 4.22, Cu is primarily held in fraction 4 (60.1-81.2%) at all stations from the Tees estuary, except site 42. None of the other metals shows such a high concentration in this fraction. Cu does not occur in detectable levels in fraction 1 (at any sites) or fraction 2, with the exception of sites 40, 41, 42, and 43. A high percentage of Cu is also found in fraction 5 (18.1-37.8%). Much lower contents are associated with fractions 3 (0.7-5.4%) and 2 (0.0-1.0 %).

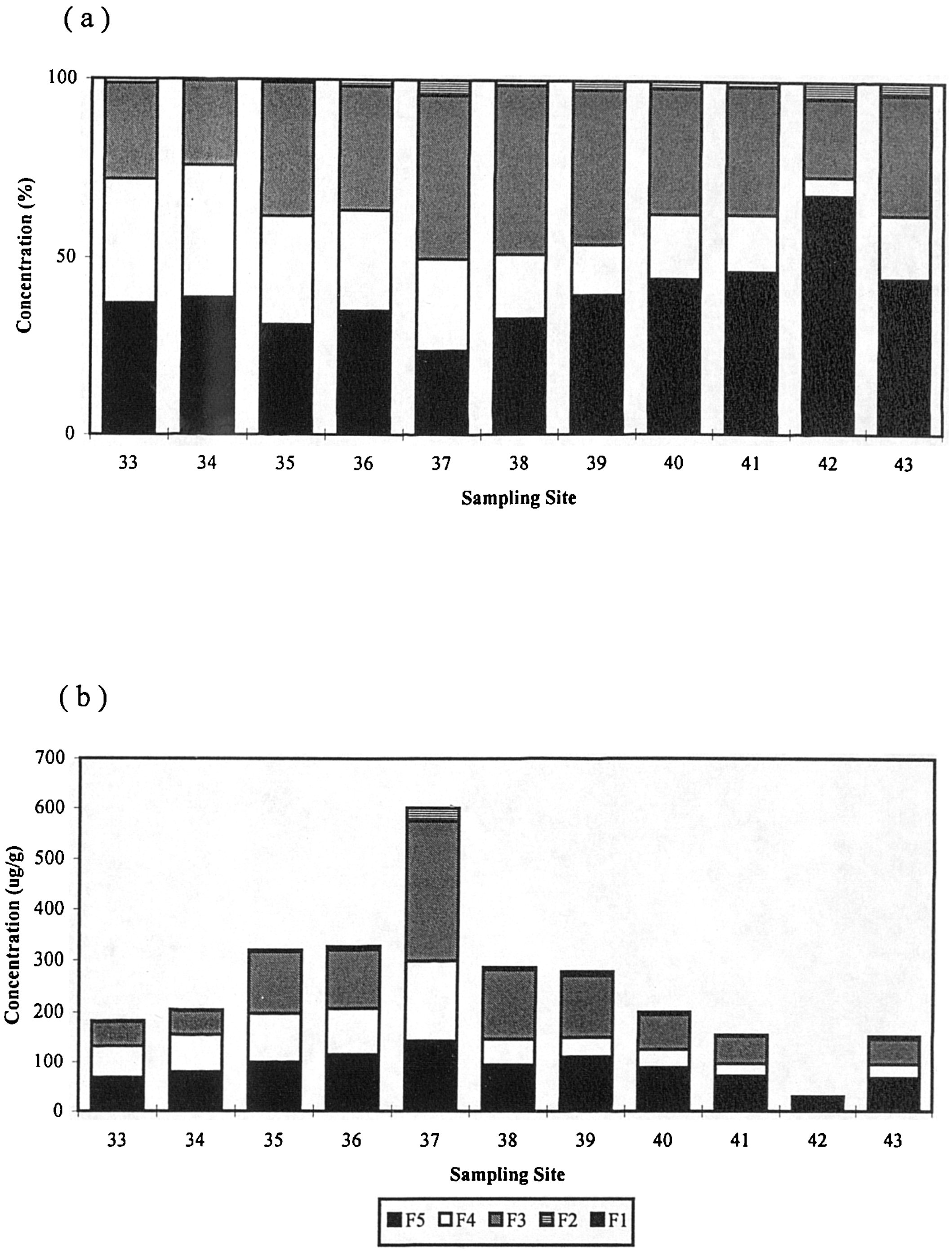


Figure 4.20 Percentage distribution (a) and absolute concentration (b) of Cr in the five geochemical phases in the surface sediments from the Tees Estuary. F1 - F5 as for Fig. 4.16.

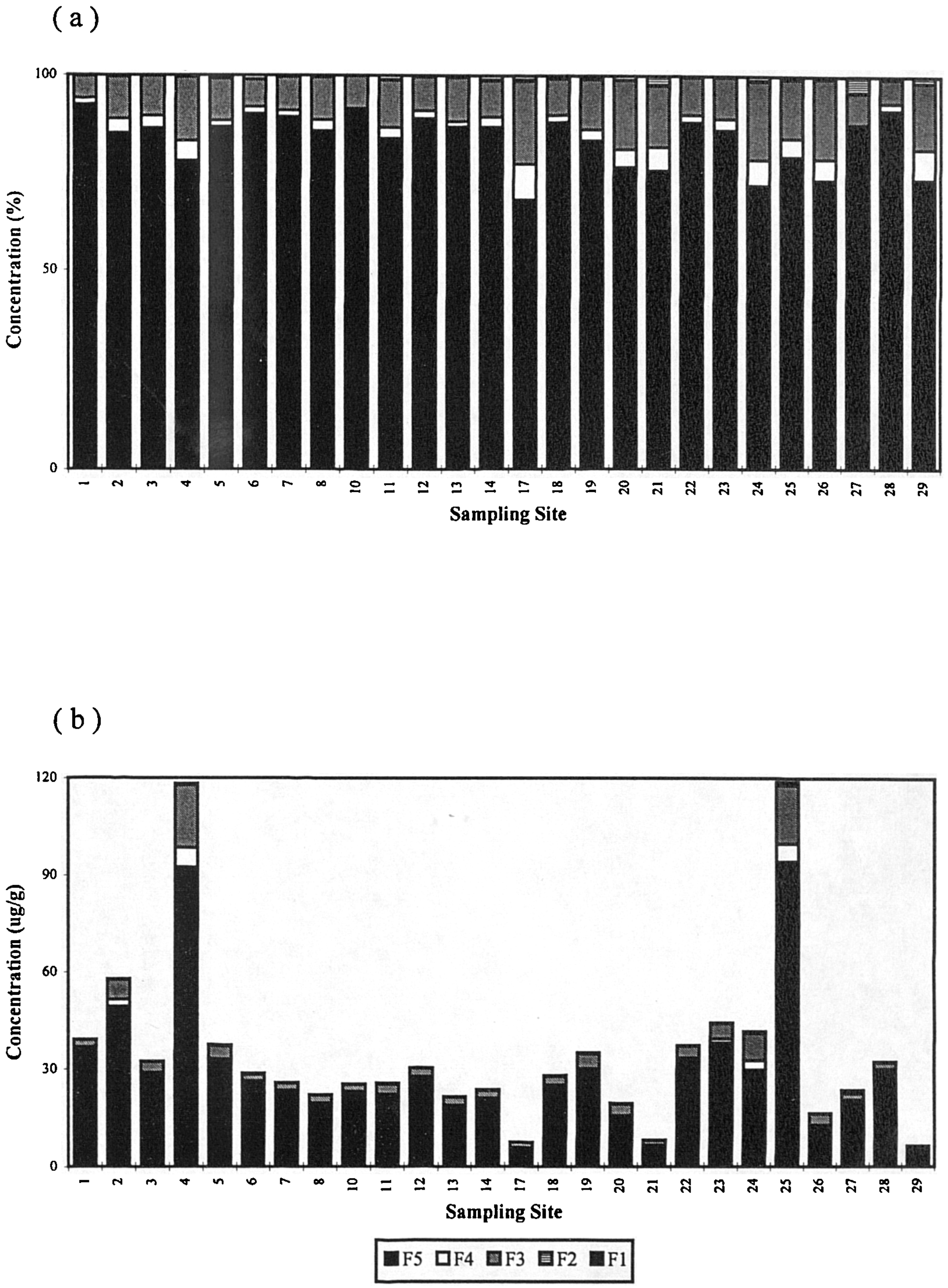


Figure 4.21 Percentage distribution (a) and absolute concentration (b) of Cr in the five geochemical phases in the surface sediments from Tees Bay. F1 - F5 as for Fig. 4.16.

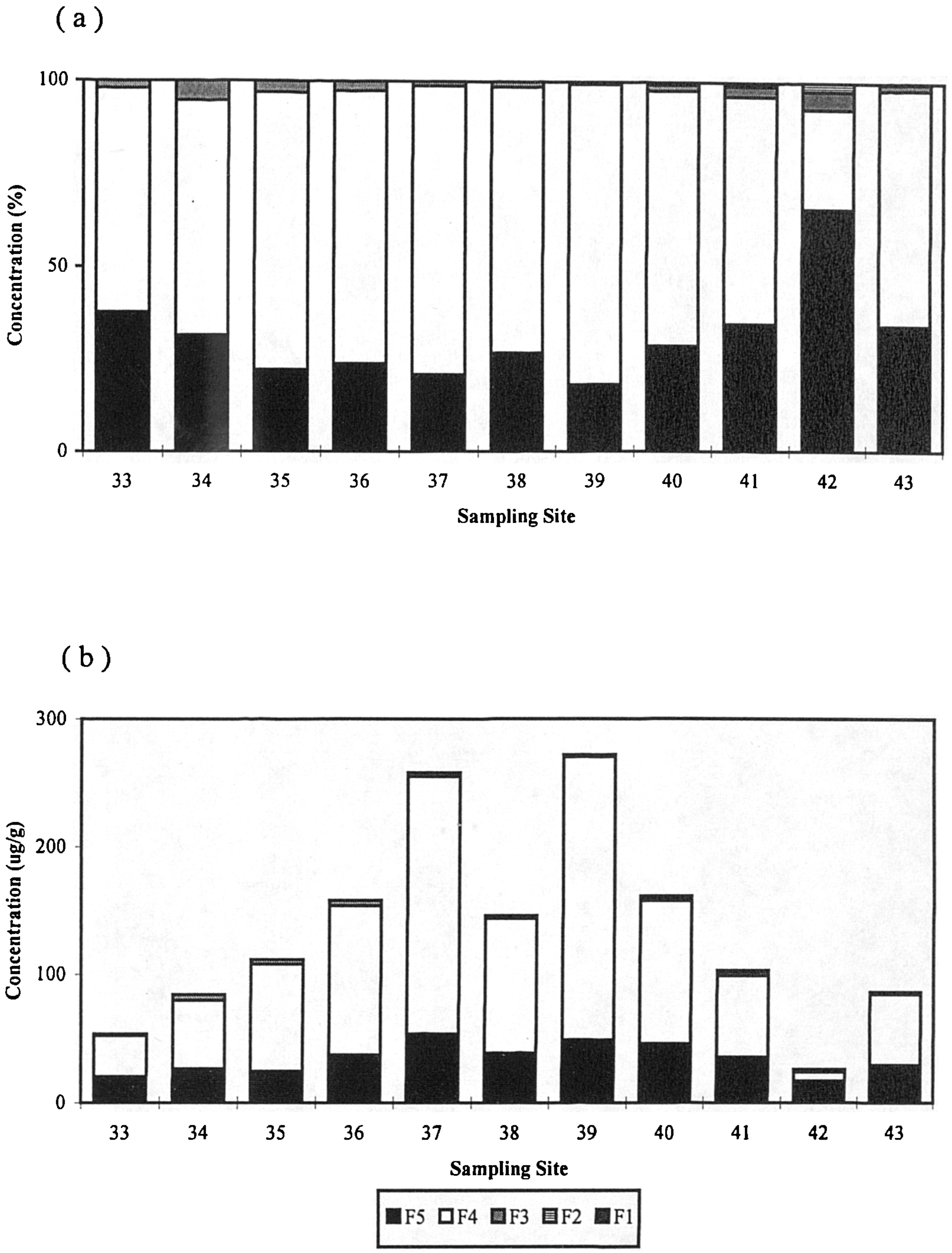


Figure 4.22 Percentage distribution (a) and absolute concentration (b) of Cu in the five geochemical phases in the surface sediments from the Tees Estuary. F1 - F5 as for Fig. 4.16.

Site 42, is different from the other estuarine samples (Fig. 4.22). It has much lower total Cu content and fraction 5 (65.6%) contributes substantially to the total. The enhanced importance of fraction 5 is accompanied by a corresponding decrease in the proportion of Cu associated with fraction 4 (27.0%).

With the exception of sites 4 and 25, Cu in sediments from all sites in Tees Bay are also dominated by fraction 5 (e.g. residual). Apart from the abundant levels of fraction 5 in these sediments, Cu is also associated in decreasing order with fractions 4, 3 followed by fraction 2 (Fig. 4.23). At sites 4 and 25, which are composed mainly of silt and clay, 98.4 and 98.6% of the total Cu are still partitioned between fraction 4 and 5, but, for these sediments, fraction 4 becomes the principal hosts.

4.3.5 Ni

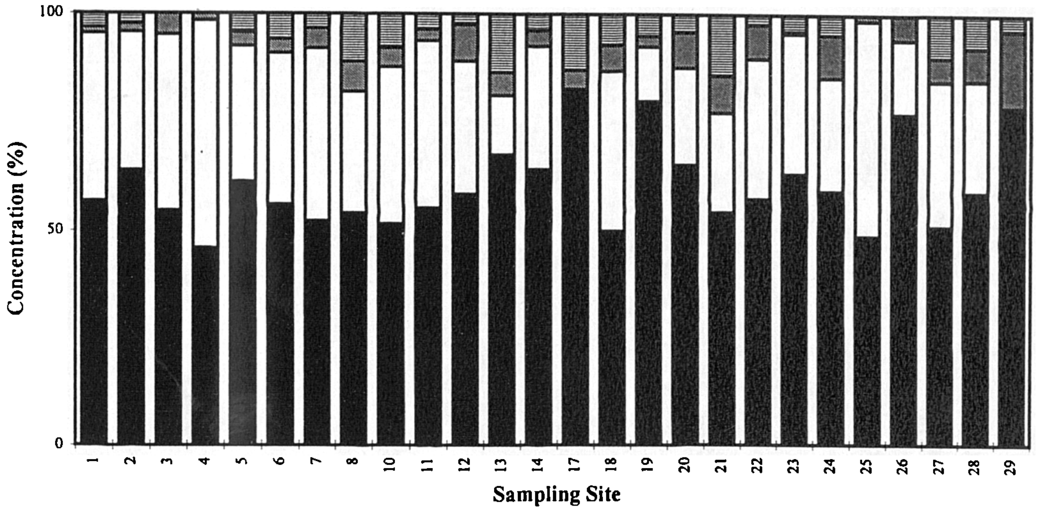
Of all the metals studied, the total nickel concentration in the Tees sediments is amongst the lowest and it does not show any significant variation. The partitioning of Ni (Figs. 4.24 and 4.25), in the surface layers of the sediment samples collected from both the Tees estuary and Bay regions, is characterized by the importance of Ni in fraction 5 (64.1-91.8%), and by the absence in fraction 1. Moderate contributions are afforded by fraction 3 (1.8-17.3%) and 4 (5.3-21.8%), whereas the contribution of fraction 2 is low (0.5-8.7%).

4.3.6 Pb

Pb, next to Zn, is the most abundant trace metal present in the study area. The various fractions of Pb are found at all sites in the surface sediments of the Tees estuary (Fig. 4.26). Pb in fraction 3, as with Zn, accounts for a very high proportion of the total (40.5-60.9%). The importance of fraction 5 is also similar to Zn (20.6-32.6 and 25.9-33.6% for Pb and Zn, respectively), but fraction 4 is less important for Pb (5.4-15.3%), when compared to Zn. Fraction 2 (3.1-20.5%) accounts for a low proportion of the total Pb, whilst Pb in fraction 1 is present at low but detectable levels in most samples (<0.1-0.7%), except for sites 34, 39 and 42.

The partitioning of Pb in the sites from Tees Bay (Fig. 4.27) suggests that a major portion of metal is held in fraction 3 (28.8-66.9%) with moderate amounts associated with fractions 2 (7.9-28.9%) and 5 (16.4-45.5%), except at sampling site 21

(a)



(b)

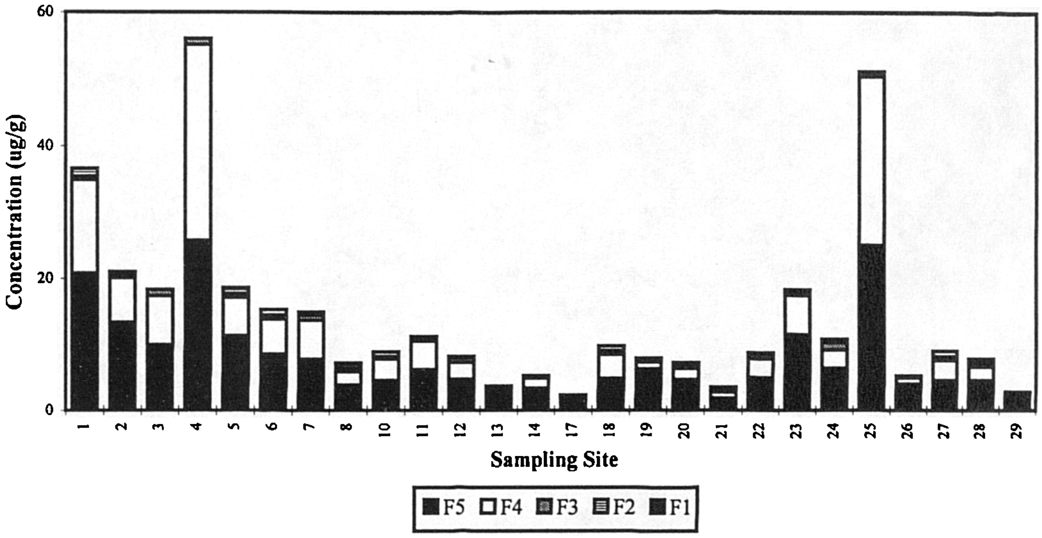


Figure 4.23 Percentage distribution (a) and absolute concentration (b) of Cu in the five geochemical phases in the surface sediments from Tees Bay. F1 - F5 as for Fig. 4.16.

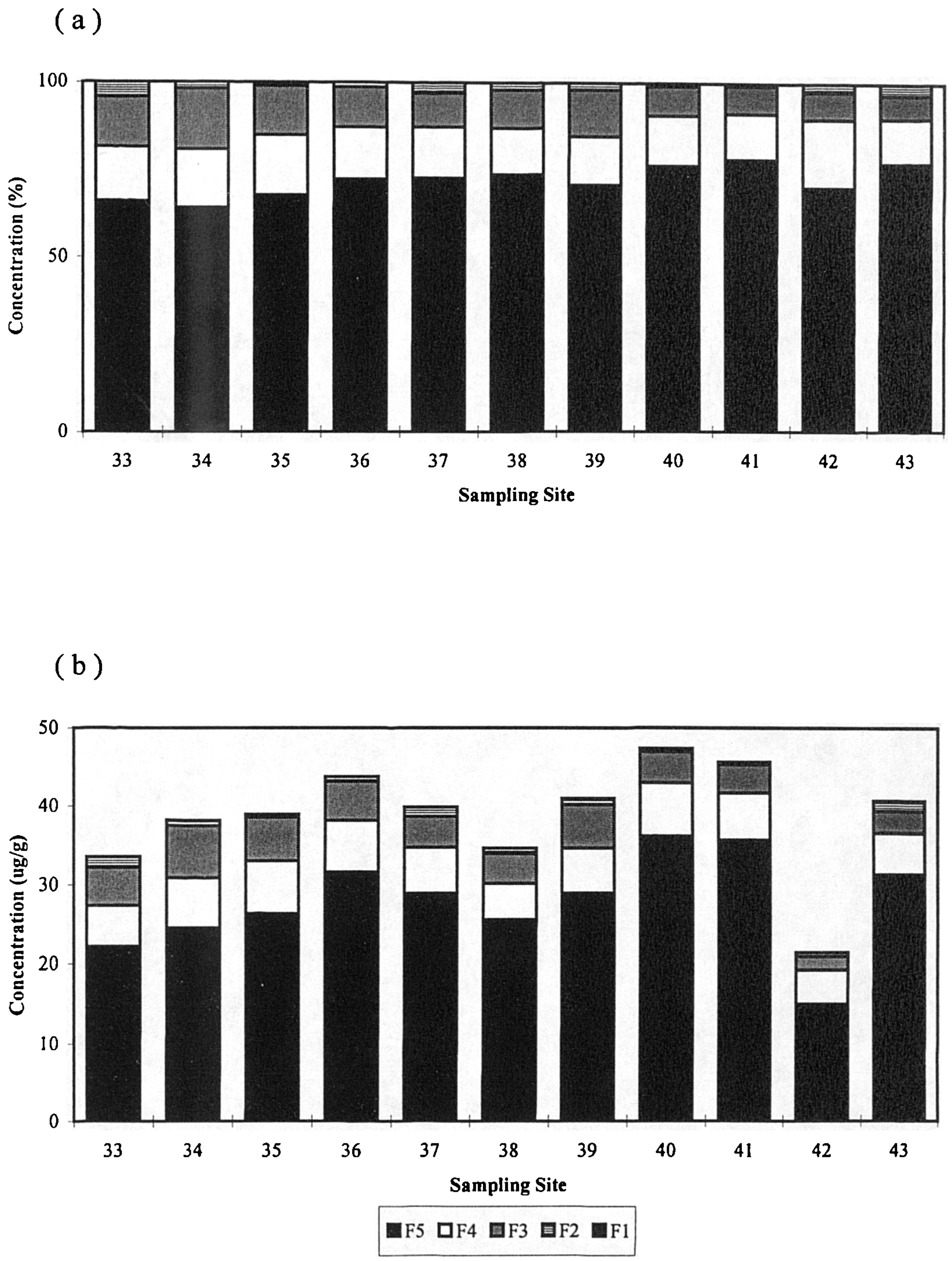


Figure 4.24 Percentage distribution (a) and absolute concentration (b) of Ni in the five geochemical phases in the surface sediments from the Tees Estuary. F1 - F5 as for Fig. 4.16.

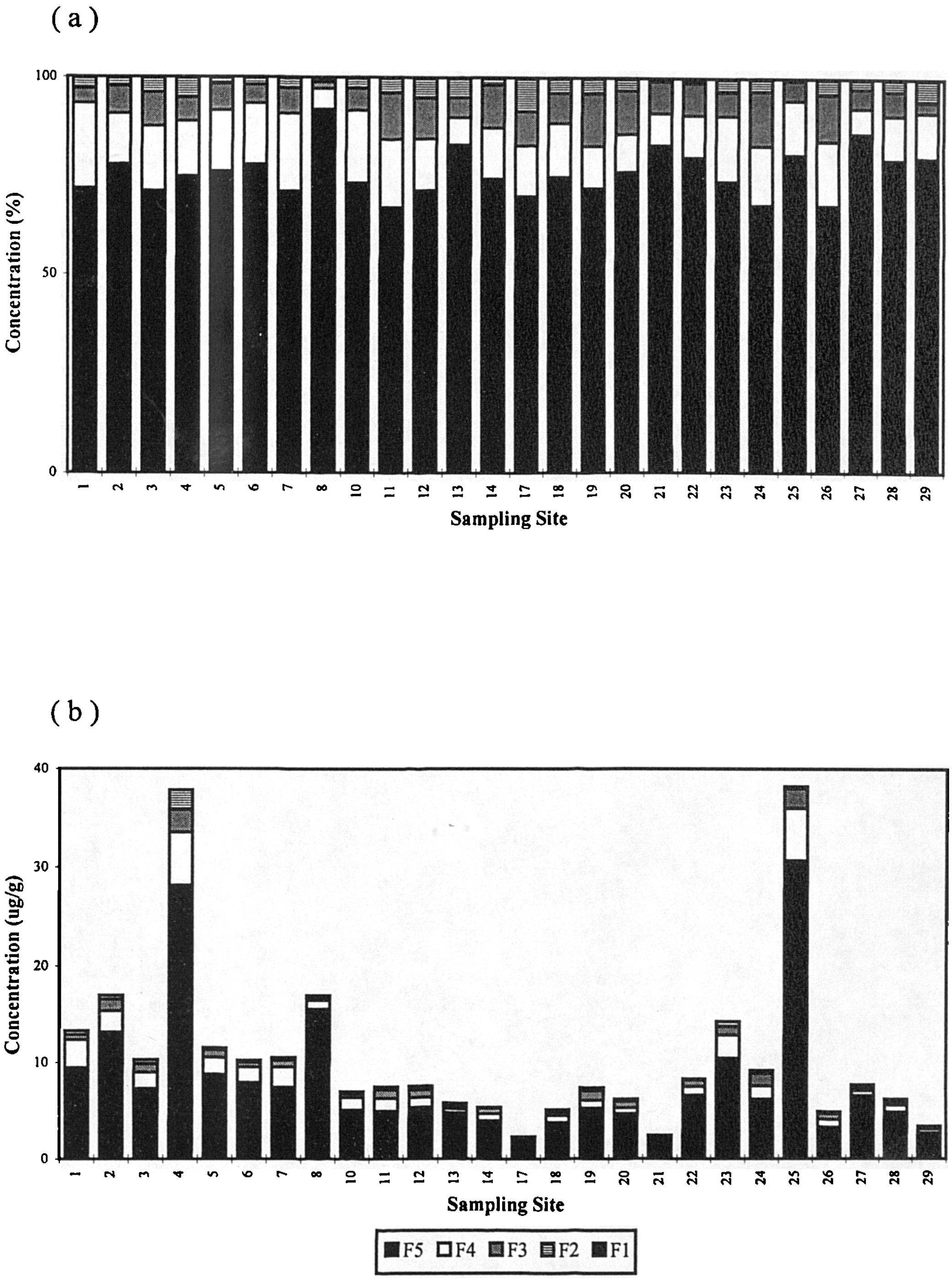


Figure 4.25 Percentage distribution (a) and absolute concentration (b) of Ni in the five geochemical phases in the surface sediments from Tees Bay. F1 - F5 as for Fig. 4.16.

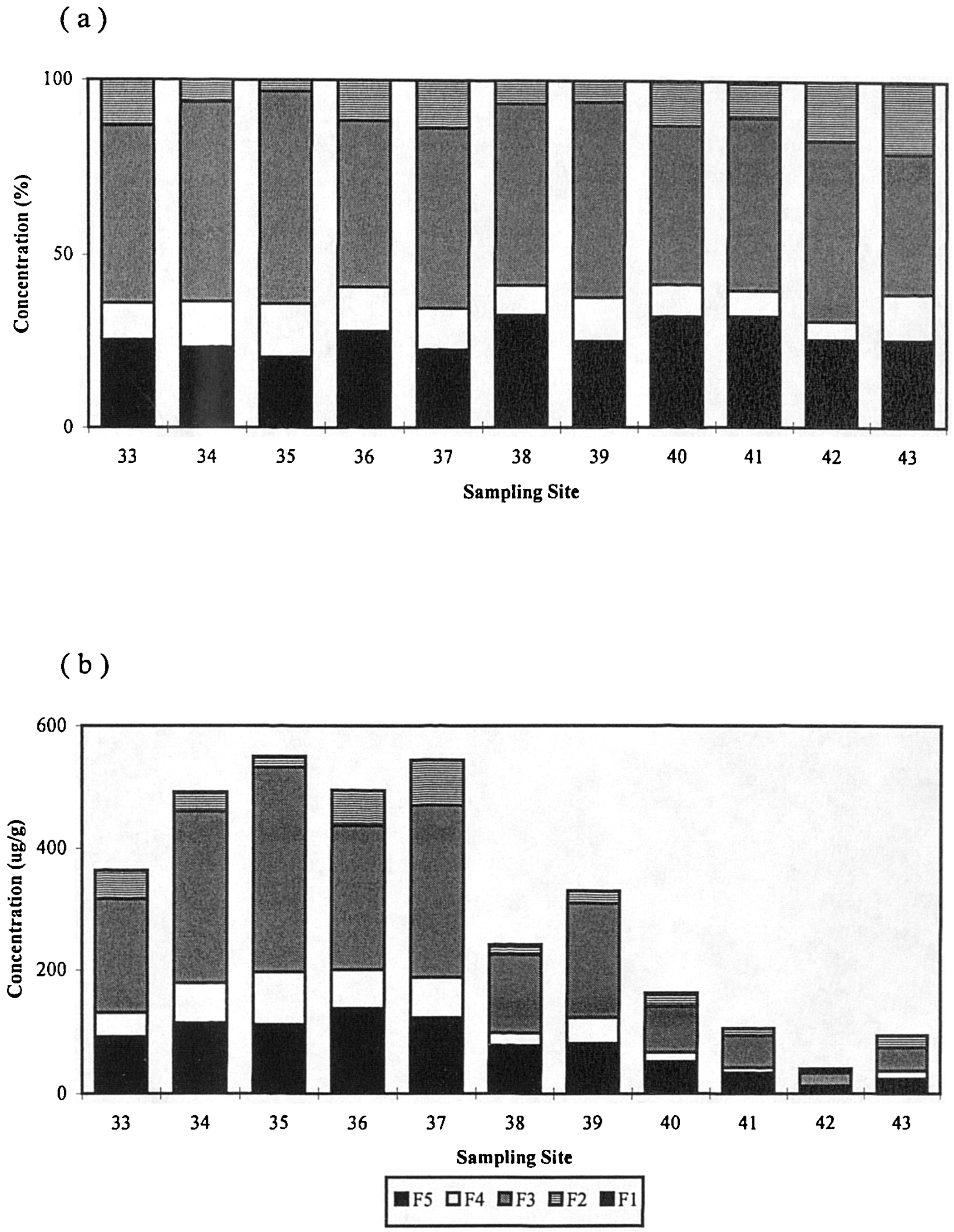


Figure 4.26 Percentage distribution (a) and absolute concentration (b) of Pb in the five geochemical phases in the surface sediments from the Tees Estuary. F1 - F5 as for Fig. 4.16.

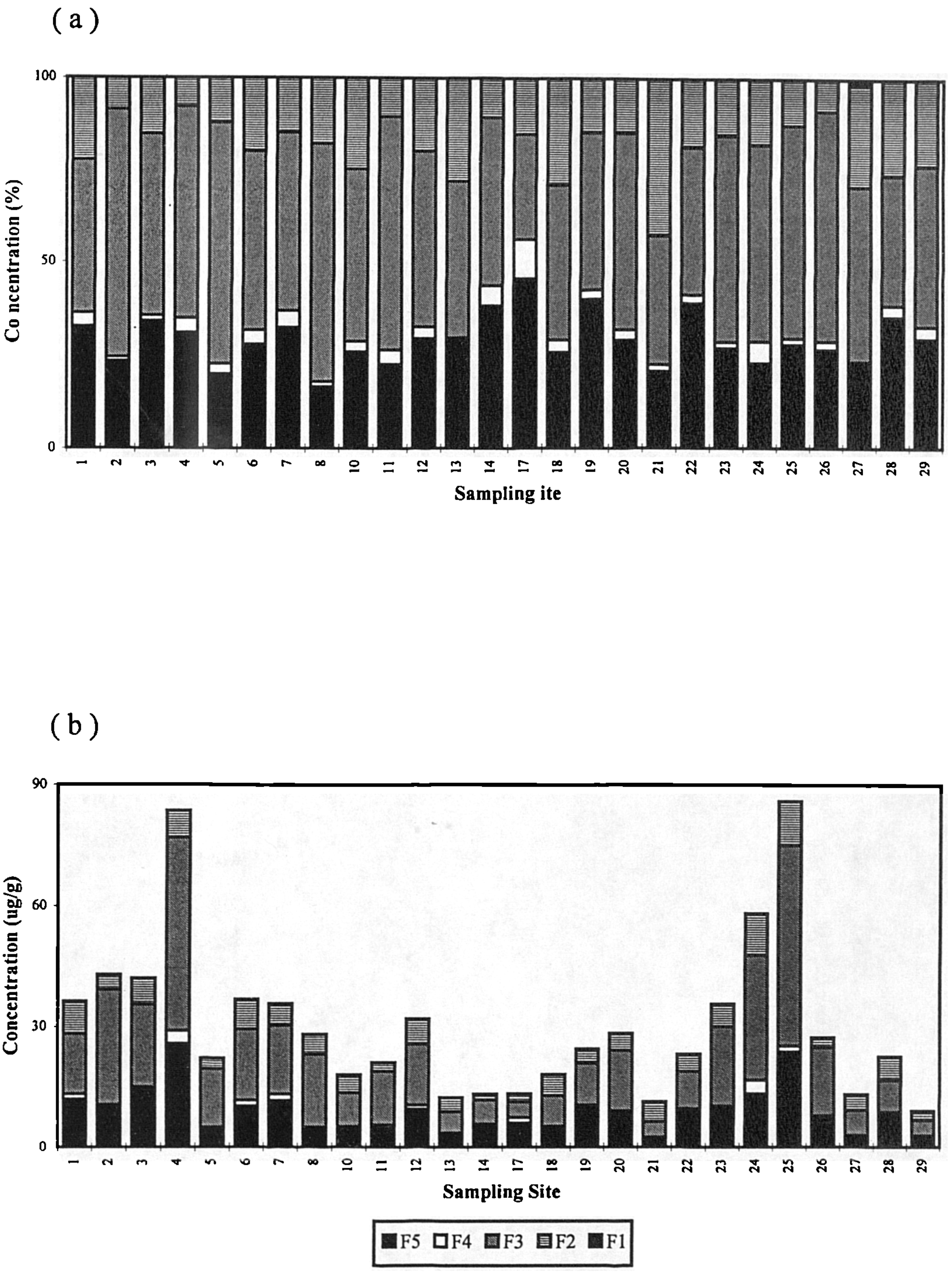


Figure 4.27 Percentage distribution (a) and absolute concentration (b) of Pb in the five geochemical phases in the surface sediments from Tees Bay. F1 - F5 as for Fig. 4.16.

in which the percentage held in fraction 2 (42.9%) is higher than fraction 3 (34.8%). At this site much less Pb is associated with fraction 4 and there is no detectable Pb in fraction 1.

4.3.7 Zn

Figures 4.28 and 4.29 illustrate the distribution (% and ug g^{-1}) of the different Zn fractions in the surface sediments from the Tees estuary and Tees Bay. For these sites in the estuary, with the exception of site 42, fraction 3 is the principal host phase for Zn (28.8-51.3%). Fractions 5 and 4 are the next most important fractions, containing approximately 25.9-33.6 and 16.0-32.0% of the total Zn, respectively. The proportions of the other fractions, fraction 1 and fraction 2 are low, containing <1% and 2.5-8.8% of the total Zn, respectively. At sites 42, which have the lowest Zn concentrations in the estuary, fraction 5 becomes of great relative importance (55.9%).

Samples collected from the sites in Tees Bay (sites 1 to 29; Fig. 4.29) continue the trend observed by site 42 (in the lower reaches of the estuary) in that fraction 5 hosts the bulk of the total Zn of the sediment (50.6-68.2%). Appreciable contributions of total Zn are noted for fractions 3 (16.4-38.5%), 2 (2.4-11.5%), and 4 (5.5-11.3%) fractions. This feature is accompanied by the absence of Zn associated with fraction 1.

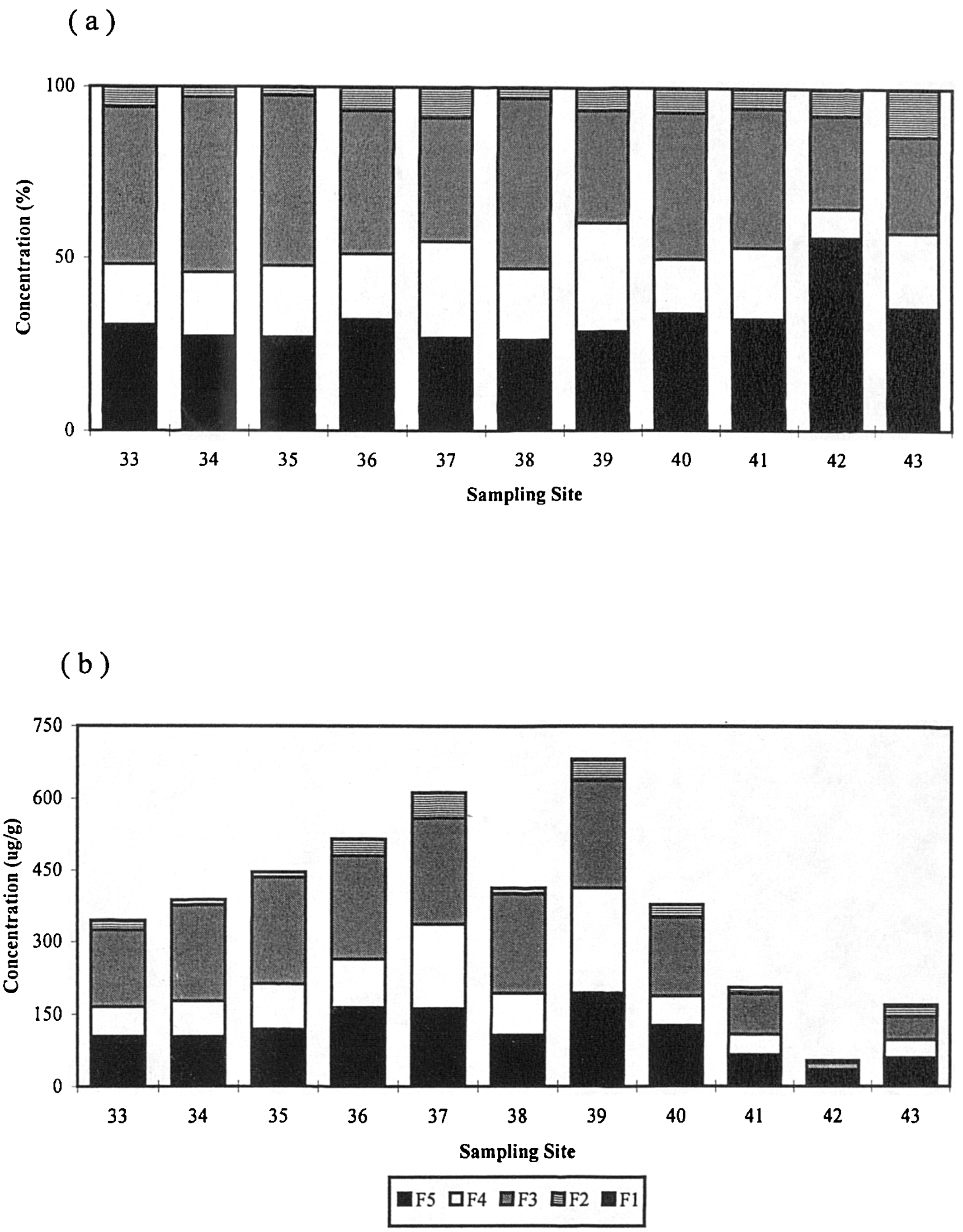


Figure 4.28 Percentage distribution (a) and absolute concentration (b) of Zn in the five geochemical phases in the surface sediments from the Tees Estuary. F1 - F5 as for Fig. 4.16.

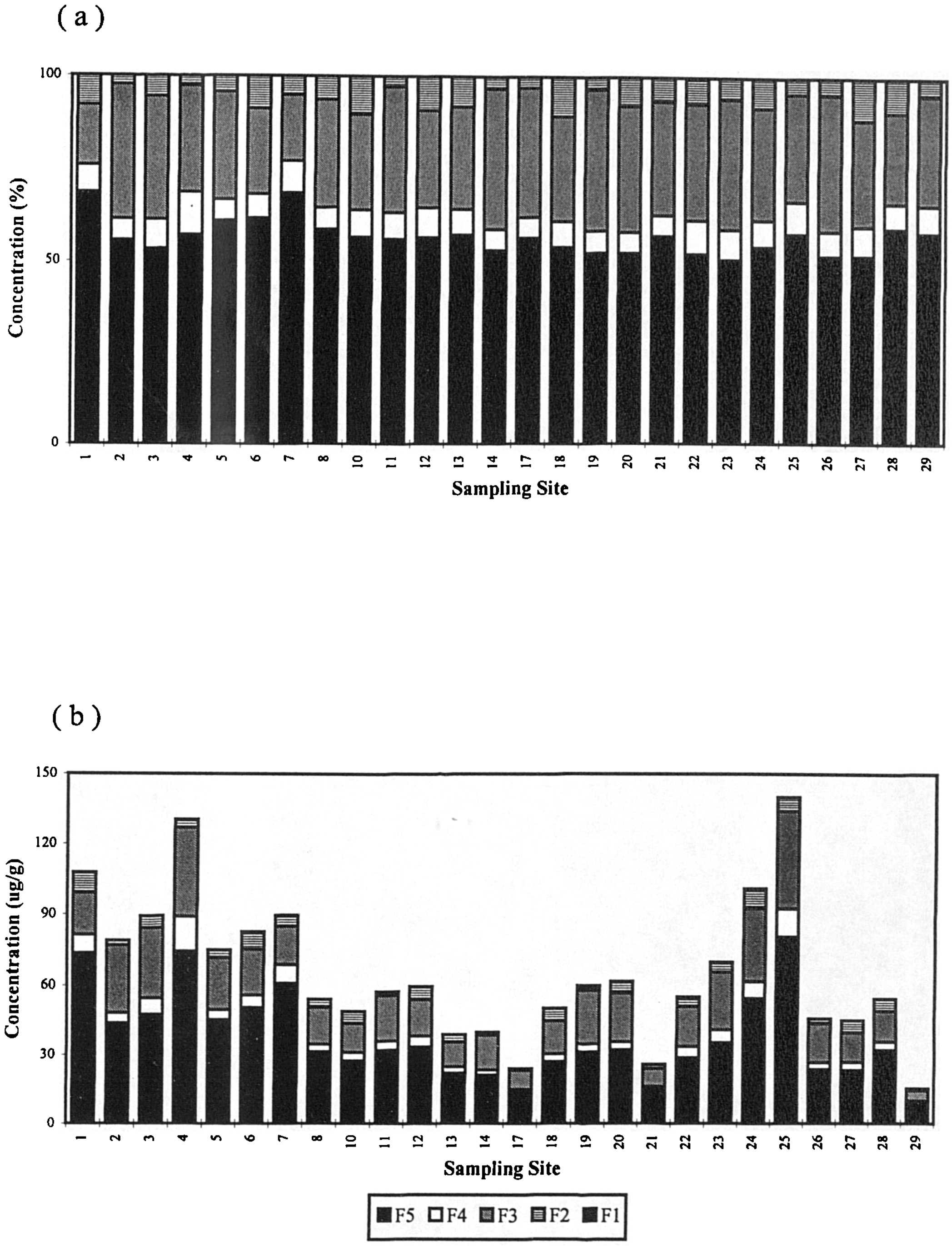


Figure 4.29 Percentage distribution (a) and absolute concentration (b) of Zn in the five geochemical phases in the surface sediments from Tees Bay. F1 - F5 as for Fig. 4.16.

4.4 Summary

Surface sediment samples were taken from 37 sites along the Tees Bay and the Tees estuary, and analysed for grain size, carbon content, total metal content, and metal partitioning.

The Tees estuary sediments are largely clay-silts, with coarser sediments found at sites 33, adjacent to Newport Bridge, 38, in the mid-estuary, ands 42 and 43, at the estuary mouth. All are organic rich, varying between 3.96% and 12.41%. Organic carbon is relatively constant above site 38, but shows a general trend of increasing concentration with increasing distance down-stream beyond this point. Concentrations of metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) are generally high, when compared with Tees Bay sediments, and mean average decrease in the order Zn > Pb > Cr > Cu > Ni > Co > Cd. Sediments at site 42 exhibit the lowest total metal contents, as a result of their sandy nature. The partitioning patterns of Cr, Pb and Zn, which are the three most abundant metals in the estuary, are similar, with fractions 3 (reducible), 5 (residual), and 4 (oxidizable) being of greatest significance. The distribution of Cd between the various sequential fractions show that fractions 5 and 3 contains a higher proportion of the element than do fractions 4 (oxidizable) and 2 (carbonate). However, Cd is also the only element for which fraction 1 (exchangeable) is significant. Cu is distributed uniquely with only fractions 5 and 4 found to be significant host phases. Of these, fraction 4 is dominant. Co and Ni, which are not highly enriched in these sediments, are hosted largely by fraction 5, although fraction 3 carries a significant proportion of Co, and the increase of Co at site 39 and beyond is due largely to an increasing concentration in this fraction.

The distributions of grain size, organic carbon contents and the metals in the surface sediments from Tees Bay are illustrated in contour maps. These maps show that the sediments are largely organic-poor, and generally coarser, with organic-rich clayey silts sediments found at sites 4 and 25 (the most seaward sites at the northern and southern ends of the Bay, respectively). The metal concentrations are distributed in a similar manner. The highest metal concentrations are found at the sites which have clayey-silts with high organic carbon contents and the lowest concentrations are observed at the sites which have a high sand with low organic carbon contents. Both of these trends are statistically significant (see Table 5.14; Chapter 5). In Tees Bay sediments, the partitioning patterns of Cd, Co, Ni and Pb are similar to those found in the Tees estuary. Cr and Zn are still partitioned between fractions 3, 5 and 4, but fraction 5 becomes the principle host. The distribution of Cu which is not highly enriched in these sediments, is dominated by fraction 5 followed by fraction 4.

Chapter Five

Sediment Composition and Trace Metal Geochemistry

5.0 Sediment Composition and Trace Metal Geochemistry

5.1 Sediment composition

5.1.1 Grain size distribution

The grain size distributions for the sediments collected from Tees Bay are illustrated in Figure 4.2 (see Chapter 4). With the exception of sites 4 and 25 the sediments are dominated by sand grade particles (median sand content of 92%), and fall largely into the sand field of Shepard (1954). Silt (2-63 µm) and clay (<2 µm) grade particles have mean concentrations of only 10.4% and 4.5%, respectively, but reach 59% and 17%, respectively, at site 4, and 59 and 25% at site 25 (Fig 4.2) where the sediments are classified as clayey-silts. The generally low silt + clay contents observed in Tees Bay, are consistent with the earlier observations of Taylor (1979). This author noted low silt + clay contents at North Hartlepool, Longscar, Teesmouth, Redcar and Saltburn, locations which are close to stations 1, 10, 13, 23 and 26, respectively, of this study. Finer sediments such as the clayey-silts occurring at sites 4 and 25 were not reported however.

For the Tees estuary, the surface sediments at all sites except site 42 are dominated by silt and clay grade particles (Fig. 4.3) and fall largely into the clayey-silt field of Shepard (1954). Shillabeer and Tapp (1990) have previously reported silt + clay contents of >95% for much of the estuary, approximately 20% higher than the present data suggest. This difference may result from the different techniques employed; Shillabeer and Tapp (1990) having employed dry sieving. Sand grade particles have a mean concentration of 20.3%, but reach 69% in the sandy-silt at site 42, near the mouth of the estuary. Coarser sediments, classified as silty-sands were also found at site 33, near Newport Bridge, and at site 38, in the middle of the estuary, whereas those classified as sand-silt-clay were found at site 43, adjacent to the North Gare Sands, at the mouth of the estuary. The relatively high sand content (27%) measured at site 33 is consistent with the tendency for grain size to increase near the Portrack sewage works reported by Shillabeer and Tapp (1990), but the coarser sediments occurring at sites 38 and 43 were not noted by these authors.

5.1.2 Organic carbon

The organic carbon contents of the Tees Bay sediments ranged between 0.22% at site 29 and 8% at site 4, with a median of 0.63% (Table 4.3). The highest organic carbon contents were found at sites 4 and 25 which are composed mainly of clayey-silt particles, and the higher organic carbon contents at these two sites are probably a result of their finer grain size. With the exception of sites 1, 2, 5, 6, 7 and 8, the lowest organic carbon contents (<1.0%) are observed at the sites which have a high sand content. The relatively high total organic carbon contents measured in the sandy sediments at sites 1, 2, 5, 6, 7 and 8 are probably due to the presence of coal fragments in these sediments, as discussed in Chapter 6.

The Tees estuary sediments are all organic-rich, varying between 3.96% organic carbon at site 33 and 12.41% at site 42, with a median of 5.36%. Organic carbon is relatively constant between sites 33 and 38, but shows a general trend of increasing concentration with increasing distance downstream beyond this point (Fig. 5.1). The sandy sediment at site 42 is particularly enriched in organic carbon, especially when its sandy nature is considered. At this site the organic matter is possibly in the form of coal particles with similar hydrodynamic properties to sand grains. Davies *et al.* (1991) measured the volatile solid content by ignition at 450°C as an indication of the organic carbon content. They observed no trends in this parameter along the estuary, although their data showed considerable scatter.

5.2 Total trace element geochemistry

5.2.1 Comparison with previous studies of Tees Bay and the Tees Estuary

Comparing trace element data from different studies can be problematic because of the lack of uniformity in the sampling methods, sample digestion procedures and analytical techniques used in the different studies being compared. Nevertheless, some comparisons have been made below to put the data collected in this study into context, on both a local and global scale. The raw unnormalized data are used in the following discussion to ensure consistency with the other studies under consideration.

For the Tees Bay sediments, differences in concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn between 1979 and 1991 can be investigated by comparing the data from

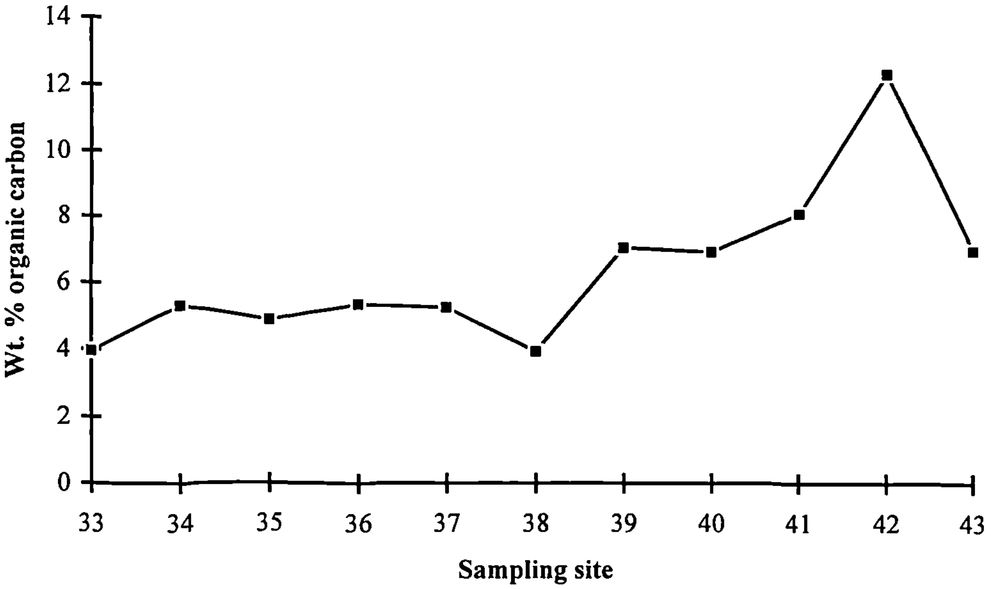


Figure 5.1 Organic carbon contents (%TOC) in the Tees Estuary. The maximum TOC occurs in the sandy sediments of site 42.

this study with an earlier study published by Taylor (1979). Five of the locations sampled by Taylor (1979) are located in the area covered by this study, with his stations North Hartlepool, Longscar, Teesmouth, Redcar and Saltburn corresponding to my locations 1, 10, 13, 23 and 26, respectively.

Metal concentrations at individual stations in 1979 and 1991 are compared in Table 5.1. For Cd, Co, and Cr, the data from this study are significantly different (at the 95% confidence level) to the concentrations reported by Taylor (1979). In contrast, concentrations of Cu, Ni, Pb and Zn, found in this study, are not significantly different (at the 95% confidence level) to those reported by Taylor (1979). For Co and Cr, the discrepancy between our values and the previous work probably arises as a result of the different digestion methods used. Aqua regia (HNO_3/HCl = 3:1) digestion, as used by Taylor (1979) for the release of metals from Tees Bay sediments, has a low extraction efficiency, releasing approximately 65% of the total Co and Cr present (Brugmann, 1995), whereas digestion using mixtures of $HF/HNO_3/HClO_4$, as used in this study, have been shown to be much more effective than aqua regia for the release of Cr and other metals from marine sediment matrices (Loring and Rantala, 1988). For Cd, the aqua regia digestion has a high extraction efficiency, releasing approximately 100% of the total Cd (Brugmann, 1995), suggesting that the Cd concentrations observed in this study are generally higher than those reported by Taylor (1979).

Table 5.1 Comparison of metals determined in this study (stations 1, 10, 13, 23 and 26) with those for adjacent sites published by Taylor (1979).(N.B. data of Taylor (1979) are mean averages of 8 samples except for Longscar and Redcar where *n* = 7 and 9, respectively).

Sample Location	**Metal Concentrations ug g^{-1}**						
	Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
N. Hartlepool	0.2	5.9	7.3	7.5	11.4	48	66.7
1	3.2	16.9	44.1	31.3	13.8	39.1	110.3
Longscar	0.2	6.6	7.9	9.7	9.0	35.9	57.7
10	2.6	11.5	29.3	9.5	7.9	20.3	59.7
Teesmouth	0.2	5.6	6.9	3.9	7.4	42.0	53.3
13	3.1	10.1	25.4	4.0	6.8	12.4	43.9
Redcar	0.2	4.7	7.5	5.7	7.6	28.6	51.6
23	3.8	16.3	41.3	18.7	15.1	40.8	68.6
Saltburn	0.2	5.0	8.9	5.4	7.2	32.6	49.4
26	2.0	14.6	17.2	5.3	5.2	17.8	48.9

A review of previous trace metal concentration data for the Tees estuary, that of Murray and Norton (1979) and Delo and Burt (1988), has been published, along with new data by Davies *et al.* (1991). These authors studied the extent of metal contamination in the Tees estuary and commented on changes in metal concentrations through time. They found that parts of the Tees estuary are moderately to strongly polluted in terms of total metal concentrations. They also found that concentrations of Cr, Cu and Zn in the Tees estuary had decreased significantly over the time period studied (1979-1991), and that Cd, Ni and Pb concentrations had shown a slight decline. When the data of this study are added to those presented by Davies *et al.* (1991) (Table 5.2) the decreases in Cu and Zn through time are confirmed, as is the possible lowering of Pb concentration. Data for Cd, Cr and Ni are less abundant, but the mean Cr concentration determined in this study is much lower than that of Murray and Norton (1979), although higher than that reported by Davies *et al.* (1991). As discussed above this increase probably reflects different digestion procedures. For Cd and Ni, the concentrations determined in this study are closer to those of Murray and Norton (1979) than those of Davies *et al.* (1991), although in the case of Ni differences in digestion procedures may also play a role here too.

Table 5.2 Previous investigations of heavy metals in sediments from the River Tees (after Davies *et al.*, 1991), and other north-east streams.

Sample Location	**Mean Metal Concentrations ug g^{-1}**							**Reference**
	Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	
R. Tees	3.6	-	493	234	40	325	766	Murray and Norton, (1979)
Dredged sediments in R. Tees 1981	-	-	-	205	-	379	688	Delo and Burt (1988)
Bed sediments in R. Tees 1986	-	-	-	187	-	260	486	Delo and Burt (1988)
Mid Channel sediments in R. Tees 1991	1.8	-	80.7	120	26.1	249	473	Davies *et al.* (1991)
Stream sediment from north-east England	1.3	26	148	24	51	276	381	British Geological Survey (in press)
Tees Estuary	6.1	35.8	251.6	123.2	40.2	322.6	407.5	This study

Trace element concentrations determined in this study have also been compared with metal concentrations in stream sediments from north-east England (British Geological Survey, in Press; Table 5.2). The concentrations of Cd, Co, Cr and

Cu found in the present study are significantly higher (at the 95% confidence level) than those of the stream sediments whereas measured Ni, Pb and Zn concentrations are not significantly different to those of north-east stream sediments. It should be noted that the stream sediment data represent the <150 μm fraction of the sediment, and are thus not strictly comparable with the bulk sediment analyses used in the present study, although as the major portion of the sediment taken from the Tees estuary sites is finer than 150 μm, discrepancies should be small.

5.2.2 Comparison with studies of other estuarine and coastal marine areas

A comparison of the mean values of the measured metals in Tees Bay with those obtained from other coastal marine areas around the world is shown in Table 5.3. These data allow the metal concentrations observed in Tees Bay to be put into a global context. The data are discussed on an element by element basis below.

Cd: The Tees Bay sediments contain concentrations of Cd (2.9 ug g^{-1}) which are an order of magnitude greater than those of sediments from unpolluted (e.g. the north-western coast of the Arabian Gulf, 0.3 ug g^{-1}) or relatively unurbanized or unindustrialized areas (e.g. the southern Californian coastal baseline, 0.3 ug g^{-1}). Sediments from the highly industrialized Belledune Harbour in Canada however contain much higher Cd concentrations (43.6 ug g^{-1}) than those measured in Tees Bay. The contents of Cd in Tees Bay sediments are comparable to those found off other industrialized or urbanized areas such as those of the south east coast of India and Tokyo Bay (2.4 and 1 ug g^{-1}, respectively).

Co: The mean Co concentration in Tees Bay sediment (14.9 ug g^{-1}) is lower than the 22 ug g^{-1} reported for the slightly polluted sediments from the Baltic Sea, but higher than those of the pristine Grand Desert Beach, Canada (4.3 ug g^{-1}) or the unpolluted north-western coast of the Arabian Gulf (2 ug g^{-1}). Sediments from the highly industrialized Belledune Harbour in Canada, which are not heavily polluted by Co, contain comparable Co concentrations (12.3 ug g^{-1}) to those measured in Tees Bay.

Cr: The Cr contents found in Tees Bay sediments (38.9 ug g^{-1}) are higher than those found in the pristine sediments of Grand Desert Beach (10.2 ug g^{-1}), but lower than those of polluted sediments from industrialized or urbanized areas such as south

Table 5.3 Average concentrations (ug g^{-1}) of trace metals in Tees Bay compared with those found in some nearshore and open sea sediments, reported in the literature.

Location	Cd	Co	Cu	Cr	Ni	Pb	Zn	Ref.	comment
Grand Desert Beach, Canada	0.2	4.3	8.7	10.2	7.5	5.4	41.5	1	a control sediment from a non-industrialized area
Southern Californian coastal baseline	0.3	-	8.3	22.0	9.7	6.1	43.0	2	unpolluted
North-western coast of Arabian Gulf	0.3	2.0	2.6	-	10.1	3.6	13.7	3	unpolluted
Baltic Sea	-	22.0	78.0	-	43.0	25.0	110.0	4	slightly polluted by Co, Cu, Pb and Zn
Wadden Sea	0.5	-	22.0	84.0	37.0	37.0	103.0	5	slightly polluted by Cd, Pb and Zn
Mid-Coast Maine, USA	0.4	-	20.3	34.9	19.9	21.7	66.8	6	slightly polluted by Cd and Pb
Sydney shelf, Australia	-	-	48.0	-	53.0	38.0	115	7	slightly polluted by Pb and Zn
Southern Atlantic coast of Spain	9.0	-	221.0	67.0	46.0	116.0	1000.0	8	polluted by Cd, Cu, Pb and Zn
Dalhousie Harbour, Canada	1.0	8.7	17.7	24.6	23.4	29.3	519.5	1	polluted by Cd, Pb and Zn
South east coast of India	2.4	-	17.0	138.0		53 .0	62.0	9	polluted by Cd, Cr and Pb
Tokyo Bay, Japan	1.0	-	49.7	71.1	30.5	47.0	275.7	10	polluted by Cd, Pb and Zn
Belledune Harbour, Canada	43.6	12.3	269	41.6	22.5	1638	6285.5	1	highly polluted by Cd, Pb and Zn
Tees Bay	2.9	14.9	14.8	38.9	11.8	32.6	69.9	11	

References:

1- Samant *et al.* (1990).
2- Word and Mearns (1979).
3- Al-Hashimi and Salam (1985).
4- Manheim (1961).
5- Laane (1992).
7- Larsen and Gaudette (1995).
7- Birch and Davey (1995).
9- Izquierdo *et al.* (1997).
9- Subramanian and Mohanachandran (1990).
10- Fukushima *et al.* (1992).
11- This study.

east coast of India (138 ug g^{-1}). Concentrations of Cr found in the present study are comparable to those found in the highly industrialized (Belledune Harbour, Canada; 41.6 ug g^{-1}) or slightly polluted (Mid-Coast Maine; 34.9 ug g^{-1}) areas, which are not specifically polluted by Cr.

Cu: The mean Cu concentration of 14.8 ug g^{-1} reported for the sediments of Tees Bay is lower than those reported for polluted sediments from the southern Atlantic coast of Spain Canada (221 ug g^{-1}) and Belledune Harbour in Canada (269 ug g^{-1}). Sediments from slightly polluted areas (e.g. the Baltic Sea) also contain higher Cu concentrations (78 ug g^{-1}) than those measured in Tees Bay. The contents of Cu in Tees Bay sediments are higher than those found in the pristine sediments of Grand Desert Beach (8.7 ug g^{-1}), but are comparable to those found in unpolluted sediment, such as those of Dalhousie Harbour (17.7 ug g^{-1}) and the south east coast of India (17 ug g^{-1}).

Ni: The levels of Ni found in the sediments of Tees Bay (11.8 ug g^{-1}) are slightly higher than those found in the pristine sediments of Grand Desert Beach (7.5 ug g^{-1}), but are comparable to those reported for unpolluted sediments, such as the southern Californian coastal baseline and north-western coast of the Arabian Gulf (9.7 and 10.1 ug g^{-1}, respectively).

Pb: The Pb concentration in the sediments from Tees Bay (32.6 ug g^{-1}) is comparable to those found in the slightly polluted sediments of the Baltic and Wadden Seas (25 and 37 ug g^{-1}, respectively), and to those concentrations found in sediments of industrialized or urbanized areas, such as the Sydney shelf, Tokyo Bay and the south east coast of India (38, 47 and 53 ug g^{-1}, respectively). Concentrations of Pb found in the present study are higher than those of the pristine Grand Desert Beach (5.4 ug g^{-1}) or unpolluted north-western coast of the Arabian Gulf (3.6 ug g^{-1}), but well below those found in the heavily polluted sediments of Belledune Harbour, Canada (1638 ug g^{-1}).

Zn: The Tees Bay sediments contain concentrations of Zn (69.9 ug g^{-1}) which are two orders of magnitude lower than those found in the highly polluted sediments of Belledune Harbour, Canada (6285.5 ug g^{-1}), and are lower than those concentrations found in the sediments of industrialized or urbanized areas, such as the southern Atlantic coast of Spain, Dalhousie Harbour and Tokyo Bay (1000, 519.5 and

275.7 ug g^{-1}, respectively). The Zn contents found in Tees Bay sediments are also lower than those found in the slightly polluted sediments of Baltic and Wadden Seas, but comparable to those found in unpolluted sediments from Mid-Coast Maine and the south east coast of India (66.8 and 62, respectively). Sediments from the non-industrialized Grand Desert Beach in Canada contains lower Zn concentrations (41.5 ug g^{-1}) than those measured in Tees Bay.

In summary, comparison of the total metal concentrations measured in Tees Bay with data from similar environments around the world suggests that mean levels of Cd and Pb are similar in magnitude to those of polluted areas, while Co, Cr,Cu, Ni and Zn concentrations are generally similar to those of unpolluted areas.

For the Tees estuary, Table 5.4 summarizes the mean metal concentrations observed here and those from other polluted and unpolluted rivers and estuaries reported by Davies *et al.* (1991). The rivers and estuaries compared were polluted and unpolluted stretches of the Rhine (Germany), the Weser Estuary (Germany) and the Huanghe Estuary (China). As can be seen from Table 5.4, with the exception of Ni for which concentration in the Tees estuary are low, the mean metal concentrations determined in this study, are similar to the concentrations found in moderately to strongly polluted European estuaries.

Metal concentrations found in the Tees estuary have also been compared (Table 5.5) to those of 19 other UK estuarine sediments, reported by Bryan and Langston (1992). The mean Cd concentration of 6.13 ug g^{-1} found in the Tees estuary (this study) is considerably higher than the mean of 2.17 ug g^{-1} reported for sediments of the Tyne estuary by Bryan and Langston (1992); the Tyne having the highest Cd concentrations reported for estuaries by these authors. The mean Co and Cr concentrations (35 and 251 ug g^{-1}, respectively) of the Tees estuary are also higher than those of any other UK estuaries for which there is published data, by a considerable margin in the case of Cr, although differences in digestion procedure efficiencies probably play a role in this. The mean concentrations of Cu, Ni, Pb and Zn (123.2, 40.2, 323.6 and 407.5 ug g^{-1}, respectively) in sediments from the Tees estuary are within the upper range of values observed for UK estuarine sediments, and are comparable with metal concentrations in sediments from the Tyne, Restronguet Creek, Gannel and the Tamar estuaries. It is apparent, therefore, that on the basis of

Table 5.4 Concentrations of metals reported from unpolluted river systems and well known polluted areas (after Davies *et al.*, 1991).

	Metal Concentrations ug g^{-1}								
Sample Location	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Ref.**	**Comments**
Haunghe Estuary		21.6	63.7	22	46.5	21.6	71.3	1	Concentrations are relatively lower than most world estuaries.
Weser Estuary	2.4		62	42	58	154	393	2	Average contents in sediments of dredging materials.
	2.71		34.7	23.4	24.6	63.7	272	2	Dredge materials.
Rhine River	4	19	121	86	152	155	520	3	Moderately polluted stretch.
Lower Rhine River	9		338	202		118	921	4	
Rhine River	28	35	397	397	167	333	1096	5	Strongly polluted stretch.
Tees Estuary	6.1	35.7	251.5	123.2	40.2	323.6	407.5	6	

Reference:-
1- Zhang *et al.* (1988).
2- Calmano *et al.* (1982).
3- Banet *et al.* 1972 (in Forstner and Wittmann, 1981).
4- Calmano & Schumann (in Forstner, 1983).
5- Patchneelam, 1975 (in Forstner and Wittmann, 1981).
6- This study.

Table 5.5 Average concentrations of metals (ug g^{-1}, dry weight) in sediments from 19 UK estuaries (reported in Bryan and Langston, 1992) and the Tees estuary (reported in this study).

Sample No	Cd	Co	Cr	Cu	Ni	Pb	Zn
Restronguet Creek	1.53	21	32	2398	58	341	2821
Fal	0.78	9	28	648	23	150	750
Tamar	0.96	21	47	330	44	235	452
Gannel	1.35	26	24	150	38	2753	940
Tyne	2.17	11	46	92	34	187	421
Mersey	1.15	13	84	84	29	124	379
Humber	0.48	16	77	54	39	113	252
Medway	1.08	11	53	55	26	86	220
Poole	1.85	11	49	50	26	96	165
Severn	0.63	15	55	38	33	89	259
Hamble	0.34	10	37	31	19	56	105
Loughor	0.47	10	207	27	21	48	146
Dyfi	0.62	17	32	24	33	166	212
Wyre	0.35	8	37	20	17	44	122
Avon	0.08	10	28	18	23	68	82
Teift	0.17	10	28	13	23	25	87
Axe	0.17	7	27	12	14	26	76
Rother	0.13	6	29	11	15	20	46
Solway	0.23	6	30	7	17	25	59
Tees	6.13	35.8	251.5	123.2	40.2	323.6	407.5

the data collected in this study concentrations of Cd, Co and Cr are higher than most other UK estuaries, whilst Cu, Ni, Pb and concentrations are similar to those reported by Bryan and Langston (1992).

5.2.3 Comparison of Tees Bay and Tees Estuary geochemistry

The mean metal concentrations in the sediments of Tees Bay and the Tees estuary are summarized in Table 5.6a along with their standard errors. It is apparent that the sediments from the Tees estuary have higher concentrations of all of the metals studied. Whether these differences are statistically significant has been determined by performing t-tests on the differences between the concentrations of each metal in the estuary and those in the bay (Table 5.6b). The results of these tests (Table 5.6b) are that all of the metals measured have significantly higher concentrations in the sediments of the Tees estuary than those of Tees Bay ($P<0.01$).

Within the studied sediments, considerable compositional variations are observed. Proportions of clay and silt are generally higher in the sediments of the Tees estuary than in those from Tees Bay, with the bay sediments being predominantly sandy. Thus, the observed, and statistically significant, differences in metal concentration noted above need not be a result of different pollutant loadings, but may merely reflect the differing sediment characteristics. For this reason it was considered useful to test the differences between metal concentrations in the Bay and the estuary again, having removed the influence of grain size variation as much as possible by means of normalizing the metal concentration to a grain size proxy.

In the literature, several different approaches for such normalization have been proposed (Loring, 1991). Often a certain grain size fraction (<2, <20 or <63 μm) is used. This will compensate for the effect of variation of grain size in sediments containing a mixture of clay, silt and sand particles, where the sand (<63 μm) and sometimes even the coarse silt fraction (20-63 μm) will dilute metal concentrations. Alternatively, chemical parameters such as Al, Fe, organic carbon, or Li may be used (see reviews by De Groot *et al.*, 1976, 1982; Trefry *et al.*, 1976; Forstner and Wittmann, 1981; Wu, 1984; Loring, 1990, 1991; Luoma, 1990).

Aluminium is the most widely used normalizer for trace metal data from estuarine and coastal environments (Bruland *et al.*, 1974,; Goldberg *et al.*, 1979;

Table 5.6a Means and standard errors of the total metal concentrations (ug g^{-1}, dry weight) for the sediments from Tees Bay and the Tees estuary.

Metal	**Location**	***n***	**Mean**	**Standard error of mean**
Cd	Tees Bay	26	2.91	0.18
	Tees Estuary	11	6.13	0.58
Co	Tees Bay	26	14.85	1.32
	Tees Estuary	11	35.79	3.45
Cr	Tees Bay	26	38.85	5.69
	Tees Estuary	11	251.64	41.68
Cu	Tees Bay	26	14.74	2.89
	Tees Estuary	11	123.22	21.90
Ni	Tees Bay	26	11.77	1.71
	Tees Estuary	11	40.20	2.52
Pb	Tees Bay	26	32.61	3.93
	Tees Estuary	11	322.60	65.86
Zn	Tees Bay	26	69.93	6.14
	Tees Estuary	11	407.48	65.73

Table 5.6b t-test for equality of mean metal concentrations in the Tees.

Metal	**Mean difference between Bay and Estuary**	**Standard error of difference**	**Significant (2-tailed)**
Cd	-3.22	0.61	0.000
Co	-20.94	3.69	0.000
Cr	-212.79	42.07	0.000
Cu	-108.48	22.09	0.001
Ni	-28.43	3.04	0.000
Pb	-289.99	65.98	0.001
Zn	-337.55	66.02	0.000

Trefry *et al.*, 1985; Windom *et al.*, 1989; Schropp *et al.*, 1990; Din, 1992; Ravichandran *et al.*, 1995). This is because it is a structural element of the clays with which the bulk of the trace metals are associated and because of its high natural concentration and minimal anthropogenic contamination (Daskalakis and O'Connor, 1995). Metal to Aluminium (metal /Al) ratios have often used to assess the extent of trace metal pollution in sediments and to evaluate pollution histories (Bertine and Goldberg, 1977).

Loring (1991) has questioned the usefulness of aluminium in high latitude areas which have been subject to glaciation. He has observed that such sediments may contain aluminium-bearing feldspars in the coarse sediment fraction which cause a reduction in the strength of the aluminium/clay relationship. In such situations he prefers the use of lithium. However, Rowlatt and Lovell (1994) tested both Al and Li in a great number of sediment samples around England and Wales and concluded that the two normalizers give similar results.

Iron (Fe), a clay mineral indicator element, was used by Rule (1986), as an alternative to Al, as a normalizing parameter for grain size in coastal and estuarine sediments from the inner Virginia shelf. Fe, however, may not always be the best candidate for normalization because its total concentration in many nearshore sediments can be distorted by the accumulation of iron compounds in these areas and because it is also susceptible to enrichment from anthropogenic sources in these areas (Loring, 1991; Din, 1992).

Windom *et al.* (1989) analyzed a great number of estuarine and coastal sediment samples, from the southeastern United States, for correlations with total organic carbon (TOC). They found that some metals, such as Cd, do covary with TOC but far less strongly than with Al. A weakness of using TOC as a normalizer is the fact that TOC itself is subject to considerable augmentation by human activity and is often a contaminant (Daskalakis and O'Connor, 1995).

In the present study, Al has been used, as it is most generally accepted as one of the best of the potential normalizing parameter. Table 5.7a summarizes the metal/Al ratios for the sediments from Tees Bay and the Tees estuary. As with the raw metal concentrations, the mean normalized metal contents are higher in the sediments from the Tees estuary than in those from Tees Bay. The differences are significant at

Table 5.7a Means and standard errors of the normalized metal concentrations (ug g^{-1}, dry weight) for the sediments from Tees Bay and the Tees estuary.

Metal	**Location**	***n***	**Mean**	**Standard error of mean**
Cd/Al	Tees Bay	26	0.24	0.01
	Tees Estuary	11	0.37	0.03
Co/Al	Tees Bay	26	1.19	0.07
	Tees Estuary	11	2.15	0.20
Cr/Al	Tees Bay	26	3.04	0.35
	Tees Estuary	11	14.96	2.30
Cu/Al	Tees Bay	26	1.13	0.18
	Tees Estuary	11	7.36	1.29
Ni/Al	Tees Bay	26	0.92	0.11
	Tees Estuary	11	2.42	0.12
Pb/Al	Tees Bay	26	2.57	0.24
	Tees Estuary	11	19.21	3.77
Zn/Al	Tees Bay	26	5.63	0.37
	Tees Estuary	11	24.41	3.90

Table 5.7b t-test for equality of mean metal/Al ratios in the Tees.

Metal	**Mean difference between Bay and Estuary**	**Standard error of difference**	**Significant (2-tailed)**
Cd/Al	-0.13	0.04	0.003
Co/Al	-0.96	0.21	0.001
Cr/Al	-11.92	2.33	0.000
Cu/Al	-6.23	1.31	0.001
Ni/Al	-1.50	0.16	0.000
Pb/Al	-16.64	3.77	0.001
Zn/Al	-18.78	3.91	0.001

the 99% confidence level for all metals (t-test, Table 5.7b), and this leads to the conclusion that the sediments of the Tees estuary are enriched in metals in comparison with the sediments of Tees Bay and that these differences are not the result of the different grain size distributions.

5.2.4 Quantification of pollution

The great number of geochemical investigations carried out in coastal marine areas, adjacent to highly populated cities and heavily industrialized areas, have demonstrated that estuaries are potential pollutant traps (Forstner and Wittmann, 1981). It is here that the substantial quantities of contaminants transported by rivers enter the marine system and it is in estuarine and coastal marine sediments that they may be deposited (Forstner and Wittmann, 1981; Fletcher *et al.*, 1994).

Anthropogenic contamination of such sediments results in the presence of metals in concentrations above their natural background levels, but to quantify the extent of such anthropogenic input, it is first necessary to determine the natural background, or pre-industrial, levels of these metals, in the sediments of the area under study (Forstner and Wittmann, 1981; De Groot *et al.*, 1982). In the absence of data on local sediment background levels, a quantitative assessment of the magnitude of any metal enrichment in a given area may be obtained by comparison to Turekian and Wedepohl's (1961) average shale composition. This provides a quick and practical means of tracing the degree of anthropogenic contamination over geological background levels and is often used as a global base-line average for particulate associated metals (e.g. Elsokkary and Muller, 1990; Davies *et al.*, 1991; Fletcher *et al.*, 1994).

Such comparisons assume that average shale can be used to represent typical metal concentrations in the fine grained sediments, and may not always be valid, but are commonly made to quantify the extent of metal pollution (Sahu and Bhosale, 1991). Metal concentrations in alternative compilations such as the average near-shore sediment of Wedepohl (1960) and the global fluvial sediment composition of Bowen (1979) are tabulated in Table 5.8 together with average shale concentrations. For most of the elements studied, metal concentrations in these different compilations do not differ greatly.

Table 5.8 Compilations of global background metal from the literature.

Sample Location	Metal Concentrations ug g^{-1}							Reference
	Cd	Co	Cr	Cu	Ni	Pb	Zn	
1- World average shale	0.3	19	90	45	68	20	95	Turekian & Wedepohl (1961)
2- Near-shore sediments	-	13	100	48	55	20	95	Wedepohl (1960)
3- Global average value of fluvial sediments	0.3	9	90	33	2	19	95	Bowen (1979)
4- Sandstone	0.02	0.3	15	35	2	7	16	Turekian & Wedepohl (1961)

Having determined the likely background concentrations of the elements studied in sediments, it is possible to calculate enrichment factors (EFs) relative to the chosen reference (i.e. EF = concentration of metal in sample/concentration of metal in reference). Enrichment factors >1 indicate that there is an enrichment of that element compared to the reference used and enrichment factors of <1.0 indicate that the element is depleted in the sample suite relative to the reference. Such enrichment factors have been calculated for the sediments of Tees Bay and the Tees estuary (Tables 5.9 and 5.10).

For Tees Bay (Table 5.9) all of the metals studied, with the exception of Cd and Pb, have enrichment factors which are significantly lower (at the 95% confidence level) than 1.0. Only Cd and Pb, of the metals studied have enrichment factors which exceed 1.0 at the 95% confidence level. In the Tees estuary (Table 5.10) all of the metals studied, with the exception of Ni, have enrichment factors which are greater than 1.0 at the 95% confidence level, and are thus significantly enriched in the estuarine sediments. Enrichment factors for Ni in the Tees estuary are significantly less than 1.0 (at the 95% confidence level) demonstrating that Ni concentrations observed in these sediments are lower than the global average shale concentration.

Apparent from Tables 5.9 and 5.10 are the greater enrichment factors of the sediments from the Tees estuary. For Zn, Cr, Cu and Co, mean concentrations in the Tees estuary were ~ 4.3, 2.8, 2.7, and 1.9 times, respectively, greater than the average shale compilation while the enrichment factors for the Tees Bay suite were all significantly less than 1.0. Enrichment factors of Cd and Pb were significantly greater than 1.0 in both the bay and the estuary, but the degree of enrichment is greater in the estuary, especially in the case of Pb.

Table 5.9 Metal enrichment factors (the ratio between metal in the sample/metal in average shale) for the sediments from Tees Bay.

Sample No	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	10.67	0.89	0.49	0.70	0.20	1.96	1.16
2	16.67	0.95	0.79	0.48	0.27	2.27	0.88
3	8.67	1.09	0.42	0.36	0.16	2.29	0.96
4	17.33	1.97	1.57	1.57	0.57	5.00	1.68
5	8.33	0.77	0.50	0.51	0.21	1.39	0.95
6	9.00	0.70	0.34	0.34	0.18	1.83	0.83
7	10.00	0.96	0.36	0.32	0.19	1.92	0.88
8	8.00	0.47	0.25	0.18	0.31	1.54	0.70
10	8.67	0.61	0.33	0.21	0.12	1.02	0.63
11	11.67	0.65	0.31	0.26	0.12	1.02	0.63
12	9.67	0.76	0.38	0.17	0.14	1.77	0.65
13	10.33	0.53	0.28	0.09	0.10	0.62	0.46
14	7.67	0.41	0.28	0.11	0.10	1.05	0.44
17	4.33	0.31	0.09	0.06	0.03	0.65	0.31
18	8.00	0.59	0.37	0.26	0.09	1.01	0.53
19	8.67	0.52	0.40	0.18	0.12	1.51	0.68
20	12.00	0.79	0.22	0.20	0.11	1.60	0.75
21	6.33	0.46	0.09	0.08	0.04	0.67	0.31
22	9.00	0.82	0.50	0.24	0.15	1.30	0.64
23	12.67	0.86	0.46	0.42	0.22	2.04	0.72
24	9.33	0.86	0.57	0.26	0.16	2.51	1.16
25	15.33	1.59	1.15	0.98	0.53	3.79	1.29
26	6.67	0.77	0.19	0.12	0.08	1.39	0.51
27	6.00	0.48	0.29	0.18	0.14	0.66	0.48
28	8.00	0.77	0.52	0.20	0.11	1.04	0.71
29	9.33	0.74	0.06	0.07	0.06	0.59	0.19
Mean	9.71	0.78	0.43	0.33	0.17	1.63	0.74
Min.	4.33	0.31	0.06	0.06	0.03	0.59	0.19
Max	17.33	1.97	1.57	8.52	0.57	5.00	1.68
Standard deviation	3.10	0.35	0.32	0.33	0.13	1.00	0.33

Table 5.10 Metal enrichment factors (the ratio between metal in the sample/metal in average shale) for the sediments from the Tees Estuary.

Sample No	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
33	15.33	1.44	1.85	1.16	0.46	17.90	3.44
34	19.33	1.65	2.48	1.84	0.56	23.88	4.15
35	22.67	1.58	3.06	2.26	0.58	28.27	5.16
36	22.00	1.87	3.51	2.93	0.67	26.89	5.67
37	29.00	1.77	6.41	5.35	0.67	33.98	7.59
38	19.67	1.59	3.48	2.76	0.56	11.00	4.13
39	32.67	2.93	3.55	5.82	0.69	15.83	8.18
40	20.67	2.69	2.43	3.33	0.72	8.06	4.08
41	17.33	2.50	1.85	2.28	0.69	5.13	2.19
42	8.67	0.85	0.40	0.55	0.31	1.83	0.69
43	17.33	1.84	1.17	1.83	0.60	4.70	1.89
Mean	20.42	1.88	2.80	2.74	0.59	16.13	4.29
Min.	8.67	0.85	0.40	0.55	0.31	1.83	0.69
Max.	32.67	2.93	6.41	5.82	0.72	33.98	8.18
Standard deviation	6.45	0.60	1.54	1.61	0.12	10.92	2.29

However, as the Tees Bay sediments are sandy (section 5.1.1) the compilation of global shale concentrations may not be the most suitable reference against which to calculate enrichment factors. An alternative, which may be more appropriate, is the average composition of sandstone of Turekian and Wedepohl (1961) (Table 5.8). Using this as a guide to the background metal concentrations in the sediments of Tees Bay results in the enrichment factors tabulated in Table 5.11. These are significantly greater than 1.0 (at the 95% confidence level) for all elements except Cu, indicating that all of the metals except Cu are significantly enriched in the Tees Bay sands, relative to average sandstone. Compared to the enrichment factors calculated by using average shale as a reference (Table 5.9), the enrichment factors calculated relative to sandstone are higher, especially for Cd, Co, and Ni. This is a result of the much lower metal concentrations in the Turekian and Wedepohl (1961) average sandstone relative to the average shale compilation, and reflects the lower metal concentrations in quartz and feldspar dominated sandstones relative to clay dominated shales (Forstner and Wittmann, 1981).

Difficulty in identifying appropriate reference concentrations for the two different sample suites, which differ greatly in grain size distribution, limits the simple approach described above. A more sophisticated means of calculating enrichment factors, which accounts for grain size variation has been followed below.

Salomons and Forstner (1984) describe an alternative method for calculating enrichment factors. They suggest defining the enrichment factor as the ratio between the metal/Al ratio of the sample and metal/Al ratio in average shale. The enrichment factors calculated in this way are listed in Tables 5.12 and 5.13. These confirm the observations obtained by using the former method, that the highest enrichment factors are found in the Tees estuary sediments. For the Tees estuary, all EFs calculated by this method are significantly greater than 1.0 for all metals, except for Ni which is significantly less than 1.0 (at the 95% confidence level). For Tees Bay, all EFs are significantly less than 1.0 (at the 95% confidence level) for all metals, except for Co and Zn which are not significantly different to 1.0, and Cd and Pb which are significantly greater than 1.0 (at the 95% confidence level). This observation leads to the conclusion that sediments from Tees Bay have lower enrichment factors than those

Table 5.11 Metal enrichment factors (the ratio between metal in the sample/metal in sandstone) for the sediments from Tees Bay.

Sample No	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	160	56.33	2.94	0.89	6.90	5.59	6.89
2	250	60.00	4.75	0.62	9.05	6.49	5.24
3	130	69.33	2.51	0.46	5.55	6.54	5.69
4	260	124.67	9.41	2.01	19.35	14.29	9.99
5	125	49.00	3.03	0.66	7.00	3.97	5.61
6	135	44.33	2.05	0.44	6.25	5.21	4.90
7	150	60.67	2.13	0.41	6.30	5.49	5.24
8	120	30.00	1.53	0.23	10.55	4.39	4.14
10	130	38.33	1.95	0.27	3.95	2.90	3.73
11	175	41.33	1.88	0.33	4.20	2.90	3.77
12	145	48.33	2.29	0.22	4.70	5.06	3.86
13	155	33.67	1.69	0.11	3.40	1.77	2.74
14	115	25.67	1.69	0.14	3.30	2.99	2.63
17	65	19.67	0.53	0.08	1.15	1.86	1.87
18	120	37.33	2.21	0.33	3.00	2.87	3.16
19	130	33.00	2.41	0.23	4.10	4.30	4.03
20	180	50.33	1.32	0.25	3.80	4.57	4.44
21	95	29.33	0.53	0.11	1.45	1.91	1.83
22	135	52.00	3.02	0.30	5.00	3.70	3.81
23	190	54.33	2.75	0.53	7.55	5.83	4.29
24	140	54.33	3.43	0.34	5.50	7.16	6.88
25	230	100.67	6.91	1.26	17.85	10.83	7.63
26	100	48.67	1.15	0.15	2.60	3.97	3.06
27	90	30.67	1.73	0.23	4.65	1.89	2.84
28	120	48.67	3.11	0.25	3.80	2.97	4.22
29	140	46.67	0.39	0.09	2.10	1.69	1.15
Mean	145.58	49.51	2.59	0.42	5.89	4.66	4.37
Min.	65.00	19.67	0.39	0.08	1.15	1.69	1.15
Max.	260.00	124.67	9.41	2.01	19.35	14.29	9.99
Standard deviation	46.48	22.36	1.93	0.42	4.35	2.86	1.96

Table 5.12 Metal enrichment factors (the ratio between metal/Al in the sample and metal/Al in average shale) for the sediments from Tees Bay.

Sample No	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	11.82	0.99	0.55	0.78	0.23	2.19	1.30
2	16.76	0.96	0.80	0.49	0.27	2.31	0.90
3	9.69	1.23	0.47	0.40	0.18	2.59	1.08
4	16.92	1.93	1.54	1.54	0.56	4.93	1.66
5	10.58	0.99	0.65	0.66	0.26	1.78	1.21
6	10.73	0.84	0.41	0.41	0.22	2.20	0.99
7	12.18	1.17	0.44	0.39	0.23	2.36	1.08
8	10.54	0.63	0.34	0.23	0.41	2.04	0.93
10	11.50	0.81	0.44	0.28	0.16	1.36	0.84
11	14.86	0.84	0.40	0.33	0.16	1.31	0.82
12	12.48	0.99	0.50	0.22	0.18	2.31	0.85
13	14.68	0.76	0.40	0.13	0.14	0.89	0.66
14	11.47	0.61	0.43	0.16	0.15	1.58	0.67
17	7.44	0.54	0.15	0.10	0.06	1.13	0.54
18	9.53	0.71	0.44	0.31	0.11	1.21	0.64
19	11.05	0.67	0.52	0.23	0.15	1.94	0.87
20	15.36	1.02	0.28	0.25	0.14	2.07	0.97
21	9.15	0.67	0.13	0.12	0.06	0.98	0.45
22	10.69	0.98	0.60	0.28	0.18	1.55	0.77
23	14.44	0.98	0.53	0.48	0.25	2.35	0.83
24	10.68	0.99	0.66	0.30	0.19	2.90	1.34
25	14.56	1.52	1.10	0.94	0.50	3.63	1.23
26	8.57	0.99	0.25	0.15	0.10	1.80	0.67
27	8.85	0.72	0.43	0.27	0.20	0.98	0.71
28	11.62	1.12	0.76	0.29	0.16	1.53	1.04
29	12.58	1.00	0.09	0.09	0.08	0.80	0.26
Mean	11.87	0.95	0.51	0.38	0.21	1.95	0.90
Min.	7.44	0.54	0.09	0.09	0.06	0.80	0.26
Max.	16.92	1.93	1.54	1.54	0.56	4.93	1.66
Standard deviation	2.52	0.30	0.30	0.31	0.12	0.91	0.30

Table 5.13 Metal enrichment factors (the ratio between metal/Al in the sample and metal/Al in average shale) for the sediments from the Tees Estuary.

Sample No	Cd	Co	Cr	Cu	Ni	Pb	Zn
33	14.75	1.39	1.80	1.12	0.44	17.39	3.34
34	17.39	1.49	2.25	1.67	0.51	21.69	3.76
35	20.46	1.44	1.79	2.05	0.53	25.77	4.70
36	19.17	1.64	3.09	2.57	0.59	23.67	4.99
37	23.86	1.46	5.32	4.43	0.56	28.24	6.30
38	18.47	1.50	3.30	2.61	0.53	10.43	3.91
39	31.03	2.79	3.40	5.57	0.66	15.19	7.84
40	17.96	2.35	2.13	2.92	0.63	7.07	3.58
41	14.82	2.15	1.60	1.96	0.60	4.43	1.89
42	9.40	0.93	0.44	0.60	0.33	2.00	0.75
43	15.45	1.65	1.54	1.64	0.53	4.23	1.70
Mean	18.43	1.71	2.51	2.47	0.54	14.56	3.89
Min.	9.40	0.93	0.44	0.60	0.33	2.00	0.75
Max.	31.03	2.79	5.32	5.57	0.66	28.24	7.84
Standard deviation	5.58	0.52	1.28	1.44	0.09	9.46	2.06

from the Tees estuary, and that these remain lower even when corrected for grain size variation by using Salomons and Forstner (1984) method.

5.2.5 Controls of the total metal concentrations in Tees Bay and the Tees Estuary

5.2.5.1 Relationships between metal levels and textural characteristics of the sediments

The relationships between metal concentrations and the textural characteristics of the sediments have been investigated in this study by the calculation of Pearson correlation coefficients (Tables 5.14 and 5.15) between the raw metal concentrations, and the percentages of sand, silt, clay and TOC in the sediment. In Tees Bay (Table 5.14), the correlation structure reflects the close relationship between metal concentration and sediment texture, with correlations of 0.72 or greater being recorded between every metal concentration and the silt and clay contents of the sediment. These correlations are all significant at the 99% confidence level. The positive significance of these coefficients indicates that as clay and silt concentrations in the sediment increase, then so do total metal concentrations. This observation is consistent with the findings of previous investigations (e.g. Brannon *et al.*, 1977; Oakley *et al.*, 1981; Cauwet, 1987), namely that finer-grained (clay and silt dominated) sediments have relatively high metal concentrations due to their large specific surface area and the strongly adsorptive properties of the finer sediment particles.

Table 5.14 Correlation matrix showing the coefficient between different pairs of variable measured in the sediments of Tees Bay.

	Cd	Co	Cr	Cu	Ni	Pb	Zn	Sand	Silt	Clay	TOC
Cd	1.00										
Co	0.78**	1.00									
Cr	0.78**	0.89**	1.00								
Cu	0.75**	0.90**	0.93**	1.00							
Ni	0.75**	0.84**	0.90**	0.91**	1.00						
Pb	0.76**	0.92**	0.91**	0.90**	0.90**	1.00					
Zn	0.69**	0.85**	0.87**	0.88**	0.83**	0.92**	1.00				
Sand	-0.73**	-0.87**	-0.91**	-0.88**	-0.91**	-0.89**	-0.77**	1.00			
Silt	0.72**	0.88**	0.91**	0.90**	0.91**	0.90**	0.77**	-0.99**	1.00		
Clay	0.74**	0.81**	0.85**	0.82**	0.87**	0.84**	0.74**	-0.96**	0.93**	1.00	
TOC	0.67**	0.84**	0.91**	0.95**	0.93**	0.87**	0.84**	-0.87**	0.88**	0.80**	1.00

** = Significant at P<0.0I.

The strong and highly significant correlations between TOC and metal concentrations, in Tees Bay, may imply either a primary association (e.g. adsorption of metals onto sedimentary organic particles), or a secondary relationship to grain size in which the organic carbon content increases with increasing clay content in the sediments, and it is the high clay contents which result in elevated metal concentrations (e.g. Stumm and Morgan, 1981; Loring, 1984; Calvert *et al.*, 1985; Krumgalz, 1989; Kuijpers *et al.*, 1993; Palanques and Diaz, 1994).

Relationships in the sediments from the Tees estuary are more complex (Table 5.15). For the estuarine sediments, all metals are negatively correlated with TOC although these correlations are only significant for Pb (at the 95% confidence level). This is probably due to the presence of the sandy sediment at site 42 which is particularly enriched in organic carbon due to the presence of coal particles, but which has very low metal contents, typical of the coarser sediments found in Tees Bay.

Table 5.15 Correlation matrix showing the coefficient between different pairs of variable measured in the sediments of Tees Estuary.

	Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Sand**	**Silt**	**Clay**	**TOC**
Cd	1.00										
Co	0.63*	1.00									
Cr	0.82**	0.24	1.00								
Cu	0.95**	0.66*	0.81**	1.00							
Ni	0.73*	0.86**	0.57	0.71*	1.00						
Pb	0.59	-0.08	0.76**	0.42*	0.27	1.00					
Zn	0.95**	0.45	0.85**	0.89	0.58	0.74**	1.00				
Sand	-0.67*	-0.75*	-0.51	-0.56	-0.93**	-0.42	-0.57	1.00			
Silt	0.66*	0.69*	0.49	0.51	0.86**	0.44	0.58	-0.97**	1.00		
Clay	0.55	0.70*	0.44	0.53	0.87**	0.27	0.40	-0.83**	0.67*	1.00	
TOC	-0.45	-0.10	-0.56	-0.25	-0.38	-0.63*	-0.51	0.62*	-0.72*	-0.24	1.00

* = Significant at $P<0.05$.
** = Significant at $P<0.01$.

If the Tees estuary data are re-calculated without the sandy sediment from site 42 somewhat different results are obtained (Table 5.16), with positive and significant relationships being observed between TOC and the concentrations of Co and Ni. Davies *et al.* (1991), in their study of the Tees estuary sediments, reported that organic matter abundance did not influence metal concentrations.

Metal concentrations are positively correlated with the finer components of the Tees estuary sediment (clay and silt) and are negatively correlated with the sand content. However, only for Ni are these relationships significant at the 99% confidence level whilst the relationship is significant at the 95% confidence level for Cd and Co (Table 5.15). Essentially the same relationships are observed in the edited data set (Table 5.16) with Co and Ni being negatively correlated with the sand content of the sediment (at the 95% confidence level) and positively correlated with the finer sediment fractions.

Table 5.16 Correlation matrix showing the coefficient between different pairs of variable measured at all sites from the Tees estuary, except site 42.

	Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Sand**	**Silt**	**Clay**	**TOC**
Cd	1.00										
Co	0.43	1.00									
Cr	0.74*	-0.08	1.00								
Cu	0.95**	0.56	0.75*	1.00							
Ni	0.51	0.80**	0.31	0.65*	1.00						
Pb	0.46	-0.44	0.70*	0.28	-0.11	1.00					
Zn	0.94**	0.22	0.80**	0.86*	0.33	0.67*	1.00				
Sand	-0.38	-0.70*	-0.12	-0.41	-0.89*	-0.05	-0.27	1.00			
Silt	0.33	0.56	0.02	0.29	0.61	0.11	0.32	-0.77**	1.00		
Clay	0.26	0.52	0.16	0.35	0.76*	-0.03	0.09	-0.78**	0.19	1.00	
TOC	0.13	0.82**	-0.27	0.24	0.73*	-0.54	-0.17	-0.68*	0.31	0.73*	1.00

* = Significant at $P<0.05$.

** = Significant at $P<0.0I$.

5.2.5.2 Possible anthropogenic sources

Of the seven metals investigated, the Cd and Pb concentrations are consistently above normal levels, in the surface sediments of both the Tees estuary and Tees Bay. These elements also exhibited the greatest degree of metal enrichment in Tees Bay (between 4.3-17.3 and 1.1-5.0 fold enrichments for Cd and Pb, respectively; Table 5.9) and the Tees estuary (between 8.7-32.7 and 1.8-33.9 fold enrichments for Cd and Pb, respectively; Table 5.10). According to Forstner and Wittmann (1981) even when it difficult to establish an association between enhanced metal concentrations in sediments and a given source of pollution, one can postulate that moderate enrichment factors of 2-10 times in recent sediments originate from mixed input of industrial, urban domestic, and agricultural sources. Since Cd and Pb enrichment factors go well above these values, at most sites in this study, some extra (or more specific) sources have to be postulated.

Cd is widely distributed in the earth's crust, but is particularly associated with Zn and it is produced commercially as by-product of Zinc smelting (Williams and Harrison, 1984). Cd has been used in quantity since about 1950 and total world production is about 15 000-18 000 t yr^{-1} (Clark, 1992). The principal uses of Cd are as stabilizers and pigments in plastic, paints, printing inks and in electroplating, but substantial amounts are used in solders and other alloys and in batteries (Fergusson, 1990; Clark, 1992). Less than 10% of the Cd used in these primary products is recycled and the rest must be assumed to be released to the environment (Clark, 1992). Other anthropogenic inputs of the Cd to the environment are: fumes, dust, and waste water from lead and zinc mining and refining as well as from Cd production; rinsing water from electroplating; the iron, steel, and non-ferrous metal industries; zinc used in galvanized coatings of metals; wear of automobile tyres; coal and heating oils; sewage sludge and phosphate fertilizers (Clark, 1992).

Cd is concentrated in the middle reach of the estuary, between sites 37 and 39, with concentrations above site 36 being similar to those below site 40. In this middle region, Cd concentrations are 29.0 and 32.7 times greater than background levels, whereas they do not exceed 19.3 fold enrichment in the upper and lower reaches. This distribution is generally consistent with the observations of Davies *et al.* (1991), who noted peak concentrations of Cd in the middle and upper estuary, between locations corresponding to our sites 34-39, and lower concentrations of this metal near the mouth of the estuary. The high levels of Cd, in the middle region of the estuary, probably result from a combination of factors including industrial discharges, urban runoff, agriculture runoff and inputs from weathering and erosion of the highly mineralized Pennine Hills and the effects of past mining activities in those hills (North Sea Task Force, 1993). As shown in Table 5.2, the mean concentration of Cd found in the Tees estuary is significantly higher (at the 95% confidence level) than that of steam sediment from north-east of England, reported by the British Geological Survey (in Press). This suggests that there are probably anthropogenic inputs to the estuary above that which could be attributed to the past mining activities on the Pennine Hills.

The consumption of Pb has risen dramatically during this century, showing a significant increase over the last 30 years, with the total production of about 43 million t yr^{-1} (Clark, 1992). Much Pb in metallic form, in battery casing and plates, in sheet and pipes, is recovered and recycled, but most Pb used in compound form is lost to the environment. Automobile production uses a large proportion of the Pb, in car batteries, petrol additives and solder. As a result, urban runoff from road surfaces and atmospheric deposition constitute important sources of Pb in the environment (Laxin and Harrison, 1977; Kersten, 1988; Lewis and McIntosh, 1989; Rognerud *et al.*, 1993). Other possible sources of lead in industrial areas include marine vessels repair, leaded fuel used by a heavy traffic of marine vessels, effluent from industrial plants and factories, sewage sludge dumping (Abu-Hilal and Badran, 1990; Machiwa, 1992), mining (North Sea Task Force, 1993; Rowlatt and Lovell, 1994) and probably paint fragments from old buildings and automobiles (Machiwa, 1992).

The highest Pb values occur off the upper and middle reaches of the Tees estuary, a similar observation to that made by Davies *et al.* (1991) . Pb varies between 17.9 and 34.0 fold enrichment over background levels above site 37, decreasing beyond this point to a 4.7 fold enrichment at site 43, near the mouth of the estuary. The higher levels of Pb in the sediments from the upper and middle reaches of the estuary are probably due to the presence of major sources of Pb pollution, and intensive human activities in this area. These include ship and boat activities, oil and other petroleum product from boats, ships and the oil refinery, sewage and industrial discharges, urban runoff from road surfaces and atmospheric deposition of petrol combustion products, inputs from weathering and erosion of the highly mineralized Pennine Hills and the effects of past mining activities in those hills. Mean Pb concentrations in the estuary are higher than local stream sediments (British Geological Survey, in Press) but this difference is not significant at the 95% confidence level. Direct anthropogenic inputs in the estuary need not, therefore, be large.

5.3 Metal Partitioning

5.3.1 Summary of partitioning data and comparison with other studies

Several methods for determining the different forms of metals in sediments have been described in the scientific literature (Chapter 2), the most widely used of which are based on sequential chemical extractions. In such procedures several increasingly aggressive reagents are used consecutively to extract metal from operationally-defined phases within the sediment. Partitioning is not only very useful for determining the degree of association of the metals in the sediments and to what extent the may be remobilized into the environment (Forstner *et al.*, 1990), but also for distinguishing those metals with a lithogenic origin from those with an anthropogenic origin. According to Salomons and Forstner (1980), Calmano and Forstner (1983) and Rubio *et al.* (1991), metals with an anthropogenic origin are mainly obtained in the first extractions, while in the last stage of the process, the residual fraction is obtained, corresponding to metals with lithogenic origins.

In the present study, the sequential extraction procedure proposed by Tessier *et al.* (1979), and modified by Ajayi and Van Loon (1989), was used. This is a five step extraction procedure, the data from which are discussed below on a phase by phase basis. The data are summarized in Tables 4.8 and 4.9 (see Chapter 4), and the full data set is presented in the Appendix.

5.3.1.1 Fraction 1 (the exchangeable fraction; F1)

The exchangeable fraction of a sediment-bound metal is weakly held by van der Waals, London and Coulomb forces (Samant *et al.*, 1990) and equilibrates easily and rapidly with the surrounding pore water. As such, exchangeable elements are often considered to be highly bioavailable (Tessier *et al.*, 1980).

Cr, Cu and Ni were not found in detectable quantities in the exchangeable fraction of the Tees sediments, and exchangeable forms of Co, Pb and Zn make up less than 1% of the total amounts of these metals present (Table 4.9). In contrast, for Cd the exchangeable fraction is a significant metal host, and exchangeable Cd occurs at all of the sites studied. However, the proportions of exchangeable Cd are lower in the marine sediments than in those from the estuary (2.6 and 5.7% of the total Cd, respectively), probably due to the ion-exchange action of sea water (Forstner and Stoffers, 1981). Similar distributions have been previously noted for Cd in both the marine (Samant *et al.*, 1990; Giordano *et al.*, 1992; Abu-Hilal, 1993; Mat *et al.*, 1994) and estuarine sediments (Pardo *et al.*, 1990; Surija and Branica, 1995).

High concentrations of trace metals in this fraction may be regarded as a pollution indicator (Forstner and Wittmann, 1981). However, even for Cd, only a small proportion of the total metal present occurred in this fraction (0.4-9.2 and 0.4-

8.3% in the Tees estuary and Bay sediments, respectively; Table 4.9), and in terms of its important as a metal host, fraction 1 is probably the least geochemically significant fraction in the studied sediments.

5.3.1.2 Fraction 2 (the carbonate fraction; F2)

Concentrations of most trace metals in fraction 2 exceed those found in the previous fraction. In Tees Bay, the amounts of Cd, Co and Pb in fraction 2 make up 15.8, 10.4 and 18.4%, respectively, of the total metal concentrations, whereas in the Tees estuary, the proportions are lower, with only 9.6, 5.1 and 11.0% of the total Cd, Co and Pb, respectively, being leached in extraction 2. The proportions of Cr, Cu, Ni and Zn associated with this fraction are low throughout (0.9, 5.3, 3.3 and 6.3%, respectively, in Tees Bay, and 2.2, 0.4, 2.0 and 6.4%, respectively, in the Tees estuary).

Since carbonates are regarded as inefficient metal carrier phases (Kruaskopf, 1956; Horowitz, 1985; Sigg, 1987), high metal concentrations in this fraction are often explained by the poor selectivity of the methods used. Desorption of metals from other phases, such as Fe-Mn oxides (Pickering, 1986; Martin *et al.*, 1987) and from organic matter coatings (Slavek, 1982; Horowitz and Elrick, 1987), during fraction 2 extraction is common and for this reason some researchers have named this fraction as the exchangeable at pH 5 fraction (Martin *et al.*, 1987) or specifically sorbed (Pickering, 1986). Apparently, the higher the metal concentrations in sediments, the greater quantity of a metal which can be desorbed from these phases. However, there was no apparent increase in the fraction 2 metal concentration with an increase in the total metal contents for the Tees estuary sites. Hence, although the percentages of Cd, Co and Pb obtained in fraction 2 were relatively high (Table 4.9), it might be assumed that some of the metals were associated with carbonates.

5.3.1.3 Fraction 3 (the reducible fraction; F3)

This fraction is generally believed to reflect the concentration of metals adsorbed to oxides/hydroxides of Mn and Fe, which form coatings on particulate materials, and which can be mobilized under low redox potentials or acid conditions (Arakel and Hongjun, 1992). The Mn and Fe oxides/hydroxides play an important role in scavenging heavy metals (Jenne, 1968; Tessier *et al.*, 1979; Waldichuck, 1985) from solution and by means of coprecipitation and dissolution reactions they can be an important factor controlling the behaviour of the metals associated with them (Bryan, 1971 ; Luoma and Bryan, 1978 ; Waldichuk, 1985; Fukai and Huynh-Ngoc, 1986).

Fraction 3 was found to contain between 26-50% of the total Cd, Co, Pb and Zn in the sediments from Tees Bay and lesser amounts of Cr, Cu and Ni (5-12%; Table 4.9). For the Tees estuary sediments this fraction is associated with 28-50% of the total Cd, Cr, Pb and Zn, but only 3-15% of Co, Cu and Ni. For Pb, fraction 3 is more significant than for the other metals studied, with 24.6-51.3% of the total Pb occurring in this fraction, and with this proportion being similar for the marine and estuarine sediments, even though Pb concentrations are lower in Tees Bay than in the estuary. These findings of a high percentage of Pb associated with F3 are in agreement with earlier studies (Salomons and Forstner, 1980; Tessier *et al.*, 1980; Rauret *et al.*, 1988; Jordao and Hickless, 1989; Pardo *et al.*, 1990; Jha *et al.*, 1990; Abu-Hilal, 1993). Fraction 3 is also a major host for Zn in the sediments from the Tees estuary, with 40.9% of the total concentrations of this metal occurring in this form. This result is similar to those reported by several workers on freshwater sediments (Chester and Stoner, 1975; Tessier *et al.*, 1980; Hickey and Kittrick, 1984; Pardo *et al.*, 1990).

5.3.1.4 Fraction 4 (the oxidizable fraction; F4)

Previous studies have shown that the oxidizable fraction, which is composed of organic matter and sulphides, can be an important metal host, especially in polluted sediments (Forstner and Wittmann, 1981; Kersten and Forstner, 1990), where it can dominate the trace metal distribution (Ridgway and Price, 1987). This fraction is not considered very mobile or available, since it is thought to be associated with high molecular weight, stable humic substances, which would only release small amounts of metal during diagenesis (Garcia-Miragaya and Sosa, 1994), whilst the sulphide minerals are stable in the absence of oxygen (Mat *et al.*, 1994).

This fraction was the least important as a host for Cd, with only 6.3% of the Cd in the Tees estuary sediments occurring in this phase, and with Cd concentrations in Tees Bay being undetectable (Table 4.9). The undetectable Cd concentrations in fraction 4 of the Tees Bay sediments are consistent with the data previously reported by Abu-Hilal (1993) for sediments from the Gulf of Aqaba. Fraction 4 is a minor host for Co and Pb, with approximately 3.0% of the total concentrations of these metals in the sediments from Tees Bay occurring in this form, and with 8.7-11.0% of the metal bound sediments in the Tees estuary being released in this stage. For Cr and Zn fraction 4 hosts 3.3-7.0% of the total in sediments from Tees Bay, and approximately 21.0% of the total in the Tees estuary sediments. Fraction 4 contained moderate percentages of Ni in both the marine and the estuarine sediments (13.4 and 15.1%, respectively). The data, in Table 4.9, also shows that percentages of all metals in fraction 4 are higher in the estuarine sediments than in those from the marine, probably due to the high TOC content of the Tees estuary sediments.

However, in terms of the proportion of the total metal held, this fraction is the most important as a host for Cu (Table 4.9). In Tees Bay, fraction 4 makes up 29.0% of the total Cu present in the sediments, and for the sediments from the Tees estuary this increases to 65.8%. This is probably an indication of the well-known close association of Cu with organic matter (Tessier *et al.*, 1980; Forstner and Patchineelam, 1981; Hickey and Kittric, 1984). The partitioning of Cu observed here is similar to that found by Salomons and Forstner (1980), Tessier *et al.* (1980), Rauret. (1988), Jordao and Hickless (1989), Pardo *et al.* (1990) and Gadh *et al.* (1993). However, Jha *et al.* (1990) have reported that Cu, in sediments of Yamuna River at Delhi, shows preference for the Fe-Mn oxide fraction. Gibbs (1977), in Amazon and Yukon sediments, and Tessier *et al.* (1979), in St. Marcel and Pierreville sediments, found high percentages of Cu in the residual fraction and a much lower contribution from Fe-Mn oxides and organic matter. The present study suggests that Cu is present predominantly in fractions 4 and 5.

5.3.1.5 Fraction 5 (the residual fraction; F5)

The residual (or lithogenic) fraction corresponds to metals with a natural origin and is the most stable and least bioavailable of all of the phases extracted, since metals in this phase are associated with detrital silicate minerals, resistant sulphides, and refractory organic material (Tessier *et al.*, 1979; Samant *et al.*, 1990; Garcia-Miragaya and Sosa, 1994; Boughriet *et al.*, 1994). Salomons and Forstner (1980), Calmano and Forstner (1983) and Rubio *et al.* (1991) demonstrated that metals in uncontaminated sediments tend to be concentrated in the lithogenic fraction, whereas metals resulting from anthropogenic input tend to be concentrated in the first four (non-lithogenic) phases, which have a greater tendency for remobilization. Table 5.17 shows the mean proportions of the lithogenous and non-lithogenous fractions in the sediments from Tees Bay and the Tees estuary.

It is apparent that the lithogenous fraction is most significant for Co and Ni, which are not highly enriched in the sediments, and which indicates that these metals are probably terrestrially derived and not highly bioavailable. These results resemble those reported by other workers in freshwater and coastal marine sediments (Tessier *et al.*, 1979 and 1980; Samant *et al.*, 1990). The data in Table 5.17, also highlight the variation in the importance of the lithogenic fraction as a host for Cr, Cu and Zn between the sediments from Tees Bay and those from Tees estuary. In the marine sediments the residual fraction is the principal host phase, for these metals which are probably largely terrestrially derived and unlikely to be reactive in the sedimentary and diagenetic environment. These are consistent with the data previously reported by Samant *et al.*, (1990), for the sediments from Dalhousie Harbour, and Izquierdo *et al.* (1997), for the sediments from Cadiz Bay.

In contrast, the partitioning characteristics of the estuarine sediments show that the lithogenous fraction is less important for these metals, indicating the more polluted nature of the estuarine sediments for these metals. This is in agreement with metal partitioning studies of sediments from polluted European rivers such as the Elbe and Rhine (Salomons and Forstner, 1980), Weser (Calmano and Forstner, 1983), Iguacu (De Souza *et al.*, 1986), Pisuerga (Pardo *et al.*, 1990), and with recent measurements of metal distribution in the suspended sediment of the Humber and Mersey Estuaries (Comber *et al.*, 1995).

For Pb, the residual fraction is less significant than for the other metals studied, with 28.9- 26.7% of the total Pb occurring in this fraction, and with this proportion being similar for the marine and estuarine sediments. The partitioning of Pb observed in this study is in agreement with those of other workers for coastal marine (Abu-Hilal, 1993; Izquierdo *et al.*, 1997) or estuarine sediments (Tessier *et al.*, 1980; Rauret *et al.*, 1988; Jha *et al.*, 1990; Pardo *et al.*, 1990). For Cd, the residual phase accounts for about half of the total Cd present in both the marine and estuarine

Table 5.17 The mean proportions of metals (%) in the lithogenous and non-lithogenous fractions for the sediments from Tees Bay and the Tees Estuary.

Metal	Location	*n*	lithogenous fraction[a]	Non-Lithogenous fraction[b]
Cd	Tees Bay	26	46.61	53.39
	Tees Estuary	11	50.91	49.09
Co	Tees Bay	26	59.97	40.03
	Tees Estuary	11	70.09	29.91
Cr	Tees Bay	26	83.68	16.32
	Tees Estuary	11	40.03	59.97
Cu	Tees Bay	26	60.34	39.66
	Tees Estuary	11	31.28	68.72
Ni	Tees Bay	26	75.56	24.44
	Tees Estuary	11	71.75	28.25
Pb	Tees Bay	26	28.90	71.10
	Tees Estuary	11	26.66	73.34
Zn	Tees Bay	26	56.44	43.56
	Tees Estuary	11	32.11	67.89

[a] = residual fraction.

[b] = F1+F2+F3+F4.

sediments. Similarly high concentrations of Cd in the residual phase of sediments from three Brazilian Estuaries have also been noted by De Souza *et al.* (1986).

To summarize, the distributions of the metals studied between the five fractions extracted are detailed below on an element to element basis.

Cd: In the sediments from the Tees estuary, the bulk of Cd is located in fractions 5 and 3. Similar results are obtained for the sediments from Tees Bay. The high proportions of Cd associated with fraction 5 found in this study are, however, different to those reported by Elsokkary and Muller (1990), Pardo *et al.*, (1990) and Gadh *et al.*, (1993) in polluted river sediments, where the contribution of the residual fraction was much lower.

Co: Co appeared mainly in fraction 5, in both the estuarine and marine sediments. The partitioning profiles observed here are similar to those reported by Tessier *et al.* (1979), in St. Marcel and Pierrville sediments, and Samant *et al.* (1990), in New Brunswick sediments. Furthermore, the results reported here contrast with those reported by Prohic and Kniewald (1987) and Pardo *et al.*, (1990).

Cr: The partitioning of Cr differs significantly between the marine and estuarine sediments. In the former (marine sediments) high percentages of the total Cr occurred in fraction 5 (83.62%) then as the intensity of pollution increased, in the estuarine sediment, a large proportion of total Cr occurred in fraction 3 (35.3%). For this metal, therefore, contributions from pollutant inputs do appear to move into host phases which are different from those containing contributions from natural inputs. The high proportions found for Cr in fraction 3 are in agreement with those of other workers for freshwater (Forstner *et al.*, 1982) or coastal marine sediments (Sadiq, 1992; Boughriet *et al.*, 1994). However, Hong and Forstner (1984), Abaychi and Douabul (1986) and Abu-Hilal (1993) have reported that Cr in sediments of Yellow river, Arabian Gulf and Jordan Gulf of Aqaba, respectively, shows preference for the residual fraction.

Cu: Relative to other trace metals, Cu has a very distinctive partitioning signature, with high percentages of the metal load being located in fractions 4 and 5. The most remarkable feature of this metal is its strong association, in the sediments from Tees estuary, with fraction 4. This trend is typical for this metal in sediments (Salomons and Forstner, 1980). The second most important category is fraction 5. The coarser sediments, from both the Tees Bay and Tees estuary, shows a different behaviour with respect fractions 4 and 5. In these sediments, fraction 5 contains the highest percentages of this metal. These results resemble those reported by other workers in freshwater and coastal marine sediments (Gibbs, 1977; Samant *et al.*, 1990; Nair *et al*, 1991). Those locations high in silt and clay in Tees Bay (sites 4 and 25), which have the highest Cu concentrations in the Tees Bay, were found to contain high percentages of total Cu in fraction 4, indicating a close relationship of this species with the textural class of sediments.

Ni: This metal has a partitioning pattern similar to that described for Cu in coarser sediments, appearing mainly fractions 5 and 4. However, because of the low concentrations of Ni determined in this study, which were less than the average shale or the average shale/Al ratio, the host components appear to be the same in the marine and estuarine sediments. According to the Ni partitioning data gathered from different sedimentary environments (Gupta and Chin, 1975; Tessier *et al.*, 1980; El Ghobary and Latouche, 1986; Zhang *et al.*, 1988; Samant *et al.*, 1990), it appears that the most important fraction of Ni is the residual and that the mobile fraction of Ni is relatively low. This partitioning may be due to the general fact that in the unpolluted sediment Ni is more often in lattice position than in the soluble or mobile form. As indicated by other workers (Gibbs, 1977; Hong and Forstner, 1984; Pardo *et al.*, 1990), this kind of distribution is also significantly different from that encountered in polluted estuarine systems such as Amazon, Yakon, Rhine, and Pisuerga, where the first fractions become largely predominant.

Pb: Pb concentrations in the upper 5 cm of sediments at all Tees Bay and the Tees estuarine sites, except sites 13, 17, 21 and 29, exceed that for uncontaminated sediments (19 ug g^{-1}) reported by Turekian and Wedepol (1961). The highest percentage of Pb corresponded to fractions 3 and 5. These hosts appear to be the same in both the Tees Bay and the Tees estuarine sediments (with the exception of site 21). In all cases, fraction 4 accounts only for a small percentages in the metal load, especially in the Tees Bay sediments. At site 21 a high percentage of Pb is held by fraction 2 for which no suitable explanation can be offered.

Zn: Similarly to Cr, the association of Zn with fractions 3 and 5 differs significantly between the marine and estuarine sediments. There is a possibility that

Zn tends to have higher affinity for fraction 3 than fraction 5 in polluted sediments. The high values found in the Tees estuary sediments for Zn associated with fraction 3 are not surprising as the information gathered by several workers (Chester and Stoner, 1975; Gupta and Chen, 1975; Tessier *et al.*, 1980; Hickey and Kittrick, 1984; El Ghobary and Latouche, 1986) on the Zn partitioning within different environments, suggests that an important fraction of Zn in the sediment is associated with Fe-Mn oxides. In the marine sediments, there are very considerable differences in the partitioning signatures of Zn. The metal in these sediments has a differential behaviour with respect to fractions 3 and 5. In these sediments, however, fraction 5 contain the highest percentages of this metal. These results resemble those reported by other workers in coastal marine sediments (Samant *et al.*, 1990; Izquierdo *et al.*, 1997).

5.3.2. Relationship between metal partitioning and total metal abundance

Pearson correlation coefficients between the total concentration of each metal and the percentage of each metal in each of the five fractions have been calculated to provide an understanding of the relationship between metal abundance and partitioning in the sediments from Tees Bay and the Tees estuary (Tables 5.18 and 5.19, respectively).

In the sediments from Tees Bay (Table 5.18) the most striking relationship is that between the total metal concentration, and the proportion of the metal in fraction 2. This relationship is negative and significant at the 99% confidence level for Cd, Co, Cu and Pb. Thus as the total Cd, Co, Cu and Pb concentrations increase, the proportion of these metals which are associated with fraction 2 decreases (Fig. 5.2). These relationships are highly significant, despite the observation that, apart from Pb, fraction 2 is not a major host for these metals. For Pb, however, the mean proportion of the total associated with fraction 2 is 18.42% (Table 4.9). Also apparent (Table 5.18) are the positive, and highly significant (at 95% confidence level), relationships between the total Co, Cu and Zn concentrations and the percentages of these metals in fraction 4. This indicates that increases in total Co, Cu and Zn are related to increasing metal abundance (Fig. 5.3). However, even at those sites with the highest metal concentrations this fraction accounts for only 10 and 12% of the total Co and Zn (Figs. 5.3a and 5.3c).

Table 5.18 Pearson correlation coefficients for the percentage of each metal in each fraction and the total metal concentrations for sediments from Tees Bay. Significance (2-tailed) in parentheses.

	Sequential Leaching Stage (%)				
Metal	**F1**	**F2**	**F3**	**F4**	**F5**
Cd	-0.38 (0.054)	-0.54** (0.005)	0.05 (0.825)	-	0.38 (0.054)
Co	0.28 (0.173)	-0.59** (0.001)	-0.30 (0.138)	0.69** (0.000)	0.41* (0.036)
Cr	-	-0.30 (0.143)	-0.01 (0.971)	-0.03 (0.884)	0.05 (0.799)
Cu	-	-0.50** (0.009)	-0.50** (0.009)	0.69** (0.000)	-0.49** (0.011)
Ni	-	-0.27 (0.184)	-0.34 (0.091)	0.09 (0.647)	0.20 (0.330)
Pb	-0.20 (0.333)	-0.52** (0.007)	0.44* (0.024)	-0.04 (0.865)	-0.03 (0.887)
Zn	-0.06 (0.778)	-0.17 (0.422)	-0.29 (0.151)	0.56** (0.003)	0.29 (0.152)

** = Correlation is significant at the 0.01 confidence level (2-tailed).
* = Correlation is significant at the 0.05 confidence level (2-tailed).

There are no significant correlations involving fraction 1, and those involving fractions 3 and 5 are less consistent than those discussed above. Correlations between metal concentrations, and the proportion of metal in fraction 3 are generally negative except for Cd and Pb, and only for Cu and Pb are the correlations significant (at the 95% confidence level). The positive relationship between the total Pb concentration and the percentage of Pb in fraction 3 possibly reflects on the tendency of Pb to associate mainly with fraction 3 (Table 4.9). Correlations between total metal concentrations and the proportion of fraction 5 is generally positive apart from Cu, although only for Co and Cu are the observed correlations significant (at the 95 and 99% confidence levels, respectively). The highly significant negative correlation coefficient between the total Cu content and the percentage of Cu in fraction 5 is probably a result of the lesser importance of the residual fraction, in those samples which have a high proportion of the total Cu occurring in fraction 4; i.e. it is a dilution effect.

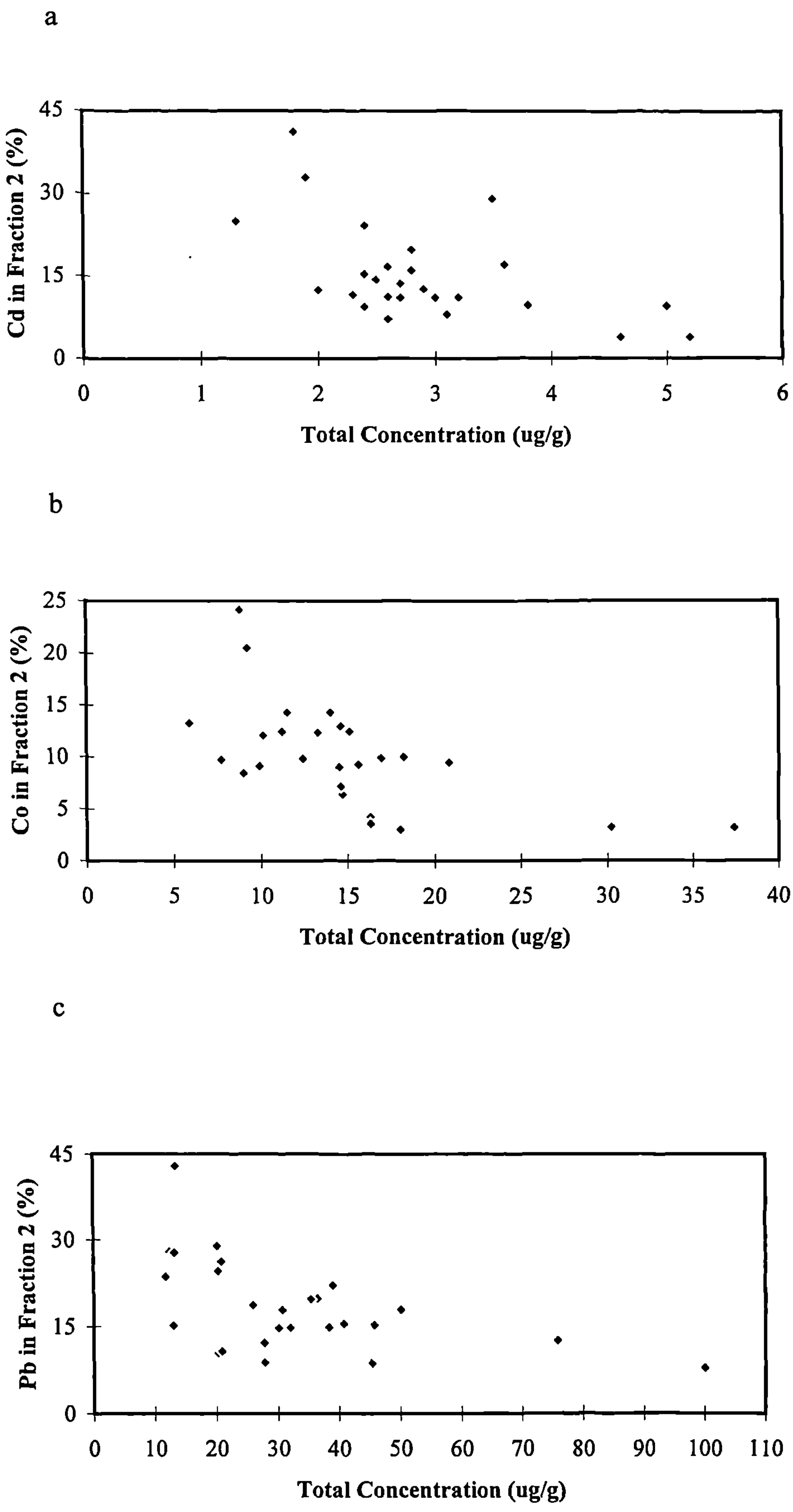


Figure 5.2 Relationship of the percentage of a): Cd, b): Co, and c): Pb in Fraction 2 with respect to their total concentrations in the sediments of Tees Bay.

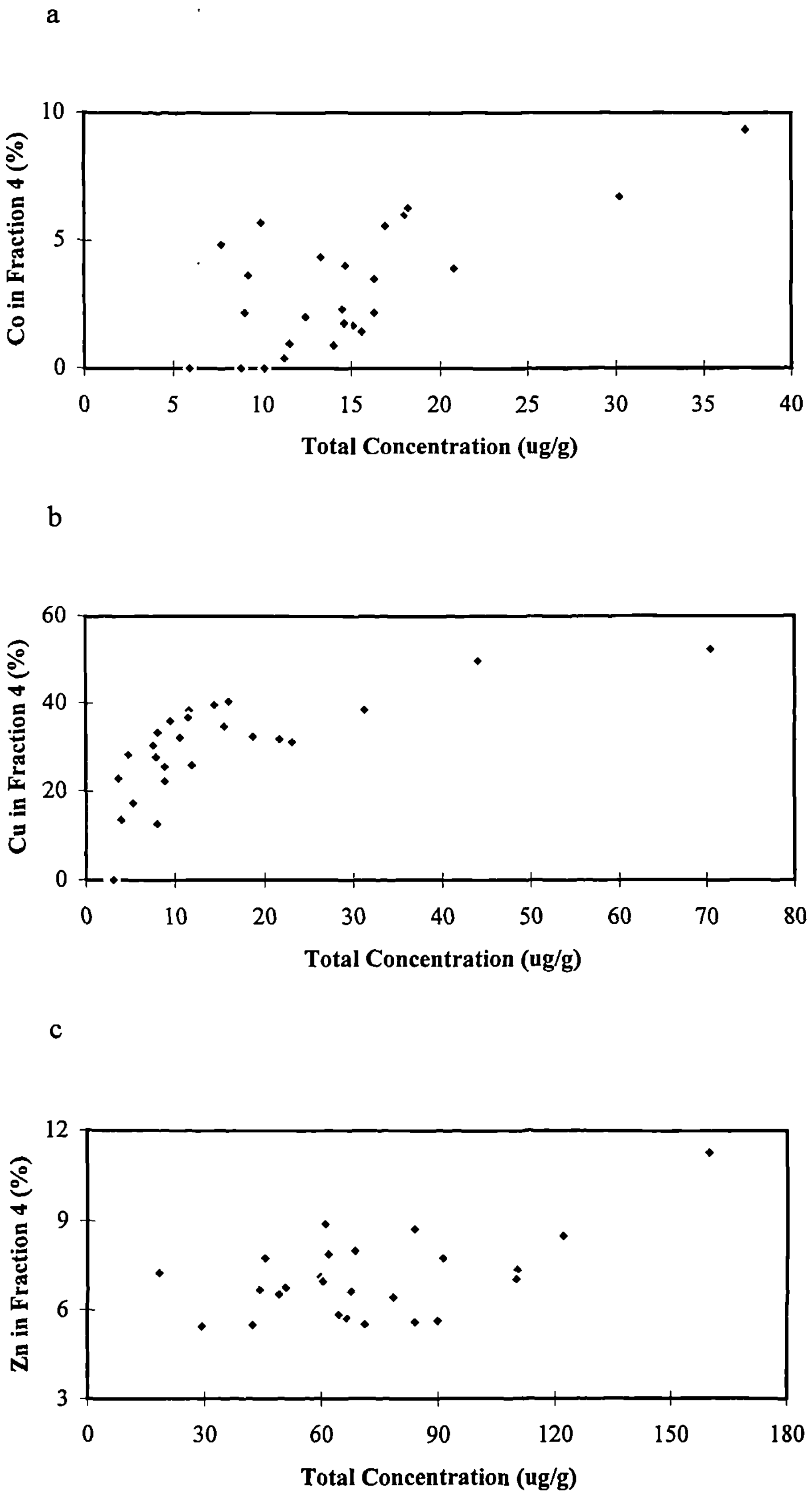


Figure 5.3 Relationship of the percentage of a): Co, b): Cu, and c): Zn in Fraction 4 with respect to their total concentrations in the sediments of Tees Bay.

For the Tees estuary, the correlations between total concentrations of each metal, and the percentage of each metal in each of the five fractions are summarized in Table 5.19. None of the correlations between total metal concentrations, and the metal proportion in fraction 1 are significant and although correlations between the total metals and those associated with fraction 2 tend to be negative, only for Cd is this relationship significant (at the 95% confidence level, but not at the 99% confidence level). The tendency for negative correlations here is consistent with the correlation structure observed for the Tees Bay sediments discussed above, with the proportion of Cd in fraction 2 becoming increasingly important in those samples having low Cd concentration (Fig. 5.4).

Table 5.19 Pearson correlation coefficients for the percentage of each metal in each fraction and the total metal concentrations for sediments from the Tees Estuary. Significance (2-tailed) in parentheses.

	Sequential Leaching Stage (%)				
Metal	**F1**	**F2**	**F3**	**F4**	**F5**
Cd	-0.16 (0.637)	-0.66* (0.026)	0.71* (0.014)	0.37 (0.258)	-0.45 (0.156)
Co	-0.31 (0.368)	0.10 (0.770)	0.09 (0.791)	0.65* (0.031)	-0.23 (0.492)
Cr	-	0.05 (0.884)	0.74** (0.009)	0.32 (0.334)	-0.84** (0.001)
Cu	-	-0.46 (0.155)	-0.69* (0.020)	0.76** (0.007)	-0.75** (0.009)
Ni	-	-0.47 (0.146)	-0.07 (0.849)	-0.73* (0.011)	0.49 (0.127)
Pb	-0.36 (0.280)	-0.44 (0.178)	0.49 (0.129)	0.68* (0.022)	-0.59 (0.058)
Zn	0.53 (0.092)	-0.22 (0.524)	0.17 (0.614)	0.79** (0.004)	-0.66* (0.028)

** = Correlation is significant at the 0.01 confidence level (2-tailed).
* = Correlation is significant at the 0.05 confidence level (2-tailed).

Metal proportions in fraction 3 are strongly correlated with the total for Cd, Cr and Cu. For Cd and Cr the relationships are positive; i.e. the higher the total Cd and Cr contents, the more important fraction 3 is (Fig. 5.5). For Cu, however, there is a negative relationship between the total concentration and the percentage in fraction 3. Thus as total Cu increases the importance of fraction 3 as a Cu carrier declines (Fig. 5.5c).

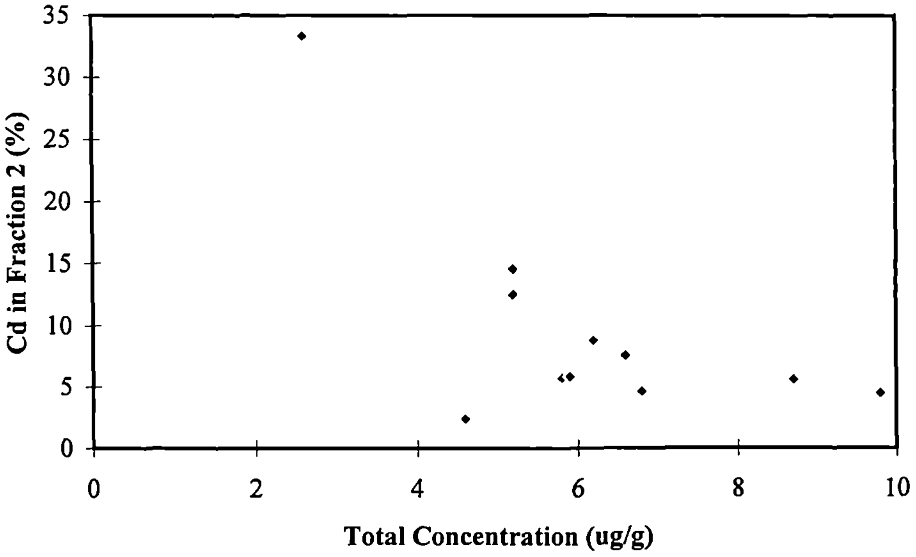


Figure 5.4 Relationship of the Percentages of Cd in fraction 2 with respect to their total concentrations in the sediments of the Tees Estuary.

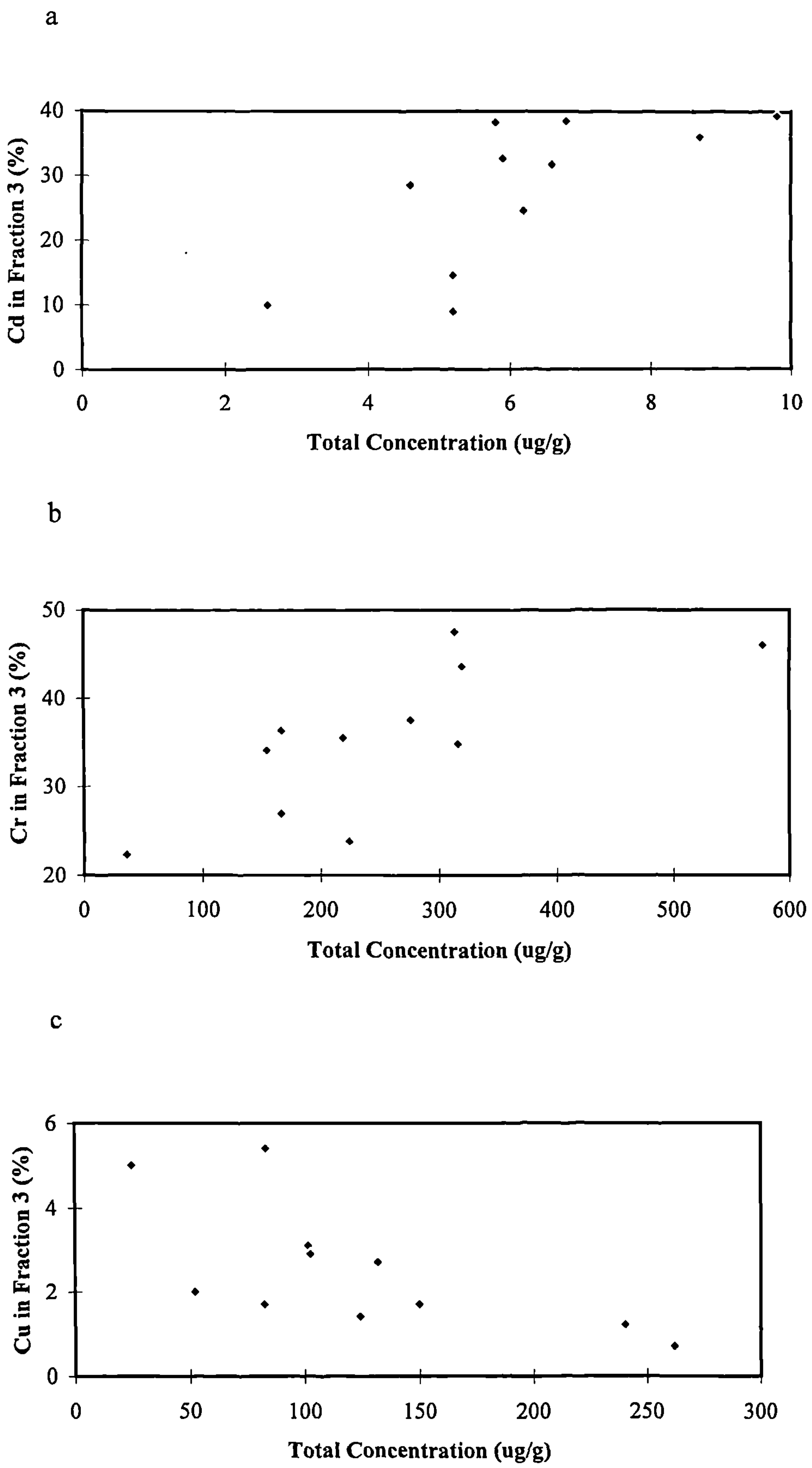


Figure 5.5 Relationship of the percentage of a): Cd, b): Cr, and c): Cu in Fraction 3 with respect to their total concentrations in the sediments of the Tees Estuary.

As in Tees Bay the proportion of the metals associated with fraction 4 tends to be positively correlated (except Ni) with the totals and only for Cd and Cr is this relationship not significant. This suggests the importance of fraction 4 carrier for Co, Cu, Pb and Zn increases as the total metal concentration increases, although even in the richest samples this fraction accounts for only 14% and 16%of the total Co and Pb, respectively (Figs 5.6a and 5.6b). A negative, but still significant (at the 95% confidence level) correlation occurs between the total Ni concentration and the percentage of Ni in fraction 4, with fraction 4 increasing in importance in samples having low Ni concentrations (Fig. 5.6c).

The proportions of Cd, Co, Cr, Cu, Pb and Zn in fraction 5 are negatively correlated with their total concentrations, but the coefficients are not significant for Cd, Co and Pb. The correlations are significant for Cr, Cu and Zn, which are among the more abundant metals in the estuary, and the coefficient is almost significant for Pb, the other abundant metal studied. The coefficients indicate that increases in total Cr, Cu, Zn, and to a lesser extent Pb are accompanied by a decrease in the importance of the residual fraction (Fig. 5.7). This relationship, which is clearly strong in the sediments from the estuary was much less strong in the sediments from Tees Bay. In the Tees estuary the relationship probably reflects the lowering of the importance of the residual (or lithogenic) fraction in those samples with high metal concentrations resulting from anthropogenic inputs.

5.3.3. Relationship between metal partitioning and textural characteristics of the sediments

Correlation matrices summarizing the relationships between the percentage of each metal in each of the fractions extracted, and the sand, silt, clay and TOC contents of the Tees Bay and Tees estuary sediments are presented in Tables 5.20 and 5.21, respectively.

In the Tees Bay sediments, the proportions of the metals bound to fraction 2 are positively correlated with the sand contents, and negatively correlated with the clay contents, but these correlations are not always significant (Table 5.20). Significant correlations with the sand contents are observed for Co (at the 99% confidence level), Cd and Cu (at the 95% confidence level). This suggests that

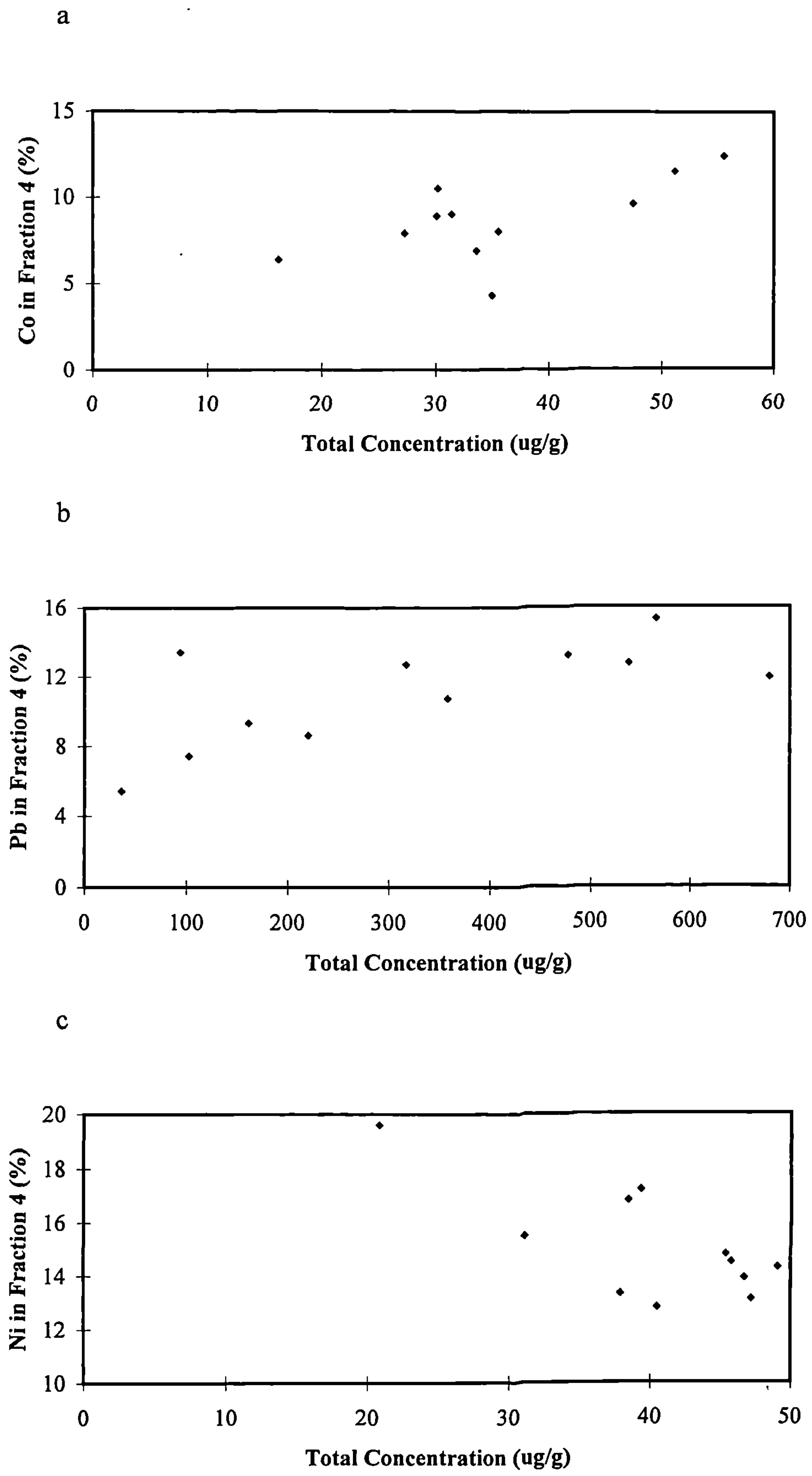


Figure 5.6 Relationship of the percentage of a): Co, b): Pb, and c): Ni in Fraction 4 with respect to their total concentrations in the sediments of the Tees Estuary.

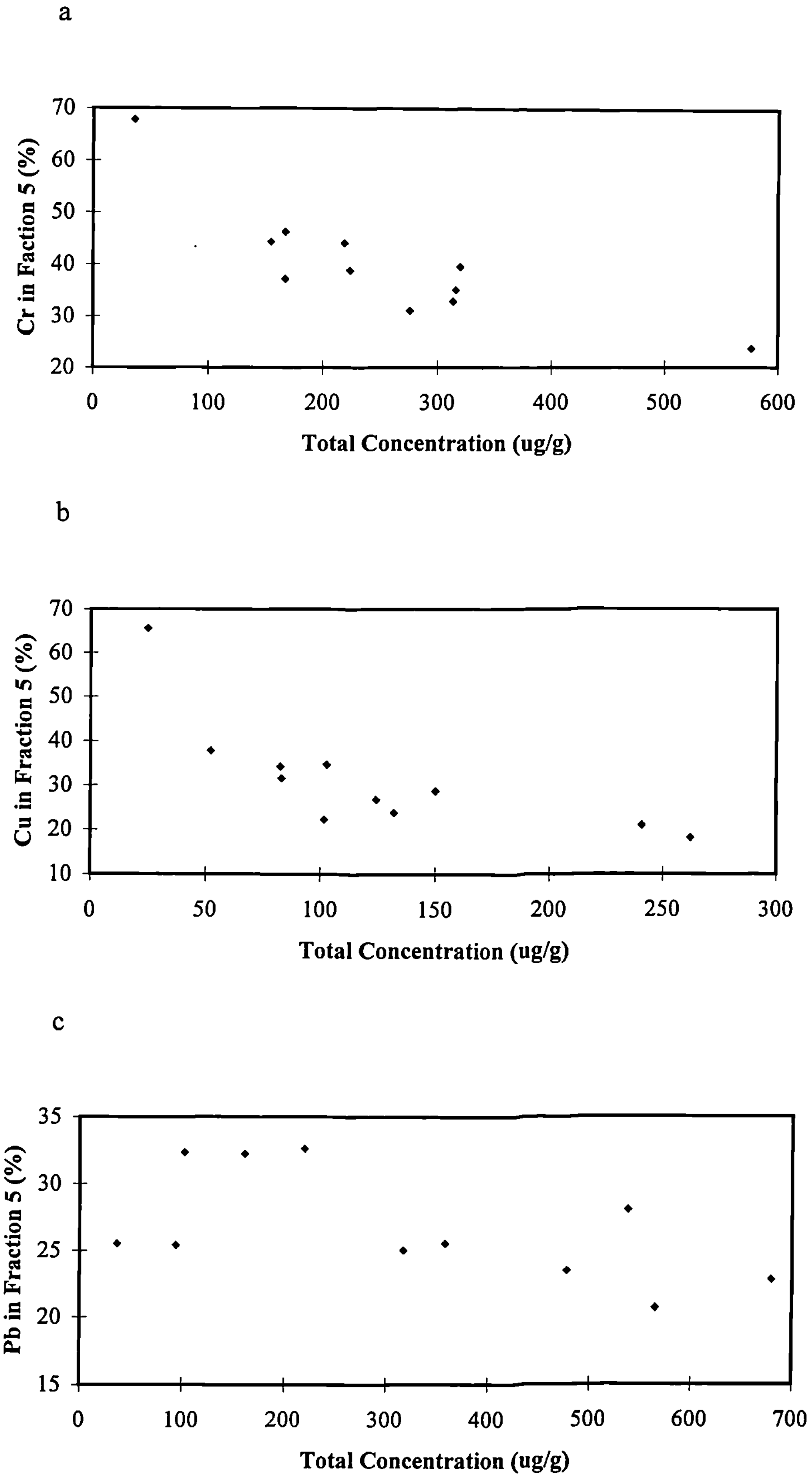


Figure 5.7 Relationship of the percentage of a): Cr, b): Cu, and c): Pb in Fraction 5 with respect to their total concentrations in the sediments of the Tees Estuary.

Table 5.20 Pearson correlation coefficients for the percentage of each metal in each fraction and the textural parameters of the sediments from Tees Bay. Significance (2-tailed) in parentheses.

Metal	Textural characteristics of the sediment	F1	F2	F3	F4	F5
Cd	Sand	0.12 (0.574)	0.48* (0.014)	0.17 (0.413)	-	-0.48* (0.013)
	Silt	-0.12 (0.571)	-0.46* (0.019)	-0.19 (0.360)	-	0.48* (0.013)
	Clay	-0.13 (0.533)	-0.51** (0.008)	-0.11 (0.605)	-	0.45* (0.020)
	TOC	-0.07 (0.724)	-0.43* (0.027)	-0.14 (0.493)	-	0.42* (0.032)
Co	Sand	-0.12 (0.952)	0.57** (0.002)	0.42* (0.031)	-0.67** (0.000)	-0.55** (0.004)
	Silt	-	-0.56** (0.003)	-0.40* (0.044)	0.66** (0.000)	0.52** (0.007)
	Clay	0.03 (0.903)	-0.60** (0.001)	-0.47* (0.017)	0.64** (0.000)	0.61** (0.001)
	TOC	-0.02 (0.912)	-0.54** (0.005)	-0.48* (0.493)	0.73** (0.000)	0.54** (0.004)
Cr	Sand	-	0.23 (0.268)	-0.15 (0.471)	-0.12 (0.555)	0.11 (0.592)
	Silt	-	-0.20 (0.325)	0.16 (0.442)	0.13 (0.537)	-0.12 (0.554)
	Clay	-	-0.27 (0.157)	0.11 (0.586)	0.10 (0.618)	-0.07 (0.725)
	TOC	-	-0.20 (0.319)	0.08 (0.703)	0.06 (0.760)	-0.05 (0.818)
Cu	Sand	-	0.48* (0.013)	0.44* (0.026)	-0.62** (0.001)	0.43* (0.030)
	Silt	-	-0.47* (0.014)	-0.43* (0.031)	0.62** (0.001)	-0.43* (0.028)
	Clay	-	-0.48* (0.12)	-0.47* (0.016)	0.59** (0.002)	0.38 (0.059)
	TOC	-	-0.41* (0.036)	-0.43* (0.029)	0.61** (0.001)	-0.44* (0.023)
Ni	Sand	-	0.16 (0.443)	0.16 (0.442)	-0.15 (0.479)	-0.03 (0.871)
	Silt	-	-0.13 (0.534)	-0.15 (0.466)	0.13 (0.522)	0.03 (0.885)
	Clay	-	0.22 (0.275)	-0.17 (0.395)	0.18 (0.375)	0.04 (0.857)
	TOC	-	-0.18 (0.378)	-0.29 (0.147)	0.18 (0.382)	0.09 (0.661)
Pb	Sand	0.09 (0.667)	0.37 (0.067)	0.35 (0.083)	0.15 (0.480)	0.04 (0.854)
	Silt	-0.07 (0.723)	-0.36 (0.068)	0.33 (0.097)	-0.13 (0.540)	-0.03 (0.901)
	Clay	-0.13 (0.537)	-0.36 (0.072)	0.38 (0.058)	-0.20 (0.328)	-0.07 (0.729)
	TOC	-0.10 (0.619)	-0.40* (0.046)	0.41* (0.036)	-0.04 (0.849)	-0.13 (0.520)
Zn	Sand	0.04 (0.851)	0.29 (0.144)	-0.13 (0.951)	-0.61** (0.001)	0.02 (0.911)
	Silt	-0.03 (0.874)	-0.30 (0.142)	0.02 (0.920)	0.65** (0.000)	-0.04 (0.835)
	Clay	-0.06 (0.789)	-0.29 (0.158)	0.02 (0.936)	0.49* (0.011)	0.01 (0.985)
	TOC	-0.06 (0.770)	-0.32 (0.108)	-0.19 (0.346)	0.54** (0.004)	0.27 (0.180)

** = Correlation is significant at the 0.01 confidence level (2-tailed).

* = Correlation is significant at the 0.05 confidence level (2-tailed).

Table 5.21 Pearson correlation coefficients for the percentage of each metal in each fraction and the textural parameters of the sediments from the Tees estuary. Significance (2-tailed) in parentheses.

Metal	Textural characteristics of the sediment	F1	F2	F3	F4	F5
Cd	Sand	-0.14 (0.701)	-0.43 (0.220)	0.03 (0.933)	0.32 (0.363)	0.06 (0.875)
	Silt	-0.33 (0.348)	0.02 (0.956)	0.37 (0.299)	-0.47 (0.173)	-0.10 (0.774)
	Clay	0.54 (0.109)	0.63 (0.051)	-0.40 (0.248)	-0.04 (0.920)	0.01 (0.969)
	TOC	0.57 (0.877)	0.77** (0.009)	-0.56 (0.095)	-0.12 (0.963)	0.40 (0.250)
Co	Sand	0.12 (0.742)	0.17 (0.641)	-0.33 (0.354)	-0.31 (0.381)	0.29 (0.424)
	Silt	-0.29 (0.454)	-0.04 (0.914)	0.48 (0.156)	0.67* (0.033)	-0.51 (0.130)
	Clay	0.08 (0.828)	-0.22 (0.543)	0.03 (0.937)	-0.18 (0.616)	0.06 (0.860)
	TOC	0.50 (0.144)	-0.42 (0.229)	0.43 (0.214)	0.13 (0.729)	-0.31 (0.383)
Cr	Sand	-	-0.09 (0.798)	-0.08 (0.830)	0.30 (0.403)	-0.25 (0.483)
	Silt	-	-0.36 (0.314)	-0.05 (0.899)	-0.07 (0.852)	0.19 (0.591)
	Clay	-	0.49 (0.152)	0.16 (0.651)	-0.39 (0.268)	0.19 (0.590)
	TOC	-	0.29 (0.418)	0.03 (0.943)	-0.65* (0.040)	0.70* (0.025)
Cu	Sand	-	-0.48 (0.158)	-0.06 (0.865)	-0.31 (0.379)	0.38 (0.274)
	Silt	-	0.20 (0.581)	0.28 (0.438)	0.33 (0.355)	-0.43 (0.216)
	Clay	-	0.54 (0.106)	-0.18 (0.626)	0.16 (0.665)	-0.17 (0.647)
	TOC	-	0.75* (0.012)	-0.11 (0.771)	-0.07 (0.855)	0.06 (0.877)
Ni	Sand	-	0.74* (0.015)	0.25 (0.479)	0.04 (0.915)	-0.36 (0.302)
	Silt	-	-0.82* (0.004)	0.21 (0.567)	0.28 (0.433)	-0.04 (0.923)
	Clay	-	-0.33 (0.356)	-0.59 (0.073)	-0.33 (0.347)	0.59 (0.073)
	TOC	-	-0.44 (0.207)	-0.55 (0.102)	-0.50 (0.146)	0.64* (0.048)
Pb	Sand	-0.34 (0.293)	0.09 (0.805)	0.50 (0.890)	0.001 (0.997)	-0.16 (0.665)
	Silt	-0.05 (0.885)	-0.50 (0.138)	0.28 (0.434)	0.04 (0.923)	0.19 (0.607)
	Clay	0.62 (0.058)	0.35 (0.315)	-0.35 (0.322)	-0.04 (0.920)	0.06 (0.873)
	TOC	0.65* (0.042)	0.26 (0.465)	-0.37 (0.294)	-0.20 (0.578)	0.28 (0.426)
Zn	Sand	-0.32 (0.373)	-0.07 (0.858)	0.24 (0.503)	-0.11 (0.754)	-0.31 (0.379)
	Silt	0.37 (0.297)	-0.42 (0.231)	0.26 (0.473)	-0.11 (0.760)	-0.01 (0.976)
	Clay	0.13 (0.730)	0.51 (0.136)	-0.62 (0.057)	0.28 (0.430)	0.49 (0.153)
	TOC	-0.26 (0.460)	0.46 (0.183)	-0.61 (0.064)	0.22 (0.539)	0.60 (0.067)

** = Correlation is significant at the 0.01confidence level (2-tailed).
* = Correlation is significant at the 0.05 confidence level (2-tailed).

fraction 2 becomes increasingly important as a host for Co, Cd and Cu in samples having high sand content (Fig. 5.8) and that its importance declines in the more clay rich samples. The relationship between metal partitioning and grain size is less clear for fraction 3. Most of the correlations are positive although only for Co and Cu is the relationship significant (at the 95% confidence level). For these elements at least, fraction 3 is quantitatively a more important metal host in the sandier sediments. Relationships between the proportions of total metals in fraction 4 and the sand contents tend to be negative. This is significant for Co, Cu and Zn (at the 99% confidence level) and is probably due to the well known trend for organic matter to be higher in finer sediments. This suggestion is further supported by the significant and positive correlations between the percentages of Co, Cu and Zn in fraction 4 and the TOC content of the sediments (Fig. 5.9), as well as between these three metals in fraction 4 and the fine grain size fractions (silt and Clay) of the sediments (Fig. 5.10). The relationship between the percentage of metal in fraction 5 and the sand content of the sediments is negative and significant for Cd and Co, and positive and significant for Cu. This suggests that for Cd and Co there may be residual bound metal in the finer sediments (clay and silt), whereas for Cu, the residual bound metal is mainly in the coarser residual fraction.

As in section 5.2.5.1, the correlation coefficients for the Tees estuary sediments are calculated after removing the data from site 42 from the data set. The resulting correlation matrices are presented in Table 5.21. due to the small number of data points very few of the correlations are significant and meaningful interpretation is difficult. However, it is apparent from the data in Table 5.21 that the percentages of all metals, except Cr, in fraction 4 are poorly correlated with the TOC content of the sediments, suggesting that the TOC does not influence the concentrations of these metals in this fraction, in the Tees estuary. For Cr there is a negative significant relationship (at the 95% confidence level) between the TOC content of the sediments and the percentage of Cr in fraction 4. Thus as TOC content increases the importance of Cr associated with fraction 4 diminishes.

It can also be seen from the data in Table 5.21 that the sand content of the sediments is negatively correlated with the percentage of Ni in fraction 2 (at the 95% confidence level), and that it does not show any significant correlations with metals in

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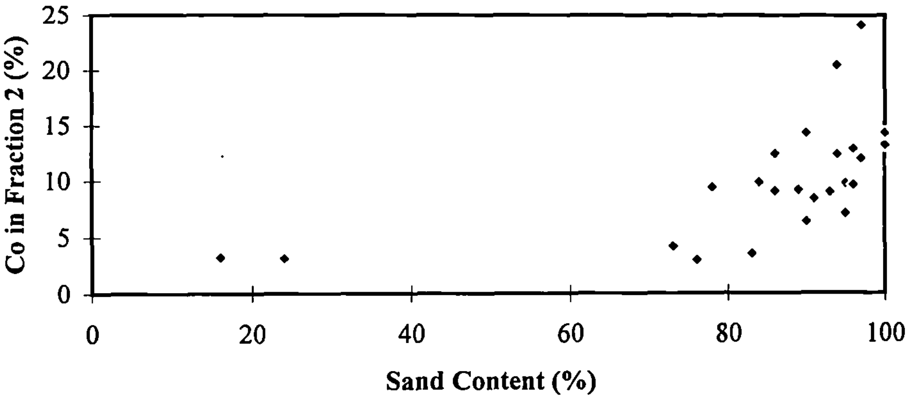

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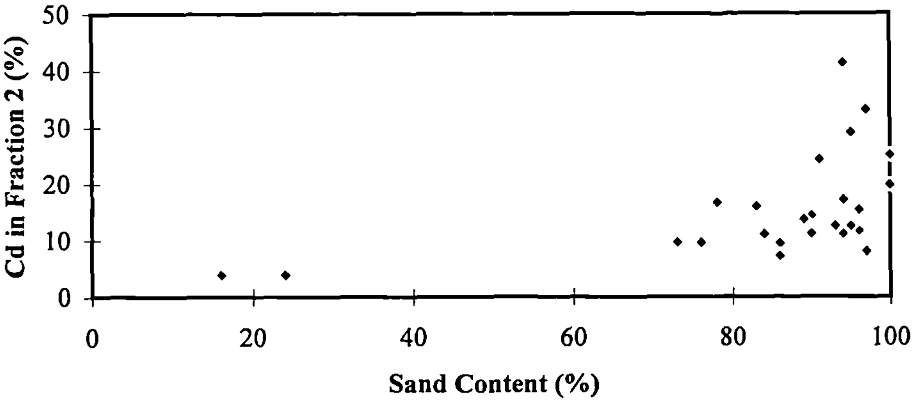


c

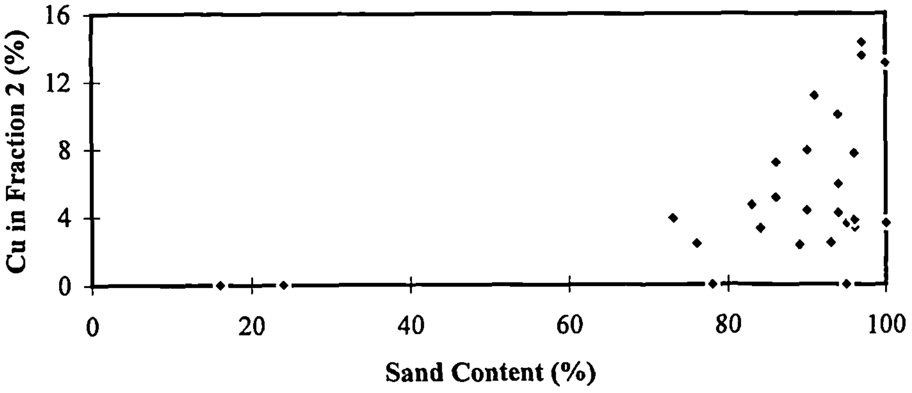
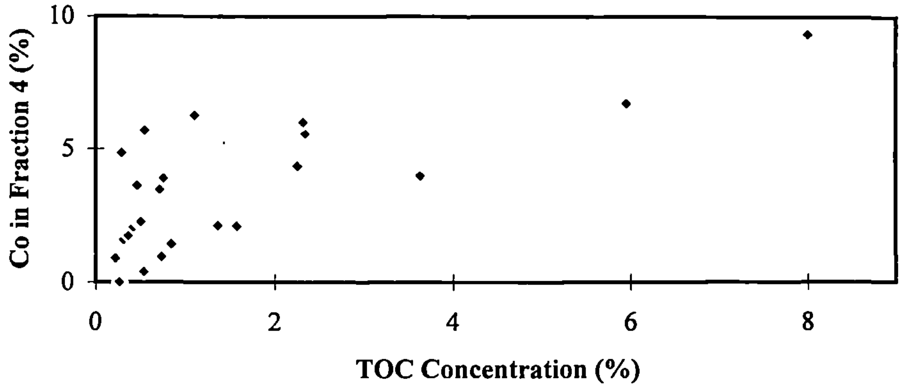
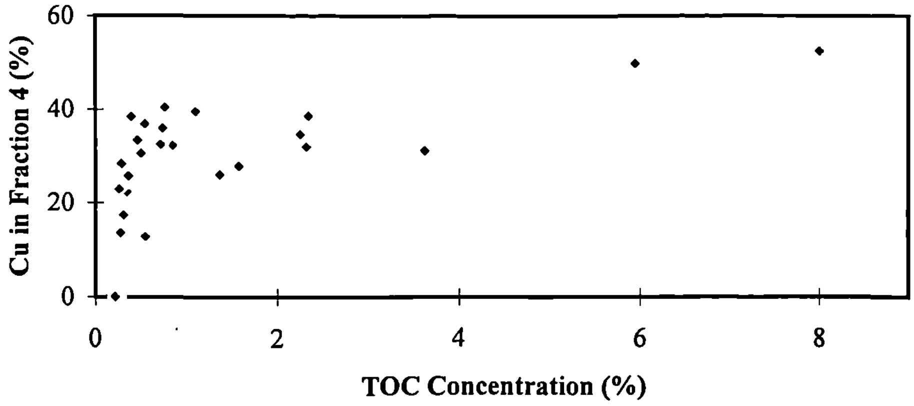


Figure 5.8 Relationship of the percentage of a): Co, b): Cd, and c): Cu in with respect to the sand content in the sediments of Tees Bay.

a



b



c

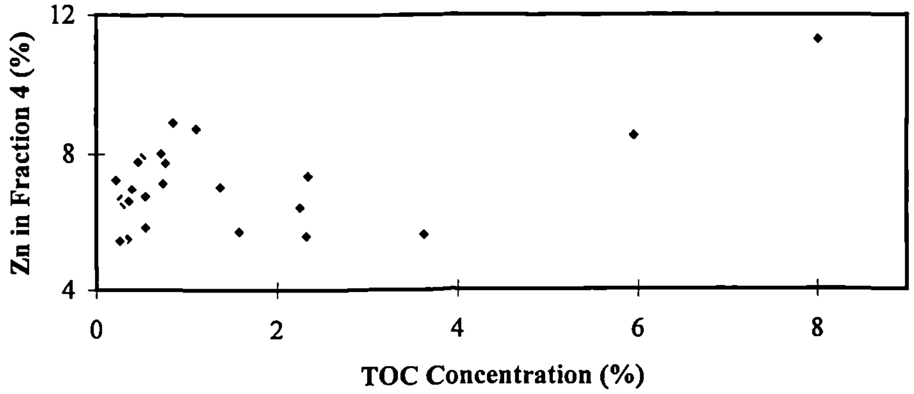
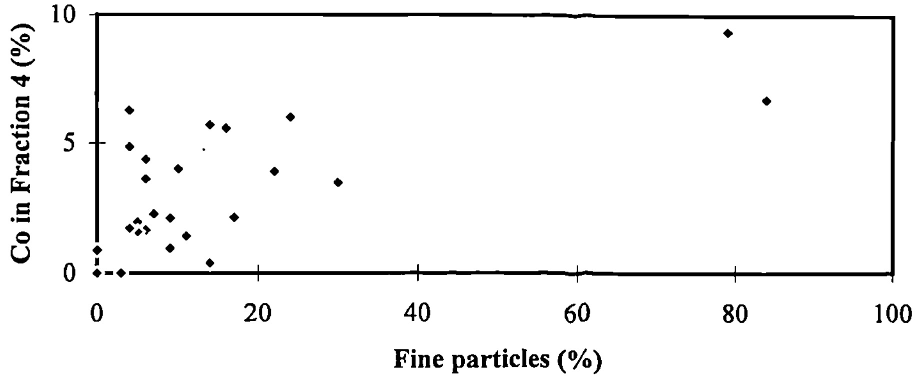
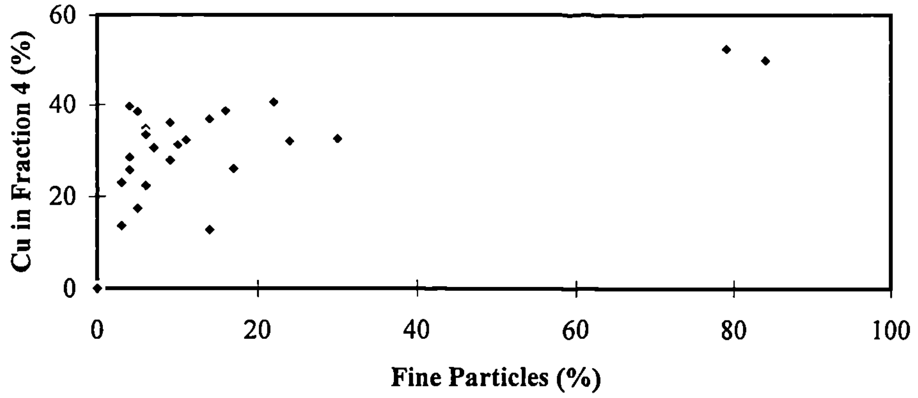


Figure 5.9 Relationship of the percentage of a): Co, b): Cu, and c): Zn in fraction 4 with respect to the TOC content in the sediments of Tees Bay.

a



b



c

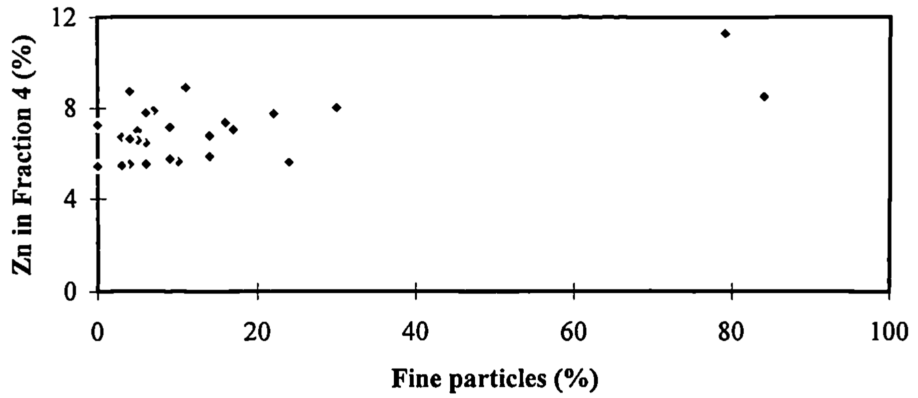


Figure 5.10 Relationship of the percentage of a): Co, b): Cu, and c): Zn in fraction 4 with respect to the fine particles contents (silt+clay) content in the sediments of Tees Bay.

any other fractions. The silt content of the sediments is significantly correlated with the percentage of Co in fraction 4 and with the percentage of Ni in fraction 2, and the clay content of the sediments does not show any significant correlations with metal partitioning. This indicates that the textural characteristics of the sediments do not influence the partitioning of most metals, in the Tees estuary, to the same extent as in the sediments from Tees Bay.

5.4 Summary

1- With the exception of Ni, concentrations of all metals in sediment samples from the Tees estuary are generally above natural background levels. Sediment at site 42 exhibited the lowest total metal concentrations, as a result of the predominantly sandy nature. In Tees Bay, concentrations of Co, Cr, Cu, Ni and Zn are lower than those of average shale at all sites other than sites 4 and 25. Cd and to a lesser extent Pb were present in concentrations above the geochemical background levels.

2- All of the metals measured (Cd, Co, Cr, Cu, Ni, Pb and Zn) have significantly higher concentrations in the sediments of the Tees estuary than in those of Tees Bay ($P<0.01$). These significantly higher concentrations remain apparent when the data are normalized to remove the effect of grain size variation, suggesting that the sediments of the Tees estuary are enriched in metals in comparison with the sediments of Tees Bay and that these differences are not the result of the different grain size distributions.

3- The high concentration of metals found in this study are generally consistent with those of Davies *et al.* (1991), and also confirm the systematic decline in Cu and Zn concentrations, and the probable lowering of Pb concentrations over time, as suggested by Davies *et al.* (1991). The data also revealed elevated concentrations, for Cd, Cr and Co, compared to those reported in 19 other UK estuaries.

4- Comparison of the mean values of metals in Tees Bay sediments with an earlier study reported by Taylor (1979) showed that the mean concentrations of Cd, Co, and Cr found in this study are significantly higher (at the 95% confidence level) to the concentrations reported by Taylor (1979), whilst the concentrations of Cu, Ni, Pb and Zn, found in this study, are not significantly higher (at the 95% confidence level) to those reported by Taylor (1979). Further comparison of the mean metal concentrations measured in Tees Bay with data from similar environments around the world suggests that mean levels of Cd and Pb are similar in magnitude to those of slightly to moderately polluted areas, while Co, Cr, Ni and Zn concentrations are generally similar to those of unpolluted areas.

5- Sediment characteristics, such as particle size and TOC content, significantly influence the geographical distribution of metals in Tees Bay. Positive and significant (at the 99% confidence level) correlations are found between increasing metal concentrations and increasing TOC content and fine-grained fraction. This suggests that the highest metal concentrations, in Tees Bay sediments, are generally found in the fine-grained organic sediment, while the sandy sediment commonly exhibited the lowest level of the metals analyzed. For the Tees estuary, metals are negatively correlated with TOC although these correlations are only significant for Pb at the 95% confidence level. This is probably due to the presence of the sandy sediment at site 42 which is particularly enriched in organic carbon due to the presence of coal particles, but which has very low metal contents. If the Tees estuary data are re-calculated without the sandy sediment from site 42, it was found that the TOC content is positively correlated with metals, but only for Co is the relationship significant at the 99% confidence level whilst the relationship is positively significant at the 95% level for Ni. These observations are found to be in agreement with the findings of Davies *et al.* (1991) that the TOC content does not influence metal concentrations in the Tees estuary sediments.

6- Metal partitioning, which is of critical importance in assessing the likely behaviour of metals in the aquatic system, was determined using a five-stage sequential leaching technique based on that of Tessier *et al.* (1979). This is the first study to report metal partitioning for Tees Bay and the Tees estuary sediments. The application of this technique, to sediment samples from Tees Bay and the Tees estuary, showed that the partitioning characteristics of a number of trace metals differed among the host components. It was also shown that the partitioning of some trace metals were different in marine and estuarine sediments. In Tees Bay sediments, the most abundant fraction for all metals except Cd and Pb is the residual one. The metal associated with this fraction cannot be remobilized under the conditions normally encountered in nature. The partitioning patterns of Cd and Pb, which are the highly enriched metals in these sediments, are similar, with fractions 3 and 5 being of greatest significance. In the Tees estuary sediments, there is much more metal pollution than on the Tees Bay. The percentages of Cr, Cu and Zn associated with the residual fraction are notably lower than those obtained on the Tees Bay. Cr, Pb and Zn are associated with fractions 3, 5 and 4. Cd, is similar, with fraction 1 also significant. Cu associated with fractions 4 and 5, and Co and Ni are hosted mainly by fraction 5.

7- The association of Cr, Cu, Pb and Zn, which are among the more abundant metals in the studied sediments, with fractions 3 and 5 differs significantly between the marine and estuarine sediments. There is a possibility that these metals tend to have higher affinity with fraction 3 (for Cr, Pb and Zn) or 4 (for Cu) than fraction 5 in polluted sediments. The proportions of Cr, Cu, Pb and Zn in fraction 5 are negatively correlated with their total concentrations, but the coefficients are not significant for Pb. The correlations are significant for Cr, Cu and Zn, which are among the more abundant metals in the estuary, and the coefficient is almost significant for Pb, the other abundant metal studied. The coefficients indicate that increases in total Cr, Cu, Zn, and to a lesser extent Pb are accompanied by a decrease in the importance of residual fraction. This relationship, which is clearly strong in the sediments from the estuary, was much less strong in the sediments from Tees Bay. In the Tees estuary the relationship probably reflects the lowering of the importance of the residual (or lithogenic) fraction in those samples with high metal concentrations resulting from anthropogenic inputs.

Chapter Six

Aliphatic Hydrocarbons

6.0 Aliphatic Hydrocarbons

6.1 Introduction

With the great increase in worldwide transportation of petroleum and petroleum products (refined oil, solvent, and plastics to name only a few), concern has grown over the extent and effect of accidental spills and other inputs to the aquatic environment. Elevated petroleum hydrocarbon levels, from different sources (e.g. oil spills, sewage outfalls and tanker ballast waste water), have been observed in most estuarine and coastal sediments around the world (Farrington *et al.*, 1977; LaFlamme and Hites, 1978). In recent years, increasing emphasis has been placed on the transport and fate of petroleum hydrocarbons in estuarine and coastal waters. Since these compounds are largely hydrophobic and lipid soluble, a major transport mechanism of these compounds in riverine and estuarine systems is via their association with suspended particulates (Van Vleet and Quinn, 1977; Hamilton, *et al.*, 1984), which are finally trapped in sediments. Field studies have shown that hydrocarbons from oil spills are able to persist in sediments for long periods of time (Blumer and Sass, 1972).

The pressure of industrial development and rising populations in the coastal zone is likely to result in increased pollutant loadings of petroleum hydrocarbons to the estuaries. The Tees estuary, which receives about 0.5×10^6 m^3 day^{-1} of the industrial effluents (Johnston *et al.*, 1991), is also subjected to major inputs of organic chemicals, in largely unknown amounts, from agricultural and street run-off, untreated sewage and waste water discharges, atmospheric fall-out, and ship and boat traffic. A major fraction of petroleum consists of aliphatic hydrocarbons which may be used to detect its presence in the environment (Al-Saad, 1987). Aliphatic hydrocarbons are among the most important contaminants of the aquatic environment. Despite its importance, no published data concerning the fate of aliphatic hydrocarbons in the Tees are available.

The aims of the present chapter are to survey the aliphatic hydrocarbons in sediments from Tees bay and the Tees estuary and to establish the importance of parameters derived from these hydrocarbons for the estimation of aquatic environment pollution.

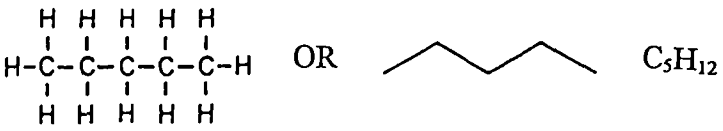
6.2 Aliphatic hydrocarbons

Aliphatic hydrocarbons, alkanes (paraffins) and cycloalkanes (naphthenes), are composed entirely of carbon and hydrogen, and contain no aromatic rings. They are straight- cyclic or branched-chain compounds. They can be saturated (no double bonds) or unsaturated (i.e. contain double or triple bonds).

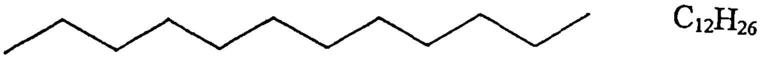
Alkanes are saturated compounds - that is all the carbon atoms are linked to other atoms by four single bonds, the maximum possible. Saturated hydrocarbons (alkanes) are widespread natural products on earth, and are primarily the products of living processes (Streitwieser and Heathcock, 1985). The straight-chain structures (normal alkanes or paraffins) are the simplest hydrocarbons (Fig. 6.1). They occur in a continuous homologous series in most crude oils and usually form a major component of crudes and most refined products except lubricating oils. Differences in *n*-alkane series may be used to indicate the presence of petroleum-derived materials, in particular to differentiate between petrogenic and biogenic sources (e.g. Readman *et al.*, 1986; Colombo *et al.*, 1989). On the other hand, iso-branched alkanes, a specific term for an alkane with a methyl branch at C-2, are usually present in relatively high concentration. Theoretically, the branches could be several, or even many, carbon linkages long. However, it is characteristic of the isoalkanes (isoparaffins) found in petroleum that they are predominantly those with single carbon atom (methyl) branches. From C_9 upwards, the most abundant branched alkanes (isoalkanes) are isoprenoids (i.e. are based on linked isoprene structures) with pristane and phytane (Fig. 6.1) being the most abundant (Butt *et al.*, 1985).

Cycloalkanes, or naphthenes, are the cyclopentane and cyclohexane series having five and six carbon atoms, respectively, in the ring (Fig. 6.2). They are saturated compounds (alkanes) but have a number of atoms bonded to form saturated rings (Butt *et al.*, 1985). Up to five rings may be joined together (or condensed) in the more complex molecules. Many naphthenes contain the biogenic-indicative isoprene structure. Triterpanes have the basic structure of six isoprene units which form molecules containing five condensed 6-membered rings (e.g. oleanane; Fig. 6.2) or four 6-membered and one 5-membered rings (e.g. hopane; Fig. 6.2). Depending on the length and number of side chains present, triterpanes usually contain 27-35 carbon atoms. Steranes contain only four rings, three 6-membered and one 5-membered, with

Normal paraffins

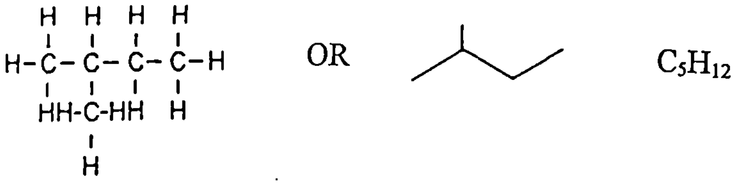


Normal pentane



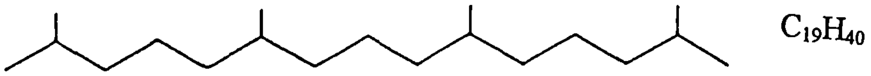
Normal dodecane

Isoparaffins



Isopentane or 2-methylpentane (isoprene structure)

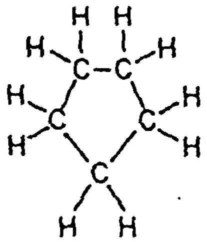
Isoprenoids



Pristane (2, 6, 10, 14-tetramethylpentadecane)

Phytane (2, 6, 10, 14-tetramethylhexadecane)

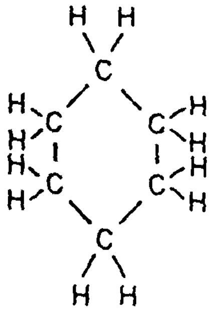
Figure 6.1. Examples of normal and isoparaffins.



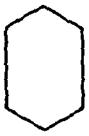
OR

C_5H_{10}

Cyclopentane



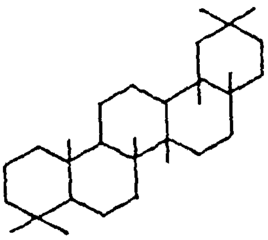
OR



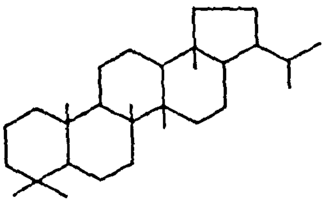
C_6H_{12}

Cyclohexane

Triterpanes

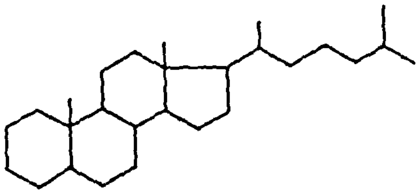


Oleanane $C_{30}H_{52}$



C_{30}-Hopane $C_{30}H_{52}$

Steranes



Cholestane $C_{27}H_{48}$

Figure 6.2. Examples of naphthenes occurring in petroleum.

a total of 27-30 carbon atoms (e.g. cholestane; Fig. 6.2). Triterpanes and steranes in the geosphere have been widely studied for geochemical reasons and are accepted as being derived from precursor triterpenoids and sterols in living systems (Butt *et al.*, 1985). They are present in low relative abundance in oils and coal and are generally resistant to weathering and bacterial degradation (Albaiges and Albrecht, 1979; Volkman *et al.*, 1992).

6.3 Results

For the purpose of this study, sediment samples, from Tees Bay and the Tees estuary, will be designated by the station numbers where metals were measured (Chapter 3, Figs. 3.1 and 3.2, respectively). Data for several stations were not collected because these samples were used for other purposes. The grain size analysis and total organic carbon (TOC), carbonate carbon and sulphur concentrations, in the surface sediments from Tees Bay and the Tees estuary, are presented in Chapter 4 (section 4.1) and discussed in Chapter 5 (section 5.1).

6.3.1 Normal alkanes (*n*-alkanes) and unresolved complex mixture (UCM)

Examples of gas chromatograms of aliphatic hydrocarbons isolated from the surface sediments from Tees Bay and the Tees estuary are shown in Figures 6.3 and 6.4, respectively. These chromatograms clearly show that the dominant identified components in the aliphatic hydrocarbons are *n*-alkanes which are present as a homologous series from about C_{14} or C_{15} to C_{33} for all samples. They also show that the distributions of *n*-alkanes in the samples from both areas are generally different. Quantitative results obtained from the chromatograms of *n*-alkanes isolated from the sediment extracts of Tees Bay and the Tees estuary are listed in Tables 6.1 and 6.2, respectively. In these two tables the concentration of *n*-alkanes have been determined, and are expressed in terms ug g^{-1} dry weight. Data in Tables 6.3 and 6.4, on the other hand, are the percentages of each *n*-alkanes to total *n*-alkanes, in sediments from both areas.

Peak identification was performed by comparison with retention times of authentic standards and by GC/MS (including selective ion monitoring: *m/z* 85 for *n*-alkanes; *m/z* 217 for steranes; *m/z* 191 for terpanes). *n*-Alkane distributions are,

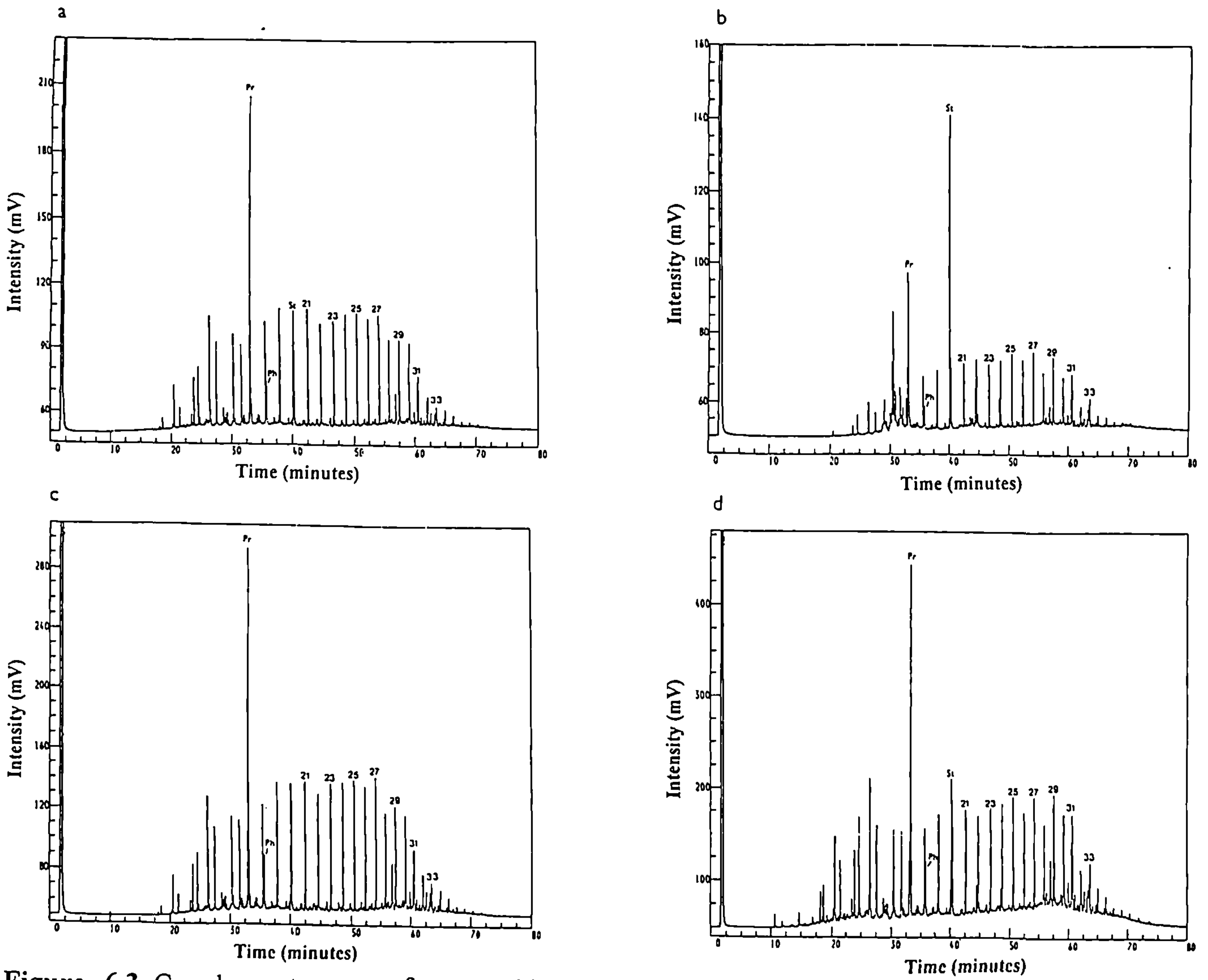


Figure 6.3. Gas chromatograms of saturated hydrocarbons in sediments from Tees Bay: a) site 1; b) site 20; c) site 5; and d) site 25. St, internal standard (1- eicosene); Pr, pristane; Ph, phytane. Numbers *n* (16-33) indicates carbon numbers of *n*-alkanes. Chromatographic conditions are described in Chapter 3.

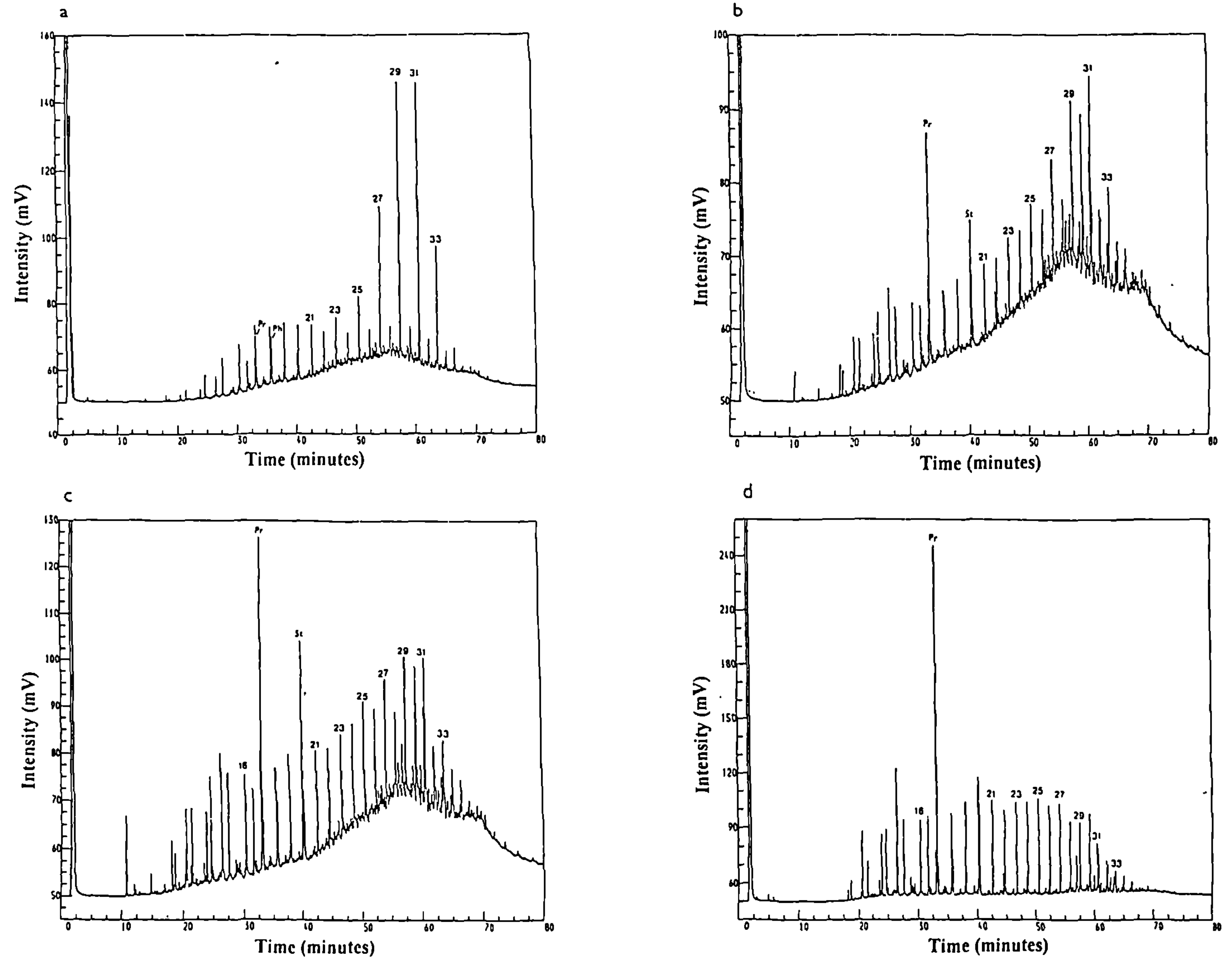


Figure 6.4. Gas chromatograms of saturated hydrocarbons in sediments from the Tees Estuary: a) site 33 (group A); b) site 38 (group B); c) site 40 (group C); and d) site 42 (group D). Peak identification and chromatographic conditions as for Fig. 6.3.

Table 6.1 *n*-Alkanes concentrations (ug g^{-1}, dry weight) in surface sediments from Tees Bay.

Sample No.	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}
1	1.16	1.07	1.25	1.34	1.44	1.46	1.28	1.37	1.43	1.48	1.33	1.42	1.04	1.08	1.55	0.68	0.51	0.28
2	0.51	0.48	0.52	0.60	0.66	0.61	0.53	0.58	0.63	0.67	0.55	0.71	0.46	0.70	0.83	0.60	0.36	0.29
3	0.28	0.22	0.24	0.26	0.31	0.29	0.27	0.27	0.28	0.31	0.26	0.31	0.22	0.28	0.32	0.24	0.15	0.11
4	2.33	1.96	2.59	2.76	2.89	2.80	2.40	2.70	2.77	3.18	2.68	3.29	2.23	3.14	4.51	2.77	1.57	1.38
5	1.65	1.59	1.88	1.98	2.04	2.21	1.98	2.09	2.19	2.33	2.08	2.25	1.65	1.79	2.62	1.06	0.79	0.42
6	1.90	1.17	1.17	1.29	1.44	1.42	1.34	1.43	1.53	1.57	1.40	1.48	1.10	1.14	1.73	0.70	0.51	0.37
10	0.28	0.25	0.25	0.28	0.9	0.30	0.28	0.29	0.30	0.32	0.28	0.31	0.23	0.25	0.32	0.16	0.10	0.07
13	0.07	0.08	0.03	0.03	0.06	0.04	0.06	0.04	0.04	0.04	0.03	0.04	0.03	0.04	0.05	0.04	0.02	0.02
14	0.02	0.06	0.04	0.05	0.06	0.06	0.06	0.06	0.06	0.07	0.06	0.07	0.05	0.06	0.07	0.05	0.02	0.03
17	0.03	0.04	0.03	0.03	0.05	0.03	0.04	0.03	0.03	0.03	0.03	0.04	0.02	0.04	0.04	0.03	0.01	0.01
18	0.20	0.19	0.21	0.23	0.26	0.26	0.23	0.25	0.25	0.29	0.24	0.30	0.19	0.29	0.35	0.23	0.12	0.11
20	0.04	0.09	0.08	0.09	0.13	0.10	0.13	0.14	0.16	0.17	0.15	0.15	0.10	0.13	0.15	0.10	0.06	0.08
21	0.23	0.21	0.21	0.23	0.24	0.27	0.27	0.28	0.30	0.32	0.28	0.32	0.22	0.27	0.30	0.16	0.12	0.12
22	0.01	0.02	0.03	0.03	0.06	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.01	0.1
24	0.23	0.29	0.30	0.33	0.40	0.36	0.32	0.33	0.34	0.38	0.32	0.38	0.24	0.33	0.44	0.26	0.15	0.12
25	2.61	1.78	2.32	2.51	2.91	2.79	251	2.79	2.76	3.10	2.62	3.26	1.95	2.97	2.09	2.11	0.94	0.86
26	0.03	0.03	0.02	0.03	0.04	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.03	0.04	0.06	0.03	0.02	0.02
27	0.11	0.09	0.09	0.10	0.11	0.11	0.10	0.12	0.11	0.12	0.11	0.12	0.08	0.10	0.13	0.08	0.05	0.04
28	0.22	0.16	0.17	0.19	0.20	0.22	0.21	0.25	0.26	0.28	0.25	0.26	0.20	0.21	0.22	0.014	0.08	0.10
29	0.01	0.04	0.03	0.02	0.04	0.03	0.04	0.02	0.02	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.01	0.01

Table 6.2 *n*-Alkanes concentrations (ug g^{-1}, dry weight) in surface sediments from the Tees Estuary.

Sample No.	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}
33	2.72	2.99	3.20	2.92	3.33	2.81	2.09	2.79	1.69	4.38	1.89	8.26	1.57	13.65	4.07	14.32	1.99	6.96
34	1.84	1.57	1.57	1.72	1.75	2.06	1.54	2.50	2.42	5.17	1.89	8.35	2.63	14.59	4.25	20.43	2.95	10.89
35	1.74	1.65	1.61	1.57	2.26	2.20	1.87	2.73	2.71	4.62	2.17	6.66	2.06	10.39	6.74	14.61	3.03	8.24
36	2.10	1.78	1.91	2.75	2.08	2.77	1.98	2.72	2.37	6.55	2.88	8.43	3.40	15.53	10.79	18.35	4.47	8.62
37	1.72	1.75	1.95	2.50	2.63	2.40	1.80	2.60	2.44	4.22	2.26	6.00	2.71	8.36	8.30	12.06	3.66	7.59
38	2.82	2.57	2.66	2.62	3.27	3.32	2.43	2.96	3.18	5.02	3.23	5.78	2.75	7.40	7.15	9.64	3.74	3.85
39	2.50	1.27	1.75	2.28	2.20	2.06	1.80	2.28	2.09	3.16	2.08	4.12	1.51	4.16	5.29	5.66	2.74	3.96
40	2.57	2.1	2.41	2.47	3.23	2.83	2.53	2.67	3.14	3.49	2.80	3.89	2.18	4.02	5.51	4.24	2.19	1.95
41	2.75	2.33	2.67	2.84	3.37	3.07	2.71	2.86	3.02	3.77	3.06	3.78	2.46	3.99	4.54	3.61	1.82	1.56
42	3.39	2.92	3.45	3.72	4.21	4.17	3.63	3.96	4.11	4.35	3.82	4.15	2.93	3.24	5.66	2.33	1.80	1.06
43	2.18	1.96	2.03	2.29	2.30	2.32	2.23	2.59	2.81	3.14	2.63	3.27	2.16	2.78	3.90	2.61	1.41	2.29

Table 6.3 *n*-Alkanes concentrations (%) in surface sediments from Tees Bay.

Sample No.	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}
1	5.47	5.04	5.89	6.33	6.79	6.89	6.06	6.48	6.74	6.98	6.30	6.70	4.92	5.13	7.32	3.23	2.39	1.33
2	5.00	4.66	5.09	5.81	6.40	5.95	5.13	5.63	6.10	6.50	5.37	6.90	4.45	6.78	8.06	5.87	3.52	2.78
3	6.14	4.82	5.20	5.69	6.59	6.18	5.92	5.87	6.08	6.59	5.70	6.74	4.70	6.15	6.93	5.19	3.14	2.37
4	4.87	4.09	5.40	5.75	6.02	5.84	5.00	5.62	5.79	6.62	5.60	6.87	4.65	6.54	9.40	5.78	3.27	2.87
5	5.05	4.86	5.77	6.08	6.26	6.76	6.08	6.42	6.73	7.14	6.37	6.90	5.07	5.49	8.03	3.24	2.44	1.29
6	8.36	5.15	5.16	5.70	6.37	6.28	5.92	6.29	6.74	6.90	6.19	6.53	4.84	5.04	7.61	3.07	2.24	1.63
10	6.27	5.41	5.50	6.13	6.40	6.67	6.06	6.44	6.52	7.03	6.21	6.78	4.96	5.40	6.97	3.42	2.28	1.54
13	8.83	10.70	3.85	4.09	8.21	5.36	7.75	4.76	4.81	5.50	4.54	5.82	3.53	5.22	6.05	5.68	2.43	2.88
14	1.86	5.85	4.69	5.35	6.56	5.95	6.61	6.30	6.63	7.16	6.18	7.18	4.84	6.78	7.09	5.38	2.55	3.02
17	5.56	7.79	4.71	5.35	8.13	5.92	7.30	5.37	5.48	6.11	5.17	6.42	3.86	6.34	6.66	5.04	2.52	2.26
18	4.72	4.48	4.95	5.49	6.11	6.22	5.58	6.04	5.93	6.87	5.72	7.05	4.52	6.93	8.41	5.52	2.84	2.61
20	1.79	4.59	3.81	4.25	6.16	5.13	6.52	6.72	7.69	8.11	7.13	7.60	4.86	6.46	7.46	4.99	2.76	3.95
21	5.34	4.82	4.87	5.40	5.48	6.16	6.15	6.44	6.90	7.41	6.45	7.28	5.03	6.23	6.81	3.78	2.66	2.78
22	2.46	4307	5.93	5.42	12.04	6.24	6.73	5.77	5.75	6.45	5.38	6.53	4.01	5.58	6.65	5.45	2.82	2.73
24	4.1	5.35	5.50	5.91	7.18	6.44	5.73	6.00	6.11	6.84	5.84	6.89	4.36	6.03	7.96	4.78	2.79	2.16
25	6.09	4.14	5.40	5.85	6.78	6.50	5.85	6.51	6.44	7.23	6.12	7.61	4.54	6.92	4.88	4.93	2.20	2.01
26	4.65	5.57	3.91	4.21	6.33	4.91	5.70	5.71	6.41	6.80	5.89	7.08	4.36	7.22	9.52	5.34	3.41	2.99
27	6.01	5.31	5.03	5.47	6.29	6.02	5.95	6.66	6.39	6.82	6.04	6.80	4.77	5.84	7.24	4.39	2.83	2.16
28	6.02	4.51	4.69	5.14	5.51	5.98	5.93	6.83	7.27	7.80	6.88	7.24	5.39	5.93	6.10	3.88	2.25	2.63
29	2.42	9.12	6.68	4.44	9.00	5.78	8.17	5.03	4.98	6.08	5.18	6.28	4.37	5.97	6.53	5.35	2.89	1.72

Table 6.4 *n*-Alkanes concentrations (%) in surface sediments from the Tees Estuary.

Sample No.	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}
33	3.33	3.66	3.92	3.57	4.09	3.44	2.56	3.41	2.07	5.37	2.31	10.12	1.92	16.72	4.99	17.55	2.44	8.53
34	2.09	1.78	1.79	1.95	1.99	2.33	1.75	2.84	2.74	5.87	2.14	9.48	2.98	16.55	4.82	23.18	3.35	12.36
35	2.27	2.15	2.10	2.04	2.94	2.86	2.43	3.56	3.53	6.01	2.82	8.67	2.68	13.51	8.76	19.01	3.94	10.72
36	2.11	1.79	1.92	2.76	2.09	2.78	1.99	2.73	2.38	6.59	2.90	8.48	3.42	15.62	10.85	18.45	4.50	8.66
37	2.29	2.33	2.61	3.33	3.51	3.20	2.40	3.47	3.26	5.63	3.02	8.00	3.61	11.16	11.07	16.09	4.88	10.13
38	3.79	3.46	3.58	3.52	4.40	4.46	3.27	3.98	4.27	6.75	4.34	7.77	3.70	9.94	9.61	12.96	5.03	5.17
39	4.91	2.50	3.44	4.47	4.31	4.05	3.54	4.48	4.10	6.20	4.09	8.10	2.97	8.16	10.39	11.12	5.38	7.78
40	4.73	3.89	4.44	4.55	5.96	5.22	4.67	4.93	5.79	6.44	5.16	7.17	4.02	7.41	10.16	7.82	4.04	3.60
41	5.08	4.29	4.92	5.24	6.22	5.66	5.00	5.28	558	6.96	5.64	6.96	4.54	7.37	8.37	6.67	3.36	2.88
42	5.39	4.65	5.49	5.91	6.70	6.63	5.77	6.30	6.53	6.92	6.07	6.60	4.65	5.15	9.00	3.71	2.86	1.68
43	4.85	4.37	4.51	5.11	5.13	5.17	4.97	5.76	6.27	6.98	5.86	7.29	4.81	6.19	8.68	5.82	3.14	5.10

however, readily evaluated without GC/MS from the relative distribution of peaks, numbering from the characteristic paired *n*-alkanes/isoprenoids: *n*-C_{17}/pristane (C_{17}/Pr) and *n*-C_{18}/phytane (C_{18}/Ph). These components are apparent in all the saturated hydrocarbon fractions from gas chromatography.

The aliphatic hydrocarbon distributions in surficial sediments from Tees Bay (Fig. 6.3) are mainly characterized by the presence of *n*-alkanes, with a dominance of the long chain ($C_{>20}$) over the short chain ($C_{<20}$) homologues, and by a chromatographically small and narrow unresolved complex mixture (UCM or "hump") of branched and cyclic hydrocarbons, which were not quantified. However, the geographic distribution of total resolvable *n*-alkanes (*n*-C_{16} to *n*-C_{33}) in surface sediments of Tees Bay is relatively uniform at all sites, with slight regional differences seen for the UCM.

In comparison with the Tees Bay sediments, the total resolvable *n*-alkanes (*n*-C_{16} to *n*-C_{33}) in surface sediments of the Tees estuary varied greatly, with regional differences seen for the UCM and in the composition of *n*-alkanes. Generally, the GC analysis of these samples showed that the sampling sites could be divided into four distinct groupings of stations based on composition (Fig. 6.4a-d). Chromatograms of saturated hydrocarbons extracted from sediments at stations 33 and 34, in the upper reaches of the estuary, are quite similar. The *n*-alkanes in these two sediments (e.g. site 33; Fig. 6.4a) show a bimodal distribution with a maximum at C_{31}. The bimodal distribution maximizes in the range C_{16} to C_{20} with no odd/even or even/odd predominance, and from C_{21} to C_{33} with a remarkable odd-carbon number predominance. A hump of an unresolved mixture was also present in these two samples, higher than those found in Tees Bay sediments. On the other hand, the distribution of *n*-alkanes in the seven samples collected from the middle section of the estuary (sites 35 to 41) are variable. Samples 35 and 36, both from the middle reaches of the estuary, continue the same trend observed by sites 33 and 34 in that the *n*-alkanes show a bimodal distribution and the UCM level is relatively higher compared to samples from all sites in Tees Bay. The three samples from the middle reaches of the estuary (sites 37, 38 and 39) clearly show that the UCM is highly increased in this part of the estuary. Sediment extracts from these three sites (e.g. site 38; Fig. 6.4b) also show bimodal *n*-alkane distributions, with no predominance of odd carbon number homologues in the range n-C_{16} to n-C_{24}, and a high odd/even predominance over the range n-C_{25} to n-C_{33}. In the case of the last two samples from the middle of the estuary (sites 40 and 41), chromatograms of aliphatic hydrocarbons extracted from these two sediments are quite different. The n-alkanes (n-C_{16} to n-C_{33}), in these two sediments (e.g. site 40; Fig. 6.4c), show a bimodal distribution with a maximum at n-C_{33}, with only a slight odd carbon number predominance between n-C_{25} and n-C_{33}, and the UCM is relatively similar to those of sites 33 and 34. The GC profile of the saturated fractions from the lower reaches of the estuary (sites 42 and 43) are completely different from those of stations 33, 34, 35, 36, 37, 38 and 39. The aliphatic hydrocarbon distribution in sediments from station 43 is characterized by a small UCM between n-C_{14} and n-C_{33} and by homologous series of straight chain alkanes superimposed on this UCM. The n-alkanes show a bimodal distribution maximizing at n-C_{30} with a slight predominance of odd carbon number chains observed between n-C_{25} and n-C_{33}. In contrast, the n-alkanes isolated from site 42 sediments (Fig. 6.4d) show a unimodal distribution with a maximum at n-C_{30}, but with no predominance of odd carbon numbered molecules larger than n-C_{25}, and a very narrow UCM.

6.3.2 Isoprenoid hydrocarbons

In addition to n-alkanes and a chromatographically unresolved complex mixture (UCM) of branched and cyclic hydrocarbons, a series of isoprenoid hydrocarbons are present in the aliphatic hydrocarbon mixture of all samples analyzed. The common isoprenoid alkanes pristane (i-C_{19}) and phytane (i-C_{20}) are common constituents of all sediments, but their relative abundance varies greatly. Pristane is more abundant relative to phytane and is the most dominant hydrocarbon seen on the gas chromatogram of fraction 1 at all sites, from both the marine and riverine sediments (Tables 6.5 and 6.6, respectively), except sites 33, 34, 35 and 36 (see Tables 6.1 and 6.2 for comparison). The pristane/phytane (Pr/Ph) ratio ranges from 3.2 to 8.2 in Tees Bay sediments (Table 6.5), and from 1.2 to 7.8 in the Tees estuarine sediments (Table 6.6). Pristane is almost always dominant over n-C_{17}. The n-C_{18} homologue, on the other hand, is predominant over phytane for all samples from Tees Bay and a few sediment samples from the Tees estuary (sites 40, 41, 42 and 43),

Table 6.5 Concentrations (ug g^{-1}, dry weight) of isoprenoid hydrocarbons and ratios for some selected hydrocarbons calculated from the gas chromatographic data of Tees Bay sediments.

Sample No.	Pr	Ph	Pr/Ph	Pr/C_{17}	Ph/C_{18}
1	5.07	0.72	7.1	4.8	0.6
2	2.63	0.38	6.9	5.5	0.7
3	1.01	0.15	6.9	4.6	0.6
4	13.24	1.73	7.6	6.8	0.7
5	8.25	1.20	6.9	5.2	0.6
6	5.67	0.74	7.6	4.9	0.6
10	0.96	0.14	6.9	3.9	0.6
13	0.11	0.03	3.9	1.4	1.0
14	0.18	0.03	6.6	3.2	0.6
17	0.12	0.02	7.1	2.8	0.7
18	1.00	0.14	6.9	5.3	0.7
20	0.33	0.05	6.7	3.5	0.6
21	0.97	0.14	7.1	4.7	0.7
22	0.09	0.02	5.4	4.4	0.6
24	1.48	0.21	7.2	5.0	0.7
25	13.22	1.61	8.2	7.4	0.7
26	0.10	0.02	5.5	3.0	0.8
27	0.35	0.05	6.9	3.7	0.6
28	0.69	0.10	6.8	4.2	0.6
29	0.08	0.02	3.2	1.8	0.8

Table 6.6 Concentrations (ug g^{-1}, dry weight) of isoprenoid hydrocarbons and ratios for some selected hydrocarbons calculated from the gas chromatographic data of the Tees Estuary sediments.

Sample No.	Pr	Ph	Pr/Ph	Pr/C$_{17}$	Ph/C$_{18}$
33	4.03	3.29	1.2	1.4	1.0
34	6.62	2.97	1.2	2.3	1.9
35	4.94	3.51	1.4	3.0 -	2.2
36	6.18	3.53	1.8	3.5	1.9
37	6.43	2.83	2.3	3.7	1.5
38	11.32	2.76	4.1	4.4	1.0
39	7.55	2.04	3.7	5.9	1.2
40	9.92	1.99	5.0	4.7	0.83
41	12.8	2.05	6.3	5.5	0.8
42	18.93	2.44	7.8	6.5	0.7
43	9.43	1.49	6.3	4.8	0.7

whereas phytane becomes more abundant in the other samples from the Tees estuary (sites 33 to 39; Table 6.6).

6.3.3 Triterpanes and steranes found in the samples

The distributions of triterpanes and steranes were determined in ten selected samples from the Tees estuary and Tees Bay (sites 1, 5, 13, 20, 25, 29, 33, 38, 40 and 42), by gas chromatography/mass spectrometry. The distributions of the pentacyclic triterpanes between C_{27} and C_{35} (Table 6.7), as displayed by *m/z* 191 mass chromatograms are similar for all samples (Figs. 6.5 and 6.6), with only minor variation in the relative abundance of certain compounds. In general, the hopane distribution is characterized by the predominance of 17α(H),21β(H)-30-norhopane (C_{29}) and 17α(H),21β(H)-hopane (C_{30}), with subordinate amounts of 18α(H)-22,29,30-trisnorneohopane (Ts), 17α(H)-22,29,30-trisnorhopane (Tm), 17β(H),21α(H)-moretane, and the extended 17α(H),21β(H)-homohopane. The homohopane series comprises 22S and 22R doublets (60:40) for C_{31} to C_{35}. These triterpanes all posses thermally altered configurations, consistent with the maturity levels experienced in the formation of petroleum; they cannot be from biota in the environment.

The distributions of steranes in the same eight samples are shown by the mass chromatograms of *m/z* 217 in Figures 6.7 and 6.8. Steranes between C_{27} and C_{30} carbon number were found in sediment samples (Table 6.7). The *m/z* 217 mass chromatograms all contain the same constituents, with significant differences in the relative amounts of C_{27} and C_{29} diasteranes; although there are no consistent differences between the sediments from the Tees estuary and Tees Bay. The dominant *steranes are 20S and 20R epimers of* C_{29}-5α(H),14α(H),17α(H) and of C_{29}-5α(H),14β(H),17β(H)-steranes. In addition to steranes, diasteranes were relatively abundant in all samples. The major diasteranes were C_{27} and C_{29} epimers with the C_{29} component dominants. However, despite the general similarities that exist among the *m/z* 191 and 217 mass chromatograms of the samples, marked difference in the ratios of triterpanes and steranes were found. Table 6.8 lists the values of various ratios of these compounds.

Table 6.7 Identification of Triterpanes and Steranes shown in Figures 6.5-6.8.

Peak	**Triterpanes (*m/z* 191)**	
1	18α (H)-22,29,30-Trisnorneohopane (Ts)	C_{27}
2	17α (H)-22,29,30-Trisnorhopane (Tm)	C_{27}
3	17α (H),21β (H)-Norhopane	C_{29}
4	17β (H),21α (H)-Norhopane (Normoretane)	C_{29}
5	17α (H),21β (H)-Hopane	C_{30}
6	17β (H),21β (H)-30-Norhopane	C_{29}
7	17β (H),21α (H)-Moretane	C_{30}
8	17α (H),21β (H)-Homohopane(22S)	C_{31}
9	17α (H),21β (H)-Homohopane(22R)	C_{31}
10	17β (H),21β (H)-Hopane	C_{30}
11	17β (H),21α (H)-Homohopane	C_{31}
12	17α (H),21β (H)-Bishomohopane(22S)	C_{32}
13	17α (H),21β (H)-Bishomohopane(22R)	C_{32}
14	17α (H),21β (H)-Trishomohopane(22S)	C_{33}
15	17α (H),21β (H)-Trishomohopane(22R)	C_{33}
16	17α (H),21β (H)-Tetrakishomohopane(22S)	C_{34}
17	17α (H),21β (H)-Tetrakishomohopane(22R)	C_{34}
18	17α (H),21β (H)-Pentakishomohopane(22S)	C_{35}
19	17α (H),21β (H)-Pentakishomohopane(22R)	C_{35}

Peak	**Steranes (*m/z* 217)**	
A	13β(H),17α(H)-Dicholestane(20S)	C_{27}
B	13β(H),17α(H)-Dicholestane(20R)	C_{27}
C	13β(H),17α(H)-Dicholestane(20S)	C_{28}
D	13β(H),17α(H)-Dicholestane(20R)	C_{28}
E	13β(H),17α(H)-Dicholestane(20S)	C_{29}
F	13β(H),17α(H)-Dicholestane(20R)	C_{29}
G	24-ethyl-5α (H),14α (H),17α (H)-cholestane(20S)	C_{29}
H	24-ethyl-5α (H),14β (H),17β (H)-cholestane(20S)	C_{29}
I	24-ethyl-5α (H),14β (H),17β (H)-cholestane(20R)	C_{29}
J	24-ethyl-5α (H),14α (H),17α (H)-cholestane(20R)	C_{29}

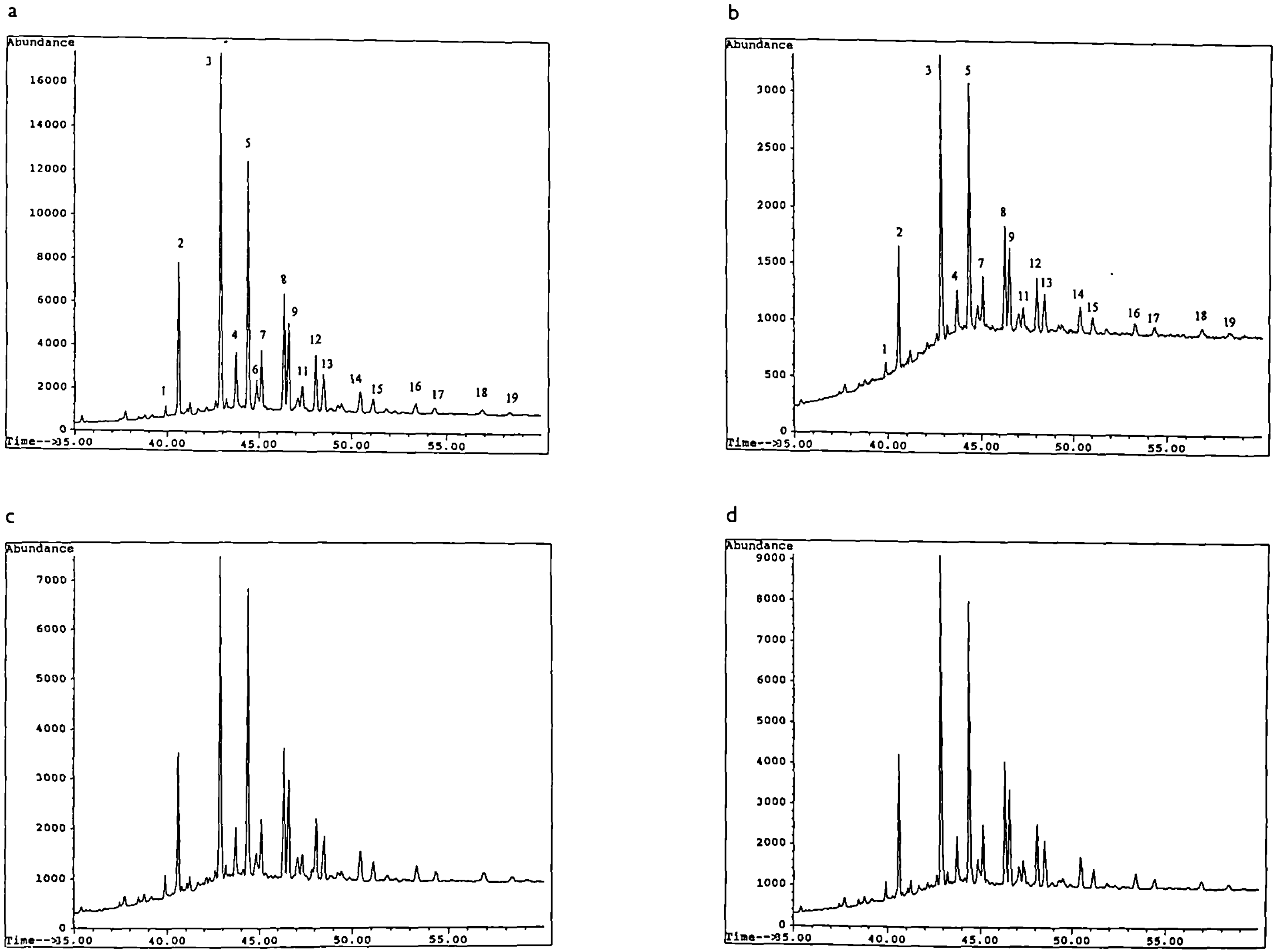


Figure 6.5. *m/z* 191 mass fragmentograms showing triterpanes in sediment samples from Tees Bay: a) site 1; b)site 20; c) site 5; and d) site 25. Peak assignments as in Table 6.7.

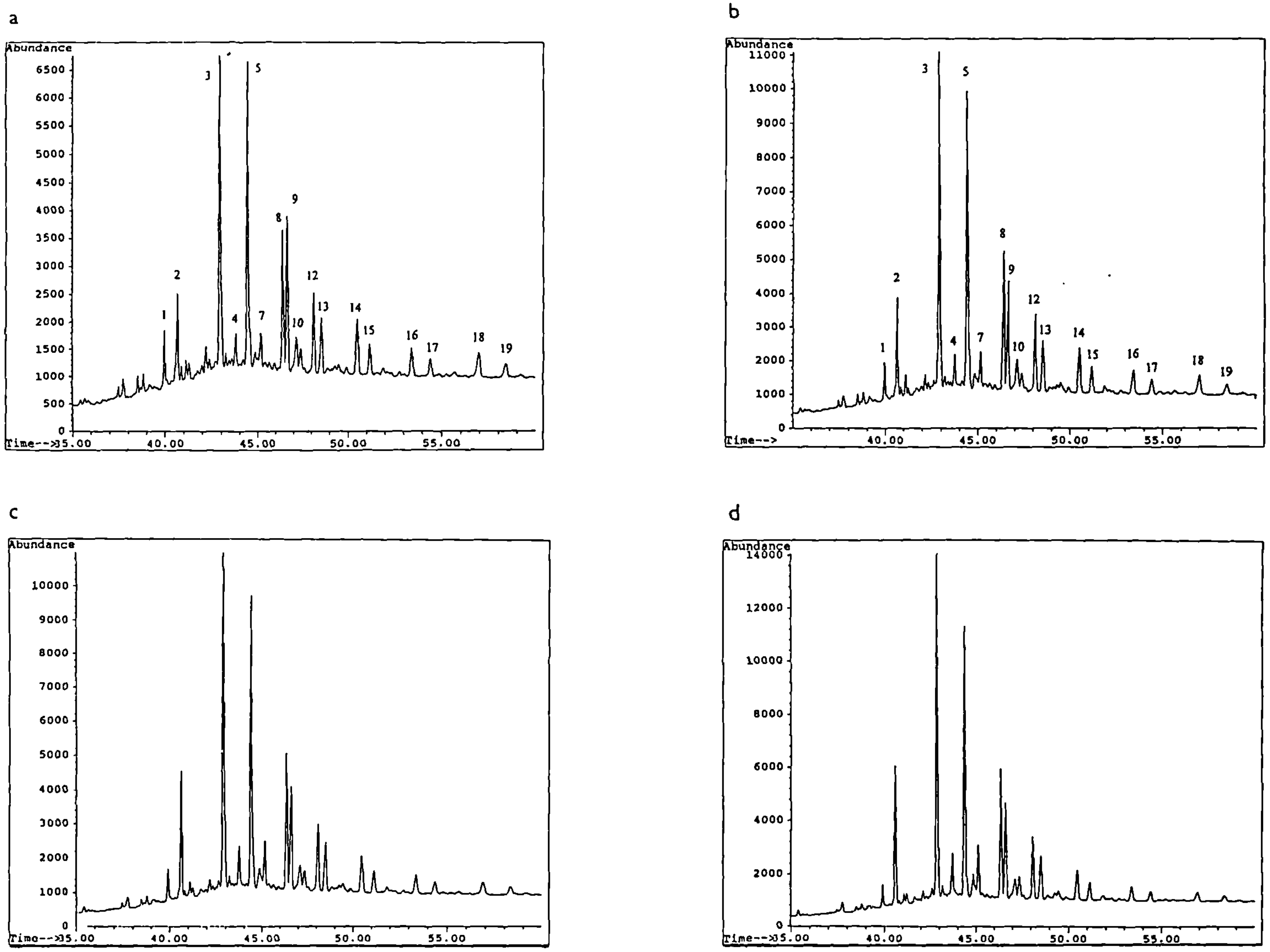


Figure 6.6. *m/z* 191 mass fragmentograms showing triterpanes in sediment samples from the Tees Estuary: a) site 33; b)site 38; c) site 40; and d) site 42. Peak assignments as in Table 6.7.

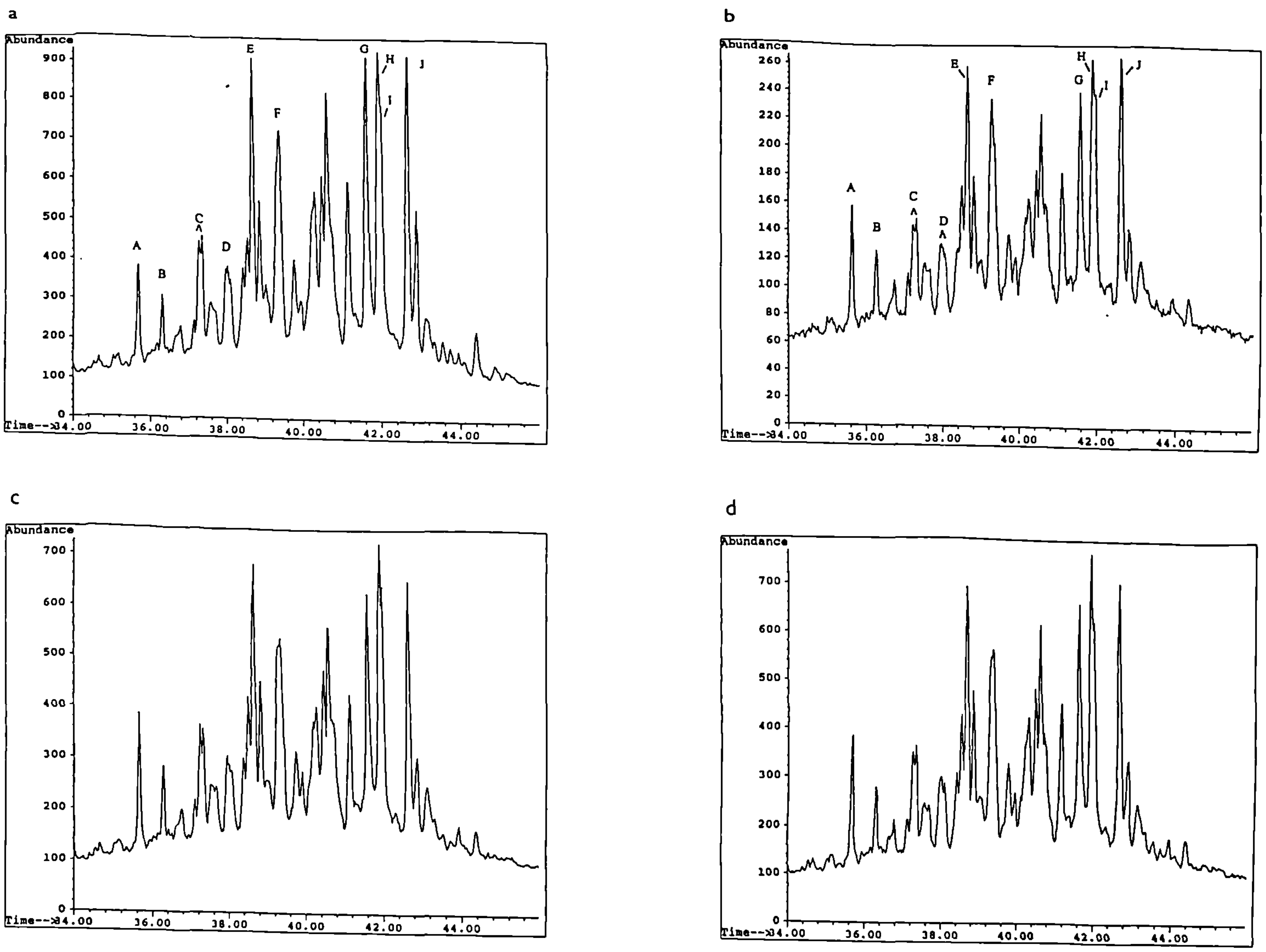


Figure 6.7. *m/z* 217 mass fragmentograms showing steranes in sediment samples from Tees Bay: a) site 1; b)site 20; c) site 5; and d) site 25. Peak assignments as in Table 6.7.

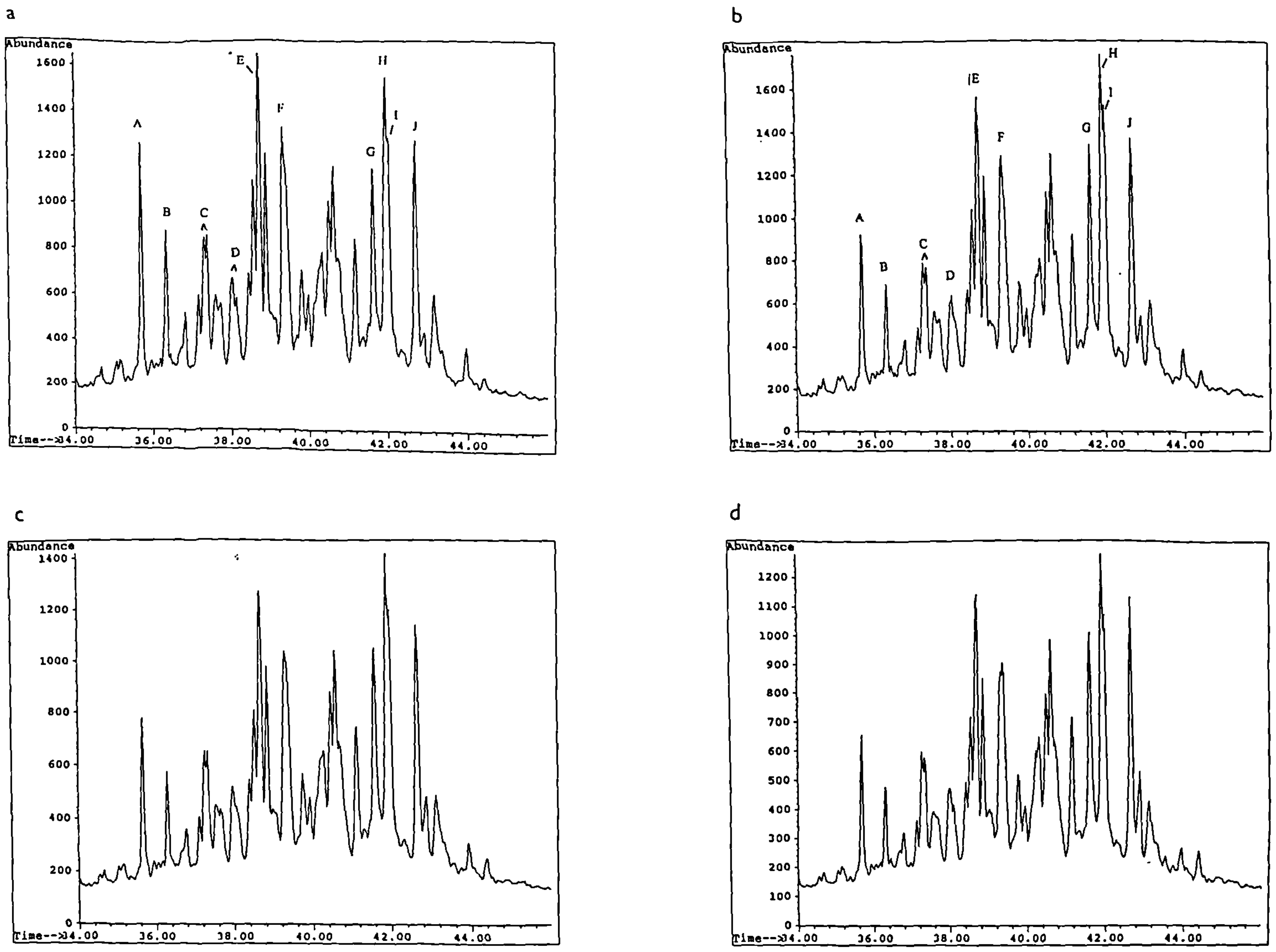


Figure 6.8. *m/z* 217 mass fragmentograms showing steranes in sediment samples from the Tees estuary: a) site 33; b)site 38; c) site 40; and d) site 42. Peak assignments as in Table 6.7.

Table 6.8 Distributions of Triterpanes and Steranes in sediments from Tees Bay and the Tees Estuary.

Sample No.	*m/z* 191			*m/z* 217		Major Terpane	Major Sterane
	Tm / Ts	$C_{29}\alpha\beta/C_{30}\alpha\beta$	$C_{31}\ \alpha\beta\ \frac{S}{S+R}$	$\alpha\beta DC_{27}/\alpha\alpha\alpha C_{29}$	$\alpha\alpha\alpha C_{29}\frac{S}{S+R}$		
1	9.79	1.26	0.48	0.26	0.54	$C_{29}\alpha\beta$	$C_{29}\alpha\beta\beta(R)$
13	7.16	1.04	0.46	0.50	0.51	$C_{29}\alpha\beta$	$C_{29}\alpha\alpha\alpha(R)$
5	7.74	0.98	0.47	0.25	0.51	$C_{29}\alpha\beta$	$C_{29}\alpha\alpha\alpha(R)$
20	7.21	1.00	0.45	0.30	0.54	$C_{29}\alpha\beta$	C29αββ(R)
25	5.27	1.09	0.44	0.33	0.79	$C_{29}\alpha\beta$	C29αββ(R)
29	9.69	0.70	0.46	0.16	0.15	$C_{29}\alpha\beta$	$C_{29}\alpha\alpha\alpha(R)$
33	1.31	1.00	0.53	0.84	0.49	$C_{29}\alpha\beta$	C29αββ(R)
38	2.24	1.06	0.45	0.42	0.54	$C_{29}\alpha\beta$	C29αββ(R)
40	3.61	1.02	0.44	0.48	0.54	$C_{29}\alpha\beta$	C29αββ(R)
42	6.18	1.14	0.48	0.43	0.52	$C_{29}\alpha\beta$	C29αββ(R)

(see Table 6.7. for identifications)

6.4 Discussion

The fingerprint of *n*-alkanes in the environment is characteristic of their origin (Neff and Anderson, 1981; Volkman *et al.*, 1992). There are no literature data regarding the type of *n*-alkanes in the sediments from the Tees estuary and Tees Bay; the present study is the first. In this study the distribution and quantity of aliphatic hydrocarbons in sediments collected from various parts of Tees Bay and the Tees estuary have been determined, and will be discussed in the following sections.

6.4.1 Concentrations

Tables 6.9 and 6.10 list values of selected gravimetric parameters over each study area. These parameters have been used in the literature (e.g. Gearing *et al.*, 1976) to characterize different environments, and here illustrate the geographical changes in the organic matter over the Tees estuary and Tees Bay. The abrupt change in sediment texture is responsible for some of the variation seen in data. The quantity of hydrocarbons in a sediment is another reflection of its environmental history. As shown in Tables 6.9 and 6.10, the extractable organic matter (EOM) concentrations in the surface sediments, from both the Tees estuary and Tees Bay, varied greatly by one to two orders of magnitude (0.29-8.76 mg/g dry sediment), the highest value being recorded in the Tees estuary.

Concentrations of *n*-alkanes in the sediment samples from Tees Bay and the Tees estuary (Tables 6.9 and 6.10, respectively) are quite different, with the highest concentrations occurring in Tees estuary samples. This could be a result of continuous deposition of saturated hydrocarbons derived from different pollutant sources (petrogenic and/or biogenic) *via* the river Tees and/or the highly urbanized and industrialized areas located very close to the estuary. These values can be compared, for instance, with the hydrocarbon levels in several British and Spanish estuaries: 10-100 ug g^{-1} (Readman *et al.*, 1986) and 1-250 ug g^{-1} (Grimalt *et al.*, 1986) respectively, or those from sediments adjacent to effluent discharge sites of a sewage treatment plant in Chesapeake Bay, USA (2-150 ug g^{-1}; Brown and Wade, 1984). In general, the levels of sedimentary hydrocarbons in all samples from the Tees estuary and in most samples from the Tees Bay (except 13, 14, 17, 22, 26 and 29) are similar to those of these samples, which correspond to petroleum polluted areas. In contrast, the

Table 6.9 Concentrations of extractable organic matter (EOM), *n*-alkanes, isoprenoids, and ratios for some selected hydrocarbons calculated from the gas chromatographic data in surface sediments from Tees Bay.

Sample No.	**EOM mg/g**	***n*-alkanes (ΣC_{16}-C_{33}) ug/g**	**% of high M.W. odd *n*-alkanes***
1	3.42	21.14	23.4
2	1.12	10.30	28.8
3	1.31	4.63	27.1
4	4.57	47.93	28.7
5	3.47	32.61	24.1
6	3.07	22.68	23.2
10	1.65	4.54	24.2
13	1.52	0.76	25.1
14	0.80	0.95	29.5
17	0.29	0.56	26.2
18	1.85	4.21	29.0
20	1.37	2.03	31.1
21	1.45	4.35	27.5
22	0.91	0.50	26.7
24	1.50	5.51	26.7
25	3.51	42.8	28.7
26	0.39	0.61	29.4
27	0.40	1.75	26.0
28	1.30	3.62	27.5
29	1.11	0.49	25.4

EOM= Extractable organic matter (ug/g of dry sediment).

* % of high molecular weight odd *n*-alkanes = % C_{25}, C_{27}, C_{29}, C_{31} and C_{33} to total *n*-alkanes (ΣC_{16}-C_{33}).

Table 6.10 Concentrations of extractable organic matter (EOM), *n*-alkanes, isoprenoids, and ratios for some selected hydrocarbons calculated from the gas chromatographic data in surface sediments from the Tees Estuary.

Sample No.	EOM mg/g	*n*-alkanes (ΣC_{16}-C_{33}) ug/g	% of high M.W. odd *n*-alkanes*
33	7.48	81.62	58.3
34	6.60	88.12	67.4
35	7.44	76.85	57.9
36	7.08	99.48	57.8
37	7.08	74.96	51.0
38	6.31	74.41	42.6
39	5.16	50.92	41.4
40	5.83	54.23	32.4
41	8.76	54.22	30.8
42	6.52	62.89	24.1
43	2.52	44.90	31.4

* = as in Table 6.9.

hydrocarbon levels the sediment samples at sites 13, 14, 17, 22, 26 and 29, from Tees Bay, are lower than those of these samples, suggesting that these sites are less polluted.

Although gravimetry does not differentiate between biogenic and anthropogenic sources of hydrocarbons, its values usually reflect the degree of pollution within a certain area (Farrington *et al.,* 1976). In addition to the differences in saturated hydrocarbon concentrations, between marine and estuarine sediments, the surface sediments displayed considerable variation between individual sites. Like trace metals (Chapter 5), the variability in hydrocarbon content per station is the largest for the Tees estuary, suggesting that the industrialized and urbanized area, located very close to the Tees estuary, are a probable source of at least some of these hydrocarbons. In contrast the low values found in all Tees Bay sediments, except sites 4 and 25, correspond to sediments composed essentially of sand. Previous studies in which sediment samples were fractionated by grain size have shown that the combined silt + clay fraction (<66 µm) may accumulate about 20-30 times more hydrocarbons than the sand fraction (>66 µm) (Grimalt *et al.,* 1984). It can also be seen from the data that there are differences in the hydrocarbon contents in the various regions of the Tees Bay. Generally, saturated hydrocarbons in Tees Bay were observed in low concentrations, as compared with those of Tees estuary, representing roughly 1.5-14% of the total extractable organic matter (EOM). Sediments from the northern part of Tees Bay have the higher hydrocarbon levels, whereas sediments from the southern part and those close to estuary mouth have the lowest (Table 6.9). The hydrocarbon content is higher in offshore relative to nearshore sediments in the area, consistent with the trend observed with organic carbon values (TOC). However, in Tees Bay, the hydrocarbons are low in coarse-grained sediments and higher in fine-grained sediments, suggesting that sediment texture strongly influence the geographical distribution of these hydrocarbons.

The two offshore sediments at the southern and northern ends of the Tees Bay (sites 4 and 25) have saturated hydrocarbon concentrations distinctly greater than sediments at other stations. The higher concentrations found at these two stations may be due to the presence of significant quantities of fine particles and high TOC values, compared to sediments from other sites. This apparent linkage of the aliphatic hydrocarbon concentrations and fine particles has been shown for sediments before (Burns *et al.,* 1982; Kennicutt *et al.,* 1987), and will be discussed in Chapter 7 (section 7.5.3). Likewise, the sediments at sites 1, 3, 5 and 6 in the northern part of the Tees Bay appear to be intermediate in character between the two offshore sediments and the other sediments in the Bay.

In the Tees estuary, different trends were found for saturated hydrocarbons, particle size and TOC. Generally, the highest concentrations were found in the middle and upper reaches of the estuary and the lowest concentration was found near the mouth of the estuary (site 43). The clayey-silt sediment at site 36 was the most contaminated sample. This sediment contains lower TOC content, compared to the coarser sediment from site 42, which contains high sand and TOC contents (69% sand content and 12.4% TOC content). In addition, for the sandy sediment from site 42, in the lower reaches of the estuary, the concentration of saturated hydrocarbons was higher than those of some clayey-silt sediments in the middle section of the estuary. It seems, therefore, that the concentration of aliphatic hydrocarbons observed in the surficial sediments of Tees estuary do not relate to the grain size or %TOC (see Chapter 7, section 7.5.3), but appear to be governed mainly by their proximity to potential pollution or anthropogenic sources.

6.4.2 *n*-Alkanes and UCM

The nature of the hydrocarbon geochemistry of the region is further revealed by the quantitative and qualitative distribution of the individual hydrocarbon components within the sediments. Many features of the hydrocarbon distributions shown by gas chromatograms are similar throughout the study region although some striking inconsistencies were found. Gas chromatograms of sediment hydrocarbons are comprised of two general features, the resolved and unresolved complex mixture (UCM). The total quantity of saturated hydrocarbons (fraction F1) includes resolved and UCM materials. The representative F1 (saturates) distributions of sediments from the Tees estuary and Tees Bay contained detectable quantities of all normal alkanes with between 16 and 33 carbon atoms (Figs. 6.3 and 6.4). In a few coarser sediments, such as at sites 22 and 29, some of these compounds were undetectable or present in only trace amounts. The predominant components in the aliphatic fraction vary from one sampling area to another. The gas chromatographic analyses of the sediment extracts of Tees Bay and Tees estuary (Figs. 6.3 and 6.4, respectively) show conclusively that aliphatic hydrocarbons in the sediments vary enormously depending upon whether the source is a heavily polluted one or not. *n*-Alkanes with a chain-length range of C_{16}-C_{33} are present in nearly all sediments which reflect several types of contributions (Tables 6.1 and 6.2). Odd carbon numbered *n*-alkanes lower than *n*-C_{21}, such as *n*-C_{15} and *n*-C_{17}, are commonly found in algae (Clark and Blumer, 1967; Youngblood and Blumer, 1973). C_{20}-C_{28} modal *n*-alkane distributions without carbon number preference and maximizing around *n*-C_{23} may result from bacterial activities (Johnson and Calder, 1973; Hatcher *et al.,* 1977; Grimalt *et al.,* 1985, 1987) and C_{25}-C_{35} odd carbon numbered *n*-alkane distributions are indicative of contributions from epicuticular waxes of higher plants (Eglinton and Hamilton, 1967). In addition mixtures of *n*-alkanes without any odd carbon number predominance may be representative of petroleum inputs. In this case, the occurrence of an unresolved complex mixture of hydrocarbons (UCM) and of a series of acyclic isoprenoids, particularly pristane and phytane, is also usually observed (Farrington and Tripp, 1977; Thompson and Eglinton, 1978).

In general, the *n*-alkane distributions in sediments from all sites, except sites 33, 34, 35, 36, 37, 38 and 39, are similar, in that they are dominated by long chain *n*-alkanes with a slight or no odd/even or even/odd predominance. In contrast, the hydrocarbon profiles in sediments from sites 33, 34, 35, 36, 37, 38 and 39 and to a lesser extent sites 40, 41 and 43 (Fig 6.4a-c) are markedly skewed towards the longer chain *n*-alkanes, and show a pronounced odd/even predominance in the *n*-alkane range C_{25}-C_{33}. This difference in *n*-alkane distributions may reflect different sources. The combined concentration of these five odd alkanes ($\Sigma C_{25\text{-}33}$; Table 6.10) are highest in sediments from the upper reaches of the estuary and decrease towards the mouth of the estuary. A possible explanation for the proportionally high content of these alkanes might be the extensive runoff from land during the sampling period, carrying higher plants debris. Resuspension of old terrestrial material from the bottoms, due to the unstable water mass, might also be of importance (Broman *et al.,* 1987). The dramatic decrease in concentrations of plant wax hydrocarbons in sediments near the mouth of the estuary (sites 40-43) demonstrates that these hydrocarbons were not introduced to the lower reaches of the estuary by the flood plume. In general, the predominance of the *n*-C_{23} through *n*-C_{33}, odd chain *n*-alkanes was a major feature of most of the gas chromatograms from Tees estuary. These *n*-alkanes (C_{23}-C_{33}) are described as being characteristic of aliphatic hydrocarbons derived from terrestrial plants and marsh grasses (Farrington and Tripp, 1977). Quantitatively, this predominance of odd chain n-alkanes (C_{23}-C_{33}) can be expressed by the carbon preference index (CPI) and odd-even *n*-alkane predominance index (OEPI), which will be discussed below. Gas chromatograms of these surface sediments, from the Tees estuary, are similar to patterns observed by Ajayi and Poxton (1987) for contaminated surface sediments from the Forth estuary.

In addition to *n*-alkanes from C_{16} to C_{33}, all chromatograms show varying degrees of an unresolved complex mixture (UCM) of branched and cyclic alkanes, seen as humps in the chromatograms. The sediment UCM is a common constituent of petroleum (Kennicutt *et al.,* 1987), and usually taken as being indicative of degraded or chronic oil pollution (Thompson and Eglinton, 1978). There have been suggestions that a UCM can result from bacterial degradation of other organic matter (Venkatesan and Kaplan, 1982), but clear evidence for this is lacking. It should also be noted that a UCM is always accompanied by hydrocarbon biomarkers indicative of petroleum products (see below). The presence of a UCM and petroleum biomarkers can also indicate the presence of hydrocarbons derived from the weathering of ancient rocks (Rowland and Maxwell, 1984). Too few data are presently available to quantify the importance of this as a source of geologically old organic matter in marine sediments, but in most sediments the concentrations would be in the low-ppm range.

In the present study, the highest relative levels of UCM are found in the sediments of the Tees estuary, especially at sites 37, 38 and 39 in the middle section of the estuary, and the lowest in the Tees Bay (Figs 6.3 and 6.4). This may correspond either to the lowest level of saturated hydrocarbons found at Tees Bay or to different sources of hydrocarbons in the Tees estuary sediments. In general, the hydrocarbon profiles of all sediment samples collected from the Tees Bay and one sediment sample collected from the Tees estuary (site 42) are similar, in that they are dominated by a very narrow UCM (Figs 6.3 and 6.4d), with low CPI or OEPI and no odd carbon number predominance, indicative of material from petrogenic sources. A low CPI has also been reported for sediments from Biscayne Bay, Florida (Corcoran *et al.*, 1983). In that study, it was concluded that some of the sediments were petroleum contaminated. This was based primarily on the large unresolved complex mixture (UCM, indicative of petroleum contamination; see NAS, 1985; UNEP, 1991) that dominated the chromatograms of the sediments (Corcoran *et al.*, 1983). In contrast to that study, only a trace of UCM was found in the chromatograms of all sediment samples taken from Tees Bay and one sediment collected from the Tees estuary (site 42). This lack of a large UCM indicates that petroleum contamination of the sediments is doubtful. Furthermore, NAS (1985) warns against attributing particular hydrocarbon distributions to oil pollution based solely on low CPI or OEPI values, since a smooth distribution of C_{20}-C_{30} alkanes has been reported for various other environmental samples (Davis, 1968; NAS, 1985; Nishimura and Baker, 1986). Inferences based on OEPI (C_{22}-C_{30}) are also weakened by reports of bacterial reworking of hydrocarbons in both sediments and in the water column, resulting in no odd-to-even carbon preference (Grimalt *et al.*, 1987; Ramos *et al.*, 1989). Bacterial reworking of longer chain *n*-alkanes may account for the lack of an odd-numbered carbon preference in sediments observed in this study, particularly in the bay sediments. The aliphatic hydrocarbon distributions in the Tees Bay were characterized by a very narrow UCM and no odd carbon predominance (Fig. 6.3). The UCM was associated with variable amounts of resolved *n*-alkanes in the range C_{16}-C_{33}. A narrow UCM in Swiss lake sediments has been attributed to fossil hydrocarbons eroded from surrounding sedimentary rocks (Giger *et al.*, 1980), although an alternative source may be from the degraded detritus of algae and other microorganisms (Johnson and Calder, 1973; Cranwell, 1978, Cox *et al.*, 1982). An unambiguous origin for the UCM in these sediments cannot be assigned from the aliphatic hydrocarbon data alone. However, a predominant UCM in the gas chromatograms of the corresponding aromatic fractions (as shown in Chapter 7) of these samples indicates the sediments have been contaminated by a petroleum source.

In addition, the narrow shape of the UCM and the lack of higher molecular weight components which are commonly found in ancient sediments or sediments contaminated by petroleum suggests that the sediments were contaminated by a refined petroleum product, such as a fuel or diesel oil. Essentially similar hydrocarbon patterns have been described in suspended particulate matter and sediments near sewage outfalls and have been attributed to runoff of petroleum products (Eganhouse *et al.,* 1981; Brown and Wade, 1984).

In contrast, the hydrocarbon profiles of the estuarine sediments are markedly different in that they are dominated by elevated levels of UCM (Fig. 6.4 a-c). UCM levels systematically increase from the upper reaches of the estuary towards the middle and then decrease in the lower reaches of the estuary. This increase in UCM level in the middle section of the estuary, particularly at sites 37, 38 and 39, is probably caused by discharges from a number of chemical and petrochemical works, plus the domestic sewage from the adjacent urban population. Johnston *et al.* (1991) state that some 0.5×10^6 m^3 of industrial effluents were being discharged daily, with 75% of the total issuing from just three sites in the middle section of the estuary (see Fig. 3.2; Chapter 3). UCM compounds, associated with anthropogenic sources, and terrigenous *n*-alkanes, associated with waxy plant detritus are found mixed together in many sediments (e.g. Han and Calvin, 1969; Thomposon and Eglinton, 1978; Boehm, 1984; Readman *et al.,* 1986). This is clearly shown in the chromatograms of hydrocarbons from most sediments in the River Tees (e.g. Fig. 6.4a-c), which show a strong predominance of odd-chain lengths even though heavily contaminated with petroleum hydrocarbons.

6.4.3 *n*-Alkane indexes

Molecular level and bulk parameters can be used to estimate the relative importance of hydrocarbon sources at a given location. These parameters or indices are based on the premise that hydrocarbon sources have unique fingerprints (i.e. certain recognizable suites of compounds). To better understand the dynamics of hydrocarbons in Tees Bay and Tees estuarine sediments several aliphatic indices have been calculated from F1 chromatograms in an attempt to improve the discrimination between contaminated and uncontaminated sites. These indices are :

6.4.3.1 Carbon preference indices (CPI)

CPI values of *n*-alkanes for marine and estuarine sediments have been discussed in relation to hydrocarbon sources by several workers (Farrington and

Meyers, 1976; Gearing *et al.*, 1976; Wakeham and Carpenter, 1976; Thompson and Eglinton, 1978; Matsumoto, 1983; Boehm, 1984; Ajayi and Poxton, 1987; Kennicutt *et al.*, 1987; Sandstrom, 1988; Pelletier *et al.*, 1991; Al-Saad and Al-Timari, 1993). In general, the CPI values of *n*-alkanes for polluted environments are close to unity (one).

For the sediments from the Tees estuary and Tees Bay, the CPI values were calculated according to Cooper and Bray (1963), from the carbon chain length of C_{16}-C_{20} and C_{20}-C_{33}. The CPI values over the low molecular weight range *n*-C_{16} to *n*-C_{20} ($CPI_{16\text{-}20}$) are relatively uniform with sediment location and geographical differences. These values lie in the range of approximately 1.0 (0.57-1.09; Tables 6.11 and 6.12) reported for a variety of hydrocarbon sources including marine plankton, higher plants, and crude oils (Gearing *et al.*, 1976; Barrick *et al.*, 1980).

In contrast, carbon preference indices over the range *n*-C_{20} to *n*-C_{33} ($CPI_{20\text{-}33}$) are variable in sediments from Tees Bay and the Tees estuary (ranged from 0.96-1.23 and 0.96 to 3.32, respectively), as shown in Tables 6.11 and 6.12. The *n*-alkanes generally showed distinct odd over even predominance, with the highest values being recorded at some sites (33, 34, 35 and 36) from the Tees estuary (ranges from 2.21-3.53; Tables 6.11 and 6.12). Such high CPI values suggest considerable *n*-alkane inputs from non-petroleum sources (Clark and Blumer, 1967; Davies *et al.*, 1981; Douglas *et al.*, 1981) especially land-plant derived biogenic hydrocarbons which are dominated by C_{27}, C_{29}, C_{31} and C_{33} *n*-alkanes (Eglinton *et al.*, 1962; Clark, 1966; Douglas and Eglinton, 1966). The CPI range found in these sediments is somewhat below the $CPI_{20\text{-}33}$ range of 4-10 reported for vascular land plants (Clark and Bulmer, 1967; Caldicott and Eglinton, 1973), but above values of <2 typical of most aquatic plants, bacteria, and petroleum (Gearing *et al.*, 1976 and references therein). This predominance, of the odd carbon number higher molecular weight *n*-alkanes, can be expressed by an odd-even *n*-alkane predominance index (OEPI) which is defined by Farrington and Tripp (1977) as:

$$\frac{2(n\text{-}C_{27} + n\text{-}C_{29})}{n\text{-}C_{26} + 2(n\text{-}C_{28}) + n\text{-}C_{30}}$$

The rationale for the formulation of OEPI, which indicates that the plant epicuticular waxes are present (Eichmann *et al.*, 1979), is similar to that for the

Table 6.11 Ratios for some selected hydrocarbons calculated from the gas chromatographic data in surface sediments from Tees Bay.

Sample No.	**CPI ($C_{20\text{-}33}$)**	**CPI ($C_{16\text{-}20}$)**	**OEPI ($C_{26\text{-}30}$)**	**RHL**	**Major constituents**
1	0.99	0.95	1.01	2.39	Pr, C_{30}, C_{25}, C_{21}
2	1.11	0.97	1.23	2.71	Pr, C_{30}, C_{27}, C_{29}
3	1.08	0.91	1.17	2.52	Pr, C_{30}, C_{27}, C_{25}
4	1.06	0.91	1.10	2.83	Pr, C_{30}, C_{27}, C_{25}
5	0.98	0.96	1.01	2.57	Pr, C_{30}, C_{25}, C_{27}
6	0.96	0.87	0.99	2.25	Pr, C_{16}, C_{30}, C_{25}
10	1.02	0.97	1.05	2.37	Pr, C_{30}/C_{25} , C_{27}
13	1.02	1.20	1.25	1.80	Pr ,C_{17} , C_{16}, C_{20} /C_{22}
14	1.08	1.35	1.22	3.11	Pr, $C_{30}/C_{25}/C_{27}$
17	1.05	1.15	1.31	2.16	Pr, C_{20}, $C_{22}/C_{27}/C_{29}$
18	1.12	0.97	1.21	2.88	Pr, C_{30}, C_{25}/C_{29}
20	1.03	1.23	1.16	2.85	Pr, C_{25}, C_{24}, C_{27}/C_{30}
21	1.06	0.99	1.16	2.86	Pr, C_{25}/C_{27}, C_{30}
22	1.02	0.83	1.21	2.34	Pr, C_{20}
24	1.06	1.03	1.15	2.56	Pr, C_{30}, C_{20}, C_{25}/C_{27}
25	1.23	0.84	1.45	2.54	Pr, C_{27}, C_{25}, C_{29}
26	1.01	1.05	1.18	3.05	Pr, C_{30} , C_{29}
27	1.05	0.96	1.11	2.56	Pr, C_{30}, C_{25}, C_{27}
28	1.06	0.92	1.11	2.87	Pr, C_{25}, C_{24}/C_{27},
29	0.99	1.18	1.20	2.16	Pr, $C_{17}/C_{20}/C_{22}$

$CPI_{20\text{-}33}$: Carbon preference index calculated, according to Copper and Bray (1963), between n-C_{20} and n-C_{33}.

$CPI_{16\text{-}20}$: Carbon preference index calculated, according to Copper and Bray (1963), between n-C_{16} and n-C_{20}.

OEPI ($C_{26\text{-}30}$) = odd-even predominance between n-C_{26} to n-C_{30}.

RHL= Ratio of higher to lower molecular weight n-alkanes (RHL= C_{21}-C_{33}/C_{16}-C_{20})

Table 6.12 Ratios for some selected hydrocarbons calculated from the gas chromatographic data in surface sediments from the Tees Estuary.

Sample No.	**CPI (C_{20-33})**	**CPI (C_{16-20})**	**OEPI (C_{26-30})**	**RHL**	**Major constituents**
33	3.42	0.95	4.82	3.34	C_{31}, C_{29}, C_{27}, C_{25}
34	3:16	0.98	4.08	9.42	C_{31}, C_{29}, C_{27}, C_{25}
35	2.16	0.90	2.62	7.90	C_{31}, C_{29}, C_{27}, C_{25}
36	2.21	1.13	2.34	8.38	C_{31}, C_{29}, C_{27}, C_{25}
37	1.29	1.04	1.80	6.10	C_{31}, C_{29}, C_{30}, Pr
38	1.23	0.91	1.66	4.33	Pr, C_{31}, C_{29}, C_{30}
39	1.07	0.87	1.59	4.09	Pr, C_{31}, C_{30}, C_{29}
40	1.09	0.87	1.25	3.24	Pr, C_{31}, C_{30}, C_{29}
41	1.02	0.90	1.24	2.88	Pr, C_{30}, C_{29}, C_{27}
42	0.96	0.92	0.96	2.56	Pr, C_{30}, C_{25}, C_{20}
43	1.04	1.00	1.12	3.17	Pr, C_{30}, C_{27}, C_{25}

For the identification of $CPI_{(C20-33)}$, $CPI_{(C16-20)}$, $OPEI_{(C26-30)}$, and RHL see Table 6.11.

Carbon Preference Index (CPI) as devised by Bray and Evans (1961). These formulations are summarized in Tissot and Welte (1981).

Sediments exhibiting primarily terrigenous inputs have OEPI values from 2 to 6 indicating a greater relative amount of the odd carbon *n*-alkanes, *n*-C_{27} and *n*-C_{29}. Petroleum is on the opposite end of the OEPI scale with a OEPI approximately equal to 1.0 in most instances (Tissot and Welte, 1981). The OEPI is an indicator of the general source of hydrocarbons and is independent of absolute concentrations of gross hydrocarbon parameters. Interpretation of odd-even alkane predominance can be potentially complicated by the presence of certain bacteria which have been shown to exhibit high molecular weight *n*-alkane distributions showing no odd carbon preference (Han and Calvin, 1969). The OEPI value is close to 1.0 for all Tees Bay sediments, but ranged from 0.96 to 4.82 for sediment samples from the estuary. However, these values are generally within the range of values previously reported for recent marine sediments (ratio values typically up to 10; Gearing *et al.,* 1976; Wong *et al.,* 1976; Farrington and Tripp, 1977; Keizer *et al.,* 1978). This index decreased with increasing distance from the upper reaches of estuary (Table 6.12), reflecting a decreasing amount of plant waxes transported across the Bay.

6.4.3.2 Ratio of higher to lower molecular weight *n*-alkanes (RHL)

This index (RHL = C_{21}-C_{33}/C_{16}-C_{20}) may principally reflect the extent of the contribution of higher plants, soils and combustion products of fossil fuels to the total contents of *n*-alkanes (Matsumoto, 1982). It may also indicate the degree of the presence of land-derived biogenic hydrocarbons in polluted sediments. However, the RHL values tend to increase with the bacterial degradation of *n*-alkanes, because the degradation rate of the lower molecular weight n-alkanes is greater than those of the higher molecular weight ones (Bailey *et al.,* 1973).

The RHL values for the sediments from Tees Bay ranged from 1.80 to 3.11 (Table 6.11), which is significantly lower than those of the Tees estuary sediments (ranged from 2.6-9.4; Table 6.12) at most sites. This finding is also consistent with the observation that the major constituents of the hydrocarbons, UCM, *n*-alkanes and $CPI_{20\text{-}33}$ values, in the sediments of Tees estuary, are different to those of the Tees Bay. However, the high RHL values for the Tees estuary sediments may be attributed to the preferential degradation of lower molecular weight *n*-alkanes and/or selective deposition of higher plant debris, which may contain higher molecular weight *n*-alkanes (Matsumoto, 1983).

6.4.3.3 Major components

The major hydrocarbon (MH) is the highest *n*-alkane concentration. This index is often around C_{18} for oily samples (Clark and Finley, 1973), C_{15}, C_{17}, or C_{19} for marine algae (Lytle and Lytle, 1979), and C_{31} for vascular plants.

The major hydrocarbons in the sediments of Tees Bay were the higher molecular weight *n*-alkanes ($>C_{20}$) and pristane. In addition lower molecular weight *n*-alkanes, e.g. *n*-C_{17}, were also found as major hydrocarbons, in sediments collected near the mouth of the estuary (sites 29 and 13). Since *n*-C_{17} is the principle aliphatic hydrocarbon in many marine organisms, including blue green algae, plankton, benthic algae and fish, a marine source for this hydrocarbon in these two sediments is most likely. Similar results have been previously reported for marine sediments (e.g. Zheng and Van Vleet, 1988; Mille *et al.*, 1992; Snedaker *et al.*, 1995).

In the sediments from the Tees estuary, the major constituents of the hydrocarbons were mainly higher molecular weight *n*-alkanes, with a maximum at C_{31}, C_{20}, C_{21}, C_{24}, C_{25}, C_{27}, C_{29}, or C_{30} (Table 6.11). In addition, pristane was also a major constituent in sediments from both the middle (sites 38, 39, 40) and upper (sites 41, 42 and 43) reaches of the estuary. The predominant resolved materials are the higher molecular weight *n*-alkanes, C_{25}-C_{33}, with odd carbon predominance indicative of material from biogenic sources (Farrington and Meyers, 1976). In addition, the elevated levels of UCM at all stations in the Tees estuary, with the exception of site 42, clearly suggests the presence of additional anthropogenic sources from the highly urbanized and industrialized areas.

6.4.4 Isoprenoid hydrocarbons

The aliphatic hydrocarbon fraction was mainly characterized by the presence of isoprenoid hydrocarbons, which are commonly considered in geochemical studies (Didyk *et al.*, 1978; ten Haven *et al.*, 1987; Powell, 1988). The common isoprenoid alkanes pristane (*i*-C_{19}) and phytane (*i*-C_{20}) are common constituents of most sediments, but their relative abundances vary considerably (Volkman *et al.*, 1992). Pristane and phytane were detected in all sediment samples from Tees Bay and Tees estuary, but their relative abundance vary greatly. They are often found to be among the dominating saturated hydrocarbons in crude oils, weathered petroleum and coal, and thus are often considered as good indicators of petroleum contamination (e.g. Volkman and Maxwell., 1986; Broman *et al.,* 1987). Pristane also occurs biogenically, for example in plankton, while phytane is rarely found in biogenic material. However, the presence of pristane in an environmental sample does not confirm incorporation of petroleum hydrocarbons (Carlsberg, 1980).

Generally, pristane and phytane were detected in all sediment samples from Tees Bay and Tees estuary, but their relative abundance vary greatly (Tables 6.5 and 6.6). From these two Tables it can be seen that the concentration of pristane in the sediment samples from Tees Bay and the Tees estuary is much higher than those of *n*-alkanes (C_{16} - C_{33}) at all sites, from both areas, except 33, 34, 35, 36 and 37. It is therefore unlikely that localized benthic organisms, for example copepods, which are known to contain high concentrations of pristane (Blumer *et al.,* 1964), are a major source of this compound to the coarse bottom sediments. Petroleum is also an unlikely source of pristane to these sediments since the phytane and UCM is very low (Han and Calvin, 1969) in the coarse sediments. These sediments do not have the correspondingly high concentrations of the other isoprenoids expected to accompany the abundance of pristane, and thus there appears to be an additional sources of pristane. A possible source of some of the pristane in these sediments might be coal fragments. To confirm this observation a coal sample, collected from the northeast coast of England (Whitley Bay), was extracted and analysed, by using the same method adapted in the present study. Figure 6.9 shows the gas chromatogram obtained from the saturated hydrocarbon fraction of the coal sample. This chromatogram shows principally a series of *n*-alkanes between *n*-C_{14} and *n*-C_{35}, and the absence of the hump called UCM. Pristane and phytane, which are the major branched alkanes, are also found in this sample (216.53 and 19.33 ug g^{-1}, respectively), but the level of pristane is much higher than phytane as well as those of *n*-alkanes. It can also be seen from the gas chromatogram of F1 fraction extracted from coal (Fig 6.9) that pristane is the most dominant hydrocarbon. This finding is similar to that observed in sediment

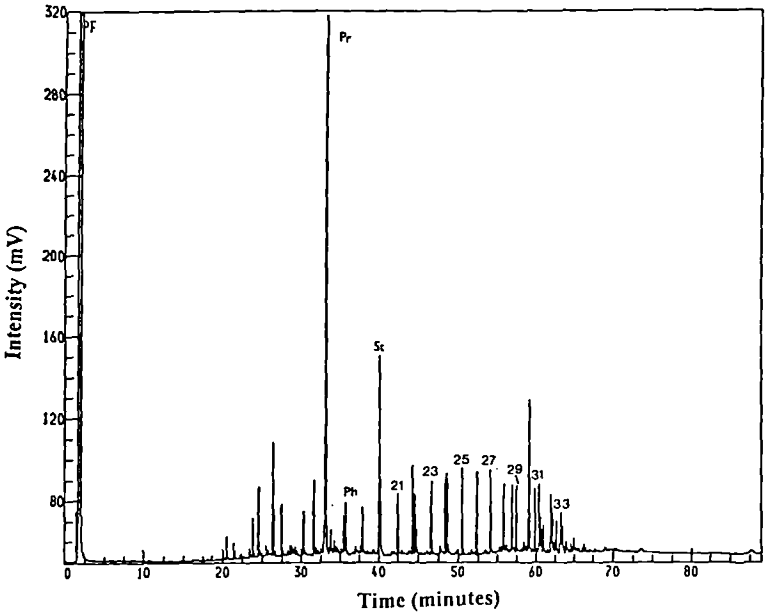


Figure 6.9. Gas chromatogram of saturated hydrocarbons in the coal sample. Peak identification and chromatographic conditions as for Fig. 6.3.

samples from all sites, except 33-36, suggesting that the high level of pristane in these sediments could be a result of continuous deposition of aliphatic hydrocarbons derived from coal. Similar distributions have been found in many other sediments around the world (Hamilton *et al.*, 1984; Barrick and Prahl, 1987).

Phytane, which is used as a marker compound for petroleum as it is usually absent in uncontaminated samples (Burns *et al.*, 1982), is rarely found in biogenic material, with a possible exception of some bacteria (Shaw and Baker, 1978; Venkatesan and Kaplan, 1982; NAS, 1985), but it might also be a natural product of post depositional reactions involving the catalytic hydrogenation of phytadienes and/or phytol (Blumer and Snyder, 1965). However, the presence of phytane in surface sediments is usually attributed to fossil fuels (Carlberg, 1980). In the present study, phytane was somewhat unusual in that its concentrations was consistently low in both regions despite the differences in EOM. These concentrations are comparable with those found in sediments of Saanich Inlet (Brown *et al.*, 1972), the Dead Sea (Nissenbaum *et al.*, 1972), Lake of Washington (Wakeham and Carpenter, 1976) and Southeast Florida (Snedaker *et al.*, 1995).

The ratio of pristane to phytane varies between oils and is thought to reflect the depositional environment of the original source rocks (Didyk *et al.*, 1978). This ratio can be used to fingerprint the oil and in a few favourable cases can be used to identify the source of an oil spillage. In the present study, the Pr/Ph ratios generally showed distinct pristane over phytane in all sediment samples from Tees Bay (3.2-8.2; Tables 6.5) and the Tees estuary (1.2-7.8; Table 6.6), with the lowest ratios being recorded at sites 33 and 34, from the upper section of the estuary, (1.2 and 1.2, respectively, Table 6.6). These low values fall in the Pr/Ph range of 0.6-1.3 reported for a petroleum source (Meinschein, 1969; Brown *et al.*, 1972; Zafiriou *et al.*, 1972; Reed *et al.*, 1977, Venkatesan *et al.*, 1980). In contrast the Pr/Ph ratios found in all other sediment samples is higher than those of petroleum but lower than Pr/Ph ratio of 11.2, calculated from the coal sample extracted in the present study, and may represents mixed contributions from these two sources.

Ph/C_{17} and Ph/C_{18} represent the pristane to *n*-heptadecane and phytane to *n*-octadecane ratios, respectively. These two ratios usually range from 0.7 to 3.0 for petroleum (Meinschein, 1969; Brown *et al.*, 1972; Zafiriou *et al.*, 1972; Reed *et al.*, 1977). In the present study the Pr/C_{17} ratios exceed levels of 0.7-3.0, suggested for a petroleum source at all sites, except 13, 17, 26, 29, 33, 34 and 35, but lower than the Pr/C_{17} ratio (12.9) found in the coal sample. Sediments from sites 13, 29, 33, 34 and 35 show the lowest ratios of Pr/C_{17}, indicative of primarily petroleum hydrocarbon sources.

In contrast, ratios of Ph/C_{18} in the sediment samples from both areas are much lower than those of Pr/Ph and Pr/C_{17}. In the Tees Bay, stations 2, 4, 13, 17, 18, 21, 24, 25, 26 and 29 show values (Table 6.5), in the range of 0.7-3.0 (Venkatesan *et al.*, 1980), suggestive of petroleum inputs. However, all other stations show low values, suggesting that these stations are relatively less polluted. For the Tees estuary, all sediments show values indicative of petroleum inputs. It should also be noted that sediments from sites 34, 35 and 36 show values (1.9, 2.2 and 1.9, respectively; Table 6.6) relatively higher than the Ph/C_{18} ratio of the coal sample (Ph/C_{18}=1.6).

It is apparent, therefore, that Pr/Ph and Pr/C_{17} ratios will be dominantly controlled by the amount of coal, and in this condition this ratio can not be used to positively distinguish biogenic and petroleum sources.

6.4.5 Triterpanes and steranes

As mentioned above, the aliphatic hydrocarbon distributions in all sediments from Tees Bay and one sediment from the Tees estuary were characterized by a very narrow UCM and no odd carbon predominance which might suggest biological origin (non petroleum). More detailed analysis using gas chromatography/mass spectrometry (GC/MS) often shows that these sediments contain high amounts of non-biogenic alkanes which are usually attributable to oil pollution. This can be confirmed by identifying compounds that are unique to petroleum. These compounds must have distinctive structures and be resistant to biodegradation. Some good examples include polycyclic alkanes such as hopanes, steranes and diasteranes. Distributions of these hydrocarbons in oil residues, tars and sediments are readily fingerprinted by monitoring characteristic fragment ions for each hydrocarbon class using selected ion monitoring mode of the capillary GC/MS (e.g. Thompson and Eglinton, 1978; Albaiges, 1980; Jones *et al.*, 1986).

The mass fragmentograms of triterpanes (*m/z* 191; Figs 6.5 and 6.6) and steranes (*m/z* 217; Figs. 6.7 and 6.8), obtained from the GC/MS analysis of the hydrocarbons in surface sediments from Tees Bay and the Tees estuary are remarkably similar. Figures 6.5 and 6.6 show the *m/z* 191 mass fragmentograms of sediment samples from Tees Bay and the Tees estuary, respectively. This ion occurs in the spectra of hopanes, hopenes and some other triterpenoid hydrocarbons, and is commonly used to fingerprint oil contamination in sediments. Among the triterpanes, pentacyclic triterpanes (or hopanes) have also been used for tracing hydrocarbons of petrogenic origin (Dastillung and Albrecht, 1976; Venkatesan and Kaplan, 1982; Urdal *et al.,* 1986; Broman *et al.,* 1987).

The GC/MS SIM of *m/z* 191 (Figs. 6.5 and 6.6) indicates the presence of pentacyclic triterpanes. The 17α(H),21β(H)-hopane series is the major series; *i.e.* C_{27} and C_{29-35} (peaks 1-19; Table 6.7). The C_{29} and C_{30} homologs (norhopane and hopane) are the dominant members in all samples (peaks 3 and 5). The 17α(H) 21β(H) hopanes larger than C_{30} occur as mixtures of C-22 R and S diastereoisomeric pairs, with two isomers in a ratio of approximately 60:40 (e.g. peaks 8:9, 11:13) in all samples, with the exception of the sediment sample from site 33 (Fig 6.6a) where this ratio is different (Peak 9 higher than peak 8). These features in these samples with the above exception are typical of the distributions of the same compounds in many crude oils and thermally mature rocks (e.g. Mackenzie *et al.*, 1980; Seifert and Moldowan, 1980), suggesting petrogenic inputs into these surface sediments (Pym *et al.,* 1975; Dastillung and Albrecht, 1976; Quirk *et al.,* 1980). In addition, the GC/MS chromatogram of terpanes (*m/z* 191) of the coal sample extracted in the present study (Fig. 6.10a), is similar to those of the sediment samples from both area (Figs. 6.5 and 6.6).

Figures 6.7, 6.8 and 10b show the *m/z* 217 mass fragmentogram obtained from the saturated hydrocarbon fractions of sediment samples from Tees Bay, the Tees estuary and the coal sample. The distribution is dominated by components identified from their mass spectra as steranes (e.g. peaks G-J). Moreover the major isomers present are those with 14β(H),17β(H) sterochemistry (e.g. peaks H,I). These, and 14α (H),17α(H) isomers are present as both 20S and 20R epimers (Figs. 6.7, 6.8 and 10b; peaks G and J) in approximately equal amounts; again features which are typical of

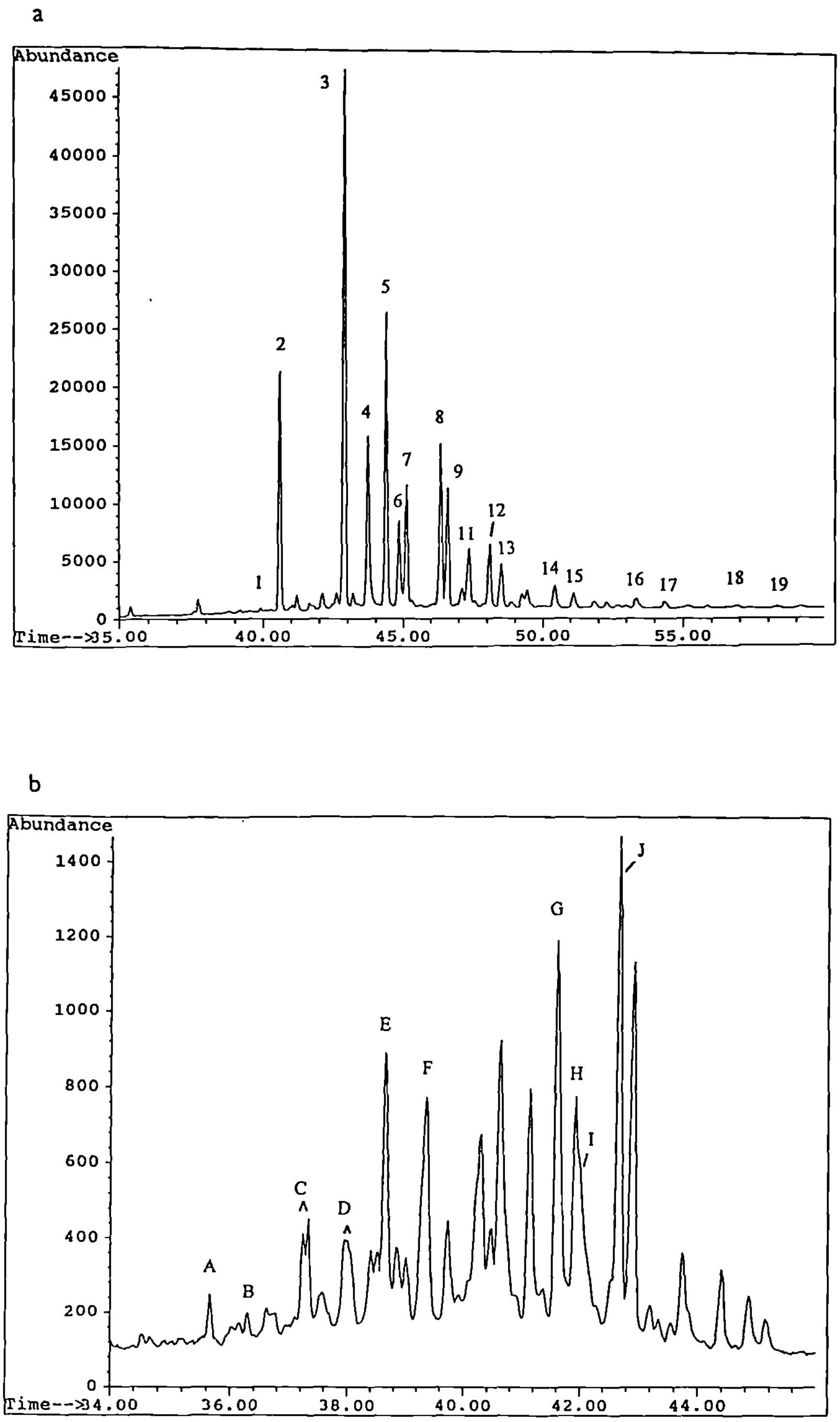


Figure 6.10. Mass fragmentograms showing a) triterpanes (*m/z* 191) and b) steranes (*m/z* 217) in the coal sample. Peak assignments as in Table 6.7.

many crude oils and thermally mature rocks (Seifert and Moldowan, 1978; Mackenzie *et al.*, 1980). In addition, all sediment samples from both areas indicate the presence of the 20S epimer of C_{27} and C_{29} diasteranes as major components (peaks A and E; Figs 6.7 and 6.8), with the C_{29} component dominating. However, in all samples, except sample 33 (Fig. 6.8a), the 20S epimer of the C_{29} diasterane is much higher than that of the 20S epimer of the C_{27} diasterane. This finding is similar to the distributions of the same compounds in the coal sample (Fig 6.10b), suggesting that these samples may received a distinguishable contribution of coal. In contrast, in the sediment sample from site 33 the 20S epimer of the C_{29} diasterane is only a little higher than that of the 20S epimer of the C_{27} diasterane, suggesting a contribution of oil into this sediment.

By contrast, Figure 6.6a shows the *m/z* 191 mass fragmentogram obtained for a saturated hydrocarbon fraction of sediment 33. At this station the second eluting homohopane isomer 22R (peak 9), which is thought to be biogenic (Quirk *et al.*, 1980), is present in a slightly higher concentration than the first, but a series of C_{32}-C_{34} hopanes of petroleum-type, with pairs of C-22 diasteromers in ratios comparable to crude oils is also present (peaks 12:13, 14:15; Fig. 6.6a). The presence of this complex mixture of hopanes provides convincing evidence that petroleum and biogenic both contribute to the hydrocarbons in this sediment. Figure 6.8a shows the corresponding *m/z* 217 mass fragmentogram which is dominated by the geologically epimerized sterane isomers as in other sites (Figs. 6.7 and 6.8 b-d).

Thus, the conclusion from the triterpane and sterane distribution is that the sediment at sampling site 33, which had the same *n*-alkane distribution and UCM as those of sites 34, 35 and 36 has received a distinguishable contribution of both biological and petroleum origin hydrocarbons. In contrast, all other samples from both areas have received a large contribution of petrogenic origin hydrocarbons (e.g. petroleum and/or coal).

6.5 Summary

1- Surface sediment samples were taken from 30 sites along the Tees estuary and Tees Bay, and analysed for saturated hydrocarbons. This is the first study to report *n*-alkanes data for Tees Bay and Tees estuary sediments.

2- The Tees estuary are much more contaminated than Tees Bay sediments as is evident from the concentration of hydrocarbons. In addition, the relatively low concentrations of hydrocarbons which are present in most sites of Tees Bay reflect the generally low concentrations of organic matter in these predominantly sandy sediments.

3- Sediment characteristics, such as particle size composition and total organic carbon content, significantly influence the geographical distribution of *n*-alkanes in Tees Bay only. In the surface sediments from the Tees estuary the concentrations of aliphatic hydrocarbons appear to be governed mainly by their proximity to potential pollution or anthropogenic sources, and do not relate to the grain size and/or TOC contents.

4- The representative *n*-alkane distributions of sediments from the Tees estuary and Tees Bay contained detectable quantities of all normal alkanes with between 16 and 33 carbon atoms (Figs. 6.3 and 6.4). The predominant components in the aliphatic fraction vary from one sampling area to another. Several parameters are used in the present study as indicators of natural or anthropogenic hydrocarbons pollution (e.g. CPI, OEPI, UCM, Pr/Ph). These parameters are not sufficient to determine the source of pollution. On the basis of the mass fragmentograms of triterpanes (*m/z* 191) and steranes (*m/z* 217), which have been proposed as being useful fingerprints of oils (e.g. Pym *et al.*, 1975; Seifert and Moldowan, 1978; Jones *et al.*, 1986), it is evident that the *n*-alkanes in all sediments from Tees Bay and most sediments from the Tees estuary (except sites 33, 34, 35 and 36) derived mainly from fossil fuel sources (petroleum and coal). On the other hand, sediments from sites 33, 34, 35 and 36 show the presence of hydrocarbons of both petroleum/coal and biological origin.

Chapter Seven

Polyaromatic Hydrocarbons

7.0 Polyaromatic Hydrocarbons

7.1 Introduction

Every year 230,000 t of polycyclic aromatic hydrocarbons (PAHs) reach the marine environment and are ubiquitously distributed world-wide (Law, 1986). The investigation of these compounds is of great scientific interest, since several of them show a high carcinogenic and mutanogenic activity (Bridboard *et al.*, 1976; Payne *et al.*, 1978; Lipiatou and Saliot, 1991a). The solubility of PAHs in water is low and decreases with increasing molecular weight. Due to their hydrophobic nature (log K_{ow}=3-8; Witt, 1995), the concentrations of dissolved PAHs in seawater are very low. Otherwise the PAHs are easily associated with particulate matter and finally deposited in the sediment (Witt, 1995). Knowledge of the sources and global distribution of polycyclic aromatic hydrocarbons in sedimentary environments is important because of the effects these compounds can have on biological systems. In addition to their potential toxicity, the chemical stability of PAHs makes them useful indicators of specific anthropogenic and diagenetic contributions to sedimentary deposits.

This chapter aims to assess the occurrence and distribution of PAHs in sediments of the Tees Bay and Tees estuary, and compares concentrations in this area with those found in the sediment samples from a number of different geographical areas. In addition possible relationships between PAHs and sediment characteristics will be evaluated and potential origins identified.

7. 2 Polycyclic Aromatic Hydrocarbons

The terms aromatic hydrocarbons and polycyclic or polynuclear aromatic hydrocarbons (PAHs) are commonly used in an operational sense. They imply C-H compounds containing benzenoid structures; the remainder of the molecule, often the largest part of it, may consist of straight or branched chains, of olefinic groups or of saturated hydrocarbon rings (Youngblood and Blumer, 1975).

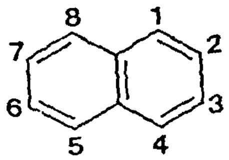
PAHs are composed of two or more fused aromatic rings. Two rings are said to be fused when a pair of carbon atoms are shared. The resultant structure is a molecule with all the carbon and hydrogen atoms lying in a single plane. Naphthalene ($C_{10}H_8$), which consists of two fused rings, is the lowest molecular weight member of the PAH group of chemicals, while the ultimate in fused ring systems is graphite, an allotropic form of carbon. However, of primary concern are those PAHs that are environmentally mobile, and these range from naphthalene (MW 128.16) to coronene ($C_{24}H_{12}$; MW 300.36). Within this range exist a large number of PAHs differing in the number and position of aromatic rings and in the number, chemistry and position of substituents on the basic ring system.

Physical and chemical characteristics of PAHs vary in a more or less regular fashion with molecular weight. Resistance to oxidation and reduction tends to decrease with increasing molecular weight, while vapour pressure and aqueous solubility decrease almost logarithmically with increasing molecular weight. As a result, PAHs of differing molecular weight vary substantially in their behaviour and distribution in the environment.

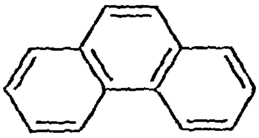
On the basis of their properties and their molecular weight, two classes of PAHs can be distinguished, *i.e.* the two- and three-ring aromatics from naphthalene to anthracene, and the four- to six-ring aromatics from fluoranthene to indeno(1,2,3-c,d)pyrene. The low-molecular-weight two- and three-ring PAHs have a significant acute toxicity, whereas some of the higher-molecular-weight PAHs show a high carcinogenic potential (Neff, 1979; Varansi, 1989).

Polycyclic aromatics have been studied for well over a century and during this time many of them have been unsystematically named. Some of these names reflect a particular attribute of the chemical, such as colour in the case of fluorene or the shape as in the case of coronene. Others have names reflecting the initial isolation of the compound from coal tar, such as naphthalene and pyrene. These names have passed into general use and it has proved impractical to change them when systematic nomenclature was introduced.

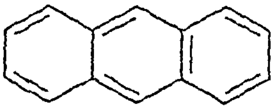
Several systems of nomenclature have been used to describe PAH ring structures. However the system adopted by the International Union of Pure and Applied Chemistry (IUPAC) is the one generally used. Selected structures of some environmentally important PAHs can be seen in Figure 7.1.



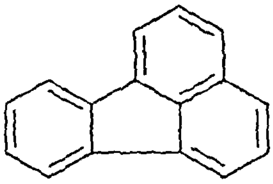
Naphthalene



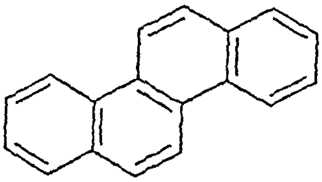
Phenanthrene



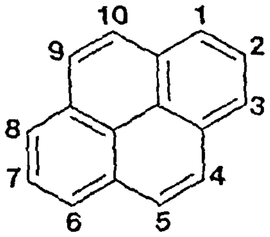
Anthracene



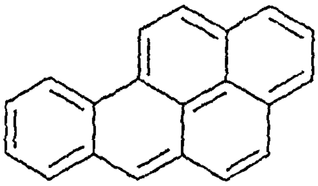
Fluoranthene



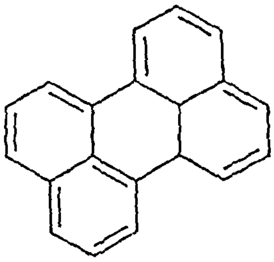
Chrysene



Pyrene



Benzo(a)pyrene



Perylene

Figure 7.1. Structures of selected polyaromatic hydrocarbons.

7.3 Results

Examples of PAH chromatograms, isolated from the extracts of Tees Bay and Tees estuarine sediments, are shown in Figs. 7.2 and 7.3, respectively. These chromatograms clearly illustrate the presence of a series of polycyclic aromatic hydrocarbons (PAHs) in addition to a small or narrow unresolved complex mixture (UCM), for all samples. It can also be seen from Figures.7.2 and 7.3 that there are differences in the relative abundance of alkylated PAHs compared to unsubstituted PAHs. Quantitative results obtained from the chromatograms of the PAH compounds (non-alkylated or unsubstituted PAHs) isolated from extracts of Tees Bay and Tees estuarine surface sediments are listed in Tables 7.1 and 7.2, respectively. In these two tables the concentration of 14 unsubstituted PAHs, i.e. naphthalene (N), biphenyl (Bi), fluorene (F), phenanthrene(P), anthracene (A), dibenzothiophene (DBT), fluoranthene (Fl), pyrene(Pyr), chrysene (Chr), benzo(*a*)anthracene (BaA), benzofluoranthene (BF), benzo(*e*)pyrene (BePyr), benzo(*a*)pyrene (BaPyr) and perylene (Per), have been determined. Concentrations of some alkylated compounds, *i.e.* methyl and dimethylnaphthalenes (1-methylnaphthalene, 1-MN; 2-methylnaphthalene, 2-MN; 2,6-dimethylnaphthalene, 2,6-DMN), methylbiphenyls (3-methylbiphenyl, 3-MBi; 4-methylbiphenyl, 4-MBi), methyl phenanthrenes (3-methylphenanthrene, 3-MP; 2-methylphenanthrene, 2-MP; 9-methylphenanthene, 9-MP; 1-methylphenanthrene, 1MP) and methyldibenzothiophenes (4-methyldibenzothiophene, 4-MDBT; 2,3-methyldibenzothiophene, 2,3-MDBT; 1-methyldibenzothiophene, 1-MDBT), were also estimated by measuring respective peak heights and assuming a response factor the same as the unsubstituted compounds. Measurable concentrations of these PAH compounds were also found in all sediments from Tees Bay and Tees estuary (Table 7.3 and 7.4, respectively). Concentrations in these tables (7.1 - 7.4) are expressed in terms of ng g^{-1} sediment dry weight. Data in Tables 7.5 to 7.8, on the other hand, are the percentages of each individual PAH to total PAH, in sediment samples from both areas. The sum of these substituted and unsubstituted PAHs, in sediments from Tees Bay and Tees estuary, is referred to here as total PAH (Table 7.9). GC retention data relative to reference standards and literature data (Lee *et al.*, 1976,1978; Radke *et al.*, 1982; Jones, 1986; Wise *et al.,* 1988) were used for the identification of PAHs as well as GC/MS data from the same samples.

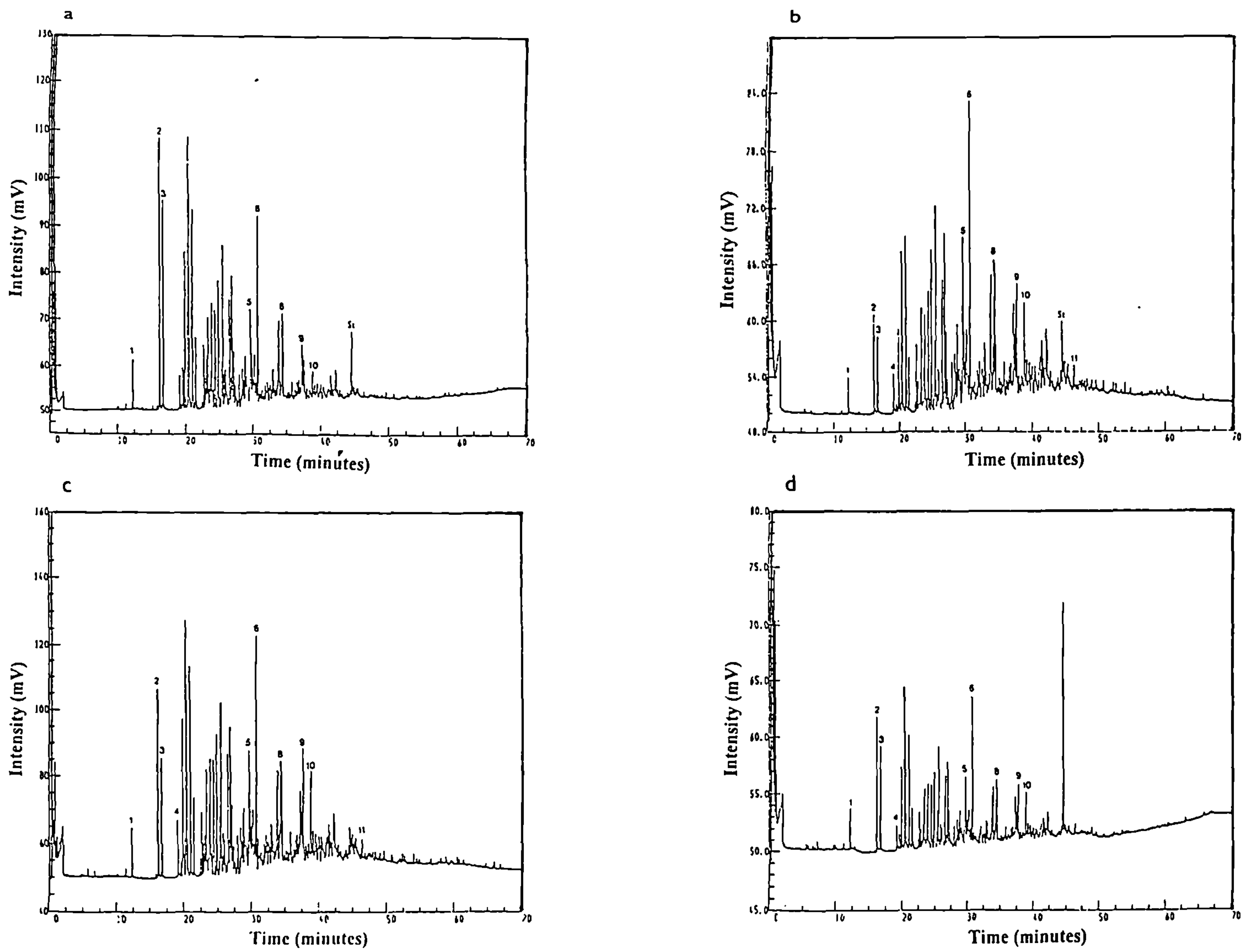


Figure 7.2. Gas chromatograms of PAHs in sediments from Tees Bay: site 1 (a), site 4 (b), site 20 (c) and site 25 (d). PAH peak identification: 1, naphthalene; 2, 2-methylnaphthalene; 3, 1-methylnaphthalene; 4, biphenyl; 5, dibenzothiophene; 6, phenanthrene; 7, anthracene; 8, methylphenanthrenes; 9, fluoranthene; 10, pyrene; 11, chrysene; 12, benzofluoranthene; 13, benzo(e)pyrene; 14, benzo(a)pyrene; 15, perylene. St = standard (1,1, binaphthyl). Chromatographic conditions are described in Chapter 3.

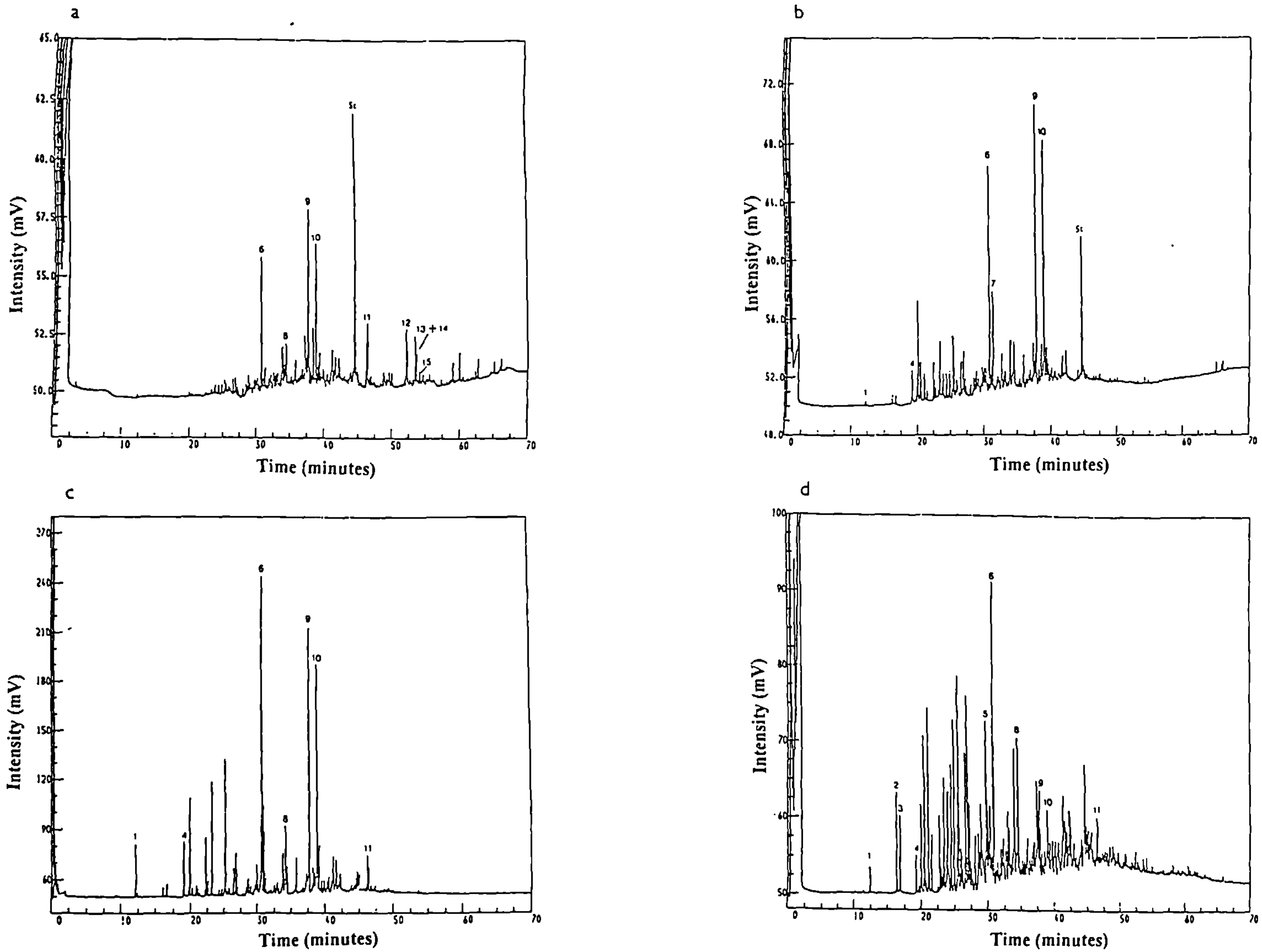


Figure 7.3. Gas chromatograms of PAHs in sediments from the Tees Estuary: site 33 (a), site 35 (b), site 37 (c) and site 42 (d). PAH peak identification and chromatographic conditions as for Fig. 7.2.

Table 7.1 Unsubstituted aromatic hydrocarbon concentrations (ng g^{-1}, dry weight) for sediment samples from Tees Bay.

Sample No.	N	Bi	F	P	A	DBT	Fl	Pyr	BaA	Chr	BF	BeP	BaP	Per
1	482.2	278.6	253.1	2005.0	n.d	163.9	202.3	294.5	46.7	64.5	3.0	7.7	7.8	0.4
2	79.6	103.5	126.3	769.9	40.7	48.7	249.3	244.9	161.9	232.5	73.5	55.5	29.9	4.7
3	83.4	82.6	96.1	574.3	44.6	47.9	190.1	216.6	41.1	46.9	2.4	4.9	7.6	0.4
4	580.7	525.0	687.8	4257.6	254.7	276.3	1495.6	1563.1	387.2	431.8	13.1	49.6	52.5	3.4
5	334.3	268.6	367.8	2684.4	n.d.	223.3	424.4	510.0	367.0	546.2	147.8	163.2	61.9	-
6	728.9	255.0	267.6	1686.9	n.d.	145.0	268.0	215.5	242.1	421.5	106.3	105.2	39.7	-
10	15.2	0.3	10.0	182.1	9.6	14.6	31.6	50.1	2.2	3.6	0.0	0.1	0.1	n.d.
13	5.8	5.7	5.8	38.7	2.6	3.1	17.9	23.4	3.4	4.8	0.4	0.7	1.0	0.1
14	4.6	3.4	7.7	60.6	3.6	5.0	19.5	21.7	8.3	13.4	3.3	3.4	2.0	0.3
17	10.1	6.7	6.4	43.7	3.0	3.7	16.2	15.4	5.8	8.6	2.1	2.6	1.6	0.2
18	17.0	25.5	27.2	180.0	17.4	11.5	69.7	68.8	41.2	59.5	17.4	15.3	12.4	2.1
20	10.1	17.1	20.8	119.1	9.3	10.5	2.7	0.3	4.9	2.2	3.9	4.1	3.7	0.5
21	23.0	27.8	36.7	236.6	14.0	18.7	2.2	4.7	4.8	4.8	n.d.	0.5	1.7	n.d.
22	0.1	2.1	3.7	28.6	1.6	1.9	0.7	0.9	3.2	0.1	3.1	2.6	1.7	0.3
24	89.7	126.8	179.5	1127.4	110.8	82.3	39.4	529.2	67.2	85.5	66.5	49.7	55.3	8.1
25	916.7	978.9	1082.2	7356.7	622.5	463.4	2763.1	259.0	431.7	419.1	18.6	38.2	67.8	3.9
26	4.8	4.9	5.1	33.0	4.3	2.5	14.0	14.1	8.1	13.7	5.3	4.1	2.6	0.4
28	23.9	2.7	21.3	131.5	6.7	10.8	30.9	33.4	18.6	36.6	11.8	11.6	3.0	n.d.
29	0.0	0.2	1.5	12.4	1.2	1.0	4.5	5.1	0.9	1.6	n.d.	0.2	0.2	n.d.

n.d. = not detected

Table 7.2 Unsubstituted aromatic hydrocarbon concentrations (ng g^{-1}, dry weight) for sediment samples from the Tees Estuary.

Sample No.	N	Bi	F	P	A	DBT	Fl	Pyr	BaA	Chr	BF	BeP	BaP	Per
33	21.3	8.2	75.1	676.5	62.5	55.9	1093.1	931.5	514.2	743.6	712.4	294.8	224.4	86.4
34	6.0	3.7	95.3	1168.9	168.4	82.6	1882.0	1612.9	856.2	1397.3	1029.0	419.2	338.6	100.6
35	55.0	378.7	574.4	2156.6	250.1	208.9	3240.5	2893.7	69.2	55.8	0.4	2.0	3.0	0.2
36	25.6	184.9	516.3	2646.5	247.4	161.9	4052.0	3094.6	742.6	675.8	17.5	47.5	86.7	7.4
37	5681.6	5087.9	19558.2	88683.4	11713.1	4973.6	84757.3	70605.6	8020.0	5083.5	12.5	78.3	9.6	n.d.
38	952.6	1357.6	1421.8	4618.8	521.7	395.6	5031.6	4729.3	16.1	88.3	n.d.	6.5	25.3	1.4
39	82.0	326.1	1228.0	3536.4	371.2	48.8	4482.1	3554.7	1845.7	1700.1	57.3	161.2	288.6	25.8
40	89.7	1037.5	997.9	4664.2	427.2	286.0	3238.5	2844.4	71.2	85.9	358.5	278.0	271.3	48.2
41	2029.7	965.5	870.1	4603.2	313.8	346.9	536.4	352.7	521.1	541.7	26.7	73.6	21.2	8.4
42	477.2	632.6	783.0	6191.9	n.d.	377.7	15.2	40.7	1015.0	69.3	173.5	222.3	144.9	14.2
43	759.0	353.9	355.4	2098.1	132.3	145.0	884.1	808.8	265.2	305.9	42.2	58.0	63.3	5.8

n.d. = not detected.

Table 7.3 Substituted aromatic hydrocarbon concentrations (ng g^{-1}, dry weight) for sediment samples from Tees Bay.

Sample No.	1-MN	2-MN	2,6-DMN	4-MBi	3-MBi	MP (3)	MP (2)	MP (9)	MP (1)	4-MDBT	2,3-MDBT	1-MDBT
1	2004.7	2930.2	1661.2	454.8	147.3	484.2	655.2	754.6	532.3	85.6	61.7	44.7
2	103.6	140.9	130.1	140.7	52.6	191.7	254.1	294.6	229.0	28.2	30.1	14.4
3	159.4	223.4	204.9	114.0	40.1	137.7	188.1	205.7	170.1	24.6	24.4	12.3
4	994.0	1371.3	1192.3	722.6	251.7	995.8	1291.8	1559.5	1184.2	147.8	167.2	80.2
5	2041.5	2611.0	1829.0	506.6	166.7	685.5	939.4	1055.4	857.3	115.2	89.9	59.6
6	1990.6	2658.9	1511.8	385.8	127.1	431.2	622.7	666.9	560.5	73.3	59.1	35.9
10	12.1	17.1	2.1	2.4	1.0	50.8	72.8	82.5	66.1	8.7	7.5	3.9
13	13.1	18.7	17.6	6.7	2.3	8.2	11.1	13.0	9.7	1.6	1.3	0.8
14	6.7	8.80	12.7	8.8	3.0	14.6	21.7	22.5	20.5	2.8	2.0	1.2
17	32.8	44.4	31.9	9.3	3.3	10.2	15.3	15.5	13.9	1.8	1.6	0.9
18	26.3	34.8	48.4	34.4	12.2	42.6	58.7	68.6	51.1	6.7	7.4	4.0
20	50.9	65.0	62.0	22.9	8.1	27.5	38.0	42.0	32.8	0.4	4.4	2.5
21	96.3	135.8	130.9	40.0	14.1	55.3	75.8	91.8	61.7	2.0	1.9	1.2
22	1.0	1.0	4.1	4.3	1.6	6.1	9.1	9.8	8.6	1.0	0.9	0.5
24	337.6	448.5	467.1	128.3	48.0	194.6	256.0	271.3	225.5	9.6	10.9	4.8
25	2433.6	4226.5	3958.2	919.3	322.3	1331.0	1859.5	2303.2	1326.9	208.6	226.4	109.5
26	10.5	13.6	13.1	6.7	2.9	8.1	11.8	13.1	11.2	0.2	1.3	0.8
28	63.6	85.9	77.8	29.3	9.7	31.3	46.5	49.6	43.9	5.4	5.5	3.0
29	0.1	0.1	0.7	1.2	0.2	2.9	4.4	4.8	4.2	0.5	0.5	0.2

Table 7.4 Substituted aromatic hydrocarbon concentrations (ng g^{-1}, dry weight) for sediment samples from the Tees Estuary.

Sample No.	1-MN	2-MN	2,6-DMN	4-MBi	3-MBi	MP (3)	MP (2)	MP (9)	MP (1)	4-MDiBT	2,3-MDiBT	1-MDiBT
33	7.3	12.8	6.5	17.4	10.5	131.1	183	158	137.3	46.8	n.d.	13.4
34	2.8	2.6	0.9	5.4	4.5	189.8	244.4	227.7	181.6	51.2	17.0	17.2
35	84.7	120.3	225.5	166.1	78.3	294.9	352.5	332.9	249.6	92.9	20.1	30.0
36	30.1	41.6	53.1	148.4	75.5	375.5	477.5	450.2	357.2	70.8	30.0	32.3
37	1061.6	933.9	110.3	1238.0	n.d.	3637.4	4080.2	2901.5	2294.6	488.6	129.4	269.6
38	2342.7	3378.0	1853.4	626.8	321.8	720.9	974.4	1010.4	708.5	34.1	15.8	8.3
29	48.8	73.3	27.1	366.9	223.9	567.8	753.7	762.7	556.8	28.3	16.0	19.9
40	254.5	391.0	675.8	718.8	309.9	951.7	1205.3	1357.2	1016.0	62.4	44.4	66.7
41	5404.9	8021.7	3657.2	839.2	312.8	1010.8	1398.1	1648.5	1110.3	28.6	67.3	14.2
42	1184.5	1671.8	1539.5	1026.7	368.8	1456.5	2018.8	2292.4	1736.7	65.8	62.7	48.5
43	1987.1	3149.1	1517.2	321.7	118.7	426.9	602.2	692.0	491.7	68.2	54.3	35.6

n.d. = not detected

Table 7.5 Unsubstituted aromatic hydrocarbon composition (as % of total PAH) for sediment samples from Tees Bay.

Sample No.	N	Bi	F	P	A	DBT	Fl	Pyr	BaA	Chr	BF	BeP	BaP	Per	Unsub. PAH
1	3.5	2.0	1.9	14.7	0.0	1.2	1.5	2.2	0.3	0.5	<0.1	0.1	0.1	<0.1	28.0
2	2.1	2.7	3.3	20.1	1.1	1.3	6.5	6.4	4.2	6.1	1.9	1.4	0.8	0.1	58.0
3	2.8	2.8	3.3	19.5	1.5	1.6	6.5	7.4	1.4	1.6	0.1	0.2	0.3	<0.1	48.9
4	2.8	2.6	3.3	20.7	1.2	1.3	7.3	7.6	1.9	2.1	0.1	0.2	0.3	<0.1	51.5
5	2.0	1.6	2.2	15.7	0.0	1.3	2.5	3.0	2.2	3.2	0.9	1.0	0.4	0.0	35.8
6	5.3	1.9	2.0	12.3	0.0	1.1	2.0	2.3	1.8	3.1	0.8	0.8	0.3	0.0	33.4
10	2.4	<0.1	1.5	28.2	1.5	2.3	4.9	7.7	0.3	0.6	0.0	0.0	0.0	0.0	49.4
13	2.7	2.6	2.7	17.8	1.2	1.4	8.2	10.8	1.6	2.2	0.2	0.3	0.5	0.1	52.1
14	1.6	1.2	2.7	21.5	1.3	1.8	6.9	7.7	2.9	4.8	1.2	1.2	0.7	0.1	55.6
17	3.3	2.2	2.1	14.2	1.0	1.2	5.3	5.0	1.9	2.8	0.7	0.8	0.5	0.1	41.1
18	1.8	2.7	2.8	18.7	1.8	1.2	7.3	7.2	4.3	6.2	1.8	1.6	1.3	0.2	58.8
20	1.8	3.0	3.7	21.1	1.6	1.9	0.5	0.1	0.9	0.4	0.7	0.7	0.7	0.1	37.0
21	2.1	2.6	3.4	21.9	1.3	1.7	0.2	0.4	0.4	0.4	0.0	0.0	0.2	0.0	34.7
22	0.1	2.1	3.8	29.0	1.6	1.9	0.7	0.9	3.2	0.1	3.1	2.6	1.7	0.3	51.3
24	1.8	2.5	3.6	22.5	2.2	1.6	0.8	10.5	1.3	1.7	1.3	1.0	1.1	0.2	52.1
25	2.6	2.8	3.1	21.2	1.8	1.3	8.0	0.7	1.2	1.2	0.1	0.1	0.2	<0.1	44.5
26	2.3	2.3	2.4	15.7	2.0	1.2	6.7	6.7	3.9	6.5	2.5	2.0	1.2	0.2	55.6
28	3.0	0.3	2.7	16.6	0.8	1.4	3.9	4.2	2.3	4.6	1.5	1.5	0.4	0.0	43.2
29	0.0	0.4	3.1	25.4	2.5	2.0	9.2	10.4	1.8	3.3	0.0	0.4	0.4	0.0	58.9

Table 7.6 Unsubstituted aromatic hydrocarbon composition (as % of total PAH) for sediment samples from Tees Estuary.

Sample No.	N	Bi	F	P	A	DBT	Fl	Pyr	BaA	Chr	BF	BeP	BaP	Per	Unsub. PAH
33	0.3	0.1	1.2	10.9	1.0	0.9	17.6	15.0	8.3	11.9	11.4	4.7	3.6	1.4	88.4
34	0.1	<0.1	0.9	11.6	1.7	0.8	18.6	16.0	8.5	13.8	10.2	4.1	3.4	1.0	90.6
35	0.5	3.2	4.8	18.1	2.1	1.8	27.1	24.2	0.6	0.5	<0.1	<0.1	<0.1	<0.1	82.8
36	0.2	1.3	3.5	18.1	1.7	1.1	27.7	21.1	5.1	4.6	0.1	0.3	0.6	0.1	85.4
37	1.8	1.6	6.1	27.6	3.6	1.5	26.4	22.0	2.5	1.6	<0.1	<0.1	<0.1	0.0	94.7
38	3.1	4.4	4.6	14.8	1.7	1.3	16.1	15.2	0.1	0.3	0.0	<0.1	0.1	<0.1	61.5
39	0.4	1.5	5.8	16.7	1.8	0.2	21.2	16.8	8.7	8.0	0.3	0.8	1.4	0.1	83.7
40	0.4	4.8	4.6	21.4	2.0	1.3	14.9	13.1	0.3	0.4	1.6	1.3	1.2	0.2	67.6
41	5.8	2.8	2.5	13.3	0.9	1.0	1.5	1.0	1.5	1.6	0.1	0.2	0.1	<0.1	32.3
42	2.0	2.7	3.3	26.2	0.0	1.6	0.1	0.2	4.3	0.3	0.7	0.9	0.6	0.1	43.0
43	4.8	2.2	2.3	13.3	0.8	0.9	5.6	5.1	1.7	1.9	0.3	0.4	0.4	<0.1	39.9

Table 7.7 Substituted aromatic hydrocarbon composition (as % of total PAH) for sediment samples from Tees Bay.

Sample No.	1-MN	2-MN	2,6-DMN	4-MBi	3-MBi	MP (3)	MP (2)	MP (9)	MP (1)	4-MDBT	2,3-MDBT	1-MDBT	Sub. PAH
1	14.7	21.5	12.2	3.3	1.1	3.6	4.8	5.5	3.9	0.6	0.5	0.3	72.0
2	2.7	3.7	3.4	3.7	1.4	5..0	6.6	7.7	6.0	0.7	0.8	0.4	42.0
3	5.4	7.6	7.0	3.9	1.4	4.7	6.4	7.0	5.8	0.8	0.8	0.4	51.1
4	4.8	6.7	5.8	3.5	1.2	4.8	6.3	7.6	5.8	0.7	0.8	0.4	48.5
5	12.0	15.3	10.7	3.0	1.0	4.0	5.5	6.2	5.0	0.7	0.5	0.3	64.2
6	14.5	19.4	11.0	2.8	0.9	3.1	4.5	4.9	4.1	0.5	0.4	0.3	66.6
10	1.9	2.6	0.3	0.4	0.2	7.9	11.3	12.8	10.2	1.3	1.2	0.6	50.6
13	6.0	8.6	8.1	3.1	1.1	3.8	5.1	6.0	4.5	0.7	0.6	0.4	47.9
14	2.4	3.1	4.5	3.1	1.1	5.2	7.7	8.0	7.3	1.0	0.7	0.4	44.4
17	10.7	14.5	10.4	3.0	1.1	3.3	5.0	5.0	4.5	0.6	0.5	0.3	58.9
18	2.7	3.6	5.0	3.6	1.3	4.4	6.1	7.1	5.3	0.7	0.8	0.4	41.2
20	9.0	11.5	11.0	4.0	1.4	4.9	6.7	7.4	5.8	0.1	0.8	0.4	63.0
21	8.9	12.5	12.1	3.7	1.3	5.1	7.0	8.5	5.7	0.2	0.2	0.1	65.3
22	1.0	1.0	4.2	4.4	1.6	6.2	9.2	9.9	8.7	1.0	0.9	0.5	48.7
24	6.7	8.9	9.3	2.6	1.0	3.9	5.1	5.4	4.5	0.2	0.2	0.1	47.9
25	7.0	12.2	11.4	2.7	0.9	3.8	5.4	6.6	3.8	0.6	0.7	0.3	55.5
26	5.0	6.5	6.2	3.2	1.4	3.9	5.6	6.2	5.3	0.1	0.6	0.4	44.4
28	8.0	10.8	9.8	3.7	1.2	3.9	5.9	6.2	5.5	0.7	0.7	0.4	56.8
29	0.2	0.2	1.4	2.5	1.0	5.9	9.0	9.8	8.6	1.0	1.0	0.4	41.1

Table 7.8 Substituted aromatic hydrocarbon composition (as % of total PAH) for sediment samples from the Tees Estuary.

Sample No.	1-MN	2-MN	2,6-DMN	4-MBi	3-MBi	MP (3)	MP (2)	MP (9)	MP (1)	4-MDiBT	2,3-MdiBT	1-MDiBT	Sub. PAH
33	0.1	0.2	0.1	0.3	0.2	2.1	2.9	2.5	2.2	0.8	0.0	0.2	11.6
34	<0.1	<0.1	<0.1	0.1	<0.1	1.9	2.4	2.3	1.8	0.5	0.2	0.2	9.4
35	0.7	1.0	1.9	1.4	0.7	2.5	3.0	2.8	2.1	0.8	0.2	0.3	17.2
36	0.2	0.3	0.4	1.0	0.5	2.6	3.3	3.1	2.4	0.5	0.2	0.2	14.6
37	0.3	0.3	<0.1	0.4	0.0	1.1	1.3	0.9	0.7	0.2	<0.1	0.1	5.3
38	7.5	10.8	5.9	2.0	1.0	2.3	3.1	3.2	2.3	0.1	0.1	<0.1	38.5
29	0.2	0.3	0.1	1.7	1.1	2.7	3.6	3.6	2.6	0.1	0.1	0.1	16.3
40	1.2	1.8	3.1	3.3	1.4	4.4	5.5	6.2	4.7	0.3	0.2	0.3	32.4
41	15.6	23.1	10.5	2.4	0.9	2.9	4.0	4.7	3.2	0.1	0.2	<0.1	67.7
42	5.0	7.1	6.5	4.3	1.6	6.2	8.5	9.7	7.3	0.3	0.3	0.2	57.0
43	12.6	20.0	9.6	2.0	0.8	2.7	3.8	4.4	3.1	0.4	0.3	0.2	60.1

Table 7.9 Total PAH (unsubstituted + substituted) concentrations (ng g $^{-1}$) in sediment samples from Tees Bay and the Tees estuary.

Sample No.	Sum of Unsub. PAHs[a]	Sum of Sub. PAHs[b]	Total PAHs[c]
Tees Bay			
1	3809.7	9816.5	13626.2
2	2220.9	1610.0	3830.9
3	1438.9	1504.7	2943.6
4	10578.4	9958.4	20536.8
5	6098.9	10957.1	17056.0
6	4581.7	9123.3	13705.0
10	219.5	327.0	646.5
13	113.4	104.1	217.5
14	156.8	125.3	282.1
17	126.1	180.9	307.0
18	565.0	395.2	960.2
20	209.2	356.5	565.7
21	375.5	679.8	1055.3
22	50.6	48.0	98.6
24	2617.4	2402.2	5019.6
25	15421.8	19225.0	34646.8
26	116.9	93.3	210.2
28	342.8	451.5	794.3
29	28.8	20.1	78.9
Tees Estuary			
33	5499.9	724.1	6224.0
34	9160.9	945.1	10106.0
35	9888.5	2047.8	11936.3
36	12506.7	2142.2	14648.9
37	304264.6	17145.1	321409.7
38	19166.6	11995.1	31161.7
39	17708.0	3445.2	21153.2
40	14698.5	7053.7	21752.2
41	11211.0	23513.6	34724.6
42	10157.5	13472.7	23630.2
43	6277.0	9464.7	15741.7

[a] Sum of the concentrations of unsubstituted PAHs.
[b] Sum of the concentrations of substituted PAHs.
[c] Sum of the concentrations of all PAHs.

Generally, the results of aromatic fractions from the sediments follow the trend seen in the trace metals and aliphatic hydrocarbons, in that a more or less clear division can be made between Tees Bay aromatic fractions on the one hand, and those of Tees estuary on the other. From Table 7.9 it can be seen that the highest levels of PAHs in the study area can be found in the Tees estuary, particularly at site 37. In addition some sites in Tees Bay (site 4 and 25) also have high PAH concentrations similar to those of some sites in the Tees estuary (e.g. sites 41 and 42). However, it is more notable that the Bay samples have lower values.

In the Tees Bay there is a definite trend in that the highest concentrations of PAHs were found along the two offshore sites, at the southern and northern ends of the bay (sites 4 and 25; Table 7.9). As one moves towards nearshore, these levels progressively fall and reach a minimum at site 29, around the seaward end of the estuary. On the other hand, gas chromatograms of PAHs extracted from surface sediment samples of Tees Bay (e.g. sites 1, 4, 20 and 25; Fig. 7.2) are quite similar and contain many peaks of unsubstituted (parent PAH) and substituted PAHs, with no significant regional differences seen for the distribution of individual PAH compounds. The major PAHs are the same at all of the Tees Bay sampling sites and can be seen to be: alkylated naphthalenes (methyl and dimethylnaphthalene, AN), phenanthrene (P) and alkylated phenanthrenes (monomethylphenanthrenes, MP). Naphthalene (N), fluorene (F), biphenyl (Bi), dibenzothiophene (DBT), fluoranthene (Fl), pyrene (Pyr), chrysene (Chr) and benzo(*a*)anthracene (BaA) are also found at all sites but their concentrations are much lower than those of the major PAHs. Trace amounts of perylene were detected in most sediments, and anthracene occurs at trace levels in all samples.

As previously stated, the concentrations of PAHs in the Tees estuary were, in general, higher than the concentrations found on the Tees Bay. Generally, the PAH concentrations found at the eleven sampling sites, collected from three regions of the Tees estuary (the upper, the middle and the lower reaches of the estuary), are distributed fairly irregularly between these sites (Table 7.9). The sites in the upper Tees region (sites 33 and 34) have higher PAH concentrations than most Tees Bay sediments (except sites 1, 4, 5, 6 and 25), but were the lowest found in the estuary. In contrast, PAH levels at sites of the middle reaches of the estuary (sites 35-41) varied widely, with site 37 having by far the highest PAH concentrations found in the present study. Other sites of this region (sites 35, 36 and 38-41) also have high PAH concentrations but much lower than those of site 37. On the other hand, as one moves seaward of the middle reaches of the estuary the PAH concentrations decrease, reaching a minimum at site 43. However, these most seaward of the Tees estuary sampling sites (42 and 43) have higher levels of PAHs compared to sites 33 and 34 in the upper reaches of the estuary and sites 35, 36, 39 and 40 in the middle reaches of the estuary.

In addition, the chromatograms of the aromatic fractions extracted from the Tees estuary samples show that the PAH distributions are not the same for all sediments (e.g. sites 33, 35, 37 and 42; Fig. 7.3). These differences may indicate different sources of PAHs in surface sediments. The PAH gas chromatograms from sites 38-43 (e.g. site 42; Fig. 7.3) are similar to each other and continue the same trend observed by Tees Bay sediments, in that two-, three- and four-ring PAHs, as well as two- and/or three-ring alkylated PAH homologues, become the major peaks. On the other hand, the chromatograms of sites 35, 36 and 37 (e.g. sites 35 and 37; Fig. 7.3) show the presence of the same unsubstituted PAH peaks but with only minor amounts of alkylated PAHs compared to those of sites 38-43. A significant change in the PAH distribution is noted in the chromatograms of the two sediments from the upper reaches of the estuary (sites 33 and 34), where the relative abundance of the major individual PAH compounds are quite different to those of other sites from both areas (e.g. Site 33; Fig. 7.3). The major peaks found at these two sites were: fluoranthene (Fl), pyrene (Pyr), chrysene (Chr), phenanthrene (P), benzo(*a*)anthracene(BaA), benzofluoranthene (BF), benzo(*e*)pyrene (BePyr) and benzo(*a*)pyrene (BaPyr). Thus, these two sites have greater relative abundance of chrysene (Chr), benzo(*a*)anthracene (BaA), benzofluoranthene (BF), benzo(*e*)pyrene (BePyr) and benzo(*a*)pyrene (BaPyr) as compared to other sites from Tees Bay and Tees estuary.

If the data set is considered as a whole, the major PAHs present at all sites in the system, except sites 33-37, are two-, three- and four- ring PAH compounds (e.g. alkylated naphthalene, phenanthrene, methylphenanthrenes, fluorene and pyrene). In contrast, for sites 33-37 the major PAHs are three- four and/or five-ring PAH.

7.4 Discussion

7.4.1 Concentrations

PAHs are ubiquitous in sedimentary environments, with background levels of between 0.010 ug g^{-1} and 0.015 ug g^{-1} (10-15 ng g^{-1}) being found in deep sea sediments (Hites *et al.*, 1980). The identity and concentrations of PAH compounds, ranging in molecular weight from naphthalene (two-rings) to perylene (five-rings) and including alkyl substituted compounds, from each of the thirty sites along the study area are presented in Tables 7.1-7.4. The wide range of concentrations of these compound groupings suggests an influence of human activity on the present levels of these hydrocarbons. In general, in the present study, the total PAH concentrations (Table 7.9) vary from 48.9 to 34646.8 ng g^{-1} (0.049-34.65 ug g^{-1}), with a mean value of 6134.3 ng g^{-1} (6.13ug g^{-1}), for Tees Bay sediments and 6224.0- 321409.7 ng g^{-1} (6.22-321.41 ug g^{-1}), with a mean value of 46589.9 ng g^{-1} (46.59 ug g^{-1}), for Tees estuary sediments. These concentrations are generally higher than background levels in deep sea sediments that are considered to be contaminated (10-15 ng g^{-1}; Hites *et al.*, 1980), and likely to be biologically significant (Rainio *et al.*, 1986; McDonald Environmental Sciences Ltd., 1992), as discussed below.

The PAH concentrations vary over a relatively wide range, between the individual sites from both area (Table 7.9), and follow a similar trend to the *n*-alkane and metal concentrations, suggesting that the elevated PAH concentrations may be related to anthropogenic influences. It may be noted that PAH concentrations in Tees Bay correlate extremely well with data for total *n*-alkanes, as discussed below (Section 7.5.3.), suggesting a common anthropogenic source of these contaminants. The highest concentrations of total PAHs (Table 7.9) occur in the Tees estuary and some sites in Tees Bay (sites 1, 2, 4, 5, 6, 24 and 25), ranging from 3830.9 ng g^{-1} (3.8 ug g^{-1}) at site 2 to 321409.7 ng g^{-1} (321.4 ug g^{-1}) at site 37. These levels are similar to, or exceed 3.8-6.8 ug g^{-1}, the levels considered to cause deleterious biological effects (McDonald Environmental Sciences Ltd., 1992; Burt and Ebell, 1995).

The higher overall concentrations of PAHs in the Tees estuary compared to Tees Bay could be a result of continuous deposition of PAHs derived from industrial discharges, heavy commercial shipping and boating activities, an adjacent major roadway and the riverine input *via* the river Tees. As observed for aliphatic hydrocarbons and metals, the highest total PAHs concentrations occur in sediments from site 37 (in the middle reaches of the estuary). It is not unexpected that the PAH concentrations in this sample would be high, due to the proximity of the sampling location to a heavily industrialized area (LaFlamme and Hites, 1978). The elevated levels in this zone suggests that PAHs were deposited in the sediments close to their discharge points and that physical mechanisms such as currents and tides have dispersed the sedimentary PAHs to only a limited extent. The upper reaches of the estuary, on the other hand, showed the lowest levels of PAHs apparently receiving a lower input of PAHs than those of other estuarine stations.

PAH concentrations also followed a similar trend to those of *n*-alkanes in Tees Bay, which suggests petrogenic inputs at these sites (see Chapter 6, section 6.5.4). The highest concentrations of both aliphatic and aromatic hydrocarbons are found in the sediments from the two offshore areas (sites 25 and 4), and the PAH concentrations show a general decrease from north to south (Table 7.9). The lowest concentration (48.9 ng g^{-1}) is observed, as for *n*-alkanes and metals, at station 29. This value is similar to concentrations reported for the Adriatic (ranged from 12-174 ng g^{-1}; Marcomini *et al.*, 1986), and could indicate atmospheric deposition (Lipiatou and Saliot, 1991a).

Varying amounts of naphthalene (two-ring) and phenanthrene (three-rings) homologous series, including the parent (unsubstituted) compound and their alkylated derivatives (Tables 7.1-7.4), are found in the sediment samples from both areas, as well as the four-ringed compound groupings of fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, and five-ringed compound groupings of benzofluornathene, benzo(*e*)pyrene and benzo(*a*)pyrene. The fact that the percentages of each individual PAH are similar between all sites in Tees Bay (Tables 7.5 and 7.7) and some sites in Tees estuary (sites 38, 39, 40, 41, 42 and 42; Tables 7.6 and 7.8) suggests that these compounds are being supplied from a common anthropogenic source. The high percentages of fluoranthene and pyrene in sites 33-37, on the other hand, may suggest that another source of these compounds also exists for these samples. However, in nearly every sample, most PAH determined were the same as those found in a great diversity of environments and can be regarded as ubiquitous in sediments worldwide (LaFlamme and Hites, 1978; Wakeham *et al.*, 1980; Prahl *et al.*, 1984; Johnson *et al.*, 1985). Many of these PAH have been shown to be the result of combustion of a variety of fuels under many different sets of conditions (Yu and Hites, 1981; Yergy and Risby, 1982; Grimmer *et al.*, 1983; Ramdahl, 1983). Although PAH are also present in small amounts in petroleum and coal and their refined products, these sources are easily characterizable by a predominance of substituted PAH over unsubstituted PAH. It is evident therefore that the dominant PAH compounds in the sediments studied are probably derived from fossil fuels through both urban run-off and combustion sources, as discussed below (section 7.5.4.).

The PAHs are of special environmental interest because of the carcinogenic properties of some of them (BaA, Chr, BF, BePyr and BaPyr). In Tees Bay, these carcinogenic PAHs vary from 1-16.1% of the total PAHs, with the most potent carcinogen, BaPyr, comprising 0.1-1.7% of the total. Tees estuarine samples exhibit a generally higher proportion of carcinogenic PAHs than in Tees Bay, comprising 1-47% of the total PAHs, with BaPyr varying from 0.1-3.6% of the total PAHs. Benzo(*a*)pyrene shows much higher concentrations in Tees estuary (3-338.6 ng g^{-1}) than those previously reported for example in the coastal Mediterranean Sea (ranged from 72-170 ng g^{-1}; Lipiatou and Saliot, 1991b).

7.4.2 Current Situation of Tees Bay and Tees Estuarine sediment

The concentrations of individual PAHs in surface sediments of the Tees Bay and Tees Estuary (Tables 7.1-7.4) have not been reported before, and are given in Tables 7.1 to 7.4. In order to discuss the extent of individual PAH levels in these regions, average concentrations from this study are compared to results reported from a number of different geographical areas (Table 7.10) from other locations in the UK and overseas. Most of the literature values are reported as ug g^{-1} so the results of this study have been converted to ug g^{-1}. Since aromatic hydrocarbons are often extracted and analysed differently from one study to the next, these data are intended as a guide only. These data indicate that Tees river estuarine sediments contain higher levels than sediments from the relatively unurbanized and unindustrialized areas such as Ross and Buurdekin rivers (Australia), Amazon River system (Brazil), and Monchaltorfer River (Switzerland), or sediments from indutrialized ports such as Humber Bay (U.K.), Gladstone and Townsville Harbours (Australia). However, sediments from other

Table 7.10 Reported average concentrations (ug/g) of individual PAH compounds in surface sediments from different geographical areas.

Location	P	A	Fl	Pyr	BaA	Chr	BF	BePyr	BaPyr	Per	Reference
Monchaltorfer River, Switzerland (moderately urbanized)	0.21	0.02	0.39	0.33	-	-	-	0.15	0.19	0.03	Giger & Schaffiner (1978)
Usk River, U.K. (Industrialized)	9.0^a	-	30.0	0.50	-	25.0	-	24.0	11.0	-	Eglinton *et al.* (1975)
Sydney Harbour, Nova Scotia, Canada (industrialized)	57.0	-	52.72	36.60	36.76	17.65	-	10.41	10.15	-	Sirota *et al.* (1983)
Charles River, MA, U.S.A. (highly urbanized)	- 5.0^a	- -	8.35 15.0	7.50 13.0	1.40 21.0^b	- -	- -	- 0.33^c	1.30 -	0.62 -	Heit & Tan (1979) Hites *et al.* (1980)
Elizabeth River, VA, U.S.A. (highly urbanized)	25.0	-	42.0	28.0	11.0	19.0	-	6.0	9.0	-	Bieri *et al.* (1986)
Amazon River System, Brazil (mostly remote)	0.005	-	0.003	0.003	-	-	-	0.0009^c	-	-	Hites *et al.* (1980)
Yarra River Estuary, Vic., Australia (highly urbanized)	-	-	-	-	-	-	-	-	1.83	1.23	Bagg *et al.* (1981)
Gladstone Harbour, Qld., Australia (Coal port)	-	-	-	0.27	0.18	0.01	-	-	0.82	-	Smith *et al.* (1985)
Ross River, Qld., Austeralia (rural)	-	-	0.06	0.04	0.02	0.02	-	-	0.04	-	Smith *et al.* (1985)

Table 7.10 Continued.

Location	P	A	Fl	Pyr	BaA	Chr	BF	BePyr	BaPyr	Per	Reference
Burdekin river, Qld., Australia (some boating activity)	-	-	0.01	0.01	<0.0	<0.01	-	-	<0.01	-	Smith *et al.* (1985)
Brisbane River Estuary, Qld. Australia (urbanized & industrialized)	0.45	0.11	0.89	0.80	0.30	0.43	-	0.28	0.38	0.36	Kayal & Connell (1989)
Mersey Estuary Dee Estuary Tamar Estuary	0.75 0.06 0.79	- - -	1.01 0.08 1.88	0.79 0.06 1.15	0.33 0.03 0.65	0.44 0.03 0.69	0.63 0.04 0.76	0.04 0.03 0.55	0.51 0.03 0.76	- - -	Readman *et al.* (1986)
Humber Bay, North Sea U.K. side	0.67-0.32^d	0.06-0.33	0.42-1.86	0.46-1.50	0.10-0.55	0.16-0.84	-	0.22-0.68	0.13-0.68	-	Klamer &Fomsgaard (1993)^d
Tees Bay	1.13	0.06	0.31	0.22	0.10	0.13	0.03	0.03	0.03	<0.01	This work
Tees Estuary	11.0	1.25	9.93	8.32	1.27	0.98	0.22	0.15	0.13	0.03	This work

[a] = phenanthrene + anthracene.

[b] = Benzo(a)anthracene + chrysene.

[c] = benzofluoranthene + benzo(e)pyrene + benzo(a)pyrene.

[d] = range in concentrations of PAHs in Humber Bay surface sediments are used by this reference.

highly industrialized or urbanized areas, such as Usk River (U.K.), and Charles and Elizabeth Rivers (U.S.A.), and Sydney Harbour (Canada), generally exhibit much larger PAH levels. While the data for the highly urbanized Yarra River are incomplete, they suggest much higher PAH levels than the Tees River estuary. It can also be seen from the data in Table 7.10 that PAH levels in the Tees estuary are an order of magnitude or more above those found in sediments of other industrialized and/or urbanized estuaries in the U.K., such as the Mersey, Dee and Tamar.

Further comparison with published data (Table 7.10) showed that PAH concentrations obtained in this study from Tees Bay sediments are of the same order of magnitude as those obtained from the Monchaltorfer River (Switzerland), which include moderately urbanized. PAH levels in Tees Bay are also well below those found in highly industrialized or urbanized areas of the U.K. (Usk River), U.S.A. (Charles and Elizabeth Rivers), Canada (Sydney Harbour) and Australia (Yarra River), as well as those estuaries from industrialized and/or urbanized of the U.K. (Mersey and Tamar) and Australia (Brisbane), but higher than those sediments from the relatively unurbanized and unindustrialized or remote areas. It is interesting to note that the industrial ports of Gladstone and Townsville Harbours have low urbanization but comparable PAH concentrations to the Tees Bay. Furthermore, Table 7.10 reveals that PAH concentrations in Tees Bay are also comparable to those reported from Humber Bay which were considered to be polluted due to anthropogenic influences arising out of industrialization and urbanization in this area (Klamer and Fomsgaard, 1993).

From a comparison of the PAH concentrations found in the Tees Bay and Tees estuary against those from other contaminated and uncontaminated areas, it is evident that the Tees estuary, and to a lesser extent Tees Bay, contains elevated levels of this class of chemical.

7.4.3 PAH levels in relation to sediment characteristics

As stated previously (see Chapter 4, section 4.1.2.), the sediments of the Tees Bay and Tees Estuary range from sandy material to clayey-silt sediments containing a high amount of organic carbon. As for metals and aliphatic hydrocarbons, the concentrations of PAHs in the sediment samples show wide variations, depending on the kind of sediment. In Tees Bay, for example, the highest concentrations of PAHs are generally found, as expected, in the clayey-silt sediments (sites 4 and 25), due to their high organic carbon contents, while the sandy sediments commonly exhibit the lowest levels of PAHs analyzed. In contrast, in the Tees estuary concentrations of PAHs in the sediments followed a different trend to those of the Tees Bay with higher concentrations being found in the muddy sediment from the middle reaches of the estuary (site 37) which contains a lower TOC content compared to the sandy sediment from the lower reaches of the estuary (site 42). According to other authors (Lee *et al.*, 1978; Neff, 1979; Boehm and Farrington, 1984; Johnson *et al.*, 1985; Chiou *et al.*, 1985; Boehm and Requejo, 1986; Van Vleet *et al.*, 1987; Pereira *et al.*, 1992; Witt, 1995), PAHs in sediments are mainly associated with organic matter, thereby indicating the importance of organic carbon in the sorption of non-ionic compounds to sediments (Chiou *et al.*, 1985*).* However, in about 30% of data from the study of Johnson *et al.* (1985) and in other studies (Matsushima, 1979; Bagg *et al.*, 1981) no obvious correlation was observed. In addition, an inverse relationship has sometimes been found between the organic carbon and PAH concentrations in sediments (Martel *et al.*, 1986). In this latter case, organic matter from a paper mill was suggested to have a diluting effect on PAH levels. Moreover, the association of PAHs with certain size fractions in sediments has been reported by Matsushima (1979), Brassell and Eglinton (1980) and Boehm and Farrington (1984).

In the present study a correlation matrix was produced to investigate the relationship between the concentrations of PAHs, *n*-alkanes, grain size and TOC, in the sediment samples from Tees Bay and the Tees estuary (Tables 7.11 and 7.12, respectively). According to Table 7.11, the total PAH and *n*-alkane concentrations in Tees Bay are positively correlated, to one another (at the 99% significance level), and are also positively correlated with TOC, clay and silt but negatively correlated to sand particles (at the 99% significance level). This finding clearly shows the greater association of PAHs and *n*-alkanes with TOC and to a lesser extent silt grade particles, than with clays. It also indicates that these two hydrocarbon classes may be, but not necessarily, being preserved in the same way.

In contrast, in Tees estuarine sediments PAHs and *n*-alkanes are positively correlated to one another and are also inversely correlated to TOC and sand, but these correlations are not significant. Clay is positively, and weakly, correlated to PAHs but showed insignificantly an inverse relationship to *n*-alkanes. Silt, on the other hand, shows a different trend to that of clay, in that it inversely correlated to PAHs but weakly correlated to *n*-alkanes. This indicates that the concentrations of PAHs and *n*-alkanes in surficial sediments of the Tees estuary do not relate to grain size or %TOC.

Table 7.11 Correlation matrix showing the coefficient between different pairs of variables measured in Tees Bay.

	***n*-alkanes**	**PAH**	**Clay**	**Silt**	**Sand**	**TOC**
***n*-alkanes**	1.00					
PAH	0.95**	1.00				
Clay	0.75**	0.80**	1.00			
Silt	0.82**	0.81**	0.93**	1.00		
Sand	-0.82**	-0.82**	-0.87**	-0.99**	1.00	
TOC	0.97**	0.89**	0.74**	0.88**	-0.77**	1.00

* = Significant at $P<0.05$.
** = Significant at $P<0.01$.

Table 7.12 Correlation matrix showing the coefficient between different pairs of variables measured in the Tees Estuary.

	***n*-alkanes**	**PAH**	**Clay**	**Silt**	**Sand**	**TOC**
***n*-alkanes**	1.00					
PAH	0.06	1.00				
Clay	-0.16	0.30	1.00			
Silt	0.16	-0.01	0.67*	1.00		
Sand	-0.06	-0.09	-0.83**	-0.97**	1.00	
TOC	-0.51	-0.12	-0.24	-0.72*	0.61*	1.00

* = Significant at $P<0.05$.
** = Significant at $P<0.01$.

7.4.4 Distributions of PAHs along the Tees Bay and Tees estuary

The aromatic fraction was composed of both alkylated and non-alkylated hydrocarbons. As can be seen from the data in Tables 7.1 to 7.4 a variety of different PAHs ranging from naphthalene (two rings) to perylene (five rings) were detected and quantified. Generally, two- and three-ring PAHs are most likely related to petrogenic hydrocarbon spillages, such as diesel and fuel oil, whilst four- and five-ring compounds, fluoranthene to benzo(*a*)pyrene, are primarily produced as a result of fossil fuel combustion (Bates *et al.*, 1984; Boehm and Farrington, 1984; Burt and Ebell, 1995).

Gas chromatograms of aromatic fractions isolated from extracts of Tees Bay and Tees estuarine sediments are shown in Fig. 7.2 and 7.3, respectively. These chromatograms are mainly characterized by the presence of a series of polycyclic aromatic hydrocarbon (PAH), as a complex suite of aromatic and alkyl aromatic compounds, derived from anthropogenic sources, and by a chromatographically small or narrow UCM. This hump is similar to that of a typical North Sea oil, such as Brent crude (Jones *et al.*, 1983) as well as those from polluted estuarine, lake, marine sediments (Thompson and Eglinton, 1978; Bates *et al.*, 1984; Prahl *et al.*, 1984; Readman *et al.*, 1986; Al-Saad, 1987; Leeming and Maher, 1992) and air particulates (Takada *et al.*, 1990).

These chromatograms (Figs.7.2 and 7.3) clearly illustrate variability in the distributions of PAH compounds in sediments from Tees Bay (e.g. sites 1, 4, 20 and 25) and Tees estuary (e.g. sites 33, 35, 37 and 42), suggesting multiple sources for these compounds. In general, the Tees Bay and Tees estuarine sediments contain larger amounts of the complex PAH compounds than sediments remote from areas of natural oil seeps or anthropogenic activities (Aizenshtat, 1973; Giger and Blumer, 1974; Youngblood and Blumer, 1975; LaFlamme and Hites, 1978; Venkatesan *et al.*, 1980). The PAH distributions in sediments from all sites, except 33 - 37, are broadly similar in that they are dominated by alkylated and non-alkylated PAHs with higher abundances of lower molecular weight alkylated compounds (two- and/or three-ring PAHs), indicative of a primarily petroleum hydrocarbon source (*vs* combustion-generated PAHs). The presence of alkyl derivatives of PAH is usually evidence of pollution from complex hydrocarbon mixtures (Desideri *et al.*, 1989; Green *et al.*, 1992), as petroleum products contain more alkylated than parent aromatics (Platt and Mackie, 1981). Another possible source of some of the PAH in these sediments might be coal fragments. To confirm this observation a coal sample, collected from the northeast coast of England (Whitley Bay), was extracted and analysed, by using the same method adapted in the present study. Figure 7.4 shows the gas chromatogram obtained from the polycyclic aromatic hydrocarbon fraction of the coal sample. This chromatogram is mainly characterized by the presence of a series of PAH, as a

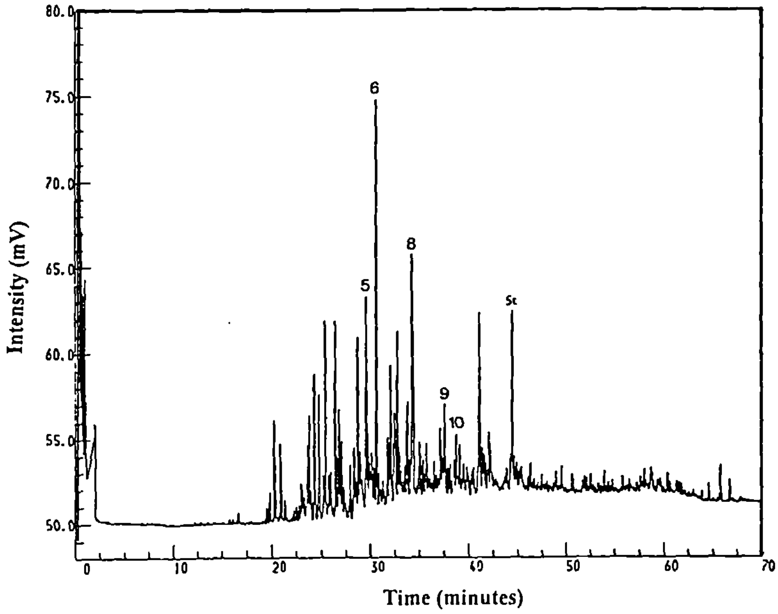


Figure 7.4. Gas chromatogram of PAHs in the coal sample. Peak identification and chromatographic conditions as for Fig. 7.2.

complex suite of aromatic and alkyl aromatic compounds, and by a chromatographically small or narrow UCM. It can also be seen from the gas chromatogram of F3 fraction, extracted from coal (Fig 7.4), that alkylated PAHs, with higher abundances of lower molecular weight alkylated compounds (three-ring PAHs), are the most dominant hydrocarbon. This finding is similar to that observed in sediment samples from all sites, except 33-37, suggesting that the high level of alkylated PAH compounds in these sediments could be a result of continuous deposition of polycyclic aromatic hydrocarbons derived from coal. Similar distributions have been found in many other sediments around the world (Barrick and Prahl, 1987).

In contrast, chromatograms for sites 33-37 (see Fig. 7.3, station 33, 35 and 37) show higher abundance of unsubstituted four-ring PAH relative to two- and three-ring PAHs and a lack of alkyl substituted PAH of lower molecular weight compounds, when compared to those of other sites. This suggests that much of the PAH in these sediments is probably derived from combustion products of fossil fuels. Those non-alkylated aromatic compounds are most certainly due to pollution from anthropogenic combustion of fossil fuels and have been widely reported to occur in surface sediments (e.g. LaFlamme and Hites, 1978; Wakeham *et al.*, 1980; Rowland and Maxwell, 1984), including those of estuaries, such as the Severn Estuary (Thompson and Eglinton, 1978; Brassell and Eglinton, 1980), the Mersey, Tamar and Dee estuaries (Readman *et al.*, 1986), and air particulates (Takada *et al.*, 1990; Leeming and Maher, 1992).

Examination of GC traces representing the two regions (Figs. 7.2 and 7.3), showed that the distribution of aromatic hydrocarbons differ in terms of the relative abundance of the major individual PAH compounds. This fact supports the above finding that the PAH compounds found in the present study are being supplied from at least two different sources.

In order to distinguish between different anthropogenic inputs, the distribution patterns of some parent PAHs and their alkylated homologs can be examined in greater detail.

Naphthalene and its alkylated derivatives are present in varying amounts in the sediment samples and these two-ring aromatic compounds are derived mainly from anthropogenic activities (Venkatesan and Kaplan, 1982). The distribution of naphthalene and its alkylated derivatives in the sediments studied, from both areas (Fig. 7.5), presents a maximum at methyl naphthalenes at all stations from both areas except for stations 22 and 29 in Tees Bay and sites 35, 36 and 40 in the Tees estuary where the distribution peaks at dimethyl derivatives. This feature, characteristic of crude petroleum (Sporstol *et al.*, 1983), is surprisingly common in both estuarine and open sea stations.

A great diversity is observed for the distribution patterns of phenanthrene and its alkylated derivatives, in Tees Bay and Tees estuarine sediments (Fig. 7.6). Such diversity of composition has been previously discussed by Hites *et al.* (1980) and Sporstol *et al.* (1983). In Tees Bay, stations 24 and 25 show a typical pyrolytic pattern with a predominance of parent compounds over alkylated derivatives. However, all other stations in the Bay show a petrogenic pattern where alkylated derivatives predominate over the parent compound. For the Tees estuarine sediments, stations 33-40 show a typical pyrolytic character, whereas the lower stations on the estuary (41-43) are undoubtedly characterized by petrogenic hydrocarbon inputs (Fig. 7.6).

Here the use of all these patterns provides complementary information for interpretation. The naphthalene series patterns show that a background content of petrogenic hydrocarbons exists in all stations. In addition, the phenanthrene series indicate the following predominant inputs: petrogenic at all stations in the study area, with an additional input of pyrogenic PAH at stations 24, 25, and 33-40, probably originating from urban-runoff, industrial activities and the riverine input *via* the river Tees, as suggested previously.

Sulphur compounds, such as dibenzothiophene and related alkylated derivatives are also identified but at low concentrations compared to those of alkylated phenanthrenes and naphthalenes (Tables 7.3 and 7.4). Their distributions present a marked maximum for the parent compounds for all stations. These patterns do not discriminate between petrogenic and pyrolytic origins (Sporstol *et al.*, 1983). Nevertheless, if the concentrations of all parent PAHs and their alkylated derivatives in each of the previously examined series of PAH are summed, and plotted as a function of the different stations, from Tees Bay and Tees estuary (Figs. 7.7 and 7.8), a similarity between the distributions of the dibenzothiophene and phenanthrene

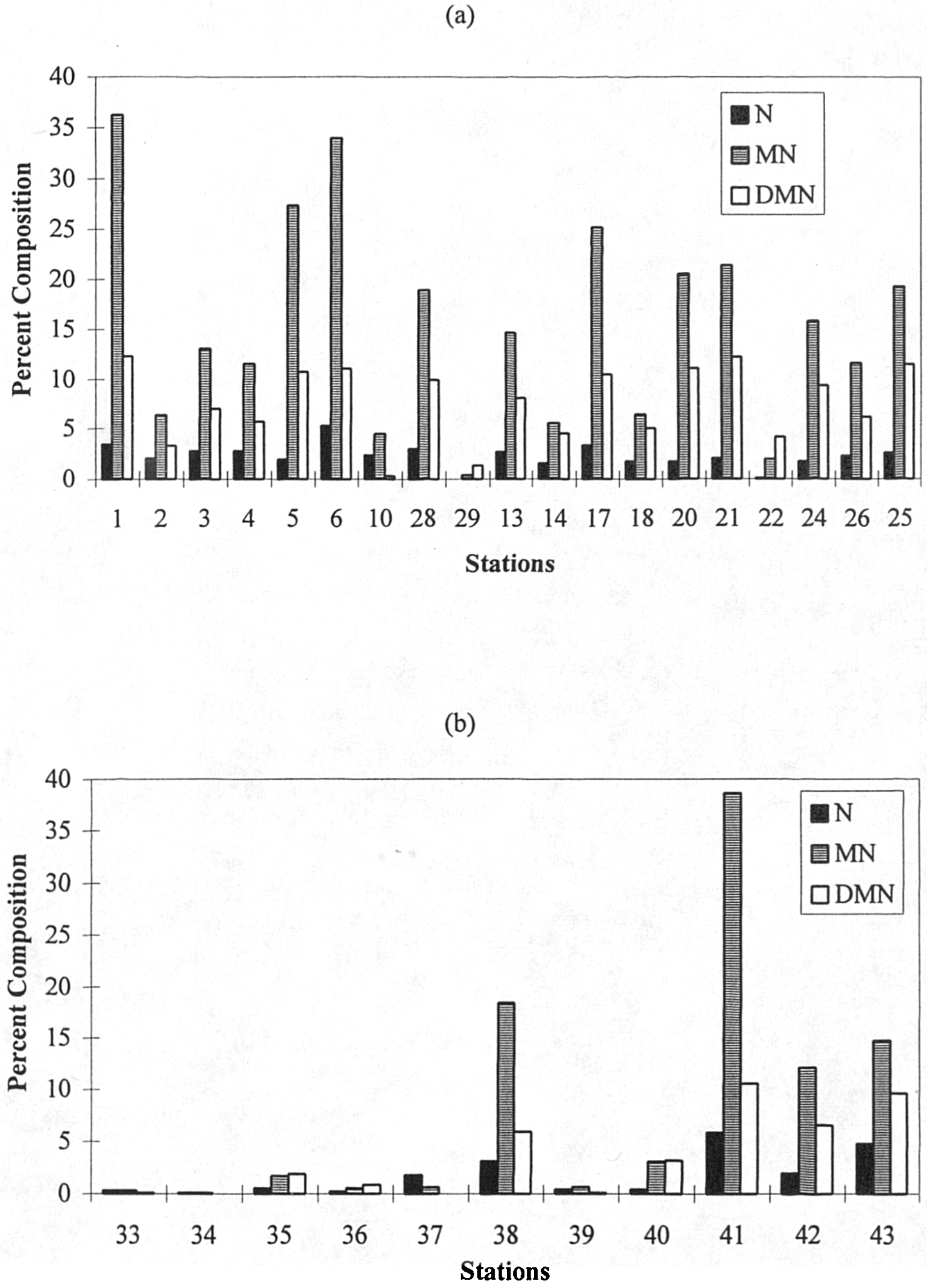


Figure 7.5. Distribution patterns of naphthalene and alkylated derivatives in surface sediments from (a) Tees Bay and (b) Tees Estuary. Concentrations are given in percent (%) of these PAH compounds to total PAHs.

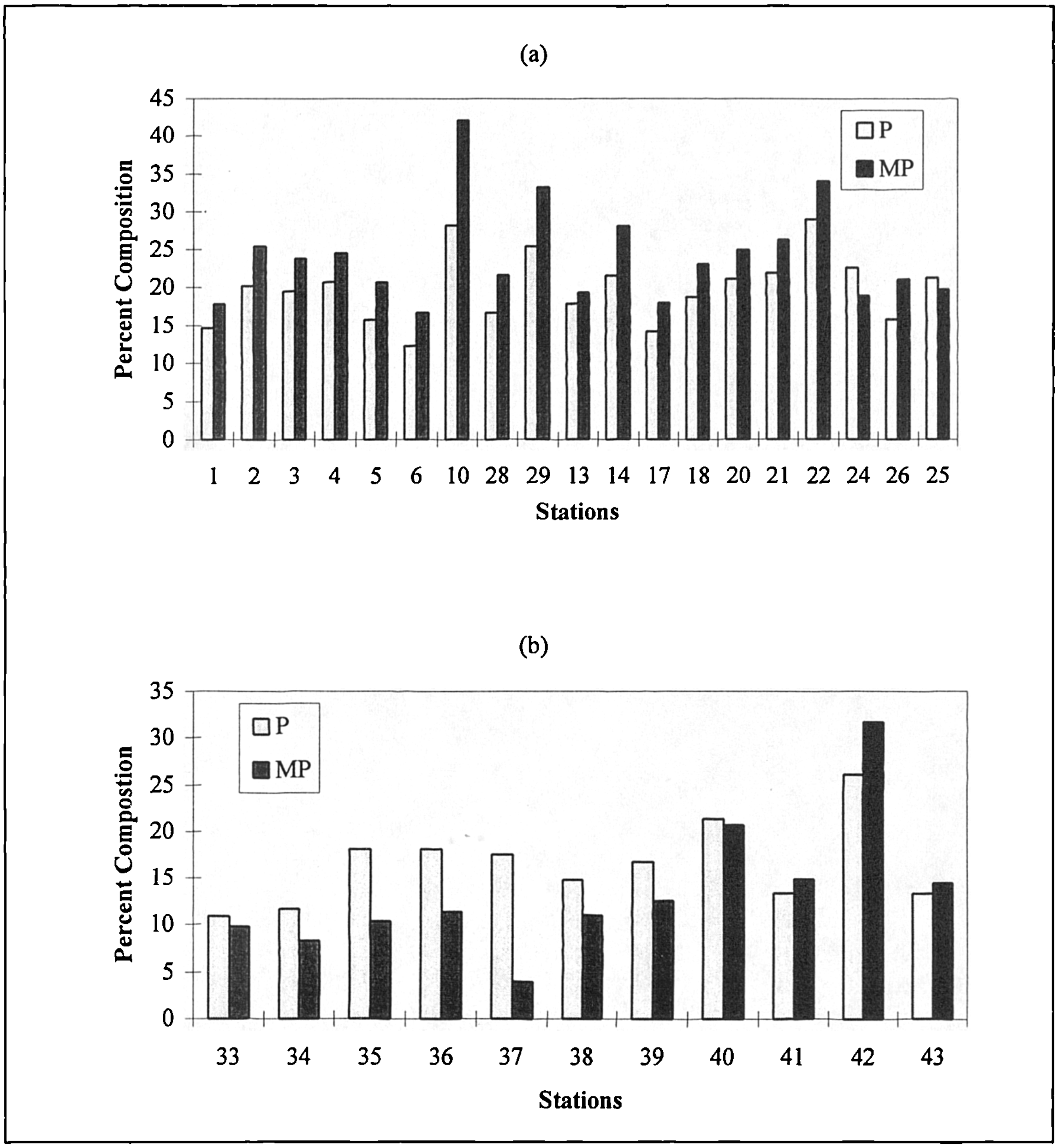


Figure 7.6. Distribution patterns of phenanthrene and alkylated derivatives in surface sediments from (a) Tees Bay and (b) Tees Estuary. Concentrations are given in percent (%) of these PAH compounds to total PAHs.

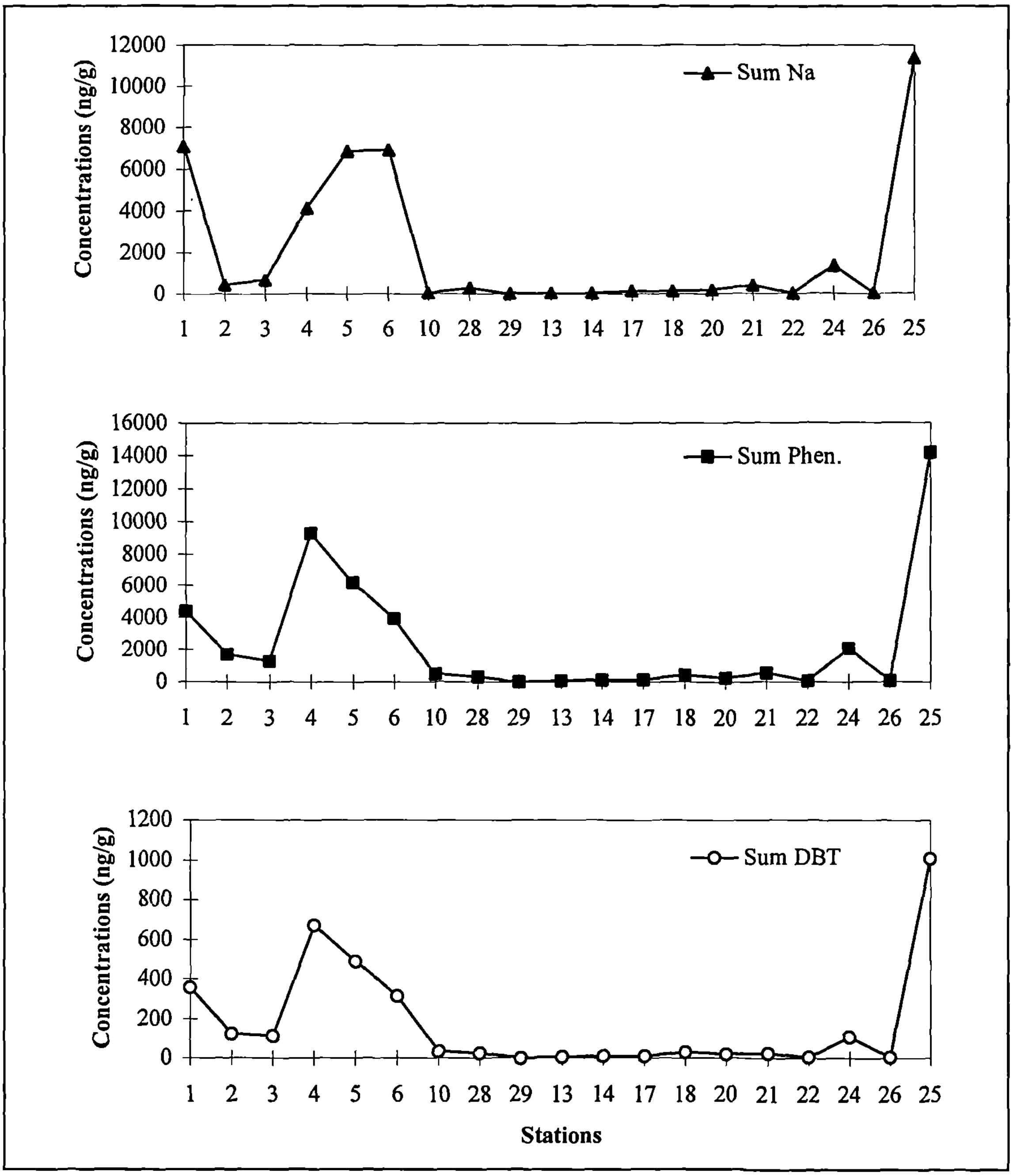


Figure 7.6. Concentrations (ng/g) of the sum of all compounds identified in surface sediments from Tees Bay in the (a) naphthalene, (b) phenanthrene and (c) dibenzothiophene series.

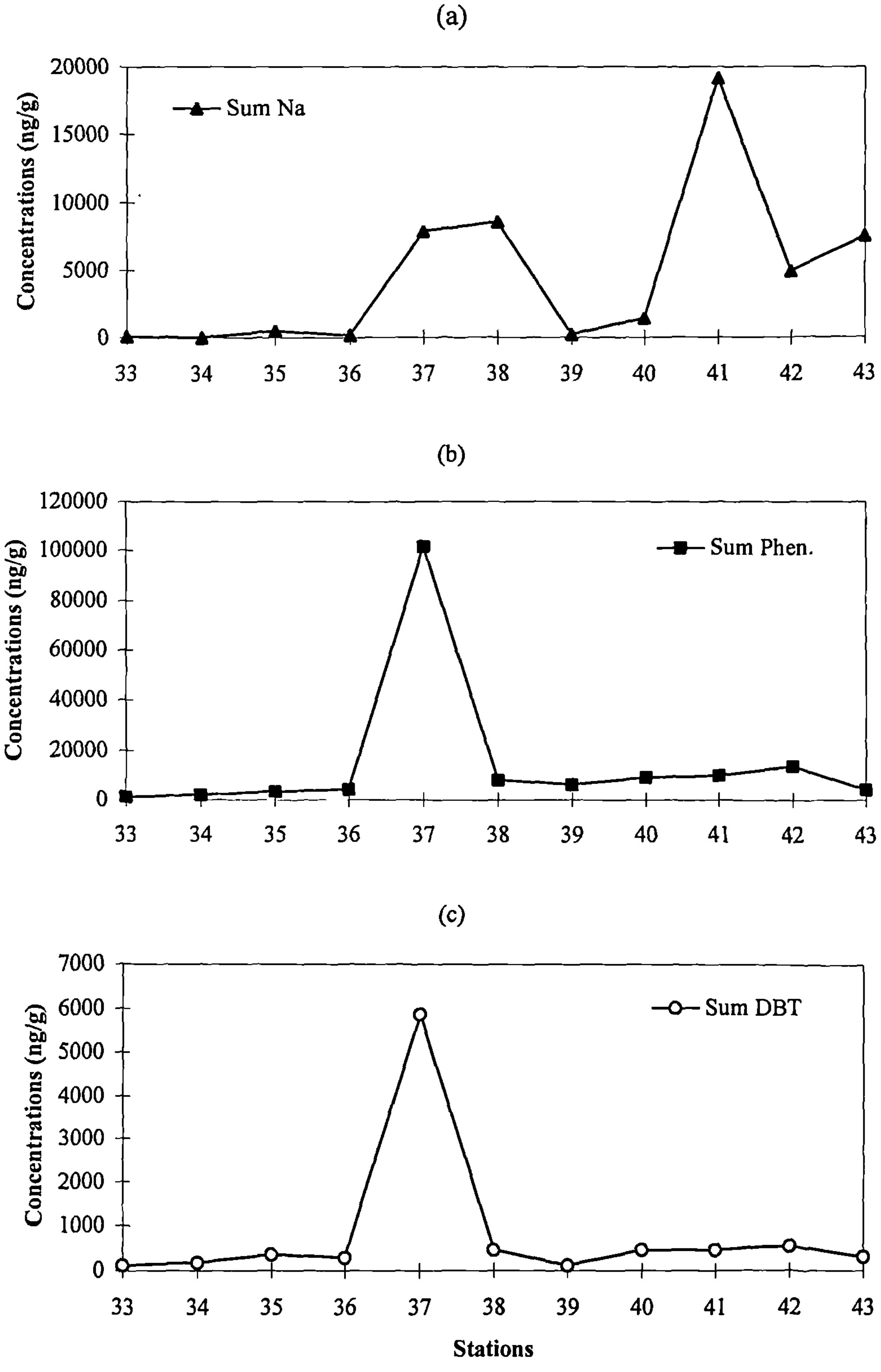


Figure 7.8. Concentrations (ng/g, dry weight) of the sum of all compounds identified in surface sediments from the Tees Estuary in the (a) naphthalene, (b) phenanthrene and (c) dibenzothiophene series.

series, in both areas, can be observed. This may suggests a common origin of these compounds (Lipiatou and Saliot, 1991b).

7.4.5 Sources of observed PAH assemblages

Sources of PAH in the aquatic environment are numerous and have been discussed in detail by Giger and Blumer (1974), Youngblood and Blumer (1975), LaFlamme and Hites (1978), and Hites *et al.* (1980). In general, the origins of PAHs entering the aquatic environment fall into two broad categories, combustion (pyrolytic or pyrogenic) and fossil fuel (petrogenic). However, perylene is thought to be of primarily *in situ* diagenetic origin (Aizenshtat, 1973; LaFlamme and Hites, 1978; Gschwend *et al.*, 1983).

The *in situ* diagenetic origin (aromatization) of naturally occurring compounds can produce PAH, but this type of formation is characterized by a relatively small number of specific compounds (LaFlamme and Hites, 1978) and not the complex mixture seen in the sediments studied. Thus it seems likely that as natural sources of PAH only contribute a minor amount of PAH to these sediments; most of the PAH found in the sediments studied are of anthropogenic origin.

As stated previously (section 7.5.4), it does appear that PAH compounds found in the Tees sediments originate from the direct input of non-combustion PAHs (e.g. fossil fuels) and to a much lesser extent from a combination with fossil fuel combustion products. The higher contribution of fossil fuel PAH sources is demonstrated by the composition of most of the samples. Fossil fuel origin for the PAHs may be indicated by greater relative abundances of alkylated naphthalenes and alkylated phenanthrene compounds compared to the unsubstituted parent compound. However, a preponderance of unsubstituted three-, four-, and five-ringed PAH in some of the samples compared with two-ringed naphthalenes, and the lack of alkyl substituted PAH also demonstrates an additional combustion-PAH-dominated assemblage at some sites. The molecular distribution of some of these PAHs found in the sediment samples at selected stations, from Tees Bay and the Tees estuary, are illustrated in Figures 7.9 and 7.10, respectively. According to these two Figures, the relative compositional profiles of PAH distributions differ between stations, and between the two areas. The different compositions indicate different possible sources.

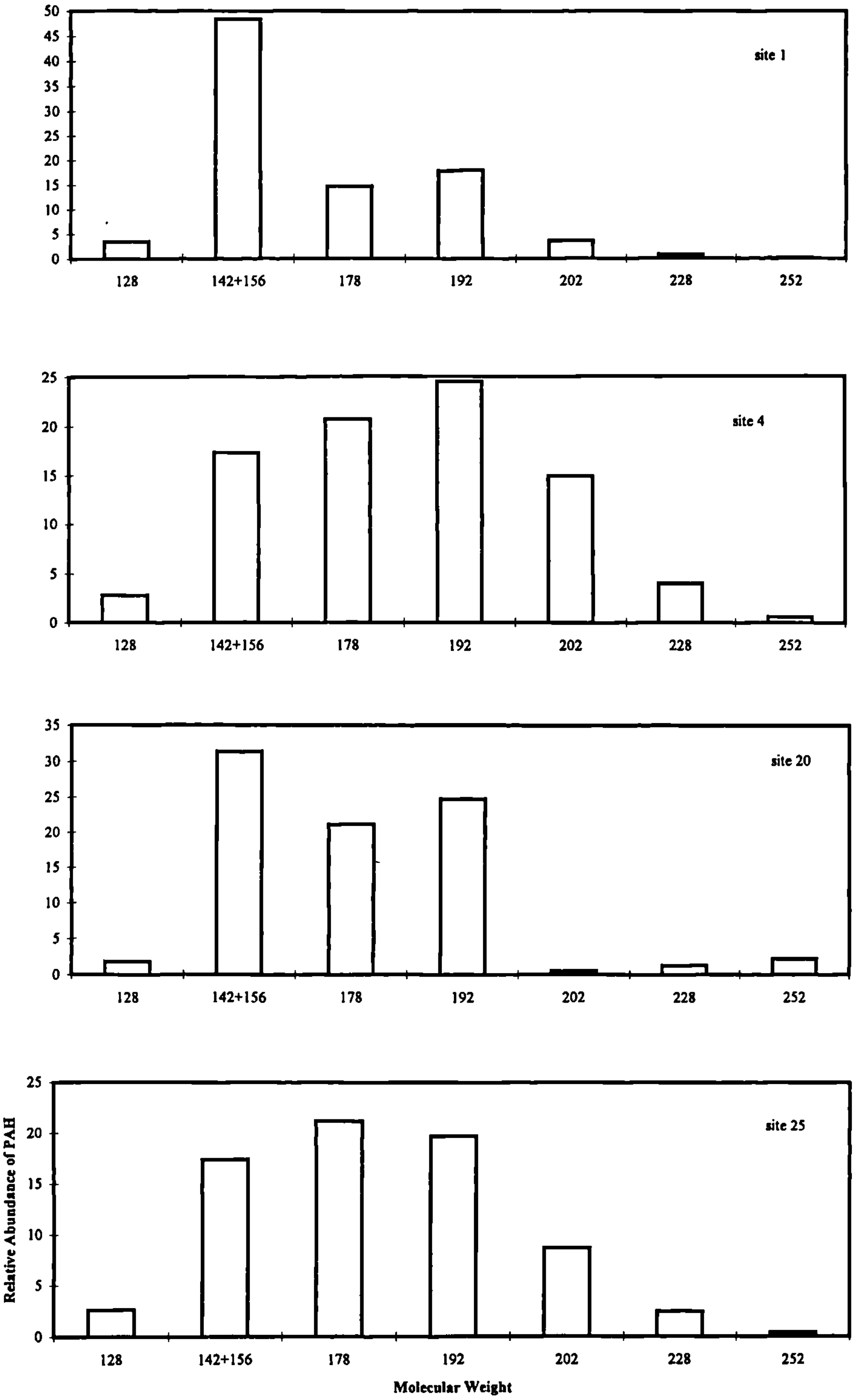


Figure 7.9. Relative (%) compositional profiles of PAH distributions in surface sediments, at selected stations, from Tees Bay. (Molecular weights: 128, naphthalene; 142+156, methyl and dimethylnaphthalene; 178, phenanthrene; 192, monomethylphenanthrene; 202, fluoranthene + pyrene; 228, benzo(a)anthracene + chrysene; 252, benzofluoranthene + benzo(*e*)pyrene + benzo(*a*)pyrene + perylene).

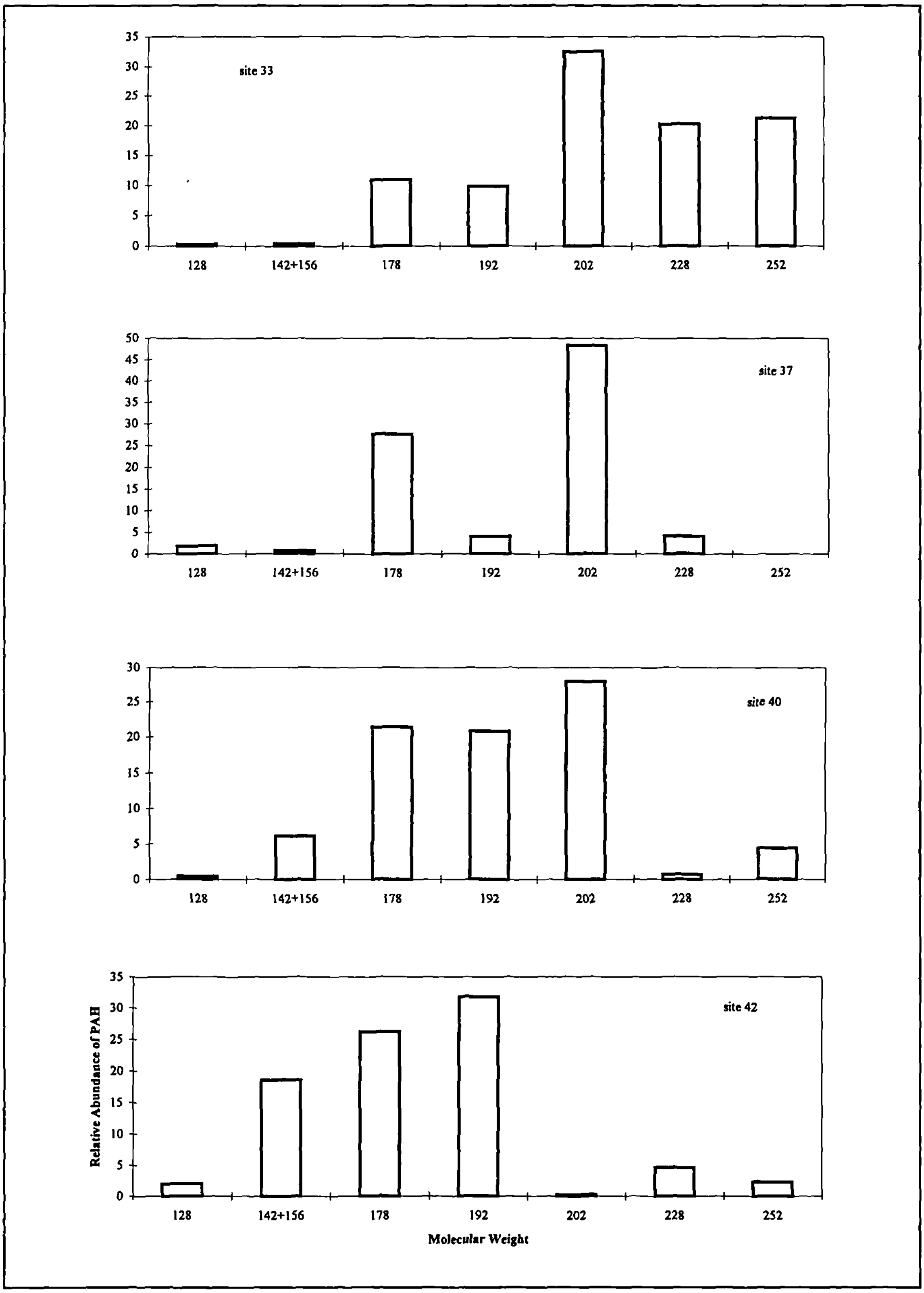


Figure 7.10. Relative (%) compositional profiles of PAH distributions in surface sediments, at selected stations, from the Tees Estuary. (Molecular weights: 128, 124 + 156, 178, 192, 202, 228 and 252, as for Fig. 7.9).

In the Tees Bay, for example, all sites, except sites 24 and 25, show characteristic patterns of non-combustion derived PAH mixtures, similar to those of crude oil (Boehm and Farrington, 1984), containing large amounts of alkylated naphthalenes (142 + 156; two rings) and phenanthrenes (192; three rings). In addition, the molecular distribution of the coal sample extracted in the present study (Fig. 7.11) is similar to those of the sediment samples from all sites in the Tees Bay except sites 24 and 25. This suggests that these samples may received a distinguishable contribution of coal. The phenanthrene/alkylated-phenanthrene distribution in sediments from other sites (24 and 25), on the other hand, differs with high levels of phenanthrene compared with the monomethylphenanthrenes. Moreover, four-ring PAH (202 and/or 228) are also relatively major components in these sediments, compared to the abundant two- and three-ring compounds (142 + 156 and 178). However, for stations 24 and 25 no dominant pattern emerges, but rather a mixed pattern of petrogenic and pyrolytic input, due to oil spillages as discussed below.

For the Tees estuary, the sediment extracts of stations 33, 34, 35, 36, 37, 39 and 40, show a wide variety of source signatures different from those of the Tees Bay. Molecular distributions of these samples (e.g. 33, 37 and 40; Fig. 7.10), taken from the Tees estuary, are dominated by non-alkylated PAHs widely attributed to combustion sources (LaFlamme and Hites, 1978) or urban drainage/street runoff (Gschwend and Hites, 1981), namely, fluoranthene and pyrene, and to lesser extent phenanthrene, chrysene and others. Alkylated homologs (142 + 156 and/or 192) are in low concentration relative to parent PAHs. However, the lower stations of the estuary (41, 42 and 43; see site 42 in Fig. 7.10 as an example) show a petrogenic pattern, like that of most of the stations in the Tees Bay and the coal sample, where alkylated derivatives predominate over parent compounds. Station 38 (Figure not shown; see Table 7.4) is of intermediate composition, similar to those of sites 24 and 25 from Tees Bay, due to the presence of significant quantities of alkylated naphthalenes in an otherwise pyrolytic pattern. This may indicate that at least some used lubricating oils and/or diesel along with PAH from combustion products are entering the Tees estuary and the Tees Bay *via* effluents, urban drains, shipping activities and atmospheric deposition. It has been suggested that the disposal of lubricating oils is a significant source of aromatic hydrocarbons in urban waterways (Brummage, 1975). The

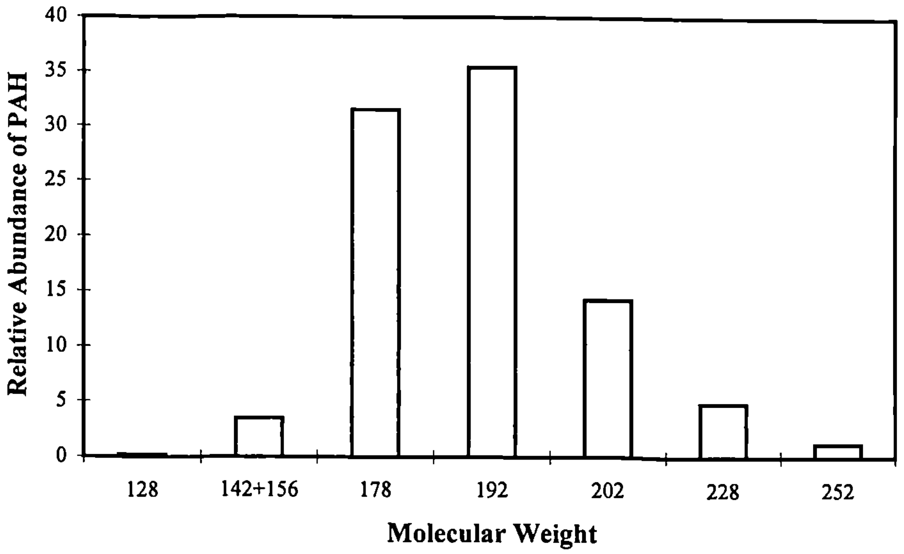


Figure 7.11. Relative (%) compositional profile of PAHs in the coal sample. (Molecular weights: 128, 124+156, 178, 192, 202, 228 and 252, as for Fig. 7.9).

presence or high abundances of alkylated naphthalenes, and to a lesser extent alkylated phenanthrenes, in these sediments suggests that oil spillages, including lubricating oil disposal, are a major source of PAH.

In addition to the molecular distributions of some of the PAH compounds, specific compositional indicators can be used to test for variability in the composition of the combustion-derived PAH mixtures recorded in Tees Bay and Tees estuarine sediments. Ratios of certain isomer pairs, and alkyl-substituted derivatives to unsubstituted compounds in a given homologous series have been used in previous studies to discriminate different PAH sources to sediments (Lake *et al.*, 1979; Gschwend and Hites, 1981; Prahl and Carpenter, 1984; Readman *et al.*, 1984; Shaw *et al.*, 1985). Although fossil fuel PAH are easily distinguished from those of combustion origin by such ratios, different sources of combustion PAH are very difficult to distinguish because they all produce strikingly similar mixtures (Youngblood and Blumer, 1975; Lee *et al.*, 1977)

Since all sediment samples in the present study contain high levels of naphthalenes, phenanthrenes and their alkylated derivatives, ratios of the polycyclic aromatic hydrocarbon methyl phenanthrene (MP) and alkylated naphthalene to their parent PAHs were examined to determine if these compounds were derived from combustion or petrogenic sources.

Phenanthrene (P) and methylphenanthrenes (MP) are characteristic components of both combustion and unburned fossil sources (Prahl and Carpenter, 1983). Phenanthrene mixtures from these two different sources are distinguished from one another by their degree of alkylation (Youngblood and Blumer, 1975). PAHs formed at high temperatures are dominated by unsubstituted species, while lower temperatures favour a higher degree of alkylation (LaFlamme and Hites, 1978; Colombo *et al.*, 1989). Thus, alkylated/nonalkylated ratios are low for pyrogenic sources and high for petrogenic sources. According to Prahl and Carpenter (1983) the MP/P ratio, which has been used for source identification of PAHs (e.g. Youngblood and Blumer, 1975; Prahl *et al.*, 1984; Barrick and Prahl, 1987; Takada *et al.*, 1991; Hostettler *et al.*, 1992), varies between 0.5 and 1.0 for combustion products and between 2 and 6 for petrogenic compounds. The results of MP/P ratios in sediment samples from Tees Bay and the Tees estuary (Tables 7.13 and 7.14, respectively)

Table 7.13 Aromatic hydrocarbon indices for sediment samples from Tees Bay.

Sample No.	MP/P[a]	AN/N[b]	ΣA-PAHs/Σparental PAHs[c]
1	1.2	13.7	2.6
2	1.3	4.7	0.7
3	1.2	7.0	1.0
4	1.2	6.1	0.9
5	1.3	19.4	1.8
6	1.4	8.5	2.0
10	1.5	2.1	1.0
13	1.1	8.5	0.9
14	1.3	6.1	0.8
17	1.3	10.8	1.4
18	1.2	6.4	0.7
20	1.2	17.6	1.7
21	1.2	15.8	1.8
22	1.2	61.0	0.9
24	0.8	14.0	0.9
25	0.9	11.6	1.2
26	1.3	7.8	0.8
28	1.3	9.5	1.3
29	1.3	n.d.	0.7

n.d. = not detected.

[a] Ratio of the sum of the concentrations of 3-methylphenanthrene (3-MP), 2-methylphenanthrene (2-MP), 9-methylphenanthrene (9-MP), and 1-methylphenanthrene (1-MP) relative to phenanthrene.

[b] Ratio of the sum of the concentrations of 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), and 2,6-dimethylnaphthalene (2,6-DMN) relative to concentration of naphthalene.

[c] Ratio of the sum of the concentrations of alkylated PAHs relative to the sum of the concentrations of nonalkylated PAHs.

Table 7.14 Aromatic hydrocarbon indices for sediment samples from the Tees Estuary.

Sample No.	MP/P[a]	AN/N[b]	ΣA-PAHs/Σparental PAHs[c]
33	0.9	1.2	0.1
34	0.7	1.1	0.1
35	0.6	7.8	0.2
36	0.6	4.9	0.2
37	0.1	0.4	0.1
38	0.7	8.0	0.6
39	0.7	1.8	0.2
40	1.0	14.7	0.5
41	1.1	8.4	2.1
42	1.2	9.2	1.3
43	1.1	8.8	1.5

[a, b, and c] Ratios as for Table 7.13.

show that samples 33-40, in the Tees estuary, and samples 24 and 25, in Tees Bay, have the lowest values (0.1-1.0) in the study area, and indicate an input of these from combustion sources. Sediments from the other stations have values clearly higher than those of the combustion range, but lower than the petroleum range. However, the MP/P ratios found in these sediments is similar to the MP/P ratio of 1.1 calculated from the coal sample, and may suggests petrogenic inputs into these surface sediments.

In addition, naphthalene, which is derived mainly from anthropogenic activities (Venkatesan and Kaplan, 1982), is present in the sediments from all sites (except site 29), but in a lower amount than phenanthrene. Alkylated naphthalenes are more abundant than the parent PAH in all samples from both areas (except site 37), but their relative abundances are quite variable among the samples, as discussed above. To express the relative abundance of alkyl substituted naphthalenes (AN), for convenience, a ratio of the concentration of methyl naphthalene (1-methylnaphthalene, 1-MN and 2-methylnaphthalene, 2-MN)) and dimethylnaphthalene (2,6-dimethylnaphthalene, 2,6-DMN) relative to that of naphthalene (N) is defined as AN/N, since these peaks are clearly resolved in the gas chromatograms. This ratio has been used previously for source identification of PAHs (Kayal and Connell, 1989; Green *et al.*, 1992). Youngblood and Blumer (1975), Brown and Starner (1978) and Brown *et al.* (1980) have noted that domination of unsubstituted compounds over their alkyl-substituted derivatives suggests a combustion origin, and a petroleum source would be indicated when substituted derivatives dominate. On the basis of the AN/N ratios (Tables 7.13 and 7.14), it is suggested that these PAH compounds in most sediments from Tees Bay and Tees estuary derived mainly from petroleum sources. Only one sediment from the studied areas (site 37) appears to have a significant contribution from combustion sources.

Other ratio in sediment samples from Tees Bay and Tees estuary, *e.g.* total alkylated PAHs to unsubstituted compounds (ΣA-PAHs/Σparental PAHs), were also examined to determine if these compounds were derived from combustion or petrogenic sources. Ratios of ΣA-PAHs/Σparental PAHs (Kayal and Connell, 1989) are reported to be in the range of 0.2-0.5 for sediments dominated by combustion PAHs, whilst ratios above this range could suggest some input from non-combustion, or petroleum derived PAHs. ΣA-PAHs/Σparental PAHs ratios in sediments from all sites, except sites 33, 34, 36, 37, 39 and 40 (Tables 7.13 and 7.14) indicate that PAHs are derived mainly from petroleum sources. However, at sites 33, 34, 36, 37, 39 and 40, within the Tees estuary, a combustion origin is also indicated.

Samples 33, 34, 35, 36, 37, 39 and 40 have the lowest values for the MP/P and ΣA-PAHs/Σparental PAHs ratios in the sample set, indicating that these compounds at these sites are derived significantly from combustion sources. Sites 38, 24 and 25 show MP/P ratios (0.7, 0.8 and 0.9, respectively) characteristic of combustion-derived PAH mixtures, but their ΣA-PAHs/Σparental PAHs ratios are clearly in the petroleum range, suggesting that the PAHs in these sediments are from mixed sources (combustion + petroleum). The MP/P ratios in sediments from other stations differ with high levels of MP (alkylated phenanthrenes) compared to P (phenanthrene). These ratios are clearly higher than those of the combustion range, lower than the petroleum range, but similar to the coal range. Moreover, ΣA-PAHs are major components in these sediments, compared to Σparental PAHs and give values higher than those of the combustion range. For these sediments, therefore, the origin of PAHs is mainly from petroleum/coal, but may contain some combustion-associated materials. In addition, the presence of petroleum derived compounds such as naphthalene also signify the importance of petroleum as a source of PAHs within these sediments.

In summary, this study of PAHs in surficial Tees Bay and estuarine sediments indicates that these compounds in the sediments originate from several sources. It is possible to differentiate them and to single out the main source of PAHs.

7.5 Summary

1- Surface sediment samples were taken from 30 sites along the Tees estuary and Tees Bay, and analysed for polyaromatic hydrocarbons (PAHs). This is the first study to report PAH data for Tees Bay and Tees estuary sediments.

2- Marked differences in the PAH concentrations are found in the sediments studied. Sediments from Tees estuary were found to contain high concentrations, which likely reflect the higher human population density in this region, when compared to those of Tees Bay. The highest concentrations within the estuarine area were found in the central region, while within the Bay area the highest concentrations were found in the offshore area. Elevated PAH concentrations, compared to background levels of deep sea sediments (10-15 ng g^{-1}; Hites *et al.*, 1980), are observed in all stations from Tees estuary, indicating higher pollution due to industrial wastes. The central part of the Tees estuary is the most highly urbanized and contained the highest concentrations of PAHs in the study area.

3- Comparing the PAH concentrations found in the present study against those from other contaminated and uncontaminated areas, reported in the literature, it is evident that the Tees estuary, and to a lesser extent Tees Bay, contains elevated levels of this class of chemical.

4- A positive and significant correlations are found between PAH levels and *n*-alkane concentrations in Tees Bay sediments, as well as between these two hydrocarbons, organic carbon content, and fine particle size (clay and slit) composition, suggesting that PAH distribution in the Bay is controlled by TOC and fine particles (slit and clay). For Tees estuarine sediments, which mostly have higher fine particles and TOC when compared to Tees Bay, an inverse relationship exists between PAHs and sediment characteristics, such as organic carbon content and particle size composition, suggesting that TOC and particle size do not significantly influence the distribution of PAH in the estuary.

5- A complex mixture of PAH compounds was identified in all sediments from both areas. Unsubstituted ring systems (i.e. parent PAH), ranging from naphthalene (two aromatic ring) to perylene (five ring), as well as substituted PAH (alkylated PAH), ranging from alkylated naphthalene to alkylated phenanthrene, were the primary components. On the basis of the distribution pattern of some PAH series, it is estimated that PAHs in all sediments from Tees Bay (except sites 24 and 25) and a few sediments from the Tees estuary (sites 41, 42 and 43) arise mainly from fossil fuels sources (petroleum and/or coal). On the other hand, other sediments from the studied areas (sites 33, 34, 35, 36, 37, 39 and 40) appear to have a more significant contribution from combustion sources and a few sediments from Tees Bay and Tees estuary (sites 24, 25, and 38) show mixed anthropogenic inputs of pyrolytic and petrogenic. Sulphur compounds are also identified in all sediments; a common origin with phenanthrenic compounds is suggested.

Chapter Eight

Polychlorinated Biphenyls

8.0 Polychlorinated Biphenyls

8.1 Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants, due to their bioaccumulative capacity and specific physico-chemical properties (Everaarts *et al.*, 1993), distributed world-wide and are highly persistent organic pollutants (Prats *et al.*, 1992). They constitute a class of theoretically 209 structurally and chemically related compounds, representing a wide range of physicochemical properties (Schulz-Bull *et al.*, 1991). Since 1930-1940 their extensive use has led to their detection in several materials; namely water, sediments, terrestrial and marine organisms, vegetables, soils, air and even in the fatty tissues of man. Concern about PCBs as environmental pollutants began in 1966 when Jensen (1966) discovered their presence in fish tissue from different parts of Sweden. This event occurred almost 40 years after PCBs became commercially available in the United States in 1929. After the discovery of their widespread environmental contamination in the 1970s, PCB production decreased, but significant quantities are still in use, primarily in older electrical equipment (Tanabe, 1988).

Polychlorinated biphenyls, widely used in industry, are structurally similar to substances such as DDT and show similar characteristics in being relatively insoluble in water, highly soluble in lipids and extremely resistant to chemical or biological degradation (Halcrow *et al.*, 1974). They have possibly been the subject of more research attention than any other group of organohalogen compounds, and are monitored continuously because of their proven toxicity to human beings and other animal and plant life (Delbeke and Joiris, 1988; Schulz-Bull *et al.*, 1991; Prats *et al.*, 1992; Tanabe *et al.*, 1994; Gribble, 1994; Tyler and Millward, 1996). Nonetheless, they still represent a challenge to the environmental chemist and ecotoxicologist who wish to understand their complex environmental fate and behavior and potential effects on ecosystems.

There are, however, few recent published reports on the background levels, occurrence and distribution of PCBs in waters and sediments of the UK. Furthermore, many of the reports concerned with sediments from the North Sea, which do exist address the mid to south east coast of England (e.g. Klamer *et al.*, 1990; Klamer and

Fomsgaard, 1993), whilst there are virtually no published reports of background contamination of the north east coast of England. At the Third International Conference on the Protection of the North Sea it was decided to reduce the loads of primary pollutants to the North Sea by 50-70% (Anon., 1990). However, there are reasons for believing that sediment quality in the area has been adversely effected by industrial activities, for example at Tees-side and Humber-side (Grogan, 1984).

The present study aims to fill part of this gap in knowledge, by an investigation of PCB levels in sediments from the Tees Bay and Tees estuarine areas. It focuses on determining distribution patterns of individual PCB congeners and compares concentrations in the area with those found in sediment samples from a number of different geographical areas. In addition, total PCB concentrations are reported as Aroclor-equivalent concentrations, based on the concentrations of isomers and congeners of a particular degree of chlorination which are resolved and summed to provide a total PCB concentration.

8.2 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) is a generic name of many isomers and congeners with different numbers of chlorine atoms substituted in biphenyl rings (Tanabe, 1988), which have 10 positions (labeled 2-6 and 2'-6' in Figure 8.1a) available for chlorine atoms (Hutzinger *at al.*, 1980).

The term PCB is used to refer to any one of 209 compounds of the general formula $C_{12}H_xCl_y$, where x = 0-9 and y = 10-x (Hutzinger *at al.*, 1980; Alfrod-Stevens, 1986). The entire set of 209 PCBs form a set of congeners. Different structural arrangements make possible 209 compounds distributed among the 10 levels of chlorination (Table 8.1). Ten levels of the 209 PCBs congeners, called homologs, can be distinguished on the basis of their degree of chlorination. For example, the first group consists of 3 PCBs containing 1 chlorine atom, while the last group consists of 1 PCB with 10 chlorines. The term isomers are applied to any PCBs of a given homolog with different chlorine substitutions; *e.g.* 2,2',3,4,4',5'-hexachlorobiphenyl and 2,2',4,4',5,5'- hexachlorobiphenyl are two of the 42 hexachlorobiphenyl isomers. Because chemical names include all the numbers of the chlorine positions on the

(a)

Numbering in the biphenyl
ring system

(b)

2,4,4'-trichlorobiphenyl
(PCB-28)

(c)

2,2',5,5'-tetrachlorobiphenyl
(PCB-52)

(d)

2,2',4,5,5'-pentachlorobiphenyl
(PCB-101)

(e)

2,3',4,4',5-pentachlorobiphenyl
(PCB-118)

(f)

2,2',3,4,4',5'-hexachlorobiphenyl
(PCB-138)

(g)

2,2',4,4',5,5'-hexachlorobiphenyl
(PCB-153)

(h)

2,2',3,4,4',5,5'-heptachlorobiphenyl
(PCB-180)

Figure 8.1. Structures of selected polychlorinated biphenyls.

biphenyl rings, such cumbersome nomenclature as 2,2',3,4,4',5,6,6'-octachlorobiphenyl (Cl_8 PCB) results (Alfrod-Stevens, 1986).

Table 8.1 Composition of PCBs by level of chlorination (from Alfrod-Stevens, 1986).

Homolog group	**Molecular formula**	**No. of isomers**
Monochlorobiphenyls	$C_{12}H_9Cl$	3
Dichlorobiphenyls	$C_{12}H_8Cl_2$	12
Trichlorobiphenyls	$C_{12}H_7Cl_3$	24
Tetrachlorobiphenyls	$C_{12}H_6Cl_4$	42
Pentachlorobiphenyls	$C_{12}H_5Cl_5$	46
Hexachlorobiphenyls	$C_{12}H_4Cl_6$	42
Heptachlorobiphenyls	$C_{12}H_3Cl_7$	24
Octachlorobiphenyls	$C_{12}H_2Cl_8$	12
Nonachlorobiphenyls	$C_{12}HCl_9$	3
Decachlorobiphenyls	$C_{12}Cl_{10}$	1
Total number of congeners		**209**

Many researchers have found the full chemical names unwieldy and have adopted various shorthand nomenclatures. However, the system devised by Ballschmiter and Zell (1980), who arranged the 209 congeners in ascending numeric order, and adopted by the International Union of Pure and Applied Chemists (IUPAC) is the one generally used (Hutzinger *at al.*, 1980; Alfrod-Stevens, 1986). This system will also be adopted in the present study. Structures of the seven ICES congeners (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180) can be seen in Figure 8.1 (b-h).

8.3 Results

Quantitative results obtained from the chromatograms of the PCB compounds isolated from extracts of Tees Bay and Tees estuarine surface sediments are listed in Tables 8.2 and 8.3, respectively. In these two tables the levels of some selected individual congeners (ICES congeners; Delbeke *et al.*, 1990; Bossi *et al.*, 1992; Law *et al.*, 1996), i.e. PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-180, and

Table 8.2 PCBs concentrations (ng g^{-1}, dry weight) in surface sediments from Tees Bay.

Sample	PCB-28	PCB-52	PCB-101	PCB-118	PCB-153	PCB-138	PCB-180	ΣICES[a]	Total PCBs[b]
1	0.11	0.09	0.19	0.12	0.09	0.10	0.10	0.80	1.93
2	0.07	0.06	0.17	0.03	0.08	0.06	0.09	0.56	1.37
3	0.03	0.13	0.11	0.04	0.09	0.05	0.05	0.50	1.10
4	0.14	0.15	1.11	0.73	1.82	1.14	0.94	6.03	14.37
5	n.d.	n.d.	0.12	0.04	0.13	0.08	0.09	0.46	1.12
10	0.08	0.03	0.10	0.05	0.13	0.05	0.08	0.52	1.22
13	trace	trace	trace	trace	trace	trace	trace	trace	trace
14	n.d.	n.d.	0.1	0.01	0.02	0.02	0.02	0.17	0.44
17	n.d.	n.d.	trace	trace	trace	trace	trace	trace	trace
18	n.d.	n.d.	trace	trace	trace	trace	trace	trace	trace
20	0.03	0.02	0.21	0.36	0.45	0.55	0.35	1.97	3.81
21	0.05	0.10	0.09	0.03	0.05	0.04	0.04	0.40	0.98
22	n.d	n.d.	trace	trace	trace	trace	trace	trace	trace
25	0.75	0.49	0.67	0.36	1.71	1.63	0.59	6.20	11.57
26	n.d.	n.d.	0.02	0.03	0.05	0.05	0.07	0.22	0.54
27	0.01	0.02	0.02	0.01	0.02	0.01	0.01	0.10	0.24
28	0.05	0.09	0.09	0.02	0.03	0.02	0.02	0.32	0.67
29	n.d.	trace	trace	trace	trace	trace	trace	trace	trace

n.d.= not detected.

[a] = the sum of the concentrations of the seven ICES congeners (28, 52, 101, 118, 153, 138 and 180).

[b] = the sum of 30 PCBs congeners, expressed as Aroclors 1260 (see Section 8.4. for more details).

Table 8.3 PCBs concentrations (ng g^{-1} dry wt.) in surface sediments from the Tees Estuary.

Sample	PCB-28	PCB-52	PCB-101	PCB-118	PCB-153	PCB-138	PCB-180	ΣICES[a]	Total PCBs[b]
33	0.09	0.49	1.09	1.14	1.46	1.69	2.02	7.98	22.98
34	0.16	0.59	1.44	0.35	0.62	0.71	1.42	5.29	17.28
35	1.99	2.66	2.24	0.91	2.73	2.32	2.56	15.41	34.67
36	3.06	0.99	4.37	3.28	4.01	4.61	4.60	24.92	55.13
37	4.46	2.68	1.94	0.59	1.27	2.14	1.18	14.26	37.67
38	0.26	0.12	0.96	0.62	1.35	1.42	0.79	5.52	12.30
39	0.44	0.13	2.11	2.86	3.20	3.53	1.99	14.26	30.59
40	0.66	0.42	1.50	0.74	2.40	0.98	1.31	8.01	22.60
41	0.52	0.85	1.22	0.45	1.77	0.65	0.69	6.15	16.62
42	0.87	1.58	1.25	0.56	0.71	0.71	0.75	6.43	13.83
43	0.10	0.03	0.59	0.31	0.93	0.39	0.38	2.73	6.96

[a] = the sum of the concentrations of the seven ICES congeners (28, 52, 101, 118, 153, 138 and 180).

[b] = the sum of 30 PCBs congeners, expressed as Aroclors 1260 (see Section 8.4. for more details).

the sum of concentrations of the seven congeners (∑ICES), are determined (Tables 8.2 and 8.3, respectively). Measurable concentrations of these PCBs are detected in almost all sediments from Tees Bay and Tees estuary. In addition, analytical results of total PCBs, expressed as Aroclor 1260, in the sediment samples from both areas are presented in Tables 8.2 and 8.3. Total PCBs correspond to the sum of the 30 congeners, i.e. PCB-28, PCB-52, PCB-95, PCB-92, PCB-101, PCB-110, PCB-151, PCB-135, PCB-149, PCB-134, PCB-146, PCB-153, PCB-141, PCB-176, PCB-138, PCB-178, PCB-187, PCB-183, PCB-185, PCB-174, PCB-177, PCB-171, PCB-172, PCB-180, PCB-170, PCB-199, PCB-203, PCB-195, PCB-194 and PCB206, identified from the reference mixture (Aroclor 1260), which were also the main components of the sediment samples.

Peaks were tentatively assigned using comparison with Aroclors 1260 and 1254 standards and ICES standards (Figs. 8.2, 8.3 and 8.4) for the seven congeners studied (IUPAC Nos: PCB-28, PCB-52, PCB-101, PCB-153, PCB-138 and PCB-180).

Examples of gas chromatograms, using an ECD, of the PCB fractions extracted from Tees Bay and Tees estuarine sediments are shown in Figures 8.5 to 8.10. A similarity in PCB chromatograms is observed when visually comparing chromatograms of samples from both areas; all chromatograms are highly complex. These chromatograms also display a variety of unknown ECD-active substances. Several compounds other than those quantified were present, most of which could, on the basis of retention times, be identified as PCBs.

Results presented in Tables 8.2 and 8.3 show the levels of PCB congeners in the surface sediments of the Tees Bay and its inflowing River in north east UK. The analyses show that PCB congeners were present in measurable concentrations in almost all samples, with the highest levels of PCBs in the study area found in the Tees estuary. In addition, considerable variations between PCB congeners were observed between individual stations. The variability in PCBs levels per station is again the largest for Tees estuary.

As apparent from the data in Tables 8.2 and 8.3, the concentration of total PCBs in the sediment samples from Tees Bay were in the low ng g^{-1} range in most samples. In the regional distribution of total PCB congeners in the surface sediments

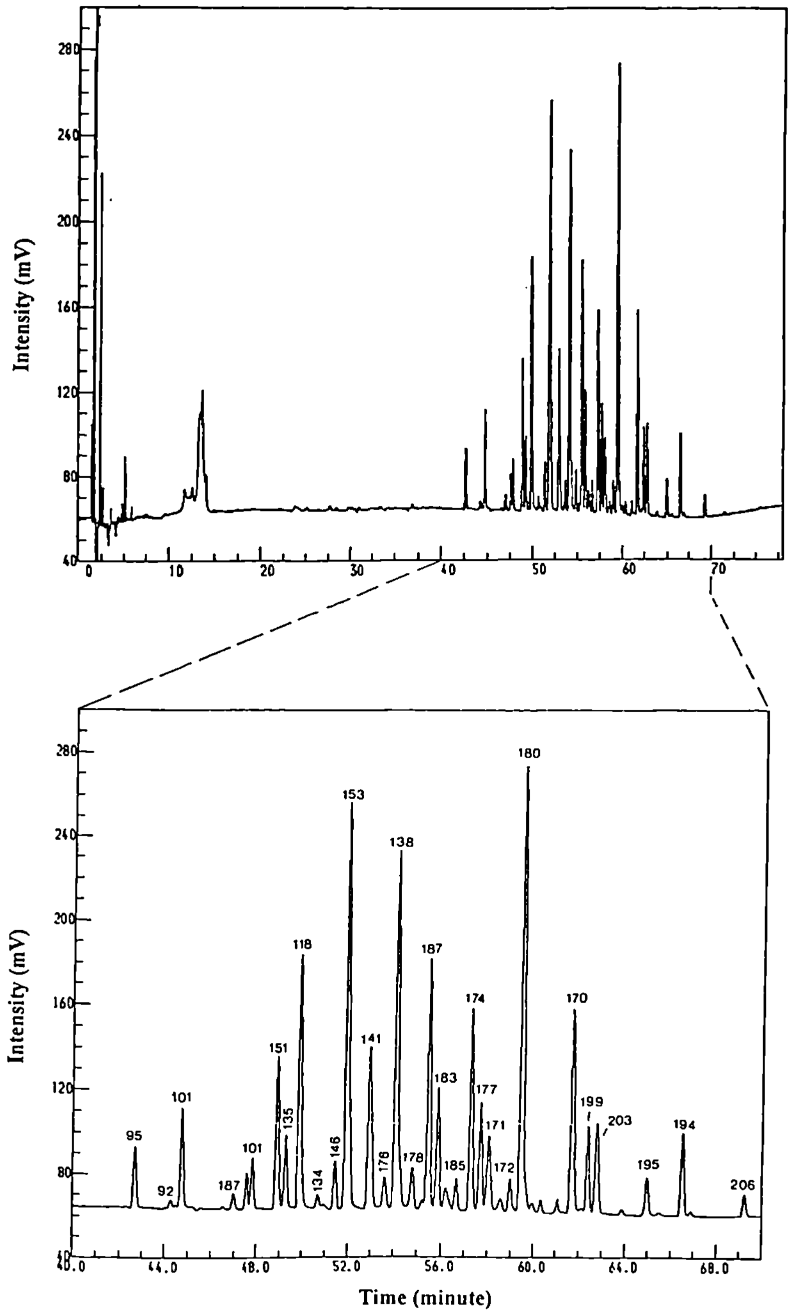


Figure 8.2. GC-ECD chromatogram of Aroclor 1260 standard. For gas chromatographic conditions see Chapter 3. PCB congeners are numbered according to IUPAC rules, as suggested by Ballschmiter & Zell (1980).

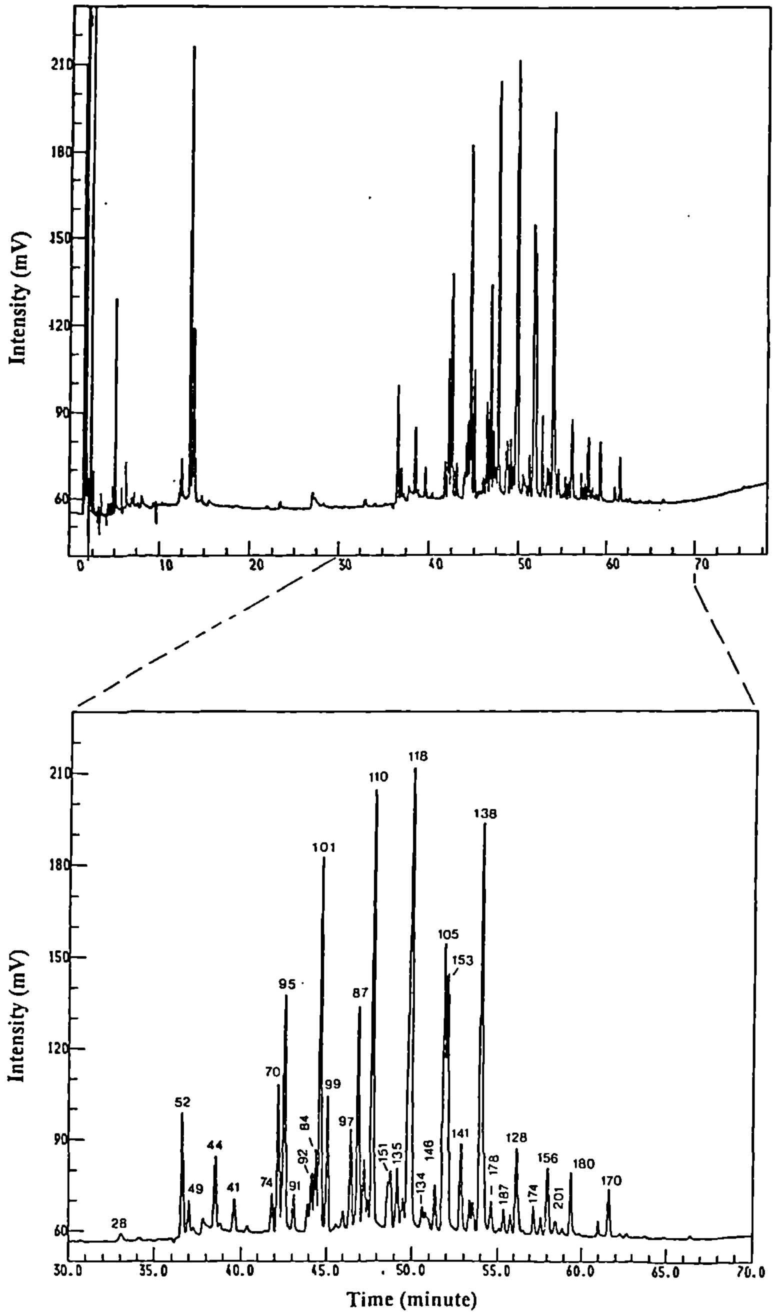


Figure 8.3. GC-ECD chromatogram of Aroclor 1254 standard. For gas chromatographic conditions and numbering system see Fig. 8.2.

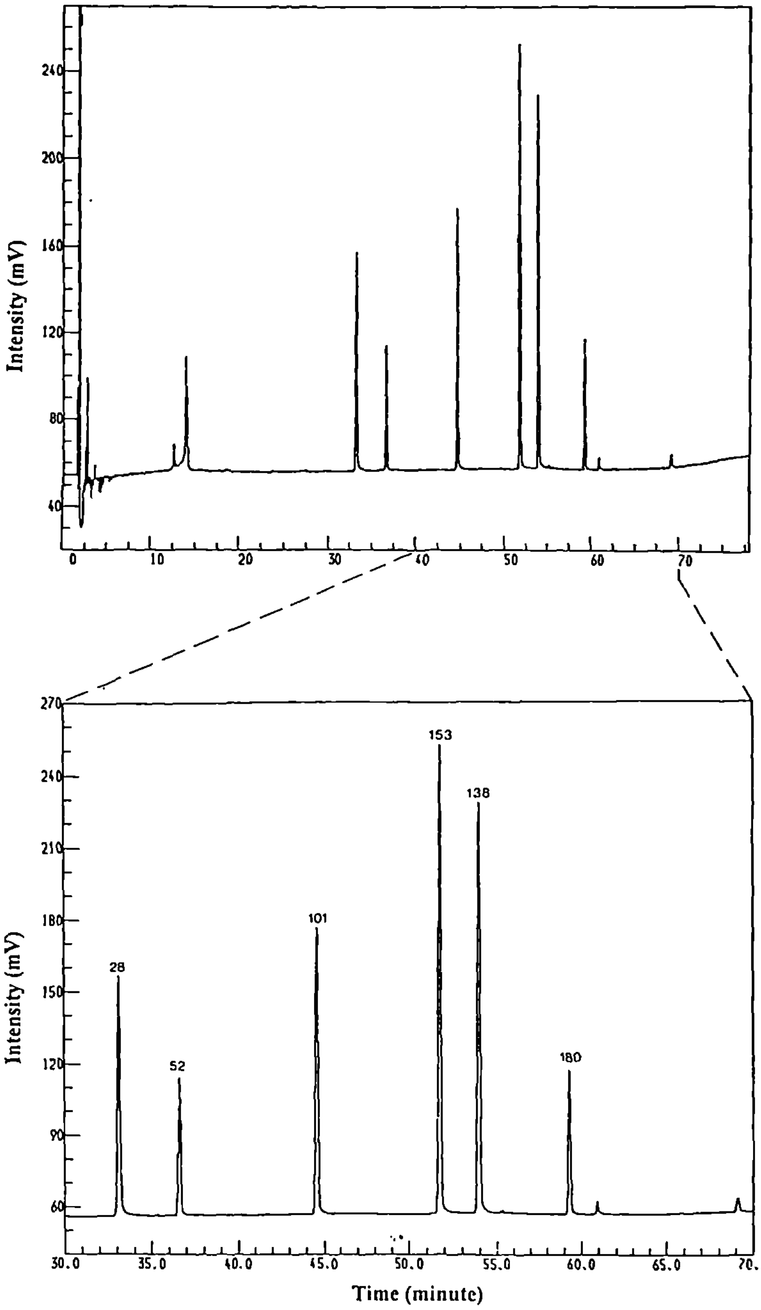


Figure 8.4. GC-ECD chromatogram of ICES standards. For gas chromatographic conditions and numbering system see Fig. 8.2.

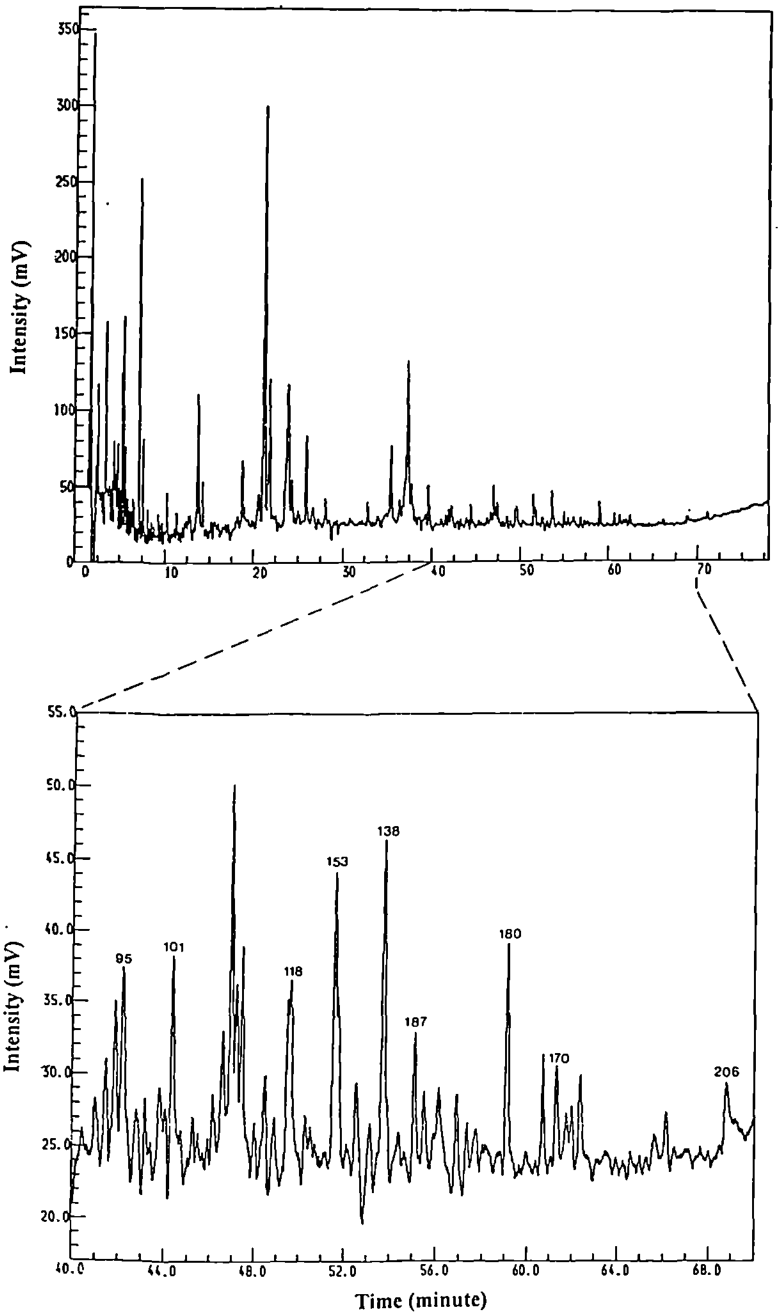


Figure 8.5. GC-ECD chromatogram of PCBs in the sediment of site 4 (Tees Bay). For gas chromatographic conditions and numbering system see Fig. 8.2.

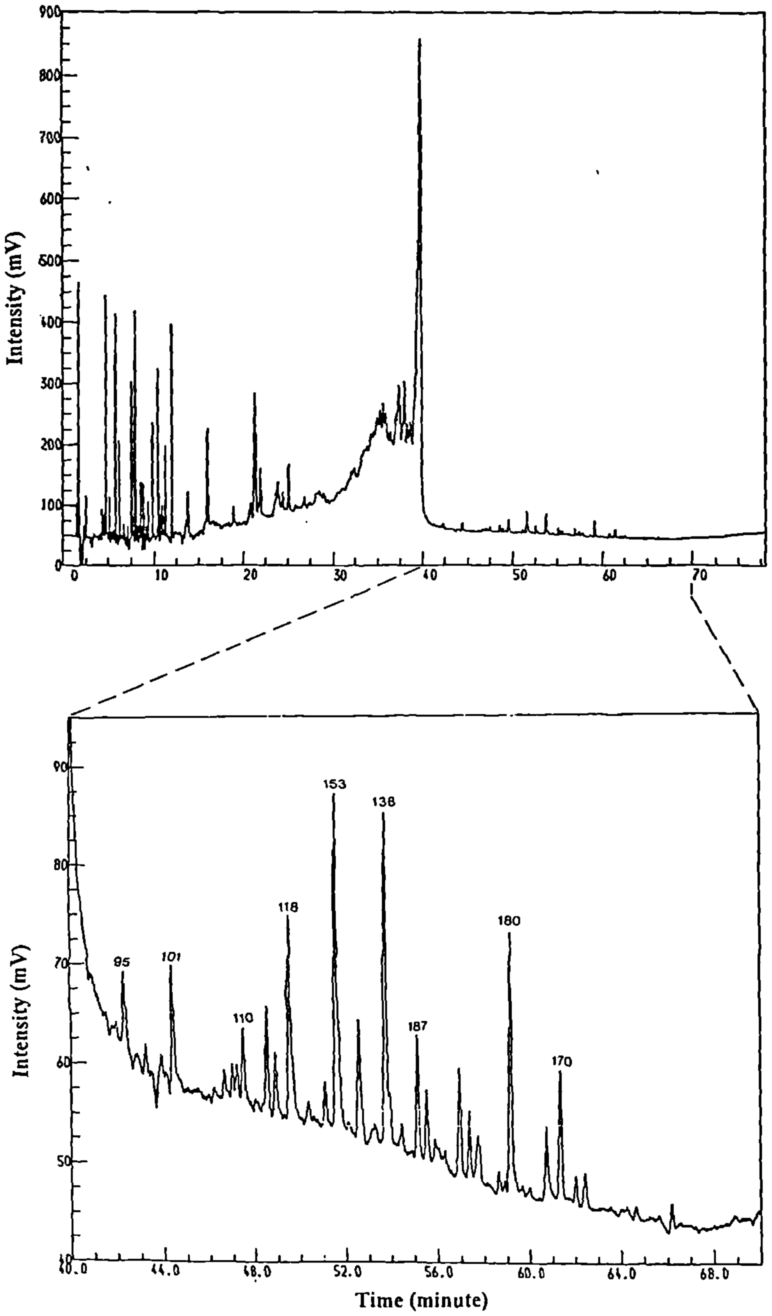


Figure 8.6. GC-ECD chromatogram of PCBs in the sediment of site 20 (Tees Bay). For gas chromatographic conditions and numbering system see Fig. 8.2.

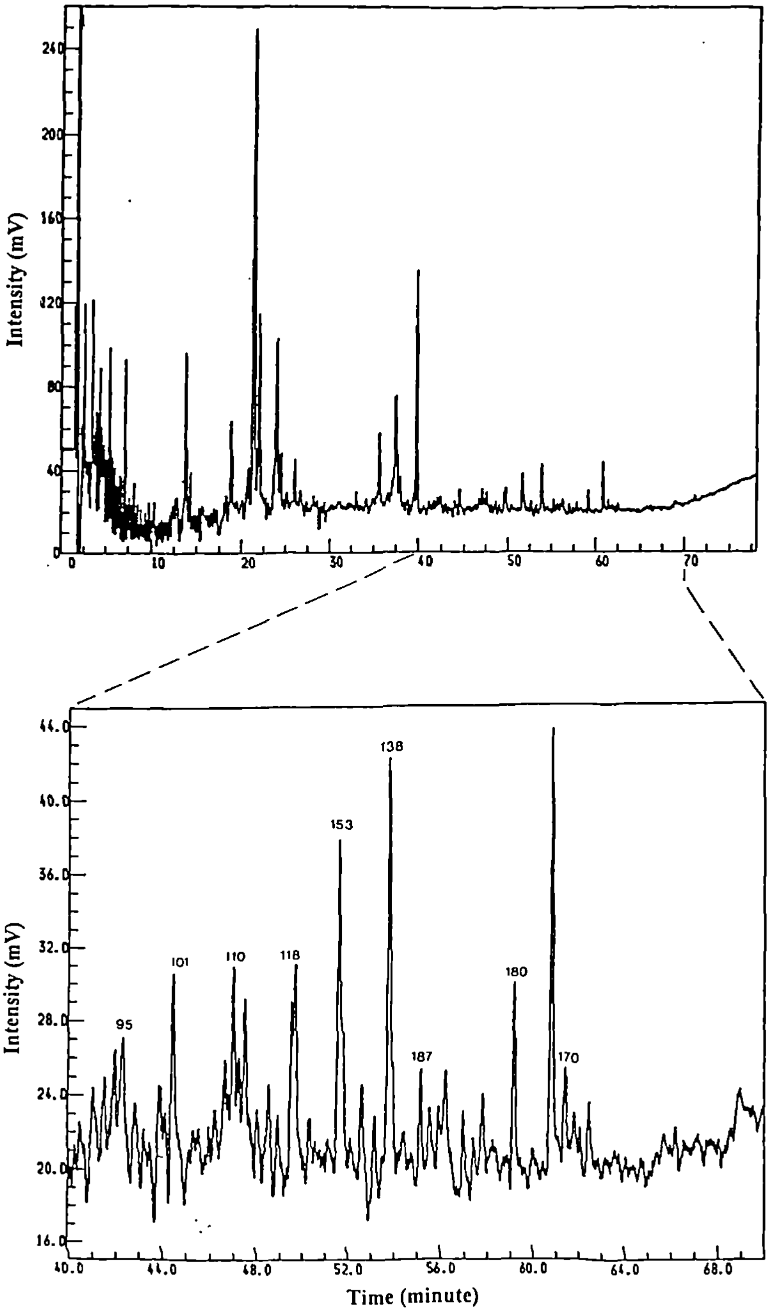


Figure 8.7. GC-ECD chromatogram of PCBs in the sediment of site 25 (Tees Bay). For gas chromatographic conditions and numbering system see Fig. 8.2.

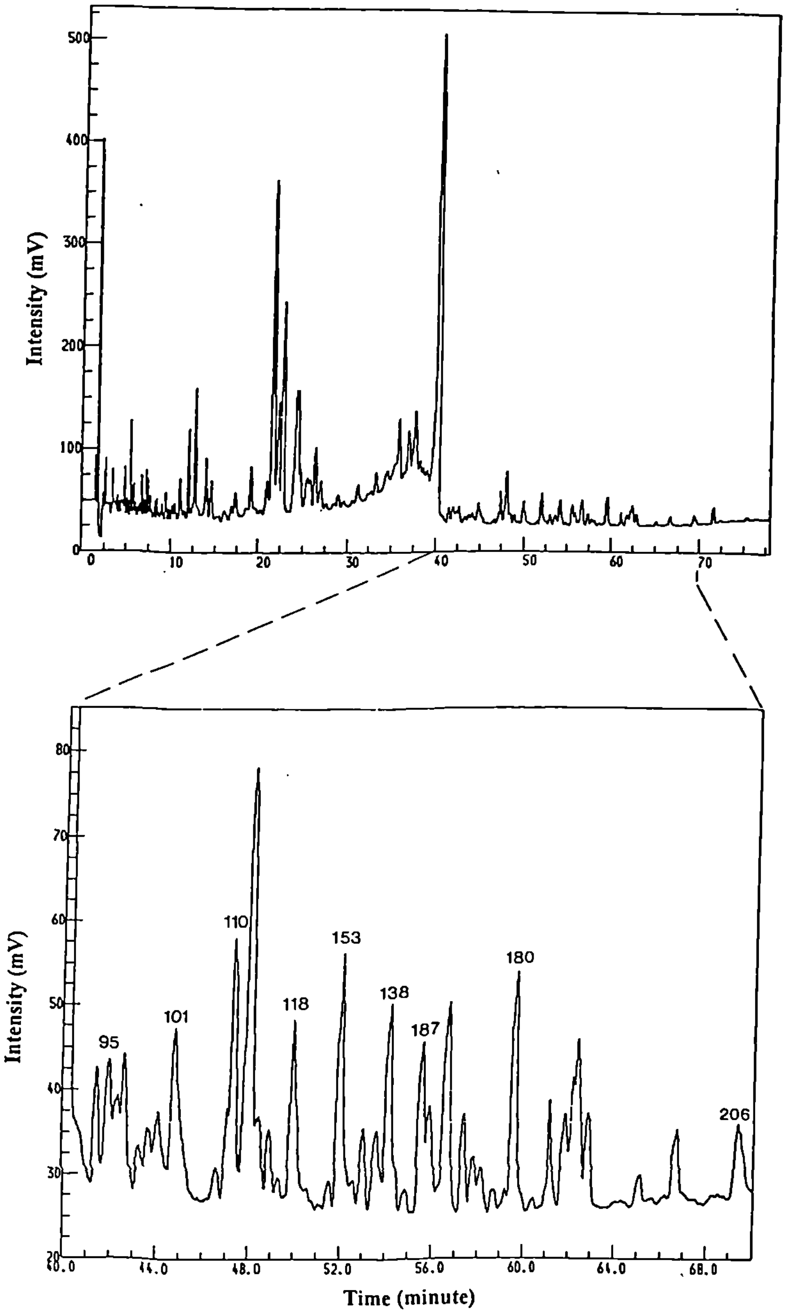


Figure 8.8. GC-ECD chromatogram of PCBs in the sediment of site 36 (Tees Estuary). For gas chromatographic conditions and numbering system see Fig. 8.2.

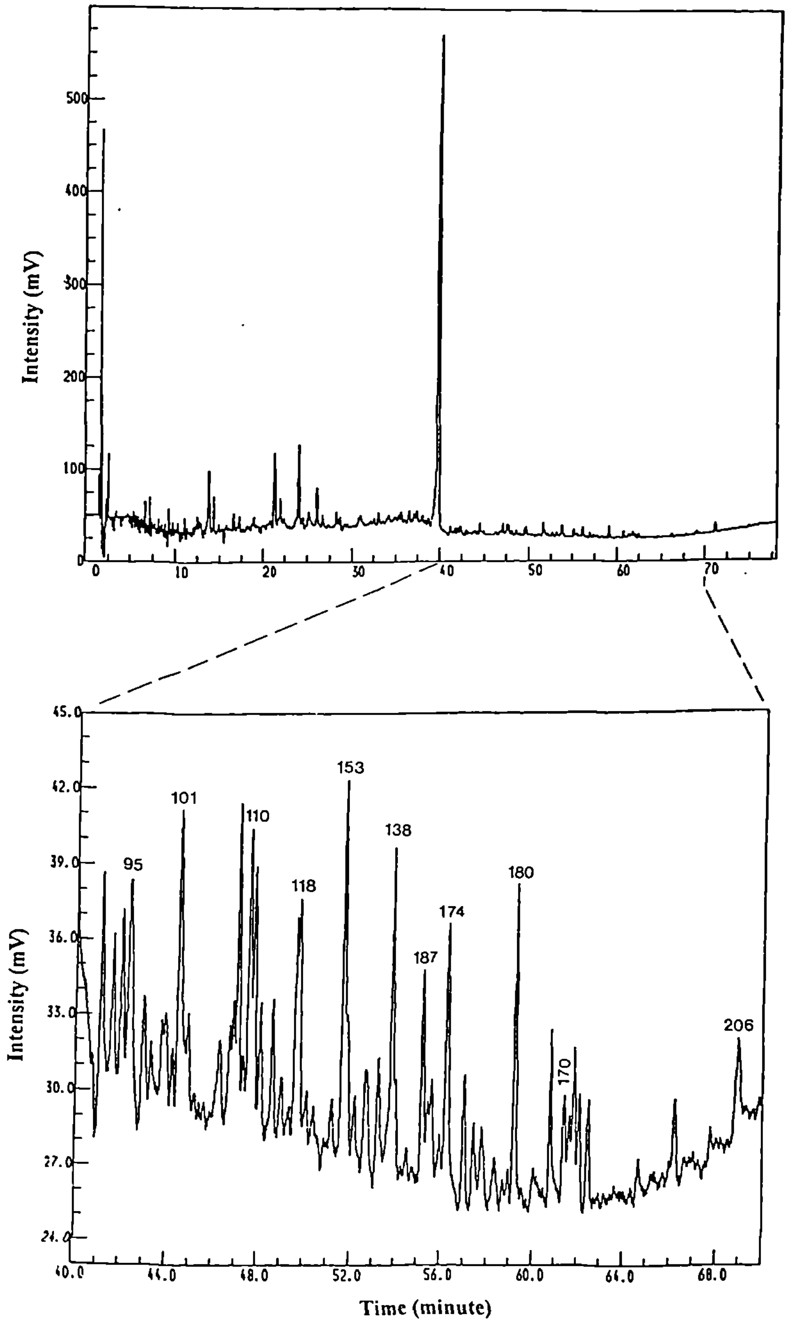


Figure 8.9. GC-ECD chromatogram of PCBs in the sediment of site 38 (Tees Estuary). For gas chromatographic conditions and numbering system see Fig. 8.2.

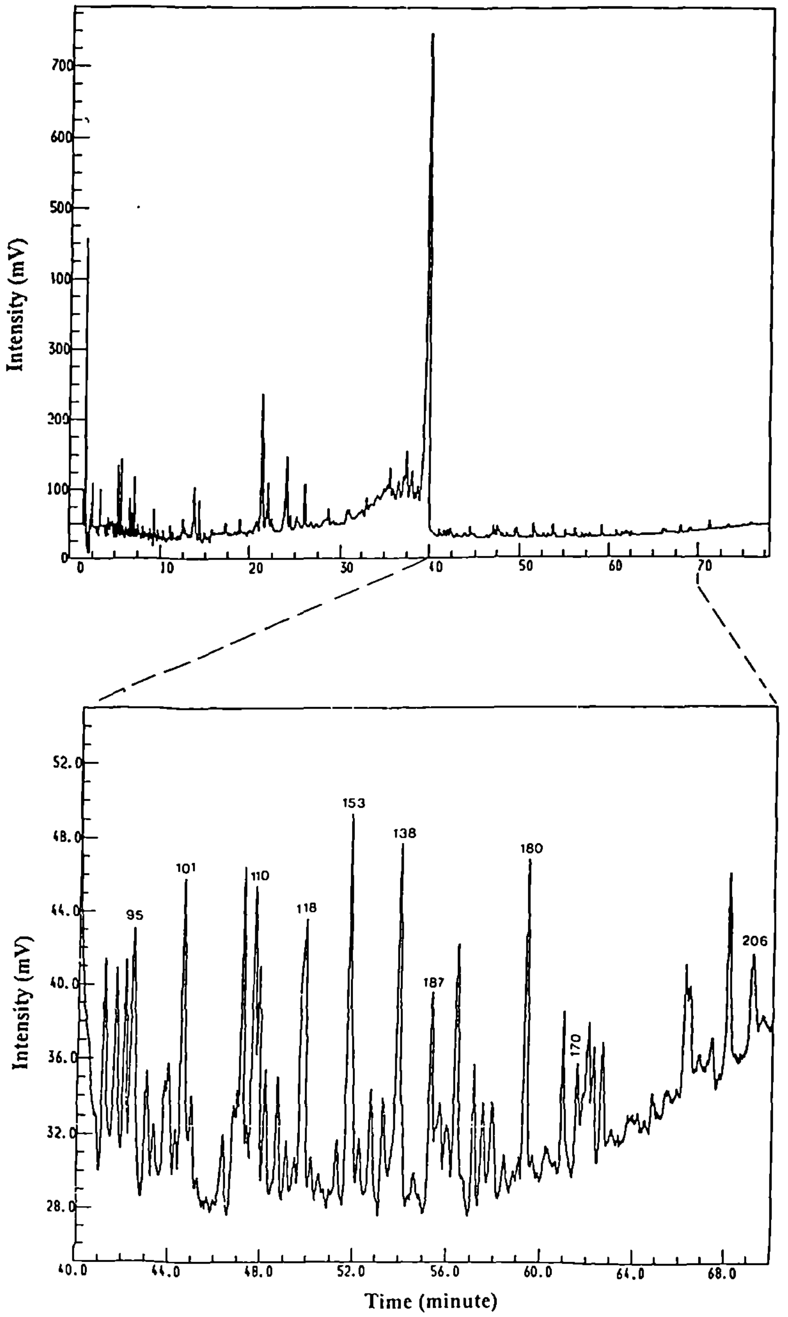


Figure 8.10. GC-ECD chromatogram of PCBs in the sediment of site 39 (Tees Estuary). For gas chromatographic conditions and numbering system see Fig. 8.2.

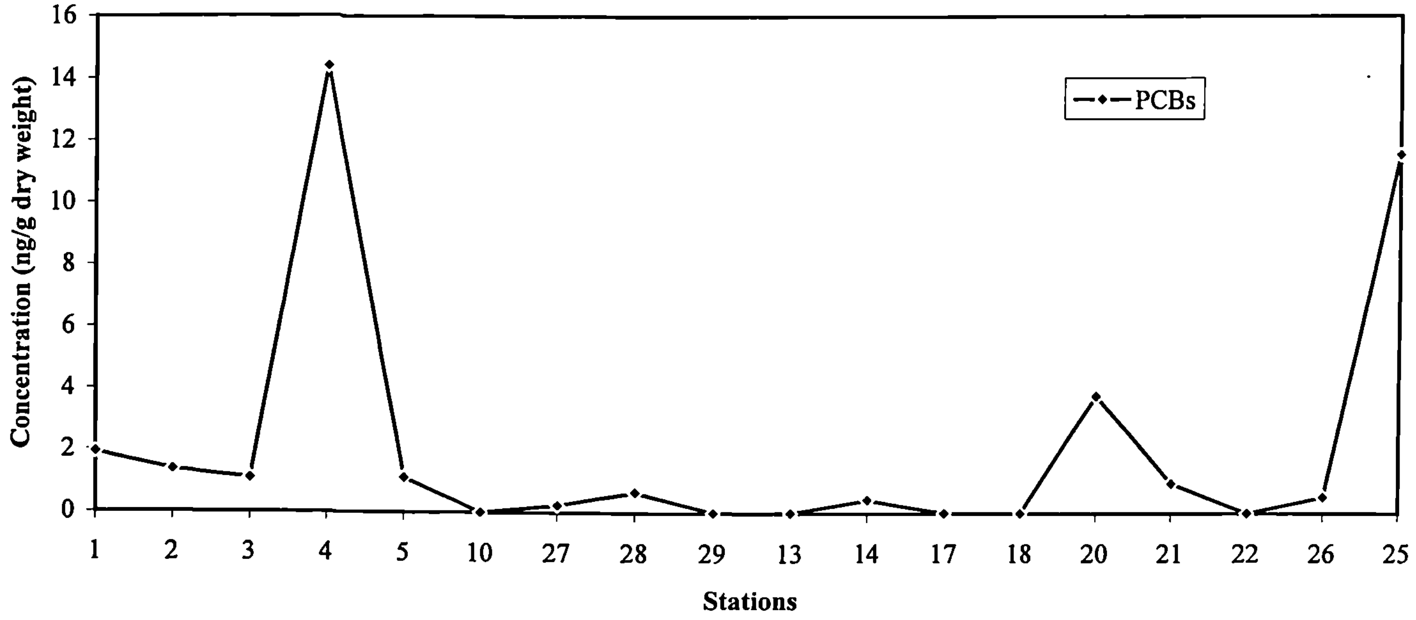


Figure 8.11. Distribution of Total PCBs in the sediments of Tees Bay.

of the Tees Bay (Fig 8.11) the highest concentrations of these compounds are detected in the offshore sediment of sites 4 (located at the northern end of the Tees Bay), with another peak in the offshore sediment of station 25 (located at the southern end of the Tees Bay). The major higher chlorinated PCB congeners are the same at all of the Tees Bay sampling sites and can be seen to be: PCB138, 153 and 180. Lower chlorinated PCB congeners with a lower chlorination degree (PCB 28, 52, 101, 118) are also important in almost all the Tees Bay sampling sites. The sediments of coastal and/or nearshore sites (1, 2, 3, 5, 20, 321, 27 and 28) have low PCB levels. Surprisingly, only trace levels of PCB congeners were detected in sediment samples collected near the mouth of the Tees estuary which are expected to receive significant quantities of contaminant discharges. However, the concentration of PCBs in these sites are lower than the offshore or nearshore sites. It appears, therefore, that within the Tees Bay there is a trend of increasing PCB concentrations as one moves from nearshore to the open sea, and in each case the major PCBs were the same.

In comparison with the Tees Bay sediments, the concentrations of PCB congeners in Tees estuarine sediments (Table 8.3 and Figure 8.12) were observed to be much higher, and exhibit considerable site specificity. The PCB congeners of the ICES primary list were detected in all samples, but their concentrations were higher than those detected in the Tees Bay area. These, higher and lower chlorinated PCB congeners, are of the same group of PCBs that are of importance in the Tees Bay. The PCB concentrations found in the Tees estuary were distributed fairly irregularly between sites (Fig. 8.12). Generally, the most highly contaminated samples along the estuary occurred in the middle reaches where high concentrations of individual chlorobiphenyls and total PCBs were found with respect to the upper (sites 33 and 34) and lower reaches (sites 42 and 43) of the estuary. Among the middle reaches of the estuary, PCBs are concentrated between sites 35, 36, 37 and 39 only, with the concentration at site 38 being similar to those detected at or below site 40 (Fig. 8.12). From this site in the middle section (site 40) to the river mouth, the PCB concentrations decrease reaching a minimum at site 43 (in the lower section of the estuary). In summary, the highest concentrations of PCBs were found at some sites in the middle section of the estuary, and further downstream these levels progressively fall to reach a minimum at site 43, near the mouth of the estuary.

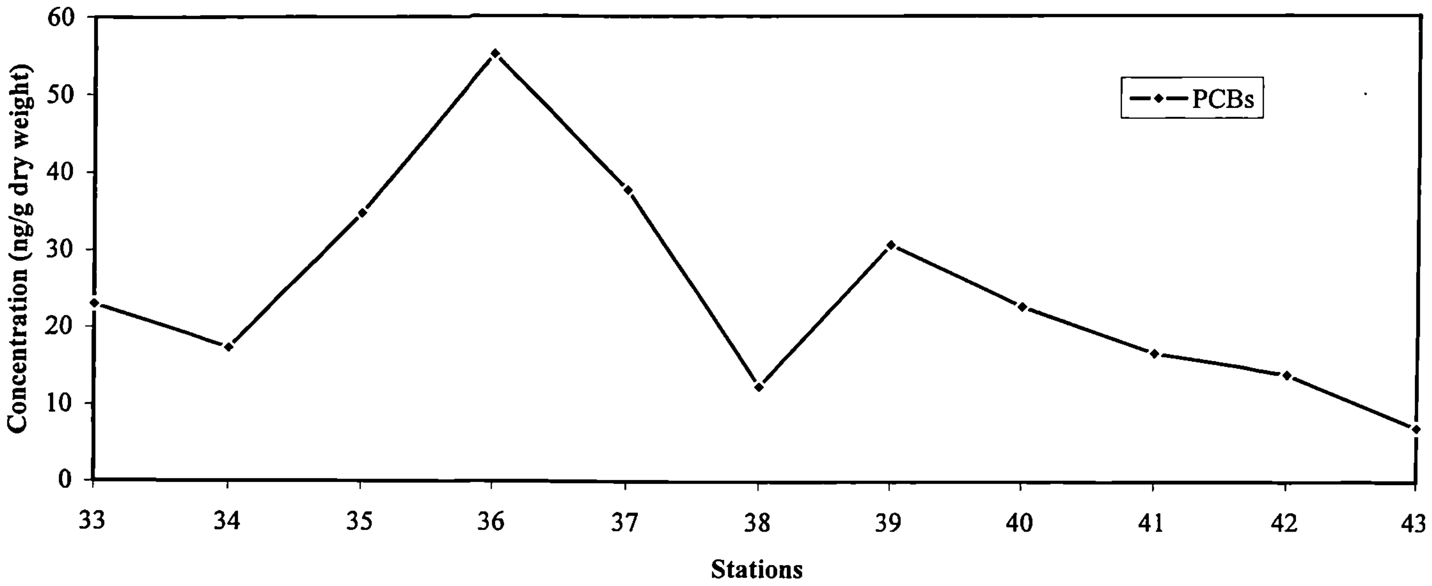


Figure 8.12. Distribution of Total PCBs in the sediments of Tees Estuary.

8.4 Discussion

For decades, PCBs have been used for a variety of industrial applications. Since 1978, the use of PCBs was restricted to non-dispersive systems. These highly toxic compounds are extremely resistant to chemical and biological degradation and may persist in the environment for several decades. The presence of PCBs in the sediments of Tees Bay and Tees estuary was, therefore, not unexpected. Previous studies have detected these compounds in sediment, water and biota samples taken from sites throughout the North Sea system (Murray, 1982; Rickard and Dulley, 1983; Marchand and Caprais, 1985; Duursma *et al.*, 1986; Delbeke *et al.*, 1990; Law *et al.*, 1996; Thompson *et al.*, 1996).

8.4.1 PCBs composition

The relative distribution of single PCB congeners as a percentage of the sum of all measured congeners is shown in Figure 8.13 for Tees Bay, Tees estuary, Aroclor 1260 and Aroclor 1254, respectively: Aroclor 1254 consists primarily of tetra-, penta-, hexa, and heptachlorobiphenyls and Aroclor 1260 consists of pent-, hexa-, hepta-, and octachlorobiphenyls. The PCB distribution pattern does not vary significantly between the bay and estuarine sediments, and presumably reflects source similarities. Surface sediments, from Tees Bay and Tees estuary (Fig. 8.13 a and b, respectively), have a composition of PCBs which is relatively similar to Aroclor 1254 and 1260 standards (Fig. 8.13 c and d, respectively), in their congener distribution patterns, but with somewhat higher concentrations of some of the more soluble tri- (PCB-28), tetra- (e.g. PCB-52) and pentachlorobiphenyls (e.g. PCBs 95, 101, 110). PCBs 153 and 180 are the main constituents in Aroclor 1260, whereas PCBs 118 and 138 predominant in Aroclor 1254 (Jones, 1988; Ballschmiter and Zell, 1980). Higher chlorinated chlorobiphenyl congeners (e.g. PCB 138, 153, 180) were detected at elevated concentrations in sediments samples from Tees Bay and Tees estuary, due to their relatively lower water solubility (Dannenberger, 1996). This observed distributional similarity, of the higher chlorinated congeners, is suggestive of an association of Aroclor 1260 and Aroclor 1254 with the sediment samples from both areas. The PCBs, therefore, are most likely derived from a point source with this chlorine composition. This evidence points to the higher urbanization/industrialization located

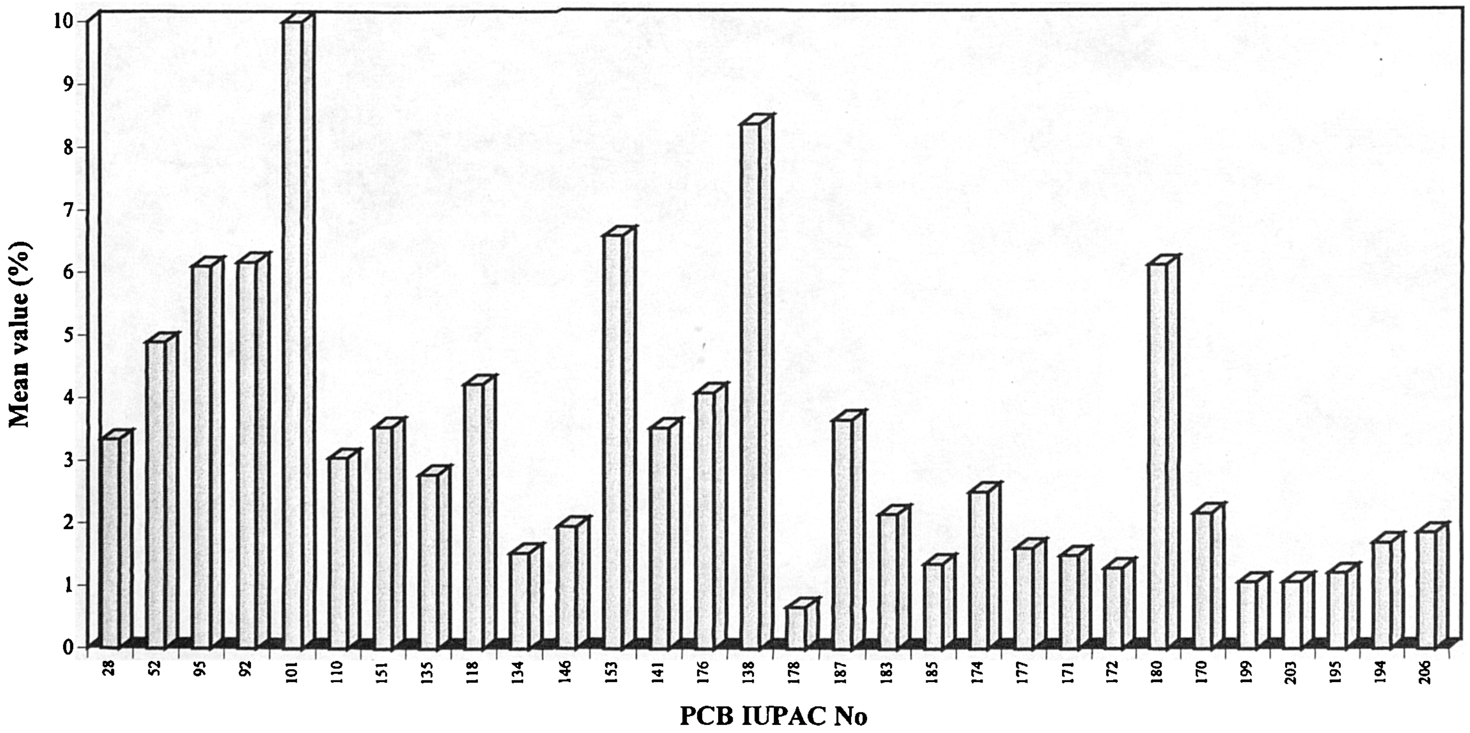


Figure 8.13a. Relative congener composition of PCBs in surface sediments from Tees Bay

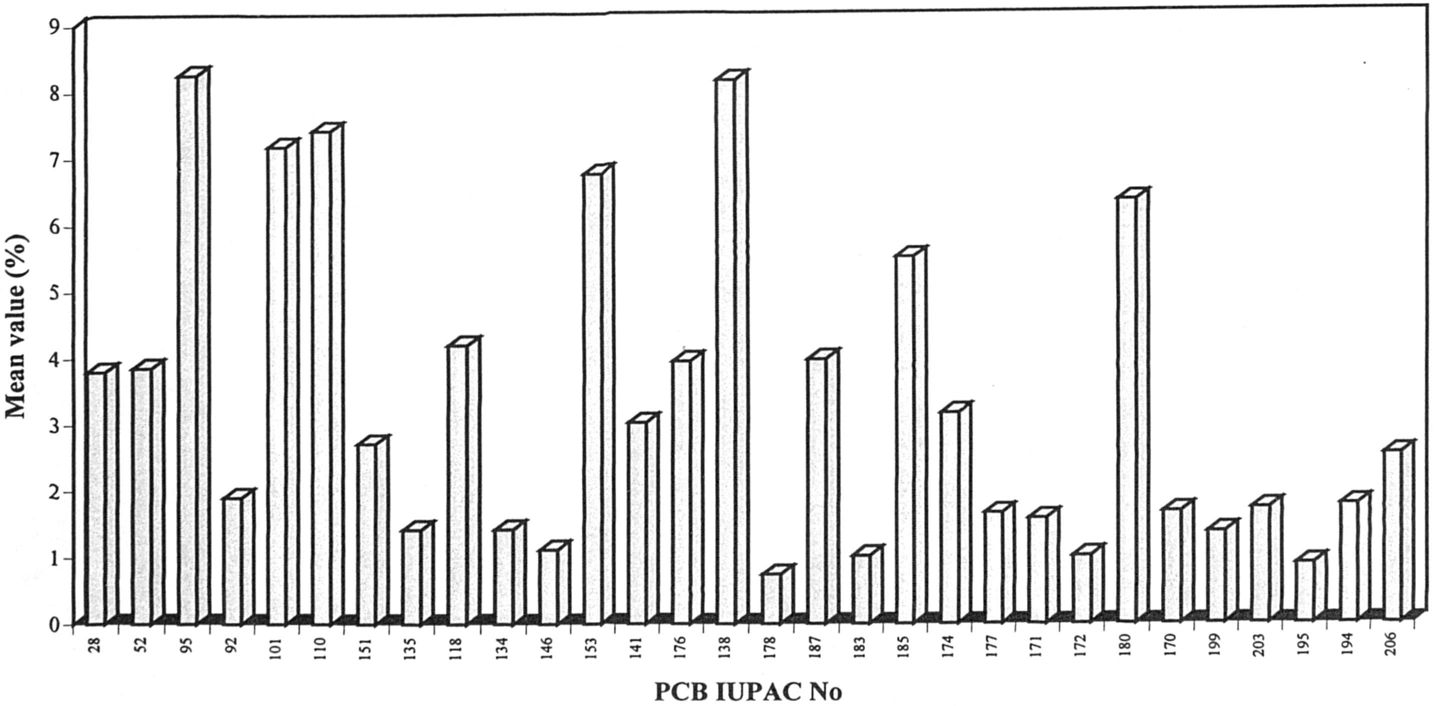


Figure 8.13b. Relative congener composition of PCBs in surface sediments from the Tees Estuary.

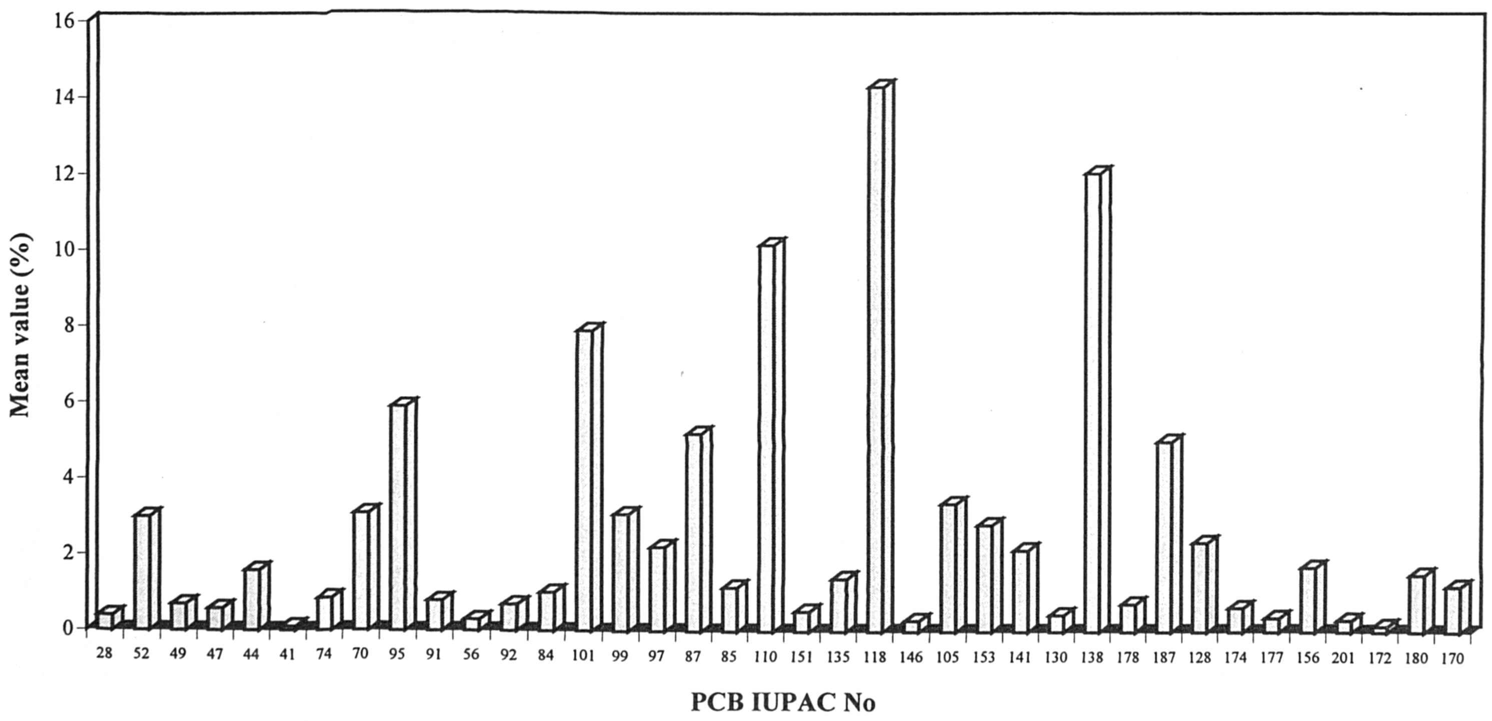


Figure 8.13c. Relative congener composition of PCBs in Aroclor 1254.

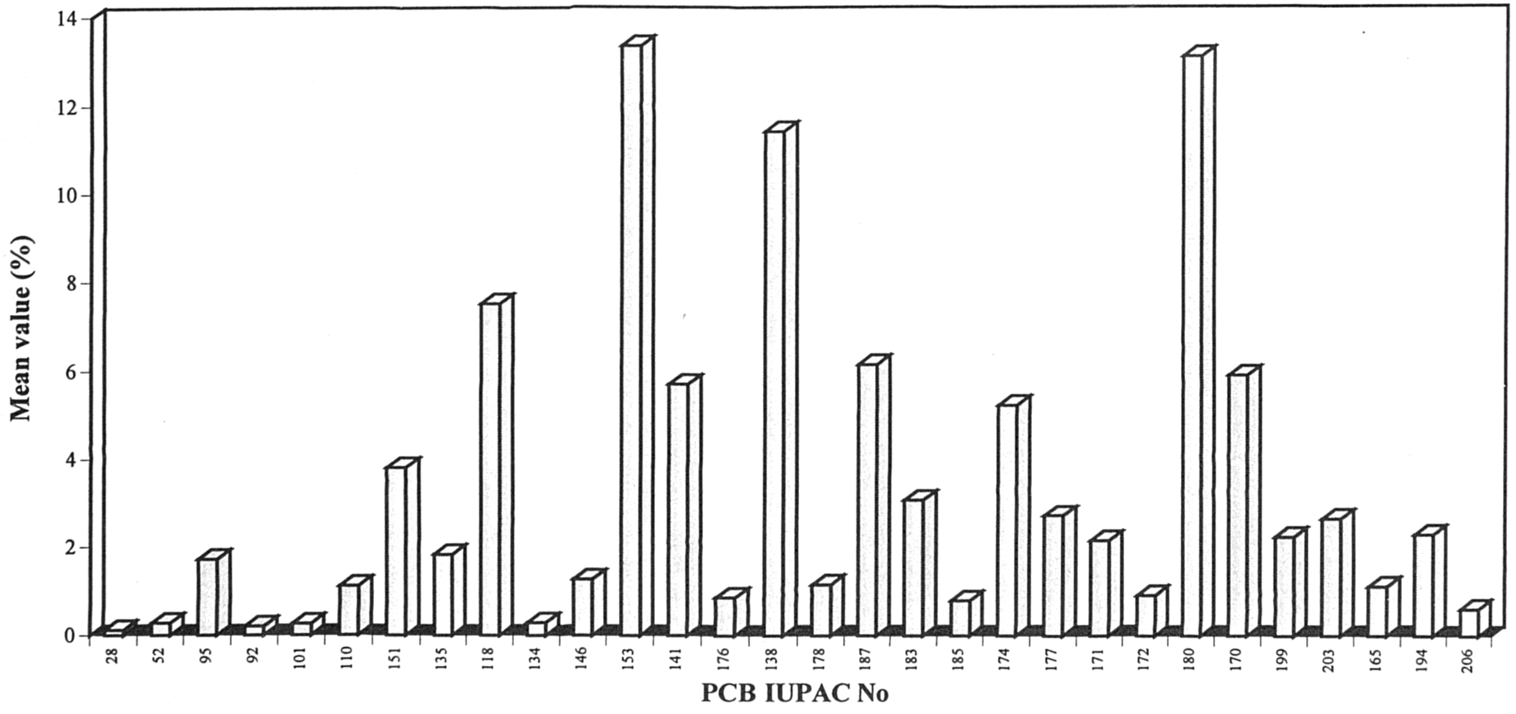


Figure 8.13d. Relative congener composition of PCBs in Aroclor 1260.

very close to the north east coast of England as the principle source for the larger PCBs. A similar observation was found for PCBs in coastal mussels of the east coast and the west coast of Scotland and of the Irish Sea (Thompson *et al.*, 1996).

In addition, the PCBs from Tees Bay and Tees estuarine sediments are also characterized by relatively high concentrations of lower chlorinated congeners (e.g. PCBs 28, 52, 101, 118), the distributions of which are highly dissimilar to Aroclor 1252 and 1260. These lower PCBs in the Tees Bay and the Tees estuarine sediments indicate additional inputs than Aroclor 1254 and 1260. However, this unusual enrichment of PCBs with 5 chlorines or less have been reported in sediments from other parts of the North Sea (e.g. the southern North Sea, Boon *et al.*, 1985; Humberside in the western North Sea, Klamer and Fomsgaard, 1993), the Irish Sea (Camacho-Ibar, 1991; Thompson *et al.*, 1996), Lake Siskiwit (Swackhamer *et al.*, 1988) and Lake Garda (Bossi *et al.*, 1992; Provini *et al.*, 1995). Similar results have also been reported in water (Schulz-Bull *et al.*, 1991) and biota (Buther, 1988) from the North Sea. Several of these authors suggested that the relative enrichment of the lower chlorinated PCBs, which can undergo long range air transportation due to their higher vapour pressure (Hites, 1990), could originate from atmospheric inputs (Swackhamer *et al.*, 1988; Camacho-Ibar, 1991; Bossi *et al.*, 1992; Provini *et al.*, 1995), from terrestrial sources.

From a comparison of Figure 8.13 (a, b, c and d), it is apparent that the distribution of the single PCB congeners in the sediment samples, both from the Tees Bay and the Tees estuary, is similar to that of Aroclor 1260 and 1254, even though a general enrichment of less chlorinated congeners can be observed. However, the similar behavior of the less chlorinated PCB congeners to that of the highly chlorinated ones in sediments from both areas indicates that sources responsible for PCB pollution are located in the north east area. This may be explained by a combinations of two contamination sources: 1) a local source, responsible for the presence of Aroclor 1260 and Aroclor 1254 and for the enrichment in the higher molecular weight congeners, and 2) an additional source arriving by long range air transport, responsible for the relative enrichment in the lower chlorinated PCB congeners. However, microbial dechlorination of PCBs is a well documented phenomenon, and such a process also results in apparent enrichment in less chlorinated congeners (e.g. Brown *et al.*, 1987; Ye *et al.*, 1992; Bedard *et al.*, 1996).

8.4.2 PCBs levels in relation to sediment characteristics:

Very large variations are encountered in the grain size and TOC of the surface sediments sampled in different places of the Tees Bay and Tees estuary (Figs. 8.14 and 8.15, respectively). Brownawell and Farrington (1986) and Colombo *et al.* (1990) have shown that the main factors controlling PCB levels in sediments are the distance from the sources and the grain size composition. Association of PCBs with total organic carbon (TOC) contents, on the other hand, has been reported by Brownawell and Farrington (1986) and Thompson *et al.* (1996). Generally, in the present study the PCB concentrations show considerable variations in the various regions of Tees Bay and Tees estuary (Figs. 8.11 and 8.12). In Tees Bay, for example, the profile of PCBs (Fig. 8.11) can be compared to either the profile of fine particles (clay and silt) or TOC (Fig. 8.14). The similarity of these profiles, especially over sites 4 and 25, is suggestive of an association of PCBs with fine-grained organic-rich sediments. This finding clearly indicates that PCB values follow the same trend as metals and hydrocarbons, being concentrated in the two offshore fine-grained organic-rich sediments (sites 4 and 25), far from industrialized area, in the northern and southern ends of the Tees Bay. PCBs are positively correlated with silt and clay and TOC contents (at the 99% significance level) and negatively correlated with sand contents of the sediments (at the 99% significance level), indicating that the highest loading of PCBs is associated with the fine grained organic particles and/or TOC.

Table 8.4 Correlation matrix showing the coefficient between different pairs of variable measured in Tees Bay.

	PCBs	**clay**	**silt**	**sand**	**TOC**
PCBs	1.00				
clay	0.85**	1.00			
silt	0.94**	0.93**	1.00		
sand	-0.94**	-0.87**	-0.99**	1.00	
TOC	0.90**	0.74**	0.88**	-0.77**	1.00

** = Significant at $P<0.01$.

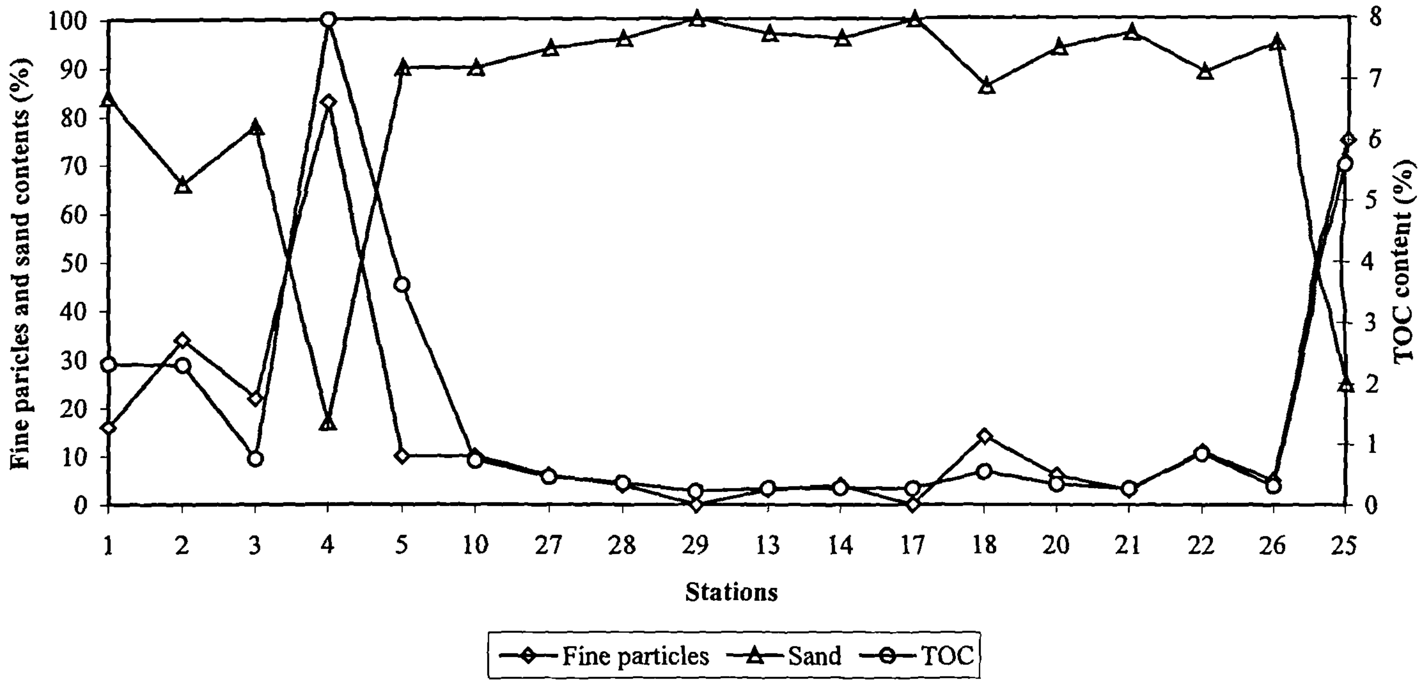


Figure 8.14. Distribution of fine particles (clay + silt), sand and TOC contents in the sediments of Tees Bay.

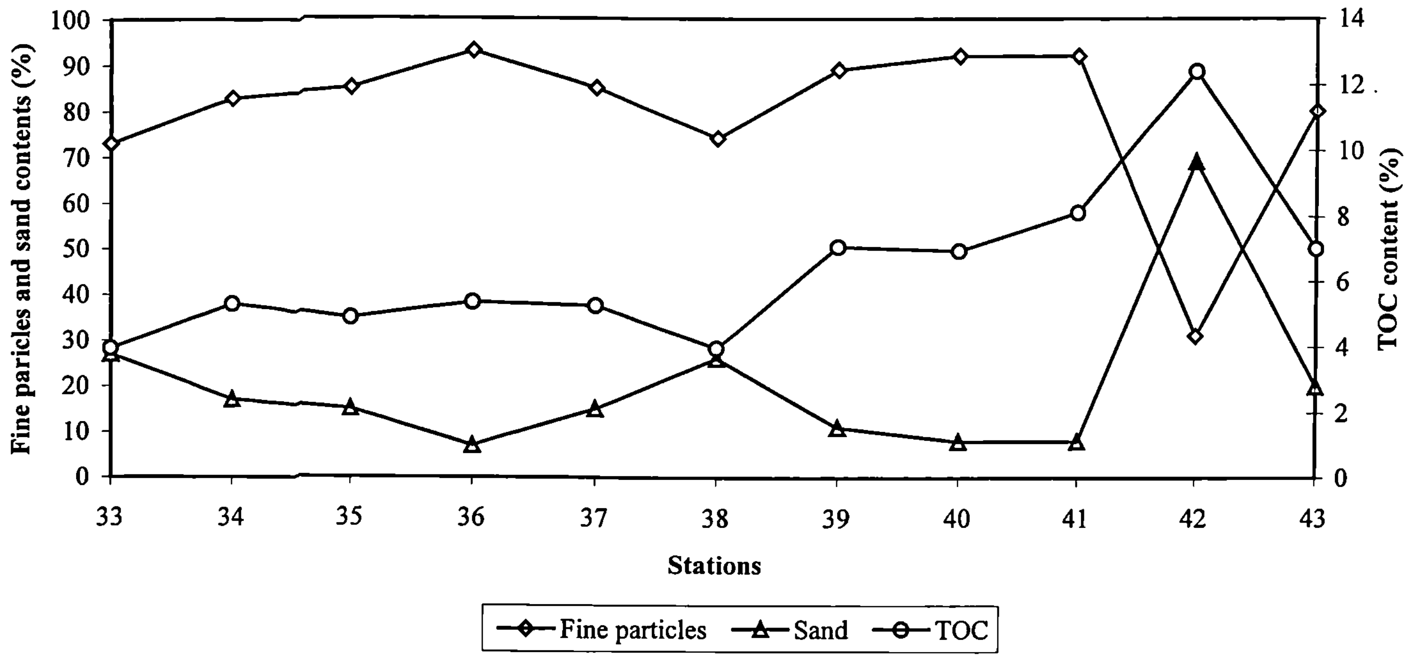


Figure 8.15. Distribution of fine particles (clay + silt), sand and TOC contents in the sediments of the Tees Estuary.

In Tees estuary, different trends were found for PCBs (Fig. 8.12), fine particles and TOC (Fig. 8.15). Sediments from sites 35, 36, 37 and 39 in the middle reaches of the estuary, which were clayey-silts (see Table 4.2; Chapter 4), were the most contaminated samples. Those sediments contains lower TOC contents (4.88, 5.36, 5.26 and 7.06%, respectively; Table 4.4; Chapter 4), compared to those of the silty sand sediment from site 42, in the lower reaches of the estuary, which contains high sand and TOC contents (69% and12.41%, respectively; Tables 4.2 and 4.4; Chapter 4). Furthermore, in the sandy sediment from site 42 concentrations of PCBs were significantly higher (13.83 ng g^{-1} dry wt) than those in the sand-silt-clay sediment of site 43 (7.01 ng g^{-1} dry wt), which contains relatively high clay and silt contents (Fig. 8.15). It seems, therefore, that the level of PCBs in these sediments are not necessarily determined by particle size and TOC content. This has been shown by the correlation of PCB level with a number of parameters (silt, clay, sand and TOC) being generally weak or poor (Table 8.5). It can be seen from the data in Table 8.5 that total PCB concentrations are positively correlated with clay and silt, and negatively correlated with sand and TOC, but these correlations are not significant. The reason for the negative correlation between PCB and TOC is not clear but could be due to the Tees estuary being relatively high in organic carbon but receiving low PCB from the highly urbanized and industrialized adjacent area. Another reason could also be due to the estuary is relatively high in organic carbon (ranged from 3.95% to 12.41% total organic carbon content; Table 4.4, Chapter 4) but is larger in area than others resulting in dilution of PCB discharges.

Table 8.5 Correlation matrix showing the coefficient between different pairs of variables measured in Tees Estuary.

	PCBs	**clay**	**silt**	**sand**	**TOC**
PCBs	1.00				
clay	0.43	1.00			
silt	0.37	0.67*	1.00		
sand	-0.42	-0.83**	-0.97**	1.00	
TOC	-0.32	-0.24	-0.72*	0.61*	1.00

* = Significant at $P<0.05$.
** = Significant at $P<0.05$.

8.4.3 Concentrations

The quantitative results, presented in Tables 8.2 and 8.3, show, as mentioned above, the level of selected PCB congeners in the surface sediments of the Tees Bay and Tees estuary. Generally, the results of PCBs fractions, extracted from Tees Bay and the Tees estuary sediments, continue the trend indicated by metals (Chapter 5), and the aliphatic (Chapter 6) and polyaromatic hydrocarbons (Chapter 7), in that the PCB concentrations varied in a relatively wide range between Tees Bay and the Tees estuary. These compounds were present in almost all sediment samples from Tees Bay and Tees estuary (with the exception of sites 10, 13, 17, 18, 22 and 29 where PCB levels are traces or nondetectable), with concentrations ranging from nondetectable to 55.13 ng g^{-1}.

In Tees Bay (Fig. 8.11), the fine-grained organic-rich surface sediments, collected from stations 4 and 25, revealed higher concentrations of PCBs (14.37 and 11.57 ng g^{-1} dry wt, respectively) in comparison with those of the sandy sediments from other stations (ranged from nondetectable to 3.81 ng g^{-1} dry wt). These results clearly show the ability of fine organic-rich sediments to accumulate large amounts of PCBs, due to their strong hydrophobic character (e.g. Brownawell and Farrington, 1986; Colombo *et al.*, 1990). These higher PCB levels were similar to, or slightly exceeding, levels of <10 ng g^{-1} dry wt in sediments of relatively uncontaminated areas such as Coos Bay or Bodega Bay (NOAA, 1987).

The increased level of PCBs in these two offshore sites (4 and 25) is in good agreement with the distributions of fine particles and TOC, as shown above. In addition, PCBs cannot be detected or found in very low concentrations in sites 13 and 29 of the Tees Bay, near the mouth of the estuary, and it seem extremely unlikely, therefore, that there is any significant direct input to marine waters from the Tees estuary. This suggests that atmospheric deposition might be the major source of PCBs in this area. Ballschmiter *et al.* (1989) observed that global equilibrium has not been reached for PCB and that environmental inputs are continuing. The atmospheric transport of PCBs to remote regions is facilitated by their long environmental half-lives and physical behaviour (Oehme and Mano, 1984; Oehme, 1991), and it has been suggested that the continuing use of large quantities of PCBs in the tropics leads to volatilization and subsequent condensation at lower temperature in high latitudes

(Tanabe *et al.*, 1994). This is supported by data obtained by Alcock *et al.* (1993) for UK agricultural soils between 1940 and 1992, which identified peak concentrations of 555 ng g^{-1} during the early 1970s with a subsequent decline in levels, reaching 12.8 ng g^{-1} in 1992. These authors concluded that the atmospheric deposition was deemed to be the main PCB input pathway for UK agricultural soils, with sample locations and proximity to industrial centers governing the degree of PCB enrichment. The similarity in concentrations between PCB loadings in these soils and the loading detected on the studied sediments implies that atmospheric deposition could well be an important pathway in coastal areas, particularly for sites located near urban areas, with sediment associated inputs of marine or fluvial origin contributing to a varying degree.

The concentrations of PCBs in the Tees estuary (Table 8.3) were higher than the concentrations found on the Tees Bay, and indicates a prevailing industrial contamination. In general, PCB levels in sediments from Tees estuary follow the same trend indicated by trace metals and hydrocarbons, in that higher concentrations of PCBs are found in the clayey-silts sediments from the middle reaches of the estuary, presumably due to localized contamination. Of the sites in the middle section of the estuary, maximum concentrations were measured at stations 35, 36, 37 and 39 (34.67, 55.13, 37.67 and 30.59 ng g^{-1} dry wt, respectively). The highest levels are recorded at site 36. Sites 38, 40 and 41, from the middle reaches of the estuary exhibited lower PCB levels (12.30, 22.60 and 16.62, respectively), but are relatively similar to those from other regions of the estuary. In this middle section of the estuary, the high PCB concentrations, at some sites, indicates that a local pollution source may exist. Urban sewage (Provini *et al.*, 1995) and industrial effluents have been reported as point sources of PCB pollution for the aquatic environment. PCB loads of up to 10-60 ug day^{-1} inhabitant and <70-732 ug day^{-1} inhabitant have been estimated for the urban sewage in France and the USA, respectively (Provini *et al.*, 1995). The river Tees receives the domestic sewage from the adjacent urban population (Shillabeer and Tapp, 1990), after simple screening and/or primary treatment only (Johnston *et al.*, 1991), plus the industrial inputs from a number of chemical and petrochemical works which discharges around 0.5×10^6 m^3 day^{-1}, with 3 sites in the middle of the estuary (see Fig. 3.2; Chapter 3) contributing around 75% of the total volume of industrial discharges (Johnston *et al.*, 1991). However, the relatively high PCB concentrations found in the middle reach of the estuary are generally consistent with the observations of Johnston *et al.* (1991), who noted that the middle section of the Tees estuary receives higher amounts of sewage and industrial discharges, between locations corresponding mostly to our sites 34-40. This observation confirms a local dumping area in which organic matter with a high complex mixture is released. These dumpings apparently contain sometimes very high, but sometime very low, PCB load. By implication, as sites 35, 36, 37 and to a lesser extent site 39, in the middle reaches of the estuary, are the sites most likely to receive direct urban/industrial inputs, from domestic and industrial discharges, this appears to be the major source of PCBs to the Tees estuary. In addition, the sediments of site 43 near the mouth of the estuary have the lowest PCB abundances, with concentrations (6.96 ng g^{-1} dry wt) that are less than those detected in other sites of the estuary. This apparent decrease of PCBs towards the mouth of the estuary must be related to the transport mechanism of PCBs: due to their low water solubility, they are essentially associated with the particulate fraction of the water column (e.g. Duursma *et al.*, 1989) and are, therefore, to a very high extent sedimented with the particulate matter. In the southern part of the North Sea, about 40% of the primary production of zooplankton is sedimenting (Joiris *et al.*, 1982). They are, therefore, transported with the water current only to a limited extent, causing lower PCB levels in areas situated at relatively greater distances from the contaminated sites.

8.4.4 Current Situation of Tees Bay and Tees Estuarine sediment:

A comparison of the observed levels of PCBs in the Tees Bay and Tees estuarine sediments with other aquatic environments is summarized in Table 8.6, to place the results of this study into a global perspective. In general, PCB concentrations, expressed as total PCB, for the Tees Bay and Tees estuarine sediment samples ranged from traces-14 and 7-55 ng g^{-1} dry wt, respectively. The total PCBs in Tees Bay sediments are lower than values for Tees estuary, and most of the other localities in Table 8.6. However, PCB concentrations in Tees Bay sediments are higher than those reported in Coos Bay (NOAA, 1987), Aliakmon River, Greece (Larsen and Fytianos, 1989), the Lagoon of Venice, Italy (Raccanelli *et al.*, 1989),

Table 8.6 Worldwide concentrations (ng g^{-1}, dry weight) of total PCBs in sediments

Location	**Total PCBs**	**Reference**
Essex Coast, UK	0.3 - 34.2	Scrimshaw *et al.* (1994)
Humber Bay, UK	3 - 19	Klamer & Fomsgaad (1993)
Humber Estuary, UK	1 - 84	Tyler & Millward (1996)
Liverpool Bay	0.08 - 38	Camacho-Ibar (1991)
Irish Sea	0.2 - 42	Thompson *et al.* (1996)
Manukau Harbour, New Zealand	0.5 - 14.2	Fox *et al.* (1988)
Axios River, Greece	4 - 24	
Aliakmon River, Greece	1 - 7	
Thermaikos Gulf, Greece	5 - 39	Larsen & Fytianos (1989)
The Lagoon of Venice	0.003 - 0.020	Raccanelli *et al.* (1989)
Rio de La Plata, Argentina	2 - 998	Colombo *et al.* (1990)
Scheldt Estuary	217 - 1068	Van Zoest & Van Eck (1990)
Jordan Valley	2 - 9	Alawi & Heidemann (1991)
California	2 - 1728	Rice *et al.* (1993)
Australia	0.5 - 790	
India	5 - 1000	
Indonesia	6 - 220	
Japan	63 - 240	
Papua New Guinea	3 - 54	
Solomon Island	1 - 5	
Taiwan	2 - 230	
Thailand	11 - 250	
Vietnam	0.2 - 140	Iwata *et al.* (1994)
Tees Bay	Traces - 14	This study
Tees estuary	7 - 55	This study

Jordan Valley, Jordan (Alawi and Heidemann, 1991) and Solomon Island (Iwata *et al.*, 1994), which were classified as relatively uncontaminated areas. They are comparable to those from other industrialized coastal regions of the world, such as Manukau Harbour, New Zealand (Fox *et al.*, 1988) and Humber Bay, UK (Klamer and Fomsgaard, 1993), which were classified as slightly polluted areas. It seems, therefore, that the levels of PCBs in Tees Bay can be classified as slightly polluted.

The highest concentrations obtained in this study are detected in sediments of the Tees estuary, and a comparison with other sedimentary aquatic environments (Table 8.6) indicates a relatively high level of contamination. However, the Tees estuary PCB concentrations are much lower than those recently reported for other highly industrialized and urbanized areas (Colombo *et al.*, 1990; Van Zoest and Van Eck, 1990, Rice *et al.*, 1993; Iwata *et al.*, 1994). Therefore, the PCB detected levels in sediments from the Tees Bay and Tees estuary are low, in general, when compared to levels measured worldwide.

8.6 Summary

1- Surface sediment samples were taken from 29 sites along the Tees Bay and Tees estuary, and analysed for PCB content. PCBs which have been recognized as a major group of environmental pollutants were determined using a method based on that of Allchin *et al.* (1989). This is the first study to report PCB data for Tees Bay and Tees estuarine sediments.

2- Sediment samples from Tees Bay and the Tees estuary have a composition of single PCB congeners similar to that of Aroclor 1260 and 1254, deviating only in a partial enrichment of lower chlorinated region, and suggested a combination of two contamination sources.

3- Sediment characteristics, such as fine particle size (clay and silt) and total organic carbon content, significantly influence the geographical distribution of PCBs in the Tees Bay only.

4- The sediments of Tees Bay and Tees estuary demonstrate the presence of PCB congeners and exhibit considerable spatial variability in their concentrations. Site-to-site variability appears high even over short distances, especially in the Tees estuary. The sediments of the Tees estuary tend to be more highly contaminated than those of the Tees Bay, particularly in the middle reaches of the estuary. There is a general decrease in PCB concentrations from the middle of the estuary to the bay area, while within the bay area, offshore sites showed higher concentrations. These marked differences and the distribution pattern, seen for the higher and the lower chlorinated PCB congeners, are indicative of the presence of multiple sources of PCBs of different degrees of chlorination (Phillips and Spies, 1988).

5- Comparing the present data with those reported in the literature the levels of PCB congeners are similar to levels found for slightly polluted areas.

Chapter Nine

Conclusions and Suggestions for Future Work

9.0 Conclusions and Suggestions for Future Work

9.1 Conclusions

9.1.1 Summary of conclusions from previous chapters

The present study was designed to investigate the distributions of metals, *n*-alkanes, PAHs and PCBs, together with metal partitioning, in the sediments of Tees Bay and the Tees estuary. The main conclusions from this work can be summarized as follows:

1- The Tees estuary sediments are largely clayey-silts, with coarser sediments found at sites 33, adjacent to Newport Bridge, 38, in the mid-estuary, and 42 and 43, at the estuary mouth. All sediments are organic-rich, varying between 3.96% and 21.41% organic carbon content, with a median of 5.36%. In contrast, Tees Bay sediments are largely sands, with clayey-silt sediments found at the most seaward sites at the southern and northern end ends of the Bay (sites 25 and 4). The organic carbon content of Tees Bay sediments varies between 0.22% and 8.00% organic carbon content, with a median of 0.63%. The highest organic carbon contents are observed in the clayey-silt sediments, whereas the lowest are found in the sandy sediments.

2- Sediment characteristics, such as the abundance of clay and silt and total organic carbon content, significantly influence the geographical distribution of metals, hydrocarbons (*n*-alkanes and PAHs) and PCBs in Tees Bay. In the sediments from the Tees estuary the concentration of inorganic and organic compounds appear to be governed mainly by their proximity to potential pollution sources, and do not relate to the grain size and/or TOC contents.

3- All of the metals measured (Cd, Co, Cr, Cu, Ni, Pb and Zn) have significantly higher concentrations in the sediments of the Tees estuary than in those of Tees Bay ($P<0.01$), and the mean averages decrease in the order Zn > Pb > Cr > Cu > Ni > Co > Cd. These significantly higher concentrations remain apparent when the data are normalized to remove the effect of grain size variation, suggesting that the sediments of the Tees estuary are enriched in metals in comparison with the sediments of Tees Bay and that these differences are not the result of the different grain size distributions.

4- In the Tees Estuary, concentrations of Cd, Co, Cr, Cu, Pb and Zn are generally above natural background levels, and are similar to the concentrations found in other moderately to strongly polluted European estuaries. The data also demonstrate that concentrations of Cd, Cr and Co are higher than those of the 19 other UK estuaries reported by Bryan and Langston (1992). The high metal concentrations found in this study are generally consistent with those of Davies *et al.* (1991), and confirm the systematic decline in Cu and Zn concentrations, and the probable lowering of Pb concentrations over the period 1979-1991, as suggested by Davies *et al.*, (1991). Variation in metal concentrations along the estuary are considerable. Pb and Zn concentrations are highest in the upper and middle reaches of the estuary, Cd, Cr and Cu are concentrated in the middle reach only (between site 37 and 39), Ni increases in concentration from Newport Bridge to the river mouth, and Co has a constant concentration above site 38, increases at site 39, and subsequently decreases to the river mouth.

5- In Tees Bay, concentrations of Co, Cr, Cu, Ni and Zn are lower than those of average shale at all sites other than 4 and 25 and this remained true even when corrections were made for grain size variation. Cd and to a lesser extent Pb were present in concentrations above the geochemical background levels. Comparison of the mean metal concentrations for Tees Bay sediments determined in this study with those of the earlier study of Taylor (1979) showed that the concentrations of Cd, Co, and Cr found in this study were significantly higher (at the 95% confidence level) than those reported by Taylor (1979), whilst the concentrations of Cu, Ni, Pb and Zn, found in this study, were not significantly higher (at the 95% confidence level). Further comparison of the mean metal concentrations measured in Tees Bay with data from similar environments around the world suggests that mean levels of Cd and Pb are similar in magnitude to those of slightly-moderately polluted areas, while Co, Cr, Ni and Zn concentrations are generally similar to those of unpolluted areas.

6- Metal partitioning, which is of critical importance in assessing the likely behaviour of metals in the aquatic system, was determined using a five-stage sequential leaching technique based on that of Tessier *et al.* (1979). This is the first study to report metal partitioning for Tees Bay and the Tees estuary sediments. The application of this technique to sediment samples from Tees Bay and the Tees estuary showed that the partitioning characteristics of the different trace metals varied. It was also shown that for some metals the partitioning differed between the marine and estuarine environments. In the Tees estuary sediments, the partitioning of Cr, Pb and Zn, which are the three most abundant metals in the Tees estuary, is generally similar at all sites, with fractions 3, 5 and 4 being of greatest importance. The distribution of Cd is dominated by fractions 5 and 3, with minor proportions of fractions 4 and 2, and Cd is also the only element for which fraction 1 is significant. Cu is distributed uniquely with only fractions 5 and 4 found to be important host fractions. Of these fraction 4 is the most significant. Co and Ni, which are not highly enriched in these sediments, are hosted largely in fraction 5, although fraction 3 also carries some Co.

7- In Tees Bay sediments, the partitioning patterns of Cd, Co, Ni and Pb are similar to those found in the Tees estuary. Cr and Zn are still partitioned between fractions 3, 5 and 4, but fraction 5 becomes the principle host. The distribution of Cu which is not highly enriched in these sediments, is dominated by fraction 5 followed by fraction 4.

8- The distributions of the organic pollutants follow a similar trend to those of metals in that sediments of the Tees estuary contained higher concentrations than those of Tees Bay.

9- The distributions of the *n*-alkanes, acyclic isoprenoids, triterpanes and steranes in Tees Bay are mainly indicative of pollution by crude oil, petroleum products and coal. A few sediment samples from the Tees estuary show the presence of both petroleum and biogenic hydrocarbons.

10- The molecular distributions and the relative concentration ratios of some alkylated and non-alkylated PAHs, in the sediment samples from both areas indicate petrogenic and/or pyrolytic sources of PAHs in the sediments studied

11- The compositions of single PCB congeners are similar to those of Aroclor 1260 and 1254. Site-to-site variability in concentration is high even over short distances, especially in the Tees estuary. The sediments of the Tees estuary tend to be more highly contaminated than those of the Tees Bay, particularly in the middle reaches of the estuary. There is a general decrease in PCB concentrations from the middle of the estuary to the bay area, while within the bay area, offshore sites showed higher concentrations. These marked differences and the distribution pattern, seen for the higher and the lower chlorinated PCB congeners, are indicative of the presence of multiple sources of PCBs of different degrees of chlorination.

9.1.2 Relationships between the inorganic and organic pollutants in the surface sediments of Tees Bay and the Tees Estuary

It has been noted above (section 9.1.1) that the inorganic and organic pollutants follow the same trend in the sediments of Tees Bay and the Tees estuary. In order to find associations between the concentrations of the metals and concentrations of the *n*-alkanes, PAHs and PCBs in the sediments, correlation coefficients have calculated for the Tees Bay and Tees estuary sample suites. As grain size appeared to be an important influence on the concentrations of all the pollutant classes determined (Chapters 5, 6, 7 and 8) the correlation with % clay, % silt and % sand were also calculated (Tables 9.1, 9.2 and 9.3).

In Tees Bay, significant and positive correlations are generally found between the concentrations of the species determined and the % silt, % clay and TOC present in the sediment, with the preferential association of all of the species measured in fine-grained organic rich sediments. Similar relationships are obtained for both the concentrations of metals and the concentrations of organic compounds (*n*-alkanes, PAHs and PCBs), suggesting that the fine-grained organic rich particles play an important role in controlling the concentrations of trace metals and organic compounds in Tees Bay sediments.

Relationships in the sediments from the Tees estuary are more complex (Table 9.2). For these sediments, concentrations of the measured metals and organic compounds are negatively correlated with TOC, although these correlations are only significant for Pb. The concentrations of all the metals measured are positively correlated with the finer components of the Tees estuary sediment (clay and silt) and are negatively correlated with the sand content. However, only for Ni are these relationships significant at the 99% confidence level whilst the relationship is significant at the 95% level for Cd and Co (Table 9.2). In the case of the organic compounds, the concentrations of PCBs are positively correlated with clay and silt and are negatively correlated with the sand content, but not significantly (Table 9.2).

Table 9.1 Correlation matrix showing the coefficient between different pairs of variables measured in the sediments of Tees Bay.

	Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	***n*-alkanes**	**PAHs**	**PCBs**	**Sand**	**Silt**	**Clay**	**TOC**
Cd	1.00													
Co	0.78**	1.00												
Cr	0.78**	0.89**	1.00											
Cu	0.75**	0.90**	0.93**	1.00										
Ni	0.75**	0.84**	0.90**	0.90**	1.00									
Pb	0.76**	0.92**	0.91**	0.90**	0.90**	1.00								
Zn	0.69**	0.85**	0.87**	0.88**	0.83**	0.92**	1.00							
***n*-alkanes**	0.64**	0.79**	0.81**	0.91**	0.90**	0.80**	0.81**	1.00						
PAHs	0.58**	0.73**	0.73**	0.81**	0.86**	0.75**	0.75**	0.95**	1.00					
PCBs	0.76**	0.91**	0.88**	0.89**	0.92**	0.92**	0.81**	0.83**	0.77**	1.00				
Sand	-0.73**	-0.87**	-0.91**	-0.89**	-0.91**	-0.89**	-0.77**	-0.82**	-0.82**	-0.94**	1.00			
Silt	0.72**	0.88**	0.91**	0.90**	0.91**	0.90**	0.77**	0.82**	0.81**	0.96**	-0.99**	1.00		
Clay	0.74**	0.81**	0.85**	0.82**	0.87**	0.84**	0.74**	0.75**	0.80**	0.85**	-0.87**	0.93**	1.00	
TOC	0.67**	0.84**	0.90**	0.95**	0.93**	0.87**	0.84**	0.97**	0.89**	0.90**	-0.77**	0.88**	0.74**	1.00

** = Significant at $P < 0.01$.

Table 9.2 Correlation matrix showing the coefficient between different pairs of variables measured at all sites from the Tees Estuary.

	Cd	Co	Cr	Cu	Ni	Pb	Zn	*n*-alkanes	PAHs	PCBs	Sand	Silt	Clay	TOC
Cd	1.00													
Co	0.63*	1.00												
Cr	0.82**	0.24	1.00											
Cu	0.95**	0.66*	0.81**	1.00										
Ni	0.73*	0.86**	0.57	0.71*	1.00									
Pb	0.59	-0.08	0.76**	0.42*	0.27	1.00								
Zn	0.95**	0.45	0.85**	0.89	0.58	0.74**	1.00							
***n*-alkanes**	-0.01	-0.46	0.29	-0.15	-0.15	0.70*	0.25	1.00						
PAHs	0.44	-0.03	0.77**	0.55	0.24	0.49	0.49	0.06	1.00					
PCBs	0.54	0.15	0.58	0.46	0.34	0.75**	0.69*	0.58	0.28	1.00				
Sand	-0.67*	-0.75*	-0.51	-0.56	-0.93**	-0.42	-0.57	-0.06	-0.09	-0.42	1.00			
Silt	0.66*	0.69*	0.49	0.51	0.86**	0.44	0.58	0.16	-0.01	0.37	-0.97**	1.00		
Clay	0.55	0.70*	0.44	0.53	0.87**	0.27	0.40	-0.16	0.30	0.43	-0.83**	0.67*	1.00	
TOC	-0.45	-0.10	-0.56	-0.25	-0.38	-0.63*	-0.51	-0.51	-0.12	-0.32	0.61*	-0.72*	-0.24	1.00

* = Significant at $P < 0.05$.
** = Significant at $P < 0.01$.

Table 9.3 Correlation matrix showing the coefficient between different pairs of variables measured in the sediments of Tees Estuary, except site 42.

	Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	***n*-alkanes**	**PAHs**	**PCBs**	**Sand**	**Silt**	**Clay**	**TOC**
Cd	1.00													
Co	0.43	1.00												
Cr	0.74*	0.08	1.00											
Cu	0.95**	0.56	0.75*	1.00										
Ni	0.51	0.80**	0.31	0.65*	1.00									
Pb	0.46	-0.44	0.70*	0.28	-0.11	1.00								
Zn	0.94**	0.22	0.80**	0.86**	0.34	0.67*	1.00							
***n*-alkanes**	-0.10	-0.65*	0.27	-0.23	-0.39	0.73*	0.22	1.00						
PAHs	0.49	-0.10	0.86**	0.58	0.28	0.50	0.49	0.05	1.00					
PCBs	0.50	0.01	0.54	0.40	0.30	0.74*	0.67*	0.57	0.27	1.00				
Sand	-0.38	-0.70*	-0.12	-0.41	-0.89*	-0.05	-0.27	0.14	-0.04	-0.50	1.00			
Silt	0.33	0.56	0.02	0.29	0.61	0.10	0.32	0.12	-0.26	0.41	-0.77**	1.00		
Clay	0.26	0.52	0.16	0.35	0.76*	-0.03	0.09	-0.32	0.32	0.36	-0.78**	0.19	1.00	
TOC	0.13	0.82**	-0.27	0.24	0.73*	-0.54	-0.16	-0.74*	-0.09	-0.19	-0.68*	0.32	0.74*	1.00

* = Significant at $P < 0.05$.
** = Significant at $P < 0.01$.

This suggests that the grain size may play, to some extent, a role in controlling the distribution of PCBs in the Tees estuary. On the other hand even poorer correlations are found between the concentrations of *n*-alkanes and PAHs and the grain size distributions of sediments in the Tees estuary. It may also be noted that Pb concentrations correlate extremely well with *n*-alkane concentrations (Table 9.2). Petroleum hydrocarbon contamination in the Tees estuary area is thought to be derived from diversified sources, including industrial discharges, urban runoff and heavy commercial shipping and boating activities. Crude oil is known to contain minor amounts of Pb (Al-Abdali *et al.*, 1996), so it seems likely that one, or probably more than one, of the above diversified oil pollutant sources are a probable source of at least some of the Pb. Significant and positive correlations are also found between the concentrations of PAHs and Cr and between PCBs and Pb and Zn, the reasons for which are not clear.

Somewhat different relationships are observed if the Tees estuary data are re-calculated without the sandy sediment from site 42 (Table 9.3), with Co and Ni being negatively correlated with the sand content of the sediment (at the 95% confidence level) and positively correlated with the TOC content and the finer sediment fractions. This suggests that the fine-grained organic rich particles play an important role in controlling the concentrations of Co and Ni in the Tees estuary sediments. It also suggests that the concentrations of all other metals and organic compounds appear to be governed mainly by their proximity to potential pollution or anthropogenic sources, and do not relate to the grain size and/or TOC contents.

9.1.3 Geochemistry of trace metals in Tees Bay and the Tees Estuary

Various studies have attempted to predict the impact of contaminated sediments on the aquatic environment by estimating the potential availability of the different metal forms, and recent studies have shown that metal partitioning is a significant influence on the bioavailability and subsequent toxicity of trace metals in sediments (Luoma and Carter, 1991; Di Toro *et al.*, 1992; Bonnevie *et al.*, 1994). Metals bound to different fractions will behave differently in the environment, and thus have different potential for remobilization, and for uptake by biota.

Trace metals in fraction 1 (e.g. the exchangeable fraction) are weakly held by van der Waals, London and Coulomb forces (Samant *et al.*, 1990), and normally constitute only a small portion of the total metals in a sediment (Kersten and Forstner, 1990). This fraction represents the capacity of the sediment to adsorb/desorb trace metals and may be influenced by changes in the ionic composition of water resulting from salinity changes (e.g. near estuaries) and/or industrial-urban pollution (Boughriet *et al.*, 1994). Fraction 2 (e.g. the carbonate fraction) represents trace metals bound to carbonates and may change with variation in pH. Since carbonates are regarded as inefficient metal carrier phases (Kruaskopf, 1956; Horowitz, 1985; Sigg, 1987), high metal concentrations in this fraction are often explained by the poor selectivity of the methods used. Desorption of metals from other phases, such as Fe-Mn oxides (Pickering, 1986; Martin *et al.*, 1987) and from organic matter coatings (Slavek, 1982; Horowitz and Elrick, 1987), during fraction 2 extraction is common and for this reason some researchers have named this fraction as the exchangeable at pH 5 fraction (Martin *et al.*, 1987) or specifically sorbed (Pickering, 1986). From a geochemical point of view, trace metals in fractions 1 and 2 are considered to be weakly bound and may equilibrate rapidly with the aqueous phase, which they are in contact, thus becoming more bioavailable. (Gambrell *et al.*, 1976; Gibbs, 1977; Rule and Alden, 1992; Comber *et al.*, 1995). Significant portions of Cd are contained in fractions 1 and 2 in both the Tees estuary sediments and those from Tees Bay. Because of the toxicity and availability of Cd this may pose a serious problem to the ecosystem. The total Pb in the sediments is also quite high, particularly in the Tees estuary, and even the small proportion in fraction 2 could cause deleterious effects. These two metals are also associated with fraction 3, which constitutes an important potential source for the release of metals to surface water under reducing conditions, as discussed below.

The behaviour of metals associated with fraction 3 (e.g. the reducible fraction) is controlled by the solubility of iron and manganese oxides (Jenne, 1968). Iron and manganese oxides and hydroxides are major trace metals hosts in estuarine sediments (Calmano and Forstner, 1983), and have been previously identified as important bioavailable metal sources (Luoma and Davis, 1983). Such iron and manganese oxides and hydroxides play an important role in scavenging trace metals from solution (Tessier *et al.*, 1979; Waldichuk, 1985; Arakel and Hongjun, 1992). Whilst such phases are stable under oxidizing conditions, they are sensitive to changes in redox conditions in the sediment, and became unstable in reducing environments. The extent and intensity of this process will vary depending on several factors associated with O_2 dynamics in the sediments (Garcia-Miragaya and Sosa, 1994). When microorganisms oxidize organic matter, they create reducing conditions which stabilize iron and manganese in their lower valency state. In this valency state, iron and manganese compounds have greater solubilities and so transfer to the aqueous phase (Samant *et al.*, 1990). Transfer of associated heavy metals to the aqueous phase is also likely during this process. Such dissolution will release metals associated with oxide phases to the pore water, possibly to the overlying water column (Petersen *et al.*, 1995), and to benthic biota. High concentrations of dissolved Mn have been observed in Tees estuary water (Laslett, 1995), and are believed to be result of transfer of dissolve $Mn^{(II)}$ from sediment pore-water to the overlying estuarine column by resuspension and/or diffusion (Laslett, 1995), confirming that $Mn^{(IV)}$ reduction is occurring within Tees estuary sediments. All metals were associated with this fraction in sediments of Tees Bay and the Tees estuary, and for some metals such as Pb, Cd, Cr, Zn and to a lesser extent Co, this fraction contained a major proportion of the total sediment burden. There is, therefore, cause for concern regarding metals associated with this fraction in the sediments because of their potential availability.

Fraction 4 (e.g. the oxidizable fraction) consists largely of organic and sulphide bound metals, and may provide an eventual sink for heavy metals (De Souza *et al.*, 1990). Chemical discrimination between organic bound and sulphide bound metals, however, is difficult (Kersten and Forstner, 1990; Papp *et al.*, 1991). This fraction is not considered very mobile or available, since it is thought to be associated to high molecular weight, stable humic substances, which would release small amounts of metals in very slow fashion (Garcia-Miragaya and Sosa, 1994). Metals precipitated with sulphides are also effectively insoluble and not easily bioavailable (Waldichuk, 1985; Rule and Alden, 1992). All metals were detected in fraction 4, except Cd in the Tees Bay sediments. The proportion of metals in this phase in Tees estuary sediments was higher than in the Tees Bay sediments, particularly for Cu and to a lesser extent Cr and Zn, reflecting the relative importance of this fraction in Tees estuary sediments. The association of Cu with organic material is well documented

(Tessier *et al.*, 1980; Forstner and Patchineelam, 1981; Hickey and Kittrick, 1984), sewage for example scavenging Cu strongly from seawater (Comber and Gunn, 1995). Thus, it is the organically bound form that Cu is most likely deposited at the sediment surface. Cu could possibly be mobilized from this phase by decomposition of the organic matter, which might be enhanced by exposure to oxidizing conditions (Rodger and Davies, 1992). Other trace metals in this fraction are normally associated with sulphides and can be made available upon an increase in the sediment redox potential (Gambrell *et al.*, 1976; Rule and Alden, 1992). Most of the Cu, and some of Cr and Zn will probably be eventually fixed as pyrite (Huerta-Diaz and Morse, 1992) and effectively be immobilized as long as the sediments remain reducing. However, dredging might expose sediments containing high concentrations of sulphide bound metals to oxygenated waters so promoting their release, and may have profound effects on the ecology of the estuary, already affected by years of heavy metals pollution.

The residual fraction, composed of detrital silicate minerals, resistant sulphides, and refractory organics (Tessier *et al.*, 1979), represents a fraction that is largely unavailable to either biological or diagenetic processes over a time scale of a year to decade (Jenne, 1977; Surija and Branica, 1995). Salomons and Forstner (1980) Calmano and Forstner (1983) Rubio *et al.* (1991) have shown that metals with an anthropogenic origin are mainly obtained in the first extractions (F1-F4; non-lithogenic or mobile fractions), while in the residual fraction (F5; immobile fraction) corresponds to metals with lithogenic origin, i.e. that which is lattice-held. Non-residual trace elements (i.e. the non-lattice part) are not a part of the silicate matrix and have been incorporated into the sediment from solution by processes such as adsorption, precipitation/co-precipitation and organic complexation. Thus, large amounts of trace metals in the non-residual fractions generally originate from polluted waters (Agemain and Chao, 1976; Chester and Voutsinou, 1981) and may provide an indication of metal pollution in the aquatic sediments (Chester and Voutsinou, 1981). The availability of certain trace metals to benthic organisms is generally correlated with the non-lithogenous fraction rather than the total metal contents of sediments (Luoma and Bryan, 1978; Langston, 1980; Tessier *et al.*, 1984; Bourgoin *et al.*, 1991). Metals that extracted in the largest percentages (>50%) in the lithogenous fraction are

Co and Ni in Tees Bay and the Tees estuary sediments, Cr, Cu, and Zn, in Tees Bay sediments, and Cd in Tees estuary sediments. Higher Cd concentrations in this fraction are hard to explain, the only likely explanation is that some of the residual Cd is probably anthropogenic. Similarly, high concentrations of Cd in the residual fraction from three Brazilian estuaries has also been reported by De Souza *et al.* (1986).

In summary, the results of the sequential extraction showed that the partitioning patterns of Cd, Cr, Cu and Zn differed between the marine and estuarine sediments. In the Tees Bay sediments the residual fraction hosted >50% of all of the metals, except Cd and Pb. In the Tees estuary, however, this fraction only accounted for >50% of the Cd, Co and Ni. The Cd concentration in the sediments studied is the lowest amongst the different element investigated but this element exhibits the greatest degree of metal enrichment in the sediments from Tees Bay and the Tees estuary. Cd is also the only element for which fraction 1 is significant and is thus readily bioavailable. As a result of the high total Pb the small amount of Pb in fraction 2 may also pose a problem to the ecosystem. High concentrations of Cd, Cr, Pb and Zn, which are the most highly enriched metals in the Tees estuary, were associated with fraction 3. This fraction constitutes an important source for release of metals to surface water under reducing conditions. Cu was the only metal significantly associated with fraction 4. This fraction is likely to have an important role as a sink for trace metals, particularly for Cu and to a lesser extent Cr and Zn.

9.1.4 Geochemistry of organic compounds in Tees Bay and the Tees Estuary

Estuarine processes play an important role in the distributions and fate of pollutants. Anthropogenic compounds, derived from terrestrial and atmospheric sources, are subject to biogeochemical processes during their residence time in estuaries. These processes ultimately determine the distribution and fate of contaminants in marine environments.

Of particular environmental concern are the so called hydrophobic organic pollutants such as petroleum hydrocarbons, PAHs and PCBs which, by virtue of their nature, under some circumstances are toxic and can adversely affect the health of biota (Reijnders, 1986; Malins *et al.*, 1988; Pridmore *et al.*, 1992; Zhou *et al.*, 1996). Most of the hydrocarbons are among the widespread and persistent environmental contaminants, and have only short residence times in the water column, due to their hydrophobic character (low water solubiliy) which leads to bioaccumulation and strong sorption onto suspended particulate matter. They are carried to the bottom water and are finally trapped in marine sediments (Dannenberger, 1996).

The data presented here are used to examine the variability of *n*-alkane, PAH and PCB composition in the sediments of Tees Bay and the Tees estuary. Sediments from areas of low net deposition in the Tees Bay, as indicated by low silt/clay and TOC content contain low levels of *n*-alkanes, PAHs and PCBs, while sediments in areas of higher deposition (i.e. high silt/clay and TOC content) have higher *n*-alkane, PAH and PCBs levels. It is important to consider coal as a hydrocarbon source when analyzing for hydrocarbons in coastal and estuarine sediments. Caution should be employed when interpreting the results of hydrocarbon analyses in these samples because of the similarity between coal-derived hydrocarbons and those hydrocarbons derived from petroleum and petroleum products.

The representative *n*-alkane distributions of sediments from the Tees estuary and Tees Bay contained detectable quantities of all normal alkanes with between 16 and 33 carbon atoms. Several parameters are used in the present study as indicators of natural or anthropogenic hydrocarbons pollution (e.g. CPI, OEPI, UCM, Pr/Ph). These parameters are not sufficient to determine the source of pollution. On the basis of the mass fragmentograms of triterpanes (*m/z* 191) and steranes (*m/z* 217), which have been proposed as being useful fingerprints of oils (e.g. Pym *et al.*, 1975; Seifert and Moldowan, 1978; Jones *et al.*, 1986), it is apparent that the *n*-alkanes in all sediments from Tees Bay and most sediments from the Tees estuary (except sites 33, 34, 35 and 36) are derived mainly from fossil fuel sources (petroleum and coal). On the other hand, a few sediments from the Tees Estuary (sites 33, 34, 35 and 36) show the presence of hydrocarbons of both petroleum/coal and biological origin.

The molecular distributions and the relative concentration ratios of some alkylated and non-alkylated PAHs, in the sediment samples from both areas indicate petrogenic (petroleum/coal) and/or pyrolytic (combustion) sources of PAHs in the sediments studied. A complex mixture of PAH compounds was identified in all sediments from both areas. Unsubstituted ring systems (i.e. parent PAH), ranging from naphthalene (two aromatic ring) to perylene (five ring), as well as substituted PAH (alkylated PAH), ranging from alkylated naphthalene to alkylated phenanthrene, were the primary components. On the basis of the distribution pattern of some PAH series, it is estimated that PAHs in all sediments from Tees Bay (except sites 24 and 25) and a few sediments from the Tees estuary (sites 41, 42 and 43) arise mainly from petrogenic sources. On the other hand, other sediments from the studied areas (sites 33, 34, 35, 36, 37, 39 and 40) appear to have a more significant contribution from combustion sources and a few sediments from Tees Bay and Tees estuary (sites 24, 25, and 38) show mixed anthropogenic inputs of pyrolytic and petrogenic.

The compositions of single PCB congeners are similar to those of Aroclor 1260 and 1254. Site-to-site variability in concentration is high even over short distances, especially in the Tees estuary. The sediments of the Tees estuary tend to be more highly contaminated than those of the Tees Bay, particularly in the middle reaches of the estuary. There is a general decrease in PCB concentrations from the middle of the estuary to the bay area, while within the bay area, offshore sites showed higher concentrations. These marked differences and the distribution pattern, seen for the higher and the lower chlorinated PCB congeners, are indicative of the presence of multiple sources of PCBs of different degrees of chlorination.

Elevated *n*-alkanes, PAHs and PCBs were determined in the studied sediments. The Tees estuary sediments are much more contaminated than the Tees Bay sediments, as indicated from the distribution and concentration of these species. Contamination of the sediments from the Tees estuary, particularly in the middle region, can be explained by its proximity to potential pollution or anthropogenic sources (i.e. urban, industrial and agricultural inputs). However, the relatively high concentrations of all the species measured in the middle reach of the estuary are generally consistent with the observations of Johnston *et al.* (1991), who noted that the middle section of the Tees estuary receives higher amounts of sewage and industrial discharges, between locations corresponding mostly to our sites 34-40. This finding indicates a local dumping area in which organic matter and metals with a highly complex mixture are released. These dumpings apparently contain sometimes very high, but sometime very low, loads of metals and organic compounds. By implication, the sites in the middle reaches of the estuary are most likely to receive direct urban/industrial inputs of metals and organic compounds, from domestic and industrial discharges. It appears that these pollutant classes are associated with the particulate fraction of the water column and are, therefore, sedimented with the particulate matter at locations not too far from the pollution source. Since it is possible to demonstrate an elevated abundance of many of these pollutants in the estuary, these compounds may present a risk to the estuary biota.

9.2 Suggestions for future work

A vast amount of future work would be possible, but with a view of supplementing the current study the most important would be:

1- Bulk chemistry of the overlying waters - to determine the exchange and partition to elements and compounds between the sediments and the overlying water;

2.- Cd is highly enriched in the studied sediments. Potential follow-up work would ideally use Scanning Electron Microscopy (SEM) to identify the dominant Cd bearing particles in the sediment, and to find out the specific sources of Cd in both the marine and estuarine areas.

3- Refined sampling scheme of sediment samples in the Tees estuary - to investigate point sources of pollutants;

4- Compare the various dissolution/extraction procedures that are commonly used to determine the total trace metals in sediments - in order to examine and improve the reliability and comparability of such metal analyses and to accurately compare the present data with published data.

5- Concentrations of trace metals within the pore waters - to examine their behaviour under changing redox conditions;

6- Quantification of the organic components studied with increasing depth within the sediments - to investigate their historical record;

7- Investigation of other organic compounds, particularly in the second and fourth fractions of the TLC plate and AF2SF2 of the column chromatography, as these were not analysed in the current study.

8- Investigate the distribution pattern of trace metals in water, sediment and biota of Tees Bay and the Tees estuary - to evaluate possible impacts of metals on the ecosystem.

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Appendix

Concentrations (ug/g) of Cd in the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
1	< 0.1	0.3	0.7	0.0	1.7	2.7	85.0
2	0.1	0.4	2.0	0.0	1.7	4.2	84.0
3	0.1	0.5	1.3	0.0	1.1	3.0	115.4
4	0.1	0.2	1.5	0.0	3.4	5.2	100.0
5	0.1	0.4	1.3	0.0	1.0	2.8	112.0
6	< 0.1	0.3	0.7	0.0	1.7	2.7	100.7
7	< 0.1	0.3	0.9	0.0	1.5	2.7	91.0
8	0.2	0.7	1.3	0.0	0.7	2.9	120.8
10	0.1	0.3	1.0	0.0	1.3	2.7	103.8
11	0.1	1.1	1.3	0.0	1.3	3.8	108.6
12	0.1	0.3	0.9	0.0	1.1	2.4	82.8
13	< 0.1	0.2	0.9	0.0	1.4	2.5	81.0
14	0.1	0.3	1.0	0.0	1.2	2.6	113.0
17	0.1	0.3	0.3	0.0	0.5	1.2	92.3
18	< 0.1	0.2	0.6	0.0	1.3	2.1	88.8
19	0.1	0.2	1.1	0.0	1.4	2.8	107.7
20	0.0	0.5	1.0	0.0	1.4	2.9	81.4
21	0.0	0.5	0.4	0.0	0.6	1.5	80.0
22	< 0.1	0.3	0.7	0.0	1.2	2.2	81.9
23	< 0.1	0.3	1.1	0.0	1.7	3.1	82.1
24	0.1	0.4	0.9	0.0	1.1	2.5	89.3
25	0.1	0.2	1.4	0.0	3.5	5.2	113.0
26	< 0.1	0.3	1.5	0.0	0.6	2.4	121.0
27	0.1	0.7	0.2	0.0	0.7	1.7	94.4
28	0.0	0.4	0.7	0.0	1.5	2.6	108.8
29	< 0.1	0.5	1.6	0.0	0.4	2.5	90.4

Concentrations (ug/g) of Co in the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
1	0.2	1.6	3.0	0.9	10.5	16.2	95.9
2	0.1	0.5	3.7	1.0	11.4	16.7	92.8
3	0.2	1.7	5.7	0.7	9.7	18.0	86.5
4	0.3	1.1	7.0	3.3	23.6	35.3	94.4
5	< 0.1	0.8	2.9	0.5	8.3	12.5	85.2
6	0.0	1.7	3.2	0.6	8.3	13.8	103.8
7	0.2	1.6	4.5	1.0	8.7	16.0	87.9
8	0.0	0.8	2.5	0.2	6.0	9.5	105.6
10	0.1	1.5	2.5	0.1	6.3	10.5	91.3
11	0.0	1.0	3.9	0.2	5.1	10.2	82.3
12	0.4	1.2	4.5	0.3	6.9	13.3	91.7
13	0.0	1.0	1.8	0.0	5.5	8.3	82.2
14	0.0	0.6	1.7	0.3	3.6	6.2	80.5
17	0.0	0.7	1.8	0.0	2.8	5.3	89.8
18	< 0.1	1.3	2.3	< 0.1	6.8	10.4	92.9
19	0.0	0.8	2.1	0.5	5.4	8.8	88.9
20	0.2	1.5	3.8	0.2	6.4	12.1	80.1
21	< 0.1	1.7	1.8	0.0	3.5	7.0	97.5
22	0.2	1.3	3.7	0.2	8.7	14.1	90.4
23	0.0	0.6	3.6	0.5	9.7	14.4	88.3
24	0.3	0.5	4.5	0.3	8.5	14.1	86.5
25	0.3	1.1	6.4	2.3	24.3	34.4	113.9
26	0.2	0.9	3.6	0.2	7.7	12.6	86.3
27	0.0	1.7	1.8	0.3	4.5	8.3	90.2
28	0.0	1.5	2.2	0.2	7.7	11.6	79.5
29	0.3	1.6	3.4	0.1	5.8	11.2	80.0

Concentrations (ug/g) of Cr in the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
1	0.0	0.1	2.2	0.6	36.2	39.1	88.7
2	0.0	0.2	6.2	2.1	49.3	57.8	81.2
3	0.0	< 0.1	3.3	1.0	27.9	32.2	85.7
4	0.0	0.5	19.3	6.0	92.5	118.3	83.8
5	0.0	0.3	4.0	0.6	32.5	37.4	82.4
6	0.0	0.3	2.0	0.5	25.9	28.7	93.5
7	0.0	0.1	2.2	0.4	23.1	25.8	80.6
8	0.0	0.1	2.4	0.6	19.0	22.1	96.5
10	0.0	< 0.1	2.1	0.2	23.0	25.3	86.4
11	0.0	0.3	3.1	0.7	21.6	25.7	91.1
12	0.0	0.1	2.6	0.6	27.1	30.4	88.4
13	0.0	0.1	2.4	0.3	18.7	21.5	84.6
14	0.0	0.3	2.2	0.6	20.6	23.7	93.3
17	0.0	0.1	1.6	0.7	5.1	7.5	94.9
18	0.0	0.2	2.6	0.5	24.7	28.0	84.6
19	0.0	0.3	4.5	1.0	29.2	35.0	97.0
20	0.0	0.2	3.5	0.9	15.0	19.6	99.0
21	0.0	0.2	1.3	0.5	6.2	8.2	102.5
22	0.0	0.1	3.6	0.7	32.8	37.2	82.1
23	0.0	0.1	4.7	1.3	38.0	44.1	106.8
24	0.0	0.5	8.4	2.8	29.8	41.5	80.6
25	0.0	0.9	18.1	5.6	94.2	118.8	114.7
26	0.0	0.1	3.4	0.9	12.0	16.4	95.3
27	0.0	1.0	1.9	0.0	20.6	23.5	90.4
28	0.0	0.2	2.0	0.6	29.4	32.2	69.0
29	0.0	0.1	1.1	0.5	4.7	6.4	110.3

Concentrations (ug/g) of Cu in the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
1	0.0	1.2	0.5	14.1	20.8	36.6	116.9
2	0.0	0.5	0.4	6.7	13.4	21.0	96.8
3	0.0	0.0	0.9	7.4	10.0	18.3	114.4
4	0.0	0.0	0.9	29.4	25.8	56.1	79.6
5	0.0	0.8	0.6	5.8	11.4	18.6	80.5
6	0.0	0.9	0.5	5.3	8.6	15.3	98.7
7	0.0	0.5	0.7	5.9	7.8	14.9	103.5
8	0.0	0.8	0.5	2.0	3.9	7.2	91.1
10	0.0	0.7	0.4	3.2	4.6	8.9	93.7
11	0.0	0.4	0.3	4.3	6.2	11.2	96.6
12	0.0	0.2	0.7	2.5	4.8	8.2	107.9
13	0.0	0.5	0.2	0.5	2.5	3.7	92.5
14	0.0	0.2	0.2	1.5	3.4	5.3	110.4
17	0.0	0.3	0.1	0.0	1.9	2.3	85.2
18	0.0	0.7	0.6	3.6	4.9	9.8	85.2
19	0.0	0.4	0.2	1.0	6.3	7.9	98.8
20	0.0	0.3	0.6	1.6	4.7	7.2	80.9
21	0.0	0.5	0.3	0.8	1.9	3.5	94.6
22	0.0	0.2	0.7	2.8	5.0	8.7	82.1
23	0.0	0.7	0.1	5.9	11.5	18.2	97.3
24	0.0	0.5	1.1	2.8	6.4	10.8	90.8
25	0.0	0.0	0.7	25.5	25.0	51.2	116.1
26	0.0	0.0	0.3	0.9	4.0	5.2	98.1
27	0.0	0.9	0.5	3.0	4.6	9.0	111.1
28	0.0	0.6	0.6	2.0	4.6	7.8	87.6
29	0.0	0.1	0.5	0.0	2.2	2.8	90.3

Concentrations (ug/g) of Ni in the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
1	0.0	0.4	0.5	2.9	9.5	13.3	96.4
2	0.0	0.4	1.2	2.2	13.2	17.0	93.9
3	0.0	0.4	0.9	1.7	7.3	10.3	92.8
4	0.0	2.0	2.3	5.3	28.2	37.8	97.7
5	0.0	0.2	0.8	1.8	8.8	11.6	82.9
6	0.0	0.2	0.5	1.6	8.0	10.3	82.4
7	0.0	0.3	0.7	2.1	7.5	10.6	84.1
8	0.0	0.2	0.3	0.9	15.6	17.0	80.6
10	0.0	0.2	0.4	1.3	5.1	7.0	88.6
11	0.0	0.3	0.9	1.3	5.0	7.5	89.3
12	0.0	0.4	0.8	1.0	5.4	7.6	80.9
13	0.0	0.3	0.3	0.4	4.8	5.8	85.3
14	0.0	0.1	0.6	0.7	4.0	5.4	81.8
17	0.0	0.2	0.2	0.3	1.6	2.3	100.0
18	0.0	0.2	0.4	0.7	3.8	5.1	85.0
19	0.0	0.3	1.0	0.8	5.3	7.4	90.2
20	0.0	0.2	0.7	0.6	4.7	6.2	81.6
21	0.0	0.0	0.2	0.2	2.0	2.4	83.4
22	0.0	0.1	0.7	0.9	6.6	8.3	83.0
23	0.0	0.5	0.9	2.4	10.5	14.3	94.7
24	0.0	0.3	1.3	1.4	6.2	9.2	83.6
25	0.0	0.2	2.0	5.3	30.7	38.2	107.0
26	0.0	0.2	0.6	0.8	3.3	4.9	94.2
27	0.0	0.2	0.4	0.5	6.6	7.7	82.8
28	0.0	0.2	0.4	0.7	4.9	6.2	81.6
29	0.0	0.2	0.1	0.4	2.7	3.4	81.0

Concentrations (ug/g) of Pb in the five geochemical phases analysed - Tees Bay.

	Sequential leaching stage (ug/g)						
Sample No.	**1**	**2**	**3**	**4**	**5**	**Sum**	**% of the Sum**
1	0.0	8.0	15.1	1.3	11.8	36.2	92.6
2	0.0	3.7	28.7	0.5	10.0	42.9	94.5
3	0.0	6.4	20.7	0.6	14.3	42.0	91.7
4	0.0	6.6	47.9	3.3	25.8	83.6	83.6
5	0.0	2.7	14.5	0.6	4.4	22.2	79.9
6	0.0	7.3	17.9	1.4	10.2	36.8	100.8
7	0.0	5.3	17.3	1.6	11.5	35.7	93.0
8	0.0	5.0	18.1	0.4	4.6	28.1	91.5
10	0.0	4.4	8.4	0.5	4.6	17.9	88.2
11	0.0	2.2	13.3	0.8	4.7	21.0	103.4
12	0.0	6.3	15.3	1.0	9.4	32.0	90.4
13	0.0	3.4	5.2	0.1	3.5	12.2	98.4
14	0.0	1.4	6.0	0.7	5.0	13.1	62.7
17	0.0	2.0	3.8	1.4	6.0	13.2	101.5
18	0.0	5.2	7.6	0.6	4.6	18.0	89.6
19	0.0	3.6	10.5	0.6	9.8	24.5	81.4
20	0.0	4.2	15.2	0.8	8.2	28.4	88.8
21	0.0	4.8	3.9	0.2	2.3	11.2	83.6
22	0.0	4.3	9.3	0.5	9.0	23.1	89.2
23	0.0	5.5	20.0	0.6	9.5	35.6	87.3
24	0.0	10.4	31.2	3.4	13.2	58.2	116.2
25	0.0	10.8	49.9	1.5	23.8	86.0	113.5
26	0.0	2.4	17.1	0.6	7.2	27.3	98.2
27	0.2	3.6	6.2	0.0	3.0	13.0	98.5
28	0.0	5.9	8.0	0.7	7.9	22.5	108.2
29	0.0	2.1	3.9	0.3	2.6	8.9	75.4

Concentrations (ug/g) of Zn in the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
1	0.0	8.6	17.7	7.9	73.5	107.7	97.6
2	0.0	1.9	28.7	4.4	43.8	78.8	93.9
3	0.0	5.0	29.8	6.9	47.5	89.2	97.9
4	0.0	3.5	37.9	14.7	74.3	130.4	81.6
5	0.0	3.2	22.0	4.2	45.4	74.8	83.3
6	0.0	7.3	19.3	5.3	50.6	82.5	105.2
7	0.0	4.6	16.1	7.8	61.0	89.5	106.8
8	0.0	3.4	16.0	3.1	31.7	54.2	81.7
10	0.0	5.1	12.8	3.5	27.7	49.1	82.2
11	0.0	1.6	19.7	4.0	32.1	57.4	95.2
12	0.0	5.5	15.8	4.7	33.6	59.6	96.4
13	0.0	3.2	10.9	2.6	22.2	38.9	88.6
14	0.0	1.3	15.3	2.2	21.2	40.0	95.0
17	0.0	0.7	8.5	1.3	13.5	24.0	80.3
18	0.0	5.4	14.4	3.4	27.1	50.3	99.4
19	0.0	2.0	23.1	3.5	31.4	60.0	93.2
20	0.0	4.9	21.2	3.4	32.3	61.8	86.9
21	0.0	1.7	8.0	1.4	14.6	25.7	88.0
22	0.0	3.9	17.5	4.9	28.7	55.1	90.3
23	0.0	4.1	24.9	5.6	35.4	70.0	102.0
24	0.0	8.3	31.1	7.1	54.6	101.1	91.9
25	0.0	5.9	41.7	11.9	80.7	140.2	114.8
26	0.0	2.1	17.1	3.0	23.7	45.9	93.9
27	0.0	5.2	13.1	3.5	23.3	45.1	99.3
28	0.0	5.1	13.6	3.6	32.1	54.4	80.6
29	0.0	0.7	4.6	1.1	8.8	15.2	82.6

Concentrations (ug/g) of Cd in the five geochemical phases analysed - Tees Estuary.

Sample No.	**Sequential leaching stage (ug/g)**					**Sum**	**% of the Sum**
	1	**2**	**3**	**4**	**5**		
33	0.3	0.1	1.2	0.1	2.5	4.2	91.3
34	< 0.1	0.3	2.0	0.3	2.6	5.2	90.0
35	0.6	0.3	2.5	0.3	2.8	6.5	95.6
36	0.6	0.5	2.1	0.3	3.1	6.6	100.0
37	0.8	0.5	3.2	1.0	3.4	8.9	102.3
38	0.1	0.3	1.7	0.5	2.6	5.2	88.1
39	0.1	0.4	3.5	0.7	4.2	8.9	90.8
40	0.2	0.5	1.4	0.2	3.4	5.7	91.9
41	0.4	0.8	0.8	0.1	3.4	5.5	105.8
42	0.2	1.0	0.3	0.1	1.4	3.0	115.4
43	0.4	0.7	0.5	0.8	3.2	5.6	107.7

Concentrations (ug/g) of Co in the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
33	0.2	2.0	3.3	2.4	22.3	30.2	110.6
34	0.5	1.3	4.6	3.4	27.8	37.6	119.7
35	0.1	1.8	4.3	3.0	24.6	33.8	112.3
36	0.1	2.4	4.3	3.4	32.2	42.4	119.1
37	0.1	2.2	3.2	2.6	29.6	37.7	112.2
38	0.1	1.8	4.9	3.7	24.9	35.4	117.2
39	0.7	3.3	14.5	6.5	27.5	52.5	94.4
40	0.2	3.7	10.0	6.9	39.2	60.0	117.2
41	0.5	1.2	8.1	5.0	37.2	52.0	109.5
42	0.4	0.6	4.2	0.9	7.9	14.0	86.4
43	0.8	1.7	3.4	1.6	29.7	37.2	106.3

Concentrations (ug/g) of Cr in the five geochemical phases analysed - Tees Estuary.

Sample No.	**Sequential leaching stage (ug/g)**					**Sum**	**% of the Sum**
	1	**2**	**3**	**4**	**5**		
33	0.0	2.3	49.2	63.5	67.9	182.9	109.7
34	0.0	0.9	48.4	75.4	78.9	203.6	91.1
35	0.0	2.7	119.8	97.8	99.2	319.5	115.9
36	0.0	5.9	113.7	92.6	114.1	326.3	103.3
37	0.0	25.7	275.8	156.1	142.3	599.9	104.0
38	0.0	4.0	135.7	52.0	93.7	285.4	91.0
39	0.0	7.1	120.7	39.7	109.2	276.7	86.5
40	0.0	4.2	70.8	36.4	87.8	199.2	91.0
41	0.0	2.1	55.7	24.7	70.9	153.4	92.0
42	0.0	1.4	6.5	1.5	19.8	29.2	80.7
43	0.0	5.5	51.5	27.2	66.9	151.1	97.9

Concentrations (ug/g) of Cu in the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
33	0.0	0.0	1.1	32.3	20.3	53.7	103.1
34	0.0	0.0	4.5	53.1	26.5	84.1	101.4
35	0.0	0.0	3.5	83.1	24.7	111.3	109.5
36	0.0	0.0	4.2	116.0	37.6	157.8	119.6
37	0.0	0.0	3.1	201.1	53.8	258.0	107.2
38	0.0	0.0	2.1	104.6	38.9	145.6	117.1
39	0.0	0.0	1.8	221.1	49.3	272.2	103.9
40	0.0	1.0	2.7	111.1	46.1	160.9	107.3
41	0.0	1.0	3.0	63.4	35.6	103.0	100.4
42	0.0	0.6	1.3	7.0	17.0	25.9	104.0
43	0.0	0.2	1.5	54.9	29.4	86.0	104.4

Concentrations (ug/g) of Ni in the five geochemical phases analysed - Tees Estuary.

Sample No.	**Sequential leaching stage (ug/g)**					**Sum**	**% of the Sum**
	1	**2**	**3**	**4**	**5**		
33	0.0	1.4	4.8	5.2	22.2	33.6	108.0
34	0.0	0.7	6.6	6.4	24.5	38.2	99.5
35	0.0	0.4	5.5	6.7	26.4	39.0	99.2
36	0.0	0.6	5.0	6.5	31.7	43.8	96.5
37	0.0	1.2	3.9	5.8	29.0	39.9	87.1
38	0.0	0.7	3.8	4.6	25.6	34.7	91.6
39	0.0	0.8	5.5	5.7	29.0	41.0	87.8
40	0.0	0.4	4.0	6.8	36.2	47.4	96.5
41	0.0	0.3	3.7	6.0	35.7	45.7	96.8
42	0.0	0.5	1.7	4.2	15.0	21.4	102.9
43	0.0	1.3	2.8	5.2	31.4	40.7	100.5

Concentrations (ug/g) of Pb in the five geochemical phases analysed - Tees Estuary.

Sample No.	**Sequential leaching stage (ug/g)**					**Sum**	**% of the Sum**
	1	**2**	**3**	**4**	**5**		
33	0.3	47.2	184.8	38.8	92.6	363.7	101.6
34	0.0	31.6	280.0	64.6	115.0	491.2	102.8
35	0.6	17.2	334.6	84.2	113.0	549.6	97.2
36	0.4	56.8	235.4	62.8	138.0	493.4	91.7
37	0.5	74.0	281.2	64.8	123.6	544.1	80.1
38	0.1	16.1	126.0	20.8	79.0	242.0	110.1
39	0.0	20.2	185.0	41.9	82.5	329.6	104.1
40	0.3	20.6	74.8	15.2	52.7	163.6	101.6
41	0.7	10.5	53.0	7.9	34.4	106.5	103.9
42	0.0	7.0	21.4	2.2	10.5	41.1	112.6
43	0.2	19.6	38.6	12.8	24.2	95.4	101.6

Concentrations (ug/g) of Zn in the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (ug/g)					Sum	% of the Sum
	1	2	3	4	5		
33	0.2	20.1	158.4	61.0	104.4	334.1	105.3
34	0.1	11.4	198.6	72.6	104.1	386.8	98.1
35	0.2	11.1	222.4	93.0	119.2	445.9	90.9
36	0.9	33.8	216.8	99.0	164.2	514.7	95.5
37	0.2	53.7	223.5	173.4	161.9	612.7	85.0
38	0.1	12.8	206.2	86.2	106.9	412.2	105.1
39	0.5	43.9	226.4	218.1	193.7	682.6	87.8
40	0.1	26.6	163.3	60.5	126.6	377.1	97.2
41	0.0	11.9	84.4	42.8	65.3	204.4	98.2
42	0.0	4.2	14.7	4.6	29.8	53.3	81.7
43	0.0	23.4	48.6	37.5	59.4	168.9	93.8

Percentage distribution of Cd between the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (%)				
	1	**2**	**3**	**4**	**5**
1	0.7	11.1	25.7	0.0	62.5
2	2.4	9.5	47.6	0.0	40.5
3	3.3	16.7	43.3	0.0	36.7
4	1.9	3.8	28.8	0.0	65.4
5	3.6	14.3	46.4	0.0	35.7
6	0.7	11.1	25.7	0.0	62.5
7	1.1	11.0	33.0	0.0	54.9
8	6.9	24.1	44.8	0.0	24.2
10	3.7	11.2	37.0	0.0	48.1
11	2.7	28.9	34.2	0.0	34.2
12	4.2	12.5	37.5	0.0	45.8
13	0.4	8.0	35.8	0.0	55.8
14	3.8	11.5	38.5	0.0	46.2
17	8.3	25.0	25.0	0.0	41.7
18	1.4	9.4	28.2	0.0	61.0
19	3.6	7.1	39.3	0.0	50.0
20	1.0	17.1	34.1	0.0	47.8
21	1.3	32.9	26.3	0.0	39.5
22	0.4	13.6	31.7	0.0	54.3
23	0.6	9.6	35.3	0.0	54.5
24	4.0	16.0	36.0	0.0	44.0
25	1.9	3.9	26.9	0.0	67.3
26	0.8	12.4	62.0	0.0	24.8
27	5.9	41.2	11.7	0.0	41.2
28	0.4	15.3	26.8	0.0	57.5
29	1.2	19.8	63.2	0.0	15.8

Percentage distribution of Co between the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
1	1.2	9.9	18.5	5.6	64.8
2	0.6	3.0	22.1	6.0	68.3
3	1.1	9.4	31.7	3.9	53.9
4	0.8	3.2	19.8	9.3	66.9
5	0.2	6.4	23.1	4.1	66.2
6	0.0	12.3	23.2	4.4	60.1
7	1.3	10.0	28.1	6.2	54.4
8	0.0	8.4	26.3	2.1	63.2
10	1.0	14.2	23.8	1.0	60.0
11	0.0	9.8	38.2	2.0	50.0
12	3.0	9.0	33.8	2.3	51.9
13	0.0	12.0	21.7	0.0	66.3
14	0.0	9.7	27.4	4.8	58.1
17	0.0	13.2	34.0	0.0	52.8
18	0.3	12.4	22.0	0.4	64.9
19	0.0	9.1	23.9	5.7	61.4
20	1.7	12.3	31.4	1.7	52.9
21	0.6	24.1	25.6	0.0	49.7
22	1.4	9.3	26.2	1.4	61.7
23	0.0	4.1	25.0	3.5	67.4
24	2.1	3.5	31.9	2.2	60.3
25	0.9	3.2	18.6	6.7	70.6
26	1.6	7.1	28.6	1.6	61.1
27	0.0	20.5	21.7	3.6	54.2
28	0.0	12.9	19.0	1.7	66.4
29	2.7	14.3	30.4	0.8	51.8

Percentage distribution of Cr between the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
1	0.0	0.3	5.6	1.5	92.6
2	0.0	0.4	10.7	3.6	85.3
3	0.0	0.1	10.2	3.2	86.5
4	0.0	0.4	16.3	5.1	78.2
5	0.0	0.8	10.7	1.6	86.9
6	0.0	1.1	7.0	1.7	90.2
7	0.0	0.4	8.5	1.6	89.5
8	0.0	0.4	10.9	2.7	86.0
10	0.0	0.1	8.3	0.8	90.8
11	0.0	1.2	12.1	2.7	84.0
12	0.0	0.3	8.6	2.0	89.1
13	0.0	0.5	11.1	1.4	87.0
14	0.0	1.3	9.3	2.5	86.9
17	0.0	1.4	21.3	9.3	68.0
18	0.0	0.7	9.3	1.8	88.2
19	0.0	0.9	12.9	2.8	83.4
20	0.0	1.0	17.9	4.6	76.5
21	0.0	2.4	15.9	6.1	75.6
22	0.0	0.3	9.7	1.8	88.2
23	0.0	0.2	10.7	2.9	86.2
24	0.0	1.3	20.2	6.7	71.8
25	0.0	0.8	15.2	4.7	79.3
26	0.0	0.6	20.7	5.5	73.2
27	0.0	4.3	8.1	0.0	87.6
28	0.0	0.6	6.2	1.9	91.3
29	0.0	1.6	17.2	7.8	73.4

Percentage distribution of Cu between the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
1	0.0	3.3	1.4	38.5	56.8
2	0.0	2.4	1.9	31.9	63.8
3	0.0	0.0	5.0	40.4	54.6
4	0.0	0.0	1.6	52.4	46.0
5	0.0	4.3	3.2	31.2	61.3
6	0.0	5.9	3.3	34.6	56.2
7	0.0	3.4	4.7	39.6	52.3
8	0.0	11.1	6.9	27.8	54.2
10	0.0	7.8	4.5	36.0	51.7
11	0.0	3.6	2.6	38.4	55.4
12	0.0	2.4	8.6	30.5	58.5
13	0.0	13.5	5.4	13.5	67.6
14	0.0	3.8	3.7	28.3	64.2
17	0.0	13.0	4.4	0.0	82.6
18	0.0	7.2	6.1	36.7	50.0
19	0.0	5.1	2.5	12.7	79.7
20	0.0	4.2	8.3	22.2	65.3
21	0.0	14.2	8.6	22.9	54.3
22	0.0	2.3	8.0	32.2	57.5
23	0.0	3.8	0.5	32.4	63.3
24	0.0	4.6	10.2	25.9	59.3
25	0.0	0.0	1.4	49.8	48.8
26	0.0	0.0	5.8	17.3	76.9
27	0.0	10.0	5.6	33.3	51.1
28	0.0	7.7	7.7	25.6	59.0
29	0.0	3.6	17.8	0.0	78.6

Percentage distribution of Ni between the five geochemical phases analysed - Tees Bay.

	Sequential leaching stage (%)				
Sample No.	1	2	3	4	5
1	0.0	3.0	3.8	21.8	71.4
2	0.0	2.4	7.1	12.9	77.6
3	0.0	3.9	8.7	16.5	70.9
4	0.0	5.3	6.1	14.0	74.6
5	0.0	1.7	6.9	15.5	75.9
6	0.0	1.9	4.9	15.5	77.7
7	0.0	2.8	6.6	19.8	70.8
8	0.0	1.1	1.8	5.3	91.8
10	0.0	2.9	5.6	18.6	72.9
11	0.0	4.0	12.0	17.3	66.7
12	0.0	5.3	10.5	13.1	71.1
13	0.0	5.1	5.2	6.9	82.8
14	0.0	1.9	11.0	13.0	74.1
17	0.0	8.7	8.7	13.0	69.6
18	0.0	3.9	7.9	13.7	74.5
19	0.0	4.1	13.5	10.8	71.6
20	0.0	3.2	11.3	9.7	75.8
21	0.0	0.8	8.3	8.3	82.6
22	0.0	1.1	8.4	10.8	79.5
23	0.0	3.5	6.3	16.8	73.4
24	0.0	3.3	14.1	15.2	67.4
25	0.0	0.5	5.2	13.9	80.4
26	0.0	4.2	12.2	16.3	67.3
27	0.0	2.6	5.2	6.5	85.7
28	0.0	3.2	6.5	11.3	79.0
29	0.0	5.9	2.9	11.8	79.4

Percentage distribution of Pb between the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
1	0.0	22.1	41.7	3.6	32.6
2	0.0	8.6	66.9	1.2	23.3
3	0.0	15.3	49.3	1.4	34.0
4	0.0	7.9	57.3	3.9	30.9
5	0.0	12.2	65.3	2.7	19.8
6	0.0	19.8	48.6	3.9	27.7
7	0.0	14.8	48.5	4.5	32.2
8	0.0	17.8	64.4	1.4	16.4
10	0.0	24.6	46.9	2.8	25.7
11	0.0	10.5	63.3	3.8	22.4
12	0.0	19.7	47.8	3.1	29.4
13	0.0	27.9	42.6	0.8	28.7
14	0.0	10.7	45.8	5.3	38.2
17	0.0	15.1	28.8	10.6	45.5
18	0.0	18.9	42.2	3.3	25.6
19	0.0	14.7	42.9	2.4	40.0
20	0.0	14.8	53.5	2.8	28.9
21	0.0	42.9	34.8	1.8	20.5
22	0.0	18.6	40.3	2.1	39.0
23	0.0	15.4	56.2	1.7	26.7
24	0.0	17.9	53.6	5.8	22.7
25	0.0	12.6	58.0	1.7	27.7
26	0.0	8.8	62.6	2.2	26.4
27	1.5	27.7	47.7	0.0	23.1
28	0.0	26.2	35.6	3.1	35.1
29	0.0	23.6	43.8	3.4	29.2

Percentage distribution of Zn between the five geochemical phases analysed - Tees Bay.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
1	0.0	8.1	16.4	7.3	68.2
2	0.0	2.4	36.4	5.6	55.6
3	0.0	5.6	33.4	7.7	53.3
4	0.0	2.7	29.1	11.2	57.0
5	0.0	4.3	29.4	5.6	60.7
6	0.0	8.8	23.4	6.5	61.3
7	0.0	5.1	18.0	8.7	68.2
8	0.0	6.3	29.5	5.7	58.5
10	0.0	10.4	26.1	7.1	56.4
11	0.0	2.8	34.3	7.0	55.9
12	0.0	9.2	26.5	7.9	56.4
13	0.0	8.2	28.0	6.7	57.1
14	0.0	3.2	38.3	5.5	53.0
17	0.0	2.9	35.4	5.4	56.3
18	0.0	10.7	28.6	6.8	53.9
19	0.0	3.4	38.5	5.8	52.3
20	0.0	7.9	34.3	5.5	52.3
21	0.0	6.6	31.2	5.4	56.8
22	0.11	7.0	31.8	8.9	52.1
23	0.0	5.8	35.6	8.0	50.6
24	0.0	8.2	30.8	7.0	54.0
25	0.0	4.2	29.7	8.5	57.6
26	0.0	4.6	37.3	6.5	51.6
27	0.0	11.5	29.0	7.8	51.7
28	0.0	9.4	25.0	6.6	59.0
29	0.0	4.6	30.3	7.2	57.9

Percentage distribution of Cd between the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
33	7.1	2.4	28.6	2.4	59.5
34	0.4	5.7	38.4	5.7	49.8
35	9.2	4.6	38.5	4.6	43.1
36	9.1	7.6	31.8	4.5	47.0
37	9.0	5.6	36.0	11.2	38.2
38	1.9	5.8	32.7	9.6	50.0
39	1.1	4.5	39.3	7.9	47.2
40	3.5	8.8	24.6	3.5	59.6
41	7.3	14.5	14.5	1.9	61.8
42	6.7	33.3	10.0	3.3	46.7
43	7.1	12.6	8.9	14.3	57.1

Percentage distribution of Co between the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
33	0.7	6.6	10.9	7.9	73.8
34	1.3	3.5	12.2	9.1	73.9
35	0.3	5.3	12.7	8.9	72.8
36	0.2	5.7	10.1	8.1	75.9
37	0.3	5.8	8.5	6.9	78.5
38	0.3	5.1	13.8	10.5	70.3
39	1.3	6.3	27.6	12.4	52.4
40	0.3	6.2	16.7	11.5	65.3
41	1.0	2.3	15.6	9.6	71.5
42	2.9	4.3	30.0	6.4	56.4
43	2.2	4.6	9.1	4.3	79.8

Percentage distribution of Cr between the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
33	0.0	1.3	26.9	34.7	37.1
34	0.0	0.4	23.8	37.0	38.8
35	0.0	0.9	37.5	30.7	31.0
36	0.0	1.8	34.8	28.4	35.0
37	0.0	4.3	46.0	26.0	23.7
38	0.0	1.5	47.5	18.3	32.8
39	0.0	2.7	39.8	15.3	42.2
40	0.0	2.1	35.5	18.3	44.1
41	0.0	1.4	36.3	16.1	46.2
42	0.0	4.8	22.3	5.1	67.8
43	0.0	3.6	34.1	18.0	44.3

Percentage distribution of Cu between the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
33	0.0	0.0	2.1	60.1	37.8
34	0.0	0.0	5.4	63.1	31.5
35	0.0	0.0	3.1	74.7	22.2
36	0.0	0.0	2.7	73.5	23.8
37	0.0	0.0	1.2	77.9	20.9
38	0.0	0.0	1.5	71.8	26.7
39	0.0	0.0	0.7	81.2	18.1
40	0.0	0.6	1.7	69.0	28.7
41	0.0	1.0	2.8	61.6	34.6
42	0.0	2.3	5.1	27.0	65.6
43	0.0	0.3	1.7	63.8	34.2

Percentage distribution of Ni between the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (%)				
	1	**2**	**3**	**4**	**5**
33	0.0	4.1	14.3	15.5	66.1
34	0.0	1.8	17.3	16.8	64.1
35	0.0	1.0	14.1	17.2	67.7
36	0.0	1.4	11.4	14.8	72.4
37	0.0	3.0	9.8	14.5	72.7
38	0.0	2.0	11.0	13.2	73.8
39	0.0	2.0	13.4	13.9	70.7
40	0.0	0.8	8.4	14.4	76.4
41	0.0	0.7	8.1	13.1	78.1
42	0.0	2.4	7.9	19.6	70.2
43	0.0	3.2	6.9	12.8	77.1

Percentage distribution of Pb between the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (%)				
	1	2	3	4	5
33	0.1	13.0	50.7	10.7	25.5
34	0.0	6.4	57.0	13.2	23.4
35	0.1	3.1	60.9	15.3	20.6
36	0.1	11.5	47.7	12.7	28.0
37	0.1	13.6	51.7	11.9	22.7
38	0.0	6.7	52.1	8.6	32.6
39	0.0	6.2	56.1	12.7	25.0
40	0.2	12.6	45.7	9.3	32.2
41	0.7	9.9	49.7	7.4	32.3
42	0.0	17.0	52.1	5.4	25.5
43	0.2	20.5	40.5	13.4	25.4

Percentage distribution of Zn between the five geochemical phases analysed - Tees Estuary.

Sample No.	Sequential leaching stage (%)				
	1	**2**	**3**	**4**	**5**
33	< 0.1	5.9	46.0	17.7	30.3
34	< 0.1	2.9	51.4	18.8	26.9
35	0.1	2.5	49.8	20.9	26.7
36	0.2	6.6	42.1	19.2	31.9
37	< 0.1	8.8	36.5	28.3	26.4
38	< 0.1	3.1	50.0	20.9	25.9
39	0.1	6.4	33.1	32.0	28.4
40	< 0.1	7.1	43.3	16.0	33.6
41	0.0	5.8	41.4	20.9	31.9
42	0.0	7.9	27.6	8.6	55.9
43	0.0	13.9	28.7	22.2	35.2