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TRACE ELEMENTS AND POLYCHLORINATED BIPHENYL (PCB) CONGENERS IN LIVERPOOL BAY SEDIMENTS

A thesis submitted in accordance with the requirements of the University of Wales
for the degree of Philosophiae Doctor

by

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DEDICATION

I dedicate this thesis to the memory of my father,

my wife's patience and support

to the support of my family throughout my career

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ABSTRACT

Some trace elements and various PCB congeners were determined in superficial sediments from Liverpool Bay. Some sediment parameters were also determined for a better understanding of the distribution of these contaminants.

Lower amounts of fine particles were found in sediments from the southern area of the sampling grid where the hydrodynamic conditions inhibit the deposition and favour the resuspension of particles with small diameter. The distribution of muddy deposits was patchy throughout the bay although the mud deposits near the Burbo Bight seem to be a permanent feature.

The concentrations of trace elements and carbon were determined in two grain size fractions. Carbon in the fine fraction increased in sediment samples with lower proportions of fine sediments probably as a result of an increase in the available surface area since these samples apparently had higher proportions of clays. This relationship was scattered suggesting that the inputs of carbon from different sources, *i.e.*, waste disposal, riverine inputs and autochthonous production, overshadow any clear trends between carbon and grain size in sediments. This observation is consistent with the distribution of $\delta^{13}C$ values. The concentration of organic matter in coarse sediments seemed to be determined by the amount of surrounding fine particles, particularly in samples with fine fraction concentrations higher than 5%.

The concentrations of all of the trace elements, except arsenic, in the coarse fraction were correlated with the organic matter content suggesting that the organic phase is an important carrier of metals in the coarse particles. In the fine fraction, however, there was a large variability in the correlations, suggesting different geochemical behaviour between trace elements. For example a contrasting behaviour was observed between mercury and arsenic since the former seemed to be associated with land derived organic matter with no correlations with the content of iron and manganese, whereas arsenic showed a strong correlation with these two elements reflecting its preference for hydrous oxides of iron and manganese. The geochemical behaviour of each particular trace element seems to play an important role in the observed distributions of the elements in Liverpool Bay sediments.

PCBs were determined in total sediments. A high correlation between PCB concentrations and the fine fraction content was observed as a result of the preferential association of these contaminants in fine particles. The distribution of normalized PCB concentrations indicated that inputs from the Mersey may be an important source of PCBs. Different patterns were observed in the PCB congener composition of the samples which reflected the different sources and degree of alteration of the "original" pattern found at the source. The changes in the composition were related to the degree of chlorination and substitution pattern since these factors control the physicochemical properties of PCB congeners.

The sediments were classified based on their elemental content and on their PCB contents by means of multivariate statistical methods. The sediments were classified in similar groups from their organic and inorganic contents, which suggested that the sources of organic and inorganic contaminants in Liverpool Bay are similar.

Chapter 1. INTRODUCTION

1.1. GENERAL INTRODUCTION

Polychlorinated biphenyls (PCBs) and some of the trace elements such as arsenic and trace metals represent two groups of organic and inorganic contaminants in the environment which are a major cause of concern due to their potential toxicological effects on living organisms including man.

With increasing frequency, waste products containing organic and inorganic toxic substances generated by a wide range of industrial processes have not been disposed of according to scientific reasoning, but rather in response to economic pressures or merely by the most convenient method (Honeyman and Santschi, 1988). As a result, many waste products have been dispersed over wide areas and in some cases at elevated concentrations, through atmospheric and aquatic reservoirs. In order to better understand the impact of toxic substances in the biosphere, it is necessary to detect their sources and determine their fate, thus, one of the main objectives of environmental chemistry has been to describe the behaviour of contaminants in natural systems based on the knowledge of their fundamental physicochemical properties (Honeyman and Santschi, 1988).

There are various sources of contaminants in the aquatic ecosystem. Atmospheric emissions from industry and households, and agricultural runoff both contribute to water pollution. However, the most important source into terrestrial and coastal aquatic systems is the direct input of wastes from industrial and domestic effluents (Forstner and Wittmann, 1979). Although these effluents contain various substances that are not considered dangerous, many of them add a disagreeable odour or taste to water and others (e.g. nutrients) may significantly upset the ecosystem without being directly harmful to humans. Other groups, however, have direct and indirect influences on humans and other living organisms and can cause grave damage. Substances in this category include inorganic contaminants such as radioactive elements, arsenic and trace metals (e.g. mercury, cadmium and lead), and also include organic compounds such as polycyclic aromatics, pesticides and PCBs.

Regardless of the mechanism of transport from the source(s), once in the marine environment a few of the contaminants are relatively unreactive and consequently their transport patterns are conceptually straightforward and mediated by water mass movements. A much greater number of these substances, however, are highly reactive and have a strong affinity for association with fine grained particles. The movements of these reactive contaminants, their removal from water, and their accumulation in the sediments are thus governed to a great extent by sedimentary processes (Olsen *et al.*, 1982). Therefore, in order to understand the transport pathways and determine the fate of contaminants in coastal marine environments, it is necessary to study the processes which control the inputs and transport of sedimentary particles.

The dynamics of fine grained particles and their associated contaminants is complex in coastal marine environments, particularly in shallow areas, because: (a) intense short term flow events (such as those induced by storms) are often more important to sediment transport than the current flow which occurs during normal conditions, (b) fine particles often undergo numerous cycles of resuspension and deposition, and (c) numerous physical, chemical and biological processes affect the fate of particles and reactive pollutants, especially in estuarine zones where fresh water mixes with sea water (Olsen *et al.*, 1982). Human activities including dredging, trawling and waste disposal might further affect the transport and composition of fine particles in the coastal areas, adding to the complexity in the understanding of the transport and fate of particle associated contaminants.

In spite of the potential problems in understanding the dynamics of sedimentary particles in coastal environments, it is common practice to assess contamination levels in aquatic systems through the determination of the concentration of the contaminants in sediments. The tracing of contamination sources by means of water analyses frequently gives rise to difficulties which might be particularly associated with analytical techniques. These problems are particularly obvious in the case of substances such as trace metals and PCBs which are not readily soluble but become rapidly fixed to particulate matter in the water column. The adsorption of these substances onto particles decreases substantially the levels in solution down to concentrations which are difficult to detect by routine methods. In the case of trace metals for example, the concentration levels in suspended particles might be three orders of magnitude higher than in solution, with typical concentrations reported in units of micrograms of metal per gram of particles (ppm) and micrograms of metal per litre of water (approximately ppb) respectively. In the case of organic compounds such as PCBs, the difference in concentrations between the dissolved (usually at the picogram per litre level) and particulate (from picogram to microgram per gram levels) phases might be even higher due to the hydrophobicity of these compounds, with typical differences being of four orders of magnitude or higher (Duursma et al. 1989).

In the case of trace elements in water, the problems in the analysis have been largely overcome by improvements in the sensitivity of analytical techniques which allow for determinations in water at ultra-low levels. On the other hand, the analysis of PCBs in seawater is still very difficult because in spite of the high sensitivity of the detectors often employed in PCB determinations, the extremely low concentrations of these compounds in solution often require handling of very large volumes of sample which make routine analyses of PCBs in solution unpractical. In a recent study of the concentrations of PCBs and pesticides in open ocean waters off the U.S. coast and in the Gulf of Mexico, Sauer *et al.* (1989) extracted ~900 l of seawater at several stations and reported not detected concentrations in most of the samples even though these large volumes permitted detection limits below 1 pg l^{-1}. Another problem arising from the handling of large volumes of water samples containing very low PCB concentrations is the possibility of contamination of the sample. Schulz *et al.* (1988) reported that the main potential sources of contamination of seawater samples are the sampler, the ship's atmosphere and the organic solvents.

In contrast to open ocean waters, the concentrations of dissolved and particulate inorganic and organic contaminants in near-shore coastal waters vary considerably in time and space, in response to variations in the composition and relative contribution of the sources, in biological productivity and in the sediment-water interactions (Kramer, 1986). Thus, even if the analytical problems associated with PCBs and trace element determinations in seawater are overcome, the short term variations (hours to days) in the concentrations of these substances in the water column may overshadow the long term variations (months to years), therefore, the study of contamination trends in time (and space) can be difficult from the study of contamination levels in the water column. In contrast to the open oceans, the highly variable coastal areas belong to territorial zones and are subject to more legislative regulations for which quality knowledge is most needed. The main goal of monitoring the coastal environments is to look at possible deviations from uncontaminated background levels and to relate changes in their composition with human influence and/or governmental policy (Kramer, 1986).

Coastal sediments seldom reflect the most recent pollution as newly deposited particles may be diluted with particles already present in the sediment. Sediments, particularly those in surface layers, are constantly reworked and homogenized by currents, turbulence, bioturbation, dredging and trawling. However, the effects of the contaminants on benthic organisms depend on the actual composition of the sediments, regardless of the time of deposition (Kramer, 1986). In areas where the conditions are appropriate and net sedimentation can occur, a contamination history can be reconstructed based on the vertical profiles of the contaminants. In general the variations in sedimentary composition are of a much longer time scale compared to the variations in the water column, and can be considered as integrators of events in time, they have been commonly used for the monitoring of contamination in coastal marine environments and other aquatic ecosystems.

Most of the studies concerned with environmental monitoring of contaminants merely report concentration data on particles, with little attention devoted to the biogeochemical processes that affect the dynamics and composition of these particles in estuarine, coastal and open ocean environments. The main processes involved in the biogeochemical cycles of particles and which, therefore, affect the dynamics of particle-associated contaminants in coastal marine environments are shown in Figure 1.1 (after Olsen *et al.*, 1982). The role which each of the processes indicated in Figure 1.1 plays in the transport and fate of a particular contaminant will depend on the source, chemical form and concentration of the contaminant, as well as on the chemical characteristics of the sorbing particle and the transporting medium. The particles involved in these cycles may be riverborne, airborne, resuspended from bottom sediments by currents and organisms, or generated within the water column by biological production, colloidal flocculation, or biodegradation (Olsen *et al.*, 1982). Some of these particles may also be derived from direct inputs from human activities such as dredging and ocean dumping of wastes such as sewage sludges and dredging spoils.

Most of the studies concerned with these processes have used geochemical signatures on particles to trace particle transport, differentiate particle sources, and quantify particle-pollutant fluxes (Olsen *et al.*, 1982). In this study, the geochemical signature of two groups of contaminants, *i.e.*, trace elements and PCBs was used to determine the possible source(s) of these contaminants in Liverpool Bay sediments.

1.1.1. Trace elements

The determination of trace metals in sediments from Liverpool Bay is part of the routine monitoring programs undertaken by the Ministry of Agriculture, Fisheries and Food (MAFF), and the North West Water Authority (NWWA), which are particularly aimed at the determination of the environmental quality of an area which receives direct inputs of wastes via dumping of domestic sewage sludges, industrial wastes and dredging materials at designated areas. As the determination of trace metals in Liverpool Bay sediments has been carried out routinely since the early 1970's, it was assumed at the beginning of this project that their behaviour, sources and fates were well understood. Therefore, the analysis of trace elements, and of trace metals in

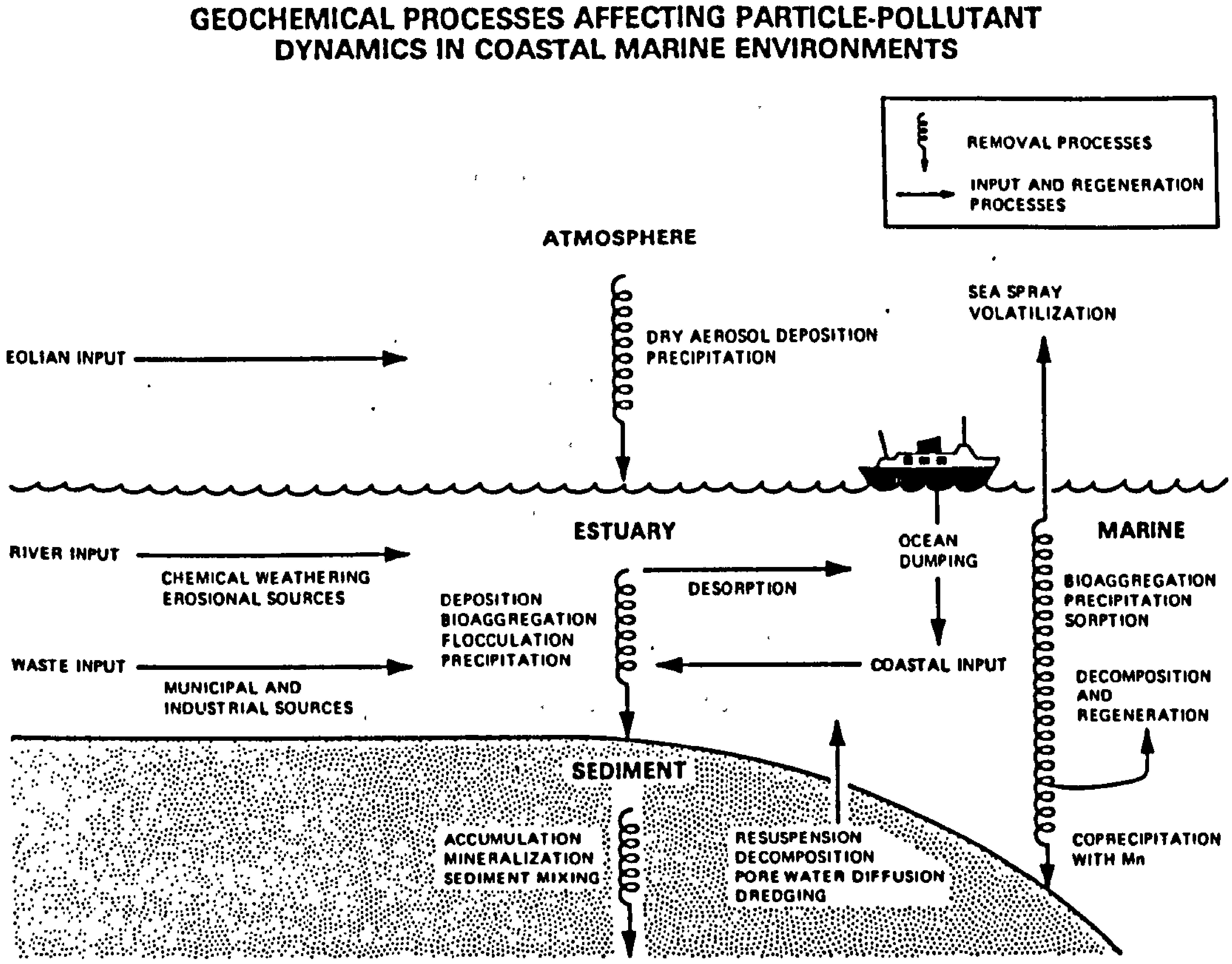

Fig. 1.1. Schematic illustration of the biogeochemical processes which affect pollutant-particle dynamics. (After Olsen *et al.*, 1982).

particular, in this study was aimed to provide a background for a better understanding of the sources and fates of PCBs in these sediments for which data have not been reported previously.

The routine determination of trace elements in environmental quality assessment is mainly due to the potential impact of some of these elements in biological systems including man. Toxic metals such as mercury, cadmium, lead and copper, and other toxic elements such as arsenic, have been extensively studied in several aquatic ecosystems, as they are produced and released into the environment in substantial quantities from various human activities including industrial processes, transportation, agriculture, etc., and they are frequently transported or directly discharged into the aquatic environment.

As some trace elements are essential for biological systems, studies of the toxicity of trace metals often follow the general trend that an undersupply leads to a deficiency, sufficient supply results in optimum conditions, but an oversupply results in toxic effects and finally death (Forstner and Wittmann, 1979). Several catastrophic episodes such as the well known case of mercury poisoning around Minamata Bay, Japan, have been reported in the literature and are often referred to in text books (e.g. see Forstner and Wittmann, 1979; Salomons and Forstner, 1984).

As the determination of metal levels in sediments can play a key role in detecting the sources of pollution in aquatic systems (Forstner and Wittmann, 1979), it is not surprising that a large number of published reports can be found in the literature regarding the levels, geochemistry, speciation and toxicity of trace elements in sediments of lakes, rivers, estuaries and coastal marine systems. It is interesting to mention that in spite of the advances in the understanding of the behaviour of metals in aquatic systems in general, and in marine sediments in particular, the monitoring programs in the Liverpool Bay area have largely been concerned only in reporting the distribution of the concentrations of some toxic metals in the sediments. Although some efforts have been made to explain these distributions in relation to the hydrodynamical processes (see for example Norton *et al.*, 1984a and 1984b) which largely control the distribution of trace elements in Liverpool Bay sediments, the geochemical aspects which may also play an important role in the behaviour of trace elements in the marine environment have not been studied or reported in the literature.

The sampling of sediments in Liverpool Bay for the present study resulted from one of the cruises of the 1988 monitoring program by MAFF and NWWA in this area. As described in the methods in Chapter 3, the trace elements were determined according to the procedures followed by MAFF. Therefore similar data to those found in previous reports by MAFF and NWWA were obtained for the trace metals which are routinely determined by these bodies, *i.e.*, mercury, cadmium, copper, chromium, nickel, lead and zinc. However, some variables which are not determined routinely by MAFF or NWWA, and that were thought to be useful for gaining an insight on the environmental behaviour of the metals mentioned above, were also determined. These variables included carbon stable isotopes, iron, manganese and aluminium. An element which is not routinely determined in Liverpool Bay sediments, and for which data were not available, *i.e.* arsenic, was also included in the elemental determinations in this study.

1.1.2. Polychlorinated biphenyls (PCBs)

In contrast to trace metals, there are no previous reports on PCBs in Liverpool Bay sediments. Also in contrast with trace metals, literature reporting these xenobiotics in marine sediments in general is very limited even though there has been a growing concern on the possible effects of PCBs in the environment, and the word PCB has become widespread in the public domain. To provide a better understanding of the complexity of the determination and the complexity of the environmental behaviour of PCBs, some basic information regarding the sources, applications, and physicochemical properties of PCBs is given in the following paragraphs.

Polychlorinated biphenyls is a term used to refer to a family of organic chemical compounds with empirical formula $C_{12}H_{10-n}Cl_n$ where n = 1-10. PCBs are produced by chlorination of the biphenyl compound which has 10 positions (labelled 2-6 and 2'-6' in Figure 1.2) available for chlorine atoms. There are a total of 209 possible structural arrangements distributed among the ten levels of chlorination (see Table 1.1). The term "congener" is applied to any of the 209 possible PCBs, as the term "isomer" can only be applied to those PCBs with the same number of chlorines in the biphenyl molecule which only differ in the substitution positions of the chlorine atoms. For example, there are a total of 209 PCB congeners, but there are only three possible monochlorobiphenyl isomers and 46 possible pentachlorobiphenyl isomers (see Table 1.1).

As the nomenclature of PCB congeners can be cumbersome, e.g. 2,2',3,3',4,4',5,6'-octachlorobiphenyl, Ballschmiter and Zell (1980) developed a scheme of numbering the PCB congeners that follows the rules of the International Union of Pure and Applied Chemists (IUPAC) of substituent characterization in biphenyls. The number of position according to this arrangement is taken as an abbreviation for the PCB structure. The structures and their corresponding IUPAC numbers of all 209 PCB congeners are shown in Table 1.2.

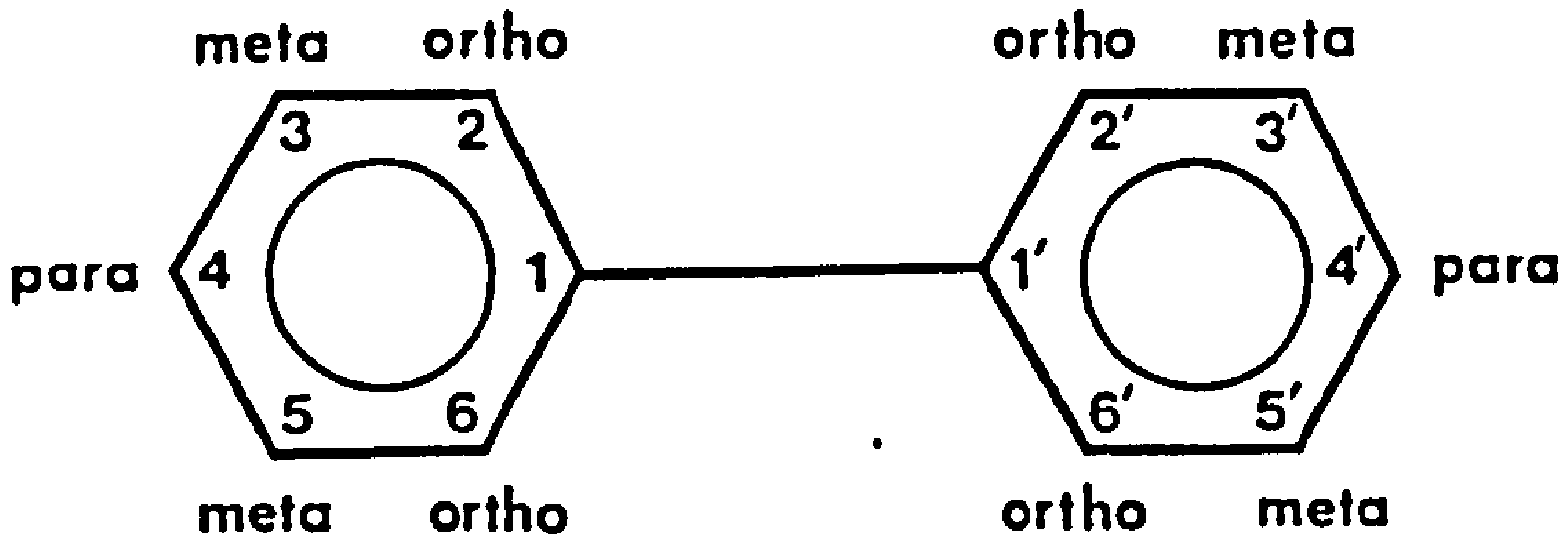

Fig. 1.2. Structure of the biphenyl molecule.

Table 1.1. Nomenclature, number of isomers, molecular weights and chlorine content of isomeric groups of PCBs. (After de Voogt and Brinkman, 1989).

Structural formula	Name (-chloro phenyl)	Number isomers	IUPAC system. number	Mol. wt.	%Cl
$C_{12}H_9Cl$	mono	3	1 - 3	188.65	18.79
$C_{12}H_8Cl_2$	di	12	4 - 15	233.10	31.77
$C_{12}H_7Cl_3$	tri	24	16 - 39	257.54	41.30
$C_{12}H_6Cl_4$	tetra	42	40 - 81	291.99	48.56
$C_{12}H_5Cl_5$	penta	46	82-127	326.43	54.30
$C_{12}H_4Cl_6$	hexa	42	128-169	360.88	58.93
$C_{12}H_3Cl_7$	hepta	24	170-193	395.32	62.77
$C_{12}H_2Cl_8$	octa	12	194-205	429.77	65.98
$C_{12}HCl_9$	nona	3	206-208	464.21	68.73
$C_{12}Cl_{10}$	deca	1	209	498.66	71.10

Table 1.2. Systematic numbering of PCB-congeners. The number is used as a synonym for the corresponding PCB congener. (After Ballschmiter *et al.*, 1989).

No.	Structure	No.	Structure	No.	Structure	No.	Structure
Monochlorobiphenyls		Tetrachlorobiphenyls		Pentachlorobiphenyls		125	2',3,4,5,6'
1	2	40	2,2',3,3'	82	2,2',3,3',4	126	3,3',4,4',5
2	3	41	2,2',3,4	83	2,2',3,3',5	127	3,3',4,5,5'
3	4	42	2,2',3,4'	84	2,2',3,3',6		
		43	2,2',3,5	85	2,2',3,4,4'	Hexachlorobiphenyls	
Dichlorobiphenyls		44	2,2',3,5'	86	2,2',3,4,5	128	2,2',3,3',4,4'
4	2,2'	45	2,2',3,6	87	2,2',3,4,5'	129	2,2',3,3',4,5
5	2,3	46	2,2',3,6'	88	2,2',3,4,6	130	2,2',3,3',4,5'
6	2,3'	47	2,2',4,4'	89	2,2',3,4,6'	131	2,2',3,3',4,6'
7	2,4	48	2,2',4,5	90	2,2',3,4',5	132	2,2',3,3',4,6'
8	2,4'	49	2,2',4,5'	91	2,2',3,4',6	133	2,2',3,3',5,5'
9	2,5	50	2,2',4,6	92	2,2',3,5,5'	134	2,2',3,3',5,6'
10	2,6	51	2,2',4,6'	93	2,2',3,5,6	135	2,2',3,3',5,6'
11	3,3'	52	2,2',5,5'	94	2,2',3,5,6'	136	2,2',3,3',6,6'
12	3,4	53	2,2',5,6'	95	2,2',3,5',6	137	2,2',3,4,4',5
13	3,4'	54	2,2',6,6'	96	2,2',3,6,6'	138	2,2',3,4,4',5'
14	3,5	55	2,3,3',4	97	2,2',3',4,5	139	2,2',3,4,4',6
15	4,4'	56	2,3,3',4'	98	2,2',3'4,6	140	2,2',3,4,4',6'
		57	2,3,3',5	99	2,2',4,4',5	141	2,2',3,4,5,5'
Trichlorobiphenyls		58	2,3,3',5'	100	2,2',4,4',6	142	2,2',3,4,5,6
16	2,2',3	59	2,3,3',6	101	2,2',4,5,5'	143	2,2',3,4,5,6'
17	2,2',4	60	2,3,4,4'	102	2,2',4,5,6'	144	2,2',3,4,5',6
18	2,2',5	61	2,3,4,5	103	2,2',4,5',6	145	2,2',3,4,6,6'
19	2,2',6	62	2,3,4,6	104	2,2',4,6,6'	146	2,2',3,4',5,5'
20	2,3,3'	63	2,3,4',5	105	2,3,3',4,4'	147	2,2',3,4',5,6
21	2,3,4	64	2,3,4',6	106	2,3,3',4,5	148	2,2',3,4',5,6'
22	2,3,4'	65	2,3,5,6	107	2,3,3',4',5	149	2,2',3,4',5',6
23	2,3,5	66	2,3',4,4'	108	2,3,3',4,5'	150	2,2',3,4',6,6'
24	2,3,6	67	2,3',4,5	109	2,3,3',4,6	151	2,2',3,5,5',6
25	2,3',4	68	2,3',4,5'	110	2,3,3',4',6	152	2,2',3,5,6,6'
26	2,3',5	69	2,3',4,6	111	2,3,3',5,5'	153	2,2',4,4',5,5'
27	2,3',6	70	2,3',4',5	112	2,3,3',5,6	154	2,2',4,4',5,6'
28	2,4,4'	71	2,3',4',6	113	2,3,3',5',6	155	2,2',4,4',6,6'
29	2,4,5	72	2,3',5,5'	114	2,3,4,4',5	156	2,3,3',4,4',5
30	2,4,6	73	2,3',5',6	115	2,3,4,4',6	157	2,3,3',4,4',5'
31	2,4',5	74	2,4,4',5	116	2,3,4,5,6	158	2,3,3',4,4',6
32	2,4',6	75	2,4,4',6	117	2,3,4',5,6	159	2,3,3',4,5,5'
33	2',3,4	76	2',3,4,5	118	2,3',4,4',5	160	2,3,3',4,5,6
34	2',3,5	77	3,3',4,4'	119	2,3',4,4',6	161	2,3,3',4,5',6
35	3,3',4	78	3,3',4,5'	120	2,3',4,5,5'	162	2,3,3',4',5,5'
36	3,3',5	79	3,3',4,5'	121	2,3',4,5',6	163	2,3,3',4',5,6
37	3,4,4'	80	3,3',5,5'	122	2',3,3',4,5	164	2,3,3',4',5',6
38	3,4,5	81	3,4,4',5	123	2',3,4,4',5	165	2,3,3',5,5',6
39	3,4',5			124	2',3,4,5,5'	166	2,3,4,4',5,6

No.	Structure	No.	Structure	No.	Structure	No.	Structure
167	2,3',4,4',5,5'	178	2,2',3,3',5,5',6	191	2,3,3',4,4',5',6	202	2,2',3,3',5,5',6,6'
168	2,3',4,4',5',6	179	2,2',3,3',5,6,6'	192	2,3,3',4,5,5',6	203	2,2',3,4,4',5,5',6
169	3,3',4,4',5,5'	180	2,2',3,4,4',5,5'	193	2,3,3',4'5,5',6	204	2,2',3,4,4',5,6,6'
		181	2,2',3,4,4',5,6			205	2,3,3',4,4',5,5',6
Heptachlorobiphenyls		182	2,2',3,4,4',5,6'	Octachlorobiphenyls			
170	2,2',3,3',4,4',5	183	2,2',3,4,4',5',6	194	2,2',3,3',4,4',5,5'	Nonachlorobophenyls	
171	2,2',3,3',4,4',6	184	2,2',3,4,4',6,6'	195	2,2',3,3',4,4',5,6	206	2,2',3,3',4,4',5,5',6
172	2,2',3,3',4,5,5'	185	2,2',3,4,5,5',6	196	2,2',3,3',4,4',5',6'	207	2,2',3,3',4,4',5,6,6'
173	2,2',3,3',4,5,6	186	2,2',3,4,5,6,6'	197	2,2',3,3',4,4',6,6'	208	2,2',3,3',4,5,5',6,6'
174	2,2',3,3',4,5,6'	187	2,2',3,4',5,5',6	198	2,2',3,3',4,5,5',6		
175	2,2',3,3',4,5',6	188	2,2',3,4',5,6,6'	199	2,2',3,3',4,5,6,6'	Decachlorobiphenyl	
176	2,2',3,3',4,6,6'	189	2,3,3',4,4',5,5'	200	2,2',3,3',4,5',6,6'	209	2,2',3,3',4,4',5,5',6,6'
177	2,2',3,3',4',5,6	190	2,3,3',4,4',5,6	201	2,2',3,3',4,5,5',6'		

The order of structures 200 and 201 is kept as originally set (Ballschmiter and Zell, 1980), though it should be reversed according to the above systematic numbering.

PCB 28, 52, 101, 138, 153 and 180 are widely used as representatives for quantitation of complex PCB mixtures.

Until the environmental health risks of PCBs were discovered, chlorinated biphenyls were thought to be one of the most successful chemical products. First synthesized in the nineteenth century, commercial production of PCBs began in 1929 (Hooper *et al.*, 1990). The total amount of PCBs produced since 1929 is approximately 1.5 million metric tonnes (de Voogt and Brinkman, 1989). Production of PCBs has probably been confined to some ten countries in the world, with the U.S.A. being the largest producer, followed by Germany, France, the U.K and Japan (de Voogt and Brinkman, 1989). Commercially, PCBs found rapid and widespread industrial use as electrical insulators, lubricants, hydraulic fluids, diffusion pump oils, cutting oils, plasticizers and liquid seals. PCBs found their way into the home as flame retardants in a number of plastics, as preservatives and protectants in rubber, in weatherproof coatings and stucco, in steel coatings, waxes, varnishes, inks, duplicating fluids and a host of other everyday items (see Hooper *et al.*, 1990, and references therein). The unique physical and chemical properties of PCB technical mixtures stimulated the extensive use of this family of mixtures in many industrial applications. Some of these properties are: a remarkable thermal stability, resistance to acids, bases and other chemical agents, stability to conditions of oxidation and hydrolysis often encountered in industrial use, low solubility in water, low flammability, high electrical resistivity, favourable dielectric constants, low vapour pressure at ambient temperature and suitable viscosity-temperature relationships (de Voogt and Brinkman, 1989).

The commercial PCB formulations are prepared by the chlorination of biphenyl using a variety of catalysts and experimental conditions (e.g. heat, pressure and reaction time). Although the electrophilic substitution by the chlorine atoms is favoured at the *ortho* and *para* positions (Fig. 1.2), the commercial products are complex mixtures of isomers and congeners with no apparent preference for chlorine substitution (Safe, 1984). Of the 209 theoretically possible congeners, a total of 132 have been reported as present in commercial mixtures at concentrations above 0.05% (Schulz *et al.*, 1989).

Commercial PCB mixtures have been sold in many countries under a variety of trade names including, for example, Aroclor (U.S.A., U.K.), Pyranol (U.S.A.), Kanechlor (Japan), Clophen (Germany), Fenchlor (Italy), Phenochlor (France), Delor (Czechoslovakia) and Sovol (U.S.S.R.). In the United States, PCBs were mainly produced by Monsanto Corporation under the trade name of Aroclor, which are, together with the German Clophen mixtures, the commercial formulations most often referred to in the literature of PCBs in environmental samples. The average chlorine content of Aroclor mixtures are 21, 32, 42, 48, 54, 60 and 61% by weight. Aroclors are designated by a four digit number, of which the first two digits are 1 and 2, representing the 12 carbons of the biphenyl skeleton, and the second two digits are the percentage of chlorine in the mix (Hooper *et al.*, 1990). Thus Aroclors 1254 and 1260 are PCB mixtures in which chlorine constitutes 54 and 60% of the total weight respectively. Within each commercial formulation only few PCB congeners tend to be the predominant components. For example, Aroclor 1254 is predominantly composed of tetra-, penta- and hexachlorobiphenyl congeners while the predominant isomeric groups in Aroclor 1260 are penta-, hexa- and heptachlorinated biphenyls (the description of the congener composition of these mixtures is given in Table 5.2, and their corresponding high-resolution gas chromatograms are shown in Fig. 5.2). A useful review with details regarding production statistics, composition, physicochemical properties and applications of PCB commercial formulations can be found in de Voogt and Brinkman (1989).

PCBs are one of the groups of contaminants in the environment which cause most serious concern because of the characteristics that made them so commercially successful. The highly nonpolar nature of PCBs results in a low dielectric constant, making them an ideal choice as an insulating coolant in electrical equipment. Nonpolarity, however, also confers low water solubility and high lipophilicity resulting in potential for the accumulation in biological tissues, and particularly in those with high lipid content. The strong electronegativity of chlorine atoms suppresses the normally reactive electron-rich carbon backbone, stabilizing the biphenyl molecule. This results in a heat-resistant fluid with excellent long term stability. Although these are desirable characteristics in oils, hydraulic fluids and preservatives, they also result in molecules that are highly resistant to physical and biological degradation (Hooper *et al.*, 1990). In general, PCB congeners with a higher number of chlorines in the molecule show lower volatility, lower aqueous solubility and higher chemical stability than the lower chlorinated congeners. As a consequence, the former persist in the environment for a longer period (see Hooper *et al.* 1990, and references therein).

The occurrence of PCBs in environmental samples was first reported in the scientific literature by Jensen in 1966. In his study, Jensen analysed several environmental extracts for the pesticide DDT and found several "unknown" peaks which interfered with the chromatographic determination of DDT in the samples. Gas chromatographic and gas chromatographic-mass spectrometric analyses confirmed that the interfering peaks were a complex series of PCBs, a widely used industrial chemical. The full significance of PCBs on health came to public attention in 1968 after the poisoning of several people by eating rice cooked in bran oil accidentally contaminated with PCBs in Yusho, Japan, and in the mid-1970s they surpassed the chlorinated insecticides as the most talked-about organochlorine pollutants (de Voogt and Brinkman, 1989).

Since the report by Jensen over 20 years ago, extensive reviews and reports on environmental PCB contamination levels have been written. However, only a small proportion of these studies discussed the distribution and occurrence of individual PCB congeners as part of the analysis of environmental samples (de Voogt *et al.*, 1990). After recognising the potential adverse effects of PCBs in the environment, many industrial nations introduced restrictions in the production, use and disposal of PCBs, and by the end of the 1970s regulations and directives restricted PCBs and PCB-containing formulations in all uses except in closed systems such as electrical capacitors (de Voogt and Brinkman, 1989).

In spite of the restrictions introduced more than a decade ago in the production and disposal of PCBs, due to the worldwide use of these xenobiotics in large quantities, they have been identified in a wide variety of environmental media and biota. Serious environmental contamination has been reported in several industrialized areas such as the Great Lakes, the Baltic Sea and Tokyo Bay (see Tanabe, 1988, and references therein). The widespread contamination with PCBs has also been evidenced by their presence in various environmental samples from polar regions such as air, water including snow and ice, fish, birds and mammals (Tanabe, 1988). PCBs have also been reported in open ocean compartments such as the atmosphere, surface and subsurface waters and biota. The widespread distribution of PCBs suggests the importance of the atmosphere as a medium of transport to remote areas (Tanabe, 1988).

Since environmental contamination with PCBs became apparent, many sample preparation procedures, gas chromatographic (GC) systems, detectors and methods for quantifying GC responses have been reported for determining the contamination extent of the environment. However, until recent advances in analytical instrumentation, most of the conventional methodology yielded only semi-quantitative data with virtually no qualitative or quantitative information on the PCB congener composition of the environmental samples (Pellizari *et al.*, 1985). The traditional method for PCB quantification was based on packed column GC and the concentrations were usually reported in terms of a particular Aroclor mixture (e.g. as Aroclor 1242, 1254 or 1260). For this quantification the detector is first calibrated using commercial Aroclor mixtures, and then the approximate commercial Aroclor profile is matched to the sample profile. The final concentration of the sample is then reported in terms of the Aroclor mixture whose pattern most closely resemble the pattern in the sample (Pellizari *et al.*, 1985). This method, as explained below, is subject to errors.

The main source of PCBs in the environment is the commercial formulations such as the Aroclor mixtures. However, as time passes after being released into the environment, the original Aroclor patterns undergo alterations, as selective weathering, degradation, biotransformation and bioaccumulation occur due to the wide range of physicochemical properties among PCB congeners. As a result, PCB patterns in environmental samples such as sediments and biota seldom resemble any particular Aroclor pattern. Thus, the quantification in terms of any Aroclor mixture would be inaccurate. Furthermore, in the case in which two or more Aroclor mixtures are the sources of PCBs in a particular sample, the quantification in terms of a single Aroclor mixture would also be inaccurate. Although some statistical methods have been used in the past (e.g. Dunn *et al.*, 1984) to match the PCB profile in samples against a single Aroclor, or combinations of different proportions of two or more Aroclors, matching the profiles still does not consider the possible alterations which occur in the environment which may lead to erroneous conclusions regarding the source of PCBs in those samples. This quantification method is further exacerbated by the production of PCB congeners in processes such as the incineration of municipal and industrial wastes, via chemical or pyrolysis reactions that are not the same as the chemical reactions used for the manufacture of commercial formulations (Pellizari *et al.*, 1985). As incidental generation does not necessarily produce a fixed pattern of PCB congeners, the analyst cannot identify and quantify these congeners based on pattern recognition from the packed column gas chromatogram. Thus, the qualitative and quantitative PCB composition of biotic and abiotic environmental samples can only be accurately described by the accurate identification and quantification of individual chlorobiphenyl congeners.

It has only been during the past few years that the technical developments in high-resolution gas chromatography (HRGC), and the detection systems, that accurate identification and quantification of PCB congeners has been possible. The low resolution of packed columns did not allow a complete separation of most of the PCB congeners in the extracts, which, therefore, eluted from the column in groups (coeluted) showing a single peak in the detector. The detector most often used in PCB determinations is an electron capture detector (ECD) which is used for the determination, in general, of electrophilic substances containing elements such as chlorine in the molecule. Any electron capturing substance passing through the detector will give a signal, thus, if two or more PCB congeners have not been resolved before entering the detector, they will appear in the chromatogram as a single peak. The main limitation of the ECD is, therefore, that it does not give any information regarding molecular composition, thus, the identification of the compounds in a sample cannot be completely unambiguous.

Gas chromatography-mass spectrometry (GC-MS) can be used to be more positive in the identification of compounds in an extract. However, the sensitivity of a mass spectrometer is not as high as that of an ECD, and often cannot be used to quantify PCBs at the relatively low concentrations often found environmental samples (Duinker *et al.*, 1988). A decrease in the possible misidentification and quantification of PCB congeners using an ECD can be achieved by improvements in the preparation of the sample extract (during the clean up of the extract to eliminate non-PCB compounds) and in the separation of the congeners in the chromatographic system.

The problems of accuracy in the identification and quantification of PCB congeners in environmental samples have been largely resolved by improvements in the methods for the preparation of the samples prior to the chromatographic analysis, and by the development of high resolution capillary columns (e.g. see review by Pellizzary *et al.*, 1985) which allow for a separation of most of the 209 PCB congeners with a single column (e.g. see Mullin *et al.*, 1984). Recently, the unambiguous identification and quantification of all PCB congeners present in the Aroclor and Clophen formulations has been reported after the complete separation of all of these congeners by multidimensional gas chromatography (Schulz *et al.*, 1989). More details in the identification and quantification procedures of PCB congeners are given in Chapter 5.

In spite of the large number of reports on PCBs appearing in the literature, the accurate determination of PCB congeners has not been possible until recently. Therefore, there is a lack of information in the literature on the levels of individual congeners in environmental samples including marine sediments. The persistent and bioaccumulative nature of PCBs has been recognised particularly in aquatic ecosystems, where the stepwise accumulation in higher-ranking predators of the food chain is common. The concern with PCB pollution in aquatic organisms has also been emphasized as the primary route of exposure to humans and domestic animals through the consumption of fish, shellfish, etc. from contaminated areas (Tanabe, 1988).

There are various recent reports on the PCB congener composition in various aquatic organisms. However, little is known about how these hydrophobic chemicals are incorporated into organisms (van der Oost *et al.*, 1988). Particles and contaminated sediments in aquatic systems can act as a source of PCBs into the food chain through ingestion by benthic organisms such as deposit feeders. It has been shown that even if direct uptake of PCBs from the water column, given its extremely low concentrations does not contribute significantly to the total concentrations in organisms, the ratio between the concentrations in the organisms and in sediments tends to be constant. This ratio may be dependent on the organic carbon content of the sediment. Thus, organic carbon standardized ratios may represent the capacity of PCBs (and other hydrophobic chemicals) to accumulate in biota of natural aquatic ecosystems (van der Oost *et al.*, 1988).

Apart from the possible environmental implications of the PCB content in aquatic sediments, the study of PCBs in sediments as model compounds for the study of various geochemical processes has been suggested (Brownawell and Farrington, 1986). Sediments from estuaries and coastal marine areas act as long or short term reservoirs for many natural and anthropogenic hydrophobic organic compounds. Sorption reactions involving sediment particles and their associated pore waters control the rates and mechanisms of transport of organic compounds between the sediments and the overlaying water column, and may also affect the bioavailability of these compounds. Other diagenetic processes such as biological and chemical transformation reactions, and physical processes such as diffusion, advection and mixing and resuspension of the sediment bed, will also affect the distribution of hydrophobic organic compounds in sediments. The relative importance of each of these processes depends on the molecular structure, biological activity and physicochemical properties of the individual organic chemicals, as well as the properties of the sedimentary environment (Brownawell and Farrington, 1986). Therefore, due to the widespread distribution of PCBs in aquatic environments and to their wide range of physicochemical properties (e.g. solubility, volatility, octanol-water partition coefficients), PCB congeners may be considered as representative of many hydrophobic organic chemicals in the marine environment (Brownawell and Farrington, 1986).

1.2. AIMS OF THE STUDY

The main aim of the present study was to determine the possible sources of various trace elements and polychlorinated biphenyl congeners in Liverpool Bay sediments.

The trace elements determined in this study included mercury, cadmium, chromium, copper, nickel, lead and zinc which are analysed routinely for monitoring purposes by British governmental institutions, and also included arsenic which had not been previously studied in sediments from Liverpool Bay.

The particular aims were:

1) to determine the spatial distribution of trace elements in two different grain size fractions in the sediments and to explain the observed distributions in terms of the possible sources including the disposal of sewage sludge, industrial wastes and dredging spoil, and the inputs from the rivers Mersey and Dee.

2) to determine the possibility of different geochemical behaviour amongst trace elements by studying their correlations with some sediment parameters including grain size, organic carbon content, organic carbon stable isotopic composition, and the content of aluminium, iron and manganese.

3) to accurately determine various PCB congeners in marine sediments.

4) to explain the observed PCB patterns in different samples in terms of the possible sources.

5) to find the relationship (if any) between the sources of PCBs and the sources of trace elements in Liverpool Bay sediments.

As this study was mainly focused on the geochemical aspects of trace elements and PCBs in an area where anthropogenic influences can be significant, an emphasis was made in explaining and discussing the possible geochemical behaviour of these contaminants, rather than discussing the possible environmental implications of the levels of these contaminants in Liverpool Bay sediments.

CHAPTER 2. BACKGROUND

4

2.1. GENERAL DESCRIPTION OF THE STUDY AREA

Liverpool Bay is an area within the Irish Sea whose precise limits have not been defined. At times the name has been used to refer to the whole of the eastern Irish Sea, but is more often used to describe that part of the Irish Sea limited to the south by the North Wales coast east of Great Ormes Head and to the east by the Lancashire coast as far north as the estuary of the Ribble River (Fig. 2.1) The seaward boundaries are not precise but are generally taken to be some 50 kilometres to the north and west of the two coasts (DOE, 1972a).

The bay is used for multiple commercial and recreational activities. Those activities include navigation, fishing, gravel extraction, sailing and boating, swimming and the use of amenity beaches, and most important, from the present work point of view, the bay is used for the disposal of sewage sludge and dredged spoil.

Fishing is one of the most important commercial activities in the region. The main commercial fish landed from this area are demersal species of which plaice is dominant, but sole, whiting, cod and rays are also important. Shellfisheries include shrimps and cockles along the landward margin of the bay and queens and scallops further offshore (Murray and Norton, 1982). The area is also an important spawning and nursery zone for several commercial species including those mentioned above.

Navigation is another important activity, especially for ships entering the port of Liverpool. These ships must pass through the bay and in particular along the Queen's and Crosby Channels for about 17 kilometres to the mouth of the River Mersey (DOE, 1972a). These channels, docks, and other areas within the River Mersey, are continuously dredged and the dredged spoil is dumped in designated areas in Liverpool Bay. Approximately three million tonnes of dredged material are dumped each year (MAFF, 1990) at two sites, Sites Y and Z (Fig. 2.1), from which Site Z receives more than 95% of the total discharges (Rowlatt *et al*, 1986).

Disposal activities of sewage sludge in Liverpool Bay started after the construction of the first sewage treatment plants near Manchester and Salford in the early 1890s (Head, 1980). Sludge disposal has continued until today, without interruption, at a designated area (Site SI) shown in Figure 2.1. Disposal of industrial wastes has taken place at the same site since the late 1960s (Norton *et al.*, 1984a). The bay also receives direct discharges of domestic and industrial wastes

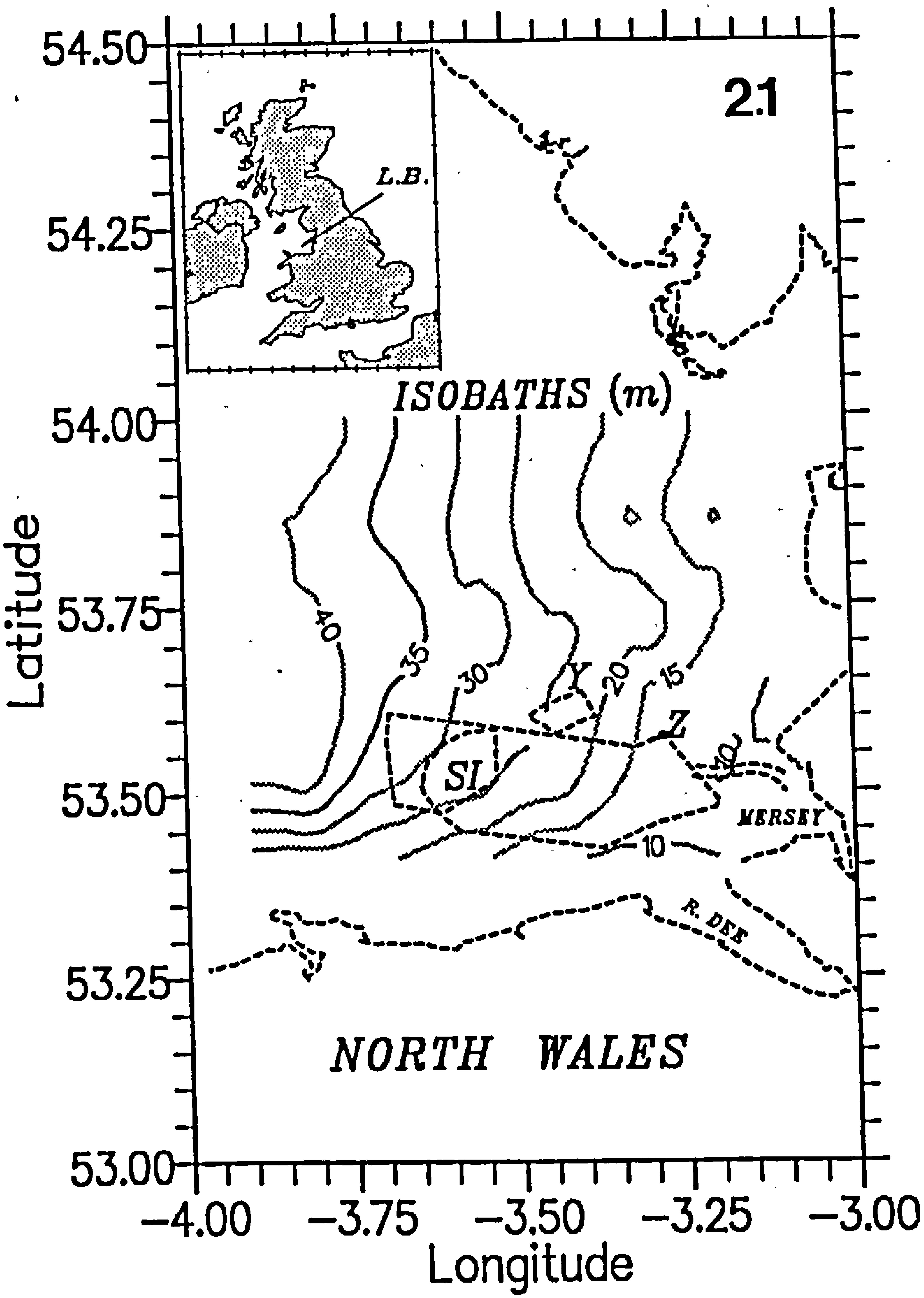

Fig. 2.1. Study area including depth contours (m). The waste disposal Sites in Liverpool Bay are indicated by SI (sewage and industrial wastes), Y and Z (dredged spoil sites). The polygon off the Mersey and the North Wales coast indicates the perimeter of the sampling grid.

from coastal outfalls, and indirectly from the discharges of effluents into the rivers flowing into Liverpool Bay. The main riverine contributions are from the rivers Mersey, Dee, and Ribble.

Several studies on the effects of dumping wastes into Liverpool Bay have been published. Most of these studies started in the early 1970s when a working party was commissioned by the Department of the Environment (DOE) to study the possible effects of the disposal at sea of sewage sludge by the Manchester and Salford Corporations after a proposal to increase the dumped amounts from 550,000 wet tonnes in 1971 to approximately 3,000,000 wet tonnes by 1976. Therefore, the main aim of the Working Party on Sludge Disposal in Liverpool Bay was "to ascertain the present conditions and to predict the likely effects of tipping significantly more sludge on the existing spoil ground in Liverpool Bay..." (DOE, 1972a).

As a result of the investigations founded by the DOE, a series of reports were published (DOE, 1972a, 1972b, 1973, 1976; DOE/NWC, 1979, 1984). These reports provided a large amount of basic information on the physical oceanography of the area, quality and quantity of the inputs, quality of the receiving water and sediments, impacts on the biota including toxicity in some species, the behaviour of the sludge after disposal both in the water column and sediments, etc.

Reports on the condition of Liverpool Bay relevant to the work presented here, have also been published by the Ministry of Agriculture, Fisheries and Food (MAFF). This Ministry is responsible for the control of dumping of wastes at sea, including the licensing of all dumping operations to exercise predischarge controls on wastes, enforcing the licensing conditions, and "carry out surveys of the areas licenced for the disposal of wastes to ensure that the marine environment and its resources are being protected." (Norton and Rolfe, 1978). Monitoring activities by MAFF have been concentrated on the investigation of dumping-related effects not fully covered in the studies founded by the DOE rather than only monitoring dumping grounds (Norton, *et al.*, 1984a). MAFF studies in Liverpool Bay and other coastal areas have been reported in the MAFF Fisheries Research Technical Report (*i.e.* Nos. 45, 1978; 47, 1978; 69, 1982; 76, 1984), and in the MAFF Aquatic Environment Monitoring Report series (*i.e.* Nos. 16, 1987; 17, 1987; 20, 1989; 22, 1990).

The aim of the following sections in this chapter is to present a background on the physical, geological, and chemical characteristics of the Liverpool Bay area. This review is particularly concerned with presenting the main factors and processes controlling the transport and deposition of sediments, and of particles derived from sewage sludge and dredged spoil discharges in this area. An understanding of these factors and processes will be necessary in the attempt to explain the distribution in the surface sediments of Liverpool Bay of the geochemical parameters, elements and PCBs determined in this study.

2.2. HYDROGRAPHY OF LIVERPOOL BAY

2.2.1. Bathimetry and freshwater inputs

Liverpool Bay is a relatively shallow, semi-enclosed water body. Most of the area lies within the 40 m isobath (Fig. 2.1) and the depth over the sewage disposal area (Site SI) is between 25 and 30 m. The depths increase almost linearly with distance from the coast with a roughly uniform slope of about 1/1000 (Halliwell, 1973).

The eastern Irish Sea receives fluvial discharges from a considerable catchment area (Fig. 2.2). The main discharges into Liverpool Bay are from the rivers Mersey, Ribble, Dee and Clwyd. The relative importance of each of these rivers in relation to the total freshwater inputs into the bay can be shown with the values reported by Miller (1985) of their mean daily flow (m^3s^{-1}). These flows, calculated from values of a period from November 1976 to December 1977 were 76.445, 38.651, 35.325, and 12.347 respectively. The influence of these freshwater discharges upon the waters of Liverpool Bay will vary seasonally, with considerable enhancement during the winter months with higher precipitation and fluvial discharges than during the summer.

2.2.2. Water circulation

In this section, a review is presented on information produced by several authors regarding the physical oceanographic processes that might be controlling, directly or indirectly, the distribution of natural sediments and the fate of the particles associated with the disposal of wastes in the Liverpool Bay area. A more detailed review of the physical oceanography of the Irish Sea in general, with description of some areas like Liverpool Bay in particular, is presented by Bowden (1980). Also a detailed review of the currents in the eastern Irish Sea is given by Howarth (1984).

As the main factors controlling the movement of water in the Irish Sea are the tides, the weather (winds in particular), and the water density gradients (Bowden, 1980), this review will cover only these aspects of the physical oceanography in the area.

2.2.2.1. Tidal currents.

The most obvious water movements in the Irish Sea are the tidal streams associated with the tidal rise and fall of water level (Bowden, 1980). The tides propagate into the Irish Sea from the

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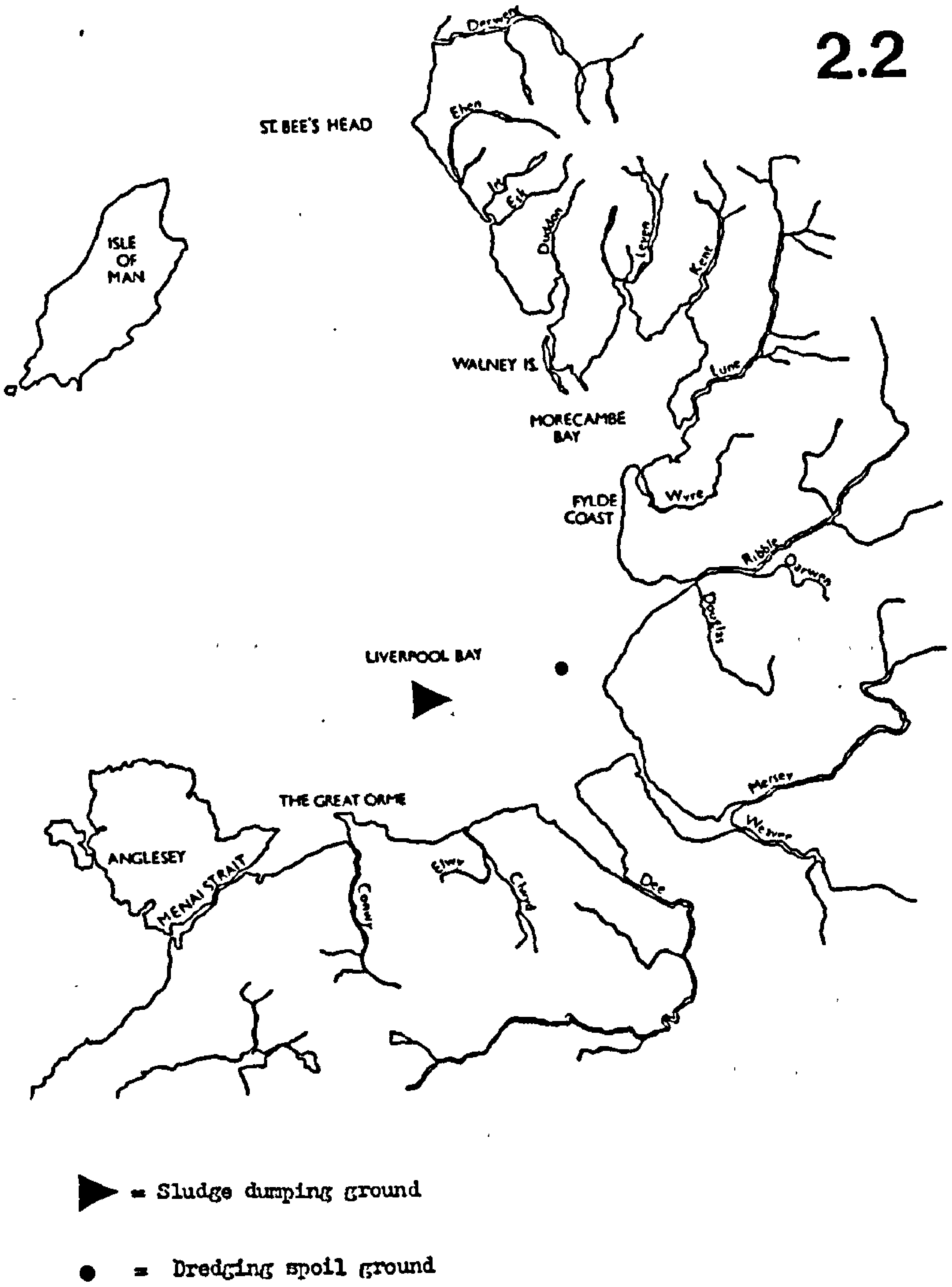

Fig. 2.2. River catchment area in the eastern Irish Sea including Liverpool Bay. (After Miller, 1985).

Atlantic Ocean through the St. George's and North Channels (Robinson, 1979). As in the Atlantic Ocean, the semi-diurnal constituents in the Irish Sea are the most important tidal components -at Liverpool 97.5% of the variance in the surface elevation record is at semi-diurnal tidal frequencies (Howarth, 1984).

Liverpool Bay is located in a macrotidal environment with spring tides of about 6 metres (DOE, 1972). In a study using one current meter near the surface and one near the seabed in the sewage disposal area, Ramster (1972a) reported maximum near surface tidal velocities of 0.91 m s^{-1} while the registered near bottom velocity was 0.63 m s^{-1} during a spring tide. The maximum near bottom velocity was 0.71 m s^{-1} as the subsurface meter registered 0.74 m s^{-1} also during a spring tide. The set of current velocities in the disposal area reported by Ramster (1972a) are in the same range as those reported by Talbot (1972) in a study with moored current meters throughout the bay. Currents exceeding 3 m s^{-1} can be found in places such as the Narrows of the River Mersey (DOE, 1972a).

In the disposal area, the general direction of the flood and ebb currents is east-west but near the coast it is influenced by estuarine channels (Best *et al.*, 1973). Tidal current ellipses in the sewage disposal area reported by Ramster (1972a) tend to be rectilinear near the surface during both spring and neap tides. On the other hand, near the bottom the ellipses are elongated during spring tides but tend to circular during neap tides.

Many of the processes and distributions (mixing, fronts, sediment transport, sediment distribution) within the Irish Sea are determined by the large spatial variation in the amplitude of the tidal current throughout this area (MAFF, 1987). Tidal movements of high frequency (periods of a few hours to one day) are the most energetic in the Irish Sea (MAFF, 1987). Tides at frequencies higher than semi-diurnal like the fourth diurnal (M_4), are not only propagated as free waves into the Irish Sea through the North and St. George's Channels, but can also be generated within this area in shallow water, particularly in the eastern side where between Liverpool and Barrow-in-Furness the M_4 amplitude exceeds 0.2 m (Howarth, 1984). M_4 is the largest component of frequency higher than semi-diurnal and has mean spring current amplitudes up to 0.15 m s^{-1} to the east of the Isle of Man, but locally these frequency currents can be enhanced near headlands, islands and estuaries (MAFF, 1987).

One of the factors controlling bedload transport is the difference between the near bottom current velocity and a critical or threshold velocity for sediment movement. Since the semi-diurnal tidal current is oscillating it can not by itself produce net bedload transport (Howarth, 1984). Tidal currents asymmetry, that is, differences in the strength between flood and ebb tidal currents, are produced by the high frequency harmonics generated in shallow water. M_4 in particular (Pingree and Griffiths, 1979) in association with the semi-diurnal component are responsible for the tidal transport of sand around the British Isles. In regions like Liverpool Bay, M_2 and M_4 combine to give a strong flood and a weaker ebb flow of longer duration (Pingree and Griffiths, 1979), resulting in significant transport eastward towards the Mersey Estuary (Howarth, 1984).

Howarth (1984) estimated the importance of the fourth diurnals in the net transport of sediment and suggested that transport due to this tidal component is of the same order as that of the mean current. This author suggested that as the amplitude of the M_4 component is proportional to the square of the amplitude of the M_2 component, transport at spring tides will be at least an order of magnitude greater than at neap tides, therefore, tidally generated net sediment transport in the eastern Irish Sea during spring tides will be important, particularly at the equinoxes.

2.2.2.2. Density currents and residual circulation

The term "residual current" is normally used to refer to the mean water flow after the tidal currents have been eliminated. Residual currents are usually calculated by taking an average over 24 h and 50 min of currents data taken at regular intervals (Dyer, 1986), in order to remove the principal semi-diurnal and diurnal tidal constituents. More sophisticated numerical filtering methods can be used to remove tidal oscillations, but little difference in the results may be observed in most cases (Dyer, 1986).

It has been mentioned before that due to the oscillatory nature of the semi-diurnal tidal component, its associated currents can not produce a net transport, therefore, the analysis of the residual currents is important to determine the direction and rates of sediment transport. It is important to mention that net sediment transport not only depends on the currents, but also on the nature (Howarth, 1984) of the sediment (whether it is cohesive like muds, or non-cohesive, like sands and gravels) and on the mode of particle transport (whether it is by bedload or by suspension).

Numerical models have shown that the residual flows through the Irish Sea are mainly caused by non-linear tides, density gradients and mean wind-stress (see MAFF, 1987, and references therein) and that the relative importance of each of these factors will vary with the location within the Irish Sea, and with the meteorological conditions.

Density currents is the term used to describe water movements associated with density gradients which are themselves due to the distribution of temperature and salinity. Although tidal

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stirring is strong, vertical salinity gradients as reported by Ramster (1972b) can occur in Liverpool Bay. Czitrom-Baus (1982) studied stratification in Liverpool Bay and the associated formation of fronts. This author reported that the main factors causing stratification in this area are the east-west baroclinic advective transport related to river discharges, and the surface heat flux, while the effect of rain is small.

According to Czitrom-Baus (1982), the relative effect of each factor on stratification in the bay has a seasonal variation. The advective transport has an estuarine-like residual circulation induced by the low-density freshwater inputs (mainly from the rivers Mersey and Dee) moving to the west at the surface, and by the transport of saline, denser water moving eastward near the bottom. During the winter, the increase in river discharges enhances the horizontal density gradients, therefore, this density driven, estuarine-like circulation in the bay is intensified. During the summer, surface heat flux contributes significantly to vertical stratification in association with low river discharges. Vertical stratification is broken by mixing processes, in particular by tidal stirring at times of low wind stress, and by wind stirring during stormy weather.

Density currents in the Irish Sea have been evaluated by several authors. One of the most relevant studies is that by Heaps and Jones (1977). In this study the authors not only present an extensive literature review on the water circulation in the Irish Sea in general and Liverpool Bay in particular, but using a three dimensional numerical model, the authors resolve the problem of conflicting theories regarding the circulation pattern of Liverpool Bay surface waters. The controversy about the surface residual circulation in the Liverpool Bay area was centred on whether the water followed a clockwise or an anticlockwise direction. Indirect evidence strongly supporting a clockwise circulation was based on plankton and chemical distributions, and also from current meter observations. On the other hand, some direct observations of residual currents and indirect observations of trace metals suggested an anticlockwise circulation (see Heaps and Jones, 1977, for discussion). Heaps and Jones showed with their model that a weak but persistent clockwise circulation was induced by density forcing, but also showed that at times, an anticlockwise flow may exist as a function of wind action (Fig. 2.3). More recently, Miller (1985) analysed nutrient distributions in surface waters of the Liverpool Bay area during various weather conditions throughout the year. Changes in the surface distributions of these parameters were consistent with changes in surface circulation in the bay, therefore, confirming indirectly the results of Heaps and Jones (1977) model.

Spencer (1984) studied the water quality in Liverpool Bay and observed the changes in the position of a density discontinuity (Fig. 2.4). This discontinuity, marked by a sharp lateral

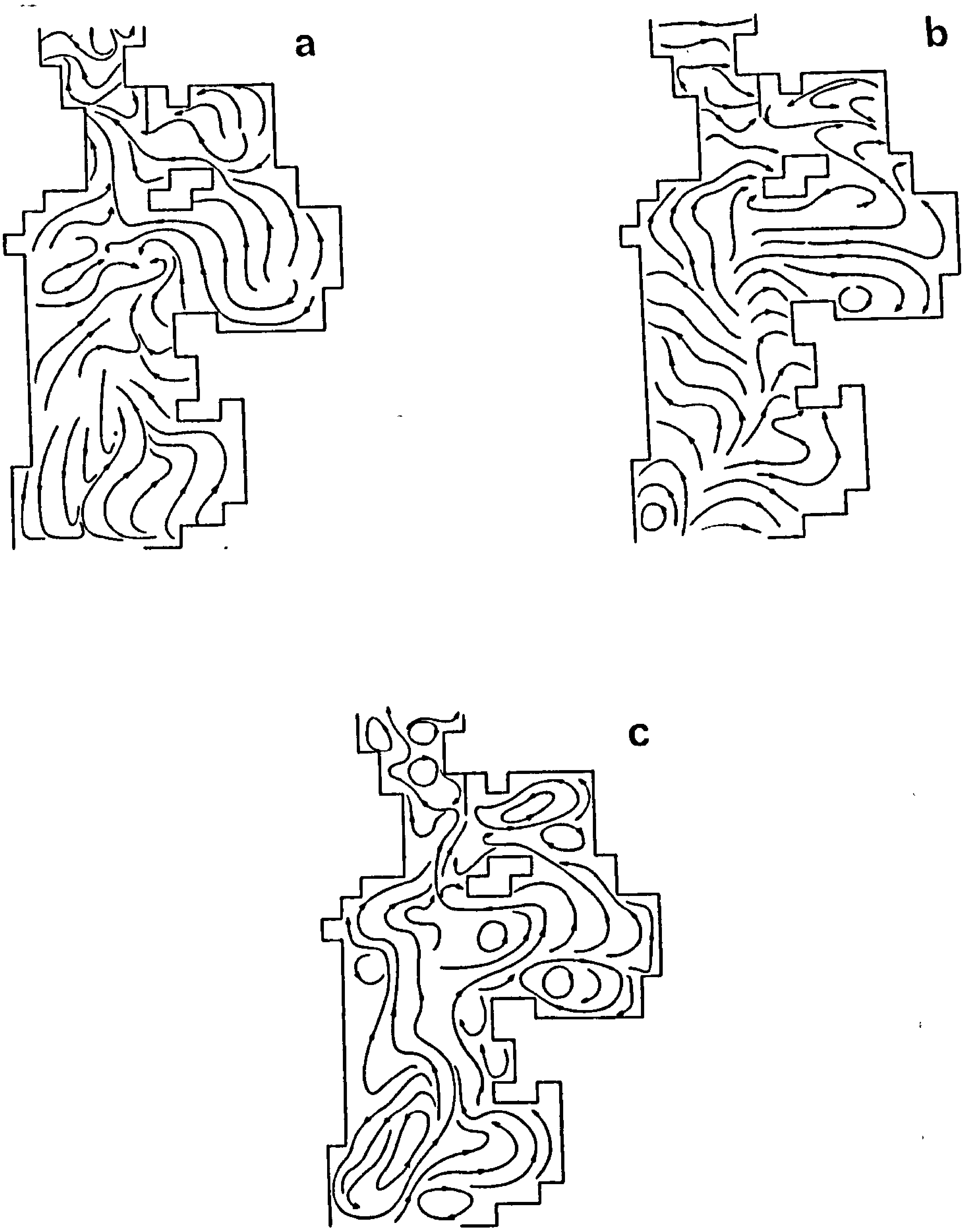


Fig. 2.3. Surface (a), bottom (b) and depth-mean (c) density current flowlines for the Irish Sea area. (After Heaps and Jones, 1977).

Fig. 2.4

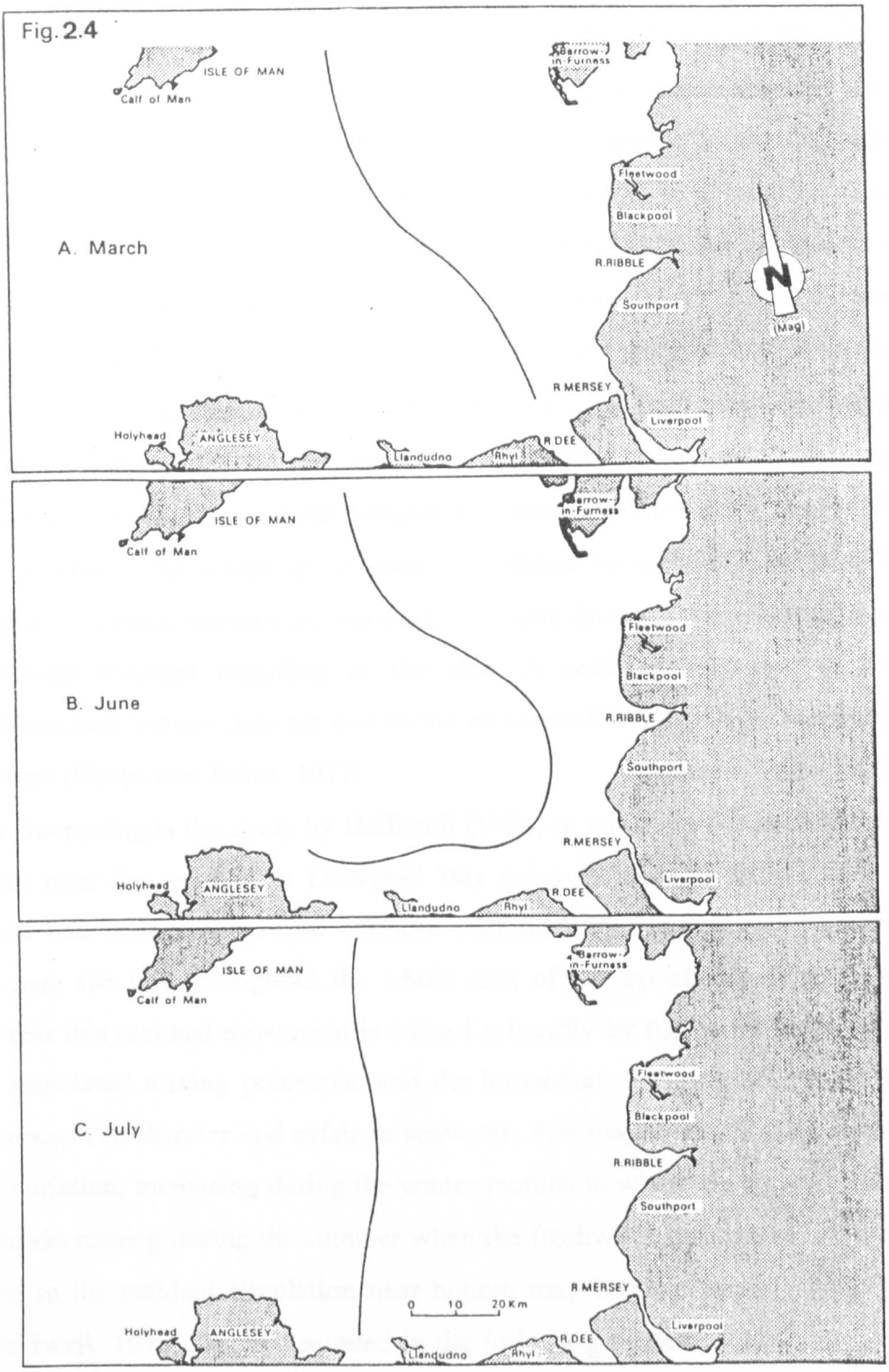


Fig. 2.4. Variations in the position of the salinity discontinuity in Liverpool Bay. (After Spencer, 1984).

gradient of salinity and/or temperature, was considered to represent the boundary between the offshore water from the central Irish Sea, and the main body of Liverpool Bay water, which is identifiably influenced by the freshwater discharges. As these discontinuities may present a restriction to lateral mixing, they may have important implications on the dispersal of soluble material dumped at sea (Spencer, 1984), or on the dispersal of contaminants associated with freshwater discharges. Foster (1984) studied the inhibition to pollutant dissipation in this area, and concluded that lateral and/or vertical density discontinuities are important features of the hydrography of the north-east Irish Sea, and that under normal meteorological conditions, major inhibitions to the free horizontal and/or vertical mixing of waters occur throughout the year, except in autumn. The autumn observations were accompanied by low wind stress suggesting that mixing processes were associated with seasonal heat loss from the surface waters (Foster, 1984).

Residual currents at the seabed are important in relation to sediment transport. In contrast to the changing near-surface circulation, near-bottom density driven residual circulation in Liverpool Bay is relatively constant regarding its direction. A persistent eastward or south-eastward direction of residual bottom currents due to the estuarine-like circulation has been reported by several authors (Heaps and Jones, 1977; Halliwell, 1973; Ramster, 1972a). Particularly interesting is the study by Halliwell (1973) in which he made direct observations of residual drift near the sea bed in Liverpool Bay using Woodhead drifters. The results, after releasing sea bed drifters in several offshore stations in the bay, showed a strong landward movement near the bed throughout the whole area of Liverpool Bay (Fig. 2.5). This author concluded that this residual movement is caused primarily by the combination of tidal currents with their associated mixing processes, and the horizontal density gradient resulting from the mixing of coastal freshwater and offshore seawater. The magnitude of the bottom currents has a seasonal variation, increasing during the winter months in which the river discharges are more intense, and decreasing during the summer when the freshwater discharges are small. The effect of the wind in the residual circulation near bottom may become important particularly during storms (Halliwell, 1973) and is discussed in the following section.

2.2.2.3. Wind driven currents

The major residual currents in the Irish Sea, are produced by wind. Under stormy conditions, wind induced surface currents can be many times greater than the density currents, however, during calm weather wind and density surface currents can be of comparable magnitude (Heaps and Jones, 1977).

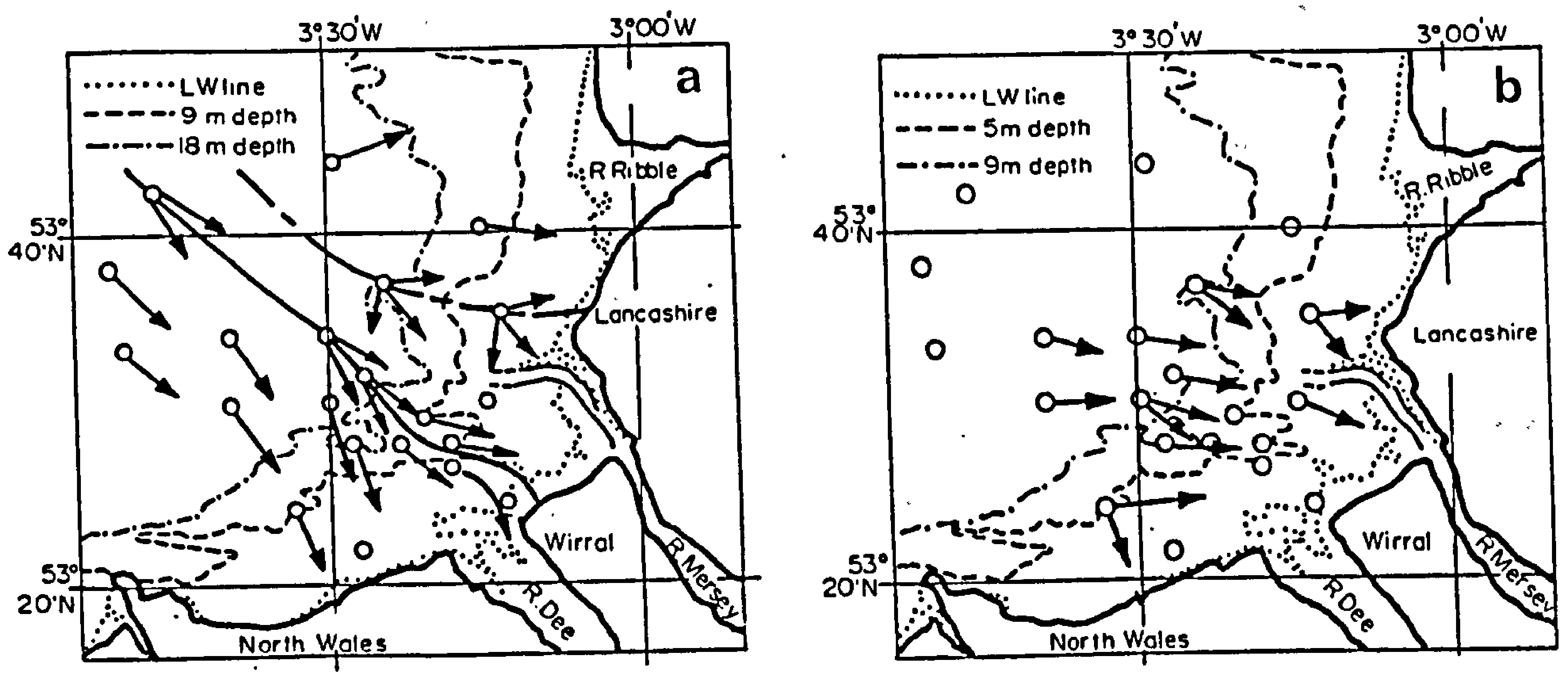


Fig. 2.5. Residual drift patterns of drifters dropped in (a) May-June 1970 and (b) February 1970 in Liverpool Bay (After Halliwell, 1973).

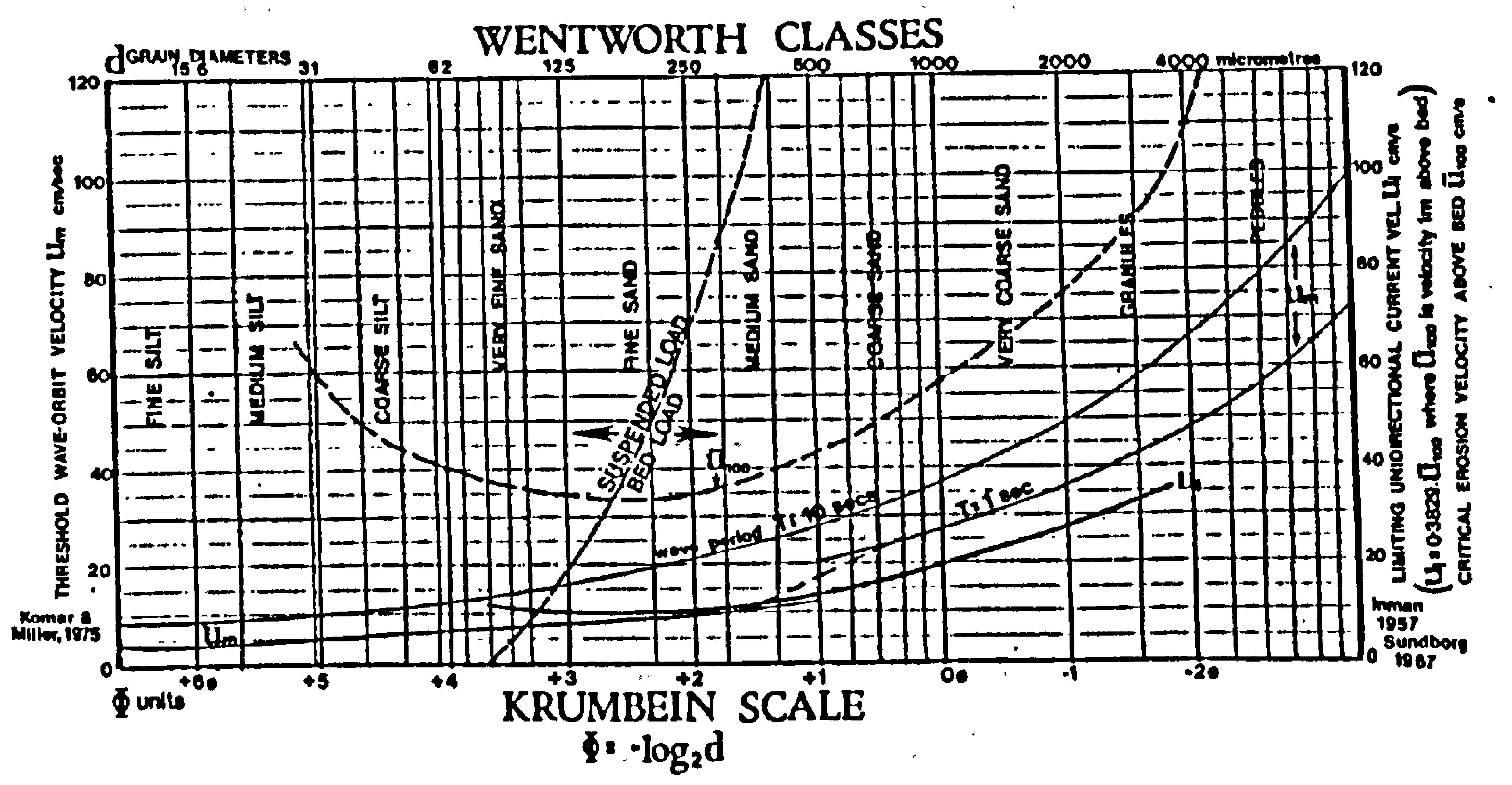


Fig. 2.6. Flow "velocities" (current speeds) needed for the initiation of movement in uncohesive, unconsolidated, well-sorted sediments composed of grains of specific gravity ca. 2.65 (i.e., quartz, cf. calcite 2.71, felspars 2.56–2.76). The wave-orbital, oscillatory, bottom currents of shallow-water Airy waves of 1 s and 10 s periods have speeds U_m, when:

$$U_m = \frac{\pi d_o}{T} = \frac{\pi H}{T \sinh(2h/L)}$$

where d_o is the near-bottom orbital diameter for an Airy wave of height (i.e. surface orbital diameter) H and wavelength L in water depth h. U_m will be the threshold velocity of grains of diameter D and specific gravity ρ_s, in water of density ρ, when empirically:

$$\frac{\rho U_m^2}{(\rho_s - \rho) g D} = 0.21 \left(\frac{d_o}{D}\right)^{1/2} \text{ for } D < 0.5 \text{ mm} \quad \text{or:} \quad \frac{\rho U_m^2}{(\rho_s - \rho) g D} = 0.46\pi \left(\frac{d_o}{D}\right)^{1/4} \text{ for } D > 0.5 \text{ mm}$$

according to Komar and Miller (1975). The corresponding thresholds under unidirectional currents have been estimated for speeds at the bed (U_l, after Inman, 1957) and 100 cm above the bed ($\bar{U}_{100}$, after Sundborg, 1967); each assumes that the bed is initially plane and horizontal. The relationship $U_l = 0.3829 \cdot \bar{U}_{100}$, given by Inman (1957), should be compared to the equivalent $U_l = 5.47 \cdot 10^{-2} \bar{U}_{100}$ given by Sternberg (1972), who defined boundary shear-stress τ_o as $3 \cdot 10^{-3} \bar{U}_{100}^2$ dynes/cm². The threshold ("limiting", "critical erosion") "velocities" are plotted here, lin-log, for the grain-size classes defined by Wentworth (1922) against the phi-scale proposed by Krumbein (1934, 1936). The limit between suspended-load transportation and bed-load transportation of these grains is from Sundborg (1967) and Sternberg (1972). (After Banner, 1979).

Observations for the eastern Irish Sea from Heaps and Jones (1977) model showed that during meteorological quiet periods with typical wind velocities of around 5 m s^{-1}, wind currents tend to dominate or be similar to surface density currents with velocities in the range of 1 to 3 cm s^{-1}. At these speeds the wind drift does not penetrate the water depth sufficiently to become superior to the bottom density currents. Characteristic near-bottom wind current velocities under these conditions are between 0 and 1 cm s^{-1}. At wind velocities higher than 5 m s^{-1}, wind-induced transport at the surface predominates over the density-induced transport, and conversely, for wind velocities below 5 m s^{-1}, the density-driven transport at the surface predominates over the wind-driven transport. A fivefold increase in wind currents will occur when wind speeds increase from 5 to 10 m s^{-1}, and this transport will dominate density-driven transport at all depths. A further fivefold increase in wind currents intensity will occur if wind velocities increase from 10 to 20 m s^{-1}, and under these conditions density currents will become comparatively insignificant. These observations are in agreement with those of Halliwell (1973) for the bed drifter study. One of the main conclusions of this author was that near bottom residual circulation was going to be affected during storms if wind speeds exceeded 30 km h^{-1} (8.3 m s^{-1}), and that if westerly wind was present at speeds higher than 50 km h^{-1} (13.9 m s^{-1}), wind generated waves would control near bed residual movement, in particular at depths less than 15 m. According to Halliwell (1973), winds from other directions in the Liverpool Bay area would only accelerate or decrease the near bed residual movement but not the direction. Heaps and Jones (1977) concluded that at the sea bed a variable flow pattern due to wind is superimposed on a relatively persistent and well established flow pattern due to density gradient.

14

2.3 SEDIMENT TRANSPORT IN LIVERPOOL BAY

It has been mentioned earlier that net sediment transport in the marine environment mainly depends on the currents at the sea bed, on the nature of the sediment, and on the mode on which sediment particles are being transported. Figure 2.6 indicates the role of grain size and current velocities in the initiation of movement of uncohesive, unconsolidated and well sorted sediments, and also shows the mode of transport in which these sediments would be transported given a particular combination of grain size and current velocity.

From data on currents in the disposal ground in Liverpool Bay given by Bowen *et al.* (1973), Norton *et al.* (1984a) calculated tidal velocities at 1 m above the sea bed (U_{100}), and from these values, calculated the corresponding friction velocities (U_*) for rough (sand and gravel) and smooth (mud) boundaries; the results are presented in Figure 2.7a. From this Figure, we can see

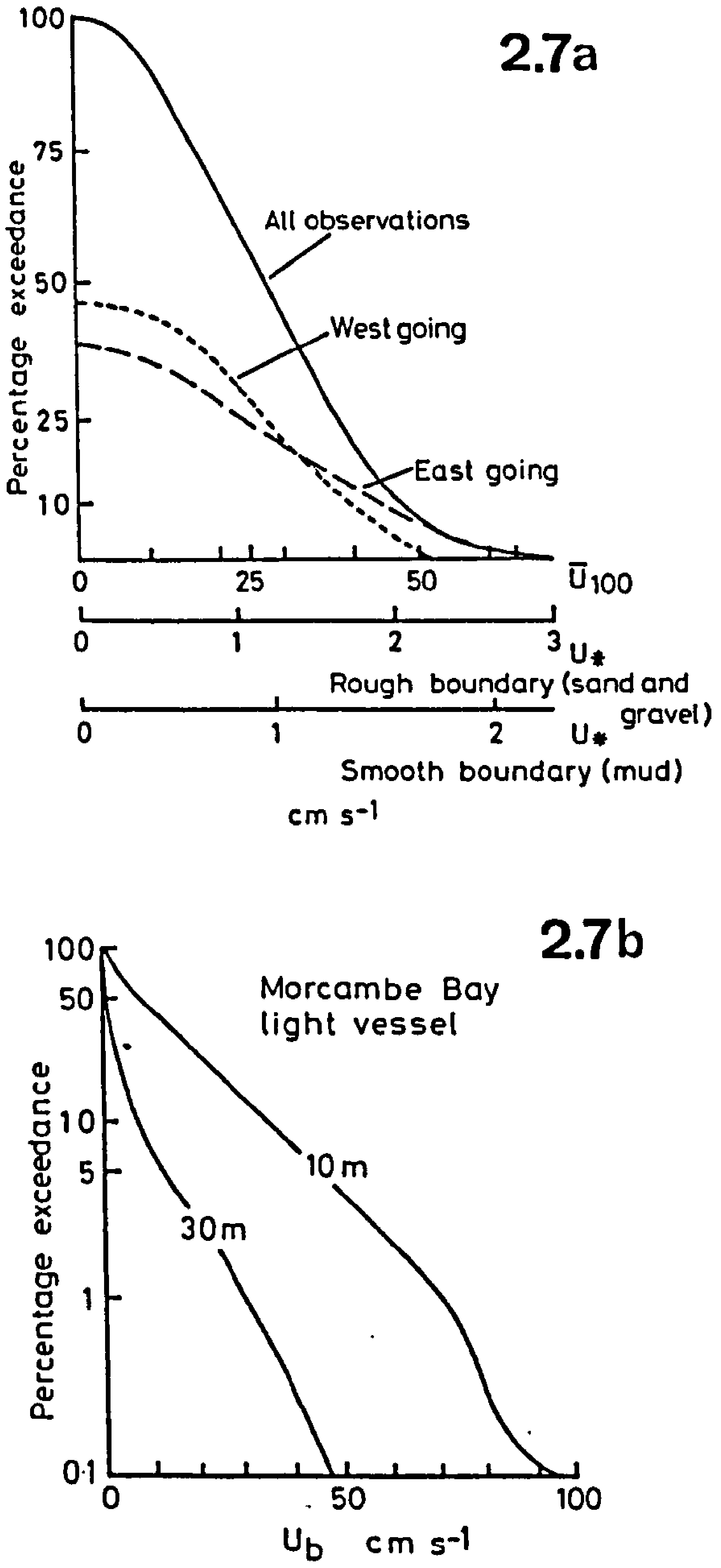


Fig. 2.7. (a) Tidal velocities 1 m above the sea bed and estimated friction velocities at the dumping ground: $\bar{U}_{100}$ = velocity 1 m above the seabed, U_* = friction velocity. (b) Wave induced near-bed velocities: U_b = maximum velocity attained during the passage of the wave. (After Norton *et al.*, 1984a).

Table 2.1. Estimated shear velocities (cm^{-1}) at Site SI and inshore. (After Norton *et al.*, 1984a).

	Dumping ground		Inshore	
	Tidal flow (rough boundary)	Wave-induced flow (30 m)	Tidal flow (smooth boundary)	Wave-induced flow (10 m)
Maximum	2.8	3.2	2.2	6.3
Value exceeded for 10% of time	2.05	0.6	1.6	2.5
Value exceeded for 50% of time	1.2	0.2	1.0	0.6

that maximum U_{100} values are around 75 cm s^{-1}; these maximum tidal velocities can move grains of up to 2000 μm in diameter (Fig. 2.6), therefore, during maximum tidal velocities most of the sediment of interest in this study will be eroded in the disposal area. For more than 15 percent of the time, values of U_{100} are higher than *ca.* 43 cm s^{-1} (Fig. 2.7a) the critical velocity for movement of 500 μm size particles, whereas approximately 30-35 percent of the time tidal currents will exceed 35 cm s^{-1}, the critical velocity for grains with size around 200 μm (Fig. 2.6). Therefore, for approximately 60 percent of the time tidal currents will not be strong enough to initiate movement of sediment particles in the dumpsite area of Liverpool Bay. An interesting feature arising from Figure 2.7a is that, due to tidal asymmetry, tidally generated currents with velocities (U_{100}) higher than 50 cm s^{-1} will occur only in an eastward or southeastward direction during the flood tide, therefore, according to Figure 2.6, sediment particles with diameter higher than 700 μm will be eroded, and transported only in the eastward or southeastward direction.

Figure 2.7 a and b, and Table 2.1 show the relative importance of tidal and wave induced currents in the possible transport of sediments in Liverpool Bay. Shear velocities in Table 2.1 show that tidal flows at the dumping ground are more important than wave-induced flows for most of the time, except during the most severe storms when maximum wave shear velocities are achieved. On the other hand, sediment transport induced by waves is relatively more important inshore than at the dumpsite as indicated by an increase in shear velocities in shallower waters. Although the main mechanism of sediment transport in Liverpool Bay may be the tidal flow, it is important to consider that tides and waves are occurring simultaneously so it is likely that the most significant transport of sediment will occur when the tidal movement is enhanced by wave motion. Sediment transport under the combined effects of tides and waves is a complex subject beyond the scope of this thesis, and a good review can be found in Dyer (1986).

The knowledge of the sediment transport paths after deposition is important to determine the sources and fates of chemicals in any study of pollutants in sediments, in particular, in an area such as Liverpool Bay where the possible sources are various, and the discharges differ in quality and quantity.

Studies of sediment transport paths in Liverpool Bay are scarce. As the direction of net sediment movement depends in part on the mode in which particles are being moved, direct observations of transport are difficult and indirect determinations of the paths become necessary.

An example of this complexity may be given if Figure 2.6 is analysed in a very simplistic manner. Considering first the case of sands with diameters of 200 and 300 μm, we can see that the threshold velocity U_{100} for both sizes is similar and around 35 cm s^{-1}. At around 40 cm s^{-1}

both grain sizes will be moving in bedload transport. If U_{100} is increased to 50 cm s^{-1}, particles of 200 μm diameter will initiate transport in suspension, and if the current velocity is increased to 60 cm s^{-1} these particles will certainly be transported in suspension whereas the bigger ones will remain in the bedload transport mode. Under these circumstances both grain sizes will be separated and will travel at different velocities and perhaps in different directions as particles in suspension will be transported more rapidly and will follow the current direction. Current velocities higher than 70 cm s^{-1} will be necessary to move particles with a 300 μm diameter in the suspended-load, therefore, it is likely that sand particles bigger than 300 μm will only be transported as bedload in Liverpool Bay even during the most severe storms.

It can be seen from Figure 2.6 that if movement of particles in the range of the very fine sand and smaller (muds) is initiated, these particles will be transported in suspension all the time, therefore, their transport paths will strongly depend on the bottom water movement paths. In the case of muds, however, further complications arise with regards to the processes of erosion and deposition due to the cohesive nature of these particles. Even though mud particles are smaller than very fine sands, higher current velocities are needed to erode muddy deposits due to the cohesive forces among particles. The higher the clay content in the mud, the greater current velocities are required to erode it.

Once in suspension, dispersed muddy particles are unlikely to be deposited unless flocculation takes place. In order for flocculation to occur, particles need to be close, therefore, the concentration of particles in suspension will be an important factor for mud deposition. Deposition of uncohesive, unconsolidated particles such as sands, is mainly controlled by one factor which also affects mud deposition, that is, the currents need to reach a critical deposition velocity below which gravity forces will dominate. These critical deposition velocities are usually smaller than critical velocities for erosion (Dyer, 1986). From the last observation it follows that once the sediments are moved, current velocities smaller than the critical erosion velocity are only required to maintain the sediments in motion. It is important to mention that natural sediments, such as those from Liverpool Bay, do not occur as single size populations but as mixtures of various grain sizes, therefore, processes of erosion and deposition will depend also on the grain size distribution within a particular area.

Several authors have reported an eastward- southeastward transport of sediments in the eastern Irish Sea. The accretion of the Mersey Estuary is one of the strongest evidences of a landward transport of sediment from Liverpool Bay. It has been estimated that only *ca.* ten percent of sedimentary material is transported into the Mersey Estuary from riverine sources, therefore, the remaining 90% is derived from the Liverpool Bay area (Taylor, 1986). In a study of siltation of the Mersey Estuary, Price and Kendrick (1963) suggested that Liverpool Bay has been an accretion area since at least 1861.

Based on a set of the strongest tidal currents and a few scattered sandwaves, Belderson (1964) suggested that some of the material passing northwards from the central or eastern side of the St. George's Channel may be transported eastward towards Liverpool Bay (Fig. 2.8a). This observation was substantiated by a model of sand transport paths resulting from tidal interactions reported by Pingree and Griffiths (1979).

More direct evidence on the possible sediment sources and transport paths within the bay have been provided by Sly (1966) and McLaren (1987). Sly (1966) presented a comprehensive report on sediment characteristics in Liverpool Bay including lithologies, detailed particle size descriptions, analysis of types of clays and fauna and flora assemblages, etc. The mean sand size values in this study decreased towards the coast and the general distribution indicated that the transport of sediment is mostly inshore. From mean sand size distributions Sly concluded that the tidal flow entering the bay is split into two main branches before reaching the sewage disposal site. South of Latitude 53°30' one stream follows a winding ESE course, while the other and more important tidal stream, North of 53°30', flows in a generally eastward direction with a strong flow towards the Mersey. These observations are in accord with the observations by Halliwell (1973) of bottom residual transport with bed drifters (Fig. 2.5). Observations of mean mud size by Sly (1966) showed no significant trends, but its size composition suggested that the present mud particles are derived from reworking of Boulder Clays deposits in the banks of the estuary and from sources in the Irish Sea. Regarding the source of muds Kirby (1987) concluded that the marginal estuaries in the Eastern Irish Sea are sinks rather than sources of sediments and pointed at the erosion of mud deposits within the Irish Sea (Fig. 2.8b) as the source of mud within this area.

The only study specifically designed to determine sediment transport paths in Liverpool Bay found in this literature review is the one by McLaren (1987). This author determined sediment transport patterns in the bay using a model based on the relative changes in complete grain size distributions of the bottom sediments. The results from this model (Fig. 2.9) revealed a preferential eastward direction of sediment transport, as sediments became finer, better sorted, and more negatively skewed in this direction. A second southeastward transport direction was also determined, with no other transport direction being found. McLaren concluded that very fine sand (125µm mode) is the size most easily transported in the eastward direction whereas fine

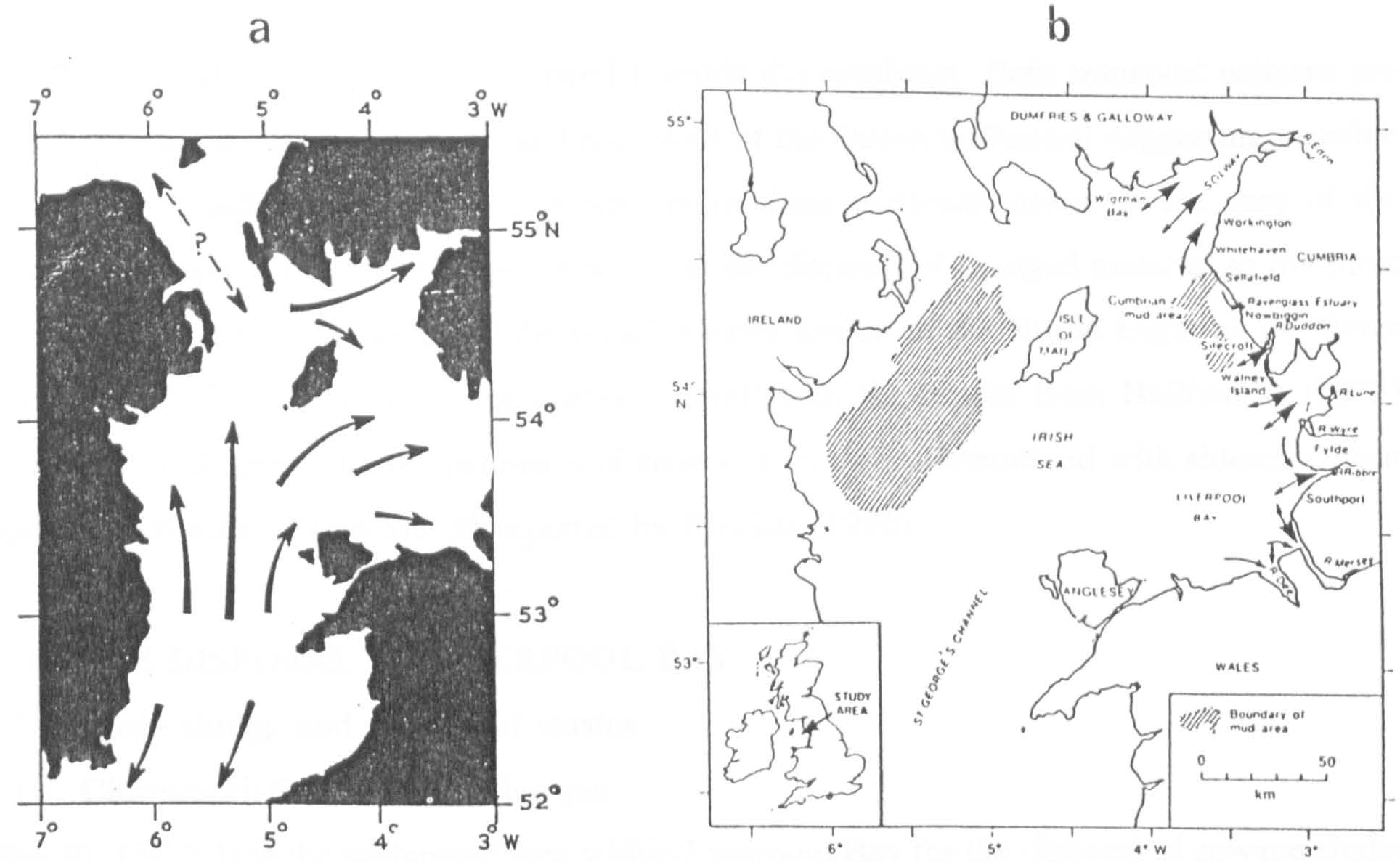


Fig. 2.8. (a) Bed transport patterns in the Irish Sea suggested by the set of strongest tidal currents and a few scattered sand waves. (After Belderson, 1964). (b) Postulated sediment transport pathways in the coastal margin of the eastern Irish Sea. The size of the arrow head indicates relative scale of exchange. (After Kirby, 1987).

2.9

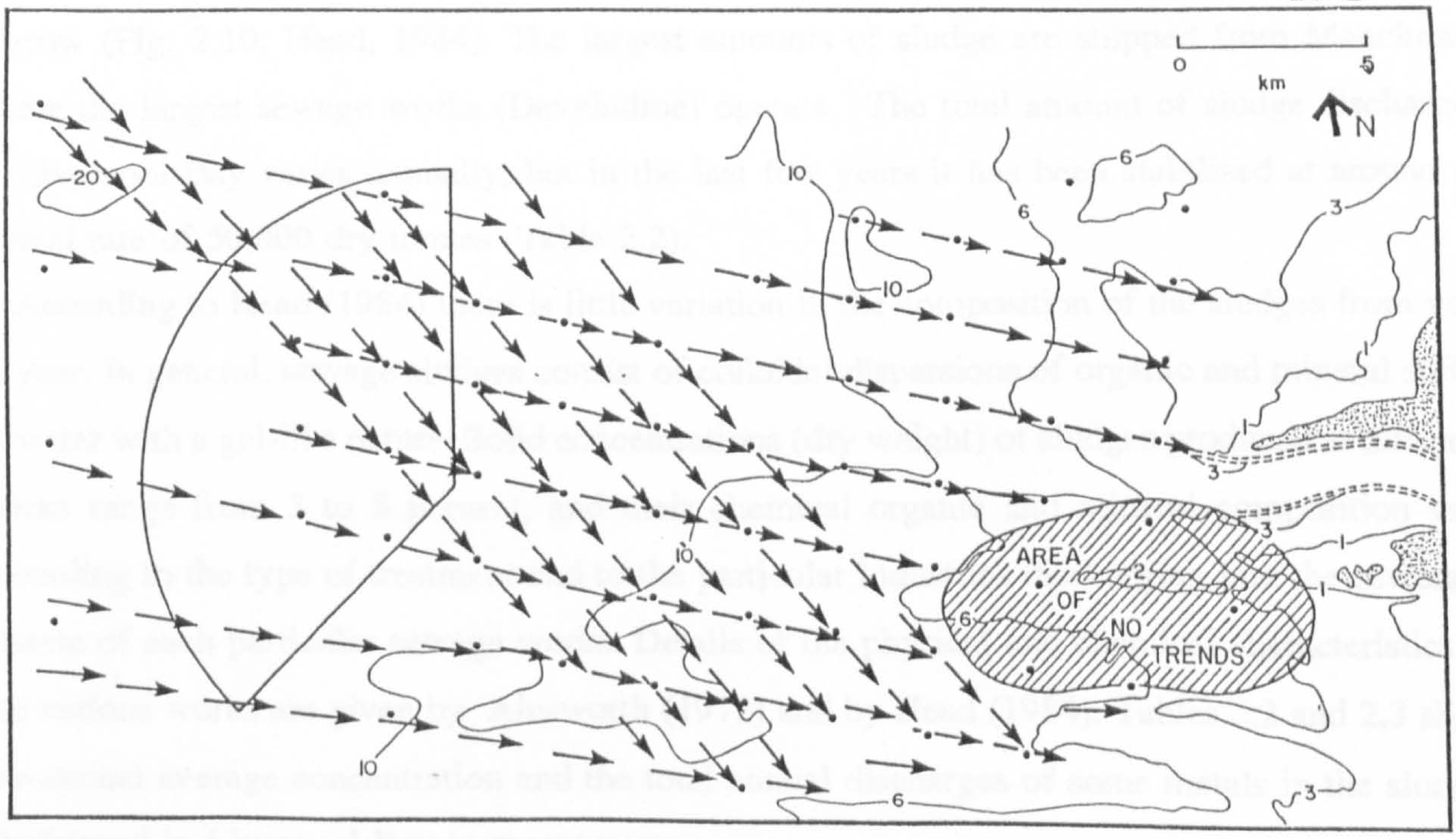


Fig. 2.9. Net sediment transport paths in Liverpool Bay derived from the complete grain-size distribution of several sediment samples. (After McLaren, 1987).

sand (250μm mode) is preferentially moved towards the southeast. Both transport patterns are interrupted near the Burbo Bight area and northwest of the Queen's Channel suggesting possible contributions of sediment from different sources in these particular areas. In the case of the northwest of Queen's Channel the author points at the disposal of dredged material as the most likely source of extra sediment, and the possible extra source in the Burbo Bight as the River Mersey. Results from this study also correlated well with the results from Halliwell's (1973) drifter study, and agree with the pathways of sediment transport determined with sidescan sonar images of bedforms around Site SI reported by Rowlatt (1986).

2.4. WASTE DISPOSAL IN LIVERPOOL BAY

2.4.1. Sewage sludge and industrial wastes

2.4.1.1. Characteristics of the discharges

Site SI (Fig. 2.1) is the designated area within Liverpool Bay for the disposal of sewage sludge and industrial wastes, most of it, generated within the catchment area presented in Figure 2.10 which includes the large conurbations and industrialized areas of the north west of England such as Merseyside and Manchester, and of North Wales.

Sewage sludges from the sewers in the region are received at various works where some kind of treatment, ranging from primary treatment to sludge digestion, will be given before the sludge is loaded and shipped to the disposal area from Manchester, Warrington, Salford, Runcorn or Barrow (Fig. 2.10; Head, 1984). The largest amounts of sludge are shipped from Manchester where the largest sewage works (Davyhulme) operate. The total amount of sludge discharged in Liverpool Bay varies annually, but in the last few years it has been stabilized at around an annual rate of 50,000 dry tonnes (Table 2.2).

According to Head (1984) there is little variation in the composition of the sludges from year to year. In general, sewage sludges consist of colloidal dispersions of organic and mineral solids in water with a gel-like nature. Solid concentrations (dry weight) of sludges produced at different works range from 3 to 8 percent, and their chemical organic and mineral composition vary according to the type of treatment and to the particular industries discharging into the sewerage system of each particular sewage works. Details of the physical and chemical characteristics of the various works are given by Ainsworth (1972) and by Head (1984). Tables 2.2 and 2.3 show the annual average concentration and the total annual discharges of some metals in the sludges discharged in Liverpool Bay in recent years.

2.10

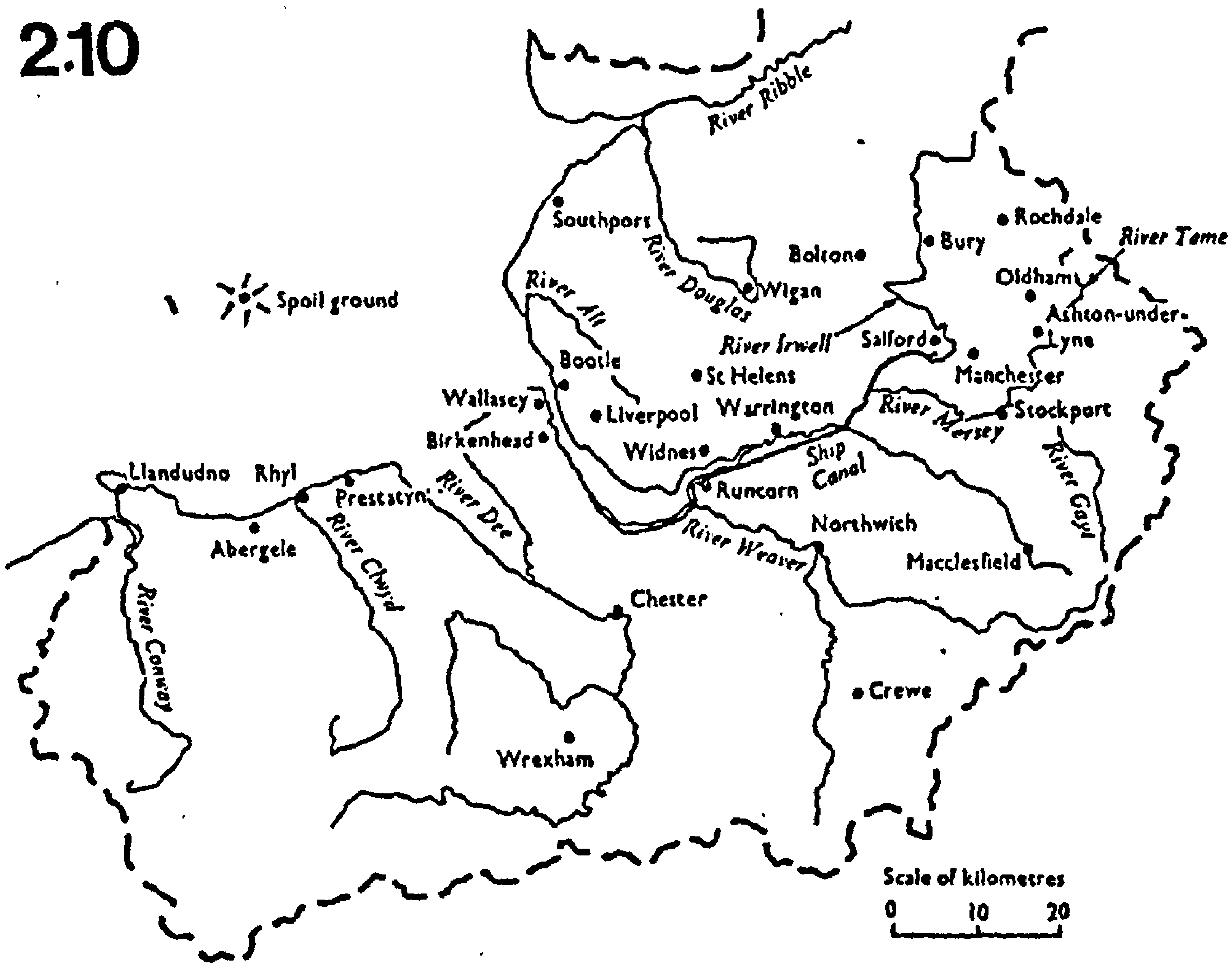


Fig. 2.10. Liverpool Bay and its catchment area. Some of the areas with largest population and industrial developments are indicated in this map. The main streams drainig directly or indirectly into the bay are also shown. (After Best *et al.*, 1973).

Table 2.2. Annual sewage sludge discharges at Site SI in Liverpool Bay and concentration of some trace metals in these sludges. (Unpublished data from North West Water, England).

LIVERPOOL BAY SLUDGE TO SEA - CONTAMINANT CONCENTRATIONS

Sludge quantities are tonnes per calendar year
Metal concentrations are mg kg^{-1} dry solids

YEAR	WET SLUDGE	DRY SLUDGE	Hg	Cd	Cu	Zn	Pb	Cr	Ni
1975		62 816	37	24		3485			
1976	1 586 888	70 386	38	30	1565	3665	780	1320	170
1977	1 688 805	69 983	36	29	1660	3360	940	1840	230
1978	1 664 605	65 244	14	30	1530	3525	890	1685	170
1979	1 650 472	69 626	10	24	1165	2900	790	1265	230
1980	1 805 969	71 350	11	20	950	3290	840	1090	140
1981	1 685 711	71 459	14	16	755	1960	925	840	75
1982	1 610 711	63 635	14	14	630	2075	960	740	95
1983	1 381 268	52 370	7.8	12	535	2560	955	690	115
1984	1 445 050	52 915	7.6	11	550	2155	815	755	125
1985	1 500 235	54 650	7.7	13	695	1920	880	895	75
1986	1 488 841	48 016	7.9	15	690	1830	875	980	110
1987	1 621 517	49 901	5.8	12	641	1985	640	1060	120
1988	1 625 321	45 309	4.2	11	640	1545	660	795	100
1989	1 642 680	50 545	3.5	11	685	1580	570	845	120

Table 2.3. Annual trace metal loads discharged at Site SI in Liverpool Bay. (Unpublished data from North West Water, England).

LIVERPOOL BAY SLUDGE TO SEA - CONTAMINANT LOADS

All quantities are tonnes per calendar year

YEAR	WET SLUDGE	DRY SLUDGE	Hg	Cd	Cu	Zn	Pb	Cr	Ni
1975		62 816	2.3	1.5		219			
1976	1 586 888	70 386	2.7	2.1	110	258	55	93	12
1977	1 688 805	69 983	2.5	2.05	116	235	66	129	16
1978	1 664 605	65 244	0.9	1.95	100	230	58	110	11
1979	1 650 472	69 626	0.7	1.7	81	202	55	88	16
1980	1 805 969	71 350	0.8	1.4	68	235	60	78	10
1981	1 685 711	71 459	0.52	1.14	54	140	66	60	5.4
1982	1 610 711	63 635	0.60	0.87	40	132	61	47	5.9
1983	1 381 268	52 370	0.41	0.64	28	134	50	36	6.0
1984	1 445 050	52 915	0.40	0.60	29	114	43	40	6.7
1985	1 500 235	54 650	0.42	0.69	38	105	48	49	4.2
1986	1 488 841	48 016	0.38	0.73	33	88	42	47	5.4
1987	1 621 517	49 901	0.29	0.61	32	99	32	53	5.9
1988	1 625 321	45 309	0.19	0.50	29	70	30	36	4.4
1989	1 642 680	50 545	0.18	0.54	35	80	29	43	6.2

Industrial wastes discharged at Site SI, either directly or indirectly (mixed with sewage sludges), originate from several industries in the region. As an example of the variety of sources of industrial waste, a list of the principal type of industries discharging wastes in the Manchester area sewerage system is presented: petrochemicals, dyestuffs, pharmaceutical, general chemicals, textiles, rubber, brewing, food, paper, detergents, etc. (Ainsworth, 1972). Industrial wastes dumped at Site SI constitute only a small proportion of the total solids annually discharged at this site (Table 2.4), and their contribution to the total metal input at this site is less than 0.5% (Norton *et al.*, 1984b).

2.4.1.2. Sewage sludge behaviour after disposal

Approximately 7000-8000 wet tonnes of sewage sludge, equivalent to *ca.* 200 t of dry solids, is dumped each weekday at Site SI, usually at low tide (Rowlatt, 1986). Sewage disposal vessels with capacity ranging from 500 to 3000 t, discharge their cargoes while moving at velocities of 2-3 m s^{-1}; up to four vessels may discharge during any one tide (Norton *et al.*, 1984a).

Crickmore (1972a) studied the initial behaviour of sludge dumped at Site SI, and estimated a dilution of the sludge of 1 to 200 immediately after the discharge. Due to this high initial dilution, even big differences in density of the sludges did not reflect in different initial vertical spreading of the sludges. Based on experimental observations of settling velocities of sludge particles and on field observations, Crickmore (1972) concluded that the settling velocity of the sludge solids is low, and that the time for the sludge particles to reach the sea bed will be primarily a function of vertical diffusion, under non-stratified conditions of the water column in which his field observations took place.

Crickmore (1972a) suggested that the assumption of neutral stability of the water column is applicable for most of the flood and over high water, but during the ebb vertical salinity gradients may be established. Transport of sludge particles towards the bottom, due to eddy diffusion, may be inhibited if vertical density gradients are established (Crickmore, 1972a; Barret *et al.*,1972; Talbot, 1972). Barret *et al.*, (1972) and Talbot (1972), estimated that under non-stratified conditions sludge particles would be dispersed down to the sea bottom in 2-2.5 h, with eddy diffusion acting as the most important transport agent.

Barret *et al.* (1972) studied the sludge dispersion in sea water by following the distribution of sewage sludge, labelled with silver-110m before being discharged at Site SI. The main observations of these authors were that: suspended sludge particles were rapidly dispersed in the horizontal along the prevailing tidal stream; vertical mixing of sludge was more intense during

Table 2.4. Inputs of sewage sludge, industrial wastes, and dredged spoil via dumping at various sites in the Irish Sea including Liverpool Bay in 1984. (After MAFF, 1987).

Location	Total weight	Organics	Solids	Cd	Cr	Cu	Ni	Pb	Zn	Hg	Ocs	N	P
Liverpool Bay													
Sites 114-120 incl.													
Industrial	28 924	1 894	4 527	0	0	0.1	0.1	0	0.5	0	0	77	-
Sewage sludge	1 279 050	49 303	49 303	0.6	41.1	26.4	3.1	47.4	143.1	0.3	3.6	2.232	838
Dredge spoil	3 545 000	-	1 371 947	1.1	113.3	103.3	60.9	191	560.7	3.1	0.1	-	-
Holyhead Site 111													
Dredge spoil	10 400	-	10 088	0	0.2	1.2	0.8	1.7	2.2	0			
Outer Morecambe Bay													
Sites 122/124													
Dredge spoil	688 500	-	513 400	0	6.9	12.3	0	20.7	34.4	0.5			
Cumbria Coast													
Site 127 Dredge spoil	119 600	-	59 800	0	1.2	1.2	0	4.8	7.2	0			
128 " "	353 600	-	176 800	0.2	7.1	7.1	17.7	31.8	0.1	0			
132 " "	85 600	-	42 800	0	1.7	4.3	0	3.4	8.6	0			

the flood tide than on the ebb; and that the concentration of sludge particles in the water also decreased by deposition.

During periods of stratification when sludge transport towards the bottom is inhibited, horizontal circulation becomes a dominant factor in sewage sludge dispersal in the bay. Conditions for stratification are met during calm periods with low wind stress, and high freshwater discharges during the winter or large heat fluxes during the summer (Czitrom-Baus, 1982). According to Rowlatt (1986), during these periods sewage particles retained in surface waters will probably follow the clockwise circulation pattern, typical of density driven circulation and move south and west before settling into the south-eastward flow of bottom waters (see text above, Section 2.2.2). Sludge particles with smallest size will be transported longer distances in the horizontal due to their smallest settling velocities, whereas larger particles will settle through the water column and reach the bottom more quickly. However, chemical, physical and/or biological processes such as oxidation, flocculation, zooplankton ingestion and faecal pellets formation may play an important role on sedimentation rates by enhancing or reducing the particles size (Rowlatt, 1986).

Rowlatt (1986) estimated that considering the period of initial settlement to be 2 h (Talbot, 1972), and a typical tidal velocity to be 80 cm s^{-1}, the settlement of sludge particles at the sea bed would be pronounced about 6 km east of Site SI. In this calculation it is also necessary to consider that most of the discharges take place at low water, therefore, initial sludge movement after the disposal will be in the direction of the flood when maximum vertical mixing occurs and, as a consequence, vertical stratification is not present to inhibit eddy diffusion. This calculation was substantiated by the distribution of faecal bacteria in sediments observed by the author (Fig. 2.11), and by the distributions of metals reported by McLaren (1987) where maximum concentrations are reported approximately 5 km east of the dumping ground.

Once deposited on the sea bed the sludge particles may flocculate or become associated with sediment particles (Rowlatt, 1986). Crickmore (1972b), following the radiolabelled sewage sludge study by Barret *et al.* (1972), studied the dispersion of the sludge on the sea bed and concluded that the two main factors controlling the near-bed sludge behaviour were the tangential shear from water currents and the type of bed on which particles fall. This author suggested that bed composition is more important than zonal differences in current velocity in relation to retention of sludge particles. Interstices in gravelly sediments providing shelter from shear forces exerted by flow, and cohesive forces associated with smooth muddy sediments inhibit further resuspension of sludge particles once deposited, whereas agitation of surface layers of sandbeds

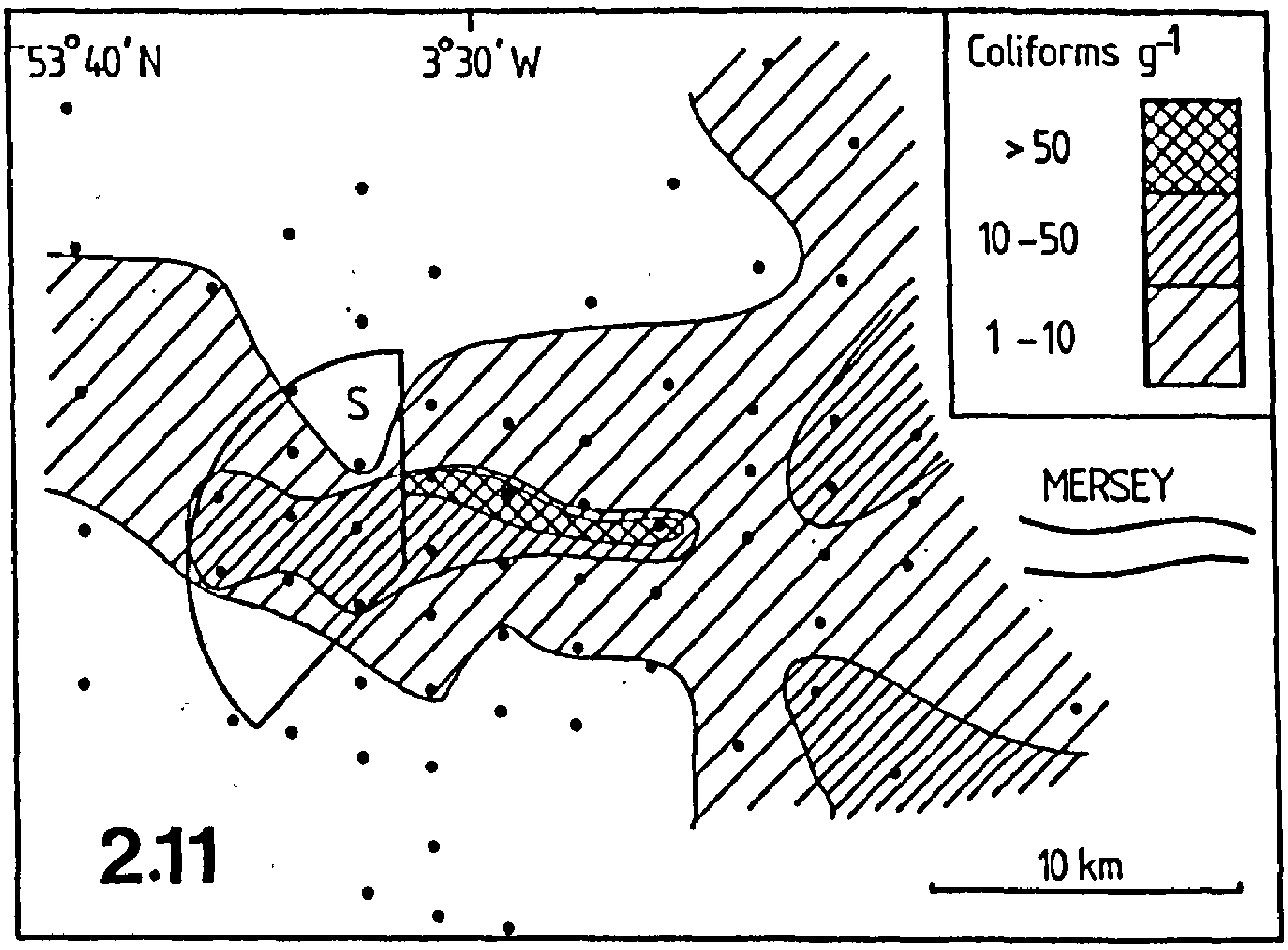


Fig. 2.11. Distribution of faecal coliform bacteria in Liverpool Bay sediments, 1980. (After Rowlatt, 1986).

associated with ripple movement acts against retention of deposited sludge particles. Crickmore (1972b) found a correlation between the distribution of the radiotracer and muddy zones in the bay, and this correlation was weaker only near the release area, suggesting an initial association of sludge particles to the sediment irrespective of its composition. Sludge particles may initially move as bedload in association with sand deposits in the general south to southeastward direction previously mentioned in this chapter, but as the critical tidal shear stress values are exceeded for 60% of the time over sand but never over mud near Site SI, sludge particles resuspension from sand deposits will occur more than half of the time and not at all over muddy deposits due to tidal currents (Rowlatt, 1986). Once resuspended the sludge particles will move in the direction of bottom residual currents towards the east-southeast most of the time, and will be deposited in zones where the conditions for mud deposition occur, therefore, becoming preferentially associated to muddy deposits. In contrast to sandy deposits, muddy deposits near the dumpsite will only be disturbed during stormy conditions (Crickmore, 1972b).

In agreement with the general patterns of near-bottom water and sediment transport, Crickmore (1972b) detected the presence of radiolabelled sludge distributed along a line in the direction of the tidal currents, and in muddy deposits of the coastal area of North Wales, the Dee Estuary, and preferentially in the Mersey Estuary. As there are very few areas within the bay where permanent deposition of fine particles can take place, sludge particles are subjected to multiple cycles of deposition and resuspension, which lead to a wide dispersion of sewage sludge throughout the sediments of Liverpool Bay (Crickmore, 1972b).

2.4.2. Dredged material

Sites Y and Z (Fig. 2.1) are the designated areas within Liverpool Bay for the disposal of wastes originating from the maintenance dredging of the channel approaches to the River Mersey, the river itself, the docks and harbours along its length, and the Manchester Ship Canal (Norton *et al.*, 1984a). The dredged spoils annually dumped in the bay amount to approximately three million tonnes, 95% of which is discharged at Site Z. The major part of this material is sand (~70%) and the remaining (~30%) are muds containing the bulk of the trace metal contaminants (Rowlatt *et al.*, 1986). Table 2.4 shows the annual amount of metals and other chemicals discharged in Liverpool Bay in 1984, as compared to their loads into the bay via dumping of sewage and industrial wastes.

Rowlatt *et al.* (1986) studied the effect of dredging spoil disposal on sediments in an area around the "new" Site Z (Fig. 2.1) and the "old" Site Z located approximately 3 km to the north-east. These authors suggested that the mud fraction from the dredging material is rapidly moved away from the disposal site, as the possibility of it being covered by sand deposition was discarded after the analysis of cores taken at the old site. Fine particulate material including cohesive sediments in this shallow area (~10 m deep, Fig. 2.1) is more likely to be moved by tidal action and stirred by waves during storms than particles in deeper areas, therefore, dispersion of fine particles in this Site is favoured. Sands in this area are also mobile but the shoaling of the old Site Z during recent years suggests that the dispersive capacity of sands in this zone is limited (Rowlatt *et al*, 1986).

Although the largest quantity of material dumped in Liverpool Bay is dredged spoil (Table 2.4), it is important to consider that this is mainly a redistribution of sediment material, often of a transient nature, as most of this sediment is returned back into the Mersey system by currents (MAFF, 1987; Halliwell, 1973; Agar and McDowell, 1972).

2.4.3. Other discharges

Apart from dumping of sewage sludges, industrial wastes and dredged spoil at designated sites, Liverpool Bay receives direct or indirect discharges of wastes from coastal sources. These inputs can be categorized in: river inputs, sewage effluent discharges, discharges of untreated sewage, and industrial effluents. Considering that the general transport of sediment and bottom water residuals are predominantly towards the coastal areas in the bay, it is likely that coastal point sources such as sewage outfalls will have only a localized effect near the discharge point rather than an effect in the whole bay. However, dissolved materials may enter the general circulation system in Liverpool Bay and therefore even point sources may have a more generalized effect over the bay.

The potential effects on water and sediment quality of the chemicals from all the different sources will depend on the exact nature of the material discharged as well as the location of the discharge, and is difficult to predict. Table 2.5 shows a summary of the relative contributions of the main sources of inorganic contaminants into Liverpool Bay, more detailed information about inputs from the various particular sources is given by Osbaldeston (1984). In general it can be said that dredged spoil dumping is the largest source of nickel, lead and mercury, and a large source of copper and zinc, while sewage sludge dumping is a major input of copper and is secondary with respect to the other metals particularly mercury. River discharge is the main source of cadmium with important contributions of copper and nickel whereas direct sewage and industrial discharges constitute the largest inputs of zinc and major sources of mercury (Norton

Table 2.5. Inputs of trace metals from various sources into Liverpool Bay in 1976 (t yr^{-1}). (After Norton *et al.*, 1984b).

Source	Hg	Cd	Cu	Pb	Zn	Cr	Ni
River discharge	0·3	34	75	ND	155	80	98
Direct sewage/ industrial discharges	2·8	16	53	47	1490	153	74
Dumped sewage sludge	2·7	2·2	110	55	265	93	13
Dumped industrial wastes	0	0	0·7	0·4	0·9	0·1	0·1
Dumped dredged spoils	4·4	1·3	110	330	800	145	105

et al., 1984b, c). No data have been found with regards to atmospheric inputs into Liverpool Bay, therefore, the importance of these inputs can not be assessed. However, it is expected that atmospheric pollutants will be evenly spread (before being redistributed once in the water and sediments) over a small area such as Liverpool Bay, therefore, it is unlikely to expect spatial variations in the distribution of pollutants within this area attributable to atmospheric inputs.

2.5. EFFECTS OF WASTE DISPOSAL IN LIVERPOOL BAY

2.5.1. Water quality studies

Several reports on the effects of waste disposal on water quality in Liverpool Bay have been published most of them under the auspices of the DOE, MAFF, and/or the North West Water Authority (NWWA). Most of these studies are only concerned on the effects of the discharges on concentrations of nutrients and/or trace metals, leaving the effects on other pollutants, particularly of organics such as PCBs, virtually unknown.

2.5.1.1. Nutrients

Investigations on nutrient concentrations have shown that the main sources of these dissolved species into Liverpool Bay are from the river inputs particularly from the Mersey (Abdullah and Royle, 1973; Spencer, 1972,1984; Foster *et al.*, 1985, 1982, 1977; Miller, 1985). Most of these nutrients originate from the discharges of treated and untreated sewage into the River Mersey and its estuary. The dispersion of freshwater into the bay controls the final distributions of nutrients, particularly during the winter months when primary productivity is minimal and, as a consecuence, biological nutrient consumption is negligible (Spencer, 1984). The dependence of nutrient concentrations on the dispersion of freshwater is reflected in high correlations between salinity and nutrients (Abdullah and Royle, 1973; Spencer, 1984; Foster *et al.*, 1985), and in the consistency amongst water circulation patterns and nutrient distributions particularly studied in surface waters (Foster *et al.*, 1985; Miller, 1985). During the summer these correlations are weakened by lower freshwater discharges and an increase in the biological consumption of nutrients by the phytoplankton (Spencer, 1984; Foster *et al.*, 1985).

The contribution of sewage sludge dumping to the overall nutrient enrichment in the bay is minimal as compared to freshwater inputs, and due to the rapid dispersion of the sludge after disposal, it is likely that a particular discharge will only have a very localised effect around Site SI for a short period. However, as freshwater discharges are reduced during the summer and the sludge discharges remain relatively constant throughout the year, sewage sludge effects on nutrient concentrations will be more important during the summer than in winter (Spencer, 1984). More detailed information on the effects of waste discharges in the bay on nutrients can be found in the references quoted above.

2.5.1.2. Trace metals

Most of the studies on trace metals in the water column of Liverpool Bay, both in the dissolved and particulate phases, have been particularly designed to assess the effects of sewage sludge disposal at Site SI (Norton *et al.*, 1984c; Rowlatt *et al.*, 1984; Burrows and Sharples, 1973; Spencer, 1984). However, other studies of dissolved metals in the bay with a more general scope have been also published (Nimmo *et al.*, 1989; Abdullah and Royle, 1973). Although the density of sampling stations in most of these works does not permit the evaluation of local effects such as sludge dumping at Site SI or dredged spoil disposal at Sites Z and Y, there is an obvious general pattern of decreasing concentrations of dissolved metals away from the freshwater discharges particularly from the Rivers Mersey and Dee, suggesting that river inputs are the main source of dissolved metals in the bay.

Norton *et al.*(1984c) measured the concentrations of zinc, copper, cadmium and nickel in solution and suspension in an area within and around Site SI, and determined the short term effects (sampling at the end of a week when ~40,000 wet tonnes were dumped) and long term effects (sampling three days after the last discharge) of sludge dumping in the water quality. High negative correlations between all dissolved metals and salinity were found for the whole area in both samplings, suggesting that the riverine and estuarine discharges are the most important sources of these dissolved species in the bay. However, when only the samples within Site SI where considered, these authors found that whereas zinc and copper concentrations remained highly correlated with salinity, no significant correlations between salinity and the concentrations of cadmium or nickel were found when the survey took place after dumping. These authors concluded that, immediately after a discharge, some of the cadmium and nickel present in the sludges may dissolve producing a very local and short lived effect on the concentrations in solution of these metals whereas copper and zinc remained strongly associated to the particulate phase and, therefore, no apparent local effects are observed for these metals in solution. These observations are consistent with laboratory experiments with sewage sludge in seawater showing that the loss of metals from the particulate phase during the first 48 h is small, with cadmium being the most labile followed by nickel (Norton *et al.*, 1984c). In a study of the chemical speciation of dissolved metals including nickel, copper and iron in Liverpool Bay, Nimmo *et al.*

(1989) confirmed the local effect on dissolved nickel concentrations caused by sludge dumping. These authors suggested that this sewage-derived dissolved nickel is largely present in the colloidal fraction whereas dissolved nickel from other sources is largely in the labile fraction of the total dissolved metal. Nimmo *et al.* (1989) had dissolved copper results also in agreement with Norton *et al.* (1984c) findings, although the former noted elevated labile dissolved copper levels around the mid-North Wales coast and a similar increase in the seston concentrations around this area. Localised coastal quarry waste deposits were suggested as possible sources of this dissolved copper (Nimmo *et al.*, 1989).

Literature regarding concentrations of dissolved metals in Liverpool Bay, other than the mentioned previously, is scarce. Even mercury which is one of the metals that causes more environmental concern does not seem to have been studied in detail in the waters of the bay, however, several references can be found for the River Mersey and its estuary (see Campbell *et al.*,1986 and references therein). It is possible that, as suggested by Campbell *et al.* (1986), the strong adsorption of mercury onto particles may inhibit an enrichment of local waters after disposal at Site SI making sludge dumping an unlikely important source of dissolved mercury in the bay, however, these authors found a seawards increase in dissolved mercury and its source was not positively identified. On the other hand, MAFF (1990) reported concentrations of total dissolved, reactive dissolved and total in unfiltered water mercury decreasing away from the River Mersey. The steep gradient in the concentrations of the total mercury in unfiltered water suggest that mercury from estuarine and point sources is quickly adsorbed by suspended sediments, leaving only a very small proportion of mercury in the dissolved phases as suggested by the fairly weak gradients in the surface water distributions of total dissolved and reactive dissolved mercury presented by MAFF (1990).

Regarding the particulate phase, in the survey three days after dumping Norton *et al.* (1984c) observed that the mean concentration of metals on suspended particles at Site SI was not significantly higher than in the rest of the bay, suggesting that the dispersion and/or settlement of the sludge particles during the three days after disposal was fairly complete. On the other hand, immediately after dumping all metals showed significantly higher concentrations in particles within Site SI than in the surroundings. Given the contrast of results between the two surveys these authors concluded that sewage sludge disposal at Site SI has a marked local effect on the concentrations of metals on suspended particles, but this effect is short-lived. Rowlatt *et al.* (1984) suggested that this effect lasts around 1-2 days, although it is important to consider that the period of the effect after a particular discharge will depend on the meteorological and hydrographic conditions (tides and stratification particularly) prevailing during and after the discharge. In a study of metals in bed sediments and in suspended particles near the bottom in the Eastern Irish Sea, Rowlatt *et al.* (1984) found concentrations in suspension of copper, zinc and nickel (26.5, 301 and 31.9 $\mu g\ g^{-1}$ respectively) close to their "benchmark" values (~24,~240, and ~32 $\mu g\ g^{-1}$ respectively) for samples collected near Site SI two days after the last sewage sludge discharges. These authors suggested that these particles were probably transported into the Liverpool Bay area from relatively clean zones offshore, as could be expected from the known sediment transport and bottom residual circulation pathways.

2.5.1.3. Polychlorinated biphenyls

No background information could be found in relation to PCBs in solution and/or suspension in Liverpool Bay, therefore it is difficult to point out the main possible sources of these xenobiotics in the dissolved and particulate phases in this area. However, it is likely that as in the case of nutrients and heavy metals, freshwater inputs of dissolved PCBs into the bay may be important. The study by Nimmo *et al.* (1989) point at the river Mersey and the Dee as possible significant contributors of dissolved organic matter (fluorescent material) into the bay, this observation was substantiated by the highly significant correlation between fluorescent material and salinity. MAFF (1990) also reported an inverse linear relationship between salinity and the log of total hydrocarbons in solution which also suggests that the River Mersey is an important source of dissolved organic substances, however, samples were taken at only seven positions in the bay therefore the possible contributions from other sources can not be evaluated. This author reported considerable scatter in plots of total hydrocarbons vs suspended particulate material concentrations, therefore, no discernible relationships amongst these two variables could be established.

2.5.2. Quality of biota

In order to determine the quality of fish and shellfish for human consumption, and to assess the possible risk posed by the contaminant levels to fish and shellfish stocks, MAFF has carried out continuous surveys around the British coastal areas including Liverpool Bay. Although it is apparent from these surveys that, for the most parts, neither fish and shellfish nor man are at risk from the reported levels of contaminants, monitoring of biota has continued in order to use fish and shellfish as indicators of changes in marine environmental quality occurring as a result of changes in the quality and quantity of waste discharges into the coastal marine environment.

Analyses of biota have been mainly focused to assess the levels of toxic metals, particularly copper, zinc, cadmium, lead and mercury, and the levels of organic substances particularly chlorinated pesticides and PCBs. Most of the information that follows has been obtained from the reports by Franklin (1987), MAFF (1990), and Murray and Norton (1982) which present results on fish and shellfish from the 1977-1984 and 1984-1987 monitoring programmes by MAFF, and include references for more detailed information on this subject.

Results from samples taken in Liverpool Bay showed that none of the species of fish and shellfish presented any significant spatial variations for any of the metals analysed, as would be expected in view of the relatively small area sampled and the mobility of the fish (Murray and Norton, 1982). Therefore, as it is has been difficult to relate the level of contaminants to a particular discharge such as sewage sludge inputs or coastal inputs, most of the results of quality in biota reported for Liverpool Bay are compared with other areas in England and Wales.

Mercury in fish from Liverpool Bay and Morecambe Bay are the highest around the coastal zones of England and Wales. Only these two areas show concentrations near the upper level of the guidelines adopted by the Joint Monitoring Programme (JMP) of the Oslo and Paris Commissions (MAFF, 1990; Franklin, 1987). Even though mercury concentrations in fish from these two areas are the highest, mercury levels are below the limit of the Environmental Quality Standard (EQS) of 0.30 $\mu g\ g^{-1}$ wet weight, furthermore, there seems to be a trend of reduction of mercury levels in fish in Liverpool Bay as shown by the annual average concentrations of 0.29, 0.26, 0.27, 0.23, 0.20, and 0.20 $\mu g\ g^{-1}$ for the period of 1982 to 1987. High levels of mercury in the bay are probably related to the presence of chlor-alkali plants in the industrial area surrounding the Mersey river and estuary. Mercury levels in shellfish from Liverpool Bay are not particularly elevated in comparison to other areas (Franklin, 1987; MAFF, 1990; Murray and Norton, 1982).

With regard to other metals, there is no apparent indication of serious contamination of fish by copper, cadmium, lead and zinc as compared to other regions. The same observation can be applied to these metals in shellfish, with the exception of lead in mussels that present levels higher than several other areas but still about half the limit specified in the Food Regulations for shellfish of 10 $\mu g\ g^{-1}$ wet weight (Franklin, 1987; MAFF, 1990).

Some organochlorine compounds in fish liver tissue and shellfish from Liverpool Bay present elevated concentrations in relation to other coastal areas. Particularly elevated are the levels of dieldrin, DDE and TDE in whiting liver, and PCBs in liver tissue in whiting, plaice and dab. Total PCB concentrations in these species were ~5.1, ~1.2, and ~2.2 $\mu g\ g^{-1}$ respectively, and in the upper category of the JMP guidelines (>5.0 μg g^{-1} for cod liver, that may represent roundfish in general, and >1.0 μg g^{-1} for flounder liver representing flatfish) (Franklin, 1987). As the knowledge of the inputs of these substances is limited, it is difficult to assess the sources of organochlorine enrichment in the biota from the Liverpool Bay area. However, the estimated input of PCBs into the bay via dumping of around 0.8 kg d^{-1}, as compared with the estimated 0.12 kg d^{-1} entering the Thames Estuary in a larger amount of sludge, suggests that sewage sludge disposal at Site SI may be a significant source of the high levels of PCBs in fish and shellfish in Liverpool Bay (Murray and Norton, 1982).

CHAPTER 3. METHODS

3.1. SAMPLING

Surface sediment samples were taken at each of the seventy stations shown in Figure 3.1, by means of a 0.1 m^2 Day grab. This type of grab has been extensively used for sediment surveys by MAFF and UCNW because of its reliability and ease of operation. This grab permits seabed sampling down to a maximum depth of 15 cm with sediment structures and sediment surface generally remaining intact, and loose organic floccules present at the sediment/water interface appear to be retained (Eagle *et al.*, 1978).

After recovering the grab, the top 3 cm of sediment were subsampled with an acid washed plastic spoon for the trace element analysis and with a solvent cleaned metal spoon for the PCBs analysis. The sediments for trace element determinations were stored in heavy duty plastic bags and sediments for PCBs in glass jars with aluminium caps, precleaned as described below in Section 3.4. Both sets of samples were immediately frozen on board and transferred to freezers in the laboratory once on land. All samples were stored frozen until analysed.

3.2. TRACE ELEMENT ANALYSIS

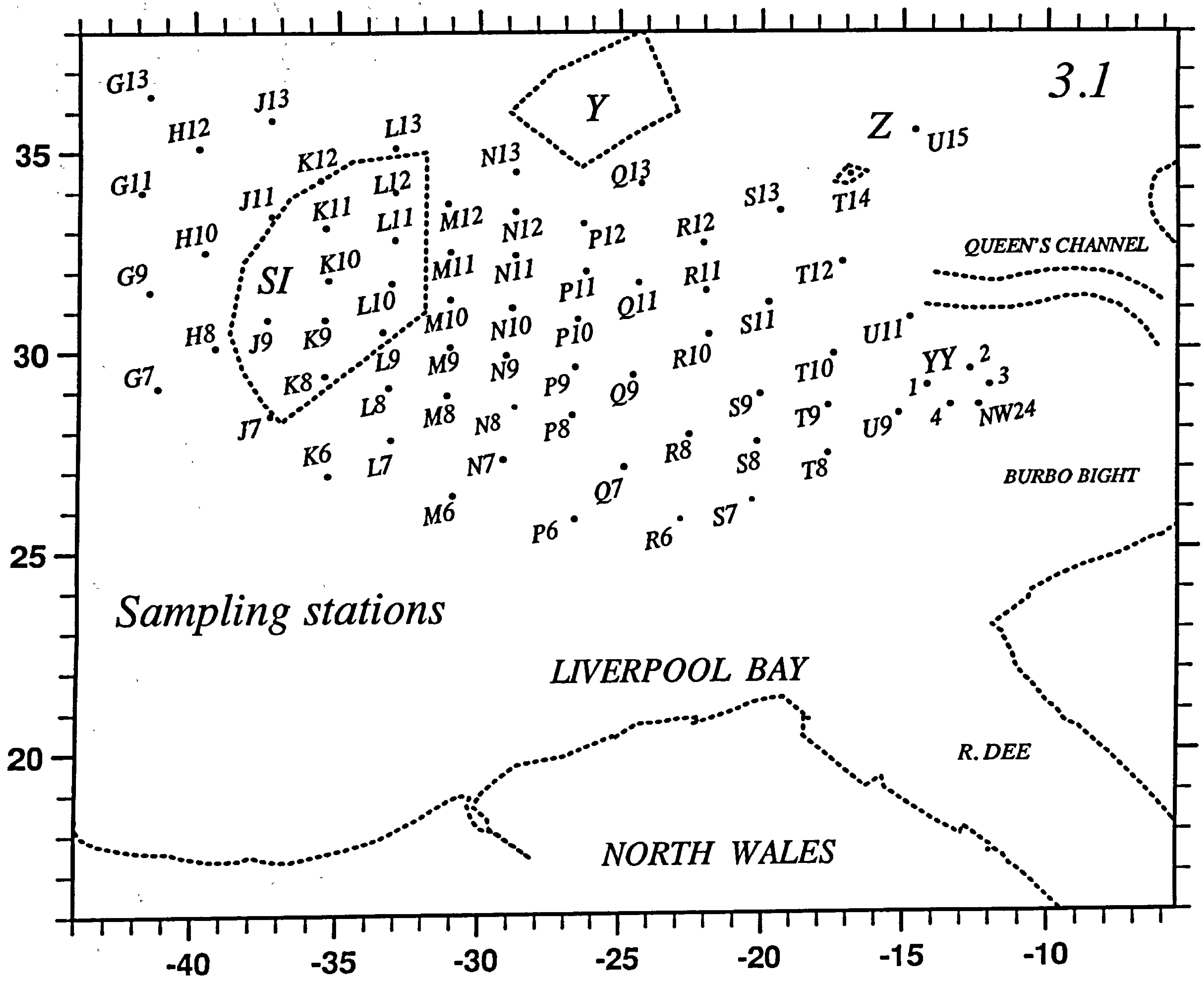
3.2.1. Glassware and plasticware cleaning

All the glassware and plasticware used in the trace element analyses was cleaned prior to its use to avoid sample contamination. The cleaning procedure consisted of thoroughly rinsing the material with tap water, soaking in a 10% nitric acid solution for at least 24 h, thoroughly rinsing with tap water, and finally rinsing three times with distilled water.

3.2.2. Sample fractionation

Sediment samples were defrosted overnight at room temperature. Once defrosted, the whole sample was transferred into a 2 litre plastic beaker and homogenised by hand using a plastic spatula. Depending on the amount of fine material in the sediments, between 100 and 500 g of sample were taken from the plastic beaker and placed in a wet sieving system. A set of stainless steel sieves was used in the fractionation. The mesh of the sieves was 90, 500 and 4000 µm. The resulting fractions (*i.e.* <90, 90-500, and 500-4000 µm) were transferred to glass dishes and dried for 48 h in an oven at 65°C. The fraction >4000 µm was discarded. Once dry each

Fig.3.1. Location of the seventy stations in Liverpool Bay in which superficial sediment samples were taken for the present study. The values in the coordinate axes are in minutes west of 3°W (X axis) and minutes north of 53°N (Y axis). The coordinates for each of the sampling positions are given in Appendix B1.


3.1
Sampling stations
LIVERPOOL BAY
NORTH WALES
QUEEN'S CHANNEL
BURBO BIGHT
R. DEE
Y
Z
SI
YY
G13
H12
J13
L13
K12
N13
Q13
U15
G11
J11
L12
K11
M12
N12
P12
R12
S13
T14
H10
L11
M11
N11
P11
R11
T12
G9
K10
L10
Q11
M10
N10
P10
S11
U11
H8
J9
K9
L9
M9
N9
P9
Q9
R10
T10
G7
K8
L8
M8
N8
P8
S9
T9
U9
J7
K6
L7
N7
Q7
R8
S8
T8
M6
P6
R6
S7
1
2
3
4
NW24
35
30
25
20
-40
-35
-30
-25
-20
-15
-10

sediment fraction was cooled in a desiccator to room temperature and weighed using an analytical balance. The grain size distribution is reported as the contribution in dry weight of each of the three fractions to the bulk (<4000 µm) sediment dry weight. The dry fractions <90 µm and 90-500 µm (referred throughout the text as "fine" and "coarse" fractions respectively) were transferred to acid washed glass vials and stored in a freezer until analysed for trace elements. The elemental content in the 500-4000 µm fraction was not determined.

Sediment subsamples for the determination of aluminium were prepared separately. For this analysis, approximately 10 g of the bulk sediment were wet sieved only through a 500 µm sieve. The <500 µm fraction (referred throughout the text as the "total sediment") was dried, and pulverized for 5 minutes in a micro-mill (Pulverisette-7, Fritsch) with agate bowls. The resulting powder was kept in a glass vial with plastic top and stored in a freezer until analysed.

3.2.3. Sample digestion

3.2.3.1. Fine fraction

Teflon bomb digestions

Approximately 1 g of sample was weighed in an analytical balance and transferred into a 20 ml teflon, screw-top, reaction vessel. 5 ml of cool concentrated (AnalaR) nitric acid (BDH, England) were slowly added to the sample to avoid excessive frothing. Once frothing had ceased the teflon bombs were tightly closed and put in a boiling water bath for a 2 h period.

After cooling the bombs to room temperature under a tap water stream, the contents of the bomb were transferred to a plastic centrifuge tube. The teflon bomb was rinsed twice with 1 ml diluted nitric acid (2%, v/v) and each time the contents were transferred to the plastic centrifuge tube. The extract was centrifuged at 2500 rpm for 25 minutes to precipitate the remaining sediment. The supernatant solution was transferred into a 20 ml volumetric flask and was made up to final volume with diluted nitric acid. The final extract was transferred to a 50 ml polyethylene bottle with screw-top and stored frozen until analysis. The trace elements analysed in this extract were: cadmium, chromium, copper, nickel, lead and zinc.

For analytical quality control, one procedure blank and one reference sediment sample with certified concentrations for various elements (BCSS-1, National Research Council Canada) was run with each batch of 15 samples. The results for the elemental determinations in certified sediments are shown in Table 3.1.

Table 3.1. Results for the determination of various elements in two certified reference sediments (BCSS-1 and MESS-1; National Research Council Canada). Conf. Int. represents the reported 95% confidence intervals r.s.d. represents the relative standard deviation.

		CERTIFIED VALUE		THIS STUDY		
Reference material	Element	Mean (μg g^{-1})	Conf. Int. (±μg g^{-1})	mean (μg g^{-1})	s.d. (μg g^{-1})	r.s.d. (%)
BCSS-1	Cd[a]	0.25	0.04	0.255	0.017	6.7
	Cr[a]	123	14	40.2	2.0	5.1
	Cu[a]	18.5	2.7	13.0	0.4	3.0
	Ni[a]	55.3	3.6	52.5	2.5	4.8
	Pb[a]	22.7	3.4	21.7	1.0	4.5
	Zn[a]	119	12	115	22	18.9
MESS-1	Hg[b]	0.171	0.014	0.197	0.011	5.6
	As[b]	10.6	1.2	10.24	0.85	8.3
	Cd[b]	0.59	0.10	0.59	0.04	6.8
	Cr[b]	71	11	26.2	2.9	11.1
	Cu[b]	25.1	3.8	19.1	1.0	5.2
	Ni[b]	29.5	2.7	19.3	0.7	3.6
	Pb[b]	34.0	6.1	31.8	3.0	9.4
	Zn[b]	191	17	144	5.6	3.9
	Fe[bd]	4.36	0.25	2.77	0.11	4.0
	Fe[cd]	4.36	0.25	3.98	0.16	4.0
	Mn[b]	513	25	272	18.7	6.9
	Mn[c]	513	25	501	12.5	2.5
	Al[cd]	11.03	0.38	10.74	0.06	0.6

Notes:

[a] Teflon bomb extractions with HNO_3 (see text).
[b] Open beaker extractions with H_2O_2:HNO_3.
[c] Teflon bomb extractions with HCl:aqua regia.
[d] Concentrations are given in percent.

Open beaker digestions

As the recovery of mercury with the teflon bomb digestions of the certified sediment BCSS-1 was both low and imprecise, an open beaker digestion method (Eagle *et al.*, 1978) was adopted for this analysis. In this case, 1 g of sample was put in a 50 ml glass beaker, and 5 ml of a cool 1:1 mixture of concentrated (AnalaR) nitric acid and (AnalaR) hydrogen peroxide (30% w/v, BDH) were added slowly. Once frothing had decreased, the beakers were placed in a hot block digester at 70°C and a watch glass was put on top of each beaker. The samples were digested for a 2 h period and once digested the extracts were cooled to room temperature. The remaining part of the procedure was similar to the one described above for the teflon bomb digestions.

The elements analysed in this extract were mercury and arsenic. Iron and manganese were also analysed in this extract after a 1 to 10 dilution. One procedure blank and one reference sediment MESS-1 (NRC, Canada) were analysed with each batch of 15 samples. The reason for the change in reference material was only because the reference BCSS-1 was not available in our laboratory when these digestions were carried out. The results for the analysis of MESS-1 samples are shown in Table 3.1.

3.2.3.2. Coarse fraction

Digestions for the coarse fraction were similar to the open beaker method described above with few modifications. In this case a 10 g sample of the 90-500µm fraction was used. Once in the beaker, 7 ml of cool concentrated nitric acid were added first to avoid excessive frothing due to the calcareous nature of several samples. Once frothing had substantially decreased, 7 ml of cool hydrogen peroxide were added. The samples were digested , diluted and stored as described in the open beaker method for the fine fraction. All elements were analysed in this extract.

3.2.3.3. Digestions for aluminium analysis

The samples for aluminium determinations were prepared following the method recommended by Loring (1987, pages 129 and 130) for total metal determination. Depending on the amount of fine material in the sediments, between 100 and 450 mg of the powdered sample prepared for this analysis were transferred into a teflon bomb. 1 ml of aqua regia (hydrochloric acid and nitric acid, 3:1) were added, followed by 6 ml of concentrated hydrofluoric acid (AnalaR, BDH). After closing the teflon bombs tightly, the samples were reacted in a boiling water bath for 1 h and cooled to room temperature under a tap water stream. Once cool, the digested samples were transferred into plastic 50 ml volumetric flasks containing 5.6 g of boric acid (GPR grade, BDH), approximately 20 ml distilled water, and 100 mg potassium chloride (AnalaR, BDH). The flasks were shaken until the dissolution of solutes was completed and the solutions were made up to volume. The final solutions were transferred into screw-top polyethylene bottles and stored in a freezer until analysis.

Aluminium was the only metal analysed in this extract. One procedure blank and one MESS-1 reference sediment was run with each batch of 15 samples.

3.2.3.4. Sewage sludge digestions

One sample of digested sewage sludge from Sandon Dock, Liverpool, of the type that is disposed in Liverpool Bay was kindly provided by North West Water Fazakerley laboratory.

This sample, containing approximately 1.2% of solids, was dried at 70°C for 48 h, and manually homogenized with a mortar and pestle. Three subsamples of approximately 250 mg were digested following the open beaker method for the fine fraction. Unfortunately one of the samples was lost during the final stages of the procedure, thus, results were obtained only for a duplicate analysis. One procedure blank was also run together with the sewage sludge subsamples. All elements except aluminium were analysed in the final sludge extract.

3.2.4. Spectrometric determinations

All the elements were analysed by atomic absorption spectrometry using a Varian Spectra-10ABQ atomic absorption spectrometer equipped with a deuterium background correction facility. The analytical conditions for each analysis in the spectrometer are shown in Table 3.2.

A VGA-96 atomization unit was used for the graphite furnace determinations. Graphite atomization tubes with L'vov platforms (Slavin *et al.*, 1983) were used in these determinations. Details of the furnace parameters and the sampler conditions are provided in Appendix A. A Varian VGA-76 system was used in the determination of mercury by the cold vapour technique (Hatch and Ott, 1968).

The precision for the determination of elements in the certified sediments was, in general, better than ±10% and in various cases was better than ±5% (see relative standard deviations, r.s.d. in Table 3.1). Only in the case of zinc the precision was lower (r.s.d.=18.9 and 11.1%), however, considering that the differences in the concentration of most elements among several sediment samples of Liverpool Bay are higher (see Chapter 4) than the analytical variations, the precision of the elemental determinations in this study can be considered as good.

Table. 3.2. Analytical conditions for the determination of elements by atomic absorption spectrometry. The wavelenght is expressed in nm. All the measurements were made in the peak height mode.

Element	Atomization method	Flame type	Wave lenght	Background correction	Calibration range (μg l^{-1})
Al	FA[a]	N/A[d]	309.3	Off	5-150
As	GFA[b]	---	193.7	On	0.150-4.000
Cd	GFA	---	228.8	On	0.015-0.050
Cr	FA	N/A	357.9	Off	2.0-10.0
Cu	FA	A/A[e]	324.8	Off	2.0-10.0
Fe	FA	A/A	386.0	Off	30-300
Hg	CV[c]	---	253.7	Off	0.005-0.050
Mn	FA	N/A	279.5	Off	1.5-40
Ni	FA	A/A	232.0	Off	1.00-5.00
Pb	FA	A/A	217.0	On	5.0-30.0
Zn	FA	A/A	213.9	Off	5.0-30.0

Notes:

[a] Flame atomization
[b] Graphite furnace atomization
[c] Cold vapour (hydride generation) technique
[d] Nitrous oxide/acetylene flame
[e] Air/acetylene flame

3.3. ORGANIC CARBON AND $\delta^{13}C$

3.3.1. Fine fraction

The total organic carbon concentrations in the fine sediments and their carbon stable isotope ratios ($\delta^{13}C$) were analysed by Europa Scientific Ltd. (Crewe, England) using a Europa Scientific CHN interfaced to a Mass Spec analyser, after removal of carbonates with sulphurous acid (BDH sulphur dioxide solution 5% w/v) following the procedure described by Shaw (1959).

The removal of carbonates consisted of adding 5 ml of sulphurous acid to a sample of approximately 100 mg dry fine sediment contained in a 10 ml glass vial. The samples were placed in a desiccator under a continuous vacuum until the excess acid was completely evaporated. The procedure was repeated with additions of only 1 ml of acid until the carbonate was completely removed. Prior to its introduction into the CHN-MS analyser, a subsample of approximately 20 mg was taken from the sediment remaining in the vial and transferred into a tin capsule and weighed in an analytical balance.

The precision of the total organic carbon, nitrogen and carbon isotopic ratios were good. In the case of the total carbon and nitrogen determinations the precision was better than ±10% (in terms of r.s.d.), and the precision reported for the $\delta^{13}C$ determinations was better than ±0.2‰.

3.3.2. Coarse fraction

An estimate of the carbon content on the coarse fraction was determined by loss on ignition (Williams, 1985). For this estimation a 10 g dry sample of the 90-500μm fraction was put in a preweighed porcelain crucible. The crucible was put in a furnace programmed at 500°C for approximately 12 hours. The crucibles were transferred into a desiccator and cooled to room temperature. Once cool, the crucibles were weighed and the difference in weight before and after igniting the samples was calculated.

3.4. POLYCHLORINATED BIPHENYL DETERMINATIONS

The procedure adopted in this study for the preparation of the sediment sample prior to the chromatographic analysis was largely based in the method reported by Boon *et al.* (1985). Briefly, the main steps in the sample preparation consist of: (a) extraction of the organic fraction of the sediments with organic solvents (hexane and acetone), (b) clean up of the organic extract with an aluminium oxide adsorbent to separate the organochlorine components from polar molecules such as pigments and lipidic materials which may interfere with the PCB determinations during the chromatographic analysis, and (c) separation (fractionation) of the PCB conegeners from other organochlorine substances (mainly pesticides such as p,p'-DDT, dieldrin, α- and γ-HCH, etc.; Boon *et al.*, 1985) which, may coelute and interfere with the determination of some PCB congeners. The clean up and fractionation steps with liquid solid chromatographic columns using alumina and silica columns for each step respectively, was originaly reported by Holden and Marsden (1969).

Only minor modifications to the method reported by Boon *et al.* (1985) were made in this study, and were particularly related with the preparation of the reagents. The main difference with the procedure reported by Boon *et al.* (1985) was the use of copper instead of mercury for the precipitation of sulfur during the clean up step (elemental sulfur from sediments interferes with the gas chromatographic determination of organochlorines by saturating the electron capture detector for a long period if present at high levels, or by showing few characteristic peaks if present at low levels, Jensen *et al.*, 1977).

3.4.1. Glassware cleaning

All glassware employed in this analysis was thoroughly cleaned prior to sample processing. The glassware was thoroughly rinsed with hot tap water and left overnight in a hot Decon 90 (Decon Laboratories Ltd., England) solution in distilled water (approximately 5%, v/v). Then the glassware was rinsed thoroughly with hot tap water followed by distilled water (the distilled water used in the analysis was kept in glass containers to avoid possible contamination with PCBs from plastic materials). Finally the glassware was transferred into an oven at 250-300°C for at least 4 h. The glassware that was not going to be used immediately was wrapped in aluminium foil. Before any piece of glassware was used, it was rinsed with acetone followed by hexane. No problems of sample contamination by glassware were encountered after this cleaning procedure.

3.4.2. Pretreatment of reagents.

3.4.2.1. Solvents

All of the solvents employed in these analyses were obtained from Rathburn Chemicals (Walkerburn, Scotland). Hexane and dichloromethane were HPLC grade and acetone was glass distilled grade. The quality of the solvents was tested by concentrating 200 ml of the solvent down to 1 ml and analysed for PCB residues. In the case of acetone and dichloromethane, the volume was taken to near dryness and dissolved to 1 ml with hexane before analysing in the gas chromatograph with electron capture detector (see below). The quality of the solvents was very good, thus, there was no need for redistillation before use. Only one interfering peak was found, with a retention time similar to that of PCB congener No. 170 (see Chapter 1 for details of the systematic numbering of PCB congeners). This peak is shown in the chromatogram corresponding to the procedure blank shown in Figure 3.2.

3.4.2.2. Sodium sulphate activation

Anhydrous sodium sulphate (Na_2SO_4, AnalaR, BDH) was Soxhlet extracted overnight with a 1:1 mixture of acetone and hexane. After air drying in a fumehood, the sodium sulphate was activated in an oven at 350°C for 4 h. After cooling to room temperature in a desiccator, the reagent was transferred into a stoppered glass flask and stored in a desiccator under vacuum until needed.

3.4.2.3. Aluminium oxide (alumina) activation

This reagent was prepared in batches of approximately 100 g. Aluminium oxide (70-230 mesh ASTM, Merk 1077) was baked for 4 h at 650 °C. After cooling in a desiccator to nearly room temperature, the reagent was transferred to a stoppered beaker, weighed, and deactivated by addition of glass distilled water previously extracted three times with hexane. The amount of water added was equivalent to 4% of the weight of the aluminium oxide, and was added dropwise by means of a 500 µl syringe. After adding the water, the beaker was stoppered and shaken for approximately 20 minutes. This reagent was stored under vacuum in a desiccator until needed.

3.4.2.4. Silica gel activation

The silica gel 60 (70-230 mesh ASTM, Merk 7734) activation and storage was similar to that for the alumina procedure. The only difference was that for the silica deactivation, 5% of water was added.

3.4.2.5. Copper activation

Copper turnings (BDH) were activated following the procedure described by Fisher *et al.*(1983). 10% nitric acid was added to the turnings to remove surface oxides. Solvent extracted distilled water was used for rinsing the activated copper several times, followed by rinsing twice with acetone and finally rinsing twice with hexane. After decanting the hexane, the copper

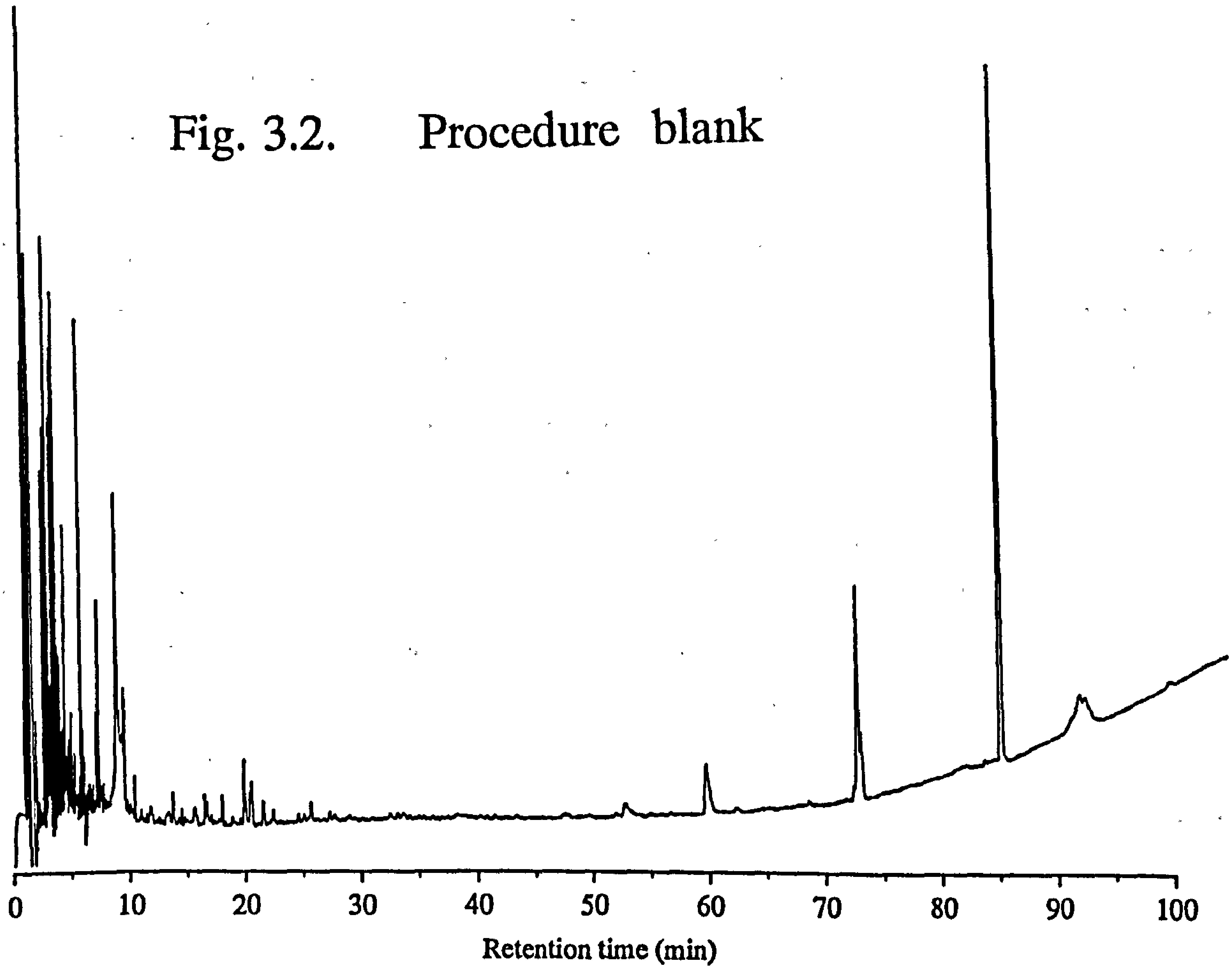


Figure 3.2. Gas chromatogram for the procedure blank in PCB determinations. (see chromatographic conditions in the text).

turnings were dried under a stream of nitrogen and stored in a stoppered beaker in a desiccator under vacuum.

3.4.3. Sample extraction

Before the extraction, the bulk sediment was lyophilized. Some of the samples were lyophilized in our laboratory but most of the samples were freeze dried elsewhere (Dr G. Wolff, Liverpool University). The dry sediment was sieved through a 500 µm stainless steel sieve and the <500 µm fraction was kept for the analysis of PCBs.

Depending on the proportion of fine material present in the sample, a subsample of between 15 and 70 g was weighed in a 100 ml glass beaker. Some activated sodium sulphate was mixed with the sediment to improve the solvent penetration through the sediment during the extraction.

The samples were transferred to "home made" glass fibre thimbles each one made with half of a 25.7 cm diameter Whatman GF/D filter (the thimbles were extracted for 4 h with acetone:hexane 1:1 before being used). Each thimble with sample was placed in a 60 ml Soxhlet extractor and spiked with 10 µl of a 5.1 µg/ml octachloro-naphthalene (OCN) solution used as an internal standard (the OCN was obtained as a powder from Greyhound Chromatography, Birkenhead, England, and dissolved in hexane). The receiving 250 ml round bottom flask contained 3 solvent-extracted boiling chips and approximately 5 g of activated copper. 80 ml of acetone and 80 ml of hexane were added to the system and the sediment samples were extracted overnight for approximately 14 h.

The extract was concentrated to approximately 5 ml using a macro Kuderna-Danish concentrator (Supelco), transferred to a graduated test tube and blown down to 1 ml under a gentle stream of nitrogen while heating in a block digester at *ca.* 45°C. A few extra copper turnings were added to the final concentrate to eliminate any remaining sulphur not precipitated during the Soxhlet extraction.

3.4.4. Extract clean up

3.4.4.1. Column preparation

Borosilicate glass columns (250 x 6 mm I.D.) with a solvent reservoir at the top and a taper at the bottom end were employed in both clean up and fractionation steps. For the clean up step, a glass wool fibre ball previously extracted with acetone and hexane was inserted in the tapered end to support the packing agent. The column was dry packed with the activated alumina by pouring 2 g of the powder measured by volume in a calibrated vial. The sides of the column were gently tapped with a piece of soft plastic tubing to ensure a good packing of the column. A small amount of activated anhydrous sodium sulphate, equivalent to approximately 5 mm of column, were added to the top of the alumina to ensure dryness of the extract before contact with the alumina, thus, avoiding changes in the activity of the adsorbent due to possible traces of water being present in the extracts.

3.4.4.2. Extract clean up

To eliminate any possible traces of contaminants the packed column was eluted first with 7 ml of dichloromethane followed by 7 ml of hexane. The solvents were carefully added through the walls of the column by means of pasteur pipettes (cleaned as above for the glassware). Once the hexane had passed through the column and the surface of the sodium sulphate started to dry, the 1 ml sediment extract was added to the top of the column with a pasteur pipette. A measuring cylinder was used to collect the eluting solvent. When the surface of the extract was level with the top of the column packing, an extra 1 ml used for rinsing the test tube containing the extract was added in a similar manner. This step was repeated once more and finally 12 ml of hexane were added to the reservoir to elute the PCBs. After discarding the first 2 ml (equivalent to the volume of hexane remaining within the packing in the column before adding the extract), the following 10 ml were recovered in a 10 ml graduated test tube. This eluate was concentrated to 1 ml in a block digester at 50°C under a gentle stream of nitrogen and a few copper turnings were added.

The volume of eluate to recover from the clean up step was determined by passing through a similar column a standard solution of PCBs (CLB1-D, described below in analytical techniques) which was also spiked with a mixture of p,p'-DDE and p,p'-DDT. After collecting an initial eluate of 5 ml, eluates of 1 ml were collected. Although most of the congeners eluted within the first 6 ml, congener No. 15 was completely recovered only after 8 ml, thus, to ensure total recovery of all PCBs, and to avoid different recoveries due to variations amongst different alumina batches, a 10 ml volume was fixed as the elution volume for the clean up step.

3.4.5. Organochlorine fractionation

The final step of the sample preparation consisted of separating the PCBs from other organochlorines that may coelute with some congeners during the chromatographic analysis. In this step, a liquid-solid chromatography was used with activated silica as adsorbent which was packed and precleaned following the procedure previously described for the clean up step.

The volume of the eluate to recover after discarding the first 2 ml, was determined for each new silica batch. In this case eluates of 0.5 ml were recovered after collecting the first 6 ml eluate. The final recovery volume varied between 8 and 9.5 ml for all the silica batches used in this work. This volume was initially determined as in Boon, *et al.* (1985), *i.e.*, as the volume in which p,p'-DDE and p,p'-DDT were separated (all PCBs are supposed to be present in the first eluate together with the DDE), however, it was later determined as the volume in which all the congeners in the PCB standard mixture CLB1-D were recovered. The latter change took place due to the fact that when testing the recovery of the CLB1-D PCB standard mixture, some significant traces of few congeners were present in the DDT fraction and a major proportion (approximately 50%) of congener number 15 was present in this fraction.

After recovering the eluate in a graduated 10 ml test tube, the extract was concentrated in a block digester under a stream of nitrogen to a volume of approximately 1 ml. The extract was then transferred to a receiving vessel from a micro Kuderna-Danish concentrator with 0.01 ml divisions, and after rinsing the test tube three times with approximately 0.5 ml of hexane and transferring the rinsings to the receiving vessel, the extract was concentrated under a stream of nitrogen to a final volume of between 0.2 and 1.0 ml. The final extracts were transferred to clean 2 ml glass vials with foil lined caps, and two or three copper turnings were added to each one to ensure no traces of sulphur were present in the extract during the chromatographic analysis. The extracts were stored in a freezer until analysed.

3.4.6. Gas-chromatographic determination of PCB congeners

The determination and quantification of the PCB congeners was performed by high resolution gas-liquid chromatography using a Carlo Erba HRGC 5160 equipped with a ^{63}Ni electron capture detector (ECD), and connected to a Spectra Physics ChromJet SP4400 integrator. A DB-5 (J&W Scientific) 60 m capillary column (0.25 mm I.D., 0.25 µm film thickness) was used for the separation and quantification in all samples. 20 samples were re-analysed using a 30 m, 0.32 mm I.D., 0.25 µm film thickness DB-1701 column (J&W Scientific) for confirmation of the identity of various congeners. A 1 µl sample was injected on-column, and the oven program for the DB-5 column was as follows: isothermal at 60°C for 2 min, 60-180°C ballistic heating, isothermal at 180°C for 20 min, 180-220°C at 1°C min^{-1}, 220-300°C at 2°C min^{-1} and finally isothermal at 300°C for 35 min. The carrier and make up gas were hydrogen and nitrogen respectively. The carrier linear velocity was approximately 55 cm sec^{-1}, and the make up pressure was 110 kPa. The detector temperature was 320°C and the electrometer (Carlo Erba, ECD 400) was operated in the constant current mode. The integrator was set at a chart speed of 0.25 cm min^{-1} and attenuation 16x. Congeners were quantified based on peak heights.

The chromatographic conditions for the DB-1701 column were as follows: isothermal at 60°C for 2 min, 60-170°C at 10°C min^{-1}, isothermal at 170°C for 25 min, 170-210°C at 1°C min^{-1}, at 210° for 0 min, 210-275°C at 3°C min^{-1}, and isothermal at 275° for 30 min. The ECD temperature was 300°C and the carrier gas linear velocity was approximately 42 cm sec^{-1}. All other parameters remained as in the DB-5 column analysis described above.

Peak identification was based on relative retention times (RRT) using the internal standard (OCN) as reference peak (RRT=1); the retention time for OCN varied between 85.24 and 85.88 min for the whole period of analysis of approximately seven weeks. Variations in the retention times from one day to another were due to small variations in the gas flows settings, particularly the carrier gas, that were switch down after each working day to save gas. The maximum variations in the retention positions in a particular day were of about 0.2 min.

A set of standard solutions, CLB-1 (National Research Council, Canada), with pure, synthetic chlorinated biphenyl congeners was used for the calibration and identification in the chromatographic analysis. The set consists of four mixtures (CLB-1-A, -B, -C, and -D), each one containing a group of 14 or 15 individual congeners, and a total of 51 different chlorinated biphenyls of established identity. A description of the composition of the CLB-1 standard solutions with the relative retention time for each congener, from each of the two columns, can be found in Chapter 5 (Section 5.1). Two sets of calibration mixtures were prepared for the calibration of the gas chromatograph. The first set contained the standard solutions CLB-1-A and CLB-1-D spiked with the internal standard and with a mixture of 3 congeners (No. 126, 158, and 169) not present in the CLB-1 standards. The latter mixture was prepared from solutions of pure congeners obtained from Greyhound Chromatography (Birkenhead, England). The second set of calibration mixtures included standards CLB-1-B and CLB-1-C, spiked with OCN and congener No. 28 (Greyhound Chromatography) which was not present in the CLB-1 standard mixtures.

Each of the two calibration sets contained eight calibration solutions covering an 80 fold range in concentration. For example, the concentration range for congener 138 was from 0.42 to 33.60 ng ml^{-1}, whereas that for congener No. 15 was from 7.75 to 620 ng ml^{-1}. Each standard was injected in duplicate and a calibration curve was drawn for each individual congener. In the few cases in which coelution of two or more congeners occurred, the calibration curve represented the summation of the concentration of both congeners. That was the case for congeners 159+187 and congeners 171+202. After mixing the calibration solutions of the different sets, that is, when the solution injected in the gas chromatograph contained all 55 individual congeners some more coeluting peaks were observed. The coeluting peaks in the DB-5 column were 40+103, 77+154, 159+187+182, 171+202, 196+203, 195+208. The chromatograms showing the performance of both DB-5 and DB-1701 columns for the mixture containing all congeners are shown and discussed in detail in Chapter 5 (Section 5.1; see Table 5.1 and Fig. 5.1).

The precision and accuracy of the chromatographic analysis were determined from the analysis of two technical PCB mixtures (Aroclor 1254 and Aroclor 1260) obtained as concentration solutions from Greyhound Chromatography (England). The precision and accuracy of the overall procedure were determined from the analysis of two reference sediment materials with certified values for some individual congeners (sediments HS-1 and HS-2, National Research Council Canada). Contrary to trace element determinations, there is no standardized analytical procedure for individual PCB congener determinations which has been adopted at an international level and, as in the present study, laboratories have been adapting and modifying methods for the determination of PCBs according to their specific needs and equipment availability. Therefore, as the method used in this study resulted from adaptations of different reported procedures, the results of the accuracy and precision determinations, together with a critical evaluation and a discussion of the method are presented in Chapter 5 (Section 5.1).

CHAPTER 4. SEDIMENT PARAMETERS AND TRACE ELEMENTS

4.1. SEDIMENT PARAMETERS

In order to determine the fate of anthropogenically derived chemical substances through the study of their distributions in sediments, it is necessary to consider the factors affecting the contaminant-particle associations and to take into account the processes controlling the sediment transport within the surveyed area.

Heavy metals and PCBs (amongst other contaminants) become appreciably associated with particles when discharged into turbid aquatic environments (Olsen *et al.*, 1982). This association may result from: (1) ion exchange, precipitation, or hydrophobic interactions with the particle surface, (2) co-precipitation with iron and manganese hydrous oxides, (3) complexation with organic substances bound or aggregated with particles, (4) incorporation into mineral lattices, organisms or faecal material, or (5) flocculation of colloidal organic matter and inorganic matter during river and sea water mixing (Olsen *et al.*, 1982).

Literature regarding the association between metals and suspended or seabed sediments in aquatic systems is abundant due to the possible toxic effects of these substances in the environment. Metals in sediments can be partitioned among different phases on the surface of the particles. The most important phases for metal binding in aquatic sediments are: (1) the aluminosilicate minerals; (2) hydrous oxide coatings of iron, manganese and aluminium; (3) organic matter coatings; and (4) to a lesser extent carbonates (Forstner and Wittmann, 1979; Lion *et al.*, 1982; Millward and Moore, 1982; Feely *et al.*, 1983; Luoma and Davis, 1983; Tessier *et al.*, 1985; Santschi *et al.*, 1990). The partitioning of a metal ion amongst these phases is influenced by: (1) the binding capacity of each phase; (2) the binding intensity of the metal ion to each phase; (3) the abundance of each phase in the sediment; (4) solution parameters such as pH and dissolved ligand concentrations which may influence the speciation of dissolved metal ions; and (5) the concentration of other metal ions which may compete with trace metals for the available binding sites (Luoma and Davis, 1983). Each of these influencing factors have been studied in certain detail by numerous authors and various reports have appeared in the literature. Some useful reviews can be found in Forstner and Wittmann (1979); Olsen *et al.* (1982); Luoma and Davis (1983); Honeyman and Santschi (1988) and Santschi *et al.* (1990).

In the present study, an estimation of the abundance of each of the most important sedimentary phases (*i.e.* organic coatings and hydrous iron/manganese oxides) was determined by bulk chemical analyses. The organic coatings were estimated only in terms of the total organic carbon in the fine fraction, and total organic matter in the coarse fraction, without specific determination of the chemical composition (e.g. humic and fulvic acids content) of these organic materials which may influence the adsorption of metals. The iron/manganese hydrous oxide content was estimated by the analysis of iron and manganese after a partial sediment extraction with nitric acid and hydrogen peroxide (this method extracts the inorganic and organic coatings without dissolving the sediment inorganic matrix). Iron and manganese oxyhydroxides can exist in various forms (for examples see Luoma and Davis, 1983; Santschi *et al.*, 1990) depending on the prevailing physicochemical conditions, and each of these forms may have very different metal binding capacities (for examples see Luoma and Davis, 1983); therefore, bulk determinations of iron and manganese in sediments can only serve as rough indicators of the abundance of hydrous oxides of these elements in the surface of the sedimentary particles.

In the present study, the possible metal association with particular sedimentary phases was investigated through statistical analyses. Statistical relationships have been used in the past by several authors for this purpose (e.g. see Thomas, 1972; Van de Meent *et al.*, 1985; Sigg *et al.*, 1987; Schults *et al.*, 1987; van der Weijden and Middelburg, 1989; Gardner *et al.*, 1990). However, it is necessary to consider that a correlation between a metal and a specific phase is not necessarily an evidence of the chemical association of the metal with that particular phase; this problem is more evident when a metal shows high correlations with more than one phase. Although attempts by various authors have been made to selectively extract and analyse each of the main sedimentary chemical phases and their associated metals, there is at present no method that can specifically extract each particular phase without possible alteration or co-extraction of other phases. The sequential extractions method to determine the adsorption of metals to specific phases in sediments has been employed by several authors, however, the various limitations found in this procedure and in particular the lack of general validation make of this method (see Nirel and Morel, 1990) a tool that is difficult to apply in practical terms for the assessment of metal contamination in sediments when a large number of chemically heterogeneous samples is to be analysed.

A review in the present knowledge of the factors controlling sediment transport in Liverpool Bay has already been presented in Chapter 2. In the present Chapter, the results on the analyses of sediment parameters involved in contaminant-particle associations are presented and discussed.

The results of the analyses of various elements are also discussed in this Chapter (the raw data of these analyses are shown in Appendix B.1 to B.4).

4.1.1. Grain size distributions

Fine grained particles generally have greater affinity for pollutants relative to coarser particles because they have greater surface area per unit weight, providing larger areas for the deposition of organic and inorganic coatings that may act as scavengers of substances such as PCBs and heavy metals in aquatic systems (Olsen *et al.*, 1982; Luoma and Davis, 1983). Fine sediments are also enriched in layered aluminosilicate minerals which contain more binding sites per unit area than other minerals such as quartz (main component of larger sedimentary particulates such as sands) which is relatively unreactive compared to organic and clay phases (Olsen *et al.*, 1982). This greater affinity of fine particles for contaminants is reflected in higher concentrations in fine than in coarse sediments, this observation in turn, indicates that the grain size distribution within sediment samples, is a critical variable to determine in any study of sediment contamination.

It is not surprising, then, that in most studies of contaminant concentrations in bulk sediments, high correlations are found between the amount of fine sediments in the samples and the contaminant concentrations. Therefore, the spatial distribution of the concentrations of a contaminant in bulk sediments from a particular area will reflect the grain size composition of the sediments in that particular area (for examples see Thomas, 1972; Forstner and Wittmann, 1979; Kramer, 1986).

One of the several methods (see Forstner and Wittmann, 1979; Cauwet, 1987) for correction of grain size effects in the assessment of contamination in sediments that has been most commonly used, is the separation by sieving of the bulk sample into two or more grain size fractions for their analyses. Several studies have been only focused on the study of the finer fractions as contaminants tend to concentrate in these particle sizes and coarse sediments are only regarded as diluting factors. However, various authors have reported relatively high concentrations of trace metals in coarse grained sediments, therefore, the contribution of the coarse sediments as metal carriers within bulk sediments has to be taken into consideration, in particular if the fraction of fine material within those sediments is small (Kramer, 1986; Cauwet, 1987; Brook and Moore, 1988; Grant, 1990; Martincic *et al.*, 1990).

In the present study, two sediment fractions were analysed for trace element content: a fine fraction consisting of sediments smaller than 90 μm in diameter, and a coarse fraction including sediments in the size range between 90 and 500 μm. These size fractions were chosen as the heavy metal part of this project was initiated as part of a monitoring program for North West Water Authority which follows the guidelines for environmental monitoring from the Ministry of Agriculture Fisheries and Food (see methods in Eagle *et al.*, 1978). The upper limit in the fine fraction (90 µm) was adopted by MAFF "...because naturally-occurring marine sediments below approximately 90 µm tend to be bound together in agglomerates and, consequently, require different drying and separating techniques from the coarser fraction, which can be simply oven dried. This is, therefore, the finest size at which it is possible to physically separate two fractions without having agglomerated fine material retained with the coarser fraction. The upper limit of the coarser fraction analysed (500 µm) was selected because of the difficulties of preparing representative samples for analysis with coarser material" (Eagle *et al.*, 1978).

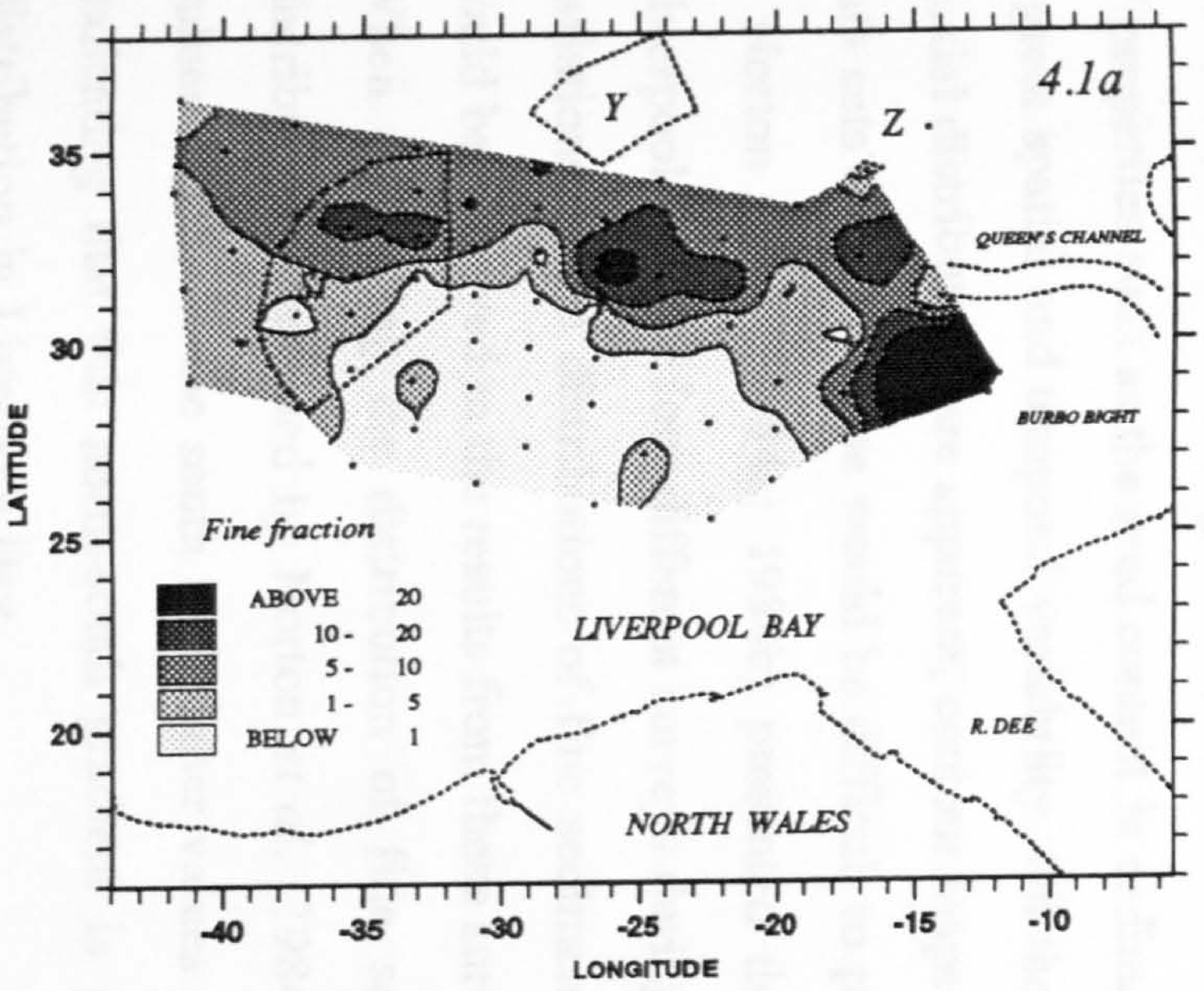
4.1.1.1. Fine fraction in bulk sediments

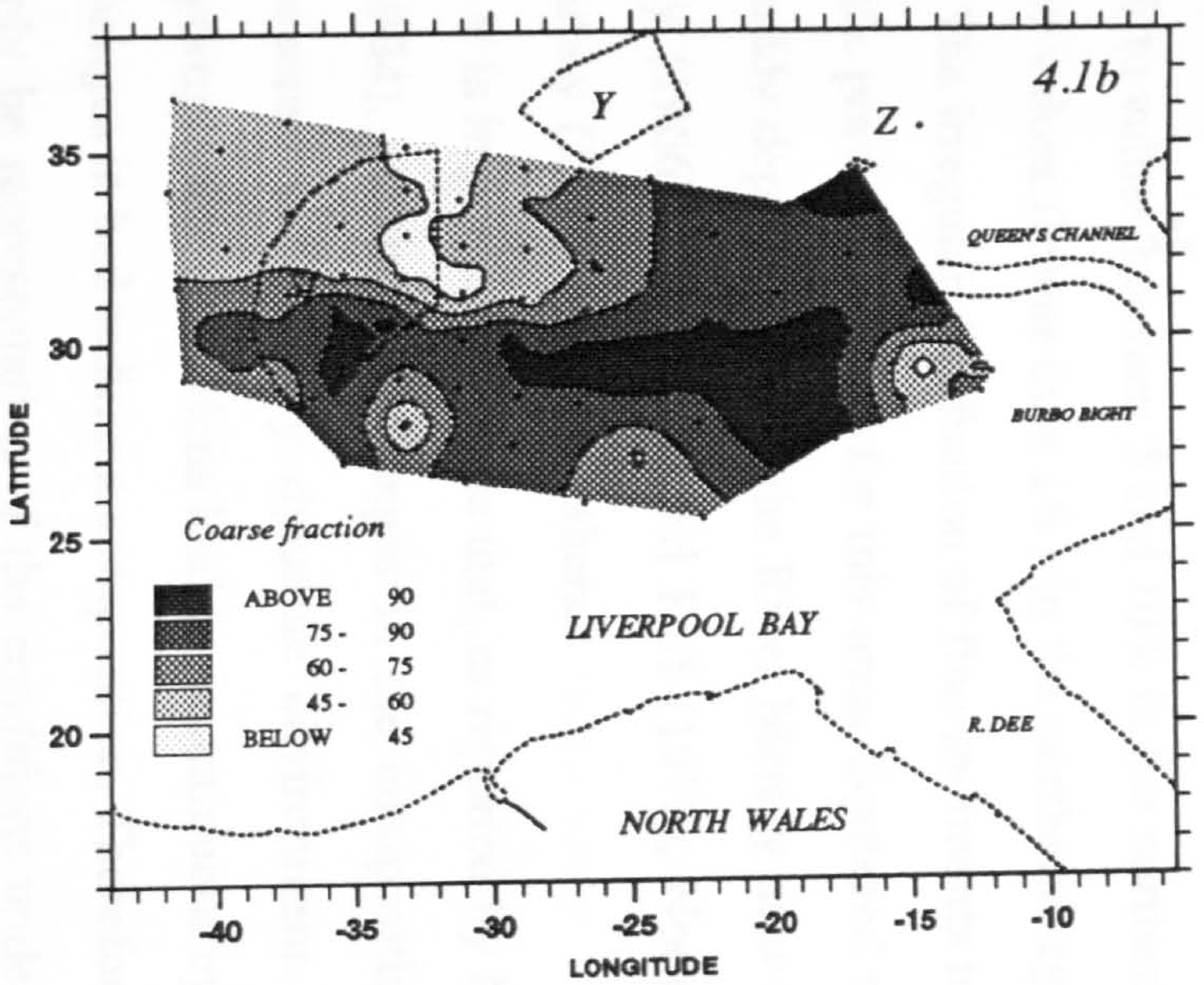
The "fine fraction", as previously defined in this thesis, contains the sediment grains smaller than 90 µm in diameter. According to Wentworth's grain size scale (Dyer, 1986, pp. 16-17), this fraction will contain particles of clay and silt (muds) and a fraction of very fine (62.5-125 µm) sands.

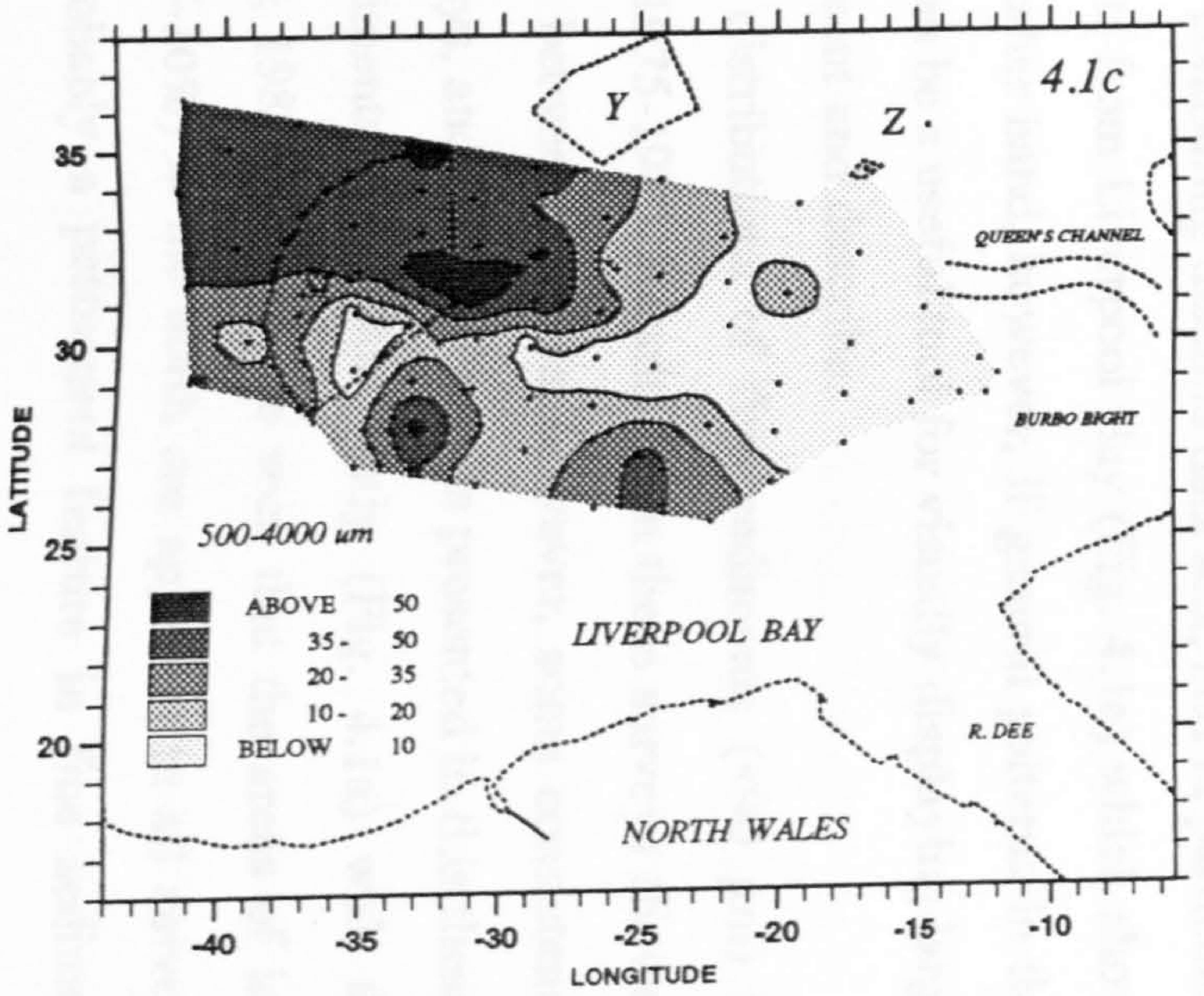
Figure 4.1a shows the distribution of the fine fraction in the bulk (<4000 µm) sediments. The mean value for all seventy samples was ~7%. The highest values, ranging from 24 to 59%, were found in the Burbo Bight area near the mouth of the Mersey Estuary, in samples U-9, YY-1 to YY-4 and NW-24 (see Figure 3.1 for the location and identification of stations), with sample YY-1 showing the highest value. Other stations with a relatively high proportion of fine material were K-11 (12%) and L-11 (~14%) located within the sewage sludge disposal area (Site SI), and stations P-11 (31%), Q-11 (11%), R-11 (17%) and T-12 (14%). Values for each of the 70 samples taken in this study can be found in Appendix B.3.

Figure 4.1a shows that muddy sediments are distributed in patches within the sampling area, however, a general trend in the distribution of fine sediments can be observed. Excluding muddy patches and the Burbo Bight samples, bulk sediments from Liverpool Bay contain less than 10% of fine material with values increasing from south to north. The lowest values can be found in the southern region including stations labelled with numbers 6 to 9 between transects G and S (27 stations). Fourteen stations in this region had values lower than 0.5% of fine material, with a minimum of 0.07% at station S-7; seven stations had values between 0.5% and 1%, and three stations values between 1 and 2%.

Fig.4.1. Distribution of the grain size fractions in "bulk" sediments (<4000 μm), (a) fine fraction (<90 μm), (b) coarse fraction (90-500μm), (c) 500-4000 μm fraction. Values are given as a percentage dry weight.


4.1a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Fine fraction
ABOVE 20
10 - 20
5 - 10
1 - 5
BELOW 1
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.1b
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Coarse fraction
ABOVE 90
75 - 90
60 - 75
45 - 60
BELOW 45
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.1c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
500-4000 um
ABOVE 50
35 - 50
20 - 35
10 - 20
BELOW 10
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10

Stations labelled with the number 10 can be considered as a boundary between the zones of lower values in the south and higher values in the north. A gradient can be observed around these stations particularly in the central region where in a short distance values increase from less than 1% to values of between 5 and 10% in the northern region. Only stations N-11 and S-11 presented low values (lower than 1%) in the northern region.

The irregular distribution of fine sediments in Liverpool Bay found in this study is consistent with previous reports for this area. Scattered small muddy patches along the bay, with larger muddy deposits toward the River Mersey near the Queen's Channel have been also reported by Sly (1966), Crickmore and Kiff (1972), Norton *et al.*(1984a; 1984b), Rees (1984), Kiff and Nunny (1984) amongst others.

It is important to stress that, as reported by Norton *et al.* (1984a; 1984b) and Kiff and Nunny (1984), continuous changes in the composition of sediment in Liverpool Bay take place in response to the highly dynamic environment. Both long term and short term variations in hydrographic conditions lead to a continuous cycle of erosion and deposition, producing constant changes in bed sediment composition. Therefore, samples taken during one particular survey can only be representative of the conditions under which the survey took place and care must be taken if generalisations are to be made from a single survey.

Contour maps such as that shown in Figure 4.1a are presented throughout this thesis aiming to present an overall picture of the distribution of the property presented in a given map. However, the author recognises the limitations of contouring discrete data sets, and in particular of properties such as the mud content in sediments from Liverpool Bay (Fig. 4.1a) which show a great spatial and temporal variability. On the other hand, however, if general patterns in the spatial distributions are apparent, contour maps can be a useful tool for visually displaying large data sets that otherwise would be difficult to present and describe.

Norton *et al.* (1984a; 1984b) presented the distributions of fine sediments (<90 μm) in Liverpool Bay for four different surveys during 1975-1980. Results from these surveys showed variations in the distributions of fine sediments between surveys, however, some consistency could be observed in the results from these surveys, and with the results presented in this thesis. When comparing the distribution of fine sediments from this study (Fig. 4.1a) with the distributions presented by Norton *et al.* (1984a; 1984b), it can be seen that the areas of low values (<5%) in the south and higher values (5-10%) in the north are apparent in all surveys indicating that this north-south gradient is probably a permanent feature in fine sediment distribution in Liverpool Bay.

The presence of a north-south gradient in the fine sediment distribution in Liverpool Bay is probably related to the topography of the region, as stations from the southern part of the sampling grid are shallower and closer to the North Wales coast than those in the north. It has been reported (e.g. Howarth, 1984) that currents intensify toward the North Wales coast, therefore, the shear stress on the sea bottom is stronger in this region than over deeper water sediments, making the deposition of fine material more unlikely. In a study of radiolabelled sewage sludge dispersion on the seabed in Liverpool Bay, Crickmore (1972b) found that although some of the sludge released in the dumping ground area was transported and deposited in muddy areas of beaches along the North Wales coast, no evidence of radioactive sewage sludge deposition was found in the sediments some 10 to 15 km off the coast, and suggested that in this tracer free area, characterized by "clean" sea bed conditions, bed shears would be sufficiently high to prevent retention of sludge particles; this observation may also be applied to fine grained sediments. Crickmore and Kiff (1972) also reported a "clean" bed in the area off the North Wales coast inshore of the 20 m depth contour with less than 1% of the sediment being finer than 60 µm.

In contrast to the fine sediment distributions presented by Norton *et al.* (1984a; 1984b), Figure 4.1a shows no "tongue" of high fine sediment values immediately outside the Queen's Channel extending west towards Site SI. The maximum concentrations of fine sediments in the present study were found nearer to the Burbo Bight area, southeast from the area of maximum values reported by Norton *et al.* These authors showed that these mud deposits change in size and position with time, therefore, this discrepancy in the position of maximum concentrations of fine sediments near the Mersey is probably due to the natural variations in the sediment composition in this hydrodynamicaly complex area.

There is no evident enrichment of fine particles in or near Site SI (Fig. 4.1a), therefore, it seems that no significant alteration in the physical characteristics of the natural sediments in Liverpool Bay occur due to sludge dumping activities. It has been extensively reported (e.g. Crickmore, 1972a; 1972b; Barret *et al.*, 1972) that after disposal, sludge solids, composed mainly of <90 µm particles (Norton *et al.*, 1984b), are rapidly dispersed over large areas in Liverpool Bay before reaching the sea bed. The principal direction of sludge movement is towards the coastal areas and the main accumulation of sludge residues occurs in existing natural mud deposits, as there is a similarity in settling velocities and hydrodynamical behaviour between sludge particles and fine inorganic particles (Crickmore, 1972b).

Sample T-14, taken at Site Z where approximately three million tonnes of dredged spoil are dumped every year (Rowlatt *et al.*, 1986), shows no particular enrichment in fine sediments even though approximately 30% of the discharges consist of mud size sediments. In a detailed study on the effects of spoil dumping in the sediment composition around this area, Rowlatt *et al.* (1986) observed no particular enrichment in fine sediments near this area due to the discharges and suggested that the mud fraction of the dredged material is rapidly transported away from the site. Therefore, this area is non-accumulating with respect to mud probably due to the shallowness of the Site (~10 m depth), where under normal tidal conditions , fine sediments are likely to be transported and even cohesive mud deposits would be subject to redistribution during storms (Rowlatt *et al.*, 1986).

4.1.1.2. Coarse and 500-4000 µm fractions in bulk sediments

In the present study the "coarse fraction" includes particles in the range of 90 to 500 µm. In Wentworth's classification this fraction includes medium sands (250-500 µm), fine sands (125-250 µm) and a fraction of the very fine sands (62.5-125 µm). In the 500-4000 µm range, coarse sands (500-1000 µm), very coarse sands(1000-2000 µm) and granules (2000-4000 µm) are included.

The distribution of the coarse fraction in bulk sediments is shown in Figure 4.1b. Values ranged from 31% at station M-10 to 99% at station Q-9, with a mean value for seventy samples of approximately 71%. An irregular distribution of this fraction can be observed in Figure 4.1b, however, there is an apparent gradient with values increasing from the northwest toward the southeast of the sampling grid. In the northwestern region, including samples labelled 10 to 13 in transects G to N, values lower than 60% were present, whereas in the southern and eastern areas the coarse fraction contributed more than 75% of the bulk sediment weight, with the exception of samples from the Burbo Bight area, and the patches of low values centred at stations L-7 and Q-7 (see Appendix B.3). The region of highest coarse fraction in the south-east contained 10 samples with values above 90%. A high value (~96%) was also found in sample T-14 taken at Site Z.

Values for the 500-4000 µm fraction ranged from less than 0.8% at stations T-14 and Q-9 to a maximum of ~69% at station M-10. Figure 4.1c shows the distribution of this fraction in the bulk sediments. In this figure an opposite trend to that of the distribution of the coarse fraction (Fig. 4.1b) can be observed. In this case the zone of maximum values is in the northwestern region with values ranging from ~58% to ~69% whereas the low values (<10%) are found in the eastern region. All values in the Burbo Bight area were lower than 8% (Appendix B.3).

The opposite distribution of the coarse and the 500-4000 µm fractions is reflected in the linear correlation coefficient between these two fractions. When all seventy samples were considered in the calculations, a $r= -0.812$ coefficient (highly significant $p<<0.001$) was obtained, however, when the values from samples containing more than 20% of fine material (7 samples) were excluded, the linear correlation coefficient increased to -0.977. No significant correlations were observed between these two variables and the concentration of fine fraction in the bulk sediments.

Decreasing amounts of material coarser than 500 µm toward the Mersey have been previously reported (Sly, 1966; Norton *et al.*, 1984a). Norton *et al.* (1984a) reported naturally occurring gravels (>4000 µm) at the sewage dumping ground and to the west and southeast of the site; these gravels were often accompanied by very coarse sands and granules. These authors also presented an eastern boundary of coarse sand population, roughly coinciding with the isoline separating the areas of 500 to 4000 µm fraction with values higher than 20% to the northwest and lower than 20% towards the east and southeast (Fig. 4.1c). The gravel deposits offshore, with their associated coarse sand populations, will only be rarely disturbed as threshold velocities (promoted both by tidal and wave induced flows) for the movement of these particles will be rarely attained (Norton *et al.*, 1984a); therefore, the areas of high concentrations of material coarser than 500 µm in Site SI and to the west of the site most be an almost permanent feature of the grain size distribution in the bay.

Norton *et al.* (1984a) described in some detail the sediment dynamics in Liverpool Bay. The eastward and southeastward transport of medium and fine sands originating from the Irish sea (see the literature review in this subject Chapter 2) is a relatively continuous process as shear velocities required for initiating the movement of these particle sizes (1.5 and 1.4 cm s^{-1} for 350-500 and 180-350 µm sand populations respectively; these sizes are denoted as medium A and medium B populations in Norton *et al.* report) are attained for approximately 40% of the time in Liverpool Bay. During neap tides these sands will not be transported as maximum shear velocities are in the order of 1.0 cm s^{-1} under these tidal conditions (Norton *et al.*, 1984a). Under some conditions (shear velocities above 2.1 cm s^{-1}) finer sands will be transported in suspension whereas medium sands will only be transported as bedload. These different transport mechanisms produce sorting of sands reflected in polymodal sand distributions as those reported by Norton *et al.* 1984a. These authors agreed with Sly (1966) in reporting finer and better sorted sand populations towards the Mersey. Norton *et al.* (1984a) also reported fine sand populations (defined by these authors as the 125-180 μm fraction) occurring only in restricted areas including the vicinity of site Z and samples with "above average" concentrations of mud.

4.1.1.3. Fine fraction in "total" sediments

The distributions of the fractions within the bulk sediments previously discussed are intended to provide a general idea of the grain size composition of the sediments from Liverpool Bay. This grain size composition is usually a good indicator of the hydrodynamical conditions prevailing at the area during the sampling period . However, chemical analyses were only carried on sediments <500 μm in diameter, therefore, only the contributions of the fine and coarse fractions to these "total" (<500 μm) sediments will directly reflect the grain size effects on the concentrations and distributions of the chemical parameters reported and discussed later in this thesis.

Figure 4.2a shows the distribution of the fine fraction in the total sediments. The distribution pattern presented in this figure shows no obvious difference to the one presented in Figure 4.1a for the fine fraction in the bulk sediments. The mean value for all samples in this case was 8.8% and the maximum and minimum values were ~61% and 0.08% respectively.

The contribution of the coarse fraction to the total sediments is presented in Figure 4.2b. It is not surprising that this distribution is exactly the opposite to that shown in Figure 4.2a as both fractions add up to 100% of the total sediments. This figure is presented, however, to stress the importance of the coarse sediments as metal carriers, particularly in those situations in which the coarse fraction is by far the major component of the total sediments.

The coarse fraction in the total sediments had a mean value of ~91% for the seventy samples taken in this study; the minimum and maximum values were ~40% and >99.9% respectively. Figure 4.2b shows that the coarse fraction is a very large component of the total sediments of the southern region, with values above 95% in all the samples excluding those from the Burbo Bight area. A large proportion of samples in this region (26 samples) had values larger than 99% (see Appendix B.3).

4.1.2. Aluminium in the total fraction

The distribution of the aluminium concentration in total sediments is discussed in this section, as this measurement is often used as an indicator of the clay content of sediments (Forstner and Wittmann, 1979).

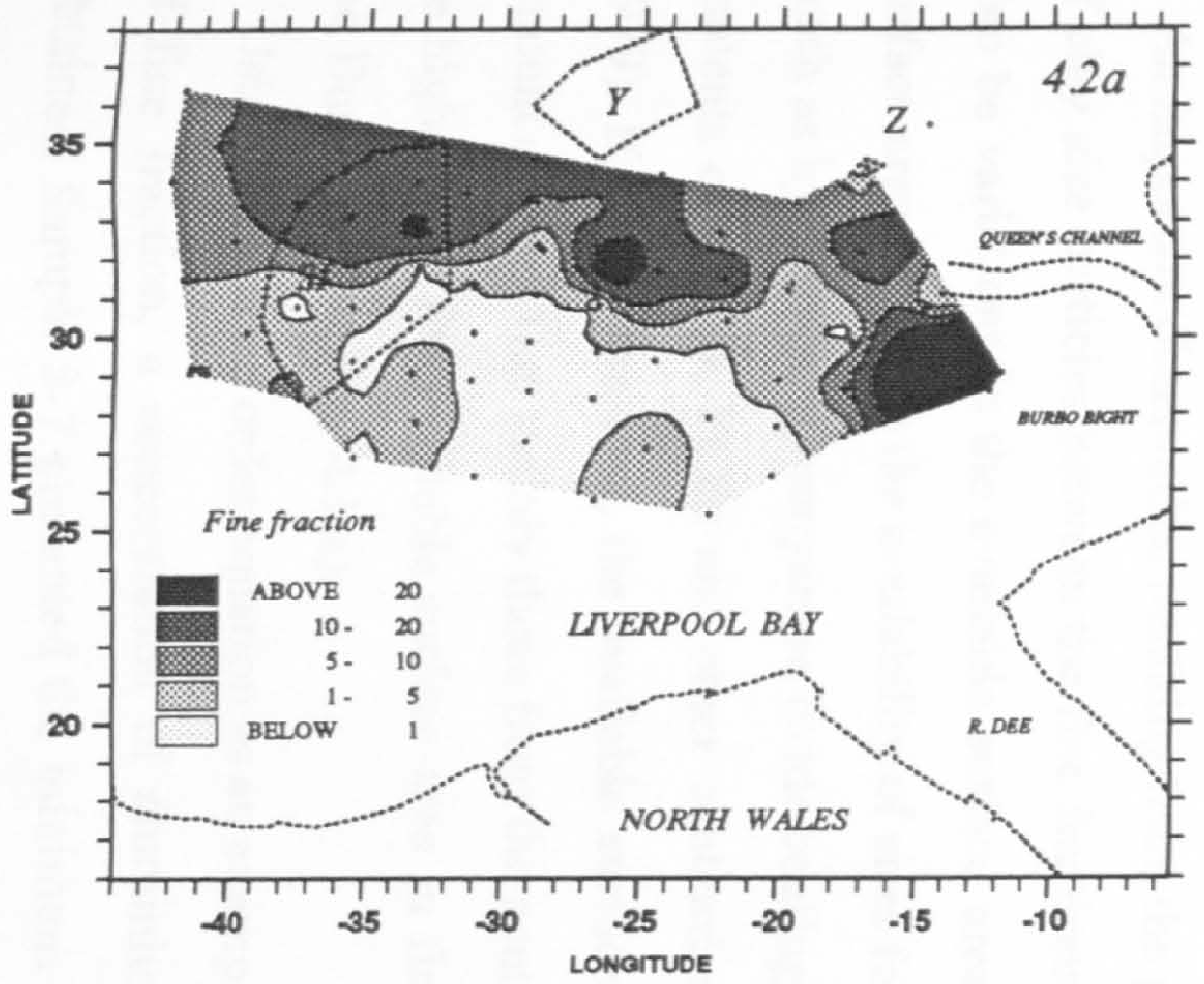
Clays have often been reported as the main metal carriers in aquatic sediments due, in part, to their high surface to volume ratio, which increases the chances of metals to adsorb onto their surface as compared to larger particles. Electrical charges on the surface of clay particles also increase the preference of metal ions for this particular sediment component. On the other hand, other components of natural sediments such as quartz, feldspars and carbonates are relatively metal poor and are considered to dilute the bulk sediment metal concentrations. For these reasons, aluminium in sediments has been used by several authors to "normalize" (correct concentrations due, in this case, to grain size effects) metal concentrations in sediments and particulate material (see for example Windom *et al.*, 1989; Duinker, 1981; Ridgway and Price, 1987; Kemp *et al.*, 1976).

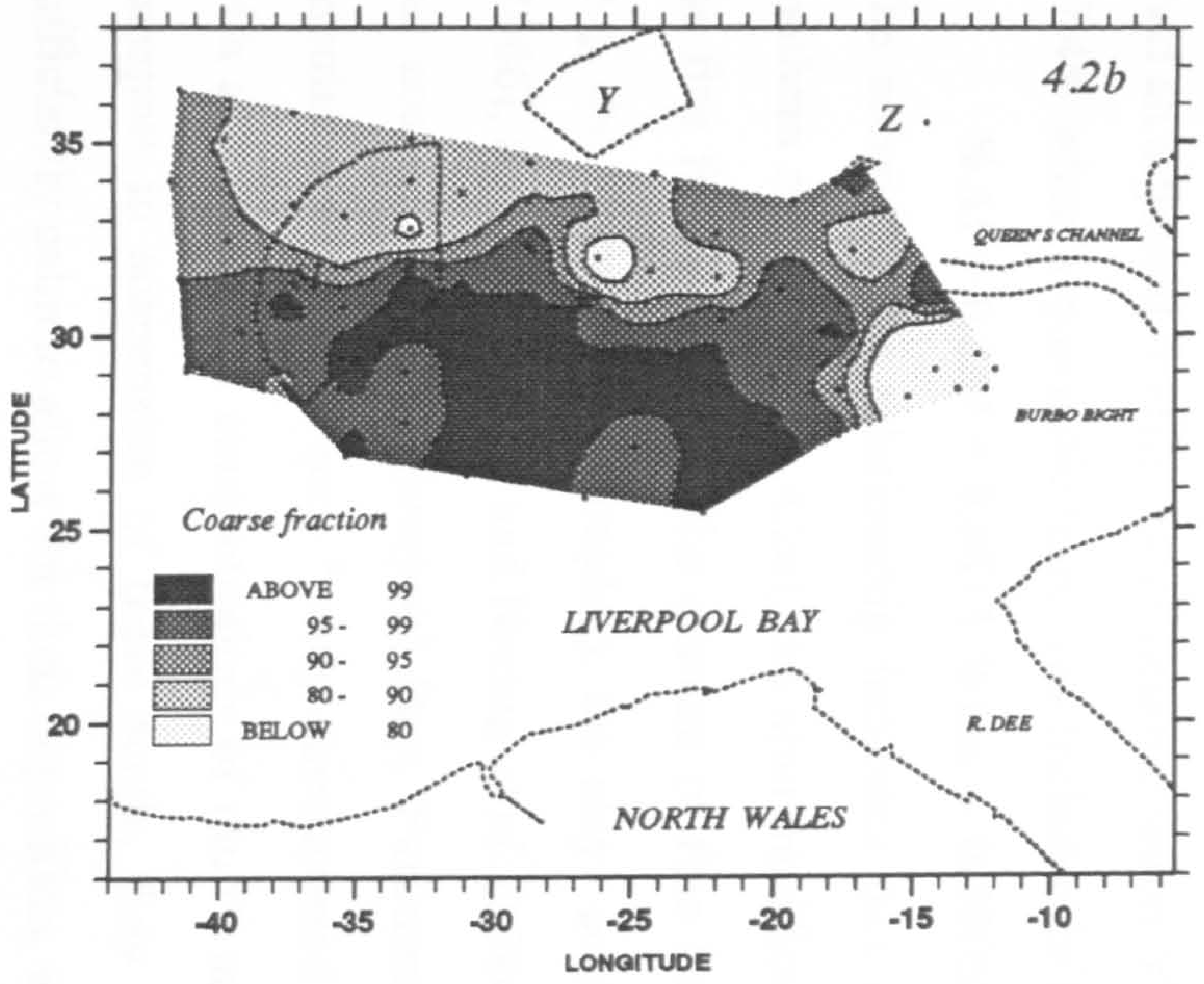
There are no previous records in the literature of aluminium analyses in sediments from Liverpool Bay, with the exception of a study by Rowlatt *et al.* (1986). These authors studied the effect of the disposal of dredged materials in the sediments around Site Z and normalized the concentrations of mercury, chromium, copper and zinc to that of the aluminium content in the sediments. Unfortunately, only three stations in the present study (T-12, T-14 and U-15; see Fig. 3.1) coincide with the region studied by Rowlatt *et al.*, therefore, it is difficult to make comparisons. The study of trace metals against an aluminium background has been recently recommended by other authors studying metals in sediments from Liverpool Bay (Rowlatt, 1988; McLaren, 1987), therefore, the author of this thesis hopes that the aluminium data presented here may provide a useful baseline for comparisons with future metal surveys in the region.

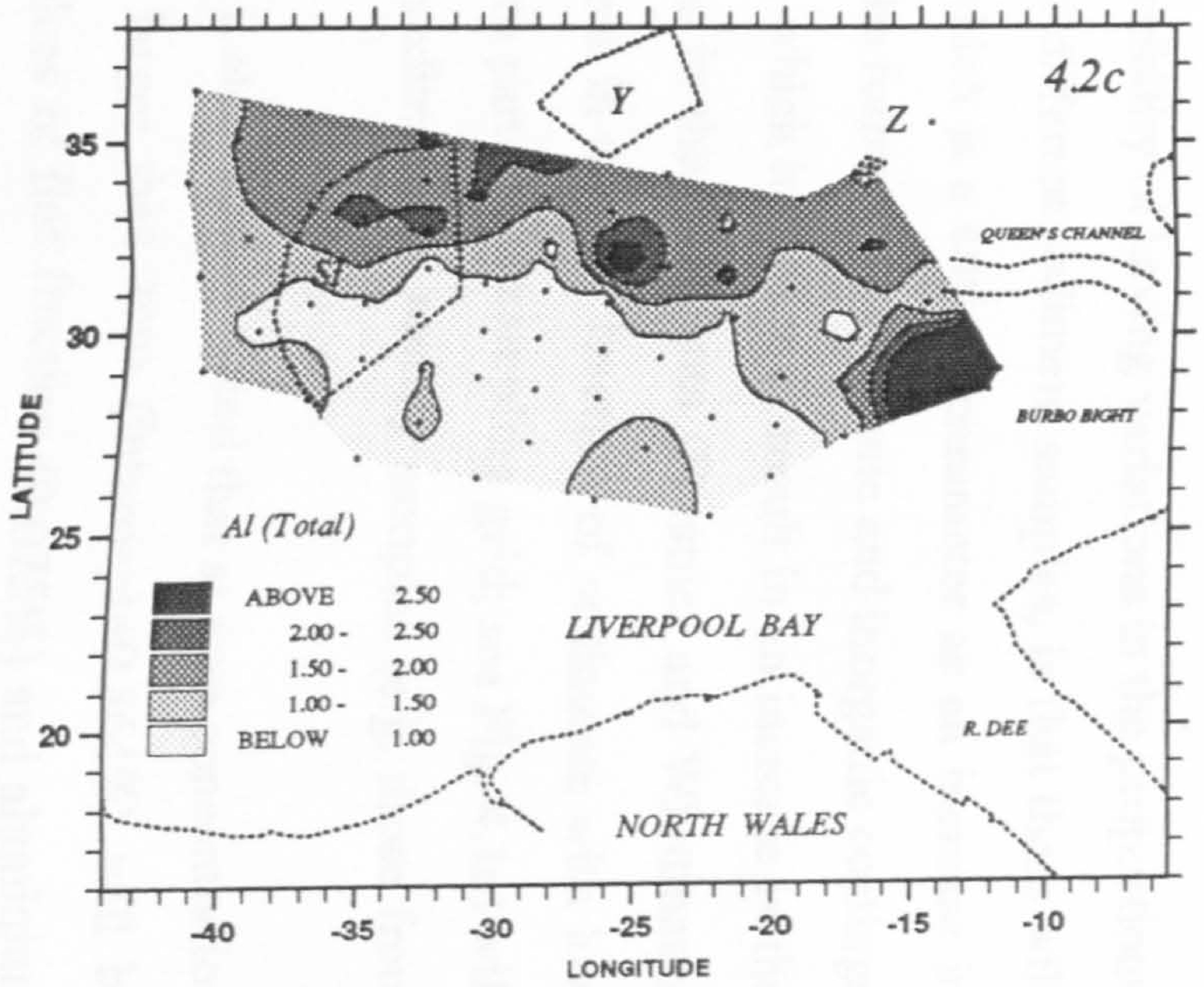
The distribution of the percentage of aluminium in the total sediment is showed in Figure 4.2c. This distribution closely resembles that of the fine fraction in the total sediment (Fig. 4.2a). Values for aluminium in the Burbo Bight area had a range from 2.71% at station NW-24 to 4.01% at station YY-1 (maximum value in the whole sampling area). The gradient from north to south showed values above 1.5% in the north (with a maximum of 3.20% at station P-11), and values below 1% in the south (with a minimum of 0.70% at station S-7).

The observed relationship between the distribution of fine fraction and the aluminium concentration (Figs. 4.2a and 4.2c) was not unexpected as an increase in muds may imply an increase in the clay content in the sediment. A highly significant linear correlation coefficient ($r=0.972$, $n=70$, $p<<0.001$) was obtained between these two variables, which suggested that the aluminosilicate component may represent an almost constant fraction of the fine sediments. A closer inspection of the relationship between these two variables (Fig. 4.3), however, indicates

Fig.4.2. Distribution of the percentage in dry weight of (a) fine fraction, (b) coarse fraction and (c) aluminium in the total (<500 μm) sediments.


4.2a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Fine fraction
ABOVE 20
10 - 20
5 - 10
1 - 5
BELOW 1
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.2b
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Coarse fraction
ABOVE 99
95 - 99
90 - 95
80 - 90
BELOW 80
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.2c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Al (Total)
ABOVE 2.50
2.00 - 2.50
1.50 - 2.00
1.00 - 1.50
BELOW 1.00
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10

that their association can be better described by a second order model than a linear one. The regression equation for a linear fit,

$$\%\mathrm{Al} = 0.953 + 0.0572\ \%\mathrm{fine},$$

had an adjusted coefficient of determination (r^2) of 94.3%, whereas this coefficient increased to 97.4% when a quadratic term was included in the regression

$$\%\mathrm{Al} = 0.864 + 0.0813\ \%\mathrm{fine} - 0.00052\ (\%\mathrm{fine})^2.$$

The second order relationship indicates that at low concentrations of fine fraction (*i.e.* the southern region in Fig. 4.2a), the aluminosilicate component constitutes a higher proportion of the fine fraction, and as the amount of fine fraction in the total (and bulk) sediment increases (e.g. the Burbo Bight samples), the clay contribution to the <90 μm fraction decreases. Sly (1966), McLaren (1987) and Norton *et al.* (1984a) reported an increase in the fine sands towards the coastal areas of Liverpool Bay. Furthermore, Norton *et al.* (1984a) reported fine sand populations (125-180 μm) "..only encountered in the vicinity of site Z,..., and often associated with above average concentrations of mud", and suggested that due to the ease of erosion and transport in suspension of these sands, they will occur only in areas where conditions are sufficiently calm to allow for their deposition, which in Liverpool Bay coincide with areas where mud deposits will occur. Therefore, the decrease in the contribution of the clay component to the fine fraction, as the amount of fines in the sample increases, can be explained by an increase in the contribution of the very fine sands (size range 62.5-125 μm) which where included in this <90 μm sedimentary fraction (*i.e.* sands with diameters 62.5-90 μm).

An important observation resulting from the possibility of having variations in the proportions of clay size particles between the fine fractions of different sediment samples, is that there will also be variations in the available surface area which is a critical parameter as an increase in surface area increases the availability of sites for the formation of organic and inorganic coatings (such as hydrous iron/manganese oxide coatings), which in turn may result in an increase in the contents of metals, PCBs and other contaminants in the sediments (Forstner and Whittmann, 1979). If this is the case, the available surface area in the fine fraction of sediments with low amount of fines (*i.e.* mainly those from the southern part of the sampling grid; see Fig. 4.1a) will be higher than the available surface area in fine sediments of muddy samples (e.g. those from the Burbo Bight; Fig. 4.1.a).

Using the second order equation as an example, it also must be noted that at zero concentration of fine fraction, a concentration of aluminium larger than zero (intercept=0.864%) will be obtained. Sample S-7 presented the minimum values of fine fraction (0.075%) and aluminium

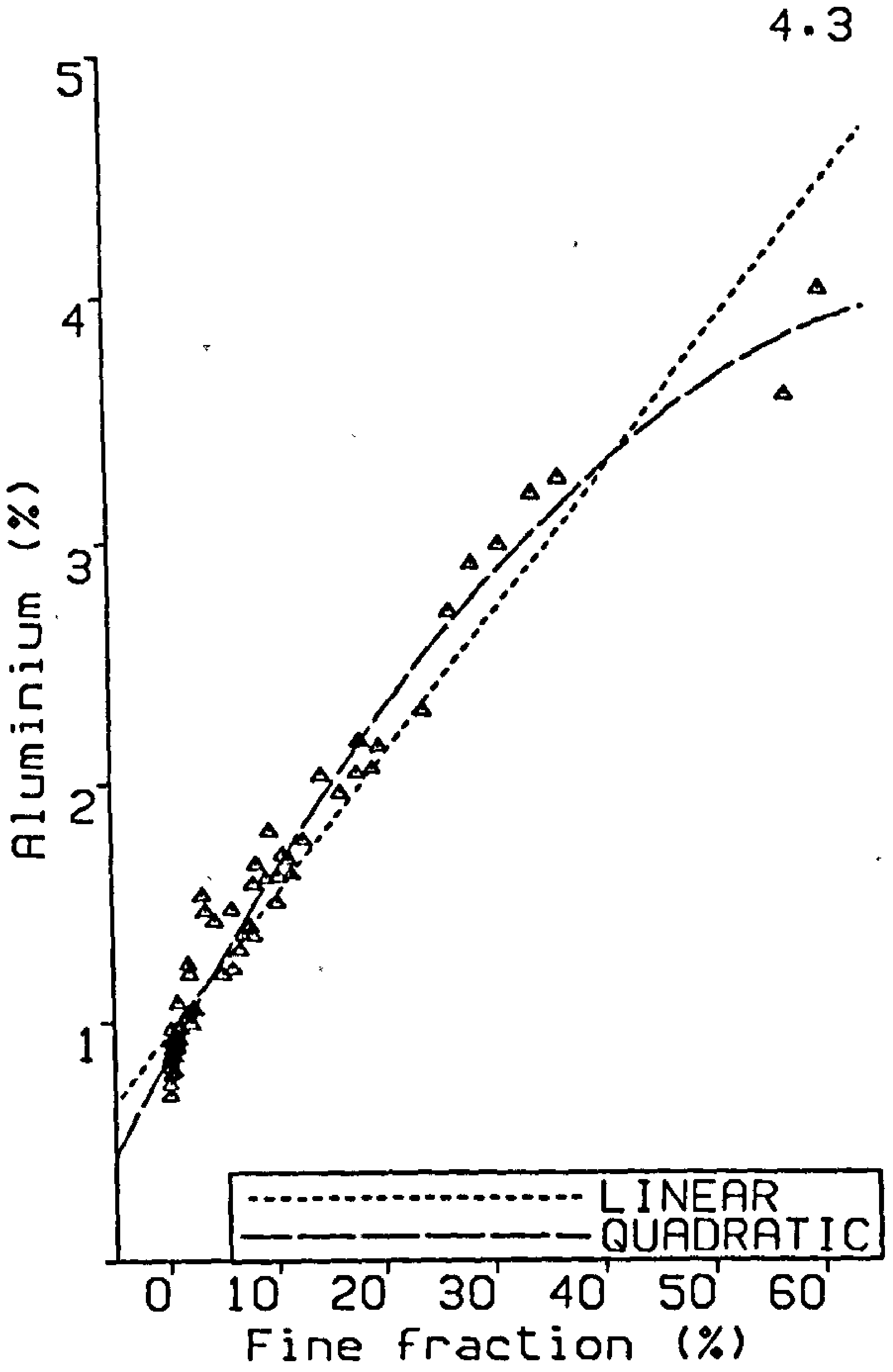


Fig.4.3. Scatter plot of the aluminium content versus the fine fraction content in the total sediments including the first and second order regression lines.

(0.70%), indicating that not all the aluminium in the total fraction was supplied by the aluminosilicate component in the fine fraction, but at least a fraction of it was present in the coarse sediments. A qualitative (visual) inspection of the coarse fraction in the sediments with very low amounts of fine material indicated that most of it was composed of clean sands, therefore, as these sediments are mainly composed of quartz (low in aluminosilicate minerals) the aluminium in the coarse fraction may be present as aluminium oxide coatings in the surface of the particles. The presence of oxides of iron/manganese in the surface of these particles was evident as the colour of their surfaces was reddish-brown, this observation suggesting that other oxides such as aluminium oxides are likely to occur.

4.1.3. Organic carbon and nitrogen

4.1.3.1. Organic carbon in the fine fraction

The total organic carbon distribution in fine sediments from Liverpool Bay is shown in Figure 4.4a. Carbon concentrations ranged from a minimum of 1.24% (station R-10) to a maximum of 3.05% (station K-8) and had a mean value of 2.03% (69 samples). The highest concentrations (>2.5%) were found as patches at stations K-8, M-8, M-9, M-10, N-10 and S-9 (Appendix B.4); the largest patches were found in the southeastern borders of Site SI. Excluding the region outside the Queen's Channel (Fig. 4.4a), there is a general trend of increasing values from less than 1.75% in the northwest of the sampling region to values higher than 2.25% towards the south and southeast. Samples from the Burbo Bight area showed a relatively large variation in total organic content with values ranging from 1.59% (sample YY-3) to 2.31% (station YY-2); stations T-12, T-14 (Site Z) and U-15 immediately out (west and northwest) of the Queen's Channel presented concentrations of 1.40, 1.45 and 1.35% respectively.

The organic carbon concentrations found in this study are within ranges previously reported for sediments in this area. Kiff and Nunny (1984) reported carbon concentrations in sediments <63 μm within a range of 1.6 to 3.2% with the distributions presenting no particular trends, although slight elevations in the southeastern area of Site SI were observed. These authors found no evidence of any significant change in organic carbon concentrations between six surveys in a three year period. Norton *et al.* (1984a) reported concentrations in <90 μm sediments ranging from less than 1% to 4.5%, with the lowest concentrations occurring in the offshore and southwestern areas, and an increase in values throughout the eastern inshore parts of the bay. Elevations in concentration were found, in particular, at, or immediately inshore from Site SI with values between 2.0 and 4.5%; these elevations were particularly noticeable during one of their four annual surveys (1978 survey), which showed an organic carbon distribution (see Fig. 12 in Norton *et al.*, 1984a) similar to the one reported in this study (Fig. 4.4a).

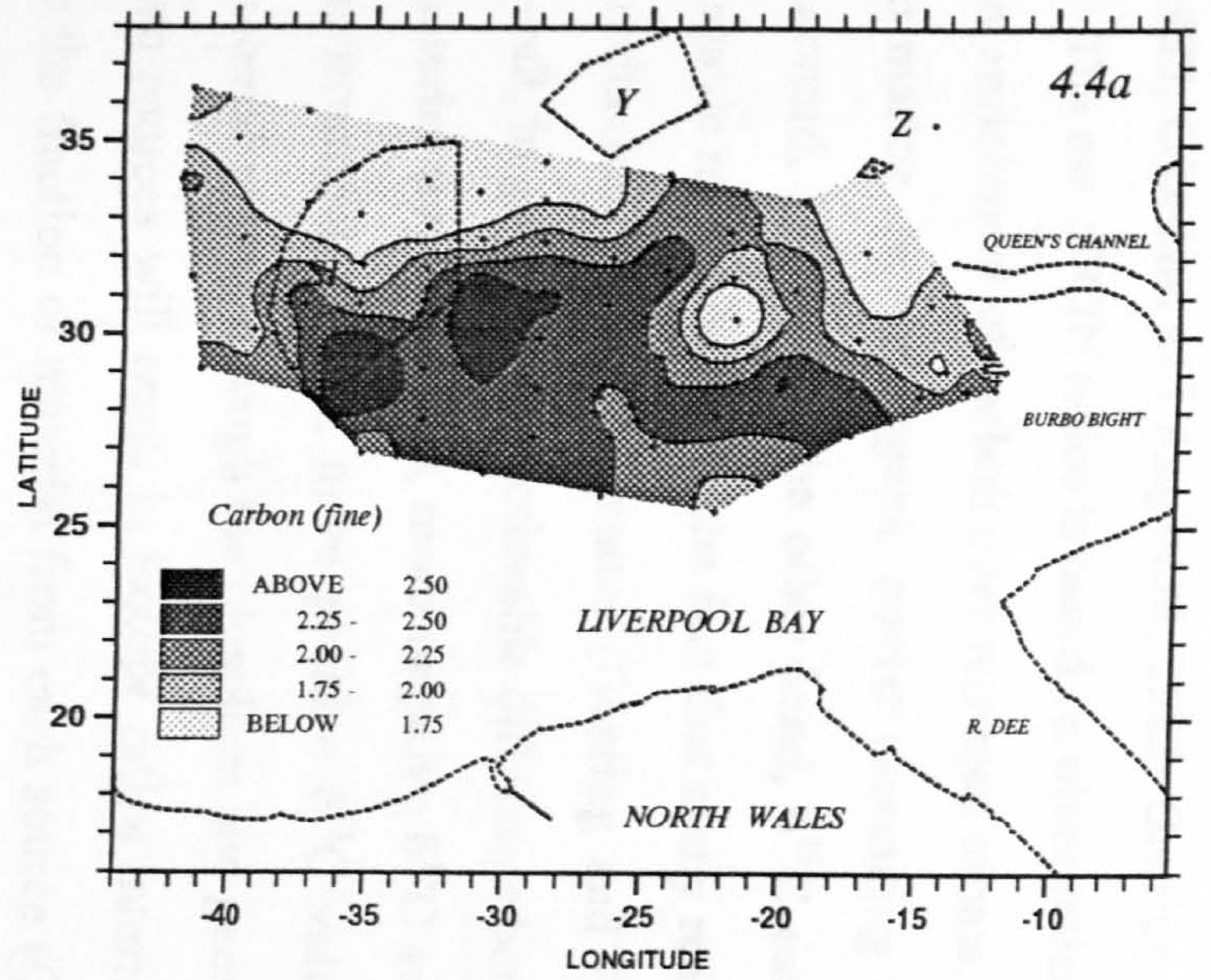
It is clear that, although carbon concentrations seem to remain within a relatively constant range with time (Kiff and Nunny, 1984), carbon distributions change (see Fig. 12 in Norton *et al.*, 1984a) as sediment grain size distributions change in response to variations in hydrodynamical conditions that control sediment transport in Liverpool Bay. Therefore, generalizations in the distribution pattern of organic carbon in fine sediments presented in this study must be viewed with caution if comparisons with other surveys are to be made. However, if factors controlling the distribution of organic carbon in sediments are considered, it may be possible to draw some general conclusions with regard to distributions of organic carbon in the sediments from Liverpool Bay.

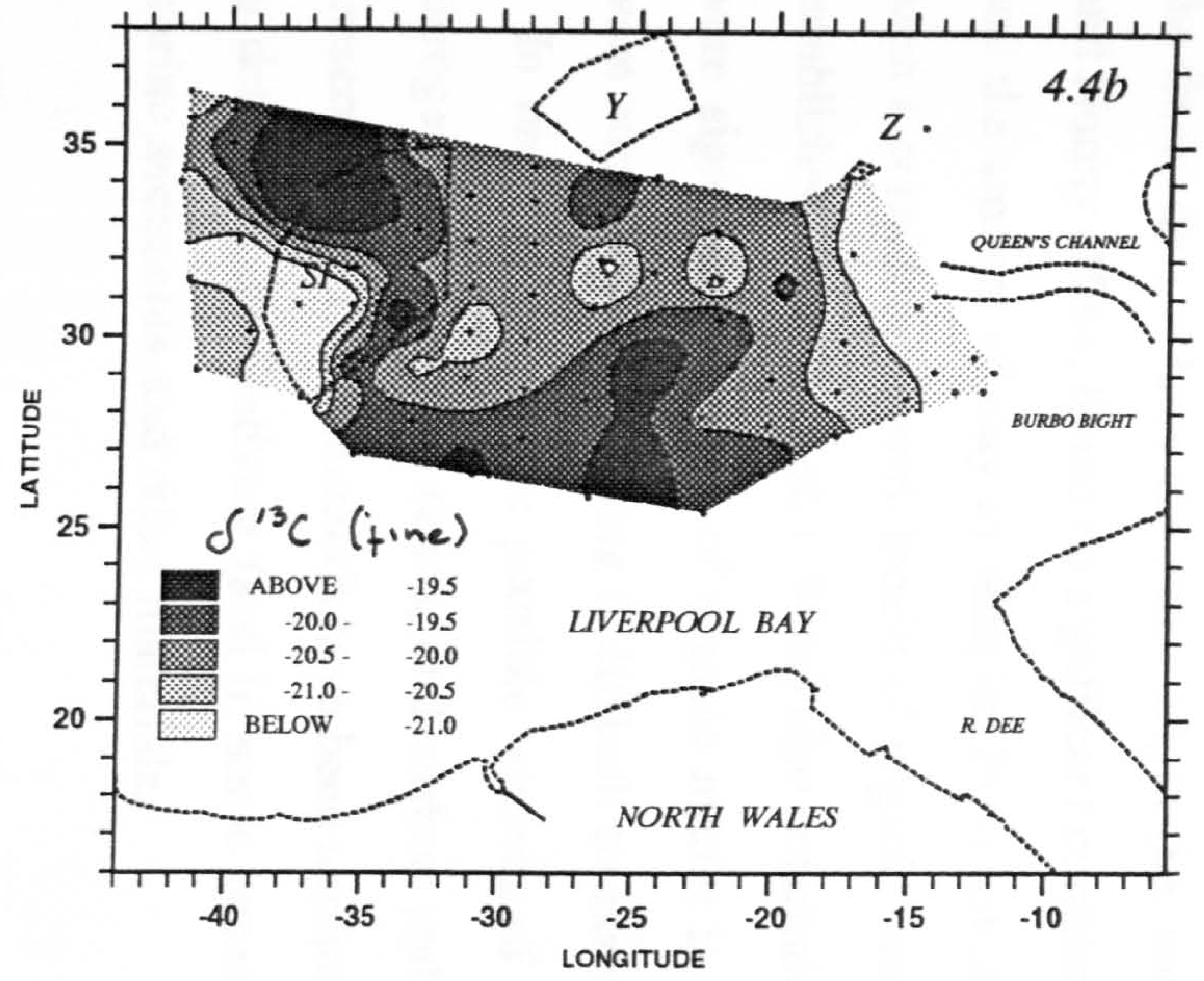
Highly significant ($p<<0.001$) negative linear correlations were obtained between the organic carbon content in the fine fraction, and the logarithm of the concentrations of aluminium ($r=-0.495$) and the percentage of fine fraction ($r=-0.519$) in the total sediments. As shown in Figure 4.5a, these negative correlations indicate that organic carbon in fine sediments increases as the amount of fine material in the total sediment decreases. It has been previously suggested, from Figure 4.3, that the proportion of clays within the fine fraction increases in samples containing lower amounts of fine fraction in the total sediments and vice versa. If this observation is true, then the surface area per unit weight in the fine fraction is higher in sediments with lower fines (southern area Fig. 4.2a), therefore, a higher organic content in these sediments is not unexpected (Fig. 4.4a).

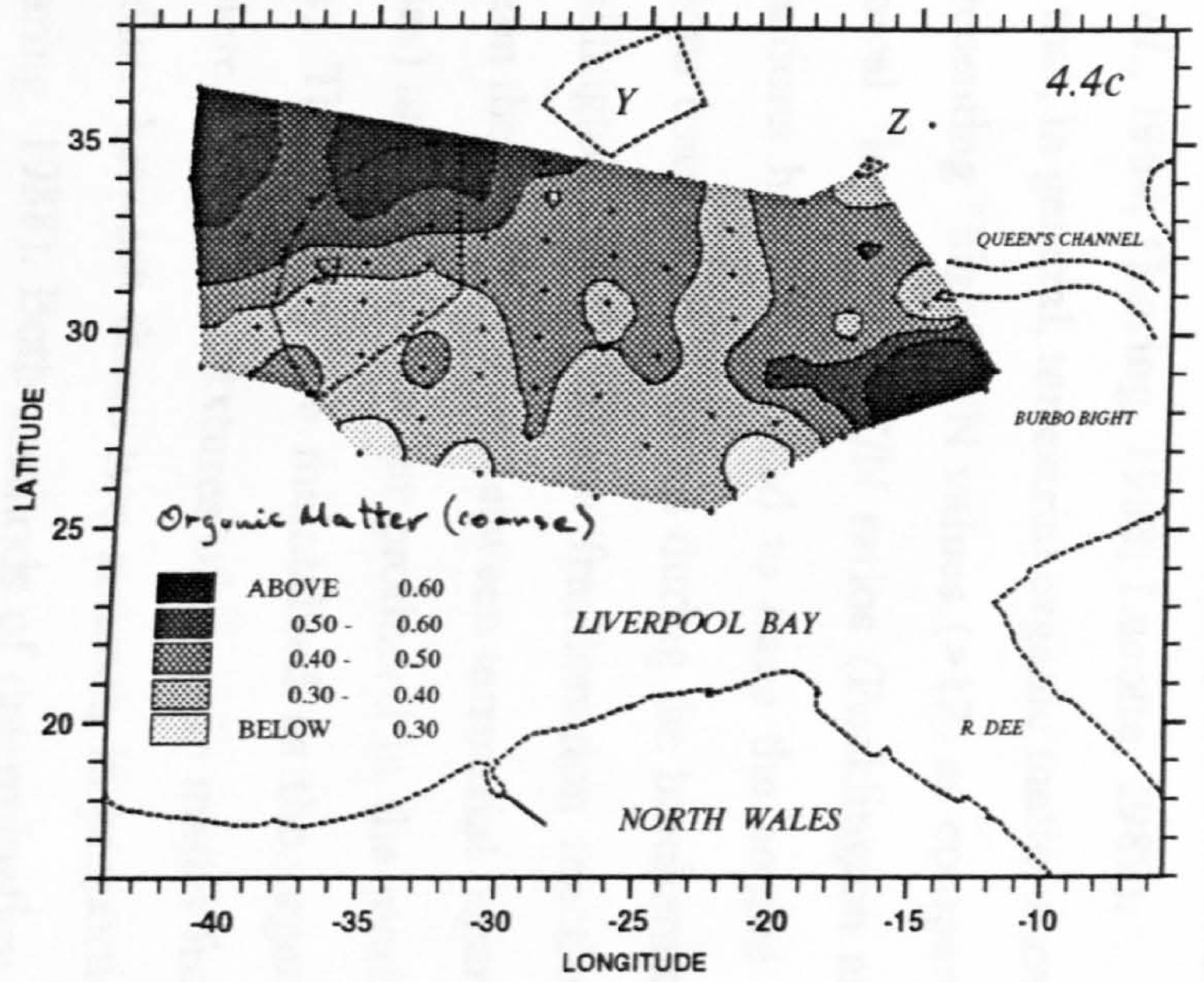
The significance in the correlation between organic carbon and the fine fraction and aluminium in total sediments only indicates that there is an overall tendency of carbon to increase as these variables decrease, however, as indicated by the determination coefficients ($r^2=0.27$ for carbon vs fine fraction; $r^2=0.24$ for carbon vs aluminium), the fine fraction and the aluminium content in the total fraction can only predict about 25% of the variance in the organic carbon content in fine sediments (see also the scatter in the data presented in Fig. 4.5a), therefore, other factors have to be considered to explain the distribution of the organic carbon values reported in the present study.

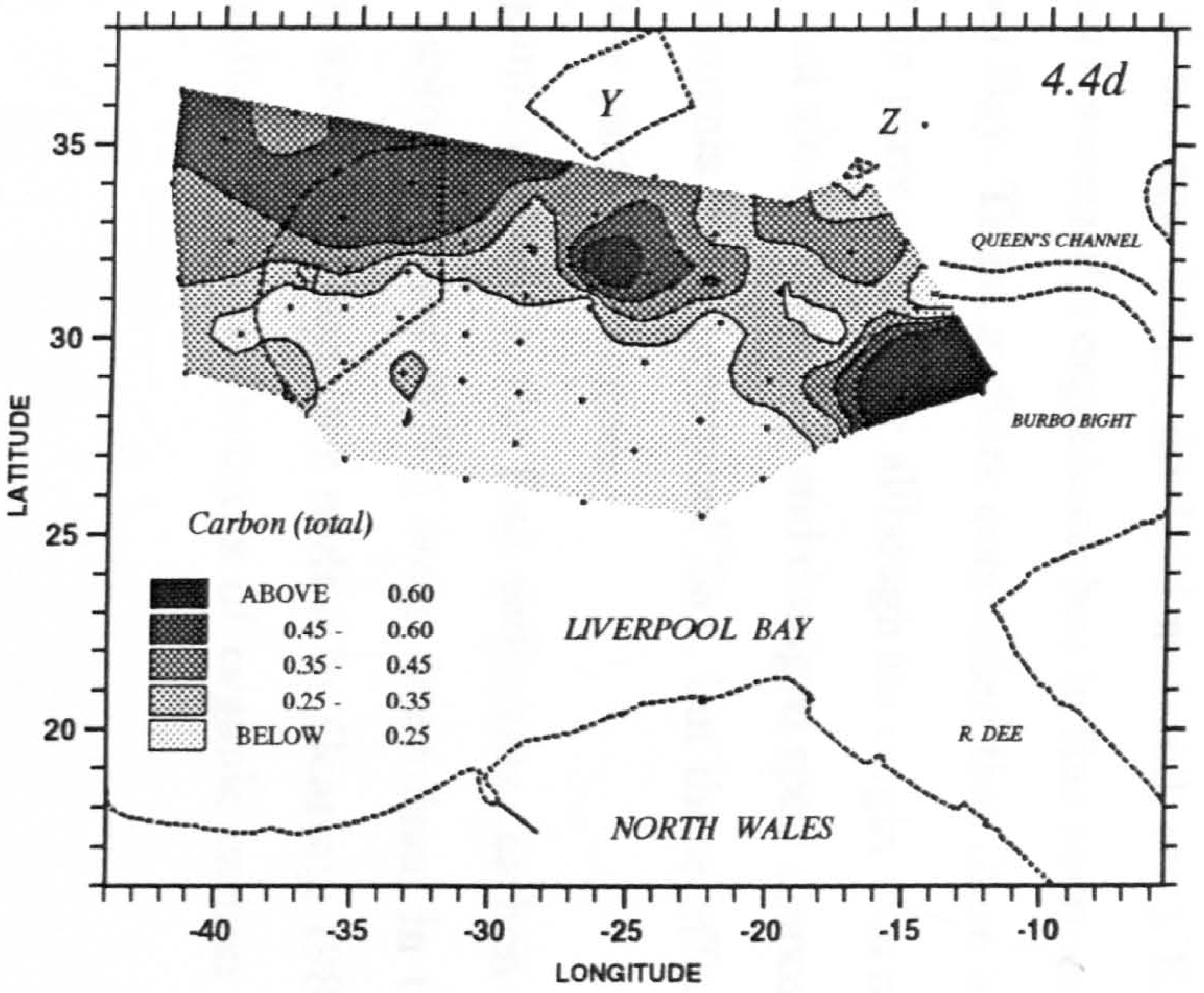
The scatter in the data presented in Figure 4.5a indicates that samples with similar amount of fine material may have substantially different carbon contents. It would be expected that, if the source of organic carbon was the same for all particles, the primary factor controlling the carbon distribution in the sediments would be the available surface area for deposition, therefore, it

Fig.4.4. Distribution of (a) organic carbon (%) and (b) $\delta^{13}C$ (‰) values in the fine fraction, (c) organic matter content (%) in the coarse fraction and (d) organic carbon in the total fraction(%).


4.4a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
SJ
Carbon (fine)
ABOVE 2.50
2.25 - 2.50
2.00 - 2.25
1.75 - 2.00
BELOW 1.75
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.4b
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
SJ
δ¹³C (fine)
ABOVE -19.5
-20.0 - -19.5
-20.5 - -20.0
-21.0 - -20.5
BELOW -21.0
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.4c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
SJ
Organic Matter (coarse)
ABOVE 0.60
0.50 - 0.60
0.40 - 0.50
0.30 - 0.40
BELOW 0.30
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.4d
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
SJ
Carbon (total)
ABOVE 0.60
0.45 - 0.60
0.35 - 0.45
0.25 - 0.35
BELOW 0.25
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10

would be roughly controlled by the grain size distribution. However, if different sediments receive carbon depositions from different sources and at different rates, the grain size effect on the carbon distribution may be overshadowed. This effect is increased if the particles (particularly the fines) do not have the same origin (i.e. natural, sewage sludge, dredged material, etc.). Kiff and Nunny (1984) found no significant correlations between the organic carbon in fine sediments and the amount of clay in samples from Liverpool Bay. These authors concluded that there has been a considerable enrichment of organic matter in parts of the bay although its origin was not established. Norton *et al.* (1984a) also concluded that sludge dumping and dredged spoil disposal were significant sources of organic matter in sediments from Liverpool Bay, but these effects were superimposed making it difficult to assess the particular sources.

In order to assess the possible sources of organic carbon in the fine sediments, carbon to nitrogen (C/N) atomic ratios, and carbon stable isotopes ratios ($\delta^{13}C$) were determined in the present study. These methods have been applied by several authors (see review by Gearing, 1988) to determine qualitatively (and in some cases quantitatively) the sources of organic carbon in marine sediments and other materials.

4.1.3.2. C/N ratio and carbon stable isotopes ratio ($\delta^{13}C$) in fine sediments.

The sources of organic matter (particularly marine vs terrigenous) in estuarine and coastal areas have been studied by several authors through determinations of C/N atomic ratios and/or $\delta^{13}C$ (e.g. Sackett, 1964; Pocklington and Leonard, 1979; Burnett and Schaefer, 1980; Tan and Strain, 1983; Giordani and Angiolini, 1983; Gearing *et al.*, 1984; Gearing, 1988; Lucotte, 1989).

The use of C/N ratios is based on observations that, in general, terrestrial organic matter shows an enrichment of carbon over nitrogen atoms, presenting "high" C/N values (>12) as compared to marine derived organic matter presenting typical "low" (<10) C/N ratios (Pocklington and Leonard, 1979). On the other hand, $\delta^{13}C$ estimations have been used to trace the source of organic matter based on the fact that many reactions fractionate isotopes during the biochemical production of organic matter (Gearing and Pocklington, 1990). These fractionation reactions result, in general, in a noticeable difference between the $^{13}C/^{12}C$ ratios between terrestrial organic material (typically low, more negative $\delta^{13}C$ values) and organic matter produced in the marine environment (higher, more positive $\delta^{13}C$ values). These ratios are maintained as the organic material moves through the biosphere and geosphere, therefore, mixtures of organic matter from two sources will result in isotope ratios intermediate between those two sources, in proportion to the fraction of material from each source (Gearing, 1988). Both methods of determination of

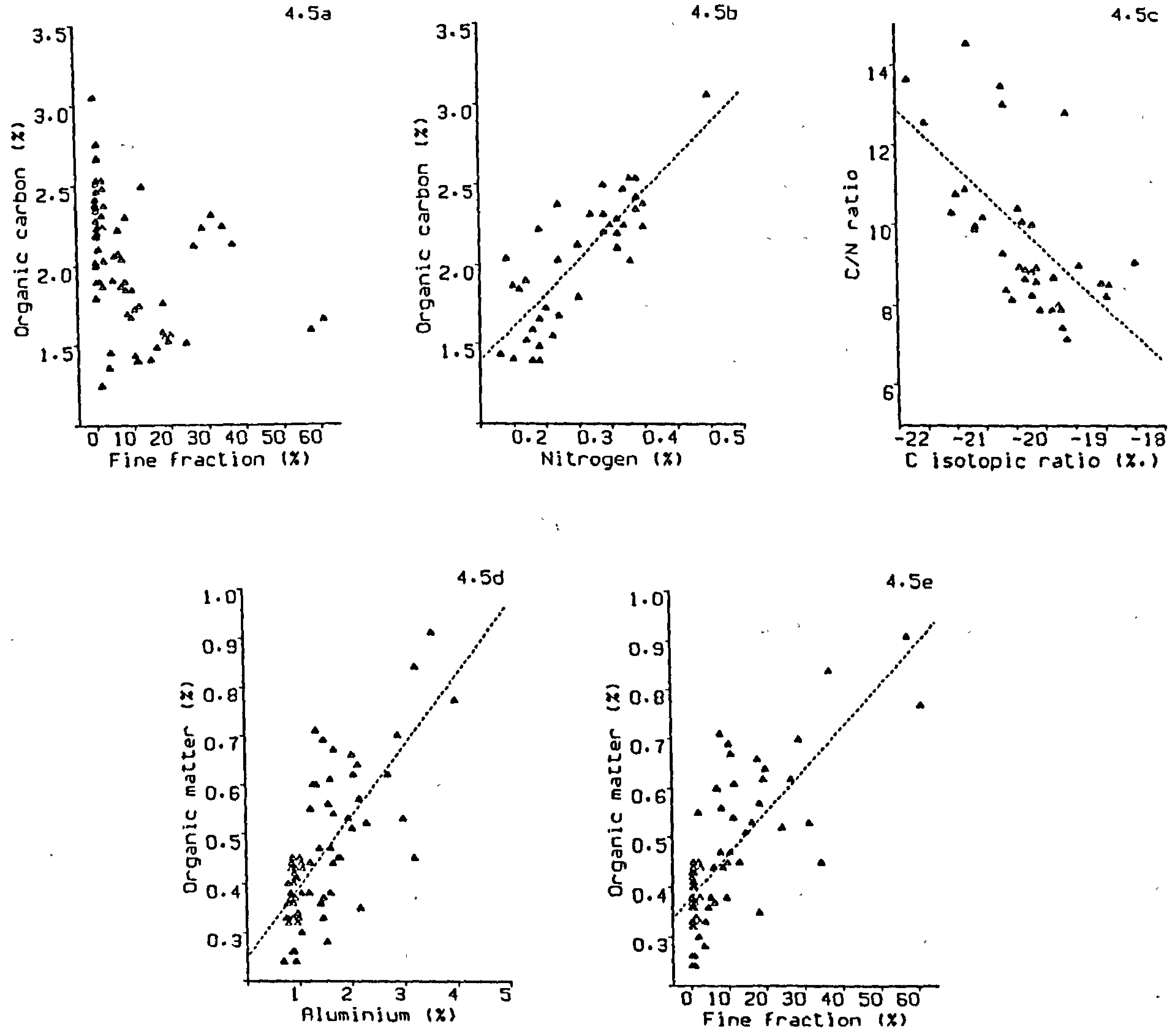


Fig.4.5. Scatter plots of (a) the organic carbon in the fine sediments vs the fine fraction content, (b) the organic carbon vs nitrogen in fine sediments, (c) carbon:nitrogen ratio vs $\delta^{13}C$ values in fine sediments, (d) organic matter in the coarse fraction vs aluminium in the total sediments and (e) organic matter in coarse sediments vs the fine fraction content.

organic matter sources have their limitations since, large variability within a source may occur, making differences between two different sources less obvious. For example, terrestrial plants with different photosynthetic pathways (i.e. C_3 or C_4) usually present large differences in $\delta^{13}C$ values, with C_3 plants showing values around -27.0‰ whereas C_4 plants show values around -13.0‰. Marine diatoms show values around -20.0‰ whereas nanoplankton shows values around -23.0‰ (Gearing, 1988). Another limitation, important with regard to the Liverpool Bay area, is that if more than two sources of organic material are present (e.g. riverine, sewage sludge, dredged spoil, autochthonous, etc.), the determination of $\delta^{13}C$ or C/N values can only be used to roughly determine the possible sources but it will be difficult to assess the contribution of each source to the total organic matter in a particular sample. When more than two carbon sources are present, the determination of other stable isotope ratios (e.g. nitrogen, hydrogen and sulphur isotopes) and other variables such as lignin oxidation products can be useful for tracing and quantifying the individual contribution of each source to the total carbon in a particular sample (Gearing, 1988). Bearing in mind these limitations, $\delta^{13}C$ determinations have been very useful for a variety of studies in ecosystems, particularly estuaries and unpolluted coastal areas, where there are only two dominant sources of carbon with considerable isotopical differences (see review by Gearing, 1988).

The distribution of $\delta^{13}C$ values in fine sediments from Liverpool Bay observed in the present study, is presented in Figure 4.4b. The eastern region, closer to the Mersey Estuary, shows a gradient with decreasing (more negative) values towards the coast indicating inputs of terrigenous organic carbon from the Mersey Estuary. In the region of low values outside the Queen's Channel a range between -21.02‰ at station T-14 (Site Z) to -21.57‰ at station YY-3 can be found. The lowest values of $\delta^{13}C$ in the bay as a whole, however, were found at stations J-7 (-22.31‰) and J-9 (-22.02‰) in the southern most region of Site SI; also within Site SI sample K-9 showed a very low (-21.49‰) value. Patches of low $\delta^{13}C$ were also found around stations L-8 (-20.71‰), M-9 (-20.83‰), P-11 (-21.16‰) and R-11 (-21.15‰).

The highest (more positive) values, more typical of organic matter of marine origin, were found in the northwestern sector of the sewage disposal site (Fig. 4.4b), with values higher than -19.10‰ at stations K-11, K-12, L-9 and a maximum of -18.49‰ at station J-11. The central-southern region, where the lowest proportions of fine fraction were found, was also an area of relatively high $\delta^{13}C$ values (>-20.00‰) with maxima at stations Q-7 (-19.28‰) and Q-9 (-19.06‰).

Unfortunately, several of the samples (32 of a total of 70) analysed for organic nitrogen were below the detection limit of the instrument. The number of analysed samples did not allow for drawing a reliable contour map for comparisons with other variables. However, a similar distribution to the organic carbon content (Fig. 4.4a) is expected as indicated by the high linear correlation ($r=0.818$, $n=38$, $p<<0.001$) between carbon and nitrogen in the samples. This relationship, represented in Figure 4.5b, was expected as the nitrogen and carbon content in a sediment must increase if the total organic matter in the sample increases.

The C/N atomic ratios for the 38 samples determined in this study are presented in Figure 4.6. The mean value for all samples was approximately 9.9 with a minimum of 7.1 and a maximum of 17.0. It can be observed that samples from the Burbo Bight region had homogeneous ratios of around 10. However, the highest ratios, characteristic of terrestrial organic matter, were observed in the southern part of the sewage disposal site (atomic ratios ~13) and in three samples in the extreme northwestern part of the sampling region where the maximum value was observed (station G-11, Fig. 4.6). Most of the samples between Site SI and the region outside the Queen's Channel presented ratios lower than 9.0 with the exception of stations M-12 (10.4) and Q-11 (10.0). The lowest ratios were found in the central-southern region with values lower than 8.3 and the minimum of 7.1 at station S-7, these values suggesting that most of the organic matter in sediments from this area is predominantly of marine origin.

A relationship between the carbon stable isotopes ratio and the C/N ratio was found in the fine sediments analysed in this study. A significant correlation ($r=-0.538$, $n=38$, $p<<0.001$) between these two variables was observed, indicating that in general, high C/N ratios correspond to low $\delta^{13}C$ values, both characteristic of a higher content of land derived organic matter as compared to low C/N ratios and higher (less negative) $\delta^{13}C$ values indicating higher proportions of marine organic carbon (Fig. 4.5c). Figure 4.5c indicates that there is a general tendency in the relationship between the isotopic composition and the C/N ratios in the organic matter in sediments from Liverpool Bay, however, the dispersion in the data indicates that more than two carbon sources exist, each of the sources with different organic matter composition.

The low $\delta^{13}C$ values (<-21.0‰) and high C/N ratios (>12.6) in the southern part of Site SI indicate a possible significant contribution of land-derived organic matter to the total organic matter in sediments from this area. Analyses of three sewage sludge samples similar to the material dumped at Site SI showed $\delta^{13}C$ values around -24.0‰ and C/N ratios around 15. Therefore, it is possible that a significant proportion of the organic matter in sediments from the southern region of Site SI is from the sewage sludge discharges in the region. An interesting

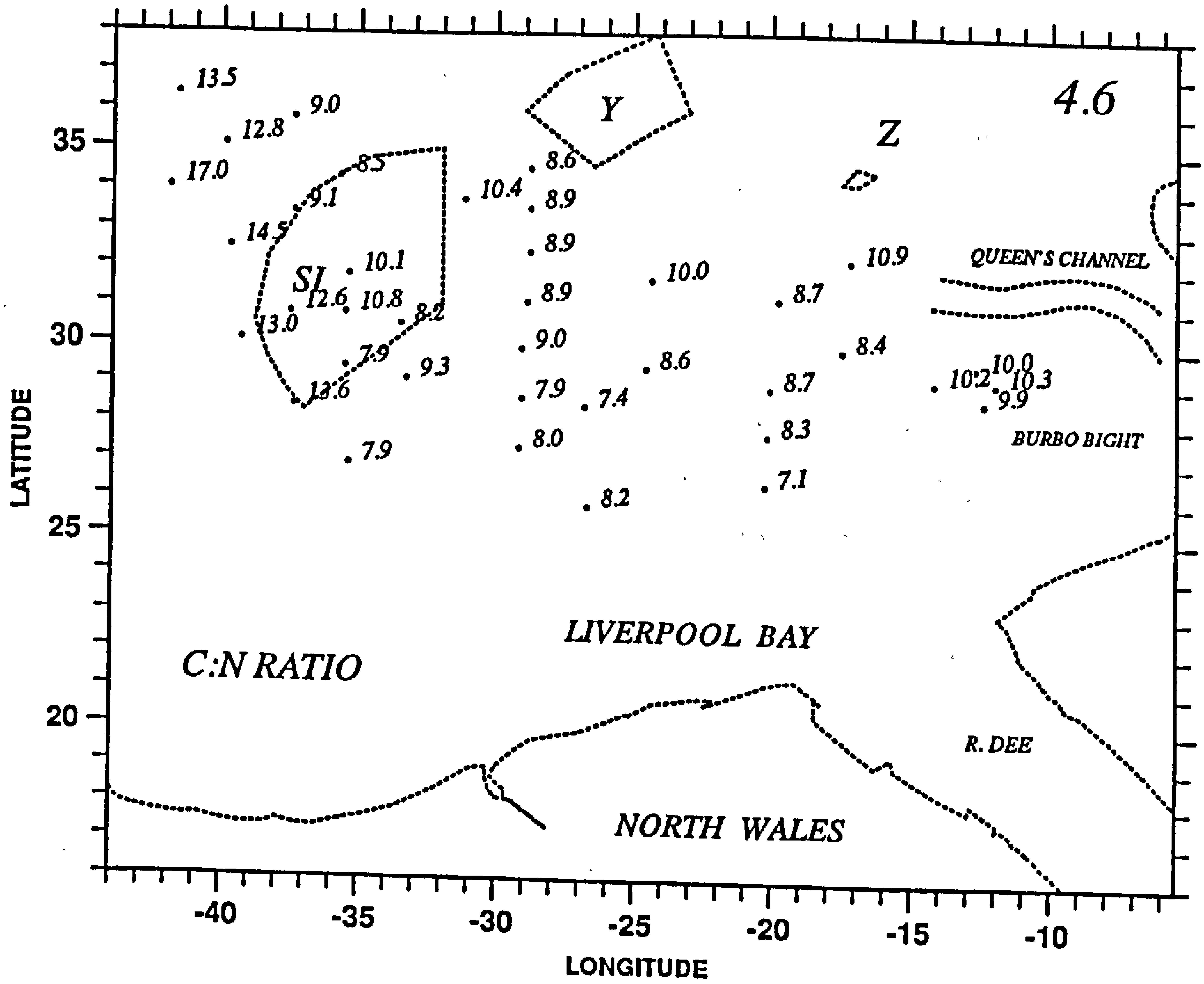


Fig.4.6. Distribution of the carbon:nitrogen atomic ratio values in the fine sediments.

observation is that the sewage disposal area is subdivided in several sectors for the control of the discharges, and that from early 1988 the dumping activities have been concentrated in the extreme southern sector of Site SI (P.C. Head, North West Water, pers.comm.); this observation supports the hypothesis that the observed values of $\delta^{13}C$ and C/N ratios in this area result from the disposal of sewage sludge.

Another area with low $\delta^{13}C$ (less than -21.0‰) values and relatively high (~10) C/N ratios is that near the Queen's Channel, outside the Mersey Estuary. Figure 4.4b shows that there is an apparent gradient of $\delta^{13}C$ values in this area indicating the influence of the run-off from the River Mersey exporting some organic matter with higher proportions of land derived organic carbon than the natural organic matter in the bay which contains a higher proportion of marine organic carbon. The $\delta^{13}C$ values found in this study for the whole area are within ranges reported for other coastal and estuarine sediments (see Gearing *et al.*, 1977; Tan and Strain, 1983) although in general the values found in the present study, even the ones near the Mersey, seem to be within ranges more characteristic of organic matter of marine origin. This observation would not be unexpected since, according to the sediment transport patterns discussed in chapter two, the net transport of particles (and their associated organic matter) is from the bay towards the Mersey Estuary (according to Taylor, 1986, ~90% of the sediment in the estuary is transported from Liverpool Bay and the remainder from riverine and other inputs), therefore, the organic matter tends to be transported in the sedimentary phase from the bay toward the land. The gradient shown in Figure 4.4b may be a result of organic matter being transported in solution out of the Mersey and being flocculated and precipitated outside the Queen's Channel. A large proportion of riverine organic matter is precipitated during estuarine mixing, flocculation increasing with increasing salinity (Forstner and Wittmann, 1979). Carbon isotope studies (Gearing *et al.*, 1977) suggest that natural inputs of terrestrial organic matter into marine systems are very limited and that this organic matter plays only a small part in determining the $\delta^{13}C$ value of the total organic carbon in continental margin sediments. This observation suggests that the patches of low (less than -20.5‰) $\delta^{13}C$ values found in the present study may be related to the discharges of wastes into Liverpool Bay rather than to natural or riverine inputs of organic matter.

The lack of a significant correlation between the total organic carbon content and the stable isotopic ratio, and between organic carbon and C/N ratios indicate that the total amount of carbon in the sediments is not necessarily an indicator of anthropogenic effects. For example, station K-8 in the southeastern limits of Site SI presented the maximum total organic carbon concentration (3.05%). This observation may lead to the conclusion that, given the location of the sample, this enrichment of carbon is due to the discharges of sewage sludge in this area, however, this sample presented one of the lowest C/N ratios (7.9) and a relatively high (-19.7‰) $\delta^{13}C$ value both characteristic of marine derived organic matter. On the other hand, another sample with high carbon content was M-9 (2.76%). This sample presented a relatively low $\delta^{13}C$ value (-20.8), indicating the possible contribution of organic matter derived from sewage sludge discharges. Stations J-7 and J-9 did not show total organic carbon values significantly above the average for the whole region (~2.03%), however, these samples presented the highest $\delta^{13}C$ values (-22.3 and -22.0‰ respectively). Some samples containing high proportions of fine fraction, particularly the muddy patches around stations P-11, R-11 and T-12 (Fig. 4.2a) also presented low stable isotope values indicating the presence of sewage sludge derived organic matter. This observation is consistent with the results by Crickmore (1972b) as this author found evidence of radiolabelled sewage sludge particularly associated to the mud patches to the east of the sewage disposal site.

The three samples in the extreme northwest sector of the sampling grid with C/N ratios above 13 (stations G-11, G-13 and H-10) also showed relatively low $\delta^{13}C$ values (-20.7, -20.8 and -21.3‰ respectively) indicating possible inputs of organic matter derived from the sewage sludge discharges. It must be remembered, however, that although the disposal of sewage sludge could be an important source of organic matter from a local point of view, several possible sources of organic matter remain which have not been considered, therefore, the observations about the possible contributions of sewage derived organic matter should be considered as tentative.

4.1.3.3. Organic matter in the coarse fraction

Figure 4.4c shows the distribution of an estimation of the organic matter in the coarse sediments as determined by loss on ignition at 550°C. Excluding the area outside the Queen's Channel, a gradient of decreasing concentrations from values higher than 0.50% in the northwestern region to values lower than 0.40% in the southeast can be observed. The highest values in the northwestern region were found at stations G-13 (0.71%) and H-12 (0.69%) whereas the lowest values in the southern region were found at stations M-6 (0.26%), P-6 (0.26%) and S-7 (0.24%). The mean organic matter concentration for the whole region was ~0.46%. Samples from the Burbo Bight area had the highest organic matter concentrations in the whole sampling area, with a value up to 0.91% at station YY-3, however, sample YY-2 had a concentration of only ~0.53% emphasizing the great variability in sediment characteristics from this muddy zone already shown with the organic carbon content of the fine sediments. A tongue of increasing carbon content in coarse sediments out of the Queen's Channel is an interesting feature shown in Figure 4.4c. A less obvious tongue in the same position, with increasing values of the percentage of coarse material towards the channel and decreasing values of fine sediments, is presented in Figures 4.2a and 4.2b.

Due to analytical limitations it was not possible to determine the organic carbon content nor the organic nitrogen content in coarse sediments. The same detection limitations did not allow for a determination of the carbon stable isotopes ratio in this fraction, therefore, an assessment of the possible sources of organic matter in the coarse fraction is even more difficult than that of the carbon in the fine fraction (see discussion above). An examination of the relationship (if any) between the organic matter in the coarse fraction and other parameters such as grain size distributions and organic carbon in the fines, however, may yield some information regarding the sources of this organic matter in coarse sediments.

Highly significant linear correlations ($p<<0.001$) were found between the organic matter content in the coarse fraction and the aluminium concentration ($r=0.734$) and fine fraction concentration ($r=0.752$) in the total sediment. These relationships presented in Figures 4.5d and e indicate that, in general, the organic matter in the coarse sediments increases as the amount of fine material increases. This observation suggests that coarse sediments may be getting part of their organic matter from the fine particles, richer in organic matter. The regression equation obtained for the relationship with aluminium was

$$\mathbf{O.M. = 0.250 + 0.142\ \%Al,}$$

($r^2=53.2\%$, $F=79$), whereas the equation with the percentage fine fraction was

$$\mathbf{O.M. = 0.381 + 0.0085\ \%fine,}$$

($r^2=56.0\%$, $F=88.7$). The correlation coefficients indicate that the relationship between the organic matter in the coarse fraction and the amount of fine particles in the samples is significant, however, as indicated by the determination coefficients (r^2 values) in the regression analyses, only approximately 55% of the variance in the organic matter content of coarse sediments can be explained by the variations in the amount of fine particles in the sample. A closer inspection in these relationships indicated that, at concentrations of fine fraction in the total sediment lower than 5% (i.e. those samples in the southern region, Fig. 4.2a), there was no significant relationship between the amount of fine fraction and the organic content in coarse sediments ($r=0.051$, $n=38$) or between the aluminium content and the organic matter ($r=0.317$, $n=33$). This observation indicates that the organic carbon content in the coarse sediments is only significantly influenced by the transfer of carbon from the fine particles when there is a high enough (>5%) amount of fine particles coexisting with the coarser material. When the amount of fine fraction was lower than 5% (% aluminium lower than ~1.2), the organic matter content in coarse sediments varied without particular trends between 0.24 and 0.45% (Fig. 4.5d and e).

4.1.3.4. Organic carbon in total sediments

The amount of organic carbon in the total sediments was computed, first, by transforming the organic matter data in the coarse sediments to organic carbon values by the use of an empirical factor (O.C.=O.M./1.887; Gearing and Pocklington, 1990); and second, by adding the contribution of the fine and the coarse sediments to the total organic carbon taking into consideration the carbon concentration in each fraction, and the contribution (in weight) of each fraction to the total sediment weight.

The distribution of the organic carbon content in the total sediments is shown in Figure 4.4d. Excluding minor details, this distribution is similar to that of the distribution of the fine fraction in the total sediments (Fig. 4.2a), suggesting that the organic carbon content in the total sediments depends on the amount of fine material present in the sample. The mean value for the whole region was ~0.40% and the maximum and minimum values were 1.19% and 0.14% respectively.

The correlation coefficient between the organic carbon in the total fraction and aluminium in the same fraction was r=0.965; a similar coefficient was obtained with the percentage fine fraction (r=0.964). The regression equations were:

total carbon = -0.0867 + 0.317 %Al, (r^2=93.1%), and

total carbon = 0.211 + 0.0186 %fine, (r^2=92.9%).

The determination coefficients indicate that approximately 93% of the variance of the organic carbon in the total sediment can be explained by the variations in the amount of fine material in the samples. The relationship between the organic carbon in total sediments and the amount of fine material in the sample is usually a common feature of natural organic matter distribution in marine sediments (Romankevich, 1978; Pocklington and Leonard, 1979; Norton *et al.*, 1984a) as the surface area in the sediments increases with the decrease in grain size. Therefore, it is not surprising that when the total sediment is analysed without fractionation, a good correlation between these two variables may be found.

The importance of analyzing different sediment fractions can be highlighted with one example. Sample G-9 presented organic carbon concentrations of 2.0 and 0.19% in the fine and coarse fractions respectively. The organic carbon value in the total sediment (0.20%) being very similar to the concentration in the coarse fraction indicates that the main carrier of carbon in the total sediment at this station was the coarse material. This observation is hardly surprising considering that the coarse fraction constituted ~99.8% of the total sample weight. However, this observation could not be made with certainty if the organic carbon was only measured directly in the total sample. The importance of coarse sediments as carriers of chemical substances such as organic matter and contaminants (e.g. heavy metals and PCBs) in the marine environment has been neglected or simply overlooked as the fine sediments tend to show higher concentrations of these substances. However, in areas such as Liverpool Bay where most of the sediment contains substantial amounts of coarse material and muddy samples are only confined to small patches when considering the whole area, overlooking the role of the coarse fraction as a carrier of chemical materials implies overlooking a very important component in the organic carbon and pollutants budget in the area. This subject is further explored in the following sections concerning the heavy metals, arsenic and PCBs in sediments from Liverpool Bay.

4.1.4. Iron and manganese distributions

Hydrous oxides of iron, manganese and aluminium represent significant sinks of heavy metals in aquatic systems (Forstner and Wittmann, 1979). These oxides, particularly those of iron and manganese, readily sorb or co-precipitate cations and anions even at low concentrations, therefore, these phases are important in controlling heavy metal distributions in aquatic systems (Forstner and Wittmann, 1979). The importance of hydrous iron and manganese oxides as surfaces for metal sorption is extensively documented for particles in diverse aquatic systems (e.g. Balzer, 1982; Lion *et al.*, 1982; Millward and Moore, 1982; Olsen *et al.*, 1982; Luoma and Davis, 1983; Laxen, 1984; Tessier *et al.*, 1985; Sigg *et al.*, 1987). These oxides normally occur as coatings on sediment surfaces, or as discrete small particles of iron (Sigg *et al.*, 1987) and manganese (Luoma and Davis, 1983) oxides.

Iron oxides in sediments occur in a continuum of states, ranging from a highly amorphous oxyhydroxide, which forms upon precipitation, to increasingly crystalline solids which form as the initial precipitate ages (Luoma and Davis, 1983). Freshly precipitated amorphous iron oxides have greater metal binding capacity than the crystalline forms because the former present greater specific surface area (~600 m^2 g^{-1}) than the later (e.g. goethite has an area of 30-50 m^2 g^{-1}) as crystallization reduces the surface area of the solid (Luoma and Davis, 1983). The difference on metal sorption capacity of different forms of iron oxyhydroxides indicate that the predominance of one or another form in a particular sediment will be reflected in the amount of metal bound to iron species in that sediment. Therefore, a determination of total iron in the sediment surface can only be used as a rough indicator of iron hydroxides content in such sediment, but the capacity of those oxides will depend on the particular forms present and can not be determined with precision with this particular determination.

The binding capacities of hydrous manganese oxides are similar to those for amorphous iron oxides, but significantly greater than the capacities of crystalline hydrous iron oxides (Luoma and Davis, 1983). Manganese in sediments, however, may occur simultaneously as manganese oxides, manganese carbonate and organically bound manganese (Luoma and Davis, 1983), therefore, as in the case of iron, the determination of total manganese in the surface of the sediments can only be used a rough indicator of the manganese oxide content in these surfaces. It is important to mention, however, that at present there are no methods which quantitatively differentiate either amorphous from the various crystalline forms of iron oxides, or the various forms of manganese oxides in the sediments; therefore, the study of possible metal-sediment associations with iron or manganese oxides through statistical analysis remains as a useful option.

4.1.4.1. Iron concentrations in fine sediments

The distribution of the percentage of iron in the fine sediments is shown in Figure 4.7a. The maximum values were found in the central region of the sampling grid along an axis in an east-west line. This line included stations K-8, L-9 (both within the SE of Site SI), M-10, N-10 and Q-9 with concentrations of 3.06%, 4.54% (maximum), 3.22%, 4.52% and 4.30% respectively. The mean iron concentration for the whole region (67 samples) was 2.18%. Most samples in the area to the west and north of Site SI presented values in the range of 1.70% to 2.00%, the only exception being at station G-9 showing an iron concentration of 2.58% (see Appendix B.1). Concentrations in the Burbo Bight area were not particularly elevated showing values within a range of 1.61% (sample YY-3) to 2.29% (sample YY-2), these values were close to, or below the mean concentration for the whole region. The area of lowest iron concentrations in fine sediments was found in a zone to the northwest outside the Queen's Channel mouth, near Site Z, with values of 1.36% (minimum), 1.43% and 1.40% at stations T-10, T-12 and T-14 (Site Z) respectively.

The distribution of iron in the fine fraction (Fig. 4.7a) shows no particular enrichment of this metal at the stations near the Mersey Estuary nor at the stations near Site Z. This observation indicates that the iron inputs from the Mersey River and from the discharges of dredged material into Liverpool Bay do not constitute significant sources of contamination of sediments in the bay with this element. The area of highest iron concentrations in the central region of the sampling grid extending eastward from Site SI, may reflect the inputs of sewage sludge derived iron. However, the concentration of this metal in the sewage sludge analysed in this study (~1.98%), suggests that sewage sludge disposal would not contribute to a significant enrichment of iron above the possible natural levels in the bay; that is, if the fine fraction of one particular sediment sample consisted of 100% sludge particles, the iron concentration for this fraction in that particular sample would be similar to the average concentration for the whole bay (2.18%). Campbell *et al.* (WRc unpublished report for North West Water Authority, England) reported iron concentrations around 2% in digested sludge samples from Davyhulme (Manchester) sewage treatment works from which a large proportion of the sludges discharged at Site SI originate. These authors concluded that the iron, manganese and nickel in these sludges may result from the supply of these elements in particulate form from non-industrial sources, such as runoff and weathering. Therefore, as particles in the sewage sludges discharged at Liverpool Bay do not seem to be enriched in iron above natural levels during sludge treatment, it is unlikely that the disposal of sewage sludge would be reflected in an enrichment of this metal in the sediments from this area.

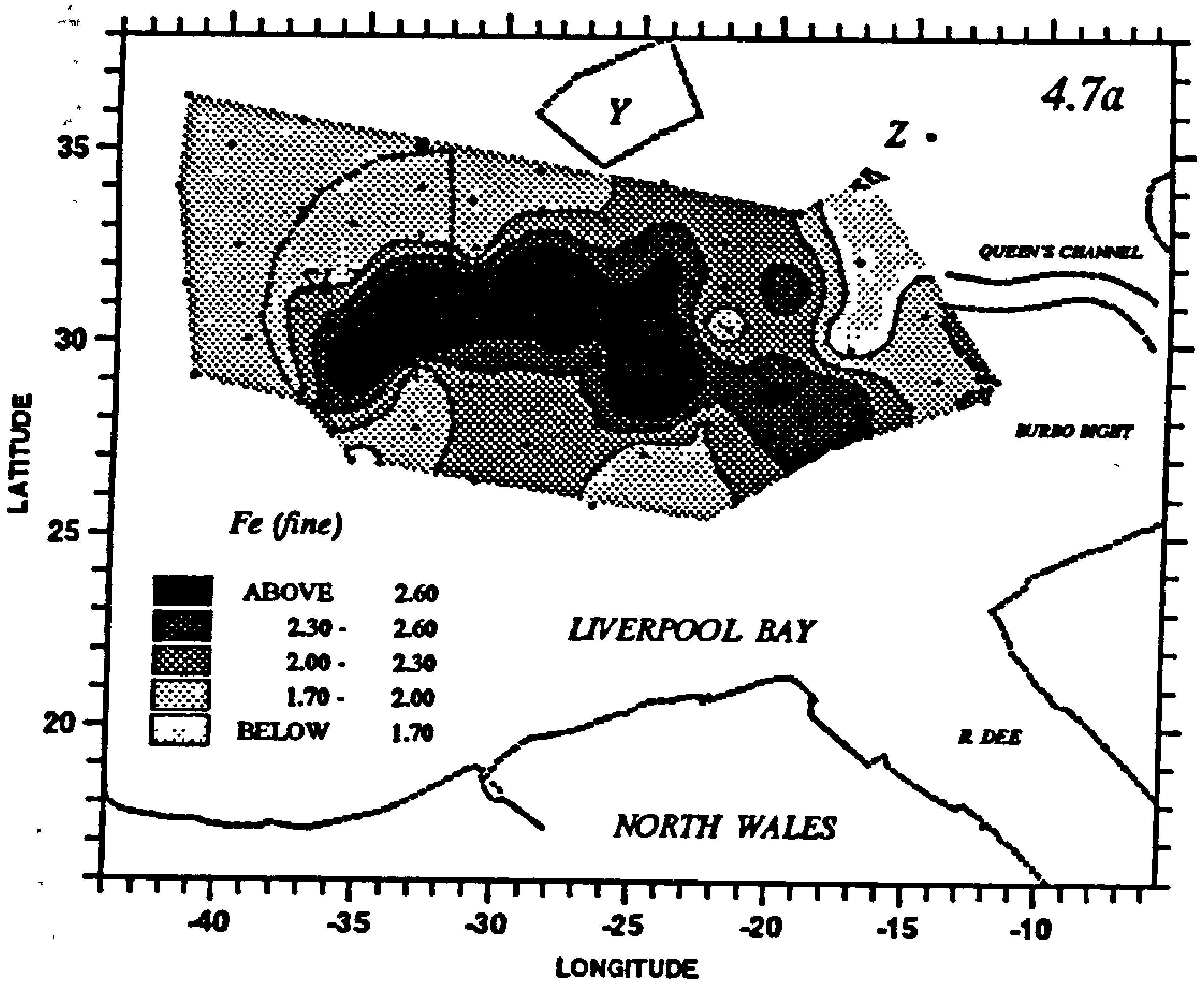
Kiff (1984) studied the concentration of some metals in different grain size fractions in sediments at four sites in Liverpool Bay and suggested that iron and manganese showed distributions indicating a predominance of natural sources for these metals; evidence of relatively high inputs of iron from natural sources was found by Kiff (1984) as high concentrations of magnetite (Fe_3O_4) and chromite ($FeCr_2O_4$) were present in the heavy mineral fractions analysed.

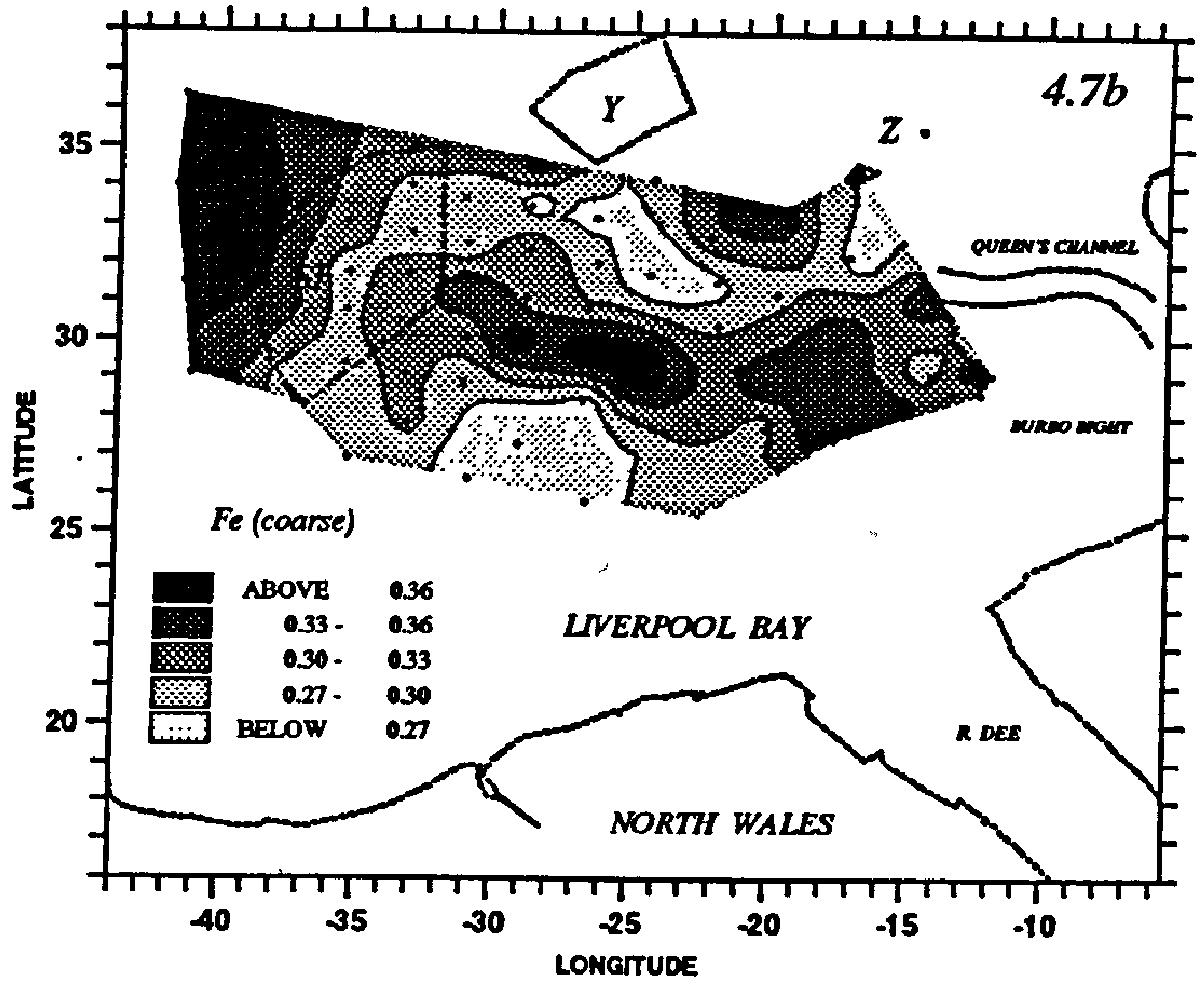
The iron concentrations in the finest fractions observed by Kiff (1984) were within the range of concentrations observed in the present study. Rowlatt (1988) determined iron concentrations in sediments from Liverpool Docks, the Mersey Estuary, and several samples from Burbo Bight. This author analysed bulk sediments, therefore, his results are only comparable with the calculated values for the total sediments from this study. The concentrations in the total sediments from the Burbo Bight area in the present study ranged from 0.80 to 1.2%, these results are consistent with the values reported by Rowlatt (1988) in this particular area. In spite of the importance of iron as a metal carrier in aquatic systems, no previous studies were found in the literature (apart from the two mentioned above) reporting iron concentrations in sediments from Liverpool Bay, therefore, the present study may provide the first relatively large data set reporting this variable, which is important in geochemical studies of trace elements in marine sediments.

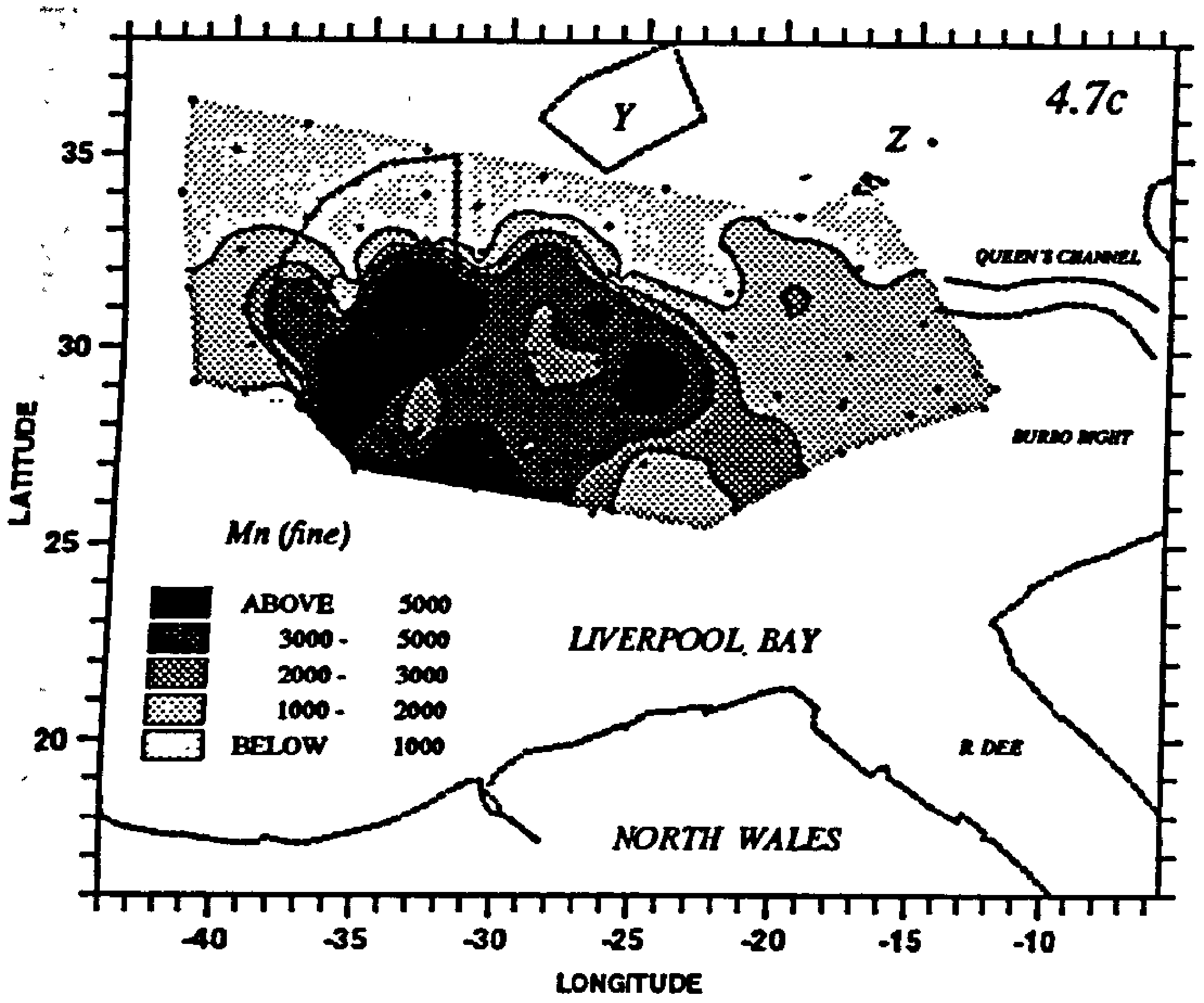
The distribution of iron in fine sediments (Fig. 4.7a) is, in general, similar to the distribution of organic carbon (Fig. 4.4a). The relationship amongst these two variables can be observed in Figure 4.8a and is reflected in a significant correlation coefficient ($r=0.539$, $p<<0.001$). A correlation between iron and organic carbon in sediments has often been reported (Sholkovitz *et al.*, 1978; Forstner and Wittmann, 1979; Olsen *et al.*, 1982; Luoma and Davis, 1983). Iron and organic materials tend to form surface coatings on particles and usually correlate well with the amount of fine sediment in a sample as a function of the available surface area (Luoma and Davis, 1983), therefore, the significant correlation between organic carbon and iron in the fine sediments in the present study is probably a result of a covariance of both variables (rather than a direct chemical association between iron and organic materials) as a function of the available surface area for the formation of coatings. However, the correlation can also be a result of a close physicochemical association between iron and organic material in the sediments (e.g. through the formation of iron-organic colloids, Sholkovitz *et al.*, 1978); this possible association in the sediment has been observed in the water column in Liverpool Bay where, in a study of chemical speciation of some metals, Nimmo *et al.* (1989) observed significant iron-organic associations. With the information available in the present study it is not possible to establish the exact cause of the iron-organic carbon correlation, however, it is possible that both factors mentioned above are playing a role in the sediments analysed in this study.

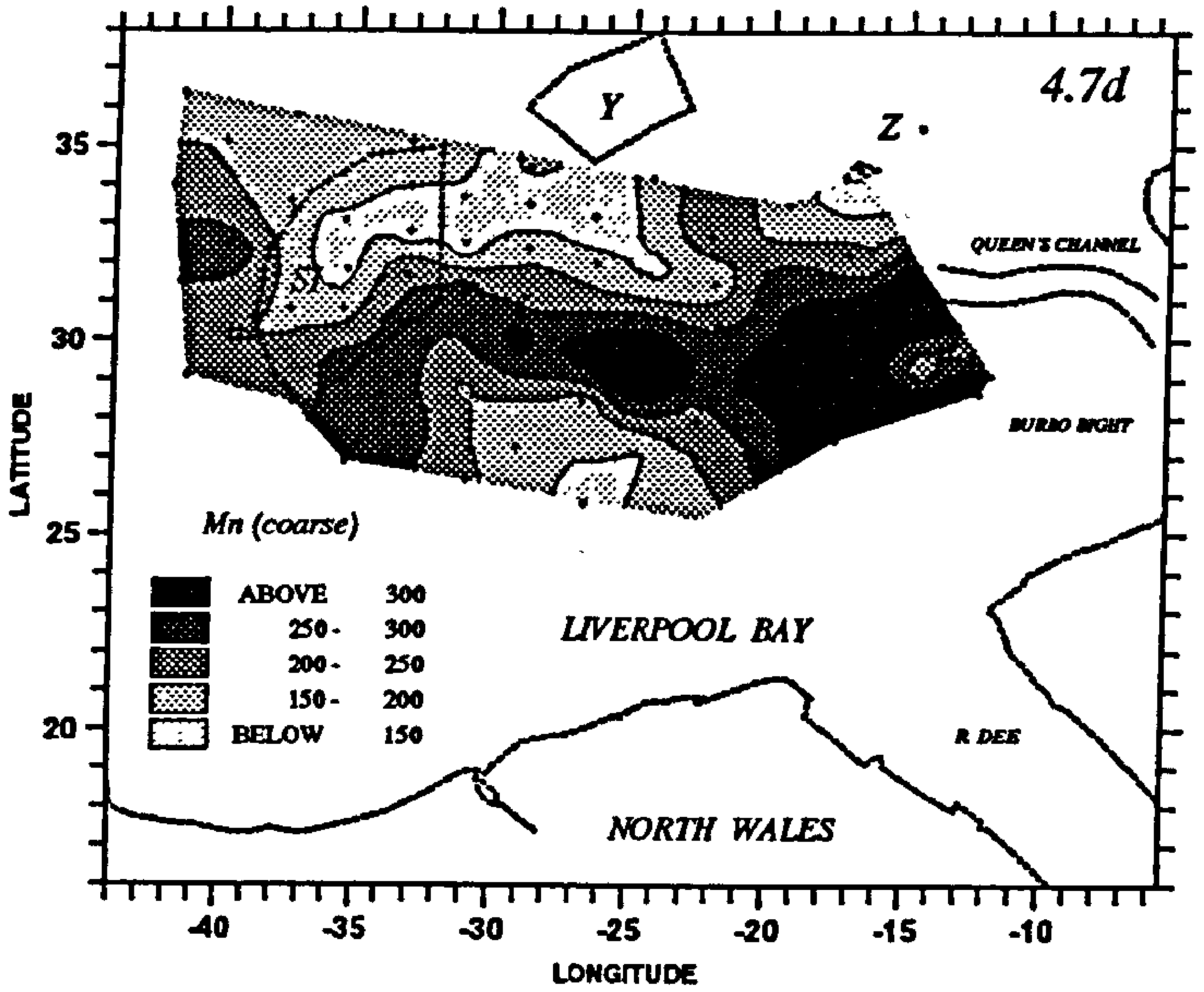
The relationship between the iron in fine sediments and the amount of fines in the total fraction is presented in Figure 4.8b. The correlation coefficient between the iron concentration and the logarithm of the fine fraction concentration ($r=-0.430$, $p<0.001$) indicates that, as in the case of the organic carbon, higher concentrations were present in sediments where the fine fraction was lower. This observation, as in the case of the organic carbon, may suggest that the fine fraction in the sediments with lower percentage of fines may contain a larger proportion of small sized particles such as clays (see discussion for the aluminium distribution), which provide higher surface areas for the precipitation of organic and inorganic coatings. Hornung (1986; cited by Cauwet, 1987) reported that the proportion of large grained sediment (e.g. sands) does not affect the distribution of metals in the fine fraction, if the latter remains higher than 5%, but if the fine sediment represents only a very small fraction, the enrichment effect is enhanced and metal concentrations in fine particles are higher. Unfortunately, Cauwet (1987) did not discussed the possible reasons for this enrichment effect. Enrichment in sediments with low fines was not

Fig.4.7. Distribution of iron concentrations (%) in (a) the fine fraction, (b) coarse fraction, and of manganese concentrations (μg g^{-1}) in the (c) fine fraction and (d) coarse fraction.


4.7a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Fe (fine)
ABOVE 2.60
2.30 - 2.60
2.00 - 2.30
1.70 - 2.00
BELOW 1.70
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE


4.7b
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Fe (coarse)
ABOVE 0.36
0.33 - 0.36
0.30 - 0.33
0.27 - 0.30
BELOW 0.27
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE


4.7c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Mn (fine)
ABOVE 5000
3000 - 5000
2000 - 3000
1000 - 2000
BELOW 1000
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE


4.7d
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Mn (coarse)
ABOVE 300
250 - 300
200 - 250
150 - 200
BELOW 150
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE

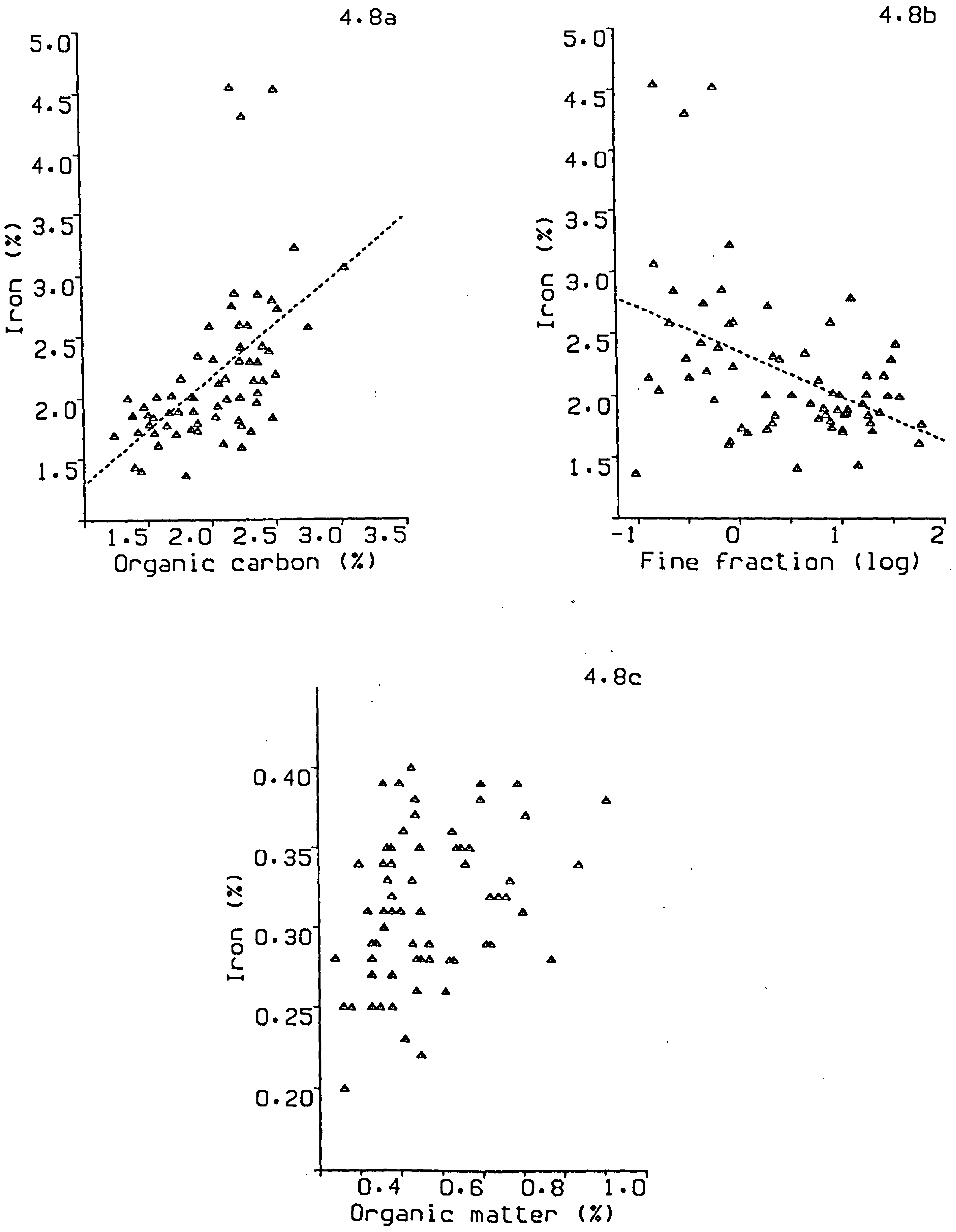


Fig.4.8. Scatter plots of (a) iron vs organic carbon in fine sediments, (b) iron in the fine fraction vs logarithm of fine fraction content, (c) iron in coarse vs organic matter content in coarse sediments.

only observed in the cases of iron and organic carbon in this study, but was also observed for most of the other elements (except mercury) and particularly in the manganese concentrations discussed below.

4.1.4.2. Iron concentrations in the coarse fraction

Figure 4.7b shows the distribution of iron in coarse sediments. This figure shows an enrichment area in the central region, similar to that for iron in fine sediments (Fig. 4.7a). Concentration values of 0.36%, 0.38%, 0.39% and 0.40% (maximum) were found in samples from stations M-10, N-9, P-9 and Q-9 respectively. In contrast to the iron in fine sediments, iron in the coarse fraction presents an enrichment in the samples west to Site SI. Samples from transects G and H had a range from 0.35% in samples G-7 and H-8, to 0.39% in samples G-9, H-10 and H-12. The lowest values were recorded in the south at stations M-6, N-7, P-6 and P-8 with concentrations of 0.25%, 0.23%, 0.20% (minimum) and 0.25% respectively. The mean value for all samples (67) was 0.31%. Iron in the coarse sediments from Burbo Bight presented a wide range from 0.28% in samples YY-1 and YY-2 to 0.38% in sample YY-3.

It is difficult to determine from the distribution pattern presented in Figure 4.7b, the possible sources of iron in the coarse sediments. The correlation between iron in the coarse sediments with iron in the fine sediments was non significant, indicating that there was no overall relationship between the iron in the different grain sizes, however, the highest values in the central region were present in both fractions indicating a possible common source. The amount of fine sediments in three of the samples with highest iron in the coarse sediments (stations N-9, P-9 and Q-9) was 0.64, 0.89 and 0.31%, therefore, it seems unlikely that the high iron concentrations in these samples were a result of iron transfer from the coexisting fine particles. It is possible that part of the relatively high iron values may result from iron inputs in solution from the rivers Dee and Mersey as some of the coarse sediments from stations nearest their mouths present high concentrations; once in the bay iron precipitation from solution may occur in coarse particle surfaces. Stations in the Burbo Bight (except YY-3) had iron concentrations in coarse sediments near or below the mean value (around 0.31%), therefore, considering that these samples are the most influenced by the River Mersey, if inputs from the Mersey are important for iron enrichment in coarse particles, large amounts of fine material and organic matter in these samples may be promoting re-dissolution or limiting iron precipitation due to low redox potentials in which iron oxide formation is less favourable (Forstner and Wittmann, 1979).

The high concentrations in the region to the west of Site SI are difficult to explain. According to sand transport patterns in this region (e.g. see McLaren, 1987), these coarse particles are being transported from offshore toward the east. In Figure 4.7b, the decreasing iron concentrations towards the central parts (except zone of high values) of the sampling grid may suggest that as these coarse particles are being transported, iron is being lost from their surfaces, however, the mechanism responsible for this removal would difficult to assess, although could be explained as a result of abrasion of the coatings as suggested by Cerling and Turner (1982) for iron and manganese release from riverine coarse (1.2 to 3.3 mm in diameter) sediments. Another possibility is that, within the sand fraction, the coarser sand populations that seem to be dominant in the area west from Site SI (Norton *et al.*, 1984a) contain higher iron concentration tha~~t~~n the finer sands which are more abundant in the eastern sector of Liverpool Bay (Norton *et al.*, 1984a). Iron and manganese enrichment in coarse sands, in relation to finer sands, has been previously reported in riverine sediments (Cerling and Turner, 1982; Brook and Moore, 1988). Brook and Moore (1988) quoted several other studies finding this enrichment in coarse sediments and explained it as probably a result of an increase in iron and manganese coating thickness with increasing particle size, either due to long residence times of coarse particles in oxygenated, relatively high velocity currents, or to greater supply of iron and manganese oxides in the coarser, more permeable (more exposed) sediments than finer, less permeable material.

As in the case of the fine fraction, iron and organic matter in the coarse sediments were correlated ($r=0.368$, $p=0.002$) although in this case the correlation is weaker. Figure 4.8c shows that there is a general trend for iron concentrations in the coarse sediments to increase as the organic matter content in the sediments increases. This general trend indicates that both variables are probably being partially controlled by a common factor, probably a physicochemical iron-organic matter association as the role of the surface area in these coarse particles may be less important that in the fine sediments. However, as indicated by the dispersion of the data and by the significant but low correlation, different factors controlling these variables may be playing a more important role. In contrast to the organic matter, iron in coarse sediments does not correlate with the amount of fine fraction in the total sediment. In the case of the organic matter the correlation was explained as a possible transfer from the abundant fine particles to the coarse particles probably just by physical contact between particles, therefore, this transfer may not occur with iron as the concentration of iron in the coarse particles is independent of the amount of surrounding fine particles.

4.1.4.3. Manganese in fine sediments

The distribution of manganese concentrations in fine sediments is shown in Figure 4.7c. An enrichment of this metal can be observed in the central-southern part of the sampling area, including the southern part of Site SI. The highest values were found at stations J-9, K-8, L-9, L-10, M-6, P-10 and Q-9 with concentrations of 5500, 10200, 22900 (maximum), 8700, 13700, 6100 and 8400 μg g^{-1} respectively. Values decreased towards the northwestern part of the sampling grid where concentrations lower than 1000 μg g^{-1} were found. The lowest concentrations were found at stations J-11, J-13, K-10, K-11, L-11, L-12, L-13 and M-12 with values no higher than 600 μg g^{-1} and a minimum of 530 μg g^{-1} at station J-11. The mean concentration for all samples analysed (67) was 2549μg g^{-1}. In the Burbo Bank area manganese concentrations were between 1050 (station YY-3) and 1490 μg g^{-1} (station YY-2). Low manganese concentrations were also found at stations T-12 and T-14 (Site Z) with values of 870 and 680 μg g^{-1} respectively.

The distribution of manganese in fine sediments was, in general, similar to the iron distribution (see Fig. 4.7c and 4.7a). This similarity is reflected in a significant correlation coefficient ($r=0.638$, $p<<0.001$) and is also represented in a plot of manganese versus iron shown in Figure 4.9a. As in the case of iron, there seem to be no significant inputs of manganese from the River Mersey or from the discharges of dredged spoil in Liverpool Bay. As in the case of iron, the possible role of dumping sewage sludge in the manganese enrichment in the central area including part of Site SI can be evaluated from the concentrations of this metal in sewage sludges. The concentration of manganese in the digested sludge analysed in the present study was 642 μg g^{-1}; this value is similar to the concentration for Davyhulme works digested sludge reported by Campbell *et al.* (WRc unpublished report for North West Water Authority, England) of 661 μg g^{-1}. The concentration of manganese in the sludge was more than an order of magnitude lower than the concentration at stations with highest manganese values (*i.e.* L-9, M-6, K-8, Q-9 and L-10) above 8000 μg g^{-1}. Concentrations in the sludge were approximately only 25% of the mean concentration (2549 μg g^{-1}) for the whole area, therefore, it is unlikely that sewage sludge disposal in Liverpool Bay contributes significantly to the manganese levels observed in the sediments.

The possibility of natural inputs of manganese had to be explored as the inputs of sewage, dredged spoil and discharges from the Mersey did not seem to explain the elevation of manganese concentrations in fine sediments. The area of higher manganese concentrations was in the south, nearer to the North Wales coast, probably suggesting inputs from the land in this region. The presence of mineralized areas in North Wales is well known as mining of minerals such as sphalerite and galena was an important activity in the past (Elderfield *et al.*, 1971). High concentrations of several elements including manganese are reported for sediments in this area in a geochemical atlas of England and Wales (Imperial College of Science and Technology, 1978). Manganese concentrations above 4000 µg g^{-1} were reported in this atlas, in samples of sediments <200 µm in diameter taken from tributaries, the main stream and the estuary of the River Conwy draining into Liverpool Bay; it is possible that if metal analyses had been carried on the fraction <90 µm fraction, higher concentrations would have been observed. Therefore, natural inputs of manganese from the mineralized areas of North Wales seems to be a reasonable explanation for the observed high values in fine sediments in Liverpool Bay.

Manganese in fine sediments was significantly ($p<<0.001$) correlated with the organic carbon content in this fraction ($r=0.633$), with aluminium ($r=-0.657$) and with fine sediment content ← 2 ($r=-0.813$) in the total sediment. Figure 4.9b shows a general trend of manganese concentrations increasing as the organic carbon concentrations increase. This relationship between manganese and carbon is probably a result of a covariance as a function of the available surface area, rather than a physicochemical association between these two variables. The stronger correlation of manganese with the percentage of fine fraction in the total sediment, as compared to that with organic carbon, may be evidence of a strong control of manganese concentrations by the grain size composition. The relationship between manganese in fine sediments and the fine sediment content in total sediments is presented in Figure 4.9c, and the relationship with the aluminium content is presented in Figure 4.9d (note that data are plotted as logarithm values). These figures show that manganese concentrations increase rapidly as the amount of fine sediments in the sample decreases. The same behaviour was observed for iron and carbon concentrations (Figs. 4.8b and 4.5a respectively), however, the enrichment of manganese in samples with lower fine sediment contents is much more evident. For example, the highest manganese concentrations were above 8000 µg g^{-1}, that is, more than three times the average for the whole region (2549 µg g^{-1}) and the maximum (22900 µg g^{-1}) was nine times higher than the mean. On the other hand, the maximum iron value (4.54%) was only 2.1 times the mean concentration (2.18%) whereas the highest carbon concentration (3.05%) was only 1.5 times higher than the mean (2.03%). From figures 4.9c and 4.9d it can be seen that the general trend in the relationship between manganese and grain size descriptors is somewhat disrupted by the samples with highest amounts of fine sediments. These samples, forming a distinctive group of seven in the lower right of the plots, corresponded to the stations in the Burbo Bight area (NW-24, YY-1, YY-2, YY-3

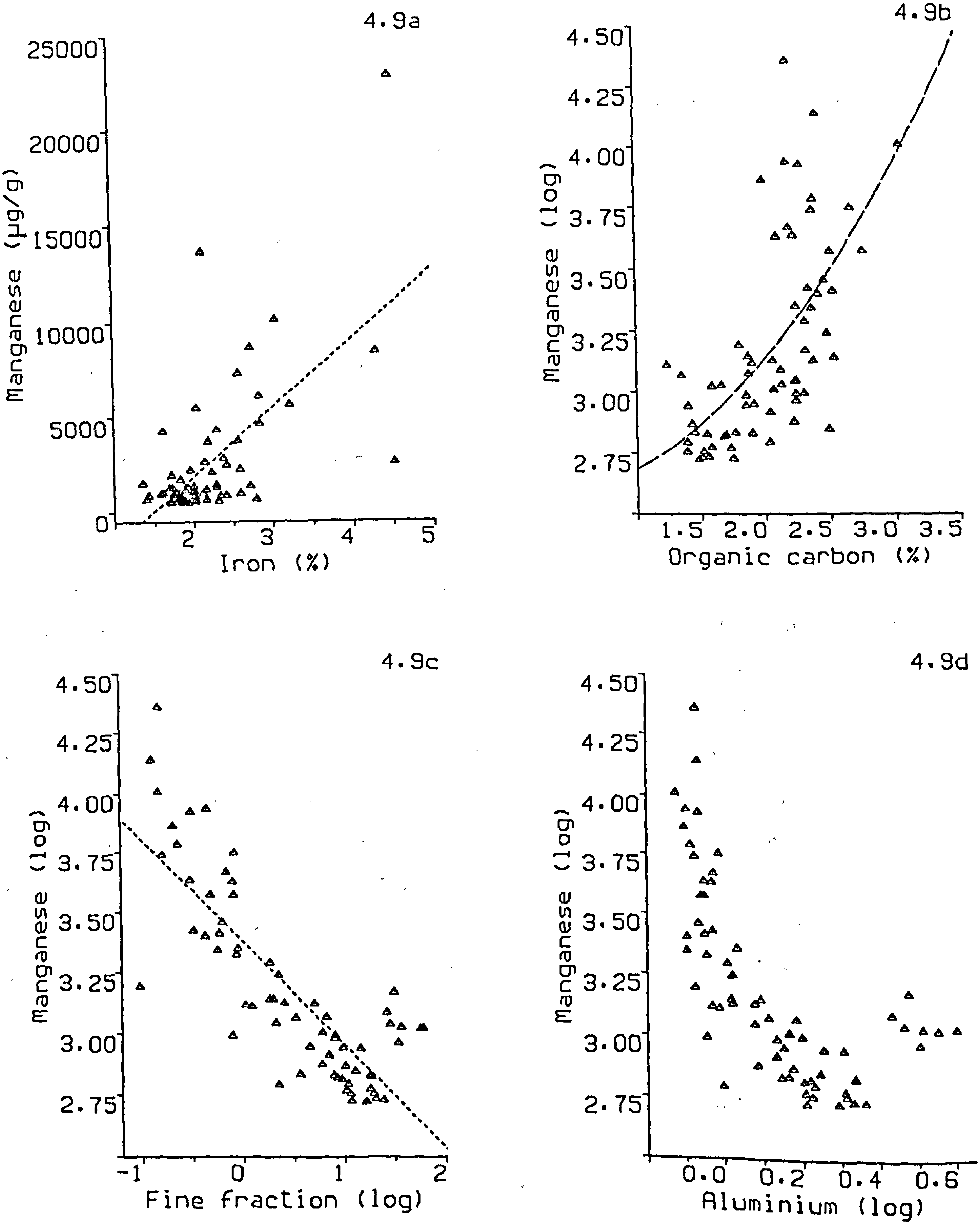


Fig.4.9. Scatter plots of (a) manganese vs iron in fine sediments, (b) logarithm of manganese vs organic carbon in fine sediments (c) logarithm of manganese in fine sediments vs logarithm of fine fraction content and (d) logarithm of manganese in fine sediments vs logarithm of aluminium content.

and YY-4), station T-9 (near Burbo Bight) and station P-11. The position of the samples may suggest that inputs from the River Mersey may be influencing the manganese concentrations in these stations, as compared to the remaining stations where only one common source is the main contributor to the manganese observed in these sediments. When the seven samples mentioned above were not included in the correlation analyzes, the correlation coefficients between manganese and aluminium, and manganese and percentage fine fraction increased significantly to $r=-0.806$ and $r=-0.879$ respectively. A regression analysis indicated that approximately 77% of the variance in the manganese concentrations in fine sediments could be predicted by the variations in the amount of fine material in the total sample; the regression equation obtained was:

$$\text{log-Mn}_{\text{fine}} = 3.38 - 0.527\ \text{log-\%fine}, \quad (n=60,\ F=198,\ p<<0.001).$$

4.1.4.4. Manganese in coarse sediments

Figure 4.7d shows the distribution of manganese in the coarse fraction. As in the case of iron (Fig. 4.7b) this distribution shows an enrichment of manganese in the central region along an east-west line, with the maximum concentration (440 $\mu g\ g^{-1}$) in sample Q-9, and a region of high values (higher than 300 $\mu g\ g^{-1}$) in most of the samples to the southeast of transect S, excluding stations YY-1 and YY-2 showing values lower than 200 $\mu g\ g^{-1}$. The lowest value was found at station N-12 (92 $\mu g\ g^{-1}$) within an area of values lower than 150 $\mu g\ g^{-1}$ including stations K-10, K-11, L-11, M-11, M-12, N-12, P-12 and Q-11. The sample from Site Z (station T-14) also had a low value of 119 $\mu g\ g^{-1}$. The mean concentration for the whole region was 222 $\mu g\ g^{-1}$.

The similarity in the distributions of manganese and iron in the central region may suggest a common source of these metals in this particular section of the bay. A significant correlation ($r=0.526$, $p<0.001$) between these two elements was observed, this correlation is reflected in the similarities observed in figures 4.7b and 4.7d. However, when comparing these two figures, obvious differences appear as also indicated by the magnitude of the correlation coefficient and the scatter of the data presented in Figure 4.10a. The main difference between the distributions of iron and manganese in the coarse fraction was that manganese did not show the gradient of increasing concentrations towards the west and northwest of Site SI, previously discussed for the iron distribution. The region near Burbo Bight with relatively high values (>300 $\mu g\ g^{-1}$) as compared to the mean, included stations YY-3, YY-4, NW-24, U-9, U-11, T-8, T-9, T-10 and S-9. Some of these stations are under the influence of the discharges from the River Mersey and probably from the River Dee, therefore, it is possible that the content of manganese in coarse

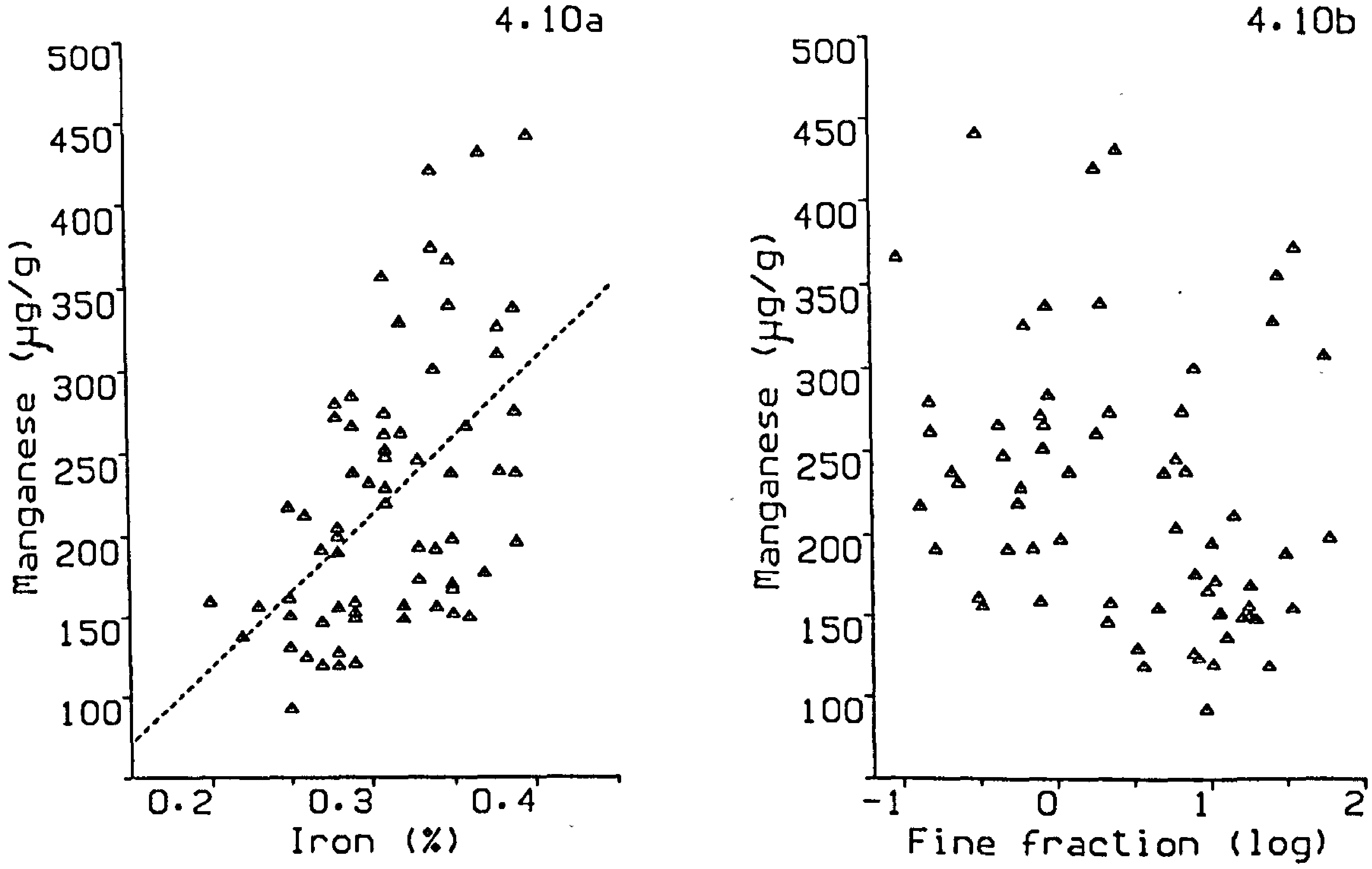


Fig.4.10. Scatter plots of (a) manganese vs iron in coarse sediments and (b) manganese in coarse sediments vs logarithm of fine fraction content.

sediments may be significantly affected by riverine discharges, as opposed to the manganese content in fine sediments which do not appear significantly enriched by these inputs.

Manganese in the coarse sediments, as opposed to iron, did not present a correlation with the organic matter content, and showed a weak linear correlation ($r=-0.313$, $p=0.010$) with the amount of fine sediments in the total fraction, after a logarithmic transformation of the data. The relationship between manganese in coarse sediments and the amount of fines in the sample presented in Figure 4.10b, shows a large scatter in the data which does not allow one to draw a firm conclusion on the significance of this relationship. However, when the seven samples (P-11, U-9, NW-24, YY-1, YY-2, YY-3 and YY-4) with the highest amount of fine sediments (higher than 26%) were excluded from the correlation analysis, the correlation between manganese concentrations in the coarse fraction and the percentage of fines increased significantly to a value of $r=-0.515$ ($n=60$, $p<0.001$). This observation indicates that if the muddiest samples are not considered, higher concentrations of manganese in the coarse fraction (as in the fine fraction) are to be found, in general, in sediments with lower concentrations of fine particles.

4.2. TRACE ELEMENT DISTRIBUTIONS

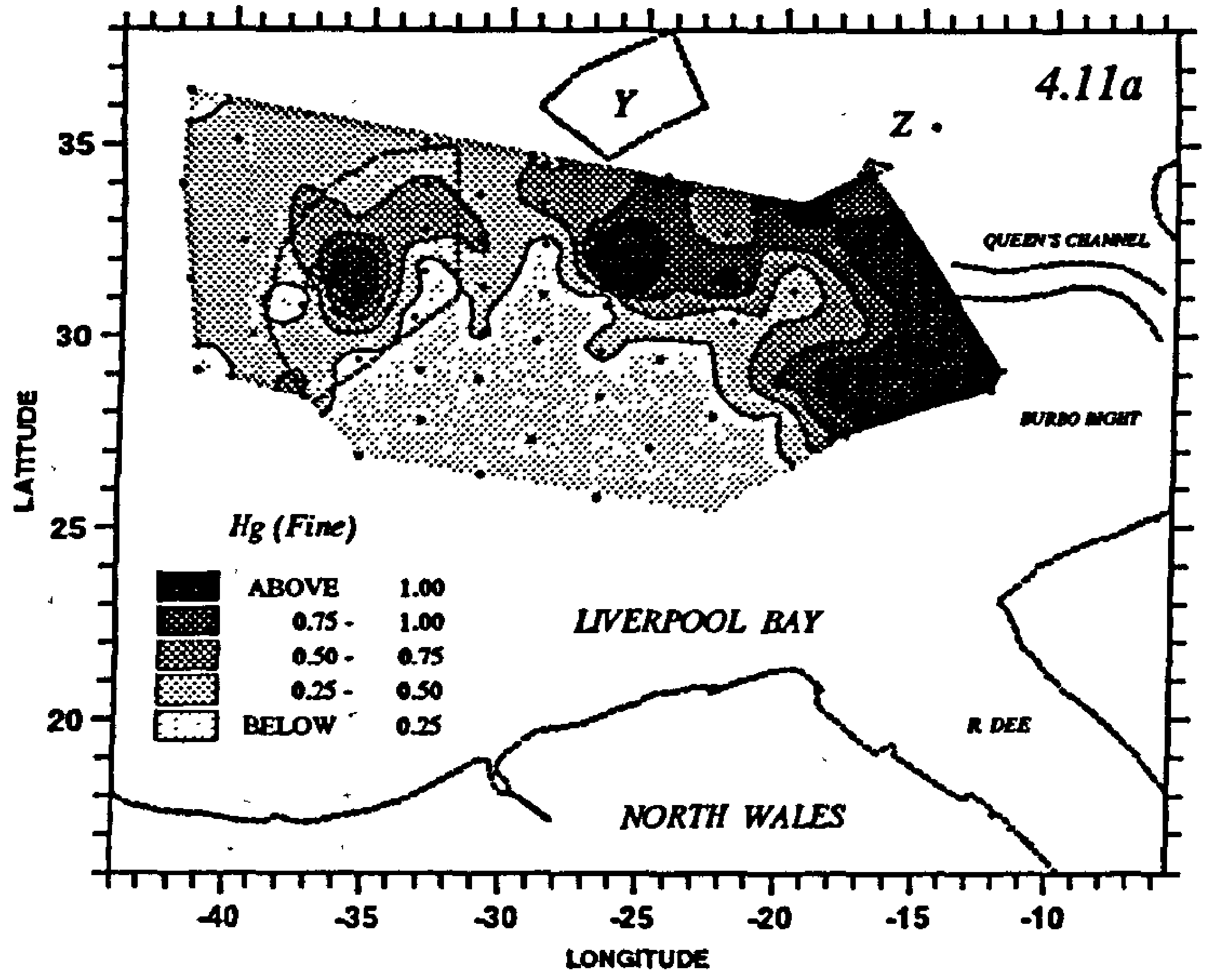
4.2.1. Mercury

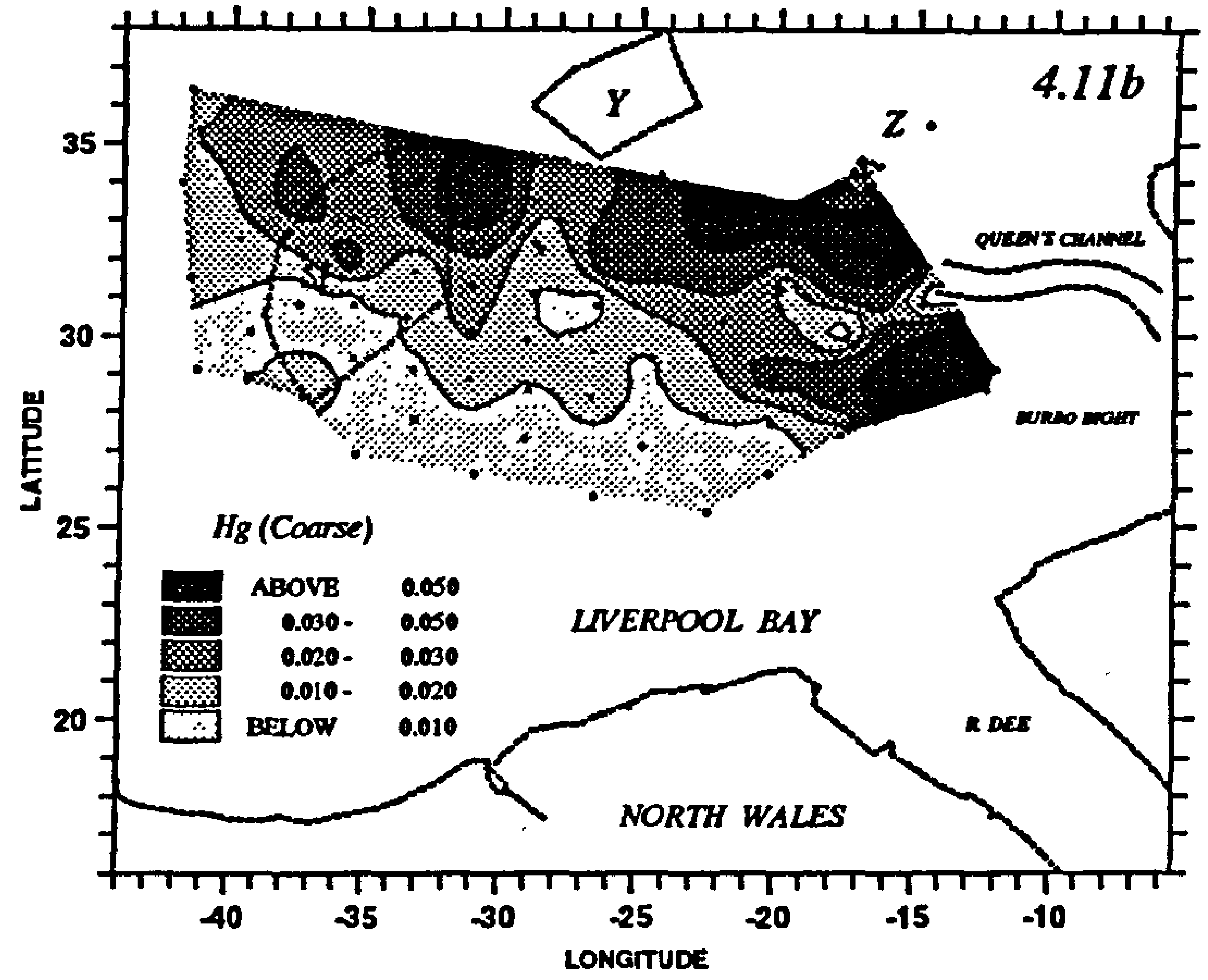
4.2.1.1. Mercury in the fine fraction

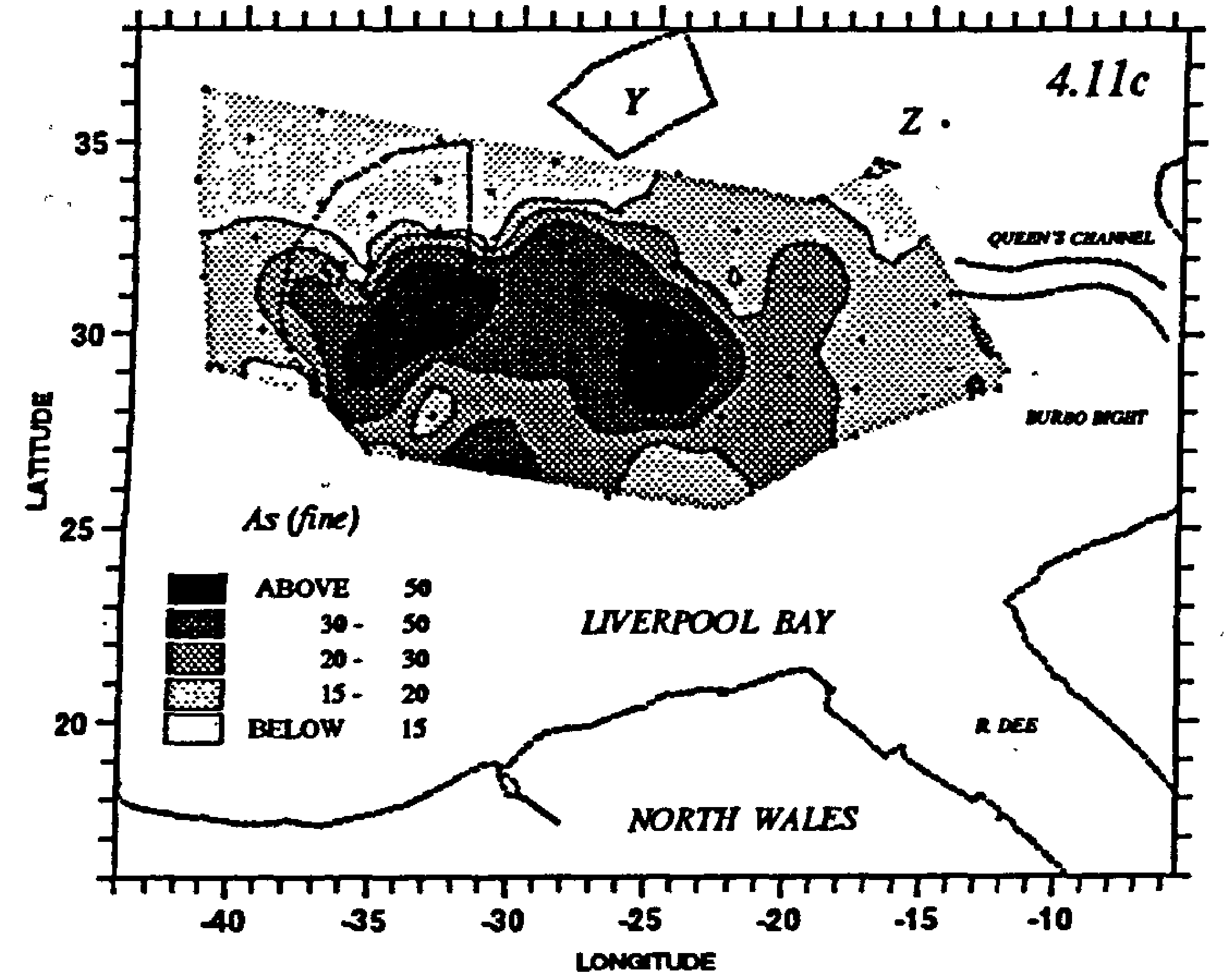
The distribution of mercury in the fine sediments, shown in Figure 4.11a, shows some similarities to the distributions of the fine sediment fraction (Fig. 4.2a) and that of aluminium in the total sediments (Fig. 4.2c). Mercury concentrations lower than 0.25 μg g^{-1} were found in the southern region, with a minimum of 0.02 μg g^{-1} at station M-6, and values around or lower than 0.1 μg g^{-1} at stations M-8, N-7, N-11, P-6, P-8, P-10 and Q-9. The mean value for the whole sampling region (67 samples) was 0.56 μg g^{-1}. Three areas of mercury enrichment can be observed in Figure 4.11a. The first is centred in Site SI around station K-10 with a concentration of 1.41 μg g^{-1}; the second is south of Site Y where the maximum value for the whole sampling grid (2.09 μg g^{-1}) was found at station P-11; the third and larger area was found around the stations nearest to the Queen's Channel and the Burbo Bight, with most values over 1.00 μg g^{-1} and up to 1.56 μg g^{-1} at station NW-24.

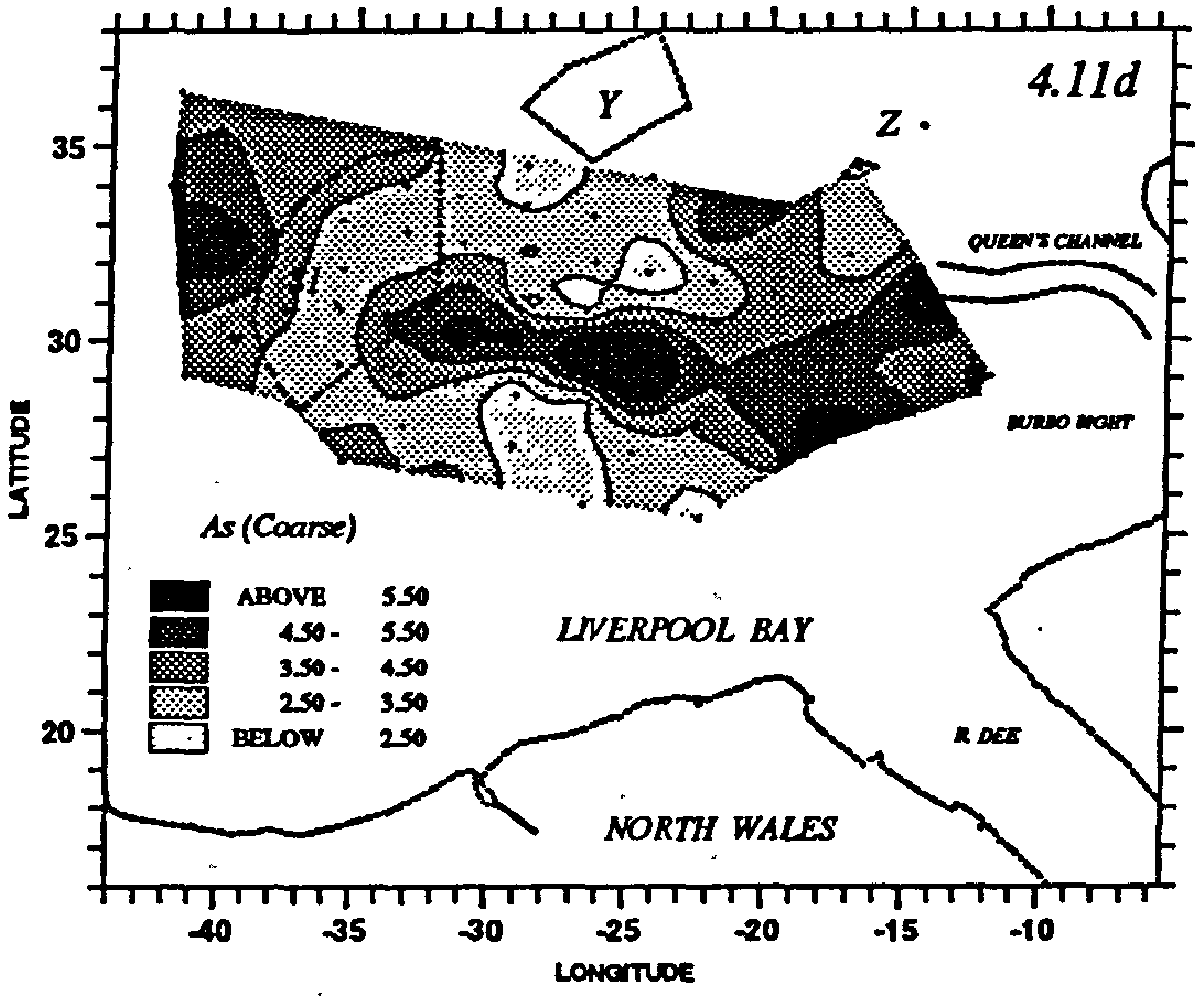
The concentrations of mercury reported here are, in general, within ranges previously reported for this area in a similar grain size fraction. For example, McLaren (1987) reported a range of mercury concentrations (in sediments <63 μm) between 0.78 and 1.88 μg g^{-1} and Norton *et al.*

Fig.4.11. Distribution of mercury in (a) fine sediments and (b) coarse sediments, and of arsenic in (c) fine sediments and (d) coarse sediments. Concentrations values are in μg g^{-1}.


4.11a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Hg (Fine)
ABOVE 1.00
0.75 - 1.00
0.50 - 0.75
0.25 - 0.50
BELOW 0.25
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.11b
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Hg (Coarse)
ABOVE 0.050
0.030 - 0.050
0.020 - 0.030
0.010 - 0.020
BELOW 0.010
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.11c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
As (fine)
ABOVE 50
30 - 50
20 - 30
15 - 20
BELOW 15
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.11d
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
As (Coarse)
ABOVE 5.50
4.50 - 5.50
3.50 - 4.50
2.50 - 3.50
BELOW 2.50
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10

(1984b) reported concentrations between 0.7 and 1.8 $\mu g\ g^{-1}$ in sediments <90 μm, both reports included a similar sampling grid to that used in the present study. Law *et al.* (1989) reported values from 0.08 to 2.6 $\mu g\ g^{-1}$ in <90μm sediments from the whole northeastern Irish sea with the highest concentrations occurring near the Mersey.

The distribution of mercury in the fine fraction shown in Figure 4.11a reveals the three main sources of this metal into Liverpool Bay. The largest mercury source into the bay, as reported by several authors (e.g. Jones, 1978; Campbell *et al.*, 1986), is that from the River Mersey and its estuary which receive substantial amounts of mercury-contaminated effluents from chlor-alkali industries (Campbell *et al.*, 1986). The gradient of decreasing mercury concentrations westwards from the Queen's Channel is evidence of the Mersey inputs, however, these inputs seem to be partially superimposed to inputs from discharges of dredging spoils at sites Y and Z which also show nearby mercury enrichments. Evidence of the effects of sewage dumping on mercury levels in the sediments is shown by the enrichment in the middle of Site SI, however, as previously discussed, sediment and sludge transport is towards the east of Liverpool Bay, therefore, part of the sewage derived mercury may be contributing to the enrichment observed in the area near the Mersey. Jones (1978) calculated mercury inputs into Liverpool Bay from the Mersey as 5-10 tonnes per year, from dredged spoil as 3-7 tonnes per year and from sewage sludge dumping as 1-2 tonnes per year, therefore, the high values in the eastern part of Liverpool Bay (Fig. 4.11a) may be largely due to the discharges from the main source of mercury into Liverpool Bay, *i.e.* the Mersey river and estuary.

Mercury in fine sediments presented a high correlation with both aluminium and fine fraction concentration in the total sediments. The correlation coefficient between mercury and the logarithm of the aluminium content was $r=0.745$ ($p<<0.001$) whereas the correlation between the logarithm of mercury and the logarithm of the fine fraction was $r=0.769$ ($p<<0.001$). The corresponding regression equations were

$$\mathbf{Hg = 0.321 + 1.90\ log\text{-}\%Al}, \ (r^2=56\%,\ F=82), \text{ and}$$

$$\mathbf{log\text{-}Hg = -0.641 + 0.441\ log\text{-}\%fine}, \ (r^2=59\%,\ F=94).$$

The correlations between mercury and the grain size descriptors indicate that the concentrations of mercury in fine sediments increased as the content of fine sediments in the total sediment increased. These relationships, represented in Figures 4.12a and 4.12b, showed that the highest concentrations of mercury in the fine fraction were found in the muddiest samples, which are particularly distinguishable in Figure 4.12a as a group of seven points with aluminium (logarithm) values higher than 0.40 (stations P-11, U-9, NW-24 and YY-1 to YY-4). Mercury

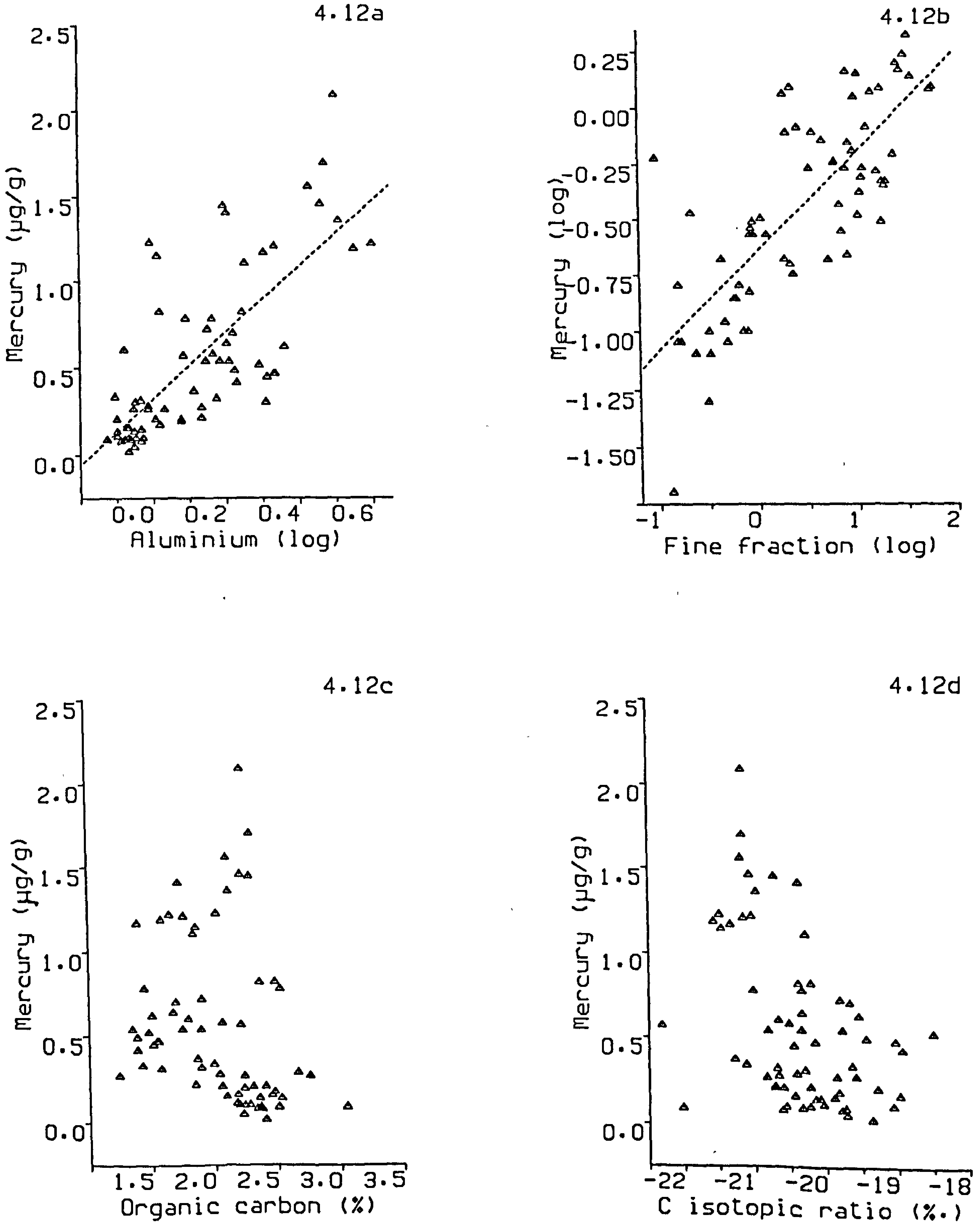


Fig.4.12. Scatter plots of (a) mercury in fine sediments vs logarithm of aluminium, (b) logarithm of mercury in fine sediments vs logarithm of fine fraction content, (c) mercury vs organic carbon in fine sediments and (d) mercury vs $\delta^{13}C$ values in fine sediments.

in the fine fraction did not show positive significant correlations with any other sediment parameter, indicating that the mercury in Liverpool Bay fine sediments is mainly controlled by the fine particle content in the total sediment, however, as showed by the determination coefficients from the regression analyses and by the dispersion in the data in figures 4.12a and b, only approximately 60% of the mercury variance can be predicted by the variations in fine particle content of the sediments.

Thomas (1972) summarized the adsorption processes by which mercury may be bound in a sediment as follows: (1) cationic adsorption or co-precipitation adsorption on to iron oxide surfaces; (2) irreversible adsorption of mercury by sulfide surfaces; (3) mercury ion-humate complexes stable between pH 3 to 6; (4) covalently-bonded sulfo-organometallic compounds; and (5) adsorption by clays. Several authors (e.g. Rae and Aston 1981, 1982; Craig and Moreton, 1986; Langston, 1985; Taylor, 1986) have reported a high correlation between the organic carbon and the mercury content in sediments from the River Mersey and its estuary. This observation, also reported in other areas (e.g. Crecelius *et al.*, 1975), has led some of these authors to the conclusion that the association of the mercury with the sediment is through interactions with the organic matter. However, most of these studies have been carried on bulk sediments and high correlations with the amount of fine material within the samples were also reported, and as Taylor (1986) mentioned, although significant correlations have been shown in the Mersey, any causal relationship has still not been proven. Norton *et al.* (1984a) also reported significant correlations between mercury and carbon in fine sediments in Liverpool Bay, although the significance in the correlations changed between surveys and even reported a non-significant correlation in one of the surveys (see Table 8 in Norton *et al.*, 1984a). On the other hand, very low or non-significant correlations have been observed for some freshwater, coastal and marine sediments in other areas (Cranston, 1976; Kemp *et al.*, 1976; Thomas, 1972; Taylor, 1986), this observation indicating that the mercury association with organic matter in sediments is not a general rule. In fact, Thomas (1972) and Senaratne and Dissanayake (1989) reported mercury associations with iron and manganese hydroxides in lake and coastal marine sediments respectively.

Based on observations of Rae and Aston (1981) on coastal intertidal sediments in the northeastern Irish Sea including Liverpool Bay, on studies by Norton *et al.* (1984a) on Liverpool Bay sediments, and on the studies in the River Mersey mentioned above, a correlation between mercury and the organic matter and between mercury and content of fines in sediments from Liverpool Bay in the present study could be expected. However, although the correlation with the content of fine particles in the samples was observed, a significant negative correlation was observed in the case of carbon (r=-0.411, p=0.001 for the logarithm of Hg vs organic carbon). This observation indicated that there was in general, an opposite trend between these two variables (see Fig. 4.12c). Significant negative correlations between the logarithm of the mercury concentration and the logarithm of the manganese concentration (r=-0.695, p<<0.001) and the logarithm of mercury versus the organic nitrogen concentration (r=-0.411, p=0.001) were also observed.

The negative correlation of mercury and organic carbon does not necessarily reflect a lack of a mercury-organic matter association, but as also indicated by the negative correlation with manganese, is probably only a result of the strong negative correlation between organic carbon (and manganese) and the amount of fine material in the samples. As already indicated in the discussion of carbon, the organic carbon was particularly enriched in the sediments (see Fig. 4.4a) containing very low amounts of fine material particularly seen in the southern region (see Fig. 4.2a), whereas concentrations of mercury (Fig. 4.11a) were lowest in this area of the bay. The complexity of the relationship between mercury and carbon is a result of the possible different sources of these substances. Whereas mercury is mainly derived from anthropogenic sources and is mainly associated to terrigenous organic material in the River Mersey system, organic matter in sediments from the bay may be derived from the western section of the Irish Sea, from local inputs mainly due to primary production, from riverine inputs and from discharges of wastes in the different disposal sites. The natural marine inputs of organic matter into sediments from Liverpool Bay may be overshadowing the mercury-organic matter relationship previously reported in sediments in the bay (Rae and Aston, 1981; Norton *et al.*, 1984a) and in sediments from the Mersey river and estuary (Rae and Aston 1981, 1982; Craig and Moreton, 1986; Langston, 1985; Taylor, 1986) . Evidence supporting a possible specific association between mercury and land derived organic matter in sediments from Liverpool Bay, is provided by a significant ($p<0.001$) correlation observed between the mercury and the carbon stable isotopes ($r=-0.450$). This relationship, presented in Figure 4.12d, indicates that mercury concentrations in fine sediments generally increase as the $\delta^{13}C$ values become more negative, and as already discussed, more negative $\delta^{13}C$ values indicate higher proportions of land derived organic matter; in other words, Figure 4.12d indicates that mercury increases as the proportion of land derived organic carbon increases for these samples.

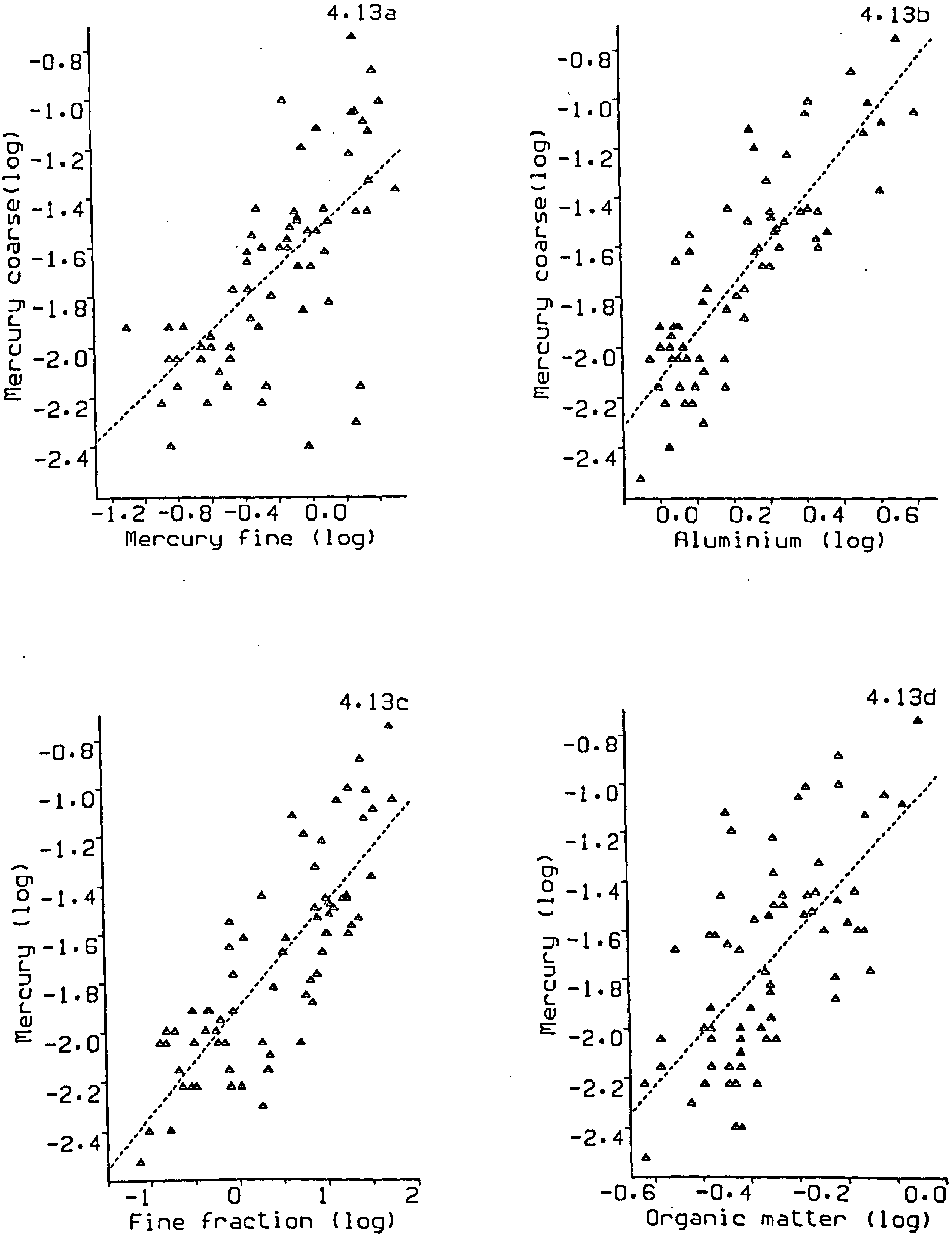


Fig.4.13. Scatter plots of logarithm of mercury in coarse sediments vs (a) logarithm of mercury in fine sediments, (b) logarithm of aluminium content, (c) logarithm of fine fraction content and (d) logarithm of organic matter content in coarse sediments.

4.2.1.2. Mercury in the coarse fraction

As in the fine fraction, a gradient of increasing concentrations from south to north was present for the distribution of mercury in the coarse fraction (Fig. 4.11b). The mean mercury concentration in the coarse material for all (70) samples was 0.030 µg g^{-1}. In the southern region of low values, concentrations for most samples were lower than 0.010 µg g^{-1} and a minimum of 0.003 µg g^{-1} was found a station S-7. Values higher than 0.020 µg g^{-1} were found at stations in the northern region with concentrations higher than 0.060 µg g^{-1} in some samples (M-12, Q-13, R-12, S-13 and T-12). The highest values were found at stations in Burbo Bight with concentrations in the range of 0.074 µg g^{-1} (station YY-4) to 0.178 µg g^{-1} (station YY-3). Stations T-14 and U-15, the nearest to Site Z, presented concentrations below the mean value (0.024 and 0.021 µg g^{-1} respectively). It is interesting to note that the concentrations at stations U-11 and T-10, immediately out of the mouth of the Queen's Channel were very low (0.005 and 0.004 µg g^{-1} respectively).

In general, the distribution of mercury in both fine and coarse fractions was similar. A high correlation between mercury in fine and coarse fractions was observed (r=0.684 after a logarithmic transformation of both variables), and as shown in Figure 4.13a, the highest variability in this relationship occurred at low mercury concentrations in the coarse fraction (values lower than -2.15 in logarithmic scale, equivalent to values lower than 0.007 µg g^{-1}). If concentrations lower than 0.007 µg g^{-1} in the coarse fraction were excluded, the correlation between fine and coarse fractions increased to r=0.798 (n=56), this correlation indicates that the mercury distribution in the coarse fraction could be largely described by the distribution in the fine sediments through a linear regression

log-Hg_{coarse} = -1.34 + 0.659 log-Hg_{fine}, (r^2=63%, F=94.4).

The correlation between mercury in fine and coarse fractions is a result of the large effect of the amount of fine particles in the total sediment on the mercury levels in fine and coarse particles. After a logarithmic transformation of the data, large correlations of the mercury in the coarse fraction with the aluminium and fine fraction content in the total sediment were observed (r=0.853 and 0.822 respectively). These correlations show that the parameters related to the amount of fine fraction in the total sediments were good predictors of the mercury content in the coarse sediments (see also Figs. 4.13b and c). The regression equations were:

log-Hg_{coarse} = -1.95 + 1.83 log-%Al, (r^2=72%, F=182), and

log-Hg_{coarse} = -1.91 + 0.428 log-%fine fraction, (r^2=68%, F=141).

A positive significant ($r=0.666$, $p<<0.001$) correlation was observed between mercury concentrations and the organic matter content in the coarse sediments (see Fig. 4.13d). Although, as previously indicated, a correlation itself does not confirm a chemical association, the lack of correlation between the mercury contents and other geochemical parameters (e.g. iron and manganese contents) in the coarse fraction may suggest that mercury in the coarse sediments is specifically associated with the organic matter at the surface of coarse particles. The previous observation, together with the fact that a high correlation between the organic matter content in the coarse fraction and the amount of fine particles in the total sediment was also observed (see Section 4.1.3. in this Chapter), may suggest that the mercury is being transferred from the fine particles associated with the terrigenous organic matter to the coarse particles, presumably by physical contact between particulates.

In summary, the distribution presented in Figure 4.11b indicates that mercury in coarse sediments largely originates from the Mersey. The largest mercury concentrations, observed in the Burbo Bight samples, coincide with the largest organic matter values (see Figs. 4.13d and 4.4c) and the largest amount of fine material (Fig. 4.2a and 4.2c). The low values immediately outside Queen's Channel result from relatively low amounts of fine material (see Fig. 4.2a) being deposited in this area as a result of intense tidal currents, therefore, this high currents may be maintaining coarse sediments in this section relatively clean. The area of high values to the north and west of Queen's Channel is also probably due to the Mersey inputs as coarse sediments closer to Site Z (stations T-14 and U-15) probably derived from the dredged spoil discharges, presented lower concentrations than the nearby samples. The high concentrations in the northeastern area of Site SI coincide with samples containing high amounts of fine particles and also high organic matter values (see Figs. 4.2a and 4.4c), these high values are probably a result of mercury inputs from sewage sludge disposal, however, this hypothesis is difficult to confirm with the available information. The region of low values in the south probably resulted from the lack of deposition of fine particles in this relatively shallow area were currents intensify, leaving the coarse sediments relatively free of the effects of the contact with contaminated fine particles. It is interesting, however, that within this area a sample was present (station J-7) which contained a high amount of fines (~6%) compared with the surrounding samples and a slight organic matter and mercury enrichment in the coarse sediments. This relative enrichment probably reflects the recent inputs of sewage sludge that, as previously mentioned in the δ^{13}C discussion (see Section 4.1.3.), have been concentrated in this section of the dumping ground from early 1988 (P.C. Head, North West Water, pers. comm.).

4.2.2. Arsenic

4.2.2.1. Arsenic in the fine fraction

The distribution of arsenic in fine sediments (Fig. 4.11c) was very similar to those of iron (Fig. 4.7a) and manganese (Fig. 4.7c). The maximum concentration of 144 μg g^{-1} was found at station L-9. Most of the stations in the central region of the sampling grid had high values with concentrations above 30 μg g^{-1}, and values above 50 μg g^{-1} at stations G-9, K-8, L-10, M-10, N-11, P-10 and a value of 131 μg g^{-1} at station Q-9. The mean value for all samples (67) was 26 μg g^{-1}. The northwestern region, with values lower than 15 μg g^{-1}, had a minimum of ~9 μg g^{-1} at station N-13. Samples form Burbo Bight had concentrations below the mean, between 16 μg g^{-1} (station YY-3) and 22 μg g^{-1} (station YY-2). Samples near Site Z (e.g. T-12, T-14, U-15) also had concentrations below the mean (15, 14 and 16 μg g^{-1} respectively).

The distribution of arsenic in fine sediments (Fig. 4.11c) seems to indicate that the disposal of sewage sludge could be the cause of this element's enrichment in the central region of the sampling grid including the southern sector of Site SI. However, as in the case of iron and manganese, arsenic levels in the sewage sludge (16.2 μg g^{-1}) are lower than the mean concentration for the whole region (~26 μg g^{-1}) and nearly one order of magnitude lower than the highest recorded concentration at station L-9 (144 μg g^{-1}). Thus, the main source of arsenic into Liverpool Bay seems to be the natural inputs from the mineralized areas of North Wales; this hypothesis is based on previous reports of arsenic levels in this region. For example, Thornton *et al.* (1975) reported arsenic concentrations between 5 and 65 μg g^{-1} in the fraction <200 μm of sediments from the River Conwy tributaries draining mineralized areas in North Wales. Arsenic values in the <200 μm fraction higher than 150 μg g^{-1}, and high values near the Conwy Estuary are reported in a geochemical atlas of England and Wales (Imperial College of Science and Technology, 1978). Other trace elements are also present in very high concentrations in the sediments of the tributaries and the estuary of the River Conwy, particularly zinc and lead, resulting from the mining activities of sphalerite and galena in the past (Elderfield *et al.*, 1971). Therefore, mine tailings could be the source of the relatively high arsenic levels found in the fine fraction of the sediments analysed in this study. Unfortunately the arsenic data presented in this thesis could not be compared with other data for the region as there are no previous reports in the revised literature of arsenic in sediments from Liverpool Bay, however, natural enrichments of arsenic in coastal sediments have been previously reported for other regions. For example, Windom *et al.* (1989) reported arsenic enrichments in unpolluted coastal sediments of the southeast coast of U.S.A. of approximately seven times above the predicted natural levels, which they attributed to inputs from phosphate rich minerals. Therefore, in contrast with mercury which mainly derives from anthropogenic inputs, arsenic levels in Liverpool Bay seem to be within the limits of the natural variability of this element.

The highest correlations of arsenic with sediment parameters in the fine sediments were found with manganese and iron concentrations. The highest correlation ($r=0.916$, $p<<<0.001$) between arsenic and manganese was obtained after a logarithmic transformation of both variables, this relationship is represented in Figure 4.14a and can be described by the following equation:

$$\log\text{-}As_{fine} = -0.607 + 0.603 \log\text{-}Mn_{fine}, \ (r^2=84\%, F=337).$$

The correlation coefficient between arsenic and iron concentrations was $r=0.806$, and the regression equation describing this relationship (see also Fig. 4.14b) was:

$$As_{fine} = -40.5 + 30.3 \ Fe_{fine}, \ (r^2=64\%, F=120).$$

The high correlation of arsenic with iron and manganese was not unexpected as hydrous iron and manganese oxides have been reported as the main carrier phases of arsenic in freshwater and marine sediments (Langston, 1983, 1985; Peterson and Carpenter, 1986; Belzile, 1988). Furthermore, it has been suggested that the arsenic is specifically associated to the iron component in aquatic particles (Edenborn *et al.*, 1986; Belzile and Tessier, 1990; Carpenter *et al.*, 1978; Mok and Wai, 1989), rather than to iron and manganese hydroxides indistinctively. This specific arsenic-iron association (according to Salomons and Forstner, 1984) may be due to the fact that under normal pH conditions in aquatic environments, δ-MnO_2, amongst other mineral phases, is negatively charged therefore exerts stronger affinity for transition metal cations (e.g. Cu, Ni and Zn), whereas iron oxides present a positive charge that permits the association of elements with aqueous anionic charge such as phosphate and arsenic. It is important, however, to mention that the possibility of arsenic uptake by manganese oxide phases in sediments has also been suggested. For example Takamatsu *et al.* (1985) concluded from their study of arsenic in lake sediments that hydrous manganese oxides, positively charged from the adsorption of Mn(II) ions, could play a significant role in the accumulation of arsenic on the surface of particulates.

The possibility of a specific association of arsenic with iron or manganese was explored by analyzing the arsenic:iron and arsenic:manganese ratios in the fine sediments (see Figs. 4.15a-c). Assuming that the main source of arsenic and manganese into Liverpool Bay is common to both (*i.e.* the mineralized areas of North Wales), Figure 4.15a indicates that in sediments near the source (represented by high arsenic and iron values, see also Fig. 4.14b) arsenic is enriched in relation to iron and, as particles from the mineralized areas are transported within the bay, the arsenic appears to be diluted by the iron phase of fine particles with a different origin (e.g. from

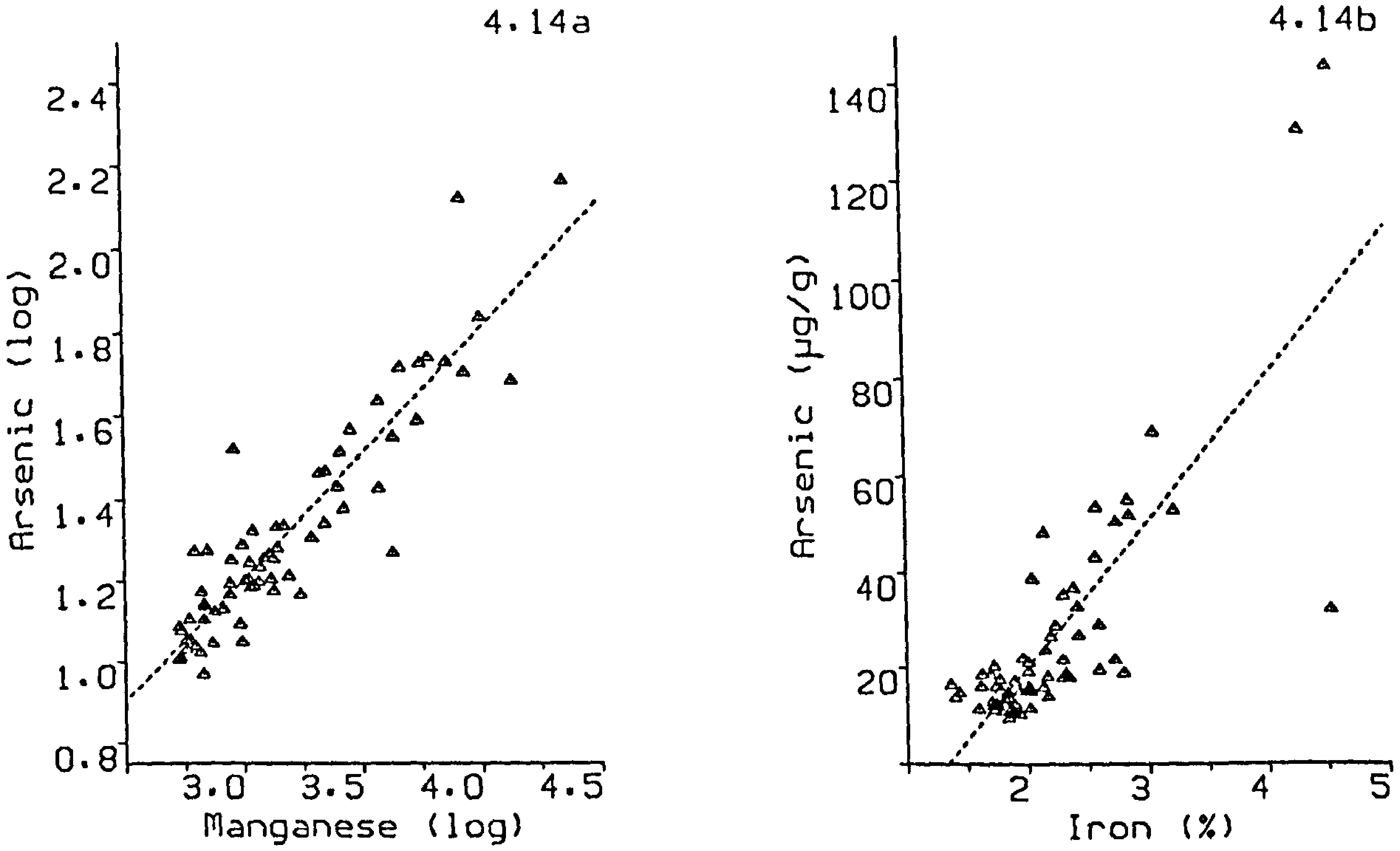


Fig.4.14. Scatter plots of (a) logarithm of arsenic vs logarithm of manganese and (b) arsenic vs iron in the fine sediments.

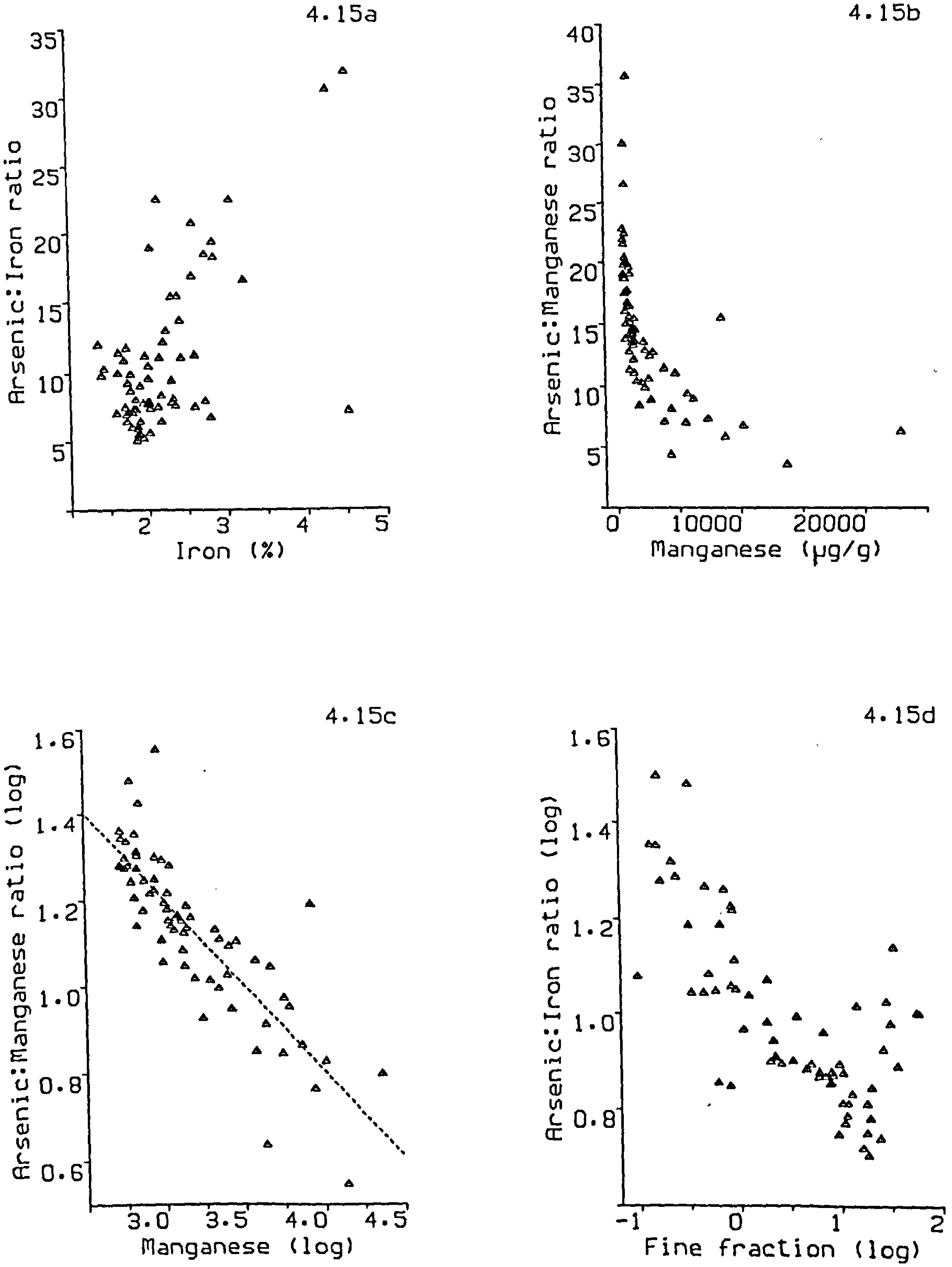


Fig.4.15. Scatter plots of (a) the arsenic:iron ratio (x 10^4) vs iron in fine sediments, (b) arsenic:manganese ratio (x 10^3) vs manganese in fine sediments, (c) logarithm of arsenic:manganese ratio vs logarithm of manganese in fine sediments and (d) logarithm of arsenic:iron ratio in fine sediments vs logarithm of fine fraction content.

the western section of the Irish Sea) and the arsenic:iron ratio decreases almost linearly (in Fig. 4.15a, $r=0.624$, $p<<0.001$). Conversely, sediments near the source (represented by high manganese values in Figs. 4.15 b and c) present a low arsenic:manganese ratio indicating that, although both elements are present in high concentrations (see also Fig. 4.14a), manganese concentrations are proportionally much higher than arsenic. As particles from the mineralized areas are transported within the bay, arsenic remains more associated to the solid phase whereas manganese is mobilized more rapidly. Therefore, the arsenic:manganese ratio increases with distance from the source. The lower mobility of arsenic may be due to its association to iron phases that are in turn less mobile (less soluble) than manganese hydroxide solid phases in surface sediments (Edenborn, *et al.*, 1986; Belzile and Tessier, 1990; Mok and Wai, 1989). The high correlation between arsenic and manganese may therefore indicate a common source rather than a direct geochemical association between these two elements.

The arsenic:iron ratio in the fine fraction presented a high correlation with the amount of fines in the total sediments ($r=-0.728$, $p<<0.001$, after logarithm transformation of both data sets). Figure 4.15d indicates that there was a clear tendency of the arsenic:iron ratio to decrease as the amount of fine material increased. Therefore, in general, muddier samples were depleted in arsenic when compared to samples with low fines, however, this general tendency was overshadowed in samples from Burbo Bight (see data points with values >1.40 in the logarithm of percentage of fine in Fig. 4.15d) probably due to arsenic inputs from the Mersey. When samples from the Burbo Bight region were excluded from the calculations, the correlation coefficient for the relationship presented in Figure 4.15d increased to $r=-0.853$ and the following regression equation was obtained:

$$\text{log-As:Fe}_{\text{fine}} = 1.07 - 0.243\ \text{log-\%fine},\ (r^2=72\%,\ F=155,\ n=60).$$

Not unexpectedly, a high correlation was also observed between arsenic in the fines and aluminium in the total sediment ($r=-0.538$ and -0.726 after exclusion of the seven muddiest samples; both variables in logarithm).

A significant correlation was obtained for the arsenic (after logarithm transformation) and organic carbon concentrations ($r=0.633$, $p<<0.001$), and also with organic nitrogen ($r=0.647$, $p<0.001$). This correlations could suggest a possible arsenic-organic matter association, however, the strong association between arsenic and iron/manganese hydrous oxides extensively reported (Langston, 1983, 1985; Peterson and Carpenter, 1986; Belzile, 1988), and the fact that after the inclusion of carbon in a multiple regression analysis no significant increase in the variance of arsenic already explained by the iron content was observed, seem to suggest that the significant correlation between carbon and arsenic in the fine fraction only reflects a covariance due to a similar effect of the amount of fine material in total sediments on both variables.

4.2.2.2. Arsenic in the coarse fraction

As in the case of arsenic in the fine fraction, arsenic in the coarse fraction (Fig. 4.11d) showed a similar distribution to iron (Fig. 4.7b) and manganese (Fig. 4.7d). A mean arsenic concentration value of 3.82 µg g^{-1} was obtained for all (70) samples. High concentrations in the central region were aligned in a west-east line along stations L-9 (4.73 µg g^{-1}), M-9 (6.30 µg g^{-1}), N-9 (6.12 µg g^{-1}), P-9 (7.38 µg g^{-1}) and reaching the maximum at station Q-9 (8.22 µg g^{-1}). Values above 4.50 µg g^{-1} were also observed in samples from the west of Site SI at stations G-9, G-11 and H-10. Values above 5.00 µg g^{-1} were registered in the eastern region at stations S-9, T-8 and U-11. Concentrations in the Burbo Bight area ranged between 3.60 µg g^{-1} (station YY-1) and 4.72 µg g^{-1} (station YY-3). The lowest concentrations were observed at stations Q-11 and P-10 (1.46 and 1.82 µg g^{-1}), and at stations N-7 and N-8 (1.92 and 1.81 µg g^{-1} respectively).

The similarity between arsenic and iron, and arsenic and manganese distributions in coarse sediments indicates, as in the fine fraction, a possible strong geochemical association between these elements. High correlation coefficients ($r=0.740$ and 0.739, $p<<0.001$) were observed between arsenic and both iron and manganese, these correlations are reflected in the high degree of linearity shown in Figure 4.16a and b. The arsenic:iron and arsenic:manganese ratios in the coarse sediments (Fig. 4.16c and d) presented a generally similar trend to that in the fine sediments (Fig. 4.15c and d), therefore, the same observation can be applied in both grain size fractions regarding the possible specific arsenic-iron association in the sediments from Liverpool Bay, and the discussion on the possible sources of iron in the coarse sediments presented in Section 4.1.4. may be applied to arsenic. Non-significant correlations were observed between arsenic in the coarse fraction and other important parameters such as organic matter, aluminium and the fine fraction content in the sediments.

4.2.3. Cadmium

4.2.3.1. Cadmium in the fine fraction

The distribution of cadmium in fine sediments is shown in Figure 4.17a. In spite of the patchiness of the distribution, three areas of cadmium enrichment can be identified. The largest enrichment zone was found in the southern region of the sewage disposal area, with concentrations higher than 0.75 µg g^{-1} in most samples and values above 1.20 µg g^{-1} at stations

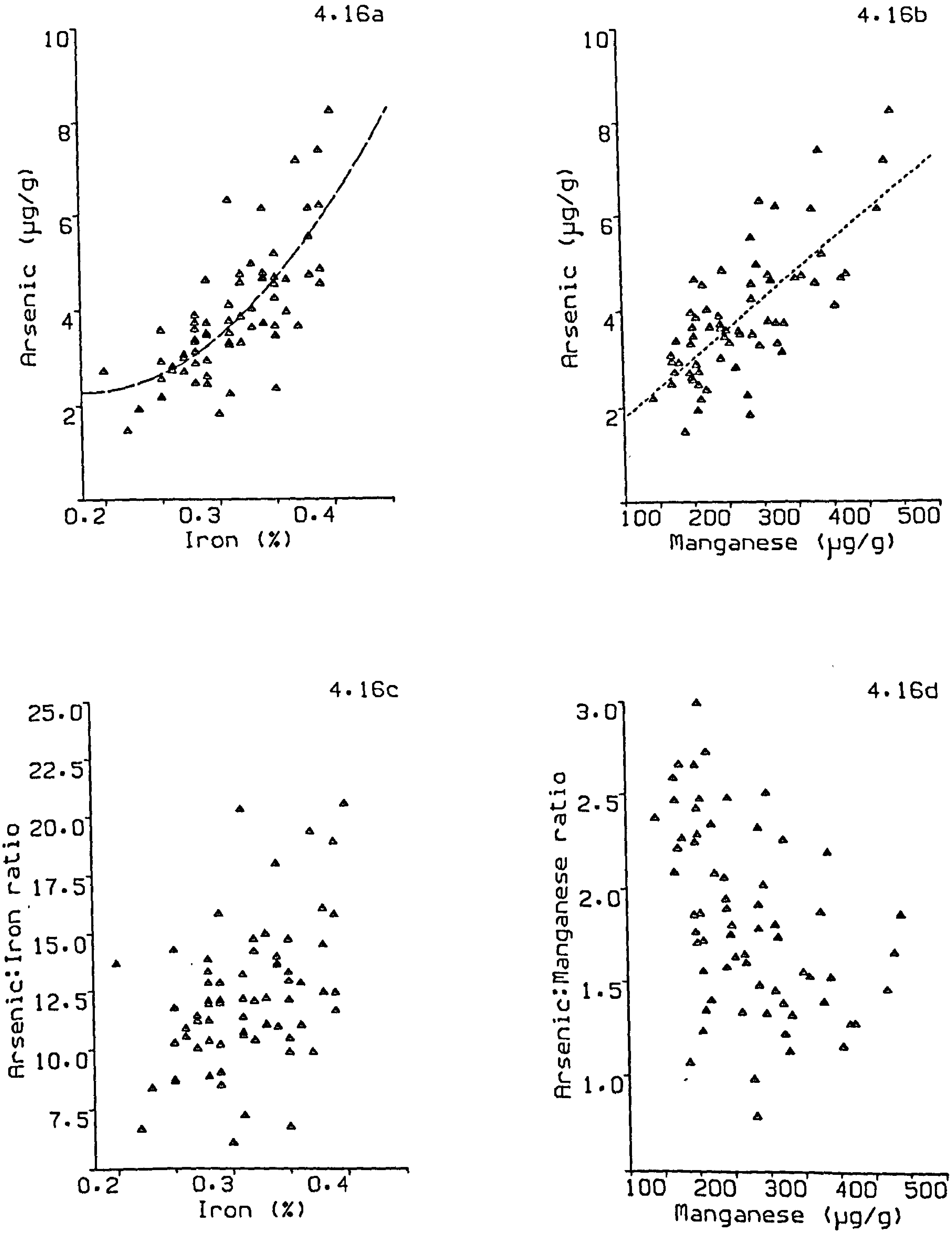
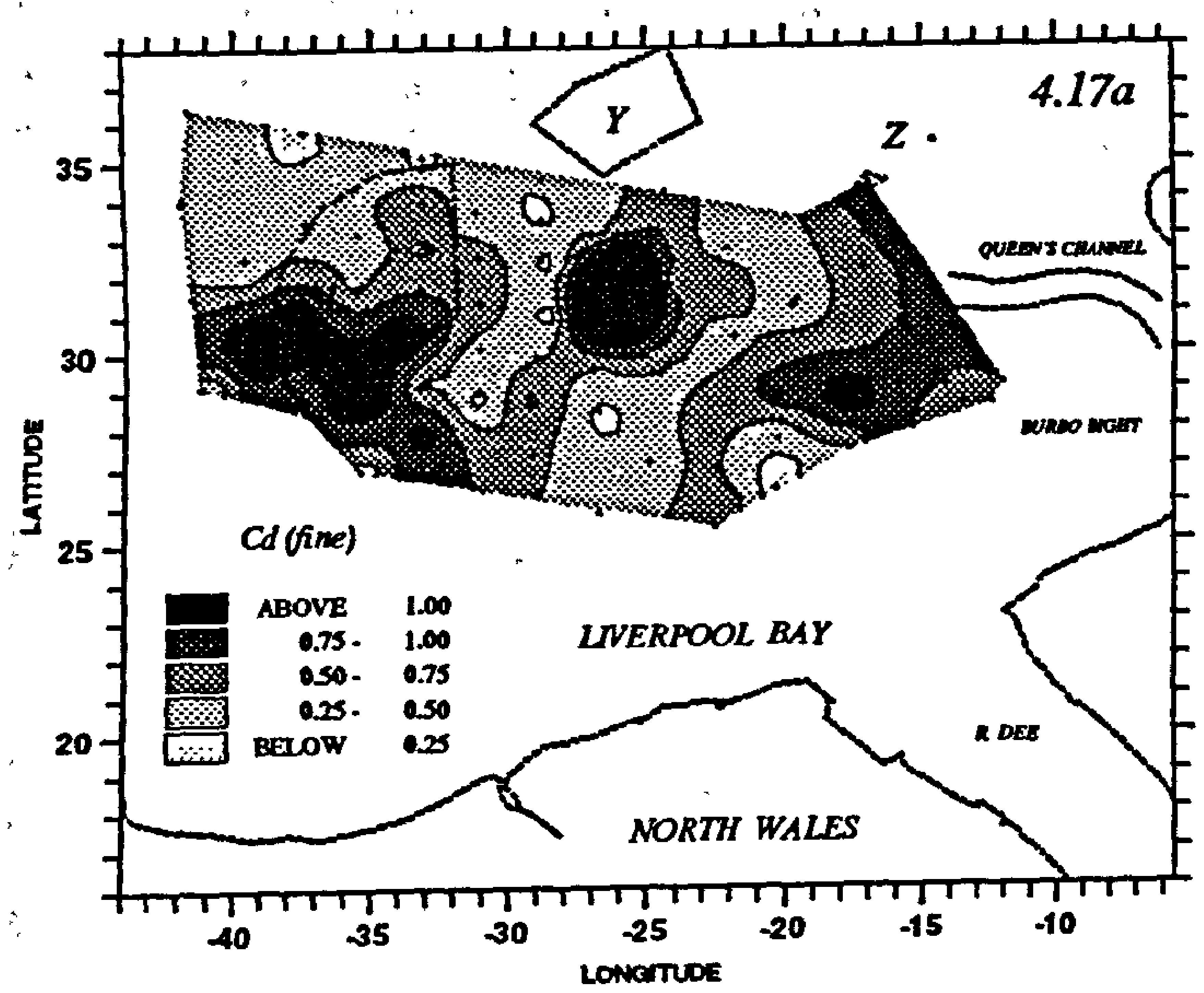
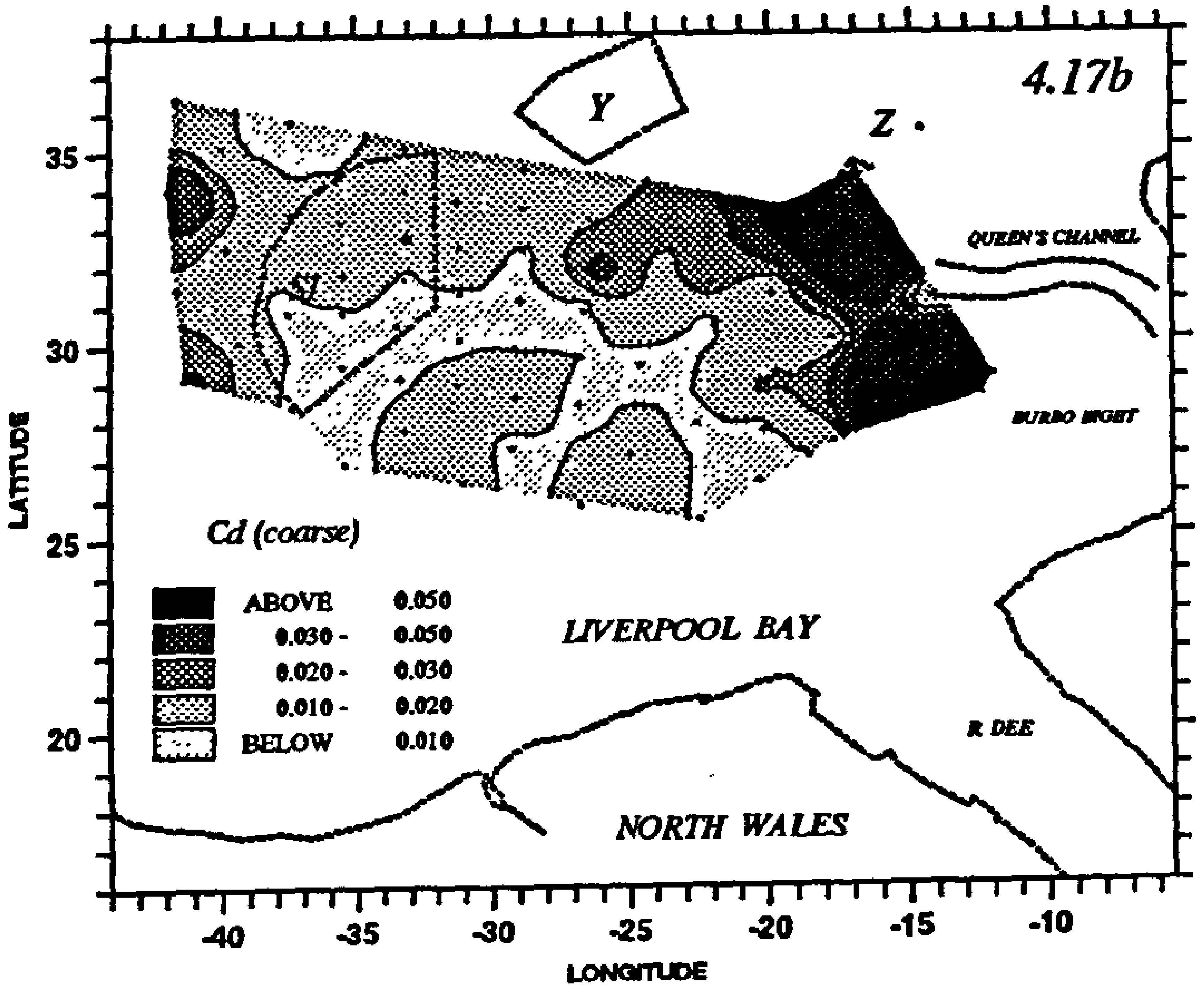
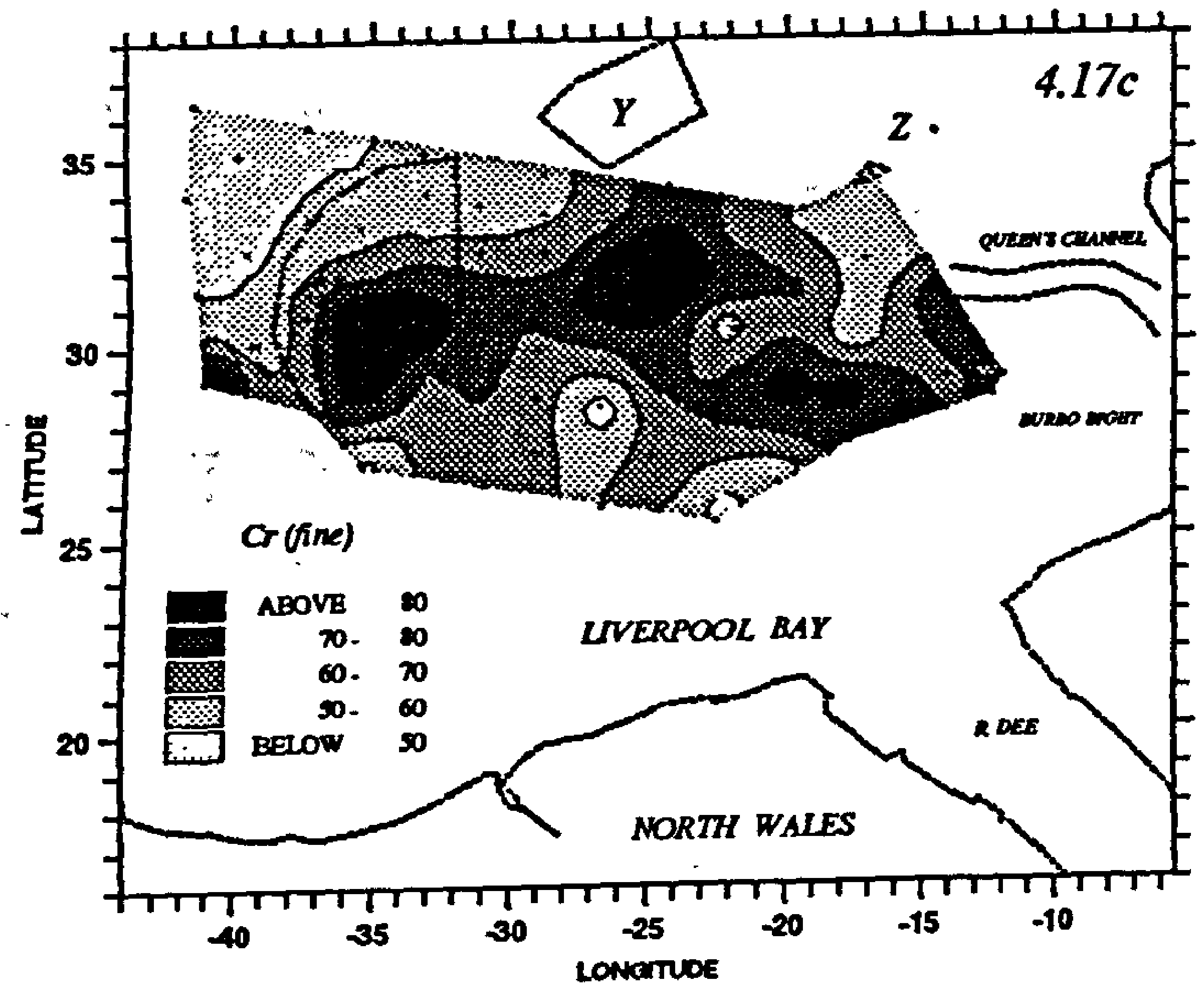


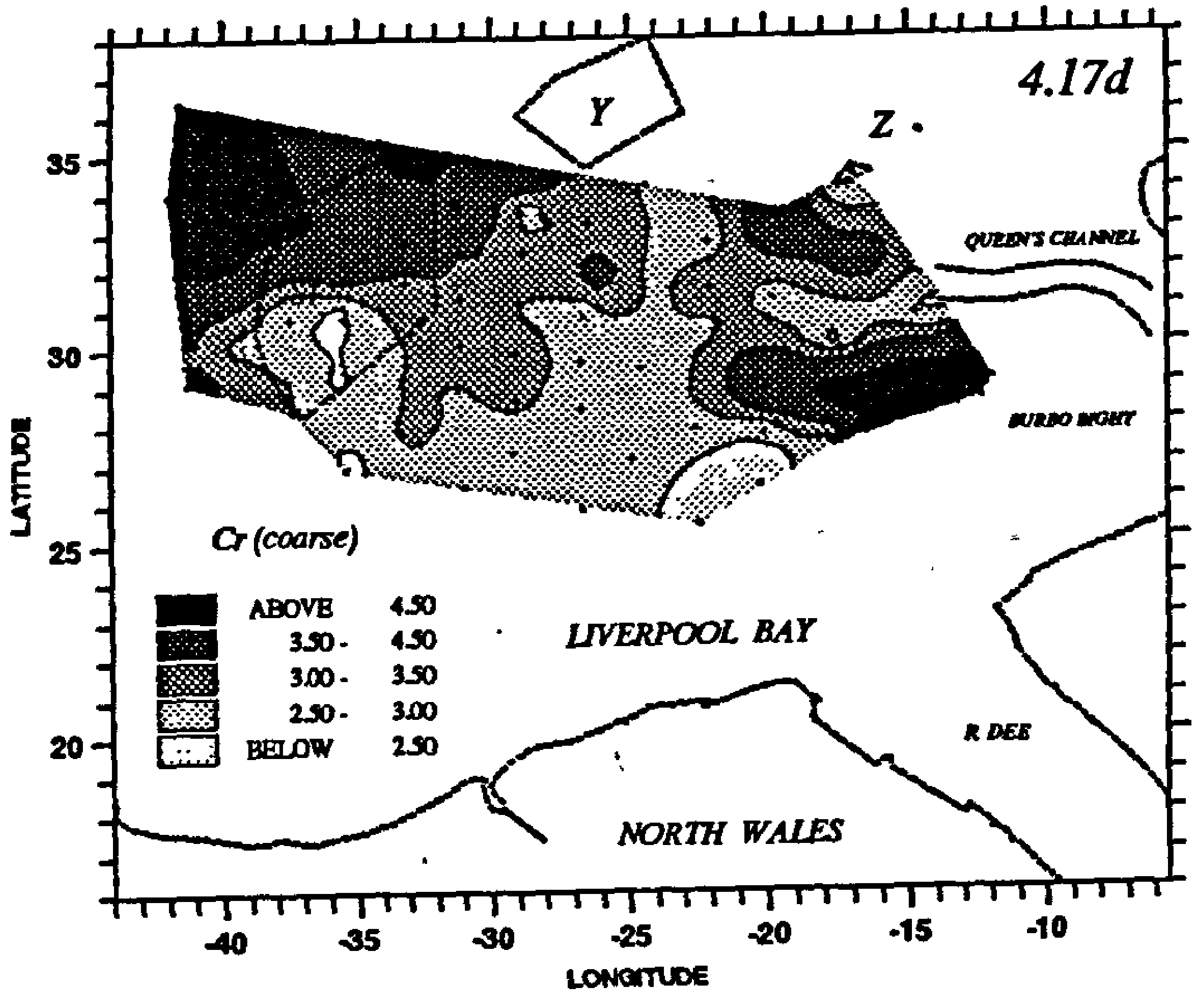
Fig.4.16. Scatter plots of (a) arsenic vs iron, (b) arsenic vs manganese, (c) arsenic:iron ratio ($x10^4$) vs iron and (d) arsenic:manganese ratio ($x10^2$) vs manganese in coarse sediments.

Fig.4.17. Distributions of cadmium in (a) fine sediments and (b) coarse sediments, and of chromium in (c) fine sediments and (c) coarse sediments. Concentration values are in μg g^{-1}.


4.17a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Cd (fine)
ABOVE 1.00
0.75 - 1.00
0.50 - 0.75
0.25 - 0.50
BELOW 0.25
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.17b
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Cd (coarse)
ABOVE 0.050
0.030 - 0.050
0.020 - 0.030
0.010 - 0.020
BELOW 0.010
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.17c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Cr (fine)
ABOVE 80
70 - 80
60 - 70
50 - 60
BELOW 50
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10


4.17d
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Cr (coarse)
ABOVE 4.50
3.50 - 4.50
3.00 - 3.50
2.50 - 3.00
BELOW 2.50
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10

G-9, H-8, J-9, K-8 and L-9. The maximum value of 2.46μg g^{-1} was found in sample P-11, centred in a patch of high values in the central part of the sampling grid, between Site SI and Queen's Channel. The average cadmium concentration for the whole region was 0.65 μg g^{-1}. There was also an enrichment of cadmium in samples near the Queen's Channel with a value up to 1.24 μg g^{-1} in sample T-9. Samples from the Burbo Bight showed a range of cadmium concentrations from 0.66 to 0.81 μg g^{-1}, that is, concentrations in this area were only slightly above the mean concentration. Low concentrations were found toward the north and northwestern part of the sampling grid, where values were lower than 0.50 μg g^{-1}, and in some cases (stations J-13, L-13, N-10, N-11 and N-12) lower than 0.22 μg g^{-1}. The minimum cadmium concentration for the whole region was 0.11 μg g^{-1} at station S-7.

The distribution of cadmium in the fine sediments seems to reflect the main sources of this metal into the bay. This distribution, however, is difficult to explain based on possible specific cadmium associations with a particular sedimentary phase (or phases) as this metal, in contrast to any of the other of the elements analised, did not present significant correlations with any of the sediment parameters, with the exception of a low correlation ($r=-0.32$, $p=0.008$) with $\delta^{13}C$.

The correlation of cadmium with $\delta^{13}C$, and its distribution (Fig. 4.17a) indicate that the main sources of this metal are the land derived discharges from the River Mersey and the sewage sludge disposal at Site SI. MAFF (1987) reported an estimation of cadmium loads discharged into Liverpool Bay of 1.6, 2.7, 3.7 and ~12 kilograms per tide from sewage sludge dumping, dredge spoil, other discharges (probably referring to direct trade and sewage effluents) and the Mersey Estuary respectively.

Considering that cadmium inputs from the Mersey are much larger than other inputs it would probably be expected to find the highest concentrations near the Queen's Channel, however, the highest concentrations were found at station P-11 and in the southern part of Site SI. The fact that cadmium levels in samples from the Burbo Bight (probably the area most influenced by the Mersey inputs) were lower than in other areas, may be due to the peculiar chemical behaviour of cadmium as compared to other trace metals. Cadmium adsorption onto sediment particles is influenced by the salinity of the water, particularly the presence of chloride ions that tend to form complexes with cadmium, and decrease adsorption and favour desorption of cadmium from particles (Salomons and Eysink, 1981; Lion *et al.*, 1982; Forstner, 1984; Comans and van Dijk, 1988). Therefore, a large proportion of the cadmium entering Liverpool Bay from the Mersey runoff may remain in solution (according to Sadiq, 1989, the major chemical form of cadmium in standard seawater is $CdCl_2^{\circ}$, a neutral species with a low affinity for sorption) in contrast to other metals such as mercury which tends to remain strongly associated to the sediments and as a consecuence shows particularly high concentrations in the sediments from samples near to Queen's Channel including Burbo Bight.

The lack of correlation with any particular phase observed in the present study may be, in part, related to the widely reported relatively low tendency of cadmium to adsorb onto particles as compared to other trace elements (Forstner and Wittmann, 1979; Olsen *et al.*, 1982; Balistrieri and Murray, 1984). According to Sadiq (1989) the low tendency of cadmium to sorb may be the reason for contradicting reports on cadmium adsorption with regard to the specific phases to which this metal associates in sediments. For example, Davies-Colley *et al.* (1984) reported iron oxides as the main phase to which cadmium associates in aerobic estuarine sediments with relatively low contributions from organic and manganese phases. Cadmium associations with iron and manganese oxides have also been suggested by Rosental *et al.* (1986), Brook and Moore (1988) and others; these reports also suggest a minor association with organic matter. Windom *et al.* (1989) reported the organic phases as probably the most important carriers of cadmium in unpolluted sediments from the southeast coast of U.S.A., whereas Lion *et al.* (1982) also suggested a control of cadmium adsorption by organic coatings. Brook and Moore (1988) indicated an strong tendency of cadmium (also manganese and zinc) to increase with decreasing particle size, whereas Libert (1987) suggested that cadmium partitioning between liquid and sedimentary phases was dependent on sediment concentrations but was not dependent on the total surface area, that is, the sediment size.

It is evident from the previous discussion that reports on cadmium associations in sediments, although well documented, are sometimes contradictory and may be strongly dependent on the sediment characteristics, and on the concentration of each sedimentary phase in particular. Another obvious controlling factor is the sources of this element. In Liverpool Bay, the high values in the sewage dumping ground are probably due to the discharges in this area (the concentration of cadmium in the sewage sludge was 11.90 $\mu g\ g^{-1}$, that is, 18.6 times the mean cadmium concentration for the whole region), however, a considerable proportion of cadmium from the original sludge load may be lost from the particulate phase into solution when sludge particles come in contact with seawater. Desorption experiments cited in Forstner and Wittmann (1979) showed a high release of cadmium (93% in 4 weeks) from sewage sludge particles after contact with seawater, this metal presented, by far, the highest desorption when compared to other metals such as copper, nickel, lead, zinc, chromium, manganese and iron showing desorptions of 69, 63, 58, 38, 0, 0 and 0%, respectively. In a study of some metals in particulate and dissolved phases, Norton *et al.* (1984c) suggested that dumping of sewage at Site SI was not a significant source of dissolved metals (zinc, copper, cadmium and nickel) into Liverpool Bay, however, these authors observed elevations on dissolved cadmium and nickel levels in some samples at the dumping ground. These elevations were explained as a possible result of desorption from sewage sludge particles. On the other hand, in the same study, significant negative correlations of dissolved metals and salinity indicated that the most important sources of dissolved metals into Liverpool Bay are the riverine and estuarine discharges.

To add to the complexity of cadmium distributions in fine sediments from Liverpool Bay, cadmium levels higher that 5 μg g^{-1} are reported for sediments in the mineralized areas of North Wales (Imperial College of Science and Technology, 1978), making natural sources, if not a significant contributor to the overall cadmium levels, possible sources of localized enrichments of this metal in sediments from the bay. On the other hand, it has been reported that phytoplankton has a strong ability to bind cadmium (compared to other toxic metals) from solution (Golimowski *et al.*, 1990), therefore, natural phytoplankton populations in Liverpool Bay, exposed to dissolved cadmium originating mainly from riverine runoff, could represent a source of this metal to the sediments, from deposition of cells after death.

4.2.3.2. Cadmium in the coarse fraction

Figure 4.17b shows the distribution of cadmium in coarse sediments. This distribution has similar features to the distribution of the fine fraction in the total sediments (Fig. 4.2a). An area with several values lower than 0.010 μg g^{-1} was present in the southern region, with a minimum of 0.005 μg g^{-1} at station K-8. Most samples in the north were within 0.010 and 0.020 μg g^{-1}. The mean value for the whole area was 0.027 μg g^{-1}. The highest values were found in the Burbo Bight samples with a range from 0.063 μg g^{-1} at station YY-2, to 0.188 μg g^{-1} at station YY-1. As in the case of mercury (Fig. 4.11b), the concentration of cadmium in the coarse sediments immediately outside the Queen's Channel (U-11 and T-10) was low (0.012 and 0.009 μg g^{-1}, respectively).

Cadmium in coarse sediments presented highly significant correlations with the amount of fine fraction and aluminium in the total sediment. The corresponding correlation coefficients after logarithmic transformation of the variables were r=0.661 and 0.778 respectively. As indicated by the correlation with mercury (r=0.767) and a comparison with the distribution of this metal (Fig. 4.11b), cadmium and mercury presented similar distributions suggesting potentially similar sources and associations in the sediment. The correlation between cadmium and organic matter (r=0.616) and the lack of correlation with iron and manganese indicates that cadmium is probably associated to the organic phase in coarse sediments. In general, the discussion regarding the sources of mercury may in general hold for cadmium, that is, the inputs from the Mersey may be the main source of this metal in the coarse sediments in the eastern sector of the bay, and also, cadmium in coarse particles may originate by transfer from the fine particles. However, contrary to the mercury distribution, cadmium was not particularly enriched in the samples from the north of Site SI even though these samples contained relatively high content of organic matter (see Fig. 4.4c). This observation may be explained by the stronger mercury-organic matter association as compared to the cadmium-organic matter association (Olsen *et al.*, 1982) together with the higher solubility of cadmium. In other words, more cadmium than mercury may be lost into solution during the transfer from the fine particles, therefore, only in areas such as the Burbo Bight where the amount of fine particles is very high and where there is a constant riverine input (also occurring in the area northwest of Queen's Channel) is the transfer of cadmium from fine particles to coarse particles noticeable. On the other hand, a direct adsorption of dissolved cadmium onto the organic matter in coarse particles near the Mersey may occur, and/or organic matter from the Mersey carrying cadmium (and other elements) may be deposited onto the surface of the coarse particles rather than being transferred from finer particles; the possibility of two or more of these mechanisms occurring simultaneously is not unlikely.

4.2.4. Chromium

4.2.4.1. Chromium in the fine fraction

Figure 4.17c shows the distribution of chromium in fine sediments. This metal presented higher concentrations in the central region along an east-west line, with values higher than 70 μg g^{-1} in most samples (except at station R-10 with 54 μg g^{-1}). Maximum concentrations were found at stations K-8, K-9 and L-9 (within Site SI) with values of 90, 95 and 91 respectively, and in samples P-10, P-11 and Q-11 with values of 85, 95 and 96 μg g^{-1} respectively. Sediments from Burbo Bight showed values from 62 (station YY-3) to 84 μg g^{-1} (station YY-2). The mean concentration for the whole region (70 samples) was 65 μg g^{-1}. In the northwestern region of the sampling area values lower than 50 μg g^{-1} were found, with the minimum of 38 μg g^{-1} at station H-12. Low values were also found near Site Z, at stations T-10, T-12 and T-14 with concentrations of 53, 55 and 51 μg g^{-1} respectively.

As partially suggested by comparison of Figure 4.17c with Figures 4.7a and 4.4a, chromium in the fine sediments correlated significantly with iron and organic carbon concentrations

($r=0.571$ and 0.588 respectively, $p>0.001$; see also Figure 4.18a and b). No significant correlations were found with other sediment parameters, indicating that chromium in the fine sediments may be specifically associated with the organic matter or hydrous iron oxides (or both).

Although the possible association of chromium with manganese oxides in aquatic sediment surfaces has been suggested (Feely *et al.*, 1983), in the present study the lack of correlation with manganese concentrations may indicate that no association of chromium with oxides of manganese is taking place in Liverpool Bay sediments or if it exists, this association is not important. On the other hand, the specific association of chromium with manganese oxides in the study by Freely *et al.* (1983) could not be confirmed, however, given the metal extraction procedure used by those authors, the association of chromium with iron oxides remained as a possibility. The possible specific association of chromium with iron oxyhydroxides in aquatic particles has been suggested by several authors (e.g. Loring, 1981; Sigg *et al.*, 1987; Angelidis and Grimanis, 1989). Sigg *et al.* (1987) suggested that chromium is preferentially bound to iron oxide surfaces as, under oxic conditions, chromium should, in thermodynamic equilibrium, occur as Cr(VI) and the CrO_4^{2-} ion could be bound to positively charged surfaces of iron oxides.

Significant association of chromium with organic phases has also been reported (Forstner and Wittmann, 1979; Rosental *et al.*, 1986; Angelidis and Grimanis, 1989, Golimowski *et al.*, 1990). In the case of associations with organic matter chromium exists probably in the Cr(III) oxidation state which is readily complexed with organic forms onto sediment particles (Rosental *et al.*, 1986) as chromium species in this oxidation state such as $Cr(H_2O)_6^{3+}$, $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$ (Golimowski *et al.*, 1990) are positively charged. Therefore, the magnitude of the correlation coefficients with iron and organic carbon may indicate a possible association of chromium with both phases in the fine sediments from the present study. It is possible that the association with iron phases is more important as a stepwise regression analysis using iron and carbon as predictors indicated iron as a better predictor for the chromium variations in the fine sediments. The multiple regression equation resulting from this analysis (after the exclusion of samples L-9, N-10 and Q-9 representing obvious outliers, see Fig. 4.18a) was:

$$\mathbf{Cr_{fine} = 12.8 + 15.0\ Fe_{fine} + 10.4\ carbon_{fine}}\ (r^2=44.2\%,\ F=25.5);$$

approximately 90% of the variance explained through this equation could be accounted for by the the variations of iron.

The lack of a stronger correlation between chromium and iron or the organic matter may be due to the different sources of these substances. It has been already mentioned that iron in

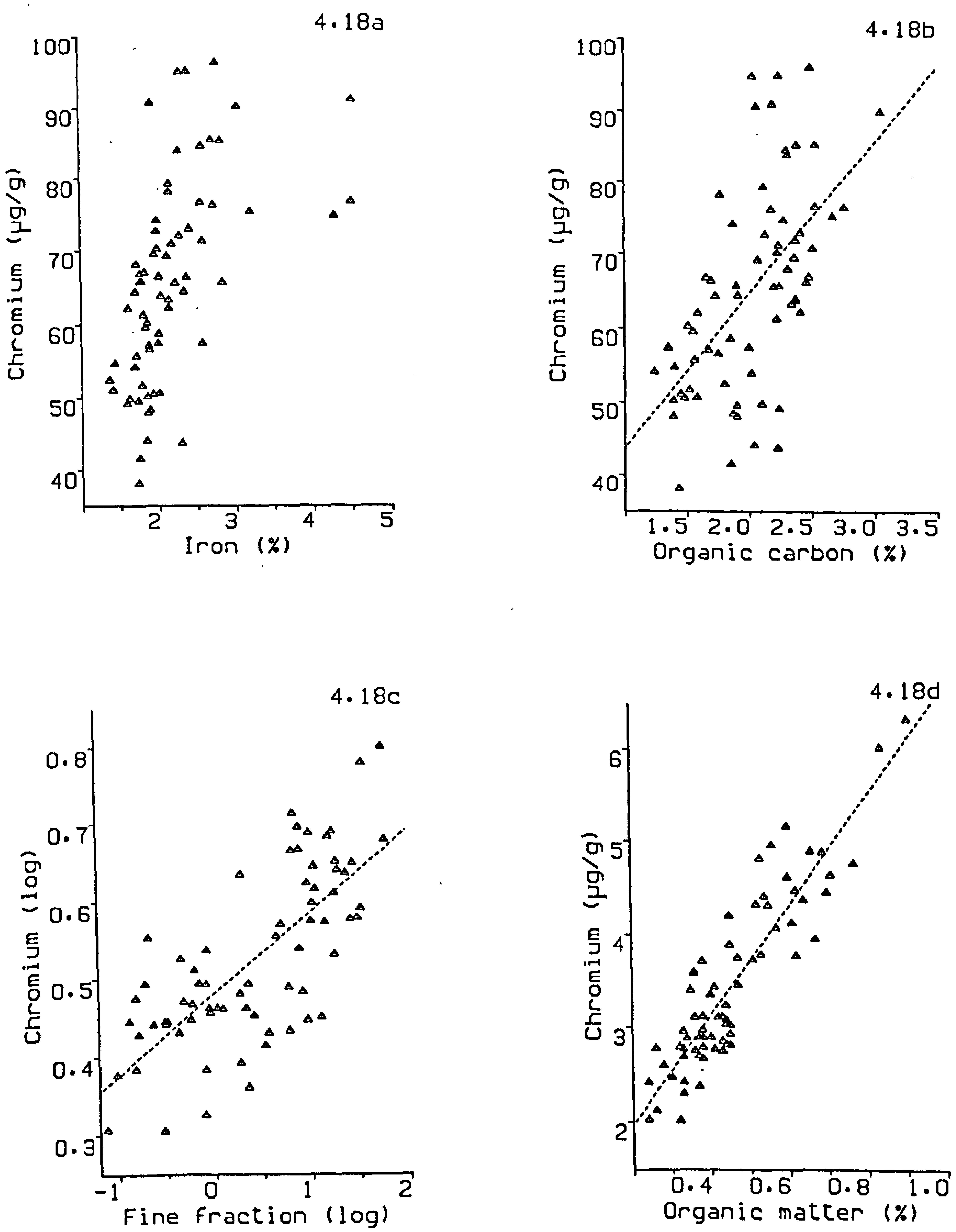


Fig.4.18. Scatter plots of (a) chromium vs iron in fine sediments, (b) chromium vs organic carbon in fine sediments, (c) logarithm of chromium in fine sediments vs logarithm of fine fraction and (d) chromium vs organic matter content in coarse sediments.

Liverpool Bay may have some important contributions from the mineralized areas of North Wales. On the other hand, the highest chromium levels (~60 µg g^{-1}) reported in sediments from the mineralized areas of North Wales (Imperial College of Science and Technology, 1978) were similar to the mean concentration for the whole bay in the present study (65 µg g^{-1}), therefore natural inputs of chromium from the North Wales mineral areas may be unimportant. An important source of chromium into the bay seems to be the sewage sludge disposal at Site SI as the concentration in the analysed sludge sample (885 µg g^{-1}), similar to concentrations reported by North West Water Authority (845 µg g^{-1}, see Table 2.2), was approximately 14 times higher than the mean concentration for the fine sediments in this study.

Data reported by MAFF (1987) indicate that the largest source of chromium into Liverpool Bay is the disposal of dredge spoil mainly at Site Z (approximately 113 tonnes in 1984) whereas sludge dumping and the Mersey discharges seem to contribute each less than half this amount (approximately 42 tonnes in 1984 respectively), it is important, however, to note that the concentrations of chromium in dredged spoil and sludge particles may have been similar as approximately three times more dredged spoil was discharged in Liverpool Bay that year.

Samples nearer Site Z (T-14 and U-15) did not show a particular enrichment of chromium and even presented concentrations (51 and 57 µg g^{-1} respectively) below the mean for the whole region. This observation is probably due to the rapid removal of fine sediments from this area (Rowlatt *et al.*, 1986; see also review of sediment transport in the bay in Chapter 2) and possible dilution with cleaner fine sediments. On the other hand, samples from Burbo Bight presented concentrations above the mean and a high concentration (84 µg g^{-1}) at station YY-2 also showing a relatively high organic carbon (2.31%) and iron concentration (2.29%) as compared to samples nearby. Chromium concentrations found in the present study were in general agreement with previously reported values in fine sediments in Liverpool Bay (e.g. Norton *et al.*, 1984b; Kiff, 1984; Kiff and Nunny, 1984; McLaren, 1987; Law *et al.*, 1989) and even the position of the maximum values in the central region seems to agree with the distributions presented by Norton *et al.*(1984a, 1984b).

Finally, a comment on the level of contamination of chromium in fine particles in Liverpool Bay can be made. McLaren (1987) reported background values of metals in sediments from this area, including chromium with a value of 25 ± 6 µg g^{-1}. Using this value as a reference, the average enrichment value (mean concentration divided by background concentration) for the whole bay was ~2.6 with a range from 1.52 to 3.84. Therefore, it can be said that there is a measurable impact from human activities on the chromium levels in sediments from the whole of the sampling region considering that the main inputs of chromium into Liverpool Bay are anthropogenic.

4.2.4.2. Chromium in the coarse fraction

Chromium concentrations in coarse sediments (Fig. 4.17d) presented a similar distribution to that of organic matter shown in Figure 4.4c. The zone of high values in the northwestern part had concentrations above 4.50 $\mu g\ g^{-1}$ at stations G-11, G-13, H-10, H-12, J-11 and L-13. The mean concentration for the whole region was 3.46 $\mu g\ g^{-1}$. Chromium concentrations gradually decreased toward the central and southern areas where values between 2.50 and 3.00 $\mu g\ g^{-1}$ were found in most of the samples. Minimum values were recorded at station K-9 (2.30 $\mu g\ g^{-1}$) within Site SI and stations R-6 and S-7 (2.02 and 2.03 $\mu g\ g^{-1}$ respectively). High chromium concentrations were observed in sediments from Burbo Bight with values ranging from 3.78 $\mu g\ g^{-1}$ at station NW-24 to 6.31 $\mu g\ g^{-1}$ at station YY-3. Low values in the vicinity of the Queen's Channel at stations T-10 and U-11 with concentrations of 2.38 and 2.47 $\mu g\ g^{-1}$ respectively.

Chromium in coarse sediments was strongly correlated with the amount of fines and aluminium in the total sediments. The correlation coefficients after logarithmic transformation of the data were r=0.734 (see also Fig. 4.18c) and 0.717 ($p<<0.001$) respectively; the regression equations were:

$$\text{log-}Cr_{coarse} = 0.481 + 0.104\ \text{log-\%fine},\ (r^2=53.2,\ F=79),\ \text{and}$$

$$\text{log-}Cr_{coarse} = 0.475 + 0.421\ \text{log-\%Al}\ (r^2=50.8\%,\ F=72).$$

This metal, as in the cases of cadmium and mercury, may be transferred from the fine particles to the coarse particles, and as indicated by Figure 4.18c, the higher the amount of fine particles for interaction, the higher the metal being transferred to the coarse particles.

There seems to be a specific control of the chromium content in the coarse fraction by the amount of organic matter present in these particles. Whereas no correlation was found between chromium and manganese in this fraction and the correlation with the iron, although significant was relatively low (r=0.423, p=0.001), a very high correlation was found with the organic matter content (r=0.899, $p<<0.001$). The regression equation for the relationship between chromium and organic matter in the coarse fraction, also represented in Figure 4.18d was:

$$Cr_{coarse} = 0.796 + 5.84\ \text{O.M.},\ (r^2=80.5\%,\ F=286).$$

The variance explained by the inclusion of iron as a predictor in a multiple regression analysis did not increase, indicating that in the coarse sediments the correlation between chromium and iron was probably a result of a covariation, and that chromium in coarse particles is specifically associated with the organic matter in the sediment; Rosental *et al.* (1986) also reported that most of the chromium in coarse sediments in their study was associated with organic matter. Therefore, the discussion of the distribution of organic matter in the coarse fraction (see Section 4.1.3 and Fig. 4.4c) also applies to the distribution of chromium shown in Figure 4.17d.

4.2.5. Copper

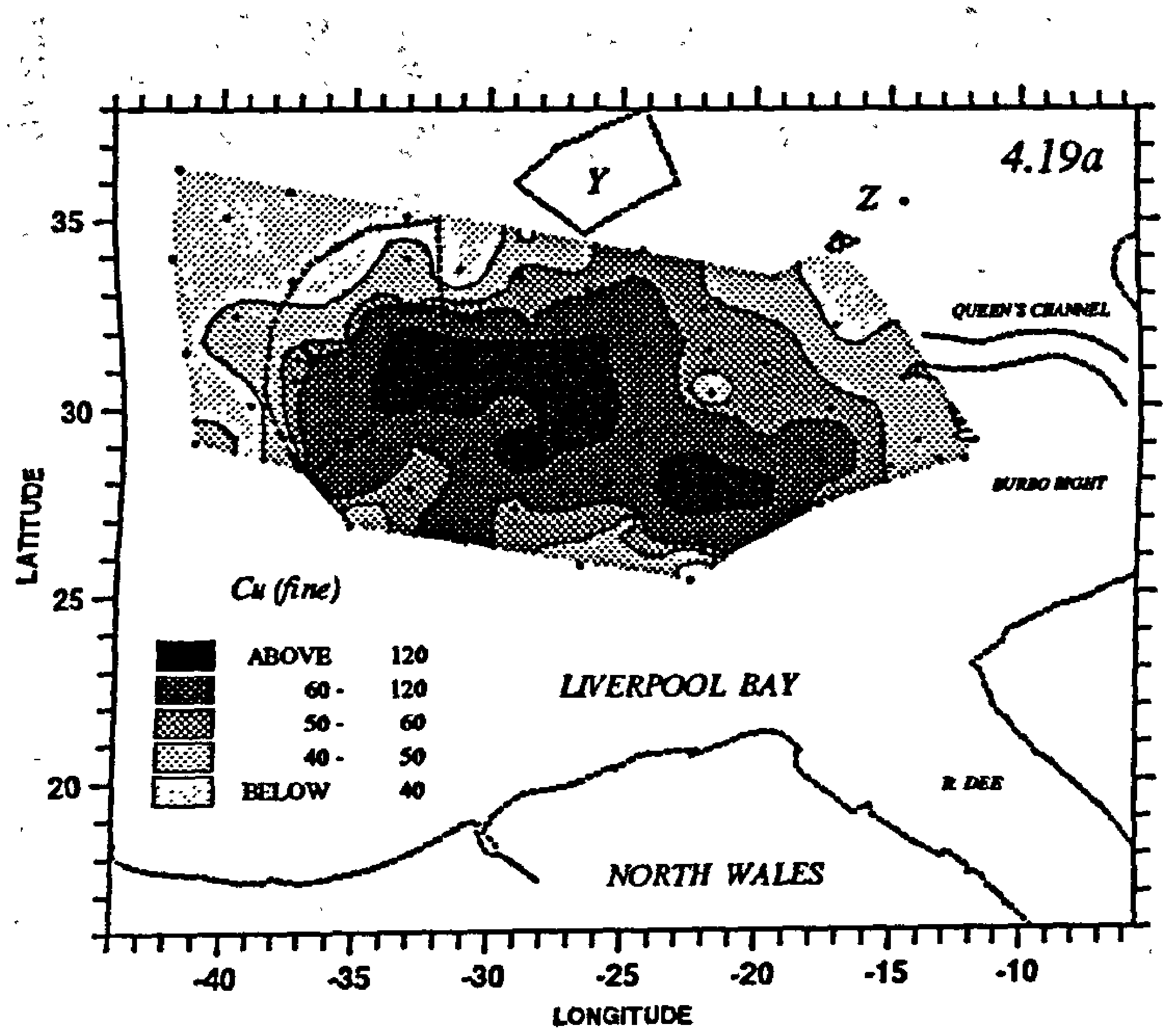
4.2.5.1. Copper in the fine fraction

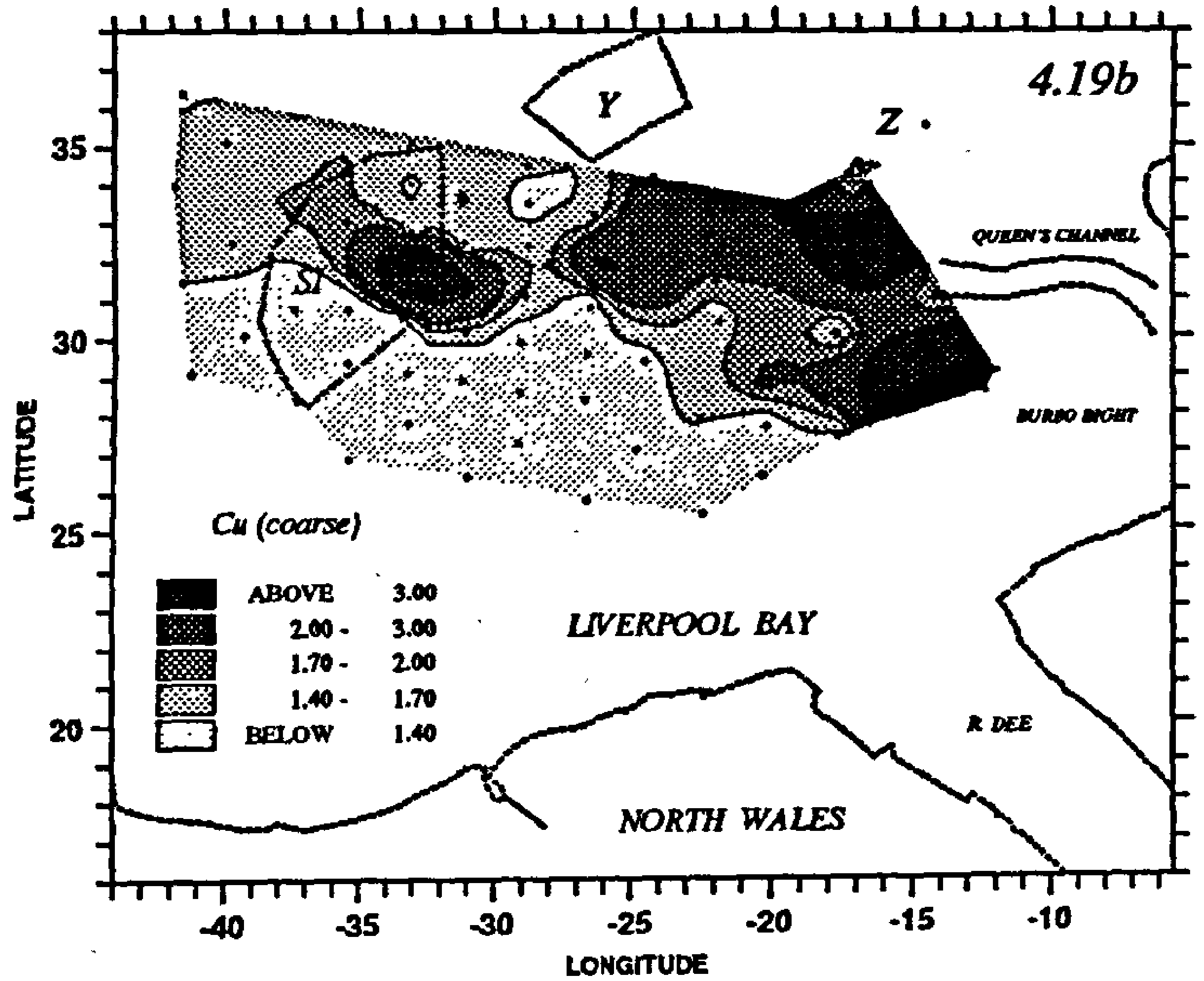
The distribution of copper in fine sediments (Fig. 4.19a) partially resembles the distributions of iron and organic carbon (Fig 4.7a. and 4.4a respectivelly). The central region of the sampling grid showed the highest concentrations, distributed within an elongated zone with the major axis orientated in an west-east line. High values in the central region were recorded at stations L-9 (157 µg g^{-1}), L-10 (168 µg g^{-1}), M-9 (144 µg g^{-1}), M-10 (173 µg g^{-1}), N-8 (168 µg g^{-1}), P-9 (176 µg g^{-1}) and the maximum at station N-10 (225 µg g^{-1}). Stations G-9, R-8 and S-8 also had high concentrations (199, 175 and 166 µg g^{-1} respectively). The mean copper concentration for the whole region was 71 µg g^{-1}. The lowest values were found in the northwestern corner of the sampling region with a minimum concentration of 23 µg g^{-1} at station H-12, and low values at G-11 (28 µg g^{-1}), G-13 (25 µg g^{-1}) and J-13 (30 µg g^{-1}). Concentrations below the overall mean, with values between 37 µg g^{-1} (sample YY-3) and 52 µg g^{-1} (sample YY-2), were found in the samples from the Burbo Bight. Samples from stations near Site Z (T-12, T-14 and U-15) also showed copper concentrations lower than the overall mean (37 and 36 and 69 µg g^{-1} respectively).

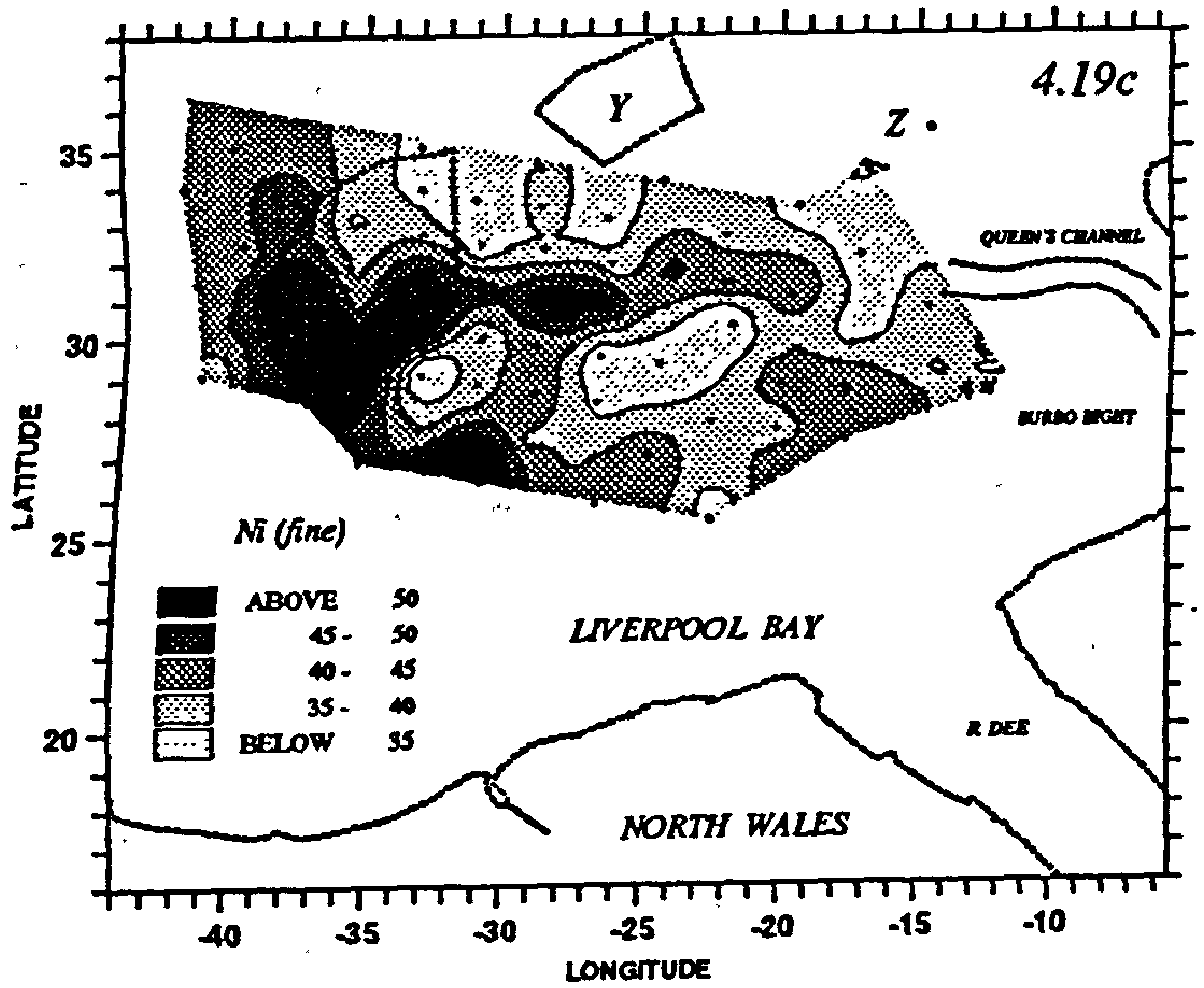
The distribution of copper in fine sediments shown in Figure 4.19a may suggest that the main source of this metal in sediments from Liverpool Bay is the discharges of sewage sludge at Site SI. This observation is consistent with reports of annual copper discharges in the bay from several sources (Norton *et al.*, 1984c; MAFF, 1987), and with previously reported copper distributions in fine sediments from this area (Norton *et al.*, 1984b).

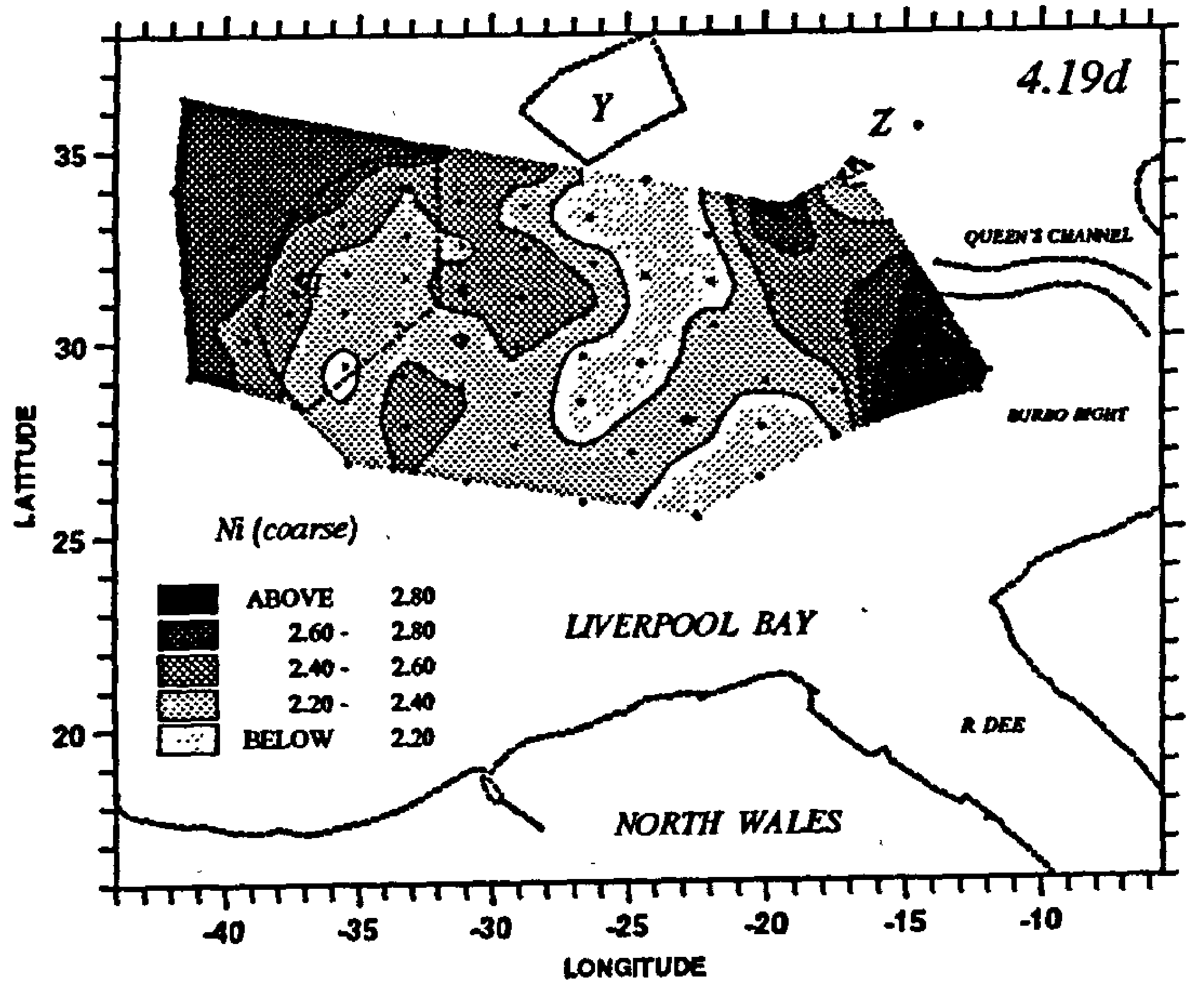
Although annual copper discharges from the River Mersey are reported to be similar to the discharges from sludge dumping (Norton *et al.*, 1984c; MAFF, 1987), the lack of copper enrichment in sediments near the Mersey may be related to the different speciation of copper in both sources. Whereas copper from the sewage sludge is probably largely associated to particles, copper from the Mersey may be largely in solution. Nimmo *et al.* (1989) and Norton *et al.* (1984c) reported dissolved copper in Liverpool Bay originating mainly from riverine inputs, as dissolved copper correlated (negatively) strongly with salinity even in samples near Site SI.

Fig.4.19. Distributions of copper in (a) fine sediments and (b) coarse sediments, and of nickel in (c) fine sediments and (d) coarse sediments. Concentration values are in μg g^{-1}.


4.19a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Cu (fine)
ABOVE 120
60 - 120
50 - 60
40 - 50
BELOW 40
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.19b
Y
Z
S1
QUEEN'S CHANNEL
BURBO BIGHT
Cu (coarse)
ABOVE 3.00
2.00 - 3.00
1.70 - 2.00
1.40 - 1.70
BELOW 1.40
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.19c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Ni (fine)
ABOVE 50
45 - 50
40 - 45
35 - 40
BELOW 35
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.19d
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Ni (coarse)
ABOVE 2.80
2.60 - 2.80
2.40 - 2.60
2.20 - 2.40
BELOW 2.20
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10

Furthermore, Nimmo *et al.* (1989) reported approximately 99% of dissolved copper in this area is mainly present as copper-organic complexes, and metal-organic complexes have a hydrophilic character which increases their solubility and mobilization from solid phases (Olsen *et al.*, 1982). This observation is consistent with reports of possible copper release from particles into solution during estuarine mixing (Salomons and Eysink, 1981) and with the considerable partitioning of copper observed in the liquid phase of estuarine systems such as the Rhine (Golimowsky *et al.*, 1990). Therefore, copper being transported form the Mersey river and estuary into the bay will tend to remain in solution and will not directly enrich the sediment particles in areas such as Burbo Bight.

The enrichment of copper inside and east of Site SI is due, in part, to the high levels of this metal in the sewage sludge (~649 $\mu g\ g^{-1}$) which is approximately 9 times higher than the mean value for the whole region (see Table 4.1 for comparison with other elements). After sewage is discharged, a large proportion of copper may remain associated to particles and deposited on the seabed. Norton *et al.* (1984c) observed no obvious effects of sludge dumping in the levels of dissolved copper around Site SI, this observation being consistent with reports of minimum effects of salinity on the association of copper with solid phases (Millward and Moore, 1982; Forstner, 1984) as opposed to elements such as cadmium which tend to desorb more readily from particles when they come into contact with saline water (see cadmium discussion in Section 4.2.3). On the other hand, it is important to consider that although considerable redissolution of copper may not take place immediately after sewage disposal, there is a report, from observations in laboratory, of 25% of copper from sewage solids being released after only four days in contact with seawater and also of copper remobilization from sediments as a result of degradation of the organic matter associated to these particles (Paulson *et al.*, 1991). Therefore, copper associated with particles both in bed sediments and in suspension may also represent an important source of dissolved copper in Liverpool Bay waters, but may not produce obvious local effects, as in the case of cadmium, due to a relatively slower desorption rate which is dependant upon the rate of organic matter degradation.

The possibility of specific associations of copper with a particular sedimentary phase in the fine fraction was difficult to establish as the correlations of the logarithm of copper with organic carbon ($r=0.623$), logarithm of iron ($r=0.705$) and logarithm of manganese ($r=0.645$) were all highly significant ($p<<0.001$) and similar.

An association of copper with the organic matter in fine sediments from Liverpool Bay is not unexpected, as the organic fraction of sediments and suspended particles in aquatic systems has

Table 4.1. Descriptive statistics[a] for the concentration[b] of elements in the fine fraction. Statistics for grain size descriptors and other sediment parameters, and the results for the analysis of a digested sewage sludge sample are also shown in this table.

	n	mean	sd	rsd	min	max	$\frac{max}{min}$	Sludge	slud mean
Hg	67	0.56	0.48	85.7	0.02	2.09	105	2.71	4.8
Cd	70	0.65	0.47	72.3	0.11	2.46	22.3	11.9	18.6
Cr	70	65	14	21.3	38	96	2.5	885	13.6
Cu	70	71	48	68.2	23	225	9.7	649	9.1
Ni	70	41	9.2	22.6	25	68	2.7	107	2.6
Pb	70	234	225	95.7	70	1214	17.2	689	2.9
Zn	70	280	127	45.0	135	904	6.7	1425	5.1
As	67	25.7	23.9	92.7	9.3	144	15.5	16.2	0.62
Mn	67	2549	3609	142	531	22900	43	642	0.25
Fe	67	2.18	0.63	28.9	1.36	4.54	3.3	1.98	0.91
C	69	2.03	0.39	19.2	1.24	3.05	2.5	27.8	13.7
N	38	0.25	0.07	30.8	0.13	0.45	3.5	2.06	8.2
C/N	38	8.46	1.89	22.3	6.12	14.6	2.4	12.9	nd
$\delta^{13}C$	69	-20.3	0.76	3.7	-22.3	-18.5	nd	-23.9	nd
Al	70	1.46	0.74	50.7	0.70	4.01	5.7	nd	nd
Fine	70	8.79	12.6	143	0.08	61.01	763	nd	nd
Coar	70	91.21	12.6	13.8	39.0	99.9	2.56	nd	nd

Note: [a] The statistical descriptives include: number of samples (n), mean concentration in sediments, standar deviation (sd), relative standar deviation (rsd), minimum, maximum, ratio between maximum and minimum, mean concentration in the sludge and the ratio between the concentration in the sludge and the mean concentration for the n sediment samples.

[b] The units of concentration for all the elements are μg g^{-1}, except for Fe which is in percent. The units for organic carbon and nitrogen are in percent whereas the $\delta^{13}C$ values are in ‰. The aluminium, fine fraction and coarse fraction are given as a percent of the total (<500 μm) sediments.

nd= not determined.

been widely reported as the dominant compartment of copper in the non-detrital fraction (e.g. Oakley *et al.*, 1981; Olsen *et al.*, 1982; Davies-Colley *et al.*, 1984; Hirata, 1985; Rosental *et al.*, 1986; Hall and Chang-Yen, 1989; Brook and Moore, 1988; Szefer, 1990); this metal is probably complexed with the organic matter (Rosental *et al.*, 1986) particularly with humic acids (Oakley *et al.*, 1981). Although the preference of copper for organic phases may be suggested by high Cu(II)-organic matter stability constants, the partitioning of copper (and other metals) in sediments will also depend on the abundance of each particular phase available for metal associations (Luoma and Davis, 1983). Therefore, as the possible association of copper with hydrous oxides of iron has also been established (Millward and Moore, 1982; Lion *et al.*, 1982; Davies-Colley *et al.*, 1984; Laxen, 1985; Tessier *et al.*, 1985), it is likely that copper in fine sediments in Liverpool Bay is partitioned amongst organic and iron phases. The overall trend of increasing copper concentrations as organic carbon and iron concentrations increase is represented in Figure 4.20a and b.

Although copper associations with manganese oxides may also occur (Olsen *et al.*, 1982; Feely *et al.*, 1983), the correlation between manganese and copper became non-significant when the samples with copper concentrations higher than 100 $\mu g\ g^{-1}$ were excluded from the correlation calculations. Therefore, for the majority of samples ($n=55$) there was no covariation between copper and manganese that could suggest an association of copper with manganese oxides.

A close analysis of the copper concentrations in some of the samples may provide a good example of the difficulty in determining with certainty the sources of metals in Liverpool Bay sediments. Figure 4.20c indicates that copper was negatively correlated with the amount of fine sediments in the total sample ($r=-0.543$, $p<0.001$), therefore, as in the case of iron, carbon, manganese and arsenic, the highest copper concentrations were found in samples with very small amount of fine fraction. For example, sample L-9 showing the highest manganese concentration (22,900 $\mu g\ g^{-1}$), also showed one of the highest copper concentrations (157 $\mu g\ g^{-1}$). Having established the possibility of sediments with high levels of manganese being derived from the mineralized areas in North Wales, and considering that copper concentrations higher than 60 $\mu g\ g^{-1}$ have been reported in sediments from the mineralized areas and the Conwy Estuary (Imperial College of Science and Technology, 1978), the possibility of copper in these samples being derived from "natural" sources is not unlikely (very high copper levels in the Anglesey coast, related to copper mining activities in Parys Mountain in the past, are also found in this report). Furthermore, other possible inputs of copper from North Wales have been suggested as Nimmo *et al.* (1989) found elevated concentrations in dissolved copper near the mid-North Wales coast

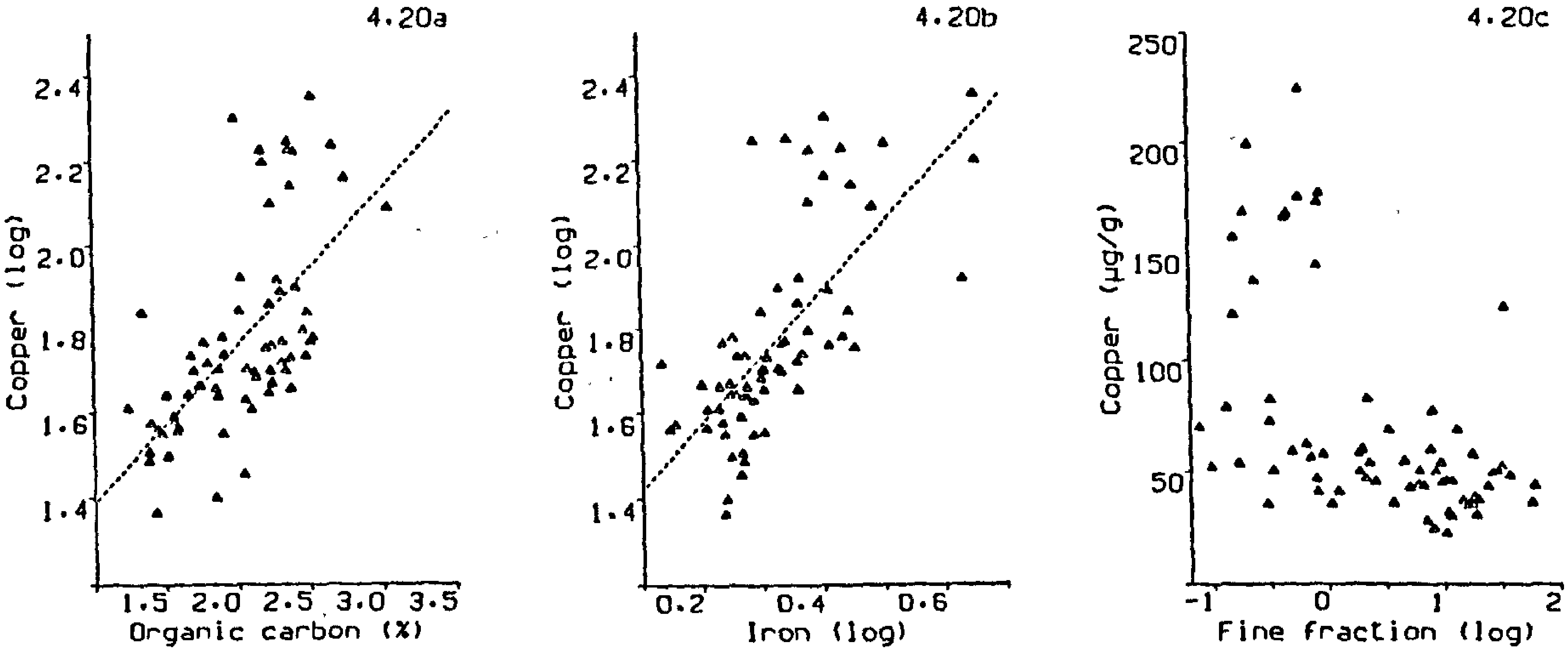


Fig.4.20. Scatter plots of (a) the logarithm of copper vs organic carbon in fine sediments, (b) the logarithm of copper vs the logarithm of iron in fine sediments and (c) copper in fine sediments vs the logarithm of fine fraction content.

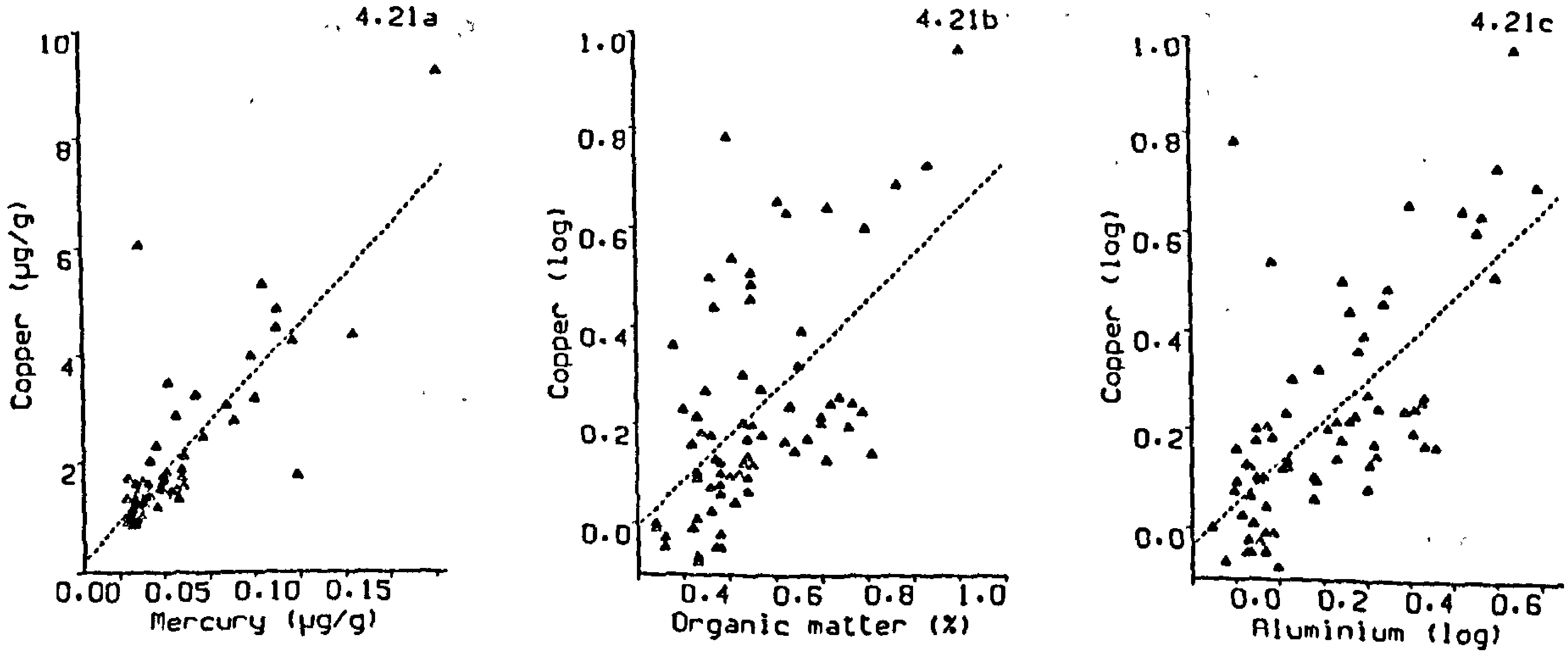


Fig.4.21. Scatter plots of (a) copper vs mercury in coarse sediments, (b) the logarithm of copper vs organic matter content and (c) the logarithm of copper in coarse sediments vs the logarithm of aluminium content.

coinciding with an increase in seston concentrations, these authors explained this phenomenon as a possible result of coastal quarry waste deposits in this region. Sample L-9 however, was within the possible immediate influence of sewage sludge discharges at Site SI and copper in this sample may have originated from sewage inputs rather than from natural sources (copper may also originate from both sources). This picture becomes more complex if samples K-8 and K-9 are considered. Although these samples were taken within a short distance and within the sector where recent sewage dumping takes place in the southern part of Site SI, they showed substantially different manganese (10200 and 622 $\mu g\ g^{-1}$ for K-8 and K-9 respectively) and $\delta^{13}C$ values (-19.73 and -21.49‰ respectively). Whereas the above average copper concentration at station K-9 (83 $\mu g\ g^{-1}$), together with the manganese and $\delta^{13}C$ values, point at the sewage sludge as the source of copper enrichment in this sediment, it is difficult to conclude beyond doubt that the copper enrichment in the nearby station K-8, showing a concentration of 121 $\mu g\ g^{-1}$, is due to the sewage discharges as the manganese and $\delta^{13}C$ values do not substantiate this possibility. The same observation as sample K-8 can be made in the case of sample L-9 showing a $\delta^{13}C$ value (-18.97‰), one of the highest in the whole region. It is also possible that (assuming that the high levels of manganese and iron in samples K-8 and L-9 are due to inputs from the mineralized areas) sediment particles with high content of iron/manganese oxyhydroxides collected copper from solution during transport in Liverpool Bay waters.

The distribution of copper in the present study was visually compared with the distributions presented by Norton *et al.* (1984a, see Fig. 16 in these authors report). From this comparison it was obvious that high copper concentrations around stations L-10, M-10 and N-10 seem to be a more or less permanent feature, therefore, it is possible that the high copper concentrations near the apex at Site SI are a result of "old" sewage discharges, prior to 1988. As sewage disposal activities were concentrated in the extreme south of this Site from early 1988, high values around the southern extreme section of Site SI may at least partially result from "recent" sewage discharges. From all the previous observations, it is obvious that more information is needed, particularly on the possible extent of influence of metal inputs from the mineralized areas in North Wales that, to date, have not been given any importance or have been simply overlooked in studies of metal levels in sediments from Liverpool Bay.

Another possible source of copper into sediments in Liverpool Bay that has not been studied and therefore reported is the contribution by phytoplankton debris. Although inputs from organic debris precipitation may not create localized effects ("hot spots") in copper distributions in the sediments, its signal may be superimposed to the that from other sources. Nimmo *et al.* (1989)

reported that the total dissolved copper levels in Liverpool Bay were around ten times higher than those observed in open oceans. From studies of metals in dissolved and particulate phases in the Dutch Rhine-Meuse delta, Golimowsky *et al.* (1990) reported that copper in solution was taken up to a great extent by phytoplankton. Hirata (1985) reported similar copper concentrations in particulate matter and coastal sediments (37 and 38 µg g^{-1} respectively) in Hiro Bay, Japan, and slightly higher concentrations in the phytoplankton (46 µg g^{-1}). Therefore, copper derived from phytoplankton debris may be an important source of total copper in the surface of sediments in Liverpool Bay, and these contributions may even overshadow the correlations between copper and organic carbon that could be expected from the review on reports mentioned earlier.

Finally, copper concentrations in fine sediments from Liverpool Bay were compared to "baseline" levels (representative of natural inputs) and "benchmark" levels (concentrations in fine sediments outside the direct influence of Site SI, mainly from the northern part of the eastern Irish Sea) reported by Rowlatt *et al.* (1984). As indicated by these authors, the benchmark value of ~27 µg g^{-1} suggests that sediments in eastern Irish Sea as a whole present some general level of contamination as compared to the baseline value of ~17 µg g^{-1}. However, there is an obvious copper enrichment in sediments from Liverpool Bay in particular, as the mean concentration for the whole region in the present study (~71 µg g^{-1}) was approximately 4.2 times above the baseline and 2.6 times above the benchmark values. The minimum copper concentration (~23 µg g^{-1}) was, as could be expected from the least influenced sediments, close to the benchmark value and around 1.4 times the baseline value, whereas the highest value (~225 µg g^{-1}) was 13 times above the baseline and 8.3 times above the benchmark values. Furthermore, even if samples with the highest copper levels (>90 µg g^{-1}) were not considered assuming that they originated from the mineralized areas, the overall mean would be approximately 50 µg g^{-1}, that is, 2.9 times the baseline value and 1.9 times the benchmark value. From these observations and previous reports (Rowlatt *et al.*, 1984; Norton *et al.*, 1984a; 1984b) it is concluded that the anthropogenic inputs of copper in Liverpool Bay, regardless of the specific sources and mechanisms of transport, have resulted in significant contamination of sediments in this region.

4.2.5.2. Copper in the coarse fraction

Copper in the coarse fraction (Fig. 4.19b) presented a distribution very similar to that of mercury (Fig. 4.11b). The mean concentration for the whole region was 1.99 µg g^{-1}. The highest values were recorded near the Mersey with a maximum of 9.25 µg g^{-1} at station YY-3 in the Burbo Bight; within the same area, station YY-4 presented a value of 3.96 µg g^{-1}. Copper concentrations decreased toward the west and south, to a region of values lower than 1.40 $\mu g\ g^{-1}$ in most of the stations labelled with numbers 6, 7 and 8. The lowest concentrations were recorded at stations K-8 and K-9 with values of 0.86 and 0.84 $\mu g\ g^{-1}$ respectively. Stations T-10 and U-11 immediately outside the Queen's Channel also showed low values (1.34 and 1.70 respectively) as was the case for most of the metals in this fraction which are described above. An enrichment area around station L-10 (6.03$\mu g\ g^{-1}$) in the dumping ground was also observed.

As suggested by the similarity in the distributions of copper and mercury shown in Figures 4.19b and 4.11b, there was a high correlation ($r=0.820$, $p<<0.001$) between these two metals in the coarse sediments in the present study. Therefore, the discussion regarding the possible sources and associations of mercury in this fraction also apply (in general) to copper and only a brief description of the copper correlations in these sediments will be given.

The only obvious difference in the distributions of mercury and copper was the presence of high values of copper around stations L-10 and M-10 (Fig. 4.19b) which were not present in the mercury distribution (Fig. 4.11b); on the other hand mercury showed a relative enrichment at station M-12 not present in the copper distribution (see outliers marked in Fig. 4.21a). High copper values in coarse sediments around stations L-10 and M-10 were also reported by Norton *et al.* (1984a; see Fig. 15 in this reference) and coincide with high levels in the fine fraction (see discussion above) probably as a result of a more or less stable sediment deposit with a strong influence of sewage sludge discharges prior to 1988, as already suggested in the discussion of the distribution of copper in fine sediments.

The lack of correlation with iron and manganese, and the significant correlation with the organic matter content ($r=0.567$, $p<0.001$) suggests that, as in the cases of all the metals previously discussed, the organic matter is the main carrier of copper in coarse sediments in Liverpool Bay. It should be noted, however, that the correlation of organic matter with copper (see also Fig. 4.21b) is lower than with any other of the previously discussed metals (see Table 4.2), in spite of the widely reported copper-organic matter association in sediments (e.g. Oakley *et al.*, 1981; Olsen *et al.*, 1982; Davies-Colley *et al.*, 1984; Hirata, 1985; Rosental *et al.*, 1986; Hall and Chang-Yen, 1989; Brook and Moore, 1988; Szefer, 1990). As suggested in the discussion of copper in fine sediments, it is possible that copper (and cadmium) correlations with the organic matter content in coarse sediments may be somewhat overshadowed by inputs of copper associated with organic matter from phytoplankton debris, combined with losses into solution of copper associated with land derived (mainly sewage derived) organic matter as the latter is degraded.

Table 4.2a. Correlation matrix for elements and sediment parameters in fine sediments. The coefficient is the Pearson's correlation coefficient, the number of data included in the calculation is in parenthesis and P represents the two-tailed significance level.

	Hg	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**As**	**Mn**	**Fe**	**$\delta^{13}C$**
Hg	1.0000 (67) P= .	.2720 (67) P= .026	.3098 (67) P= .011	-.2308 (67) P= .060	-.2184 (67) P= .076	-.3728 (67) P= .002	-.1029 (67) P= .407	-.3045 (67) P= .012	-.3932 (67) P= .001	-.1945 (67) P= .115	-.4503 (66) P= .000
Cd	.2720 (67) P= .026	1.0000 (70) P= .	.3979 (70) P= .001	.3478 (70) P= .003	.3466 (70) P= .003	.4552 (70) P= .000	.5712 (70) P= .000	.3026 (67) P= .013	.3008 (67) P= .013	.1864 (67) P= .131	-.2908 (69) P= .015
Cr	.3098 (67) P= .011	.3979 (70) P= .001	1.0000 (70) P= .	.2731 (70) P= .022	.4405 (70) P= .000	.3536 (70) P= .003	.5920 (70) P= .000	.3940 (67) P= .001	.2923 (67) P= .016	.5714 (67) P= .000	-.1879 (69) P= .122
Cu	-.2308 (67) P= .060	.3478 (70) P= .003	.2731 (70) P= .022	1.0000 (70) P= .	.3640 (70) P= .002	.5389 (70) P= .000	.5663 (70) P= .000	.4150 (67) P= .000	.6238 (67) P= .000	.4459 (67) P= .000	.0094 (69) P= .939
Ni	-.2184 (67) P= .076	.3466 (70) P= .003	.4405 (70) P= .000	.3640 (70) P= .002	1.0000 (70) P= .	.6896 (70) P= .000	.6945 (70) P= .000	.5250 (67) P= .000	.4944 (67) P= .000	.6585 (67) P= .000	.0198 (69) P= .872
Pb	-.3728 (67) P= .002	.4552 (70) P= .000	.3536 (70) P= .003	.5389 (70) P= .000	.6896 (70) P= .000	1.0000 (70) P= .	.8855 (70) P= .000	.8198 (67) P= .000	.8447 (67) P= .000	.6601 (67) P= .000	.1728 (69) P= .156
Zn	-.1029 (67) P= .407	.5712 (70) P= .000	.5920 (70) P= .000	.5663 (70) P= .000	.6945 (70) P= .000	.8855 (70) P= .000	1.0000 (70) P= .	.8527 (67) P= .000	.8428 (67) P= .000	.7539 (67) P= .000	.0618 (69) P= .614
As	-.3045 (67) P= .012	.3026 (67) P= .013	.3940 (67) P= .001	.4150 (67) P= .000	.5250 (67) P= .000	.8198 (67) P= .000	.8527 (67) P= .000	1.0000 (67) P= .	.8784 (67) P= .000	.8057 (67) P= .000	.2417 (66) P= .051
Mn	-.3932 (67) P= .001	.3008 (67) P= .013	.2923 (67) P= .016	.6238 (67) P= .000	.4944 (67) P= .000	.8447 (67) P= .000	.8428 (67) P= .000	.8784 (67) P= .000	1.0000 (67) P= .	.6381 (67) P= .000	.2725 (66) P= .027
Fe	-.1945 (67) P= .115	.1864 (67) P= .131	.5714 (67) P= .000	.4459 (67) P= .000	.6585 (67) P= .000	.6601 (67) P= .000	.7539 (67) P= .000	.8057 (67) P= .000	.6381 (67) P= .000	1.0000 (67) P= .	.2316 (66) P= .061
$\delta^{13}C$	-.4503 (66) P= .000	-.2908 (69) P= .015	-.1879 (69) P= .122	.0094 (69) P= .939	.0198 (69) P= .872	.1728 (69) P= .156	.0618 (69) P= .614	.2417 (66) P= .051	.2725 (66) P= .027	.2316 (66) P= .061	1.0000 (69) P= .
O.C.	-.2135 (66) P= .085	.2262 (69) P= .062	.5877 (69) P= .000	.4437 (69) P= .000	.5359 (69) P= .000	.4713 (69) P= .000	.5242 (69) P= .000	.4340 (66) P= .000	.4088 (66) P= .001	.5387 (66) P= .000	-.0931 (69) P= .447

Tab.4.2acont..(2)

N	-.3390 (36) P= .043	.0938 (38) P= .575	.5193 (38) P= .001	.2255 (38) P= .173	.6246 (38) P= .000	.5894 (38) P= .000	.5729 (38) P= .000	.4689 (36) P= .004	.4662 (36) P= .004	.5625 (36) P= .000	.3250 (38) P= .046
C/N	.1010 (36) P= .558	.1376 (38) P= .410	-.3013 (38) P= .066	.0997 (38) P= .552	-.3859 (38) P= .017	-.3990 (38) P= .013	-.3569 (38) P= .028	-.2826 (36) P= .095	-.2841 (36) P= .093	-.3156 (36) P= .061	-.5381 (38) P= .000
Al	.7435 (67) P= .000	.0708 (70) P= .560	.0550 (70) P= .651	-.2790 (70) P= .019	-.3594 (70) P= .002	-.4491 (70) P= .000	-.2601 (70) P= .030	-.3432 (67) P= .004	-.3888 (67) P= .001	-.2908 (67) P= .017	-.2544 (69) P= .035
>500	-.3854 (67) P= .001	-.1575 (70) P= .193	-.3023 (70) P= .011	.0762 (70) P= .531	-.0080 (70) P= .947	-.0289 (70) P= .812	-.1774 (70) P= .142	-.1300 (67) P= .294	-.0634 (67) P= .610	-.0538 (67) P= .666	.2158 (69) P= .075
Fine	.6591 (67) P= .000	.0758 (70) P= .533	.0485 (70) P= .690	-.2364 (70) P= .049	-.3029 (70) P= .011	-.3737 (70) P= .001	-.2199 (70) P= .067	-.2834 (67) P= .020	-.3196 (67) P= .008	-.2653 (67) P= .030	-.2631 (69) P= .029

	O.C.	**N**	**C/N**	**Al**	**>500**	**Fine**
Hg	-.2135 (66) P= .085	-.3390 (36) P= .043	.1010 (36) P= .558	.7435 (67) P= .000	-.3854 (67) P= .001	.6591 (67) P= .000
Cd	.2262 (69) P= .062	.0938 (38) P= .575	.1376 (38) P= .410	.0708 (70) P= .560	-.1575 (70) P= .193	.0758 (70) P= .533
Cr	.5877 (69) P= .000	.5193 (38) P= .001	-.3013 (38) P= .066	.0550 (70) P= .651	-.3023 (70) P= .011	.0485 (70) P= .690
Cu	.4437 (69) P= .000	.2255 (38) P= .173	.0997 (38) P= .552	-.2790 (70) P= .019	.0762 (70) P= .531	-.2364 (70) P= .049
Ni	.5359 (69) P= .000	.6246 (38) P= .000	-.3859 (38) P= .017	-.3594 (70) P= .002	-.0080 (70) P= .947	-.3029 (70) P= .011
Pb	.4713 (69) P= .000	.5894 (38) P= .000	-.3990 (38) P= .013	-.4491 (70) P= .000	-.0289 (70) P= .812	-.3737 (70) P= .001
Zn	.5242 (69) P= .000	.5729 (38) P= .000	-.3569 (38) P= .028	-.2601 (70) P= .030	-.1774 (70) P= .142	-.2199 (70) P= .067

Tab. 4.2a cont..(3)

As	-.4340 (66) P= .000	.4689 (36) P= .004	-.2826 (36) P= .095	-.3432 (67) P= .004	-.1300 (67) P= .294	-.2834 (67) P= .020
Mn	.4088 (66) P= .001	.4662 (36) P= .004	-.2841 (36) P= .093	-.3888 (67) P= .001	-.0634 (67) P= .610	-.3196 (67) P= .008
Fe	.5387 (66) P= .000	.5625 (36) P= .000	-.3156 (36) P= .061	-.2908 (67) P= .017	-.0538 (67) P= .666	-.2653 (67) P= .030
$\delta^{13}C$	-.0931 (69) P= .447	.3250 (38) P= .046	-.5381 (38) P= .000	-.2544 (69) P= .035	.2158 (69) P= .075	-.2631 (69) P= .029
O.C.	1.0000 (69) P= .	.8182 (38) P= .000	-.2265 (38) P= .171	-.3943 (69) P= .001	-.1515 (69) P= .214	-.3507 (69) P= .003
N	.8182 (38) P= .000	1.0000 (38) P= .	-.7234 (38) P= .000	-.4718 (38) P= .003	-.4805 (38) P= .002	-.4285 (38) P= .007
C/N	-.2265 (38) P= .171	-.7234 (38) P= .000	1.0000 (38) P= .	.1523 (38) P= .361	.3596 (38) P= .027	.1409 (38) P= .399
Al	-.3943 (69) P= .001	-.4718 (38) P= .003	.1523 (38) P= .361	1.0000 (70) P= .	-.1106 (70) P= .362	.9717 (70) P= .000
>500	-.1515 (69) P= .214	-.4805 (38) P= .002	.3596 (38) P= .027	-.1106 (70) P= .362	1.0000 (70) P= .	-.0955 (70) P= .432
Fine	-.3507 (69) P= .003	-.4285 (38) P= .007	.1409 (38) P= .399	.9717 (70) P= .000	-.0955 (70) P= .432	1.0000 (70) P= .

Table 4.2b. Correlation matrix for elements and sediment parameters in the fine fraction after logarithmic tranformation of all data. (see Table 4.3a for details).

	Hg	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**As**	**Mn**	**Fe**	**δ^{13}C**
Hg	1.0000 (67) P= .	.2492 (67) P= .042	.1441 (67) P= .245	-.3273 (67) P= .007	-.2872 (67) P= .018	-.5641 (67) P= .000	-.2388 (67) P= .052	-.5021 (67) P= .000	-.6946 (67) P= .000	-.2827 (67) P= .020	.3923 (66) P= .001
Cd	.2492 (67) P= .042	1.0000 (70) P= .	.4120 (70) P= .000	.2488 (70) P= .038	.2690 (70) P= .024	.2496 (70) P= .037	.4762 (70) P= .000	.3010 (67) P= .013	.2172 (67) P= .078	.1104 (67) P= .374	.3173 (69) P= .008
Cr	.1441 (67) P= .245	.4120 (70) P= .000	1.0000 (70) P= .	.2515 (70) P= .036	.5783 (70) P= .000	.4079 (70) P= .000	.6786 (70) P= .000	.4866 (67) P= .000	.3144 (67) P= .010	.6100 (67) P= .000	.1966 (69) P= .105
Cu	-.3273 (67) P= .007	.2488 (70) P= .038	.2515 (70) P= .036	1.0000 (70) P= .	.3405 (70) P= .004	.4465 (70) P= .000	.4909 (70) P= .000	.4040 (67) P= .001	.4896 (67) P= .000	.4433 (67) P= .000	-.0034 (69) P= .978
Ni	-.2872 (67) P= .018	.2690 (70) P= .024	.5783 (70) P= .000	.3405 (70) P= .004	1.0000 (70) P= .	.8111 (70) P= .000	.8173 (70) P= .000	.7273 (67) P= .000	.6454 (67) P= .000	.7046 (67) P= .000	.0127 (69) P= .918
Pb	-.5641 (67) P= .000	.2496 (70) P= .037	.4079 (70) P= .000	.4465 (70) P= .000	.8111 (70) P= .000	1.0000 (70) P= .	.8621 (70) P= .000	.8974 (67) P= .000	.8878 (67) P= .000	.6937 (67) P= .000	-.1551 (69) P= .203
Zn	-.2388 (67) P= .052	.4762 (70) P= .000	.6786 (70) P= .000	.4909 (70) P= .000	.8173 (70) P= .000	.8621 (70) P= .000	1.0000 (70) P= .	.8799 (67) P= .000	.7742 (67) P= .000	.7666 (67) P= .000	.0293 (69) P= .811
As	-.5021 (67) P= .000	.3010 (67) P= .013	.4866 (67) P= .000	.4040 (67) P= .001	.7273 (67) P= .000	.8974 (67) P= .000	.8799 (67) P= .000	1.0000 (67) P= .	.9156 (67) P= .000	.7902 (67) P= .000	-.0865 (66) P= .490
Mn	-.6946 (67) P= .000	.2172 (67) P= .078	.3144 (67) P= .010	.4896 (67) P= .000	.6454 (67) P= .000	.8878 (67) P= .000	.7742 (67) P= .000	.9156 (67) P= .000	1.0000 (67) P= .	.6201 (67) P= .000	-.1209 (66) P= .333
Fe	-.2827 (67) P= .020	.1104 (67) P= .374	.6100 (67) P= .000	.4433 (67) P= .000	.7046 (67) P= .000	.6937 (67) P= .000	.7666 (67) P= .000	.7902 (67) P= .000	.6201 (67) P= .000	1.0000 (67) P= .	-.2033 (66) P= .102
δ^{13}C	.3923 (66) P= .001	.3173 (69) P= .008	.1966 (69) P= .105	-.0034 (69) P= .978	.0127 (69) P= .918	-.1551 (69) P= .203	.0293 (69) P= .811	-.0865 (66) P= .490	-.1209 (66) P= .333	-.2033 (66) P= .102	1.0000 (69) P= .
O.C.	-.3914 (66) P= .001	.1917 (69) P= .114	.5834 (69) P= .000	.4459 (69) P= .000	.6098 (69) P= .000	.6079 (69) P= .000	.6181 (69) P= .000	.6187 (66) P= .000	.6185 (66) P= .000	.5831 (66) P= .000	.1235 (69) P= .312
N	-.4831 (36) P= .003	-.0280 (38) P= .867	.5670 (38) P= .000	.1874 (38) P= .260	.7556 (38) P= .000	.7825 (38) P= .000	.6994 (38) P= .000	.6322 (36) P= .000	.6678 (36) P= .000	.5981 (36) P= .000	-.2954 (38) P= .072

Tab. 4.2b cont...(2)

C/N	.2812 (36) P= .097	.2400 (38) P= .147	-.2967 (38) P= .070	.0943 (38) P= .573	-.5057 (38) P= .001	-.5597 (38) P= .000	-.4522 (38) P= .004	-.3393 (36) P= .043	-.3942 (36) P= .017	-.3306 (36) P= .049	.5654 (38) P= .000
Al	.7453 (67) P= .000	.0810 (70) P= .505	-.0077 (70) P= .950	-.3019 (70) P= .011	-.4683 (70) P= .000	-.6810 (70) P= .000	-.3749 (70) P= .001	-.5376 (67) P= .000	-.6572 (67) P= .000	-.3442 (67) P= .004	.2098 (69) P= .084
>500	-.3181 (67) P= .009	-.2863 (70) P= .016	-.3137 (70) P= .008	.1405 (70) P= .246	-.1049 (70) P= .387	-.0574 (70) P= .637	-.2628 (70) P= .028	-.2023 (67) P= .101	-.0844 (67) P= .497	-.1204 (67) P= .332	-.2125 (69) P= .080
Fine	.7694 (67) P= .000	-.0129 (70) P= .916	-.0615 (70) P= .613	-.3627 (70) P= .002	-.5430 (70) P= .000	-.8111 (70) P= .000	-.5259 (70) P= .000	-.6961 (67) P= .000	-.8126 (67) P= .000	-.4167 (67) P= .000	.2127 (69) P= .079

	O.C.	N	C/N	Al	>500	Fine
Hg	-.3914 (66) P= .001	-.4831 (36) P= .003	.2812 (36) P= .097	.7453 (67) P= .000	-.3181 (67) P= .009	.7694 (67) P= .000
Cd	.1917 (69) P= .114	-.0280 (38) P= .867	.2400 (38) P= .147	.0810 (70) P= .505	-.2863 (70) P= .016	-.0129 (70) P= .916
Cr	.5834 (69) P= .000	.5670 (38) P= .000	-.2967 (38) P= .070	-.0077 (70) P= .950	-.3137 (70) P= .008	-.0615 (70) P= .613
Cu	.4459 (69) P= .000	.1874 (38) P= .260	.0943 (38) P= .573	-.3019 (70) P= .011	.1405 (70) P= .246	-.3627 (70) P= .002
Ni	.6098 (69) P= .000	.7556 (38) P= .000	-.5057 (38) P= .001	-.4683 (70) P= .000	-.1049 (70) P= .387	-.5430 (70) P= .000
Pb	.6079 (69) P= .000	.7825 (38) P= .000	-.5597 (38) P= .000	-.6810 (70) P= .000	-.0574 (70) P= .637	-.8111 (70) P= .000
Zn	.6181 (69) P= .000	.6994 (38) P= .000	-.4522 (38) P= .004	-.3749 (70) P= .001	-.2628 (70) P= .028	-.5259 (70) P= .000
As	.6187 (66) P= .000	.6322 (36) P= .000	-.3393 (36) P= .043	-.5376 (67) P= .000	-.2023 (67) P= .101	-.6961 (67) P= .000
Mn	.6185 (66) P= .000	.6678 (36) P= .000	-.3942 (36) P= .017	-.6572 (67) P= .000	-.0844 (67) P= .497	-.8126 (67) P= .000

Tab.4.2b cont..(3)

Fe	.5831 (66) P= .000	.5981 (36) P= .000	-.3306 (36) P= .049	-.3442 (67) P= .004	-.1204 (67) P= .332	-.4167 (67) P= .000
$\delta^{13}C$	.1235 (69) P= .312	-.2954 (38) P= .072	.5654 (38) P= .000	.2098 (69) P= .084	-.2125 (69) P= .080	.2127 (69) P= .079
O.C.	1.0000 (69) P= .	.7857 (38) P= .000	-.2321 (38) P= .161	-.4747 (69) P= .000	-.1032 (69) P= .399	-.5087 (69) P= .000
N	.7857 (38) P= .000	1.0000 (38) P= .	-.7841 (38) P= .000	-.5517 (38) P= .000	-.3833 (38) P= .018	-.6822 (38) P= .000
C/N	-.2321 (38) P= .161	-.7841 (38) P= .000	1.0000 (38) P= .	.2851 (38) P= .083	.2711 (38) P= .100	.4583 (38) P= .004
Al	-.4747 (69) P= .000	-.5517 (38) P= .000	.2851 (38) P= .083	1.0000 (70) P= .	-.0983 (70) P= .418	.9305 (70) P= .000
>500	-.1032 (69) P= .399	-.3833 (38) P= .018	.2711 (38) P= .100	-.0983 (70) P= .418	1.0000 (70) P= .	.0136 (70) P= .911
Fine	-.5087 (69) P= .000	-.6822 (38) P= .000	.4583 (38) P= .004	.9305 (70) P= .000	.0136 (70) P= .911	1.0000 (70) P= .

Copper in coarse sediments was also highly correlated ($p<<0.001$) with the percentage of fines ($r=0.720$) and aluminium ($r=0.756$ after logarithmic transformations; see also Fig. 4.21c) in the total sediment, indicating that the amount of copper and other metals in coarse sediments is largely controlled by the amount of fines in the sediment sample.

4.2.6. Nickel

4.2.6.1. Nickel in the fine fraction

Nickel concentrations in fine sediments were irregularly distributed throughout the bay (Fig. 4.19c). There was no apparent general trend in the distribution of this metal with the exception of an obvious enrichment area, with values above 50 μg g^{-1}, in the southern section of the sewage dumping ground. The highest values recorded in this area were at stations J-9 (68 μg g^{-1}), K-8 (60 μg g^{-1}) and L-9 (68 μg g^{-1}). The mean concentration for all samples was 41 μg g^{-1} and the minimum value, 25 μg g^{-1}, was found at station L-8. In general, samples from the northeastern region of the sampling grid showed concentrations below the mean value with samples near Site Z showing concentrations lower than 33 μg g^{-1}. Samples from the Burbo Bight showed concentration values near or below the overall mean ranging from 33 μg g^{-1} (station YY-3) to 42 μg g^{-1} (station YY-2).

The distribution of nickel in fine sediments shown in Figure 4.19c suggests that the main source of enrichment of this metal in sediments from Liverpool Bay is from the discharges of sewage sludge in the southern part of Site SI. However, reports of annual metal discharges into the bay from several sources (Jones, 1978; Norton *et al.*, 1984c; MAFF, 1987) indicate that nickel inputs from sewage sludge discharges at Site SI are very low as compared with inputs from the Mersey and from discharges of dredged spoils at sites Z and Y. In fact, the concentration of nickel in the sewage sludge was 107 μg g^{-1}, that is 2.7 times the average concentration for the fine sediments in the whole region.

Although the enrichment of nickel in the south of Site SI is obvious (Fig. 4.19c), the range of values for this metal in the whole region was not as high as for other elements previously discussed with the exception of chromium. Table 4.1 shows that the relative standard deviation for nickel (21.3%) in fine sediments was, together with chromium (22.6%) very low, indicating that the distribution of these metals in the fine sediments was more homogeneous, the ratio between the highest and lowest concentrations was 2.5, as compared with mercury showing a ratio of 105 and copper showing a ratio of 9.7 (see Table 4.1). A more homogeneous distribution of nickel, as compared to other elements, may be related to its relatively lower levels in sewage sludge (see Table 4.1) and also to the lower affinity of nickel for particles as compared to other metals.

Balistrieri and Murray (1984), for example, reported the following affinity sequence for metal interactions with marine interfacial sediments: Pb>Fe>Mn>Cu>Zn>Ni>Cd (only the metals of interest in this thesis were taken from the original sequence reported). This sequence is consistent with the study of Tessier *et al.* (1985) in which binding strengths of several elements for iron oxides are reported. It is possible, therefore, that the relatively high values of nickel (also observed in the case of cadmium) in the south of Site SI represent only a very localized effect related to sewage disposal, but this effect is rapidly attenuated as fast desorption from the sediments takes place during the transport of these particles through the bay. Evidence of possible desorption of nickel from sewage sludge was reported by Nimmo *et al.* (1989) who found particularly high levels of colloidal inorganic nickel only near Site SI. High levels of dissolved nickel around the sewage disposal area were also reported by Norton *et al.* (1984c) who suggested that sludge dumping was only producing very local and patchy effects and of limited significance. Considering Liverpool Bay as a whole, however, the main inputs of dissolved nickel (Abdullah and Royle, 1973; Nimmo *et al.*, 1989; Norton *et al.*, 1984c) are those from the discharges of the Mersey river and estuary.

Although nickel inputs from the Mersey are much larger than the discharges from sludge dumping (Jones, 1978; Norton *et al.*, 1984c; MAFF, 1987), most of the nickel from the Mersey apparently remains in solution, therefore, an enrichment of the sediments near the Mersey (Fig. 4.19c) would not be expected. Even sediment particles transported out of the Mersey Estuary may lose some of the nickel into the aqueous phase before entering the bay as suggested by observations of possible nickel redissolution during estuarine mixing (Salomons and Eysink, 1981).

Nickel correlations with organic carbon (r=0.444), iron (r=0.446) and manganese (r=0.624) in the fine fraction were all significant ($p<0.001$) but relatively low. The low correlations of nickel with iron and organic matter may suggest that this element does not show a specific affinity for one particular sedimentary phase in the study area. Possible nickel associations with organic phases have been reported (Hirata, 1985; Rosental *et al.*, 1986) in marine sediments and also a possible specific association with iron oxides has been reported (Loring, 1981; Olsen *et al.*, 1982). There are also reports of similar distributions of nickel amongst oxide and organic phases (Tessier *et al.*, 1985; Brook and Moore, 1988) and of partitioning in various degrees onto iron oxides, manganese oxides and organic fractions (see literature review in Forstner and Patchineelam, 1981). Therefore, nickel in fine sediments from Liverpool Bay may be distributed amongst iron and organic phases in various degrees, probably depending to a large extent on the relative amount of each phase in each sample. The covariations of nickel with organic carbon and iron concentrations are represented in Figure 4.22a and b respectively.

Although nickel associations with manganese oxides may also occur (Suarez and Langmuir, 1976; Olsen *et al.*, 1982; Feely *et al.*, 1983; Jha *et al.*, 1990), the correlation between manganese and nickel became non-significant if the 9 samples with manganese concentrations higher than 5000 $\mu g\ g^{-1}$ were excluded from the correlation calculations. Therefore, for the majority of samples (n=58) there was not an apparent covariation between nickel and manganese that could suggest a possible association of nickel with manganese oxides. It was interesting to notice, however, that for samples with manganese concentrations above 2000 $\mu g\ g^{-1}$ a general trend of increasing nickel concentrations as manganese concentrations increased was observed (Fig. 4.22c). For example, samples from stations K-8, M-6 and L-9 showed the highest manganese concentrations (10200, 13700 and 22900 $\mu g\ g^{-1}$ respectively) and some of the highest nickel concentrations (60, 68 and 68 $\mu g\ g^{-1}$ respectively), whereas their corresponding $\delta^{13}C$ values (-19.73, -19.36 and -18.97 ‰) did not suggest high levels of sewage derived carbon. This observation may suggest that some of the nickel could derive from the mineralized areas of North Wales where nickel concentrations higher than 60 $\mu g\ g^{-1}$ have been reported in sediments (Imperial College of Science and Technology, 1978). It is of interest to note that Kiff (1984) reported relatively high nickel values around transect K (Site SI) and suggested that this nickel probably originated from North Wales. On the other hand, relatively high values of nickel were found at stations J-7 and J-9 (51 and 68 $\mu g\ g^{-1}$ respectively) which also showed very low $\delta^{13}C$ values (-22.30 and -22.02 ‰ respectively) indicating a possible strong influence from sewage discharges, however, whereas sample J-7 showed a low manganese concentration (756 $\mu g\ g^{-1}$), sample J-9 had a high concentration (5512 $\mu g\ g^{-1}$). The only obvious difference amongst samples J-7 and J-9 was the amount of fine fraction in the total sediment (6.02 and 0.16% respectively) and, as already discussed (see Fig. 4.9c and Section 4.1.4), manganese seems to be highly related ($r=-0.812$ after logarithmic transformation of both variables) to this parameter whereas in the case of nickel, the correlation with the amount of fine material in the sample was significant but low ($r=-0.401$, $p\approx0.001$, after logarithmic transformation of the percentage of fine fraction), but became non-significant when the 9 samples with highest manganese concentrations were excluded from the calculations.

Nickel concentrations in fine sediments from Liverpool Bay in the present study were comparable with previously reported concentration in this area (Norton *et al.*, 1984a, 1984b;

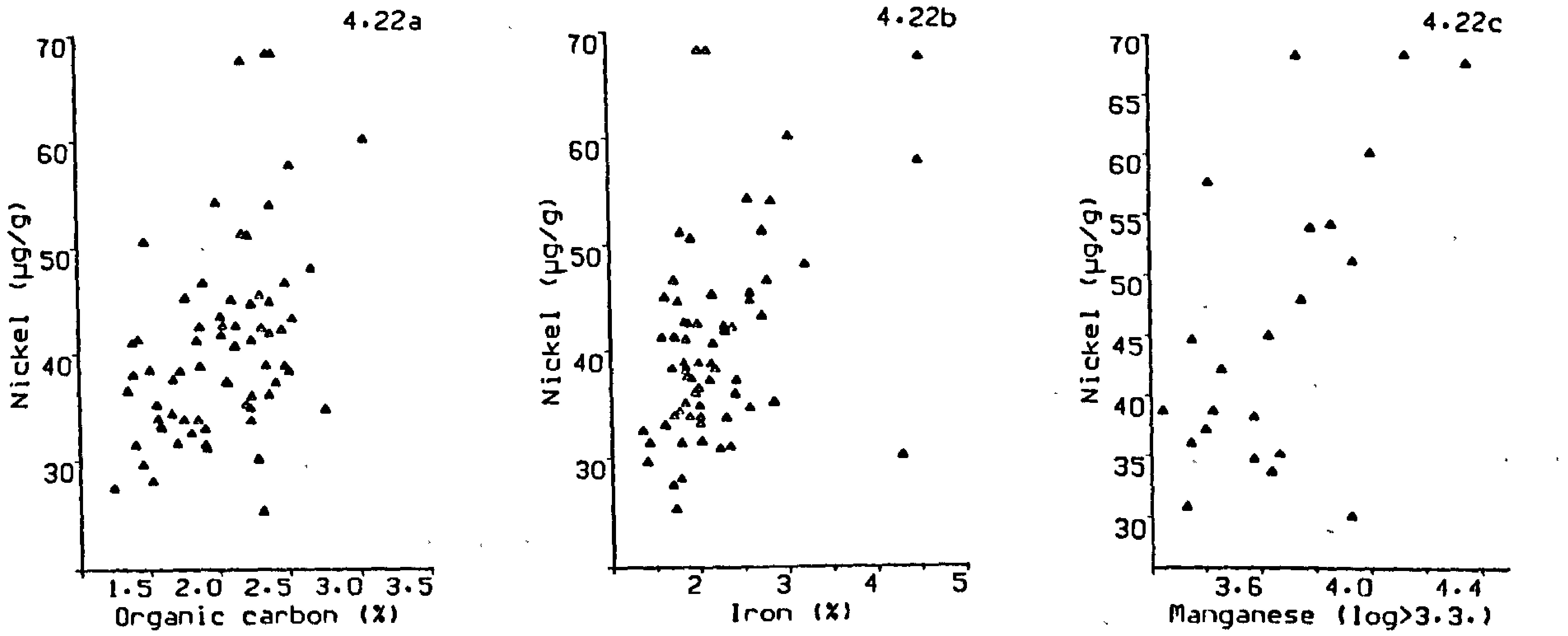


Fig.4.22. Scatter plots of nickel vs (a) organic carbon, (b) iron and (c) logarithm of manganese (only values higher than 3.3 are plotted; see text for explanation) in fine sediments.

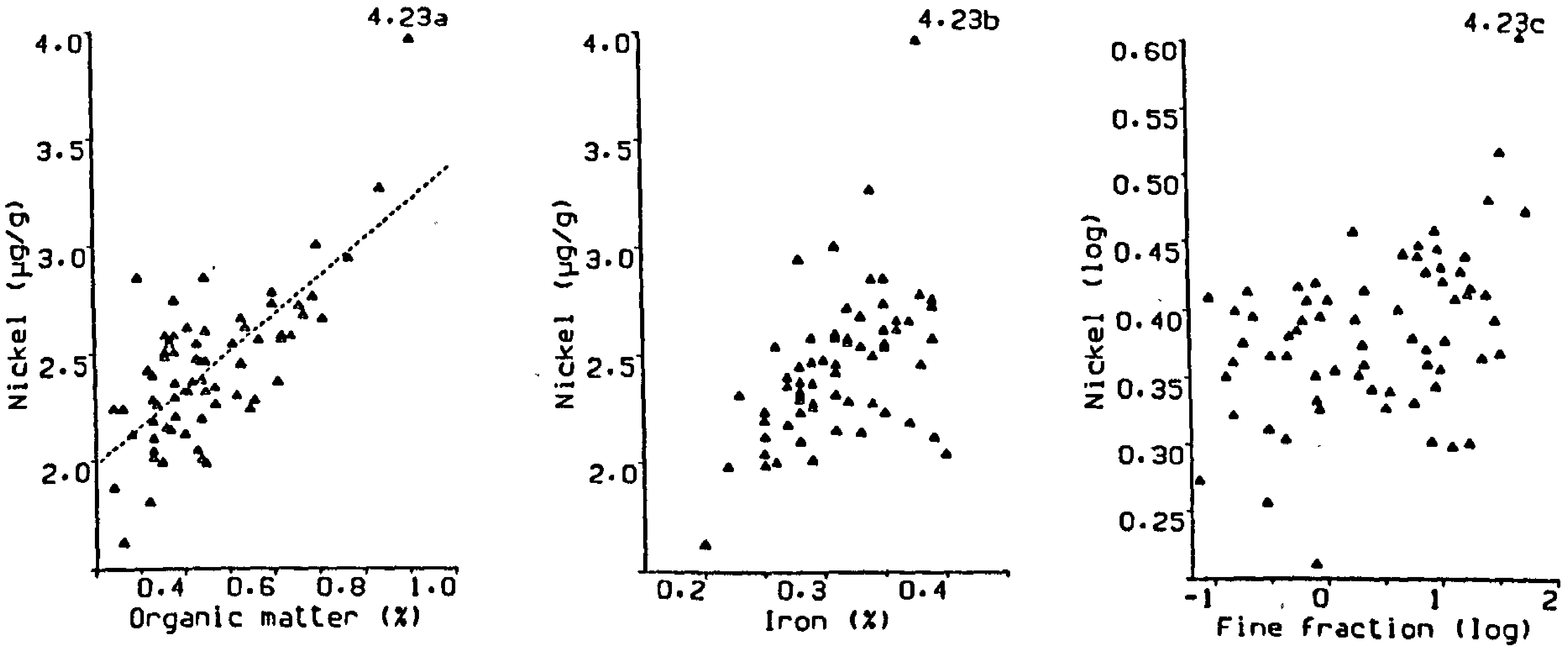


Fig.4.23. Scatter plots of (a) nickel vs organic matter in coarse sediments, (b) nickel vs iron in coarse sediments and (c) logarithm of nickel in coarse sediments vs logarithm of fine fraction content.

McLaren, 1987; Law *et al.*, 1989). As in the case of copper, nickel concentrations were compared with the baseline levels and benchmark levels reported by Rowlatt *et al.* (1984). The similarity between the baseline (27 µg g^{-1}) and benchmark (32 µg g^{-1}) values indicates that sediments in the eastern Irish Sea as a whole present a low level of contamination as compared to copper. ← A nickel enrichment in sediments from the Liverpool Bay area in particular was apparent, as the mean concentration for the whole sampling region in the present study (~40 µg g^{-1}) was approximately 1.5 times above the baseline and 1.3 times above the benchmark values. The minimum nickel concentration (~25 µg g^{-1}) was below but very close to the baseline value indicating that some sediments present natural levels of this metals, whereas the highest value (~68 µg g^{-1}) was 2.5 times above the baseline and 2.1 times above the benchmark values. From these observations and previous reports (Rowlatt *et al.*, 1984; Norton *et al.*, 1984a; 1984b) it is concluded that the anthropogenic inputs of nickel in Liverpool Bay, regardless of the specific sources, have not resulted in significant contamination of sediments in this region. The lack of nickel enrichment in fine sediments, however, does not mean that there is not contamination of Liverpool Bay due to human activities, but is probably reflecting the relatively low affinity of this element for particles as compared to other metals. Therefore, if studies of environmental impact of nickel in Liverpool Bay are designed, these studies should pay particular attention to nickel levels in solution.

4.2.6.2. Nickel in the coarse fraction

Figure 4.19d shows the distribution of nickel in the coarse sediments. Some similarities between this distribution, and the distribution of organic matter (Fig. 4.4c) can be observed. The highest values were found in samples from the Burbo Bight area, with a maximum concentration of 3.96 µg g^{-1} at station YY-3 whereas the lowest value in this area in particular was found at station YY-2 showing a concentration of 2.45 µg g^{-1}. Nickel values decreased away from the Burbo Bight, reaching a minimum at around transect P, where at station P-6 the lowest value (1.62 µg g^{-1}) for the whole region was observed. Nickel concentrations increased again towards the western region of the sampling area, reaching values between 2.60 and 2.80 µg g^{-1} in northern samples from transects G and H. The mean concentration value for all samples was 2.43 µg g^{-1}. Samples from the stations near Site Z (T-14 and U-15) showed concentrations below the overall mean with values of 2.18 and 2.12 µg g^{-1} respectively.

Nickel in the coarse fraction had a high correlation with the organic matter content ($r=0.718$, $p<<0.001$; see also Fig. 4.23a). This observation suggests that, as in the cases of mercury, McLaren, 1987; Law *et al.*, 1989). As in the case of copper, nickel concentrations were compared with the baseline levels and benchmark levels reported by Rowlatt *et al.* (1984). The similarity between the baseline (27 µg g^{-1}) and benchmark (32 µg g^{-1}) values indicates that sediments in the eastern Irish Sea as a whole present a low level of contamination as compared to copper. A nickel enrichment in sediments from the Liverpool Bay area in particular was apparent, as the mean concentration for the whole sampling region in the present study (~40 µg g^{-1}) was approximately 1.5 times above the baseline and 1.3 times above the benchmark values. The minimum nickel concentration (~25 µg g^{-1}) was below but very close to the baseline value indicating that some sediments present natural levels of this metals, whereas the highest value (~68 µg g^{-1}) was 2.5 times above the baseline and 2.1 times above the benchmark values. From these observations and previous reports (Rowlatt *et al.*, 1984; Norton *et al.*, 1984a; 1984b) it is concluded that the anthropogenic inputs of nickel in Liverpool Bay, regardless of the specific sources, have not resulted in significant contamination of sediments in this region. The lack of nickel enrichment in fine sediments, however, does not mean that there is not contamination of Liverpool Bay due to human activities, but is probably reflecting the relatively low affinity of this element for particles as compared to other metals. Therefore, if studies of environmental impact of nickel in Liverpool Bay are designed, these studies should pay particular attention to nickel levels in solution.

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Nickel in the coarse fraction had a high correlation with the organic matter content ($r=0.718$, $p<<0.001$; see also Fig. 4.23a). This observation suggests that, as in the cases of mercury, cadmium, chromium and copper, the organic matter in the coarse sediments represents the main carrier phase of nickel. As in the case of chromium in the coarse fraction, however, a significant correlation was also found between nickel and the iron concentrations ($r=0.510$, $p<0.001$; see also Fig. 4.23b) suggesting a that the hydrous iron oxides may be playing a significant role as nickel carriers in the coarse sediments, but are not as important as the organic matter. This observation is supported by an increase in the explained variance of nickel when iron was included as a second predictor in a multiple regression analysis; the resulting equation from this analysis was:

$$\mathrm{Ni}_{coarse} = 1.13 + 1.41\ \mathrm{O.M.} + 2.13\ \mathrm{Fe}_{coarse},\ (r^2=55\%,\ F=41.9).$$

In contrast to most of the previously discussed metals, nickel in coarse sediments did not show a significant correlation (after the exclusion of 4 samples with the highest nickel concentrations) with the amount of fine fraction in the total sediments. In the case of mercury, cadmium, chromium and copper, the significant correlation with the amount of fine fraction indicated that these metals in coarse sediments may be transferred from the fine sediments, therefore, the total amount of metal in the coarse particles would depend on the number of surrounding fine particles available for metal transfer. In the case of nickel, however, the lack of correlation with the amount of fine sediments (see Fig. 4.23c) indicates that amount of nickel in coarse particles is independent of the amount of coexisting fine particles and, therefore, the correlation with the organic matter content may indicate that nickel in coarse sediments is being adsorbed from solution probably in association with organic constituents. A second possibility is that if nickel in coarse sediments is being transferred from the fine particles, this effect is being overshadowed by re-dissolution from coarse sediment particles, this observation probably reflected in a more homogeneous distribution of nickel values in the coarse sediments throughout Liverpool Bay as indicated by a relatively low relative standard deviation (~14%) when compared to other elements (see Table 4.3).

4.2.7. Lead

4.2.7.1. Lead in the fine fraction

Lead in the fine fraction (Fig 4.24a) showed a similar distribution to those shown for arsenic (Fig. 4.11c), manganese (Fig. 4.7c) and iron (Fig. 4.7a). The highest concentrations were found at stations G-9, K-8, L-9 (maximum), M-10 and P-10 with values of 865, 698, 1214, 707 and 1000 $\mu g\ g^{-1}$ respectively. The mean concentration for the whole area was 234 $\mu g\ g^{-1}$. The northwestern region of low values showed concentrations below 100 $\mu g\ g^{-1}$ and a minimum of 70 $\mu g\ g^{-1}$ at station H-12. Low concentrations were also measured in samples T-12 (90 $\mu g\ g^{-1}$)

Table 4.3. Descriptive statistics[a] for the concentration[b] of elements in the coarse fraction. The statistical descriptors for the organic matter content in this fraction are also shown in the table.

	n	mean	sd	rsd	min	max	max/min	fine/coar
Hg	70	0.030	0.033	110	0.003	0.178	59	19.3
Cd	70	0.027	0.039	146	0.005	0.188	37.6	24.9
Cr	70	3.46	0.93	27	2.02	6.31	3.1	18.9
Cu	70	1.99	1.49	72	0.84	9.25	11.0	35.6
Ni	70	2.43	0.35	14	1.62	3.96	2.4	16.8
Pb	70	8.96	3.44	38	3.30	19.9	6.0	26.1
Zn	70	24.7	14.8	60	10.4	75	7.2	11.3
As	70	3.82	1.36	35	1.46	8.22	5.6	6.7
Mn	67	223	82	37	92	441	4.8	11.5
Fe	67	0.31	0.05	15	0.20	0.40	2.0	7.0
OM	70	0.46	0.14	30.4	0.24	0.91	3.8	8.4

Note: [a] The statistical descriptives include: number of samples (n), mean concentration in sediments, standar deviation (sd), relative standar deviation (rsd), minimum, maximum, ratio between maximum and minimum, and the ratio between the mean concentration in the fine fraction and the mean concentration in the coarse fraction.

[b] The units of concentration for all the elements are $\mu g\ g^{-1}$, except for Fe which is in percent. The units for the organic matter content are in percent.

Table 4.4a. Correlation matrix for elements and sediment parameters in the coarse fraction without data transformation. (see Table 4.2a for details).

	Hg	Cd	Cr	Cu	Ni	Pb	Zn	As	Mn	Fe	O.M.
Hg	1.0000 (70) P= .	.7691 (70) P= .000	.6146 (70) P= .000	.8198 (70) P= .000	.5362 (70) P= .000	.5260 (70) P= .000	.6818 (70) P= .000	.0611 (70) P= .615	.0419 (67) P= .736	.0474 (67) P= .703	.6417 (70) P= .000
Cd	.7691 (70) P= .000	1.0000 (70) P= .	.5809 (70) P= .000	.7972 (70) P= .000	.6159 (70) P= .000	.4326 (70) P= .000	.6865 (70) P= .000	.0732 (70) P= .547	.1715 (67) P= .165	.0410 (67) P= .742	.6163 (70) P= .000
Cr	.6146 (70) P= .000	.5809 (70) P= .000	1.0000 (70) P= .	.5519 (70) P= .000	.7318 (70) P= .000	.5358 (70) P= .000	.4434 (70) P= .000	.1801 (70) P= .136	-.0070 (67) P= .955	.4234 (67) P= .000	.8990 (70) P= .000
Cu	.8198 (70) P= .000	.7972 (70) P= .000	.5519 (70) P= .000	1.0000 (70) P= .	.5811 (70) P= .000	.5834 (70) P= .000	.6828 (70) P= .000	.0890 (70) P= .464	.1828 (67) P= .139	.0959 (67) P= .440	.5666 (70) P= .000
Ni	.5362 (70) P= .000	.6159 (70) P= .000	.7318 (70) P= .000	.5811 (70) P= .000	1.0000 (70) P= .	.3664 (70) P= .002	.3961 (70) P= .001	.1986 (70) P= .099	.2241 (67) P= .068	.5101 (67) P= .000	.7175 (70) P= .000
Pb	.5260 (70) P= .000	.4326 (70) P= .000	.5358 (70) P= .000	.5834 (70) P= .000	.3664 (70) P= .002	1.0000 (70) P= .	.7281 (70) P= .000	.5523 (70) P= .000	.4336 (67) P= .000	.4337 (67) P= .000	.4626 (70) P= .000
Zn	.6818 (70) P= .000	.6865 (70) P= .000	.4434 (70) P= .000	.6828 (70) P= .000	.3961 (70) P= .001	.7281 (70) P= .000	1.0000 (70) P= .	.4548 (70) P= .000	.5496 (67) P= .000	.2686 (67) P= .028	.4348 (70) P= .000
As	.0611 (70) P= .615	.0732 (70) P= .547	.1801 (70) P= .136	.0890 (70) P= .464	.1986 (70) P= .099	.5523 (70) P= .000	.4548 (70) P= .000	1.0000 (70) P= .	.7401 (67) P= .000	.7390 (67) P= .000	.1513 (70) P= .211
Mn	.0419 (67) P= .736	.1715 (67) P= .165	-.0070 (67) P= .955	.1828 (67) P= .139	.2241 (67) P= .068	.4336 (67) P= .000	.5496 (67) P= .000	.7401 (67) P= .000	1.0000 (67) P= .	.5263 (67) P= .000	.0758 (67) P= .542
Fe	.0474 (67) P= .703	.0410 (67) P= .742	.4234 (67) P= .000	.0959 (67) P= .440	.5101 (67) P= .000	.4337 (67) P= .000	.2686 (67) P= .028	.7390 (67) P= .000	.5263 (67) P= .000	1.0000 (67) P= .	.3679 (67) P= .002
O.M.	.6417 (70) P= .000	.6163 (70) P= .000	.8990 (70) P= .000	.5666 (70) P= .000	.7175 (70) P= .000	.4626 (70) P= .000	.4348 (70) P= .000	.1513 (70) P= .211	.0758 (67) P= .542	.3679 (67) P= .002	1.0000 (70) P= .
Al	.8053 (70) P= .000	.7852 (70) P= .000	.6985 (70) P= .000	.6925 (70) P= .000	.5215 (70) P= .000	.3978 (70) P= .001	.5041 (70) P= .000	-.0794 (70) P= .514	-.1233 (67) P= .320	-.0481 (67) P= .699	.7343 (70) P= .000
>500	-.2249 (70) P= .061	-.3319 (70) P= .005	.2228 (70) P= .064	-.1576 (70) P= .193	.1536 (70) P= .204	-.1221 (70) P= .314	-.5557 (70) P= .000	-.2391 (70) P= .046	-.3694 (67) P= .002	.1287 (67) P= .299	.1821 (70) P= .131

Tab. 4.4a cont..(2)

Fine	.8004 (70) P= .000	.8151 (70) P= .000	.7007 (70) P= .000	.7196 (70) P= .000	.5775 (70) P= .000	.3708 (70) P= .002	.4902 (70) P= .000	-.0514 (70) P= .673	-.0678 (67) P= .586	-.0023 (67) P= .985	.7524 (70) P= .000

	Al	**>500**	**Fine**	**Coarse**
Hg	.8053 (70) P= .000	-.2249 (70) P= .061	.8004 (70) P= .000	-.8004 (70) P= .000
Cd	.7852 (70) P= .000	-.3319 (70) P= .005	.8151 (70) P= .000	-.8151 (70) P= .000
Cr	.6985 (70) P= .000	.2228 (70) P= .064	.7007 (70) P= .000	-.7007 (70) P= .000
Cu	.6925 (70) P= .000	-.1576 (70) P= .193	.7196 (70) P= .000	-.7196 (70) P= .000
Ni	.5215 (70) P= .000	.1536 (70) P= .204	.5775 (70) P= .000	-.5775 (70) P= .000
Pb	.3978 (70) P= .001	-.1221 (70) P= .314	.3708 (70) P= .002	-.3708 (70) P= .002
Zn	.5041 (70) P= .000	-.5557 (70) P= .000	.4902 (70) P= .000	-.4902 (70) P= .000
As	-.0794 (70) P= .514	-.2391 (70) P= .046	-.0514 (70) P= .673	.0514 (70) P= .673
Mn	-.1233 (67) P= .320	-.3694 (67) P= .002	-.0678 (67) P= .586	.0678 (67) P= .586
Fe	-.0481 (67) P= .699	.1287 (67) P= .299	-.0023 (67) P= .985	.0023 (67) P= .985
O.M.	.7343 (70) P= .000	.1821 (70) P= .131	.7524 (70) P= .000	-.7524 (70) P= .000

Tab. 4.4a cont..(3)

```
Al             1.0000      -.1106       .9717      -.9717
              (   70)     (   70)     (   70)     (   70)
              P= .        P= .362     P= .000     P= .000

>500           -.1106      1.0000      -.0955       .0955
              (   70)     (   70)     (   70)     (   70)
              P= .362     P= .        P= .432     P= .432

Fine            .9717      -.0955      1.0000     -1.0000
              (   70)     (   70)     (   70)     (   70)
              P= .000     P= .432     P= .        P= .000

Coarse         -.9717       .0955     -1.0000      1.0000
              (   70)     (   70)     (   70)     (   70)
              P= .000     P= .432     P= .000     P= .
```

Table 4.4b. Correlation matrix for elements and sediment parameters in the coarse fraction after logarithmic data transformation. (see Table 4.2a for details).

	Hg	Cd	Cr	Cu	Ni	Pb	Zn	As	Mn	Fe	O.M.
Hg	1.0000 (70) P= .	.7238 (70) P= .000	.7046 (70) P= .000	.7884 (70) P= .000	.3821 (70) P= .001	.6673 (70) P= .000	.5924 (70) P= .000	.0902 (70) P= .458	-.1503 (67) P= .225	.0140 (67) P= .911	.6663 (70) P= .000
Cd	.7238 (70) P= .000	1.0000 (70) P= .	.5644 (70) P= .000	.7632 (70) P= .000	.4818 (70) P= .000	.4357 (70) P= .000	.6340 (70) P= .000	.0916 (70) P= .451	.0312 (67) P= .802	.0128 (67) P= .918	.5059 (70) P= .000
Cr	.7046 (70) P= .000	.5644 (70) P= .000	1.0000 (70) P= .	.5750 (70) P= .000	.7124 (70) P= .000	.5982 (70) P= .000	.3487 (70) P= .003	.2377 (70) P= .048	-.0250 (67) P= .841	.4338 (67) P= .000	.8857 (70) P= .000
Cu	.7884 (70) P= .000	.7632 (70) P= .000	.5750 (70) P= .000	1.0000 (70) P= .	.4877 (70) P= .000	.6667 (70) P= .000	.6730 (70) P= .000	.1512 (70) P= .212	.1391 (67) P= .262	.1028 (67) P= .408	.5561 (70) P= .000
Ni	.3821 (70) P= .001	.4818 (70) P= .000	.7124 (70) P= .000	.4877 (70) P= .000	1.0000 (70) P= .	.3835 (70) P= .001	.3019 (70) P= .011	.2717 (70) P= .023	.2448 (67) P= .046	.5565 (67) P= .000	.6748 (70) P= .000
Pb	.6673 (70) P= .000	.4357 (70) P= .000	.5982 (70) P= .000	.6667 (70) P= .000	.3835 (70) P= .001	1.0000 (70) P= .	.7336 (70) P= .000	.5820 (70) P= .000	.3996 (67) P= .001	.4538 (67) P= .000	.5267 (70) P= .000
Zn	.5924 (70) P= .000	.6340 (70) P= .000	.3487 (70) P= .003	.6730 (70) P= .000	.3019 (70) P= .011	.7336 (70) P= .000	1.0000 (70) P= .	.5582 (70) P= .000	.5397 (67) P= .000	.2935 (67) P= .016	.3212 (70) P= .007
As	.0902 (70) P= .458	.0916 (70) P= .451	.2377 (70) P= .048	.1512 (70) P= .212	.2717 (70) P= .023	.5820 (70) P= .000	.5582 (70) P= .000	1.0000 (70) P= .	.6899 (67) P= .000	.7433 (67) P= .000	.1765 (70) P= .144
Mn	-.1503 (67) P= .225	.0312 (67) P= .802	-.0250 (67) P= .841	.1391 (67) P= .262	.2448 (67) P= .046	.3996 (67) P= .001	.5397 (67) P= .000	.6899 (67) P= .000	1.0000 (67) P= .	.5350 (67) P= .000	.0462 (67) P= .710
Fe	.0140 (67) P= .911	.0128 (67) P= .918	.4338 (67) P= .000	.1028 (67) P= .408	.5565 (67) P= .000	.4538 (67) P= .000	.2935 (67) P= .016	.7433 (67) P= .000	.5350 (67) P= .000	1.0000 (67) P= .	.3985 (67) P= .001
O.M.	.6663 (70) P= .000	.5059 (70) P= .000	.8857 (70) P= .000	.5561 (70) P= .000	.6748 (70) P= .000	.5267 (70) P= .000	.3212 (70) P= .007	.1765 (70) P= .144	.0462 (67) P= .710	.3985 (67) P= .001	1.0000 (70) P= .
Al	.8530 (70) P= .000	.7778 (70) P= .000	.7174 (70) P= .000	.6948 (70) P= .000	.4597 (70) P= .000	.4401 (70) P= .000	.4178 (70) P= .000	-.0534 (70) P= .660	-.2552 (67) P= .037	-.0417 (67) P= .738	.7207 (70) P= .000
>500	-.2201 (70) P= .067	-.3970 (70) P= .001	.1097 (70) P= .366	-.2477 (70) P= .039	.1371 (70) P= .258	-.2594 (70) P= .030	-.7206 (70) P= .000	-.3247 (70) P= .006	-.3650 (67) P= .002	-.0102 (67) P= .935	.0951 (70) P= .433

Tab. 4.4b cont..(2)

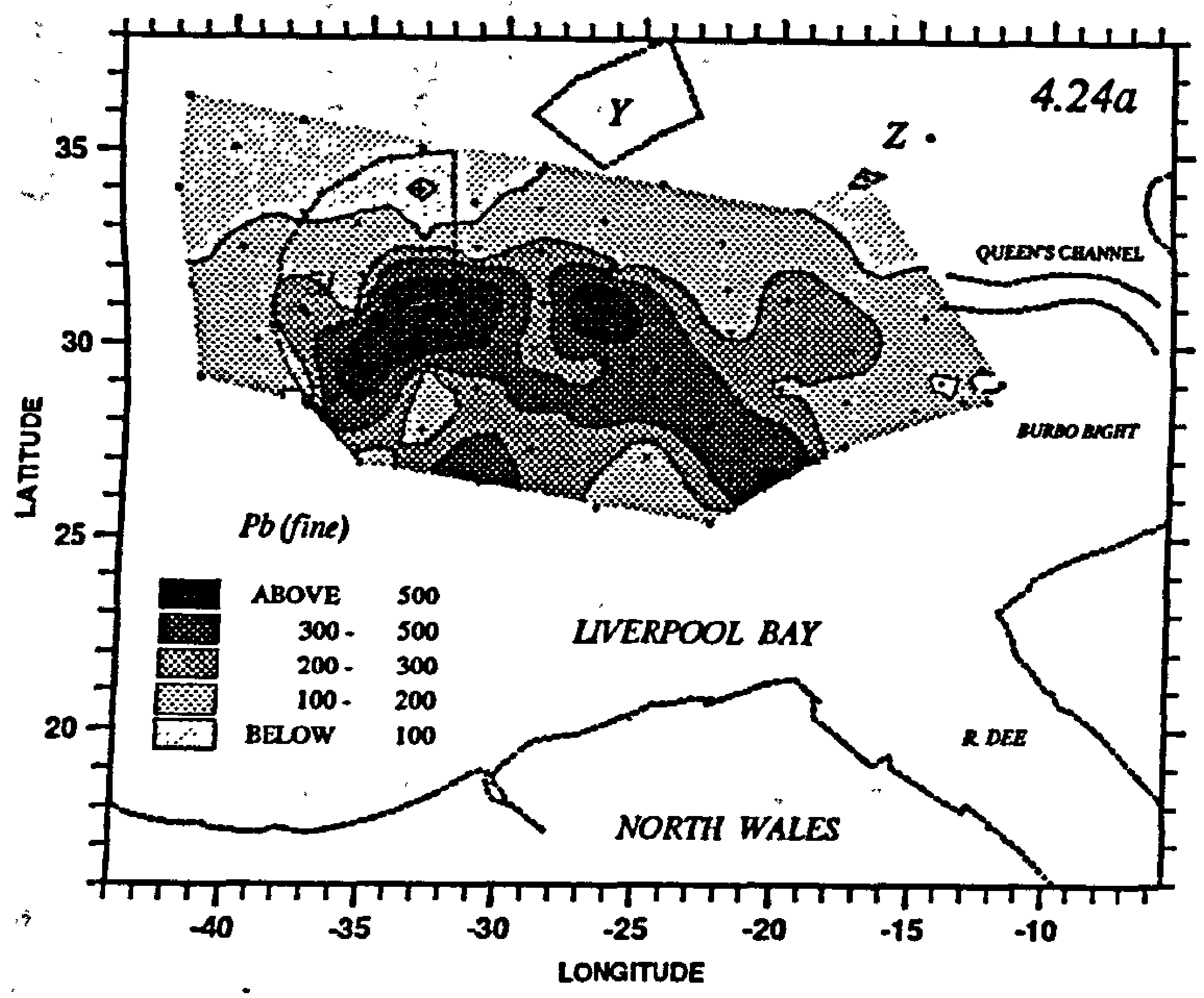
Fine	.8217 (70) P= .000	.6612 (70) P= .000	.7340 (70) P= .000	.6085 (70) P= .000	.4381 (70) P= .000	.4683 (70) P= .000	.3297 (70) P= .005	.0074 (70) P= .952	-.3138 (67) P= .010	.0146 (67) P= .906	.7188 (70) P= .000
Coarse	-.6908 (70) P= .000	-.7468 (70) P= .000	-.6255 (70) P= .000	-.6820 (70) P= .000	-.5351 (70) P= .000	-.3727 (70) P= .001	-.4467 (70) P= .000	-.0110 (70) P= .928	.0376 (67) P= .763	-.0145 (67) P= .908	-.6595 (70) P= .000

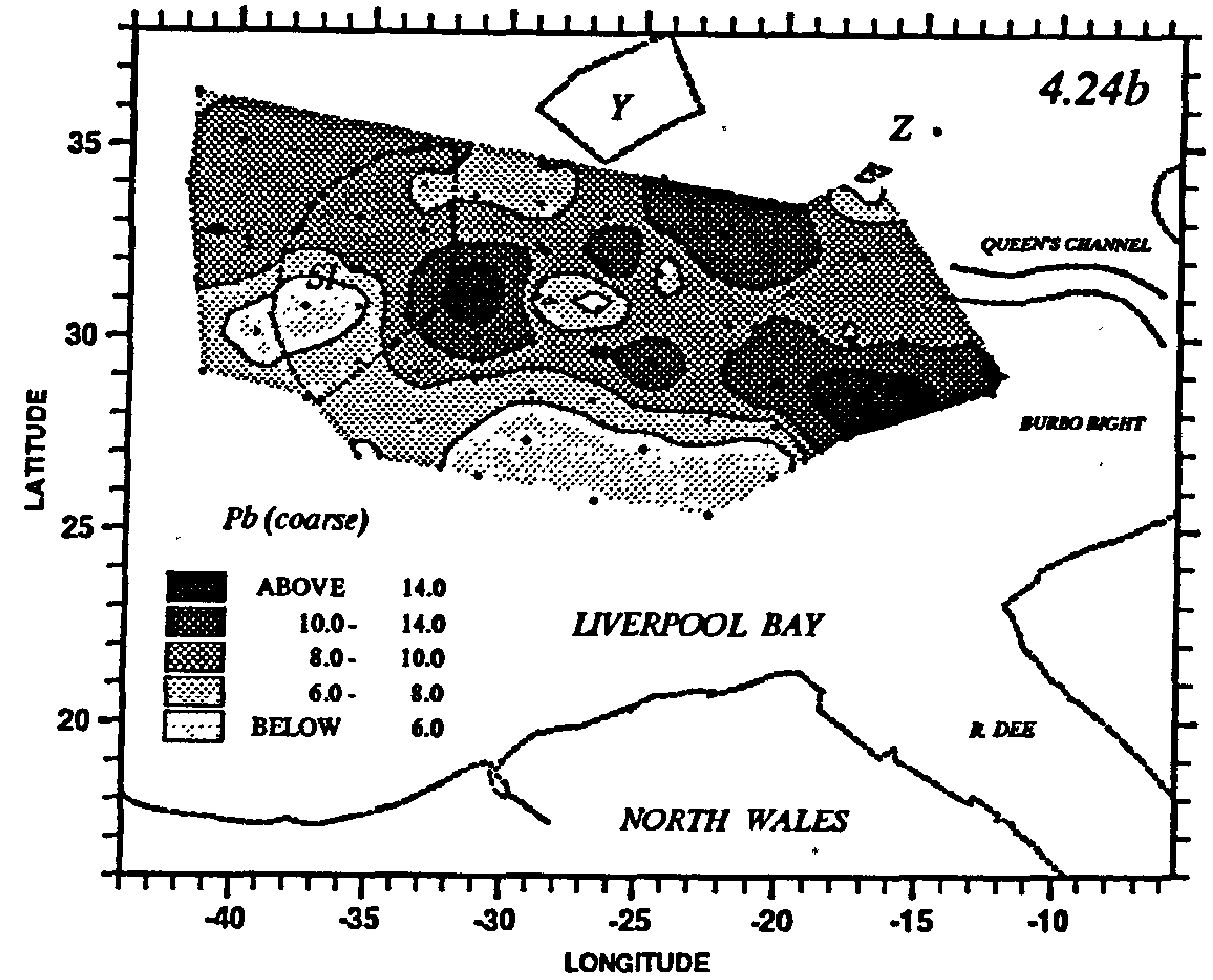
	Al	**>500**	**Fine**	**Coarse**
Hg	.8530 (70) P= .000	-.2201 (70) P= .067	.8217 (70) P= .000	-.6908 (70) P= .000
Cd	.7778 (70) P= .000	-.3970 (70) P= .001	.6612 (70) P= .000	-.7468 (70) P= .000
Cr	.7174 (70) P= .000	.1097 (70) P= .366	.7340 (70) P= .000	-.6255 (70) P= .000
Cu	.6948 (70) P= .000	-.2477 (70) P= .039	.6085 (70) P= .000	-.6820 (70) P= .000
Ni	.4597 (70) P= .000	.1371 (70) P= .258	.4381 (70) P= .000	-.5351 (70) P= .000
Pb	.4401 (70) P= .000	-.2594 (70) P= .030	.4683 (70) P= .000	-.3727 (70) P= .001
Zn	.4178 (70) P= .000	-.7206 (70) P= .000	.3297 (70) P= .005	-.4467 (70) P= .000
As	-.0534 (70) P= .660	-.3247 (70) P= .006	.0074 (70) P= .952	-.0110 (70) P= .928
Mn	-.2552 (67) P= .037	-.3650 (67) P= .002	-.3138 (67) P= .010	.0376 (67) P= .763
Fe	-.0417 (67) P= .738	-.0102 (67) P= .935	.0146 (67) P= .906	-.0145 (67) P= .908

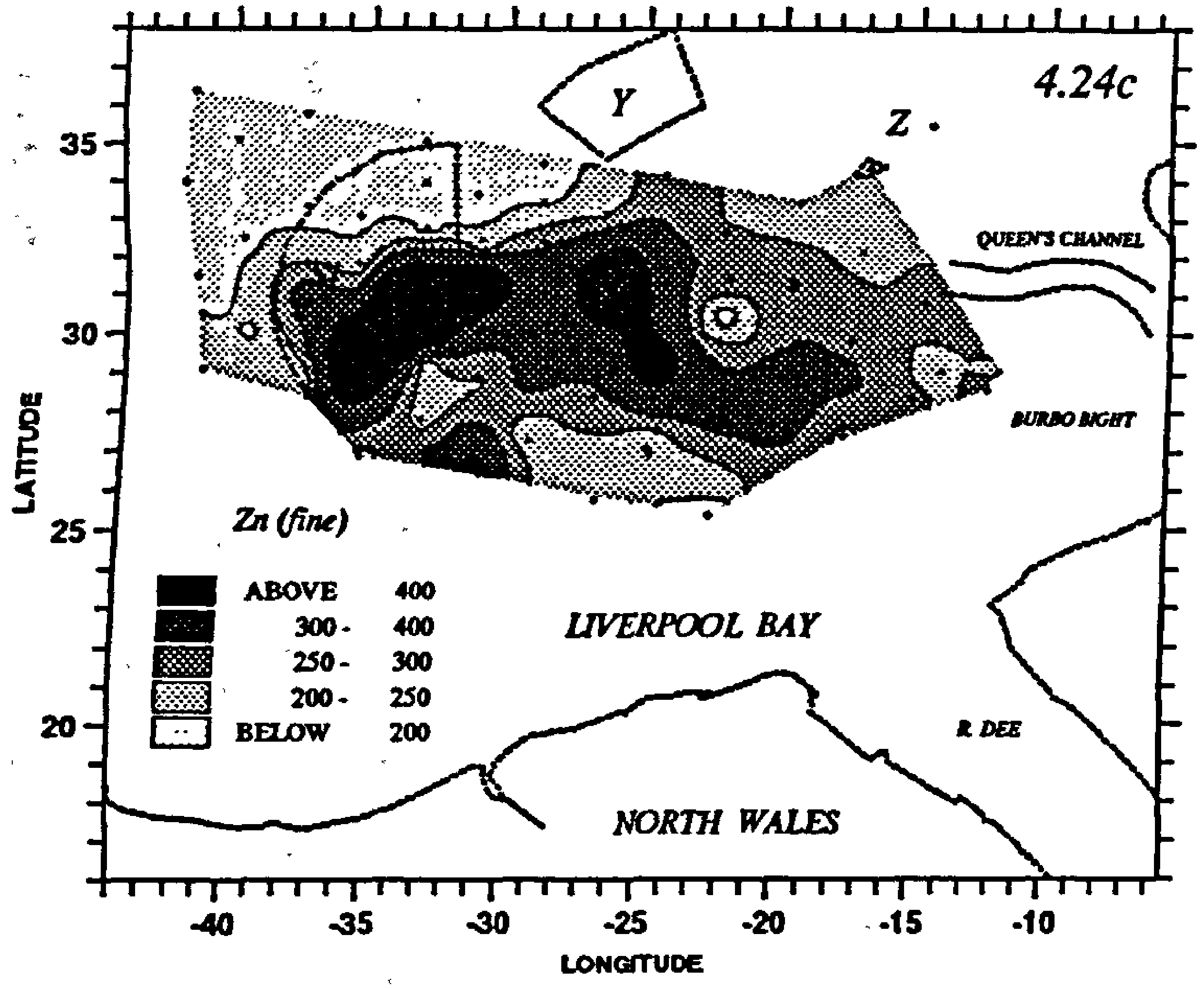
Tab. 4.4b cont..(3)

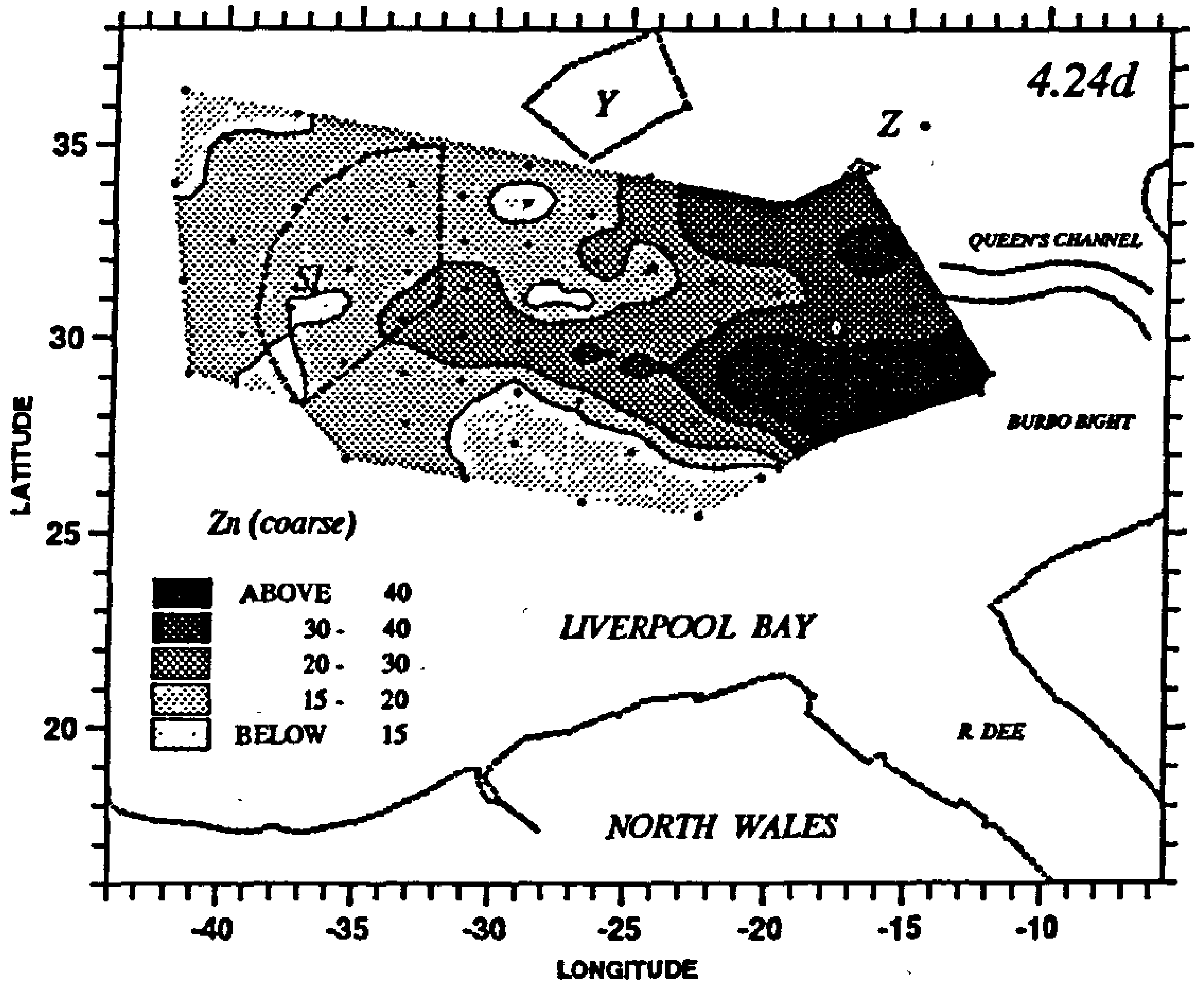
```
O.M.            .7207       .0951       .7188      -.6595
             (    70)    (    70)    (    70)    (    70)
             P=  .000    P=  .433    P=  .000    P=  .000

Al             1.0000     -.0983       .9305      -.8477
             (    70)    (    70)    (    70)    (    70)
             P=  .       P=  .418    P=  .000    P=  .000

>500           -.0983     1.0000       .0136       .1472
             (    70)    (    70)    (    70)    (    70)
             P=  .418    P=  .       P=  .911    P=  .224

Fine            .9305      .0136      1.0000      -.7033
             (    70)    (    70)    (    70)    (    70)
             P=  .000    P=  .911    P=  .       P=  .000

Coarse         -.8477      .1472      -.7033      1.0000
             (    70)    (    70)    (    70)    (    70)
             P=  .000    P=  .224    P=  .000    P=  .
```

Fig.4.24. Distributions of lead in (a) fine sediments and (b) coarse sediments, and of zinc in (c) fine sediments and (d) coarse sediments. Concentration values are in µg g^{-1}.


4.24a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Pb (fine)
ABOVE 500
300 - 500
200 - 300
100 - 200
BELOW 100
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.24b
Y
Z
S1
QUEEN'S CHANNEL
BURBO BIGHT
Pb (coarse)
ABOVE 14.0
10.0 - 14.0
8.0 - 10.0
6.0 - 8.0
BELOW 6.0
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.24c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Zn (fine)
ABOVE 400
300 - 400
250 - 300
200 - 250
BELOW 200
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10


4.24d
Y
Z
S1
QUEEN'S CHANNEL
BURBO BIGHT
Zn (coarse)
ABOVE 40
30 - 40
20 - 30
15 - 20
BELOW 15
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
-40
-35
-30
-25
-20
-15
-10

and T-14 (89.3 $\mu g\ g^{-1}$) near Site Z. Lead concentrations in the fine sediments from the Burbo Bight were considerably lower than the overall mean with the highest value in sample YY-2 (127 $\mu g\ g^{-1}$) and the lowest value in sample YY-3 (82 $\mu g\ g^{-1}$).

The similarity of the distribution of lead with the distributions of arsenic, manganese and iron in fine sediments is reflected in good correlations between lead and arsenic (r=0.898), manganese (r=0.888) and iron (r=0.694) after logarithmic transformation of all variables. From Figure 4.25a it could be suggested that arsenic and lead probably have similar sources, as well as similar geochemical associations in the sediment. Regarding the possible geochemical associations in the sediments, a similarity between these two elements is suggested by the correlations of lead with manganese (see Fig. 4.25b) and iron (see Fig. 4.25c), which indicate a possible specific association of lead with the hydrous iron/manganese oxides in fine sediments; the possible association of arsenic with these oxides has already been discussed (see Section 4.2.2). As already indicated by the correlation coefficient, a large percentage of the variance of lead could be predicted by variations in the manganese concentrations through the equation:

$\textbf{log-Pb}_{fine} = \textbf{0.101} + \textbf{0.670 log-Mn}_{fine},$ (r^2=78.5%, F=242; see also Fig. 4.25b).

A preferential association of lead with hydrous iron/manganese oxides in fine sediments from Liverpool Bay is very likely as this association has been widely reported for several types of aquatic particles and soils (Forstner and Patchineelam, 1981; Loring, 1981; Warren, 1981; Lion *et al.*, 1982; Sakata, 1985; Kersten *et al.*, 1988; Prosi, 1989; Jha *et al.*, 1990). It is important, to mention, however, that a highly significant correlation (r=0.623, p<<0.001) was obtained between the logarithm of lead concentration and the organic carbon concentration in the fine fraction. Although lead correlations with manganese and iron were higher, indicating that the variations of lead concentrations could be better explained by variations in manganese and iron concentrations which in turn could suggest a preference of lead for oxide coatings, associations of lead with organic coatings in the same sediments can also occur (Kemp *et al.*, 1976; Warren, 1981; Hirata, 1985; Brook and Moore, 1988; Hall and Chang-Yen, 1989).

Whether the correlation between lead and organic carbon reflects a chemical association or it is only a result of a covariance between these two variables as a result of the grain size composition of the samples is difficult to assess. As in the cases of iron, manganese and organic carbon, lead showed a significant negative correlation with the amount of fine sediments in the samples (r=-0.811 for the logarithm of both variables; see also Fig. 4.25d), indicating that lead was also particularly enriched in sediments with lower amount of fine particles. This trend is particulary emphasized when aluminium is used as an indicator of the amount of fine particles

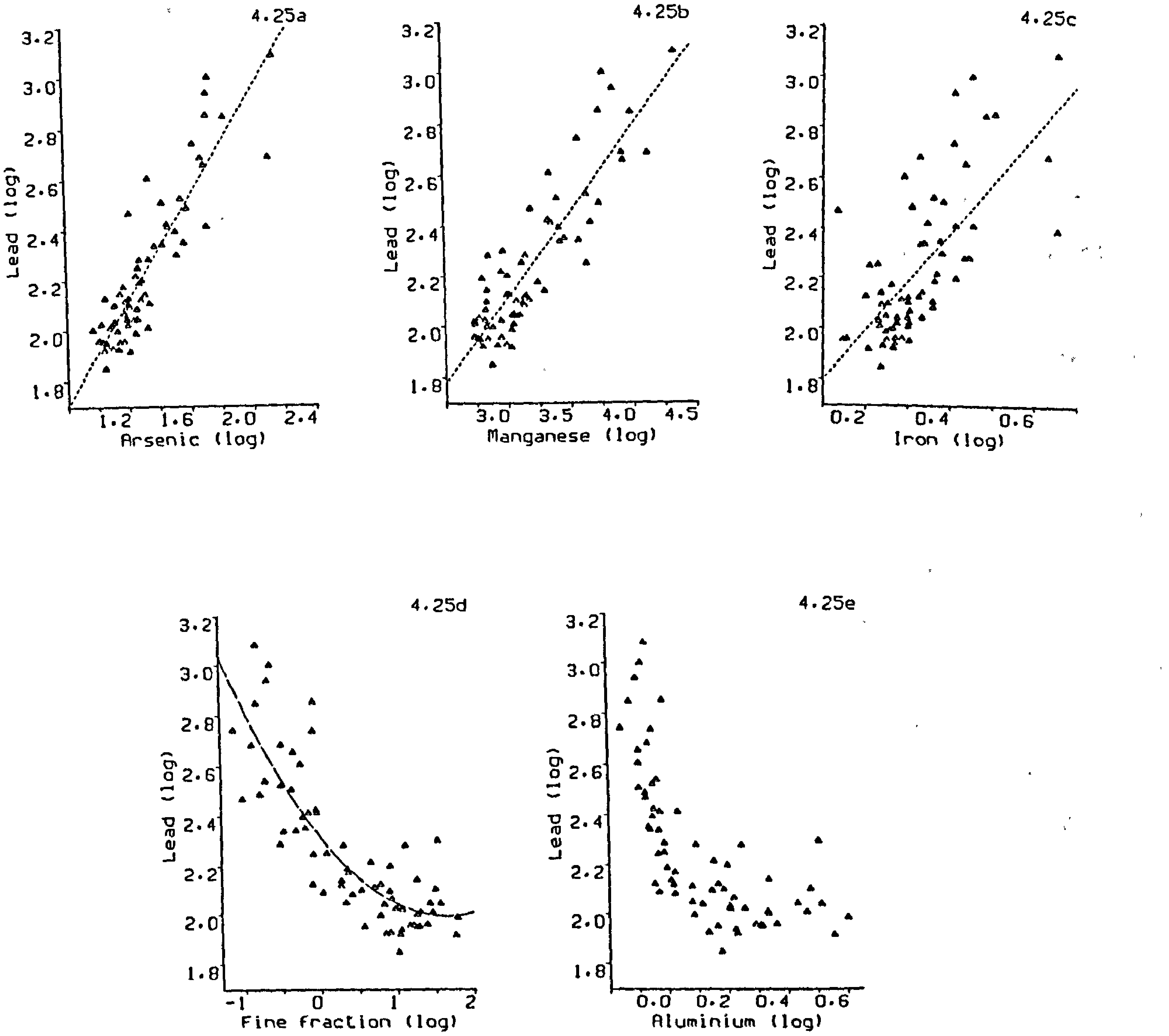


Fig.4.25. Scatter plots of the logarithm of lead in fine sediments vs (a) logarithm of arsenic, (b) logarithm of manganese, (c) logarithm of iron, (d) logarithm of fine fraction content and (e) the logarithm of aluminium content.

in the total sediment samples (see Fig. 4.25e). The possibility of having higher available surface areas in sediments with lower amounts of fine fraction has already been discussed (see Section 4.1.2), and Figure 4.25e indicates a sharp increase in lead concentrations as aluminium decreases, particularly from aluminium concentrations lower than ~1.5% (equivalent to approximately 5% of fine fraction; see Fig. 4.3). From these observations, it seems that the available surface area has an strong effect on the concentrations of lead (also on manganese, iron and organic carbon), and this effect becomes more significant in samples with a percentage of fine fraction lower than 5% (see also Fig. 4.25d).

Regarding the possible sources of lead in the fine fraction, the similarity between the distribution of this element and the distribution of arsenic (Fig. 4.25a) would probably suggest that both elements originate from the same source(s). As in the case of arsenic, lead could be derived from the mineralized areas of North Wales, as the mining activities that took place in the region were related to the extraction of two principal ore minerals (Elderfield *et al.*,1971): sphalerite (ZnS) and galena (PbS). Not surprisingly, very high concentrations of lead and zinc, together with other elements related to sphalerite and galena ores (such as arsenic and manganese), have been reported in sediments from tributaries, the main stream and the estuary of the River Conwy which drains mineralized areas in North Wales (Elderfield *et al.*, 1971; Imperial College of Science and Technology, 1978; Elderfield *et al.*, 1979). Elderfield *et al.* (1971) reported a concentration range for lead in sediments <85 μm in the Conwy Estuary between 85 and 600 μg g^{-1} with an average of 250 μg g^{-1}, and a range for zinc between 300 and 2000 μg g^{-1} with an average of 900 μg g^{-1}. These authors suggested that higher concentrations of these metals may be found after periods of flooding when more material from the mineral deposits may be washed into the streams and carried into the estuary. Considering that the average lead concentration in the present study was 234 μg g^{-1} and that the highest values (up to ~1200 μg g^{-1}) were found together with high concentrations of arsenic, manganese, iron and other elements, all of these exceeding the concentrations in sewage sludge (the concentration of lead in the analysed sewage sample was 689 μg g^{-1}), inputs of these elements from the mineralized areas seems to be a reasonable explanation, particularly in sediment samples where "anomalous" high concentrations were measured. Furthermore, Norton *et al.* (1984a) reported lead concentrations in fine sediments from Liverpool Bay exceeding the average concentrations in sludge particles and suggested that an "additional" source of inorganic lead may have been present. These authors concluded that it was not possible to tell whether this was due to a transient increase in sludge lead concentrations or to the dumping of an industrial waste contaminated with high concentrations of lead. Most of the high values in Norton *et al.* (1984a) study occurred to the south of Site SI (see Fig. 19; 1980 survey) where probably very low concentration of fine fraction were observed (where the probability of deposition of dumped wastes is lower according to these authors and previous studies already discussed in Chapter 2) and closer to possible influence from material derived from the North Wales coast, therefore, an alternative explanation to the high concentrations found in these authors report could be inputs from the mineralized areas in North Wales. In the report by Norton *et al.* (1984a), during the 1980 survey in which particularly high concentrations of lead occurred, zinc (see Fig 17 in these authors report) presented a relatively similar enrichments at the same stations as lead.

In contrast to arsenic, iron and manganese, however, the inputs of lead from sewage dumping in Liverpool Bay at Site SI are significant. This observation is hardly surprising as domestic wastes mix in the sewage system with water from runoff in streets, which may collect large amounts of lead originating from petrol combustion (Prosi, 1989). These observations, together with the reported very high affinity of lead towards particles (Ballistrieri and Murray, 1984), may explain the high concentrations of lead in sewage sludges (689 $\mu g\ g^{-1}$ in the sludge analysed in this study). As compared to mercury, cadmium and nickel, large amounts of lead are discharged annually into the bay via sewage sludge dumping (see Table 2.3), and although the quantities of copper, chromium and zinc annually discharged are higher than those of lead, these differences are not reflected in the fine sediment concentrations as lead values are similar to those of zinc, and higher than those of copper and chromium (see Table 4.1) and figures 4.24a, 4.24c, 4.19a and 4.17c).

The concentration of lead in the sludge was approximately 2.9 times the mean concentration for the sediments in the whole bay as compared to values lower than 1 for iron, manganese and arsenic (see Table 4.1). When the relationship between lead and manganese (Fig. 4.25b) was analysed in more detail, it was observed that the strong correlation between these variables was emphasized by samples with high lead and manganese contents. Data were split in two sets, one including samples with manganese concentration higher than 2000 $\mu g\ g^{-1}$ and the other one samples with concentrations lower than this value. The corresponding correlation coefficients between lead and manganese (in logarithmic scale) were 0.711 and 0.441 respectively, this observation indicating that although in both cases the correlations were significant which probably underlines the possible lead-manganese associations, the association seems to be more significant in samples with very high concentrations of manganese which are probably the most influenced by the inputs from mineralized areas. Sediments with manganese concentrations in the fine fraction lower than 2000 µg g^{-1} correspond to those with a percentage of fine fraction higher than 1% (see Fig. 4.9c). Therefore, lead concentrations in sediments with the lowest amounts of fine fraction (lower than 1%) may be more directly associated to inputs from mineralized areas whereas sediments with higher amounts of fines, where deposition of sludge derived particles is more likely (see Chapter 2), are more affected by sewage-derived lead. This observation is probably reflected in the apparent loss on the trend of decreasing lead concentrations as the amount of fine fraction increases observed in samples with values higher than 1% (0 in logarithmic scale) in Figure 4.25d.

Lead concentrations in the fine sediments were compared with the baseline and benchmark values reported for this metal by Rowlatt *et al.* (1984). The reported benchmark value (60 µg g^{-1}) was three times above the baseline value (20 µg g^{-1}) indicating and overall contamination of the eastern Irish Sea sediments without considering Liverpool Bay. The average concentration in the present study (234 µg g^{-1}) was 11.7 times above the baseline and 3.9 times above the benchmark values, whereas the minimum and maximum values (70 and 1214 µg g^{-1}) were 3.5 and 60.7 times above the baseline value, and 1.1 and 20.2 times above the benchmark value. From these observations it can be concluded that fine sediments in Liverpool Bay are considerably contaminated with lead, as a result of high inputs via sewage sludge disposal and due to the high tendency of this metal to associate with sediments. The high overall mean concentration of lead may be, in part, caused by inputs from the mineralized areas in North Wales, however, even if the highest values were excluded, a mean concentration of approximately 135 µg g^{-1} (median value in Table 4.1) could be expected which is 6.8 times above the baseline and 2.5 times above the benchmark values.

4.2.7.2. Lead in the coarse fraction

Figure 4.24b shows the distribution of lead in the coarse sediments. Low values were found in samples from the southern region with concentrations lower than 8.0 µg g^{-1} and several samples with values lower than 6.0 µg g^{-1}. The minimum concentration value (3.3 µg g^{-1}) was found in samples R-6 and S-7. Station T-14 in Site Z also had a low value (5.3 µg g^{-1}). The average concentration value for the whole region was 9.0 µg g^{-1}. An area of high concentrations similar to that shown for copper (Fig. 4.19b) was found near Site SI around stations L-9, L-10, M-9, M-11, N-9 with values above the mean and a maximum of 19.9 µg g^{-1} at station M-9. High concentrations were also found in a line at stations S-9 (14.2 µg g^{-1}), T-8 (13.9 µg g^{-1}), T-9 (17.2

μg g^{-1}) and U-9 (17.7 μg g^{-1}). Samples from the Burbo Bight showed a range of concentrations above the mean from 9.4 μg g^{-1} (station YY-2) to 15.9 μg g^{-1} (station YY-3).

The distribution of lead (Fig. 4.24b) in the coarse sediments from Liverpool Bay was partially similar to the distribution of copper (Fig. 4.19b), particularly regarding the area of low concentrations in the south and the area of high values at the apex of Site SI. However, lead did not show a gradient of increasing concentrations towards the Mersey as obvious as that shown in the distribution of copper (also present in the distributions of mercury, cadmium and zinc). This observation indicates that lead concentrations in the coarse fraction are not as affected by the inputs from the Mersey as the concentrations of mercury, cadmium and zinc.

The concentration of lead in coarse sediments did not seem to be as strongly affected as other metals by the amount of fine fraction in the samples, as indicated by a low correlation between the logarithm of lead and the logarithm of the percentage of fine sediments (r=0.469, see also Fig. 4.26a). When aluminium was used as an indicator of the amount of fine fraction in the sediments (r=0.440, Fig. 4.26b), the lack of dependence on the amount of fine sediments of the lead concentrations in coarse sediments became more obvious. Also in contrast with all the metals previously discussed, the correlation between lead and the organic matter in coarse sediments was relatively low (r=0.527 after logarithmic transformation of both variables, see also Fig. 4.26c). Low but significant correlations were observed between lead and manganese concentrations (r=0.434), and lead and iron concentrations (r=0.454 after logarithmic transformation of both variables, see also Fig. 4.26d).

A strong affinity of lead towards sediment particles in general (Ballistrieri and Murray, 1984) and strong binding strengths of this metal with hydrous iron/manganese oxides in particular (Tessier *et al.*, 1985) have been reported. Therefore, the low correlations between lead and the amount of fine material in the total sediments may indicate a lower transfer (as compared to other metals) of this metal from fine sediment particles towards coarse particles as a consequence of a strong association of lead to the fine sediments in Liverpool Bay.

The low correlations of lead with organic matter, iron and manganese may be due to a lack of a specific association of lead with one particular sedimentary phase in the coarse particles, in contrast to a possible preference of lead for association with iron/manganese oxides in the fine particles previously discussed in this Section. For example, Figure 4.26b indicates that some of the samples with low amounts of fine fraction showed high concentrations of lead in the coarse fraction. As discussed in Section 4.1.3 (see Fig. 4.5e), the organic matter content in coarse sediments decreased as the amount of fine material in the samples decreased, therefore, some of

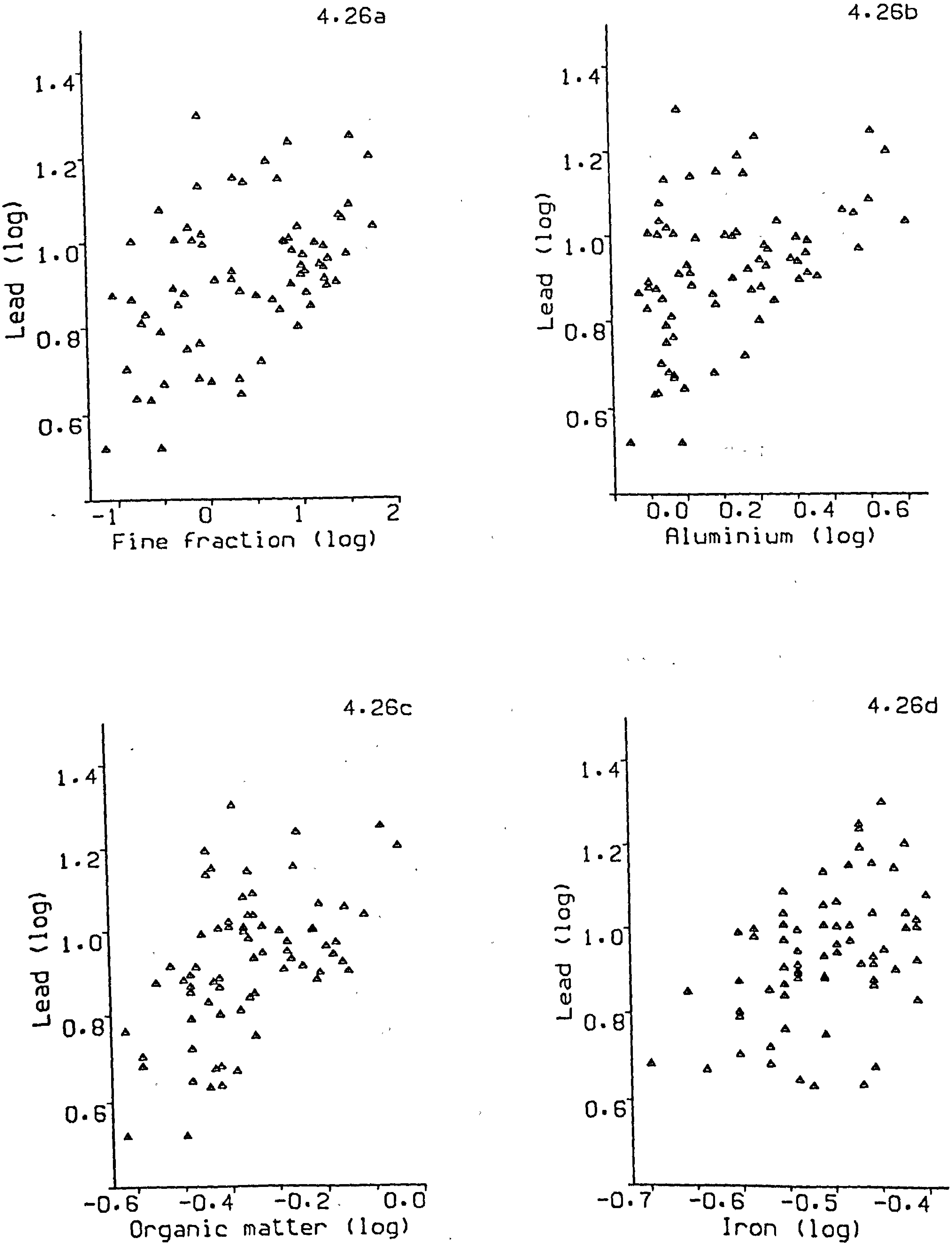


Fig.4.26. Scatter plots of the logarithm of lead in coarse sediments vs (a) logarithm of the fine fraction content, (b) logarithm of aluminium content, (c) logarithm of the organic matter content and (d) logarithm of iron.

the high lead concentrations in coarse sediments occurred in samples with low amounts of organic matter (see Fig. 4.26c). As indicated in Figure 4.26d, the high values of lead observed in samples with low amounts of fines can be explained by an enrichment in the iron content, therefore, lead in coarse sediments of samples with low amounts of fines may be preferentially carried in the iron oxide coatings, whereas lead may be preferentially carried in the organic phases of coarse sediments coexisting with high amounts of fines, also showing a high organic matter content, such as those sediments from the Burbo Bight region.

4.2.8. Zinc

4.2.8.1. Zinc in the fine fraction

The distribution of zinc in the fine fraction (Fig. 4.24c) was very similar to the distribution of lead (Fig. 4.24a) discussed above. The mean concentration of zinc for the whole area was 280 μg g^{-1}. The concentrations in the area of high values in Site SI were 591 μg g^{-1} in sample K-8, a maximum of 904 μg g^{-1} in sample L-9 and 548 μg g^{-1} at station M-10. As in the cases of other elements, station G-9 had a high concentration of zinc (607 μg g^{-1}) as compared to other stations nearby. The lowest values in the northwestern region were found at stations H-12 (minimum), G-11 and G-13, with concentrations of 135, 158 and 153 μg g^{-1} respectively. Samples from the Burbo Bight area had concentrations near or below the overall mean value (*e.g.* 288 and 209 μg g^{-1} at stations YY-2 and YY-3 respectively).

The high similarity in the distributions of zinc and lead (see Fig. 4.24a and c) and the high correlation amongst these two variables (r=0.862 after logarithmic transformation of both variables; see also Fig. 4.27a) suggest that zinc and lead may have similar sources and similar geochemical associations in the fine sediments from Liverpool Bay. Therefore, as most of the discussion regarding the possible sources and associations of lead in the fine fraction also applies to zinc, the following paragraphs are mainly focused on some differences observed between these two metals.

As in the case of lead, after a logarithmic transformation of the data high correlations of zinc with manganese (r=0.744) and iron (r=0.766) were observed (see also Fig. 4.27b and c), suggesting zinc associations with hydrous iron/manganese oxides in the fine sediments from Liverpool Bay. Possible associations of zinc with oxide phases have been reported for various aquatic particles (Warren, 1981; Millward and Moore, 1982; Feely *et al.*, 1983; Luoma and Davis, 1983; Tessier, 1985; Kersten *et al.*, 1988; Angelidis and Grimanis, 1989). Zinc showed a similar correlation with organic carbon (r=0.626; see also Fig. 4.27d) as lead, and after the

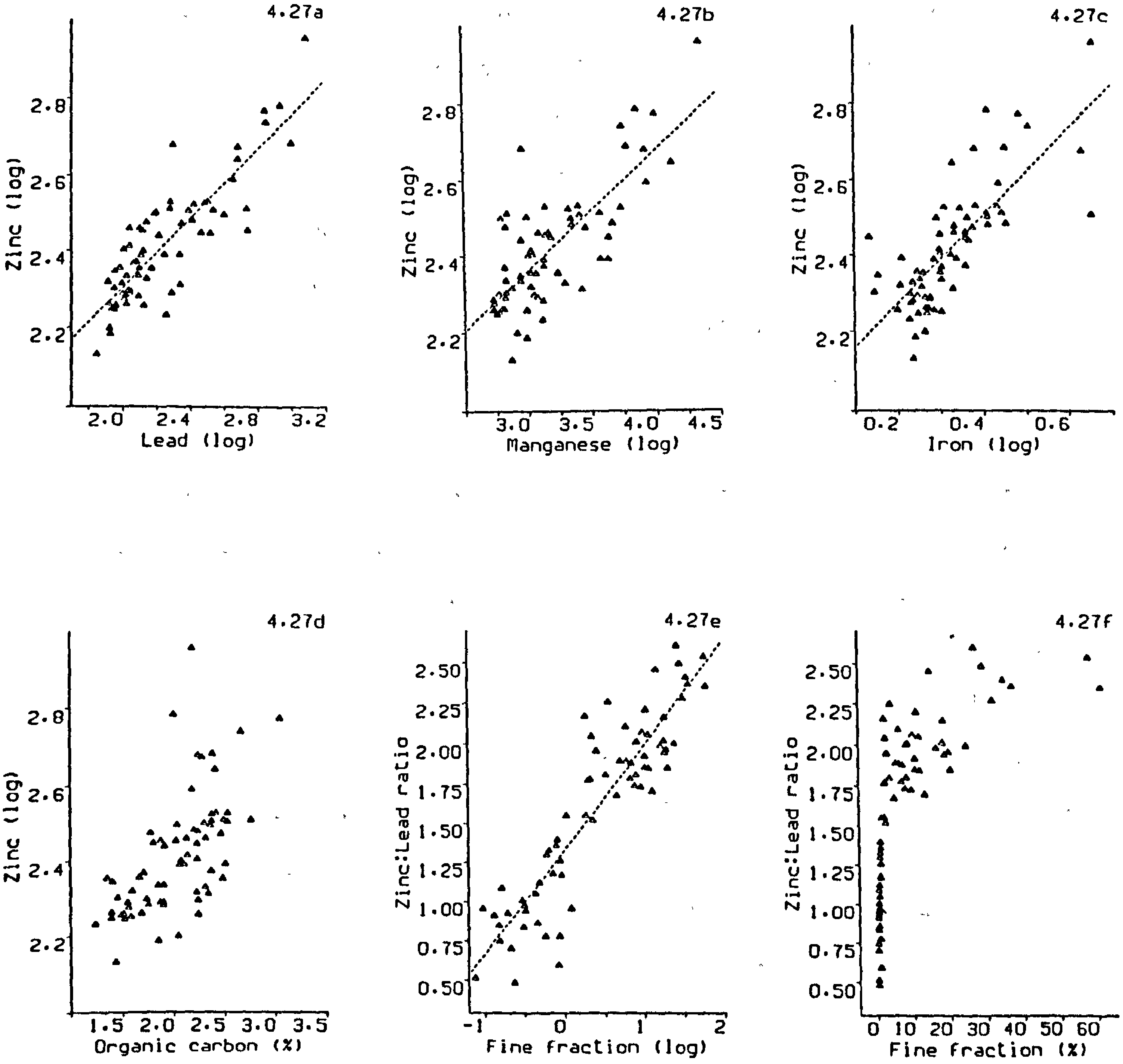


Fig.4.27. Scatter plots of the logarithm of zinc in fine sediments vs (a) logarithm of lead, (b) logarithm of manganese, (c) logarithm of iron, and (d) organic carbon, and of the zinc:lead ratio in fine sediments vs (e) logarithm of fine fraction and (f) the fine fraction content (in percent).

exclusion of the two samples with the highest zinc concentrations this correlation increased to r=0.672 probably reflecting the commonly reported stronger tendency of zinc (as compared to lead) to associate with organic phases (Hirata, 1985; Rosental *et al.*, 1986; Sigg *et al.*, 1987; Golimowski *et al.*, 1990). It is likely that zinc is partitioned amongst iron/manganese oxides and organic coatings to different degrees, depending on the sources of the fine particles and/or the physicochemical properties of the metal itself. Campbell *et al.* (1988) suggested that zinc in particles from the Mersey Estuary (largely affected by sewage and industrial inputs) may be mainly associated with organic phases, whereas Elderfield *et al.* (1979) reported zinc in sediments from the Conwy Estuary (largely affected by inputs from the mineralized areas in North Wales) associated with iron/manganese oxides.

It was mentioned in the discussion of lead distributions that sphalerite (ZnS) is one of the two principal ore minerals in the North Wales old mining zone. This observation, and reports by Elderfield *et al.* (1971), the Imperial College of Science and Technology (1978) and Elderfield *et al.* (1979) showing high zinc concentrations in sediments in the streams and estuary of the River Conwy, indicated the possibility of an effect of zinc inputs from the mineralized areas on the concentrations of this metal in the fine fraction of the sediments collected in the present study. This possibility is also supported by Kiff (1984) who reported high concentrations of magnetite and chromite in the heavy mineral fraction of some sediment samples from Liverpool Bay including the sewage dumping ground, and by a report of high concentrations of zinc (up to 800 μg g^{-1} for magnetite and 8000 μg g^{-1} for chromite) being associated with these two minerals (Warren, 1981). On the other hand, it could be possible that these heavy minerals reported by Kiff (1984) were derived from the sewage sludge and industrial waste disposal at Site SI rather than being transported from North Wales. In a study of the distribution of metals in different particle size fractions of sewage sludges (including digested sludge from the Davyhulme sewage works dumped at Site SI), Campbell *et al.* (WRc unpublished report for North West Water Authority, England) reported concentrations of lead and zinc higher than 2000 μg g^{-1} in the finest fraction (<20 μm), therefore, if heavy minerals were present in this fraction, sewage sludge dumping could account even for the highest concentrations of lead found in the present study (~1200 μg g^{-1}). In the same study, however, the concentrations of iron and manganese in the finest fraction were not particularly elevated (2.2% for iron and 757 μg g^{-1} for manganese), therefore, it seems that inputs of metals such as manganese, zinc and lead from the mineralized areas of North Wales could explain the high concentration of these elements in sediments with very low amounts of fine material where the deposition of sewage derived particles is more unlikely (see Chapter 2, Section 2.4.1).

Although the similar distribution (Fig. 4.24a and c) and the high correlation between zinc and lead (Fig. 4.27a) suggest that these metals have a similar geochemical behaviour in Liverpool Bay fine sediments, an interesting observation arose from the analysis of the ratio between these two metals. Figure 4.27e shows that the Zn:Pb ratio in the fine sediments analysed in the present study could be largely predicted by the variations in the fine fraction content of the total sediment through the equation:

$$\mathbf{Zn_{fine}/Pb_{fine} = 1.32 + 0.657\ log\text{-}\%fine,\ (r^2{=}82\%,\ F{=}314).}$$

Figure 4.27e shows that Zn:Pb ratios decreased as the amount of fine particles in the total sediments decreased, and as the concentration of both metals in the fine particles increased as the fine fraction in the sediments decreased (see Fig. 4.27d and 4.26a), proportionally higher concentrations of lead were found as the concentration of both metals increased, in other words, lead concentrations increased more rapidly than zinc concentrations. This effect is more obvious if the Zn:Pb ratio is plotted against the percentage of fine fraction without logarithmic transformation. From Figure 4.27f, it is more obvious that at concentrations of fine fraction higher than approximately 2% the Zn:Pb ratio fluctuated between 1.7 and 2.6, whereas this ratio sharply decreased from the 1.7 value at 2% of fine fraction towards a minimum of 0.48 in one of the samples (P-10) with the lowest proportion of fine sediments (0.23%), sample S-7 with the lowest amount of fine material (0.08%) showed the second lowest Zn:Pb ratio (0.51). It is interesting to note that a similar behaviour of the Zn:Pb ratios in relation to the grain size distribution in the sediments, was observed with the data reported by Law *et al.* (1989) for the <90 µm fraction of sediments in the Liverpool Bay area in particular. As an example, these authors report (see Table 5) that the sample from station 4 (near the apex of Site SI) showed the highest lead and zinc concentrations (570 and 490 µg g^{-1} respectively) and the lowest Zn:Pb ratio (0.86); this sample also had the lowest amount of <90 µm fraction (0.1%) in the whole region. On the other hand, station 1 (near Site Z) showed the highest Zn:Pb ratio (2.8) within the region (zinc and lead concentrations were 390 and 140 µg g^{-1} respectively) and a very high proportion of the <90 µm fraction in the sample (87.8%); other samples within Liverpool Bay (stations 10, 11, 13, 15 and 21) showed a Zn:Pb range from 2.1 to 2.7.

A Zn:Pb ratio of 4 was obtained with the benchmark values for these metals reported by Rowlatt *et al.* (1984) and a ratio of 2.6 was obtained for the mean concentrations of lead and zinc in 119 samples (<90 µm fraction) in the whole eastern Irish Sea including only a relatively small amount of samples from the Liverpool Bay area. These ratios may be representative of those in fine particles in sediments being transported into Liverpool Bay from the Irish Sea. A Zn:Pb ratio of approximately 2.1 was observed in the sludge. Therefore, the Zn:Pb ratio in fine particles of sediments in Liverpool Bay seems to be controlled by the relative amounts of particles contributed by each of the main sources (*i.e.* those derived from the Irish Sea, sewage sludge derived and those probably derived from the mineralized areas). It is possible that fine particles of sediments containing more than 2% of fine fraction show a relatively constant Zn:Pb ratio (between 1.7 and 2.3) because most of these particle are either derived from the eastern Irish Sea or from sewage sludges (both sources showing similar ratios). On the other hand, fine particles in sediments with a concentration of fine fraction lower than 2% may be dominated by particles (showing high concentrations of lead and zinc and a low Zn:Pb ratio) derived from the mineralized areas in North Wales. It is important to stress at this point that most of the samples with fine fraction concentrations lower than 2% occurred nearer the North Wales coast (see Fig. 4.1a), and that sediments with low amount of fines indicated hydrodynamical conditions under which the deposition of fine particles (such as those from sewage sludges) were less favourable (see Chapter 2, sections 2.3 and 2.4).

When compared with the baseline (85 $\mu g\ g^{-1}$) and benchmark (240 $\mu g\ g^{-1}$) values for zinc reported by Rowlatt *et al.* (1984), the mean value obtained for the fine sediments in the present study was 3.3 times above the baseline and 1.2 times above the benchmark values. These values indicate that although there is an obvious enrichment of zinc in fine sediments from Liverpool Bay as compared to the baseline value, the average concentration was only 20 percent above the average value for the eastern Irish Sea (as compared to a factor of 3.9 for lead) indicating that zinc is not extremely enriched in Liverpool Bay fine sediments as compared to other areas in the eastern Irish Sea which apparently are not directly affected by sewage sludge disposal, dredging spoils disposal or inputs from the rivers in the coastal areas particularly the Mersey. This observation, however, does not indicate that zinc levels in fine sediments from Liverpool Bay are low, but is a result of a relatively high benchmark value for zinc that is 2.8 times above the baseline value indicating that there is an enrichment of zinc not only in the Liverpool Bay area but in the whole eastern Irish Sea.

Finally, Table 4.1 shows that the relative standard deviation for the zinc concentrations in fine sediments in the present study (45%) and the ratio between the maximum and minimum concentrations (6.7) was lower than that for lead and other metals, indicating a relatively more homogeneous distribution of this element amongst fine particles in the bay. When compared to

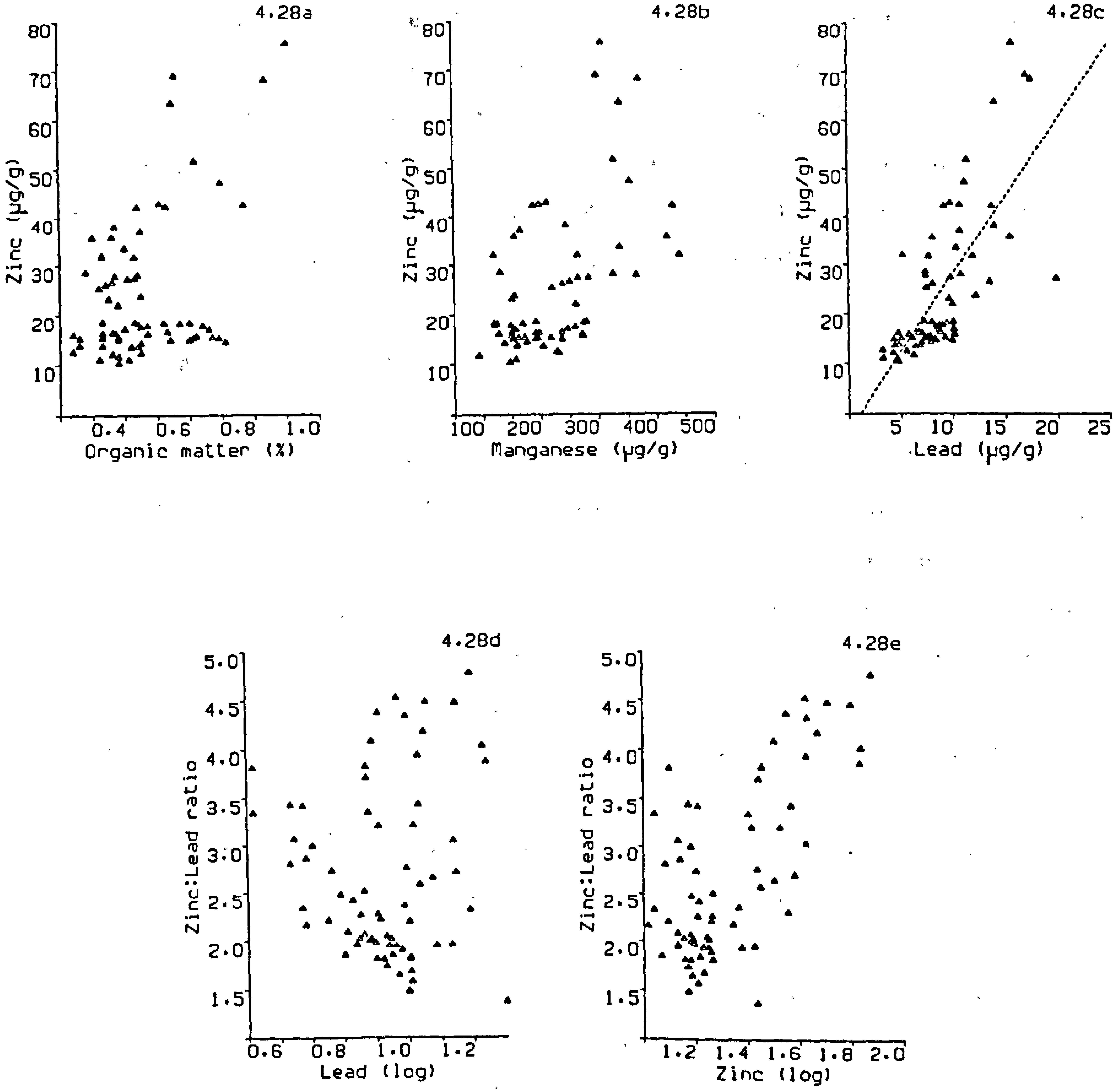


Fig.4.28. Scatter plots of the zinc concentration in coarse sediments vs (a) organic matter content, (b) manganese, and (c) lead, and of the zinc:lead ratio in coarse sediments vs (d) logarithm of lead and (e) logarithm of zinc.

lead and copper, zinc shows a lower affinity towards particles (Ballistrieri and Murray, 1984), and as in the case of copper seems to have a higher affinity for dissolved organic matter (Golimowski *et al.*, 1990) and may also play a more important role than lead in biological systems such as uptake by phytoplankton (Hirata, 1985; Sigg *et al.*, 1988). Therefore, as compared to lead, zinc shows a higher mobility and is more involved in processes leading to redisolution and precipitation which lead to a better homogenization in the distribution of this metal.

4.2.8.2. Zinc in the coarse fraction

Figure 4.24d shows the distribution of zinc in the coarse fraction. A clear gradient of increasing values from west to east can be observed. The mean concentration for the whole region was 24.7 μg g^{-1}. Most samples west from transect L had values below 20 μg g^{-1}, with some stations showing concentrations below 15 μg g^{-1} and reaching a minimum of 13.6 μg g^{-1} at station K-9. Concentrations in the central-southern area were also low, with the lowest values at stations Q-7 (10.4 μg g^{-1}), R-6 (11.0 μg g^{-1}) and S-7 (12.6 μg g^{-1}). High concentrations were found at stations S-9, T-9 and U-9 with values of 63.5, 69.0 and 68.2 μg g^{-1} respectively. The maximum value (75.6 μg g^{-1}) in the whole region was found at station YY-3 in the Burbo Bight area, where the lowest value was of 42.3 μg g^{-1} at station YY-2.

The distribution of zinc in the coarse fraction (Fig. 4.24d) indicates that inputs from the Mersey appear to be a significant source of this metal in coarse particles. In contrast to mercury, cadmium, chromium and copper, the correlation between zinc in coarse sediments and the amount of fine material in the total sediment was low (r=0.490) but significant, indicating that the concentration of this metal in coarse sediment particles may be mainly controlled by factors other than the amount of coexisting fine particles.

Also in contrast to other metals (excluding lead), zinc in coarse sediments showed a low but significant correlation with the organic matter content (r=0.434) in the particles. A significant correlation was observed between zinc and manganese (r=0.549) and no correlation was observed with the iron content, therefore, it is possible that zinc is preferentially associated with manganese oxides and organic matter in coarse particles in Liverpool Bay and the proportion in each phase might be depending on the location of the samples. Figure 4.28a shows that some samples with high organic matter content had high concentrations of zinc whereas others had low concentrations. In fact, from figures 4.24d and 4.4c it can be seen that samples showing high zinc and organic matter values are those nearer to the Mersey whereas those showing high organic matter but low zinc values are those from the extreme northwestern section of the sampling grid.

It is likely that zinc is mainly associated to organic phases in coarse sediments near the Mersey outflow as manganese concentration in samples from the Burbo Bight area (where the highest zinc and organic matter values were observed) were not the highest (see also Fig. 4.28b).

As in the fine fraction, zinc was significantly correlated with the lead content (Fig. 4.28c) in the coarse fraction (r=0.781 after the exclusion of sample M-10) which suggested that both metals may have also a similar geochemical behaviour in the coarse particles. It was interesting to note that in samples outside the influence of the Mersey, a similar trend as the one observed in the fine particles was observed in the coarse particles of lead concentrations increasing more rapidly than zinc concentrations, therefore, the Zn:Pb decreased as the concentration of both metals increased (this effect is particularly noticeable in Fig. 4.28d). In samples within the influence of the Mersey outflow, however, this trend was reversed (see Fig. 4.28e) indicating that within this area zinc concentrations increased more rapidly than lead concentration, probably as a result of higher zinc discharges than lead discharges from the Mersey Estuary which is subject to particularly high inputs of zinc from domestic and industrial sources that can be transported in solution associated with organic substances (Campbell *et al.*, 1988), in contrast to lead that due to its high reactivity may be largely associated with particles (Ballistrieri and Murray, 1984) and most of the particles in the estuary may be retained within the estuarine system rather than being transported into Liverpool Bay (see Chapter 2, Section 2.3). It was also interesting to notice that the Zn:Pb ratios in the area outside the reaches of the Mersey inputs were similar to those found in the fine particles in sediments with a fine fraction proportion higher than 2% which do not appear to be significantly affected by inputs from mineralized areas.

4.3. STATISTICAL CLASSIFICATION OF SEDIMENTS USING RATIO MATCHING

From the discussions in the previous sections, it is obvious that trace element distributions in sediments from Liverpool Bay do not only depend on the sources of each of these elements and the total amounts discharged into this area by either natural or anthropogenic inputs, but are also determined by the particular physicochemical properties of each element, specially those controlling adsorption-desorption processes. As noted in Chapter 2, the hydrodynamical conditions also play a major role in controlling the observed trace element distributions as they will ultimately determine whether particles are deposited or not in a particular area. Therefore, considering the possible multiple sources of these elements into the bay, the difference in their physicochemical properties and the continuously changing hydrodynamic conditions leading to a continuous cycle of sediment erosion-transport-deposition, it is not surprising to observe such different distributions when some of the elements discussed above are compared. However, in spite of the multiple controlling factors and the complexity of the distributions, an attempt has been made to summarize the information previously discussed. To achieve this goal, an attempt has been made to classify the sediments based on their elemental composition by means of multivariate statistical methods, in particular, by applying a technique called "ratio matching" (Anders, 1972; Poulton, 1989) for determining the similarity amongst samples, which is followed by cluster analysis used for the separation of the samples into groups or "clusters" based on their similarities.

The "ratio matching" technique used in this study to determine the degree of similarity between sediment samples was originally developed by Anders (1972) and later modified by Poulton (1989). Although this technique can be more broadly applied to various sorts of analog problems, both Anders (1972) and Poulton (1989) applied this method to determine the sources of various trace elements in sediment samples. The hypothesis on which this method is based is that sediment samples of common origin will tend to have similar ratios of the concentrations of trace pollutants (heavy metals, PCBs, etc.), whereas the absolute concentrations of the individual pollutants may vary considerably due to dilution with inert materials such as SiO_2 and $CaCO_3$ (Poulton, 1989). It is important to mention at this point that Anders (1972) and Poulton (1989) analysed total sediment samples and worked under the assumption that sedimentary particles larger than clay and silts consist mainly of "inert" minerals such as silica or calcite and that these larger particles, having less surface area per unit mass available for contaminant adsorption in comparison to the fine grained particles, will only act as "diluent" factors, in other words, it is assumed that the contribution of coarse particles to the observed total metal content in a particular sediment sample is insignificant as compared to the contribution by fine particles. It has been mentioned previously in this chapter that, if total sediments are analysed, regarding coarse sediment materials as "inert" towards metals, therefore regarding them as "diluent" factors may be questionable in several situations, particularly in areas such as Liverpool Bay where a large proportion of the sediments are sandy with only small proportions of fine grained material, and therefore, the contribution of coarse particles to the metal load in the total sediment may be significant. These statistical methods were therefore applied separately to the fine and coarse sediment fractions analysed in this study, and these analyses show that different elemental "fingerprint" can be observed in different grain size fractions within the same sample which suggest that if trace element analyses were carried on total sediments, the fingerprinting of the different fractions would have been superimposed, making the interpretation of the results more difficult than they already are.

In order to compare the samples, the first step in Anders (1972) procedure was, for each sample, to divide the concentration of each chemical component by that of each of the other components obtaining this way the "concentration ratio matrix", $\{X_{ij}\}$, which is a triangular matrix of size *m x m* where *m* is the number of chemical components involved in the analysis. In the present study, ten chemical elements in sixty seven sediment samples were included in the calculations, and the data were arranged in a data file as follows:

		Element									
		Hg	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**As**	**Mn**	**Fe**
S	S1	Hg_1	Cd_1	Cr_1	Cu_1	Ni_1	Pb_1	Zn_1	As_1	Mn_1	Fe_1
a	S2	Hg_2	Cd_2	Cr_2	Cu_2	Ni_2	Pb_2	Zn_2	As_2	Mn_2	Fe_2
m	S3	.	.	.	.	.	.	.	.	.	.
p	.	.	.	.	.	.	.	.	.	.	.
l	.	.	.	.	.	.	.	.	.	.	.
e	.	.	.	.	.	.	.	.	.	.	.
	S67	Hg_{67}	.	.	.	.	.	.	.	.	Fe_{67}

therefore, for each sediment sample a 10 x 10 triangular matrix was obtained. For example, for sample S1 (A), the concentration ratio matrix looks as follows:

$$\{X_{ij}\,(A)\} = \left|\begin{array}{llllll}
\frac{Hg}{Hg_A} & & & & & \\
\frac{Cd}{Hg_A} & \frac{Cd}{Cd_A} & & & & \\
\frac{Cr}{Hg_A} & \frac{Cr}{Cd_A} & \frac{Cr}{Cr_A} & & & \\
\cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \\
\frac{Fe}{Hg_A} & \frac{Fe}{Cd_A} & \frac{Fe}{Cr_A} & \cdot & \cdot & \frac{Fe}{Fe_A}
\end{array}\right|$$

The next step of the procedure is to compare the ratios obtained for each sample with those of all the other samples. For example, the comparison between sample S1 (A), and sample S2 (B), is carried out by forming the "ratio matrix of two samples" $\{Y_{ij}\,(AB)\}$, which is a triangular matrix obtained by dividing each of the a_{ij} elements of the concentration ratio matrix, $\{X_{ij}\,(A)\}$, for sample A, by the corresponding b_{ij} element of the "concentration ratio matrix", $\{X_{ij}\,(B)\}$ of sample B which results in a "ratio matrix of two samples" looking as follows:

$$\{Y_{ij}\,(AB)\} = \left| \begin{array}{cccccc}
\frac{\frac{\mathrm{Hg}}{\mathrm{Hg}_A}}{\frac{\mathrm{Hg}}{\mathrm{Hg}_A}} & & & & & \\
\frac{\frac{\mathrm{Cd}}{\mathrm{Hg}_A}}{\frac{\mathrm{Cd}}{\mathrm{Hg}_B}} & \frac{\frac{\mathrm{Cd}}{\mathrm{Cd}_A}}{\frac{\mathrm{Cd}}{\mathrm{Cd}_B}} & & & & \\
\frac{\frac{\mathrm{Cr}}{\mathrm{Hg}_A}}{\frac{\mathrm{Cr}}{\mathrm{Hg}_B}} & \frac{\frac{\mathrm{Cr}}{\mathrm{Cd}_A}}{\frac{\mathrm{Cr}}{\mathrm{Cd}_B}} & \frac{\frac{\mathrm{Cr}}{\mathrm{Cr}_A}}{\frac{\mathrm{Cr}}{\mathrm{Cr}_B}} & & & \\
\cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \\
\frac{\frac{\mathrm{Fe}}{\mathrm{Hg}_A}}{\frac{\mathrm{Fe}}{\mathrm{Hg}_B}} & \frac{\frac{\mathrm{Fe}}{\mathrm{Cd}_A}}{\frac{\mathrm{Fe}}{\mathrm{Cd}_B}} & \frac{\frac{\mathrm{Fe}}{\mathrm{Cr}_A}}{\frac{\mathrm{Fe}}{\mathrm{Cr}_B}} & \cdot & \cdot & \frac{\frac{\mathrm{Fe}}{\mathrm{Fe}_A}}{\frac{\mathrm{Fe}}{\mathrm{Fe}_B}}
\end{array} \right|$$

Finally, an index of the similarity between two samples A and B is obtained from the ratio matrix of the two samples by reducing the matrix $\{Y_{ij}\,(AB)\}$ to a similarity coefficient Z_{AB}. The similarity coefficient between any k and l pair of samples was defined by Poulton (1989) as an evaluation of the relative differences of all elements of the $\{Y_{ij}\,(kl)\}$ matrix from 1. For each of the $[(m \times m) - m]/2$, (m_2), off-diagonal elements in the $\{Y_{ij}\,(kl)\}$ matrix, the absolute value of the logarithm is used as a measure of the difference of each element from 1. In order to obtain a value of 1.0 for a perfect match (*i.e.* all $\{Y_{ij}\}$ values = 1.0), 1.0 is added to the logarithms, and the similarity coefficient takes the form:

$$Z_{kl} = \sum_{i=1}^{m} \sum_{j=i+1}^{m} \left[\frac{1}{|\ln\{Y_{ij}\,(kl)\}| + 1} \right] \frac{1}{(m_2)}$$

In this equation, *k* and *i* vary from 1 to *n*, where *n* is the number of samples, $Z_{kk}=1$ and $Z_{kl}=Z_{lk}$.

The similarity coefficients Z_{kl} for all samples form a "similarity coefficient matrix" of size *n x n* (67 x 67 in this study), as follows:

$$\{Z_{kl}\} = \begin{vmatrix} 1 & & & & & \\ Z_{AB} & 1 & & & & \\ Z_{AC} & Z_{BC} & 1 & & & \\ . & . & . & 1 & & \\ . & . & . & . & 1 & \\ Z_{An} & Z_{Bn} & . & . & . & 1 \end{vmatrix}$$

For an example on the calculations of the similarity coefficients the following data for three metals in three samples is considered:

	Hg	Cd	Cu
M-9	0.27	0.39	144
YY-1	1.22	0.77	44
YY-3	1.19	0.72	36

In the first step, the "concentration ratio matrix", $\{X_{ij}\}$ for each sample is calculated as follows:

$$\{X_{ij}(M9)\} = \begin{vmatrix} \frac{0.27}{0.27} & & \\ \frac{0.39}{0.27} & \frac{0.39}{0.39} & \\ \frac{144}{0.27} & \frac{144}{0.39} & \frac{144}{144} \end{vmatrix} = \begin{vmatrix} 1.0 & & \\ 1.4 & 1.0 & \\ 533 & 369 & 1.0 \end{vmatrix}$$

$$\{X_{ij}(YY1)\} = \begin{vmatrix} \frac{1.22}{1.22} & & \\ \frac{0.77}{1.22} & \frac{0.77}{0.77} & \\ \frac{44}{1.22} & \frac{44}{0.77} & \frac{44}{44} \end{vmatrix} = \begin{vmatrix} 1.0 & & \\ 0.6 & 1.0 & \\ 36 & 57 & 1.0 \end{vmatrix}$$

$$\{X_{ij}(YY3)\} = \begin{vmatrix} \frac{1.19}{1.19} & & \\ \frac{0.72}{1.19} & \frac{0.72}{0.72} & \\ \frac{36}{1.19} & \frac{36}{0.72} & \frac{36}{36} \end{vmatrix} = \begin{vmatrix} 1.0 & & \\ 0.6 & 1.0 & \\ 30 & 50 & 1.0 \end{vmatrix}$$

then, the ratio matrix $\{Y_{ij}\}$ for each pair of samples is computed

$$\{Y_{ij}\ (M9YY1)\} = \begin{vmatrix} \frac{1}{1} & & \\ \frac{1.4}{0.6} & \frac{1}{1} & \\ \frac{533}{36} & \frac{369}{57} & \frac{1}{1} \end{vmatrix} = \begin{vmatrix} 1.0 & & \\ 2.3 & 1.0 & \\ 14.8 & 6.5 & 1.0 \end{vmatrix}$$

$$\{Y_{ij}\ (M9YY3)\} = \begin{vmatrix} 1.0 & & \\ 2.3 & 1.0 & \\ 17.8 & 7.4 & 1.0 \end{vmatrix} \qquad \{Y_{ij}\ (YY1YY3)\} = \begin{vmatrix} 1.0 & & \\ 1.0 & 1.0 & \\ 1.2 & 1.1 & 1.0 \end{vmatrix}$$

and finally, the difference from 1 of each of the off-diagonal elements in each matrix is calculated with the inverse of $[|\ln \{Y_{ij}\}\ (kl)| + 1]$, e.g. in $\{Y_{ij}\ (M9YY1)\}$ the calculation for the three off-diagonal elements 2.3, 14.8 and 6.5 would be $1/[|\ln(2.3)| + 1] = 0.55$, $1/[|\ln(14.8| + 1] = 0.27$ and $1/[|\ln(6.5)| + 1] = 0.35$ respectively. The average from these three values is 0.39 and represents the similarity coefficient, Z_{M9YY1}, between samples M-9 and YY-1. The similarity coefficients between samples M-9 and YY-3 and between samples YY-1 and YY-3 would be Z_{M9YY3}=0.38 and Z_{YY1YY3}=0.91 respectively. A matrix of similarity coefficients looking as follows is the final product of these calculations:

	M-9	YY-1	YY-3
M-9	1.00		
YY-1	0.39	1.00	
YY-3	0.38	0.91	1.00

These similarity coefficients indicate that regardless the total metal concentration in the samples, the ratios between Hg, Cd and Cu in samples YY-1 and YY-3 were very similar whereas these ratios were very different to those found in sample M-9. These results would suggest that the metals mercury, cadmium and copper in the fine fraction of samples YY-1 and YY-3 have a similar source(s) and have been similarly affected by physicochemical processes (e.g. adsorption-desorption), whereas those metals in sample M-9 probably come from a different source(s) or have been affected to a different extent by physicochemical processes (or both).

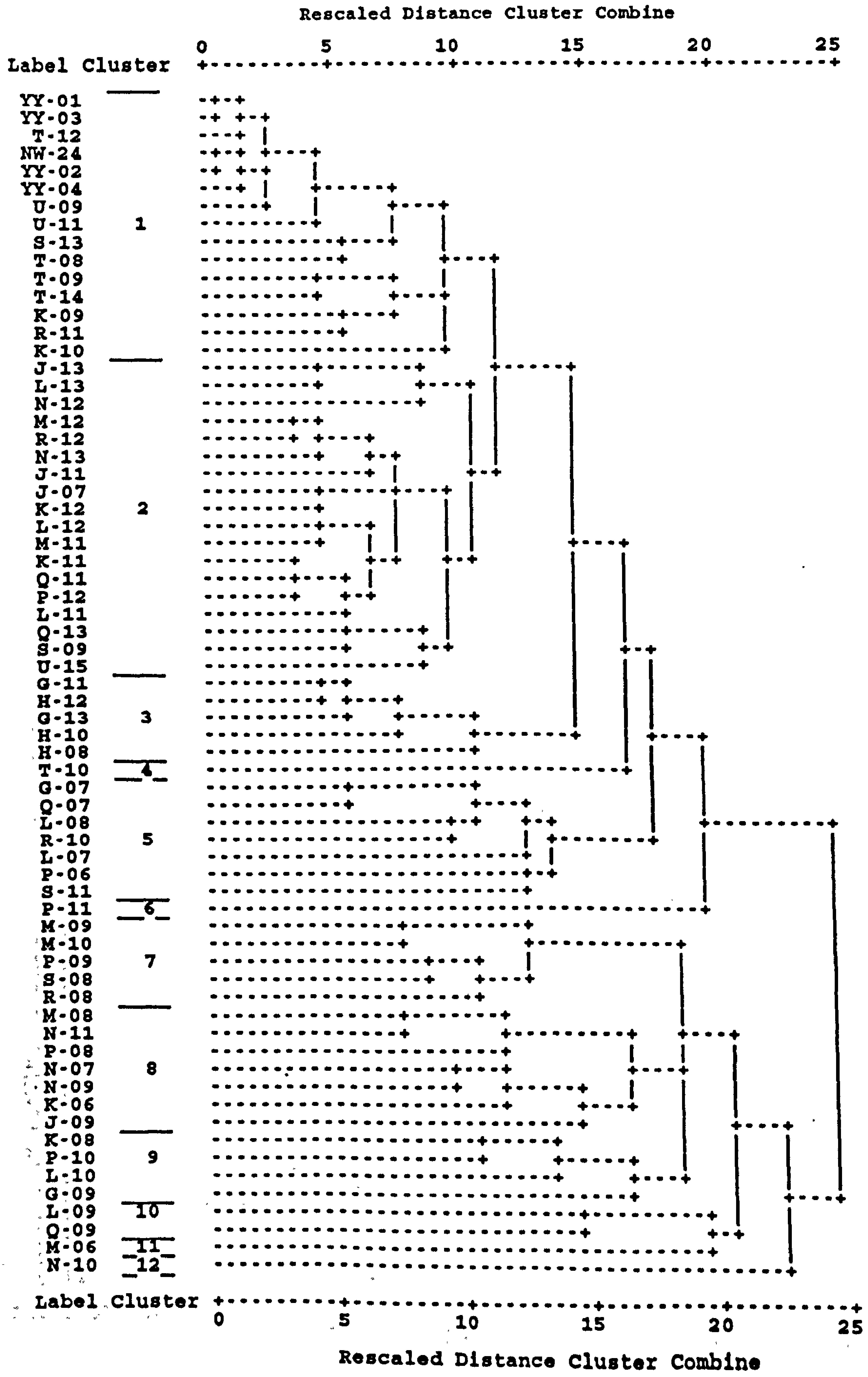
In the present study, the final product of these calculations were two triangular matrices (67 x 67) of similarity coefficients, one for data in the fine fraction and one for data in the coarse fraction. As the number of data handled during these calculations is very large (each of the similarity coefficients was obtained from a 10 x 10 "ratio matrix for two samples", and for each sample a 10 x 10 "concentration ratio" matrix was computed), all these calculations were done in a VAX computing system (UCNW) using a FORTRAN programme written by Alejandro Souza-Gómez, a fellow Mexican student from the Physical Oceanography Department (UCNW).

Using the matrix of similarity coefficients as an input, Poulton (1989) used a cluster analysis to classify the sediments into groups with similar inter-elemental ratios, therefore, into groups with similar origin. In general, the problem that cluster analysis is designed to solve is the following: given a sample of *n* objects (in this study *n*= 67 sediments) each of which has a score on *m* variables (in this case a concentration value for *m* = 10 chemical elements), devise a scheme for grouping the objects into classes so that "similar" ones are in the same class (Manly, 1986). As several clustering procedures exist and discussing them is beyond the scope of this work, the reader is referred to Manly (1986), Norusis (1985) and references therein. The clustering procedure followed by Poulton (1989) and followed in this study is a hierarchical agglomerative method which, in few words, consist of grouping the objects into bigger and bigger clusters until all objects are members of a single cluster. For example, in this study, the

Fig.4.29. Dendrograms for the cluster analysis on the similarity coefficient matrices obtained with the "ratio matching technique" applied on the content of ten elements (see text for details) in (a) fine sediments, (b) coarse sediments and (c) the fine and coarse fractions in 25 sediment samples. The vertical relative scale indicates the distance (dissimilarity) between clusters, in the horizontal the number of station (label) and the cluster membership (shown in Fig. 4.30) are indicated.

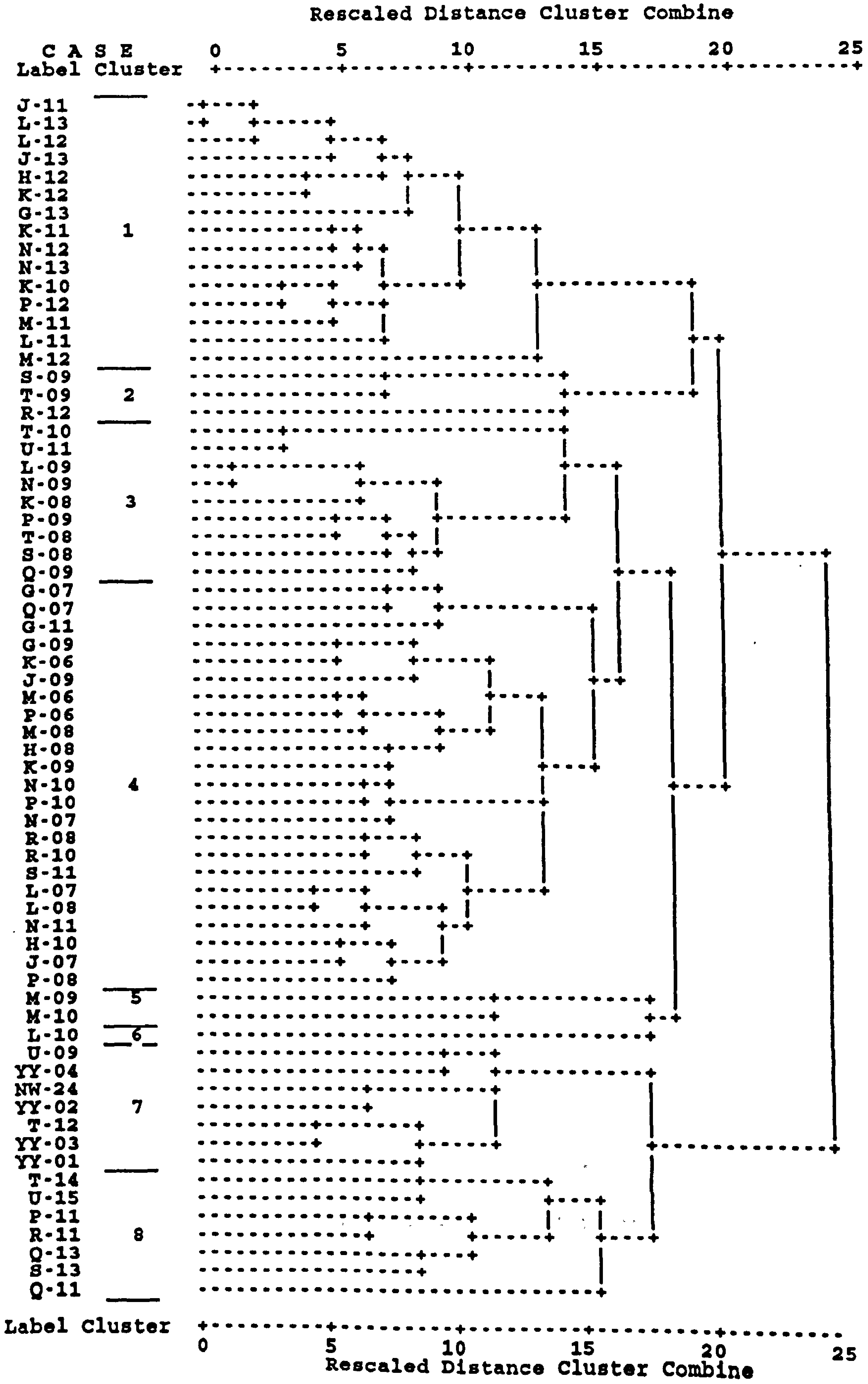
4.29a

Dendrogram using Average Linkage (fine fraction)



4.29b

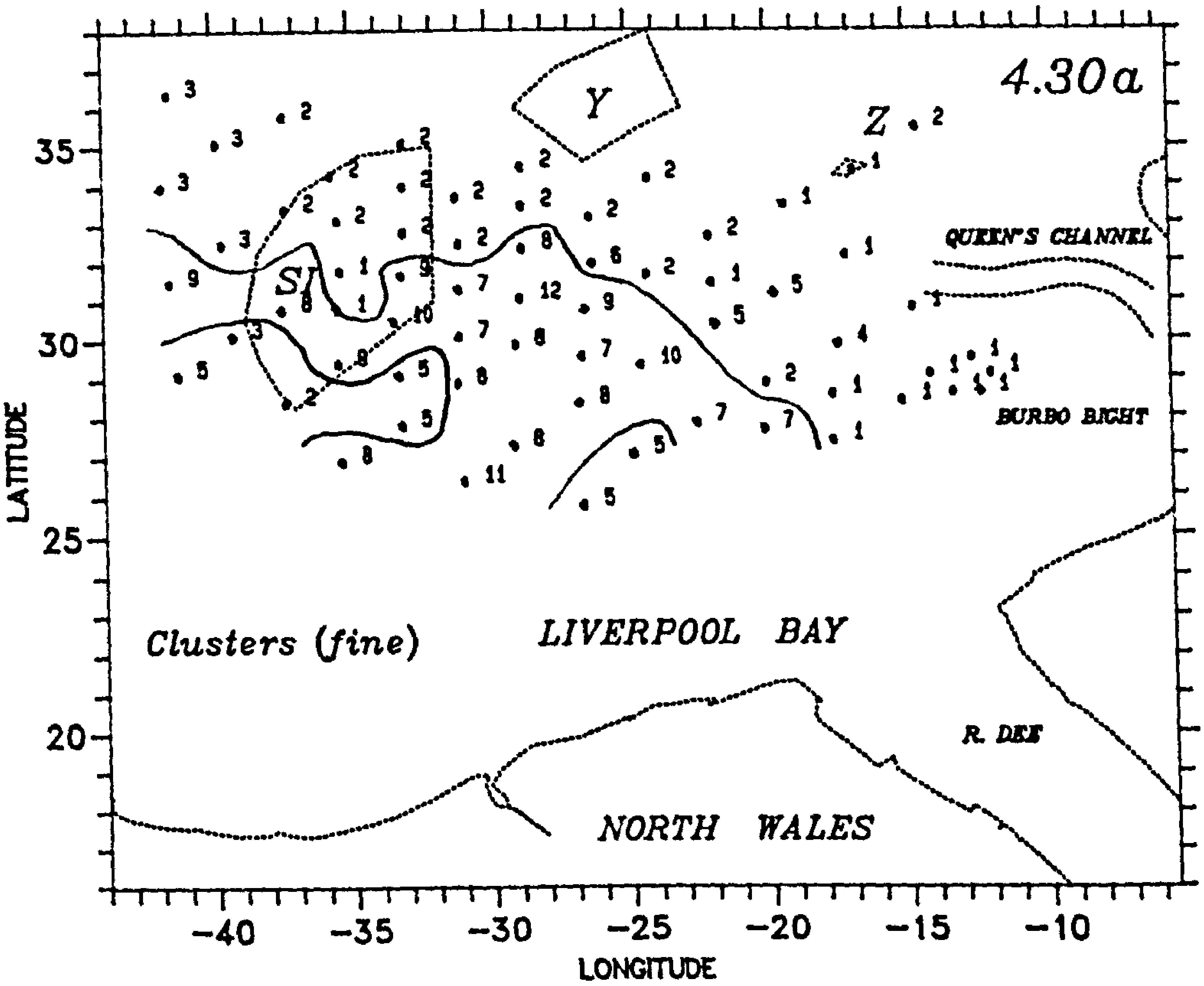
Dendrogram using Average Linkage (coarse fraction)

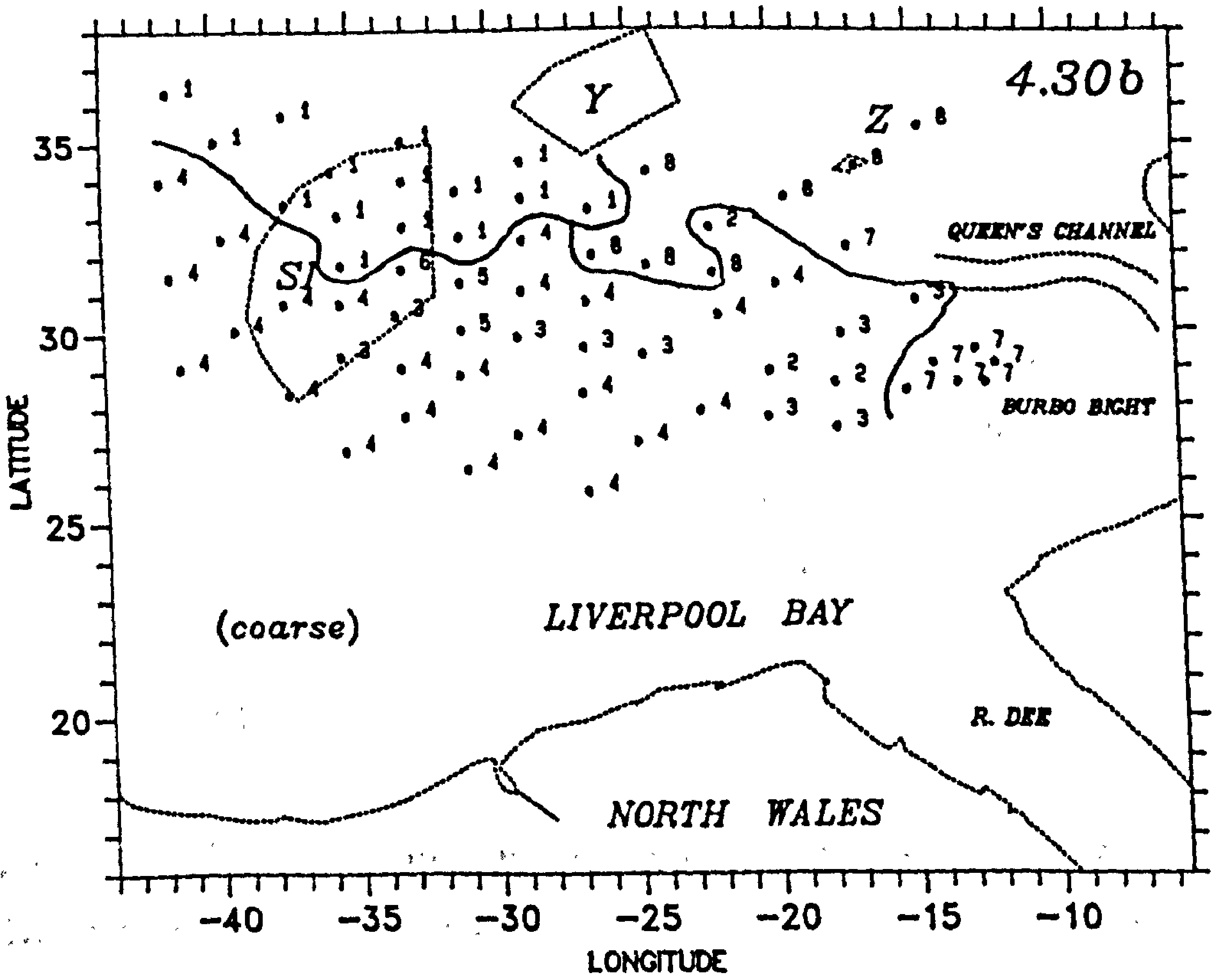


4.29c

```
Dendrogram using Average Linkage (fine fraction and coarse fraction)

                         Rescaled Distance Cluster Combine

                0         5        10        15        20        25
Label           +---------+---------+---------+---------+---------+

YY-01            -+-----+
YY-03            -+     +---+
U-11             -------+   +---------+
T-14             -----------+         +-+
S-09             -------------+-----+ | |
U-15             -------------+     +-+ +-----+
J-07             -------------------+   |     |
K-09     F       -------------------+---+     +-+
K-10             -------------------+         | +-+
T-10             -----------------------------+ | |
G-13     I       -----------------+-------------+ +---+
H-08             -----------------+               |   |
L-13             ---------------------------+-----+   +-----------+
P-06     N       ---------------------------+         |           |
YY-01c           ---------------+-----------------+   |           |
YY-03c           ---------------+                 +---+           |
P-11     E       ---------------------------------+               |
L-09             -------------------------------+-------+         |
M-06             -------------------------------+       |         |
J-09             -----------------------+-----------+   +---+     |
N-07             -----------------------+           |   |   |     |
M-09             -------------+-------------+       +---+   |     |
M-10             -------------+             |       |       +-----+
R-08             ---------------------------+---+   |       |     |
L-10             ---------------------------+   +---+       |     |
G-09             -------------------------------+           |     |
N-10             -------------------------------------------+     |
K-10             -----------------+---------+                     |
L-13             -----------------+         +---------+           |
T-14     C       -------------+---------+   |         |           |
U-15             -------------+         +---+         |           |
P-11             -----------------------+             |           |
M-09     O       -------------------+---------+       +-----------+
M-10             -------------------+         +---+   |
S-09             -----------------------------+   |   |
T-10     A       -------+-----------------------+ |   |
U-11             -------+                       | +---+
L-09             ---------------+-------+       | |
R-08     R       ---------------+       |       | |
G-09             -----------+-----+     |       +-+
J-09             -----------+     +---+ +-----+ |
M-06     S       ---------+---+   |   | |     | |
P-06             ---------+   +---+   | |     | |
H-08             -----------+-+       +-+     | |
K-09     E       -----------+         |       +-+
N-07             -----------+-------+ |       |
N-10             -----------+       +-+       |
G-13             -----------+-------+         |
J-07             -----------+                 |
L-10             -----------------------------+

Label           +---------+---------+---------+---------+---------+
                0         5        10        15        20        25

                         Rescaled Distance Cluster Combine
```

Fig.4.30. Distribution of cluster memberships obtained from a cluster analysis applied on the matrices of similarity coefficients for ten elements in (a) fine sediments and (b) coarse sediments. The similarity coefficients were calculated with the "ratio matching technique" (see text for details).


4.30a
Y
Z
SI
QUEEN'S CHANNEL
BURBO BIGHT
Clusters (fine)
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
−40
−35
−30
−25
−20
−15
−10


4.30b
Y
Z
SI
QUEEN'S CHANNEL
BURBO BIGHT
(coarse)
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
LONGITUDE
35
30
25
20
−40
−35
−30
−25
−20
−15
−10

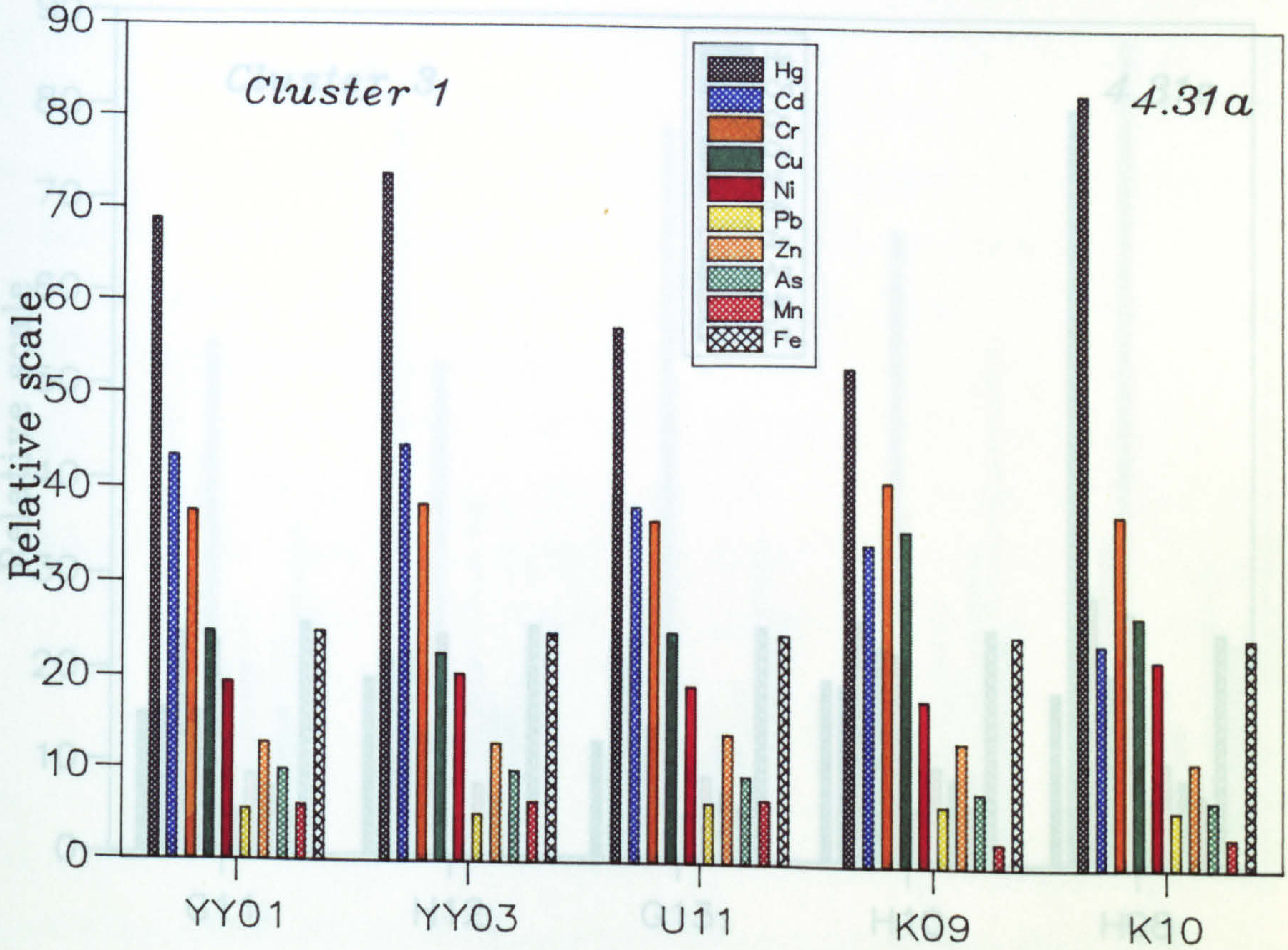
concentration of iron in that particular sample, this way, the dispersion of the values of elements showing co-variation with iron is reduced and data from different samples will be more easily represented using the same scale. For example, arsenic concentrations ranged from ~9 to 144 µg g^{-1} but once normalized with the percentage of iron, the range was from ~5 to ~30, on the other hand, zinc showed a range of concentrations from 135 to 904 µg g^{-1} and after normalization, the range was from 70 to 240. It is obvious that if normalized values of arsenic and zinc were to be represented in a bar diagram using the same scale, the range in the scale would have to be from 0 to 240 and the size of the of the bars representing arsenic would be very small. Therefore, if zinc normalized values were divided by 10, the range of arsenic and zinc would be similar. The transformation of data using multiplication or division does not affect the concept of "relative proportions" amongst elements because, regardless the absolute concentration values, if one of the elements increases by a factor of 2 from one sample to another while the other remains unchanged, the size of the bar representing the transformed data of the "enriched" element will also duplicate its size. Therefore, for data in coarse and fine fractions, after normalization with iron concentrations (in percent), mercury and cadmium values were multiplied by 100, lead and zinc were divided by 10, manganese divided by 100 and iron was multiplied by 25 in the fine and by 10 in the coarse fraction while the other elements (chromium, copper, nickel and arsenic) remained unchanged after dividing by the iron concentration.

Figure 4.31a shows examples of patterns in samples from cluster number 1. The similarity coefficients between the samples in this cluster were:

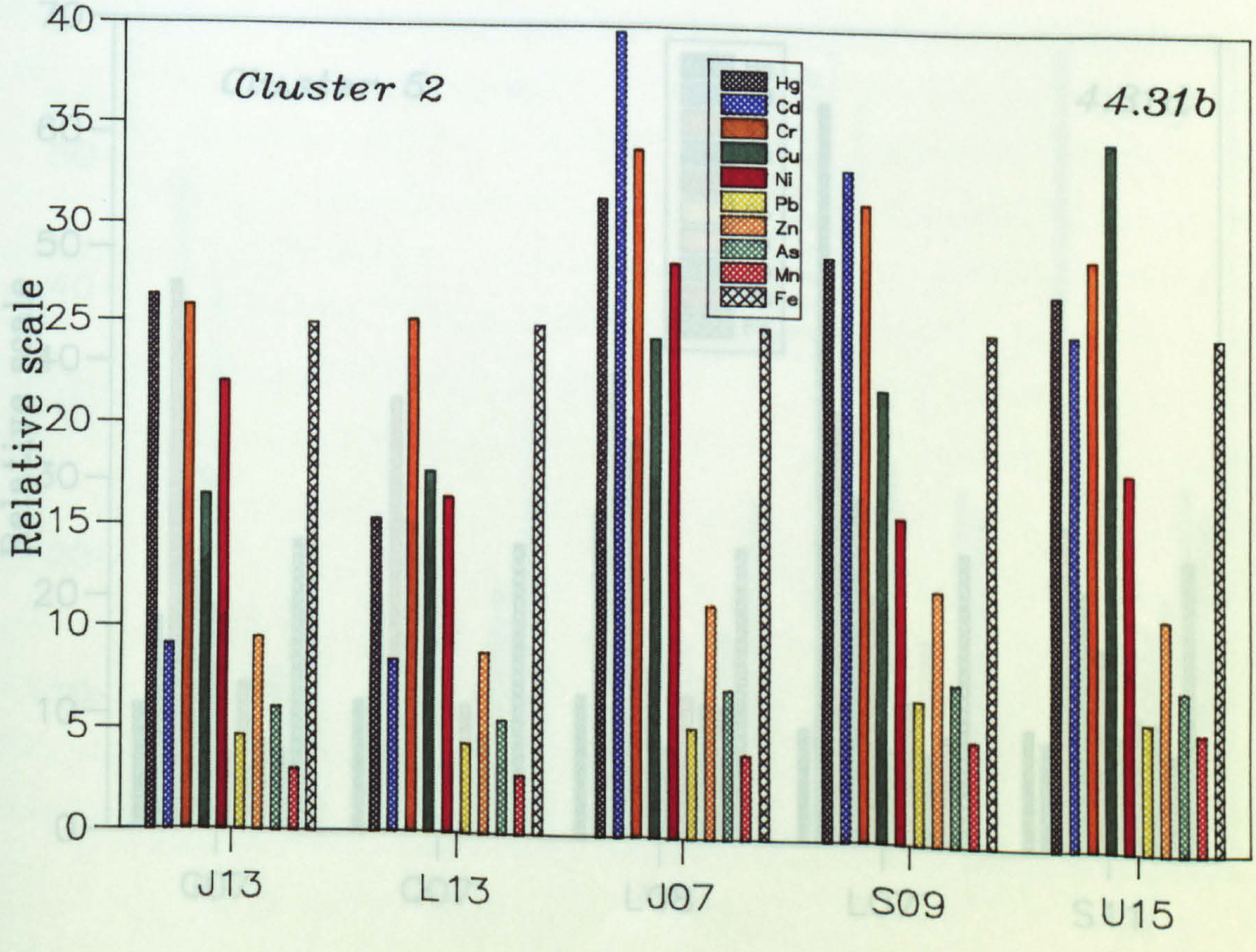
	YY-1	YY-3	U-11	K-9	K-10
YY-1	1.000	0.941	0.888	0.762	0.780
YY-3		1.000	0.867	0.736	0.766
U-11			1.000	0.798	0.758
K-9				1.000	0.791
K-10					1.000

From these coefficients, and from Figure 4.31a it can be seen that the pattern in the elemental relative proportions was very similar in samples YY-1 and YY-3 whereas the most dissimilar samples within this cluster were K-9 and YY-3. Figure 4.31a also shows that all samples within this cluster had a similar pattern in the proportions of nickel, lead, zinc, arsenic, manganese and iron, whereas differences amongst samples within this cluster were due to variations in mercury,

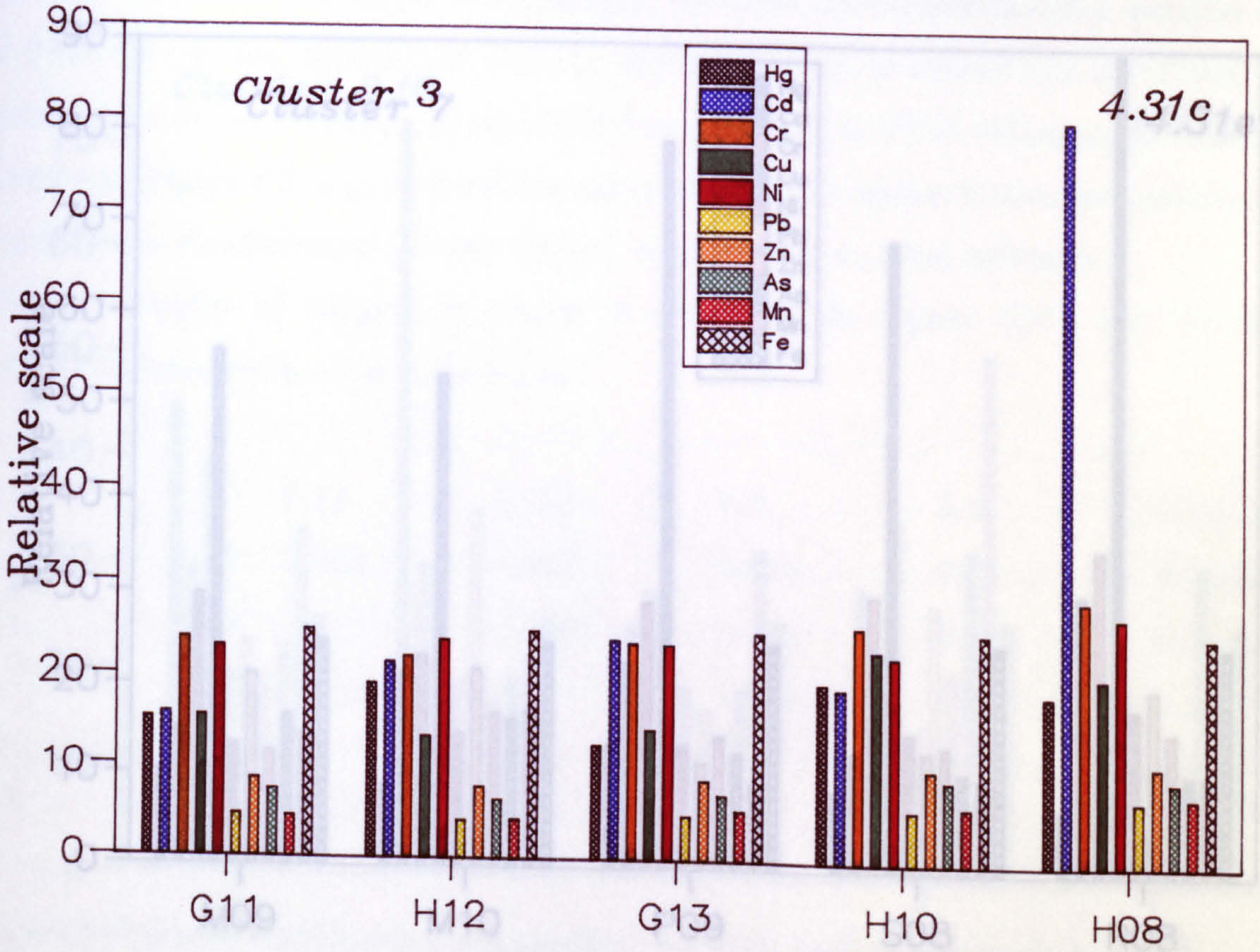
Fig.4.31. Examples of the distribution of the relative concentrations (see text for details on the calculation of these concentrations) of ten elements in fine sediments classified in (a) cluster 1, (b) cluster 2, (c) cluster 3, (d) cluster 5, (e) cluster 7, (f) cluster 8, (g) clusters 9 (samples K-8, P-10 and L-10) and 10 (samples L-9 and Q-9), and (h) samples with the lowest similarity coefficients including G-9 (cluster 9), M-6 (cluster 11), N-10 (cluster 12), P-11 (cluster 6) and T-10 (cluster 4). (see also dendrogram in Fig.4.29a).

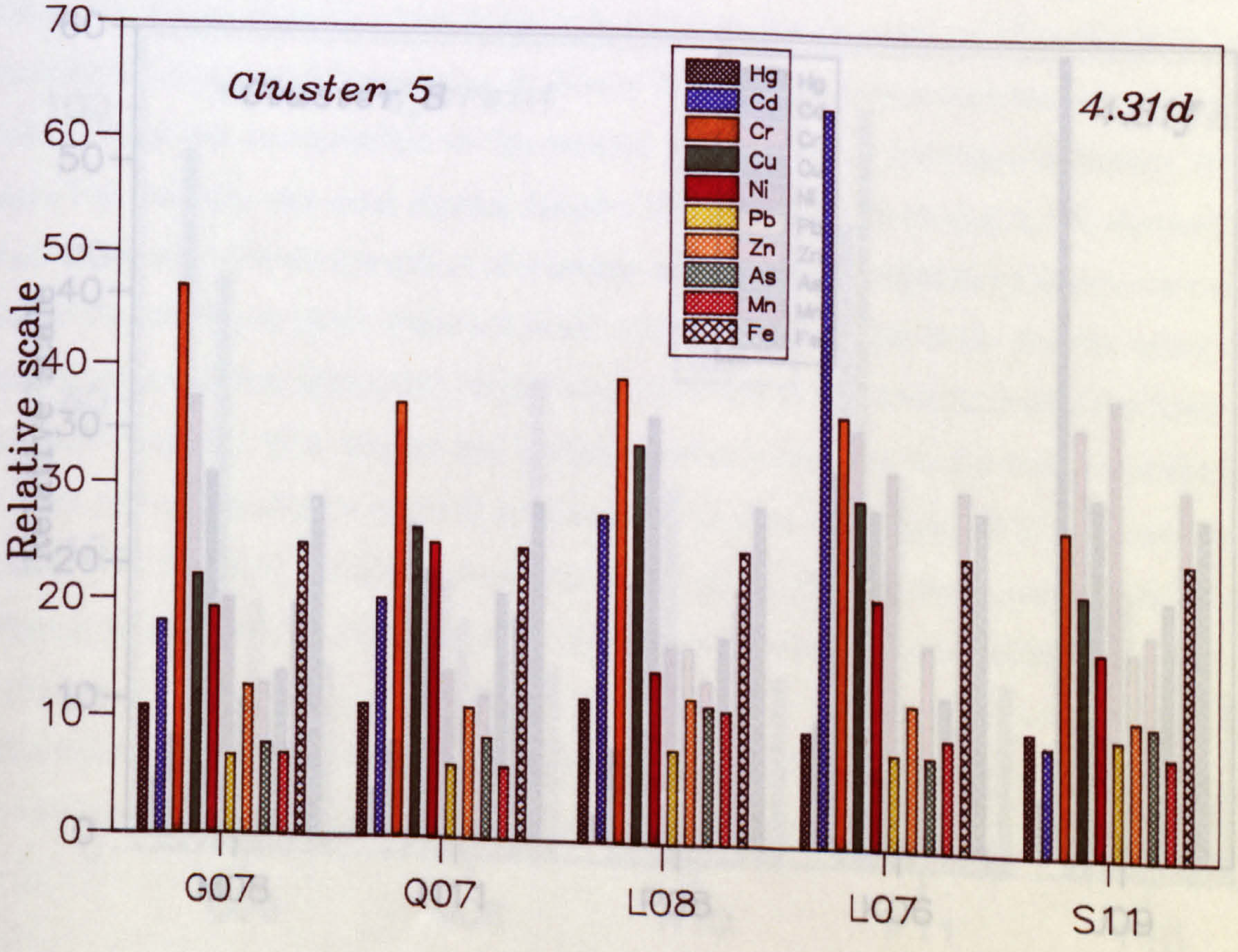


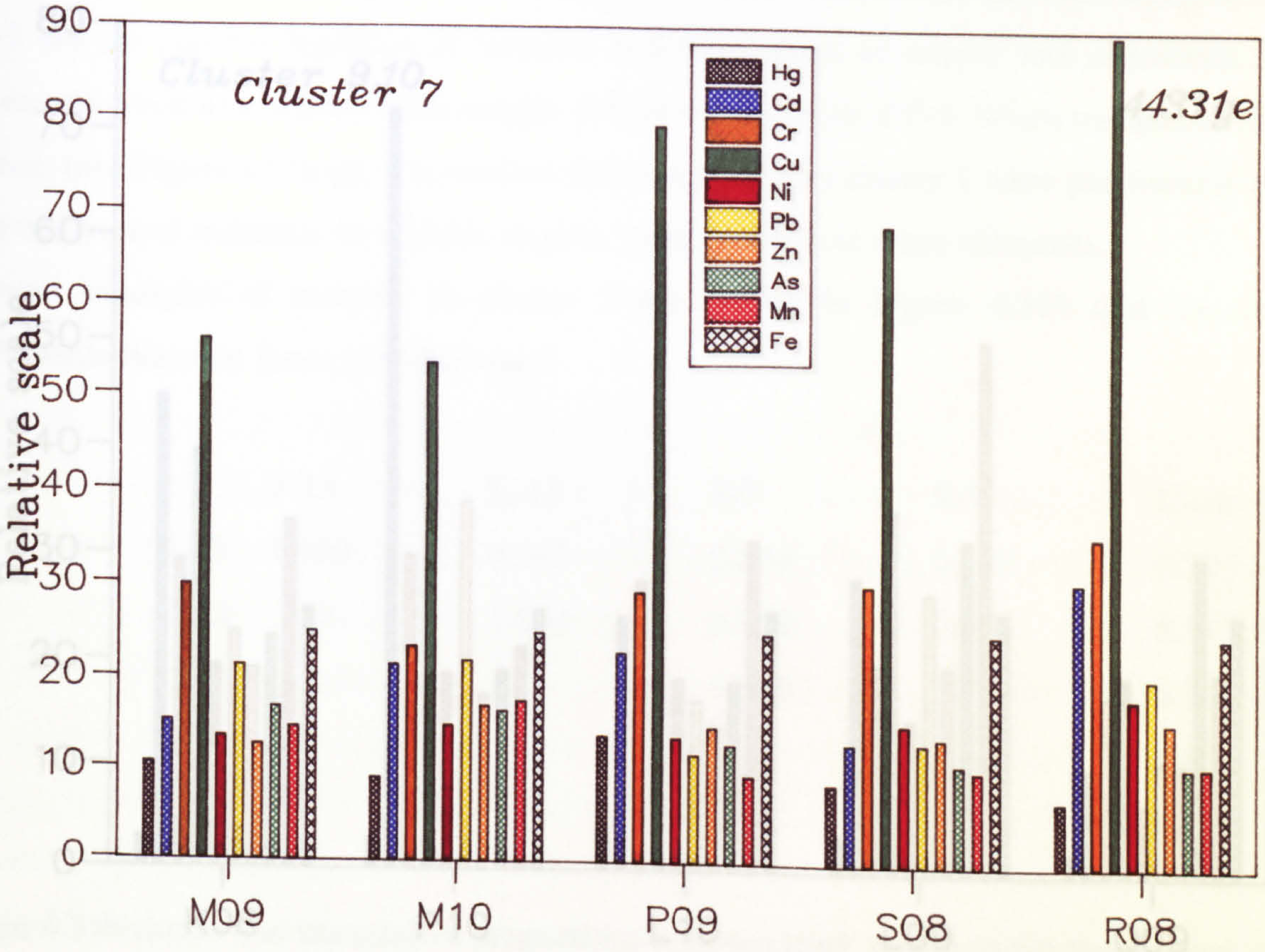
Cluster 1
4.31a
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
Relative scale
0
10
20
30
40
50
60
70
80
90
YY01
YY03
U11
K09
K10

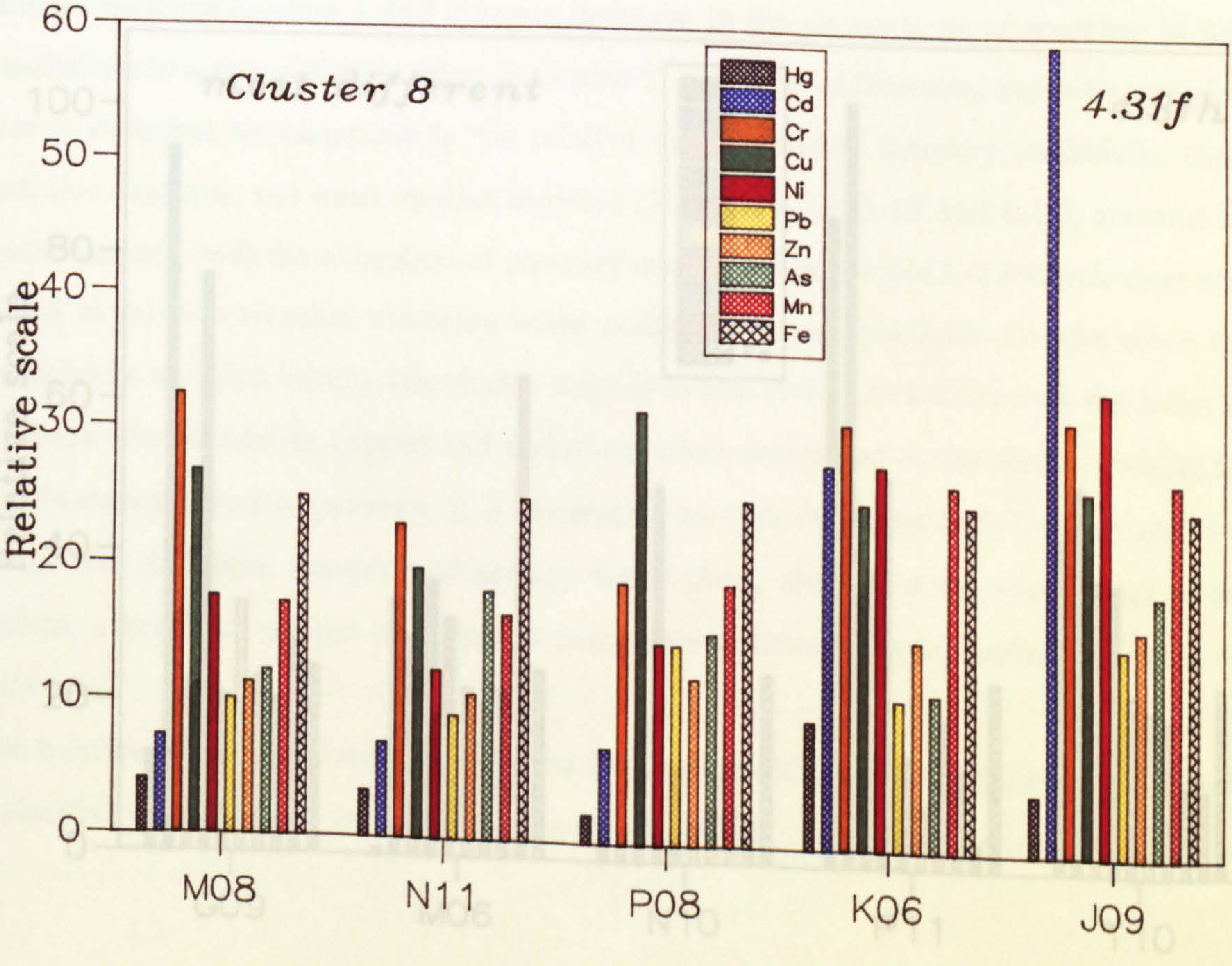


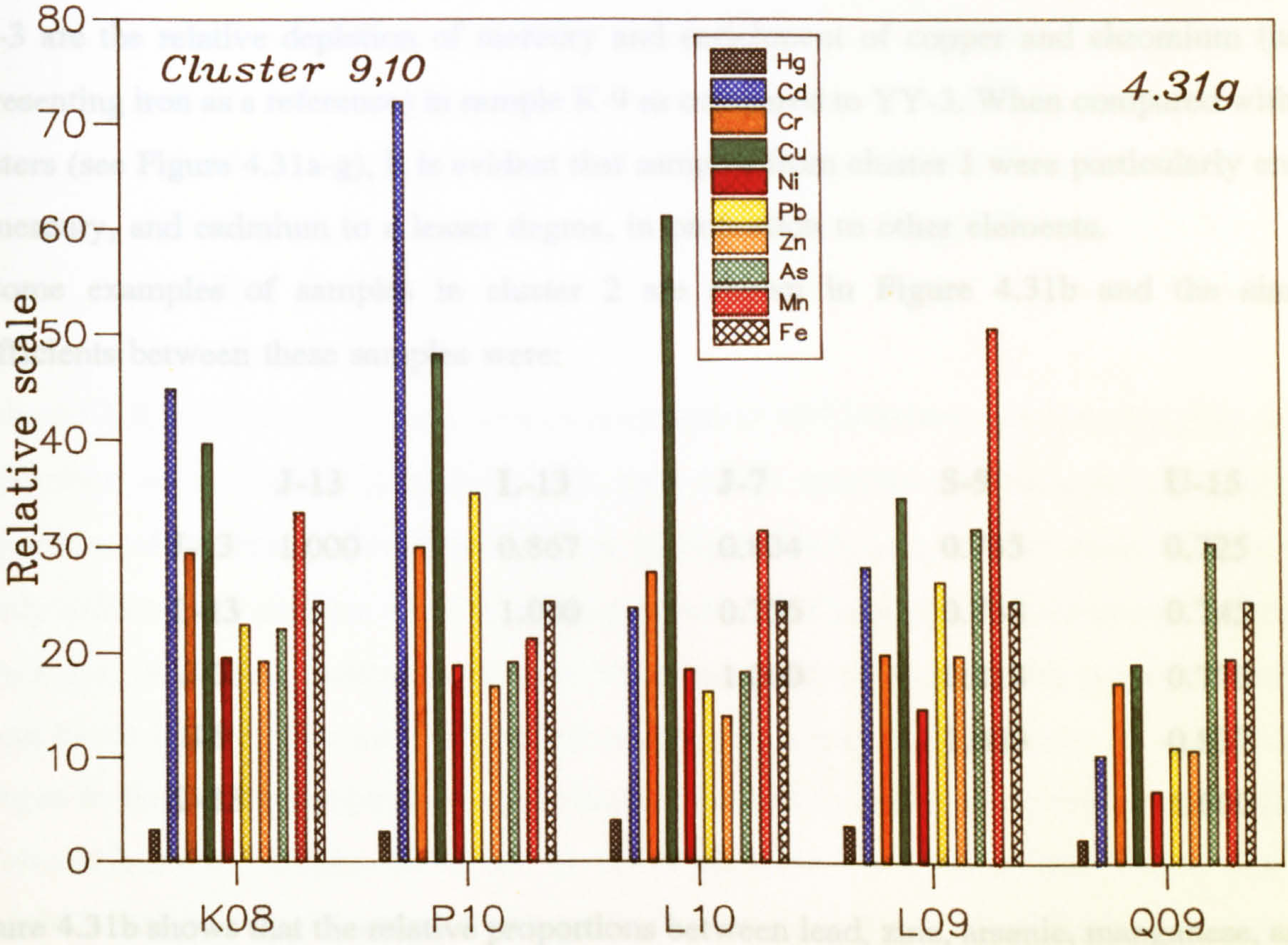
Cluster 2
4.31b
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
Relative scale
0
5
10
15
20
25
30
35
40
J13
L13
J07
S09
U15

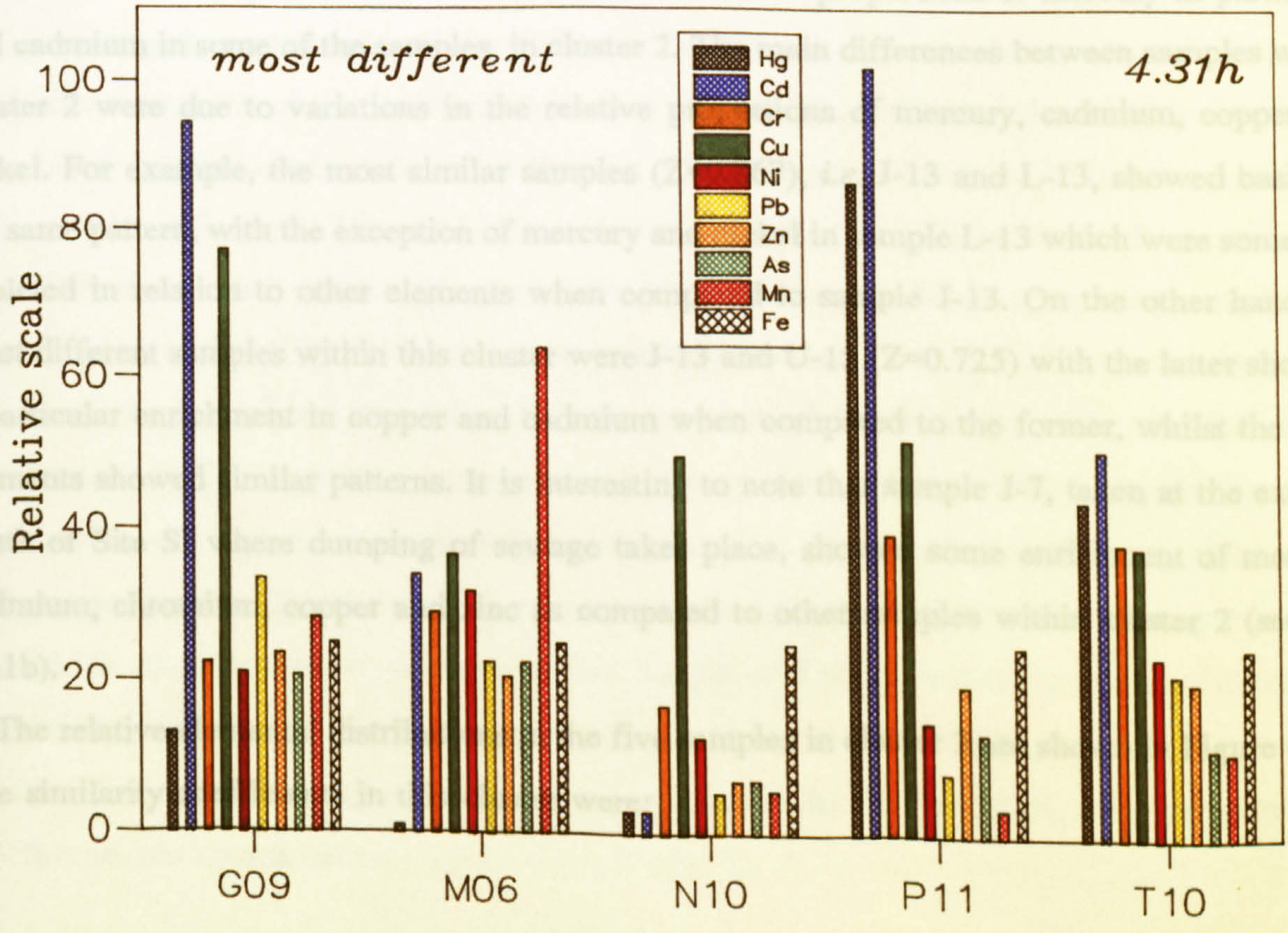

Cluster 3
4.31c
Relative scale
0
10
20
30
40
50
60
70
80
90
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
G11
H12
G13
H10
H08


Cluster 5
4.31d
Relative scale
0
10
20
30
40
50
60
70
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
G07
Q07
L08
L07
S11


Cluster 7
4.31e
Relative scale
0
10
20
30
40
50
60
70
80
90
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
M09
M10
P09
S08
R08


Cluster 8
4.31f
Relative scale
0
10
20
30
40
50
60
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
M08
N11
P08
K06
J09


Cluster 9,10
4.31g
Relative scale
0
10
20
30
40
50
60
70
80
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
K08
P10
L10
L09
Q09


most different
4.31h
Relative scale
0
20
40
60
80
100
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
G09
M06
N10
P11
T10

cadmium, chromium and copper. For example, the main differences between samples K-9 and YY-3 are the relative depletion of mercury and enrichment of copper and chromium (use bar representing iron as a reference) in sample K-9 as compared to YY-3. When compared with other clusters (see Figure 4.31a-g), it is evident that samples from cluster 1 were particularly enriched in mercury, and cadmium to a lesser degree, in proportion to other elements.

Some examples of samples in cluster 2 are shown in Figure 4.31b and the similarity coefficients between these samples were:

	J-13	**L-13**	**J-7**	**S-9**	**U-15**
J-13	1.000	0.867	0.804	0.735	0.725
L-13		1.000	0.756	0.738	0.745
J-7			1.000	0.813	0.770
S-9				1.000	0.837
U-15					1.000

Figure 4.31b shows that the relative proportions between lead, zinc, arsenic, manganese, and iron in all samples from cluster 2 were similar to those shown for cluster 1 (Fig. 4.31a). The main difference between clusters 1 and 2 was a decrease in the proportions of mercury in particular, and cadmium in some of the samples, in cluster 2. The main differences between samples within cluster 2 were due to variations in the relative proportions of mercury, cadmium, copper and nickel. For example, the most similar samples (Z=0.867), *i.e.* J-13 and L-13, showed basically the same pattern, with the exception of mercury and nickel in sample L-13 which were somewhat depleted in relation to other elements when compared to sample J-13. On the other hand, the most different samples within this cluster were J-13 and U-15 (Z=0.725) with the latter showing a particular enrichment in copper and cadmium when compared to the former, whilst the other elements showed similar patterns. It is interesting to note that sample J-7, taken at the extreme south of Site SI where dumping of sewage takes place, showed some enrichment of mercury, cadmium, chromium, copper and zinc as compared to other samples within cluster 2 (see Fig. 4.31b).

The relative elemental distributions in the five samples in cluster 3 are shown in Figure 4.31c. The similarity coefficients in this cluster were:

	G-11	H-12	G-13	H-10	H-8
G-11	1.000	0.867	0.860	0.867	0.769
H-12		1.000	0.864	0.805	0.741
G-13			1.000	0.812	0.803
H-10				1.000	0.791
H-8					1.000

In cluster 3 (Fig. 4.31c) lead, zinc, arsenic, manganese and iron seem to keep roughly the same proportions as in clusters 1 and 2, with only some increase in manganese (compare the proportions of the manganese and lead bars in Figures 4.31a-c). On the other hand, cluster 3 mainly differs from clusters 1 and 2 in the proportions of mercury and chromium which in the former are, in general, lower than in the other two clusters whereas the proportion of nickel seems to be higher. The main variations amongst samples within cluster 3 were related to changes in the relative proportions of cadmium, chromium and copper. For example, the main difference between samples G-11 and H-12 which were the most similar within this cluster (Z=0.867) seems to be a decrease in the proportion of chromium and an increase in cadmium in sample H-12 as compared to sample G-11. The most dissimilar samples within this cluster were H-12 and H-8 (Z=0.741). An obvious enrichment in cadmium can be seen in sample H-8 whereas the remaining elements seem to keep similar proportions in this sample as in sample H-12.

Cluster 4 was one of the "clusters" with only one sample, T-10, and the relative distribution of elements in this sample is shown in Figure 4.31h. This sample showed its highest similarities with samples S-9 (Z=0.775), Q-13 (Z=0.741) and U-15 (Z=0.737) in cluster 2, sample U-11 (Z=0.740) in cluster 1 and sample R-10 (Z=0.736) in cluster 5. When comparing sample T-10 (Fig. 4.31h) with S-9 (Fig. 4.31b), it can be seen that although mercury, cadmium, chromium and copper are more enriched in relation to iron in sample T-10 as compared to sample S-9 (see relative scales), the proportion amongst these elements is roughly similar (although chromium is proportionally higher in sample S-9) in both samples. On the other hand, lead, zinc, arsenic and manganese are also enriched in relation to iron in sample T-10 and lead in particular is enriched in relation to other elements in this sample, and also when compared to clusters 1, 2, 3 and 5.

Five of the seven samples in cluster 5 are shown in Figure 4.31d, and their similarity coefficients are shown below:

	G-7	Q-7	L-8	L-7	S-11
G-7	1.000	0.851	0.773	0.756	0.744
Q-7		1.000	0.788	0.760	0.722
L-8			1.000	0.769	0.742
L-7				1.000	0.717
S-11					1.000

Mercury in cluster 5 was depleted in relation to other elements as compared to clusters 1, 2, 3 and 4. The pattern in the proportions of lead, zinc, arsenic and manganese remains roughly similar to the previously mentioned clusters, particularly to cluster 3, however, more relative variations amongst these elements are observed between samples within cluster 5 than between samples within the other clusters. Other elements within this cluster had also some variations amongst samples. For example, the most similar samples within this cluster were G-7 and Q-7 (Z=0.851); the main difference between these samples was some depletion in chromium and a slight enrichment of copper and nickel in sample Q-7 as compared to G-7. On the other hand, the most dissimilar samples within cluster 5 were L-7 and S-11 (Z=0.717), with sample L-7 showing an enrichment in cadmium in particular and in chromium, copper and nickel as compared to these elements in sample S-11.

Only one sample, P-11, was classified in cluster 6. The elemental relative distributions for this sample are shown in Figure 4.31h. The largest similarities shown by sample P-11 were with samples K-9 (Z=0.741), T-9 (Z=0.755), T-12 (Z=0.720) and T-14 (Z=0.735), all of them being members of cluster 1. From figures 4.31a and h it can be seen that lead, zinc, arsenic and manganese in sample P-11 kept similar proportions amongst each other as compared with samples in cluster 1, although these elements are somewhat enriched in sample P-11 in relation to iron and nickel. The main difference between sample P-11 and those in cluster 1 in general, and sample K-9 in particular, was an enrichment of cadmium in particular, and copper, in comparison with mercury and chromium in sample P-11.

It was mentioned earlier that before all clusters were joined into a single one during the clustering procedure (see dendrogram, Fig. 4.29a), two distinctive large clusters were formed, one including the six clusters previosly described, and the other including clusters 7 to 12. The main difference between these two sets of clusters seems to be the increase in the relative proportions of lead, zinc, arsenic and manganese in relation to the other elements in clusters 7 to 12. From diagrams in Figure 4.31 it can be seen that the roughly constant proportions amongst lead, zinc, arsenic and manganese mantained throughout samples from clusters 1 to 6, has changed and varies throughout samples in clusters 7 to 12.

The main feature in samples of cluster 7 (Fig. 4.31e) is an enrichment in copper in relation to all other elements. Within this cluster, the relative proportions of mercury, cadmium,, chromium, copper and nickel seems to be kept roughly constant, and the main differences between samples within this cluster seem to be mainly related to variations in the proportions of lead, zinc, arsenic and manganese although variations in the proportions of the other elements may be significant in some samples in particular. The similarity coefficients amongst samples within cluster 7 were:

	M-9	M-10	P-9	S-8	R-8
M-9	1.000	0.829	0.742	0.793	0.719
M-10		1.000	0.724	0.758	0.736
P-9			1.000	0.812	0.770
S-8				1.000	0.788
R-8					1.000

The main differences between the two most similar samples within this cluster, M-9 and M-10, seem to be an enrichment in zinc and manganese and some depletion in chromium in sample M-10 as compared to sample M-9. On the other hand, the main differences between the two most dissimilar samples, M-9 and R-8, are due to a decrease in the proportions of arsenic and manganese, and an enrichment in cadmium and copper in particular in sample R-8 as compared to sample M-9. As compared with samples in clusters 1 to 6, most samples in clusters 7 to 12 showed an enrichment of lead in relation to zinc which has been discussed in section 4.2.8.

Five of the seven samples in cluster 8 are shown in Figure 4.31f and their similarity coefficients were:

	M-8	N-11	P-8	K-6	J-9
M-8	1.000	0.824	0.756	0.708	0.703
N-11		1.000	0.766	0.663	0.691
P-8			1.000	0.626	0.659
K-6				1.000	0.743
J-9					1.000

The most similar samples within this cluster, M-8 and N-11, mainly differed due to a relative increase in arsenic, and a decrease in chromium, copper and nickel proportions in sample N-11 as compared with sample M-8. The most dissimilar samples within this cluster were K-6 and P-8 (Z=0.626). When comparing the elemental patterns between these two samples (see Fig 4.31f) it can be seen that it is not simple, as in the previously described clusters, to establish the main similarities which allow them to be classified in the same cluster. In fact, Figure 4.29a shows that the similarities between samples within clusters 7 to 10 are much lower than the similarities between samples within clusters 1 to 5, as roughly indicated by the distance in the vertical scale of this dendrogram. Therefore, at this stage only a rough description of the elemental distributions within clusters 8 to 12 will be given.

Figures 4.31f-h show that manganese was relatively enriched in most samples in clusters 8 to 11, particularly in samples K-6, J-9, K-8, L-10, L-9, G-9 and M-6. In most of these samples arsenic, lead and zinc are also enriched in relation to other elements, particularly when compared with samples in clusters 1 to 6. It can also be seen that there was also an enrichment in cadmium in several of these samples, whereas the proportion of mercury in all of them remained very low. The five samples with the lowest overall similarities, that is, the most different within the whole area, are shown in Figure 4.31h. Sample G-9 had its highest similarities with sample M-10 (Z=0.765) in cluster 7 and P-10 (Z=0.723) in cluster 9. Sample M-6 showed its higher similarity coefficients with sample K-8 (Z=0.727) in cluster 9 and sample L-9 (Z=0.685) in cluster 10. Sample N-10 was the sample with the most different elemental ratios, being most similar to sample S-8 (Z=0.697) in cluster 7 and sample M-8 in cluster 8 (Z=0.691).

The geographical distribution of the cluster memberships shown in Figure 4.30a shows that most of the samples in cluster number 1 were found near the Mersey, however, two samples from Site SI (K-9 and K-10) were also classified in cluster 1. If, as suggested by Anders (1972) and Poulton (1989), similar inter-elemental ratios between sediment samples indicate a common source(s) of these elements, then the fine sediment samples taken from stations K-9 and K-10 may have similar sources than samples near the Mersey. According to the review on sediment transport patterns, near-bottom residual circulation and sewage sludge behaviour after being discharged (see Chapter 2), the possible explanation for finding similar sources in samples near the sewage dumping site and near the Mersey, is that some particles being dumped at Site SI have been deposited within this area whereas some of these particles may have eventually been deposited in muddier areas near the Mersey, particularly in large mud deposits such as those found in the Burbo Bight region.

In order to compare the elemental ratios in the fine sediments with the elemental ratios in the sludge, the similarities between the sludge and sediments were calculated. These similarity coefficients were low, with a range from Z=0.353 with samples M-6 and P-9, to Z=0.525 with sample P-11. Only seven sediment samples, K-9, R-11, and T-9 in cluster 1, L-12, M-11, Q-13 in cluster 2 and P-11 showed similarity coefficients with the digested sewage sludge higher than 0.500. The similarity coefficients amongst these samples were:

	P-11	**M-11**	**L-12**	**Q-13**	**K-9**	**T-9**
Slu.	0.525	0.513	0.512	0.512	0.511	0.506
P-11	1.000	0.702	0.698	0.715	0.741	0.755
M-11		1.000	0.879	0.869	0.815	0.852
L-12			1.000	0.841	0.799	0.847
Q-13				1.000	0.759	0.825
K-9					1.000	0.835

From these coefficients, it can be seen that the similarity amongst sediment samples is higher than the similarity between the samples and the sludge. However, the higher similarity between the sludge and sediments in clusters 1, 2 and 6 as compared in particular with samples in clusters 7 to 12 (the lowest similarities, showing values lower than 0.400, were with samples J-9, M-8, N-11, P-8 in cluster 8; K-8, L-10, P-10 in cluster 9; L-9, Q-9 in cluster 10; M-6 and N-10 in clusters 11 and 12) may suggest that sludge is mainly affecting the element content and ratios in sediments from clusters 1 to 6.

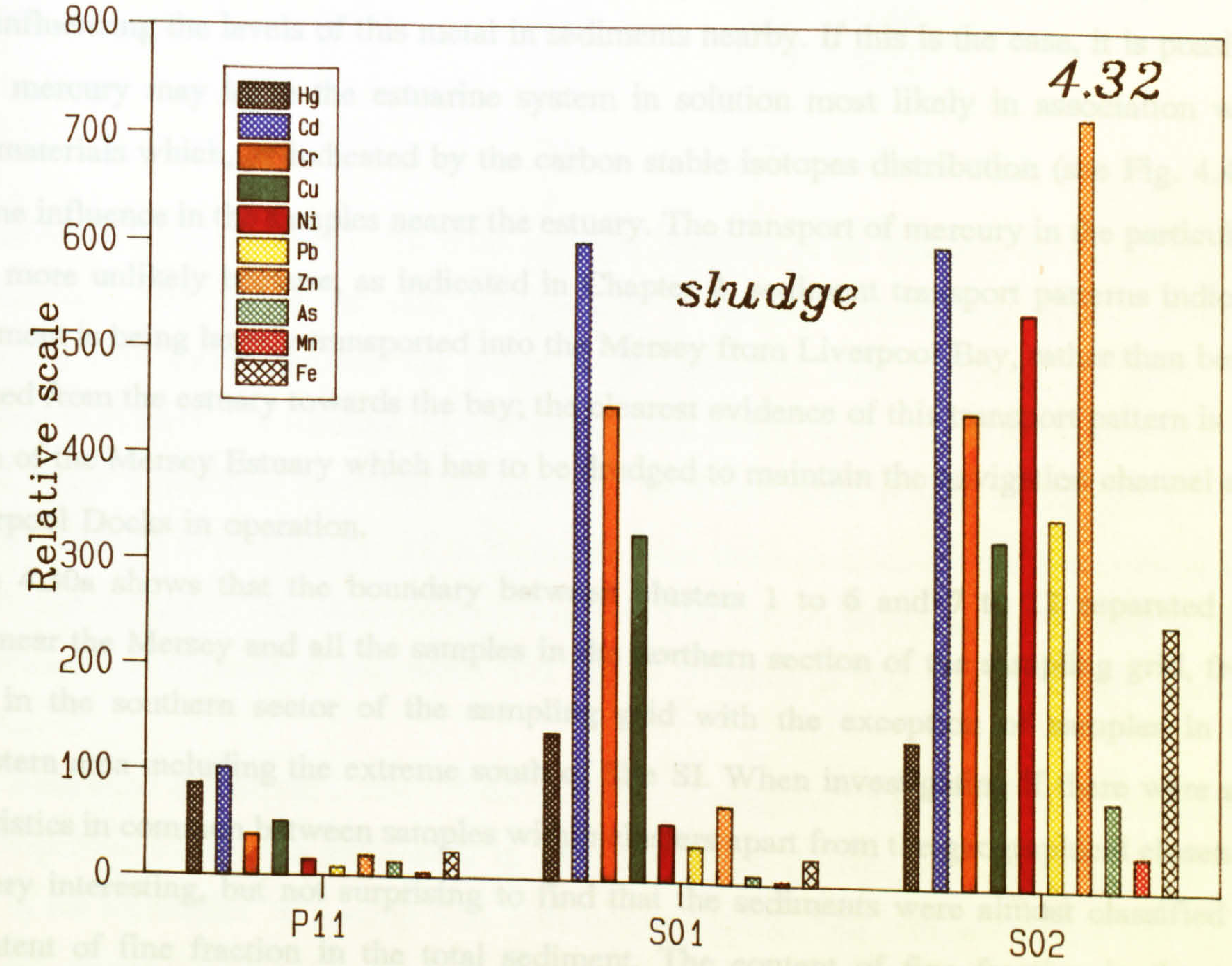
Figure 4.32 shows that the similarity between the sludge and samples in clusters 1, 2 and 6 (see Fig. 4.31a, b and h) may be due to the enrichment of mercury, cadmium, chromium, and copper in relation to nickel, lead, zinc, arsenic, manganese and iron. However, from the comparison of these figures it can be seen that this enrichment is much higher in the sludge than in the sediments. If, based on the similarities, elements in sediments such as K-9 and P-11 largely originate from sewage sludge, then mercury, cadmium, chromium and copper may be lost from the solid phase more rapidly than nickel, lead and zinc, whereas arsenic, manganese and iron do not appear to be significantly altered (note that the proportions between these three elements appear to be similar both in the sludge and in the sediments).

Figure 4.32 shows that cadmium in the sludge is significantly enriched, particularly as compared with mercury. It can be seen, however, that sediments in cluster 1 and 2 (except

Fig.4.32. Distribution of the relative concentrations of ten elements in a digested sewage sludge sample. S01 represents the relative concentrations in the sludge calculated as in the sediment samples and S02 represents the same data as in S01 except for the values of nickel, lead, zinc, arsenic, manganese and iron which are ten times higher than in S01 to facilitate a visual inspection of the pattern. The relative concentrations in the fine fraction of sample P-11 (the most similar to the sludge; see text) were included for a direct comparison of the patterns in sediment and sludge samples.

sample J-7) are more enriched in mercury than in cadmium. If the elements in clusters 1 and 2 largely derive from sludge, then an enrichment in mercury in the sediments as compared to cadmium could be explained by a faster cadmium loss into solution which would not be unexpected because, as indicated in the discussion of cadmium earlier in this chapter (see Section 4.2.3), chloride ions may compete for cadmium with solid phases when these solids are put in contact with seawater. On the other hand, most samples in cluster 1 are close to the Mersey outflow, therefore, it is possible that some mercury from the largely contaminated Mersey Estuary may be influencing the levels of this metal in sediments nearby. If this is the case, it is possible that this mercury may [illegible] the estuarine system in solution most likely in association with organic materials which, [illegible] indicated by the carbon stable isotopes distribution (see Fig. 4.4b), have some influence in the samples nearer the estuary. The transport of mercury in the particulate phase is more unlikely [illegible], as indicated in Chapter [illegible] transport patterns indicate that [illegible] being [illegible] transported into the Mersey from Liverpool Bay, rather than being transported from the estuary towards the bay; the clearest evidence of this transport pattern is the accretion of the Mersey Estuary which has to be dredged to maintain the navigation channel and the Liverpool Docks in operation.

Figure 4.10a shows that the boundary between clusters 1 to 6 and [illegible] separated the samples near the Mersey and all the samples in the northern section of the sampling grid, from samples in the southern sector of the sampling grid with the exception of samples in the southwestern [illegible] including the extreme southern line SI. When investigating if there were any characteristics in common between samples within clusters apart from the [illegible] elements it was very interesting, but not surprising to find that the sediments were almost classified by their content of fine fraction in the total sediment. The content of fine fraction in the total sediment for each sample is given in Appendix B.3. Some statistical descriptives of the fine fraction content in the samples within each cluster are given below:



sample J-7) are more enriched in mercury than in cadmium. If the elements in clusters 1 and 2 largely derive from sludge, then an enrichment in mercury in the sediments as compared to cadmium could be explained by a faster cadmium loss into solution which would not be unexpected because, as indicated in the discussion of cadmium earlier in this chapter (see Section 4.2.3), chloride ions may compete for cadmium with solid phases when these solids are put in contact with seawater. On the other hand, most samples in cluster 1 are close to the Mersey outflow, therefore, it is possible that some mercury from the largely contaminated Mersey Estuary may be influencing the levels of this metal in sediments nearby. If this is the case, it is possible that this mercury may leave the estuarine system in solution most likely in association with organic materials which, as indicated by the carbon stable isotopes distribution (see Fig. 4.4b), have some influence in the samples nearer the estuary. The transport of mercury in the particulate phase is more unlikely because, as indicated in Chapter 2, sediment transport patterns indicate that sediment is being largely transported into the Mersey from Liverpool Bay, rather than being transported from the estuary towards the bay; the clearest evidence of this transport pattern is the accretion of the Mersey Estuary which has to be dredged to maintain the navigation channel and the Liverpool Docks in operation.

Figure 4.30a shows that the boundary between clusters 1 to 6 and 7 to 12 separated the samples near the Mersey and all the samples in the northern section of the sampling grid, from samples in the southern sector of the sampling grid with the exception of samples in the southwestern area including the extreme south of Site SI. When investigating if there were any characteristics in common between samples within clusters apart from the geographical closeness it was very interesting, but not surprising to find that the sediments were almost classified by their content of fine fraction in the total sediment. The content of fine fraction in the total sediment for each sample is given in Appendix B.3. Some statistical descriptives of the fine fraction content in the samples within each cluster are given below:

Cluster	n	mean	s.d.	min.	max.
1	15	20.88	19.29	1.86	61.01
2	18	11.68	6.41	2.01	19.34
3	5	6.64	3.41	1.07	10.28
4	1	0.09	----	----	----
5	7	2.04	1.46	0.78	5.08
6	1	34.34	----	----	----
7	5	0.71	0.20	0.43	0.88
8	7	0.49	0.24	0.16	0.81
9	4	0.26	0.14	0.15	0.46
10	2	0.23	0.11	0.15	0.31
11	1	0.13	----	----	----
12	1	0.59	----	----	----

This observation indicates that, if the ratio amongst elements is an indicator of the sources of these elements, then the grain size composition is largely determining where particles contaminated with these elements are going to be deposited and, therefore, the grain size composition is indirectly controlling the elemental ratios in fine sediments in Liverpool Bay. As elemental ratios in samples classified in clusters 1 to 6 are more similar to the ratios in the sludge than samples in clusters 7 to 12, it is possible that these samples are the most affected by sewage sludge dumping. This observation is supported by reports on sewage sludge being most likely associated to deposits of sediments with higher amounts of fine fraction (see Chapter 2, Section 4.2.4).

It was mentioned in Chapter 2 that Crickmore (1972b) suggested that the seabed composition is more important than zonal differences in current velocity in relation to retention of sludge particles in the sediments. In a study with radiolabelled sludge this author found a correlation between radiotracer distributions and mud zones in Liverpool Bay and that only near the release area (Site SI) was this correlation weaker, suggesting an initial association of the sludge with sediments irrespective of their composition. Sludge particles may initially move as bedload in association with sand deposits in the general south to southeastward direction of sand transport mentioned in Chapter 2, but as the critical tidal shear stress values are exceeded for 60% over sand but never over mud near Site SI, sludge particles resuspension from sand deposits will occur more than half of the time and not at all over muddy deposits due to tidal currents (Rowlatt, 1986). Once resuspended, sludge particles will move in the direction of bottom residual currents towards the east-southeast most of the time (see Chapter 2, Section 2.2.2), and will be deposited in zones were the conditions for mud deposition occur, therefore, becoming preferentially associated to muddy deposits. In contrast to sandy deposits, muddy deposits near the dumpsite will only be disturbed during stormy conditions (Crickmore, 1972b).

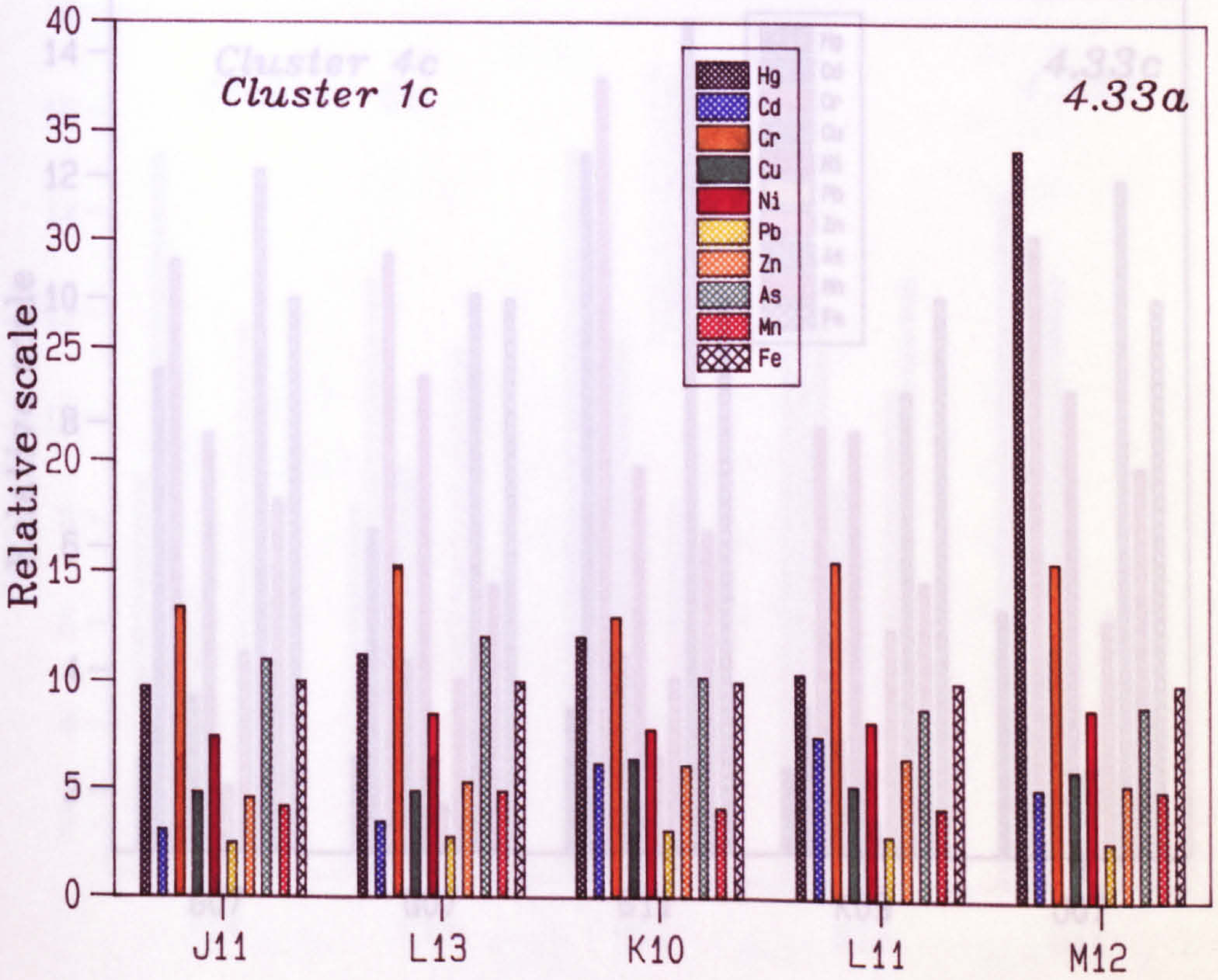
Therefore, the boundary drawn in Figure 4.30a may effectively be representing a boundary between the most affected and the least affected sediments by disposal activities in Liverpool Bay. Most of the samples in clusters 1 to 6 had average fine sediment fraction concentrations higher than 2% whereas all samples in clusters 7 to 12 had fine fraction concentrations below 0.88%. It is interesting to notice that the contents of cadmium and mercury, which may be largely anthropogenic, decreased from cluster 1 to cluster 5 (cluster 6 which was sample P-11, and was the sediment with highest similarity with the sludge, had also its highest similarities with samples from cluster 1), therefore, it seems that the sediments most affected by anthropogenic inputs of trace elements, particularly metals, are those with the highest proportions of fine particles as suggested by Crickmore (1972b). On the other hand, sediments in clusters 7 to 12 may be the ones containing the highest proportion of "naturally" derived elements, as indicated by an enrichment of arsenic and manganese in particular, which are not particularly enriched in the sewage sludge in relation to other elements (compare Fig. 4.31e-h with Fig. 4.32). Another interesting feature in Figure 4.30a is that there is a small area in the southern extreme of Site SI within the suggested boundary of most contaminated sediments, this contaminated region probably indicates the effect of the recent trend of sewage sludge disposal which only started early in 1988, few months before samples were taken for the present study.

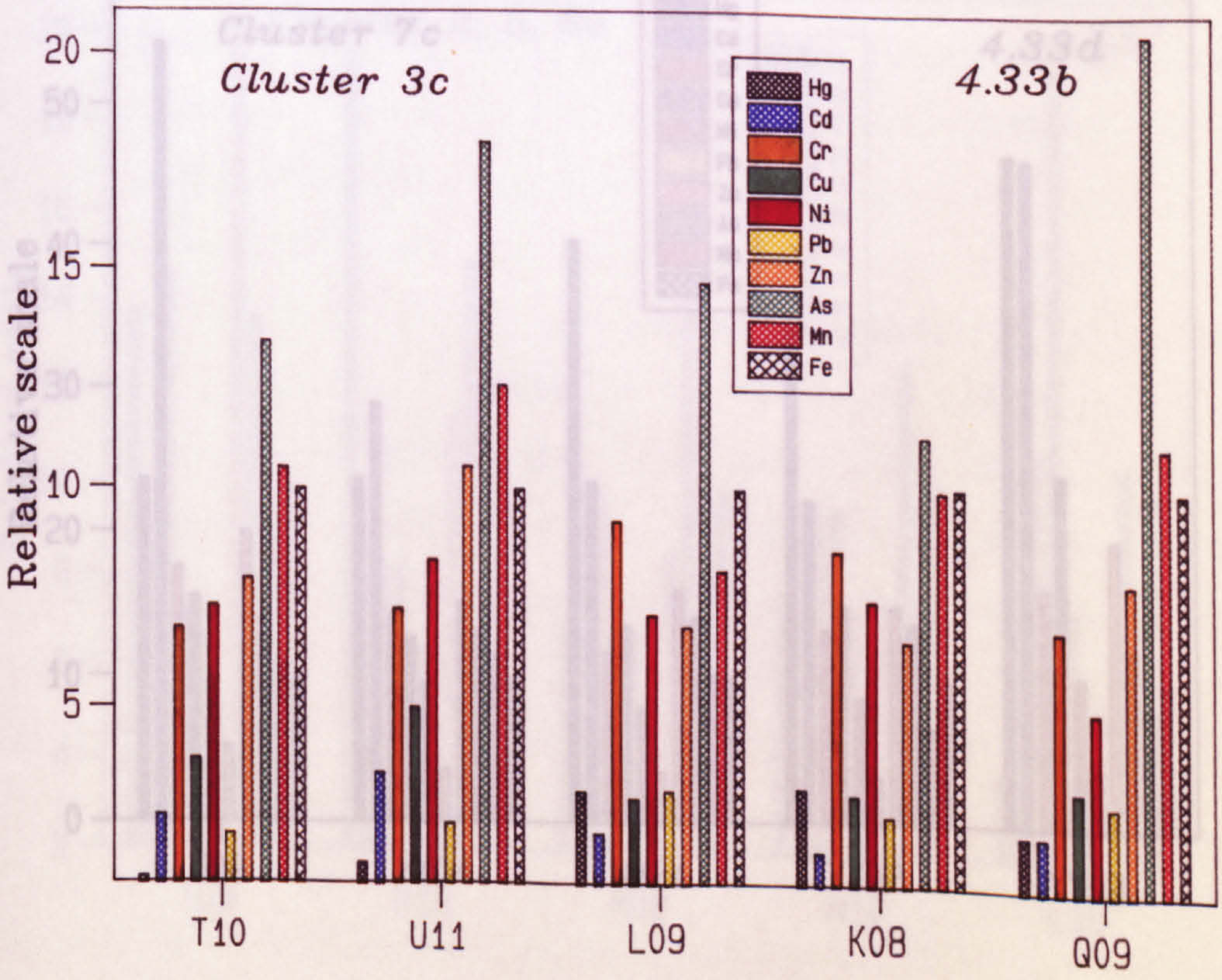
Regarding the elemental ratios in the coarse fraction, Figure 4.29b shows the dendrogram obtained for the clustering procedure which indicates that eight clusters could be clearly identified in this fraction. Only cluster number 6 contained a single sediment sample (L-10), whereas clusters number 5 and 2 contained two and three samples respectively. Some examples of the similarity coefficients between samples within each cluster are given below, and the bar diagrams for these samples are plotted in Figure 4.33a-f.

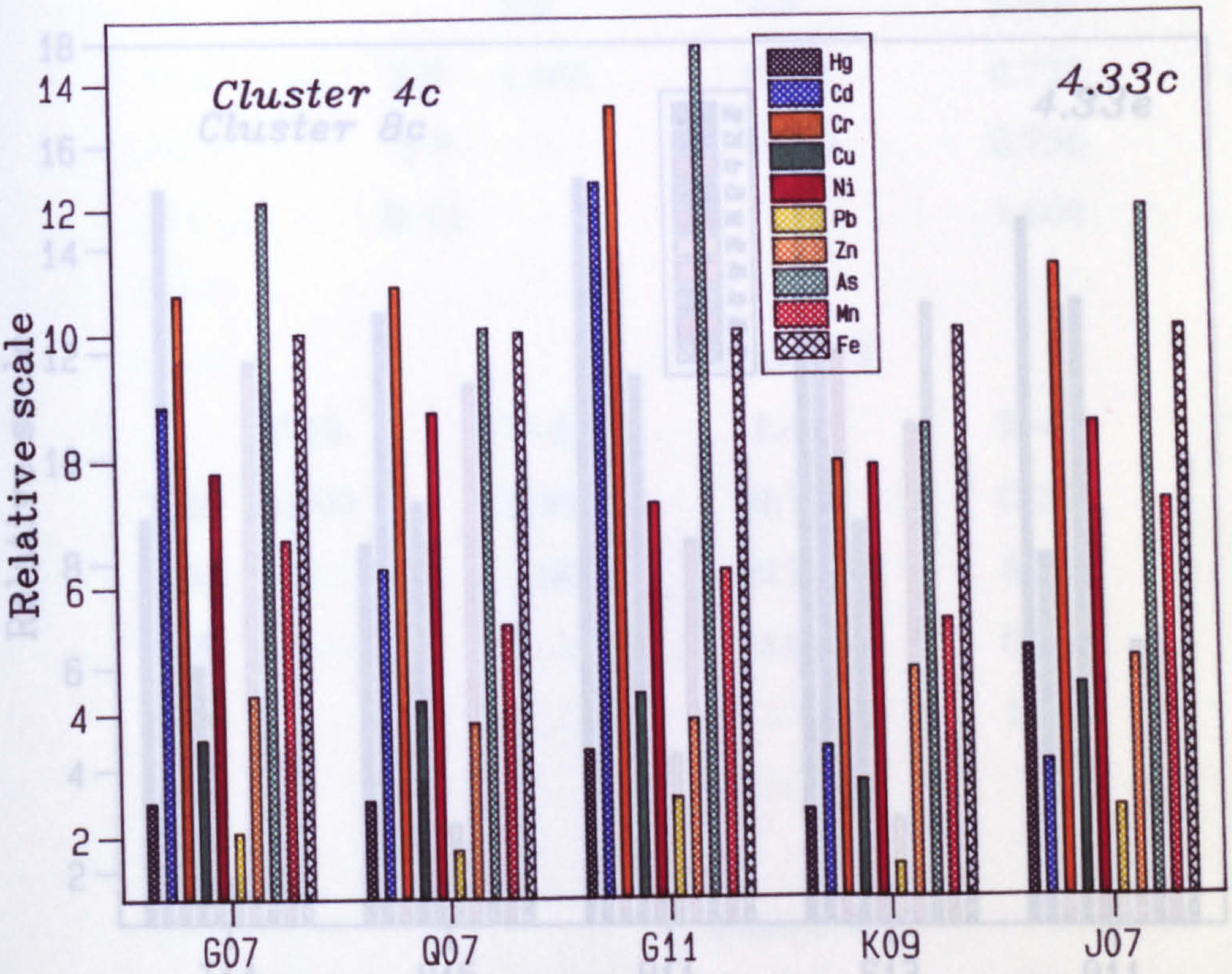
Cluster 1

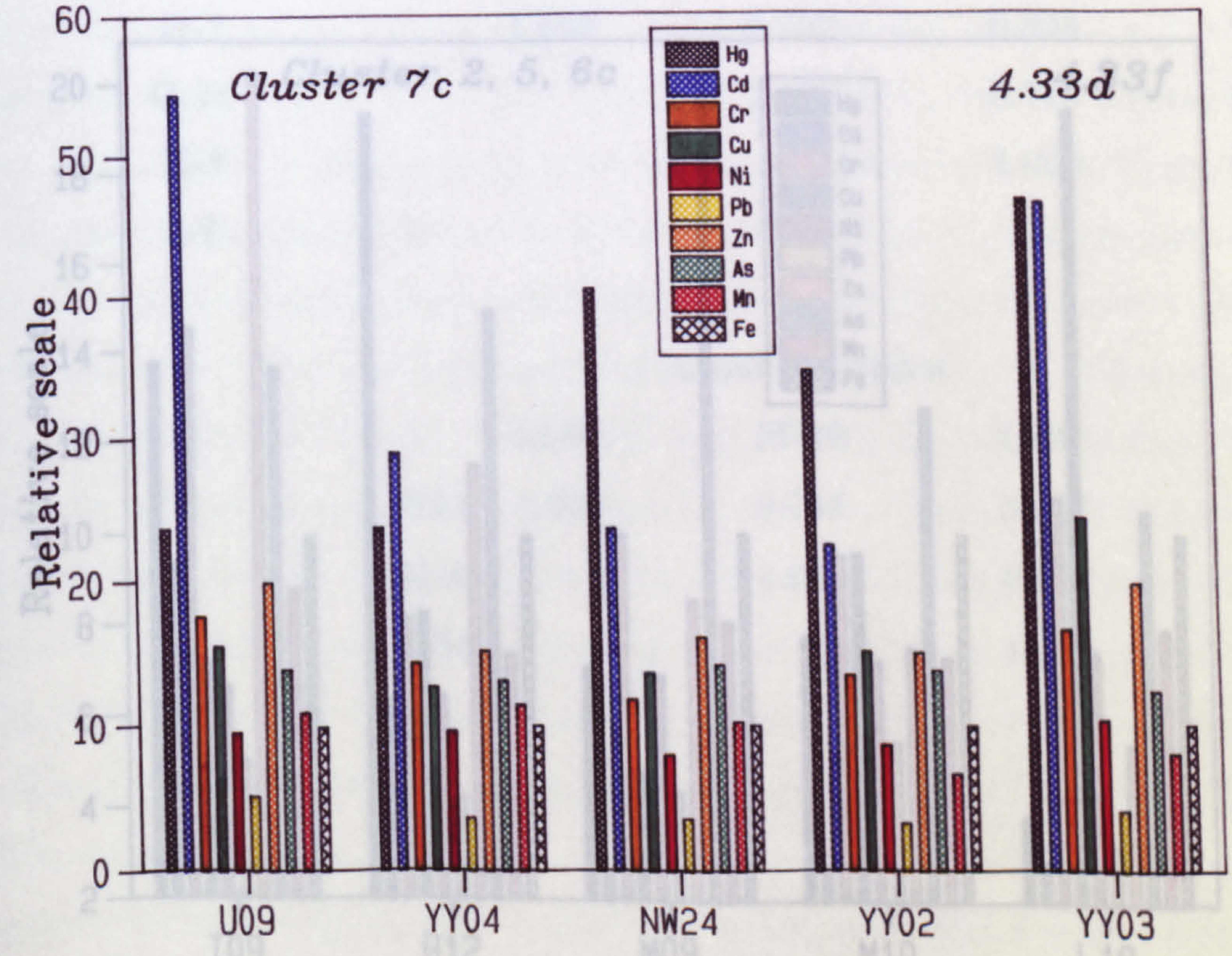
	J-11	**L-13**	**K-10**	**L-11**	**M-12**
J-11	1.000	0.943	0.814	0.803	0.767
L-13		1.000	0.807	0.804	0.780
K-10			1.000	0.868	0.780
L-11				1.000	0.787
M-12					1.000

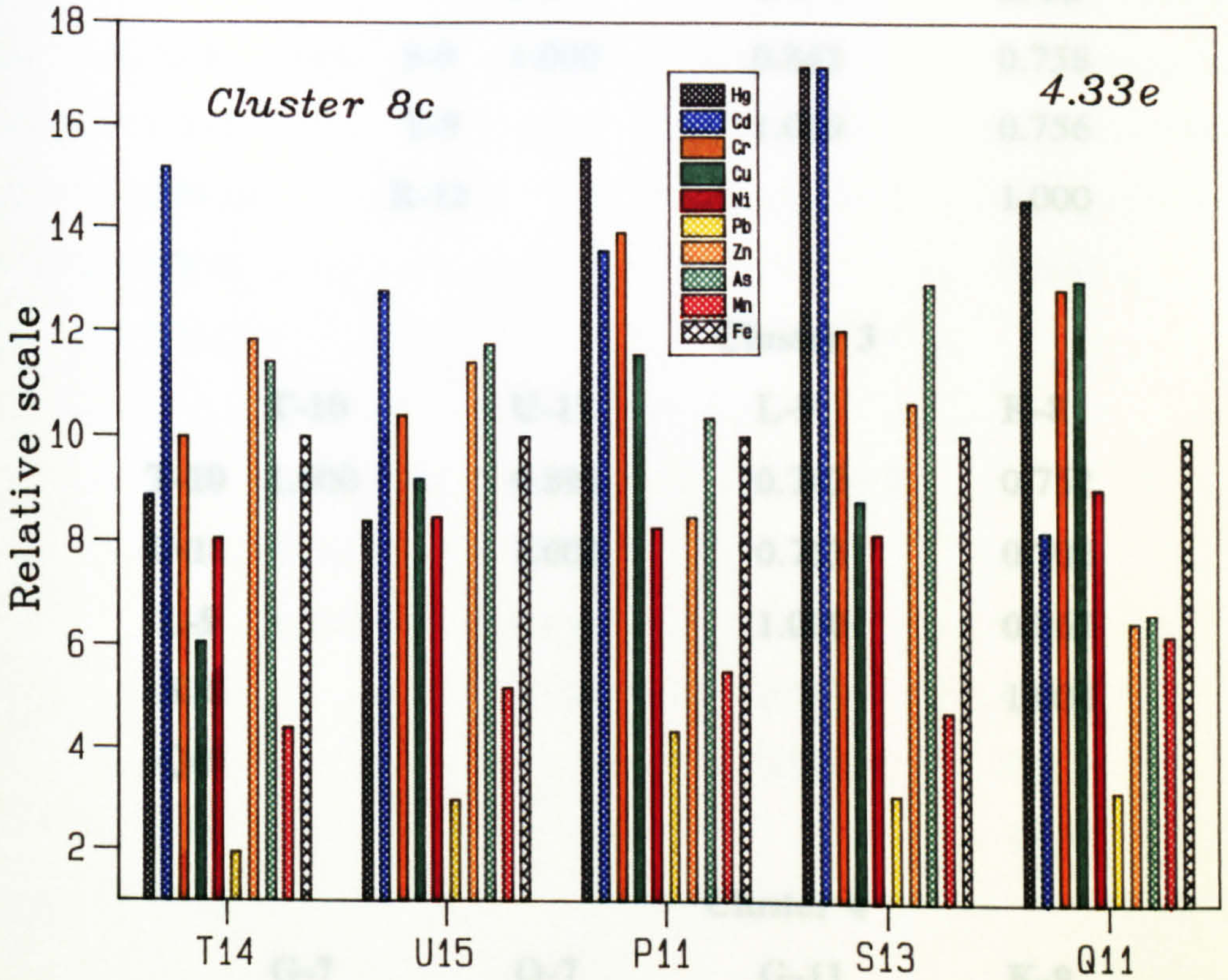
Fig.4.33. Examples of the distribution of the relative concentrations of ten elements (see text) in the coarse sediments classified in (a) cluster 1, (b) cluster 3, (c) cluster 4, (d) cluster 7, (e) cluster 8 and (f) clusters 2 (samples T-9 and R-12), 5 (samples M-9 and M-10) and 6 (sample L-10). (see also dendrogram in Fig.4.29b).

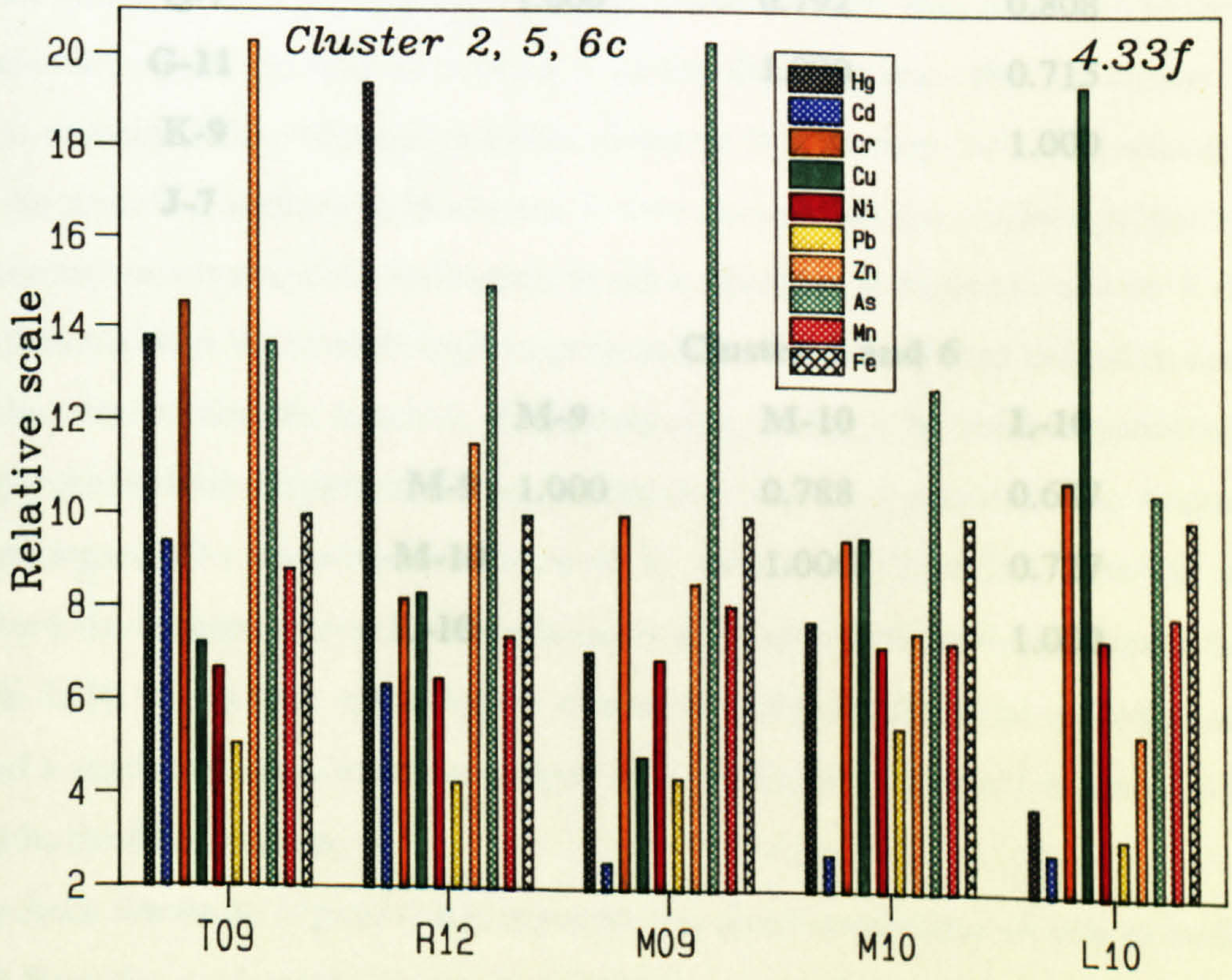

Cluster 1c
4.33a
Relative scale
0
5
10
15
20
25
30
35
40
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
J11
L13
K10
L11
M12


Cluster 3c
4.33b
Relative scale
5
10
15
20
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
T10
U11
L09
K08
Q09


Cluster 4c
4.33c
Relative scale
2
4
6
8
10
12
14
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
G07
Q07
G11
K09
J07


Cluster 7c
4.33d
Relative scale
0
10
20
30
40
50
60
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
U09
YY04
NW24
YY02
YY03


Cluster 8c
4.33e
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
Relative scale
18
16
14
12
10
8
6
4
2
T14
U15
P11
S13
Q11


Cluster 2, 5, 6c
4.33f
Hg
Cd
Cr
Cu
Ni
Pb
Zn
As
Mn
Fe
Relative scale
20
18
16
14
12
10
8
6
4
2
T09
R12
M09
M10
L10

Cluster 2

	S-9	T-9	R-12
S-9	1.000	0.842	0.758
T-9		1.000	0.756
R-12			1.000

Cluster 3

	T-10	U-11	L-9	K-8	Q-9
T-10	1.000	0.891	0.742	0.752	0.764
U-11		1.000	0.713	0.706	0.751
L-9			1.000	0.865	0.791
K-8				1.000	0.767
Q-9					1.000

Cluster 4

	G-7	Q-7	G-11	K-9	J-7
G-7	1.000	0.850	0.848	0.791	0.776
Q-7		1.000	0.792	0.808	0.763
G-11			1.000	0.715	0.742
K-9				1.000	0.789
J-7					1.000

Cluster 5 and 6

	M-9	M-10	L-10
M-9	1.000	0.788	0.687
M-10		1.000	0.727
L-10			1.000

Cluster 7

	U-9	YY-4	NW24	YY-2	YY-3
U-9	1.000	0.824	0.751	0.744	0.778
YY-4		1.000	0.833	0.806	0.748
NW24			1.000	0.862	0.766
YY-2				1.000	0.811
YY-3					1.000

Cluster 8

	T-14	U-15	P-11	S-13	Q-11
T-14	1.000	0.836	0.718	0.803	0.670
U-15		1.000	0.781	0.826	0.721
P-11			1.000	0.811	0.800
S-13				1.000	0.719
Q-11					1.000

Figure 4.30b shows the geographical distribution of the cluster memberships in the coarse fraction. When compared with Figure 4.30a it can be seen that cluster 7 in the coarse fraction corresponded approximately to cluster 1 in the fine fraction, that is, cluster 7 in the coarse fraction contained the sediment samples closer to the Mersey outfall. Looking at Figure 4.33d it can be seen that sediments in cluster 7 were those with the highest proportions of cadmium and mercury as compared to sediments in other clusters. Samples in cluster 8 (Fig. 4.33e) were the sediments with the second highest proportions of mercury and cadmium and were followed by sediments in clusters 1 and 2. It appears that, judging by the proportions of the elements amongst the various clusters in the coarse fraction, cluster 7 contained the coarse sediments with highest degree of contamination followed by clusters 8, 2 and 1, whereas clusters 3 and 4 contained the highest proportions of elements such as arsenic and manganese (see Fig. 4.33a-f). Sample L-10 which was classified in cluster 6 and was the most different to other samples, showed a particular enrichment in copper such as the one showed for samples in cluster 7 (Fig. 4.31e) in the fine fraction.

The lines drawn in Figure 4.30b separate the most contaminated coarse sediments (cluster 7 and 8) from the moderately contaminated (clusters 1 and 2) and the least contaminated (clusters 3, 4, 5 and 6). Not surprisingly, the most contaminated coarse particles were those in sediments with the highest proportions of fine material, which, as already mentioned in previous sections in this chapter, seem to be the source of several of the trace elements in coarse particles. As in the case of the fine fraction, and also indicated by the similarity in the boundaries drawn in Figures 4.30a and b, the cluster analysis for the coarse fraction separated the samples in clusters by their amount of fine fraction in the total sediment. Some statistical descriptives for the amount of fine fraction in each cluster for the coarse fraction is given below:

Cluster	n	mean	s.d.	min.	max.
1	15	13.58	5.20	7.79	19.99
2	3	5.39	3.10	2.01	8.07
3	9	0.79	0.87	0.09	2.57
4	23	1.82	2.19	0.13	7.05
5	2	0.84	0.01	0.83	0.85
6	1	0.46	----	----	----
7	7	36.69	16.90	14.54	61.01
8	7	12.35	11.10	3.35	34.34

In order to compare the similarity in the elemental ratios between the fine particles and the coarse particles within sediments, a set of 25 sediments with a wide range of fine fraction proportions were selected and the ratio matching and cluster analysis was performed on both fractions in each sample. Figure 4.29c showing the resulting dendrogram from this analysis clearly indicates that 2 main clusters were formed during this procedure, one containing all the fine fractions and the other one containing all the coarse fractions except those in samples YY-1 and YY-3. These results indicate that the elemental ratios in each fraction are, in general, significantly different from one another, which according to the basic hypothesis of this method, would indicate different sources of these elements for each fraction. The most similar fine and coarse fractions were those of samples YY-1 (Z=0.684) and YY-3 (0.704). These samples were those with the highest amounts of fine particles in the total sediments (61.0 and 57.6% respectively), which indicates that the proportions of elements are roughly preserved when these elements are transferred from fine particles to coarse particles in muddy sediments. On the other hand, the similarities between fine and coarse particles in other samples even with relatively high amounts of fine fraction were not high enough to be classified in the same cluster, for example, sample P-11 showing one of the most contaminated fine fractions, and containing relatively high amounts of these particles within the total sediment (34.3%), showed a similarity between fine and coarse fractions of Z=0.568. Other samples with contaminated fine fractions (classified in cluster 1) such as K-9 and K-10 (containing 2.2 and 10.4% of fine fraction respectively), also showed relatively low similarity coefficients (Z=0.463 and Z=0.581 respectively). Not surprisingly, sediments with very low amounts of fine material also showed relatively low similarity coefficients between the coarse and fine fractions. For example, samples G-9, L-9 and M-6 containing 0.21, 0.15 and 0.13% of fine fraction showed coefficients of Z=0.476, 0.540 and 0.497 respectively.

It is expected that in sediments with largest amounts of fine material, the coexistence between fine and coarse particles is longer than in sediments with small amounts of fine material because, as described in Chapter 2, once deposited muddy sediments are more difficult to erode than relatively clean sands as the cohesive forces between clay particles in muddy deposits plays a significant role. Therefore, coarse particles in sediments with a high amount of fine particles are not only more enriched in trace elements because they coexist with a larger amount of fines, but also because they coexist for much longer than fine and coarse particles in sandy deposits. Therefore, the longer coexistence of particles of different sizes in muddy deposits favours a more homogeneous distribution of the elements amongst these particles, resulting in higher similarity coefficients between fine and coarse particles such as those found in samples YY-1 and YY-3.

4.4. CONCLUSIONS

There is a general trend in the distribution of fine sediments in Liverpool Bay. Intermediate values (5-10%) are found in the northern areas with a decrease towards the North Wales coast to values below 1%. The distribution of muddy deposits is erratic although the muddy banks near the Burbo Bight appear to be a permanent feature.

The aluminium content suggests that the <90 μm fraction in sediments with lower amounts of fine particles (e.g. those from the southern region) has a higher proportion of clay than the <90 μm fraction of sediments with higher amounts of fines (e.g. those from the muddy areas in the Burbo Bank).

There was a negative correlation between organic carbon (and also iron and manganese) in fine particles and the amount of fine particles in the sediments. This agrees with a possible higher amount of clay in the fine fraction of sediments lower in fines, which provides a higher surface area for the formation of organic and inorganic coatings. However, the scatter in the relationship between organic carbon and grain size, and the distribution of $\delta^{13}C$ values may suggest that inputs from various sources (e.g. waste disposal, riverine and autochthonous) overshadow any clear trend between the available surface area and the amount of carbon in the sediments.

In sediments with more than 5% of <90 μm particles, the organic carbon content in coarse sediments was correlated with the amount of fine particles in the sample suggesting a possible transfer from fine particles toward coarse particles.

Mercury was the only trace element correlated with the fine sediment fraction distribution. This element also showed a low but significant correlation with $\delta^{13}C$. These observations are consistent with the anthropogenic origin of this metal, which is transported into the Bay mainly via the Mersey outfall and the disposal of sewage sludge at Site SI. Mercury may be particularly associated with the land derived fraction of the sedimentary organic matter. This may explain the lack of correlation between mercury and organic carbon which is often reported in aquatic sediments. This relationship was, however, observed in the coarse sedimentary fraction.

Arsenic was highly correlated with iron and manganese in fine and coarse sediments in agreement with the reported strong association of arsenic with iron/manganese oxyhydroxides. It is suggested that, in contrast to mercury, arsenic is mainly transported into the bay from natural sources such as the mineralized areas in North Wales. Other trace elements in this study such as lead and zinc, which may be largely derived from anthropogenic inputs, may also have some inputs from similar sources as arsenic.

Although cadmium is mainly derived from anthropogenic sources, and may be preferentially associated with the land derived organic matter in fine sediments, it shows a different distribution as compared with mercury. This difference is due to the different geochemical behaviour between these two metals, as mercury tends to remain strongly associated with particles whereas cadmium tends to desorb from particles when there is an increase in salinity.

Copper, chromium, and in a lower degree nickel, were correlated with organic carbon, iron and manganese in fine sediments suggesting a partitioning of these elements among organic and inorganic sedimentary phases. As in the case of cadmium, the role of the dissolved phase in the geochemistries of copper and nickel may be important, as redissolution may be significant. Although copper in Liverpool Bay sediments may largely result from sewage sludge inputs, there is a possibility of natural inputs from mineralized areas.

The correlation analysis suggests that the organic phases are the main trace metal carrier on coarse particles in Liverpool Bay. Only lead and zinc showed some degree of correlation with iron and manganese, which indicates a possible partitioning of these metals between organic and inorganic phases in coarse particles. The correlation of most of the trace metals in the coarse fraction with the amount of fine sediments suggests a possible transfer from fine particles toward coarse particles.

From the above it is concluded that the geochemical behaviour of elements in Liverpool Bay has to be better understood for a proper explanation of their observed distributions in superficial sediments in this complex area.

5. POLYCHLORINATED BIPHENYLS (PCBs)

5.1. VALIDATION OF THE METHOD

The occurrence of PCBs in environmental samples has been reported for more than two decades since they were first reported by Jensen (1966), however, it is only during the past ten years, and the last five years in particular, that the need for analysing these xenobiotics at the individual congener level has been recognised. Recent studies report various analytical procedures and there is, at present, no standard analytical method for the analysis of chlorobiphenyl congeners in environmental samples which has been adopted by a large number of laboratories at an international level. Therefore, in order to accurately determine the PCB composition in environmental samples, both qualitatively and quantitatively, each laboratory has to perform a careful evaluation of each step in the analytical procedure.

In this section, the chromatographic analysis of the various PCB congeners determined in this work is discussed, and this discussion is followed by some comments on the results of the analysis of sediment reference materials which can be used as indicators of the quality of the sample preparation procedure prior to the chromatographic analysis.

5.1.1. Chromatographic analysis of individual PCB congeners

Due to the worldwide use of PCBs in large quantities in the past, a widespread contamination of these xenobiotics has been detected including remote areas such as the polar regions and open ocean environments (see Tanabe, 1988, and references therein). As PCBs consist of a total of 209 theoretically possible congeners having different toxicological and biological responses (Tanabe, 1988) and as a large number of these theoretically possible congeners has been reported in various environmental samples, their accurate analysis becomes necessary. More important from the point of view of the present study, an accurate analysis of various PCB congeners was necessary because of the wide range of physicochemical properties (eg. water solubility and octanol-water partition coefficients) presented by this family of organic compounds which may lead to different geochemical behaviours (see Brownawell and Farrington, 1986 and references therein) between different congeners.

It was mentioned in the general introduction (see Chapter 1) that the common practice throughout the 1970s and early 1980s was to quantify PCBs in the environment by comparing their packed column gas chromatograms with the patterns exhibited by known amounts of individual commercial PCB formulations for example Aroclor 1254, or mixtures of these formulations such as Aroclor 1242 + 1254 + 1260 (Jones, 1988). This method of identification and quantification of PCBs relies upon matching the pattern or "fingerprint" observed in the sample against the pattern observed in a single or a mixture of commercial formulations. However, if the chromatograms of PCBs in the environmental samples can not be matched against commercial formulations, then the quantification is not possible (Jones, 1988). Due to the differences in biological, chemical and physical properties amongst PCB congeners and isomers, which lead to different degrees of partitioning amongst environmental compartments and also to different degrees of degradation, biological uptake, metabolism, etc., PCB patterns usually differ between environmental compartments as well as between animal species (Boon and Duinker, 1986), therefore, environmental samples can not often be adequately described by any commercial formulation or mixture of formulations and it would be inappropriate to report these sample PCB residues as, for example, Aroclor equivalents or Aroclor mixtures (Jones, 1988). On the other hand, high similarities in the patterns with the use of packed columns do not guarantee a high similarity in the actual congener composition (Boon and Duinker, 1986). Therefore, information regarding PCB composition in environmental samples obtained by packed column gas-chromatography can only be regarded as semiquantitative and semiqualitative.

The ambiguities associated with results obtained by packed column gas-chromatography have been overcome by the introduction of high resolution gas-chromatographic techniques aiming to determine individual PCB congeners as well defined chemical entities (Duinker *et al.*, 1988). An interesting review regarding recent advances in the analytical instrumentation side (e.g. development of capillary columns and improvement in detection systems), which has lead to higher accuracy and precision in congener-specific PCB determinations has been presented by Pellizary *et al.* (1985).

The accurate determination of specific congeners also requires the availability of these congeners for the calibration of the gas-chromatograph. Since the excellent work by Mullin *et al.* (1984) in which the synthesis, relative retention times (on a 50 m, SE-54 fused silica capillary column) and relative response factors of all 209 PCB congeners were reported, an increasing number of PCB congeners have become commercially available. It is important to mention, however, that although analysing the 209 PCB congeners in environmental samples is feasible at present, the access to all 209 congeners and the detailed instrument standardization and calibration would be extremely time-consuming and costly. Furthermore, several congeners are unlikely to occur in commercial formulations (which represent the ultimate source of PCBs in the environment) as preferential substitution patterns occur at the chlorination stage during the production of these technical mixtures (Ballschmiter *et al.*, 1989). Schulz *et al.* (1989) made a full description of the congener composition in various PCB commercial formulations and identified a total of 132 congeners; these authors have not detected any congeners additional to those reported in the commercial mixtures, in various environmental matrices such as water, suspended particles, fish, marine mammals, atmospheric vapour and aerosols.

In the present study, a total of 55 individual PCB congeners were used for the calibration of the gas-chromatograph (see Table 5.1). 51 of these congeners were obtained from the National Research Council Canada as a set (CLB-1 solutions) of four mixtures of individually synthesized chlorinated biphenyls. The quoted concentrations in the CLB-1 solutions are believed to be reliable to within 2% for most of the congeners with the exception of numbers 199 and 201, whose purities in the synthetic products were only 81 and 83% respectively (National Research Council Canada). Therefore, these solutions can be used for qualitative and quantitative determinations of individual PCB congeners. The remaining four PCB congeners (see Table 5.1) were obtained from Greyhound Chromatography (Birkenhead, England) as solutions of pure (>99% purity) congeners. Also from Greyhound, concentrated solutions of Aroclor 1254 and Aroclor 1260 were obtained, together with solutions of the pure congeners recommended by the International Council for the Exploration of the Sea (ICES), *i.e.* IUPAC Nos. 28, 52, 101, 118, 153, 138 and 180; the latter were used to corroborate the concentrations quoted for these congeners in the CLB-1 standard solutions (with the exception of congener No. 28 which is not present in the CLB-1 standards). The gas chromatograms in a DB-5 and a DB-1701 column (see section of methods in Chapter 3 for the chromatographic conditions) of a mixture of all 55 congeners are shown in Figure 5.1a and b. The relative retention times with each column and the possible coeluting congeners from the DB-5 column (based on the relative retention times reported by Mullin *et al.*, 1984; and information presented by Schulz *et al.*, 1989) are also shown in Table 5.1.

Some congeners (see Table 5.1) which were not present in the standard solutions, but constituted significant components of the Aroclors and of the sediment samples were identified by comparison of their relative retention times to those reported by Mullin *et al.* (1984) and the retention positions in the chromatograms in the present study. These congeners were quantified by using the calibration curves of one of the 54 congeners which was used in the calibration of the chromatographic system, and the specific calibration curve was selected by comparison of the relative response factors reported by Mullin *et al.* (1984). For example, congeners No 74, 70 and 95 which were

Table 5.1. Relative retention time (RRT) for the PCB congeners determined in this study. The relative retention times are for the elution of these congeners from a nonpolar (DB-5) and an intermediate pollarity (DB-1701) capillary column. The chromatographic conditions are described in the methods chapter.

CB No	Cl n	RRT DB-5	RRT OV-1701	Coelution	Notes
18	3	0.191-0.199	0.203-0.205	15	
15	2	0.193-0.201	0.210-0.214	18	
54	4	0.223-0.231	0.228	--	b
31	3	0.234-0.245	0.235-0.237	28	d
28	3	0.239-0.247	0.235-0.237	31	
52	4	0.286-0.296	0.269-0.271	73	+
49	4	0.292-0.303	0.270-0.272	38	+
44	4	0.318-0.329	0.296-0.300	--	+
40	4	0.352-0.363	0.330-0.335	103	e,+
103	5	0.354-0.365	0.307	57	b
74	4	0.380-0.388	0.353-0.358	94, 61	a,+
70	4	0.387-0.398	0.353-0.358	76, 98	a,+
95	5	0.395-0.405	0.357-0.362	80	a
121	5	0.400-0.410	0.343	--	b
60	4	0.424-0.435	0.394-0.400	56	d
92	5	0.428-0.440	0.384-0.389	84	a,+
89	5	0.433-0.444	0.405-0.409	--	a,+
101	5	0.439-0.449	0.394-0.400	90	
99	5	0.449-0.459	0.399-0.404	79	a
97	5	0.480-0.490	0.449-0.454	86	a,+
86	5	0.480-0.490	0.441	97	b
87	5	0.489-0.498	0.465-0.471	115, 111	
136	6	0.504-0.513	0.503-0.506	120	a,+
77	4	0.507-0.516	0.513-0.518	110	
110	5	0.509-0.518	0.492-0.497	77 × 77	a
154	6	0.512-0.522	0.458	--	b
82	5	0.529-0.539		--	a,d
151	6	0.534-0.543	0.502-0.505	--	
149	6	0.558-0.567	0.534-0.539	106	a
118	5	0.561-0.570	0.548-0.553	106,139,140	
143	6	0.576-0.584	0.552	134	b
134	6	0.578-0.586		143	a,+
114	5	0.583-0.591	0.565	--	
146	6	0.597-0.605	0.577-0.580	161	a,+
153	6	0.609-0.618	0.587-0.592	132, 105	
132	6	0.611-0.620	0.606-0.610	153, 105	a
105	5	0.614-0.622	0.618-0.622	132, 153	
141	6	0.634-0.641	0.623-0.628	179	
137	6	0.648-0.656	0.630-0.632	--	
138	6	0.664-0.671	0.659-0.662	160,163,164,186	
158	6	0.669-0.675	0.659-0.662	186	d
129	6	0.680-0.687	0.678-0.684	126	d
126	5	0.681-0.688	0.704	129	
182	7	0.701-0.708	0.671	187, 159	b
187	7	0.701-0.708	0.678-0.684	182, 159	d,+

Tab.5.1. cont...2

159	6	0.701-0.708	0.694	182, 187	b
183	7	0.711-0.718	0.687-0.692	--	+
128	6	0.719-0.726	0.728-0.731	--	d,+
185	7	0.731-0.738	0.716	--	+
174	7	0.747-0.754	0.740-0.744	181	a,c,+
177	7	0.758-0.765	0.749-0.753	--	a,c,+
171	7	0.767-0.773	0.744	202	
202	8	0.767-0.773	0.728-0.731	171, 156	d
156	6	0.769-0.774	0.776-0.780	202	
173	7	0.778-0.783	0.769	--	
201	8	0.781-0.787	0.757-0.760	157	+
180	7	0.805-0.808	0.802-0.806	--	+
191	7	0.816-0.821	0.816	--	+
169	6	0.840-0.843	0.878-0.882	--	d,+
170	7	0.854-0.857	0.870-0.872	190	e,d
199	8	0.870-0.873	0.870-0.872	--	d,+
203	8	0.878-0.881	0.878-0.882	196	d
196	8	0.879-0.881	0.878-0.882	203	d
189	7	0.902-0.903	0.931	--	+
208	9	0.922-0.923	0.910-0.912	195	
195	8	0.923-0.924	0.938-0.939	208	
207	9	0.934-0.935	0.924-0.925	--	+
194	8	0.954-0.955	0.975-0.976	--	+
205	8	0.960-0.961	0.982-0.983	--	+
206	9	1.003-1.004	1.007-1.009	--	+
209	10	1.041-1.041	1.024	--	+
OCN		85.34-85.88	87.78-88.11		
DDE		0.497-0.504	0.481-0.485		
DDT		0.656-0.663			
BLANK		0.854-0.857			

Notes: a)Calculated based on Mullin's RRT and confirmed by comparison with Schulz *et al.* (1989) data on Aroclor compositions.

b)Very unlikely to occur in environmental samples (Schulz *et al.*, 1989) but present in the CLB-1 standard solutions.

c)Not confirmed with a DB-1701 column due to the lack of standards.

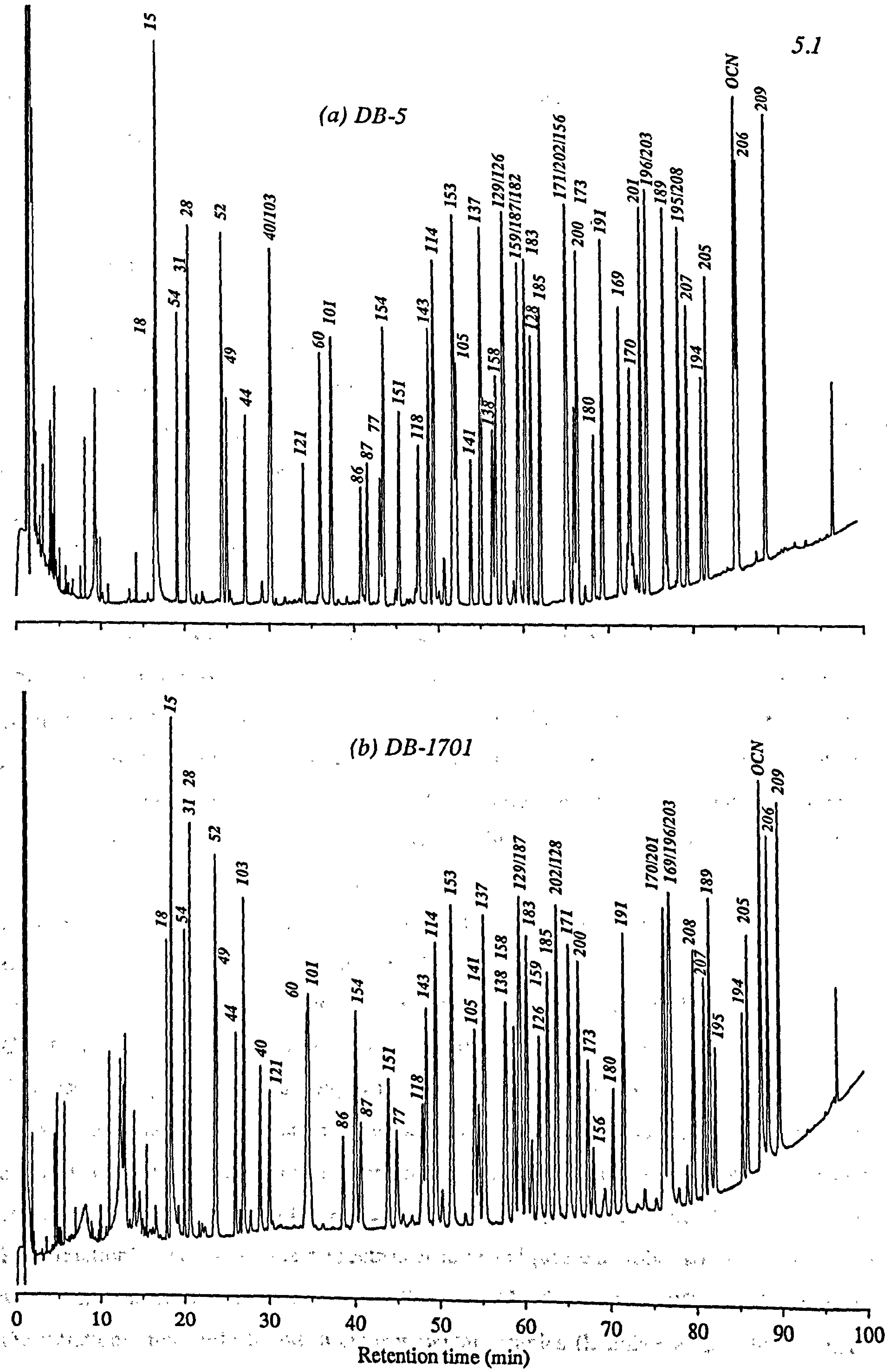
d)Difficult confirmation in DB-1701 because coelutes with other congeners.

e)Coelutes with a contaminant in the blank.

\+ According to Schulz *et al.* (1989) these congeners would elute "cleanly" from a SE-54 colum because the possible coeluting congeners are unlikely to occur at significant levels in environmental samples.

Figure 5.1. Gas chromatograms of a mixture containing the calibration standard solutions CLB-1, congener Nos. 28, 126, 158 and 169, and the internal standard octachloronaphthalene (OCN). (a) Elution from a nonpolar DB-5 and (b) an intermediate polarity, DB-1701, capillary column. The retention times are shown in the horizontal axis and the relative retention time for each congener is given in Table 5.1. The chromatographic conditions for each column are given in the Methods (Chapter 3).

5.1


(a) DB-5
15
18
54
31
28
52
49
44
40/103
121
60
101
86
87
77
154
151
118
143
114
153
105
141
137
138
158
129/126
159/187/182
183
128
185
171/202/156
200
173
180
191
169
170
201
196/203
189
195/208
207
194
205
OCN
206
209
(b) DB-1701
15
18
54
31
28
52
49
44
103
40
121
60
101
86
154
87
151
77
118
143
114
105
153
141
137
138
158
129/187
183
126
159
185
202/128
171
200
173
156
180
191
170/201
169/196/203
208
207
189
195
194
205
OCN
206
209
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

present in significant quantities in the majority of the sediment samples and were also significant components in the Aroclor 1254, were quantified by using the calibration curve for congener No. 101 in the case of congeners 74 and 70 (the relative response factors reported by Mullin *et al.*, 1984, for these three congeners were 0.668, 0.671 and 0.658 respectively) and the calibration curve for congener 52 in the case of congener 95 (their corresponding relative response factors were reported as 0.418 and 0.443 respectively). The validity of the quantification of these congeners, for which standard solutions were not available, was confirmed by the comparison of the results obtained for these congeners in the analysis of the Aroclors 1254 and 1260, with the results for the composition of these formulations reported by Schulz *et al.* (1989) who made a complete and reliable description of various PCB commercial formulations analysed by multidimensional gas-chromatography, and with the results reported by Safe *et al.* (1985) for Aroclor 1260 (see Table 5.2).

5.1.1.1. Chromatographic resolution and peak identification

The correct identification of PCB congeners based on a gas chromatogram using an electron capture detector (ECD) largely depends on a good resolution of these congeners before they reach the detector, as the identification is based on the comparison between the relative retention times of the unknown peaks in the chromatogram of the sample and the relative retention times in the chromatogram of the congeners in the standard solution(s) used for the calibration of the gas chromatograph. If two or more congeners reach the ECD simultaneously, a single peak will appear in the chromatogram and an accurate identification and quantification of these congeners will become difficult. Therefore, in an ideal gas chromatographic determination of PCB congeners, all of the congeners of interest should be completely resolved before reaching the ECD. It is important to mention that when environmental samples are analysed by HRGC-ECD (high resolution gas chromatography with ECD), even if a good resolution has been proven for the PCB congeners of interest in a calibration solution, there is still a possibility of these congeners coeluting with unknown compounds as the ECD gives a signal not only for PCBs, but for any electron-capturing substance such as chlorinated pesticides which happen to occur in the "PCB fraction". The use of mass spectrometric techniques can solve some of the problems of PCB identification but it is not generally available for routine PCB analyses at the low concentrations frequently found in environmental samples (Duinker *et al.*, 1988). Therefore, it should be kept in mind that although the ECD is very sensitive (some congeners can be detected at sub-picogram quantities) the identification of PCB congeners with this detector is not

Table 5.2. Comparison of the PCB congener composition of two technical PCB formulations, Aroclors 1254 and 1260, reported in (A) this study, (B) Schulz *et al.* (1989) and (C) Safe *et al.* (1985). The values in the table are as a percentage of the total Aroclor concentration.

CB No.	A1254		A1260		
	A	B	A	B	C
18	0.12	0.41	0.00	0.00	0.12
15	0.00	0.00	0.31	0.00	0.00
31	0.03	0.22	0.00	0.05	0.00
28	0.20	0.25	0.00	0.05	0.04
52	6.47	5.18	0.54	0.56	0.25
49	1.52	1.64	0.00	0.00	0.06
44	2.76	2.03	0.00	0.00	0.11
40	0.32	0.20	0.00	0.00	0.03
74	1.03	0.78	0.00	0.00	0.03
70	3.56	3.21	0.00	0.09	0.15
95	7.47	6.02	3.46	3.04	2.70
60	0.53	0.54	0.00	0.00	0.14
92	1.80	1.58	0.48	0.59	*
89	4.28	1.95	0.25	0.25	0.65
101	8.51	7.94	3.46	5.02	2.50
99	3.43	3.60	0.00	0.11	0.13
97	2.88	2.55	0.00	0.23	0.45
87	4.82	3.78	0.57	0.77	0.45
136	0.42	1.12	0.78	2.23	1.40
110	5.79	5.85	1.13	1.90	1.70
77	0.00	0.00	0.00	0.00	0.00
82	1.13	0.95	0.00	0.00	0.11
151	0.92	1.17	3.44	3.67	2.50
149	3.62	2.21	6.46	7.83	7.40
118	6.55	6.39	0.59	0.57	0.49
134	0.49	0.49	0.46	0.62	0.35
114	0.19	0.00	0.00	0.00	0.00
146	1.01	0.83	1.52	1.49	1.30
153	4.40	4.26	8.06	10.80	9.60
132	2.93	1.98	2.68	3.69	*
105	2.84	3.83	0.00	0.07	*
141	1.12	1.04	2.39	2.56	2.50
137	0.48	0.25	0.00	0.06	0.22
138	5.84	3.20	6.74	6.13	6.50
158	0.66	0.77	0.56	1.55	0.55
129	0.52	0.23	*	1.11	0.20

Tab. 5.2. cont....2

126	0.00	0.00	0.00	0.00	*
187	0.41	0.32	4.19	3.97	4.50
183	0.40	0.17	2.56	1.76	2.30
128	1.63	2.07	0.55	1.06	0.47
185	0.00	0.00	0.49	1.34	4.10
174	0.39	0.34	3.67	3.85	5.50
177	0.30	0.21	2.41	2.21	1.90
156	0.86	1.62	*	0.88	0.45
173	0.00	0.09	0.00	0.36	0.06
201	0.28	0.68	0.35	0.99	0.78
180	1.00	0.38	6.53	7.12	9.10
191	0.00	0.00	0.00	0.25	0.10
169	0.00	0.00	0.00	0.05	0.00
170	0.86	0.31	3.97	3.91	6.80
199	0.00	0.00	2.30	1.31	2.90
196	0.00	0.00	1.98	1.68	3.10
189	0.00	0.00	0.20	0.11	0.15
208	0.00	0.00	0.00	0.17	0.00
195	0.00	0.00	0.86	0.68	3.10
207	0.00	0.00	0.16	0.05	0.08
194	0.00	0.00	1.75	1.30	1.70
205	0.00	0.00	0.17	0.15	0.11
206	0.00	0.00	0.67	0.45	0.85
209	0.00	0.00	0.05	0.05	0.06

* Not determined.

unequivocal. Improvements in the resolution of the analysis and in the preparation of the samples (clean up) prior to the analysis can reduce the probability of coelution of specific PCB congeners with other congeners or other unknown substances.

The resolution obtained with the chromatographic conditions used during the present study was, in general, very good. Figure 5.1a shows the chromatogram obtained with a 60 m, DB-5 (equivalent to a SE-54 which is mentioned later) capillary column for a mixture containing all 55 individual PCB congeners available for the calibrations in this study. This chromatogram shows that 46 well resolved (baseline separated) or largely resolved peaks were observed with this column, and only 7 peaks contained two or three unresolved congeners. In the information provided with the CLB-1 standards, the National Research Council of Canada recommends the use of some of the congeners as "testing pairs" for the resolution during the chromatographic analysis. These pairs are congeners 86/87, 173/202, 171/201, 199/203 and 196/199 which in all cases appear as completely resolved (baseline separated) pairs in Figure 5.1a. The seven sets of unresolved congeners were: 31+28, 103+40, 129+126, 159+187+182, 171+202+156, 196+203 and 195+208.

It is obvious from Figure 5.1a that, assuming that the congeners present in the calibration solutions were the only congeners that would appear in an environmental sample, the large majority of them could be identified and quantified with accuracy as they are well resolved. However, an accurate identification (and quantification) of the unresolved congeners would be impossible with electron capture detection. For example, a peak appearing with a relative retention time of 0.680 (see Table 5.1) in an environmental sample could correspond to congeners 129 or 126, or both. The ECD would not give any information on whether congener 129 would be the only one present in the sample or, if both congeners were present, it would not be possible to determine in what proportion each of them contributes to the total signal given by the ECD. It is obvious that the problem becomes more complex if more than two congeners are coeluting as in the case of 171+202+156.

Although the accurate determination of PCB congeners requires that each of them should appear as a single peak, well resolved from other compounds, an unambiguous determination of all congeners present in commercial formulations cannot be achieved with a single column because no single column can completely resolve all congeners present in these formulations (Duinker *et al.*, 1988). The problem of insufficient resolution for some congeners from a single column has been overcome by the use of multidimensional gas chromatography with electron capture detection (MDGC-ECD) and a full description of all congeners present in various commercial formulations is now available (Schulz *et al.*, 1989). The MDGC-ECD technique involves the use of two columns of different polarities in series, each in a separate temperature-controlled oven. The eluate of the first column is carried either through the monitor ECD, producing the usual chromatogram, or through the second column and the main ECD (Schulz *et al.*, 1989). The usefulness of this technique lies in the fact that a preselected fraction from the eluate of the first column can be quantitatively transferred into the second column, therefore, only the coeluting congeners are diverted towards the second column whereas the well resolved congeners can be directed from the first column to an ECD. The chromatogram from the first column (which may be a non-polar SE-54 type capillary column) will include the majority of the PCB congeners which can be well resolved in this type of column, whereas the chromatogram from the second column (which may be of intermediate polarity such as an OV-210 type) will include only a few peaks corresponding to the congeners that cannot be resolved from the first column (Schulz *et al.*, 1989).

Unfortunately a MDGC system was not available for the present study and the application of this technique for PCB analysis had not yet been reported (in the literature reviewed by the author of this thesis). However, as special attention was paid in obtaining the maximum possible resolution from the DB-5 column, and as various congeners in the calibration solutions for this study which are present in commercial formulations can be well resolved with this type of column (Schulz *et al.*, 1989), after comparing the results of the analysis of Aroclors 1254 and 1260 in this study with the results for these Aroclors reported by Schulz *et al.* (1989) and by Safe *et al.* (1985) it is concluded that these congeners, together with those identified and quantified with the information provided by Mullin *et al.* (1984), were identified and quantified with accuracy.

A confirmation of the identity of various congeners was performed by analysing the Aroclors and several (20) samples with a DB-1701 type capillary column of intermediate polarity. Figure 5.1b shows the chromatogram for a mixture of all 55 congeners available for calibration of the chromatographic system. This chromatogram shows the same number of peaks (46) as those obtained with a DB-5 column, which indicates that both columns had a fairly similar resolution (compare Fig. 5.1 and b). However, most of the congeners coeluting with the DB-5 column were resolved in the DB-1701 column, for example, congeners 171, 202 and 156 which coelute in the DB-5 column (see Fig. 5.1a) are completely separated in the DB-1701 column (see Fig. 5.1b). On the other hand, congeners which were completely resolved in the DB-5 column (e.g. 60 and 101) coeluted in the DB-1701 column, and only in a few cases (*i.e.* 28+31 and 196+203) were pairs of congeners not resolved with either of the two columns. Therefore, in cases in which the identification of a congener or group of congeners was dubious due to possible coelution, the reported concentrations are regarded as the sum of the coeluting congeners and the discussion of these values is only limited, whereas in cases such as the one for congeners 31 and 28 in which a partial resolution was obtained (see Fig 5.1a) in the DB-5 column, a quantification was done for each congener keeping in mind that the precision in this quantification is affected by the partial coelution with other congener(s) (Duinker *et al.*, 1988) and these determination could be regarded as semiquantitative.

5.1.1.2. Description of the composition of two Aroclor mixtures

The concentrations of the PCB congeners listed in Table 5.1 were determined in two Aroclor mixtures, *i.e.* Aroclor 1254 and Aroclor 1260. The results of these analyses were compared with the results for both formulations reported by Schulz *et al.* (1989) and the results for Aroclor 1260 reported by Safe *et al.* (1985). The comparison was made with these two reports in particular because in both cases all the individual congeners reported were available as individual standards for the calibration and identification of the chromatographic systems, and the chromatographic conditions used in both (by Schulz *et al.* in particular) studies provided very good resolution and, therefore, accuracy in the determinations. The results for the composition of Aroclor 1260 in these two reports were in good agreement, with the exception of a few congeners that coelute with a SE-54 column (Schulz *et al.*, 1989) which was the only column used by Safe *et al.* (1985). As shown in Table 5.2, the results obtained in the present study were in good agreement with the results from the two studies previously mentioned.

Before discussing the results shown in Table 5.2, it is important to comment on some relevant points arising from the report by Schulz *et al.* (1989). It was previously mentioned that these authors found a total of 132 congeners at concentrations higher than 0.05% (w/w) in a series of commercial formulations, and mentioned that in studies of various types of environmental samples analysed with their MDGC-ECD technique, no additional congeners to those reported for the commercial formulations were found. This observation implies that the probability of coelution of various PCB congeners is greatly reduced as 69 of the possible total of 209 congeners are unlikely to occur in the environment as they are not present in the commercial formulations that represent the ultimate source of these xenobiotic substances (see list of the congeners not detected in the commercial formulations in Schulz *et al.*, 1989).

The explanation for the complete absence, or presence at trace levels of some of the PCB congeners is based on the concept of preferred substitution patterns (Ballschmiter *et al.*, 1987). During the synthesis of the PCB technical formulations, an electrophilic aromatic substitution reaction of biphenyl is applied and this reaction stabilizes the *o,p*-dichlorine substitution patterns (*i.e.* at the positions 2 and 4), and the substitution of additional chlorine atoms is consequently more difficult as a result of electronic and steric effects (Schulz *et al.*, 1989). On the basis of electronic effects, chlorination may occur preferentially at the 2,5-, 2,3-, 2,4- or 3,4- positions; thus, congeners No. 52 (2,2′,5,5′) and 153 (2,2′,4,4′,5,5′) are dominant components (Schulz *et al.*, 1989).

On the other hand, the ionic chlorination mechanism leads to very little 3- and 3,5- substitution (Ballschmiter *et al.*, 1987), thus, congeners No. 11 (3,3′), 14 (3,5), 39 (3,4′,5), 43 (2,2′,3,5), 58 (2,3,3′,5′), 68 (2,3′,4,5′), 72 (2,3′,5,5′), 80 (3,3′,5,5′), 108 (2,3,3′,4,5′) and 111 (2,3,3′,5,5′), amongst others, are reported as absent from the PCB technical formulations analysed by Schulz *et al.* (1989). Also absent, or present at trace levels in commercial formulations, are those congeners with all of the chlorine atoms present in one ring which include, amongst others, congeners No. 21 (2,3,4), 23 (2,3,5), 38 (3,4,5), 61 (2,3,4,5), 65 (2,3,5,6) and 116 (2,3,4,5,6) reported as absent by Schulz *et al.* (1989). The exceptions to these observations are congeners 24 (2,3,6) and 29 (2,4,5), which were the only congeners (with more than two chlorine atoms) with all the chlorine atoms on one ring reported as present (at levels lower than 0.35%) in some of the PCB formulations analysed by Schulz *et al.*, and their presence was accounted for on the basis of the favoured 2,3,6 and 2,4,5 substitution patterns. Also likely to occur only at trace levels (if at all) are those congeners with 4 or five chlorine atoms in one ring and only one or two in the other (e.g. 4+1, 5+1 and 5+2 substitution patterns, Ballschmiter *et al.*, 1987; Schulz *et al.*, 1989). Of the pentachlorobiphenyls with 4+1 substitutions only three (*i.e.*, No.88: 2,2′,3,4,6; No. 114: 2,3,4,4′,5; and No. 115: 2,3,4,4′,6) were detected at very low concentrations, while the others were not detected at all (Nos. 86, 93, 106, 109, 112 and 117). Similar observations apply to the corresponding hexachlorobiphenyls (Schulz *et al.*, 1989).

It is important to note that Schulz *et al.* (1989) included in the list of absent congeners No. 89 which is a 3+2 substituted PCB (2,2′,3,4,6′) and is reported by Schulz *et al.* as a 4+1 (therefore unlikely to occur) substituted congener. Based on the relative retention times reported by Mullin *et al.* (1984) this congener can elute cleanly on a SE-54 column and, using this report as a reference, this congener is reported as present in the Aroclor 1254 formulation analysed in the present study. In a study of the composition of technical mixtures similar to those analysed by Schulz *et al.* (1989), Ballschmiter *et al.* (1987) also reported congeners 92 and 84 as coelutants and the peak eluting after this pair as congener No. 89. This congener represents the only discrepancy between the present study and the report by Schulz *et al.* (1989) regarding the identification of the PCB congeners in the Aroclors analysed in both studies.

As part of the validation of the quantification made with the chromatographic conditions used in the present study, some comments are made in the following paragraphs regarding the data reported in Table 5.2. In this table, the results of the quantitative analysis of Aroclors 1254 and 1260 in which the congeners listed in Table 5.1 were determined, are compared with the results reported by Schulz *et al.* (1989) and Safe *et al.* (1985). The first comparison regards those congeners which were available for the calibrations, and which are reported by Schulz *et al.* (1989) as being completely resolved on a SE-54 type column and therefore, can be accurately determined with a single column. These congeners were Nos. 52, 49, 44, 40, 187, 183, 128, 185, 180, 191, 169, 199, 189, 207, 194, 205, 206 and 209 (see Table 5.1). Table 5.2 shows that the results between the three studies are largely similar, however, some differences in the quantification for these congeners were expected as the composition of Aroclors vary somewhat from one batch to another (Alford-Stevens, 1986). The differences observed with the data of Schulz *et al.* (1989) in particular are expected to be related to differences between the batches of Aroclors analysed in each study, and not due to differences in the quality of the calibration standards because part of a recent reassessment of the concentration values in the CLB-1 (National Research Council Canada) PCB solutions used in the present study, was performed by one of the authors in Schulz *et al.* (1989).

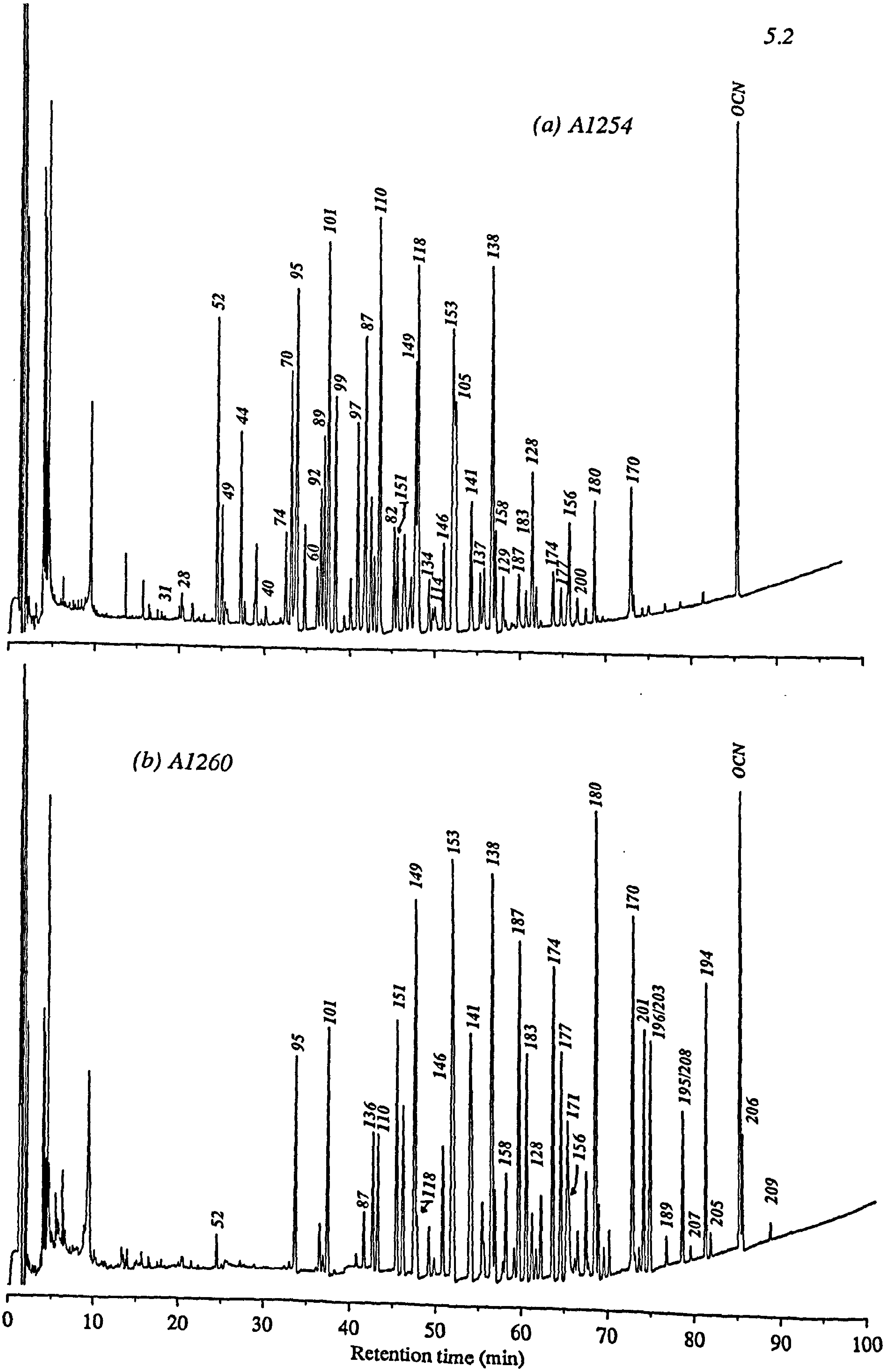
The validity of using the relative retention times and relative response factors reported by Mullin *et al.* (1984) for the identification and quantification of some congeners which can be resolved on a SE-54 column (Schulz *et al.*, 1989), and which in various cases represented significant components in the sediment chromatograms, was tested by comparing the results for these congeners (*i.e.* Nos. 74, 70, 99, 97, 136, 134, 146, 174 and 177) shown in Table 5.2. With the exception of congener No. 136, there was very good agreement in the quantification of all of these congeners, therefore, the data reported for these congeners in sediment samples can be regarded as accurate. Mullin *et al.* (1984) reported a relatively similar response factor for congener No. 136, and congeners 126 and 195 which were available as calibration standards in this study. The quantification of congener 136 gave similar results using the calibration curve of either of these congeners, therefore, the difference between the values reported in Table 5.2 for congener 136 can be due to differences amongst batches of Aroclors, or due to the possibility of the response factor for congener 136 not being similar to those for congeners 126 and 195, thus, the use of the calibrations for the latter congeners was not appropriate. From the last observations it is obvious that, as suggested by Schulz *et al.* (1989), ideally one should have available for calibration each congener which is to be determined quantitatively in a PCB analysis.

A particularly interesting set to compare is that including the congeners recommended by ICES (*i.e.* No. 28, 52, 101, 118, 153, 138 and 180) for determination in environmental samples. These congeners were originally selected because, according to Griepink *et al.* (1988), they occur in significant proportions in many environmental samples and can be separated from most matrix interferences and coeluting congeners; congener No. 118 was also selected because of its toxicity. However, Duinker *et al.* (1988; see also Schulz *et al.*, 1989) applied MDGC for the determination of these congeners and concluded that some of them may present the problem of coeluting with other congeners if a single (SE-54) column is used in the determinations. Congeners No. 52 and 180 were the only ones reported to elute as single peaks from a SE-54 column and can thus be analysed accurately using only this column. In the determination by Schulz *et al.* (1989), after the first column (SE-54), congener No. 28 coeluted with No. 31; No. 101 coeluted with No.90; No. 153 eluted closely from 132 and 105; No. 118 closely eluted with 149; and No. 138 eluted closely with 158. After the second column all of these congeners were well separated, with the exception of 28 and 31 which were only partially resolved. Table 5.2 and Figure 5.2a and b indicate that, although some of the PCB congeners recommended by ICES partially coeluted with other congeners from the DB-5 column used in the present study, the quantification of these congeners was satisfactory and the agreement with the data reported by Schulz *et al.* (1989) and Safe *et al.* (1985) was good. As suggested by the comparisons previously made for other congeners, the differences between studies found in Table 5.2 could be due to differences in the composition among Aroclor batches, however, the partial coelution with other congeners probably affect, in a minor degree, the accuracy of the results. It is important to remember that the identity and relative proportion of coeluting congeners was confirmed in several sediment samples (20) and the Aroclor mixtures by using a DB-1701 column (see for example chromatograms for Aroclors in Fig. 5.3a and b).

Most of the discussions in this chapter are focused on most of the congeners mentioned earlier, which, in general, can be considered as accurately identified and quantified. The other congeners which are listed in Table 5.1 and which have not been mentioned are those reported by Schulz *et al.* (1989) as coeluting with other congeners from a SE-54 capillary column. Some of these

Figure 5.2. Gas chromatograms (DB-5 column) of two PCB commercial formulations (a) Aroclor 1254 and (b) Aroclor 1260. The composition of these Aroclors is shown in Table 5.2. The congeners which were not present in the calibration standards (see Fig. 5.1) were identified with the relative retention times reported by Mullin *et al.* (1984). See chromatographic conditions in the methods.

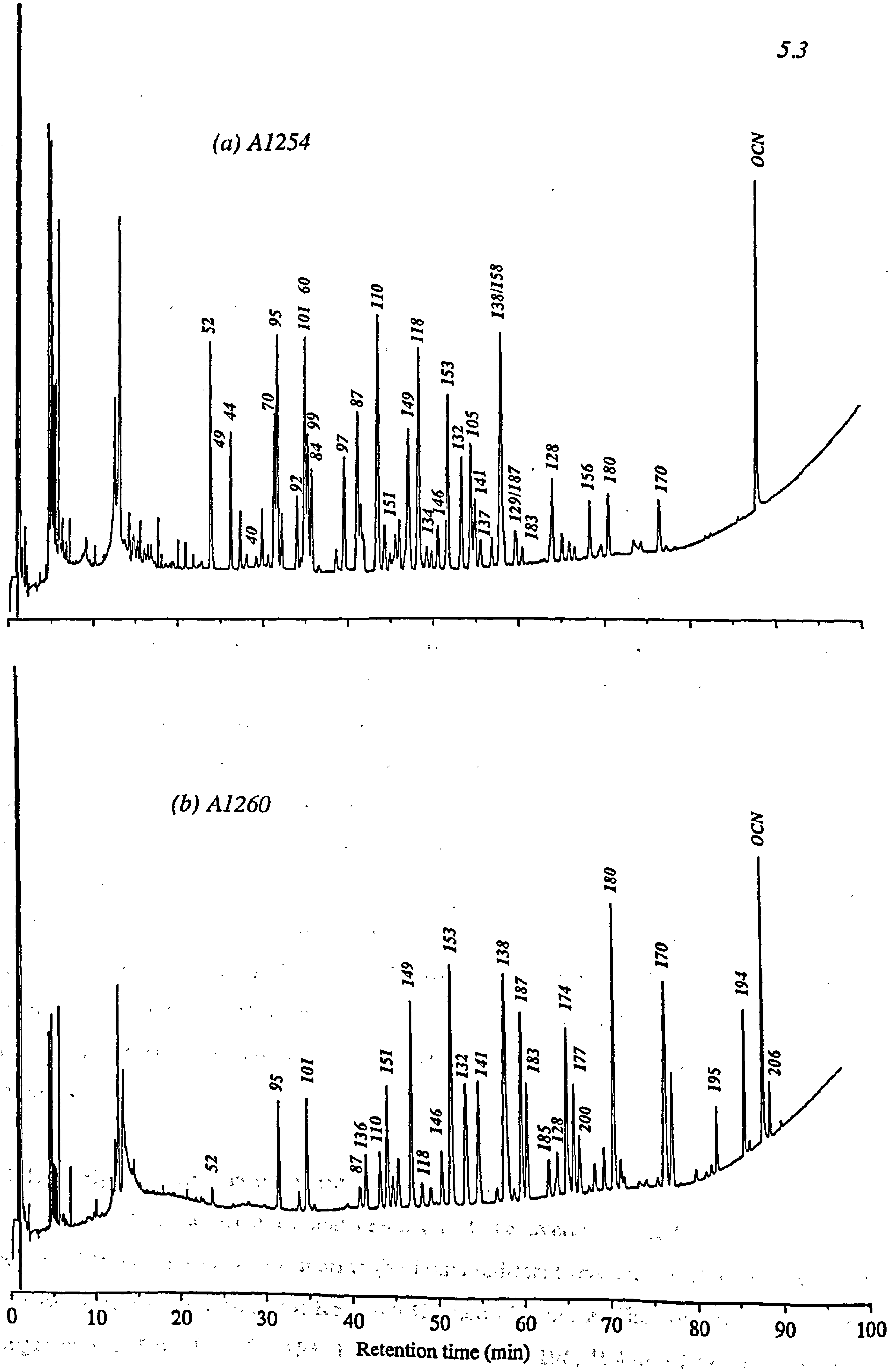
5.2



(a) A1254
28
31
40
44
49
52
60
70
74
82
87
89
92
95
97
99
101
105
110
114
118
128
129
134
137
138
141
146
149
151
153
156
158
170
174
177
180
183
187
200
OCN
(b) A1260
52
87
95
101
110
118
128
136
138
141
146
149
151
153
156
158
170
171
174
177
180
183
187
189
194
195/208
196/203
201
205
206
207
209
OCN
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.3. Gas chromatograms (DB-1701 column) of two commercial formulations (a) Aroclor 1254 and (b) Aroclor 1260.

5.3


(a) A1254
52
49
44
40
70
95
92
101
60
84
99
97
87
110
151
149
118
134
146
153
132
105
141
137
138/158
129/187
183
128
156
180
170
OCN
(b) A1260
52
95
101
87
136
110
151
149
118
146
153
132
141
138
187
183
185
128
174
177
200
180
170
195
194
206
OCN
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

congeners (*i.e.* No. 54, 103, 121, 86, 154, 143, 182 and 159) are not reported in the results for the PCBs in sediments because, although present in the calibration solutions, they are reported as unlikely to occur in environmental samples as they are absent from the technical formulations (Schulz *et al.*, 1989). The concentrations reported for most of the remaining congeners should be only regarded as tentative, as the presence and proportions of coeluting congeners could not be evaluated. Table 5.2 shows that for some of these congeners the quantification in the Aroclor mixtures was in close agreement to the values reported by Schulz *et al.* (1989) indicating that the presence of coeluting congeners did not affect severely their quantification, however, as the contribution of coeluting congeners may change in environmental samples, the accuracy in the quantification of these congeners in the Aroclors, can not be extrapolated to the sediment samples, and the values quoted for these congeners should be considered as the summation of the concentrations of all possible coeluting congeners which are also listed in Table 5.1.

The concentration values for congeners Nos. 40, 136 and 170 were not reported for the sediment samples, as congener 170 coeluted with a compound present in the blank, and Nos. 40 and 136 coeluted, in some samples, with large contaminants from the sediment. It is possible that the coeluting compound with No. 136 was DDE which had a similar relative retention time. Based on the relative retention times reported by Mullin *et al.* (1984), and on the fact that after injecting several sediment sample extracts in the DB-1701 column there was evidence of congener No. 92 coeluting with probably another PCB congener, the concentrations values for this congener in the sediments are believed to be enhanced by the presence of congener No. 84 which Schulz *et al.* (1989) reported as being well resolved in a SE-54 type column. Also based on the data reported by Mullin *et al.* (1984) the peak eluting after congeners 92+84 in the Aroclor and sediment DB-5 chromatograms has been identified as congener 89 which, as mentioned earlier, was reported by Schulz *et al.* (1989) as absent from the commercial formulations.

5.1.2. Analysis of marine sediment reference materials.

In order to test the accuracy and precision of the overall method for the determination of individual PCB congeners, two marine (harbour) sediment reference materials (HS-1 and HS-2) were obtained from the National Research Council of Canada. The concentration values for ten congeners (*i.e.* No. 101, 151, 153, 138, 180, 170, 201, 196, 194 and 209) are certified in these reference sediments, and these values have been used for testing the accuracy of the analysis.

The results for the determinations in three replicate samples of each reference sediment, of the PCB congeners with certified concentrations, are reported in Table 5.3. This table shows a good agreement between the values determined in the present study, and those reported in the certification. Considering the differences in the methodology for the PCB congener determinations, the similarity in the values shown in Table 5.3 is remarkable, however, some of the differences in the reported concentrations could have been more closely studied if more detailed information in the certification of the reference sediments was provided by the National Research Council of Canada. For example, while testing the method for PCBs analysis in sediments, the same method (with only minor modifications) was tested on biological reference material (mackerel oil CRM No. 350) produced by the Community Bureau of Reference of the Commission of the European Communities. Together with the reference oil, this Bureau provides detailed information on the certification of the material, *i.e.*, provides the data reported by the laboratories participating in the certification. Although a few of the certified congeners in the mackerel oil were slightly below the confidence limits of the certified values suggesting perhaps some losses during the treatment of the sample, the comparison of the results in our laboratory with those of the individual laboratories participating in the certification indicated that the PCB determination in our laboratory was within values reported and accepted for the determination of the certified value. Detailed information in the certified materials can be very important, particularly for those laboratories where the analysis of PCBs in environmental samples is done for the first time.

The data presented in Table 5.3 shows that the precision of the overall method was, in general, similar or better than that reported for the certified values. The average relative standard deviations for the PCB congener concentrations in reference sediments were 7 and 9% in this study, whereas those calculated with the certified values were 16 and 10% for HS-1 and HS-2 respectively. The only congener in which relatively poor precision was observed (r.s.d.=~20%) was No. 101 in sediment HS-2 (see Table 5.3). When all the congeners were considered, including those whose concentrations are not certified, the average relative standard deviation in the HS-1 sediment was 8.9%, with only congeners 18 and 137 showing values higher than 20%. For sediment HS-2 the average relative standard deviation was 12.4% with congeners Nos. 52, 87, 118, and 156 showing values higher than 20%. Although some congeners with high variability (e.g. 118 and 156) may not be fully resolved form other congeners with a DB-5 column, causing a decrease in the precision of the determinations, congeners 52 and 128 are reported to elute cleanly (under appropriate chromatographic conditions) from a non-polar column

Table 5.3. Results of the determination of some PCB congeners in two sediment reference materials, HS-1 and HS-2, from the National Research Council of Canada. The certified concentration values are also included in the table together with the relative standard deviations for the certified and determined values. The concentration values are in ng g^{-1}.

HS - 1

	this study			**certified**		
IUPAC	**mean**	**s.d.**	**r.s.d.**	**mean**	**s.d.**	**r.s.d.**
101	1.19	0.13	9	1.62	0.21	13
151	0.29	0.01	5	0.48	0.08	17
153	1.78	0.15	9	2.27	0.28	12
138	1.67	0.13	8	1.98	0.28	14
180	0.87	0.06	7	1.17	0.15	13
170	0.42	0.02	6	0.27	0.05	19
201	0.32	0.01	4	0.57	0.07	12
196	0.27	0.03	10	0.45	0.40	89
194	0.18	0.01	8	0.23	0.04	17
209	0.13	0.01	10	0.33	0.10	30
mean			7.6			16.3

HS - 2

IUPAC	**mean**	**s.d.**	**r.s.d.**	**mean**	**s.d.**	**r.s.d.**
101	6.69	1.32	20	5.42	0.34	6
151	1.62	0.18	11	1.37	0.07	5
153	8.14	0.66	8	6.15	0.67	11
138	7.95	0.70	9	6.92	0.52	8
180	4.56	0.08	2	3.70	0.33	9
170	2.19	0.18	8	1.07	0.15	14
201	1.42	0.14	10	1.39	0.09	7
196	1.16	0.12	10	1.13	0.12	11
194	0.75	0.06	8	0.61	0.07	12
209	0.61	0.02	4	0.90	0.14	16
mean			9			10

(Schulz *et al.*, 1989). The cause of the lower precision observed for these congeners, as compared to others, is difficult to assess. The recoveries for the octachloronaphthalene which was used as an internal standard were between 91 and 98% for all of the sediment samples analysed including the reference materials, therefore, no corrections were made for the concentrations determined in the samples. The precision observed for the internal standard during the analysis of the reference materials was good, with relative standard deviations of 1.4 and 3.1% for HS-1 and HS-2 respectively.

In conclusion, the method used in this work for the analysis of individual PCB congeners can be considered as satisfactory. Although the identification of several congeners can be regarded as accurate after a gas chromatographic analysis using a single column (DB-5), the confirmation of some of the identities with the use of a more polar column was important. Two reports which have been important in the validation of the method and the identification of some congeners were those by Mullin *et al.* (1984) and Schulz *et al.* (1989). Although the precision observed for some congeners was not as good as for other congeners, the overall precision can be regarded as good, in particular, when considering the large differences (more than two orders of magnitude) in concentration observed between some of the sediment samples which are reported in the following section of this chapter.

5.2. RESULTS

5.2.1. Total PCBs

As PCB congeners show a wide range of physicochemical and toxicological properties, they can be studied as well defined individual chemical entities. The main aim of this chapter is, therefore, to discuss the patterns in the distributions of the relative concentrations of the PCB congeners in sediment samples in Liverpool Bay. However, as precise determinations of individual congeners have only recently been possible, literature reporting PCB congeners in marine sediments in particular is limited as compared with studies reporting total PCBs. Hence, comments are made in the following paragraphs regarding the levels of "total" PCBs (estimated as the sum of all congeners listed in Table 5.1 present in each sample above the detection limit) in the sediments analysed in the present work. In this section comparisons are made between the total PCB levels in samples within this study, which are followed by comparisons between the results in this study and total PCB levels reported for sediments in other marine coastal systems.

5.2.1.1. Distribution of total PCBs in Liverpool Bay sediments

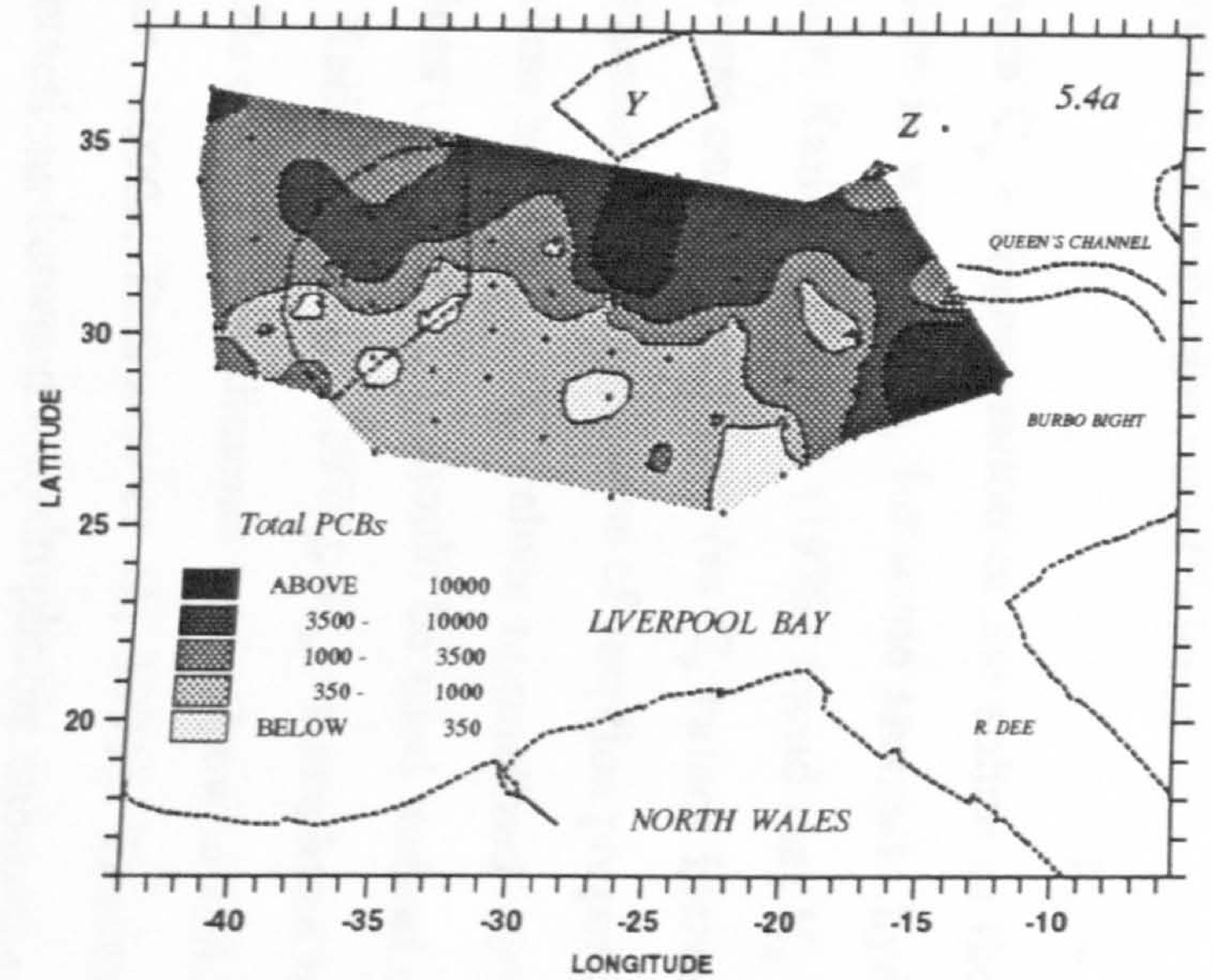
Before comparing the results for total PCBs between samples in this study, and between this and other studies, it is important to mention the possible limitations in the comparisons, particularly regarding the comparison of results between sediment samples with different sedimentological characteristics.

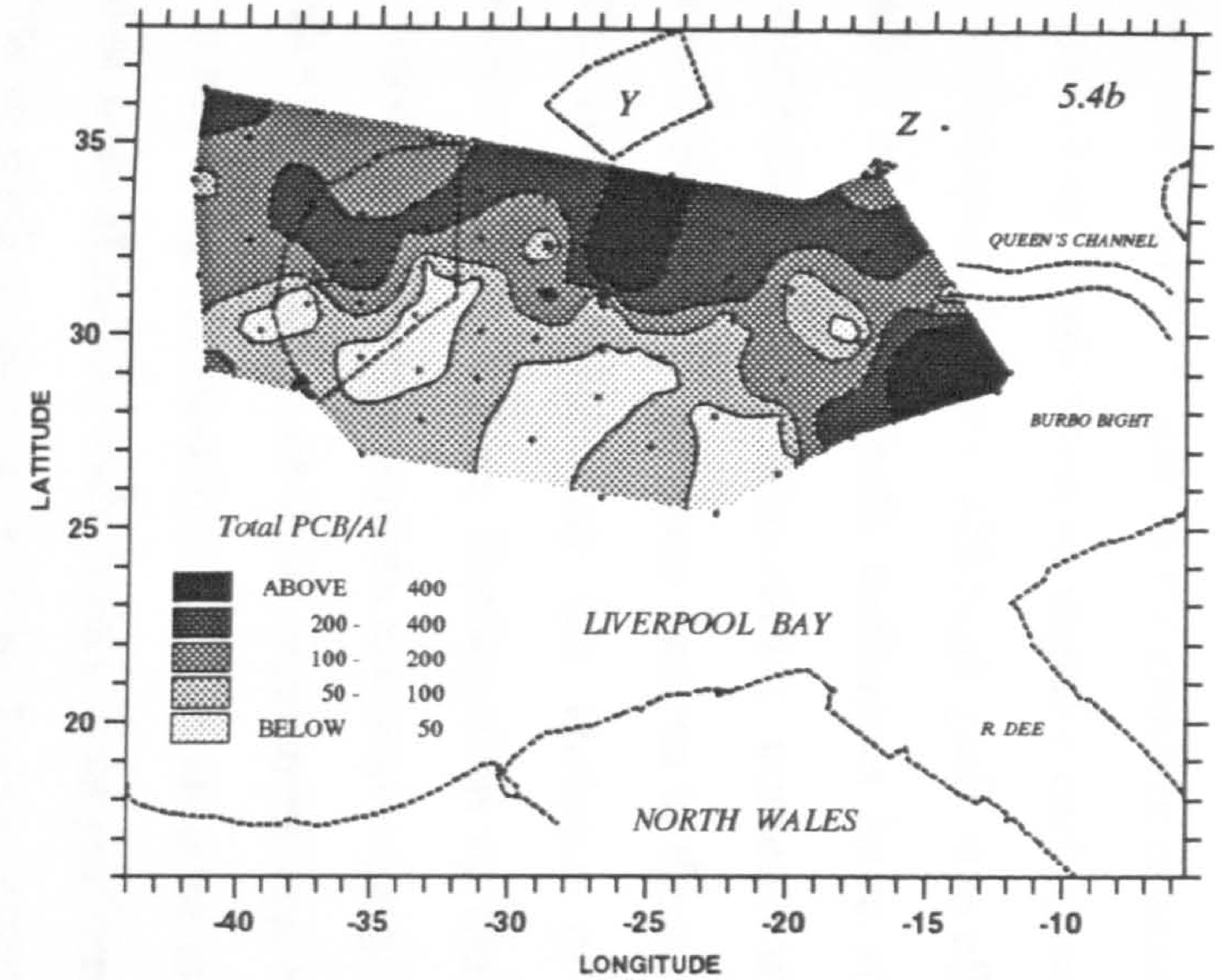
Figure 5.4a shows the distribution of total PCBs in the total fraction (<500 µm) in Liverpool Bay sediments. When this figure is compared with the distribution of fine fraction in these sediments (see Figs. 4.2a and c), it is obvious that PCB concentrations closely reflect the amount of fine material in the sediment. Not surprisingly, highly significant ($p<<0.001$) correlations were observed between PCB concentrations and the percentage of fine fraction in the total sediment ($r=0.899$), and between PCBs and the aluminium content ($r=0.892$), therefore, the results of PCBs in the total fraction shown in Figure 5.4a, more than showing areas of higher and lower contamination of the sediments may be reflecting only the distribution of fine sediments in Liverpool Bay. It was mentioned in Chapter 4 that the fractionation of sediments prior to trace element determinations was important to avoid the effect of variations in the grain size distribution between samples and, in most of the studies in which determinations of trace elements were done in the total sediments, the results were corrected or "normalized" prior to comparisons of the results between samples. As in the case of trace metals, given the higher surface area of fine particles and their higher content of organic matter, PCBs will tend to preferentially accumulate in the fine fraction of the sediments (see Section 4.1.1.), therefore, it is not surprising that the PCB content in total sediments in this study increases as the amount of fine particles in the sediment increases.

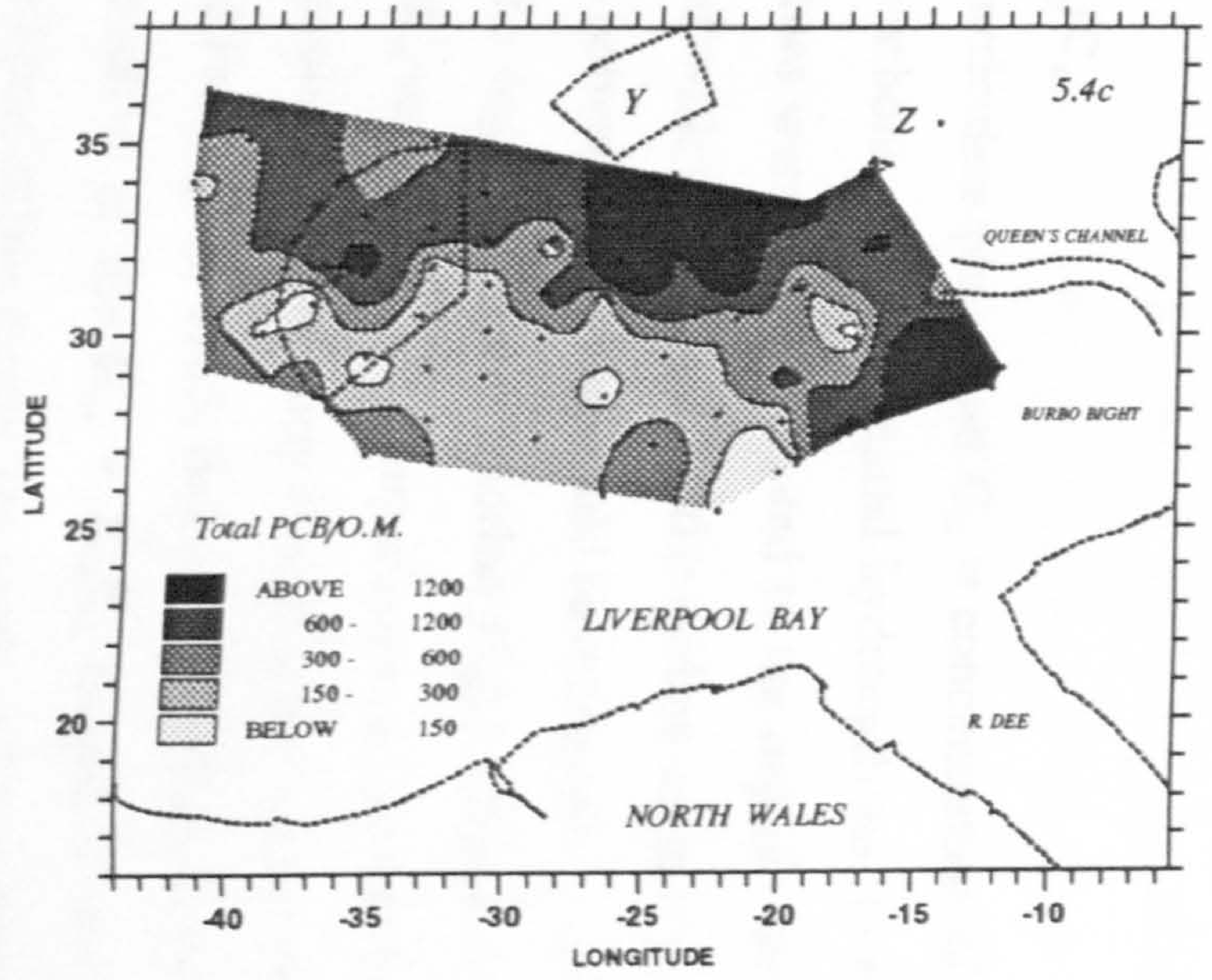
The main reason for not analysing PCBs in separate fine and coarse fractions in the present study, rather than analysing the total sediment, was that as the amount of sediment necessary for PCB determinations was comparatively much higher (up to 70 g) than for the analysis of trace elements (1 g or less), and several of the sediment samples collected were relatively small, it was estimated that for a large number of samples (~30 out of 70) collected in this study the fractionation would have yielded fine fraction subsamples smaller than 1 g, therefore, the determination of PCBs probably would have given signals below the detection limit for a large proportion of the samples.

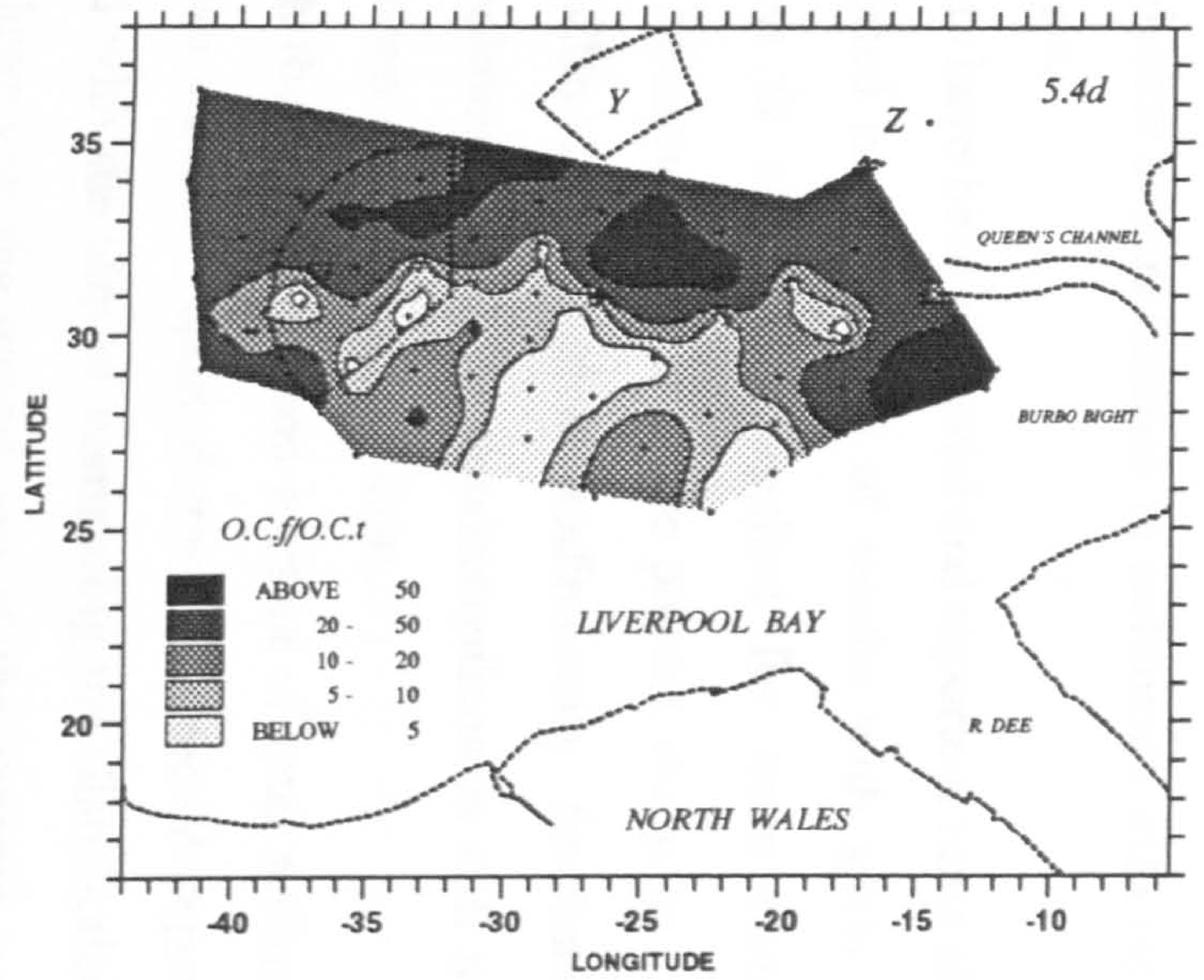
It has been mentioned (see Section 4.1.2.) that one of the techniques most commonly applied for grain size correction of trace elements determined in total or bulk sediments is normalizing the results with the aluminium content of the sediment (see for example Windom *et al.*, 1989;

Figure 5.4. Distribution of (a) total PCB concentrations in sediments from Liverpool Bay, and of these concentrations normalized with (b) the aluminium content and (c) total organic carbon content in the sediments. The units of concentration are pg g^{-1}, ng g^{-1} Al and ng g^{-1} C respectively, and the values for each sample are given in Appendix C2. The contribution in percent of the organic carbon in the fine fraction to the organic carbon in the total sediment fraction is shown in figure (d).


5.4a
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Total PCBs
ABOVE 10000
3500 - 10000
1000 - 3500
350 - 1000
BELOW 350
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE


5.4b
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Total PCB/Al
ABOVE 400
200 - 400
100 - 200
50 - 100
BELOW 50
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE


5.4c
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
Total PCB/O.M.
ABOVE 1200
600 - 1200
300 - 600
150 - 300
BELOW 150
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE


5.4d
Y
Z
QUEEN'S CHANNEL
BURBO BIGHT
O.C.f/O.C.t
ABOVE 50
20 - 50
10 - 20
5 - 10
BELOW 5
LIVERPOOL BAY
R DEE
NORTH WALES
LATITUDE
35
30
25
20
-40
-35
-30
-25
-20
-15
-10
LONGITUDE

Duinker, 1981; Ridgway and Price, 1987; Kemp *et al.*, 1976). The dependence on the grain size composition observed in the present study has also been reported in other studies in which PCBs were determined in bulk sediments (e.g. Boon *et al.*, 1985; Lohse, 1988; Duursma *et al.*, 1989; Lara and Ernst, 1990a), and Boon *et al.* (1985) suggested that from the geochemical point of view, it would be better to standardize organochlorine concentrations in sediments with respect to grain size distribution or organic carbon content.

As mentioned above, although grain size effects have been observed and reported, none of the studies of PCBs in bulk sediments have reported normalization of results with grain size descriptors such as aluminium content which is commonly applied for trace element normalizations. It is obvious that, as in the case of trace elements in the present study, to avoid grain size normalizations the analysis of PCBs in individual sedimentary fractions is recommended, however, fractionation of the sediments for PCB determinations is still not a common practice and reports are scarce (e.g. Larsen and Fytianos, 1989).

The normalization of PCB concentrations with the organic carbon content of total sediments for comparing distributions within an area is also scarcely reported (the only recent report in which normalization with carbon was performed with the aim of comparing the distribution of PCBs in surface sediments is by Lohse, 1988), however, the importance of the organic carbon content on the surface of aquatic particles has been widely reported in studies of partitioning of hydrophobic organic contaminants between dissolved and particulate phases. Karickhoff *et al.* (1979) studied the sorption of hydrophobic pollutants on natural sediments and determined the partition (distribution) coefficients

$$K_d = C_p/C_w,$$

where C_p = concentration of the solute in the particulate phase and C_w = concentration of the solute in water phase, for some aromatic hydrocarbons and chlorinated hydrocarbons. In their study, Karickhoff *et al.* (1979) found that K_d values were directly related to the organic carbon content on the sediments (as C_p values increased with an increase of the carbon content), and suggested that comparisons of sorption properties between particles should be made on an organic carbon basis, thus, K_d values normalized with the organic carbon fraction (f_{oc}), defined as K_{oc} values ($K_{oc} = K_d/f_{oc}$), should be used instead of K_d values for the comparisons. After the report by Karickhoff *et al.* (1979), K_{oc} values have been often used to study the partition behaviour of PCBs on aquatic sediments (e.g. Brownawell and Farrington, 1985; Baker *et al.*, 1986; Lara and Ernst, 1990a; Brannon *et al.*, 1991). The assumption of the $K_{oc} = K_d/f_{oc}$ model is that the interactions between a hydrophobic substance and particulate matter are weak and non-specific, resembling the simple partitioning into an organic solvent (Lara and Ernst, 1990a). If this assumption is valid, then a normalization of the total PCB concentrations with the organic carbon content of the total sediment seems to be a better choice than normalizing with aluminium for comparison of the PCB levels between the highly heterogeneous sediment samples analysed in this study. However, some limitations arise from this assumption as it has been reported that the mineral phase onto which the organic films are formed in natural sediments may play a role in the adsorption process of hydrophobic organic compounds. Murphy *et al.* (1990) reported that the mineral effects are particularly important for less hydrophobic compounds at low organic carbon concentrations in particles, whereas Lara and Ernst (1990b) observed that, after removing most of the organic matter on some marine sediments, the sorption of PCBs on the "mineral" particles became increasingly significant as the hydrophobicity of the PCB congeners and the percentage of silt-clay fraction of the sediments increased. It is apparent from these observations that the association of PCBs in aquatic sediments may not be accurately described as a simple partitioning into the organic phase, as the mineral fraction may play a direct or indirect role in the sorption process. Furthermore, it has also been reported that the composition of the organic matter plays a role in the sorption of organic compounds onto sediments (e.g. Grathwohl, 1990; Murphy *et al.*, 1990). For example, Murphy *et al.* (1990) observed that humic substances, as compared to fulvic acids, greatly enhanced the sorption of hydrophobic organic substances, and that the type of humic coating influenced the amount of substance adsorbed. These authors reported that the sorption of hydrophobic compounds was proportional to the aromatic content of the organic matter and inversely proportional to their oxygen/carbon ratio. Karickhoff *et al.* (1979) reported that, on an organic carbon basis, the sand fraction within a particular sample was considerably less effective sorbent (50-90% reduction in K_{oc}) than the fine fraction (<50 μm particles), these results probably suggesting that the composition of the organic matter was different between the sands and the fine particles in the report by Karickhoff *et al.* (1979), or that the mineral matrix played a major role in the organic substance-sediment association, or both.

From the above, it is clear that the interaction between organic substances such as PCBs and sediment particles is far from well understood, and therefore, any method used for normalization of the PCB concentrations will have advantages and disadvantages. Duursma *et al.* (1989) reported that since the organic carbon in their sediments was correlated with silt (defined as the particles <16 μm in their study), it was not at all clear whether organic matter was a better parameter than silt content for K_d corrections. In the present study, high correlations were also found between the organic carbon content in the total sediment and grain size descriptors such particles even though this correlation has been reported for the estuarine sediments in the region. However, although a correlation between mercury and organic carbon was not observed, probably suggesting that mercury concentrations were not controlled by the organic matter in fine particles, the correlation between mercury and $\delta^{13}C$ values indicated that the mercury might be associated and controlled by a specific fraction of the organic matter in fine sediments which is land derived.

As in the case of mercury, given their organic and hydrophobic nature, a specific association between PCBs and the organic matter in the sedimentary particles is expected, however, as mentioned above, apart from the quantity, the quality or composition of the organic matter is also expected to play a role in the control of the PCB concentrations in sediments. The distribution of the normalized PCB concentrations shown in Figures 5.4a and 5.4c may, thus, indicate that the higher concentrations found in the northeastern sector of the sampling grid, and in Burbo Bight, are due to inputs from the River Mersey which is also a significant source of mercury into Liverpool Bay. The transport of sediments towards the coastal areas and towards the Mersey in particular may superimpose the PCB inputs from the Mersey, with PCB inputs from sewage sludge, industrial wastes and dredged material further offshore. The possible sources of PCBs in sediments in Liverpool Bay are further explored later in this chapter through the analysis of the distribution patterns of the individual congeners.

5.2.1.2. Comparisons with PCB levels in other regions

The comparison between PCB levels in Liverpool Bay and levels reported for sediments in other regions is based on the absolute PCB concentrations (rather than the normalized concentrations), as many of the studies have been carried out in total sediments and, in some cases, a description of the sediment characteristics such as grain size composition and organic carbon content is not given. Although, as mentioned in the previous section, the comparison between the results of sediments with substantially different sedimentological characteristics may be questionable, the aim of this section is only to put the total PCB results from this study in a more global context as, surprisingly (considering the concern of the PCB contamination of the environment and the knowledge of waste disposal activities in the region), this seems to be the first data set of PCB concentrations in sediments reported for Liverpool Bay (and for coastal marine sediments in Britain) and, therefore, represents the first report on the state of PCB contamination of sediments in this area which has been extensively studied for other types of contaminants and for heavy metals in particular.

The average total PCB concentration of the sediments in this study (n=66) was 3938 pg g^{-1}. The highest concentrations were found at the stations in the Burbo Bight with values in this area ranging from 13676 pg g^{-1} at station NW-24 to a maximum of 37883 pg g^{-1} at station YY-1. Stations U-9 and P-11 also showed among the highest values in the region (17688 and 28680 pg g^{-1} respectively). It can be seen in Appendix B3 that the stations previously mentioned also contained the highest amounts of fine particles in the total sediment with values of 61, 37 and 34% of fine fraction for samples YY-1, U-9 and P-11 respectively. In the northern region of the sampling grid, where most of the samples showed fine particle concentrations higher than 5% (see Fig. 4.2a), the total PCB concentrations ranged from 1000 to 10000 pg g^{-1}. The southern sector of the sampling grid, where most of the sediments had proportions of fine fraction lower than 1%, total PCB concentrations where lower than 1000 pg g^{-1} and several samples had concentrations lower than 350 pg g^{-1} (see Fig. 5.4a and Appendix C2) and a minimum of 82 pg g^{-1} at station S-7 which also had the lowest amount of fine particles (0.08%, see Appendix B3). Other stations with total PCB concentrations lower than 150 pg g^{-1} were G-9, J-9 and T-10 with concentrations of 96, 86 and 143 pg g^{-1} respectively and fine fraction proportions of 0.21, 0.17 and 0.09% respectively.

The data for total PCBs in the present study are compared with the most recent reports of PCBs in estuarine and marine sediments (found in the literature revised by the author) which were determined in all cases by high resolution gas chromatography. In a recent review of PCBs in coastal and open ocean sediments by Fowler (1990) it is interesting to notice that the data reported for open ocean surface sediments are within the range of values found in the present study. For the Mediterranean sea, values from 0.6 to 9.0 ng g^{-1} (all mentioned concentrations will be in dry weight unless otherwise stated) are reported, whereas a concentration of 0.6 ng g^{-1} is reported for a sediment core from the Sargasso Sea. These values are compared against the range of 0.08 to ~38 ng g^{-1} found in the present study. It is important to mention, however, that all of these studies in the open ocean were done during the mid seventies, usually with packed columns and during a period in which the production and wide spread use of PCBs in the largest industrialized countries was still common, as the production of PCBs was not banned in the United States until 1977 (Knap *et al.*, 1986). Whether the comparatively large values of total PCBs (it would be expected that coastal sediments such as those in Liverpool Bay receiving inputs of urban and industrial wastes were largely more contaminated than open ocean deep sediments) found in open ocean sediments were due to analytical artifacts or were a result of much higher inputs of PCBs into the environment in the seventies is difficult to assess.

Regarding the possible effect of contamination during sampling, and during sample preparation, it is important to mention that it was not until the early eighties that improvements in the analytical procedures to reduce blanks were particularly attended to, and even recently (Mudroch *et al.*, 1989) blanks up to 45.6 ng g^{-1} (higher than the most contaminated sample in the present study) are reported. Although these blanks may have not significantly affected the conclusions by Mudroch *et al.* (1989) as their sediment samples had concentrations up to 14200 ng g^{-1}, it is obvious that they would have been completely unacceptable for the present work and for most of the studies reporting PCBs in coastal and open ocean sediments (see Fowler, 1990). As the original references reporting the open ocean data in the review by Fowler (1990) were not available at the moment of writing this discussion, it can only be said at this stage that, regarding possible analytical artifacts in those results, large differences in PCB levels in seawater have been attributed to possible contamination of the samples during collection and preparation for the analysis in the past (Schulz *et al.*, 1988). However, it is also important to mention that PCB determinations in the dissolved phases, particularly at very low levels, are much more difficult and more prone to contamination than determinations of PCBs in sediments.

On the other hand, there is evidence that the reduction of PCB inputs into the environment may be (at least partially) responsible for the relatively large values observed in open ocean sediments during the seventies. Knap *et al.* (1986) studied the flux of chlorinated synthetic organic chemical including PCBs in the deep Sargasso Sea by analysing particulates collected with sediment traps deployed at a depth of 3200 m between 1978 and 1980. In the size fraction analysed by these authors (<125 μm) which accounted for 75-90% of the material collected, the total PCB concentrations on particles ranged from 50 to 350 ng g^{-1} and had an average of ~150 ng g^{-1} which represents ~4 times the maximum concentration observed in the present study. Knap *et al.* (1986) concluded that PCBs were major contaminants on particles in the open ocean up to 1980, although production in the United States ceased in 1977.

Regarding the levels of PCBs in Liverpool Bay sediments as compared to other coastal areas, Table 5.4 shows the range of total PCB concentrations found in this study and those found in other regions which are reported in relatively recent studies. All these studies determined PCBs in sediments by glass capillary gas chromatography and some of them reported concentrations for individual congeners. Although, as indicated in Table 5.4, the calculation of total PCBs in the different studies was based on the quantification of a different number of congeners and, therefore, direct comparisons of the results can not be highly precise, a general comparison of the values can still be made as the main aim is to give a global picture of what is the status of ~~a~~

Table 5.4. Comparison of the total PCB concentrations in the sediments from Liverpool Bay with concentrations in sediments reported for various marine coastal and estuarine areas. The numbers of the congeners used to estimate the total concentration in each study (if reported) are shown in parenthesis preceded by a letter t. The concentrations of some PCB congeners taken from these references are also shown. In the column showing the sediment fraction analysed, (M) indicates that the sediments were muddy and (FS) indicates fine sands.

Table 5.4.

Location	Sediment fraction	PCB conc. range (ng g^{-1})	Reference
Liverpool Bay	Total	0.08-38 (t55 CBs) 0.007-1.60 (CB 28) 0.006-1.69 (CB 153)	This study (1991)
North Sea	Total	<0.05->2.0 (t3 CBs)	Lohse (1988)
North Sea	Total	0.27-4.7 (t21 CBs)	Boon *etal.* (1985)
North Sea coast	Suspended Particles	2.1-8.2 (CB 52) 1.8-24.6 (CB 180)	Duinker (1986)
Rhine (estuarine)	Total	~10-~60 (CB 28) ~10-~60 (CB 153)	Duursma *et al.* (1989)
Rotterdam Harbour	Total	200-512 (6 CBs) 90-105 (CB 28) 91-105 (CB 153)	Japenga *et al.* (1988)
Elbe Estuary		30.6-188 (t6 CBs) 1.5-29.4 (CB 28) 8.0-41.8 (CB 153)	
Hano Bight (Baltic)	Total Susp. Part.	0.9 ± 0.3 (t CBs) 11.2 ± 3.5 (t CBs)	Larsson (1984)
Lagoon of Venice (Adriatic coast)	Total (M)	~15 (t CBs)	Pavoni *et al.* (1987)
Thermaikos Gulf (Greece)	<63µm	5-39 (t CBs) 0.29-0.43 (CB 28) 0.64-4.19 (CB 153)	Larsen and Fytianos (1989)
Manukau Harbour (New Zealand)	Total (M)	0.5-14.2 (t51 CBs) 0.1-2.3 (CB 31?) 0.1-1.1 (CB 153)	Fox *et al.* (1988)
Junk Bay	Total	31-2200 (t CBs) 0.08-7.6 (CB 77) 0.002-0.30 (CB 126)	Kannan *et al.* (1989)
Tolo Bay & Channel (Hong Kong)		6.6-45 (t CBs) 0.057-0.085 (CB 77) <0.002-0.005 (CB 126)	
Acushnet River Estuary (Mass.)	Total	~1200 (CB 28) ~540 (CB 153)	Farrington *et al.* (1986)
New Bedford Harb. (Estuary) Mass.	Total	6100-2.1x10^{6} (t CBs) 170-170x10^{3} (CB 52) 260-54x10^{3} (CB 153)	Pruell *et al.* (1990)
New Bedford Harbor (Mass.)	Total (M)	1270-6840 (A1242) 8860-26x10^{3} (A1254)	Brownawell and Farrington (1986)
Upper Hudson River	Total (FS)	1410-16x10^{3} (t CBs)	Bush *et al.* (1987)
Buzzards Bay (New Bedford)	Total (M)	~1300 (t CBs)	Beller and Simoneit (1986)
Long Beach Harbor (Los Angeles)		~91 (t CBs)	

total PCB levels in Liverpool Bay in relation to other coastal sediments near industrialized areas. Table 5.4 also indicates that in all but one study the determinations were carried out on the total sediments which also limits the extent of this discussion although some of these studies were done in areas where net sediment deposition occurs and may have a large proportion of fine sediments and, thus, may be comparable with the sediment samples in this study in which a large proportion of fine particles was observed.

Total PCB levels in sediments from Liverpool Bay are similar to those reported for deposited sediments and suspended particles in the North Sea region. Table 5.4 shows that the values reported by Lohse (1988), Boon *et al.* (1985) and Duinker (1986) are all within the range observed in the present study. As in the present study, Boon *et al.* (1985) found a relationship between grain size composition of the sediments and PCB concentrations, and reported that sandy sediments had PCB levels below the detection limit of their analytical procedure. Lohse (1988) reported increasing concentrations (for the sum of 3 congeners, 153+138+180) towards the coastal areas in sediments from the North Sea, with highest concentrations (>2 ng g^{-1}) near the German coast, which are similar to the highest concentrations (for the sum of the same congeners) found in the present study in Burbo Bight. The trend of increasing concentrations towards the coastal zones in the North Sea is emphasized by the values reported in sediments from estuarine and harbour sediments (Duursma *et al.*, 1989; Japenga *et al.*, 1988) reaching total PCB concentrations of 512 ng g^{-1} in Rotterdam Harbour (see Table 5.4). A value of 0.9 ng g^{-1}, within the range observed in this study, was also observed in a sediment in Hano Bight (Baltic Sea). Concentrations in suspended particles (~11 ng g^{-1}) in Hano Bight were higher than those in deposited sediments (Larsson, 1984) probably suggesting that sinking particles in this region are acting as a source of PCBs in the sediments. Larsson (1984) and Fowler (1990) suggested that as the reported concentrations in sinking particles were higher than the concentration in surface sediments, some decomposition and compound recycling takes place after deposition, thus, deposited sediments may be considered as sources of PCBs into the water column. Total PCB levels in sediments from Liverpool Bay are also similar to the levels reported for other coastal areas with intense nearby industrial activity such as the Lagoon of Venice, the Thermaikos Gulf and Manukau Harbour (Table 5.4).

The fact that the PCB concentrations in Liverpool Bay sediments are similar to those of other industrialized coastal regions may suggest that the contamination levels in this area are high, particularly if comparisons could be made with more pristine areas (for which recent data are lacking or scarce) where the lack of industrial activity may indicate the lack of direct inputs of

PCBs and other contaminants. On the other hand, these values are comparatively much lower than the highest concentrations reported for sediments in some estuaries and harbours. For example, Kannan *et al.* (1989) analysed sediments in two areas in Hong Kong and reported a range of total PCB concentrations of 6.6 to 45 ng g^{-1} in the Tolo Bay and Channel, which are similar to the highest values found in Liverpool Bay, however, for Junk Bay sediments these authors reported a range from 31 to 2200 ng g^{-1}, that is, the highest value in this area was around 58 times higher than the highest value in Liverpool Bay. Bush *et al.* (1987) reported a range of total PCB concentrations of 1410-$16x10^3$ ng g^{-1} in the Upper Hudson River which has been badly polluted with direct inputs of PCBs, this range representing 37 to ~420 times the highest value in Liverpool Bay. Even higher values than those in the Hudson River have been reported by Brownawell and Farrington (1986) and Pruell *et al.* (1990) in the Acushnet River Estuary region and in the New Bedford Harbour in particular, with a range of 6100 to $2.1x10^6$ ng g^{-1} reported by Pruell *et al.* (1990), equivalent to ~160-~55000 times the highest value recorded in Liverpool Bay. According to Pruell *et al.* (1990) the concentrations of PCBs found in New Bedford Harbour sediments are the highest reported for any estuary.

The significance of the total PCB levels found in Liverpool Bay sediments, with regard to possible detrimental effects, is difficult to assess. In areas such as New Bedford Harbour, Farrington *et al.* (1986) reported that harvesting of lobsters and certain fish and bivalves is banned because of PCB concentrations in excess of the 5 μg g^{-1} wet weight edible tissue guidelines. PCB levels above 5 μg g^{-1} have been reported in liver of some fish species (cod and whiting) in Liverpool Bay between 1981 and 1984, however, total PCB levels in muscle (wet weight) were reported to be between 15 and 60 ng g^{-1} between 1983 and 1984 (Franklin, 1987). Except for a 1984 plaice sample in which the PCB level was above the upper level (50 ng g^{-1}) of the guidelines for muscle recommended by the Joint Monitoring Programme (JMP) of the Oslo and Paris Commissions, PCB concentrations in the muscle of fish from Liverpool Bay were generally low (Franklin, 1987). The method for the determination of PCBs in sediments used in the present study was tested for the analysis of biological samples, including a pooled sample of the soft parts of three hermit crabs collected around Site SI in Liverpool Bay in 1989. The total PCB level in crabs was 1400 ng g^{-1} in a lipid basis, which was equivalent to 122 ng g^{-1} wet weight. Assuming that the water content in crabs was 50%, then the PCB levels in a dry weight basis would be 244 ng g^{-1} which represents more than 6 times the highest concentration observed in sediments in the bay.

Total PCB concentrations in sediments, fish and shellfish in Liverpool Bay are much lower than in areas where severe PCB pollution has occurred, therefore, these levels may suggest that the inputs of PCBs in this region are of no serious concern, particularly as the concentrations found in fish are unlikely to pose any threat either to the fish themselves or to the people who eat them (Morris *et al.*, 1989). However, in a recent study of organochlorine concentrations in dolphins and porpoises of Cardigan Bay (which is expected to be less contaminated than Liverpool Bay) extremely high concentrations of PCBs were reported in fat-rich tissues (Morris *et al.*, 1989). The highest total PCB concentrations were found in the blubber of a bottlenose dolphin calf (290 $\mu g\ g^{-1}$) and in common porpoises (93 $\mu g\ g^{-1}$), these values being amongst the highest ever recorded for this kind of marine mammals. More important, the levels found in four of the six individuals analysed in this report could have serious implications for these animals in terms of their ability to resist disease and/or their reproductive status, and may in part be associated with observed population changes (Morris *et al.*, 1989). The high concentrations in dolphins and porpoises were not derived from local pollution, but from the animals' normal diet which did not show markedly elevated levels of organochlorines (Morris *et al.*, 1989). From these observations, it is clear that although the PCB levels in Liverpool Bay sediments are not amongst the highest reported in coastal areas, it can not be concluded that these levels pose no threat to the ecosystem. Several aquatic food chains start with benthic organisms which obtain their energy from scavenging the surface of sediment particulates. At the same time, benthic organisms may accumulate the contaminants in the sediments, particularly those which are lipophilic such as PCBs, and these pollutants may be transferred to the rest of the food chain, therefore, coastal sediments may act as sources of PCBs to the top predators such as marine mammals. The last observation leads to the conclusion that, until the transfer from sediments through the food chain of PCBs and other contaminants in the region is better understood, the significance of the levels of PCBs observed in sediments from Liverpool Bay can not be properly assessed.

5.2.2. PCB congeners

5.2.2.1. Variations in congener distribution patterns ("fingerprint")

It is obvious that the strong effect of the grain size composition on the total PCB concentrations in sediments, which has been discussed above, will be also observed in the concentrations of individual PCB congeners. The following discussion is, therefore, mainly focused on comparisons between the relative proportions ("fingerprint") of PCB congeners between samples, rather than in the distribution of the absolute concentrations of individual congeners in particular which will show a similar distribution to that shown in Figure 5.4a.

Table 5.5 shows descriptive statistics which summarize the data in Appendix C1 showing the concentrations of the PCB congeners determined in each sediment sample. In Table 5.5, the column with the number of samples in which the congeners were not determined (either because of uncertainty in the identification of the congener or because the concentrations were below the limit of detection) indicates that some congeners were quantified in all of the samples (66) analysed, and that 26 of the 55 congeners shown in the table were determined in 60 or more of the samples. All of the congeners listed in Table 5.5 were detected in sediments with a high total PCB concentration. For example, the chromatograms for samples YY-1 and P-11 (Figs. 5.5a and 5.5b respectively), which were the two stations with the highest PCB concentrations, show that not only all of the congeners listed in Table 5.5 were present at detectable levels in these sediments, but also show that many more possible PCB congeners were not determined, therefore, the values reported earlier for total PCBs are an underestimation of the "true" total PCB content in the sediments from Liverpool Bay. On the other hand, several congeners were below the detection limit in the sediments showing the lowest concentrations. For example, in the samples from stations S-7 and J-9 only 17 and 16 congeners respectively (of those included in Table 5.5) were present above the detection limit (see chromatograms in Fig. 5.6a and 5.6b).

The congeners showing the highest mean concentrations (see Table 5.5) were Nos. 153 and 138 (217 and 216 pg g^{-1} respectively) whereas the highest concentration for any of the congeners in a particular sample was found in sample YY-1 for congener 95 (1899 pg g^{-1}), with congeners 28, 118, 153, 138, 15 and 77 also showing values above 1500 pg g^{-1} at this station. On the other hand, the column showing the minimum concentration values determined for each congener (which represent the practical limit of detection for most of the congeners) indicates that the minimum quantity detected for various of the congeners was 1 pg g^{-1}. The wide range of concentrations (see minimum and maximum values and the standard deviations in Table 5.5) observed for each congener, as in the case of total PCB concentrations, reflects the heterogeneity in the grain size composition of Liverpool Bay sediments. This heterogeneity is further illustrated by the first and third quartile values (Q1 and Q3) which indicate that, if the 17 samples with highest concentrations and the 17 samples with the lowest concentrations are not considered (*i.e.* if a large proportion of the extreme values is ignored), variations in the individual congener concentrations of around one order of magnitude are still observed.

Table 5.5. Descriptive statistics for the PCB congener concentrations reported in Appendix C1, obtained with the command DESCRIBE of the statistical package MINITAB. Only the samples in which detectable amounts of the congener were present were used in the calculations. The concentrations in the table are in pg g^{-1}.

CB	n	*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN	MIN	MAX	Q1	Q3
28	66	4	179.6	74.5	132.4	314.0	38.6	7.0	1600.0	12.8	191.0
52	66	4	130.7	58.0	98.0	209.0	25.7	7.0	1080.0	15.0	139.0
101	66	4	145.6	62.5	112.8	220.0	27.1	4.0	1140.0	22.0	178.5
118	66	4	173.8	75.0	133.2	274.2	33.8	4.0	1651.0	23.0	204.8
153	66	4	217.4	104.5	175.3	317.4	39.1	6.0	1687.0	24.8	250.3
138	66	4	216.6	100.5	172.1	322.0	39.6	7.0	1792.0	23.0	253.5
180	66	4	160.0	77.0	126.1	245.8	30.3	4.0	1489.0	19.3	201.8
TICES	66	4	1220.0	578.0	949.0	1884.0	232.0	41.0	10386	148.0	1435.0
18	54	16	83.6	27.5	56.8	152.1	20.7	2.0	754.0	9.7	64.3
15	61	9	173.1	78.0	115.8	332.9	42.6	1.0	1808.0	11.0	166.5
54	9	61	36.9	34.0	36.9	30.8	10.3	8.0	112.0	14.0	41.0
31	36	34	47.9	19.5	38.3	65.1	10.8	1.0	250.0	11.5	40.0
49	64	6	116.9	39.0	80.9	221.9	27.7	2.0	1248.0	10.2	119.3
44	64	6	84.0	35.0	60.6	145.9	18.2	3.0	760.0	11.0	88.3
74	64	6	108.0	40.0	76.5	197.3	24.7	1.0	1050.0	5.3	104.0
70	66	4	119.8	43.5	88.3	205.8	25.3	3.0	1140.0	9.0	130.5
95	66	4	200.2	81.0	147.4	337.6	41.6	8.0	1899.0	19.5	241.8
60	55	15	80.7	39.0	59.0	130.2	17.6	2.0	689.0	7.0	80.0
92	62	8	105.7	42.5	75.3	187.9	23.9	2.0	1100.0	8.0	106.5
89	57	13	135.3	50.0	97.7	232.9	30.9	5.0	1300.0	14.0	127.0
99	65	5	72.6	32.0	53.8	120.2	14.9	2.0	690.0	11.0	82.0
97	62	8	47.6	17.0	33.8	81.9	10.4	1.0	450.0	6.0	53.3
87	62	8	77.4	35.5	60.5	112.7	14.3	3.0	663.0	13.8	90.8
136	62	8	82.0	24.0	58.9	144.2	18.3	2.0	680.0	7.0	93.0
110	66	4	133.4	56.5	108.2	186.3	22.9	5.0	900.0	23.0	164.7
77	10	60	330.0	97.0	214.0	494.0	156.0	19.0	1568.0	27.0	592.0
82	45	25	27.4	16.0	22.8	33.4	5.0	3.0	174.0	6.5	30.5
151	60	10	55.9	29.0	43.6	82.1	10.6	2.0	408.0	7.0	60.5
149	65	5	144.2	74.0	113.4	214.5	26.6	5.0	1113.0	14.0	161.0
134	36	34	40.0	16.5	29.4	60.6	10.1	2.0	285.0	10.0	36.3
114	21	49	60.9	36.0	53.5	59.7	13.0	7.0	256.0	20.5	99.0
146	65	5	141.4	71.0	108.1	231.1	28.7	1.0	1200.0	10.0	162.0
132	19	51	138.8	56.0	110.7	200.0	45.9	3.0	752.0	33.0	137.0
105	50	20	114.0	59.5	89.5	161.5	22.8	2.0	784.0	10.8	129.7
141	58	12	51.2	23.0	38.8	80.0	10.5	2.0	457.0	6.0	62.0
158	36	34	20.5	14.5	17.1	22.6	3.8	2.0	107.0	5.3	24.8
129	29	41	54.2	26.0	48.4	60.4	11.2	3.0	261.0	16.0	84.5
187	66	4	86.2	39.5	67.9	132.2	16.3	2.0	721.0	9.0	94.8
183	59	11	36.4	21.0	30.3	45.4	5.9	3.0	219.0	6.0	46.0
128	61	9	36.7	21.0	30.7	45.6	5.8	2.0	250.0	6.5	50.0
185	19	51	26.1	15.0	22.2	27.6	6.3	5.0	114.0	10.0	38.0
174	60	10	17.8	7.5	13.8	27.0	3.5	1.0	147.0	2.0	20.0
177	57	13	39.1	21.0	31.8	53.6	7.1	1.0	276.0	5.0	44.5
171	45	25	41.1	22.0	34.5	50.7	7.6	3.0	270.0	11.5	45.0
156	20	50	18.0	16.0	16.6	15.6	3.5	2.0	60.0	4.0	25.5
173	3	67	47.7	46.0	47.7	35.5	20.5	13.0	84.0	13.0	84.0
201	15	55	55.1	34.0	48.0	54.0	13.9	7.0	196.0	21.0	67.0
169	29	41	18.0	5.0	14.9	27.2	5.0	1.0	120.0	2.0	30.0
199	63	7	63.2	28.0	47.9	101.6	12.8	1.0	557.0	6.0	72.0
196	57	13	51.6	23.0	39.4	78.0	10.3	2.0	408.0	6.0	58.0
189	14	56	29.8	30.5	27.6	22.5	6.0	4.0	82.0	9.5	39.5
195	47	23	23.9	11.0	19.0	35.2	5.1	1.0	182.0	3.0	23.0
194	66	4	36.5	14.5	28.3	58.2	7.2	1.0	320.0	3.0	40.5
205	47	23	12.8	7.0	11.0	15.7	2.3	1.0	77.0	2.0	13.0
206	55	15	30.6	15.0	24.4	41.9	5.6	2.0	222.0	4.0	32.0
209	56	14	45.0	21.0	32.4	76.8	10.3	1.0	445.0	5.0	43.0

Figure 5.5. Gas chromatograms in a DB-5 column for sediment samples (a) YY-1 and (b) P-11. The sample weights extracted were 15 and 40 g respectively and the final extract volumes were 1 and 2 ml respectively. These sediments were classified in cluster 2.

5.5

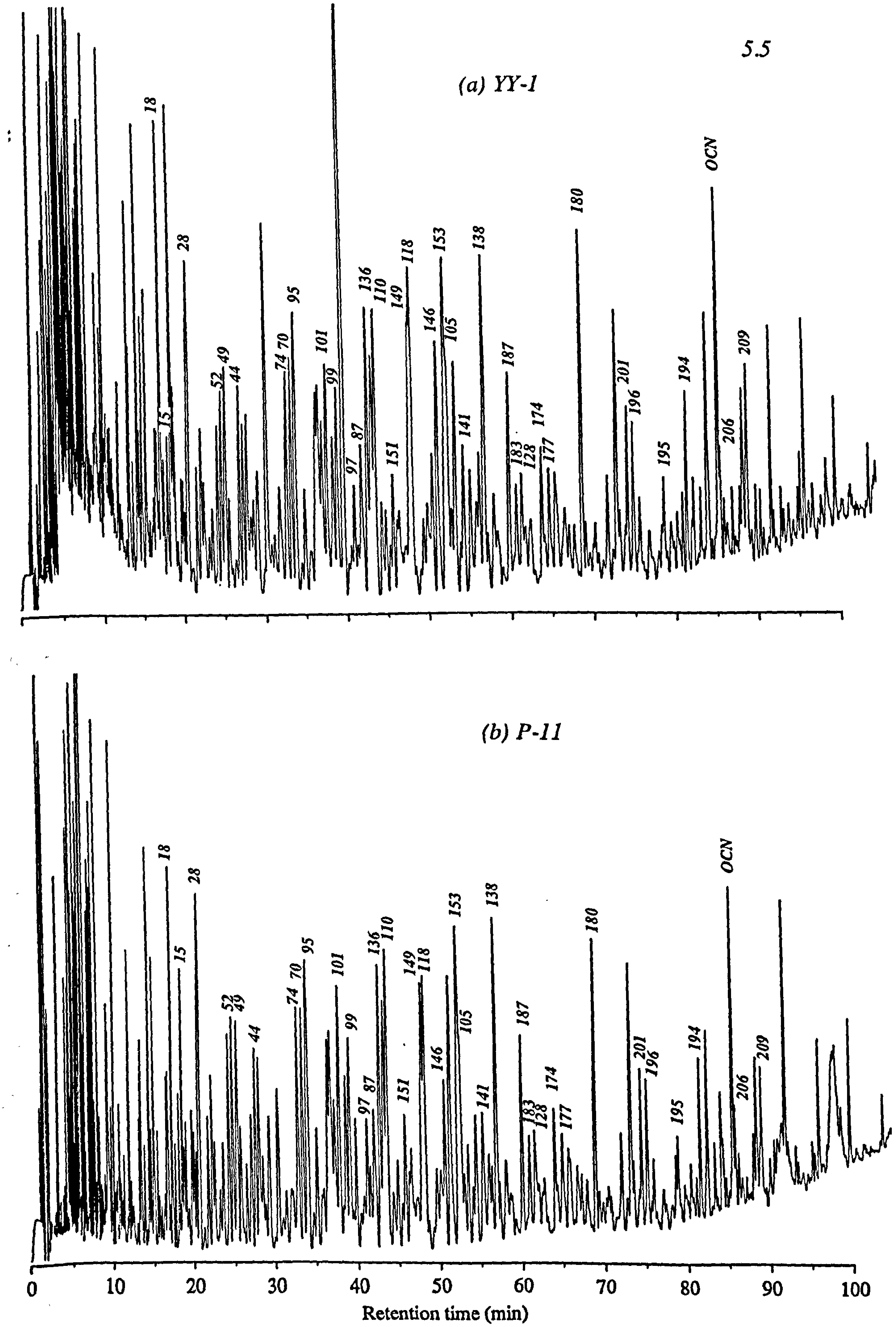
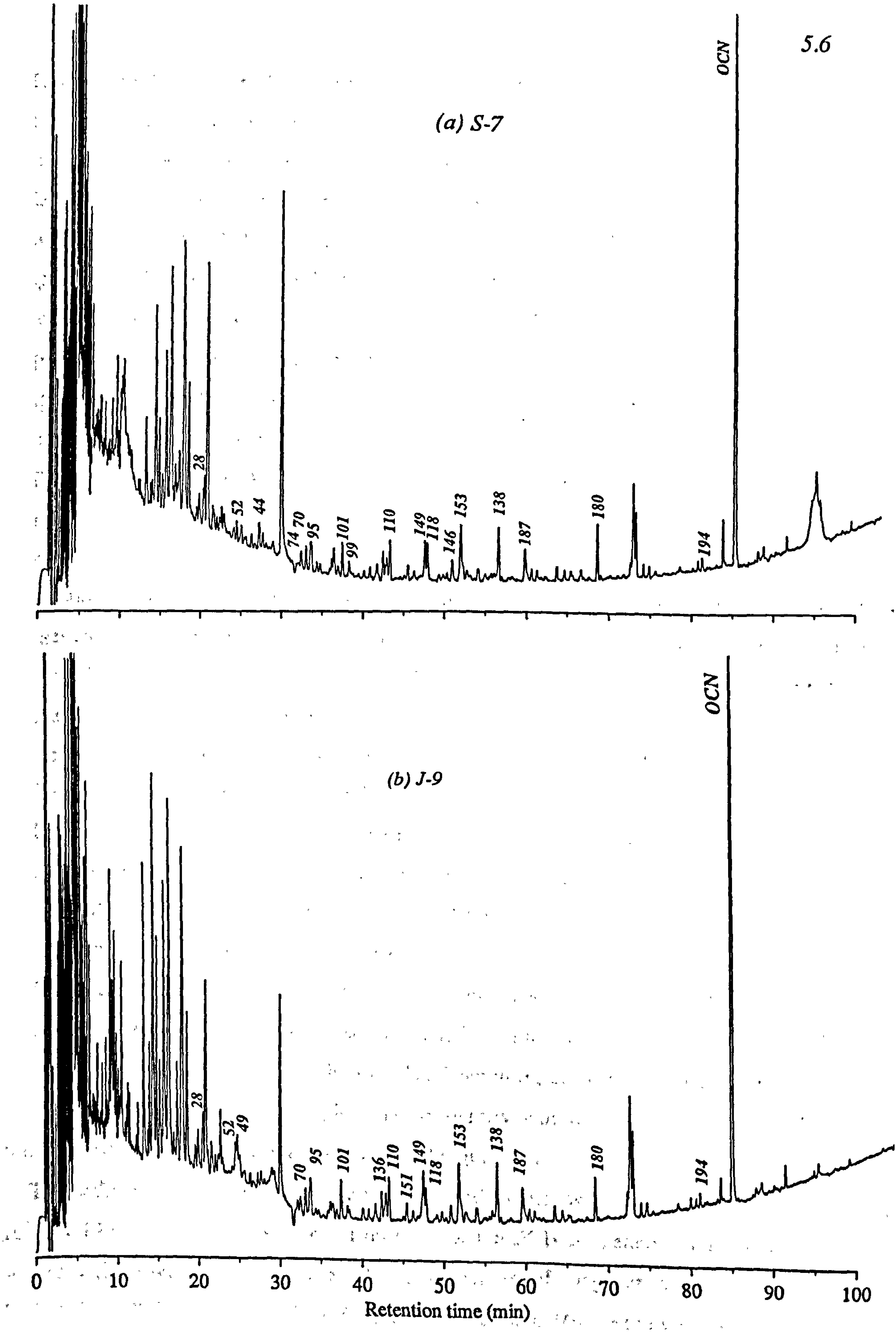

(a) YY-1
18
15
28
52
49
44
74
70
95
101
99
97
87
136
110
151
149
118
146
153
105
141
138
187
183
128
174
177
180
201
196
195
194
OCN
206
209
(b) P-11
18
15
28
52
49
44
74
70
95
101
99
97
87
136
110
151
149
118
146
153
105
141
138
187
183
128
174
177
180
201
196
195
194
OCN
206
209
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.6. Gas chromatograms in a DB-5 column for sediment samples (a) S-7 and (b) J-9. The sample weights extracted were 70 and 60 g respectively and the final extract volumes were of 0.2 ml. These sediments were classified in cluster 3.

5.6


(a) S-7
OCN
28
52
44
74
70
95
101
99
110
149
118
146
153
138
187
180
194
(b) J-9
OCN
28
52
49
70
95
101
136
110
151
149
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

To evaluate the relative abundance of each congener within the PCB group, the contribution of each congener (in percent) to the total PCB concentration in each sample was estimated, and a summary of these calculations is given in the descriptive statistics shown in Table 5.6. This table shows that, regardless of the absolute concentrations, the contribution of each particular congener to the total PCB concentration varied over a relatively narrow range. For example, congener No. 28 contributed to the total PCB content from 1.26% in sample N-10 to 8.54% in sample S-7 whereas congener No. 15 contributed 0.43% and 13.4% in samples P-8 and G-7 respectively. The first and third quartile values indicate that the contribution of individual congeners to the total PCB values varied within a much narrower range in most samples than the overall range indicated by the maximum and minimum values.

The values shown in Table 5.6 indicate that the seven ICES congeners were significant components in the sediments from Liverpool Bay with average contributions to the total PCB levels ranging from 4.34% for congener 28 to 6.26% for congener 138. This table shows that, on average, congeners 153 and 138 were the largest PCB components in the sediments and that the seven ICES congeners contributed on average 35% of the total PCBs with their contribution ranging from 22.5% up to 52.4%. In order of decreasing abundance, other significant components of the total PCBs were congeners Nos. 95 > 110 > 15 > 149 > 146 > 70 > 89 > 92 > 49 > 187 > 105 > 44 > 87 > 99 > 74, which cover a range from dichloro (No.15) to heptachloro (No. 187) biphenyls. Thus, the list of the overall 22 most abundant congeners (>2% of the total PCBs) includes one di-, one tri-, five tetra-, nine penta-, four hexa-, and two heptachlorobiphenyls. The data shown in Table 5.6, however, only represent the average contribution of each congener to the total PCB content in all samples, and some important variations in the relative contributions ("fingerprint") were observed between samples.

An analysis of the variations of each congener (one by one) within the group of PCB congeners determined in the present study would be unpractical, considering that 45 of them were determined in more than 50% of the samples. Therefore, in order to study the general trends in the PCB composition among samples, and to identify samples with similar PCBs "fingerprint", the application of multivariate statistical techniques was necessary.

The sediments in Liverpool Bay were classified by means of the "ratio matching" technique followed by cluster analysis, applied on a set of ten PCB congeners, in a similar way as they were classified based in their elemental content. The set of congeners used in the analysis, which included the ICES congeners 28 (tri-CB), 52 (tetra-CB), 101 (penta-CB), 118 (penta-CB), 153 (hexa-CB), 138 (hexa-CB) and 180 (hepta-CB), and also included congeners 70 (tetra-CB), 187

Table 5.6. Descriptive statistics for the PCB congener concentrations in Appendix C1 expressed as a percentage of total PCBs.

CB	n	nd	MEAN	MEDIAN	TRMEAN	S.D.	SEMEAN	MIN	MAX	Q1	Q3
28	66	4	4.34	4.32	4.26	1.43	0.18	1.26	8.54	3.44	4.91
52	66	4	4.37	3.41	4.07	2.55	0.31	2.24	14.21	2.82	4.71
101	66	4	4.45	3.98	4.34	1.43	0.18	2.68	8.64	3.47	4.96
118	66	4	5.17	4.93	5.06	1.50	0.18	1.97	13.22	4.32	5.72
153	66	4	6.24	6.34	6.25	1.10	0.14	3.34	8.96	5.57	6.89
138	66	4	6.26	6.22	6.24	1.38	0.17	2.79	12.02	5.54	7.11
180	66	4	4.90	4.59	4.81	1.76	0.22	1.97	9.77	3.78	5.73
TICES	66	4	35.29	34.65	35.05	5.58	0.69	22.51	52.44	32.11	38.97
18	54	16	1.60	1.38	1.57	0.69	0.09	0.66	3.48	1.07	2.15
15	61	9	4.10	3.48	3.82	2.41	0.31	0.43	13.43	2.67	4.73
54	9	61	0.28	0.24	0.28	0.13	0.04	0.14	0.60	0.21	0.31
31	36	34	0.64	0.63	0.63	0.23	0.04	0.25	1.17	0.46	0.76
49	64	6	2.43	2.41	2.44	0.60	0.08	0.98	3.49	2.05	2.88
44	64	6	2.33	2.07	2.22	0.86	0.11	1.42	5.57	1.83	2.56
74	64	6	2.16	2.20	2.16	0.66	0.08	0.66	3.70	1.68	2.68
70	66	4	2.93	2.98	2.96	0.63	0.08	0.40	4.18	2.60	3.29
95	66	4	5.60	5.11	5.43	1.75	0.22	3.23	11.34	4.63	5.95
60	55	15	1.56	1.58	1.57	0.40	0.05	0.66	2.30	1.35	1.85
92	62	8	2.47	2.52	2.47	0.56	0.07	1.31	3.66	2.10	2.84
89	57	13	2.75	2.65	2.73	0.71	0.09	1.49	4.46	2.21	3.23
99	65	5	2.17	1.97	2.11	0.68	0.08	1.32	4.20	1.70	2.54
97	62	8	1.19	1.13	1.16	0.40	0.05	0.62	2.62	0.87	1.32
87	62	8	2.24	2.00	2.18	0.69	0.09	1.31	4.59	1.80	2.60
136	62	8	1.83	1.62	1.74	1.00	0.13	0.25	5.64	1.34	2.06
110	66	4	4.32	4.03	4.28	1.08	0.13	2.25	8.20	3.68	4.95
77	10	60	2.30	2.08	2.27	1.18	0.37	0.69	4.14	1.36	3.32
82	45	25	0.63	0.59	0.62	0.15	0.02	0.42	1.00	0.51	0.70
151	60	10	1.47	1.43	1.46	0.28	0.04	1.04	2.33	1.29	1.61
149	65	5	4.07	3.89	3.98	0.94	0.12	2.51	7.98	3.52	4.43
134	36	34	0.53	0.50	0.53	0.15	0.03	0.25	0.88	0.42	0.67
114	21	49	0.74	0.60	0.61	0.64	0.14	0.35	3.48	0.50	0.71
146	65	5	3.25	3.32	3.20	1.34	0.17	0.45	11.57	2.70	3.80
132	19	51	2.21	2.14	2.02	1.21	0.28	0.84	6.92	1.83	2.26
105	50	20	2.37	2.39	2.38	0.60	0.08	0.56	3.69	2.10	2.78
141	58	12	1.19	1.19	1.19	0.22	0.03	0.56	1.98	1.07	1.30
158	36	34	0.35	0.34	0.35	0.09	0.01	0.24	0.54	0.28	0.42
129	29	41	0.65	0.63	0.64	0.17	0.03	0.39	1.13	0.51	0.74
187	66	4	2.39	2.41	2.41	0.67	0.08	0.40	3.66	2.05	2.84
183	59	11	1.14	1.06	1.10	0.43	0.06	0.58	2.47	0.84	1.35
128	61	9	1.17	1.06	1.11	0.62	0.08	0.43	5.25	0.89	1.32
185	19	51	0.27	0.27	0.27	0.04	0.01	0.21	0.35	0.25	0.30
174	60	10	0.43	0.40	0.42	0.16	0.02	0.20	1.04	0.33	0.46
177	57	13	0.93	0.92	0.92	0.23	0.03	0.38	1.49	0.81	1.07
171	45	25	0.89	0.83	0.88	0.25	0.04	0.38	1.45	0.71	1.06
156	20	50	0.68	0.66	0.69	0.14	0.03	0.41	0.88	0.60	0.82
173	3	67	0.24	0.24	0.24	0.02	0.01	0.22	0.26	0.22	0.26
201	15	55	0.78	0.57	0.68	0.63	0.16	0.39	2.47	0.48	0.63
169	29	41	0.18	0.16	0.17	0.12	0.02	0.04	0.66	0.09	0.22
199	63	7	1.55	1.54	1.57	0.47	0.06	0.28	2.64	1.43	1.84
196	57	13	1.20	1.19	1.19	0.33	0.04	0.38	2.22	1.05	1.31
189	14	56	0.23	0.23	0.23	0.05	0.01	0.17	0.34	0.19	0.27
195	47	23	0.42	0.43	0.42	0.12	0.02	0.12	0.76	0.34	0.47
194	66	4	0.93	0.95	0.93	0.28	0.03	0.25	1.80	0.81	1.08
205	47	23	0.39	0.32	0.37	0.17	0.03	0.17	0.88	0.26	0.46
206	55	15	0.80	0.74	0.79	0.26	0.04	0.25	1.56	0.62	0.95
209	56	14	0.92	0.94	0.91	0.36	0.05	0.20	1.71	0.71	1.14

(hepta-CB) and 194 (octa-CB), was selected because it covers a wide range of chlorination, and also because the congeners in the set were detected in all 66 sediment samples analysed in this study, thus, all samples could be classified.

The dendrogram resulting from the cluster analysis on the matrix of similarities is shown in Figure 5.7. It can be seen from this dendrogram that six clusters could be identified. The results from this analysis were corroborated by repeating the analysis on a second group of ten congeners covering a wide range of chlorination (*i.e.* congener Nos. 44, 70, 99, 97, 146, 128, 177, 196, 206 and 209). Although the congeners in this second set were all present only in 53 samples (as compared to 66 for those in the previous set), the samples were grouped in similar clusters to those resulting from the first analysis. The only relatively important difference between the two analyses was that with the second set of congeners samples N-7 and K-6 were classified into a separate cluster, thus, in Figure 5.7 these samples are labelled as cluster 6 and sample N-10 as cluster 7.

Figure 5.7 and the map including the cluster membership for each sample (Figure 5.8), indicate that most of the samples near the Mersey, and those from the Burbo Bight in particular, were classified in cluster 2 (a total of 14 samples were classified in this cluster). Also classified in cluster 2 was the sample from station K-9 (Site SI). With the exception of samples T-10, S-7 and U-15, all samples from transect R and eastward (see Fig. 3.1), which were not classified in cluster 2, were classified in cluster 1. With the exception of samples G-13, J-13, M-11 and N-11, all those samples shown in Figure 3.1 with labels 11 to 13 (sediments from the northern region of the sampling grid) were also classified in cluster 1. Thus, a large proportion (37 samples) of the sediment samples analysed in the present study were classified in either cluster 1 or 2 (samples from clusters 1 and 2 are separated with a line from the other clusters in Fig. 5.8). Figure 5.8 shows that most sediments in the western-southern region of the sampling grid, which includes the south of Site SI, were classified in cluster 4 (14 samples), whereas 4 samples were classified in cluster 3, 4 samples in cluster 5, 2 samples in cluster 6 and 1 sample in cluster 7. Other samples classified in cluster 5 were T-10 (near the Queen's Channel), U-15 (near the old Site Z), G-13 and J-13 (northwestern corner of the sampling grid).

Cluster 2 included some sediments with the highest PCB concentrations in the study area (the total PCB concentrations and the concentrations normalized with the organic carbon content are shown in Appendix C2). Table 5.7 shows that this cluster had a mean carbon-normalized concentration of 1585 ng g^{-1}, and included the sediments from Burbo Bight in which the highest total PCB concentration value was found at station YY-1 (3232 ng g^{-1}C). The lowest

Table 5.7. Descriptive statistics for carbon normalized total concentration of PCBs in sediments within each cluster. The concentration values are given as ng of PCBs per gram of carbon.

Cluster	mean	n	s.d.	r.s.d.	min.	max.
1	590	22	364	62	108	1334
2	1585	14	771	49	506	3232
3	149	4	196	131	42	442
4	373	14	417	112	74	1672
5+6	458	10	496	108	72	1644

Figure 5.7. Dendrogram obtained in the Cluster Analysis applied on the matrix of similarities for ten PCB congeners (see text for details).

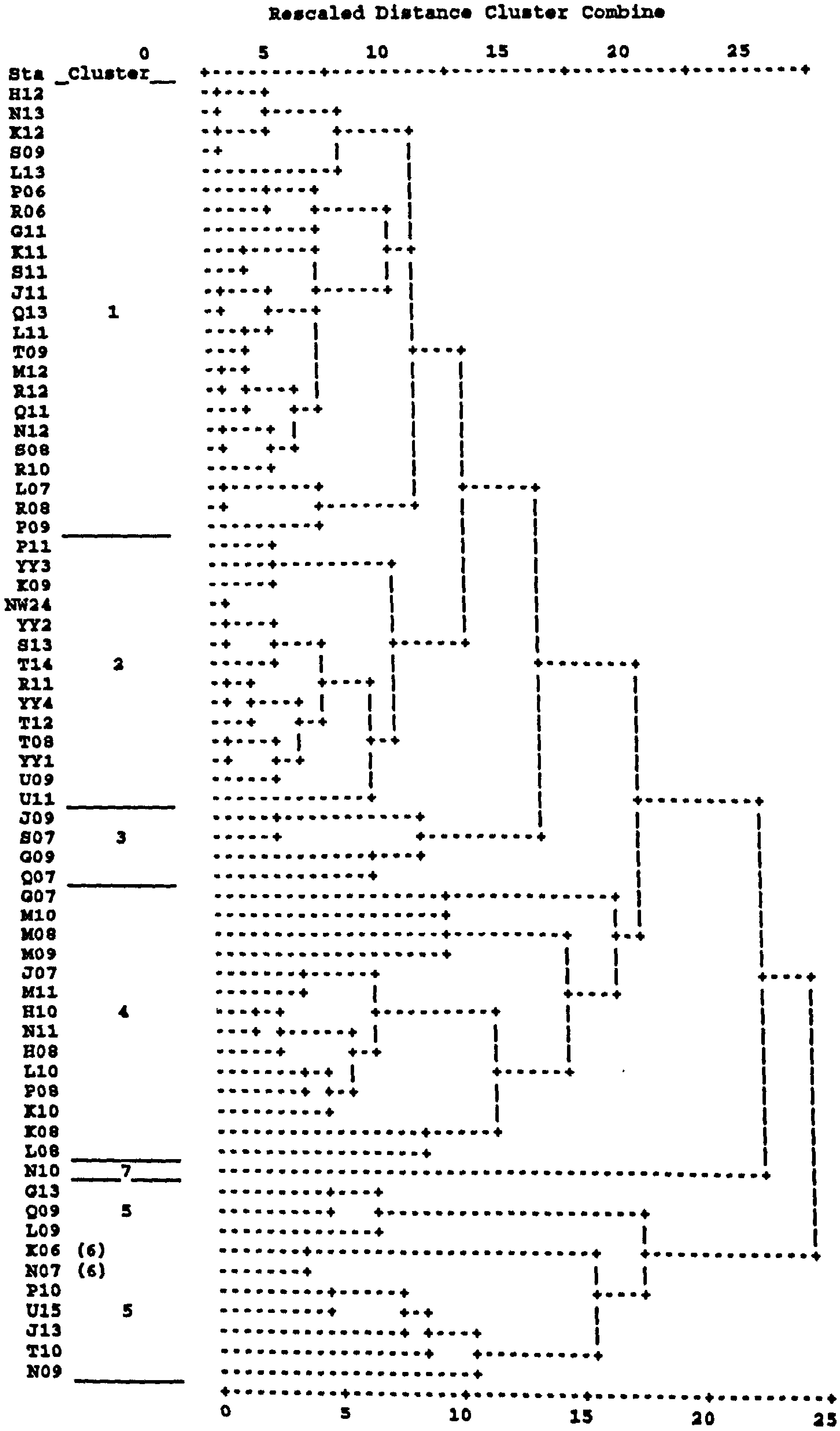
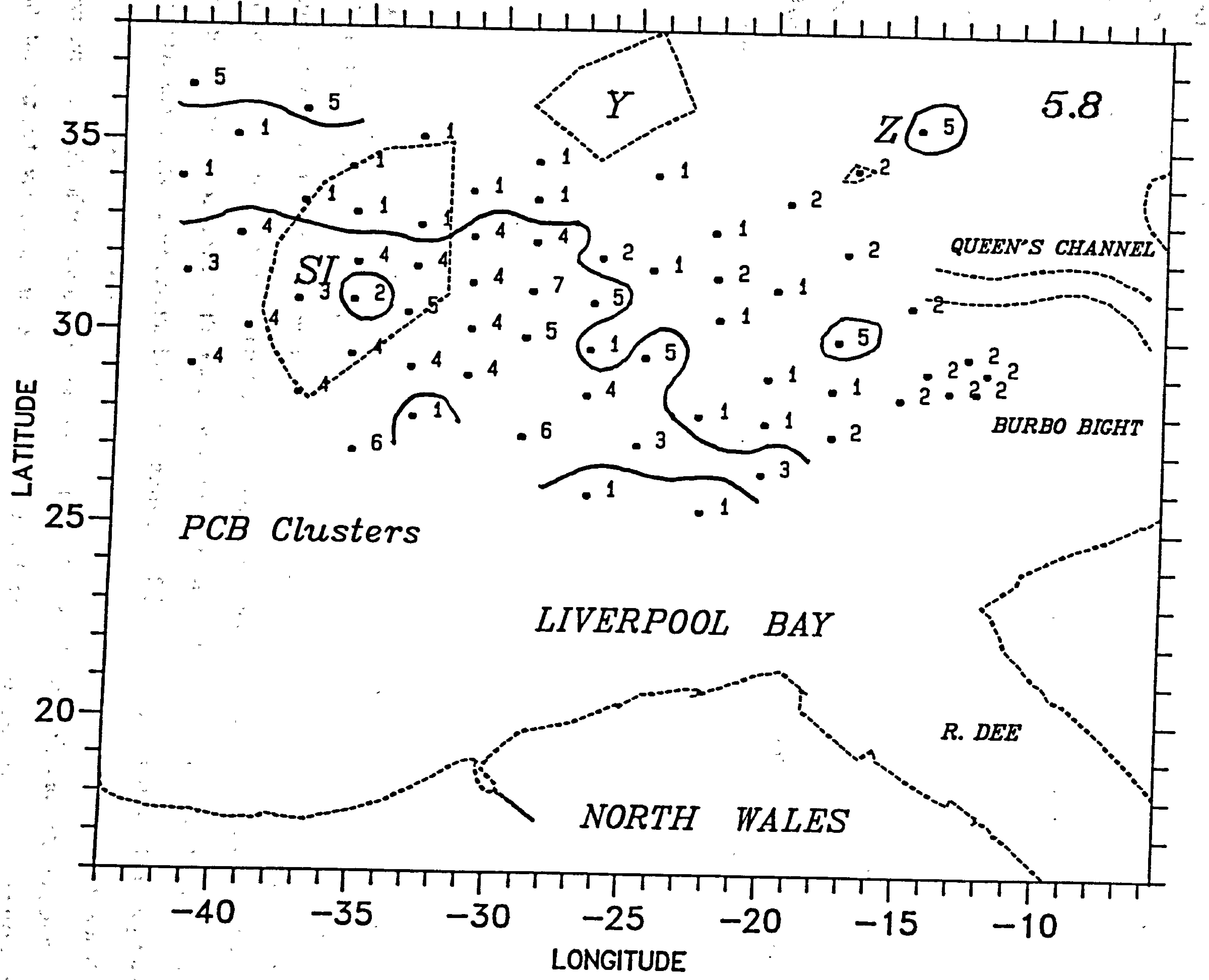


Figure 5.8. Cluster memberships obtained from a cluster analysis based on a matrix of similarities for PCB congener Nos. 28, 52, 70, 101, 118, 138, 153, 180, 187 and 194. The dendrogram from this analysis is shown in Fig. 5.7. The line in the map separates clusters 2 and 1, which are considered as the most contaminated, from clusters 3, 4, 5 and 6. (see text for details).


5.8
PCB Clusters
Y
Z
SI
QUEEN'S CHANNEL
BURBO BIGHT
LIVERPOOL BAY
R. DEE
NORTH WALES
LATITUDE
35
30
25
20
LONGITUDE
−40
−35
−30
−25
−20
−15
−10

concentration in this cluster was found at station U-11 (506 ng g^{-1}C). Although most of the sediment samples within this cluster had high amounts of fine fraction (see Appendix B3), showing a corresponding high concentration of PCBs (see discussion in the previous section), some sediments within this cluster had a relatively low amount of fine particles. For example, sediments from the Burbo Bight had fine fraction concentrations above 26%, whereas sediments from stations T-14, K-9 and U-11 had fine fraction concentrations of 3.68, 2.23 and 1.87% respectively.

Figures 5.5a and 5.5b show the chromatograms of samples YY-1 and P-11 classified in cluster 2. Further examples of sediments in this cluster are given in Figure 5.9 (including the chromatograms of samples U-11 and T-14) and 5.10 (including the chromatograms of samples K-9 and S-13). From these chromatograms it can be seen that, although there was a large difference in the total PCB concentrations and in the amount of fine particles between some sediments in cluster 2, the pattern of the congeners (particularly of those congeners used for the classification of the sediments) remained relatively constant throughout these samples, which suggests a similar source (see matrix of similarities for these samples shown below):

	K-9	P-11	S-13	T-14	U-11	YY-1
P-11	0.879	1.000				
S-13	0.818	0.802	1.000			
T-14	0.815	0.834	0.882	1.000		
U-11	0.806	0.829	0.823	0.810	1.000	
YY-1	0.822	0.827	0.892	0.867	0.867	1.000

From a qualitative inspection of the chromatograms for samples K-9 and U-11 (Fig. 5.10a and 5.9a respectively), which showed the lowest similarity within the group of congeners above, it can be seen that the proportions of not only the ten congeners used in the classification of sediments were similar, but several other congeners also showed the same pattern in the two sediments. Table 5.8, in which the mean (note that the values represent the contribution of each congener to the total value obtained for the summation of the concentration of the ten congeners; these values are referred below as the "relative concentrations") and the relative standard deviation for each of the ten congeners used in the sediment classification are shown, indicates that the largest variations in cluster 2 were found for congeners 52 (r.s.d.=22.2%), 28 (r.s.d.=12.3%) and 180 (r.s.d.=11.2%), therefore, the differences between the patterns in samples from this cluster are mainly due to variations in the relative concentrations of congener No. 52.

Table 5.8. Mean and relative standard deviations within each cluster, of the relative concentrations[a] of each of the ten PCB congeners used in the sediment classification by the ratio matching technique followed by cluster analysis (see text for details).

	Cluster 1		Cluster 2		Cluster 3	
Congener	mean	r.s.d	mean	r.s.d	mean	r.s.d
28	0.10	15.1	0.14	12.3	0.13	21.1
52	0.08	17.8	0.09	22.2	0.17	21.7
70	0.07	9.6	0.09	5.7	0.06	10.7
101	0.10	13.9	0.09	9.6	0.09	11.1
118	0.12	6.9	0.11	9.8	0.10	16.0
138	0.15	8.0	0.14	4.3	0.14	9.8
153	0.16	5.8	0.14	9.7	0.13	13.8
180	0.12	15.7	0.11	11.2	0.11	17.2
187	0.06	7.8	0.06	8.5	0.06	7.9
194	0.02	13.5	0.03	9.7	0.02	9.6

	Cluster 4		Cluster 5		Cluster 6	
Congener	mean	r.s.d	mean	r.s.d	mean	r.s.d.
28	0.07	26.1	0.09	39.7	0.08	4.2
52	0.08	17.5	0.15	32.3	0.31	5.7
70	0.05	18.4	0.08	15.0	0.10	3.7
101	0.09	18.4	0.16	10.6	0.20	2.1
118	0.14	27.9	0.13	27.8	0.08	12.2
138	0.16	8.8	0.13	20.3	0.07	6.4
153	0.16	9.5	0.13	13.2	0.08	10.5
180	0.16	22.2	0.06	20.3	0.06	3.4
187	0.06	22.2	0.04	25.1	0.02	24.6
194	0.03	32.4	0.01	28.0	0.01	0

Note [a] The relative concentration for each of these congeners in each sample was computed by dividing the absolute concentration of the congener by the sum of the concentrations of the ten congeners.

Figure 5.9. Gas chromatograms in a DB-5 column for sediment samples (a) U-11 and (b) T-14. The sample weights extracted were 70 and 60 g respectively and the final extract volumes were of 0.5 ml. These sediments were classified in cluster 2.

5.9

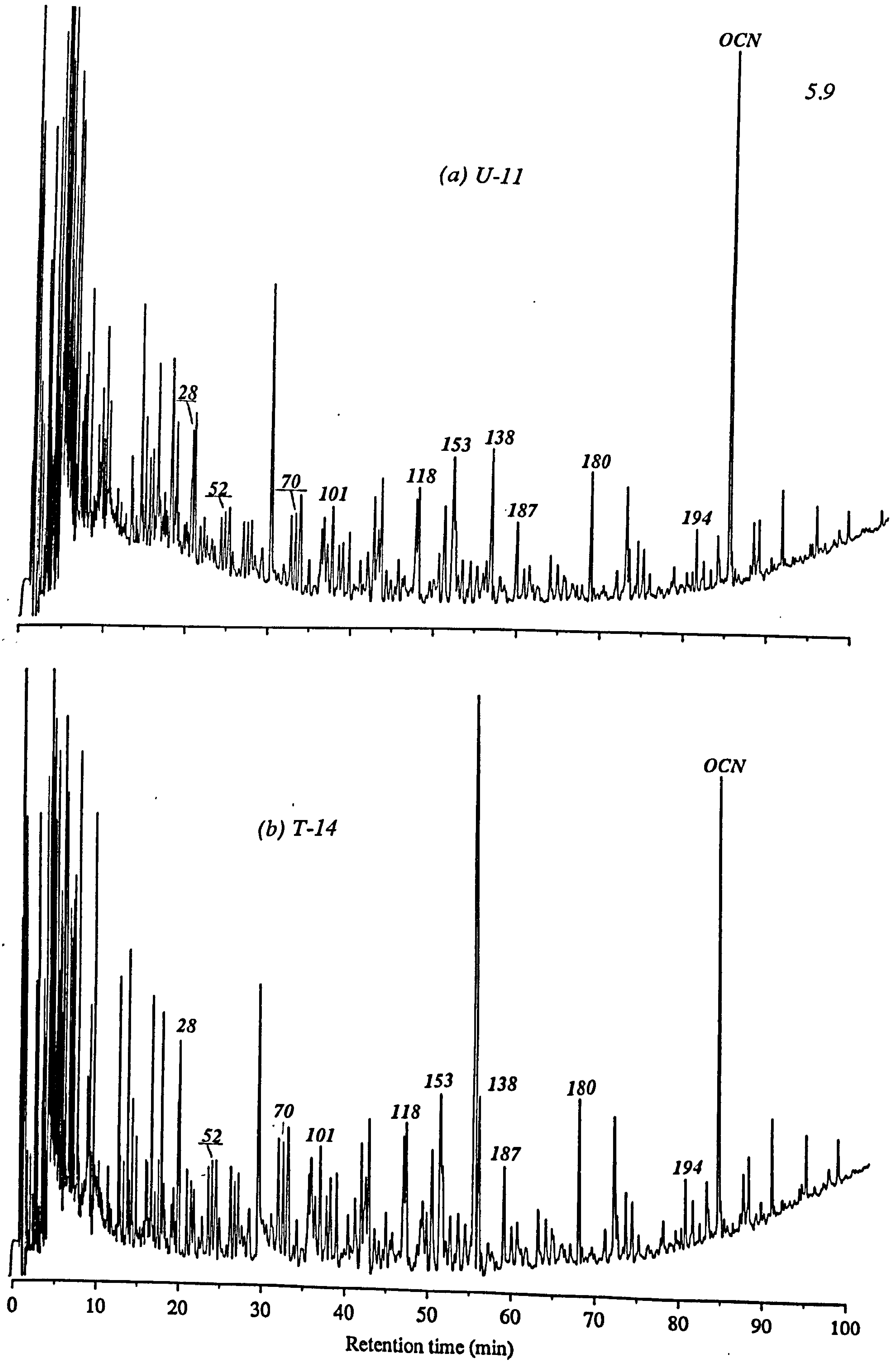
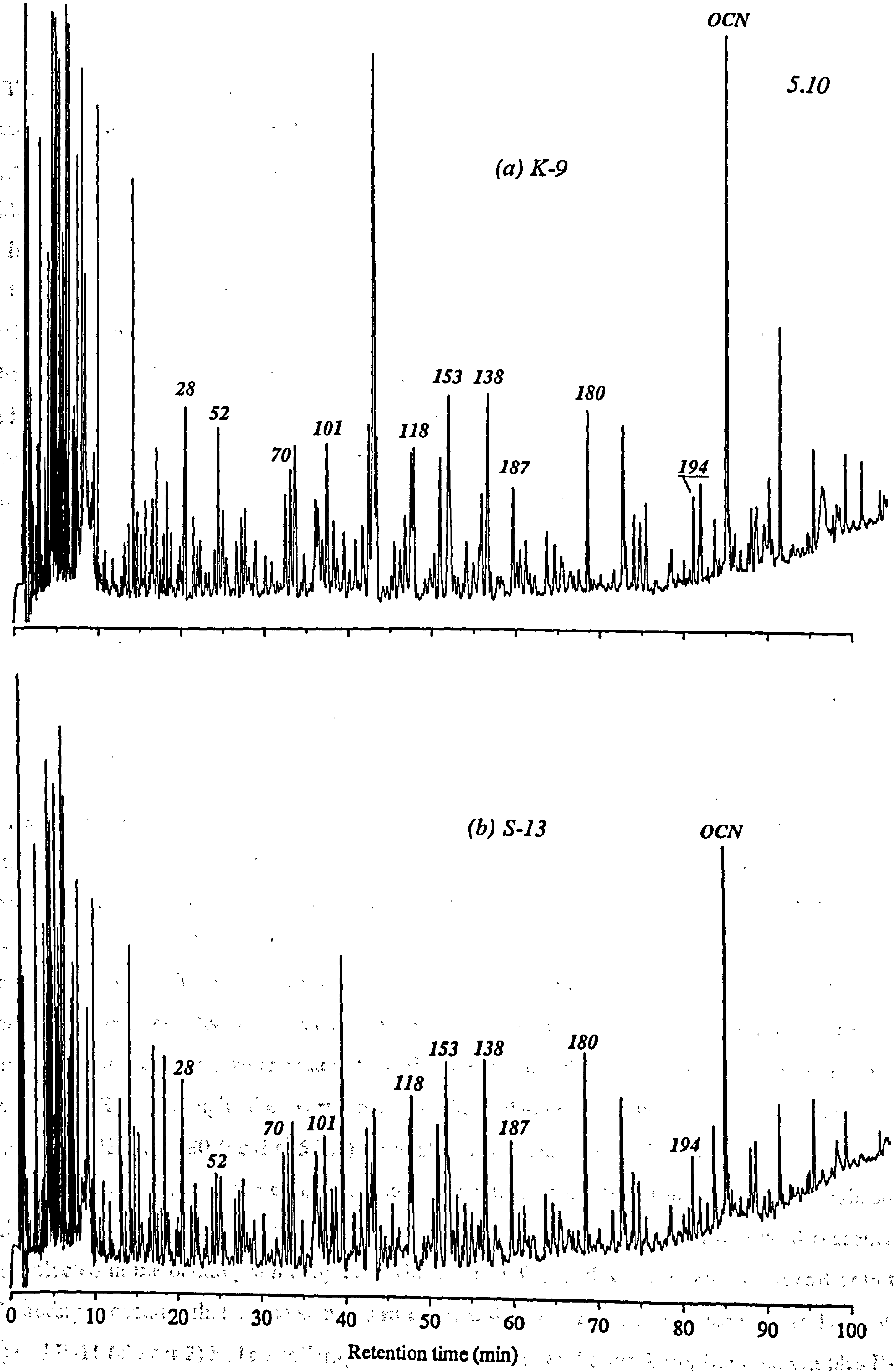

OCN
(a) U-11
28
52
70
101
118
153
138
187
180
194
(b) T-14
OCN
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.10. Gas chromatograms in a DB-5 column for sediment samples (a) K-9 and (b) S-13. The sample weights extracted were 70 and 50 g respectively and the final extract volumes were of 0.5 and 1.0 ml respectively. These sediments were classified in cluster 2.

5.10


OCN
(a) K-9
28
52
70
101
118
153
138
187
180
194
(b) S-13
OCN
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

The sediments classified in cluster 1 showed a wide range of PCB concentrations and fine fraction concentrations in the sediments. The mean concentration for 22 of the 23 samples (the organic carbon in sample P-9 was not measured) in this cluster was 590 ng g^{-1}C (see Table 5.7), with the minimum concentration value found at station R-6 (110 ng g^{-1}C) which had only 0.3% of fine fraction, and the maximum value found at station R-12 (1334 ng g^{-1}C) which had 6.1% of fine fraction. Some samples within this cluster had fine fraction concentrations higher than 15% (*i.e.* samples N-13, K-11, J-11, L-11 and M-12) and PCB concentrations above 600 ng g^{-1}C, whereas some had fine fraction concentrations lower than 1% (*i.e.* samples R-6, S-11, S-8, R-8 and P-9) and PCB concentrations lower than 260 ng g^{-1}C. The similarities between a set of six samples from this cluster covering a wide range of concentrations, and whose chromatograms are presented in Figures 5.11, 5.12 and 5.13, are shown below:

	G-11	L-11	P-6	Q-11	R-6	R-12
L-11	0.838	1.000				
P-6	0.851	0.846	1.000			
Q-11	0.846	0.903	0.813	1.000		
R-6	0.863	0.846	0.880	0.822	1.000	
R-12	0.847	0.874	0.815	0.914	0.833	1.000

As in the case of cluster 2, the patterns in the chromatograms of samples within cluster 1 remained relatively constant regardless of the total PCB concentrations or the amount of fine particles in the sediments. For example, the chromatograms of samples R-6 and R-12 (Fig. 5.11a and 5.11b) show a high similarity (Z=0.833), although the minimum and maximum PCB concentrations within this cluster were found in these samples which had 0.3 and 6.1% of fine fraction respectively. As in the case of cluster 2, the maximum variability in the patterns between samples within cluster 1 were related to variations in the relative concentration of congener 52 (r.s.d.=17.8%), although the variations in the relative concentrations of congeners 28 (r.s.d.=15.1%) and 180 (r.s.d.=15.7%) were also important (see Table 5.8).

A visual inspection of the chromatograms of samples in clusters 1 and 2 seems to indicate a relatively high similarity in the patterns between the two clusters. This similarity also seems to be reflected in the dendrogram (Fig. 5.7) which shows that both clusters are joined earlier in the clustering procedure than some samples in clusters 4 and 5. For example samples R-12 (cluster 1) and R-11 (cluster 2) had a similarity of Z=0.908, however the similarity between samples R-12 and M-12 (cluster 1) was Z=0.932 and the similarity between samples R-11 and YY-4 (cluster

Figure 5.11. Gas chromatograms in a DB-5 column for sediment samples (a) R-6 and (b) R-12. The sample weights extracted were 70 and 50 g respectively and the final extract volumes were of 0.2 and 0.5 ml respectively. These sediments were classified in cluster 1.

5.11

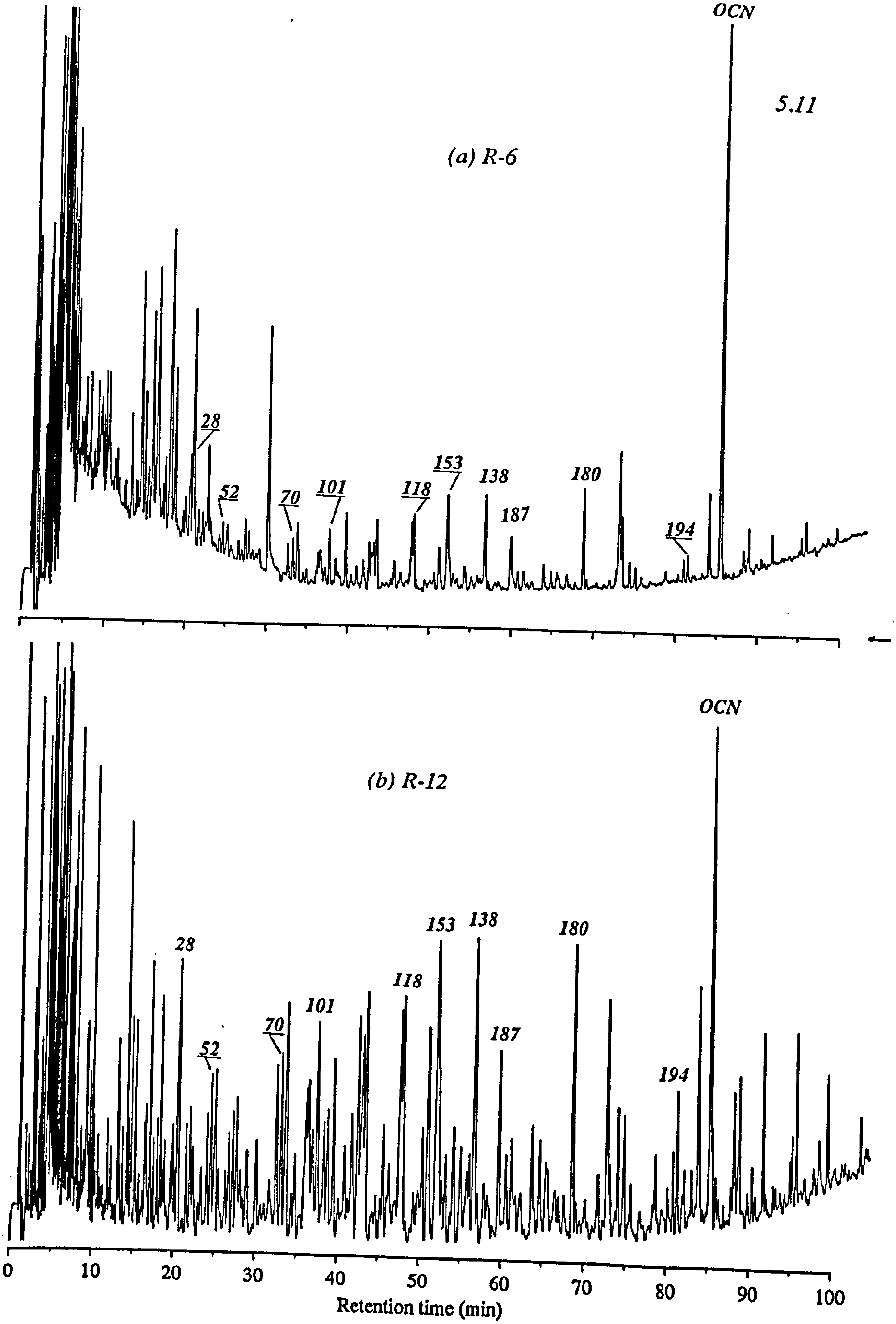

OCN
(a) R-6
28
52
70
101
118
153
138
187
180
194
OCN
(b) R-12
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.12. Gas chromatograms in a DB-5 column for sediment samples (a) P-6 and (b) L-11. The sample weights extracted were 70 and 50 g respectively and the final extract volumes were of 0.2 and 0.5 ml respectively. These sediments were classified in cluster 1.

5.12

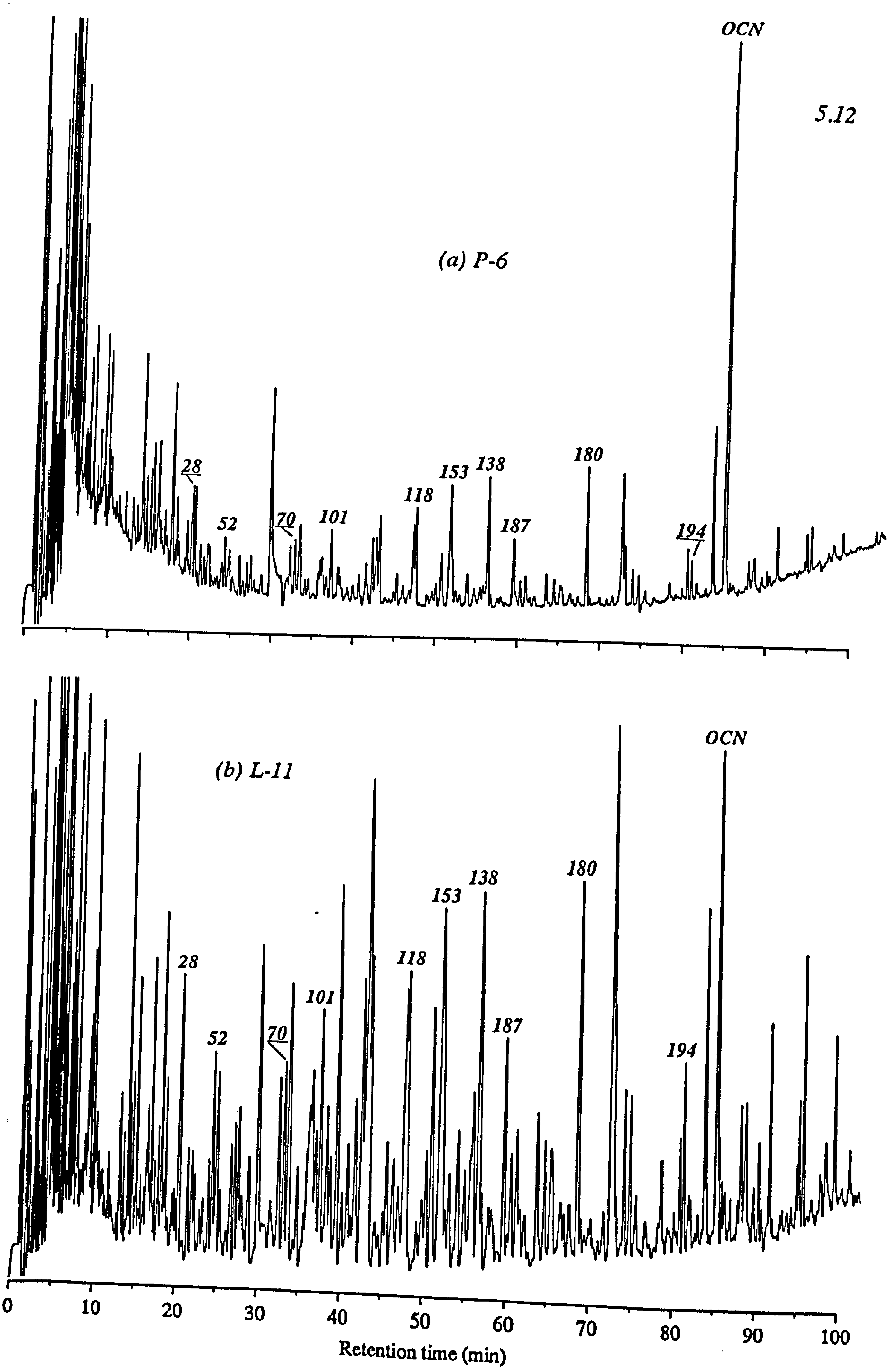
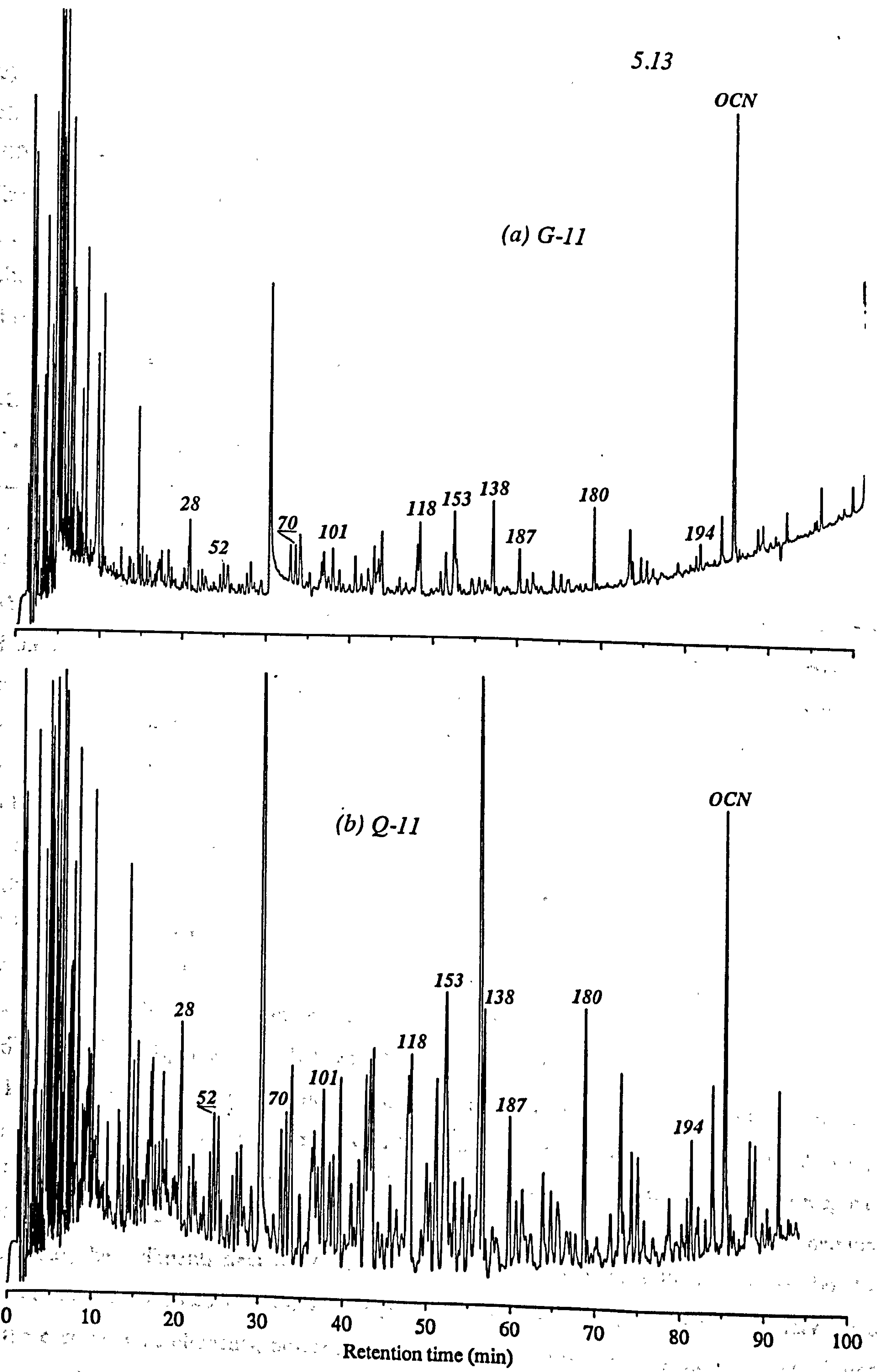

(a) P-6
OCN
28
52
70
101
118
153
138
187
180
194
(b) L-11
OCN
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.13. Gas chromatograms in a DB-5 column for sediment samples (a) G-11 and (b) Q-11. The sample weights extracted were of 50 g respectively and the final extract volumes were of 1.0 ml respectively. These sediments were classified in cluster 1.

5.13


OCN
(a) G-11
28
52
70
101
118
153
138
187
180
194
(b) Q-11
28
52
70
101
118
153
138
187
180
194
OCN
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

2) was Z=0.933. Therefore, although samples R-11 and R-12 were very similar, they were classified in different clusters because of their higher similarities with other samples which were different enough to be classified in different clusters. This observation highlights one of the limitations of the clustering procedures which are not perfect because, ideally, if samples R-11 and R-12 are similar then they should be classified in the same cluster, however, when the clustering procedure is evaluated as a whole (by cluster and not by specific samples), some differences between clusters are evident.

Figure 5.14 shows the 95% confidence intervals (obtained with the statistical package MINITAB) for the relative concentration of each of the ten congeners (used in the sediment classification) in each cluster. The comparison between the confidence intervals indicates that the main difference between the "fingerprints" of clusters 1 and 2 was due to the lower relative concentrations of congeners 28 and 70 (Figs. 5.14a and c respectively) and a slight enrichment of congener 153 (Fig. 5.14f) in cluster 1. The overlapping of the confidence intervals for the other congeners in Figure 5.14 suggests no significant differences in the relative concentrations of these congeners between clusters 1 and 2. The decrease in the concentrations of congeners 28 and 70 in cluster 1, and the chromatograms for samples in cluster 1 and 2 shown above indicate that although there is a general similarity between the two clusters, the distribution of congeners in cluster 2 was more homogeneous, that is, lower and higher chlorinated PCB congeners tend to be present in more similar proportions than in cluster 1.

The position of the stations classified in cluster 2 (see Fig. 5.8) and their higher concentrations indicate that sediments in this cluster represent those most directly affected by point sources of PCBs. It is interesting to compare Figure 5.8, in which the cluster memberships were obtained from a set of ten PCB congeners determined in total sediments, with Figure 4.30a in which the cluster memberships were obtained from ten elements determined in the fine fraction of the sediments. These figures show that, with few exceptions, sediments classified in clusters 1 to 6 in Figure 4.30a, which were also mentioned as the most directly affected by anthropogenic inputs (see discussion in Section 4.3) correspond to sediments classified in clusters 1 and 2 in Figure 5.8, and in particular, those sediments classified in cluster 1 in Figure 4.30a correspond to sediments in cluster 2 in Figure 5.8. As in the case of most trace elements, and of mercury in particular, the sediments near the Queen's Channel (and particularly those from Burbo Bight) seem to be contaminated with PCBs transported from the River Mersey and its estuary. Also as in the case of trace elements, however, sample K-9 (inside the sewage sludge disposal area in Liverpool Bay) was classified in the same cluster as those sediments nearer the Mersey. In the

Figure 5.14. 95% confidence intervals for each of the ten PCB congeners used for the statistical classification of sediments (see text). The confidence intervals were computed with the command ONEWAY in the statistical package MINITAB.

```
a)   CB28
CLUSTER      N      MEAN     STDEV  --+---------+---------+---------+----
      1     23   0.10383   0.01573                (--*--)
      2     14   0.13950   0.01720                           (---*--)
      3      4   0.12850   0.02715                    (------*------)
      4     14   0.07436   0.01942     (---*---)
      5      8   0.09400   0.03733          (----*----)
      6      2   0.08450   0.00354  (--------*---------)
                                    --+---------+---------+---------+----
 POOLED STDEV =  0.02106            0.060     0.090     0.120     0.150
```

```
b)   CB52
CLUSTER      N      MEAN     STDEV  --+---------+---------+---------+----
      1     23   0.07887   0.01400   (*)
      2     14   0.08871   0.01971    (*-)
      3      4   0.17050   0.03697            (--*--)
      4     14   0.07893   0.01381  (-*)
      5      8   0.15075   0.04869           (-*-)
      6      2   0.30850   0.01768                            (----*---)
                                    --+---------+---------+---------+----
 POOLED STDEV =  0.02360            0.080     0.160     0.240     0.320
```

```
c)   CB70
CLUSTER      N      MEAN     STDEV  -------+---------+---------+---------
      1     23   0.07148   0.00684             (-*)
      2     14   0.08714   0.00501                    (--*-)
      3      4   0.05650   0.00603   (---*---)
      4     14   0.05093   0.00937  (-*--)
      5      8   0.08287   0.01244                  (-*--)
      6      2   0.09650   0.00354                      (---*-----)
                                    -------+---------+---------+---------
 POOLED STDEV =  0.00792                 0.060     0.080     0.100
```

```
d)   CB101
CLUSTER      N      MEAN     STDEV   -+---------+---------+---------+-----
      1     23   0.09996   0.01391        (*)
      2     14   0.09271   0.00890     (-*-)
      3      4   0.09150   0.01012   (---*--)
      4     14   0.08950   0.01649     (*-)
      5      8   0.16475   0.01753                       (-*--)
      6      2   0.19800   0.00424                             (---*----)
                                     -+---------+---------+---------+-----
 POOLED STDEV =  0.01384            0.080     0.120     0.160     0.200
```

```
e)   CB118
CLUSTER      N      MEAN     STDEV  -------+---------+---------+---------
      1     23   0.12465   0.00857                           (---*--)
      2     14   0.11407   0.01119                       (---*---)
      3      4   0.10225   0.01640               (-------*-------)
      4     14   0.13907   0.03883                               (---*----)
      5      8   0.13400   0.03720                            (-----*----)
      6      2   0.07550   0.00919   (----------*----------)
                                    -------+---------+---------+---------
 POOLED STDEV =  0.02380                 0.060     0.090     0.120
```

Fig. 5.14 cont....2

```
f)  CB153
CLUSTER      N      MEAN     STDEV  ----------+---------+---------+------
       1    23   0.15839   0.00924                                 (-*-)
       2    14   0.14414   0.01403                            (-*-)
       3     4   0.13075   0.01810                     (----*---)
       4    14   0.16100   0.01526                                 (--*-)
       5     8   0.12788   0.01689                     (---*--)
       6     2   0.08100   0.00849     (-----*-----)
                                    ----------+---------+---------+------
 POOLED STDEV =  0.01335                    0.090     0.120     0.150
```

```
g)  CB138
CLUSTER      N      MEAN     STDEV  -------+---------+---------+---------
       1    23   0.15474   0.01237                              (*-)
       2    14   0.14207   0.00607                         (--*-)
       3     4   0.13550   0.01330                      (---*---)
       4    14   0.16093   0.01418                               (-*-)
       5     8   0.13363   0.02709                      (--*--)
       6     2   0.06600   0.00424  (-----*-----)
                                    -------+---------+---------+---------
 POOLED STDEV =  0.01435                 0.070     0.105     0.140
```

```
h)  CB187
CLUSTER      N      MEAN     STDEV  ---+---------+---------+---------+---
       1    23  0.063739  0.004938                                 (-*-)
       2    14  0.059000  0.004992                            (--*--)
       3     4  0.057750  0.004573                        (----*----)
       4    14  0.063143  0.014016                              (-*--)
       5     8  0.036625  0.009180              (---*---)
       6     2  0.023000  0.005657  (------*-------)
                                    ---+---------+---------+---------+---
 POOLED STDEV = 0.008335             0.016     0.032     0.048     0.064
```

```
i)  CB180
CLUSTER      N      MEAN     STDEV  ---+---------+---------+---------+---
       1    23   0.12022   0.01890                       (-*-)
       2    14   0.10657   0.01189                   (--*--)
       3     4   0.10800   0.01857                 (----*----)
       4    14   0.15686   0.03480                             (--*--)
       5     8   0.06338   0.01289       (---*---)
       6     2   0.06150   0.00212   (------*-------)
                                    ---+---------+---------+---------+---
 POOLED STDEV =  0.02165             0.040     0.080     0.120     0.160
```

```
j)  CB194
CLUSTER      N      MEAN     STDEV  -+---------+---------+---------+-----
       1    23  0.024174  0.003270                               (-*--)
       2    14  0.025786  0.002486                                (--*--)
       3     4  0.019000  0.001826                     (-----*-----)
       4    14  0.025357  0.008205                                (--*--)
       5     8  0.012125  0.003399              (---*---)
       6     2  0.006000  0.000000  (-------*--------)
                                    -+---------+---------+---------+-----
 POOLED STDEV = 0.004661           0.0000    0.0080    0.0160    0.0240
```

discussion of trace elements the similarity in the composition of sediments in station K-9 and stations from Burbo Bight was explained by a possible transport of the sludge particles towards the Burbo Bight, although, it was also mentioned that trace element inputs from sewage sludge may be superimposed on inputs from the River Mersey run-off, which were particularly suggested by the high levels of mercury in the sediments from Burbo Bight, as this heavy metal is discharged in substantial quantities in the Mersey Estuary. The association of mercury with the organic matter in sediments has been reported for estuaries in this region, therefore, particulate PCBs, which are certainly associated to the organic component of sediments, are expected to be transported in a similar way to particulate mercury in this region. Thus, the high levels of PCBs in the Burbo Bight sediments and the similarity of the congener distributions with other sediments near the Mersey may be evidence of PCB inputs from the freshwater run-off into the bay.

As mentioned in Chapter 2, the direction of net sediment transport in this region is from the bay towards the Mersey, therefore, the input of sediment-associated contaminants from the Mersey towards Liverpool Bay may be limited. However, it is evident from Figure 4.4b (showing the distribution of $\delta^{13}C$ values) that the transport of organic materials from the Mersey towards Liverpool Bay is reflected in the composition of the organic matter in the sediments near the Mersey outfall. This land derived organic matter is probably transported in the water column as dissolved or colloidal organic matter which will eventually flocculate or be adsorbed onto particles and be deposited in the vicinity of the Queen's Channel entrance. Further evidence of the transport of land derived organic matter towards Liverpool Bay was reported by Nimmo *et al.* (1989). These authors reported that the rivers Dee and Mersey appeared to be significant sources of fluorescent material (probably consisting mainly of freshwater fulvic acids) to Liverpool Bay. Several studies of partitioning of organic contaminants and of PCBs in particular (e.g. Brannon *et al.*, 1991; Brownawell and Farrington, 1986; Baker *et al.*, 1986; Gschwend and Wu, 1985) between water and particles have stressed the importance of considering the dissolved organic matter in the studies of partitioning, as hydrophobic substances may remain in "apparent" solution in possible association with organic colloids which are not retained by filters and, thus, are operationally included in the dissolved phase. For example, Baker *et al.* (1986) studied the influence of colloids on sediment-water partition coefficients of PCBs and suggested that the presence of colloidal-sized, non-settling microparticles played a significant role in decreasing the apparent K_d values of PCBs by increasing their apparent solubility. These authors concluded that since organic contaminants associated with colloidal matter are subject neither to sedimentation nor to volatilization they may have longer residence times in the water column, whereas the aggregation and settling of destabilized colloids in the presence of larger particles may, however, rapidly remove this fraction under proper hydrodynamic conditions, thus, the geochemistry of organic pollutants in natural waters is closely tied to the behaviour of colloids. Brownawell and Farrington (1986) reported apparent oversaturation in the concentration of PCB congeners in pore waters of a marine sediment and also concluded that organic colloids may play a critical role in the biogeochemistry of PCBs in sediments. These reports suggest that, due to the apparent significant inputs of dissolved organic matter from riverine sources, and from the Mersey runnoff in particular, the input of PCBs in "solution" into Liverpool Bay may be significant, these inputs are reflected in the relatively high PCB concentrations in sediments from Burbo Bight and in the similar pattern of the PCB congeners in those sediments with a relatively low amount of fine particles (e.g. samples U-11 and T-14) which are within the influence of the freshwater runnoff from the Mersey.

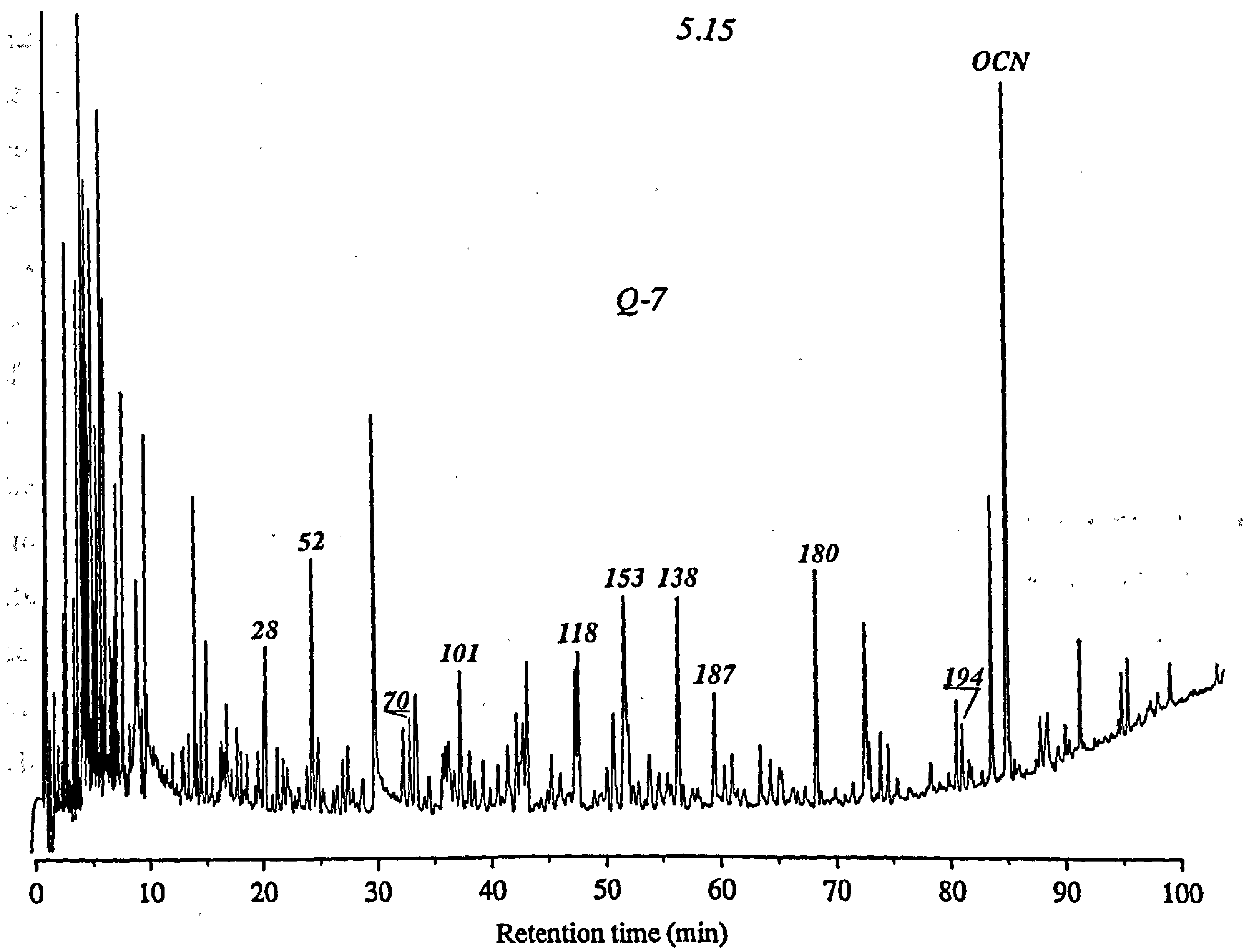
The general similarity between the pattern of PCB congeners in sediments from clusters 1 and 2 suggests that these sediments are being mainly affected by the same source(s), however, the decrease in the relative concentrations of congeners 28 and 70 in sediments in cluster 1 as compared to sediments in cluster 2 may be due to a faster loss of these congeners into solution. The PCB congener composition of sediments in cluster 2 may reflect more closely the congener composition from the sources as they are the most directly affected by the inputs. Due to differences in the physicochemical properties amongst congeners, the longer the particles and their associated PCBs have been transported, the higher the alteration of the "original" fingerprint will be, due in particular, to differences in water solubility and partitioning between water and sediments (K_d values). For example, a recent review on various physicochemical properties of PCB congeners by Shiu and Mackay (1986), including aqueous solubilities and octanol-water partition coefficients (K_{ow}), reported aqueous solubilities for congeners 28, 70, 153 and 194 of 160, 41, 1 and 0.2 mg m^{-3} respectively, and log K_{ow} values of 5.80, 5.90, 6.90 and 7.10 respectively. Therefore, the higher solubility and lower partitioning into solid phases (a relationship between PCB congener K_{oc} values and their sediment-water partition coefficients, K_p or K_{oc} , has been widely reported; see for example Baker *et al.*, 1986; Brownawell and Farrington, 1985; Lara and Ernst, 1990a) shown by congeners 28 and 70 may cause a faster release of these congeners into solution during transportion, thus, sediments in cluster 1 which may have the same source of PCBs as sediments in cluster 2, have a more altered PCB pattern as they have probably been in transport for a longer period.

Only four samples were classified in cluster 3 (*i.e.* samples G-9, J-9, Q-7 and S-7; see Fig. 5.8). The similarities between these four samples were:

	G-9	J-9	Q-7	S-7
J-9	0.813	1.000		
Q-7	0.814	0.773	1.000	
S-7	0.850	0.880	0.803	1.000

The amount of fine particles in these sediments was low (0.21, 0.17, 2.14 and 0.08% for samples G-9, J-9, Q-7 and S-7 respectively) and the mean normalized PCB concentration was also low (149 ng $g^{-1}C$) with the maximum found at station Q-7 (442 ng $g^{-1}C$) and the minimum found at station J-9 (42 ng $g^{-1}C$). In spite of the low amounts of fine material and PCB concentrations, the pattern of the congener distribution in the sediments within this cluster (see chromatograms in Figures 5.6 and 5.15) was, in general, similar to those patterns shown by sediments in cluster 1 and 2. As shown in Figure 5.14, the confidence intervals of the higher chlorinated congeners in cluster 3 overlap with those in clusters 1 and 2, and the only difference with these clusters is due to a higher relative concentration of congener 52 and a lower relative concentration of congener 70 in the sediments of cluster 3. As congeners 52 and 70 are tetrachlorinated it may be expected that, in general, they would have similar solubilities and show similar geochemical behaviour. However, there are some variations in the physicochemical properties between PCB isomers which are related to the substitution positions of the chlorine atoms in the biphenyl ring, and, it seems that the three-dimensional configuration of the PCB molecules also plays a role in the physicochemical behaviour of the PCB congeners. For example, the aqueous solubility reported by Shiu and Mackay (1986) for congener 52 (30 mg m^{-3}) is lower than the solubility for congener No. 70 (41 mg m^{-3}) whereas the log K_{ow} values for these congeners were reported as 6.10 and 5.90 respectively. Therefore, based on the solubilities and the octanol-water partition coefficients, it is expected that congener No. 70 would be more mobile than congener 52, which could explain a reduction of congener 70 in relation to congener 52 in sediments from cluster 3, assuming that they originated from a similar source as PCBs in sediments from clusters 1 and 2. However, this observation would suggest that if congener 70 is being lost into solution faster than congener 52 as a result of their respective solubilities and K_{ow} values, the same behaviour (which was not observed) would also be expected for congener 28 which also shows a higher solubility and lower K_{ow} than congener 52. It is possible that a clear trend in the relative concentrations of congeners 28 and 52 is overshadowed by their high variability in sediments

Figure 5.15. Gas chromatogram in a DB-5 column for sediment sample Q-7. The sample weight extracted was of 60 g and the final extract volume was of 0.5 ml. This sediment was classified in cluster 3.


5.15
Q-7
OCN
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

within cluster 3, as these congeners showed relative standard deviations of 21.7 and 21.1% respectively (see Table 5.8).

A more evident shift in the PCB congener distribution pattern in sediments of Liverpool Bay was observed in the samples classified in cluster 4. The chromatograms of some sediments in this cluster are shown in Figures 5.16, 5.17 and 5.18. From these chromatograms it is evident that the lower chlorinated congeners are less abundant than the higher chlorinated congeners in the sediments of this cluster. The chromatograms also show that within cluster 4, samples K-10 and L-10 (Fig. 5.16a and b) had a congener pattern more similar to the patterns shown by sediments in clusters 1, 2 and 3, as compared to samples M-11 and J-7 (Fig. 5.18a and b) which showed the most altered patterns. Therefore, figures 5.16, 5.17 and 5.18 seem to reflect different degrees of alteration of the "original" pattern exemplified by sediments classified in cluster 2 such as those from stations YY-1 and P-11 (Fig. 5.5) and station K-9 (Fig. 5.10a). Although the shift in the PCB pattern in sediments of cluster 4 is evident from the chromatograms, this shift is further emphasized by the confidence intervals in Figure 5.14 which show that, as compared to other clusters, congeners 28, 52, 70 and 101 in cluster 4 were at the lower end of the relative concentration values, whereas congeners 118, 153, 138, 187, 194 and particularly 180, were at the higher end of the relative concentration values. The similarities for six sediment samples in cluster 4 are shown below:

	J-7	K-8	K-10	L-10	M-8	M-11
K-8	0.798	1.000				
K-10	0.813	0.711	1.000			
L-10	0.832	0.762	0.852	1.000		
M-8	0.732	0.687	0.684	0.689	1.000	
M-11	0.863	0.758	0.851	0.845	0.684	1.000

The main differences amongst sediments within this cluster, as suggested by the relative standard deviations in Table 5.8 were due to variations in the relative concentrations of congeners 194 (r.s.d.=32.4%), 118 (r.s.d.=27.9%) and 28 (r.s.d.=26.1%). The mean total PCB concentration for this cluster (373 ng g^{-1}C, see Table 5.7) was lower than the means for clusters 1 and 2 but higher than for cluster 3. The lowest concentration within cluster 4 was found at station K-8 (74 ng g^{-1}C) and the maximum was found at station K-10 (1672 ng g^{-1}C) which is located within Site SI, and was considered as one of the most directly affected by anthropogenic inputs of trace elements (see Fig. 4.30a and the discussion in Section 4.3). Excluding sample K-10, all sediments within

Figure 5.16. Gas chromatograms in a DB-5 column for sediment samples (a) K-10 and (b) L-10. The sample weights extracted were of 40 and 50 g respectively and the final extract volumes were of 1.0 and 0.2 ml respectively. These sediments were classified in cluster 4.

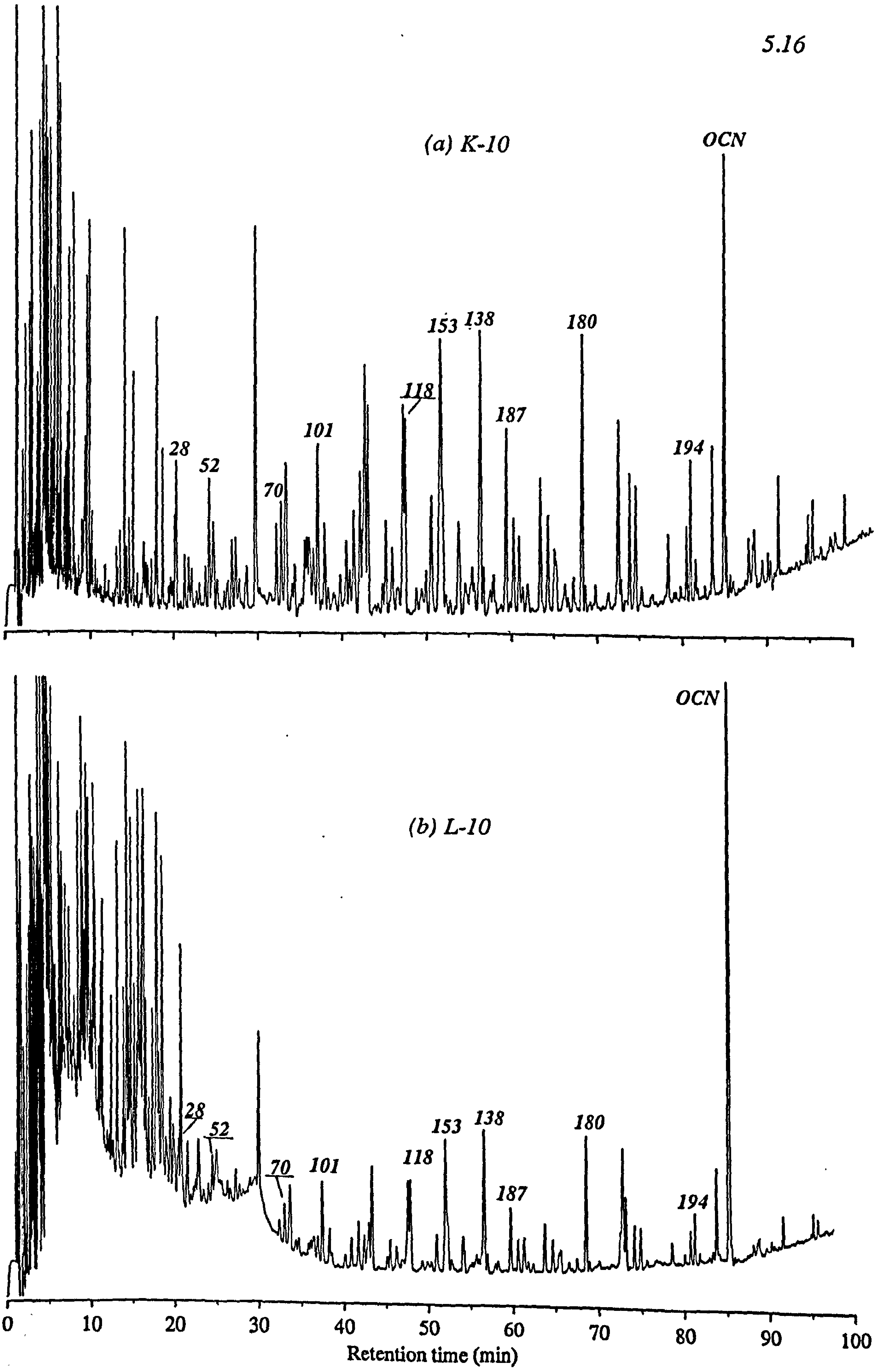

(a) K-10
OCN
28
52
70
101
118
153
138
187
180
194
(b) L-10
OCN
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.17. Gas chromatograms in a DB-5 column for sediment samples (a) K-8 and (b) M-8. The sample weights extracted were of 70 g respectively and the final extract volumes were of 0.2 ml respectively. These sediments were classified in cluster 4.

5.17

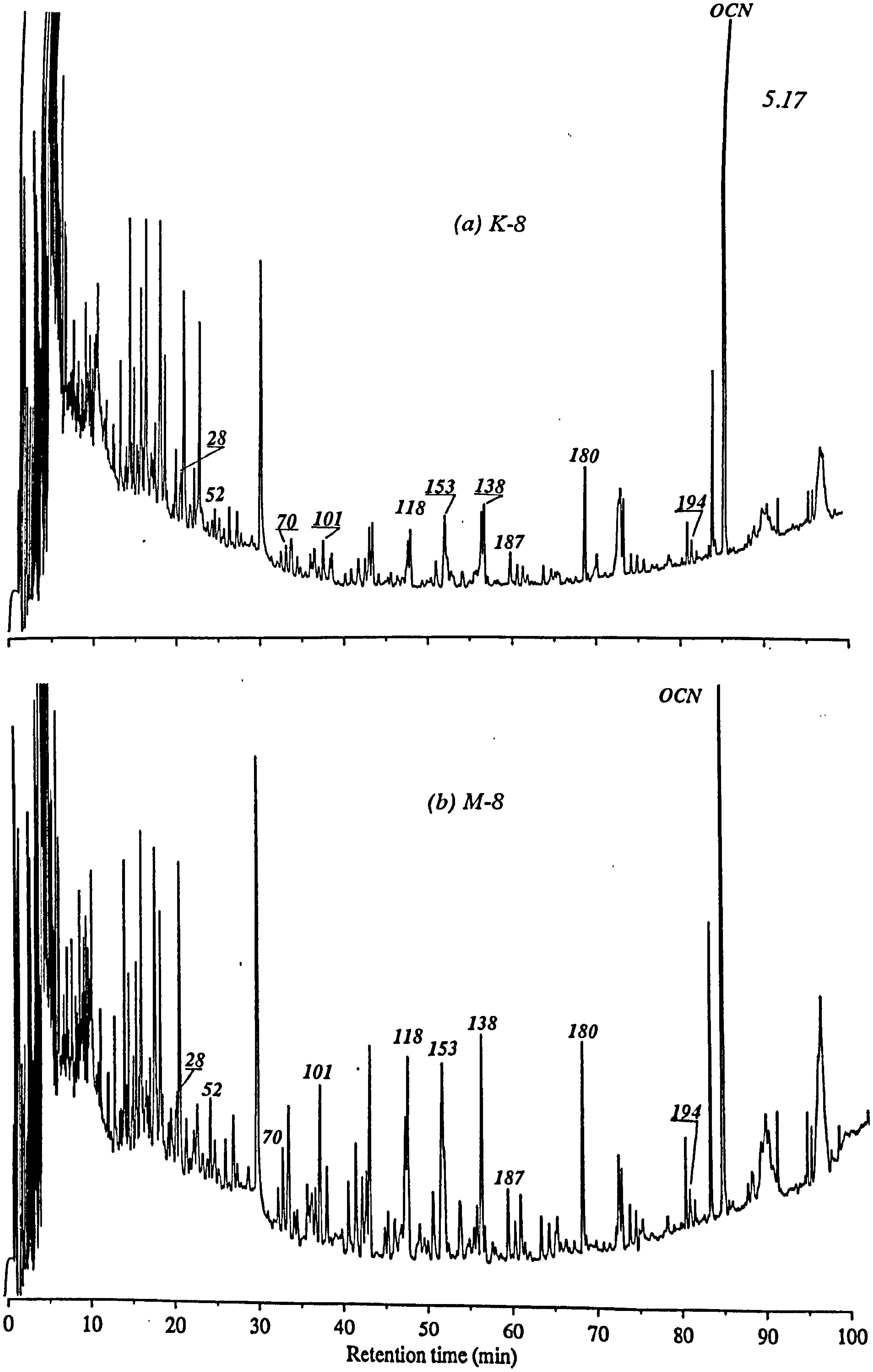
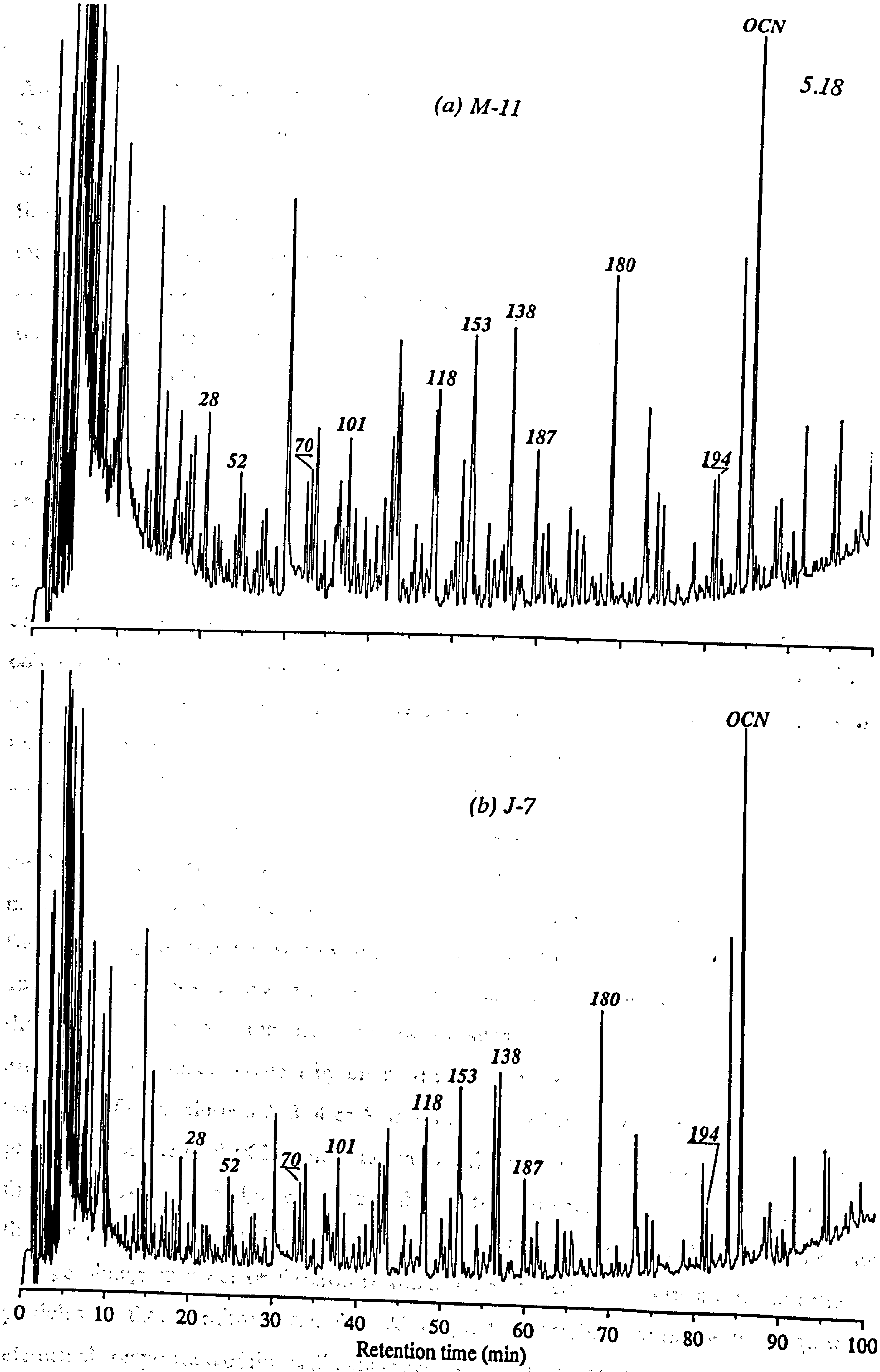

OCN
(a) K-8
28
52
70
101
118
153
138
187
180
194
OCN
(b) M-8
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.18. Gas chromatograms in a DB-5 column for sediment samples (a) M-11 and (b) J-7. The sample weights extracted were of 60 g respectively and the final extract volumes were of 0.5 ml respectively. These sediments were classified in cluster 4.


OCN
(a) M-11
28
52
70
101
118
153
138
187
180
194
OCN
(b) J-7
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

5.18

this cluster had fine fraction concentrations lower than 8%, and eight of them had concentrations lower than 1%, with a minimum of 0.15% found at station K-8 (see Appendix B3). As compared with most samples in clusters 1 and 2, sediments in cluster 4 showed relatively low amounts of fine particles and, in cases of 8 of the 14 samples, the coarse fraction of the sediment constituted the largest sedimentary component (>99%) and was probably the main carrier of the total PCB load in this sediment. If this was the case, then the pattern of the PCB congeners in these sediments suggests that the organic composition of particles in these samples is affected by sources such as sludge dumping and/or inputs from the River Mersey. This observation is based on the assumption that the PCB patterns reflect an altered form of the original pattern which is more closely described by those in cluster 2. A higher alteration in the congener pattern in sediments which are further from the sources, and have a low amount of fine material, can be explained by the sedimentary PCB congeners having a higher exchange with the water column, as water exchange through particles in coarser sediments is favoured by higher porosities as compared, for example, with muddy deposits in which the porewater exchange with the water column is limited by lower porosities. Therefore, the higher the "flushing" of the coarser sediments with water containing lower concentrations of PCBs, the higher the redissolution of PCB congeners will be (and in particular of those lower chlorinated congeners with higher aqueous solubilities and lower sediment partition coefficients).

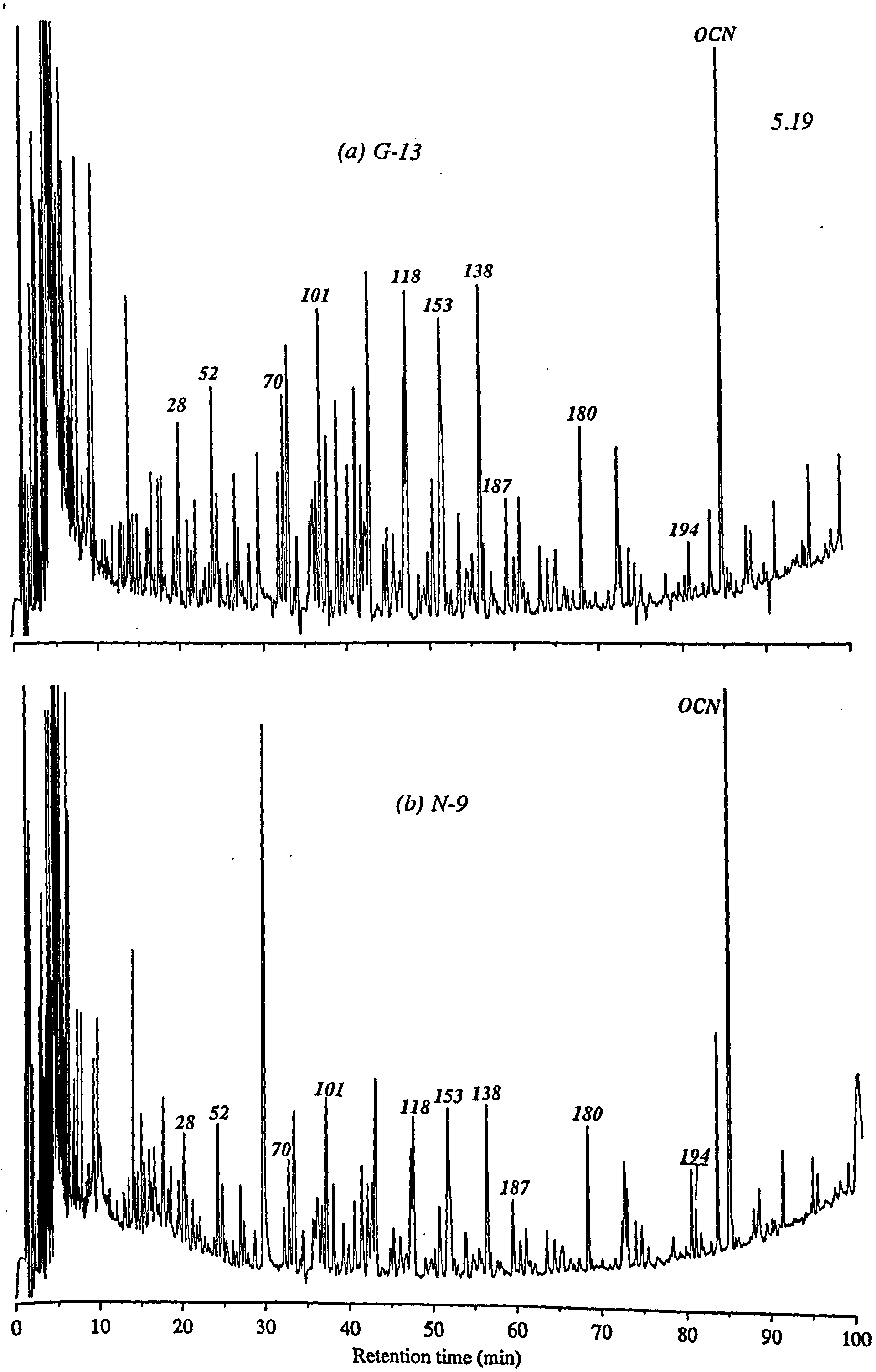
It is important to mention, however, that if the coarse particles are the carriers of the bulk of the PCB loads in sediments containing a very low amount of fine particles, and if their PCB patterns indicate an influence on the organic composition by discharges of sewage sludge and/or freshwater inputs from the Mersey in particular, this influence was not obvious in the elemental composition of these coarse particles. Figure 4.30b indicates (see also text in Section 4.3) that the coarse fraction of sediments with low amounts of fine particles did not show an obvious effect on their element content by inputs from the Mersey or sludge discharges at Site SI, and were classified in clusters 2, 3, 4 or 5. If, on the other hand, the strong correlation between the grain size and the total PCB concentration in sediments of Liverpool Bay indicates that even in the sediments with very low amounts of fine particles the main carrier of the total PCB load are the fine particles, then the PCB patterns of sediments in cluster 4 would suggest that inputs via sewage sludge disposal or freshwater runnoff are affecting the organic composition of fine particles in these sediment samples. Although this possible influence is suggested by the elemental composition of fine sediments near the extreme southern section of Site SI (*i.e.* samples G-7, H-8, J-7 and L-8, see Fig. 4.30a) and other samples (*i.e.* samples H-10, K-10, M-11), it was not obvious in the elemental composition of fine particles at stations K-8, L-10, M-9, M-9, M-10, N-11 and P-8, whose elemental composition has been proposed as resulting mainly from the inputs of elements from natural sources.

An interesting shift in the PCB congener composition was observed in the sediments classified in clusters 5 and 6. An opposite trend in the composition which has been previously discussed was observed in clusters 5 and 6, that is, a dominance in the abundance of PCB congeners with a lower degree of chlorination was observed. For example, Figures 5.19, 5.20 and 5.21 show the chromatograms for five sediment samples in cluster 5. The congener distribution pattern in sample G-13 (Fig. 5.19a) was the most similar to the pattern for sediments in clusters 2 and 1, although the higher proportion of lower chlorinated congeners such as Nos. 52 and 101, as compared to congener 180 is evident in this chromatogram when compared to the chromatograms for sediments in clusters 1 and 2. The chromatograms for samples N-9 (Fig. 5.19b), P-10 (Fig. 5.20a) and U-15 (Fig. 5.20b) show a further degree of enrichment of the lower chlorinated congeners which is even more emphasized in sample J-13 (Fig. 5.21). The sediments in cluster 6 (only samples N-7 and K-6 were included in this cluster) showed the PCB patterns with the highest relative concentrations of lower chlorinated congeners (see Fig. 5.22). The confidence intervals shown in Figure 5.14 indicate that, as compared to clusters 1, 2, 3 and 4, sediments in clusters 5 and 6 showed, in general, higher relative concentrations of congeners 52, 70 and particularly 101, and lower concentrations of congeners 187, 180 and 194. The similarities between some samples in cluster 5 were:

	G-13	J-13	N-9	P-10	U-15
J-13	0.677	1.000			
N-9	0.752	0.733	1.000		
P-10	0.702	0.792	0.764	1.000	
U-15	0.741	0.811	0.840	0.848	1.000

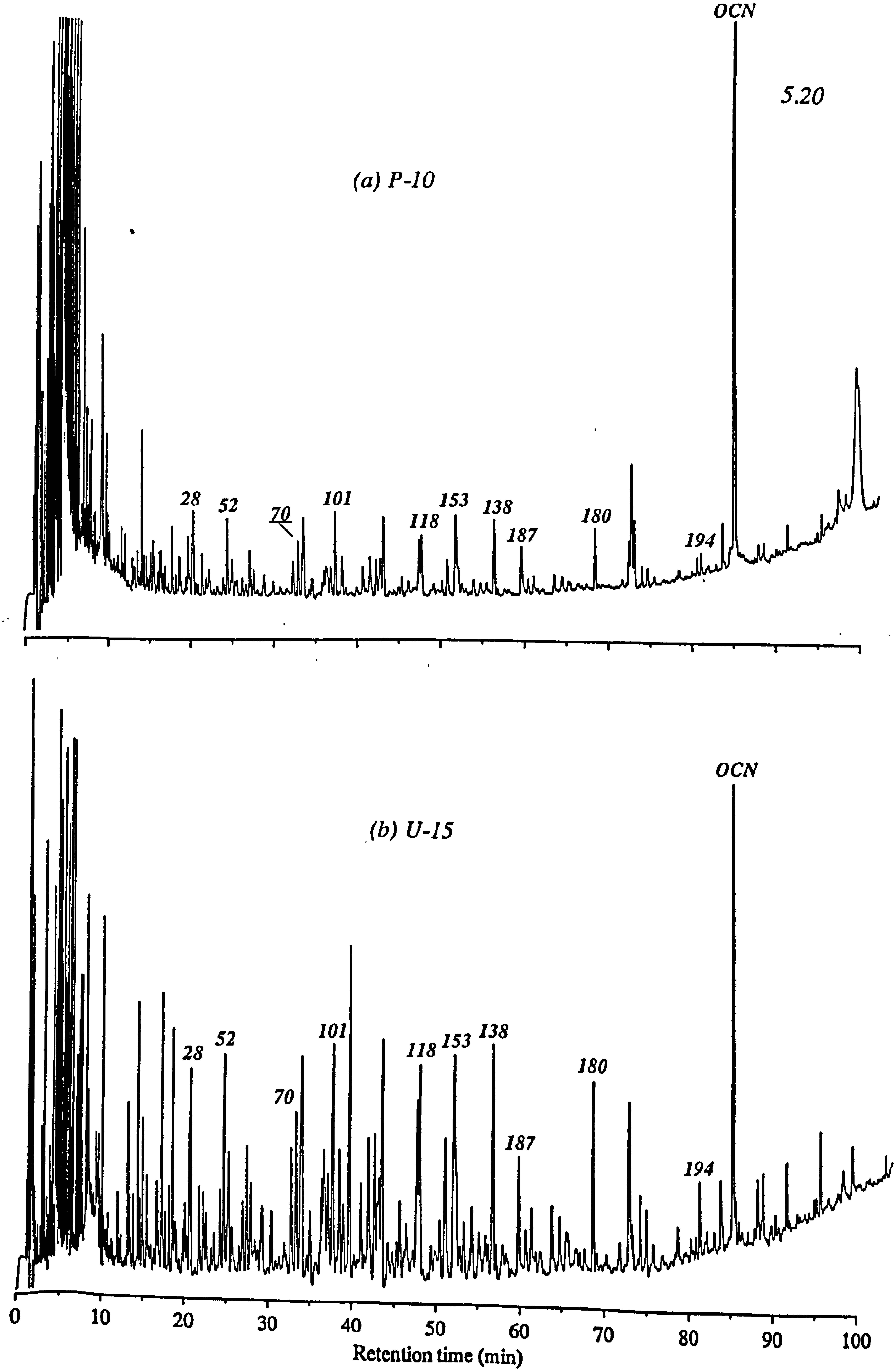
and the similarity between samples N-7 and K-6 in cluster 6 was 0.869. The mean total PCB concentration in sediments in clusters 5 and 6 was 458 ng g^{-1}C, with the maximum observed in sample U-15 (1644 ng g^{-1}C) and the minimum observed in sample T-10 (72 ng g^{-1}C). Seven of the sediment samples (*i.e.* samples K-6, L-9, N-7, N-9, P-10, Q-9 and T-10) included in clusters 5 and 6 had very low amounts of fine fraction (lower than 0.9%) whereas the remaining three samples (*i.e.* samples G-13, J-13 and U-15) had a fine fraction content of more than 3% and up to 11.4% at station J-13. The main differences in the PCB patterns among samples within cluster

Figure 5.19. Gas chromatograms in a DB-5 column for sediment samples (a) G-13 and (b) N-9. The sample weights extracted were of 50 and 70 g respectively and the final extract volumes were of 0.5 and 0.2 ml respectively. These sediments were classified in cluster 5.


5.19

(a) G-13
OCN
28
52
70
101
118
153
138
187
180
194
(b) N-9
OCN
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

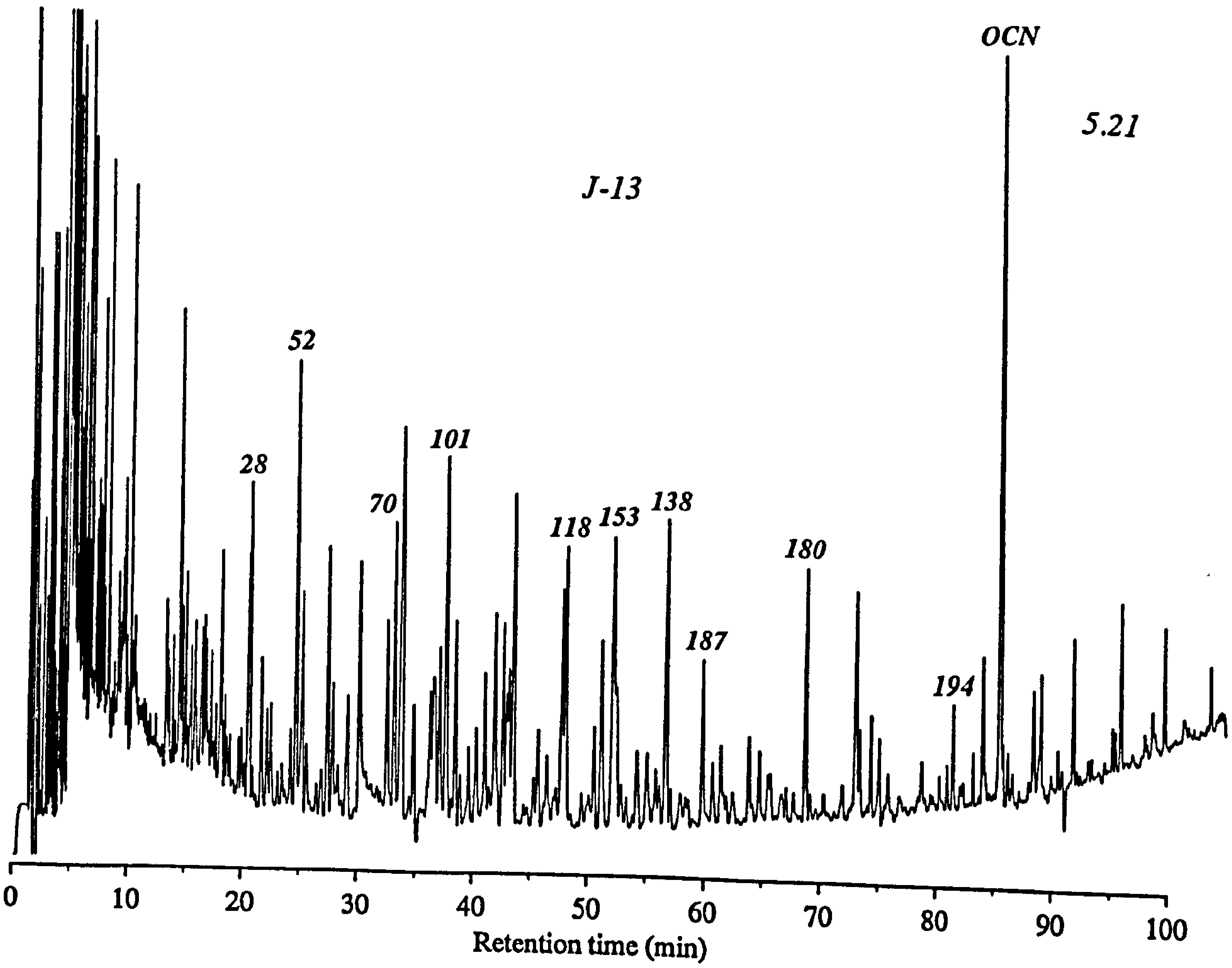
Figure 5.20. Gas chromatograms in a DB-5 column for sediment samples (a) P-10 and (b) U-15. The sample weights extracted were of 60 g respectively and the final extract volumes were of 0.2 and 0.5 ml respectively. These sediments were classified in cluster 5.



5.20

OCN
(a) P-10
28
52
70
101
118
153
138
187
180
194
OCN
(b) U-15
28
52
70
101
118
153
138
187
180
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

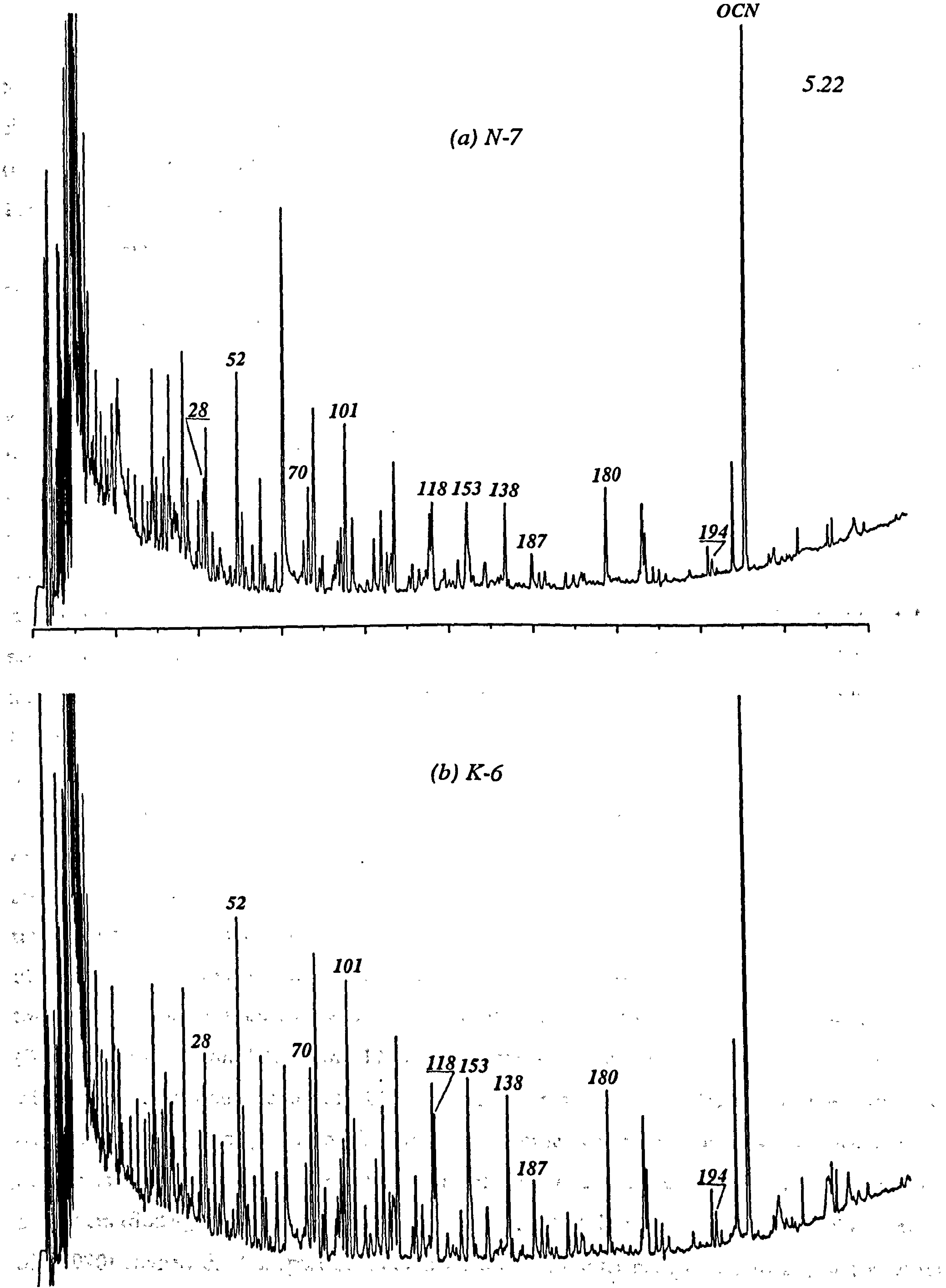
Figure 5.21. Gas chromatogram in a DB-5 column for sediment sample J-13. The sample weight extracted was of 60 g and the final extract volume was of 0.5 ml. This sediment was classified in cluster 5.



OCN
5.21
J-13
52
28
70
101
118
153
138
180
187
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

Figure 5.22. Gas chromatograms in a DB-5 column for sediment samples (a) N-7 and (b) K-6. The sample weights extracted were of 70 g respectively and the final extract volumes were of 0.2 ml respectively. These sediments were classified in cluster 6.

5.22


OCN
(a) N-7
52
28
101
70
118
153
138
180
187
194
(b) K-6
52
101
28
70
118
153
138
180
187
194
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

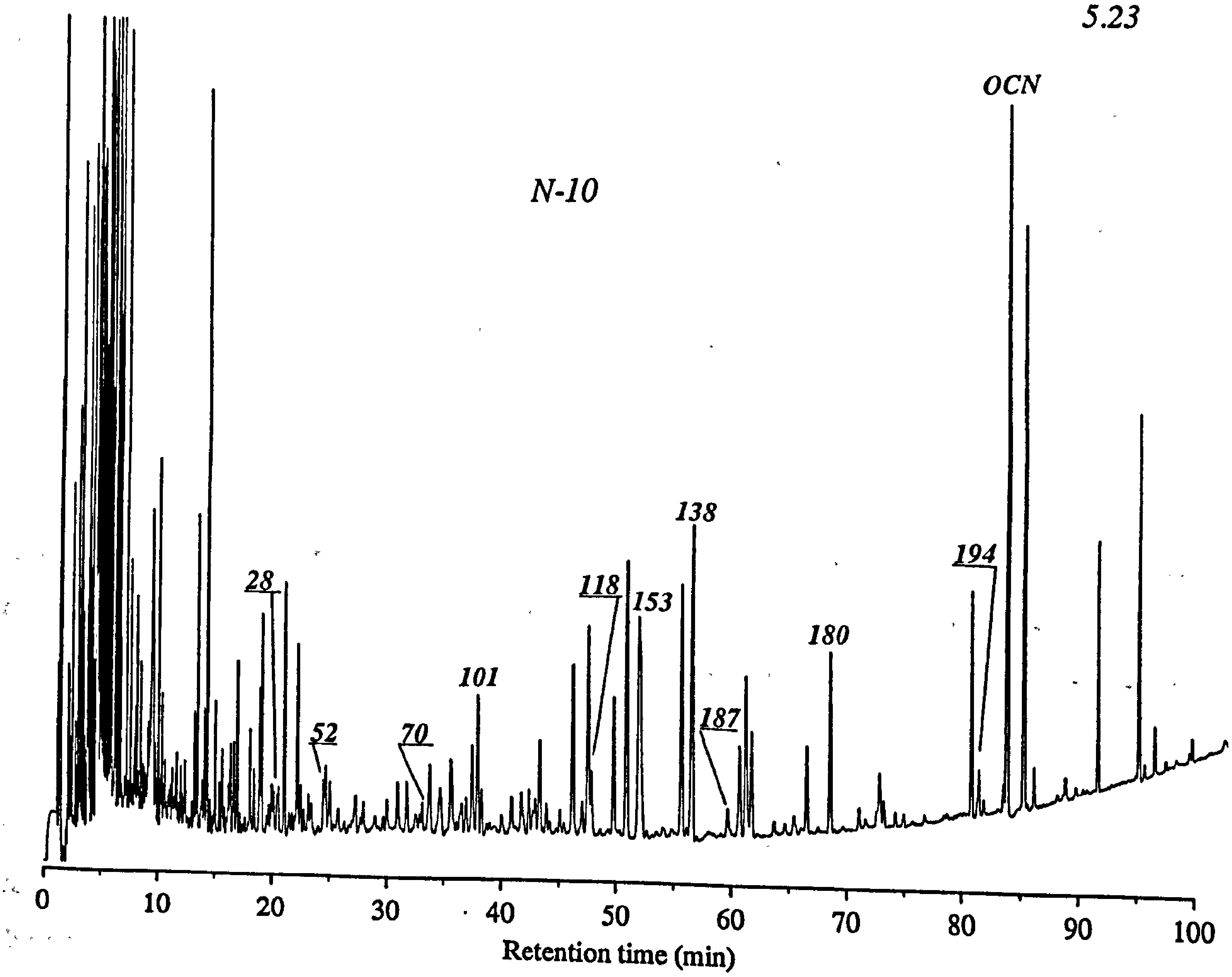
5 were due to variations in the relative concentrations of PCB congeners at both ends of the chlorination range as indicated by the relative standard deviations for congeners 28 (r.s.d.=39.7%), 52 (r.s.d.=32.3%), 187 (r.s.d.=25.1%) and 194 (r.s.d.=28.0%), although congener 118 also showed a relatively high variability (r.s.d.=27.8%).

The substantially different pattern in the distribution of PCB congeners in sediments from clusters 5 and 6 suggests that the main source of PCBs in these samples was different to the source(s) of PCBs for sediments in clusters 1, 2, 3 and 4 which, as mentioned above, seem to be related to inputs from the River Mersey and its estuary and/or associated to inputs of wastes at the designated areas within Liverpool Bay. In the case of the first four clusters, it is suggested that the PCB congener distribution pattern in sediments of cluster 2 reflect more closely the PCB composition of the source(s), and the patterns shown by sediments in clusters 1, 3 and 4 represent different states of alteration of the "original" pattern. The different degrees of alteration of the original pattern are probably due to the desorption of PCB congeners, which will occur at different rates according to the solubility of each congener and its tendency to associate with sediment particles, with the solubility generally decreasing and the K_p increasing with increasing number of chlorine atoms in the biphenyl ring. Therefore, sediments in cluster 4 represent the highest degree of alteration of the original pattern and indicate the highest solubility and/or desorption tendency of the PCB congeners with lower chlorine contents.

The distribution pattern of the PCB congeners in sediments in clusters 5 and 6 can be explained by a higher contribution to the total PCB load, of PCBs associated to sediments from the Irish Sea which, according to the sediment transport patterns described in Chapter 2, are transported eastward into Liverpool Bay. The main transport mechanism responsible of the ubiquitous distribution of stable contaminants such as PCBs far from point sources, and even toward remote areas such as the arctic region and open ocean waters is via the atmosphere (Sodergen *et al.*, 1990; Atlas *et al.*, 1986). Therefore, it is expected that atmospheric deposition will be a more important source of PCBs in offshore areas than in nearshore areas where riverine and direct inputs through waste disposal may become dominant. The less chlorinated PCB congeners have a higher vapour pressure and rate of volatilization than the more chlorinated congeners (Sodergen *et al.*, 1990; Shiu and Mackay, 1986). In a laboratory system, Sodergen *et al.* (1990) studied the transport of incinerated organochlorine compounds to air, water, water microlayer and organisms and reported that the less chlorinated congeners were more quickly transferred to the air, and since the proportions of these congeners was high in the air, they were partitioned to the water more extensively and thus became more available for uptake by fish than the highly chlorinated congeners. If, due to a higher volatility, lower chlorinated congeners are enriched in the atmospheric compartment, it is expected that the zones more affected by atmospheric deposition will be more enriched by lower chlorinated congeners. Eisenreich (1987) reported that atmospheric deposition was probably an important mechanism of transport of PCBs into Lake Superior water and sediments during periods of high precipitation, whereas Larsson (1984) also reported that sedimentation rates in two Swedish lakes and in a marine coastal sampling station (Hano Bight in the southern Baltic) strongly suggested that the atmosphere was the source of PCBs in these localities. Therefore, it seem reasonable to assume that the main source of PCBs into offshore waters and sediments in the Irish Sea is the atmosphere, and, if so, the PCB congener distribution pattern may show a dominance of lower molecular weight congeners. The influence by offshore particles on the organic composition of the sediments in clusters 5 and 6 with fine fraction concentrations lower than 1%, is consistent with the classification of these samples in the "non-contaminated" clusters determined by their elemental composition (see Figs. 5.8, 4.30a and 4.30b).

All the similarities of the sediment sample from station N-10 with the other sediment samples were below 0.6, indicating that the pattern in this sample (see Fig. 5.23) of ten the congeners used for the classification of the sediments was very different. Apart from the differences in the distribution of the ten congeners used in the classification, this sample showed a marked difference in the distribution of the other congeners. For example, as compared to all of the chromatograms previously shown, Figure 5.23 shows that this sample was particularly enriched in certain congeners whereas others seem to be depleted. The total normalized concentration in this sample was 786 ng $g^{-1}C$ which is relatively high in relation to the amount of fine particles in the sediment which was 0.60%. Although the amount of organic carbon and the $\delta^{13}C$ value did not show any particular anomaly, the elemental composition of this sample was also unusual and showed very low similarities with the other sediments in the bay. As the PCB congener and elemental compositions of the sediment did not follow any particular trend in relation to the other sediment samples, it can only be speculated that perhaps some debris associated to the sewage sludge disposal at Site SI, or the remains of a benthic organism in the sample may have caused the unusual composition of this particular sediment.

Figure 5.23. Gas chromatogram in a DB-5 column for sediment sample N-10. The sample weight extracted was of 60 g and the final extract volume was of 1.0 ml. This sediment was classified in cluster 7 and showed the lowest similarities.


5.23
OCN
N-10
138
194
28
118
153
180
101
187
52
70
0
10
20
30
40
50
60
70
80
90
100
Retention time (min)

5.2.2.2. Differences in the geochemical behaviour of PCB isomers

The complexity of the geochemical behaviour of PCB congeners is due to the considerable variability in the various physicochemical properties observed within this family of hydrophobic organic contaminants. The variability in these properties, although considerably related to the degree of chlorination amongst congeners, is also influenced by differences in the substitution pattern within isomeric groups, *i.e.*, PCB congeners with the same number of chlorines, but different substitution positions of the chlorine atoms, may show differences in solubility, volatility, etc. (see, for example, the review on physicochemical properties of PCBs reported by Shiu and Mackay, 1986).

The relationship between the structure and the toxicity of PCB congeners is one of the best examples of the effects of the substitution patterns on the properties of PCBs. It is well known that only a small number of congeners are extremely toxic, *viz.* Nos. 77, 126 and 169, and that this toxicity is related to the planar configuration adopted by these congeners. The ability for a congener to adopt a planar configuration depends on the substitution positions of the chlorine atoms (De Voogt *et al.*, 1990). The preferred conformation for all PCB congeners, including the non-*ortho* substituted congeners, is a non-planar one, however, the lack of *ortho* chlorine atoms exerts a minimum steric hindrance of rotation about the 1,1′ bond and the planar configuration can be adopted with a minimum energy requirement. If one chlorine atom is introduced in an *ortho* position, the energy requirement for free rotation of the phenyl-phenyl bond significantly increases and this effect is enhanced by the introduction of more *ortho* chlorine atoms. Changes in the substitution pattern have a considerable effect on the activity of the PCB congener, with toxicity decreasing (but not necessarily disappearing) as the planarity of the molecule decreases due to an increase in the ortho chlorine substitutions. According to De Voogt *et al.* (1990), the position of the chlorine atoms has a greater influence on the microsomal activity of PCBs than the number of chlorine atoms in the molecule, particularly within the group of tri- to heptachlorinated congeners.

The three-dimensional configuration of the PCB congeners may also play a significant role in their behaviour in the aquatic environment and their partitioning amongst different compartments such as sediments, the water column and air. In recent reports, some observations have been made in relation to the structure and the properties of PCB congeners which can lead to a better understanding of the PCB distribution in the different environmental compartments. For example, Lara and Ernst (1989) who studied the partitioning of PCBs between water and dissolved humic substances reported an increase in the partitioning (K_h) of congeners into the organic phase as the number of chlorines increased, this observation was consistent with reports of a correlation between the molecular weight of PCBs and K_{ow} (e.g. see data reported by Shiu and Mackay, 1986). These authors also reported differences between isomers, with K_h decreasing as the number of *ortho* chlorines increased, and also decreasing with the presence of *meta* chlorines adjacent to *ortho* chlorine atoms. Regarding the number of *ortho* chlorines, Hawker and Connel (1988) reported the lowest K_{ow} value for the tetrachlorobiphenyl with the four chlorines at *ortho* positions, whereas the highest K_{ow} values (around one order of magnitude higher) were reported for tetrachlorobiphenyls without *ortho* substitution. In relation to the effect of the *meta* chlorines adjacent to *ortho* chlorines, Rapaport and Eisenreich (1984) suggested that the reduction on K_{ow} values for congeners with chlorines at 2,2' and 3,3' positions was due to the *meta* substituents "pushing" the *ortho* chlorines toward the 1,1' bond, forcing a more non-planar configuration. Although there is some relation between the structure and the properties of PCB congeners, this relationship is not completely understood. Murphy *et al.* (1987) recently studied the solubilities, vapour pressures and Henry's law constants (HLCs) and reported that "the trends in the solubilities and vapour pressures were surprisingly uneventful", as the differences between individual compounds were not large, or statistically significant. On the other hand, however, from a closer inspection of the data some trends could be observed such as lower HLC for congeners with 2,3 and 2,3,5 substitution on one or both rings, or higher solubilities and vapour pressures for congeners with 2,3,6 substitution.

Although the behaviour of PCB congeners in the environment may be influenced by many more factors than those influencing their behaviour under laboratory conditions in which the above observations were made, an attempt was made to examine the possibility of obvious different behaviours amongst congeners within specific isomeric groups in the sediment samples analysed in the present study. To achieve this aim, a principal component analysis was performed on a data set including five tetra-, seven penta-, four hexa-, three hepta- and three octachlorobiphenyl congeners. As the grain size had a large effect on the absolute concentration of each congener, it was obvious that the data had to be normalized before the analysis which, otherwise, would have resulted in a single principal component (related to grain size) explaining a very large percentage of the total variance of the data set. To avoid grain size effects, the concentration of each of the congeners in each sample used in the analysis was divided by the concentration of congener No. 138 in that particular sample. This way, regardless of the absolute concentrations, the ratio **congener X / congener 138** remained constant if congener X had a similar behaviour to congener 138. As the principal component analysis is based on the matrix of correlations, only the congeners which showed some variations in comparison to congener 138 could be used in the analysis. For example, some of the congeners not included in the analysis were 153 and 180, as the ratios **CB-153 / CB-138** and **CB-180 / CB-138** remained relatively constant throughout the sediment samples in Liverpool Bay.

The principal component analysis was performed with the statistical package SPSS-X of the VAX mainframe system at UCNW. The reliability of the analysis was tested with the Kaiser-Meyer-Olkin measure of sampling adequacy which gave a coefficient of 0.81. The Bartlett test of sphericity was also highly significant, therefore, the results from the principal component analysis were reliable (see Norusis, 1985 for details of the tests recommended before a factor analysis and a detailed description on a Factor analysis on SPSS-X).

Table 5.9 shows the communalities (explained variance) for each congener, the eigenvalues and the percentage of the variance explained by each of the four principal components extracted in the analysis. This table shows that 87.5% of the total variance of the data set was explained by four components, although the first two components explain more than 70% of this variance. The column showing the communalities also shows that with these four components more than 80% of the variance of all but two of the congeners can be explained. Table 5.10 shows a matrix with the loadings for the congeners on each component. Briefly, this table shows that three of the tetrachlorinated congeners (*i.e.* Nos. 44, 52 and 70) were highly loaded (explained by) on the first principal component. Of the tetrachlorinated congeners, No. 74 was highly loaded on component 3, whereas congener 49 was equally loaded to both components 3 and 1. Congener 70 also showed some obvious load on component 3. All of the pentachlorinated congeners (*i.e.* Nos. 87, 95, 97, 99, 101 and 110), except 118, showed a high load on the first component whereas No. 118 showed some loading on this component but was mainly loaded on the fourth principal component. Of the hexachlorinated congeners, Nos. 149 and 159 were mainly loaded on principal component 1 whereas No. 146 was highly loaded on component three and 128 was highly negatively loaded on component three and significantly loaded on component four. With the exception of congener 174, all of the hepta- and octachlorinated congeners (*i.e.* Nos. 177, 187, 194, 196 and 199) were highly loaded on component 2. Although the load of congener 174 on the second principal component was obvious, it was largely (and negatively) loaded on component 4.

The principal component analysis indicated that some of the congeners within each specific isomeric group showed different behaviour to that of their isomers. To facilitate the interpretation of the analysis, the confidence intervals for each congener were computed using the clusters

Table 5.9. Final statistics obtained with the procedure FACTOR of the SPSS-X statistical package. This table shows that four Principal Components were extracted explaining 87.5% of the total variance. The communalities obtained for each congener with these four components are also shown in the table.

```
CONGENER         COMMUNALITY  *  FACTOR   EIGENVALUE    PCT OF VAR    CUM PCT
                              *
 44                   .91612  *     1      10.20876          46.4        46.4
 49                   .86558  *     2       5.26413          23.9        70.3
 52                   .85882  *     3       2.49414          11.3        81.7
 70                   .96216  *     4       1.27307           5.8        87.5
 74                   .94580  *
 87                   .94605  *
 95                   .94938  *
 97                   .82203  *
 99                   .94062  *
 101                  .97331  *
 110                  .87637  *
 118                  .82543  *
 128                  .83490  *
 146                  .90839  *
 149                  .81378  *
 151                  .80050  *
 174                  .77784  *
 177                  .67241  *
 187                  .84160  *
 194                  .92293  *
 196                  .86807  *
 201                  .91802  *
```

Table 5.10. Matrix of the loads for various PCB congeners on each principal component after a VARIMAX rotation of the originally extracted components. Data from a total of 54 sediment samples were used in the PCA.

		PRINCIPAL COMPONENT			
IUPAC No.	Cl n	1	2	3	4
44	4	.93433	-.09160	.17466	.06525
49		.63045	.15626	.66308	-.06342
52		.92368	-.07488	-.00092	-.00586
70		.84693	-.12115	.47598	.06025
74		.25183	.13232	.92895	.04386
87	5	.88404	-.31065	-.13861	.22094
95		.95306	-.09971	.17329	.03281
97		.83516	-.30402	.09564	.15153
99		.91432	-.14916	-.04848	.28293
101		.94129	-.27248	-.03174	.10969
110		.79339	-.22344	-.18401	.40387
118		.43399	-.27072	-.12408	.74054
128	6	.04781	.10008	-.75577	.50141
146		-.15393	.32431	.87336	.12946
149		.86194	.10902	.09046	-.22531
151		.82636	.32357	-.03688	-.10760
174	7	.09630	.49308	-.12192	-.71454
177		-.13406	.75488	.13822	-.25591
187		.03835	.91156	-.02170	-.09333
194	8	-.20507	.87783	.23143	-.23818
196		-.15641	.91477	.06458	-.05120
201		-.13097	.94365	.10176	-.00614

formed with the sediment classification previously discussed. The hypothesis on which this discussion is based, is that the ratio **congener X / congener 138** of sediments in cluster 2 would represent more closely the ratio of these congeners near the source. If this ratio decreased toward clusters 1 and 4 (cluster 3 was not considered as the congeners used in the principal component analysis were only all present in one sample of this cluster), then congener X is being lost from the sediments in these clusters at a faster rate than congener 138. On the other hand, if the ratio **congener X / congener 138** increased from cluster 2 towards clusters 1 and 3, then congener X is being released at a slower rate than congener 138. Differences in the rate of release of these congeners into solution may be due to differences in their solubilities, strength of sorption onto sediment particles, or both.

The confidence intervals for tetrachlorinated congeners are shown in Figure 5.24. The ratio of the means between cluster 4 and 2, and between 1 and 2 shows that, in general, all of these congeners were lost from the sediments at a faster rate than congener 138, which was expected by the observations in the discussion of the previous section. The main point in the present discussion is the observation that the tetrachlorinated congener which showed a large difference in the principal component loadings, *i.e.* 74, was lost at a much faster rate (see Fig. 5.24e) than any other of the tetrachlorinated congeners. It is also important to observe that congener 49, which also showed a significant load on component three, also showed a relatively fast rate of loss from the sediments. Therefore, these observations seem to suggest that component three represents those congeners with a fast rate of release from the sediments in relation to congener 138.

From the analysis of the structures of the tetrachlorinated congeners it is obvious that the main difference between congener 74 and the other congeners is that the former is the only one with three chlorine atoms in one biphenyl ring and one chlorine in the other (Table 5.11). If the solubility is the main property controlling the release of PCBs from sediments, it would be expected that congener 74 showed a slower release than the other isomers, as its aqueous solubility is lower probably due to having only one *ortho* chlorine substitution (see Table 5.11). The higher octanol water partition coefficient (K_{ow}) would also suggest a possibly stronger association of congener 74 to the sedimentary organic matter as compared with the other isomers. On the other hand, however, this congener also shows a relatively high HLC (see Table 5.11) which indicates a higher tendency of this congener to be lost from solution into the vapour phase which may accelerate the transport from the solid (sediment) to the liquid (seawater) phase. Unfortunately there are only few studies in which the partition coefficients of PCBs between marine sediments and seawater are reported (e.g. Lara and Ernst, 1990a, Brownawell and

Figure 5.24. 95% confidence intervals for each of tetrachlorinated PCB isomers used in the Principal Component analysis (see text). The confidence intervals were computed with the command ONEWAY in the statistical package MINITAB.

```
a) CB44
   CLUSTER    N      MEAN     STDEV  --+---------+---------+---------+----
       2     14   0.41043   0.06779              (---*----)
       1     22   0.31036   0.06204      (---*--)
       4     11   0.28782   0.07952   (----*----)
       5      5   0.57100   0.26186                        (-------*------)
                                     --+---------+---------+---------+----
 POOLED STDEV =   0.09980            0.24      0.36      0.48      0.60
```

```
b) CB49
   CLUSTER    N      MEAN     STDEV  -+---------+---------+---------+-----
       2     14    0.5728    0.1076                          (----*---)
       1     22    0.3684    0.0811          (---*--)
       4     11    0.3006    0.0740   (----*----)
       5      5    0.4532    0.2196             (-------*-------)
                                     -+---------+---------+---------+-----
 POOLED STDEV =    0.1057           0.24      0.36      0.48      0.60
```

```
c) CB52
   CLUSTER    N      MEAN     STDEV  -+---------+---------+---------+-----
       2     14    0.6272    0.1538       (---*---)
       1     22    0.5164    0.1347     (--*--)
       4     11    0.4937    0.0790   (---*---)
       5      5    1.2308    0.7501                      (-----*------)
                                     -+---------+---------+---------+-----
 POOLED STDEV =    0.2501           0.35      0.70      1.05      1.40
```

```
d) CB70
   CLUSTER    N      MEAN     STDEV  -+---------+---------+---------+-----
       2     14   0.61436   0.05524                     (--*--)
       1     22   0.46532   0.05272            (-*-)
       4     11   0.33236   0.04129  (--*--)
       5      5   0.70240   0.19711                         (----*---)
                                     -+---------+---------+---------+-----
 POOLED STDEV =   0.07507           0.30      0.45      0.60      0.75
```

```
e) CB74
   CLUSTER    N      MEAN     STDEV  ------+---------+---------+---------+
       2     14   0.55543   0.07100                                (--*---)
       1     22   0.37632   0.07484                (--*--)
       4     11   0.22609   0.07883   (---*---)
       5      5   0.36620   0.14261            (------*-----)
                                     ------+---------+---------+---------+
 POOLED STDEV =   0.08249                0.24      0.36      0.48      0.60
```

Table 5.11. Physicochemical properties reported for some of the PCB congeners used in the Principal Component Analysis. The aqueous solubilities (S) are in µg L^{-1} and the Henry's Law Constants (HLC) are in atm m^3 $mol^{-1}x10^{-4}$.

IUPAC No.	Structure	Ortho Cl	[a]S	[a]HLC	[b]log K_{ow}	[c]log K_h	[d]log K_{oc}
44	2,2',3,5'	2	100	1.9	6.00	nd	nd
49	2,2',4,5'	2	78	2.8	6.10	nd	nd
52	2,2',5,5'	2	112	2.4	6.10	nd	nd
70	2,3',4',5	1	36	1.9	5.90	nd	nd
74	2,4,4',5	1	30	2.1	6.10	nd	nd
87	2,2',3,4,5'	2	29	1.3	6.50	3.75	nd
95	2,2',3,5',6	3	54	2.0	6.40	3.70	5.68
97	2,2',3',4,5	2	28	1.5	6.60	nd	5.83
99	2,2',4,4',5	2	22	2.1	6.60	nd	nd
101	2,2',4,5,5'	2	26	1.8	6.40	3.86	5.81
110	2,3,3',4',6	2	28	1.1	nd	3.79	nd
118	2,3',4,4',5	1	13	0.9	6.40	nd	nd
128	2,2',3,3',4,4'	2	6	0.6	7.00	nd	6.28
138	2,2',3,4,4',5'	2	7	0.8	7.00	4.60	6.22
146	2,2',3,4',5,5'	2	7	0.9	nd	4.58	nd
149	2,2',3,4',5',6	3	12	1.5	6.80	nd	nd
151	2,2',3,5,5',6	3	13	1.6	nd	4.41	6.05
174	2,2',3,3',4,5,6'	3	5	0.5	nd	nd	nd
177	2,2',3,3',4',5,6	3	4	0.3	nd	4.90	nd
187	2,2',3,4',5,5',6	3	4	0.8	nd	4.90	nd
194	2,2',3,3',4,4',5,5'	2	0	0	7.10	5.36	6.41
196	2,2',3,3',4,4',5,6'	3	0	0	nd	nd	nd
199	2,2',3,3',4,5,5',6'	3	0	0	nd	5.31	nd

Notes: [a] Data from Murphy *et al.* (1987)

[b] Data from Shiu and Mackay (1986)

[c] Data from Lara and Ernst (1989)

[d] Data from Lara and Ernst (1990a)

Farrington, 1986) and these studies did not report data for many of the congeners used in this analysis. Therefore, although there is an obvious structural difference between congener 74 and the other isomers, it is difficult to explain how this structure induces a faster loss from the sediments in Liverpool Bay.

Figure 5.25 shows that the only pentachlorinated congener being lost at a faster rate than congener 138 was No. 95, however, its loss was not as apparent as for congener 74 and was highly loaded on principal component 1. The fast rate of loss from the sediment for congener 95 is consistent with its higher solubility which is probably induced by the three chlorine atoms in *ortho* positions. This configuration would probably also create a weaker association of this congener with sediments, as the lower planarity produces a lower surface area of contact with the sediment. Lara and Ernst (1990a) reported significantly lower sediment-water partition coefficients (K_d) for congener 95 as compared to congeners 97 and 101 (Table 5.11), which is consistent with the observation of a possible easier release of the former from the sediment surface. Among the pentachlorinated congeners only No. 118 showed a significant loading to a principal component (component 4) other than 1. The difference between this congener and other isomers could not be assessed in terms of its ratios with congener 138, because as shown in Figure 5.25 this congener had a relatively similar behaviour to the other isomers. However, an important structural difference can be observed for this congener, as it was the only one within the group which has only one *ortho* chlorine substitution in the molecule. In fact, this congener is one of the group of PCBs which causes more environmental concern because it has a relatively high toxicity related to its configuration which tends to be more planar than the majority of congeners, and is present at significant levels in the environment as compared to the most toxic congeners which are present at low levels in the technical formulations, and therefore in the environment (De Voogt *et al.*, 1990).

An interesting group to compare is the hexachlorinated congeners, as in terms of number of chlorines they should have a closer relationship with congener 138. Table 5.10 shows that congeners 149 and 151 were highly loaded on principal component 1, and which, as for other congeners loaded to this component (see Figs. 5.24 and 5.25) the confidence intervals in Figure 5.26 show that they had a relatively faster rate of release from sediments as compared to isomer 138, although this release was not as strong as for those congeners more loaded on the third principal component such as No. 146. The faster rate of release of congeners 149 and 151 can be explained, as in the case of congener 95, as related to their lower degree of planarity due to the three *ortho* chlorine substitutions in their molecules. The number of *ortho* chlorine

Figure 5.25. 95% confidence intervals for each of pentachlorinated PCB isomers used in the Principal Component analysis (see text). The confidence intervals were computed with the command ONEWAY in the statistical package MINITAB.

```
a) CB87
   CLUSTER   N      MEAN     STDEV  -+---------+---------+---------+-----
      2     14   0.32707   0.03464   (--*--)
      1     22   0.32986   0.05301    (-*-)
      4     11   0.34100   0.06427    (--*--)
      5      5   0.61260   0.06816                              (----*----)
                                    -+---------+---------+---------+-----
 POOLED STDEV =  0.05293           0.30      0.40      0.50      0.60

b) CB95
   CLUSTER   N      MEAN     STDEV  --+---------+---------+---------+----
      2     14    0.9660    0.1168             (--*--)
      1     22    0.8005    0.1213        (--*-)
      4     11    0.6518    0.1204  (---*--)
      5      5    1.3496    0.4658                         (----*----)
                                    --+---------+---------+---------+----
 POOLED STDEV =   0.1767            0.60      0.90      1.20      1.50

c) CB97
   CLUSTER   N      MEAN     STDEV  -+---------+---------+---------+-----
      2     14   0.20521   0.05905         (--*---)
      1     22   0.17082   0.03188     (-*--)
      4     11   0.16336   0.03767   (--*---)
      5      5   0.33260   0.03725                           (-----*----)
                                    -+---------+---------+---------+-----
 POOLED STDEV =  0.04243           0.140     0.210     0.280     0.350

d) CB99
   CLUSTER   N      MEAN     STDEV  ---+---------+---------+---------+--
      2     14   0.32200   0.05726     (--*---)
      1     22   0.30905   0.06105    (--*--)
      4     11   0.30182   0.06870  (---*---)
      5      5   0.53940   0.09161                          (-----*-----)
                                    ---+---------+---------+---------+--
 POOLED STDEV =  0.06482              0.30      0.40      0.50      0.60

e) CB101
   CLUSTER   N      MEAN     STDEV  ---------+---------+---------+------
      2     14    0.6535    0.0810      (-*--)
      1     22    0.6599    0.1099       (*-)
      4     11    0.5742    0.0955  (--*--)
      5      5    1.3100    0.1943                               (---*---)
                                    ---------+---------+---------+------
 POOLED STDEV =   0.1100                    0.75      1.00      1.25

f) CB110
   CLUSTER   N      MEAN     STDEV  -+---------+---------+---------+-----
      2     14    0.6364    0.0809  (--*---)
      1     22    0.6469    0.0902   (--*--)
      4     11    0.6638    0.0947   (---*---)
      5      5    0.9652    0.1428                       (---*-----)
                                    -+---------+---------+---------+-----
 POOLED STDEV =   0.0943           0.60      0.75      0.90      1.05

g) CB118
   CLUSTER   N      MEAN     STDEV  -----+---------+---------+---------+
      2     14    0.8024    0.0781   (---*----)
      1     22    0.8051    0.0854     (---*--)
      4     11    0.8015    0.1191   (---*-----)
      5      5    1.0054    0.0998                     (-------*-------)
                                    -----+---------+---------+---------+
 POOLED STDEV =   0.0929                0.80      0.90      1.00      1.10
```

Figure 5.26. 95% confidence intervals for each of hexachlorinated PCB isomers used in the Principal Component analysis (see text). The confidence intervals were computed with the command ONEWAY in the statistical package MINITAB.

```
a) CB128
   CLUSTER   N       MEAN     STDEV   --------+---------+---------+--------
      2     14    0.14743   0.02691    (-----*-----)
      1     22    0.17386   0.02367                (----*---)
      4     11    0.20527   0.03697                          (------*------)
      5      5    0.19640   0.02485                    (---------*---------)
                                      --------+---------+---------+--------

 POOLED STDEV =   0.02788                   0.150     0.175     0.200


b) CB146
   CLUSTER   N       MEAN     STDEV   -+---------+---------+---------+-----
      2     14    0.71636   0.04425                              (---*---)
      1     22    0.55091   0.08643                 (--*--)
      4     11    0.41009   0.11419    (---*----)
      5      5    0.44460   0.13750    (------*------)
                                      -+---------+---------+---------+-----
 POOLED STDEV =   0.08995            0.36      0.48      0.60      0.72


c) CB149
   CLUSTER   N       MEAN     STDEV   ---+---------+---------+---------+---
      2     14    0.66607   0.03868               (-----*-----)
      1     22    0.63273   0.06850            (---*----)
      4     11    0.58736   0.10477   (------*-----)
      5      5    0.71060   0.09803                  (---------*--------)
                                      ---+---------+---------+---------+---
 POOLED STDEV =   0.07447              0.560     0.630     0.700     0.770


d) CB151
   CLUSTER   N       MEAN     STDEV   ---------+---------+---------+-------
      2     14    0.24914   0.02781                 (---------*--------)
      1     22    0.23986   0.03649              (-------*------)
      4     11    0.23600   0.03412         (----------*----------)
      5      5    0.23420   0.04983   (---------------*---------------)
                                      ---------+---------+---------+-------
 POOLED STDEV =   0.03523                    0.220     0.240     0.260
```

substitutions, and the 2,3,6 configurations also increase the solubility of these congeners. The effect of the different number of chlorines in the biphenyl rings of congener 151 may also affect the sorption of this congener onto the sediment. This observation is consistent with a lower K_d for congener 151 as compared with the K_d for 138 reported by Lara and Ernst (1990a). On the other hand, it was not possible to explain the relatively faster loss of congener 146 which shows properties relatively similar to congener 138, although Lara and Ernst (1989) reported a slightly lower K_h for congener 146 than for 138 (Table 5.11). Congener 128 was the only PCB in the whole group included in this analysis which showed a relative increase in its ratio with congener 138. Figure 5.26 shows that this increase was probably significant, suggesting that congener 138 was lost at a faster rate compared to congener 128. Although this difference is difficult to explain from the structure of congener 128, as it would probably show a lower planarity than congener 138 due to the two *meta* chlorines being adjacent to the two *ortho* chlorines and hence forcing a more non-planar configuration, it is consistent, on the other hand, with reported physicochemical properties for this congener which shows lower solubility, a low HLC, and its K_ds are also reported higher than that of congener 138 (see Table 5.11).

The congeners with a higher molecular weight than that of congener 138 were highly loaded on principal component 2. Therefore, the first two components seem to be also related to the degree of chlorination of the PCB congeners. Although there was some degree of variability of the ratios of these congeners with congener 138, there seemed to be no clear overall trend of a decrease or increase of the ratios from cluster 2 towards clusters 1 and 4 (Fig. 5.27). The fact that these congeners with higher chlorination than that of 138 were more loaded on principal component 2, and showed a near zero or a slightly negative load on component 1, and the opposite trend was observed for most of those congeners with a lower chlorination than congener 138, may suggest that the variations in the ratios with congener 138 between highly chlorinated and lower chlorinated congener, although minor (as indicated by the overlapping of confidence intervals), occurred in opposite directions, *i.e.*, when the ratio of higher chlorinated congeners increased, the ratios in the lower chlorinated decreased and *viceversa*. This observation is consistent with the discussion in the section above. The high and negative load of congener 174 on principal component 4, which reflects an opposite behaviour of this congener as compared to congener 118 could not be explained.

From the principal component analysis it is clear that the molecular configuration, as well as the degree of chlorination are playing a significant role in the behaviour of PCB congeners in Liverpool Bay sediments. Although some of the observations could be explained by the effect

Figure 5.27. 95% confidence intervals for each of hepta- and octachlorinated PCB isomers used in the Principal Component analysis (see text). The confidence intervals were computed with the command ONEWAY in the statistical package MINITAB.

```
a) CB174
   CLUSTER   N      MEAN     STDEV  -------+---------+---------+---------
      2     14   0.07457   0.00983                     (----*----)
      1     22   0.06764   0.01732                   (---*---)
      4     11   0.07818   0.02973                      (-----*-----)
      5      5   0.04420   0.01173   (-------*--------)
                                    -------+---------+---------+---------
 POOLED STDEV =  0.01879                 0.040     0.060     0.080
```

```
b) CB177
   CLUSTER   N      MEAN     STDEV  -----+---------+---------+---------+-
      2     14   0.16057   0.01156                          (----*-----)
      1     22   0.15309   0.02127                        (---*----)
      4     11   0.16409   0.04000                          (------*-----)
      5      5   0.11260   0.03409   (--------*--------)
                                    -----+---------+---------+---------+-
 POOLED STDEV =  0.02577               0.100     0.125     0.150     0.175
```

```
c) CB187
   CLUSTER   N      MEAN     STDEV  ---------+---------+---------+-------
      2     14   0.41543   0.03119                         (----*-----)
      1     22   0.41209   0.04232                         (----*---)
      4     11   0.41491   0.09998                        (-----*-----)
      5      5   0.30080   0.08293  (--------*--------)
                                    ---------+---------+---------+-------
 POOLED STDEV =  0.06085                   0.300     0.360     0.420
```

```
d) CB194
   CLUSTER   N      MEAN     STDEV  ----------+---------+---------+------
      2     14   0.18157   0.01636                             (----*----)
      1     22   0.15764   0.01713                       (---*---)
      4     11   0.16509   0.05817                        (----*-----)
      5      5   0.10140   0.03629   (-------*-------)
                                    ----------+---------+---------+------
 POOLED STDEV =  0.03187                    0.105     0.140     0.175
```

```
e) CB196
   CLUSTER   N      MEAN     STDEV  --+---------+---------+---------+----
      2     14   0.22407   0.02283                         (---*---)
      1     22   0.18864   0.02729                  (---*--)
      4     11   0.22555   0.06549                        (----*----)
      5      5   0.12960   0.03986   (------*------)
                                    --+---------+---------+---------+----
 POOLED STDEV =  0.03864            0.100     0.150     0.200     0.250
```

```
f) CB199
   CLUSTER   N      MEAN     STDEV  -+---------+---------+---------+-----
      2     14   0.30093   0.03312                            (----*----)
      1     22   0.26355   0.03156                      (---*---)
      4     11   0.28518   0.07231                        (-----*-----)
      5      5   0.18820   0.06618  (--------*-------)
                                    -+---------+---------+---------+-----
 POOLED STDEV =  0.04677           0.150     0.200     0.250     0.300
```

of the chlorine substitution pattern on the physicochemical properties of each congener, the behaviour of some congeners is more difficult to explain. So far, the discussion has been focused on the relationship between the structure, the physicochemical properties, and the behaviour of the PCB congeners in the sediment samples. However, one aspect of the environmental behaviour of PCBs which is not well understood and the significance of which is not known is the extent of the environmental degradation of the PCB congeners, in particular, by bacteria.

Reports on microbial degradation in the environment are contradictory. Quensen *et al.* (1990) incubated aquatic sediments from two sites with PCB technical mixtures and found differences in the rates and types of modification of the PCB composition, which suggested that there are different PCB-dechlorinating microorganisms at different sites, with characteristic specificities for PCB dechlorination. These authors quoted some studies in which the aerobic biodegradation of PCBs is reported to be more limited than the anaerobic dehalogenation which implied that the latter can be a more important process of PCB degradation in the environment. Brown *et al.* (1987) also reported that the microbial degradation of PCBs in sediments appeared to be more important in the anoxic regions of the sediments. On the other hand, however, Pardue *et al.* (1988) reported that mineralization rates for a PCB mixture in sediments were significantly higher under aerobic conditions than under anaerobic conditions, although the maximum rates occurred under moderately aerobic (microaerophilic) conditions. Larsson and Lemkemeier (1989) studied aerobic degradation in lake sediments and reported a low mineralization which could even have been observed because of experimental artifacts, thus, implying that aerobic PCB mineralization in these sediments was unimportant. Oliver *et al.* (1989) studied the PCB congener distribution in sediments from Lake Ontario and concluded that anaerobic dehalogenation was not important (if occurring at all) in these sediments. Finally, the PCB congener distribution patterns in sediments from the Hudson River, which is severely polluted with PCBs, were postulated by Brown *et al.* (1987) to result from microbial anaerobic dehalogenation which could be an important process of depuration of these sediments, however, Bush *et al.* (1987) suggested that the changes in the PCB patterns in these sediments could also be explained by the effect of physicochemical processes and are not necessarily the result of anaerobic microbial dechlorination.

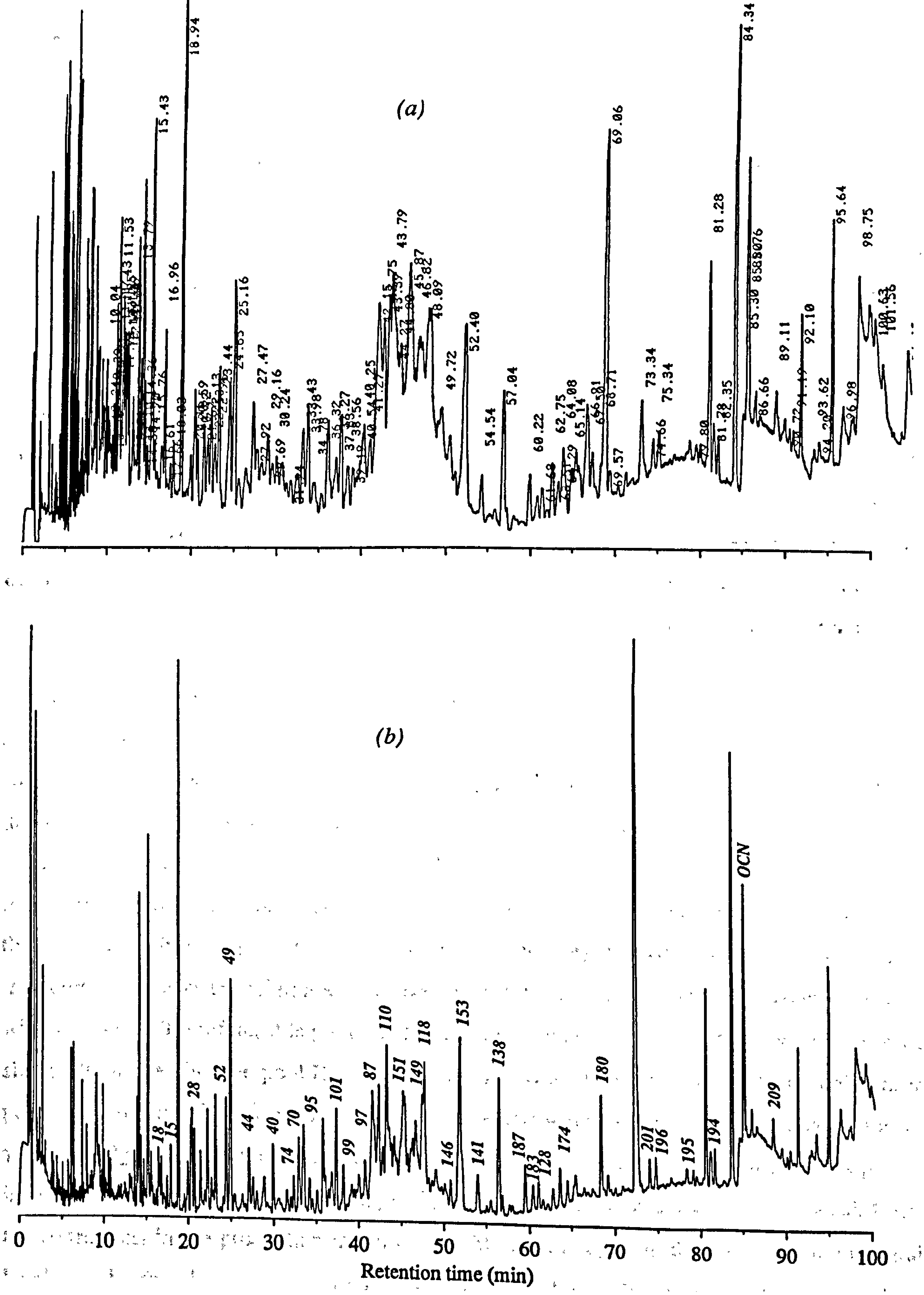
It is clear from the above, that the role of bacterial mineralization of PCBs in the environment is not clear. The changes in the PCB patterns in sediments from Liverpool Bay could be largely explained by physicochemical processes, although the possible role of microbial activity on these sediments is not known. If important, anaerobic dehalogenation would only be significant in the muddy areas which represent the only sediments where reducing conditions can be established. However, most of the sediments in Liverpool Bay have low amounts of fine particles which allows them to be more easily disturbed and transported either by suspension or as beadload which, in any case, would favour aerobic conditions. It has been mentioned that the hydrodynamical conditions in this area favour the constant movement of fine sediments in particular which are the main PCB carriers, therefore, considering Liverpool Bay as a whole, aerobic degradation of PCBs would be more likely than anoxic dehalogenation. The constant movement of sediment particles in Liverpool Bay also favours desorption of PCBs from sediments as the equilibrium between the solid and liquid phases is unlikely to be established due to the constant "renewal" of the water which is in direct contact with the sediment particles. Based on the changes in the congener patterns observed between cluster 2 and clusters 1, 3 and 4 in particular, it is suggested that desorption from sediments is the main mechanism responsible of the observed changes, as microbial dehalogenation would lead to an enrichment rather than a depletion of lower chlorinated congeners. The importance of bacteria in the geochemical behaviour of PCBs in the environment should, however, not be underestimated as even if they do not directly degrade PCB congeners, they indirectly contribute to the transfer of these contaminants from the sediments to the water column by mineralizing the organic matter to which most of the sedimentary PCB load may be associated.

5.2.2.3. PCBs in sewage sludge

The treatment of the sewage sludge sample prior to the chromatographic determination was similar to the procedure already described for PCB determinations in sediments. However, as indicated by the chromatogram in Figure 5.28a, the clean up procedure did not eliminate some unknown substance(s) which interfered with the chromatographic determination, even though only 0.5 g of sludge sample were extracted, as compared with up to 70 g of sample used in the analysis of sediments. The sludge extracts were subjected to further clean up with thin layer chromatography which produced no improvements in the chromatograms, and finally were treated with concentrated sulphuric acid which decreased but did not eliminate the interferences (see Fig. 5.28b). The lack of time did not allow for a close inspection of the possible effect of these extra steps in the clean up of the sludge sample, therefore, the quantitative analysis of the sewage sludge should be regarded as tentative. It is felt, however, that as a treatment of reagents and materials used in these steps was given, *i.e.*, the thin layer plates, the water and the sulphuric acid were extracted with acetone and hexane before use, the possible effects could be related to losses

Figure 5.28. Gas chromatograms in a DB-5 column for a sewage sludge extract (a) before and (b) after sulphuric acid treatment of the sample (see text for details). The weight of sample extracted was 0.5 g and the final volume of the extract was 1.0 ml.

Sewage sludge



rather than contamination of the extracts with PCBs. Therefore, if any alterations occurred during the treatment, the concentration values for the individual PCB congeners reported in Table 5.12 are underestimated.

Table 5.12 shows that the mean total PCB concentration in the sewage sludge analysed was ~320 ng g^{-1}. This value was 8.4 times higher than the highest concentration (37.8 ng g^{-1}), 81 times higher than the overall mean (3.9 ng g^{-1}) and 4000 times higher than the lowest concentration (0.08 ng g^{-1}) found in Liverpool Bay sediments. When the degree of enrichment of PCBs in the sludge is compared with the enrichment of the elements determined in the present study (see Table 4.1), it is obvious that sewage sludge may be an important source of these organic contaminants into Liverpool Bay. For example, Table 4.1 shows that the heavy metals with the highest enrichment in the sludge in relation to the mean concentration in sediments were cadmium (18.6) and chromium (13.6), as compared with a factor of 81 for PCBs. The total PCB concentrations found in the present study are in agreement with the concentrations reported by McIntyre and Lester (1984) for PCBs in sewage sludges from various works throughout Great Britain. These authors reported a mean value of 340 ng g^{-1}, and a range of 10 to 21500 ng g^{-1}, with no trends in the PCB concentrations in relation to the type treatment given to the sewage sludges prior to their disposal.

The "low" PCB concentrations in Liverpool Bay sediments, as compared with the concentrations in the sludge, may be largely due to the behaviour and characteristics of the sludges which are dumped in this area. It was mentioned in Chapter 2 (see Section 2.4.1.1.) that these sludges consist, in general, of colloidal dispersions of organic and mineral solids in water. It was also mentioned above that several authors suggest that organic colloids play a significant role in the geochemistry of PCBs, as these contaminants seem to be strongly associated with these colloids. It is expected that the sewage sludge organic colloids will be more easily transported in the water column as compared with settling solids which will become associated with sediments. Therefore, it is possible that a large fraction of the total PCB load in the sewage sludge discharged in Liverpool Bay will remain in and be transported in the water column. It is possible, therefore, that a large proportion of the PCBs which are discharged in association with sewage sludge are made readily available for uptake into the aquatic food chains (for zooplankton ingestion for example) through the large dispersion of these wastes after their disposal. Despite the restrictions in the production and use of PCBs which began in the mid 1970's, measurable levels can be found even in remote areas of the globe due to the presence of these xenobiotics in the mobile environmental compartments such as the water column and the atmosphere.

Table 5.12. Concentration of some PCB congeners in three replicate samples from a digested sludge. The mean of the three determinations is also given, together with the mean of each congener represented as a percentage of the total PCB concentration which is given in the last row of the column. The concentration units in the sludge are pg g^{-1}.

IUPAC No.	Slu1	Slu2	Slu3	mean	Percen. total
18	19040	9520	8330	12297	3.85
15	23250	7750	7750	12917	4.04
31	17420	6700	6030	10050	3.15
28	22000	13000	12000	15667	4.90
52	20020	20020	18480	19507	6.11
49	18720	56940	49140	29120	9.12
44	9000	9000	8400	8800	2.75
74	3600	4500	3600	3900	1.22
70	9000	9900	9000	9300	2.91
95	12320	13860	12320	12833	4.02
92	1800	1800	1800	1800	0.56
89	6160	7280	6720	6720	2.10
101	14400	16200	13500	14700	4.60
99	6540	6540	5450	6177	1.93
97	3600	4500	3600	3900	1.22
87	9360	14430	15210	13000	4.07
136	*	2000	2400	2200	0.69
110	10880	16640	17280	14933	4.67
151	6120	8670	10710	8500	2.66
149	8820	10080	11340	10080	3.16
118	15600	17160	15990	16250	5.09
146	3050	3050	3050	3050	0.95
153	25850	22000	22000	23283	7.29
105	*	4200	3360	3750	1.17
141	3360	3640	3360	3453	1.08
138	14700	17220	16380	16100	5.04
158	1200	1200	1200	1200	0.38
187	4600	5060	4600	4753	1.49
183	3650	3650	3650	3650	1.14
128	2500	3500	3000	3000	0.94
174	800	1200	1200	1067	0.33
177	1840	1840	1840	1840	0.58
180	*	*	9570	9570	3.00
201	3080	3520	3080	3227	1.01
196	2800	2800	2450	2683	0.84
194	1920	1920	1920	1920	0.60
205	2310	2640	2310	2420	0.76
209	1840	1840	1840	1840	0.58
TOTAL	**311150**	**335770**	**323860**	**319457**	---

* not determined

Eisenreich (1987) reported that of the approximately 5.7 x 10^8 Kg of PCBs which have been commercially produced, approximately 2 x 10^8 Kg (~35% of the total) remain in mobile environmental reservoirs, and that the major fluxes are associated to processes of particle transport and settling, volatilization, and sediment resuspension and diffusion, whereas sediments represent a large sink/source of PCBs in water bodies.

Unfortunately no reports were found in the literature regarding the congener specific composition of PCBs in sewage sludge, therefore, the data reported in this study could not be compared. Table 5.12 shows that all of the ICES congeners were important components of the total PCBs with individual contributions higher than 3%. This table also shows that most of the results between replicates were consistent, however, large variations in the concentrations of some congeners were observed. For example, congener 49 showed the largest contribution (~9%) to the average total PCB concentration, however, one of the replicates had a concentration lower than that of congener 153. Table 5.12 indicates that the lower chlorinated congeners showed, in general, higher concentrations than the more chlorinated congeners, which resulted in higher similarities between the fingerprint in the sludge and sediments classified in cluster 5 above. For example, the highest similarities of the sludge were found with samples T-10 (Z = 0.824) and U-15 (Z = 0.847) classified in cluster 5 and whose PCB pattern is suggested to result largely from the effect of atmospheric deposition on sediments offshore Liverpool Bay and are, therefore, considered as the least affected by direct inputs from rivers or waste disposal in this area. On the other hand, however, the sludge pattern also showed a significant similarity with some samples from cluster 1 (e.g, Z = 0.797 for sample L-13) and cluster 2 (e.g., Z = 0.791 for sample K-9 which is within Site SI). The chromatogram in Figure 5.28b shows that, in general, the distribution of PCB congeners in the sewage sludge did not show a marked or distinctive pattern compared with previously described chromatograms, which may reflect common PCB sources in the sewage sludge and sediments in Liverpool Bay.

5.3. CONCLUSIONS

The clean up procedure used in this study was satisfactory for the accurate determination of various PCB congeners in marine sediments. This clean up procedure, however, was not satisfactory for the analysis of sewage sludge samples.

The grain size effect observed in the PCB determinations in this study can be overcome by fractionation of the sediments before the analysis.

The distribution of the aluminium and carbon normalized total PCB concentrations indicates an enrichment of PCBs in muddy sediments, similar to the enrichment of mercury. The inputs of PCBs from the Mersey and from waste disposal may, therefore, be significant.

The levels of PCB contamination in Liverpool Bay are similar to those reported for other industrialized areas such as the North Sea coast, however, these levels are much lower than those reported for areas heavily polluted with PCBs. The significance of the PCB concentrations in Liverpool Bay sediments, in relation to potential adverse ecological effects, can not be evaluated without an understanding of the transfer of these xenobiotics through the food chain in this area.

The different patterns observed in the distribution of PCB congeners in sediments may reflect different sources of these substances into Liverpool Bay. It is suggested that PCBs in those sediments classified in clusters 5 and 6 are mainly derived from atmospheric deposition in the Irish Sea, and that PCBs in sediments from clusters 1, 2, 3 and 4 are mainly derived from riverine and waste disposal inputs. Within the latter group, the pattern observed in cluster 2 may reflect more closely the PCB composition of the source(s), and the patterns shown by sediments in clusters 1, 3 and 4 represent different states of alteration of the original pattern.

The changes in the congener patterns may be largely explained by the differences in physicochemical properties such as the aqueous solubility and K_{ow}, however, the possible role of microbial alteration of PCB congeners may be important.

CHAPTER 6. CONCLUDING REMARKS

Liverpool Bay is a shallow and highly dynamic coastal environment. The continuous flow of tidally induced currents, occasionally intensified by storms, results in constant stirring which modifies the sediment composition by resuspension of fine particles and/or by bedload transport of coarser grains. As a consequence, the distribution of natural and anthropogenically derived chemical substances which become appreciably associated with sedimentary particles in this region is largely controlled by the hydrodynamic conditions.

The distributions of trace elements and PCBs in the superficial sedimentary particles throughout Liverpool Bay may, therefore, be largely explained in terms of the net transport patterns of water and sediments in this area, in association with the possible inputs of these contaminants. The main inputs of these contaminants may result from the disposal of sewage sludge and industrial wastes at Site SI, the disposal of dredging spoils at Sites Y and Z, and from the contaminated outflow from the rivers Mersey and Dee.

Once the contaminants have been associated with the natural sedimentary particles they will be subject to diagenetic processes such as biological and chemical transformation reactions. The geochemical behaviour of a particualr contaminant will depend on the physicochemical properties, chemical form, biological activity, etc., of that particular substance, as well as on the composition of the sedimentary particles.

In the case of trace elements the partition among different phases on the surface of the particles can occur. The most important phases for metal binding in aquatic sediments are the aluminosilicate minerals, hydrous oxide coatings of iron, manganese and aluminium, and organic matter coatings. If different metals show different preference for specific phases, they might be differentially adsorbed onto or desorbed from sediment particles, according to the content of each phase in the particles. For example, mercury shows a strong affinity towards the organic sedimentary phases whereas lead shows strong affinity toward iron/manganese oxides. As the organic matter in the particles is degraded mercury might be released into the water column whereas lead may remain associated to the oxide phase in sediment particles. Therefore, the metal composition in the sediment will not only depend on the original source of those metals, but also on the specific geochemical behaviour of each of the metals.

The geochemical behaviour of trace metals is well documented and many books and reviews on this subject can be found in the literature. However, previous studies of metals in Liverpool

Bay sediments, largely resulting from monitoring programs by governmental agencies, have only reported the distribution of their concentrations throughout the bay. These distributions have been largely explained in terms of the location of the possible sources and the water circulation patterns with their associated sediment transport patterns. On the other hand, little or no information has been reported on the possible effects which the difference in geochemical behaviour among metals in sediments can have on the observed distributions.

In this study, the abundance of some of the more important sedimentary phases was estimated by means of bulk chemical determinations. The possible preferential associations of trace elements with any of the phases was then inferred by correlation analyses. Although more selective chemical extraction procedures, such as sequential extractions, could give more precise information on the possible sedimentary phases to which elements are associated, the application of these methods in the present study was considered impractical. The large number of samples and their chemical heterogeneity would have required a laborious validation of the sequential extraction method for the different types of sedimentary conditions found in Liverpool Bay. On the other hand, early during this project, the main aim of determining the trace elements was to provide some background information for an understanding of the distribution of PCBs in the same sediment samples.

In spite of the limitations of using bulk chemical analyses for estimating the concentrations of the sedimentary phases, some interesting observations have resulted from these determinations especially when compared with the trace element content of the samples.

From the grain size distributions it is concluded that, although the particle size composition of Liverpool Bay sediments may change in response to constant changes in the hydrodynamical conditions, there is a general trend in the distribution of the grain size in bulk sediments. As in this study, previous reports indicate that sediments in the southern section of Liverpool Bay are low in fine particles. This results from a decrease in the depth of the water column toward the North Wales coast which intensifies the coastal currents and the shear stress over the sedimentary deposits. Therefore, even though the deposition of fine particles in this area may be possible during calm conditions, fine particles can be easily resuspended from the bottom sediments when currents intensify. Wave induced turbulence can also be an important process associated to the resuspension and sediment transport in these shallow areas. Sediments towards the northern region of the bay tend to increase in their fine particle content, and the highest amounts of fine particles are found outside the Queen's Channel around Burbo Bight.

If the aluminium content is a good indicator of the amount of clay in Liverpool Bay sediments, the second order relationship between the amount of fine particles and the aluminium content in total sediments suggests that the <90 µm fraction of sediments with low amount of fines (e.g. those from the southern area) has a higher proportion of clays than the <90 µm fraction in sediments from muddy areas.

As a possible explanation of the relationship between aluminium content and the grain size distribution it was suggested that the muddy deposits, particularly in the Burbo Bank, may contain higher amounts of very fine sands (which is the 62.5-125 µm fraction). A preferential transport of very fine sands toward this area has been previously reported. In this study, the limit of 90 µm separating the fine and coarse fractions was chosen following the methods recommended by MAFF (Eagle *et al.*, 1978), and which have been followed by NWWA for trace metal monitoring purposes. However, in many of the studies where sediments are fractionated for trace metal determinations, the limit between fine and coarse fractions is often reported as ~63 µm. It is recommended that the use of the 90 µm limit should be avoided. The standardization of the analytical methods used in the determination of environmental contaminants results in more comparable data sets. Sandy particles often show different geochemical properties than smaller sized particles such as silts and clays. The difference in grain size which determines the available surface area for the deposition of organic and inorganic phases can partially explain the differences between sands and smaller particles, however, the different nature of mineral matrices can also be important in the control of the concentrations of trace elements on the particles. Thus, from the geochemical point of view the use of 63 µm as the limit between fine and coarse sediments results an obvious better choice than the use of 90 µm which includes a mixture of clays, silts and very fine sands in the fine fraction.

The distribution of organic carbon in fine sediments showed a low but significant negative correlation with the amount of fine particles and aluminium which may be explained by a higher proportion of clays in the fine fraction of sediments low in fines. An increase in clays would result in a higher surface area available for organic coating formation. The scatter between the relationship of carbon and grain size suggests, however, that the inputs of carbon from various sources including waste disposal, riverine inputs and autochthonous production, may overshadow the possible correlations between carbon and grain size which have been reported in other areas.

The distribution of $\delta^{13}C$ values also reflects the possibility of various sources of organic carbon into Liverpool Bay sediments. There is evidence of terrestrial inputs of carbon from the River Mersey inputs as a gradient can be seen in the samples near the Queen,s Channel entrance. The inputs of land derived carbon from sewage sludge disposal is also suggested by high $\delta^{13}C$ values near an area within Site SI where the discharges have been concentrated since early 1988. The presence of low $\delta^{13}C$ values indicated the possible dominance of marine derived organic carbon in some sediment samples.

The organic matter content in coarse sediments was correlated with the amount of fine particles in the total sediments. This observation suggested that some transfer of carbon from fine toward coarse particles might be occurring. However, this possible transfer seems to occur only when the amount of fine particles surrounding coarse particles is high, *i.e.*, at fine fraction concentrations higher than ~5%.

The distribution of the concentrations of iron and manganese in Liverpool Bay sediments did not appear to be significantly influenced by inputs from the River Mersey or from sewage sludge disposal at Site SI. Relatively high concentrations of these elements were found in fine particles of sediments with low amounts of fine fraction. As in the case of carbon, this observation suggested the availability of higher surface areas for the deposition of hydrous oxide coatings of manganese and iron.

The distribution of iron and manganese in coarse particles showed patterns difficult to explain. The low and negative correlation between manganese and the fine particle content may suggest that the formation of oxide coatings in coarse particles with low amount of fine particles is favoured by the higher exposure of the particles to oxidizing conditions, as opposed to muddy deposits where the formation of oxide coatings may be inhibited by lower redox potential.

Mercury was the only trace metal in the fine fraction showing a high correlation with the fine particle content in the total sediments. Mercury in fine particles was not particularly correlated to any other sediment parameter, with the exception of a low correlation with the $\delta^{13}C$ values. The low correlation with $\delta^{13}C$ values may indicate that the correlation which is often reported for carbon and mercury in sediments was probably overshadowed by natural inputs of organic matter. Mercury in Liverpool Bay fine sediments may be associated to land derived organic matter in particular, thus, as this organic matter might be mixed at different ratios with marine derived organic matter, the content of mercury is not necessarily a function of the total organic carbon in the sample, but depends on the composition of this organic matter. The mercury-carbon association in sediments often reported was probably observed more clearly in the coarse sedimentary fraction. The correlation between mercury and grain size suggests that, given the location of the muddy areas, this element is largely transported into the bay from the River Mersey and from sewage sludge disposal in the bay.

Arsenic showed contrasting behaviour when compared with mercury in Liverpool Bay sediments. The high correlation between arsenic and iron and manganese in both fine and coarse particles, agrees with the reported preference of arsenic for the hydrous oxide coatings of these elements on the surface of aquatic particles. Whereas mercury is largely derived from human activities in the region, arsenic (as well as iron and manganese) seems to be derived from inputs from mineralized areas. The fine particles in some of the sediments with low amount of fine fraction showed very high concentrations of arsenic and manganese. These concentrations were many times higher than in the sewage sludge samples, and were comparable with levels of these elements reported in sediments from streams in the mineralized areas of North Wales.

Lead and zinc may be largely derived from anthropogenic inputs into Liverpool Bay as their levels in sewage sludges, for example, as compared to the mean sediment concentrations are high. The correlation between these elements and the concentrations of manganese, iron and arsenic may also indicate possible inputs of lead and zinc from mineralized areas. The main mining activities which took place in the past were related to the extraction of sphalerite and galena which are minerals from which zinc and lead are extracted, thus, it is not surprising that high levels of these metals have been reported in sediments from the mineralized areas in North Wales. It is suggested that the "anomalously" high values of these elements which may be found in Liverpool Bay sediments can be explained by the inputs from mineral sources. These observations are not intended to undermine the importance that the inputs of lead, zinc and other substances from anthropogenic discharges may have on the levels of toxic elements in Liverpool Bay sediments. Anthropogenic inputs have caused an enrichment of metals not only in this area, but in the whole of the eastern Irish Sea as indicated by the reported background sedimentary levels and the concentrations reported in this and other studies.

A specific association of zinc and lead with the hydrous oxide phases in sediments has often been reported, thus, the correlations among these variables found in this study seem to agree with this association. However, the correlation of lead and particularly zinc with the organic carbon content on the sediments may also suggest an association with the organic sedimentary coatings. The preference for association of one element with a particular phase does not exclude the partition of the element among other phases in the sediment.

From the above it is concluded that the geochemical aspects of the distribution of trace elements in superficial sediments from Liverpool Bay have to be better understood for a proper explanation of the distribution of these elements.

A low correlation was found between cadmium concentrations and $\delta^{13}C$ values, whereas no correlations were observed between this trace metal and the other sediment parameters in the fine fraction. This observation suggests that, as in the case of mercury, cadmium is mainly derived from anthropogenic sources and is preferentially associated to the organic phases in the sediment. The different distributions of cadmium and mercury observed in Liverpool Bay fine sediments may be a result of a substantial difference in the geochemical behaviour of these elements. In general, mercury tends to remain associated with particles whereas cadmium tends to desorb from the particulate phases when the salinity of the water increases. Thus, the enrichment of mercury in the Burbo Bight fine sediments may be due to inputs from the river Mersey since this metal will remain in association with particles if these are transported from the estuarine waters in the Mersey to the coastal waters in Liverpool Bay. Although cadmium seems to be an important contaminant in the Mersey Estuary, its transport into the bay may be largely in solution as this element will tend to desorb from the particulate phase during transport from estuarine to coastal waters.

From the correlation analyses, it is possible to suggest that copper is associated with the organic phases in the fine sediments in the bay. This association has been proposed by reports in the literature on the preferential adsorption of copper by organic coatings in aquatic particles. The possible association between copper and iron/manganese oxides has also been suggested in previous reports and cannot be disregarded in Liverpool Bay sediments since copper and iron were significantly correlated. The distribution of copper in Liverpool Bay fine sediments was complex and, although sewage sludge disposal has been recognised as the main input of this element into the bay, the observations from this study may suggest possible inputs from non anthropogenic mineral sources.

Chromium also showed significant correlations with organic carbon and iron which is in agreement with reports of the association of chromium in these sedimentary phases. Nickel, on the other hand, showed similarly low but significant correlations with carbon, iron, manganese and the percentage of fine fraction. Accordingly, the lack of specificity of nickel for sedimentary phases has also been reported. The distribution of the concentrations of this trace metal in fine sediments was relatively homogeneous as a possible result of a higher solubility of this element in relation to the other elements in this study which tend to remain more strongly bound onto particulate phases.

Based on the correlation analyses, it is suggested that the organic matter is the most important carrier phase of trace metals in coarse sedimentary particles in Liverpool Bay. Only lead and zinc showed some correlation with the iron and manganese contents in coarse particles indicating a possible lower specificity for organic coatings than the other metals, *i.e.*, mercury, cadmium, copper, nickel and chromium. It seems that the coexistence of coarse particles with a higher amount of fine particles increases the levels of trace metals in the former. Thus, it is possible that trace metals are transferred from fine toward coarse sediments in association with the organic matter. Arsenic was the only element with no correlation with the organic matter in coarse sediments. The high correlations with iron and manganese reflect the strong affinity of arsenic for oxide coatings.

The correlations between trace elements and sediment parameters suggested different types of trace element-sediment associations. The geochemical behaviour of trace elements seems to play an important role in the control of the concentrations of these elements on the sediment particles. The possible impact of waste disposal in Liverpool Bay can be partially determined from the distribution of the concentrations of toxic elements in superficial sediments and the knowledge of the water circulation and sediment transport pattern. However, these distributions are also affected by the geochemical behaviour of each particular trace element.

It is recommended that in studies of the distributions of trace elements in Liverpool Bay sediments the geochemical behaviour of each trace element should be taken into consideration. Thus, more specific studies on the sediment-trace element associations in Liverpool Bay are needed. The potential significance of inputs of trace elements from natural sources should also be evaluated by a closer inspection of the mineralogical composition of the sediments.

The method used in this study for the determination of various PCB congeners was satisfactory for the sediment samples, but the clean up was not satisfactory for the sewage sludge samples.

The grain size effect on the concentration of PCBs in the total sediments was not unexpected as these organic compounds show a strong affinity for small sized particles. The "correction" of the total PCB concentrations by normalization with either the organic matter content and with the aluminium content resulted in similar distributions of the normalized values. These distributions showed similarities with the distributions of mercury in coarse and fine sediments. Thus, after grain size correction, higher concentrations of PCBs were found in the sediments with high amounts of fine particles. The distribution of total PCBs suggests that the main sources of PCB contamination in the Bay are the inputs from the River Mersey and from sewage sludge disposal.

The level of PCB contamination in Liverpool Bay sediments is similar to those levels reported in other areas such as in the North Sea coast. The PCB levels found in this study are much lower than in sediments from areas where severe contamination with PCBs is reported. The significance of the PCB levels in Liverpool Bay sediments, in relation to potential adverse effects, can not be properly evaluated. Sediments can act as a source of PCBs into aquatic food chains where biomagnification may occur. Thus, even if the levels in Liverpool Bay sediments are low as compared to other areas, they may still be high enough to cause detrimental effects at the higher levels in the food chain.

It is suggested that the patterns of the PCB congener distribution in Liverpool Bay sediments indicate two main different types of sources. One type of source, best reflected in the muddy sediments of the Burbo Bight, are the direct inputs of PCBs from river discharges and waste disposal activities in Liverpool Bay. Several degrees of alteration of the "original" PCB pattern were observed, and the changes were mainly explained in terms of the different physicochemical properties among congeners. The second main source is the transport of contaminated sediments from the Irish Sea, which show a PCB pattern suggesting atmospheric deposition as the original source of PCBs into the offshore waters and sediments of the Irish Sea.

Differences in the behaviour of isomers were also observed, which resulted from differences in the configuration (planarity) of the PCB molecule. An increase in the number of *ortho* chlorine substitutions in the biphenyl ring increases the torsion of the molecule which may result in a decrease in the surface area for contact with particle surfaces. Thus, isomers with more *ortho* chlorines will tend to desorb more easily from the sedimentary particles. Although some generalizations could be made regarding the geochemical behaviour of PCB congeners and their molecular configuration, the behaviour of some congeners could not be explained in these terms.

It is recommended that the determinations of PCBs in Liverpool Bay sediments are carried out in different grain size fractions. In the case of trace elements, the different "signatures" in fine and coarse fractions were related to different transport patterns, thus, PCBs in this study were probably a result from the combination of the patterns in the fine and coarse particles. However, the strong correlation between total PCBs and the amount of fine particles in the sediment probably indicates that, even in total sediments with low amount of fines, the main contribution to the total PCB loads in the sediments came from the fine particles.

The sediments in Liverpool Bay were classified according to the trace element and PCB "fingerprints" by the application of multivariate statistical. There was a good agreement between the clusters resulting from the analyses on both data sets. Not surprisingly, the classification suggested that the major sources of the inorganic contaminants are also the major sources of organic contaminants.

It is suggested that, for a better understanding of the effects of waste disposal on the distributions of contaminants in Liverpool Bay sediments, the dynamical oceanography and sediment transport patterns as well as the geochemical behaviour of each particular organic and inorganic contaminant of interest should be considered. When large data sets are produced, the application of multivariate statistical methods can assist in the interpretation of the results.

REFERENCES

Abdullah, M.I. and Royle, L.G. (1973). Chemical evidence for the dispersion of River Mersey run-off in Liverpool Bay. Est. Coast. Mar. Sci. 1, 401-409.

Agar, M. and McDowell, D.M. (1972). The sea approaches to the Port of Liverpool. (Discussion). Proc. Instn. Civ. Engrs. U.K. 51, 609-620.

Ainsworth, G. (1972). Composition of sludge. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 1. pp. 1-7.

Alford-Stevens, A.L. (1986). Analyzing PCBs. Environ. Sci. Technol. 20, 1194-1199.

Anders, O.U. (1972). Ratio matching - a statistical aid for discovering generic relationships among samples. Anal. Chem. 44, 1930-1933.

Angelidis, M. and Grimanis, A.P. (1989). Geochemical partitioning of Co, Cr, Fe, Sc, and Zn in polluted and non-polluted marine sediments. Environ. Pollut. 62, 31-46.

Atlas, E., Bidleman, T. and Giam, C.S. (1986). Atmospheric transport of PCBs to the Oceans. In: *PCBs and the environment.* Vol. I., J.S. Waid (Ed.). CRC Press, Boca Raton, Florida. 79-100.

Baker, J.E., Capel, P.D. and Eisenreich, S.J. (1986). Influence of colloids in sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. Environ. Sci. Technol. 20, 1136-1143.

Balistriery, L.S. and Murray, J.W. (1984). Marine scavenging: trace metal adsorption by interfacial sediment from MANOP Site H. Geochim. Cosmochim. Acta. 48, 921-929.

Ballschmiter, K. and Zell, M. (1980). Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fresenius Z. Anal. Chem. 302, 20-31.

Ballschmiter, K., Rappe, C. and Buser, H.R. (1989). Chemical properties, analytical methods and environmental levels of PCBs, PCTs, PCNs and PBBs. In: *Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and related products.* R.D. Kimbrough and A.A. Jensen (Eds.). Elsevier, Amsterdam. pp. 47-69.

Ballschmiter, K., Scafer, W., and Buchert, H. (1987). Isomer-specific identification of PCB congeners in technical mixtures and environmental samples by HRGC-ECD and HRGC-MSD. Fresenius Z. Anal. Chem. 326, 253-257.

Balzer, W. (1982). On the distribution of iron and manganese at the sediment/water interface: thermodynamic versus kinetic control. Geochim. Cosmochim. Acta. 46, 1153-1161.

Banner, F.T. (1979). Sediments of the north-western European shelf. In: *The North-West European Shelf Seas: the sea bed and the sea in motion I. Geology and sedimentology.* F.T. Banner, M.B. Collins and K.S. Massie (Eds.). Elsevier, Amsterdam. pp. 271-300.

Barrett, M.J., Munro, D. and White, K.E. (1972). Sludge dispersion in sea water. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 9, pp. 145-169.

Belderson, R.H. (1964). Holocene sedimentation in the western half of the Irish Sea. Mar. Geol. 2, 147-163.

Beller, H.R, and Simoneit, B.R.T. (1986). Polychorinated biphenyls and hydrocarbons. Distributions among bound and unbound lipid fractions of estuarine sediments. In: *Organic marine geochemistry.* Sohn, M.L. (Ed.). A.C.S., Washington D.C. pp. 198-213.

Belzile, N. (1988). The fate of arsenic in sediments of the Laurentian Trough. Geochim. Cosmochim. Acta. 52, 2293-2302.

Belzile, N. and Tessier, A. (1990). Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim. Cosmochim. Acta. 54, 103-109.

Best, R., Ainsworth, G., Wood, P.C., and James, J.E. (1973). Effects of sewage sludge on the marine environment: a case study in Liverpool Bay. Proc. Instn. Civ. Engrs. U.K. 55, 43-66.

Boon, J.P., and Duinker, J.C. (1986). Monitoring of cyclic organochlorines in the marine environment. Environ. Monit. Asses. 7, 189-208.

Boon, J.P., Van Zantvoort, M.B., Govaert, M.J.M.A., and Duinker, J.C. (1985). Organochlorines in benthic polychaetes (*Nephtys spp.*) and sediments from the southern North Sea. Identification of individual PCB components. Neth. J. Sea Res. 19, 93-109.

Bowden, K.F. (1980). Physical and dynamical oceanography of the Irish Sea. In: *The North-West European Shelf Seas: the sea bed and the sea in motion II. Physical and chemical oceanography, and physical resources.* F.T. Banner, M.B. Collins and K.S. Massie (Eds.). Elsevier Amsterdam. pp. 391-413.

Brannon, J.M., Myers, T.E., Gunnison, D. and Price, C.B. (1991). Nonconstant polychlorinated biphenyl partitioning in New Bedford Harbor sediment during sequential batch leaching. Environ. Sci. Technol. 25, 1082-1087.

Brook, E.J. and Moore, J.N. (1988). Particle-size and chemical control of As, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in bed sediment from the Clark Fork River, Montana (U.S.A.). Sci. Tot. Environ. 76, 247-266.

Brown,Jr.,J.F., Wagner, R.E., Feng, H., Bedard, D.L., Brennan, M.J., Carnahan, J.C and May, R.J. (1987). Environmental dechlorination of PCBs. Environ. Toxicol. Chem. 6, 579-593.

Brownawell, B. and Farrington, J. (1986). Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment. Geochim. Cosmochim. Acta. 50, 157-169.

Brownawell, B.J. and Farrington, J.W. (1985). Partitioning of PCBs in marine sediments. In: *Marine and estuarine geochemistry.* Sigleo, A.C. and Hattory, A. (Eds.). Lewis Publishers. pp. 97-120.

Burnett, W.C. and Schaeffer, O.A. (1980). Effect of ocean dumping on $^{13}C/^{12}C$ ratios in marine sediments from the New York Bight. Est. Coast. Mar. Sci. 11, 605-611.

Burrows, E.M. and Sharples, E.J. (1973). Bio-assay of sea water. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 3: Report for 1972-73. (Department of the Environment). HMSO, London. Appendix A. pp. 21-43.

Bush, B., Shane, L.A., Wahlen, M., and Brown, M.P. (1987). Sedimentation of 74 PCB congeners in the Upper Hudson River. Chemosphere. 16, 733-744.

Campbell, J.A., Chan, E.Y.L., Riley, J.P., Head, P.C., and Jones, P.D. (1986). The distribution of mercury in the Mersey Estuary. Mar. Pollut. Bull. 17, 36-40.

Campbell, J.A., Whitelaw, K., Riley, J.P., Head, P.C., and Jones, P.D. (1988). Contrasting behaviour of dissolved and particulate nickel and zinc in a polluted estuary. Sci. Tot. Environ. 71, 141-155.

Carpenter, R., Peterson, M.L. and Jahnke, R.A. (1978). Sources, sinks and cycling of arsenic in the Puget Sound region. In: *Estuarine interactions*. M.L. Wiley (Ed.). Academic Press. pp. 459-480.

Cauwet, G. (1987). Influence of sedimentological features on the distribution of trace metals in marine sediments. Mar. Chem. 22, 221-234.

Cerling. T.E. and Turner, R.R. (1982). Formation of freshwater Fe-Mn coatings on gravel and the behaviour of ^{60}Co, ^{90}Sr, and ^{137}Cs in a small watershed. Geochim. Cosmochim. Acta. 46, 1333-1343.

Comans, R.N.J. and van Dijk, C.P.J. (1988). Role of complexation processes in cadmium mobilization during estuarine mixing. Nature. 336, 151-154.

Craig, P.J. and Moreton, P.A. (1986). Total mercury, methyl mercury and sulphide levels in British estuarine sediments-III. Wat. Res. 20, 1111-1118.

Cranston, R.E. (1976). Accumulation and distribution of total mercury in estuarine sediments. Est. Coast. Mar. Sci. 4, 695-700.

Crecelious, E.A., Bothner, M.H. and Carpenter, R. (1975). Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9, 325-333.

Crickmore, M.J. (1972a). Sludge dispersion on the sea bed. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 10, pp. 171-208.

Crickmore, M.J. (1972b). Initial behaviour of sludge. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 5, pp. 45-54.

Crickmore, M.J. and Kiff, P.R. (1972). Bed sediments: particle size. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 12, pp. 273-286.

Czitrom-Baus, S.P.R. (1982). *Density stratification and an associated front in Liverpool Bay.* Ph.D. thesis, University of Wales.

Davies-Colley, R.J., Nelson, P.O. and Williamson, K.J. (1984). Copper and cadmium uptake by estuarine sedimentary phases. Environ. Sci. Technol. 18, 491-499.

de Voogt, P. and Binkman, U.A.Th. (1989). Production, properties and usage of polychlorinated byphenyls. In: *Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and related products*. R.D. Kimbrough and A.A. Jensen (Eds.). Elsevier, Amsterdam. pp. 3-45.

de Voogt, P., Wells, D.E., Reutergardh, L., and Brinkman. U.A.Th. (1990). Biological activity determination and occurrence of planar, mono- and di-ortho PCBs. Intern. J. Environ. Anal. Chem. 40, 1-46.

Department of the Environment and National Water Council. (1979). *Sewage sludge disposal in Liverpool Bay. Research into Effects, 1975 to 1977.* Part 1. General. Department of the Environment, London, Standing Technical Committee Report. 16, 44 pp.

Department of the Environment. (1984). *Sewage sludge disposal in Liverpool Bay. Research into Effects, 1975 to 1977.* Part 2. Appendices. Report of a Liverpool Bay Working Group. Department of the Environment. HMSO, London. 194 pp.

Department of the Environment. (1972a). *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Vol. 1. Main report. HMSO, London. 36 pp.

Department of the Environment. (1972b). *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Vol. 2. Appendices. HMSO, London. 483 pp.

Department of the Environment. (1973). *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Vol. 3. Report for 1972-73. HMSO, London. 96 pp.

Department of the Environment. (1976). Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay. Vol. 4. Report for 1973-75. HMSO, London. 188 pp.

Duinker, J.C. (1986). The role of small, low density particles on the partition of selected PCB congeners between water and suspended matter (North Sea area). Neth. J. Sea Res. 20, 229-238.

Duinker, J.C. (1981). Partition of Fe, Mn, Al, K, Mg, Cu and Zn between particulate organic matter and minerals, and its dependence on total concentrations of suspended matter. In: *Holocene Marine Sedimentation in the North Sea Basin.* S.-D. Nio, R.T.E. Shuttenhelm and Tj.C. van Weering (Eds.). Blackwell Scientific Pubs., Oxford. pp. 451-459.

Duinker, J.C., Schultz, D.E., and Petrick, G. (1988). Selection of chlorinated biphenyl congeners for analysis in environmental samples. Mar. Pollut. Bull. 19, 19-25.

Dunn, W.J. III, Stalling, D.L., Schwartz, T.R., Hogan, J.W., Petty, J.D., Johansson, E. and Wold, S. (1984). Pattern recognition for classification and determination of polychlorinated biphenyls in environmental samples. Anal. Chem. 56, 1308-1313.

Duursma, E.K., Nieuwenhuize, J. and Van Liere, J.M. (1989). Polychlorinated biphenyl equilibria in an estuarine system. Sci. Tot. Environ. 79, 141-155.

Dyer, K.R. (1986). *Coastal and estuarine sediment dynamics*. Wiley, London. 342 pp.

Eagle, R.A., Norton, M.G., Nunny, R.S. and Rolfe, M.S. (1978). *The field assessment of effects of dumping wastes at sea: 2. Methods*. Fish. Res. Tech. Rep. MAFF Direct. Fish. Res., Lowestoft, 47, 24 pp.

Edenborn, H.M., Belzile, N., Mucci, A., Lebel, J. and Silverberg, N. (1986). Observations on the diagenetic behavior of arsenic in a deep coastal sediment. Biogeochemistry. 2, 359-376.

Eisenreich, S.J. (1987). Chemical limnology of nonpolar organic contaminants: polychlorinated biphenyls in Lake Superior. In: *Sources and fates of aquatic pollutants*. R. A. Hites and S.J. Eisenreich (Eds.). Advances in Chemistry 216. ACS, Washington, D.C. pp. 393-469.

Elderfield, H., Hepworth, A., Edwards, P.N. and Holliday, L.M. (1979). Zinc in the Conwy River and Estuary. Est. Coast. Mar. Sci. 9, 403-422.

Elderfield, H., Thornton, L., and Webb, J.S. (1971). Heavy metals and oyster culture in Wales. Mar. Pollut. Bull. 2, 44-47.

Farrington, J.W., Davies, A.C., Brownawell, B.J., Tripp, B.W., Clifford, C.H., and Livramento, J.B. (1986). The biogeochemistry of polychlorinated biphenyls in the Acushnet River Estuary, Massachusetts. In: *Organic marine geochemistry*. Sohn, M.L. (Ed.), A.C.S., Washington, D.C. pp. 174-197.

Feeley, R.A., Massoth, G.J., Paulson, A.J. and Gendron, J.F. (1983). Possible evidence for enrichment of trace elements in the hydrous manganese oxide phases of suspended matter from an urbanized embayment. Estuarine Coastal Mar. Sci. 17, 693-708.

Fisher, J.B., Petty, R.L., and Lick, W. (1983). Release of polychlorinated biphenyls from contaminated lake sediments: Flux and apparent diffusivities of four individual PCBs. Environ. Pollut. Ser. B. 5, 121-132.

Forstner, U. (1984). Effects of salinity on the metal sorption onto organic particulate matter. Neth. Inst. Sea Res. Pub. Ser. 10, 195-209.

Forstner, U. and Patchineelam, S.R. (1981). Chemical associations of heavy metals in marine deposits with special reference to pollution in the German North Sea. Rapp. P.-v. Reun. Cons. int. Explor. Mer. 181, 49-58.

Forstner, U. and Wittmann, T.W. (1979). *Metal pollution in the aquatic environment.* Springer-Verlag, Berlin Heidelberg New York, 486 pp.

Foster, P. (1984). Inhibition to pollutant dissipation in the north-east Irish Sea. Mar. Pollut. Bull. 15, 222-225.

Foster, P., Beardall, J., Voltolina, D., and Savidge, G. (1985). The effect of wind, phytoplankton and density discontinuities upon ammonia distributions in Liverpool Bay. Est. Coast. Shelf Sci. 20, 463-475.

Foster, P., Pugh, K.B., Hunt, D.T.E., Foster, G.M., and Savidge, G. (1977). Influence of wind upon water quality in Liverpool Bay. Mar. Pollut. Bull. 8, 11-12.

Foster, P., Voltolina, D., Spencer, C.P., Miller, I. and Beardall, J. (1982). A seasonal study of the distributions of surface state variables in Liverpool Bay. III. An offshore front. J. Mar. exp. Mar. Biol. Ecol. 58, 19-31.

Fowler, S.W. (1990). Critical review of selected heavy metal and chlorinated hydrocarbon concentrations in the marine environment. Mar. Environ. Res. 29, 1-64.

Fox, M.E., Roper, D.S., and Thrush, S.F. (1988). Organochlorine contaminants in surficial sediments of Manukav Harbour, New Zealand. Mar. Pollut. Bull. 19, 333-336.

Franklin, A. (1987). *The concentration of metals, organochlorine pesticide and PCB residues in marine fish and shellfish: results from MAFF fish and shellfish monitoring programmes, 1977-1984.* Aquat. Environ. Monit. Rep. MAFF Direct. Fish. Res., Lowestoft. 16, 38 pp.

Gardner, J.V., Dean, W.E. and Alonso, B. (1990). Inorganic geochemistry of surface sediments of the Elbro shelf and slope, nothwestern Mediterranean. Mar. Geol. 95, 225-245.

Gearing, J.N. (1988). The use of stable isotope ratios for tracing the nearshore-offshore exchange of organic matter. In: *Lecture Notes on Coastal and Estuarine Studies* 22. B.O. Jansson (Ed.). Springer-Verlag. pp. 69-101.

Gearing, J.N. and Pocklington, R. (1990). Organic geochemical studies in the St. Lawrence Estuary. In: *Oceanography of a large-scale Estuarine System. The St. Lawrence.* M.I. El-Sabh, N. Silverberg (Eds.). Coastal and Estuarine Estudies 39. Springer-Verlag, New York. pp. 170-201.

Gearing, J.N., Gearing, P.J., Rudnick, D.T., Requejo, A.G. and Hutchins, M.J. (1984). Isotopic variability of organic carbon in a phytoplankton-based, temperate estuary. Geochim. Cosmochim. Acta. 48, 1089-1098.

Gearing, P., Plucker, F.E. and Parker, P.L. (1977). Organic carbon stable isotope ratios of continental margin sediments. Mar. Chem. 5, 251-266.

Giordani, P. and Angiolini, L. (1983). Chemical parameters characterizing the sedimentary environment in a NW Adriatic coastal area (Italy). Est. Coast. Shelf Sci. 17, 159-167.

Golimowski, J., Merks, A.G.A. and Valenta, P. (1990). Trends in heavy metal levels in the dissolved and particulate phase in the Dutch Rhine-Meuse (MAAS) delta. Sci. Tot. Environ. 92, 113-127.

Grant, A. (1990). Multivariate statistical analyses of sediment geochemistry. Mar. Pollut. Bull. 21, 297-299.

Grathwohl, P. (1990). Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implications on K_{oc} correlations. Environ. Sci. Technol. 11, 1687-1693.

Griepink, B., Wells, D.E. and Frias Ferreira, M. (1988). *The certification of the contents (mass fraction) of chlorobiphenyls (IUPAC Nos 28, 52, 101, 118, 138, 153 and 180) in two fish oils.* Community Bureau of Reference. Commision of the European Communities. Report EUR 11520 EN. Luxemburg. 84 pp.

Gschwend, P.M. and Wu, S. (1985). On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. Environ. Sci. Technol. 19, 90-96.

Hall, L. and Chang-Yen, I. (1989). An evaluation of the extraction efficiencies of some common extractants for Fe, Cr, Mn, Ni, Pb, and Cu on five grain-size fractionated, tropical marine sediments. Environ. Pollut. 56, 51-63.

Halliwell, A.R. (1973). Residual drift near the sea bed in Liverpool Bay: an observational study. Geophys. J. R. astr. Soc. 32, 439-458.

Hatch, W.R. and Ott, W.L. (1968). Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry. Anal. Chem. 40, 2085-2087.

Hawker, D.W. and Connell, D.W. (1988). Octanol-water partition coefficients of polychlorinated biphenyl congeners. Environ. Sci. Technol. 22, 382-387.

Head, P.C. (1980). The environmental impact of the disposal of sewage sludge in Liverpool Bay. Prog. Wat. Tech. 13, 27-38.

Head, P.C. (1984). Sludge disposal data. In: *Sewage sludge disposal in Liverpool Bay. Research into Effects 1975-1977*, Part 2, Appendices. Report of a Liverpool Bay Working Group. Department of the Environment, London. Appendix A, pp. 1-8.

Heaps, N.S. and Jones, J.E. (1977). Density currents in the Irish Sea. Geophys. J. R. astr. Soc. 51, 393-429.

Hirata, S. (1985). Phosphorus and metals bound to organic matter in coastal sediments- an investigation of complexes of P, Cu, Zn, Fe, Mn, Ni, Co and Ti by inductively coupled plasma-atomic emission spectrometry with sephadex gel chromatography. Mar. Chem. 16, 23-46.

Holden, A.V. and Marsden, K. (1969). Single-stage clean-up of animal tissue extracts for organochlorine residue analysis. J. Chromatogr. 44, 481-492.

Honeyman, B.D. and Santschi, P.H. (1988). Metals in aquatic systems. Environ. Sci. Technol. 22, 862-871.

Hooper, S.W., Pettigrew, C.A. and Sayler, G.S. (1990). Ecological fate, effects and prospects for the elimination of environmental polychlorinated biphenyls (PCBs). Environ. Toxicol. Chem. 9, 655-667.

Hornung. (1986). Problems associated with monitoring heavy metals in marine organisms and sediments. IX Int. Symp. on the chemistry of the Mediterranean, Primosten, Yugoslavia.

Howarth, M.J. (1984). Currents in the Eastern Irish Sea. Oceanogr. Mar. Biol. Ann. Rev. 22, 11-52.

Imperial College of Science and Technology. (1978). *The Wolfson geochemical atlas of England and Wales*. Applied Geochemistry Group, Imperial College of Science and Technology, London. Clarendon Press, Oxford.

Japenga, J., Wagenaar, W.J., Smedes, F., and Salomons, W. (1987). A new, rapid clean-up procedure for the simultaneous determination of different groups of organic micropollutants in sediments; application in two European estuarine sediment studies. Environ. Technol. Lett. 8, 9-20.

Jensen, S. (1966). Report of a new chemical hazard. New Scientist. 32, 612.

Jensen, S., Renberg, L. and Reutergardh, L. (1977). Residue analysis of sediment and sewage sludge for organochlorines in the presence of elemental sulfur. Anal. Chem. 49, 316-318.

Jha, P.K., Subramanian, V., Sitasawad, R., and Van Grieken, R. (1990). Heavy metals in sediments of the Yamuna River (a tributary of the Ganges), India. Sci. Tot. Environ. 95, 7-27.

Jones, K.C. (1988). Determination of polychlorinated biphenyls in human foodstuffs and tissues: suggestions for a selective congener analytical approach. Sci. Total Environ. 68, 141-159.

Jones, P.D. (1978). *Studies of the marine geochemistry of mercury and other heavy metals*. Ph.D. thesis, University of Liverpool.

Kannan, N., Tanabe, S., Okamoto, T., Tatsukawa, R. and Phillips, D.H. (1989) Polychlorinated biphenyls (PCBs) in sediments in Hong Kong: a congener-specific approach to the study of coplanar PCBs in aquatic sediments. Environm. Pollut. 62, 223-235.

Karickhoff, S.W., Brown, D.S., and Scott, T.A. (1979). Sorption of hydrophobic pollutants on natural sediments. Wat. Res. 13, 241-248.

Kemp, A.L.W., Thomas, R.L., Dell, C.I. and Jaquet, J.-M. (1976). Cultural impact on the geochemistry of sediments in Lake Erie. J. Fish. Res. Board Can. 33, 440-462.

Kersten, M., Dicke, M., Kriews, M., Naumann, K., Schmidt, D.S., Schulz, M., Schwikowski, M., and Steiger, M. (1988). Distribution and fate of heavy metals in the North Sea. In: *Pollution of the North Sea. An assessment.* W. Salomons, B.L. Bayne, E.K. Duursma, U. Forstner (Eds.). Springer Verlag. pp. 300-347.

Kiff, P.R. and Nunny, R.S. (1984). Bed sediment surveys. In: *Sewage Sludge Disposal in Liverpool Bay. Research into effects 1975 to 1977.* Part 2, Appendices. Report of a Liverpool Bay Working Group. Department of the Environment. London. Appendix D, pp. 73-99.

Kiff, P.R. (1984). *Heavy metal determinations on sediments. Particle size dependence I.* Report No. DE 72. Hydraulics Research Ltd., Wallingford, England. 7 pp.

Kirby, R. (1987). Sediment exchanges across the coastal margins of NW Europe. J. Geol. Soc. London. 144, 121-126.

Knap, A.H., Binkley, K.S. and Deuser, W.G. (1986). Synthetic organic chemicals in the deep Sargasso Sea. Nature. 319, 572-574.

Kramer, C.J. (1986). Monitoring of abiotic compartments for trace metals: difficulties, strategies and use of surveys. Environ. Monit. Asses. 7, 169-187.

Langston, W.J. (1985). Assessment of the distribution and availability of arsenic and mercury in estuaries. In: *Estuarine Management and Quality Assessment.* J.G. Wilson and W. Halcrow (Eds.). Plenum Press, New York. 131-146.

Langston, W.J. (1983). The behaviour of arsenic in selected United Kingdom estuaries. Can. J. Fish. Aquat. Sci. 40 (Suppl. 2). 143-150.

Lara, R. and Ernst, W. (1990a). Sorption of polychlorinated biphenyls on marine sediments. I. The role of the organic carbon content. Environ. Technol. 11, 83-92.

Lara, R. and Ernst, W. (1990b). Sorption of polychlorinated biphenyls on marine sediments. II. Effect of the removal of sediment organic matter. Environ. Technol. 11, 93-97.

Lara, R. and Ernst, W. (1989). Interaction between polychlorinated biphenyls and marine humic substances. Determination of association coefficients. Chemosphere. 19, 1655-1664.

Larsen, B. and Fytianos, K. (1989). Organochlorine compounds and PCB congeners in contaminated sediments. Sci. Tot. Environ. 86, 273-279.

Larsson, P. (1984). Sedimentation of polychlorinated biphenyls (PCBs) in limnic and marine environments. Wat. Res. 18, 1389-1394.

Larsson, P. and Lemkemeier, K. (1989). Microbial mineralization of chlorinated phenols and biphenyls in sediment-water systems from humic and clear-water lakes. Wat. Res. 23, 1081-1085.

Law, R.J., Fileman, T.W., Fileman, C.F., and Limpenny, D.S. (1989). The distribution of hydrocarbons and metals in the North-eastern Irish Sea prior to development of the Morecambe Bay gas field. Oil Chem. Pollut. 5, 285-320.

Laxen, D.P.H. (1984). Adsorption of Cd, Pb and Cu during the precipitation of hydrous ferric oxide in a natural water. Chem. Geol. 47, 321-332.

Libert, Y. (1987). Mesures d'adsorption du cadmium sur les sediments du Lac de Comabbio-Italie du nord. Environ. Technol. Lett. 8, 189-196.

Lion, L.W., Altmann, R.S. and Leckie, J.O. (1982). Trace-metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of Fe/Mn oxide and organic surface coatings. Environ. Sci. Technol. 16, 660-666.

Lohse, J. (1988). Ocean incineration of toxic wastes: a footprint in North Sea sediments. Mar. Pollut. Bull. 19, 366-371.

Loring, D.H. (1981). Potential bioavailability of metals in eastern Canadian estuarine and coastal sediments. Rapp. P.-v. Reun. Cons. int. Explor. Mer. 181, 93-101.

Loring, D.H. (1987). *A final report on the ICES intercalibration for trace metals in marine sediments (1/TM/MS).* ICES Coop. Res. Rep. No. 143. Copenhagen.

Lucotte, M. (1989). Organic carbon isotope ratios and implications for the maximum turbidity zone of the St Lawrence upper estuary. Est. Coast. Shelf Sci. 29, 293-304.

Luoma, S.N. and Davis, J.A. (1983). Requirements for modelling trace metal partitioning in oxidized estuarine sediments. Mar. Chem. 12, 159-181.

MAFF. (1987). *Irish Sea status report of the Marine Pollution Monitoring Management Group.* R.R. Dickson (Ed.). Aquat. Environ. Monit. Rep., MAFF Direct. Fish. Res., Lowestoft. 17, 83 pp.

MAFF. (1990). *Monitoring and surveillance of non-radioactive contaminants in the aquatic environment, 1984-1987.* A. Franklin (Ed.). Aquat. Environ. Monit. Rep. MAFF Direct. Fish. Res., Lowestoft. 22, 60 pp.

Manly, B.F.J. (1986). *Multivariate statistical methods. A primer.* Chapman and Hall, London. 159 pp.

Martincic, D., Kwokal, Z. and Branica, M. (1990a). Distribution of zinc, lead, cadmium and copper between different size fractions of sediments I. The Limski Kanal (North Adratic Sea). Sci. Tot. Environ. 95, 201-215.

Martincic, D., Kwokal, Z. and Branica, M. (1990b). Distribution of zinc, lead, cadmium and copper between different size fractions of sediments II. The Krka River estuary and the Kornati Islands (Central Adriatic Sea). Sci. Tot. Environ. 95, 217-225.

McIntyre, A.E. and Lester, J.N. (1984). Occurrence and distribution of persistent organochlorine compounds in U.K. sewage sludges. Water, Air, Soil Pollut. 23, 397-415.

McLaren, P. (1987). *Sediment transport and the dispersal of sewage sludge in Liverpool Bay.* North West Water Authority (U.K.), Report. 46 pp.

Miller, I.D. (1985). *Nutrient distributions in relation to a thermohaline discontinuity in the north-east Irish Sea.* Ph.D. thesis, University of Wales.

Millward, G.E. and Moore, R.M. (1982). The adsorption of Cu, Mn and Zn by iron oxyhydroxide in model estuarine solutions. Wat. Res. 16, 981-985.

Mok, W.M. and Wai, C.M. (1989). Distribution and mobilization of arsenic species in the creeks around the Blackbird mining district, Idaho. Wat. Res. 23, 7-13.

Morris, R.J., Law, R.J., Allchin, C.R., Kelly, C.A., and Fileman, C.F. (1989). Metals and organochlorines in dolphins and porpoises of Cardigan Bay, West Wales. Mar. Pollut. Bull. 20, 512-523.

Mudroch, A., Onuska, F.I., and Kalas, L. (1989). Distribution of polychlorinated biphenyls in water, sediment and biota of two harbours. Chemosphere. 18, 2141-2154.

Mullin, M.D., Pochini, C.M., McCrindle, S., Romkes, M., Safe, S. and Safe, L.M. (1984). High-resolution PCB analysis: synthesis and chromatographic properties of all 209 PCB congeners. Environ. Sci. Technol. 18, 468-476.

Murphy, E.M., Zachara, J.M. and Smith, S.C. (1990). Influence of mineral-bound humic substances on the sorption of hydrophobic organic compounds. Environ. Sci. Technol. 24, 1507-1516.

Murphy, T.J., Mullin, M.D. and Meyer, J.A. (1987). Equilibration of polychlorinated biphenyls and toxaphene with air and water. Environ. Sci. Technol. 21, 155-162.

Murray, A.J. and Norton, M.G. (1982). *The field assessment of effects of dumping wastes at sea: 10. Analysis of chemical residues in fish and shellfish from selected coastal regions around England and Wales.* Fish. Res. Tech. Rep. MAFF Direct. Fish. Res., Lowestoft. 69, 42 pp.

Nimmo, M., van den Berg, C.M.G. and Brown, J. (1989). The chemical speciation of dissolved nickel, copper, vanadium and iron in Liverpool Bay, Irish Sea. Est. Coast. Shelf Sci. 29, 57-74.

Nirel, P.M.V. and Morel, F.M.M. (1990). Pitfalls of sequential extractions. Wat. Res. 24, 1055-1056.

Norton, M.G. and Rolfe, M.S. (1978). *The field assessment of the effects of dumping wastes at sea: 1. An introduction.* Fish. Res. Tech. Rep., MAFF Direct. Fish. Res., Lowestoft. 45, 9 pp.

Norton, M.G., Franklin, A., Rowlatt, S.M., Nunny, R.S. and Rolfe, M.S. (1984a). *The field assessment of effects of dumping wastes at sea: 12. The disposal of sewage sludge, industrial wastes and dredged spoils in Liverpool Bay.* Fish. Res. Tech. Rep., MAFF Direct. Fish. Res., Lowestoft. 76, 49 pp.

Norton, M.G., Rowlatt, S.M. and Nunny, R.S. (1984b). Sewage sludge dumping and contamination of Liverpool Bay sediments. Est. Coast. Shelf Sci. 19, 69-87.

Norton, M.G., Jones, P.G.W., Franklin, A. and Rowlatt, S.M. (1984c). Water quality studies around the sewage sludge dumping site in Liverpool Bay. Est. Coast. Shelf Sci. 19, 53-67.

Norusis, M.J. (1985). *SPSSX advanced statistics guide.* McGraw-Hill, New York. 505 pp.

Oakley, S.M., Nelson, P.O. and Williamson, K.J. (1981). Model of trace-metal partitioning in marine sediments. Environ. Sci. Technol. 15, 474-480.

Oliver, B.G., Charlton, M.N. and Durham, R.W. (1989). Distribution, redistribution, and geochronology of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in Lake Ontario sediments. Environ. Sci. Technol. 23, 200-208.

Olsen, C.R., Cutshall, N.H. and Larsen I.L. (1982). Pollutant-particle associations and dynamics in coastal marine environments:a review. Mar. Chem. 11, 501-533.

Osbaldeston, P.J. (1984). Inputs into Liverpool Bay. In: *Sewage Sludge Disposal in Liverpool Bay. Research into Effects 1975 to 1977.* Part 2, Appendices. Report of a Liverpool Bay Working Group. Department of the Environment, London. Appendix B. pp. 9-20.

Pardue, J.H., DeLaune, R.D., and Patrick, Jr., W.H. (1988). Effect of sediment pH and oxidation-reduction potential on PCB mineralization. Water, Air, and Soil Pollut. 37, 439-447.

Paulson, A.J., Curl Jr., H.C. and Cokelet, E.D. (1991). Remobilization of Cu from marine particulate organic matter and from sewage. Mar. Chem. 33, 41-60.

Pavoni, B., Sfriso, A., and Marcomini, A. (1987). Concentration and flux properties of PCBs, DDTs and PAHs in a dated sediment core from the lagoon Venice. Mar. Chem. 21, 25-35.

Pellizzari, E.D., Moseley, M.A., and Cooper, S.D. (1985). Recent advances in the analysis of polychlorinated biphenyls in environmental and biological media. J. Chromatogr. 334, 277-314.

Peterson, M.L. and Carpenter, R. (1986). Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washington coast and Saanich Inlet, B.C. Geochim. Cosmochim. Acta. 50, 353-369.

Pingree, R.D. and Griffiths, D.K. (1979). Sand transport paths around the British Isles resulting from M_2 and M_4 tidal interactions. J. mar. biol. Ass. U.K. 59, 497-513.

Pocklington, R. and Leonard, J.D. (1979). Terrigenous organic matter in sediments of the St. Lawrence Estuary and Saguenay Fjord. J. Fish. Res. Board Can. 36, 1250-1255.

Poulton, D.J. (1989). Statistical zonation of sediment samples using ratio matching and cluster analysis. Environ. Monit. Assess. 12, 379-404.

Price, W.A. and Kendrick, M.P. (1963). Field and model investigations into the reasons for siltation in the Mersey Estuary. Proc. Instn. Civ. Engrs. (UK). 24, 473-518.

Prosi, F. (1989). Factors controlling biological availability and toxic effects of lead in aquatic organisms. Sci. Tot. Environ. 79, 157-169.

Pruell, R.J., Norwood, C.B., Bowen, R.D., Boothman, W.S., Rogerson, P.F., Hackett, M., and Butterworth, B.C. (1990). Geochemical study of sediment contamination in New Bedford Harbor, Massachusetts. Mar. Environ. Res. 29, 77-101.

Quensen III, J.F., Boyd, S.A. and J.M. Tiedje. (1990). Dechlorination of four commercial polychlorinated biphenyl mixtures (Aroclors) by anaerobic microorganisms from sediments. Appl. Environ. Microbiol. 56, 2360-2369.

Rae, J.E. and Aston, S.R. (1981). Mercury in coastal and estuarine sediments of the Northeastern Irish Sea. Mar. Pollut. Bull. 12, 367-371.

Rae, J.E. and Aston, S.R. (1982). The role of suspended solids in the estuarine geochemistry of mercury. Wat. Res. 16, 649-654.

Ramster, J.W. (1972a). Current measurements. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 6. pp. 55-79.

Ramster, J.W. (1972b). Salinity, temperature and density distribution. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 4. pp. 31-44.

Rapaport, R.A. and Eisenreich, S.J. (1984). Chromatographic determination of octanol-water partition coefficients (K_{ow}'s) for 58 polychlorinated biphenyl congeners. Environ. Sci. Technol. 18, 163-170.

Rees, E.I.S. (1984). Evaluation of side-scan sonar for locating muddy deposits in Liverpool Bay. In: *Sewage Sludge Disposal in Liverpool Bay. Research into effects 1975 to 1977.* Part 2, Appendices. Report of a Liverpool Bay Working Group. Department of the Environment. Appendix E, pp. 100-112.

Ridgway, I.M. and Price, N.B. (1987). Geochemical associations and post-depositional mobility of heavy metals in coastal sediments: Loch Etive, Scotland. Mar. Chem. 21, 229-248.

Robinson, I.S. (1979). The tidal dynamics of the Irish and Celtic Seas. Goephys. J. R. astr. Soc. 56, 159-197.

Romankevich, E.A. (1978). *Geochemistry of organic matter in the ocean.* Springer-Verlag, Berlin. 334 pp.

Rosental, R., Eagle, G.A. and Orren, M.J. (1986). Trace metal distribution in different chemical fractions in nearshore sediments. Est. Coast. Shelf Sci. 22, 303-324.

Rowlatt, S.M. (1986). The transport of sewage-derived copper in Liverpool Bay. Rapp. P.-v. Reun. Cons. int. Explor. Mer. 186, 475-485.

Rowlatt, S.M. (1988). *Metal contamination in sediments from Liverpool Docks and the Mersey Estuary.* Marine Environmental Quality Committee, ICES. C.M. 1988/E:12. 10 pp.

Rowlatt, S.M., Law, R., Harper, D. and Limpenny, D. (1984). *Sewage sludge dumping and the composition of sediments and suspended particulate matter in the eastern Irish Sea.* Marine Environmental Quality Committee, ICES. C.M. 1984/E:9. 4 pp.

Rowlatt, S.M., Rees, H.L. and Rees, E.I.S. (1986). *Changes in sediments following the dumping of dredged materials in Liverpool Bay.* Marine Environmental Quality Committee, ICES. C.M. 1986/E:17 (mimeo). 7 pp.

Sackett, W.M. (1964). The depositional history and isotopic organic carbon composition of marine sediments. Mar. Geol. 2, 173-185.

Sadiq, M. (1989). Marine chemistry of cadmium: a comparison of theoretical and field observations. Environ. Technol. Lett. 10, 1057-1070.

Safe, S. (1984). Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs): biochemistry, toxicology, and mechanism of action. Crit. Rev. Toxicol. 13(4) 319-395.

Safe, S., Safe, L. and Mullin, M. (1985). Polychlorinated biphenyls: congener-specific analysis of a commercial mixture and a human milk extract. J. Agric. Food Chem. 33, 24-29.

Sakata,M. (1985). Diagenetic remobilization of manganese, iron, copper and lead in anoxic sediment of a freshwater pond. Wat. Res. 19, 1033-1038.

Salomons, W. and Eysink, W.D. (1981). Pathways of mud and particulate trace metals from rivers to the southern North Sea. In: *Holocene Marine Sedimentation in the North Sea Basin.* S.-D. Nio, R.T.E. Shuttenhelm and Tj.C.E. van Weering (Eds.). Blackwell Scientific Pubs., Oxford. pp. 429-450.

Salomons, W. and Forstner, U. (1984). *Metals in the hydrocycle.* Springer-Verlag, Berlin. 349 pp.

Santschi, P., Hohener, P., Benoit, G. and Buchholtz-ten Brink, M. (1990). Chemical processes at the sediment-water interface. Mar. Chem. 30, 269-315.

Sauer, T.C., Jr., Durell, G.S., Brown, J.S., Redford, D. and Boehm, P.D. (1989). Concentrations of polychlorinated pesticides and PCBs in microlayer and seawater samples collected in open-ocean waters off the U.S. east coast and in the Gulf of Mexico. Mar. Chem. 27, 235-257.

Schults, D.W., Ferraro, S.P., Ditsworth, G.R. and Sercu, K.A. (1987). Selected chemical contaminants in surface sediments of Commencement Bay and Tacoma Waterways, Washington, USA. Mar. Environ. Res. 22, 271-295.

Schulz D.E., Petrick, G. and Duinker, J.C. (1989). Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. Environ. Sci. Technol. 23, 852-859.

Schulz, D.E., Petrick, G., and Duinker, J.C. (1988). Chlorinated biphenyls in North Atlantic surface and deep water. Mar. Pollut. Bull. 19, 526-531.

Senaratne, A. and Dissanayake, C.B. (1989). The geochemistry of mercury in some coastal sediments from Sri Lanka. Chem. Geol. 75, 183-190.

Shaw, K. (1959). Determination of organic carbon in soil and plant material. J. Soil Sci. 10, 316-326.

Shiu, W.Y. and Mackay, D. (1986). A critical review of aqueous solubilities, vapor pressures, Henry's Law constants, and octanol-water partition coefficients of the polychlorinated biphenyls. J. Phys. Chem. Ref. Data. 15, 911-929.

Sholkovitz, E.R., Boyle, E.A. and Price, N.B. (1978). The removal of dissolved humic acids and iron during estuarine mixing. Earth Planet. Sci. Lett. 40, 130-136.

Sigg, L., Sturm, M. and Kistler, D. (1987). Vertical transport of heavy metals by settling particles in Lake Zurich. Limnol. Oceanogr. 32, 112-130.

Slavin, W., Carnick, G.R., Manning, D.C. and Proszkowska, E. (1983). Recent experiences with the stabilized temperature platform furnace and Zeeman background correction. Atomic Spectroscopy. 4, 69-86.

Sly, P.G. (1966). *Marine geological studies in the Eastern Irish Sea and adjacent estuaries, with special reference to sedimentation in Liverpool Bay and River Mersey.* Ph.D. thesis, University of Liverpool.

Sodergren, A., Larssson, P., Knulst, J. and Bergovist, C. (1990). Transport of incinerated organochlorine compounds to air, water, microlayer, and organisms. Mar. Pollut. Bull. 21, 18-24.

Spencer, C.P. (1972). Plant nutrient and productivity study. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 16. pp. 357-401.

Spencer, C.P. (1984). Water quality surveys. In: *Sewage Sludge Disposal in Liverpool Bay. Research into Effects 1975 to 1977.* Part 2, Appendices. Report of a Liverpool Bay Working Group. Department of the Environment, London. Appendix C. pp. 21-72.

Suarez, D.L. and Langmuir, D. (1976). Heavy metal relationships in a Pennsylvania soil. Geochim. Cosmochim. Acta. 40, 589-598.

Szefer, P. (1990). Interelemental relationships in organisms and bottom sediments of the southern Baltic. Sci. Tot. Environ. 95, 119-130.

Takamatsu, T., Kawashima, M. and Koyama, M. (1985). The role of Mn^{2+}-rich hydrous manganese oxide in the accumulation of arsenic in lake sediments. Wat. Res. 19, 1029-1032.

Talbot, J.W. (1972).Transport and dispersion of soluble material. In: *Out of Sight, Out of Mind. Report of a working party on sludge disposal in Liverpool Bay.* Volume 2. Appendices. (Department of the Environment). HMSO, London. Appendix 11. pp. 209-271.

Tan, F.C. and Strain, P.M. (1983). Sources, sinks and distribution of organic carbon in the St. Lawrence Estuary, Canada. Geochim. Cosmochim. Acta. 47, 125-132.

Tanabe, S. (1988). PCB problems in the future: foresight from current knowledge. Environ. Pollut. 50, 5-28.

Taylor, D. (1986). Changes in the distribution patterns of trace metals in sediments of the Mersey Estuary in the last decade (1974-83). Sci. Tot. Environ. 49, 257-295.

Tessier, A., Rapin, F. and Carignan, R. (1985). Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. Geochim. Cosmochim. Acta. 49, 183-194.

Thomas, R.L. (1972). The distribution of mercury in the sediments of Lake Ontario. Can. J. Earth Sci. 9, 636-651.

Thornton, I., Watling, H. and Darracott, A. (1975). Geochemical studies in several rivers and estuaries used for oyster rearing. Sci. Tot. Environ. 4, 325-345.

Van de Meent, D., De Leeuw, J.W., Schenck, P.A. and Salomons, W. (1985). Geochemistry of suspended particulate matter in two natural sedimentation basins of the River Rhine. Wat. Res. 19, 1333-1340.

van der Oost, R, Heida, H. and Opperhuizen, A. (1988). Polychlorinated biphenyl congeners in sediments, plankton, molluscs, crustaceans, and eel in a freshwater lake: implications of using reference chemicals and indicator organisms in bioaccumulation studies. Arch. Environ. Contam. Toxicol. 17, 721-729.

van der Weijden, C.H. and Middelburg, J.J. (1989). Hydrogeochemistry of the River Rhine: long term and seasonal variability, elemental budgets, base levels and pollution. Wat. Res. 23, 1247-1266.

Warren, L.J. (1981). Contamination of sediments by lead, zinc and cadmium: a review. Environ. Pollut. Ser. B. 2, 401-436.

Williams, P.J. le B. (1985). Analysis: organic matter. In: *Practical Estuarine Chemistry: a Handbook.* P.C. Head (Ed.). Cambridge University Press. pp. 160-200.

Windom, H.L., Schropp, S.J., Calder, F.D., Ryan, J.D., Smith Jr., R.J., Burney, L.C., Lewis, F.G. and Rawlinson, C.H. (1989). Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. Environ. Sci. Technol. 23, 314-320.

APPENDIX A. Furnace parameters used for the determinations of arsenic and cadmium by graphite-furnace atomic absorption spectrometry. L'vov platforms were used with the atomizations tubes. 5 µl sample volumes were injected into the furnace together with 5µl of matrix modifier (nickel nitrate for arsenic and phosphoric acid for cadmium) and 10 µl of blank (nitric acid 1% v/v).

FURNACE PARAMETERS FOR ARSENIC

Step No.	Temperature (C)	Time (sec)	Gas flow (L/min)	Read Command
1	100	10.0	3.0	NO
2	250	70.0	3.0	NO
3	350	30.0	3.0	NO
4	600	10.0	3.0	NO
5	1300	5.0	3.0	NO
6	1300	10.0	3.0	NO
7	1300	1.0	0.4	NO
8	2800	1.2	0.4	YES
9	2800	2.0	0.4	YES
10	2800	8.0	3.0	NO

FURNACE PARAMETERS FOR CADMIUM

Step No.	Temperature (C)	Time (sec)	Gas flow (L/min)	Read Command
1	110	10.0	3.0	NO
2	250	60.0	3.0	NO
3	350	30.0	3.0	NO
4	600	10.0	3.0	NO
5	900	10.0	3.0	NO
6	900	10.0	3.0	NO
7	900	1.0	0.2	NO
8	2800	1.2	0.2	YES
9	2800	3.0	0.2	YES
10	2800	8.0	3.0	NO

APPENDIX B.1. Concentration of elements in the fine fraction. The concentration units for all elements except Fe are µg g^{-1}. Concentration units for Fe are in percent.

Sta.	Lon.	Lat.	Hg	Cd	Cr	Cu	Ni	Pb	Zn	As	Mn	Fe
G07	-41.30	29.10	0.21	0.35	91	43	37	130	245	15	1347	1.93
G09	-41.60	31.50	0.34	2.44	58	199	54	865	607	53	7316	2.58
G11	-41.90	34.00	0.28	0.29	44	28	43	84	158	13	822	1.84
G13	-41.60	36.40	0.22	0.42	41	25	41	85	153	12	966	1.74
H08	-39.30	30.10	0.32	1.39	50	35	47	123	191	16	1316	1.73
H10	-39.70	32.50	0.37	0.36	48	44	43	110	195	17	1183	1.89
H12	-39.90	35.10	0.33	0.37	38	23	41	70	135	11	739	1.72
J07	-37.40	28.40	0.57	0.72	61	44	51	99	207	13	756	1.81
J09	-37.50	30.80	0.09	1.21	64	54	68	307	335	39	5512	2.04
J11	-37.40	33.40	0.52	0.31	51	35	51	91	180	10	531	1.93
J13	-37.40	35.80	0.49	0.17	48	31	41	86	177	11	572	1.86
K06	-35.40	26.90	0.15	0.45	50	40	45	177	246	19	4281	1.62
K08	-35.50	29.40	0.09	1.37	90	121	60	698	591	69	10200	3.06
K09	-35.50	30.80	1.23	0.80	95	83	42	154	314	19	622	2.31
K10	-35.40	31.80	1.41	0.41	64	46	38	107	199	13	589	1.70
K11	-35.50	33.10	0.47	0.43	56	38	34	102	189	12	543	1.71
K12	-35.70	34.30	0.42	0.46	50	32	38	83	183	11	625	1.85
L07	-33.20	27.80	0.18	1.16	67	54	39	148	226	15	1744	1.83
L08	-33.30	29.10	0.21	0.48	68	58	25	138	214	20	1957	1.72
L09	-33.50	30.50	0.16	1.28	91	157	68	1214	904	144	22900	4.54
L10	-33.20	31.70	0.11	0.67	76	168	51	453	389	51	8692	2.74
L11	-33.10	32.80	0.62	0.47	60	44	38	91	182	10	540	1.86
L12	-33.10	34.00	0.54	0.75	57	46	34	104	192	12	535	1.89
L13	-33.10	35.10	0.31	0.17	51	36	33	89	179	11	596	2.01
M06	-31.00	26.40	0.02	0.73	62	79	68	482	439	48	13700	2.14
M08	-31.20	28.90	0.09	0.16	71	59	38	220	246	27	3759	2.19
M09	-31.10	30.10	0.27	0.39	77	144	35	547	325	43	3764	2.57
M10	-31.10	31.30	0.29	0.69	75	173	48	707	548	53	5660	3.22
M11	-31.10	32.50	0.54	0.75	66	60	31	125	217	13	679	1.79
M12	-31.20	33.70	0.45	0.30	52	31	28	90	176	11	572	1.78
N07	-29.20	27.30	0.08	0.53	63	50	39	218	205	24	2669	2.14
N08	-29.10	28.60	*	0.80	64	168	45	348	322	*	*	*
N09	-29.10	29.90	0.16	0.45	66	62	42	224	297	37	2882	2.38
N10	-28.90	31.10	0.14	0.14	77	225	58	247	321	32	2602	4.52
N11	-28.80	32.40	0.10	0.20	66	56	35	258	304	52	4680	2.85
N12	-28.80	33.50	0.64	0.22	57	54	37	105	182	11	655	1.88
N13	-28.80	34.50	0.47	0.28	60	39	35	100	195	9	673	1.84
P06	-26.70	25.80	0.10	0.17	49	46	41	133	181	11	984	1.59
P08	-26.80	28.40	0.05	0.16	44	72	34	334	279	35	4349	2.30
P09	-26.70	29.60	0.31	0.51	66	177	31	265	333	29	2127	2.23
P10	-26.60	30.80	0.08	2.05	85	137	54	1000	483	55	6119	2.84
P11	-26.30	32.00	2.09	2.46	95	125	36	199	479	33	925	2.41
P12	-26.40	33.20	0.70	0.45	66	50	32	116	234	15	664	2.02
Q07	-24.90	27.10	0.20	0.36	66	47	45	111	198	15	1113	1.77
Q09	-24.60	29.40	0.10	0.45	75	82	30	484	473	131	8472	4.30
Q11	-24.40	31.70	0.82	0.66	96	69	47	191	324	19	707	2.79
Q13	-24.30	34.20	0.72	0.98	64	55	31	165	275	18	894	2.34
R06	-22.50	25.40	*	0.70	48	35	33	194	195	*	*	*
R08	-22.60	27.90	0.14	0.60	70	175	36	403	313	22	2211	1.96
R10	-21.90	30.40	0.27	0.37	54	41	27	179	171	18	1293	1.69
R11	-22.00	31.50	1.21	0.72	78	58	45	139	299	14	681	2.16
R12	-22.10	32.70	0.58	0.41	69	50	37	133	251	16	1018	2.12

S07	-20.30	26.40	*	0.11	54	70	44	553	284	*	*	*
S08	-20.20	27.70	0.21	0.32	73	166	37	322	338	27	2521	2.42
S09	-20.10	28.90	0.78	0.90	85	60	43	191	338	22	1394	2.72
S11	-19.80	31.20	0.27	0.24	71	57	45	259	302	29	2254	2.59
S13	-19.40	33.50	1.11	0.45	59	45	34	105	216	16	881	2.01
T08	-17.70	27.40	0.82	0.49	72	45	42	121	235	18	1342	2.29
T09	-17.70	28.60	1.45	1.24	85	78	45	158	317	19	990	2.59
T10	-17.50	29.90	0.60	0.69	53	52	33	294	281	16	1559	1.36
T12	-17.20	32.20	1.17	0.73	55	37	31	90	222	15	877	1.43
T14	-16.90	34.40	0.78	0.79	51	36	30	89	201	14	684	1.40
U09	-15.20	28.40	1.36	0.73	73	48	43	110	259	15	1072	1.99
U11	-14.80	30.80	1.15	0.77	74	50	39	132	285	19	1397	2.00
U15	-14.60	35.50	0.54	0.50	58	69	37	126	227	16	1168	2.00
NW24	-12.40	28.60	1.56	0.75	79	50	41	111	288	18	1229	2.16
YY01	-14.20	29.10	1.22	0.77	67	44	34	97	227	18	1063	1.77
YY02	-12.70	29.50	1.70	0.81	84	52	42	127	288	22	1487	2.29
YY03	-12.00	29.10	1.19	0.72	62	37	33	82	209	16	1056	1.61
YY04	-13.40	28.60	1.46	0.66	70	50	35	102	254	21	1102	2.00

APPENDIX B.2. Concentration of elements in the coarse fraction. The concentration units for all elements except Fe are in $\mu g\ g^{-1}$. Concentration values for Fe are in percent.

Sta.	Hg	Cd	Cr	Cu	Ni	Pb	Zn	As	Mn	Fe
G07	0.009	0.031	3.72	1.26	2.74	7.30	15.1	4.24	237	0.35
G09	0.007	0.011	3.58	1.18	2.58	6.74	16.3	4.54	237	0.39
G11	0.013	0.047	5.16	1.64	2.78	9.98	14.8	5.52	238	0.38
G13	0.017	0.014	4.64	1.38	2.66	7.94	14.4	3.66	176	0.37
H08	0.006	0.016	2.90	0.90	2.54	4.74	16.2	3.46	197	0.35
H10	0.016	0.011	4.62	1.59	2.73	10.04	18.2	6.18	274	0.39
H12	0.025	0.012	4.88	1.68	2.76	8.36	15.1	4.84	195	0.39
J07	0.014	0.009	3.08	1.24	2.38	6.91	13.6	3.34	204	0.28
J09	0.004	0.008	2.68	0.90	2.50	4.34	14.9	3.72	191	0.34
J11	0.035	0.011	4.82	1.72	2.66	8.86	16.4	3.96	149	0.36
J13	0.030	0.007	4.42	1.40	2.62	8.52	14.8	3.66	151	0.35
K06	0.006	0.009	2.42	0.98	2.24	5.80	15.9	3.74	271	0.28
K08	0.009	0.005	2.42	0.86	2.10	7.32	18.4	3.14	279	0.28
K09	0.007	0.010	2.30	0.84	2.28	4.44	13.6	2.46	158	0.29
K10	0.035	0.018	3.76	1.86	2.26	8.80	17.8	2.96	120	0.29
K11	0.027	0.013	4.38	1.80	2.58	9.11	17.7	3.32	148	0.32
K12	0.025	0.010	3.96	1.74	2.68	9.32	15.3	4.02	172	0.33
L07	0.008	0.012	3.12	1.32	2.58	7.66	15.5	3.32	273	0.31
L08	0.009	0.009	3.03	1.31	2.46	8.54	17.4	3.77	260	0.31
L09	0.010	0.007	2.98	0.95	2.29	10.07	22.0	4.73	261	0.32
L10	0.012	0.009	3.36	6.03	2.32	10.13	17.0	3.28	247	0.31
L11	0.029	0.021	4.34	1.46	2.30	8.04	18.3	2.48	119	0.28
L12	0.033	0.013	4.13	1.34	2.37	7.58	15.2	3.47	152	0.29
L13	0.036	0.011	4.89	1.56	2.72	8.71	16.9	3.86	156	0.32
M06	0.009	0.014	2.78	0.90	2.24	5.06	15.2	3.58	217	0.25
M08	0.012	0.015	2.96	1.02	2.40	7.11	16.1	3.02	191	0.27
M09	0.022	0.008	3.11	1.50	2.15	13.60	26.6	6.30	251	0.31
M10	0.028	0.010	3.44	3.46	2.62	19.90	27.2	4.62	265	0.36
M11	0.032	0.014	3.46	1.50	2.34	10.19	16.1	3.38	127	0.28
M12	0.099	0.015	4.48	1.74	2.58	7.88	15.6	2.62	148	0.29
N07	0.006	0.008	2.78	1.10	2.32	4.69	11.0	1.92	156	0.23
N08	0.010	0.020	3.11	1.26	2.37	6.46	13.5	1.81	*	*
N09	0.011	0.008	3.24	1.16	2.46	10.84	28.0	6.12	326	0.38
N10	0.009	0.007	2.94	1.58	2.60	5.62	12.4	2.24	228	0.31
N11	0.009	0.009	3.12	1.60	2.54	10.12	18.4	3.64	192	0.33
N12	0.021	0.012	2.80	1.20	2.20	6.32	11.7	2.18	92	0.25
N13	0.025	0.015	4.08	1.48	2.56	8.18	18.2	2.36	169	0.35
P06	0.007	0.009	2.12	0.94	1.62	4.82	13.8	2.74	159	0.20
P08	0.012	0.007	2.78	1.26	2.04	6.16	15.3	2.16	161	0.25
P09	0.012	0.010	2.90	1.24	2.12	10.44	33.5	7.38	337	0.39
P10	0.006	0.007	2.76	1.06	2.48	4.30	12.1	1.82	231	0.30
P11	0.043	0.038	3.90	3.24	2.32	12.23	23.8	2.90	155	0.28
P12	0.029	0.017	3.04	1.48	2.00	9.52	18.1	2.74	124	0.26
Q07	0.007	0.017	2.90	1.14	2.36	4.81	10.4	2.72	146	0.27
Q09	0.009	0.009	2.76	1.32	2.04	11.98	31.8	8.22	441	0.40
Q11	0.032	0.018	2.82	2.86	1.98	7.04	14.3	1.46	137	0.22
Q13	0.076	0.042	3.60	3.18	2.50	15.52	35.9	4.64	155	0.34
R06	0.006	0.009	2.02	0.98	1.80	3.30	11.0	2.32	*	*
R08	0.010	0.008	2.80	1.44	2.42	7.56	25.3	3.52	219	0.31
R10	0.024	0.008	2.89	1.52	2.26	8.14	26.1	3.51	237	0.29
R11	0.035	0.024	3.40	1.85	1.99	9.75	23.1	2.57	150	0.25
R12	0.064	0.021	2.71	2.75	2.14	14.08	38.2	4.95	245	0.33

S07	0.003	0.008	2.03	1.00	1.87	3.30	12.6	3.42	*	*
S08	0.010	0.009	2.70	1.23	2.01	7.79	31.8	4.61	265	0.29
S09	0.036	0.021	4.33	2.10	2.24	14.23	63.5	5.17	339	0.35
S11	0.017	0.012	2.86	2.01	2.47	9.89	27.4	3.73	283	0.29
S13	0.060	0.060	4.21	3.07	2.85	10.83	37.2	4.53	166	0.35
T08	0.015	0.012	2.83	1.36	2.19	13.88	42.2	7.16	431	0.37
T09	0.047	0.032	4.96	2.46	2.28	17.19	69.0	4.66	300	0.34
T10	0.004	0.009	2.38	1.34	2.56	7.50	27.8	4.66	366	0.35
T12	0.088	0.108	3.74	4.50	2.54	9.93	42.9	2.83	212	0.26
T14	0.024	0.041	2.70	1.64	2.18	5.26	32.0	3.08	119	0.27
U09	0.081	0.185	6.01	5.31	3.26	17.68	68.2	4.76	373	0.34
U11	0.005	0.012	2.47	1.70	2.85	8.18	35.7	6.12	420	0.34
U15	0.021	0.032	2.60	2.30	2.12	7.46	28.5	2.94	130	0.25
NW24	0.130	0.076	3.78	4.38	2.56	11.54	51.7	4.56	329	0.32
YY01	0.089	0.188	4.76	4.84	2.94	10.83	42.6	3.60	199	0.28
YY02	0.097	0.063	3.79	4.26	2.45	9.36	42.3	3.89	189	0.28
YY03	0.178	0.177	6.31	9.25	3.96	15.84	75.6	4.72	309	0.38
YY04	0.074	0.090	4.46	3.96	3.00	11.32	47.2	4.10	356	0.31

APPENDIX B3. Grain size distributions in bulk (<4000 μm) and total (<500 μm) sediments. All values are given as a percentage dry weight. The concentration (in percent) of aluminium in the total fraction is also shown.

	BULK (<4000 μm)			TOTAL (<500 μm)		
Sta	Fine	Coar	>500	Fine	Coar	Al
G07	3.27	60.93	35.80	5.09	94.91	1.20
G09	0.13	59.19	40.69	0.21	99.79	0.79
G11	4.30	56.68	39.02	7.05	92.95	1.36
G13	4.31	49.31	46.38	8.03	91.97	1.36
H08	0.95	87.93	11.11	1.07	98.93	0.93
H10	3.77	52.03	44.20	6.76	93.24	1.30
H12	6.36	55.53	38.11	10.28	89.72	1.50
J07	4.17	65.10	30.73	6.02	93.98	1.22
J09	0.12	72.43	27.45	0.17	99.83	0.84
J11	9.27	47.80	42.93	16.25	83.75	1.96
J13	6.82	53.16	40.02	11.38	88.62	1.68
K06	0.71	86.78	12.51	0.82	99.18	0.93
K08	0.15	96.87	2.98	0.15	99.85	0.75
K09	2.07	90.85	7.08	2.23	97.77	0.99
K10	6.04	51.81	42.16	10.44	89.57	1.61
K11	11.91	47.67	40.42	19.99	80.01	2.15
K12	7.04	57.97	34.99	10.83	89.17	1.70
L07	0.99	42.42	56.59	2.28	97.72	1.05
L08	1.37	71.31	27.33	1.88	98.12	1.02
L09	0.14	92.05	7.81	0.16	99.84	0.85
L10	0.19	40.44	59.37	0.46	99.54	0.80
L11	13.60	42.66	43.74	24.17	75.83	2.30
L12	6.18	46.92	46.90	11.65	88.35	1.62
L13	8.48	38.99	52.53	17.87	82.13	2.04
M06	0.12	88.50	11.39	0.13	99.87	0.86
M08	0.40	81.59	18.01	0.49	99.51	0.87
M09	0.72	85.22	14.06	0.84	99.16	0.89
M10	0.27	31.04	68.69	0.86	99.14	0.97
M11	4.40	52.03	43.57	7.79	92.21	1.40
M12	10.29	42.92	46.79	19.34	80.66	2.06
N07	0.28	83.32	16.40	0.33	99.67	0.93
N08	0.17	89.54	10.29	0.19	99.81	0.92
N09	0.60	93.55	5.84	0.64	99.36	0.86
N10	0.34	57.36	42.29	0.60	99.40	0.89
N11	0.34	48.16	51.50	0.71	99.29	0.94
N12	6.38	62.12	31.50	9.31	90.69	1.60
N13	10.37	46.11	43.51	18.37	81.63	2.17
P06	0.62	77.85	21.53	0.79	99.21	0.90
P08	0.27	85.70	14.04	0.31	99.69	0.89
P09	0.87	96.89	2.24	0.89	99.11	0.90
P10	0.16	68.79	31.05	0.23	99.77	0.82
P11	31.03	59.30	9.68	34.35	65.65	3.20

P12	6.45	70.41	23.14	8.39	91.61	1.66
Q07	1.28	58.54	40.18	2.14	97.86	1.20
Q09	0.31	98.89	0.79	0.32	99.68	0.86
Q11	11.22	76.02	12.76	12.86	87.14	1.76
Q13	4.32	90.50	5.18	4.56	95.44	1.42
R06	0.21	71.14	28.65	0.29	99.71	0.97
R08	0.49	85.83	13.68	0.57	99.43	0.80
R10	1.12	90.11	8.76	1.23	98.77	0.97
R11	16.57	75.37	8.06	18.03	81.97	2.17
R12	5.42	83.60	10.98	6.09	93.91	1.47
S07	0.07	89.29	10.64	0.08	99.93	0.70
S08	0.41	95.18	4.41	0.43	99.57	0.80
S09	1.99	97.13	0.87	2.01	97.99	1.24
S11	0.79	85.43	13.79	0.91	99.09	1.08
S13	9.47	88.61	1.92	9.66	90.34	1.80
T08	2.54	96.14	1.32	2.58	97.42	1.05
T09	8.00	91.08	0.92	8.08	91.92	1.58
T10	0.09	93.19	6.72	0.09	99.90	0.84
T12	14.24	83.71	2.05	14.54	85.46	2.03
T14	3.66	95.81	0.53	3.68	96.32	1.46
U09	34.19	58.49	7.32	36.90	63.10	3.26
U11	1.75	91.92	6.33	1.87	98.13	1.04
U15	3.26	94.02	2.71	3.36	96.64	1.53
NW24	24.67	67.98	7.35	26.63	73.37	2.71
YY01	59.30	37.90	2.80	61.01	38.99	4.01
YY02	31.08	67.94	0.98	31.39	68.61	2.99
YY03	55.20	40.60	4.20	57.62	42.38	3.58
YY04	26.57	65.84	7.59	28.75	71.25	2.91

APPENDIX B4. Organic carbon (OC) and organic matter (OM) concentrations (in percent) in fine and coarse fractions. The concentrations of nitrogen (%) and $\delta^{13}C$ values (in ‰) in fine sediments and an estimation of the organic carbon content in the total fraction are also shown in this appendix. C/N represents the atomic ratio between carbon and nitrogen.

	FINE FRACTION (< 90 µm)					COARSE FRACTION (90-500 µm)		TOTAL (<500µM)
Sta	OC	OM	N	C/N	$\delta^{13}C$	OM	OC	OC
G07	2.06	3.89	*	*	-20.60	0.38	0.20	0.30
G09	2.00	3.77	*	*	-21.12	0.36	0.19	0.19
G11	2.04	3.85	0.14	17.0	-20.66	0.60	0.32	0.44
G13	1.85	3.49	0.16	13.5	-20.71	0.71	0.38	0.50
H08	1.90	3.59	0.17	13.0	-20.68	0.37	0.20	0.21
H10	1.87	3.53	0.15	14.5	-21.28	0.60	0.32	0.42
H12	1.43	2.70	0.13	12.8	-19.63	0.69	0.37	0.47
J07	2.22	4.19	0.19	13.6	-22.31	0.44	0.23	0.35
J09	2.37	4.47	0.22	12.6	-22.02	0.38	0.20	0.20
J11	1.48	2.79	0.19	9.1	-18.49	0.53	0.28	0.48
J13	1.39	2.62	0.18	9.0	-19.43	0.54	0.29	0.41
K06	2.10	3.96	0.31	7.9	-19.88	0.24	0.13	0.14
K08	3.05	5.76	0.45	7.9	-19.73	0.33	0.17	0.18
K09	2.03	3.83	0.22	10.8	-21.49	0.33	0.17	0.22
K10	1.73	3.27	0.20	10.1	-20.37	0.47	0.25	0.40
K11	1.56	2.94	*	*	-19.02	0.64	0.34	0.58
K12	1.39	2.62	0.19	8.5	-18.93	0.67	0.35	0.47
L07	2.48	4.68	*	*	-19.82	0.38	0.20	0.25
L08	2.31	4.36	0.29	9.3	-20.71	0.45	0.24	0.28
L09	2.19	4.13	0.31	8.2	-18.97	0.38	0.20	0.20
L10	2.18	4.11	*	*	-20.04	0.40	0.21	0.22
L11	1.51	2.85	*	*	-19.53	0.52	0.28	0.57
L12	1.75	3.30	*	*	-19.77	0.61	0.32	0.49
L13	1.58	2.98	*	*	-20.29	0.66	0.35	0.57
M06	2.41	4.55	*	*	-19.36	0.26	0.14	0.14
M08	2.51	4.74	*	*	-20.33	0.33	0.17	0.19
M09	2.76	5.21	*	*	-20.83	0.36	0.19	0.21
M10	2.67	5.04	*	*	-20.40	0.41	0.22	0.24
M11	1.90	3.59	*	*	-20.34	0.47	0.25	0.38
M12	1.52	2.87	0.17	10.4	-20.44	0.62	0.33	0.56
N07	2.34	4.42	0.34	8.0	-19.78	0.41	0.22	0.22
N08	2.37	4.47	0.35	7.9	-20.09	0.42	0.22	0.23
N09	2.46	4.64	0.32	9.0	-20.43	0.44	0.23	0.25
N10	2.53	4.77	0.33	8.9	-20.15	0.45	0.24	0.25
N11	2.20	4.15	0.29	8.9	-20.23	0.43	0.23	0.24
N12	1.68	3.17	0.22	8.9	-20.33	0.38	0.20	0.34
N13	1.55	2.92	0.21	8.6	-20.15	0.57	0.30	0.53
P06	2.24	4.23	0.32	8.2	-20.56	0.26	0.14	0.15
P08	2.23	4.21	0.35	7.4	-19.71	0.33	0.17	0.18
P09	*	*	*	*	*	0.40	0.21	*

P10	2.38	4.49	*	*	-20.61	0.36	0.19	0.20

App.B4. cont.. (2)

P11	2.24	4.23	*	*	-21.16	0.45	0.24	0.93
P12	1.70	3.21	*	*	-19.66	0.44	0.23	0.36
Q07	2.24	4.23	*	*	-19.28	0.38	0.20	0.25
Q09	2.28	4.30	0.31	8.6	-19.06	0.43	0.23	0.23
Q11	2.49	4.70	0.29	10.0	-20.21	0.45	0.24	0.53
Q13	1.91	3.60	*	*	-19.80	0.36	0.19	0.27
R06	1.90	3.59	*	*	-19.59	0.32	0.17	0.17
R08	2.36	4.45	*	*	-20.09	0.32	0.17	0.18
R10	1.24	2.34	*	*	-19.58	0.34	0.18	0.19
R11	1.77	3.34	*	*	-21.15	0.35	0.19	0.47
R12	2.07	3.91	*	*	-20.51	0.37	0.20	0.31
S07	2.02	3.81	0.33	7.1	-19.64	0.24	0.13	0.13
S08	2.41	4.55	0.34	8.3	-20.22	0.33	0.17	0.19
S09	2.53	4.77	0.34	8.7	-20.33	0.55	0.29	0.34
S11	2.24	4.23	0.30	8.7	-19.85	0.43	0.23	0.25
S13	1.85	3.49	*	*	-20.28	0.45	0.24	0.39
T08	2.37	4.47	*	*	-20.38	0.44	0.23	0.29
T09	2.30	4.34	*	*	-20.71	0.56	0.30	0.46
T10	1.80	3.40	0.25	8.4	-20.66	0.37	0.20	0.20
T12	1.40	2.64	0.15	10.9	-21.33	0.51	0.27	0.44
T14	1.45	2.74	*	*	-21.02	0.33	0.17	0.22
U09	2.13	4.02	*	*	-20.97	0.84	0.44	1.07
U11	1.87	3.53	*	*	-21.46	0.30	0.16	0.19
U15	1.35	2.55	*	*	-20.81	0.28	0.15	0.19
NW24	2.12	4.00	0.25	9.9	-21.18	0.62	0.33	0.81
YY01	1.66	3.13	0.19	10.2	-21.04	0.77	0.41	1.17
YY02	2.31	4.36	0.27	10.0	-21.16	0.53	0.28	0.92
YY03	1.59	3.00	0.18	10.3	-21.57	0.91	0.48	1.12
YY04	2.23	4.21	*	*	-21.06	0.70	0.37	0.90

Appendix C1. Concentration of individual PCB congeners in total sediment samples. Concentrations are in pg g^{-1}.

CONGENER

Sta	28	52	101	118	153	138	180	TICES	18	15	54	31
G07	37	45	49	59	101	93	124	508	15	194	*	*
G09	8	10	5	7	6	8	6	50	*	*	*	*
G11	70	46	36	74	82	80	61	449	12	78	*	13
G13	110	177	306	275	220	252	80	1420	42	78	*	*
H08	10	9	10	16	20	18	15	98	7	*	*	*
H10	113	96	113	146	186	184	127	965	30	97	*	*
H12	122	68	120	143	156	161	103	873	33	86	*	11
J07	42	45	56	76	87	98	110	294	10	32	*	*
J09	7	7	5	4	7	7	4	41	*	11	*	*
J11	194	128	195	234	333	343	250	1677	53	172	*	26
J13	129	295	191	107	108	119	68	1017	64	97	*	8
K06	29	99	67	23	29	23	20	290	20	22	*	*
K08	7	7	5	8	9	10	13	59	*	11	*	*
K09	82	88	61	61	86	86	57	521	21	83	*	*
K10	200	212	259	322	468	467	359	2287	59	97	*	17
K11	140	92	162	185	242	258	200	1279	42	116	8	17
K12	85	54	77	111	135	134	80	676	18	39	*	*
L07	24	29	29	33	43	37	46	241	*	21	*	*
L08	11	15	14	27	33	35	44	179	3	11	*	*
L09	7	15	24	26	19	23	7	121	2	11	*	*
L10	12	15	16	17	24	24	21	129	*	*	*	*
L11	190	162	176	226	314	323	244	1635	65	271	17	23
L12	*	*	*	*	*	*	*	*	*	*	*	*
L13	140	108	166	172	212	193	110	1101	36	78	*	13
M06	*	*	*	*	*	*	*	*	*	*	*	*
M08	10	15	28	37	32	37	27	186	9	11	*	*
M09	13	22	24	71	37	38	40	245	*	11	*	*
M10	10	9	13	27	36	34	34	163	*	*	*	*
M11	79	64	75	115	156	156	157	802	20	65	*	8
M12	200	125	169	210	289	281	207	1481	52	145	*	29
N07	13	51	31	13	12	10	10	140	10	11	*	*
N08	*	*	*	*	*	*	*	*	*	*	*	*
N09	14	24	32	26	26	23	17	162	9	11	*	*
N10	25	51	53	39	147	238	92	645	69	129	*	22
N11	11	11	12	18	21	22	14	109	9	11	*	*
N12	130	108	135	164	193	197	171	1098	24	78	*	13
N13	270	139	252	296	369	357	247	1930	71	233	*	40
P06	13	11	10	15	17	17	17	66	3	11	*	*
P08	10	9	9	14	18	14	16	90	*	1	*	*
P09	13	18	24	23	27	24	21	150	*	11	*	3
P10	13	18	15	10	13	11	7	87	6	13	*	1
P11	1430	1080	1080	1030	1170	1250	840	7880	650	1740	40	250
P12	*	*	*	*	*	*	*	*	*	*	*	*
Q07	46	116	49	54	69	61	65	460	15	32	*	3
Q09	10	18	32	28	25	29	10	152	3	11	*	*
Q11	250	169	198	261	402	336	244	1860	*	233	34	40
Q13	83	58	86	88	140	130	93	678	25	65	*	11
R06	11	9	8	11	13	12	12	76	*	11	*	*
R08	10	13	12	16	18	18	20	107	7	33	*	*
R10	26	22	29	37	43	46	30	233	12	16	*	*
R11	450	250	281	322	481	457	333	2574	104	388	*	75
R12	195	108	149	174	236	223	165	1250	77	233	*	30
S07	7	7	4	5	7	7	6	43	*	*	*	*
S08	13	11	12	16	20	19	16	107	3	11	*	*
S09	100	58	90	112	147	145	86	738	35	65	*	14
S11	20	18	26	34	43	46	33	220	9	22	*	3
S13	290	139	171	250	330	307	226	1713	48	155	*	40
T08	175	122	131	203	225	220	187	1263	55	161	*	22
T09	95	62	77	97	140	145	107	723	18	39	*	13
T10	10	11	9	7	8	8	4	57	2	11	*	*
T12	244	164	186	193	275	249	218	1529	134	291	11	33
T14	146	58	64	83	108	103	74	636	60	97	*	14
U09	833	590	510	780	953	875	653	5194	377	388	*	145
U11	46	33	35	43	39	51	39	286	21	28	*	7
U15	138	199	188	143	154	152	88	1062	60	129	*	17
NW24	750	385	473	556	756	767	544	4231	268	581	*	134
YY01	1600	1027	1140	1651	1687	1792	1489	10386	754	1808	112	246
YY02	700	400	486	616	858	731	551	4342	309	620	34	107
YY03	860	616	612	694	891	907	551	5131	357	465	34	161
YY04	725	385	450	536	797	777	652	4322	298	581	42	117

Appendix C1. cont...(2)

CONGENER

Sta	49	44	74	70	95	60	92	89	99	97	87	136
G07	42	22	19	34	58	*	*	*	23	11	26	12
G09	*	5	2	3	8	*	2	*	2	*	*	5
G11	23	18	27	36	77	16	30	*	22	9	20	8
G13	66	90	77	149	262	57	90	165	131	81	162	26
H08	6	6	5	6	13	*	6	6	6	3	6	15
H10	39	37	56	67	116	34	37	49	68	22	59	35
H12	56	50	75	85	128	59	83	68	55	25	59	40
J07	33	22	22	34	51	18	25	*	27	15	31	27
J09	3	*	*	3	9	*	*	*	*	*	*	2
J11	87	77	100	135	197	80	120	103	85	60	93	111
J13	88	120	64	120	244	44	63	117	77	41	76	28
K06	23	39	12	33	90	7	16	32	23	14	27	2
K08	2	5	1	3	9	*	4	*	5	1	*	3
K09	36	32	39	51	71	31	36	30	23	16	26	*
K10	136	97	101	146	250	78	97	126	109	79	136	255
K11	70	66	81	108	193	62	99	92	71	41	84	100
K12	51	33	50	54	85	43	63	50	38	22	37	34
L07	15	13	12	17	29	8	10	14	15	5	16	9
L08	11	11	6	8	18	3	6	7	8	5	11	9
L09	3	6	3	9	20	2	4	10	11	8	14	2
L10	8	6	2	7	18	*	*	8	9	4	9	4
L11	133	90	117	135	285	72	120	112	82	45	96	*
L12	*	*	*	*	*	*	*	*	*	*	*	*
L13	66	69	77	99	162	62	90	92	71	41	78	54
M06	*	*	*	*	*	*	*	*	*	*	*	*
M08	6	12	5	13	24	7	8	14	12	9	18	7
M09	14	13	9	14	29	*	14	14	11	6	14	11
M10	14	11	3	5	15	3	7	6	6	*	6	7
M11	49	37	45	53	96	31	55	42	36	26	45	93
M12	122	82	113	129	241	83	127	112	82	39	85	110
N07	12	20	5	15	40	3	8	16	11	6	12	3
N08	*	*	*	*	*	*	*	*	*	*	*	*
N09	13	13	8	17	33	*	12	15	14	9	16	7
N10	33	*	*	8	64	*	*	33	45	15	26	7
N11	6	9	5	8	15	4	8	6	6	3	7	7
N12	94	60	117	99	139	51	90	73	65	36	70	64
N13	140	114	171	189	308	117	174	146	109	63	121	112
P06	6	4	6	8	15	4	6	5	6	3	6	5
P08	4	6	5	5	13	*	7	*	6	3	6	3
P09	10	9	8	14	22	6	9	13	11	6	11	8
P10	5	8	5	9	18	3	4	7	9	3	7	3
P11	960	740	900	900	1540	550	840	800	570	380	430	540
P12	*	*	*	*	*	*	*	*	*	*	*	*
Q07	26	18	22	26	45	15	22	19	23	8	21	13
Q09	6	11	5	14	24	3	8	14	12	9	16	3
Q11	164	114	153	171	308	101	150	151	87	81	125	152
Q13	39	37	41	56	103	31	48	44	32	19	42	30
R06	3	6	4	5	13	3	4	*	5	2	3	3
R08	4	7	5	8	15	4	9	6	6	3	6	5
R10	16	14	16	22	31	12	18	19	13	9	13	11
R11	224	180	236	270	462	161	248	280	123	113	161	335
R12	117	78	99	117	216	74	102	95	55	32	66	76
S07	*	3	1	3	9	*	3	*	3	*	*	*
S08	7	5	6	9	15	5	9	10	6	3	6	5
S09	59	40	53	64	109	36	48	58	41	26	45	28
S11	13	12	15	17	29	10	23	16	11	8	15	10
S13	133	102	162	180	262	105	174	129	87	54	90	76
T08	120	80	105	124	218	70	95	128	55	53	75	68
T09	62	45	59	68	100	39	72	62	38	18	39	36
T10	3	4	3	4	11	2	4	5	6	3	4	*
T12	171	116	152	180	269	110	135	193	95	67	95	93
T14	59	45	68	68	96	41	65	54	32	15	34	25
U09	572	350	480	495	898	305	390	523	272	225	293	420
U11	22	24	26	29	50	21	32	32	19	6	18	13
U15	75	83	71	105	212	45	80	93	77	45	81	23
NW24	429	285	405	450	655	273	375	420	245	113	215	220
YY01	1248	760	1050	1140	1899	689	1100	1300	690	450	663	680
YY02	452	300	396	468	708	273	372	504	218	108	218	224
YY03	562	348	522	558	832	211	252	616	262	216	304	560
YY04	409	255	405	428	616	263	345	560	245	113	205	210

Appendix C1 cont.... (3)

C O N G E N E R

Sta	110	77	82	151	149	134	114	146	132	105	141	158
G07	51	*	7	26	63	*	*	30	*	*	20	*
G09	6	*	*	*	5	*	*	3	*	*	*	*
G11	45	*	*	*	44	*	*	43	*	25	*	*
G13	218	28	39	43	154	15	*	88	95	116	43	22
H08	12	*	*	4	9	*	*	10	*	6	4	*
H10	120	*	*	51	126	*	*	76	*	63	35	*
H12	110	*	16	37	101	10	*	98	*	68	26	*
J07	56	*	8	21	55	*	*	36	23	28	16	5
J09	5	*	*	2	6	*	*	*	*	*	*	*
J11	167	*	27	88	235	24	*	152	*	105	68	24
J13	107	*	16	30	84	10	*	71	*	47	18	7
K06	32	*	4	12	29	3	*	7	10	*	6	*
K08	7	*	*	*	6	*	*	3	*	2	*	*
K09	57	24	8	20	58	*	*	63	33	32	15	*
K10	264	*	36	115	331	23	48	175	160	157	95	30
K11	150	*	25	48	151	9	*	122	*	*	45	18
K12	80	*	13	28	76	12	*	76	*	*	20	*
L07	26	*	*	11	25	*	*	15	*	10	8	*
L08	23	*	3	7	22	4	*	12	*	11	6	2
L09	25	*	3	4	14	*	*	5	*	10	4	*
L10	17	*	*	6	14	*	*	7	*	*	6	*
L11	182	190	29	64	189	18	26	180	113	124	62	22
L12	*	*	*	*	*	*	*	*	*	*	*	*
L13	141	*	22	41	126	12	*	110	*	88	32	12
M06	*	*	*	*	*	*	*	*	*	*	*	*
M08	31	*	4	7	14	*	*	10	*	18	6	2
M09	27	*	4	7	*	*	*	16	*	*	6	2
M10	23	*	4	9	26	*	*	13	*	*	7	2
M11	91	44	15	32	100	10	*	74	51	58	28	10
M12	172	*	27	57	173	19	*	172	*	123	53	15
N07	17	*	*	4	9	*	*	3	3	2	2	*
N08	*	*	*	*	*	*	*	*	*	*	*	*
N09	28	*	4	7	20	*	*	10	*	11	5	*
N10	48	*	15	*	158	*	69	229	137	*	*	*
N11	16	*	*	5	10	*	*	10	*	8	4	*
N12	141	*	20	46	120	*	*	134	*	67	34	*
N13	237	*	38	82	233	31	32	244	*	164	64	20
P06	10	*	*	4	10	*	*	8	6	7	4	*
P08	11	*	*	4	9	*	*	9	*	5	3	*
P09	23	*	3	7	19	2	*	11	*	*	5	*
P10	11	*	*	3	8	*	*	1	*	3	*	*
P11	900	660	120	370	950	210	140	990	530	540	280	80
P12	*	*	*	*	*	*	*	*	*	*	*	*
Q07	40	*	*	17	45	*	*	30	*	19	13	*
Q09	27	*	4	6	19	3	*	8	*	*	5	2
Q11	224	*	32	82	214	31	*	244	*	*	76	20
Q13	77	*	12	38	97	10	*	76	46	45	29	7
R06	8	*	*	4	8	*	*	6	*	*	2	*
R08	12	*	*	4	10	*	*	9	*	4	3	*
R10	31	*	*	11	29	5	*	23	*	19	8	2
R11	280	*	44	108	315	38	56	343	*	231	98	25
R12	138	62	22	59	161	21	22	146	55	107	50	14
S07	5	*	*	*	5	*	*	3	*	*	*	*
S08	12	*	*	4	9	*	*	11	*	10	4	*
S09	88	*	13	32	89	10	8	76	56	61	29	8
S11	30	*	5	11	30	3	*	21	*	*	8	3
S13	198	*	26	77	202	31	26	214	*	147	62	16
T08	131	133	19	47	142	23	24	137	76	96	48	12
T09	83	*	13	33	85	12	13	82	*	65	28	6
T10	8	*	*	*	6	*	*	4	*	2	*	*
T12	164	*	25	61	161	38	36	187	*	147	65	15
T14	75	19	10	28	74	10	19	74	41	58	20	5
U09	544	569	87	213	599	122	107	620	386	413	210	47
U11	39	*	6	16	34	*	7	39	*	32	11	*
U15	139	*	19	36	108	15	13	86	64	63	28	8
NW24	512	*	73	191	488	76	64	534	*	389	161	40
YY01	853	1568	174	408	1113	285	256	1200	752	784	457	107
YY02	486	*	75	184	491	110	102	549	*	428	174	40
YY03	448	*	*	204	567	110	115	622	*	260	190	48
YY04	464	*	65	179	488	76	96	534	*	420	161	40

Appendix C1 cont..... (4)

C O N G E N E R

Sta	129	187	183	128	185	174	177	171	156	173	201	169
G07	*	52	24	15	5	10	19	19	9	*	*	*
G09	*	3	*	*	*	*	*	*	*	*	*	*
G11	*	37	*	15	*	4	9	*	*	*	*	*
G13	17	48	26	55	*	8	21	22	24	*	*	*
H08	*	7	4	4	*	1	3	*	*	*	*	*
H10	*	86	46	37	*	15	35	*	22	*	*	*
H12	15	61	24	25	*	9	26	20	17	*	*	*
J07	*	33	15	19	*	7	13	19	*	*	*	*
J09	*	3	*	*	*	*	*	*	*	*	*	*
J11	19	151	53	53	15	42	56	35	34	*	19	2
J13	*	42	18	21	*	7	17	15	*	*	*	2
K06	*	9	5	4	*	2	3	3	*	*	*	*
K08	*	3	3	2	*	1	*	*	*	*	*	*
K09	*	31	16	16	*	6	13	13	*	*	*	*
K10	44	224	91	81	19	70	98	67	45	*	*	*
K11	17	87	33	45	10	22	39	32	*	*	17	2
K12	*	53	18	22	*	6	21	*	15	*	*	*
L07	*	16	10	8	*	2	5	*	5	*	*	*
L08	*	11	6	7	*	2	5	*	4	*	*	*
L09	*	3	3	5	*	1	*	*	*	*	*	*
L10	*	10	7	6	*	2	4	*	*	*	*	*
L11	22	124	47	68	11	30	48	41	26	*	25	4
L12	*	*	*	*	*	*	*	*	*	*	*	*
L13	17	71	26	33	8	10	30	22	*	*	*	2
M06	*	*	*	*	*	*	*	*	*	*	*	*
M08	*	9	7	8	*	2	3	4	4	*	*	*
M09	*	11	6	7	*	2	5	6	*	*	*	*
M10	*	13	7	7	*	3	6	5	*	*	*	*
M11	11	59	24	27	6	13	25	26	15	*	*	2
M12	27	112	41	47	12	20	43	34	*	*	26	5
N07	*	3	*	2	*	*	*	*	*	*	*	*
N08	*	*	*	*	*	*	*	*	*	*	*	*
N09	*	9	5	5	*	1	3	*	3	*	*	*
N10	*	8	49	104	*	*	*	*	*	*	49	*
N11	*	9	5	4	*	1	3	*	2	*	*	*
N12	*	78	37	30	*	12	32	36	*	*	*	*
N13	35	143	51	60	15	20	55	45	*	*	34	8
P06	*	8	4	3	*	1	2	3	*	*	*	*
P08	*	8	4	4	*	1	3	*	2	*	*	*
P09	*	11	5	5	*	2	4	5	*	*	*	*
P10	*	5	*	*	*	1	*	*	*	*	*	*
P11	170	510	180	160	70	90	180	160	*	*	150	80
P12	*	*	*	*	*	*	*	*	*	*	*	*
Q07	*	29	15	13	*	5	8	15	*	*	*	*
Q09	*	7	5	6	*	1	2	*	3	*	*	*
Q11	35	138	51	55	19	24	60	54	*	*	34	12
Q13	15	59	21	19	*	8	23	19	*	*	*	3
R06	*	6	3	2	*	1	1	*	*	*	*	*
R08	*	8	4	4	*	1	3	4	*	*	7	*
R10	3	17	9	7	*	3	6	7	*	*	*	1
R11	65	207	73	75	24	40	86	67	*	*	53	15
R12	26	90	33	38	10	16	37	27	*	*	21	8
S07	*	3	*	*	*	*	*	*	*	*	*	*
S08	*	9	4	4	*	1	3	4	*	*	*	*
S09	15	58	21	25	*	8	25	19	19	*	*	3
S11	*	16	7	7	*	3	7	6	*	*	*	1
S13	35	124	44	45	*	20	46	45	29	*	*	12
T08	25	90	27	40	11	18	35	26	*	*	28	8
T09	17	58	26	22	*	10	23	22	*	*	*	4
T10	*	2	*	*	*	*	*	*	*	*	*	*
T12	60	109	36	34	12	20	37	39	22	13	*	35
T14	*	42	18	15	*	7	17	19	*	*	*	3
U09	131	376	110	133	44	80	146	105	*	46	*	47
U11	9	25	13	9	*	4	8	10	*	*	*	1
U15	15	50	18	25	*	8	21	19	*	*	*	2
NW24	130	299	128	113	*	50	126	113	*	*	*	30
YY01	261	721	219	250	114	147	276	270	*	84	196	120
YY02	122	313	102	100	38	40	129	108	60	*	67	40
YY03	104	359	131	70	53	64	147	108	*	*	101	40
YY04	109	311	128	113	*	60	126	113	*	*	*	30

Appendix C1 cont.... (5)

C O N G E N E R

Sta	199	196	189	195	194	205	206	209
G07	35	32	*	11	26	7	19	*
G09	1	*	*	*	1	*	*	*
G11	22	11	*	*	12	*	*	9
G13	26	19	*	5	14	*	15	12
H08	5	4	*	*	3	2	3	2
H10	55	39	*	10	33	*	28	11
H12	39	23	*	9	23	7	21	26
J07	24	16	*	5	13	8	12	13
J09	*	*	*	*	1	*	*	*
J11	86	53	8	19	53	11	29	28
J13	28	18	*	7	16	5	15	21
K06	4	3	*	*	2	2	2	2
K08	2	*	*	*	1	*	*	*
K09	24	18	*	7	15	7	11	13
K10	159	118	*	42	93	25	46	29
K11	59	37	*	17	37	12	30	28
K12	33	23	*	8	18	8	15	32
L07	11	7	*	*	6	4	8	5
L08	7	6	*	2	4	4	4	6
L09	1	*	*	*	1	*	*	*
L10	8	6	*	2	4	*	*	*
L11	79	65	10	23	54	13	30	39
L12	*	*	*	*	*	*	*	*
L13	42	30	*	13	25	8	15	28
M06	*	*	*	*	*	*	*	*
M08	5	4	*	*	2	2	3	2
M09	8	7	*	2	5	3	5	3
M10	9	6	*	2	6	2	4	2
M11	40	31	4	11	27	7	19	21
M12	72	57	*	18	45	12	32	40
N07	1	*	*	*	1	*	*	*
N08	*	*	*	*	*	*	*	*
N09	6	4	*	1	3	2	3	4
N10	*	*	*	*	14	*	*	4
N11	7	6	*	1	3	1	4	3
N12	53	35	*	10	31	10	30	37
N13	92	63	*	23	55	16	37	55
P06	4	3	*	*	2	2	3	1
P08	5	4	*	*	3	2	3	2
P09	8	6	*	1	4	2	4	3
P10	2	*	*	*	1	*	*	*
P11	400	300	60	120	220	*	150	200
P12	*	*	*	*	*	*	*	*
Q07	20	13	*	3	9	5	9	8
Q09	4	3	*	*	2	*	2	1
Q11	88	70	*	29	62	20	44	60
Q13	33	23	*	9	21	5	15	21
R06	3	2	*	*	2	*	3	3
R08	6	4	*	*	3	2	3	5
R10	13	9	*	3	7	3	7	9
R11	149	109	24	42	90	25	65	86
R12	59	47	10	18	38	10	30	44
S07	*	*	*	*	1	*	*	*
S08	6	4	*	1	3	1	3	5
S09	35	29	*	12	25	7	19	29
S11	11	9	*	3	7	2	4	6
S13	75	60	*	18	48	16	37	55
T08	64	45	8	23	39	11	28	54
T09	40	32	*	12	28	8	19	32
T10	1	*	*	*	1	*	*	*
T12	80	59	18	21	50	12	32	52
T14	28	20	*	7	17	*	12	21
U09	293	216	41	100	168	44	111	253
U11	19	14	*	3	11	*	11	12
U15	31	22	*	8	18	*	15	19
NW24	209	157	37	59	126	41	93	138
YY01	557	408	82	182	320	77	222	445
YY02	220	168	39	62	139	40	104	156
YY03	246	189	39	73	154	40	104	166
YY04	231	175	37	65	144	49	93	161

Appendix C2. Total PCB concentrations (tPCB) and normalized total concentrations with aluminium (PCB/Al) and total organic carbon (PCB/OC). The units of concentration are pg g^{-1}, ng g^{-1} Al and ng g^{-1} C respectively.

Station	tPCB	PCB/Al	PCB/OC
G07	1444	120	488
G09	96	12	49
G11	1114	82	254
G13	4069	299	822
H08	266	29	124
H10	2599	200	614
H12	2597	173	547
J07	1306	107	370
J09	86	10	42
J11	4832	247	1015
J13	2890	172	701
K06	794	85	555
K08	133	18	74
K09	1516	153	702
K10	6755	420	1672
K11	3621	168	621
K12	1870	110	400
L07	607	58	240
L08	454	45	164
L09	305	36	150
L10	303	38	137
L11	5256	229	916
L12	*	*	*
L13	3153	155	553
M06	*	*	*
M08	488	56	262
M09	537	60	253
M10	402	41	169
M11	2384	170	631
M12	4486	218	803
N07	359	39	160
N08	*	*	*
N09	473	55	191
N10	1980	222	786
N11	315	34	130
N12	3164	198	933
N13	5990	276	1128
P06	273	30	177
P08	231	26	128
P09	421	47	*
P10	223	27	114
P11	28680	896	3097
P12	*	*	*
Q07	1084	90	442
Q09	401	47	171
Q11	5702	324	1080
Q13	2032	143	755
R06	192	20	110
R08	321	40	176
R10	687	71	356
R11	8767	404	1861
R12	4136	281	1334
S07	82	12	64
S08	305	38	165
S09	2278	184	678
S11	633	59	257
S13	5218	290	1324
T08	4160	396	1444
T09	2204	139	480
T10	143	17	72
T12	5314	262	1222
T14	2068	142	932
U09	17688	543	1658
U11	967	93	506
U15	3108	203	1644
NW24	13676	505	1697
YY01	37883	945	3232
YY02	14339	480	1562
YY03	16143	451	1440
YY04	13882	477	1534

APPENDIX D. ABBREVIATIONS

$\delta^{13}C$ = carbon isotopic ratio in the sample in relation to the carbon isotopic ratio of a standard.

δ-MnO_2 = one form of amorphous manganese oxide mineral.

r = Pearson's correlation coefficient.

r^2 = coefficient of determination.

p = two-tailed significance level for the correlation coefficient.

s.d. = standard deviation.

r.s.d. = relative standard deviation.

Z = similarity coefficient.

OCN = octachloronaphthalene.

RRT = relative retention time.

ECD = electron capture detector.

DB-5 = stationary phase with 95% dimethyl-(5%)-diphenyl-polysiloxane.

DB-1701 = stationary phase with 86% dimethyl-(14%)-cyano-propylphenyl-polysiloxane.

K_d = distribution coefficient between a solid and an aqueous phase.

K_{ow} = octanol-water partition coefficient.

K_{oc} = distribution coefficient between sedimentary and aqueous phases normalised with the organic carbon content.

K_h = distribution coefficient between the dissolved humic phase and the aqueous phase.

MAFF = Ministry of Agriculture, Fisheries and Food (U.K.)

NWWA = North West Water Authority (U.K.)

ICES = International Council for the Exploration of the Sea.

IUPAC = International Union of Pure and Applied Chemists.