

# CHEMICAL DYNAMICS IN NORTH SEA ESTUARIES AND PLUMES

by

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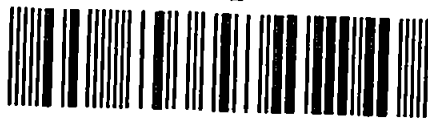
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## DECLARATIONS

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other C.N.A.A. or University award. This study was financed with the aid of a studentship from the Natural Environment Research Council, and carried out in collaboration with Plymouth Marine Laboratory.

A programme of advanced study was undertaken, which included a final year honours course in colloid chemistry, supervised micro and mainframe computer instruction, and a post-graduate course on analysis and hazard assessment of marine pollution.

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

### Publications

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Chemistry *R and D Topics in Analytical Chemistry*. Plymouth Polytechnic, July 1988.

Turner, A., Millward, G.E., Bale, A.J. and Glasson, D.R. Particulate Trace Metals in the Humber Estuary and its North Sea Plume. Oral presentation, EBSA 18 Symposium *North Sea - Estuaries Interactions*. Newcastle University, August-September 1988.

Millward, G.E., Turner, A., Glasson, D.R. and Glegg, G.A. Intra- and Inter-Estuarine Variability of Particle Microstructure. Oral presentation, International Symposium *The Fate and Effects of Toxic Chemicals in Large Rivers and Their Estuaries*. Quebec City, October 1988.

Turner, A. Trace Metals in Sediments from the Clyde, Elbe, Humber, Mersey and Tamar Estuaries. Invited lecture delivered to the Institut für Hydrobiologie und Fischereiwissenschaft. Hamburg University, November 1988.

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North Sea Project Workshop. POL Bidston, February 1990.

Turner, A., Millward, G.E., Bale, A.J., Morris, A.W. and Clifton, R.J. The Partition of Radiotracers Between Dissolved and Particulate Phases in the North Sea. Oral presentation, NERC Geocolloids Meeting. Polytechnic South West (Plymouth), April 1990.

Turner, A. *Radiochemical Studies*. Oral Presentation, North Sea Project Workshop. POL Bidston, May 1990.

Millward, G.E., Turner, A., Bale, A.J., Clifton, R.J. and Morris, A.W. Heterogeneous Chemical Reactivity of Radioisotopes in North Sea Estuarine Plumes. Poster presentation, European Research Conference *Particles in Natural Waters and in Water Technology*. Il Cioco (Italy), September 1990.

Turner, A., Millward, G.E., Bale, A.J., Clifton, R.J. and Morris, A.W. The Solid-Solution Partitioning of Radiotracers in the North Sea. Poster presentation, Challenger Society *U.K. Oceanography '90*. Polytechnic South West (Plymouth), September 1990.

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### **External Visits**

*University of Hull, Department of Zoology.* Survey planning of Humber Estuary. November 1987.

*Southampton University, Department of Oceanography.* Co-ordination of North Sea Project sampling campaigns; processing and analysis of particulate trace metals using ultra-clean facilities; preparations for conference presentations. April and July 1988, August 1989, February and August 1990.

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*Yorkshire Water Authority, Leeds.* Plans for parallel sampling/monitoring during Humber plume cruises; data acquisition. September 1988.

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# CHEMICAL DYNAMICS IN NORTH SEA ESTUARIES AND PLUMES

Andrew Turner

## ABSTRACT

Observational and experimental studies have been undertaken in the southern North Sea environment, including five major estuaries (Humber, Thames, Scheldt, Weser and Elbe), with the aim of elucidating the mechanistic and kinetic details of trace metal reactivity required for the refinement of pollutant transport models.

The results of a systematic investigation of suspended particle characteristics (BET specific surface area and porosity, carbon content, Fe and Mn oxide coatings) indicated that, although there exists significant yet explicable variability among the North Sea estuaries, such compositional factors do not exert an observable influence on solid-solution interactions. Furthermore, chemical reactivity was not usually demonstrable from observations of leachable particulate trace metals as phase interactions impart relatively little influence on their concentrations; particulate metal distributions therefore generally conformed with mixing of fluvial and marine material unless perturbed by major anthropogenic sources as in the Humber.

Solid-solution redistributions were revealed by following the partitioning of artificial radiotracers in a series of carefully controlled experiments in which salinity and suspended solids concentration gradients were simulated by mixing river and sea water end-member samples. Relationships between salinity and the solid:solution concentration of radiotracers as quantified by a distribution coefficient ( $K_D$ ) indicated substantial desorption from particles of  $^{109}\text{Cd}$  and  $^{137}\text{Cs}$ , conservative behaviour of  $^{65}\text{Zn}$ , and oxidative removal from solution of  $^{54}\text{Mn}$ .

Radiochemical techniques applied *in situ* to study solid-solution partitioning in the southern North Sea established a more significant role of particle composition (in particular, estuarine-derived versus plankton-rich material) in regulating trace metal behaviour in offshore waters. This finding was corroborated by distinct seasonal contrasts in measured particulate metal concentrations; whereas most metals (Fe, Mn, Cu, Pb, Zn) were enriched during winter when detrital and terrigenous components from fluvial/resuspension inputs dominate, Cd was elevated during summer in tandem with amplification of the biomass.

These results provide a valuable basis for both future long-term pollutant monitoring programmes, and the conceptual development of estuarine chemical flux models, specifically the incipient Plymouth Marine Laboratory model of the Humber plume.

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# CHAPTER 1: INTRODUCTION

## 1.1: NORTH SEA POLLUTION

The North Sea supports a diversity of social and economic interests, including the exploitation of a rich fishery stock and abundant oil and gas fields. However, associated with runoff from a densely populated and highly industrialized catchment is an apparently ceaseless influx of waste materials. The North Sea has also been regarded as a convenient recipient and effective disperser of dumped industrial and sewage wastes and an ideal site for organochlorine incineration.

The declining health of North Sea waters has reflected its inability to tolerate an overwhelming anthropogenic burden. The balance of the ecosystem is particularly sensitive to these disturbances and concern was voiced over this issue at the *Second International Conference on the Protection of the North Sea* (Scientific and Technical Working Group, 1987). For example, an increase in the supply of nutrients to the North Sea has enhanced phytoplankton production and caused a shift in species population including those generating toxic substances that can be transmitted to higher trophic levels. More specifically, the demise of a large bloom in the German Bight in September 1981 caused a severe O<sub>2</sub> depletion and consequent extensive mortality of benthic organisms (Earll, 1987). Fish diseases have frequently been linked with regions of elevated metal concentrations, and in particular in the vicinity of dumpsites, although causal relationships have not yet been clarified (Bucke and Watermann, 1988; Dethlefsen, 1988).

Pollution prevention of the north east Atlantic (encompassing the North Sea) was the objective of two conventions introduced in the early 1970s; viz. the Oslo and Paris Conventions relating to offshore dumping and land-based discharges respectively (Grogan, 1985). However, a recent spate of publicity and pressure from environmental groups has called for more immediate and effective remedial action. Thus, at the *Second International Conference on the Protection of the North Sea*, Ministers agreed to reduce drastically the inputs of dangerous

substances (Ministerial Declaration, 1987).

The response of the scientific community has culminated in the initiation of large-scale multi-disciplinary investigations such as the *Circulation and Pollutant Transfer in the North Sea* project of Hamburg University (Sündermann, 1988; Sündermann and Degens, 1989) and the water quality modelling programmes of Delft Hydraulics Laboratory (van Pagee *et al.*, 1986 de Ruijter *et al.*, 1987; van Pagee *et al.*, 1988; see also Taylor, 1987). In the U.K., several oceanographical institutes are currently engaged in the *North Sea Project*, sponsored by the Natural Environment Research Council (NERC).

## 1.2: THE NERC NORTH SEA PROJECT

The ultimate aim of the NERC *North Sea Project* (1987-1992) is the development of a prognostic three-dimensional water quality transport model of the southern North Sea. Parallel objectives involve defining seasonal cycles and elucidating non-conservative processes.

Observational studies necessary to validate the model were undertaken on board *RRS Challenger* during 12-day survey cruises every month for 15 months (August 1988-October 1989). Master variables and current profiles were recorded underway, and water samples (and occasional atmospheric and sediment core samples) for chemical analyses were taken at discrete spatial intervals. Each survey cruise was interspersed with 14-day process cruises aimed at more detailed study of specific phenomena such as dispersion of estuarine discharges, frontal dynamics, metal-bloom interactions, sediment resuspension, sand wave transport and air-sea gas exchange.

However, some more fundamental problems must be addressed. For instance, it is implicit that a 50% reduction of pollutant supply to rivers and estuaries decided at the *Second International Conference on the Protection of the North Sea* (Ministerial Declaration, 1987) is matched by an equivalent reduction in supply to North Sea waters, and this is difficult to verify, as estuarine chemistry is so poorly defined.

### 1.3: THE PHYSICAL AND CHEMICAL NATURE OF ESTUARIES

An estuary may be defined as a partially enclosed water body having free connection with the open sea and influenced by fresh water runoff from land drainage (Bowden, 1967; Pritchard, 1967). Although this description fails to emphasize certain fundamental hydrological qualifications and is therefore unrealistic for estuaries globally (Fairbridge, 1980), it suffices as a physical definition for the estuaries under examination in this work.

Estuaries have been conveniently classified in terms of physiography (Dyer, 1973; Fairbridge, 1980) and on the basis of circulation and mixing characteristics, hence vertical salinity stratification (Pritchard, 1952; Hansen and Rattray, 1966; Bowden, 1967; Dyer, 1973) which is controlled by river flow and tidal currents. Thus, river flow dominates in a *salt-wedge* estuary, giving rise to a sharp halocline, whereas tidal mixing dominates in a *well-mixed* estuary in which vertical salinity gradients are absent (Pritchard, 1952; Dyer, 1973); an intermediate situation arises in a *partially-mixed* type.

Likewise, from a chemical point of view, an estuary may be defined simply as a region in which sea water is diluted with fresh water from land drainage (Burton, 1976). The resulting sharp gradients in physico-chemical parameters of ionic strength (salinity), temperature, dissolved O<sub>2</sub> concentration, pH and redox potential, and compositional changes of suspended particulate matter, give rise to complex behaviour of many chemical constituents such as nutrients, organic matter and trace metals. Natural estuarine circulation processes also generate a pronounced region of high suspended solids concentration known as the turbidity maximum zone or TMZ (Inglis and Allen, 1957; Postma, 1967; Schubel, 1969; Allen *et al.*, 1980; Jouanneau and Latouche, 1981; Wellershaus, 1981), which is of special interest to the internal cycling of these constituents (Elbaz-Poulichet *et al.*, 1984; Ackroyd *et al.*, 1986; Donard and Bourg, 1986; Morris, 1986; Cossa and Noël, 1987).

It is perhaps more appropriate for estuarine chemists to divide an estuary

into two zones (Bourg, 1988) on the basis of the evolution of the major dissolved components (Dyrssen and Wedborg, 1980; Millero, 1981a; Mantoura and Morris, 1983). The demarcation of the *mixing zone*, in which the relative contribution to salinity from the major anions and cations varies, and the *dilution zone*, in which the relative composition remains essentially constant, is conveniently the 1 ‰ isohaline (Bourg, 1988), and this should be considered as the true river water - ocean water (or fresh water - brackish water) interface (Morris *et al.*, 1978; Bourg, 1988). The chemical and biological significance of the very low salinity region (*mixing zone*) has been recognized in the Tamar Estuary (Morris *et al.*, 1978; Morris, 1986) in which, for example, a fivefold increase in dissolved Mn concentration and threefold reduction in dissolved Cu concentration were observed (Morris *et al.*, 1978).

#### 1.4: TRACE METALS IN ESTUARIES

Heavy metals have practically been defined from fundamental atomic chemistry theory on the basis of their position in the periodic table (Burrell, 1974) or their specific gravity (Martin and Coughtrey, 1982; Parker, 1984; Trevors *et al.*, 1986). Trace metals (or trace elements) are considered by biochemists as those elements essential to organisms for metabolism in extremely small concentrations (Stenesh, 1975; Allaby, 1983); Eisler (1981) has arbitrarily quantified *trace* as < 100 µg/g dry weight of organism. Bruland (1983) has discussed trace or minor elements occurring in sea water, presumably filtered, at concentrations < 1 part per million. However, in all scientific fields these terms have been treated synonymously and rather flexibly in order conveniently to encompass a wider variety of elements (including non-metals) of interest. In particular these elements have been referred to with toxicological and pollution connotations, and it would perhaps, therefore, be more desirable to classify metals on the basis of some (environmentally) relevant yet more specific concept. For example, Wood (1974) devised a scheme according to toxicity and availability, and Nieboer and Richardson



(1980) classified metals on the basis of their affinity for different ligands, which was related to their chemical behaviour in biological systems. Throughout this work, however, the term *trace metal* has been adopted and conveniently describes all metals under investigation including the more abundant metals, Fe and Mn, which are usually discussed in the context of particle composition.

In the aquatic environment trace metals exist in solution as free (hydrated) ions, or complexed by inorganic anions (e.g.  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ) and organic ligands (e.g. fulvic and humic acids), and in solid form in various associations (Section 1.6). The operational distinction between the two phases of solid and solution is commonly related to size (0.4 or 0.45  $\mu\text{m}$ ), practical separation being achieved through filtration. Colloidal sized particles are consequently included in the solution phase.

It is because of their persistence, toxicity and accumulation in the aquatic food chain (Bryan, 1976; Davies, 1978; Wood and Wang, 1983) and their accelerated release to the hydrosphere through anthropogenic inputs (Förstner and Wittman, 1979; Förstner, 1980; Salomons and Eysink, 1979; Moore and Ramamoorthy, 1984; Salomons and Förstner, 1984) that trace metals have received a great deal of attention. These effects are compounded in estuaries where industrial and urban settlements are concentrated and productivity is high. Trace metal monitoring has thus become an integral component of estuarine water quality management programmes (Rickard and Dulley, 1983; Woodward, 1984; Sayers, 1986; Taylor, 1986; Leatherland and Halcrow, 1988; Head *et al.*, 1990; Müller *et al.*, 1990). Moreover, the behaviour and distributional features of trace metals in estuaries must be understood in order to determine fluxes to the oceans and refine geochemical mass balance models (Mackenzie and Garrels, 1966; Boyle *et al.*, 1974; Brewer, 1975; Turekian, 1977; Martin and Meybeck, 1979; Martin and Whitfield, 1983). Figure 1.1 schematically illustrates the pathways of trace metals in an estuarine environment. Natural weathering processes provide riverine and aeolian fluxes, and domestic waste disposal, refuse incineration, fossil fuel burning and the discharge of waste materials from metal refining, chemical

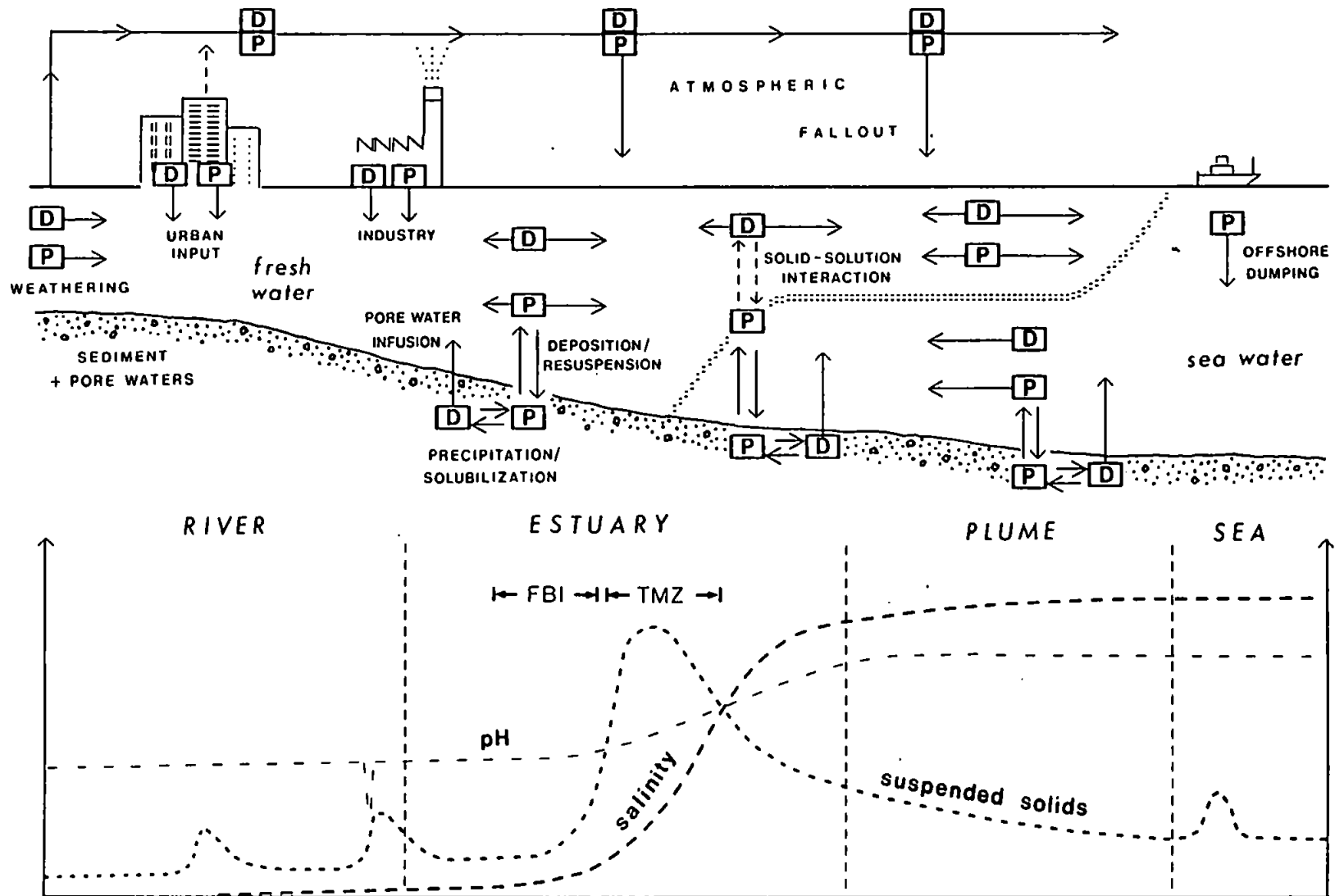


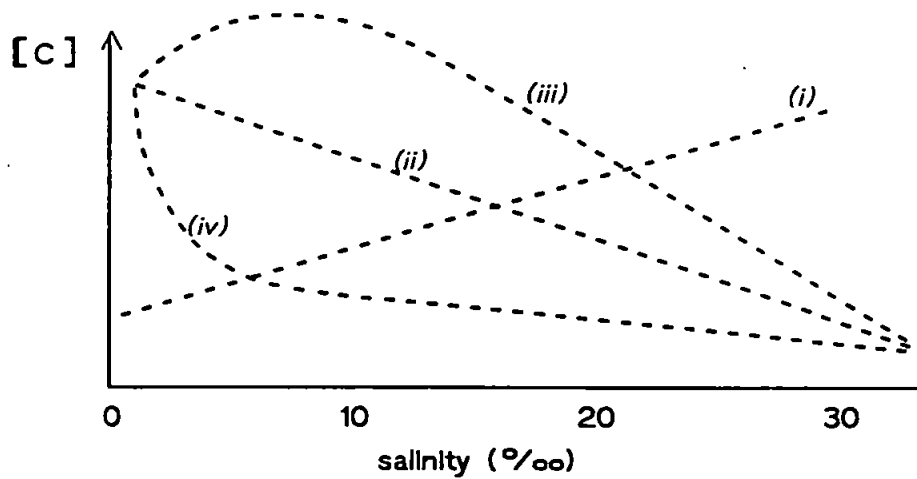
Figure 1.1: Schematic representation of the evolution of important master variables, and pathways of trace metals (D = dissolved; P = particulate) at the river-ocean boundary.

industries and cement production are important anthropogenic sources (Förstner, 1980; Hutton and Symon, 1986). A landward flux of material dumped offshore (industrial waste, dredged spoil and sewage sludge) may also contribute to the estuarine trace metal budget.

## 1.5: TRACE METAL REACTIVITY IN ESTUARIES

Chemical reactivity in estuaries results in trace metal speciation transformations, including dissolved-particulate interactions (Figure 1.1) involving sorption and ion exchange processes, as well as removal from solution by precipitation and flocculation. Such interactions have frequently been inferred circumstantially from field data manifested by deviations of dissolved constituents from simple two end-member mixing, *i.e.* a linear relationship with a conservative constituent such as salinity or chlorinity (Liss, 1976). It is implicit that a positive deviation necessitates some solubilization from the particles and a negative deviation some removal (scavenging) mechanism from solution. Commonly observed distributions of dissolved constituents are illustrated in Figure 1.2. Such simple interpretations are, however, restricted to systems for which subsidiary inputs are small and end-member concentrations fairly constant (Loder and Reichard, 1981; Mantoura and Morris, 1983; Schemel and Sharp, 1990). Subsidiary inputs could include release from pore waters (Elderfield and Hepworth, 1975; Evans *et al.*, 1977; Gobeil *et al.*, 1981; Morris *et al.*, 1982a; Emerson *et al.*, 1984; Keeney-Kennicutt and Presley, 1986) and direct anthropogenic discharges (Klinkhammer and Bender, 1981; Andreae *et al.*, 1983; Sanders, 1985; Paulson *et al.*, 1989; see Figure 1.1).

The large-scale removal of dissolved Fe on estuarine mixing (Figure 1.2) is the result of de-stabilization of Fe-humic colloids by the major sea water cations and subsequent flocculation (Eckert and Sholkovitz, 1976; Boyle *et al.*, 1977; Zhiqing *et al.*, 1987). However, such generalizations cannot be made for other metals, as it would appear (Figure 1.2) that their estuarine chemistries are more sensitive to



|                                       | Constituent, C    | Estuary                    | Reference   |
|---------------------------------------|-------------------|----------------------------|---|
| (i) Conservative, sea water source    | alkalinity        | Delaware                   | Sharp <i>et al.</i> (1982)                              |
|                                       | As                | Ogeechee, Satilla Savannah | Waslenchuk and Windom (1978)                            |
|                                       | Br/I              | Tamar                      | Upstill-Goddard and Elderfield (1988)                   |
|                                       | <sup>137</sup> Cs | Severn                     | Uncles (1979)   |
|                                       | F                 | Purna                      | Zingde and Mandalia (1988)                              |
| (ii) Conservative, river water source | Mo                | Southampton Water          | Head and Burton (1970)                                  |
|                                       | Cu                | outer Forth                | Balls and Topping (1987)                                |
|                                       | DOC               | Severn                     | Mantoura and Woodward (1983)                            |
|                                       | DOC, Mn, Zn       | Beaulieu                   | Holliday and Liss (1976);<br>Moore <i>et al.</i> (1979) |
|                                       | DOC, silicate     | Delaware                   | Sharp <i>et al.</i> (1982)                              |
|                                       | Mn, silicate      | St. Lawrence               | Subramanian and d'Anglejan (1976)                       |
|                                       | Ni                | Amazon plume               | Boyle <i>et al.</i> (1982)                              |
|                                       | nitrate           | Tamar                      | Morris <i>et al.</i> (1981)                             |
|                                       | Se                | Southampton Water          | Measures and Burton (1978)                              |
|                                       | Zn                | Rhine                      | Duinker and Nolting (1976)                              |
| (iii) Release to solution             | Cd                | Changjiang                 | Elbaz-Poulichet <i>et al.</i> (1987)                    |
|                                       | Cd                | Weser                      | Calmano <i>et al.</i> (1985)                            |
|                                       | Cu                | Ems                        | Duinker <i>et al.</i> (1985)                            |
|                                       | Cu                | Ogeechee                   | Windom <i>et al.</i> (1983)                             |
|                                       | Si                | Peconic                    | Wilke and Dayal (1982)                                  |
| (iv) Removal from solution            | Co, Fe, Mn        | Delaware                   | Sharp <i>et al.</i> (1982)                              |
|                                       | Colloidal Al,     | Patuxent                   | Sigleo and Helz (1981)                                  |
|                                       | C, Fe             |                            |   |
|                                       | Cu, Fe            | Rhine                      | Duinker and Nolting (1976;1977)                         |
|                                       | Fe                | Beaulieu                   | Holliday and Liss (1976)                                |
|                                       | Fe                | Peconic                    | Wilke and Dayal (1982)                                  |
|                                       | Fe                | US east coast estuaries    | Boyle <i>et al.</i> (1977)                              |
|                                       | Hg                | St. Lawrence               | Cossa <i>et al.</i> (1988)                              |
| Si                                    | Conwy             | Hydes and Liss (1977)      |   |

Figure 1.2: Examples of profiles of dissolved constituent concentration, [C], versus salinity.

a variety of phenomena. As an example, Cd behaves conservatively in the Elbe (Duinker *et al.*, 1982b) but is removed from solution in the Rhine Estuary (Duinker and Nolting, 1977). Release of Cd from particles in the Changjiang Estuary has been attributed to the formation of stable soluble chloro-complexes (Elbaz-Poulichet *et al.*, 1987), whereas solid-solution exchange in the Scheldt Estuary has been largely accounted for in terms of the evolution of its sulphide compound in response to the redox chemistry of the system (Duinker *et al.*, 1982a; Zwolsman and van Eck, 1990). Moreover, temporal intra-estuarine variability may be linked with the changing prevalent hydrological regime. This is sometimes manifested by a relationship between fresh water end-member concentration and river discharge (Waslenchuk, 1979; Windom *et al.*, 1983), or by different curvature in the longitudinal profile of the constituent concentration (Eaton, 1979; Huang *et al.*, 1988).

Estuarine trace metal behaviour is therefore very complex and, not surprisingly, poorly understood. A greater knowledge of specific processes has been derived from laboratory experiments performed under well-defined conditions. For example, Sholkovitz (1978) studied the nature and extent of flocculation of trace elements by mixing filtered river and sea waters. This approach has also been adopted in order to study the flocculation of rare earth elements (Hoyle *et al.*, 1984). Salomons (1980) investigated the adsorption of Cd and Zn onto River Rhine sediment in an artificial medium by varying the chlorinity, pH and sediment concentration, and Millward and Moore (1982) similarly studied Cu, Mn and Zn uptake by well characterized iron hydroxides in relation to ionic strength and pH.

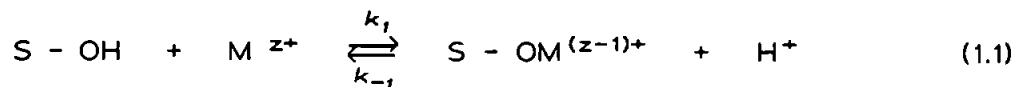
A further insight into estuarine chemical reactivity has been derived from the equilibrium speciation of trace metals in solution as predicted from thermodynamic theory (Mantoura *et al.*, 1978; Dyrssen and Wedborg, 1980; Millero, 1981b; Turner *et al.*, 1981). More recent speciation models have incorporated adsorption onto a solid phase in which surface sites are envisaged as conventional ligands (Bourg, 1983; Mouvet and Bourg, 1983; Bourg, 1987).

## 1.6: ESTUARINE PARTICULATE MATTER

The particulate phase obviously plays a complex yet key role in controlling the chemical behaviour and transport of trace metals in estuaries. The solid substrate is a heterogeneous composition of various mineral phases including clays, quartz, feldspars, and carbonates, derived from catchment and coastal erosion processes and atmospheric fallout, and is coated with Fe and Mn hydroxides and organics of both marine and terrestrial origin. Additional solid material is introduced anthropogenically through industrial and sewage discharges, and atmospheric deposition of fly ash and colliery waste, and produced *in situ* both chemically (flocculation) and biologically (primary production). Transport of the particulate phase is not, however, a simple function of water movement. Particles may be subject to many cycles of deposition and resuspension in an estuary, giving rise to a relatively long residence time and thereby enhancing potential for pollutant accumulation. For example, the flushing time (*i.e.* the time required to replace the accumulated fresh water at the rate of river discharge; Dyer, 1973; 1981) of the Tamar Estuary is typically no more than 20 days (Uncles *et al.*, 1983), whereas calculations indicate that particles remain for 1.4 years in the TMZ alone (Bale, 1987). Thus, particle reactive elements and hydrophobic compounds such as polychlorinated biphenyls have a considerably greater residence time in an estuarine system than soluble constituents.

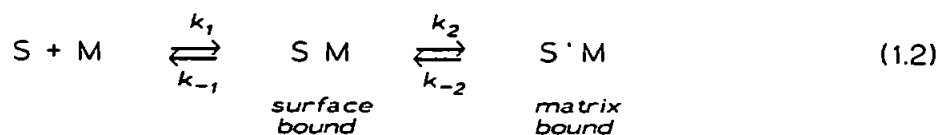
The surface properties of the particulate phase are particularly important in determining the behaviour and fate of trace metals in aquatic environments (Stumm and Morgan, 1981; Olsen *et al.*, 1982; Bourg, 1983; Loring *et al.*, 1983; Salomons and Förstner, 1984; Honeymann and Santschi, 1988; Clegg and Sarmiento, 1989) largely as a result of the sorptive properties of coatings of hydrous Fe-Mn oxides (Benjamin and Leckie, 1981; Lion *et al.*, 1982; Balistrieri and Murray, 1983; 1986; Davies-Colley *et al.*, 1984; Balls, 1986; Johnson, 1986; Adediran and Kramer, 1987; Aualitia and Pickering, 1987) and organic matter (Hunter and Liss, 1979; Tanoue and Handa, 1979; Balistrieri *et al.*, 1981; Tipping, 1981; Davis, 1982; Lion *et al.*, 1982; Hunter, 1983; Davies-Colley *et al.*, 1984;

Davis, 1984; Rashid, 1985; Adediran and Kramer, 1987). These surfaces contain ionizable functional groups, and the adsorption of a metal ion ( $M^{z+}$ ) can be described in terms of competition with protons for surface sites (S-OH) as follows (Schindler, 1975; Schindler *et al.*, 1976; Li, 1981; Mouvet and Bourg, 1983):



where S may be the Fe and Mn of oxide coatings or the C of carboxyl and hydroxyl groups of organic coatings, and  $k_1$  and  $k_{-1}$  are the reaction rate constants.

The specific surface area (SSA) provides a conceptual measure of particle reactivity (Martin *et al.*, 1986; Glegg *et al.*, 1987) and has been attributed largely to the chemical properties of these surface coatings. Furthermore, an extension of this technique has recently enabled particle porosity to be examined and its role in terms of the kinetic and mechanistic details of sorption reactions to be interpreted (Glegg *et al.*, 1987). These reactions consist of two distinct stages, whereby ions are initially adsorbed relatively rapidly onto the particle surface, followed by a slow internal migration into pores (Nyffeler *et al.*, 1984; Glegg *et al.*, 1987; Jannasch *et al.*, 1988; Moore and Millward, 1988). Soil scientists have also invoked these types of reaction, and it has been suggested that the relative rate of diffusion involved in the second stage is dependent on ionic diameter and binding strength of the metal (Brümmer *et al.*, 1988; Barrow *et al.*, 1989). Equation 1.1 can therefore be modified as follows (Nyffeler *et al.*, 1984; Moore and Millward, 1988):



where, for convenience, sites on the particle surface and within the particle matrix are represented by S and S' respectively.

There has, however, been lacking a systematic investigation into the surface microstructure of estuarine particles in conjunction with particulate trace metal concentrations, in particular those (available) metals located at the particle surface.

Investigations into particle-metal associations have tended to focus on total metal concentrations, *i.e.* metal concentrations determined by neutron activation, or by atomic absorption or any other suitably sensitive techniques following complete destruction of the particle matrix by treatment with HF. This approach has been criticized on the basis of removing detrital metals that are unable to participate in short-term biogeochemical reactions (Jones, 1978; Martin *et al.*, 1987; Tessier and Campbell, 1987; Yeats and Dalziel, 1987). A more environmentally significant fraction may be removed by treatment with a weaker acid attack (Duinker *et al.*, 1974; Malo, 1977; Loring, 1978; 1979; Luoma and Bryan, 1978; 1981; Langston, 1980; 1986). Such a leachable fraction is not necessarily indicative of a biologically available fraction as information is, unfortunately, lacking on the specific mechanisms by which organisms extract nutrients from solid material (Förstner, 1987). Nevertheless, metal bioavailability has occasionally been related to removal by mild leaches (Luoma and Bryan, 1981; Ray *et al.*, 1981; Diks and Allen, 1983). In particular, a combination of weak acid-reducing agent potentially provides a good indicator of a bioavailable fraction (Salomons and Förstner, 1980), especially if particle ingestion is the main accumulation route and acidic/reducing conditions prevail in the intestinal tract (Tessier and Campbell, 1987).

The application of sequential extractants of increasing strength designed to remove successively metals associated with various phases, such as carbonates, Fe-Mn oxides and organics, has enabled the particulate metal speciation to be investigated (Guy *et al.*, 1978; Tessier *et al.*, 1979; Calmano and Förstner, 1983; Rapin *et al.*, 1983; Rosental *et al.*, 1986; Kersten and Förstner, 1987; Martin *et al.*, 1987; Prohic and Kniewald, 1987), assuming each attack is both selective and specific to one phase.



## 1.7: ESTUARINE-COASTAL INTERACTION

Plumes are regions in which estuarine discharges impinge on the adjacent coastal waters and therefore represent the final stages of estuarine mixing, occurring outside the estuary proper. Although plume hydrography has been extensively documented, there exists very limited information on plume chemistry.

Low density, buoyant discharges emanating from a *stratified* or *salt-wedge* estuary and overlying denser ambient sea water beyond the estuary mouth, are the classic form of plume. Examples include the Amazon (Edmond *et al.*, 1981), Connecticut (Garvine, 1974), Fraser (Royer and Emery, 1985), Great Whale (Ingram, 1981), Mississippi (Wright and Coleman, 1971) and Po (Grancini and Cescon, 1973). Although the hydrographic conditions of the North Sea and its estuaries generally ensure a substantial degree of vertical mixing between river/estuary and coastal waters, it is worth considering the theoretical and observational aspects of buoyant plumes, as the inherent principles can be extrapolated to most forms of discharge.

Ideally, a buoyant plume thins vertically as it expands laterally in hyperbolic form (Defant, 1960; Officer, 1976; Bowden, 1983), the Coriolis force tending to deviate the plume anticyclonically. However, field observations have demonstrated an overwhelming influence of instantaneous and seasonal or more stochastic hydrographic and meteorological conditions on plume behaviour (Garvine, 1974; 1975; 1977; Stronach, 1981; Ingram and Larouche, 1987). Such short- and long-term variability has very significant implications for offshore pollutant dispersal. For example, a causal relationship exists between the hydrographic conditions within an estuary and those occurring in the outflow, and, as the former is known to influence the concentrations and behaviour of constituents in the estuary (Eaton, 1979; Waslenchuk, 1979; Yeats and Bowers, 1982; Mantoura and Woodward, 1983), it seems reasonable to assume that these effects are translated to the plume waters. Physical (mixing) timescales within the plume, which are sensitive to hydrodynamic factors, may impose important constraints on

chemical reactions which are kinetically slow, and hence affect the form (speciation) of contaminants dispersed offshore. Furthermore, the initial dispersion direction may be controlled to a large extent by meteorological conditions, although in the long-term averaged conditions will establish a prevalent regime of pollutant dispersal which is likely to be identified.

## 1.8: STUDY SITES

### 1.8.1: The North Sea

#### 1.8.1.1: Hydrography

The North Sea is a shallow shelf sea of surface area almost 600 000 km<sup>2</sup> according to the conventional boundaries (Eisma, 1987), and has free connection with North Atlantic waters to the north, and to the south via the English Channel. Additional, low salinity water enters from the Baltic Sea to the east, and from land drainage of northern Europe, and outflowing water is confined mainly along the Norwegian coast.

The residual surface current regime is principally wind driven, tidal and density effects playing a lesser role, and exhibits a general cyclonic gyre (Hill, 1973; Kautsky, 1973; Hill and Dickson, 1978; Lee, 1980; Backhaus and Maier-Reimer, 1983). Whereas in the winter the whole system is essentially well-mixed vertically, the combination of water depth and horizontal tidal stream velocity determines the vertical structure during the summer months. Thus, insolation creates a seasonal thermocline in the central and northern parts, although to the south the water column remains well-mixed (Pingree and Griffiths, 1978). The boundaries of these regimes are characterized by strong gradients in temperature and salinity (Simpson and Hunter, 1974; Pingree and Griffiths, 1978; James, 1983), and at the surface may cause a convergence of debris and host visible transitions in suspended solids concentration and colour (Eisma, 1987; Holligan *et al.*, 1989). The North Sea has been sub-divided on vertical structure criteria (Hill and Dickson, 1978), although other, more arbitrary schemes have been conceived. For example,

a water mass classification was devised by Laevastu (1963), which was modified by Lee (1980) in the light of more recent physical and chemical observations, and a series of nine rigid boxes has been described by ICES (see Oceanography Sub-Group, 1987; Reid *et al.*, 1988) according to their hydrodynamical and biological properties.

A summary of the principal hydrographical features of the North Sea is given in Table 1.1.

Table 1.1: Principal hydrographic features of the North Sea.

| Parameter  | Minimum   | Maximum                      |
|--|---|------------------------------|
| Depth (m)  | <10 (various coastal environments, especially in the south) | >200 (off Norwegian coast)   |
| Mean surface temperature (°C)                      |   |                              |
| <i>winter</i>                                      | 2.5 (German Bight)  | 7.0 (northern border)        |
| <i>summer</i>                                      | 12.5 (northern border)                                      | 18.0 (German Bight)          |
| Mean surface salinity (‰)                          |   |                              |
| <i>winter</i>                                      | 29 (German Bight)   | 35.3 (northern border)       |
| <i>summer</i>                                      | 30 (German Bight)   | 35.2 (northern border)       |
| Maximum tidal current speed - mean springs (knots) | 0.25 (Skagerrak)  | 4 (Orkney; off Elbe Estuary) |
| Tidal range - mean springs (m)                     | <0.5 (Skagerrak, extending into central regions)            | 6.5 (The Wash)               |
| Stratification                                     | (SE English coast; Rhine delta)                             | (off Norwegian coast)        |
| Residence time (days)                              | <200 (off Norwegian coast)                                  | 1500 (NE Scotland)           |

Information taken from Lee and Ramster (1981) except for residence time, *i.e.* time required for water in a particular locality to exit North Sea as predicted from a 2-dimensional model (Prandle, 1984).

### 1.8.1.2: Suspended Sediment

The sources of suspended sediment to the North Sea have been discussed and quantified by McCave (1973) and Eisma (1981). The major supply is associated with the inflowing water masses of the North Atlantic, Baltic and rivers. Smaller, yet substantial quantities are introduced through cliff erosion, notably along the coasts of Holderness and East Anglia (McCave, 1987), atmospheric fallout and primary production. Transport, although highly non-conservative, is generally linked with the water circulation and the resulting distribution exhibits an increase in concentration from north to south, with the highest concentrations (>10 mg/l) occurring off the East Anglian and Dutch coasts (Eisma and Kalf, 1987; Sündermann, 1988). The instantaneous and more localized distribution may also, under appropriate weather conditions, reflect resuspension of bottom deposits.

The budget is balanced by an export to the North Atlantic, and by deposition in the tidal flats of the Wash (Evans and Collins, 1975) and Wadden Sea (Postma, 1961), and offshore in the German Bight, Skagerrak/Kattegat and Norwegian Channel through the effects of suspended sediment accumulation by gyres and subsequent settling (Eisma and Kalf, 1987; Eisma and Irion, 1988).

Table 1.2: Elemental composition of suspended sediment material from the North Sea environment.

|               | %   |     |     |    |     | Reference                      |
|---------------|-----|-----|-----|----|-----|--------------------------------|
|               | Al  | Ca  | Fe  | Si | POC |                                |
| North Sea     | 3   | 5   | 3   | 12 | 4   | Nolting and Eisma (1988)       |
| Elbe Estuary  | 6   | 2.5 | 4   | 25 | 3   | Duinker <i>et al.</i> (1982b)  |
| Rhine Estuary | 3.8 | 6.5 | 3.9 | 16 | 4.6 | } Nolting <i>et al.</i> (1989) |
| Rhine River   | 3.6 | 4.8 | 5.1 | 13 | 4.5 |                                |
| Thames River  | 5.2 | 4.2 | 6.3 | -  | -   | Habib and Minski (1982)        |

Considering its sources, the bulk composition of North Sea suspended sediment should reflect that of estuarine material (Section 1.6), but with an enhanced biogenic component. The elementary composition of North Sea material has recently been investigated by Nolting and Eisma (1988), and the contents of the major elements are compared with those for selected river and estuarine environments of the North Sea catchment in Table 1.2. No significant differences are apparent, although North Sea POC values are low according to Sündermann (1988) who gives a mean of 8.0% for the winter and 21.0% for the summer, thereby also illustrating strong seasonality differences for this particular constituent. The distribution of the major components indicates an increase from north to south with the exception of Ca, which decreases in an easterly direction (Nolting and Eisma, 1988).

#### 1.8.1.3: Trace Metals

Although trace metal studies of the North Sea are not necessarily recent (Dutton *et al.*, 1973; see also Burton and Young, 1980), it is now accepted that early investigations of trace metals in sea water were flawed because of contamination during sampling and processing. With the development of ultra-clean shipboard facilities (Magnusson and Rasmussen, 1982; Freimann *et al.*, 1983; Mart *et al.*, 1985; Harper, 1988; Bordin *et al.*, 1988; Morley *et al.*, 1988) and improved analytical techniques (Danielsson *et al.*, 1978; Kremling *et al.*, 1983; Li and van den Berg, 1989), revised baseline concentrations for the North Sea have been substantially reduced (Table 1.3) and have reached a general consistency between different laboratories (Balls, 1985c).

Attention has focussed on the dissolved phase, and on specific regions of the North Sea such as the Southern Bight and bordering coastal environs (Duinker and Nolting, 1976; 1977; 1978; 1982; Duinker and Kramer, 1977; Nolting, 1986; Baeyens *et al.*, 1987a; 1987b) and the German Bight (Schmidt, 1980; Mart *et al.*, 1985; Mart and Nürnberg, 1986; Schmidt *et al.*, 1986). Estuaries are the largest land-based non-atmospheric source of trace metals to the North Sea (Grogan,

1985), and not surprisingly the concentrations of dissolved metals often bear some inverse relationship with salinity (Duinker and Nolting, 1982; Jones and Jeffries, 1983; Nolting, 1986; Kremling and Hydes, 1988). This effect is exemplified in Table 1.3, which demonstrates a progressive reduction of dissolved Cd, Cu and Pb concentration with distance from river sources, and is magnified in the form of trace metal/salinity fronts separating coastal and open sea waters (Balls, 1985b; 1985c). However, conservative mixing is not generally observed, and this can be attributed to the variety of end-members of diverse characteristics, as well as substantial inputs from the atmosphere (Cambray *et al.*, 1979; Balls, 1989b), pore waters (Kremling, 1983; Nolting, 1986; Westerlund *et al.*, 1986) and dumping activities (Murray *et al.*, 1980; Schmidt, 1980; Norton *et al.*, 1981; Spaans, 1987). Moreover, field studies suggest that both biological (Mart *et al.*, 1982) and geochemical (Brügmann *et al.*, 1985) removal processes are important offshore.

Table 1.3: Dissolved trace metal concentrations in various compartments of the North Atlantic showing a progressive reduction with distance from a large river source. Figures in parentheses demonstrate a reduction in baseline levels cited for the North Sea associated with improved sampling/analytical techniques.

|                     | $\mu\text{g/l}$ |       |      | Reference   |
|---------------------|-----------------|-------|------|---|
|                     | Cd              | Cu    | Pb   |   |
| North East Atlantic | 0.007           | 0.06  | 0.03 | Balls (1985b; 1985c); Brügmann <i>et al.</i> (1985)         |
| Open North Sea      | 0.016           | 0.25  | 0.06 | Brügmann <i>et al.</i> (1985); Kremling and Hydes (1988)    |
|                     | (0.1)           | (0.4) | -    | Jones <i>et al.</i> (1973; cited in Burton and Young, 1980) |
| Dutch/Belgian coast | 0.033           | 0.93  | 0.15 | Mart <i>et al.</i> (1982)                                   |
| Rhine Estuary       | 0.1             | 3     | 0.3  | Golimowski <i>et al.</i> (1990)                             |
| Rhine River         | 0.7             | 4.5   | 1.0  | van der Weijden and Middelburg (1989)                       |

Little information exists on suspended particulate trace metals in the North Sea. Both dissolved and particulate concentrations have been published for the U.K. coastal waters (Balls, 1985a) and the Southern Bight (Duinker and Nolting, 1977), and although such analyses were undertaken for the entire North Sea by Jones and Jeffries (1983), very few data are presented. The most comprehensive distributions of particulate metals are those total (elementary) contents given by Nolting and Eisma (1988) and Sündermann (1988; see also Kersten *et al.*, 1988), although no simultaneous sampling for dissolved analyses was undertaken. Distributions are ambiguous but the concentrations are higher in the northern regions, *i.e.* a reversal of the major element distributions (Nolting and Eisma, 1988).

### 1.8.2: North Sea Estuaries

The locations of the estuaries under investigation are shown in Figure 1.3, and their principal hydrographic features are given in Table 1.4. Despite their different

Table 1.4: Physical features of the five North Sea estuaries.

|         | Catchment<br>area<br>(km <sup>2</sup> ) | River flow,<br>mean (range)<br>(m <sup>3</sup> /s) | Tidal range<br>at mouth, n/s*<br>(m) | Vertical<br>stratification | Flushing<br>time<br>(days) |
|---------|---|--|--------------------------------------|----------------------------|----------------------------|
| HUMBER  | 27 000                                  | 246 (60-450)                                       | 3.5/6.2                              | well mixed                 | up to 40                   |
| THAMES  | 9 900                                   | 82 (9-210)   | 3.3/5.1                              | well mixed                 | 20-75                      |
| SCHELDT | 21 580                                  | 100 (40-350)                                       | 4.0                                  | well mixed                 | 60                         |
| WESER   | 44 304                                  | 326 (120-1181)                                     | 3.4                                  | well mixed                 | 2-50                       |
| ELBE    | 148 500                                 | 726 (145-3620)                                     | 2.5/3.3                              | partially stratified       | 4-7                        |

\*Neaps/springs.

**Sources of information.** HUMBER: Gameson, 1976; Woodward, 1984; Morris, 1988; calculations using model held by Yorkshire Water Authority. THAMES: Inglis and Allen, 1957; Department of Scientific and Industrial Research (1964); Morris, 1988. SCHELDT: Nihoul *et al.*, 1978 and references therein; Duinker *et al.*, 1979b. WESER: Lüneburg *et al.*, 1975; Duinker *et al.*, 1982c; Grabemann *et al.*, 1990; Müller *et al.*, 1990. ELBE: Duinker *et al.*, 1982b; Salomons *et al.*, 1987; Tent, 1987.

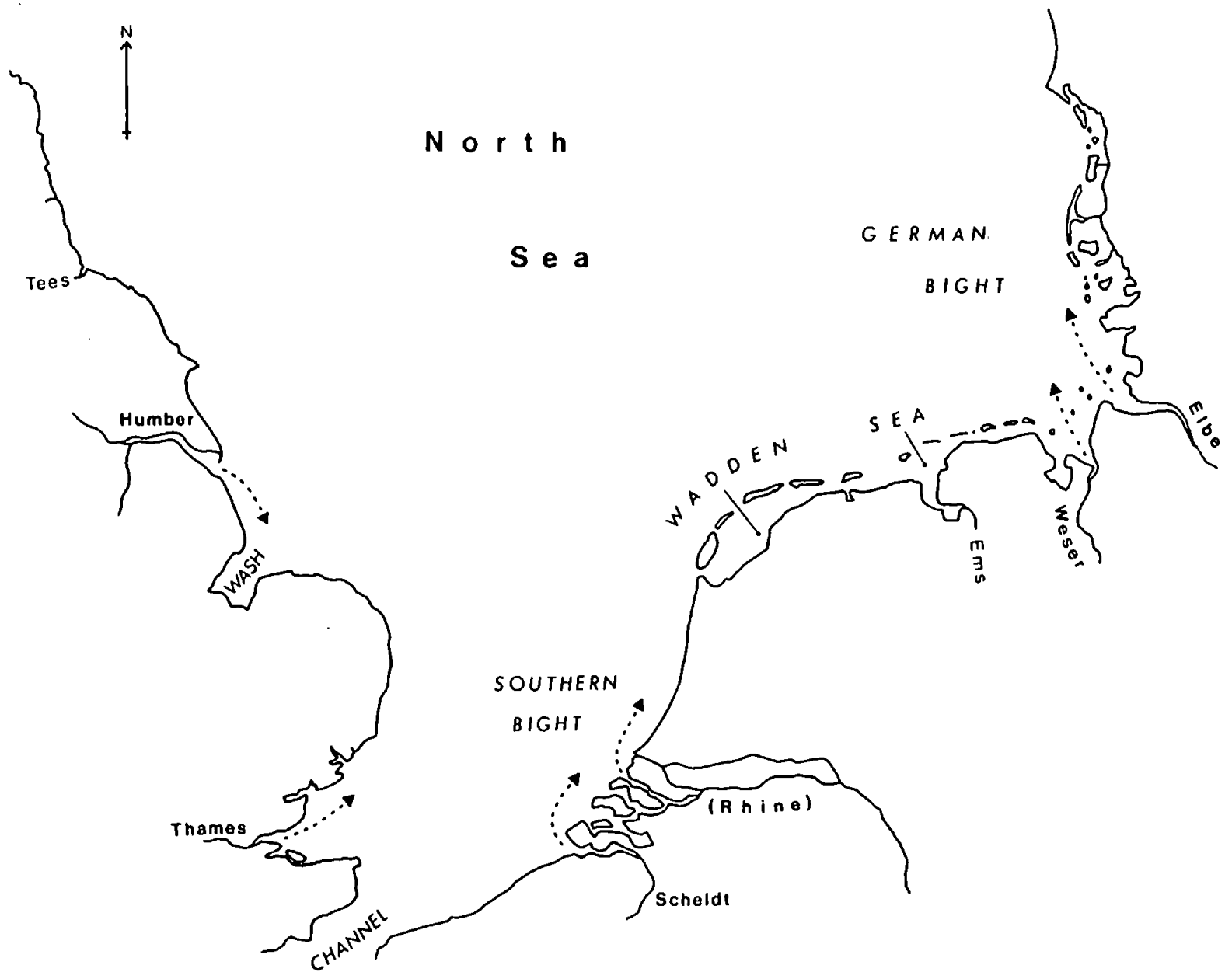


Figure 1.3: Location of the five estuaries in relation to the southern North Sea. Arrows indicate initial direction of plume dispersion.



sizes, in terms of catchment area or fresh water discharge for example, these estuaries are physiographically and hydrographically similar; thus they fit the description of shallow coastal plain type estuaries (Dyer, 1973; Fairbridge, 1980), and are classified as *partially-/well-mixed* (Pritchard, 1952). This is in contrast to the largest North Sea estuary of the Rhine, in which a large river flow and small tidal range create strong vertical salinity stratification (Duinker *et al.*, 1979b). The flushing time is short (only a few days; Duinker *et al.*, 1979b) and is therefore likely to impose important restraints on chemical reactions which are kinetically slow. Furthermore, the disruption of natural estuarine circulation by extensive channeling has prevented the development a TMZ (Eisma and Irion, 1988).

Table 1.5: Previous investigations into leachable metal fractions of suspended particulate matter in North Sea estuaries.

| Estuary                | Sampling logistics  | Sample pre-treatment   | Reference  |
|------------------------|---|--|--|
| Göta                   | 3 axial profiles;<br>S=0-25‰  | unfiltered sample, 0.015M HNO <sub>3</sub><br>+0.01M H <sub>2</sub> O <sub>2</sub> at 120°C for 1 hour   | Danielsson <i>et al.</i><br>(1983)               |
| Elbe/<br>Weser         | axial profile;<br>S=0-27‰   | centrifuged or filtered<br>a) 0.1M NH <sub>2</sub> OH·HCl+0.01M HNO <sub>3</sub> ,<br>12 hours shaking<br>b) 0.2M C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> +0.2M C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> ,<br>24 hours shaking | Schoer <i>et al.</i><br>(1983)                   |
| Scheldt                | 2 anchored tidal<br>stations  | retention on 0.45 µm filter, low<br>temperature ash, HCl (pH 2)  | Valenta <i>et al.</i><br>(1986)                  |
| Elbe                   | axial profile;<br>S=0-32‰   | acidify unfiltered sample with HCl<br>(strength not specified)   | Schmidt <i>et al.</i><br>(1986)                  |
| Elbe,<br>Weser,<br>Ems | 2 anchored tidal<br>stations and axial<br>section of outer<br>estuary | retention on 0.45 µm filter,<br>low temperature ash,<br>0.1M HCl for 18 hours  | Duinker <i>et al.</i><br>(1982b; 1982c;<br>1985) |
| Rhine,<br>Meuse        | axial profile (no S<br>given) and anchored<br>tidal station           | retention on 0.45 µm filter,<br>low temperature ash,<br>0.1M HCl for 18 hours  | Nolting <i>et al.</i><br>(1989)                  |

The catchments of these North Sea estuaries support extensive regions of urbanization and industrialization and consequently supply high BOD levels to the upper estuarine waters, leading to a depletion of dissolved O<sub>2</sub> (van der Veen and Huizenga, 1980; Tent, 1987; Morris, 1988; Wollast, 1988; Grabemann *et al.*, 1990). This problem is compounded in the Scheldt Estuary by the long water residence time (Table 1.4) resulting in a considerable (tens of kilometres) permanent stretch of anoxia (Wollast, 1988). Although certain constituents (such as Ni and PCBs) behave conservatively, the chemical distributions of others (Mn, Cd, Cu, V and Zn) are profoundly affected by these extreme redox conditions during their seaward transit (Duinker *et al.*, 1979b; 1982a; van der Sloot *et al.*, 1985; Wollast, 1988; Zwolsman and van Eck, 1990).

Although a leachable fraction of metals in suspended sediment has occasionally been determined for the continental estuaries, a diversity of sampling logistics and leaching reagents (compiled in Table 1.5) renders direct comparisons invalid. Duinker and co-workers (Duinker *et al.*, 1982b; 1982c; 1985; Nolting *et al.*, 1989) have generated a suite of leachable metal data for several estuaries, but there appears to have been no attempt at inter-estuary comparisons.

### 1.8.3: North Sea Plumes

The major North Sea outflows are those of the continental estuaries draining northern Europe, and the large British estuaries of the Humber and Thames. Their physical features, especially immediately offshore, are largely related to hydrographic conditions within their respective estuaries, which have been discussed in Section 1.8.2.

The discharges of the Rhine, Elbe and Humber are identified by extensive offshore gradients of constituents such as salinity and nutrients (Folkard and Jones, 1978; Harding and Nichols, 1987), dissolved Al (Hydes and Liss, 1977), artificial fluorescent materials (Suijlen and van Leussen, 1990) and trace metals (Lee and Ramster, 1981; Jones and Jeffries, 1983). Satellite images have also distinguished these plume water bodies by their characteristically high suspended

solids concentrations and distinctive temperatures (Szekielda *et al.*, 1988; Holligan *et al.*, 1989).

The largest outflow emanates from the Rhine Estuary, whose water masses can be detected in the Dutch Wadden Sea some considerable distance along the coast (Zimmerman and Rommets, 1974; van Bennekom *et al.*, 1975). The Rhine outflow is, however, atypical of the North Sea, as its estuary is stratified (Section 1.8.2) and immediately offshore forms a buoyant discharge which is strongly affected by the Coriolis force (van Alphen *et al.*, 1988).

The most conspicuous and extensive plume is that of the Elbe. Discharging into the shallow and dynamic waters of the German Bight, the plume normally heads north as a distinct water body, often as far as the island of Sylt (Schmidt *et al.*, 1986). The fresh water input of the Elbe is augmented by neighbouring estuaries such as the Weser and Eider, and consequently the German Bight is characterized by the lowest salinity and most extreme seasonal temperature variations of the North Sea (Lee and Ramster, 1981; Table 1.1).

The physical aspects of the outflows of the Tees, Tyne and Humber have been described and parameterized by Lewis (1990). The Tees and Tyne plumes exhibit vertical stratification; however, they are only of very local significance, as their inherent fresh water discharges and estuarine inter-tidal volumes are small. In contrast, the shallow, dynamic and macrotidal environment of the Humber Estuary (Table 1.4) and adjacent coastal waters, coupled with a large fresh water flow results in a well-mixed plume of considerable extent. The local residual current regime directs the diffusing plume immediately south towards the Wash (Figure 1.3).

In the longer-term, estuarine water masses are carried by the wind driven residual North Sea circulation (Section 1.8.1.1), and their transport has been simulated using three-dimensional (Hainbucher *et al.*, 1987) or vertically averaged two-dimensional (van Pagee *et al.*, 1986; de Ruijter *et al.*, 1987) hydrodynamic models, with the aim of assessing pollutant dispersal. Passive, conservative behaviour is a tacit assumption, although the latter model can cater for simple first order decay of constituents. However, non-conservative effects have already

been emphasized (Section 1.8.1.3), and although solid-solution transformations (as well as sediment-water interfacial exchange processes, and sediment dynamics) have been incorporated into conceptual models (Taylor, 1987), vital mechanistic and kinetic details of such interactions, which are needed in order to refine transport models, are lacking.

## 1.9: AIMS OF PRESENT STUDY

The primary objective of this investigation is to elucidate mechanisms of metal reactivity in various compartments of the southern North Sea, including several large estuaries and their neighbouring coastal (plume) environments, that would assist the development and validation of pollutant transport models, in particular a model of the dispersion of the Humber outflow currently being developed at Plymouth Marine Laboratory.

In the estuarine environments attention would focus on the role of the particulate phase, with emphasis on surface properties and an available fraction of metals. In the North Sea and plume regions both dissolved and particulate metal distributions would be generated in collaboration with Southampton University Department of Oceanography as a pre-requisite for the *North Sea Project*, and complementary *in situ* radiotracer experiments would assist interpretation of these data.

## CHAPTER 2: PARTICLE COMPOSITION AND TRACE METAL REACTIVITY IN THE NORTH SEA ESTUARINE ENVIRONMENTS

### 2.1: SAMPLING AND ANALYTICAL METHODS

A summary of the sampling and analytical methods employed in this Chapter is shown in the form of a flow diagram in Figure 2.1.

#### 2.1.1: Sampling in Estuaries

##### 2.1.1.1: Suspended Sediment

Surface water samples of up to 20 l were taken in polyethylene carboys during axial profiles of the five estuaries (Figures 2.2a-e) in order to yield approximately 500 mg solid material. This was achieved either directly by hand from a small craft at discrete sampling points, or via a pumped supply on board a moving vessel. Separation of the suspended sediment involved either filtration through 0.45  $\mu\text{m}$  pore size Millipore or Sartorius cellulose acetate filters, under  $\text{N}_2$  pressure or vacuum, or continuous flow centrifugation onto removable teflon panels lining the interior of the rotating bowl (van der Sloot and Duinker, 1981). Recovery of material began *in situ*, filtration of an individual sample normally being complete within 30 minutes and by centrifugation within 15 minutes. Samples were subsequently washed with up to 50 ml distilled deionized water in order to remove salt, a process which has been shown not to desorb loosely bound metals (Duinker *et al.*, 1979a), freeze dried (Edwards High Vacuum Limited), and stored under vacuum dessication until required.

In addition, several samples were taken from a variety of locations in the North Sea itself (Figure 2.2f) by pressure filtration of water samples collected by either a pumped supply or General Oceanics (*Go-Flo*) bottles mounted on the CTD cast of *RRS Challenger* (Section 3.12), and centrifugation of up to 200 l (recovery taking up to 3 hours).

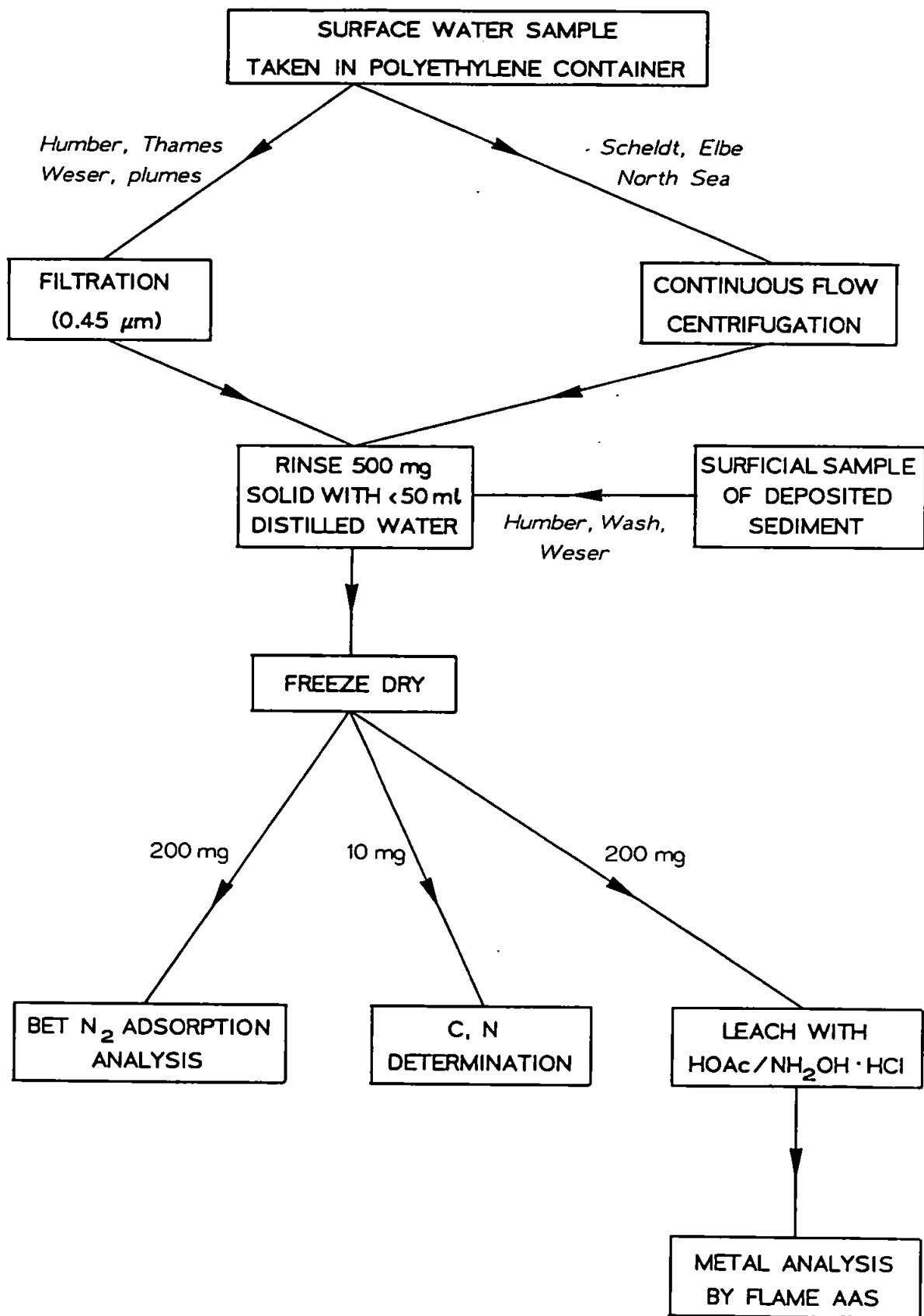


Figure 2.1: Flow diagram of methods of collection, processing and analysis of sediment samples.

Table 2.1: Summary of sampling techniques employed in the North Sea environment.

| Survey Dates        | Vessel                | Water sample collection <sup>1</sup> | Solid recovery <sup>2</sup> | Number of samples |
|---------------------|-----------------------|--------------------------------------|-----------------------------|-------------------|
| <u>Humber</u>       |                       |                                      |                             |                   |
| Jan. 1988           | fishing craft         | direct                               | HPF                         | 19                |
| July 1989           | aluminium dory        | direct                               | HPF                         | 11                |
| <u>Thames</u>       |                       |                                      |                             |                   |
| Feb. 1989           | <i>RRS Challenger</i> | pump                                 | HPF                         | 8                 |
| Mar. 1989           | aluminium dory        | direct                               | HPF                         | 6                 |
| <u>Scheldt</u>      |                       |                                      |                             |                   |
| Feb. 1987           | Ministry of           | pump                                 | CFC                         | 12                |
| May 1987            | Public Works          | pump                                 | CFC                         | 13                |
| Aug. 1987           | (NL) vessel           | pump                                 | CFC                         | 12                |
| <u>Weser</u>        |                       |                                      |                             |                   |
| Aug. 1989           | <i>RV Weserluchs</i>  | pump                                 | VF                          | 15                |
| <u>Elbe</u>         |                       |                                      |                             |                   |
| June 1988           | <i>RV Valdivia</i>    | pump                                 | CFC                         | 10                |
| <u>Humber plume</u> |                       |                                      |                             |                   |
| Dec. 1988           | <i>RRS Challenger</i> | pump/ <i>Go-Flo</i>                  | HPF                         | 4                 |
| May 1990            | <i>RRS Challenger</i> | pump/ <i>Go-Flo</i>                  | HPF                         | 3                 |
| <u>Thames plume</u> |                       |                                      |                             |                   |
| Feb. 1989           | <i>RRS Challenger</i> | pump                                 | HPF                         | 2                 |
| <u>North Sea</u>    |                       |                                      |                             |                   |
| Mar. 1987           | <i>RV Valdivia</i>    | pump                                 | CFC                         | 4                 |
| <u>S. North Sea</u> |                       |                                      |                             |                   |
| July 1988           | <i>RV Valdivia</i>    | pump                                 | CFC                         | 3                 |

<sup>1</sup> Surface water samples taken directly by hand (direct), abstracted from a pumped supply on board (pump), or taken from deployed General Oceanics bottles (*Go-Flo*).

<sup>2</sup> HPF = high pressure filtration through 0.45  $\mu\text{m}$  filters

VF = vacuum filtration through 0.45  $\mu\text{m}$  filters

CFC = continuous flow centrifugation

Master variables (salinity, temperature, pH, dissolved O<sub>2</sub> concentration) were recorded *in situ* at each discrete sampling station. In addition, automated



continuous data logging was available during the surveys of the Scheldt and Weser Estuaries, and during sampling on board *RRS Challenger*. A continuous data logging facility was also available during the winter survey of the Humber when the *Magpie* system (LTH Electronics Limited) was being tested. Suspended solids concentrations were determined from the washed (distilled water) and dried (at 110°C for 12 hours) masses retained on pre-weighed Whatman GF/C filters after filtration of up to 3 l samples.

The details of which particular sampling methods were employed in each environment are given in Table 2.1.

Samples have also been taken during axial profiles of the Mersey and Tamar Estuaries by high pressure filtration and are occasionally referred to in the discussion (Section 2.2).

Although it has been demonstrated that samples collected by filtration and centrifugation do not always yield consistent metal concentrations (Duinker *et al.*, 1979a; Etcheber and Jouanneau, 1980; Horowitz, 1986) it is considered that such differences are not sufficiently large as to obscure any genuine trends and features of inter-estuarine variability (van Eck, 1982, cited in van der Weijden and Middelburg, 1989; G. Zwolsman, pers. comm.).

#### 2.1.1.2: Deposited Sediment

Scrapes of recently exposed sediment from the surficial oxic layer were taken using a PTFE spatula from the inter-tidal regions of the Humber during April and November of 1988 (Figure 2.2a) and from each morphological sub-zone of the Wash embayment (Evans, 1965) at Freistone shore during November 1988 (Figure 2.2f). Sub-tidal sediments were taken from the estuaries of the Humber (November 1988) and Weser (August 1989) using a 0.1 m<sup>2</sup> van Veen grab. About 10 g samples were stored cool in acid cleaned plastic pots and subsequently washed with distilled deionized water through cellulose acetate Millipore filters (0.45 µm) and freeze dried.

In addition, samples were taken from the inter-tidal zones of the Esk, Tamar and Thames (Figure 2.2b), and sub-tidal deposits of the Clyde and Loch Goil (a

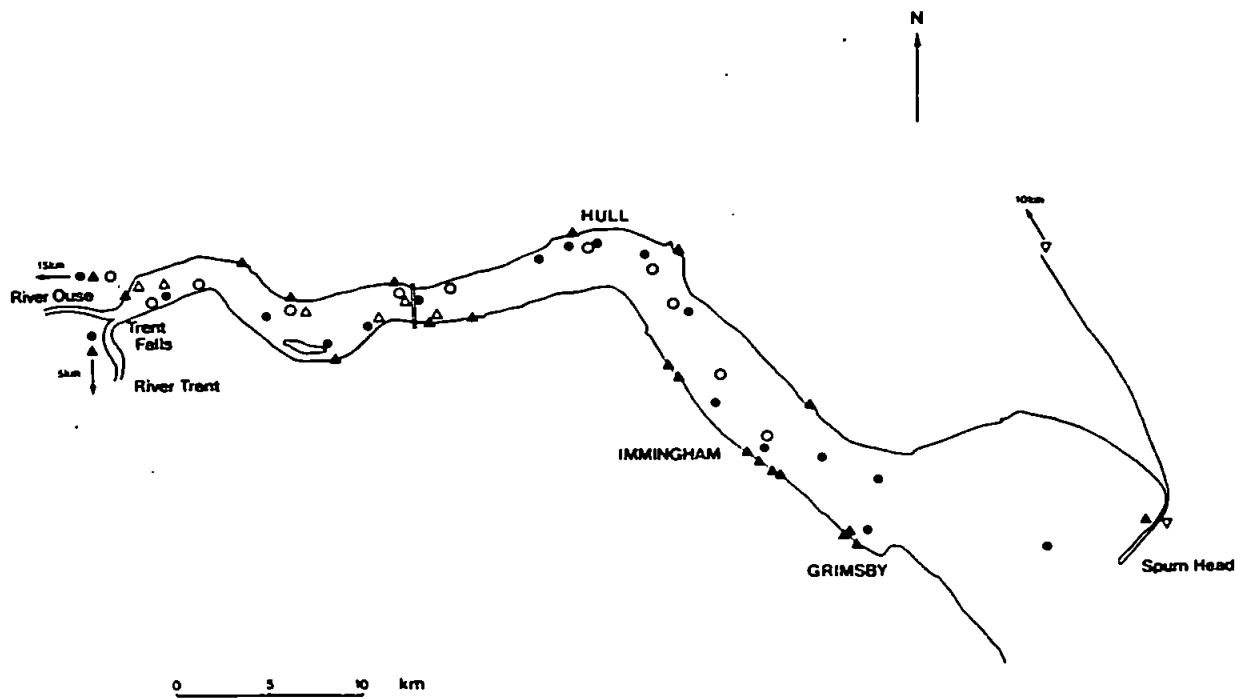


Figure 2.2a: Sampling locations in the Humber Estuary. Suspended sediment: Jan. 1988 (●); July 1989 (○). Deposited sediment: inter-tidal (▲); sub-tidal (Δ); coastal sand (▽).

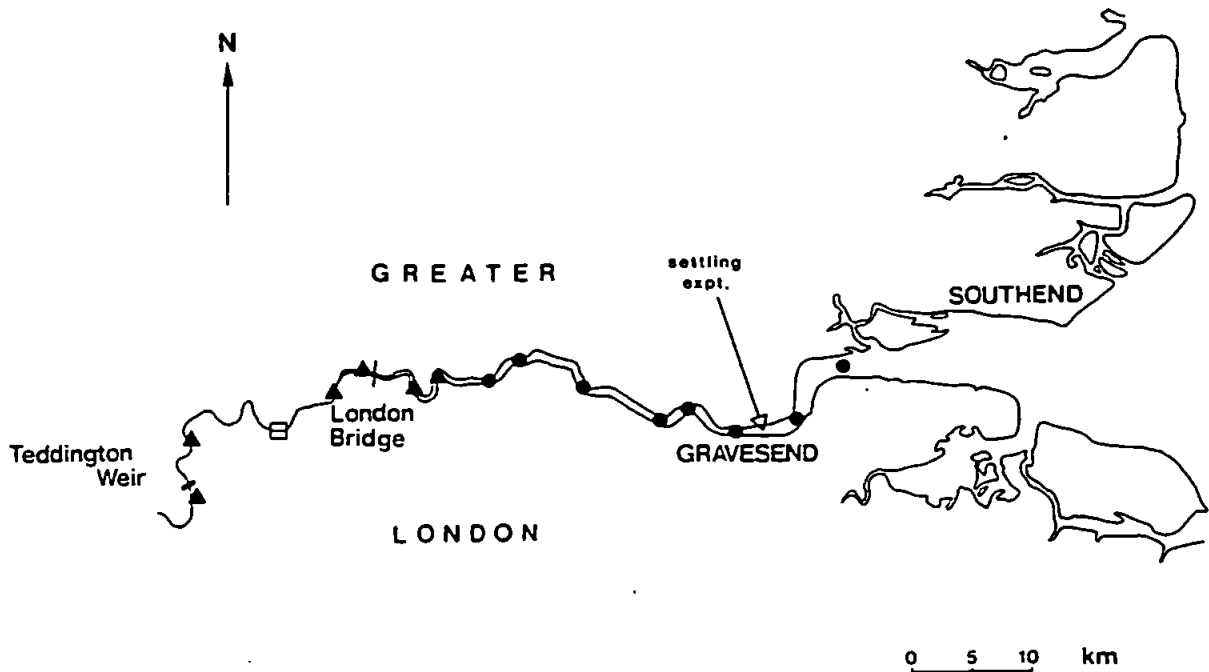


Figure 2.2b: Sampling locations in the Thames Estuary. Suspended sediment: Feb. 1989 (●); Mar. 1989 (▲). Inter-tidal sediment (□).

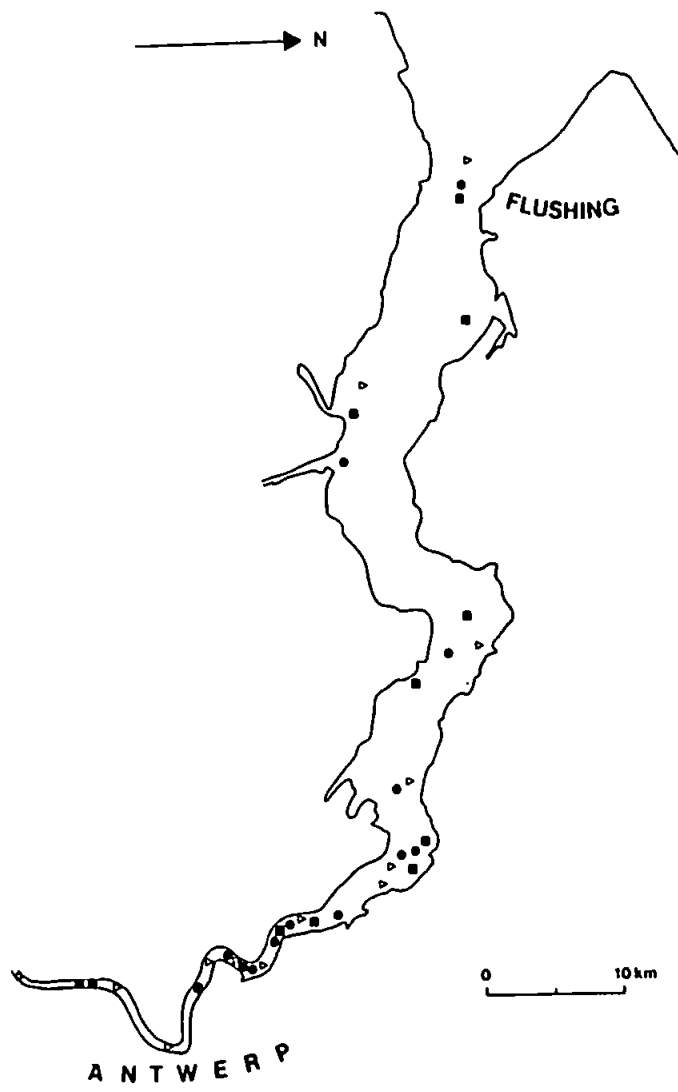


Figure 2.2c: Sampling locations for suspended sediment in the Scheldt Estuary. Feb. 1987 ( $\triangleright$ ); May 1987 ( $\bullet$ ); Aug. 1987 ( $\blacksquare$ ).

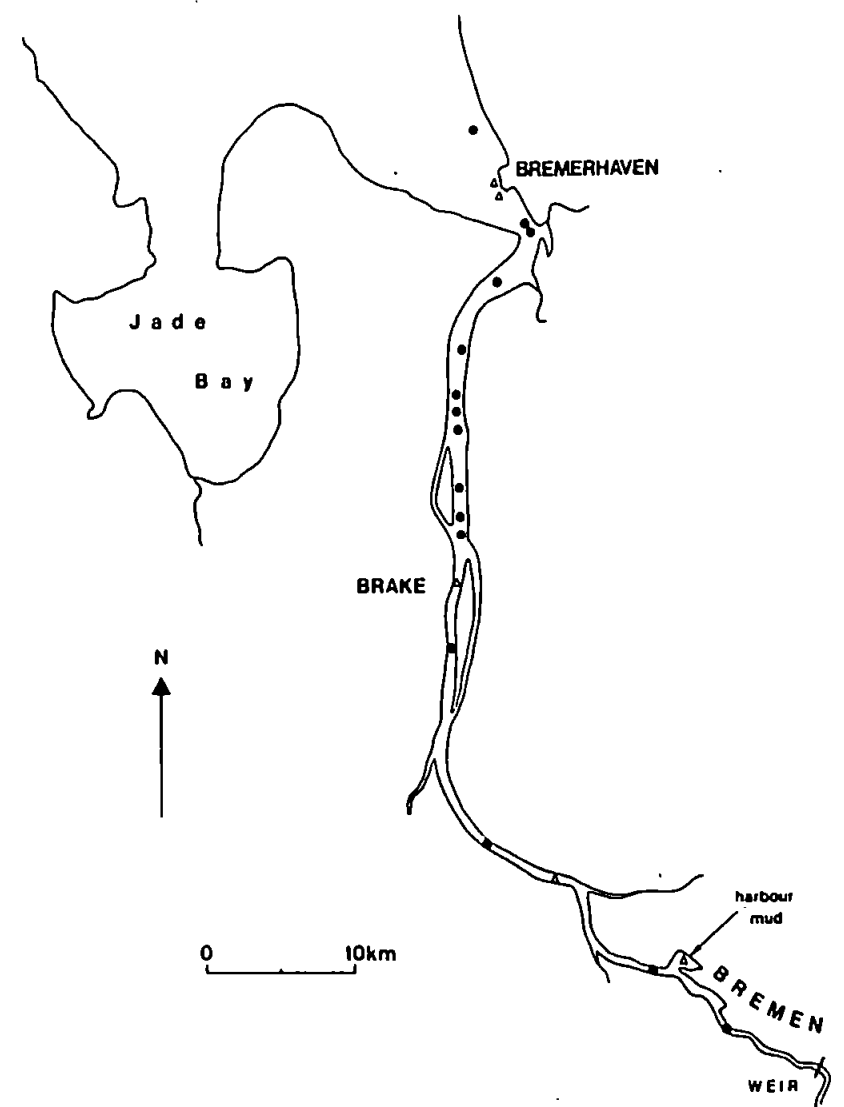


Figure 2.2d: Sampling locations in the Weser Estuary, Aug. 1989. Suspended sediment ( $\bullet$ ); sub-tidal sediment ( $\Delta$ ).

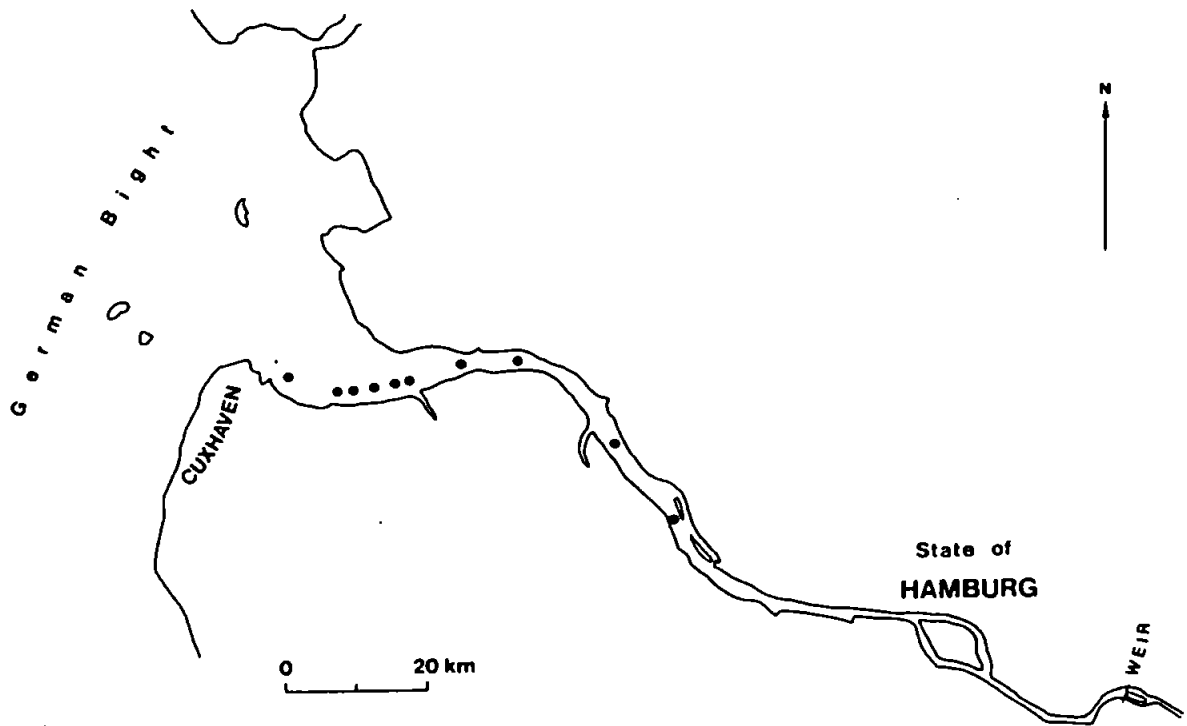


Figure 2.2e: Sampling locations for suspended sediment in the Elbe Estuary, June 1988.

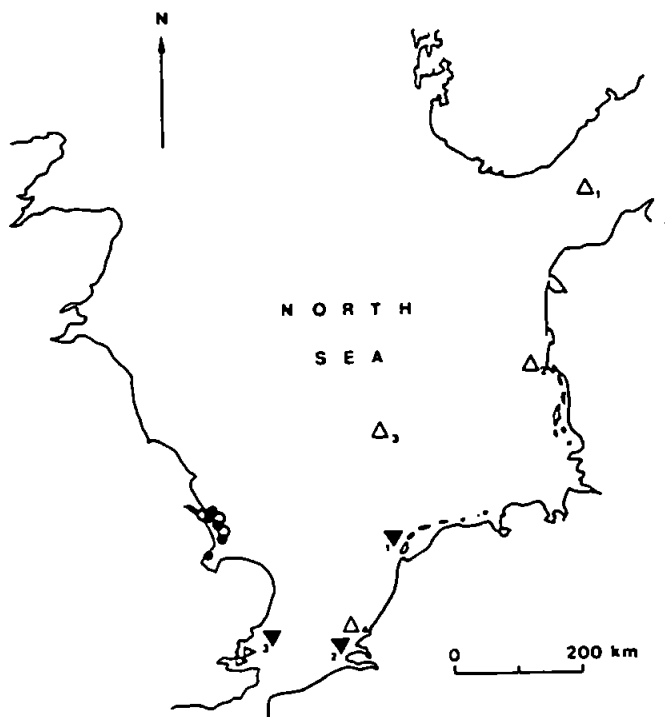


Figure 2.2f: Sampling locations in the North Sea. Suspended sediment: Humber plume Dec. 1988 (●) and May 1990 (○); Thames plume Feb. 1989 (▴); southern North Sea transect July 1988 (▼ 1. Dutch coast, 2. Rhine plume and 3. English coast); samples collected by M. Kersten (Harburg Technical University, F.R.G.) during Jan.-Mar. 1987 as part of inter-laboratory comparisons (Table 2.5 and Section 2.2.3.5) (Δ 1. Skagerrak, 2. Danish coast, 3. algal bloom and 4. Rhine plume). Deposited sediment: Wash (\*).

sea loch branch of the Firth of Clyde; Farmer, 1983) for general experimental and method development usage.

## 2.1.2: Chemical Analysis

### 2.1.2.1: Leaching Procedure

A combination of weak acid/reducing agent (*viz.* acetic acid/hydroxylamine-hydrochloride) was selected to leach metals associated with the Fe-Mn hydroxide coatings (Chester and Hughes, 1967; Tessier *et al.*, 1979). This type of attack is potentially indicative of a bioavailable fraction (Salomons and Förstner, 1980) and was also found to be efficient in removing the phases that are largely responsible for the surface microstructural properties (Glegg, 1987), yet causing minimal damage to the underlying matrix (Chester and Hughes, 1967; Duinker *et al.*, 1974).

The time dependence of this leach was investigated over a period of five days on three samples of diverse composition (Figure 2.3): suspended material from the low salinity region of the Scheldt Estuary; sandy inter-tidal sediment from the Esk Estuary; sub-tidal, Mn-rich sediment from Loch Goil. Whereas Mn release reaches equilibrium quickly, Fe, after a relatively rapid initial release, is leached continually more slowly over the remaining period in an almost linear fashion. In most instances the release of other metals was consistent with the behaviour of Fe, and this was interpreted as a relatively rapid destruction of the surface Fe-Mn hydroxide coatings, followed by a slower continual attack of the underlying lithogenous phase. The slope tends to become linear at around 16 hours and this was therefore chosen as an arbitrary leaching time. Aware of all inherent problems in adopting such (leaching) procedures (Tipping *et al.*, 1985; Martin *et al.*, 1987) this leach was consistently applied to give an operational (*i.e.* not necessarily specific) measure of metals associated with the Fe-Mn hydroxide phase. Details of preparation and experimental application are now described.

A 0.05M solution of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (BDH AnalaR grade) was made up in 25% glacial HOAc (BDH AristaR grade), and approximately 20 ml were added to

Fe, Mn  
 $\mu\text{g/g}$

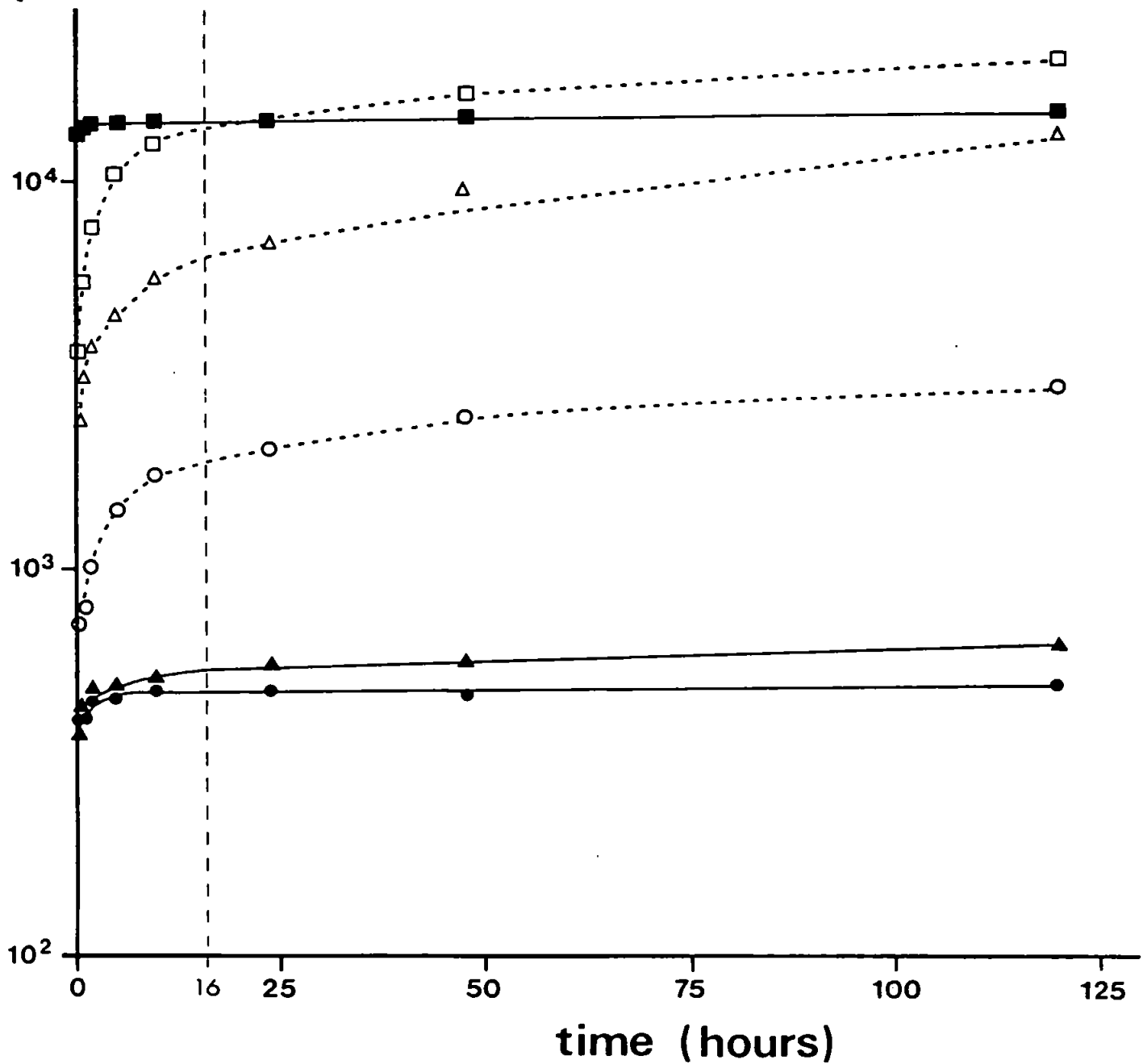


Figure 2.3: Iron (open symbols) and Mn (closed symbols) release from sediments by acetic acid/hydroxylamine-hydrochloride as a function of time. Deposited: Esk Estuary (O, ●); Loch Goil (□, ■). Suspended: Scheldt Estuary during winter (Δ, ▲).

150–350 mg accurately weighed ( $\pm 0.1$  mg) freeze dried sample at room temperature in covered 35 ml glass vials for 16 hours. The final mixture was filtered with washings (Milli-Q water) through a 22 mm diameter Millipore cellulose acetate filter of pore size  $0.45 \mu\text{m}$  mounted in a glass Millipore vacuum filtration assemblage, and the filtrate transferred into a volumetric flask (25 or 50 ml) and topped up with Milli-Q water. Procedural blanks were prepared in a similar fashion for every 7 or 8 samples. All glassware involved had been previously soaked in acid (approximately 15% HCl + 5% HNO<sub>3</sub>) for at least 24 hours and rinsed thoroughly with Milli-Q water.

#### 2.1.2.2: Metal Analysis

Solutions were analyzed for metals (Fe, Mn, Co, Cr, Cu, Ni, Pb and Zn) by atomic absorption spectrophotometry using an Instrumentation Laboratory 151 in the flame mode and employing conditions recommended by the operator's manual, or appropriate modifications (Table 2.2). Three or four working standards (BDH Spectrosol) were prepared in the leaching solution encompassing the range appropriate for the samples (*i.e.* either all or part of the linear range). The most sensitive wavelengths were used for all elements with the exception of Pb for which interference and suppression effects could be reduced by using an alternative wavelength. Dilutions were often necessary for Zn analyses but less sensitive wavelengths were also employed for solutions of high Fe and Mn concentrations.

Samples were aspirated into an air-acetylene flame for all metal analyses with the exception of Cr for which a nitrous oxide-acetylene flame has been recommended (Loring and Rantala, 1988; Harper *et al.*, 1989). Several Al analyses undertaken also involved use of the latter flame type. Deuterium lamp background correction was generally unnecessary and only tended to enhance instrument background noise, and blank signals were generally < 5% of the smallest sample signal for all metals.

Table 2.2: Instrument conditions for atomic absorption analysis of North Sea estuarine samples.

| Element | Wavelength (nm) | Bandpass (nm) | Flame                                       | Background correction | Working range ( $\mu\text{g/ml}$ ) | Detection limit ( $\mu\text{g/ml}$ ) |
|---------|-----------------|---------------|---|-----------------------|------------------------------------|--------------------------------------|
| Al      | 309.3           | 1.0           | $\text{N}_2\text{O}_2\text{-C}_2\text{H}_2$ | off                   | 1-12                               | 0.25                                 |
| Fe      | 248.3           | 0.3           | air- $\text{C}_2\text{H}_2$                 | off                   | 1.0-4.0                            | 0.025                                |
|         | 386.0           | 0.3           | air- $\text{C}_2\text{H}_2$                 | off                   | >5.0                               | 0.2                                  |
| Mn      | 279.5           | 0.5           | air- $\text{C}_2\text{H}_2$                 | off                   | 0.5-2.5                            | 0.025                                |
|         | 403.1           | 0.3           | air- $\text{C}_2\text{H}_2$                 | off                   | 2-40                               | 0.5                                  |
| Co      | 240.7           | 0.3           | air- $\text{C}_2\text{H}_2$                 | off                   | 0.015-0.2                          | 0.015                                |
| Cr      | 357.9           | 0.5           | $\text{N}_2\text{O}_2\text{-C}_2\text{H}_2$ | off                   | 0.05-0.8                           | 0.05                                 |
| Cu      | 324.7           | 1.0           | air- $\text{C}_2\text{H}_2$                 | off                   | 0.02-1.0                           | 0.02                                 |
| Ni      | 232.0           | 0.5           | air- $\text{C}_2\text{H}_2$                 | off                   | 0.05-0.5                           | 0.05                                 |
| Pb      | 283.3           | 0.5           | air- $\text{C}_2\text{H}_2$                 | off                   | 0.05-0.6                           | 0.05                                 |
| Zn      | 213.9           | 1.0           | air- $\text{C}_2\text{H}_2$                 | on                    | 0.1-0.8                            | 0.1                                  |
|         |                 |               |   |                       | >0.8, dilutions                    |                                      |

Table 2.3: Coefficient of variation (%) on metal analyses of n replicate sediment samples leached.

| Sample                 | n | Al  | Fe   | Mn  | Co  | Cr  | Cu   | Ni  | Pb  | Zn   |
|------------------------|---|-----|------|-----|-----|-----|------|-----|-----|------|
| Scheldt <sup>1</sup>   |   |     |      |     |     |     |      |     |     |      |
| (Feb. 1987)            | 3 | 6.9 | 6.7  | 4.5 | 5.3 | 4.8 | 11.2 | -   | 6.3 | 4.4  |
| (May 1987)             | 6 | 14  | 14.9 | 6.5 | 9.4 | 16  | 24.3 | 8.8 | 7.4 | 14.8 |
| Loch Goil <sup>2</sup> |   |     |      |     |     |     |      |     |     |      |
| (April 1988)           | 5 | 16  | 9.6  | 2.7 | 13  | 5.1 | 11.0 | 9.0 | 18  | 19.0 |
| Weser <sup>2</sup>     |   |     |      |     |     |     |      |     |     |      |
| (Aug. 1989)            | 5 | 7.1 | 5.0  | 4.6 | 7.6 | -   | 16   | 8.8 | 15  | 7.7  |

<sup>1</sup> Suspended material.

<sup>2</sup> Deposited material.



Several duplicate or triplicate samples were run in each batch of analyses, and the coefficient of variation on replicate samples is shown in Table 2.3. Analyses were usually complete within 10 days of leaching, although calibration with freshly prepared standards on several samples demonstrated no deterioration after 7 weeks.

### 2.1.2.3: Carbon and Nitrogen

The total carbon and nitrogen contents were determined by chromatographic separation of the gases emitted on combustion of the samples in a Carlo-Erba 1106 elemental analyzer. Between 1 and 15 mg sample were accurately weighed out ( $\pm 1 \mu\text{g}$ ) on a Cahn microbalance into aluminium capsules, along with varying weights of standard (acetanilide; Elemental Micro-Analysis Limited) in order to cover a sufficiently wide range of signal. The capsules were pre-cleaned by successive 10 minute washings with chloroform, acetone and Milli-Q water in an ultrasonic bath, and dried at  $100^\circ\text{C}$  for 12 hours. Duplicates or triplicates of each sample, as well as the standards and capsule blanks were introduced into the furnace tube from a carousel.

Table 2.4: Carbon determinations on three reference sediments.

|          | C (%)           |            |
|----------|-----------------|------------|
|          | Certified*      | Measured   |
| MESS - 1 | $2.99 \pm 0.09$ | 2.94; 2.92 |
| BCSS - 1 | $2.19 \pm 0.09$ | 2.21; 2.18 |
| PACS - 1 | $3.69 \pm 0.11$ | 3.71; 3.70 |

\* National Research Council for Canada (1987).

The analytical reproducibility for both C and N was generally better than 5%; for example, analyses of 5 aliquots of Bremen harbour mud from the Weser Estuary (Figure 2.2d) gave a mean and standard deviation of  $5.68 \pm 0.16$  for C

(coefficient of variation = 2.8%) and  $0.56 \pm 0.084$  for N (coefficient of variation = 1.5%).

Analysis of marine reference sediments run in duplicate gave results within the certified values (National Research Council for Canada, 1987; Table 2.4).

### 2.1.3: Physical Analysis - Surface Microstructure

#### 2.1.3.1: Background

Techniques that have been adopted in order to study the surface area of marine/estuarine sediment material include Hg porosimetry (Weiler and Mills, 1965), and adsorption by cetyl pyridinium bromide (CPB) dye (Mayer and Fink, 1980; Mayer, 1982), Ar gas (Kulp and Carr, 1952; Elbaz-Poulichet *et al.*, 1982; 1984; Martin *et al.*, 1986), N<sub>2</sub> gas (Glegg, 1987; Glegg *et al.*, 1987; Titley *et al.*, 1987; Millward *et al.*, 1989; 1990) and water vapour (Slabaugh and Stump, 1964).

Quantification of surface area is, however, very sensitive to the particular analytical method employed. In this work a gravimetric multi-point BET (Brunauer *et al.*, 1938) N<sub>2</sub> adsorption technique has been employed, and it must therefore be appreciated that all results discussed refer to the specific surface area (SSA) as determined by this technique. Table 2.5 compares the results obtained by the presently adopted method with those obtained by one-point BET N<sub>2</sub> adsorption, and ethylene glycol-monoethyl ether (EGME) adsorption. It is apparent that the one-point BET N<sub>2</sub> adsorption method yields slightly higher surface areas than the multi-point method, whereas the EGME technique yields surface areas an order of magnitude higher although the results are highly ( $r^2 = 82.7\%$ ) and significantly ( $p = 0.003$ ) correlated. Surface area determination is also dependent on the sample pre-treatment. For example, Elbaz-Poulichet *et al.* (1982) oven dried suspended sediment samples at 105°C prior to Ar adsorption, and various chemical treatments were a pre-requisite for CPB surface area determinations of sediment material (Mayer, 1982). These somewhat vigorous preparative techniques, especially the latter, therefore fail to enable the original native surface structure to be examined by the ensuing respective method. In this work careful and consistent

sample preparation has been adhered to in order to keep the natural structure intact. Thus, freeze drying, considered the most suitable drying method (Weiler and Mills, 1965; Glegg, 1987), and subsequent storage under vacuum desiccation in order to prevent pore damage by adsorbed water vapour (Egashira and Aomine, 1974) have been observed.

This procedure, now outlined, yields an operational measurement of surface area which is not necessarily assumed to be representative of the surface available for adsorbing metals or other constituents in the aquatic environment.

Table 2.5: A comparison of surface areas as determined by three different techniques.

| Sample                     | m <sup>2</sup> /g   |   |                                 |
|----------------------------|---|---|---------------------------------|
|                            | Multi-point BET<br>N <sub>2</sub> adsorption <sup>1</sup> | One-point BET<br>N <sub>2</sub> adsorption <sup>2</sup> | EGME<br>adsorption <sup>3</sup> |
| <i>SUSPENDED SEDIMENT</i>  |   |   |                                 |
| Rhine plume                | 5.0   | 7.4   | -                               |
| Danish coast               | 9.3   | 14.6  | -                               |
| Skagerrak                  | 0.8   | 3.1   | -                               |
| North Sea algal bloom      | <1  | 3.7   | -                               |
| <i>DEPOSITED SEDIMENT</i>  |   |   |                                 |
| Esk Estuary (sand)         | 0.2   | -   | 3.3                             |
| Esk Estuary (mud)          | 4.7   | -   | 37.6                            |
| Clyde Estuary              | 2.2   | -   | 22.2                            |
| Humber Estuary             | 19.1  | -   | 95.3                            |
| Loch Goil                  | 21.0  | -   | 188.0                           |
| <i>SYNTHETIC MATERIALS</i> |   |   |                                 |
| Montmorillonite            | 67.5  | -   | 247.5                           |
| Illite                     | 76.9  | -   | 250 (220*)                      |

<sup>1</sup> This work.

<sup>2</sup> M. Kersten (Harburg Technical University, F.R.G.).

<sup>3</sup> G. Williams (Imperial College of Science and Technology, London).

\* Srodon *et al.* (1986).

### 2.1.3.2: Surface Area Determination

Between 100 and 300 mg sample were accurately weighed out ( $\pm 0.1$  mg) into an aluminium bucket and outgassed in the apparatus, for which a full description can be found in Carter (1983), by means of vacuum pump plus cold trap to constant weight; this was usually achieved within 10 hours. The sample was then cooled to 77°K by surrounding it with liquid N<sub>2</sub> and the uptake of successive doses of N<sub>2</sub> gas (at 40 mm Hg intervals, taking approximately 25 minutes to equilibrate) was monitored by a CI Electronics microbalance. The SSA was then calculated from the BET equation (Brunauer *et al.*, 1938):

$$\frac{P}{X(P_o - P)} = \frac{1}{X_m C} + \left[ \frac{(C-1)}{X_m C} \times \frac{P}{P_o} \right] \quad (2.1)$$

where P is the pressure of N<sub>2</sub> around the sample, P<sub>o</sub> the saturated vapour pressure of N<sub>2</sub>, X<sub>m</sub> the weight of N<sub>2</sub> adsorbed at monolayer coverage (*i.e.* a completely filled, single molecular layer), X the weight of N<sub>2</sub> adsorbed at pressure P, and C is a constant related to the heat of adsorption of the first layer of gas. Plotting P/[X(P<sub>o</sub> - P)] versus P/P<sub>o</sub> (for the range 0.05 < P/P<sub>o</sub> < 0.3) yields a straight line (Figure 2.4) from which the slope and intercept are used to determine X<sub>m</sub>. The SSA, in m<sup>2</sup>/g, is then calculated from the following:

$$SSA = X_m \times L \times A_N \quad (2.2)$$

where L is the number of N<sub>2</sub> molecules in 1 mg and A<sub>N</sub> is the area of the N<sub>2</sub> molecule, assumed 0.162 nm<sup>2</sup> (Adamson, 1982).

### 2.1.3.3: Porosity Studies

Continual dosing beyond P/P<sub>o</sub> = 0.3 to P/P<sub>o</sub> = 1.0 results in multi-layer adsorption, pore filling and capillary condensation. Subsequent desorption often

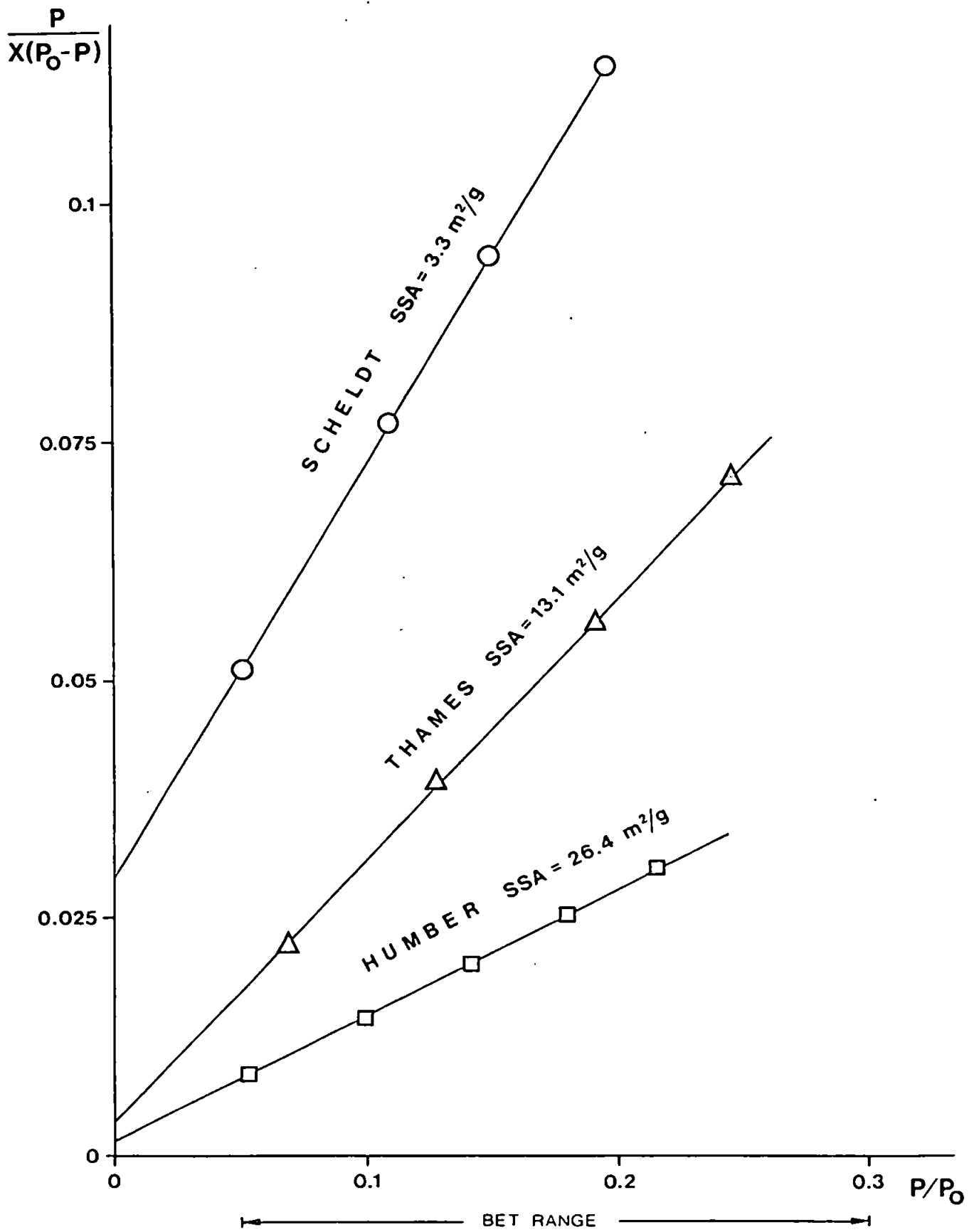


Figure 2.4: Examples of plots of  $P/[X(P_0 - P)]$  versus  $P/P_0$  used in the determination of SSA.

results in characteristic hysteresis patterns in the isotherms for which classifications have been devised (Gregg and Sing, 1982). Hysteresis is possible because condensation (during adsorption) can only occur in the presence of pre-existing solid surfaces when  $P < P_0$ , and at a specific  $P$  value dependent on the pore radius (Equation 2.3), whereas evaporation (during desorption) can occur spontaneously if the pressure is low enough. The hysteresis can yield valuable qualitative information, including the nature of the pore shapes. Furthermore, semi-quantitative information can be obtained as  $P/P_0$  can be translated into equivalent pore diameters via the *Kelvin Equation* assuming pores are cylindrical (Gregg and Sing, 1982) as follows:

$$\ln \frac{P}{P_0} = - \frac{2 \gamma V}{r R T} \quad (2.3)$$

where  $\gamma$  is the surface tension of the adsorbed  $N_2$ ,  $V$  the molar volume of  $N_2$ ,  $r$  the pore radius,  $R$  the universal gas constant and  $T$  the temperature.

Key samples were dosed beyond the BET range (Figure 2.4) with  $N_2$  up to  $P/P_0 = 1$  at intervals of 100 mm Hg allowing up to 45 minutes for each equilibration, followed by desorbing via the pump and cold trap at similar intervals.

#### 2.1.3.4: General Considerations

The microbalance was regularly calibrated with accurate aluminium weights, and the methodology was occasionally checked against standard reference materials.

The theoretical analytical accuracy of the SSA determination is dependent on the mass of sample,  $m$  (mg), and magnitude of SSA ( $m^2/g$ ) (sample reactivity), and, assuming that 1 mg  $N_2$  is equivalent to 3.5  $m^2$ , can be determined as follows:

$$\text{accuracy (\%)} = \frac{10^4}{(3.5 \times \text{SSA} \times m)} \quad (2.4)$$

For example, 200mg adsorbate of SSA  $15 \text{ m}^2/\text{g}$  would yield an accuracy of about 1%. However, reproducibility on sediment material was reduced owing to the inhomogeneity of samples; the mean and standard deviation of five analyses on separate aliquots of Bremen harbour mud was  $11.7 \pm 1.0 \text{ m}^2/\text{g}$  giving a coefficient of variation of 8.5%.

As the amount of material recovered from waters of low turbidity was occasionally below 150mg, metal analysis (Section 2.1.2.2) was necessary on the same material after BET analysis. Although potential risks of contamination were recognised, metal concentrations determined on untreated and BET analyzed aliquots were the same to within the analytical errors given in Table 2.3.

## 2.2: RESULTS AND DISCUSSION

### 2.2.1: Hydrography and Water Chemistry

The hydrographic conditions encountered during each survey are summarized in Table 2.6, and examples of master variable distributions determined at each sampling station (Weser) and logged automatically (Humber winter survey) are shown in Figures 2.5a and 2.5b.

Estuarine mixing gave rise to normal seaward increases (winter) or decreases (summer) of temperature and salinity profiles exhibited S-shape curvature (Figures 2.5a and 2.5b) typical for *partially-/well-mixed* estuaries. In the Weser Estuary, however, salinity only fell to 2.2 ‰, thereafter increasing slightly in a landward direction (Figure 2.5a). This is the result of the anthropogenic release of  $\text{Cl}^-$  ions from the potash mining industry upstream of the tidal weir (Figure 2.2d; Lüneburg *et al.*, 1975) and salinity (or chlorinity) cannot therefore be regarded as a truly conservative index in the upper reaches of this estuary.

Seaward increases in pH were the result of mixing of relatively low pH river water (7-7.5) with higher pH sea water (around 8), and distributions generally conformed with carbonate chemistry (Mook and Koene, 1975), although the pH at the mouth of the Humber Estuary during winter was low (about 6.5; Figure 2.5b) as a result of the acidic discharge ( $180\,000 \text{ m}^3 \text{ H}_2\text{SO}_4/\text{annum}$ ) from the titanium dioxide manufacturing plant on the south bank (Newell *et al.*, 1984).

Estuarine circulation generated a distinct TMZ in most, but not all instances (Table 2.6; Figure 3.5) at the fresh water/brackish water interface (FBI). The TMZ was also associated with an  $\text{O}_2$  minimum (Figures 2.5a and 2.5b), probably as a result of consumption by particulate organic carbon trapped in this region (Morris *et al.*, 1982b).



Table 2.6: Hydrographic conditions at the sampling sites during surveys in the North Sea environment. Mean  $\pm$  one standard deviation and range of determinands given.

| Survey Date<br>(No. samples) | Salinity<br>(‰)              | Temperature<br>(°C)          | Suspended solids<br>(mg/l) | Dissolved oxygen<br>(mg/l)   | pH                        | River flow<br>(m <sup>3</sup> /s) | Tidal state<br>** |
|------------------------------|------------------------------|------------------------------|----------------------------|------------------------------|---------------------------|-----------------------------------|-------------------|
| <u>Humber</u>                |                              |                              |                            |                              |                           |                                   |                   |
| Jan. 1988<br>(19)            | 8.6 $\pm$ 9.1<br><0.5-25.9   | 6.2 $\pm$ 0.4<br>5.5-6.9     | 135 $\pm$ 62*<br>35-248    | 11.3 $\pm$ 0.49<br>10.3-12.2 | 7.3 $\pm$ 0.24<br>6.5-7.5 | 234                               | f                 |
| July 1989<br>(11)            | 11.9 $\pm$ 8.6<br>0.5-25.0   | 20.0 $\pm$ 1.4<br>18.4-22.5  | 223 $\pm$ 187<br>45-693    | -<br>-                       | 7.7 $\pm$ 0.11<br>7.5-7.9 | 52                                | f,e               |
| <u>Thames</u>                |                              |                              |                            |                              |                           |                                   |                   |
| Feb./Mar.<br>1989 (14)       | 10.0 $\pm$ 10.3<br>0.3-27.4  | -<br>-                       | 143 $\pm$ 126*<br>19-424   | -<br>-                       | -<br>-                    | 101/<br>160                       | f,e               |
| <u>Scheldt</u>               |                              |                              |                            |                              |                           |                                   |                   |
| Feb. 1987<br>(12)            | 9.9 $\pm$ 8.6<br>0.6-26.0    | 3.4 $\pm$ 0.96<br>2.2-4.6    | 100 $\pm$ 65<br>26-239     | 5.1 $\pm$ 4.3<br>0.15-10.7   | 7.5 $\pm$ 0.29<br>7.1-8.0 | 196                               | f,e               |
| May 1987<br>(13)             | 10.1 $\pm$ 8.7<br>0.9-27.5   | 13.0 $\pm$ 1.32<br>10.6-14.3 | 88 $\pm$ 86*<br>8-223      | 4.3 $\pm$ 4.8<br>0.1-11.0    | 7.9 $\pm$ 0.51<br>7.4-8.8 | 116                               | f,e               |
| Aug. 1987<br>(12)            | 11.7 $\pm$ 9.1<br>0.6-26.7   | 19.7 $\pm$ 0.43<br>19.0-20.2 | 53 $\pm$ 48*<br>16-167     | 3.3 $\pm$ 3.0<br>0.1-7.4     | 7.5 $\pm$ 0.20<br>7.2-7.9 | 162                               | f,e               |
| <u>Weser</u>                 |                              |                              |                            |                              |                           |                                   |                   |
| Aug. 1989<br>(15)            | 6.8 $\pm$ 6.5<br>2.2-23.6    | 19.7 $\pm$ 0.88<br>17.5-20.3 | 108 $\pm$ 112*<br>19-426   | 6.8 $\pm$ 1.1<br>5.4-8.7     | 7.8 $\pm$ 0.21<br>7.6-8.3 | 127                               | f,e               |
| <u>Elbe</u>                  |                              |                              |                            |                              |                           |                                   |                   |
| June 1988<br>(10)            | 11.2 $\pm$ 9.4<br><1-26.9    | 18.2 $\pm$ 0.74<br>17.3-19.4 | 100 $\pm$ 94*<br>13-289    | -<br>-                       | 7.8 $\pm$ 0.32<br>7.3-8.3 | 463                               | f,e               |
| <u>Humber plume</u>          |                              |                              |                            |                              |                           |                                   |                   |
| Dec. 1988<br>(4)             | 31.5 $\pm$ 2.1<br>28.8-33.8  | 6.8 $\pm$ 0.31<br>6.5-7.2    | 70 $\pm$ 64<br>15-139      | -<br>-                       | -<br>-                    | -<br>-                            | -<br>-            |
| May 1990<br>(3)              | 33.5 $\pm$ 0.42<br>33.2-34.0 | 11.2 $\pm$ 0.45<br>10.7-11.6 | 7.4 $\pm$ 4.0<br>3.7-11.6  | -<br>-                       | -<br>-                    | -<br>-                            | -<br>-            |
| <u>Thames plume</u>          |                              |                              |                            |                              |                           |                                   |                   |
| Feb. 1989 (2)                | 34.1                         | 6.8                          | 42.2                       | -                            | -                         | -                                 | -                 |
| <u>S. North Sea</u>          |                              |                              |                            |                              |                           |                                   |                   |
| July 1988 (3)                | > 31.5                       | -                            | < 2                        | -                            | -                         | -                                 | -                 |

\* Denotes occasion when well developed TMZ was observed.

\*\* f = flood tide; e = ebb tide.

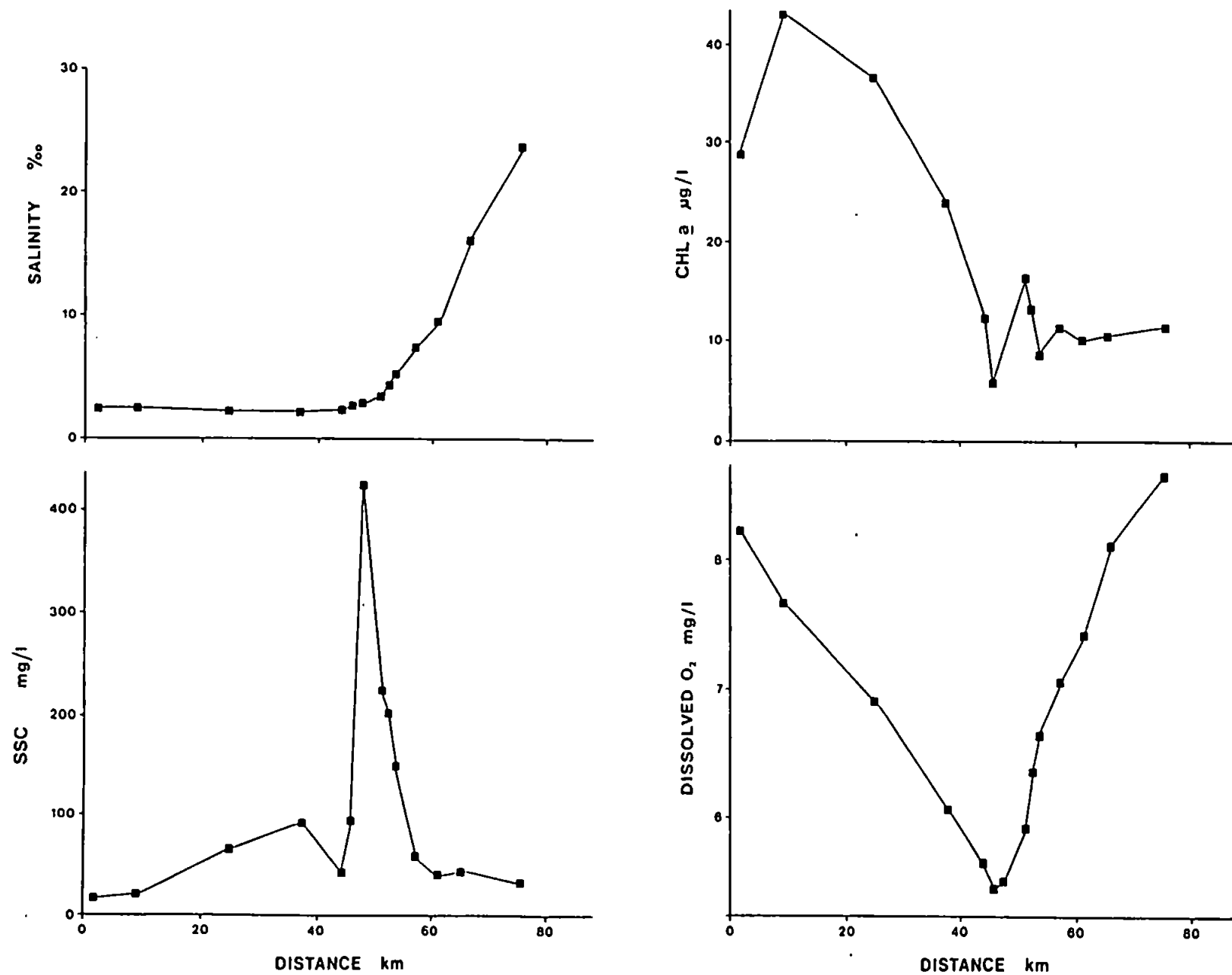


Figure 2.5a: Distributions of salinity, chlorophyll a (chl a; determined spectrophotometrically after hot ethanol extraction by B. Schuchardt, University of Bremen, FRG), suspended solids concentration (SSC) and dissolved O<sub>2</sub> in the Weser Estuary.

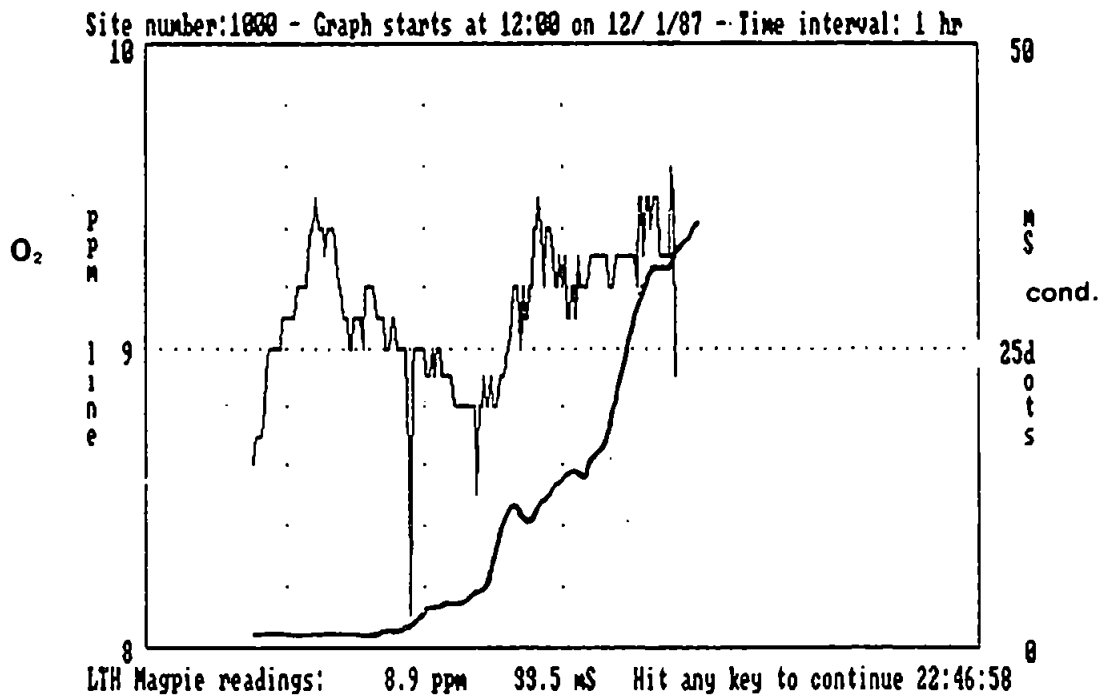
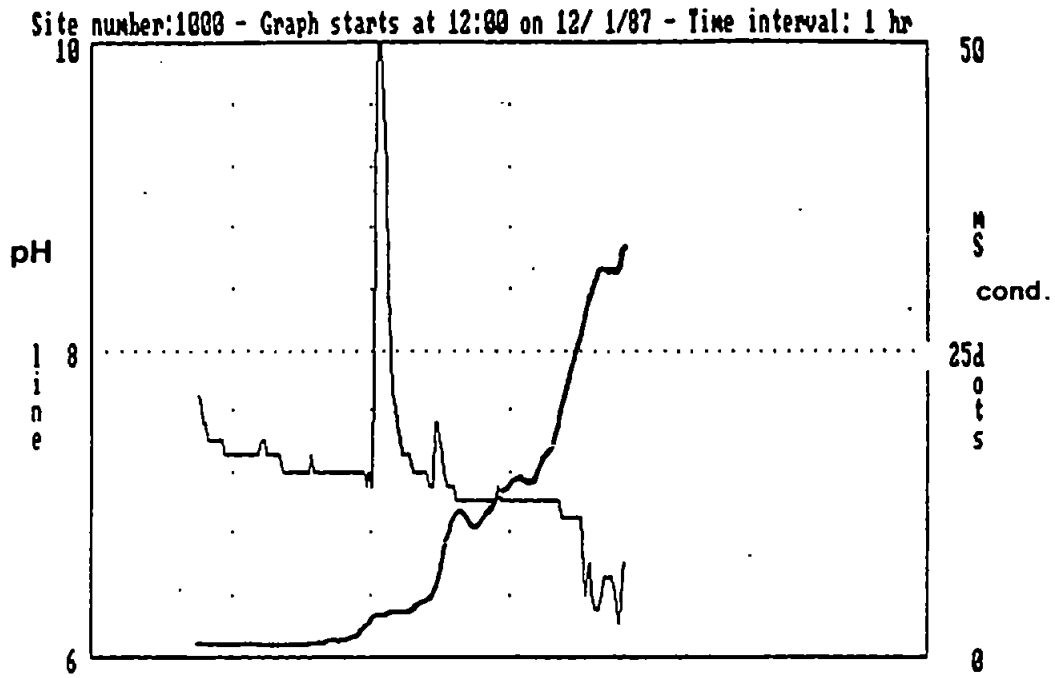


Figure 2.5b: LTH Magpie outputs of continuously logged pH and dissolved O<sub>2</sub> against a reference of conductivity in Humber Estuary during winter. The pH ranges from 6.5 towards the mouth to over 10 in the low salinity region. Although the former was supported by pH records from a portable meter, the latter probably resulted from some instrumental instability.

## 2.2.2: Particle Composition

A summary of the particle characteristics for each survey is given in Table 2.7.

### 2.2.2.1: Surface Areas - Axial Profiles

Axial profiles of SSA are illustrated in Figures 2.6a-2.6c. A common trend is frequently apparent consisting of an increase of SSA in low salinity waters culminating in the vicinity of the TMZ, thereafter decreasing seaward. A further decrease is observed offshore in the plume waters of the Humber and Thames, and in the open waters of the southern North Sea. A low salinity peak in SSA has also been noted in the estuaries of the Gironde and Loire (Elbaz-Poulichet *et al.*, 1982; Martin *et al.*, 1986), and Tamar (Glegg *et al.*, 1987; Titley *et al.*, 1987; this work), and it has been postulated that the destruction of flocs and/or the *in situ* formation of Fe and Mn oxide coatings on the particle surface are responsible (Martin *et al.*, 1986). As this peak is coincident with high turbidity waters the available sites for adsorption per litre in this region are further enhanced. Indeed the TMZ has often been implicated as an important location for sorption reactions (Bewers and Yeats, 1978; Elbaz-Poulichet *et al.*, 1984; Ackroyd *et al.*, 1986; Donard and Bourg, 1986; Morris, 1986; Cossa and Noël, 1987).

In contrast, a low salinity peak in SSA is not observed in the absence of a distinct TMZ (Humber summer, Scheldt winter). Rather uniform SSAs in the Mersey Estuary were encountered in concert with a uniform suspended solids distribution (Millward *et al.*, 1990); a TMZ is not readily observed in this estuary (P.C. Head, pers. comm.) because of trapping of material at the head associated with extensive dredging operations and canalization.

Table 2.8 lists a series of synthetic and natural samples and their respective SSAs as determined by a BET N<sub>2</sub> adsorption technique. Iron and Mn oxides have high SSAs compared with many other natural and synthetic materials and their importance to estuarine particle microstructure has been emphasised (Martin *et al.*, 1986; Glegg *et al.*, 1987; Titley *et al.*, 1987). However, no striking or



SSA  
m<sup>2</sup>/g

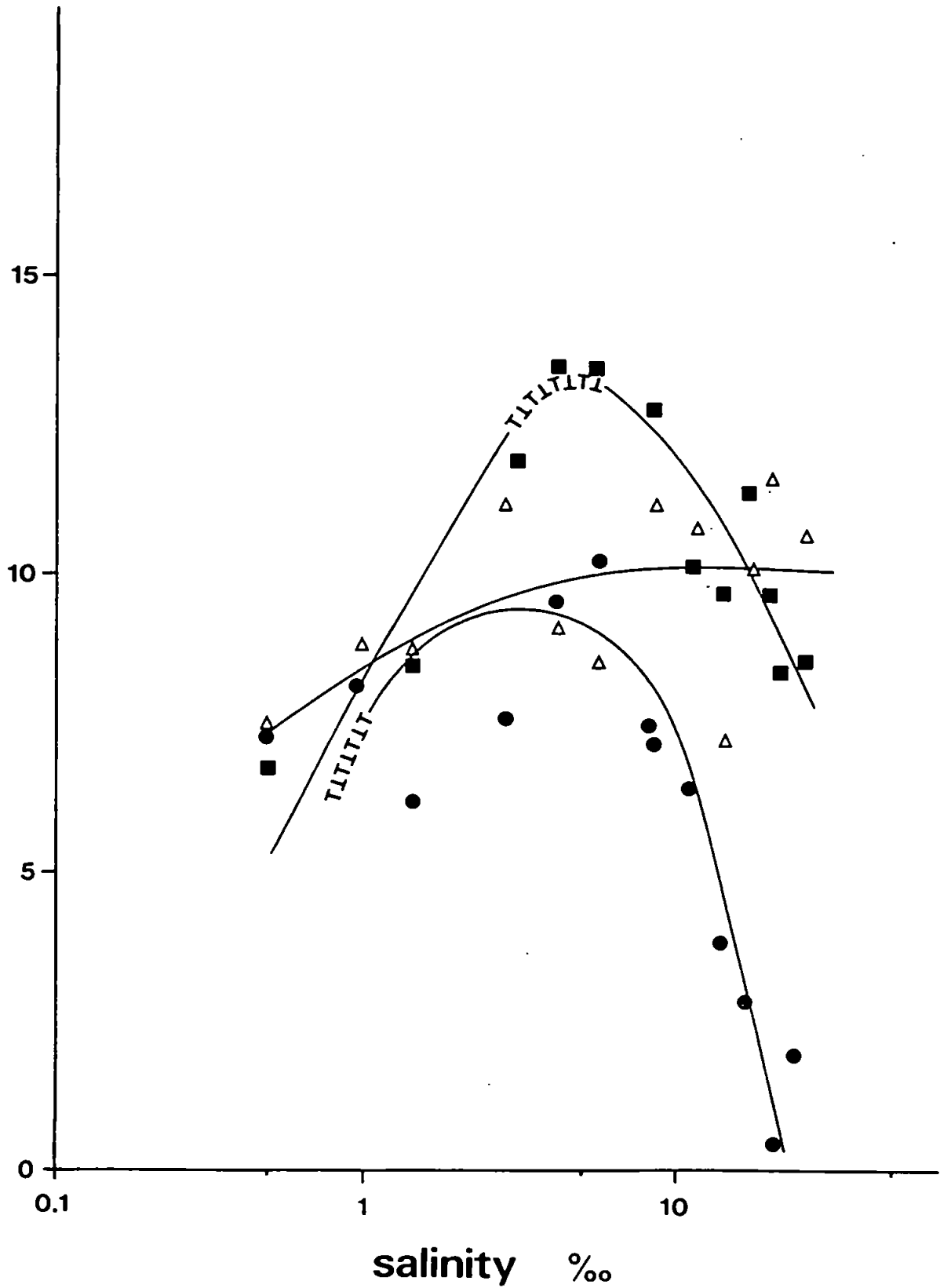


Figure 2.6 (continued): b. Scheldt winter (Δ), spring (●) and summer (■).

SSA  
m<sup>2</sup>/g

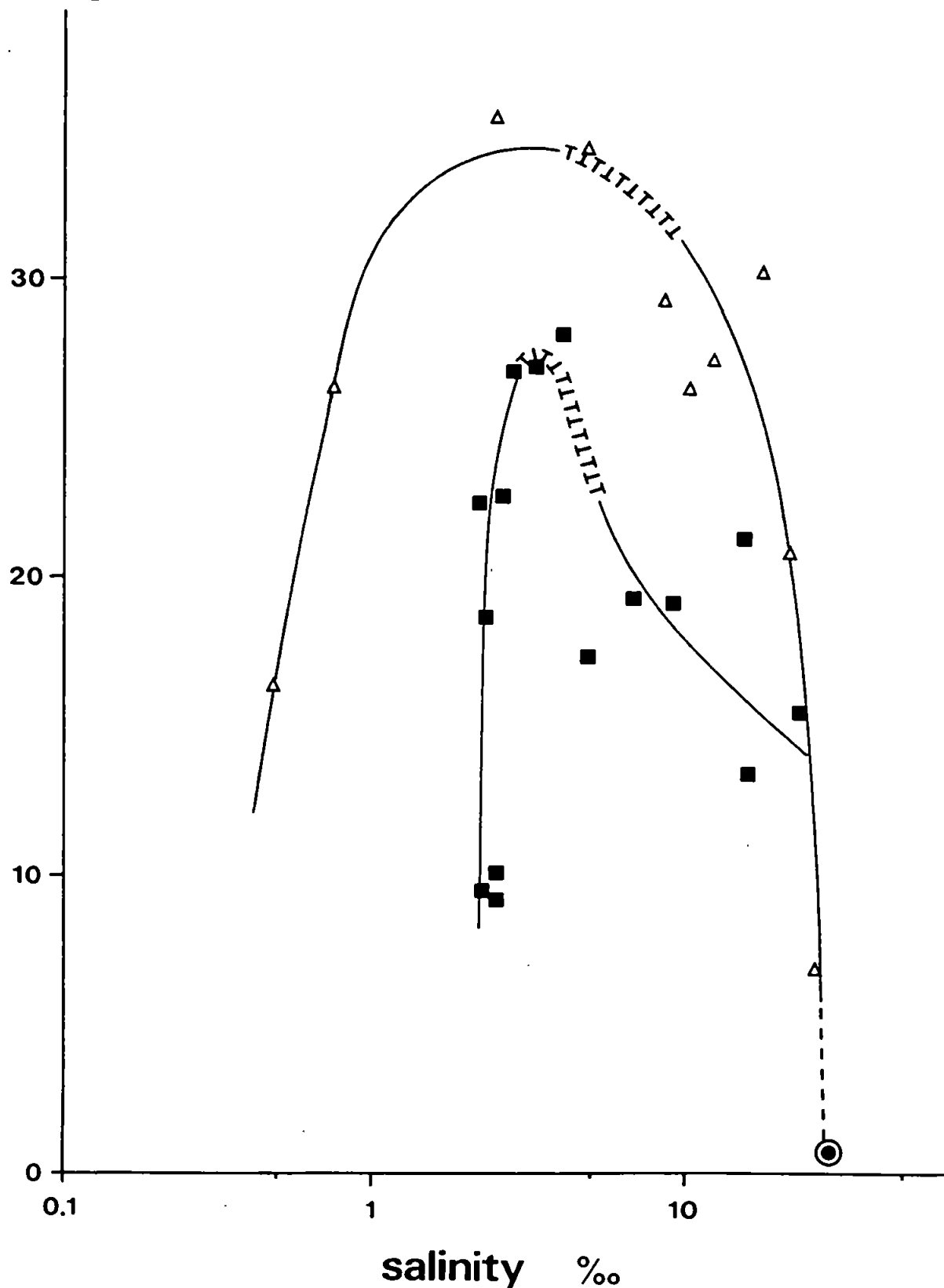


Figure 2.6 (continued): c. Weser (■) and Elbe (Δ), and mean SSAs of southern North Sea samples (●).

Table 2.7: Summary of particle composition analyses of suspended sediment samples from the North Sea environment. Mean  $\pm$  one standard deviation,  $\mu \pm 1\sigma$ , and range, R, of n sample analyses given.

| Survey Date           | Statistical parameters | BET SSA (m <sup>2</sup> /g) | Fe (mg/g)       | Mn (mg/g)       | Fe:Mn          | C (%)           | C:N            |
|-----------------------|------------------------|-----------------------------|-----------------|-----------------|----------------|-----------------|----------------|
| <u>Humber</u>         | n                      | 18                          | 19              | 19              | 19             | 18              | 18             |
| <i>Jan. 1988</i>      | $\mu \pm 1\sigma$      | 24.0 $\pm$ 6.5              | 12.0 $\pm$ 5.8  | 0.99 $\pm$ 0.18 | 12.9 $\pm$ 8.7 | 5.4 $\pm$ 0.4   | 9.7 $\pm$ 1.4  |
|                       | R                      | 9.8-38.3                    | 4.8-29.1        | 0.64-1.29       | 5.5-39.3       | 4.8-5.8         | 6.7-11.5       |
|                       | n                      | 11                          | 11              | 11              | 11             | 11              | 11             |
| <i>July 1989</i>      | $\mu \pm 1\sigma$      | 25.2 $\pm$ 3.9              | 10.4 $\pm$ 1.22 | 1.38 $\pm$ 0.13 | 7.6 $\pm$ 0.6  | 4.8 $\pm$ 0.5   | 15.6 $\pm$ 3.4 |
|                       | R                      | 16.3-29.5                   | 9.02-13.2       | 1.23-1.69       | 6.9-9.1        | 4.3-6.1         | 11.5-21.4      |
| <u>Thames</u>         | n                      | 14                          | 14              | 14              | 14             | 14              | 14             |
| <i>Feb./Mar. 1989</i> | $\mu \pm 1\sigma$      | 12.3 $\pm$ 4.0              | 4.86 $\pm$ 1.13 | 0.70 $\pm$ 0.14 | 7.1 $\pm$ 1.7  | 7.1 $\pm$ 2.2   | 9.9 $\pm$ 2.0  |
|                       | R                      | <5-19.2                     | 3.72-8.26       | 0.50-0.94       | 4.5-10.0       | 4.8-11.1        | 5.2-13.0       |
| <u>Scheldt</u>        | n                      | 12                          | 12              | 12              | 12             | 12              | 12             |
| <i>Feb. 1987</i>      | $\mu \pm 1\sigma$      | 9.7 $\pm$ 1.5               | 3.20 $\pm$ 0.38 | 0.70 $\pm$ 0.21 | 5.1 $\pm$ 1.9  | 6.1 $\pm$ 1.1   | 13.7 $\pm$ 2.9 |
|                       | R                      | 7.3-11.6                    | 2.63-3.77       | 0.39-1.07       | 2.9-8.2        | 4.1-7.8         | 9.4-17.6       |
|                       | n                      | 13                          | 13              | 13              | 13             | 12              | 12             |
| <i>May 1987</i>       | $\mu \pm 1\sigma$      | 6.2 $\pm$ 2.9               | 2.56 $\pm$ 1.10 | 0.62 $\pm$ 0.18 | 4.7 $\pm$ 2.4  | 8.6 $\pm$ 3.7   | 9.5 $\pm$ 3.2  |
|                       | R                      | <1-10.3                     | 0.70-3.64       | 0.39 $\pm$ 0.93 | 0.9-7.1        | 4.7-15.8        | 5.2-12.9       |
|                       | n                      | 12                          | 12              | 12              | 12             | 12              | 12             |
| <i>Aug. 1987</i>      | $\mu \pm 1\sigma$      | 10.5 $\pm$ 2.2              | 2.70 $\pm$ 0.61 | 0.77 $\pm$ 0.25 | 4.0 $\pm$ 2.1  | 6.6 $\pm$ 1.4   | 12.6 $\pm$ 2.8 |
|                       | R                      | 6.8-13.7                    | 2.02-3.67       | 0.40-1.14       | 2.7-8.1        | 5.0-9.5         | 8.1-16.7       |
| <u>Weser</u>          | n                      | 15                          | 15              | 15              | 15             | 15              | 15             |
| <i>Aug. 1989</i>      | $\mu \pm 1\sigma$      | 18.8 $\pm$ 6.3              | 5.95 $\pm$ 0.64 | 2.43 $\pm$ 1.27 | 2.9 $\pm$ 0.9  | 6.3 $\pm$ 2.1   | 10.4 $\pm$ 2.2 |
|                       | R                      | 9.3-28.2                    | 4.46-7.17       | 1.25-5.06       | 1.4-3.8        | 4.8-11.4        | 7.0-13.6       |
| <u>Elbe</u>           | n                      | 10                          | 10              | 9               | 9              | 10              | 10             |
| <i>June 1988</i>      | $\mu \pm 1\sigma$      | 25.6 $\pm$ 8.6              | 6.6 $\pm$ 0.95  | 3.08 $\pm$ 0.35 | 2.2 $\pm$ 0.2  | 6.9 $\pm$ 1.7   | 10.4 $\pm$ 2.1 |
|                       | R                      | 7.2-35.5                    | 5.0-8.3         | 2.58-3.62       | 1.9-2.4        | 4.6-10.0        | 6.7-13.2       |
| <u>Humber plume</u>   | n                      | 4                           | 4               | 4               | 4              | 4               | 4              |
| <i>Dec. 1988</i>      | $\mu \pm 1\sigma$      | 12.8 $\pm$ 3.3              | 8.75 $\pm$ 3.60 | 0.91 $\pm$ 0.10 | 9.4 $\pm$ 3.2  | 4.3 $\pm$ 0.4   | 17.1 $\pm$ 2.1 |
|                       | R                      | 8.5-15.7                    | 5.16-12.6       | 0.77-0.98       | 6.7-12.9       | 3.9-4.7         | 14.5-19.1      |
|                       | n                      | 3                           | 3               | 3               | 3              | 3               | 3              |
| <i>May 1990</i>       | $\mu \pm 1\sigma$      | 9.0 $\pm$ 3.2               | 6.90 $\pm$ 2.16 | 0.84 $\pm$ 0.13 | 8.1 $\pm$ 1.4  | 6.0 $\pm$ 0.6   | 11.3 $\pm$ 1.9 |
|                       | R                      | 5.9-12.3                    | 5.06-9.28       | 0.70-0.96       | 7.2-9.7        | 5.4-6.1         | 9.2-12.9       |
| <u>Thames plume</u>   | n                      | 2                           | 2               | 2               | 2              | 2               | 2              |
| <i>Feb. 1989</i>      | $\mu$                  | 10.7                        | 4.35            | 0.50            | 8.9            | 4.0             | 13.7           |
| <u>S. North Sea</u>   | n                      | 3                           | 3               | 3               | 3              | 3               | 3              |
| <i>July 1988</i>      | $\mu \pm 1\sigma$      | 0.8 $\pm$ 0.7               | 1.6 $\pm$ 0.69  | 0.38 $\pm$ 0.27 | 5.7 $\pm$ 4.2  | 22.9 $\pm$ 12.3 | 8.0 $\pm$ 1.2  |
|                       | R                      | <0.1-1.4                    | 1.2-2.4         | 0.22-0.69       | 1.7-10.0       | 8.7-30.3        | 6.6-9.0        |



consistent correlation was found for individual samples between SSA and leachable Fe and Mn (*i.e.* quantification of oxide coatings; Figure 2.16). On the other hand, the implicated role of organics to the surface properties of estuarine particles has been to reduce the SSA by pore blocking (Weiler and Mills, 1965; Elbaz-Poulichet

Table 2.8: BET N<sub>2</sub> adsorption specific surface areas (SSA) of naturally occurring and synthetic materials.

| Material                      | SSA (m <sup>2</sup> /g) | Reference                   |
|-------------------------------|-------------------------|-----------------------------|
| <i>NATURAL</i>                |                         |                             |
| Coastal sand                  | <0.1                    | This work                   |
| Soil Organic Matter           | <1                      | Chiou <i>et al.</i> (1990)  |
| Shelf sediments               | 2-20                    | Weiler and Mills (1965)     |
| Calcareous ooze               | 3-30                    | Weiler and Mills (1965)     |
| Slope sediments               | 10-45                   | Weiler and Mills (1965)     |
| Continental terrace sediments | 2-53                    | Slabaugh and Stump (1964)   |
| Siliceous ooze                | 18-70                   | Weiler and Mills (1965)     |
| Deep ocean red clay           | 25-90                   | Weiler and Mills (1965)     |
| Lepidocrocite                 | 258                     | This work                   |
| <i>SYNTHETIC</i>              |                         |                             |
| Humic acid                    | 0.7                     | Glegg (1987)                |
| Kaolinite                     | 7.6; 9.9                | This work                   |
| Montmorillonite               | 67.5                    | This work                   |
| Illite                        | 76.9                    | This work                   |
| Lepidocrocite                 | 97-121                  | Crosby <i>et al.</i> (1983) |
| Amorphous FeOOH               | 159-234                 | Crosby <i>et al.</i> (1983) |
| Ground MnO <sub>2</sub>       | 147                     | Guy <i>et al.</i> (1975)    |
| Amorphous MnO <sub>2</sub>    | 470                     | This work                   |

*et al.*, 1982; Martin *et al.*, 1986; Jednacak-Biscan and Juracic, 1987; Glegg *et al.*, 1987; Titley *et al.*, 1987). Total C content includes carbonates and is therefore not a measure of organic C, although Figure 2.7 demonstrates the close relationship between the two parameters in a North Sea estuarine environment. Furthermore, measurements have demonstrated that CaCO<sub>3</sub> has a relatively low BET SSA (Suess, 1973; Pravdic *et al.*, 1981) and it may therefore be more appropriate to

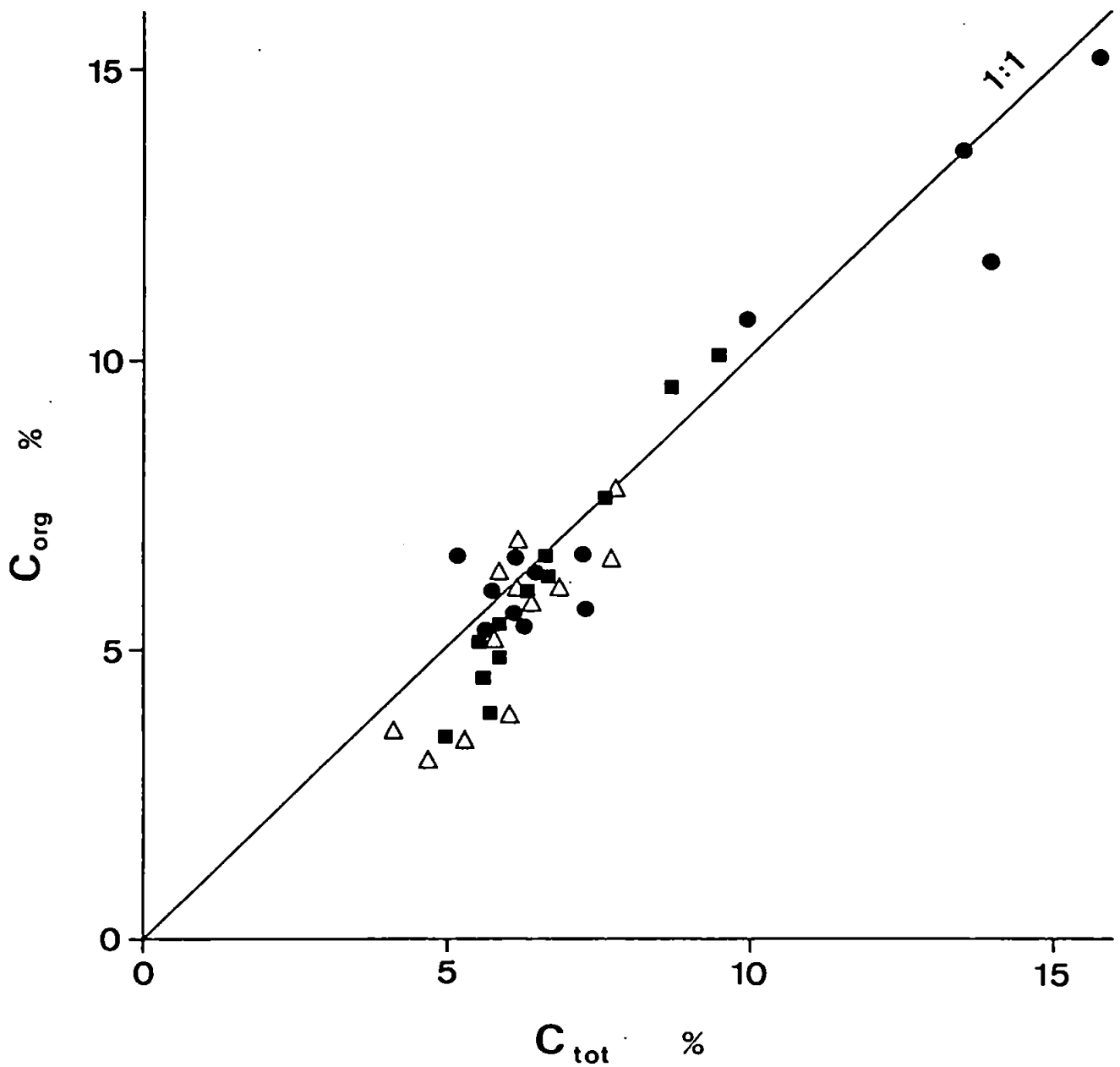


Figure 2.7: Organic carbon ( $C_{org}$ ; determined by G. Zwolsman, University of Utrecht, N.L.) versus total carbon ( $C_{tot}$ ) for the Scheldt Estuary.

Winter ( $\Delta$ ):  $C_{tot} = 2.97 + 0.581 C_{org}$ ;  $r^2 = 66.4\%$ ;  $p \leq 0.0005$ .

Spring ( $\bullet$ ):  $C_{tot} = 0.202 + 1.03 C_{org}$ ;  $r^2 = 93.9\%$ ;  $p \leq 0.0005$ .

Summer ( $\blacksquare$ ):  $C_{tot} = 2.65 + 0.640 C_{org}$ ;  $r^2 = 95.4\%$ ;  $p \leq 0.0005$ .

consider carbonaceous material in general as presenting a relatively inert BET adsorption surface. Once more, however, a clear relationship between C contents and SSAs for individual samples was not apparent (Figure 2.16). Correlation of SSA with an index intended as a ratio of active oxide coatings to inert organic coatings/carbonaceous content [*i.e.* (Fe + Mn)/C] met with varying degrees of significance ranging from  $p \leq 0.0005$  (Scheldt during spring, Weser and Elbe), to  $p > 0.5$  (Thames, and Scheldt during winter).

The relationship between particle size and SSA was investigated by a series of settling experiments. Suspensions of freshly prepared Tamar mud in estuary water (about 5 g/l) were allowed to settle through 1 m in glass columns for different time intervals up to 2 hours and the remaining suspended material in each instance was filtered (0.45  $\mu\text{m}$ ) and freeze dried prior to BET analysis (Section 2.1.3.2). In addition, a similar approach was adopted *in situ* during *RRS Challenger* cruise CH46 (Section 3.1.2).

The results are shown in Figure 2.8 (see also Figure 3.2) and demonstrate that a reduction in particle size, as inferred from Stoke's law and measured directly by a laser diffraction particle sizer (Malvern Instruments; Bale *et al.*, 1989), is accompanied by an increase in SSA. The median particle diameter (MPD, in  $\mu\text{m}$ ) of Tamar material was related to the SSA by the following equation:

$$\text{MPD} = 30.9 - 1.24 \text{SSA} \quad (2.5)$$

for which  $r^2 = 85.3\%$  and  $p \leq 0.0005$ .

The inference of these observations is that physical factors, in particular those conducive of particle size sorting within the TMZ (Postma, 1967; Schubel 1969; Gobeil *et al.*, 1981; Bale *et al.*, 1984), are primarily responsible for an estuarine SSA longitudinal profile; the role of chemical factors, although intuitively likely to be important, could not be established.

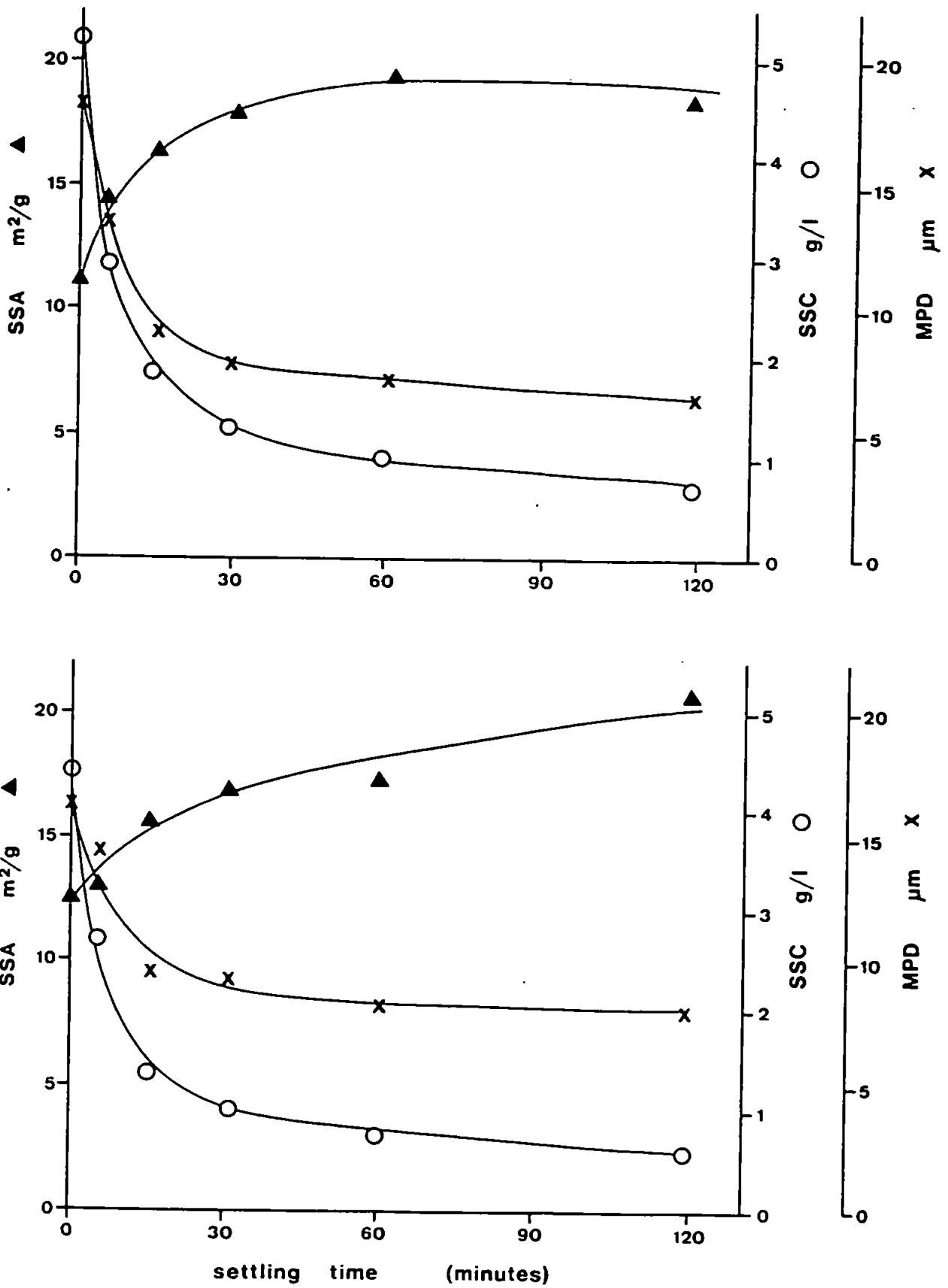


Figure 2.8: SSA, suspended solids concentration (SSC), and mean particle diameter (MPD) of Tamar sediment remaining in suspension during two settling experiments in 1 m glass columns as a function of time.

### 2.2.2.2 Iron and Manganese - Axial Profiles

Axial profiles of particulate Mn vary between estuaries (Figure 2.14). Rather constant concentrations are encountered in the Humber Estuary, although a slight seaward increase is evident in the summer. Uniform concentrations are also a feature of the Thames and Elbe Estuaries, whereas a seaward decrease is observed in the Weser in tandem with all other metals (Section 2.2.3.1). In the Scheldt Estuary during all surveys a maximum of particulate Mn occurs in the salinity range 15-25 ‰. This accords with the model of Duinker and co-workers describing the behaviour of Mn in this estuary (Duinker *et al.*, 1979b; 1982a; Wollast *et al.*, 1979) whereby dissolved Mn(II) is oxidized downstream of the anoxic zone in response to an increase of pH and dissolved O<sub>2</sub> into less soluble species of higher oxidation states (MnOOH and MnO<sub>2</sub>).

Particulate Fe profiles (Figure 2.14) are in general similar to those of Mn. The occurrence of the maxima in the Scheldt profiles at lower salinities (2-5 ‰) can be explained in terms of the more rapid oxidation kinetics of Fe(II) in aqueous systems (Sung and Morgan, 1980; 1981) in concert with removal of colloidal Fe material through flocculation (Moore *et al.*, 1979; Boyle *et al.*, 1977; Sholkovitz, 1978).

### 2.2.2.3: Surface Areas, Iron and Manganese - Inter-Estuarine Variability

The magnitude of SSA follows the order:

Humber = Elbe > Weser > Thames > Scheldt > North Sea.

In the Humber particles are rich in amorphous Fe as a result of the discharge of vast quantities of acid-iron waste by the titanium dioxide manufacturing industry (65 000 tonnes are discharged annually according to Newell *et al.*, 1984) and the rapid and effective precipitation of anthropogenic Fe in the Humber Estuary is therefore responsible for high SSAs.

Iron concentrations in the Elbe Estuary are somewhat lower than in the Humber and high SSAs are probably more the result of elevated leachable Mn

concentrations. Elevated particulate Mn is also a feature of the Weser Estuary (Table 2.7) and of the adjoining German Bight (Nolting and Eisma, 1988; Section 3.2.2.2). The origin of high particulate Mn in this environment may be the result of a similar but accentuated mechanism to that which accounts for the uptake of Mn in the Tamar Estuary (Morris *et al.*, 1982a). The rapidly accreting and anoxic harbour regions of Hamburg (Elbe) and Bremen (Weser) induce a reduction of Mn(IV) in the sediments to more soluble Mn(II) which subsequently diffuses into the water column, a process enhanced by disturbance of the sediment by tidal stress. Transport downstream is accompanied by uptake onto the suspended solid phase as the O<sub>2</sub> concentrations improve and turbidity increases. A rapid removal of Mn from solution has been observed at low salinities in the Elbe (Duinker *et al.*, 1982b) and Weser (Figure 2.18) in support of this hypothesis.

Figure 2.9 shows the relationship between mean SSA and important compositional parameters described in Section 2.2.2.1 for the surveys of the North Sea environment. Also presented are the results from the Mersey and Tamar although these have not been included in the regression analyses. SSA is best correlated with Fe + Mn, and although C effects a reduction in SSA, this is only obvious at high (> 10%) C contents. The implication is that chemical factors, primarily Fe and Mn oxide coatings, are responsible for the general inter-estuarine variability in SSAs.

#### 2.2.2.4: Porosity

Full adsorption-desorption isotherm plots were very similar; examples from the Humber and Scheldt are shown in Figure 2.10. Although the end of the desorption limb is (tentatively) extrapolated back to the origin, complete reversibility was not achieved. Irreversibility was also demonstrated by a reduction in SSA on successive determinations on the same sample aliquot. Trapped N<sub>2</sub> molecules may be associated with similar sized pores to their molecular diameter, or result from some physical alteration of the adsorbate or adsorbent during the experiment. The characteristic shape of these isotherms can be described in terms of a hybrid of

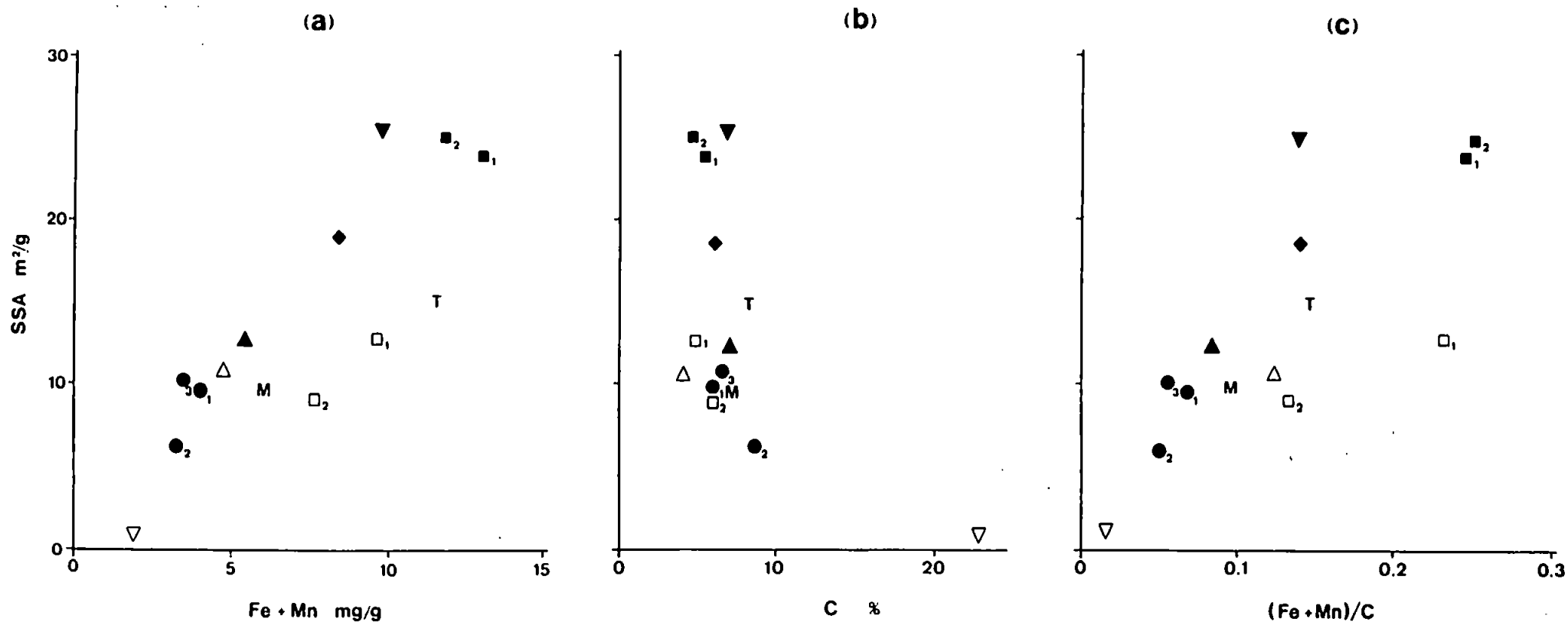


Figure 2.9a-c: Relationship between SSA and compositional parameters. Symbols represent mean values of the surveys. Estuaries: Humber (■) during winter (1) and summer (2); Thames (▲); Scheldt (●) during winter (1), spring (2) and summer (3); Weser (◆); Elbe (▼); Mersey (M); Tamar (T). North Sea: Humber plume (□) during winter (1) and spring (2); Thames plume (Δ); southern North Sea (▽).

a:  $SSA = 0.54 + 0.00191(Fe + Mn)$ ;  $r^2 = 74.5\%$ ;  $p \leq 0.0005$ .

b: No significant correlation ( $p > 0.05$ ).

c:  $SSA = 4.04 + 77.0[(Fe + Mn)/C]$ ;  $r^2 = 55.8\%$ ;  $p = 0.003$ .

Type II and Type IV isotherms (*i.e.* non-porous/mesoporous solids; Gregg and Sing, 1982). This is not surprising as major component adsorbates such as montmorillonite (Stul, 1985; this work), kaolinite (this work) and Fe oxyhydroxides (Crosby *et al.*, 1983; Marsh *et al.*, 1984; this work) exhibit these type of isotherms. The hysteresis signifies slit shaped pores (Millward *et al.*, 1989) of diameters in the range <0.5 to >20 nm as calculated from the *Kelvin Equation* (Equation 2.3), assuming  $V = 34.7 \text{ cm}^3/\text{mol}$ ,  $\gamma = 8.72 \times 10^{-7} \text{ J/cm}^2$  and  $R = 8.314 \text{ J/K.mol}$ . Pore size distribution studies on sediment material indicate that those of diameter 3-5 nm are most important to the SSA (Slabaugh and Stump, 1964; Weiler and Mills, 1965; Millward *et al.*, 1989) which are therefore amply able to accommodate adsorbing metal ions of radii of the order of  $10^{-1} \text{ nm}$  (Wealt and Astle, 1979) and may be instrumental to a second stage diffusion controlled reaction (Equation 1.2).

The minimum mesopore (*i.e.* pores of diameter 2-50 nm; Sing, 1982) volumes were estimated from the following equation (Glegg, 1987):

$$PV = \frac{X_{(0.96-0.38)} V}{M} \quad (2.5)$$

where PV is the pore volume ( $\text{cm}^3/\text{g}$ ), M is the molecular mass of  $\text{N}_2$  and X the weight adsorbed in the partial pressure range 0.38 - 0.96 (corresponding to pore sizes between 2 and 50 nm).

For North Sea estuarine samples, PV ranges from  $0.47 \times 10^{-2} \text{ cm}^3/\text{g}$  for a Scheldt sample during spring (Figure 2.10b) of low SSA ( $3.9 \text{ m}^2/\text{g}$ ) and Fe + Mn concentration ( $2.5 \text{ mg/g}$ ), and high C content (10.0%), to  $2.7 \times 10^{-2} \text{ cm}^3/\text{g}$  for a Humber winter sample (Figure 2.10a) in the vicinity of an acid-iron discharge (Figure 2.6a) of high SSA ( $38.3 \text{ m}^2/\text{g}$ ) and Fe + Mn concentration ( $30.0 \text{ mg/g}$ ), and low C content (5.3%). The lowest PV measured ( $0.35 \times 10^{-2} \text{ cm}^3/\text{g}$ ) was that of a sample from the Skagerrak (Figure 2.2f; SSA =  $0.8 \text{ m}^2/\text{g}$ ; Fe + Mn =  $0.7 \text{ mg/g}$ ; C = 23.7%).



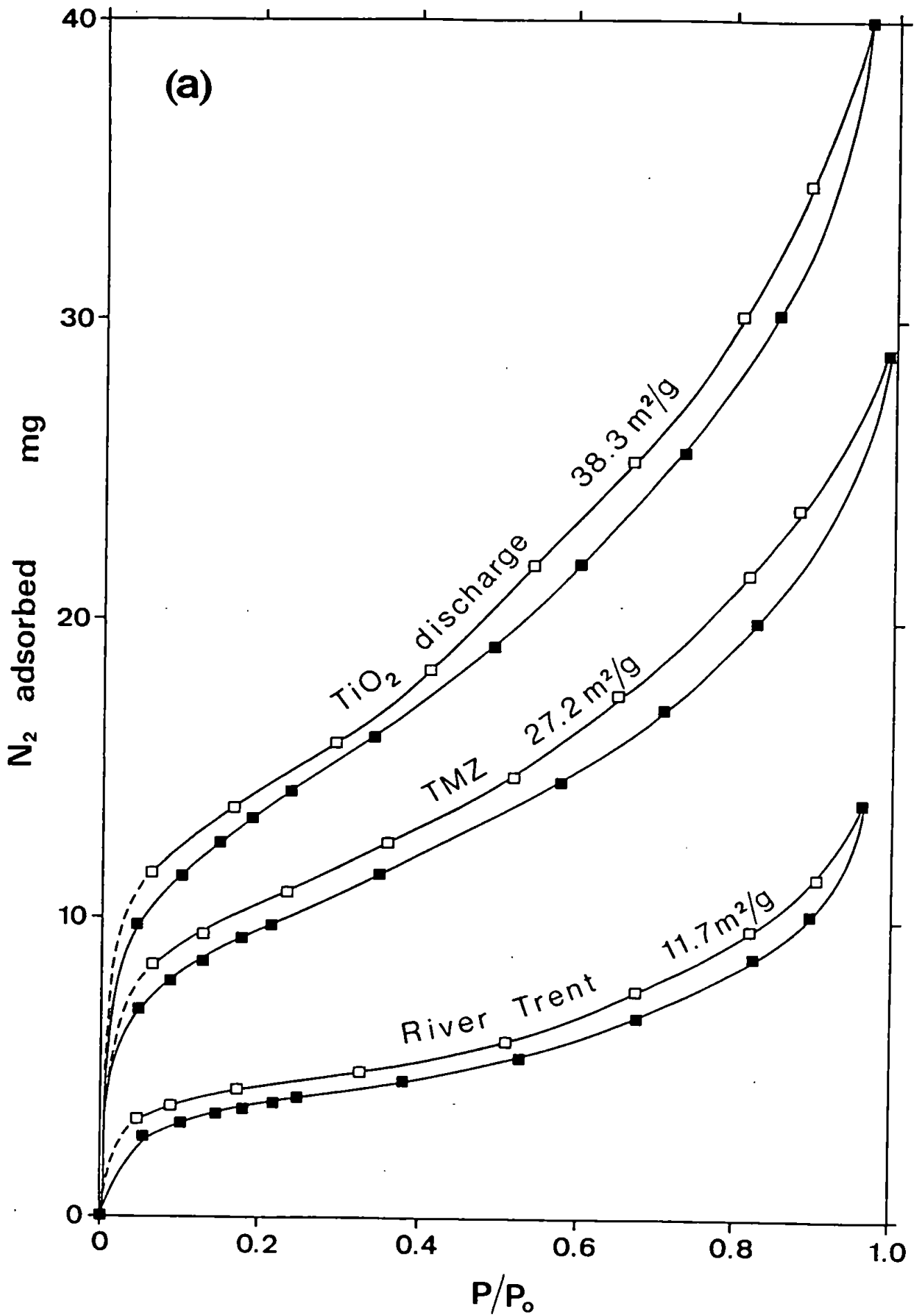


Figure 2.10: The adsorption (■) and desorption (□) of  $N_2$  onto suspended sediments of location and SSA as annotated.

a. Humber winter samples.

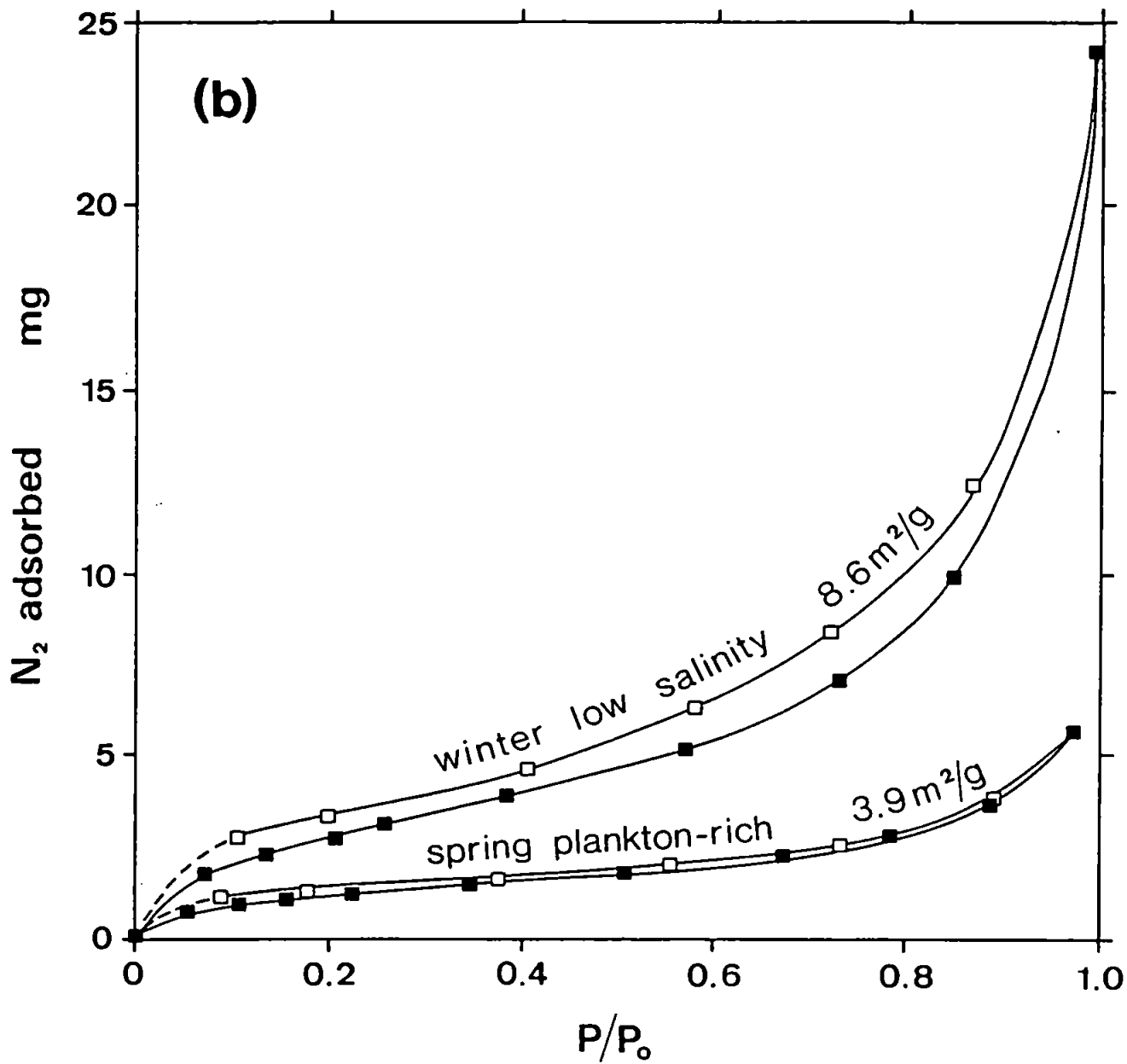


Figure 2.10 (continued): b. Scheldt samples.

PV was a linear function of SSA and the relationship could be described by the following equation:

$$PV = 0.884 + 0.0447 SSA \quad (2.7)$$

for which  $r^2 = 55.8\%$  and  $p \leq 0.0005$ .

#### 2.2.2.5: Iron:Manganese Ratio

The ratio of Fe to Mn gauges simply the relative importance of each oxide phase to the particle surface properties. It has also been used to distinguish on a geographical basis different populations of particles in the Southern Bight and coastal environs (Duinker and Nolting, 1976). It is interesting to note that a reduction in this ratio is encountered in an anticlockwise direction around the North Sea (Table 2.7; in tandem with the general North Sea current circulation); *i.e.*:

|         |             |   |        |   |                 |   |       |   |       |
|---------|-------------|---|--------|---|-----------------|---|-------|---|-------|
|         | Humber      | > | Thames | > | Scheldt         | > | Weser | > | Elbe. |
| (Fe:Mn) | (12.9; 7.6) |   | (7.1)  |   | (5.1; 4.5; 4.0) |   | (2.9) |   | (2.2) |

The results of Duinker and Nolting (1976) indicate that a total (as opposed to leachable) particulate Fe:Mn ratio of about 50 is characteristic of the suspended matter of the Rhine Estuary. It is not unreasonable to assume that most particulate Mn and about 10% Fe is removed from North Sea estuarine material by the leach adopted in the current research (Section 2.2.3.5). Therefore, the leachable Fe:Mn ratio in the Rhine Estuary can be expected to be around 5:1 which would fit nicely into the geographical trend above. Using total metal data for the Elbe Estuary (Duinker *et al.*, 1982b) a leachable Fe:Mn ratio of 2.0 was calculated, very close to that derived directly in this work. This encouraged similar translations using published data for the Tees (Taylor, 1982) and Ems (Duinker *et al.*, 1985) which gave values of 14 and 2.7 respectively, again in accord with the

geographical sequence above (cf. Figure 1.3).

These results are plotted in Figure 2.11 in which the North Sea is divided arbitrarily into three zones (west, south and east) according to the magnitude of the Fe:Mn ratio. Results of the analyses of samples taken along the southern North Sea transect and those supplied as part of the inter-laboratory exercise (Figure 2.2f) are also plotted in Figure 2.12. Although highest off the English coast in the western North Sea, and a minimum in the Skagerrak to the east, the geographical pattern is modified as additional factors to estuarine inputs become important in controlling particulate Fe and Mn distributions, in particular the seasonal cycling of redox potential in surface sediments (Dehairs *et al.*, 1989). Nevertheless, an extensive and distinctive geographical variability in Fe:Mn ratio has been demonstrated, manifested by a transition from the estuaries situated in the north/west (high leachable Fe) to those in the south/east (high leachable Mn). Intuitively, this should be reflected by particulate trace metal patterns according to their relative affinity for the individual (Fe and Mn) hydroxide phases (Takematsu, 1979; Davies-Colley *et al.*, 1984; Aualiitia and Pickering, 1987); however, no such trends could be discerned from the trace metal data of Section 2.2.3.

#### 2.2.2.6: Carbon and C:N Ratio

The different properties of marine and terrestrial plants and living matter have enabled the origin of particulate organic material to be deduced on the basis of its organic carbon to total or organic nitrogen ratio (Loder and Hood, 1972; Loring, 1975; Müller, 1977; Walsh *et al.*, 1981).

Proteins are the major N compounds of living organisms and are characterized by low C:N ratios, and living matter therefore has a low C:N ratio. For example, bacteria, benthic animal organisms and zooplankton have similar C:N ratios of 4-6 (Bordowskiy, 1965a; 1965b; Nagata, 1986). Lower plants, the mass organic matter producers in the sea, are also rich in proteins. Phytoplankton are therefore also characterized by C:N ratios of around 6 (Bordowskiy, 1965a; Banse, 1974). In contrast, higher (land) plants are the major organic matter contributors to

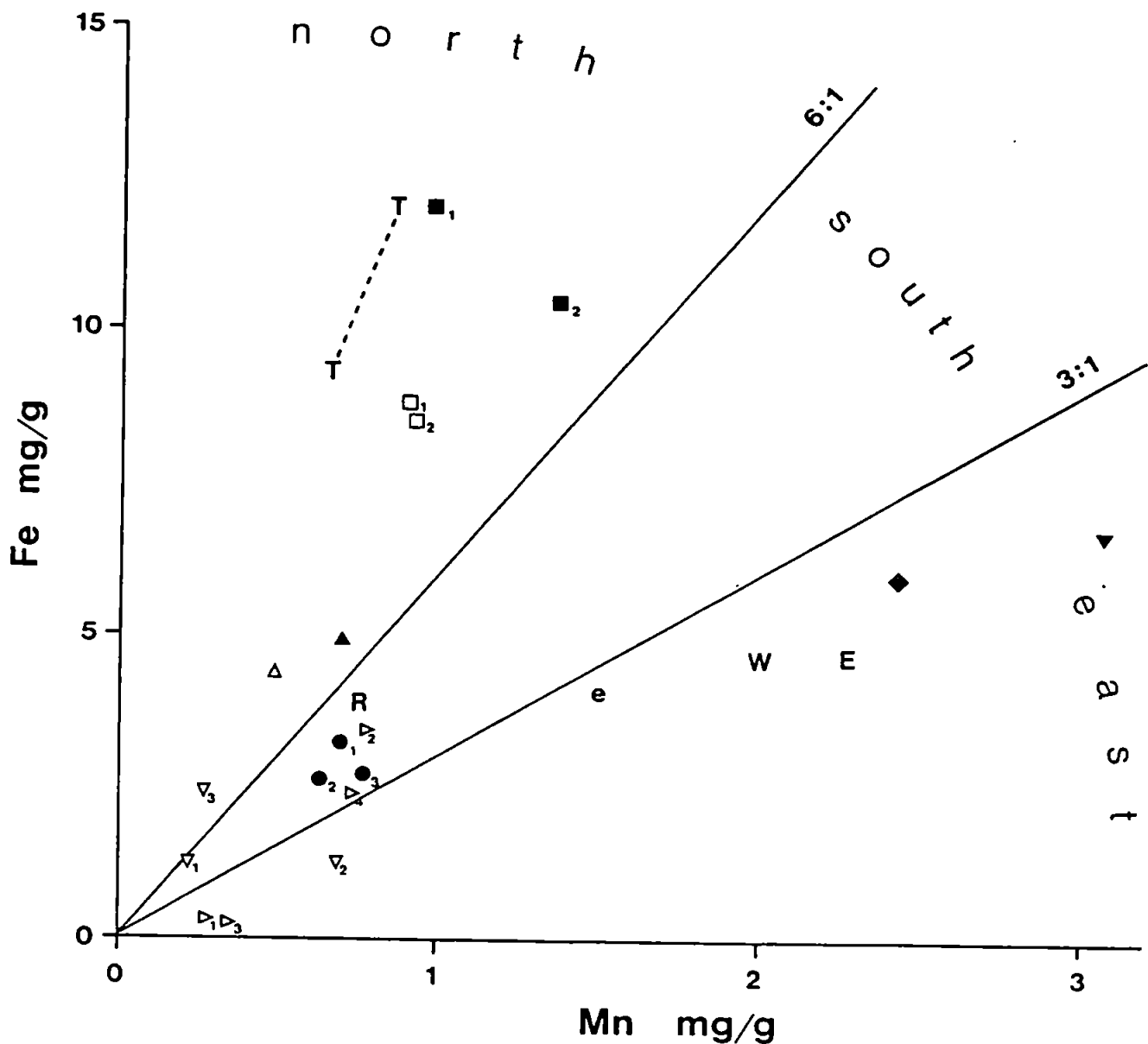


Figure 2.11: Particulate leachable Fe versus Mn concentrations in the North Sea environment. Symbols as in Figure 2.9 represent mean values of the estuarine surveys. Individual North Sea samples for the southern transect ( $\nabla$ ) and supplied for the inter-laboratory comparisons ( $\triangleright$ ) are numbered according to their location in Figure 2.2f. Positions of lettered symbols are derived from published values of total particulate Fe and Mn concentrations for the estuaries of the Rhine (R; Duinker and Nolting, 1976), Ems (e; Duinker *et al.*, 1985), Weser (W; Duinker *et al.*, 1982c) and Elbe (E; Duinker *et al.*, 1982b). Although a ratio of Fe:Mn could be derived for the Tees (T; Taylor, 1982), absolute concentrations could not, and a range of anticipated concentrations is therefore presented.

terrestrial aquatic environments and have relatively low protein contents, and high carbohydrate content of high C:N ratio (Bordowskiy, 1965b; Walsh *et al.*, 1981). Thus, soils and limnic sediments are characterized by appreciably higher C:N ratios than freshly deposited marine sediments (Müller, 1977). For example, the C:N ratio of particulate material in the Amazon River is  $> 10$  compared with a value of  $< 6$  in the euphotic zone of the adjacent continental shelf (Walsh *et al.*, 1981).

Although the determinands in this study were total C and N contents the close resemblance of the former in magnitude to its organic component has been demonstrated (Figure 2.7). Furthermore, analysis of estuarine sediments established that a large fraction of total N (80–95%) is organically associated (Simon and Kennedy, 1987). Therefore, the origins of organic matter, hence possible origins of particles in this study, are now discussed in terms of their total C:N ratios.

Mean carbon versus nitrogen contents are plotted in Figure 2.12. For the North Sea estuarine environments suspended sediment C:N ratios lie close to the 10:1 line indicative of terrestrially dominated material. According to Table 2.7 the highest C:N ratios occur in the Humber during summer ( $15.6 \pm 3.4$ ) in association with the lowest C contents ( $4.8 \pm 0.5$ ) whereas the lowest C:N ratios occur in the Scheldt during spring ( $9.5 \pm 3.2$ ) when productivity was high in the outer estuary in association with the highest C contents ( $8.6 \pm 3.7$ ). More open North Sea samples exhibit higher C contents and lower C:N ratios indicative of a high biomass. Deposited sediments have high C:N ratios, perhaps because of the abundance of  $\text{CaCO}_3$  phases amongst more coarse material. Presumably this would also account for the fact that C in deposited sediments from the Humber/Wash environment was significantly ( $p \leq 0.0005$ ) correlated positively with SSA (an indicator of bulk sediment grain size; Section 2.2.3.6), whereas C:N was significantly ( $p = 0.008$ ) correlated inversely. However, high *organic* C:N ratios have been noted in the deposited sediments of the Humber plume region (10–15; Murray *et al.*, 1980) and Rhine Estuary (14–21; de Groot, 1973) and an alternative explanation for high C:N ratios in sediment deposits would be related to the expulsion of N compounds

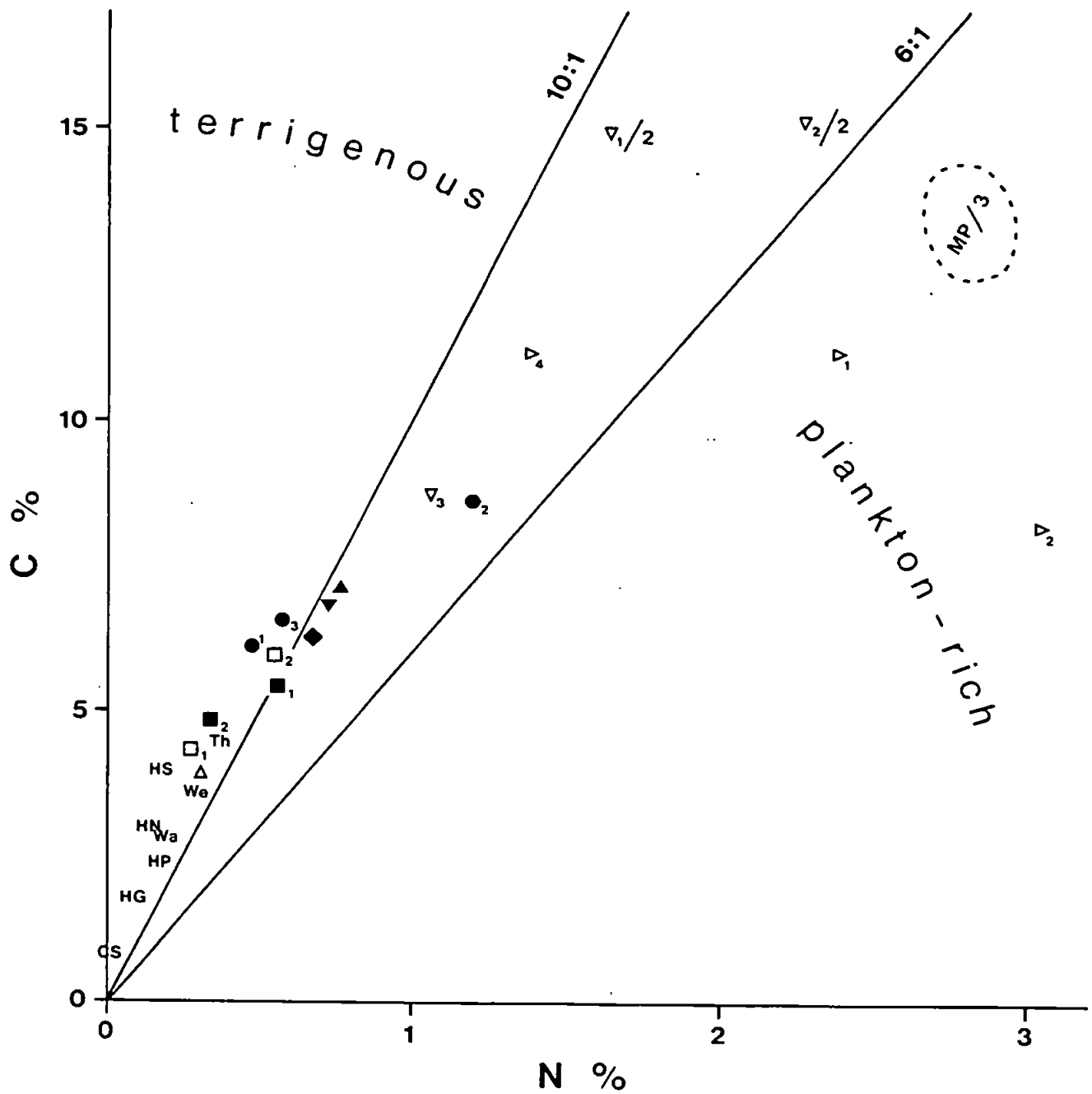


Figure 2.12: Total C versus total N for the North Sea environment. Symbols are as for Figures 2.9 and 2.11. Lettered positions refer to deposited sediment samples: Humber north bank (HN), south bank (HS), sub-tidal (HG), plume (HP, Murray *et al.*, 1980) and coastal sand (CS); Wash (Wa); Weser (We); Thames (Th); Mediterranean phytoplankton samples (MP, Härstedt-Romeo, 1982).

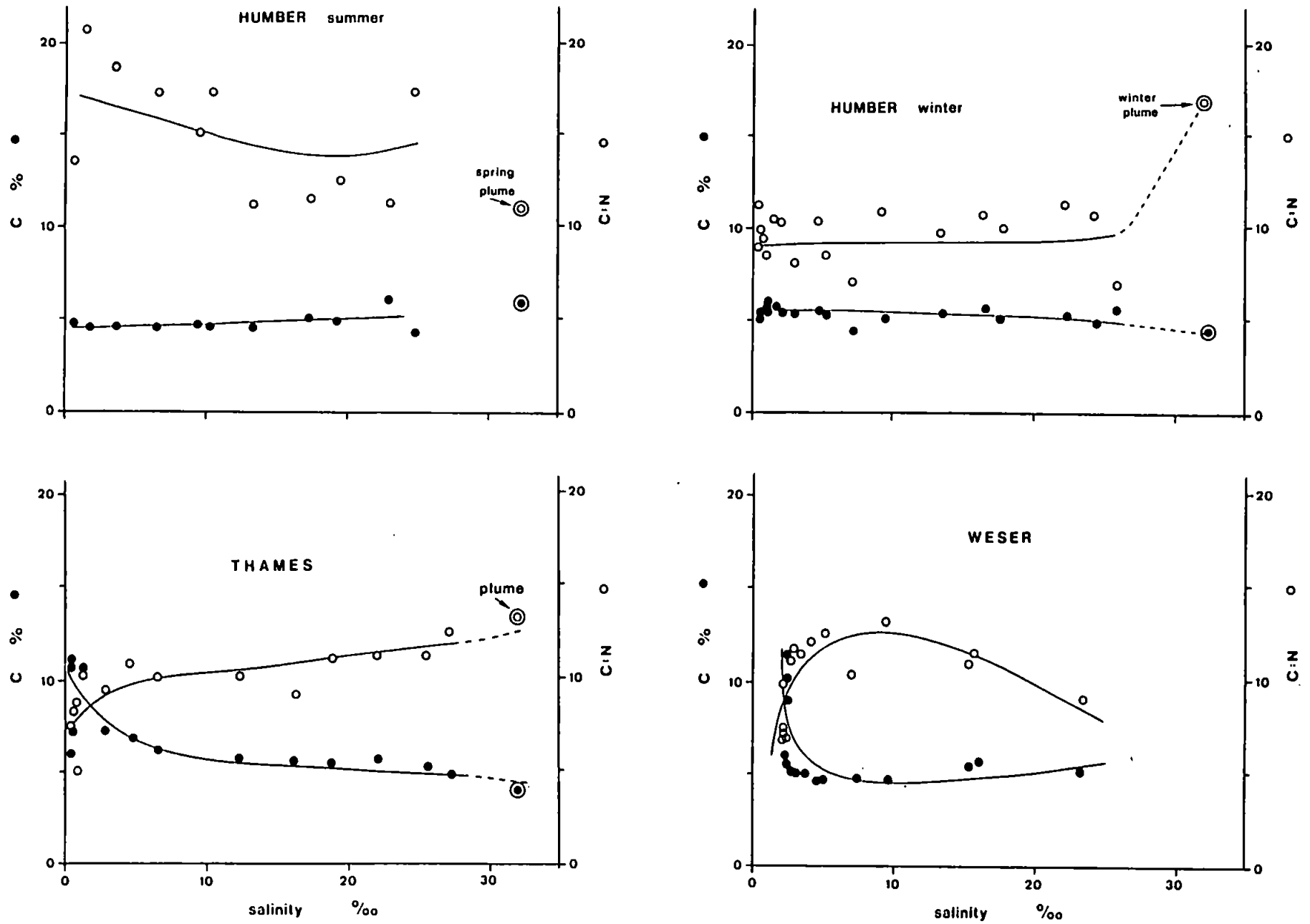


Figure 2.13: Axial profiles of suspended particulate C and C:N for the North Sea estuaries.



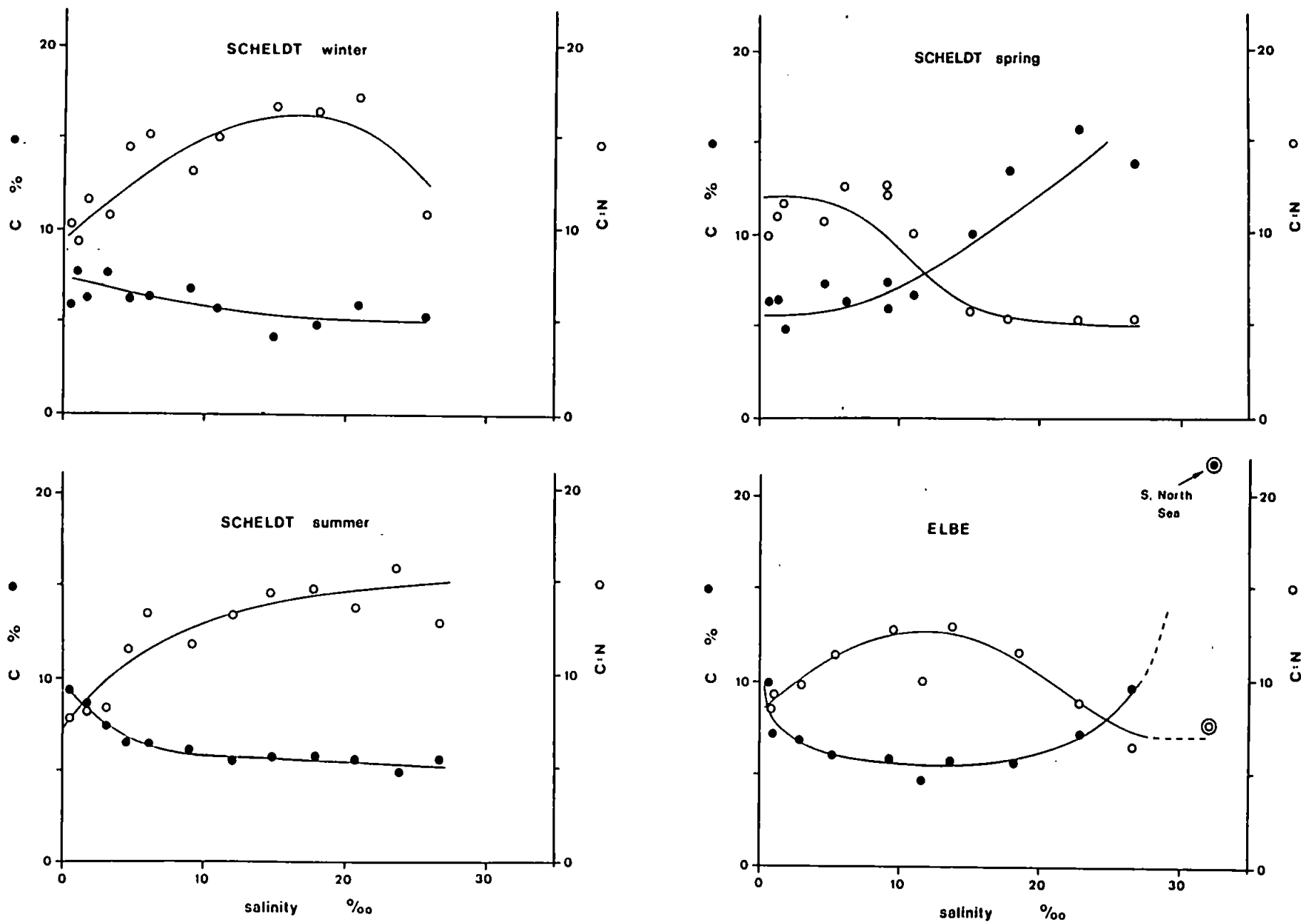


Figure 2.13 (continued).

through their rapid diagenetic recycling (Degens, 1970).

Axial estuarine plots of C and C:N for suspended material are shown in Figure 2.13. Distributions of C in the Humber Estuary are rather uniform, and the Elbe is characterized by a mid-estuary minimum suggesting some consumption on estuarine mixing. The samplings of the Thames, Weser, and Scheldt during winter and summer, exhibit seaward decreases indicative of fluvial sources as the major pathways. The inferred export in such instances may, however, contribute only a small percentage to the particulate carbon budget of the North Sea compared with that derived from *in situ* primary production. This is implicated by a reversal of such a trend in the Scheldt during spring with maximum values occurring at higher salinities resulting from high productivity.

Estuarine profiles of C:N essentially mirror the corresponding C profiles. Thus, only in the Scheldt during spring is a clear seaward decrease evident conforming with the mixing of fluvial (high C:N) and marine (low C:N) material. The highest values are often found in the mid-estuarine region (Scheldt during winter and spring, Weser and Elbe). Lower upstream values could be accounted for by the existence of halophobic riverine plankton; their subsequent demise, as indicated by a reduction in chlorophyll a concentration in the Weser Estuary (Figure 2.5a) and owing to an increase of salinity and light limitation at the onset of estuarine mixing (Morris *et al.*, 1982b), results in an increase in C:N. By similar reasoning, the high C:N ratios encountered during the summer sampling of the Humber Estuary could be explained by the high turbidities (Table 2.6) limiting primary production (*cf.* Joint and Pomeroy, 1981).

### 2.2.3: Trace Metals

A summary of all estuarine metal analyses is given in Table 2.9. The number of analyses, *n*, was occasionally restricted by instrumental limits of detection (Table 2.2), or, in the early work (Humber winter and Elbe samplings), by lack of analyte volumes. Axial profiles, and the means and standard deviations of all estuarine particulate trace metal concentrations are illustrated in Figures 2.14 and

Table 2.9: Summary of trace metal analyses of suspended sediment samples from the North Sea environment. Mean  $\pm$  one standard deviation,  $\mu \pm 1\sigma$ , and range, R, of n sample analyses given.

| Survey Date         | Statistical parameters | Co                  | Cr           | Cu             | Ni             | Pb          | Zn            |
|---------------------|------------------------|---------------------|--------------|----------------|----------------|-------------|---------------|
|                     |                        | ( $\mu\text{g/g}$ ) |              |                |                |             |               |
| <u>Humber</u>       | n                      | 14                  | 17           | 19             | 6              | 6           | 19            |
| Jan. 1988           | $\mu \pm 1\sigma$      | 18 $\pm$ 7          | 37 $\pm$ 14  | 110 $\pm$ 60   | 24 $\pm$ 5     | 55 $\pm$ 8  | 510 $\pm$ 440 |
|                     | R                      | 11-29               | 17-74        | 30-240         | 19-31          | 43-68       | 250-2220      |
|                     | n                      | 11                  | 11           | 11             | 11             | 11          | 11            |
| July 1989           | $\mu \pm 1\sigma$      | 13.3 $\pm$ 0.9      | 33 $\pm$ 3   | 21 $\pm$ 6     | 25.5 $\pm$ 2.0 | 39 $\pm$ 6  | 242 $\pm$ 46  |
|                     | R                      | 12.3-15.0           | 26-38        | 14-32          | 20.4-27.8      | 29-49       | 208-370       |
| <u>Thames</u>       | n                      | 14                  | 13           | 14             | 11             | 14          | 14            |
| Feb./Mar. 1989      | $\mu \pm 1\sigma$      | 11 $\pm$ 3          | 19 $\pm$ 3   | 27 $\pm$ 10    | 26 $\pm$ 9     | 73 $\pm$ 18 | 290 $\pm$ 180 |
|                     | R                      | 6-15                | 16-24        | 16-45          | 15-44          | 46-113      | 130-730       |
| <u>Scheldt</u>      | n                      | 12                  | 12           | 12             | 12             | 12          | 12            |
| Feb. 1987           | $\mu \pm 1\sigma$      | 13 $\pm$ 2          | 24 $\pm$ 8   | 19 $\pm$ 8     | 21 $\pm$ 6     | 37 $\pm$ 4  | 400 $\pm$ 220 |
|                     | R                      | 10-17               | 11-33.5      | 9-32           | 13-31          | 31.5-45     | 100-770       |
|                     | n                      | 13                  | 13           | 13             | 13             | 13          | 13            |
| May 1987            | $\mu \pm 1\sigma$      | 10 $\pm$ 1          | 20 $\pm$ 8   | 21 $\pm$ 10    | 24 $\pm$ 4     | 36 $\pm$ 8  | 380 $\pm$ 160 |
|                     | R                      | 8-12                | 7-29         | 7-44           | 14-31          | 22-47       | 90-550        |
|                     | n                      | 12                  | 12           | 12             | 12             | 12          | 12            |
| Aug. 1987           | $\mu \pm 1\sigma$      | 10 $\pm$ 2          | 15.5 $\pm$ 7 | 13 $\pm$ 11    | 16.5 $\pm$ 6   | 33 $\pm$ 9  | 250 $\pm$ 160 |
|                     | R                      | 8-13                | 8-30         | 3.5-43         | 12-34          | 24-60.5     | 80-610        |
| <u>Weser</u>        | n                      | 15                  | 15           | 15             | 15             | 15          | 15            |
| Aug. 1989           | $\mu \pm 1\sigma$      | 12.9 $\pm$ 2.0      | 8 $\pm$ 2    | 11.8 $\pm$ 8.7 | 18.6 $\pm$ 4.5 | 45 $\pm$ 8  | 255 $\pm$ 143 |
|                     | R                      | 10.5-17.0           | 5-12         | 5.5-35.1       | 13.6-27.6      | 31-64       | 134-585       |
| <u>Elbe</u>         | n                      | 4                   | 4            | 10             | 4              | 4           | 10            |
| June 1988           | $\mu \pm 1\sigma$      | 17 $\pm$ 2          | 22 $\pm$ 5   | 17 $\pm$ 7     | 29 $\pm$ 8     | 58 $\pm$ 5  | 470 $\pm$ 100 |
|                     | R                      | 15-19               | 15-26        | 10-31          | 21-40          | 53-65       | 360-700       |
| <u>Humber plume</u> | n                      | 4                   | 4            | 4              | 4              | 4           | 4             |
| Dec. 1988           | $\mu \pm 1\sigma$      | 12 $\pm$ 2          | 26 $\pm$ 3   | 15 $\pm$ 5     | 20 $\pm$ 2     | 52 $\pm$ 16 | 113 $\pm$ 38  |
|                     | R                      | 9-14                | 23-28        | 11-20          | 18-23          | 36-67       | 70-150        |
|                     | n                      | 3                   | 3            | 3              | 3              | 3           | 2             |
| May 1990            | $\mu \pm 1\sigma$      | 7.9 $\pm$ 0.6       | 19 $\pm$ 5   | 16 $\pm$ 3     | 30 $\pm$ 6     | 42 $\pm$ 6  | 160           |
|                     | R                      | 7.3-8.4             | 14-23        | 13-18          | 26-37          | 38-49       | 140-180       |
| <u>Thames plume</u> | n                      | 2                   | 2            | 2              | 2              | 2           | 2             |
| Feb. 1989           | $\mu$                  | 9.5                 | 7.5          | 8              | 10             | 39          | 50            |
| <u>S. North Sea</u> | n                      | -                   | -            | 3              | -              | -           | 3             |
| July 1988           | $\mu \pm 1\sigma$      | -                   | -            | 27 $\pm$ 10    | -              | -           | 210 $\pm$ 23  |
|                     | R                      | -                   | -            | 19-38          | -              | -           | 180-220       |

2.15 respectively.

### 2.2.3.1: Axial Profiles

A common underlying trend of decreasing metal concentration with increasing salinity can frequently be identified. This decrease is occasionally linear (Figure 2.16) but more often non-conservative. This trend can be interpreted by the mixing of riverborne material of high metal concentrations with marine or reworked estuarine sediment of lower metal concentrations. A similar explanation has been given to account for the seaward reduction in metal concentrations of deposited sediments in the Scheldt and Elbe, as well as the Rhine and Ems Estuaries (Müller and Förstner, 1975; Salomons and Mook, 1977). Physical mixing was the dominant process accounting for suspended solid compositional distributions in the estuaries of the Tamar (Loring *et al.*, 1983; Mantoura and Morris, 1983; Morris *et al.*, 1986) and Tay (Sholkovitz, 1979). However, sorption and other solid-solution interactions cannot necessarily be dismissed from such observations. For example, the solubilization of Zn at high salinities in the Scheldt Estuary, inferred from positive deviation of dissolved Zn from the theoretical dilution line, has been attributed to the oxidation and solubilization of the sulphide compound which formed further upstream in response to the anoxic conditions (Duinker *et al.*, 1982a; Zwolsman and Van Eck, 1990). This clearly non-conservative behaviour of Zn, although implicitly derived from the particles, is accompanied only by an unambiguous seaward decrease of particulate Zn (Duinker *et al.*, 1982a; Figure 2.14b). Measurements of suspended sediment composition will not, therefore, readily enable identification of exchange processes (Sholkovitz, 1979) as these processes generally have only a small or negligible effect on the bulk particle composition (Mantoura and Morris, 1983).

Although a seaward decrease in concentration of Hg is evident from determinations on the Elbe samples (Turner *et al.*, 1990); such a trend is partially obscured in this estuary for the metals reported here. It has been previously demonstrated that subsidiary inputs to the tidal Elbe are responsible for concealing simple dissolved trace metal mixing patterns in this estuary (Mart *et al.*, 1985).

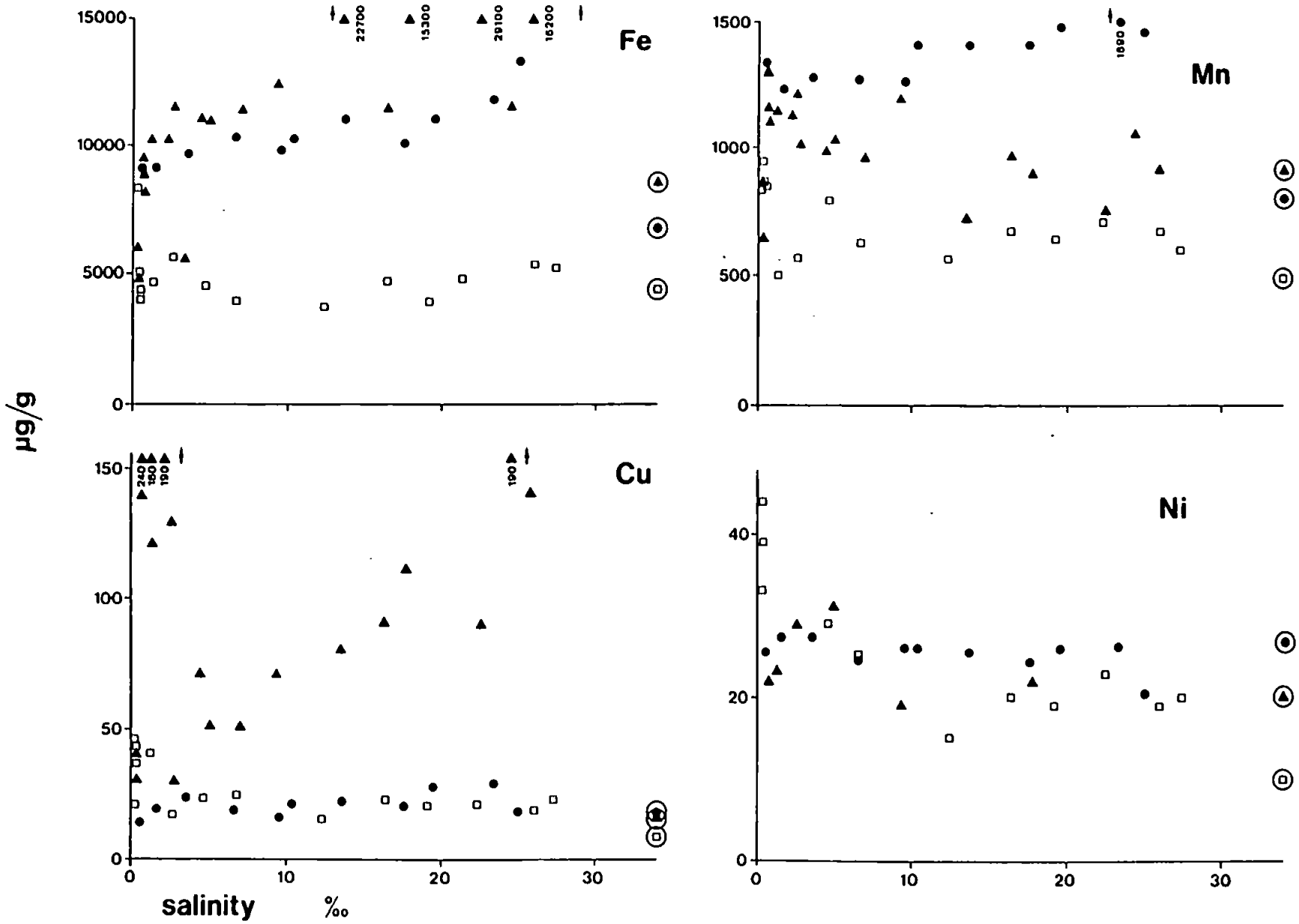


Figure 2.14a: Axial estuarine profiles of leachable particulate Fe, Mn and trace metals in the Humber during winter (▲) and summer (●), and Thames (□). Also shown are the mean values for the plumes of the Humber during winter (⊕) and spring (⊙), and Thames (⊚).

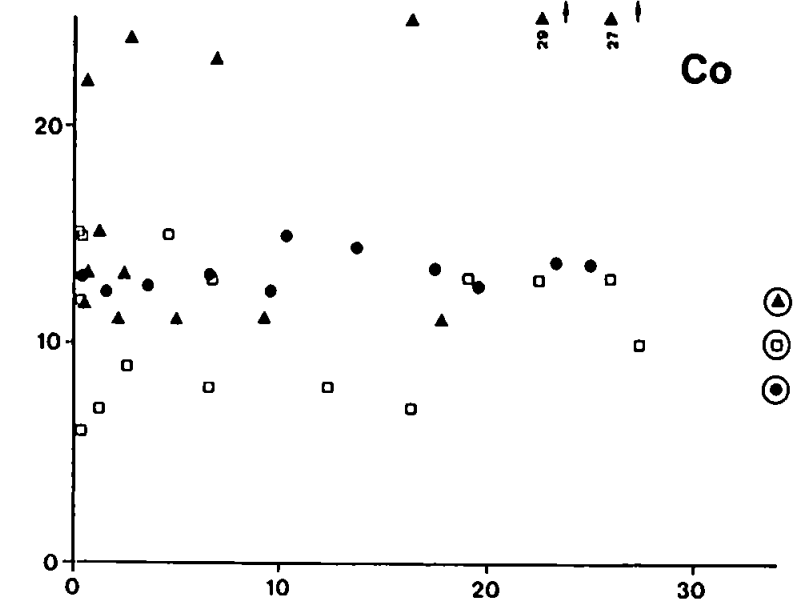
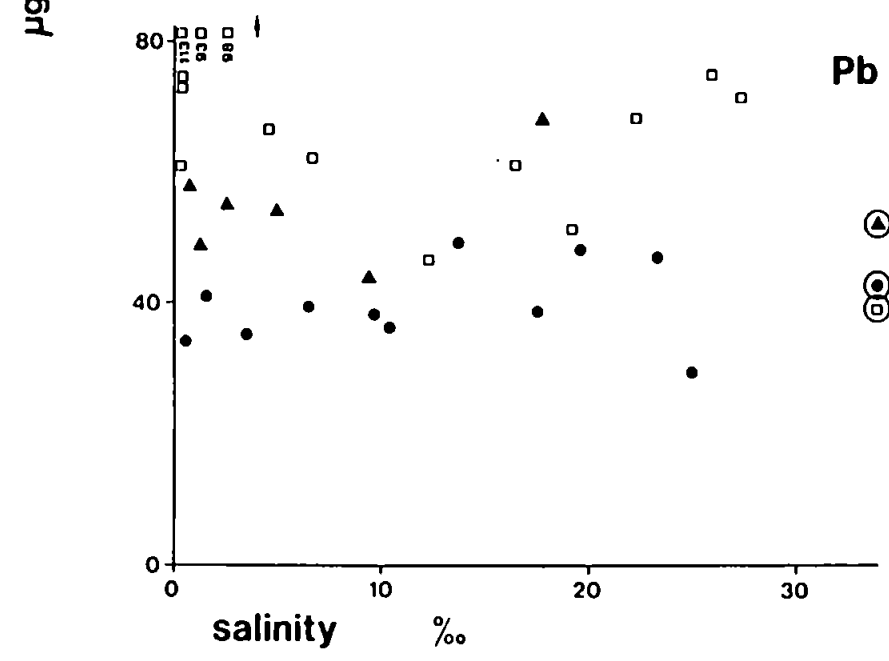
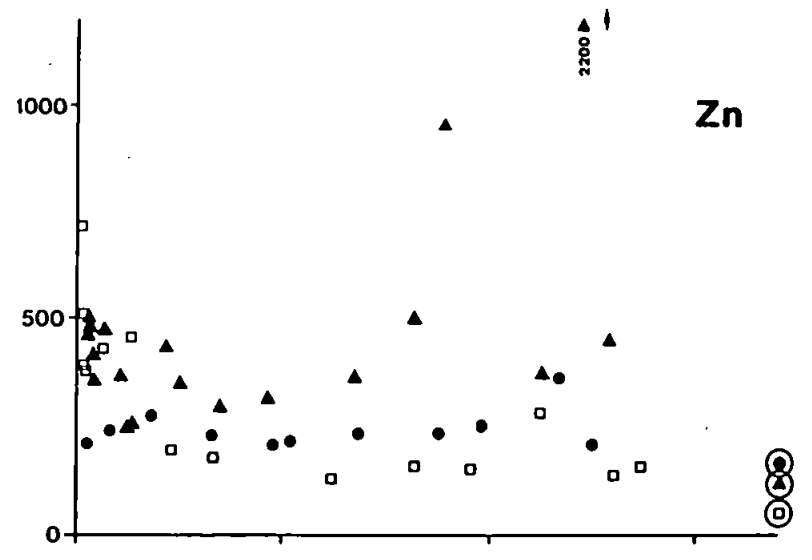
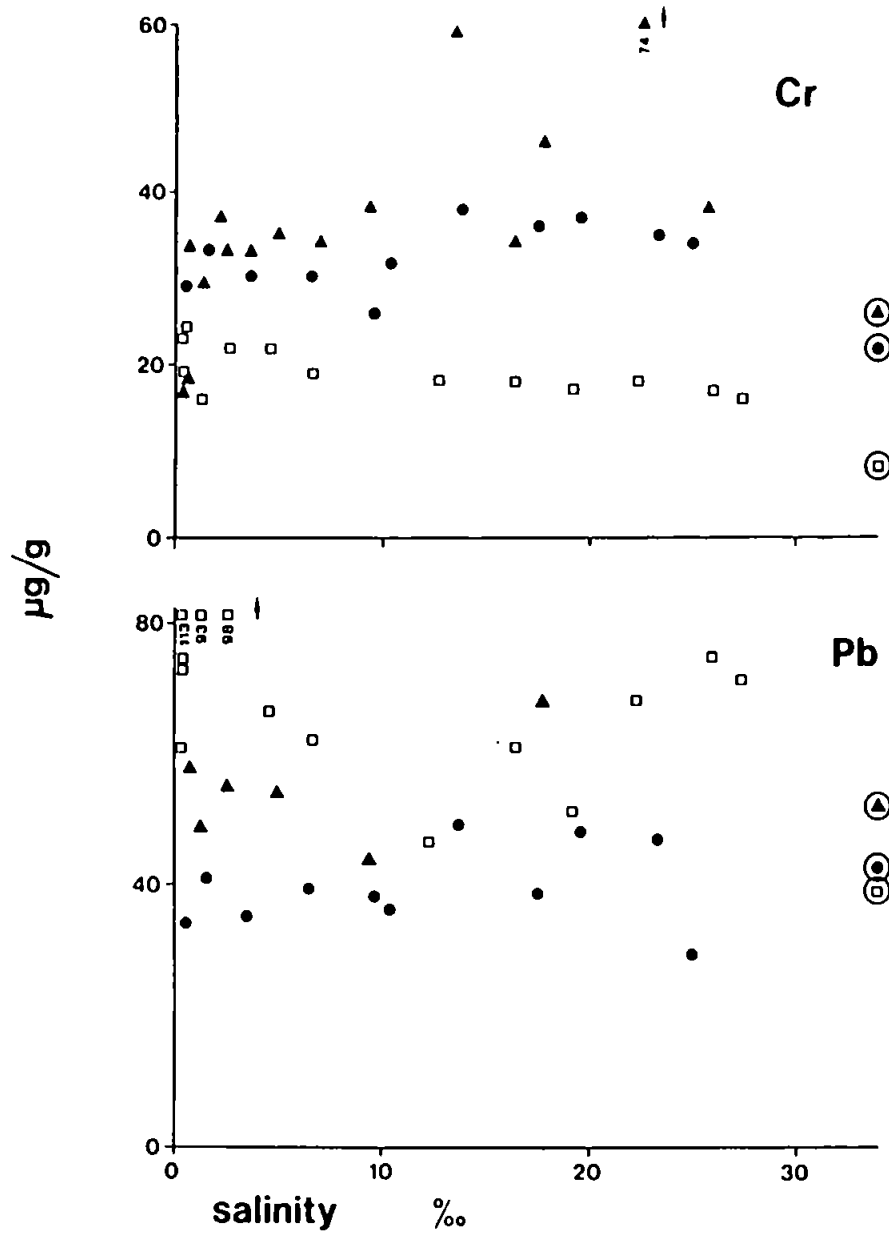


Figure 2.14a (continued).

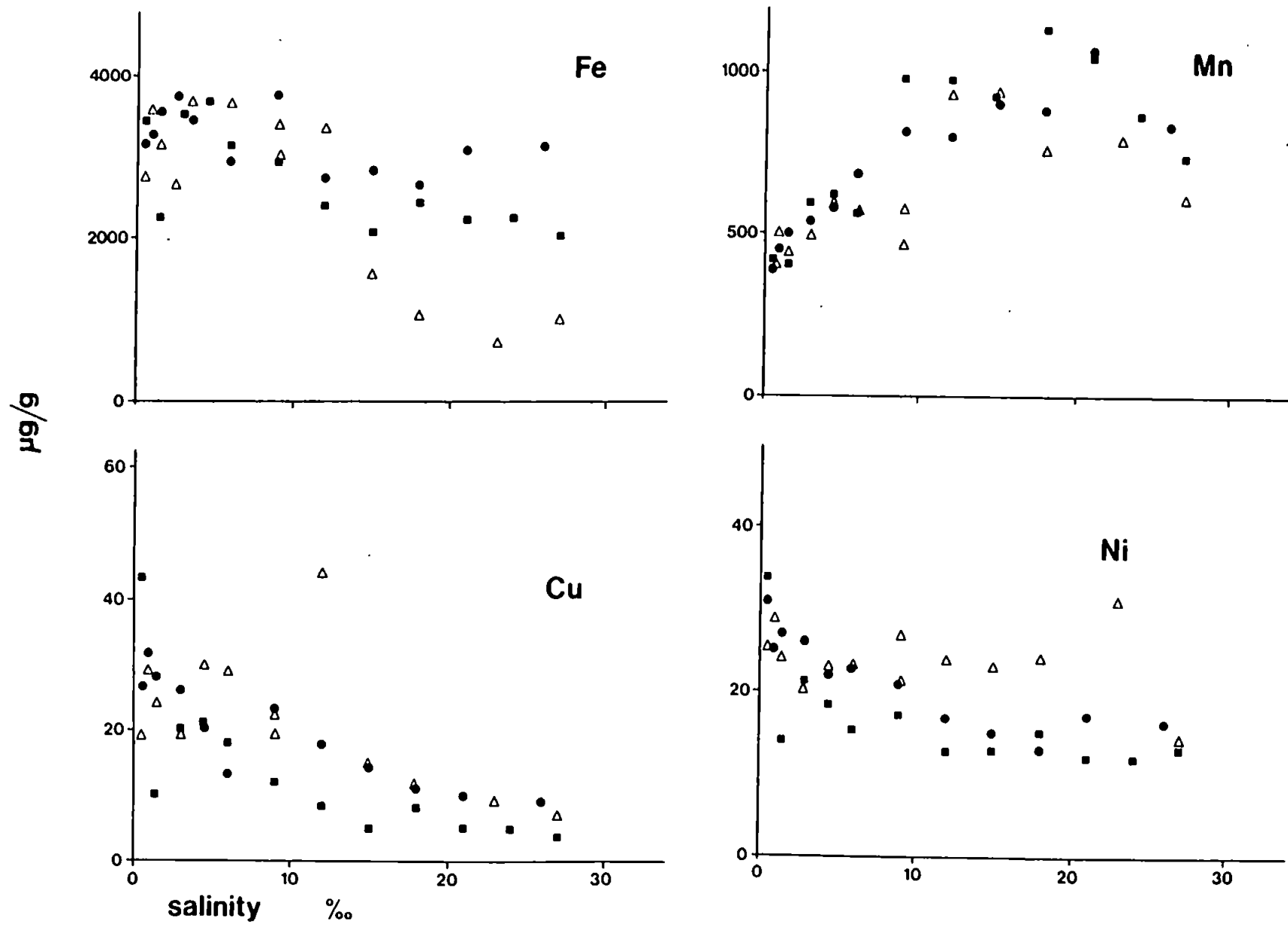
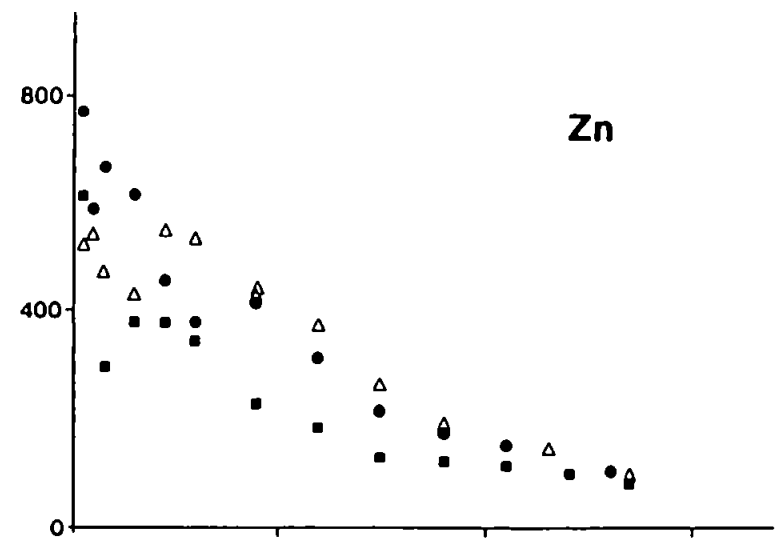
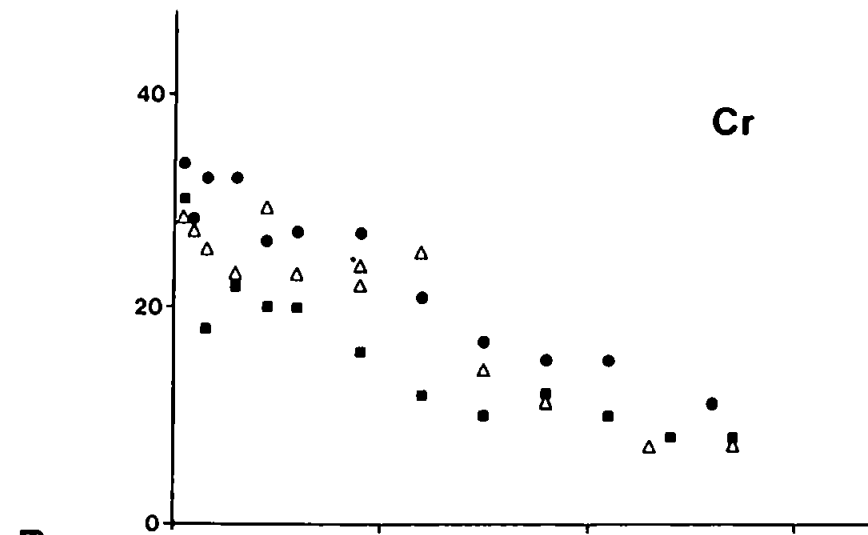


Figure 2.14b: Axial estuarine profiles of leachable particulate Fe, Mn and trace metals in the Scheldt during winter ( $\Delta$ ), spring ( $\bullet$ ) and summer ( $\blacksquare$ ).





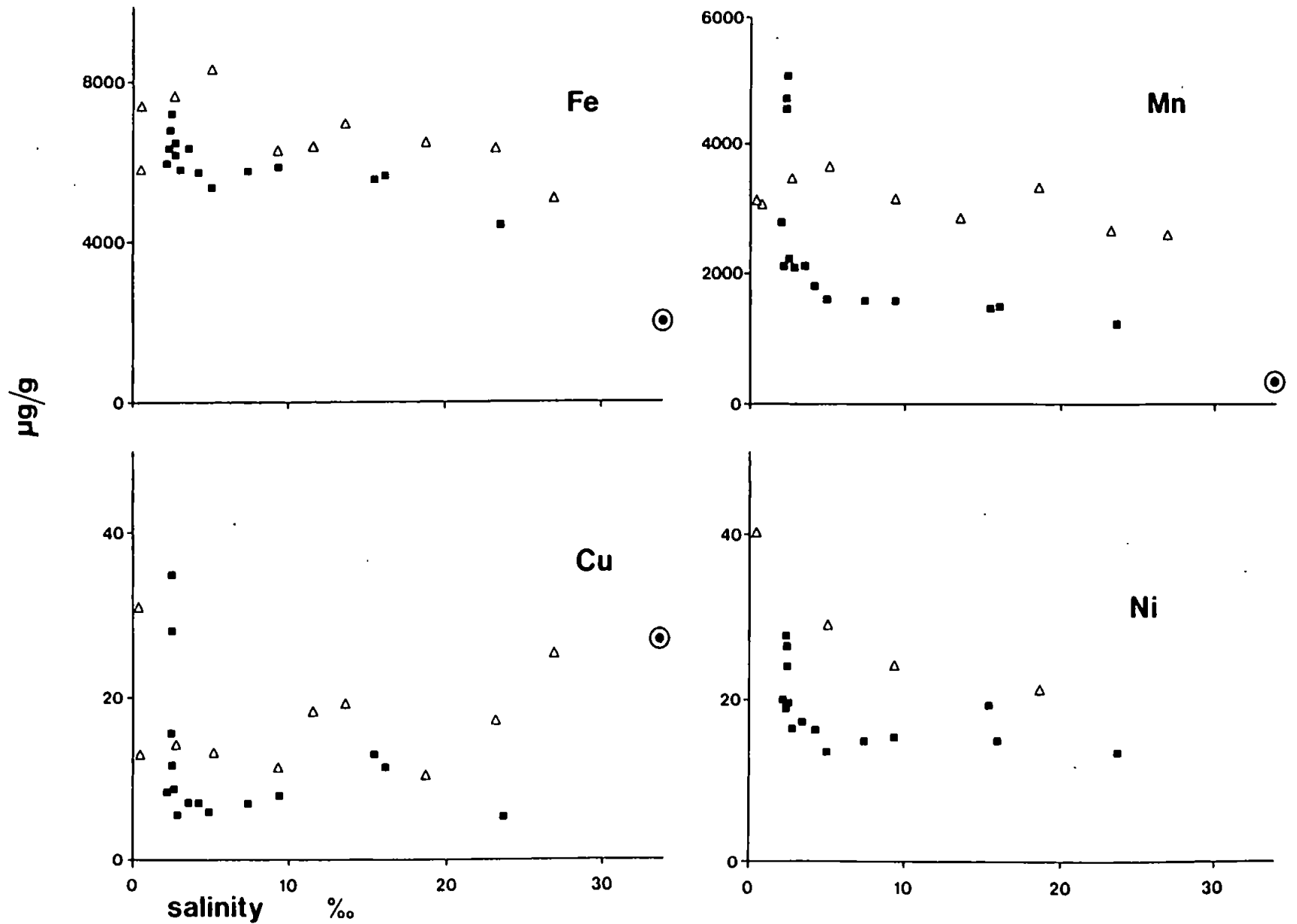


Figure 2.14c: Axial estuarine profiles of leachable particulate Fe, Mn and trace metals in the Weser (■) and Elbe (Δ). Also shown are the mean values for the southern North Sea (⊙).



Particulate metal concentrations in the Humber Estuary remain either uniform along the salinity gradient, or increase seaward, diminishing only further offshore by dispersion in the plume waters. This can be attributed to large industrial effluents towards the mouth of the estuary and an enhancement of scavenging properties of particles in this region as a result of freshly precipitated anthropogenic Fe (Section 2.2.2.3). During the winter, profiles were superimposed by *hot-spots* of elevated metal concentrations in the vicinity of these effluents. Their absence during the summer can be attributed to sampling further upstream in association with the landward migration of the salt intrusion. The effects of industrial effluents are also clearly manifested by localized perturbations in metal concentrations of inter-tidal sediment (Jaffe and Walters, 1977) and *Fucus vesiculosus* (Barnett and Ashcroft, 1985; Barnett *et al.*, 1989).

The seaward decreases of Pb and Co are generally not as conspicuous as for other metals. Particulate Pb concentrations in the coastal plume waters of the Humber during winter are not different to those occurring in the estuary itself, whereas other metals are considerably diluted. Furthermore, concentrations of Pb in the sediments of the Wash embayment to the south (lying directly in the plume path; Figure 1.3) are similar to those of sediments from the polluted south bank of the Humber Estuary where major industrial effluents are situated (Table 2.10); this is in contrast to all other metals which are considerably lower in the Wash environment and suggests that dissolved Pb is subjected to large-scale removal from solution in the plume waters. Indeed, Pb has a high particle affinity in coastal waters (Balls, 1989a) and there is abundant circumstantial evidence to suggest that removal from solution is a common phenomenon in North Sea plume regions (Balls, 1985a; Brüggmann *et al.*, 1985; Baeyens *et al.*, 1987a; D. Harper, pers. comm.). Therefore, uptake at high salinities may account for the observed particulate Pb distribution in estuarine and coastal waters and in such an instance solid-solution interactions exert an influence on particle composition, although the role of atmospheric inputs cannot be precluded (Cambray *et al.*, 1979; Norton, 1982; Schaule and Patterson, 1983; Kersten *et al.*, 1988).

Table 2.10: Mean metal concentrations, C contents and SSAs of inter-tidal sediment samples from the Humber and Wash regions.

|                            | No. of samples | SSA<br>m <sup>2</sup> /g | C<br>(%) | Fe<br>mg/g | Mn<br>mg/g | Co<br>μg/g | Cr<br>μg/g | Cu<br>μg/g | Ni<br>μg/g | Pb<br>μg/g | Zn<br>μg/g |
|----------------------------|----------------|--------------------------|----------|------------|------------|------------|------------|------------|------------|------------|------------|
| HUMBER                     |                |                          |          |            |            |            |            |            |            |            |            |
| (north bank)               | 10             | 14.9                     | 3.0      | 5.7        | 0.68       | 7          | 20         | 17         | 13         | 35         | 160        |
| (south bank)               | 11             | 14.3                     | 4.0      | 8.8        | 0.86       | 8          | 27         | 11         | 11         | 25         | 110        |
| WASH                       | 10             | 4.9                      | 2.9      | 3.0        | 0.51       | 4          | 6          | 3          | 4          | 25         | 30         |
| <u>HUMBER (south bank)</u> |                | 2.9                      | 1.4      | 2.9        | 1.7        | 2          | 4.5        | 3.7        | 2.8        | 1.0        | 3.7        |
| WASH                       |                |                          |          |            |            |            |            |            |            |            |            |

### 2.2.3.2: Inter-Estuarine Variability

Particulate trace metal concentrations are broadly similar in each estuary (Table 2.9; Figure 2.15) although slight deviations are now accounted for.

Elevated concentrations of Cu and Zn during the winter sampling of the Humber and their inherent variability can be attributed to the occurrence of *hot-spots* resulting from industrial effluents (Section 2.2.3.1), and a general elevation of Cr in the Humber environment results from its association in the ore (ilmenite) used in the manufacture of TiO<sub>2</sub> and subsequent discharge as a waste product in the acid-iron effluent. Paradoxically, the Weser, in which Cr concentrations are lowest, supports a major TiO<sub>2</sub> manufacturing plant near the estuary mouth. However, the resulting waste material is dumped off the Dutch coast where the effects are manifested by localized enhancements of Fe and Cr in the benthic sediments (Spaans, 1987). Rather high Pb concentrations in the Thames can be attributed to extensive urban runoff from the city of London and environs.

The three samples collected from the open waters of the southern North Sea during summer are high in Cu and Zn when compared with samples from the outflow regions of the polluted Humber and Thames Estuaries (Table 2.9). Moreover, Cu concentrations exceed those measured in the estuarine environments

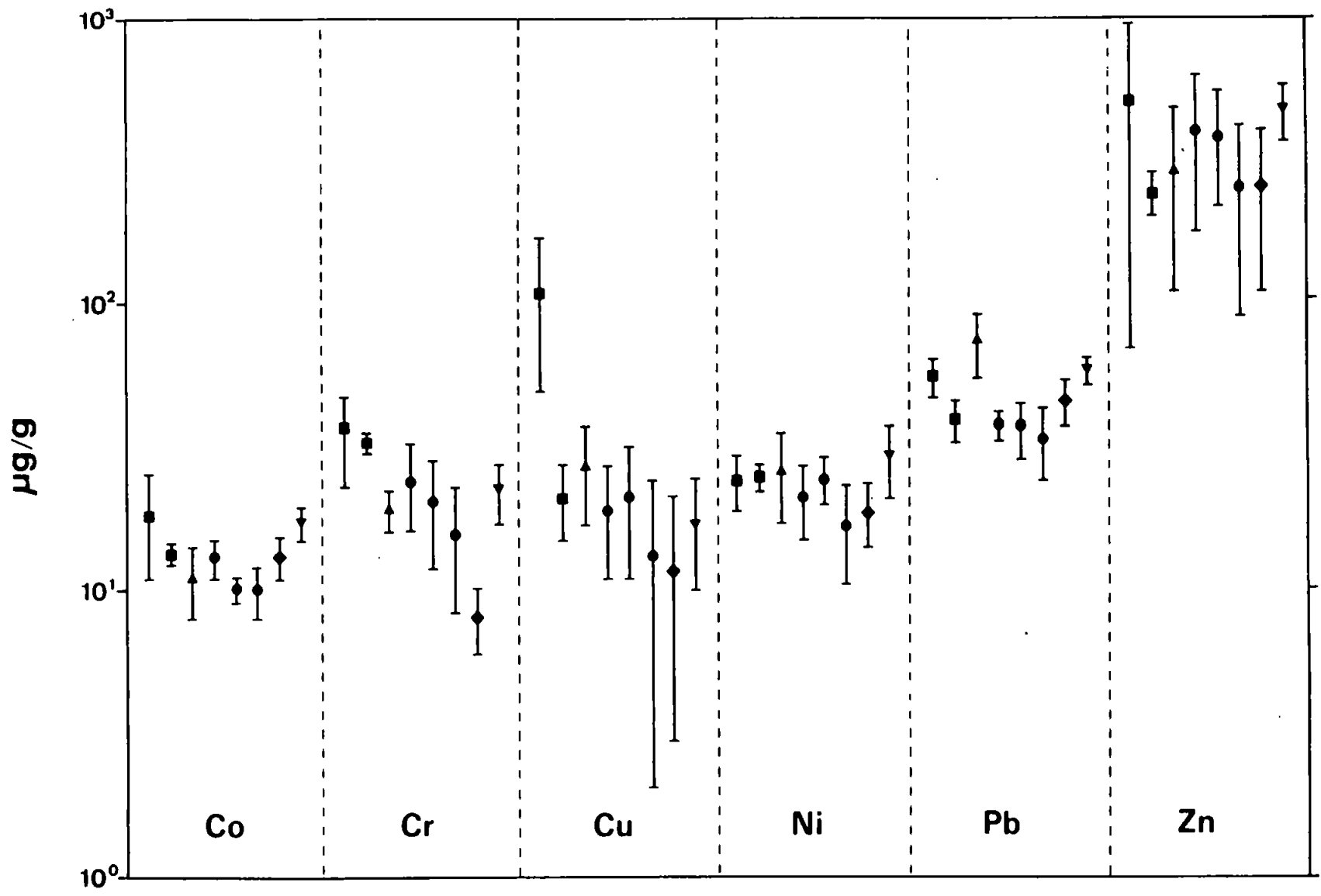


Figure 2.15: Mean  $\pm$  one standard deviation of leachable particulate trace metal concentrations in the estuaries of the North Sea. Symbols are as for Figure 2.9; multi-sampling campaigns (*i.e.* Humber and Scheldt) are illustrated chronologically from left to right.

themselves in many instances. Compositional features of these samples such as high C content and low C:N ratio (Table 2.7) suggest that elevated Cu and Zn concentrations are associated largely with biological uptake (*cf.* Morris, 1971). Furthermore, concentrations of Cu and Zn, and also Ni, are higher in the Humber plume during spring when productivity was enhanced than during winter (Table 2.9) suggesting accumulation by planktonic material, whereas the reverse pattern exists for Co, Cr and Pb. However, elevation of certain particulate metal concentrations through plankton assimilation is apparently not a general phenomenon as exemplified by the occurrence of similar metal concentrations in the outer Scheldt Estuary during each sampling campaign despite the varying abundance of biomass (as indicated by the particle compositional regimes; e.g. Section 2.2.2.5).

### 2.2.3.3: Temporal Variability

Although a difference in sampling locations in the Humber Estuary between winter and summer (Figure 2.2a) may have introduced a biasing towards higher metal concentrations during the winter survey, it is interesting to note that the metals that were most elevated in winter (Cu and Zn) were similarly enhanced in the Scheldt Estuary (Table 2.9). With the exception of Mn, other metals were also elevated during the winter surveys in both estuaries, although to a lesser extent. One interpretation is that of a relatively higher fraction of contaminated river water and associated particulate material occurring in the estuary during this season. On the other hand, Mn concentrations were higher during the summer surveys in both instances. The lower O<sub>2</sub> levels encountered in the warmer, more stagnant river waters at this time of year could accentuate release of dissolved Mn from particulate matter which is taken up at higher salinities within the estuary. However, observations of the seasonal variability of particulate Mn concentrations in the river waters of the Rhine also signify an elevation during the summer months (van der Weijden and Middelburg, 1989). A more logical explanation would therefore be enhanced oxidation at higher water temperatures (Morris and Bale, 1979; Morris *et al.*, 1982a; Keeney-Kennicutt and Presley, 1986).

#### 2.2.3.4: Inter-Parameter Relationships

A programme was written for the Minitab statistical package on the Polytechnic South West mainframe in order to identify simple linear relationships of significance ( $p \leq 0.0005$ ) between particulate metal concentrations and other parameters (salinity, suspended solids concentration, C, SSA) in each estuary; the results are presented in the form of a correlation matrix (Figure 2.16).

In only two estuaries has SSA been successfully correlated with metal concentrations. This indicates that, unlike the situation for deposited sediments where SSA is successfully related to metal concentration (Mayer and Fink, 1980; Section 2.2.3.6), this parameter does not provide an ideal measure of the capacity of particles to transport metals in suspension. Correlations are more common between trace metal and either Fe or Mn, emphasizing their sorptive properties, and between metal and C. The latter is most striking for Zn (significant positive correlation in all but two instances) and suggests an organic association. Inter-(trace) metal correlations are abundant in the Scheldt and Weser Estuaries in which seaward decreases induced by physical mixing are most pronounced (Section 2.2.3.1), but absent in the Humber in which a diversity of anthropogenic effluents create ambiguous relationships. A clear positive correlation between Cr and Fe during the winter sampling of the Humber is the result of their common occurrence in the acid-iron discharge (Section 2.2.3.2).

#### 2.2.3.5: Comparison with Total Metal Concentrations

Table 2.11 compares the amount of metals removed by the chosen leach (an operational measure of available metals) with those as determined after (almost) complete destruction of the particle matrix. Total metal determinations were carried out by inductively coupled plasma techniques following destruction by HF/HNO<sub>3</sub> for North Sea samples (M. Kersten, Harburg Technical University, F.R.G.) and for Scheldt Estuary samples (G. Zwolsman, University of Utrecht, N.L.). Weser Estuary and Loch Goil samples were analyzed for total metals following digestion in hot concentrated HNO<sub>3</sub> by total x-ray fluorescence (A.

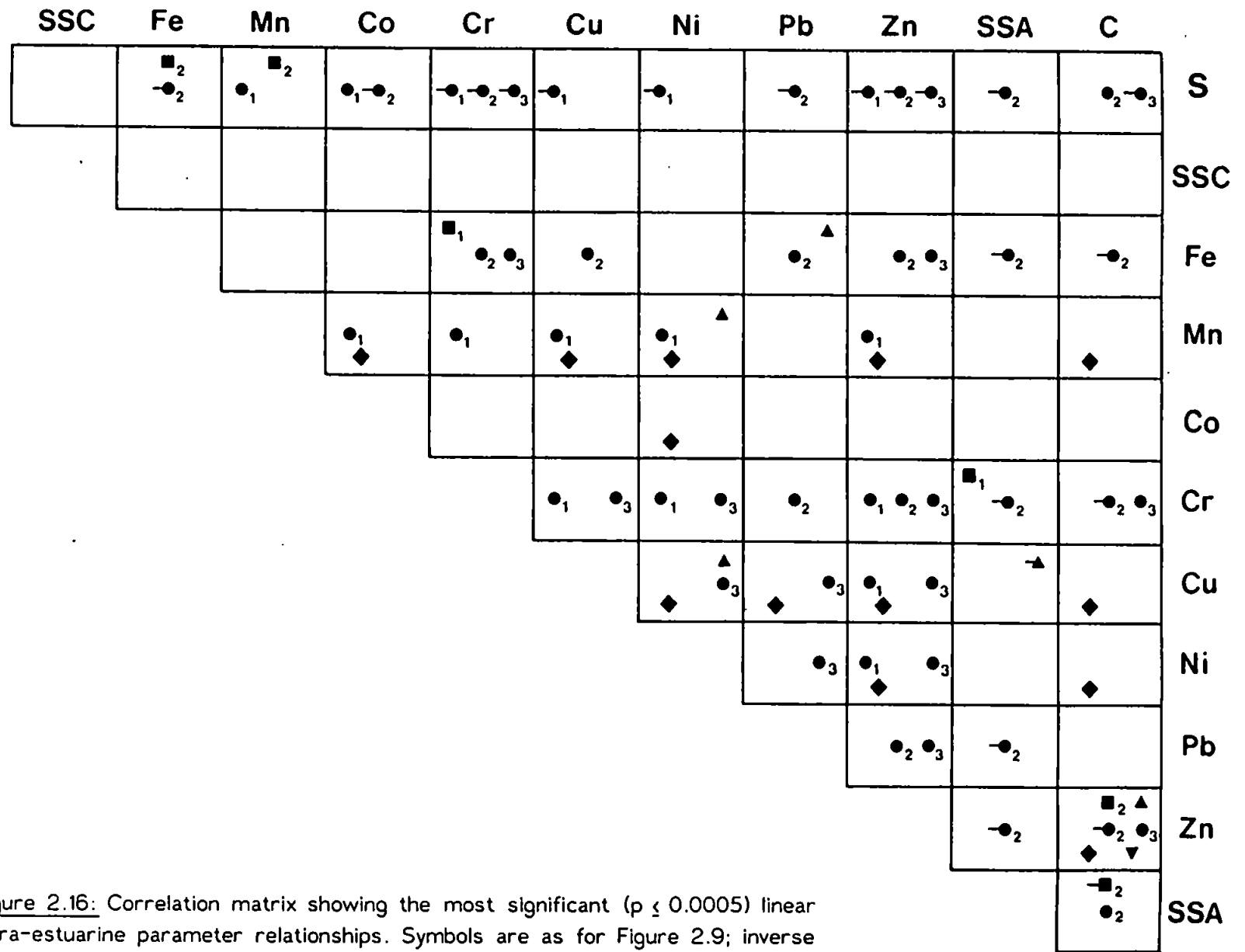


Figure 2.16: Correlation matrix showing the most significant ( $p \leq 0.0005$ ) linear intra-estuarine parameter relationships. Symbols are as for Figure 2.9; inverse relationships are negatively prefixed.



Prange, GKSS Research Centre, F.R.G.; Prange *et al.*, 1990) and atomic absorption spectrophotometry (P. Balls, Department of Agriculture and Fisheries for Scotland) respectively. Total metal contents of the marine reference sediments have been determined by a variety of independent methods (National Research Council for Canada, 1987).

Table 2.11: Percentage of leachable metals removed from sediments. Mean  $\pm$  one standard deviation of n samples given.

|           | n  | Al            | Fe            | Mn           | Co          | Cr         | Cu          | Ni          | Pb          | Zn          |
|-----------|----|---------------|---------------|--------------|-------------|------------|-------------|-------------|-------------|-------------|
| Scheldt   | 12 | 1.4 $\pm$ 0.3 | 7.5 $\pm$ 0.9 | 57 $\pm$ 8   | 86 $\pm$ 22 | 11 $\pm$ 1 | 17 $\pm$ 5  | 37 $\pm$ 4  | 31 $\pm$ 11 | 56 $\pm$ 8  |
|           | 13 | 1.5 $\pm$ 0.4 | 6.7 $\pm$ 1.4 | 60 $\pm$ 14  | 83 $\pm$ 22 | 11 $\pm$ 2 | 24 $\pm$ 13 | 49 $\pm$ 18 | 32 $\pm$ 17 | 66 $\pm$ 11 |
|           | 12 | 1.1 $\pm$ 0.5 | 6.6 $\pm$ 1.0 | 65 $\pm$ 9   | 82 $\pm$ 11 | 9 $\pm$ 1  | 17 $\pm$ 4  | 36 $\pm$ 8  | 37 $\pm$ 14 | 54 $\pm$ 7  |
| Weser     | 14 | -             | 15 $\pm$ 1.7  | 85 $\pm$ 6   | -           | 6 $\pm$ 2  | 27 $\pm$ 11 | 28 $\pm$ 7  | 40 $\pm$ 7  | 60 $\pm$ 10 |
| North Sea | 4  | -             | 15 $\pm$ 2    | 120 $\pm$ 26 | -           | <24        | -           | -           | 71 $\pm$ 21 | 96 $\pm$ 34 |
| Loch Goil | 2  | -             | 46            | 55           | -           | -          | 32          | -           | 77          | 79          |
| MESS-1    | 1  | 2.2           | 2.2           | 6.8          | 16          | 11         | 9.2         | <4          | 26          | 43          |
| BCSS-1    | 1  | 1.2           | 4.6           | 9.2          | -           | 3.1        | 7.6         | 2.5         | 24          | 23          |
| PACS-1    | 1  | 1.9           | 15            | 8.9          | 31          | 7.6        | 21          | 12          | 31          | 46          |

For the North Sea environments the ease of extraction by the leach is in the order:

$$\text{Co} > \text{Mn, Zn} > \text{Ni, Pb} > \text{Cu} > \text{Cr} > \text{Fe} > \text{Al}$$

indicating that the majority of Al, Fe and Cr is held in less accessible sites of the particle matrix, whereas Mn, Co and Zn are more bio- and geochemically mobile. Table 2.12 compares the results from this study for the Humber, Thames and Elbe with published total metal determinations from these environments, and once more a similar pattern of metal mobility can be discerned. Moreover, with the exception of Co, this sequence is very similar to that determined by van der Weijden *et al.* (1977) for the ease of desorption from Rhine suspended sediment in

Table 2.12: A comparison of leachable with published total particulate metal concentrations for the Humber, Thames and Elbe Estuaries. Concentrations in µg/g except for Fe and Mn (mg/g).

|                             |    | Concentration, mean(range) |                     | Reference<br>sampling season                |
|-----------------------------|----|----------------------------|---------------------|---|
|                             |    | LEACHABLE<br>this work     | TOTAL<br>other work |   |
| Humber<br>July 1989         | Cu | 21(14-32)                  | (28-861)            | Goulder <i>et al.</i> (1980)<br>May/July    |
|                             | Pb | 39(29-49)                  | (87-370)            |   |
|                             | Zn | 242(208-370)               | (21-343)            |   |
| Thames<br>Feb./Mar.<br>1989 | Fe | 4.86(3.72-8.26)            | 39(17-46)           | Nelson (1979)<br>June-Dec.                  |
|                             | Co | 11(6-15)                   | 19(10-26)           |   |
|                             | Cr | 19(16-24)                  | 71(50-103)          |   |
| Elbe<br>June 1988           | Fe | 6.6(5.0-8.3)               | (35-50)             | Duinker <i>et al.</i> (1982b)<br>Aug./Sept. |
|                             | Mn | 3.08(2.58-3.62)            | (1.8-3.3)           |   |
|                             | Cr | 22(15-26)                  | (30-150)            |   |
|                             | Cu | 17(10-31)                  | (30-300)            |   |
|                             | Pb | 58(53-65)                  | (50-600)            |   |
|                             | Zn | 470(360-700)               | (300-800)           |   |

artificial sea water media.

Sequential extraction techniques have previously demonstrated that Mn and Zn are relatively easily removed from suspended sediment from North Sea estuarine environments when compared with Cr, Cu and Pb (Calmano *et al.*, 1982; Calmano and Förstner, 1983). High leachable Mn and Zn fractions have also been found in samples collected from the Baltic Sea and attributed to authigenic formation (Bernard *et al.*, 1989).

However, compared with material from the North Sea and adjoining estuaries a large fraction of Fe is removed from Loch Goil samples, whereas reference sediments host a considerably larger refractory component of Mn, Co and Ni, thereby demonstrating that metal availability is also environment dependent.

### 2.2.3.6: Comparison with Deposited Sediments

It is evident from Table 2.13 that SSAs and metal concentrations of Humber and Weser sediment deposits are lower than those for suspended material from the corresponding environments. This is caused by a dilution of fine, high metal bearing resuspendable material with coarse non-porous silicate and carbonate grains of low metal adsorptive capacity in sediment deposits.

Table 2.13: A comparison of metal concentrations in deposited and suspended sediments from the Humber and Weser Estuaries.

|   | SSA                 | Fe   | Mn   | Co   | Cr | Cu   | Ni   | Pb | Zn  | C   |
|---|---------------------|------|------|------|----|------|------|----|-----|-----|
|   | (m <sup>2</sup> /g) | mg/g |      |      |    | μg/g |      |    |     | (%) |
| <u>Humber</u> suspended                     |                     |      |      |      |    |      |      |    |     |     |
| Jan. 1988                                   | 24.0                | 12.0 | 0.99 | 18   | 37 | 110  | 24   | 55 | 510 | 5.4 |
| July 1989                                   | 25.2                | 10.4 | 1.38 | 13.3 | 33 | 21   | 25.5 | 39 | 242 | 4.8 |
| deposited                                   | 14.6                | 7.31 | 0.77 | 7.5  | 24 | 14   | 12   | 30 | 130 | 3.5 |
| suspended normalized<br>with respect to SSA |                     |      |      |      |    |      |      |    |     |     |
| Jan. 1988                                   | 14.6                | 7.30 | 0.60 | 11   | 23 | 67   | 15   | 33 | 310 | 3.3 |
| July 1989                                   | 14.6                | 6.03 | 0.80 | 7.7  | 19 | 12   | 14.8 | 23 | 140 | 2.8 |
| <u>Weser</u> suspended                      |                     |      |      |      |    |      |      |    |     |     |
| Aug. 1989                                   | 18.8                | 5.95 | 2.43 | 12.9 | 8  | 11.8 | 18.6 | 45 | 255 | 6.3 |
| deposited                                   | 11.2                | 4.07 | 1.01 | 6.8  | 6  | 9.4  | 10.4 | 21 | 199 | 3.8 |
| suspended normalized<br>with respect to SSA |                     |      |      |      |    |      |      |    |     |     |
|   | 11.2                | 3.54 | 1.45 | 7.7  | 5  | 7.0  | 11.1 | 27 | 152 | 3.8 |

All metal and compositional parameters given in Figure 2.16 were positively correlated significantly ( $p \leq 0.0005$ ) for deposited sediment samples from the Humber/Wash environment; this is exemplified by plots of metals versus SSA (Figure 2.17). Metal concentration of sediment is a function of sediment grain size (Sakai *et al.*, 1986; Brook and Moore, 1988), and mineralogical and chemical textural effects (Mayer and Fink, 1980), both of which are quantified by the BET

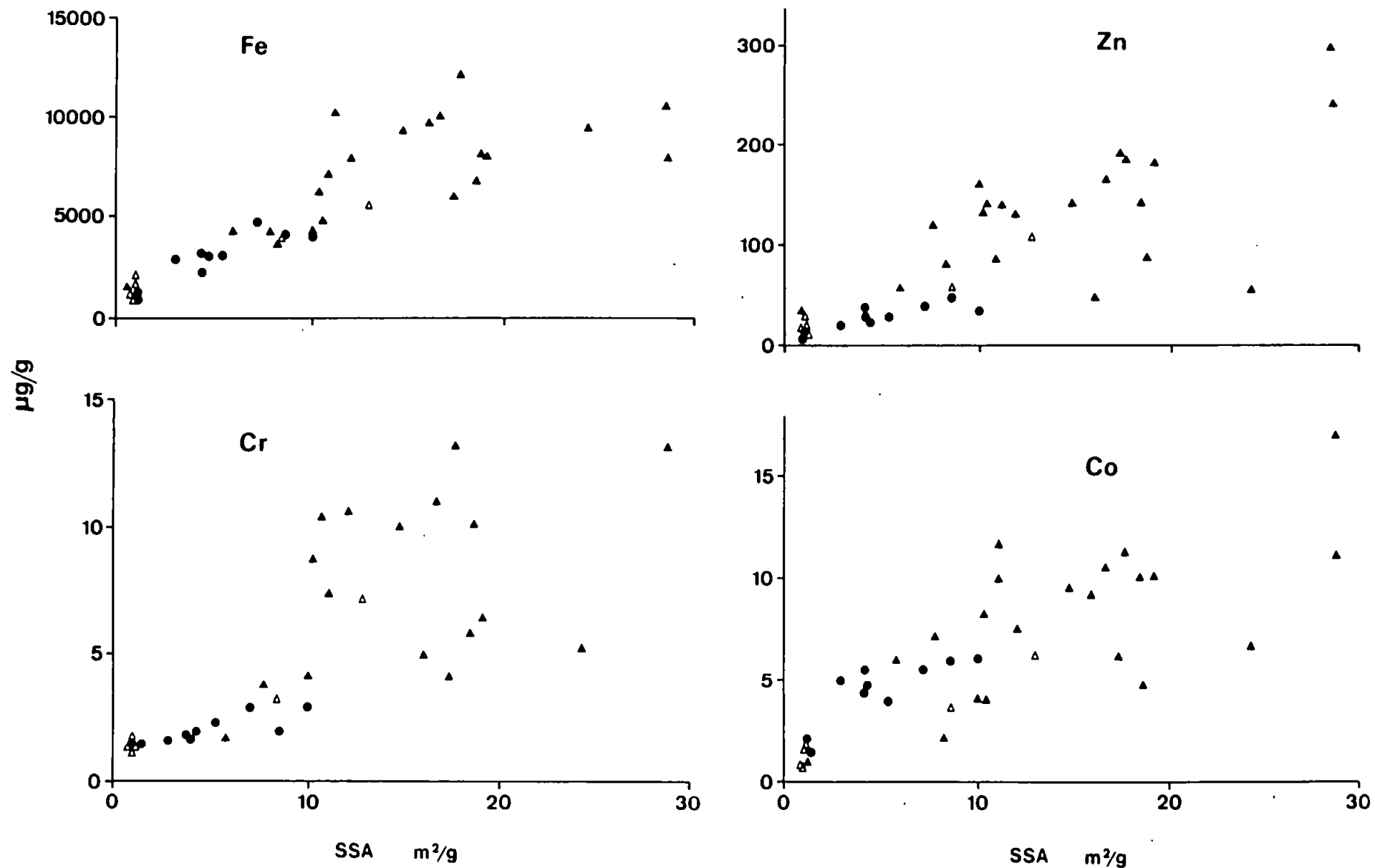


Figure 2.17: Leachable metal concentrations versus SSA of deposited sediment from the Humber ( $\blacktriangle$ , inter-tidal;  $\triangle$ , sub-tidal) and Wash ( $\bullet$ ).

Fe:  $SSA = -0.69 + 0.00203Fe$ ;  $r^2 = 69.6\%$ ;  $p \leq 0.0005$ .      Zn:  $SSA = 2.42 + 0.0865Zn$ ;  $r^2 = 65.0\%$ ;  $p \leq 0.0005$ .

Cr:  $SSA = 3.43 + 0.431Cr$ ;  $r^2 = 55.9\%$ ;  $p \leq 0.0005$ .      Co:  $SSA = -0.21 + 1.73Co$ ;  $r^2 = 64.9\%$ ;  $p \leq 0.0005$ .

method, and ultimately dependent on the hydrographical, hence sediment dynamic regime. Such linear relationships therefore reflect the extent of dilution of fine metal-rich sediment of high SSA with coarse metal poor sediment of low SSA.

Successful incorporation of Wash samples into the regression analyses suggests a common population with Humber material and some coupling between the two environments. A southward migration of Humber material in accordance with the local water circulation and subsequent accumulation in the Wash would seem a logical explanation.

After normalizing with respect to deposited sediment SSA from the respective environments, suspended sediment metal concentrations from the Humber and Weser compare favourably with deposited sediment concentrations (Table 2.13). However, Cu and Zn concentrations for the Humber winter sampling are still notably enhanced. This suggests that the industrial *hot-spots* responsible for their elevation (Section 2.2.3.1) are localized (both spatially and temporally) and do not exert a large-scale impact on the sedimentary environment of the Humber.

#### 2.2.3.7: Metal Discharges

There have been several attempts to estimate fluxes of particulate material from North Sea estuaries to coastal waters (Veenstra, 1970; Eisma, 1973; McCave, 1973) and these have formed the basis of estuarine particulate metal discharge calculations (Salomons and Eysink, 1979; Turner *et al.*, 1990). Such sediment export figures are shown in Table 2.14, along with estimates obtained from an empirically derived prediction equation (Wilmot and Collins, 1981). This equation relates sediment flux,  $y$ , in tonnes per annum, to the size of the catchment,  $x$ , in  $\text{km}^2$ , and its format is dependent on the nature of the catchment and climatological factors. For the type of catchment common to the British Isles this equation can be written as follows (Wilmot and Collins, 1981):

$$y = 60x^{0.78} \quad (2.8)$$

Estimates derived from the different sources of information are of similar

order of magnitude. However, seasonal variability is not considered and this may be very significant. For example, in winter months river discharge is higher and is associated with higher concentrations of particulate trace metals as this and other work would suggest (e.g. Yeats and Bewers, 1982), leading to a larger metal export in this season. The role of single storm events may be very important by accentuating such an effect (Huynh-Ngoc *et al.*, 1988).

Table 2.14: Estimates of estuarine sediment exports.

|         | <u>Discharge</u>               |              |               | <i>Prediction equation</i> | <u>Maintenance dredging</u>               |
|---------|--------------------------------|--------------|---------------|----------------------------|---|
|         | Veenstra (1970)                | Eisma (1973) | McCave (1973) |                            | Salomons and Eysink (1979)                |
|         | x 10 <sup>6</sup> tonnes/annum |              |               |                            | (x 10 <sup>6</sup> m <sup>3</sup> /annum) |
| Humber  | 0.1                            | 0.7          | -             | 0.17                       | 4.8                                       |
| Thames  | 0.2                            | 0.2          | -             | 0.08                       | 0.7                                       |
| Scheldt | 0.1                            | -            | 0.40          | 0.14                       | 12.5                                      |
| Weser   | 0.6                            | ┌<br>1.3     | 0.42          | 0.25                       | 10  |
| Elbe    | 0.7                            | └            | 0.84          | 0.65                       | 11  |

Although metal analyses of North Sea benthic sediments have demonstrated an influence on the nearshore zone by estuarine discharges (Nicholson and Moore, 1981; Irion and Muller, 1987; Araujo *et al.*, 1988), it must be questioned whether this inferred export of particulate material is significant. For example, studies of waste material dumped offshore often indicate a net landward transport (Kirby, 1987). Furthermore, river sediments originating from the Ems, Weser and Elbe are trapped in their respective estuarine environments under natural conditions (Irion *et al.*, 1987), although recent activities such as dredging and waterway controlling are now responsible for an escape of sediment from these German estuaries and deposition nearshore.

Calculations suggest that the dumping of dredged material in the southern

North Sea (as opposed to direct river/estuarine inputs) has an overwhelming impact on the mud budget of the North Sea (Salomons and Eysink, 1979; Table 2.14). However, the units quantifying dredged material (*viz.* m<sup>3</sup>) are not easily convertible into units of sediment mass (*viz.* tonnes), as the density and percentage of solids in the slurry vary greatly. Furthermore, it cannot always be ascertained from such figures the amount of spoil used as landfill, thereby escaping the marine environment (*cf.* Tent, 1987).

Nevertheless, the sediment discharge figures derived from the prediction equation have been chosen in order to assess the possible impact of each river system on the particulate trace metal budget of the southern North Sea. Metal concentrations at the head of each estuary or in the low salinity region have been used in the calculations, taking mean values where more than one survey was undertaken (*i.e.* Humber and Scheldt). It is assumed in these calculations that the amount of eroded material from the catchment is not trapped within the estuarine environment but exported to coastal waters, either directly by natural estuarine circulation processes, or by other means such as dredging operations. Although a tacit assumption is the absence of solid-solution interactions in the estuarine mixing zone, it appears that these have a negligible effect on the suspended sediment composition (Section 2.2.3.1).

The annual riverine exports in tonnes of leachable particulate metals are presented in Table 2.15. Also given are the corresponding estimates of dissolved metal discharges derived from combining annual average river flows (Table 1.4) with what are considered the best available estimates of fresh water end-member dissolved metal concentrations. The accuracy of these calculations is therefore limited by assuming conservative mixing.

Compared with previously published estimates (Norton, 1982; Critchley, 1984; Hill *et al.*, 1984; Grogan, 1985) the values cited here are somewhat lower. This can be attributed to the incorporation of more reliable (and usually lower) metal concentrations (through improved sampling and analytical procedures) in the calculations and consideration of a leachable particulate phase. It is also implicit

Table 2.15: Estimates of discharges (in tonnes/annum; t/a) of fluvial derived metals to the North Sea via the five estuaries. (EMC = end-member concentration).

|                     | Fe   | Mn   | Co  | Cr  | Cu  | Ni   | Pb   | Zn  | Source<br>sampling season          |
|---------------------|------|------|-----|-----|-----|------|------|-----|------------------------------------|
| <u>Humber</u>       |      |      |     |     |     |      |      |     |                                    |
| <i>Dissolved</i>    |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/l}$ | -    | -    | -   | 1.8 | 8   | 12.5 | 0.75 | 35  | Gardiner (1982)                    |
| Discharge t/a       | -    | -    | -   | 14  | 60  | 100  | 6    | 270 | Dec./Jan.                          |
| <i>Particulate</i>  |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/g}$ | 9000 | 1200 | 15  | 30  | 60  | 25   | 40   | 350 | This work                          |
| Discharge t/a       | 1500 | 200  | 3   | 5   | 10  | 4    | 7    | 60  | Jan./July                          |
| <u>Thames</u>       |      |      |     |     |     |      |      |     |                                    |
| <i>Dissolved</i>    |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/l}$ | -    | -    | -   | 2   | 5   | 8    | 1    | 30  | D. Harper<br>(pers. comm).         |
| Discharge t/a       | -    | -    | -   | 5   | 13  | 20   | 3    | 80  | Feb./Mar.                          |
| <i>Particulate</i>  |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/g}$ | 5000 | 900  | 10  | 23  | 40  | 35   | 75   | 600 | This work                          |
| Discharge t/a       | 400  | 70   | <1  | 2   | 3   | 3    | 6    | 50  | Feb./Mar                           |
| <u>Scheldt</u>      |      |      |     |     |     |      |      |     |                                    |
| <i>Dissolved</i>    |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/l}$ | 90   | 300  | -   | 1.4 | 1.0 | -    | -    | 10  | G. Zwolsman<br>(pers. comm).       |
| Discharge t/a       | 280  | 950  | -   | 4.4 | 3.2 | -    | -    | 32  | Seasonal mean                      |
| <i>Particulate</i>  |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/g}$ | 3000 | 450  | 10  | 30  | 30  | 30   | 40   | 600 | This work                          |
| Discharge t/a       | 420  | 60   | 1   | 4   | 4   | 4    | 6    | 80  | Feb./May/Aug.                      |
| <u>Weser</u>        |      |      |     |     |     |      |      |     |                                    |
| <i>Dissolved</i>    |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/l}$ | 5    | 40   | -   | -   | 2.7 | 3.5  | 0.10 | 8   | Figure 2.18                        |
| Discharge t/a       | 50   | 400  | -   | -   | 30  | 40   | 1    | 80  | Aug.                               |
| <i>Particulate</i>  |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/g}$ | 6500 | 4700 | 15  | 12  | 30  | 28   | 60   | 600 | This work                          |
| Discharge t/a       | 1600 | 1200 | 4   | 3   | 8   | 7    | 15   | 150 | Aug.                               |
| <u>Elbe</u>         |      |      |     |     |     |      |      |     |                                    |
| <i>Dissolved</i>    |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/l}$ | 50   | 50   | 0.2 | -   | 10  | 6    | 0.3  | 20  | Mart et al. (1985)                 |
| Discharge t/a       | 1100 | 1100 | 3   | -   | 230 | 140  | 7    | 460 | ? Duinker et al.<br>(1982b). Sept. |
| <i>Particulate</i>  |      |      |     |     |     |      |      |     |                                    |
| EMC $\mu\text{g/g}$ | 7000 | 3100 | 19  | 20  | 20  | 35   | 60   | 600 | This work                          |
| Discharge t/a       | 4600 | 2000 | 12  | 13  | 13  | 20   | 40   | 390 | June                               |



from earlier flux calculations that river flows were combined with total (*i.e.* unfiltered) metal concentrations, the results therefore very much dependent on suspended solids concentrations encountered.

The results from this study indicate that the significance to the North Sea metal budget of these river systems generally reflects the sizes of the respective catchments. Thus, for the leachable particulate metal phase:

Elbe > Weser > Humber > Scheldt  $\geq$  Thames

and for the dissolved metal phase:

Elbe > Humber > Weser  $\geq$  Thames > Scheldt.

Table 2.16: Inputs of trace metals to the North Sea from the Humber and Thames Estuaries and their component sources.

|                    | Discharge |         |          |         |          |
|--------------------|-----------|---------|----------|---------|----------|
|                    | Cr        | Cu      | Ni       | Pb      | Zn       |
| <u>Humber</u>      |           |         |          |         |          |
| River-dissolved*   | 14 (8)    | 60 (55) | 100 (80) | 6 (13)  | 270 (26) |
| River-particulate* | 5 (3)     | 10 (9)  | 4 (3)    | 7 (16)  | 60 (6)   |
| Sewage**           | 41 (25)   | 9 (8)   | 2 (2)    | 7 (16)  | 71 (7)   |
| Industrial**       | 107 (64)  | 30 (28) | 19 (15)  | 25 (55) | 630 (61) |
| TOTAL              | 167       | 109     | 125      | 45      | 1031     |
| <u>Thames</u>      |           |         |          |         |          |
| River-dissolved*   | 5 (12)    | 13 (21) | 20 (26)  | 3 (5)   | 80 (25)  |
| River-particulate* | 2 (5)     | 3 (5)   | 3 (4)    | 6 (11)  | 50 (15)  |
| Sewage**           | 32 (74)   | 30 (47) | 51 (66)  | 38 (69) | 176 (54) |
| Industrial**       | 4 (9)     | 17 (27) | 3 (4)    | 8 (15)  | 19 (6)   |
| TOTAL              | 43        | 63      | 77       | 55      | 325      |

\* According to Table 2.15.

\*\* Grogan (1985).

Apparently Cu and Ni are exported primarily in the dissolved phase, whereas Fe, Mn and Pb favour the particulate phase; Zn exports exhibit similar partitioning between solid and solution.

Including metal inputs from sewage and industrial effluents to estuarine waters (Grogan, 1985), and assuming that these metals are predominantly discharged in an environmentally available form, total (*i.e.* estuarine) discharges have been calculated for the Humber and Thames Estuaries (Table 2.16). The percentage contribution from each source highlights the significance of industry in the Humber, whereas for the Thames, sewage inputs are dominant.

#### 2.2.3.8: Application of $K_D$ . Case Study - The Weser Estuary

This chapter has thus far provided very little evidence of metal reactivity in the North Sea estuaries, primarily because reactivity exerts very little influence on particle composition (Section 2.2.3.1). During the Weser Estuary survey additional filtrate and digested (hot concentrated  $\text{HNO}_3$ ) samples were analyzed by total-reflection x-ray fluorescence by A. Prange (GKSS Research Centre, FRG). Consequently, concentrations of six metals in three compartments were generated (*i.e.* total particulate, leachable particulate and dissolved) and these are plotted against distance from the tidal weir (Figure 2.2d) in Figure 2.18.

Dissolved profiles signify a rapid removal from solution of Fe and Mn in the low salinity region, and remobilization of Cu on estuarine mixing. Nickel, Pb and Zn decrease seawards although chemical reactivity is apparent in mid-estuary coincident with the FBI/TMZ. Particulate metals in both fractions decrease seaward as explained in Section 2.2.3.1.

The partitioning of a constituent between solid and solution can be conveniently quantified in terms of a distribution coefficient,  $K_D$  (*e.g.* Olsen *et al.*, 1982; Li *et al.*, 1984a). This is simply the ratio of the concentration in the solid phase,  $C_P$  in  $\mu\text{g/g}$ , to that in solution,  $C_S$  in  $\mu\text{g/ml}$ ; *i.e.*:

$$K_D = \frac{C_P}{C_S} \quad (2.9)$$

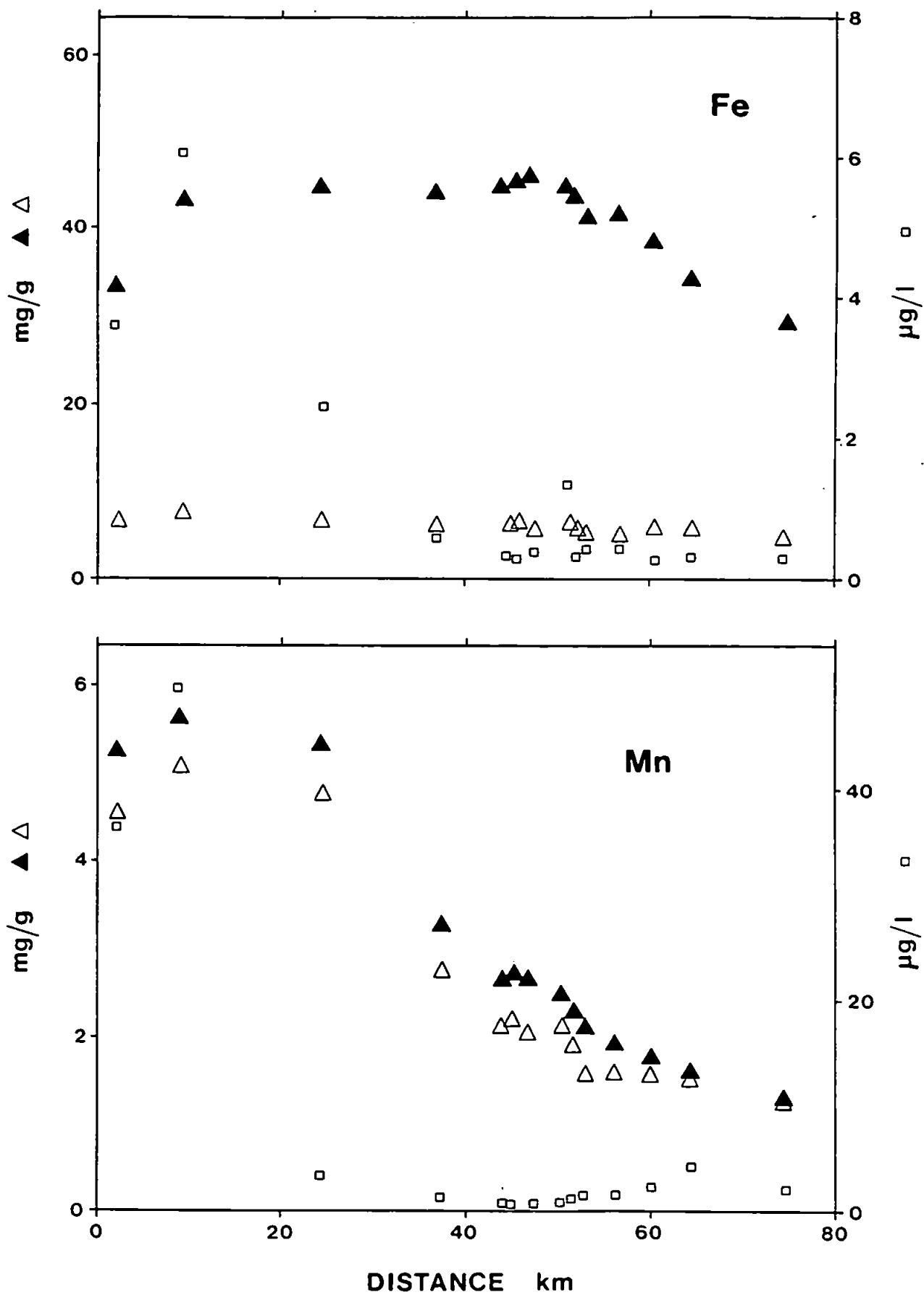


Figure 2.18: Concentrations of six metals in three compartments (▲, total particulate; △, leachable particulate; □, dissolved) as a function of distance (origin 5 km downstream of the tidal weir; Figure 2.2d) in the Weser Estuary.

a. Fe and Mn

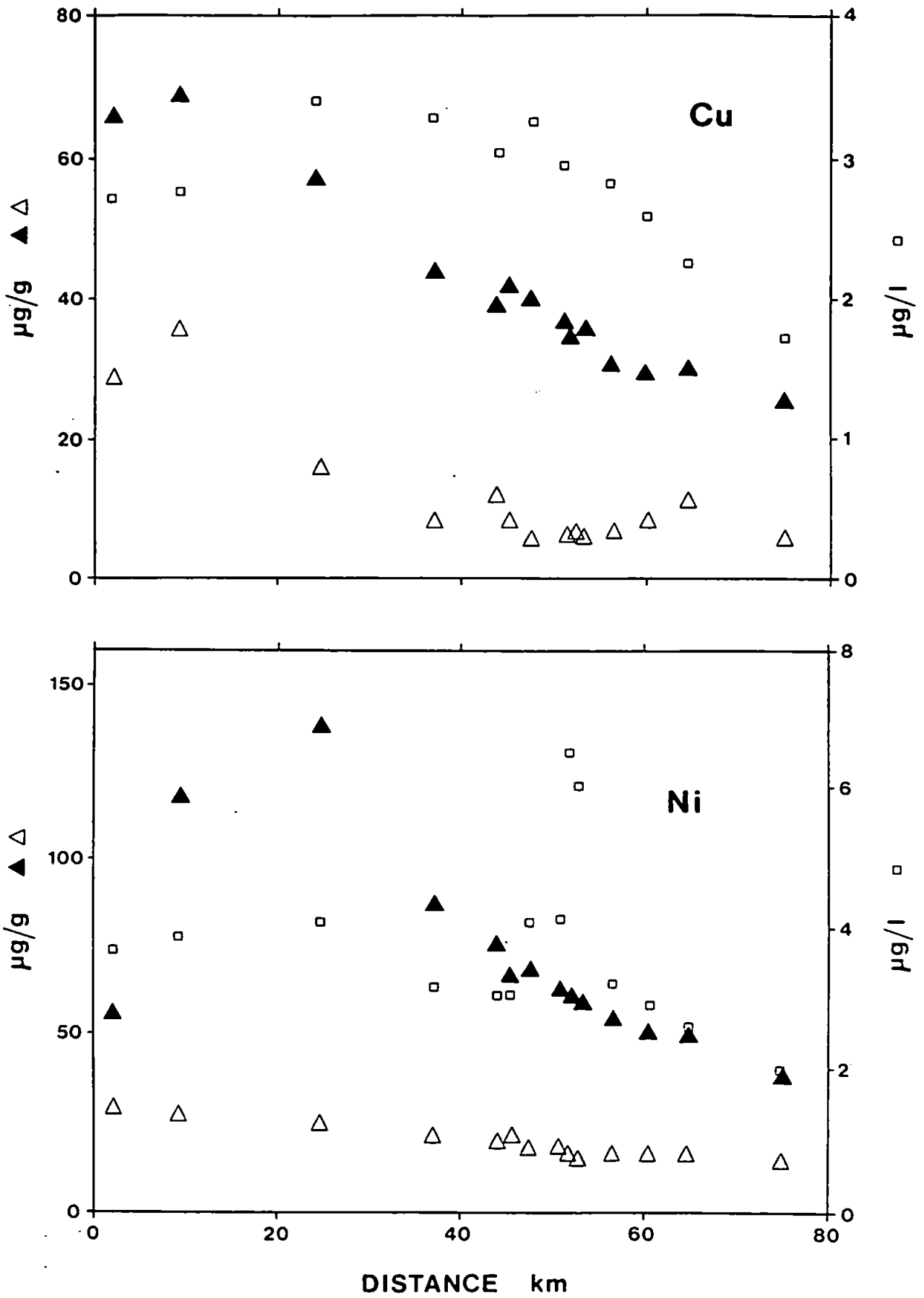


Figure 2.18 (continued): b. Cu and Ni.

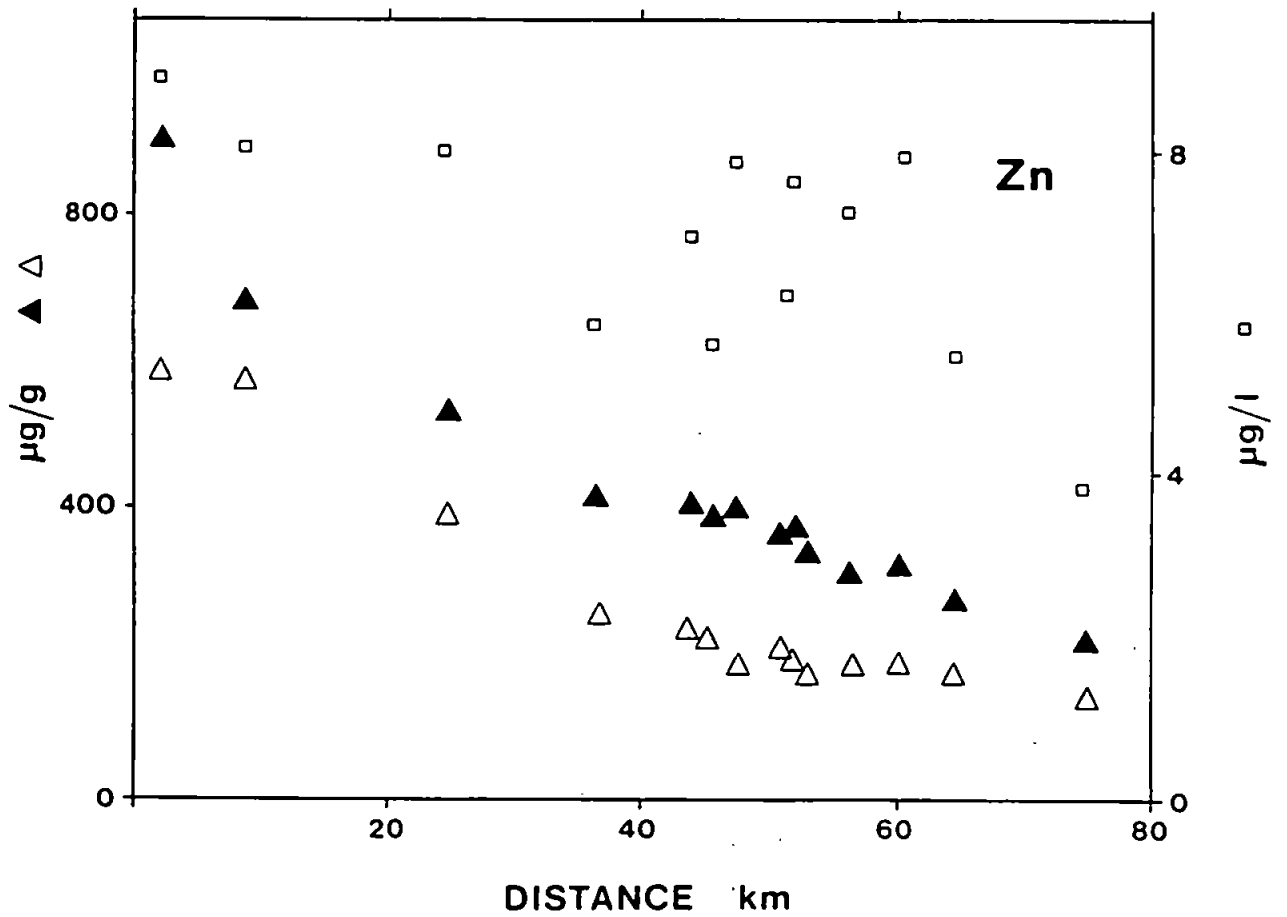
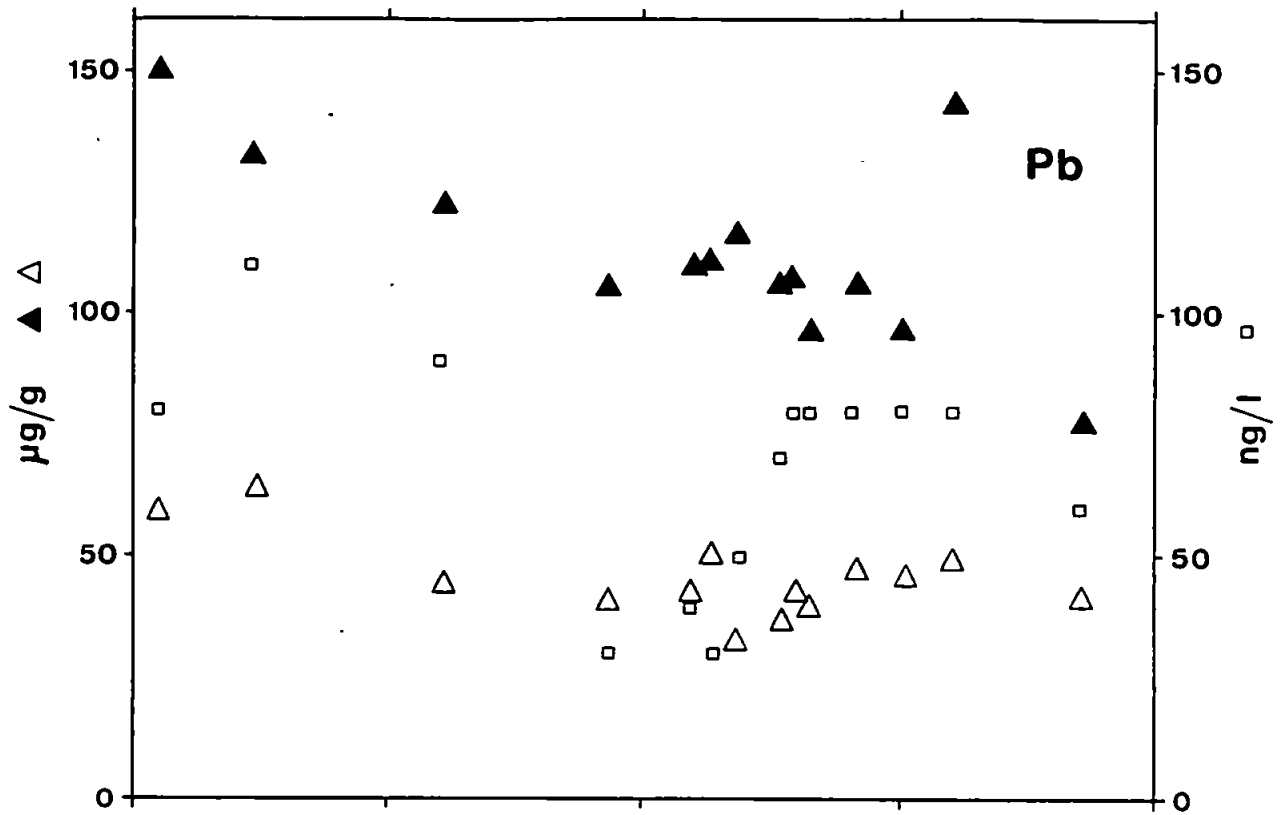


Figure 2.18 (continued): c. Pb and Zn.

and becomes dimensionless assuming that 1 ml is equivalent to 1 g. Such ratios have proven conceptually useful in elucidating element oceanic removal mechanisms and residence times (Cherry *et al.*, 1978; Whitfield and Turner, 1979; 1982; Fisher, 1986). However, other applications including trace metal studies with more environmental connotations (Valenta *et al.*, 1986; Balls, 1988; 1989a; Golimowski *et al.*, 1990) have been criticized for failing to discriminate between different solid associations (Bourg, 1987), and in particular, the solid component available for exchange processes between solid and solution (Ciceri *et al.*, 1988). Presumably  $K_D$ s based on a leachable solid fraction, or more specifically metals associated with hydrous Fe-Mn oxide coatings by operational definition (Section 2.1.2.1), yield a more meaningful interpretation of partitioning with respect to short-term biogeochemical reactivity.

The evolution of  $K_D$ s derived from leachable particulate concentrations along the estuary is shown in Figure 2.19. Particle affinity, which is gauged by the magnitude of  $K_D$ , varies from metal to metal and follows the order:



Thus, Cu, Ni and Zn favour solution whereas Fe, Mn and Pb have a stronger affinity for the particulate phase. This sequence is consistent with the affinity of metals to bind with metal oxide surfaces (Balistrieri and Murray, 1984) with the exception of Mn and Cu. An exceptionally high  $K_D$  for Mn can be accounted for by significant oxidative removal from solution (Boulegue *et al.*, 1978; Morris and Bale, 1979; Sung and Morgan, 1981; Sections 4.3.1.1 and 4.3.5.1), whereas low  $K_D$ s calculated for Cu may reflect an inefficient chemical extraction for this element.

These  $K_D$ s have some important environmental implications; their magnitudes are indicators of relative availability both biologically and geochemically, and may allow an assessment of the relative metal residence times in an estuary. For instance, Jackson and Norman (1970) estimated that during a spring tide in winter

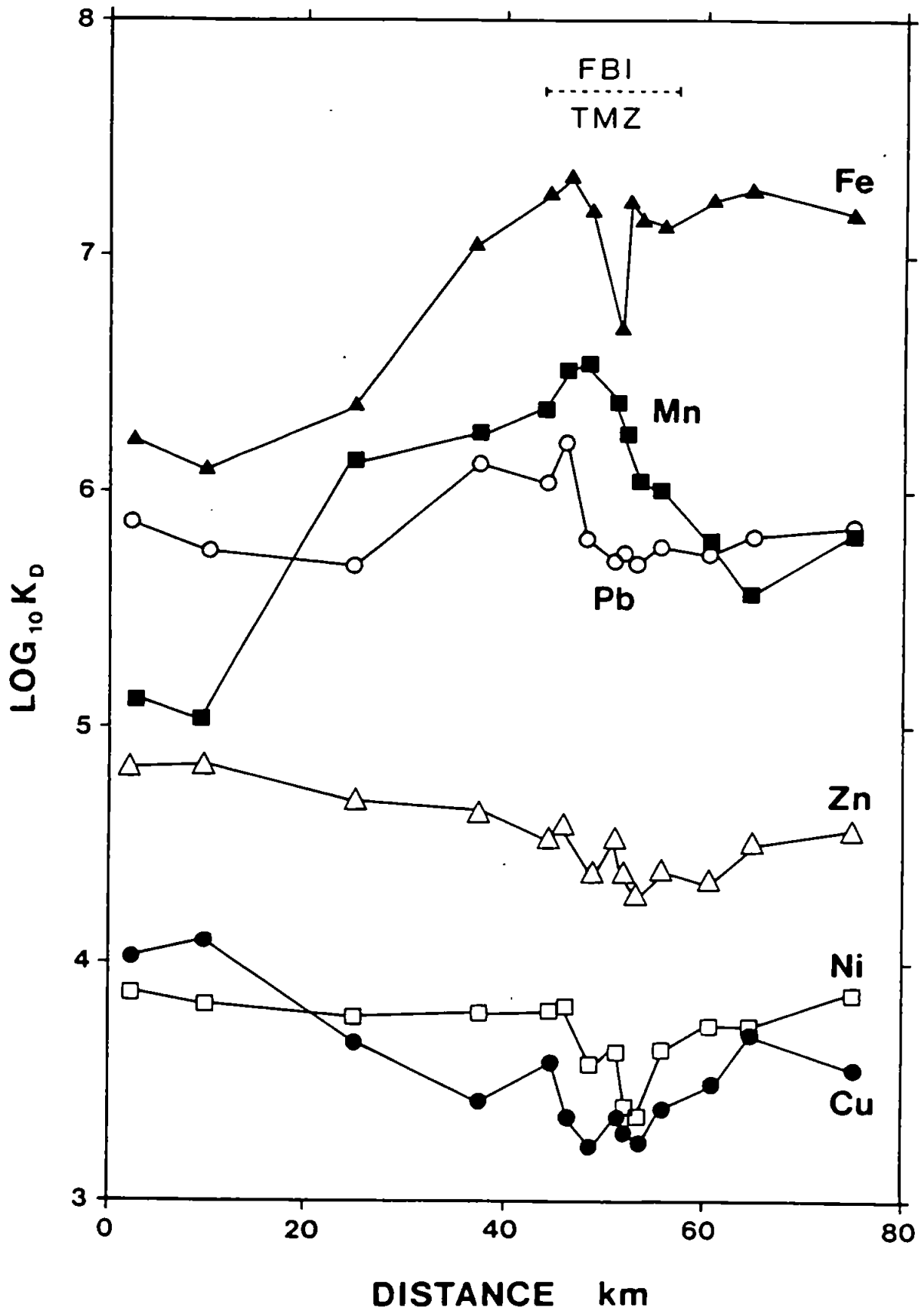


Figure 2.19: Apparent distribution coefficients,  $K_D$ s, of six metals as a function of distance in the Weser Estuary.

$3 \cdot 10^6$  tonnes of material is held in suspension in the Humber Estuary. Assuming this represents the amount of resuspendable material in the system, a crude estimate of particle residence time can be derived by dividing this figure by the rate at which material is introduced as calculated from Equation 2.8. The result of 30 years compares with a flushing time of up to 40 days (Table 1.4). Therefore, particle reactive constituents of high  $K_D$  such as Fe, Mn and Pb are expected to reside in an estuary for a period of the order of years, whereas soluble constituents (of low  $K_D$ ) such as Ni and Cu may be flushed through within a period of only a few weeks.

Although the implications of  $K_D$  transitions along the longitudinal profile to a large extent corroborate the inferences of chemical reactivity made from the dissolved distributions, interpretation of reactivity from  $K_D$ s must be made with caution. For example, a reduction of  $K_D$  for Zn with salinity may imply some release from the particles. However, both dissolved and leachable particulate Zn decrease seaward rather conservatively (Figure 2.18) and the reduction of  $K_D$  is caused by a more gradual decrease in particulate Zn compared with that for dissolved Zn. This decrease of particulate Zn is not indicative of desorption, as this would register as an input to the dissolved profile, but more likely reflects compositional changes resulting from end-member mixing. To reiterate, compositional changes as well as chemical reactivity govern these observed, or apparent  $K_D$ s, and it is important to emphasize this point as  $K_D$ s derived from a different (experimental) approach are discussed in Chapter 4 and are necessarily interpreted in a different fashion.



## 2.3: CONCLUSIONS

Both chemical and physical factors are instrumental in controlling the surface microstructure of suspendable material from the North Sea environment. Chemical effects, primarily resulting from hydrous oxide coatings of Fe and Mn, are responsible for the inter-estuarine variability in magnitude of SSA. The relative significance of Fe oxides is greatest in the Humber Estuary where substantial anthropogenic inputs are located, and diminishes in an anticlockwise direction around the coastal North Sea as the role of Mn oxides becomes more important. Physical factors are most apparent around the TMZ in which a preponderance of small particles results in high SSAs and generates a region of high scavenging potential. Chemical processes on estuarine mixing were, however, rarely detected from leachable particulate metal profiles as their influence on particle composition is minor.

Particulate trace metal concentrations exhibited little inter-estuarine variability, and estimated fluxes to the North Sea were therefore essentially a function of catchment area.

## CHAPTER 3: TRACE METAL REACTIVITY IN THE NORTH SEA. FIELD OBSERVATIONS

The distributions of particulate trace metals in the North Sea are described and interpreted in this Chapter, with emphasis on the plume environments of the Humber and Thames in which estuarine waters impinge on adjacent coastal waters.

### 3.1: SAMPLING AND ANALYSIS

#### 3.1.1: Sample Sites

Suspended sediment samples have been taken during six NERC North Sea cruises on board *RRS Challenger* for metal analysis. The aim of an initial *Shakedown* cruise (CH28 May 1988) was to assess the logistical and sampling/analytical practicalities and limitations. Sampling was subsequently undertaken during two 12-day survey cruises following a pre-determined track during summer (CH33 August 1988) and winter (CH43 January 1989) in order to provide quasi-synoptic seasonal surface distributions of particulate trace metals in the southern North Sea. In addition, samples were taken during three process cruises which focussed on specific environments of interest viz. the outflow regions of the Humber and Thames (plume cruises; CH42 December 1988 and CH46 February 1989) and suitable sites for the study of algal blooms (bloom cruise; CH50 April 1989).

During the plume cruises samples were taken around a fixed grid in the outflow regions, and at hourly intervals for 12-14 hours during two tidal anchor stations in the mouth of the Humber Estuary, and one some distance up estuary at Gravesend in the Thames Estuary (Figure 2.2b). Two algal blooms were tracked by means of an Argos buoy fitted with a submersed sail of approximately 4 m<sup>2</sup> during CH50 at a northerly site of diatoms and southerly site of *Phaeocystis* (Figure 4.1a).

### 3.1.2: Sampling Methods

Suspended solids concentrations encountered in the North Sea, especially offshore, are often lower than 1 mg/l (Eisma and Kalf, 1987), and, because of previous inferences (e.g. Section 1.8.1.3) of estuaries as major metal sources, low particulate metal concentrations were anticipated in open North Sea waters. For this reason, and the requirement of simultaneous sampling for dissolved trace metal analysis (MAFF and Southampton University Department of Oceanography), it was necessary to adopt extremely clean sampling techniques as now described.

During the survey cruises modified 10 l *Go-Flo* (General Oceanics, Florida) bottles were deployed on a stainless steel 12 bottle rosette fitted with CTD package from the starboard side of the vessel. Modifications to the *Go-Flos* included an interior PTFE lining, PTFE taps, and pressure opening and closure at depth (Morley *et al.*, 1988). Samples were routinely taken at approximately 10 m depth (near surface), and occasionally these were complemented by sampling nearer the bed of deeper waters or a distinctly stratified water column.

On completion of a CTD profile, the full bottles were transferred onto a rack (initially wooden, later adapted with fibreglass) mounted on the exterior of a clean container laboratory (Morley *et al.*, 1988) situated on the afterdeck, and connected to FEP pressure (particle-free compressed air) and filtration lines (Figure 3.1). Simultaneously, an acid cleaned (2M HCl 1 day; 1M HNO<sub>3</sub> 1 day) 142 mm diameter Nuclepore polycarbonate membrane filter of pore size 0.4 µm was mounted in an acid cleaned (50% HNO<sub>3</sub> 1 week; 50% HCl 1 week) polypropylene filter sandwich fitted with a sintered polyethylene frit of effective pore size 70 µm. This was placed vertically on the interior wet bench and connected to the filtration line (Figure 3.1), and the sample in the *Go-Flo* was filtered under pressure. The volume of filtrate was recorded after collection in a 10 l measuring cylinder and direct abstraction of 1 l samples for dissolved metal analysis. In more open waters of low transmission up to 40 l were filtered by successively connecting and evacuating several *Go-Flos* containing a common water mass.

Following filtration the sandwich was transferred to a vacuum line/water trap

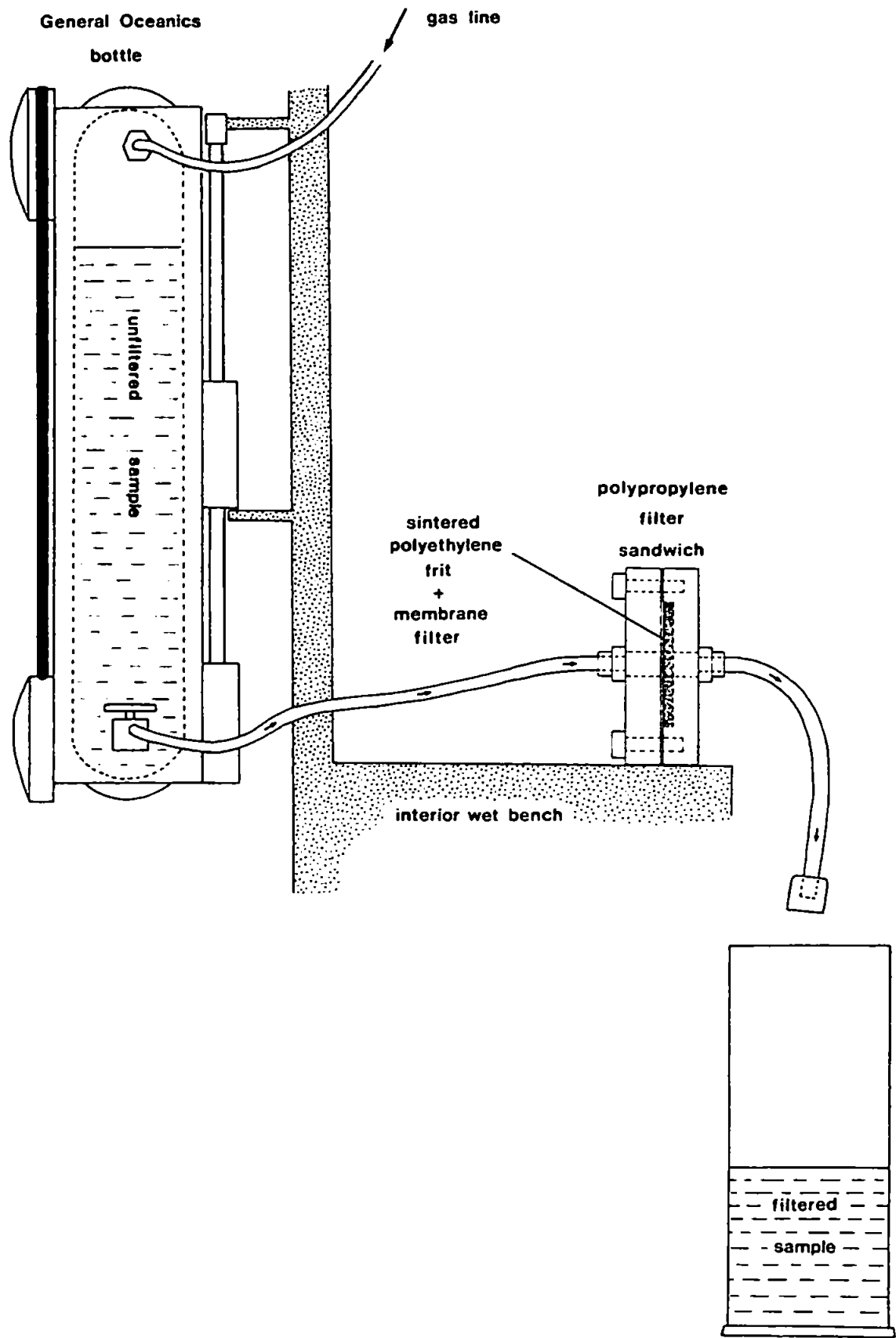


Figure 3.1: High pressure filtration system for the collection of suspended sediment and dissolved samples from the North Sea.

under a Class 100 laminar flow hood where the residue was washed with up to 30 ml sub-boiled distilled water in order to remove sea salt. During the bloom cruise, however, filter washing tended to detach delicate planktonic particles resulting in a loss of material; moreover, significant fractions of some metals including Mn and Cd are only loosely bound to plankton (Collier and Edmond, 1984) and are therefore susceptible to solubilization on washing. These filters were therefore thoroughly sucked dry without rinsing. After removal from the sandwich, filters were stored frozen ( $-18^{\circ}\text{C}$ ) in acid cleaned petri dishes.

All filter manipulations involved the use of plastic tweezers, and disposable plastic gloves were worn during all operations in the clean container and during the handling of the *Go-Flos*.

It was realized from the outset that particle settling below the tap/filtration line of the *Go-Flo* during filtration would result in preferential recovery of small, low density particles (Gardner, 1977; Calvert and McCartney, 1979). During the survey cruises if filtration proceeded slowly ( $< 0.1$  l/minute) the *Go-Flo* would occasionally be disconnected and inverted several times. In the more energetic and turbid environments of the winter plumes, although sufficient material for metal analysis could be recovered in a shorter time, the effects of settling were more apparent. This was demonstrated at the anchored tidal station of the Thames plume cruise (see Figure 2.2b) where 6 standard *Go-Flos* were fired simultaneously a few metres below the surface, and, once the CTD frame was returned on deck, samples were abstracted from each bottle at different time intervals up to 6 hours. The results are shown in Figure 3.2 and signify a rapid reduction in concentration and change in SSA of particles remaining in suspension with time; similar experiments reported in Section 2.2.2.1 exemplified the effects of settling time on particle size. An alternative method of sampling was therefore introduced during the plume cruises which overcame these problems, although CTD casts, and hence *Go-Flo* sampling, were still necessary at the anchored tidal stations. An underway pumped supply of water was provided in the clean container by means of PTFE tubing connected to a precision echo sounder (PES) deployed a

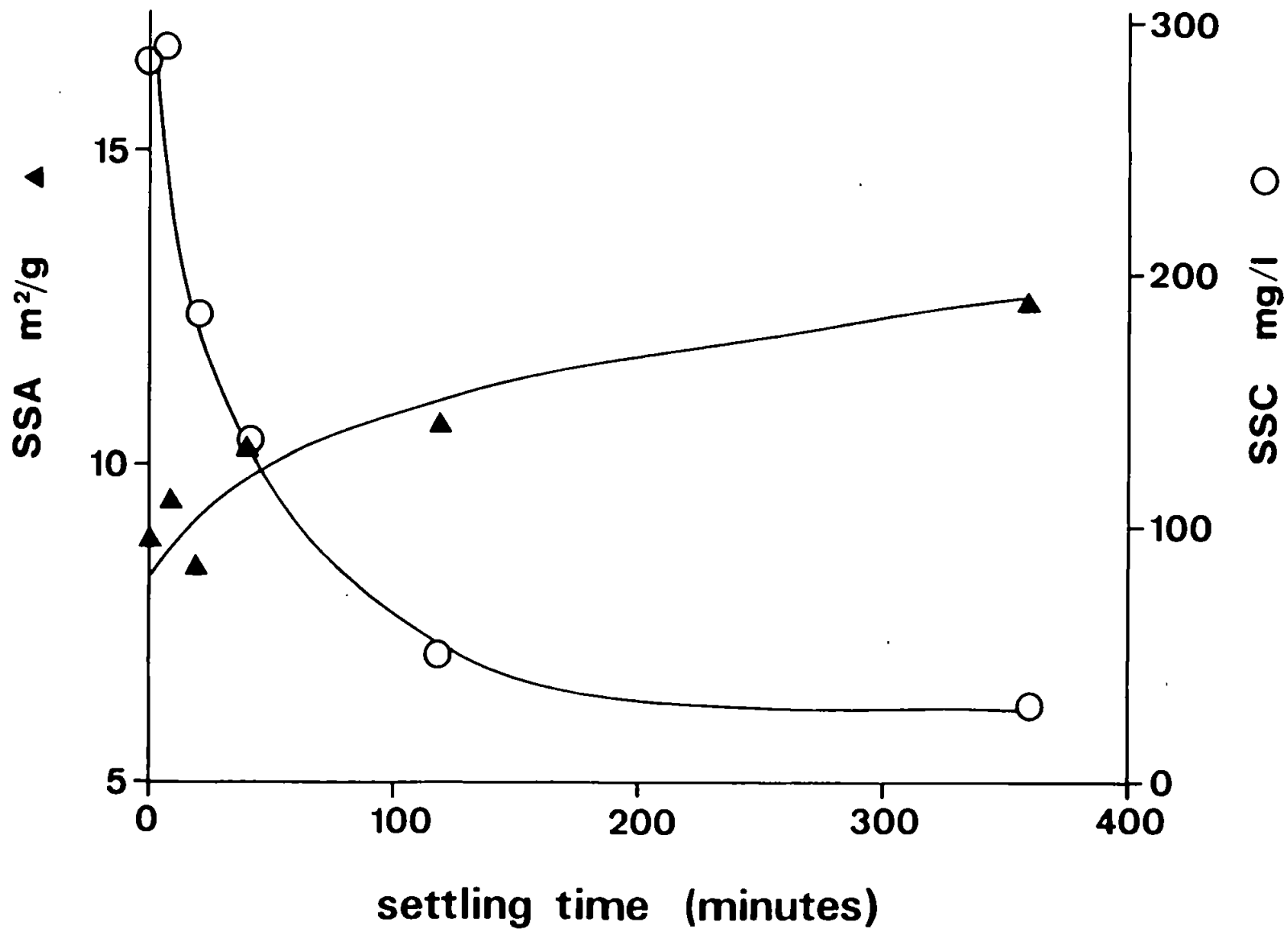


Figure 3.2: Specific surface area (SSA) and suspended solids concentration (SSC) of Thames sediment (sampled at Gravesend, low water, salinity = 23.0 ‰; Figure 2.2b) remaining in suspension in *Go-Flos* as a function of time.

few metres below the surface at the port side of the bow. After flushing the system through for at least 5 minutes with ambient water, a sample was abstracted into a 10 l PTFE reservoir on the wet bench. The reservoir was then connected to gas and filtration lines and regularly shaken during pressure filtration of the sample.

Essential master variable parameters were measured continuously by sensors flushed with the non-toxic supply, and recorded as depth profiles at the CTD stations (Figure 3.3).

### 3.1.3: Determination of Suspended Solids Concentration

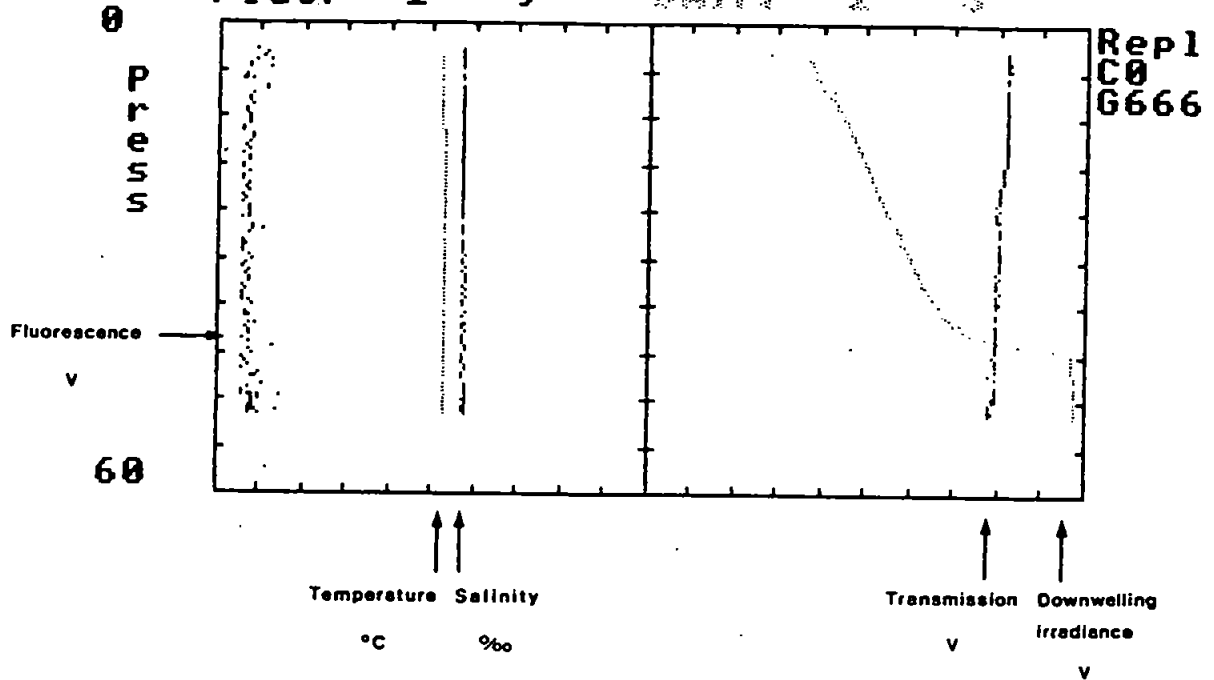
All samples were retained on Nuclepore membrane filters and air dried to constant weight in a Class 100 laminar flow hood. Initially (CH28 and CH33), in order to derive the masses of dry solid material the mean weight of two acid cleaned blank filters was subtracted from the mass of each sample plus filter. Subsequently, however, it was found that although the coefficient of variation of the filter weights was small, the range could exceed that of the mass of recovered sediment. For example, the weights of a suite of 7 blank filters gave a mean and standard deviation of  $134.0 \pm 3.1$  mg (coefficient of variation = 2.3%) and a range of 9.2 mg which compares with the lowest sediment loadings retained on filters (< 5 mg). Therefore the weights of individual filters were determined after removal of all excess leached solids and subtracted from the sample plus filter masses (CH42 and CH43). For the remaining cruises (CH46 and CH50) filters were pre-weighed after acid cleaning and stored in recorded sequence in their original container.

The suspended solids concentration was determined from the mass of dry material on the filter and the filtrate volume recorded during operations in the clean container.

Suspended solids concentrations were also routinely determined after filtration of up to 6 l sample, taken from either a *Go-Flo* immediately after arrival on deck or from the PES supply, through pre-weighed Whatman GF/C filters (pore size 1.2

(a) 266/1 Mon, 15 Aug 1988.05:27:16 49m

|       |    |   |    |       |    |   |   |
|-------|----|---|----|-------|----|---|---|
| Temp  | 22 | - | 16 | Trans | 0  | - | 5 |
| Sal   | 32 | - | 36 | XXXXX | 0  | - | 1 |
| Fluor | -1 | - | 9  | Downw | -2 | - | 3 |



(b) 244/1 Sat, 13 Aug 1988.05:08:35 84m

|       |    |   |    |       |   |   |   |
|-------|----|---|----|-------|---|---|---|
| Temp  | 22 | - | 14 | Trans | 0 | - | 5 |
| Sal   | 33 | - | 36 | XXXXX | 0 | - | 1 |
| Fluor | -1 | - | 9  | Downw | 0 | - | 4 |

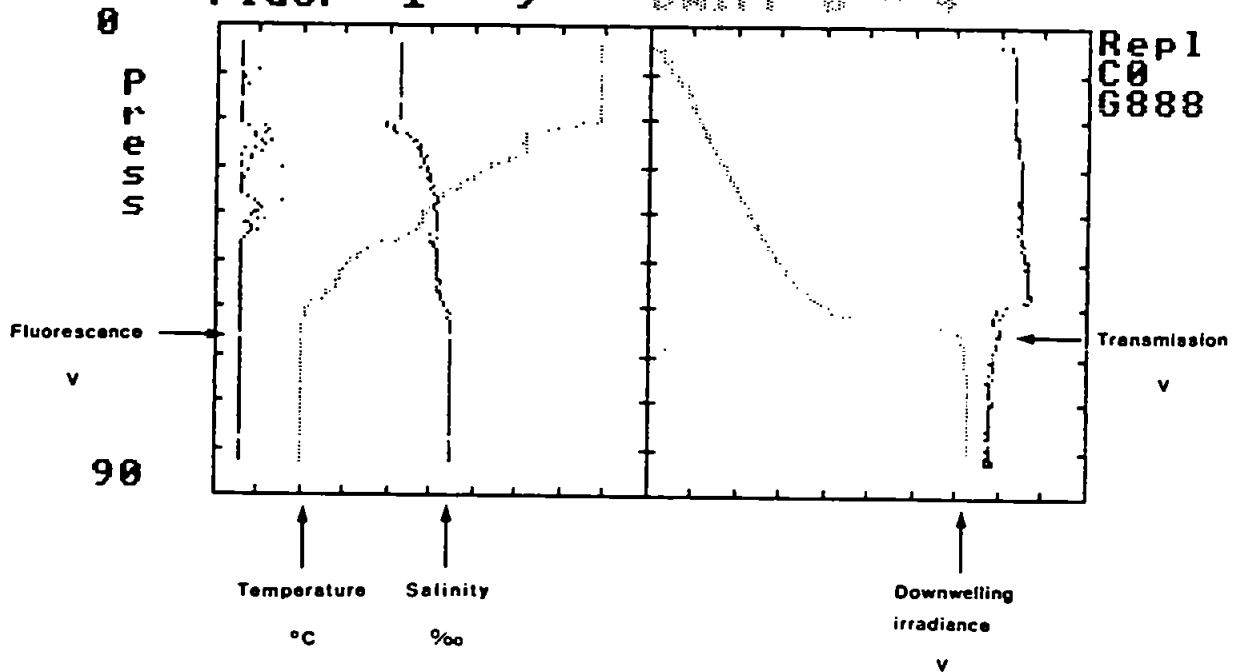


Figure 3.3: Examples of recorded CTD depth profiles during CH33 (locations given in Figure 3.12). a. Well-mixed water column to the north of the Humber Estuary mouth. b. Stratified water column off the northern English coast.



$\mu\text{m}$ ; Section 2.1.1.1), and these results are compared with the corresponding suspended solids concentrations determined from the masses of material retained on Nuclepore filters in Table 3.1. Both data sets are highly and significantly correlated in all instances with the exception of the bloom cruise, despite comparing material often collected from different sources (*i.e.* standard *Go-Flo* versus modified *Go-Flo*) and of different particle size (*i.e.*  $>1.2 \mu\text{m}$  versus  $>0.4 \mu\text{m}$ ); problems of settling and mass determination are therefore not apparent. Lack of correlation for the bloom cruise can be attributed to inaccuracies associated with the determination of very low masses ( $< 5 \text{ mg}$ ) retained on the Whatman filters rendered by very low turbidities and rapid pore clogging by glutinous planktonic matter.

Table 3.1: A comparison of suspended solids concentrations ( $\text{mg/l}$ ) derived from Nuclepore (NUC) and Whatman GF/C (GFC)\* filtration.

| Cruise number | Sampling method | n  | Regression equation                | $r^2$ (%) | p             |
|---------------|-----------------|----|------------------------------------|-----------|---------------|
| CH33          | <i>Go-Flo</i>   | 47 | NUC = $0.818 + 0.702 \text{ GFC}$  | 84.2      | $\leq 0.0005$ |
| CH42          | <i>Go-Flo</i>   | 30 | NUC = $-7.37 + 1.13 \text{ GFC}$   | 91.8      | $\leq 0.0005$ |
| CH42          | <i>PES</i>      | 10 | NUC = $-0.75 + 0.987 \text{ GFC}$  | 82.8      | $\leq 0.0005$ |
| CH43          | <i>Go-Flo</i>   | 52 | NUC = $-0.444 + 0.900 \text{ GFC}$ | 88.2      | $\leq 0.0005$ |
| CH46          | <i>Go-Flo</i>   | 16 | NUC = $16.1 + 0.791 \text{ GFC}$   | 75.3      | $\leq 0.0005$ |
| CH46          | <i>PES</i>      | 34 | NUC = $-14.5 + 1.45 \text{ GFC}$   | 95.2      | $\leq 0.0005$ |
| CH50          | <i>Go-Flo</i>   | 9  | not significant                    | -         | $> 0.05$      |

\*Determined by T.J. Moffat for CH33 and CH43 (Polytechnic South West, Plymouth).

### 3.1.4: Sample Leaching

It was decided that the extraction procedure adopted for estuarine samples (Section 2.1.2.1) could not be suitably applied to the North Sea samples for the following reasons. Firstly, it was necessary from a practical point of view to reduce the number of manipulations when dealing with significantly larger batches

of samples; moreover, as considerably lower masses of samples were involved (often < 10 mg) this would reduce the risk of contamination. Secondly, the extraction efficiency of the HOAc/NH<sub>2</sub>OH·HCl leach, although environmentally significant, is relatively poor for certain metals (Section 2.2.3.5) and this may have frequently rendered detection difficult. A 0.1M HCl leach (Duinker *et al.*, 1974) was avoided as this may be subject to neutralization by the dissolution of certain sediment components hence impair the extraction of certain metals such as Cu (G.Bryan, pers. comm.). A 1M HCl attack was preferred as this is potentially strong enough to release a substantial proportion of metals, yet is thought to predict metal bioavailability in sediments (Luoma and Bryan, 1978; 1981; Langston, 1980).

Table 3.2: Metal removal from suspended sediments by HOAc/NH<sub>2</sub>OH·HCl given as a percentage of metal removal by 1M HCl. Mean±one standard deviation of n sample determinations given.

|                                 | n | Fe     | Mn     | Cu     | Pb     | Zn     |
|---------------------------------|---|--------|--------|--------|--------|--------|
| Humber Estuary<br>Jan. 1988     | 4 | 27±4.7 | 84±4.1 | 59±6.5 | 26*    | 82±9.5 |
| Elbe Estuary<br>June 1988       | 4 | 21±1.7 | 90±12  | 25±3.7 | 42±6.6 | 84±6.6 |
| Southern North Sea<br>July 1988 | 1 | 15     | 73     | 44     | -      | 72     |

\* n = 2.

Table 3.2 compares the concentrations of metals released from suspended sediment samples from the North Sea environment by HOAc/NH<sub>2</sub>OH·HCl and 1M HCl. Evidently the latter leach removes a significantly larger fraction of Fe, Cu and Pb indicating dissolution of more refractory components.

Samples plus filters were leached in covered 100 ml PTFE beakers with 1M HCl (BDH AristaR grade) for approximately 12 hours under a Class 100 laminar flow

hood. Samples of mass up to 100 mg were leached in 15 ml whereas the occasional higher mass samples were leached in 25 ml. The residual mixture of leachate plus solids removed from the filter, and rinsings of 1M HCl, were transferred into volumetric flasks (25 or 50 ml). Procedural blanks were prepared likewise by leaching blank filters.

All glass- and PTFE-ware employed had been soaked in Micro detergent (1 hour), followed by 50% HCl (>12 hours), and rinsed out thoroughly with Milli-Q water.

### 3.1.5: Metal Analysis

Solutions were analyzed by atomic absorption techniques (*cf.* Section 2.1.2.2) for the six metals considered most appropriate to the interests of the *North Sea Project* (*viz.* Fe, Mn, Cd, Cu, Pb and Zn). Determinations of Fe, Mn, Cu and Zn, and Pb for plume cruise samples, were performed using a Pye Unicam SP9 under the conditions outlined in Table 3.3. For each sample and standard (BDH Spectrosol) 3 or 4 aliquots of 200  $\mu$ l were pipetted manually into an air-acetylene flame via a PTFE microcup connected to the end of the aspiration tubing and absorbance peaks were recorded on a Perkin-Elmer S6 chart recorder. Blanks were usually less than the instrumental limits of detection (Table 3.3), and interferences were found to pose no major problems on comparison of linear plots derived from standards and sample standard additions. Dilutions were occasionally necessary for Fe, Mn and Zn analyses of survey cruise samples; however, it was more practical to adopt less sensitive wavelengths for analyses of plume cruise samples of high Fe and Mn concentrations.

Remaining analyses (*i.e.* Cd and Pb) were performed on a Varian-Techtkon in the flameless mode using a Perkin Elmer HGA 76B graphite furnace with an AS-1 autosampler according to conditions as recommended in the operator's manual with minor modifications. Aliquots introduced to the graphite tube were treated by the following programme:

Table 3.3: Instrumental conditions for atomic absorption analysis of North Sea samples.

| <i>MODE</i>      |   |                 |               |                       |  |                                      |
|------------------|---|-----------------|---------------|-----------------------|--|--------------------------------------|
| Element          | Cruises                                 | Wavelength (nm) | Bandpass (nm) | Background correction | Working range ( $\mu\text{g/ml}$ )                                       | Detection limit ( $\mu\text{g/ml}$ ) |
| <i>FLAME</i>     |   |                 |               |                       |  |                                      |
| Fe               | CH 33; CH 43;<br>CH 50                  | 248.3           | 0.2           | off                   | 0.2-4.0<br>>4.0, dilutions   | 0.05                                 |
|                  | CH 42; CH 46                            | 392.0           | 0.2           | off                   | 50-500   | 5                                    |
| Mn               | CH 33; CH 43;<br>CH 50                  | 279.5           | 0.2           | off                   | 0.05-3.0<br>>3.0, dilutions  | 0.03                                 |
|                  | CH 42; CH 46                            | 403.1           | 0.2           | off                   | 3.0-15.0   | 0.3                                  |
| Cu               | CH 33; CH 42;<br>CH 43; CH 46;<br>CH 50 | 324.7           | 0.2           | off                   | 0.02-0.8   | 0.02                                 |
| Pb               | CH 42; CH 46                            | 283.3           | 0.5           | off                   | 0.2-3.0  | 0.2                                  |
| Zn               | CH 33; CH 42;<br>CH 43; CH 46;<br>CH 50 | 213.9           | 0.2           | on                    | 0.01-0.6<br>>0.6, dilutions  | 0.01                                 |
| <i>FLAMELESS</i> |   |                 |               |                       |  |                                      |
| Cd               | CH 33; CH 42;<br>CH 43; CH 46;<br>CH 50 | 228.0           | 0.5           | on/off                | $10^{-3}$ - $3 \cdot 10^{-3}$<br>> $3 \cdot 10^{-3}$ , dilutions         | $10^{-4}$                            |
| Pb               | CH 33; CH 43;<br>CH 50                  | 217.0           | 1.0           | off                   | $3 \cdot 10^{-3}$ - $2 \cdot 10^{-2}$<br>> $2 \cdot 10^{-2}$ , dilutions | $5 \cdot 10^{-4}$                    |

- (1) dry @ 100°C, 15 seconds;
- (2) ash @ 400°C, 10 seconds;
- (3) atomize @ 2000°C, 4 seconds;
- (4) burn @ 2250°C, 2 seconds.

Blank signals for Cd and Pb were generally below 1 ng/ml and 3 ng/ml respectively, although several Cd blanks generated with the plume sample suite exceeded 5 ng/ml. There were no demonstrable interferences using the method of standard additions except for Pb analyses of CH50 samples which have therefore been omitted from the results.

## 3.2: RESULTS AND DISCUSSION

### 3.2.1: Plumes

#### 3.2.1.1: Hydrography

Mean daily river flows (essentially a measure of the driving force of plume development) for the Humber and Thames are given in Table 3.4 for the periods during and 40 days (approximating their flushing times; Table 1.4) prior to sampling. Flows are evidently low (especially for the Thames) when compared with the 10 year monthly averaged values and reflect the abnormally dry weather conditions of this particular winter.

Table 3.4: River flows to the Humber and Thames Estuaries. Mean  $\pm$  one standard deviation (and range) of mean daily values given.

|                   | Dates          | Flow (m <sup>3</sup> /s)   | Source of information |
|-------------------|----------------|----------------------------|-----------------------|
| <u>Humber</u>     |                |                            |                       |
| During sampling   | 22-29/12/88    | 297 $\pm$ 103 (190-450)    | NRA Severn-Trent /    |
| 40 previous days  | 12/11-21/12/88 | 216 $\pm$ 150 (94-634)     | Yorkshire Regions     |
| Mean for November | (1964-1973)    | 275                        | Gameson (1976)        |
| Mean for December | (1964-1973)    | 430                        |                       |
| <u>Thames</u>     |                |                            |                       |
| During sampling   | 13-17/2/89     | 15.6 $\pm$ 9.7 (10.3-33.0) | NRA Thames            |
| 40 previous days  | 4/1-12/2/89    | 22.8 $\pm$ 9.8 (8.5-46.0)  | Region                |
| Mean for January  | (1978-1987)    | 200                        | NRA Thames<br>Region  |
| Mean for February | (1978-1987)    | 180                        |                       |

The salinity distributions in the plumes are shown in Figure 3.4; isohalines have been redrawn from non-tidally corrected computer interpolations of continually logged salinity data at intervals emphasizing the salient features.

The Humber plume, arbitrarily bounded by the 34.2 ‰ isohaline, heads in a south/south easterly direction coupled with the local residual circulation. The pool of low salinity water to the south east of the mouth and bounded by the 33.0

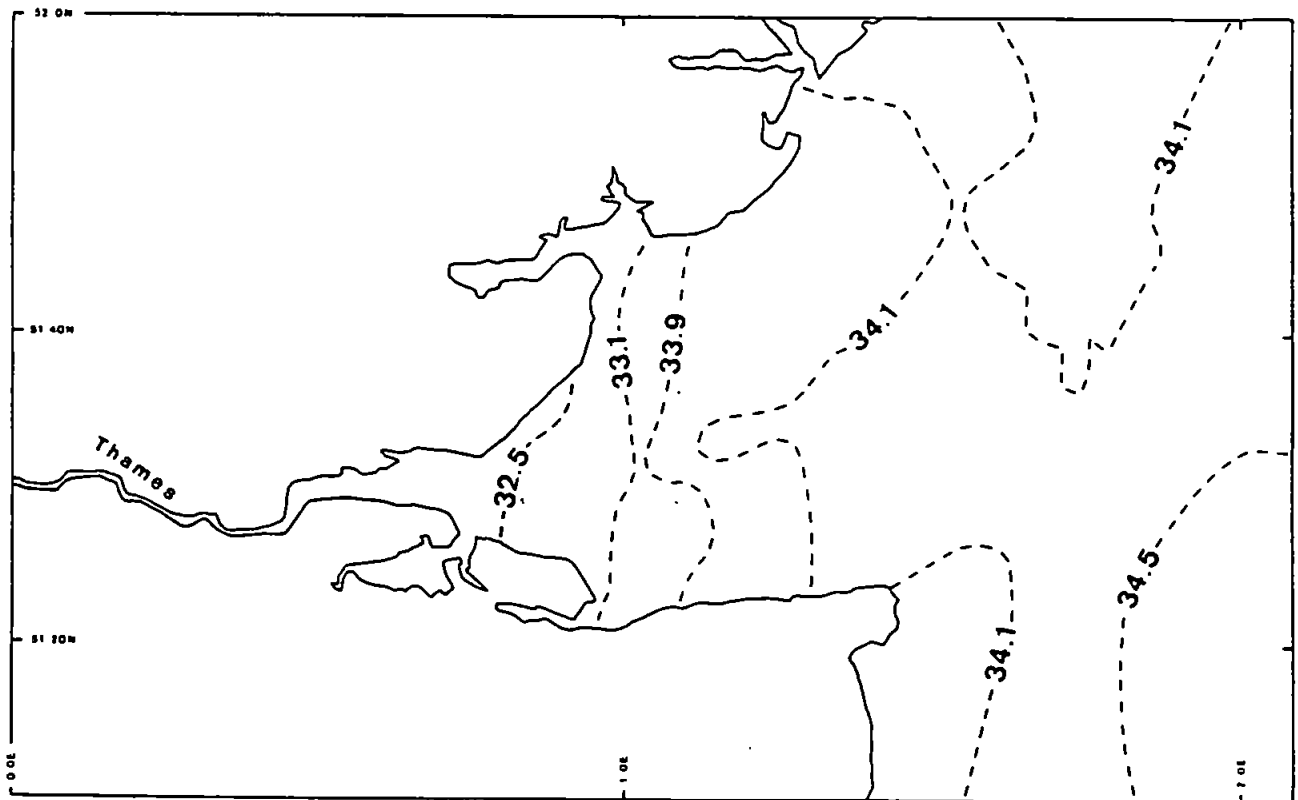
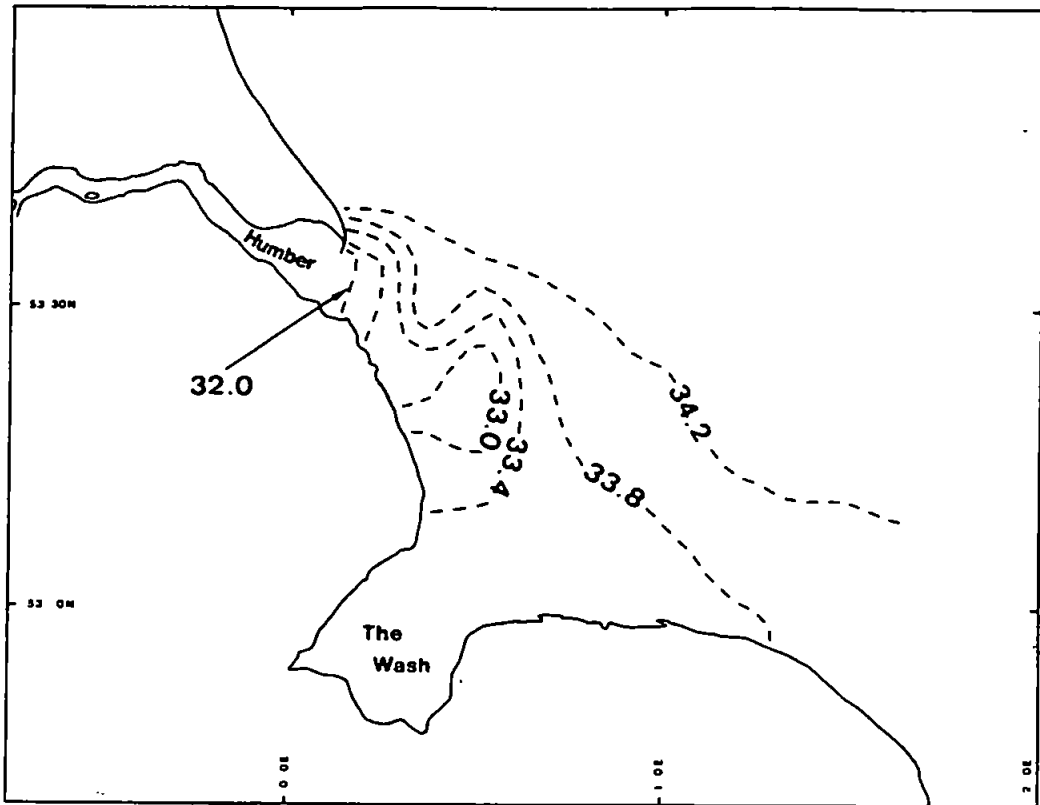


Figure 3.4: Near surface salinity distributions (‰) observed in the Humber and Thames plumes during sampling.

SSC  
mg/l

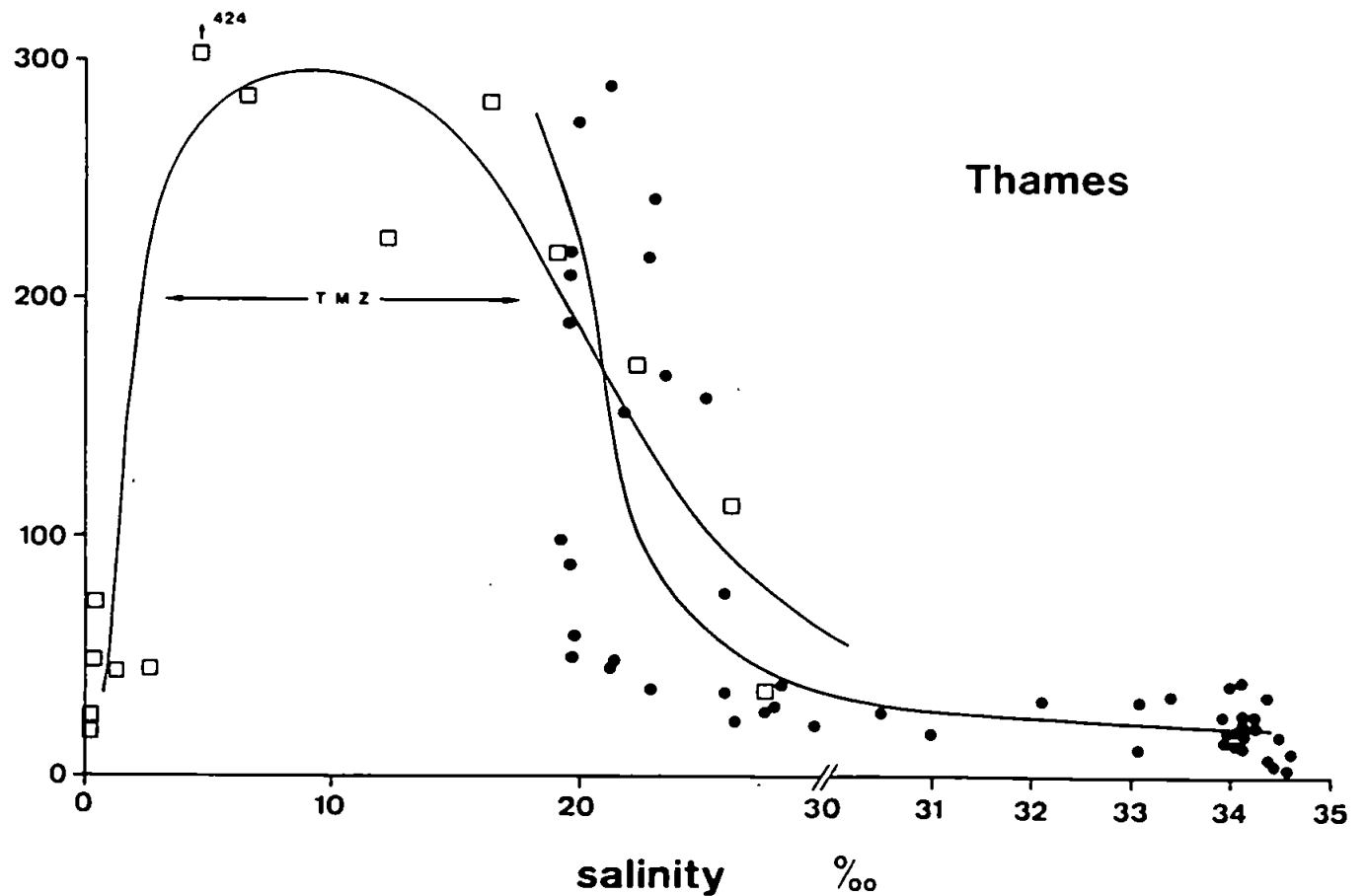
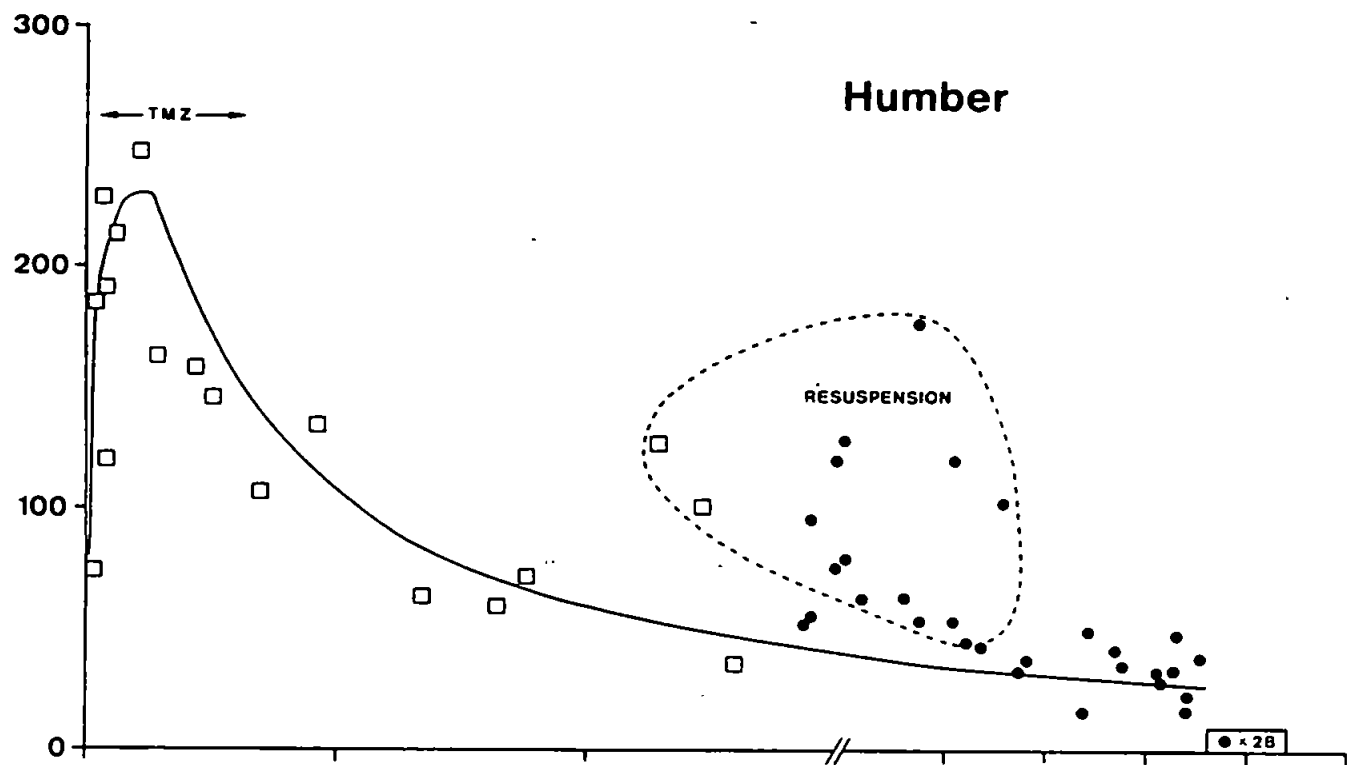


Figure 3.5: Distribution of suspended solids in the estuaries (□; winter surveys) and plumes (●) of the Humber and Thames.



‰ isohaline is reminiscent of tidally cut-off patches observed by Lewis (1990) off the mouth of the Tees Estuary. However, in this instance the feature is more likely an artifact created by the contouring package in response to lack of data towards the coast.

Although a reduction in salinity is apparent with distance from the mouth of the Thames Estuary, the plume is not well-defined. Thames water is quickly dissipated in high salinity English Channel water entering from the south.

CTD cast data indicated that the water columns within the plumes were well-mixed; vertical stratification was only apparent during maximum current velocity at the anchored tidal stations.

Figure 3.5 shows the suspended solids distributions in the plumes; the axes have been expanded in order to accommodate data from the respective estuarine environments (Section 2.2.1). Concentrations decrease offshore from the outer estuaries although this trend is superimposed by elevated concentrations in the Humber plume suggesting that a large component of material is derived from resuspension of marine or reworked estuarine deposits.

#### 3.2.1.2: Metal Distributions

Particulate metal concentrations for the Humber and Thames plumes are summarized in Table 3.5. Copper and Pb were not detectable in several samples from the outer reaches of the Humber plume owing to the low masses of solid recovered (<15 mg); Cd analyses were often complicated by the small peak heights resulting from low concentrations associated with particles in these outflow regions (Section 3.2.2.4; *cf.* Balls, 1985a) which often failed to exceed the rather high blank signals of these sample suites (Section 3.1.5).

Distributions of particulate Fe, Mn, Cu and Zn in the Humber plume were similar (exemplified by Fe and Zn in Figure 3.6a) and linear correlations between these metals (shown in Figure 3.8) were very significant. Concentrations were highest along the coast from the mouth of the Humber Estuary to the Wash, and lowest to the north of the Humber away from the influence of the outflow, and

|                   | salinity<br>(‰)  | SSC<br>(mg/l)   | Fe<br>mg/g       | Mn<br>mg/g      | Cd<br>μg/g    | Cu<br>μg/g      | Pb<br>μg/g   | Zn<br>μg/g   | Fe:Mn          |
|-------------------|------------------|-----------------|------------------|-----------------|---------------|-----------------|--------------|--------------|----------------|
| <u>CH42</u>       |                  |                 |                  |                 |               |                 |              |              |                |
| n                 | 58               | 58              | 58               | 58              | 21            | 43              | 32           | 57           | 58             |
| $\mu \pm 1\sigma$ | 32.75 $\pm$ 1.73 | 33.4 $\pm$ 38.8 | 26.0 $\pm$ 9.81  | 0.91 $\pm$ 0.15 | 0.5 $\pm$ 0.4 | 25.6 $\pm$ 8.0  | 105 $\pm$ 13 | 136 $\pm$ 50 | 27.9 $\pm$ 7.8 |
| R                 | 28.59-34.36      | 0.9-177         | 8.41-43.91       | 0.58-1.19       | 0.1-1.6       | 6.8-37.7        | 77-137       | 65-289       | 12.3-38.7      |
| <u>CH46</u>       |                  |                 |                  |                 |               |                 |              |              |                |
| n                 | 50               | 50              | 50               | 50              | 30            | 50              | 46           | 50           | 50             |
| $\mu \pm 1\sigma$ | 28.57 $\pm$ 5.93 | 66.5 $\pm$ 78.2 | 20.68 $\pm$ 2.96 | 0.55 $\pm$ 0.12 | 0.4 $\pm$ 0.3 | 32.1 $\pm$ 15.7 | 112 $\pm$ 34 | 120 $\pm$ 38 | 38.3 $\pm$ 6.0 |
| R                 | 19.31-34.65      | 2.0-289         | 13.44-25.99      | 0.37-0.78       | 0.1-1.7       | 9.8-55.7        | 48-180       | 73-182       | 28.7-49.0      |

Table 3.5: Summary of hydrographic conditions and particulate metal concentrations during the plume cruises. Mean $\pm$ 1 standard deviation ( $\mu \pm 1\sigma$ ) and range (R) of n determinations given; for metals, n was occasionally limited by the instrumental limits of detection.

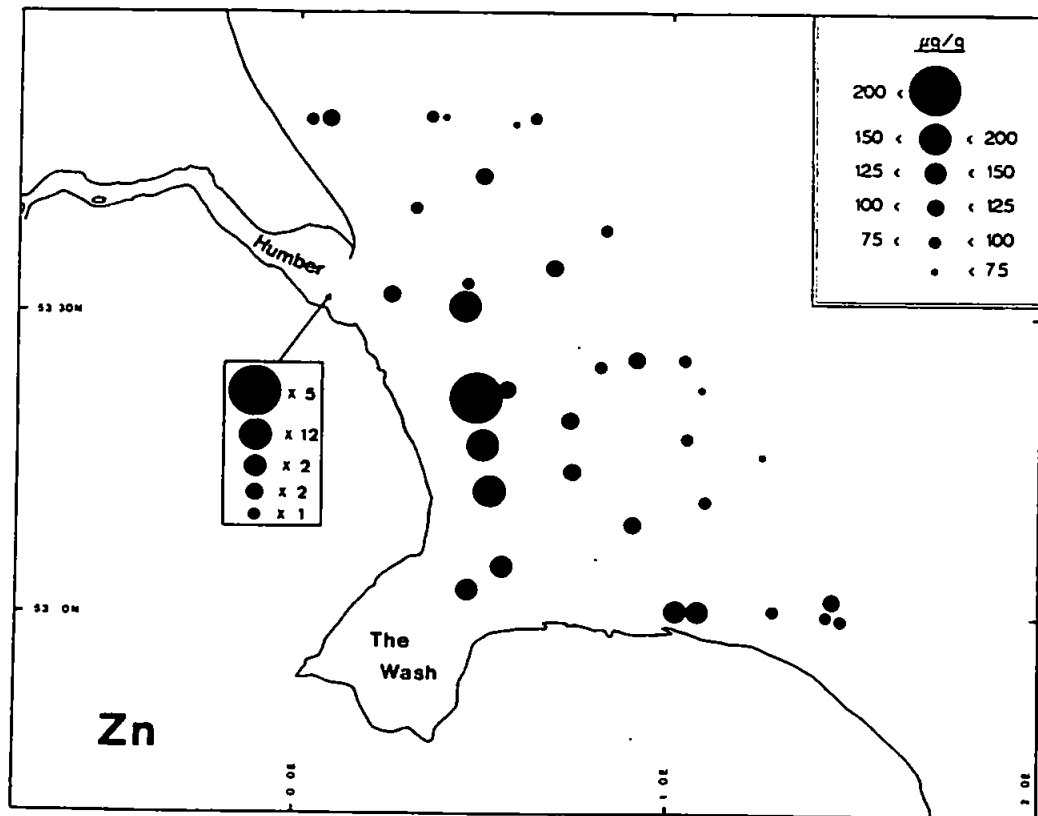
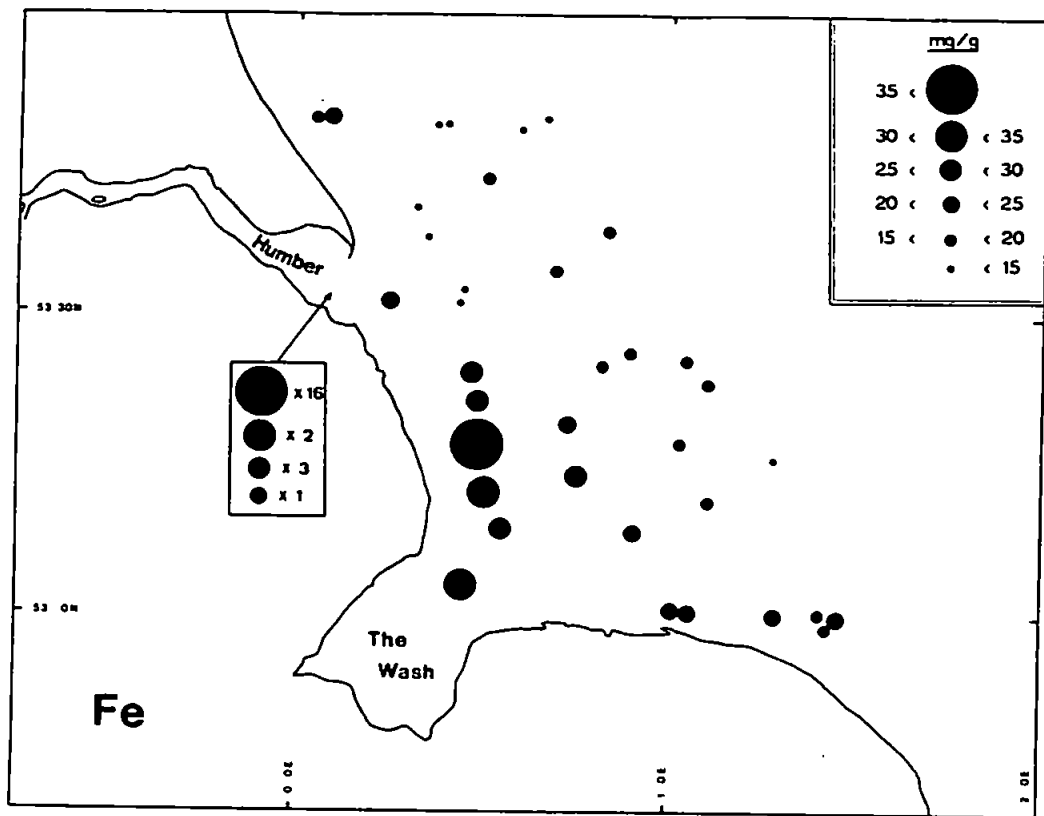


Figure 3.6a: Distributions of particulate Fe and Zn in the Humber plume. Boxed data points refer to anchored tidal station.

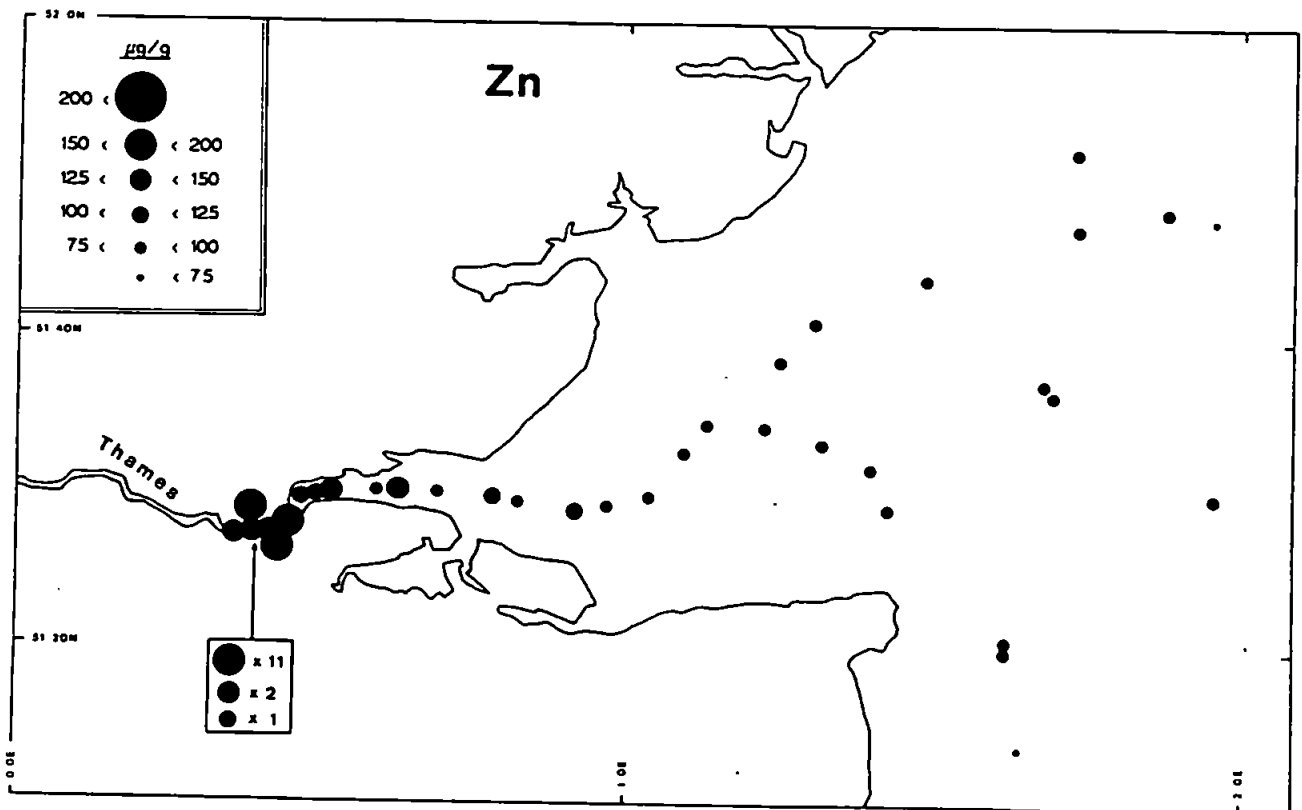
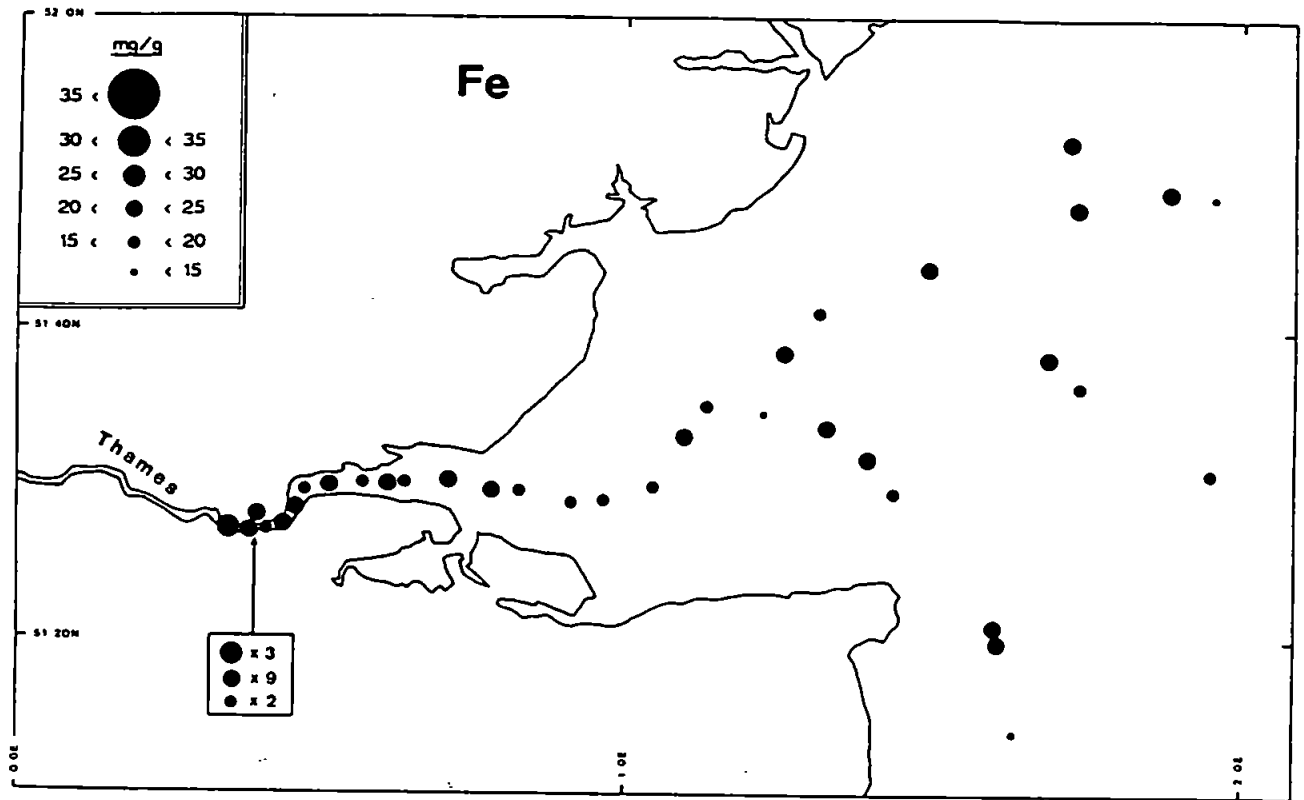


Figure 3.6b: Distributions of particulate Fe and Zn in the Thames plume. Boxed data points refer to anchored tidal station.

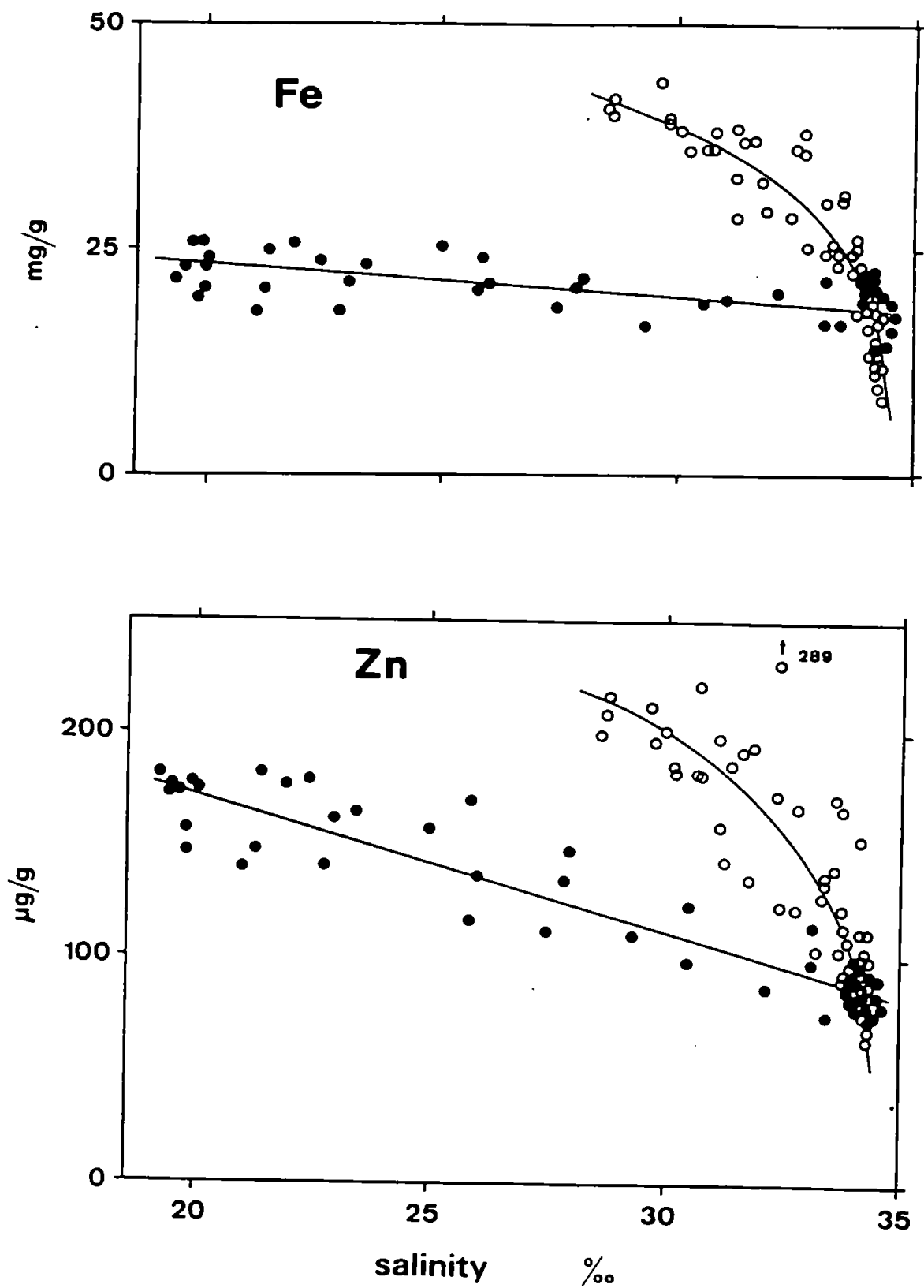


Figure 3.7: Particulate Fe and Zn concentrations versus salinity in the Humber (O) and Thames (●) plumes.

beyond the 34.2 ‰ isohaline. Distributions of these particulate metals therefore essentially reflected an inverse salinity distribution. Although concentrations were significantly correlated inversely with salinity (Figure 3.8) suggesting that estuarine-derived material is diluted in the plume with material of lower metal concentrations derived from offshore and local erosion, convex profiles better describe the relationship as exemplified by Fe and Zn in Figure 3.7. A more uniform Pb profile concords with observations and inferences of Section 2.2.3.1 regarding efficient removal from solution at high salinities, whereas an increase in Cd with salinity may reflect its dissimilar behaviour to other metals (Sections 3.2.2.8 and 3.2.2.10) or the aforementioned analytical difficulties.

The distributions of Fe and Zn in the Thames plume and outer estuary are shown in Figure 3.6b and typify all metals with the exception of Cd. Although a small decrease in particulate metal concentrations seaward of the anchored tidal station is apparent, concentrations within the plume region are rather uniform. Nevertheless, these distributions gave rise to inverse linear relationships of metal concentrations with salinity (Figure 3.7) and significant inter-metal linear correlations (Figure 3.8).

The regression analyses of particulate metal concentrations with salinity for the Thames yield significantly smaller fresh water end-member concentrations and shallower gradients when compared with the Humber (Table 3.6). Although the end-members of the Humber are overemphasized because of large direct industrial inputs to its estuarine waters, the inference is that the Humber represents a larger source of particulate metals to the North Sea than the Thames. Moreover, a steeper gradient to the Humber particulate metal - salinity profiles suggests that either its plume is capable of more effective dispersion, or that estuarine-derived material is rapidly diluted in the large flux of suspended sediment entering the region from cliff erosion to the north (McCave, 1987).

Particulate metal concentrations as a function of tidal state at anchored stations in the Humber and Thames are illustrated in Figure 3.9. It is, however, difficult to establish whether the underlying trends are inversely related to salinity

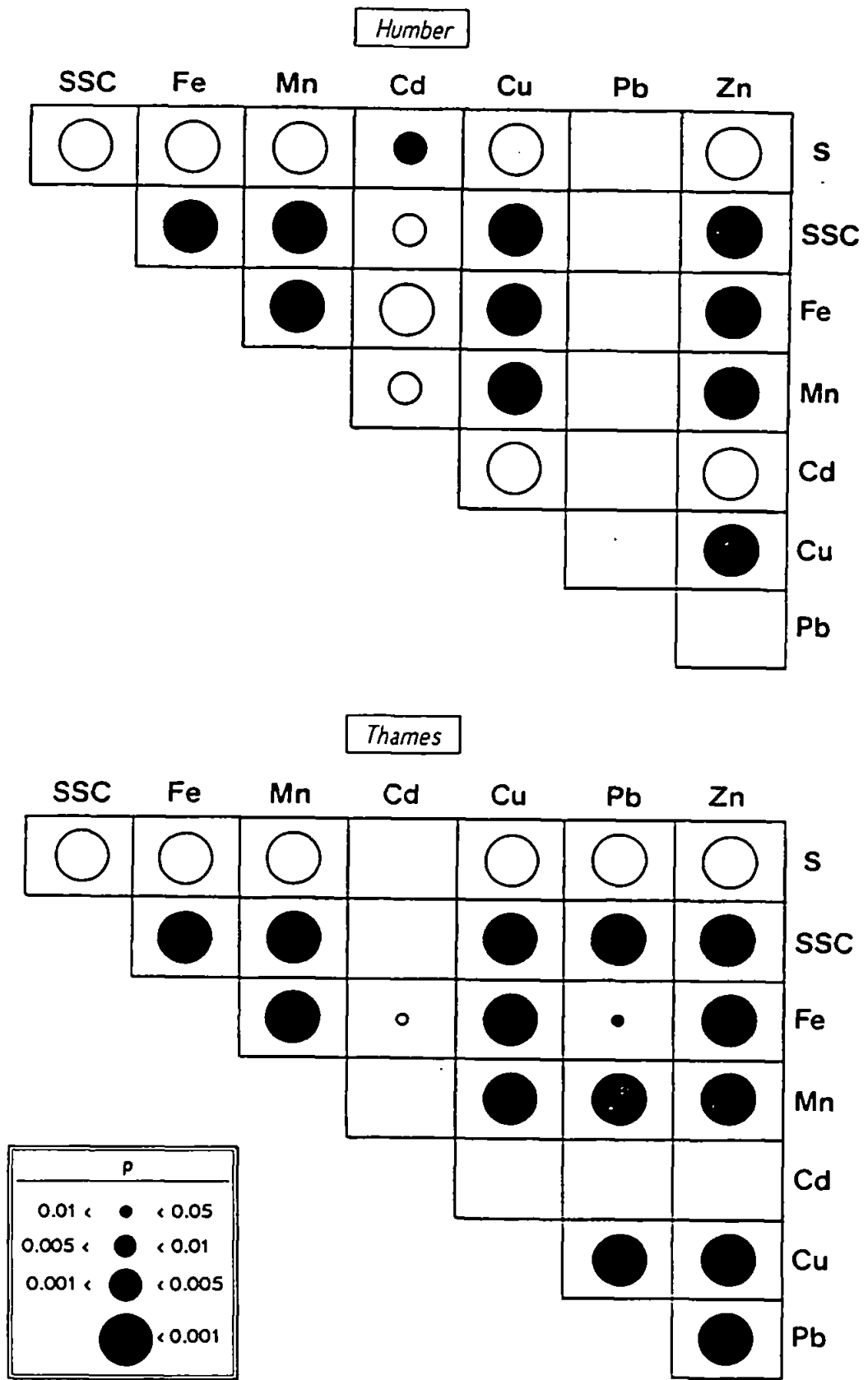


Figure 3.8: Correlation matrices for Humber and Thames plume measurements of salinity, SSC and particulate metal concentrations, identifying significant positive (closed circles) and negative (open circles) linear relationships.

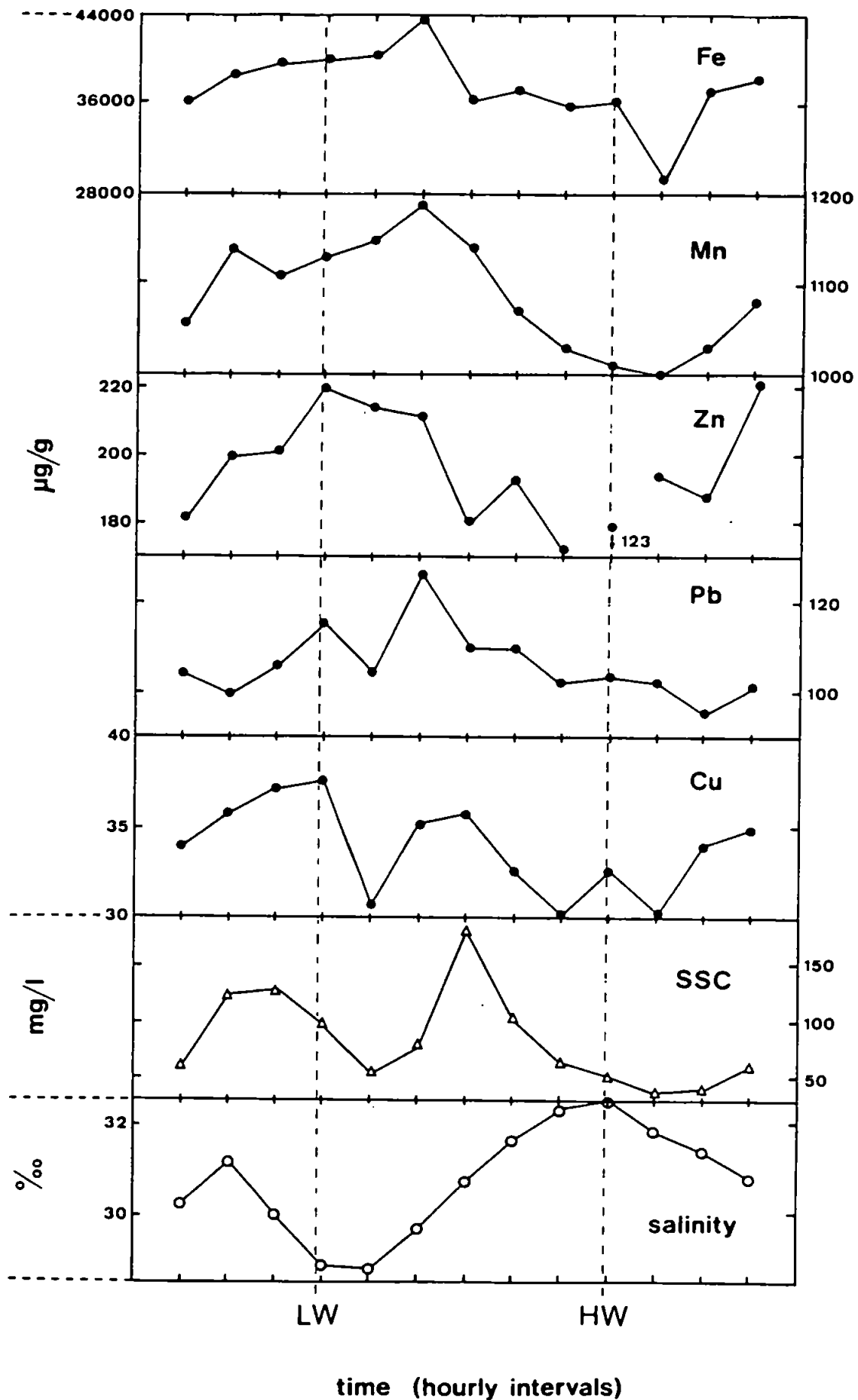


Figure 3.9: Evolution of salinity, SSC and particulate metal concentrations over a tidal cycle. Cadmium data have been omitted owing to fewer determinations and analytical difficulties. HW = high water; LW = low water.

a. Mouth of the Humber Estuary.



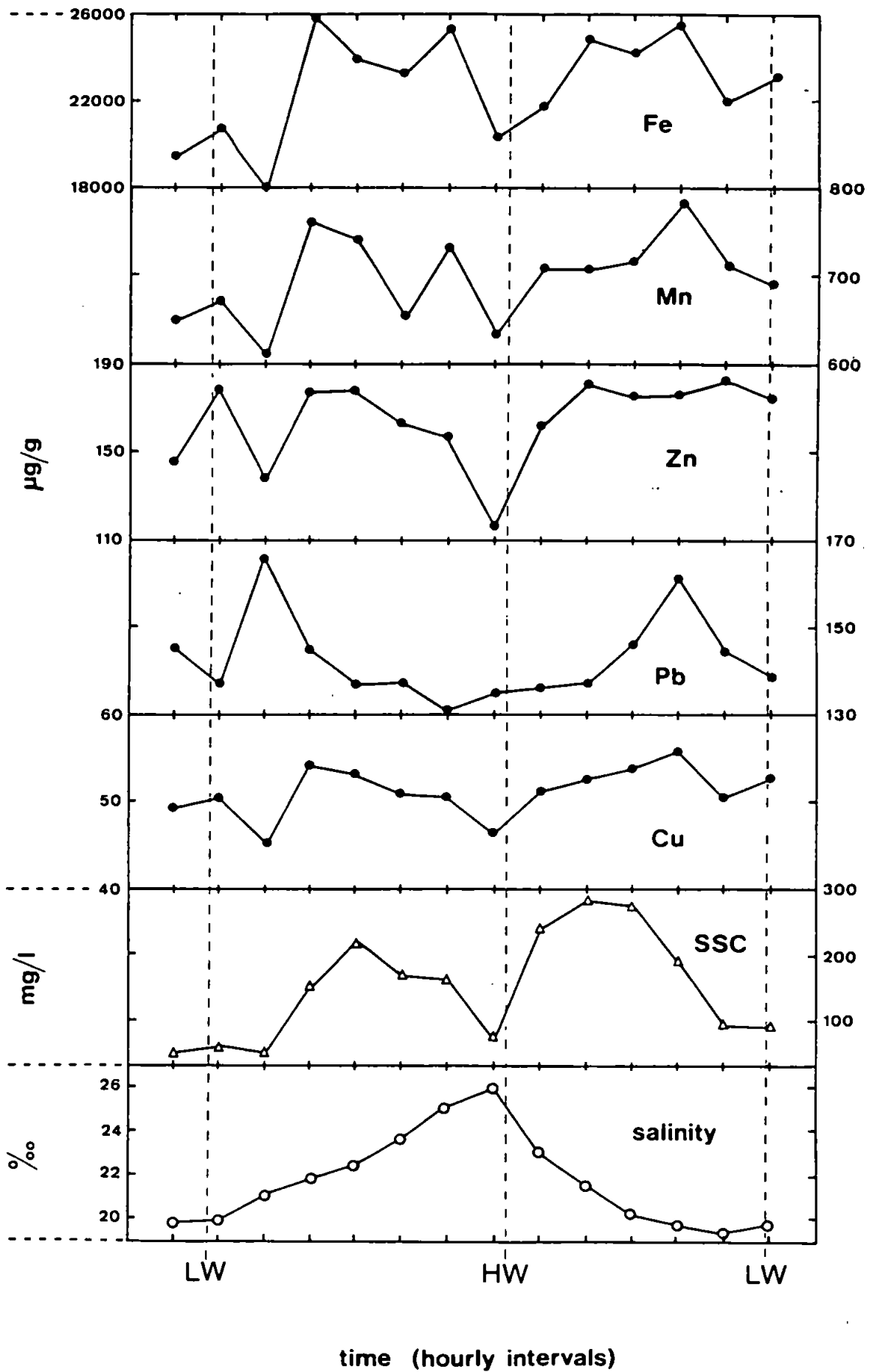


Figure 3.9 (continued): b. Thames Estuary, Gravesend.

(e.g. Zn Humber) as indicated by earlier observations, or related to the suspended solids concentration (e.g. Fe Thames) hence tidal current velocity suggesting that temporarily suspended material is the major carrier of particulate metals.

Table 3.6: Regression equations describing the relationships between salinity and particulate metal concentrations, of significance as given in Figure 3.8, in the Humber and Thames plumes.

| Humber                         | Thames               |
|--------------------------------|----------------------|
| Fe = 19.2 - 5.06 S             | Fe = 28.2 - 0.264 S  |
| Mn = 2.97 - 0.063 S            | Mn = 1.07 - 0.0179 S |
| Cu = 152 - 3.92 S              | Cu = 104 - 2.50 S    |
| Pb; not significant (p > 0.05) | Pb = 241 - 4.57 S    |
| Zn = 908 - 23.6 S              | Zn = 292 - 6.00 S    |

### 3.2.2: North Sea

A summary of the hydrographic conditions and metal analyses for near surface (10 m depth) samples from CH33 (summer) and CH43 (winter) is given in Table 3.7; their distributions are now discussed.

All parameters were initially plotted out using a UNIRAS interactive graphics contouring package (UNIMAP) in compliance with other participants of the *North Sea Project* (Hydes and Edmunds, 1989) as exemplified for underway logged salinity data (CH33 and CH43) and particulate Fe and Zn determinations (CH33) in Figures 3.10 and 3.11 respectively. However, poor sampling spatial resolution in the central regions of the southern North Sea, and in particular across the northern transect (Figure 3.12), did not inspire a great deal of confidence in this approach. Real data were therefore plotted for each discrete sampling station as circles of size representative of concentration (Figures 3.13 and 3.14).

To assist the description of the data, a series of boxes has divided the

|                   | salinity<br>(‰)  | SSC<br>(mg/l) | Fe<br>mg/g      | Mn<br>mg/g      | Cd<br>μg/g    | Cu<br>μg/g    | Pb<br>μg/g    | Zn<br>μg/g  | Fe:Mn          |
|-------------------|------------------|---------------|-----------------|-----------------|---------------|---------------|---------------|-------------|----------------|
| <u>CH33</u>       |                  |               |                 |                 |               |               |               |             |                |
| n                 | 48               | 49            | 49              | 49              | 48            | 34            | 49            | 47          | 49             |
| $\mu \pm 1\sigma$ | 33.69 $\pm$ 1.05 | 2.5 $\pm$ 2.7 | 4.46 $\pm$ 4.23 | 0.74 $\pm$ 0.56 | 3.3 $\pm$ 2.0 | 7.9 $\pm$ 5.9 | 67 $\pm$ 40   | 63 $\pm$ 38 | 7.8 $\pm$ 6.4  |
| R                 | 31.12-34.94      | 0.4-12.8      | 0.36-17.5       | 0.05-2.70       | 0.9-8.9       | 1.6-29.2      | 7-178         | <10-175     | 0.6-22.7       |
| <u>CH43</u>       |                  |               |                 |                 |               |               |               |             |                |
| n                 | 56               | 56            | 55              | 56              | 39            | 43            | 56            | 56          | 55             |
| $\mu \pm 1\sigma$ | 33.90 $\pm$ 1.19 | 4.9 $\pm$ 7.1 | 12.8 $\pm$ 6.16 | 0.87 $\pm$ 0.46 | 1.8 $\pm$ 1.1 | 22 $\pm$ 11   | 276 $\pm$ 123 | 98 $\pm$ 41 | 16.6 $\pm$ 8.0 |
| R                 | 30.07-35.05      | 0.2-37.4      | 1.05-40.0       | 0.36-2.23       | <0.1-4.4      | <7-72         | 110-620       | 42-250      | 2.4-46.6       |

Table 3.7: Summary of near surface hydrographic conditions and particulate metal concentrations during the survey cruises. Mean  $\pm$  1 standard deviation ( $\mu \pm 1\sigma$ ) and range (R) of n determinations given; for metals, n was occasionally restricted by the instrumental limits of detection.

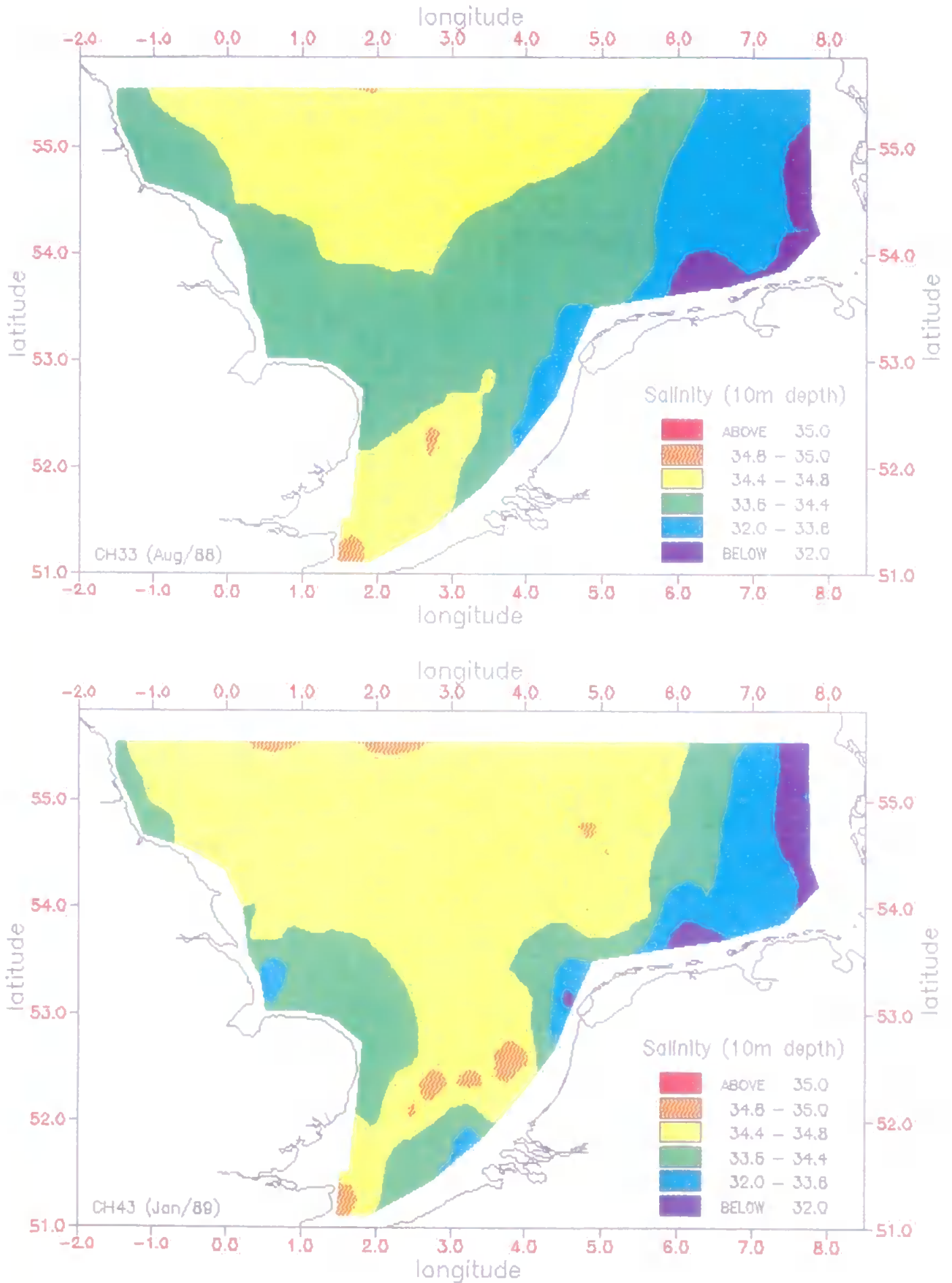


Figure 3.10: UNIMAP generated near surface salinity distributions during survey cruise samplings (courtesy of T.J. Moffat, Polytechnic South West, Plymouth).

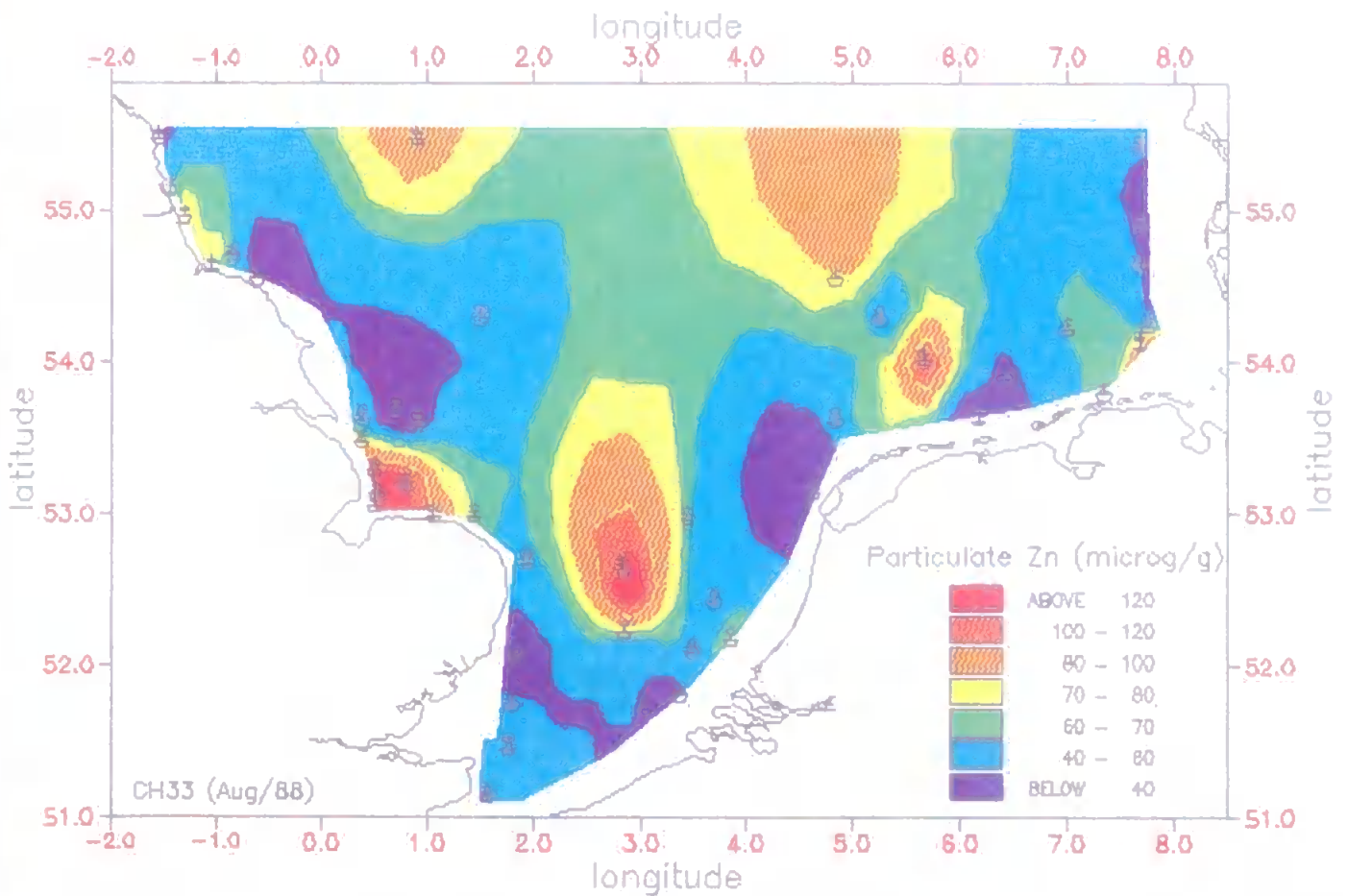
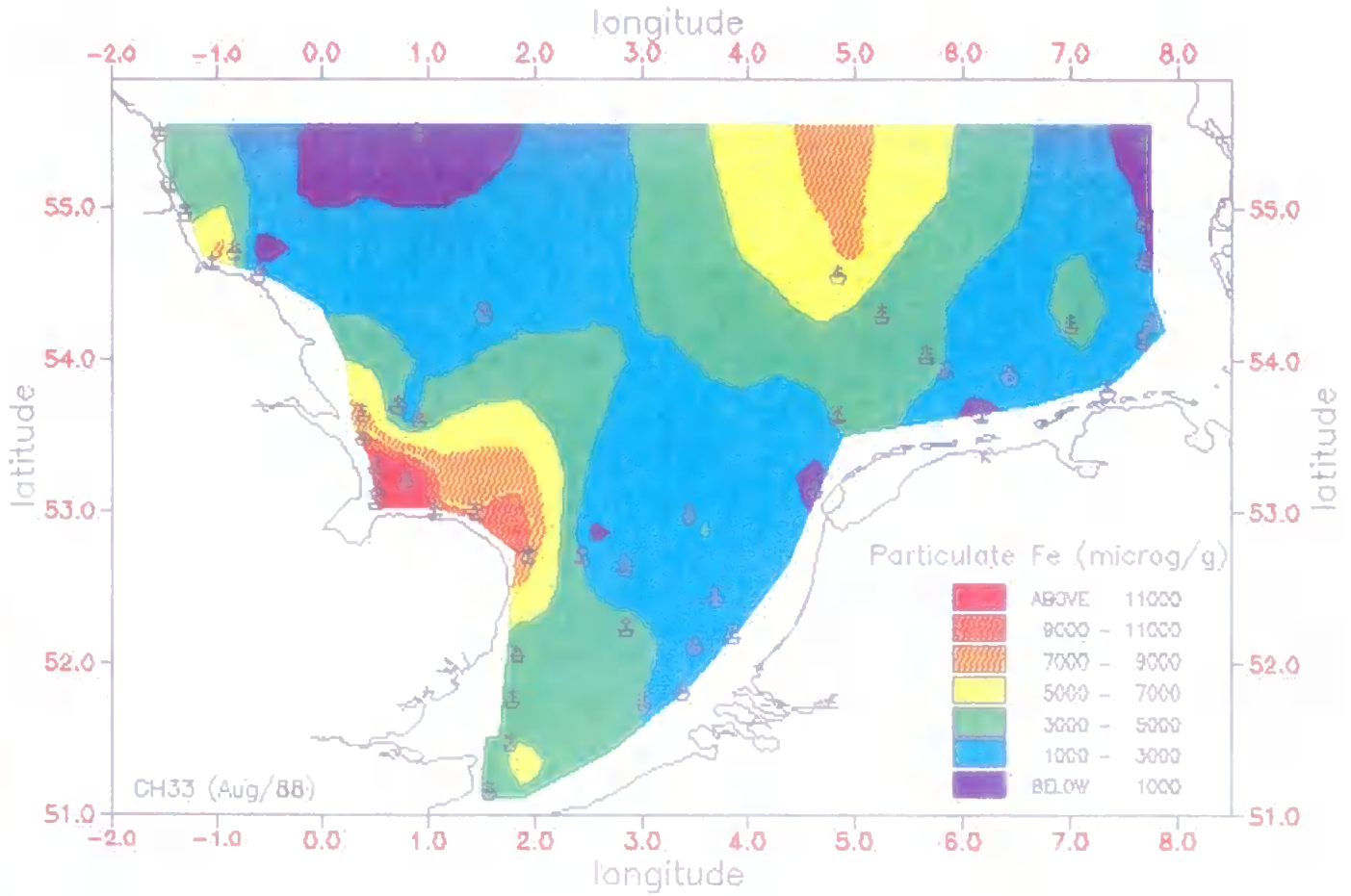


Figure 3.11: UNIMAP generated near surface particulate Fe and Zn distributions for summer survey cruise; boat symbols show sampling locations (courtesy of T.J. Moffat, Polytechnic South West, Plymouth).

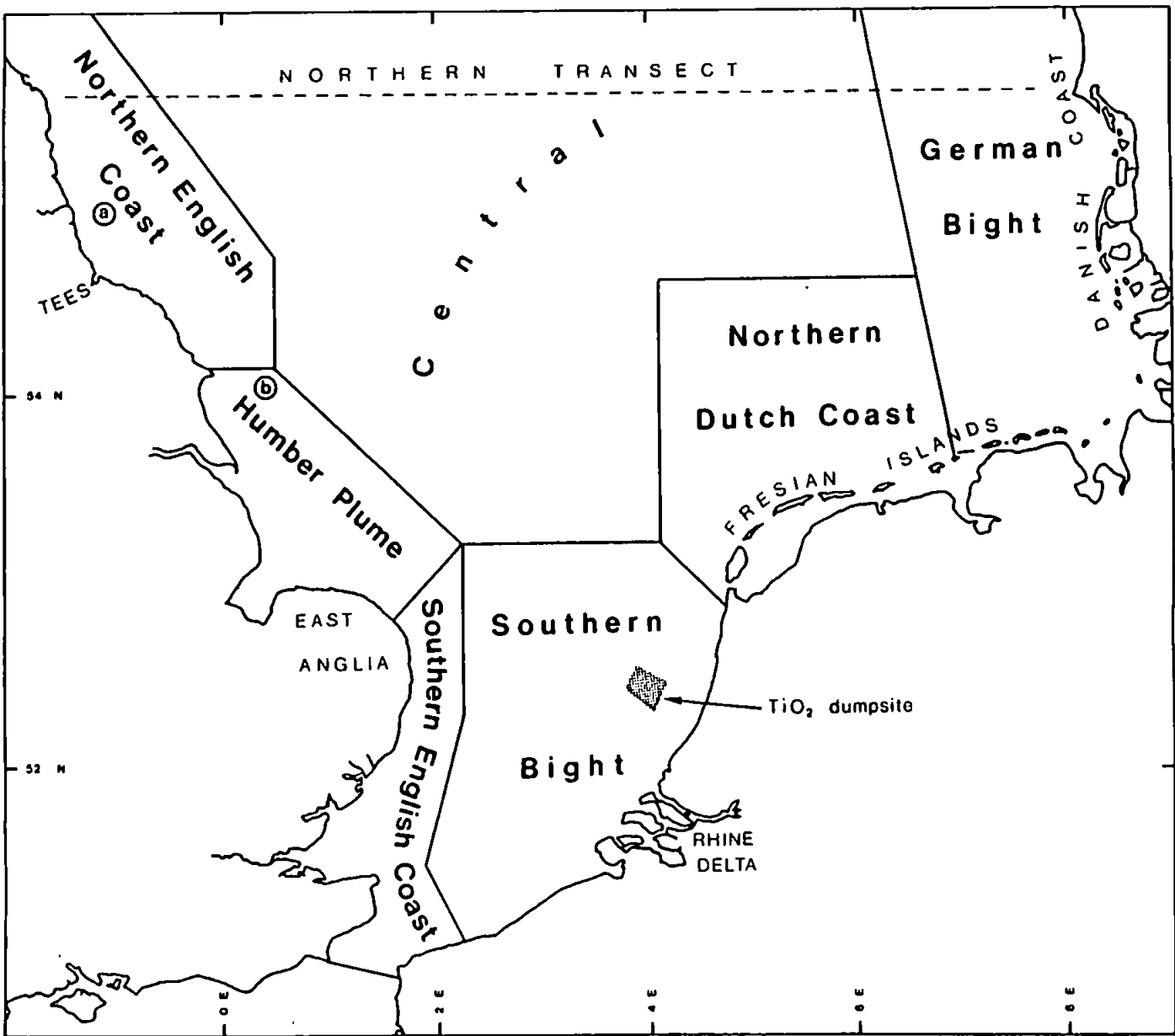


Figure 3.12: Division and location map of the southern North Sea. Positions of CTD casts a and b (cf. Figure 3.3) are circled.

southern North Sea arbitrarily on a regional basis (Figure 3.12).

### 3.2.2.1: Suspended Solids (*Figure 3.1.3*)

Concentrations of suspended solids generally decrease offshore and are highest along the English coast south of the Humber Estuary where active erosion occurs (McCave, 1987). Concentrations are higher by a factor of two and more variable during winter because of enhanced supply from fluvial inputs, resuspension and cliff erosion.

### 3.2.2.2: Iron and Manganese (*Figures 3.14a and 3.14b*)

During summer elevated Fe concentrations occur along the English coast and are highest in the Humber plume (up to 17.5 mg/g), off the Tees Estuary (10.6 mg/g) and off East Anglia (11.0 mg/g). The lowest concentrations (< 1.0 mg/g) are found in the German Bight along the Danish coast and off the Fresian Islands; the lowest value measured (0.36 mg/g) occurs along the northern transect in more open central waters.

During winter the mean Fe concentration is almost three times higher and the distribution is more uniform. Seasonal differences are smallest for the Humber plume (concentrations vary by a factor of < 2) and largest along the Danish coast (concentrations 30 times higher during winter). The highest Fe concentration measured during winter was 40 mg/g off the Dutch coast and this coincides with the dumpsite for acid-iron waste from the titanium dioxide manufacturing industries of continental Europe (Spaans, 1987).

Summer Mn concentrations are highest in the German Bight and northern Dutch coast sectors (maximum 2.7 mg/g). Concentrations also exceed 1.0 mg/g in certain regions off the English coast north of East Anglia (e.g. 1.2 mg/g off Tees Estuary and up to 1.08 mg/g in the Humber plume). The lowest values (<0.25 mg/g) occur off the southern English coast and in the central Southern Bight, and off the Fresian Islands; the minimum value measured of 0.05 mg/g is located on the northern transect in the central waters, although at 50 m depth

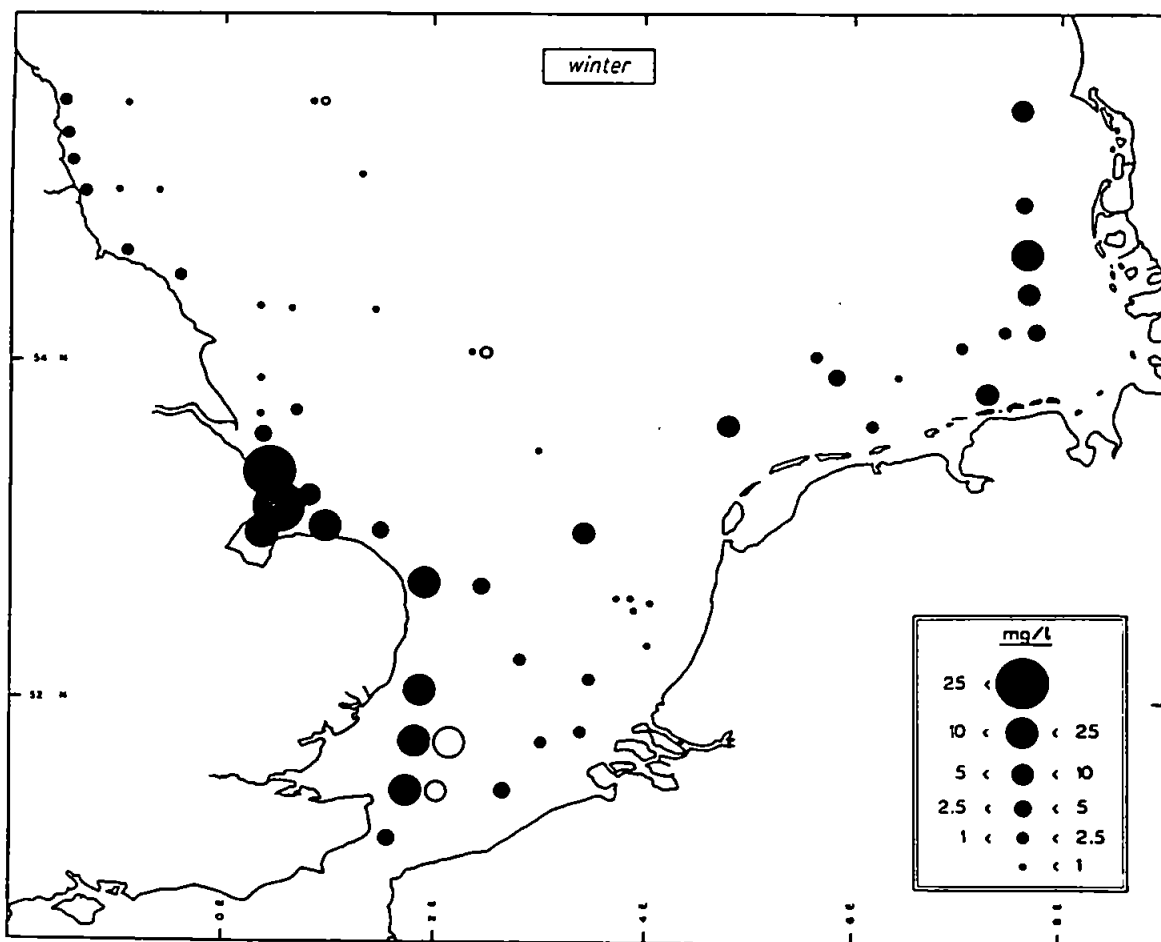
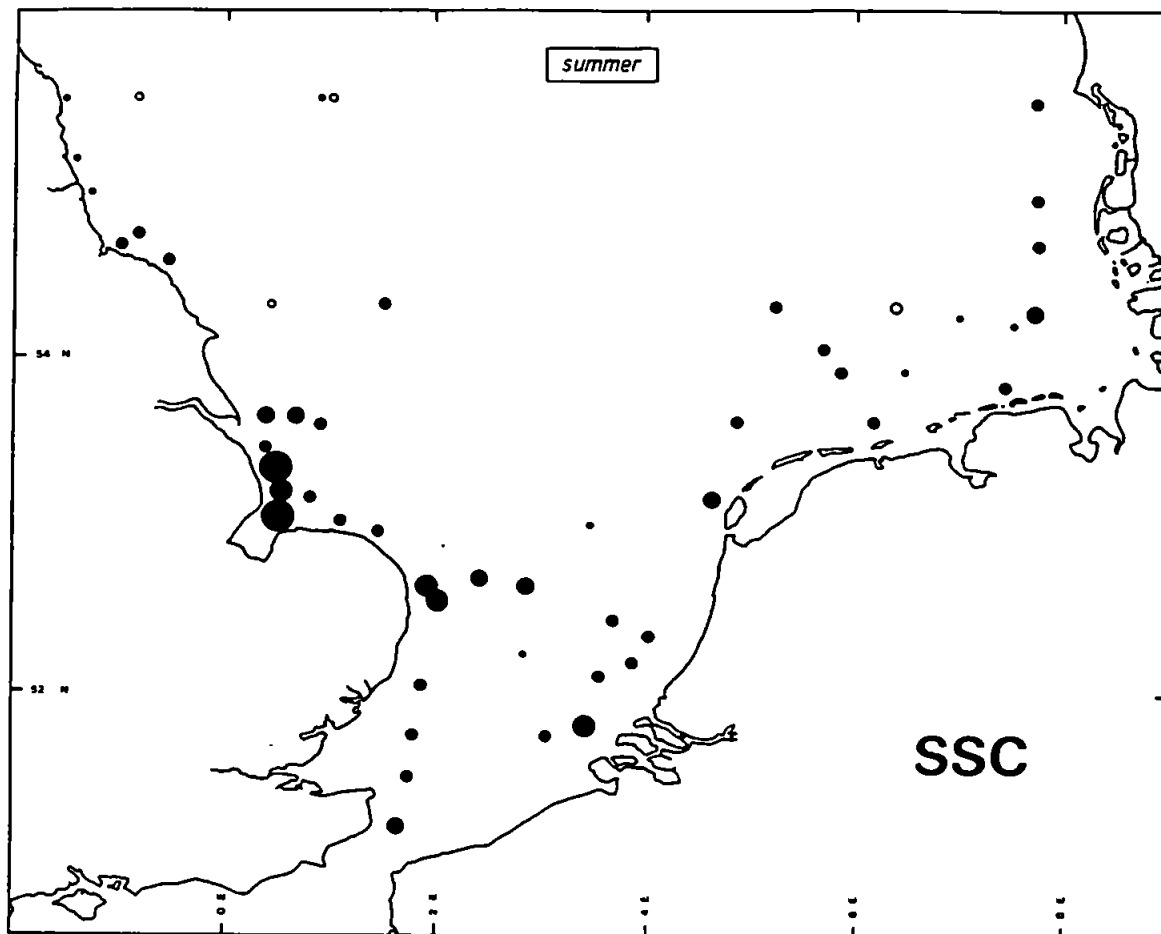


Figure 3.13: Summer (CH33) and winter (CH43) distributions of suspended solids in the southern North Sea. Closed circles are near surface values and adjacent open circles are near bed values from common CTD casts.



the Mn concentration is elevated by a factor of 40.

Mean winter concentrations are slightly elevated and the winter distribution is more uniform, although localized maxima occur off the northern English coast (up to 2.23 mg/g) and in the German Bight (2.16 mg/g). Elevated Mn is also found at the location identified as the dumpsite, reflecting the composition of the discharge which contains approximately 500 mg/l Mn (Spaans, 1987).

### 3.2.2.3: Iron:Manganese (*Figure 3.14c*)

The role of hydrous Fe and Mn hydroxides in controlling certain particle surface and compositional properties has been discussed in Section 2.2.2, and the ratio of Fe:Mn, which assesses the relative contribution of each oxide phase, has been implicated as a geographical marker (Section 2.2.2.5). In the North Sea during summer this ratio is highest along the English coast south of the Humber with a maximum of 22.7 occurring in the Humber plume. Values decrease both north- and eastwards and the lowest ratios are encountered in the German Bight with a minimum of 0.6 at the most north-easterly position. The decline in Fe:Mn ratio to the east is particularly notable and it is possible to conceive the existence of a *front* in the Southern Bight between ratios of 5 and 10 separating English coastal waters from continental waters.

Mean winter values are double because of the elevated Fe concentrations and a northerly and/or easterly decrease is now absent.

### 3.2.2.4: Cadmium (*Figure 3.14d*)

Summer concentrations of Cd are highest in the Southern Bight (maximum 8.9  $\mu\text{g/g}$ ) and along the coastal waters of continental Europe (maximum 8.3  $\mu\text{g/g}$  to the north of the Fresian Islands). Concentrations are also high off the northern English coast: 5.0  $\mu\text{g/g}$  off the Tees Estuary; 5.8  $\mu\text{g/g}$  off the Tyne Estuary; 5.5  $\mu\text{g/g}$  to the east of the Humber Estuary. Along the English coast south of the Humber to the Thames, Cd concentrations are lowest and are between 0.9 and 2.1  $\mu\text{g/g}$ .

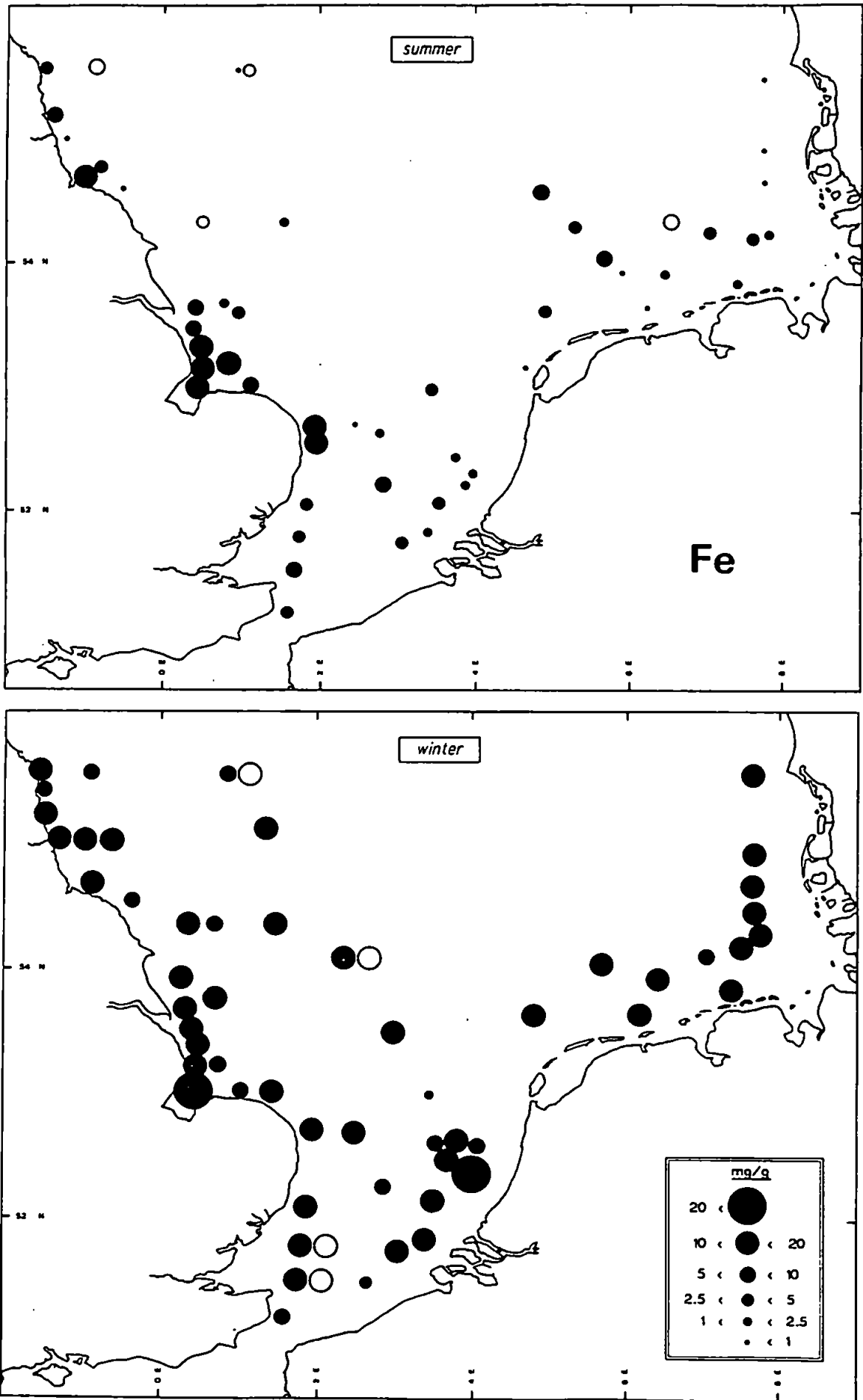


Figure 3.14: Summer (CH33) and winter (CH43) distributions of particulate metals in the southern North Sea. Closed circles are near surface values and adjacent open circles are near bed values from common CTD casts.

a. Fe.

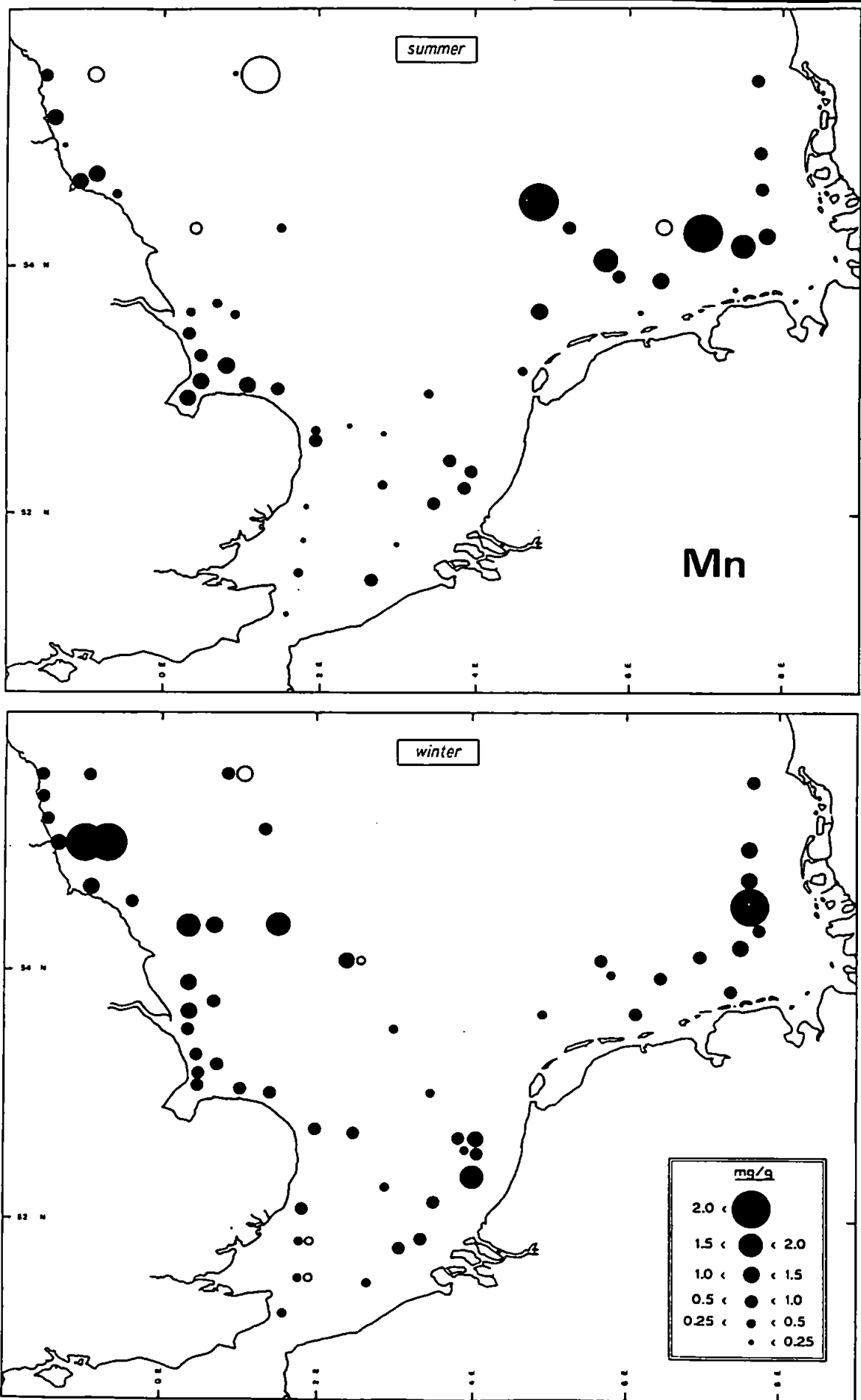


Figure 3.14(continued): b. Mn.

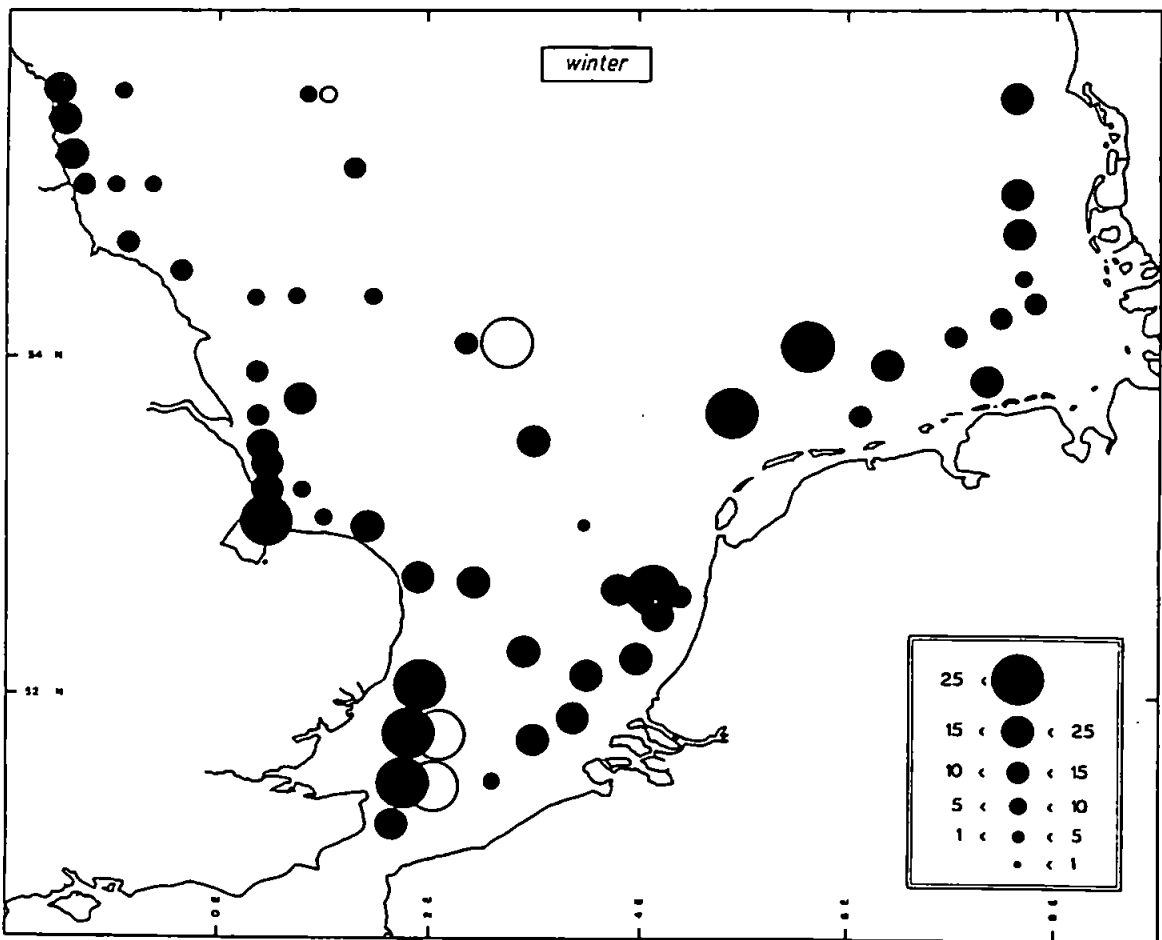
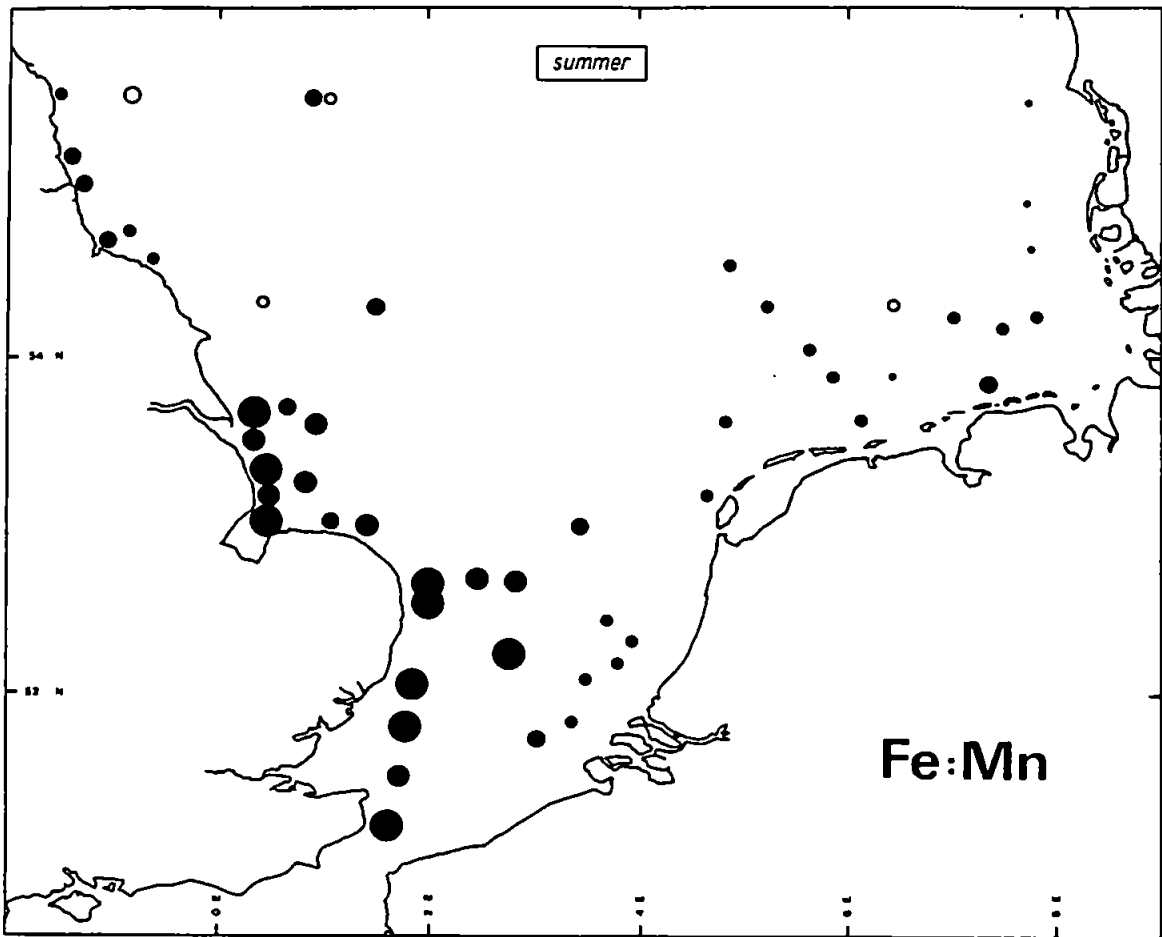


Figure 3.14 (continued): c. Fe:Mn.

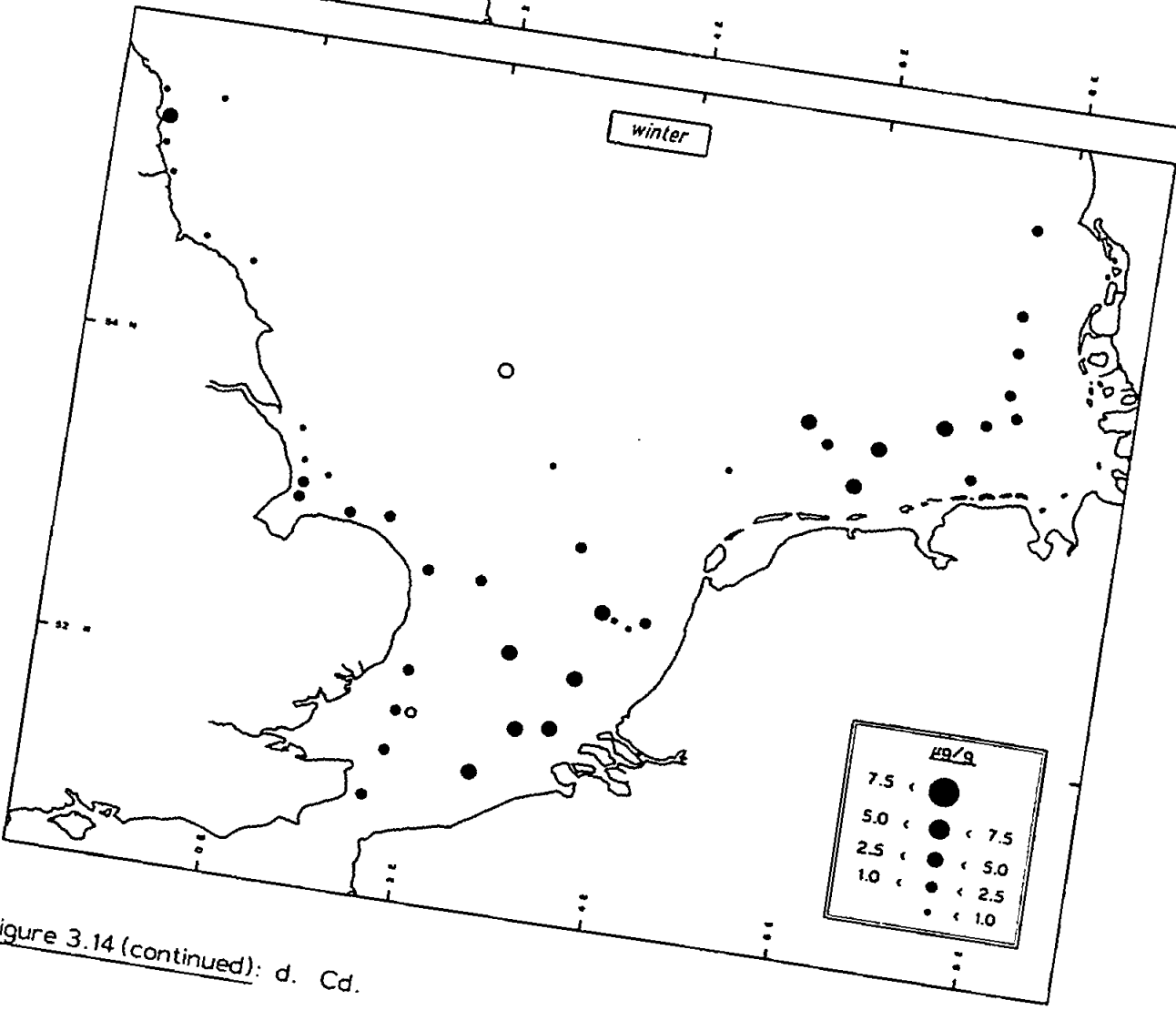
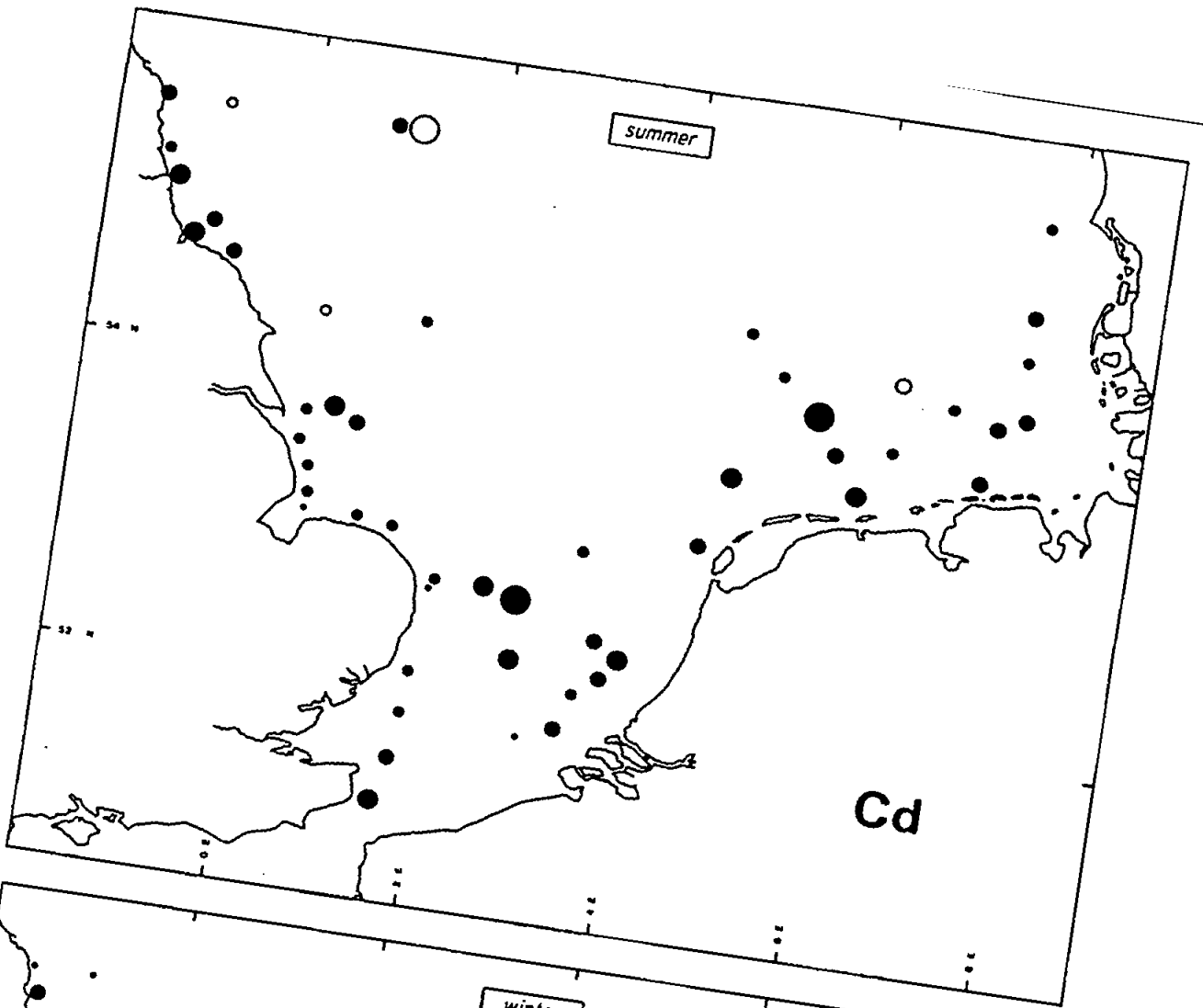


Figure 3.14 (continued): d. Cd.

During winter mean concentrations are almost halved. The highest concentrations occur in the Southern Bight off the Rhine Delta with a maximum of  $4.4 \mu\text{g/g}$ , and in the northern Dutch coastal waters where concentrations reach  $2.9 \mu\text{g/g}$ . Along the entire English coast with the exception of a single sample in the north, concentrations are below  $2.5 \mu\text{g/g}$  with a minimum value of  $< 0.1 \mu\text{g/g}$  off North Yorkshire.

#### 3.2.2.5: Copper (Figure 3.14e)

During summer the highest Cu concentration ( $29.2 \mu\text{g/g}$ ) is found in the centre of the Southern Bight. High concentrations are found off the English coast to the north of East Anglia with a maximum of  $18.1 \mu\text{g/g}$  off the Tees Estuary. The lowest concentrations ( $< 2.5 \mu\text{g/g}$ ) are encountered in the continental coastal waters.

During the winter mean concentrations are almost three times higher. The highest values are found along the English coast north of the Humber Estuary ( $23 - 72 \mu\text{g/g}$ ); concentrations are also high at two sites in the open waters of the central North Sea ( $33$  and  $42 \mu\text{g/g}$ ) and one site in the German Bight ( $43 \mu\text{g/g}$ ). The lowest concentrations occur off the southern English coast and in the Southern Bight with a minimum value measured at  $< 7 \mu\text{g/g}$  off the Rhine Delta.

#### 3.2.2.6: Lead (Figure 3.14f)

The highest concentration of Pb measured during summer ( $225 \mu\text{g/g}$ ) is at 50 m depth in central waters along the northern transect. High surface concentrations are found along the English coast with a maximum value of  $178 \mu\text{g/g}$  off East Anglia, and in the central Southern Bight (maximum  $148 \mu\text{g/g}$ ) and northern Dutch coastal waters ( $168 \mu\text{g/g}$ ). The lowest concentrations are found in the German Bight ( $7-44 \mu\text{g/g}$ ) and in the open central waters ( $21 \mu\text{g/g}$ ;  $27 \mu\text{g/g}$ ).

Mean winter concentrations of Pb are enhanced by a factor of four and the distribution is more uniform. Concentrations in excess of  $500 \mu\text{g/g}$  were

measured in winter off the northern English coast (maximum 620  $\mu\text{g/g}$ ), and along the continental coast of the Southern Bight (maximum 540  $\mu\text{g/g}$ ) where summer concentrations were about 50  $\mu\text{g/g}$ . The highest concentration (750  $\mu\text{g/g}$ ) is found at depth in central waters at the same locality as during summer. Lowest values occur off the southern English coast (minimum 100  $\mu\text{g/g}$  at the surface and 85  $\mu\text{g/g}$  at depth).

#### 3.2.2.7: Zinc (Figure 3.14g)

Zinc concentrations during summer are highest in the Humber plume, with a maximum of 175  $\mu\text{g/g}$  in the Wash; localized maxima are found in more open waters of the Southern Bight (146  $\mu\text{g/g}$ ), northern Dutch coast (125  $\mu\text{g/g}$ ) and German Bight (133  $\mu\text{g/g}$ ). The lowest concentrations (< 25  $\mu\text{g/g}$ ) are encountered in the coastal waters to the east of the Humber Estuary, in the vicinity of the Fresian Islands, and off the Rhine Delta.

During winter the mean concentration is higher by 50%; the maximum concentration measured is 250  $\mu\text{g/g}$  at the location identified as a dumpsite for acid-iron waste in the Southern Bight. High concentrations are also found in the German Bight (up to 224  $\mu\text{g/g}$ ), Humber plume (up to 124  $\mu\text{g/g}$ ) and in central waters (166 and 167  $\mu\text{g/g}$ ). The lowest concentrations are encountered off the English coast north of the Humber (minimum 42  $\mu\text{g/g}$ ) and in the Southern Bight (minimum 50  $\mu\text{g/g}$ ).

#### 3.2.2.8: General Considerations

These descriptions have demonstrated the patchiness of particulate metal distributions even on relatively short spatial scales within individual boxes sub-dividing the southern North Sea (Figure 3.12), including the occurrence of inexplicable *hot-spots* of elevated metal concentrations in remote offshore waters. This patchiness is reduced in winter, when mean concentrations for all metals except for Cd are increased. Presumably higher winter concentrations are the result of enhanced wind/wave activity hence resuspension of bottom deposits, for

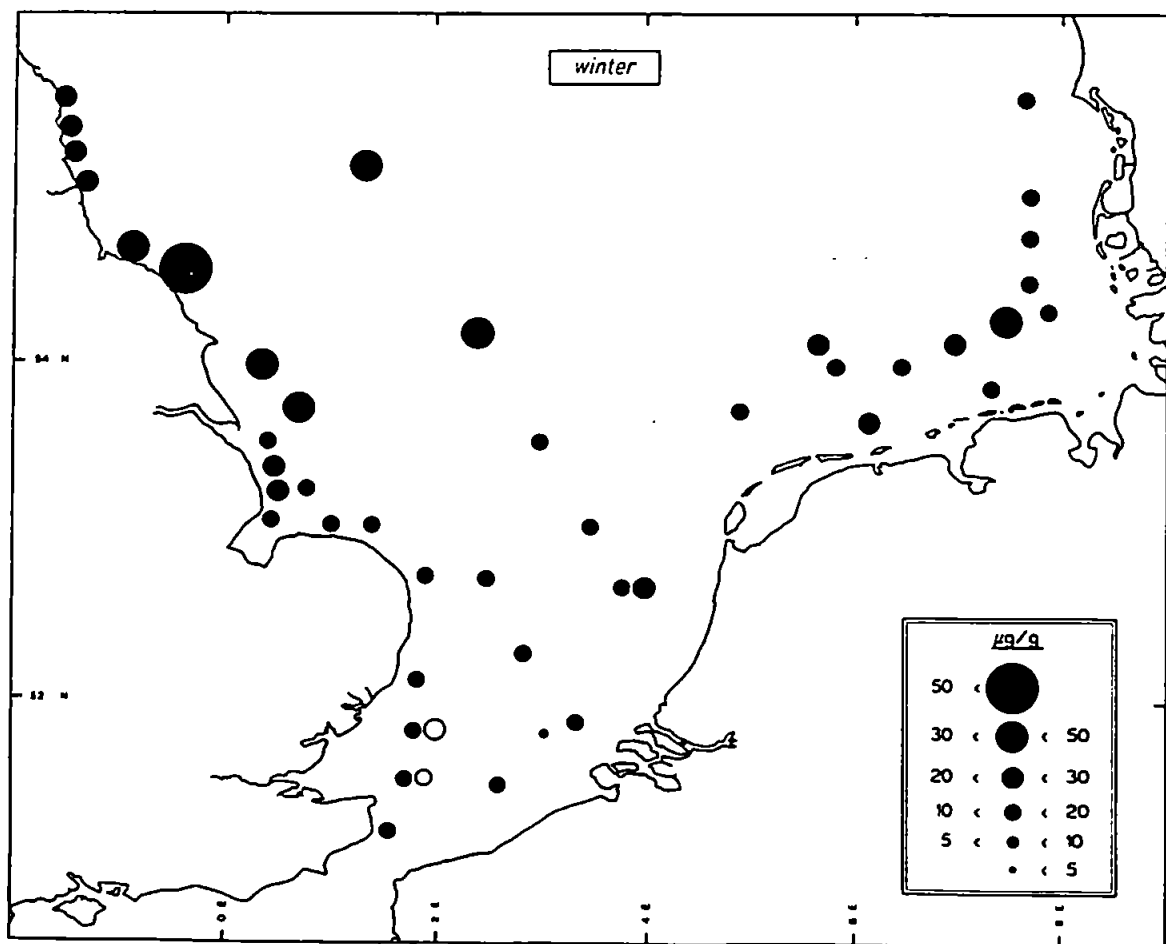
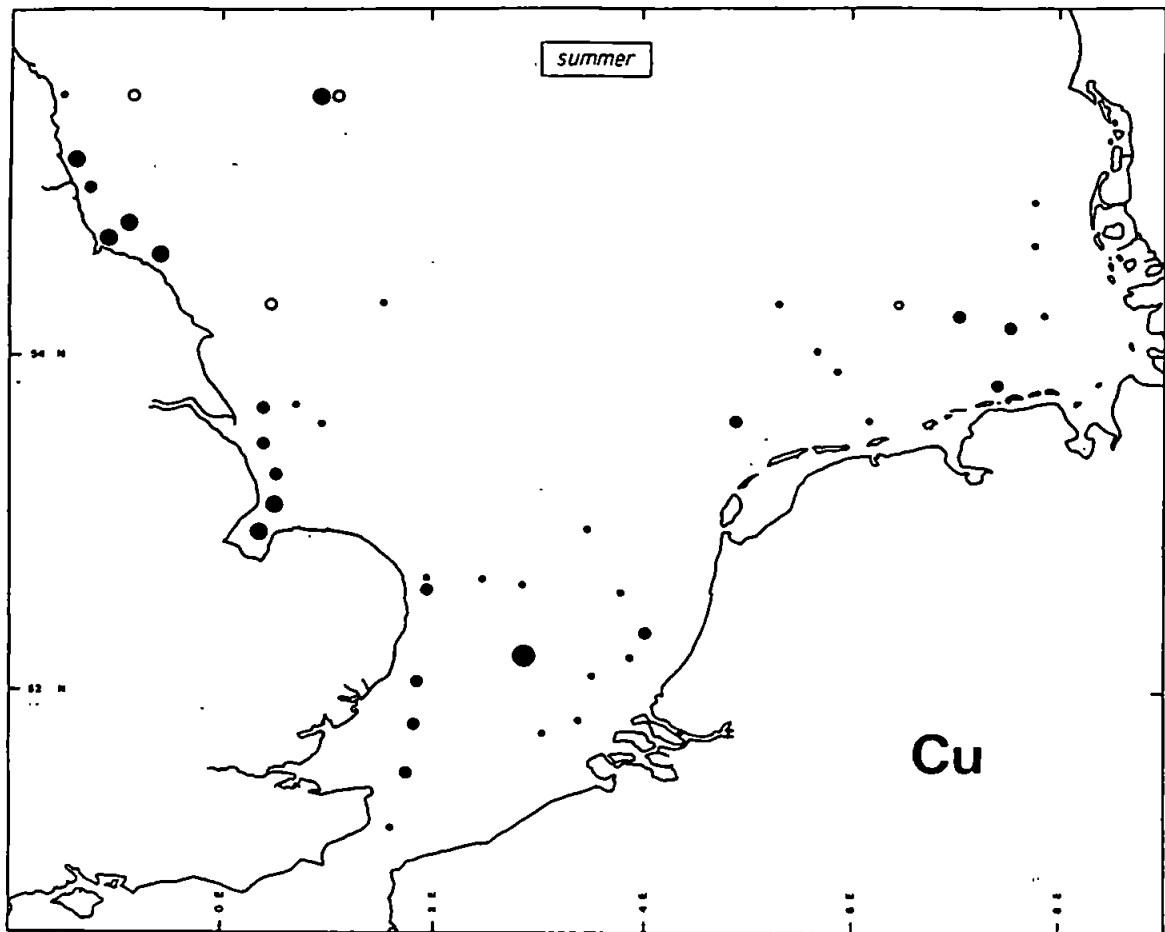


Figure 3.14 (continued): e. Cu.



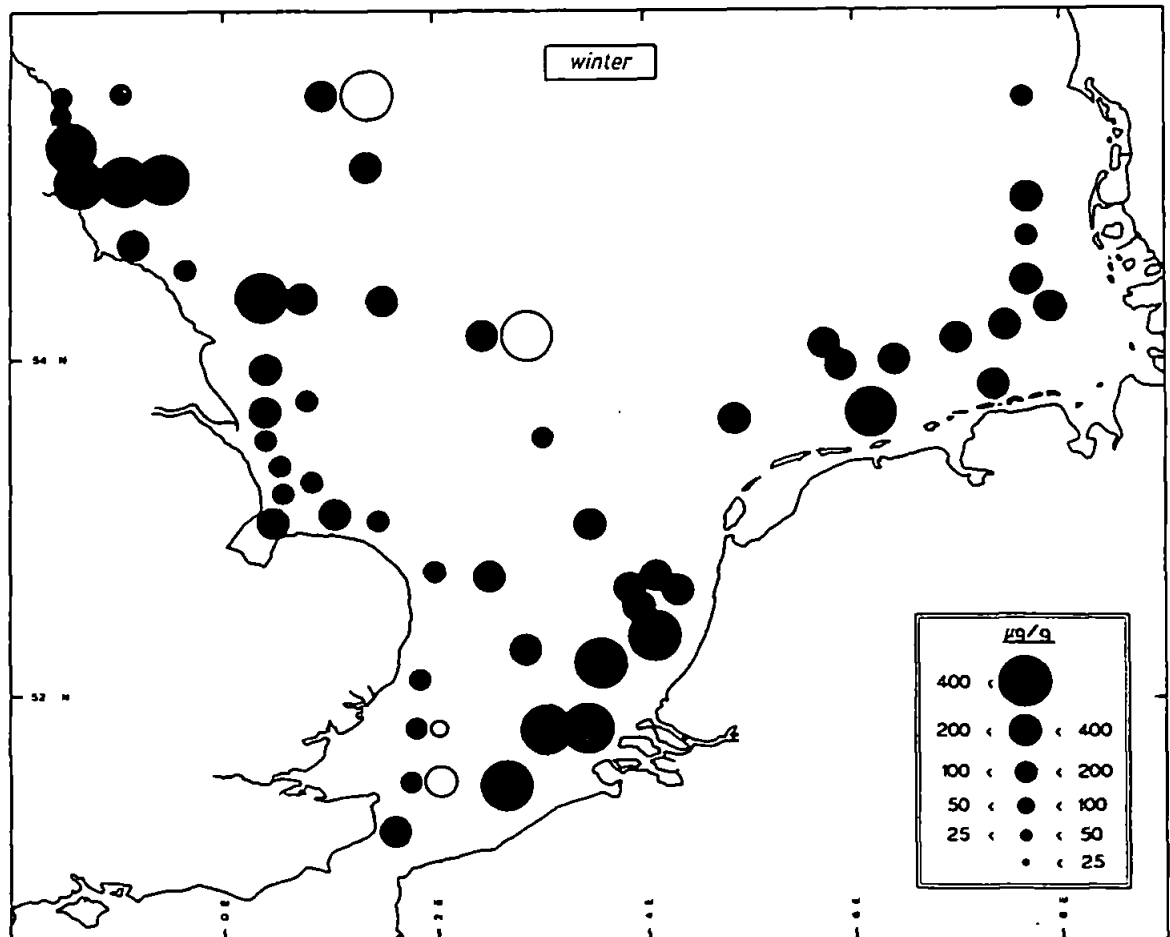
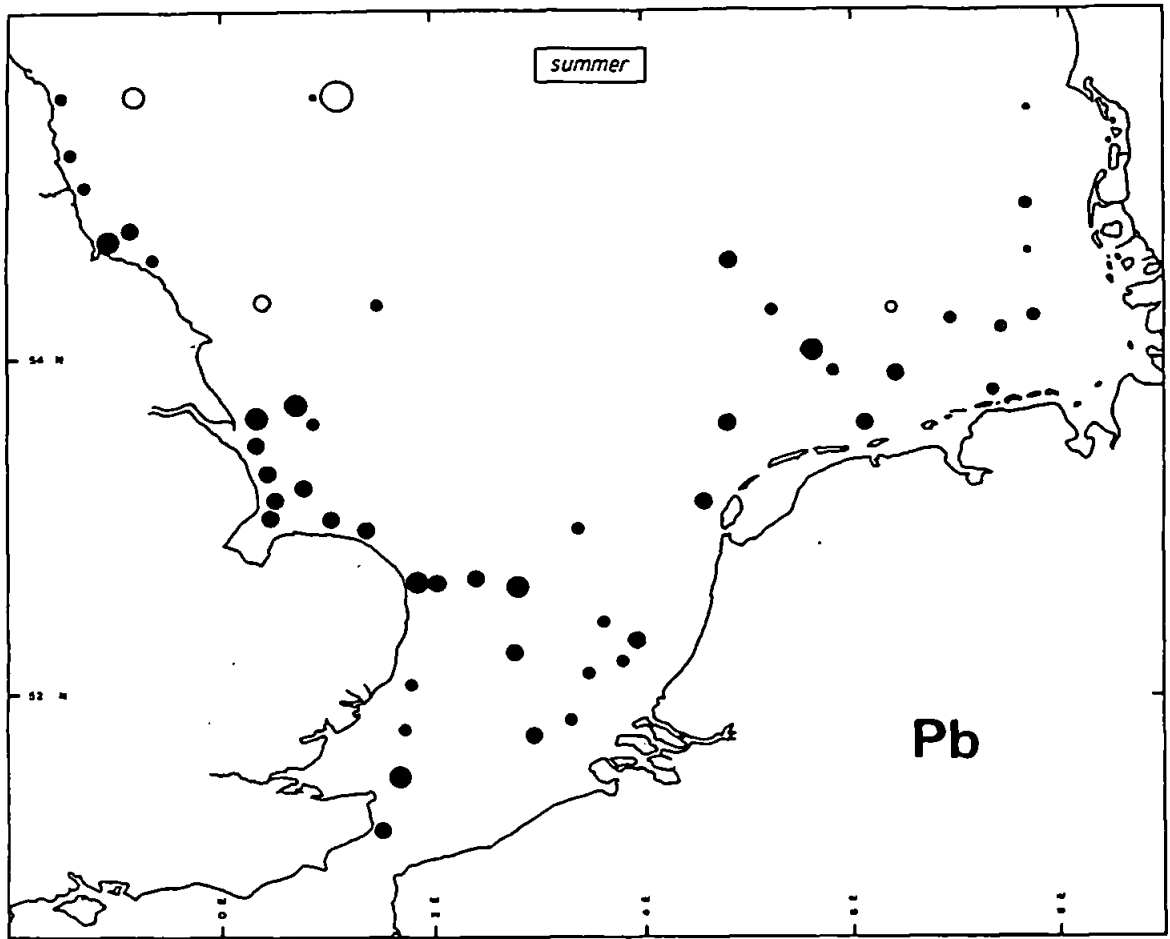


Figure 3.14 (continued): f. Pb.

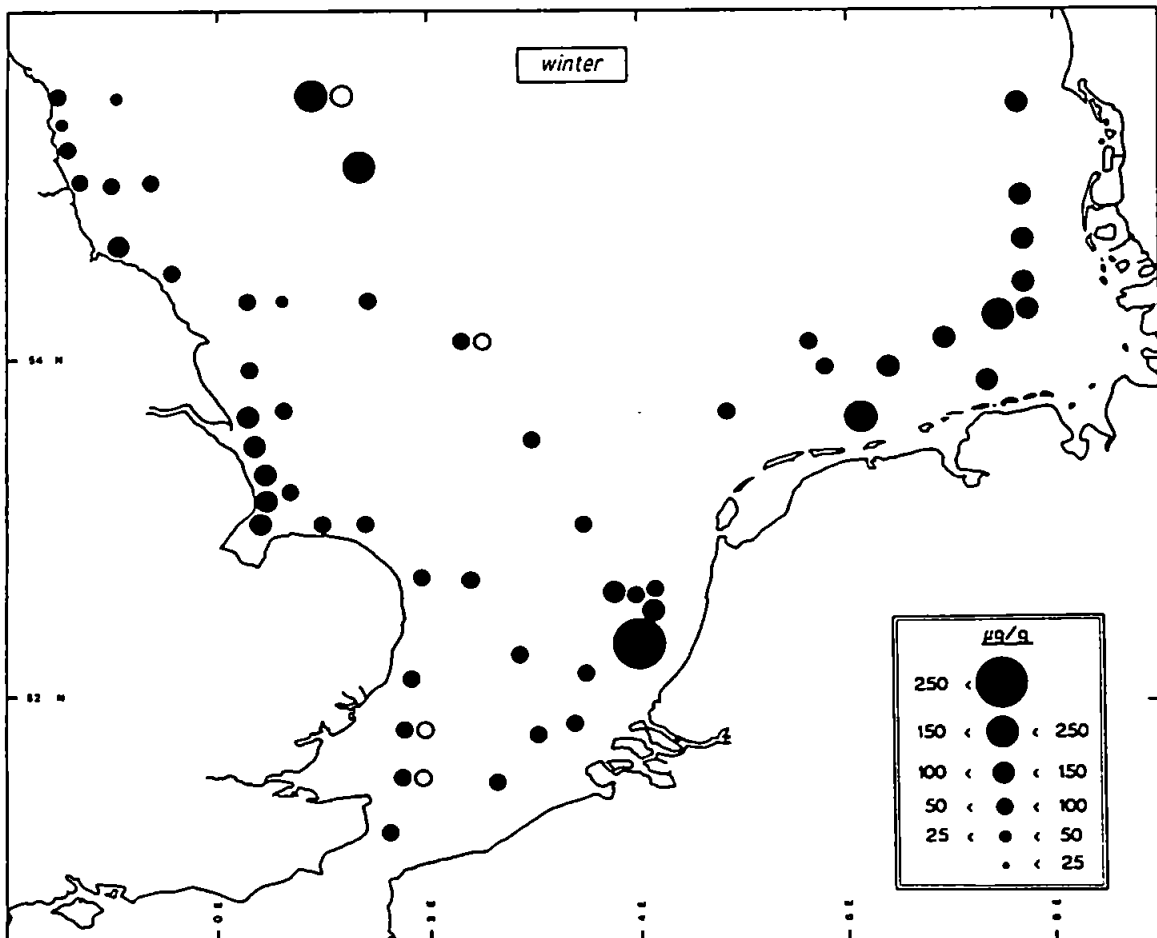
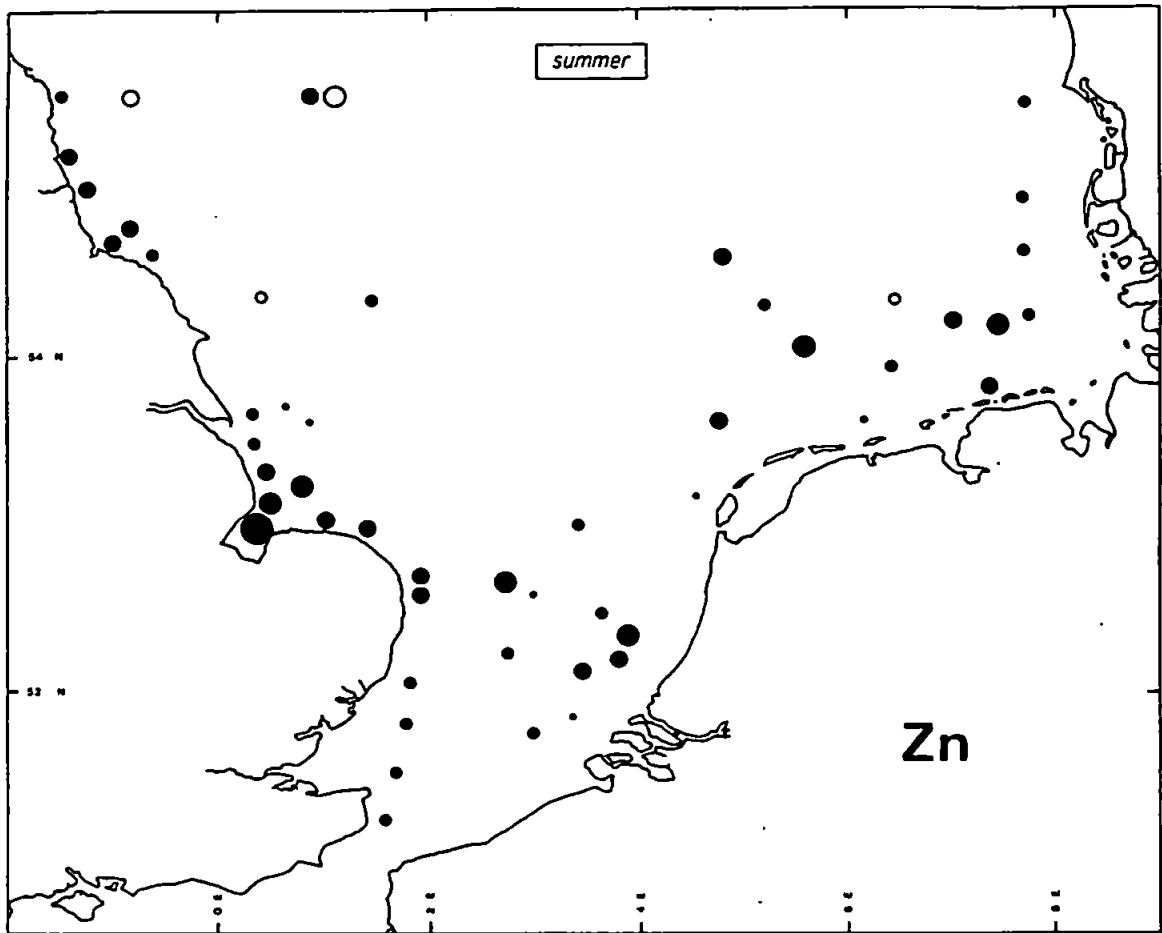


Figure 3.14 (continued): g. Zn.

which there is evidence to suggest metal enrichment (Sections 3.2.2.2 and 3.2.2.6), and an increased supply of fluvial, and perhaps atmospheric (e.g. Pb) particulate metals. Moreover, enhanced physical mixing during winter may give rise to a greater penetration into the southern North Sea of North Atlantic and northern North Sea waters, which are evidently enriched in particulate trace metals (Section 1.8.1.3). Similarly, less spatial variability encountered during winter can be attributed to more effective mixing of suspended material from these sources. Manganese, which displays less seasonal variability, is also affected by its redox chemistry. Thus, winter enrichment through resuspension and fluvial inputs, is partially offset by a slower and less effective oxidative precipitation under the cooler water conditions (Section 2.2.3.3). On the other hand Cd is enriched in summer (higher mean concentration and number of samples exceeding the detection limit; Table 3.4); this can be explained by its affinity for organic phases, in particular planktonic material (Section 4.3.1.3), and the occurrence of an enhanced particulate biogenic component in the water column during summer (Section 1.8.1.2).

Total (elementary) particulate metal distributions for the entire North Sea during winter are also rather patchy (Kersten *et al.*, 1988; Nolting and Eisma, 1988). The magnitudes of particulate metal concentrations presented in this work compare favourably with total values cited in Nolting and Eisma (1988) for Mn, Cd, Pb and Zn suggesting effective removal from the particles by the chosen leach (1M HCl); however, total Fe and Cu contents are considerably higher than leachable concentrations, indicative of a significant resistant (detrital) component.

### **3.2.2.9: Estuarine Effects**

From the data presented it is difficult to directly identify or assess the impact of estuaries as sources of particulate metals to the North Sea. During the summer when metal-rich bed deposits are relatively undisturbed, the Tees and Humber can be recognized as sources of Fe and Cu. Iron-rich particles emanating from the titanium dioxide industry on the Humber (Section 2.2.2.3) can be traced

in the Humber plume as far as the East Anglian coast. Although an anthropogenic release of Fe to the Tees Estuary could account for elevated levels in Tees Bay, a significant contribution is likely from coastal erosion of Fe-rich mineral bearing rocks in this vicinity (Taylor, 1979). The cruise track was too far offshore to detect any influence of the Thames and the continental estuaries on the particulate metal distributions. Although elevated summer concentrations of Mn in the German Bight suggest an input from the Mn-rich estuaries of the Weser and Elbe (Section 2.2.2.3), a substantial contribution may also result from O<sub>2</sub> deficiencies in the subsurface waters of the German Bight (von Westernhagen and Dethlefsen, 1983) which would effect reduction and solubilization of particulate Mn that consequently reprecipitates in the aerated surface waters. The summer North Sea distribution of Fe:Mn can be related to the anticlockwise reduction observed in the estuarine environments (Section 2.2.2.5); however, a cause or effect relationship cannot be established.

#### 3.2.2.10: Inter-Parameter Relationships

The results of the linear regression analyses for summer and winter North Sea data are shown in the form of correlation matrices in Figure 3.15.

An inverse correlation with salinity, *i.e.* indicative of a fluvial source, was significant only for Zn during winter. Significant linear relationships with suspended solids concentration were found for Fe, Pb and Zn during summer, and inverse relationships were found for Cd and Pb during winter. However, in most instances the relationship could better be described by some inverse non-linear function (Figure 3.16). Kersten *et al.* (1988) demonstrated that particulate metals in the North Sea during winter could be grouped according to their relationship with suspended solids concentration. These observations were interpreted in terms of a relationship between the concentration and particle size distribution (hence metal composition) of suspended material (*cf.* Duinker, 1983). Thus, at high suspended solids concentrations relatively large temporarily suspended particles dominate, and at low suspended solids concentrations fine material of high metal concentration

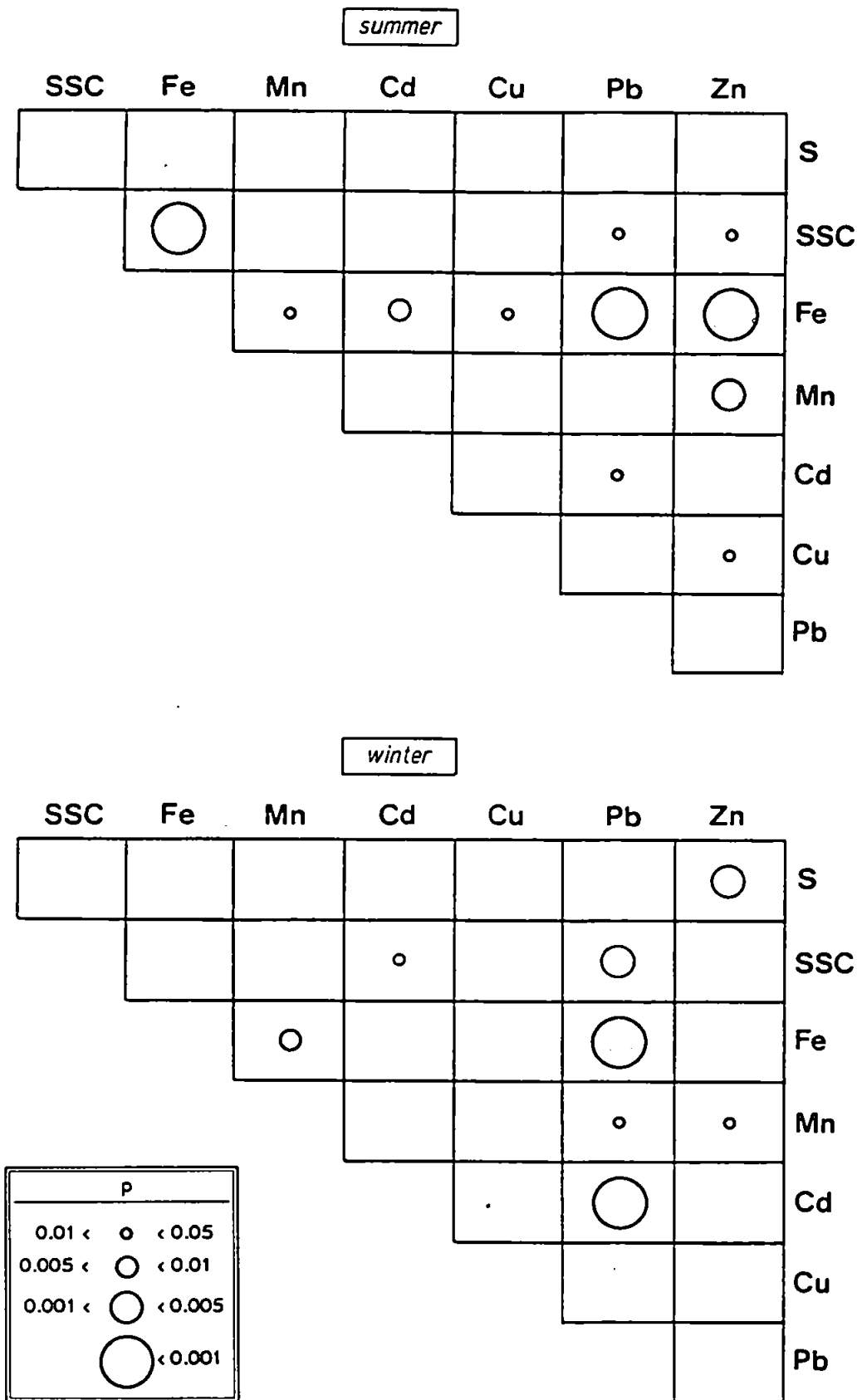


Figure 3.15: Correlation matrices for summer (CH33) and winter (CH43) measurements of salinity, SSC and particulate metal concentrations, identifying significant positive (closed circles) and negative (open circles) linear relationships.

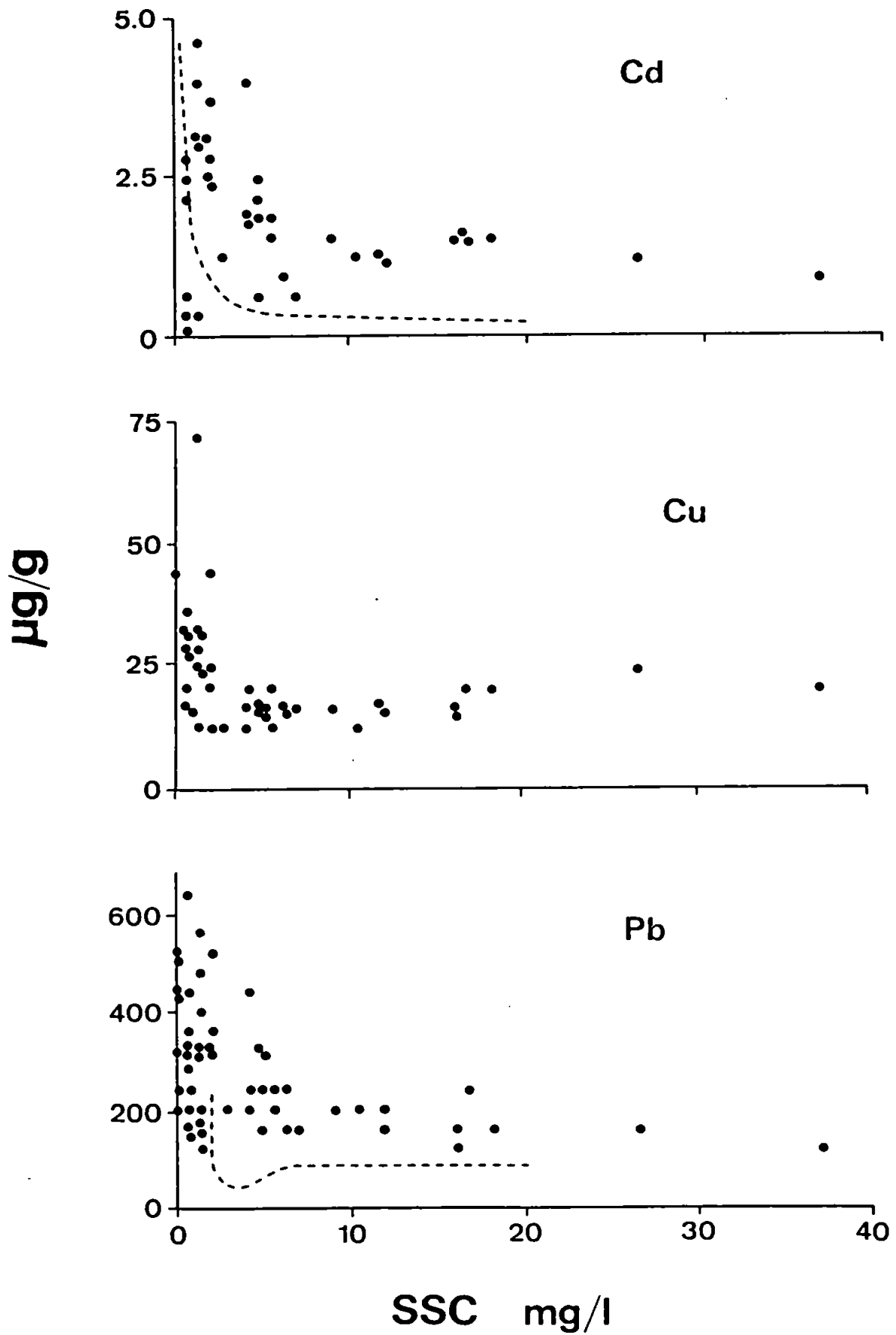


Figure 3.16: Particulate Cd, Cu and Pb concentrations versus SSC for the North Sea during winter. Dashed lines are eye-drawn best fit lines representing data given by Kersten *et al.* (1988).

dominates; the asymptote of metal concentration may therefore reflect deposited sediment values, and from Figure 3.16 these are 1.0  $\mu\text{g/g}$ , 15  $\mu\text{g/g}$  and 100  $\mu\text{g/g}$  for Cd, Cu and Pb respectively. However, this interpretation contests previous ideas as resuspended material in winter was invoked as a major source of particulate metals (Section 3.2.2.8).

Positive correlation with Fe was significant for Mn and Pb during winter and for all metals during summer except for Cd which was inversely correlated. This suggests an Fe oxide association for most metals and a dissimilar (probably biogenic) association for Cd. Zinc was significantly correlated with Mn during both cruises suggesting that Mn oxide phases are important solid associations for this metal. Inter-trace metal correlations were restricted to Cu-Zn during summer, and Pb-Cd during summer and winter.

The results from these regression analyses are in contrast to those for a North Sea estuary such as the Scheldt or Weser (Section 2.2.3.4), or the plumes of the Humber and Thames (Section 3.2.1.2), in which metals are significantly correlated inversely with salinity and inter-metal relationships are abundant (indicative of dilution of a common fluvial/estuarine source). In this respect an estuary or plume may be described as a relatively *well-defined* or *simple* system; the North Sea metal distribution is far more complex and reflects highly non-conservative mixing of a diversity of end-members of differing histories and composition.

### 3.2.3: Metal Association with Plankton

Table 3.8 gives the metal concentrations associated with the plankton sampled during CH50. Although variable amongst the same community (coefficients of variation often exceed 100%), the means of concentrations for all metals (especially Mn and Zn) are higher in the diatom bloom compared with the *Phaeocystis* bloom.

A comparison of these concentrations with those for the outflow regions of the Humber and Thames (Table 3.5) indicates that whereas Fe and Mn are elevated in the detrital material of estuarine plumes, Cd has a significantly higher

|                    | salinity<br>(‰)  | SSC<br>(mg/l)   | Fe<br>mg/g      | Mn<br>mg/g        | Cd<br>μg/g    | Cu<br>μg/g  | Pb | Zn<br>μg/g    | Fe:Mn          |
|--------------------|------------------|-----------------|-----------------|-------------------|---------------|-------------|----|---------------|----------------|
| <u>Diatoms</u>     |                  |                 |                 |                   |               |             |    |               |                |
| n                  | 9                | 9               | 9               | 9                 | 9             | 3           | -  | 9             | 9              |
| $\mu \pm 1\sigma$  | 34.74 $\pm$ 0.03 | 0.58 $\pm$ 0.19 | 3.54 $\pm$ 2.62 | 0.39 $\pm$ 0.14   | 2.8 $\pm$ 1.1 | 69 $\pm$ 76 | -  | 125 $\pm$ 202 | 8.6 $\pm$ 4.9  |
| R                  | 34.69 - 34.77    | 0.29 - 0.95     | 0.92 - 8.75     | 0.16 - 0.62       | 1.5 - 5.2     | <12 - 157   | -  | 28 - 660      | 5.7 - 18.3     |
| <u>Phaeocystis</u> |                  |                 |                 |                   |               |             |    |               |                |
| n                  | 7                | 7               | 7               | 7                 | 7             | 2           | -  | 7             | 7              |
| $\mu \pm 1\sigma$  | 34.95 $\pm$ 0.40 | 1.88 $\pm$ 0.76 | 2.68 $\pm$ 1.96 | 0.084 $\pm$ 0.058 | 2.4 $\pm$ 0.6 | 24          | -  | 38 $\pm$ 18   | 30.9 $\pm$ 5.5 |
| R                  | 34.04 - 35.12    | 1.17 - 3.31     | 0.46 - 6.56     | 0.020 - 0.20      | 1.6 - 3.0     | <7 - 30     | -  | 17 - 61       | 23.0 - 38.8    |

Table 3.8: Summary of hydrographic conditions and particulate metal concentrations during the bloom cruise (CH50). Mean  $\pm$  1 standard deviation ( $\mu \pm 1\sigma$ ) and range (R) of n determinations given; for metals, n was occasionally restricted by the instrumental limits of detection. Lead determinations have been omitted because of interference problems encountered during analysis.



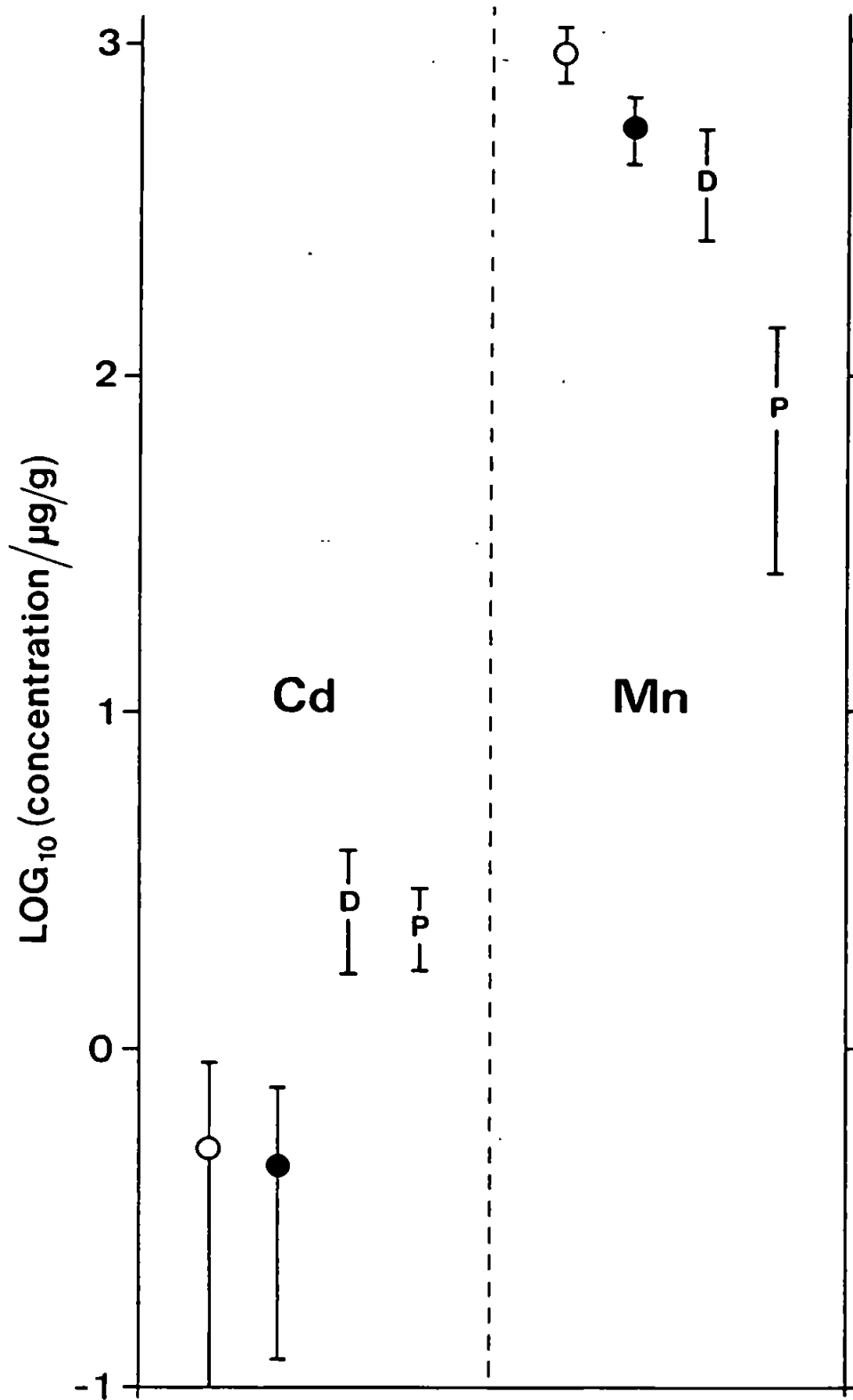


Figure 3.17: Mean  $\pm$  one standard deviation of particulate Cd and Mn concentrations in the plumes of the Humber (O) and Thames (●), and in the blooms of diatoms (D) and *Phaeocystis* (P).

association with planktonic material supporting previous inferences that the biomass is the major carrier of sorbed Cd in the marine environment (Rebhun and Ben-Amotz, 1984). These regional differences are illustrated in Figure 3.17 for Mn and Cd, and are accounted for in terms of particle composition and metal-solid reaction mechanisms in Chapter 4 (Section 4.3.3).

### 3.3: CONCLUSIONS

Distributions of particulate metals in the southern North Sea are spatially very variable. This patchiness is reduced during winter (compared with summer) when material is better mixed under more turbulent conditions.

Analysis of estuarine-derived material and plankton samples suggests that seasonal variability in particulate metal concentrations can largely be accounted for by a shift in particle population. Thus, whereas Cd concentrations are highest in summer in association with a higher biomass, other metals are elevated during winter when detrital components from resuspension and fluvial inputs culminate; inverse relationships between metal concentrations and salinity as evidence of estuarine inputs are, however, restricted to nearshore dispersing plume environments.

## CHAPTER 4: TRACE METAL REACTIVITY IN THE NORTH SEA. RADIOCHEMICAL STUDIES

### 4.1: INTRODUCTION

The use of radioisotopes has provided a powerful and flexible means of studying trace metal behaviour in aquatic systems. Applications have included responses of plankton (Fisher, 1986; Nucho and Baudin, 1989), exchange processes at the sediment-water interface (Duursma and Bosch, 1970; Santschi, 1985; Santschi *et al.*, 1984; 1987) and the nature (Balistrieri and Murray, 1984; Li *et al.*, 1984b) and rates (Hesslein *et al.*, 1980; Nyffeler *et al.*, 1984; 1986) of solid-solution interactions. Furthermore, such studies have been directed at a diversity of environments including lakes, coastal waters and the deep ocean.

The prime attraction of radiochemistry lies in the simplicity and specificity of the analysis (Amdurer *et al.*, 1982) which offers rapid, contamination-free and multi-element determinations. Moreover, high sensitivity renders only a small addition (spike) necessary to an enclosed system, thereby effecting minimal perturbation to natural conditions. However, the limitations associated with radiochemistry must not be overlooked. Foremost is the tacit assumption that radioisotopes replicate stable analogue isotope behaviour, although this has been demonstrated for fresh water systems (Anderson *et al.*, 1987). Practical problems may arise from sample isolation including wall adsorption or the change of solid substrate composition through aggregation (Benes *et al.*, 1988), and, unless additional studies are conducted in order to elucidate the nature and rates of reactions, interpretation of the data may prove conceptually difficult.

In this Chapter, radiochemical techniques have been carefully developed in order to study *in situ* the solid-solution partitioning of trace metals in North Sea coastal waters.

### 4.2: SAMPLING AND EXPERIMENTAL PROCEDURES

#### 4.2.1: Sample Collection and Incubation

Fieldwork was undertaken during four NERC North Sea cruises; *viz.* three

plume cruises of the Humber (CH42 and CH65) and Thames (CH46), and the bloom cruise (CH50). Whereas CH42 and CH46 represented winter conditions (Section 3.1.1), CH65 (May 1990) was characterized by high spring productivity.

Sampling was undertaken around the grids of the respective cruises (Section 3.1.1; Figure 4.1); 100 ml samples were taken from either standard *Go-Flo* bottles or the *PES* pumped supply in a polyethylene measuring cylinder and immediately transferred to 150 ml polyethylene pots in the constant temperature laboratory to which 100  $\mu$ l spike of cocktail consisting of  $\gamma$ -emitting  $^{109}\text{Cd}$ ,  $^{137}\text{Cs}$ ,  $^{54}\text{Mn}$  and  $^{65}\text{Zn}$  (Amersham International) in chloride form (1M HCl, BDH AnalaR grade) was added at sub-picomolar concentrations. These particular isotopes were selected on the basis of practicality (sufficiently long half-life, and high  $\gamma$ -emission and instrument detection efficiency) and their contrasting behaviour and chemical speciation in aquatic systems (Table 4.1).

The reduction of pH by 1.5 units resulting from spiking was buffered by the addition of 100  $\mu$ l  $\text{NH}_3$  (BDH AnalaR grade) diluted accordingly (to < 0.5M) with Milli-Q water. The pH of a sample from the Thames plume was found to remain stable ( $7.96 \pm 0.11$ ) for at least 7 days under these conditions.

Table 4.1: Details of radioisotopes used in this study.

| Isotope           | Energy (keV) | Detection efficiency (%) | $\gamma$ -Emission (%) | Half-life (days) | Sea water speciation (%)*      | Reason for studying            |
|-------------------|--------------|--------------------------|------------------------|------------------|--------------------------------|--------------------------------|
| $^{109}\text{Cd}$ | 88.0         | 3.90                     | 3.8                    | 453              | Cl (97)                        | very toxic                     |
| $^{137}\text{Cs}$ | 661.6        | 1.10                     | 84.6                   | 11000            | Free (93)                      | reactor released radionuclide. |
| $^{54}\text{Mn}$  | 834.8        | 0.70                     | 100                    | 312              | Free (58);<br>Cl (37)          | important scavenging agent     |
| $^{65}\text{Zn}$  | 1115.5       | 0.54                     | 50.8                   | 244              | Free (46);<br>Cl (35); OH (12) | well documented                |

\* Calculated for model sea water at pH 8.2 (Turner *et al.*, 1981).

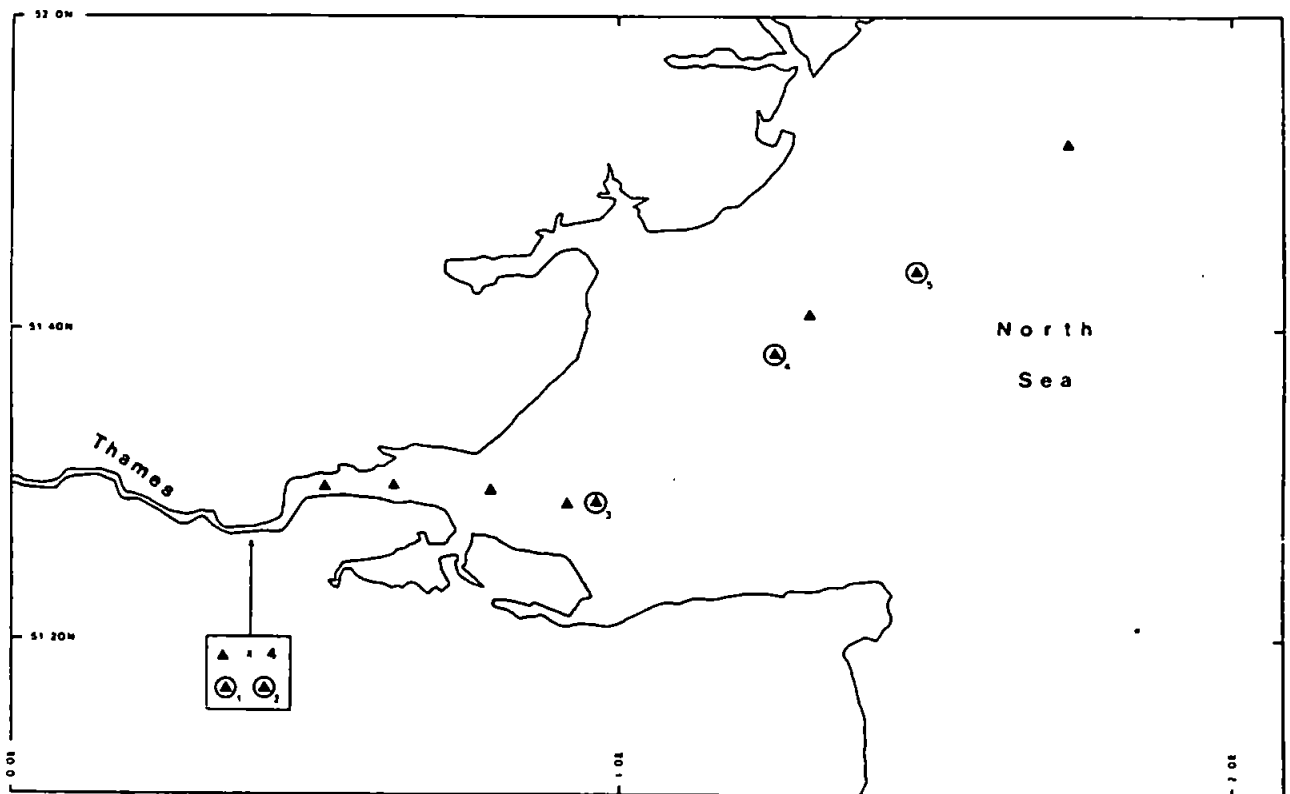
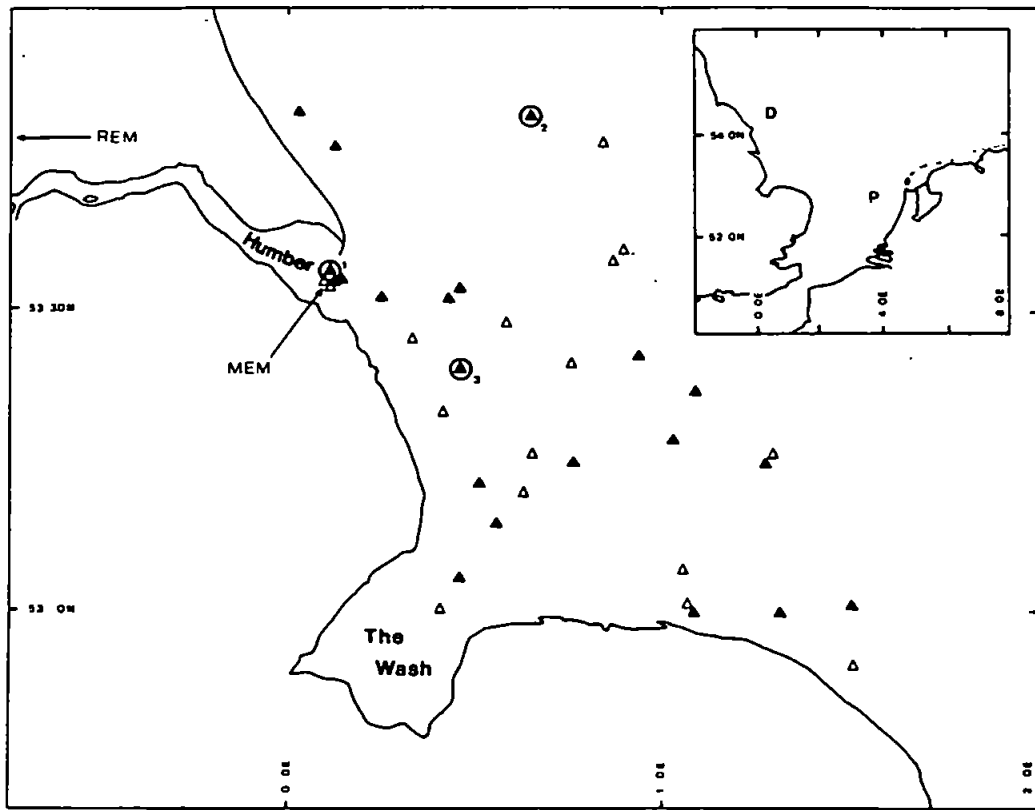


Figure 4.1: Sampling locations for radiochemical studies in the southern North Sea. Circled symbols represent time dependent experiments. a: Humber plume during winter (▲) and spring (Δ); REM and MEM are end-member samples for the mixing experiments (Section 4.2.3.1); inset shows the location of the diatom (D) and *Phaeocystis* (P) blooms. b: Thames plume.

Table 4.2 gives the concentrations of dissolved stable metal analogues in U.K. North Sea coastal waters and concentrations in the reactor vessel (stable- and radioisotopes) resulting from the addition of a spike. These serve to illustrate that spiking is responsible for a negligible increase in both metal concentrations and chlorinity.

The sample was sealed, placed in a plastic bag and incubated at ambient sea water temperature. For the plume samples this was achieved by suspending the vessel by means of nylon wiring in a cell constructed from a 35 dm<sup>3</sup> polyvinyl chloride container which was continually flushed with sea water from the ship's non-toxic supply at a rate of approximately 3l/minute in the constant temperature laboratory (Figure 4.2). Diatom and *Phaeocystis* samples taken during CH50 were left under natural light by a window; sea water temperature was maintained by the temperature regulator in the laboratory.

Table 4.2: Concentrations of dissolved metal and chloride ions in reactor vessel after spike addition.

|           | cocktail      |                 | sea water * |
|-----------|---------------|-----------------|-------------|
|           | radio-isotope | stable -isotope | background  |
| Cd (ng/l) | 0.23          | 0.59            | 25          |
| Cs (ng/l) | 0.11          | 4.5             | 400         |
| Mn (ng/l) | 0.017         | 0.76            | 300         |
| Zn (ng/l) | 0.04          | 0.29            | 600         |
| Cl (%)    | -             | 0.01            | 1.85        |

\*Sources of information. Cd, Zn; preliminary analyses of PES samples from CH42 (Section 3.1.1) by M. Althaus, Southampton University Department of Oceanography; Cs; mean oceanic concentration (Brewer, 1975; Martin and Whitfield, 1983); Mn; North Sea concentration (Kremling and Hydes, 1988).

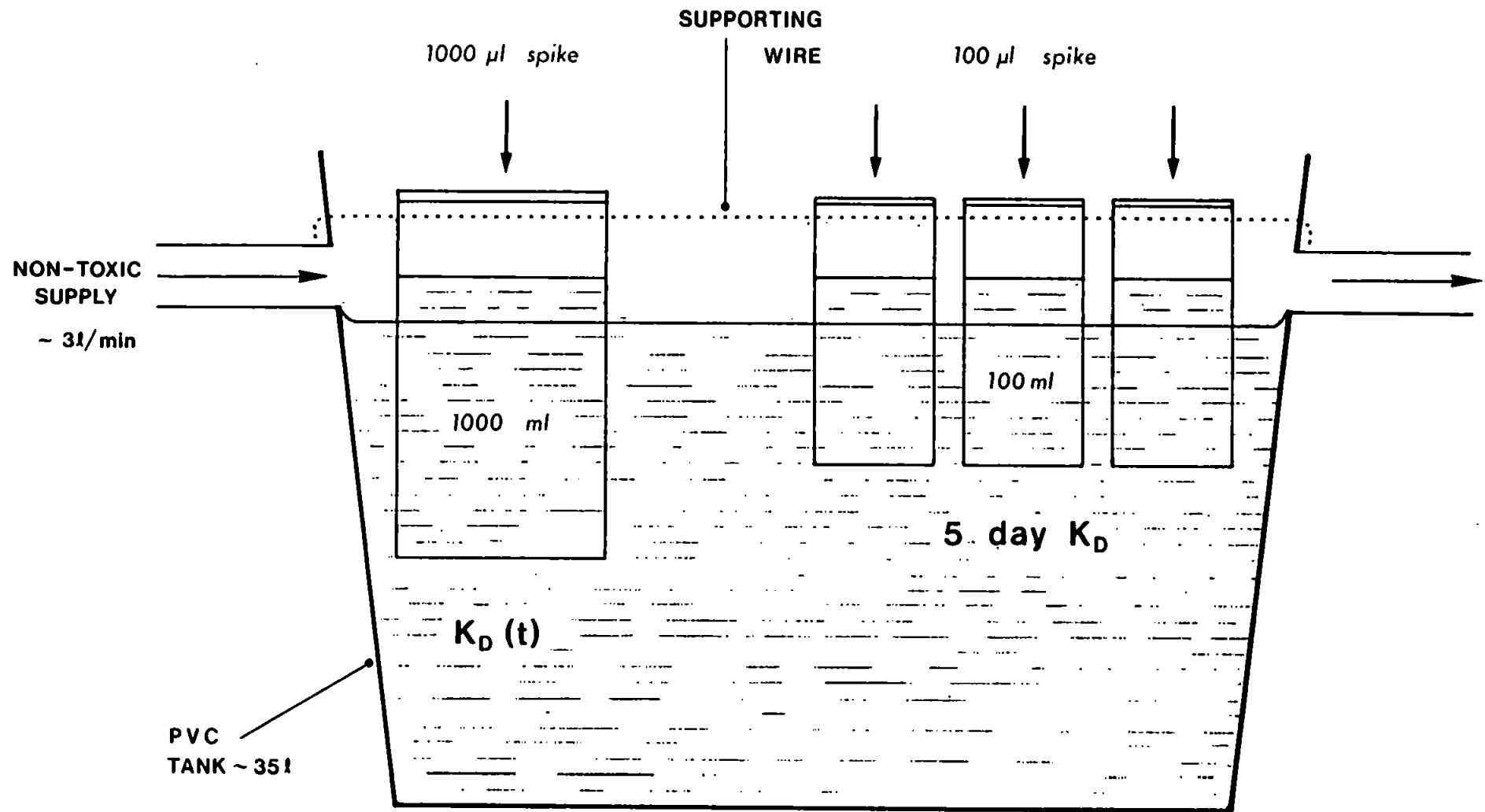


Figure 4.2: Construction of the continuously flushed cell for the incubation of spiked samples.



After 5 days ( $\pm 10$  hours) the samples were carefully sucked into a 50 ml Millipore polyethylene syringe in two stages and filtered through Millipore cellulose acetate filters of pore size  $0.45 \mu\text{m}$  and diameter 22 mm mounted in a Millipore (*Swinex*) filter sandwich. In the most turbid waters, filtration became difficult and time consuming and only 30 or 50 ml was successfully filtered. It was anticipated that this problem would be compounded for the mixing experiments (Section 4.2.3) and during CH65 and therefore larger filter sandwiches were used in order to accommodate 47 mm diameter filters. The filtrate was collected in a fresh 150 ml polyethylene pot and spiked with 1 ml 50%  $\text{HNO}_3$  (BDH AnalaR grade) for preservation, sealed, wrapped in a plastic bag and stored at room temperature.

The filter was allowed to dry briefly on paper tissue and subsequently placed centrally in a 50 mm diameter petri dish which was wrapped in plastic and stored likewise.

In order to determine the rates of these solid-solution interactions several 1 l samples were taken in larger (1-1.5 l) polyethylene containers during the plume cruises and spiked with 1 ml cocktail and 1 ml dilute ammonia. The reactor vessel was stirred gently at regular intervals with a PTFE spatula. At discrete time intervals ranging from 5 minutes to 5 days after spiking, subsamples were taken and treated as described above.

The influence of temperature on the experiments was investigated during CH65 by subjecting replicate samples to a range of temperatures typical of North Sea coastal waters (Lee and Ramster, 1981); viz.  $4^\circ\text{C}$  (fridge),  $11^\circ\text{C}$  (ambient water temperature on this occasion) and  $20^\circ\text{C}$  (constant temperature laboratory).

Disposable rubber gloves were worn during all operations and filters were manipulated with Millipore tweezers. The reactor vessels, measuring cylinder, *Swinex*-syringe units and PTFE spatulas had been previously soaked in detergent (1 hour) and 50%  $\text{HNO}_3$  (1 day) and rinsed thoroughly with Milli-Q water; items that were reused were recleaned likewise.

The extent of wall adsorption (Amdurer *et al.*, 1982; Benes *et al.*, 1988) was assessed by counting spiked samples of 100 ml filtered sea water left for 5 days

and recounting the empty polyethylene pots after having refiltered the solutions into fresh pots; the resulting filters were counted in order to quantify filter blanks. The empty pots were subsequently rinsed with 10% HNO<sub>3</sub> and recounted in order to assess the efficiency of acid cleaning reusable plastic-ware involved in the sampling routine. The results of this exercise are shown in Table 4.3 and demonstrate that the loss of isotope from solution is very small and ranges from an undetectable amount for <sup>109</sup>Cd to 5% for <sup>65</sup>Zn, and that HNO<sub>3</sub> is effective in removing residual isotope.

Table 4.3: Significance of wall adsorption and blanks, and efficiency of acid wash.

|  | Disintegration counts in 1000 seconds |                   |                  |                  |
|--|---------------------------------------|-------------------|------------------|------------------|
|  | <sup>109</sup> Cd                     | <sup>137</sup> Cs | <sup>54</sup> Mn | <sup>65</sup> Zn |
| <b>SAMPLE 1</b>                            |                                       |                   |                  |                  |
| Spiked solution after 5 days               | 6717                                  | 6846              | 7640             | 5433             |
| Empty container after refiltering solution | 0                                     | 19                | 83               | 42               |
| Container after 10% HNO <sub>3</sub> rinse | 0                                     | 15                | 20               | 7                |
| Filter blank                               | 0                                     | 19                | 279              | 236              |
| <b>SAMPLE 2</b>                            |                                       |                   |                  |                  |
| Spiked solution after 5 days               | 5611                                  | 5887              | 6386             | 4648             |
| Empty container after refiltering solution | 0                                     | 6                 | 51               | 53               |
| Container after 10% HNO <sub>3</sub> rinse | 0                                     | 8                 | 5                | 2                |
| Filter blank                               | 0                                     | 23                | 155              | 154              |
| Mean of 3 instrument blanks                | 0                                     | 4                 | 12               | 6                |

#### 4.2.2: Counting Procedure

Filter and filtrate samples were retained in plastic bags and counted on a high resolution Ge crystal (Li drifted) coaxial detector (E.G. and G. Ortec) with live time correction connected to a Canberra Series 80 Multichannel Analyzer. Disintegrations were counted for 1000 seconds and this gave statistical counting errors ( $\pm 0.5\sigma$ ) of < 2% for filtrate samples and varying errors ranging from < 1%

to > 300% for filter samples. The high errors were generally associated with  $^{109}\text{Cd}$  and  $^{137}\text{Cs}$  on filters having low masses of material collected in the Humber plume.

The differential sensitivity of the counter towards *flat* petri dishes (filters) and *cylindrical* pots (filtrates) was evaluated by counting 100  $\mu\text{l}$  aliquots of cocktail absorbed into 22 mm diameter filters in 50 mm diameter petri dishes, and spiked

Table 4.4: Example of geometry factor, *f*, calculation - filtrate sample (100ml): filter sample. Mean  $\pm$  one standard deviation of 5 determinations given.

|  | Counts in 1000 seconds |                   |                   |                   |
|--|------------------------|-------------------|-------------------|-------------------|
|  | $^{109}\text{Cd}$      | $^{137}\text{Cs}$ | $^{54}\text{Mn}$  | $^{65}\text{Zn}$  |
| <i>FILTRATE</i> : 100 $\mu\text{l}$ cocktail +<br>100ml sea water in pot | 3333 $\pm$ 184         | 3481 $\pm$ 154    | 3890 $\pm$ 213    | 2782 $\pm$ 144    |
| <i>FILTER</i> : 100 $\mu\text{l}$ cocktail on<br>filter in petri dish    | 15022 $\pm$ 494        | 12010 $\pm$ 320   | 12783 $\pm$ 371   | 8836 $\pm$ 144    |
| filtrate : filter, <i>f</i>  | 0.222 $\pm$ 0.015      | 0.290 $\pm$ 0.015 | 0.305 $\pm$ 0.021 | 0.315 $\pm$ 0.017 |

into 100ml filtered sea water in 150 ml polyethylene pots (Table 4.4). Geometry corrections were also necessary for different filtrate volumes (*viz.* 30, 50 and 100 ml) and were similarly evaluated by counting respective volumes of spiked filtered sea water. Occasional filters that curled up on drying during storage were flattened by adding a few drops of water to ensure a uniformly flat distribution (*i.e.* consistent geometry).

Replicate samples taken after 5 days from a 1 l reactor vessel indicate considerably better reproducibility for filtrate samples compared with filter samples (Table 4.5). This can be attributed to the loss of material during filter manipulations, for example to the handling tweezers and *Swinex* O-ring, and to imperfect subsampling of the particle population.

Table 4.5: Details of disintegration counts after 1000 seconds on n replicate samples taken after 5 days from an incubated 1 l reactor vessel:  $\mu \pm 1\sigma$  = mean  $\pm$  one standard deviation; C.V. = coefficient of variation.

|          |                   | $^{109}\text{Cd}$ | $^{137}\text{Cs}$ | $^{54}\text{Mn}$ | $^{65}\text{Zn}$ |
|----------|-------------------|-------------------|-------------------|------------------|------------------|
| SOLUTION | n                 | 5                 | 5                 | 5                | 5                |
|          | $\mu \pm 1\sigma$ | 8449 $\pm$ 187    | 7620 $\pm$ 280    | 2319 $\pm$ 65    | 3978 $\pm$ 112   |
|          | C.V. (%)          | 2.2               | 3.7               | 2.8              | 2.8              |
| FILTER   | n                 | 6                 | 6                 | 6                | 6                |
|          | $\mu \pm 1\sigma$ | 2347 $\pm$ 235    | 927 $\pm$ 97      | 12070 $\pm$ 1257 | 3911 $\pm$ 325   |
|          | C.V. (%)          | 10.0              | 10.5              | 10.4             | 8.3              |

#### 4.2.3: Mixing Experiments

In the light of initial results (Section 4.3.4) the dependence on salinity and suspended solids concentration was examined in more detail during CH65 by constructing a series of carefully controlled model estuaries. Previous laboratory experiments aimed at elucidating the effects of salinity and other master variables on metal behaviour have frequently employed artificial media and/or solid substrates (van der Weijden *et al.*, 1977; Salomons, 1980; Millward and Moore, 1982; Davies-Colley *et al.*, 1984) and the validity of extrapolation to natural systems must be questioned. Where suspensions constitute natural components other conditions have not been observed realistically such as excessive (Aston and Duursma, 1973) or inadequate (Li *et al.*, 1984a) suspended solids concentrations. In the present experiments simulated salinity and suspended solids concentration gradients considered appropriate to the types of estuaries under investigation were achieved by mixing, *in situ*, proportions of native and freshly collected end-member samples.

##### 4.2.3.1: End-Member Sampling and Processing

The river end-member (REM) was collected from shore in a 10 l carboy from the River Ouse (Figure 4.1) as far upstream as practically possible before the

major river confluences in order to encompass water derived from the whole catchment. Site accessibility was also limited to near high water (HW -2 hours) and the resulting salinity (Figure 4.3) as determined by titration with  $\text{AgNO}_3$  (Strickland and Parsons, 1972) was not as *fresh* as desirable bearing in mind the chemical significance of the very low salinity region (Section 1.3). The suspended solids concentration was determined after subsample filtration of 100 ml through Whatman GF/C filter papers as described in Section 2.1.1.1 and is shown in Figure 4.3 along with important particle characteristics determined on freeze dried solid ( $0.45 \mu\text{m}$ ) samples (Sections 2.1.2 and 2.1.3). The suspended solids concentration of this water body was varied by mixing proportions of filtered ( $0.45 \mu\text{m}$ ) and unfiltered sample within 2 hours of collection as follows:

$$\begin{aligned} \text{REM}_{\text{unfiltered}} &= \text{REM}_A \\ 1 \text{ REM}_{\text{unfiltered}} + 1 \text{ REM}_{\text{filtered}} &= \text{REM}_B \\ 1 \text{ REM}_{\text{unfiltered}} + 3 \text{ REM}_{\text{filtered}} &= \text{REM}_C \end{aligned}$$

The resulting samples ( $\text{REM}_A$ ,  $\text{REM}_B$  and  $\text{REM}_C$ ) were transported cool to the vessel immediately.

About 10 l sea water (marine end member; MEM) were taken at low water in the mouth of the Humber Estuary (Figure 4.1) during CH65 from a standard *Go-Flo* bottle. Particle characteristics and the suspended solids concentration were determined as above and the salinity was read off the accurate on board thermo-salinograph (Figure 4.3).

#### 4.2.3.2: End-Member Mixing

The mixing experiments commenced within 48 hours of REM collection. The salinity was controlled by varying REM:MEM in the ratios 4:0, 3:1, 2:2, 1:3 and 0:4, where each unit represents 25 ml. The suspended solids concentration was controlled by mixing each REM (A, B and C) in these proportions. Thus, 100 ml volume was used in each mix and these were spiked and incubated for five days

as described in Section 4.2.1. The conditions in each model estuary (A, B and C) are illustrated in Figure 4.3 assuming that particle concentration behaves conservatively, *i.e.* mass balance. Suspended solids concentrations were high and well controlled and consequently filter residues were easier to manipulate without loss rendering a higher accuracy to these results:

The only artificial constraints imposed upon this experiment were temperature alterations during transportation and storage, sample isolation, and spike addition (Table 4.2).

#### 4.2.4: Calculations

The results of the 5-day incubations have been represented in terms of a distribution coefficient,  $K_D$  (Section 2.2.3.8), which provides a straightforward quantification of the solid-solution partitioning. It should not necessarily be implicit of equilibrium or reversibility (Olsen *et al.*, 1989); thus, the time dependent (kinetic) partitioning has also been represented by this parameter,  $K_D(t)$ . The nature of the experimental procedure renders a new format (Duursma and Bosch, 1970; Bale, 1987):

$$K_D = \frac{C_P}{C_S} \times \frac{1.025 \times 10^5}{m.f} \quad (4.1)$$

Here,  $C_P$  and  $C_S$  are the activities associated with filter and filtrate respectively. Filter blanks and wall adsorption were found to be small compared with typical sample signals (Table 4.3). Furthermore, they were assessed in the absence of pre-existing particles and are therefore considered to represent overestimates. Thus, neither these effects, nor background counts which were negligible (Table 4.3), have been incorporated into the calculations. The detection limit was arbitrarily defined as 100 counts per 1000 seconds, corresponding approximately to a 20% counting error. The dry weight of material loaded on the filter,  $m$ , was commonly <0.5 mg and consequently difficult to determine directly. This was therefore derived from the mass retained on Whatman GF/C filters after filtration

|                         | REM          | MEM               |
|-------------------------|--------------|-------------------|
| Location / tide         | Ouse / HW -2 | Humber mouth / LW |
| Salinity (‰)            | 1.7          | 30.8              |
| SSC (mg/l)              | 440          | 30.5              |
| SSA (m <sup>2</sup> /g) | 31.4         | 20.6              |
| Fe (mg/g)               | 10.1         | 11.2              |
| Mn (mg/g)               | 1.32         | 1.05              |
| C (%)                   | 4.9          | 5.2               |
| C:N                     | 15.8         | 13.9              |

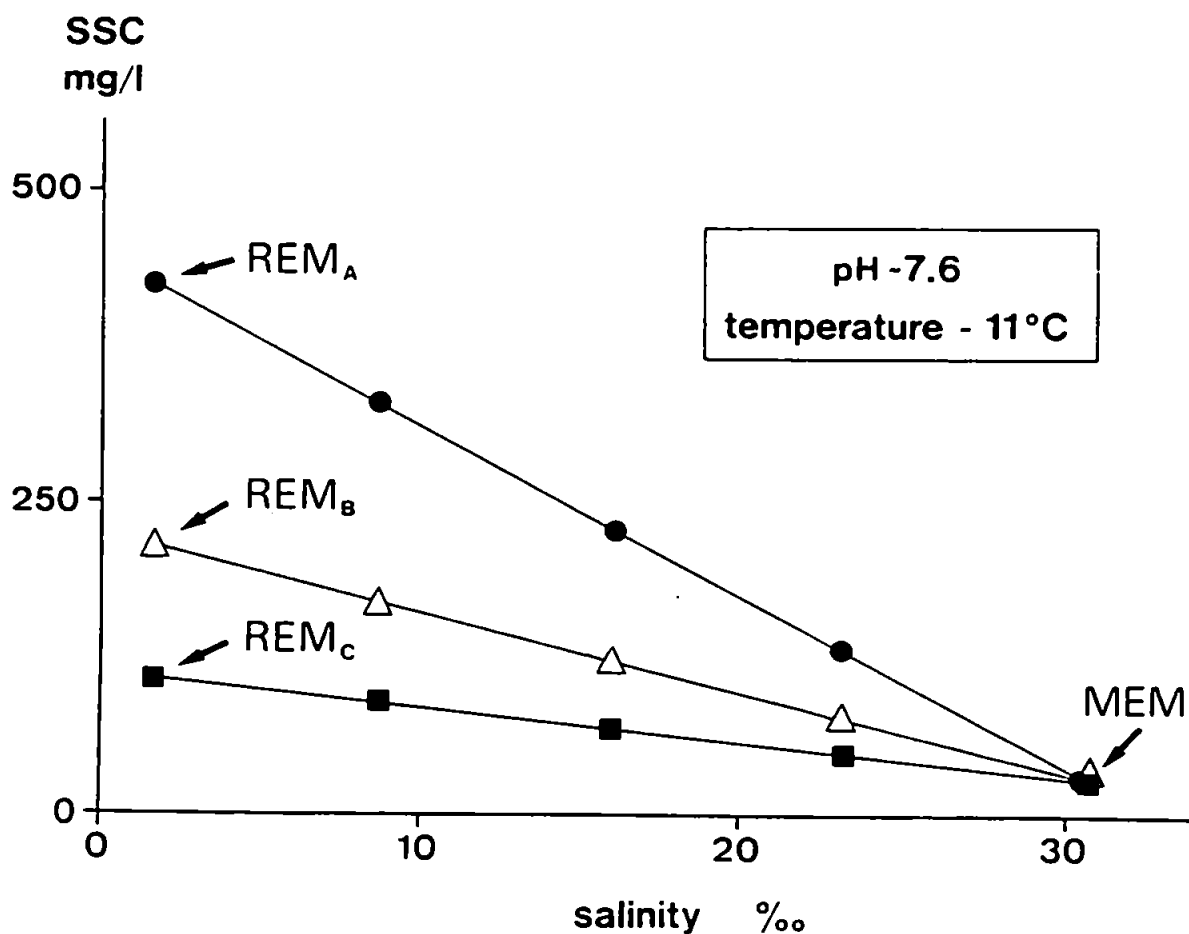


Figure 4.3: Water and particle characteristics of end-member samples, and theoretical (salinity and suspended solids concentration, SSC) and measured (temperature and pH) conditions in the model estuaries A (●), B (Δ) and C (■).

of up to 3 l (Section 3.1.3). Geometry differences are considered by insertion of the appropriate factor,  $f$  (Section 4.2.2), and the constant in the numerator accounts for the density of sea water.

#### 4.2.5: Filter Leaching

The nature of the radioisotope-particle interactions was investigated further by conducting a series of leaching experiments. After counting, several filters from both the kinetic and equilibrium experiments were remounted in Millipore *Swinex*-syringe systems and 15 ml 1M HCl (BDH AnalaR grade) were passed through over a period of 12 hours at room temperature. This was an attempt to simulate the leaching performed on membrane filters prior to trace metal analysis (Section 3.1.4). After drying briefly on tissues, the filters were replaced centrally in new petri dishes and recounted. This procedure was then repeated using different filters with 15 ml 1M  $\text{NH}_4\text{OAc}$  (ammonium acetate; BDH Analar grade) at pH 7 for 40-60 minutes, *i.e.* an exchangeable fraction (Calmano and Förstner, 1983), and 25 ml filtered ( $0.4 \mu\text{m}$ ) sea water of salinity 34 ‰ (collected during the winter survey cruise, CH43) for 20 hours, which had been freshly filtered ( $0.45 \mu\text{m}$ ) immediately prior to use, *i.e.* desorption in sea water. Several filters from the mixing experiment were leached with 50 ml volumes of 1M  $\text{NH}_4\text{OAc}$ , 1M HCl and 50%  $\text{HNO}_3$  after assembling in a Millipore vacuum filtration unit. The percentage removal,  $r$ , was calculated from the counts on the untreated filter,  $C_P$ , and following leaching,  $C_L$ . The time lapse in days,  $t$ , between determinations often exceeded one month and for  $^{109}\text{Cd}$ ,  $^{54}\text{Mn}$  and  $^{65}\text{Zn}$  the decay was accounted for from the known half life ( $t_{0.5}$ ; Table 4.1) and exponential decay law as follows:

$$r(\%) = 10^2 - \left[ \frac{10^2 \cdot C_L}{C_P \cdot e^{\ln 0.5 \cdot (t/t_{0.5})}} \right] \quad (4.2)$$



## 4.3: RESULTS AND DISCUSSION

The results of the time dependent studies describing the approach to equilibrium are reported before the 5-day  $K_D$  values. However, in order to interpret the data it is worth first considering the likely types of reaction of the radioisotopes with the particles.

### 4.3.1: Mechanisms of Isotope Uptake by Particles

#### 4.3.1.1: Manganese

The formation of particulate Mn is principally the result of precipitation of oxidized Mn (II). Although theoretically a kinetically slow process in aquatic systems, observed oxidation rates have been reconciled with an autocatalytic mechanism, whereby pre-existing or freshly generated  $MnO_2$  phases encourage further precipitation (Morgan, 1967; Crerar and Barnes, 1974; Kessick and Morgan, 1979; Morris and Bale, 1979), and effective microbially mediated oxidation (Chapnick *et al.*, 1982; Emerson *et al.*, 1982; Tebo *et al.*, 1984; Vojak *et al.*, 1985; Sunda and Huntsman, 1987).

Oxidation of Mn (II) is also induced by the steep microgradients in  $O_2$  (and pH) adjacent to cells resulting from photosynthesis (Richardson *et al.*, 1988) and this may be significant in the plankton-rich samples, although as Mn is a required micronutrient direct uptake is also likely (Sunda and Huntsman, 1985; 1986).

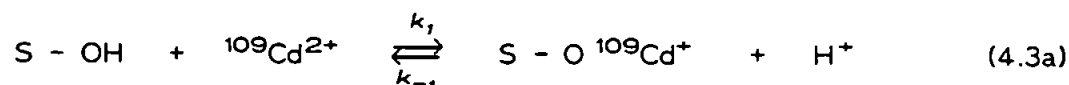
#### 4.3.1.2: Caesium

The uptake of Cs by inorganic phases in aquatic systems is largely related to the mineral structure and results in ions bound either non-selectively to external or planar surfaces of clays, or fixed selectively in less accessible wedge and/or interlattice sites (Sawhney, 1972; Evans *et al.*, 1983).

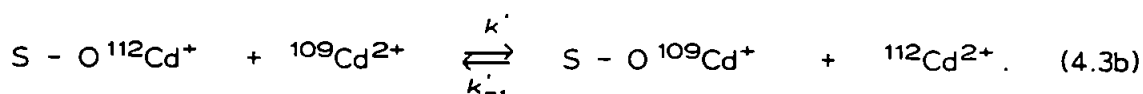
#### 4.3.1.3: Cadmium and Zinc

Cadmium and Zn adsorb onto a variety of inorganic phases, in particular Fe

and Mn oxides (Takematsu, 1979; Lion *et al.*, 1982; Balistrieri and Murray, 1983; Davies-Colley *et al.*, 1984; Aualiitia and Pickering, 1987) and the inherent mechanism can be described by Equation 1.1. Conceivably, adsorption of the radioisotope occurs in conjunction with an isotopic exchange mechanism with stable counterparts already adsorbed. Thus, considering Cd, adsorption onto the particle surface, S, can be written as:



and the isotopic exchange reaction can be written as:



In addition, Cd has a high affinity for a variety of organic phases including river sediments (Suzuki *et al.*, 1979), faecal pellets (Fowler, 1977) and phytoplankton (Rebhun and Ben-Amotz, 1984; Valenta *et al.*, 1986; Golimowski *et al.*, 1990; Section 3.2.3). The specific uptake mechanisms by plankton are uncertain, although both active and passive (*i.e.* involving no metabolism) mechanisms have been invoked (Rebhun and Ben-Amotz, 1984; Fisher *et al.*, 1984; Trevors *et al.*, 1986). Active mechanisms would seem a logical interpretation of observed oceanic Cd - phosphorus relationships (Bruland *et al.*, 1978; Boyle and Husted, 1983; Collier and Edmond, 1984). Passive uptake is probably primarily adsorption according to surface complexation formation (Equation 4.2) with functional groups of cell walls (Xue *et al.*, 1988).

#### 4.3.2: $K_D$ Kinetics

Examples of the evolution of  $K_D$  with time,  $K_D(t)$ , are shown in Figure 4.4.

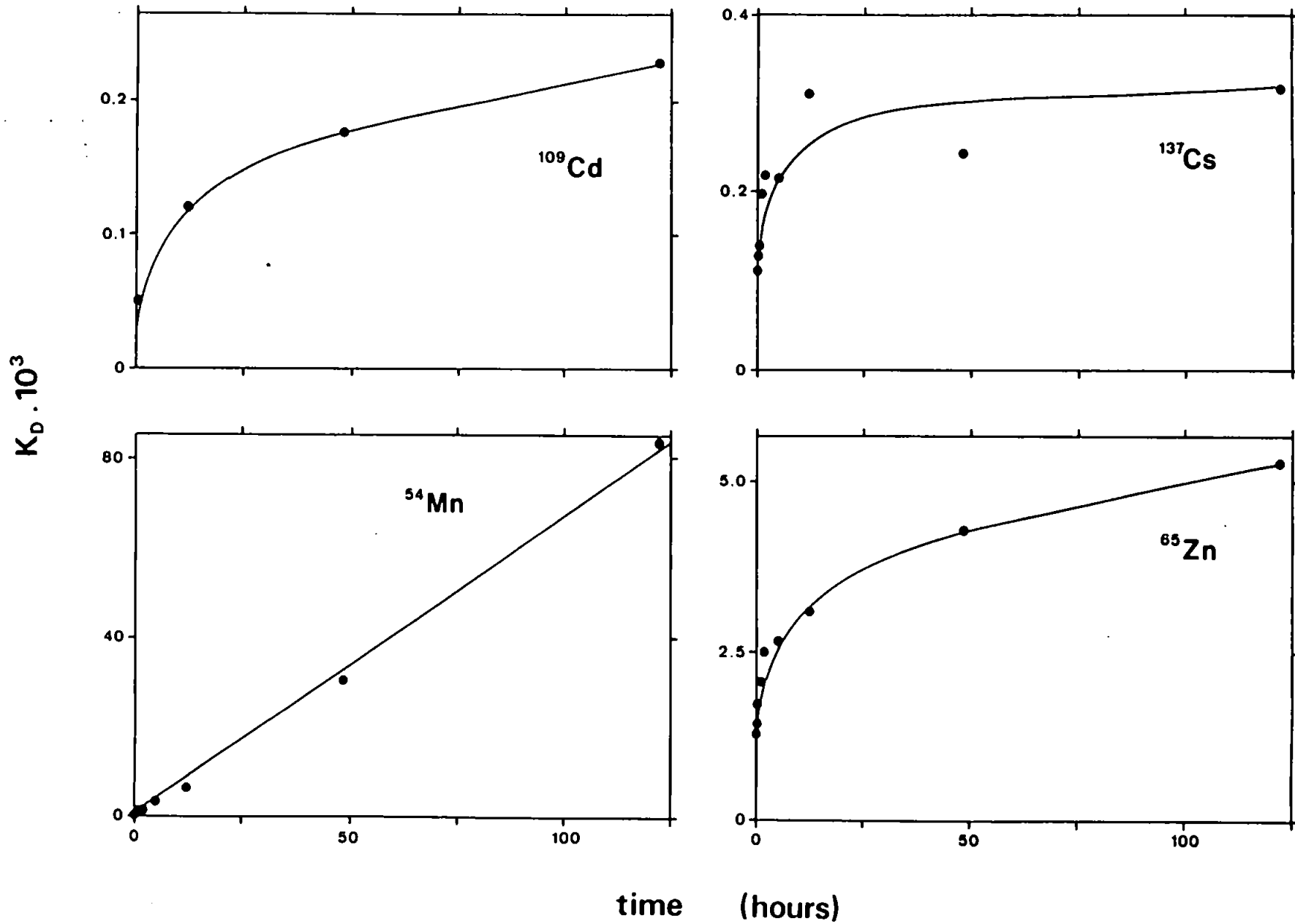


Figure 4.4a: Time dependent  $K_D$  profiles for Humber plume sample number 3 (location given in Figure 4.1a).

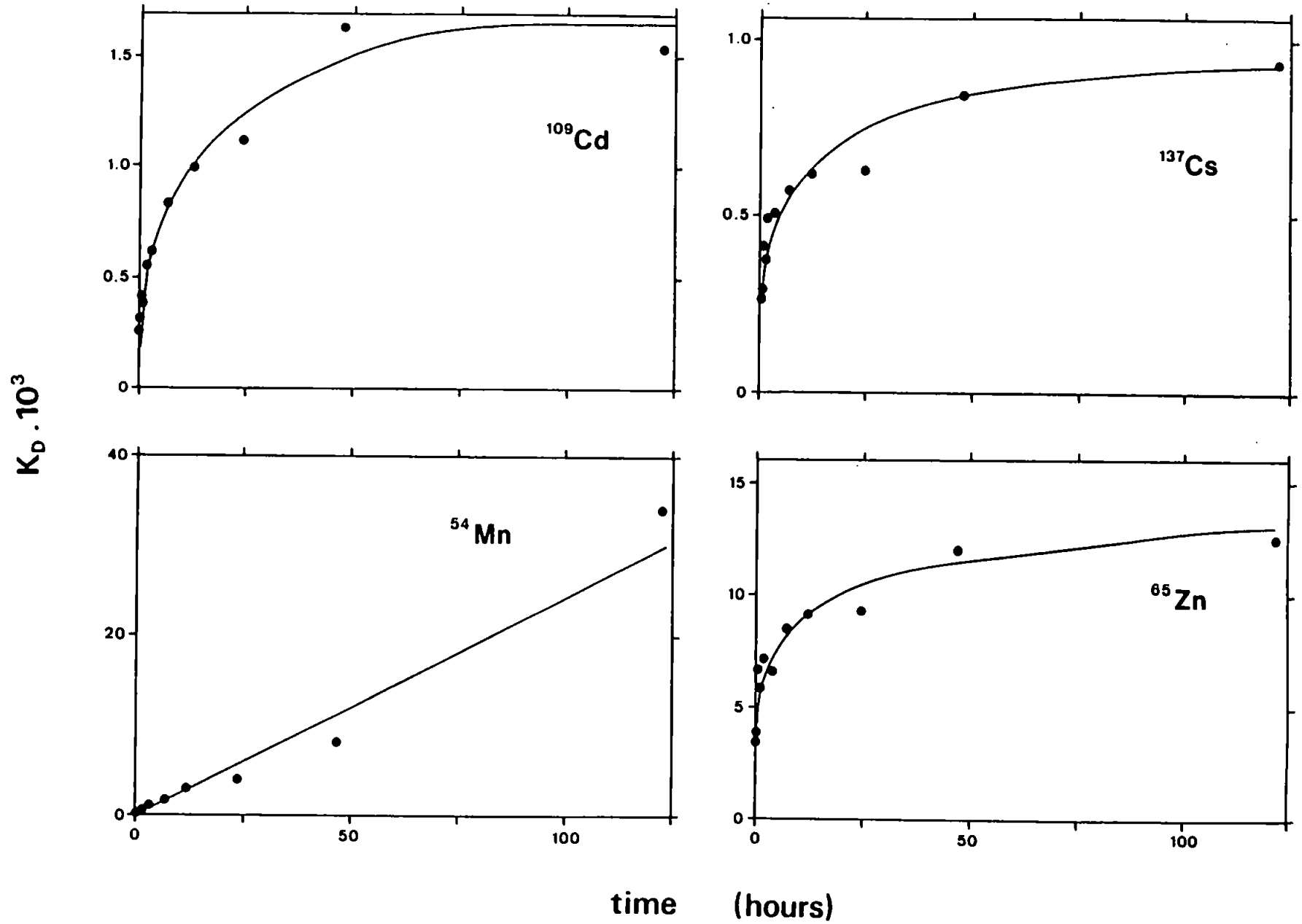


Figure 4.4b: Time dependent  $K_D$  profiles for Thames plume sample number 1 (location given in Figure 4.1b).

#### 4.3.2.1: Manganese

Manganese displays a linear increase in  $K_D$  throughout the 5-day incubation period and equilibrium is not established; regression analysis indicates a high and significant correlation (Table 4.6). Thus, a linear Mn oxidation rate characteristic of estuaries, whether induced by autocatalysis (Morris and Bale, 1979) and/or bacteria (Sunda and Huntsman, 1987), also continues offshore in coastal waters. The rate varies by an order of magnitude from 56.4 to 677  $\text{hour}^{-1}$ , and is related to the final 5-day  $K_D$  value (Table 4.6) by the following equation:

$$(K_D \text{ Mn})_{5\text{-day}} = 123 \cdot \frac{d(K_D \text{ Mn})}{dt} - 933 \quad (4.4)$$

for which  $r^2 = 97.3\%$  and  $p \leq 0.0005$ . This can, therefore, be applied to predict rates of change of  $K_D$  from known 5-day values in plume waters and according to data of Table 4.7 yields rates ranging from 90.5 - 1410  $\text{hour}^{-1}$  and 125 - 1800  $\text{hour}^{-1}$  for the Humber and Thames plumes respectively.

The initial uptake (over a period of a few days) of  $^{54}\text{Mn}$  from sea water by marine interfacial sediments - sea water was succeeded by a distinctly slower stage reaction continuing beyond 50 days in laboratory experiments conducted by Nyffeler *et al.* (1984); this behaviour was also echoed by Fe and Co and presumably reflects their oxidation chemistries. If such a protracted second stage reaction were an extension of the linear  $^{54}\text{Mn}$  oxidation process observed for Humber- and Thames-derived suspended material - sea water then equilibrium conditions would not be satisfied within the plume grids as delineated in Figure 3.4 as these regions are normally flushed within similar timescales (de Ruijter *et al.*, 1987).

Magnification of the time dependent profiles over the initial (< 2 hours) stages (Figure 4.5) indicates a positive intercept through the ordinate (although this is not always apparent from the regression analyses), *i.e.* a finite  $K_D$  at time zero. Taking the origin as a point, necessary from the nature of the experiment in which  $^{54}\text{Mn}$  was introduced in solution as chloride (Section 4.2.1), gives rise to

curvature in the trend over a short (< 0.3 hours) period indicative of adsorption; thus, removal of Mn in saline waters may be characterized by a three stage reaction. The relative significance of adsorption was assessed from the ratio of the intercept, I, of the best fit straight line of the initial (up to 2 hours) data points, to the 5 day  $K_D$  value (Table 4.6; Sunda and Huntsman, 1987); in all but one experiment, adsorption accounts for < 1% of the total particulate  $^{54}\text{Mn}$  formed.

Table 4.6: Details of  $^{54}\text{Mn}$  kinetic experiments.

| Experiment | $K_D$ versus time                        |                        | 5 day $K_D$<br>( $\cdot 10^3$ ) | I    | I/5 day $K_D$<br>( $\cdot 10^2$ ) |
|------------|--|------------------------|---------------------------------|------|-----------------------------------|
|            | $\frac{d(K_D)}{dt}$ ( $\text{hr}^{-1}$ ) | $r^2$ ( $\rho$ )       |                                 |      |                                   |
| HUMBER 1   | 56.4                                     | 94.4 ( $\leq 0.0005$ ) | 7.13                            | -    | -                                 |
| 2          | 522                                      | 97.1 ( $\leq 0.0005$ ) | 64.2                            | 1960 | 3.1                               |
| 3          | 677                                      | 99.7 ( $\leq 0.0005$ ) | 83.7                            | 389  | 0.46                              |
| THAMES 1   | 357                                      | 93.7 ( $\leq 0.0005$ ) | 34.2                            | 137  | 0.40                              |
| 2          | 139                                      | 96.1 ( $\leq 0.0005$ ) | 17.4                            | 89.9 | 0.52                              |
| 3          | 391                                      | 99.9 ( $\leq 0.0005$ ) | 47.9                            | 366  | 0.76                              |
| 4          | 349                                      | 96.5 ( $\leq 0.0005$ ) | 45.2                            | 400  | 0.88                              |
| 5          | 420                                      | 99.8 ( $\leq 0.0005$ ) | -                               | 237  | -                                 |

The blank controls (Section 4.2.4; Table 4.3) indicate that particulate  $^{54}\text{Mn}$  formation (> 0.45  $\mu\text{m}$ ) cannot proceed in the absence of pre-existing particles by, for example, oxidative precipitation (Morris and Bale, 1979) or flocculation (Sholkovitz, 1976; 1978). It would appear, therefore, that Mn oxidation can only occur in the presence of freshly formed (by adsorption onto existing particles) particulate Mn.

#### 4.3.2.2: Cadmium, Caesium and Zinc

The time dependent  $K_D$  profiles of  $^{109}\text{Cd}$ ,  $^{137}\text{Cs}$  and  $^{65}\text{Zn}$  are characterized by a rapid initial uptake onto particles within 25 hours. It is difficult

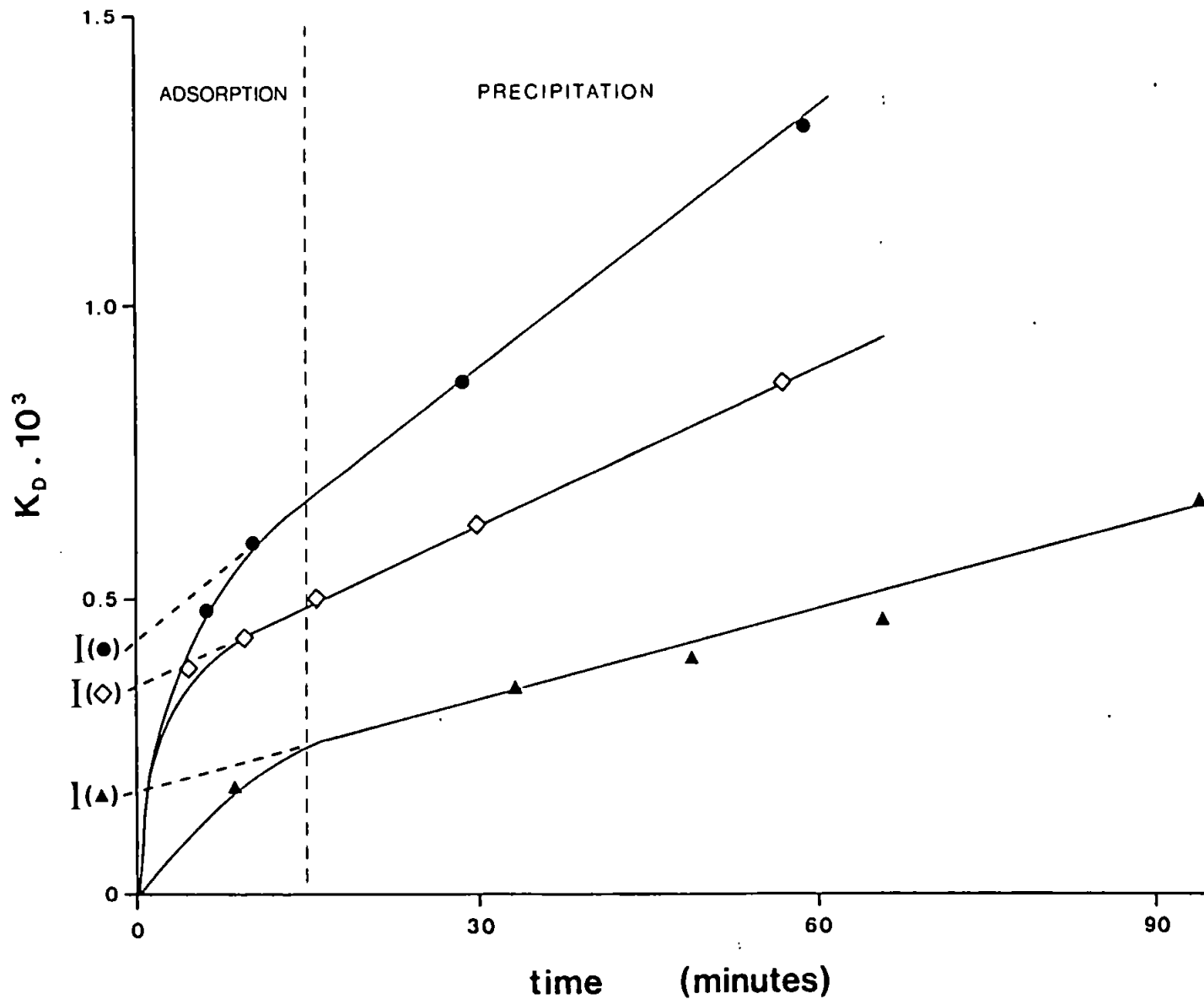


Figure 4.5: Examples of the early stages of the time dependent  $K_D$  profiles for  $^{54}\text{Mn}$ ; Humber 3 ( $\bullet$ ), Thames 1 ( $\blacktriangle$ ) and Thames 4 ( $\diamond$ ). Intercepts,  $I$ , have been derived from extrapolation (dashed lines) of the linear stages of the reactions.

to establish from the data whether subsequently equilibrium is established or a slower uptake mechanism is occurring. These data could not be matched with a double exponential profile when delivered to a maximum likelihood curve fitting package on the Polytechnic South West mainframe system. The scatter to the data probably reflects the failure to maintain a uniform, hence consistent suspended solids concentration in the reactor vessel despite occasional stirring (Section 4.2.2).

There is, however, increasing evidence to suggest that for metals such as Cd and Zn the reaction consists of two distinct stages as described by Equation 1.2 (Glegg, 1987; Jenne and Zachara, 1987; Moore and Millward, 1988; Brummer *et al.*, 1988; Jannasch *et al.*, 1988; Barrow *et al.*, 1989), although the second stage is not necessarily controlled by a diffusion process into the particle matrix. For example, it has been suggested that a second stage could be related to exchange reactions with  $Mg^{2+}$  ions which cover natural particles in sea water (Nyffeler *et al.*, 1984). More recently the role of colloids has been invoked whereby rapid formation of metal-colloid and metal-particle associations (*i.e.* adsorption) is followed by a slow coagulation of colloids with filterable ( $>0.45 \mu m$  diameter) particles (Honeyman *et al.*, 1988; Honeyman and Santschi, 1989). If this were the case, data could be easily misinterpreted as the colloidal fraction is, by experimental definition, included in the dissolved phase (Section 1.4). Furthermore, biologically mediated reactions are often observed to proceed in two stages (Davies, 1978; Romeo and Gnassia-Barelli, 1983; Xue *et al.*, 1988); adsorption onto external cell surfaces is followed by diffusive transport into cells.

The mechanisms of sorption kinetics of  $^{137}Cs$  may be understood from its interaction with soils (Kirk and Staunton, 1989) involving diffusion of ions into interlattice sites of micaceous clays. The reaction rate is governed by interlattice geometry and therefore dependent on type of mica and extent of weathering. Micaceous clays (muscovite) were identified, although not quantified, by x-ray diffraction studies (Philips P1710 diffractometer using a  $Cu-\alpha$  source of wavelength 0.154 nm) on suspended sediment in the estuarine and coastal environments of the North Sea; examples for the Humber are shown in Figure 4.6. It is



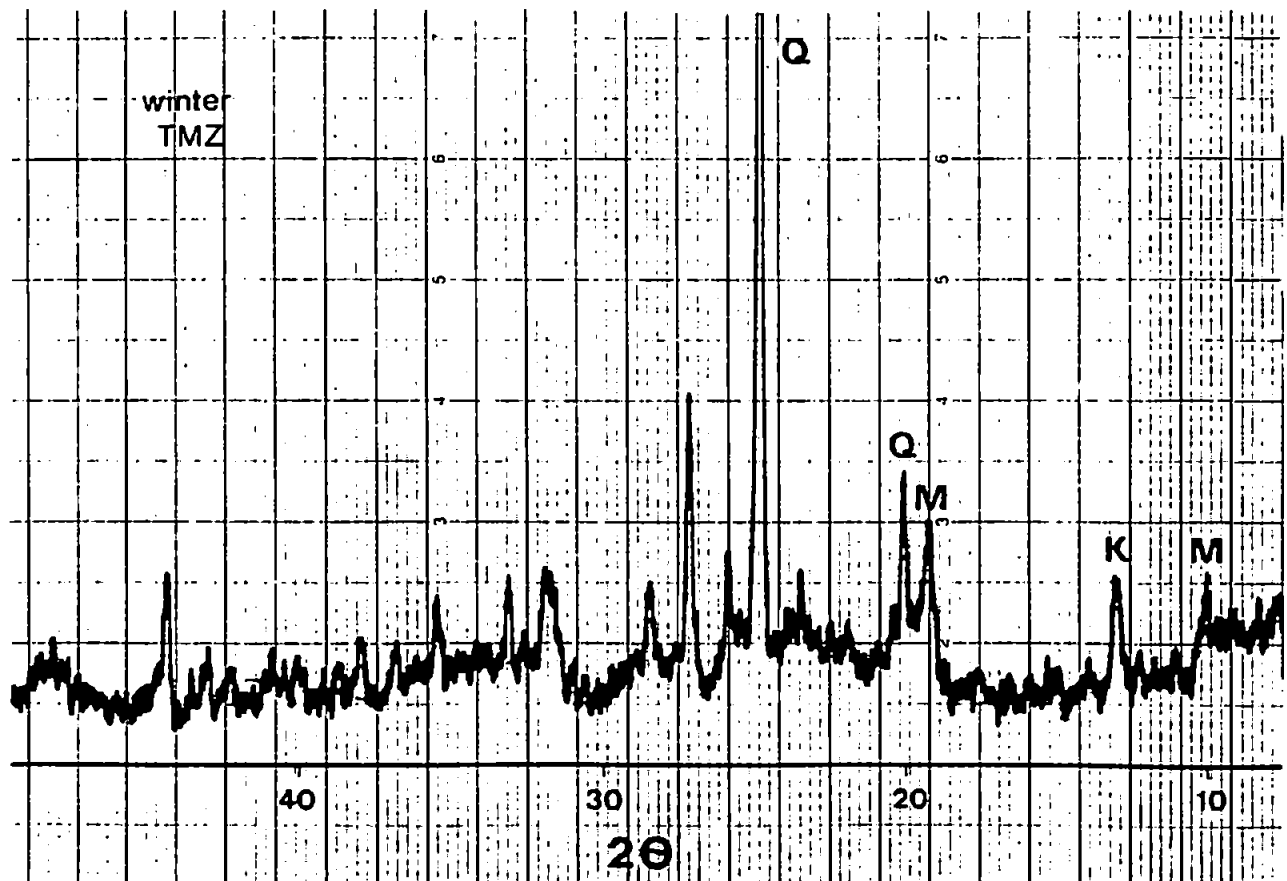
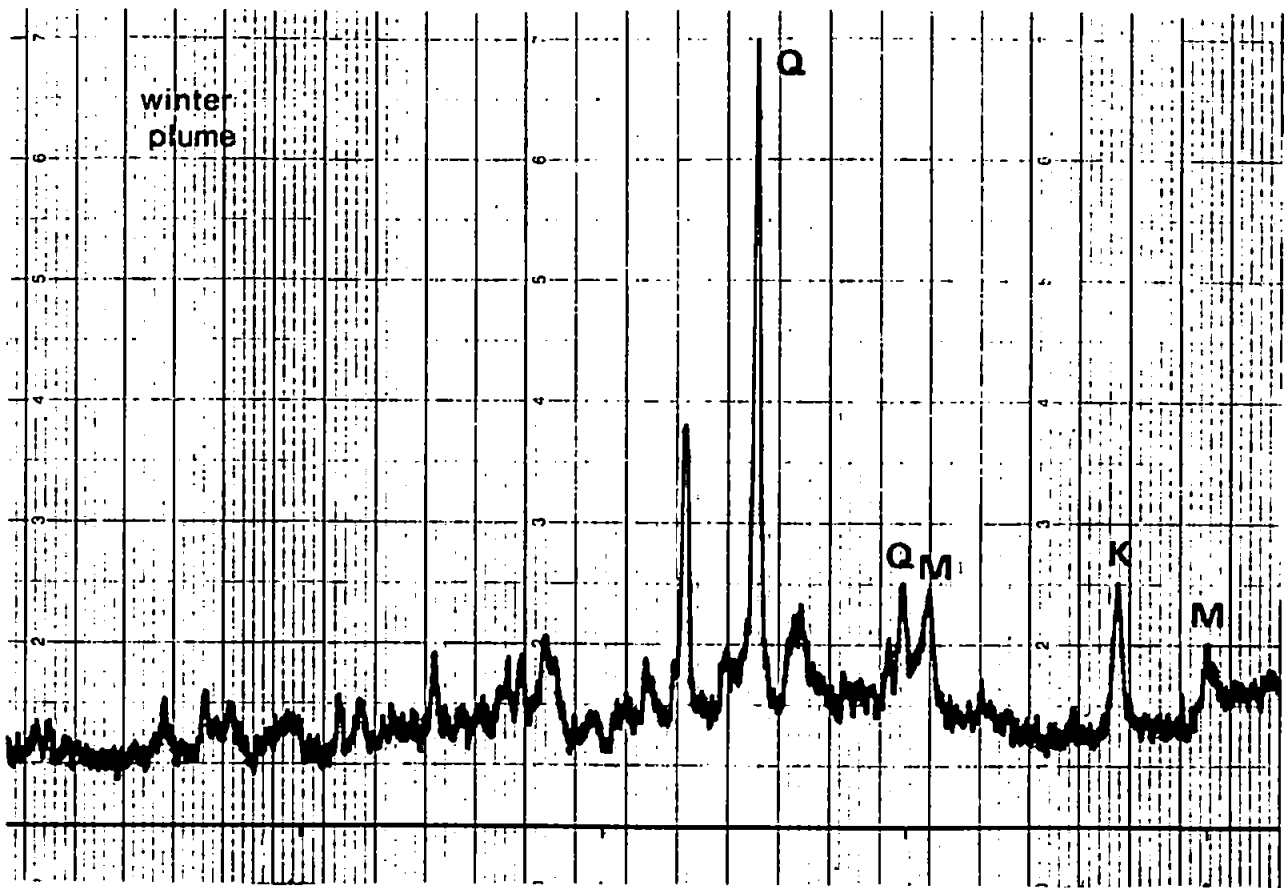


Figure 4.6: Identification of the major crystalline components of suspended sediments from the Humber environment. K = kaolinite; M = muscovite; Q = quartz.

suggested, therefore, that  $^{137}\text{Cs}$  is taken up in two stages by Humber and Thames plume particles by a fast adsorption onto external mineral surfaces (Section 4.3.1.2) followed by a slow migration into interlattice sites of micaceous clay components.

#### 4.3.3: Five-Day $K_D$ s

The results of the 5-day  $K_D$ s for each environment are given in Table 4.7. Figure 4.7 illustrates the results for  $^{109}\text{Cd}$  and  $^{54}\text{Mn}$ , and it is worth emphasizing the remarkable resemblance to the corresponding plot of measured stable particulate metal concentrations (Figure 3.17).

The magnitudes of  $K_D$ s for the plume samples are in the order:

$$^{54}\text{Mn} > ^{65}\text{Zn} > ^{109}\text{Cd}, ^{137}\text{Cs}$$

indicating that  $^{54}\text{Mn}$  has a relatively high particle affinity, whereas  $^{109}\text{Cd}$  and  $^{137}\text{Cs}$  favour solution. This sequence, together with magnitudes, is generally consistent with results from other natural sea water - sediment substrate partitioning investigations using these radioisotopes (Aston and Duursma, 1973; Stanners and Aston, 1981; Li *et al.*, 1984a; 1984b; Nyffeler *et al.*, 1984; Santschi *et al.*, 1984; 1987).

Although levels in the Humber and Thames plumes are quite variable the means of sample suites follow the sequence:

$$\text{Humber (May)} > \text{Humber (December)} > \text{Thames (February)}.$$

Particle affinity is enhanced by diatoms for  $^{109}\text{Cd}$  and  $^{65}\text{Zn}$  by an order of magnitude, and for  $^{54}\text{Mn}$  by a smaller amount. *Phaeocystis* effects a reduced affinity, especially for  $^{54}\text{Mn}$ , although this is still higher than plume particle uptake for  $^{109}\text{Cd}$  and  $^{65}\text{Zn}$ . Plankton filter counts for  $^{137}\text{Cs}$  were always below the limit of detection.

Presumably the temporal differences in Humber plume  $K_D$ s can be explained in terms of elevated productivity / plankton uptake during spring. Thus, there is a

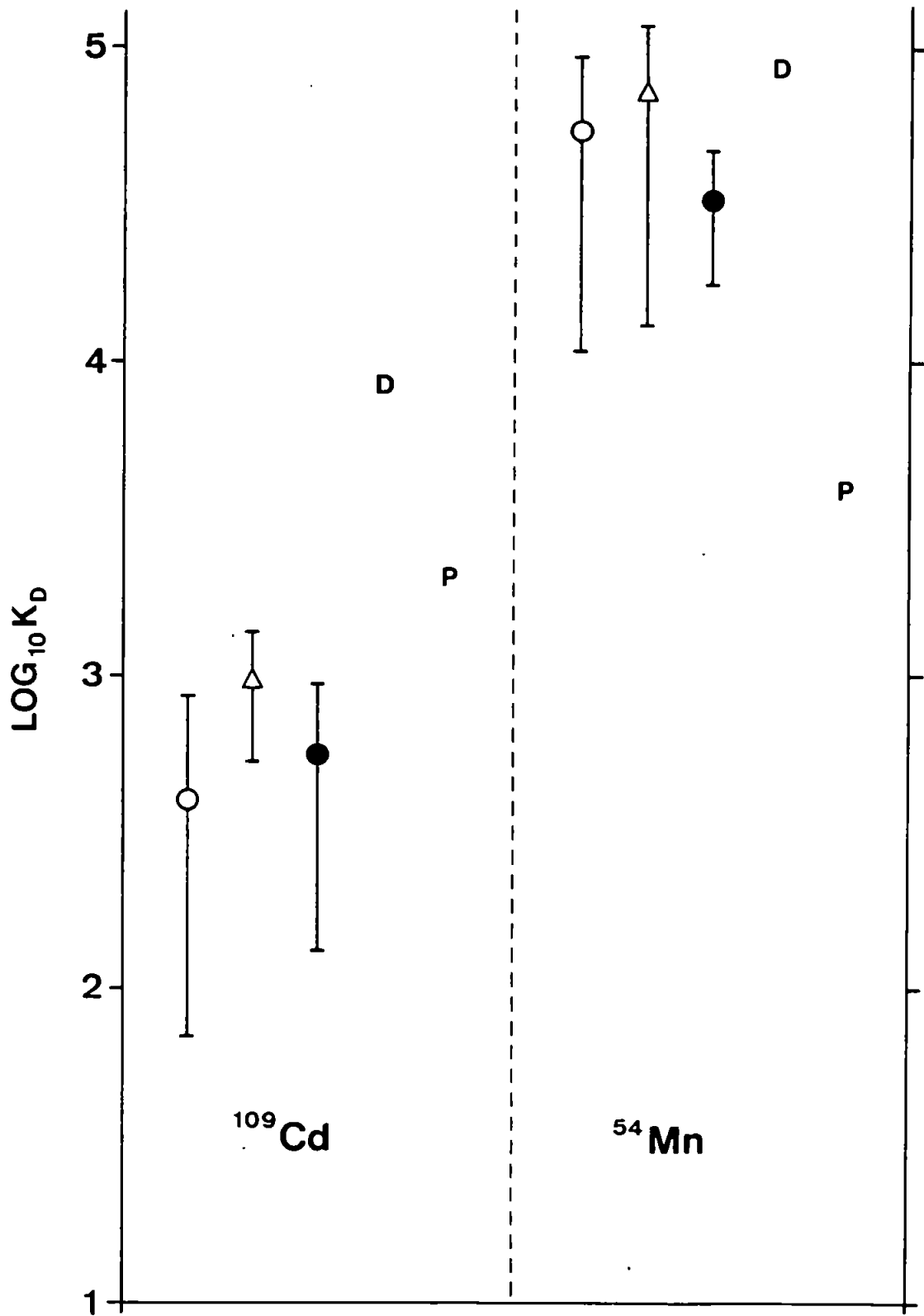


Figure 4.7: Mean ( $\pm$  one standard deviation) of  $K_D$ s for  $^{109}\text{Cd}$  and  $^{54}\text{Mn}$ ; Humber plume during winter (O) and spring ( $\Delta$ ); Thames plume ( $\bullet$ ); diatoms (D); *Phaeocystis* (P).

Table 4.7: Five-day incubation  $K_D$ s;  $\mu \pm 1\sigma$  = mean  $\pm$  one standard deviation, and R = range of the number of samples above the limit of detection (n).

|                       |                   | $K_D \cdot 10^3$  |                   |                  |                  |
|-----------------------|-------------------|-------------------|-------------------|------------------|------------------|
|                       |                   | $^{109}\text{Cd}$ | $^{137}\text{Cs}$ | $^{54}\text{Mn}$ | $^{65}\text{Zn}$ |
| <b>HUMBER PLUME</b>   |                   |                   |                   |                  |                  |
| <i>December, 1988</i> | n                 | 6                 | 5                 | 18               | 18               |
|                       | $\mu \pm 1\sigma$ | 0.40 $\pm$ 0.33   | 0.51 $\pm$ 0.46   | 53.2 $\pm$ 41.8  | 5.43 $\pm$ 5.86  |
|                       | R                 | <0.10 - 1.05      | <0.16 - 1.34      | 10.2 - 173       | 1.44 - 27.4      |
| <i>May, 1990</i>      | n                 | 15                | 3                 | 16               | 16               |
|                       | $\mu \pm 1\sigma$ | 0.95 $\pm$ 0.43   | 0.56 $\pm$ 0.15   | 70.4 $\pm$ 56.9  | 8.76 $\pm$ 3.64  |
|                       | R                 | 0.33 - 1.88       | <0.22 - 0.73      | 14.4 - 221       | 2.6 - 14.9       |
| <b>THAMES PLUME</b>   |                   |                   |                   |                  |                  |
| <i>February, 1989</i> | n                 | 10                | 10                | 10               | 10               |
|                       | $\mu \pm 1\sigma$ | 0.53 $\pm$ 0.40   | 0.31 $\pm$ 0.19   | 32.8 $\pm$ 14.3  | 3.66 $\pm$ 1.53  |
|                       | R                 | 0.26 - 1.62       | 0.17 - 0.84       | 10.4 - 55.6      | 1.46 - 5.94      |
| <b>DIATOMS</b>        |                   |                   |                   |                  |                  |
| <i>April, 1989</i>    | n                 | 4                 | -                 | 4                | 4                |
|                       | $\mu$             | 7.42              | -                 | 86.6             | 29.3             |
| <b>PHAEOCYSTIS</b>    |                   |                   |                   |                  |                  |
| <i>April, 1989</i>    | n                 | 1                 | -                 | 1                | 1                |
|                       | $\mu$             | 2.08              | -                 | 3.9              | 8.06             |

noticeable elevation in  $K_D$  for  $^{109}\text{Cd}$ , borne out not only by a doubling of the mean  $K_D$  but also by a significant increase in the number of detectable Cd filter samples, and only a small increase for  $^{137}\text{Cs}$  coupled with a reduced number of analyses.

Figure 4.8 suggests the reactions of the radioisotopes with the particles are encouraged at higher temperatures and this could account for some observed temporal variability. Although it seems reasonable to assume a relationship between temperature and Mn oxidation rate (cf. Section 2.2.3.3), it is suspected that higher temperatures are conducive of particle production and therefore the effect observed in Figure 4.8 may simply reflect experimental artifact. Moreover, results reported earlier (e.g. Section 3.2.3) suggest that the role of particle composition

Table 4.8a: Hydrographic conditions associated with radiochemical sampling campaigns; mean  $\pm$  one standard deviation ( $\mu \pm 1\sigma$ ) and range (R) of parameters at sampling sites given.

|              |                   | Salinity (‰)   | Temperature (°C) | Suspended solids (mg/l) |
|--------------|-------------------|----------------|------------------|-------------------------|
| HUMBER PLUME |                   |                |                  |                         |
| Dec. 1988    | $\mu \pm 1\sigma$ | 33.6 $\pm$ 1.3 | 7.5 $\pm$ 0.7    | 17.2 $\pm$ 16.9         |
|              | R                 | 28.8-34.3      | 6.4-8.3          | 2.2-55.2                |
| May, 1990*   | $\mu \pm 1\sigma$ | 33.5 $\pm$ 1.1 | 10.8 $\pm$ 1.0   | 7.9 $\pm$ 6.6           |
|              | R                 | 30.8-34.3      | 9.8-12.6         | 3.5-30.8                |
| THAMES PLUME |                   |                |                  |                         |
| Feb. 1989    | $\mu \pm 1\sigma$ | 28.0 $\pm$ 5.1 | 7.1 $\pm$ 0.5    | 85.7 $\pm$ 97.9         |
|              | R                 | 21.1-34.4      | 6.5-8.1          | 16.4-324.9              |
| DIATOMS      |                   |                |                  |                         |
| Apr. 1989    | $\mu$             | 34.7           | 7.0              | 1.13                    |
| PHAEOCYSTIS  |                   |                |                  |                         |
| Apr. 1989    | $\mu$             | 35.0           | 8.4              | 2.49                    |

\* Salinity and temperature data are based on only 9 sample sites as data for the remaining 7 sites were not available at the time of writing.

Table 4.8b: Particle composition encountered or anticipated during radiochemical sampling campaigns. Mean of 3 or 4 analyses given.

|                                     | Fe (mg/g) | Mn (mg/g) | Fe/Mn | C (%) | C/N  | SSA (m <sup>2</sup> /g) |
|-------------------------------------|-----------|-----------|-------|-------|------|-------------------------|
| HUMBER PLUME <sup>1</sup>           |           |           |       |       |      |                         |
| Dec. 1988                           | 8.75      | 0.91      | 9.4   | 4.3   | 17.1 | 12.8                    |
| May 1990                            | 6.90      | 0.84      | 8.3   |       |      | 9.0                     |
| THAMES PLUME <sup>2</sup>           |           |           |       |       |      |                         |
| Feb. 1989                           | 4.66      | 0.58      | 8.3   | 4.6   | 13.0 | 11.6                    |
| PLANKTON RICH MATERIAL <sup>3</sup> |           |           |       |       |      |                         |
|                                     | 1.6       | 0.38      | 5.7   | 22.9  | 8.0  | 0.8                     |

<sup>1</sup> As Table 2.7.

<sup>2</sup> Mean of 4 samples from the plume and outer estuary at salinities  $> 20$  ‰.

<sup>3</sup> Samples from the southern North Sea during summer (Table 2.7).

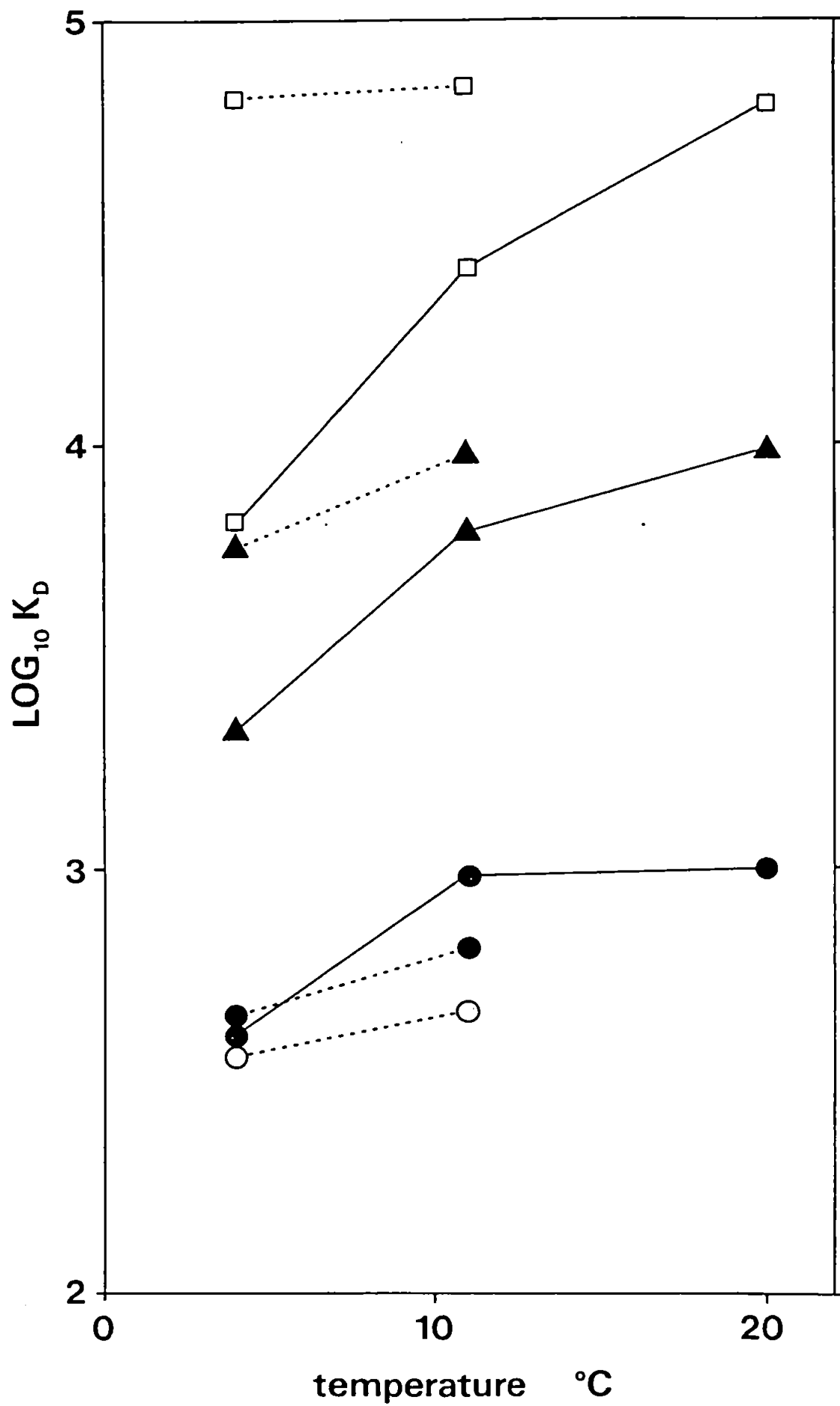


Figure 4.8: Effects of temperature on  $K_D$  for two samples from the Humber plume during spring;  $^{109}\text{Cd}$  (●);  $^{137}\text{Cs}$  (○);  $^{54}\text{Mn}$  (□);  $^{65}\text{Zn}$  (▲).

is more significant to these regional and temporal differences in  $K_D$ .

Table 4.8 summarizes the hydrographic conditions encountered at the sampling sites, and lists some important particle properties which are characteristic of these environments as determined by the techniques outlined in Sections 2.1.2 and 2.1.3. Thus, relatively high leachable Fe and Mn concentrations, reflected by a high BET specific surface area (SSA) of plume samples, suggests that uptake is largely controlled by the reaction with hydrous Fe and Mn oxide coatings (Takematsu, 1979; Lion *et al.*, 1982; Millward and Moore, 1982; Davies-Colley *et al.*, 1984), whereas the high C content and low SSA of plankton-rich material invites a biologically mediated interpretation. The specific mechanisms of these isotope-particle interactions can now therefore be referred to Section 4.3.1. Thus,  $^{109}\text{Cd}$  distributions can be explained by its high affinity for planktonic phases compared with Fe and Mn oxides. Presumably differences in uptake of  $^{109}\text{Cd}$  (and more notably  $^{54}\text{Mn}$ ) observed between diatom and *Phaeocystis* communities are related to the different cellular characteristics; whereas diatoms are encased in a siliceous material, *Phaeocystis* present a slimy organic surface. In contrast, a small uptake of  $^{137}\text{Cs}$  by plankton, corroborated by similar observations using picoplankton (Fisher, 1985), suggests that this element is inert to cellular material; perhaps an analogy can be drawn with another Group 1 ion,  $\text{Na}^+$ , which is weakly and minimally adsorbed to cell walls through ionic charge bonding to carboxyl groups and sulphates (Crist *et al.*, 1981).

#### 4.3.4: $K_D$ Relationships with Master Variables In Plumes

No unambiguous dependence of  $K_D$  for any metal on salinity or suspended solids concentration could be discerned. It was assumed that more subtle relationships did in fact exist, but were masked by the inherent practical and analytical limitations, in particular those responsible for loss of material from filters (Table 4.5). Considering inter-metal  $K_D$  ratios eliminated errors associated with filter manipulations and established the following relationships.

Zinc was chosen as a reference isotope as previous radiochemical studies

suggest that its partitioning is relatively insensitive to environmental change (Aston and Duursma, 1973; Olsen *et al.*, 1989). Figure 4.9 shows a linear decrease of  $K_D^{109\text{Cd}} / K_D^{65\text{Zn}}$  and  $K_D^{137\text{Cs}} / K_D^{65\text{Zn}}$  with salinity for plume samples. The regression analyses are for the Thames plume for which a greater range of salinity was encompassed, and indicate a high degree of significant correlation. These relationships suggest, relative to  $^{65}\text{Zn}$ , desorption from the particles with an increase of salinity. For  $^{109}\text{Cd}$ , this is probably the result of the formation of highly soluble and stable chloro-complexes (Edmond *et al.*, 1985; Bourg, 1987; Elbaz-Poulichet *et al.*, 1987). Caesium exists in sea water predominantly as the free ion,  $\text{Cs}^+$  (Table 4.1), and a more plausible explanation for the observed desorption would therefore be enhanced competition for available adsorption sites (occupied non-selectively; Section 4.3.1.2) by major sea water cations, and in particular  $\text{K}^+$  (Aston and Duursma, 1973; Stanners and Aston, 1981; Kamineni *et al.*, 1986; Ticknor *et al.*, 1989). A salinity induced desorption of Cs has also been inferred from both field observations (Olsen *et al.*, 1981; 1989; Zucker *et al.*, 1984) and laboratory experiments (Aston and Duursma, 1973; Patel *et al.*, 1978; Stanners and Aston 1981). The regression analyses indicate that the rate of desorption with salinity relative to  $^{65}\text{Zn}$  of  $^{109}\text{Cd}$  is essentially double that of  $^{137}\text{Cs}$ , and that extrapolation back to fresh water yields respective relative values of 0.6 and 0.3.

Plankton samples are characterized by high ratios of  $K_D^{109\text{Cd}} / K_D^{65\text{Zn}}$  (Figure 4.9) and this can be related to preferential assimilation of Cd, as well as Cd substitution for Zn in certain plankton macromolecules (Price and Morel, 1990); higher ratios encountered in the Humber plume during spring when compared with winter can be accounted for by enhanced productivity.

Although  $K_D^{54\text{Mn}} / K_D^{65\text{Zn}}$  was not correlated with salinity, this ratio was significantly positively correlated with suspended solids concentration for the Humber plume during December ( $r^2 = 44.9\%$ ;  $p = 0.001$ ). It has been demonstrated that both the rate of Mn oxidation (Morris and Bale, 1979) and its distribution coefficient (Li *et al.*, 1984b) increase with increasing particle concentration, and



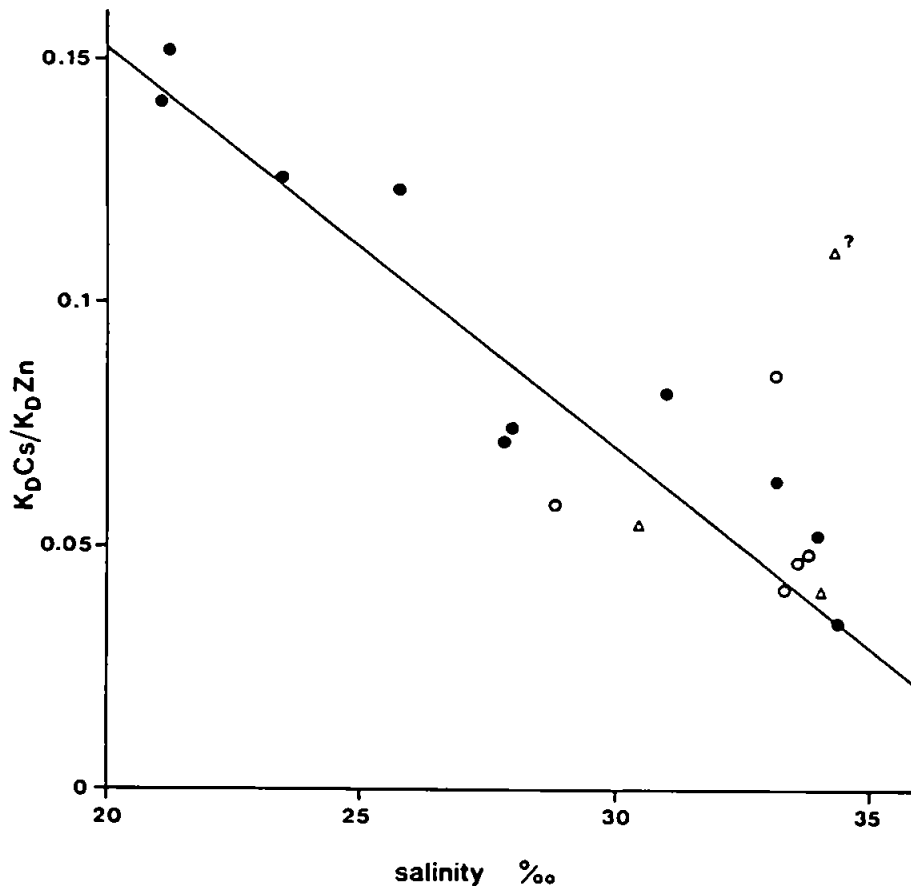
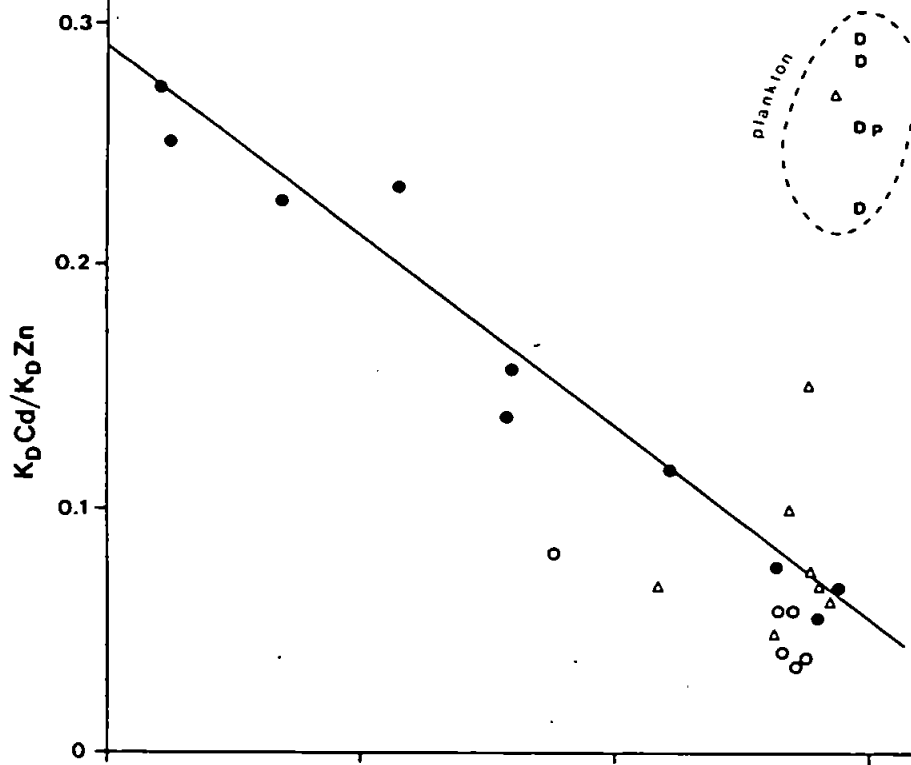


Figure 4.9: Relationship between salinity and  $K_D$  ratios; symbols are as for Figure 4.7. Regression analyses for Thames samples:

$$K_D^{109}\text{Cd} / K_D^{65}\text{Zn} = 0.601 - 0.0159S; \quad r^2 = 94.6\%; \quad p \leq 0.0005$$

$$K_D^{137}\text{Cs} / K_D^{65}\text{Zn} = 0.304 - 0.00757S; \quad r^2 = 89.2\%; \quad p \leq 0.0005$$

presumably this reflects a relationship between rate of oxidation and concentration of autocatalytic sites. However, lack of such a correlation with other sample suites suggests that local variability in particle composition is also a very important factor (Morris and Bale, 1979).

#### 4.3.5: Mixing Experiments

##### 4.3.5.1: $K_D$ Dependence on Salinity

Profiles of  $K_D$ s in the model estuaries are shown in Figure 4.10.

Zinc is apparently independent of salinity indicating a successful choice for the basis of isotope ratios (Section 4.3.4).

As indicated by the previous results (Section 4.3.4) both  $^{109}\text{Cd}$  and  $^{137}\text{Cs}$  are subject to desorption with salinity. The effect is greater for  $^{137}\text{Cs}$  for which  $K_D$  changes by almost an order of magnitude along the salinity gradient, compared with a corresponding factor of about 4 for  $^{109}\text{Cd}$ . Desorption is not a linear function of salinity as predicted from Figure 4.9; concave profiles result in fresh water end-member  $K_D$  values relative to  $^{65}\text{Zn}$  of at least 0.4 and 1.0 respectively.

Manganese displays an increase in  $K_D$  with salinity of more than an order of magnitude. This contests the results of earlier investigations (Evans and Cutshall, 1973; Li *et al.*, 1984a) in which a slight desorption was noted. It is suggested that the low suspended solids loadings involved (not specified by the former authors but evidently low; < 18 mg/l given by the latter authors) imparted a high proportion of adsorbed Mn (compared with oxidized species) which undergoes desorption as a result of increased salinity through exchange with major sea water cations.

The results reported here concord with those of Morris *et al.* (1982a) derived from laboratory experiments using Tamar waters. In more detail, it is worth considering the sag in  $K_D$  at 9 ‰ which is a feature of all three models. A minimum in efficiency of removal from solution over similar salinities was also demonstrated in Tamar waters (Morris *et al.*, 1982a; Vojak *et al.*, 1985). The reduction in removal rate at the onset of estuarine mixing was attributed to

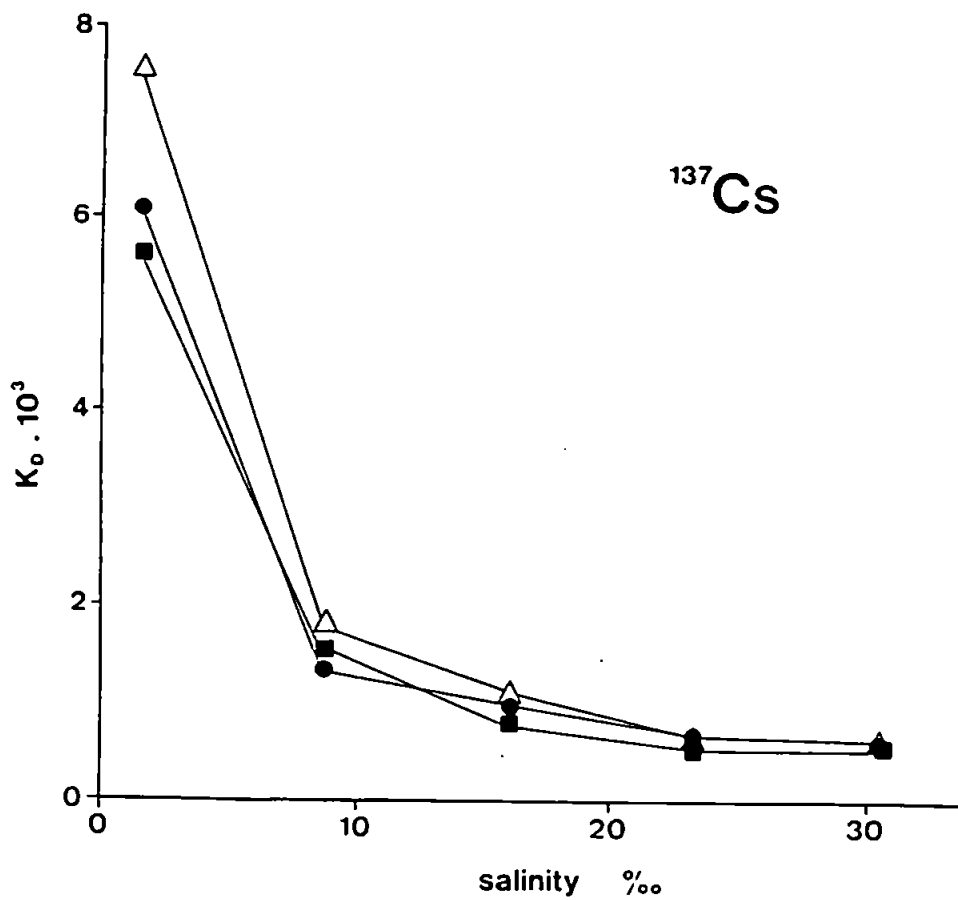
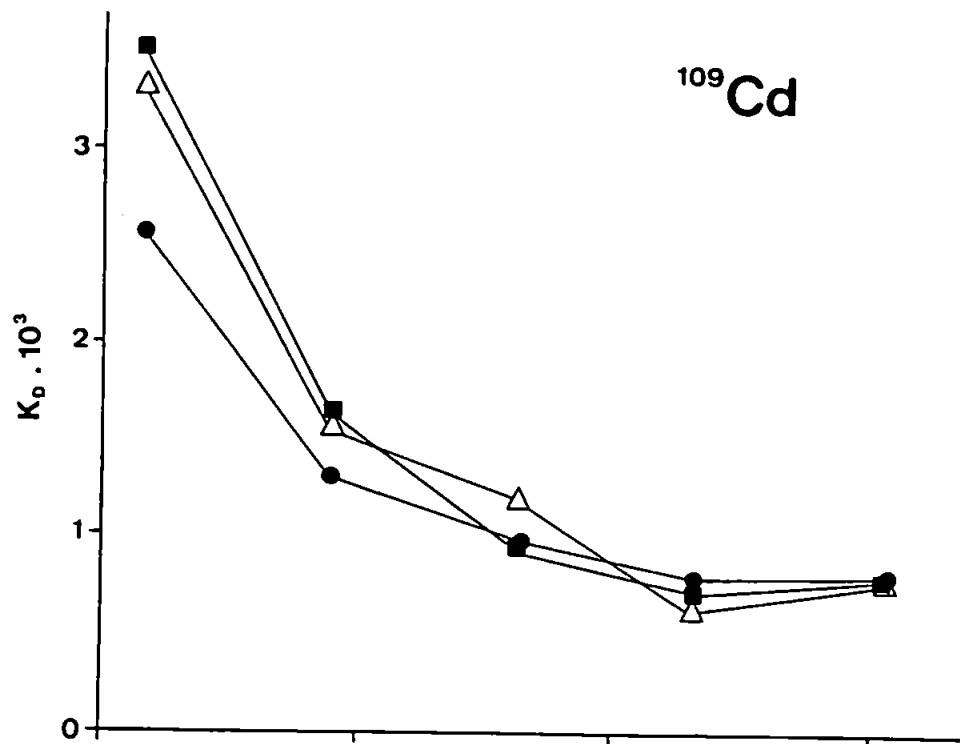


Figure 4.10: Effect of simulated salinity and suspended sediment gradients on  $K_D$ . Symbols refer to model estuaries A, B and C as in Figure 4.3.

a. <sup>109</sup>Cd and <sup>137</sup>Cs.

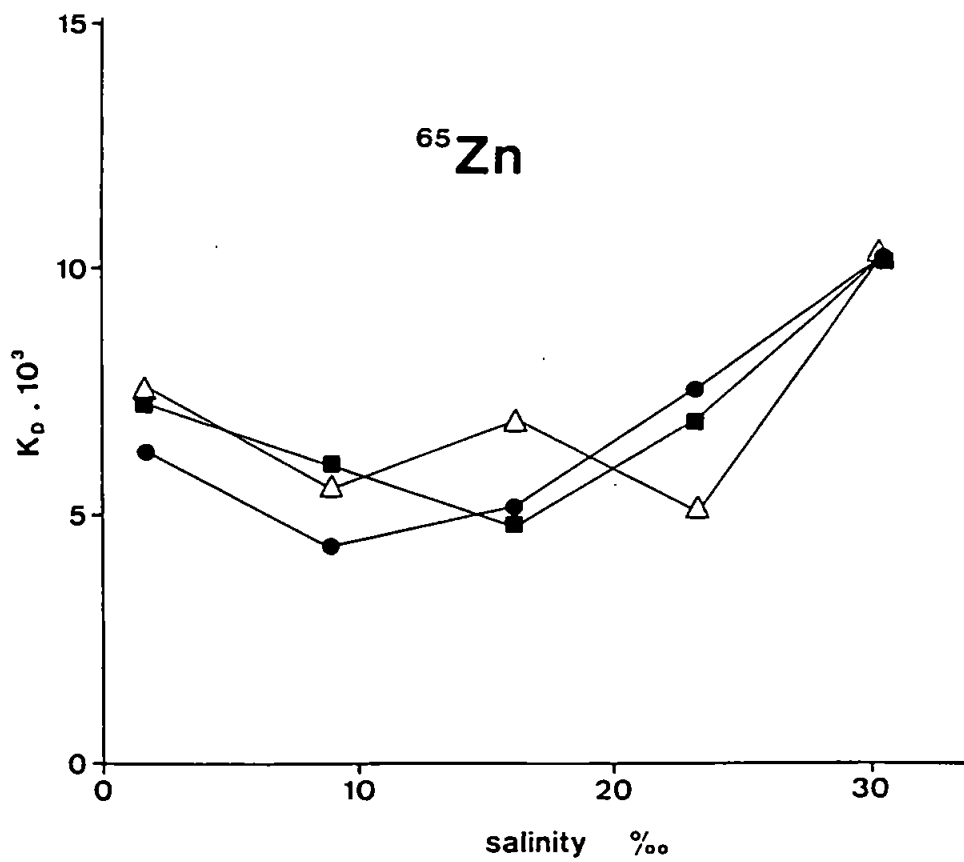
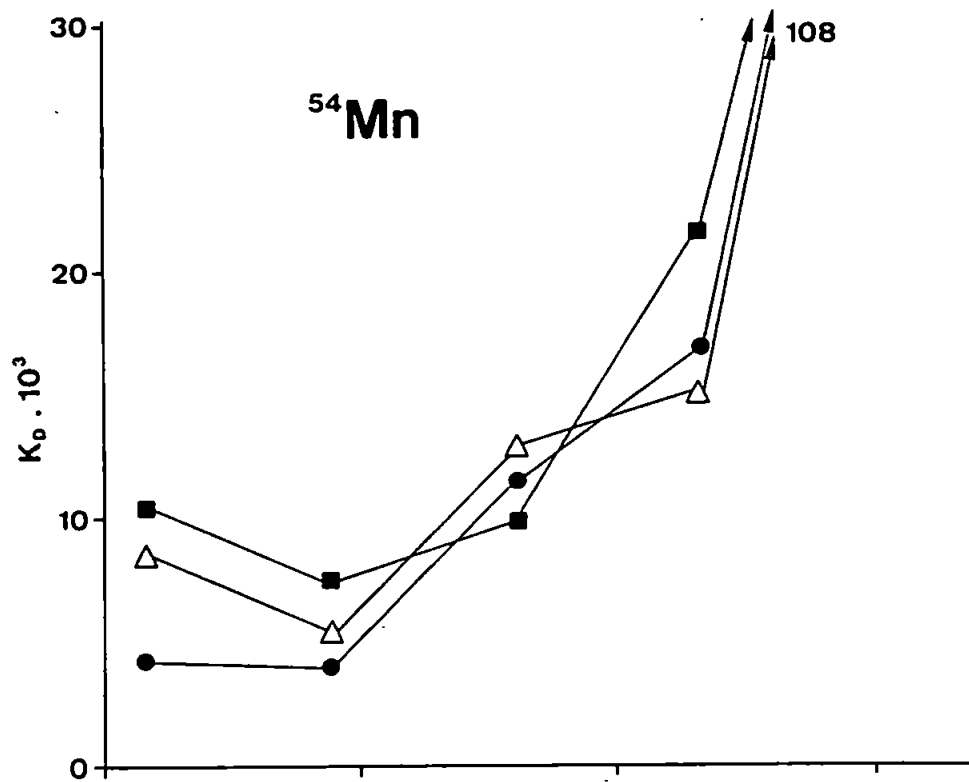


Figure 4.10 (continued): b. <sup>54</sup>Mn and <sup>65</sup>Zn.

competition for active catalytic sites by the major sea water cations and the subsequent increase was related to an increase of dissolved Mn, in particular mid-estuarine enhancements resulting from localized inputs such as mobilization of reduced Mn from resuspended bed sediment (Morris *et al.*, 1982a). Although inhibition of Mn oxidation by increasing sea water cations could readily account for an initial decrease in  $K_D$  observed in the present study, Mn distributions in Tamar samples cannot be extrapolated to Humber waters derived from mixing.

Presumably the REM sample was deficient in dissolved  $O_2$  (*cf.* Gameson, 1982; Edwards and Lai, 1984) and it is possible that reaeration was not complete during sampling and filtration; consequently, a dissolved  $O_2$  gradient was created in the model estuaries. Thus, an increase in  $O_2$  with salinity could account for an increase in  $^{54}\text{Mn } K_D$ . Alternatively and/or additionally, it has been demonstrated that soluble organic matter may retard Mn oxidation by complexing the oxidizable species (Wilson, 1980). It is not unreasonable to assume that a decrease of dissolved organic carbon (DOC), especially humics, hence complexing capacity with salinity exists in the model estuaries (*cf.* Moore *et al.*, 1979; van Bennekom and Salomons, 1981; Ittekkot *et al.*, 1982; Mantoura and Woodward, 1983) which would be responsible for an increase in Mn oxidation with salinity.

It is suggested that the combination of such effects (*i.e.* resulting from gradients in  $O_2$  and DOC, and salinity directly) is responsible for the observed  $^{54}\text{Mn}$  distribution; these ideas are presented in Figure 4.11.

#### 4.3.5.2: $K_D$ Dependence on Suspended Solids Concentration

The mixing experiments revealed no clear dependence of  $K_D$  on suspended solids concentration (*i.e.* physical processes). Although a relationship was established by Duursma and Bosch (1973) their experiments were conducted in the presence of unrealistic solids concentrations (of the order g/l). However, more recent laboratory experiments (Li *et al.*, 1984b) and field observations (McKee *et al.*, 1986; Balls, 1989a) have demonstrated that, for several metals (with the exception of Mn; Section 4.3.4) the solid:solution distribution decreases with

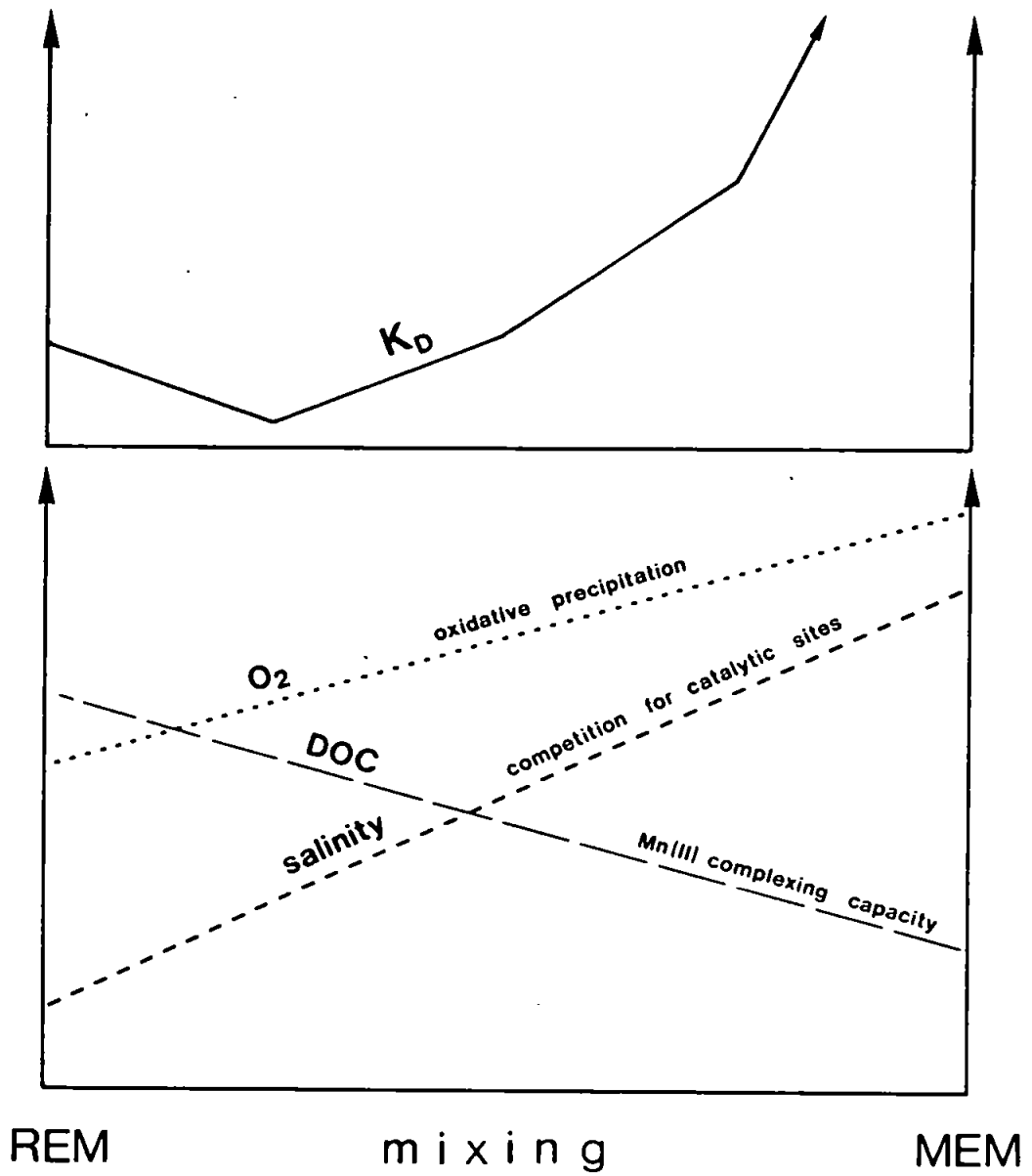


Figure 4.11: Hypothetical gradients of salinity, dissolved organic carbon (DOC) and dissolved O<sub>2</sub> resulting from end-member mixing, and their influence on <sup>54</sup>Mn K<sub>D</sub>.

increasing particle load in coastal waters. It is conceivable that such field observations are the result of an inverse relationship between particulate metal concentration and suspended solids concentration as exemplified in Figure 3.16. Nevertheless, the results of this study signify an overwhelming influence of salinity on metal solid-solution partitioning.

#### 4.3.6: Isotope Removal from Filters

The results of all leaching experiments are given in Table 4.9, and those for  $^{109}\text{Cd}$  and  $^{137}\text{Cs}$  are illustrated in Figure 4.12. Evidently  $^{109}\text{Cd}$  is the most loosely held isotope to particles and is removed from plume samples by filtered sea water suggesting a fully reversible adsorption; removal by sea water for other

Table 4.9: Removal,  $r$ , of isotopes from filter samples. Mean  $\pm$  one standard deviation ( $\mu \pm 1\sigma$ ) of  $n$  determinations given.

| <i>Treatment</i>                |                          |                   | <i>r</i> (%)      |                   |                  |                  |
|---------------------------------|--------------------------|-------------------|-------------------|-------------------|------------------|------------------|
|                                 |                          |                   | $^{109}\text{Cd}$ | $^{137}\text{Cs}$ | $^{54}\text{Mn}$ | $^{65}\text{Zn}$ |
| Humber and Thames winter plumes | <i>filtered seawater</i> | $n$               | 8                 | 6                 | 7                | 8                |
|                                 |                          | $\mu \pm 1\sigma$ | 99 $\pm$ 1.3      | 43 $\pm$ 17       | 36 $\pm$ 12      | 46 $\pm$ 12      |
|                                 | $\text{NH}_4\text{OAc}$  | $n$               | 6                 | 6                 | 8                | 8                |
|                                 |                          | $\mu \pm 1\sigma$ | 98 $\pm$ 2.4      | 38 $\pm$ 12       | 42 $\pm$ 15      | 55 $\pm$ 10      |
|                                 | <i>HCl</i>               | $n$               | 7                 | 7                 | 8                | 8                |
|                                 |                          | $\mu \pm 1\sigma$ | all 100           | 63 $\pm$ 9.3      | 99 $\pm$ 0.5     | 95 $\pm$ 3.3     |
| Kinetic experiment (Thames)     | $\text{NH}_4\text{OAc}$  | $n$               | 8                 | 8                 | 8                | 8                |
|                                 |                          | $\mu \pm 1\sigma$ | 89 $\pm$ 7.5      | 17 $\pm$ 16       | 49 $\pm$ 9.0     | 36 $\pm$ 11      |
| Humber spring plume             | $\text{NH}_4\text{OAc}$  | $n$               | 1                 | 1                 | 1                | 1                |
|                                 |                          | $\mu$             | 70                | 48                | 15               | 51               |
| Mixing experiment B             | $\text{NH}_4\text{OAc}$  | $n$               | 5                 | 5                 | 5                | 5                |
|                                 |                          | $\mu \pm 1\sigma$ | 75 $\pm$ 6.7      | 30 $\pm$ 7.2      | 15 $\pm$ 7.3     | 48 $\pm$ 12      |
| REM <sub>A</sub>                | <i>HCl</i> *             | $n$               | 1                 | 1                 | 1                | 1                |
|                                 |                          | $\mu$             | 98                | 64                | 96               | 98               |
|                                 | $\text{HNO}_3$ *         | $\mu$             | 100               | 90                | 100              | 99               |

\*Sequential extraction.

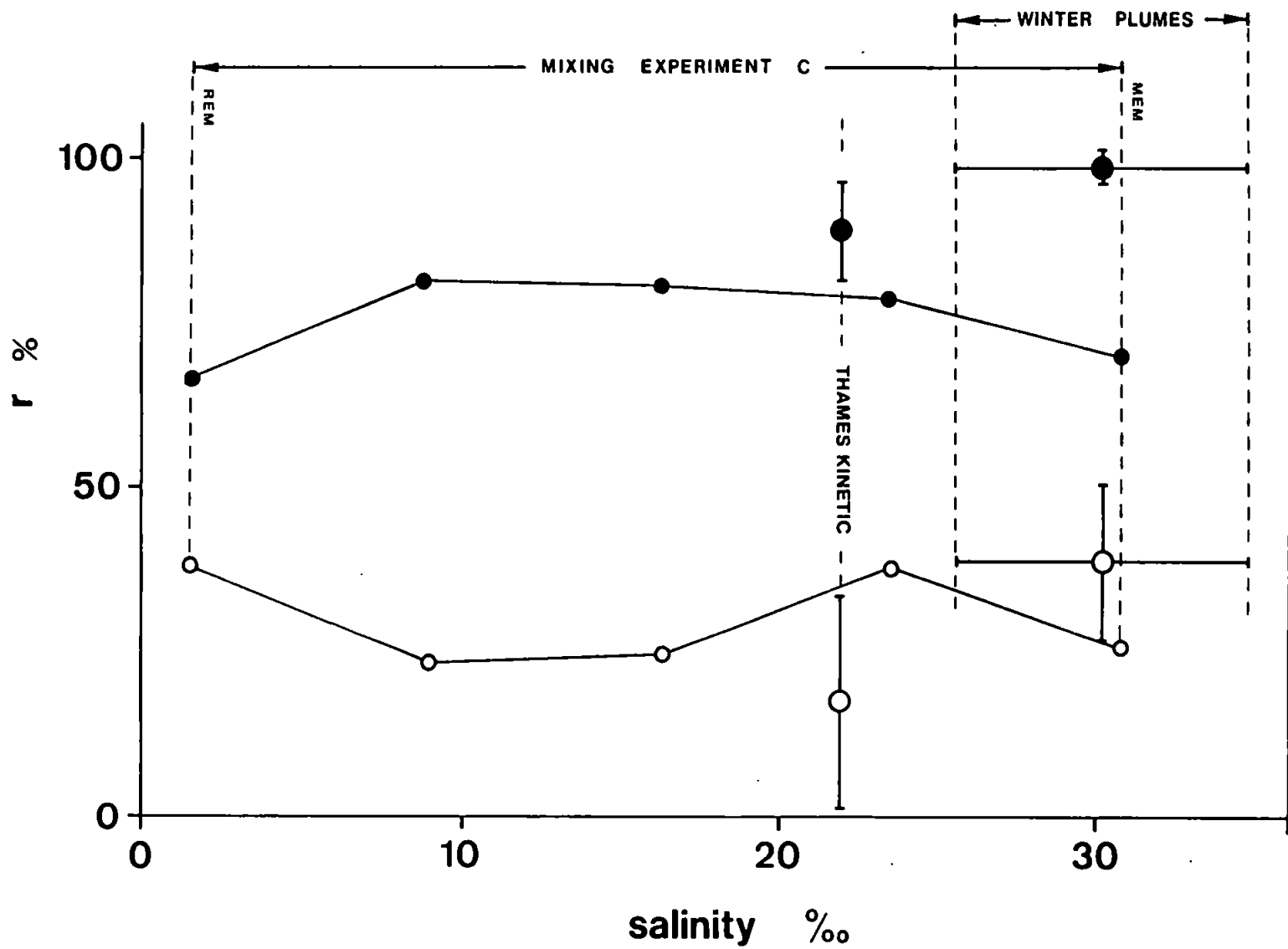


Figure 4.12: Removal,  $r$ , of  $^{109}\text{Cd}$  (●) and  $^{137}\text{Cs}$  (○) from filter samples by  $\text{NH}_4\text{OAc}$  treatment.



isotopes is about 40%. Ammonium acetate is equally effective in removal, probably by similar mechanisms of ion exchange (Cd, Cs and Zn) and attack of oxide phases (Mn). Whereas 1M HCl can recover almost all  $^{109}\text{Cd}$ ,  $^{54}\text{Mn}$  and  $^{65}\text{Zn}$ , significant resistance is offered by  $^{137}\text{Cs}$  ions; even treatment of  $\text{REM}_A$  with 50%  $\text{HNO}_3$  failed to release 10% of the adsorbed  $^{137}\text{Cs}$ . This irreversibility, which has also recently been demonstrated with clay bearing stream gravel deposits (Cerling *et al.*, 1990), can be accounted for by migration of Cs ions into wedge and/or interlattice sites (Section 4.3.2.1) where access by other cations is very limited (Sawhney, 1972; Evans *et al.*, 1983). It must be appreciated that the extent of salinity induced Cs desorption inferred from Figure 4.10 cannot conceivably be reconciled with such a large fraction of irreversibly held ions and has, therefore, been overestimated.

Leaching a series of filters generated from a kinetic experiment and a series derived from a mixing experiment with  $\text{NH}_4\text{OAc}$  did not establish a dependence of removal on time of isotope-solid phase exposure and salinity respectively (Figure 4.12).

Recovery of  $^{109}\text{Cd}$  and  $^{54}\text{Mn}$  by  $\text{NH}_4\text{OAc}$  from mixing experiment and Humber (spring) plume samples was low when compared with earlier (winter) plume samples (Table 4.9). Treatment of the former filters was undertaken shortly (less than two days) after initial counting which itself was undertaken within a few days of returning from sea. In contrast, winter plume samples were counted at least two weeks after collection and leached up to 4 weeks later. The occurrence of some ageing process, for example associated with the demise of the surface microstructural properties (Crosby *et al.*, 1983; Glegg, 1987), is therefore invoked to explain how  $^{109}\text{Cd}$  and  $^{54}\text{Mn}$  ions become more accessible with time.

#### 4.3.7: Comparison with Observational Studies

Although results from the current research have generally been reconciled with published results, it must be questioned whether the implications from this

process oriented study can be related directly with field observations in the specific environments under investigation. For instance, the similarity between 5-day  $K_D$ s and measured particulate metal concentrations has already been noted (Section 4.3.3).

A conservative seaward decrease of dissolved Zn in the Humber Estuary is generally observed (Gardiner, 1982; Edwards *et al.*, 1987), substantial mid-estuarine inputs probably reflect large industrial discharges (*cf.* Section 2.2.3.2). Balls (1985a) observed conservative Cd behaviour in the outer Humber and, although Water Authority analyses only just exceed their limits of detection, data presented could be interpreted in terms of an upper estuary input from desorption (Gardiner, 1982; Edwards *et al.*, 1987). These observations therefore support  $K_D$ s derived for this estuary from the mixing experiment (Section 4.3.5.1).

Radiochemically-derived  $K_D$ s for the Humber plume are compared with stable isotope equivalents (Table 4.10) derived from either preliminary CH42 metal data corresponding to PES stations (*i.e.* with less emphasis on anchored tidal stations; Section 3.1.2), or, where not analyzed, from the literature. The magnitudes of both sets of  $K_D$ s follow the same sequence, although the stable  $K_D$ s are higher than those derived from the radiochemical experiments by an order of magnitude or more. The discrepancy is attributable to the incorporation of total, or near total particulate metal concentrations in the stable calculations thereby including metals held in resistant phases which are unable to participate in short-term biogeochemical reactions simulated by the radioisotopes. The ratio of radiochemical to stable  $K_D$  therefore gives an estimate of the fraction of *reactive* particulate metal and is about 1:50 for all metals.

Complementary field and experimental observations suggest that the application of radiotracers to reproduce stable trace metal counterpart behaviour is justified for marine environments and therefore encouraged the use of 5-day  $K_D$ s as a predictive tool for the Humber Estuary as exemplified in the following Section.

Table 4.10: Comparison of  $K_D$ s derived from radio- and analogue stable-isotope data.

|    | $K_D \cdot 10^3$           |                             | Stable concentration <sup>1</sup> |                                 |
|----|----------------------------|-----------------------------|-----------------------------------|---------------------------------|
|    | radio-isotope <sup>2</sup> | stable-isotope <sup>3</sup> | dissolved ( $\mu\text{g/l}$ )     | particulate ( $\mu\text{g/g}$ ) |
| Cd | 0.40                       | 20                          | 0.025                             | 0.5                             |
| Cs | 0.51                       | 20                          | 0.40                              | 8.0                             |
| Mn | 53                         | 2900                        | 0.30                              | 850                             |
| Zn | 5.4                        | 210                         | 0.60                              | 120                             |

<sup>1</sup> Sources of information. Dissolved Cd, Cs, Mn and Zn; as Table 4.2: particulate Cd, Mn, Zn; analyses of PES samples from CH42: particulate Cs; based on concentrations in fine sediments of North Sea estuaries (Förstner *et al.*, 1982; Salomons and Mook, 1987).

<sup>2</sup> December 1988 values.

<sup>3</sup>  $K_D = \frac{\text{particulate concentration}}{\text{dissolved concentration}} \cdot 1025$

#### 4.3.8: $K_D$ Predictive Concept

Figure 4.13a shows the mean 5-day  $K_D$ s for  $^{109}\text{Cd}$  at each salinity of the mixing experiment and the corresponding dissolved concentration of Cd as determined during an axial survey by the Water Authorities (Edwards *et al.*, 1987). The concentration of reactive (Section 4.3.7) Cd associated with the particulate phase as calculated from Equation 2.9 predicts a seaward decrease from about 0.4 to 0.1  $\mu\text{g/g}$ . Applying this approach to Zn also gives rise to a seaward particulate decrease (Figure 4.13b); this is observed for leachable particulate Zn in the Thames, Scheldt and Weser estuaries (Section 2.2.3.1) and would therefore probably occur in the Humber if unperturbed by large industrial effluents. Figure 4.13c predicts an upper estuary peak in dissolved Mn from mean 5-day  $K_D$ s (although far from equilibrium values) and observed (Section 2.2.2.2) and modelled (Figure 4.3) HOAc/ $\text{NH}_2\text{OH} \cdot \text{HCl}$  leachable particulate Mn profiles.

Although reactive and leachable particulate concentrations have implicitly been referred to interchangeably, a reactive component of the particles was not

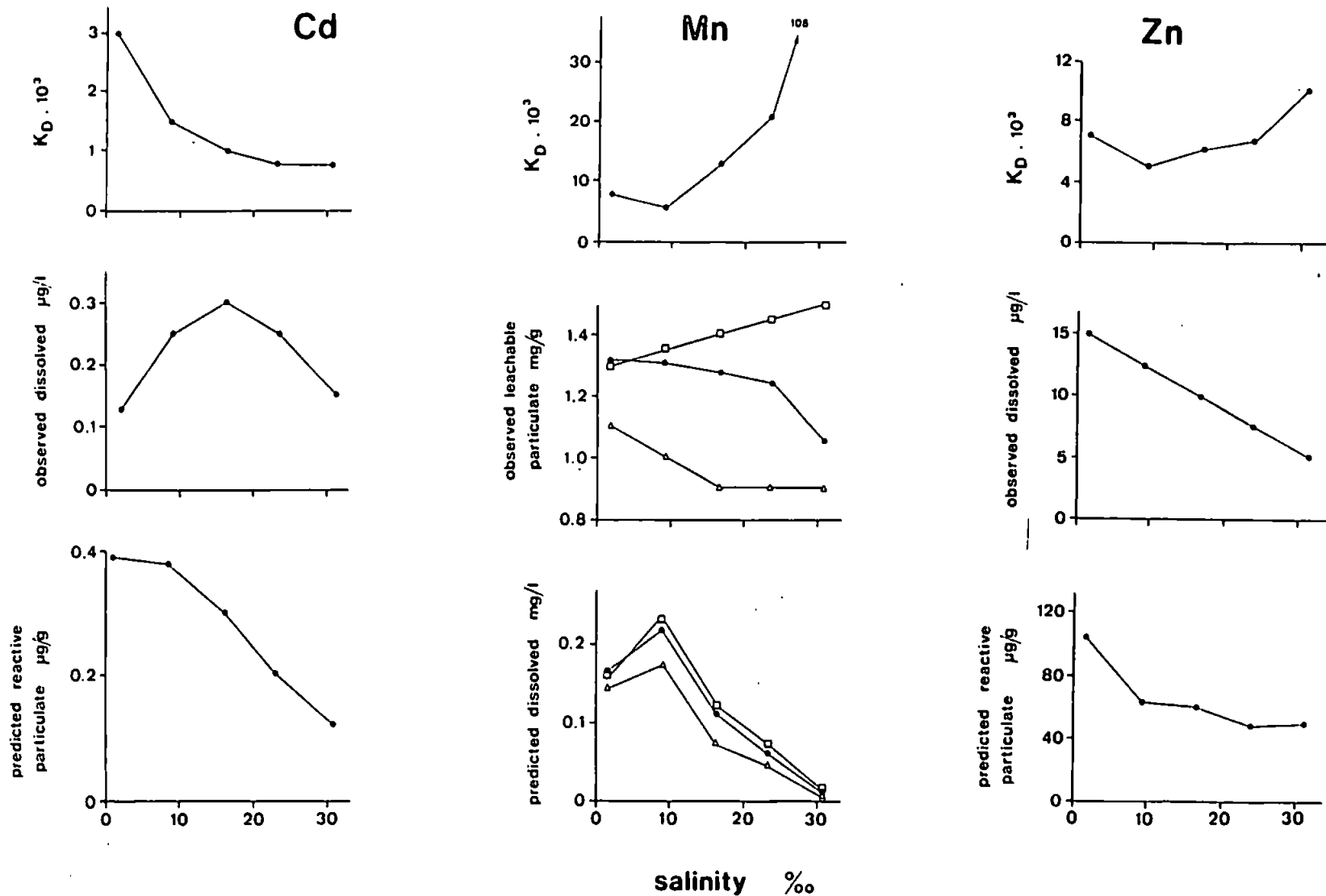


Figure 4.13: The use of 5-day  $K_D$ s to predict the distributions of particulate reactive Cd and Zn from published dissolved concentrations (Edwards *et al.*, 1987), and dissolved Mn from particulate leachable distributions observed during the winter ( $\Delta$ ) and summer ( $\square$ ) estuary surveys and in the mixing experiment ( $\circ$ ).

determined by the leach described and operationally defined in Section 2.1.2.1. A reactive particulate phase is considered a marker of chemical reactivity, whereas measured leachable distributions described in Chapter 2 (Section 2.2.3) did not readily enable identification of solid-solution interactions.

#### 4.4: CONCLUSIONS - Implications for Offshore Transport

From the evidence presented in this Chapter it is possible to conceive the likely mechanisms of solid-solution interaction and modes of transport offshore from estuarine sources in the North Sea for certain metals.

Riverine Mn responds to slow oxidation kinetics producing precipitated Mn oxide phases, and despite an increase in rate with salinity, there is no evidence to suggest that equilibrium is met within the flushing times of the coastal plume environments.

Cadmium, Cs and Zn interact with the solid phase by rapid initial adsorption (within 25 hours), probably followed by a slow migration of ions into the porous microstructure as characterized in Section 2.2.2. Although reversible for Cd, Cs ions lodge into interlattice sites of (micaceous) clays. Riverborne Cd and Cs become more soluble along a salinity gradient and their preference for solution in winter plumes will ensure effective offshore dispersal. During high productivity Cd is assimilated by plankton and therefore subject to biological recycling and enhanced residence time in coastal waters; Cs is unaffected by plankton and its use as a conservative tracer in shelf waters is therefore justified (Kautsky, 1973; 1985; Prandle, 1984). These conclusions have important implications for the fate of reactor released Cs radionuclides: if discharged into a fresh water environment a significant fraction of Cs will associate with sediments where it will remain irreversibly incorporated, possibly for geological time-scales; if disposed of in saline waters Cs will favour solution and hence dispersal.

## CHAPTER 5: CONCLUSIONS. IMPLICATIONS FOR TRANSPORT MODELLING AND FURTHER WORK

### 5.1: LONG-TERM MONITORING

This research has generated a comprehensive distributional scenario of particle composition (including operational measures of surface microstructure, and Fe and Mn oxide coatings) and particulate trace metals in the North Sea and key sub-environments (estuaries, plumes, algal blooms).

For the first time particulate leachable metal concentrations have been compared in five major North Sea estuaries from the U.K. and continental Europe. This has been possible through common sampling logistics and systematic analytical procedures and has established valuable baseline concentrations. Such a consistent approach is recommended for future long-term monitoring programmes in order to assess the effectiveness of pollutant discharge reductions on suspended sediment concentrations entering the North Sea. This reduction may, however, be difficult to verify over timescales implemented at the *Second International Conference on the Protection of the North Sea* (Ministerial Declaration, 1987) as calculations have indicated that estuarine particle residence time is of the order of tens of years. Therefore, an essential goal of any long-term monitoring programme will be to discriminate between any changes in pollutant discharges and the continual leakage of trace metals to the North Sea from contaminated estuarine sediments over decadal timescales. Ideally, a similar approach should be extended to the North Sea in order that the extrinsic effects of these reductions be evaluated.

### 5.2: ESTUARINE GEOCHEMISTRY

The concentrations of leachable particulate Fe and Mn, which have been implicated as being important to particle surface and compositional properties, are geographically very variable within the North Sea estuarine environments. For

instance, comparing mean values of summer axial distributions for three estuaries:

Humber; Fe = 10.4 mg/g and Mn = 1.38 mg/g

Scheldt; Fe = 2.70 mg/g and Mn = 0.77 mg/g

Elbe; Fe = 6.6 mg/g and Mn = 3.08 mg/g.

Particulate leachable trace metal concentrations, however, exhibit little inter-estuarine variability and minor perturbations (such as elevated Cr in the Humber) can be identified with known major anthropogenic sources. Chemical reactivity was not usually demonstrable from observations of estuarine particulate metal distributions as the reactive component of particulate metals represents only a small proportion of more refractory metals which are attacked even by mild leaches. Thus, compositional (either total or leachable metal) measurements will only normally establish a dilution of fluvial-derived material (metal-rich) by marine-derived (metal-poor) material unless either solid-solution interactions involve substantial mass transfer, as exemplified by large-scale Mn precipitation at high salinities in the Scheldt Estuary, or the system is affected significantly by direct anthropogenic discharges, as in the Humber.

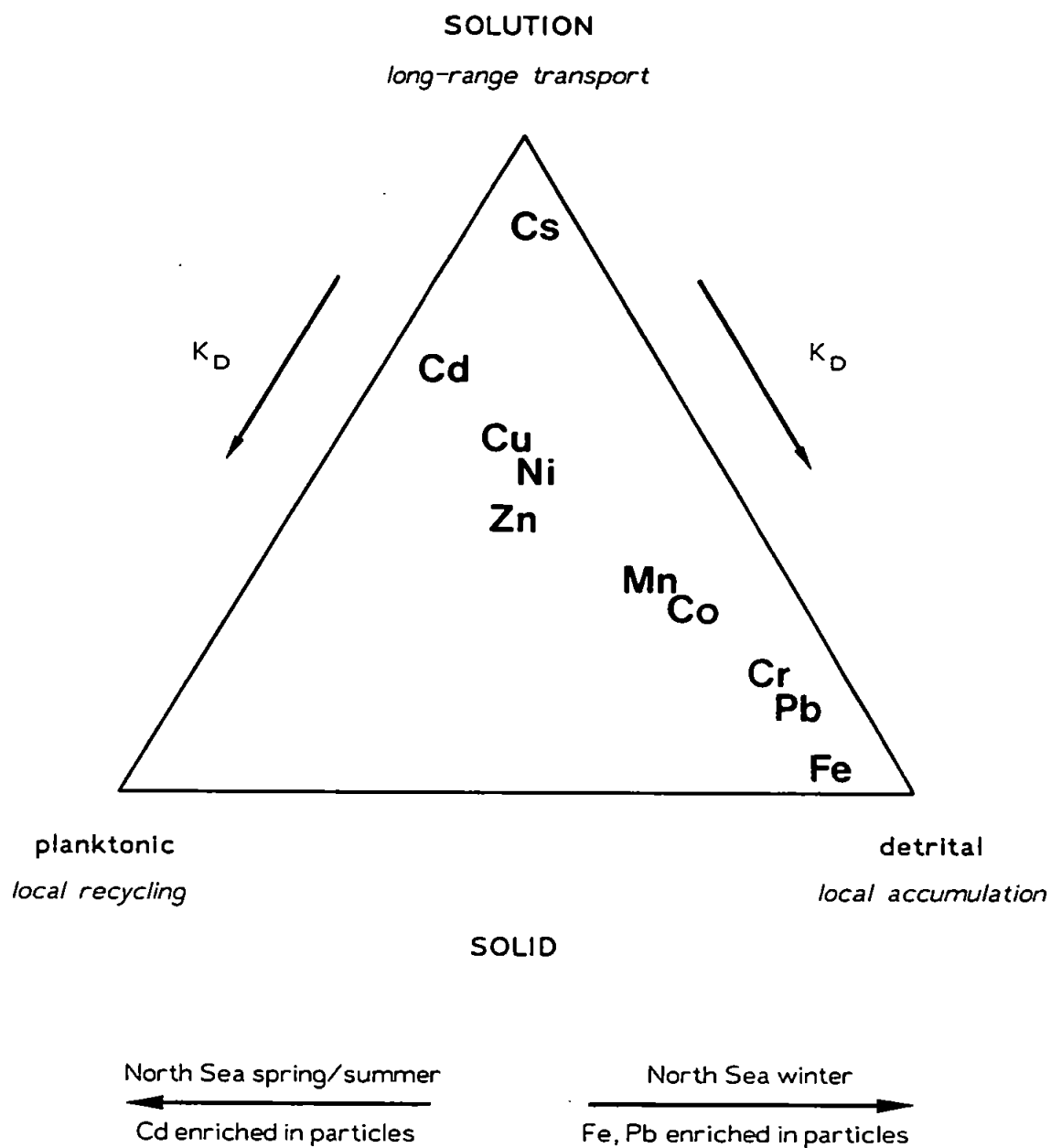
Estuarine chemical reactivity was more successfully investigated by simulating conditions considered appropriate to a North Sea estuary in mixing experiments and following the redistribution between solid and solution phases of artificially introduced radioisotopes. The results were expressed as the ratio of solid to solution concentration in the form of a distribution coefficient,  $K_D$ . Over a salinity range of 30 ‰ the  $K_D$ s for  $^{109}\text{Cd}$  and  $^{137}\text{Cs}$  were reduced by factors of 4 and 9 respectively indicating considerable solubilization. Whereas the partitioning of  $^{65}\text{Zn}$  remained essentially constant over this salinity range, the  $K_D$  for  $^{54}\text{Mn}$  increased by more than an order of magnitude. The phase redistribution of Mn can be accounted for in terms of oxidative removal from solution, and its behaviour in estuarine systems will therefore be governed to a large extent by the redox regime.



### 5.3: CONCEPTUAL SUB-MODELLING

Experimental studies indicate that in the outflow regions of estuaries, where chemical behaviour is likely to determine the long-term fate of many constituents, although metals may still respond to small salinity transitions, the role of particle composition is more significant. Isotopes of  $^{109}\text{Cd}$ ,  $^{137}\text{Cs}$  and  $^{65}\text{Zn}$  interact with the solid phase rapidly, and it is difficult to establish whether initial surface adsorption (within 25 hours) is succeeded by a slower reaction (such as diffusion into the microporous structure of the particles) or equilibrium conditions are met. Whereas  $^{109}\text{Cd}$  is relatively inert to particles common to winter estuarine plumes ( $K_D \sim 5 \cdot 10^2$ ) it is more effectively sequestered by organic-rich planktonic particles during spring and summer ( $K_D > 10^3$ ). Thus, although Cd may be modelled as a quasi-conservative constituent under winter conditions, seasonal shifts in particle population result in local recycling and render its longer-term fate more difficult to evaluate. Although more particle reactive ( $K_D \geq 10^4$ ), a similar inference can be made about the behaviour of Zn in estuarine plumes. In contrast,  $^{137}\text{Cs}$  has little affinity for all solid substrates ( $K_D \leq 5 \cdot 10^2$ ), hence its successful application as a water mass tracer (e.g. Kautsky, 1985). Although  $^{54}\text{Mn}$  is characterized by a high  $K_D$  ( $10^4 - 10^5$ ) there is still scope for considerable transport offshore in solution as oxidative removal is slow and protracted compared with typical flushing times of estuarine plumes.

The behaviour of other metals in estuarine plumes not studied in such experimental approaches can be conceived from observational investigations of the estuarine environments and the southern North Sea. In particular, it is of interest to consider their solid-solution partitioning, and to assess their relative affinities for two different solid phases, *i.e.* planktonic and estuarine-derived (hereafter termed detrital). Thus, Cu and Ni have relatively low particle affinities, as observed in apparent  $K_D$ s derived from leachable particulate and dissolved metal concentrations in the Weser Estuary and inferred from estuarine metal discharge estimates for both solid and solution phases. However, elevated concentrations in



**Figure 5.1:** Ternary diagram showing metal affinities for three compartments (solution, and planktonic and detrital solid associations) in North Sea plumes. Shown in italics at each apex are the likely fates of metals within a timescale of one year.

the Humber plume during spring compared with winter suggest that particle affinity is enhanced by planktonic material. On the other hand, similar observations indicate that Fe, Cr and Pb have a high affinity for detrital material and suggest that plankton effect a reduced affinity. This latter inference is substantiated for Fe and Pb by an enhancement of their particulate concentrations in the southern North Sea during winter (biomass depleted) compared with summer (biomass elevated) by factors of 3 and 4 respectively, and further for Fe by direct measurements of concentrations in winter plume material ( $> 20$  mg/g) and plankton ( $< 4$  mg/g).

These deductions allow all metals studied to be grouped according to their relative affinities for three phases (solution, and detrital and plankton-rich solid associations) in the form of a ternary diagram (Figure 5.1). Although several of the observations which form the basis of this diagram have been derived from specific environments, the essence of this investigation suggests that such a grouping is critical to an understanding of the behaviour, hence transport and fate of trace metals in coastal shelf seas. Furthermore, it is conceivable that the relative affinity of metals for these three phases is ultimately related to some fundamental chemical property (*cf.* Nieboer and Richardson, 1980; Turner *et al.*, 1981).

The behaviour of two contrasting metals (Cd and Mn) during their transit to coastal environments following release in a fresh water environment are conceptualized by simple box models and linked with hypothetical physical timescales in Figure 5.2.

#### 5.4: TRANSPORT MODELLING

To date, North Sea prognostic transport models have been restricted to the spreading of conservative constituents from estuarine sources (*e.g.* van Pagee *et al.*, 1986). In order that such models be fully capable of assessing the impact and fate of pollutants discharged to coastal shelf seas, the inherent hydrodynamic timescales must be coupled with chemical timescales and sediment dynamics.

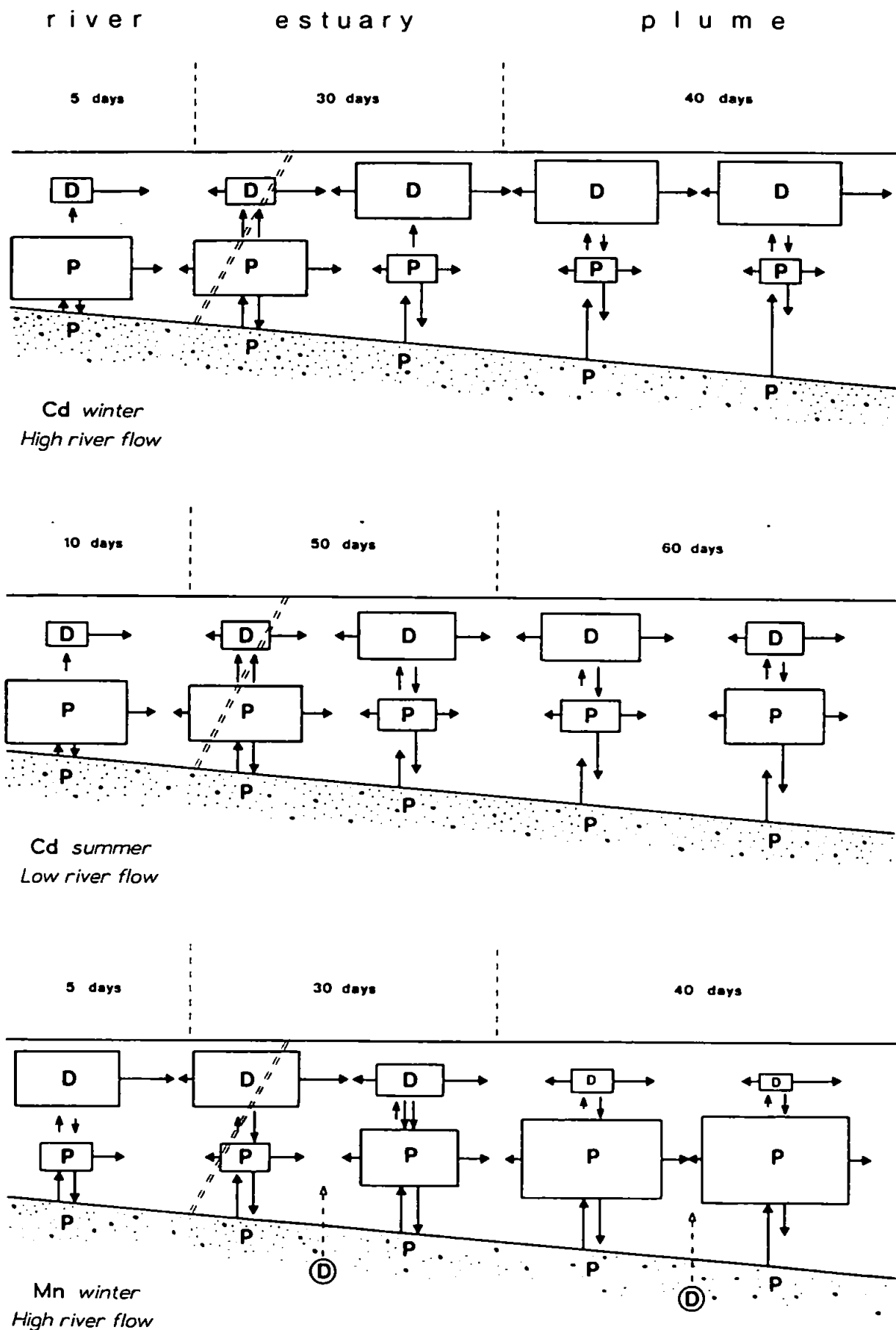


Figure 5.2: Conceptual box models of the behaviour of Cd and Mn during transit from fresh to coastal waters. Double dashed line represents fresh water - brackish water interface. Timescales refer to hypothetical flushing times for dissolved (D) constituents in each compartment (river, estuary, plume); these are enhanced for the particulate phase (P) because of deposition and resuspension.

This study has provided important mechanistic details of chemical reactivity occurring within estuarine plumes which will prove highly beneficial to model development from a conceptual basis. In particular, the successful application of radiochemical techniques should encourage this type of approach in order to evaluate rate constants for solid-solution interactions, provided problems hindering the subsampling of a representative particle population can be overcome.

An understanding of sediment transport may be derived theoretically, necessitating frequent measurements of such parameters as turbulence, and the concentrations and particle size spectra of suspended solids (West *et al.*, 1990). However, observational studies of suitable tracers currently being developed such as fluorescent resins (Spanhoff and Suijlen, 1990) offer a potentially more feasible solution to this problem.

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## APPENDIX 1: PUBLISHED WORK

In: *Estuarine Water Quality Management. Coastal and Estuarine Studies Volume 36* (Michaells, W. ed.). Springer-Verlag (Berlin):

### AN INTERCOMPARISON OF PARTICULATE TRACE METALS FROM FOUR LARGE ESTUARIES

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#### ABSTRACT

Suspended sediment samples have been taken during axial profiles of four major estuaries (viz. Mersey, Humber, Elbe and Thames) and analysed in a consistent manner for trace metals and specific BET surface area. The results indicate that a great deal of inter-estuarine variability exists.

#### INTRODUCTION

The Mersey, Thames, Humber (UK) and Elbe (FRG) are large, partially/well mixed macrotidal estuaries. Furthermore, all are industrialized with long histories of pollution problems. The former estuary discharges into Liverpool Bay (Irish Sea), whereas the remainder discharge into the North Sea, and both are shelf sea regions of growing concern regarding levels of toxic materials.

One form of pollution that has received much attention over the past two decades is that of trace metals (Salomons and Förstner, 1984). Trace metals occur in the water column in solution and associated with the suspended solid material.

It was the aim of this investigation to determine the levels of leachable (i.e. perhaps representative of bioavailable or geochemically reactive) particulate trace metals in each of the aforementioned estuaries in order to gain a basic insight into inter-estuarine variability, and relate such levels to physical properties of the particles as determined by BET analysis. The latter analyses are discussed in detail in a separate paper (Millward et al., 1989). However, combining the results of both trace metal and BET analysis may allow a fuller assessment of inter-estuarine geochemical variability.

#### SAMPLING AND ANALYTICAL METHODS

Between 10 and 20 samples of 1-10 l were taken during axial profiles of the Mersey, Humber and Thames and filtered through 0.45 µm Millipore filters (142 mm diameter) under N<sub>2</sub> pressure. The residue material was washed with about 20 ml distilled water and transferred into plastic pots for freeze-drying. During the

Elbe profile and for the Mersey samples for Hg analysis, a continuous flow centrifuge (10' rpm) was employed to collect material on teflon strips lining the interior of the rotating bowl. Samples were subsequently washed with distilled water and freeze-dried.

The salinity was monitored with an MC-5 T-S bridge and subsamples were taken to determine the suspended solids concentration ( $\text{mg l}^{-1}$ ) by filtration through Whatman GF/F papers.

Table 1. Hydrodynamic conditions during sampling

|                             | Salinity Range<br>& | Suspended Solids Range<br>$\text{mg l}^{-1}$ |
|-----------------------------|---------------------|--|
| Mersey (Nov. 1987)          | 0.4 - 31.9          | 50 - 155                                     |
| Mersey (July 1988; Hg only) | 27.7 - 33.5         | 1 - 47                                       |
| Humber (Jan. 1988)          | < 0.5 - 25.9        | 35 - 248                                     |
| Elbe (June 1988)            | < 0.5 - 31.3        | 13 - 289                                     |
| Thames (Feb. 1989)          | 4.7 - 27.4          | 35 - 424                                     |
| Thames (March 1989)         | 0.4 - 4.5           | 17 - 70                                      |

The surface areas of samples were determined using a gravimetric BET N<sub>2</sub> adsorption technique (Crosby et al., 1983) and trace metals were determined using conventional flame AA techniques following leaching with 25 % acetic acid + 0.05 M hydroxylamine hydrochloride (Chester and Hughes, 1967; Tessier et al., 1980). The particulate Hg levels were determined by cold vapour AAS following leaching by dilute HNO<sub>3</sub>.

#### RESULTS AND DISCUSSION

The results are expressed as means, standard deviations, ranges and coefficients of variation in Table 2. Although sampling was undertaken during different seasons and under different hydrodynamic conditions (Table 1), the significance of which to trace metal levels and distributions has previously been demonstrated (e.g. Morris et al., 1986), some useful comparisons can be made. Trace metal levels are generally highest in the Humber Estuary (especially for Cu and Cr; Fig. 1a, Table 2) reflecting the large industrial inputs, as is the Fe content (Fig. 1b). The latter is largely derived from two titanium dioxide manufacturing plants and, as Fe is very BET reactive (Crosby et al., 1983; Marsh et al., 1984), this leads to large surface areas and enhances scavenging properties of Humber particulates. The surface areas of Elbe material are equally high. However, the particles are relatively Fe poor (Fig. 1b, Table 2) and the high Mn contents (Table 2) suggest that this element is more significant to the surface properties.

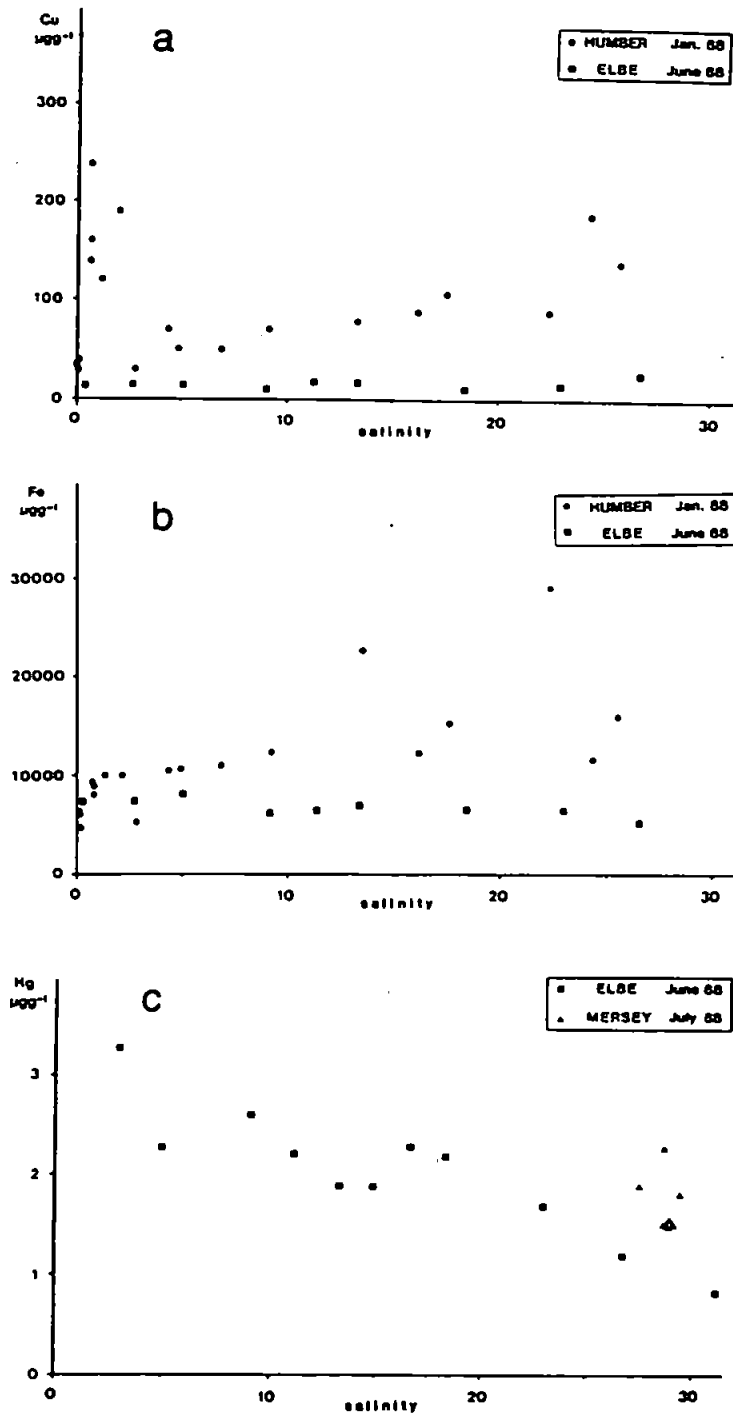


Figure 1. Profiles of the particulate trace metal levels. a) Cu, Humber and Elbe; b) Fe, Humber and Elbe; c) Hg, Elbe and Mersey

One suggestion regarding the origin of such high Mn levels is the mobilization of reduced Mn from the anoxic sediments of Hamburg Harbour, and subsequent uptake onto particles downstream as the  $O_2$  levels in the water column improve and the turbidity increases. Trace metal levels and coefficients of variation are lower than in the Humber, possibly because of the absence of such large industrial discharges to the lower tidal waters. In fact much of the trace metal burden of the Elbe may have been derived from the industrialized regions of the eastern European countries in the upper catchment, and subsequently diluted by the large volume of water downstream.

**Table 2.** Particulate trace metal levels in the four estuaries (n = number of samples; R = range; CV = coefficient of variation).

|        | Statistical parameter | Fe $mgg^{-1}$ | Mn $mgg^{-1}$ | Zn $mgg^{-1}$ | Cu $\mu gg^{-1}$ | Pb $\mu gg^{-1}$ | Cr $\mu gg^{-1}$ | Hg $\mu gg^{-1}$ | SSA $m^2 g^{-1}$ |
|--------|-----------------------|---------------|---------------|---------------|------------------|------------------|------------------|------------------|------------------|
| Mersey | $\bar{x} \pm \sigma$  | 4.8±0.8       | 1.2±0.3       | 0.31±0.08     | 30±13            | -                | -                | 1.4±0.4          | 9.6±2.2          |
|        | n                     | 9             | 10            | 10            | 10               | -                | -                | 11               | 10               |
|        | R                     | 3.5-6.5       | 0.7-1.6       | 0.23-0.50     | 20-60            | -                | -                | 0.7-2.3          | 6-14.9           |
|        | CV, %                 | 17            | 25            | 26            | 43               | -                | -                | 28               | 23               |
| Humber | $\bar{x} \pm \sigma$  | 12.5±5.7      | 0.99±0.17     | 0.53±0.43     | 110±60           | 55               | 37±144           | -                | 24.0±6.3         |
|        | n                     | 19            | 19            | 19            | 19               | 6                | 14               | -                | 18               |
|        | R                     | 4.8-29.1      | 0.64-1.29     | 0.25-2.22     | 30-240           | -                | 17-74            | -                | 9.8-38.3         |
|        | CV, %                 | 48            | 17            | 81            | 55               | -                | 38               | -                | 26               |
| Elbe   | $\bar{x} \pm \sigma$  | 6.6±0.9       | 3.08±0.33     | 0.47±0.10     | 17±6             | 58               | 22               | 2.0±0.6          | 25.6±8.1         |
|        | n                     | 10            | 9             | 10            | 10               | 4                | 4                | 11               | 10               |
|        | R                     | 5.0-8.3       | 2.58-3.62     | 0.36-0.70     | 10-31            | -                | -                | 0.8-3.3          | 7.2-35.5         |
|        | CV, %                 | 14            | 11            | 21            | 35               | -                | -                | 30               | 32               |
| Thames | $\bar{x} \pm \sigma$  | 4.9±1.1       | 0.70±0.13     | 0.29±0.17     | 27±10            | 73±17            | 19±3             | -                | 12.3±13.9        |
|        | n                     | 14            | 14            | 14            | 14               | 14               | 13               | -                | 14               |
|        | R                     | 3.7-8.3       | 0.42-0.94     | 0.13-0.73     | 16-45            | 51-113           | 16-24            | -                | 5.0-19.2         |
|        | CV, %                 | 22            | 19            | 59            | 37               | 23               | 16               | -                | 32               |

The surface area and Fe contents of the Mersey Estuary are low compared with the Humber and Elbe, and trace metal levels are somewhat lower than anticipated bearing in mind the abundance of industrial discharges to the tidal waters. This may be interpreted as coarse material of low adsorptive capacity being carried in suspension. A similar situation exists for the Thames Estuary, viz. low surface areas and Fe contents. The relatively low levels of trace metals such as Zn and Cr may be a result of the low BET reactivity as in the Mersey, and associated with the lack of large industrial effluents. The relatively high levels of Pb on the other hand, may be expected in an estuary receiving vast quantities of urban runoff.

Regarding the Hg results, although less comprehensive, it is worth mentioning that an almost conservative seaward decrease in the Elbe was noted (Fig. 1c). The Hg levels in the Mersey (Fig. 1c) also decrease seawards. Although levels in this estuary are lower than in the Elbe, it should be borne in mind that sampling

was undertaken at higher salinities and extrapolation back to freshwater would yield a significant Hg burden in the Mersey, which would be consistent with previous observations (Airey and Jones, 1982; Campbell et al., 1986). Much of this Hg load is derived from anthropogenic discharges, notably the chlor-alkali industry, as well as effective scavenging of Hg from solution (Airey and Jones, 1982; Campbell et al., 1986).

Using previously published estimates of sediment discharges (Veenstra, 1970), the possible impact on the North Sea particulate trace metal budget may be assessed for the Elbe, Humber and Thames (Table 3). Because of its far greater water and sediment discharge, the Elbe provides the largest contribution of particulate trace metals to the North Sea through its input to the German Bight. Material derived from the Humber is discharged in a distinct but poorly dispersing plume (Lewis, undated) which is likely to have more of an impact on the local nearshore environment.

Table 3. Approximate discharge of particulate trace metals from the Humber, Elbe and Thames estuaries.

|        | Approximate sediment discharge*<br>(tons/annum) | Cr | Cu | Fe<br>(tons/annum) | Mn   | Pb | Zn  |
|--------|---|----|----|--------------------|------|----|-----|
| Humber | 10 <sup>6</sup>                                 | 4  | 10 | 1200               | 100  | 5  | 50  |
| Elbe   | 7 · 10 <sup>6</sup>                             | 15 | 10 | 4600               | 2220 | 40 | 300 |
| Thames | 2 · 10 <sup>6</sup>                             | 4  | 5  | 1000               | 150  | 15 | 60  |

\* Veenstra, 1970

#### CONCLUSIONS

Particulate trace metals studies in four large estuaries have shown that levels in the Humber are much higher than those in the Thames and Mersey, probably as a result of the abundance of large industrial discharges and the high (BET) reactivity of particles in the former estuary. The levels of particulate trace metals in the Elbe are generally intermediate, although its impact on the North Sea particulate trace metal budget is larger than that of the Humber through its far greater sediment discharge.

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