

Interim Report

R&D Project 016

**PARTITIONING OF CONTAMINANTS BETWEEN WATER AND  
SEDIMENT**

WRc plc

November 1991

R&D 016/3/N

ENVIRONMENT AGENCY



001526

**PARTITIONING OF CONTAMINANTS BETWEEN WATER AND SEDIMENT**

A M Gunn, H R Rogers, C J Whalley

<b>Environmental Agency</b>
<b>Thames Region</b>
<b>Library Catalogue</b>
Class No. ....
Accession Code ..... <b>ACFB</b> .....

Research Contractor:  
WRc plc  
Henley Rd Medmenham  
PO Box 16 Marlow  
SL7 2HD

National Rivers Authority  
Rivers House Waterside Drive  
Almondsbury Bristol BS12 2UD

NRA Interim Report 016/3/N

National Rivers Authority  
Rivers House Waterside Drive  
Almondsbury Bristol BS12 2UD

Tel: 0454 624400  
Fax: 0454 624409

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Internal: Limited  
External: Restricted

Research-contractor

This document was produced under R&D Contract 016 by:

WRc plc  
Henley Road Medmenham  
PO Box 16 Marlow  
SL7 2HD

Tel: 0491 571531  
Fax: 0491 579094

WRc report N° NR 2927/4209

NRA Project Leader

The NRA's Project Leader for R&D Contract 016:

E Douglas - Northumbria Region

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## EXECUTIVE SUMMARY

The partitioning of contaminants between water and suspended particulate exerts a major influence on their transport and environmental impact. WRC has consequently been contracted to investigate the effects of a variety of important dissolved and particulate phase parameters on the partitioning behaviour of specific organic and trace metal contaminants. This report discusses progress achieved during the period November 1990 to September 1991.

Recent effort on organic contaminants has concentrated on the application of radiotracer techniques, with the main compounds under study being atrazine and gamma-hexachlorocyclohexane. For atrazine, results have indicated that sorption processes are only important at extremely high solids concentrations. Gamma-HCH, however, has been found to exhibit significant partitioning over the typical range of particulate levels found for the Humber. For both compounds, partition coefficients have shown a dependence on salinity and particulate concentrations. Application of equilibrium dialysis has established that neither show any great affinity for natural colloidal material.

An investigation of the kinetics of adsorption processes for trace metals has indicated that these cannot readily be explained in terms of simple first order reversible kinetics. A multi-step kinetic model has therefore been proposed and relevant adsorption and desorption rate constants have been determined. The importance of dissolved phase natural organic ligands in controlling partitioning has also been demonstrated. For cadmium, dissolved phase chloro complexation has been established to be a major controlling factor throughout the saline reaches of the Ouse/Humber. *In-situ* speciation of metals associated with riverine and estuarine particulates has been investigated by use of sequential extraction procedures, and data obtained in this way have been compared with results from laboratory sorption studies.

## KEY WORDS

Organic contaminants, trace metals, suspended sediment, equilibrium partitioning, speciation, kinetics.

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## 1. INTRODUCTION

The partitioning of contaminants between dissolved and particulate phases has a major influence on their transport, fate and effects. The WRC has therefore been contracted by the NRA to investigate the main factors influencing the partitioning behaviour of priority trace metal and organic pollutants. Initial findings have been discussed in previous reports (PRS 2262-M September 1989, NR 2573 October 1990) while the present report covers progress for the period November 1990 to August 1991.

Work on organic contaminants has concentrated on investigation of the partitioning behaviour and speciation of atrazine and gamma-hexachlorocyclo-hexane (g-HCH) in estuarine waters. Particular emphasis has been placed on evaluating the importance of pesticide binding to naturally occurring colloids. This has involved the application of size-based speciation procedures such as equilibrium dialysis and filtration. The influence of physicochemical parameters such as salinity and suspended solids concentration on contaminant partitioning behaviour has also been studied.

The approach adopted for laboratory studies of trace metal partitioning has continued along the lines of that described previously (NR 2573), with all unnecessary manipulation of particulates (eg prefiltration, centrifugation) being avoided and natural suspended matter rather than bed sediments being employed. A second major survey of the Humber system has now been carried out (April 1991) and in conjunction with this, laboratory studies of the influence of particulate phase speciation on partitioning have been initiated. Attention has recently also been directed towards the study of kinetics of adsorption/desorption processes.



## 2. PARTITIONING OF ORGANIC CONTAMINANTS

### 2.1 Background

The partitioning of contaminants between dissolved and particulate phases in natural waters is an important process that influences the fate, transport and bioavailability of contaminants. However, most of our knowledge about aquatic organic contaminant partitioning processes is largely based on the extrapolation of soil data. There is a need for more information on the partitioning of priority pollutants in fresh and saline waters in order that their transport, fate and toxicity may be adequately assessed. Most water quality studies concerned with organic contaminants either report total concentrations or at best differentiate between 'dissolved' and particulate forms based on filtration. The concept and importance of solution phase speciation is well established for trace metals (Neubecker and Allen 1983), and it is generally accepted that for many metals it is the free metal ion that is bioavailable and hence the toxic form (Apte *et al* 1988). Several reports (Carter and Suffet 1982, Landrum *et al* 1984) suggest that the same is true for organic contaminants i.e. association with particulates, colloidal material and macromolecular organics reduces bioavailability and toxicity.

Most previous work has involved using preconcentrated natural samples (Wijayratne and Means 1984, Beckett *et al* 1990) or extraction techniques that underestimate the extent of colloidal/humic interactions (Landrum *et al* 1984).

Atrazine is widely used in the UK in total weed control in non-agricultural situations such as on railways and industrial sites and has been designated as a priority UK Red-list chemical with the aim of reducing its discharge into the environment. Recently, Italy, France, Denmark, Germany and the Netherlands introduced restrictions on the usage of atrazine in order to reduce inputs to ground and surface waters. This action was prompted because of concern over the presence of atrazine in drinking water above levels permitted by the EC Drinking Water Directive ( $0.1 \mu\text{g l}^{-1}$ , Cartwright *et al* 1991).

Hexachlorocyclohexane is a List I priority pollutant and its use has been limited in the UK in order to reduce inputs to the environment. Both atrazine and  $\gamma$ -HCH were chosen for study because of their priority status as environmental contaminants.

The aims of this work were to develop physico-chemical techniques that could be used to investigate the speciation of organic contaminants, to use these techniques to examine the extent of atrazine and hexachlorocyclohexane ( $\gamma$  isomer) binding to colloidal material, and to obtain information on partitioning processes for these contaminants in estuarine and freshwaters.

Radiolabelled contaminants were used in these studies as model contaminants to expedite rapid, precise analysis at near to realistic environmental concentrations. Their use allowed rigorous methodological development that would otherwise not have been possible using conventional time-consuming analytical methods such as GCMS. However, it should be borne in mind that radiotracers will only provide valid data on partitioning phenomena over a time frame where degradative transformation of the labelled compounds can be assumed to be negligible.

## 2.2 Experimental

$^{14}\text{C}$ -labelled atrazine (specific activity  $4.29 \text{ MBq mg}^{-1}$ ) and  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH, 'lindane'; activity  $8.06 \text{ MBq mg}^{-1}$ ) were from Amersham International UK. Stock solutions of atrazine ( $1.3 \mu\text{g l}^{-1}$ ) and  $\gamma$ -hexachlorocyclohexane were prepared in deionised/activated carbon filtered water and stored at  $4 \text{ }^\circ\text{C}$  in the dark. The concentrations of radiolabel in standards and sample solutions were determined using liquid scintillation counting. Five ml of sample was mixed with 10 ml of scintillation cocktail (Instagel, Canberra/Packard) in a polyethylene scintillation vial and counted for 10 min. on a Beckman LS9800 or LS6000SE liquid scintillation counter using the manufacturers recommended conditions.

### 2.2.1 Sample storage experiments

Three sizes of Pyrex glass bottle (1000 ml, 500 ml and 250 ml) were checked for adsorption losses of radiolabelled atrazine and g-HCH over the 24 hour duration of the partitioning experiments. Each bottle was thoroughly cleaned in a laboratory grade washing machine (three phase wash cycle : detergent solution, acetic acid and deionised water washes) and dried before use. The bottles were filled with borehole water (Medmenham source, hardness 275 mg CaCO<sub>3</sub> l<sup>-1</sup>) and spiked with radiotracer to give a final concentration of either 1.3 µg l<sup>-1</sup> atrazine (5.55 KBq l<sup>-1</sup>) or 0.92 µg l<sup>-1</sup> g-HCH (7.4 KBq l<sup>-1</sup>). Each treatment was replicated five times. The solutions were stored at room temperature (~20 °C) for 24 hours in darkness and aliquots of solution were then taken from each bottle and analysed.

### 2.2.2 Losses during filtration and ultrafiltration

Losses of atrazine and g-HCH during filtration of samples were evaluated by filtering 200 ml aliquots of spiked borehole water containing either 1.3 µg l<sup>-1</sup> atrazine or 0.92 µg l<sup>-1</sup> g-HCH through the following filters: Whatman GF/F (straight from the box), Whatman GF/F (pre-ashed overnight at 500 °C), Millipore 0.45 µm cellulose nitrate/acetate, Anotec 0.2 µm and 0.02 µm. A glass and PTFE Sartorius filtration assembly with a hand powered vacuum suction pump were used for the filtrations. In addition, 50 ml aliquots of spiked borehole water were filtered through Sartorius SM145-29 ultrafilters (5000 MWCO) using an Amicon 8050 ultrafiltration unit under positive nitrogen pressure. The membranes were first washed to remove preservatives as advised by the manufacturers. All treatments were replicated five times. The activities of the filtrates were measured and compared to freshly prepared standards.

### 2.2.3 Equilibrium dialysis

Spectrapor 6, 1000 MWCO dialysis membrane (Cole Palmer), 24.2 mm diameter, 30 cm length was thoroughly washed with deionised/activated carbon filtered water, closed at one end with a dialysis clip (Medicell, UK) and then filled

with 75 ml of deionised/activated carbon filtered water. The cell was suspended in a Pyrex glass bottle containing 1000 ml of spiked borehole water and the solution was continuously stirred with a magnetic flea. Five ml aliquots were withdrawn from the dialysis cell and the outer solution using a micropipette at intervals and analysed. A similar procedure was used for the river and estuarine samples. One litre aliquots of filtered water from each site were spiked with  $6.5 \mu\text{g l}^{-1}$  atrazine, equilibrated for 24 hours and then dialysed for 66 hours. Aliquots of the dialysate and outer solution were taken at the start and finish of the experiment. Hexachlorocyclohexane dialyses were carried out with pre-equilibrated samples that had been filtered to  $<0.45 \mu\text{m}$  and dialysed as above.

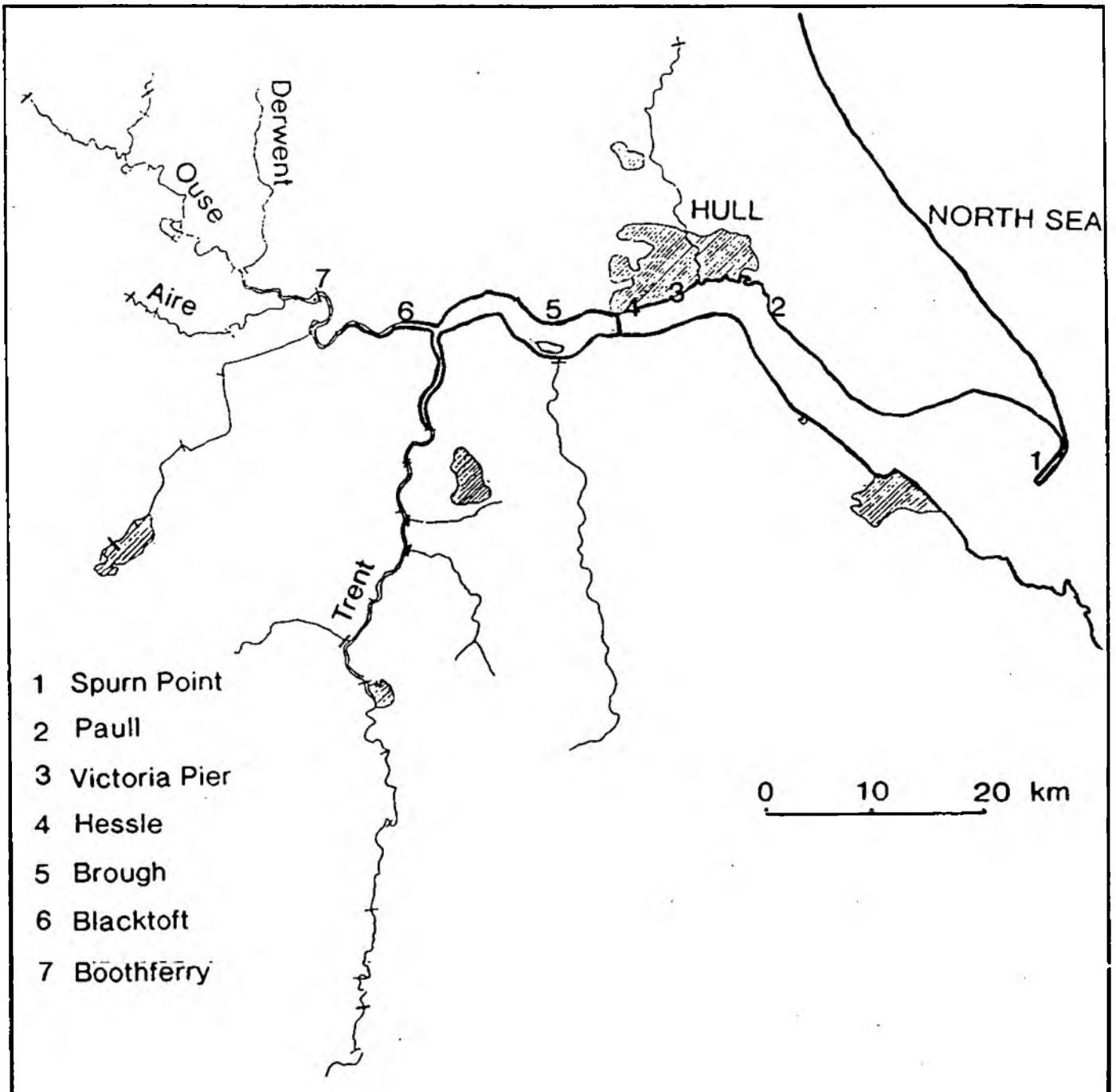
#### **2.2.4 Collection of estuarine and river samples**

Water and sediment samples were collected from five sites in the Humber estuary on 15.11.90 and 22.4.91 (Figure 2.1). Sampling sites were selected to give a compromise between covering the geographical span of the estuary and a broad range of salinities. Twenty litre surface water samples were collected at each site. At the Blacktoft site, a sample of unconsolidated mud was scraped from the surface of an intertidal mudflat, close to the waters' edge. Salinity and water temperature measurements were recorded at each site using an MC5 bridge salinometer. Samples were immediately transported back to the laboratory and refrigerated at  $4 \text{ }^\circ\text{C}$ . Partitioning experiments were conducted within 72 hours of collection. River Thames water (Medmenham) was used for the freshwater experiments.

#### **2.2.5 Analysis**

Dissolved organic carbon was determined using a high temperature catalytic method (Suzuki and Sugimura 1988). Suspended sediment concentrations were determined gravimetrically following filtration, and sediment organic carbon was determined by ashing at  $550 \text{ }^\circ\text{C}$ . Background levels of atrazine and  $\text{g-HCH}$  were obtained by GC-MS. Atrazine was determined in GF/F filtered samples by gas chromatography-nitrogen phosphorus detection following extraction into

Figure 2.1 . Humber estuary sampling sites



dichloromethane, drying by freezing and concentration by Kuderna Danish and nitrogen stream evaporation. Quantification was carried out by an internal standard procedure using prometryne as internal standard.

Hexachlorocyclohexane was determined by negative ion chemical ionisation mass spectrometry after extraction into pentane, drying by freezing and nitrogen stream evaporation. The g-HCH was quantified using  $^{13}\text{C}_6\text{-d}_6\text{-HCH}$  as an internal standard.

### 2.2.6 Partitioning experiments

The partitioning behaviour of g-HCH and atrazine was investigated in separate experiments. Each bulk water sample was shaken thoroughly to ensure resuspension of settled material and 250 ml aliquots carefully transferred to clean Pyrex bottles. Each solution was spiked with radiotracer ( $6.5 \mu\text{g l}^{-1}$  atrazine;  $0.92 \mu\text{g l}^{-1}$  g-HCH), capped and equilibrated for 24 hours with continuous gentle agitation. Samples were then filtered (GF/F) and the 'dissolved' phase radiotracer concentration determined. All experiments were performed in triplicate. Additional saline experiments were carried out at high solids concentrations, which were representative of the near sediment/water interface. Suspended sediment concentrations were increased by adding wet sediment from the Blacktoft site to each 250 ml aliquot. The experiment was then continued as above.

The partition coefficient can be defined as :

$$K_p = \frac{\text{sediment concentration (ppm)}}{\text{water concentration (ppm)}} \quad (1)$$

Further, it can be shown that:

$$K_p = \frac{(\text{initial counts} - \text{final counts}) \times 10^6}{\text{final counts} \times \text{SSC (mg l}^{-1}\text{)}} \quad (2)$$

where initial counts are the counts obtained from control solutions (no sediments added).

Partition coefficients were calculated from Equation 2. The organic carbon normalised partition coefficient,  $K_{oc}$  was calculated from:

$$K_{oc} = \frac{K_p}{f_{oc}}$$

where  $f_{oc}$  is the fractional organic carbon content.

## 2.3 Results

### 2.3.1 Methodological studies.

Sample storage tests indicated that adsorptive losses during the 24 hours were negligible for both atrazine and g-HCH. No significant losses of atrazine or g-HCH were observed during the filtration procedures, however, 24.1% of the atrazine and 91% of the g-HCH was lost during ultrafiltration through MWCO 5000 SM145-29 ultrafilters. Experiments were repeated with pre-filtered borehole water and similar losses were observed. The use of ultrafiltration was therefore abandoned.

Dialysis equilibrium was attained within 28 hours for the atrazine and within 24 hours for the g-HCH. The concentration in the surrounding water showed no change during the course of the experiment (aside from that expected through dilution by the contents of the dialysis cell) indicating negligible adsorption to the dialysis membrane.

### 2.3.2 Estuarine field studies

Parameters measured at each site are presented in Tables 2.1 and 2.2. Atrazine was detected at all sites, and g-HCH at only one site (Table 2.3). However, their concentrations were below  $170 \text{ ng l}^{-1}$  and were therefore low compared to the spiked concentrations.

**Table 2.1 Estuarine survey data (15.11.90) - Atrazine**

Site	Salinity ‰	Temp. °C	pH	SSC mg l <sup>-1</sup>	DOC mg C l <sup>-1</sup>
Boothferry	<0.2	10	7.47	1339	8.1
Blacktoft	3.2	9	7.57	2220	6.4
Brough	7.5	9	7.86	1333	9.3
Victoria Pier	12.8	9	7.75	894	4.7
Spurn	30.6	9	7.84	111	3.4

**Table 2.2 Estuarine survey data (22.4.91) - g-HCH.**

Site	Salinity ‰	Temp. °C	pH	SSC mg l <sup>-1</sup>	DOC mg C l <sup>-1</sup>
Spurn	32.5	11.5	8.1	2209	2.84
Paull	22.5	8.6	7.8	392	3.29
Hessle	13.0	8.9	7.4	787	4.12
Brough	9.5	9.0	7.4	1116	9.56
Blacktoft	1.9	8.3	7.1	1713	5.41

**Table 2.3 Background levels of atrazine and g-HCH in Humber estuary (22.4.91)**

Site	Atrazine conc. ng l <sup>-1</sup>	g-HCH conc. ng l <sup>-1</sup>
Spurn	40	<1
Paull	120	<1
Hessle	110	<1
Brough	110	4
Blacktoft	170	<1

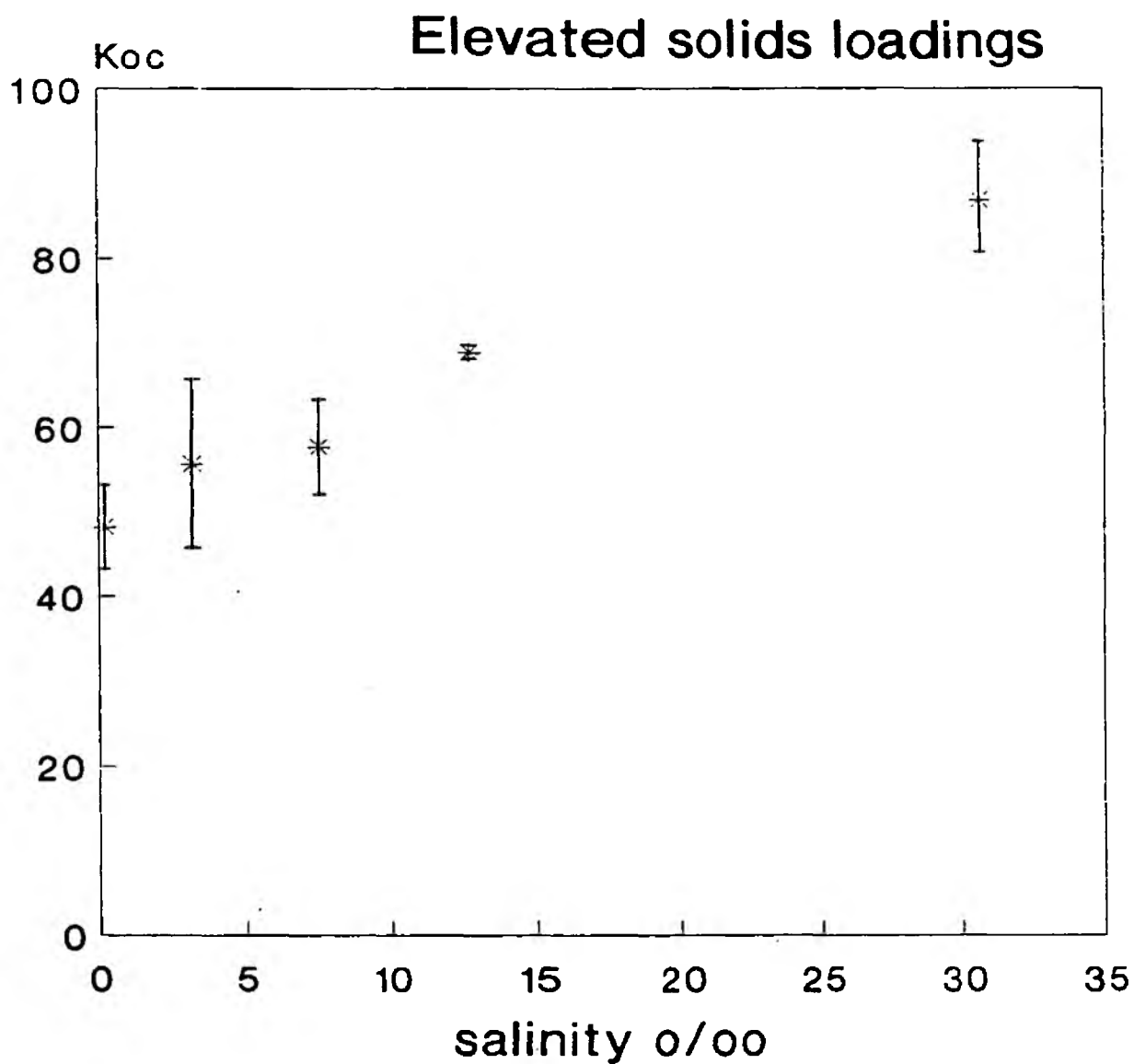


### 2.3.3 Partitioning experiments

When determining partition coefficients in the manner described in this report it is important to take into account the limitations of the experimental approach. Radiotracers may contain small concentrations of radioactive impurities that will partition differently (with higher or lower affinity) to the target compound. The presence of impurities can lead to errors when very high or little sorption is observed. To compensate for this potential error, it was considered that the edges of the detection window were defined by 5% and 95% adsorption of the added radiotracer. The lower limits of detection for  $K_p$  are therefore  $52632/SSC$  ( $mg\ l^{-1}$ ) and the upper limit was  $1.9 \times 10^7/SSC$  ( $mg\ l^{-1}$ ). Any partition coefficients outside this range were regarded as being potentially unreliable and were not used.

At natural suspended sediment concentrations typical of the Humber estuary ( $0.01-2.5\ g\ l^{-1}$ ) a negligible amount of atrazine adsorbed to the particulate phase. Sorption was only observed in the experiment where the levels of suspended solids were elevated by addition of extra sediment and the  $K_p$  increased with increasing salinity. The  $K_{oc}$  increase seawards is probably a result of a salting-out effect (Figure 2.2). The resulting partitioning data are presented in Table 2.4 and are compared to other literature data in Table 2.5. The added sediment was 57.7% dry weight and had an organic carbon content of 5.01%. Dialysis experiments indicated that >99% of added atrazine was dialysable and suggests that either atrazine is present in true solution or conceivably in association with low molecular weight (<1000) dissolved organics such as fulvic acids. Previous studies by Wang *et al* (1990) suggest that atrazine associates with fulvic acids (number averaged molecular wt <1000, wt averaged molecular wt ~5000) either by hydrogen bonding with hydroxyl groups or by a charge transfer interaction. Wijayarathne and Means (1984) found that atrazine associated with estuarine colloidal material with an average molecular weight of ~10 000 using gel permeation techniques. However, molecular weight distributions and macromolecular functional groups characteristics of fulvic acids will probably vary with water source and this may account for the differences in observed fraction association between this and other studies. A recent report by Jota and Hassett (1991) suggests that considerably more hydrophobic contaminants such as 2,2',5,5'-tetrachlorobiphenyl also have

Figure 2.2. Plot of Atrazine Koc vs salinity  
for Humber estuary 15.11.90



High solids loadings



measurable binding with dissolved organics with molecular weights less than 1000, although the main association is with higher molecular weight fractions.

**Table 2.4 Humber estuary partition coefficient data : atrazine elevated solids levels**

Site	SSC g l <sup>-1</sup>	K <sub>p</sub>	K <sub>oc</sub>	logK <sub>oc</sub>	S ‰
Boothferry	82.12	2.41	48.2	1.68	<0.2
Blacktoft	83.00	2.78	55.6	1.75	3.2
Brough	82.11	2.88	57.6	1.76	7.5
Victoria Pier	81.67	3.44	68.8	1.84	12.7
Spurn	80.89	4.34	86.8	1.94	30.6

**Table 2.5 Comparison of partition coefficients: atrazine**

	log K <sub>oc</sub>
Pereira and Rostad (1990)	2.0
Karickhoff (1981)	2.17
This work (high solids, 0-31 ‰ sal.)	1.68-1.94

Gamma-hexachlorocyclohexane showed appreciable association with suspended particulates >0.45 µm and log K<sub>oc</sub> values (Table 2.6) were comparable to those previously reported in the literature (Karickhoff 1981).

**Table 2.6 Humber estuary partition coefficient data : g-HCH**

Site	SSC mg l <sup>-1</sup>	K <sub>p</sub>	K <sub>oc</sub>	logK <sub>oc</sub>	S ‰
Blacktoft	1713	215.1	2723	3.43	1.9
Brough	1116	259.8	2383	3.38	9.5
Hessle	787	334.3	3799	3.58	13.0
Paull	392	447.1	4757	3.68	22.5
Spurn	2209	237.3	2637	3.42	32.55

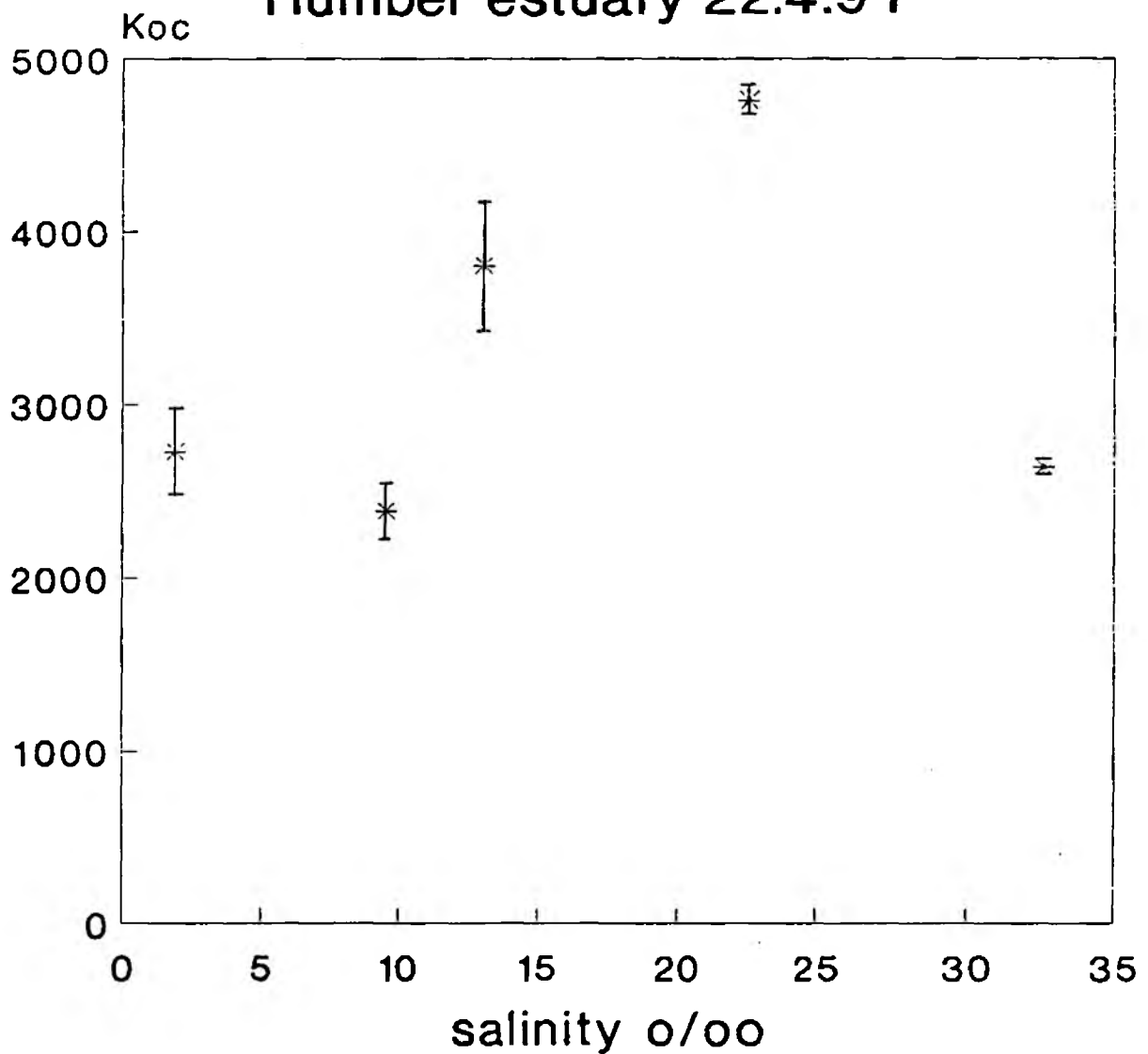
Salinity has a significant effect on K<sub>oc</sub> (Figure 2.3), but it is not a linear relationship. However, there appeared to be a correlation between K<sub>oc</sub> and estuarine solids loadings (Figure 2.4). The same relationship was also observed in freshwater samples from the Thames that were enriched with bottom sediment (Figure 2.5), with a decrease in K<sub>oc</sub> with increased solids loadings. These observations agree with the particle interaction model proposed by DiToro (1985) and Mackay and Powers (1987). The model suggests that loose surface sorption of contaminants can easily be reversed at high solids loadings because of collision-induced desorption. Equilibrium dialysis indicated that in all experiments, greater than 90% of the g-HCH was dialysable, suggesting that it was present in true solution or possibly associated with low molecular weight organics.

#### 2.4 Conclusions

The partitioning behaviour and speciation of atrazine and gamma-hexachloro-cyclohexane (g-HCH) in estuarine waters has been investigated. Particular emphasis was placed on evaluating the importance of pesticide binding to naturally occurring colloids. This involved the application of size-based speciation procedures such as equilibrium dialysis. Experiments using radiolabelled pesticides as model contaminants indicated that over the 24 hour time frame of the experiments, the sorption of atrazine onto suspended sediments was not a significant process.

Figure 2.3. Plot of g-hexachlorocyclohexane Koc vs salinity

Humber estuary 22.4.91



natural solids loadings

Figure 2.4. Plot of g-hexachlorocyclohexane Koc vs. Suspended solids conc. Humber estuary 22.4.91

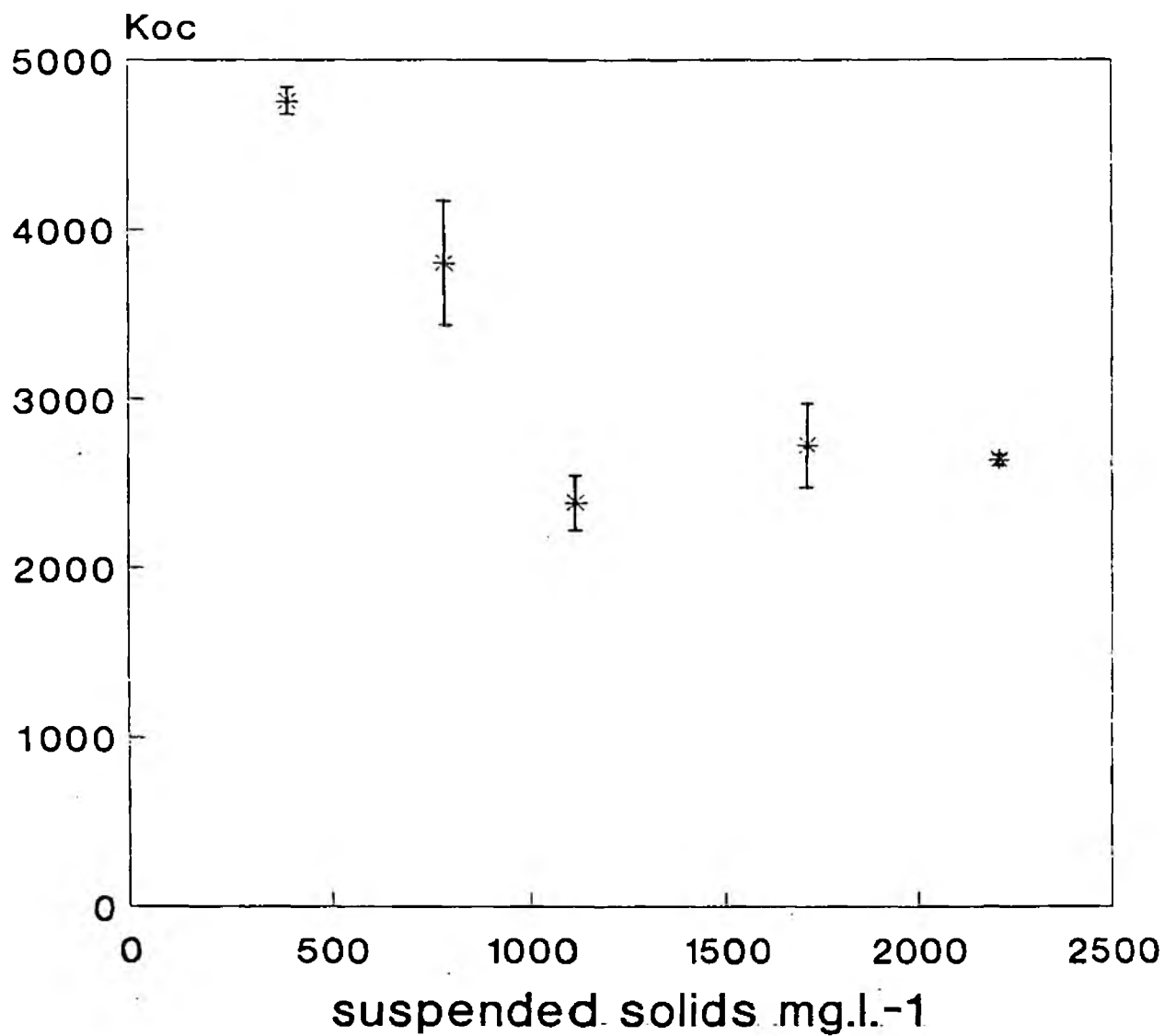
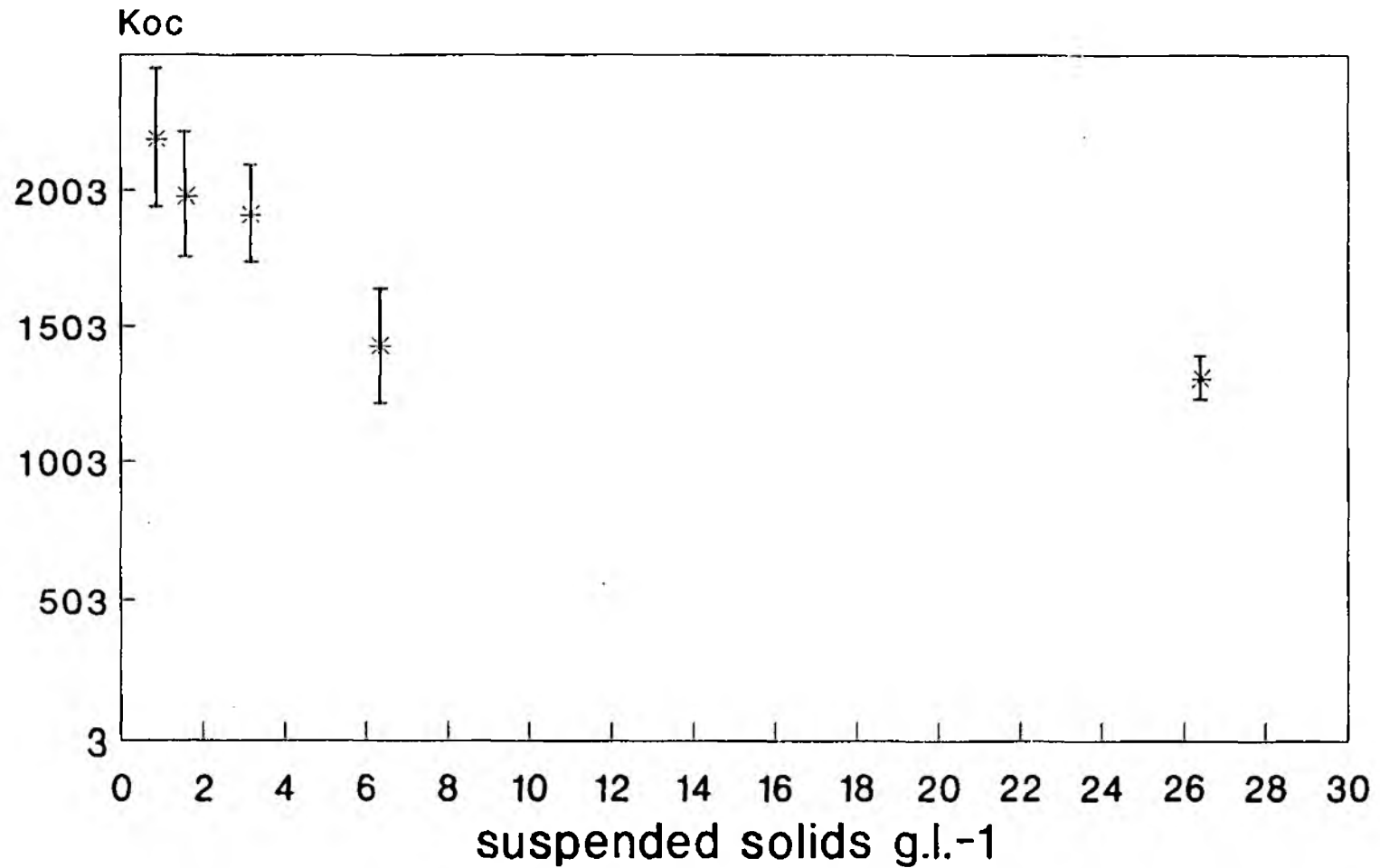


Figure 2.5. Plot of  $\gamma$ -hexachlorocyclohexane  $K_{oc}$  vs  
suspended solids conc. River Thames 18.3.91  
Elevated solids loadings



RIVER THAMES WATER, ELEVATED SOLIDS



Equilibrium dialysis indicated that the two compounds showed little affinity for natural colloids and that  $<0.45 \mu\text{m}$  fractions were probably present in true solution. The measured partition coefficients showed a dependence on salinity and particulate concentrations.

At suspended sediment concentrations typical of the Humber estuary water column ( $<2.5 \text{ g l}^{-1}$ ) a negligible amount of atrazine sorbs to the particulate phases ( $>0.45 \mu\text{m}$ ). Sorption was only observed at high solids concentrations (ca.  $80 \text{ g l}^{-1}$ ) which were representative of the highly turbid zones close to the bed sediment/water interface. Under these conditions, the partition coefficient was shown to vary with salinity. At this high sediment concentration, between 16.2% (in freshwater) and 25.8% (at the saline end-member) of added atrazine was sorbed to particulates.

In contrast, g-HCH exhibited significant partitioning over the typical concentration range for suspended sediments in the Humber estuary. For instance, at a suspended sediment concentration of  $1 \text{ g l}^{-1}$ , 17.7% of added g-HCH would be partitioned onto suspended solids at the freshwater end of the estuary rising to a maximum of 30.9% at a salinity of 22 ‰. Further field studies including other estuaries are required to confirm these predictions.

Equilibrium dialysis was found to be a simple method for investigating the solution phase speciation of organic contaminants. In particular, it is not subject to preconcentration artefacts or adsorption losses which are significant drawbacks of other speciation methods. Experiments indicated that in filtered estuarine samples atrazine and g-HCH are associated with the dialysable fraction ( $<1000 \text{ MW}$ ) and are most likely present in true solution or possibly in association with low molecular weight organics. Interactions with high molecular weight estuarine colloids seem to be unimportant for these compounds.

### 3. TRACE METAL PARTITIONING

#### 3.1 Investigation of effect of natural organic ligands on partitioning equilibria

Earlier work has indicated that significant differences in sorption behaviour can sometimes occur between metal present in samples at the time of collection and that added in subsequent laboratory experiments. In particular, it has been noted that adsorption to vessel walls can sometimes be very much greater for metal spikes than for unamended samples. A possible explanation for this lies in the fact that much of the riverine or estuarine 'dissolved' metal can be either complexed by natural organic ligands or associated with natural colloidal material (Apte and Gardner 1991, Amdurer *et al* 1983, Haekel 1984, Mayer *et al* 1983). On addition of metal in the form of free aquo ion in laboratory experiments, the levels used could possibly exceed the available complexation capacity and therefore show a stronger tendency towards adsorption. Alternatively, adsorption to either vessel walls or particulates could be favoured kinetically over the timescale of the experiment.

In order to establish the importance of such effects a series of three experiments was undertaken using samples from the River Aire:

- Expt 1 A relatively clean filtered upstream sample was used as a base and mixed with aliquots of a contaminated downstream sample to provide a range of 'natural' metal levels. Adsorption to vessel walls was then compared with that for similar metal concentrations spiked into the upstream sample as free aquo ion.
- Expt 2 A similar regime to that for Expt 1 was used but with the addition of a model particulate phase to increase adsorption sites.
- Expt 3 Adsorption of free aquo ion spikes was compared for a filtered untreated, UV irradiated and Chelex 100 resin treated downstream sample.

The general experimental design for sorption studies has been described previously (WRC report NR 2573), and is illustrated in Figure 3.1.

Equilibration was carried out by mechanical shaking of the samples in the dark. All plasticware was cleaned in 5% nitric acid and rinsed with deionised water prior to use. Samples were preserved in 0.2% nitric acid.

### 3.1.1 Comparison of vessel wall adsorption of 'natural' metal spikes with that of free aquo ion spikes.

A water sample from a 'clean' upstream site was taken, and spiked with either a pH adjusted stock metal solution or with an aliquot of a metal polluted downstream sample from the same river, so that approximately the same concentrations would occur in concurrently spiked samples. The downstream sample, with its essentially similar water quality, was seen as the best approximation to a 'natural' metal spike. It is recognised however, that sewage and agricultural inputs, for example, may have altered the nutrient and organic loading.

The upstream River Aire sample was collected at Gargrave (G) and the downstream sample at Snaith (S). Both were prefiltered to 0.4  $\mu\text{m}$ , and then Gargrave was spiked either with a standard made up from stock metal solutions ('standard' spike), or with increasing amounts of Snaith ('mixed river' spike) so that the total volume was 30 ml:

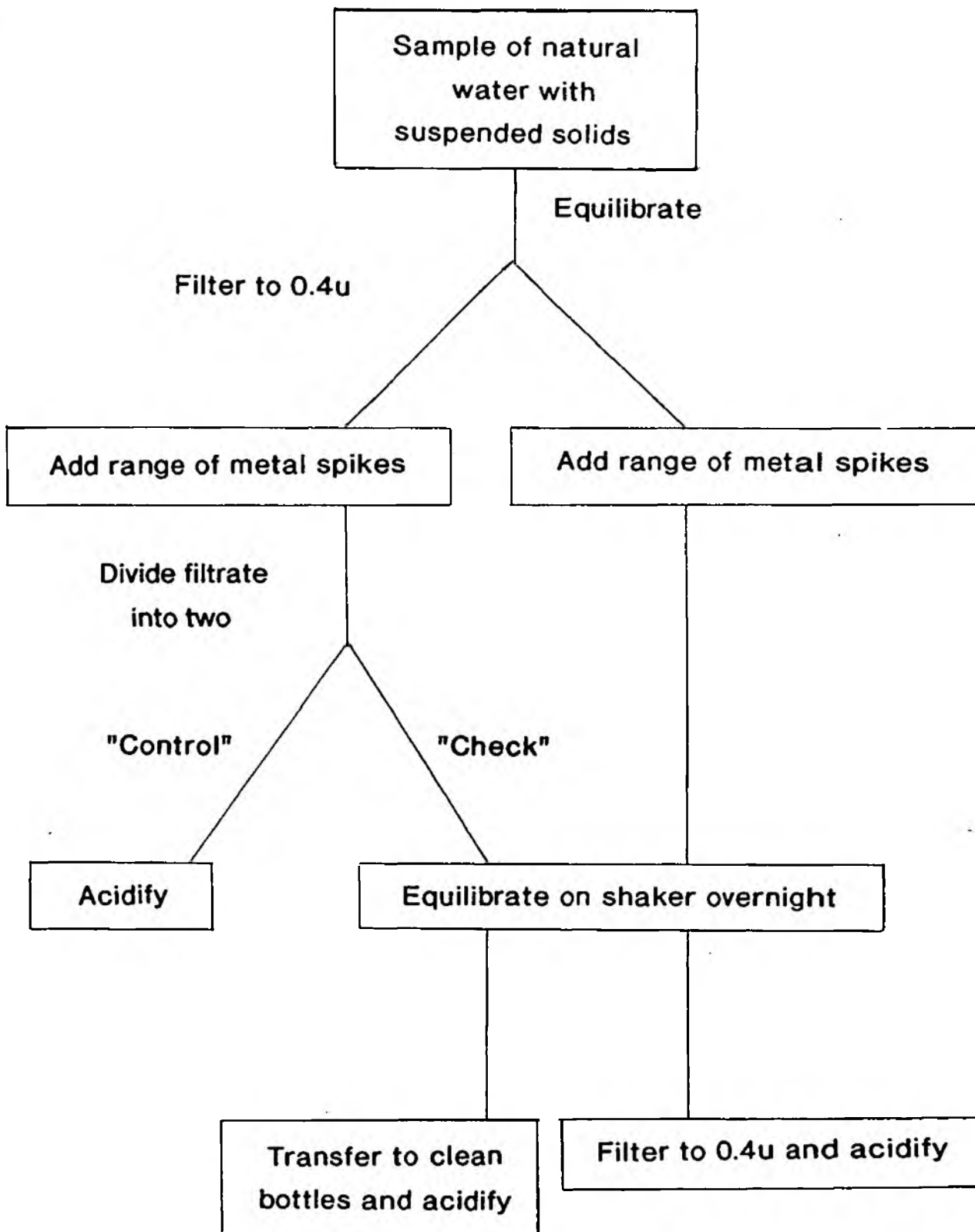
Ratio of Gargrave to Snaith samples in 'mixed river' spike series :

Spike	1	2	3	4	5
	1G	9G:1S	2G:1S	1G:1S	1S

Metal added in the 'standard' spike series was set at levels to give comparable concentrations to those which would result from the river water mixes.

Replicate samples were carried out upon Spikes 1, 3 and 5 for both series. The waters were allowed to equilibrate in Nalgene polyethylene bottles for 20 hours before being transferred to new bottles and acidified.

Fig 3.1 : Outline of experimental method



## Results

The pH of the Snaith sample was 6.8, while that from Gargrave was ca. 7.2 (but of low ionic strength). Their mixing was thus unlikely to have resulted in large precipitative losses.

The metals included in the test were cadmium, chromium, copper and nickel. For cadmium, chromium and copper, there was no evidence of important adsorption to the vessel walls for either series of samples. Mean recoveries of the 'standard' spikes were 106%, 104% and 91%, respectively. For copper the mean recovery of standard spikes was 77% compared with 98% for the 'mixed river' spikes. Although not significant, this therefore suggested a possible tendency for the metal to be more subject to adsorptive loss when introduced as the free ion.

Given that this preliminary experiment had resulted in little metal sorption to vessel walls, a second test was therefore conducted along similar lines but with inclusion of a model particulate phase. This is described in Section 3.1.2 below.

### **3.1.2 Comparison of adsorption of 'natural' metal spikes and free aquo ion spikes in presence of micro-crystalline cellulose**

For this experiment it was considered essential to employ identical particulate material for each test sample. Since these were to be prepared from bulk samples collected at different sites it was not possible to follow the preferred procedure of using unamended natural suspended matter. The option of spiking with a bulk suspension of particulates from one of the sites was also ruled out because of the possibility of release of organic ligands and/or colloids during the equilibration period. For this reason a synthetic model particulate phase, micro-crystalline cellulose (MCC), was adopted. This was added to the prefiltered samples after being acid-washed and rinsed with deionised water until a constant pH was measured in the supernatant liquid. In addition, "control" and "check" (Figure 3.1) samples without solids were also run, to give an indication of vessel wall losses and actual spike levels in the

experiment. ("Control" samples were acidified immediately after spiking, while "check" samples were prefiltered and equilibrated alongside other samples, before being transferred into new bottles.)

## Results

The MCC was introduced at a concentration of 63 mg/l. Test samples of 50 ml volume were equilibrated for ca. 20 hours before being transferred into new bottles. Two replicates of each sample were performed. As before, 'standard' spikes were introduced directly to the Gargrave sample and 'mixed river' spikes were prepared by addition of increasing proportions of Snaith sample as follows:

Ratio of Gargrave to Snaith samples in 'mixed river' series:

Spike	1	2	3	4	5	6	7
	1G	9G:1S	4G:1S	3G:2S	2G:3S	1G:4S	1S

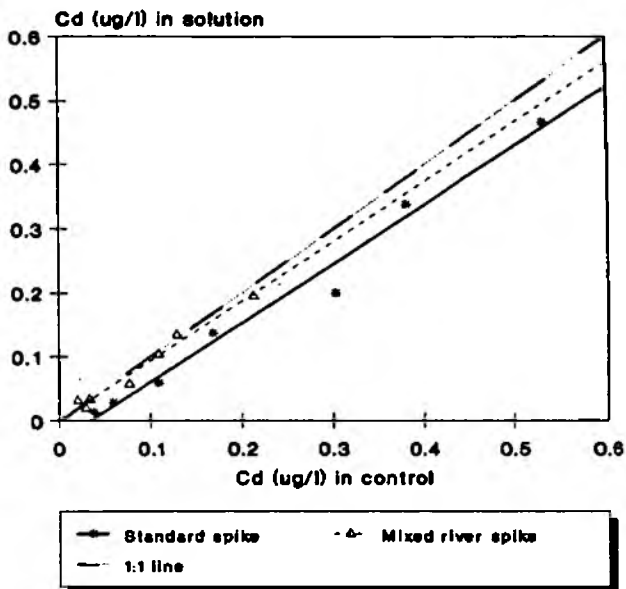
Results obtained are illustrated in Figures 3.2a-d. The dashed line (1:1) is included to provide a marker of zero adsorption (ie if all the metal added had remained in solution).

Cadmium - The 'mixed river' spikes proved indistinguishable from the 1:1 line indicating negligible adsorption to the substrate. Although 'standard' spikes gave consistently lower dissolved phase concentrations, the level of adsorption indicated remained minimal.

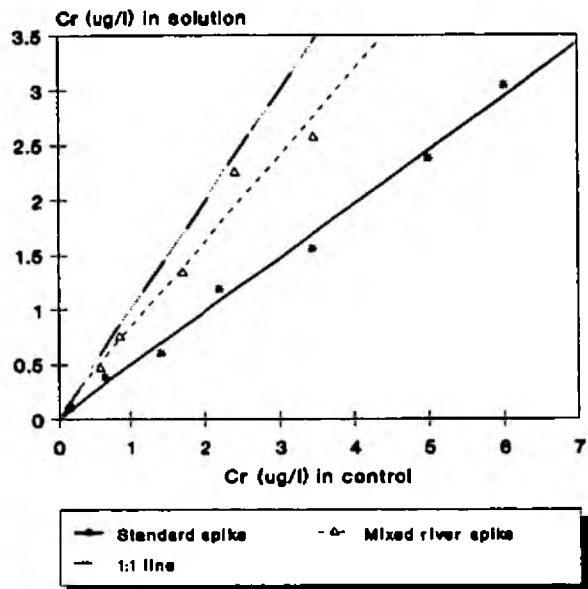
Copper - The degree of adsorption observed was slightly higher than for cadmium and again there was an indication of somewhat greater adsorption for the 'standard' spikes.

Chromium - By far the most significant effect was observed in this case. Responses for the 'mixed river' spikes demonstrated only low levels adsorption while 'standard' spikes consistently showed losses in the region of 50%. This strongly suggests organic ligands and/or colloidal material play an important part in controlling chromium

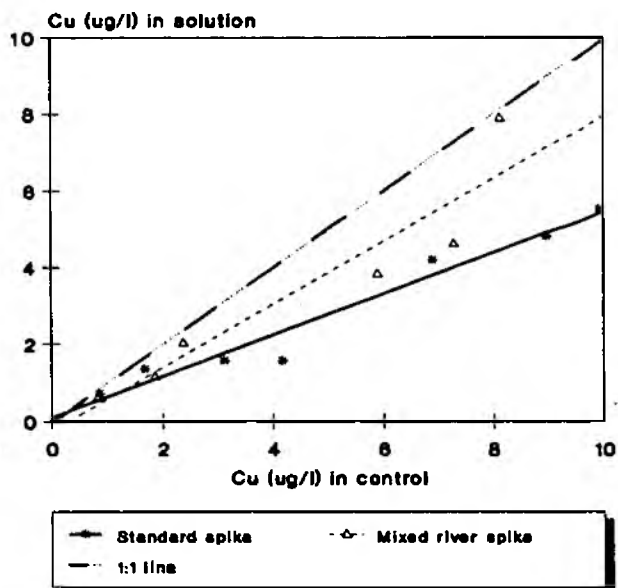
**Fig 3.2a Cadmium adsorption onto mcc**



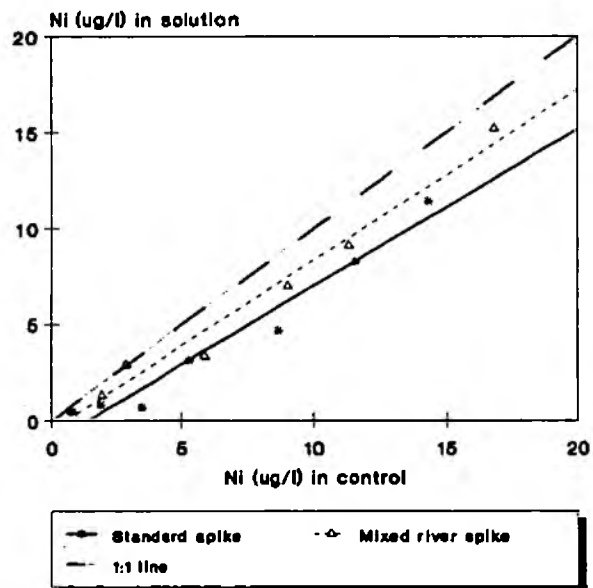
**Fig 3.2b Chromium adsorption onto mcc**



**Fig 3.2c Copper adsorption onto mcc**



**Fig 3.2d Nickel adsorption onto mcc**



partitioning in the sample. It must be noted, however, that oxidation state differences between the 'standard' spike and chromium present in the sample initially could also have an influence.

Nickel - The picture for nickel was almost identical to that for cadmium, with little adsorption occurring even for the 'standard' spike.

These results suggest that, for studies where appreciable adsorption occurs, the presence of dissolved phase natural organics/colloids may be an important factor in controlling partitioning behaviour. The finding is clear for chromium, and to a lesser extent copper. However, to test the hypothesis for cadmium and nickel it would be necessary to carry out further tests at a much higher solids loading.

### **3.1.3 Comparison of vessel wall adsorption of free aquo ion spikes for untreated, UV irradiated and Chelex 100 resin treated samples**

Having established certain differences in sorption behaviour for metals present in samples at the time of collection and that added in laboratory experiments, a further series of tests were set up to investigate the significance of natural organic ligands in more detail.

The tests were carried out using river water from the Aire at Snaith. Four sets of samples were run: one deionised water set which was used to provide analytical confirmation of spike levels, and three using prefiltered river water from Snaith. Losses to vessel walls only were examined, with 15 ml samples in 50 ml bottles giving a relatively large surface area for adsorption during the overnight equilibration. The river water was divided into:

- a) a filtered sample (S);
- b) an UV-irradiated (UV) sample; and
- c) a Chelex-100 (C) treated sample.



The untreated filtered sample was used to give background information on adsorptive behaviour of 'standard' laboratory spikes. The treatment with UV irradiation was carried out to break down natural organic ligands in the sample and release complexed metals. Chelex treatment was intended to remove much of the metal already present in the sample while leaving its natural organics content essentially intact.

## Results

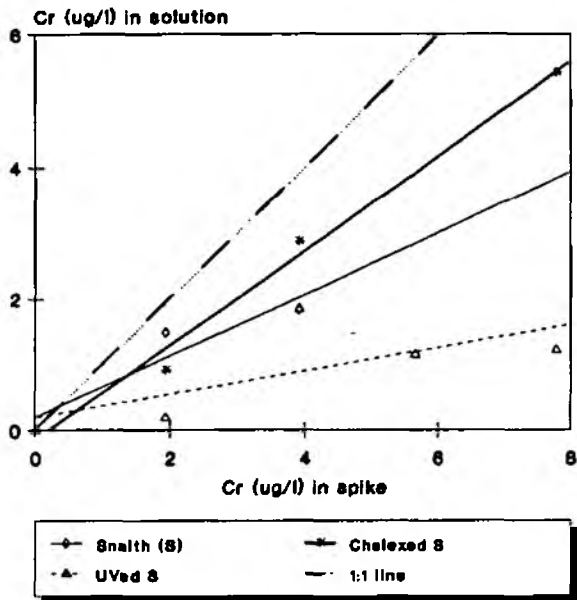
See Figures 3.3a-c. Data are presented with their respective initial metal concentrations subtracted from each spike level, and plotted against the spike concentration found in the deionised water sample set (control).

Chromium - Adsorptive losses occurred in all cases, with those in the untreated (S) and Chelex-treated (C) samples not being significantly different from each other. Chromium which would normally have been organically-bound (UV) however, showed greater losses. This suggests that organic complexation of this metal plays an important role in preventing adsorption to the sediment, a point noted previously by Mayer *et al* (1983).

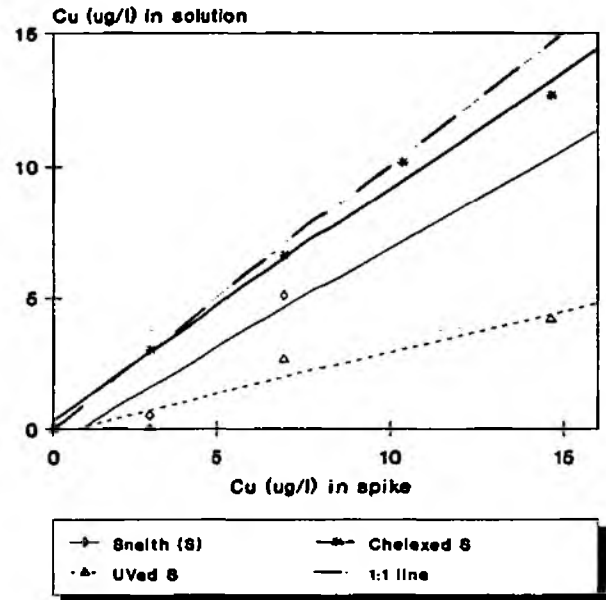
Copper - Again there is a spread of data, depending upon the treatment the river water received. Where the sample had much of its initial metal load removed (C), there is no significant adsorption to bottle surfaces, reflecting the strong attraction organic ligands and copper have for each other (Apte *et al* 1990). Data for the untreated water S are scattered, but lie between C and UV, suggesting that some of the added copper has been organically-complexed and/or held in solution. Copper added to the UV-treated sample is subject to high adsorption, with only c. 30% of the spike remaining in solution.

Nickel - In general there was little adsorption in any of the samples for this metal. This reflects the low laboratory  $K_p$ s generally found for nickel.

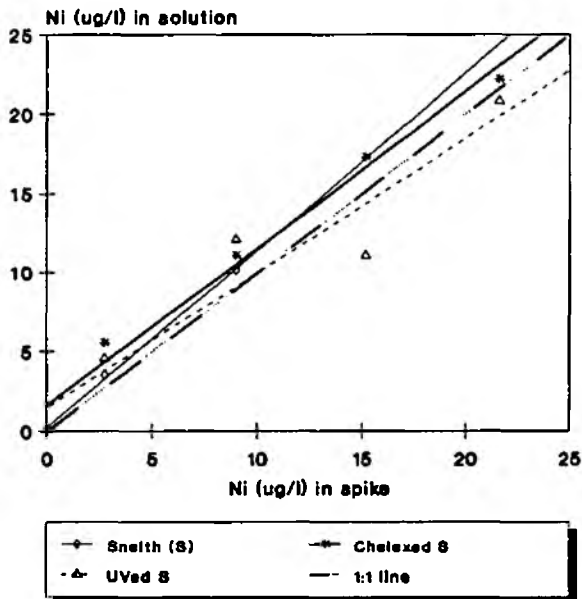
**Fig 3.3a Effect of UV/Chelex treatments on Cr adsorption**



**Fig 3.3b Effect of UV/Chelex treatments on Cu adsorption**



**Fig 3.3c Effect of UV/Chelex treatments on Ni adsorption**



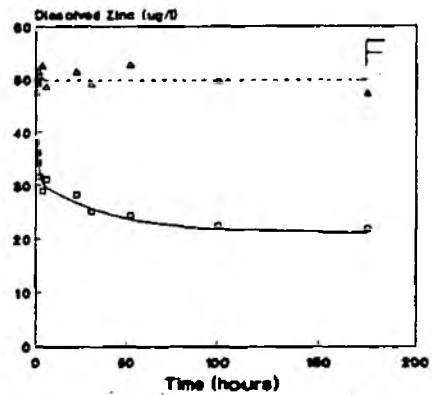
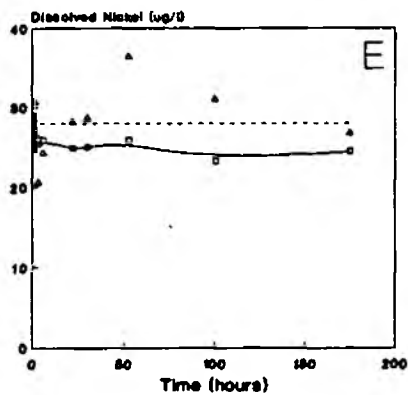
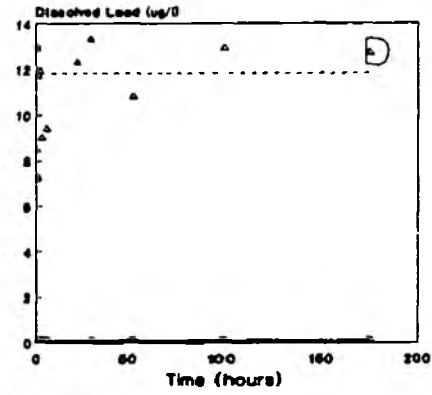
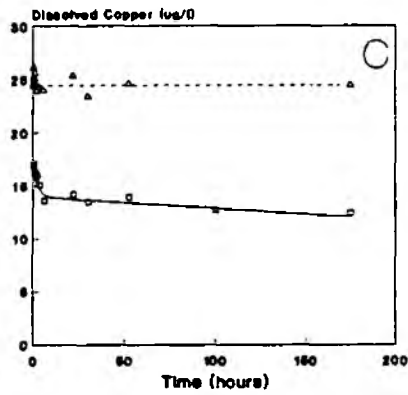
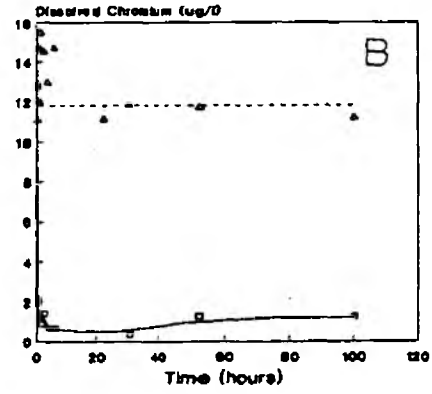
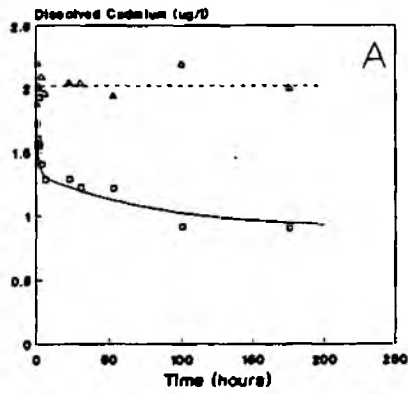
These data provide information upon the constituents of natural waters which are important in keeping metals in the dissolved phase. Adsorption to solid phase materials generally represents reduced metal availability and transport. The Chelex-treated samples gave straight line graphs close to the zero adsorption line, suggesting plenty of capacity to keep dissolved metals in solution, (except in the case of metals which have high laboratory partition coefficients). Untreated Snaith samples generally showed some ability to keep metals in solution, although this was lower than in the Chelex-treated ones. Marked differences were found in the UV-irradiated sample however; clearly organic ligands play an important role in retaining metals in solution.

### **3.2 Investigation of kinetics of sorption to Humber suspended particulate matter**

The kinetics of adsorption of trace metals to natural suspended particulate matter in the Humber were investigated using a bulk sample of medium salinity (13 ppt) and solids concentration of 130 mg/l. This was collected from the Hessele site during the April 1991 survey. A four litre sample was simultaneously spiked with 2 µg/l Cd, 10 µg/l Cr and Pb, 20 µg/l Cu and Ni, and 40 µg/l Zn. Subsamples were then taken at 0.08, 0.25, 0.5, 0.8, 1.25, 2, 3.25, 5.5, 22, 30, 52.5, 100 and 175 hour intervals and analysed for "dissolved" metal contents after separation both by filtration to 0.4 µm and by centrifugation at 6000 rpm. Throughout the equilibration period the bulk sample was shaken mechanically and kept in darkness. A control sample spiked with the same metal levels, but for which all suspended particulates had previously been removed by filtration, was taken through an identical procedure.

Results obtained are shown in Figure 3.4. With the exception of chromium there were no important differences between data obtained with phase separation carried out by centrifugation and that obtained after filtration. Mean results are therefore displayed in the plots. For chromium, there was some evidence of introduction of contamination during the centrifugation process and only filtration data are shown in this case.

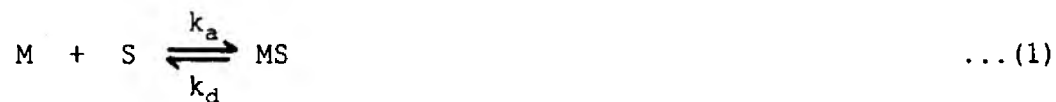
Fig 3.4 Adsorption kinetics on Humber Estuary suspended particulate matter



The general trend in metal behaviour was found to be an initial rapid adsorption during the first five minutes, followed by slower uptake until an approach to equilibrium partitioning was apparently reached by the end of the 175 hour period. For chromium and lead, levels dropped extremely rapidly to close to or below detection limit, while nickel levels remained close to that of the control. This was in line with expectation, based on previous partition coefficient measurements, but meant that it was not possible to use the data to study kinetic processes for these metals in greater detail.

To date, considerably less attention has been devoted by other workers to the study of the kinetics of trace metal adsorption and desorption than to measurements of equilibrium partitioning. The relative merits of the two approaches have been discussed by Honeyman and Santschi (1988) and Morris (1990). Clearly, residence times within the system of interest are a major consideration in this respect.

In terms of kinetics, the simplest possible model for sorption at a solid surface would be a reversible first-order process which can be expressed as:



where M is the metal ion and S is a solid phase sorption site.

Thus the rate of change of metal concentration with time:

$$\begin{aligned} d[M]/dt &= k_d \cdot [MS] - k_a \cdot [M] \cdot [S] \\ &= k_d \cdot [MS] - k_a \cdot SK \cdot P \cdot [M] \\ &= k_d \cdot [MS] - k_a' \cdot P \cdot [M] \end{aligned} \quad \dots(2)$$

where SK is the concentration of sites per kilogram of solids and P is the particle concentration in solution in kg/l.

For computation of the adsorption and desorption rate constants from dissolved phase/time profiles it is more appropriate to use the integrated form:

$$[M]_t = [M]_o \left| \frac{k_d + k_a \cdot P \cdot \exp\{-(k_a \cdot P + k_d) \cdot t\}}{k_a \cdot P + k_d} \right| \quad \dots (3)$$

Now, given that at equilibrium  $d[M]/dt = 0$ :

$$k_a' / k_d = [MS] / (P \cdot [M])$$

and since the equilibrium partition coefficient:

$$K_p = ([MS]/P) / [M]$$

it follows that:

$$k_d = k_a' / K_p \quad \dots (4)$$

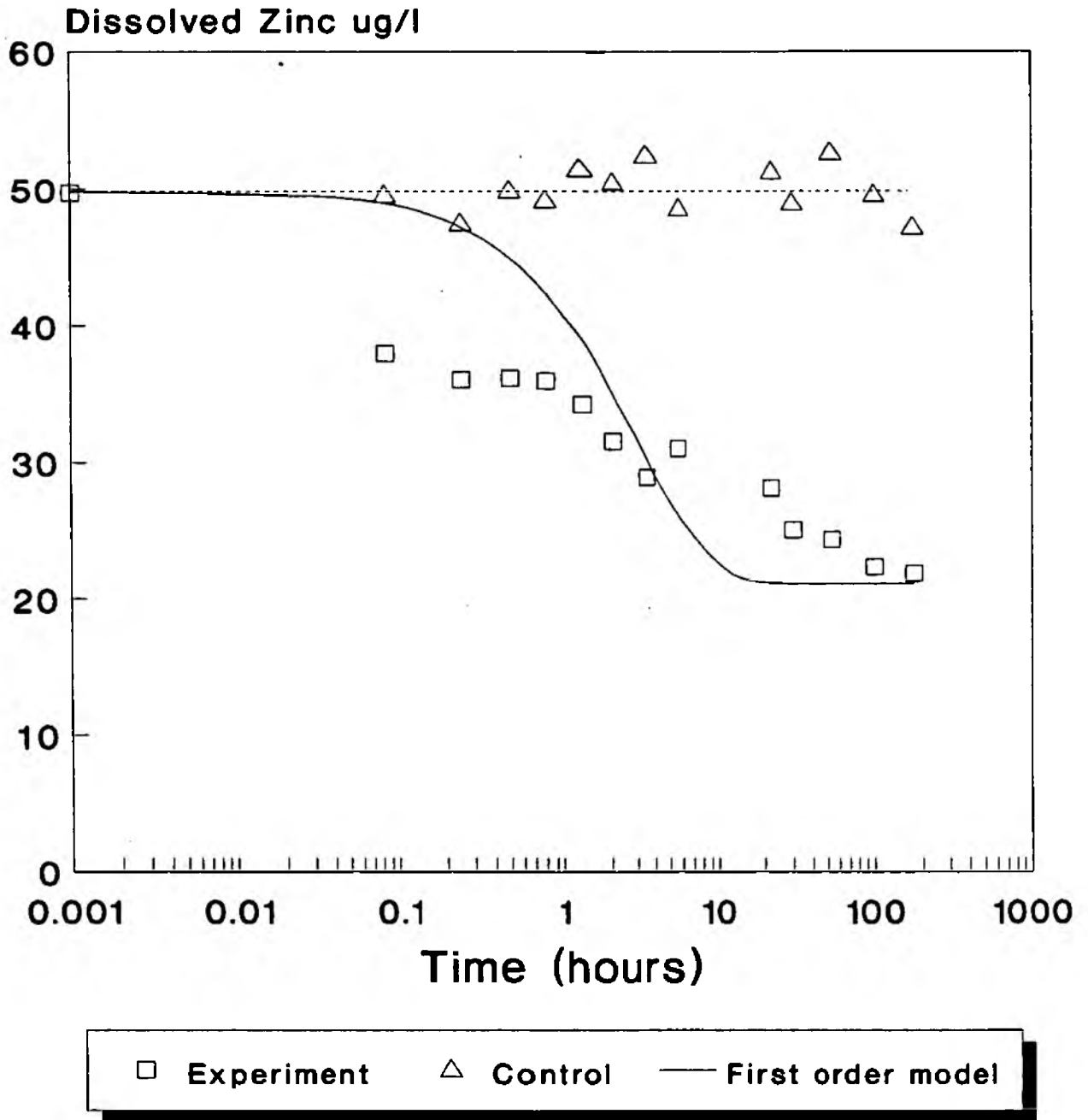
and equation (3) then reduces to:

$$[M]_t = [M]_o \left| \frac{1/K_p + B \cdot \exp\{-k_a \cdot (B + 1/K_p) \cdot t\}}{B + 1/K_p} \right| \quad \dots (5)$$

To determine the suitability of this simple model, quasi-equilibrium partition coefficients for cadmium, copper and zinc were calculated from the 175 hour dissolved phase concentrations, and best-fits to the observed sorption/time plots were computed by iteration of  $k_a$ . This quickly revealed that at best a very poor fit could be obtained, with serious underestimation of the rate of adsorption in the early stages coupled with overestimation of the rate of attainment of equilibrium. An example is shown for the case of zinc in Figure 3.5. This is presented as a semi-logarithmic plot to demonstrate more clearly the poorness of fit in the initial stages of the sorption process.

Similar difficulties in fitting a simple kinetic model have been experienced by other workers. For instance, Nyffeler *et al* (1984) found that for long term experiments (ca. 100 day) on bed sediment material resuspended in seawater, the partitioning of radiotracers proved difficult to fit to first order kinetics at time periods of greater than two to four days. They therefore proposed a two-stage sequential first order model which gave a reasonable fit to their data. More recently, Jannasch *et al* (1987) have reported results for

**Fig 3.5 Fit of first order reversible kinetic model to zinc sorption data**



radiotracer partitioning on marine particles that suggest the existence of four distinct processes with timescales of <1 min/, ca. 20 min., ca. 4 hours and several days.

Returning to our own data for the Humber system, Table 3.2 shows partition coefficients for cadmium, copper and zinc calculated after equilibration times of 5 minutes, 22 hours and the full period of 175 hours. The 5 minute  $K_p$ 's indicate the extent of extremely rapid sorption processes while the 22 hour data is included for comparative purposes, since the majority of other reported experiments have been carried out over such a timescale.

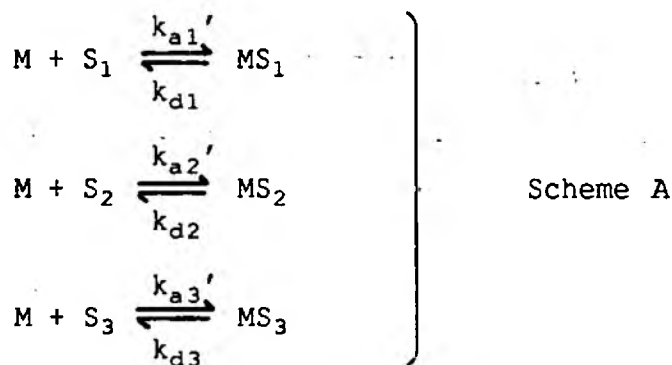
**Table 3.1 Variation of trace metal partition coefficients for Humber suspended particulates with time of equilibration**

	$K_p$ 5 min.	$K_p$ 22 hr	$K_p$ 175 hr
Cadmium	$2.3 \times 10^3$	$4.6 \times 10^3$	$10.0 \times 10^3$
Copper	$5.0 \times 10^3$	$8.5 \times 10^3$	$12.2 \times 10^3$
Zinc	$2.9 \times 10^3$	$7.6 \times 10^3$	$13.6 \times 10^3$

From Table 3.1 it can be seen that the rapid processes occurring within the initial 5 minute period constitute an important proportion of the overall sorption. Such processes may actually occur even more rapidly but for the present experimental arrangement it was not possible to achieve phase separation over a shorter timescale. However, examination of the data obtained over the first few hours of equilibration indicated that a distinct sorption stage was already complete within the initial five minutes. For all three metals a second stage was then evident over the period up to ten hours, followed by a much slower step continuing to the end of experiment at 175 hours.

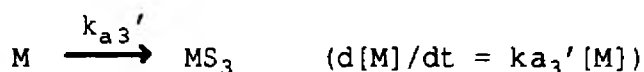
By a process of iteration best fits to the observed data were therefore obtained on the basis of three independent first order reversible processes covering these timescales, ie:





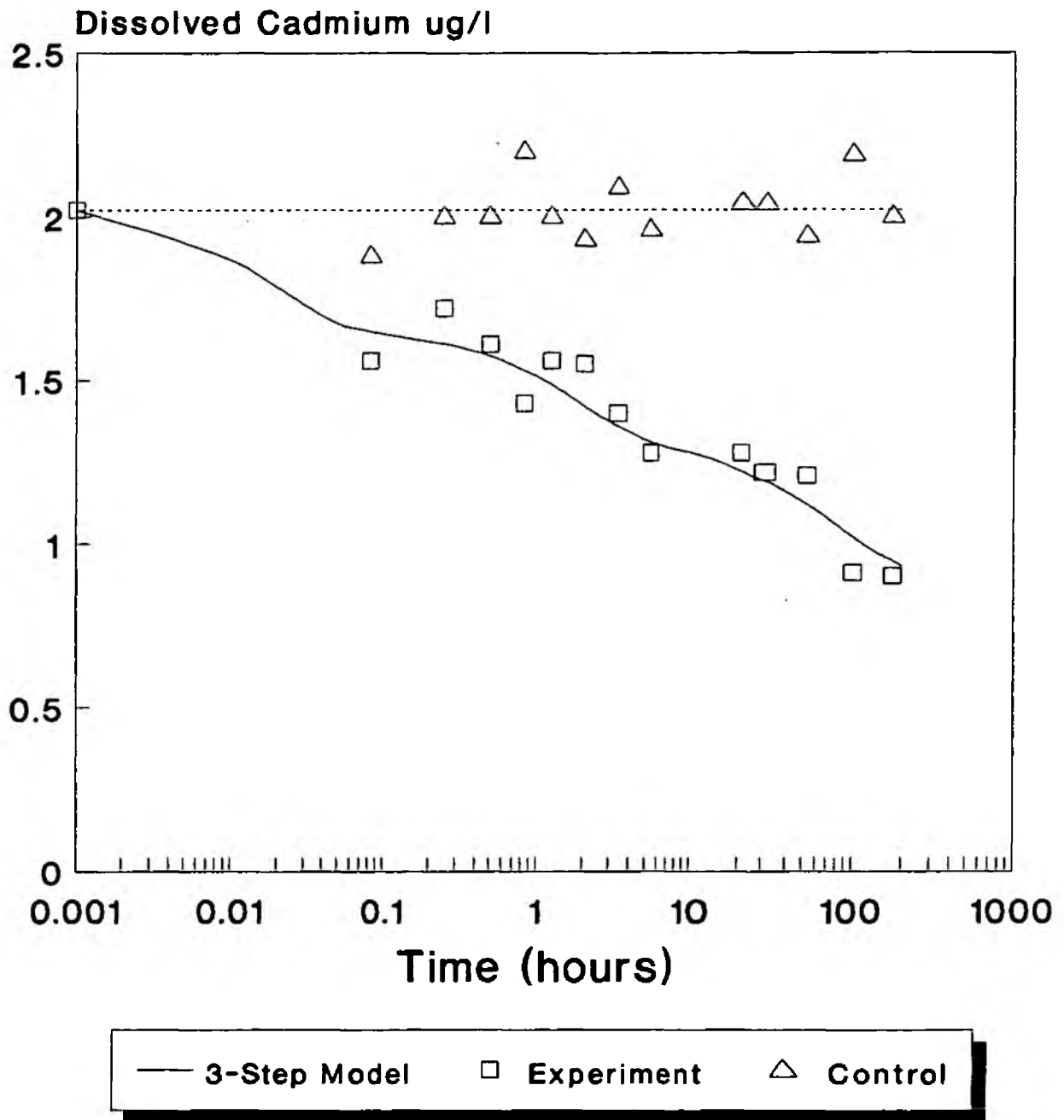
It was further assumed that the relative rates of the three processes were such that only one was controlling the overall rate at any one time and that each had fully reached equilibrium before the subsequent stage became dominant.

Results obtained in this way demonstrate an extremely good fit in all cases, and are shown in Figure 3.6a-c (again in the form of semi-log plots). Given that no data were available for times of less than five minutes, rate constants for the first stage were computed such that equilibrium for the first step was just achieved within the timescale; these must therefore be taken as limiting constants indicating the slowest possible reactions compatible with the observed behaviour. Full results for the best fit constants for each of the three proposed stages are listed in Table 3.2. In the case of copper, the final sorption stage was apparently still some way from equilibrium after 175 hours and this was therefore modelled on the basis of simple non-reversible first order kinetics, which proved adequate within the available timescale:

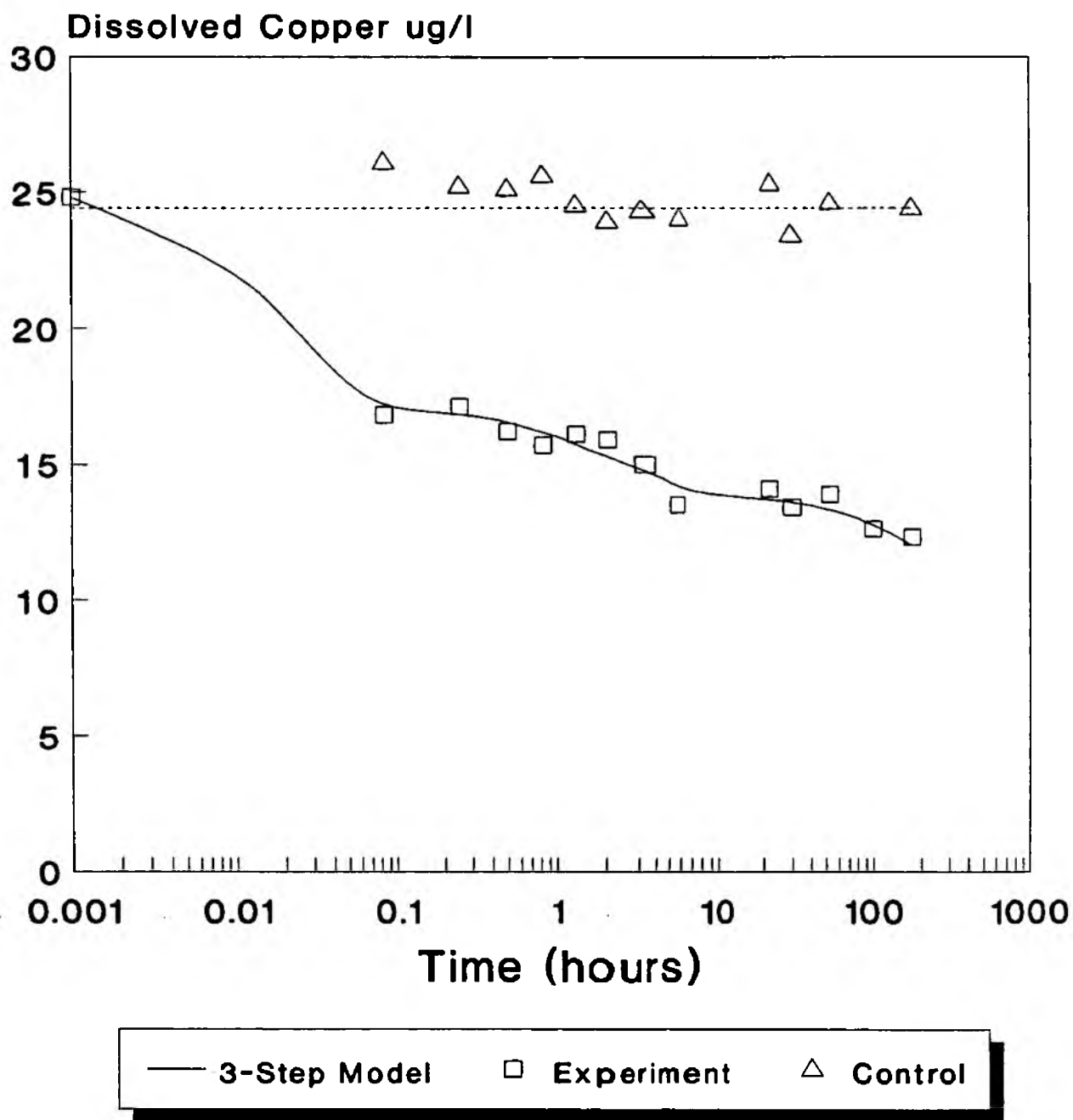


The above model (Scheme A), based on parallel sorption to a series of sites of widely varying metal binding strengths, thus appears adequate for mathematical prediction of trace metal sorption behaviour to natural suspended sediments. Conceptually, however, such behaviour is equally likely to occur via a series of serial sorption reactions, as suggested by Jannasch *et al* (1987):

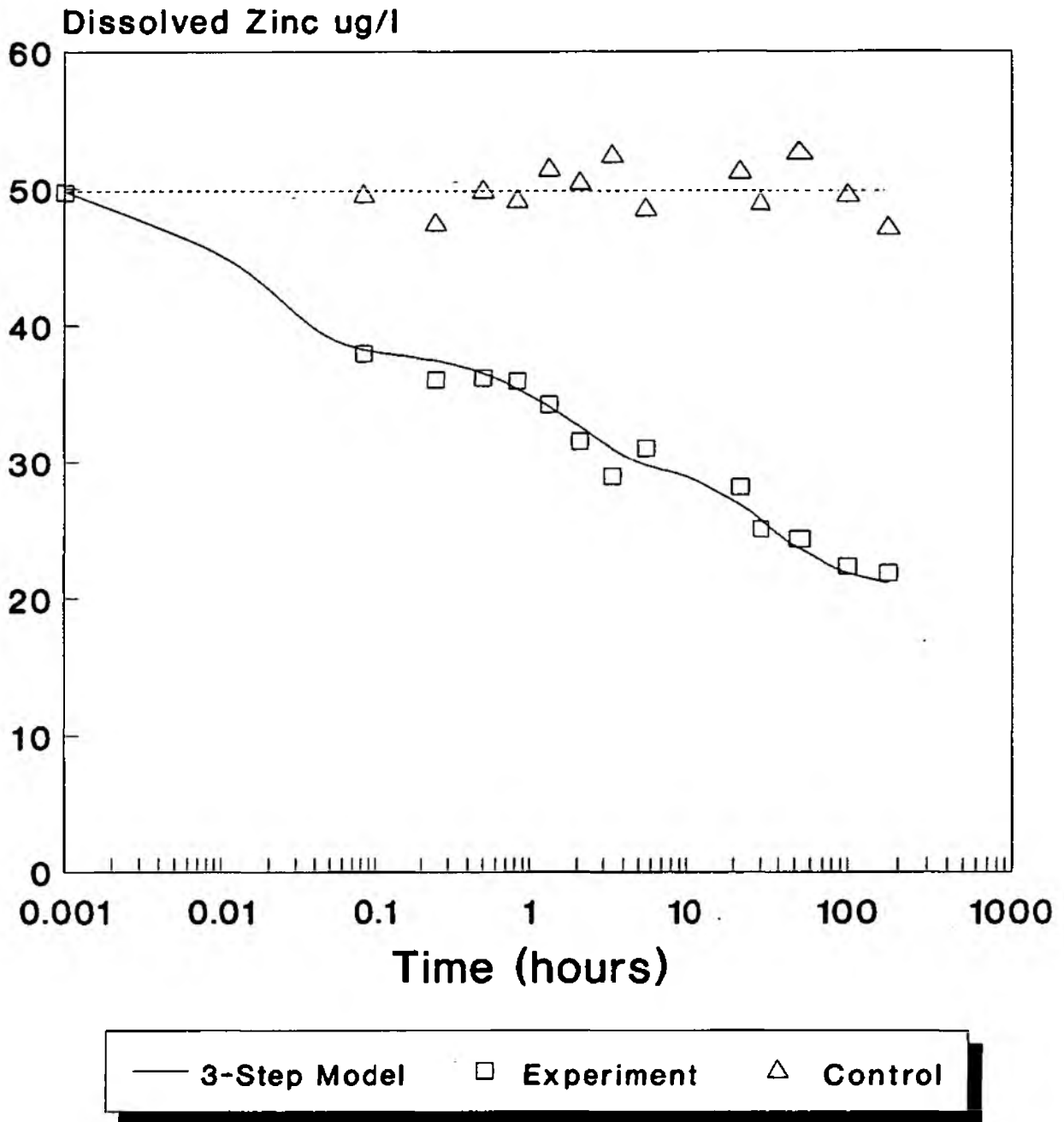
Fig 3.6a Adsorption kinetics of cadmium on Humber Estuary suspended particulates



**Fig 3.6b Adsorption kinetics of copper on Humber Estuary suspended particulates**



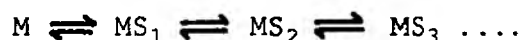
**Fig 3.6c Adsorption kinetics of zinc on Humber Estuary suspended particulates**



**Table 3.2 Computed rate constants (hr<sup>-1</sup>) for 3-stage first order reversible model fitted to experimental sorption data**

	Copper	Cadmium	Zinc
$k_{a1}'$	$1.2 \times 10^5$	$7.0 \times 10^4$	$1.0 \times 10^5$
$k_{b1}$	$2.4 \times 10^1$	$3.8 \times 10^1$	$3.5 \times 10^1$
$k_{a2}'$	$8.0 \times 10^2$	$8.0 \times 10^2$	$1.0 \times 10^3$
$k_{b2}$	$3.0 \times 10^{-1}$	$3.5 \times 10^{-1}$	$3.2 \times 10^{-1}$
$k_{a3}'$	$9.6 \times 10^0$	$3.0 \times 10^1$	$7.0 \times 10^1$
$k_{b3}$	---	$8.8 \times 10^{-3}$	$1.7 \times 10^{-2}$

Scheme B



This can be envisaged as an initial rapid sorption to surface sites followed by slow migration into occluded sites within the pores of the particulate material. In practice, from the data presently available it is impossible to distinguish between these two possible mechanisms. Nevertheless, given the very good fits obtained, the Scheme A constants given in Table 3.2 should prove highly useful for incorporation in environmental fate models.

**3.3 Influence of particulate concentration on rapid (<5 minute) sorption processes**

Given the relative importance of adsorption processes occurring within a five minute contact time, and the fact that such sorption is likely to be readily reversible, it was decided to undertake further study on the effect of particulate concentration on partition coefficients measured after this short equilibration period (rather than for the 24-hour period employed in previous work - Report NR 2573).

The basic approach used was similar to that for earlier experiments and involved spiking a range of metal levels into both an unamended Hessele sample (particulate concentration 650 mg/l) and the same sample diluted with a

prefiltered aliquot of itself to give a solids concentration of 150 mg/l). These were then shaken for five minutes and rapidly filtered to separate the dissolved phase.

Six metals were employed in the test: cadmium, copper, nickel, chromium, zinc and arsenic. In the case of chromium, nickel and arsenic no significant differences in behaviour were observed for the two solids levels; however, establishment of accurate adsorption isotherms proved impossible because only very small changes in dissolved phase concentrations occurred for nickel and arsenic, while chromium proved to be almost completely adsorbed.

For cadmium, copper and zinc, observed adsorption isotherms are shown in Figure 3.7a-c. These clearly demonstrate no significant differences for the two solids levels, which is very encouraging from the modelling point of view. Overall mean partition coefficients for the three metals are shown in Table 3.3.

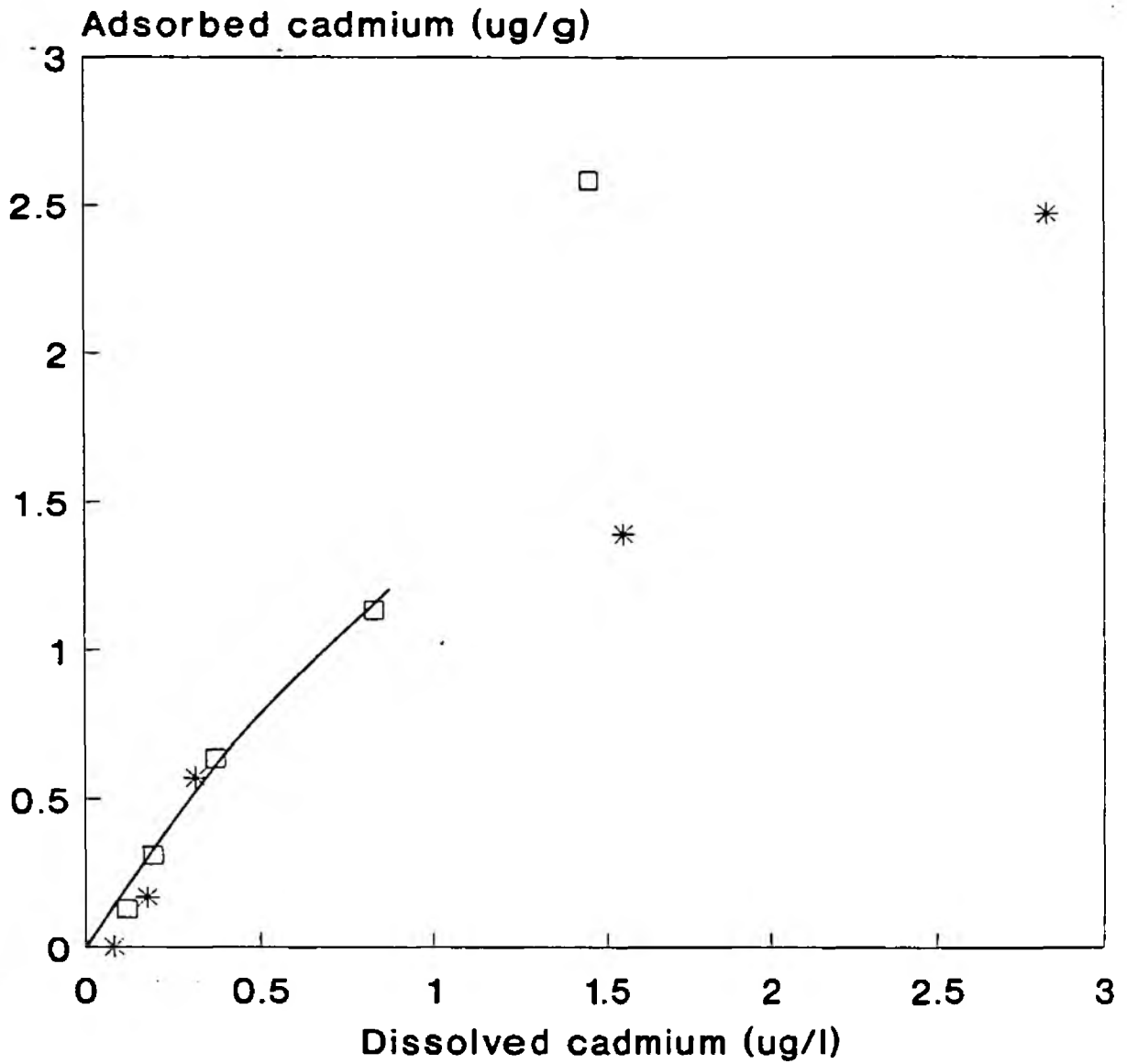
**Table 3.3 Mean five-minute partition coefficients for data obtained at solids levels of 150 mg/l and 650 mg/l**

	$K_p$ 5 min
Cadmium	$1.5 \times 10^3$
Copper	$6.7 \times 10^3$
Zinc	$3.0 \times 10^3$

### 3.4 Humber field survey

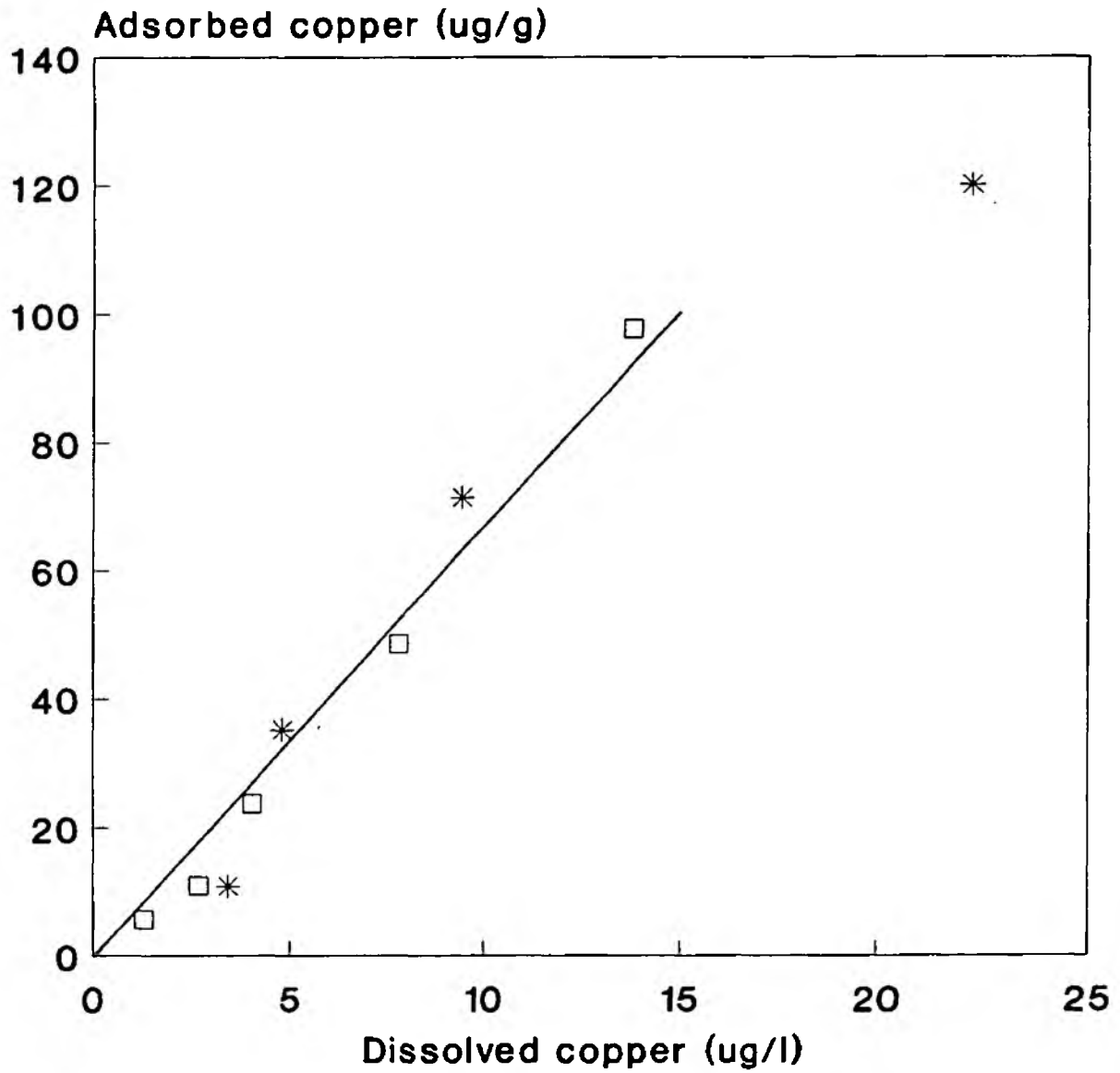
A field survey was carried out upon the Humber river system on 22 April 1991, in a similar fashion to that performed in September 1989 (NR 2573, 1990). Water samples were taken by two teams during one tidal cycle, with one team collecting freshwaters and the other saline waters. See Figure 3.8 for sampling sites. The survey was carried out in spring rather than autumn to check for seasonal variations in metal levels and partitioning behaviour.

**Fig 3.7a Particulate concentration effect on 5-minute adsorption isotherms**



\* 150 mg/l solids      □ 680 mg/l solids

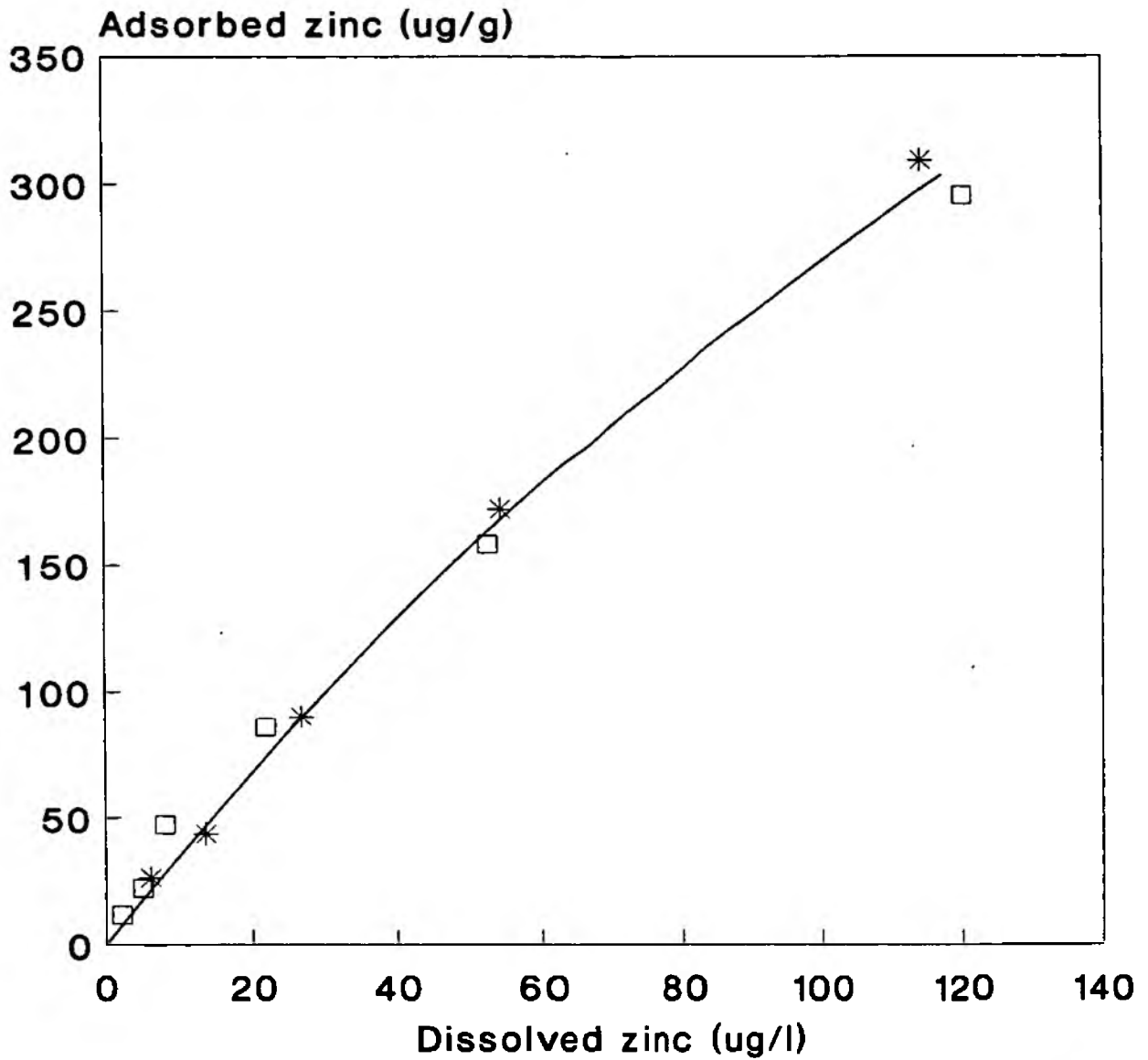
**Fig 3.7b Particulate concentration effect on 5-minute adsorption isotherms**



\* 150 mg/l solids      □ 680 mg/l solids

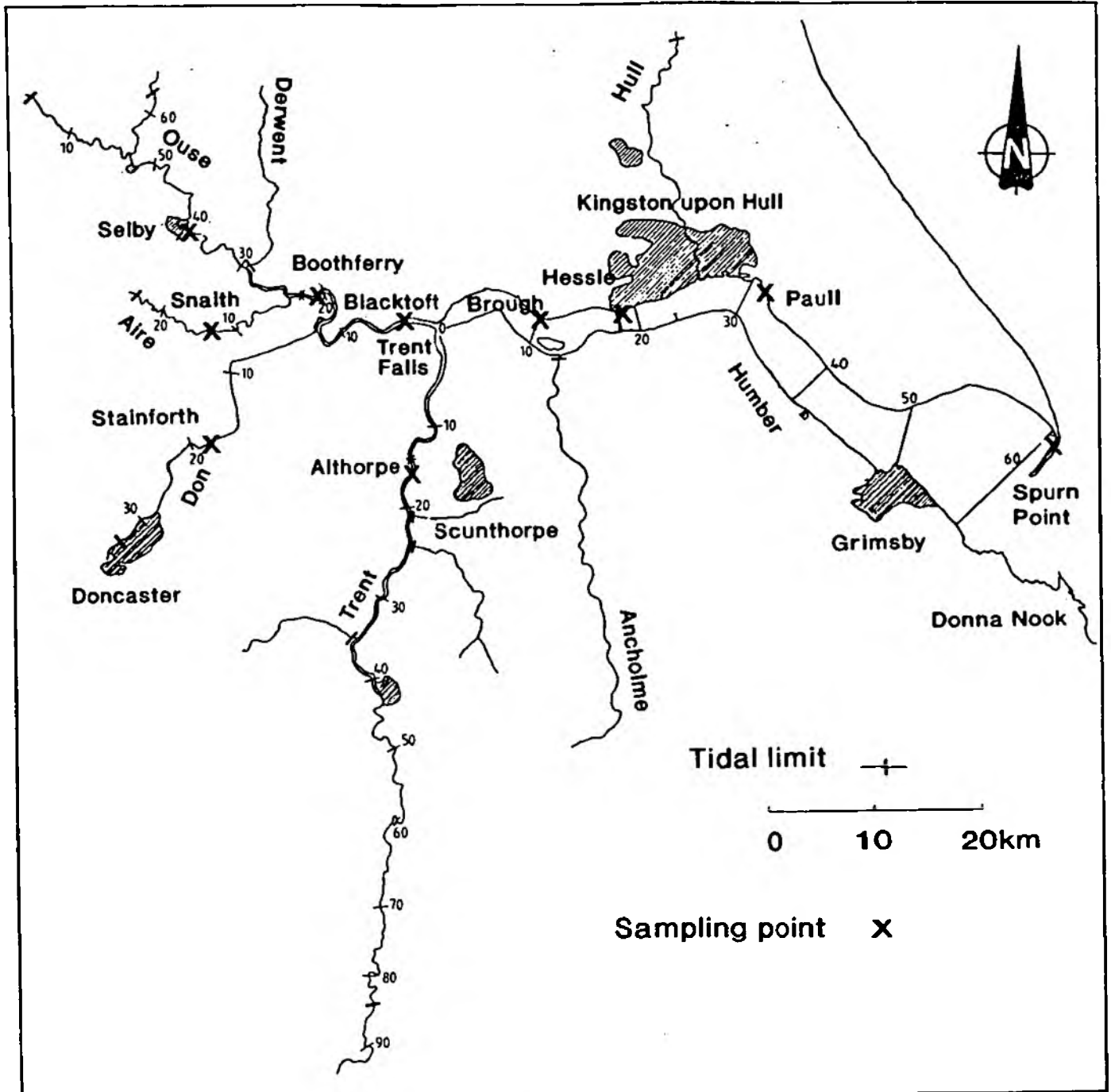


**Fig 3.7c Particulate concentration effect on 5-minute adsorption isotherms**



\* 150 mg/l solids      □ 680 mg/l solids

Fig 3.8 The Humber Estuary



## Aqueous and particulate metal concentrations in the Humber Estuary

Samples were filtered through acid-washed 0.4  $\mu\text{m}$  Nuclepore membranes immediately after collection, although some of the freshwater samples, with high colloidal loading, were stored for a few hours. Data from the previous survey suggest that this should not have greatly altered the partitioning between solid and solution phase. Duplicate filtrations of 200-250 ml were performed, in order to provide particulate material for sequential and nitric acid "total" digestions, and to reduce the significance of any contamination. In accordance with the previous survey, suspended solids were seen as giving the best indication of *in situ*  $K_p$ s.

Deionised water (DIW) blanks were run through the filter units at all sites. Quality control standards were spiked into both DIW and prefiltered samples, which were then poured into clean filter units and re-filtered. All samples were preserved at 0.2%  $\text{HNO}_3$ .

## Results

See Table 3.4 for details of sample characteristics. The temperature varied between 8-9  $^{\circ}\text{C}$ , except at Spurn where the highest reading of 11.5  $^{\circ}\text{C}$  was obtained. pH levels were all in the range 7-8. Dissolved oxygen (DO) measurements at the freshwater sites suggest that the water was well-oxygenated (anoxic conditions may lead to remobilisation of metals from sediment). DOC levels (measured by high temperature oxidation) were generally higher in the freshwater inputs than in the estuary. The sharp peak at Brough may be caused by the sewage outfall just upstream of the sampling point. POC levels (measured by loss on ignition) show little variation down the estuary, apart from a small peak at Brough. Levels of suspended solids covered a large range (14-6400 mg/l). The lowest amounts were found in the rivers, while the highest concentration found was at Spurn. The sample at this end-member site was taken from a point further inland than during the previous survey, since access was restricted by storm damage. A high particle loading in the sample may have led to some settling of the solids during subsampling for filtration; despite vigorous agitation, as the filtrations were carried out after pouring off some

**Table 3.4. Humber field survey 22/4/91 : Sample characteristics**

Site	Time of sampling	Temp °C	pH	Conductivity uMho	Salinity ppt	DO %	DOC mg/l	POC %	Suspended solids mg/l
Althorpe	17.10	9.6	8.1	900	-	88	8.62	*	314
Boothferry	18.20	8.6	7.8	900	-	77	5.96	*	156
Selby	12.30	9.1	8.0	*	-	91	10.36	*	23
Snaith	13.40	9.9	7.5	895	-	81	7.25	*	14
Stainforth	16.00	9.6	7.5	1000	-	77	4.85	*	18
Blacktoft	19.05	8.3	7.1	2150	1.9	*	5.41	8.0	1590
Brough	16.15	9.0	7.4	*	9.0	*	9.56	10.9	876
Hessle	17.40	8.9	7.4	*	13.0	*	4.12	8.8	1751
Paull	14.30	8.6	7.8	*	22.5	*	3.29	9.4	680
Spurn	12.50	11.5	8.1	*	32.6	*	2.84	9.0	6400

water into a bulk container, the solids concentration measured may have been anomalously high.

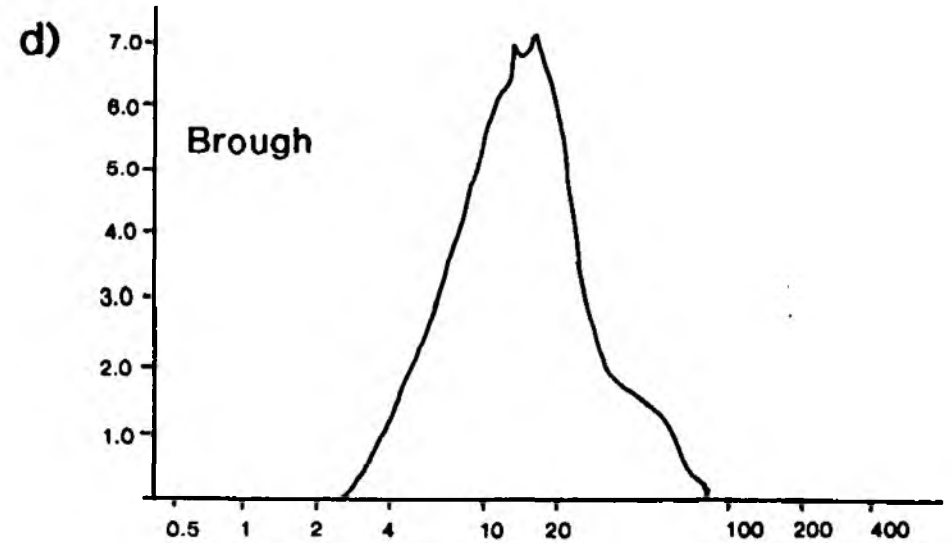
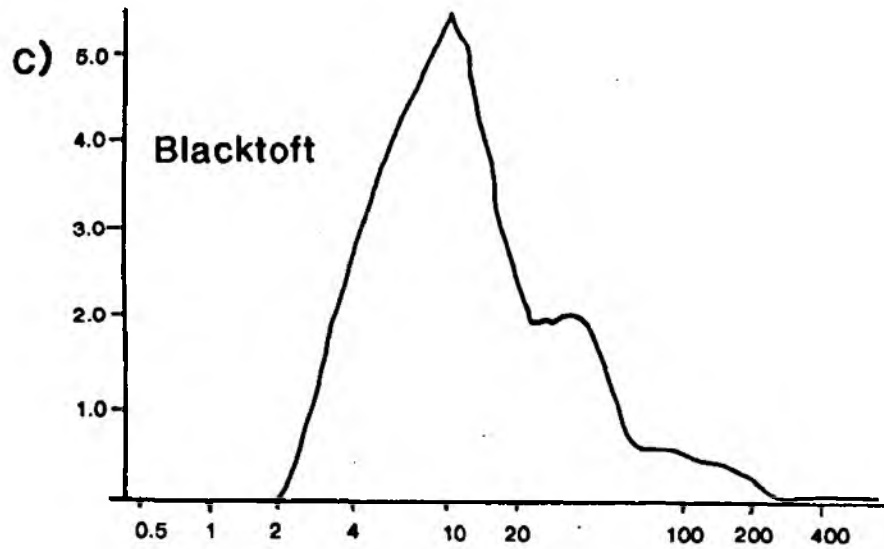
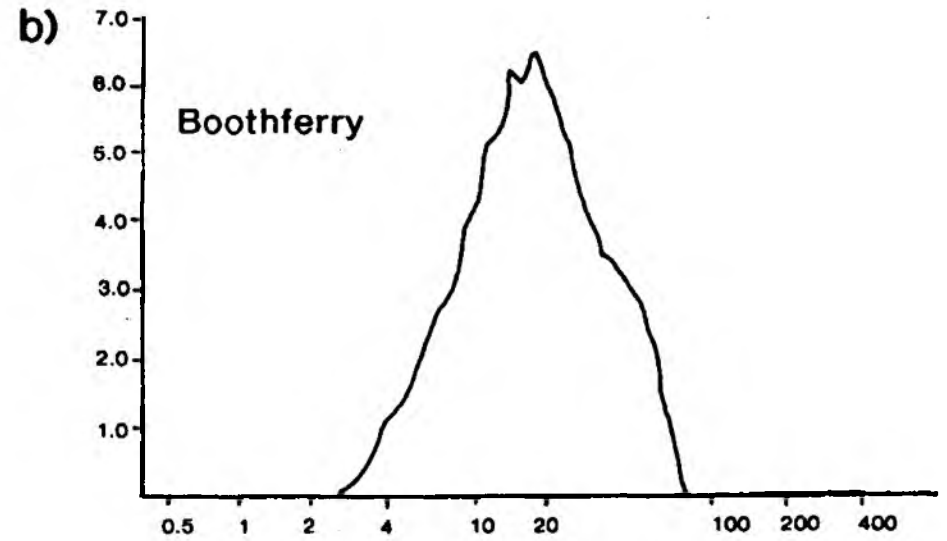
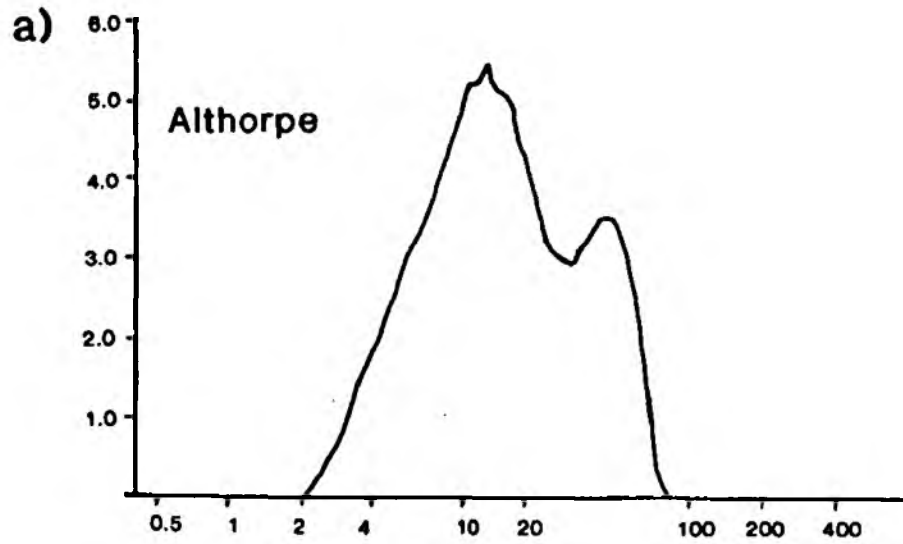
See Figure 3.9a-g for particle size curves for suspended sediment at the various sites, determined on a Coulter LS100 laser counting system. Particle size is an important variable; smaller particles have a higher surface area, and therefore generally have a greater capacity for adsorption in relation to their weight than do larger ones. There was quite a small variation in median particle diameters (10.6-15.3  $\mu\text{m}$ ), with the largest being found in the rivers (at Althorpe and Boothferry), and the smallest at Blacktoft. Most of the samples show a shoulder in the 20-80  $\mu\text{m}$  range. Larger particles were present to a small extent at Blacktoft and Spurn, as shown by Figures 3.9 c and f. Larger particles might be expected at the mouth of the river, since sandy sediments are common here; the unusual sampling site may account for the low proportion of sand in this sample. The small range of particle diameters suggests that adsorption differences caused by surface site variations were of low significance during the survey - a useful observation in modelling terms if further work confirms that this behaviour is consistent.

### **Analysis**

Analysis of aqueous samples for cadmium, copper, nickel and lead was carried out on a Perkin Elmer 4000 graphite furnace AAS according to the method of Apte and Gunn (1987). Chromium was analysed on the same instrument following the method of Apte *et al* (1991). Arsenic was analysed by electrothermal atomisation on a custom-built hydride generation system. Zinc was analysed by flame AAS on a Philips 9000. "Total" metal concentrations in sediments were found by concentrated nitric acid digestion; the sample and acid were heated at 100 °C for two hours, allowed to cool and 2 ml 100 v/v hydrogen peroxide added, before heating the mixture for a further two hours.

See Figures 3.10 a-f for graphs of aqueous and particulate metal concentrations found during the survey. The low levels of solids found at Selby, Snaith and Stainforth meant that particulate concentrations are not available for these sites. Also, the particulate data given for Paull and Spurn (salinities 22.5 and 32.6 ppt) must be considered as guide values only, since a small amount of the solids were lost during the digestion procedure.

Fig 3.9 Particle size of suspended solids collected along the Humber system



Particle size (um)

Fig 3.9 contd

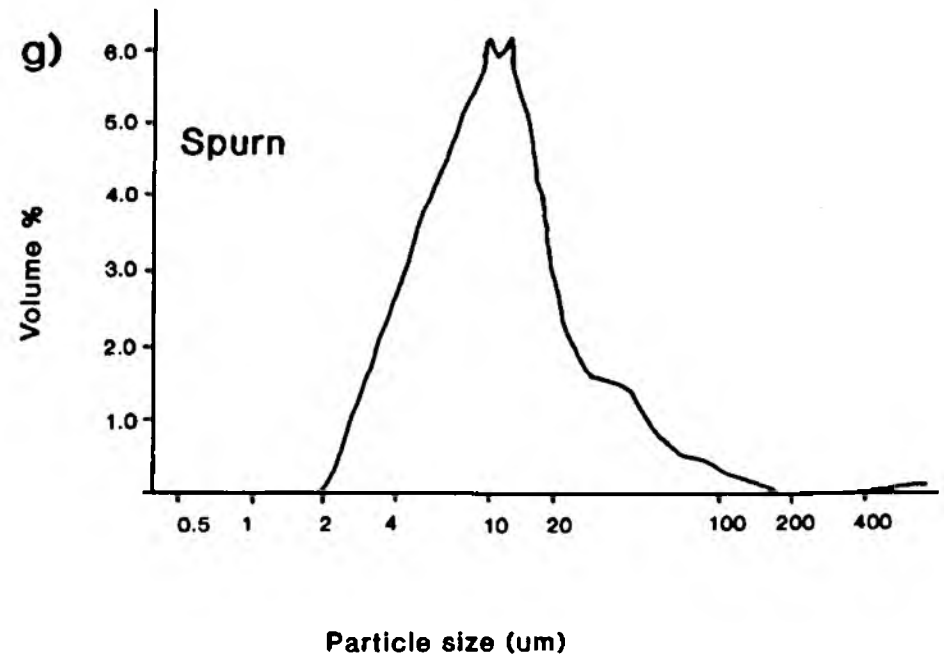
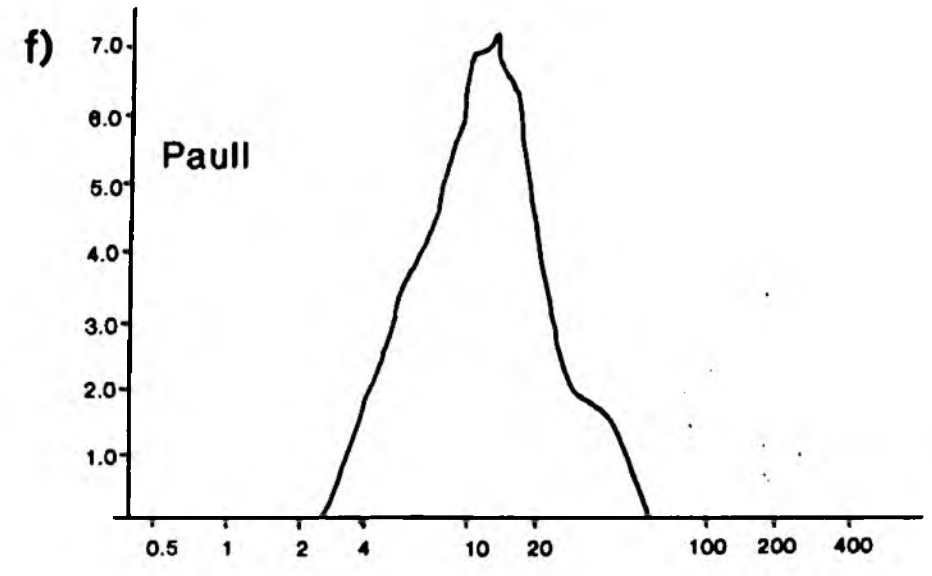
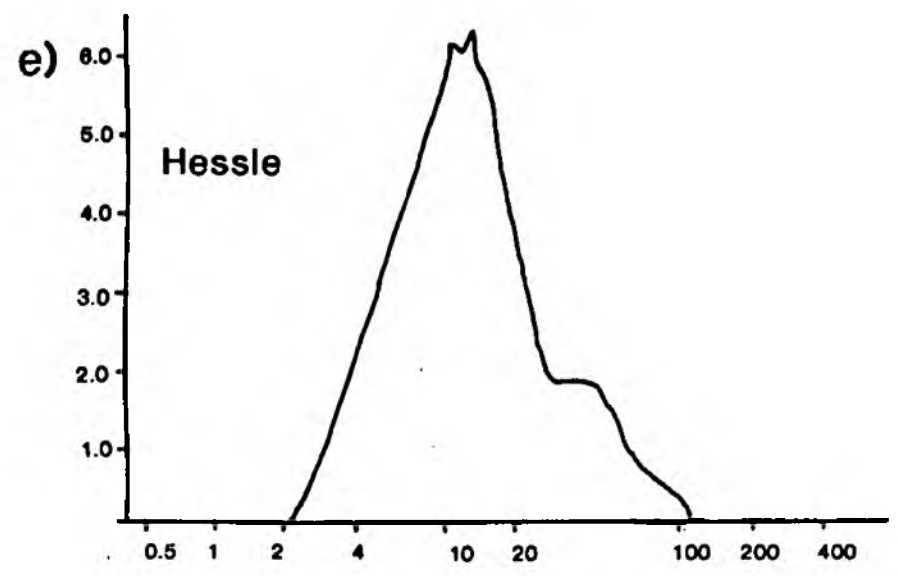
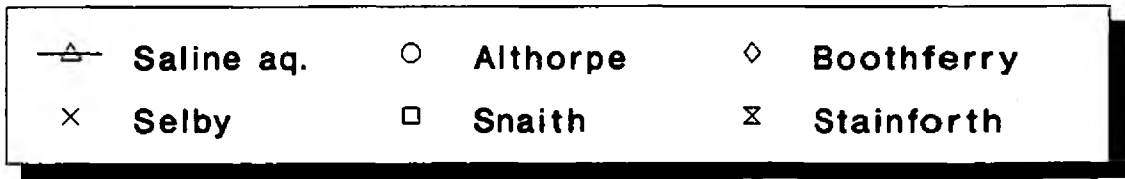
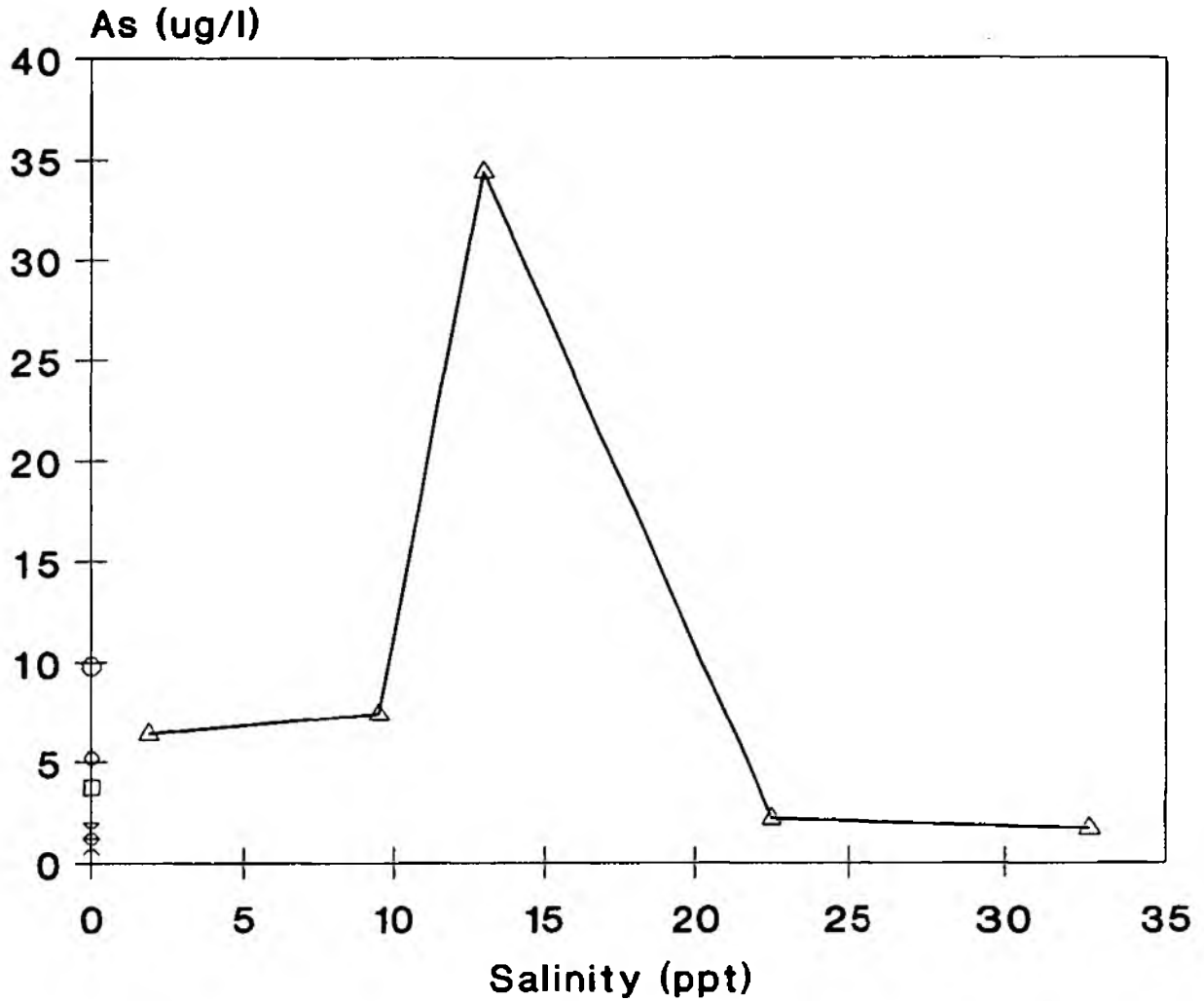
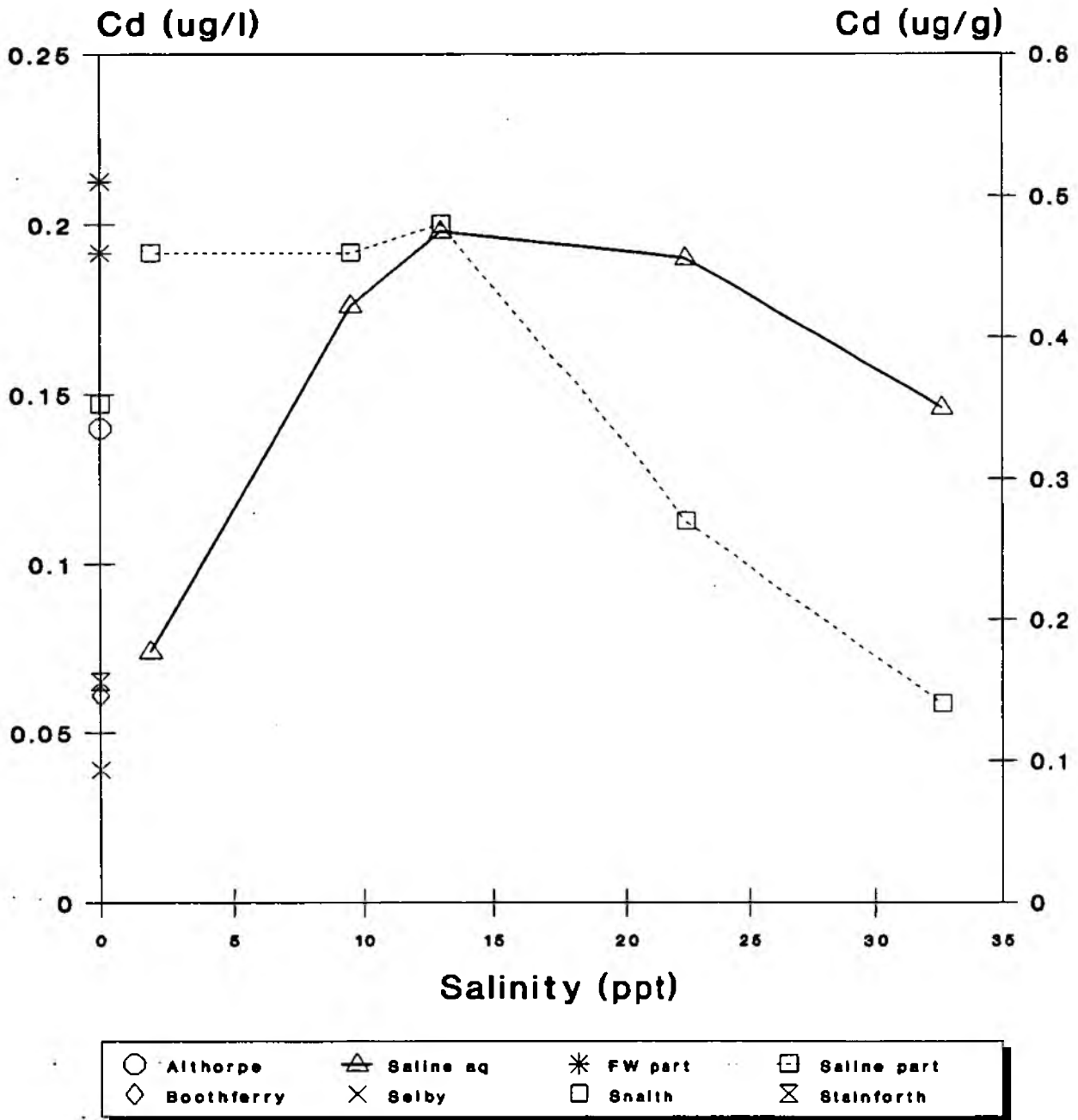


Fig 3.10a Aqueous arsenic in the Humber system

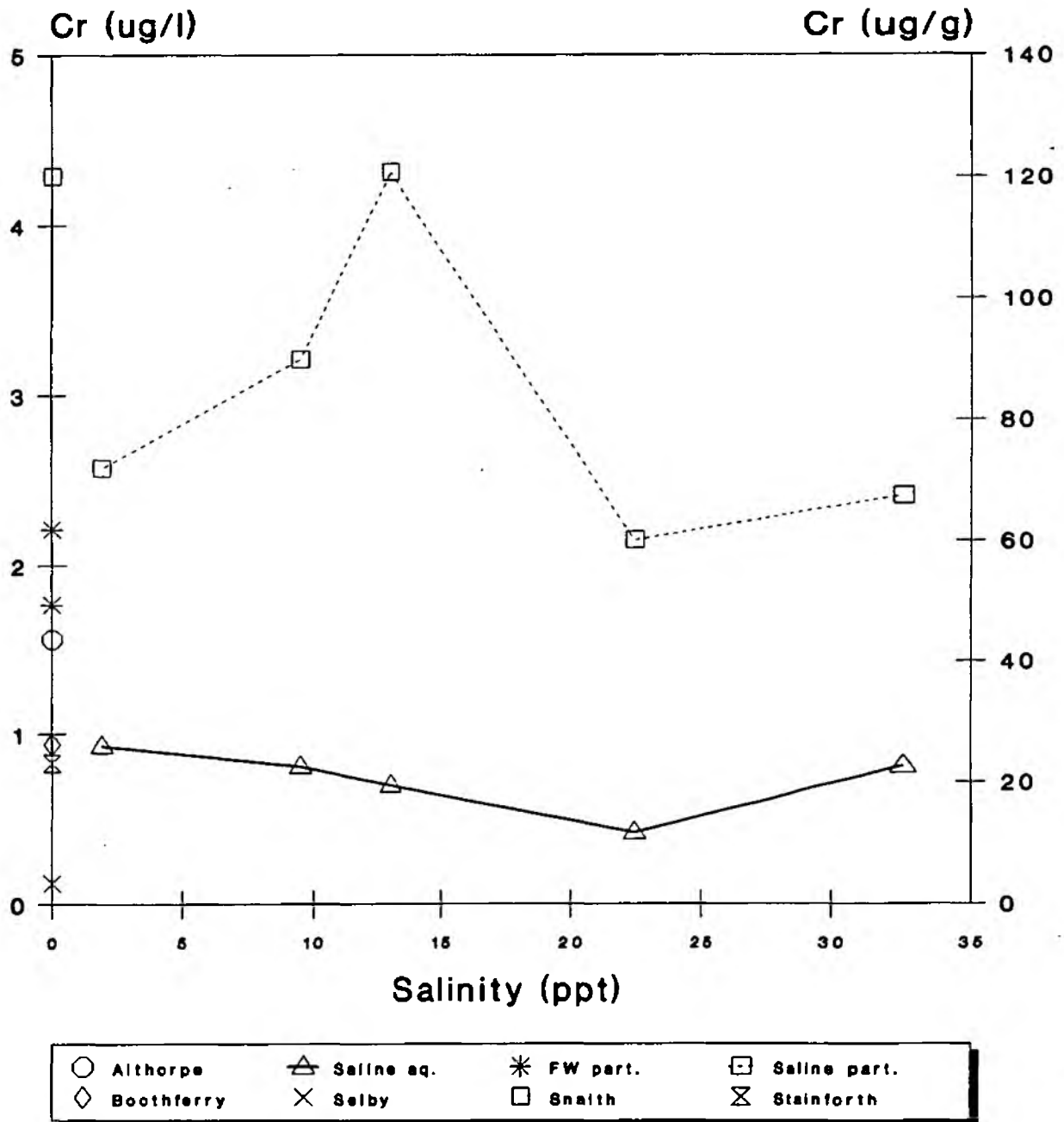




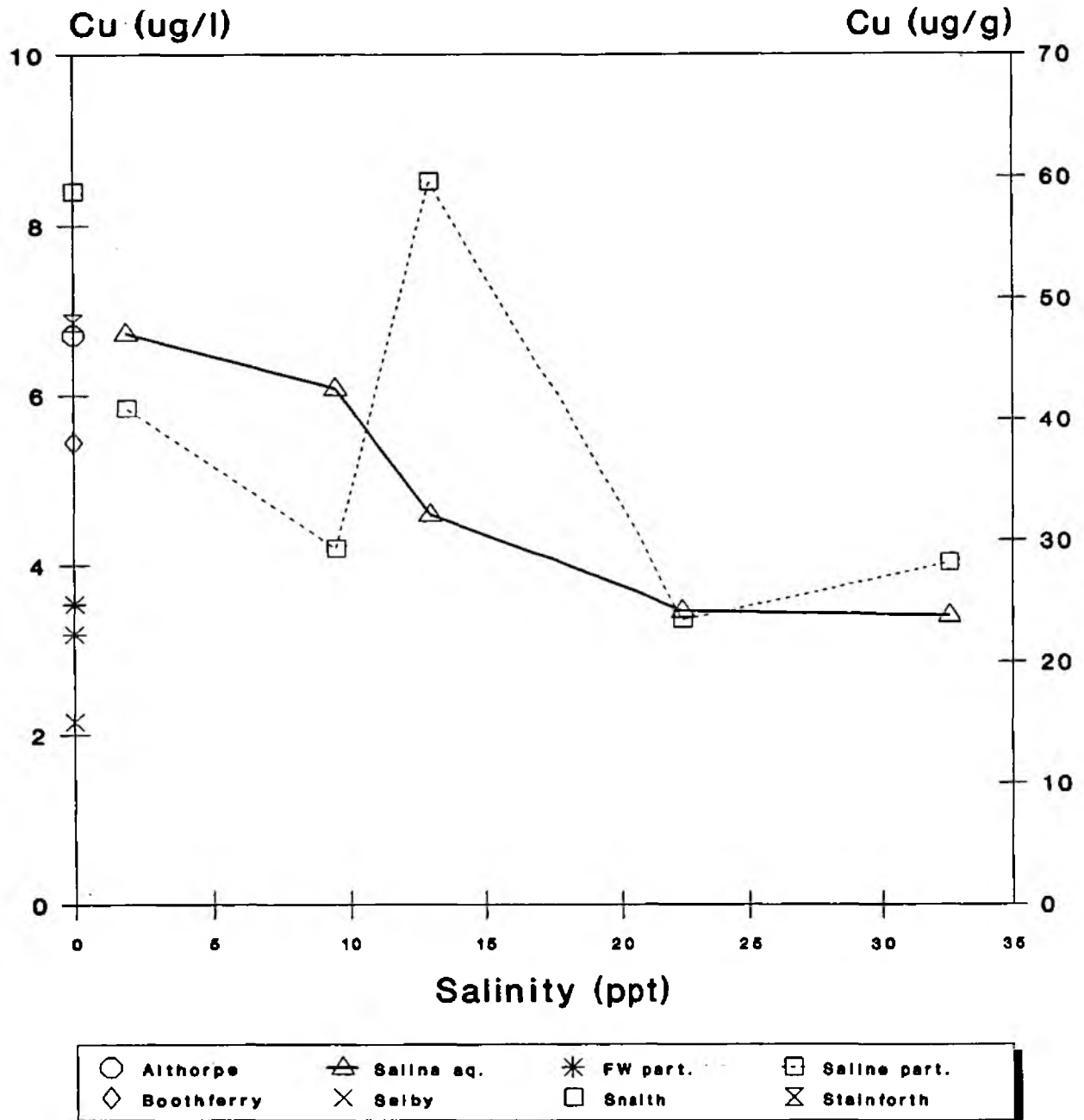
# Fig 3.10b Cadmium in the Humber system



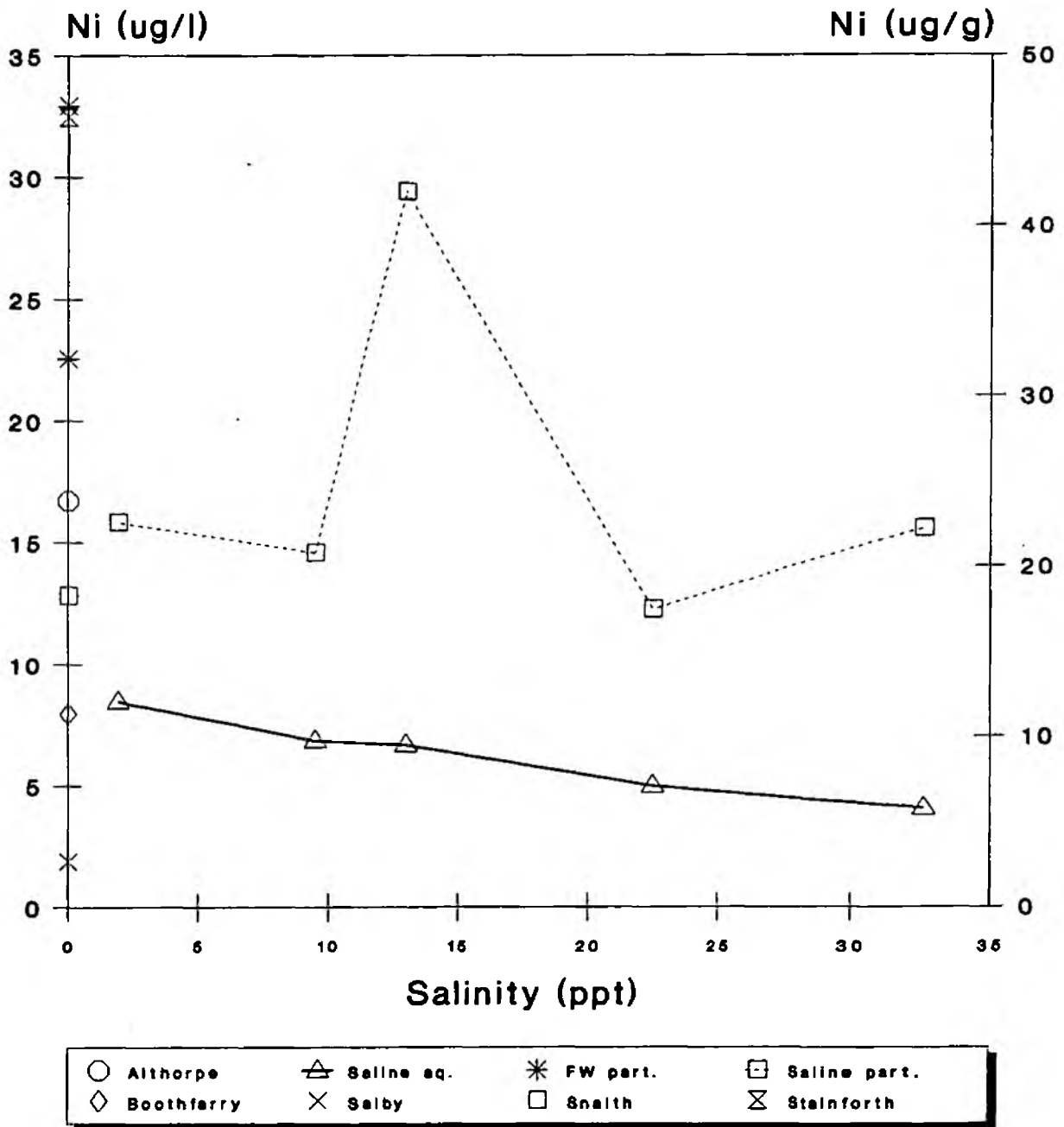
# Fig 3.10c Chromium in the Humber system



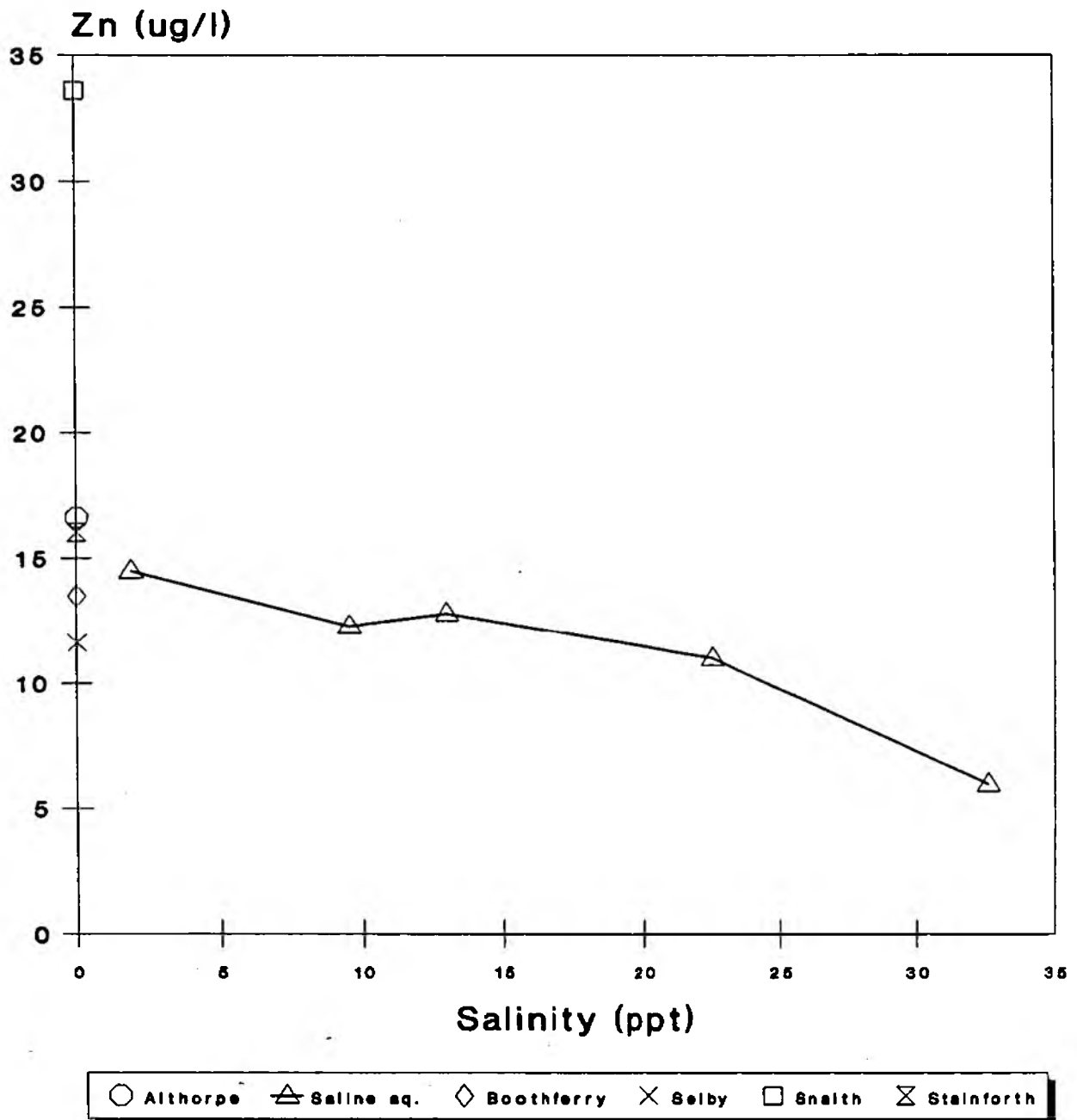
# Fig 3.10d Copper in the Humber system



# Fig 3.10e Nickel in the Humber system



# Fig 3.10f Aqueous zinc in the Humber system



- Arsenic - Levels in the rivers ranged from 0.8 µg/l (Selby) to 9.8 µg/l (Althorpe). The aqueous concentrations in the estuary were generally in the range 1.7 µg/l (Spurn) to 7.4 µg/l (Brough), decreasing towards the sea. However, there was a very high level of 34.4 µg/l found in the sample taken at Hessle; this is thought to result from the effluent plume from a metal refinery near Brough.
- Cadmium - Freshwater concentrations were in the range 0.039 µg/l (Boothferry) to 0.147 µg/l (Snaith). High concentrations, found in the Aire and the Trent, come from rivers with highly industrialised catchments. Particulate cadmium levels in the rivers examined were of about 0.5 µg/g. Saline aqueous concentrations show a wide range of 0.074 µg/l (Blacktoft) to 0.198 µg/l (Hessle), with the broad peak within the estuary probably being caused in part by discharges and input from the Trent. However, increased dissolved phase chloro-complexation at higher salinities (see Section 3.5.1) may also be important. Measurements of cadmium in the suspended sediment show fairly constant concentrations between Blacktoft and Hessle with a range of 0.46-0.48 µg/g. This then drops sharply to 0.14 µg/g at Spurn - again, possibly as a result of chloro-complexation.
- Chromium - Levels of dissolved chromium in the rivers generally ranged from 0.12 µg/l at Selby to 1.56 µg/l at Althorpe, although a high concentration of 4.29 µg/l was recorded at Snaith. Particulate levels in the suspended solids were 49.5 µg/g at Althorpe and 61.9 µg/g at Boothferry. Levels of chromium in estuarine waters showed small variation of between 0.42 µg/l (Paull) and 0.93 µg/l (Blacktoft). There is steady dilution until Spurn, when there is an unexpected increase in the aqueous concentration. The particulate levels show a range of 60.1-120.8 µg/g, peaking at Hessle. The increase in both aqueous and particulate metal concentrations at Spurn is rather surprising; but the unusually high suspended solids loading observed here on this occasion may have had some bearing on this.

Copper - Aqueous concentrations in the freshwaters range from 2.2 µg/l (Selby) to 8.4 µg/l (Snaith). Levels in the suspended sediment in the rivers tested were 22.3 µg/g (Althorpe) and 24.8 µg/g (Boothferry). Estuarine aqueous copper concentrations decreased from 6.7 µg/l at Blacktoft to 3.4 µg/l at the saline end-member. Particulate levels were in the range 23.5-59.6 µg/l and again peaked at Hessle.

Nickel - Levels of dissolved nickel in the rivers ranged from 1.9 µg/l (Selby) to 32.5 µg/l (Stainforth). Particulate concentrations measured were 32.2 µg/g (Boothferry) and 47.1 µg/g (Althorpe). Aqueous levels range from 4.1 µg/l (Spurn) to 8.4 µg/l (Blacktoft), showing a steady decline in concentration down the estuary. This suggests essentially conservative behaviour, in line with the low  $K_p$ 's found for this element in laboratory experiments. Particulate data show similar trends to copper and chromium, with a sharp peak in concentration at Hessle of 42.0 µg/g.

Lead - A graph is not shown for these data, since few significant dissolved phase results have been determined for this metal. The only aqueous concentration recorded above the detection limit was at Snaith, of 0.35 µg/l. (Extremely high partition coefficients for lead in estuarine waters mean that most of it is sorbed to particulate material.) Levels found for particulates were 59.7 µg/g at Althorpe, 73.0 µg/g at Boothferry and 55.6 µg/g at Brough. Examination of preliminary data for the other sites suggest concentrations of about 50 µg/g between Blacktoft and Hessle, falling to about half this level at Paull and Spurn.

Zinc - Aqueous levels in the rivers ranged from 11. µg/l (Selby) to 16.6 µg/g (Althorpe), with the exception of the high concentration of 33.6 µg/l at Snaith. Zinc in saline waters shows a slight fall in concentration between Blacktoft (14.5 µg/l) and Paull (12.8 µg/l), but then a steeper fall to 6 µg/l at Spurn. This gradual decline indicates essentially conservative behaviour, but with possibly some release from particulates in the increased ionic strength environment encountered in the upper reaches of the estuary.

## **General observations from dissolved and particulate metal profiles for the two Humber field surveys**

Lowest aqueous concentrations in the rivers were found at Selby on the River Ouse, with the greatest generally being found at Snaith on the River Aire (excepting Althorpe on the Trent for highest arsenic levels, and Stainforth on the Don for nickel). These levels come from rivers with highly industrialised and populated catchments; analysis of upstream samples from these rivers has shown aqueous metal concentrations at or close to limits of detection. Low levels recorded at Selby, above the point where the Aire meets the Ouse, may be also explained by the lack of large populated or industrialised areas upstream. There is a shortage of freshwater particulate data upon which to base comparisons, caused (during both surveys) by very low solids levels in some of the rivers examined. Table 3.5 shows maximum and minimum levels found in dissolved and solid phases during these studies:

Freshwater aqueous data showed similar behaviour, except for higher values of arsenic at Dunham and nickel at Selby (1989), and zinc at Snaith (1991). Particulate data were more variable, with cadmium and copper showing significantly higher levels in the sediment in 1989, while nickel and lead were more concentrated in the 1991 study. However, this variation may merely reflect the limited number of sites for which metals data are available in the solid phase.

Saline data are comparable between the surveys; in 1991 dissolved arsenic was higher (with the presumed discharge plume level found at Hessle), while copper and nickel were slightly elevated in the suspended sediment.

### **Analytical quality control**

Field blanks were run through the filter units and membranes at all sites. Table 3.6 shows blank concentrations and gives limits of detection (lod) data for the analyses.



**Table 3.5 Comparison of maximum and minimum concentrations in dissolved and particulate phase data during surveys in September 1989 and April 1991**

Sample		As	Cd	Cr	Cu	Ni	Pb	Zn
FW aqueous µg/l								
1989 min	T	4.9	S 0.05	S 0.31	S 4.8	S 7.4	<lod	S 2.7
max	A	9.7	T 0.82	A 6.19	A 8.7	T 35.4	T 0.8	T 18.2
1991 min	S	0.8	B 0.06	S 0.12	S 2.2	S 1.9	<lod	S 11.6
max	L	9.8	N 0.15	N 4.29	N 8.4	F 32.5	N 0.4	N 33.6
FW particulate								
1989 min µg/g	S	1.8	S 1.6	*	S 12.1	S 9.4	S 37.0	S 15.5
max	A	6.9	A 4.1	*	A 75.8	A 15.3	A 46.6	A 27.2
1991 min	*		B 0.51	L 49.5	L 22.3	B 32.2	L 59.7	*
max	*		L 0.46	B 61.9	B 24.8	L 47.1	B 73.0	*
SW aqueous µg/l								
1989 min	P	1.6	P 0.12	P 0.18	P 1.7	P 2.9	<lod	P 2.4
max	B	9.1	H 0.32	R 0.77	B 7.9	B 10.6	<lod	C 9.7
1991 min	P	1.7	C 0.07	U 0.42	P 3.4	P 4.1	<lod	P 6.0
max	H	34.4	H 0.20	C 0.93	C 6.7	C 8.4	<lod	C 14.5
SW particulate								
1989 min µg/g	P	15.5	H 0.15	*	P 8.6	C 11.0	P 29.9	V 19.0
max	H	24.7	R 0.44	*	R 20.8	H 17.9	H 52.0	R 51.4
1991 min	*		P 0.14	U 60.1	U 23.5	U 17.5	*	*
max	*		H 0.48	H120.8	H 59.6	H 42.0	*	*

**NOTES**

NB 1989 Boothferry had a salinity of 3.2 ppt

**Freshwater (FW) abbreviations**

S = River Ouse at Selby  
 A = River Aire at Beal  
 T = River Trent at Dunham  
 F = River Don at Stainforth  
 L = River Trent at Althorpe  
 B = River Ouse at Boothferry  
 N = River Aire at Snaith

**Seawater (SW) abbreviations**

P = Spurn  
 C = Blacktoft  
 H = Hessle  
 R = Brough  
 V = Victoria Pier  
 U = Paull

Solids data available for Rivers Ouse at Selby and Aire at Beal (1989), for Rivers Ouse at Boothferry and Trent at Althorpe (1991)

**Table 3.6 Field blanks and limits of detection for survey analyses**

Metal	N <sup>o</sup> of samples	Mean concn in blank	sd	lod µg/l
As	11	<lod	-	0.5
Cd	12	<lod	0.013	0.03
Cr	12	<lod	0.018	0.15
Cu	12	<lod	0.094	0.07
Ni	12	<lod	0.142	0.03
Pb	11	<lod	0.067	0.59
Zn	11	<lod	0.235	0.05

These data show that the blanks were at acceptable levels.

Table 3.7 shows recovery of metals spiked into prefiltered samples: a freshwater (Althorpe) and a saline sample (Hessle). These were then re-filtered in the field. The percentage recovery was measured against the spike concentration found from spiking into an equivalent volume of 250 ml DIW.

**Table 3.7 Quality control (QC) sample percentage recovery**

	As	Cd	Cr	Cu	Ni	Pb	Zn
Freshwater QC	94.7	101.9	55.1	108.6	*	80.4	75.7
Saline QC	104.5	87.5	54.2	80.9	88.6	30.6	72.4
Nominal spike (µg/l)	20	0.5	2	10	20	1	20

Recoveries appear to be satisfactory, except in the cases of metals which have high partition coefficients ( $K_p$ s). In these instances (Cr, Pb and Zn) metal may have sorbed onto the walls of the filter unit and the filter membrane. The losses are in contrast to the situation suggested by results obtained in Sections 3.1.1 and 3.1.2 above, where there were few problems with such

adsorptive losses. Copper, which also has quite a high  $K_p$  may be less subject to adsorptive losses here because of its high affinity for organic ligands. These are less abundant in saline waters and may account for the greater losses in the Hessele sample over the Althorpe sample. The large loss of lead in the saline sample is probably caused by precipitation, although a spike of 10 µg/l into a 4 litre volume did not show such large losses in a saline sample (3.2). While adsorption to filtration vessels for chromium and lead have been recorded in previous QC tests (NR 2573, 1990), the amount of "lost" metal has not been as significant in the past as it was here. It should be noted, however, that the nature of the spike used in the tests (ie 'free' ion) may have resulted in greater losses than appropriate to metal already present in the real samples.

#### **3.4.2 Sequential extraction of Humber sediments**

The speciation of metals bound to particulate matter is an important consideration as regards metal availability, with ready dissolution into the water column providing opportunity for metals transport and uptake by organisms. More tightly bound metal may be essentially irreversibly adsorbed, so that the partition coefficient found by straight nitric acid digestion may not adequately describe the amount of "active" metal. A sequential extraction procedure of sediments collected during the 1991 survey was therefore performed, in order to determine the most significant phases in this respect.

The procedure used was a combination of that suggested by Tessier *et al* (1979) and Gunn and Winnard (1989). Preliminary investigations indicated that when the amount of sediment to be extracted was low (eg <200 mg from 250 ml filtrate), the initial step in the Tessier method (extraction with 1M  $MgCl_2$  pH7) produced extracts below the analytical limit of detection. Therefore the first step used was the stronger ammonium acetate/calcium chloride extraction of Gunn and Winnard's method. It should be noted that, because of the variety and continuum nature of metal binding to environmental particulates, sequential extractions can only provide operational definitions of sediment speciation. Analysis was carried out on a Perkin Elmer 4000 graphite furnace.

### Sequential extraction procedure :

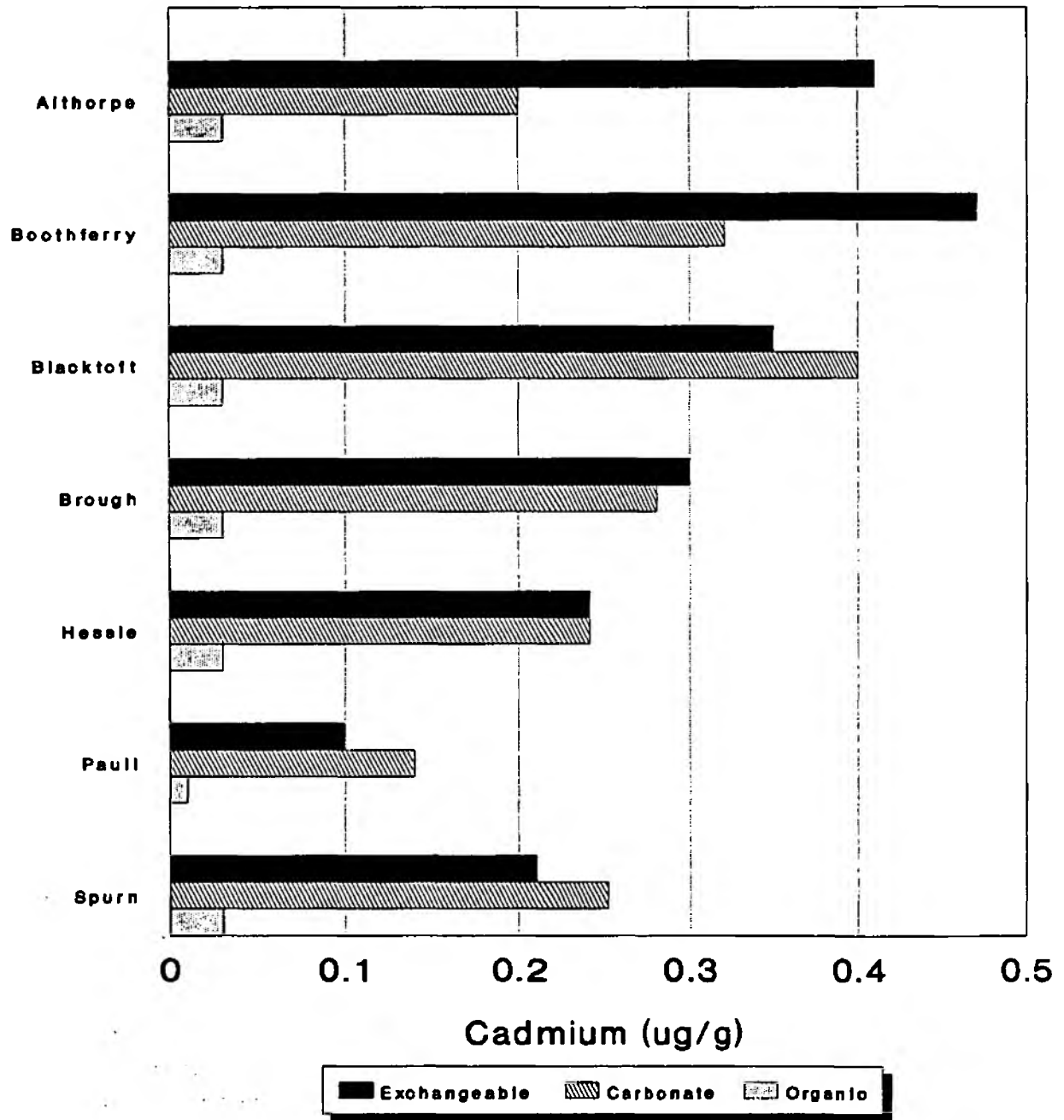
1. **Exchangeable/adsorbed** - 1M ammonium acetate/0.25M calcium chloride pH6, shaken for 3 hours
2. **Carbonate** - 1M sodium acetate pH5 shaken for 6 hours
3. **Reducible** - 0.04M hydroxylamine hydrochloride in 25% v/v acetic acid, heated at 96 °C for 6 hours
4. **Organic** - 0.02M nitric acid and 30% hydrogen peroxide heated at 85 °C for 2 hours; addition of hydrogen peroxide after cooling and heated at 85 °C for 3 hours. After cooling 3.2M ammonium acetate in 20% nitric acid was added and the mixture diluted.
5. **Residual** - Aqua regia heated for 4 hours at 100 °C

Volumes of reagent were adjusted to allow for differing quantities of sediment which had been collected from the 200-250 ml *in situ* filtration.

### Results

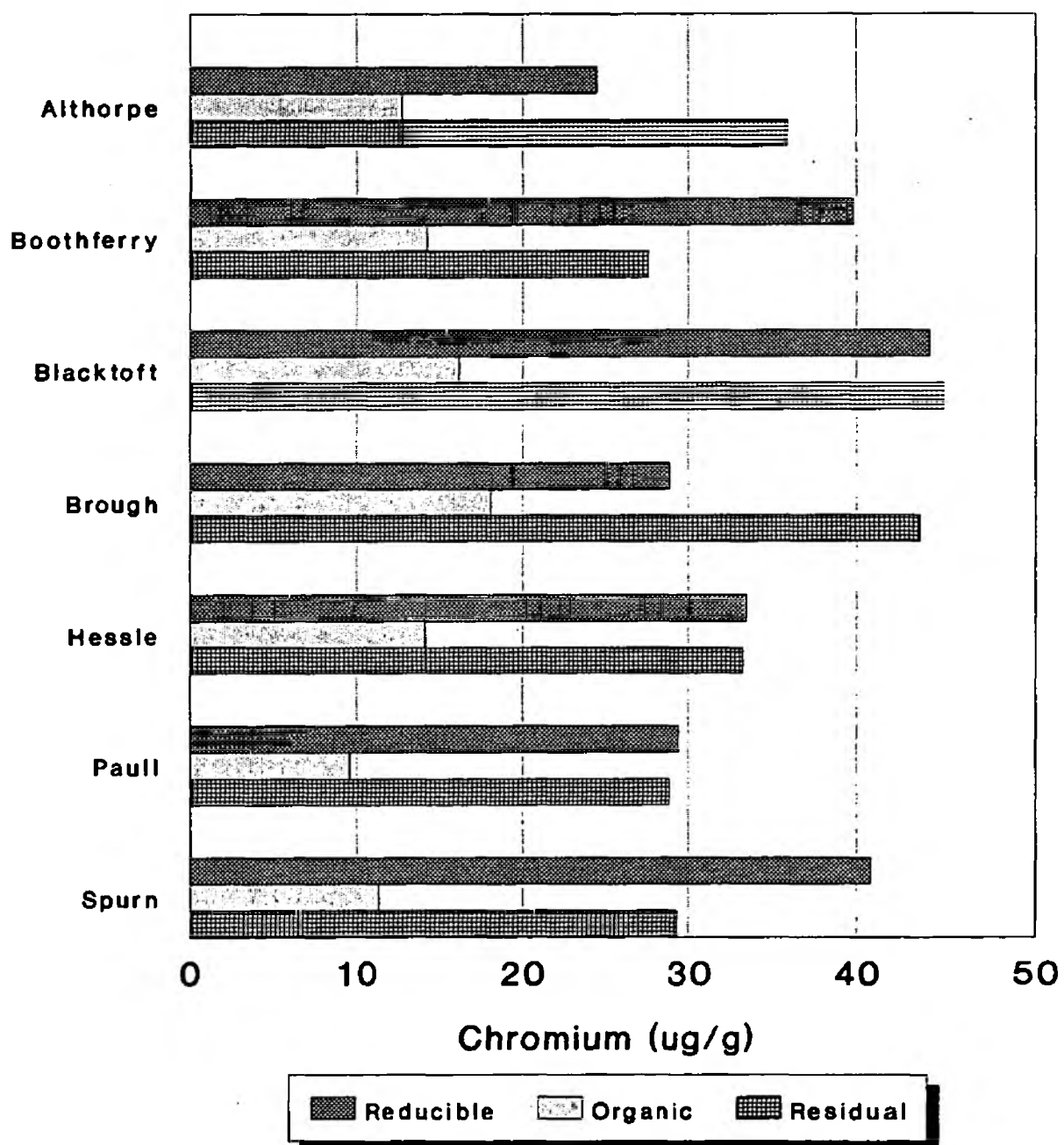
See Figures 3.11a-e for histograms of metal speciation by site as determined by the above procedure. Some data sets are not yet available for this report, ie those for reducible cadmium, exchangeable and carbonate-bound chromium. However, preliminary analyses carried out upon these phases suggest they are of minor importance in terms of the bulk speciation of these metals. A small amount of sediment and solution was lost in the early stages of digestion of the organic phase for Spurn, and the residual phase of Paull. Thus the data for these points (and residual at Spurn) are included merely as a guide to metals behaviour.

**Fig 3.11a Cadmium speciation in Humber suspended sediments**

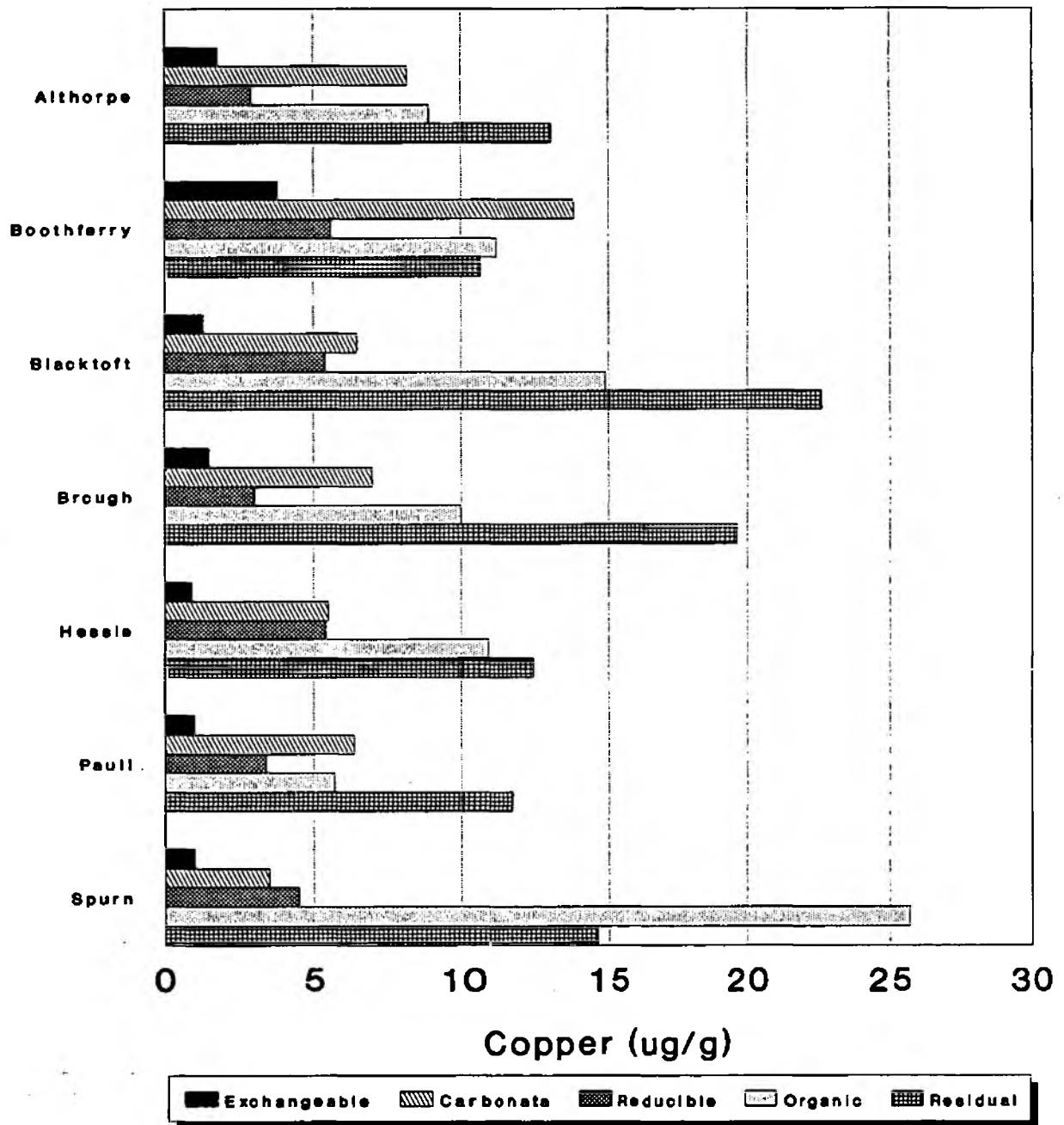


Residual cadmium below detection limit

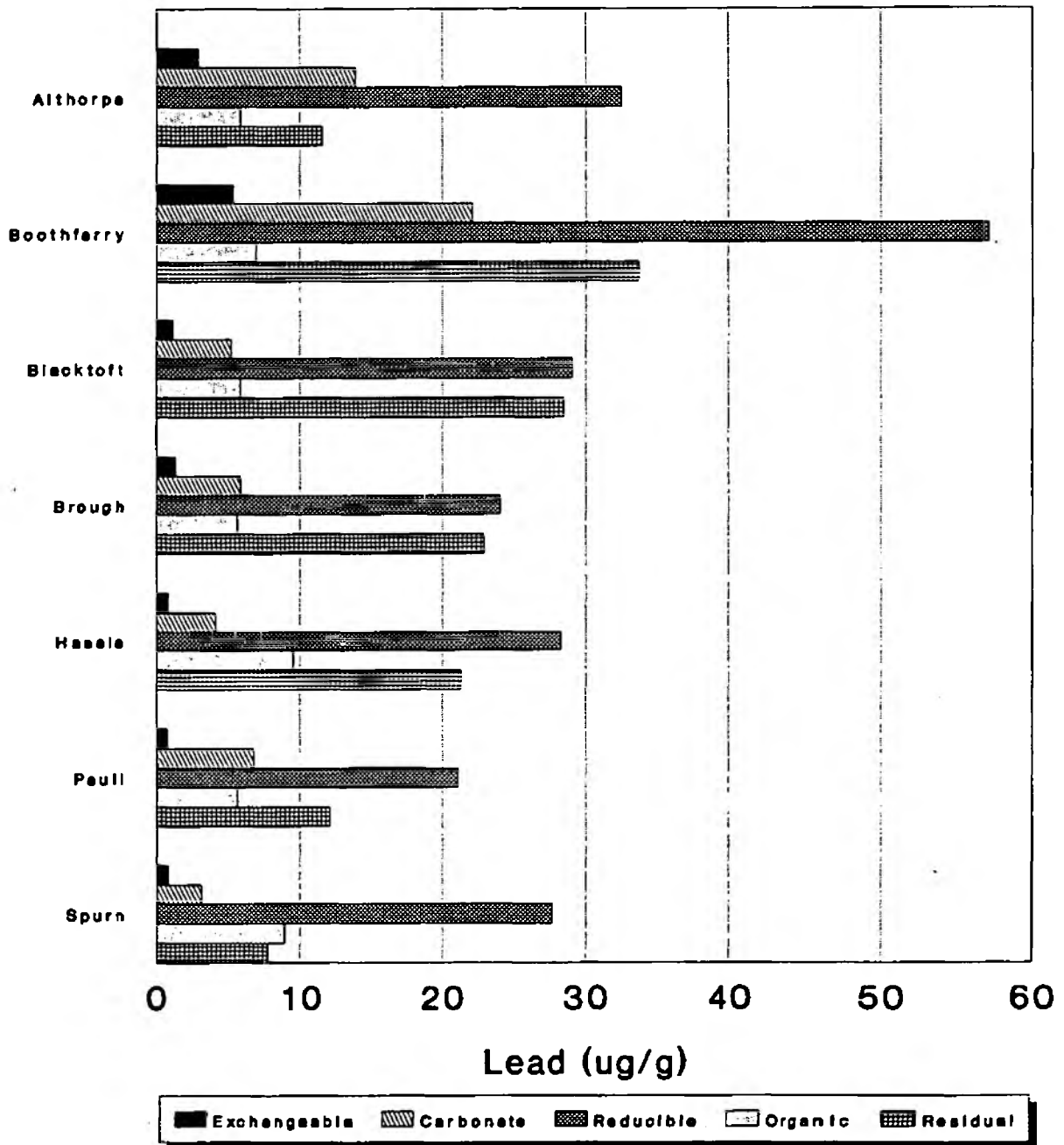
**Fig 3.11b Chromium speciation in Humber suspended sediments**



**Fig 3.11c Copper speciation in Humber suspended sediments**

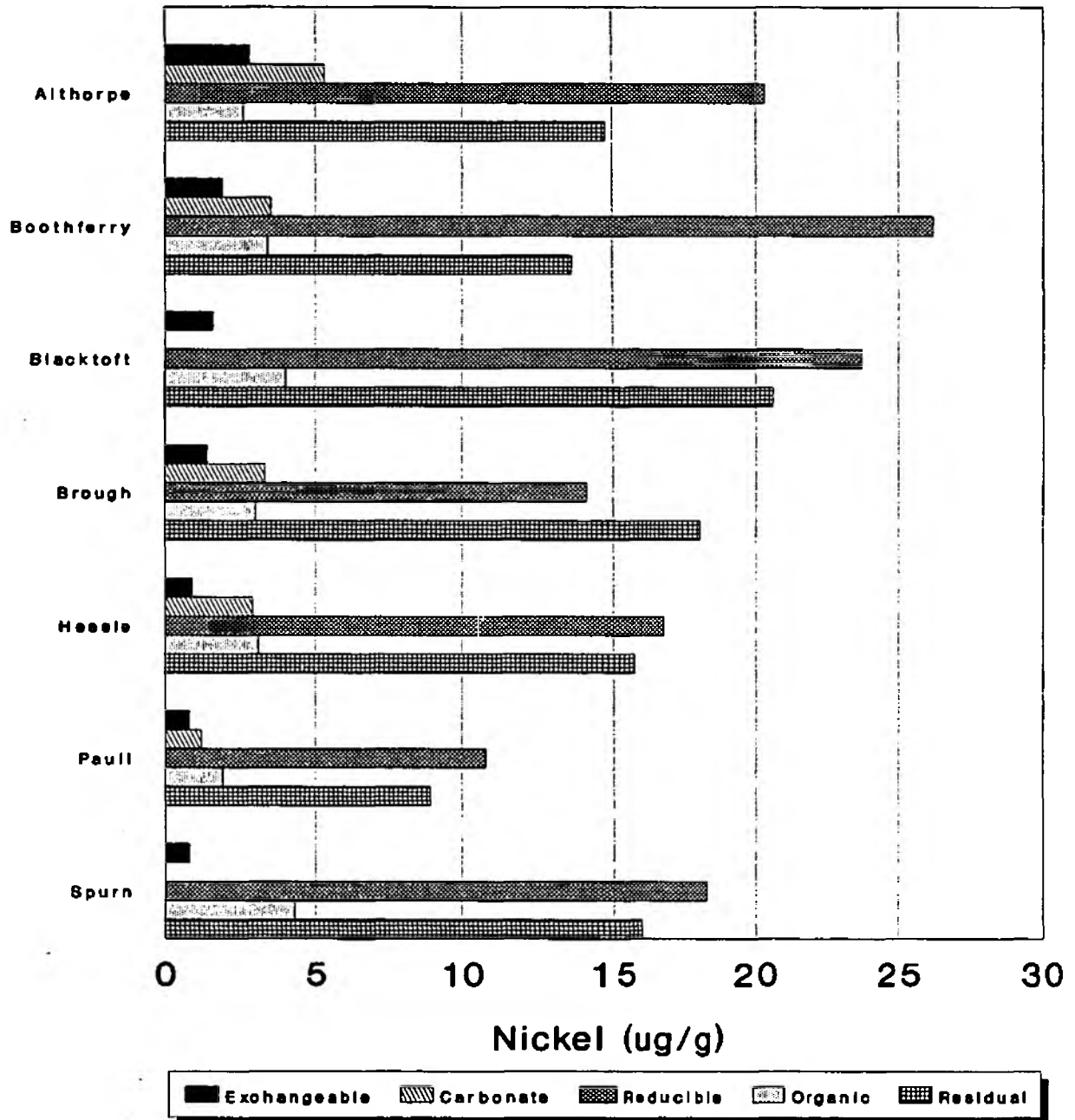


**Fig 3.11d Lead speciation in Humber suspended sediments**





**Fig 3.11e Nickel speciation  
in Humber suspended sediments**



Carbonate data for Blacktoft and Spurn not yet available

Cadmium - Most of the cadmium present on the solids was present in the weakly bound phases (exchangeable and carbonate). In freshwater sediments (Althorpe and Boothferry), the exchangeable phase was predominant (0.41-0.47 µg/g), while in those from saline sites, the first two phases examined were of approximately equal significance, at levels between 0.2-0.4 µg/g. Data are not yet available for the reducible phase. Organically-bound cadmium formed an extremely low (0.01-0.03 µg/g) proportion of the total; the amount remaining in the residual fraction was below the detection limit. There was a general decrease in concentrations down the estuary to Paull, whereupon there was a small rise at Spurn. The decrease in exchangeable metal concentrations on going from fresh to saline water was expected, since sediments entering a region of high ionic strength are subject to a variety of physical and chemical influences, such as ion exchange, precipitation, coagulation etc. In addition, strong chloro-complexation of cadmium may desorb these lightly bound forms. The high proportion of cadmium in weakly bound phases is clearly important in terms of this metal's potential bioavailability/toxicity.

Chromium - Data for the reducible, organic and residual phases are available, while preliminary screening suggests low concentrations in the first two digests. There was little difference between the freshwater and saline sediments, with most of the metal being found in the reducible and residual fractions (24-49 µg/g). Concentrations in the organic phase ranged between 9-18 µg/g, and decreased slightly down the estuary. The high amounts of chromium on the relatively strongly bound reducible and residual phases reflects the very high partition coefficients observed for this element.

Copper - In the freshwater sediments, the carbonate, organic and residual phases were all of roughly the same importance (10-14 µg/g), while that in the exchangeable was present at about twice the concentration found in the saline samples (at 2-4 µg/g as opposed to 0.8-1.6 µg/g). In the saline suspended sediments, most copper

was found in the residual phase (11-20 µg/g), followed by that which was organically-bound. Carbonate-bound copper was present at about the same concentration as that in the reducible phase (3-5 µg/g), except at Brough and Paull (6-7 µg/g). The presence of a significant amount of copper in the organically-bound phase reflects the strong affinity of this metal for organic ligands.

Lead - Lead was found to be enhanced in the freshwater weakly bound phases relative to that in the saline sediments: 2.9-5.3 µg/g in the exchangeable fraction compared to 0.7-1.3 µg/g; 13-22 µg/g carbonate-bound compared to 3-7 µg/g, with this decrease presumably resulting from competition by major ions in the higher ionic strength estuarine environment. Reducibly-bound lead was the most significant form in both freshwater and saline sediments (21-57 µg/g), followed by the residual fraction, which showed a progressive decrease with increasing salinity downstream of Blacktoft. Lead in the organic phase was present at approximately the same level (5-9 µg/g) at all sites.

Nickel - Exchangeable nickel was present at between 0.7-2.8 µg/g and demonstrated a progressive decrease in concentration down the estuary. Carbonate-bound data for Blacktoft and Spurn are not yet available, but in general these appeared to be present at about the same concentration as in the organically-bound phase (1-4 µg), which again generally dropped down towards the mouth of the estuary. Reducible metal levels (10-26 µg/g) generally had the highest nickel concentrations, followed by those in the residual fraction (8-21 µg/g). There was a gradual decline in nickel concentrations in these two fractions from Blacktoft to Paull. However, at Spurn there was an apparently anomalous increase in concentrations in the three more strongly bound phases. The high levels of nickel present in reducible and residual fractions suggests that much of this metal may not be readily releasable under oxic environmental conditions.

### **General comments upon sediment speciation data**

Several metals demonstrate a concentration in the reducible and residual phases. Of these, the residual may be considered as of no immediate environmental concern, as release from this fraction is unlikely.

Reducibly-bound metal may be released under anoxic conditions, such as may exist in aquatic bed sediments, whereupon eg benthic organisms may take up remobilised metal. Major exceptions to this speciation pattern are cadmium and copper. Cadmium was concentrated in the most weakly bound phases (exchangeable and carbonate), - it is thus chemically quite straightforward for this highly toxic metal to pass back into the water column and become available to a wide range of organisms. Copper was concentrated in the residual and organic phases - while the former may be of little concern, the liposolubility of the latter may allow ready uptake by sediment-ingesting organisms. In general more metal was present on the weakly bound phases in freshwaters, which is in line with removal from these fractions as a result of competition by major ions at higher salinities.

### **3.5 Humber system partition coefficients determined by laboratory experiment**

This part of the study was carried out with two main objectives: (i) to look at variations in partitioning of added metal throughout the Humber system; and (ii) to compare data with *in situ* partition coefficients and with results of solid phase sequential extractions for samples filtered on-site in the April 1991 survey.

Samples used in the study were collected during the field survey and stored in the dark at 4°C for a month prior to use. Metal spikes were added to 200 ml subsamples in Nalgene polyethylene bottles and equilibrated overnight, with shaking, before being filtered through 0.4 µm Nuclepore membranes. All samples were run in duplicate and, as previously, spiked, filtered control samples were also taken through the procedure. The levels of metal spikes (pH ca. 2.2) employed were adjusted in the different samples to allow for the differing amounts of solids known to be present; for each sample a range of four concentrations were added to establish the adsorption isotherms.

Partition coefficients for arsenic, cadmium, copper, nickel, and zinc, determined from the slopes of the essentially linear portions of the adsorption isotherms, are shown in Figure 3.12.

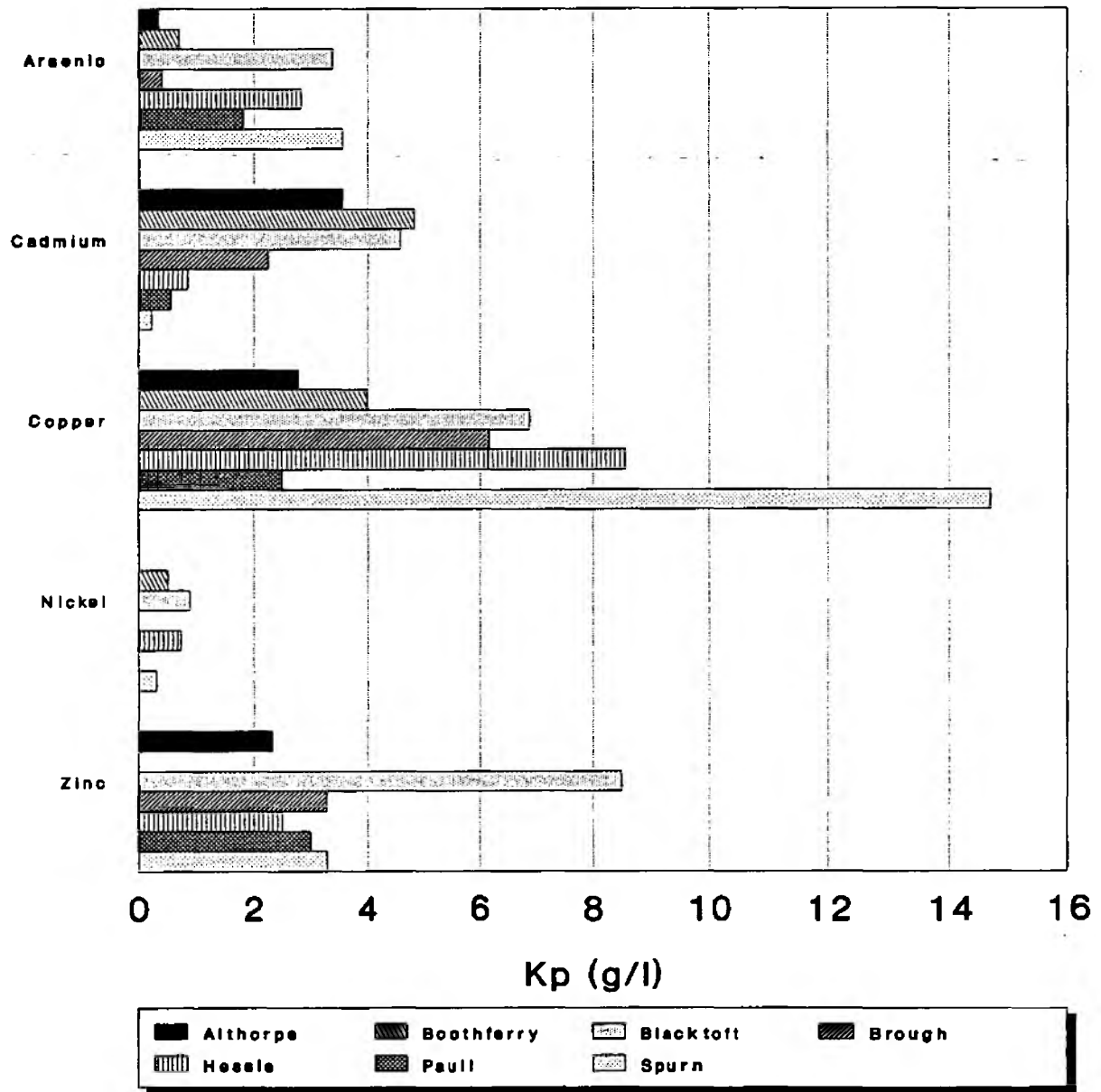
These are in broad agreement with earlier findings, with nickel showing the lowest  $K_p$ 's and zinc and copper the highest. Looking at trends throughout the system the most striking observation is of a dramatic decrease in  $K_p$ 's for cadmium with increasing salinity. The importance of this lies in the fact that the dissolved phase speciation of cadmium in the estuarine environment is known to be strongly influenced by chloro-complexation. This is demonstrated in Figure 3.13 (taken from French and Hunt 1986), which illustrates results of thermodynamic equilibrium calculations of cadmium speciation as a function of salinity. It should be noted that these calculations take no account of possible complexation by natural organic ligands. The example shown is for an estuary with a river at pH 7 but, as hydroxy complexation is relatively unimportant, the situation would not be noticeably different for other river pH's.

In order to examine the theory that chloro-complexation might account for the observed decrease in  $K_p$  values on moving down the Humber system, free cadmium ion concentrations were computed for each of the samples and the adsorption isotherms replotted as  $\mu\text{g}$  adsorbed Cd per gram of solids versus ng free aqueous Cd ion per litre of solution. The effect of this recalculation is shown in Figure 3.14a-b. From this it can be seen that the extremely wide variation in the unamended isotherms is essentially eliminated and partitioning throughout the system can now be reasonably described in terms of a single free ion based partition coefficient  $K_p(\text{Cd}^{2+}\text{aq}) = 1.4 \times 10^4$ .

A similar effect of chloro-complexation has previously been reported by Comans (1988) for synthetic test samples and a single solid phase. The fact that such a good correlation is observed here indicates that other variables within the Humber system, eg solids concentration, pH, organic ligands, colloids etc, are of only minor importance in comparison.

The other interesting finding of the study was that, with the exception of an anomalously low result for the Paull site, there was a tendency for  $K_p$  values

# Fig 3.12 Laboratory-determined Kps in Humber system



Data not available for nickel  
at Althorpe, Brough or Spurn,  
or zinc at Boothferry

Fig 3.13 Inorganic speciation of cadmium in an estuary with a river at pH7

(from French and Hunt, 1986)

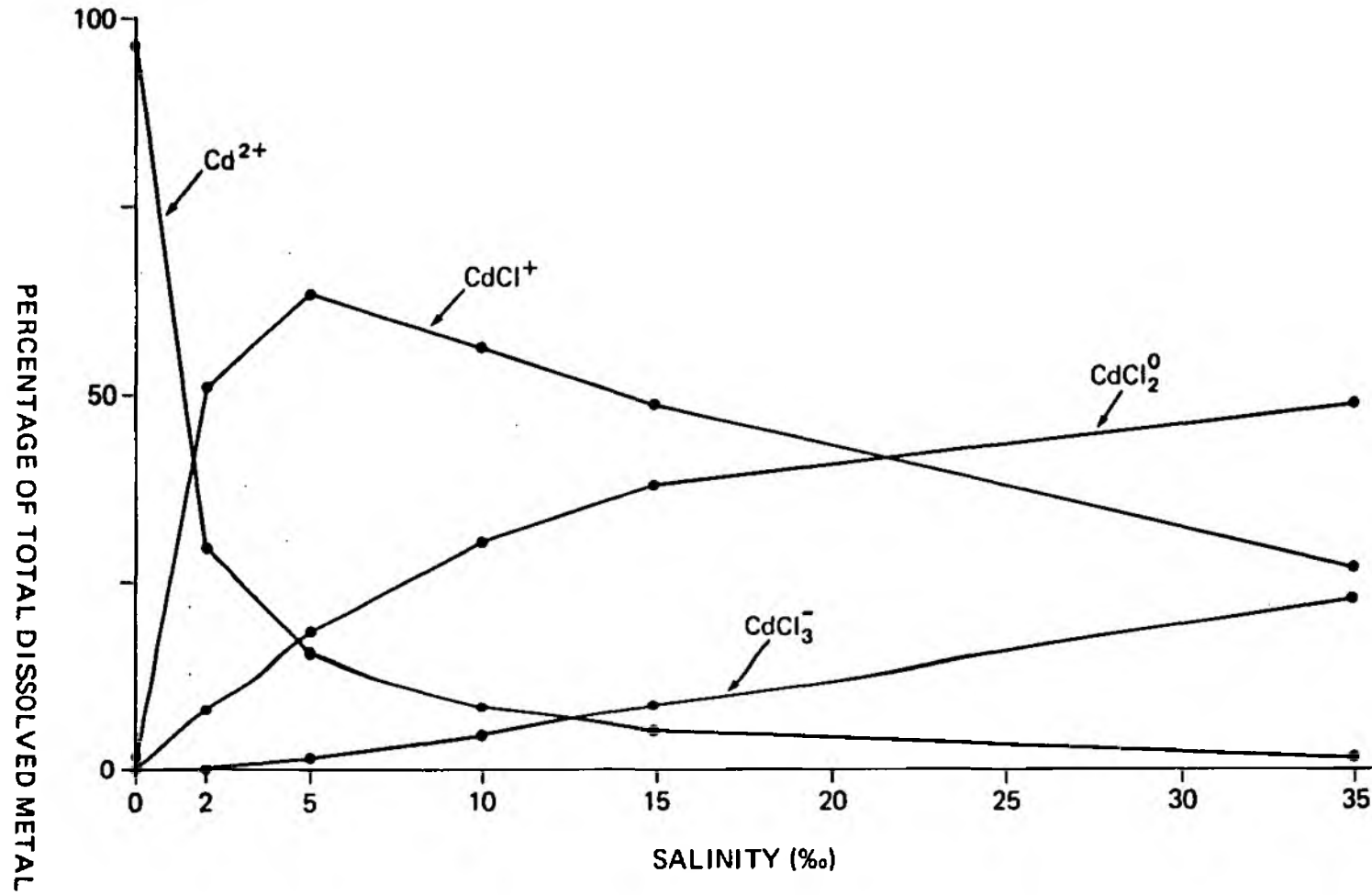


Fig 3.14a Cadmium adsorption isotherms for Humber Estuary samples

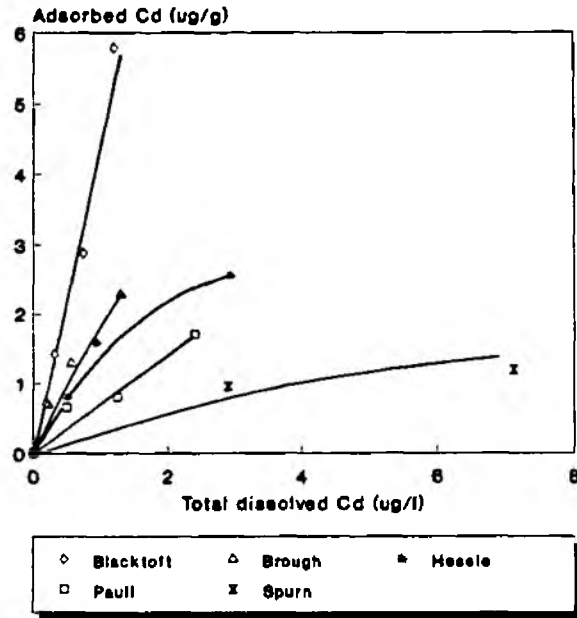
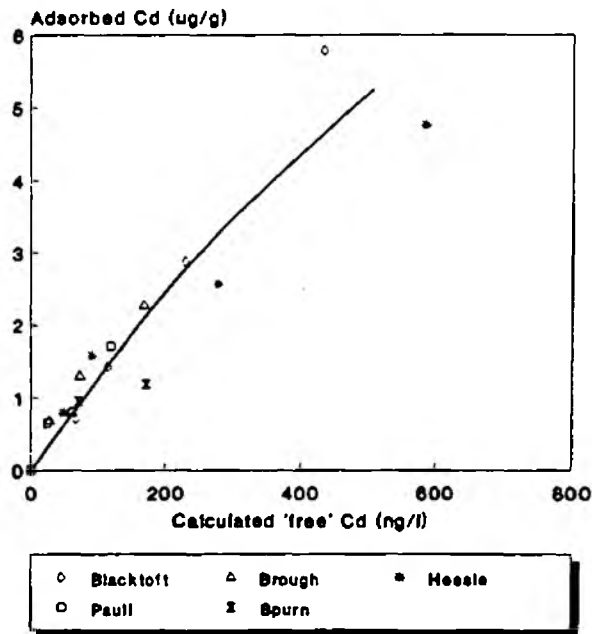


Fig 3.14b Data replotted against dissolved phase as free Cd ion content





for copper to show an increase with increasing salinity throughout the system. This is not readily explainable in terms of inorganic complexation. However, copper is well known to bind strongly to natural organic ligands and the concentration of such ligands has been shown (Apte *et al* 1987) to generally decrease with increasing salinity for the Humber Estuary. A possible explanation of the observed data might therefore lie in inhibition of adsorption through complexation by these dissolved phase organics. This would also tie in with our findings of the effect of UV irradiation on extent of adsorption of copper on Humber particulates (see Section 3.1.3).

### 3.6.1 Comparison of partition coefficients

The data found in the experiments and survey described above have yielded information which may be used in evaluating the partition coefficients at various points in the Humber system. The range of field and experimental measurements made should provide a body of information from which to determine how reproducible field and laboratory partition coefficients are, and which phases of the sorbed metal are important in determining  $K_p$ . Table 3.8 therefore compares data collected in the course of this study. Partition coefficients are shown as those found by "total" nitric acid digestion (1989 and 1991), and as found by the sum of the sequential extracts (1991), with the assumption being that the release of metals from particulates will be in the order:

exchangeable --> carbonate --> reducible --> organic --> residual  
(1)                      (2)                      (3)                      (4)                      (5)

so that the progressive addition of  $K_p$  worked out at each stage should point to the most important phases in terms of reversible partitioning. The results obtained by calculated adsorption in laboratory experiment (3.5 above) are included to provide a comparison of field and laboratory results. Data in parentheses are those for which there was known experimental error (in the digestion process) - they are included to give a general indication of the partition coefficient at that point. It should be noted that the total metal present as determined by sequential extraction was usually higher than that found by nitric acid digestion alone, suggesting greater efficiency by the former method.

**Table 3.8. Comparison of field and laboratory partition coefficients**

Metal	Site	Kp from Field Surveys			(kg/l)
		1991 total	1991 seq total	1989 total	Kp from lab expt
As	Althorpe	*	*	*	3.4 E2
	Boothferry	*	*	1 E4	6.9 E2
	Blacktoft	*	*	*	3.4 E3
	Brough	*	*	1 E4	4.0 E2
	Hessle	*	*	2 E4	2.8 E3
	Paull	*	*	*	1.8 E3
	Spurn	*	*	*	3.6 E3
Cd	Althorpe	3.6 E3	*	*	3.6 E3
	Boothferry	7.5 E3	*	6 E3	4.8 E3
	Blacktoft	6.2 E3	*	4 E3	4.6 E3
	Brough	2.6 E3	*	2 E3	2.3 E3
	Hessle	2.0 E3	*	3 E3	0.9 E3
	Victoria Pier	*	*	3 E3	*
	Paull	1 E3	*	*	0.6 E3
	Spurn	1 E3	*	*	0.2 E3
Cr	Althorpe	3.2 E4	5 E4	*	*
	Boothferry	6.6 E4	9 E4	*	*
	Blacktoft	7.7 E4	12 E4	*	*
	Brough	11.1 E4	11 E4	*	*
	Hessle	17.3 E4	12 E4	*	*
	Paull	(14 E4)	16 E4	*	*
	Spurn	(8 E4)	(10 E4)	*	*
Cu	Althorpe	3.3 E3	5.2 E3	*	2.8 E3
	Boothferry	4.6 E3	8 E3	7 E3	4.0 E3
	Blacktoft	6.7 E3	8.3 E3	7 E3	6.9 E3
	Brough	4.8 E3	6.8 E3	8 E3	6.2 E3
	Hessle	13.0 E3	7.6 E3	10 E3	8.6 E3
	Victoria Pier	*	*	10 E3	*
	Paull	(7 E3)	8.1 E3	*	2.5 E3
	Spurn	(10 E3)	(11.6 E3)	*	14.7 E3

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Kp from progressive seq digests

(1)	(1+2)	(1+2+3)	(1+2+3+4)
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*	*	*	*
*	*	*	*
*	*	*	*
*	*	*	*
*	*	*	*
*	*	*	*
2.9 E3	4.3 E3	*	*
7.7 E3	13.0 E3	*	*
4.7 E3	10.1 E3	*	*
1.7 E3	3.3 E3	*	*
1.2 E3	2.4 E3	*	*
*	*	*	*
0.5 E3	1 E3	*	*
1.4 E3	3 E3	*	*
*	*	*	*
*	*	*	*
2.2 E2	*	*	*
0.3 E2	*	*	*
*	*	*	*
<lod	*	*	*
1.2 E2	*	*	*
2.7 E2	1.5 E3	1.9 E3	3.3 E3
7.0 E2	3 E3	4.3 E3	6 E3
2.2 E2	1.3 E3	2.2 E3	4.6 E3
2.5 E2	1.4 E3	1.9 E3	3.5 E3
1.9 E2	1.4 E3	2.6 E3	4.9 E3
*	*	*	*
2.8 E2	1.5 E3	3.1 E3	4.8 E3
2.9 E2	1.3 E3	2.6 E3	(7 E3)

Table 3.8 continued

Metal	Site	Kp from Field Surveys			(kg/l)	Kp from progressive seq digests			
		1991 total	1991 seq total	1989 total	Kp from lab expt	(1)	(1+2)	(1+2+3)	(1+2+3+4)
Ni	Althorpe	2.8 E3	2.7 E3	*	*	1.7 E2	4.8 E2	1.7 E3	*
	Boothferry	4.1 E3	6.1 E3	5 E3	5.0 E2	2.4 E2	6.8 E2	4.0 E3	*
	Blacktoft	2.7 E3	*	5 E3	8.8 E2	1.8 E2	*	*	*
	Brough	3.0 E3	5.8 E3	7 E3	*	2.0 E2	6.8 E2	2.8 E3	*
	Hessle	6.3 E3	5.9 E3	8 E3	7.2 E2	1.4 E2	5.7 E2	3.1 E3	*
	Victoria Pier	*	*	8 E3	*	*	*	*	*
	Paull	(4 E3)	4.7 E3	*	*	1.6 E2	4.1 E2	2.6 E3	*
	Spurn	(7 E3)	*	*	3.1 E2	1.9 E2	*	*	*
Zn	Althorpe	*	*	*	2.3 E3	*	*	*	*
	Boothferry	*	*	20 E3	*	*	*	*	*
	Blacktoft	*	*	9 E3	8.5 E3	*	*	*	*
	Brough	*	*	7 E3	3.3 E3	*	*	*	*
	Hessle	*	*	10 E3	2.5 E3	*	*	*	*
	Paull	*	*	*	3.0 E3	*	*	*	*
	Spurn	*	*	*	3.3 E3	*	*	*	*

Notes : 1989 "Hessle" site sample was taken from south side of river

Paull replaced Victoria Pier site in 1991 survey

seq = sequential extraction

total = nitric acid digestion

sequential extraction codes : 1 = exchangeable; 2 = carbonate; 3 = reducible; 4 = organic; 5 = residual

total of sequential digests for chromium made up of main phases ie 3, 4 and 5

\* = data not yet available

## Results

The lack of availability of some results at this time, means that additive data from the sequential extractions is limited. Blanks in the sequential procedure were generally below the detection limit, although some contamination was found in the organic phase for cadmium, chromium, lead and nickel, and in the reducible and residual phases for chromium.

- Arsenic - The partition coefficients found in the 1989 field survey were significantly higher than those found from laboratory spiking experiments. This is likely to indicate that much of the arsenic *in situ* exists in more strongly bound phases, playing little part in readily reversible sorption processes. However, results from sequential digests from the 1991 survey are awaited to confirm this.
- Cadmium - *In situ* partition coefficients from the 1991 and 1989 surveys were generally similar, and were also close to those found by laboratory experiment. This is in line with the hypothesis that the bulk of the cadmium *in situ* is present on solid phase sites for which sorption processes are readily reversible. Agreement between laboratory experiment  $K_p$  data and those derived from the exchangeable phase of the sequential extraction procedure was in fact extremely good, while the combination of exchangeable and carbonate phases accounted for essentially all of the cadmium partitioning on Humber suspended sediment.
- Chromium - Total and sequential data given for 1991 were similar, but note that the sequential data are made up of those from reducible, organic and residual phases only. The partition coefficient for the exchangeable extract is ca. 100 times lower than the total found *in situ* reflecting the strong binding of chromium to particulate matter.

- Copper - Data were generally comparable between the *in situ*- and laboratory-determined partition coefficients. The  $K_p$  given by the exchangeable phase is about 100 times lower than that found to occur in the field; however, addition of the carbonate phase brings the  $K_p$  up to the same order of magnitude as the *in situ* determinations. The reducible phase does not seem to exert much effect, while the inclusion of the organic phase brings the partition coefficient to similar levels to those found from either the total digestions or by laboratory experiment. The major phases controlling copper sorption therefore appear to be carbonate and organically-bound metal, and all phases in the sequential extraction scheme apart from the residual appear relevant in terms of estimating reversible partitioning.
- Nickel -  $K_p$ s found on the 1991 survey, determined by total digestion and sequential extraction were similar, but tended to be slightly lower than those found in 1989. Partition coefficients found in the laboratory experiment however, were about ten times lower than those found in the field. As for arsenic, this suggests the presence *in situ* large amounts of Ni which is not readily desorbed over short timescales. Sequential extraction data indicate that the important phases in this respect are the exchangeable and carbonate, with  $K_p$ s calculated after these two steps agreeing well with the lab data. Inclusion of the reducible phase, however, provides data of a similar order of magnitude to the total *in situ*; this suggests that sorption processes for iron- and manganese-bound nickel may be the slow step in equilibration.
- Zinc - Data available at present for zinc are limited. *In situ*  $K_p$ s for the 1989 survey proved somewhat higher than those from lab experiment but a more detailed assessment of this element's behaviour awaits further results.

### 3.6.2 General comments on comparison of $K_p$ data

Partition coefficient data determined by both sequential extraction and by nitric acid "total" digestion were generally similar.  $K_p$ s for 1989 and 1991 are similar, although results from the earlier survey tended to be slightly higher. Breaking down the partition coefficient into various phases provided useful information upon which species are important in governing the sorptive processes of a particular metal. The most significant phases in this respect seem to be the exchangeable for cadmium, the carbonate and organic for copper and the reducible for nickel. Comparison of the various methods allows the reproducibility of techniques used to be assessed and highlights areas where laboratory experiments do not adequately represent field conditions. Kinetic constraints, for instance, may prove extremely important in terms of modelling the likely impact of changing discharge practices on contaminant behaviour in polluted systems.

#### 4. GENERAL DISCUSSION AND FURTHER WORK

Ongoing work on the influence of physicochemical parameters on the partitioning of contaminants between dissolved and particulate phases is of benefit to the NRA in a number of areas.

Firstly, a basic understanding of the partitioning of most priority pollutants in estuarine and freshwater systems is generally lacking. The provision of sound fundamental chemical behavioural data is essential as a basis for the development of improved environmental fate models. Similarly, such data will also be of direct use in setting and maintaining discharge consents of effluents to surface waters. The demonstration that partitioning of both pesticides and trace metals can be markedly influenced by factors such as salinity, suspended solids and dissolved natural organics is particularly important in this respect.

While the majority of existing models depend solely on equilibrium partition coefficients, our initial studies of the kinetics of sorption processes have shown these to be extremely complex. Sediment transport models under development for the NRA at WRC already include provision for simple first order reversible kinetics for contaminant sorption but for certain applications the addition of multi-step processes may now have to be considered.

In conjunction with associated work at WRC on toxicity and bioavailability of sediment bound contaminants, the study also has implications for addressing future questions on setting EQSs that incorporate both 'dissolved' and particulate components.

The next phase of the project will involve effort in three main areas:

1. Field and laboratory studies of trace metals partitioning behaviour will be extended to a second major UK river/estuary system. The selection of system for study will be made through consultation with the NRA.
2. A second phase of the studies on kinetics of metals partitioning will involve measurements of rates of desorption from Humber suspended



particulates. This is extremely important in terms of practical reversibility of sorption under changing environmental conditions. To this end, differences in desorption kinetics will be examined after prior adsorption of spiked metals over a range of equilibration periods. Desorption from 'naturally' contaminated particulates after transfer to a 'clean' system will also be investigated.

3. For organics, work will be extended to investigate the partitioning behaviour of other priority contaminants from the Red-List using the techniques used in the earlier work. Contaminants for study will include a polychlorinated biphenyl congener and possibly a compound with ionic character such as pentachlorophenol. Field samples will be collected from both the Humber and another estuary to provide natural aqueous media for the radiotracing experiments.

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