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Investigation of Partitioning of Contaminants between Water and Sediment

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Investigation of Partitioning of Contaminants between Water and Sediment

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EXECUTIVE SUMMARY

The partitioning of contaminants between water and suspended sediment exerts a major influence upon their transport and toxic effects. Sound physicochemical data for contaminant-particle interactions in aqueous systems are therefore essential for the development of effective environmental management models. WRc have carried out a three year NRA funded project to investigate the major factors influencing contaminant partitioning. This has involved a programme of research, concentrating initially on the Ouse/Aire/Trent/Humber system, and followed by the Mersey estuary. Work on the partitioning behaviour of organic contaminants has been focused on compounds selected from the UK Red List i.e. atrazine and gamma-hexachlorocyclohexane in estuarine waters. Particular emphasis has been placed on evaluating the importance of pesticide binding to naturally occurring colloids. The influence of physicochemical parameters such as salinity and suspended solids concentration on contaminant partitioning behaviour has also been established. Similar parameters have been investigated for trace metals, for which the importance of dissolved phase natural organic ligands in controlling partitioning equilibria has also been evaluated. Marked differences have been found for the partitioning of cadmium and copper in the Humber and Mersey estuaries. Partition coefficients have been found to be very much higher in the Mersey, with substantial removal to suspended particulates occurring within the estuary. A preliminary study of the kinetics of trace metal partitioning has resulted in the development of a multi-step reversible first order model. This draft of the Project Report provides a discussion of the experimental data obtained in the study, together with implications for EQS and discharge consent setting, sediment quality criteria, contaminant monitoring programmes, and environmental fate modelling. A more general discussion of the outputs can be found in the corresponding draft of the R&D Note (016/7/N).

KEY WORDS

Organic contaminants, trace metals, equilibrium partitioning, speciation, colloids, kinetics.

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1. INTRODUCTION

Although water is sometimes called the 'universal solvent', few chemicals have such a strong association with it that they remain entirely in the dissolved phase when the solution comes into contact with other environmental phases, be they solids such as soils or biota, gas i.e. the atmosphere, or other dissolved species such as humic material. The distribution of chemicals between the truly dissolved solution phase and other phases is called partitioning and at equilibrium this partitioning is usually characterised by a partition or distribution coefficient (K) which is the ratio of the concentration of the chemical in the phase of interest to the concentration in solution i.e.:

$$K = \frac{\text{concentration in phase of interest}}{\text{concentration in solution}}$$

Partitioning of chemicals is of critical importance in assessing or understanding their environmental behaviour for a number of reasons:

1. Once a chemical partitions onto or into a particle its hydrodynamic behaviour becomes controlled by that of the particle. For example a pollutant may concentrate and localise in sediment downstream of a discharge.

2. After partitioning the chemical will be exposed to a different microbiological and chemical environment resulting in more or less rapid degradation and possibly different breakdown products.

3. A chemical may have different bioavailability and therefore different toxicity when partitioned into other phases.

In the aquatic environment the most important critical partitioning process is that between the dissolved and the particulate bound phases and this has been the major focus of this study.

Although these two phases seem to be intuitively distinct and readily distinguishable, given more thought or experience it is clear that there are both practical and theoretical difficulties in making the distinction as the following factors will illustrate:

1. What constitutes a particle? Some 'particles' of clay for example may be of comparable size (≤1 µm) to some colloidal or even macromolecular dissolved organic species so an analytical scheme based on filtration or centrifugation separation may or may not separate all the 'particles' from the dissolved phase.

2. Are all dissolved species the same? The answer is obviously no but how can they be distinguished? It is known that trace metals form soluble molecular complexes with ligands such as chloride or NTA. Also metals and hydrophobic organic chemicals can associate in some way with naturally occurring dissolved humic matter. Most importantly it has been demonstrated that pollutants associated with dissolved natural organic material are usually less bioavailable than when in free solution.

It is clear from the above that a precise distinction between dissolved and particulate-bound pollutants is only feasible when it is characterised not by the theoretical understanding of the separation, but by the operation that performs the separation e.g. filtration, dialysis etc. A range of phase separation procedures have been used during our experimental studies and the possible influence of specific sample handling methods on partitioning results has been considered.

2. OVERVIEW OF WATER/SEDIMENT PARTITIONING

2.1 Introduction

An understanding of the factors controlling the transfer of contaminants between dissolved and particulate phases in aquatic systems provides a basis for describing the transport, sedimentation, bioaccumulation and biodegradation of contaminants of environmental concern. Figure 2.1 illustrates schematically some of the processes affecting the transport and fate of contaminants in the aquatic environment. This section briefly outlines the main physical and chemical factors that influence the partitioning behaviour of organic contaminants and trace metals.

2.2 Partition coefficient

Equilibrium partitioning of contaminants between dissolved and particulate phases is commonly represented by a partition coefficient Kp.

$$K_p = \frac{\text{mass of compound/kg of solid}}{\text{mass of compound/litre of solution}}$$

K_p is an empirical term rather than a true equilibrium constant. For non-polar organics it has been found that partitioning to solids is related to their organic carbon content and a more useful parameter is Koc where:

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

(f_{oc} is the organic carbon weight percentage in the sorbing solids.) The partition coefficient normalised for sorbate organic carbon content (K_{oc}) has been shown experimentally to be related to other parameters, such as the octanol-water partition coefficient (K_{ow}) (Briggs 1981) and solubility (Karickhoff *et al* 1979). These and other factors influencing partitioning are discussed in Section 3.

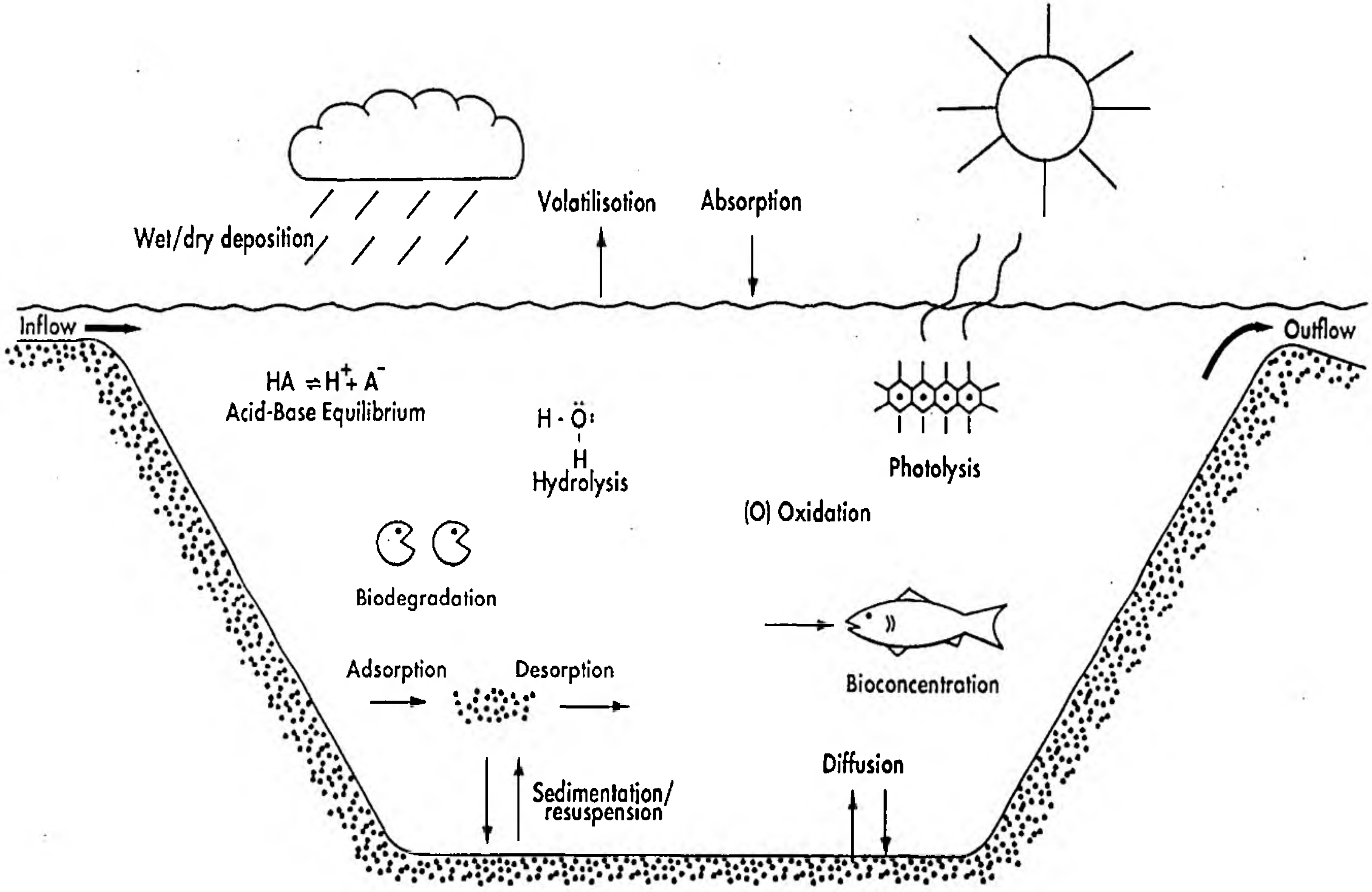


Figure 2.1 Physicochemical processes in the aquatic environment

2.3 Characterisation of organic partitioning

The likelihood of a chemical partitioning onto particulate material is controlled to a great extent for non-polar organic compounds by their hydrophobicity. This can be described as the incompatibility or the lack of affinity of non-polar compounds for water. The higher the degree of hydrophobicity, the more likely that an organic pollutant will partition onto natural suspended particulate matter which provides a range of different inorganic and organic sorptive sites with which hydrophobic organic contaminants can associate.

2.4 Characterisation of trace metal partitioning

Natural aquatic particulate matter is a complex mixture of geochemical phases, exhibiting widely varying metal binding characteristics. However, considerable experimental evidence exists (Llon *et al* 1982; Jenne *et al* 1984) to suggest that sorption of trace metal cations on such solids is strongly influenced by the presence of hydrous oxides of iron and manganese, and by surface coatings of natural organics such as humic substances; clay and zeolite mineral sites may also contribute.

Much information has, as a result, been obtained for pure mineral phases and has contributed to the development of detailed conceptual surface complexation models in which sorption is likened to solution phase complexation (Honeymman and Santschi 1988; and references therein). Support for this hypothesis is provided by the observation that equilibrium binding constants from such models tend to be closely correlated with hydrolysis constants of the respective metals (Shindler and Stumm 1987).

On theoretical grounds this approach has much to commend it and can readily be applied alongside existing well established solution phase speciation models. This has led to a tendency among some workers (Bourg 1987) to dismiss the simpler empirical partition coefficient approach to metals partitioning as of extremely limited value. However, in practice, difficulties in obtaining adequate accurate input data can be a problem in implementation of surface complexation models, and use is therefore still made of the partition coefficient. Our own feeling is that partition coefficient data can be a valuable aid to modelling the transport and fate of trace metals, provided both its empirical and conditional nature is borne in mind. Furthermore, there is no reason why the partition coefficient approach cannot itself be incorporated in an overall model including solution phase speciation data.

3. FACTORS CONTROLLING WATER/SEDIMENT PARTITIONING

3.1 Organic contaminants

A variety of physical and chemical parameters need to be considered when assessing the factors that influence the partitioning of organic contaminants in aquatic systems. In this section a short summary of these various factors is presented. The effects of a variety of factors on sorption processes in soil have been extensively reviewed (Bailey and White 1970; Browman and Chesters 1975; Hamaker and Thompson 1972). The laboratory studies carried out in this project concentrated on the main factors affecting the interaction of trace levels of hydrophobic organic compounds with suspended particulate matter and sediments in natural waters. The partitioning behaviour of polar, less hydrophobic chemicals is not as well understood.

3.1.1 Solubility

Solubility is one of the most important parameters that affects the fate and transport of organic chemicals in the environment and has been widely used to predict the partition coefficients of organic contaminants (Mailhot and Peters, 1988). Apart from temperature, solubility is also influenced by other parameters such as salinity, dissolved organic matter and pH.

3.1.2 Hydrophobicity

Hydrophobic organic compounds exhibit molecular character that is essentially non-polar and show low affinity for, and solubility in aqueous solutions. As a consequence hydrophobic contaminants tend to migrate to water surfaces or associate with suspended solid materials establishing a condition of dynamic equilibrium between dissolved and solid-sorbed states. The hydrophobicity or lipophilicity of organic compounds is commonly expressed as the octanol-water partition coefficient, K_{ow}, which is a distribution coefficient of solute monomers between an aqueous phase and an octanol organic phase (Leo *et al* 1971).

3.1.3 Volatility

Vaporisation is an important transfer pathway for organic chemicals from aqueous systems to the atmosphere (Dilling 1977). The physicochemical properties that control the exchange processes of organic compounds between the liquid and gas phases include solubility, molecular weight and the vapour pressure of the chemical. Other physical factors that influence phase transfer are flow velocity, depth, turbulence, the character of the air-water boundary and suspended particle content. Adsorption of an organic contaminant onto suspended particulate material reduces its chemical activity and affects the vapour density and volatization rate.

3.1.4 pH

Acid-base exchange processes can be important in controlling the speciation and behaviour of chemicals in aqueous systems. The degree of ionisation of organic contaminants can influence both their solubility and tendency for particle adsorption. The ionic character of particulate sorbate sites is also influenced by the ambient pH of the aqueous system. The variation in partition coefficient with pH is thought to result from changes in the chemical characteristics of the sorbate binding sites on the sorbent particle surface.

3.1.5 Ionic strength

The solubility of organic compounds in aqueous solutions is known to be affected to a minor extent by the presence of dissolved inorganic salts. Generally, the solubility of organic compounds decreases with increasing ionic strength and the relationship between salt concentration and the molar solubility of non-polar organic compound is described by the Setchenow equation (Hashimoto *et al* 1984):

$$\log (So/S) = KsCs$$

where S and S_o are the molar solubilities in salt solution and pure water respectively, Ks is the salting out parameter characteristic of the compound and C_s is the molar salt concentration. The salting-out effect on organic contaminants is likely to be most important in estuarine systems where large gradients in ionic strength are encountered. The influence of this parameter on both trace metal and organic contaminant partitioning has been investigated in this study.

3.1.6 Dissolved organic carbon (DOC)

A large proportion of the dissolved organic carbon (DOC) in natural waters consists of polymeric humic material (colloidal organic matter). Carter and Suffet (1982) and Landrum *et al* (1984) indicated that the binding of hydrophobic compounds to dissolved organic carbon was an important process in determining the distribution of such compounds in the aquatic environment.

In general, no distinction is usually made between the concentration of free dissolved compound and free compound plus humic bound compound in the aqueous phase. For compounds that are strongly bound to humic material e.g. DDT, the actual aqueous phase concentration may be significantly greater than the freely dissolved concentration (Chiou *et al* 1984) in the presence of DOC.

3.1.7 Particulate organic carbon (POC)

Natural sediments are usually inorganic minerals coated with organic and inorganic polyelectrolytes. The primary site of sorption of hydrophobic chemicals is organic matter which is associated with the mineral substrate. The mineral sites only contribute a substantial sorptive capacity at low organic matter contents. Natural organic matter is present in all soil and natural water systems. Carbohydrates, amino acids, proteins, fatty acids, phenols, lignin and isoprenoids have been isolated. Organic matter may form a surface coating on the mineral (clay) particles. It is a well established fact that particles with high organic matter content have a greater affinity for hydrophobic compounds than do particles with a low organic content.

The initial demonstration of the importance of the particulate organic carbon content of sediments in the sorption of neutral organic compounds can be credited to the work of Lambert (1967 and 1968) and Kenaga and Goring (1980).

Sediments are heterogeneous materials with varying chemical composition and particle size distributions; thus the Kp value for a contaminant varies with different sediment, to reduce this variability it is customary to normalise Kp values with measurable sediment properties. Several investigators (Karickhoff *et al* 1979; Means *et al* 1980; Brownawell and Farrington 1986) have observed that sorption of hydrophobic organic compounds can be correlated to the organic carbon content of the sorbent. Karickhoff *et al* (1979) developed a relationship which accounts for both the octanol-water partition coefficient of the sorbate and the particulate organic carbon content of the sorbent using sorption data from hydrophobic solutes (pyrene and methoxychlor) and aquatic sediment samples.

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21$$

K_{oc} is the partition coefficient normalised in terms of the organic carbon associated with the sorbent (see Section 2.2).

'Carbon-referenced' sorption has been tested for a wide variety of compounds and sediment/soils (Kenaga and Goring 1980; Karickhoff 1981). Agreements between calculated and measured Koc's were good, generally agreeing within a factor of 3 (0.48 log units). This was comparable to typical deviations in Koc's reported for a given compound on widely differing sediments or soils. Generally there is less data available on the effect of DOC; but the indication is that DOC is not as important in controlling the distribution and bioavailability of hydrophobic compounds as particulate organic carbon (POC). This could be due to the fact that DOC levels usually occur in the microgram to milligram per litre range whereas POC levels in sediment are typically in the 0.5 to 5% range.

3.1.8 Particle size and sediment surface area

Sediment particle size distribution may range from very small colloidal particles of less than 0.1 µm in diameter to large sand particles several millimetres in diameter. It is the smaller clay and silt particulates that are most likely to be involved in sorption reactions because their surface organic coatings have a large hydrophobic surface area. Sediment particle size has been identified as a secondary factor in the sorption of hydrophobic chemicals to natural sediments (Karickhoff *et al* 1979).

The specific area of particles appear to be proportional to the reciprocal of the average particle size irrespective of differences in particle properties. Correlations between specific surface area and contaminant concentration factor of adsorbing material have been observed (Hiraizumi *et al* 1979). The surface area dependence therefore seems to be a surrogate for particle size.

3.1.9 Suspended solids concentration

Sediments are complex mixtures of a number of solid phases that may include clays, silica (sand), silt, metal oxides, carbonates, and viable organic matter which interacts with and coats clay surfaces and biological detritus (including a living bacterial/algal population).

Organic contaminant sorption behaviour has been shown to be affected by variations in suspended sediment concentration (Lotse *et al* 1968). Contaminant to sediment ratio can have a pronounced effect on the extent of sorption and an inverse relationship between particle (adsorbing solid) concentration and partition coefficient has been observed (O'Connor and Connolly 1980). Partition coefficients can increase as much as an order of magnitude for every order of magnitude decrease in solids concentration.

3.1.10 Temperature

Temperature is an important parameter that influences the rate of chemical and biological processes in aquatic systems. It is probably only of minor importance when considering overall partitioning effects although it should be considered from a kinetic viewpoint.

3.1.11 Molecular surface area

Regression analysis has shown that the relationship between the calculated total molecular surface area (TSA) and the octanol/water partition coefficient (K_{ow}) for hydrophobic compounds such as PCB's can be expressed as a linear function (Doucette and Andren, 1987). However since TSA is also highly correlated with water solubility it seems reasonable to consider that it as an alternative measure for hydrophobicity.

3.2 Trace metals

It is important to understand that the partition coefficient K_p is not a true thermodynamic equilibrium constant for a single adsorption/desorption reaction but a complex empirical term, the value of which is dependent on both the nature of the particulate matter under consideration and a variety of solution phase parameters. As such, K_p data obtained under a particular set of field or experimental conditions are applicable to that set of conditions alone. This need not be a major obstacle to the approach, however, provided that measurements are made over the entire range of conditions likely to be encountered in the situation to which the model is to be applied. The more important factors which must be considered in this respect are discussed below.

3.2.1 Particle size and composition of particulate matter

The relevance of grain size effects to metals partitioning has been reviewed by Salomons and Forstner (1984). Clearly, an inverse relationship exists between particle size and surface area to mass ratio. Thus, available surface site densities can be expected to be much higher for smaller particles. The resulting tendency for metals to concentrate in finer particles must always be borne in mind when comparing data from different sites. In many laboratories conventional practice in the determination of metal contents of bottom sediments is to sieve to 63 µm (clay-silt fraction) prior to digestion and analysis.

As discussed in Section 2.4., metals can bind to natural particulates at a variety of different sites, dependent on chemical composition. Detailed sequential chemical extraction schemes (Tessier *et al* 1979; Rapin and Forstner 1983) have consequently been established in an attempt to determine the proportion of metals associated with each of the major particulate geochemical phases. Such schemes have been reviewed in a previous WRc report (Towner and Campbell 1987). While they can provide much useful information, and have been employed in this study, it must be emphasised that without exception they rely on entirely operational separations of the various fractions (exchangeable, carbonate, reducible, organic etc.) and some lack of selectivity of the different extractants is generally evident.

3.2.2 pH

Many studies have demonstrated the crucial role of pH in controlling sorption of metals on both pure mineral and natural particulate surfaces. Changes in pH affect not only the availability of adsorption sites but also the surface charge on the particulates and, as a result of hydrolysis reactions, the speciation of the dissolved phase metal. Typically, an extremely abrupt increase in the degree of adsorption is observed over a narrow range of 1 - 2 pH units (the so called 'adsorption edge').

3.2.3 Hardness

Competition for surface sorption sites by major cations such as calcium and magnesium has been demonstrated to inhibit trace metal adsorption, although the magnitude of such effects can be extremely variable. Differences in the relative affinities of major ions and trace metals for various binding sites therefore require further elucidation. The possible relevance of inhibition of adsorption by trace metals competing for similar sites must also be addressed.

3.2.4 Salinity

Changes in salinity during estuarine mixing can influence metal partitioning in a number of ways. Firstly, while Na^+ will be much less effective in competing for adsorption sites than Ca^{2+} and Mg^{2+}, the extremely high concentrations reached mean that such effects cannot be discounted. More important, however, is the complexing ability of Cl^- which can greatly reduce the aqueous phase 'free' ion content of certain metals, in particular Cd^{2+} (Bourg 1987; Comans and Van Dijk, 1988). The rapid increase in ionic strength experienced at the freshwater/estuarine interface also has a profound effect on the physicochemical characteristics of the particulate matter, for example through flocculation of dissolved natural organic matter.

3.2.5 Temperature

Although temperature is likely to affect both the kinetics of adsorption/desorption reactions and equilibrium partitioning, this is one aspect which appears to have received relatively little attention. In the case of laboratory experiments it is certainly important that equilibration is carried out at a temperature relevant to the water body of interest; ideally, at least two appropriate temperatures should be tested.

3.2.6 Solution phase metal speciation

The above mentioned situation of inhibition of Cd adsorption to particulates by chloride complexation in the estuarine environment is a prime example of the influence of solution phase speciation on partitioning. Such effects can be interpreted in terms of competition between dissolved phase complexants and solid phase adsorption sites. However, it is a mistake to assume necessarily that only the free metal ion is involved in sorption processes. Indeed, complexation can in practice either increase or decrease trace metal sorption (Jenne and Zachara 1984). The importance of inorganic ligands such as hydroxide, carbonate, chloride, sulphate, phosphate etc. can readily be deduced, as speciation models for these are well established. Unfortunately, available thermodynamic data for natural organic ligands are often entirely lacking or of dubious accuracy. Ongoing research at WRc for the NRA has shown that such ligands dominate solution phase speciation for some important metals such as copper and zinc (Gardner and Ravenscroft 1991, Ravenscroft and Gardner 1991).

3.2.7 Particle concentration

One of the most surprising experimental findings on partitioning is a marked dependency of Kp on the concentration of adsorbing particles. Several laboratory studies have demonstrated an essentially linear decrease in Kp with increasing suspended solids loading, in some cases over several orders of magnitude of concentration (O'Connor and Connolly, 1980; DiToro 1986). More recently, a similar finding has been reported from a compilation of field data for coastal waters (Balls 1989). The explanation for this particle concentration effect is presently the subject of some controversy. One school of thought (Morel and Gschwend 1987) is that it is merely an experimental artefact resulting from the presence of colloidal material with a strong tendency to bind metals, but not separated from the aqueous phase by the filtration or centrifugation procedure employed. An alternative is that it is a genuine effect caused by either: (i) an additional particle interaction induced desorption reaction (DiToro *et al* 1986); or (ii) aggregation of particulates at high solids levels leading to a reduction in surface area and surface site concentration. A final possibility worthy of consideration Gardner and Gunn (1989) is the release of particulate associated natural organic ligands to the dissolved phase in the course of the experiment - the subsequent concentration, and hence effect, of such ligands would be greater the higher the solids loading.

3.3 Importance of kinetics in trace metal partitioning

The vast majority of studies undertaken to date have concentrated solely on an equilibrium approach to trace metal partitioning on the grounds that sorption rates were assumed to be extremely rapid. While this may be valid for surface sorption on many model mineral phases, recent work using natural sediments or suspended matter (Jannasch *et al* 1988; Millward 1989; Unger *et al* 1988) has demonstrated the significance of relatively slow sorption processes, with equilibration periods of up to 100 days or more being required. Multi-step first order kinetic models have been proposed (Jannasch *et al* 1988; Nyfeller *et al* 1984) in which very fast initial sorption is followed by much slower and extended uptake. A possible rationalisation for this is in terms of rapid binding to surface sites followed by much slower transport to sites within pores in the particle interior. Coagulation of colloids could also result in surface sorbed metals being occluded within the coagulated particles and hence difficult to desorb (Li *et al* 1984).

Regardless of mechanism, the importance of kinetic processes as a factor in the transport of metals by particulates depends on the relative time scales of such processes and particle residence times in the system of interest. During this study we have attempted to adopt an all-embracing approach involving estimation of both equilibrium partition coefficients and, where relevant, associated adsorption and desorption rate constants.

3.4 Methods of equilibration

Adsorption methods can be either batch or flow measurements depending on how sorption equilibrium is reached between the solid and the solution. In batch methods a known mass sediment is added to a known volume of solution of known initial concentration. The suspension is agitated and after equilibrium is achieved the sediment and solution are separated usually by centrifugation or filtration. The equilibration concentration of the supernatant is then measured and the change in solution concentration attributed to sorption in the sediment. Chemical losses due to volatilisation, adsorption on container walls, photochemical reactions, biodegradation must be accounted for in blank runs without sediment present. Because of their simplicity batch methods were the main techniques used to study sorption on sediments during our studies.

4. INVESTIGATION INTO PARTITIONING OF ORGANIC CONTAMINANTS IN AQUEOUS SYSTEMS

4.1 Introduction

The investigations of the partitioning behaviour of organic contaminants was carried out in two phases. The first phase involved experimental assessments of the desorption of a 'naturally' occurring pollutant from river sediments. The second phase involved investigations of the main physical and chemical factors influencing partitioning behaviour of specific Red List compounds in river and estuarine waters.

4.1.1 Sediment desorption experiments

The process of desorption from resuspended sediments artificially enriched with hydrophobic organic contaminants has been studied extensively (Karickhoff 1980, Horzempa and DiToro 1983, DiToro and Horzempa 1982, Karickhoff and Morris 1985, Shorten, Elzerman and Mills 1990, Miller and Weber 1984, Oliver 1985, Wu and Gschwend 1986, Coates and Elzerman 1986). However, our initial laboratory investigations focused on a study of the desorption of 'naturally' incorporated contaminants from resuspended river sediment fractions under controlled temperature conditions with variable suspended solids concentration. The rate at which equilibrium conditions between 'dissolved' and 'particulate' phases are reached have been estimated. This work has provided data on the desorption behaviour of a contaminant (nonylphenol) that has not been studied previously to our knowledge.

4.1.2 Partitioning of Red List compounds in fresh and estuarine waters

The second phase of the work concentrated on the investigation and validation of novel and rapid procedures for the study of contaminant sorption in natural waters. Recent research suggests that the colloidally-bound fraction may comprise a significant proportion of total organic contaminants in natural waters (Carter and Suffet, 1982; Jota and Hasset, 1991). The toxicological significance of colloidally-bound organic contaminants has yet to be evaluated, but they may be of reduced toxicity and bioavailability, as has been shown for trace metal complexes (Apte *et al* 1988). The second phase of the work on organic contaminants investigated contaminant partitioning between particulate, colloidal and dissolved phases, and assessed the importance of the colloidally-bound fraction for two Red List compounds. The following operational definitions were used.

Particulate fraction - material >0.45 µm nominal diameter
Dissolved fraction - the solvated organic molecule
Colloidal fraction - the fraction of the contaminant bound to naturally occurring colloidal or organic humic substances, i.e. <0.45 µm but not truly dissolved.

The programme of work had the following aims:

- to evaluate the use of radiolabelled organic contaminants as a means of obtaining rapid and precise measurements in environmental modelling experiments;

- to develop rigorous, validated methods for the measurement of dissolved, colloidally bound and particulate organics in natural water samples;

- to investigate the organic speciation and partitioning of persistent non-polar contaminants in natural waters.

The main aspects of the second phase of the work on organics were:

1. Selection of Red List compounds for study.

   The criteria for selection were:

   - available in ^{14}C-radiolabelled form
   - of intermediate polarity
   - persistent
   - not exhaustively studied by other workers

2. Establishment of ^{14}C laboratory facilities and gaining of proficiency with the techniques.

3. Methodological investigations:

   - investigation of losses due to adsorption onto container walls and minimisation of these effects;

   - investigation of losses during filtration and ultrafiltration - comparison of different filter types;

   - investigation of equilibrium dialysis as a method for fractionating dissolved and colloidal phases;

   - development of an experimental protocol for the fractionation of particulate, dissolved and colloidal species (the 'three phases').

4. Partitioning experiments

   The partitioning behaviour of chosen UK 'Red List' organic contaminants between the three phases was investigated using samples from the Humber estuary, River Thames and the Mersey estuary. Turbid water samples were collected and used with the minimum of adulteration. The following experiments were carried out using radiolabelled priority pollutants:

   - measurement of partition coefficients;

   - effect of sediment concentrations;

   - effect of ionic strength (salinity);

   - kinetics of sorption processes.

4.2 Sediment desorption experiments

4.2.1 Investigations of organic contaminant desorption equilibrium

Most studies reported in the literature on the partitioning of organics between solid and aqueous phases have concentrated on quantifying the sorption process (characterised by a sediment/water partition coefficient) and studies on the desorption of chemicals from sediments have been more limited. Sediments can act as pollutant sources in two ways:

- contaminants on bottom sediments can desorb into pore water and then diffuse into overlying waters; and
- bottom sediment particles may be resuspended in the water column due to turbulent mixing or dredging and desorption of chemicals can occur.

In view of the possible role that polluted sediments can play as contaminant sources the desorption approach to studying contaminant partitioning has been investigated. In order to assess the influence of time on the desorption of organic contaminants desorption experiments were carried out under controlled temperature conditions with variable suspended solids (sediment) concentrations.

4.2.2 Bulk sediment collection

Bulk sediment from the River Aire in Yorkshire which receives industrial and domestic effluent from various sources was collected in early November 1989. Approximately 10 kg of contaminated muddy sediment was obtained with a van Veen grab at Fleet Weir east of Rothwell (Ordnance Survey Grid Reference 38.28). The bulk sample was stored in pre-cleaned methanol-rinsed, dried glass Beatson jars (500 ml) prior to work-up.

4.2.3 Batch desorption experiments

Aliquots of the bulk sediment (200 g) were suspended in 20 ml of River Aire water, poured on to a 500 micron stainless steel sieve and pushed through gently with a spatula. The <500 µm fractions were combined and subsequently air-dried at room temperature for 2-3 days. Dried sediment was stored at 4 °C for immediate use or at -20 °C for longer term storage. This material served as a standard 'naturally' contaminated sediment for use in desorption experiments. An accurately weighed sample of the sediment was introduced directly into the aqueous phase (1 litre) for desorption experiments.

All bottles were tightly stoppered and no reagent was added to halt microbiological activity to avoid possible disturbance of desorption processes. Triplicate batches of sediment/water mixtures (500 mg l^{-1}) plus a blank (no sediment) were incubated at 10 °C and shaken for the following time periods; 30 min, 5 hours, 24 hours and 72 hours. After the filtration and extraction of the sediment and aqueous phases no further clean up of the samples generated was undertaken. At the end of the incubation period the content of each bottle was filtered through a Whatman GF/F filter (previously ashed overnight at 550 °C). If immediate extraction was not possible the aqueous filtrate phase was stored at 4 °C. The sediment fraction (+ filter paper) was placed in teflon-lined screw-capped glass bottles with 10 ml of n-hexane; these were stored at -20 °C prior to extraction.

4.2.4 Extraction of particulate and aqueous phases

The sediment and filter paper were extracted three times with n-hexane (3 x 10 ml) for 5 minutes using a Lucas Dawe Ultrasonics Soniprobe (pulsed mode). Extracts were reduced to 1 ml using a N_2 gas stream prior to either direct GC-FID analysis or further sample clean up. After filtration the 1-litre aqueous phase was transferred to a 2-litre separating funnel, and extracted by shaking three times with n-hexane (3 x 30 ml). The hexane extracts were combined and stored at -20 °C overnight in teflon-lined screw cap glass bottles to remove traces of water. Sample extracts were concentrated to 1 ml with a nitrogen gas stream and stored prior to analysis in 1.5 ml capacity glass vials.

4.2.5 Sample clean-up and analysis

Capillary GC-FID (Perkin Elmer 8310 gas chromatograph) was initially used to screen the crude particulate and aqueous sample extracts for the presence of organic contaminants. GC-MS analysis was used to identify unknown contaminants observed in both particulate and aqueous extracts. This exercise enabled the identification of specific contaminants that underwent desorption. Particulate and aqueous sample extracts were desulphured using the tetra-butyl ammonium sulphite method of Rogers *et al* (1989). After sulphur removal samples (1 ml) were cleaned up using Florisil (magnesium silicate 60-100 mesh pre-baked at 650 °C, 1% deactivated, topped with pre-baked sodium sulphate) column chromatography. The column was initially eluted with n-hexane (5 ml) and then with 10% diethyl ether in hexane (10 ml). Eluates were reduced to 1 ml by nitrogen gas stream evaporation.

4.2.6 Identification of specific sediment contaminants

In preliminary experiments the sample extracts were not subjected to clean-up because at this stage only a screening of components amenable to gas chromatography was required. Comparison of chromatograms from triplicate samples and blanks clearly indicated the presence of a characteristic cluster of peaks consistently present in the particulate and aqueous phases of the samples which was not present in the blank samples. GC-MS analysis of a desulphured extract of the <500 micron fraction of the sediment identified the characteristic cluster of peaks as nonylphenol isomers (fragment masses 29, 45, 57, 71, 85, 107, 121, 135, 149). The mass spectrum of the nonylphenol identified in the desulphured sediment extract is shown in Figure 4.1. The recovery efficiency of nonylphenol from sediments was greater than 85% (Table 4.1.). These preliminary results showed that nonylphenols would serve as useful model contaminants for further desorption studies. Nonylphenols are widely used in pesticide formulations (McLeese *et al* 1980) and as raw materials for the production of polyoxyethylene derivatives. Their presence in river water, treated municipal water, digested sewage sludges and tap water has also been reported (Sheldon and Hites 1978). Nonylphenol is a major degradation product of nonylphenol ethoxylates; a group of compounds employed as non-ionic surfactants.

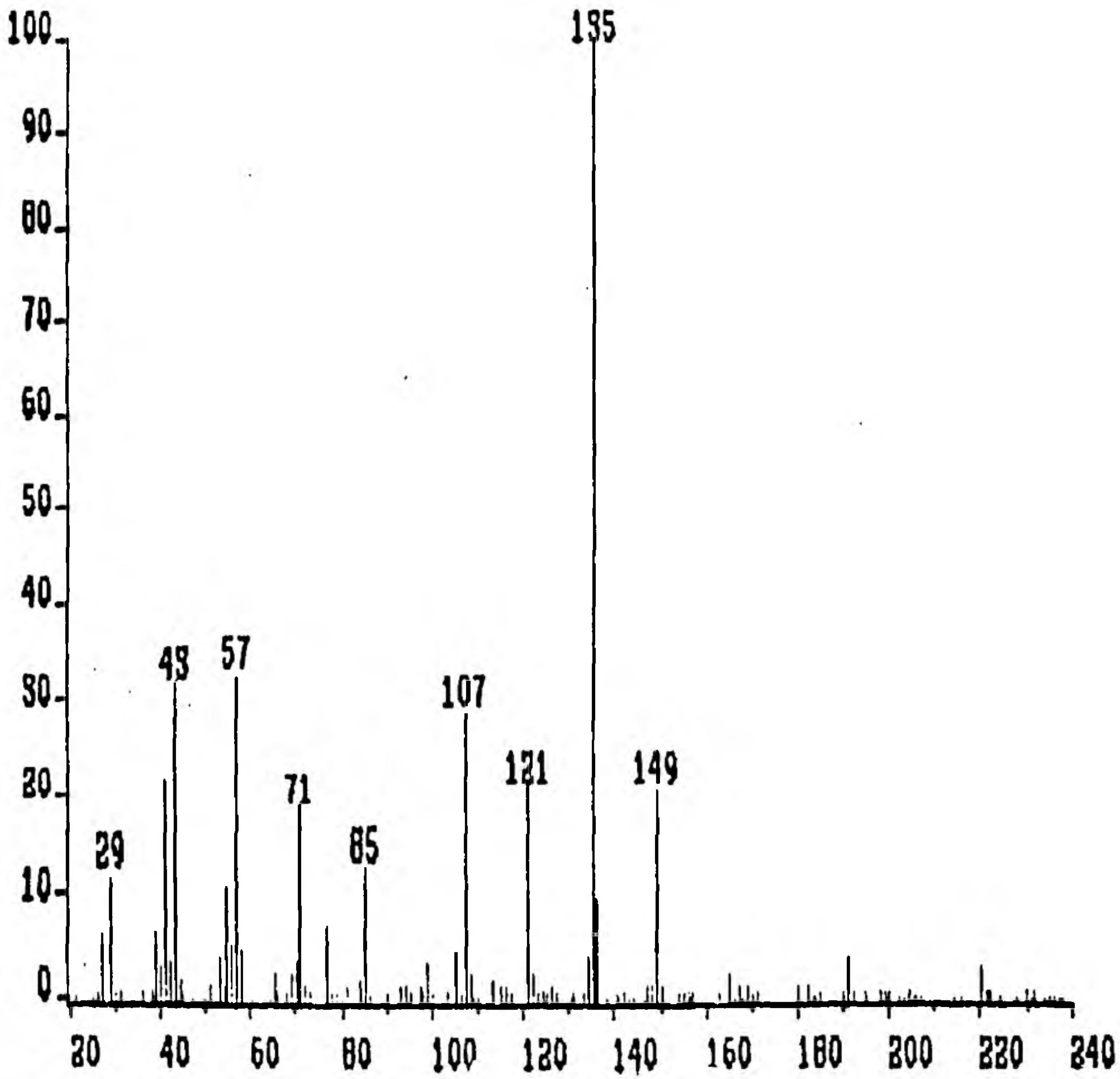


Figure 4.1. Mass spectrum of nonylphenol in extract from contaminated River Aire sediment

Quantitative results from the preliminary desorption experiment are presented with equilibrium partition coefficients (K_p and K_{oc}) for nonylphenol in Table 4.2. Quantification of the nonylphenol concentrations in both aqueous and particulate phases were based on the summation of GC-FID peak heights of five characteristic peaks consistently present in all sample extracts and in the technical grade standard of nonylphenol. Nonylphenol is a mixture of ring and chain isomers so several peaks were used in quantification. The external standard was a technical grade mixture of nonylphenol (Fluka).

An unresolved complex mixture (UCM) of contaminants was present in all crude particulate extracts but not in cleaned-up extracts. The presence of a UCM is usually indicative of gross pollution with petroleum hydrocarbons. Aqueous phase samples showed an increase in nonyl phenol concentration over a 24 hr period indicating desorption from the resuspended sediment into the aqueous phase. It was thus assumed that initial equilibrium had been reached within this 24 hr period.

Recovery data for nonylphenol (technical grade) from standard and spiked aqueous and sediment samples taken through the complete extraction and clean-up process is shown in Table 4.1.

Table 4.1 - Recovery efficiency for nonyl phenol

Nonyl phenol spike level	Procedure	% recovery
0.025 mg l^{-1} standard	Sulphur removal followed by florisil column chromatography on 1 ml	99
0.05 mg l^{-1} standard	aliquots	85.2
500 mg l^{-1} sediment spiked with 0.051 mg l^{-1} technical grade nonylphenol	As above using 1 ml extracts of spiked sediment and deionised	86
1 litre deionised water spiked with 0.051 mg l^{-1} technical grade nonylphenol	water samples	91

Table 4.2 Desorption of nonylphenol from contaminated sediment over a 24 hour period (sediment concentration 400 mg l^{-1})

Desorption period	Nonylphenol concentration* $\mu g\ l^{-1}$ Aq.	$\mu g\ l^{-1}$ Part.	CV Aq.	Part.	$\log K_p$	$\log K_{oc}$
30 mins	5.2	44	18	33		
5 hours		7.5	34	18	22	
24 hours	7.3	37	7	7	3.7	4.96

*quantified using five major GC peaks

4.3 Investigations of the partitioning of atrazine and g-hexachlorocyclohexane

The partitioning of contaminants between dissolved and particulate phases in natural waters is an important process that influences their fate, transport and bioavailability. 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.

Several studies have demonstrated that dissolved organic matter can increase the apparent aqueous solubility of hydrophobic organic compounds as a result of the presence of hydrophobic sites such as alkyl chains on the natural organic matter. The resulting organic chemical: DOC complex would be held in solution or colloidal dispersion by hydrophilic sites such as carboxylic acid, phenolic and hydroxyl groups on the DOC (Hassett and Anderson 1979; Boehm and Quinn 1973; Poirrier *et al* 1972).

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 ($0.1\ \mu g\ l^{-1}$, 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 g-HCH were chosen for study because of their priority status as environmental contaminants.

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). The aims of this work were to develop physicochemical 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 (both abiotic or biotic) of the labelled compounds can be assumed to be negligible.

4.3.1 Experimental

^{14}C-labelled atrazine (specific activity 4.29 MBq mg 1-1) and gamma-hexachlorocyclohexane (g-HCH, 'lindane'; activity 8.06 MBq mg 1-1) were from Amersham International UK. Stock solutions of atrazine (1.3 µg l^{-1}) and gamma-hexachlorocyclohexane were prepared in deionised/activated carbon filtered water and stored at 4 °C in the dark. The concentrations of radiolabel in standards and sample solutions were determined using liquid scintillation counting. The 5 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.

4.3.2 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 l^{-1} CaCO3 l^{-1}) and spiked with radiotracer to give a final concentration of either 1.3 µg l^{-1} atrazine (5.55 KBq l^{-1}) or 0.92 µg l^{-1} g-HCH (7.4 KBq l^{-1}). 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.

4.3.3 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^{-1} atrazine or 0.92 µg l^{-1} 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.

4.3.4 Equilibrium dialysis

Dialysis technique

Carter and Suffet (1982) developed a dialysis method for partitioning of compounds with low to moderate lipophilicity (low-intermediate Kow's). pp'DDT was used as a model pollutant, humic acid as sorbent. The humic acid solution (or buffered water for controls) was placed in a dialysis bag which was shaken in a solution of radio labelled DDT for four days at 25 °C. At the end of this period aliquots removed from the dialysis bag and the solution outside the dialysis bag were hexane extracted. The dialysis tubing was chosen so that humic material was retained inside the bag while the DDT diffused freely through the bag. In a dialysis experiment it was assumed that the DDT inside the bag consisted of two fractions, one fraction was free, dissolved DDT, the other fraction was bound to humic materials. Since the free DDT diffused through the dialysis bag the concentration of free DDT was the same inside and outside the bag. The bound concentration was then measured as the difference between the DDT concentration inside and outside the dialysis bag. This approach has been used in our studies.

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. The 5 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 µg l^{-1} atrazine, equilibrated for 24 hours and then dialyzed for 66 hours. Aliquots of the dialyzate 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 µm and dialyzed as above.

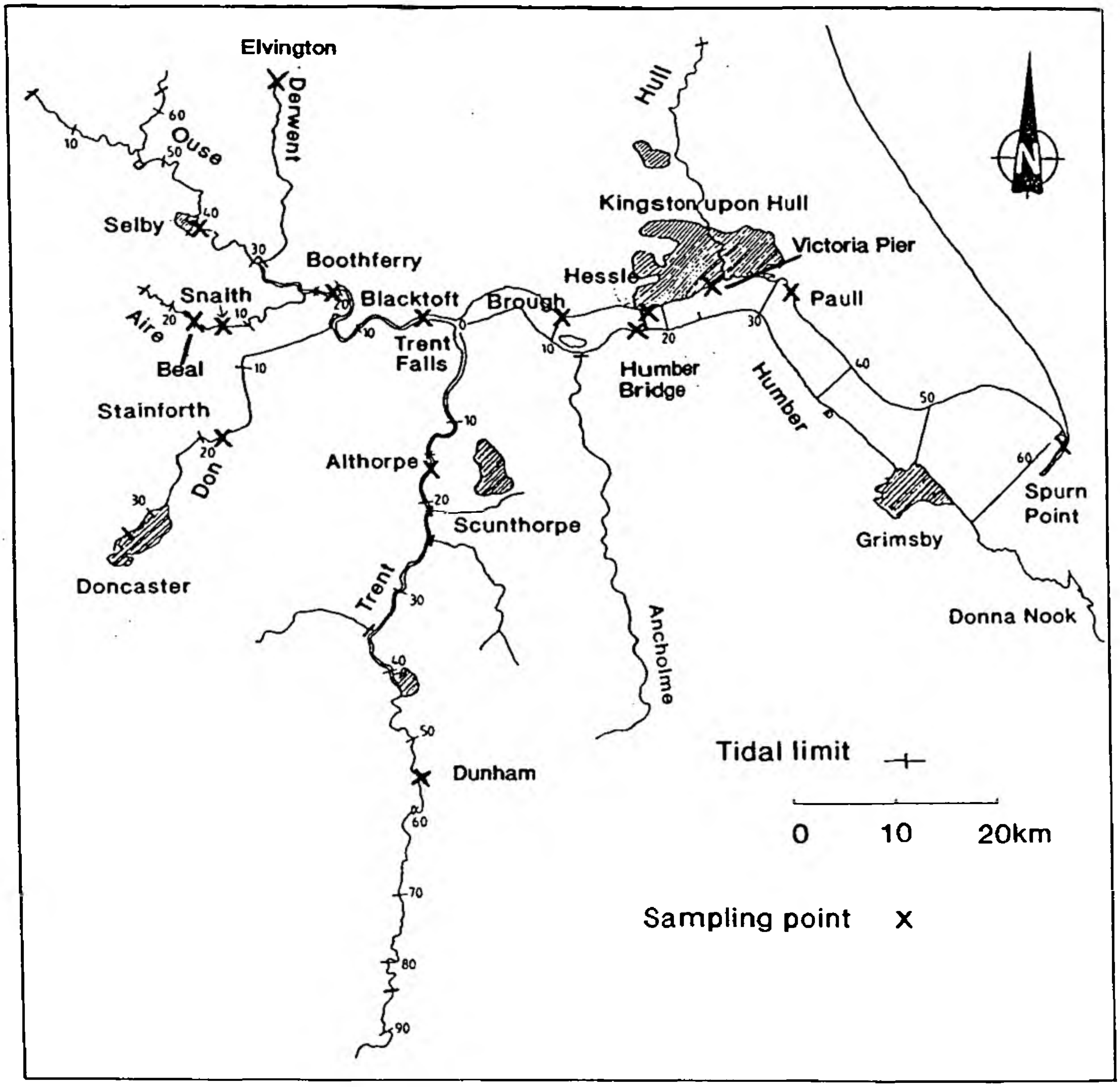
4.3.5. Collection of estuarine and river samples

Water and sediment samples were collected from five sites in the Humber estuary on 15.11.90 and 22.4.91 (Figure 4.2). 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 mud flat, 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 °C. Partitioning experiments were conducted within 72 hours of collection. River Thames water (Medmenham) was used for the freshwater experiments. The Humber survey was followed by a complementary exercise on the Mersey estuary (Figure 4.3.) which was intended to provide partitioning data for another major estuary. The main Mersey sampling site was at Fiddlers Ferry in the upper estuary where samples were taken over the period of a flood tide (23.1.92) in order to cover a range of salinities.

4.3.6 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 °C. Background levels of atrazine and g-HCH were obtained by GC-MS. Atrazine was determined in GF/F filtered samples by

Figure 4.2 Sampling sites in the Humber system



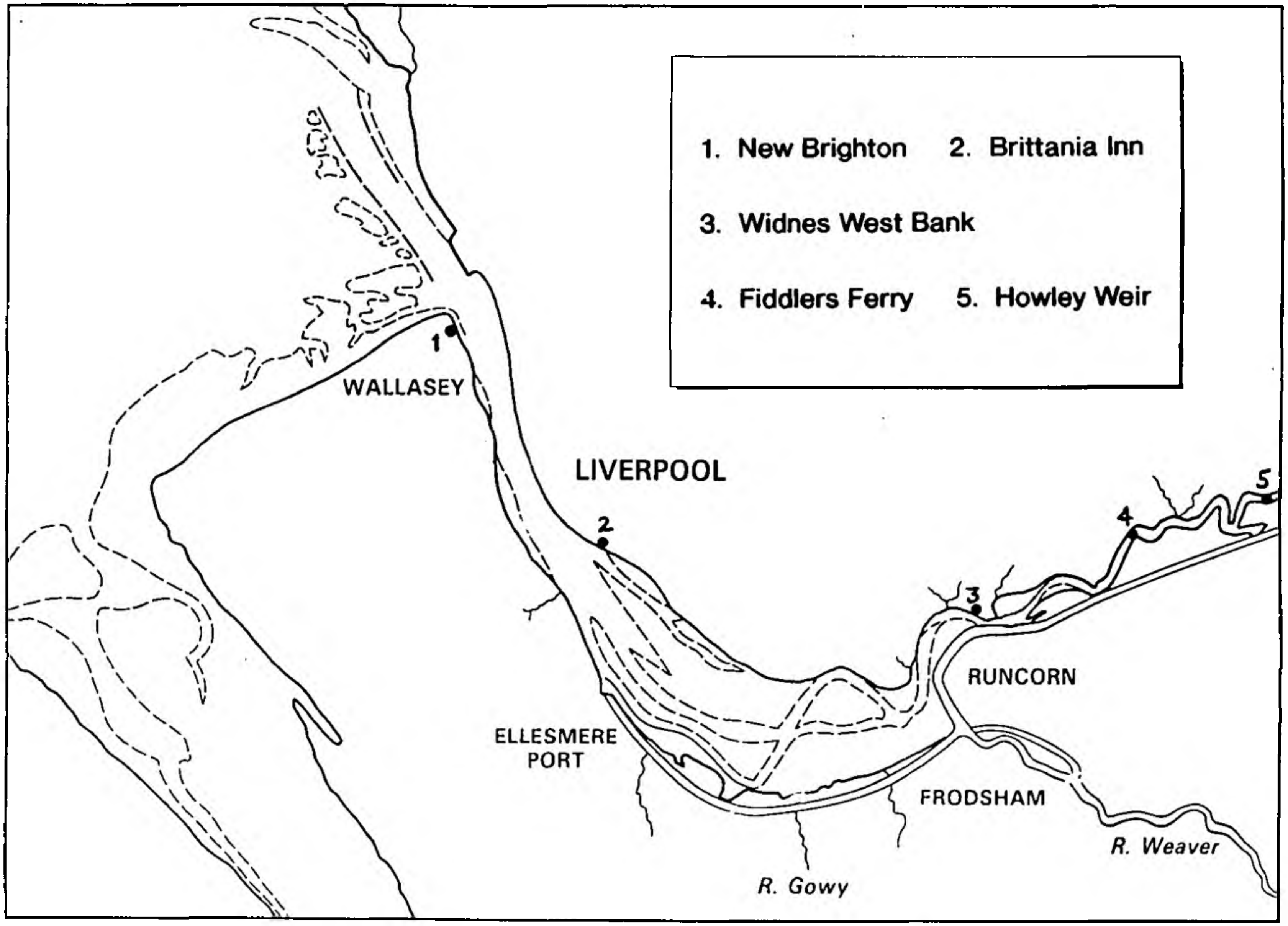


Figure 4.3 Sampling sites in the Mersey estuary

gas chromatography-nitrogen phosphorus detection following extraction into 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 $^{13}C_6$-d_6-HCH as an internal standard.

4.3.7 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 µg l^{-1} atrazine; 0.92 µg 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 :

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

Further, it can be shown that:

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

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.

4.3.8 Results - 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 (MWCO<5000). Experiments were repeated with pre-filtered borehole water and similar losses were observed. The use of ultrafiltration was therefore abandoned. The results of these tests are presented in Table 4.3.

Table 4.3 Percentage recoveries of atrazine and g-HCH following filtration

Filter type	Percentage recovery* Atrazine	 g-HCH
GF/F untreated	101±2%	102±2%
GF/F ashed	100±1%	106±5%
Millipore 0.45 µm	99±1%	102±2%
Anotec 0.2 µm	100±0.5%	-
Anotec 0.02 µm	100±1%	100±2%
UF(<5000 MWCO)	75.9±6%	9±3%

* calculated using data from five replicated filtrations

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.

4.3.9 Estuarine field studies

Parameters measured at each site on the Humber are presented in Tables 4.4 and 4.5. Atrazine was detected at all sites, and g-HCH at only one site (Table 4.6). However, their concentrations were below 170 ng l^{-1} and were therefore low compared to the spiked concentrations. Although analytical data for atrazine and g-HCH in the Mersey samples were not obtained during this work, previous WRc work has shown that dissolved g-HCH levels are typically less than 50 ng l^{-1} (Rogers *et al* 1990).

Table 4.4 Estuarine survey data (15.11.90) - Atrazine

Site	Salinity °/oo	Temp. °C	pH	SSC mg l^{-1}	DOC mg C l^{-1}
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 4.5 Estuarine survey data (22.4.91) - g-HCH

Site	Salinity °/oo	Temp. °C	pH	SSC mg l^{-1}	DOC mg C l^{-1}
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 4.6 Background levels of atrazine and g-HCH in Humber estuary (22.4.91)

Site	Atrazine conc. ng l^{-1}	g-HCH conc. ng l^{-1}
Spurn	40	<1
Paull	120	<1
Hessle	110	<1
Brough	110	4
Blacktoft	170	<1

4.3.10 Results - 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 1.9×10^7/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 4.4). The resulting partitioning data are presented in Table 4.7 and are compared to other literature data in Table 4.8. The added sediment was 57.7% dry weight and had an organic carbon

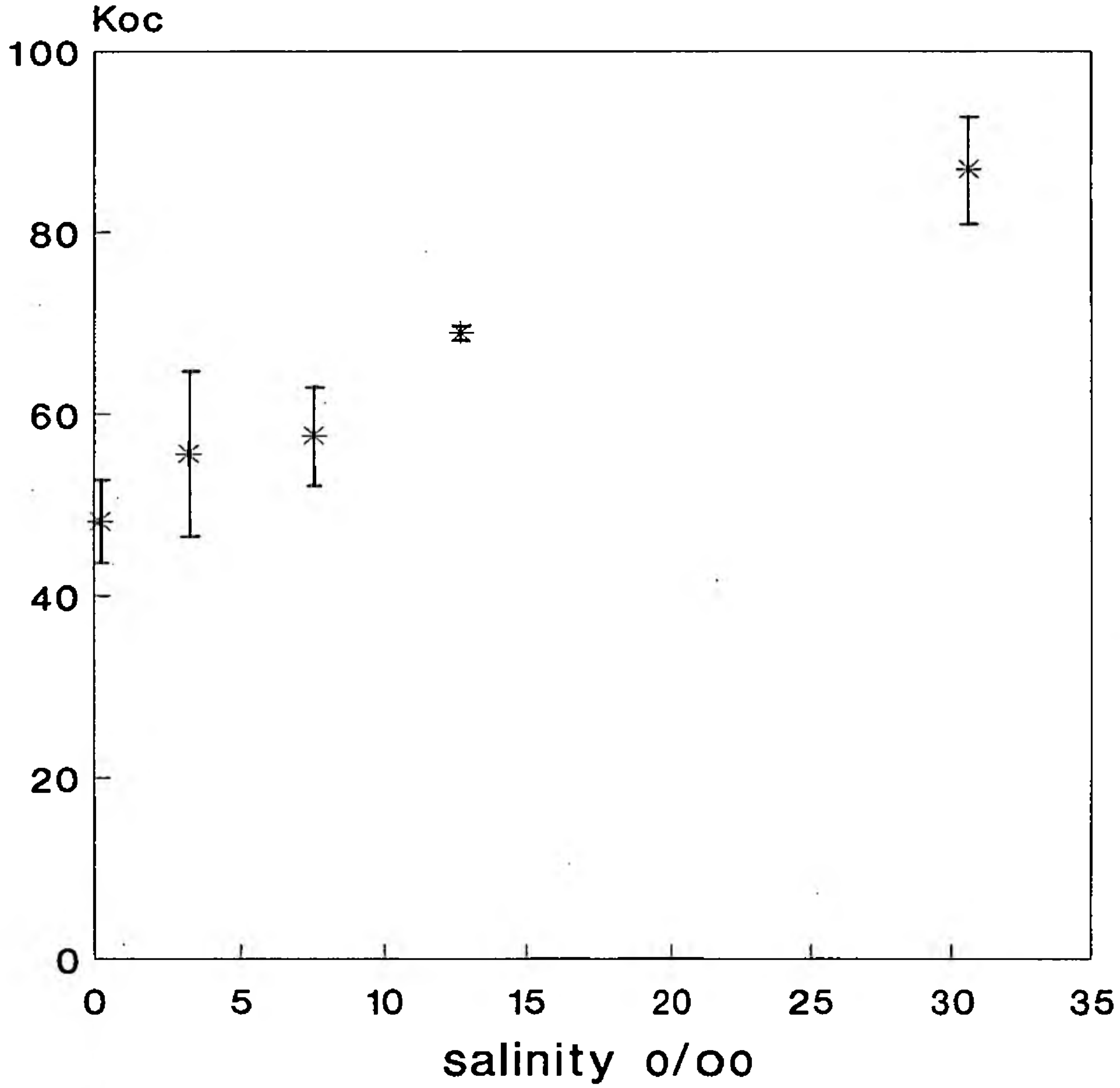


Figure 4.4. Plot of atrazine Koc vs salinity for Humber estuary 15.11.90

(elevated solids loading)

content of 5.01%. Dialysis experiments indicated that >99% of added atrazine was dialyzable 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. Wijayaratne 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 measurable binding with dissolved organics with molecular weights less than 1000, although the main association is with higher molecular weight fractions.

Table 4.7 Humber estuary partition coefficient data: atrazine elevated solids levels

Site	SSC $g\ l^{-1}$	K_p	K_{oc}	$\log K_{oc}$	S $^o/_{oo}$
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 4.8 Comparison of partition coefficients: atrazine

	log K_{oc}
Pereira and Rostad (1990)	2.0
Karickhoff (1981)	2.17
This work (high solids, 0-31 $^o/_{oo}$ sal.)	1.68-1.94

Gamma-hexachlorocyclohexane showed appreciable association with suspended particulates >0.45 µm and log K_{oc} values for the Humber and Mersey (Tables 4.9 and 4.10) were comparable to those previously reported in the literature (Karickhoff 1981).

Table 4.9 Humber estuary partition coefficient data: g-HCH

Site	SSC g l^{-1}	K_p	K_{oc}	logK_{oc}	S $^o/_{oo}$
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 did not appear to show a simple correlation with g-HCH K_{oc} in either the Humber or the Mersey (Figures 4.5 and 4.6). However, there was a correlation between K_{oc} and estuarine solids loadings in the Humber (Figure 4.7), although not in the Mersey (Figure 4.8). The same relationship was also observed in freshwater samples from the Thames that were enriched with bottom sediment (Figure 4.9), with a decrease in K_{oc} 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

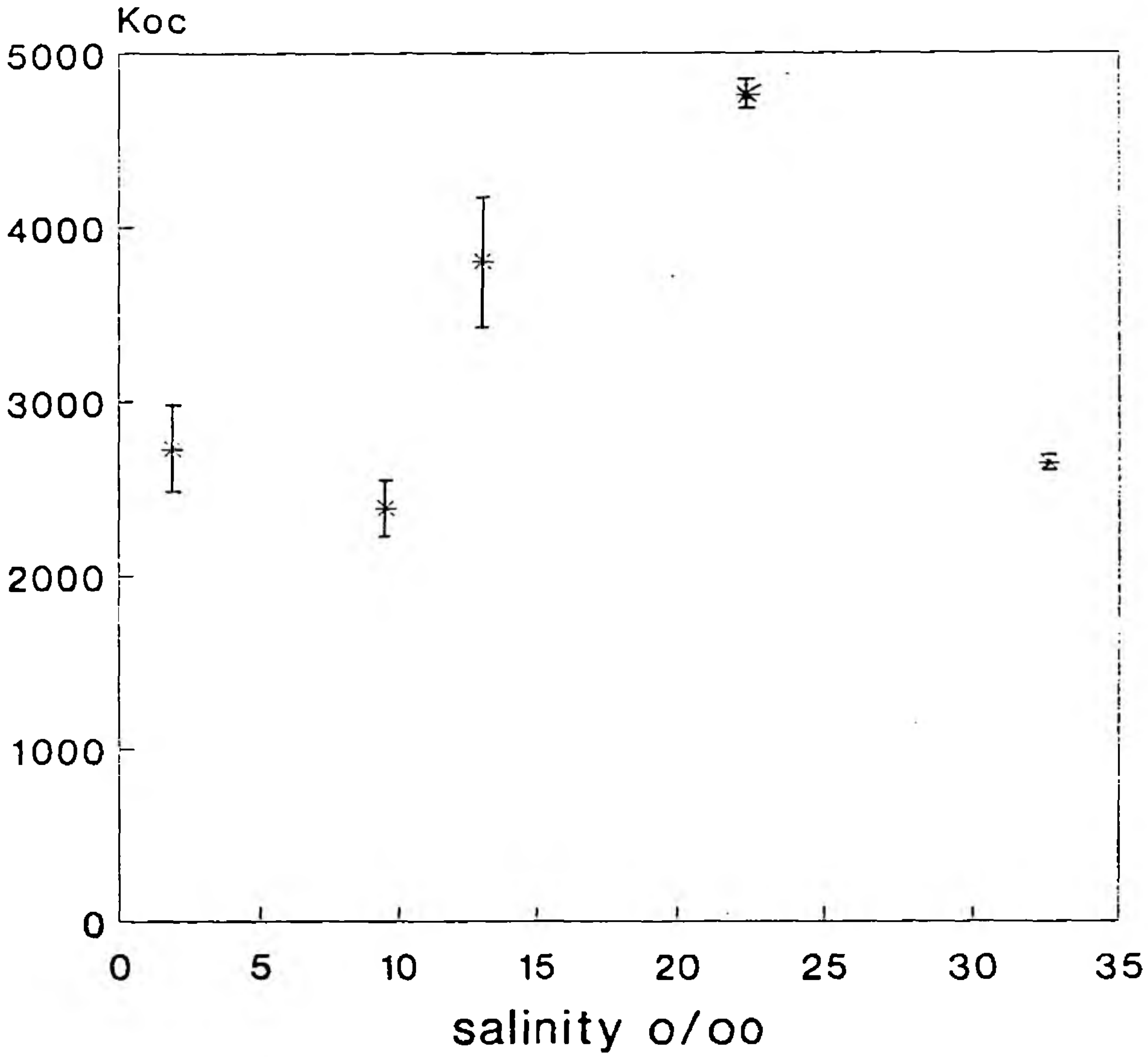


Figure 4.5. Plot of g-HCH Koc vs salinity for Humber estuary 22.4.91

natural solids loadings

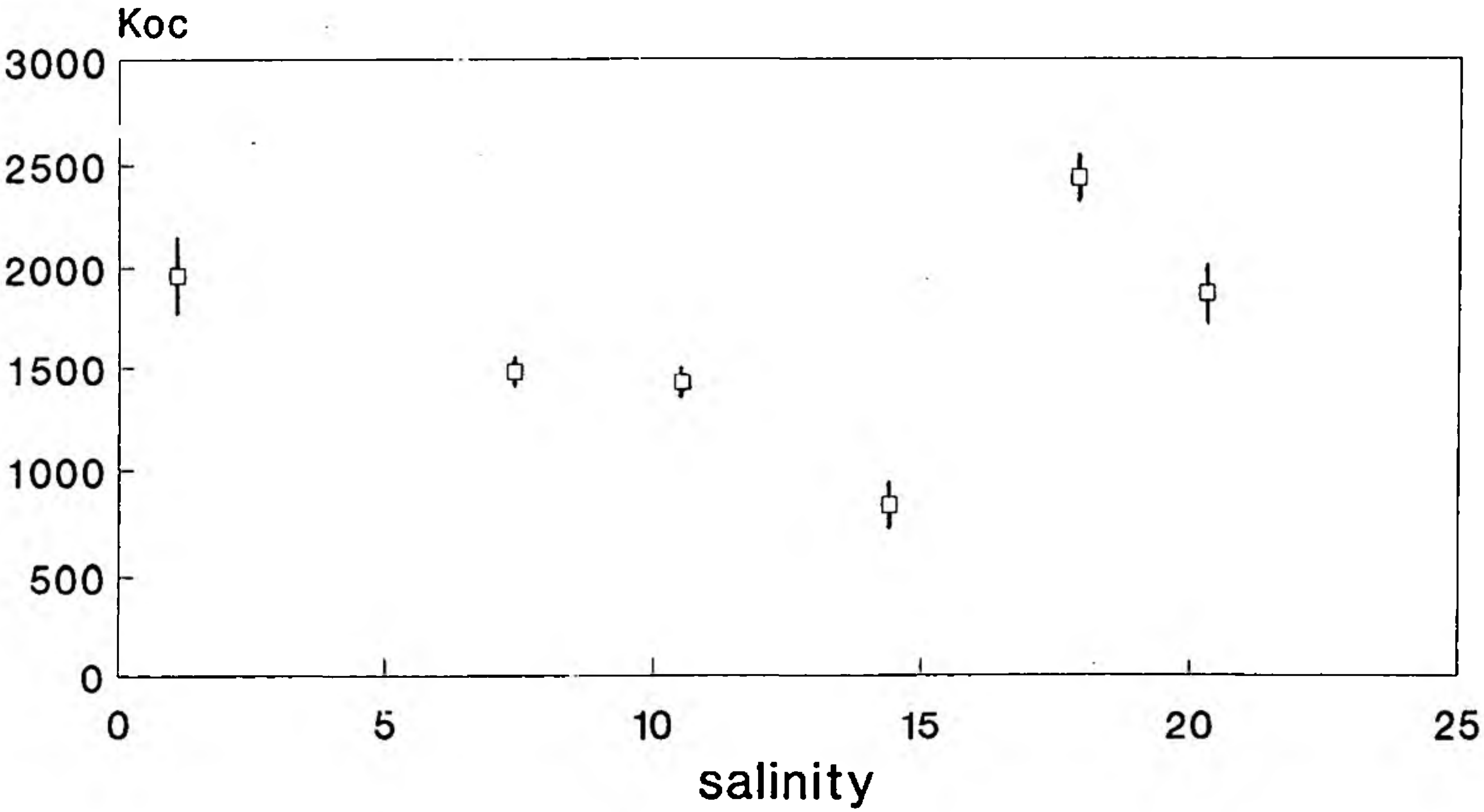


Figure 4.6. Plot of g-HCH Koc vs salinity for Mersey estuary 23.1.92

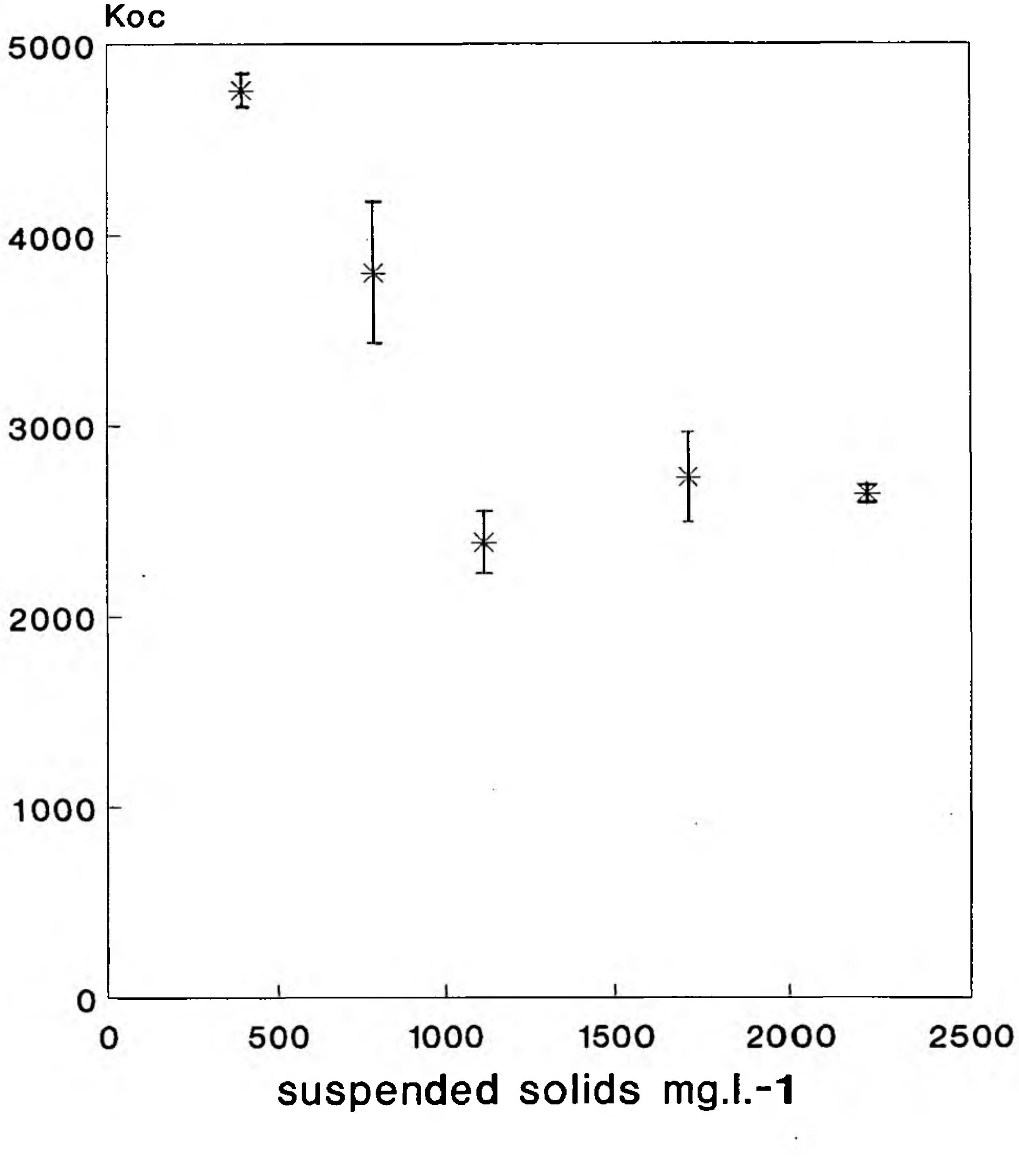


Figure 4.7. Plot of g-HCH Koc vs suspended solids conc. Humber estuary 22.4.91

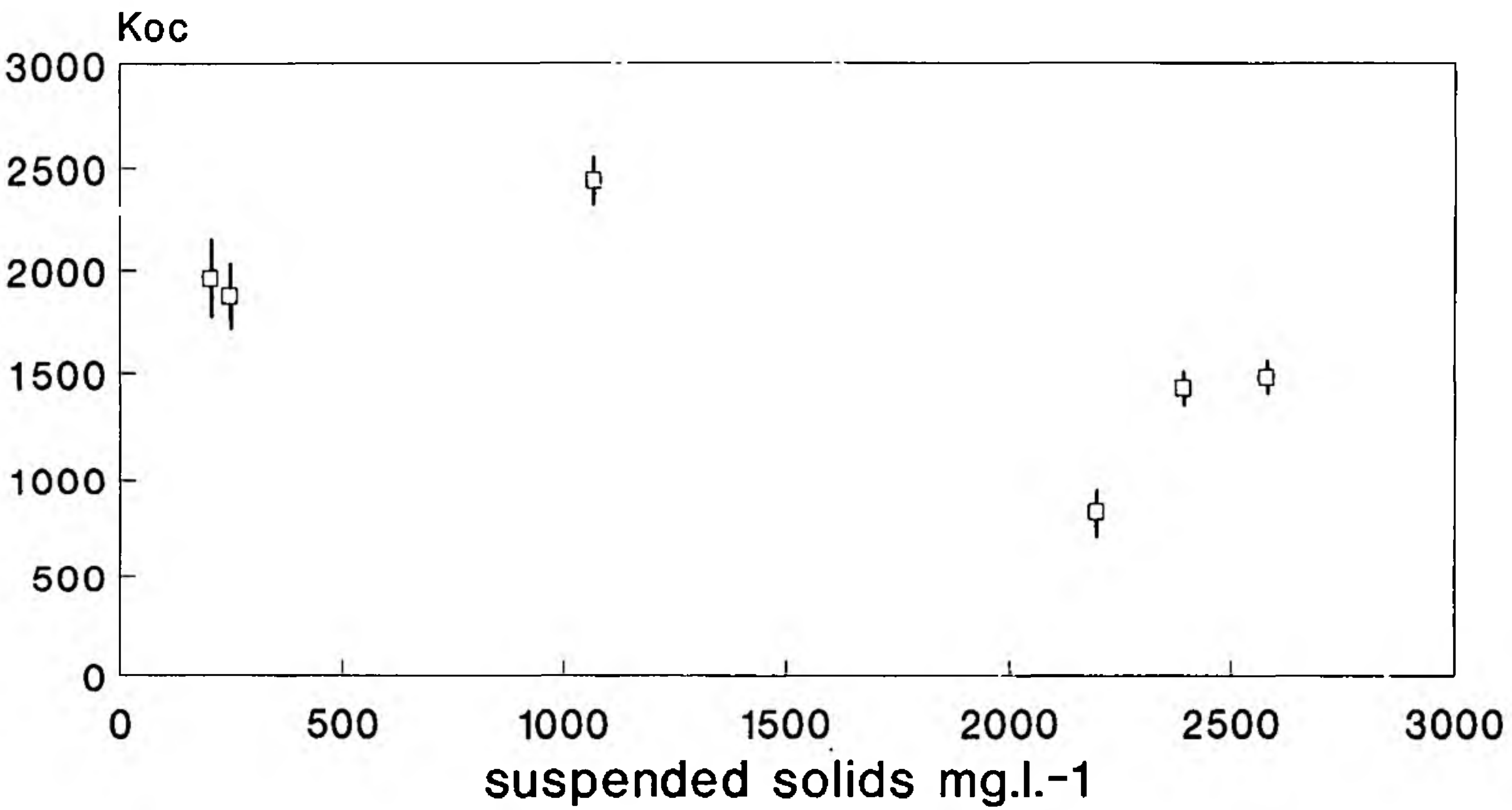


Figure 4.8. Plot of g-HCH Koc vs suspended solids conc. Mersey estuary 23.1.92

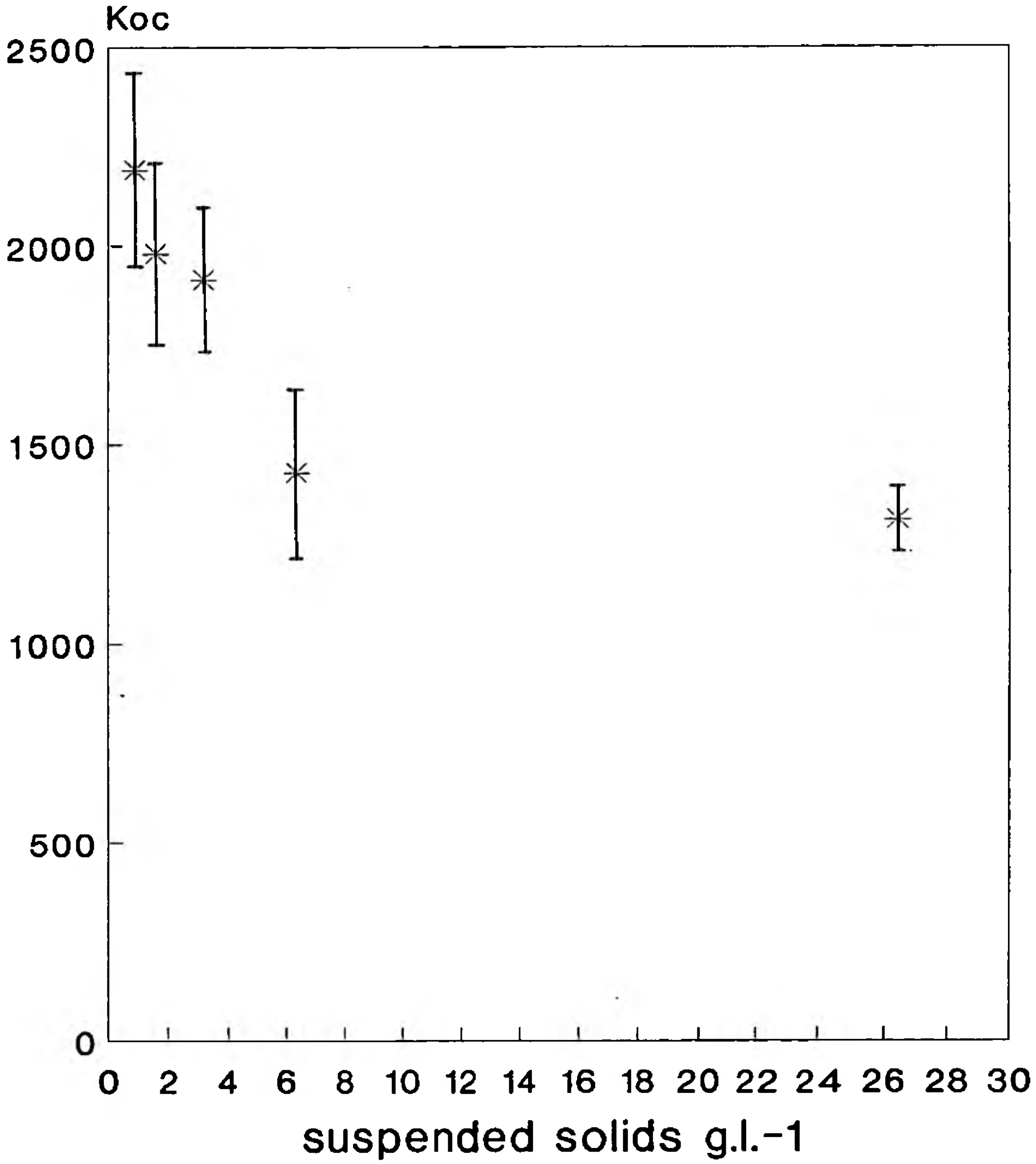


Figure 4.9. Plot of g-HCH Koc vs suspended solids conc.

River Thames 18.3.91 (elevated solids loading) solids loadings because of collision-induced desorption. Equilibrium dialysis indicated that in all experiments, greater than 90% of the g-HCH was dialyzable, suggesting that it was present in true solution or possibly associated with low molecular weight organics. The absence of any clear K_{oc} vs suspended solids relationship in the Mersey may have been due to instability in the samples caused by the presence of sewage.

Table 4.10 Mersey estuary partition coefficient data: g-HCH (23.1.92 survey samples)

Site	SSC g l^{-1}	K_p	K_{oc}	$\log K_{oc}$	S °/oo
Fiddlers Ferry 1	202	431	1959	3.29	1.1
Fiddlers Ferry 2	2578	101.6	1481	3.17	7.4
Fiddlers Ferry 3	2391	106.5	1428	3.15	10.5
Fiddlers Ferry 4	2194	49.1	830	2.92	14.4
Fiddlers Ferry 5	1064	189.1	2437	3.39	17.9
Widnes West Bank	244	218.8	1875	3.27	20.3

4.3.11 Kinetics of g-HCH sorption - experimental

Experiments were carried out to investigate the rate of attainment of sorption equilibrium for g-HCH in turbid estuarine water. Triplicate sub-samples (250 ml) from a bulk sample of Mersey estuary water collected from Fiddlers ferry (20.2.92; 285 mg l^{-1} suspended solids; 1.6 °/oo salinity) were spiked with ^{14}C-g-HCH at a level of 0.9 µg l^{-1} and mixed by shaking in darkness for periods from between 1 minute and 24 hours. After mixing samples were filtered through 0.45 um membrane filters and analysed. Unspiked samples mixed for the same period were used to prepare spiked calibration standards.

4.3.12 Kinetics of g-HCH sorption - results

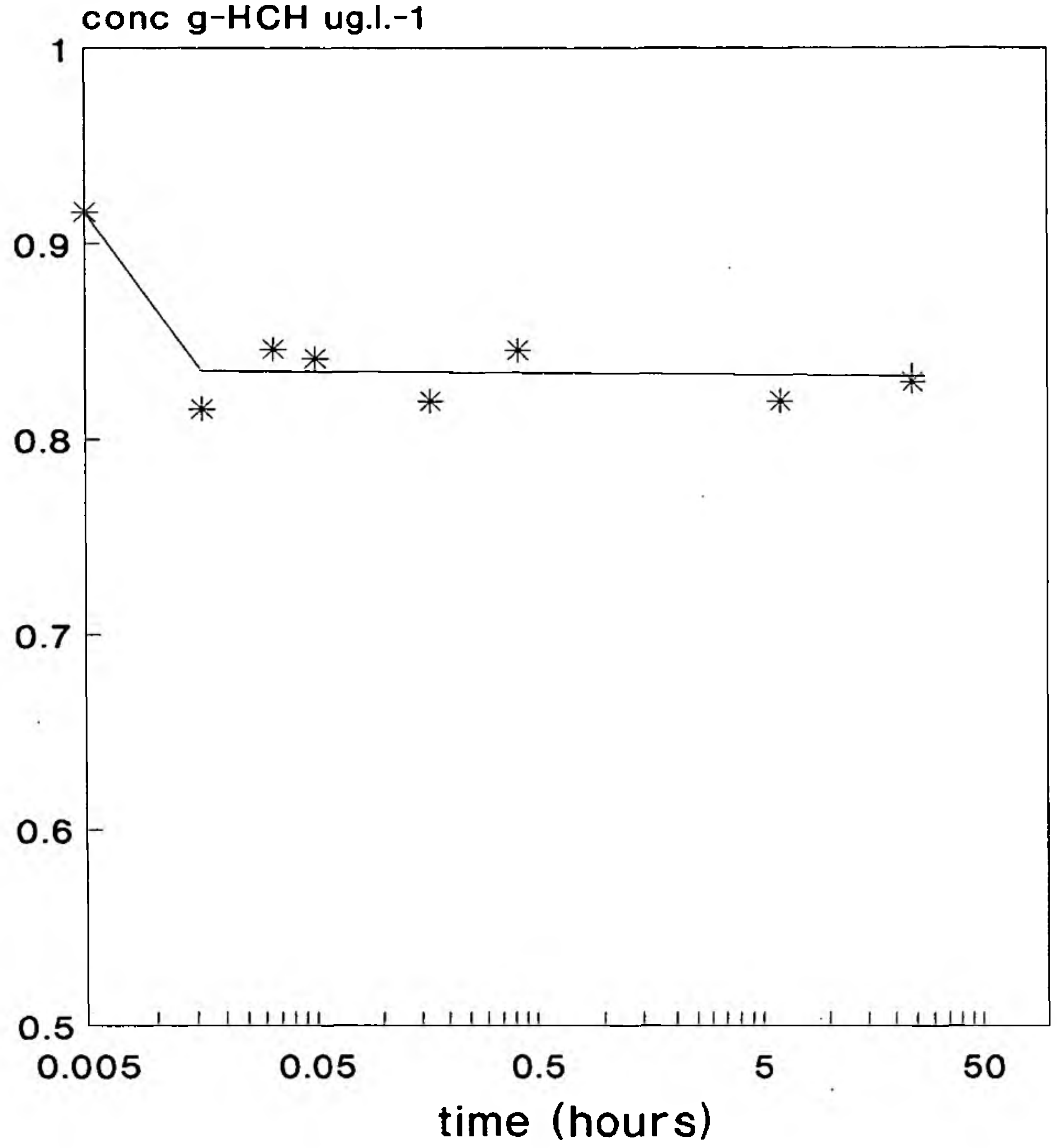
The results of the kinetics experiments carried out in Mersey estuary water are shown graphically in Figure 4.10. It appears that equilibrium is reached relatively quickly and certainly within the first couple of minutes of mixing. Over the 24 hour period of the experiments there was no further detectable shift in the equilibrium. It is likely that these relatively short term observations correspond to a rapid sorption of the g-HCH to the surfaces of particles. However, other workers have suggested that intra-particle diffusion of residues may occur in the longer term and thus render them less available for desorption (Karickhoff 1981). Intra-particle diffusion may occur over an extended period at a slow rate but was not detectable during the duration of our experiments.

4.4 Conclusions

The partitioning behaviour and speciation of atrazine and gamma-hexachlorocyclohexane (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.

Equilibrium dialysis indicated that the two compounds showed little affinity for natural colloids and that <0.45 µm 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 g l^{-1}) a negligible amount of atrazine sorbs to the particulate phases (>0.45 µm). Sorption was only observed at high solids concentrations (ca. 80 g l^{-1}) which were representative of the highly turbid zones close to the bed sediment/water interface. Under these conditions, the partition coefficient



Salinity 1.6 o/oo, Susp.solids 285 ppm

Figure 4.10. Kinetics of g-HCH sorption to Mersey estuary particulates

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 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 $^{o}/_{oo}$.

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 dialyzable fraction (<1000 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.

5. TRACE METAL PARTITIONING

5.1 Field and laboratory approaches to investigation of metal partitioning

Investigations of solid/solution phase partitioning of trace metals can be conducted by either field or laboratory based studies. Both approaches have their pros and cons.

Field measurements have the advantage that they are directly relevant to the setting for which the proposed model is intended to apply but obtaining samples over the entire range of expected conditions may in practice prove difficult. Furthermore, in many situations it is by no means certain that equilibrium will exist between solid and solution phases at the time of sampling. Should a post sampling equilibration period prove necessary then many of the benefits of the approach will be lost.

The main attraction of laboratory studies is that they readily permit determination of the effects of a wide range of pertinent variables in a controlled fashion. Unfortunately, discrepancies frequently occur when extrapolating the results of such studies to field situations. A problem with many of the investigations reported to date is that experimental conditions have been determined largely on the basis of the capabilities of inadequate analytical methodology. As a result, metals and/or particulate matter loadings have often been inappropriately high.

The difficulty of lack of sensitivity at the analytical stage has frequently been overcome in lab equilibration experiments by use of radio-isotopes. However, for certain priority contaminant metals either no isotope may be available, or none of sufficient activity. Copper is a prime example. For the present study conventional analytical methodology has therefore been applied to compare field and laboratory data. To this end a previously established micro-scale rapid extraction/ETAAS procedure for EQS compliance monitoring of metals in saline waters (Apte and Gunn 1987) has been modified to permit precise determination of the much lower metal levels commonly present in coastal waters.

Sample handling problems, including contamination and adsorption to filtration and/or storage vessels are common to both lab and field studies, and must be closely monitored. For laboratory experiments, microbial activity can provide a further complication. The importance of such activity has been investigated by (Jannasch *et al* 1988) by pretreating particulate matter with NaN_3.

A final but very important point to be addressed in any study is the means of separation of 'dissolved' and 'particulate' phases. Neither centrifugation nor filtration necessarily provide adequate discrimination and experimental artefacts in the form of an apparent particle concentration dependency of Kp can result. The conventional water industry procedure is base upon filtration to 0.4 µm or 0.45 µm and this cut-off has therefore been adopted for much of this study. Filtration to smaller size cut-offs (0.2 µm or less) may reduce but not necessarily eliminate phase separation artefacts. The extent to which they distort partitioning data can nevertheless still be monitored by careful experimental design.

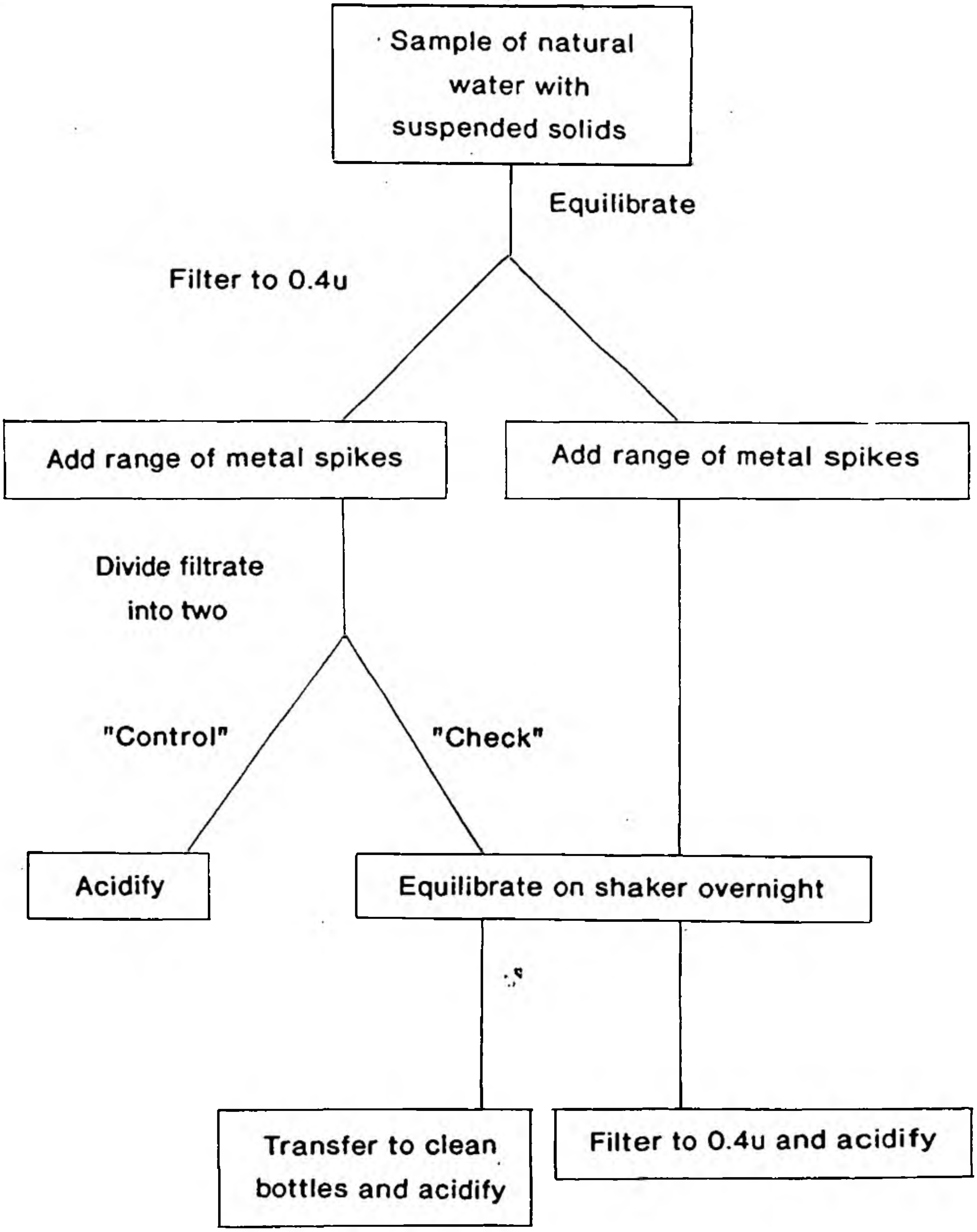
5.2 Experimental design and performance testing for laboratory adsorption tests

5.2.1 Experimental design

The majority of experiments on partitioning equilibria in the Humber used natural waters and suspended particulates from the system, subjected to as little pre-manipulation as possible. The aim generally was to establish adsorption isotherms under particular conditions of interest. General experimental features were similar, and are described here.

An outline of the procedure used is shown in Figure 5.1. All plastic equipment and containers were precleaned with 10% v/v HNO_3 and thoroughly rinsed with deionised water. A sample of the test natural water was equilibrated with natural suspended particulate matter for at least 48 hours. At the end of this time, aliquots of 50-250 ml, depending upon experiment, were transferred to polyethylene containers and spiked as appropriate with standard solution. At

Fig 5.1 Outline of experimental method



the same time, similar aliquots were filtered through acid-washed 0.4 µm Nuclepore membranes housed in Nuclepore polycarbonate pressure filtration units. These were then spiked and half of the solution was immediately acidified with 2 ml/l HNO_3 ('control'). The remainder ('check') was retained in similar containers to the spiked, unfiltered samples.

The spiked and 'check' samples were then put on an orbital shaker and allowed to equilibrate for the period of interest. The spiked samples were then filtered and acidified as above, while the 'check' samples were transferred to new bottles and acidified. The latter gave information as to the amount of metal adsorbed onto the walls of the bottles, which could be a source of significant losses.

Analysis was carried out using hydride generation for arsenic on a Perkin Elmer 603, and graphite furnace atomic absorption for cadmium, chromium, copper, lead and nickel on a Perkin Elmer 4000. Saline analyses were performed using methodology based on that described by Apte and Gunn (1987) for cadmium, copper, lead and nickel. Standard additions were made for the other determinations as required. Zinc was determined either by graphite furnace or flame atomic absorption on a Philips PU9200.

Plots showing the adsorbed metal (µg/kg) against that found in solution were then drawn up. Adsorbed metal was calculated according to the following:

$$M_{ads}(\mu g/kg) = \frac{S - (F-U)\ \mu g/l}{\text{mass of solids present kg/l}}$$

where S is spike concentration, F is the final metal concentration found in solution and U is the metal concentration in the unspiked sample.

The partition coefficient was taken from the gradient of the linear portion of the adsorption isotherm plot:

$$K_p = \frac{\text{Concn of adsorbed metal}\quad (\mu g/kg \text{ of particulate material})}{\text{Concn of dissolved metal } (\mu g/l \text{ of solution})}$$

5.2.2 Comparison of adsorption for single and mixed metal spikes

The aim here was to establish whether the addition of one metal as a spike, and its consequent adsorption, was affected by the presence of other spiked metals.

Competition between metals for sites on the solids might affect observed partition coefficients. However, the use of mixed spikes would greatly reduce the workload when performing sorption experiments.

Saline water from Hessle was taken. A spike was added to each set of seven bottles (500 ml samples), of either one metal or a mixed spike. Other experimental details were as described above.

The data generally did not show any significant difference between single and mixed metal spikes and this allowed the use of mixed spikes in later experiments. This approach is probably also more realistic when considering typical environmental conditions.

5.2.3 Reproducibility of adsorption data

This investigation was designed to find out how reproducible results from spiking experiments were. Six replicates of a series of mixed metal spikes into 200 ml samples from Blacktoft were performed. Two replicates at each spiking level were buffered to the natural sample pH (7.4) using the non-complexing biological buffer MOPS, in order to check whether possible pH changes during equilibration led to altered adsorption.

Significant differences between the buffered and non-buffered samples were not apparent, and these samples were therefore included in the statistical treatment of the data. Confidence intervals ($p=0.05$) were calculated for both the aqueous phase (2-sided) and the adsorbed phase (1-sided).

In general, the replicated data showed acceptable levels of variation. However, the experiment highlighted the need for replicate samples to be run during adsorption tests, to ensure that firm conclusions can be drawn.

Adsorption to the walls of the bottles was measured for the second spike. Table 5.1 shows percentage losses by this route. These changes occurred in a slightly saline sample (~5 ppt). Significant losses occurred in the case of chromium, copper and zinc. The occurrence of such losses is clearly an important consideration when interpreting laboratory adsorption experiments.

Table 5.1 Percentage losses by adsorption to walls of bottle during replicates experiment

Metal	% Loss during equilibration
As	2 ± 3.1
Cd	4 ± 0.4
Cr	32 ± 5.0
Cu	24 ± 4.3
Ni	3 ± 3.5
Zn	31 ± 5.7

5.3 Analytical quality control for field studies

Field blanks of deionised water filtered through acid-washed 0.4 µm polycarbonate membranes were routinely run at each sampling site. Example means and standard deviations for each metal for the September 1989 survey are given in Table 5.2.

Table 5.2 Field blank data

Metal	Mean concentration in field blank µg/l	Standard deviation µg/l
As	<lod - 0.2	-
Cd	<lod - 0.05	0.014
Cr	<lod - 0.1	0.05
Cu	<lod - 0.5	0.27
Ni	<lod - 0.5	0.09
Pb	<lod - 0.5	0.07
Zn	<lod - 2	0.69

Note: n=15

Variability of the field blank data was in no case greatly different from the within batch standard deviations of analytical blanks for the methods used for final analysis. Blank data are therefore satisfactory.

Field controls of saline and fresh waters were also run at several sites. A known water sample was spiked and immediately filtered in order to check for systematic error. Table 5.3 shows the percentage changes in concentrations found.

Table 5.3 Percentage change in field control concentrations (Whalley and Gardner 1990)

Metal	Percentage change in concentration Fresh water		Saline water	
	n		n	
As	5	-2.76 ± 2.90%	4	+1.60 ± 4.34
Cd	4	-3.37 ± 1.23	4	-6.65 ± 2.72
Cr	3	-10.37 ± 6.71	3	-17.46 ± 16.2
Cu		*	4	-2.26 ± 5.32
Ni	4	-4.57 ± 2.68	3	-0.35 ± 8.57
Pb	4	-4.50 ± 4.04	3	-27.5 ± 8.43
Zn	5	-7.44 ± 2.19	*	

These data suggest that in general there were no major problems in the filtering method, although there could be significant losses for chromium and lead. Those for lead in the seawater are thought to be because of the relatively high spike (4 µg/l) for this medium resulting in precipitation out of some of the metal. Those for chromium are thought to have been caused by adsorption to the filter, and represent an unavoidable source of error in the procedures used.

The results of replicate filtrations and analyses made of the Victoria Pier sample are given in Table 5.4, along with their 2-sided confidence intervals (p=0.05).

From these data, the standard deviation upon the mean only exceeded 5% for Cd (5.9%), Cr (7.1%) and Zn (7.1%). For the latter two cases this can be explained by proximity of the determinand concentrations to the LOD of the final analytical methods. Thus, procedures used in filtration and analysis are of an acceptable level of reproducibility.

Table 5.4 Precision-testing of filtration and analysis using water from Victoria Pier

Metal	n	Mean µg/l	Standard deviation µg/l	Confidence interval (p=0.05) µg/l
As	5	5.5	0.04	± 0.05
Cd	5	0.35	0.02	± 0.259
Cr	4	0.27	0.02	± 0.14
Cu	4	4.6	0.15	± 0.25
Ni	5	7.2	0.22	± 0.33
Pb	5	<lod		
Zn	5	5.0	0.36	± 0.44

5.4 Influence of suspended particulate concentration on partitioning equilibria

The aim here has been to assess the effect of different solids concentrations on the uptake of spiked metal (see Section 3.2 for discussion of the particle concentration effect). Two main tests have been carried out.

In the first, a portion of water sample from Selby with a very high natural suspended particulate concentration was filtered. The filtrate was then used to dilute unfiltered samples, so that three solids levels were obtained (undiluted, a 7 times and 50 times dilution). In determining adsorption isotherms at these very different solids loadings, the levels of metal spikes added were varied according to the mass of solids present. This was necessary because it has been found that as a general rule in partitioning measurement, there is a very narrow experimental window of spiking concentrations which will result both in accurately determinable changes in dissolved and particulate phase concentrations, and in sorption within the linear portion of the isotherm.

Samples (200 ml) were equilibrated in 250 ml bottles overnight. The measured solids levels were:

S1	5298 mg/l
S2	756 mg/l
S3	85 mg/l

Experimental partition coefficients are shown in Table 5.4 and are comparable to those found at Selby during the 1989 Humber survey. They show the trend S3>S2>S1; i.e. there is a greater tendency for the metals to go on to the solid phase at low solids levels.

Table 5.5 Laboratory partition coefficients for different suspended solids loadings

Sample	K_p			
	Arsenic	Copper	Nickel	Zinc
S1	2.5×10^2	1.3×10^4	1.0×10^3	7.0×10^3
S2	3.7×10^2	2.9×10^4	1.5×10^3	1.5×10^4
S3	2.1×10^3	1.1×10^5	4.4×10^3	1.7×10^4

The existence of such a particle concentration effect is of course of great importance if partition coefficients are to be used for estuarine modelling purposes where solids loadings can vary widely. However, the magnitude of the effect is lower than has been found in some earlier studies; it also varies in extent for the different metals.

One possibility which had to be examined was whether the relationship between solids and Kp was merely an artefact of adsorption to vessels during equilibration. This can be proportionately larger for the smaller spikes used in low solids samples. However, of the elements for which Kp data were obtained here, only copper exhibited marked differences in percentage sorption losses for the different spiking levels. This increased from 9% loss of the mid-spike (1500 µg/l) for the high solids run to 21% loss on 210 µg/l at mid solids and 33% loss on 30 µg/l at low solids. Despite this complication, recalculation of K_p values after applying appropriate corrections for sorption to vessel walls did not result in any major differences in the extent to which these varied with particulate concentration.

The possibility that the use of 0.4 μ membranes for phase separation had contributed to the observed effects was looked at also by filtering aliquots of selected test samples through 0.1 μ and 0.015 μ Nuclepore membranes. If non-separable particulate matter and/or dissolved phase ligands were the main cause of observed K_p variations, then the concentration of such species would have to be greater with greater particulate concentration. The present test has been carefully designed to minimise the likelihood of this occurrence, but colloid aggregation/desegregation and ligand sorption processes during preparation of the test samples cannot be completely ruled out.

Blank corrected data for dissolved phase metal concentrations through the different pore size membranes are shown in Table 5.6.

Table 5.6 Comparison of solution concentrations found with different filter sizes

Unspiked			Low spike			Mid-spike		High spike	
	A	B	A	B	C	A	B	A	B
Cd	0.00	0.03	0.98	0.64	0.63	5.92	5.53	8.40	8.27
Cu	5.6	5.7	12.5	15.7	10.9	27.4	18.7	42.0	33.6
Ni	4.5	4.2	*	*	*	879	950	1540	1520
Zn	2.9	2.1	17.2	20.6	*	49.9	66.6	161	197

Notes: A = concentration found in 0.4 μ filtered solution
B = concentration found in 0.1 μ filtered solution
C = concentration found in 0.015 μ filtered solution

In the majority of cases no important differences were observed. However for copper, which exhibited the largest variation in K_p values, there appeared to be greater retention of the mid and high spikes by the 0.1 μ membrane than at 0.4 μ (the high result for the low spike at 0.1 μ may be the result of contamination during handling). There is also a slight indication of differences in cadmium retention for the different pore sizes, particularly at the low spike level.

A second test involved assessment of the effect of solids concentration on the kinetics of trace metal partitioning. Full details of experimental procedures are given later in Section 5.9. However, in brief, the time dependence of partition coefficients was first determined for trace metals spiked into a Blacktoft sample with suspended solids concentration amended to 160 mg/l (prepared by dilution of the base sample with prefiltered sample). This data was then used to predict partitioning behaviour for unamended sample which had a natural suspended particulate loading of 1000 mg/l.

The partitioning experiment was then repeated for the high solids sample. Results are shown in Figure 5.2, along with predicted behaviour based on the observed partitioning at 160 mg/l solids level. Once again, there was some evidence for a lower tendency for metals to partition to the solid phase at the higher particulate loading. The trend was clearest for cadmium and arsenic, but negligible for copper.

To conclude, these investigations have shown some evidence for a 'particle concentration effect' for Humber system suspended solids. This is important in relation to environmental modelling. However, the effect is not as large as been indicated in earlier work.

5.5 Investigation of effect of natural organic ligands on partitioning equilibria

In the course of the project it became clear 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

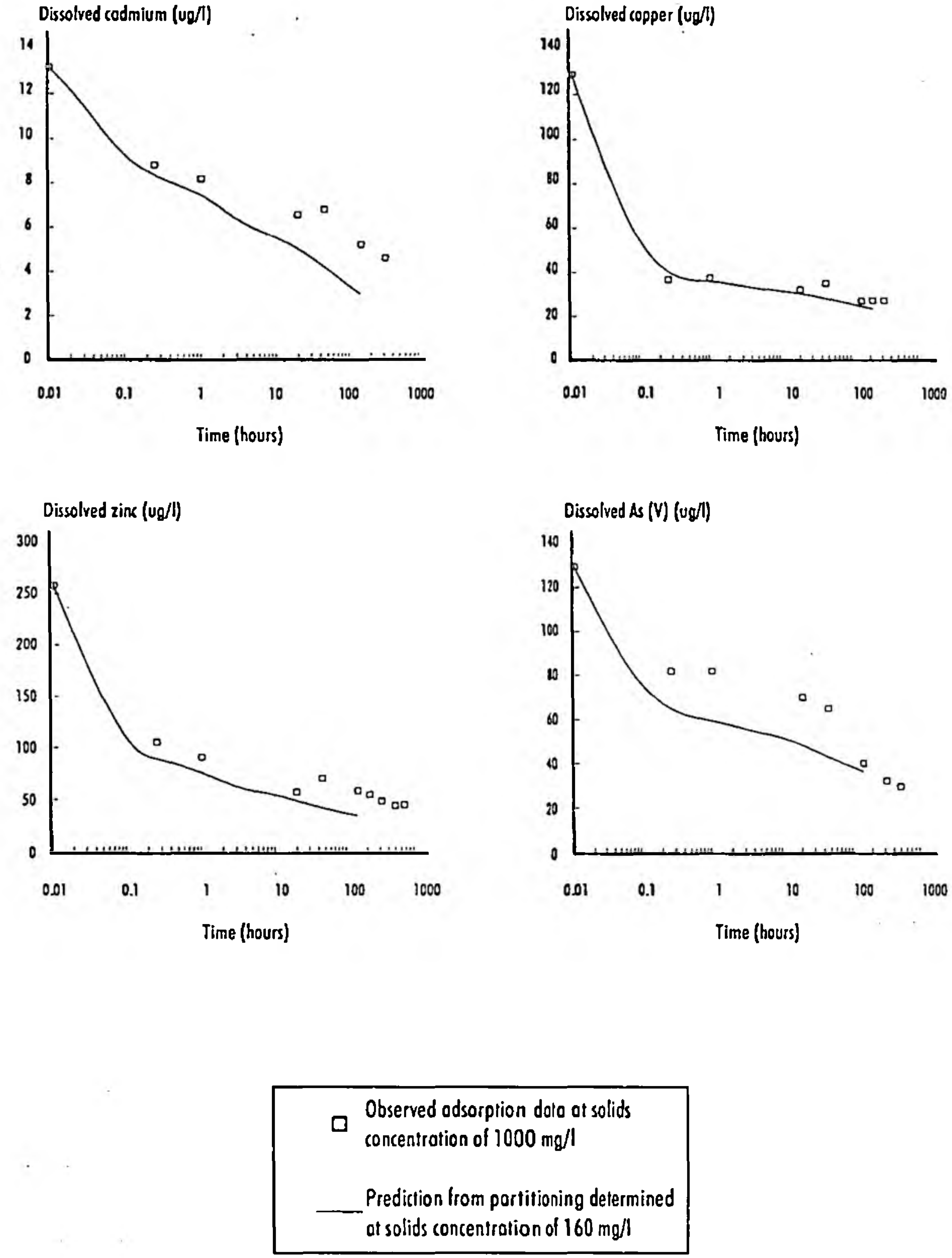


Figure 5.2 Effect of suspended solids concentration on trace metal partitioning kinetics

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.

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

5.5.1 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 µm, 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.

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 5.5.2 below.

5.5.2 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 5.1) 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^{-1}. 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 5.3a-d. The dashed line (1:1) is included to provide a marker of zero adsorption (i.e. if all the metal added had remained in solution).

Fig 5.3a Cadmium adsorption onto mcc

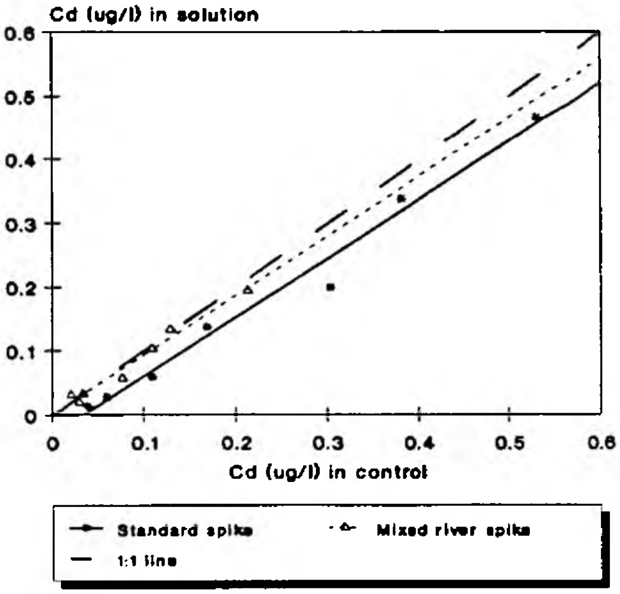


Fig 5.3b Chromium adsorption onto mcc

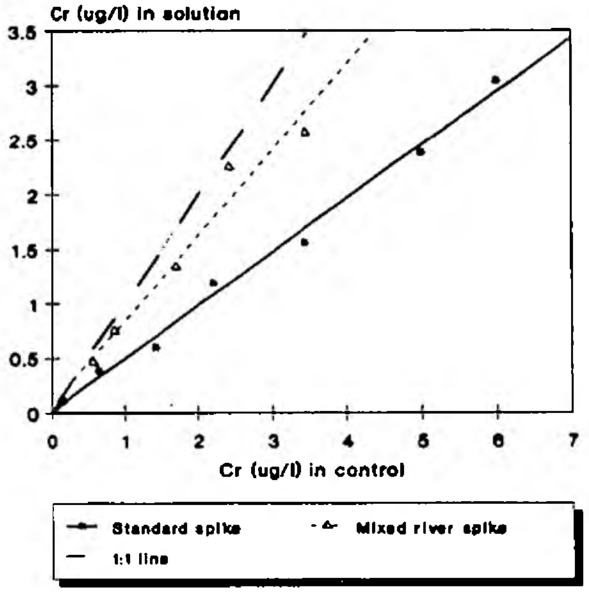


Fig 5.3c Copper adsorption onto mcc

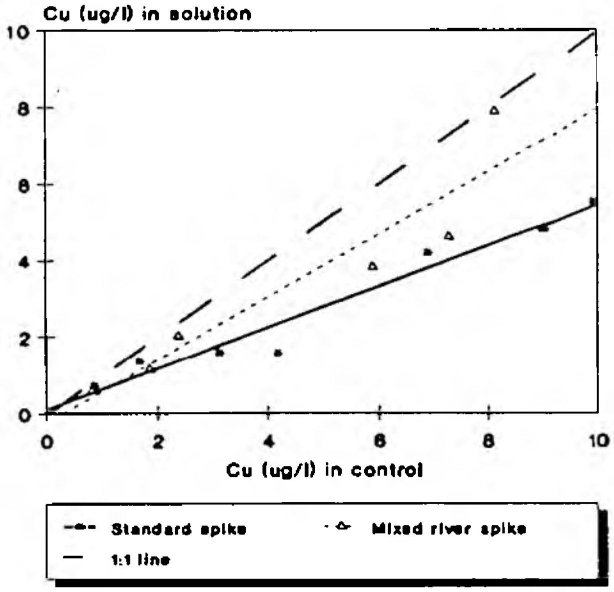
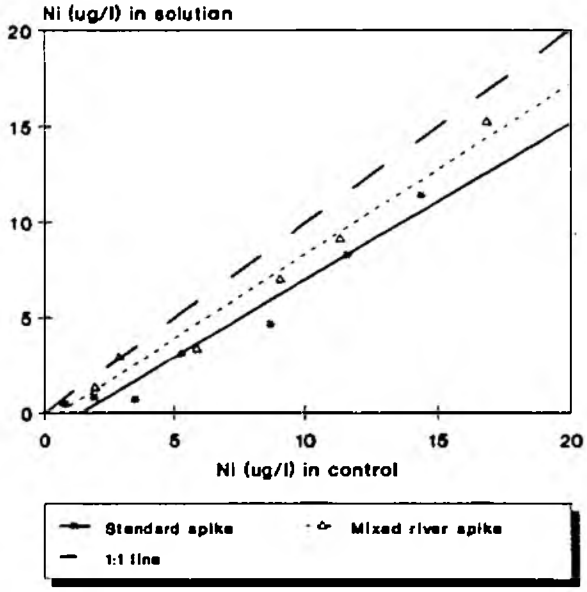


Fig 5.3d Nickel adsorption onto mcc



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 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.

5.5.3 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:

- o a filtered sample (S);
- o an UV-irradiated (UV) sample; and
- o 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 5.4a-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

Fig 5.4a Effect of UV/Chelex treatments on Cr adsorption

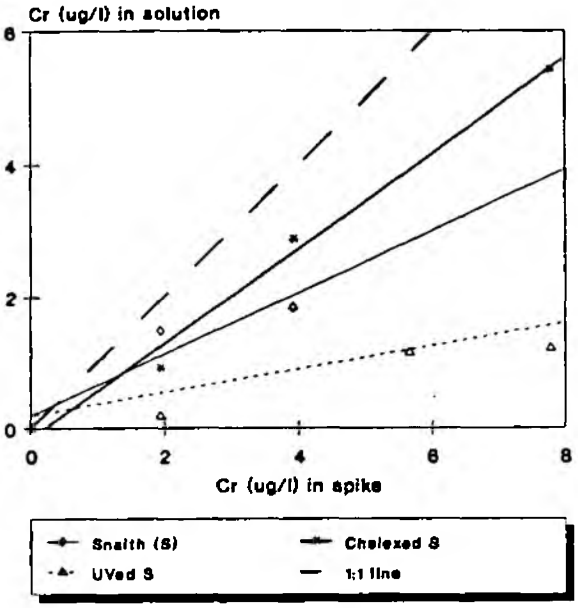


Fig 5.4b Effect of UV/Chelex treatments on Cu adsorption

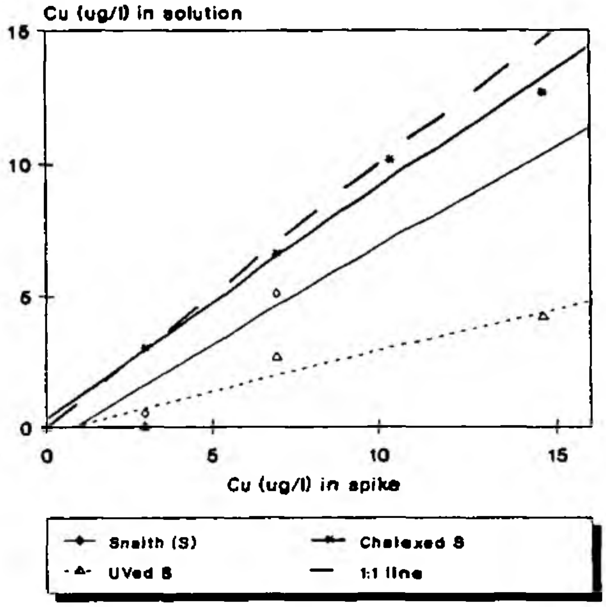
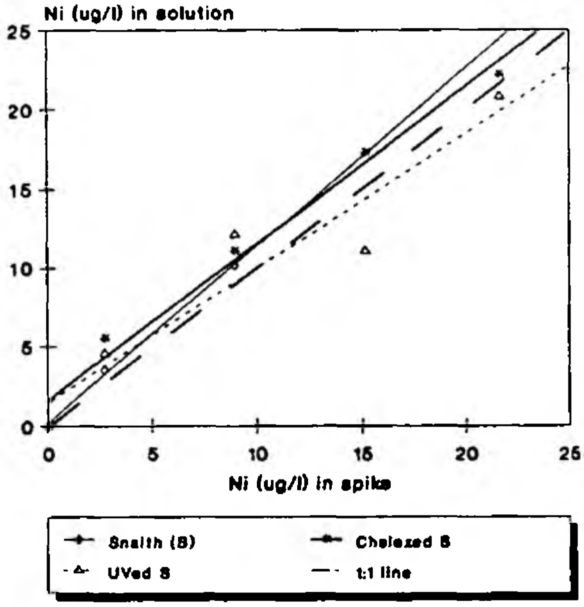


Fig 5.4c Effect of UV/Chelex treatments on Ni adsorption



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_ps generally found for nickel.

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.

5.6 The Humber system

5.6.1 Survey characteristics

An approach involving concentration of studies primarily on a single large river/estuary system (the Humber) has been adopted. The Humber system was selected for a variety of reasons. Primarily, it represents a system with widely differing inputs. These range from the almost unpolluted River Derwent, to rivers such as the Trent, Ouse, Aire and Don, which pass through large industrial, as well as agricultural areas. Associated sewage and industrial waste inputs create one of the more polluted UK estuaries.

The chemistry of the region where saline water meets fresh water is characterised by a variety of interactions. Increasing pH can cause precipitation of some metals, and higher concentrations of major ions create greater competition for surface sites. Meanwhile, altered redox states affect solution/solid equilibria, and flocculation and desegregation processes work concurrently (Burton 1976). The presence of both point and diffuse source inputs into the estuary complicate the situation further.

In the course of the project two intensive field surveys of the Humber system were carried out in September 1989 and April 1991. These studies used two teams to sample water from both saline and freshwater sites during a single tidal cycle, in order to look at the *in situ* partitioning of trace metals. A further survey covering the saline reaches and the freshwater Ouse only, was undertaken in October 1991.

Locations of sampling sites employed in the three surveys are shown in Figure 4.2. Measured characteristics of water sampled at each of the sites are listed in Tables 5.7 to 5.9.

Table 5.7 Characteristics of water sampled during 6 September 1989 Humber survey

Site/ River	Distance from Trent Falls km	pH	Salinity ppt	Conductivity µS	Solids mg/l
Trent @	-65	7.5	-	11012	*
Derwent	-50	7.8	-	572	3
Selby (Ouse)	-40	7.2	-	670	5560
Aire	-35	7.1	-	1105	7
Boothferry (Ouse)	-20	7.2	3.2	-	2860
Blacktoft	-3	7.2	6.3	-	2800
Brough	10	7.6	15.1	-	393
Brough @	10	7.6	13.6	-	98
Humber Bridge	18	7.6	19.8	-	227
Victoria Pier	25	7.5	23.8	-	356
Spurn Point	60	7.9	32.3	-	44

Note: @ = water sampled on 7/9/89. Data is shown on graphs below for information.

Table 5.8 - Characteristics of water sampled during 22 April 1991 Humber survey

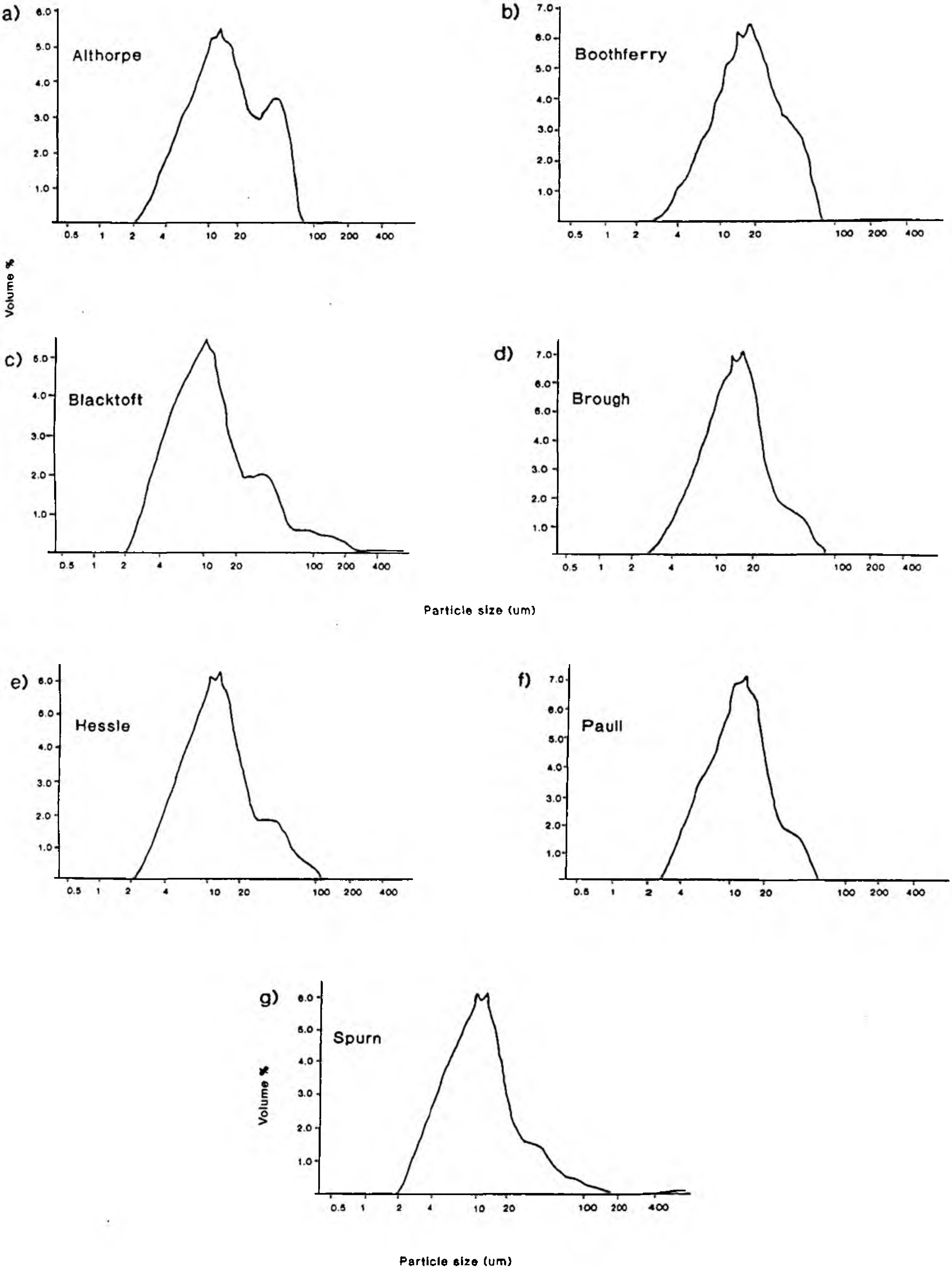
Site/ River	pH	Temp °C	Salinity ppt	DOC mg/l	POC %	Suspended solids mg/l
Althorpe (Trent)	8.1	9.6	-	8.62	-	314
Boothferry (Ouse)	7.8	8.6	-	5.96	-	156
Selby (Ouse)	8.0	9.1	-	10.36	-	23
Snaith (Aire)	7.5	9.9	-	7.25	-	14
Stainforth (Don)	7.5	9.6	-	4.85	-	18
Blacktoft	7.1	8.3	1.9	5.41	8.0	1590
Brough	7.4	9.0	9.0	9.56	10.9	876
Hessle	7.4	8.9	13.0	4.12	8.8	1751
Paull	7.8	8.6	22.5	3.29	9.4	680
Spurn	8.1	11.5	32.6	2.84	9.0	6400

Table 5.9 Characteristics of water sampled during 2 October 1991 Humber survey

Site	Salinity ppt	Suspended solids mg/l
Boothferry	0.8	412
Blacktoft	9.0	992
Hessle	23.3	303
Paull	24.6	123
Spurn	33.4	564

Figure 5.5a-g shows 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 µm), 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 µm range. Larger particles were present to a small extent at Blacktoft and Spurn, as shown by Figures 5.5 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

Fig 5.5 Particle size of suspended solids collected along the Humber system



proportion of sand in this sample. The small range of particle diameters suggests that adsorption differences caused by surface area variations were of low significance during the survey - a useful observation in modelling terms if this behaviour proves consistent.

5.6.2 Aqueous phase profiles

Ranges of dissolved phase metal concentrations in freshwater samples are summarised in Table 5.10, which shows maximum and minimum levels found for the September 1989 and April 1991 surveys. In general, the freshwater data showed similar behaviour, except for higher values of arsenic at Dunham and nickel at Selby (1989), and zinc at Snaith (1991). 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.

Table 5.10 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

Notes:

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

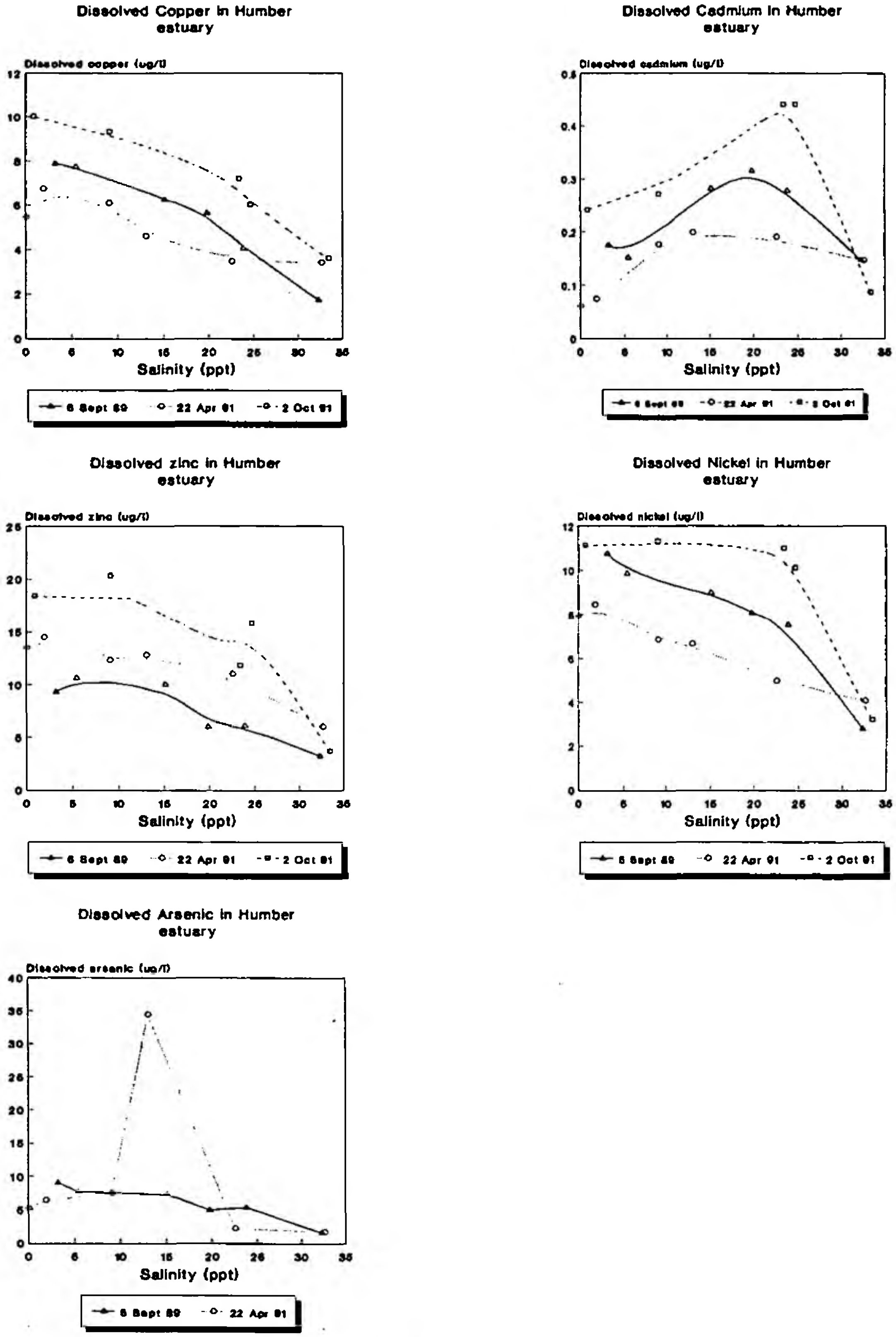
Aqueous data for saline Ouse/Humber samples, and the freshwater Ouse end-member, are shown plotted against salinity in Figure 5.6. Patterns of behaviour for the different metals proved very similar on all occasions. Saline end-member concentrations at Spurn Point showed little variation, while differences in freshwater concentrations (Boothferry bridge) could be explained by variations in metal discharge and/or freshwater flow.

The only marked discrepancy between profiles was observed for arsenic on the September 1989 and April 1991 surveys. In the former case, levels essentially followed a conservative dilution line, falling from 9.1 to 1.6 µg/l. For the 1991 survey most concentrations were within this range. However, a sharp peak of 34.4 µg/l was found for the Hessle sample. This can be explained in terms of the sample catching the effluent plume of a metal refinery near Brough, which is known to be a major discharger of arsenic.

Positive deviations from conservative behaviour were also observed for nickel, particularly for the October 1991 survey. Although release from suspended particulates during estuarine mixing could contribute to this, laboratory studies carried out within this project indicated that dynamic particulate sorption processes are considerably less significant for nickel than for other elements under study. The effect can therefore more readily be explained in terms of influx of nickel from the Trent and from direct discharges to the Humber.

For all three surveys, copper demonstrated similar behaviour, with only very slight (positive) deviations from conservative dilution. Such deviations were more pronounced for zinc and partitioning data indicates that desorption from solids transported from rivers with high zinc loadings (Trent and Aire) may partly explain this.

Cadmium consistently exhibited broad peaks in aqueous concentrations within the estuary. Diffuse discharges and input from the Trent may contribute to this but desorption from particulate matter as a consequence of dissolved phase chloro-complexation should also be considered as a factor. This effect is discussed in more detail in Section 5.6.5.



Dissolved Copper in Humber estuary

Dissolved Cadmium in Humber estuary

Dissolved zinc in Humber estuary

Dissolved Nickel in Humber estuary

Dissolved Arsenic in Humber estuary

Figure 5.6 Dissolved phase metal vs salinity profiles for Humber estuary

5.6.3 Effect of sample storage time prior to phase separation

At each of the sites, four filtrations of the collected water sample were made - two at the time of collection (to), one after five hours (t5) and one after twenty-four hours (t24). The sample at Blacktoft was filtered at t0, t24 and t36. The aim of sub-sampling over a time period was to determine whether partitioning between solid and aqueous phases altered significantly. This is of importance both to establish the extent of partitioning equilibria *in situ* and in finding out the short term stability of samples from field experiments.

Table 5.11 shows how metal concentrations varied at three sites of varying salinity. Comparison of the two samples collected at t0 shows that reproducibility was generally good.

From these results, it may be taken that changes in aqueous concentrations arising from interactions between the solid and dissolved phases in the collected sample were generally of low significance. Thus it would appear that partitioning closely approaches equilibrium *in situ* over wide reaches of the river/estuary system. Relative stability was maintained even in samples for which a large increase in dissolved oxygen content occurred during storage (e.g. from ~1 mg l^{-1} to ~8 mg l^{-1} for both Selby and Boothferry). On the other hand, a few important changes were observed. For instance, the sample taken at Brough on the day after the main survey showed an initial high dissolved phase chromium content of 0.85 µg l^{-1} which then dropped to a level (0.32 µg l^{-1}) much more akin to those prevalent throughout the estuary on the previous day. One possibility is that when taken, the sample contained recently discharged dissolved phase chromium which then very rapidly equilibrated with the associated particulates - laboratory experiments have shown Humber solids to have a very high affinity for this metal.

Overall, the relative stability of dissolved metal concentrations with respect to storage time is an important finding in terms of partitioning processes in the Humber system. It should not, however, be taken as a general indication that filtration of samples can be delayed until transported to the laboratory. For example, in a similar storage test on a low salinity sample from the Mersey Estuary we have observed dramatic release of copper from particulates over a very short timespan. Changes in lead and zinc levels have also been observed for Mersey samples.

Table 5.11 Effect of storage time on dissolved phase data for October 1989 Humber Survey
Data from samples taken 6/9/89 unless stated

SITE	TIME	AQUEOUS METAL CONCENTRATION (ug/l) As	Cd	Cr	Cu	Pb	Ni	Zn
Trent 7/9/89	t0	4.9	0.16	1.27	5.0	0.5	37.0	17.9
	t0	4.8	0.18	1.20	5.6	0.9	32.8	17.6
	t5	5.0	0.18	0.76	5.1	0.8	36.5	18.1
	t24	5.0	0.23	1.21	6.2	0.9	35.3	19.2
Derwent	t0	0.6	0.03	0.18	0.7	<lod	1.4	<lod
	t0	0.6	0.04	0.29	1.1	<lod	1.3	<lod
	t5	0.6	0.01	*	0.7	<lod	1.0	0.5
	t24	0.5	0.03	0.26	0.7	<lod	1.0	<lod
Selby	t0	9.5	0.04	0.28	4.6	0.1	8.5	2.5
	t0	9.7	0.05	0.34	5.1	0.3	7.6	3.2
	t5	9.7	0.05	0.31	4.4	0.1	6.9	1.6
	t24	9.7	0.05	0.32	5.0	0.1	6.6	2.7
Aire	t0	9.6	0.11	6.47	8.2	<lod	17.3	16.6
	t0	9.9	0.12	7.10	9.4	<lod	17.7	16.4
	t5	9.8	0.11	*	8.8	<lod	17.3	15.6
	t24	9.7	0.12	5.00	8.4	<lod	16.7	15.1
Boothferry	t0	9.1	0.18	*	7.9	<lod	10.7	*
	t5	9.1	0.13	0.52	7.7	<lod	10.8	3.3
	t24	9.0	0.13	0.52	8.0	<lod	10.2	3.2
Blacktoft	t0	7.8	0.16	0.30	7.6	<lod	9.9	9.1
	t0	7.6	0.14	0.35	7.6	<lod	9.9	12.2
	t24	9.1	0.14	0.32	7.7	<lod	9.1	9.7
	t36	9.1	0.14	0.32	8.0	<lod	8.6	7.7
Brough	t0	7.9	0.28	*	6.0	<lod	9.0	11.3
	t0	6.7	0.29	*	6.6	<lod	9.5	8.8
Brough 7/9/89	t0	7.7	0.21	0.93	4.5	<lod	8.0	9.5
	t0	7.9	0.22	0.77	5.0	<lod	8.9	9.1
	t5	8.4	0.22	0.32	5.2	<lod	8.6	8.6
	t24	8.5	0.26	*	6.1	<lod	8.7	8.0
Humber Bridge	t0	4.9	0.33	0.22	5.2	<lod	7.9	5.5
	t0	5.0	0.30	0.25	6.1	<lod	8.3	6.5
	t5	5.3	0.32	0.29	5.3	<lod	10.0	5.5
	t24	5.3	0.33	0.24	5.2	<lod	7.6	5.6
Victoria Pier	t0	5.4	0.26	0.24	4.1	<lod	7.4	6.9
	t0	5.4	0.29	0.26	4.0	<lod	7.7	5.4
	t5	5.6	*	0.20	4.4	<lod	7.6	4.3
	t24	5.7	0.33	0.22	4.4	<lod	7.5	4.7
Spurn Point	t0	1.6	0.14	0.17	1.8	<lod	2.7	3.0
	t0	1.5	0.15	0.18	1.7	<lod	2.8	3.5
	t5	1.7	0.13	0.20	1.7	<lod	2.9	1.9
	t24	1.6	0.15	0.18	1.6	<lod	3.0	1.3

5.6.4 Sequential extraction of suspended particulates

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 April 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 (e.g. <200 mg l^{-1} 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 pH 6, shaken for 3 hours.
2. **Carbonate** - 1M sodium acetate pH 5 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 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.

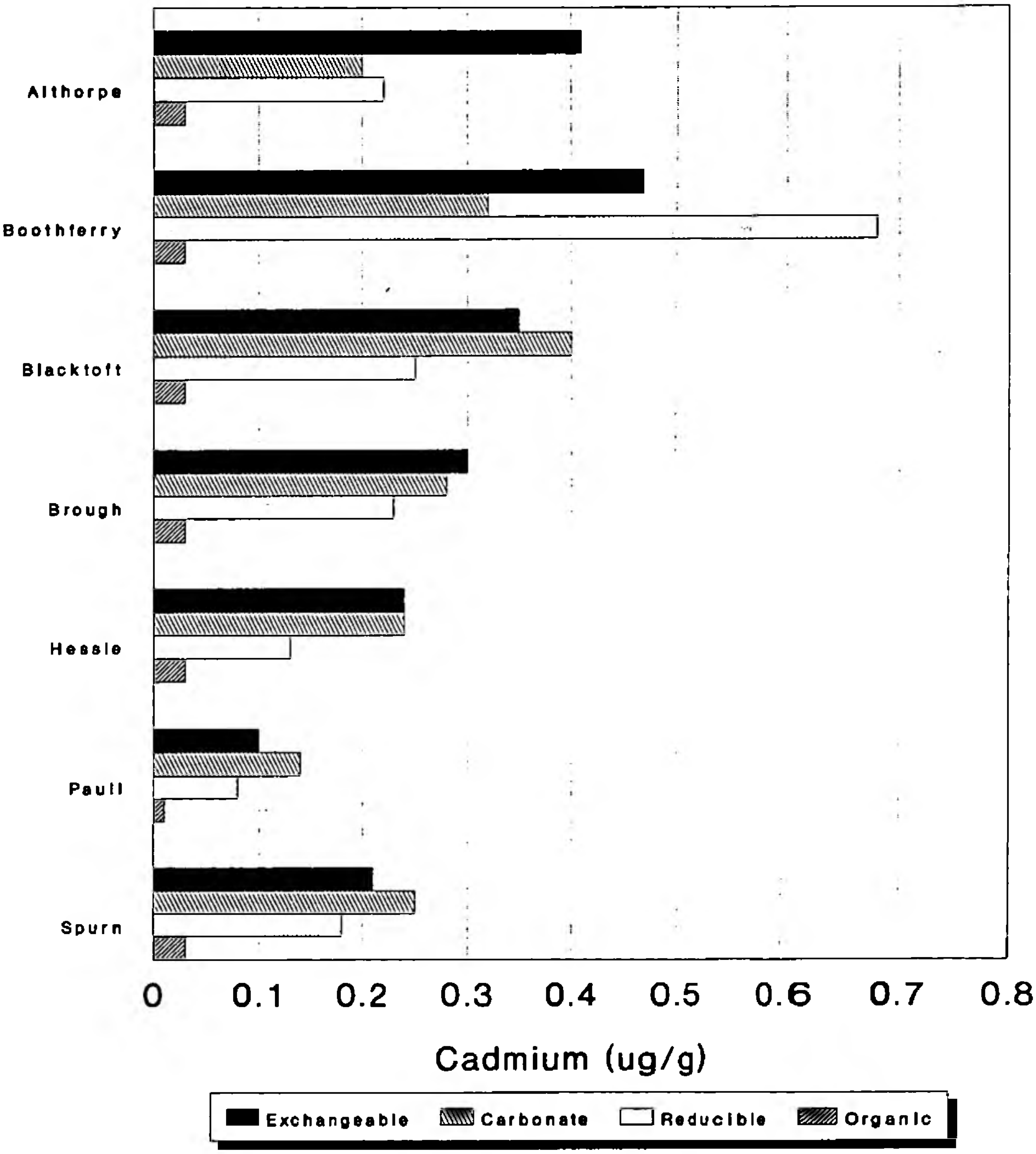
Results

See Figures 5.7a-f for histograms of metal speciation by site as determined by the above procedure. 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.

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).

Fig 5.7a Cadmium speciation in Humber suspended sediments



Residual cadmium below detection limit

Fig 5.7b Chromium speciation in Humber suspended sediments

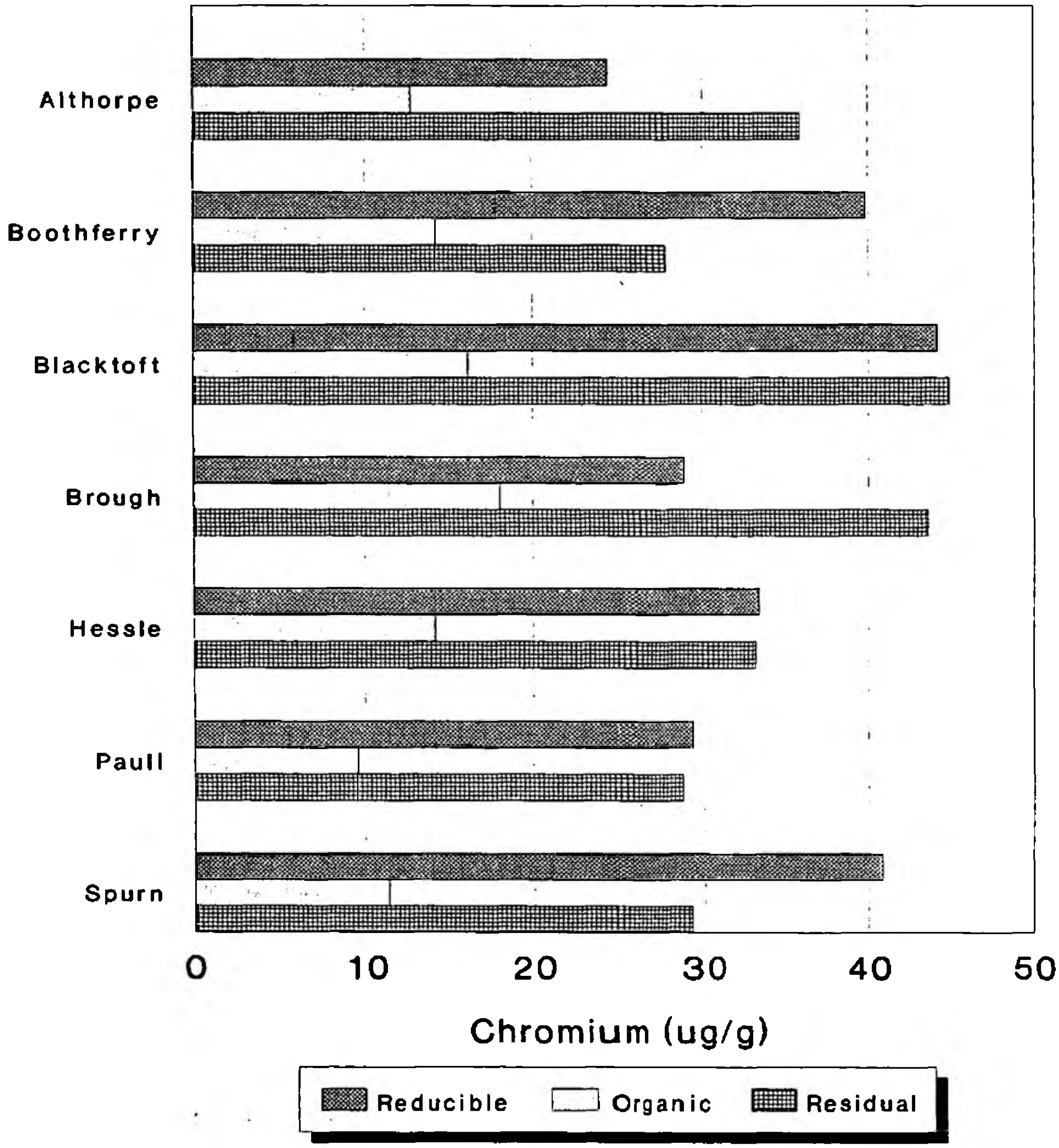


Fig 5.7c Copper speciation in Humber suspended sediments

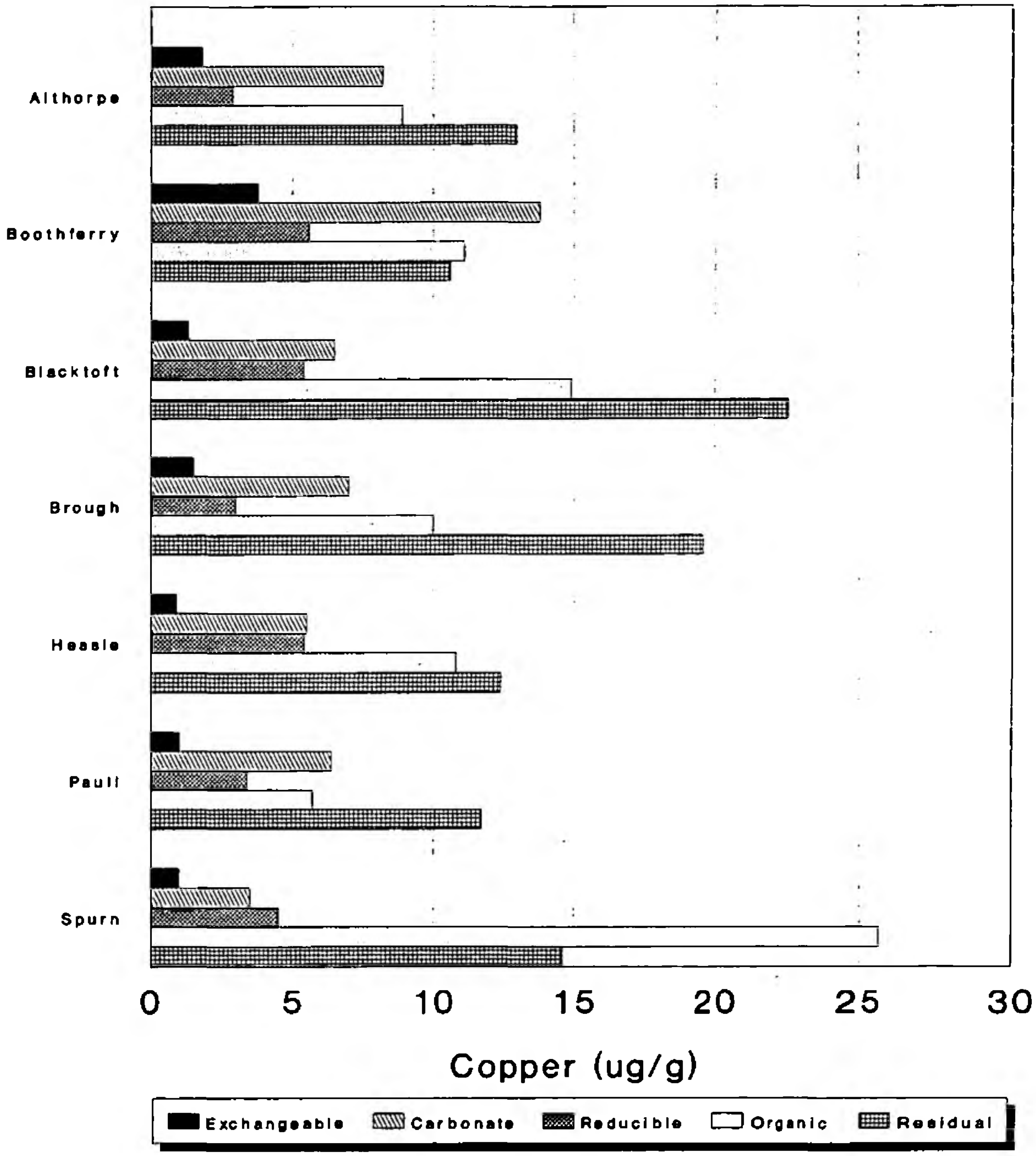


Fig 5.7d Lead speciation in Humber suspended sediments

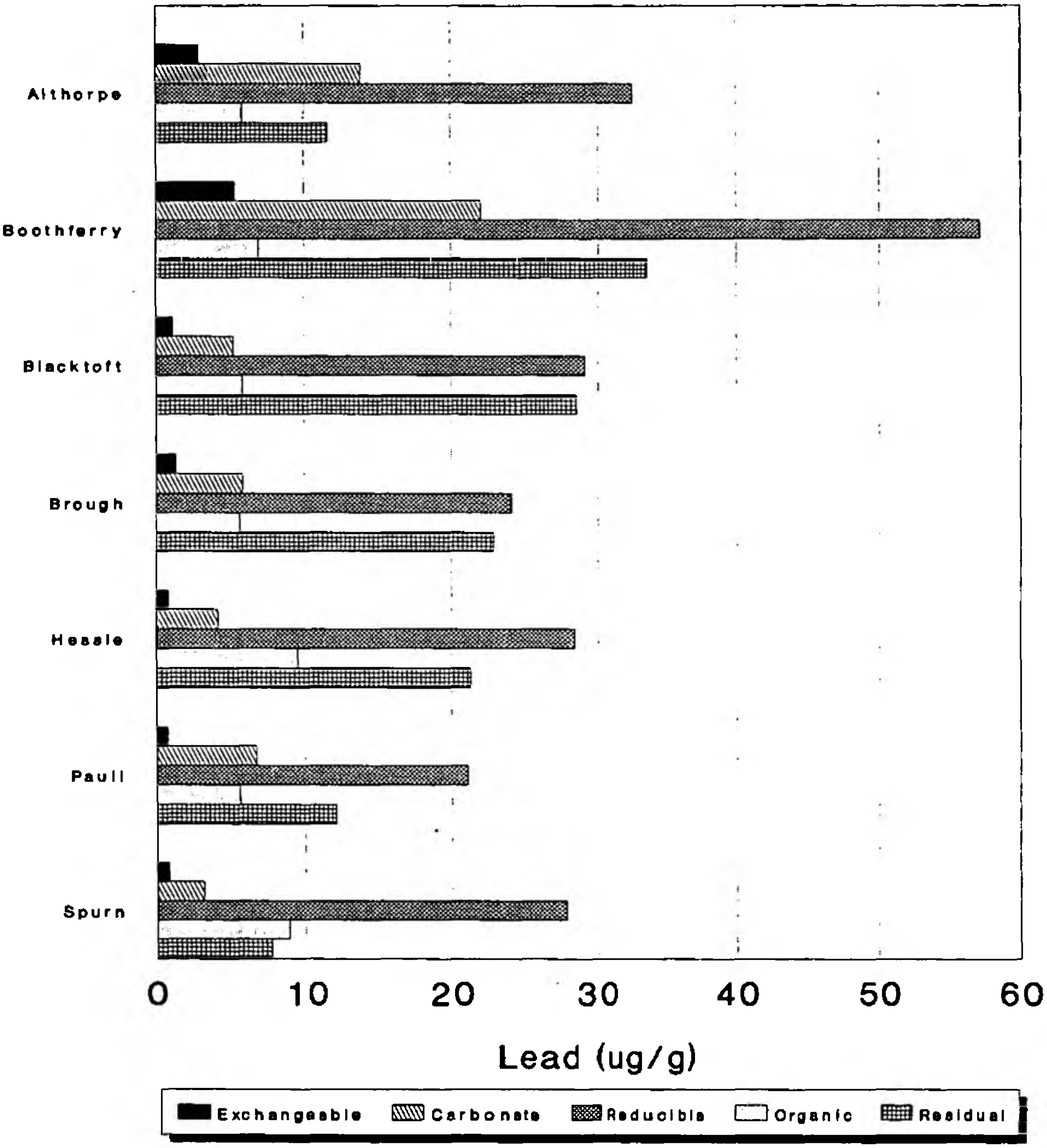
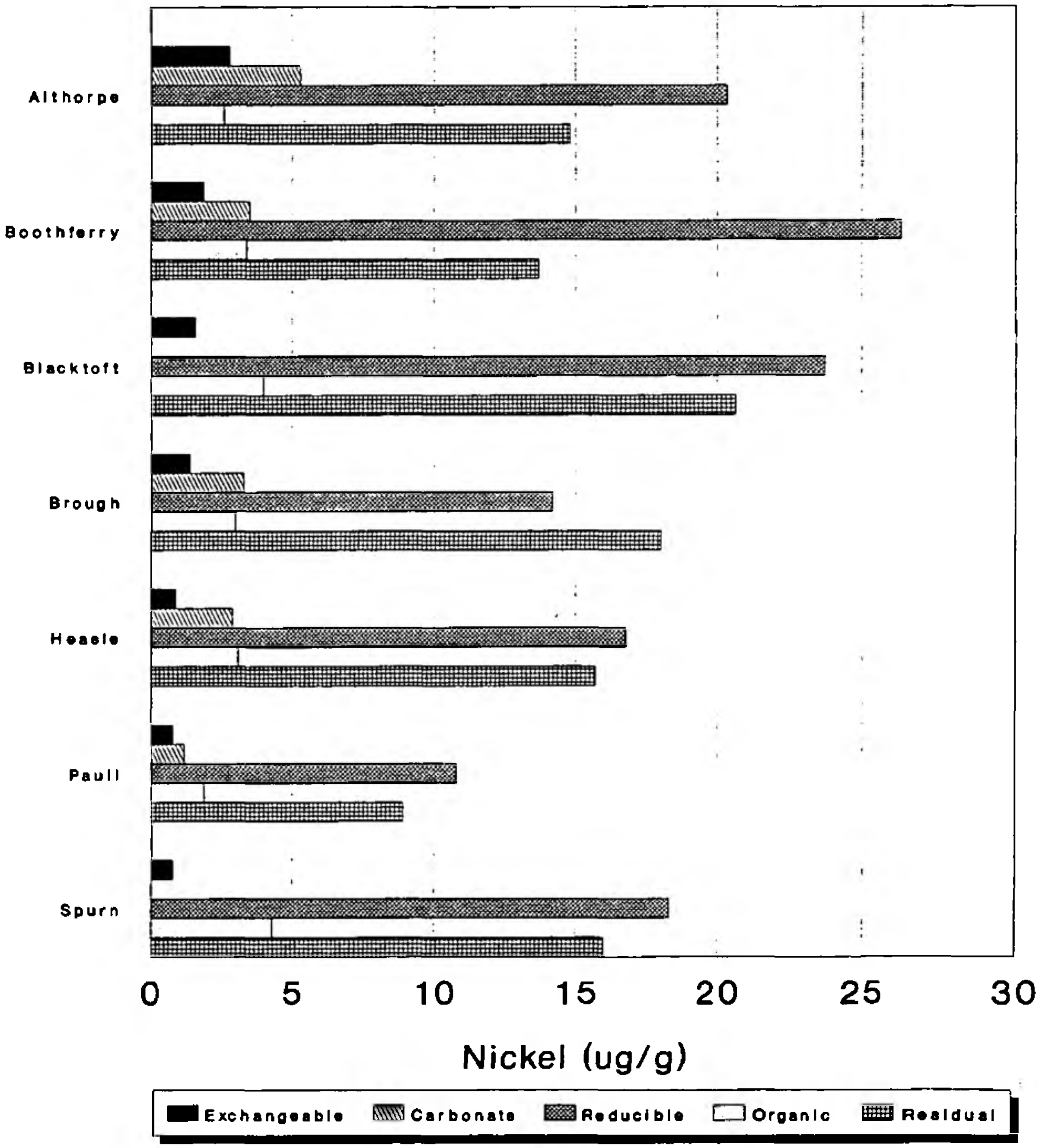
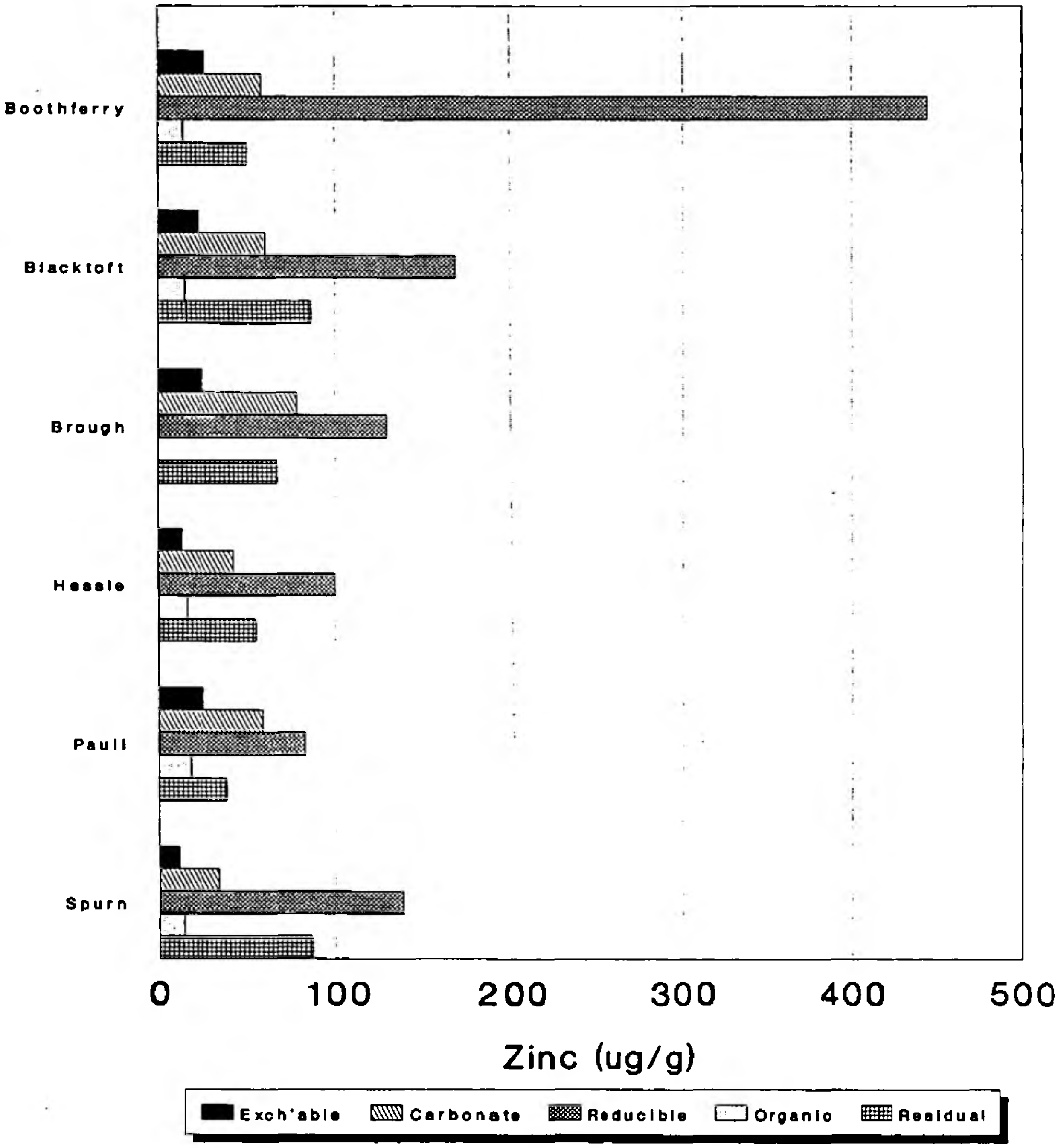


Fig 5.7e Nickel speciation
in Humber suspended sediments



Carbonate data for Blacktoft and Spurn not yet available

Fig 5.7f Zinc speciation in Humber suspended sediments



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 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.

Zinc - For all samples examined, the reducible phase proved dominant. This feature was most prominent for the Boothferry sample collected at the freshwater/saline interface, which suggests co-precipitation of zinc on flocculating iron oxyhydroxides.

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 e.g. benthic organisms may take up remobilized 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.

5.6.5 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 5.8.

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 5.9, 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.

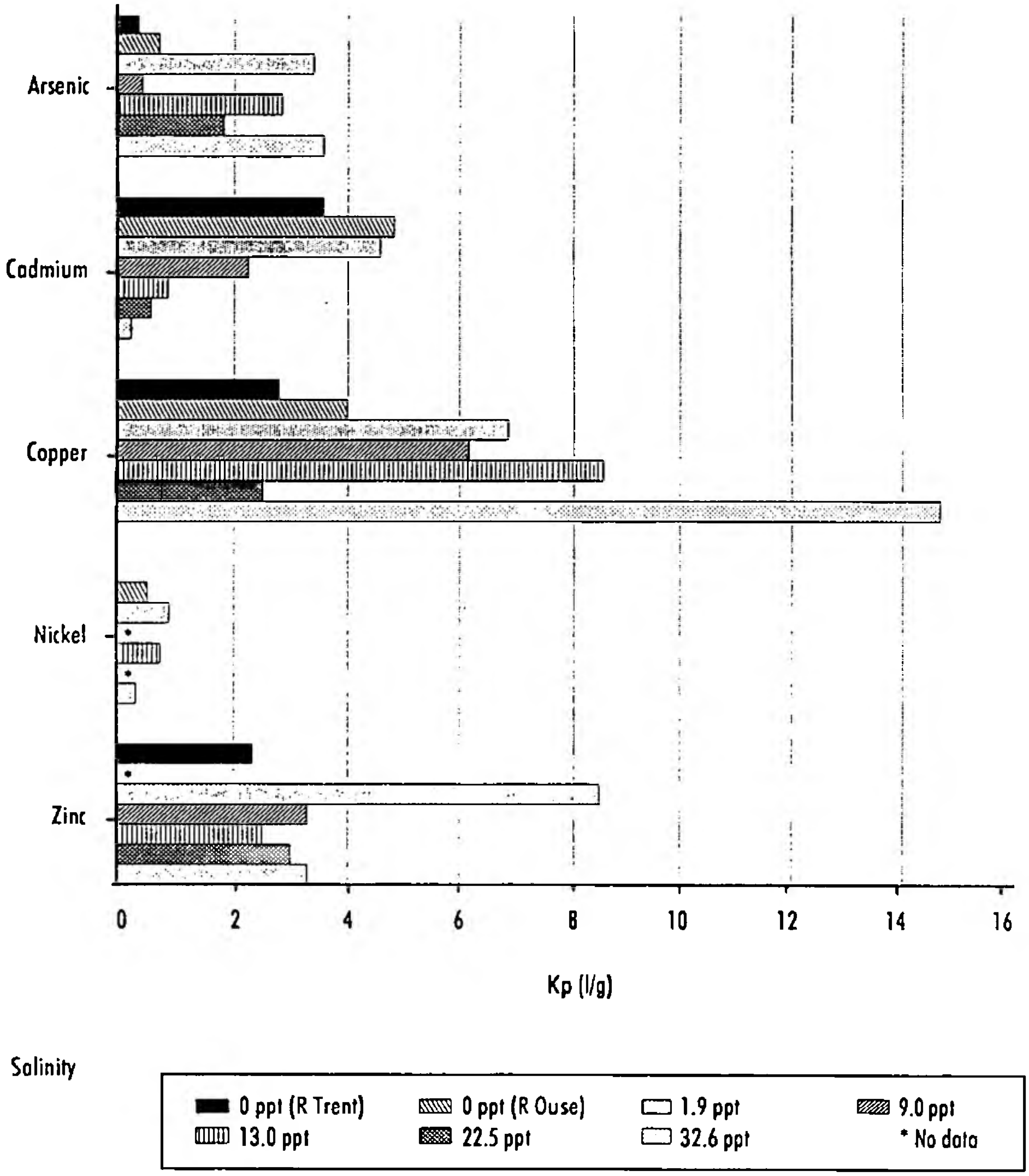
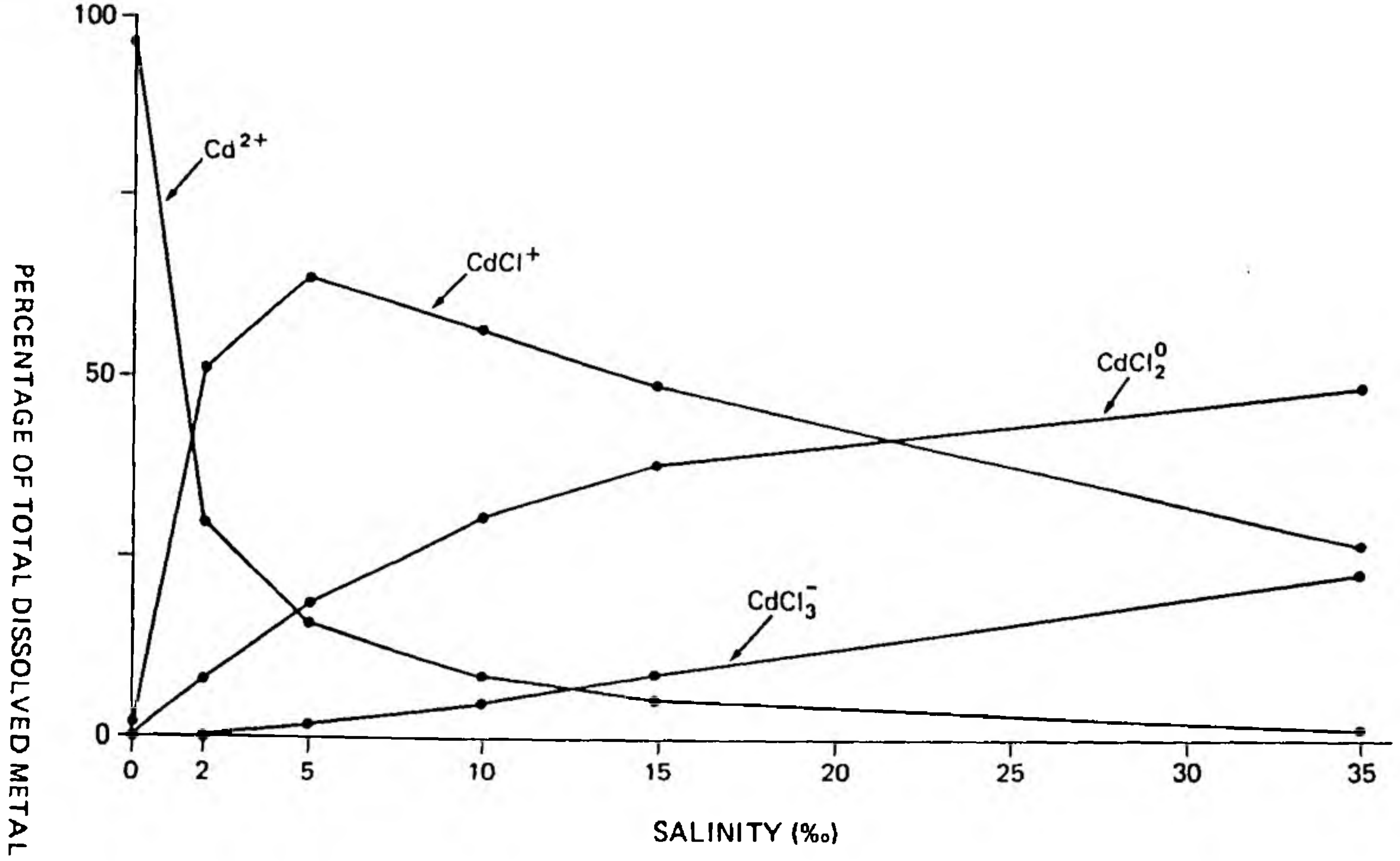


Figure 5.8 Partition coefficients for Humber estuary suspended particulates (determined from adsorption isotherm data)

Fig 5.9 Inorganic speciation of cadmium in an estuary with a river at pH7

(from French and Hunt, 1986)



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 µg 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 5.10a-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 $K_p(Cd^{2+}aq) = 1.4 \times 10^4$.

A similar effect of chloro-complexation has previously been reported by Comans and van Dijk (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, e.g. 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 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 the sorption behaviour of copper in Humber samples (Section 5.5).

5.6.6 Comparison of field and laboratory partition coefficients

The data found in the field and in the experiments 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

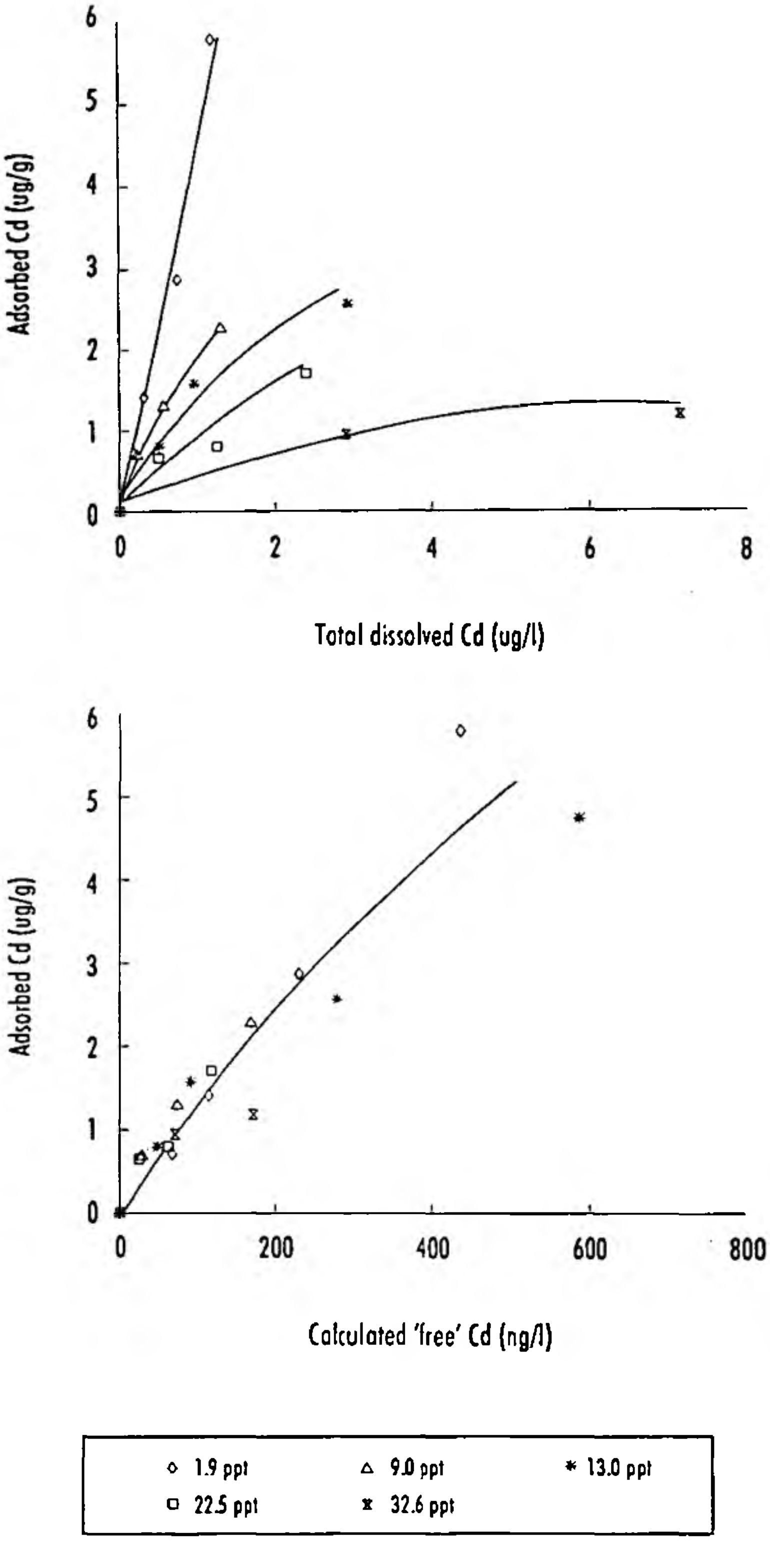


Figure 5.10 Influence of dissolved phase chloro-complexation on cadmium adsorption isotherms for Humber estuary suspended particulates

phases of the sorbed metal are important in determining K_p. Table 5.12 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 (5.6.5 above) are included to provide a comparison of field and laboratory results. 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.

Discussion

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, insufficient sample volume in sequential digests from the 1991 survey precluded confirmation of 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.

Table 5.12 Comparison of field and laboratory partition coefficients

Metal	Site		Kp from field surveys		(kg/l) Kp from lab expt
		1991 total	1991 seq	1989 total	
As	Althorpe	*	*	*	3.4 x 10^{2}
	Boothferry	*	*	1 x 10^{4}	6.9 x 10^{2}
	Blacktoft	*	*	*	3.4 x 10^{3}
	Brough	*	*	1 x 10^{4}	4.0 x 10^{2}
	Hessle	*	*	2 x 10^{4}	2.8 x 10^{3}
	Paull	*	*	*	1.8 x 10^{3}
	Spurn	*	*	*	3.6 x 10^{3}
Cd	Althorpe	3.6 x 10^{3}	*	*	3.6 x 10^{3}
	Boothferry	7.5 x 10^{3}	25 x 10^{3}	6 x 10^{3}	4.8 x 10^{3}
	Blacktoft	6.2 x 10^{3}	15 x 10^{3}	4 x 10^{3}	4.6 x 10^{3}
	Brough	2.6 x 10^{3}	5 x 10^{3}	2 x 10^{3}	2.3 x 10^{3}
	Hessle	2.0 x 10^{3}	4 x 10^{3}	3 x 10^{3}	0.9 x 10^{3}
	Victoria Pier	*	*	3 x 10^{3}	*
	Paull	1. x 10^{3}	2 x 10^{3}	*	0.6 x 10^{3}
	Spurn	1. x 10^{3}	*	*	0.2 x 10^{3}
Cr	Althrope	3.2 x 10^{4}	5 x 10^{4}	*	*
	Boothferry	6.6 x 10^{4}	9 x 10^{4}	*	*
	Blacktoft	7.7 x 10^{4}	12 x 10^{4}	*	*
	Brough	11.1 x 10^{4}	11 x 10^{4}	*	*
	Hessle	17.3 x 10^{4}	12 x 10^{4}	*	*
	Paull	*	16 x 10^{4}	*	*
	Spurn	*	*	*	*
Cu	Althorpe	3.3 x 10^{3}	5.2 x 10^{3}	*	2.8 x 10^{3}
	Boothferry	4.6 x 10^{3}	8 x 10^{3}	7 x 10^{3}	4.0 x 10^{3}
	Blacktoft	6.7 x 10^{3}	8.3 x 10^{3}	7 x 10^{3}	6.9 x 10^{3}
	Brough	4.8 x 10^{3}	6.8 x 10^{3}	8 x 10^{3}	6.2 x 10^{3}
	Hessle	13.0 x 10^{3}	7.6 x 10^{3}	10 x 10^{3}	8.6 x 10^{3}
	Victoria Pier	*	*	10 x 10^{3}	*
	Paull	*	8.1 x 10^{3}	*	2.5 x 10^{3}
	Spurn	*	*	*	14.7 x 10^{3}
Ni	Althorpe	2.8 x 10^{3}	2.7 x 10^{3}	*	*
	Boothferry	4.1 x 10^{3}	6.1 x 10^{3}	5 x 10^{3}	5.0 x 10^{2}
	Blacktoft	2.7 x 10^{3}	6.2 x 10^{3}	5 x 10^{3}	8.8 x 10^{2}
	Brough	3.0 x 10^{3}	5.8 x 10^{3}	7 x 10^{3}	*
	Hessle	6.3 x 10^{3}	5.9 x 10^{3}	8 x 10^{3}	7.2 x 10^{2}
	Victoria Pier	*	*	8 x 10^{3}	*
	Paull	*	4.7 x 10^{3}	*	*
	Spurn	*	*	*	3.1 x 10^{2}

	Kp from progressive seq digests		
(1)	(1 + 2)	(1 + 2 + 3)	(1 + 2 + 3 + 4)
*	*	*	*
*	*	*	*
*	*	*	*
*	*	*	*
*	*	*	*
*	*	*	*
*	*	*	*
2.9 x 10^3	4.3 x 10^3	*	*
7.7 x 10^3	13.0 x 10^3	24 x 10^3	25 x 10^3
4.7 x 10^3	10.1 x 10^3	13 x 10^3	14 x 10^3
1.7 x 10^3	3.3 x 10^3	5 x 10^3	5 x 10^3
1.2 x 10^3	2.4 x 10^3	4 x 10^3	4 x 10^3
*	*	*	*
0.5 x 10^3	1. x 10^3	2 x 10^3	2 x 10^3
1.4 x 10^3	3. x 10^3	*	*
*	*	*	*
*	*	*	*
2.4 x 10^2	*	*	*
0.3 x 10^2	*	*	*
*	*	*	*
<lod	*	*	*
1.2 x 10^2	*	*	*
2.7 x 10^2	1.5 x 10^3	1.9 x 10^3	3.3 x 10_3 X
7.0 x 10^2	3/ x 10^3	4.3 x 10^3	6 x 10^3
2.2 x 10^2	1.3 x 10^3	2.2 x 10^3	4.6 x 10^3
2.5 x 10^2	1.4 x 10^3	1.9 x 10^3	3.5 x 10^3
1.9 x 10^2	1.4 x 10^3	2.6 x 10^3	4.9 x 10^3
*	*	*	*
2.8 x 10^2	1.5 x 10^3	3.1 x 10^3	4.8 x 10^3
2.9 x 10^2	1.3 x 10^3	2.6 x 10^3	*
1.7 x 10^2	4.8 x 10^2	1.7 x 10^3	*
2.4 x 10^2	6.8 x 10^2	4.0 x 10^3	*
1.8 x 10^2	*	*	*
2.0 x 10^2	6.8 x 10^2	2.8 x 10^3	*
1.4 x 10^2	5.7 x 10^2	3.1 x 10^3	*
*	*	*	*
1.6 x 10^2	4.1 x 10^2	2.6 x 10^3	*
1.9 x 10^2	*	*	*

Table 5.12 Continued......

Metal	Site		Kp from field surveys		(kg/l)		Kp from progressive seq digests		
		1991 total	1991 seq	1989 total	Kp from	(1)	(1 + 2)	(1 + 2 + 3)	(1 + 2 + 3 + 4)
Zn	Althorpe	3. x 10^4	*	*	2.3 x 10^3	3.4 x 10^3	6.7 x 10^3	13 x 10^3	*
	Boothferry	3. x 10^4	4 x 10^4	20 x 10^3	*	1.9 x 10^3	6.3 x 10^3	39 x 10^3	40 x 10^3
	Blacktoft	2. x 10^4	3 x 10^4	9 x 10^3	8.5 x 10^3	1.6 x 10^3	5.7 x 10^3	17 x 10^3	18 x 10^3
	Brough	2. x 10^4	2 x 10^4	7 x 10^3	3.3 x 10^3	2.0 x 10^3	8.4 x 10^3	19 x 10^3	*
	Hessle	*	2 x 10^4	10 x 10^3	2.5 x 10^3	1.0 x 10^3	4.3 x 10^3	12 x 10^3	13 x 10^3
	Paull	2. x 10^4	2 x 10^4	10 x 10^3	3.0 x 10^3	2.3 x 10^3	7.6 x 10^3	15 x 10^3	17 x 10^3
	Spurn	2. x 104	5 x 10^4	*	3.3 x 10^3	1.9 x 10^3	7.5 x 10^3	30 x 10^3	33 x 10^3

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

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_ps 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_ps 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 - *In situ* and sequential extraction K_ps for zinc in the 1989 and 1991 surveys also proved appreciably higher than those from lab experiment. The dominant phase in the sequential extraction profiles was found to be the reducible phase, particularly for the Boothferry sample. The latter was collected near the freshwater/saline interface region, where flocculation of colloidal iron would be at its most pronounced. Partition coefficients within the saline reaches of the estuary did not vary markedly.

To conclude, partition coefficient data determined by both sequential extraction and by nitric acid 'total' digestion showed similar trends. K_ps for 1989 and 1991 were similar, although results from the earlier survey tended to be slightly higher. Breaking down the partition coefficient into various phases provided useful information on which species are important in governing sorptive for the different metals. The most significant phases in this respect seem to be the exchangeable for cadmium, the organic for copper and the reducible for nickel and zinc. 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.

5.7 Ythan Estuary

5.7.1 Adsorption tests on Ythan Estuary sample

Partitioning in a relatively unpolluted system was also investigated. The aim here was to study effects occurring at lower total concentrations of metal than is feasible in more polluted systems. Of particular interest was the possible extent to which natural organic ligands might lead to increased dissolved phase metal levels under such conditions.

Samples of water and bed sediment were collected from the Ythan river and estuary in NE Scotland (note: natural suspended solids levels were too low for direct use). These were mixed in proportion in order to produce a solution of 9 ppt salinity and 916 mg/l suspended solids. Three replicates of samples containing solids were performed, and samples to check for adsorption to the vessel during equilibration were run for all spikes.

Partition coefficient data are given in Table 5.13, along with those found in laboratory experiments for Selby and Blacktoft.

The partition coefficients found from different experiments with water from different sites are generally of similar magnitude, although the K_p for nickel is ten times greater at Blacktoft than at Ythan. The partition coefficient for cadmium at Selby is about ten times larger than at Blacktoft. The affinity of the solids for cadmium at Selby is probably a reflection of the chloro-complexation of the metal in saline waters, resulting in a higher dissolved phase level (and lower K_p) at Blacktoft. The similarity of partition coefficients from such different sites (i.e. saline and fresh water, polluted and relatively clean estuaries), is encouraging in terms of general modelling applicability.

Table 5.13 Partition coefficients for metals at Ythan, Selby and Blacktoft

Metal	Kp µg/kg		
	Ythan	Selby	Blacktoft
As	6.6×10^2	2.6×10^2	6.7×10^2
Cd	1.6×10^3	6.8×10^3	8.1×10^2
Cu	2.4×10^4	1.3×10^4	1.5×10^4
Ni	7.7×10^2	1.0×10^3	6.7×10^3
Zn	4.4×10^3	6.5×10^3	4.4×10^3

Adsorption to the walls of the bottles during equilibration occurred here in the case of copper (mean of 19% lost) and nickel (mean of 9% lost). There was no apparent trend in which spikes were most prone to losses.

5.8 Mersey Estuary

5.8.1 Survey characteristics

Although effort on the project has been concentrated mainly on the Humber system it was felt essential to also obtain comparative data for a second major estuary and the Mersey was selected to this end. The Mersey receives a wide range of industrial discharges and is one of the most polluted estuaries in the UK. Sewage discharges, although substantially reduced over the last decade, also remain important.

Two surveys were carried out to investigate partitioning processes for the system in December 1991 and January 1992. Locations of the sampling sites employed are shown in Figure 4.3. Measured characteristics of water sampled at each of the sites are listed in Tables 5.14 and 5.15.

Table 5.14 Mersey field survey 10/12/91: Sample characteristics

Site	Salinity ppt	pH	Temp °C	DOC mg/l	Suspended solids mg/l
Howley	0.0	7.22	6.5	11.0	7.2
Fiddlers Ferry I	4.4	7.31	4.5	11.2	1311
Fiddlers Ferry II	8.0	7.37	3.2	10.6	205
Widnes West Bank	21.5	7.41	4.0	4.13	61.6
New Brighton*	28.0	-	3.5	1.34	15.3

* Sampled on 11/12

Table 5.15 Mersey field survey 23/1/92: Sample characteristics

Site	Salinity ppt	pH	Temp °C	DOC mg/l	Suspended solids mg/l
Howley	0	7.51	4.2	11.7	11.1
Fiddlers Ferry I	1.0	7.30	4.2	10.9	202
Fiddlers Ferry II	7.4	7.79	1.9	8.36	2578
Fiddlers Ferry III	10.5	7.59	2.0	6.54	2391
Fiddlers Ferry IV	14.4	7.50	1.6	3.89	2194
Fiddlers Ferry V	17.9	7.74	2.0	2.01	1060
Widnes West Bank	20.3	7.81	2.4	2.80	244
Brittania Inn	27.6	8.03	3.6	0.9	311
New Brighton*	26.5	-	3.0	1.1	69.0

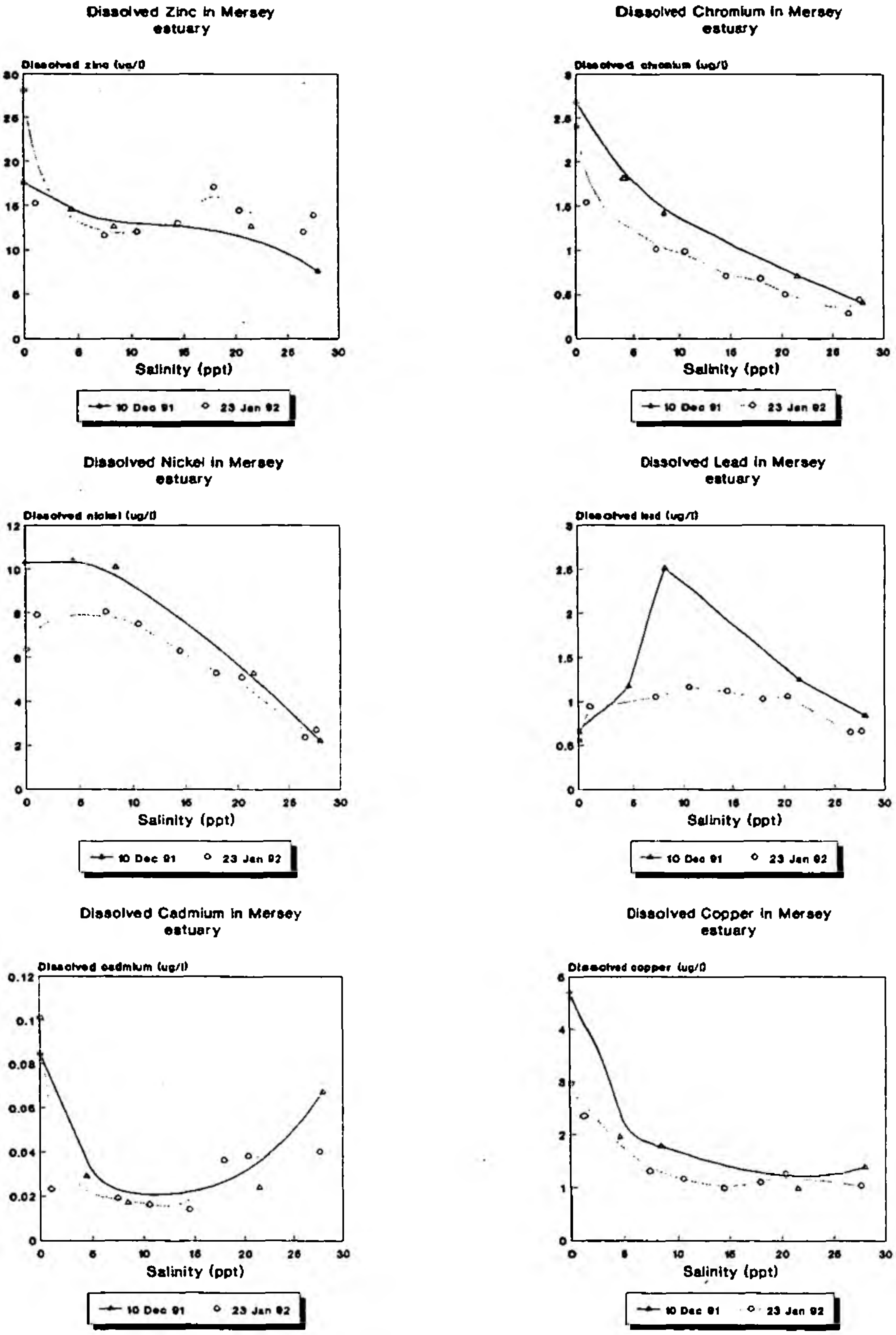
* Sampled on 24/2/92

5.8.2 Aqueous phase profiles

Data for dissolved phase cadmium, copper, nickel, lead, zinc and chromium plotted against salinity are shown for the December 1991 and January 1992 surveys in Figure 5.11.

In general, metals behaviour proved to be very consistent between the two surveys. However, in contrast to the Humber, where most metals showed either essentially conservative behaviour, or positive deviations from the simple two end-member mixing line, there was clear evidence in the Mersey for removal from the dissolved phase at the freshwater/saline interface and low salinity regions. This effect was most pronounced for copper and cadmium, but was also noticeable for chromium and zinc.

Nickel, on the other hand, showed positive deviations from conservative dilution at low salinity. The profiles obtained were similar in both shape and concentration range to those reported for earlier surveys (Campbell *et al* 1988) carried out between 1980 and 1984. The most likely cause at that time was considered to be industrial discharges to the waters of the upper reaches of the estuary. Interestingly, these earlier surveys also showed pronounced maxima in the zinc profiles at salinities in the range 20-25 ppt. Concentrations at the maxima were typically 40-60 µg l^{-1} compared ca. 15 µg l^{-1} at similar salinities for the present surveys. Although release from disturbed sediments and physical mixing of interstitial pore waters was recognised as a



Dissolved Zinc in Mersey estuary

Dissolved Chromium in Mersey estuary

Dissolved Nickel in Mersey estuary

Dissolved Lead in Mersey estuary

Dissolved Cadmium in Mersey estuary

Dissolved Copper in Mersey estuary

Figure 5.11 Dissolved phase metal vs salinity profiles for Mersey estuary possibility, the main cause of the influx was suggested to be discharges of untreated domestic wastewater. Major reductions in the levels of such discharges to the North bank of the estuary have been achieved in recent years through introduction of a new treatment works. The markedly lower levels, and absence of mid-estuarine maximum, for our own recent surveys may therefore be a direct consequence of such remedial measures.

The high levels of lead observed in the 5-20 ppt salinity region are considered to be the result of discharges from a major alkyl lead plant in the area. A detailed study of alkyl lead concentrations in the estuary has been reported previously by Riley and Towner (1984).

5.8.3 Particulate phase metal concentrations and speciation

For the January 1992 Mersey survey, the *in situ* partitioning of trace metals was investigated by application of the sequential extraction procedures described earlier (Section 5.6.4) to suspended particulate mater collected at the various sites on 0.4 μ Nuclepore polycarbonate membrane filters. Sequential extractions, rather than straightforward nitric acid/peroxide digestion, were adopted to provide information on the nature of binding of metals to specific geochemical phases within the particulate matrix. Care was taken to adjust filtration volumes to, as far as practically possible, provide similar solids loadings on membrane filters for all sites. Reagent volumes were also selected to provide similar sample/reagent ratios in all cases.

Results obtained for the various phases are displayed in Figures 5.12a-f. Although total concentrations varied, there was a good degree of consistency in speciation trends for the different metals with those found for the Humber system. Thus, the most important phases were identified as:

Cadmium:	exchangeable, carbonate and reducible;
Chromium:	reducible, organic and residual;
Copper:	organic and residual;
Nickel:	reducible and residual;
Lead:	reducible and residual;
Zinc:	reducible.

Fig 5.12a Cadmium speciation in Mersey suspended sediments

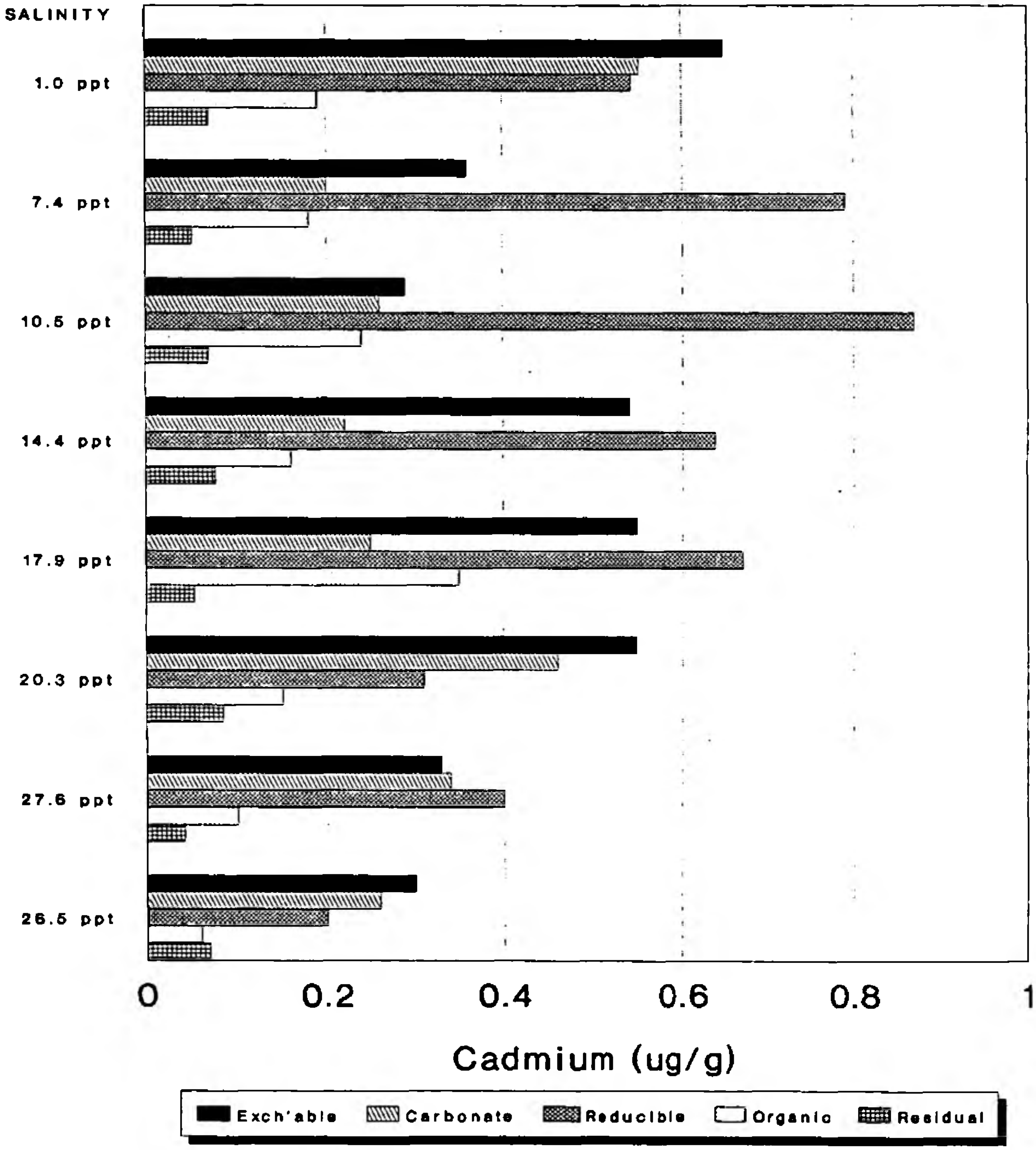


Fig 5.12b Chromium speciation in Mersey suspended sediments

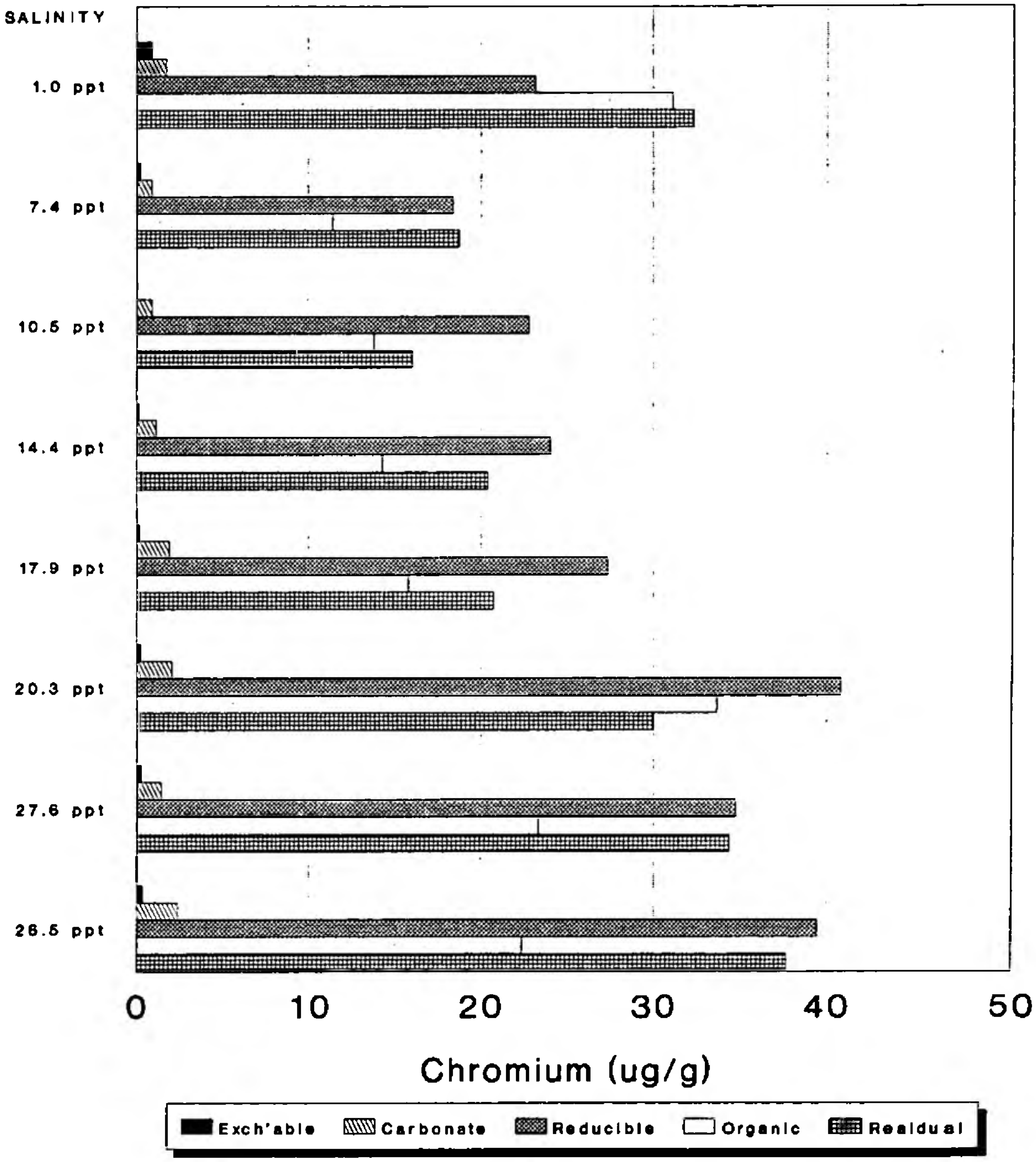


Fig 5.12c Copper speciation in Mersey suspended sediments

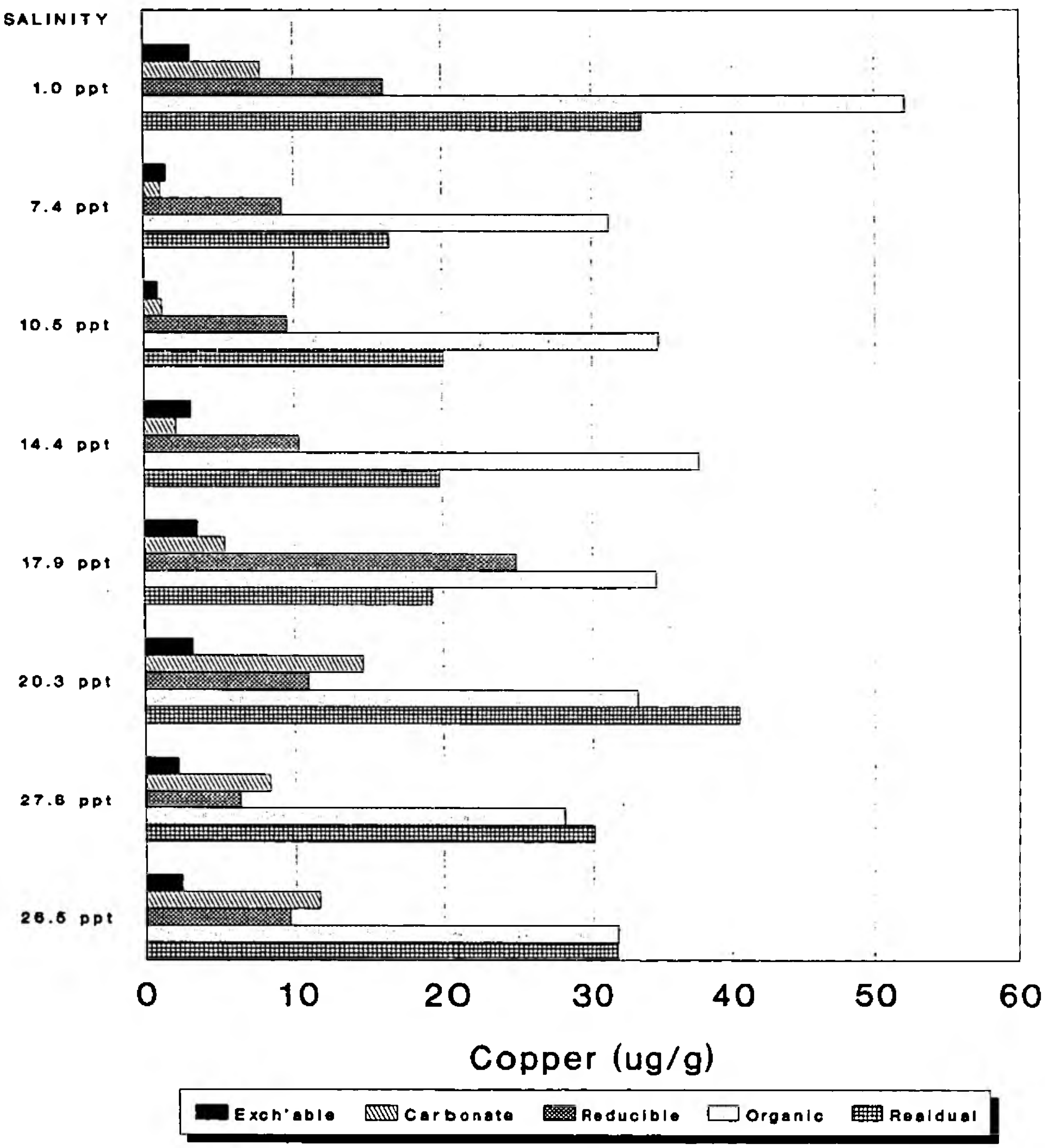


Fig 5.12d Lead speciation in Mersey suspended sediments

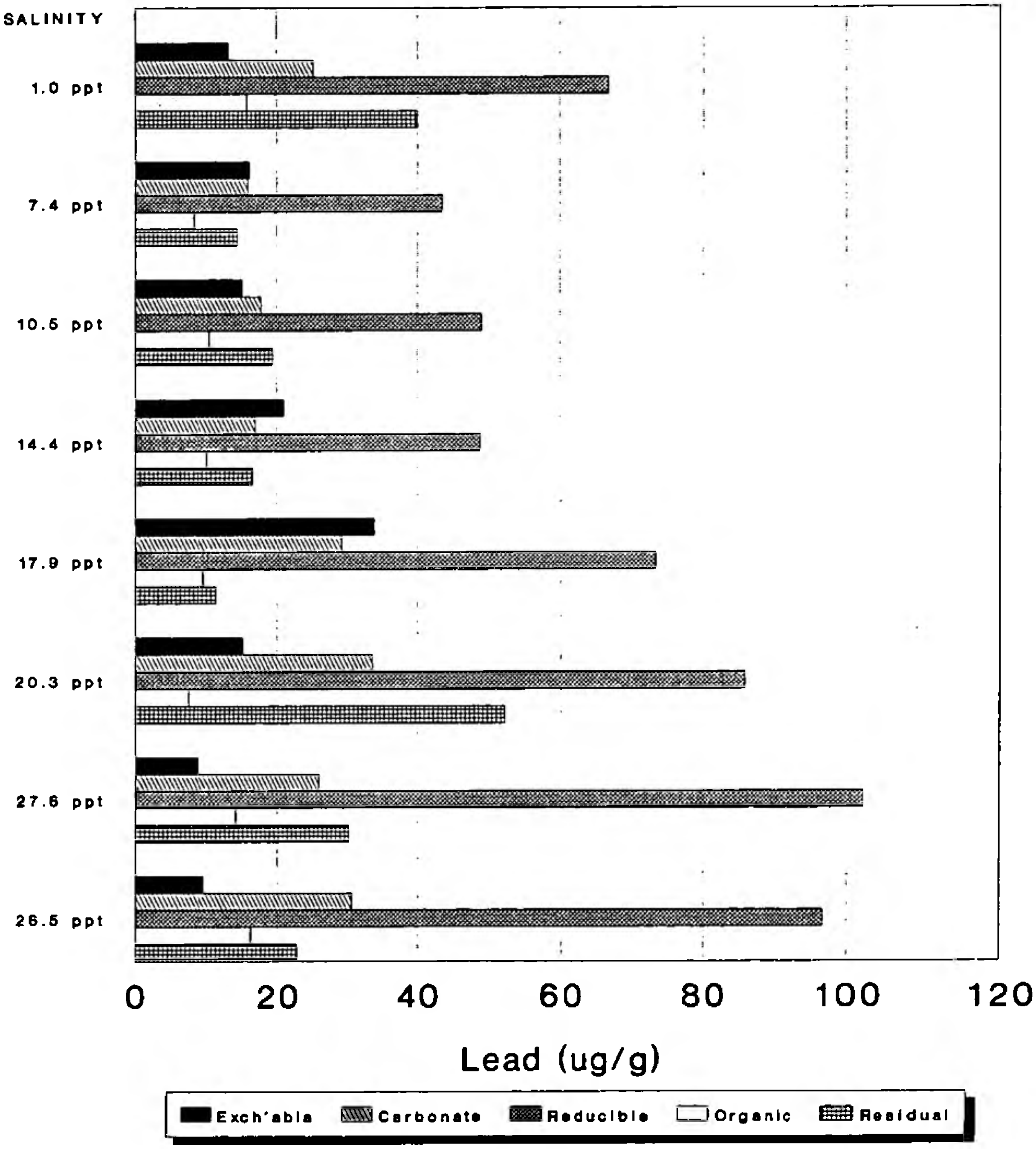


Fig 5.12e Nickel speciation in Mersey suspended sediments

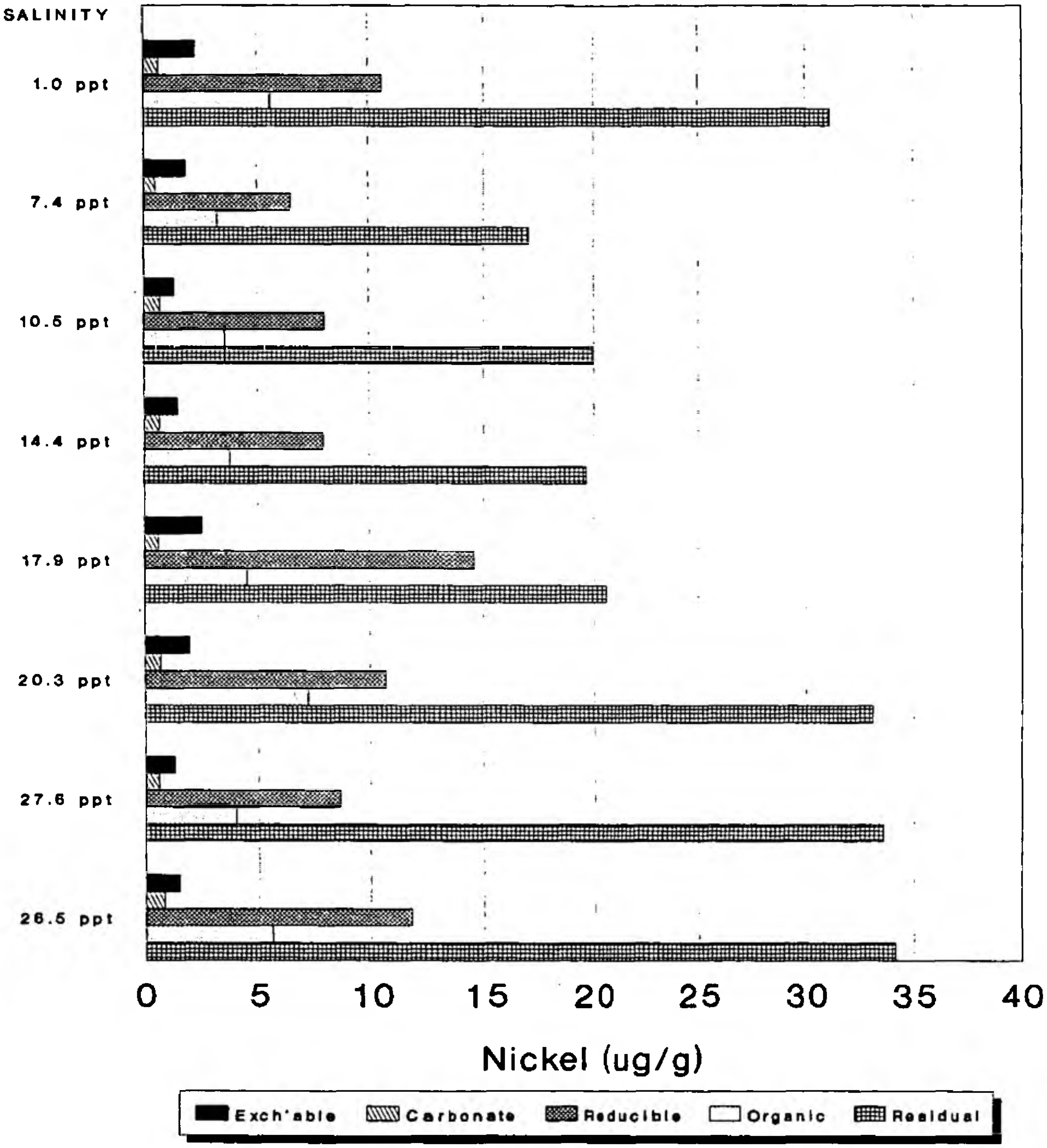
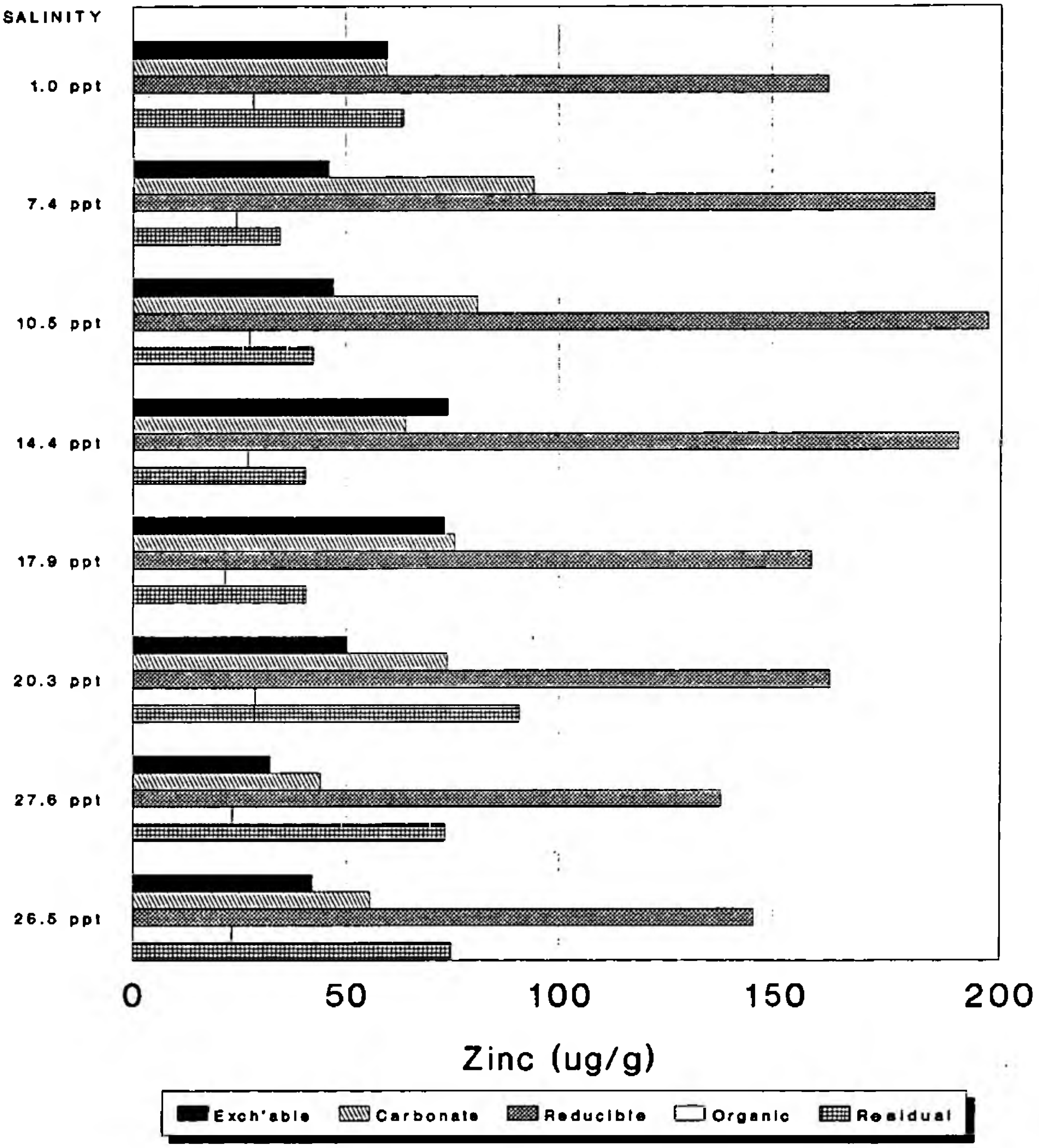


Fig 5.12f Zinc speciation in Mersey suspended sediments



By summation of the data for all phases, it was possible to determine *in situ* partition coefficients for each metal and these are plotted in Figure 5.13. Note that as these may well include a proportion of strongly bound metal not in dynamic equilibrium with the dissolved phase, they cannot be directly compared in absolute terms with the laboratory determined partition coefficients shown in Figure 5.8 for the Humber system. However, a number a number of consistent trends are evident. In particular, the cadmium coefficients again show a tendency to decrease with increasing salinity, while those for copper show a progressive increase. Hence, chloro-complexation appears to play an equally important part in controlling the partitioning behaviour of cadmium as was found for the Humber. A decrease in the levels of dissolved phase copper-complexing organic ligands with increasing salinity could account for the observed trend for this element, although no firm confirmatory evidence is available.

In order to explain the very high levels of removal of copper and cadmium from solution in the upper reaches of the Mersey, it is useful to compare the sequential extraction derived partition coefficients with those obtained in a similar manner for the Humber. In both cases, these were approximately an order of magnitude higher for the Mersey than for the Humber, indicating a much greater propensity to scavenge these metals. The reasons for this are not known but one possibility may lie in the relatively high levels of sewage discharged to the Mersey estuary. While considerable reductions have been achieved in recent years, such discharges remain important in the upper reaches of the system where cadmium and copper removal is evident. Previous work at WRc (Comber and Gunn 1991) has indicated that following mixing of sewage sludge and seawater, an initial rapid scavenging of both metals occurred with subsequent slow release as microbial degradation of the solids progressed. The observed increase in dissolved cadmium concentrations in the lower Mersey may in part be a consequence of the aforementioned chloro-complexation but ingress of metal released from degrading sewage sludge in the vicinity of the Liverpool Bay disposal ground may also contribute.

For nickel, zinc and chromium, the magnitude of partition coefficients was found to be similar in both estuaries. Chromium, particularly in the Mersey, exhibited more pronounced increases with increasing salinity than those for copper. This effect has not been studied in greater detail, but again may be a

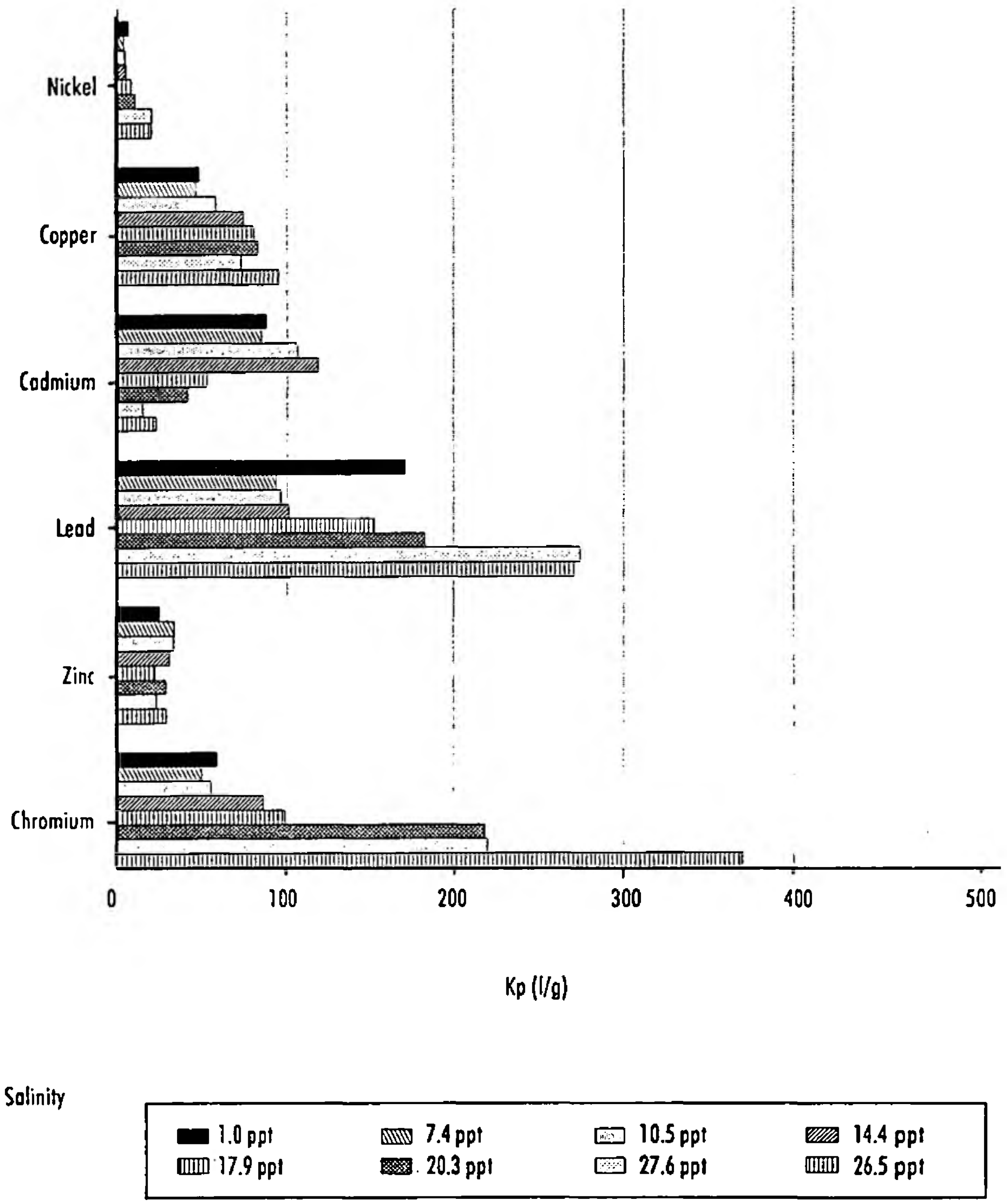


Figure 5.13 Partition coefficients for Mersey estuary suspended particulates (determined from sequential extraction data)

reflection of the influence of dissolved or colloidal natural organic material on partitioning processes. Dissolved lead levels in Mersey sample aliquots filtered 24 hours after the time of collection were found to be consistently lower than those filtered on-site. This is interesting, given that alkyl lead has previously been shown to behave very conservatively within the estuary (Riley and Towner 1984). However, total lead levels in our surveys were much lower than earlier data; the proportion of inorganic lead (which shows a much stronger tendency to adsorb to particulates) may now be much higher.

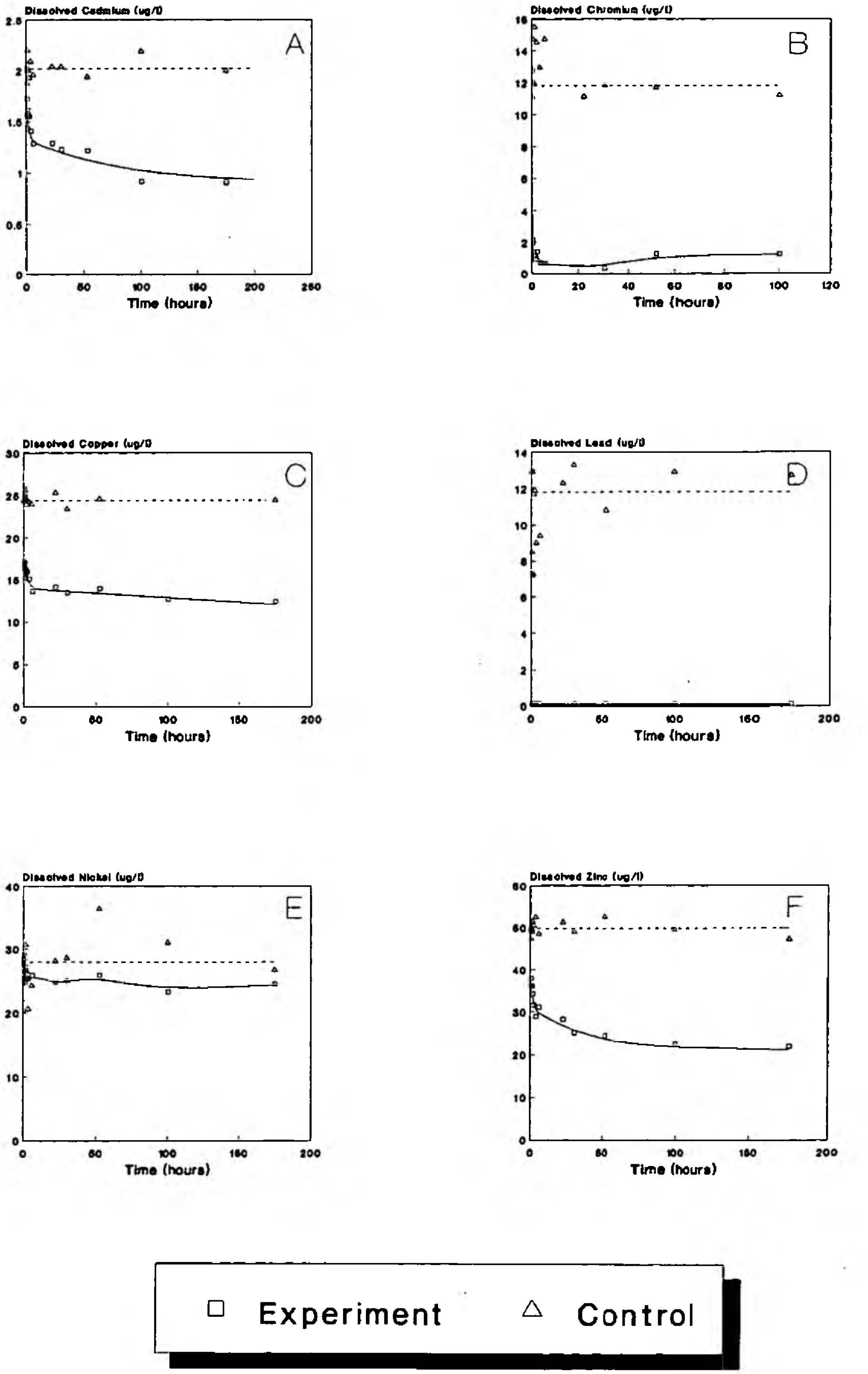
5.9 Investigation of kinetics of sorption to estuarine suspended particulate matter

5.9.1 Development of multi-step kinetic model

The kinetics of adsorption of trace metals to natural suspended particulate matter in the Humber were initially investigated using a bulk sample of medium salinity (13 ppt) and solids concentration of 130 mg/l. This was collected from the Hessle site during the April 1991 survey. A four litre sample was simultaneously spiked with 2 µg l^{-1} Cd, 10 µg l^{-1} Cr and Pb, 20 µg l^{-1} Cu and Ni, and 40 µg l^{-1} 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 5.14. 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 5.14 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:

$$M + S \underset{k_d}{\overset{k_a}{\rightleftharpoons}} MS \qquad (1)$$

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

Thus the rate of change of metal concentration with time:

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

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:

$$[M]_t = [M]_o\left[\frac{k_d + k_a'.P.\exp(-(k_a'.P + k_d).t)}{k_a'.P + k_d}\right] \qquad (3)$$

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

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

and since the equilibrium partition coefficient:

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

it follows that:

$$k_d = k_a'/K_p \tag{4}$$

and equation (3) then reduces to:

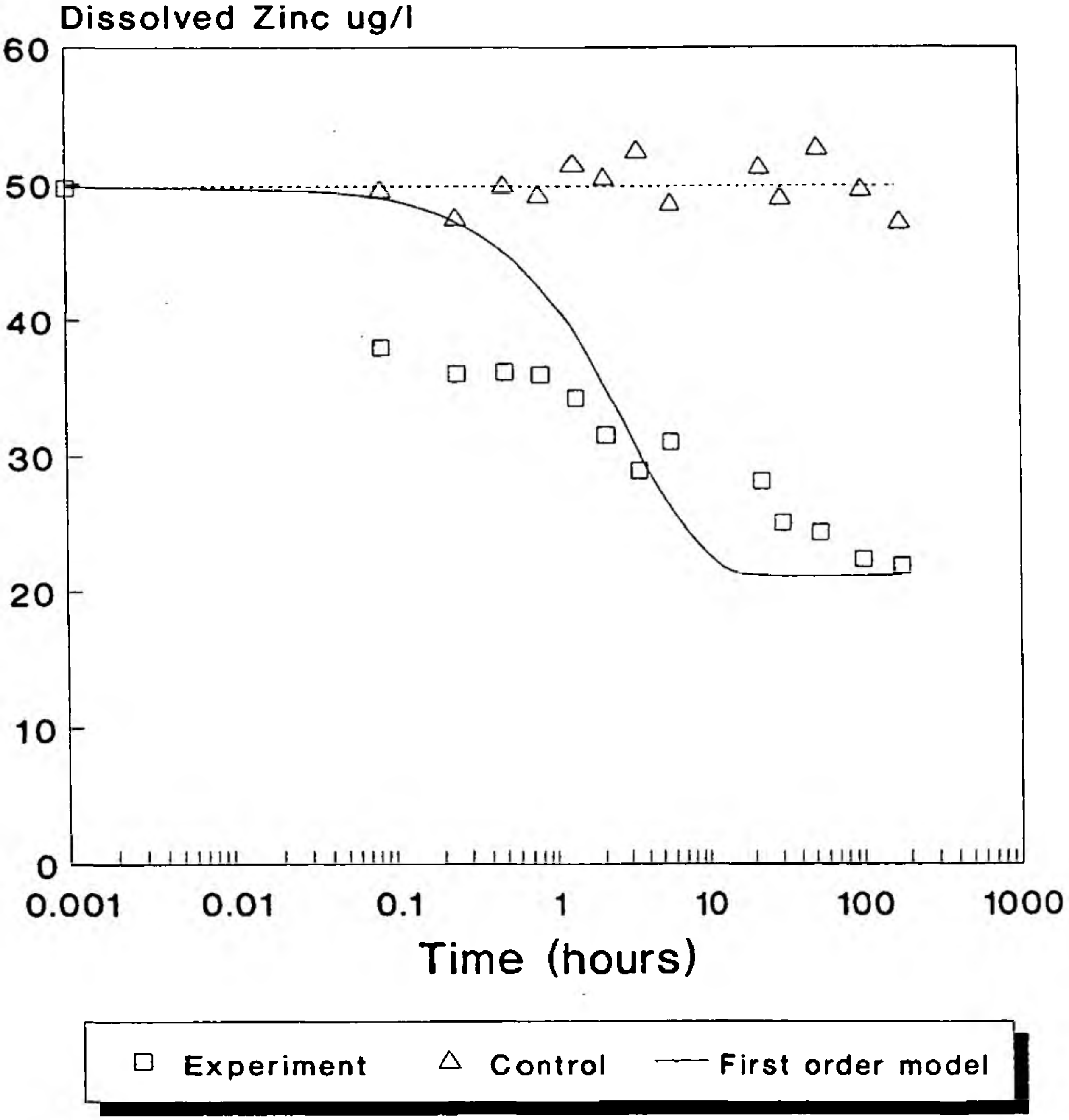
$$[M]_t = [M]_o \left[\frac{1/K_p + P.\exp\{-k_a'.(P + 1/K_p).t\}}{p + 1/K_p} \right] \tag{5}$$

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 5.15. 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* (1988) have reported results for 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 5.16 shows partition coefficients for cadmium, copper and zinc calculated after equilibration times of five minutes, 22 hours and the full period of 175 hours. The five minute

Fig 5.15 Fit of first order reversible kinetic model to zinc sorption data



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 5.16 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	2.3×10^3	4.6×10^3	10.0×10^3
Copper	5.0×10^3	8.5×10^3	12.2×10^3
Zinc	2.9×10^3	7.6×10^3	13.6×10^3

From Table 5.16 it can be seen that the rapid processes occurring within the initial five 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 equilibrate over ca. 200 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, i.e.:

$$\left.\begin{array}{l} M + S_1 \underset{k_{d1}}{\overset{k_{a1}'}{\rightleftharpoons}} MS_1 \\[2ex] M + S_2 \underset{k_{d2}}{\overset{k_{a2}'}{\rightleftharpoons}} MS_2 \\[2ex] M + S_3 \underset{k_{d3}}{\overset{k_{a3}'}{\rightleftharpoons}} MS_3 \end{array}\right\} \qquad \text{Scheme A}$$

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 5.16a-c (again in the form of semi-log plots). Full results for the best fit constants for each of the three proposed stages are listed in Table 5.17. Given that no data were available for times of less than five minutes, partition coefficients rather than rate constants were computed for the initial rapid stage.

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* (1988):

Scheme B

$$M \rightleftharpoons MS_1 \rightleftharpoons MS_2 \rightleftharpoons MS_3 \; \ldots .$$

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 5.17 should prove highly useful for incorporation in environmental fate models.

5.9.2 Application to prediction of desorption profiles

A second series of experiments were undertaken, to test both the applicability of the model to samples from different sites within the Humber system, and its usefulness in prediction of desorption profiles.

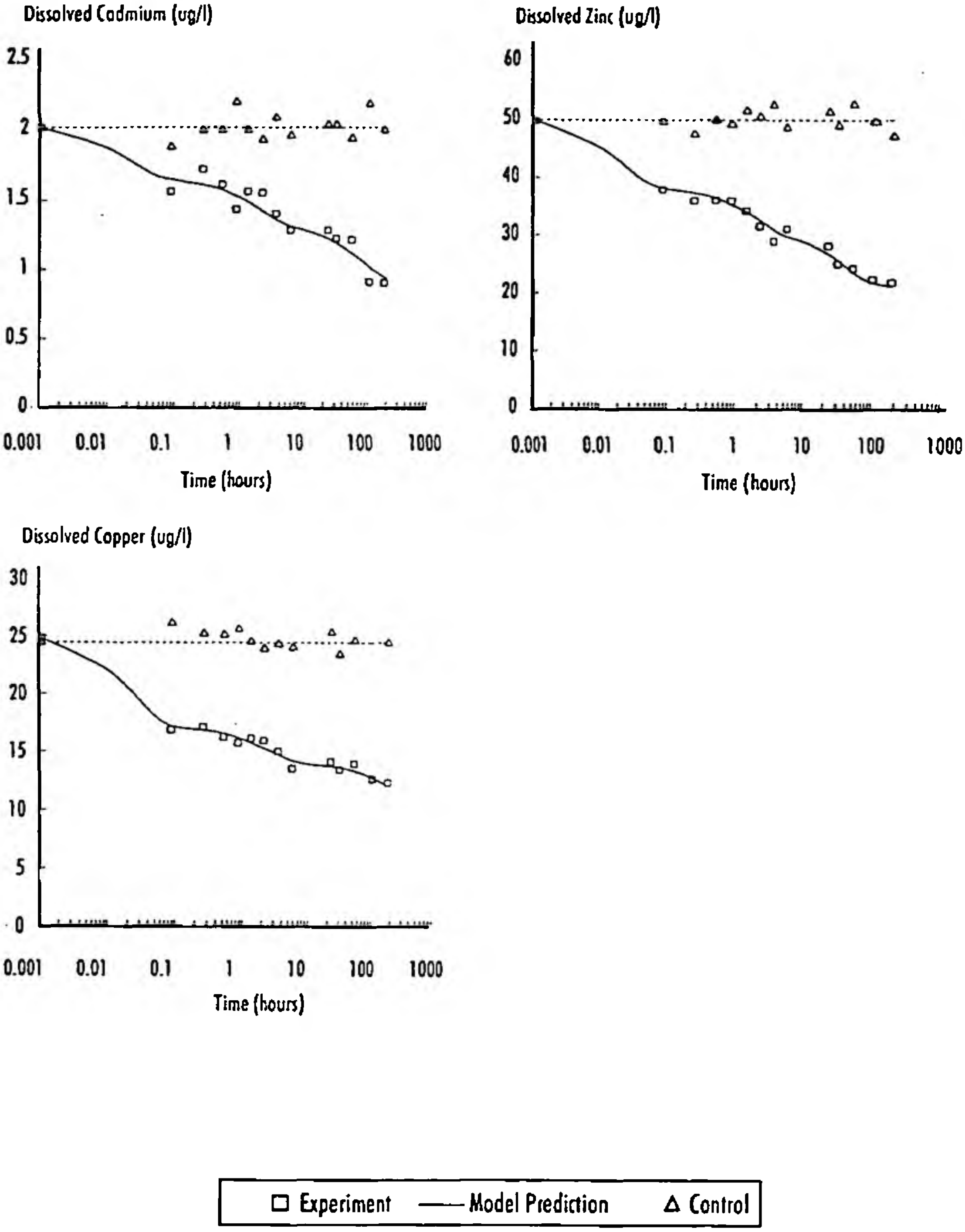


Figure 5.16 Fit of multi-step kinetic model to observed trace metal adsorption profiles

Table 5.17 Computed rate constants (hr^{-1}) and initial stage partition coefficients for 3-stage first order reversible model fitted to Hessle experimental sorption data

	Copper	Cadmium	Zinc
K_{p1}	4.9×10^3	1.8×10^3	2.1 x 103
k_{a2}'	1.2×10^3	9.0×10^2	1.5×10^3
k_{d2}	3.0×10^{-1}	3.1×10^{-1}	4.8×10^{-1}
k_{a3}'	4.0×10^1	5.0×10^1	1.5×10^2
k_{d3}	9.9×10^{-3}	1.1×10^{-2}	1.9×10^{-2}

The base sample for these studies, collected from Blacktoft Jetty in October 1991, had a salinity of 9 ppt and a suspended solids concentration of 1000 mg/l. This was initially subjected to a similar adsorption test to that carried out for the April 1991 Hessle sample. The suspended solids concentration was adjusted to 165 mg l^{-1} by dilution with filtered sample and additions of 2 µg l^{-1} Cd, 20 µg l^{-1} Cu and 40 µg l^{-1} Zn were made. Arsenate (20 µg l^{-1} as As) was also included to establish whether a similar kinetic model was applicable to anionic metal species as that derived for cations.

Figure 5.17 shows adsorption vs time profiles predicted for the Blacktoft sample using the rate constant data from the Hessle model (Model 1) plotted alongside the observed experimental data. Considering the differences in both time and location of sample collection, the observed fit is reasonable, particularly for zinc. For cadmium, for which the poorest fit was obtained, the final dissolved phase concentration was underestimated by approximately 20%. In order to provide a better data set to test the reversibility of the model in desorption situations, rate constants were recomputed to provide best fits to the Blacktoft experimental results. The degree of adjustment required was not great, however, and the timescales for equilibration of the three steps were maintained at five minutes, 10 hours and 200 hours. Fits obtained in this way are displayed in Figure 5.17 (Model 2), along with that for arsenate; associated rate constants are given in Table 5.18.

Figure 5.17 Predicted and experimental adsorption kinetics for Blacktoft Humber sample

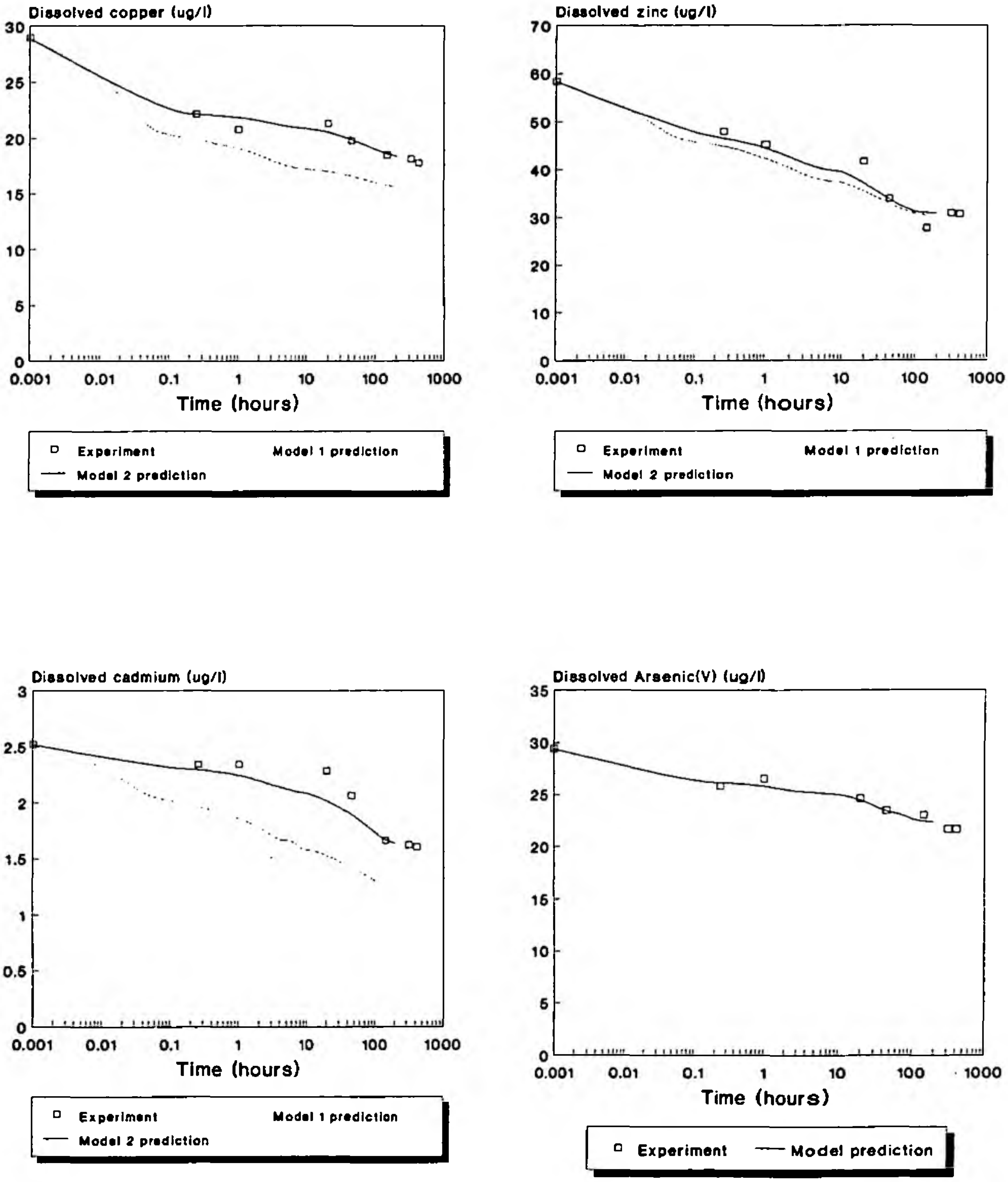


Table 5.18 Computed rate constants (hr^{-1}) and initial stage partition coefficients for model fitted to Blacktoft experimental adsorption data

	Zinc	Cadmium	Copper	Arsenic(V)
K_{p1}	2.1×10^3	5.6×10^2	3.1×10^3	1.1×10^3
k_{a2}'	1.1×10^3	2.9×10^2	3.5×10^2	2.5×10^2
k_{d2}	3.5×10^{-1}	3.1×10^{-1}	3.0×1^{-1}	4.0×10^{-1}
k_{a3}'	1.5×10^2	3.0×10^1	3.0×10^1	3.0×10^1
k_{d3}	1.9×10^{-2}	1.1×10^{-2}	9.7×10^{-3}	1.7×10^{-2}

Two series of desorption tests were then undertaken to establish the reversibility of sorption process by examination of desorption kinetics after prior adsorption of spiked metals over equilibration periods of ten minutes and six days. Adsorption was carried out on the unamended (i.e. 1000 mg l^{-1} solids) Blacktoft sample, at spike levels of 12 µg l^{-1} for Cd, 120 µg l^{-1} for As(V) and Cu, and 240 µg l^{-1} for Zn. After the appropriate equilibration period, an aliquot of sample was removed and filtered to 0.4 µ to determine the extent of adsorption. The remainder was then rapidly diluted and mixed, in 5:1 ratio, with prefiltered, unspiked sample.

In order to model desorption from different initial starting points, it was necessary to employ the general solution to the reversible first order reaction (equation 1) which takes the form:

$$[M]_t = [M]_o \left[\frac{([M] + [MS])k_d + ([M].k_a'.P - [MS].k_d)\exp\{-(k_a'.P + k_d).t\}}{(k_a'.P + k_d)} \right] \quad (6)$$

Concentrations of metals in solid phase sites corresponding to each of the model kinetic steps were first calculated for the ten minute and six day adsorption situations. Predicted behaviour over 200 hours subsequent to dilution with the filtered, unspiked sample was then computed.

Figures 5.18 and 5.19 compare these predictions with observed experimental data for the two cases. For all determinands, the agreement was extremely good, which indicates clear reversibility of sorption processes over the timescales studied. Thus, commonly reported hysteresis effects, whereby observed desorption is markedly lower than that predicted from partitioning in adsorption studies, appear to be a simple function of the equilibration times adopted in many studies, rather than any true reflection of irreversibility. Because desorption rate constants are consistently much lower than adsorption constants, if equivalent equilibration times of say, 24 hours, are used for both adsorption and desorption experiments, then some hysteresis is inevitable.

For the present study, final dissolved phase concentrations, for both the adsorption situations and the two desorption cases examined, demonstrate remarkable consistency for all four elements. In order to illustrate more fully the applicability of the model, Figures 5.20 and 5.21a/b show examples of the predicted migration of zinc between the dissolved phase and the three model solid phase sites. For simplicity, the solid phase sites have been designated 'fast', 'medium' and 'slow', dependent on their relative equilibration timescales. Looking at an adsorption profile first (Figure 5.20 - Hessle sample), we can see that dissolved phase levels fall very rapidly during the first five minutes as the fast sites equilibrate. As metal then migrates to the 'medium' sites over the next ten hours, levels in the 'fast' sites decrease accordingly to maintain equilibrium with the changing dissolved phase concentrations. Finally, and most importantly in terms of subsequent desorption behaviour, the most pronounced changes in the period between ten and 200 hours are not in the aqueous concentrations but in movement between sites on the solid phase. Thus, total particulate concentrations do not change greatly but 'slow' sites go from a position of minor importance to become the dominant solids form.

If we now consider the desorption situations, Figure 5.21a shows observed and predicted behaviour for the case where the adsorption contact time has been limited to ten minutes. An extremely interesting feature here is that the initial dissolved concentration (ca. 30 $\mu g\ l^{-1}$ Zn) is almost identical to that predicted at final equilibrium. The observed desorption and subsequent slow readsorption of some 20 $\mu g\ l^{-1}$ Zn therefore demonstrates unequivocally the

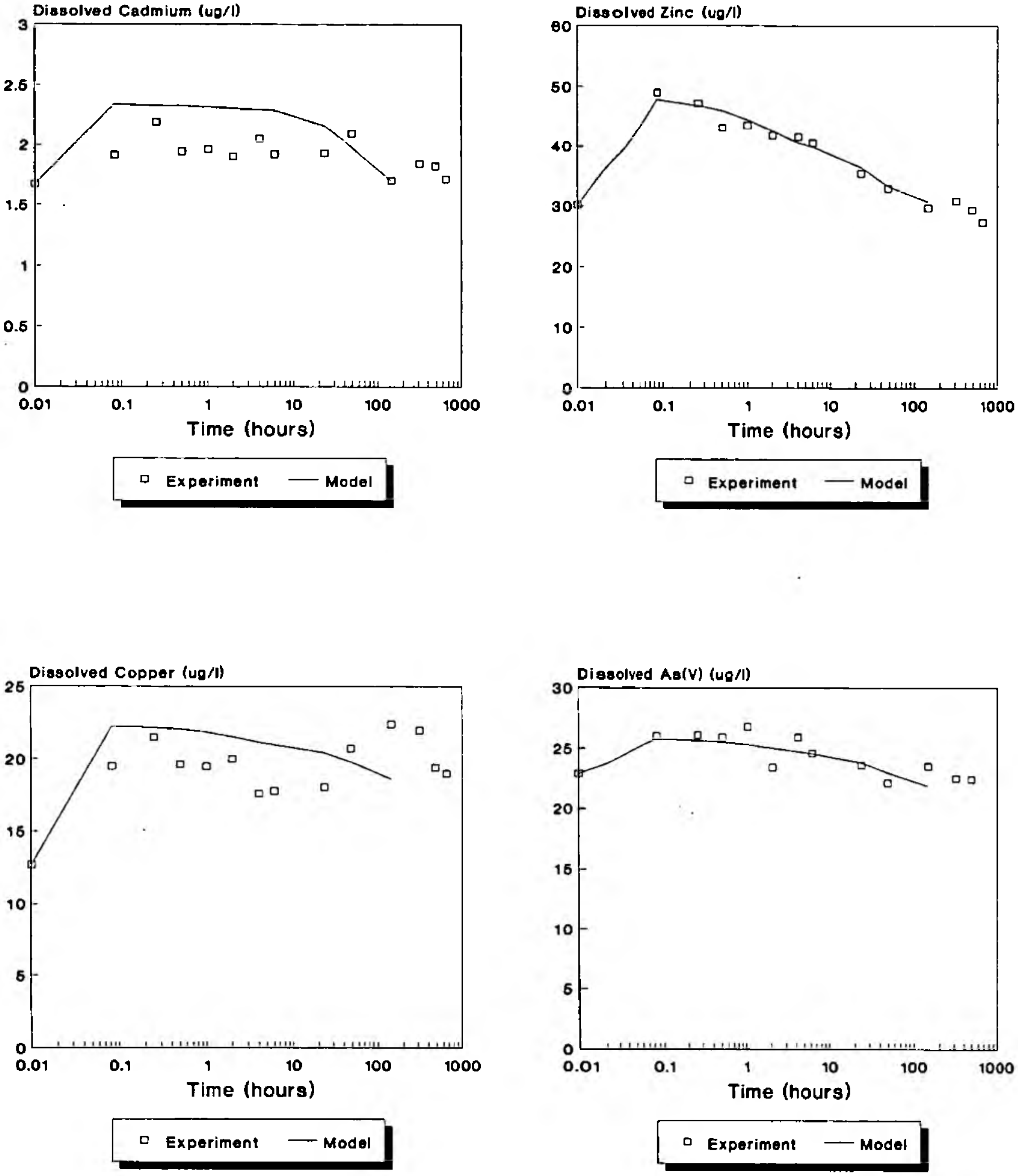


Figure 5.18 Desorption of metals from Humber suspended particulates following 10 minute adsorption period

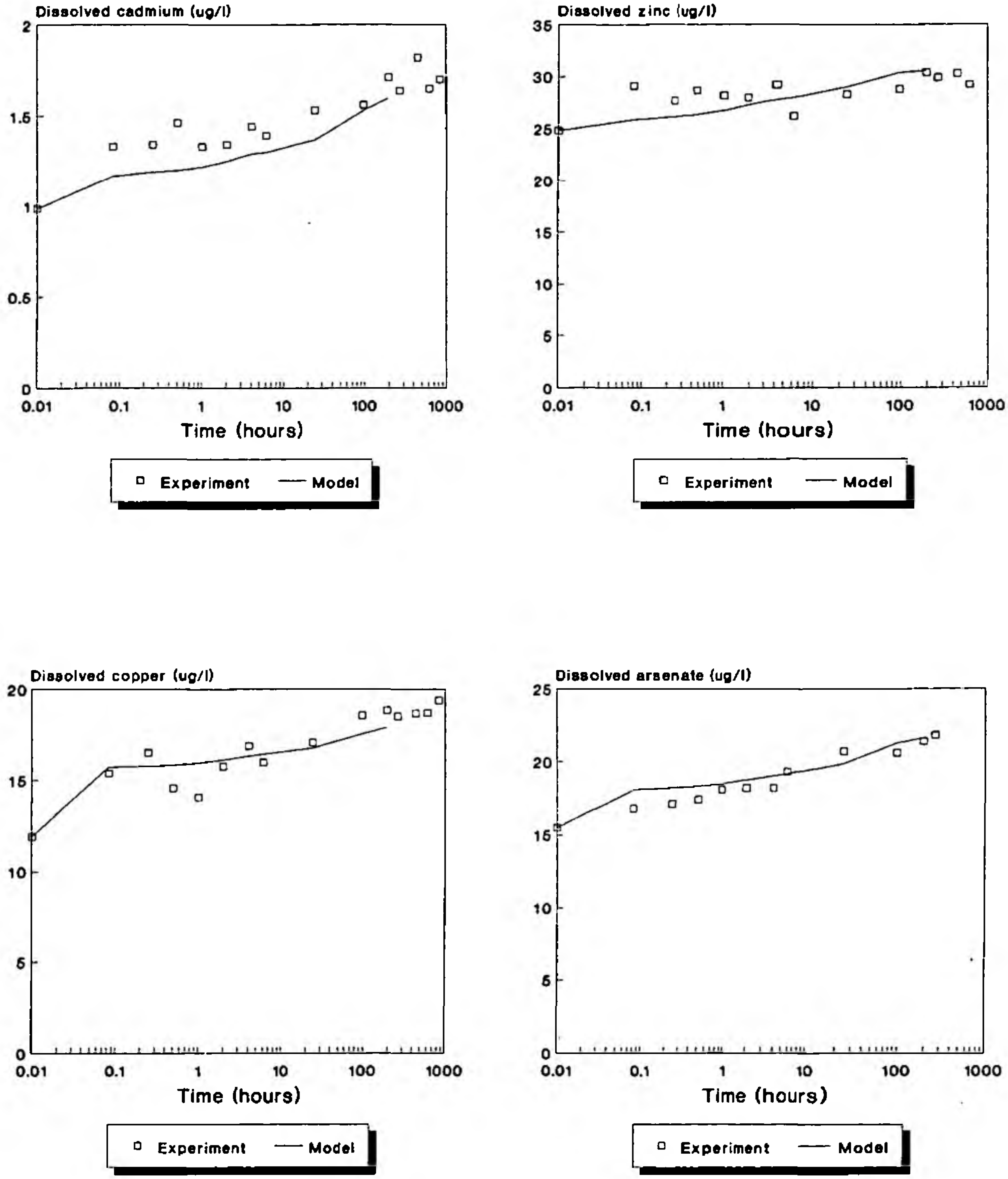


Figure 5.19 Desorption of metals from Humber suspended particulates following 6 day adsorption period

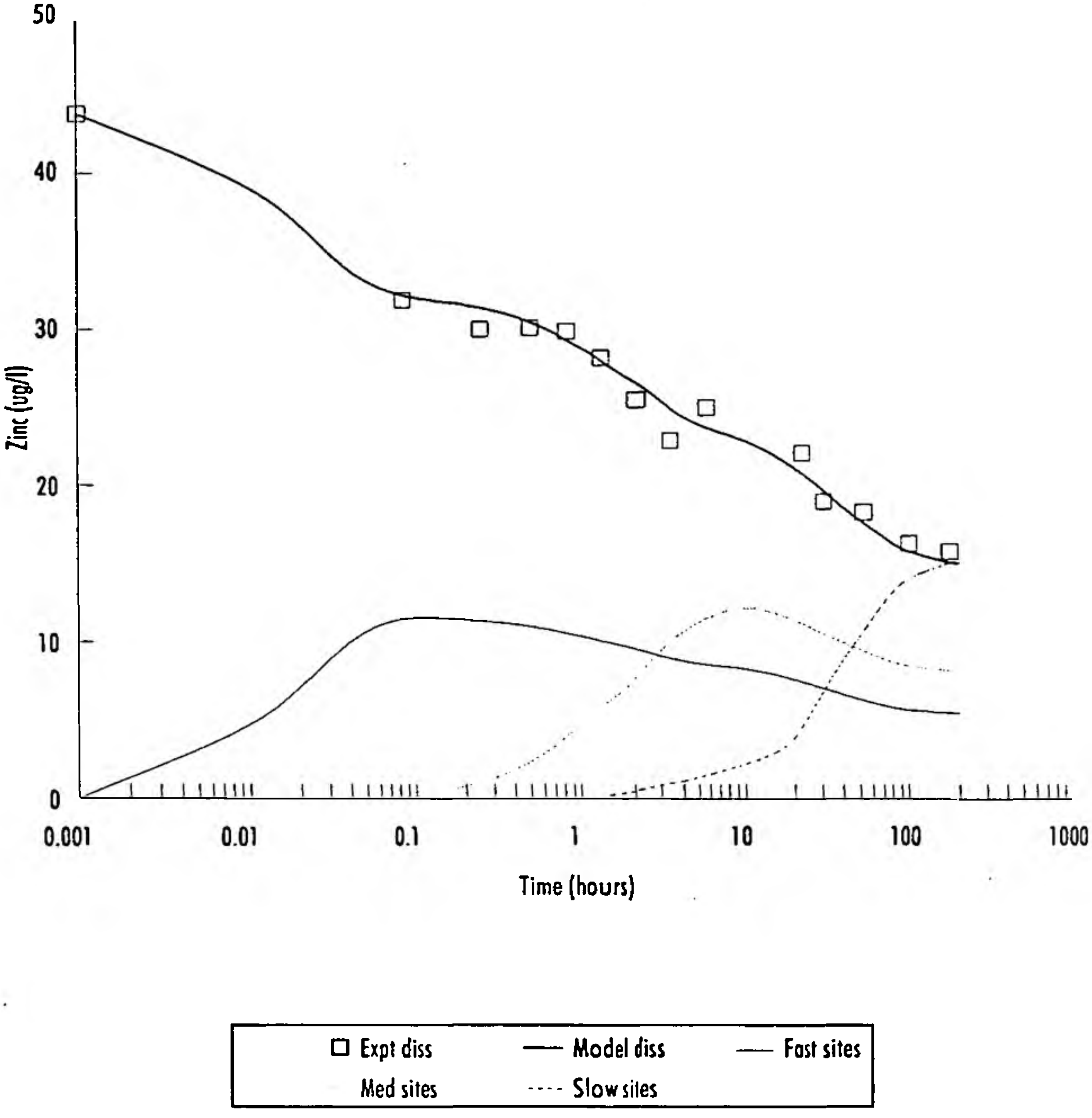


Figure 5.20 **Computed zinc concentrations on solid phase sites during adsorption to Humber suspended particulates**

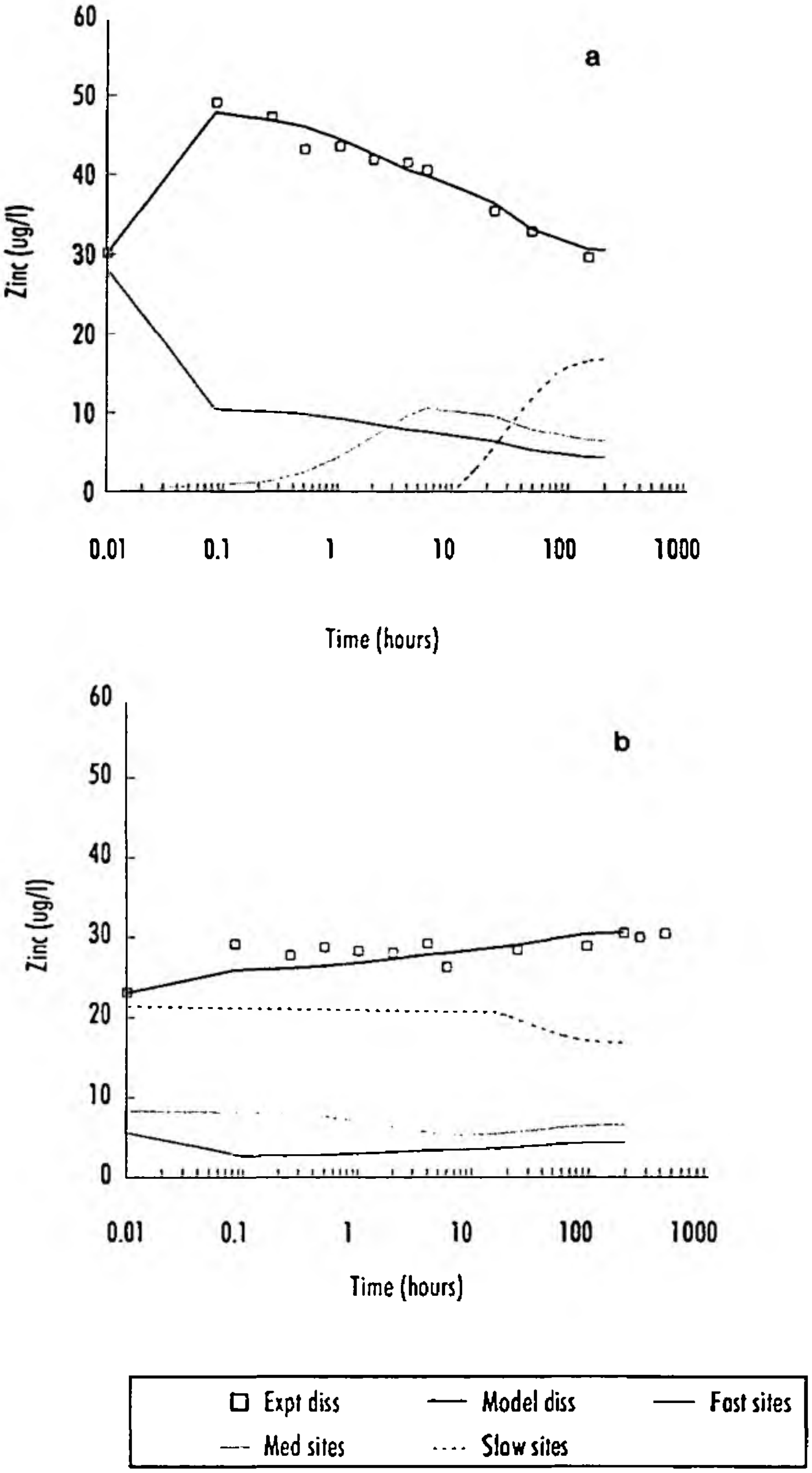


Figure 5.21 Desorption of zinc from Humber suspended particulates following adsorption over varying contact times

importance of inherently distinct physicochemical sites exhibiting differing sorption kinetics. Any simple single-site kinetic or equilibrium model would predict that dissolved concentrations would not change from the initial 30 µg l^{-1} level in such a situation. However, observed behaviour is readily explained in terms of the multi-site model. Thus, although initial dissolved and total particulate levels are close to the equilibrium values, relative site-occupancy on the particulate phase is very much in a state of disequilibrium. As only ten minutes has been allowed for adsorption, essentially all the solid phase zinc is on 'fast' sites. Following dilution, these are initially overoccupied and a rapid release of 20 µg l^{-1} Zn is required for them to re-equilibrate with the dissolved phase. At this stage, the 'medium' and 'slow' sites are virtually unoccupied and progressive readsorption therefore occurs over the following 200 hours, with the 'slow' sites eventually becoming the dominant solid phase form.

Turning to Figure 5.21b, the contact time during adsorption has now been extended such that 'fast', 'medium' and 'slow' sites are now all near to equilibrium. On dilution with filtered sample of low zinc content, all sites are then over-occupied and, in turn, release metal to compensate. 'Slow' sites are dominant, however, and the net effect is therefore a slow bleed to the dissolved phase. Equilibrium concentrations for both the dissolved phase and all three solid site types are identical to those for the 10-minute adsorption case.

6. CONCLUSIONS

1. Radiochemical techniques are ideal for carrying out short term investigations of the partitioning behaviour of organic contaminants in natural waters.

2. The partitioning behaviour of atrazine and g-HCH in fresh and saline waters can be influenced by physicochemical factors such as suspended solids concentration and salinity. However, the effect of such factors may not be critical if partitioning data are to be used in generalised models. For most modelling purposes it may be sufficient to use averaged partition coefficient values.

3. Atrazine exhibits little particulate association at suspended solids concentrations typical of the water column in most estuarine or freshwater environments. For monitoring and compliance monitoring for atrazine the analysis of only dissolved fractions of samples should therefore be sufficient.

4. Salinity gradients may significantly influence atrazine partitioning onto solids at very high suspended solids loadings (>10 g l^{-1}). This observation would only be of relevance from a contaminant fate viewpoint in highly turbid zones such as those that may be encountered immediately above disturbed bed sediment. The salinity correlation with partition coefficient at high solids may be attributed to an ionic strength or salting-out effect.

5. High suspended solids concentrations can result in a decrease in the g-HCH partition coefficient. This effect is probably caused by particle-induced desorption at high particle densities (the so-called 'DiToro' effect). Such effects may be relevant in areas where there are considerable gradients in suspended solids concentrations such as estuaries.

6. Our investigations of colloidal speciation indicate that atrazine and g-HCH do not associate with dissolved organic materials with nominal molecular weights of greater than 1000. Literature information suggests that this is not the case for more hydrophobic contaminants such as PCBs. It has been suggested that the speciation of organic contaminants with dissolved organic macromolecules may play an important role in influencing their bioavailability or toxicity. However, our results indicate that for atrazine and g-HCH interaction with high molecular weight or colloidal species is probably not a major factor.

7. Dialysis of filterable aqueous fractions (nominally <0.45 µm) showed that atrazine and g-HCH residues are present either in true solution or are in association with low molecular weight materials such as fulvic acids. These fractions may be more bioavailable than colloidally associated residues of other contaminants, such as PCBs, that have been shown in other studies to associate more strongly with humic materials.

8. An investigation of the kinetics of g-HCH sorption to estuarine particulates showed that initial equilibration appears to be a rapid process (<5 mins).

   However, other work has suggested that intra-particle diffusive processes may take place over longer time periods, resulting in contaminants becoming less available for desorption with time. These processes were not investigated in this study but are relevant when considering contaminant availability following dredging activities or during resuspension of historically contaminated sediment under storm conditions.

9. Particle concentration effects similar to those observed for atrazine and g-HCH also occur for a variety of trace metal contaminants. However, the extent to which the effects distort partitioning data is less than has been suggested by previous research and is not considered a major obstacle to use of the partition coefficient approach to contaminant modelling.

10. Binding to dissolved phase natural organic ligands or colloids can play a crucial role in controlling the partitioning behaviour of trace metals between 'dissolved' and particulate phases. Prime examples are copper and chromium.

11. The partitioning of cadmium in estuarine environments is dominated by the influence of dissolved phase complexation by chloride ion. In the Humber estuary, the effect is sufficiently prominent that the order of magnitude variability in partition coefficients within the system is effectively eliminated by recalculation of a single free cadmium ion based partition coefficient, after accounting for inorganic complexation at the various salinities.

12. Sequential chemical extraction procedures, despite suffering from some lack of selectivity between operationally defined phases, can provide valuable information on the nature of trace metal binding to aquatic particulate matter and an indication of which forms of particulate bound matter are most relevant in terms of dynamic adsorption/desorption processes *in situ*.

13. Strong contrasts in metal partitioning behaviour are evident between the Humber and Mersey estuaries. For the Humber, the majority of metals show either essentially conservative behaviour, or positive deviations from simple end-member mixing. In the Mersey, however, removal of cadmium, copper, chromium and zinc occurs at the freshwater/saline interface and low salinity regions. The effect is most pronounced for cadmium and copper, and is reflected in very much higher partition coefficients for these elements on Mersey suspended particulates. Discharges of sewage to the upper estuary may have an important bearing on this finding, as both metals are known to exhibit a strong affinity for sewage derived particulate matter.

14. Initial studies of sorption kinetics for trace metals indicate that complex multi-step processes are involved with equilibration times varying from minutes to weeks. For periods up to 200 hours, adsorption of a range of cationic (cadmium, copper, zinc) and anionic (arsenate)

species can be accurately modelled on the basis of three-step first order reversible kinetics. The same model is also capable of predicting desorption kinetics following resuspension of particulate spiked metals over widely varying adsorption timescales.

7. IMPLICATIONS FOR THE NRA

Implications for contaminant monitoring programmes

Partitioning data obtained for atrazine indicate that the analysis of only dissolved phase concentrations should be sufficient for compliance monitoring purposes. Binding to particulate matter need only be considered at very high solids loadings (>10 g l^{-1}), e.g. for samples collected immediately above bed sediments, or for samples collected following storm events where appreciable soil erosion has occurred. However, for compounds of medium hydrophobicity such as g-HCH, analysis of both dissolved and particulate fractions may routinely be required. For instance, at suspended solids levels commonly encountered in the Humber estuary, our data indicates that up to 30% of the g-HCH may be associated with the particulate fraction.

Our studies have clearly demonstrated the existence of solid phase sites exhibiting very slow rates of adsorption and desorption of trace metals. Indications from recent literature are that similar processes are also relevant to organic contaminants. There are important implications for contaminant monitoring programmes here, since laboratory spiking data obtained after short-term equilibration with the sample matrix can no longer be considered an adequate test of analytical method performance. 'Slow' sites, which would not be addressed by such testing, are likely to be much less accessible to typical extraction agents than 'fast' surface sites.

The finding that contaminant partitioning can fluctuate during sample storage implies that, if separate determinations of dissolved and/or particulate concentrations are to be monitored, then samples should be filtered as soon as possible after collection. Ideally, this should be carried out on-site but if this is impractical, then samples should be transferred rapidly to the laboratory and filtered immediately on arrival.

Implications for EQS setting and discharge consents

Most water quality studies either report total contaminant concentrations or at best differentiate between 'dissolved' and particulate forms based on filtration. It is generally accepted that for trace metals it is the free metal ion that is the most bioavailable and hence toxic form, and it has been suggested that the same is true for organic contaminants. At present, environmental quality standards (EQSs) do not differentiate between dissolved and particulate associated organic pollutant fractions. However, data from this study and from other work has shown that this simplistic approach may give a biased view of water quality. For contaminants for which it is accepted that the partitioning to solids markedly reduces toxicity, there is scope for the consideration of an increase in discharge consents above that based on simple conservative dilution in receiving waters. The partitioning data provided in this study can thus assist in the setting and maintenance of the discharge consents of effluents to surface waters.

Implications for future sediment quality criteria

At present there are no accepted standard UK methods for assessing the toxicity of sediment-bound contaminants. Although the equilibrium partitioning (EP) approach provides a useful tool for predicting the environmental impact of particulate associated contaminants in the water column it does have some limitations when applied to bed sediments. One problem with using the EP approach is the fact that water quality standards for single contaminants cannot be readily applied to mixtures and are thus at present only appropriate where a single contaminant is likely to account for most of the adverse toxic effects of a sediment. There are also kinetic implications here, in that contaminants may become irreversibly sorbed to sediments over long periods and consequently be unavailable for release to pore waters and uptake by biota. Furthermore, it is possible, as has been suggested in the case of PAHs (Landrum 1989), that bioavailability of sediment bound contaminants may in some cases be controlled by desorption kinetics.

Implications for contaminant fate modelling

The empirical partition coefficient approach can provide a viable basis for modelling the transport and fate of contaminants in the aquatic environment. Partitioning data provided in the course of this project should prove valuable through incorporation in environmental fate (e.g. EXAMS) and estuarine water quality models employed by the NRA.

Our studies have demonstrated that associations of atrazine and g-HCH with dissolved or colloidal natural organic matter are of minor importance for a range of freshwater and estuarine samples. The use of a single solid:solution phase partition coefficient is therefore recommended for modelling the behaviour of these contaminants. For more hydrophobic organic compounds, on the other hand, there are indications from the literature that partitioning behaviour can be strongly influenced by binding to organic macromolecules. For such cases, the inclusion of a second coefficient to account for these associations will be necessary for effective modelling applications. This also applies for trace metals which demonstrate strong affinities for natural organic ligands, e.g. copper and chromium. Research aimed at determining the concentrations and binding strengths of such ligands is currently being carried out for the NRA at WRc.

Existing sediment transport models developed for the NRA at WRc already incorporate a very simple model for trace metal sorption kinetics. However, these can now be substantially improved by inclusion of the multi-step processes established in the present study.

Implications for further research

It is recommended that research on the equilibrium partitioning of contaminants in freshwater and estuarine systems should be extended to provide further data on the most important factors influencing the partitioning of more hydrophobic compounds than those examined here. Additional data is also required for species of more polar character (e.g. chlorophenols).

The implications of kinetics of sorption processes are most obvious under rapidly changing environmental conditions such as exist e.g. during mixing of freshly discharged effluents with receiving waters, or in response to storm events. Dramatic improvements in our ability to predict contaminant behaviour under such conditions should be achieved by employing a kinetic as opposed to simple equilibrium model. Further information on desorption kinetics would also assist in prediction of the effect of remedial measures on the quality of historically contaminated sediments. Again, the equilibrium partitioning approach may prove inadequate in cases where the contaminant has been bound to particulates over an extended timescale.

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