

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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SUMMARY

I BACKGROUND

The partitioning of contaminants between water and suspended sediment is a major influence on their transport and toxic effects. A better understanding of partitioning is needed for the development of environmental management models.

II OBJECTIVES

To investigate the factors affecting, and the effects of, the partitioning of major organic and inorganic contaminants between the dissolved and particulate phases.

III RESUME

Two concurrent studies on contaminant partitioning are being undertaken, one concerned with the physico-chemical processes controlling partitioning and the other with the influence of partitioning on toxicity. This first progress report is a joint one for the two studies.

For the toxicity study, progress has been achieved in:

- a) Defining biological and chemical requirements for investigating sediment toxicity and the effects of contaminant partitioning.
- b) Culture and test protocol development for two marine species.
- c) Establishing programmes of research into bioavailability and epibenthic species test development.
- d) Identifying species for future investigation, with overall aim of achieving a range of tests covering all aquatic media and routes of exposure.

For the physico-chemical study:

- a) Existing literature has been reviewed and the major factors controlling water/sediment partitioning identified.
- b) Laboratory and field approaches to investigation of partitioning have been critically evaluated.
- c) A programme of research, concentrating initially on the Ouse/Aire/Trent/Humber system, has been started.
- d) The likely influence of dissolved phase natural organic ligands on metal partitioning has been investigated by computer modelling.

SECTION 1 - INTRODUCTION

Although water is sometimes called the "universal solvent", this is a myth. Few chemicals have such a strong association with water 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 ie 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 ie:

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

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

- a) 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.
- b) 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.
- c) A chemical will 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 is the major focus of the two studies for which this is the first progress report. One study is concerned with the physico-chemical

process involved in partitioning and the other is concerned with assessment of the biological implications of partitioning. It is vital that these two studies are closely co-ordinated and in order to emphasise the links this first progress report is a joint one. For the physico-chemical study, the report includes a detailed review of available literature on partitioning of organic contaminants, together with a broad overview of important factors controlling trace metal partitioning. A paper on the influence of natural organic ligands on metal partitioning has also been incorporated as an Appendix.

1.1 PARTITIONING IN THE AQUATIC ENVIRONMENT

The major objective in these two projects is to study and evaluate the significance of solution phase and particulate phase partitioning. These two phases seem to be intuitively distinct and readily distinguishable, however 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 size of particle constitutes a particle? Some "particles" of sand for example may be of comparable size ($\leq 1 \mu\text{m}$) 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. Further it has been demonstrated that pollutants associated with dissolved humic 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 eg filtration, dialysis etc.

SECTION 2 - OVERVIEW OF WATER/SEDIMENT PARTITIONING

2.1 ORGANICS

2.1.1 Introduction

Current interest in the environmental fate of organic contaminants has generated the need for an increased understanding of the degree and nature of partitioning between the dissolved and particle bound phases. An understanding of the factors controlling the transfer of contaminants between these phases in aquatic systems provides a basis for describing the transport, sedimentation, bioaccumulation and biodegradation of organic contaminants of environmental concern. Figure 1 illustrates schematically some of the processes affecting the transport and fate of organic contaminants in the aquatic environment. This review briefly outlines the main physical and chemical factors that influence the partitioning behaviour of organic contaminants.

2.1.2 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.

2.1.3 Equilibrium sorption

Sorption is usually represented graphically in terms of isotherms which show the relationship between the contaminant concentration in the

sorbed phase to that in solution. Sorption equilibrium is attained when the sorbate fugacities in the sorbed (f_s) and aqueous (f_w) phases are equal.

$$f_s = f_w$$

The fugacity of a substance in a given phase is a measure of its escaping tendency from that phase^(1,2).

The fugacity can be related to the pollutant concentration in each phase,

$$C_w = f_w Z_w \text{ and } C_s = f_s Z_s$$

where Z is the fugacity capacity factor of the particular phase concerned.

Assuming a total number of moles M of the contaminant in the system and a volume V for each of the two phases,

$$M = C_s V_s + C_w V_w$$

$$= f_s (V_s Z_s + V_w Z_w)$$

Mackay et al⁽³⁾ defined fugacity capacities as follows:

$$Z_w = 1/H = S/p$$

where S is solubility, P is vapour pressure and H is the Henry's Law constant

$$Z_s = \frac{K}{H}$$

where K is the partition coefficient for the contaminant between the solid phase and water.

The partition coefficient of a contaminant can be expressed as the ratio of sorbate fugacity capacity (Z_s) and solute fugacity capacity (Z_w).

$$\text{ie } \frac{C_s}{C_w} = \frac{Z_s}{Z_w} = K$$

In general it is impracticable to directly measure the partition coefficient (K) for all organic contaminants in natural waters because of their diversity and because of the complexity of sorbing material (suspended particles, biota etc). As a result estimations of partitioning have usually involved the measurement of other physical properties eg solubility, which are correlated to partitioning to predict partitioning behaviour.

2.1.4 Partition coefficient

Equilibrium partitioning can be represented by a partition coefficient K_p .

$$K_p = \frac{\text{mass of compound/g. solid}}{\text{mass of compound/ml. solution}}$$

K_p is really an 'apparent' partition coefficient since it has been found that for non-polar organics the partitioning to solids is related to their organic carbon content and a more useful parameter is K_{oc} where

$$K_{oc} = K_p \frac{1}{f_{oc}}$$

(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. Many relationships have been derived two of the most widely used link K_{oc} to octanol-water partition coefficient (K_{ow})⁽⁴⁾ and solubility⁽⁵⁾:

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

and

$$\log K_{oc} = -0.54 \log S + 0.44$$

Kow is defined as the partition coefficient between octanol and water and was first introduced in the study of the physical chemistry of pharmaceuticals. It has been frequently used to predict the bioconcentration of organic contaminants by fish⁽⁶⁾.

Empirical relationships between octanol-water partitioning coefficients and solubility allows values for Koc to be estimated for many physically different contaminants by using pre-determined and catalogued physical parameters.

2.2 TRACE METALS

2.2.1 Nature of binding

Natural aquatic particulate matter is a complex mixture of geochemical phases, exhibiting widely varying metal binding characteristics.

However, considerable experimental evidence exists^(7,8) 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⁽⁹⁾ (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⁽¹⁰⁾.

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⁽¹¹⁾ 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.

SECTION 3 - FACTORS CONTROLLING WATER/SEDIMENT PARTITIONING

3.1 ORGANICS

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 review of these various factors is presented. The effects of a variety of factors on sorption* processes in soil have been extensively reviewed^(12,13,14) and hence this review will concentrate 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.

- * sorption - accumulation of dissolved substances by solid particles
- sorbent - sediment or dissolved organic matter
- sorbate - contaminant

3.1.1 Solubility

The solubility of a chemical in water may be defined as the maximum amount of the chemical that will dissolve in pure water at a specified temperature. 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⁽¹⁵⁾. Apart from temperature, solubility is also influenced by other parameters such as salinity, dissolved organic matter and pH. These factors will be discussed separately.

Karickhoff et al⁽⁵⁾ investigated the relationship between coarse silt and clay particle adsorption and sorbate aqueous phase concentrations ie $X = K_p C$.

where X = concentration of sorbate on the sediments
 C = equilibrium solution sorbate concentration
 K_p = partition coefficient

At sorbate water concentrations approaching 60-70% of the sorbate aqueous solubility the sorption isotherms deviated from linearity indicative of increased sorption. The adsorption isotherms for pyrene and methoxychlor were within experimental error of the respective desorption isotherms, hysteresis effects were not observed and the sorption appeared to be reversible.

Chiou et al⁽¹⁶⁾ experimentally determined the n-octanol-water partition coefficients and aqueous solubilities of a variety of organic compounds including aliphatic and aromatic hydrocarbons, organochlorine and organophosphorus pesticides and PCB's (Table 1). A linear relationship was observed between log (octanol-water partition coefficient) and log (aqueous solubility) which covered a wide range of solubilities (10^{-3} to 10^4 ppm) and partition coefficients (10 to 10^7) (Figure 2).

Water solubility is commonly used to estimate partition coefficients using empirical linear regression equations. Means et al⁽¹⁷⁾ found a significant negative correlation between log K_{oc} and log water solubility for a group of polynuclear aromatic hydrocarbons (pyrene, 3 methylcholanthrene, dibenzanthracene and 7,12 dimethyl benz-a-anthracene).

$\text{Log } k_{oc} = -0.82 \text{ log water solubility} + 4.07$ ($r^2 = 1.000$) (Table 2).

Table 1 - Solubilities and partition coefficients of various compound⁽⁶⁾

Compound	Solubility in water, ppm	Log (n-octanol/ H ₂ O partition coeff
Benzene	820 (22 °C)	2.13
Toluene	470 (16°)	2.69
Fluorobenzene	1540 (30°)	2.27
Chlorobenzene	448 (30°)	2.84
Bromobenzene	446 (30°)	2.99
Iodobenzene	340 (30°)	3.25
p-Dichlorobenzene	79 (25°)	3.38
Naphthalene	30	3.37
Diphenyl ether	21 (25°)	4.20
Tetrachloroethylene	400 (25°)	2.60
Chloroform	7950 (25°)	1.97
Carbon tetrachloride	800	2.64
p,p'-DDT	0.0031-0.0034 (25°)	6.19
p,p'-DDE	0.040 (20°)	5.69
Benzoic acid	2700 (18°)	1.87
Salicylic acid	1800 (20°)	2.26
Phenylacetic acid	16 600 (20°)	1.41
Phenoxyacetic acid	12 000 (10°)	1.26
2,4-D	890 (25°)	2.81
2,4,5,2',5'-PCB	0.010 (24°)	6.11
2,4,5,2',4',5'-PCB	0.00095 (24°)	6.72
4,4'-PCB	0.062 (20°)	5.58
Phosmet	25 (25°)	2.83
Malathion	145 (20°)	2.89
Fenitrothion	30	3.38
Dicapthon	6.25 (20°)	3.58
Parathion	24	3.81
Phosalone	2.15 (20°)	43.0
Methyl chlorpyrifos	4.76 (20°)	4.31
Dialifor	0.18	4.69
Ronnel	1.08 (20°)	4.88
Chlorpyrifos	0.4 (23°)	5.11
Dichlofenthion	0.245 (25°)	5.14
Leptophos	0.0047 (20°)	6.31

Table 2 - Water solubilities and octanol-water partition coefficients for selected PAHs⁽¹⁷⁾

Compound	Water solubility µg/L	Octanol-water partition coeff, K_{ow}
Pyrene	135 ± 13	124 000 ± 11 000
7,12-dimethylbenzanthracene	24.4 ± 4.2	953 000 ± 59 000
3-methylcholanthrene	3.23 ± 0.17	2 632 000 ± 701 000
1,2,5,6-dibenzanthracene	2.49 ± 0.81	3 170 000 ± 883 000

Mailhot and Peters⁽¹⁵⁾ used regression analysis to relate partition coefficients to solubility for 300 organic compounds from 10 chemical families. Figure 3 shows the linear relationship between log K_{ow} and log solubility for 66 halogenated hydrocarbons and 14 organophosphates. Schwarzenbach et al⁽¹⁸⁾ reported good correlation between octanol-water partition coefficients and aqueous solubility for a group of mono- and di-nitrophenols.

The predictive capabilities of aqueous solubility sorption models can be improved when the 'crystal energy' contribution of solutes that are solids at room temperature are taken into account⁽¹⁹⁾.

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 sorption of hydrophobic compounds by solid materials has been reported by a number of investigators^(20,21,22,23).

The hydrophobicity or lipophilicity of organic compounds can be expressed as the octanol-water partition coefficients, K_{ow} . K_{ow} is a distribution coefficient of solute monomers between an aqueous phase and an octanol organic phase⁽²⁴⁾.

Karickhoff et al⁽⁵⁾ described a linear relationship between K_{oc} and K_{ow} (Figure 4).

$$K_{oc} = 0.63 K_{ow} (r^2 = 0.96)$$

$$\text{or } \log K_{oc} = 1.00 \log K_{ow} - 0.21 (r^2 = 1.00)$$

They investigated sediment/water systems where the aqueous solution concentration for the aromatic and chlorinated hydrocarbons studied (Table 3) were considerably below the water solubility of the compounds. As the water solubility was approached the K_{ow} value showed a slight dependence on compound concentration. The concept of linear partitioning is assumed to be valid only at low solute concentrations. It is likely that linear partitioning will be observed in the natural aquatic environment since organic contaminants are usually present at concentrations below their aqueous solubility (trace levels). The use of the octanol-water partition coefficient as a key parameter in assessing the potential environmental behaviour of hydrophobic chemicals is now well established.

Table 3 - Sorption dependence on sorbate properties⁽⁵⁾

Compound	Water solubility		K x 10 ⁻³	K x 10 ⁻³	$\frac{K_{oc}}{K_{ow}}$
	Mole reaction x 10 ⁹	ppb			
Pyrene	12	135	84	150	0.56
Methoxychlor	6.3	120	80	120	0.67
Naphthalene	4 460	31 700	1.3	2.3	0.57
2-Methylnaphthalene	3 220	25 400	8.5	13	0.65
Anthracene	7.57	73	26	35	0.74
9-Methylantracene	24.4	261	65	117	0.56
Phenanthrene	130	1 290	23	117	0.62
Tetracene	0.037	0.5	650	800	0.81
Hexachlorobiphenyl	0.048	0.95	1 200	2 200	0.55
Benzene	410 000	1 780 000	0.083	0.13	0.64

Deviations from the linear relationship between K_{oc} and K_{ow} have been observed with compounds of high hydrophobicity (log K_{ow} >5) and has been

attributed to their higher affinity for non-settling microparticles or organic macromolecules (colloids) that remain in the aqueous phase during laboratory sorption tests leading to an enhancement of the apparent aqueous phase concentration and an underestimation of the sorption coefficient^(25,26). Schrap and Oppenhuizen⁽²⁷⁾ have suggested the use of a reference compound (not sensitive to the third phase) to quantify the sorption of hydrophobic contaminants on sediments, ie differences between sediments normalised with a reference chemical rather than with organic carbon content.

3.1.3 Volatility

Vaporisation is an important transfer pathway for organic chemicals from aqueous systems to the atmosphere⁽²⁸⁾. The physico-chemical 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 volatisation rate.

The partition coefficient between water and air, H (Henry's law constant) can be calculated using the following formula:

$$H = \frac{C_{air}}{C_{water}} = \frac{16.04 P M}{TS}$$

C_{air}, C_{water} are equilibrium concentrations in the air and water phases

P = vapour pressure of the pure solute

M = gram molecular weight of solute

T = temperature

S = solubility of solute in water (ppm)

Organic compounds such as hydrocarbons and chlorinated hydrocarbons (eg PCB's) have high activity coefficients in water and therefore will evaporate at high rates and have short half lives in water bodies⁽²⁹⁾.

Low molecular weight polycyclic aromatic hydrocarbons (PAH's) possess properties which suggest that their volatility in solution may be significant as compared with the higher molecular weight PAH's (4 or more aromatic rings)⁽³⁰⁾. Readman *et al*⁽³¹⁾ showed increasing particulate affinity (higher log Kp) with molecular weight of PAH's in Tamar Estuary sediments. Benz-a-pyrene showed 100 times greater affinity for Tamar sediment than the more volatile PAH's such as naphthalene. Naphthalene, phenanthrene and anthracene characterised by high solubility and vapour pressure exhibited a complex distribution in the estuary and were significantly enriched in the water while the higher molecular weight PAH's were found in surface sediments and suspended particulates.

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.

Wijayarathne and Means⁽³²⁾ found a significant decrease in the sorption of benzene, naphthalene and anthracene to natural estuarine colloids when the ambient pH (8.01) of natural water was decreased to 5.0 or increased to 9.0. The decrease in Koc values was attributed to changes occurring within the polymeric structure of the colloids (Figure 5).

Horzempa and Di Toro⁽³³⁾ studied the effect of systematic variations in pH on the adsorption of 2,4,5,2',4',5' hexachloro biphenyl to 200 mg l⁻¹ suspensions of montmorillonite clay. Partition coefficients (ratio of adsorbed concentration ng kg⁻¹ to aqueous concentration ng l⁻¹) decreased as solution pH levels were increased from pH 6 to pH 8. Values of partition coefficients for acidic solutions (pH <6) were 2-3

times greater than those observed under more basic conditions ($\text{pH} > 7$) (Figure 6).

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. pH was found not to have any significant effect on the sorption of dieldrin to montmorillonite clay (a major constituent of aquatic sediments)⁽³⁴⁾.

An example of the effect of pH on the speciation of an organic contaminant is provided by quinoline. Quinoline is an organic base which when solution pH is below the compound pKa (4.9) exists primarily as a cation. Quinoline adsorption was markedly higher in acid sub-soils (preferential adsorption of the cationic species) than in basic sub-soils⁽³⁵⁾, suggesting a cationic adsorption mechanism as the major mode of quinoline binding. The neutral quinoline molecule is weakly sorbed when particulate organic carbon is low, therefore contrasting sorption behaviour is observed for the cationic and neutral form.

Sorption of non-dissociated chlorophenols and their conjugate bases (phenolates) has been described by Schellenberg *et al*⁽³⁶⁾. In natural waters where the pH does not exceed the pKa of the phenol by more than one log unit phenolate sorption could be neglected, although highly chlorinated phenols such as tetra- and pentachlorophenol are present in water at ambient pH as phenolate anions (an increase in the number of chloro substituents leads to an increase in acidity and hydrophobicity; thus the phenols with more chloro substituents are more likely to be ionised at environmental pH values). Sorption of these ionic species (phenolate) has to be considered in studies of the transport and the fate of these compounds (Figure 7).

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⁽³⁷⁾:

$$\log (S_o/S) = K_s C_s$$

where S and S_o are the molar solubilities in salt solution and pure water respectively, K_s 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.

In experiments designed to evaluate the effect of solution ionic strength on 2,4,5,2'4'5' hexachlorobiphenyl adsorption the NaCl concentrations of 200 mg l⁻¹ montmorillonite suspensions were systematically varied⁽³⁸⁾. The partition coefficient appeared to be only slightly influenced by increasing sodium chloride concentration from 10⁻⁴M to 10⁻²M (Figure 8).

CaCl₂ exerted a different effect; the partition coefficient increasing from 11 000 l kg⁻¹ to >25 000 l kg⁻¹ over a 10⁻⁴M to 10⁻²M concentration range. This was explained by increased aqueous Ca²⁺ concentrations flocculating fine suspended clay particles that have been reported to resist centrifugation⁽³⁸⁾. The removal from solution of HCBP adsorbed on to such particles would have the effect of decreasing measured values of aqueous concentration of HCBP and increasing the calculated value of the partition coefficient.

Incremental addition of NaCl (0-20 mg ml⁻¹ in 2 mg ml⁻¹ increment) to a silt-pyrene suspension resulted in a linear increase in K_p (a 15% increase in K_p with 20 mg ml⁻¹ salt content)⁽⁵⁾.

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⁽³⁹⁾ and Landrum et al⁽⁴⁰⁾ 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.

The solubilisation of hydrophobic organic pollutants in water by humic materials has been reported^(26,41).

Addition of DOC to the aqueous phase reduced the sorption of DDT to sediments but had no effect on the sorption of lindane; DDT binds strongly to humic material but lindane only slightly. The DOC increased the amount of DDT in the soluble phase⁽⁴²⁾, Figure 9. In the absence of added DOC the sediment-water partition coefficient for DDT was 20,650; in the presence of 6.95 mg l⁻¹ added DOC, K_p was 5170. As illustrated in Figure 9a addition of DOC to the aqueous phase had no observed effect on the sediment water partitioning behaviour of lindane, K_p 84 and 90 in the absence and presence of added DOC respectively. Lindane does not appear to bind to a significant extent to humic materials.

O'Connor and Connolly⁽⁴³⁾ proposed that the observed decrease in sediment-water partition coefficient with increasing sediment concentration could be explained by the release of dissolved organic colloidal material from the sediment to the water phase. The amount of this material released increases with the sediment: water ratio (non-settling microparticles)^(44,25).

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 eg DDT, the actual aqueous phase concentration may be significantly greater than the freely dissolved concentration⁽⁴⁵⁾ in the presence of DOC.

Landrum et al⁽⁴⁸⁾ used column chromatography in the form of Sep-pak C₁₈ cartridges to separate humic bound pollutants (benzo[a]pyrene, anthracene, biphenyl, pp'DDT, PCB) from freely dissolved pollutant (humic bound pollutant passed through while the unbound pollutants were retained by the cartridge). This showed that the partition coefficients

(grams of pollutant bound per gram of organic carbon + grams of pollutant freely dissolved per millilitre) did not depend on pollutant concentration but was inversely proportional to the concentration of dissolved organic carbon in solution. At low DOC (1-2 mg humic acid l^{-1}) the partition coefficient was equal to the octanol-water partition coefficient. A decrease in apparent partition coefficients with increased humic acid concentration had been previously reported⁽³⁹⁾.

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^(46, 47, 48).

Dissolved humic material can compete with sediment or suspended particles for binding of contaminants (the binding can be reversible with an affinity comparable to that of the organic content of sediment particles⁽⁴⁹⁾). The empirical regression equation determined for DOC was $\log K_{ow} = 0.97 \log K_{doc} + 0.48$ which is similar to the relationship between K_{ow} and $K_{particulate\ OC}$ ⁽⁵⁾ (viz $\log K_{oc} = 1.00 \log K_{ow} - 0.21$) Wijayarathne & Means⁽³²⁾ carried out quantitative sorptive studies of PAH's on natural estuarine colloids. They compared K_{oc} values for benzene, naphthalene and anthracene on natural colloidal material and found them to be high when compared with pond sediment K_{oc} values.

	K _{oc} (estuarine colloidal organic matter)	K _{oc} * (sediment)
Benzene	920	83
Naphthalene	4060	1300
Anthracene	510000	2600

* Karickhoff et al⁽⁵⁾

Previous studies with the herbicides atrazine and linuron had suggested that colloidal organic matter was of the order of 10-35 times better as a sorptive substrate than sediment organic matter⁽⁵⁰⁾.

3.1.7 Particulate organic carbon

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^(51,52) and Kenaga and Goring⁽⁵³⁾.

The partitioning of hydrophobic compounds between water and particulate organic carbon is normally described by a linear sorption isotherm.

$$C_s = K_p C_w$$

C_s = concentration of compounds on the sediment

C_w = concentration of compounds in water

K_p ($l\ kg^{-1}$) = partition coefficients

This applies rigorously only to adsorption partitioning processes in which the equilibrium solution phase concentration is very low ($<100\ \mu g\ l^{-1}$).

Sediments are heterogeneous materials with varying chemical composition and particle size distributions; thus the K_p value for a contaminant varies with different sediment, to reduce this variability it is customary to normalise K_p values with measurable sediment properties. Several investigators^(5,17,54) have observed that sorption of hydrophobic organic compounds can be correlated to the organic carbon content of the sorbent. Karickhoff et al⁽⁵⁾ 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 (particulate organic carbon partition coefficient)

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

—
f_{oc}

(f_{oc} = fractional mass of organic carbon in the sediment.)

Karickhoff et al⁽⁵⁾ observed a generally good relationship between K_p and K_{oc} but noted deviations for sandy soils having a low organic carbon content (f_{oc} < 0.001). The K_{oc} values in the latter cases were lower by approximately a factor of two than those determined for high organic content silty sediments. A similar effect was observed for the sorption of lindane on a high organic carbon soil and a sandy low organic carbon aquifer material⁽⁵⁵⁾. Garnas et al⁽⁵⁶⁾ demonstrated that the highest partitioning of kepone occurred with a sediment fraction (clay) exhibiting the highest percentage of organic matter (Figure 10).

'Carbon-referenced' sorption has been tested for a wide variety of compounds and sediment/soils^(53,57). Agreements between calculated and measured K_{oc}'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 (10^3 - 10^4 fold difference).

3.1.8 Particle size

Sediment particle size has been identified as a secondary factor in the sorption of hydrophobic chemicals to natural sediments⁽⁵⁾. The primary particle size effect was a reduction of Koc for sand particles (>50 μm) relative to Koc for sediment fines (<50 μm). Karickhoff and Brown⁽³⁸⁾ studied the distribution of sorbed paraquat as a function of particle size (sand through to clay) in five natural sediments. Adsorption isotherms were measured for individual size fractions on one sediment; sand (>64 μm), coarse silt (64-20 μm) medium clay (0.2-0.08 μm). Paraquat concentration peaked in clay or fine silt fractions and showed a 20-50 fold reduction in the medium and coarse silts and a 1000 fold reduction in sand (Table 4 and Figure 11).

Table 4 - Paraquat distribution in natural sediments⁽³⁸⁾

Size fraction *	Total fraction mass g	Total paraquat mg	Sediment paraquat conc ppm	Paraquat as % of CEC
Georgia local stream I				
Sand	833.0	0.8	1	0.26
C silt	44.9	0.9	21	0.35
M silt	32.7	1.7	52	0.69
F silt	14.0	4.6	330	3.3
C clay	13.6	13.6	1000	4.6
M clay	0.53	0.4	760	-
F clay	0.40	0.06	150	-
* C = coarse, M = medium, F = fine				
% Paraquat recovered = 90%				

Generally an inverse relationship between particle size and sorption has been observed^(22, 58). Variations in partition coefficients for a given hydrophobic organic chemical among different sediments and among different size fractions within a given sediment can be related to differences in organic carbon content⁽⁵⁷⁾.

In natural aquatic sediments the particle size (and settling speeds) vary over a wide range; for a typical sediment this range may be over two orders of magnitude for particle diameters. Particle size and settling speeds (if particle is spherical with a known density) are related by Stokes' Law

$$W_s = \frac{gd^2}{18\mu} (ps-p)$$

W_s = settling speed
 d = particle diameter
 ps = particle density
 μ = viscosity of water
 p = density of water

In reality, most particles are not spherical and individual particles tend to aggregate together into flocs (groups of particles tightly bound together). Because of this aggregation the effective diameter and density of a particle can change with time and the diameter and the settling speed of such particles are not related by Stoke's Law. Aggregation of particles depends on the rate of particle collisions which itself is primarily dependent on Brownian motion, differential settling and fluid shear. The aggregation of particles may have a significant effect on the sorption of contaminants and their transport to sediments. 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.

3.1.9 Suspended solid 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 (see section on particulate organic carbon) and biological detritus (including a living bacterial/algal population).

Lotse et al⁽⁷³⁾ demonstrated that lindane (γ -hexachlorocyclohexane) adsorption on to a lake sediment was affected by sediment suspension concentration, lindane to sediment ratio and lindane concentration as well as organic matter content. By varying the sediment concentration (varying the amount of lake sediment added to 40 ml of lindane solution with an initial concentration of 1.86 ppm) the amount of lindane sorbed per milligram of sediment varied. Figure 12 shows that the lindane to sediment ratio has a pronounced effect on the extent of lindane adsorption. At a ratio of 0.1 microgram lindane per milligram of sediment 90% of the lindane was adsorbed by sediment 6, 40% by sediment 4. At 2 microgram lindane per milligram of sediment 30% and 8% of the added lindane was adsorbed by sediment 6 and 4 respectively.

An inverse relationship was described⁽⁴³⁾ between particle (adsorbing solid) concentration and partition coefficient. Partition coefficients were observed to increase as much as an order of magnitude for every order of magnitude decrease in solids concentration (Figure 13).

A significant increase in partitioning of four hydrophobic pollutants (chlorobenzene, naphthalene, 2,5,2'-trichlorobiphenyl and 2,4,5,2',4',5'-hexachlorobiphenyl) between water and lake sediments as solids concentration decreased was reported by Voice et al⁽⁴⁴⁾, confirming the findings of O'Connor and Connolly⁽⁴³⁾. The study was conducted at solute concentrations as close as possible to those found in the natural environment (Figure 14). After least squares multiple linear regression analysis of the data the following equation was developed.

$$\log K_{oc} = 0.748 \log K_{ow} - 0.648 \log S - 0.131 \log f_{oc} + 0.364$$

where

S = solids concentration in milligrams per litre

K_{oc} = organic carbon normalised partition coefficient

f_{oc} = fraction of solids by weight composed of organic carbon

K_{ow} = octanol/water partition coefficient

The observed change in the partitioning behaviour due to solids concentrations was suggested as being due to a transfer of sorbing (solute binding) material from the solid phase to the liquid phase during the course of the partitioning experiment. This material is not removed from the liquid phase during the separation procedure and leads to an overestimate of the solution phase concentration. The amount of material contributed to the liquid phase (proportional to the amount of solid phase present) was suggested to be a measure of the capacity of the liquid phase to accommodate solute which in turn depends on the concentration of solids in the system.

In contrast to the findings already described Karickhoff et al⁽⁵⁾ reported that their isotherms for pyrene and methoxychlor on several

sediments were independent of sediment concentration ($10^3 - 4 \times 10^5 \text{ mg l}^{-1}$) in dilute suspensions ie changes in sediment concentration did not affect partitioning. Decreasing adsorbent concentration from 10^6 mg l^{-1} to $3 \times 10^5 \text{ mg l}^{-1}$ resulted in a significant increase in 2,4,5-T adsorption⁽⁵⁹⁾.

Further conflicting opinions were put forward by Bowman and Sans⁽⁶⁰⁾ who obtained adsorption isotherms for several insecticides (parathion, dieldrin, chlorpyrifos) in sandy loam and found no evidence that altering adsorbent concentration exerted any influence on the partitioning of insecticides between adsorbent and solution phases.

A study of the effect of sediment concentration on PCB sorption to lake sediment and clay⁽³¹⁾ showed that partition coefficients increased as sediment concentration decreased from 1000 mg l^{-1} to 50 mg l^{-1} (Table 5).

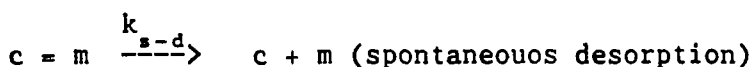
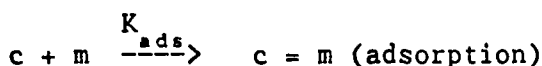
Table 5 - Isotherm parameters⁽³¹⁾

Adsorbent	Aqueous phase	Adsorbent concentration (m) mg/L	Partition coefficient (π_a) L/kg
Saginaw Bay Station No 50	Distilled water	55	17 100 (0.27)*
Saginaw Bay Station No 50	Distilled water	220	12 300 (0.14)
Saginaw Bay Station No 50	Distilled water	1 100	9 910 (0.20)
Montmorillonite	Distilled water	50	10 600 (0.40)
Montmorillonite	Distilled water	200	6 690 (0.09)
Montmorillonite	Distilled water	1 000	2 900 (0.20)
Montmorillonite	2 mM NaHCO ₃	55	16 200 (0.26)
Montmorillonite	2 mM NaHCO ₃	1 100	2 100 (0.19)

* Coefficient of variation

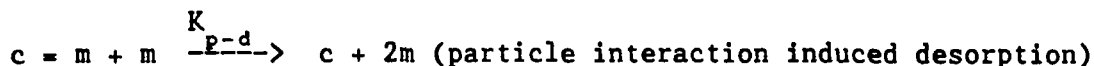
Carter and Suffet⁽³⁹⁾ have suggested the possibility that dissolved organic materials may cause the decline in partition coefficients with higher suspended solid loading. Gschwend and Wu⁽²⁵⁾ have demonstrated that non-settling organic material (micro or macroparticles) have an impact on observed partition coefficients (ie the existence of a third sorbing phase which is not removed from the supernatant by separation techniques such as centrifugation). Variations in the concentration of this non-settling matter would explain the variations in Kp.

A second explanation of the suspended solids concentration effect was put forward by Di Toro⁽⁶¹⁾ who in order to explain the effect of solids on partitioning proposed a 'particle interaction' model that involved an additional desorption reaction. Particle-particle collisions would be sufficiently energetic to dislodge the accumulated contaminant and at a higher particle concentrations collisions are more frequent. This was expressed in terms of rate constants:



where c = chemical concentration in water mg l⁻¹
m = particle concentration
c+m = reversibly sorbed chemical concentration

Additional desorption reaction



The sorption process is viewed as being a loose surface accumulation which can be disrupted by collisions between particles. Mass transfer analysis predicted that when a significant fraction of the sorbate is sorbed, collision induced desorption becomes important and limits the sorbed concentrations to approximately an equal amount to that in solution.

3.1.10 Temperature

Temperature is an important parameter that influences the rate of chemical and biological processes in aquatic systems and its role in affecting sorption processes has been considered in several studies. Huang⁽³⁴⁾ reported no effect on the sorption of dieldrin to montmorillonite clay in the temperature range 10-30 °. A significantly reduced adsorption on aquifer sand at 40 ° compared with 5 ° for lindane and dieldrin has been reported⁽⁵⁸⁾. Zachura et al⁽³⁵⁾ measured sorption isotherms for quinoline on acid and basic sub-soils at 5 °, 15 ° and 35 ° in order to define the temperature induced variation in sorption. Highest adsorption occurred at 5 °, least at 35 °.

3.1.11 Molecular surface area

Doucette and Andren⁽⁶²⁾ developed a relationship between the calculated total molecular surface area (TSA) and the octanol/water partition coefficient (Kow) for hydrophobic compounds such as PCB's, polychlorinated dioxins and polychlorinated furans. Regression analysis showed that the relationship could be expressed as a linear function:

$$\log Kow = 0.0238 (TSA) - 0.142 \quad (R^2 = 0.924)$$

Hawker and Connell⁽⁶³⁾ reported that the TSA of thirteen PCB congeners was highly significantly correlated with log Kow. However since TSA is also highly correlated with water solubility it seems likely that it is simply acting as an alternative measure for hydrophobicity.

3.1.12 Sediment surface area

Hiraizumi et al⁽⁶⁴⁾ suggested that sediment surface area may play a significant role in partitioning. The percentage of the fine particle portion of the sediment ie the ratio of the fine mud under 50 µm in particle diameter to the whole sediment, was found to be proportional to the specific surface area of the sediment. Representative particle size of every sieved fraction of sea bed sediment was observed to have an inverse relation to its specific surface area suggesting that the average particle size correlates to its specific surface area among the

adsorbing materials of similar properties. The same relationship was examined for various adsorbing agents - phytoplankton, zooplankton, coarse sand, activated and acid clay. Irrespective of vast differences in particle properties the specific area of the particle seems to be proportional to the reciprocal of the average particle size. Correlations were obtained between specific surface area and PCB concentration factor of adsorbing material. The surface area dependence therefore seems to be another surrogate for particle size (see 3.1.8)

3.2 MEASUREMENT OF PARTITIONING

When sorption measurements are made in the laboratory the main objective is to determine the change in solution concentration when a known volume of solution is equilibrated with a known amount of adsorbent ie sediment. The data is plotted as an adsorption isotherm (equilibrium plot of C_s versus C_w).

Figure 15 shows typical isotherms for the adsorption of organic compounds on sediment from dilute aqueous solution.

Figure 15(a) indicates that K_p is constant and equal to the slope of the isotherm. Linear adsorption isotherms are commonly found for low molecular-weight organic solutes with low aqueous solubilities at very low concentration (less than half their aqueous solubility). The isotherms are linear because the solute/sediment interaction is non-specific ie hydrophobic solute does not interact strongly with specific surface sites in the sediment.

Typical non-linear adsorption isotherms are shown in Figure 15(b) where the slope of the isotherm decreases and in Figure 15(c) where slopes increase with increasing concentration. These isotherms are typically fitted to the Freundlich equation:

$$C_s = K_f C_w^{1/n}$$

and are defined by the Freundlich parameters K_f and n . K_f increases with C_w for $n < 1$ and decreases with C_w for $n > 1$.

Non-linear isotherms in the dilute concentration range indicate that the organic solute is adsorbing on specific sites on the sediment.

The Langmuir isotherm shown in Figure 15(d) is characterised by an initial linear portion followed by a decrease in isotherm slope to a limiting plateau. This type of isotherm results from adsorbate molecules filling a finite number of adsorption sites.

In this review attention is focused on the sorption of hydrophobic solutes. Hydrophobic solute sorption is generally non-specific and the adsorption isotherms are linear. This makes it possible to normalise the slope of the isotherm with the organic carbon content of the sediment.

3.2.1 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 $m(g)$ of sediment is added to a known volume $V (ml)$ of solution of known initial concentration $C_w^o (\mu g\ ml^{-1})$. The suspension is agitated and after equilibrium is achieved the sediment and solution are separated usually by centrifugation. The equilibration concentration of the supernatant C_w^* is measured and the change in solution concentration ($\Delta C = C_w^o - C_w^*$) attributed to sorption in the sediment. The amount sorbed at equilibrium is calculated from

$$C_s^* = \frac{V\Delta C}{m}$$

Measurement of C_s^* at several values of C_w^o gives the adsorption isotherm. Chemical losses due to volatilisation, adsorption on container walls, photochemical reactions, biodegradation must be accounted for in blank runs without sediment present.

In the flow equilibration methods⁽⁶⁵⁾ solution of known concentration C_o is continuously passed through a column of adsorbent of mass m . The

concentration of the effluent solution is monitored and the amount sorbed is calculated by integrating the breakthrough curve as a function of time after accounting for the dead volume of the apparatus. The flow method has certain advantages. Measurements of the amount sorbed are more precise. Sample handling is minimised and volatilisation losses can be eliminated if the effluent is continuously monitored on-line.

Because of their simplicity batch methods continue to be used almost exclusively to study sorption on sediments.

3.2.2 Octanol/water partitioning coefficients (K_{ow})

The magnitude of the partition coefficient for a specific organic compound (pollutant) in a particular system is often related to the octanol/water partition coefficient of the pollutant. Measurement of K_{ow} by traditional centrifugation (centrifuge tube) or shake flask methods are very time consuming^(66,67,68,69). The use of alternate methods has been suggested for highly hydrophobic compounds (log K_{ow} >5)⁽⁶²⁾ since their precise concentration in the aqueous phase is difficult to measure in small volumes, also emulsion problems arise.

(a) Generator column technique⁽⁷⁰⁾

In this method an octanol solution of the compound is sorbed to a solid support in a column. The quantity of the compound in a mobile phase of water or octanol saturated water which is passed through is determined.

(b) Gas or Liquid Chromatographic solute retention data

A highly significant linear relationship between log K_{ow} and log of the relative retention time on a non-selective GC stationary phase has been reported^(63,71). Rapaport and Eisenreich⁽⁷²⁾ determined the K_{ow} of 58 polychlorinated biphenyl congeners of Aroclor 1242 and 1254 mixtures by reverse phase C₁₈ HPLC. The method was rapid and clean (emulsion formation did not occur) compared with traditional methods. The linear regression $\log K_{ow} = 2.88 + 3.37 \log k^1$ was

developed where k^1 = capacity factor of the solute

($k^1 = \frac{tr-to}{to}$) tr = retention time of solute

to to = void volume retention time

other investigators have developed empirical correlations between Kow and HPRPLC retention time for hydrophobic organic compounds⁽⁷³⁻⁷⁸⁾.

3.2.3 Direct measurement of sediment/water partitioning

Karickhoff et al⁽⁵⁾ reported isotherm determinations involving the equilibration of variable concentrations of compounds with constant concentration of sediment. The amount of compound added to the sediment sample was chosen to give 50% and 10% respectively of the compound's water solubility. Subsequent to compound-sediment equilibration, suspensions were either centrifuged at 20 000 rpm for 60 minutes (stainless steel or glass tubes fitted with teflon lined screw caps) or filtered through 'Zitex' membranes (2-5 μm pore size). Filtering and centrifugation separations gave comparable isotherms.

(a) Dialysis technique

Carter and Suffet⁽³⁹⁾ 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 4 days at 25 °. 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 (Figure 16).

(b) Reverse phase technique-separation on Sep-pak C₁₈ cartridges

A reverse-phase separation technique was described by Landrum et al⁽⁴⁰⁾ to determine the binding of ¹⁴C-radiolabelled organic pollutants such as PAH's, PCB's to humic materials in aqueous solution. The humic-bound pollutant was separated from the 'freely dissolved' pollutant by using a Sep-pak C₁₈ cartridge. Humic bound pollutant passed through while the unbound pollutants were retained on the cartridge. The reverse phase partition coefficients tended to decrease as the humic acid concentration increased.

(c) Reverse phase technique-liquid chromatography

Rapaport and Eisenreich⁽⁷²⁾ suggested that the partitioning behaviour of an organic solute between the reverse phase, stationary phase and the mobile phase in a HPRPLC system is analogous to that involved in water:sediment/soil sorptive processes and proposed the use of this technique (already described for K_{ow}) for estimating sediment partition coefficients. Chin et al⁽⁷⁹⁾ correlated HPRPLC retention parameters to organic carbon normalised partition coefficients (K_{oc}). The results yielded a relationship between log K_{oc} and log solute retention time (t_c).

$$\log K_{oc} = 2.78 \log t_c + 2.17$$

(solutes: carbon tetrachloride, cis-chlordane, 1,2,4 trichlorobenzene, 4,4'PCB, 2,5,2'PCB, 2,2,'4,5 PCB and lindane). (Table 6 and Figure 17).

Table 6 - Logarithms of normalised carbon partition coefficients and retention times for target compounds⁽⁷⁹⁾

Compound	log (K_{oc})	Log(t_c)
2,2',4,5-PCB (OSH)	5.64	1.22
2,5,2'-PCB (OSH)	5.21	1.06
4,4'-PCB (OSH)	5.27	1.13
Chlordane (OSH)	5.57	1.25
Trichlorobenzene (OSH)	4.61	0.89
CCl ₄ (Michawye)	2.62	0.39
Lindane (Michawye)	3.42	0.67
1,2,4-TCB (Michawye)	3.98	0.89
2,5,2'-PCB (Michawye)	4.46	1.06
Chlordane	5.15	1.25

3.3 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. Among the more important factors which must be considered in this respect are:

3.3.1 Particle size and composition of particulate matter

The relevance of grain size effects to metals partitioning has been reviewed by Salomons and Forstner⁽⁸⁰⁾. 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 prior (clay-silt fraction) prior to digestion and analysis. For the present work, size characterisation is seen an important means of particle classification.

As discussed in Section 2.2.1, metals can bind to natural particulates at a variety of different sites, dependent on chemical composition. Detailed sequential chemical extraction schemes^(81,82) 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⁽⁸³⁾. While they can provide much useful information, it must be emphasised that without exception they rely on entirely operational separations of the various fractions (exchangeable, carbonate, reducible, organic etc) and a lack of adequate selectivity of the different extractants is generally evident.

3.3.2 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').

3.3.3 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 inhibition of adsorption by trace metals competing for similar sites must also be addressed.

3.3.4 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+} ^(11,84). The rapid increase in ionic strength experienced at the freshwater/estuarine interface also has a profound effect on the physico-chemical characteristics of the particulate matter, for example through flocculation of dissolved natural organic matter.

3.3.5 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.

3.3.6 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⁽⁸⁾. 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, which may play a dominant role, are often entirely lacking or of dubious accuracy.

3.3.7 Particle concentration

One of the most surprising experimental findings on partitioning is a marked dependency of K_p on the concentration of adsorbing particles. Several laboratory studies have demonstrated an essentially linear decrease in K_p with increasing suspended solids loading, in some cases over several orders of magnitude of concentration^(43,85). More recently, a similar finding has been reported from a compilation of field data for coastal waters⁽⁸⁶⁾. The explanation for this particle concentration effect is presently the subject of some controversy. One school of thought⁽⁸⁷⁾ 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⁽⁸⁵⁾; 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 is the release of particulate associated natural organic ligands to the dissolved phase in the course of the experiment (see Appendix A) - the subsequent concentration, and hence effect, of such ligands would be greater the higher the solids loading.

3.4 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^(88,89,90) 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^(88,91) 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⁽⁹²⁾.

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

SECTION 4 - 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. In the present study is intended wherever possible to employ conventional analytical methodology which can be applied directly 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⁽⁹³⁾ 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⁽⁸⁸⁾ 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 K_p (see Section 2) can result. The conventional water industry procedure of filtration to $0.4\ \mu\text{m}$ or $0.45\ \mu\text{m}$ will often not be suitable. Filtration to smaller size cut-offs ($0.2\ \mu\text{m}$ or less) will 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.

SECTION 5 - PREVIOUS WRc LABORATORY AND FIELD STUDIES ON ORGANICS PARTITIONING

WRc has recently been involved with several specific field investigations into the sources and fates of organic contaminants in both rivers and estuaries. The distribution of organic contaminants between aqueous and particulate phases was recognised as an important aspect of all these studies, and where possible the partitioning behaviour of specific contaminants has been investigated. Some data resulting from these studies is presented in this section to provide examples of recent WRc work in this area.

a) Fate studies in rivers

A recent WRc study was carried out to investigate the behaviour and fate of organic contaminants in a river using a sewage effluent as a point discharge of organic pollutants for study⁽⁹⁴⁾. Samples of the sewage effluent, receiving water and river sediments were analysed at a number of points downstream of the discharge and showed the presence of a range of compounds with widely differing physicochemical properties. In summary, these investigations showed that the aqueous concentrations of these compounds were mainly controlled by simple dilution, and that those compounds with the highest octanol/water partition coefficients (log Kow) were strongly associated with particulate matter, and that they were found in the sediment at the greatest distance from the discharge. Table 7 shows the major compounds identified in water and suspended particulate samples by GC-MS analysis. Partitioning data for specific contaminants including log Kp, and log Koc values were calculated using field data for aqueous and particulate concentrations, and particulate organic carbon content. These data are shown in Table 8 with log Kow data obtained from the literature. Work on this project is still in progress and it is intended that field data will be used in environmental fate models such as the USEPA EXAMS (EXAMS = exposure analysis modelling systems).

Table 7 - Major compounds identified in water and suspended particulate samples

Compound	Upstream		STW effluent		Downstream	
	Water	Particle	Water	Particle	Water	Particle
Alkanes (<u>n</u> -, branched and cyclic)		x		x		x
C ₃ Alkylbenzenes			x		x	
C ₁₀ to C ₁₃ -Alkylbenzenes				x		x
Benzaldehyde	x		x		x	
Benzothiazole	x		x		x	
Caffeine	x		x		x	
4-Chloro-3,5-dimethylphenol			x		x	
Cholesterol		x		x		x
Coprostanol		x		x		x
Cyclohexanone	x		x		x	
Dichlorobenzene, <u>o</u> , <u>m</u> and <u>p</u>			x		x	
2,6-Di- <u>i</u> sopropylphenol			x		x	
Hexadecanal		x		x		x
Hexanal	x		x		x	
1-Methyl-4-(1-methylethyl)-3-cyclohexen-1-ol	x		x		x	
Octadecanal				x		x
Octadecenal				x		x
Octene					x	
Oleic acid	x	x	x	x	x	x
Palmitic acid	x	x	x	x	x	x
Pentachlorophenol	x		x		x	
Phenol			x		x	

Table 7 - continued

Compound	Upstream		STW effluent		Downstream	
	Water	Particle	Water	Particle	Water	Particle
Squalene		x		x		x
Stearic acid	x	x	x	x	x	x
Styrene			x		x	
Tri- <u>n</u> -butylphosphate			x		x	
2,4,6-Trichlorophenol			x		x	
a,a,4-trimethyl-3-cyclohexene-1-methanol	x		x		x	
Tris(2-butoxyethyl)phosphate			x		x	
Tris(2-chloroethyl)phosphate	x		x		x	
Xylene, <u>o</u> , <u>m</u> and <u>p</u>	x		x		x	

Table 8 - Calculated concentrations of the selected compounds in water, particulate and sediment phases

(a) Water

Compound	Approximate conc in particles (ng mg ⁻¹)	log K _{ow}	log K _{oc}	log Kp	Calculated water conc (ng l ⁻¹)
oleic acid	50-250	5.36	4.96	4.44	1800-9100
palmitic acid	250-500	6.2	5.79	5.27	1300-2700
stearic acid	250-500	8.23	7.79	7.27	13-27
4-phenyldodecane	0.5-5	8.76	8.32	7.80	0.0079-0.079
cholesterol	500-750	9.5	9.05	8.53	1.5-2.2
squalene	50-250	9.86	9.41	8.89	0.064-0.32
coprostanol	875-1125	10.71	10.25	9.73	0.16-0.21

(b) Particulate

Compound	Approximate conc in water (ng l ⁻¹)	log K _{ow}	log K _{oc}	log Kp	Calculated particle conc (ng mg ⁻¹)
styrene	10-100	2.95	2.57	2.05	0.0011-0.011
1,4-dichlorobenzene	5-50	3.37	2.99	2.47	0.0015-0.015
1,2-dichlorobenzene	5-50	3.38	3.00	2.48	0.0015-0.015
1,3-dichlorobenzene	5-50	3.48	3.10	2.58	0.0019-0.019
4-chloro-3,5-dimethyl phenol	10-100	3.50	3.12	2.60	0.004-0.04
tri-n-butylphosphate	10-100	4.00	3.61	3.09	0.012-0.12
2,6-di-isopropylphenol	10-100	4.72	4.32	3.80	0.06-0.6
tris(2-butoxyethyl) phosphate	10-100	4.78	4.38	3.86	0.072-0.72

Table 8 - continued

(c) Sediment

Compound	Approximate conc in water (ng l ⁻¹)	log K _{oc}	log K _p	Calculated sediment conc (µg g ⁻¹)
styrene	10-100	2.57	0.30	2.0x10 ⁻⁵ -2.0x10 ⁻⁴
1,4-dichlorobenzene	5-50	2.99	0.72	2.6x10 ⁻⁵ -2.6x10 ⁻⁴
1,2-dichlorobenzene	5-50	3.00	0.73	2.7x10 ⁻⁵ -2.7x10 ⁻⁴
1,3-dichlorobenzene	5-50	3.10	0.83	3.4x10 ⁻⁵ -3.4x10 ⁻⁴
4 chloro-3,5-dimethyl- phenol	10-100	3.12	0.85	7.1x10 ⁻⁵ -7.1x10 ⁻⁴
tri-n-butyl phosphate	10-100	3.61	1.34	2.2x10 ⁻⁴ -2.2x10 ⁻³
2,6-di-isopropylphenol	10-100	4.32	2.05	0.0011-0.011
tris(2-butoxyethyl) phosphate	10-100	4.38	2.11	0.0013-0.013
oleic acid	1800-9100*	4.96	2.69	0.9-4.5
palmitic acid	1300-2700*	5.79	3.52	4.5-9
stearic acid	13-27	7.79	5.52	4.5-9
4-phenyl dodecane	0.0079-0.079*	8.32	6.05	0.009-0.09
cholesterol	1.5-2.2*	9.05	6.78	9-14
squalene	0.064-0.32*	9.41	7.14	0.9-4.5
coprostanol	0.16-0.21*	10.25	7.98	16-20

* Calculated from particulate concentration, see (a)

b) Laboratory studies of the effect of dissolved organic material on the solubility of organic contaminants

The interaction of organic contaminants with dissolved organic compounds has been recognised as an important factor influencing their solubility and chemical reactivity. A recent WRc project⁽⁹⁵⁾ investigated the association of DDT with natural dissolved organic matter, and with humic and fulvic acids. Partition coefficients for the distribution of DDT between the solution and sorbed on humic and fulvic acids or dissolved organic matter were determined in laboratory experiments. The partition coefficients were measured in the absence of suspended particulates and the amount of DDT that associated with humic acid or aquatic organic matter ranged from 4.3-8.1% (Table 9). This study showed the importance of dissolved organic material in influencing the partitioning of a hydrophobic contaminant in natural waters. Further work is needed to assess the role of dissolved organic material in associations with other contaminants with different physicochemical properties.

Table 9 - The partition coefficient of DDT in solutions with different dissolved organic content

Water sample	DOC mg l ⁻¹	pH	Partition coefficient
Fluka humic acid solution	6.4	6.5-7	1.5 (± 0.07) × 10 ⁵ n=3
Suwannee Stream humic acid solution	8.8	6.5	4.0 (± 0.16) × 10 ³ n=3
Grassholm water	8.1	6	5.2 (± 0.38) × 10 ³ n=3
Suwannee Stream fulvic acid solution	9.3	6.5-7	ND*
Islay water	16.3	6	5.5 (± 0.3) × 10 ³ n=3
River Thames water	3.6	7.5-8	2.0 (± 0.1) × 10 ⁴ n=3

* ND - Not determinable because the concentration of bound DDT was below the GC detection limit

c) Estuarine investigations - toluene

Investigations into the distribution and partitioning of toluene have been carried out in a major estuary. GC-MS analysis with deuterated surrogate internal standards has been used to determine the concentrations of toluene in both the dissolved and particulate phases of water samples from throughout the tidal estuary. Toluene was detected in both the dissolved and the particulate phases of all samples (Table 10), but there was no correlation between particulate concentration and suspended solids concentration of samples. Partition coefficients for individual samples ranged from 2.72-4.50, and this variation may be due to differences in suspended particle sizes between samples, and variations in dissolved organic carbon concentration and salinity.

Table 10 - Concentrations of toluene in 'particulate' and 'dissolved' phases of water samples from a UK estuary

Salinity	Suspended solids (mg l^{-1})	Dissolved conc ($\mu\text{g l}^{-1}$)	Particulate conc ($\mu\text{g g}^{-1}$)	Log Kp
29.97	118	8.7	5.1	2.77
29.46	81	11.2	83.3	3.87
29.35	58	0.5	15.9	4.50
25.89	417	3.2	3.5	3.04
20.75	48	8.3	8.6	3.02
15.68	682	1.0	1.1	3.04
14.55	110	14.9	7.8	2.72
7.30	159	2.6	17.5	3.83
8.38	739	0.8	4.7	3.77

* Kp = conc. in particulate phase ($\mu\text{g g}^{-1}$)

conc in dissolved phase ($\mu\text{g ml}^{-1}$)

SECTION 6 - OUTLINE OF PROPOSED STUDY

6.1 ORGANICS

Initial experimental work will involve the assessment and development of a procedure for the preparation of natural sedimentary material for use in laboratory desorption experiments. Bulk sediment samples from the River Aire and River Humber will be size fractionated and fractions of known importance in contaminant adsorption processes will be used as a stock matrix for subsequent laboratory experiments. Experimental conditions will be kept as simple as possible in preliminary work and investigations of parameters considered important in influencing contaminant partitioning will be limited to suspended solids concentration and temperature in the first instance.

The following experiments will undertaken in the laboratory in the first 12 months of the programme of work.

- i) Desorption experiments using natural resuspended sediment fractions will be carried under controlled temperature conditions.
- ii) Experiments will be carried out to determine the rate at which equilibrium conditions are achieved.
- iii) The use of natural sedimentary material should enable observations to be made of the partitioning behaviour of organic contaminants associated with a real sediment matrix. Suspended matter and 'dissolved' phase associated contaminants will be analysed initially by GC-FID, GC-ECD and GC-MS.

Future work

After completion of initial experiments, investigations will be extended to study the range of controlling factors that influence organic contaminant partitioning behaviour.

6.2 TRACE METALS

Experimental work will be designed to assess the effects of the most important of the factors discussed in Section 3 so that the transport and fate of heavy metals in aquatic systems may be predicted. The approach to be adopted will be to concentrate primarily on a single river system and to co-ordinate research on metals with that on organic compounds. Aspects such as sampling and the characterisation of sediment and water quality will then be common to both programmes. The river currently under consideration as a major river for which questions of partitioning are highly relevant is the Ouse/Humber. Freshwaters from other sources will also be examined to include other types of waters. Effort will be directed mainly towards partitioning occurring with naturally suspended material rather than that in bed sediments.

The following series of tests are proposed on freshwaters and estuary samples. These will take place over the first 18 months of the three-year programme.

- a) Studies of the fractionation of metals naturally present in a series of water/suspended sediment samples. Tests to determine whether or not partitioning is at equilibrium. Examination of the effect of solution pH and of changes in the level of particulate matter on sorption.
- b) Studies of the adsorption of added dissolved metal by natural sediment at different particulate levels. These will provide details of the kinetics of adsorption.
- c) Evaluation of the adsorption isotherm - the relationship between adsorption of a given metal and the concentration of the metal present. Corresponding studies of desorption to throw light on the reversibility of sorption.

Future years work

Further work to examine the effects of temperature, redox status and, where appropriate, the role of dissolved ligands in determining partitioning.

SECTION 7 - EFFECTS OF PARTITIONING ON TOXICITY

7.1 INTRODUCTION

As has been noted above, sediments are a major sink for many anthropogenic environmental contaminants and may, over the long term, also be a major source of contaminants to the biosphere. Whilst contamination of the water column may largely be controlled by regulating discharges, chronically contaminated sediments may continue to present problems even after the complete cessation of a discharge.

There are at present no formally defined methods in the UK for evaluating the effects of sediment contamination on aquatic biota. This need is currently being addressed by WRc under a number of programme headings. The establishment of such methods is necessarily an integral part of any programme to investigate the effects of contaminant partitioning on toxicity. Equally important, standard criteria and methods must be developed for the sampling, handling, storage, characterisation and manipulation of sediments used in geochemical and biological studies. These aims must be realised for freshwater, estuarine and marine environments.

The study of effects of partitioning on toxicity can be approached in a number of ways:

Geochemical

- a) By investigation of near-natural systems, using in situ contaminated sediments impacted by real effluents.
- b) By investigation, in laboratory systems, of the effects of pure chemicals or mixtures of pure chemicals.

Biological

- c) By investigation of factors controlling availability and uptake of contaminants - ie effects considered in terms of tissue burdens of contaminants.
- d) By investigation of whole-organism endpoints such as mortality, growth, fecundity and energy metabolism.

In evaluating the importance of contaminant partitioning, it is necessary to devise tests to take account of different possible routes of exposure. It is, for instance, widely recognised that for some contaminants toxicity is closely related to sediment pore-water concentrations. The importance of the particulate phase cannot be neglected however; to be of long-term utility, any test systems must have the capacity to evaluate the significance of exposure via pore-water contact and direct ingestion of contaminated particles. This requires the availability of organisms which can be experimentally exposed to pore-water and particulate phases jointly and separately.

Although, in related contexts, the importance of sensitive indigenous species is recognised, for the programme under consideration here the use of easily cultured cosmopolitan species is more appropriate. This approach makes practicable a large and continuing process of comparative testing.

7.2 PROGRAMME STRATEGY

The biological effects study programme, based on the above considerations, can be summarised as follows.

7.2.1 Geochemistry

- a) Define sediment handling methods - (chemists).
- b) Define standard lab testing system - (artificial sediment).

7.2.2 Biology

- a) Develop programme to investigate the relationship between experimentally introduced/in situ contaminants and availability.
- b) Devise pragmatic methods for investigating the importance of different routes of exposure.
- c) Select, for marine, freshwater and estuarine environments, suitable test organisms for a) and b), and establish standard culture methods to ensure the routine availability of uniformly-aged specimens of known environmental history.
- d) Develop appropriate methods for determining acute and chronic lethal, and sublethal endpoints.
- e) Where appropriate, intercalibrate tests developed via a) to d) with already established biological effects tests, to permit the wider application of routine partitioning effects assessment.

The development of procedures under the above headings will follow the requirements of good scientific practice, with the aim of establishing well-documented and clearly defined standard methods. It is thus desirable to establish collaboration with centres of excellence and expertise in relevant fields of research.

7.3 PROGRESS TO DATE

This section outlines in greater detail the needs identified, and describes practical progress achieved.

7.3.1 Geochemistry

In the first instance, and to simplify the chemical problems, work will be conducted on oxidised sediments only.

- a) Uniform procedures for sediment handling are being defined in collaboration with inorganic and organic chemists. Liaison has been established with research organisations in the UK and abroad (eg USA; ASTM and EPA; Netherlands; TNO) with the aim of achieving a degree of uniformity which will promote comparability of published work.
- b) In order to establish a reliable laboratory test system, it is considered that an 'artificial' sediment (or sediments) should be defined, analogous to standard artificial waters already widely used in aquatic toxicity testing. Such a sediment will be defined in terms of: particle-size distribution; sand, clay and silt composition; organic content. These characteristics will be, to some extent, dependent on the choice of test species.

Numerical criteria for defining a standard sediment should be determined in consultation with recognised centres of expertise. This aspect of the programme will facilitate the testing of pure chemicals and of hypotheses concerning pure chemicals; it should prove to be of long term value in a predictive context.

7.3.2 Biology

Initially, two approaches are being adopted in support of objectives 7.2.2a) and b) as defined above.

- a) A programme of research has been commissioned at the Plymouth Marine Laboratory, to investigate in detail the effects of physico-chemical heavy metals by the estuarine oligochaete Tubificoides benedeni. Tubificoides is an infaunal organism which is exposed to contaminants via pore-water contact and particle ingestion. This work will take as a starting point a previous study conducted at WRC on the relationship between metal speciation and uptake in Tubificoides, which in turn was a development of a similar study of a freshwater sediment-oligochaete system.

- b) In order to separate the effects of different routes of exposure, simple physical methods will be used, in the first instance, to prepare separate phases from contaminated sediment. Pore-water will be extracted by centrifugation or pressure techniques. Repeated elutriation with water will be used to leach readily desorbed contaminants; the toxicity of the residual, strongly-adsorbed contaminants will be evaluated in comparison with the toxicity of eluted contaminants. The toxicity of whole sediments, pore-water, 'residually-contaminated' sediments and elutriate will be tested using appropriate infaunal species.

The responses to pore-water and elutriates should also be calibrated against well established dissolved phase tests on elutriates (eg Daphnia, oyster embryo larval test) where appropriate. These tests are rapid and sensitive, and may prove to be a useful surrogate in screening procedures. To investigate the toxicity of particulate-sorbed contaminants alone, but under equilibrium partitioning conditions, tests should be developed using epibenthic species. Such organisms feed on sediment-surface particles, but do not burrow within the sediment and are thus not exposed to ambient pore-water contaminant concentrations.

It may be necessary to investigate the importance of re-suspended sediments as a source of contamination. For fine particles, this might best be accomplished by using as test species filter feeders, which can ingest resuspended material directly.

For the above tests, lab protocols must be defined which satisfy the requirements of good quality control; uniformity of test organisms, acceptability of control animals survival, and supporting chemical analysis. The maintenance and characteristics of lab cultures must be documented, and quality criteria defined.

The aims identified in 7.2.2c) and d) are presently being addressed:

Infaunal test species have been selected for the estuarine and marine environments. Corophium volutator, an estuarine amphipod crustacean,

and Capitella capitata, a marine polychaete worm, are both sediment dwelling organisms which feed on particulate material. Culture methods for these species, and for the oligochaete Tubificoides, have been developed. All three species have been maintained in breeding laboratory colonies for more than nine months.

Effort is now being devoted to rigorously defining culture characteristics and maintenance requirements, and to developing handling methods and test end points which are amenable to good quality control. The aim of culture characterisation is to determine the scale and conditions necessary to produce adequate numbers of juvenile organisms for routine testing purposes.

Preliminary acute lethal tests have been conducted with both Corophium and Capitella exposed to a range of contaminants. These studies have the aim of both estimating suitable concentration ranges for sublethal (growth and development) tests and developing handling and exposure methods. In related studies, the relative practicality of using different life history stages is under investigation. Test protocols are being evaluated against a criterion of control survival; protocol definitions will be based on the best achievable results from a range of highly replicated test systems.

The midge Chironomus riparis, which has an infaunal larval phase, has been identified as an appropriate freshwater test organism.

Asellus aquaticus, an isopod crustacean, has been selected as an epibenthic freshwater test organism. Equivalent species for the marine and estuarine environment have not yet been finally chosen; amphipods (genera Gammarus and Chaetogammarus) and mysids are probable candidates.

7.4 FUTURE WORK

7.4.1 Geochemistry

Methods will be defined, appropriate for the collection, storage and manipulation of oxidised sediments. Attention will be focused on sediments with predominantly salt and clay components, as these fractions are most closely associated with both adsorbed contaminants and with the organic material on which infaunal organisms feed. Where a variety of methods are available (eg in extracting sediment pore water), intercalibration of these methods may be necessary to determine the degree, and acceptability, of functional equivalence.

'Artificial' sediments will be developed.

Such sediments must be based on readily available stocks of components with defined and reproducible characteristics. These components may be either derived from a standard source (or sources) of uncontaminated natural sediment or material, or be of laboratory reagent grade (eg clay, fine sand). Experience in the United States has indicated that organic (humic) material may be added as peat, although there is uncertainty as to the adequacy with which this can mimic the effects of natural organic particle coatings.

Broadly, the procedure envisaged is as follows:

- a) Define, for each test organism the range of sediment characteristics (psd, % clay, salt, sand organic) which support acceptable survival, growth and reproduction.
- b) Investigate natural and synthetic sources of these components.
- c) Assemble model sediments and test suitability.
- d) Compile stocks of components which prove acceptable.

- e) Compile documentation on components (sources, characteristics) and on suitability of derived sediments.

7.4.2 Biology

Work in progress with *Capitella* and *Corophium* will continue with the aim of developing sublethal and lethal methods respectively for direct sediment toxicity assessment. For both taxa, the immediate priorities are:

- a) To improve definition of culture methods.
- b) To develop satisfactory test protocols; this will be tested against the criterion of 'best achievable' control performance and will require comprehensive investigation of a range.
- c) To identify the most practicable stage of early life history with which to initiate tests.

Investigation of the physico-chemical and biological factors influencing metal bioavailability to *Tubificoides* should commence in September/October 1989; the project will run for three years.

A three year project will also be established to refine existing culture methods, for the freshwater isopod *Asellus*, and to develop and validate procedures for using this species as an epibenthic sediment toxicity test organism.

During the next quarter, literature will be collated relating to marine gammarid and mysid culture characteristics and general biology, with the aim of selecting an appropriate epibenthic species for marine sediment tests.

Work towards developing a freshwater infaunal test using *Chironomus* will commence. In the first instance, centres of expertise in the culture of this organism will be approached for assistance in acquiring an established and proven culture system.

If progress in developing test protocols and culture methods permits, it may be possible to begin the process of intercalibrating sediment toxicity tests with standard dissolved phase tests of elutriates.

Existing methods for measuring filtration rates in marine molluscs can be adapted, if necessary, to assess the effects of resuspended sediment.

REFERENCES

1. MACKAY D. Finding fugacity feasible. Environ Sci Technol (1979), 13, 1218-1223.
2. DOBBS A J, MOORE K and PIPER S E. Environmental concentrations and predicted equilibrium distribution for some organic chemicals. WRC Report 1168-M/EV 8527. (1986).
3. MACKAY D, PATERSON S, CHEUNG B and NEELY W B. Evaluating the environmental behaviour of chemicals with a level III fugacity model. Chemosphere (1985), 14, 335-374.
4. BRIGGS G G. Theoretical and experimental relationship between soil adsorption, octanol-water partition coefficients, water solubilities and bioconcentration factors. J Agric Fd Chem (1981), 29, 1050-1059.
5. KARICKHOFF S W, BROWN D S and SCOTT T A. Sorption of hydrophobic pollutants on natural sediments. Water Research (1979), 13, 241-248.
6. CHIOU C T, FREED V H, SCHMEDDING D W and KOHNERT R L. Partition coefficients and bioaccumulation of selected organic chemicals. Environ Sci Technol (1977), 11, 475-478.
7. LLON L W, ALTMANN R S and LECKIE J O. Trace-metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of contributions of Fe/Mn oxide and organic surface coatings. Environ Sci Technol (1982), 16, 660-666.
8. JENNE E A and ZACHARA J M. Factors influencing the sorption of metals. In: Fate and effects of sediment-bound chemicals in aquatic systems, edited by K L Dickson, A W Maki and W A Brungs. Pergamon Press, New York, pp83-98. (1984).
9. HONEYMAN B D and SANTACHI P H. Metals in aquatic systems. Environ Sci Technol (1988), 22, 862-871.

10. SHINDLER P W and STUMM W The surface chemistry of oxides, hydroxides and oxide minerals. In: Aquatic surface chemistry: Chemical processes at the particle-water interface, edited by W Stumm, 83-110. Wiley-Interscience, New York. (1987).
11. BOURG A C M. Trace metal adsorption modelling and particle-water interactions in estuarine environments. Continental Shelf Research (1987), 7, 1319-1332.
12. BAILEY G W and WHITE J L. Factors influencing the adsorption, desorption and movement of pesticides in soil. Residue Rev (1970), 32, 29-92.
13. BROWMAN M G and CHESTERS G. The solid-water interface: transfer of organic pollutants across the solid-water interface. In: Fate of pollutants in the air and water environment Part I, edited by I H Suffett. pp49-105, Wiley Interscience, New York. (1975).
14. HAMAKER J W and THOMPSON J M. Adsorption. In: Organic chemicals in the soil environment Vol I, edited by C M Goring and J W Hamaker pp49-143, Dekker, New York. (1972).
15. MAILHOT H and PETERS R H. Empirical relationships between the 1-octanol/water partition coefficient and nine physico chemical properties. Environ Sci Technol (1988), 22, 1479-1488.
16. CHIOU C T, FREED V H, SCHMEDDING D W and KOHNERT R L. Partition coefficient and bioaccumulation of selected organic chemicals. Environ Sci Technol (1977), 11, 475-478.
17. MEANS J C, WOOD S G, HASSETT J J and BANWART W L. Sorption of PAH's by sediment and soils. Environ Sci Technol (1980), 14, 1524-1528.
18. SCHWARZENBACH R P, STIERLI R, FOLSOM B R and ZEYER J. Compound properties relevant for assessing the environmental partitioning of nitrophenols. Environ Sci Technol (1988), 22, 83-92.

19. TSONOPOULOS C and PRAUSNITZ J M. Activity coefficients of aromatic solutes in dilute aqueous solution. Ind Engng Chem Fund (1971), 10, 593-599.
20. HUANG J C and LIAO C S. Adsorption of pesticides by clay minerals. J Sanit Engng Div ASCE (1970), 96, 1057-1078.
21. LELAND H V, BRUCE W N and SHIMP N F. Chlorinated hydrocarbon insecticides in sediments of southern Lake Michigan. Environ Sci Technol (1973), 7, 833-838.
22. RICHARDSON E M and EPSTEIN E. Retention of three insecticides on different size soil particles suspended in water. Soil Sci Soc Am Proc (1971), 35, 884-887.
23. LOTSE E G, GRAETZ D A, CHESTERS G, LEE G B and NEWLAND L W. Lindane adsorption by lake sediments. Environ Sci Technol (1968), 2, 353-357.
24. LEO A, HANSCH C and ELKINS D. Partition coefficients and their uses. Chem Rev (1971), 71, 525-616.
25. GSCHWEND P M and WU S. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. Environ Sci Technol (1985), 19, 90-96.
26. CHIOU C T, MALCOLM R L, BRINTON T T and KILE D E. Water solubility enhancement of organic pollutants and pesticides by dissolved humic and fulvic acids. Environ Sci Technol (1986), 20, 502-508.
27. SCHRAP M S and OPPERHUIZEN A. Quantifying the sorption of organic chemicals on sediments. Chemosphere (1989), 18, 1883-1893.
28. DILLING W L. Interphase transfer processes II. Evaporation rates of chloro methanes, ethanes, ethylenes, propanes and propylenes from dilute aqueous solutions. Comparison with theoretical predictions. Environ Sci Technol (1977), 11, 405-409.

29. MACKAY D and WOLKOFF A W. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ Sci Technol (1973), 7, 611-614.
30. SOUTHWORTH G R. Role of volatilisation in removing PAH's from the aquatic environment. Bull Environ Contam Toxicol (1979), 21, 507-514.
31. READMAN J W, MANTOURA R F C, RHEAD M M and BROWN L. Aquatic distribution and heterotrophic degradation of PAH's in the Tamar estuary. Estuarine Coastal and Shelf Science, (1982), 14, 369-389.
32. WIJAYARATNE R D and MEANS J C. Sorption of polycyclic aromatic, hydrocarbons by natural estuarine colloids. Marine Environ Res (1984), 11, 77-89.
33. HORZEMPA L M and DI TORO D M. PCB partitioning in sediment-water systems: the effect of sediment concentration. J Environ Qual (1983), 12, 373-380.
34. HUANG J C. Effect of selected factors on pesticide sorption and desorption in the aquatic system. J Water Pollut Cont Fed (1971), 43, 1739-1748.
35. ZACHARA J M, AINSWORTH C C, FELICE L J and RESCH C T. Quinoline sorption to subsurface materials: role of pH and retention of the organic cation. Environ Sci Technol (1986), 20, 620-627.
36. SCHELLENBERG K, LEUENBERGER C and SCHWARTZENBACH R P. Sorption of chlorinated phenols by natural sediments and aquifer materials. Environ Sci Technol (1984), 18, 652-657.
37. HASHIMOTO Y, TOKURA K, KISHI H and STRACHAN W M J. Prediction of seawater solubility of aromatic compounds. Chemosphere (1984), 13, 881-888.
38. KARICKHOFF S W and BROWN D S. Paraquat sorption as a function of particle size in natural sediments. J Environ Qual (1978), 7, 246-252.

39. CARTER C W and SUFFET I H. Binding of DDT to dissolved humic materials. Environ Sci Technol (1982), 16, 735-740.
40. LANDRUM P F, NIHART S R, EADLE B J and GARDNER W S. Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters. Environ Sci Technol (1984), 18, 187-192.
41. WERSHAW R L, BURCAR P J and GOLDBERG M C. Interaction of pesticides with natural organic material. Environ Sci Technol (1969), 3, 271-273.
42. CARON G, SUFFET I H and BELTON T. Effect of dissolved organic carbon on the environmental distribution of non polar organic compounds. Chemosphere (1985), 14, 993-100.
43. O'CONNOR D J and CONNOLLY J P. The effect of concentration of adsorbing solids on the partition coefficient. Water Research (1980), 14, 1517-1523.
44. VOICE T C, RICE C D and WEBER W J Jr. Effect of solids concentrations on the sorptive partitioning of hydrophobic pollutants in aquatic systems. Environ Sci Technol (1983), 17, 513-518.
45. CHIOU C T, PORTER P E and SHOUP T D. Comments on partition equilibria of non-ionic organic compounds between soil organic matter and water. Environ Sci Technol (1984), 18, 295-297.
46. HASSETT J P and ANDERSON M A. Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems. Environ Sci Technol (1979), 13, 1526-1529.
47. BOEHM P D and QUINN J G. Solubilisation of hydrocarbons by the dissolved organic matter in sea water. Geochim et Cosmochim Acta (1973), 37, 2459-2477.

48. POIRRIER M A, BORDELON B R and LASETER J L. Adsorption and concentration of dissolved ¹⁴Carbon-DDT by colouring colloids in surface water. Environ Sci Technol (1972), 6, 1033-1035.
49. MCCARTHY J F and JIMENEZ B D. Interactions between PAH's and dissolved humic materials: binding and dissociation. Environ Sci Technol (1985), 19, 1072-1076.
50. MEANS J C and WIJAYARATNE R. Role of natural colloids in the transport of hydrophobic pollutants. Science (1982), 215, 968-970.
51. LAMBERT S M. Functional relationship between sorption in soil and chemical structure. J Agric Fd Chem (1967), 15, 572-576.
52. LAMBERT S M. Omega(Ω) a useful index of soil sorption equilibria. J Agric Fd Chem (1968), 16, 340-343.
53. KENAGA E E and GORING C A I. Relationship between water solubility, soil sorption, octanol-water partitioning and bioconcentration of chemicals in biota. In: Aquatic Toxicology, edited by J G Eaton, P R Parish and A C Hendricks. ASTM No STP 707. American Society of Testing and Materials. (1980).
54. BROWNAWELL B J and FARRINGTON J W. Bio geochemistry of PCB's in interstitial waters of coastal marine sediment. Geochim et Cosmochim Acta (1986), 50, 157-169.
55. MILLER C T and WEBER W J Jr. Sorption of hydrophobic organic pollutants in saturated soil systems. J Contam Hydrol (1986), 1, 243-246.
56. GARNAS R L, BOURQUIN A W and PRITCHARD P H. Appendix C to the EPA Kepone Mitigation Project Report EPA 440/5-78. (1978).
57. KARICKHOFF S W. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere (1981), 10, 833-846.

58. BOUCHER F R and LEE G F. Adsorption of lindane and dieldrin pesticides on unconsolidated aquifer sand. Environ Sci Technol (1972), 6, 538-548.
59. KOSKINEN W C and CHENG H H. Effects of experimental variables on 2,4,5-T adsorption-desorption in soil. J Environ Qual (1983), 12, 325-330.
60. BOWMAN B T and SANS W W. Partitioning behaviour of insecticides in soil-water systems: 1. Adsorbent concentration effects. J Environ Qual (1985), 14, 265-269.
61. Di TORO D M. A particle interaction model of reversible organic chemical sorption. Chemosphere (1985), 14, 1503-1538.
62. DOUCETTE W J and ANDREN A W. Correlation of octanol/water partition coefficients and total molecular surface area for highly hydrophobic aromatic compounds. Environ Sci Technol (1987), 21, 821-824.
63. HAWKER D W and CONNELL D W. Octanol-water partition coefficients of polychlorinated biphenyl congeners. Environ Sci Technol (1988), 22, 382-387.
64. HIRAIZUMI Y, TAKAHASHI M and NISHIMURA N. Adsorption of PCB's on sea bed sediment, marine plankton and other adsorbents. Environ Sci Technol (1979), 13, 580-584.
65. PODOLL R T and MABEY W R. Factors to consider in conducting laboratory sorption/desorption tests. In: Fate and effects of sediment bound chemicals in aquatic systems, edited by K L Dickson, A W Maki and W A Brungs, pp99-108, Pergamon Press. (1987).
66. HAQUE R and SCHMEDDING D W. A method of measuring the water solubility of hydrophobic chemicals: solubility of five polychlorinated biphenyls. Bull Envir Contam Toxic (1975), 14, 13-18.

67. KARICKHOFF S W and BROWN D S. Determination of octanol-water distribution coefficients, water solubilities and sediment/water partition coefficients for hydrophobic organic pollutants. EPA 600/4-79-032 US Envir Prot Agency, Athens, Georgia. (1979).
68. SUTTON C and CALDER J A. Solubility of higher molecular weight n-paraffins in distilled water and sea water. Environ Sci Technol (1974), 8, 654-657.
69. MILLER M M, WASIK S P, HUANG G, SHIU W and MACKAY D. Relationship between octanol/water partition coefficient and aqueous solubility. Environ Sci Technol (1985), 19, 522-529.
70. WOODBURN K B, DOUCETTE W J and ANDREN A W. Generator column determination of octanol/water partition coefficients for selected PCB congeners. Environ Sci Technol (1984), 18, 457-459.
71. MILLER M M, GHODBANE S, WARIK S P, TEWARI Y B and MARTIRE D E. Aqueous solubilities, octanol/water partition coefficient and entropies of melting of chlorinated benzenes and biphenyls. J Chem Engng Data (1984), 29, 184-190.
72. RAPAPORT R A and EISENREICH S J. Chromatographic determination of octanol-water partition coefficients for 58 PCB congeners. Environ Sci Technol (1984), 18, 163-170.
73. McCALL J M. Liquid-liquid partition coefficients by HPLC. J Med Chem (1975), 18, 549-552.
74. VIETH G D, AUSTIN N M and MORRIS R T. A rapid method for estimating Log P (partition coefficient) for organic chemicals. Water Research (1979), 13, 43-47.
75. EADSFORTH C V and MOSER P. Assessment of reverse-phase chromatographic methods for determining partition coefficients. Chemosphere (1983), 12, 1459-1475.

76. D'AMBOISE M and HANAI T. Hydrophobicity and retention in reverse phase liquid chromatography. J Liquid Chromat (1982), 229-244.
77. McDUFFIE B. Estimation of octanol/water partition coefficients for organic pollutants using reverse-phase HPLC. Chemosphere (1980), 10, 73-83.
78. BURKHARD L P, KUEHL D W and VIETH G. Evaluation of reverse phase liquid chromatography/mass spectrometry for estimation of n-octanol/water partition coefficients for organic chemicals. Chemosphere (1985), 14, 1551-1560.
79. CHIN Y P, PEVEN C S and WEBER W J Jr. Estimating soil/sediment partition coefficients for organic compounds by high performance reverse phase liquid chromatography. Water Res (1988), 22, 873-881.
80. SALOMONS W and FORSTNER U. Metals in the hydrocycle. Springer-Verlag, Berlin. (1984).
81. TESSIER A, CAMPBELL P G C and BISSON M. Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem (1979), 51, 844-851.
82. RAPIN F and FORSTNER U. Sequential leaching techniques for particulate metal speciation: the selectivity of various extractants. In: Management and control of heavy metals in the environment, CEP Consultants, Edinburgh, pp1074-1077. (1983).
83. TOWNER J V and CAMPBELL J A. The partitioning of trace metals in sediments: a review of chemical extraction procedures. WRc Report PRS 1313-M. (1987).
84. COMANS R N J and VANDIJK C P J. Role of complexation processes in cadmium mobilisation during estuarine mixing. Nature (1988), 336, 151-154.

85. DI TORO D M, MAHONY J D, KIRCHGRABER P R, O'BYRNE A L, PASQUALE L R and PICCIRILLI D C. Effects of non-reversibility, particle concentration and ionic strength on heavy metal sorption. Environ Sci Technol (1986), 20, 55-61.
86. BALLS P W. The partition of trace metals between dissolved and particulate phases in European coastal waters: a complication of field data and comparison with laboratory studies. Netherlands Journal of Sea Research (1989), 23, 7-14.
87. MOREL F M M and GSCHWEND P M. The role of colloids in the partitioning of solutes in natural waters. (1987).
88. JANNASCH H W, HONEYMAN B D, BALISTRIERI L S and MURRAY J W. Kinetics of trace metal uptake by marine particles. Geochim Cosmochim (1988), 52, 567-577.
89. MILLWARD G E. New directions in aquatic adsorption studies presented at NERC Geocolloids Discussion Group Meeting, Lancaster, April. (1989).
90. UNGER M A, MACINTYRE W G and HUGGET R J. Sorption behaviour of tributyltin on estuarine and freshwater sediments. Environ Toxicol Chem (1988), 7, 907-915.
91. NYFFELER U P, LI Y H and SANTSCHI P H. A kinetic approach to describe trace-element distribution between particles and solution in natural aquatic systems. Geochim Cosmochim Acta (1984), 48, 1513-1522.
92. LI Y H, BURKHARDT L, BUCHHOLTZ M, O'HARA P and SANTSCHI P H. Partition of radiotracers between suspended particles and seawater. Geochim Cosmochim Acta (1984), 48, 2011-2019.
93. APTE S C and GUNN A M. Rapid determination of copper, nickel, lead and cadmium in small samples of estuarine and coastal waters by liquid/liquid extraction electrothermal atomic absorption spectrophotometry. Anal Chim Acta (1987), 193, 147-156.

94. WATTS C D and MOORE K. The transport and fate of organic pollutants in rivers - a progress report on project 4233. WRc Report PRU 1592-M. (1987).
95. FIELDING M, WATTS C D and ZHU X R. The association of DDT with dissolved humic and fulvic acids and with dissolved organic matter in natural waters. WRc Report LR 1352-M. (1986).

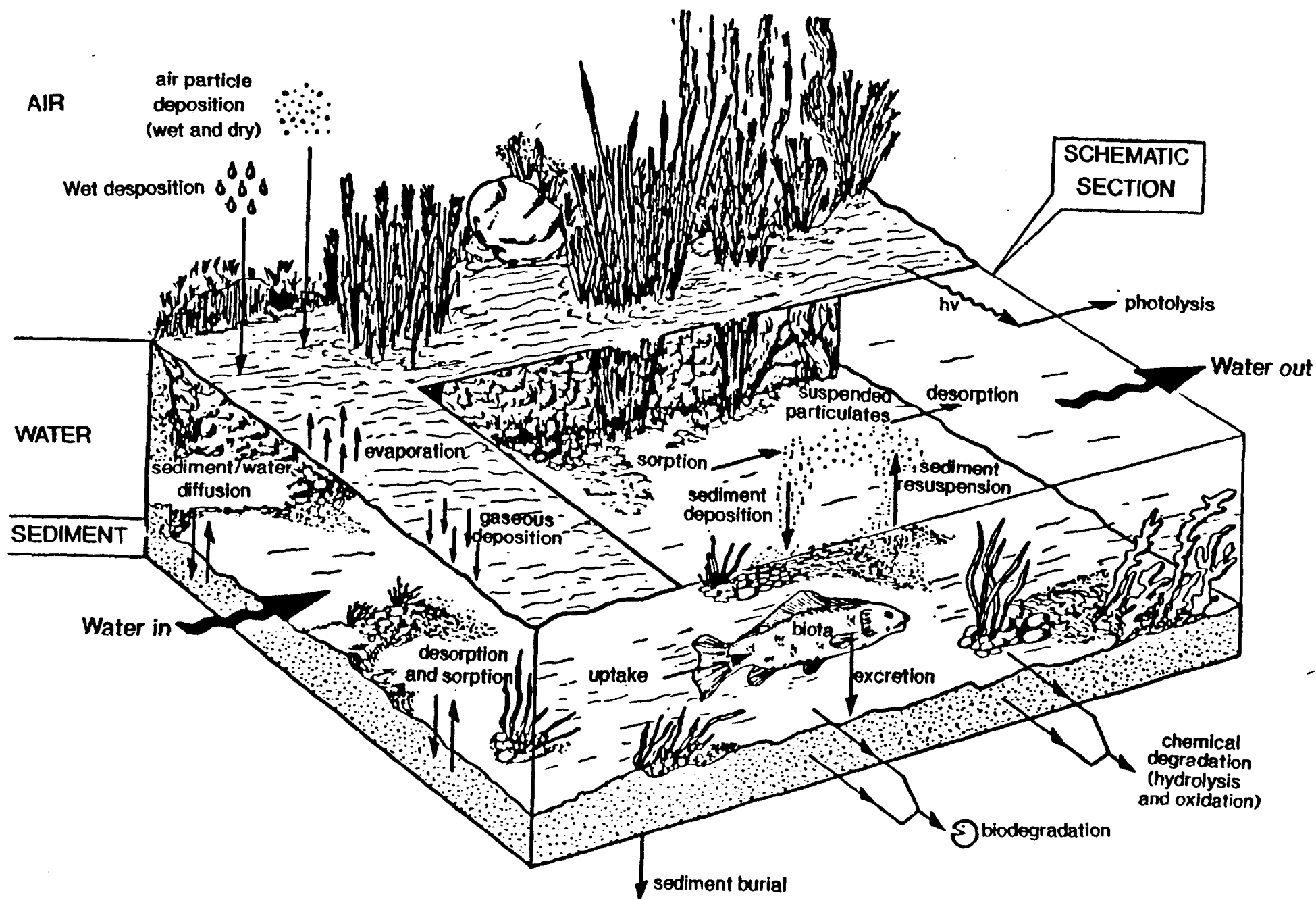


Figure 1. Processes affecting the fate of organic contaminants in the aquatic environment

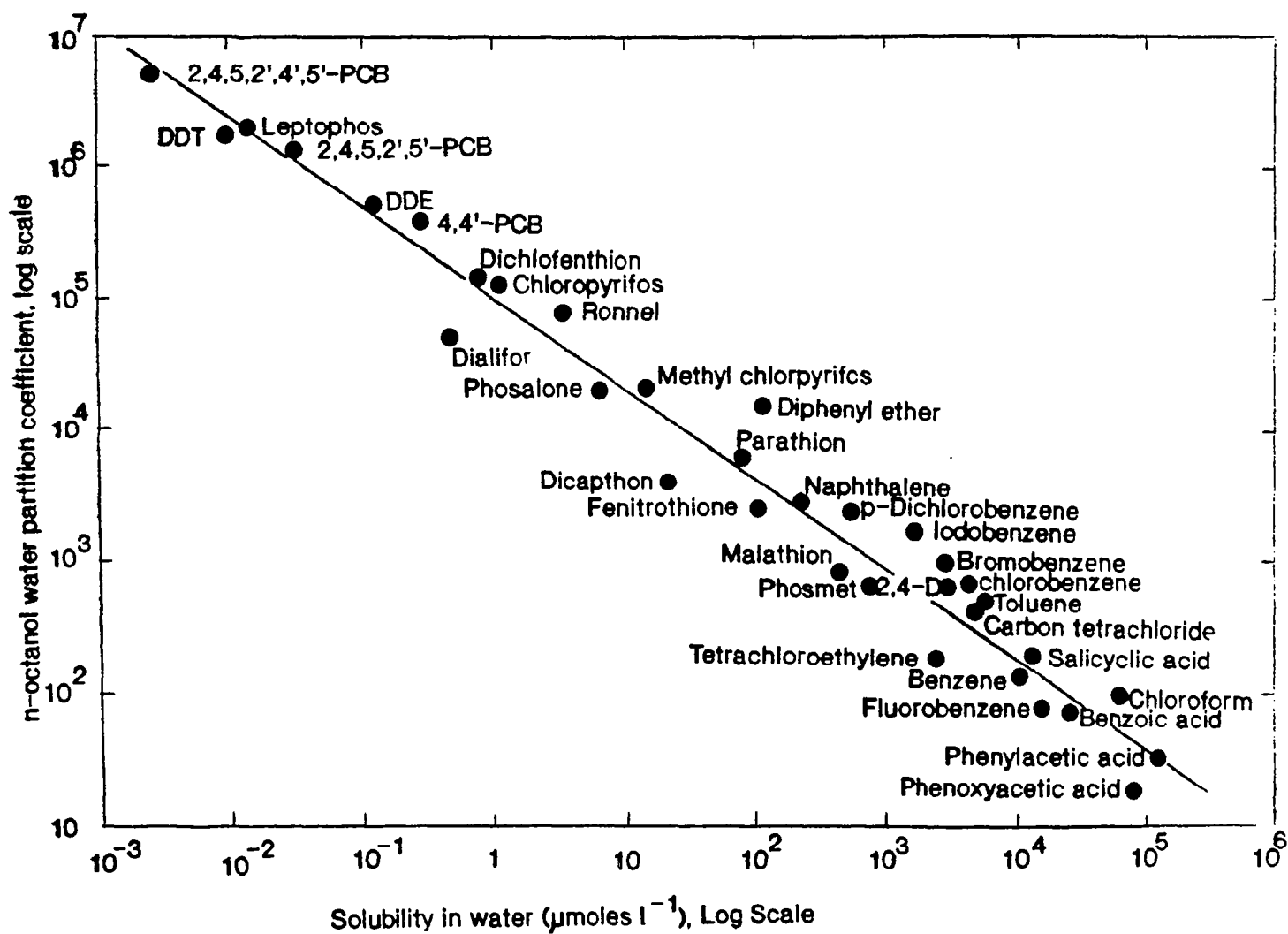


Figure 2. Partition coefficients and aqueous solubilities of various organic chemicals at room temperature⁽⁶⁾

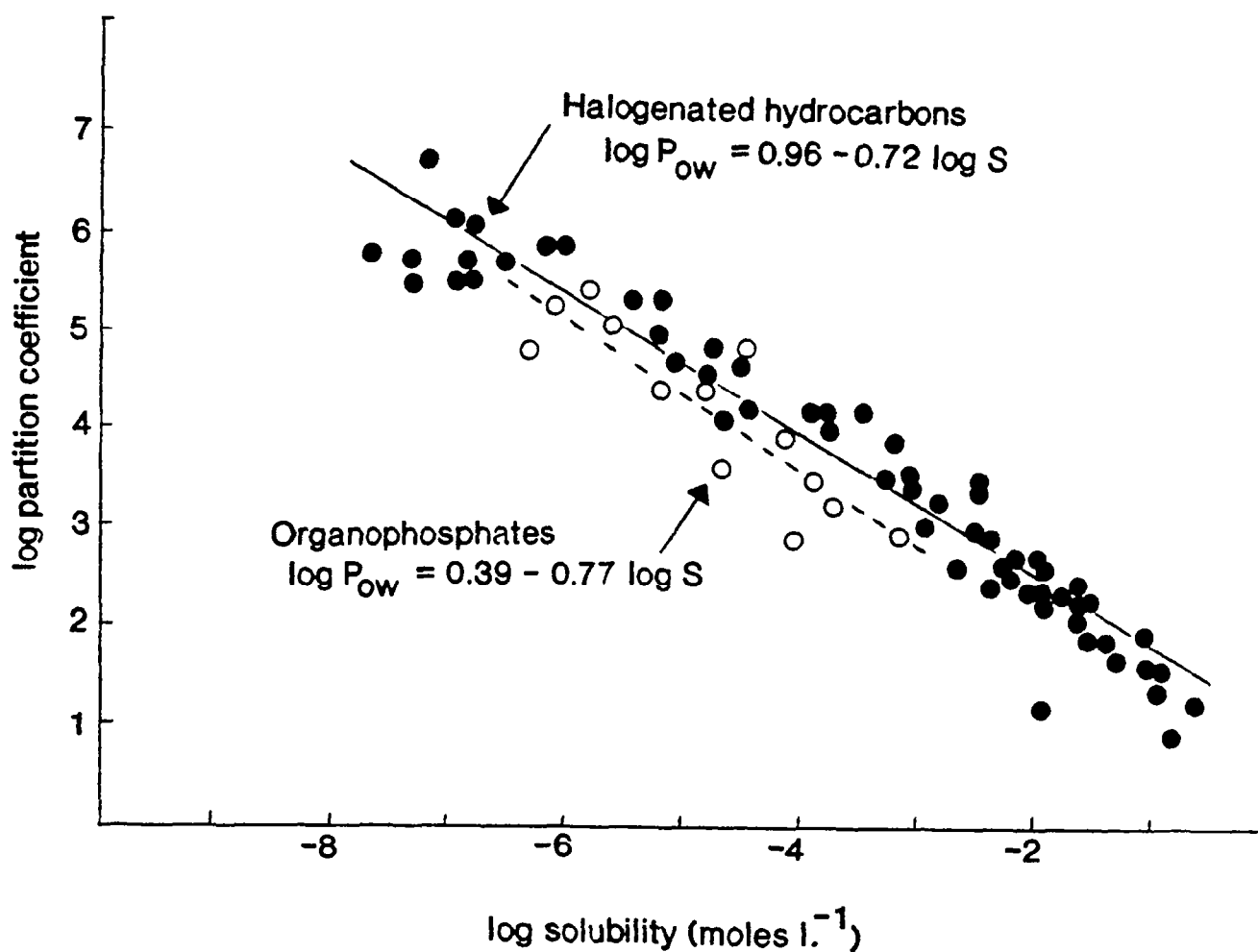


Figure 3. Relationship between log 1-octanol/water partition coefficient and log solubility for halogenated hydrocarbons ($n=65$, $r^2 = 0.944$, $MSE=0.138$) and organophosphates ($n=13$, $r^2=0.751$, $MSE=0.202$)⁽¹⁵⁾

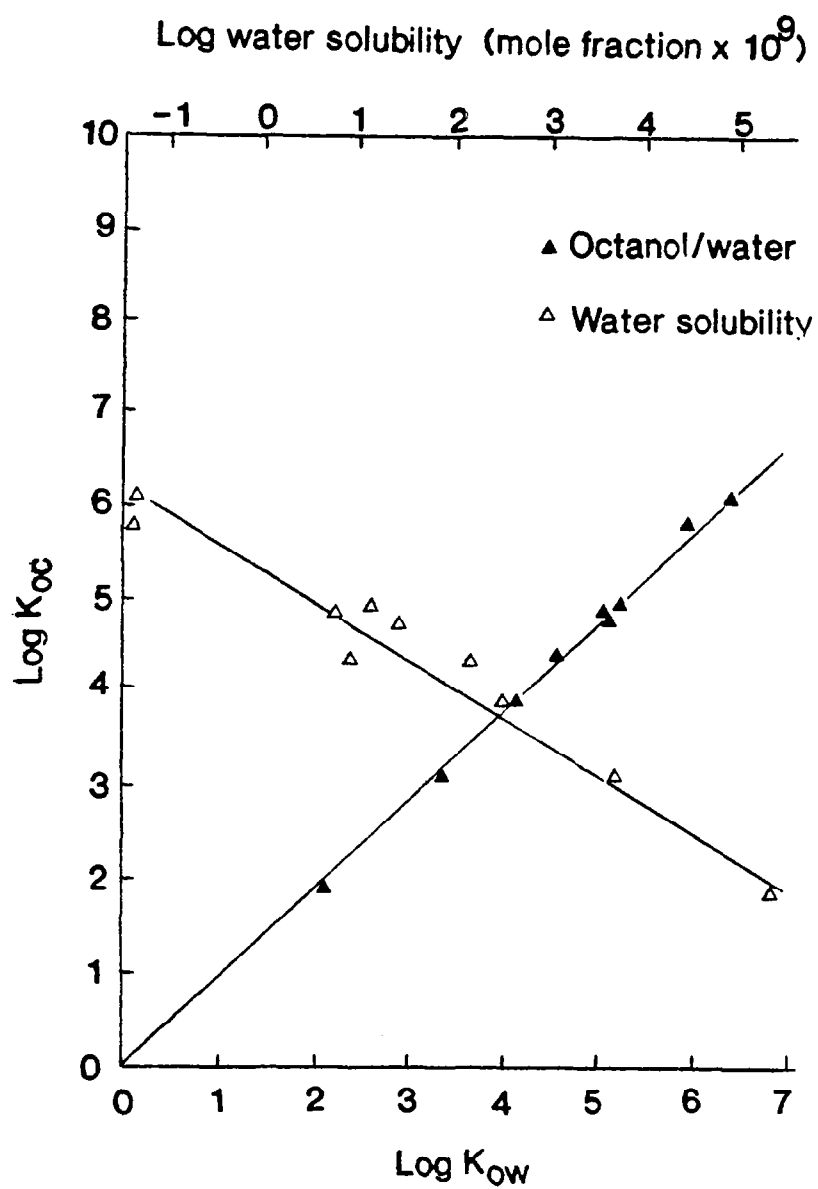


Figure 4. Sorption K_{oc} as a function of compound water solubility and octanol/water distribution coefficients⁽⁵⁾

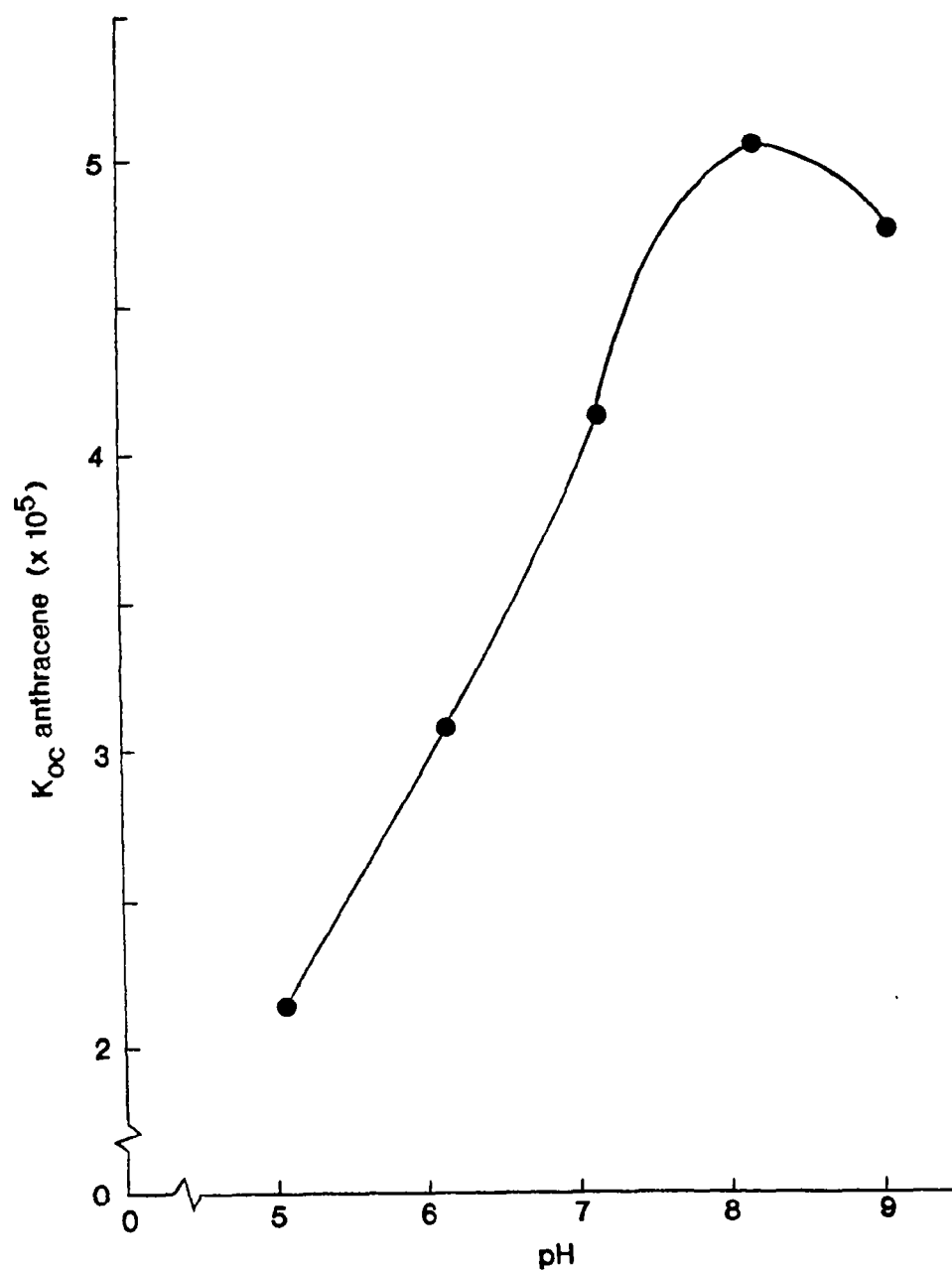


Figure 5. Effects of changes in pH on the K_{OC} values of anthracene⁽³²⁾

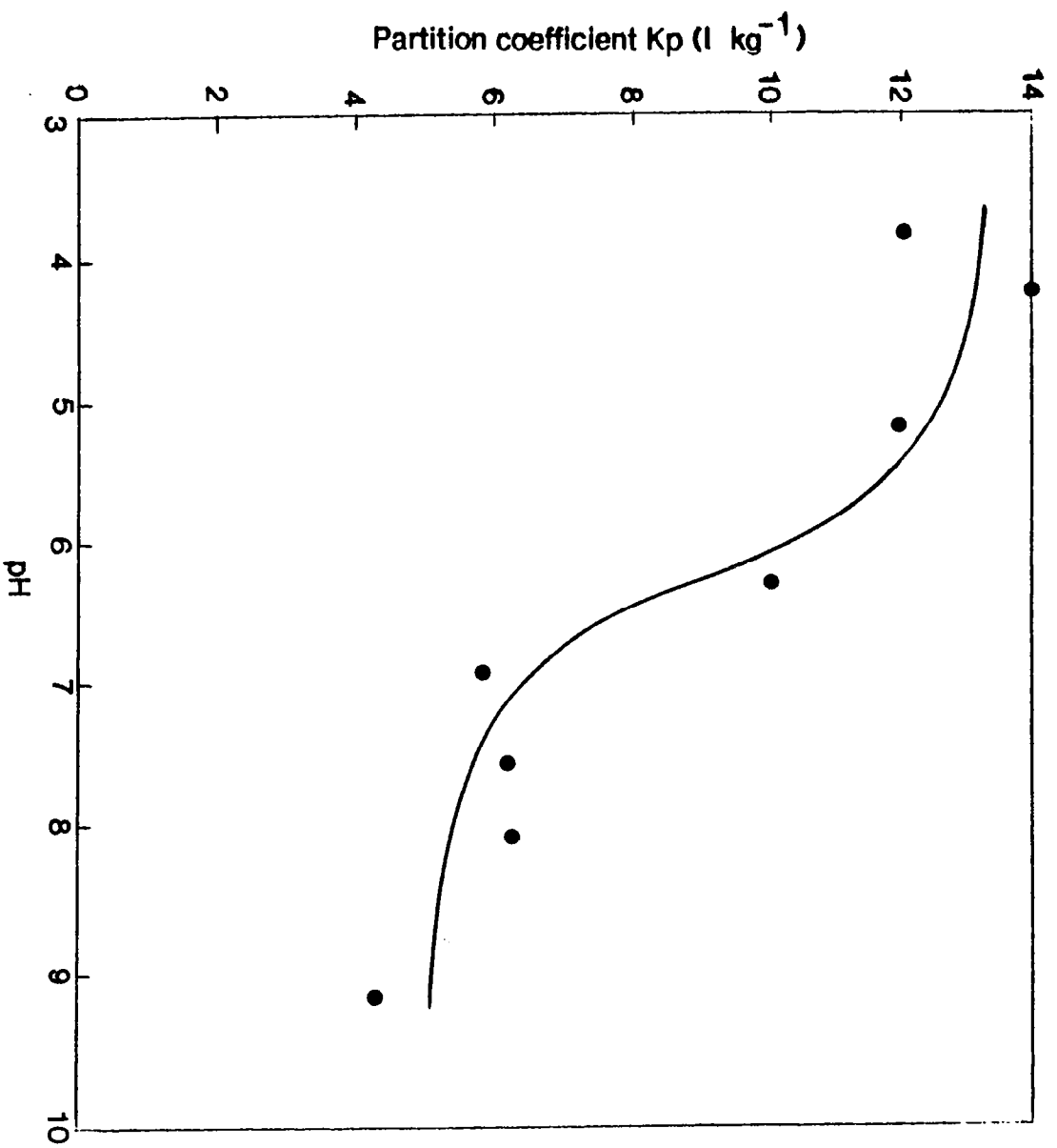


Figure 6. Effect of pH variations on partition coefficient - montmorillonite,
 $m = 200 \text{ mg l}^{-1}$ (33)

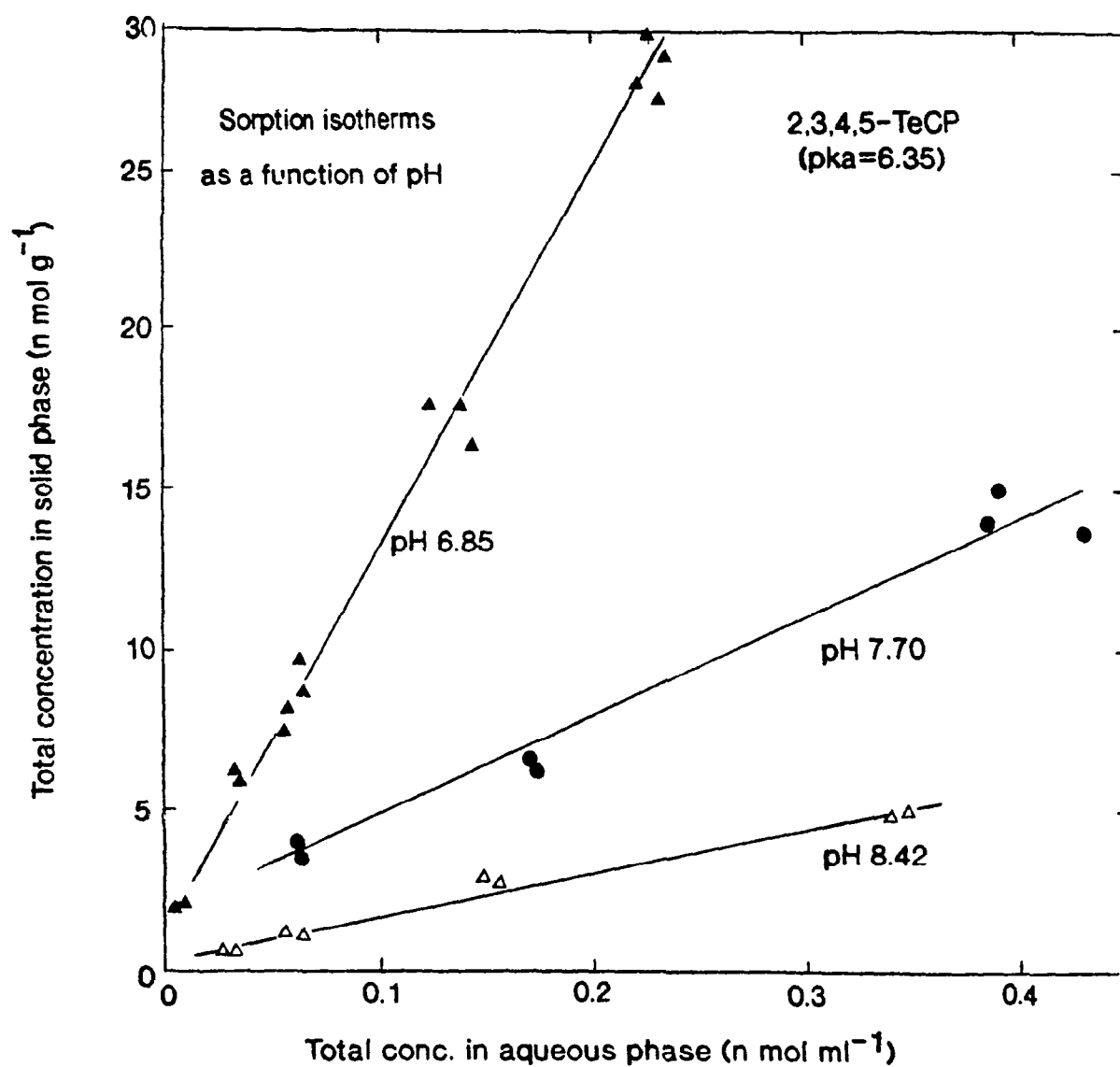


Figure 7. Sorption isotherms for 2,3,4,5-tetrachlorophenol at different pH values⁽³⁶⁾

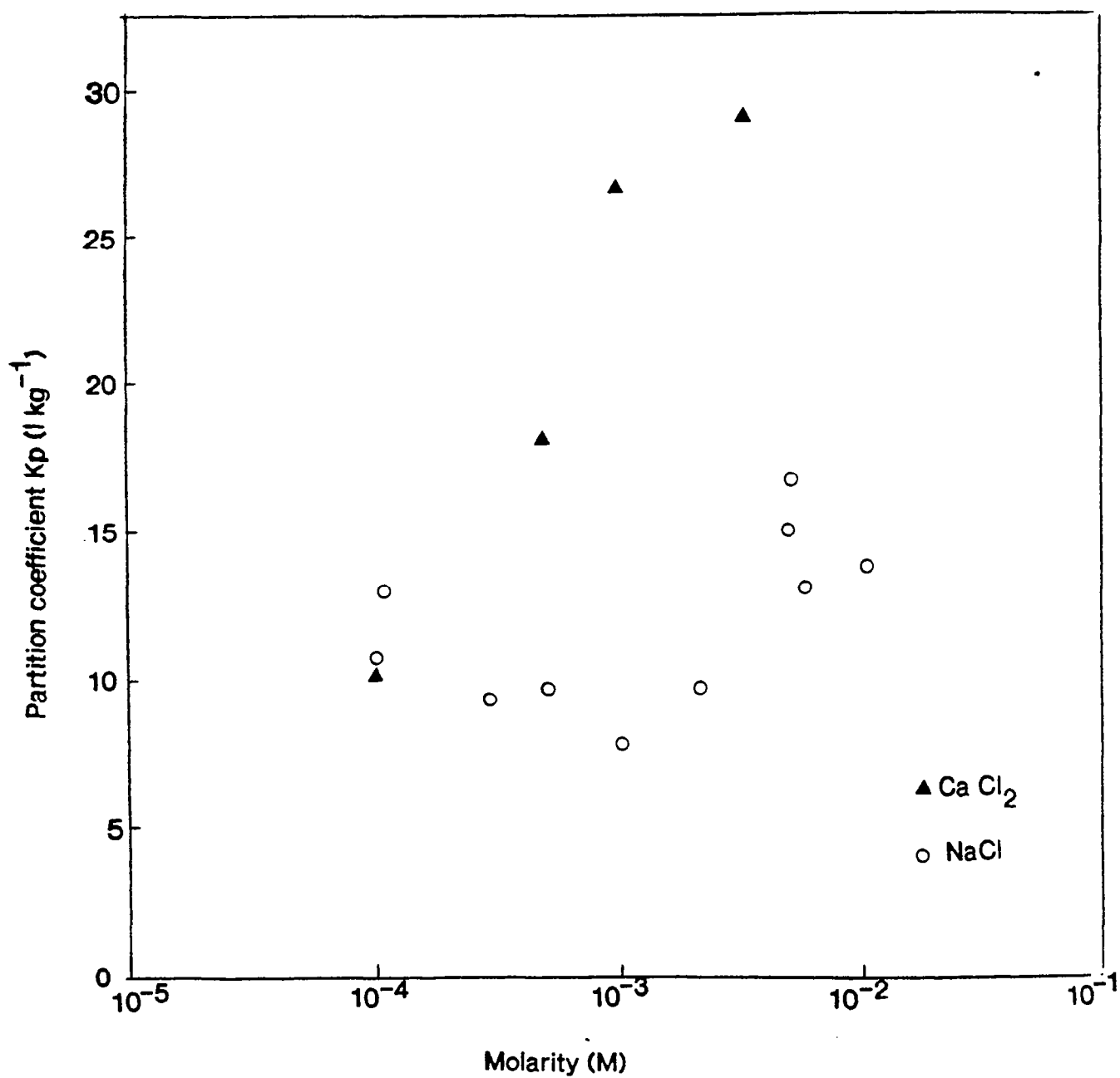


Figure 8. Effect of ionic strength variation on partition coefficient montmorillonite, $m = 200 \text{ mg l}^{-1}$ (33)

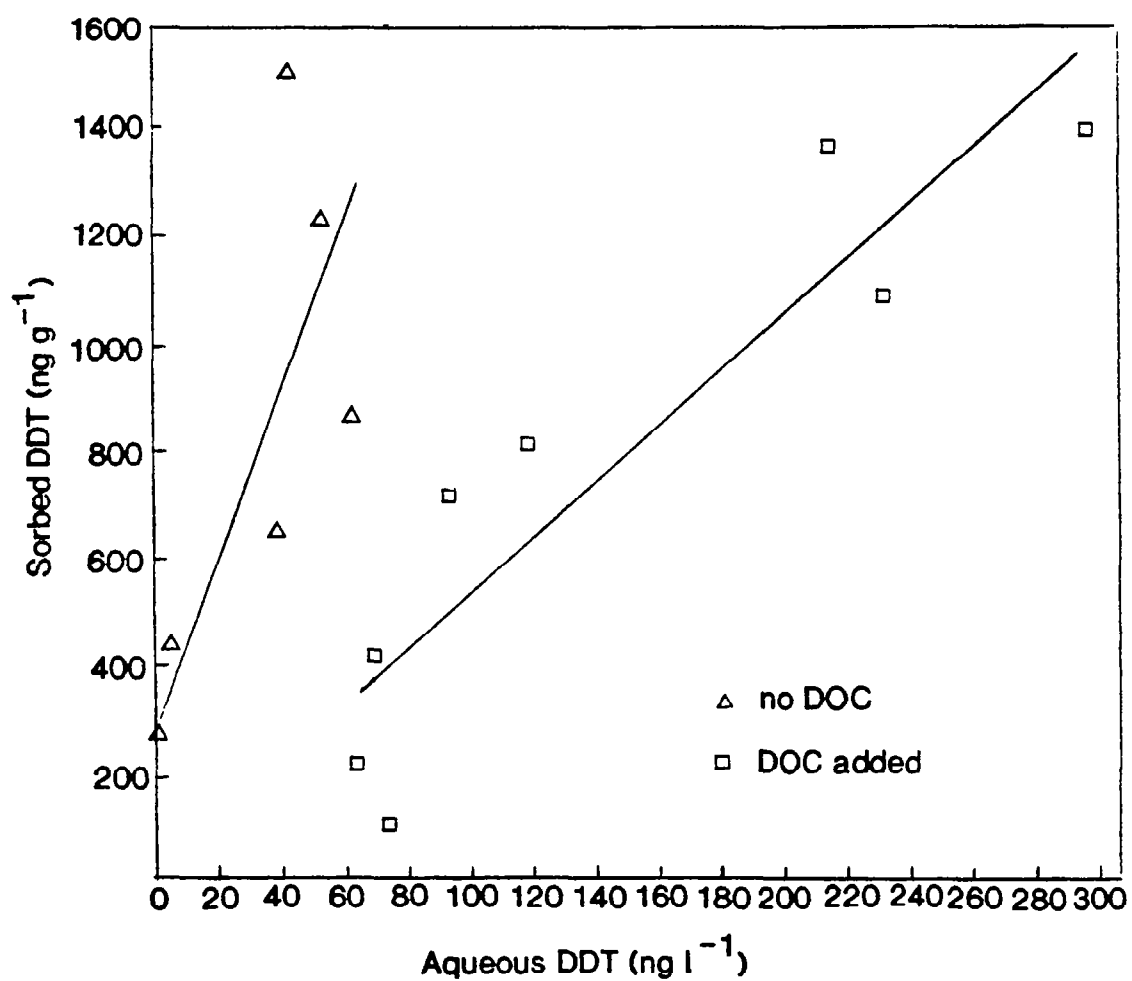


Figure 9. Effect of DOC on DDT partitioning⁽⁴²⁾

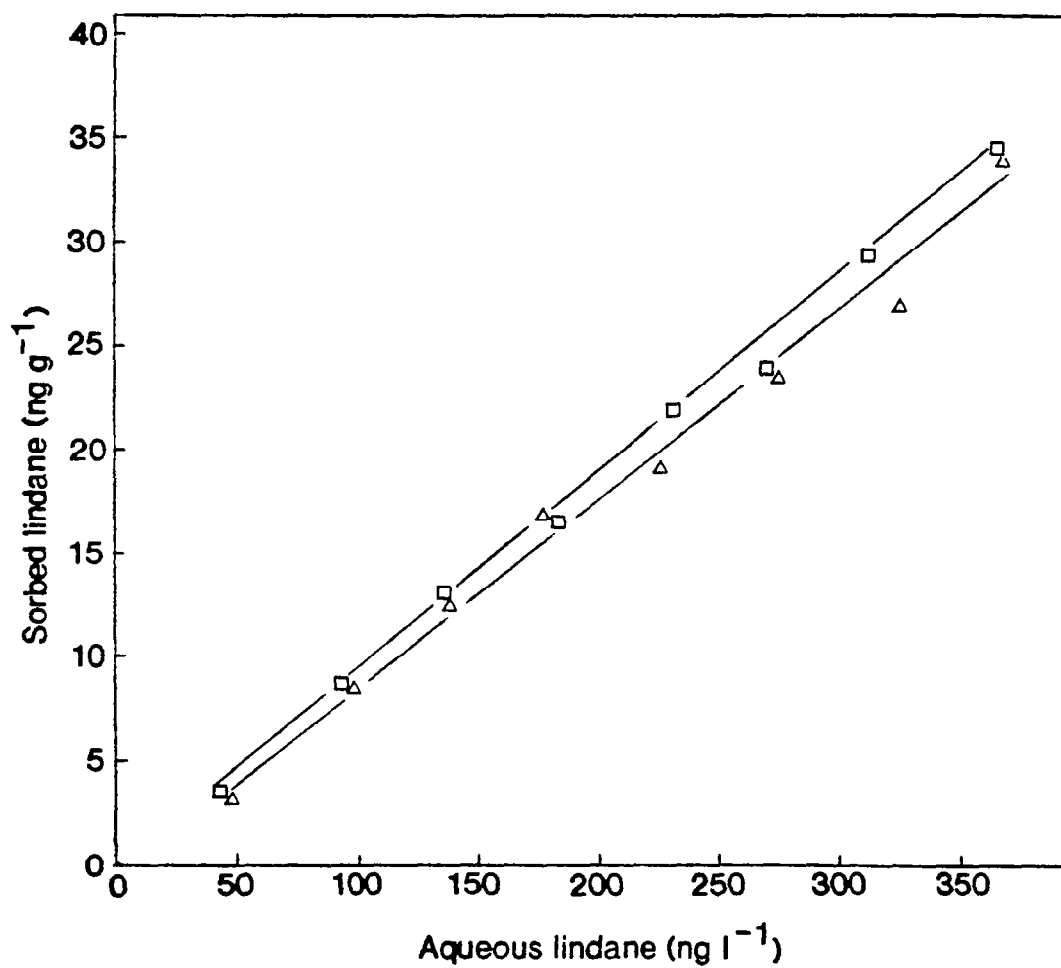


Figure 9a. Effect of DOC on lindane partitioning⁽⁴²⁾

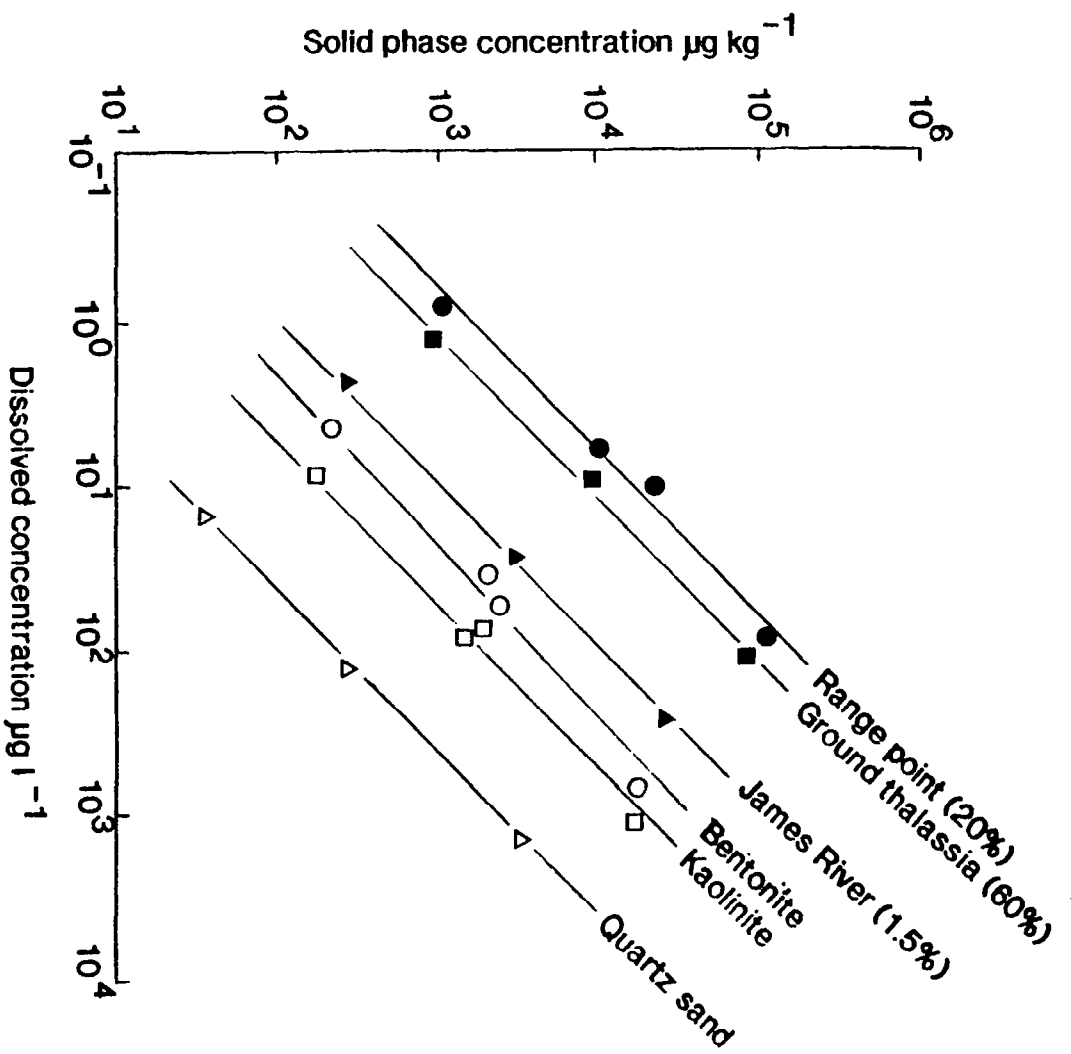


Figure 10. Adsorption isotherms for Kepone on various solids types.
(The organic matter content is shown in parentheses) (43)

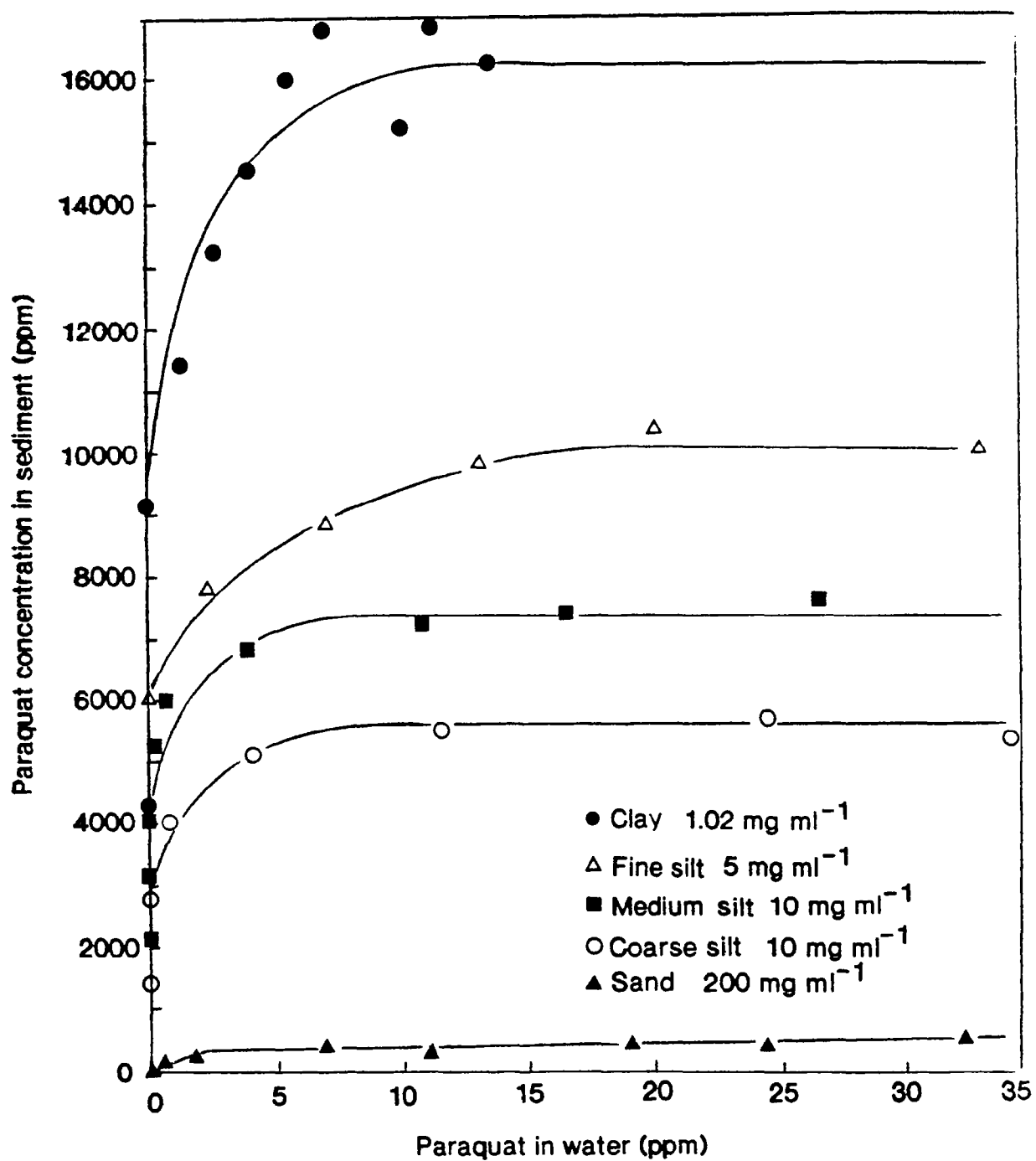


Figure 11. Adsorption isotherms - paraquat on Georgia I sediments (38)

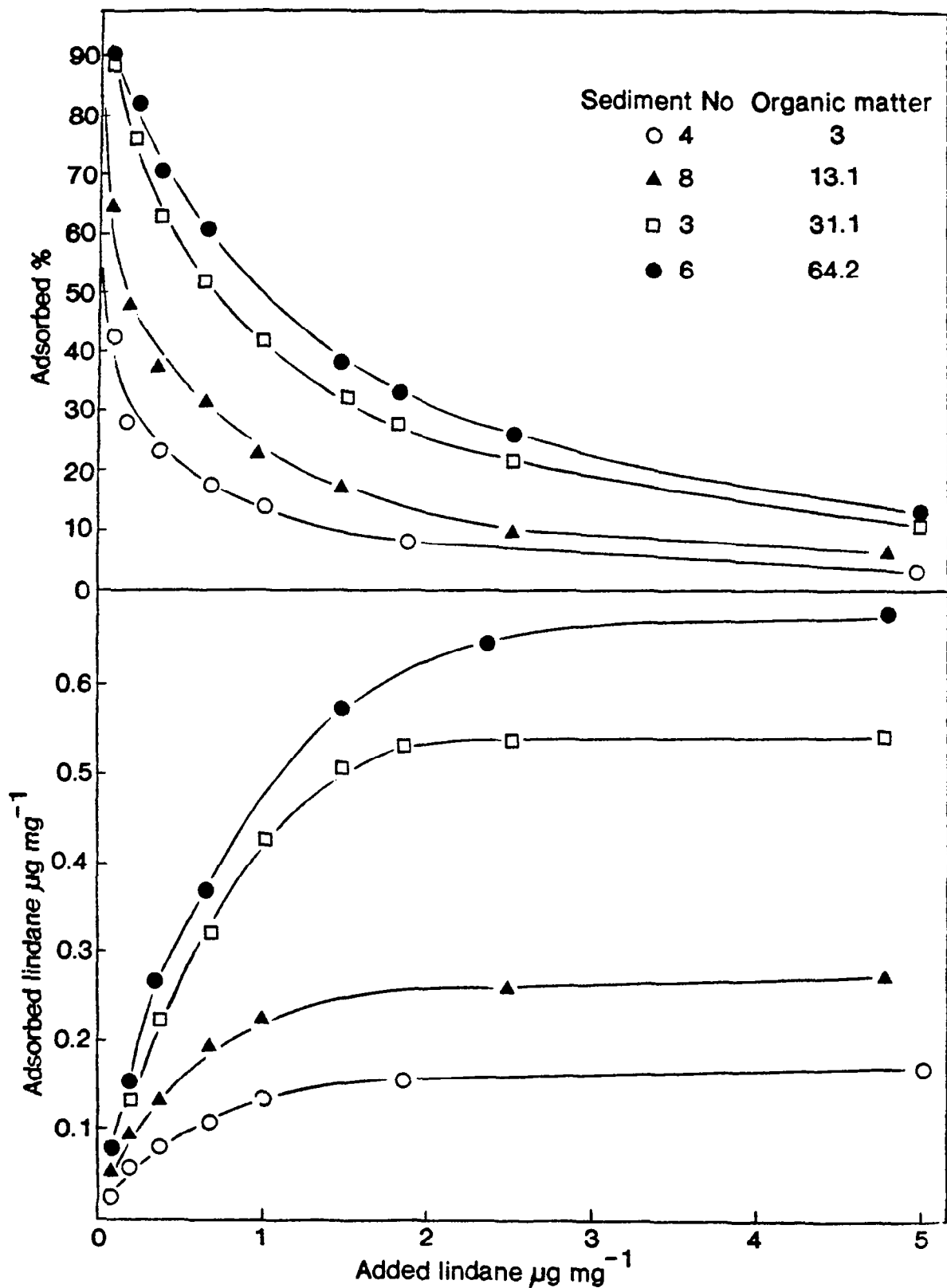


Figure 12. Lindane adsorption by sediments as a function of lindane to sediment ratio⁽²³⁾

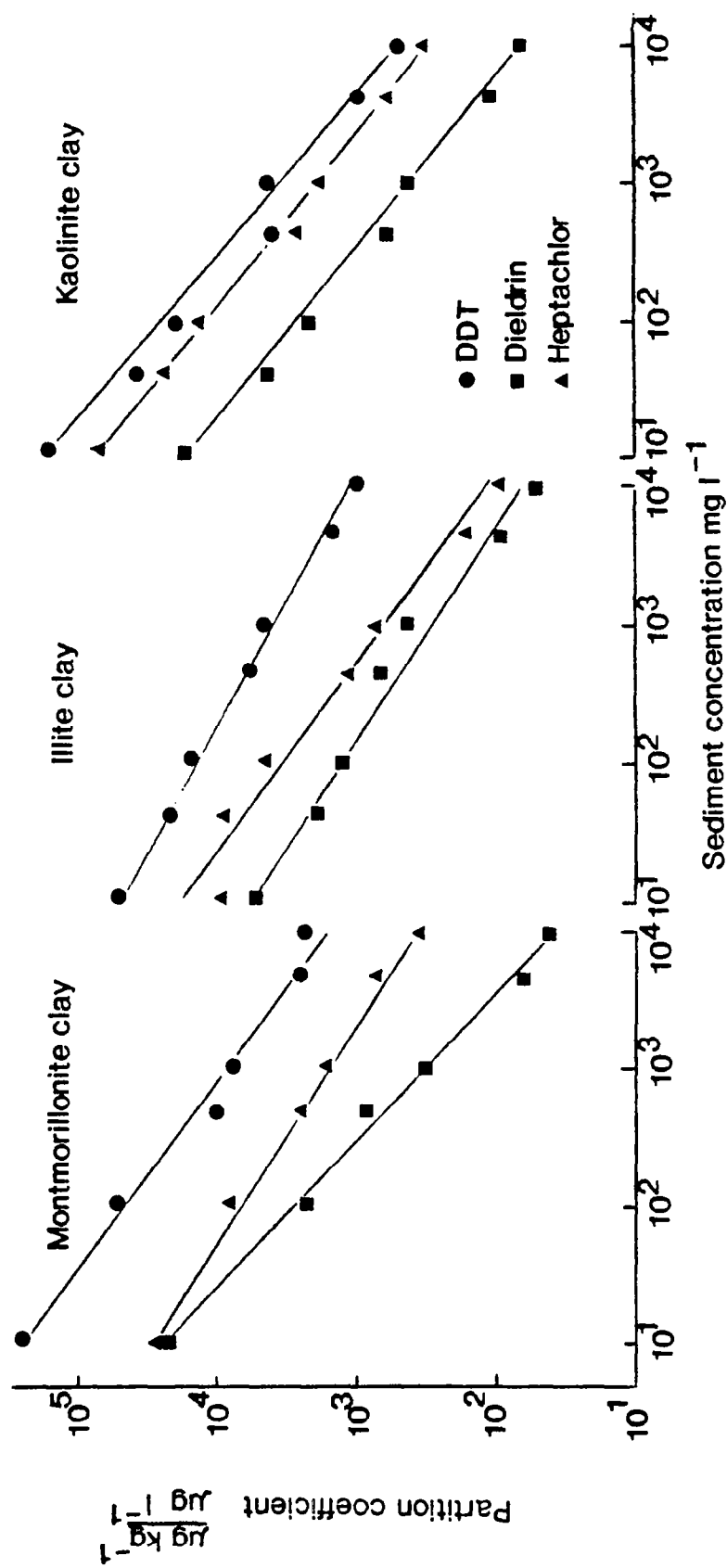


Figure 13. Correlation of partition coefficient and concentration of solids for chlorinated hydrocarbons on clay (43)

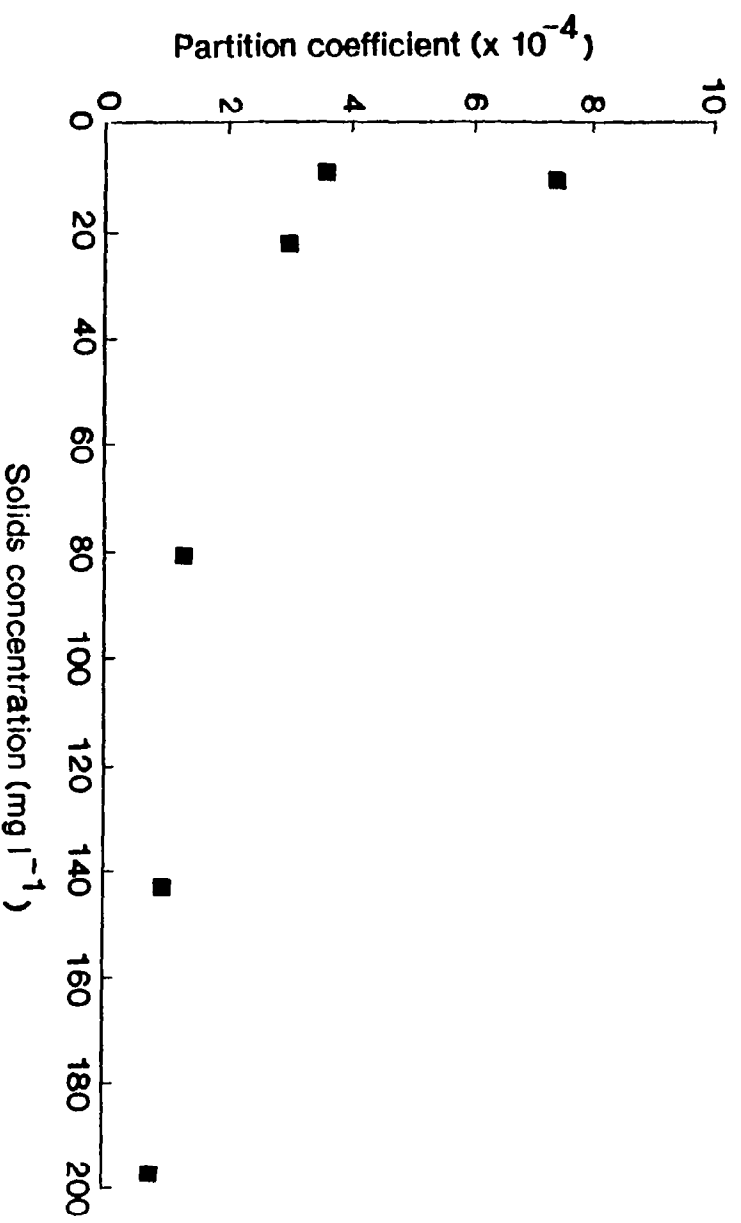
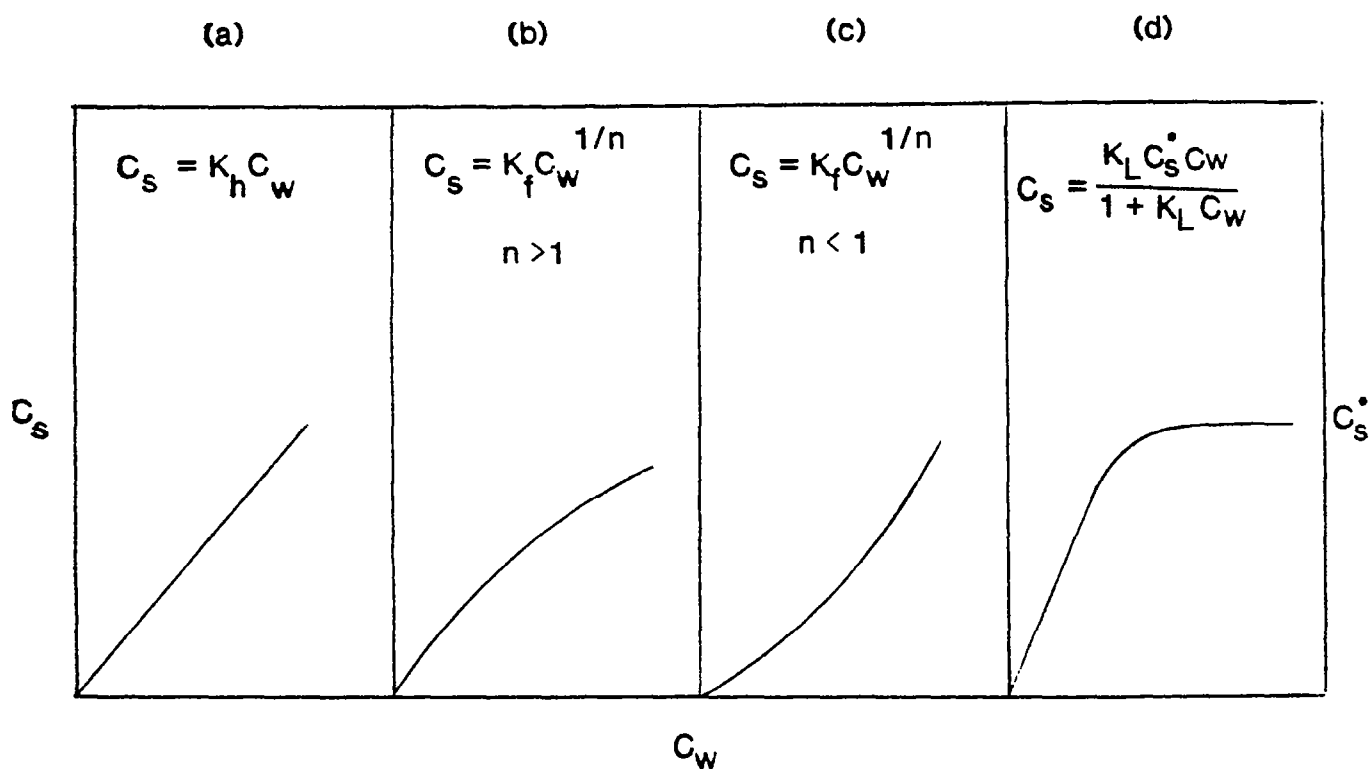


Figure 14. Dependence of the partition coefficient on solids concentration
for 2,4,5,2',4',5'-hexachlorobiphenyl and Lake Michigan sediment (OGH) ⁽⁴⁴⁾



K_f and K_h are Freundlich constants.

K_L is the Langmuir parameter

C_s = amount of chemical sorbed per unit mass of sediment

C_w = amount of chemical in aqueous phase per unit mass of solution

C_s^* is the amount sorbed at monolayer capacity

Figure 15. Typical isotherms for the adsorption of organics on sediment from dilute aqueous solution. (65)

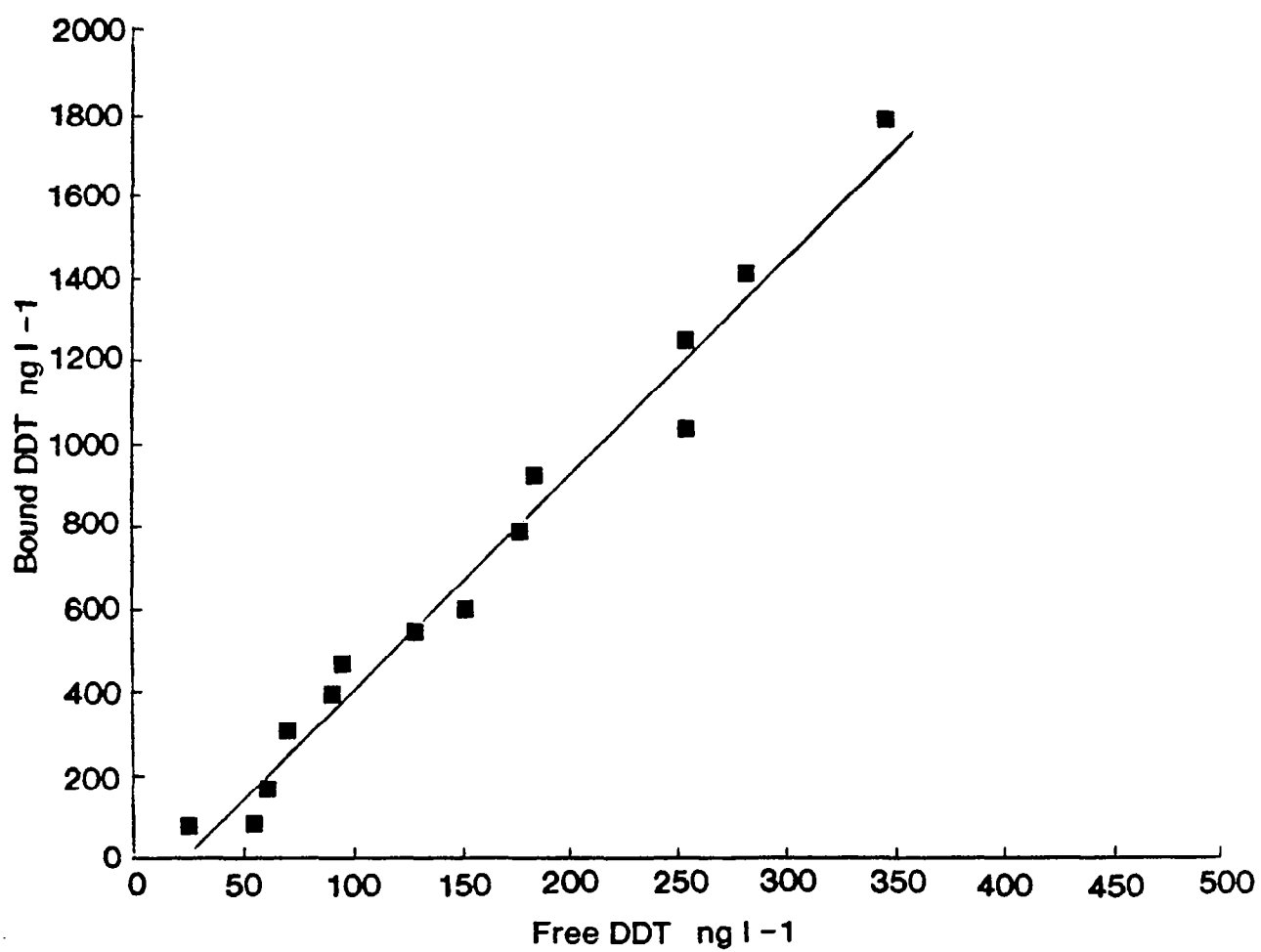


Figure 16. Typical dialysis results: (Boonton humic acid) = 16.2 mg l⁻¹
pH 8.3; I 0.01⁽³⁹⁾

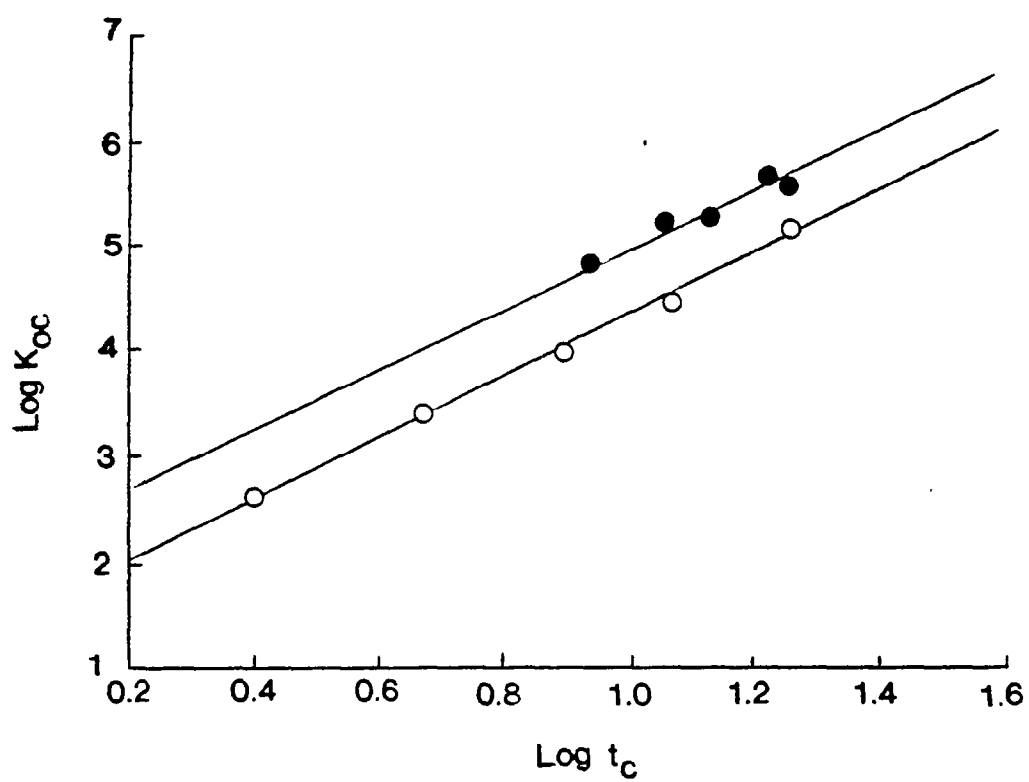


Figure 17. Correlation between K_{oc} and t_c .

● OSH sediment ○ Michawye sediment⁽⁷⁹⁾

APPENDIX A

THE EFFECT OF NATURAL LIGANDS ON TRACE METAL PARTITIONING

**THE EFFECT OF NATURAL LIGANDS ON TRACE METAL
PARTITIONING**

PRU 2183-M

JUNE 1989

THE EFFECT OF NATURAL LIGANDS ON TRACE METAL PARTITIONING

Report No: PRU 2183-M

June 1989

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UNRESTRICTED

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1. INTRODUCTION

The behaviour of potentially hazardous substances in the aquatic environment is known to be dependent on the form in which they are present. An important factor influencing the speciation of such substances (notably heavy metals and trace organics) is the interaction between dissolved and particulate phases. The toxicity to aquatic life and the tendency to be transported within water systems has been shown to be markedly different for dissolved species compared with those associated with particulate material. An understanding of partitioning is therefore required if the impact and fate of contaminants is to be modelled and controlled.

A key parameter of many partitioning models is the so called equilibrium partition coefficient, K_p . This quantity is usually expressed as a ratio of the concentration of adsorbed substance versus the concentration in solution.

$$K_p = \frac{\text{concentration of adsorbed (M/Kg of particulate matter)}}{\text{concentration of dissolved (M/L of solution)}}$$

The numerical value of K_p will depend on a number of factors: the nature of the contaminant; the type of particulate matter under consideration (eg particle size, surface properties, chemical composition); the physical and chemical properties of the solute (eg ionic strength, pH, other dissolved species). For a given system and excluding any of the substance which is not freely exchangeable, it might be assumed that a single coefficient would describe the equilibrium partitioning between dissolved and particulate phases. With one important proviso, this assumption has been shown to be valid for both organics and trace metals. Any changes in partitioning have been found to be broadly explicable in term of existing knowledge of solution and surface chemistry. The feature which has been difficult to explain is the fact that K_p is not observed to be constant with respect to changes in the concentration of suspended particulate matter (1). Measured values for K_p have been observed to increase as the concentration of suspended solids is decreased.

Two explanations of this phenomenon have been put forward. Some workers have attributed the "particle concentration effect" to an experimental artefact produced by the presence of a fraction of suspended material which is not separated from (and is therefore included in) the dissolved phase. Gschwend and Wu (2) have reported that when this "non separable particulate phase" is removed by washing the sediment used in determining K_p for organic compounds, the particle concentration effect disappears. In contrast, DiToro et al (3), in an experiment in which the effects of a "third phase" on metal adsorption is held constant for different dilutions, have reported that the particle concentration effect was still observed. They conclude that a more complex view of partition is needed; a mechanism of desorption caused by interactions between particles, in addition to spontaneous sorption/desorption processes, is postulated.

Although these different explanations may both have their merits under different circumstances, they remain tentative. We propose that more emphasis should be placed on the study of variations in measured values of K_p which arise from factors known to be important in natural waters. The role of naturally occurring organic macromolecules or dissolved organic materials has been noted as of potential significance (4,5,6) but has not followed up in relation to metal complexation. The existence of naturally occurring organic ligands with an affinity for trace metals is well known (eg 7,8,9). We feel that such ligands are likely to play a key role in the partition of trace metals and, possibly, organic compounds.

Our interest in partitioning of environmental contaminants stems primarily from the desire to model the fate and speciation of trace metals contained in sewage sludge which is disposed of at sea. The purpose of this paper is (i) to examine the potential importance of naturally occurring ligands to the partitioning of trace metals, and (ii) to model the likely variation of measured K_p with respect to dilution, on the basis of current estimates of ligands present in sewage sludge and seawater.

SECTION 2 - MODELLING

Consider a system in which an organic ligand, LIG, is in equilibrium with dissolved metal, M_d , and the metal-ligand complex MLIG. The equilibrium is expressed in terms of the constant K_{lig} :

$$K_{lig} = \frac{[MLIG]}{[M_d] \cdot [LIG]} \quad (1)$$

The dissolved metal is also in equilibrium with metal associated with suspended material in a ratio given (in the absence of dissolved metal-organic species and ignoring irreversible binding) by the partition coefficient, K_p :

$$K_p = \frac{[M_s]}{[M_d]} \quad (2)$$

where $[M_s]$ is the number of moles of metal adsorbed per kilogram of solid.

The observed partition coefficient, $K_{p, obs}$, will include metal associated with ligand as part of the dissolved phase:

$$\text{ie } K_{p, obs} = \frac{[M_s]}{[MLIG] + [M_d]} \quad (3)$$

The total metal concentration in the system is $[MTOT]$ M/L.

$$[MTOT] = ([MSL]/DFS) + [MSW] \quad (4)$$

where $[MSL]$ and $[MSW]$ are the concentrations of metal associated with the sludge and in the seawater, respectively. DFS is the factor by which the sludge is diluted (the dilution of seawater by sludge is ignored).

$$[M_s] = ([MTOT] - [MLIG] - [M_d])DFS/SS \quad (5)$$

$$[M_d] = [M_s]/K_p = \frac{([MTOT] - [MLIG])}{(1 + K_p \cdot SS/DFS)} \quad (6)$$

(SS is the suspended solids concentration of the sludge in Kg/l)

From (1), (2) and (6):

$$K_{lig} = \frac{[MLIG] \cdot (DFS/SS + K_p)}{([MTOT] - [MLIG]) \cdot ([LTOT] - [MLIG]) \cdot DFS/SS} \quad (7)$$

([LTOT] is the total ligand concentration in M metal equivalent/L)

For a given system, DFS, [MTOT], SS, and K_{lig} , can be regarded as known or measurable, K_p is constant and, for the purpose of the model, known. Equation (7) can be rearranged to a quadratic in [MLIG], the solution of which gives values for [MLIG], given the above parameters. This provides a way of comparing the values of observed partition coefficient, $K_{p, obs}$, (excluding any measurement error) with the idealised value, K_p , to model the effect of organic ligands on the assessment of metal partitioning.

For the disposal of sewage sludge at sea, the ligand or ligands concerned can be derived from the sludge itself or can be present, naturally, in the seawater. These two sources have been separated to allow each to be varied independently (though the same stability constant is used for ligand-metal complexes regardless of source).

The choice of input values for the model will be determined by the concentration of the metal concerned, the concentration of a ligands and the strength of their affinity for the metal. The following parameters were chosen on the basis of what is known concerning copper complexation in seawater and the composition of what might be regarded as the component of sewage sludge which remains suspended in seawater.

Parameter	Value chosen	Basis of choice/reference
True partition coefficient (K_p)	10^5	~ for copper (1,10,11) Note 1.
Ligand concentration in the dissolved phase (seawater)	5×10^{-8}	Measured in Severn estuary for copper complexation (12), and (13,14)
Ligand concentration in sludge	10^{-5} to 10^{-3}	Values obtained by Plymouth Marine Laboratory under contract to WRC using ligand titration techniques. Note 2.
Metal-ligand complex concentrations and (15)	10^7 to 10^{11}	See references for ligand stability constant
Metal concentration in sewage sludge	10^{-4}	Typical for suspended fraction (after 1 hour settling) of sludge used in sea disposal
Sludge suspended solids	1% by weight	" " Note 3
Dilution ratio	1 to 10^6	(16,17)

Note 1. Values for metal partitioning coefficients given in the references cited vary in the range 10^4 to 10^6 .

Note 2. The ligand concentration in the sludge is assumed to be released to the dissolved phase on dilution with seawater. The value given is inferred from tests carried out on a sludge diluted onehundredfold with seawater.

Note 3. Total solids in sludges disposed of to sea may be 2% to 4%. A value of 1% is taken to represent the lighter, non-settling fraction.

SECTION 3 - RESULTS

The results of modelling are shown for complexing ligands of strengths in Figures 1 to 3. In all cases the partition coefficient, K_p , is set at 10^5 . Two separate, competing effects are apparent. The first is the increase in observed/measured partition coefficient as dilution is

increased. This is effectively the same phenomenon as that noted by O'Connor and Connolly (1) and subsequently investigated by other workers (eg 2,3,18). The sources of this effect may be different in different situations, but in the case of sewage sludge the variation of observed K_p with dilution is explicable as a product of complexation. It appears that the value for K_p observed at highest dilution is nearest to the true value. At lower dilutions, the effect of ligands in the dissolved phase is to increase the proportion of metal in solution and hence to depress the partition coefficient.

The second effect amounts to a titration of metal derived from the added solid phase with ligands naturally present in solution. For the most strongly complexing ligands, the consequence of this is to reduce the observed value of the partition coefficient at higher dilutions to a value very much less than its theoretical level (Figure 3).

In combination, these two effects tend to lead to the underestimation of the value of K_p which, in truth, applies for the metal/solid/solution system under consideration. This negative bias in the observed K_p is complicated by being strongly dependent on the dilution at which any measurements are made. The measurement of partition coefficients by estimation of dissolved and particulate metal, either in natural systems or those to which solids and metal have been added, is likely to be subject to such errors. This calls into question the use of such partition coefficients to model equilibrium partitioning of metals between particulate and dissolved phases for conditions (especially dilution) which differ from those which have been tested directly.

This proviso is more restrictive than it might seem at first since the ability to make reliable analytical determinations of dissolved and particulate metal limits the dilutions which can be examined to (say) 500 to 1000 times. Such dilution ratios are relatively small compared with those which occur during the first few hours in the disposal of sludge at sea. Jenkins and Gibbs (16) report dilution factors for whole sludge of 1,000 to 6,000 in the first 2 hours. Duedall et al (17) report lower dilutions (around 20x) 2 hours after a spot dump.

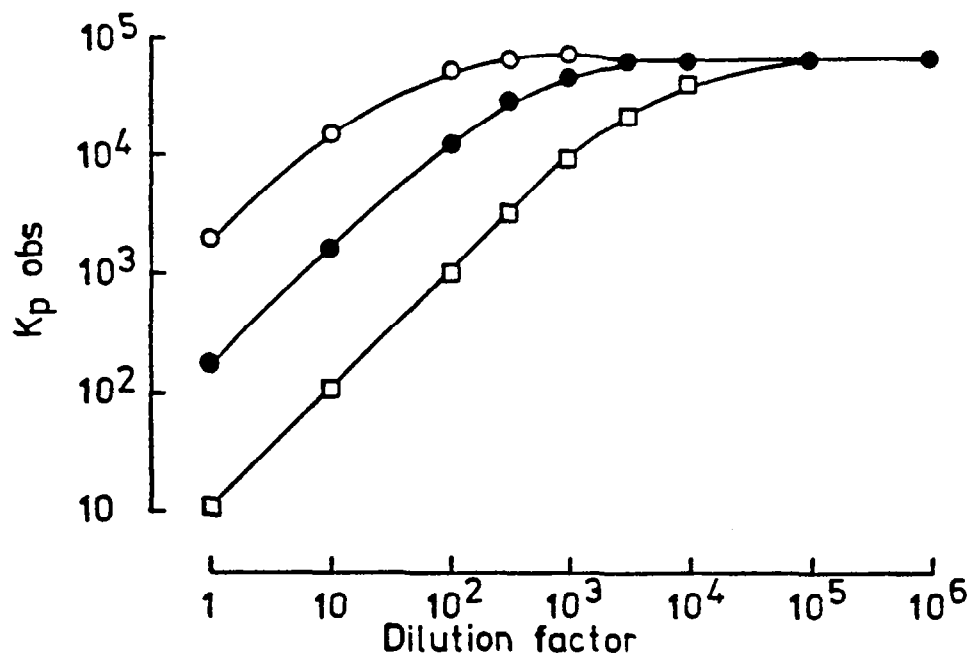


Figure 1. Effect of dilution on observed partition coefficients for ligand-metal complex of stability constant $K=10^7$. Concentrations of ligand in undiluted sludge: $\square 10^{-3}M$; $\bullet 10^{-4}M$; $\circ 10^{-5}M$.

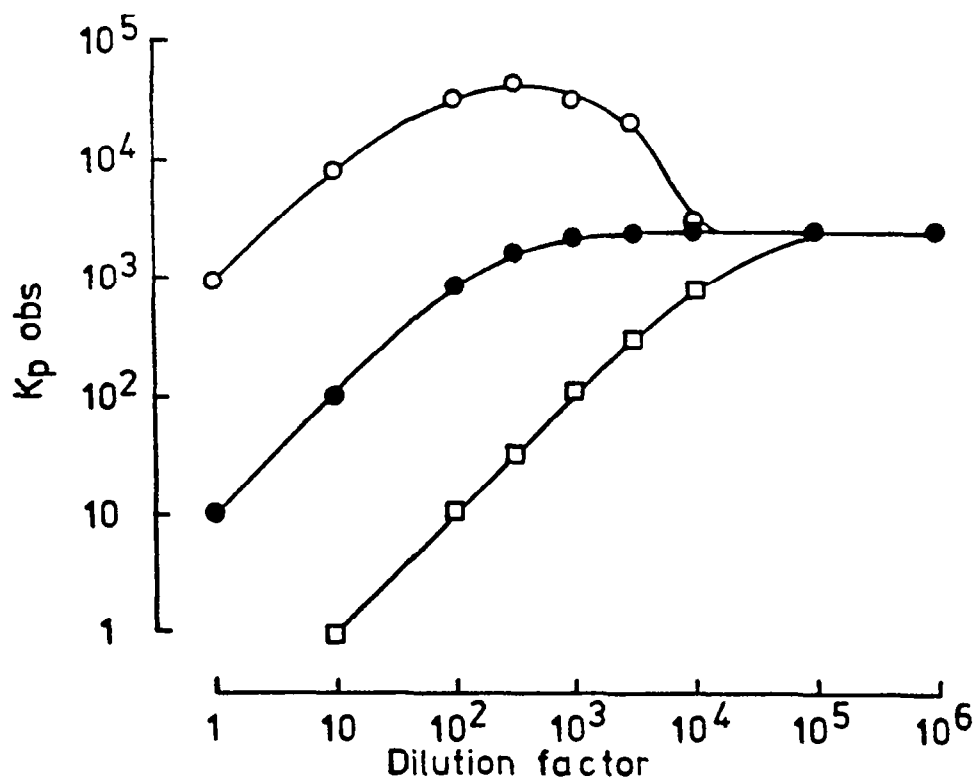


Figure 2. Effect of dilution on observed partition coefficients for ligand-metal complex of stability constant $K=10^9$. Concentrations of ligand in undiluted sludge: $\square 10^{-3}M$; $\bullet 10^{-4}M$; $\circ 10^{-5}M$.

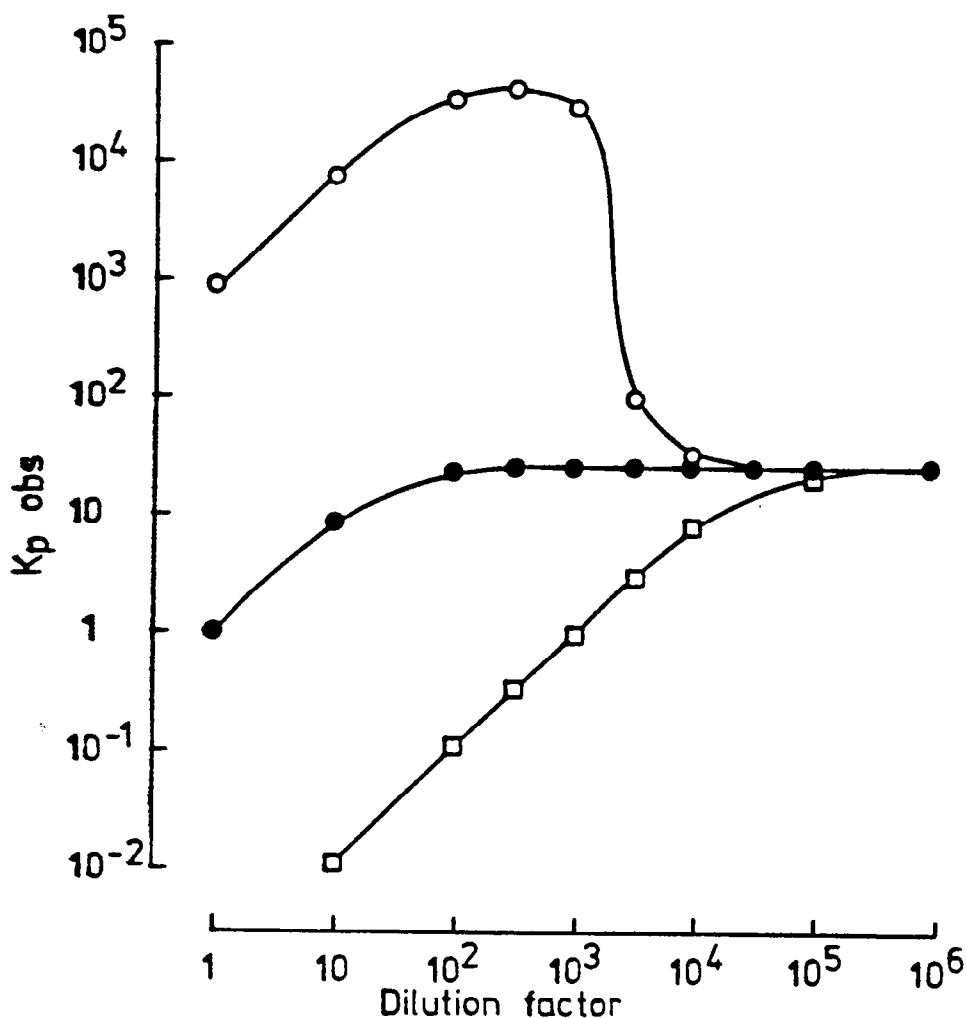


Figure 3. Effect of dilution on observed partition coefficients for ligand-metal complex of stability constant $K=10^{11}$. Concentrations of ligand in undiluted sludge: $\square 10^{-3} \text{ M}$; $\bullet 10^{-4} \text{ M}$; $\circ 10^{-5} \text{ M}$.

Whilst it might be expected that the suspended fraction of sludge would not be diluted as quickly as whole sludge (because of lower rates of sedimentation), over the period of several days before equilibrium is established between solid and liquid phases (10) it is clear that dilution factors of over 10,000 could apply. In this case, the naturally occurring suspended matter in seawater would be likely to predominate. This has not been modelled, but needs to be borne in mind when partition coefficients are being measured.

The validity of measured EQUILIBRIUM partition coefficients is even more questionable when it is realised that, in practice, their determination often involves the assumption that equilibrium has been reached. Merely separating dissolved and particulate metal - whether in naturally occurring samples or in those to which additions of metal or solids have been made - does not answer the question of whether or not equilibrium between dissolved and particulate phases is achieved within the time in which the two phases are in contact - ie before sedimentation or further dilution causes separation (19).

The parameters used in the above model have been chosen to apply to copper, a metal known to have a strong affinity for organic species. For other metals, where organic complexation may not be so important, the effects will not be so large. However, few metals have no association with natural ligands so these effects cannot be assumed to be unimportant. The effect of inorganic speciation (20) may also be important.

SECTION 4 - CONCLUSIONS

1. Equilibrium partition coefficients, obtained by a simple, single separation of dissolved and particulate materials, are of limited value in modelling the fate of metals. Serious errors in the estimated division of metal between the dissolved and particulate phases are likely, unless the partition coefficient used in modelling is measured under conditions identical to those of interest. This implies the need to make measurements at a range of dilutions as well as taking into account other physical and chemical factors. Partition coefficients obtained in this way may still prove useful as empirical predictors of metal speciation.
2. Measurements of partition coefficients made in an artificial system excluding natural dissolved organic ligands will tend to yield a value which underestimates the proportion of metal in the dissolved phase for natural systems. The relationship between a partition coefficient obtained at one dilution and that applying at another is not easily predicted. Among other factors, it

depends on the strength of any ligand-metal complexes and on the relative quantities of ligand released from the solid phase and that already present in the aqueous phase.

3. Although the influence of complexation demonstrated here is not the sole possible explanation of any variation of K_p obs with dilution, it is certain to be important for many metals in organic rich systems, such as those involving sewage sludge, where relatively large quantities of natural ligands are present.
4. A greater understanding of the kinetics of partitioning together with the effects of dilution is required. Specifically, it is desirable that estimates be made of the likely partitioning of metal which may occur between the dissolved and particulate phases at the appropriate dilution and within the time available as dilution and dispersion occurs.

REFERENCES

1. O'CONNOR D J and CONNOLLY J P. The Effect of Concentration of Adsorbing Solids on the Partition Coefficient. Water Res, (1980), 14, 1517-1523.
2. GSCHWEND P M and WU S. On the Constancy of Sediment-water Partition Coefficients of Hydrophobic Organic Pollutants. Environ Sci Technol, (1985), 19, 90-96.
3. DI TORO D M, MAHONY J D, KIRCHGRABER P R, O'BYRNE A L, PASQUALE L R and PICCIRILLI D C. Effects of Non-reversibility, Particle Concentration and Ionic Strength on Heavy Metal Sorption. Environ Sci Technol, (1986), 20, 55-61.
4. BOURG A C M. Trace Metal Adsorption Modelling and Particle-Water Interactions in Estuarine Environments. Continental Shelf Research, (1987), 7, 1319-1332.
5. VOICE T C, RICE C P and WEBER W J. Effect of Solid Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems. Environ Sci Technol., (1983), 17, 513-518.
6. CARTER C W and SUFFET I H. Binding of DDT to Natural Humic Substances. Environ Sci Technol, (1982), 9, 101, 735-740.
7. BUCKLEY P J M, and VAN DEN BERG C M G. Copper Complexation Profiles in the Atlantic Ocean. Marine Chemistry, (1986), 19, 281-296.
8. RUZIC I. Theoretical aspects of the direct titration of natural waters and its information yield for trace metal speciation. Anal Chim Acta, (1982), 140, 99-113.
9. NEUBECKER T A and ALLEN H E. The measurement of complexation capacity and conditional stability constants for Ligands in Natural Waters. A Review. Water Res, (1983), 17, 1-14.

10. ROHATGI N and CHEN K Y. Transport of Trace Metals by Suspended Particulates on Mixing with Seawater. Journal of the Water Pollution Control Federation, (1975), 47, 2298-2316.
11. HONEYMAN B D and SANTACHI P H. Metals in Aquatic Systems. Environ Sci Technol, (1988), 22, 862-871.
12. APTE S C, GARDNER M J and RAVENSCROFT J E. Submitted to Marine Chemistry.
13. KRAMER C J M. Apparent Copper Complexation Capacity and conditional stability constants in north Atlantic waters. Mar Chem, (1986), 18, 335-349.
14. VAN DEN BERG C M G, BUCKLEY P J, HUANG Z Q and NIMMO M. An electrochemical study of the speciation of copper, zinc and iron in two estuaries in England. Est Coastal Mar Sci, (1986), 22, 479-486.
15. APTE S C, GARDNER M J and RAVENSCROFT J E. An Evaluation of Voltammetric Titration Procedures for the Determination of Trace Metal Complexation in Natural Water by use of Computer Simulation. Anal Chim Acta, (1988), 212, 1-21.
16. JENKINS W A and GIBBS R J. Settling and Dispersion of Ocean Dumped Sewage Sludge. Marine Pollution Bulletin, (1988), 19, 120-124.
17. DUEDELL I W, O'CONNERS H B, OAKLEY S A and STANFORD H M. Short-term Water Column Perturbations Caused by Wastewater Sludge Dumping in the New York Bight Apex. Journal of the Water Pollution Control Federation, (1977), 2074-2080.
18. MACKAY D and POWERS B. Sorption of Hydrophobic chemicals from Water: A Hypothesis for the Particle Concentration Effect. Chemosphere, (1987), 16, 745-757.
19. NYPFELER U P, LI Y H and SANTACHI P H. A Kinetic Approach to Describe Trace-element Distribution Between Particles and Solution in Natural Aquatic Systems. Geochimica et Cosmochimica Acta, (1984), 48, 1513-1522.

20. COMANS R N J and VAN DIJK C P J. Role of Complexation Processes in Cadmium Mobilisation During Estuarine Mixing. Nature, (1988), 336, 151-154.

