

**THE INFLUENCE OF SURFACTANTS
ON THE SORPTION OF
PHENANTHRENE IN NATURAL WATERS**

TRACEY LOUISE JONES-HUGHES

Ph. D. 2002

DEDICATION

For my parents, my husband Russell

and

my son Thomas

who gave me every reason to persevere

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ON THE SORPTION OF
PHENANTHRENE IN NATURAL WATERS**

by

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Department of Environmental Sciences
Faculty of Science
University of Plymouth

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and

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THE INFLUENCE OF SURFACTANTS ON THE SORPTION OF PHENANTHRENE IN NATURAL WATERS

Tracey Louise Jones-Hughes

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are widely recognised as harmful, persistent organic pollutants, whilst surfactants are more easily degraded but their ubiquitous use both domestically and industrially ensures their presence in natural waters. Owing to both their hydrophobic and hydrophilic properties, surfactants are capable of both adsolubilisation and solubilisation of co-contaminants, hence, their presence in natural waters is considered extremely significant. The purpose of this research was to determine how surfactants and PAHs influence each other in estuaries where both are co-disposed. This study is the first to employ environmentally realistic concentrations of surfactants and to use natural particles in order to determine how changes in surfactant behaviour impinge on the sorption of a representative PAH to sediment.

The experimental method employed involved tracing the solubility and sorption of a ^{14}C -labelled PAH (phenanthrene) in the presence of representative surfactants from the three main groups, i.e., anionic, nonionic and cationic. Initially the four compounds were examined in isolation at two temperatures (8°C and 20°C), salinities and particle concentrations. The next stage involved incorporating each surfactant with phenanthrene in the same experiment and repeating the range of variables.

Solubility and adsorption of phenanthrene in the presence of Triton X-100, sodium dodecyl sulphate (SDS) or hexadecyltrimethylammonium iodide (HDTMA) proved to be highly complex. The adsorption, expressed as a Freundlich coefficient, K_F , was generally nonlinear and varied according to surfactant type, salinity, temperature, and contact sequence. The overriding influence, however, was sediment particulate matter (SPM) concentration. On some occasions the surfactants in isolation displayed unusual

particle concentration effects (PCE), such as an increase of surfactant in the aqueous phase as the SPM concentration increased. Despite this, they all generally exaggerate the more typical PCE displayed by phenanthrene, where the particle-water partition coefficient is reduced as particle concentration increases. This effect is then modified by temperature and contact sequence, which has important environmental implications with regard to removal or release of compounds stored within sediments. However, overall, at environmentally relevant concentrations, the surfactants appear to enhance sorption, rather than solubility, with HDTMA the most effective surfactant at removing phenanthrene from the aqueous phase.

Author's declaration

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award.

This study was carried out in collaboration with BMT Marine Information Systems Limited and AstraZeneca.

A programme of advanced study was undertaken which included guided reading in topics relating to environmental and estuarine organic chemistry. Training was given in the safe use of radioisotopes and analysis of ^{14}C radiotracers using scintillation counting. Instruction was also given in a wide-range of analytical methodologies including radio-GC, radio-HPLC, ICP- atomic emission spectrophotometry and multi-point BET nitrogen gas adsorption.

Publications

Turner, A., Hyde, T. L. & Rawling, M.C. (1999) Transport and retention of hydrophobic organic micropollutants in estuaries: implications of the particle concentration effect. *Estuarine, Coastal and Shelf Science*, **49**, 733-746.*

*See Appendix B.

Conferences and presentations

British Organic Geochemistry Society, University of Plymouth, 16-17 July 1998.

Oral presentation : *The Role of Surfactants on the Sorption of Hydrophobic Organic Micropollutants in Estuaries.*

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Poster Presentation: *The Role of Surfactants on the Sorption of Hydrophobic Organic Micropollutants in Estuaries.*

Young Researchers Radiochemical Methods Meeting, University of Manchester, 9 June 1999.

Oral Presentation: *The use of Radiotracers to Establish Particle-Water Partitioning of Organic Contaminants in Natural Waters*

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Courses and external visits

Meetings were held with colleagues at AstraZeneca, Brixham, to discuss data and plan future work.

Signed...*T. J. M.*.....

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CHAPTER 1: INTRODUCTION

1.1. General Introduction

As the human demand for energy and materials continues to grow, the disposal of anthropogenic chemicals into the environment inevitably rises. While many of these chemicals are incorporated into apparently innocuous formulations such as cosmetics, concern is directed towards substances which display toxic, persistent properties (e.g. polycyclic aromatic hydrocarbons) and high volume products (e.g. detergents).

Natural waterbodies are especially prone to contamination due to the assortment of fluxes entering both directly and indirectly i.e., the disposal of domestic and industrial waste, surface run off, ground water leaching, and long range atmospheric transport. In particular, estuaries, as a result of their convenient coastal location, are especially vulnerable to point discharges of domestic and industrial wastes.

Without the added environmental stress of pollution, extreme variations in physico-chemical conditions pre-ordain estuaries as an exceptionally unforgiving environment for organisms to inhabit. This is because estuaries are highly complex systems experiencing variations in salinity, pH and dissolved oxygen concentration (Turner & Tyler, 1997). Furthermore, the estuarine sediments are subject to advection and dispersion, particle settling, flocculation, coagulation, interfacial entrapment, resuspension, bioturbation and organic matter trapping (Santschi *et al.*, 1997). Regardless of these conditions, estuaries remain zones of high productivity, frequently supporting complex ecosystems, including the larval development of various aquatic species (Quiroga *et al.*, 1989).

Being able to identify contaminant behaviour within a polluted estuary requires not only a comprehensive understanding of the existing physico-chemical processes but also a consideration of co-disposed compounds. It is becoming increasingly clear that

other compounds within a waste stream, whether they are believed to be deleterious to the environment or not, may exert a significant influence on the fate of the chemical under investigation (Edwards *et al.*, 1991; Jafvert, 1991; Liu *et al.*, 1991; Haigh, 1996; Tiehm *et al.*, 1997; Guha *et al.*, 1998). Therefore, before the behaviour of discharged pollutants can be assessed, the estuarine and contaminant system needs to be simplified.

Two groups of compounds which feature heavily in industrial and domestic waste streams are hydrophobic organic micropollutants (HOMs) and surfactants. HOMs encompass a huge number of anthropogenic organic compounds which are ubiquitous and persistent in the environment. Examples of HOMs include phthalate esters, polychlorinated biphenyls (PCBs) and, the type of compound of interest here, polycyclic aromatic hydrocarbons (PAHs) (Rawling *et al.*, 1998). HOMs are described as such because they display high solubilities in many nonpolar solvents contrasted by an extremely low solubility in water. Their potential to bioaccumulate coupled with the ability of some of these chemicals to induce carcinogenic, mutagenic or teratogenic responses in receiving organisms requires a thorough understanding of their fate and transport in order to minimise unfavourable environmental repercussions (Kennish, 1997).

Conversely, surfactants, as a result of their amphiphilic nature, are soluble in both polar and nonpolar solvents. They are generally considered easily degradable with wide variations in toxicity (Haigh, 1996). Although surfactants are certainly pollutants in their own right, much interest now revolves around their ability to significantly influence the solubility or sorption of other contaminants in aquatic systems.

1.2 General Properties of Polycyclic Aromatic Hydrocarbons

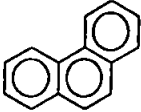
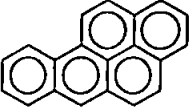
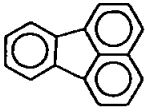
Polycyclic aromatic hydrocarbons (PAHs), also known as polynuclear aromatic hydrocarbons, are nonpolar and comprise of two or more fused benzene rings in linear,

angular or cluster arrangements with unsubstituted groups possibly attached to one or more rings (Mackay & Yeun, 1983). The principal characteristic of PAHs, with regard to this study, is their extremely low aqueous solubility, ranging from 32 mg L⁻¹ for naphthalene to <0.001 mg L⁻¹ for perylene, countered by a high solubility in organic solvents such as *n*-octanol (Laha & Luthy, 1991). As a result, in aqueous-sediment systems, PAHs will favourably transfer out of the aqueous phase and sorb onto the solid phase. It is this property which influences PAH behaviour since sorption, or a lack of, will have a bearing on the mobility and bioavailability of organic contaminants. A parameter frequently used to estimate the preference of a PAH and other HOMs for organic compartments such as animal lipids or sedimentary organic matter, over an aqueous phase is the *n*-octanol-water partition coefficient, K_{ow} . This coefficient describes the distribution of the compound, at equilibrium, between *n*-octanol and water and provides a direct assessment of hydrophobicity or of the tendency to partition from water to organic media (Mackay *et al.*, 1992):

$$K_{ow} = \frac{C_o}{C_w} \quad (1.1)$$

where C_o is the concentration of the compound in *n*-octanol (w/v), and C_w is the concentration of the compound in the aqueous phase (w/v). Examples of log K_{ow} and aqueous solubility for selected PAHs are presented in Table (1.1).

Table 1.1: General properties of selected PAHs (Mackay *et al.*, 1992).

	Phenanthrene	Benzo(a)pyrene	Fluoranthene
			
Property	C ₁₄ H ₁₀	C ₂₀ H ₁₂	C ₁₆ H ₁₀
Mol. Wt. (g mol ⁻¹)	178.2	252.3	202.3
Melting point (°C)	101	175	111
Boiling point (°C)	339	495	375
Vapour pressure at 25°C (Pa)	0.02	7.00 × 10 ⁻⁷	1.23 × 10 ⁻³
Aqueous solubility at 25°C (mg L ⁻¹)	1.10	0.0038	0.26
Log K _{ow} at 25°C	4.57	6.04	5.22

Global studies of PAHs in sediments provide evidence of their ubiquity (see Table 1.2) while the similarity of sediment PAH patterns to each other and to air particulate matter indicate that anthropogenic combustion of fossil fuels are the major source of PAHs (Miles & Delfino, 1999). Air masses passing over extremely industrialised regions have been known to accumulate high PAH loads (20 to 30 ng m⁻³) (Kennish, 1997), which emphasises the significance of long-range atmospheric dispersion processes. PAHs can also enter aquatic ecosystems from other anthropogenic sources such as domestic and industrial wastewater, urban and agricultural run off, waste incineration, fuel use and spills (Miles & Delfino, 1999). Natural sources of PAHs include forest fires, volcanic eruptions and synthesis by bacteria, plants and fungi (Kennish, 1997). Unfortunately, the combustion derived PAHs are relatively resistant to degradation as compared to oil-derived aromatic hydrocarbons which can be rapidly biodegraded in sediments (Readman *et al.*, 1987).

Table 1.2: Concentrations of PAHs in natural waters.

Environmental Matrix	Phenanthrene	Fluoranthene	Benzo(a)pyrene	ΣPAH
<u>Aqueous phase (ng L⁻¹)</u>				
<u>River and lake</u>				
Lac Saint Louis	8.1 ^a	4.1 ^a	0.48 ^a	21.8 ^a
St Lawrence River, Canada	3.0 ^b	3.7 ^b	1.1 ^b	23.1 ^b
<u>Estuarine and marine</u>				
Tamar, UK	8.8 ^c	10.4 ^c	9.1 ^c	97.3 ^c
<u>Suspended sediment (µg g⁻¹)</u>				
Tamar, UK	1.04 ^c	0.76 ^c	0.74 ^c	9.96 ^c
<u>Surficial sediment (µg g⁻¹)</u>				
<u>River and lake</u>				
Escura, Portugal	0.05 ^d	0.08 ^d	0.02 ^d	0.8 ^d
Starolesnianske, Slovakia	0.60 ^d	1.95 ^d	0.77 ^d	18.0 ^d
<u>Estuarine and marine</u>				
Tamar, UK	0.36 ^c	0.80 ^c	0.72 ^c	4.89 ^c
Plymouth Sound, UK	0.37 ^c	0.52 ^c	0.31 ^c	3.75 ^c
Florida, USA - Background	0.05-13.5 ^f	0.05-22 ^f	0.24-6.6 ^f	0.04-113 ^f
Florida, USA - Impacted	0.05-228 ^f	0.06-85 ^f	0.18-9.5 ^f	0.05-1086 ^f

Sources: ^aMackay & Hickie, (2000); ^bPham *et al.*, (1999); ^cReadman *et al.*, (1982); ^dFernández *et al.*, (1999); ^eWoodhead *et al.*, (1999); ^fMiles & Delfino, (1999).

1.3. Partitioning, fate and transport of PAHs in aquatic systems

The entry of an organic contaminant into an aquatic system may result in several outcomes as identified in Figure 1.1, hence the difficulties in predicting pollutant behaviour. The pathways illustrated are subject to the chemistry of the contaminant and changes in physico-chemical conditions, therefore they are each evaluated in detail in the following sections.

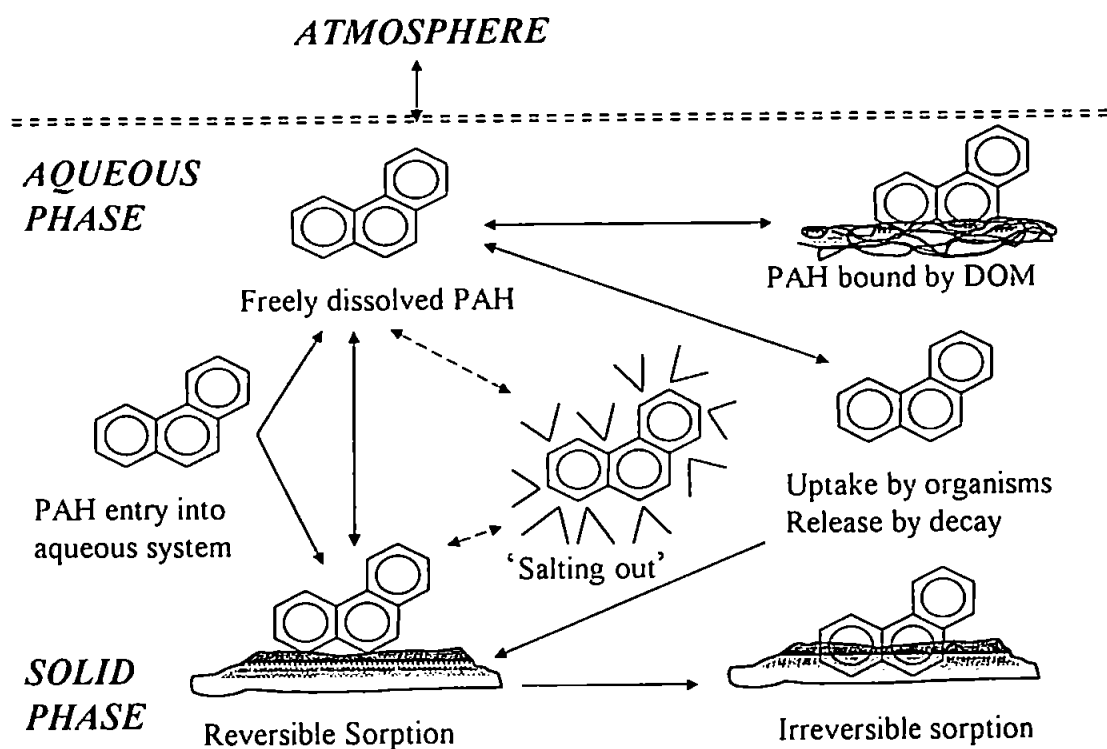


Figure 1.1: Summary of PAH behaviour (shown as phenanthrene) in an aquatic environment

1.3.1. Air-water partitioning

Although PAHs generally display low vapour pressures, they also have very low aqueous solubilities. Therefore, in surface waters under environmental temperatures it is possible for these compounds to appreciably transfer into the atmosphere (Jones & Voogt, 1999). Volatilised HOMs may then undergo long distance transport either as a gas or adsorbed to atmospheric particles until they are ultimately removed by atmospheric deposition or rain washout. The relative escaping tendency of a compound existing as vapour molecules as opposed to being dissolved in water is described by Henry's law constant (K_H) (Schwarzenbach *et al.*, 1993);

$$K_H = \frac{P_i}{C_w} \text{ (Pa m}^3 \text{ mol}^{-1}\text{)} \quad (1.2)$$

where P_i is the partial pressure and C_w is aqueous molar concentration.

Mackay & Yuen (1983) established significant rates of volatilisation for compounds with $K_H > 10^{-1}$ kPa m³ mol⁻¹ although it can still be significant at values around 10^{-3} kPa m³ mol⁻¹, particularly with increased wind velocity (see Table 1.3 for PAH values). Furthermore, Baker & Eisenreich (1990) found appreciable transfer of PAHs and PCBs from Lake Superior to the atmosphere during summer months where weather conditions were found to play an important role.

Table 1.3: Henry's Law constant for selected PAHs (Schwarzenbach *et al.*, 1993)

PAH	K_H at 25°C (kPa m ³ mol ⁻¹)
Phenanthrene	3.2×10^{-3}
Fluoranthene	1.0×10^{-3}
Benzo(a)pyrene	4.6×10^{-5}

1.3.2. Particle-water interactions

By virtue of their extremely low aqueous solubility and subsequent high solubility in organic solvents, PAHs favourably transfer out of the aqueous phase and sorb onto the solid phase, whereby a dynamic equilibrium is established (Voice & Weber, 1983). The mechanisms of PAH sorption to a particle are complex and yet to be fully understood, although physical sorption via van der Waals forces and specific polar interactions (i.e., hydrogen bonding) appears to be the principal mechanisms (Goss & Schwarzenbach, 2001). Van der Waals bonding arises as the PAH from the aqueous phase approaches the surface of a solid sorbent and electron distributions interact to induce additional dipole-dipole moments resulting in a net attraction (Carey, 1992). Conversely, hydrogen bonding only occurs between complementary compounds and therefore may not always be present (Goss & Schwarzenbach, 2001). As PAHs contain π electrons they behave as hydrogen acceptors. However, with regard to hydrophobic molecules in an aqueous solvent, these comparatively weak bonding forces are enhanced by a

substantial thermodynamic gradient driving the molecules out of solution, even before reaching maximum solubility. This combined effect is known as 'hydrophobic bonding' (Tanford, 1980). The energy driving hydrophobic molecules out of solution is due to the structural organisation of H₂O molecules resulting in a number of generally unfavourable enthalpic and entropic contributions to the excess free energy of the solution. For example (Tanford, 1980):

- (i) The organic solute must overcome water:water interactions, since unlike an ionic or polar solute it is unable to form strong bonds with water molecules to compensate for the distortion of these bonds.
- (ii) Although water molecules displaced to make a cavity for the organic compound salvage their water:water interactions elsewhere in solution, the remaining water molecules lining the cavity must interact with fewer water molecules. This becomes increasingly energetically unfavourable the larger the organic molecule.
- (iii) The water molecules immediately surrounding the organic solute have strong interactions with the nearest neighbour water molecules only on one side away from the organic molecule. This situation appears to result in a 'solidifying of positions and orientations' of these cavity-lining water molecules.

1.3.2.1 The influence of particle type on PAH sorption

Due to the nonpolar nature of PAHs, a favourable sorption site would evidently be a hydrophobic one, such as particulate organic matter (POM) consisting of proteins, polysaccharides, lipids and humic or fulvic substances (Santschi *et al.*, 1997). Hydrophobic compounds are thought to be able to pervade the mass of flexible, organic chains of POM to become effectively dissolved in a non-aqueous medium (Schwarzenbach *et al.*, 1993). Jepsen *et al.* (1995) revealed the importance of organic

matter on the mobility of HOMs by observing their sorption to sediment stripped of organic matter to be reduced by a factor of 16. This is because most natural minerals are polar and form hydrogen bonds with water. Hydrogen bonds are energetically unfavourable for an HOM to replace because of the greater interaction energy per unit surface area of water (Mader *et al.*, 1997).

The perceived influence of organic matter on PAH sorption suggests that the hydrophobic bonding occurs in a fashion similar to dissolution in an organic solvent, hence the use of K_{ow} s to predict PAH uptake by natural particles (Zhou & Rowland, 1997). Yet, despite this widely accepted interpretation of PAH behaviour, the rather simplified view of organic matter as a bulk organic solvent has been unable to account for nonlinear, slow, hysteretic behaviour of PAHs and other HOMs exhibited in some studies (Huang & Weber, 1997b). Consequently, suggestions have been made that POM consists of both a highly amorphous swollen matrix, whereby the partitioning is rapid, linear and reversible, and a hard, relatively condensed matrix, where sorption becomes irreversible (see Figure 1.2.; Huang and Weber, 1997a; Di Toro *et al.*, 1986; Luthy *et al.*, 1997). The distinction between the two forms of POM is thought to be a result of different diagenetic histories. Weathering of organic matter results in changes in the relative amount of oxygen-containing functional groups and the H/C or O/C atomic ratios, leading to variations in polarity, aromatic carbon content and sorption capacity (Huang & Weber, 1997a). However, the argument for the two organic matter domains has been rejected by some researchers on the grounds that to be feasible, the amorphous organic matter needs to be micrometers thick, which is not supported by microscopic observations, and the time required for the sorbate to diffuse through glassy organic matter would be size dependent, yet this is not the case for data obtained on aquifer sands (Luthy *et al.*, 1997). Fortunately this conceptual argument is not paramount to these studies, only the behaviour of the labile PAH will be investigated as this fraction

is considered to be more susceptible to co-existing contaminants and the more significant activity in the short time-scale employed (Weber & Huang, 1996).

Despite thermodynamic unfavourability, adsorption of PAHs onto minerals does occur and becomes important with sediments consisting of a relatively low organic carbon content, ($f_{oc} < 0.001$) (Schlautman & Morgan, 1994). Potential sorption sites on inorganic geosorbent surfaces include (Luthy *et al.*, 1997):

- (i) external surfaces;
- (ii) swelling clay interlayer surfaces;
- (iii) internal surfaces that can be classified based on sorbate behaviour: macropores (larger than 50 nm), internal mesopores (pore diameters 2-50 nm) and micropores (pore diameter < 2 nm).

It is therefore apparent that the heterogeneous nature of natural particles with structurally and/or chemically distinct components, as indicated in Figure 1.2, will influence adsorption or desorption of the sorbate.

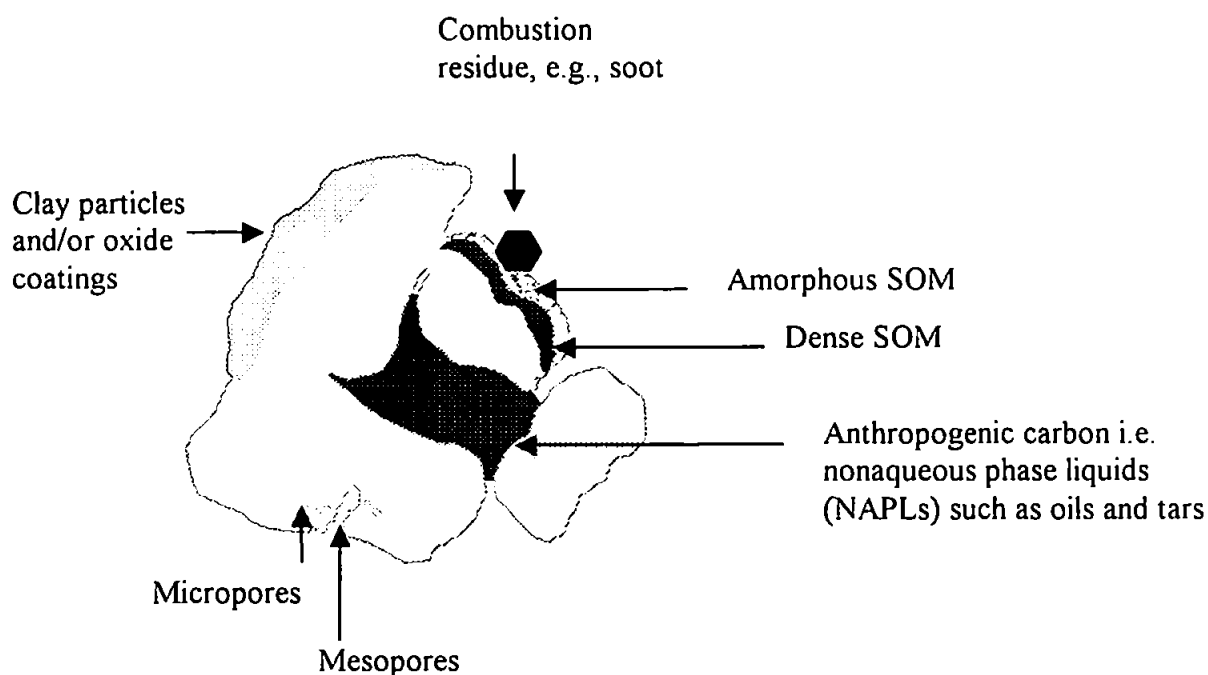


Figure 1.2: Conceptual summary of potential sorption sites (adapted from Luthy *et al.*, 1997)

The inclusion of anthropogenic contaminants within the particle will also impact on sorbate behaviour, for example sorption of PAH from water to the highly aromatic matrix of soot particles has been found to be 35 to 250 times higher than predictions based on bulk organic carbon (Bucheli & Gustafsson, 2000). Subsequently, actual sorption may involve a number of processes, but generally one type will dominate.

1.3.2.2. Distribution coefficients

The overall process of sorption can be described graphically by plotting compound concentration in the sorbed phase versus compound concentration in solution. However, several models have been developed to describe this relationship and yet still no single model has been found to be generally applicable. For the purposes of this research two simple models have been selected, described by Freundlich and linear isotherms:

$$P = K_F C^n \quad (1.3)$$

$$P = K_D C \quad (1.4)$$

where P is the concentration of the compound in the particulate phase (w/w), C is the concentration of the compound in the dissolved phase (w/v), K_F is the Freundlich coefficient, n is a measure of nonlinearity of the isotherm and K_D is the linear coefficient or partition coefficient. Examples of the two models are displayed in Figure 1.3.

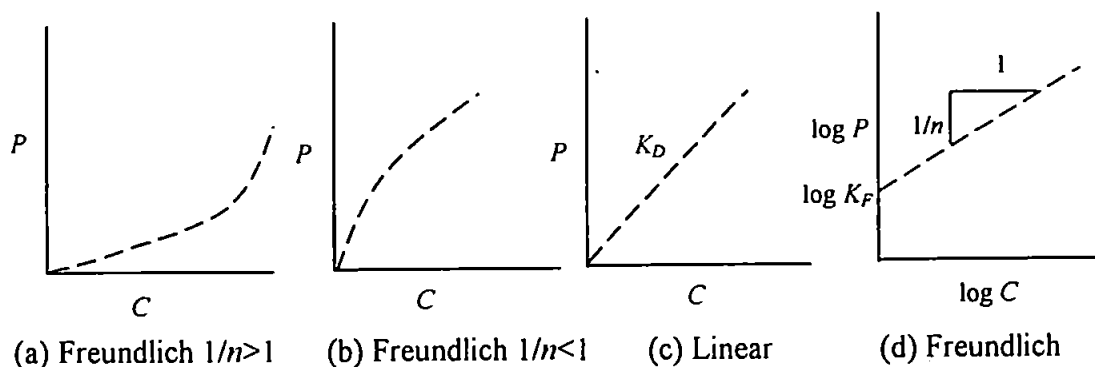


Figure 1.3: Plots of Freundlich and linear isotherms (adapted from Voice & Weber, 1983).

Since organic matter is recognised as being key to the sorption of PAHs, the linear partition coefficient is often normalised to the organic carbon content of sorbents giving the organic carbon normalised partition coefficient (K_{oc}):

$$K_{oc} = \frac{K_D}{f_{oc}} \quad (1.5)$$

where f_{oc} is the organic carbon fraction of the particles. Table 1.4 highlights the fluctuating influence of POM composition on K_{oc} for phenanthrene, therefore reported values must be used with some caution.

Table 1.4: Variation in K_{oc} values for phenanthrene due to different POM facies (Kleineidam *et al.*, 1999).

Log K_{oc}	Organic Constituent
<4.7	POM adsorbed to mineral grain surfaces, humic substances, humic and fulvic acids, humin
4.9-5.6	Wood tissue (huminite), spore, pollen, cuticle, resin algae
5.6-6.1	Amorphous organic matter, autochthonous algae
6.3-6.7	Opaque particles, charcoal, vitrinitic plant remains, coal particles.

1.3.2.3 PAHs in the aqueous phase

Despite their low aqueous solubilities PAHs also occur in the dissolved phase and may exist as either freely dissolved or, more probably, associated with colloids and dissolved organic matter (DOM). Once again, the hydrophobic characteristics of the compound induce a substantial thermodynamic gradient driving the solute out of solution and enhancing the formation of van der Waals and hydrogen bonding forces between the solute and organic matter in the aqueous phase. DOM is probably the most important colloidal material in the transport of hydrophobic compounds (Schlautman & Morgan, 1993) and is operationally defined as the fraction of total organic matter that passes through a specified filter pore diameter (usually 0.45µm). Organic substances which

pass through may not be truly dissolved species, therefore the fraction occupying the size range >1 nm to <0.4 μ m is generally defined as colloidal (Sigleo & Means, 1990).

DOM is composed of a variety of compounds such as proteins, polysaccharides, lipids and humic substances (Sanstchi *et al.*, 1997), which, in an aqueous solution, may aggregate to form micelle-like structures, with a hydrophilic exterior surrounding a hydrophobic core (Weber & Huang, 1996). Compounds such as PAHs are able to permeate through the outer casing and enter the more agreeable hydrophobic core, subsequently enhancing its apparent solubility. The affinity of PAHs for DOM is correlated with large DOM molecules abundant in aromatic structures coupled with a significant proportion of ionisable acidic functional groups thought to open the structure of DOM subsequently exposing more hydrophobic cavities (McCarthy *et al.*, 1989). Colloids, on the other hand, comprise of a carbohydrate-proteinaceous matrix often in association with crystalline clay minerals and trace metals (Wijayaratne & Means, 1984). Intriguingly, these structures have been found to have a greater affinity for PAHs and other HOMs than sediment/soil organic matter, possibly be due to differences in size and positional availability of sites for hydrophobic bonding (Wijayaratne & Means, 1984). It is clear then that the existence of both colloids and DOM in the aqueous phase have important implications regarding contaminant fate. Their ability to increase the apparent solubility of HOMs will enhance the transport and influence the bioavailability of these organic compounds.

An additional parameter affecting the solubility and subsequent sorption of PAHs is a phenomenon known as 'salting out', (see also Figure 1.1.). This occurs in solutions of high ionic concentration, where the hydration spheres of the dissociated ions tightly bind the water molecules, reducing the volume of water available to accommodate the compound (Schwarzenbach *et al.*, 1993). As a result, PAH solubility is reduced in saline waters, where the more saline the solution, the lower the solubility

of the compound, although the magnitude of this effect is determined by the hydrophobicity of the compound (see Section 3.1.1.). The influence of salinity on the solubility of an organic compound can be quantitatively defined by the empirical Setschenow relationship (Xie *et al.*, 1997):

$$\log\left(\frac{S_o}{S}\right) = \sigma M \quad (1.6)$$

where S_o and S are the solubilities of the solute in water and salt solutions respectively, σ (L mol^{-1}) is the Setschenow or salting out constant and M (mol L^{-1}) is the molar concentration of the salt solution. This relationship can be adapted to natural waters in the following way:

$$\log\left(\frac{S_r^{rw}}{S_r^{sw}}\right) = \sigma_r M \quad (1.7)$$

where S_r^{rw} and S_r^{sw} are the relative solubility of the solute in river and sea water respectively, σ_r is the relative solubility constant and M is the effective molar concentration of sea water (assumed to be 0.5 mol L^{-1}).

High salinity also alters the influence of particles on PAH behaviour by (i) inducing compression of the electrical double layer (Zhou & Rowland, 1997), this being the ionic diffuse layer of counterions surrounding the surface charge of a particle, and (ii) causing the electrostatic potential to fall off more quickly with distance subsequently enhancing the ability of the PAH to displace water dipoles from the particle surface (Hunter, 1987). Therefore, PAHs which enter an estuary and encounter the raised ionic concentration of the saline intrusion are likely to be transferred to sediments and effectively 'trapped' rather than flushed out to sea. This is confirmed by Murphy *et al.* (1988) who estimated that 90% of hydrocarbons entering Puget Sound

Estuary, Washington, were deposited in estuarine sediments. The trapping effect may also be compounded by 'salting out' of DOM resulting in increased accumulation of organic matter coatings on particles subsequently enhancing PAH sorption. Therefore the following relationship, a variation of equation 1.7, may be applied to establish whether sorption enhanced in seawater is due to salting out of the PAH alone or because of additional influences caused by modifications in DOM/POM (Means, 1995):

$$\log\left(\frac{K_F^{sw}}{K_F^{rw}}\right) = \sigma_p M - \log \gamma_p \quad (1.8)$$

where K_F^{sw} and K_F^{rw} are the Freundlich coefficients ($L g^{-1}$) in seawater and river water, respectively (determined from the linear adsorption isotherms), σ_p is an adsorption salting constant, M is the effective molar concentration of seawater and γ_p is the activity coefficient of the compound in the estuarine sediment particulate organic matter. Assuming that the organic matter of the particles approximates an ideal reference phase, γ_p will approach unity and the term on the right hand side of the equation is removed.

Overall, however, the magnitude and direction of the salt effect has been observed to be a complicated function of pH, divalent ion concentration and the organic molecule under investigation (Brunk *et al.*, 1997).

1.3.3. Aquatic toxicity, bioavailability and bioconcentration

Assessment of toxicity and bioavailability of PAHs to aquatic organisms is a relatively complex task since there are several routes of exposure i.e., ingestion of particles, exposure to overlying water, feeding on contaminated organisms and exposure to interstitial water (Landrum *et al.*, 1994). Hence, the body burdens of PAHs will vary according to (Kennish, 1997):

- (i) the chemistry of the contaminant;

- (ii) surrounding physico-chemical conditions and associated bioavailability;
- (iii) organism behaviour such as feeding habits;
- (iv) variable capacities of the organisms to metabolise them;
- (v) concentration of PAHs in aquatic system and individual compartments.

The bioconcentration of HOMs, defined as a measure of the concentration of HOM in the protein and lipid material in contrast to the surrounding aqueous medium (Mallon & Harrison, 1984), generally displays a positive correlation with $\log K_{ow}$. This is to be expected since, analogous to octanol, the lipids of an aquatic organism may be viewed as a suitably hydrophobic phase for the HOM to partition into. At the extremes of $\log K_{ow}$, however, this relationship tends to struggle, which is thought to be a result of a dissolved organic carbon or lipid phase within the aqueous system (Verhaar *et al.*, 1999).

Regardless of the concentration of the PAH in the aqueous or solid phase, the uptake by an organism will be limited by the bioavailability of the compound. Both dissolved and sedimentary organic matter can exert a considerable influence on the bioavailability of PAHs, by acting as additional hydrophobic phases to partition into. However, while some studies have detected a decrease in bioavailability of PAHs to aquatic organisms as a result of binding to dissolved humic substances, other studies indicate the contrary (Sigleo & Means, 1990). Nam *et al.* (1998) reported that as the organic carbon content of soil particles increased, so did the proportion of phenanthrene sequestered. This was accompanied by a subsequent reduction in bioavailability e.g., 47% of phenanthrene mineralised by an added bacterium after 100 days for soil containing 3% organic carbon as opposed to 63% for soil containing 1% organic carbon. Furthermore, the origin of the PAH also appears to be important. Baumard *et al.* (1998a) observed a reduced availability of pyrogenic compounds to mussels whereas

petroleum hydrocarbons were accumulated at high levels. Table 1.5 gives an example of PAH body burdens in three aquatic organisms.

Table 1.5: Concentration of PAHs in aquatic organism tissues (ng g⁻¹ dry weight) (Baumard *et al.*, 1998b)

Organism	Phenanthrene	Fluoranthene	Benz(a)pyrene	ΣPAH
<i>Mytilus galloprovincialis</i> (mussel)	10.4 ^a	5.66 ^a	0.66 ^a	39.0 ^a
	16.3 ^b	4.68 ^b	1.32 ^b	50.3 ^b
<i>Serranus scriba</i> (fish)	19.2 ^a	25.8 ^a	1.26 ^a	87.4 ^a
	24.6 ^b	3.12 ^b	N.Q.	33.9 ^b
<i>Mullus barbatus</i> (fish)	5.31 ^a	2.32 ^a	0.01 ^a	14.7 ^a
	10.9 ^c	3.19 ^c	0.01 ^c	18.3 ^c

^aFort Brescou, France, ^bLeucate Harbour, France, ^cArgeles sur Mer, France, N.Q. – not quantified.

The higher molecular weight (MW) PAHs are more strongly adsorbed to sediment than the lighter molecules (Mackay *et al.*, 1992). As a result they are more prone to bioaccumulation by non-selective deposit feeders (uptake of PAH via particulate material in addition to aquatic medium), than organisms which actually live in the sediment but feed on overlying detritus and plankton (Woodhead *et al.*, 1999). This is of some concern since although lower molecular weight PAHs, such as phenanthrene, pyrene and fluoranthene, may be acutely toxic, the higher-MW compounds, when ingested, can form metabolites that are active carcinogens in aquatic organisms (Kennish, 1997). PAHs known to be carcinogenic compounds include benz(a)pyrene (also classified as mutagenic), chrysene, benz[a]anthracene, benzo[b]fluoranthene and dibenz [a, h] anthracene (Grimmer, 1983). Fish are generally less susceptible to the adverse effects of PAHs due to their ability to metabolise many xenobiotics, however, elevated PAH concentrations in sediments have been associated with incidents of liver neoplasms, impaired immune systems and endocrine disruption (Woodhead *et al.*, 1999). Concentrations of PAH in sediments considered responsible for inducing liver cancer are variable e.g. ΣPAH concentrations of 181 µg kg⁻¹ and 41,200 µg kg⁻¹ dry

weight for the brown bull head catfish from Lake Munuscong and the Cuyahoga River respectively (Baumann, *et al.*, 1991). In general, however, amphipods appear to be more sensitive to sediment-associated PAH than fish, where sublethal effects on osmoregulation have been shown at ΣPAH concentrations as low as approximately 6000 µg kg⁻¹ (Alden & Butt, 1987).

1.3.4. Degradation

Principal PAH removal from aquatic systems is via biological transformation, where microbial metabolism especially by bacteria, exceeds metabolism by other organisms, particularly in highly contaminated areas. However, photooxidation either via direct photolysis reactions or by photooxygenated reactions involving singlet oxygen ozone and other oxidising agents can be important in PAH removal from the water column as displayed in Table 1.6 (Kennish, 1997).

Table 1.6: Half lives of selected PAHs in environmental matrices (days) (Howard *et al.*, 1991)

	Fluoranthene	Benzo(a)pyrene	Phenanthrene
Soil ^a	140-440	57-530	16-200
Air ^b	0.08-0.84	0.01-0.05	0.08-0.84
Surface water ^c	0.88-2.63	0.01- 0.05	0.13- 1.04
Ground water ^d	280-880	114-1059	32 – 402

Half lives were based upon the high and low degradation rates of the most important degradation process within a particular medium. ^a Based upon aerobic soil die-away test data; ^b based upon photooxidation half-life in air; ^c based upon aqueous photolysis half-life; ^d based upon estimated unacclimated aqueous aerobic biodegradation half-life

Once adsorbed by the solid phase, PAHs exhibit increased resistance to photo- and biodegradation and hence, may accumulate indefinitely (Burgos *et al.*, 1999). Mechanisms believed to inhibit biodegradation include intraparticle diffusion into a microporous sorbent, intraorganic matter diffusion into solid phase organic matter and polymerisation or covalent binding to humic substances (Burgos *et al.*, 1999). Various studies also suggest that particle sorbed PAHs are biodegraded to a residual

concentration that ceases to decrease with time or which decreases very slowly over years with continued treatment (Luthy *et al.*, 1997).

1.4 General Properties of Surfactants

Surfactants are currently the subject of extensive and widespread research. Considerable attention is being focused on their potential to modify sites contaminated by both organic and metal contaminants, the intrinsic behaviour of surfactants *per se* and also their influence on co-existing pollutants. The word surfactant is a contraction of the term surface active agent and applies to molecules comprising of a polar and a nonpolar region (Rosen, 1989). It is these amphiphilic properties which permits dissolution of surfactants in both oil and water, adsorption at interfaces and solubilisation of hydrophobic compounds in micelles and/or adsorbed layers. As a result surfactants are indispensable for a number of technologies including detergency, emulsification, dispersion, coating, wetting flotation, petroleum recovery, lubrication and adhesion (Sharma, 1995). It is hardly surprising that surfactants now seem to be omnipresent and can be found in formulations from pharmaceuticals to cosmetics, although their major use by far is as household products as illustrated in Figure 1.4.

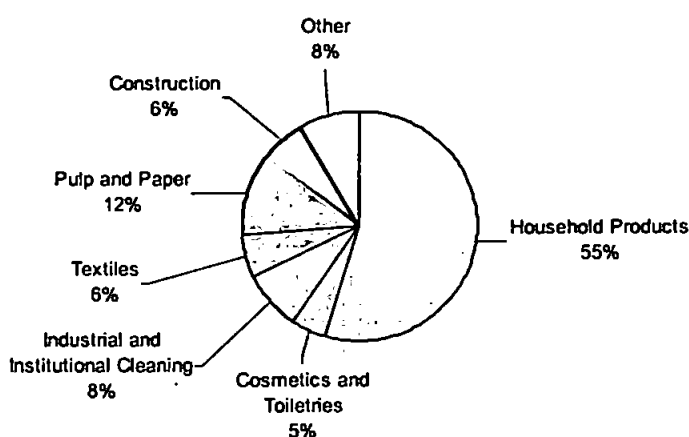


Figure 1.4: Surfactant usage by application area in Western Europe, 1995 (Karsa *et al.*, 1999).

Prior to the late nineteenth century, the only man-made surfactant was soap. However, its ineffectiveness in hard or acidic water coupled with a crucial shortage in Germany after World War 1, encouraged the development of synthetic soap substitutes (Singer & Tjeerdema, 1993). As a result, synthetic surfactants have been used increasingly in consumer and industrial cleaning formulations since the late 1940's to the point where the annual worldwide surfactant demand has reached over 10 million tonnes (Thomas, 1999). Figure 1.5 displays the projected increase of surfactant use over 10 years.

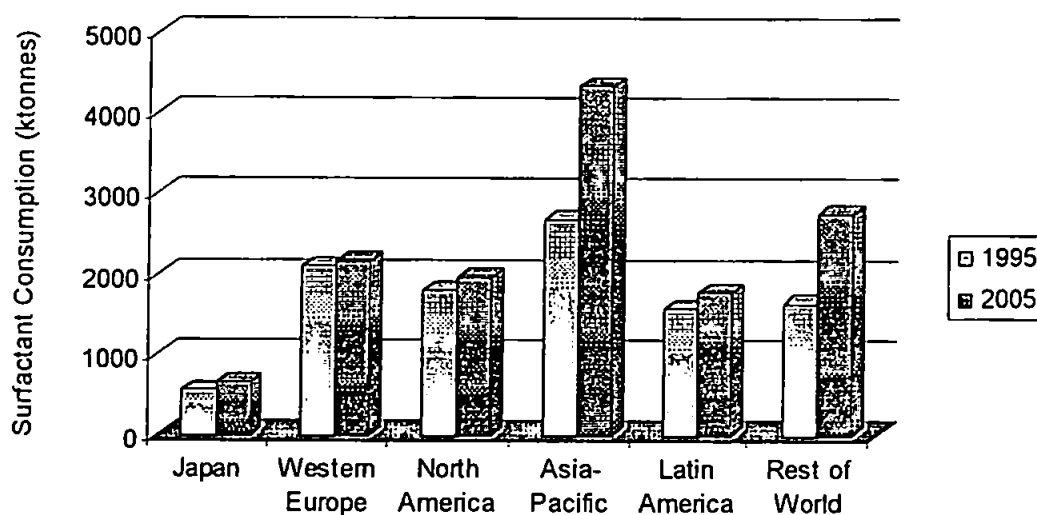


Figure 1.5: Increase in surfactant use between 1995 and 2005 (Karsa *et al.*, 1999)

The key source raw materials for production of both high volume surfactants and many specialities are derived from oleochemical (manufactured from natural fats and oils) and/or petrochemical (Karsa *et al.*, 1999). Since these chemicals are used so extensively and almost invariably in aqueous solutions, the potential to enter aquatic and terrestrial systems is obvious. It is therefore becoming ever more important to understand their influence on receiving systems.

Surfactants are broadly characterised as anionic, cationic, nonionic or amphoteric, according to the nature of the hydrophile existing in an aqueous solution as indicated in Table 1.7. (Singer & Tjeerdema, 1993). This is because chemical characteristics displayed due to variations in the hydrophobic tails (degree of branching, carbon number, aromaticity) are generally less pronounced than those due to the head group (West & Harwell, 1992).

Table 1.7: Classification of surfactants according to hydrophile (West & Harwell, 1992)

Ionic type	Example	Molecular Structure
Anionic	Sodium dodecyl sulphate (SDS)	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$
Nonionic	Octylphenol polyethoxylate (Triton X-100)	$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{C}_6\text{H}_4 - (\text{OCH}_2\text{CH}_2)_9\text{OH}$
Cationic	Hexadecyltrimethyl ammonium bromide (HDTMA)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_{16}\text{H}_{33} - \text{N}^+ - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \text{Br}^-$
Amphoteric	N-dodecyl-N,N-dimethyl betaine	$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$

Since the chemistry of surfactants is so diverse, each class, other than the amphoteric, will be considered individually in the following sections. Amphoteric surfactants comprise of both an acidic and a basic group so, depending on the pH of the solution, they can behave as either anionic, nonionic or cationic species. Therefore the amphoteric surfactants may be considered a subgroup of the other three (Attwood & Florence, 1983).

1.4.1. Nonionic surfactants

Currently, the most widely used surfactants in Western Europe are nonionic, as indicated in Figure 1.6. Their prevalence is largely because it is possible to vary the average chain length of the hydrophobe and the degree of ethoxylation of the hydrophile so that a range of properties can be formulated (Thomas, 1999).

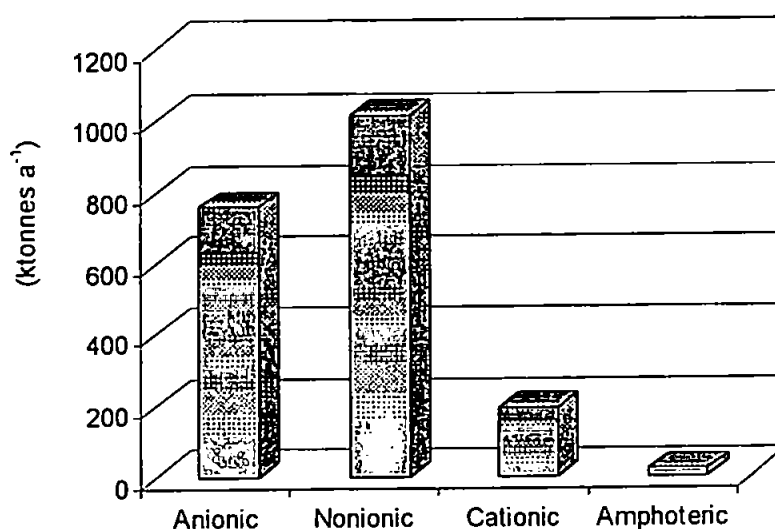


Figure 1.6: Annual surfactant use for 1996 in Western Europe (Karsa *et al.*, 1999).

Nonionic surfactants have distinct hydrophilic and hydrophobic regions but no net electrical charge. There are many different types of nonionic surfactants, generally derived from linear and highly branched fatty alcohols, alkylphenols or fatty acids (Thomas, 1999). Table 1.8 lists the most common nonionic surfactants and their uses.

Table 1.8: Main nonionic surfactants and their uses (Rosen, 1989)

Nonionic Surfactant	Common uses
Polyoxyethylenated alkylphenols (APE)	Mainly industrial use due to low degradability. Emulsifying agents, foam control agents, detergents, dye retarders
Polyoxyethylenated straight chain alcohols (AE)	Emulsifying agent, heavy duty liquid detergent
Polyoxyethylenated polyoxypropylene glycols	Pigment dispersant, scale removal, foam control agent, petroleum demulsifiers
Polyoxyethylenated mercaptans	Textile detergent, metal cleaning, shampoos.
Long chain carboxylic acid esters	Food, pharmaceutical and cosmetic emulsifiers

Inspection of Table 1.8 emphasises the prevalence of the ethylene oxide (EO) oligomers as the hydrophilic group of choice for nonionic surfactants in commercial preparations. These EO units can range from one to forty within a surfactant molecule, occasionally including propylene oxide units to depress foaming properties, but this has been known to adversely affect surfactant biodegradability (Holt *et al.*, 1992). Alternative hydrophiles originating from sugar chemistry such as polyols (e.g. sorbitol) and glycosides are beginning to receive renewed attention although their use is largely in food applications (Swisher, 1987).

While the extensive use of nonionic surfactants has led to concern regarding environmental contamination, information for specific formula concentrations found in natural water systems is sparse, as indicated in Table 1.9. The significantly high concentrations for two streams in Israel reflect the large usage and poor biodegradability

of alkylphenol ethoxylates however, the removal of nonionic surfactants even via sewage treatment varies according to plant type (Giger *et al.*, 1984).

Table 1.9: Concentrations of nonionic surfactants in aquatic systems (Holt *et al.*, 1992)

Compound	Environmental Compartment	Concentration
	<u>River water</u>	($\mu\text{g L}^{-1}$)
Nonionics	Rhine, Germany	20-80
APE	2 rivers, Japan	20-70
Nonionics	2 streams, Israel	1600-2600
Nonionics	Avon, U.K.	8
	<u>Seawater</u>	($\mu\text{g L}^{-1}$)
NP1EO-NP13EO	Marine water	19.6
NPE	Coastal water	0.85
	<u>Marine sediment</u>	(mg kg^{-1})
NPE		0.1-6.6
	<u>River sediment</u>	(mg kg^{-1})
NP	Rhine	0.9
NP1EO	Rhine	0.8
NP2EO	Rhine	0.7

APE – alkylphenoethoxylates, NP- nonylphenol, EO- ethylene oxide units.

The oligomeric distribution is also dependent on environmental compartment, particularly with regard to metabolites of APEs since unlike other surfactants their EO chain is gradually reduced as they are degraded which results in the compound becoming increasingly hydrophobic (Ahel & Giger, 1993b). Therefore the dissolved phase is more likely to contain APEs with longer ethoxylates whereas sediments may become a pool for alkylphenol and alkylphenols with short ethoxylate chains (Holt *et al.*, 1992).

1.4.2. Anionic surfactants

Anionic surfactants are the second most widely used class after nonionics. The most common anions are sulphonate, sulphate and more rarely phosphate. As many as sixty sub-groups have been listed, of which only seven were not sulphonated or sulphated products (Painter, 1992). Some of the commonly used types of surfactants are listed in Table 1.10

Table 1.10: Main nonionic surfactants and their uses (Painter, 1992)

Surfactant	Structure	Applications
Alkyl aryl sulphonates (ABS, LAS)	$RC_6H_4SO_3H^+$	Most widely used due to excellent deterative power and low cost. Cleaning agent in heavy duty grade washing powders and liquids.
Alkyl sulphates Primary (LPAS)	$RCH_2OSO_3Na^+$	Wool-washing agents and in light- and heavy-duty laundry formulations. Used in speciality products including toothpastes, shampoo, foods, pharmaceuticals.
Secondary (AS)	$\begin{matrix} R_1CHOSO_3Na^+ \\ \\ R_2 \end{matrix}$	
Alkyl ethoxylate sulphate (AES)	$R(OCH_2CH_2)_nOSO_3Na^+$ R (primary or secondary)	In light-duty liquid detergents to improve foaming characteristics
Alkane sulphonate	RSO_3H^+ R (primary or secondary)	In detergents similar to AS
α -olefine sulphonates (AOS)	$RCH:CHCH_2SO_3Na^+$ $RCHOH(CH_2)_nSO_3Na^+$	Excellent foaming and detergency in hard water

Information on environmental concentrations of anionic surfactants proves to be even more limited than for nonionic surfactants. Most investigations concern linear alkylbenzene sulphonates since this is the most widely used type within the anionic class. Fortunately, most anionic surfactants are rapidly degraded during sewage treatment, hence the low concentrations in Table 1.11, yet direct discharge into natural

waters still occurs, particularly in third world countries, where more surfactants pass directly to surface waters than to sewage treatment works (Mukherjee *et al.*, 1993).

Table 1.11: Environmental concentrations of LAS (Painter, 1992)

Sample location	Concentration
<u>River water</u>	(mg L ⁻¹)
Rhine, Germany	0.009-0.035
UK polluted sites	0.2-0.5
<u>Seawater</u>	(mg L ⁻¹)
Tokyo Bay	<0.003-0.014
<u>River sediment</u>	(mg kg ⁻¹)
U.S.A, near outfall	174-275
Downstream	12
<u>Marine sediment</u>	(mg kg ⁻¹)
Tamagawa Estuary, Tokyo	0.5-24

1.4.3. Cationic surfactants

Cationic surfactants are an extremely important group of compounds with regard to commercial use and environmental consequences. The hydrophile is a positively charged nitrogen, therefore since most solid surfaces are negatively charged, cationic surfactants have a particular affinity for them and actually impart special characteristics to the substrate e.g. antistatic properties to textiles (Cross, 1994). Cationic surfactants are also well known for their germicidal properties (Singer, 1994). These characteristics have been extensively manipulated for a wide variety of applications, as is evident in Table 1.12.

The major commercial cationic surfactants are the quaternary ammonium compounds (QACs). Nonquaternary cationics may be sensitive to high pH, polyvalent anions and inert electrolyte in the aqueous phase whereas QACs are generally insensitive to these additives (Rosen, 1989). QACs comprise of a permanently charged

pentavalent nitrogen with at least one alkyl chain approximately C10 or longer as the hydrophobe (Boethling & Lynch, 1992).

Table 1.12: Important cationic surfactants and their uses (Rosen, 1989)

Surfactant	Basic Structure	Applications
Long-chain amines and their salts	$ \begin{array}{c} R_1 \\ \\ R - N^+ - H \cdot X^- \\ \\ R_2 \end{array} $	Emulsifying agent at pH below 7. Corrosion inhibitor for metal surfaces to protect them from water, salts, acids. Anticaking agent for fertiliser, ore flotation collectors, adhesion promoters for painting damp surfaces
Quaternary ammonium salts (QACs)	$ \begin{array}{c} R \\ \\ R_3 - N^+ - R_1 \\ \\ R_2 \end{array} \quad X^- $	Unaffected by pH change – textile softener, emulsifying agent, germicide, disinfectant, hair conditioner, oral antiseptic
Polyoxyethylenated chain amines	long RN[(CH ₂ CH ₂ O) _x H] ₂	Used to improve tensile strength of regenerated cellulose filaments and to keep spinnerets free of incrustations. Emulsifying agent

R refers to an alkyl group and X an anion.

As QACs are strongly sorbed by a wide variety of materials i.e., activated sludge, sediments, clay, minerals, proteins and cell walls of microorganisms, low concentrations are expected in receiving waters (Table 1.13). However, these compounds can be extremely toxic even at such low levels (Boethling & Lynch, 1992).

Table 1.13: Environmental concentrations of QACs (Boethling & Lynch, 1992)

Compound	Sample location	Concentration
	<u>River</u>	($\mu\text{g L}^{-1}$)
Cationic	Main, West Germany	5-10
DA18DMAC ^a	Bonn, West Germany	6-12
DTDMAC ^b	Millers River, USA	<2
DTDMAC ^b	Otter River, USA (downstream from WTW)	24
DTDMAC ^b	Blackstone River USA (downstream from WTW)	17
DTDMAC ^b	Rapid Creek USA (downstream from WTW)	33
	<u>Sediment</u>	(mg kg^{-1})
DTDMAC ^b	Rapid Creek, USA (0.8 -88km from sewage outfall)	<3 - 67

^aDADMAC – dialkyl dimethylammonium chloride, ^bDTDMAC- ditallow dimethyl ammonium chloride

1.4.4 Unusual properties of surfactants

As a result of their amphiphilic nature surfactants display unusual properties, one of the most important being their ability to form micelles once they reach a point known as the critical micelle concentration (CMC). The CMC is a narrow concentration range which can be determined empirically from the sharp inflection of a physical property as a function of concentration, e.g. surface tension, turbidity, conductivity (Hunter, 1987). Below the CMC, solutions consist of singly dispersed molecules or monomers, however as the concentration increases, the molecules aggregate via interaction between their hydrophobic tails to form micelles (Hall & Tiddy, 1981). If the concentration proceeds further than the CMC, the monomer concentration remains approximately constant while additional molecules form more micelles (Singer & Tjeerdema, 1993). Once the solubility limit is exceeded, however, a new phase of either a hydrated solid or liquid is formed (Painter, 1992). Table 1.14 lists the CMCs for three well known surfactants.

Table 1.14: CMCs for selected surfactants

Surfactant	Conditions	CMC (mg L ⁻¹)
Sodium dodecyl sulphate (SDS)	H ₂ O 25°C	3461 ^a
	H ₂ O 40°C	3172 ^a
	0.1M NaCl 25°C	720 ^a
	*	2200 ^b
Triton X-100	*	130 ^b
		195 ^c
Hexadecyltrimethylammonium iodide (HDTMA)	H ₂ O 25°C	335 ^a
	*	361 ^c

^aRosen, (1989); ^b Liu & Chang, (1997); ^c Kile & Chiou, (1989). * Conditions not stated, assumed to be 25°C in H₂O

Micelles contain tens or hundreds of molecules which are oriented with their hydrophobic groups clustered together, the hydrophilic ends extending outwards (Tanford, 1980). They can take several forms, their shape determining various properties of the surfactant, in particular its capacity to solubilise co-existing hydrophobic compounds. The major types of micelles appear to be (Rosen, 1989):

- (i) Relatively small spherical structures, aggregation number less than 100.
- (ii) Elongated cylindrical, rodlike micelles with hemispherical ends (prolate ellipsoids).
- (iii) Large flat lamellar micelles (disklike extended oblate spheroids).
- (iv) Vesicles – more or less spherical structures consisting of lamellar micelles arranged in one or more concentric spheres with an aqueous interior.

Micellisation takes place in order to minimise the distortion of the aqueous phase by the hydrophobic region of the surfactant molecule. Forces opposing this involve electrostatic repulsion from neighbouring, similarly charged surfactants and the loss of freedom for the monomer due to being restricted in the micelle (Rosen, 1989). Nonionic

surfactants, however, are not subject to electrostatic repulsion and therefore have much lower CMCs than ionic surfactants (see Table 1.14) (Attwood & Florence, 1983). Other factors which may influence the CMC include changes in temperature and additives in the liquid phase. These can alter the size, shape and aggregation number of the micelle and hence the CMC (Hunter, 1987).

As indicated in Table 1.14 for SDS, the addition of a neutral electrolyte to aqueous solutions of ionic surfactants reduces the CMC and increases the aggregation number by minimising the electrical repulsion between hydrophilic head groups (Hall & Tiddy, 1981). The effect is more noticeable for anionics than cationics, whereas nonionics have been known to display an increase and decrease in CMC on the addition of an electrolyte. The change of CMC for nonionics has been attributed mainly to 'salting out' or even 'salting in' of the hydrophobic groups rather than an effect on the hydrophilic groups (Meguro *et al.*, 1987). Inclusion of organic materials can also alter the CMC, for example it is reduced by alcohols as they decrease the work required for micellisation and, with regard to ionic surfactants, decrease the repulsion between the headgroups (Rosen, 1989).

The effect of temperature on the CMC is also complex, seeming to initially decrease to a minimum with an increase in temperature and then increase as the temperature rises further. An increase in temperature results in the dehydration of the hydrophilic group, encouraging micellisation, yet it also disrupts the structured water surrounding the hydrophobic group subsequently hindering micellisation (Rosen, 1989). It therefore depends on the strength of these two effects whether the CMC increases or decreases at a particular temperature.

Temperature also exerts an influence on the solubility of the surfactant, and, rather unusually, an increase can reduce the solubility of some surfactants. For ionic

surfactants there is a dramatic increase in solubility above a temperature known as the Krafft point (T_k) (see Figure 1.7).

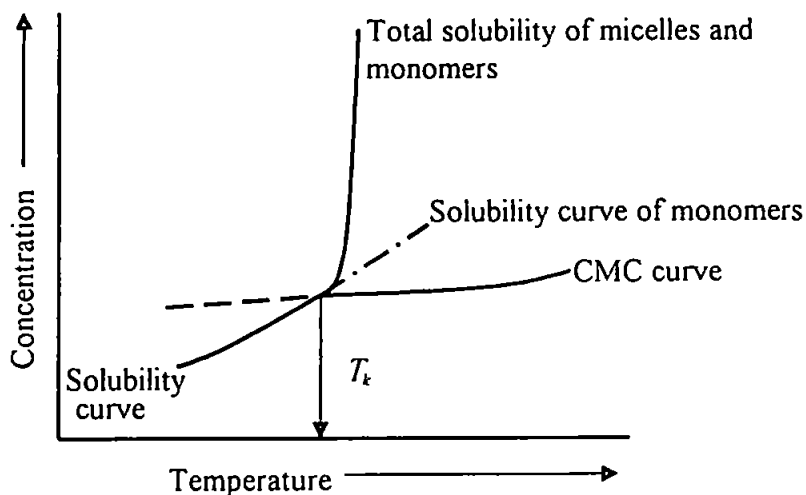


Figure 1.7: The effect of temperature on the solubility of an ionic surfactant (Attwood & Florence, 1983)

The Krafft point is defined as the temperature at which monomer solubility equals the CMC (West & Harwell, 1992). This effect can be explained by considering a solution at T_k containing a surfactant concentration well in excess of monomer solubility. If the temperature increases to just above the Krafft point there will be a slight increase in the solubility of the monomers. However, the excess solid surfactant will also begin to go into solution as micelles, as the total surfactant in solution now exceeds the CMC (Attwood & Florence, 1983). The response to temperature change is very different for nonionic surfactants where Krafft points are not usually observed since, as previously mentioned, they display relatively low CMCs, which would drive the Krafft point to temperatures close to or below the freezing point of water (Holt *et al.*, 1992). Interestingly, increasing the temperature of a nonionic surfactant solution with a concentration above its CMC results in turbidity and eventually phase separation. The temperature at which this takes place is referred to as a cloud point and is believed to be due to a noticeable increase in aggregation number of the micelles and the decrease in

intermicellar repulsions resulting from the dehydration of the ethylene oxide groups (Meguro *et al.*, 1987). The micelles eventually grow so large that the solution becomes visibly turbid, although on cooling they revert back to a clear solution (Rosen, 1989). Krafft and cloud points for surfactants should be treated with caution however, since just as the CMC varies with the concentration of an added electrolyte so will the Krafft and cloud points, as illustrated in Figure 1.8.

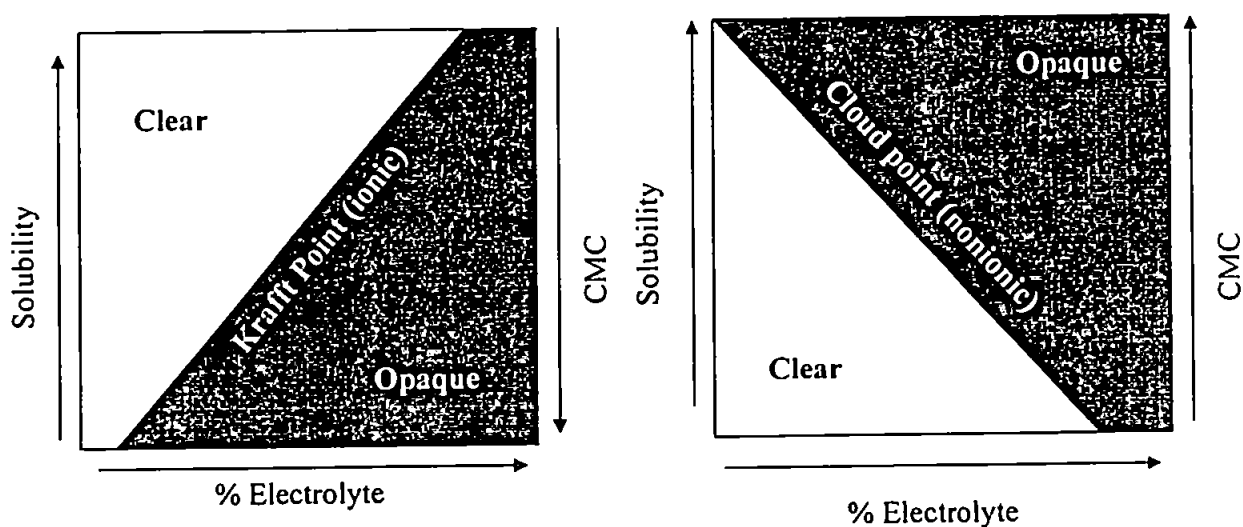


Figure 1.8: Dependence of Krafft and cloud points on electrolyte concentration (adapted from Fairchild *et al.*, 1999)

1.5. Partitioning, fate and transport of surfactants in aquatic systems

1.5.1. Surface activity

It is clear from Section 1.4 that the removal of the hydrophobic portion of the surfactant molecule from its aqueous environment is an entropically favourable process. This allows the highly structured water to become disordered again and also removes constraints on the hydrocarbon chains (Attwood & Florence, 1983). For these reasons the molecules will tend to accumulate at the air-water or oil-water interface orientated so that the hydrophobic portion penetrates into the gaseous or oil phases. The molecule remains anchored by the hydrophilic head group which resides in the aqueous phase (see Figure 1.9)

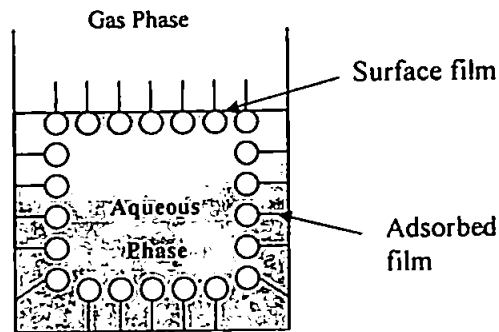


Figure 1.9: Schematic of surfactant interfacial activity (Singer & Tjeerdema, 1993)

The existence of surfactant molecules in the surface layer causes some water molecules to be replaced by the hydrocarbon groups in the nonpolar tail. Since the intermolecular attraction between water molecules and nonpolar groups are less than those between water molecules, the surface tension is therefore reduced (Attwood & Florence, 1983). The decrease of surface tension is less dramatic for ionic than nonionic surfactants due to repulsion between headgroups impeding surface adsorption (Ingram & Ottewill, 1991).

The extent of surface activity for ionic surfactants can be influenced by the addition of an electrolyte, which minimises repulsion between the ionic head groups allowing closer packing in the surface layer (Ingram & Ottewill, 1991). As expected, electrolyte addition has only a slight effect on nonionic surfactants due to their uncharged nature. Temperature appears to have little effect on surface adsorption, although increased temperature produces a slight decrease for ionics (Attwood & Florence, 1983).

1.5.2. Particle-water interactions

The adsorption of surfactants at the solid-liquid interface is influenced by three main factors (Rosen, 1989):

- (i) The nature of the structural groups on the solid surface – whether the surface contains highly charged sites or nonpolar groupings;
- (ii) The molecular structure of the surfactant being adsorbed – whether it is ionic or nonionic and whether the hydrophobic group is long or short, straight chain or branched, aliphatic or aromatic;
- (iii) The environment of the aqueous phase – its pH, electrolyte content, the presence of any additives and its temperature.

As implied above, surfactant adsorption is an extremely complex process. The main mechanisms are displayed in Table 1.15. Generally, ionic surfactants will adsorb onto hydrophobic sorbents by dispersion forces, with the hydrophobic group close to the surface and the hydrophilic group oriented toward the aqueous phase (Rosen, 1989). As adsorption continues, the adsorbed molecules may become more perpendicular to the surface with head groups oriented towards the water making the surface more hydrophilic (Sharma, 1995). Conversely adsorption of an ionic surfactant onto an oppositely charged surface will occur via electrostatic interaction, with the hydrophilic head group oriented toward the oppositely charged surface and the hydrophobic group away, making the surface water repellent (Sharma, 1995).

Table 1.15: Mechanisms of surfactant adsorption (adapted from Rosen, 1989)

Schematic	Mechanism	
	<p>Ion Exchange - replacement of counterions adsorbed onto the substrate from the solution by similarly charged surfactant ions</p>	
	<p>Ion Pairing - adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counterions</p>	
	<p>Acid-base interaction - via either hydrogen bond formation between substrate and adsorbate or Lewis acid-Lewis base reaction</p>	
	<p>Adsorption by polarisation of pi electrons - occurs when there is attraction between adsorbate with electron-rich aromatic nuclei and adsorbent with strongly positive sites.</p>	
	<p>Adsorption by dispersion forces - via van der Waals forces between adsorbent and adsorbate molecules. Acts independently and as a supplementary mechanism to other types e.g., assists in displacement of equally charged inorganic ions from substrate by ion exchange</p>	
		<p>Hydrophobic bonding - occurs when the mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an aqueous environment becomes large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains. Adsorption of surfactant molecules onto or adjacent to other surfactant molecules already adsorbed may occur by this mechanism.</p>
Uncharged	Charged surface	

The adsorption of nonionic surfactants at solid-liquid interfaces appears to be less complex than that of ionic surfactants since they are not directly subject to ion exchange and ion pairing chemistry. Nonionics adsorb onto surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface depending upon the nature of the surface (Rosen, 1989). These surfactants may adsorb via the polarisation of pi electrons or by dispersion forces acting between the surfactant and adsorbent through hydrogen bonding between polyoxyalkylene groups and suitable hydroxyl or amino groups on the adsorbent (von Rybinski & Schwuger, 1987).

The complexity of the aforementioned particle-water interactions of surfactants suggests that a number of scenarios may take place if the surfactant is introduced in a natural aquatic environment. Figure 1.10 illustrates several possibilities.

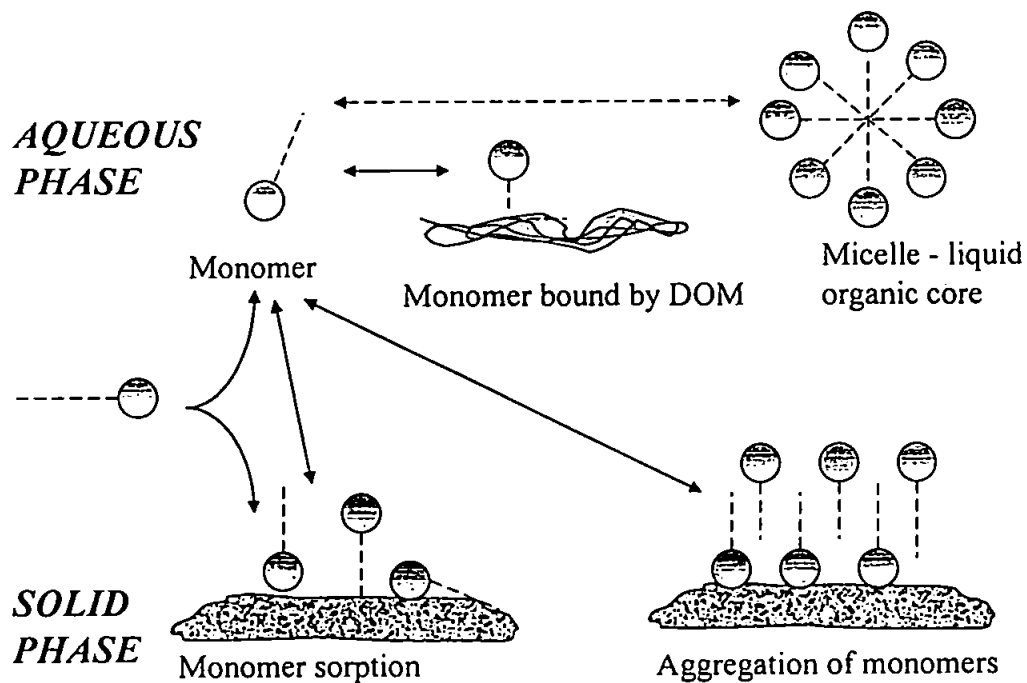


Figure 1.10: Schematic of surfactant behaviour in natural waters

While the extent of surfactant adsorption to natural particles will be variable, some generalisations can be made. For example, sediments are usually negatively charged, therefore there is likely to be a significant interaction between cationic surfactant head groups and the particle. Conversely an anionic surfactant would experience more repulsion and less sorption. With regard to nonionic surfactants there may be hydrogen bonding between ethoxylate chains and silicon oxide surfaces, or hydrophobic bonding with organic matter, although sorption may be either high or low, depending on the water solubility of the surfactant (West & Harwell, 1992). Unfortunately, information on any surfactant association with dissolved humic substances, which could affect their fate, transport and toxicity, is limited. However, this is believed to take place, primarily due to hydrophobic interactions between alkyl chains of surfactant molecules and nonpolar regions of humic substances (Traina *et al.*, 1996).

Another important property of surfactant adsorption is the local aggregates formed on solid surfaces, as indicated in Figure 1.10. These aggregates have been referred to as hemimicelles, admicelles, surface micelles and more recently solloids (Sharma, 1995). The general consensus appears to be that the term admicelle applies to a bilayer structure and hemimicelle for monolayer aggregates. The formation of surface aggregates occurs at higher surfactant concentrations when adsorbed monomers re-orientate so that their nonpolar tails extend into the aqueous phase (Edwards *et al.*, 1994). This realignment, believed to be due to strong mutual attractions between the hydrophobic regions of adjacent surfactant molecules, continues with the addition of surfactant molecules until monolayers form (Sharma, 1995). As the surfactant concentration increases further still, monomers begin to sorb onto the newly created monolayers due to the mutual attraction of the hydrophobic moieties in the bulk solution and in the monolayers to form bilayers (Edwards *et al.*, 1994).

Surfactant partitioning is, as expected, susceptible to surrounding physico-chemical conditions. Addition of a neutral electrolyte will reduce sorption of ionic surfactants onto an oppositely charged sorbent and enhance sorption onto a similarly charged sorbent (Mukerjee *et al.*, 1995). This is a result of decreased attraction between oppositely charged species and the decreased repulsion between similarly charged species at higher ionic concentrations. Increases in salt concentration can encourage salting out of nonionic surfactants, as is evidenced by the decrease in CMC with increasing ionic strength (Brownawell *et al.*, 1997). This would therefore enhance sorption.

Temperature increase will generally reduce the efficiency and effectiveness of adsorption of ionic surfactants whereas it usually causes an increase in the adsorption of nonionic surfactants containing a polyoxyethylene chain (Rosen, 1989). This is due to a reduced solute-solvent interaction via dehydration of the polyoxyethylene group as temperature is raised (Rosen, 1989).

1.5.3. Aquatic toxicity, bioavailability and bioconcentration.

In general, surfactants are toxic to aquatic organisms by interaction with biological membranes due to their interfacial activity. In the case of fish for example, the surfactant may adsorb on the gill membranes and interfere with oxygen uptake, leading to suffocation (Thomas, 1999). The most toxic surfactants are, however, QACs which display highly effective germicidal activity, although gram-negative bacteria are generally less sensitive to QACs than gram-positive bacteria (Singer, 1994). The substantial capacity of microorganisms to sorb QACs is well known since these compounds are attracted to negatively charged materials such as bacterial proteins. However, the germicidal mode of action for QACs may be a result of several biological responses, from a direct effect on proteins (denaturation and disruption) and cell

membranes, to impaired metabolic reactions and enzyme systems (Singer, 1994). Fortunately, this germicidal activity has little effect on microorganisms in waste water treatment systems since QACs form 1:1 complexes with anionic surfactants, which are substantially less toxic (Sullivan, 1983). Uncomplexed QACs, which may find their way into natural water bodies, are acutely toxic in the milligram per litre range and lower to aquatic organisms (e.g. algae, fish, molluscs, and shrimp) (Boethling & Lynch, 1992).

Table 1.16: Toxicity of quaternary ammonium compounds (Boethling & Lynch, 1992)

Test Species	Cationic surfactant	LC ₅₀ (mg L ⁻¹)
<i>Daphnia magna</i> (water flea)	ATMAC ^a	1.2-5.8
<i>Idus melanotus</i> (golden orfe)	ATMAC ^a	0.36-8.6
<i>Planorbis corneus</i> (water snail)	ATMAC ^a	0.73-23
<i>Lepomis macrochirus</i> (bluegill sunfish)	Hyamine 3500 ^b	0.5

^aAlkyltrimethyl ammonium chloride including A₁₂TMAC, A₁₄TMAC, A₁₆TMAC, A₁₈TMAC and A_{20/22}TMAC; ^bAn alkyldimethylbenzylammonium chloride.

QACs are also toxic to algae and possibly higher plants with an inhibited growth of green algae (*Chlorella sp.*) and great duckweed (*Spirodela oligorhiza*) reported at 3 to 5 mg L⁻¹ (Boethling, 1994). Despite the acute sensitivity of aquatic organisms to QACs, rather surprisingly they exhibit low toxicity towards humans and other mammals (Singer, 1994).

The majority of nonionic surfactants for use in domestic detergents yield LC₅₀ values within the range 1-10 mg L⁻¹ as displayed in Table 1.17. A trend which is visible in Table 1.17 becomes even more clear in Table 1.18, where the toxicity of alcohol ethoxylates and alkyphenol ethoxylates decreases with an increase in the degree of ethoxylation and with reduction in the alkyl chain length of the hydrophobe (Thomas, 1999).

Table 1.17: Toxicity of nonionic surfactants (Holt *et al.*, 1992)

Test organism	Surfactant	Concentration (mg L ⁻¹)
		<u>96hr EC₅₀</u>
<i>Selenastrum</i> (algae)	OPE	0.21
<i>Mycrocystis</i> (algae)	OPE	7.40
		<u>48hr LC₅₀</u>
<i>Daphnia Magna</i> (macroinvertebrate)	APE	18.3
		<u>48hr LC₅₀</u>
<i>Mysidopsis bahia</i> (estuarine crustacean)	OPEO _{1..5}	2-7
	OPEO ₅	2 or less
	tp-NPEO ₉	2 or less
	tp-NPEO ₄₀	>100
		<u>24hr LC₅₀</u>
Blue gill (<i>Lepomis macrochirus</i> - fish)	Triton X-100	16.2
	Triton X-45	3.5

OPE – octylphenol ethoxylate

Table 1.18: The influence of EO units on toxicity (Thomas, 1999)

		Fish LC ₅₀ (mg L ⁻¹)	Daphnia LC ₅₀ (mg L ⁻¹)	Algae IC ₅₀ (mg L ⁻¹)
C ₉ -C ₁₁ alcohol	2.5EO	4-7	2.5-4	1.4
	5EO	8-12	5-7	7
	8EO	12-24	9-17	47
C ₁₂ -C ₁₅ alcohol	3EO	0.6-1.8	0.14	0.4-0.75
	7EO	0.5-2.4	0.4-0.95	0.9-2.9
	11EO	1.2-2.8	-	-

One of the more well known problems associated with nonionic surfactants involves polyethoxylated nonylphenols (R-C₆H₄-(OCH₂-CH₂)_nOH, where R=C₉H₁₉, and n=6-18) which, due to the highly branched nonyl group and phenol ring, display only low to moderate biodegradability (Fytianos *et al.*, 1997). Despite current efforts to reduce their use, nonylphenol ethoxylates remain one of the largest volume groups of nonionic surfactants. Furthermore, the metabolite, nonylphenol which is acutely toxic to aquatic organisms, has also induced sublethal toxic effects at concentrations as low as 6 µg L⁻¹ and has been implicated as an endocrine disrupter (Shang *et al.*, 1999). This

problem is compounded by the ability of nonylphenol to significantly accumulate in various aquatic organisms (Ahel & Giger, 1993a).

As indicated in Table 1.19, anionic surfactants appear to be the least toxic of the three surfactant classes, with fish being the most sensitive organism (Thomas, 1999). Most correlations between toxicity and chain length show an increasing toxicity with increasing chain length (Painter, 1992).

Table 1.19: Toxicity of anionic surfactants (Painter, 1992)

	Fish LC ₅₀ (mg L ⁻¹)	Daphnia LC ₅₀ (mg L ⁻¹)	Algae IC ₅₀ (mg L ⁻¹)
C ₁₁₋₆ LAS	3-10	9-14	10-300
C ₁₃ -C ₁₈ sec alkane sulphonate	3-24	8.7-13.5	-
C ₁₂ -C ₁₈ alcohol sulphate	3-20	5-70	60
C ₁₂ -C ₁₄ alcohol + 2EO sulphonate	1.4-2.0	1-50	65
C ₁₄ -C ₁₈ α-olefin sulphonate	39	33	-
di-C ₈ -sulphosuccinate	39	33	-

1.5.4. Degradation

Degradation may occur by abiotic processes such as hydrolysis or photolysis. However, biodegradation is the process by which the majority of substances are degraded in the environment. The extent of modification will range from slight to complete mineralisation of the parent compound. Ultimate biodegradability describes the breakdown of the substance into simple molecules such as carbon dioxide, methane, ammonia, nitrite, nitrate or sulphate ions, whereas partial degradation may yield relatively stable metabolites with more damaging environmental consequences than the original compound (Thomas, 1999). This is unfortunately the case with the nonionic alkylphenol polyethoxylates (APE), where their associated toxicity and accumulation problems are due to the mechanisms of degradation. Unlike alcohol ethoxylate surfactants, derived from straight chain primary or secondary alcohols, which undergo

rapid and ultimate biodegradation, APE degradation is more gradual and often incomplete (Holt *et al.*, 1992). This is demonstrated by an observation where two linear alcohol ethoxylates were converted to greater than 75% of their theoretical yields of carbon dioxide in 30 days yet the more highly branched compounds achieved much less degradation with NPE9 reaching less than 30% yield in 30 days (Holt *et al.*, 1992). The biodegradation is impeded because the hydrophile is initially attacked at the ethoxylate end. Therefore, as the EO_n chain is sequentially shortened by one EO group the metabolites become progressively more hydrophobic, as displayed in Figure 1.11. These lipophilic metabolites, especially the fully de-ethoxylated products such as nonylphenol are more toxic to aquatic organisms than the parent compounds (Naylor *et al.*, 1992).

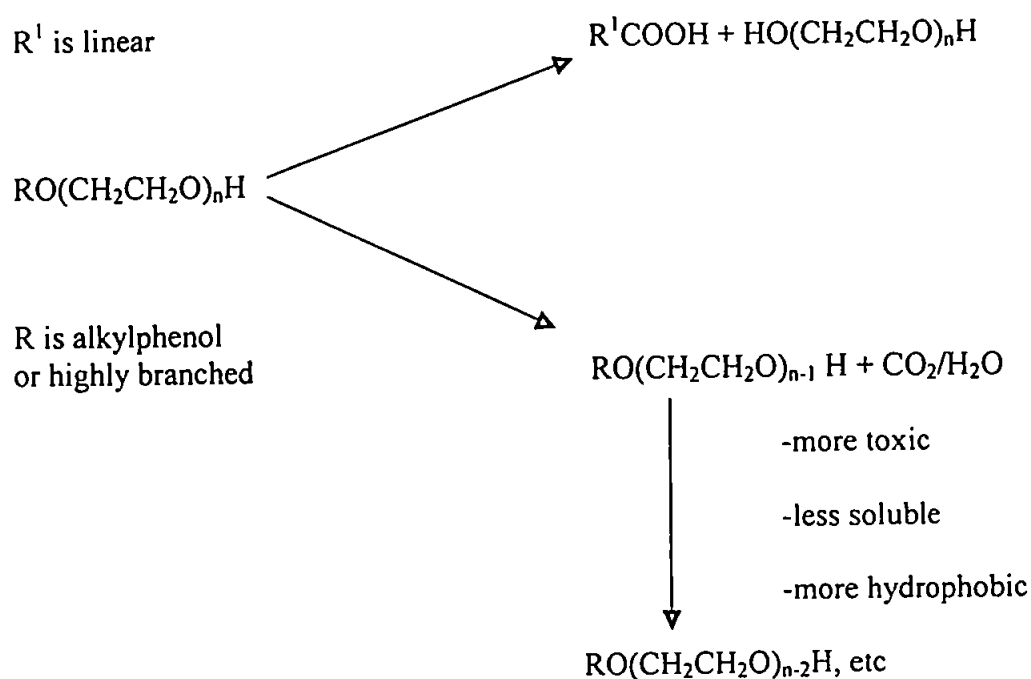


Figure 1.11: Biodegradation of alcohol and alkyphenol ethoxylates (Thomas 1999)

It is generally agreed that linear primary alkyl sulphates are the most rapidly degraded class of surfactants (Singer & Tjeerdema, 1993). Reported biodegradation rates include 90% removal from a 10 ppm solution of Chesapeake Bay water within 2 days and from a 75mg L^{-1} solution of Cadiz Bay (Spain) water within 21 days (Singer & Tjeerdema,

1993). More highly branched sulphate esters however undergo considerably slower degradation.

With regard to QACs, monoalkyl quaternaries are likely to be most rapidly and trialkyl quaternaries least rapidly biodegraded (Swisher, 1987). Studies have shown A₁₈TMAC, A₁₇₋₂₀TMAC and A₁₈DMBAC to be removed from river water without added bottom sediment within 30 to 40 days (Boethling & Lynch, 1992). Ultimate degradation of 100 µg L⁻¹ A₁₆TMAB and A₁₈TMAB has been demonstrated to occur with no detectable lag and half-lives of 2 to 3 days, although DA₁₈DMAC was not appreciably degraded in 9 weeks in sediment-free water (Boethling & Lynch, 1992). Other investigations indicate that a number of variables significantly influence QAC biodegradation including biomass, acclimation, aeration, temperature and organic and inorganic nutrients (Swisher, 1987). Sorption may also inhibit degradation, although this appears to be dependent on sorbent type, e.g., montmorillonite, a swelling clay, or kaolinite which is nonswelling (Xu & Boyd, 1995c). QACs may also undergo photooxidation, as suggested by a reported reduction in which the carbon and hydrogen contents of DA₁₈DMAC decreased from 75 to 55.4% and 13.8 to 8.9% respectively with 16 to 72h exposure to UV light (Boethling, 1994).

1.6. Behaviour of PAHs in a surfactant solution

The influence of a surfactant on the environmental fate of PAHs is very complex and poorly understood, yet the consequences of such interactions can be extremely important. At concentrations above the CMC, surfactant micelles have the ability to preferentially partition PAHs and other hydrophobic compounds from solution, a process termed solubilisation, which results in an increase in apparent solubility (see Figure 1.12). Solubilisation in aqueous media is important in areas such as the

formulation of products containing water-insoluble ingredients e.g. detergency (removal of oily soil), separation of materials and enhanced oil recovery (Rosen, 1989).

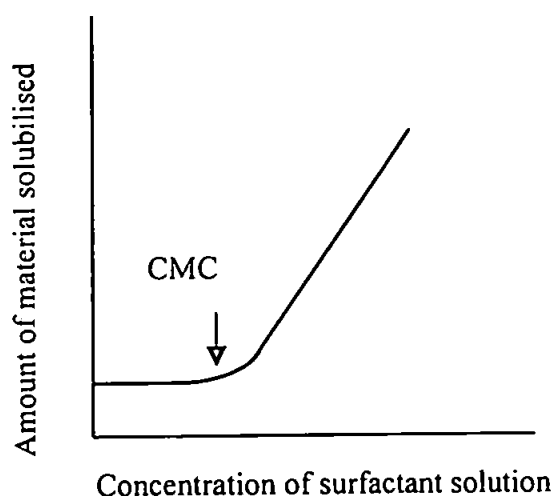


Figure 1.12. Surfactant solubilisation of solvent insoluble compound

Micelles formed by ionic surfactants have an inner hydrocarbon core, an outer ionic layer and an intermediate region known as the palisade layer. For most non-polar hydrophobic compounds, the locus of solubilisation is the hydrocarbon core of the micelle (Attwood & Florence, 1983). Therefore the amount of PAH solubilised depends on surfactant structure, aggregation number, micelle geometry, ionic strength and chemistry, temperature, solubilise chemistry and solubilise size (Edwards *et al.*, 1991). Furthermore, since the PAH partitions into the liquid organic core of the micelle it is not unreasonable to expect a correlation between the micelle-water partition constant (K_m) and other organic solvent-water partition constants for PAHs. However, due to Laplace pressure acting across the curved micelle-water interface, the solubility of a hydrophobic solute in a micelle will be less than its solubility in a bulk hydrocarbon solvent (Valsaraj & Thibodeaux, 1989). Edwards *et al.*, (1991) found $\log K_m$ to be a linear function of $\log K_{ow}$ for a given surfactant solution. Therefore, while a correlation

can be obtained it will be specific to a certain surfactant due to differences in micelle structure and subsequent solubilising capacity.

At concentrations below the CMC, the surfactant molecules are in the form of monomers which, although less effective than micelles, may increase the apparent solubility of sparingly soluble organic compounds (Iglesias-Jimenez *et al.*, 1996). This has been displayed for DDT which exhibits significant solubility enhancement below the CMC of the Triton series and Brij 35 (Kile & Chou, 1989). In this case solubility enhancement is thought to occur because commercial grade surfactants such as Triton and Brij 35 have no distinct CMC value. Therefore, since monomers of similar chain lengths tend to self associate, monomers with long hydrophobic groups will associate at lower concentrations while monomers with shorter hydrophobic groups associate at higher concentrations enabling micelles to form below the operationally defined CMC (Jafvert *et al.*, 1994). For other surfactant types, dimer or trimer formation may also occur below CMC.

As changes in surrounding physico-chemical conditions affect surfactant and PAH interactions, similar changes are likely to affect solubilisation, although this can be difficult to predict. For example Ko *et al.*, (1998) found micellar phenanthrene partition coefficients to increase with increasing ionic strength for anionic surfactant SDS, but not for Tween 80, a nonionic surfactant.

1.6.1 Air-water partitioning

There is very little information on the influence of surfactants on the air-water partitioning of PAHs, other than a study presented by Anderson, (1992) where the presence of SDS and an alcohol ethoxylate resulted in substantial reductions in the apparent Henry's constant of benzene, toluene and o-xylene. Presumably this was due

to the uptake of the aromatic compounds by into the favourable hydrophobic environment of the surfactant molecules, preventing transport to the air-water interface.

1.6.2. Particle-water interactions

As indicated in Figure 1.13, the extent to which surfactants impinge on PAH and other HOMs distribution in an aquatic system depends on (Jafvert *et al.*, 1994):

- (i) The effects of HOM sorption reactions with sedimentary materials;
- (ii) HOM solubilisation or sorption by micellar or monomer surfactant;
- (iii) Surfactant interactions with sediment.

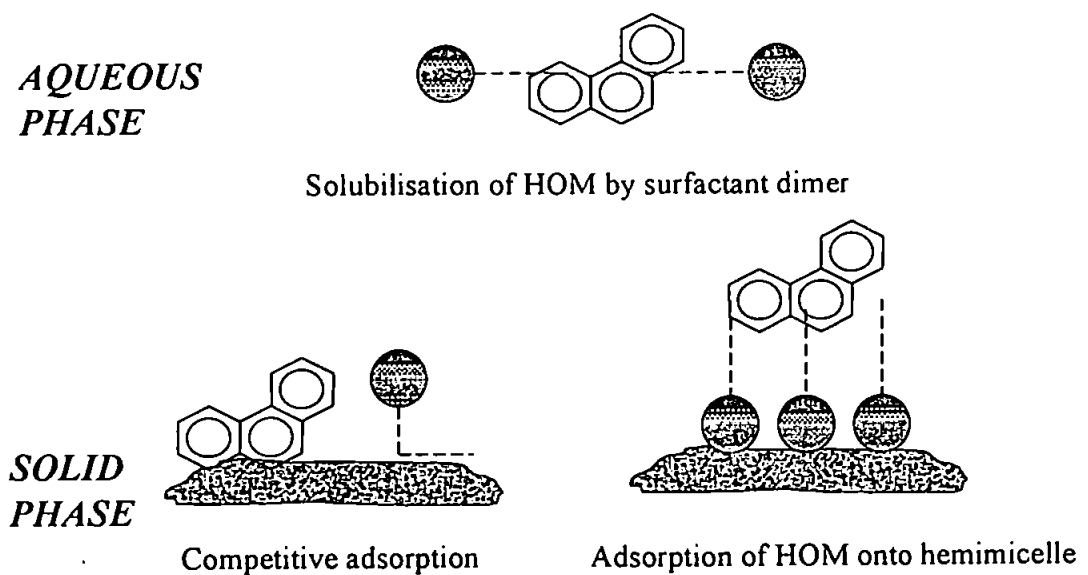


Figure 1.13: Influence of a surfactant on HOM partitioning

In a similar way to solubilisation by micelles in solution, surfactant aggregates sorbed to solid surfaces are also capable of solubilising nonpolar molecules. Solubilisation by adsorbed surfactant layers has been termed surface solubilisation, coadsorption or adsolubilisation (Sharma, 1995). This phenomenon is demonstrated most effectively by cationic surfactants which are retained by negatively charged sediment particles. Their

head on sorption means the hydrophobic tails are exposed and available for PAH sorption. Furthermore, although natural organic matter and the hydrophobic region of surfactant aggregates are mechanistically similar in PAH uptake from water, the effectiveness of the latter is much greater natural organic matter which can have a highly polar functional group content (Lee *et al.*, 1989).

Surfactants are also able to enhance desorption of PAHs already adsorbed to particles. This occurs mainly by increasing matrix diffusivities by sorption, penetration and swelling of micropores (Yeom & Ghosh, 1998). Surfactant sorption will reduce interfacial tension between the water and POM, allowing the water to wet the more hydrophobic regions of the POM. As the water content increases, the tortuosity is reduced (Deitsch & Smith, 1995). However the effectiveness of a surfactant on solubilising a PAH from sediment depends on (Liu *et al.*, 1991):

- (i) The interaction of PAH with monomers;
- (ii) The extent of PAH sorption onto particle;
- (iii) The sorption of surfactant on soil and its effect on increasing wettability of soil;
- (iv) The partitioning of aqueous phase PAH with micelles.

1.6.3. Bioavailability and biodegradation

The effect of surfactants on PAH biodegradation is rather indistinct. Some studies have reported an enhanced rate of biodegradation of naphthalene and phenanthrene in the presence of nonionic surfactants, while others noted a strong inhibition of biodegradation (Guha & Jaffe, 1996). Whether the surfactant is above or below its CMC seems to have some significance on bioavailability, as does surfactant type since surfactants with similar structures may have different biological effects. Triton X-114, which differs from Triton X-100 only by containing two fewer ethoxylate groups,

inhibited phenanthrene mineralisation, whereas Triton X-100 enhanced mineralisation within the same 6 day incubation period (Tsomides *et al.*, 1995).

The effect of surfactants on biodegradation may be indirect, for example by solubilising the PAH it may become readily available for microbial degradation. It seems, however, that surfactants actually increase the instantaneous rate, rather than the extent of desorption and therefore microorganisms have more substrate continuously made available (Aronstein *et al.*, 1991). The extent of aging may also be important, for example, Triton X-100 has been shown to significantly enhance phenanthrene mineralisation in 10 month old soil but had no effect in 2 day old soil (Tsomides *et al.*, 1995).

1.7. Research Aim and Objectives

Although the sorption of PAHs and surfactants to natural particles has been extensively investigated, the fate and transport of both types of compounds within the same system under changing environmental conditions is extremely complex and remains poorly understood. A large number of researchers have tended to use elevated rather than environmental contaminant concentrations (Liu & Chang, 1997; Iglesias-Jimenez *et al.*, 1996; Edwards *et al.*, 1994) possibly due to the difficulties of analysis at these levels. However, extrapolating generated trends down to realistic concentrations is often fraught with problems because of nonlinearity effects. Therefore, the objective of this study is to investigate the influence of three representative surfactants at typical environmental concentrations, on the partitioning behaviour of a PAH according to a range of variables e.g. temperature, time, salinity, particle concentration. To achieve this an empirical approach involving water and sediment samples taken from the Plym Estuary, UK, spiked with ^{14}C -labelled compounds was employed. Via this technique the

sorptive behaviour and interactions of selected compounds can be manipulated under controlled laboratory conditions.

The overall aim of this research is to improve the understanding of the fate and transport of HOMs and surfactants in aquatic systems both in isolation and as co-disposed contaminants. The objectives necessary to accomplish this were as follows:

- (i) develop a method originally employed for the addition of HOMs to natural samples under a range of environmental conditions to include surfactants;
- (ii) establish the influence of selected variables on the particle-water partitioning behaviour of phenanthrene, surfactants, and phenanthrene associated with surfactants;
- (iii) quantify the solubility and sediment-water partitioning of phenanthrene, surfactants, and phenanthrene associated with surfactants, in order to evaluate potential remediation options, and to enhance the accuracy and applicability of pollution transport models.

2.1. Introduction

There is currently an abundance of techniques for analysing surfactants, including high performance liquid chromatography, UV, infrared and NMR spectroscopy, paired ion extraction and thin layer chromatography (Swisher, 1987). However these systems and the conditions for analysis need to be adapted according to surfactant type both within and between classes. With regard to PAHs, gas chromatography – mass spectrometry is often the chosen method, although this requires extraction and concentration of analytes in addition to clean up procedures, which are both time consuming and prone to sample loss or contamination (Neilson, 1994). For this study it was necessary to employ a method that facilitated the use of environmental concentrations of contaminants, yet ensured a complete recovery and could be used for all four compounds both in isolation and together. Furthermore, a procedure was required that enabled an investigation into the effect of environmental variables, such as salinity, particle concentration and temperature, since a thorough appreciation of co-disposed contaminant behaviour according to these changes is lacking. An approach was therefore modified, which permitted the use of typical environmental concentrations of contaminants and replicated, as closely as possible, the processes that may occur between these co-existing compounds in natural waters. The existing approach involved equilibrating a ^{14}C -labelled HOM with an aqueous sample turbidised with particles (Means *et al.*, 1980; Zhou & Rowland, 1997; Rawling *et al.*, 1998). The concentration of the compound existing in the solid or aqueous phase could then be established, after phase separation, by detecting the radioactivity in the aqueous phase via liquid scintillation counting. A mass balance would then be used to calculate the concentration of the compound on the solid phase. This well established method, along with some necessary modifications, is described in detail in Section 2.7.

2.2. Experimental strategy

The surfactants used in this study were chosen for their well-characterised properties and because they represent commercially important compounds. A surfactant from each major class type was employed, as displayed in Table 2.1. Triton X-100 is an octylphenol polyethoxylate (OPE) with an average of 9.5 EO units. All Triton surfactants are molecularly heterogenous because of variable ethylene oxide (EO) chain lengths in the monomers (Kile & Chiou, 1989). The anionic surfactant is sodium dodecyl sulphate (SDS) which is an alkyl sulphate, and the QAC is hexadecyl trimethyl ammonium bromide (HDTMA).

Table 2.1: Surfactants selected for study

Surfactant	M wt (g mol ⁻¹)	Aqueous solubility @ 25°C (g L ⁻¹)	Molecular formula
Triton X-100	~ 625	Soluble in all proportions	$\underbrace{\text{C}_8\text{H}_{17}-\text{C}_6\text{H}_4}_{\text{Hydrophobe}} - \underbrace{(\text{OCH}_2-\text{CH}_2)_{9.5}\text{OH}}_{\text{Hydrophile}}$
SDS	288.4	100	$\underbrace{\text{CH}_3(\text{CH}_2)_{11}}_{\text{Hydrophobe}} \underbrace{\text{SO}_4^-}_{\text{Hydrophile}} \underbrace{\text{Na}^+}_{\text{Counterion}}$
HDTMA	363.9	36	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_{16}\text{H}_{33} - \text{N}^+ - \text{CH}_3 \\ \quad \swarrow \\ \text{CH}_3 \quad \text{Hydrophile} \\ \text{Hydrophobe} \end{array} \quad \underbrace{\text{Br}^-}_{\text{Counterion}}$

The chosen PAH was phenanthrene, a three ring polycyclic aromatic hydrocarbon (PAH) (Table 1.1), which has well-defined environmental properties and concentrations. Phenanthrene is a moderately hydrophobic compound which exists in relatively high concentrations in polluted aqueous environments. Although phenanthrene and its

metabolites are not acutely toxic, carcinogenic or mutagenic, it is useful as a model substrate to approximate behaviour of more harmful compounds (Laor *et al.*, 1998).

Since the particle-water interactions of PAHs and surfactants influence their fate and transport in aquatic systems, and, in turn, partitioning behaviour is largely controlled by the solubility of a compound, an understanding of how aqueous physicochemical characteristics affects solubility is integral to sorption studies. Furthermore, should both PAHs and surfactants exist as co-disposed contaminants, then the relative solubility of the PAH may be modified and the complexity of the situation increases. Hence, it makes sense to consider each compound in isolation before both are included in the same system. To this end, the solubility of all four compounds as affected by changes in physicochemical properties of water were investigated, followed by a repetition where phenanthrene was included with each surfactant type (Figure 2.1).

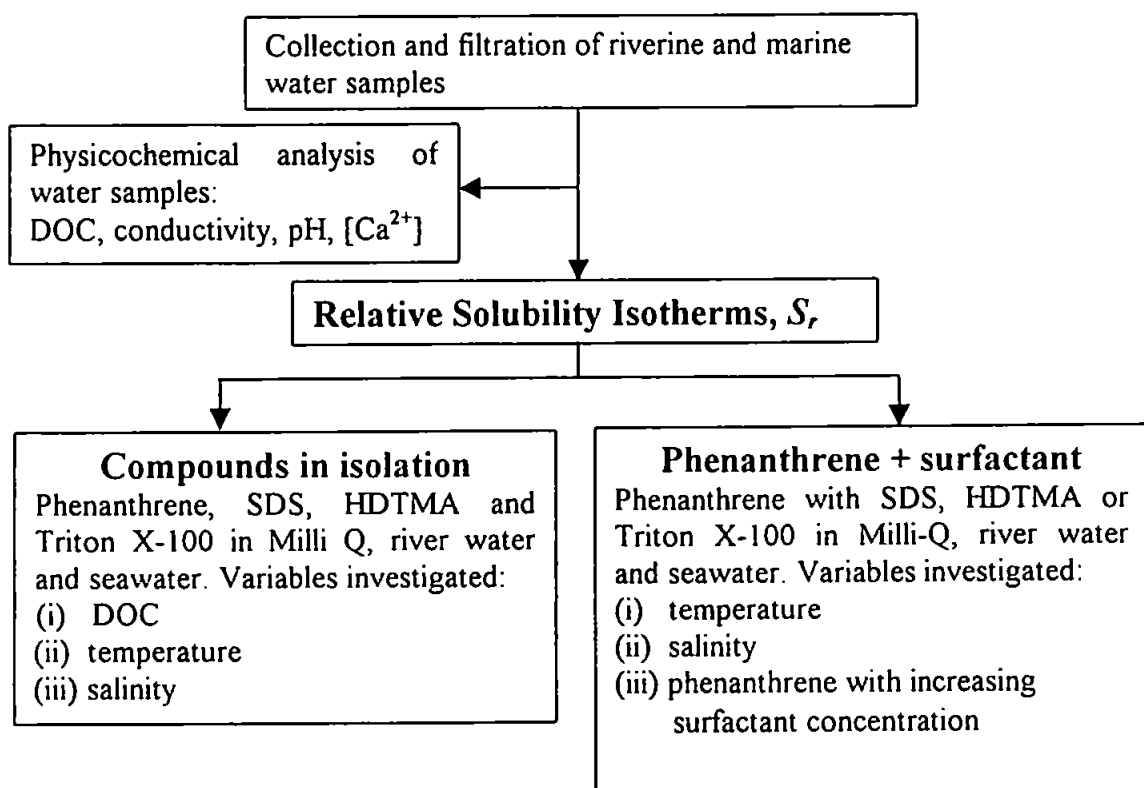


Figure 2.1: Summary of experimental strategy for the study of the relative solubility of phenanthrene and surfactants, where DOC is dissolved organic carbon.

Dissolved organic carbon (DOC) and salinity have been reported as significant variables in the solubility of HOMs (Wijayarathne & Means, 1984; Murphy *et al.*, 1988; Means, 1995; Sanstchi *et al.*, 1997) and were therefore selected as key variables to investigate for all compounds. The role of DOC, with regard to surfactants, is somewhat unclear, whereas salinity is better defined and appears to be a much more influential factor (Traina *et al.*, 1996; Ingram & Ottewill, 1991; Mukerjee *et al.*, 1995; Brownawell *et al.*, 1997). Surfactants may experience a change in solubility with a change in temperature, and therefore experiments were carried out at both 20°C and approximately 8°C ($\pm 2^\circ\text{C}$), in order to reflect changing environmental conditions (Attwood & Florence, 1983). While a change in pH can also exert an influence on surfactants, particularly anionic and cationic types (Rosen, 1989), limited availability of time, equipment and reagents dictated that this variable had to be forfeited. Furthermore, since the pH range in estuaries is typically between about 6.5 and 8, fluctuations in this range were unlikely to induce significant variations in surfactant behaviour. Nevertheless, the pH of collected water samples was regularly monitored and proved to be relatively constant (Table 3.1).

Once the influence of aqueous physico-chemical properties on compound solubility had been established, it was then necessary to incorporate natural particles to observe sorption characteristics. Variables included suspended particulate matter (SPM) concentration, salinity, contact sequence of contaminants, time (kinetics) and temperature (Figure 2.2.).

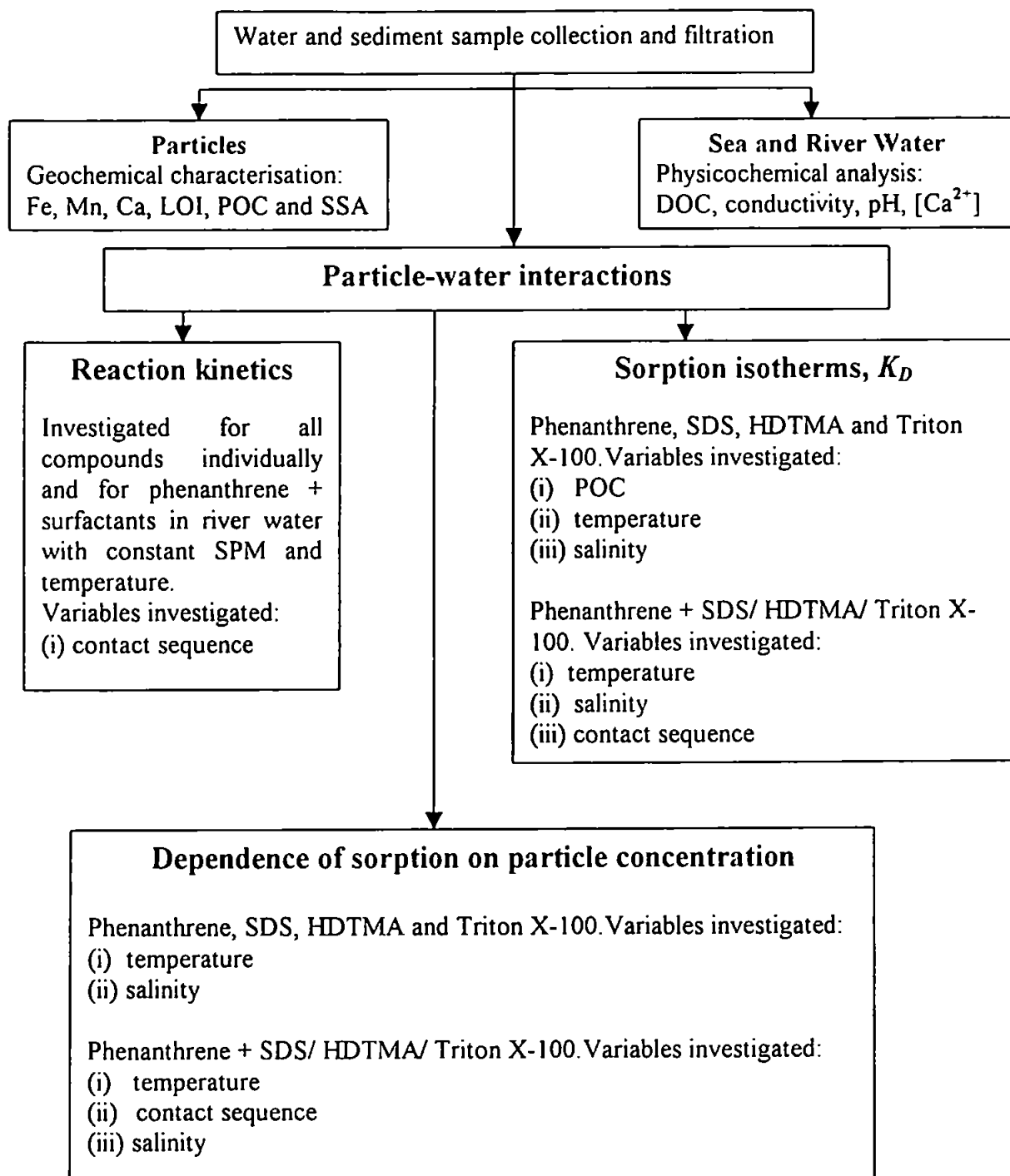


Figure 2.2: Summary of experimental strategy for phenanthrene and surfactants with particles, where LOI is loss on ignition, POC is particulate organic carbon, SSA is specific surface area, SPM is suspended particulate matter, DOC is dissolved organic carbon.

2.3. Site description

Water samples were obtained from the riverine and marine end members of the Plym Estuary in Plymouth, Devon ($52^{\circ}07'50\text{N } 04^{\circ}07'75\text{W}$) (Figure 2.3). The Plym Estuary, which is 7 km long and well-mixed with a tidal range of 2 to 3 m, was chosen to represent a typical urban estuary. It drains the granitic moorland of Dartmoor incorporating deciduous and coniferous woodland, with a lower catchment flanked by several industries including landfill, sewage treatment works and a china clay works. Surficial oxic sediment was collected from the intertidal mud flats.

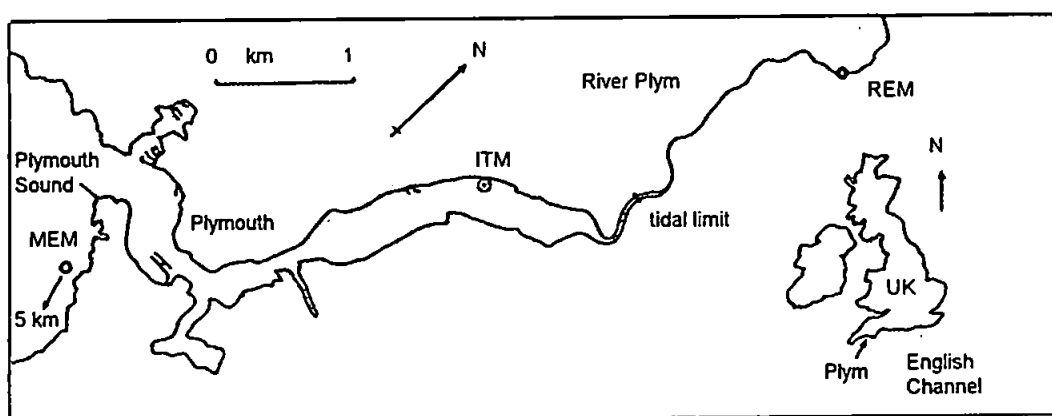


Figure 2.3: The Plym Estuary and sample areas. REM and MEM are river and marine end-member samples, respectively and ITM is the intertidal estuarine mud sample.

2.4. Sample collection and characterisation

2.4.1. Riverine and marine water samples

Glass pyrex bottles which had been cleaned with Decon[®] and then ashed (8 hours at 500°C) to remove any adsorbed organic contamination, were used to collect both river and sea water. The samples were then filtered via ashed Whatman GF/F filters (pore size $0.7\ \mu\text{m}$) and stored in the original pyrex bottles at 4°C in the dark. In order to ensure the integrity of the samples was not affected over time (e.g. the formation of organic colloids) the water samples were used within 1 month and fresh samples were

collected when necessary. The physicochemical properties of each batch was monitored (Table 3.1).

2.4.2. Estuarine sediment samples

Surface sediment samples were collected in clean glass jars, divided and frozen in portions until required so that the same particles were used throughout the study. The <63 μm (mud) fraction was chosen to represent suspended sediment, the most significant transport medium for HOMs (Voice & Weber, 1983). Sediment required for use was thawed and separated from the bulk sample by passing the sample through a 63 μm nylon mesh and washed through with small amounts of river water. The concentration of the sediment slurry was estimated by filtering a known aliquot in triplicate via GF/F filters which were then dried and weighed. The remainder of the sediment slurry was stored in a glass jar at 4°C in the dark for a maximum of 4 weeks.

2.4.3. Water characterisation

The pH and conductivity of the water was determined in the field using a calibrated HI 9025 microcomputer pH meter and HI 9635 microprocessor conductivity / TDS meter, respectively. Further water characterisation included dissolved organic carbon (DOC) and calcium concentration. DOC analysis required 100 mL of each water sample to be filtered through ashed 47 mm diameter Whatman GF/F filters (pore size 0.7 μm). Since immediate analysis was impractical, the filtrate was acidified with 1% phosphoric acid (AristaR) and stored in ashed glass bottles, ensuring the glass stopper was secure and no air bubbles were present. This method of sample preservation is a potential source of contamination (Kramer *et al.*, 1994), therefore a similar procedure was performed using Milli-Q for a background reading to be established (ranging from 0.25 to 0.78 mg L^{-1}). The samples were then stored at 4°C in the dark until the DOC could be determined on a

Schimidzu TOC-5000 total organic carbon analyser, which has a limit of detection of $\sim 0.001 \text{ mg L}^{-1}$. Calcium analysis was determined via a Perkin Elmer Optima 3000 ICP atomic emission spectrophotometer (AES) calibrated using Ca standards at a wavelength of 317.9 nm.

2.4.4. Sediment characterisation

In order to establish the Fe, Mn and Ca concentration on the $<63 \mu\text{m}$ sediment particles, approximately 700 mg of freeze-dried sediment was extracted with 0.05 M hydroxylamine hydrochloride in 25% v/v acetic acid (BDH AristaR) for 24 hours at room temperature. The digests were performed in triplicate and analysed on the Perkin Elmer Optima 3000 ICP-AES, calibrated using multi-element acidified standards at wavelengths of 317.9 nm for Ca, 257.6 nm for Mn and 238.2 nm for Fe. Procedural blanks were below the limits of detection.

The total carbon of the sediment was determined on dried sediment (10 mg) via the Schimidzu TOC-5000 total organic carbon analyser, while the specific surface area of the sediment was established using the multi-point BET nitrogen gas adsorption technique on a freeze-dried sample (Millward *et al.*, 1990). Loss on ignition (LOI) was also performed where sediment was collected on an ashed 47 mm diameter Whatman GF/F filter (pore size $0.7 \mu\text{m}$) of a known weight. The sediment and filter were dried, re-weighed, combusted in a Carbolite ESF3 Muffle furnace at 550°C for 5 h and then weighed again.

2.5. Radiotracer Procedures

A well-established method employed to determine the particle-water partitioning behaviour of ^{14}C - HOMs (Turner & Tyler, 1997; Rawling, 1998; Zhou *et al.*, 1999), was refined to incorporate surfactants and to ensure complete recovery of the compound

under investigation. The most significant advantages of this approach are its sensitivity, providing a means for employing concentrations at typical environmental levels (i.e., ng L^{-1}), and the ability to directly determine the concentration of the compound in both aqueous and solid phases. This method does, however, require caution with regard to handling compounds which are both toxic and radioactive. Hazards were kept to a minimum by working on a spill tray within a fume cupboard on a bench area that was labelled and designated for radioactive use only. Diluted solutions were used in the laboratory while the original stock was held in the University's radiochemical store. Gloves, protective clothing, goggles and an 'organic-fume' mask were worn during experimental work.

2.5.1. Radioactive compounds used for this study

Both phenanthrene-9- ^{14}C and sodium dodecyl-1- ^{14}C sulfate (SDS) were purchased from Sigma[®] Chemical Company. The purity of these compounds were reported as $\geq 98\%$ and $\geq 95\%$ respectively (see Section 2.5.2).

Once received, phenanthrene was diluted in hexane to make a stock solution of $1.85 \times 10^6 \text{ Bq mL}^{-1}$. This was diluted again in hexane for laboratory use to $3.7 \times 10^4 \text{ Bq mL}^{-1}$, where a $25 \mu\text{L}$ aliquot would provide 925 Bq of radioactivity. The SDS solution was stored as received since it was contained in a vial with a resealable septum. This was necessary in order to minimise contamination by microbes since SDS is particularly susceptible to biodegradation. As a result any dilutions made were used within a week. In order to use environmentally and practically realistic concentrations, radiolabelled SDS was added to a non-radiolabelled SDS-Milli Q solution ($5 \mu\text{L}$ added at $1.1 \times 10^4 \text{ Bq } \mu\text{L}^{-1}$ in 2 mL of non-radiolabelled solution at $1 \mu\text{g } \mu\text{L}^{-1}$). This concentration would provide approximately 700 Bq for a $25 \mu\text{L}$ spike. Both phenanthrene and SDS were stored in the dark at 4°C .

The cationic surfactant, hexadecyltrimethyl ammonium iodide (HDTMA) was provided by Tocris Cookson (U.K. agents for the American Radiolabelled Company). The stock solution, received as HDTMA in ethanol, was stored at 4°C in the dark undiluted. As with SDS, radiolabelled HDTMA was added to a solution containing the non-radiolabelled compound in Milli-Q (14 μL added at $3.7 \times 10^3 \text{ Bq } \mu\text{L}^{-1}$ to a 2 mL non-radiolabelled solution at $1 \mu\text{g } \mu\text{L}^{-1}$) to give a 25 μL spike activity of $\sim 650 \text{ Bq}$. However, unlike SDS, HDTMA precipitates at 4°C therefore the solution was kept at room temperature.

Unfortunately, despite a comprehensive search of chemical companies (including Procter & Gamble, 3M, Shell UK, Uniqema (a subsidiary of ICI), DuPont, NEN (New England Nuclear), Unilever, Lancaster Synthesis, Sigma, ARC (Tocris Cookson), Amersham and Moravek), it was not possible to source a radiolabelled non-ionic surfactant without incurring the costs of custom synthesis. As a compromise, a non-labelled, non-ionic surfactant Triton X-100 was used. This can easily be detected by UV-Vis spectrophotometry. However the limits of detection are much higher, and so significantly greater concentrations were required in the experiments (Section 2.7.5).

2.5.2. Monitoring radiochemical purity

In order to confirm the integrity of the radiolabelled compounds it was necessary to check their purity. This was particularly important for three reasons (Touchstone & Dobbins, 1983):

- (i) To ensure the compound does not degrade during the incubation, since the results may differ from that of the original compound.

- (ii) The high sensitivity of scintillation counting would detect low levels of incidental material. This may behave differently to the compound of interest and subsequently affect results.
- (iii) Autoradiolysis can occur in compounds of high specific activity resulting in chemical changes. This can be reduced by storing samples at low temperatures and in dilute solutions. However, if the solvent is attacked and, like water, is highly reactive, long-lived excited species such as free radicals or ions are formed and further complications result.

While the determination of phenanthrene purity is reasonably straightforward, the analysis of surfactants can be problematic. They have a tendency to adsorb to any available surface and are nonvolatile without derivatization (Armstrong & Stine, 1983). Although a number of techniques exist, such as spectrometric, titrimetric and ion-selective electrode methods, they are limited by being selective for specific functional groups, leading to positive responses for a range of homologous, isomeric and even structurally dissimilar surfactants (Armstrong & Stine, 1983). As a result, liquid chromatography (LC) and thin layer chromatography (TLC) are frequently selected as the most suitable methods since these are both not only effective in separating identically charged surfactants, but also mixtures containing surfactants from more than one class. Furthermore, TLC used in conjunction with liquid scintillation counting is an extremely sensitive method for use with radiolabelled compounds; hence this was the chosen technique to determine the purity of the original solutions of SDS, HDTMA and phenanthrene. In order to ensure degradation during incubation of the compounds with particles was minimal, TLC was also performed on a solvent wall rinse from the glass centrifuge tube for each compound.

2.5.2.1. Radiochemical thin layer chromatography

The 20 x 20 cm TLC plates were prepared in the laboratory, with glass as a backing material, using a Desaga Moving Hopper Spreader. A silica gel slurry was applied at a thickness of 0.25 mm and left to dry at room temperature overnight. The plates were then activated in an oven at 115°C for two hours. This aim of this process is to deactivate very active sites in order to encourage a more uniform hydrogen-bonding mechanism, subsequently producing more reproducible separations (Touchstone & Dobbins, 1983). Once the plates had cooled, a microsyringe (10 µL) was used to spot the analytes 1cm from the bottom (2 µL of the stock solution and 5 µL of wall rinse). The plates were then transferred to a glass tank lined with filter paper and containing the appropriate mobile phase (100 mL), as indicated in Table 2.2. The tanks were covered and left to equilibrate for 30 minutes to ensure the atmosphere inside was saturated with the solvent vapour.

Table 2.2: The solvent-sorbent system for each compound

¹⁴ C Compound	Adsorbent	Solvent System
Phenanthrene ^a	Silica gel	<i>n</i> -hexane
SDS ^b	Silica gel	Dichloromethane:Methanol:Acetic Acid (8:1:0.75)
HDTMA ^b	Silica gel	Dichloromethane:Methanol:Acetic Acid (8:1:0.75)

^a Zweig & Sherma, (1972); ^b Armstrong & Stine, (1983)

Once the solvent front had travelled 15 cm, the plates were removed and left in the fume hood until the residual solvent had evaporated. The adsorbent was then removed in 2 mm segments and deposited into a scintillation vial. Milli Q (1 mL) was added to form a suspension, followed by Insta-Gel scintillation cocktail (2 mL). Each vial was then

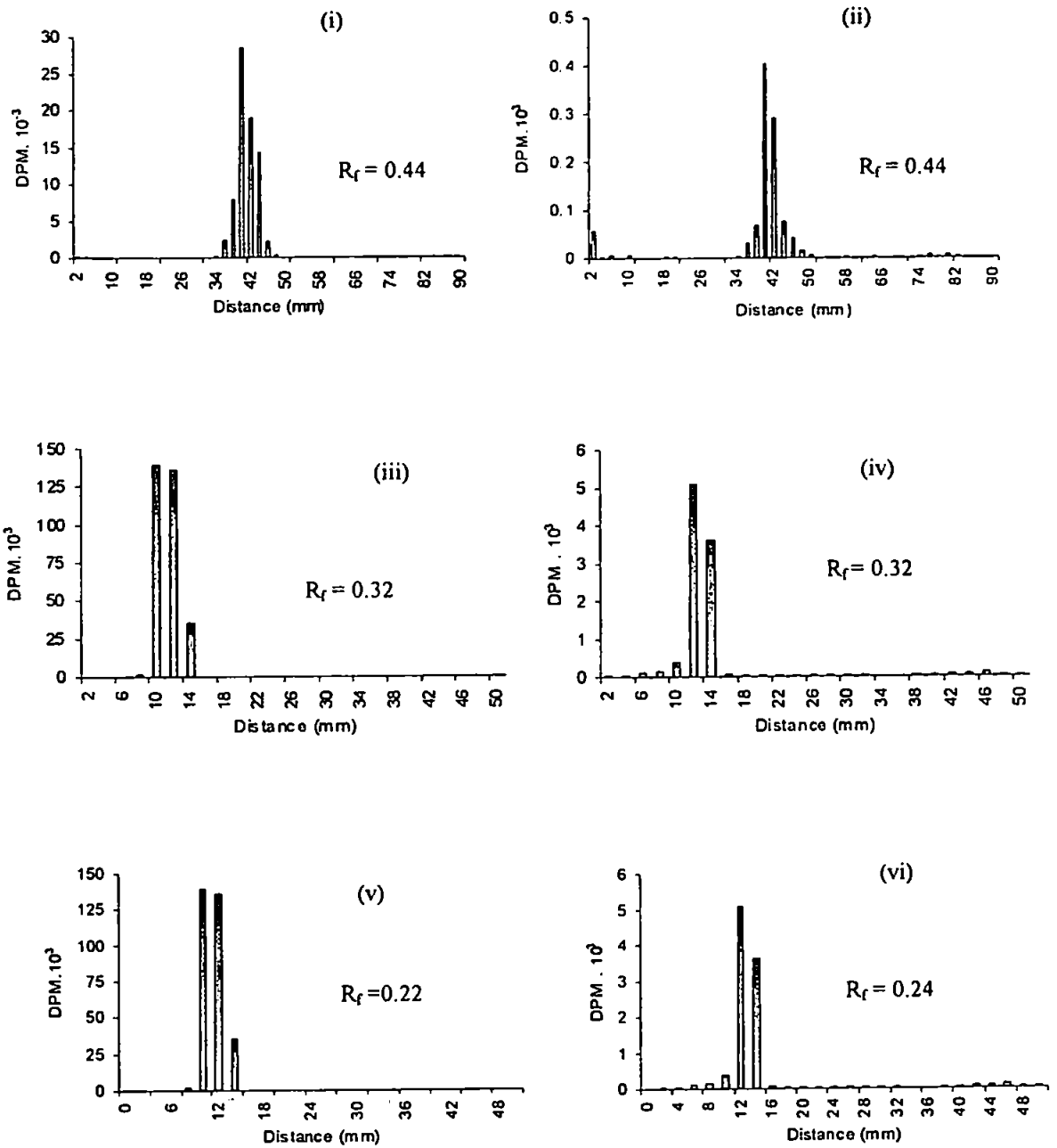


Figure 2.4: Radio-TLC profiles for (i) phenanthrene stock (ii) phenanthrene rinse (iii) SDS stock, (iv) SDS rinse, (v) HDTMA stock, (vi) HDTMA rinse. R_f is the relative front.

Table 2.3: Purity of radiolabelled compounds

Compound	Specific activity ^a (mCi mmol ⁻¹)	¹⁴ C labelling	Compound purity (%)	Radio-chemical purity pre-incubations (%)	Radio-chemical purity post-incubations (%)
Phenanthrene	46.9	9- ¹⁴ C	≥99	≥98	90
SDS ^b	53.5	1- ¹⁴ C	≥95	≥97	97
HDTMA ^c	55	methyl- ¹⁴ C	≥99	≥99	92

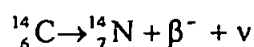
^aSpecific activity of a radioisotope defines its radioactivity related to the amount of material (Goulding, 1994); ^bSDS- sodium dodecyl sulphate; ^cHDTMA- hexadecyl trimethyl ammonium iodide.

With regard to the surfactants, efforts taken to hinder biodegradation during partitioning experiments appeared to be successful, whereas phenanthrene seems to be subject to some losses. This may be misleading however, since unlike the surface active SDS and HDTMA, phenanthrene sorption to the glass walls is minimal. Therefore, despite pre-concentration, the phenanthrene collected from the solvent rinse of the walls proved to be very close to background radiation counts and hence less definitive. Losses over the short time scale employed are unlikely to occur since photodegradation was inhibited by equilibration of samples in the dark and estimates of phenanthrene biodegradation in soil indicate a minimum half life of 16 days (Table 1.6., Section 1.3.4.).

2.6. Liquid scintillation counting

The most commonly used methods of detecting radioactivity are based on the ionisation of gases, the excitation of solids or solutions, or the ability of radioactivity to expose photographic emulsions (Goulding, 1994). The detection method employed for this investigation encompasses one of the oldest principles for quantitatively determining radioactivity, a process known as scintillation. This involves detecting the photons of light (scintillations) that are produced when radiation strikes a fluor (Skoog & Leary, 1992). Carbon-14, which is used as a radiolabel for this study, undergoes beta decay

resulting in negatron formation:



where ν represents a neutrino of no particular significance in analytical chemistry and β^- is a negatron, an electron that is formed when one of the neutrons in the nucleus is converted to a proton (Skoog & Leary, 1992). For low energy beta emitters such as carbon-14, liquid scintillation counting (LSC) is particularly suitable, since the sample is added directly to a scintillation cocktail containing a solvent and one or more fluors which are easily accessible to the weakly penetrating beta particles (Geary, 1986). The light emitted by the organic solvent when bombarded with radioactivity is accepted by a primary fluor which itself fluoresces at a longer wavelength than the organic solvent. As the emitted light is not always detected with very high efficiency, this can be overcome by a secondary fluor or wavelength shifter.

Two LSCs were employed for this study, Ultima Gold for holding an aqueous sample, and Insta-Gel Plus for particle suspensions. Ultima Gold (Packard Canberra) contains di-isopropylnaphthalene as the solvent with 2,5-diphenyloxazole (PPO) and 1,4-bis-(2-methylstyryl)benzene (bis-MSB) as the primary and secondary scintillators, respectively. Insta-Gel Plus contains the same scintillators with 1,2,4-trimethylbenzene as the solvent.

2.6.1. Evaluation of the liquid scintillation counting method

Liquid scintillation holds several advantages over other methods employed for the detection and quantification of radioactive decay including (Goulding, 1994):

- (i) the rapidity of fluorescence decay (10^{-9} s), meaning high count rates are possible;
- (ii) high counting efficiencies particularly for low energy β -emitters;
- (iii) ability to accommodate different sample types, e.g., liquids, solids suspensions and gels;

- (iv) the general ease of sample preparation;
- (v) the ability to count separately different isotopes in the same sample, therefore allowing dual labelling;
- (vi) scintillation counters are highly automated and so large numbers of samples can be counted automatically and built in computer facilities carry out many forms of data analysis.

As indicated above, liquid scintillation counting has become an extremely sophisticated technique, therefore many of its associated problems have been overcome. Some disadvantages remain, however, and these include the following (Goulding, 1994):

- (i) Optical quenching. This occurs with use of dirty scintillation vials which absorb emitted light before it reaches the photomultiplier. Disposable plastic vials were used for this investigation and gloves were worn to handle samples, subsequently minimising surface contamination and the likelihood of optical quenching.
- (ii) Photon quenching. This is caused when heterogeneous mixtures affect interactions between neutron and scintillators leading to variable results. This may also be due to high salt concentration and extreme pH.
- (iii) Colour quenching. A coloured sample will absorb light emitted within the scintillation cocktail before it leaves the sample vial.
- (iv) Chemical quenching. Chemicals existing in the sample modify the transfer of energy from the solvent to the primary fluor or between the primary and secondary fluor.
- (v) Chemiluminescence. This is caused by the production of light via chemical reactions in the sample, independent of the excitation of the solvent and fluor

system by radioactivity. Chemiluminescence may occur in samples with an alkaline pH or in the presence of peroxides, tissue solubilizers or chlorophyll.

- (vi) Phospholuminescence. This arises from constituents of the sample absorbing light and re-emitting it. Pigmented samples are most likely to phosphoresce.
- (vii) Self-absorption. Low energy, β emitters, may exhibit self-absorption, where radiation is absorbed by the sample itself. This can be a problem if the sample is particulate or collected on a membrane filter.

2.6.2. Determination of absolute counts

Even in the absence of a radiolabelled sample, the existence of natural radiation (e.g cosmic radiation) means that the scintillation counter will still register a count. Employing coincidence counting and lead shielding can minimise this, however, the background value must always be noted and subtracted.

Another factor to be taken into account when calculating isotope activity is that since the emission of radioactivity is random, repeated measurements of isotope activity, at equal intervals, will result in counts that vary over a range of values but cluster near the centre of the range. Therefore, while a single count cannot be assumed to be true, the mean of large counts are likely to be more accurate. The accuracy of this mean will, however, depend on the spread of the data. In order to minimise this variation, a counting precision of 1%, or 40000 counts per minute, is preset providing a 95% confidence level for the count (i.e. 95% of values lie within 1% of the mean). If counts were low a 20 minutes maximum counting period was used, although this resulted in a lower counting precision.

An occasional complication encountered with scintillation counting is that of quenching, which reduces the light output from the sample and affects the accuracy of the counts per minute. While some interferences cannot be accounted for, chemical and

colour quenching can themselves be quenched. Therefore by employing quench correction it is possible to determine the counting efficiency of each sample so that relative sample activity (CPM) can be converted into absolute sample activity in disintegrations per minute (DPM):

$$DPM = \frac{[CPM - BKG]}{[E]} \quad (2.1)$$

where BKG is the background count and E is the counting efficiency. Fortunately, the instrument employed for this study, the Beckman LS6500 Multi-purpose Scintillation System, is particularly advantageous in that it has an installed Auto DPM mode. This means each isotope has a stored quench curve, automatically correcting for counting efficiency and calculating the samples absolute count. Auto DPM Calibration is performed at the factory with unquenched standards and stored until recalibration at 6 monthly intervals by Beckman technicians.

An additional useful facility on the Beckman LS6500 Scintillation Counter is the Lum-Ex for luminescence correction (Beckman Operating Manual, 1993). This ensures counts of actual radioactive disintegrations within the sample are distinguished from other light producing events such as chemiluminescence. If the Lum-Ex is shown to be over 5% for a sample an effort was made to establish and amend the problem.

2.7. Experimental procedure

The range in characteristics between the compounds employed in this study coupled with the desire to improve the rigour of the original procedure (Section 2.1; Section 2.7.2) has evolved a number of different methodologies. The intention of this method development was to enable direct determination of the compound concentration in both the particulate and aqueous phases, rather than relying on mass balances to estimate sorbed activities as in conventional approaches. This would eliminate assumptions associated with such calculations and reduce inherent errors.

2.7.1. Sediment preparation

The < 63 μm fraction of sediment was separated from the bulk sample by passing the sample through a 63 μm pore nylon mesh, agitated with small amounts of river water. The resultant slurry was transferred into a clean glass jar and stored at 4°C in the dark. Dilutions were made, as required, with filtered river or seawater at sediment concentrations of 1 mg mL^{-1} and 6 mg mL^{-1} , to provide a working solution for the experiments.

The < 63 μm particles were then added to filtered river or seawater, reaching a final volume of 20 mL for all samples, with a range of suspended particulate matter (SPM) concentrations from 20-600 mg L^{-1} . These concentrations reflect typical sediment concentrations (10-600 mg L^{-1}) in the turbidity maximum zone, an area where alluvial particles are thought to coagulate and settle and considered to be largely responsible for pollutant trapping within estuaries (Brunk *et al.*, 1997).

In order to determine the influence of particulate organic matter (POM) on the partitioning of the compounds, several experiments were performed with sediment devoid of its organic coating. This was achieved by reacting hydrogen peroxide (20mL) with freeze-dried estuarine particles (1g). The mixture was left for 24 hours, until the effervescing had ceased. Milli Q (20mL) was then added and the solution was centrifuged for 30 minutes at 3000 rpm. The supernatant was removed, the particles were rinsed with Milli Q and centrifuged again. This was repeated once more and dilutions were then made in UV-irradiated river or seawater at a concentration of 50 mg L^{-1} . Prior to use the UV-irradiated water was placed in the dark for 6 days since exposure to the UV-lamp provided a possible source of phospholuminescence (Rawling, 1998).

2.7.2 Existing approach for studying phenanthrene solubility and sorption

The chief concerns addressed for the original method of determining the particle-water partitioning of PAHs, such as phenanthrene, included:

- (i) elimination of the carrier solvent (i.e., *n*-hexane), prior to the addition of the turbidised water sample, to prevent formation of an emulsion;
- (ii) complete recovery of HOM adsorbed onto glassware in order to employ mass balance technique, therefore avoiding problems associated with direct counting of particles.

The following procedure, summarised in Figure 2.5, was developed with regard to the points mentioned above. The first step required the removal of the carrier solvent, in this case hexane. This was simply achieved by using a glass microsyringe, which had been rinsed with *n*-hexane, to transfer between 10 and 25 μL (300-900 Bq) of the phenanthrene/hexane solution onto the wall of a clean glass centrifuge tube (30 mL). Each concentration throughout the study was examined in quadruplicate to monitor precision and reproducibility. The carrier solvent was then allowed to evaporate under the fume hood, leaving the phenanthrene adsorbed to the glass. This was necessary to prevent the formation of an emulsion, which would alter the behaviour of phenanthrene. A filtered or turbidised water sample (20 mL) was immediately added for either relative solubility experiments or particle-water incubations, respectively. Ground-glass stoppers were placed in the centrifuge tubes and covered with aluminium foil to minimise photolysis of phenanthrene. The samples were then left to equilibrate on a wrist action shaker (350 rpm) at 20°C for 16 hours, after which, the glass stoppers were removed and the samples were centrifuged (3000 rpm for 30 minutes) in order to separate the solid from the aqueous phase. This step is omitted for relative solubility work, where the effect of different aqueous matrices on the solubility of the compounds

is investigated. Using a glass pipette, 1 mL of the supernatant was transferred to a vial containing Ultima Gold-LSC cocktail (4 mL) so that the activity of ^{14}C -phenanthrene in the dissolved phase could be determined. Since hydrophobic compounds are known to adsorb to glass, the pipette was rinsed in hexane (1 mL), which was also added to LSC (4 mL). The surplus supernatant and sediment pellet were then discarded and replaced with hexane (6 mL) to extract any residual phenanthrene adsorbed to the glass walls. The tubes were again covered with aluminium foil, agitated at 20°C for 16 hours when ultimately the hexane (1 mL) was transferred to LSC (4 mL) and the activity recorded.

The concentration of phenanthrene on the particles is determined via mass balance by incorporating the activity values obtained in the dissolved phase and solvent rinses (Section 2.7.2.1). However to determine absolute counts it was necessary to establish a background count (BKG) by incorporating 1 mL of the aqueous solution in 4 mL of liquid scintillation cocktail. As for the radiolabelled samples, this was done in quadruplicate. If this produced a relative standard deviation (RSD) below 10% then the mean BKG was used. However, occasionally the random nature of negatron emission can cause erratic counts. Therefore, if the RSD was greater than 10% then one of the values was discarded (Rawling, 1998). The limit of detection (LOD) was calculated from the sample mean (\bar{x}) and standard deviation (S_{n-1}) of the BKG as indicated in Table 2.3.

$$\text{LOD} = \bar{x} + (3s_{n-1}) \quad (2.2)$$

Table 2.4: Background counts and limits of detection for scintillation counting of employed matrices

Matrix	BKG (CPM)	S_{n-1} (CPM)	LOD (CPM)	RSD (%)
Milli-Q	18	1.2	21	6.8
River water	17	0.7	19	3.8
Sea water	19	1.4	23	7.1
<i>n</i> -hexane	23	0.53	25	2.3

BKG is the mean background activity, $n=4$, in counts per minute (CPM), S_{n-1} is the standard deviation, LOD is the limit of detection and RSD is the relative standard deviation of the background count.

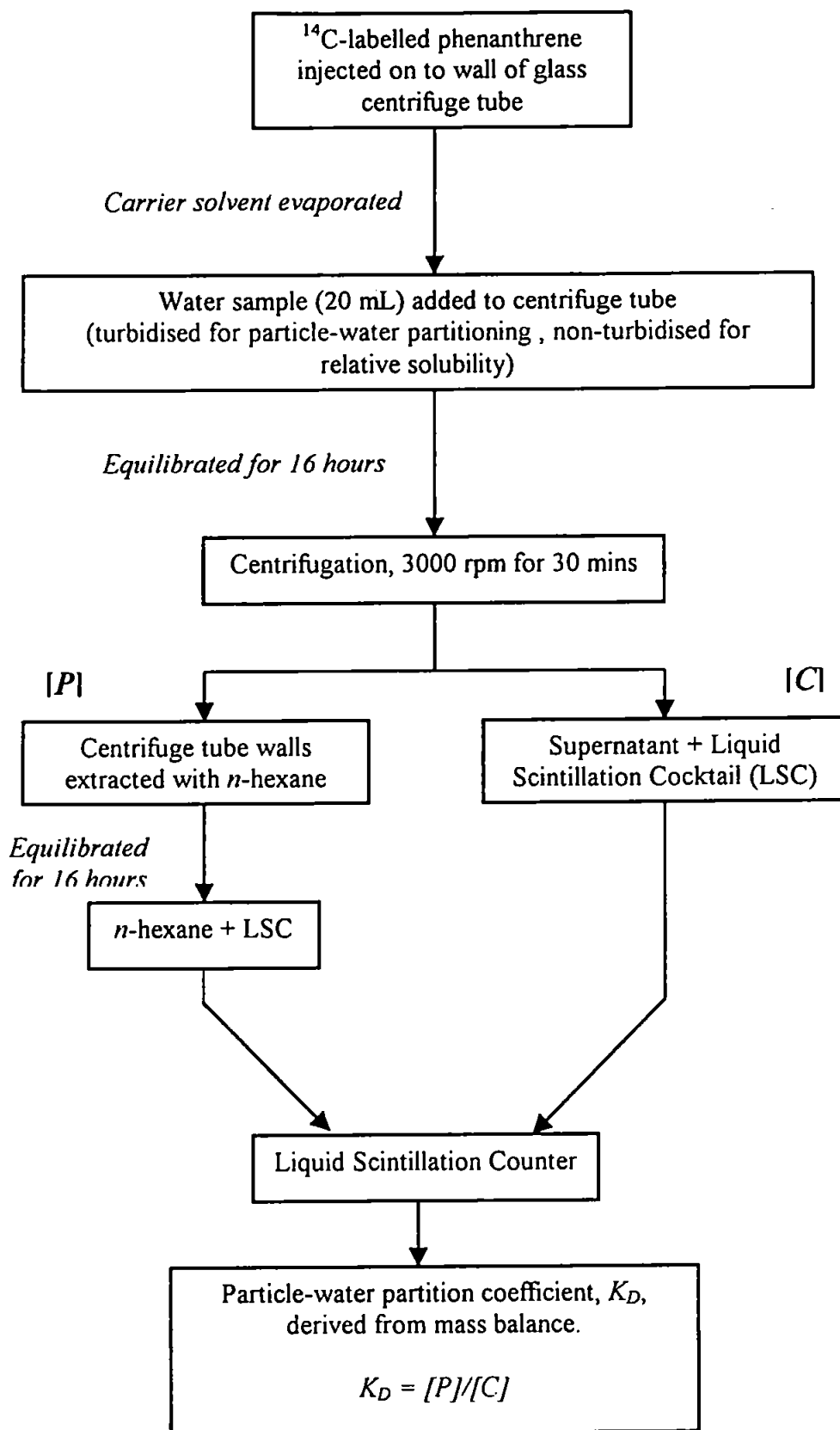


Figure 2.5: Summary of original approach incorporating a mass balance technique to calculate K_D (P and C are the concentrations of the compound in the particulate and aqueous phase, respectively); (adapted from Rawling, 1998).

2.7.2.1. Partitioning and relative solubility calculations for original phenanthrene approach

In order to understand how different conditions influenced the behaviour of the compounds under investigation, their relative solubility was determined using the following equation, where each compound concentration was examined in quadruplicate:

$$S_r = \left[\frac{A_c + A_r}{Spec.Act.} \right] \cdot rmm \quad (2.3)$$

where S_r is the relative solubility of the compound (g L^{-1}) according to the added mass of the compound, temperature, matrix and possible incorporation of co-solute, A_c is the aqueous activity (Bq mL^{-1}), A_r is the activity of the pipette rinse, rmm is the relative molecular mass of the ^{14}C -labelled compound (g mol^{-1}) and $Spec. Act.$ is the specific activity of the compound (Bq mmol^{-1}),

Since it was originally assumed that the particles would form a heterogeneous mixture with LSC and due to quenching or self-absorption, could not be counted directly for carbon-14, a mass balance equation was employed to calculate the particle water partition coefficient:

$$K_D = \frac{P}{C} \quad (2.4)$$

$$K_D = \left[\frac{(A_o - ((A_c + A_r) + A_w))}{(A_c + A_r)} \right] \times \left[\frac{V}{M} \right]$$

where K_D is the partition coefficient (mL g^{-1}), P is the compound concentration in the particulate phase (w/w), C is the compound in the aqueous phase (w/v), A_o is the activity of the original spike, A_c is the activity in the aqueous phase, A_r is the activity of

the pipette rinse, A_w is the activity adsorbed onto the walls of the centrifuge tube, V is the volume of water (mL), and M is the mass of particles (g) in the sample.

2.7.2.2 Evaluation of original approach for phenanthrene

Since the K_D was determined by mass balance, it was of primary importance to ensure that any losses of phenanthrene, other than to the particles, were minimised. If this were not the case the K_D would be significantly over estimated. As a result several steps were taken to address this issue. Loss of phenanthrene during evaporation of the carrier solvent was a potential problem that needed to be quantified. This was simply achieved by injecting a 25 μL spike of phenanthrene dissolved in hexane onto the wall of a glass scintillation vial. The hexane was left to evaporate over a range of time intervals, from 5 to 30 minutes, before the addition of Ultima Gold-LSC. The sample was then counted for carbon-14 to determine the percentage recovery of phenanthrene. The results, displayed in Figure 2.6, indicate that significant loss occurs after 10 minutes and is therefore preventable by adding the water sample before this time has elapsed.

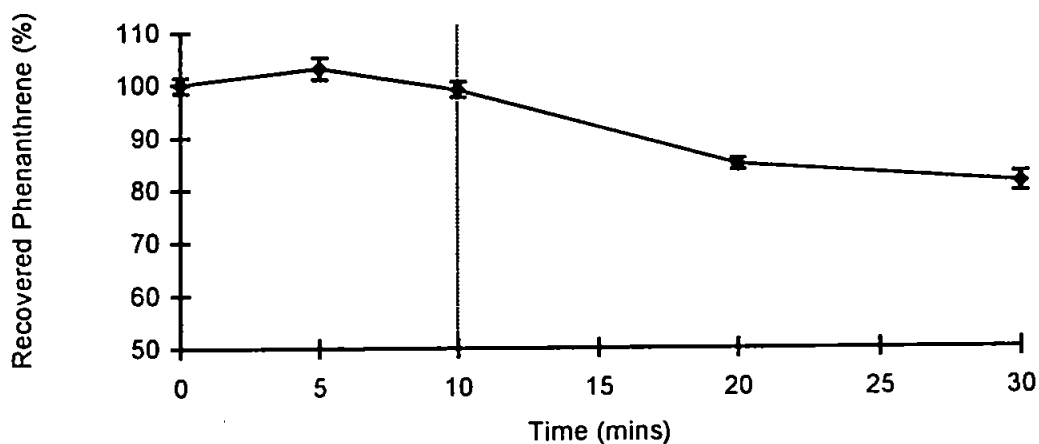


Figure 2.6: Volatilisation of phenanthrene during evaporation of hexane, where significant losses are shown to occur after 10 minutes ($n = 4$ for each data point).

In order to locate further areas of phenanthrene loss, e.g., irreversible sorption to glassware, the aforementioned procedure was performed in the absence of particles. The concentration in the aqueous phase and the glassware rinses were determined and compared to the initial concentration of phenanthrene added. Thus, an estimate of phenanthrene recovery was made, as displayed in Figure 2.7, which ranged from a mean of 88 to 97%.

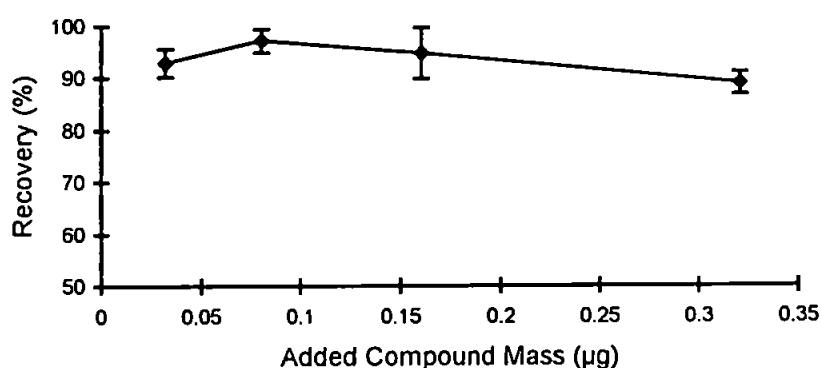


Figure 2.7: Recovery of phenanthrene as a function of added compound mass, where $n=4$ and standard deviations are shown.

Figure 2.7. also shows the effect of increased volumes of phenanthrene spikes, and therefore compound mass, on recovery. A decreased recovery is evident at a phenanthrene mass of $0.33 \mu\text{g}$ corresponding to a volume of $100 \mu\text{L}$ in hexane. Rather than irreversible wall adsorption, which at approximately 3 % or less is minimal for phenanthrene, the loss is more likely to be a result of volatilisation due to the longer time required to evaporate the carrier solvent.

In order to establish whether changes in the characteristics of the water sample adversely affected recovery, a comparison was made between three aqueous matrices. Increased ionic concentration may be expected to reduce the solubility of phenanthrene and hence increase glass wall adsorption. However, as evident in Table 2.4, this does not seem to be the case and overall, the recovery of phenanthrene is very good.

Table 2.5: Percentage recovery of phenanthrene for each experimental phase corresponding to water type

Matrix	% Recovery, $\bar{x} \pm s_{n-1}$			Recovery (%) $\bar{x} \pm SD$
	Aqueous Phase	Pipette Rinse	Wall Rinse	
Milli Q	92.7 ± 2.2	4.9 ± 0.05	1.3 ± 0.01	98.9 ± 2.2
River water	90.2 ± 3.9	2.9 ± 0.4	2.6 ± 0.1	95.7 ± 3.9
Sea Water	93.7 ± 0.2	5.8 ± 0.4	1.7 ± 0.4	101.2 ± 0.6

where \bar{x} is the sample mean, $n = 4$, s_{n-1} is the standard deviation and SD is the standard deviation

Unfortunately a further loss, not evident when estimating recovery via solubility experiments, was occurring. This came to light during a modification of the original methodology (Section 2.7.3.) involving phenanthrene extraction from the particles, where less than 50% of the mass was repeatedly obtained. A process of elimination indicated the centrifugation step to be responsible for the deficit. Previously, the tubes were centrifuged uncovered since it was assumed that hydrophobic compounds with low volatilities would be adsorbed onto the particles or the tube walls. Therefore any loss from the aqueous phase would be minimal. However, PAHs display relatively high fugacities (escaping tendencies) in both air and water, and as a result exchange between these phases can be considerable (Schwarzenbach *et al.*, 1993). Figure 2.8. displays the effect covering and exposing tubes has on the K_D for phenanthrene on Plym sediment as a function of particle concentration. The effect is greater at low sediment concentrations, since although the K_D is higher, the absolute concentration of phenanthrene in the aqueous phase is greater, as shown in Figure 2.9, and therefore the losses more significant.

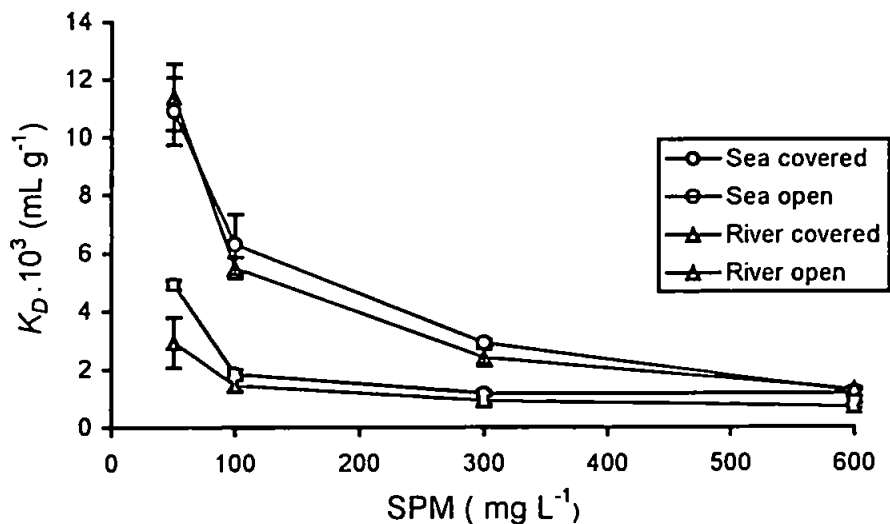


Figure 2.8: The influence of air-water transfer of phenanthrene on mass balance determinations of K_D , where $n = 4$ and standard deviations are shown.

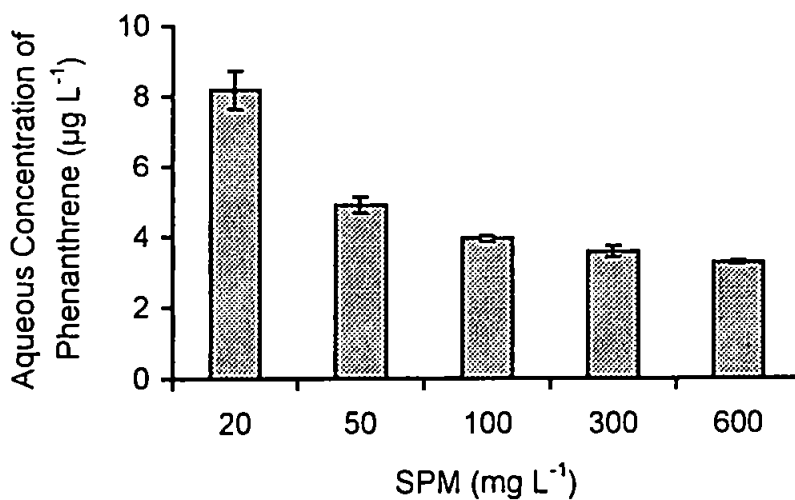


Figure 2.9. Aqueous concentration of phenanthrene as a function of particle concentration in covered tubes.

In order to appreciate how a compound with a low volatility and boiling point of 340°C can be so readily lost from the aqueous phase, its behaviour at the air-water interface needs to be understood. The air-water transfer of a compound is dictated by its diffusivity in air and in water and is described by the air-water partition constant, otherwise known as Henry's Law constant, K_H . The Henry's Law constant quantifies

the fugacity of a compound existing as vapour molecules as opposed to being dissolved in water (Stumm & Morgan, 1996). The diffusivity represents the speed of the random walk of molecules moving by Brownian motion through the surrounding medium. The larger the chemical the slower the progress since the mean velocity of their thermal motion is reduced and their increased cross sectional area reduces their mean free path (Schwarzenbach *et al.*, 1993). This is displayed in Table 2.5. which shows the diffusivity and transport times through water for a variety of chemicals via molecular diffusion.

Table 2.6: Transport times of three organic chemicals through water

	Methane	Phenanthrene	Benz(a)pyrene
	$D_w = 3.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_w = 0.89 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_w = 0.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
	Henry's Constant (L atm mol ⁻¹) = 660.690	Henry's Constant (L atm mol ⁻¹) = 0.0260	Henry's Constant (L atm mol ⁻¹) = 0.0012
Depth (cm)	Time in water		
0.1	2.7 min	9.3 min	11 min
0.5	1.1 h	4 h	4.6 h
1	4.6h	15 h	18h
10	19 days	65 days	77 days

D_w or molecular diffusivity in water, calculated from Schwarzenbach *et al.*, (1993) and estimated using $[(D_w O_2)(mwO_2/mw \text{ (chemical)})]^{0.5}$

As indicated in Table 2.5, molecular diffusion is microscopically, rather than macroscopically significant, particularly where aqueous turbulence is diminished such as at the air-water interface. Since the act of centrifugation increases the liquid surface area to volume ratio, the extent of aqueous molecular diffusivity of phenanthrene may increase and hence enhance transfer as the system attempts to reach equilibrium. Equilibrium is of course achieved much more quickly if the tube is covered, subsequently reducing loss of the solute from the aqueous phase. Over larger distances transport by advection is faster and enhanced by air and water turbulence, which may also occur during centrifugation to increase phenanthrene loss to the atmosphere.

2.7.3. Modified approach for phenanthrene (I)

As discussed in Section 2.7.2.2, attempts were made to move away from the mass balance approach in order to minimise potential artefacts and reduce the element of uncertainty. The first attempt involved extracting the particle directly for carbon-14, as outlined in Figure 2.10.

The particle extraction was achieved by discarding 18 mL of the supernatant after the usual equilibration and centrifugation steps, once the 1 mL had been taken for determining aqueous concentration. The sediment pellet was resuspended in the remaining 1 mL of water directly transferred to a clean glass centrifuge tube. The original tube was rinsed with 1 mL of river water or seawater from the same batch used for the experiment, and this was also added to the fresh tube. The particles were then mixed with ethanol (6 mL) and left to equilibrate at 20°C for 16 hours on a wrist action shaker (300 rpm). Ethanol was the chosen solvent for the first extraction since it is polar enough to be miscible with water but hydrophobic enough to offer a preferable phase for phenanthrene to partition into. This step is likely to recover phenanthrene from the 1 mL of water used to resuspend the sediment, which can be subtracted since this value is known, and also the readily available phenanthrene, which has partitioned into the particulate amorphous organic matter or directly onto the minerals. Once the first extraction was complete the particles were centrifuged (3000 rpm for 30 mins) and the ethanol supernatant (1 mL) was added to LSC and counted for carbon-14. Again, the remainder of the supernatant was discarded leaving only 1 mL in which to resuspend the pellet.

In order to reach phenanthrene taken up by the more condensed refractory organic matter a more nonpolar solvent was necessary. Therefore the ethanol was replaced with *n*-hexane (6 mL). The sediment/hexane solution was treated in a similar manner to the previous extraction and the supernatant counted for carbon-14.

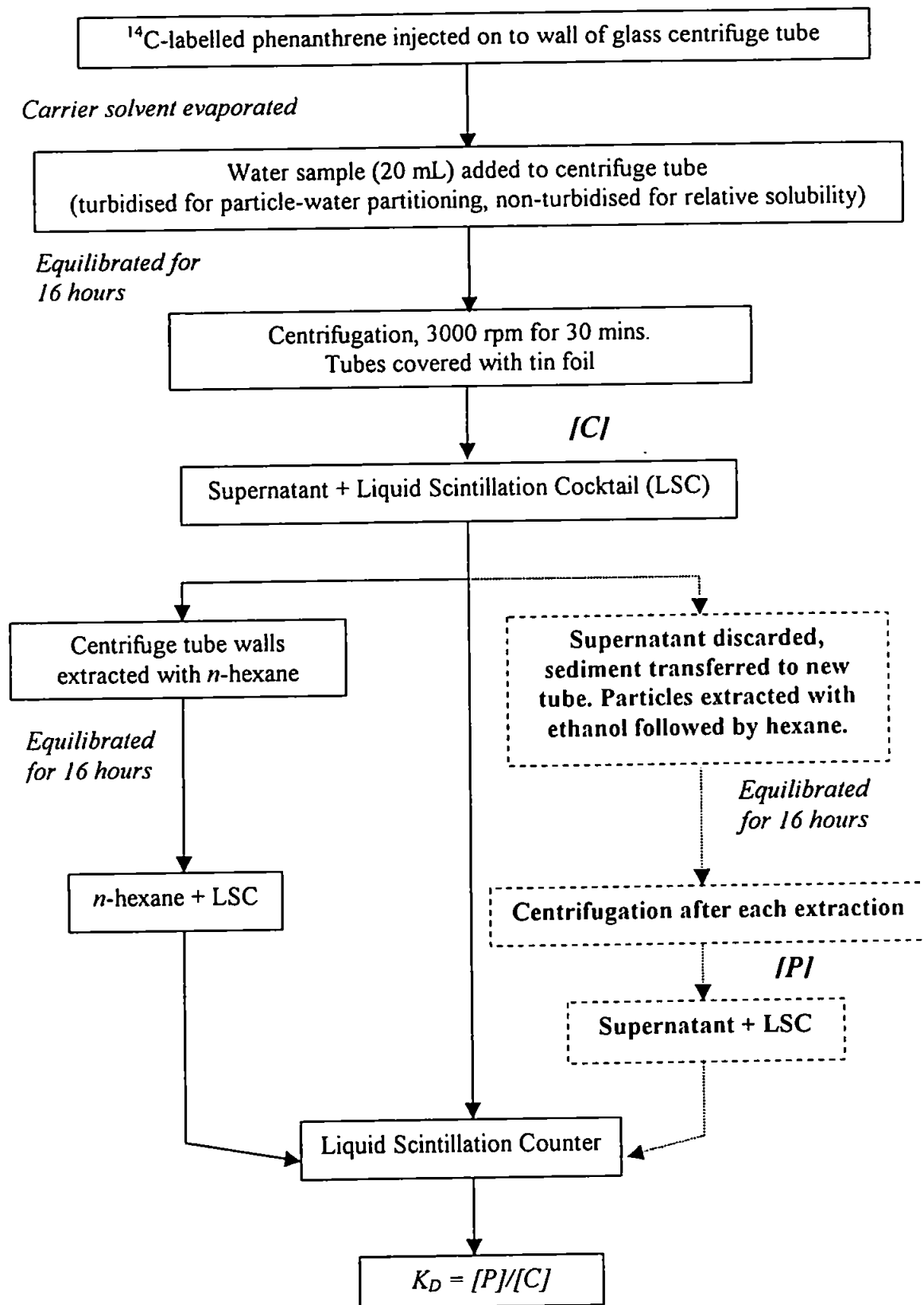


Figure 2.10: Modified approach for phenanthrene incorporating a two-step particle extraction. P and C are the concentrations of phenanthrene in the solid and the aqueous phase, respectively.

2.7.3.1. Partitioning and relative solubility calculations for phenanthrene approach (I)

The direct recovery of phenanthrene from the particles removes the need for mass balance calculations and determines directly the concentration on the particles and the particle-water partition coefficient:

$$K_D = \left(\frac{A_p}{A_c} \right) \times \left(\frac{V}{M} \right) \quad (2.5)$$

where, K_D is the partition coefficient (mL g^{-1}), A_p is the activity in the solid phase rinse, A_c is the activity in the aqueous phase, V is the volume of water (mL) in the centrifuge tube, and M is the mass of particles (g) in the centrifuge tube.

2.7.3.2. Evaluation of modified approach (I)

Using the modified approach, recoveries were acceptable at 90 to 97%. However, as illustrated in Figure 2.11, the first particle rinse of ethanol proved to be reasonably efficient at recovering phenanthrene, generally around 7% of the original spike, whereas the second rinse with hexane produced less than 1%.

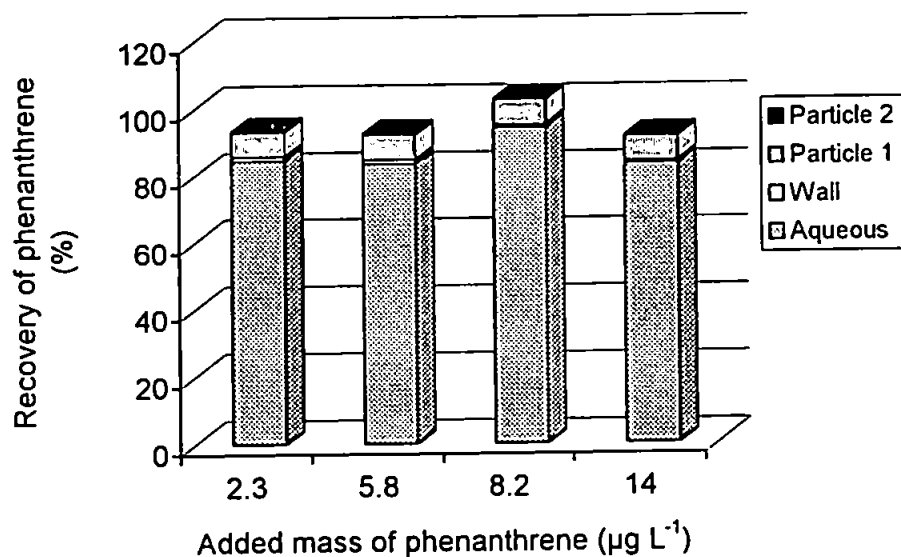


Figure 2.11: Recovery of phenanthrene from each step in modified method (I) using Plym sediment at an SPM of 50 mg L^{-1} . Particle 1 denotes the ethanol rinse and particle 2 the hexane rinse

Since phenanthrene is relatively soluble, in comparison to other PAHs, it is readily taken up by ethanol. Furthermore, as the equilibration time is only 16 hours, phenanthrene is unlikely to have had sufficient time to pass into the more condensed organic matter. Therefore the hexane rinse was deemed superfluous and subsequently neglected.

It is also important to note that with this method, water associated with the solids after centrifuging will contain dissolved solute and will therefore be extracted with the particle rinse. As a result there will be a slight overestimation of sorbed phenanthrene. This artefact was not investigated further since a second modification to the method was already under consideration.

2.7.4 Modified approach for phenanthrene (II)

Although modified approach (I) proved to acceptable by providing good recoveries of phenanthrene, it was particularly labour intensive and time consuming. Investigations therefore continued into improving the protocol further. Fortunately a type of scintillation cocktail came to light which removed any need to extract phenanthrene from the particles, since it permitted the direct counting of the particles. Unlike Ultima Gold used for the aqueous phase, this cocktail, known as InstaGel Plus, forms a homogeneous, gel-like suspension with particles in solution. Therefore, since there is no settling and subsequent photon quenching, the radioactivity on the particles can be accurately detected by scintillation counting. Self-absorption may pose a problem for long-term incubations where organic compounds become incorporated into the particle, however due to the time period employed for this work only surface sorption is likely to take place.

The experimental design employing InstaGel Plus is shown in Figure 2.12. which displays a protocol very similar to the original method, with the additional step of

counting particles directly. To do this the turbidised sample is gently shaken to ensure the particles are suspended and the mixture is homogeneous. An aliquot (1 mL) of the water sample is then added to the InstaGel Plus (2 mL) contained in a plastic vial and shaken. A gel is then formed which maintains the particles in suspension so they can then be counted for carbon-14.

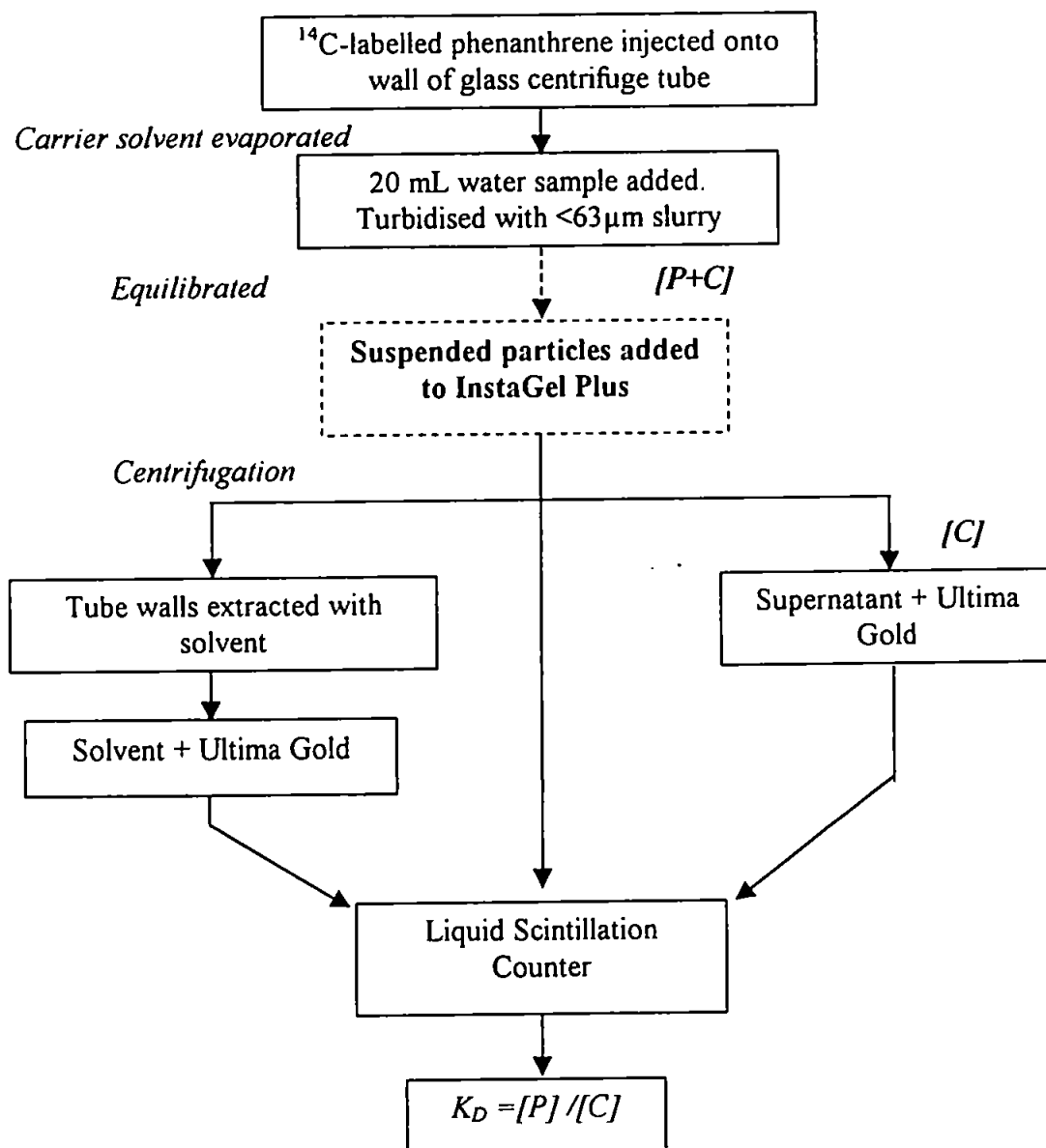


Figure 2.12: Second modification of original approach enabling the use of direct particle counting

2.7.4.1. Partitioning and relative solubility calculations for phenanthrene approach (II)

The method for calculating the particle-water partition coefficient for the above protocol is very similar to that in Section 2.7.3.2. However, because the solid and particulate phase are mixed when added to InstaGel, the concentration of phenanthrene in the aqueous phase needs to be subtracted in order to determine the concentration on the particles:

$$K_D = \left[\frac{(A_p - A_c)}{A_c} \right] \times \left[\frac{V}{M} \right] \quad (2.6)$$

where, K_D is the partition coefficient (mL g⁻¹), A_p is the activity in the particle rinse, A_c is the activity in the aqueous phase, V is the volume of water (mL) in the centrifuge tube and M is the mass of particles (g) in the centrifuge tube.

2.7.4.2. Evaluation of phenanthrene approach (II)

The recoveries using this method were 93 to 105%. Intra and inter-sample variability were a concern with regard to higher SPM concentrations which may display self-absorption, however, as indicated in Figure 2.13, this proved to be minimal.

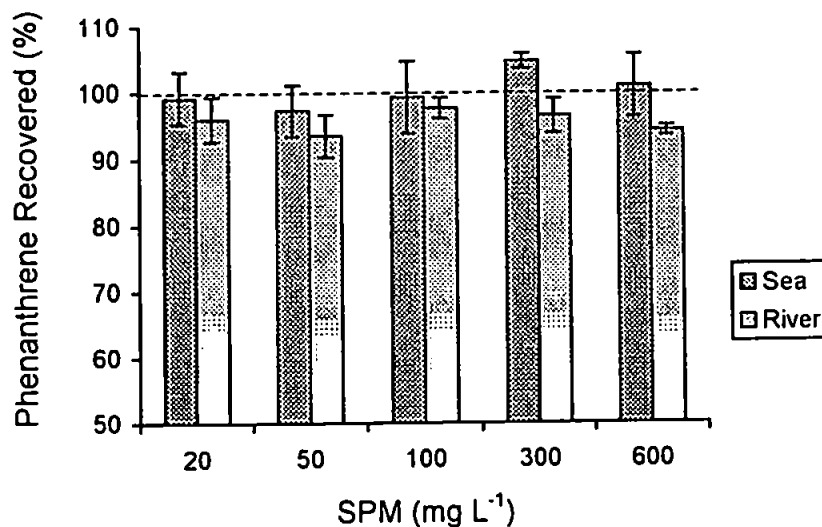


Figure 2.13: Variation in phenanthrene recovery as a function of particle concentration using Plym sediment

2.7.5. Approach for SDS and HDTMA

The protocol described for phenanthrene methodology (II) incorporating InstaGel Plus was used for investigations into the partitioning behaviour of SDS and HDTMA with three notable amendments. The first one being that since the surfactants are dissolved in Milli-Q, there was no organic solvent that needed to be evaporated. The second, and more significant change, was the inclusion of a microbial inhibitor. Surfactants are particularly susceptible to biodegradation (Section 1.5.4.), therefore samples were poisoned prior to surfactant addition with HgCl_2 (100 μL per 300 mL at 3.5%).

Ionic surfactants are known to display Krafft points at a particular temperature whereas nonionic surfactants have cloud points (Section 1.4.4.), therefore some experiments were performed within the range of 8-10°C, as well as 20°C, in order to simulate typical ranges in environmental temperatures. This was achieved by placing the mechanical shaker in the fridge. However, a different method of separation was needed, as centrifugation for 30 minutes would restore the tubes to at least room temperature, if not higher. Therefore the particles were allowed to settle in the fridge for 4 h, according to a loose interpretation of Stokes' Law, assuming particles to be spherical with a radius of 1 μm :

$$V_s = \frac{2g(p_s - p_w)}{9\mu} r^2 \quad (\text{m s}^{-1}) \quad (2.7)$$

where v_s is the settling velocity of a particle with density p_s through a fluid with density p_w , r is the radius of the sphere, g is the acceleration due to gravity and μ is the dynamic viscosity of the fluid ($\text{kg m}^{-1} \text{s}^{-1}$). Using quartz spheres ($p_s = 2650 \text{ kg m}^{-3}$), Schwarzenbach *et al.*, (1993) determined V_s to typically be $3.6 \times 10^6 \text{ m}^{-1} \text{s}^{-1}$ for water at 20°C ($\mu = 10^{-3} \text{ kg m}^{-1} \text{s}^{-1}$). Therefore, since the depth of water in the centrifuge tube is 5 cm, it would take approximately 4 hours for a particle of radius 1 μm to fall this far.

2.7.5.1. Evaluation of approach for SDS and HDTMA

It was important to assess how the addition of a microbial inhibitor influenced the sorption of surfactants to particles. As discussed in Section 1.5.2, the addition of an electrolyte can influence surfactant behaviour. Table 2.6. shows the addition of HgCl₂ enhances the true K_D slightly, however, as alternative methods such as autoclaving may alter the chemical composition of organic matter (Cosovic & Kozarac, 1993) and due to potential surfactant biodegradation without it, HgCl₂ addition was considered necessary.

Table 2.7. Influence of HgCl₂ on surfactant partitioning

$\bar{x} \pm s_{n-1}$ $n = 4$	SDS (2.5 mg L ⁻¹)		HDTMA (2.5 mg L ⁻¹)	
	With HgCl ₂	Without HgCl ₂	With HgCl ₂	Without HgCl ₂
K_D (mL g ⁻¹) at SPM of 50mg L ⁻¹	1588 ± 86	954 ± 22	(2.2 ± 0.2) × 10 ⁴	(1.4 ± 0.2) × 10 ⁴

The inclusion of reduced temperature, as an additional parameter, required an assessment of the settling technique as opposed to centrifugation for separation of the particles from the aqueous phase. A comparison was therefore made between these two procedures at 20°C using phenanthrene as the solute, since at the time SDS was the only alternative. As phenanthrene exhibits greater sorption to particles it was more likely to highlight any discrepancies. Figure 2.14 indicates that there was very little difference between the two methods of separation.

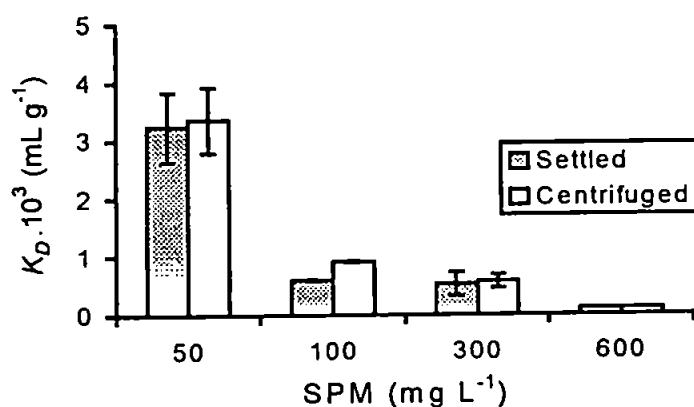


Figure 2.14: Variability between phase separation methods with increasing SPM using Plym sediment and river water where $n = 4$ and standard deviations are shown.

2.7.6. Approach for Triton X-100

As previously mentioned, a source of radiolabelled nonionic surfactant could not be found. Therefore as a compromise stable Triton X-100 was chosen since it can be easily detected via UV/Vis spectrophotometry. However, this required a return to the mass balance method and protocol described in Section 2.7.2. where instead of analysing the supernatant via a scintillation counter, the solution was placed in a quartz cuvette (suitable for wavelengths below 350nm) and analysed at a wavelength of 274.8nm (Sun *et. al.*, 1995) in a Perkin Elmer Lambda 7 UV/Vis spectrophotometer. Calibration was performed using Triton X-100 in Milli-Q at a range of 25 to 250 mg L⁻¹. Blanks were included for each water sample and sediment concentration. A second disadvantage was that due to the limits of detection, glassware rinses proved pointless since the concentrations of adsorbed Triton X-100 were too low. As a result concentrations adsorbed to particles would be slightly overestimated.

2.7.7. Approach for phenanthrene and surfactants

The combination of radiolabelled phenanthrene and non-radiolabelled surfactants in the same incubation invites two experimental approaches. For example, phenanthrene may be added to particles already equilibrated with a surfactant or the surfactant may be added to particles already equilibrated with phenanthrene. The addition of a surfactant to a solution already containing ¹⁴C-phenanthrene follows the method previously described in Section 2.7.4, (Figure 2.12) with the inclusion of HgCl₂. The reverse of this, i.e., equilibrating with surfactant first, involves the direct transfer of equilibrated water + particles + surfactant to a centrifuge tube which contains phenanthrene only, since the carrier solvent of phenanthrene needs to be evaporated off. The concentrations used for all surfactants ranged from 250 µg L⁻¹ to a maximum of 2.5 mg L⁻¹ in order to

ensure any changes in partitioning behaviour are visible whilst maintaining concentrations close to environmental levels.

2.7.7.1. Evaluation of approach for phenanthrene and surfactants

The influence of HgCl_2 on phenanthrene partitioning was investigated for experiments with surfactants. Figure 2.15 shows no effect on phenanthrene alone, whereas Figure 2.16 highlights the importance of using a biological inhibitor with the inclusion of the readily biodegradable surfactant SDS.

The nonlinearity of phenanthrene sorption displayed in Figure 2.16 may be a result of the SDS reaching various stages of degradation. Initially the hydrophilic head group is released by alkyl sulphatase producing bacteria to produce 1-dodecanol (Singer & Tjeerdema, 1993). Since this metabolite is more hydrophobic than the parent compound it will sorb onto particles and provide additional nonpolar sites for phenanthrene, hence the increased sorption.

Possible surfactant losses during the transfer phase i.e., adherence to glass walls, particularly for the positively charged surfactant HDTMA, will occur. However losses were around 10% or less for samples containing an SPM of 50 mg L^{-1} . This is unlikely to have a large influence on the particle-sorbed HDTMA.

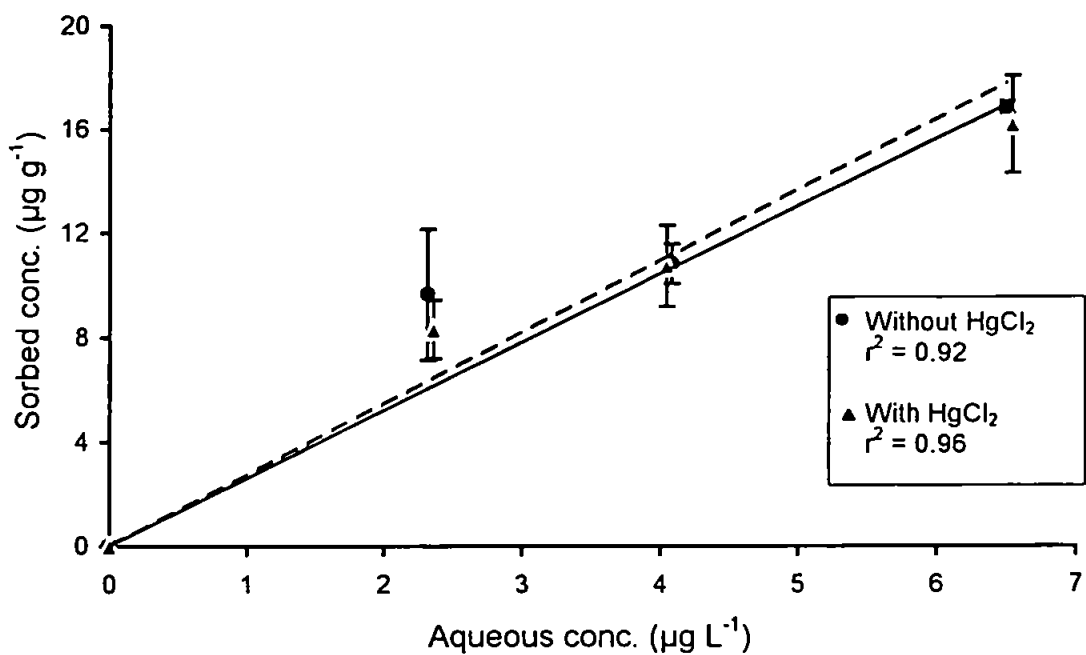


Figure 2.15: Sorption of phenanthrene to Plym sediment (50 mg L^{-1}) in river water, where $n=4$ and standard deviations are shown

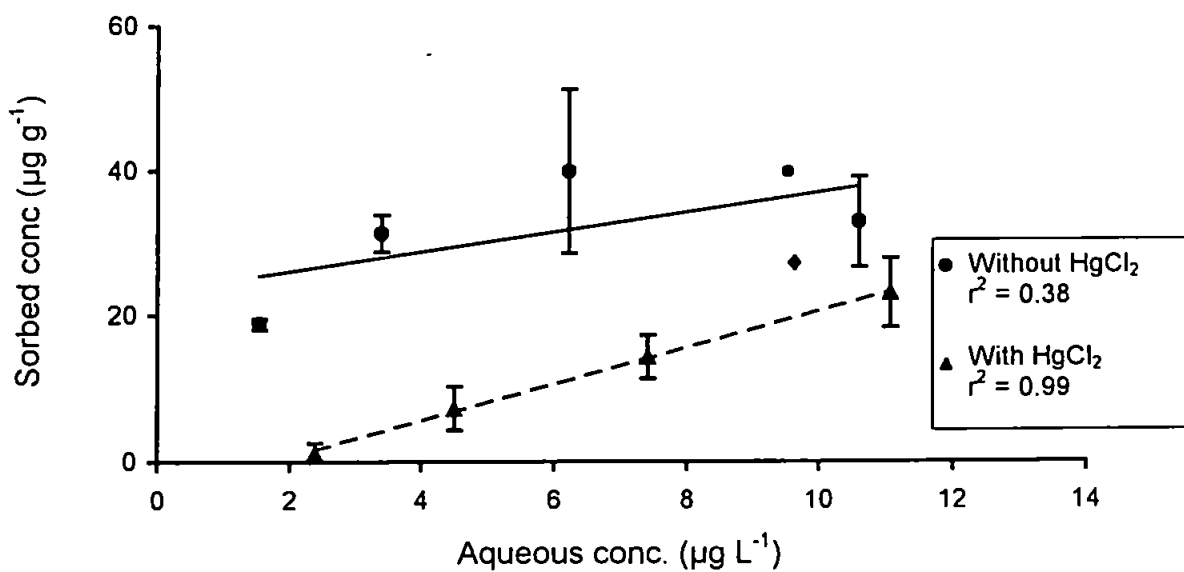


Figure 2.16: Sorption of phenanthrene to Plym sediment (50 mg L^{-1}) in a river water-SDS system (2.5 mg L^{-1}), where $n=4$ and standard deviations are shown.

CHAPTER 3: PHENANTHRENE - RESULTS AND DISCUSSION

3.1. Relative solubility

Environmental processes, such as sorption to sediment, transport and bioaccumulation are strongly influenced by the aqueous solubility of a hydrophobic organic micropollutant (HOM) (Whitehouse, 1984). As a result, there is a need to establish how this property is influenced by changes in aquatic physico-chemical conditions such as those displayed in Table 3.1.

Table 3.1: Physico-chemical properties of water samples employed

Sample	Conductivity (μS)	pH	[Ca ²⁺] (mg L ⁻¹)	DOC (mg L ⁻¹)
English Channel Sea				
$\bar{x} \pm s_{n-1}$, n= 4	$43 \pm 7 \times 10^3$	8.06 ± 0.16	na	1.81 ± 1.09
Range	36 - 52 x 10 ³	7.84 - 8.20		0.84 - 3.20
River Plym				
$\bar{x} \pm s_{n-1}$, n= 4	100 ± 35	6.86 ± 0.37	1.83 ± 0.45	1.57 ± 0.22
Range	74 - 152	6.50 - 7.30		0.72 - 1.85
Milli Q	0.056	5.00 - 7.00	nd	0.25 - 0.61

Where \bar{x} is the sample mean, s_{n-1} is the sample standard deviation, n is the number of samples, na is not analysed and nd is not detected.

To a degree, the solubility of an HOM can be estimated theoretically, for example the aqueous solubility of HOMs can often be successfully correlated with the molecular surface area or volume of the compound (within a congeneric series). The assumption employed is that the larger the interfacial area of the molecule the greater the loss of entropy due to the arrangement of surrounding water molecules. According to Zhang and Gobas (1995), however, this is a very simplified view and the process actually revolves around the increased energy requirement of the larger molecules to leave the pure (subcooled) liquid phase.

Differences in solubility due to variations in aquatic matrices may be more accurately defined empirically e.g., in this investigation, by comparing the activity of ^{14}C -phenanthrene in the aqueous phase relative to the total activity of the compound added. This is subsequently known as the relative solubility of a compound, S_r , (Equation 2.3).

3.1.1. Relative solubility isotherms

Relative solubility isotherms were produced for phenanthrene over a concentration range similar to that found in the environment (approximately 1 to 20 $\mu\text{g L}^{-1}$). The experiments were performed using three water types, with and without removal of dissolved organic carbon (DOC) by UV irradiation, and at a constant temperature of either $8 \pm 3^\circ\text{C}$ or $20 \pm 1^\circ\text{C}$ (Figure 3.1; Tables 3.2 & 3.4).

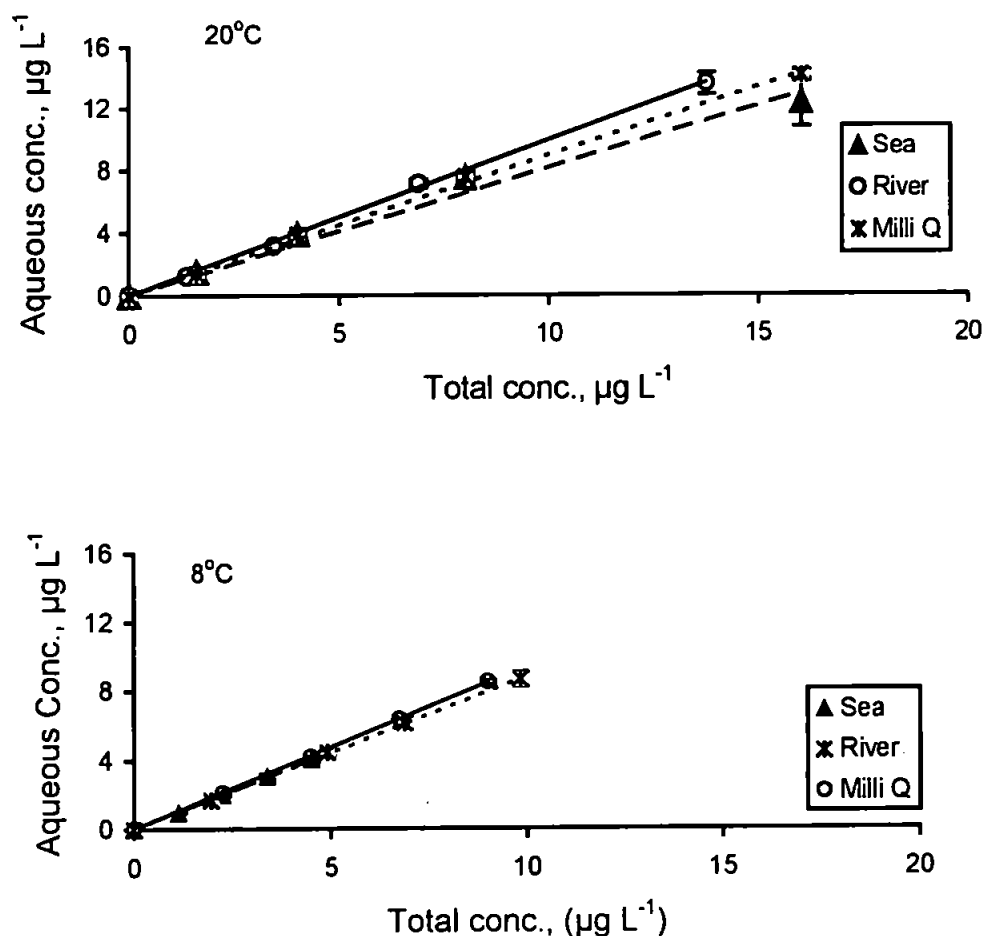


Figure 3.1: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater at 20°C and 8°C , where the mean value and standard deviations are shown ($n=4$).

Table 3.2: Relative solubility isotherm equations for phenanthrene in three aqueous matrices at 20°C derived from data fitting of Figure 3.1

Aqueous Matrix n = 4	Equation	r ²	P value
Milli-Q	y = 0.89x	0.998	<0.001
Plym river water	y = 0.99x	0.999	<0.001
Seawater	y = 0.81x	0.982	<0.001

As indicated in Table 3.2. by the r^2 and P values, all the isotherms are appropriately described by a linear equation. This is to be expected since the phenanthrene concentrations employed are well below the published saturated solubility of 1.1 mg L⁻¹ (Schwarzenbach *et al.*, 1993). In comparison to Milli-Q, river water appears to enhance the phenanthrene solubility slightly, possibly via adsorption to dissolved organic matter (DOM). Although the effect is minimal here, phenanthrene may exist in one of two phases in the aquatic system, either freely dissolved or associated with DOM. The influence of DOM on the environmental fate of hydrophobic organic molecules remains under some debate. While the ability of DOM to increase HOM solubility is in no doubt, the extent of sorption is subject to DOM characteristics and aquatic physico-chemical conditions (McCarthy *et al.*, 1989; Brunk *et al.*, 1997; Raber *et al.*, 1998). Furthermore, how this behaviour is reflected in HOM bioavailability often appears contradictory and remains poorly understood (Sigleo & Means, 1990).

The salting out of neutral organic compounds from aqueous solutions with a high ionic concentration is well known (Turner & Rawling, 2001) (Section 1.3.2.) and this phenomenon can be quantitatively described by the empirical Setschenow relationship (Equation 1.6). Published values for phenanthrene give a Setschenow constant in the region of 0.330 L mol⁻¹ (Schwarzenbach *et al.*, 1993) which in comparison to other PAHs such as benzo(a)pyrene and anthracene with respective values of 0.199 and 0.35 L mol⁻¹ (Hashimoto *et al.*, 1984; Means, 1995), suggests it is susceptible to salting out. Perhaps of more environmental significance, however, is the

relative solubility salting constant (σ_s) (Equation 1.7) which reflects potential changes in solubility due to estuarine mixing (Rawling *et al.*, 1998). Since the gradient of the solubility isotherms in river and seawater are compared, DOC effects as well as salinity are taken into consideration. The relative solubility salting constant for phenanthrene is calculated to be 0.17 L mol^{-1} which, in comparison to the published Setschenow constant, appears low for a hydrophobic compound. While this may be due to the low concentration of phenanthrene employed, both Hashimoto *et al.*, (1984) and Whitehouse (1984) reported only a slight reduction in phenanthrene solubility despite large changes in salinity (Figure 3.2.). This implies that despite thermodynamic unfavourability, even in seawater the aqueous phase is still able to accommodate the phenanthrene molecule.

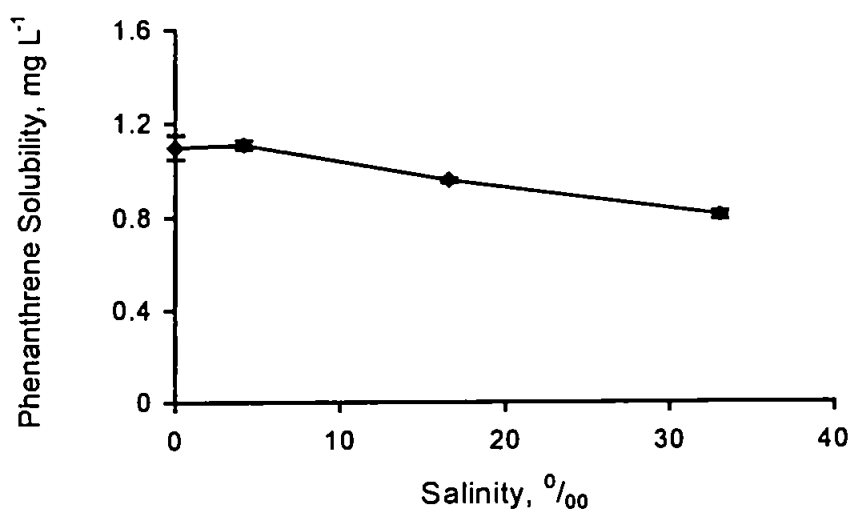


Figure 3.2: Solubility of phenanthrene according to salinity (Whitehouse, 1984)

The effect of temperature on the solubility of phenanthrene has been shown by some researchers to be important. While it is reasonable to expect phenanthrene solubility to decline with increasing temperature, since in energy terms it becomes more expensive to dissolve the solid, some investigations have shown phenanthrene solubility to be more influenced by temperature than salinity, as exhibited in Table 3.3.

Table 3.3: Solubility of phenanthrene (mg L^{-1}) according to temperature and salinity (Whitehouse, 1984)

Salinity ‰	Temperature ($^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$)		
	4.6	12.9	25.3
0	0.36 ± 0.01	0.56 ± 0.02	1.10 ± 0.05
4.14	0.34 ± 0.00	0.52 ± 0.00	1.11 ± 0.02
16.6	0.30 ± 0.01	0.48 ± 0.01	0.96 ± 0.01
33.1	0.24 ± 0.00	0.40 ± 0.00	0.81 ± 0.02

The results displayed below (Table 3.4) do not reflect this trend and display a minimal difference in solubility between 8°C and 20°C with only a slight increase in river water solubility and a small decrease in seawater solubility. However, again, this may be due to the low, but environmentally realistic, concentrations employed.

Table 3.4: Relative solubility isotherm equations for phenanthrene in three aqueous matrices derived from data fitting of Figure 3.1

Aqueous Matrix n = 4	20°C			8°C		
	Equation	r^2	P value	Equation	r^2	P value
Milli-Q	$y = 0.89x$	0.998	<0.001	$y = 0.88$	0.999	<0.001
Plym river water	$y = 0.99x$	0.999	<0.001	$y = 0.94$	0.998	<0.001
Seawater	$y = 0.81x$	0.982	<0.001	$y = 0.89$	0.999	0.006

The final potentially influential characteristic on phenanthrene behaviour to be investigated is dissolved organic carbon. This was removed in the river and seawater by UV irradiation. Once again this only appeared to have a minimal effect, although perhaps this is not so surprising since both the river and seawater employed here have very low DOC concentrations of approximately 1.81 mg L^{-1} and 1.57 mg L^{-1} , respectively (Figure 3.3; Table 3.5).

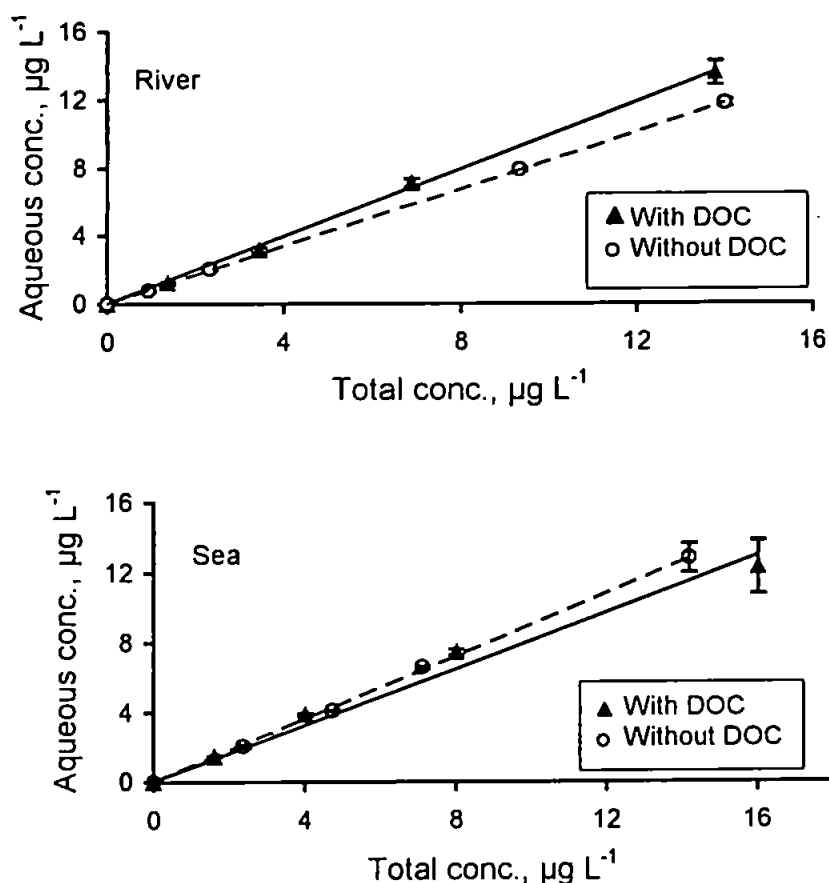


Figure 3.3: Relative solubility isotherms for phenanthrene in Plym river water and seawater with OC removed, where the mean value and standard deviations are shown (n=4).

Table 3.5: Relative solubility isotherm equations for phenanthrene in Plym river water and seawater before and after DOC removal

Aqueous Matrix n = 4	Equation	r ²	P value
River water	y = 0.99x	0.999	<0.001
River water with DOC removed	y = 0.84x	1.000	0.009
Sea water	y = 0.81x	0.982	<0.001
Sea water with DOC removed	y = 0.89x	0.997	<0.001

Phenanthrene solubility in river water displays a slight decrease in solubility with no DOC, whereas in seawater with DOC removed it actually appears to increase. For these two seawater values, however, the difference is minimal and they remain lower than the DOC free Milli Q. Furthermore, the existence of DOC in seawater may not necessarily provide an effective phase for phenanthrene sorption, since the DOC itself may be

affected by the high ionic concentration. The effect of ionic strength on hydrophobic organic compound binding to DOC is difficult to interpret, although it is thought to be a combined function of pH, divalent ion concentration and specific organic macromolecule studied (Brunk *et al.*, 1997). According to McCarthy *et al.*, (1989) binding of an HOM to DOM requires the existence of an open structure to provide access to hydrophobic domains within the DOM. It has been suggested that seawater changes the conformation of DOM, by folding or contraction of hydrophobic regions (Means, 1995). This could minimise HOM sorption and any potential solubility enhancement, resulting in no change for phenanthrene solubility in seawater either with or without DOM.

3.1.2. Summary of phenanthrene relative solubility

The low concentrations of phenanthrene employed, which were chosen in order to reflect environmental concentrations, appear to mask the hydrophobic tendencies associated with its aqueous solubility. Slight salting out was evident. However according to other researchers, this minimal reduction in solubility is not unusual for phenanthrene. Hence, it is possible that the saline intrusion within an estuary is not an effective pollutant trap for phenanthrene and it may continue to be transported seawards. The seasonal implications of reduced contaminant solubility are clearer, where adsorption would be expected to increase during the colder months, to be released again in potentially much higher concentrations as the temperature increases. In this case, however, typical environmental concentrations of phenanthrene apparently are largely unaffected by such temperature changes. Finally, the existence of DOC exerted some influence on phenanthrene solubility, but to a much greater extent in river than seawater. It appears that in seawater, DOC is less effective as an additional sorptive phase for phenanthrene.

3.2. Particle-water interactions of phenanthrene

The behaviour of organic pollutants is often distinct from that of the supporting aqueous matrix, therefore, since the determination of relative solubility alone is not sufficient to predict pollutant fate and transport, there is a need to examine sorption processes and their environmental significance (Laor & Rebhun, 1997). Sorption, defined here as the uptake of dissolved compound by particles, has a profound influence on the environmental impact of PAHs, affecting related processes such as bioavailability and degradation. It is this property which is often exploited in the treatment of water and wastes and frequently governs the extent to which a pollutant is released and moves through the environment (Voice & Weber, 1985). As mentioned in Chapter 1, a number of attractive forces may exist between a molecule and a sorbent. However, for nonpolar organic compounds such as PAHs, sorption is dominated by hydrophobic interactions, where physical sorption from the action of van der Waals forces is amplified by a substantial thermodynamic gradient forcing the molecules out of solution (Voice & Weber, 1983). Therefore, while many PAHs may have a similar affinity for a given natural sorbent surface, it is the affinity for water which determines the difference in sorption behaviour (Karickhoff, 1984). However, despite a general trend toward an inverse relationship, attempts to correlate aqueous solubility with sorption have been poor (Voice & Weber, 1983). As a result, the majority of studies on the sorption of PAHs and other HOMs have been carried out empirically using suspended particles which are considered to be the main transport medium. Yet many of these studies have employed concentrations far in excess of environmental concentrations and there is some danger in extrapolating these results to environmental levels. Hence, in order to achieve a better understanding of phenanthrene sorption mechanisms at environmental concentrations, suspended particulate matter (SPM) was included in the reaction vessels. In addition to the previous variables studied i.e., salinity, temperature and organic carbon, time (kinetics) and particle concentration were also included. A summary of the experimental strategy is displayed in Figure 2.2 and the

geochemical properties of the estuarine sediment employed are displayed in Table 3.6.

Table 3.6: Plym sediment geochemical characteristics ($\bar{x} \pm s_{n-1}$, n= 3)

Fe (mg g ⁻¹)	Mn (mg g ⁻¹)	Fe/Mn	Ca (mg g ⁻¹)	LOI (%)	Total Carbon (%)	SSA (m ² g ⁻¹)
3.48 ± 0.09	0.047 ± 0.001	74	4.67 ± 0.16	11.6 ± 0.24	2.1	3.7

LOI is loss on ignition, SSA is specific surface area, \bar{x} is the sample mean, s_{n-1} is the sample standard deviation and n is the number of samples

3.2.1. Reaction kinetics

Prior to assessing the influence of other variables on phenanthrene partitioning it was necessary to determine the rate of phenanthrene uptake and the length of time required to reach a sorption equilibrium, since this will establish the importance of phenanthrene sorption on its environmental fate (Voice & Weber, 1983). While it is understood that reaching absolute equilibrium may take months or even years for a hydrophobic organic compound, there is an initial period of rapid sorption which is reversible i.e., the sorbed compound is easily desorbed, and where comparatively high concentrations of the compound may be taken up by the particle (Luthy *et al.*, 1997). This stabilises to a point where further sorption is much slower, irreversible and involves lower concentrations. For the purposes of this work, which is concerned with short-term mechanisms, the point of interest will be once the initial rapid sorption has ceased. Therefore there was a need to confirm that the 16 hour incubation period was suitable for the determination of consistent particle-water partition coefficients after a rapid pseudo-equilibrium had been reached. In order to verify this, the particle-water partition coefficient, K_D (mL g⁻¹) (Equation 1.3.), was established for phenanthrene over a time period of 14 days at an SPM of 50 mg L⁻¹ (Figure 3.4). The initial phenanthrene sorption appeared to be reasonably rapid, stabilising at approximately 2 hours when a maximum of 14% of the original spike has been adsorbed. Following this further sorption was limited. Initially

this was thought to be due to loss of compound within the particle, subsequently undetected by the scintillation counter since the radioactive particle is not in contact with scintillation cocktail. However, detection was unlikely to be the problem, since the average recovery was over 90 percent, and calculations by mass balance methods produced similar results. Even for compounds displaying much greater hydrophobicity, stage 2 often only accounts for a relatively small amount of sorption (Rawling, 1998).

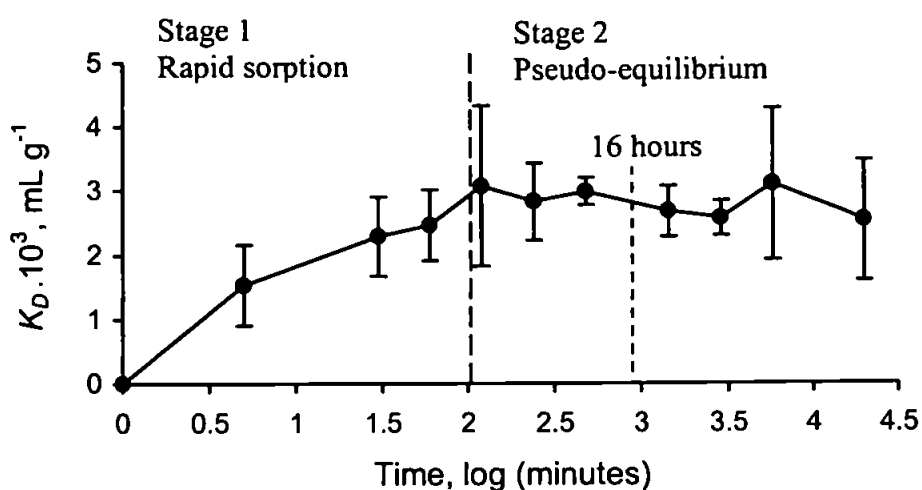


Figure 3.4: Partition coefficients for phenanthrene in Plym river water as a function of time, where the mean value and standard error are shown (n=4).

The existence of co-solutes may reduce the extent and rate of uptake of phenanthrene, as demonstrated by White and Pignatello (1999) with pyrene and phenanthrene. Since natural particles and water are employed here co-solute contamination is a possibility. In addition, there appears to be some variability in rate of phenanthrene uptake, probably due to the sorbent employed (Table 3.7.). For example Kleineidam *et al.* (1999) reported a 7 day period to reach equilibrium on minerals, whereas Kan *et al.* (1994) estimated 1 to 4 days on soil.

Table 3.7: HOM sorption characteristics according to type of sorbent (adapted from Luthy, *et al.*, 1997)

Characteristic	SORBENT			
	Amorphous OM	Condensed OM	Mineral Surface	Microporous Minerals
Kinetics	Fast	Slow; sorption-desorption hysteresis	Fast	Slow ;sorption-desorption hysteresis
Isotherm	Linear	Possibly linear after long equilibration, nonlinear if variable size matrix spaces	Linear because of competition with water	Nonlinear if pore size is variable
Competitive	No	Yes	No, coverage is small with abundance of weakly attractive sites	Yes due to limited number of high energy sites
Solvent extractability	High	Low	High	Low

3.2.2 Sorption Isotherms

Equilibrium sorption isotherms were produced following the experimental procedure described in section 2.2, using river and seawater with an SPM of 50 mg L⁻¹ at a constant temperature of either 20°C or 8°C. The isotherms can then be described graphically by plotting phenanthrene concentration in the sorbed phase versus phenanthrene concentration in solution. As previously described (Section 1.3.2.2), although several models have been developed to describe this relationship no single model has been found to be generally applicable. Therefore, since surfactants rarely display linear sorption isotherms, for comparative purposes, the Freundlich isotherm has been most widely used throughout this study and will be used to quantitatively describe phenanthrene partitioning (Table 3.8). However, sorption data displayed graphically are not fitted to a model to prevent

masking any changes in trends, such as inflections, s-shapes and intercepts.

The adsorption isotherms for phenanthrene reveal that n deviates from unity, indicating the isotherms are nonlinear (Table 3.8; Figure 3.5). Similarly Weber & Huang, (1996) also established nonlinear isotherms for phenanthrene sorption on to sediment (Table 3.9). The n values of less than 1 for both river and sea water may be due to several variables including:

- (i) the occupation of a limited number of attractive adsorption sites, therefore as the concentration increases sorption is hindered by the less favourable sites available (Schwarzenbach *et al.*, 1993);
- (ii) the existence of co-solutes which have been shown to influence PAH sorption, by sorbing competitively, although White & Pignatello (1999) reported that while pyrene suppressed phenanthrene sorption it increased the linearity of the isotherm;
- (iii) sediment heterogeneity, which will be discussed in more detail later.

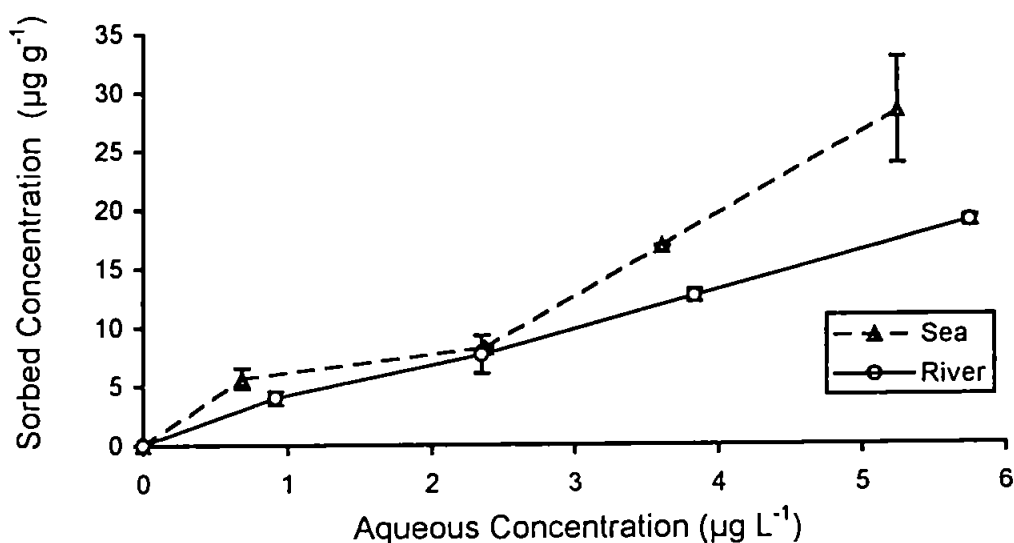


Figure 3.5: Sorption isotherms for phenanthrene in Plym river and seawater at 20°C using Plym particles with an SPM concentration of 50 mg L⁻¹, where $n = 4$ and standard deviations are shown.

Table 3.8: Freundlich isotherm variables for phenanthrene derived from data fitting of Figure 3.5 using Plym particles with an SPM concentration of 50 mg L⁻¹

	<i>n</i>	<i>K_F</i> (L g ⁻¹)	<i>r</i> ²	P value
Plym river water	0.84	4.10	0.993	0.005
Seawater	0.75	6.44	0.884	0.08
Published Values				
EPA-23 sediment ^a (2.35%) ^c	0.73 ^b	1.72	0.99	
EPA-22 sediment ^a (1.69%) ^c	0.89 ^b	0.73	1.00	

Source: ^a Weber & Huang, (1996); ^b SPM 300 mg L⁻¹; ^c organic carbon content.

As displayed in Table 3.8, sorption of phenanthrene to sediment in sea water is enhanced due to salting out. Readman *et al.*, (1982), who found little correlation between salinity and PAH distribution in estuaries, suggested the effect of salting out somewhat inconsequential at low salinities. Zhou *et al.*, (1999) also found a poor correlation, reporting that this may be due to the heterogenous nature of the SPM particles (e.g. soot fraction, different particle sizes) rather than the insignificance of salinity. However, in order to determine whether the slightly higher *K_F* for phenanthrene in seawater is due to a reduction in its solubility or an effect caused by changes in DOM/POM the following adsorption salting constants (σ_p) can be compared (Equation 1.8) (Means, 1995; Rawling *et al.*, 1998).

For phenanthrene, the adsorption salting constant, using a value of 0.5 as the effective molar concentration of seawater, is 0.39 L mol⁻¹, compared to a relative solubility salting constant of 0.17 L mol⁻¹. The increase in salting constant indicates that additional processes other than salting out in solution are taking place. Suggestions generally revolve around changes to POM, such as a reduction in the negative charge when mixed with saline waters, thereby enhancing phenanthrene sorption or changes in the conformation of the POM encouraging trapping of compounds (Means, 1995).

Table 3.8. also includes some published values which highlight the variability in estimated partition coefficients for phenanthrene. In comparison to this study, the sediment concentrations employed were much higher and this has important implications for compound partitioning (Section 3.2.3.). Furthermore, while it is well known that the

organic carbon content in sediments is of extreme importance in PAH sorption, the type of organic matter has now been shown to be increasingly significant (Kleineidam *et al.*, 1999).

Sediment organic matter heterogeneity is known to significantly impact on the sorption behaviour of contaminants, as displayed in Table 3.9. Samples containing predominantly coal-like particulate organic matter showed the higher partition coefficients, the highest nonlinearity and the slowest sorption kinetics. Therefore even if coal particles represent only a small fraction of the sediment (<3%), sorption can be much higher than anticipated (Karapanagioti *et al.*, 2000). Additionally, field data has shown no evidence of a linear correlation between K_D and f_{oc} , which challenges the previous concept of outer organic matter coatings as a simple, rubbery phase (Zhou *et al.*, 1999).

Table 3.9: Variability in phenanthrene sorption according to type of organic matter (Karapanagioti *et al.*, 2000)

Dominant organic matrix	f_{oc} (%)	n	K_F (L g ⁻¹)	r^2
AOM ^a in clay matrix	5.90 ± 0.640	0.57 ± 0.020	30 ± 2.5	0.99
POM ^b coal	1.6 ± 0.076	0.55 ± 0.024	33 ± 2.1	0.98
POM in clay matrix	0.16 ± 0.014	0.74 ± 0.036	0.23 ± 0.0 37	0.97
AOM coating	0.10 ± 0.004	0.89 ± 0.091	0.043 ± 0.015	0.89
Canadian River Alluvium sample	0.44 ± 0.027	0.65 ± 0.021	1.1 ± 0.0 85	0.99

^aAOM: amorphous organic matter; ^bPOM: particulate organic matter

While sorption of PAHs to mineral surfaces is thought to be insignificant when the f_{oc} of a soil or sediment is greater than 0.1% weight, natural sediments are intrinsically heterogeneous and therefore mineral surfaces may still influence sorption (Schwarzenbach *et al.*, 1993). Figure 3.6 and Table 3.10 display data regarding the adsorption of phenanthrene to particles which have had the organic carbon stripped and the water samples irradiated with UV light (Section 2.7.1).

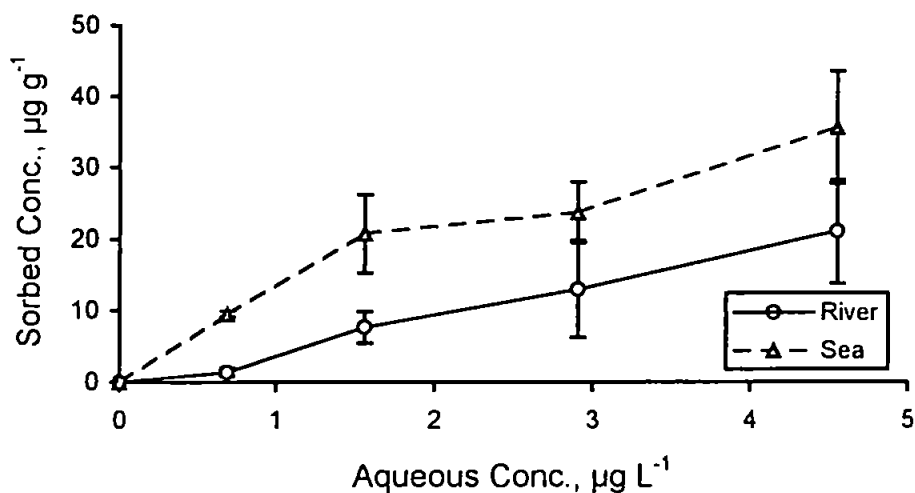


Figure 3.6: Sorption isotherms for phenanthrene with POC removed from Plym particles at an SPM concentration of 50 mg L^{-1} and DOC removed from Plym river water and seawater, $n=4$ and standard deviations are shown

Table 3.10: Freundlich isotherm variables for phenanthrene derived from data fitting of Figure 3.6 using Plym particles with an SPM concentration of 50 mg L^{-1}

Aqueous Matrix $n = 4$	n	$K_F (\text{L g}^{-1})$	r^2	P value
Plym river water	0.84	4.10	0.84	0.005
Seawater	0.75	6.44	0.98	0.080
Plym river water (POC and DOC removed)	1.42	2.85	0.99	<0.001
Seawater (POC and DOC removed)	0.66	11.08	0.89	0.007

Despite the removal of organic carbon, phenanthrene sorption still occurs, although contrary to the anticipated reduction in river water, sorption in seawater has been enhanced. The removal of DOC from seawater may encourage salting out, whereas this would have less effect in river water. Furthermore, the high ionic concentration in seawater would compress the electrical double layer (Zhou & Rowland, 1997), enabling the displacement of water dipoles from the surface by HOMs (Hunter, 1987). Salinity may also influence flocculation. However, Gibbs (1983) found that natural particles with the organic coating removed flocculated more quickly than unmodified particles on coming

into contact with seawater. This effect decreased with increasing salinity however, and therefore is unlikely to be significant in this case.

The sorption of hydrophobic organic compounds on minerals alone is often observed to be much higher than predicted. This is likely to be due to the driving force of the thermodynamic effect, rather than specific interactions with the sorbent (Schlautman & Morgan, 1994). Although sorption is favoured when the sorbent is a 'swelling' or expandable clay material, kaolinite (non-swelling), the prevalent mineral under consideration here, is also capable of adsorbing PAHs. Higher sorptivity may occur on kaolinite because the siloxane and gibbsite basal planes on its surfaces contain few ionisable hydroxyl sites and hence display more hydrophobic properties (Murphy *et al.*, 1994), although it has also been suggested that PAHs may interact with the vicinal water and not directly with the mineral surface (Mader *et al.*, 1997).

The final variable on phenanthrene sorption to be examined was temperature change, which revealed some unexpected results (Figure 3.7; Table 3.11).

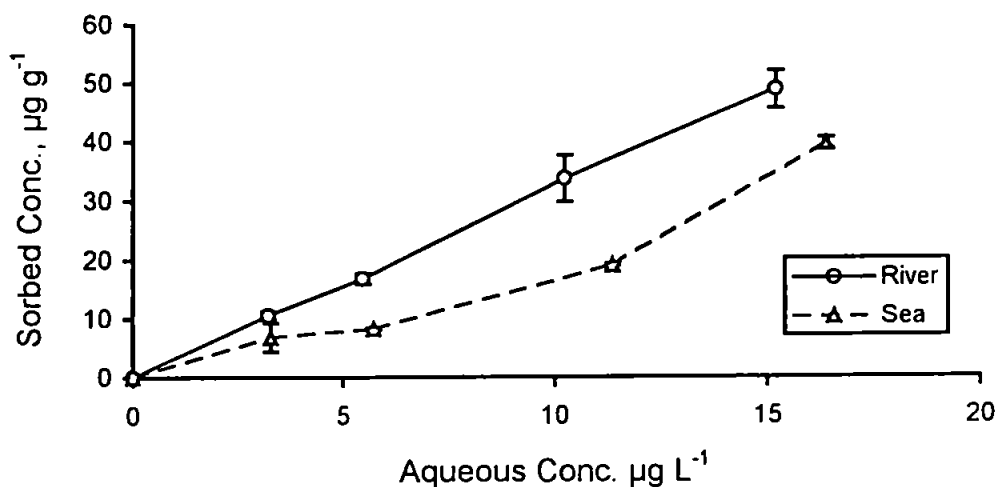


Figure 3.7: Sorption isotherms for phenanthrene at 8°C in Plym river water and seawater with Plym particles at an SPM concentration of 50 mg L⁻¹, where n = 4 and standard deviations are shown

Table 3.11: Published linear isotherm variables and Freundlich isotherm variables for phenanthrene derived from data fitting in Figure 3.7 at different temperatures and using Plym particles with an SPM concentration of 50 mg L⁻¹

Water Type	Temp. (°C)	<i>n</i>	<i>K_F</i> (L g ⁻¹)	<i>r</i> ²
Plym River	8	1.00	3.18	0.99
	20	0.84	4.10	0.99
Seawater	8	1.09	1.56	0.93
	20	0.75	6.44	0.84
Published Values				
Webster soil in deionised water ^a (2.38-3.02%) ^b	10	0.61	3.65	0.98
	25	0.65	2.08	0.99
Chelsea soil in deionised water ^a (3.30-6.41%) ^b	10	0.78	3.23	1.00
	25	0.76	2.82	1.00

^aYoung & Weber (1995), no sorbent concentration given; ^b*f_{oc}*.

Generally, for PAHs, partition coefficients increase with decreasing temperature, and, according to Schwarzenbach *et al.* (1993), the temperature effect of sorption is largely due to the temperature effect on solubility. There are some exceptions to the rule, for example naphthalene sorption has been shown to both increase and decrease at reduced temperatures (Lüers & Ten Hulscher, 1996). In contradiction to the values produced by Young & Weber (1995), the phenanthrene isotherms in this study display increasing linearity (i.e. increased values of *n*) with a reduction in temperature, and surprisingly with sorption dramatically decreased in seawater at 8°C. This discrepancy may partially be due to the chosen aqueous phase, since Young & Weber (1995) used deionised water as opposed to the natural waters employed here. It is possible that salinity in conjunction with lower temperatures is affecting the DOM, given that the solubility of phenanthrene in seawater at 8°C is greater than at 20°C. Moreover, the available sites on POM may be reduced by changes in the conformity of the organic matter induced by a decrease in temperature, subsequently reducing sorption.

3.2.3 Particle concentration effect

While the assumption of linear partitioning at low solute concentrations is widely accepted, if not strictly the case, there is a generally acknowledged phenomenon which must also be taken into account. This is known as the particle concentration effect (PCE), where the partition coefficient appears to increase as the concentration of solids is decreased, an effect that occurs with both organic and inorganic species (Voice & Weber, 1985; Santschi *et al.*, 1997). The PCE, which is displayed graphically in Figure 3.8 for phenanthrene, can be defined by a simple power law, derived from the regression of $\log K_D$ against \log SPM concentration:

$$\log K_D = \log a - b \log SPM \quad (3.1)$$

$$K_D = a SPM^b$$

where a and b are the constants equal to the intercept and the gradient of the log regression line, respectively.

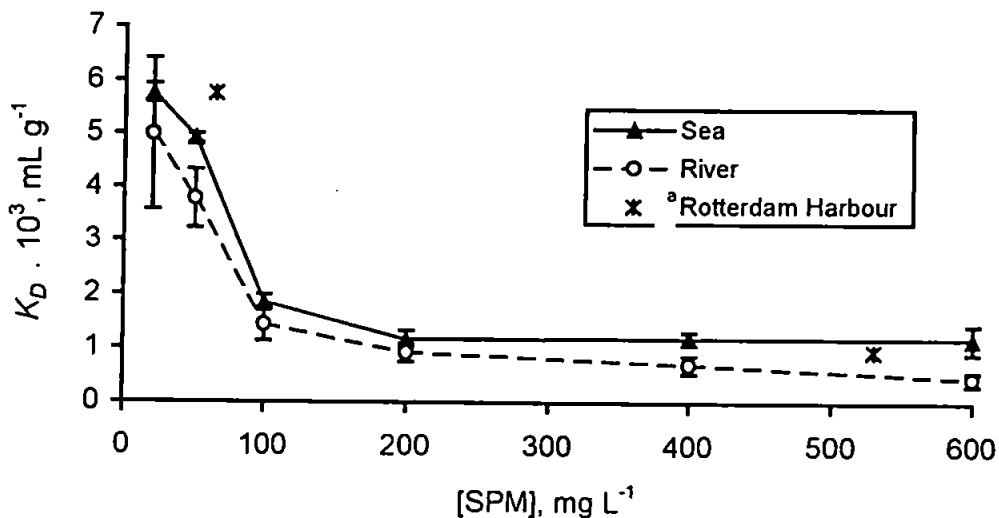


Figure 3.8: Partition coefficients, K_{DS} , for phenanthrene in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration, where $n = 4$ and standard deviations are shown (^a Hegeman *et al.*, 1995).

Values for a and b , defining phenanthrene sorption to Plym sediment are given in Table 3.12 and displayed in Figures 3.9 and 3.10. Published results are also shown in Table 3.12 for benzo[a]pyrene and 2,2',5,5'-tetrachlorobiphenyl.

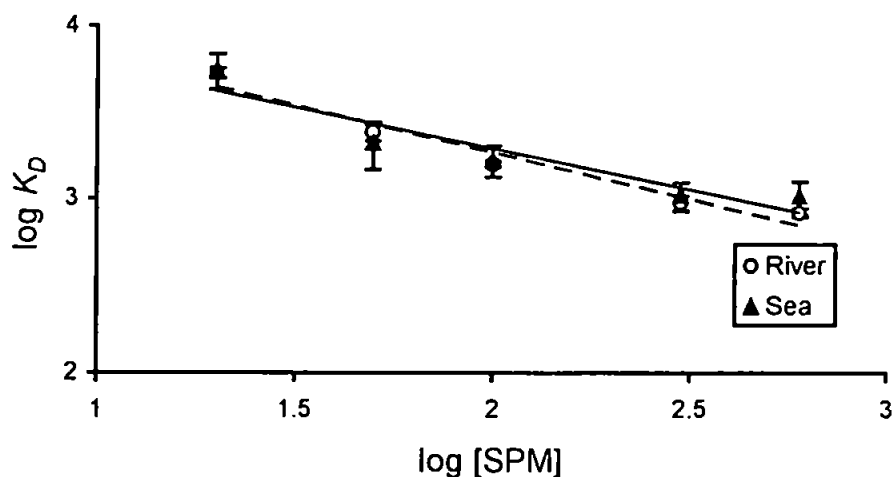


Figure 3.9: Partition coefficients as $\log K_D$ of phenanthrene as a function of \log Plym particle concentration in Plym river water and seawater at 20°C, where $n=4$ and standard deviations are shown.

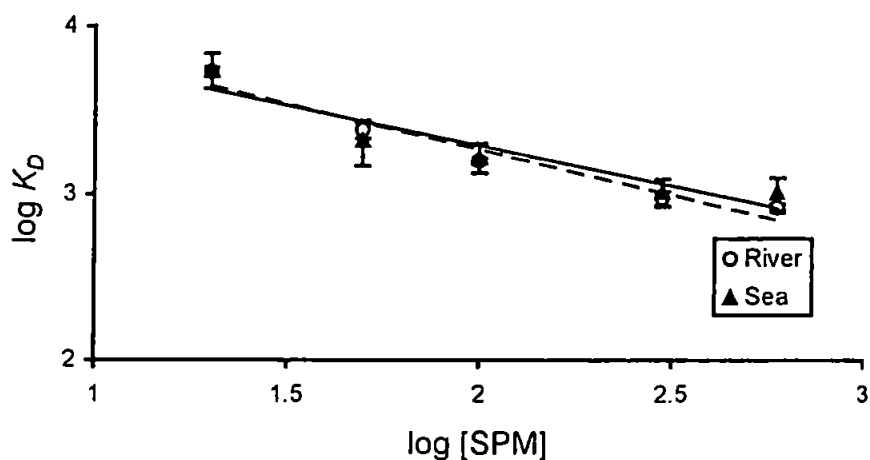


Figure 3.10: Partition coefficients as $\log K_D$ of phenanthrene as a function of \log Plym particle concentration in Plym river water and seawater at 8°C, where $n=4$ and standard deviations are shown.

Table 3.12: Model parameters defining the particle concentration effect for phenanthrene, BaP and 2,2',5,5'-TCB in the Plym estuary

Compound	Matrix		$a \cdot 10^4$	b	r^2	P value
Phenanthrene	River	8°C	2.27	0.54	0.952	0.004
		20°C	4.79	0.73	0.966	<0.001
	Sea	8°C	1.75	0.48	0.883	0.017
		20°C	2.89	0.54	0.866	0.007
^a BaP	River		20.9	0.46	0.949	0.005
	Sea		47.7	0.49	0.963	0.003
^a 2,2',5,5'-TCB	River		45.3	0.61	0.941	0.006
	Sea		39.8	0.50	0.869	0.021

^a(Rawling, 1998)

Figure 3.11 displays similar particle concentration effects for other more hydrophobic organic micropollutants, where it can be seen that compounds with larger partition coefficients have a more pronounced effect on the observed partitioning as the solid concentration increases (Zhao & Lang, 1996).

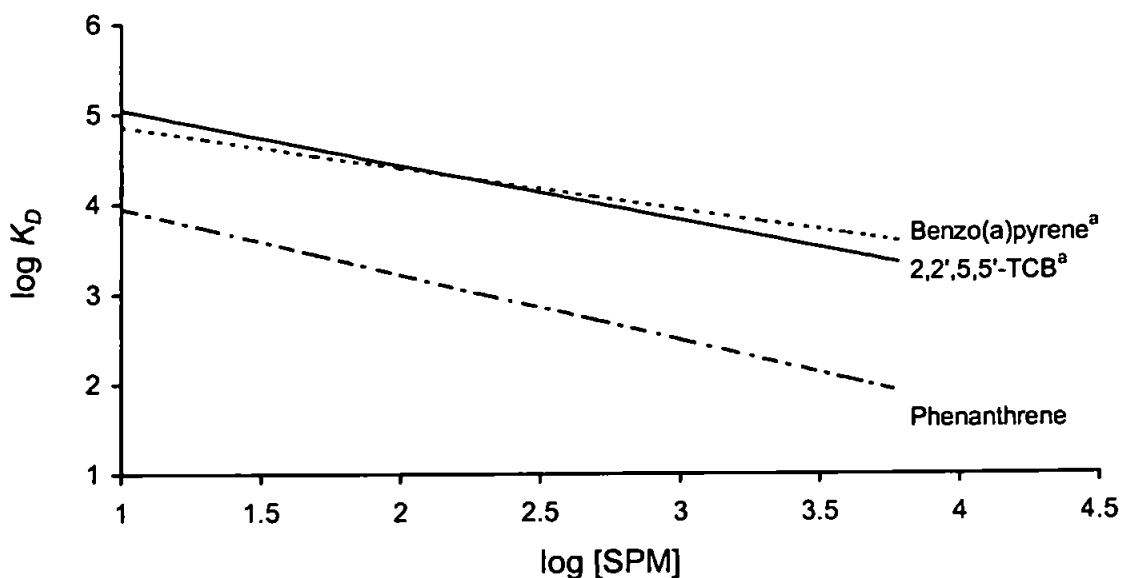


Figure 3.11: The particle concentration effect displayed by various HOMs in Plym river water (^a Rawling, 1998).

3.2.3.1 Causes of the particle concentration effect.

Although complete understanding of the causes of PCE remains elusive, the effect is frequently observed (Wijayarathne & Means 1984; Gschwend & Wu, 1985; Voice & Weber, 1985; Hegeman *et al.*, 1995; Santschi *et al.*, 1997). Suggested causes, both environmental and experimental, include the following:

- (i) The presence of non-settling particles (NSPs) in the aqueous phase, since centrifugation or filtration of particles cannot be absolute. There will always be particles smaller than the point of separation and this concentration will increase as a function of SPM (Gschwend & Wu, 1985). As a result, the higher surface area of NSPs promotes greater HOM sorption and subsequently enhances its apparent solubility (Voice & Weber, 1985; Gschwend & Wu, 1985). Wijayarathne & Means (1984) found that sorption of benzene, naphthalene and anthracene to colloids was at least an order of magnitude higher than to soil or sediment.
- (ii) As the SPM increases, particle aggregation may occur, consequently reducing sites available for adsorption. However, if this were the primary cause of the PCE, functional dependency would be expected on the particle concentration alone instead of some variation with hydrophobicity (Di Toro, 1985).
- (iii) A theory put forward by DiToro *et al.* (1986) suggested desorption of loosely sorbed HOMs by particle interaction or collisions (Mackay & Powers, 1987). This theory is supported by Perlinger & Eisenreich (1991) who employed a method which apparently refuted suggestions (i) and (ii).
- (iv) Experimental artefacts, for example, incomplete extraction of compound due to irreversible adsorption to glassware which would become less pronounced with

increasing SPM (Rawling, 1998). This is unlikely to be the cause although it may exacerbate the effect with extremely hydrophobic compounds.

- (v) Release of complexing agents from the sorbent as SPM increases, enhancing the DOM content and therefore HOM solubility (Zhao & Lang, 1996).

From a biological and dispersion point of view, the most important pollutant fraction is that left in the aqueous phase. Therefore, in order to predict contaminant behaviour, it is necessary to determine the fraction of contaminant in the solution phase (X) and the particulate phase. X can be calculated using the following equation (Turner & Tyler, 1997):

$$X = \left[\frac{1}{\left(1 + \frac{K_D SPM}{10^6}\right)} \right] \cdot 100\% \quad (3.2)$$

where K_D is in mL g⁻¹, and SPM is in mg L⁻¹.

As the K_D for PAHs is dependent on SPM concentration, this variable must be taken into account when determining X , by incorporating Equation 3.1 into Equation 3.2:

$$X = \left[\frac{1}{\left(1 + \frac{\alpha SPM^{-(b-1)}}{10^6}\right)} \right] \cdot 100\% \quad (3.3)$$

Figure 3.12 displays X for phenanthrene in river and sea water over an SPM range of 0 to 1000 mg L⁻¹ with values of α and b taken from Table 3.12. Even at an SPM of 1000 mg L⁻¹ the majority of phenanthrene is in the aqueous phase and therefore both

bioavailable and active in transport processes. Temperature does appear to play a role, however, particularly at elevated SPM in river water, where phenanthrene in the aqueous phase is reduced at 8°C, almost as much as seawater. However an extremely high SPM is still necessary in all aqueous matrices for substantial trapping of phenanthrene.

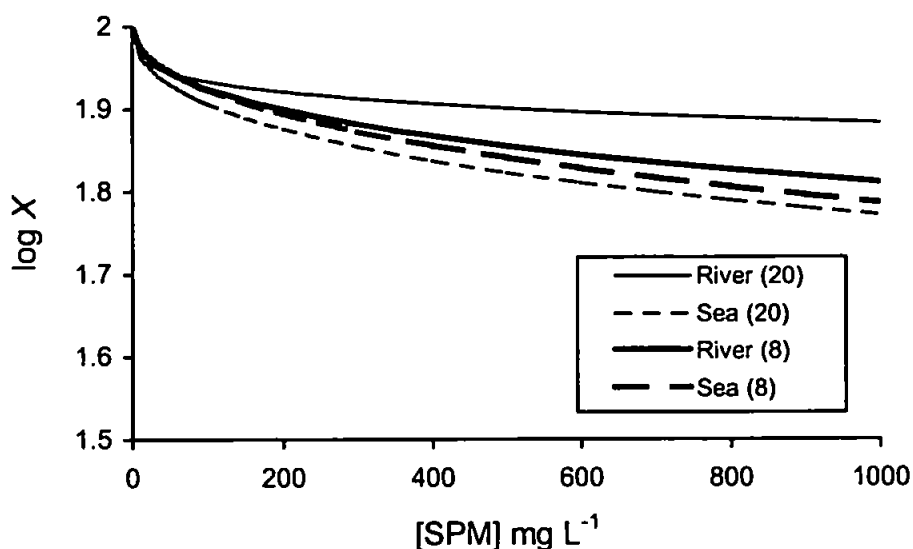


Figure 3.12: Calculated fraction of dissolved phenanthrene in river and seawater as a function of particle concentration using equation 3.3 and values of a and b in Table 3.12 with °C in parenthesis.

3.2.4. Summary of phenanthrene particle-water interactions

The variations in phenanthrene partitioning according to the aforementioned system modifications were somewhat surprising. While the sorption of phenanthrene to particles in seawater was greater than river water, comparisons with phenanthrene solubility in seawater did, however, indicate the slight elevation in partitioning may be due to physical or chemical changes in particulate organic matter, rather than merely salting out in solution. This was contradicted by the result that phenanthrene sorption to particles stripped of their organic matter was enhanced further, possibly because the aqueous phase was also devoid of organic matter, although this actually appeared to

enhance relative solubility in section 3.1.1. Temperature also had an interesting influence, in conflict with other reports, possibly due to the range of conditions employed. It seems likely that the influence of all these variables impinge on the behaviour of organic matter, which in turn affects the phenanthrene sorption. As a whole HOM sorption mechanisms are evidently extremely complex and remain poorly understood.

With regard to the PCE, despite the current lack of understanding, it is a phenomenon known to occur both in the field and the laboratory hence, this research is more concerned with the environmental implications of the PCE as opposed to the underlying causes. The results from this study reveal the significant effect the PCE has on pollutant behaviour in comparison to other variables.

CHAPTER 4: SURFACTANTS - RESULTS AND DISCUSSION

The variance in surfactant properties occurs because of their different charges, range of hydrophobic chain lengths and spatial variations in polarity (Liu *et al.*, 1992). An understanding of these properties is important in characterising the behaviour of surfactants in natural systems. Hence, as with phenanthrene, relative solubility, sorption kinetics, sorption isotherms and particle concentration effect were examined.

4.1. Relative solubility

As a rule, surfactants generally display high aqueous solubility. However, this is subject to surrounding conditions such as temperature and salinity. Therefore the influence of environmental variables on solubility were determined for three surfactants, one from each of the major groups i.e., nonionic, cationic and anionic.

4.1.1. Relative solubility isotherms for Triton X-100

As Triton X-100 is a commercial alkylphenol polyethoxylate nonionic surfactant, the number of ethoxylate (EO) groups is taken as an average value. The solubility of alkylphenol polyethoxylates (APE) varies according to the number of ethoxylate groups (hydrophilic region) as displayed in Figure 4.1. Triton X-100 has a mean of 9.5 EO groups and is therefore highly soluble in water. However, reducing the alkyl chain by one methylene group is more effective in increasing solubility than extending the hydrophilic region by one EO group, which reveals the controlling influence of the hydrophobic group on APE solubility (Ahel & Giger, 1993b).

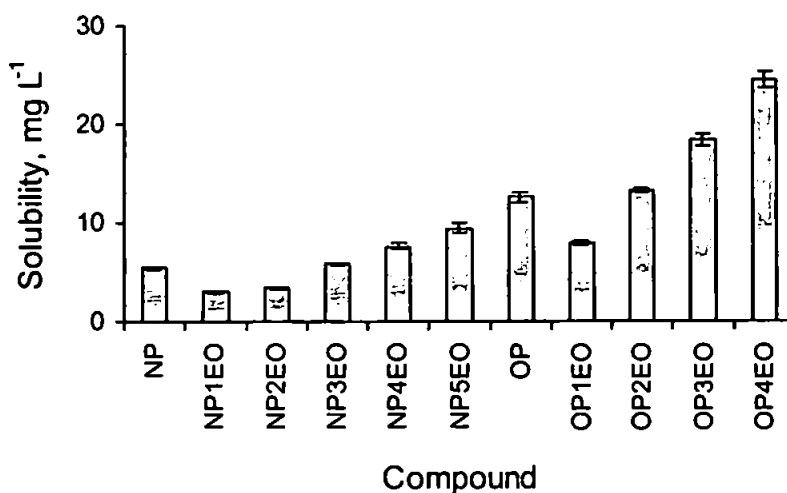


Figure 4.1: Solubilities of alkylphenol ethoxylates according to EO number of EO groups where NP and OP refers to the nonylphenol and octylphenol alkyl chain, respectively (Ahel & Giger, 1993b).

Relative solubility isotherms were produced for Triton X-100 over an enhanced concentration range (50 to 300 mg L⁻¹) since the compound was not available in a radiolabelled form. As with phenanthrene the experiments were performed using the three water types, with and without removal of dissolved organic carbon (DOC) by UV irradiation for river and seawater and at a constant temperature of either $8 \pm 2^\circ\text{C}$ or $20 \pm 1^\circ\text{C}$. Figure 4.2. displays linear relative solubility isotherms in three aqueous matrices at 20°C , with no obvious difference between them (Table 4.1). This highlights the hydrophilicity of Triton X-100, since even in a matrix of high ionic concentration there is no evidence of salting out of the tail group. As indicated in Table 4.1, however, DOC appears to exert a minor influence on Triton X-100 solubility. Since the Triton X-100 molecule has no net charge it may adsorb to DOC with either the hydrophilic or the hydrophobic group oriented toward the surface, subsequently enhancing Triton X-100 solubility. Therefore, the existence of electrolytes in river and seawater appear to have more effect in reducing Triton X-100 solubility with DOC removed.

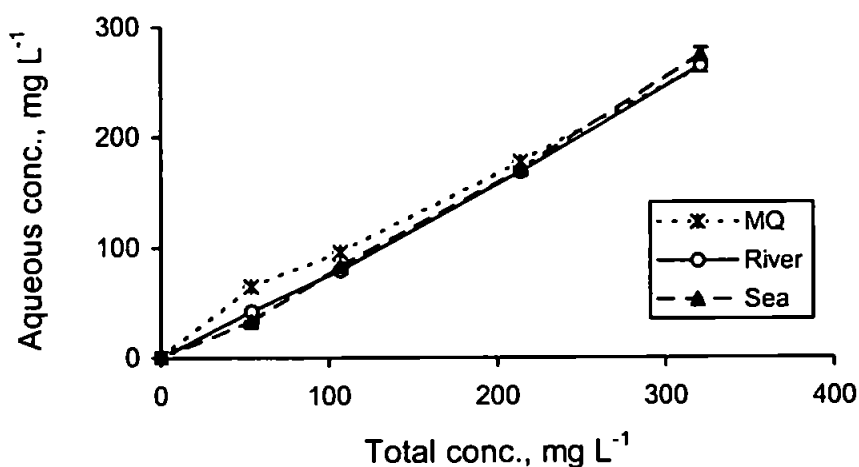


Figure 4.2: Relative solubility isotherms for Triton X-100 in Milli Q, Plym river and seawater at 20°C, where the mean value and standard deviations are shown (n=4).

Table 4.1: Relative solubility isotherm equations for Triton X-100 in Plym river water and seawater before and after DOC removal at 20°C derived from data fitting of Figure 4.2

Aqueous Matrix n = 4	Equation	r ²	P value
Milli-Q	y = 0.84x	0.999	0.001
Plym river water	y = 0.81x	0.998	<0.001
Seawater	y = 0.83x	0.994	<0.001
Plym river water with DOC removed	y = 0.76x	0.993	0.005
Seawater with DOC removed	y = 0.75x	0.998	0.002

The effect of temperature is important (Figure 4.3; Table 4.2) because the APE solubility depends on the hydration of ether functional groups through hydrogen bonds. Since hydration decreases with temperature, accordingly, the solubility of nonionic surfactants should decrease with higher temperatures (Ahel & Giger, 1993a). This is, however, contrary to the results displayed overleaf, where it may be that since we are working in a high concentration range the temperature has affected the CMC and subsequently encouraged the formation of larger micelles which would modify solubility (Section 1.4.4).

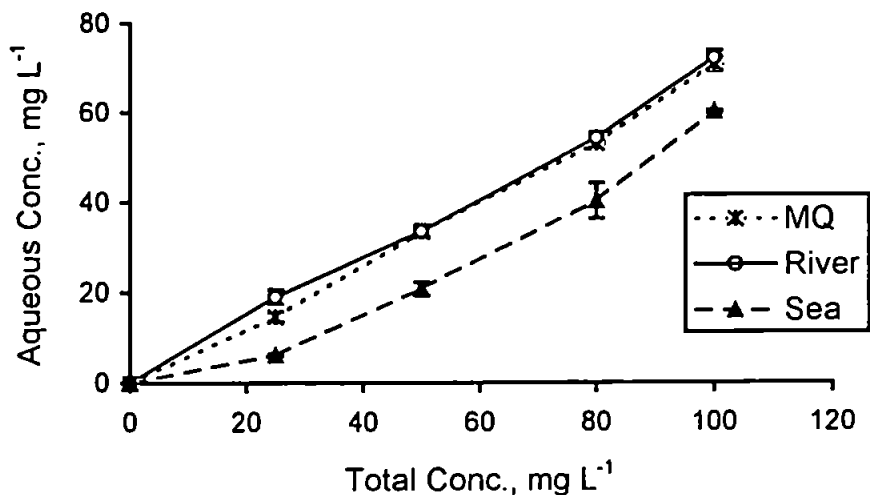


Figure 4.3: Relative solubility isotherms for Triton X-100 in Milli Q, Plym river and seawater at 8°C, where the mean value and standard deviations are shown (n=4).

Table 4.2: Relative solubility isotherm equations for Triton X-100 in three aqueous matrices at 8°C derived from data fitting of Figure 4.3.

Aqueous Matrix n = 4	Equation	r ²	P value
Milli-Q	y = 0.68x	0.995	0.001
Plym River water	y = 0.70x	0.996	0.004
Seawater	y = 0.56x	0.951	0.034

The lower temperature appears to have accentuated the effect of the high ionic concentration of seawater resulting in a reduced solubility of Triton X-100, giving a comparatively high relative solubility salting constant for a surfactant of 0.19 L mol⁻¹ (Equation 1.7). This was not calculated for the 20°C samples since no salting out took place.

4.1.2. Relative solubility isotherms for SDS

SDS displays similar, linear solubility isotherms to Triton X-100 since it is also very soluble (Figure 4.4). In comparison to Milli Q and river water, the seawater solubility of SDS appears to be slightly reduced, to give a somewhat low relative solubility salting constant of 0.09 L mol⁻¹. Although the change in solubility is small it may be due to two processes; i.e., salting out of the hydrophobic tail or a shielding effect allowing

increased SDS sorption onto the similarly charged glass wall. However, at SDS concentrations above those used in Figure 4.4 increased ionic concentration can adversely affect sorption because it causes a decrease in the CMC and subsequently reduces the concentration at which the adsorption attains a maximum (Attwood & Florence, 1983).

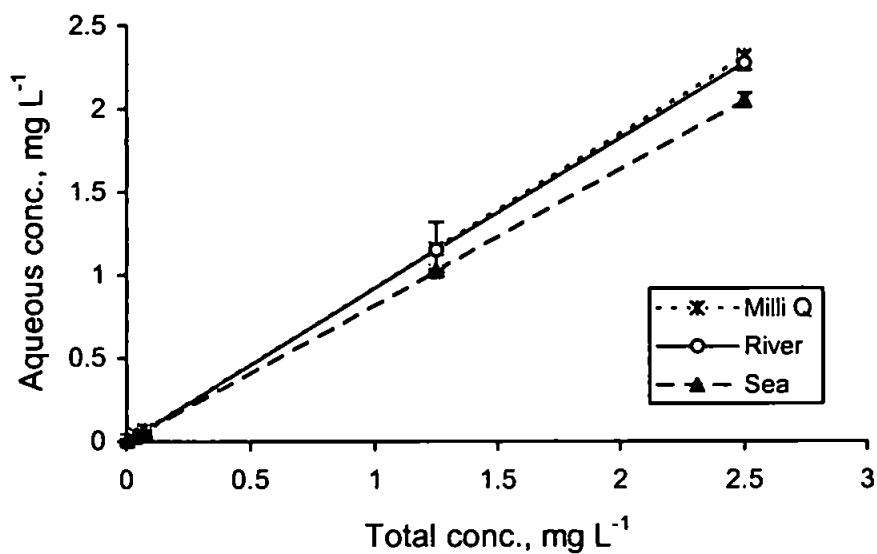


Figure 4.4: Relative solubility isotherms for SDS in Milli Q, Plym river and seawater at 20°C, where the mean value and standard deviations are shown (n=4).

Table 4.3: Relative solubility isotherm equations for SDS in three aqueous matrices at 20°C derived from data fitting of Figure 4.4.

Aqueous Matrix n = 4	Equation	r ²	P value
Milli-Q	y = 0.93x	0.999	<0.001
Plym River water	y = 0.91x	0.996	<0.001
Seawater	y = 0.82x	0.997	<0.001
River water with DOC removed	y = 0.79x	0.996	<0.001
Sea water with DOC removed	y = 0.77x	0.999	<0.001

As displayed in Table 4.3, the removal of DOC from river and seawater decreases SDS solubility. This has been revealed by other studies which suggest anionic surfactants associate with dissolved humic substances (DHS), primarily through nonpolar interactions between alkyl chains and nonpolar regions of DHS, resulting in enhanced

solubility (Traina *et al.*, 1996). As a result competitive effects may take place between salting out due to the existence of electrolytes in natural waters and enhanced solubility due to DOC.

The effect of temperature on SDS solubility is small with a relative solubility salting constant of 0.1 L mol^{-1} (Figure 4.5; Table 4.4). Although an increased temperature causes a slight decrease in SDS solubility, possibly due to the dehydration of the hydrophilic group, the effect is not visible.

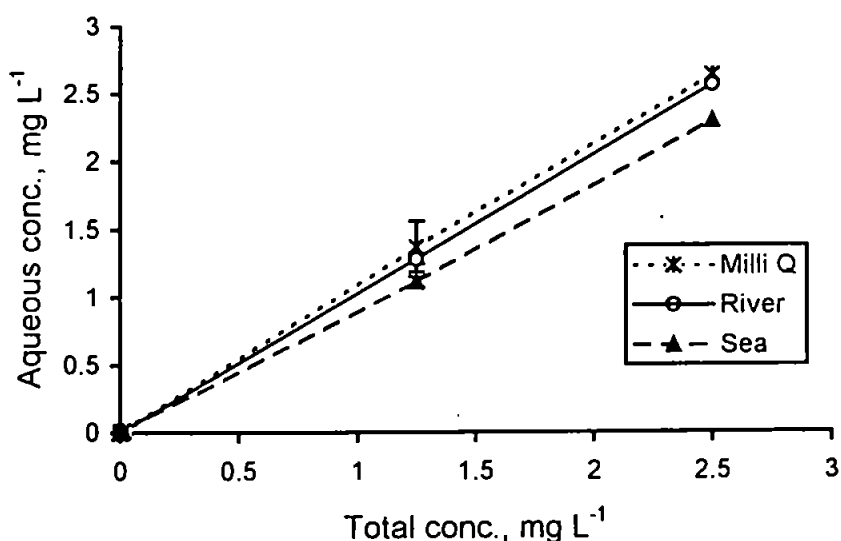


Figure 4.5: Relative solubility isotherms for SDS in Milli Q, Plym river and seawater at 8°C , where the mean value and standard deviations are shown ($n=4$).

Table 4.4: Relative solubility isotherm equations for SDS in three aqueous matrices at 8°C derived from data fitting of Figure 4.5.

Aqueous Matrix $n = 4$	Equation	r^2	P value
Milli-Q	$y = 1.06x$	0.999	<0.001
Plym river water	$y = 1.02x$	1.000	<0.001
Seawater	$y = 0.91x$	0.998	<0.001

4.1.3. Relative solubility isotherms for HDTMA

As expected, due to its lower aqueous solubility and affinity for almost any surface with a negative charge, HDTMA is much less soluble than Triton X-100 and SDS. The

solubility is lowest in seawater and a relative solubility salting constant of 0.12 L mol^{-1} is derived, since it is likely that the extensive hydrophobic region of the compound is salted out. The influence of DOC (Table 4.4) is also important, where its removal increases the salting constant to 1.1 L mol^{-1} . This may be explained by the attraction of the positively charged head group to the negatively charged DOC, subsequently minimising salting out. As the isotherms, displayed in Figure 4.6, have not been forced through a line of best fit a slight curvature is revealed, indicating that at higher concentrations of HDTMA, fewer sorption sites are available. Since the mechanism of sorption is likely to be head out, no bilayers are able to form and further HDTMA monomers are being repelled.

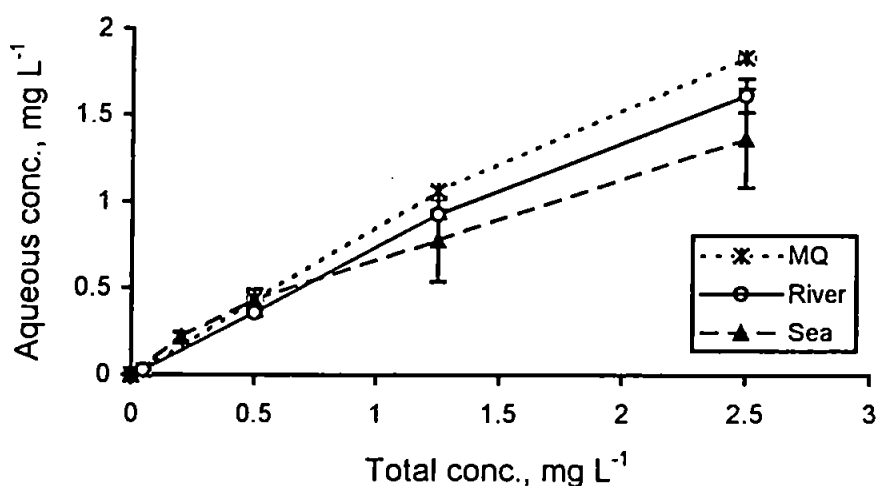


Figure 4.6: Relative solubility isotherms for HDTMA in Milli Q, Plym river and seawater at 20°C , where the mean value and standard deviations are shown ($n=4$).

Table 4.5: Relative solubility isotherm equations for HDTMA at 20°C in three aqueous matrices derived from data fitting of Figure 4.6.

Aqueous Matrix $n = 4$	Equation	r^2	P value
Milli-Q	$y = 0.76x$	0.992	<0.001
Plym river water	$y = 0.66x$	0.994	<0.001
Seawater	$y = 0.57x$	0.966	<0.001
Plym river water with DOC removed	$y = 0.47x$	0.977	0.005
Seawater with DOC removed	$y = 0.13x$	0.911	<0.001

Temperature also plays a significant role in HDTMA solubility (Figure 4.7; Table 4.5). As discussed with regard to SDS, a raised temperature will reduce the hydration of the hydrophilic region and therefore aqueous solubility. This is in contrast to results for HDTMA. However, it is possible that at reduced temperatures, particularly at high ionic concentrations, the water around the hydrophobic tail is more structured, therefore reducing entropy and solubility. It is likely that the competitiveness of these effects ultimately dictates solubility.

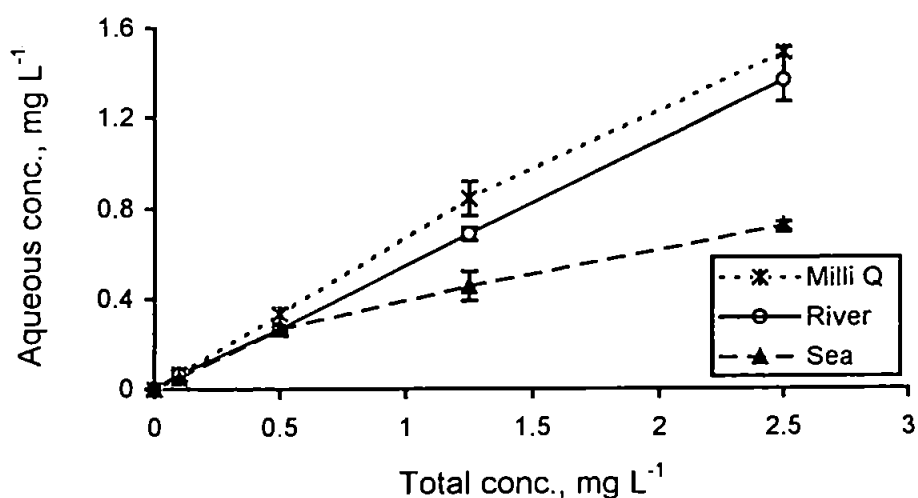


Figure 4.7: Relative solubility isotherms for HDTMA in Milli Q, Plym river and seawater at 8°C, where the mean value and standard deviations are shown (n=4).

Table 4.6. Relative solubility isotherm equations for HDTMA in three aqueous matrices at 8°C derived from data fitting of Figure 4.7.

Aqueous Matrix n = 4	Equation	r ²	P value
Milli-Q	y = 0.61x	0.994	<0.001
Plym river water	y = 0.55x	0.999	<0.001
Seawater	y = 0.31x	0.941	0.002

4.1.4. Summary of surfactant solubility

The variables investigated emphasise the complexity of surfactant behaviour and highlight the fact that surfactants need to be considered both individually and according to environmental conditions. This is to be expected for molecules with regions of opposing polarity, each with their own characteristics. In general HDTMA displays lower solubility compared to Triton X-100 and SDS. Triton X-100 appears to be more soluble than SDS at 8°C, though it should be remembered that the concentrations necessary for the nonionic surfactant will be in the vicinity of its CMC (depending on conditions) that subsequently enhance solubility.

Overall, the solubility of Triton X-100 and HDTMA is reduced by a decrease in temperature in contrast to SDS, which appears to become slightly more soluble at 8°C. The removal of DOC has a minimal influence on Triton X-100 and SDS but becomes important for HDTMA particularly in seawater. An increase in ionic concentration reduces the solubility for SDS and HDTMA, but only affects Triton X-100 at 8°C.

4.2. Particle - water interactions of surfactants

The prevalence of surfactants in modern society means that, despite wastewater treatment, surfactants still exist in surface waters. These residual surfactants may be removed from the aqueous phase and associated with sediments after discharge of treated water (Cano & Dorn, 1996). Hence, surfactant sorption onto natural particles is an important process that must be examined in experimental and modelling studies (Liu et al., 1992). As discussed in Section 1.5.2., surfactant sorption is an extremely complex phenomenon. However, in basic terms it is largely dependent on the structural groups on the solid surface, the molecular structure of the surfactant, and the conditions of the aqueous phase (Rosen, 1989).

4.2.1. Reaction kinetics

In the same way as phenanthrene, there was a need to determine the rate of surfactant uptake and time taken to reach equilibrium. This proved to be extremely rapid for all three surfactants (Figure 4.8), certainly within 30 minutes, therefore the 16h incubation period is more than adequate for the surfactants to attain equilibrium. In general there appears to be very little current information on the kinetics of surfactant sorption to sediments other than Liu *et al.*, (1992) who reported a study of two commercial nonionic surfactants reaching approximate sorption equilibrium in 1h.

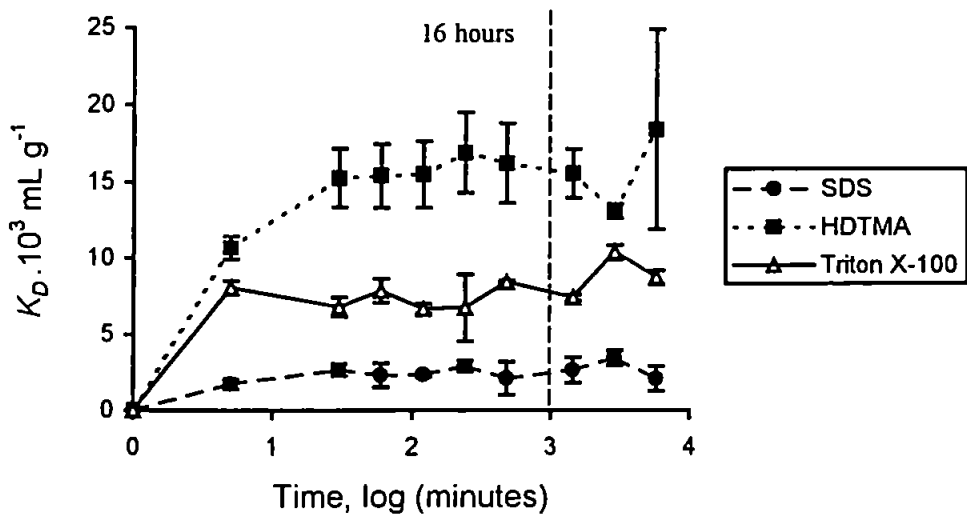


Figure 4.8: Partition coefficients for three surfactants as a function of time where the mean and standard deviations are shown

4.2.2 Sorption Isotherms

Sorption isotherms were produced, using Plym river and seawater with an SPM of 50 mg L^{-1} at a constant temperature. Since surfactant sorption is frequently nonlinear the sorption data are fitted according to the Freundlich equation (1.3) to give sorption coefficients but are displayed graphically without best-fit lines to show specific trends.

4.2.2.1. Sorption isotherms for Triton X-100

Nonionic surfactant sorption is considered less complex than ionic since no charges are involved. Sorption onto particles may occur via the polarisation of pi electrons, by dispersion forces acting between the surfactant and adsorbent or through hydrogen bonding between polyoxyalkylene groups and suitable hydroxyl or amino groups on the adsorbent (von Rybinski & Schwuger, 1987). However, the surfactant under investigation, an alkylphenol polyethoxylate (APE), is likely to sorb to the sediment primarily by a hydrophobic mechanism. This is confirmed by Kiewiet *et al.* (1996) who demonstrated the contribution of an ethoxylate fragment to partitioning to sediments as relatively small, whereas sorption partition coefficients varied by more than two log units according to changes in the length of the alkyl chain.

As anticipated, the sorption isotherms produced below for Triton X-100 in river and seawater at 20°C are nonlinear (Figure 4.9, Table 4.7). The river water isotherm at 20°C has an initially upward curvature ($n > 1$), indicating possible co-operative sorption via sorbate-sorbate interactions, visible due to the elevated concentrations necessary to detect Triton X-100 (Brownawell *et al.*, 1997). Sorption in sea water, however, is much higher than river water, despite there being very little difference between the relative solubility isotherms. It is possible that this highlights the importance of sediment organic matter, which may be salted out in seawater, leading to greater sorption to particles. This theory is supported by the similarity between partition coefficients in the samples with DOC and POC removed. In addition, although the CMC of surfactants is reduced at high ionic concentrations causing large micelles to form and subsequently maintain solubility (Section 1.4.4.), the inclusion of particles provides an alternative location for the surfactant molecules. It may well be energetically more favourable for the monomers to hydrophobically sorb to the particles than to increase the size of micelles. This is indicated by appearance of the seawater sorption isotherm which

rapidly appears to reach a maximum, indicating that head out sorption has taken place, which removes the tail from the aqueous phase but prevents bilayer formation (Figure 4.10). As a result a peak is reached where there are reduced sorption sites available and micelles may form.

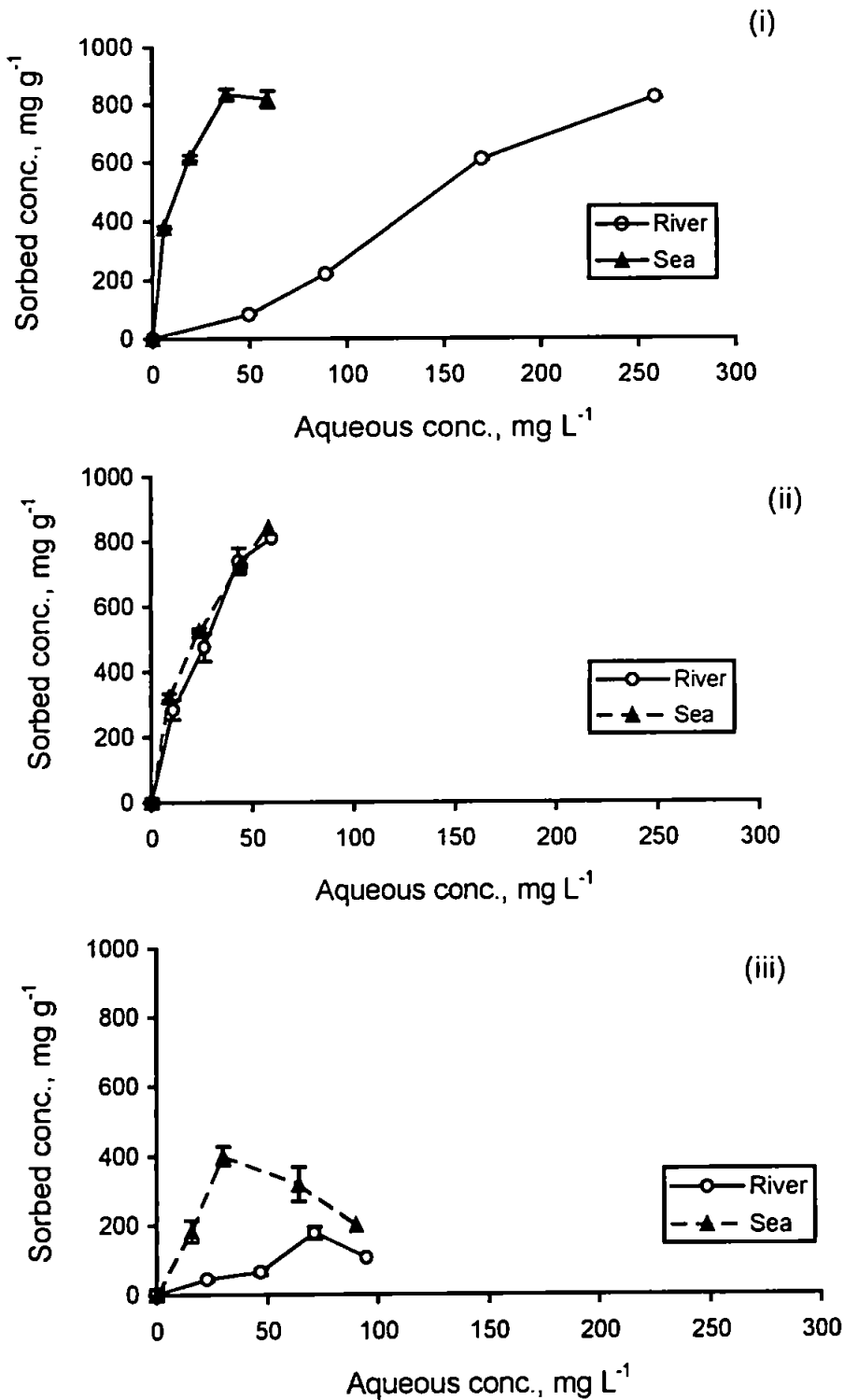


Figure 4.9: Sorption isotherms for Triton X-100 with an SPM of Plym particles of 50 mg L⁻¹ at (i) 20°C, (ii) 8°C and (iii) with DOC and POC removed, n=4 and standard deviations are shown

Table 4.7: Freundlich isotherm variables for Triton X-100 derived from data fitting of Figure 4.9 using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous Matrix n = 4	n	K_F (L g ⁻¹)	r ²	P value
Plym river water 20°C	1.42	2.89	0.983	0.008
Seawater 20°C	0.36	206	0.956	0.021
Plym river water 8°C	0.82	3.35	0.696	0.166
Seawater 8°C*	-	-	-	-
Plym river water (DOC and POC removed)	0.64	61.5	0.985	0.007
Seawater (DOC and POC removed)	0.51	107	0.999	<0.001

*Isotherm data not appropriate for regression

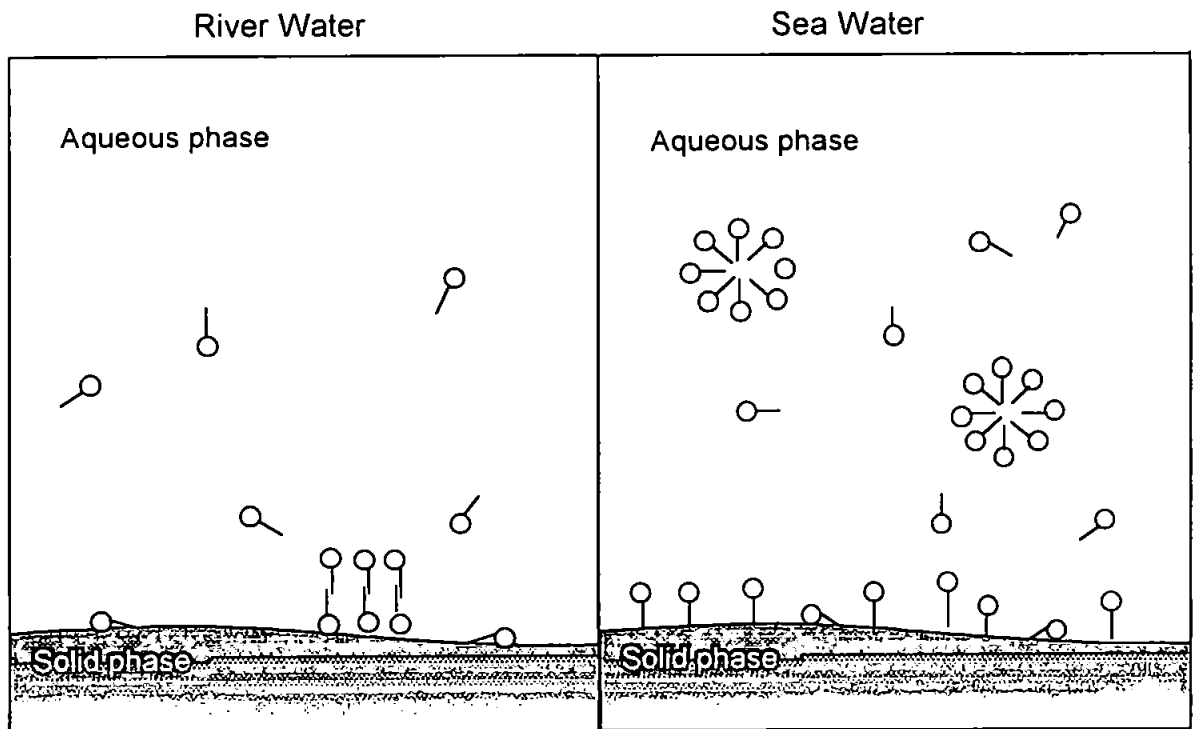


Figure 4.10: Changes in surfactant molecule orientation according to ionic concentration

In order to compare the results for Triton X-100 at 20°C in river and seawater with published values, Table 4.8 was compiled. This information highlights the importance of variables such as particle type and concentration.

Table 4.8: Published Freundlich values for nonionic surfactant sorption to natural sorbents

High Concentration Range ^a			
Homolog(mw) ^c	Sediment ^d	K_F (L kg ⁻¹) ^a	n
A13E3 (322)	EPA-12	73	0.92
A13E6 (464)	EPA-12	11	0.77
A13E9 (596)	EPA-12	1.9	0.61
Wide Concentration Range ^a			
Homolog	Sediment ^d	Log K_F ^a	n
A13E6	EPA-13	1.77	0.74
A13E6	EPA-25	1.60	0.75
A13E6	EPA-16	1.78	0.78
Commercial Surfactant (mw) ^c	Soil ^{f,g}	Log K_F ^b	n
Igepal CA-720 A8E12 (735)	Grassland soil	0.058	1.79
Tergitol NP 10 A9E10.5 (682)	Grassland soil	0.41	1.67
Brij 30 A12E4 (363)	Grassland soil	7.79	0.47
Triton X-100 A8E9.5 (628)	Grassland soil	0.86	1.34

Source: ^a Brownawell *et al.*, 1997; ^b Liu *et al.*, 1992; ^c surfactant concentration 12-240 mgL⁻¹; ^d SPM 2.5-50g L⁻¹; ^e surfactant at sub cmc concentrations; ^f SPM 11-222g L⁻¹; ^g $f_{oc} = 0.0096$

It is apparent in Table 4.8 that an increase in oxyethylene groups enhances nonlinearity and sorption, possibly by interacting with the surface by hydrogen bonding (Brownawell *et al.*, 1997). Conversely, with regard to sediment, a range of sorbents has a lesser effect, suggesting that specific interaction with the sorbent may be less significant than other forces such as hydrophobic bonding. Unfortunately a comparison of results produced in this study with those of Brownawell *et al.*, (1997) is of limited use since the SPM concentration employed here is much lower, and particle concentration has an important effect on sorption (Section 4.2.3.). It is, however, interesting to note that $n < 1$ which reflects the higher sediment concentration employed by Brownawell *et al.*, and subsequently greater available surface area. This reduces the opportunity for cooperative interactions and hence reduces sorption intensity. In contrast, the results of this study at 20°C display $n > 1$, possibly due to the reduced surface area and high surfactant concentration enforcing sorbate sorbate interactions.

Similarly, three of the published values for grassland soil have distinctly upward curving isotherms ($n > 1$). This may also be due to sorbate sorbate interactions since the soil has a very low organic carbon content potentially encouraging head on sorption by the oxyethylene groups, leaving the hydrophobic tails extended towards the aqueous phase, providing conditions for bilayer bonding (Figure 4.10).

The results in Table 4.6 display large Freundlich coefficients of Triton X-100 to samples with no organic carbon. Since $n < 1$ this indicates bilayers are unlikely to be forming. However, the non-ionic surfactant molecule may be intercalated within the mineral, which is known to occur with swelling clays (Brownawell *et al.*, 1997). Furthermore, Cano & Dorn, (1996) found nonionic surfactant sorption did not correlate well with percent organic carbon (Table 4.9) as did Podoll *et al.*, (1987) who found that the sorption of polyethylene glycols to natural sediments was related to the fraction of montmorillonite and vermiculite and not directly to fraction of organic carbon. In contrast, however, another study employing nonionic surfactants and natural sorbents displayed nonlinear sorption isotherms with the extent of sorption generally increasing with increasing organic carbon content of the sorbent, suggesting hydrophobic bonding to be most influential with regard to non-ionic surfactant sorption (Urano *et al.*, 1984). This finding was supported by Aston *et al.*, (1989), who shows that nonionic surfactants are sorbed to a greater extent onto silica dioxide particles that are chemically modified to provide a hydrophobic surface than onto unmodified silica dioxide of similar dimensions.

Table 4.9: Nonionic surfactant sorption according to OC content (Cano & Dorn, 1996)

Surfactant ^a	OC of sediment (%) ^b	K_F (L kg ⁻¹)	n	r
AE-3	2.8	500	0.83	0.99
	1.6	490	0.89	0.99
	0.3	110	0.97	0.98
AE-9	2.8	450	0.66	0.99
	1.6	590	0.56	0.98
	0.3	110	0.53	0.99

^a surfactant concentration 0.01-20 mg L⁻¹; ^bSPM 4 g L⁻¹

According to Table 4.7, a reduction in temperature from 20°C to 8°C appears to have a profound effect of nonionic surfactant behaviour, particularly in seawater. Although the data cannot be regressed, the graph shows sorption to be comparatively low (Figure 4.9), which is not unexpected since nonionic surfactants frequently display increased solubility on cooling (Section 1.4.4.), despite evidence to the contrary for the relative solubility isotherms (Section 4.1.1.). It may be that the inclusion of particles enhances or catalyses the influence of temperature, since at 20°C they provide attractive sorption sites for Triton X-100 due to its reduced solubility, whereas they are less effective at 8°C when Triton X-100 is more soluble.

4.2.2.2. Sorption isotherms for SDS

The adsorption of the anionic surfactant SDS on to negatively charged natural particles was not expected to be particularly pronounced since both are similarly charged and SDS is highly soluble in water. This is confirmed by Figure 4.11 and Table 4.10 where isotherms are produced at 20°C in river and sea water.

Table 4.10: Freundlich isotherm variables for SDS derived from data fitting of Figure 4.11 using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous Matrix n = 4	n	K _F (L g ⁻¹)	r ²	P value
Plym river water 20°C	1.09	2.48	0.998	<0.001
Seawater 20°C	1.09	2.44	0.995	<0.001
Plym river water 8°C	1.01	2.40	0.987	0.009
Seawater 8°C	1.25	8.77	0.999	<0.001
Plym river water (DOC and POC removed)	-0.94	1.34	0.366	0.395
Seawater (DOC and POC removed)	0.206	24.32	0.127	0.644

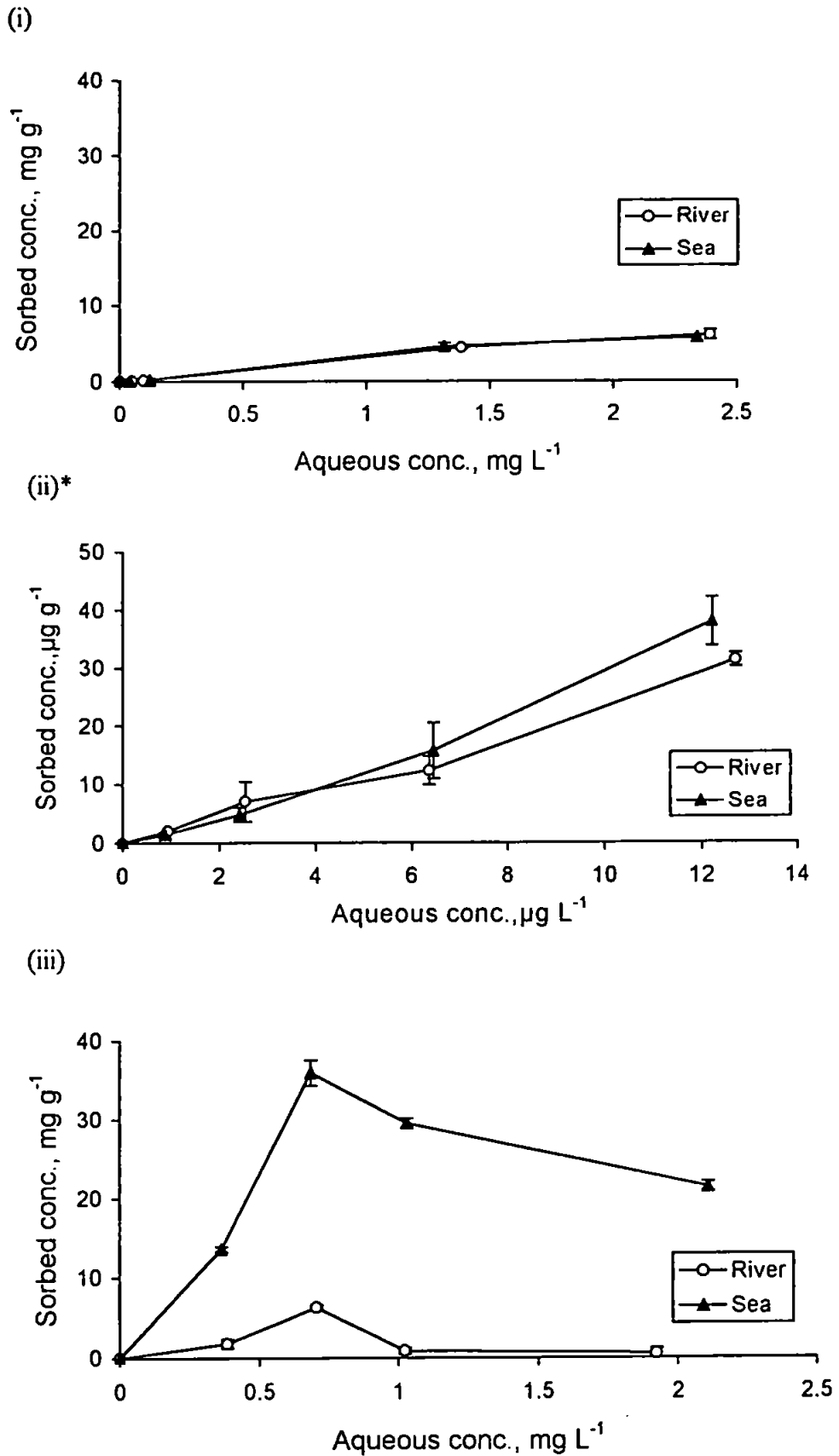


Figure 4.11: Sorption isotherms for SDS with an SPM of Plym particles of 50 mg L⁻¹ at (i) 20°C, (ii) 8°C and (iii) with DOC and POC removed, n=4 and standard deviations are shown.

* Increased concentrations of SDS omitted in error therefore smaller scale on axis. Comparisons in section 4.2.3. indicate similar trends at higher concentrations.

The sorption of SDS is generally lower than for Triton X-100, which is to be expected due to the natural repulsion between SDS and negatively charged sediment particles. Sorption of SDS at 20°C displays a linear trend in river and seawater with similar Freundlich coefficients, indicating either non-specific interactions between the alkyl chains and hydrophobic sites or an abundance of equally suitable sorption sites. Low partition values have also been reported in the literature for another type of anionic surfactant known as linear alkyl benzene sulphonate (Table 4.11).

Table 4.11: Published values for LAS sorption to sediment

Sediment (f_{oc})	Surfactant	K_D		r^2
Rapid Creek (0.99%)	LAS C10 ^a	45		>0.997
	LAS C14 ^a	2399, 2089, 3019		
Sediment (f_{oc})		K_F	n	r^2
Marine Bay of Cadiz (0.144%)	LAS C12 ^b	1071	0.81	0.97
	LAS C10 ^b	78	0.81	0.98
	LAS C11 ^b	347	0.77	0.98

^a Hand & Williams, 1987; SPM 0.07-17 g L⁻¹; surfactant ~ 100µg L⁻¹; ^b Rubio *et al.*, 1996; SPM 40g L⁻¹; surfactant 0-1000ppb; salinity 36‰.

The linearity of the isotherms in Figure 4.11(i) reveals no evidence of a change in orientation of the molecule or bilayer formation as the surfactant concentration increases. In addition, partitioning is unaffected by an increase in ionic concentration, where some shielding effect to increase sorption may have been expected between the SDS molecule and the particle. However, the concentrations employed may be too low and SDS too soluble for this to be visible. Conversely (Brownawell *et al.*, 1991) observed nonlinear sorption of C10, C12- and C14-LAS to soils and sediments where sorption increased according to increasing chain length, ionic strength or the valence of the cations in the aqueous phase. On this evidence it was concluded the LAS sorption was a result of largely nonpolar with possible electrostatic and specific chemical interactions, particularly between sorption sites, Ca²⁺ and LAS molecules.

Reducing the temperature to 8°C enhances SDS sorption in seawater (Figure 4.11 (ii); Table 4.10). The reduced temperature in a solution of high ionic concentration may enhance precipitation or salting out of the nonpolar tail. Although only very low concentrations were employed here, higher concentrations were used in section 4.2.3 where a difference is more obvious.

The removal of organic carbon produced very surprising results (Figure 4.11 (iii); Table 4.10). Since sorption of LAS to natural sediments has been shown to increase with alkyl chain length and organic carbon content, a hydrophobic mechanism is implied (DiToro *et al.*, 1990; Westall *et al.*, 1999). However, this is disputed by other research where a strong correlation between anionic surfactant sorption and percent silt rather than OC was established (Hand & Williams, 1987). The isotherms produced here are distinctly nonlinear suggesting more specific interactions rather than hydrophobic mechanisms. Greater sorption still occurs in seawater sample with no DOC/POC, possibly due to shielding of the negatively charged mineral although this did not take place with the unmodified particles. It is possible that intercalation took place with the positive charges on minerals or the dodecyl sulphate molecules may have precipitated via association with calcium, sodium and magnesium ions. According to Jafvert & Heath, (1991) at dodecyl sulphate concentrations approaching the CMC, the predominant surfactant loss to most natural soils and sediments will be precipitation. Westall *et al.*, (1999) found an increase in sorption with an increase in Ca^{2+} concentration, suggesting that the Ca^{2+} adsorbed directly on to the sediment particle subsequently reduces the negative surface charge and the electrostatic repulsions. The second theory seems more plausible since the extreme reduction in seawater solubility in Table 4.10 did not take place with the relative solubility isotherms in section 4.1.2. However, both isotherms appear to reach a point of maximum sorption and decline

sharply, suggesting active sorption sites are rapidly occupied with no bilayer formation (Figure 4.11 (iii)).

4.2.2.3. Sorption isotherms for HDTMA

The adsorption of cationic surfactants such as HDTMA in aquatic systems onto negatively charged sediment particles is anticipated because of favourable hydrophobic and electrostatic interactions. Hence, the behaviour and effect of these compounds is strongly influenced by adsorption with indirect consequences such as displacement of adsorbed metal ions (Brownawell *et al.*, 1990). The results in Figure 4.12 and Table 4.12 reflect the complex nature of these compounds.

Table 4.12: Freundlich isotherm variables for HDTMA derived from fitting of Figure 4.12 using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous Matrix	<i>n</i>	<i>K_F</i> (L g ⁻¹)	<i>r</i> ²	P value
n = 4				
Plym river water 20°C	0.65	4.59	0.988	0.006
Seawater 20°C	1.37	71.99	0.957	0.021
Plym river water 8°C	0.56	14.31	0.993	0.004
Seawater 8°C	0.38	5.68	0.721	0.151
Plym river water (DOC and POC removed)	0.67	0.55	0.959	0.024
Seawater (DOC and POC removed)	1.31	0.22	0.993	0.003

The Freundlich coefficient for HDTMA in river water at 20°C is only slightly higher than for the other two surfactants (Figure 4.12 (i)). This may be due to the low concentrations employed with too few molecules to form bilayers, or the existence of adsorbed Ca²⁺ on the particles repelling HDTMA, although the adsorption mechanism of HDTMA in the early stages of sorption is attributed to cation exchange as indicated by an equivalent cation release (Xu & Boyd, 1995c, Brownawell *et al.*, 1990). It is also possible that the surfactant is adsorbing to oppositely charged non-settling particles or DOM. In seawater, however, the sorption is much greater, possibly due to a

combination of salting out and electrostatic interactions leading to the formation of bilayers ($n > 1$). Shielding to prevent repulsion between headgroups will occur to allow closer packing (Xu & Boyd, 1995a). Other studies have demonstrated that higher ionic strength resulted in increased cationic surfactant sorption by hydrophobic bonding (Xu & Boyd, 1995c).

Reducing temperature to 8°C has an unusual effect in that seawater sorption is reduced, while the river water sorption increases drastically (Figure 4.12). The isotherms are nonlinear with $n < 1$ indicating limited favourable sorption sites and no bilayer formation. The lack of bilayer formation in sea water at 8°C, unlike at 20°C, may be due to the condensed form of the nonpolar tail. Also, the greater the electrolyte concentration, the higher the Krafft point and therefore the solubility of an ionic surfactant. It may be that the Krafft point in sea water has increased, whereas in river water it was exceeded at 8°C subsequently reducing solubility.

The effect of OC removal is unclear (Table 4.12; Figure 4.12). The sorption constants are substantially reduced in both river and seawater, however the mechanism of sorption is likely to be different in both cases. For example, on particles containing organic matter, sorption can take place either head on as an electrostatic reaction between the positively charged head and the negatively charged organic matter or mineral, or it may partition by hydrophobic interaction and van der Waals forces between the nonpolar tail and organic matter. It may be that the hydrophobic bonding between the surfactant and organic matter is at least as important as electrostatic interactions, which is not possible when the OC is removed from the particles. The type of clay will also play a role. Xu & Boyd (1995c) reported that surfactant molecules adopt a vertical arrangement on nonswelling clays, whereas on swelling clays such as montmorillonite, the molecule may form flat-lying monolayers or bilayers within the clay. It is also possible that adsorption of a positively charged surfactant onto negatively

charged minerals encourages flocculation of particles either electrostatically or by interactions between tail groups and OM subsequently reducing available sorption sites.

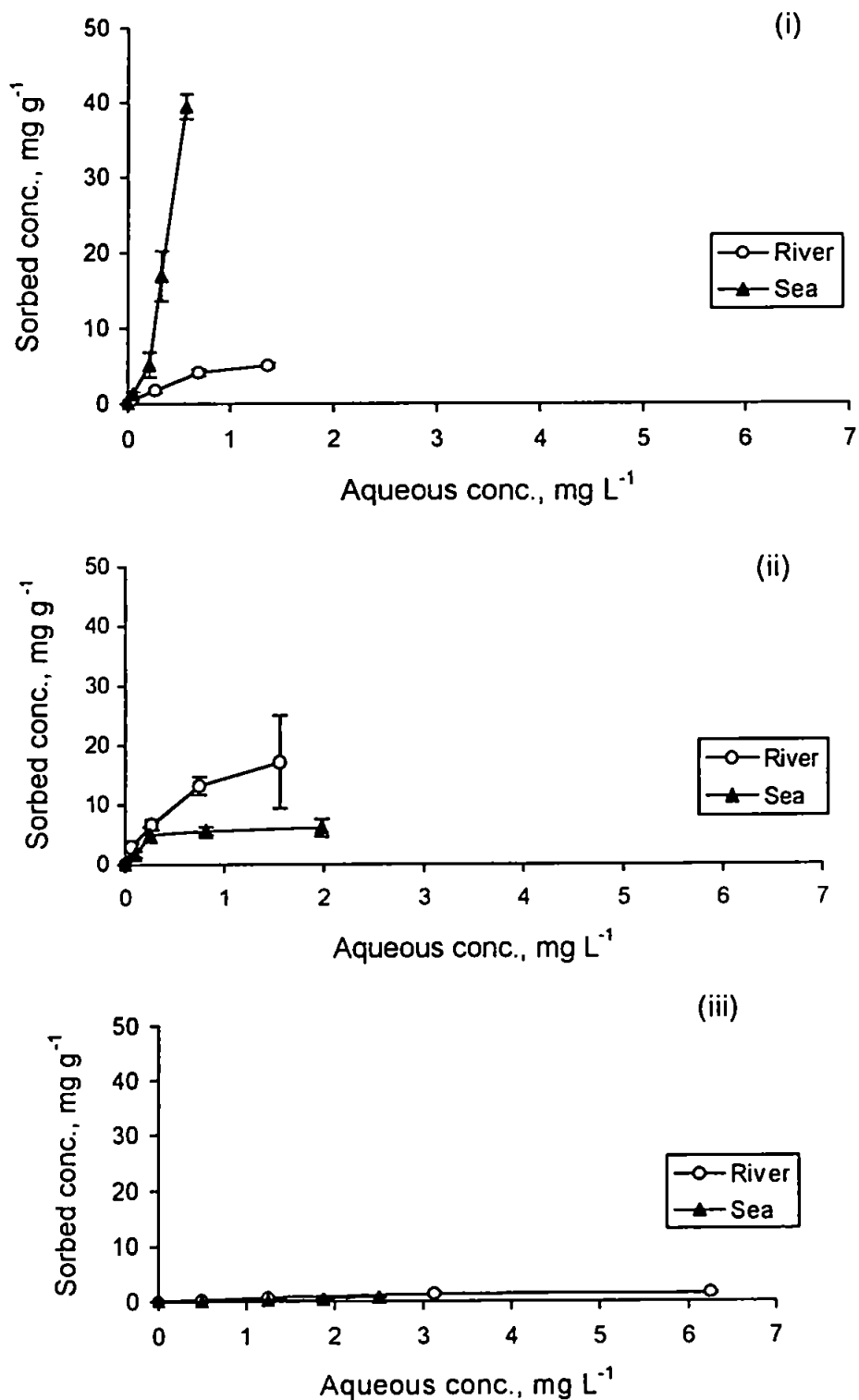


Figure 4.12: Sorption isotherms for HDTMA with an SPM of Plym particles of 50 mg L⁻¹ at (i) 20°C, (ii) 8°C and (iii) with DOC and POC removed, n=4 and standard deviations are shown.

This was shown to be the case with nonswelling clays such as kaolinite, whereas HDTMA sorption in interlayers of swelling clays can cause dispersion (Xu & Boyd, 1995a). Conversely, if hydrophobic bonding were the primary mechanism of bonding, the build up of positive charge may lead to disaggregation and dispersion of clay particles.

4.2.3 Particle Concentration Effect

The particle concentration effect is known to occur with hydrophobic compounds but so far this phenomenon appears to have received very little attention with regard to surfactants. All three surfactants investigated display a PCE, yet the extent of this varies according to surrounding conditions (Figure 4.13; Table 4.13).

Table 4.13: Model parameters defining the particle concentration effect for Triton X-100, SDS and HDTMA in the Plym estuary derived from fitting data of Figure 4.13.

Compound	Matrix	Temperature	$a \cdot 10^4$	b	r^2	P value
Triton X-100	River	20°C	0.61	0.53	0.648	0.100
		8°C	18.79	1.18	0.923	0.009
	Sea	20°C	40.12	1.03	0.999	<0.001
		8°C	2.03	0.93	0.982	0.001
SDS	River	20°C	0.60	0.56	0.717	0.070
		8°C	8.51	0.96	0.967	0.003
	Sea	20°C	0.15	0.27	0.631	0.110
		8°C	1.22	0.63	0.735	0.063
HDTMA	River	20°C	5.65	0.27	0.841	0.029
		8°C	11.70	0.55	0.836	0.030
	Sea	20°C	362.16	1.01	0.943	0.006
		8°C	0.95	0.23	0.766	0.052

Refer to equation 3.24 for constants a and b .

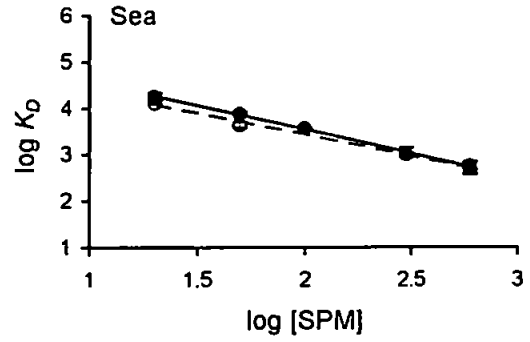
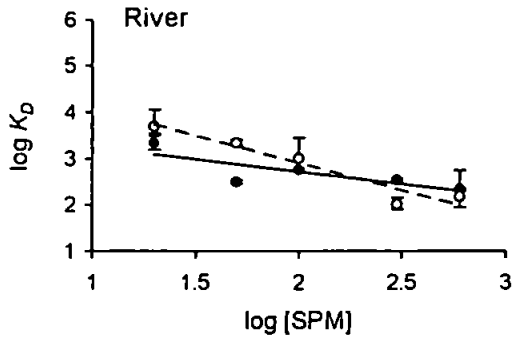
The PCE for Triton X-100, SDS and HDTMA is more significant at 8°C in river water than at 20°C, according to the factor b , while the reverse is true for seawater except for SDS. It appears that when comparing the same compound between temperatures, the

higher the initial sorption or K_D , the greater the effect of particle concentration i.e., factor b . This implies that it is probably an attribute of compound behaviour rather than conditions associated with particles in isolation such as particle aggregation/disaggregation or release of complexing agents, since this would take effect at both temperatures (section 3.2.3.1).

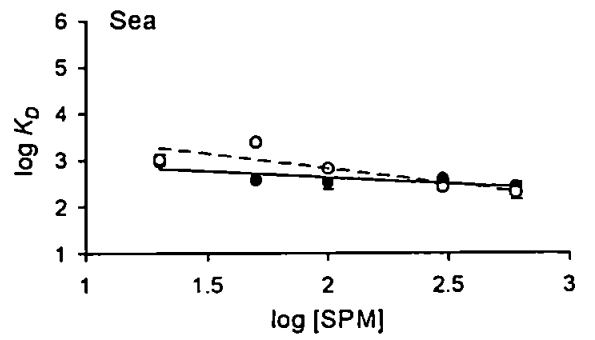
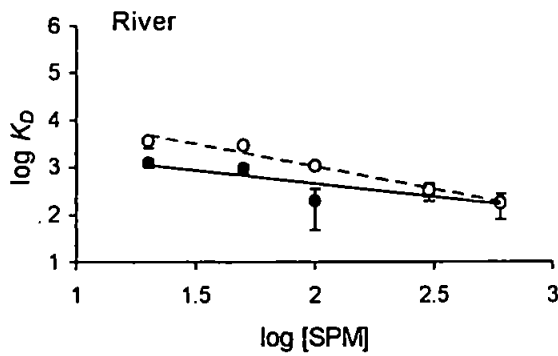
Interestingly, HDTMA displays a large PCE in seawater at 20°C but this is almost nonexistent at 8°C. As with the adsorption isotherms where reduced temperature reduced sorption, this may be due to a lack of bilayer formation since the nonpolar tail has taken on a condensed form. As a result less hydrophobic sorption is taking place leading to a reduced PCE. This effect may compete with the reduced solubility caused by a reduction in temperature.

The environmental implications of the PCE and its modification due to changes in temperature and salinity become more clear in Figure 4.14, which displays the dissolved (X ; Equation 3.3) or bioavailable fraction of surfactants using values of a and b from Table 4.13. With regard to Triton X-100, the surfactant remains largely dissolved in river water despite an increase in SPM. Indeed at 8°C sorption is reduced as SPM increases. The fraction of Triton X-100 in seawater remains relatively stable regardless of SPM although it is consistently lower at 8°C. SDS remains soluble in all matrices and is apparently unaffected by temperature or SPM, whereas the fraction of dissolved HDTMA in river water is significantly reduced with increased SPM and this is further enhanced by a reduced temperature. The fraction dissolved in seawater is reduced further again at 8°C. However, at 20°C the fraction dissolved remains very low at between 20 to 40% and is uninfluenced by a change in SPM.

Triton X-100



SDS



HDTMA

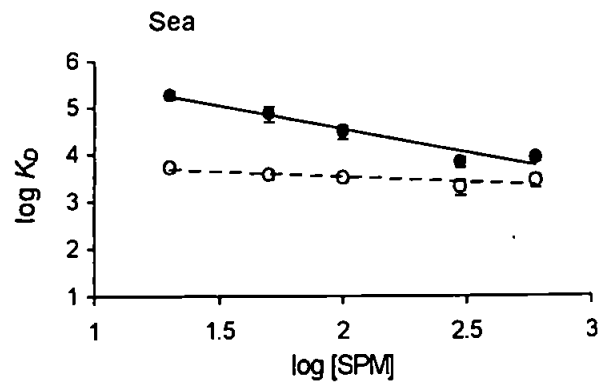
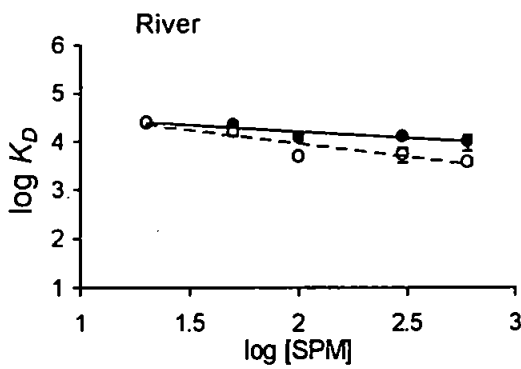


Figure 4.13: Partition coefficients as $\log K_D$ for three surfactants as a function of Plym particle concentration in river and seawater at 20°C (●) and 8°C (○).

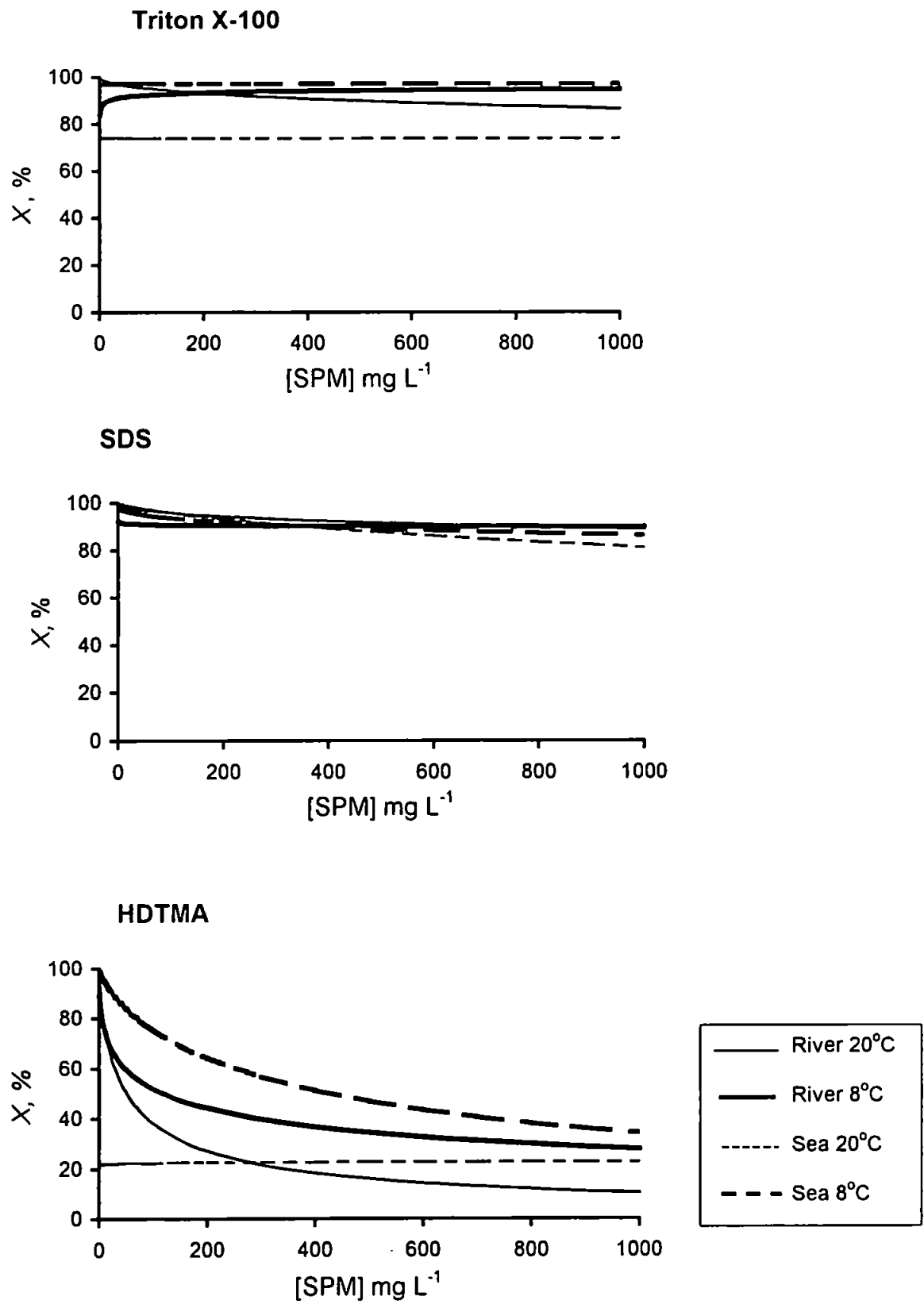


Figure 4.14: Calculated fraction of dissolved of surfactants in river and seawater as a function of particle concentration using equation 3.3 and values of a and b in Table 4.13.

4.2.4. Summary of surfactant particle water interactions

The adsorption of surfactants to natural particles proves to be extremely complex and highly susceptible to the three variables investigated i.e., temperature, salinity and OC. Sorption is generally nonlinear, although this may be an artefact of particle heterogeneity as well as a characteristic of surfactant partitioning. The PCE and fraction dissolved of all three surfactants can also vary widely depending on conditions under investigation. This emphasises the need to consider each case in isolation when attempting to model the behaviour of surfactants.

CHAPTER 5: PHENANTHRENE IN A SURFACTANT MODIFIED AQUATIC SYSTEM – RESULTS AND DISCUSSION

The introduction of surfactants to an aquatic system containing PAHs, such as phenanthrene, can produce instant and significant modifications to PAH behaviour. These changes are, however, subject to a large number of variables including surrounding environmental conditions, the existence of co-contaminants and the concentrations of the compounds of interest. In order to examine possible trends, the following selection of variables was chosen to determine the circumstances more likely to influence phenanthrene partitioning in a surfactant-aqueous system:

- Surfactant concentration: The higher the concentration the more likely the formation of polymers or micelles. Depending on whether the micelles are in the solid or aqueous phase this may increase or reduce phenanthrene solubility, known as solubilisation or adsolubilisation, respectively.
- Phenanthrene concentration: To determine whether surfactants have altered the behaviour of phenanthrene sorption to the originally linear adsorption isotherms.
- Temperature: This can have a profound effect on surfactant solubility.
- Salinity: Both phenanthrene and surfactant solubility and sorption can be influenced by salinity.
- Particle concentration: This has been shown to modify the partition coefficient of phenanthrene and surfactants.
- Contact sequence: The sorption or solubility of phenanthrene may be influenced differently depending on whether the surfactant is added before, after or simultaneously with phenanthrene.
- Kinetics: Surfactants reach sorption equilibrium relatively quickly in comparison to phenanthrene, it is therefore important to establish whether together they influence the time taken for phenanthrene to reach equilibrium.

5.1. Relative solubility

The experiments performed in this Chapter represent an amalgamation of those performed in Chapters 3 and 4. Relative solubility isotherms for phenanthrene were produced using a surfactant concentration of 2.5 mg L^{-1} . Isotherms were also produced using a constant phenanthrene concentration of approximately $5 \text{ } \mu\text{g L}^{-1}$ and a surfactant concentration up to 2.5 mg L^{-1} for SDS and HDTMA. The concentration for Triton X-100 was increased to 50 mg L^{-1} since, due to a lack of radiolabel, previous experiments were performed in this range. As a result, conditions such as point source and chronic contamination for each pollutant type would be replicated.

5.1.1. Relative solubility isotherms of phenanthrene modified with Triton X-100

The isotherms produced for phenanthrene in Triton X-100 display very little difference to phenanthrene alone, as displayed in Figure 5.1 and Table 5.1, other than the slight solubility enhancement in seawater. This suggests phenanthrene has experienced some solubilisation by partitioning into the hydrophobic tail of Triton X-100, which is more energetically favourable than the salting out process. This effect would probably be more pronounced with a more hydrophobic compound. As a non-ionic surfactant Triton X-100 is also relatively insensitive to increased ionic concentration and therefore remains effective as an aqueous pseudophase for phenanthrene (Pennell *et al.*, 1997). The comparative solubility of phenanthrene to other HOMs may also have led to its greater solubility in seawater than river water with Triton X-100, hence the relative solubility salting constant cannot be estimated. Overall, the trends for all three aqueous matrices remain linear, suggesting no competitive processes are taking place.

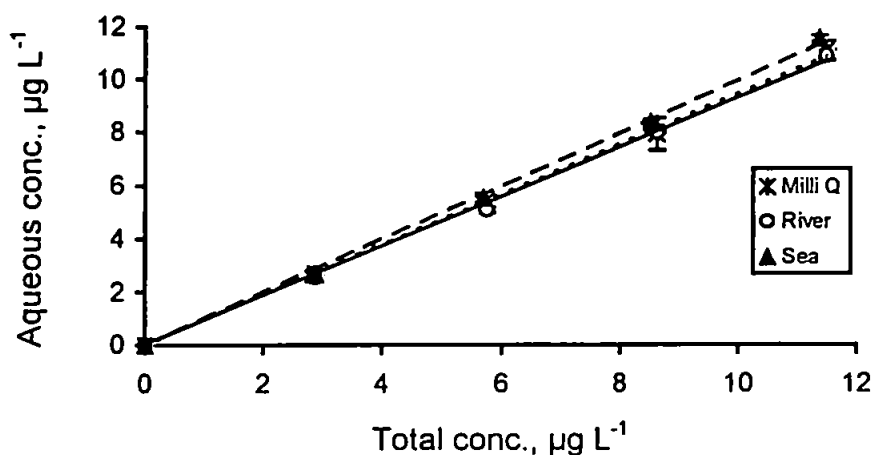


Figure 5.1: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater modified with Triton X-100 at 20°C, where the mean value and standard deviations are shown (n=4).

Table 5.1: Relative solubility isotherms for phenanthrene in three aqueous matrices modified with Triton X-100 at 20°C derived from data fitting of Figure 5.1.

Aqueous Matrix n = 4	Equation		r ^{2,a}	P value ^a
	Phenanthrene alone	Phenanthrene & Triton X-100		
Milli-Q	y = 0.89x	y = 0.95x	0.999	<0.001
River water	y = 0.99x	y = 0.93x	0.998	<0.001
Sea water	y = 0.81x	y = 1.00x	0.999	<0.001

^a r² and P value refer to the phenanthrene & Triton X-100 system

For commercial grade surfactants such as Triton X-100 there is no precise CMC value, since as monomers of similar chain lengths tend to self associate, the monomers with long hydrophobic groups will associate at lower concentrations than monomers with shorter hydrophobic groups (Jafvert *et al.*, 1994). Therefore, increasing the concentration of Triton X-100 should raise the number of polymers in solution capable of sorbing phenanthrene, subsequently enhancing apparent solubility. However, as displayed in Figure 5.2, this had no effect. This may be because phenanthrene, at the concentration employed, is relatively soluble. Furthermore, despite the indistinct CMC, the maximum concentration of Triton X-100 at 50 mg L⁻¹ is substantially below quoted values (Table 1.14). Therefore, although some polymers may exist, there are likely to be

no micelles in solution providing the more favourable phase for phenanthrene to partition into and enhancing apparent solubility.

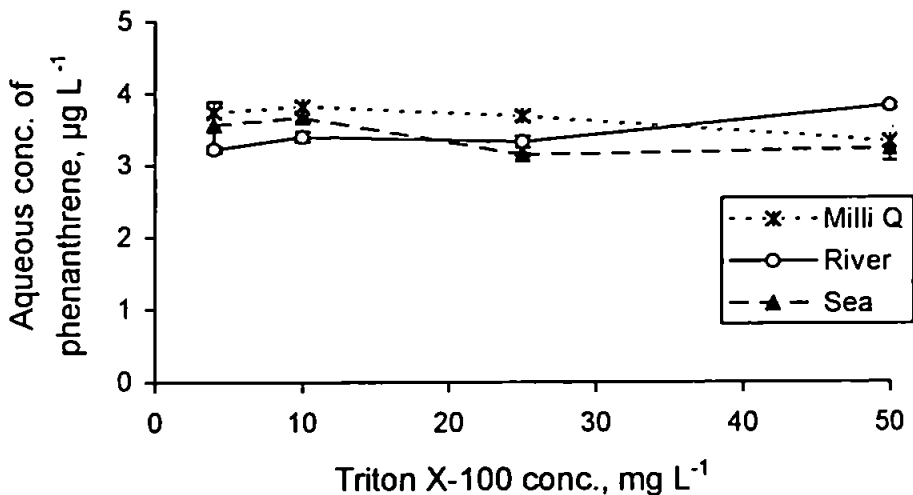


Figure 5.2: Relative solubility of phenanthrene at a concentration of 5 µg L⁻¹ according to increasing Triton X-100 concentration at 20°C.

A reduction in temperature to 8°C (Figure 5.3; Table 5.2) produces very similar results to those in Table 5.1 for 20°C, with only a slight elevation of phenanthrene solubility in seawater. Therefore, although the solubility of Triton X-100 is reduced at lower temperatures (Table 4.2), there appear to be sufficient molecules in solution to slightly solubilise phenanthrene. Again as with the 20°C results, phenanthrene in seawater is apparently more soluble than river water, although this effect is not substantial.

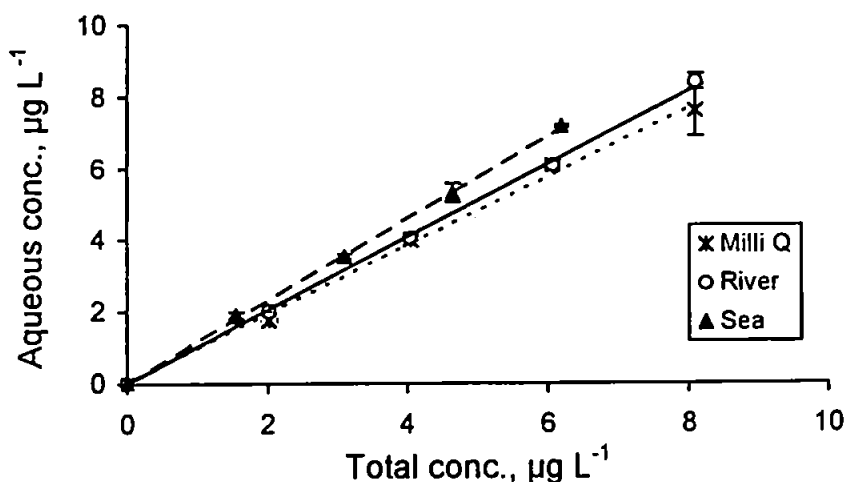


Figure 5.3: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater modified with Triton X-100 at 8°C, where the mean value and standard deviations are shown (n=4).

Table 5.2: Relative solubility isotherms for phenanthrene in three aqueous matrices modified with Triton X-100 at 8°C derived from data fitting of Figure 5.3.

Aqueous Matrix n = 4	Equation		$r^{2,a}$	P value ^a
	Phenanthrene alone	Phenanthrene & Triton X-100		
Milli-Q	$y = 0.88x$	$y = 0.96x$	0.997	<0.001
River water	$y = 0.94x$	$y = 1.02x$	0.999	<0.001
Sea water	$y = 0.89x$	$y = 1.15x$	0.997	<0.001

^a r^2 and P value refer to the phenanthrene & Triton X-100 system

5.1.2. Relative solubility isotherms of phenanthrene modified with SDS

At the low concentrations used, SDS appears to exert almost no influence on phenanthrene via solubilisation (Figure 5.4; Table 5.3). While solubility has been reduced slightly in river water and increased slightly in seawater, the changes are not significantly different. The isotherms also remain linear. Increasing the concentration of SDS appears to cause some variability, particularly in seawater (Figure 5.5). Since SDS becomes more susceptible to salinity and less soluble as its concentration increases (Figure 4.4) this may influence the behaviour of phenanthrene by providing sorption sites on the test tube glass wall.

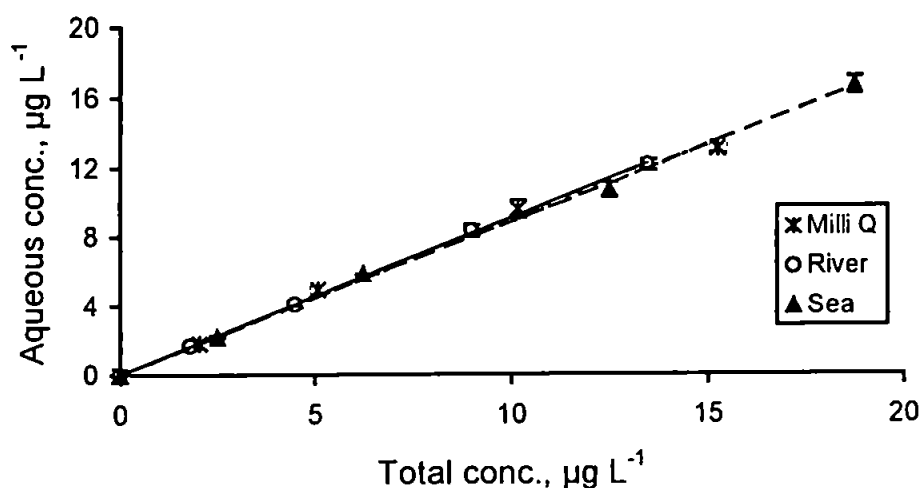


Figure 5.4: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater modified with SDS at 20°C, where the mean value and standard deviations are shown (n=4).

Table 5.3: Relative solubility isotherms for phenanthrene in three aqueous matrices modified with SDS at 20°C derived from data fitting of Figure 5.4.

Aqueous Matrix n = 4	Equation		$r^{2,a}$	P value ^a
	Phenanthrene alone	Phenanthrene & SDS		
Milli-Q	$y = 0.89x$	$y = 0.88x$	0.994	0.002
River water	$y = 0.99x$	$y = 0.91x$	0.995	<0.001
Sea water	$y = 0.81x$	$y = 0.88x$	0.999	<0.001

^a r^2 and P value refer to the phenanthrene & SDS system

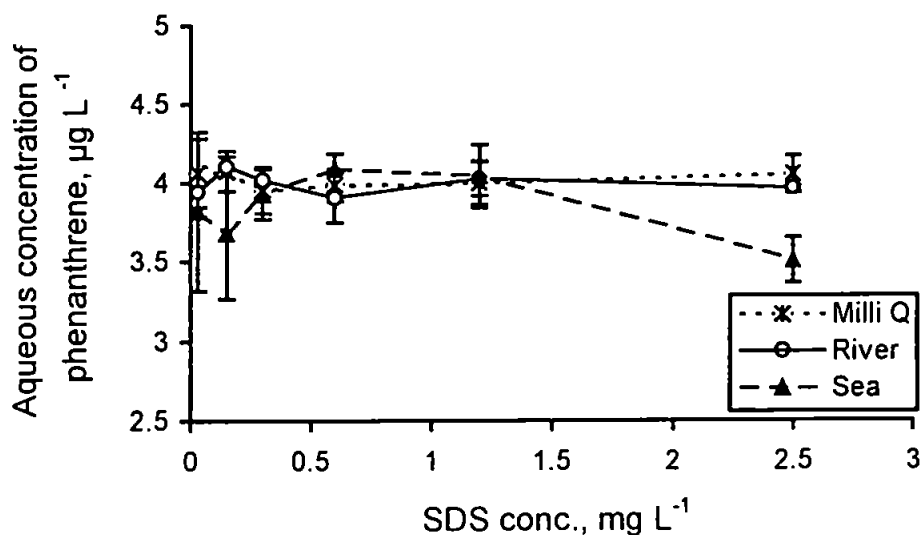


Figure 5.5: Relative solubility of phenanthrene at a concentration of 5 µg L⁻¹ according to increasing SDS concentration at 20°C, where the mean value and standard deviations are shown (n=4).

Reducing the temperature to 8°C does not appear to modify phenanthrene behaviour in the SDS systems since phenanthrene solubility with and without SDS is indistinguishable (Figure 5.6; Table 5.4). As the influence of temperature on SDS solubility is also minimal this is not surprising.

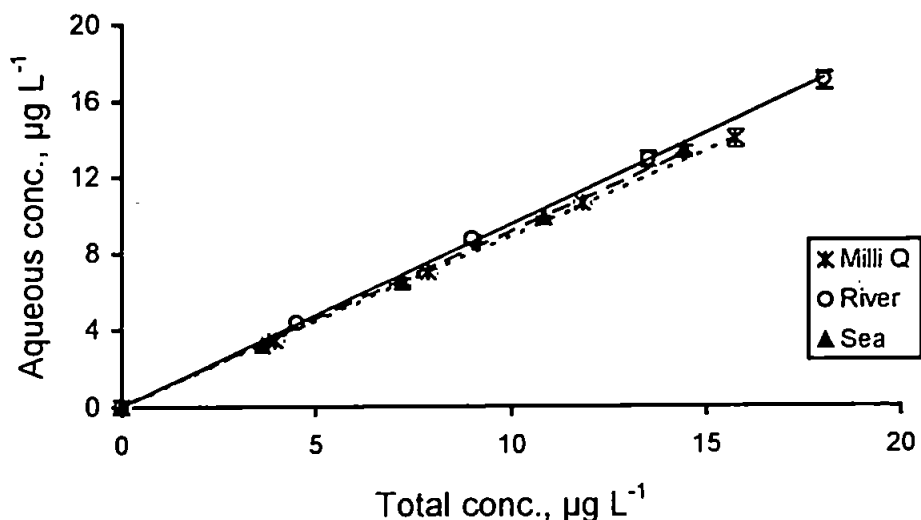


Figure 5.6: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater modified with SDS at 8°C, where the mean value and standard deviations are shown (n=4).

Table 5.4: Relative solubility isotherms for phenanthrene in three aqueous matrices modified with SDS at 8°C derived from data fitting of Figure 5.6.

Aqueous Matrix n = 4	Equation		$r^{2,a}$	P value ^a
	Phenanthrene alone	Phenanthrene & SDS		
Milli-Q	$y = 0.88x$	$y = 0.89x$	1.000	<0.001
River water	$y = 0.94x$	$y = 0.95x$	1.000	<0.001
Sea water	$y = 0.89x$	$y = 0.92x$	0.999	<0.001

^a r^2 and P value refer to the phenanthrene + SDS system

5.1.3. Relative solubility isotherms of phenanthrene modified with HDTMA

Interestingly, the behaviour of phenanthrene in an HDTMA system is unaffected. As a positively charge surfactant, HDTMA should adsorb head on to the glass walls with the hydrophobic tail available as a sorption site for phenanthrene. The end result being reduced phenanthrene solubility. The results displayed in Figure 5.7 and Table 5.5 show this is not the case. There is a slight increase for phenanthrene in Milli-Q and seawater. It may be that it is energetically more favourable for phenanthrene to enter a polymer in the aqueous phase, rather than one sorbed to the glass wall. At 2.5 mg L⁻¹ it is possible that the glass wall is saturated with HDTMA leaving surplus molecules in the aqueous phase available for phenanthrene. However, even over a range of HDTMA

concentrations (Figure 5.8), there is very little variability suggesting that HDTMA in this system exerts a minimal influence.

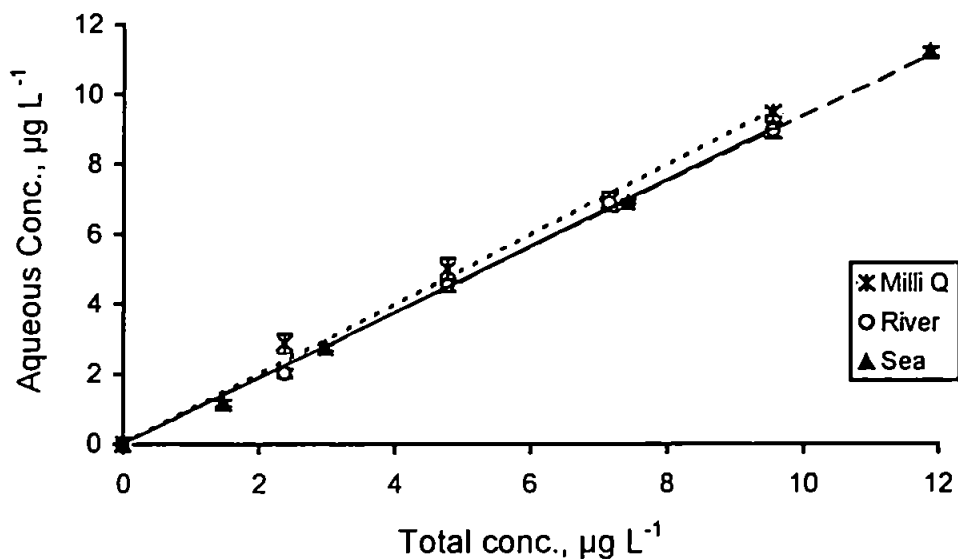


Figure 5.7: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater modified with HDTMA at 20°C, where the mean value and standard deviations are shown (n=4).

Table 5.5: Relative solubility isotherms for phenanthrene in three aqueous matrices at modified with HDTMA 20°C derived from data fitting of Figure 5.7.

Aqueous Matrix n = 4	Equation		r^2 ^a	P value ^a
	Phenanthrene alone	Phenanthrene & HDTMA		
Milli-Q	$y = 0.89x$	$y = 1.00x$	0.993	<0.001
River water	$y = 0.99x$	$y = 0.94x$	0.998	<0.001
Sea water	$y = 0.81x$	$y = 0.94x$	0.999	<0.001

^a r^2 and P value refer to the phenanthrene + HDTMA system

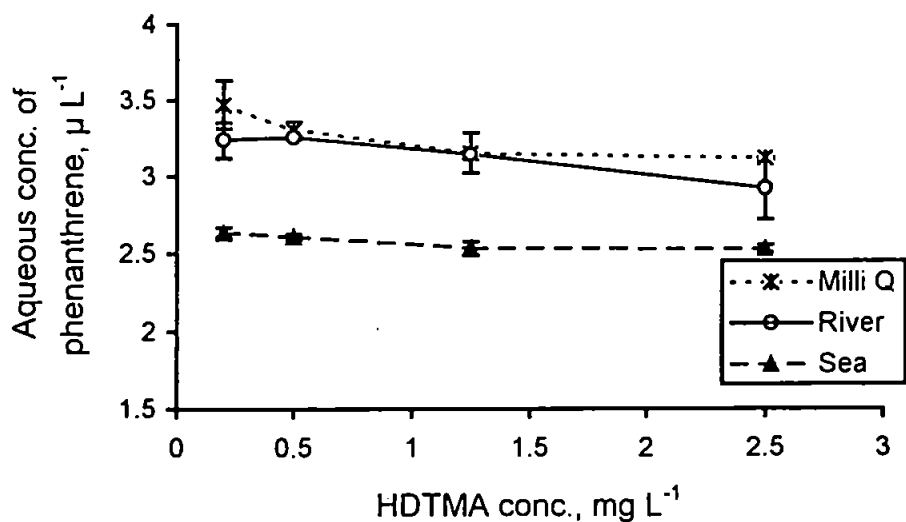


Figure 5.8: Relative solubility of phenanthrene at a concentration of 5 µg L⁻¹ according to increasing HDTMA concentration at 20°C.

Phenanthrene solubility appears to be slightly reduced at 8°C suggesting greater sorption to HDTMA on the glass walls (Figure 5.9; Table 5.6). Although this contradicts the knowledge that raising temperature reduces ionic surfactant solubility since the hydration of the hydrophilic region is reduced, it does agree with the HDTMA relative solubility results in Table 4.5.

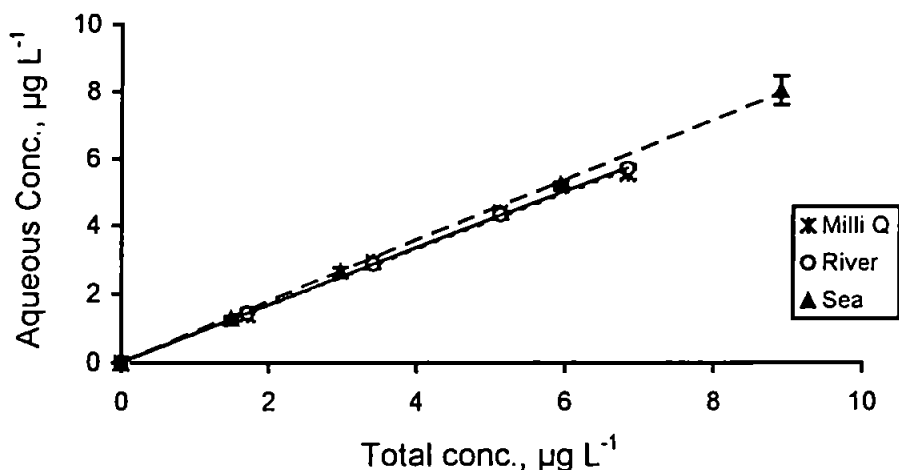


Figure 5.9: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater modified with HDTMA at 8°C, where the mean value and standard deviations are shown (n=4).

Table 5.6: Relative solubility isotherms for phenanthrene in three aqueous matrices modified with HDTMA at 8°C derived from data fitting of Figure 5.9.

Aqueous Matrix n = 4	Equation		r ^{2,a}	P value ^a
	Phenanthrene alone	Phenanthrene & HDTMA		
Milli-Q	y = 0.88x	y = 0.83x	0.998	<0.001
River water	y = 0.94x	y = 0.84x	1.000	<0.001
Sea water	y = 0.89x	y = 0.89x	1.000	<0.001

^a r² and P value refer to the phenanthrene + SDS system

5.1.4 Summary of phenanthrene relative solubility modified with surfactants

In aqueous solutions alone, it appears that at low and environmentally realistic concentrations none of the surfactants exert a significant influence on the solubility of phenanthrene (Figure 5.10).

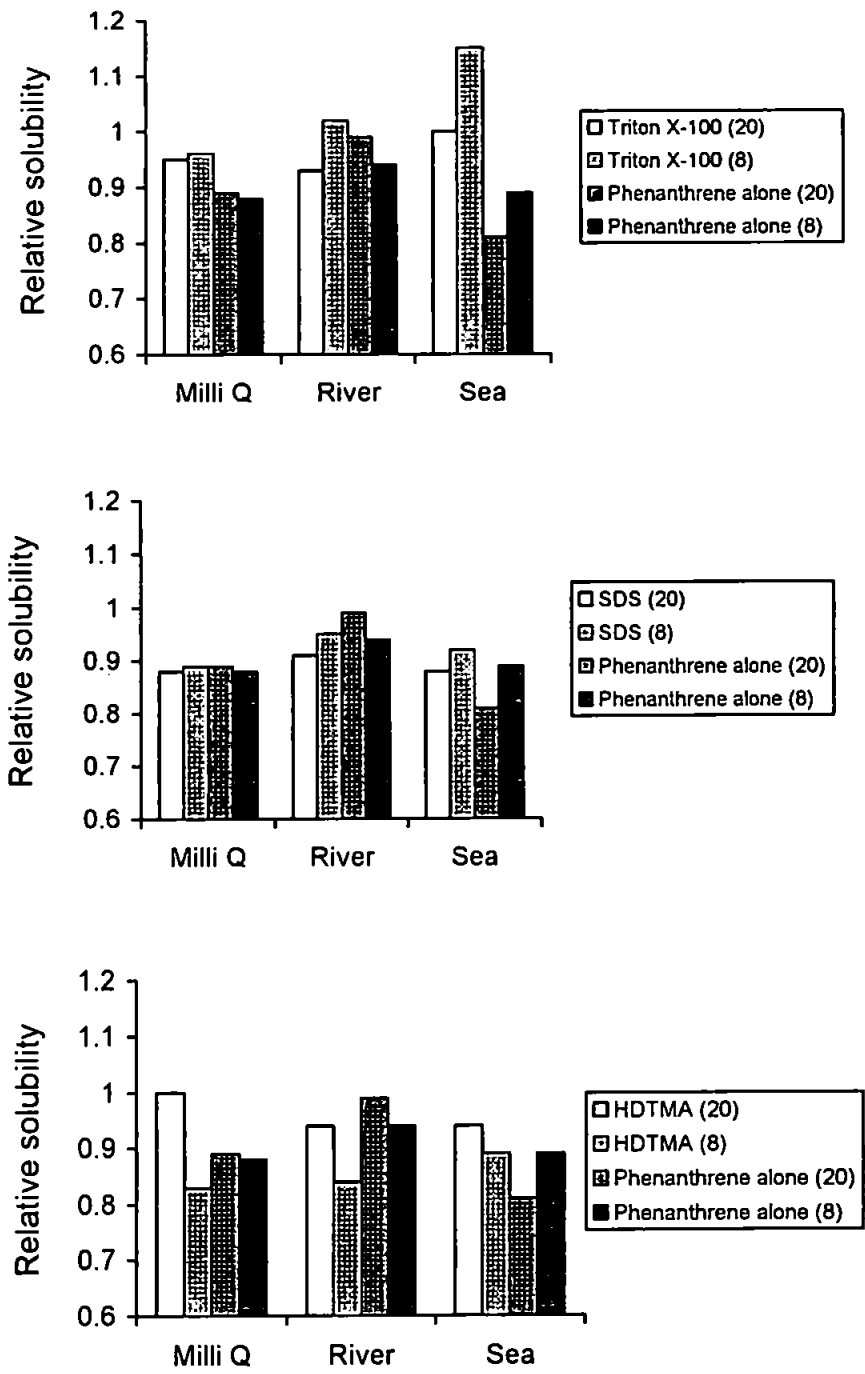


Figure 5.10: Summary of surfactant influence on phenanthrene solubility shown as gradients of relative solubility isotherms with °C in parenthesis

At reduced temperatures, Triton X-100 was the most effective surfactant at enhancing phenanthrene solubility. This may be because with ionic surfactants such as SDS and HDTMA, the hydration sphere of the ionic group extends to a large portion of the hydrophobic tail and subsequently reduces molecular forces (i.e. the van der Waals

forces) between phenanthrene and the nonpolar group of the surfactant. For nonionic surfactants, the effect of the nonionic polar group should be less significant and hence have less influence (Kile & Chiou, 1989).

5.2. Particle-water interactions of phenanthrene with surfactants

Although it would appear from section 5.1. that surfactants at low concentrations have little influence on the relative solubility of phenanthrene, the inclusion of particles considerably changes the situation. This is because surfactants are able to modify the character of the particles and as a result encourage sorption or desorption of phenanthrene. In order to establish this, the variables investigated for phenanthrene sorption alone were repeated with surfactants, i.e. time (kinetics), particle concentration, salinity, temperature and the contact sequence of the surfactant with the particle.

5.2.1 Reaction kinetics

By increasing or reducing the solubility of phenanthrene, surfactants may affect the kinetics of phenanthrene behaviour e.g. by increasing matrix diffusivities of particles and organic matter by sorption, penetration and swelling of micropores (Yeom & Ghosh, 1998) or by reducing interfacial tension between the water and SOM (Deitsch & Smith, 1995). The effect of surfactants on phenanthrene behaviour may be influenced by whether the surfactant or phenanthrene is the first to come in contact with particles, therefore the effect of contact sequence on sorption kinetics was investigated. Figure 5.11 displays the effect of contact sequence for the three surfactants on sorption kinetics of phenanthrene.

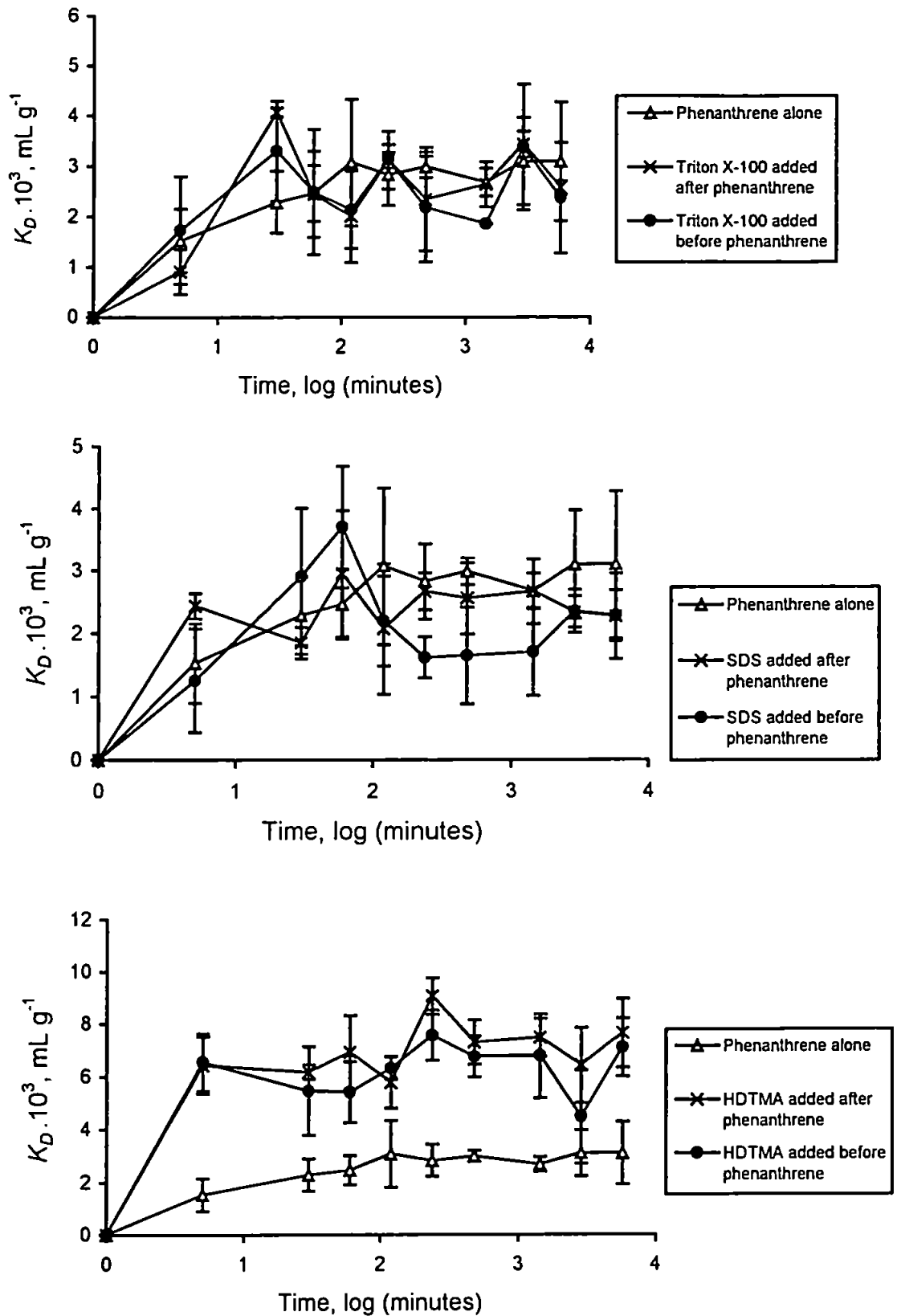


Figure 5.11: Partition coefficients for phenanthrene and surfactants in river water as a function of time, using Plym particles with an SPM concentration of 50 mg L^{-1} , where the mean value and standard deviations are shown ($n=4$)

Both contact sequences for Triton X-100 and SDS added before phenanthrene are characterised by a rapid increase in adsorption, followed by a period of desorption. This may be due to the surfactant successfully competing with phenanthrene for hydrophobic sorption sites. With regard to SDS, the negatively charged head group is likely to be repelled by the particle. Therefore the nonpolar tail group will occupy preferential sorption sites. SDS added after phenanthrene has no effect, suggesting that phenanthrene had become too strongly bound for desorption to take place. In contrast, phenanthrene added to an HDTMA system, appears unaffected by contact sequence. There is rapid sorption within 5 minutes, which is generally maintained over 7 days. The increased sorption displayed is due to the head-on sorption of the positively charged HDTMA onto particles leaving the hydrophobic tails extended into the aqueous phase. This provides additional favourable sites for phenanthrene to sorb onto.

5.2.2 Sorption isotherms

In solid-water systems, the presence of a surfactant may enhance or reduce the apparent solubility of co-existing hydrophobic organic compounds. This leads to an extremely complex picture in this case where both the PAH and surfactant may interact with each other and with the solid phase, potentially leading to altered contaminant mobility and bioavailability. As a result of this intricacy, little is known about the effects of surfactants on the partitioning of PAHs in sediment-water systems and how environmental variables may further influence this.

5.2.2.1 Sorption isotherms for phenanthrene modified with Triton X-100

The sorption of PAHs and other HOMs in a surfactant-free soil or sediment-water system is believed to be governed by a mechanism where the PAH molecules partition into the particulate organic matter phase. However, where a surfactant is added,

into the particulate organic matter phase. However, where a surfactant is added, depending on the net effect of partitioning into aqueous phase surfactant molecules or sorbed surfactant molecules, the apparent solute-particle water distribution coefficient may increase or decrease relative to the intrinsic distribution coefficient of the same solute in a surfactant free system (Sun *et al.*, 1995). Sun *et al.*, (1995) found that for a non-ionic surfactant at low concentrations below the CMC, the partition coefficient for HOMs was generally greater than in a surfactant free system, presumably due to sorption of the HOM to the particle bound surfactant (Figure 5.11), whereas at elevated surfactant concentrations, the formation of micelles acts as an additional aqueous sorptive phase leading to a lower partition coefficient.

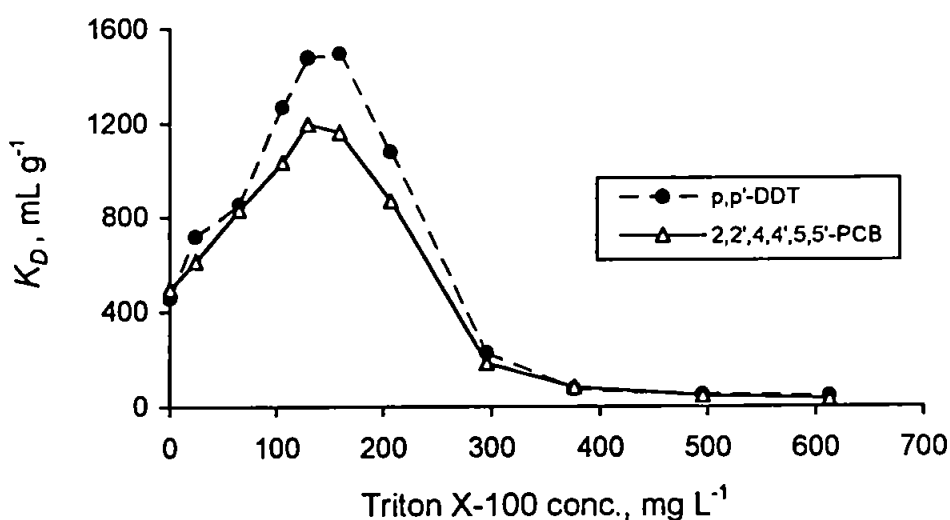


Figure 5.11: The influence of Triton X-100 on the partitioning of HOMs in a soil-water system (adapted from Sun *et al.*, 1995).

The results for this study with Triton X-100 suggest little change for phenanthrene in river water with an original K_F of 4.10 L g⁻¹ (Table 5.7; Figure 5.12). Sorption in seawater has been slightly reduced from a K_F of 6.71 L g⁻¹ suggesting phenanthrene uptake by Triton X-100 molecules in the aqueous phase is reducing the salting out effect. However, as discovered in Section 4.2.2.1, Triton X-100 displays a much higher partition coefficient in sea water than river water, possibly via head-out sorption which

will occupy hydrophobic sorption sites. As a result competitive sorption may occur between phenanthrene and Triton X-100 leading to a reduced K_F for phenanthrene. Other evidence to suggest competitive sorption is the convex nature of the isotherm, since as the phenanthrene concentration increases the rate of sorption begins to decrease. Overall, the fact that these isotherms are relatively linear in comparison to those for Triton X-100 alone, combined with the knowledge that both contact sequence and increasing concentration of surfactant has a minimal influence on phenanthrene sorption, suggests that this surfactant has little effect on phenanthrene behaviour at the concentrations investigated.

Research performed by Deitsch & Smith (1995) indicates that higher concentrations of Triton X-100 may be needed before any effect is seen. For example, 30 and 300 mg L⁻¹ had no effect on trichloroethene sorption whereas 900 and 3000 mg L⁻¹ reduced the K_{oc} from 0.073 L g⁻¹ to 0.013 L g⁻¹. These changes are suggested to be due to reduced tortuosity of the soil organic matter by reducing interfacial tension or by causing the organic matter matrix to expand. In contrast, it was also postulated that increased sorption of Triton X-100 may block more diffusive paths than are opened therefore an optimal concentration is preferable (Deitsch & Smith, 1995). Grimberg *et al.*, (1995) actually found that nonionic surfactants caused a decreased mass transfer coefficient for phenanthrene relative to water alone. However the influence of surfactants on solubilisation lead to an overall increase in phenanthrene dissolution rates.

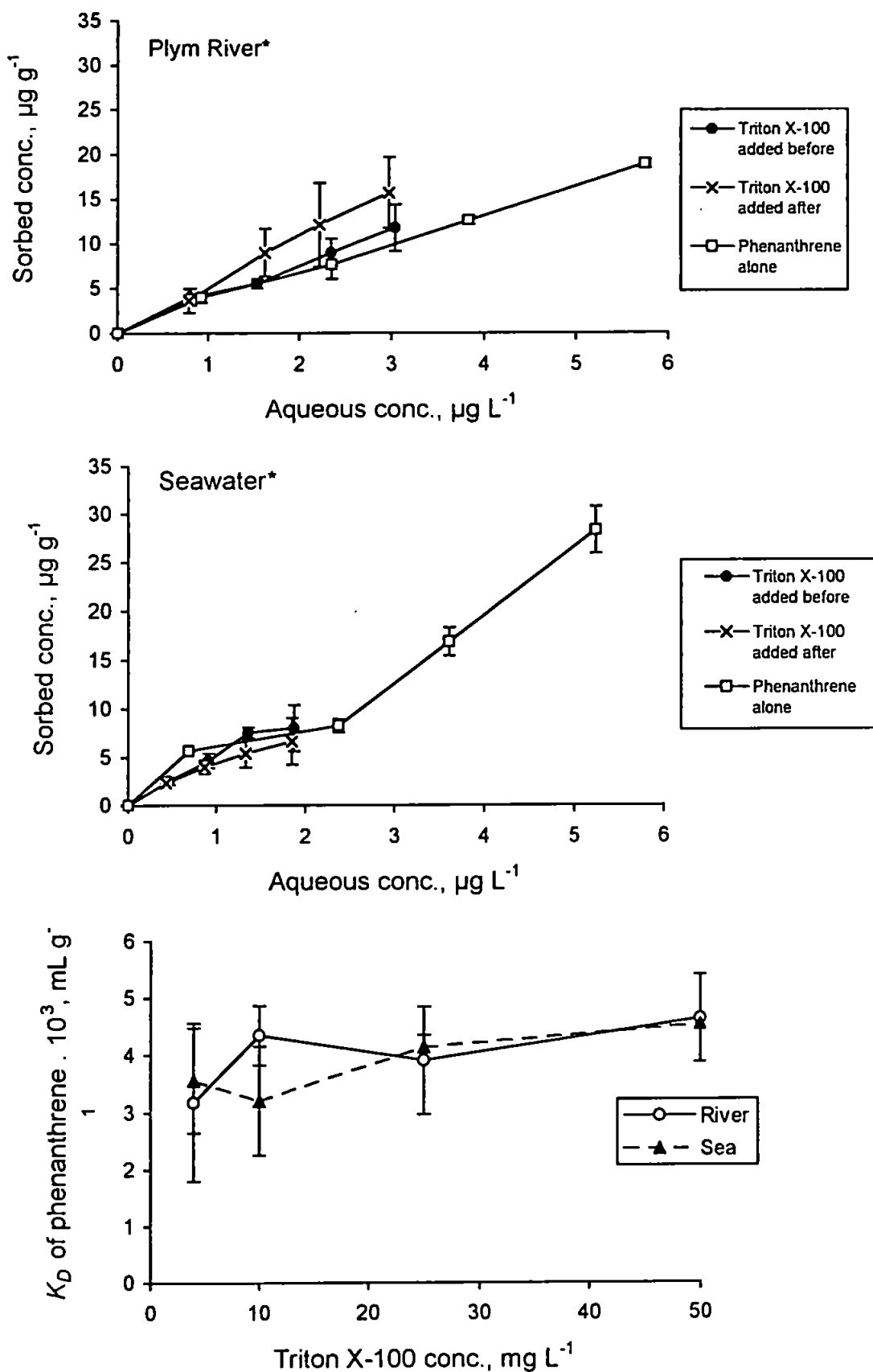


Figure 5.12: Sorption isotherms for phenanthrene with Triton X-100 at 20°C using Plym particles at an SPM concentration of 50 mg L⁻¹ where n = 4 and standard deviations are shown

* limited stock of ¹⁴C-phenanthrene prevented extension of isotherms with Triton X-100

Table 5.7: Freundlich isotherm variables for phenanthrene with Triton X-100 derived from data fitting of Figure 5.12 using Plym particles with an SPM concentration of 50 mg L⁻¹ at 20°C

Aqueous Matrix n = 4		<i>n</i>	<i>K_F</i> (L g ⁻¹)	<i>r</i> ²	P value
Plym River	Triton X-100 added before	0.80	4.53	0.957	0.003
	Triton X-100 added after	1.12	4.91	0.993	0.022
	Phenanthrene alone	0.84	4.10	0.993	0.005
Seawater	Triton X-100 added before	0.87	5.09	0.969	0.016
	Triton X-100 added after	0.71	4.35	0.998	<0.001
	Phenanthrene alone	0.75	6.71	0.884	0.08

The particle-water partition coefficient for phenanthrene in both river and seawater with the surfactant and at both temperatures is very similar. However, Triton X-100 substantially enhances phenanthrene sorption in seawater at 8°C in comparison to phenanthrene alone. Although at 8°C Triton X-100 sorption reduced, it appears that it is still able to provide additional sorption sites for phenanthrene subsequently minimising the influence of reduced temperature. (Table 5.8; Figure 5.13). Since there was also no significant difference between contact sequences no competitive sorption or modifications in particle behaviour appears to be taking place.

Table 5.8: Freundlich isotherm variables for phenanthrene with Triton X-100 derived from data fitting of Figure 5.13 using Plym particles with an SPM concentration of 50 mg L⁻¹ at 8°C

Aqueous Matrix n = 4		<i>n</i>	<i>K_F</i> (L g ⁻¹)	<i>r</i> ²	P value
Plym River	Triton X-100 added before	0.99	5.02	0.95	0.026
	Triton X-100 added after	0.97	4.88	0.96	0.019
	Phenanthrene alone	1.00	3.18	0.99	<0.001
Sea	Triton X-100 added before	0.72	4.76	0.99	0.007
	Triton X-100 added after	0.82	5.25	0.99	0.005
	Phenanthrene alone	1.09	1.56	0.93	0.006

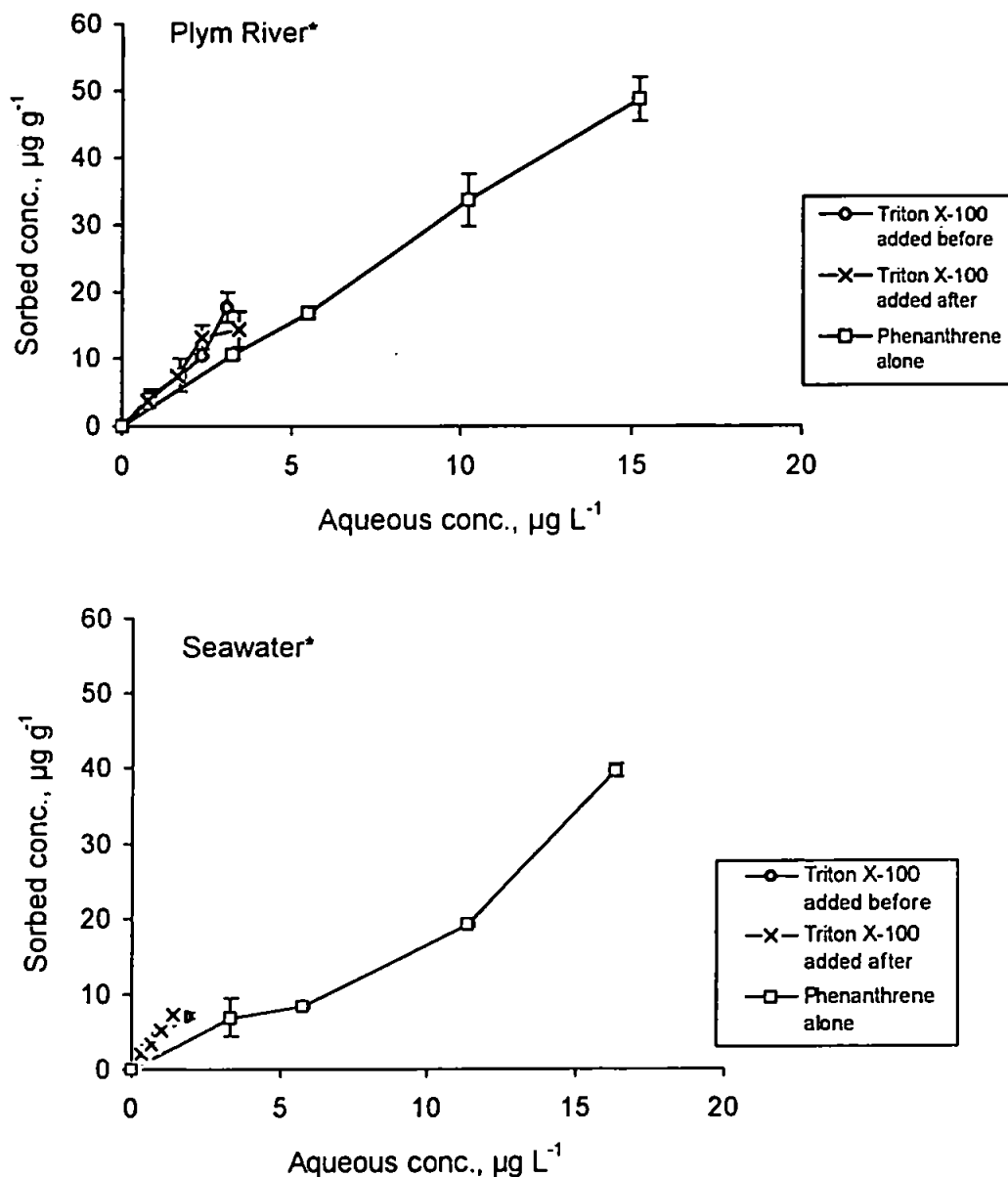


Figure 5.13: Sorption isotherms for phenanthrene with Triton X-100 at 8°C using Plym particles at an SPM concentration of 50 mg L⁻¹ where n = 4 and standard deviations are shown

* limited stock of ¹⁴C-phenanthrene prevented extension of isotherms with Triton X-100

5.2.2.2 Sorption isotherms for phenanthrene modified with SDS

Ou *et al.*, (1995) found that with low concentrations (<50 $\mu\text{g mL}^{-1}$) of the anionic surfactant type, linear alkyl benzene sulphonate, the contact sequence had an effect on phenanthrene partitioning. This study shows SDS to have a similar effect (Table 5.9; Figure 5.14). According to Ou *et al.*, (1995) this is because if the particles are

equilibrated with the surfactant prior to phenanthrene, the adsorption of phenanthrene decreases due to active sites being occupied by the surfactant. However, if the particles come into contact with phenanthrene first, the adsorption of phenanthrene is increased by partitioning into hemimicelles/admicelles formed on the solid surface.

The influence of contact sequence is similar for both river water and seawater. However, increased ionic concentration appears to raise the K_F . Since seawater, as opposed to river water, has no effect on SDS partitioning the change in K_F is likely to be an artefact of phenanthrene partitioning influenced by salting out. The profile of the seawater isotherm with SDS added after, indicates that as the phenanthrene concentration increases and available sorption sites are reduced, some solubilisation may be taking place, whereas, if only the SDS concentration is increased, in river water the K_F falls, probably due to occupied sorption sites. This is in agreement with reported results from Ou *et al.*, (1995) who used sterile water and soil with LAS and phenanthrene (Table 5.10). With seawater there is an initial increase in sorption, where perhaps the shielding effect of seawater reduces electrostatic influence of the anionic surfactant head on the hydrophobic tail, providing an additional site for phenanthrene. Closer packing of SDS molecules may also occur leaving other sites available.

Table 5.9: Freundlich isotherm variables for phenanthrene with SDS derived from data fitting of Figure 5.14 using Plym particles with an SPM concentration of 50 mg L⁻¹ at 20°C

Aqueous Matrix n = 4		<i>n</i>	K_F (L g ⁻¹)	r^2	P value
River	SDS added before	1.30	0.32	0.897	0.053
	SDS added after	1.88	1.26	0.957	0.022
	Phenanthrene alone	0.84	4.10	0.993	0.005
Sea	SDS added before	1.05	1.27	0.997	0.002
	SDS added after	0.70	2.47	0.571	0.244
	Phenanthrene alone	0.75	6.71	0.884	0.080

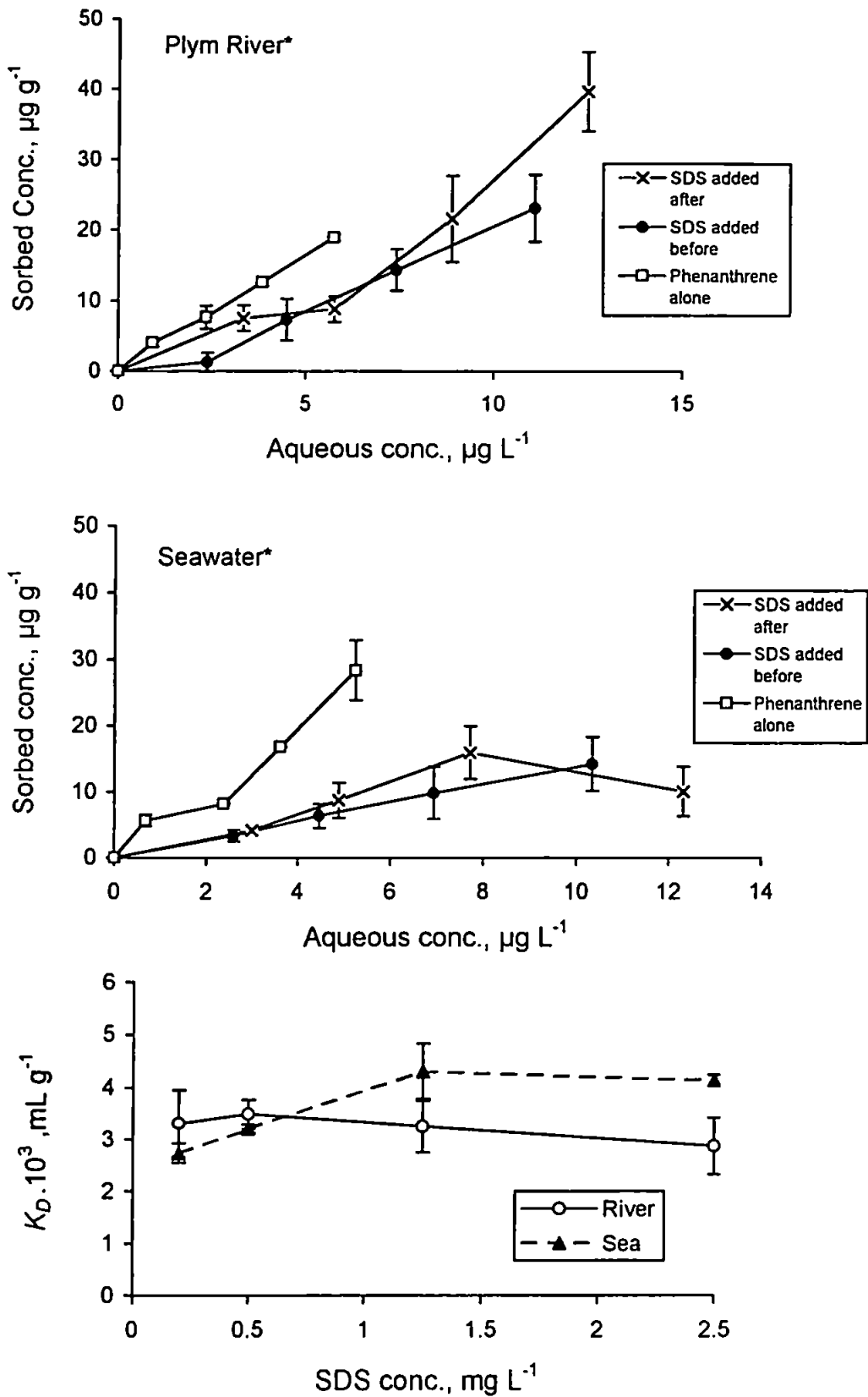


Figure 5.14: Sorption isotherms for phenanthrene with SDS at 20°C using Plym particles at an SPM concentration of 50 mg L $^{-1}$ where n=4 and standard deviations are shown

* limited stock of ^{14}C -phenanthrene prevented extension of isotherms with SDS

Table 5.10: The influence of LAS concentration on phenanthrene partitioning (Ou *et al.*, 1995)

LAS conc. (mg L ⁻¹)	0	25	500	1000
Phenanthrene, K_D (mL g ⁻¹)	251	210	112	32

Reducing the temperature appears to affect phenanthrene partitioning in a very similar way in both river and seawater (Table 5.11; Figure 5.15). While phenanthrene alone appears to display increased solubility with reduced temperature, where SDS is added before, phenanthrene becomes less soluble. Furthermore, the influence of the contact sequence is reversed in comparison to 20°C. This suggests that sorbed SDS molecules are influencing phenanthrene behaviour in some way, perhaps by increasing repulsion between negatively charged particles. This would lead to increased dispersion and more available sorption sites for phenanthrene.

Table 5.11: Freundlich isotherm variables for phenanthrene with SDS derived from data fitting of Figure 5.15 using Plym particles with an SPM concentration of 50 mg L⁻¹ at 8°C

Aqueous Matrix n = 4		<i>n</i>	K_F (L g ⁻¹)	r^2	P value
River	SDS added before	1.028	3.060	0.964	0.018
	SDS added after	1.142	1.166	0.994	0.003
	Phenanthrene alone	1.00	3.18	0.99	<0.001
Sea	SDS added before	1.025	3.656	0.998	<0.001
	SDS added after	1.076	2.125	0.982	0.009
	Phenanthrene alone	1.09	1.56	0.93	0.006

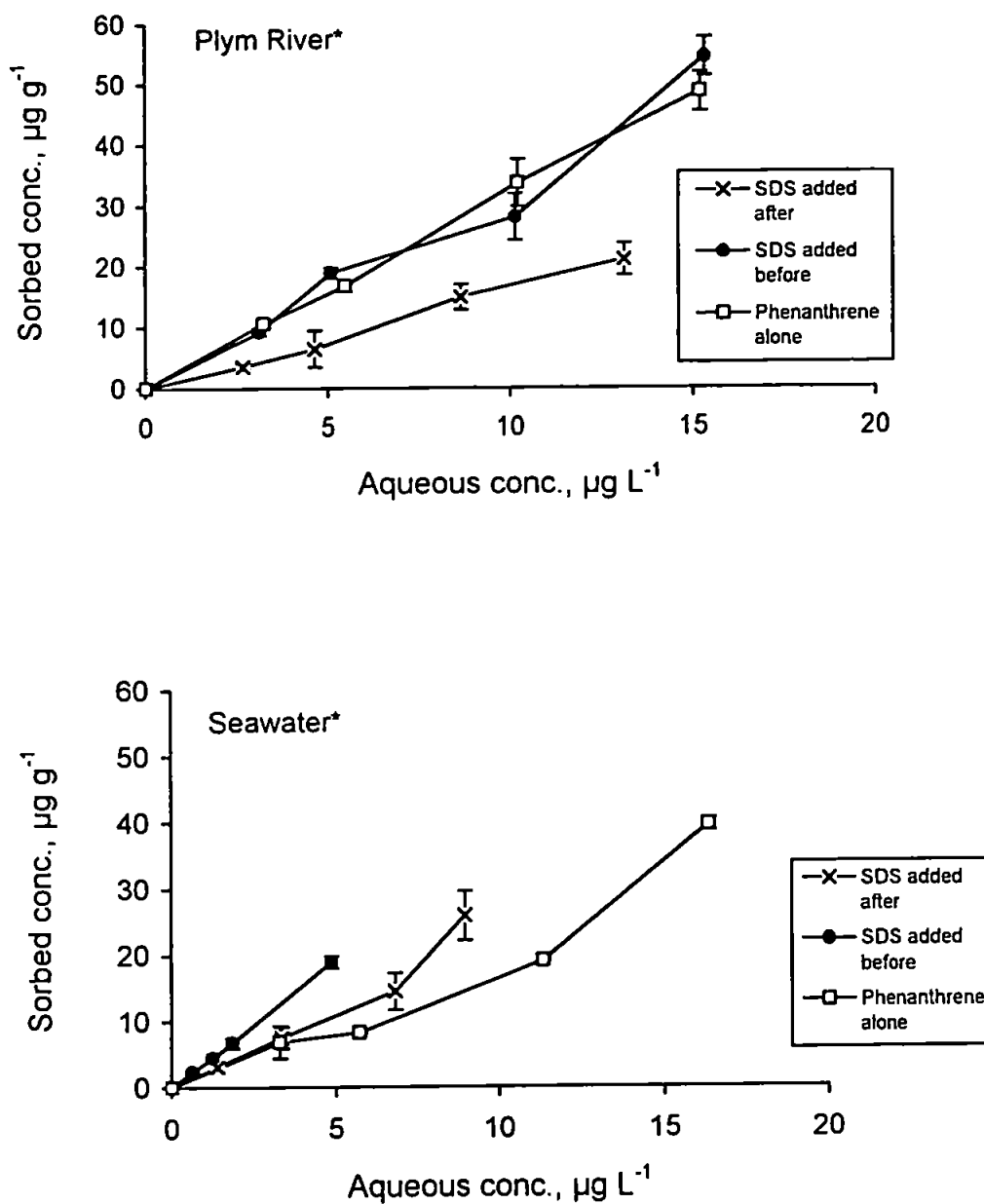


Figure 5.15: Sorption isotherms for phenanthrene with SDS at 8°C with Plym particles at an SPM concentration of 50 mg L⁻¹ where n = 4 and standard deviations are shown
 * limited stock of ¹⁴C-phenanthrene prevented extension of isotherms with SDS

5.2.2.3 Sorption isotherms for phenanthrene modified with HDTMA

As explained in Section 4.2.2.3, the adsorption of cationic surfactants such as HDTMA onto negatively charged sediment particles is liable because of complementary hydrophobic and electrostatic interactions. This results in head-on sorption of the HDTMA molecules to negatively charged particles, leaving the hydrophobic tail

exposed to the aqueous phase. This has the effect of providing additional hydrophobic sorption sites for phenanthrene, leading to increased sorption, as displayed in Table 5.12 and Figure 5.16. Similarly Lee *et al.*, (1989) found the sorption coefficients of subsurface soil treated with HDTMA increased by ~200 times for toluene, ethylbenzene and dichlorobenzene. These coefficients are so enhanced because, although natural SOM and the HDTMA organic matter phases operate in a similar manner, the HDTMA-derived OM is more effective as a sorptive phase for HOMS since it provides a better nonpolar solvent environment than natural OM, which has a high polar functional group content (Lee *et al.*, 1989).

As expected the contact sequence where HDTMA is added before phenanthrene in river water is the most effective in reducing phenanthrene solubility, since this provides readily available sorption sites. This may not be so visible in seawater, since the high ionic concentration reduces the attraction between the particle and HDTMA molecules.

Table 5.12: Freundlich isotherm variables for phenanthrene with HDTMA derived from data fitting of Figure 5.16 using Plym particles with an SPM concentration of 50 mg L⁻¹ at 20°C

Aqueous Matrix n = 4		<i>n</i>	<i>K_F</i> (L g ⁻¹)	<i>r</i> ²	P value
River	HDTMA added before	0.99	7.49	0.991	0.004
	HDTMA added after	1.28	4.62	0.993	0.003
	Phenanthrene alone	0.84	4.10	0.993	0.005
Sea	HDTMA added before	0.85	8.90	0.868	0.068
	HDTMA added after	1.18	9.68	0.990	0.005
	Phenanthrene alone	0.75	6.71	0.884	0.08

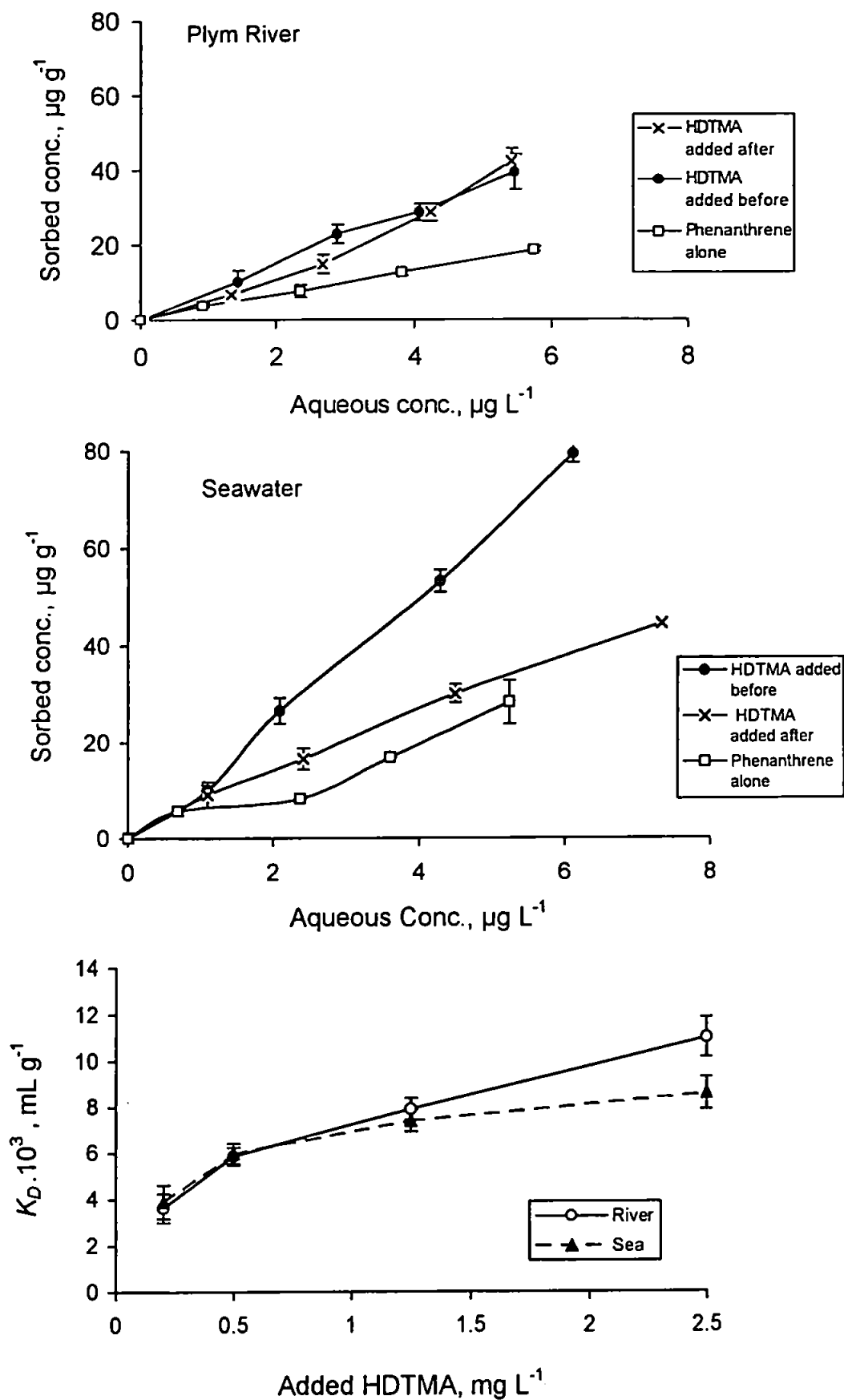


Figure 5.16: Sorption isotherms for phenanthrene with HDTMA at 20°C using Plym particles at an SPM concentration of 50 mg L⁻¹ where n = 4 and standard deviations are shown

A reduction in temperature appears to increase phenanthrene sorption in river water, but reduce it in sea water, suggesting that the combination of a lower temperature and increased salinity minimise the effectiveness of the hydrophobic tail as a sorptive phase (Figure 5.17; Table 5.13). Section 4.2.2.3. also reveals that in sea water at 8°C HDTMA sorption is vastly reduced, therefore fewer sorption sites are available for phenanthrene.

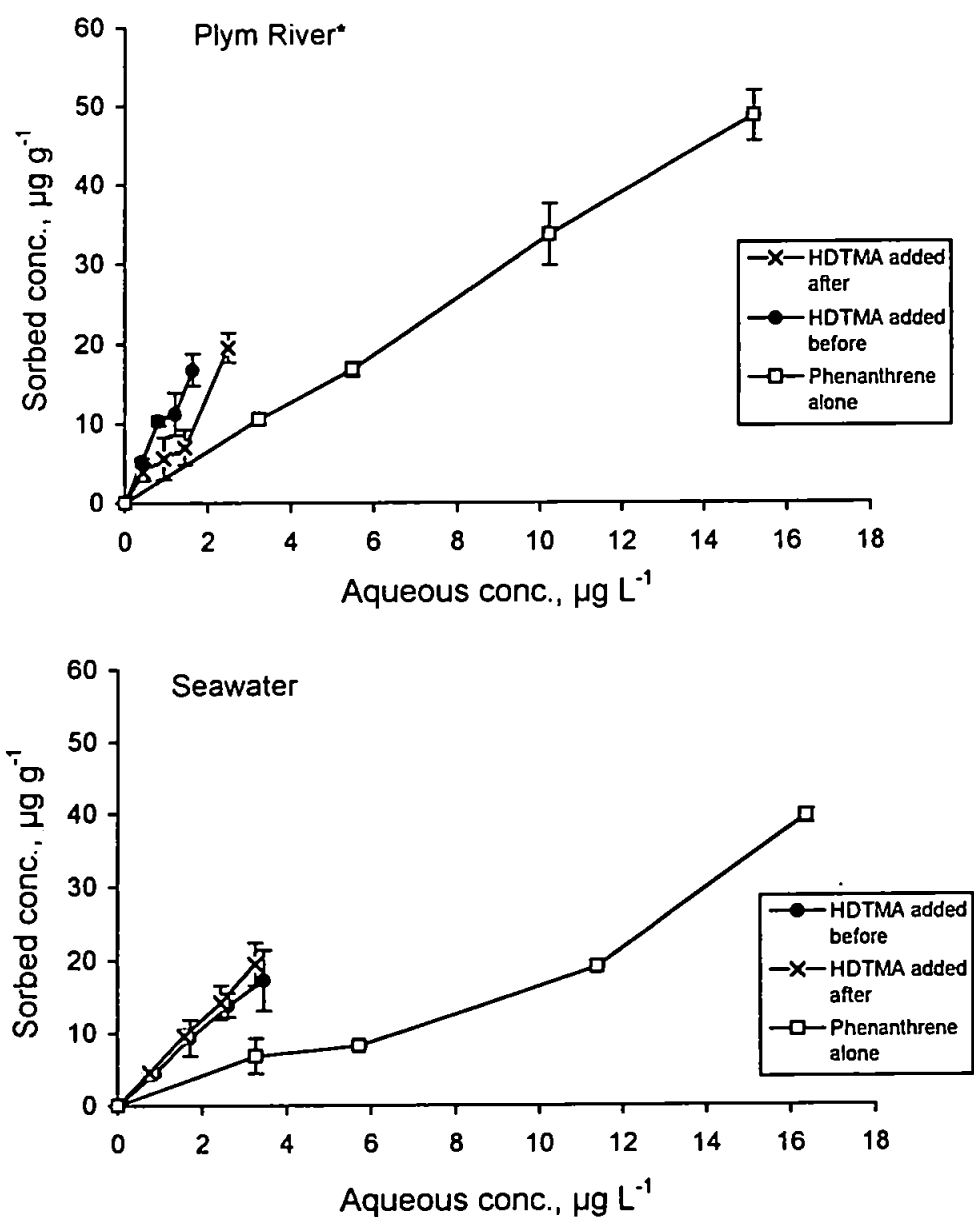


Figure 5.17: Sorption isotherms for phenanthrene with HDTMA at 8°C using Plym particles at an SPM concentration of 50 mg L⁻¹ where n = 4 and standard deviations are shown

* limited stock of ¹⁴C-phenanthrene prevented extension of isotherms with HDTMA

Table 5.13: Freundlich isotherm variables for phenanthrene with HDTMA derived from data fitting of Figure 5.17 using Plym particles with an SPM concentration of 50 mg L⁻¹ at 8°C .

Aqueous Matrix n = 4		<i>n</i>	<i>K_F</i> (L g ⁻¹)	<i>r</i> ²	P value
River	HDTMA added before	0.818	10.902	0.950	0.002
	HDTMA added after	0.896	6.729	0.872	0.066
	Phenanthrene alone	1.00	3.18	0.99	<0.001
Sea	HDTMA added before	0.996	5.207	0.995	<0.001
	HDTMA added after	0.989	6.019	0.999	0.003
	Phenanthrene alone	1.09	1.56	0.93	0.006

5.2.3 Particle Concentration Effect

The influence of surfactants on the particle concentration effect of HOMs has not previously been researched. In section 4.2.3, it was confirmed that all three surfactants display a PCE. The following section attempts to discover how this impinges on the PCE of phenanthrene. Possible influences include the following:

- (i) The flocculation or dispersion of particles may be affected which will in turn influence non-settling particles and available sorption sites for phenanthrene.
- (ii) Coating of particles by surfactants can enhance or reduce particle interactions or collisions by inducing attraction or repulsion
- (iii) The solubility of phenanthrene may be enhanced or reduced by the surfactants. This is likely to be highly dependent on contact sequence.
- (iv) The surfactant may affect the structure of DOM to enhance sorption or release of phenanthrene

Table 5.14 and Figure 5.18 display the effect of Triton X-100 on the PCE of phenanthrene in river and seawater at 8°C and 20°C. There appears to be very little difference between contact sequences at either temperature or matrix, suggesting that Triton X-100 does not compete successfully with phenanthrene for sorption sites, even

at low particle concentrations, nor does it influence particle behaviour such as flocculation or dispersion. As a result any effect it does have on phenanthrene sorption is likely to be due to solubilisation or adsolubilisation.

Temperature continues to play a significant role with regard to Triton X-100 behaviour and this has impinged on the PCE of phenanthrene, particularly for river and seawater at 8°C. Since the relative solubility of Triton X-100 is reduced at these temperatures (Figure 4.3; Section 4.1.1), it appears adsolubilisation of phenanthrene is taking place resulting in a more significant PCE. A similar process may also be occurring with increased salinity where the PCE for phenanthrene alone is less significant than with Triton X-100.

Table 5.14: Model parameters defining the particle concentration effect for phenanthrene in Triton X-100 in the Plym estuary derived from data fitting of Figure 5.18.

Compound	Matrix	a.10 ⁴	b	r ²	P value
River 20°C	Triton X-100 added before	5.37	0.63	0.968	0.016
	Triton X-100 added after	5.67	0.62	0.974	0.013
	Phenanthrene alone	4.79	0.73	0.966	<0.001
River 8°C	Triton X-100 added before	7.00	0.68	0.962	0.001
	Triton X-100 added after	8.36	0.74	0.979	0.019
	Phenanthrene alone	2.27	0.54	0.952	0.004
Sea 20°C	Triton X-100 added before	4.62	0.61	0.977	<0.001
	Triton X-100 added after	4.05	0.58	0.995	0.002
	Phenanthrene alone	2.89	0.54	0.866	0.007
Sea 8°C	Triton X-100 added before	5.92	0.62	0.990	<0.001
	Triton X-100 added after	6.91	0.62	0.982	0.001
	Phenanthrene alone	1.75	0.48	0.883	0.017

In contrast to Triton X-100, the contact sequence of SDS appears more important for both sorption isotherms and PCE (Table 5.15; Figure 5.19; Figure 5.21), where for river water, SDS added before phenanthrene reduces sorption, but generally, for seawater SDS added after phenanthrene increases sorption. This may be a case of competitive sorption in river water. Although the negatively charged SDS may be repelled by similarly charged particles, it still has a large hydrophobic component and may be attracted to DOC on the particle, reducing available sites for phenanthrene, or it may be more effectively solubilising phenanthrene before the PAH reaches the particles since overall, the sorption of phenanthrene is reduced with SDS than without it. With regard to seawater, the high ionic concentration has a shielding effect and this may encourage sorption of SDS to particles leading to possible adsorption or increased dispersion, both of which would increase phenanthrene sorption and the PCE.

Temperature has a rather unclear effect on SDS and phenanthrene behaviour. The relative solubility of SDS is greater at 8°C than 20°C. However this is not the case when particles are included, particularly in seawater, where the reverse is true. The reduced temperature apparently modifies the molecule such that the repelling negative charge of the particles is minimised. This may counteract the solubilising nature of SDS to provide some sorption sites on the hydrophobic region of the sorbed surfactant for phenanthrene. The strongest impact of SDS on the phenanthrene PCE can be seen in river water at 20°C where both PCE parameters are reduced, possibly due to effective solubilisation of the PAH.

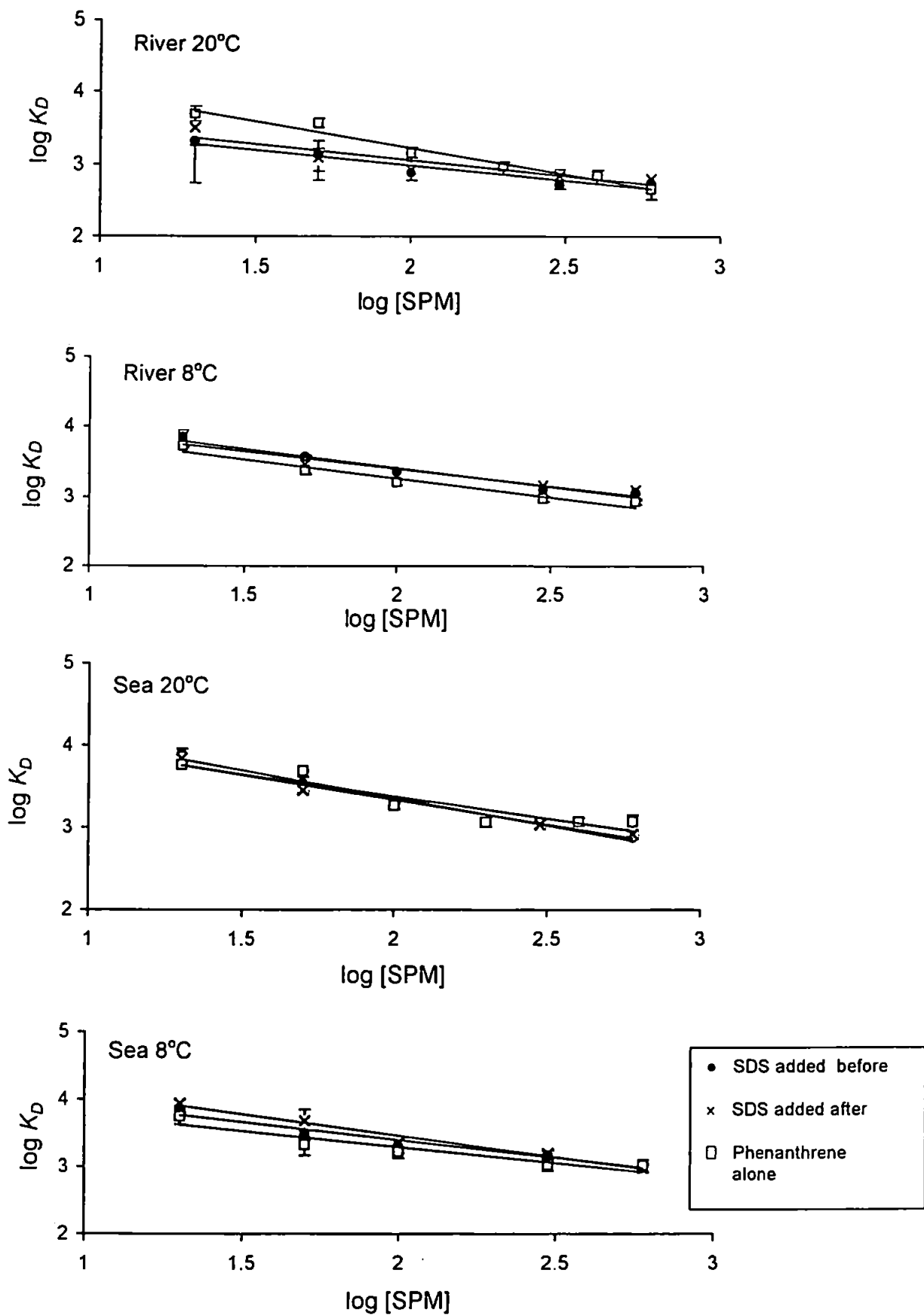


Figure 5.19: Partition coefficients as $\log K_D$ of phenanthrene as a function of particle concentration in Plym river water and seawater with SDS

Table 5.15: Model parameters defining the particle concentration effect for phenanthrene with SDS in the Plym estuary derived from data fitting of Figure 5.19.

Compound	Matrix	$a \cdot 10^4$	b	r^2	P value
River 20°C	SDS added before	0.67	0.41	0.907	0.012
	SDS added after	0.86	0.44	0.834	0.030
	Phenanthrene alone	4.79	0.73	0.966	<0.001
River 8°C	SDS added before	2.36	0.49	0.907	0.002
	SDS added after	3.28	0.55	0.968	0.012
	Phenanthrene alone	2.27	0.54	0.952	0.004
Sea 20°C	SDS added before	4.88	0.66	0.975	0.002
	SDS added after	3.44	0.60	0.968	0.002
	Phenanthrene alone	2.89	0.54	0.866	0.007
Sea 8°C	SDS added before	2.85	0.53	0.936	0.007
	SDS added after	5.51	0.64	0.973	0.002
	Phenanthrene alone	1.75	0.48	0.883	0.017

As expected HDTMA substantially increases phenanthrene sorption and therefore the PCE (Figure 5.20; Table 5.16). It is therefore thermodynamically more favourable for phenanthrene to partition into sorbed HDTMA. The contact sequence produces similar results whether HDTMA is added before or after phenanthrene, which indicates that the head on partitioning of HDTMA provides a surplus of sorption sites for phenanthrene. Furthermore, this suggests that the positively charged HDTMA is not encouraging flocculation of particles, and a subsequently reduced PCE for phenanthrene.

The reduced PCE in seawater may be due to shielding of the attractive forces between HDTMA and particles, leading to fewer sorption sites for phenanthrene and a greater chance of solubilisation since there are more HDTMA molecules in solution.

The relative solubility of HDTMA in river water is reduced at 8°C, leading to greater HDTMA sorption to particles and therefore greater phenanthrene sorption in river water. This is less clear in seawater, where with the inclusion of particles, HDTMA is more soluble at 8°C than 20°C. This is reflected in the lesser sorption of phenanthrene at the lower temperature.

CHAPTER 6: SUMMARY AND SIGNIFICANCE OF RESULTS

Frequently, data are incorporated into fate and transport models which have been calculated according to the physico-chemical properties of the HOM e.g. K_{ow} or solubility, rather than by empirical determination. This thesis has highlighted problems associated with such methods by demonstrating changes in PAH behaviour due to the co-existence of surfactants, coupled with variations in salinity, SPM and temperature (8°C and 20°C). To the author's knowledge, this is the first study which has systematically examined the sorption behaviour of a PAH together with surfactants at environmentally relevant concentrations and with the use of natural sediments.

The approach employed was laboratory based involving liquid scintillation counting originally designed for use with ^{14}C -labelled HOMs alone. This was successfully modified to both remove the need for mass balance calculations and to incorporate surfactants.

6.1 General observations

6.1.1 Phenanthrene

Owing to its moderate hydrophobicity and the use of environmentally realistic concentrations (1 to 20 $\mu\text{g L}^{-1}$), the aqueous solubility of phenanthrene was relatively unaffected by increased ionic concentration or temperature change. The removal of DOC only had a minor effect in seawater solubility experiments but was more important in river water. It may be that DOC in seawater is less suitable as a sorptive phase due to the effects of high ionic concentration.

The sorption of phenanthrene to estuarine sediment isotherms was fitted according to the Freundlich model. The generally nonlinear isotherms were thought to be due to sediment heterogeneity and multilayer sorption. The inclusion of particles enhanced a salting out effect, suggesting that the sediment was also salted out,

subsequently increasing sorption in seawater. However, as with the solubility isotherms, a reduction in temperature reduced this effect. Sorption was still shown to take place with removal of DOC and POC, but in contrast to solubility experiments, sorption actually increased in the case of seawater with OC removed. Reasons for this observation include enhanced salting out, since there was no DOC in the aqueous phase to increase phenanthrene solubility, or changes in particle properties such as increased dispersion. Alternatively, compression of the electrical double layer due to the high ionic concentration may have allowed the displacement of water dipoles from the particle surface by phenanthrene.

The particle concentration effect displayed by PAHs such as phenanthrene is well known, although, unlike more hydrophobic compounds, even with elevated SPM concentrations, the majority of phenanthrene remains in the aqueous phase (e.g. over 80% at SPM of 100 mg L^{-1}). However, this study revealed that the PCE can be modified by both temperature and water type, with the PCE being most significant at 20°C in river water.

6.1.2. Surfactants

With regard to the three surfactants, Triton X-100 was the first to be investigated, which proved to be soluble in all aqueous matrices tested with no evidence of salting out. However, the removal of DOC and reduced temperature inhibited solubility. SDS displayed slight salting out and reduced solubility with DOC removal. In contrast to Triton X-100, lower temperatures caused a small increase in SDS solubility. The reduced solubility of HDTMA in seawater compared with river water was not unexpected due to the combination of salting out of the large hydrophobic region, reinforced by the attraction of the positively charged hydrophilic region to the

negatively charged glass walls of the vessel. Solubility of HDTMA proved to be reduced further by removal of DOC and lower temperatures.

The inclusion of particles appeared to encourage salting out of Triton X-100. However, more surprisingly and contrary to the solubility isotherms, sorption was dramatically reduced at 8°C. It seems as attractive sorption sites, the particles may have enhanced the influence of temperature since the convex isotherm observed indicates competitive sorption. In river water at 20°C, sorbate-sorbate interactions, such as bilayer formation, were apparent whereas for seawater the enhanced initial sorption appeared to become competitive. This was because the high ionic concentration of seawater encouraged salting out of tails and therefore head out sorption so that bilayers could not be formed.

Sorption of SDS resulted in linear isotherms with similar Freundlich coefficients for river water and seawater, reflecting the relatively high solubility of SDS and indicating either non-specific interactions between the alkyl chains and hydrophobic sites or an abundance of equally suitable sorption sites. Reduced temperature enhanced SDS sorption in seawater possibly exacerbating a salting out effect. The removal of DOC/POC produced distinctly nonlinear isotherms indicating specific interactions between SDS and the few sorption sites available on the mineral followed by competitive sorption. HDTMA displayed enhanced sorption in seawater at 20°C, which appeared to be largely due to salting out and bilayer formation rather than merely an attraction between the positively charged surfactant and negatively charged particles, since sorption was much lower in river water. The reverse occurred at a lower temperature suggesting possible changes to the surfactant such as condensation of the nonpolar tail hindering bilayer formation. The removal of DOC/POC surprisingly appears to have had an opposing effect on sorption, therefore signifying that either hydrophobic bonding between the surfactant and organic matter was at least as

important as electrostatic interactions, or that adsorption of a positively charged surfactant onto negatively charged minerals encouraged flocculation of particles subsequently reducing available sorption sites.

All three surfactants investigated displayed a PCE, yet the extent of this varied widely according to experimental conditions. In terms of the aqueous fraction of the surfactants, which is a more environmentally relevant parameter and is established by manipulating parameters generated by the PCE, Triton X-100 remained largely dissolved in river water for example, approximately 86% was dissolved at 1000 mg L⁻¹ SPM. At 8°C the aqueous fraction actually increased as the SPM increased. Triton X-100 in seawater remained unaffected by SPM concentration, however, a reduction in temperature to from 20°C to 8°C resulted in increasing the aqueous fraction. Approximately 80% of SDS resided in the aqueous phase in all water types and was apparently unaffected by temperature or SPM concentration. In contrast, with regard to river water, the fraction of HDTMA in the aqueous phase water was significantly reduced with increasing SPM concentration to about 10% at 1000 mg L⁻¹ SPM. In seawater at 20°C HDTMA 20% was in the aqueous phase on the inclusion of particles at 20 mg L⁻¹ and was unaffected by further changes in SPM concentration, yet at 8°C the fraction in the aqueous phase was higher and reduced according to SPM concentration.

6.1.3. Phenanthrene in the presence of surfactants

The influence of surfactants on phenanthrene partitioning was highly variable, as displayed in Figure 6.1 which, as an overview, compares the behaviour of phenanthrene in the presence of surfactants with that of phenanthrene alone. This diagram reveals that an understanding of how surfactants behave in isolation is insufficient to predict changes in phenanthrene sorption due to the co-existence of these compounds.

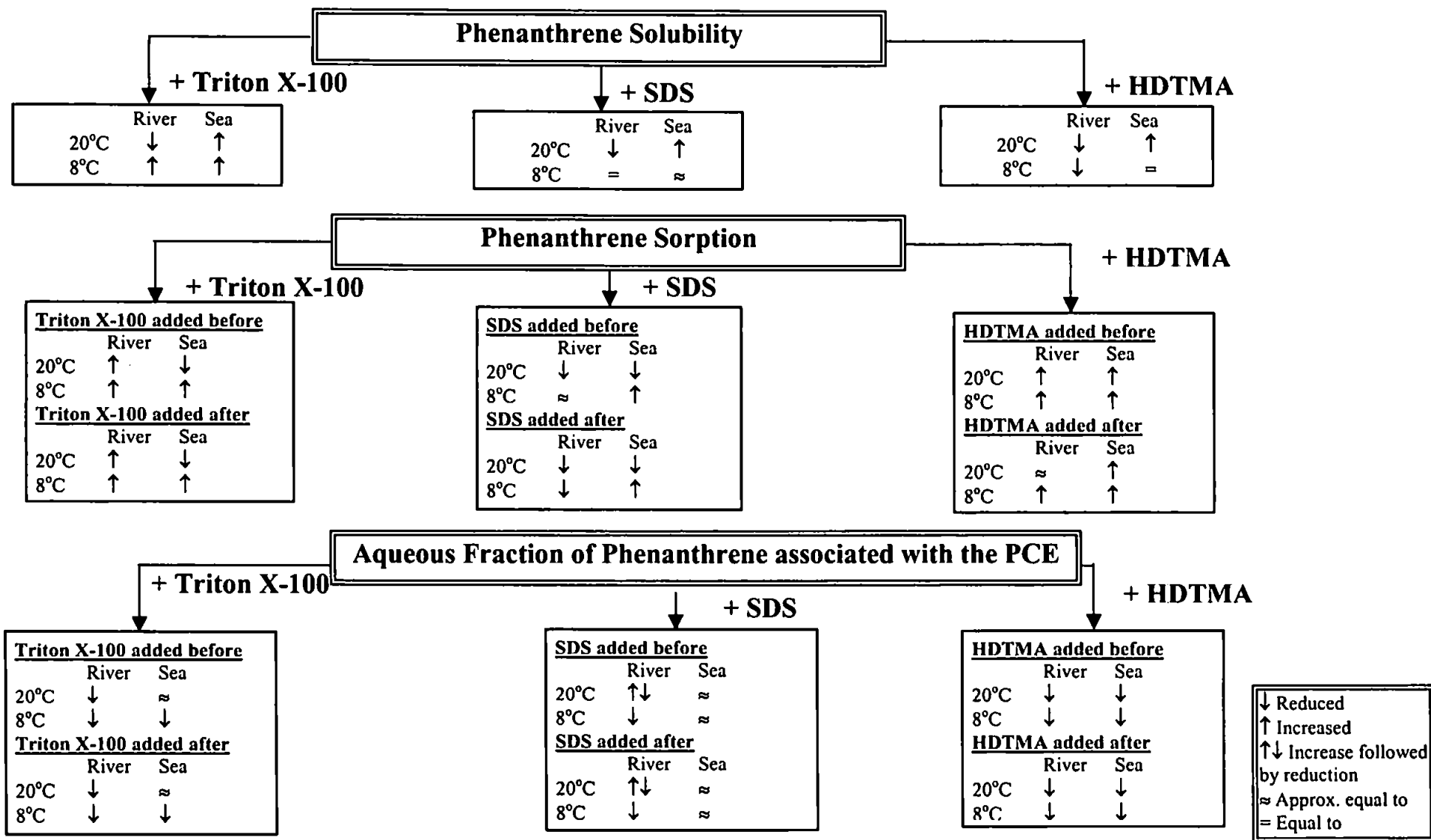


Figure 6.1 : A summary of the influence of surfactants on phenanthrene behaviour compared to phenanthrene alone

Regarding the effect of surfactants on phenanthrene solubility, Triton X-100 had only a small influence, producing a slight increase in seawater solubility contrasted by a slight decrease in river water solubility. A reduction in temperature to 8°C enhanced phenanthrene solubility, comparable to levels at 20°C. SDS had a minimal impact on phenanthrene solubility displaying a small increase in seawater and a reduction in river water, although unlike Triton X-100, this was unaffected by temperature. The insignificant effect of HDTMA on phenanthrene solubility was unexpected, since it was likely to form a hydrophobic layer on the negatively charged glass walls via head-on sorption. The hydrophobic tails would then be available as sorption sites for phenanthrene. As displayed in Figure 6.1, although there was a reduction in solubility for phenanthrene in river water, solubility in seawater actually increased. A reduction in temperature to 8°C minimised the influence of the surfactant further to produce a solubility similar to that of phenanthrene alone.

Even with the inclusion of particles, Triton X-100 had no great effect on phenanthrene sorption in river water, but, in accordance with the solubility isotherms, slightly reduced sorption in seawater. Generally, the impact of Triton X-100 on phenanthrene behaviour at 20°C was minimal, whereas reduced temperature had a more dramatic effect, particularly in seawater, by substantially enhancing phenanthrene sorption, compared to that of phenanthrene alone. Since values for phenanthrene in a Triton X-100 system at 8°C and 20°C were similar, it appears that the influence of temperature on phenanthrene alone is negated by the inclusion of this surfactant, perhaps providing thermodynamically favourable sorption sites. Since there was also no significant difference between contact sequences this suggests that modifications to particulate organic matter such as a reduction in tortuosity to enhance sorption, or a blockage of available sites by Triton X-100, did not take place.

The sorption of phenanthrene within an SDS system was reduced in both river and seawater, with SDS added before phenanthrene inhibiting sorption the most. Since generally $n > 1$, the initial uptake of phenanthrene may have been by monomers or dimers in the aqueous phase which is thermodynamically favourable. Once the sites within the surfactant molecules were occupied, adsolubilisation would take place leading to a concave isotherm. For seawater, where SDS was added after phenanthrene, $n < 1$ possibly indicating competitive sorption due to salting out of SDS. At 8°C in seawater, sorption is elevated. Since SDS sorption is increased at this temperature, adsolubilisation was a likely cause.

HDTMA, when added prior to phenanthrene in river water, had the effect of enhancing phenanthrene sorption, which was expected as a result of the surfactant's head on sorption leading to an increase in suitable sorption sites. Additional sorption did not initially appear to take place when HDTMA was added after phenanthrene although $n > 1$, hence sorption was enhanced according to increasing phenanthrene concentration. The overall sorption for the contact sequences were similar in seawater. A lower temperature had the effect of increasing phenanthrene sorption in river water, but reducing it in seawater, suggesting that the combination of a lower temperature and increased salinity minimised the effectiveness of the hydrophobic tail as a sorptive phase. As a result, since HDTMA sorption is vastly reduced in seawater at 8°C, fewer sorption sites were available for phenanthrene.

While phenanthrene with Triton X-100 displayed a PCE, Figure 6.1 indicates no obvious difference in the fraction of phenanthrene in the aqueous phase between contact sequences, temperature or water type. This suggests that Triton X-100 did not influence particle interactions such as flocculation or dispersion. Model parameters defining the PCE highlight the important role of temperature in river water, where, as the solubility of Triton X-100 is reduced at 20°C, it appears increasing adsolubilisation of

phenanthrene when compared to phenanthrene alone. The reverse was apparently true in seawater, however, overall in both water types, phenanthrene sorption was increased with the inclusion of Triton X-100.

Phenanthrene with SDS also exhibited a PCE, but by far the most profound influence was in river water, where the fraction dissolved was strongly dependent on temperature. The reduced temperature apparently modified the SDS molecule such that the repelling negative charge of the particle was minimised with SDS subsequently providing sorption sites for phenanthrene. The strongest impact of SDS on the PCE of phenanthrene was seen in river water at 20°C where both PCE parameters were reduced, possibly due to effective solubilisation of the PAH. This effect was not seen in seawater where SDS had a minimal influence.

The increase of the PCE for phenanthrene with HDTMA in river water was expected leading to a large reduction in the dissolved fraction. Since the contact sequences produced similar results (Figure 6.1), a surplus of sorption sites were therefore available for phenanthrene with the possibility of particle flocculation unlikely. The reduced PCE in seawater may have been due to shielding of the attractive forces between HDTMA and particles, leading to fewer sorption sites for phenanthrene and a greater chance of solubilisation.

6.2. Environmental Implications

The general observations above reveal the complex behaviour of surfactants and HOMs in natural waters both when alone and when co-disposed. The effect of temperature and salinity on the relative solubility of phenanthrene and surfactants was often in contrast to the effect of these variables with the inclusion of particles. Therefore, changes in solubility alone, while providing a useful insight into compound characteristics, are

insufficient for predicting compound behaviour in estuaries where suspended particles are present.

6.2.1. Phenanthrene

The environmentally realistic concentrations of phenanthrene employed coupled with its moderate hydrophobicity, appeared to mask the typical trends displayed by PAHs. Slight salting out was evident where the sorption of phenanthrene to particles in seawater was greater than in river water. As a result phenanthrene may be trapped within sediments should it encounter more saline waters. This effect maybe enhanced with an increase in SPM concentration, although, unlike more hydrophobic HOMs, even at SPM concentrations of 1000 mg L^{-1} , over 50% of the compound is predicted to remain in the aqueous phase. Somewhat surprisingly, temperature change from 20°C to 8°C proved to be important for phenanthrene in seawater by significantly reducing sorption. Therefore, in winter the saline intrusion may not always be an effective pollutant trap for HOMs and of more concern, a build up of sorbed HOMs may be re-released into the water column.

6.2.2. Surfactants

The behaviour of surfactants under changing experimental conditions was highly complex. Triton X-100 sorption in seawater was unaffected by a change in SPM concentration, therefore even in highly turbid areas Triton X-100 would remain largely in the aqueous phase. Winter conditions would enhance this solubility further, potentially favouring the transport of Triton X-100 along increased distances.

Since SDS remained extremely soluble with sorption unaffected by changes in temperature, salinity or particle concentration, it is also unlikely to be effectively removed by physico-chemical estuarine processes and may be transported for long

distances unless biodegraded. In contrast, as expected, HDTMA displayed high sorption overall even at low SPM concentrations. Therefore, a discharge of HDTMA is likely to stay close to the source, possibly accumulating up to a point where the negative charge of some particles may be overcome resulting in a net positive charge, which has implications for particle behaviour such as increased flocculation and adsorption of "-"ve charged contaminants. This effect was reduced, however, by lowering the temperature, which decreased HDTMA sorption. Since sorbed cationic surfactants such as HDTMA are often resistant to biodegradation, they may be released back into the water column in winter conditions.

6.2.3. Phenanthrene in the presence of surfactants

The inclusion of surfactants even at such a low concentration (2.5 mg L^{-1}) modified phenanthrene behaviour, with variations according to temperature, particle concentration and salinity (Figure 6.1). The addition of Triton X-100 with phenanthrene demonstrated no significant difference between contact sequence at either temperature or water type indicating no competition for sorption sites and no flocculation or dispersion taking place. However, adsolubilisation of phenanthrene did occur with in river water at 20°C . Cooler temperatures minimised this effect due to the increased solubility of Triton X-100. Therefore, in an environmental scenario, the presence of Triton X-100 would encourage sorption and possibly accumulation of phenanthrene on particles during summertime, only to be re-released at potentially much higher concentrations in winter when Triton X-100 becomes more soluble. In seawater the solubility of phenanthrene was reduced by the addition of Triton X-100 at both temperatures, however the maximum difference compared with phenanthrene alone in the aqueous phase was only 5%, therefore salinity had the stronger influence. As a

result, in areas of high ionic concentration, phenanthrene is more likely to be salted out and therefore effectively trapped, than adsorbed by Triton X-100.

The incorporation of SDS with phenanthrene in both river water and seawater displayed slightly higher sorption with SDS added after phenanthrene, therefore the time at which these two pollutants should meet in a waste stream will have implications for phenanthrene transport. Overall, however, SDS reduces phenanthrene sorption and therefore may increase the distance travelled to a more pristine environment unless both increased salinity and reduced temperatures are encountered (Figure 6.1).

HDTMA had the strongest ability to remove phenanthrene from the aqueous phase. Although no effects owing to contact sequence or temperature in river water were displayed, the overall significant reduction, even at low SPM indicated effective, potentially long term, adsorption was taking place. The extent of sorption with HDTMA in river and seawater was similar, so sorption due to the surfactant rather than salting out could be regarded as the main influence. In seawater however, there was a difference between HDTMA added before and after phenanthrene, with greatest sorption occurring with HDTMA added before. Therefore, should both compounds be discharged simultaneously at any point within an estuary, phenanthrene would be immobilised. Furthermore, if the sediments were contaminated with a cationic surfactant such as HDTMA prior to coming into contact with phenanthrene, the effect would be even more substantial.

Considering the extremely low concentrations of surfactants employed and the moderate hydrophobicity of phenanthrene, the results suggest that the influence of surfactants existing in the presence of HOMs in natural waters must be taken into account. Despite the variation in particle concentration effects displayed by the surfactants, as a rule they appear to exaggerate the PCE of phenanthrene. This effect is then enhanced or minimised by temperature change (i.e., seasonal) and time of contact,

which has important environmental implications with regard to removal or release of compounds stored within sediments. However, overall, at these levels the surfactants generally seem to enhance sorption, rather than solubility with HDTMA proving to be the most effective surfactant at removing phenanthrene from the aqueous phase.

6.3. Future Work

Four key suggestions for further work have been identified as follows:

- (1) Phenanthrene was chosen as the HOM to study owing to its well-defined environmental and chemical properties. However, in order to enhance an understanding of how surfactants affect hydrophobic compounds more generally, other PAH compounds could be investigated such as benzo[a]pyrene, pyrene or naphthalene. Furthermore, a larger range of concentrations may be examined in order to replicate both acute and chronic inputs.
- (2) A more comprehensive examination of the influence of environmental variables such as sediment type would be beneficial for pollutant transport models, in addition to characterisation of DOC and POC and their influence on the behaviour of HOMS and surfactants.
- (3) In addition, an investigation into potential synergistic effects of combinations of chemicals is necessary. For example Guha *et al.* (1998) found the solubility enhancement of naphthalene in Triton X-100 was slightly reduced in the presence of phenanthrene and/or pyrene. This highlights the difficulties in dealing with complex, mixed waters and heterogeneous particles.
- (4) A further extension of this work would be to establish how the surfactants influence uptake of HOMs by surrounding flora and fauna, since an increase in the dissolved phase due to solubilisation by surfactants does not necessarily mean the HOM is more bioavailable and able to enter the foodchain.

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GLOSSARY

ABS: alkyl benzene sulphonate, an anionic surfactant (Section 1.4.2.).

Adsolubilisation: the partitioning of a compound into a surface sorbed surfactant

AE: polyoxyethylenated straight chain alcohol or alcohol polyethoxylate, a nonionic surfactant (Section 1.4.1.).

AES: alkyl ethoxylate sulphate, an anionic surfactant (Section 1.4.2.).

AOS: α -olefine sulphonate, an anionic surfactant (Section 1.4.2.).

APE: polyoxyethylenated alkylphenol also known as alkylphenol polyethoxylate, a nonionic surfactant (Section 1.4.1.).

AS: alkyl sulphate, an anionic surfactant (Section 1.4.2.).

ATMAC: alkyltrimethyl ammonium chloride, a cationic surfactant (Section 1.5.3.).

Cloud point: temperature at which nonionic surfactants above the critical micelle concentration become turbid.

CMC: critical micelle concentration, the narrow concentration range at which surfactants form micelles (Section 1.4.4.).

DADMAC: dialkyl dimethylammonium chloride, a cationic surfactant (Section 1.4.3.).

DOC: dissolved organic carbon

DOM: dissolved organic matter.

DTDMAC: ditallow dimethyl ammonium chloride, a cationic surfactant (Section 1.4.3.).

EO: ethylene oxide, generally found as the hydrophilic region of the nonionic surfactant type APE or AE (Section 1.4.1.).

HDTMA: hexadecyltrimethylammonium usually with bromide, chloride or iodide counterion, a quaternary ammonium compound type cationic surfactant (Section 1.4.3.).

Hydrophobic: a 'water-hating' substance.

Hydrophobic organic micropollutant, HOM: a 'water-hating' organic compound detected at sub-micron concentrations in the environmental matrices.

Hydrophilic: a 'water-loving' substance.

K_D : particle-water partition coefficient (Section 1.3.2.).

K_F : Freundlich coefficient (Section 1.3.2.)

K_H : Henry's law constant (Section 1.3.1.).

K_m : micelle-water partition coefficient (Section 1.6.).

K_{oc} : organic carbon normalised partition coefficient (Section 1.3.2.).

K_{ow} : *n*-octanol-water partition coefficient (Section 1.2.).

K_s : Setschenow constant describing the salting out effect of an organic compound according to salinity (section 1.3.2.).

Krafft point: the temperature at which surfactant monomer solubility is equal to the critical micelle concentration (Section 1.4.4.)

LAS: linear alkyl benzene sulphonate, an anionic surfactant (Section 1.4.2.).

LPAS: linear primary alkyl sulphate, an anionic surfactant (Section 1.4.2.)

Micelle: an aggregation of tens or hundreds of monomers forming a hydrophobic core and hydrophilic exterior.

NP: nonylphenol, frequently found as the degradation product of the nonionic surfactant nonylphenol polyethoxylate (NPE) (Section 1.4.1.).

NPE: nonylphenol polyethoxylate, a nonionic surfactant (Section 1.5.3).

OM: organic matter.

OP: octylphenol, frequently found as the degradation product of the nonionic surfactant octylphenol polyethoxylate (OPE) (Section 1.5.3.).

OPE: octylphenol polyethoxylate, a nonionic surfactant (Section 1.5.3).

PAH: polycyclic aromatic hydrocarbon, organic compounds which comprise of two or more fused benzene rings, occasionally occur naturally although primary source is as a by-product of fossil fuel combustion.

PCB: polychlorinated biphenyl, aromatic chlorinated hydrocarbons produced commercially by the direct chlorination of biphenyl.

PCE: particle concentration effect

POC: particulate organic carbon

POM: particulate organic matter

QAC: quaternary ammonium compound, cationic surfactant (Section 1.4.3.).

SDS: sodium dodecyl sulphate, an alkyl sulphate type anionic surfactant (Section 1.4.2.).

Setschenow constant: a quantitative description of the 'salting out' effect of an organic compound (Section 1.3.2.).

Solubilisation: partitioning of a compound into surfactant molecules in the aqueous phase

SOM: sediment organic matter.

SPM: suspended particulate matter.

T_k : Krafft point (Section 1.4.4.).

Triton X-100: a nonionic surfactant of the octylphenol polyethoxylate type with an average 9.5 ethylene oxide units.

X: dissolved fraction

APPENDICES

APPENDIX A: GENERATED DATA

A1: Method Evaluation Data

A2: Relative Solubility Data

A3: Particle-Water Interaction Data – Kinetics

A4: Particle-Water Interaction Data – Sorption

A5: Particle-Water Interaction Data – Particle Concentration Effect

APPENDIX B: PUBLICATION

Turner, A., Hyde, T. L. & Rawling, M.C. (1999) Transport and retention of hydrophobic organic micropollutants in estuaries: implications of the particle concentration effect. *Estuarine, Coastal and Shelf Science*. **49**, 733-746.

APPENDIX A: GENERATED DATA

A1: Method Evaluation Data

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A3: Particle-Water Interaction Data – Kinetics

A4: Particle-Water Interaction Data – Sorption

A5: Particle-Water Interaction Data – Particle Concentration Effect

Appendix A1: Method Evaluation Data

Table A1.1: Radio-thin layer chromatography data for phenanthrene, SDS and HDTMA

Distance (mm)	Phenanthrene		SDS		HDTMA	
	Stock	Rinse DPM.10 ³	Stock	Rinse DPM.10 ³	Stock	Rinse DPM.10 ³
2	189.4	56.08	82.91	19.82	0.05	0.02
4	99.19	1.77	43.43	24.81	0.13	0.02
6	26.37	4.88	86.72	27.39	0.33	0.09
8	24.45	0.00	129.1	19.71	1.42	0.13
10	22.29	3.88	256.2	29.80	139.3	0.37
12	30.35	0.00	320.4	17.76	135.8	5.08
14	48.71	0.00	853.1	45.62	34.92	3.63
16	58.28	0.00	6694	129.5	0.22	0.07
18	29.49	2.32	19845	1702	0.09	0.03
20	27.52	1.68	1234	398.3	0.07	0.02
22	27.28	0.00	40.93	21.13	0.06	0.02
24	25.47	0.00	40.14	20.25	0.05	0.02
26	24.33	0.00	30.45	17.74	0.03	0.02
28	21.42	0.00	23.44	18.93	0.12	0.02
30	24.84	0.00	22.94	20.57	0.03	0.02
32	35.68	0.07	20.76	17.31	0.03	0.02
34	224.8	2.39	21.78	15.81	0.03	0.02
36	2426	30.97	20.14	17.99	0.02	0.02
38	7801	66.56	20.30	17.96	0.02	0.02
40	28313	401.8	18.57	18.79	0.03	0.02
42	18862	290.5	23.30	19.22	0.05	0.07
44	14223	75.24	20.15	17.91	0.05	0.06
46	2230	40.52	26.72	23.67	0.08	0.11
48	368.2	14.48	19.16	19.74	0.08	0.05
50	66.49	5.16	33.92	19.34	0.05	0.04
52	30.99	0.00	34.27	22.07	0.04	0.02
54	25.41	0.00	17.19	25.54		
56	56.92	0.00	18.93	20.87		
58	41.21	0.00				
60	61.63	0.00				
62	22.68	1.61				
64	21.68	0.00				
66	24.38	0.00				
68	19.88	0.00				
70	17.26	0.00				
74	26.02	3.02				
78	23.52	1.78				
82	19.62	1.62				
86	29.92	0.00				
90	23.67	0.00				

A1.2: Volatilisation of phenanthrene during evaporation of hexane

Time (mins)	Recovered phenanthrene (%) $\bar{x} \pm SD$
0	100 \pm 1
5	103 \pm 2
10	99 \pm 1
20	85 \pm 1
30	81 \pm 2

A1.3: Recovery of phenanthrene as a function of added compound mass

Mass of phenanthrene (μg)	Recovered phenanthrene (%) $\bar{x} \pm SD$
0.03	93 \pm 3
0.08	97 \pm 2
0.16	95 \pm 5
0.32	88 \pm 2

A1.4: The influence of air-water transfer of phenanthrene on mass balance determinations of K_D

SPM Concentration (mg L^{-1})	Sea covered	River covered	Sea uncovered	River uncovered
	K_D (mL g^{-1}) $\bar{x} \pm SD$			
50	4922 \pm 186	3780 \pm 1111	10900 \pm 1174	11400 \pm 1155
100	1844 \pm 143	1437 \pm 189	6300 \pm 1030	5500 \pm 352
300	1166 \pm 86	919 \pm 146	2900 \pm 127	2400 \pm 300
600	1185 \pm 213	707 \pm 82	1200 \pm 300	1300 \pm 54

A1.5: Aqueous concentration of phenanthrene as a function of particle concentration in covered tubes

SPM Concentration (mg L^{-1})	Aqueous concentration of phenanthrene ($\mu\text{g L}^{-1}$) $\bar{x} \pm SD$
20	8.17 \pm 0.55
50	4.90 \pm 0.23
100	3.94 \pm 0.08
300	3.56 \pm 0.15
600	3.27 \pm 0.06

A1.6: Recovery of phenanthrene from each step in modified method (I) using Plym sediment at an SPM of 50 mg L⁻¹. Particle 1 denotes the ethanol rinse and particle 2 the hexane rinse

Fraction	Added mass of phenanthrene ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$			
	2.3	5.8	8.2	14
Aqueous	85.76 \pm 0.79	83.50 \pm 0.94	94.31 \pm 1.30	83.43 \pm 0.30
Wall	1.01 \pm 0.18	1.17 \pm 0.18	0.80 \pm 0.13	0.63 \pm 0.01
Particle 1	7.65 \pm 0.05	7.62 \pm 0.27	7.53 \pm 0.31	7.47 \pm 0.37
Particle 2	0.10 \pm 0.04	0.19 \pm 0.10	0.10 \pm 0.01	0.13 \pm 0.05

A1.7: Variation in phenanthrene recovery as a function of particle concentration using Plym sediment

SPM concentration (mg L ⁻¹)	Phenanthrene recovered (%) $\bar{x} \pm \text{SD}$	
	River	Sea
20	95.97 \pm 3.36	99.20 \pm 4.00
50	93.45 \pm 3.14	97.26 \pm 3.84
100	97.56 \pm 1.56	99.21 \pm 5.44
300	96.41 \pm 2.59	104.61 \pm 1.14
600	94.14 \pm 0.75	100.93 \pm 4.69

A1.8: Variability between phase separation methods with increasing SPM using Plym sediment and river water

SPM concentration (mg L ⁻¹)	K_D (mL g ⁻¹) $\bar{x} \pm \text{SD}$	
	Settled	Centrifuged
50	3239 \pm 595	3358 \pm 559
100	599 \pm 10	914 \pm 6
300	532 \pm 203	573 \pm 110
600	106 \pm 1	103 \pm 4

A1.9: Sorption of phenanthrene to Plym sediment (50 mg L⁻¹) in river water with and without HgCl₂

Aqueous Conc. ($\mu\text{g L}^{-1}$)	Without HgCl ₂		With HgCl ₂	
	Sorbed Conc. ($\mu\text{g g}^{-1}$) $\bar{x} \pm \text{SD}$		Aqueous Conc. ($\mu\text{g L}^{-1}$)	Sorbed Conc. ($\mu\text{g g}^{-1}$) $\bar{x} \pm \text{SD}$
2.32	9.65 \pm 2.50		2.35	8.31 \pm 1.13
4.08	10.83 \pm 0.76		4.04	10.74 \pm 1.57
6.50	16.87 \pm 0.24		6.54	16.19 \pm 1.87

A1.10 Sorption of phenanthrene to Plym sediment (50 mg L⁻¹) in a river water-SDS system (2.5 mg L⁻¹) with and without HgCl₂

Without HgCl ₂		With HgCl ₂	
Aqueous Conc. (µg L ⁻¹)	Sorbed Conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous Conc. (µg L ⁻¹)	Sorbed Conc. (µg g ⁻¹) $\bar{x} \pm SD$
1.54	18.87 ± 0.74	2.38	1.26 ± 1.31
3.39	31.32 ± 2.54	4.50	7.30 ± 2.99
6.23	39.90 ± 11.32	7.41	14.34 ± 2.93
10.61	32.92 ± 6.29	11.07	23.10 ± 4.76

Appendix A2: Relative Solubility Data

A2.1: Relative solubility data for phenanthrene in Milli Q, Plym river water and seawater at 20°C

Total conc. (µg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)
1.60	1.42 ± 0.11	1.38	1.22 ± 0.10	1.60	1.48 ± 0.03	1.60
4.01	3.84 ± 0.09	3.44	3.16 ± 0.15	4.01	3.87 ± 0.09	4.01
8.02	7.50 ± 0.39	6.90	7.09 ± 0.27	8.02	7.46 ± 0.16	8.02
16.03	14.07 ± 0.35	13.79	13.56 ± 0.70	16.03	12.32 ± 1.53	16.03

A2.2: Relative solubility data for phenanthrene in Milli Q, Plym river water and seawater at 8°C

Total conc. (µg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)
2.25	2.08 ± 0.10	1.97	1.67 ± 0.07	1.13	0.97 ± 0.03	1.13
4.50	4.18 ± 0.03	4.92	4.43 ± 0.18	2.26	1.97 ± 0.03	2.26
6.75	6.32 ± 0.10	6.89	6.11 ± 0.38	3.39	3.04 ± 0.14	3.39
9.00	8.48 ± 0.14	9.84	8.66 ± 0.42	4.52	4.01 ± 0.13	4.52

A2.3: Relative solubility data for phenanthrene in Plym river water and seawater with DOC removed

Total conc. (µg L ⁻¹)	River		Sea	
	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹) $\bar{x} \pm SD$	Total conc. (µg L ⁻¹)
0.95	0.76 ± 0.06	2.37	2.05 ± 0.10	2.05 ± 0.10
2.34	2.03 ± 0.06	4.74	4.12 ± 0.39	4.12 ± 0.39
9.34	7.91 ± 0.11	7.10	6.60 ± 0.09	6.60 ± 0.09
14.02	11.78 ± 0.20	14.21	12.82 ± 0.82	12.82 ± 0.82

A2.4: Relative solubility data for Triton X-100 in Milli Q, Plym river and seawater at 20°C

Total conc. (mg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$		$\bar{x} \pm SD$	
54	64.67 ± 1.15	54	42.00 ± 2.07	54	33.00 ± 1.00	
107	95.73 ± 0.46	107	79.33 ± 1.15	107	82.67 ± 6.11	
214	177.20 ± 0.69	214	168.67 ± 3.05	214	170.67 ± 2.31	
321	263.60 ± 5.56	321	264.67 ± 3.06	321	274.67 ± 6.11	

A2.5: Relative solubility data for Triton X-100 in Milli Q, Plym river and seawater at 8°C

Total conc. (mg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$		$\bar{x} \pm SD$	
25	14.6 ± 0.85	25	19.07 ± 1.62	25	6.20 ± 0.28	
50	33.47 ± 0.92	50	33.47 ± 1.40	50	20.80 ± 1.44	
80	53.07 ± 0.46	80	54.27 ± 1.28	80	40.27 ± 3.95	
100	70.80 ± 1.44	100	72.13 ± 1.62	100	60.70 ± 0.28	

A2.6: Relative solubility data for Triton X-100 in Plym river water and seawater with DOC removed

Total conc. (mg L ⁻¹)	River		Sea	
	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$	
25	18.27 ± 1.22	25	20.40 ± 3.46	
50	36.00 ± 1.44	50	36.27 ± 0.46	
80	57.87 ± 0.23	80	58.93 ± 2.54	
100	79.87 ± 2.27	100	76.80 ± 1.6	

A2.7: Relative solubility data for SDS in Milli Q, Plym river and seawater at 20°C

Total conc. (µg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$		$\bar{x} \pm SD$	
2.74	2.63 ± 0.38	2.74	2.22 ± 0.00	2.74	1.93 ± 0.00	
5.79	5.92 ± 0.30	5.49	4.53 ± 0.13	5.49	4.05 ± 0.35	
38.44	38.39 ± 2.29	35.65	32.54 ± 2.24	35.65	32.26 ± 2.24	
76.87	66.56 ± 1.49	71.31	62.45 ± 3.93	71.31	57.00 ± 3.9	
1250	1160 ± 160	1250	1150 ± 10	1250	1020 ± 10	
2500	2310 ± 16	2500	2270 ± 40	2500	2500 ± 410	

A2.8: Relative solubility data for SDS in Milli Q, Plym river and seawater at 8°C

Total conc. ($\mu\text{g L}^{-1}$)	Milli-Q		River		Sea	
	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)
	$\bar{x} \pm \text{SD}$		$\bar{x} \pm \text{SD}$		$\bar{x} \pm \text{SD}$	
1.10	0.99 ± 0.08	2.76	2.08 ± 0.00	1.10	0.85 ± 0.10	
2.76	2.51 ± 0.11	5.51	4.18 ± 0.86	2.76	2.42 ± 0.03	
6.89	6.49 ± 0.09	8.27	6.32 ± 2.42	6.89	6.20 ± 0.10	
13.78	12.99 ± 0.36	11.02	8.48 ± 4.20	13.78	12.99 ± 0.14	
1250	1372 ± 442	1250	1281 ± 11	1250	1056 ± 52	
2500	2636 ± 186	2500	2558 ± 40	2500	2304 ± 37	

A2.9: Relative solubility data for SDS in Plym river water and seawater with DOC removed

Total conc. (mg L^{-1})	River		Sea	
	Aqueous conc. (mg L^{-1})	Total conc. (mg L^{-1})	Aqueous conc. (mg L^{-1})	Total conc. (mg L^{-1})
	$\bar{x} \pm \text{SD}$		$\bar{x} \pm \text{SD}$	
1.25	1.41 ± 0.05	2.50	1.83 ± 0.08	
3.12	2.54 ± 0.04	6.25	4.80 ± 0.05	
6.25	5.29 ± 0.44	9.37	7.21 ± 0.28	
15.63	12.10 ± 0.30	15.62	9.72 ± 0.04	

A2.10: Relative solubility data for HDTMA in Milli Q, Plym river and seawater at 20°C

Total conc. ($\mu\text{g L}^{-1}$)	Milli-Q		River		Sea	
	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)
	$\bar{x} \pm \text{SD}$		$\bar{x} \pm \text{SD}$		$\bar{x} \pm \text{SD}$	
50	27.26 ± 9.66	50	26.66 ± 18.10	50	21.80 ± 20.11	
500	433.4 ± 9.6	500	353.8 ± 17.2	500	431.3 ± 60.6	
1250	1061 ± 29	1250	922.9 ± 22.6	1250	775.4 ± 238.9	
2500	1837 ± 11	2500	1616 ± 98	2500	1369 ± 287	

A2.11: Relative solubility data for HDTMA in Milli Q, Plym river and seawater at 8°C

Total conc. ($\mu\text{g L}^{-1}$)	Milli-Q		River		Sea	
	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$)	Total conc. ($\mu\text{g L}^{-1}$)
	$\bar{x} \pm \text{SD}$		$\bar{x} \pm \text{SD}$		$\bar{x} \pm \text{SD}$	
100	67.35 ± 14.10	100	64.49 ± 27.42	100	47.66 ± 5.91	
500	336.3 ± 23.9	500	266.3 ± 18.1	500	268.4 ± 10.6	
1250	843.5 ± 75.7	1250	688.9 ± 28.4	1250	457.5 ± 65.7	
2500	1489 ± 16	2500	1365 ± 99	2500	720.8 ± 19.4	

A2.12: Relative solubility data for HDTMA in Plym river water and seawater with DOC removed

Total conc. (mg L ⁻¹)	River		Sea	
	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)	Aqueous conc. (mg L ⁻¹)	Total conc. (mg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$	
0.50	0.31 ± 0.01	0.50	0.085 ± 0.024	
1.25	0.71 ± 0.04	1.25	0.32 ± 0.02	
3.12	1.40 ± 0.06	3.12	0.45 ± 0.03	
6.25	1.60 ± 0.12	6.25	0.74 ± 0.10	

A2.13: Relative solubility data for phenanthrene in Milli Q, Plym river water and seawater modified with Triton X-100 at 20°C

Total conc. (µg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$		$\bar{x} \pm SD$	
2.87	2.70 ± 0.03	2.87	2.50 ± 0.12	2.84	2.65 ± 0.12	
5.75	5.75 ± 0.09	5.75	5.09 ± 0.11	5.68	5.53 ± 0.17	
8.62	8.62 ± 0.62	8.62	8.01 ± 0.05	8.53	8.36 ± 0.15	
11.50	11.50 ± 0.33	11.50	10.90 ± 0.20	11.37	11.54 ± 0.13	

A2.14: Relative solubility of phenanthrene at a concentration of 5 µg L⁻¹ according to increasing Triton X-100 concentration at 20°C.

Triton X-100 conc. (mg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous phenanthrene conc. (µg L ⁻¹)	Triton X-100 conc. (mg L ⁻¹)	Aqueous phenanthrene conc. (µg L ⁻¹)	Triton X-100 conc. (mg L ⁻¹)	Aqueous phenanthrene conc. (µg L ⁻¹)	Triton X-100 conc. (mg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$		$\bar{x} \pm SD$	
4	3.75 ± 0.05	4	3.22 ± 0.04	4	3.56 ± 0.32	
10	3.82 ± 0.06	10	3.40 ± 0.07	10	3.66 ± 0.04	
25	3.69 ± 0.06	25	3.32 ± 0.07	25	3.15 ± 0.02	
50	3.70 ± 0.05	50	3.39 ± 0.04	50	3.23 ± 0.17	

A2.15: Relative solubility data for phenanthrene in Milli Q, Plym river water and seawater modified with Triton X-100 at 8°C

Total conc. (µg L ⁻¹)	Milli-Q		River		Sea	
	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)	Aqueous conc. (µg L ⁻¹)	Total conc. (µg L ⁻¹)
	$\bar{x} \pm SD$		$\bar{x} \pm SD$		$\bar{x} \pm SD$	
2.02	1.76 ± 0.04	2.02	1.98 ± 0.22	1.55	1.89 ± 0.09	
4.05	3.99 ± 0.19	4.05	4.04 ± 0.06	3.10	3.53 ± 0.06	
6.07	6.09 ± 0.09	6.07	6.07 ± 0.09	4.64	5.32 ± 0.27	
8.09	7.62 ± 0.72	8.09	8.09 ± 0.21	6.19	7.18 ± 0.03	

A2.16: Relative solubility data for phenanthrene in Milli Q, Plym river water and seawater modified with SDS at 20°C

Total conc. ($\mu\text{g L}^{-1}$)	Milli-Q		River		Sea	
	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)
2.03	1.84 \pm 0.17	1.79	1.67 \pm 0.07	2.49	2.23 \pm 0.07	2.49
5.08	4.91 \pm 0.13	4.49	4.09 \pm 0.18	6.24	5.83 \pm 0.02	6.24
10.17	9.58 \pm 0.51	8.97	8.34 \pm 0.34	12.49	10.72 \pm 0.44	12.49
15.25	13.04 \pm 0.20	13.46	12.13 \pm 0.28	18.73	16.71 \pm 0.48	18.73

A2.17: Relative solubility of phenanthrene at a concentration of 5 $\mu\text{g L}^{-1}$ according to increasing SDS concentration at 20°C.

SDS conc. ($\mu\text{g L}^{-1}$)	Milli-Q		River		Sea	
	Aqueous phenanthrene conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	SDS conc. ($\mu\text{g L}^{-1}$)	Aqueous phenanthrene conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	SDS conc. ($\mu\text{g L}^{-1}$)	Aqueous phenanthrene conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	SDS conc. ($\mu\text{g L}^{-1}$)
0.03	4.06 \pm 0.22	0.03	3.94 \pm 0.16	0.03	3.82 \pm 0.50	0.03
0.15	4.07 \pm 0.13	0.15	4.10 \pm 0.07	0.15	3.68 \pm 0.41	0.15
0.3	3.95 \pm 0.15	0.3	4.02 \pm 0.07	0.3	3.93 \pm 0.16	0.3
0.6	3.98 \pm 0.10	0.6	3.91 \pm 0.15	0.6	4.10 \pm 0.09	0.6
1.2	3.99 \pm 0.15	1.2	4.02 \pm 0.11	1.2	4.04 \pm 0.20	1.2
2.5	4.05 \pm 0.12	2.5	3.96 \pm 0.02	2.5	3.50 \pm 0.14	2.5

A2.18: Relative solubility isotherms for phenanthrene in Milli Q, Plym river water and seawater modified with SDS at 8°C

Total conc. ($\mu\text{g L}^{-1}$)	Milli-Q		River		Sea	
	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)
3.94	3.42 \pm 0.08	4.37	3.61 \pm 0.13	3.61	3.21 \pm 0.08	3.61
7.88	7.02 \pm 0.15	8.72	7.21 \pm 0.15	7.21	6.47 \pm 0.19	7.21
11.81	10.60 \pm 0.11	12.92	10.82 \pm 0.38	10.82	9.84 \pm 0.04	10.82
15.75	13.96 \pm 0.43	16.98	14.43 \pm 0.43	14.43	13.38 \pm 0.21	14.43

A2.19: Relative solubility data for phenanthrene in Milli Q, Plym river water and seawater modified with HDTMA at 20°C

Total conc. ($\mu\text{g L}^{-1}$)	Milli-Q		River		Sea	
	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)
2.38	2.89 \pm 0.25	2.38	2.02 \pm 0.11	1.48	1.15 \pm 0.10	1.48
4.77	4.99 \pm 0.29	4.77	4.52 \pm 0.16	2.96	2.77 \pm 0.08	2.96
7.15	6.93 \pm 0.25	7.15	6.89 \pm 0.25	7.42	6.91 \pm 0.07	7.42
9.54	9.48 \pm 0.08	9.54	8.95 \pm 0.22	11.87	11.23 \pm 0.12	11.87

A2.20: Relative solubility of phenanthrene at a concentration of $5 \mu\text{g L}^{-1}$ according to increasing HDTMA concentration at 20°C .

	Milli-Q		River		Sea	
Triton X-100 conc. (mg L^{-1})	Aqueous phenanthrene conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Triton X-100 conc. (mg L^{-1})	Aqueous phenanthrene conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Triton X-100 conc. (mg L^{-1})	Aqueous phenanthrene conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	conc.
0.2	3.47 ± 0.16	4	3.23 ± 0.12	4	2.63 ± 0.03	
0.5	3.30 ± 0.05	10	3.25 ± 0.01	10	2.61 ± 0.02	
1.25	3.15 ± 0.13	25	3.14 ± 0.01	25	2.53 ± 0.04	
2.5	3.11 ± 0.01	50	2.92 ± 0.20	50	2.53 ± 0.02	

A2.21: Relative solubility data for phenanthrene in Milli Q, Plym river water and seawater modified with HDTMA at 8°C

	Milli-Q		River		Sea	
Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	Total conc. ($\mu\text{g L}^{-1}$)	Aqueous conc. ($\mu\text{g L}^{-1}$) $\bar{x} \pm \text{SD}$	
1.71	1.39 ± 0.05	1.71	1.43 ± 0.05	1.48	1.29 ± 0.05	
3.42	2.95 ± 0.05	3.42	2.88 ± 0.02	2.96	2.66 ± 0.13	
5.13	4.40 ± 0.06	5.13	4.33 ± 0.11	5.94	5.25 ± 0.06	
6.84	5.56 ± 0.14	6.84	5.72 ± 0.12	8.91	8.05 ± 0.44	

Appendix A3: Particle-Water Interaction Data - Kinetics

A3.1: Partition coefficients for phenanthrene in Plym river water as a function of time with a SPM concentration of 50 mg L^{-1} .

Time, log (minutes)	$K_D \cdot 10^3 \text{ (mL g}^{-1}) \bar{x} \pm \text{SD}$
0.70	1.53 ± 0.63
1.48	2.29 ± 0.61
1.78	2.46 ± 0.56
2.08	3.07 ± 1.25
2.38	2.83 ± 0.60
2.68	2.98 ± 0.21
3.16	2.67 ± 0.27
3.46	3.09 ± 0.87
3.76	3.10 ± 1.18

A3.2: Partition coefficients for Triton X-100 in Plym river water as a function of time with a SPM concentration of 50 mg L⁻¹.

Time, log (minutes)	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.70	8.04 ± 0.46
1.48	6.79 ± 0.63
1.78	7.84 ± 0.78
2.08	6.67 ± 0.30
2.38	6.73 ± 2.18
2.68	8.44 ± 0.12
3.16	7.40 ± 0.19
3.46	10.38 ± 0.48
3.76	8.71 ± 0.47

A3.3: Partition coefficients for SDS in Plym river water as a function of time with a SPM concentration of 50 mg L⁻¹.

Time, log (minutes)	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.70	1.73 ± 0.33
1.48	2.66 ± 0.40
1.78	2.30 ± 0.79
2.08	2.34 ± 0.14
2.38	2.89 ± 0.36
2.68	2.09 ± 1.09
3.16	2.64 ± 0.85
3.46	3.44 ± 0.49
3.76	2.07 ± 0.80

A3.4: Partition coefficients for HDTMA in Plym river water as a function of time with a SPM concentration of 50 mg L⁻¹.

Time, log (minutes)	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.70	10.67 ± 0.75
1.48	15.25 ± 1.89
1.78	15.39 ± 2.07
2.08	15.47 ± 2.16
2.38	16.88 ± 2.61
2.68	16.21 ± 2.60
3.16	15.54 ± 1.60
3.46	13.09 ± 2.30
3.76	18.38 ± 6.49

A3.5: Partition coefficients for phenanthrene modified with Triton X-100 in Plym river water as a function of time with a SPM concentration of 50 mg L⁻¹.

Time, log (minutes)	Triton X-100 added after phenanthrene $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	Triton X-100 added before phenanthrene $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.70	0.90 ± 0.48	1.72 ± 1.06
1.48	4.07 ± 0.09	3.30 ± 0.99
1.78	2.44 ± 0.85	2.49 ± 1.25
2.08	2.01 ± 0.91	2.14 ± 0.77
2.38	3.12 ± 0.57	3.12 ± 0.16
2.68	2.34 ± 1.03	2.18 ± 1.09
3.16	2.64 ± 0.44	1.86 ± 0.01
3.46	3.44 ± 0.26	3.38 ± 1.25
3.76	2.58 ± 0.13	2.37 ± 1.10

A3.6: Partition coefficients for phenanthrene modified with SDS in Plym river water as a function of time with a SPM concentration of 50 mg L⁻¹.

Time, log (minutes)	SDS added after phenanthrene $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	SDS added before phenanthrene $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.70	2.43 ± 0.20	1.25 ± 0.82
1.48	1.85 ± 0.25	2.90 ± 1.10
1.78	2.95 ± 1.01	3.70 ± 1.00
2.08	2.07 ± 1.04	2.19 ± 0.72
2.38	2.67 ± 0.29	1.62 ± 0.33
2.68	2.55 ± 0.57	1.64 ± 0.77
3.16	2.66 ± 0.52	1.70 ± 0.68
3.46	2.34 ± 0.25	2.35 ± 0.34
3.76	2.27 ± 0.68	2.28 ± 0.40

A3.7: Partition coefficients for phenanthrene modified with HDTMA in Plym river water as a function of time with a SPM concentration of 50 mg L⁻¹.

Time, log (minutes)	HDTMA added after phenanthrene $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	HDTMA added before phenanthrene $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.70	6.43 ± 1.07	6.54 ± 1.08
1.48	6.17 ± 0.26	5.46 ± 1.67
1.78	6.92 ± 1.39	5.42 ± 1.15
2.08	5.78 ± 0.97	6.31 ± 0.42
2.38	9.05 ± 0.69	7.55 ± 0.94
2.68	7.29 ± 0.85	6.74 ± 0.79
3.16	7.47 ± 0.73	6.77 ± 1.59
3.46	6.43 ± 1.41	4.47 ± 1.77
3.76	7.64 ± 1.31	7.09 ± 1.10

Appendix A4: Particle-Water Interaction Data - Sorption

A4.1: Sorption data for phenanthrene in Plym river water and seawater at 20°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (µg L ⁻¹)	River		Sea	
	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)
0.92	4.01 ± 0.58	0.68	5.67 ± 0.88	
2.35	7.65 ± 1.62	2.38	8.23 ± 0.11	
3.83	12.61 ± 0.51	3.61	16.86 ± 0.04	
5.75	18.92 ± 0.46	5.24	28.34 ± 4.52	

A4.2: Sorption data for phenanthrene in Plym river water and seawater at 8°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (µg L ⁻¹)	River		Sea	
	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)
3.23	10.59 ± 0.64	3.29	6.85 ± 2.45	
5.48	16.83 ± 0.89	5.74	8.29 ± 0.19	
10.24	33.70 ± 3.88	11.38	19.11 ± 0.19	
15.21	48.76 ± 3.22	16.37	39.65 ± 0.95	

A4.3: Sorption data for phenanthrene with POC removed from Plym particles at an SPM concentration of 50 mg L⁻¹ and DOC removed from Plym river water and seawater

Aqueous conc. (µg L ⁻¹)	River		Sea	
	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)
0.69	1.37 ± 0.56	0.69	9.52 ± 0.39	
1.57	7.62 ± 2.23	1.57	20.77 ± 5.46	
2.91	12.98 ± 6.79	2.91	23.72 ± 4.23	
4.55	21.02 ± 7.25	4.55	35.61 ± 7.94	

A4.4: Sorption data for Triton X-100 in Plym river water and seawater at 20°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (mg L ⁻¹)	River		Sea	
	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (mg L ⁻¹)	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (mg L ⁻¹)
49.50	83.04 ± 1.00	6.00	380.0 ± 3.0	
89.00	220.0 ± 3.46	19.20	616.0 ± 9.7	
169.5	610.0 ± 1.91	38.27	834.7 ± 19.1	
258.8	824.0 ± 2.86	59.07	818.6 ± 29.5	

A4.5: Sorption data for Triton X-100 in Plym river water and seawater at 8°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (mg L ⁻¹)	River	Aqueous conc. (mg L ⁻¹)	Sea
	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$
10.80	284.0 ± 1.00	8.80	324.0 ± 12.5
26.27	474.7 ± 30.5	23.73	525.3 ± 10.3
43.07	738.7 ± 41.6	43.73	725.3 ± 6.4
59.60	808.0 ± 40.0	57.87	842.7 ± 5.0

A4.6: Sorption data for Triton X-100 with POC removed from Plym particles at an SPM concentration of 50 mg L⁻¹ and DOC removed from Plym river water and seawater

Aqueous conc. (mg L ⁻¹)	River	Aqueous conc. (mg L ⁻¹)	Sea
	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$
22.83	43.33 ± 16.5	15.87	182.5 ± 6.7
46.75	65.00 ± 5.65	30.00	400.0 ± 30.4
71.17	176.7 ± 9.2	64.12	317.5 ± 27.1
94.75	105 ± 16.9	90.00	200.0 ± 49.8

A4.7: Sorption data for SDS in Plym river water and seawater at 20°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (µg L ⁻¹)	River	Aqueous conc. (µg L ⁻¹)	Sea
	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
1.89	2.75 ± 0.34	1.80	2.73 ± 0.05
3.76	6.10 ± 0.58	6.01	9.71 ± 1.86
48.75	80.57 ± 0.81	43.75	69.70 ± 6.03
98.31	165.8 ± 22.3	122.5	180.6 ± 14.7
1386	4417 ± 185	1317	4615 ± 234
2389	6052 ± 634	2338	5732 ± 496

A4.8: Sorption data for SDS in Plym river water and seawater at 8°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (µg L ⁻¹)	River	Aqueous conc. (µg L ⁻¹)	Sea
	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
0.95	2.02 ± 0.25	0.89	1.43 ± 0.53
2.54	7.05 ± 3.42	2.42	4.82 ± 1.15
6.37	12.32 ± 2.38	6.46	15.69 ± 4.81
12.72	31.34 ± 1.15	12.21	37.92 ± 4.19

A4.9: Sorption data for SDS with POC removed from Plym particles at an SPM concentration of 50 mg L⁻¹ and DOC removed from Plym river water and seawater

Aqueous conc. (mg L ⁻¹)	River	Aqueous conc. (mg L ⁻¹)	Sea
	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$
0.39	1.79 ± 0.32	0.36	13.55 ± 0.55
0.70	6.34 ± 1.61	0.68	35.94 ± 0.27
1.02	0.87 ± 0.68	1.03	29.50 ± 0.40
1.92	0.59 ± 0.59	2.10	21.44 ± 0.58

A4.10: Sorption data for HDTMA in Plym river water and seawater at 20°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (mg L ⁻¹)	River	Aqueous conc. (mg L ⁻¹)	Sea
	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$
0.04	0.55 ± 0.05	0.05	1.31 ± 0.26
0.27	1.80 ± 0.28	0.20	5.17 ± 1.67
0.69	4.15 ± 0.49	0.32	16.92 ± 3.31
1.36	5.11 ± 0.30	0.56	39.42 ± 1.61

A4.11: Sorption data for HDTMA in Plym river water and seawater at 8°C using Plym particles with an SPM concentration of 50 mg L⁻¹

Aqueous conc. (mg L ⁻¹)	River	Aqueous conc. (mg L ⁻¹)	Sea
	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$
0.06	3.00 ± 0.64	0.10	1.73 ± 0.50
0.26	6.72 ± 0.85	0.25	5.03 ± 1.29
0.74	13.28 ± 1.49	0.81	5.66 ± 0.68
1.56	17.24 ± 7.77	2.00	6.16 ± 1.51

A4.12: Sorption data for HDTMA with POC removed from Plym particles at an SPM concentration of 50 mg L⁻¹ and DOC removed from Plym river water and seawater

Aqueous conc. (mg L ⁻¹)	River	Aqueous conc. (mg L ⁻¹)	Sea
	Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$		Sorbed conc. (mg g ⁻¹) $\bar{x} \pm SD$
0.50	0.31 ± 0.01	0.50	0.08 ± 0.02
1.25	0.71 ± 0.04	1.25	0.32 ± 0.02
3.12	1.40 ± 0.06	1.87	0.45 ± 0.03
6.25	1.60 ± 0.12	2.5	0.74 ± 0.10

A4.13: Sorption data for phenanthrene with Triton X-100 at 20°C in Plym river water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
0.80	4.07 ± 0.93	0.79	3.63 ± 1.34
1.53	5.53 ± 0.51	1.62	8.98 ± 2.67
2.35	8.98 ± 1.52	2.22	12.10 ± 4.67
3.04	11.76 ± 2.64	2.97	15.69 ± 3.97

A4.14: Sorption data for phenanthrene with Triton X-100 at 20°C in seawater using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
0.43	2.35 ± 0.40	0.47	2.55 ± 0.40
0.86	3.99 ± 0.73	0.91	4.65 ± 0.69
1.32	5.39 ± 0.52	1.35	7.55 ± 1.46
1.85	6.62 ± 2.38	1.87	8.02 ± 2.41

A4.15: Sorption data for phenanthrene with Triton X-100 at 8°C in Plym river water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
0.76	3.68 ± 0.98	0.82	4.44 ± 0.92
1.63	7.45 ± 0.56	1.69	7.56 ± 2.44
2.34	13.21 ± 1.81	2.34	10.39 ± 0.21
3.43	14.39 ± 2.66	3.08	17.73 ± 2.25

A4.16: Sorption data for phenanthrene with Triton X-100 at 8°C in seawater using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
0.33	2.18 ± 0.52	0.46	2.73 ± 0.23
0.65	3.53 ± 0.33	0.93	4.40 ± 0.53
1.02	5.13 ± 0.66	1.42	6.59 ± 0.44
1.38	7.21 ± 0.89	1.87	7.16 ± 0.44

A4.17: Partition coefficients, K_{DS} , for phenanthrene modified with increasing concentrations of Triton X-100

Triton X-100 conc. (mg L ⁻¹)	River	Triton X-100 conc. (mg L ⁻¹)	Sea
	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$		$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
4	3.18 ± 1.37	4	3.57 ± 0.91
10	4.34 ± 0.52	10	3.21 ± 0.95
25	3.91 ± 0.93	25	4.14 ± 0.21
50	4.63 ± 0.76	50	4.53 ± 0.10

A4.18: Sorption data for phenanthrene with SDS at 20°C in Plym river water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
3.36	7.56 ± 1.82	2.38	1.26 ± 1.31
5.77	8.79 ± 1.81	4.50	7.30 ± 2.99
8.88	21.58 ± 6.14	7.41	14.34 ± 2.92
12.48	39.71 ± 5.65	11.07	23.10 ± 4.76

A4.19: Sorption data for phenanthrene with SDS at 20°C in seawater water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
3.00	4.15 ± 0.69	2.60	3.37 ± 0.89
4.89	8.75 ± 2.66	4.46	6.35 ± 1.85
7.72	15.96 ± 3.98	6.94	9.87 ± 3.97
12.31	10.04 ± 3.78	10.36	14.29 ± 4.10

A4.20: Sorption data for phenanthrene with SDS at 8°C in Plym river water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
2.67	3.60 ± 0.33	3.12	9.25 ± 0.64
4.63	6.43 ± 3.00	5.09	18.97 ± 0.89
8.66	14.93 ± 2.10	10.16	28.14 ± 3.88
13.14	21.09 ± 2.66	15.33	54.52 ± 3.22

A4.21: Sorption data for phenanthrene with SDS at 8°C in seawater water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before Triton X-100		Phenanthrene added after Triton X-100	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
1.39	3.15 ± 0.64	0.62	2.34 ± 0.24
3.35	7.52 ± 1.59	1.26	4.47 ± 0.61
6.81	14.52 ± 2.83	1.85	6.74 ± 0.81
8.96	25.87 ± 3.72	4.87	18.99 ± 0.93

A4.22: Partition coefficients, K_{DS} , for phenanthrene modified with increasing concentrations of SDS

River		Sea	
SDS conc. (mg L ⁻¹)	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	SDS conc. (mg L ⁻¹)	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.2	3.31 ± 0.64	0.1	2.74 ± 0.19
0.5	3.49 ± 0.28	0.5	3.21 ± 0.09
1.25	3.25 ± 0.49	1.25	4.30 ± 0.53
2.5	2.87 ± 0.55	2.5	4.13 ± 0.11

A4.23: Sorption data for phenanthrene with HDTMA at 20°C in Plym river water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before HDTMA		Phenanthrene added after HDTMA	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
1.33	6.99 ± 0.75	1.43	10.39 ± 2.89
2.67	14.90 ± 2.49	2.87	23.01 ± 2.47
4.23	28.77 ± 2.49	4.08	28.87 ± 2.39
5.42	42.42 ± 3.65	5.46	39.69 ± 4.70

A4.24: Sorption data for phenanthrene with HDTMA at 20°C in seawater using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before HDTMA		Phenanthrene added after HDTMA	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
1.10	9.07 ± 0.48	1.09	9.95 ± 1.13
2.42	16.49 ± 1.41	2.10	26.53 ± 2.68
4.50	30.13 ± 2.59	4.29	53.26 ± 2.24
7.34	44.55 ± 1.55	6.11	79.44 ± 1.89

A4.25: Sorption data for phenanthrene with HDTMA at 8°C in Plym river water using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before HDTMA		Phenanthrene added after HDTMA	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
0.45	3.88 ± 1.14	0.42	5.18 ± 0.52
0.95	5.61 ± 2.68	0.80	10.34 ± 0.62
1.43	7.02 ± 2.24	1.21	11.22 ± 2.67
2.50	19.58 ± 1.89	1.62	16.75 ± 2.01

A4.26: Sorption data for phenanthrene with HDTMA at 8°C in seawater using Plym particles at an SPM concentration of 50 mg L⁻¹

Phenanthrene added before HDTMA		Phenanthrene added after HDTMA	
Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$	Aqueous conc. (µg L ⁻¹)	Sorbed conc. (µg g ⁻¹) $\bar{x} \pm SD$
0.86	4.36 ± 0.30	0.77	4.61 ± 0.04
1.71	9.37 ± 2.52	1.58	9.69 ± 0.91
2.63	13.87 ± 1.64	2.44	14.26 ± 2.30
3.47	17.27 ± 4.15	3.27	19.48 ± 2.87

A4.27: Partition coefficients, K_{Ds} , for phenanthrene modified with increasing concentrations of HDTMA

HDTMA conc. (mg L ⁻¹)	River	HDTMA conc. (mg L ⁻¹)	Sea
	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$		$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
0.2	3.63 ± 0.63	0.2	3.89 ± 0.72
0.5	5.86 ± 0.39	0.5	5.98 ± 0.44
1.25	7.89 ± 0.46	1.25	7.38 ± 0.47
2.5	10.99 ± 0.86	2.5	10.99 ± 0.71

Appendix A5: Particle-Water Interaction Data – Particle Concentration Effect

A5.1: Partition coefficients, K_{Ds} , for phenanthrene in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 20°C

[SPM] mg L ⁻¹	River	[SPM] mg L ⁻¹	Sea
	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$		$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	4.99 ± 1.42	20	5.76 ± 0.17
50	3.78 ± 0.55	50	4.92 ± 0.08
100	1.44 ± 0.29	100	1.84 ± 0.14
200	0.92 ± 0.16	200	1.17 ± 0.16
400	0.71 ± 0.14	400	1.18 ± 0.12
600	0.45 ± 0.13	600	1.17 ± 0.26

A5.2: Partition coefficients, K_{Ds} , for phenanthrene in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 8°C

[SPM] mg L ⁻¹	River $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	Sea $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	5.37 ± 1.15	20	5.57 ± 1.29
50	2.41 ± 0.35	50	2.12 ± 0.65
100	1.58 ± 0.25	100	1.67 ± 0.33
300	0.94 ± 0.05	300	1.05 ± 0.19
600	0.83 ± 0.10	600	1.03 ± 0.23

A5.3: Partition coefficients, K_{Ds} , for Triton X-100 in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 20°C

[SPM] mg L ⁻¹	River $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	Sea $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	2.17 ± 0.23	20	17.77 ± 0.03
50	0.32 ± 0.13	50	7.55 ± 0.20
100	0.58 ± 0.04	100	3.70 ± 0.06
300	0.35 ± 0.12	300	1.08 ± 0.19
600	0.22 ± 0.09	600	0.57 ± 0.61

A5.4: Partition coefficients, K_{Ds} , for Triton X-100 in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 8°C

[SPM] mg L ⁻¹	River $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	Sea $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	4.96 ± 0.48	20	12.57 ± 0.40
50	2.19 ± 0.13	50	4.36 ± 0.20
100	1.02 ± 0.53	100	3.66 ± 0.10
300	0.10 ± 0.08	300	0.99 ± 0.46
600	0.15 ± 0.55	600	0.49 ± 0.38

A5.5: Partition coefficients, K_{Ds} , for SDS in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 20°C

[SPM] mg L ⁻¹	River $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	Sea $K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	1.27 ± 0.29	20	0.91 ± 0.01
50	0.95 ± 0.22	50	0.37 ± 0.05
100	0.20 ± 0.15	100	0.33 ± 0.08
300	0.32 ± 0.13	300	0.39 ± 0.03
600	0.18 ± 0.00	600	0.27 ± 0.04

A5.6: Partition coefficients, K_{DS} , for SDS in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 8°C

[SPM] mg L ⁻¹	River	[SPM] mg L ⁻¹	Sea
	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$		$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	3.64 ± 1.15	20	1.04 ± 0.03
50	2.92 ± 0.09	50	2.37 ± 0.05
100	1.08 ± 0.10	100	0.66 ± 0.09
300	0.34 ± 0.10	300	0.26 ± 0.03
600	0.17 ± 0.09	600	0.20 ± 0.06

A5.7: Partition coefficients, K_{DS} , for HDTMA in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 20°C

[SPM] mg L ⁻¹	River	[SPM] mg L ⁻¹	Sea
	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$		$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	24.50 ± 2.29	20	189.33 ± 38.27
50	23.61 ± 3.14	50	76.84 ± 28.28
100	12.58 ± 1.97	100	31.48 ± 10.55
300	12.81 ± 1.57	300	6.84 ± 1.86
600	10.07 ± 3.71	600	8.56 ± 1.56

A5.8: Partition coefficients, K_{DS} , for HDTMA in Plym river water and seawater as a function of Plym suspended particulate matter (SPM) concentration at 8°C

[SPM] mg L ⁻¹	River	[SPM] mg L ⁻¹	Sea
	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$		$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	25.05 ± 0.14	20	5.30 ± 1.13
50	16.74 ± 3.80	50	3.70 ± 0.79
100	5.01 ± 0.29	100	3.15 ± 0.65
300	5.53 ± 0.67	300	2.03 ± 2.03
600	3.81 ± 0.69	600	2.73 ± 0.81

A5.9: Partition coefficients, K_{DS} , for phenanthrene modified with Triton X-100 in Plym river water as a function of Plym suspended particulate matter (SPM) concentration at 20°C

[SPM] mg L ⁻¹	Phenanthrene added after Triton X-100	[SPM] mg L ⁻¹	Phenanthrene added before Triton X-100
	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$		$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	9.08 ± 0.99	20	9.81 ± 1.65
50	4.16 ± 0.69	50	4.48 ± 0.68
100	2.56 ± 0.60	100	2.95 ± 0.09
300	1.64 ± 0.21	300	1.79 ± 0.13
600	1.17 ± 0.18	600	1.45 ± 0.15

A5.10: Partition coefficients, K_{DS} , for phenanthrene modified with Triton X-100 in Plym river water as a function of Plym suspended particulate matter (SPM) concentration at 8°C

Phenanthrene added after Triton X-100		Phenanthrene added before Triton X-100	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	9.86 ± 3.16	20	9.66 ± 1.19
50	4.54 ± 0.45	50	4.69 ± 0.20
100	2.61 ± 0.37	100	2.10 ± 0.16
300	1.56 ± 0.09	300	1.36 ± 0.11
600	1.22 ± 0.03	600	1.14 ± 0.05

A5.11: Partition coefficients, K_{DS} , for phenanthrene modified with Triton X-100 in seawater as a function of Plym suspended particulate matter (SPM) concentration at 20°C

Phenanthrene added after Triton X-100		Phenanthrene added before Triton X-100	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	6.97 ± 2.44	20	6.86 ± 2.61
50	4.99 ± 0.83	50	4.38 ± 0.73
100	2.62 ± 0.04	100	2.92 ± 0.38
300	1.22 ± 0.03	300	1.36 ± 0.03
600	1.02 ± 0.05	600	1.02 ± 0.08

A5.12: Partition coefficients, K_{DS} , for phenanthrene modified with Triton X-100 in seawater as a function of Plym suspended particulate matter (SPM) concentration at 8°C

Phenanthrene added after Triton X-100		Phenanthrene added before Triton X-100	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	9.20 ± 2.20	20	12.20 ± 1.33
50	5.72 ± 2.19	50	5.39 ± 1.56
100	2.97 ± 0.82	100	3.47 ± 0.04
300	1.66 ± 0.07	300	1.93 ± 0.39
600	1.17 ± 0.16	600	1.39 ± 0.13

A5.13: Partition coefficients, K_{DS} , for phenanthrene modified with SDS in Plym river water as a function of Plym suspended particulate matter (SPM) concentration at 20°C

Phenanthrene added after SDS		Phenanthrene added before SDS	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	2.14 ± 1.59	20	3.18 ± 0.79
50	1.37 ± 0.77	50	1.26 ± 0.36
100	0.77 ± 0.17	100	0.84 ± 0.40
300	0.54 ± 0.07	300	0.71 ± 0.16
600	0.57 ± 0.06	600	0.65 ± 0.05

A5.14: Partition coefficients, K_{DS} , for phenanthrene modified with SDS in Plym river water as a function of Plym suspended particulate matter (SPM) concentration at 8°C

Phenanthrene added after SDS		Phenanthrene added before SDS	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	7.17 ± 1.59	20	7.11 ± 1.82
50	3.68 ± 0.28	50	2.97 ± 0.86
100	2.28 ± 0.15	100	1.99 ± 0.52
300	1.29 ± 0.24	300	1.46 ± 0.20
600	1.15 ± 0.22	600	1.25 ± 0.15

A5.15: Partition coefficients, K_{DS} , for phenanthrene modified with SDS in seawater as a function of Plym suspended particulate matter (SPM) concentration at 20°C

Phenanthrene added after SDS		Phenanthrene added before SDS	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	7.77 ± 1.92	20	6.88 ± 1.06
50	3.45 ± 0.66	50	2.85 ± 0.27
100	1.86 ± 0.21	100	1.95 ± 0.24
300	1.13 ± 0.17	300	1.09 ± 0.11
600	0.78 ± 0.04	600	0.85 ± 0.08

A5.16: Partition coefficients, K_{DS} , for phenanthrene modified with SDS in seawater as a function of Plym suspended particulate matter (SPM) concentration at 8°C

Phenanthrene added after SDS		Phenanthrene added before SDS	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	7.34 ± 1.12	20	8.74 ± 0.99
50	3.02 ± 0.42	50	4.78 ± 2.30
100	2.01 ± 0.42	100	2.24 ± 0.28
300	1.46 ± 0.22	300	1.56 ± 0.24
600	1.08 ± 0.06	600	0.95 ± 0.09

A5.17: Partition coefficients, K_{DS} , for phenanthrene modified with HDTMA in Plym river water as a function of Plym suspended particulate matter (SPM) concentration at 20°C

Phenanthrene added after HDTMA		Phenanthrene added before HDTMA	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	14.66 ± 1.14	20	14.22 ± 1.32
50	11.40 ± 0.24	50	9.84 ± 0.72
100	7.48 ± 0.97	100	5.72 ± 0.92
300	3.06 ± 0.41	300	2.46 ± 0.17
600	2.21 ± 0.09	600	1.97 ± 0.10

A5.18: Partition coefficients, K_{DS} , for phenanthrene modified with HDTMA in Plym river water as a function of Plym suspended particulate matter (SPM) concentration at 8°C

Phenanthrene added after HDTMA		Phenanthrene added before HDTMA	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	18.83 ± 2.58	20	21.74 ± 5.59
50	10.95 ± 2.28	50	9.52 ± 1.31
100	5.75 ± 0.36	100	5.39 ± 1.05
300	3.94 ± 0.89	300	3.26 ± 0.54
600	1.75 ± 0.12	600	1.87 ± 0.29

A5.19: Partition coefficients, K_{DS} , for phenanthrene modified with HDTMA in seawater water as a function of Plym suspended particulate matter (SPM) concentration at 20°C

Phenanthrene added after HDTMA		Phenanthrene added before HDTMA	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	14.45 ± 3.32	20	12.25 ± 1.61
50	6.77 ± 2.08	50	5.72 ± 1.62
100	5.06 ± 2.89	100	4.34 ± 0.49
300	3.50 ± 0.31	300	1.69 ± 0.07
600	2.05 ± 0.16	600	1.12 ± 0.04

A5.20: Partition coefficients, K_{DS} , for phenanthrene modified with HDTMA in seawater water as a function of Plym suspended particulate matter (SPM) concentration at 8°C

Phenanthrene added after HDTMA		Phenanthrene added before HDTMA	
[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$	[SPM] mg L ⁻¹	$K_D \cdot 10^3$ (mL g ⁻¹) $\bar{x} \pm SD$
20	9.74 ± 1.30	20	12.16 ± 3.99
50	6.80 ± 0.51	50	6.44 ± 1.28
100	6.67 ± 1.26	100	4.86 ± 0.65
300	2.94 ± 0.57	300	2.09 ± 0.27
600	1.39 ± 0.01	600	1.77 ± 0.20



Transport and Retention of Hydrophobic Organic Micropollutants in Estuaries: Implications of the Particle Concentration Effect

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An increase in the particle–water distribution coefficient with decreasing particle concentration, or particle concentration effect (PCE), is a common phenomenon observed in both laboratory and field studies of many hydrophobic organic micropollutants (HOMs), and is demonstrated in this work by ¹⁴C-labelled benzo[a]pyrene sorption to estuarine sediment. While the focus of most studies has been the precise cause of the PCE, a more immediate requirement from a regulatory and impact assessment standpoint is its empirical definition and incorporation into any pollution modelling or management tool.

A compilation of literature data on the sorption of HOMs to natural particles indicates that the relationship between distribution coefficient, K_D , and suspended particle concentration, SPM , is of the form: $K_D = aSPM^{-b}$. The constants a and b are compound- and site-specific and are dependent to some extent on the inadequacy of particle–aqueous phase separation (or the concentration of colloids or non-settling particles encompassed by the aqueous phase). It is proposed that, for chemical flux calculations and pollution transport considerations, a PCE algorithm of the same form is appropriate: $K_D' = a'SPM^{-b'}$. Here, a transport distribution coefficient represents the ratio of HOM concentrations discriminated according to contaminant transport properties (i.e. contaminant bound to particles which are subject to gravitational settlement, and contaminant in an aqueous phase which embraces non-settling particles), SPM , is the concentration of particles which are subject to gravitational settlement, and a' and b' are empirical constants which define the PCE derived in this way. The implications of this algorithm for the transport and fate of HOMs in estuaries are examined, and a simple model for the estuarine retention of HOMs, incorporating the PCE and accounting for compound degradation in the aqueous phase, is presented. Estuarine retention increases with increasing magnitude of a' , the particle concentration-normalized partitioning or 'hydrophobicity index', and increasing degradation half-life. For $b' < 1$, retention increases with increasing particle concentration; for $b' > 1$, the reduction in K_D' more than offsets the accompanying increase in particle concentration and a decrease in retention with increasing particle concentration is predicted.

In the absence of necessary site-specific sorption and degradation data, and hydrological and sediment transport parameters, these calculations are largely hypothetical. Nevertheless, they demonstrate the factors that affect the overall retention of HOMs by estuaries and highlight the requirement for incorporation of the PCE in any contaminant modelling framework and environmental impact evaluation.

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Keywords: organic micropollutants; estuaries; adsorption; suspended particles; transport; retention

Introduction

For the purposes of impact assessment and pollution transport modelling of aquatic environments, it is usually assumed that a single ratio defines the partitioning of a chemical between the particulate and aqueous phases (Shea, 1988; Webster & Ridgway, 1994; Millward & Glegg, 1997; Radovanovic & Koelmans, 1998). Regarding hydrophobic organic micropollutants (HOMs), such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons and many pesticides, a sediment–water partition constant may be empirically predicted from the compound's octanol–water distribution coefficient or water solubil-

ity (Sigleo & Means, 1990; Girvin & Scott, 1997; Chiou *et al.*, 1998). In estuaries, however, chemical and particle gradients resulting from tidally-assisted mixing of river and seawaters significantly modify the sediment–water partitioning, hence land–ocean fluxes, of many contaminants and the use of a single sorption constant is inappropriate. Salinity exerts an influence on the partitioning of non-polar organic chemicals through salting out effects (Means, 1995; Brunk *et al.*, 1997), but the most important sorption-controlling variable appears to be suspended particle concentration. Thus, in both laboratory and field studies an increase in partitioning with decreasing particle concentration, or particle concentration effect

(PCE), is observed (e.g. Baker *et al.*, 1986; Duinker, 1986; Mackay & Powers, 1987; Servos & Muir, 1989; Eadie *et al.*, 1990; Koelmans & Lijklema, 1992; Bergen *et al.*, 1993; Hegeman *et al.*, 1995; Zhao & Lang, 1996; Rawling *et al.*, 1998). The precise cause(s) of this effect is unclear but popular theories relate to the presence or creation of a complexing phase (e.g. organic ligands released from inter-particle collisions) or additional sorbent (e.g. colloidal particles) which is operationally included in the aqueous phase and whose concentration is some function of particle concentration (Gschwend & Wu, 1985; Pankow & MacKenzie, 1991; Santschi *et al.*, 1997).

This paper reports on the uptake of benzo[a]pyrene, a highly hydrophobic, persistent polycyclic aromatic hydrocarbon, by different size fractions of estuarine sediment over a range in particle concentrations typical of macrotidal estuaries. It is not the purpose of the paper to further our understanding of the causal mechanisms of the PCE; rather, it attempts to provide an empirical parameterization of the effect which can be used to qualitatively and quantitatively examine its implications to pollution modelling and management in the marine and estuarine environment. Specifically, the distinction between particulate and aqueous phases is re-addressed in the context of pollution transport considerations and the role of estuaries as filters or traps for land-derived HOMs is evaluated in some detail.

Methods

Sampling and sample preparation

Sampling was undertaken in the River Plym (south-west England) and its estuary, during November 1997. There are no major industrial effluents in the region, but china clay extraction in the upper catchment means that estuarine sediment is composed, in part, of this waste (Hiscock & Moore, 1986).

About 8 l river water were collected in ashed Pyrex bottles with foil-lined caps and a surficial scrape of about 250 g oxic intertidal mud from the estuary was collected using a metal spatula and stored in an ashed glass jar. On return to the laboratory, river water was filtered through a Whatman GF/F filter (pore size 0.7 μm) and stored at 4 °C, and the sediment sample was wet sieved (using filtered river water) through a 2 mm nylon mesh to remove gravel and vegetal debris and stored at 4 °C. A portion of the resulting slurry was filtered through 0.7 μm to remove residual water. The remaining slurry (equivalent to about 200 g sediment) was sieved through a series of nested meshes of decreasing pore size (0.25 mm; 0.125 mm, 0.063 μm)

TABLE 1. Mass contribution and particulate organic carbon content (POC, as mean \pm 1 SD of three determinations) of whole and sieved fractions of estuarine sediment (D =particle diameter)

D , mm	Mass contribution, %	POC, %
Whole		
<2	100	2.77 \pm 0.06
Sieved fractions		
0.25–2	1.8	16.1 \pm 1.7
0.125–0.25	58.2	2.83 \pm 0.16
0.063–0.125	5.7	2.41 \pm 0.08
<0.063	34.3	2.00 \pm 0.03

and the finest fraction was filtered through 0.7 μm to remove residual river water. Up to about 5 g of each size fraction, including the portion of whole (<2 mm) sediment, were added to about 50 ml filtered river water in ashed Pyrex bottles, resulting in slurries containing the following particle size fractions: <2 mm; 0.25–2 mm; 0.125–0.25 mm; 63 μm –0.125 mm; 0.7–0.63 μm (or <63 μm). The particle concentration of each fraction was determined by filtering a 10 ml aliquot through a pre-weighed 0.7 μm filter and weighing the dried sample, and the particulate organic carbon content of each dried sample was determined using a Shimadzu-5000 total organic carbon analyser after sample digestion in phosphoric acid. The organic carbon content and percentage mass contributions to the overall sediment sample of each size fraction are listed in Table 1.

Sorption experiments

The protocol for the incubation and radiochemical analysis of samples is outlined elsewhere (Rawling *et al.*, 1998) and summarized below.

¹⁴C-labelled benzo[a]pyrene (BaP) (Sigma Chemicals, St. Louis, MO), of specific activity 980 MBq mmol⁻¹ and radiochemical purity \geq 98%, was diluted in *n*-hexane to give a working solution of concentration about 37 Bq per μl . For the sorption isotherms, spikes of between 5 and 36 μl (equivalent to about 0.05 to 0.35 μg BaP) were dispensed into hexane-cleaned glass centrifuge tubes using a glass microsyringe and the carrier solvent was evaporated in a fume cupboard. A volume of slurry, equivalent to a dried mass of 1.5 mg sediment, was pipetted into the tube and the volume was made up to 20 ml with filtered river water (resulting in a particle concentration of 75 mg l⁻¹). To investigate the effects of particle concentration on sorption a spike of 25 μl was dispensed into the glass centrifuge tubes and varying

TABLE 2. Parameters defining the sorption of BaP to whole and sieved fractions of estuarine sediment (Equation 2; Figure 1). P and C are apparent or measured adsorbed and aqueous concentrations, respectively, and are given as the mean and propagated error of four determinations, K_D is the apparent distribution coefficient calculated from the slope of the isotherm, and K_{oc} is the organic carbon-normalized distribution coefficient

D , mm	P , $\mu\text{g g}^{-1}$	C , $\mu\text{g l}^{-1}$	$\log K_D$, ml g^{-1}	$\log K_{oc}$, ml g^{-1}	R^2	
Whole <2	19.0 ± 4.1	0.24 ± 0.08	5.11	6.67	0.96	
	48.9 ± 1.7	0.36 ± 0.07				
	88.8 ± 0.8	0.59 ± 0.04				
	134 ± 7.2	0.93 ± 0.09				
	179 ± 9.3	1.49 ± 0.32				
Sieved fractions 0.25–2	18.8 ± 1.3	0.46 ± 0.11	4.78	5.58	0.91	
	36.8 ± 2.8	0.74 ± 0.09				
	83.4 ± 6.8	1.25 ± 0.30				
	0.125–0.25	20.5 ± 1.3	0.35 ± 0.03	4.84	6.39	0.91
		46.3 ± 1.3	0.63 ± 0.07			
		87.4 ± 3.5	1.27 ± 0.21			
		135 ± 7.0	1.49 ± 0.16			
	0.063–0.125	176 ± 19.6	2.82 ± 1.02	4.47	6.09	0.86
		18.2 ± 2.3	0.29 ± 0.08			
		27.5 ± 1.4	0.45 ± 0.15			
44.7 ± 10.1		2.23 ± 0.46				
105 ± 11.2		2.60 ± 0.66				
<0.063	129 ± 26.4	4.83 ± 1.60	5.23	6.92	0.96	
	25.4 ± 1.2	0.09 ± 0.01				
	48.4 ± 1.5	0.30 ± 0.08				
	86.8 ± 3.5	0.53 ± 0.19				
	137 ± 4.0	0.68 ± 0.14				
	197 ± 4.3	1.24 ± 0.50				

volumes of slurry were added such that the particle concentration ranged between 25 and 1000 mg l^{-1} after the volume was made up to 20 ml.

Tubes were stoppered and shaken on a lateral shaker for 16 h at 20 °C in the dark and the aqueous and particulate phases were then separated by centrifugation at 3000 rpm for 30 min. One ml supernatant was pipetted into 4 ml Ultima Gold liquid scintillation cocktail (LSC; Packard-Canberra) and counted on a Beckman LS6500 scintillation counter with factory installed internal quench curves. The tube walls were then extracted twice with 6 ml *n*-hexane for 16 h each and 1 ml of both extracts was added to LSC and counted as above. Radio-GC analysis of selected 10 ml extracts, reduced to 2 μl by nitrogen purge, indicated that the radiopurity of $\geq 98\%$ was maintained throughout the incubation.

The adsorbed-aqueous distribution coefficient was determined from mass balance of the original activity and the activities of the tube extracts and supernatant. Experiments conducted in the absence of particles indicated that about 90% of the original activity was accounted for by this approach. Loss of activity is

likely to be less in the presence of particles, and, under the particle concentrations employed in this study, a small, but unquantifiable error may be introduced into the results.

All experiments were undertaken in quadruplicate and results are presented as mean values together with the combined or propagated errors resulting from each stage of the radiochemical analysis (Caulcutt & Boddy, 1983).

Results

Sorption isotherms

Data for benzo[a]pyrene (BaP) sorption to each sediment size fraction are given in Table 2 and sorption isotherms are shown in Figure 1. Isotherm data for the 0.25–2 mm diameter (D) fraction are incomplete as there was insufficient sediment sample to undertake the full range of BaP concentrations. Isotherms conform with the Freundlich equation:

$$P = KC^n \quad (1)$$

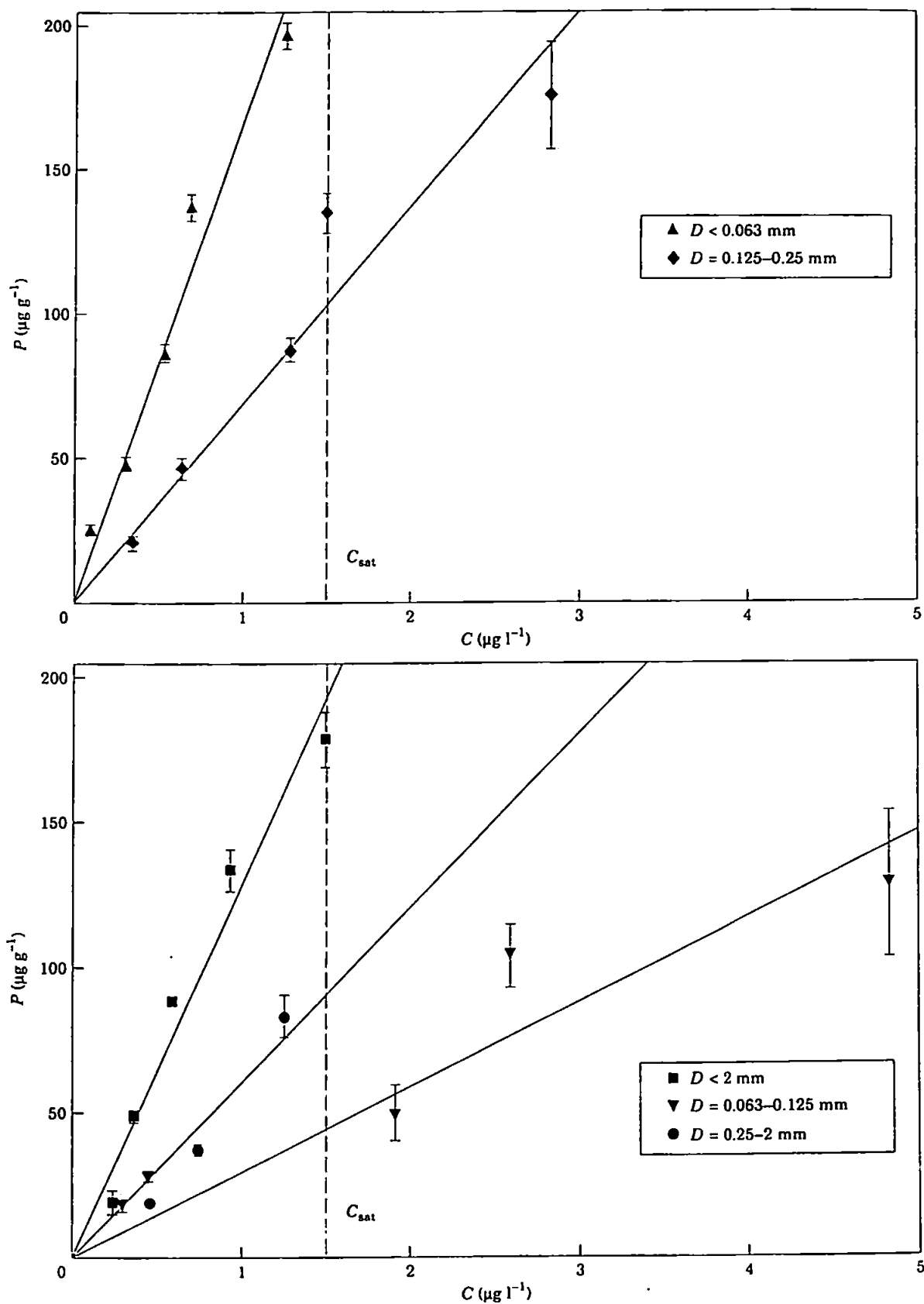


FIGURE 1. Isotherms for BaP sorption to whole and sieved fractions of Plym Estuary sediment (D =particle diameter); a suspended particle concentration of 75 mg l^{-1} was employed in all experiments. The broken line represents the saturated solubility, C_{sat} , of BaP at 20°C .

TABLE 3. Apparent distribution coefficients, K_D s, as a function of suspended particulate concentration, SPM , for BaP sorption to whole and sieved fractions of estuarine sediment, and parameters defining the regression of $\log K_D$ vs $\log SPM$ (Equation 3; Figure 2)

D , mm	SPM , $mg\ l^{-1}$ =	K_D ($\times 10^3$), $ml\ g^{-1}$					log a	b	R^2
		25	75	125	500	1000			
Whole									
<2		143 \pm 16.2	89.5 \pm 18.9	85.5 \pm 32.5	31.6 \pm 13.0	17.5 \pm 3.87	6.02	0.571	0.96
Sieved fractions									
0.25-2		123 \pm 49.5	102 \pm 17.3	102 \pm 21.5			5.26	0.123	0.89
0.125-0.25		477 \pm 64.9	111 \pm 52.3	87.0 \pm 40.8	53.5 \pm 13.2	19.9 \pm 10.4	6.61	0.755	0.93
0.063-0.125		274 \pm 48.4	116 \pm 22.0	71.1 \pm 40.3	38.9 \pm 5.1		6.30	0.653	0.97
<0.063		302 \pm 168	149 \pm 43.4	153 \pm 9.32	48.1 \pm 31.5	27.3 \pm 17.2	6.43	0.649	0.97

where P and C are the apparent or measured adsorbed (particulate) and aqueous concentrations of BaP, respectively, and K and n are constants. Despite the aqueous concentration exceeding the saturated solubility of BaP (*c.* $1.5\ \mu g\ l^{-1}$ at $20\ ^\circ C$; Schwarzenbach *et al.*, 1993) in some experiments, sorption is reasonably linear in all cases within the range of concentrations studied. Thus, assuming the sorption constant n has unit value, the slopes of the isotherms represent an apparent particle-water distribution coefficient, K_D , whose magnitude is independent of the concentration of compound present:

$$K_D = P/C \quad (2)$$

Values for K_D and K_{oc} , the organic carbon-normalized distribution coefficient, are given in Table 2, along with the statistical parameters defining the linear fits to the isotherms. The finest fraction of sediment ($D < 63\ \mu m$) has the highest K_D , but there is neither a regular reduction in K_D with increasing grain size nor a uniform distribution of K_{oc} s among the different grain sizes. The weighted sums of sorption constants in the individual fractions ($K_D = 1.01 \times 10^5\ ml\ g^{-1}$; $K_{oc} = 4.36 \times 10^6\ ml\ g^{-1}$) are similar to those of the whole sediment ($K_D = 1.29 \times 10^5\ ml\ g^{-1}$; $K_{oc} = 4.66 \times 10^6\ ml\ g^{-1}$) suggesting that adsorption is largely an additive process in heterogeneous suspensions of different particle populations.

Particle concentration effect

Apparent distribution coefficients for BaP sorption to each fraction of estuarine sediment are given as a function of suspended particle concentration (SPM) in Table 3), and the data are plotted in logarithmic form in Figure 2. Data are incomplete for the $D = 0.25-2\ mm$ and $D = 0.063-0.125\ mm$ fractions as

insufficient sediment of these size ranges was recovered from the bulk sample. Propagated errors were generally larger in these experiments (typically 20 to 50%) than in the sorption isotherm experiments ($P \sim 10\%$; $C \sim 10-30\%$). This is because counts in the aqueous phase above particle concentrations of a few hundred $mg\ l^{-1}$ were sensitive to slight contamination from solvents and glassware and from random counting errors of the instrument. Moreover, it was suspected that accurate and reproducible particle concentrations were not maintained (especially at $25\ mg\ l^{-1}$) through imperfect subsampling of the sediment slurry. Nevertheless, an inverse relationship between K_D and particle concentration (or PCE), in which K_D s are reduced by an order of magnitude over the particle concentration range studied, is evident in all cases.

Discussion

Empirical definition of the particle concentration effect

The BaP sorption data presented in Figure 2 may be defined by the empirical equation:

$$\log K_D = -b \log SPM + \log a \quad (3a)$$

or:

$$K_D = a SPM^{-b} \quad (3b)$$

where a and b represent, respectively, the particle concentration-normalized K_D (at $SPM = 1\ mg\ l^{-1}$) and the gradient of the relationship. Estimates of a and b , shown in Table 3, were derived from regressions of $\log K_D$ vs $\log SPM$ and, as with sorption isotherm constants, bear no clear relationship with sediment particle size.

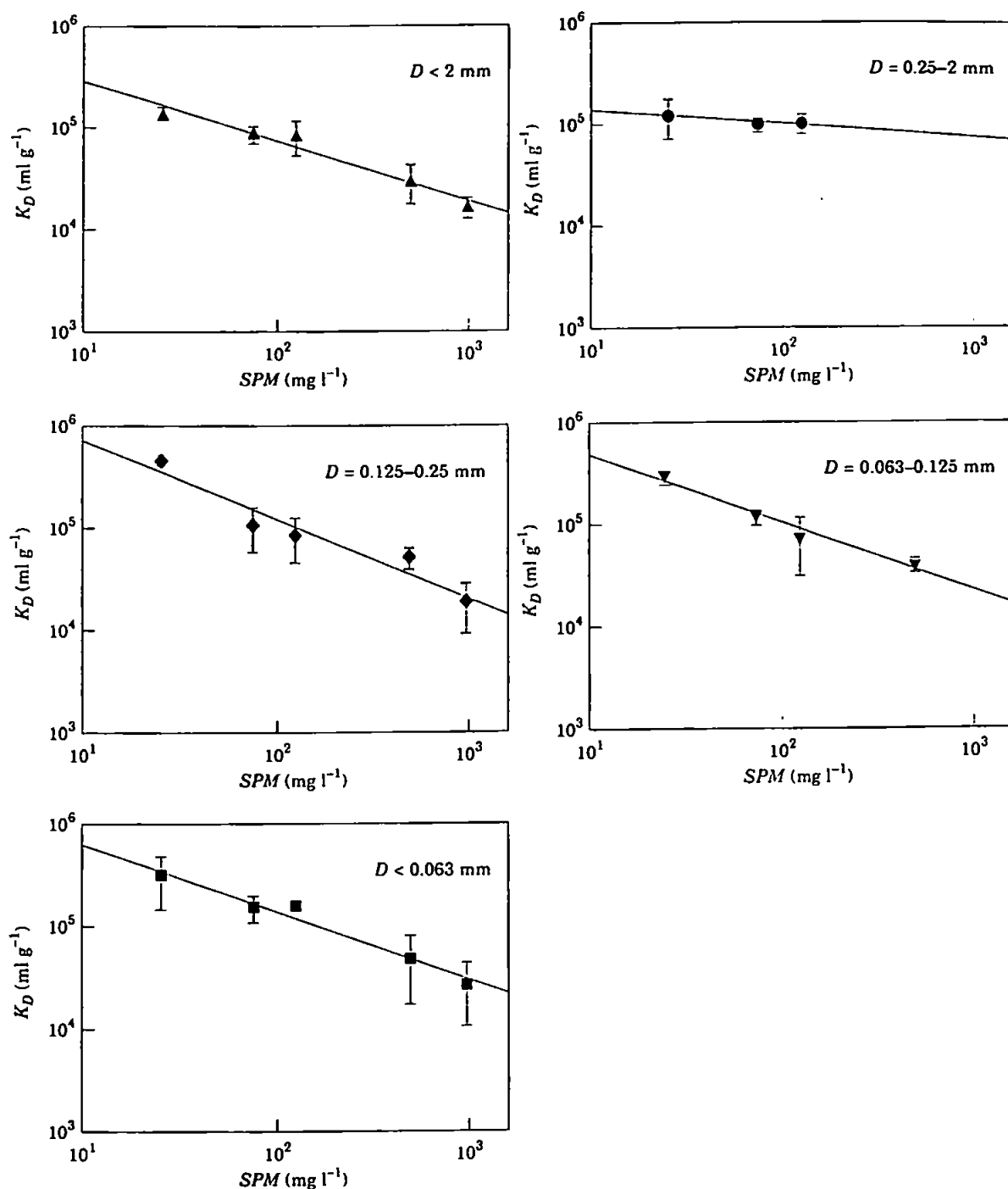


FIGURE 2. Apparent distribution coefficients, $K_{D,s}$, for BaP sorption to whole and sieved fractions of Plym Estuary sediment (D =particle diameter), versus suspended particle concentration (SPM).

Equation 3 was applied to literature data on HOM partitioning between fine (sieved or suspended) sediments and water in various environments and the resulting estimates of a and b are given in Table 4. Values are site- and compound-specific and are likely dependent to some extent on the experimental proto-

col employed (e.g. laboratory *vs* field-based), but serve to illustrate the generality of the effect. That all datasets can be defined by a common algorithm is perhaps surprising given that the concentration of colloids is environment-dependent and not a simple function of suspended particle concentration

TABLE 4. Estimates of a and b for hydrophobic organic micropollutants in various aquatic environments (K_{ow} = octanol-water distribution coefficient)

Compound	$\log K_{ow}$	Sample	SPM, mg l^{-1}	$\log a$	b	Reference
Hexachlorobenzene	5.50	<24 μm Detroit River sediment in tap water	10–2000	5.0	0.42	Jepsen <i>et al.</i> (1995)
1,3,6,8-tetrachlorodibenzo- <i>p</i> -dioxin	7.13	<100 μm Lake 304 sediment in Milli-Q water	1–1000	6.3	1.50	Servos and Muir (1989)
2,2',5,5'-tetrachlorobiphenyl	6.09	Unfiltered Lake Michigan water	0.3–1.9	5.0	0.75	Eadie <i>et al.</i> (1990)
		Unfiltered Lake Superior water	0.2–8	5.3	1.08	Baker <i>et al.</i> (1986)
		Unfiltered North Sea coastal water	1–150	6.2	0.94	Duinker (1986)
		<63 μm Plym Estuary sediment in Plym river water	10–1000	5.7	0.61	Rawling <i>et al.</i> (1998)
2,2',4,4',5,5'-hexachlorobiphenyl	7.15	Unfiltered Lake Michigan water	0.3–1.9	5.8	0.46	Eadie <i>et al.</i> (1990)
		Unfiltered Lake Superior water	0.2–8	5.4	0.54	Baker <i>et al.</i> (1986)
Benzo[a]pyrene	6.50	<63 μm Rotterdam Harbour sediment in Atlantic Ocean water	50–10 000	6.2	0.83	Hegeman <i>et al.</i> (1995)
Diethylhexyl phthalate	7.50	<63 μm Beaulieu Estuary sediment in Beaulieu river water	10–1000	6.4	1.15	Turner and Rawling (in press)

(Honeyman & Santschi, 1989; Moran *et al.*, 1996) and that variations in suspended particle concentration in the field are often accompanied by the resuspension and advection of multiple particle populations of differing characteristics (Turner *et al.*, 1994). The data also indicate a general relationship between a and K_{ow} , the octanol-water distribution coefficient; thus, the parameter a may be likened to some sort of 'hydrophobicity index'. Definition of partitioning data in terms of two empirical parameters, at least one of which may be related to a fundamental and readily available chemical property, is extremely useful as a basis for providing first-order predictions of the environmental distributions of HOMs, as demonstrated below.

Transport modelling and the retention of HOMs in estuaries

Particulate and aqueous phase definition. Most experimental evidence suggests that inadequate particle-water phase separation is at least partly responsible for the PCE (see Koelmans & Lijklema, 1992 and Zhao & Lang, 1996 and reference therein). Accordingly, HOMs which are operationally embraced by the aqueous phase include those in true solution and those complexed with dissolved organic matter and sorbed

to colloids and non-settling or non-filterable particles and whose chemical and biological properties are modified by such an association (Sigleo & Means, 1990; Santschi *et al.*, 1997; Butcher *et al.*, 1998). For example, relative to HOM in true solution, photo-reactivity may be reduced due to photon absorption by a surrounding humic medium, or enhanced by the accumulation of photochemical transients like singlet oxygen within a colloidal matrix (Gustafsson & Gschwend, 1997). The thermodynamic distinction between sorbed (or particulate) and aqueous phases is, therefore, unclear as colloidal- or organically-bound HOMs may exhibit chemical properties which are similar to either (or both) phase. There is, however, a clear physical distinction between aqueous and particulate HOMs: aqueous HOMs, regardless of their association and including colloidal and non-settling particles, are directly coupled with water movement and can be transported a considerable distance from source, whereas particulate HOMs are subject to additional physical and chemical processes such as settling, erosion and aggregation, and, neglecting possible diagenetic modification, their local residence times are significantly longer.

Specifically, the distinction between the aqueous and particulate phases should be a particle size equivalent to either neutral buoyancy or a settling rate which

is comparable with the hydrodynamic flushing time of the environment of interest (Mayer, 1982; Turner & Millward, 1994). Studies on suspended particle size distributions in lakes suggest that a particle diameter of about 10 μm affords a suitable cutoff for distinguishing conservative or 'aqueous' particles from the settling population (Baker *et al.*, 1991; Gustafsson & Gschwend, 1997). In more dynamic, tidally-influenced estuaries, where salt-induced flocculation may be important, a physical cutoff is more difficult to define, but a first-order estimate may be gained by comparing Stokesian particle settling rates with estuarine hydrodynamic flushing times. For spherical particles of diameter less than about 100 μm , the following equation defines the settling velocity, v_s , under laminar conditions:

$$v_s = \frac{(\rho_s - \rho)gD^2}{18\mu} \quad (4)$$

where ρ_s and ρ are the densities of the settling particles and water, respectively, D is particle diameter, g is the acceleration due to gravity, and μ is the dynamic viscosity of the water. The settling time, t_s , through a well-mixed water column of depth z is, therefore:

$$t_s = \frac{18\mu z}{(\rho_s - \rho)gD^2} \quad (5)$$

Particles will resist settlement and escape a semi-enclosed environment when the settling time exceeds the flushing time, τ , or, on a particle size basis, when:

$$D < \left[\frac{18\mu z}{(\rho_s - \rho)g\tau} \right]^{1/2} \quad (6)$$

A critical diameter, D_c , equal to the right-hand side of Equation 6, represents the maximum size of particles which are maintained in suspension during transit from river to sea, or the largest particles which are operationally encompassed by the aqueous phase for a given environment. Typical estuarine flushing times range from a few days to a few months (Morris, 1990; Millward & Turner, 1995) and for a dynamic viscosity of 0.015 $\text{kg m}^{-1} \text{s}^{-1}$, a particle density of 2650 kg m^{-3} and a mean water depth of 10 m, are equivalent to a range in D_c of about 8 to 25 μm . These calculations are subject to important assumptions about the nature and settling characteristics of particles in suspension (Eisma, 1993) and neglect the effects of turbulence and particle aggregation-disaggregation. However, the estimated range in diameters appears to concord with *in situ* size

measurements of particles carried in permanent suspension in the seaward flowing surface layer of stratified estuaries (Walling & Moorehead, 1989; Turner, 1999) and may, therefore, be indicative of a size cutoff appropriate for contaminant modelling in estuaries.

For the purposes of the remaining discussion, and general HOM transport considerations in estuaries, two-phase partitioning based on a particle size cutoff is appropriate. A transport distribution coefficient, K_D' , is defined thus:

$$K_D' = \frac{P_s}{C_p + C_d} \quad (7)$$

where P_s (w/w) and C_p (w/v) represent concentrations of HOM sorbed to particles which are retained and escape the estuary, respectively, C_d (w/v) is the concentration of non-particle bound (or truly dissolved/complexed) HOM, and K_D' is identical to K_D (Equation 2) when $C = C_p + C_d$ and $P = P_s$. The PCE can be redefined in terms of SPM_s , the concentration of suspended particles whose diameter exceeds D_s , as follows:

$$K_D' = a' SPM_s^{-b'} \quad (8)$$

where, in practice, the empirical constants, a' and b' , are derived by employing centrifuge conditions which achieve a particle-aqueous cutoff appropriate to that defined by Equation 6. The remaining, non-settleable particles ($D < D_s$) are either pre-existent or are formed by disaggregation during sediment resuspension or particle-particle interactions in the water column and an implicit assumption of Equation 8 is that their concentration is some function of the total particle loading.

Implications of the particle concentration effect. With respect to transport modelling, a useful value that can be calculated from the distribution coefficient and suspended particle concentration is the fraction of total HOM that exists in the aqueous phase (encompassing non-settling particles), f_c . The aqueous concentration relative to the total concentration in the water column is given as follows:

$$f_c = \frac{C_p + C_d}{C_p + C_d + P_s SPM_s} \quad (9)$$

Combining Equations 7 and 9 yields:

$$f_c = \frac{1}{1 + K_D' SPM_s / 10^6} \quad (10)$$

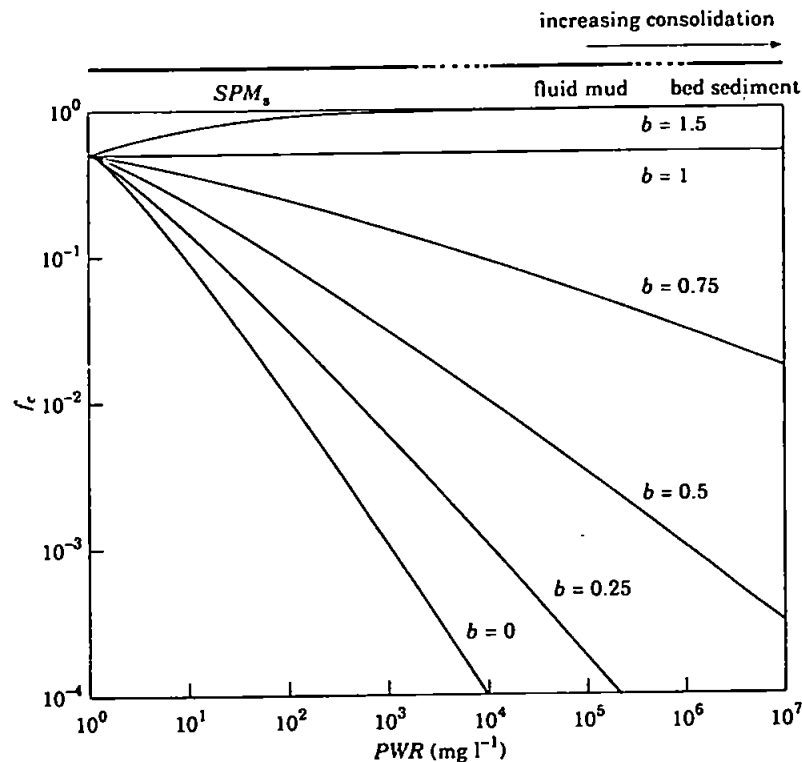


FIGURE 3. Fraction of hydrophobic organic micropollutant in the aqueous phase as a function of particle-water ratio (or particle concentration), calculated according to Equation 11 for a 'hydrophobicity index', a' , of 10^6 , and different values of b' between 0 and 1.5. The particle-water ratio embraces three modes of particle mobility: suspended particulate matter (as SPM_s); fluid mud; bed sediment.

or, incorporating the PCE (Equation 8):

$$f_c = \frac{1}{1 + a' SPM_s^{-(b'-1)}/10^6} \quad (11)$$

The fraction of total HOM that is adsorbed to suspended particles which are at least partially retained by the system, f_s , is obtained by difference:

$$f_s = 1 - f_c \quad (12)$$

Partitioning expressed in this way gauges the relative importance of each mode of transport (directly coupled with water and retarded by gravitational settlement, resuspension etc.) for a given pollutant and affords a first-order assessment of the retention capacity of the environment under study for that pollutant. Brunk *et al.* (1997) suggest that $f_s > 0.5$ represents 'significant' trapping of a pollutant by a semi-enclosed body such as an estuary or shelf sea, in that more than half will be retained by the sediment, at least with respect to the sediment turn-over timescale. This approach represents an upper-estimate of the retention capacity as it is assumed that there is a

continual supply of contaminant-depleted particles to the water column for adsorption and that contaminant degradation is negligible (see later discussion).

Figure 3 shows the fraction of HOM in the aqueous phase as a function of particle-water ratio, PWR (mg l^{-1}), calculated according to Equation 11. Since estimates of a' and b' based on a suitable particle size cutoff (Equation 8) are not available, representative values of a (10^6) and b (0–1.5) derived from Equation 3 (Tables 3 and 4) have been employed. Calculations are not extended below 1 mg l^{-1} as it is unclear whether Equation 8 (or Equation 3) is applicable when the mass contribution of colloids or non-settling particles approaches that of the total suspended particle loading (Honeyman & Santschi, 1989). Three modes of particle transport or mobility are indicated: suspended particulate matter (SPM_s , excluding colloids and non-settling particles), fluid mud (a loosely consolidated mud layer which can be entrained as a high density suspension) and bed sediment. Increasing PWR above about 10^5 mg l^{-1} is accompanied by increasing consolidation and whether or not Equations 3 and 8 can be extrapolated to these conditions is uncertain without a better understanding of the

TABLE 5. Decay constants (k) and half-lives ($t_{1/2}$) for the degradation or transformation of BaP in estuaries

	k	$t_{1/2}$	Reference
Water column			
Direct photolysis (turbid conditions; 10 m depth) ^a	0.09–0.6 days ⁻¹	1.2–7.7 days	Zwolsman (1994)
Microbial degradation (at 11.5 °C)	0.037–0.18 yr ⁻¹	3.9–19 yr	Readman <i>et al.</i> (1982)
Sediment			
Leaching by pore waters (at 11.5 °C)	0.0090 yr ⁻¹	77 yr	Readman <i>et al.</i> (1987)
Microbial degradation (at 11.5 °C)	0.24 yr ⁻¹	2.8 yr	Readman <i>et al.</i> (1987)

^aDerived from near-surface, clear water, summer conditions at 40°N.

cause(s) of the PCE and the source(s) of non-settling particles. Causes relating to inter-particle collisions are clearly inappropriate in porewaters; those relating to the concentration of pre-existing colloids and non-settling particles, which are independent of particle mobility, are potentially applicable, provided pore-water colloids and particles exhibit similar properties to such in the overlying water column and that diagenetic release or scavenging of compound-binding dissolved or colloidal organic matter is not significant.

Qualitatively, the calculations indicate a minimum fraction in the aqueous phase when $b'=0$ and there is no particle concentration-dependence of K_D' . Increasing the magnitude of b' increases the particle-concentration dependence of K_D' such that increasing particle concentration is increasingly offset by the accompanying reduction in K_D' . When $b'=1$, increasing particle concentration is directly compensated by the reduction in K_D' and a constant aqueous fraction ($f_c=0.5$ in this example) is maintained at all particle concentrations. When $b'>1$ the reduction in K_D' more than offsets the increase in particle concentration; an increase in the aqueous fraction with increasing particle concentration results and significant pollutant trapping no longer occurs ($f_c>0.5$).

These predictions clearly demonstrate the potential for error when flux and retention calculations and pollution assessment criteria are based on an invariant sorption constant. The degree of error will depend on the magnitude of b (or b'), and the PWR employed when deriving a working sorption constant in relation to the PWR in the environment under study. Sorption experiments are often undertaken in the presence of unrealistically high particle concentrations (Balistrieri & Murray, 1987; Chang *et al.*, 1987; Booi, 1993; Zhao & Lang, 1996; Kan *et al.*, 1997) and the extent of sorptive removal or retention in the environment will be underestimated according to the magnitude of b (or b'). Significantly, when $b>1$ the extent of sorptive removal from the water column increases with decreasing particle concentration; in practice, this

suggests that turbid environments (e.g. turbidity maxima) receiving waste products may assist the transport of certain HOMs to lower turbidity environments where sorption is more favourable. In contrast, (bed) sediment quality criteria derived from sorption studies employing suspensions and applying the equilibrium partitioning approach (Shea, 1988; van der Kooij *et al.*, 1991; Webster & Ridgway, 1994; Liu *et al.*, 1999) may significantly overestimate 'safe' or 'permissible' environmental concentrations.

Particle size effects and HOM degradation. In order to refine the estimates of the retention capacity of HOMs by estuaries, both the particle size-dependence of sorption and loss (e.g. volatilization) or transformation (e.g. photolytic oxidation or microbial degradation) mechanisms must be accounted for. As demonstrated above and in previous field and laboratory studies on the grain size distribution of HOMs in sediment, there is no clear relationship between sorption constants (K_D , K_{oc} , a) and the reciprocal of particle diameter (Kukkonen & Landrum, 1996; Pierard *et al.*, 1996; Koelmans *et al.*, 1997; Witt & Trost, 1999). Sorption is evidently dependent to some extent on the characteristics of the particulate organic material, including its age, degree of mineralization, surface area and aromaticity (Gauthier *et al.*, 1987; Huang & Webster, 1997; Standley, 1997). Empirical definition of this effect, although not possible with the present data, will form an essential component of accurate flux and retention calculations, as particles of different size (hence sorption capacity) are subject to different hydrodynamic controls and residence times (Dyer, 1989; Pereira *et al.*, 1996; Dellapenna *et al.*, 1998; Hughes *et al.*, 1998).

HOM loss or transformation mechanisms are generally more significant in the aqueous phase because of light extinction in the water column and the relative inaccessibility of adsorbed or occluded forms to chemical and biological processes. Transformation rates for BaP in the estuarine environment are given in

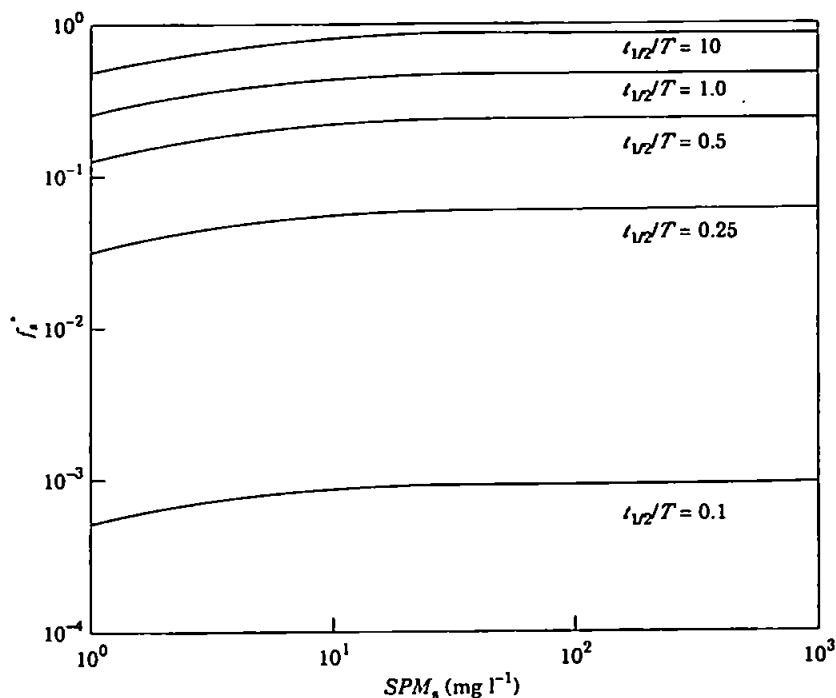


FIGURE 4. Fraction of hydrophobic organic micropollutant retained by an estuary as a function of (settleable) suspended particle concentration (SPM_s), calculated according to Equation 13 using representative values of a' and b' of 10^6 and 0.75 , respectively, and for different ratios of degradation half-life to water transit time ($t_{1/2}/T$).

Table 5. Microbial degradation in the water column is negligible compared with typical flushing times of estuaries. However, measured half-lives for direct photolysis in clear, mid-latitude, summer surface water are on the order of an hour (Payne & Phillips, 1985) and accounting for light extinction in the more turbid estuarine water column, photolysis half-lives of between about 1 and 8 days are predicted (Zwolsman, 1994). In contrast, BaP in inter-tidal estuarine sediment is largely unavailable for post-depositional transformation, including microbial degradation and leaching by porewaters, at least with respect to the residence time (typically several years) of the aerobic mixed layer. Thus, photolytic degradation is an important removal mechanism of aqueous (or, strictly, truly dissolved) BaP, while the bed sediments afford a medium-term (years) to long-term (decades) sink for the compound.

Loss or transformation of HOM from the aqueous phase that affects its medium- to long-term retention by estuarine sediment is that which occurs from its source to a region of turbidity where sorption and subsequent incorporation into the bed sediment takes place. Assuming first-order degradation kinetics, a simple correction that can be applied to Equation 11 is as follows:

$$f_s^* = \left[1 - \frac{1}{1 + a' SPM_s^{-(b'-1)}/10^6} \right] \exp(-kT) \quad (13a)$$

$$= (1 - f_t) \exp(-kT) \quad (13b)$$

The parameter f_s^* represents the overall retention of the HOM by the system and is additionally dependent on T , the transit time from the source of the HOM to the turbid zone, and k , the first-order rate constant for the transformation or degradation of the compound. The loss of HOM incurred by transformation or degradation is therefore dependent on the ratio of the reaction half-life to the water transit time; for $t_{1/2}/T < 1$ more than 50% of the compound will be lost before partitioning and partial incorporation into the sediment occurs. The effects of photolytic transformation of BaP in the aqueous phase on its overall retention by an estuary are demonstrated in Figure 4. Here, the retention, f_s^* , is plotted against (settleable) suspended particle concentration, SPM_s , calculated according to Equation 13 using representative values of a' and b' of 10^6 and 0.75 , respectively, and for different ratios of $t_{1/2}/T$ which encompasses the range in rate constant given in Table 5 and water transit times between about 1 and 10 days.

Although these calculations are compound-specific and largely hypothetical, Equation 13 serves as a useful framework for estimating the overall retention of HOMs in estuaries for which pollution inputs and particle residence times are defined and where empirical degradation and partitioning data are available. Qualitatively, the equation illustrates the variety of factors which may affect the overall reduction of HOMs, including the water temperature and bacterial density (if microbial degradation is important) and the hydrodynamic processes which control water transmit times and generate the turbidity maximum.

Conclusions

Sorption of benzo[a]pyrene to estuarine sediment is defined by a linear isotherm and exhibits a particle concentration effect (that is, an inverse relationship between the distribution coefficient, K_D , and suspended particle concentration, SPM). The particle concentration effect is common to many hydrophobic organic micropollutants (HOMs) in various aquatic environments and appears to be related to the presence or desorption of colloidal and non-settling particles which are operationally encompassed by the aqueous phase. While an understanding of the precise causal mechanisms is important in its own right, of equal importance is empirical inclusion of the effect in pollution transport models and chemical flux calculations.

The equation: $K_D = aSPM^{-b}$; where a and b are site- and compound-specific constants, appears to define the effect reported in the literature, at least over a range in suspended particle concentrations typical of the estuarine environment. A modified algorithm of the same form: $K_D' = a'SPM_s^{-b'}$; is proposed for chemical flux calculations and pollutant transport considerations. Here, a transport distribution coefficient represents the ratio of HOM concentrations discriminated according to their transport characteristics; thus, the aqueous phase embraces particles which are transported in permanent suspension through an estuary, while the particulate phase is specific to particles (of concentration SPM_s) whose long-range transport is restricted by gravitational settlement.

A model for the retention of HOMs in estuaries was developed and tested using the BaP sorption data generated in this study and its published photolytic degradation rate in the aqueous phase. Although the model demonstrates the factors which affect the estuarine retention of HOMs and serves as a framework for first-order retention estimates, accurate predictions will rely on the definition of appropriate particle

size cutoffs for transport modelling and compound-specific PCE algorithms derived according to this cutoff.

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Notation

a (or a')	'hydrophobicity index'; <i>i.e.</i> sediment-water partitioning normalized to a particle concentration of 1 mg l^{-1} .
b (or b')	gradient of $\log K_D$ (or K_D') versus $\log SPM$ (or $\log SPM_s$)
BaP	benzo[a]pyrene
C	apparent or measured aqueous concentration of HOM (w/v)
C_{sat}	aqueous concentration of HOM at saturated solubility
C_d	truly aqueous (or dissolved) concentration of HOM (w/v)
C_p	particulate concentration of HOM (w/v) which is in permanent suspension
D	particle diameter
D_s	maximum diameter of particles carried in permanent suspension
f_c	aqueous fraction (embracing non-settling particles) of total HOM in the water column
f_i	fraction of total HOM in the water column which is adsorbed to particles subject to gravitational settlement
f_s	fraction of total HOM in the water column which is retained by an estuary
g	acceleration due to gravity
HOM	hydrophobic organic micropollutant
k	decay constant for HOM degradation or transformation
K	sorption isotherm constant
K_D	apparent or measured sediment-water distribution coefficient (v/w)
K_D'	transport distribution coefficient (v/w)
K_{oc}	organic-carbon normalised distribution coefficient (v/w)
K_{ow}	octanol-water distribution coefficient
μ	dynamic viscosity
n	sorption isotherm constant
P	apparent or measured particulate (adsorbed) concentration of HOM (w/w)

P_s	concentration of particulate (adsorbed) HOM (w/w) which is subject to gravitational settlement
PCE	particle concentration effect
POC	particulate organic carbon content
PWR	particle-water ratio (w/v)
ρ	water density
ρ_s	settling particle density
SPM	apparent or measured concentration of suspended particles (w/v)
SPM ₁	concentration of suspended particles whose diameter exceeds D_s (w/v)
$t_{1/2}$	half-life for transformation or degradation of HOM
t_s	particle settling time
T	water transit time from HOM source to a zone of high turbidity
τ	estuarine flushing time
v_s	Stokesian settling velocity
z	water depth

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