The Physico-Chemical Speciation
of Polycyclic Aromatic Hydrocarbons (PAH) in Aquatic Systems

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Die physikalisch-chemische Speziation polycyclischer aromatischer Kohlenwasserstoffe (PAH) in aquatischen Systemen

Zusammenfassung. Die „physikalisch-chemische Speziation" wird dargestellt zur Beschreibung der Umweltchemie organischer Verbindungen in aquatischen Systemen. Dabei dienen die PAH als Beispiel. Es werden Meßergebnisse und experimentelle Befunde gegeben, die die Anwesenheit verschiedener physikalisch-chemischer Spezien von PAH in der Mündung des Tamar-Flusses (UK) demonstrieren. Es wird gezeigt, daß der Grad und damit der Chemismus der Teilchenbindung von PAH im Tamarfluß nicht den üblichen Sorptionsmodellen entspricht. Diese Feststellung hat beträchtliche Auswirkungen auf die Voraussehbarkeit des aquatischen Chemismus der PAH einschließlich der Verfügbarkeit dieser Verbindungen für Photooxidation und biologische Aufnahme (Toxizität).

Summary. 'Physico-chemical speciation' is presented as a concept to describe the environmental chemistry of organic compounds in aquatic systems, using polycyclic aromatic hydrocarbons as an example.

Survey data and experimental results are reported which demonstrate the presence of different physico-chemical species of PAH in the Tamar Estuary, UK.

The degree, and hence chemistry of binding of PAH to particulates in the Tamar is shown to be incompatible with current sorption modelling techniques. This finding has extensive repercussions on prediction of the aquatic chemistry of PAH, including availibility of the compounds for fates such as photo-oxidation and biological uptake/toxicity.

Introduction

The major states in which organic compounds can exist in natural waters include gaseous, truly dissolved, micelle forms, surface adsorbed onto particulates, occluded, associated with lipid films at the air/water interface, and incorporated into the biota. Factors determining the species are primarily related to the physico-chemical properties of the individual compounds, such as solubility, hydrophobicity and vapour pressure. For example, well studied pesticides

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in aquatic environments are predominantly sorbed onto particulates, whereas chlorinated phenols are primarily in solution. With homologous series (for example n-alkanes) there is a gradual change in physico-chemical properties and hence in cycling processes. The presence of solubilising agents, such as detergents in polluted environments and dissolved organics, might be expected to change the balance of the species present. Sources from which the pollutants are derived will also determine the species of compound present, for example polycyclic aromatic hydrocarbons (PAH) derived from oil would be expected to behave differently with regard to speciation than would PAH occluded in combustion particulates.

As with trace metal speciation, the physico-chemical speciation of organic compounds will ultimately control the transport, fates and biological availability/toxicity of the compounds in aquatic environments. The significance of physico-chemical speciation is exemplified for PAH in Fig. 1. The complex interactions illustrated are controlled to a high degree by the aqueous/particulate chemistry.

Of natural water bodies, estuaries are potentially most susceptible to physico-chemical speciation of organics owing to the hydrodynamic, physico-chemical and biological gradients encountered. Additionally, for micropollutant studies, estuaries are often susceptible to a multiplicity of inputs.

The approach adopted to introduce 'physico-chemical speciation of PAH in aquatic systems' will discuss results derived from survey data of 'in situ' PAH in the Tamar Estuary, UK, and relate these findings to experimental results and theory proposed for the behaviour of PAH in natural waters.

Study Area

The geographical location of the study area and positions of sampling sites are illustrated in Fig. 2. The Tamar catchment drains relatively unpolluted moorland. In contrast, urban Plymouth is situated adjacent to the lower estuary (Fig. 2). Morris et al. [19−21] have described the master variables and nutrient chemistry of the Tamar. The aquatic distribution and microbial heterotrophic degradation of PAH (Readman et al. [26]) and distribution of PAH in surface sediments (Readman et al. [28]) in the Tamar Estuary have been reported. Although the Lynher and Tavy tributaries enter the estuary, the River Tamar represents the major fresh-water source, consequently sampling has been restricted to the main estuarine axis (Fig. 2).
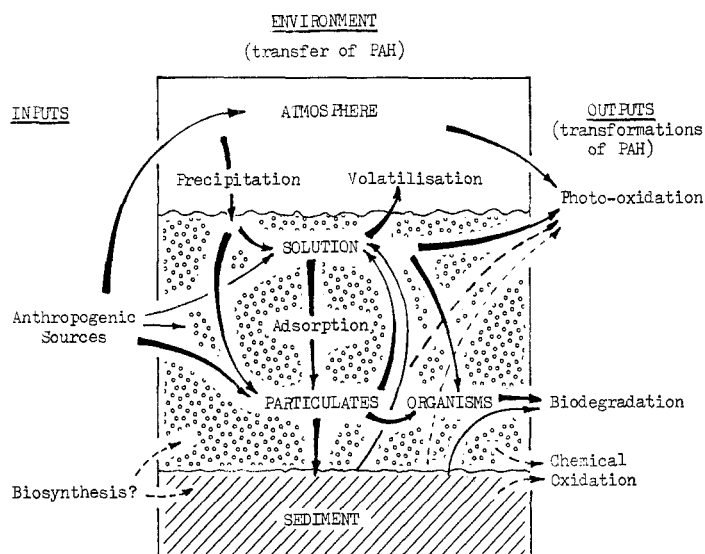
Fig. 1. Fates of PAH in the aquatic environment. Owing to the range of molecular weights (and hence physico-chemical properties) of the PAH, the relative importance of pathways will differ for individual homologues. The boldness of the arrows in the above diagram represents a subjective indication of the relative contributions for a four aromatic ring PAH. The importance of the aqueous/particulate chemistry (and hence speciation) is of special interest
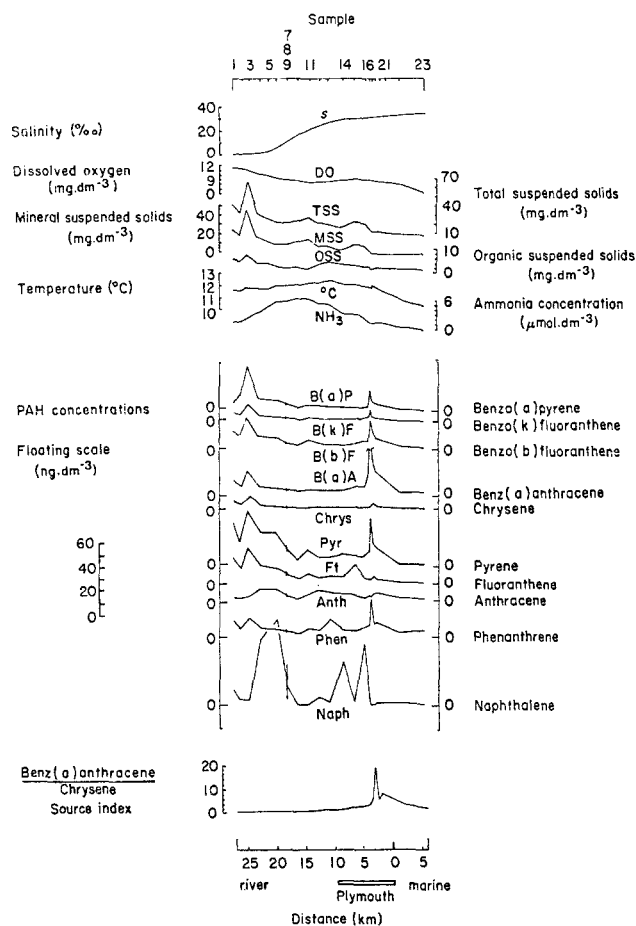

Fig. 2. Description of the Tamar Estuary and sampling stations. Water sample numbers and locations are indicated on the right hand side. The two sampling stations of waters for sorption experiments and analyses of 'dissolved' and 'particle associated' PAH are denoted by A and B. Distance upstream from the narrows (N) at the mouth of the estuary are indicated in 5 km intervals and circled. Plymouth is indicated by the hatched area with the dockyards located along the estuarine foreshore demarked by stipples. The region of the hydrodynamically generated turbidity maximum (from which suspended particulates were sampled for PAH analyses of separated particle size fractions) is identified

Fig. 3. Axial profiles of individual PAH concentrations and a selection of environmental variables in waters of the Tamar Estuary. Sample locations are shown in Fig. 2. Distances from the mouth of the estuary are shown at the bottom of the diagram and the position of Plymouth is indicated. A floating scale is used for the PAH concentrations with origins for individual compounds indicated on both sides of the diagram. Deviations from the mean of triplicate samples 7, 8 and 9 are shown as 95% confidence interval bars on the concentration plots of the individual PAH. A source index of Plymouth-specific PAH is indicated at the base of the diagram. (From Readman et al. [26])
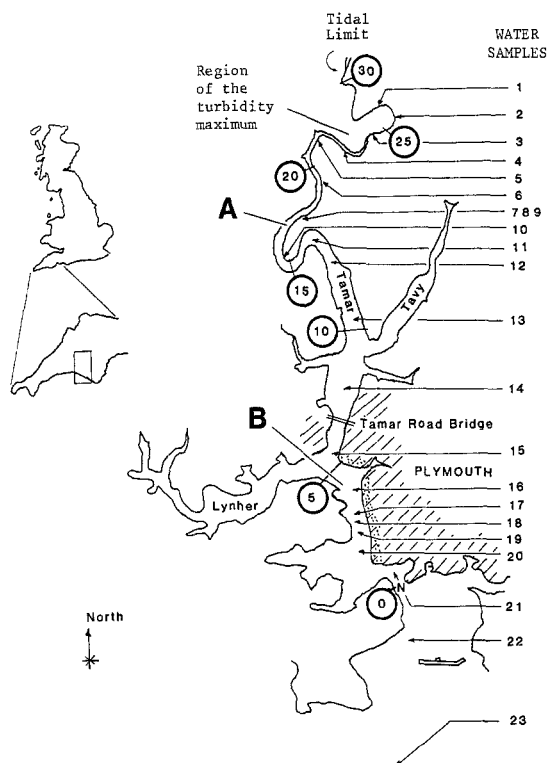
PAH in the Tamar Estuary Water Column

There is very little published data on PAH in estuaries (Herrmann and Hübner [10]; Jackim and Lake [11]; Neff [22]; Readman et al. [26]). Only Herrmann and Hübner [10] and Readman et al. [26] have reported individual PAH concentrations in estuarine waters and both discuss concentrations in context with concurrent environmental variable results (for example salinity and turbidity).

Survey data from the Tamar Estuary water column (Readman et al. [26]) is shown in Fig. 3. Results indicate the presence of different physico-chemical states of PAH. Most notably a division can be drawn between low and high molecular weight homologues. PAH comprising of four or more fused aromatic rings are highly associated with particulates (correlation coefficient 'r' typically > 0.60). In contrast, lower molecular weight homologues do not significantly correlate with particulate loading. High levels of PAH (including high molecular weight compounds) in the

127

Table 1. Equilibrium partition coefficients for two Tamar Estuary water samples obtained: (i) by calculation from the linear free energy equation $\log K_p = \log K_{ow} + \log f_{oc} - 0.21$ (Karickhoff et al. [13]), (ii) from sorption experiments (Readman [27]), (iii) by fractionation and analyses of in situ 'dissolved' and 'particle associated' PAH actually present in sub-samples of the estuarine waters (Readman [27])

	(i) $\log K_p$ calculated from a linear free energy equation (25°C)	(ii) $\log K_p$ derived from sorption experiments (20°C)	(iii) $\log K_p$ from analyses of in situ PAH (20°C)
Water sample A (see Fig. 2) Salinity 1.3‰			
Anthracene	3.10	3.55	5.56
Fluoranthene	3.46	3.68	5.52
Benz(a)anthracene	4.17	4.31	$-$[a]
Benzo(a)pyrene	4.60	4.69	6.28
Water sample B (see Fig. 2) Salinity 22.3‰			
Anthracene	2.88 (2.95)[b]	3.14	4.82
Fluoranthene	3.24 (3.35)[b]	3.74	5.32
Benz(a)anthracene	3.95 (4.06)[b]	4.43	5.21
Benzo(a)pyrene	4.38 (4.51)[b]	4.93	5.50

[a] Benz(a)anthracene was below the limits of detection in the aqueous phase and hence was not quantified in this sample

[b] Values in parentheses are corrected for the increased salinity {and hence 'salting out' (Gordon and Thorne [7]) of the PAH}. These values were *estimated* by: (a) calculation of the aqueous solubilities of the PAH at 22.3‰ salinity using published distilled water solubilities and Setschenow constants (May [18]). (b) Insertion of the solubility data into the equation of Chiou and Schmedding [4]:

$$\log K_{ow} = -0.862 \log S + 0.710$$

to calculate the differences in $\log K_{ow}$ owing to increased salinity. (c) Addition of the estimated increase in $\log K_{ow}$ to the previously used published low K_{ow} values for recalculation of K_p as previously described for column (i) using the equation of Karickhoff et al. [13].
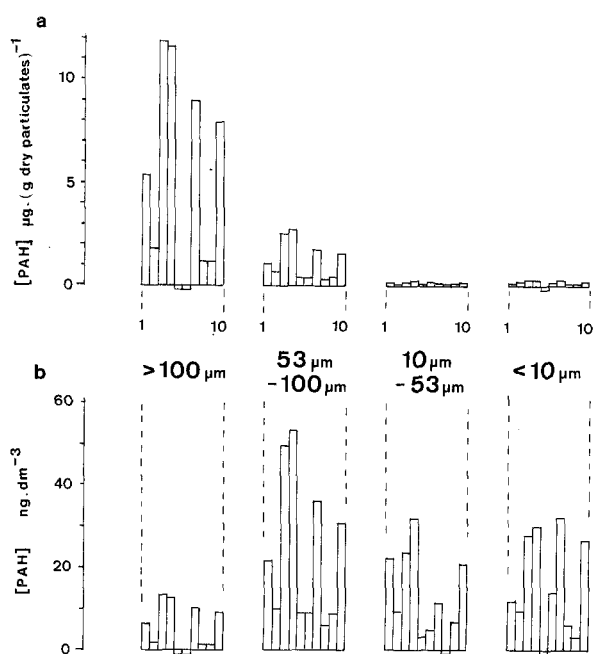

Fig. 4a, b. Histograms showing PAH concentrations and compositions in particulate size fractions of suspended solids sampled from the turbidity maximum of the estuary. For each fraction 10 bars are shown indicating individual PAH concentrations starting with *1* phenanthrene on the left and proceeding right in sequence, *2* anthracene, *3* fluoranthene, *4* pyrene, *5* benz(a)anthracene, *6* chrysene, *7* benzo(e)pyrene, *8* perylene, *9* benzo(k)fluoranthene, *10* benzo(a)pyrene. Short bars extending beyond the base line indicate that these compounds were not quantified. **a** PAH concentrations in isolated particulates [expressed in µg (g dry particulates)$^{-1}$]. **b** PAH concentrations corrected for the relative proportions of the particulate fractions in the estuarine water sampled and expressed as ng · dm^{-3}

urban region of the estuary do not correlate with suspended particulates and were probably present as transient soluble and colloidal forms. Removal of these samples from the correlation calculations for the remainder of the estuary increases the coefficient between large MW PAH and suspended particulates to $r > 0.87$ (even though concentrations of PAH in the estuary were less than 1% saturated).

The extent to which the distribution of PAH in the Tamar Estuary water column is regulated by sorption was investigated by comparing 'dissolved' and 'particle associated' PAH concentrations with partitioning of 'spiked' PAH in sub-samples of the same waters (Readman [27]). Theoretical partition was also predicted for the same samples using the linear free energy equation (Karickhoff et al. [13]):

$$\log K_p = \log K_{ow} + \log f_{oc} - 0.21$$

where K_p and K_{ow} are non-dimensional equilibrium partition coefficients of a hydrocarbon between particle and water, and *n*-octanol and water phases respectively; f_{oc} is the fractional organic carbon content (w/w) of the particulates. (Literature values for K_{ow} were obtained from Karickhoff

et al. [13]; Environmental Protection Agency Report [5]; Radding et al. [24].) Results are shown in Table 1.

K_p values derived from fractionations and analyses of in situ 'dissolved' and 'particle associated' PAH (Table 1) are in agreement with K_p values that can be calculated from equivalent data published by Lewis [16] on PAH distributions in other aquatic systems in the UK. The values are shown to be one to two orders of magnitude higher than those obtained by sorption experiments or predicted from sorption theory (Table 1). This result is highly indicative that PAH in the samples analysed are NOT in equilibrium between the aqueous and particulate phases. The difference in K_p values indicates that the PAH are considerably enriched in the particulate fraction, and are in a state that renders them unavailable for dynamic exchange with the water. Such species might include occlusion of PAH in particulates originating from combustion processes or erosion of asphalt surfaces.

To further investigate the distribution of PAH within suspended particulates, individual particle size fractions were isolated by the wet sieving of water sampled from the turbidity maximum of the estuary (Fig. 2). Fractions were subsequently analysed for PAH (according to the methods of Readman [27]; Readman et al. [25, 28]). Size fractions selected were > 100 µm; 53 µm to 100 µm; 10 µm to 53 µm and < 10 µm {corresponding approximately to sand, very

fine sand, silt and clay respectively by Wentworth Classification (Green [8])}. Results are shown in Fig. 4. Concentrations of PAH in particles > 100 μm were substantially higher (6-fold) than those in the 53 μm – 100 μm fraction and more than an order of magnitude greater than levels associated with particles < 53 μm. A proportion of the > 100 μm fraction was identified as low density organic debris. It might be expected that this fraction would contain charcoal particles and charred organic material, the densities of which are characteristically low. Prahl [23] has also reported enrichment of PAH in low density fractions of sediment. In agreement with Brassell and Eglinton [3] the sand fraction contains an order of magnitude higher concentrations of PAH than silt and clay sized fractions.

These results appear to contradict sorption theory, surface area apparently controlling concentrations of PAH to only a negligible extent. Occlusion of PAH into the particulates can be invoked to explain this observed particle size distribution.

A generally uniform PAH composition is apparent (Fig. 4), particularly in the larger particle size fractions (> 10 μm). The < 10 μm particles are, however, relatively enriched in higher molecular weight homologues, or alternatively depleted in lower molecular weight PAH. This might be attributable to preferential adsorption of the more hydrophobic higher MW compounds, although considering the evidence previously discussed a more feasible explanation might be that these smaller particles are susceptible to leaching of the more soluble lower molecular weight homologues.

The relative importance of the individual fractions in PAH composition of the total suspended particulates sampled are indicated in Fig. 4 (b). Although highest concentrations were recorded in the > 100 μm fraction, within the sample this is the fraction of least importance with regard to total PAH content.

PAH in Sediments of the Tamar Estuary

Sedimentary PAH have received considerable attention because they represent a record of the input history of the compounds into an aquatic environment. The occurence and distribution of PAH in surface sediments have been extensively investigated (Bieri et al. [1]; Blumer and Youngblood [2]; Giger and Schaffner [6]; John et al. [12]; Laflamme and Hites [14]; Lake et al. [15]; Matsushima [17]; Thompson and Eglinton [29] and others).

Readman et al. [28] have reported the distribution of PAH in the surface sediments of the Tamar Estuary. Highest concentrations were recorded at the riverine end with subsequent dilution by less polluted marine sediments resulting in a seaward trend of decreasing concentrations. A secondary maximum of PAH associated with urban Plymouth was superimposed on this trend. Although substantial variations in PAH concentrations were recorded throughout the Tamar region, PAH composition was generally uniform. A trend of change was, however, observed in sediments at the head of the estuary, where reductions in low MW PAH relative to higher MW homologues were recorded for sequential samples progressing from the tidal limit (Fig. 2) towards the mid-estuarine region. The extent to which particle size distribution (and particularly settlement of particles < 10 μm — discussed in the previous section) control this

observed pattern of PAH distribution requires further investigation. This observation might support exchange of the low molecular weight PAH from particulates to the water, which would support enrichment of 'soluble states' of these homologues identified in the previously discussed water column survey. The 'typical' PAH composition is restored in the urban region of the estuary. It is of special interest that urban discharges of differing PAH composition, such as that identified in the water column survey (water samples 16 to 20 inclusive, Figs. 2 and 3) were shown to assert only minor influence on the uniform surface sedimentary PAH composition. This might arise from dominance of a primary source buffering these less significant inputs, or alternatively these urban discharges are present in states (physico-chemical species) that are more susceptible to diffusive transport and fates such as volatilisation and photo-oxidation (as might be expected for soluble or colloidal species).

Suspended particulates in the water column were shown to contain similar levels, and compositionally reflect the larger MW PAH (MW ≥ 200) recorded in the surface sediments. This observation endorses the significance of particulate transport (and hence the influence of hydrodynamics) and might suggest that compound-selective degradation processes in the water column (for example photo-oxidation) are of only minor importance, the primary fate of these large MW compounds being sediment incorporation. Experimental results reported by Herbes et al. [9] predict that in a fresh-water system of equivalent particulate loading to the Tamar Estuary, photolysis of benz(a)-anthracene would represent a major fate of this compound, equivalent in relative importance to sediment sorption. Occlusion of PAH into the particulates would, however, remove any isomeric discrimination by photolysis and support the survey data from the Tamar Estuary.

Conclusion

Previously reported survey data of PAH and environmental variables in the Tamar Estuary water column (Readman et al. [26]) indicated the presence of different states or 'physicochemical species' of PAH. Throughout most of the estuary the large molecular weight PAH (MW ≥ 200) were shown to be highly correlated with suspended particulates (correlation coefficient 'r' > 0.87). An exception to this observed distribution was recorded for an urban Plymouth input which was judged to be present as transient soluble and colloidal species. Low molecular weight PAH (MW ≤ 200) were shown to be distributed independently of suspended particulates indicating enrichment of 'dissolved' species.

The particulate chemistry of the PAH was investigated by comparing 'dissolved' and 'particle associated' PAH concentrations with partitioning of 'spiked' PAH in sub-samples of the same estuarine waters. Equilibrium partition coefficients (K_p) calculated from the environmental analysis were shown to be one to two orders of magnitude higher than those obtained by sorption experiments. This result indicates that the PAH in the estuary are not in equilibrium between the aqueous and particulate phases, and are considerably enriched in the particulates (as might be expected for PAH occluded in particles originating from combustion or road surface abrasion).

Analyses of PAH in suspended particulate size fractions isolated from water sampled at the turbidity maximum of the

estuary revealed highest concentrations of PAH in relatively large particles ($> 53\ \mu m$), with surface area controlling PAH distribution to a negligible extent. Occlusion of the compounds in particulates can be invoked to explain this observation. A reduction in relative content of low molecular weight PAH in the smallest particle size fraction ($< 10\ \mu m$) might be attributable to selective leaching of these more soluble homologues and would support enrichment of 'soluble species' of these PAH identified in the water column survey.

PAH composition in surface sediments was generally uniform throughout the estuary. Suspended particulates in the water column were shown to contain similar levels and compositionally reflect the larger molecular weight ($MW \geq 200$) PAH. This observation demonstrates the importance of particle transport and hence the influence of hydrodynamics in controlling distribution. It might also suggest that compound-selective degradation in the water column (e.g. by photo-oxidation) is of only minor significance (the major fate of these larger molecular weight PAH being sediment incorporation). Occlusion of PAH into particulates might remove isomeric discrimination by photo-oxidation which would be expected to act primarily on dissolved species. Compositionally different PAH-rich urban discharges (as described in the water column survey) assert negligible influence on the sedimentary PAH assemblage. This might result from buffering by a dominant primary source or, alternatively, the speciation of PAH in the discharges (transient soluble and colloidal forms) might render the compounds more susceptible to diffusive transport and fates such as photo-oxidation and volatilization.

Important repercussions arise from the observations presented. In order to predict behaviour of PAH in aquatic systems the physico-chemical speciation of the compounds must be modelled. The water/particulate chemistry of PAH in the Tamar is shown to be incompatible with current sorption modelling techniques and it would appear that the degree of binding/leachability of the compounds must be quantified as a prerequisite to developing new environmentally realistic models.

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