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## USE OF LIQUID CHROMATOGRAPHY FOR THE MEASUREMENT OF ADSORPTION ISOTHERMS FOR POLYCYCLIC AROMATIC HYDROCARBONS ON COAL FLY ASHES

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### SUMMARY

The adsorption behaviour of polycyclic aromatic hydrocarbons (PAHs) on coal fly ashes was examined using frontal-analysis liquid chromatography. The experimental data were fitted to a number of theoretical isotherms and it was found that the Freundlich and Weber-Matthew models gave the most useful representation. Different parameters of these equations were used for comparative PAH adsorption studies on different fly ash samples.

Results indicated that the adsorption of PAHs on fly ash increases with increasing size of the PAH molecule. This work also showed that although the carbon content of the fly ash is the dominant factor in regulating PAH adsorption, other controlling factors such as porosity are also important.

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### INTRODUCTION

The annual world consumption of coal in electric power plants is predicted to increase to *ca.* 7000 million tonnes by the turn of the century<sup>1</sup>. A consequence of this is the increased production of organic and inorganic wastes. Polycyclic aromatic hydrocarbons (PAHs) have long been recognised as the most toxic organic pollutants associated with coal burning<sup>2,3</sup>. They are formed during the combustion process and adsorbed by fly ashes in the cooler parts of the plant<sup>4,5</sup>. Fly ash particles in the form of aerosols of respirable dimensions escape to the atmosphere via the stacks<sup>6</sup> and are therefore of considerable environmental concern.

The transport and fate of PAHs on fly ash substrates have been studied by several groups<sup>7,8</sup>. Korfmacher *et al.*<sup>7</sup> reported that fly ash-adsorbed PAHs exhibit chemical behaviour quite different from PAHs adsorbed on other substrates. Griest and Tomkins<sup>8</sup> physically fractionated stack fly ashes into adsorptive and non-adsorptive portions and concluded that the subfractions enriched in carbonaceous particles were more adsorptive and had higher levels of PAHs. Recently Eiceman and Vandiver<sup>9</sup> refuted Natusch's model<sup>10</sup> that the vapour phase adsorption of PAHs on fly ash is governed solely by a simple reversible condensation process related to the

vapour pressure. Instead, they postulated at least two separate mechanisms, chemisorption and vapour-pressure-controlled condensation. The dominant operating mechanism depends on the concentration of vaporised PAHs in the stack environment. Identifying chemisorption as a possible adsorption mode for trapping PAHs on fly ash is important, since it implies that these compounds, once released to the atmosphere, can be preserved for a considerable length of time through their association with solid fly ash particles. Poor extraction recoveries of PAHs from some fly ash samples may therefore be explained on the basis of such strong interactions<sup>11,12</sup>.

The physical and chemical parameters that control the interaction of solutes with solid substrates<sup>13,14</sup> may be characterised using adsorption isotherms, and numerous mathematical models exist for describing these adsorption processes<sup>15-17</sup>. A knowledge of the adsorptive behaviour of PAHs on fly ash will be critical to understanding the environmental control and fate of these compounds. Further, it will be of value in developing valid analytical methodologies for the accurate recovery of PAHs from such difficult matrices.

Adsorption isotherms can be studied in gaseous and liquid phases. The latter mode was chosen in this study since, by judicious selection of a solvent, a particular aspect of chemisorption could be studied. Traditionally, isotherms are obtained by either static or batch experiment, with the change in concentration of a solute being measured on addition of the adsorbent to the solution. Each experiment is equivalent to a discrete point on the adsorption isotherm. Disadvantages of this method are its slowness, the uncertainty in ascertaining the equilibrium points, and the wastage of large amounts of solute, solvents and adsorbents. Manual manipulation of large amounts of PAHs is also highly undesirable because of their extreme toxicity.

A number of chromatographic procedures based on packed columns have been developed to circumvent problems of the batch method<sup>18-20</sup>. The use of highly sensitive high-performance liquid chromatographic (HPLC) detectors is especially attractive, since they permit investigation of the adsorption of very low concentrations not accessible by other methods. Prolonged analysis times can be considerably shortened using short HPLC columns or other miniaturised microbore HPLC columns, with significant reductions in solvent and solute usage.

Among the liquid chromatographic methods used, Chuduk's elution method<sup>18</sup> and the frontal-analysis method<sup>19,20</sup> are mostly preferred. The attraction of the former is its simplicity, but the method requires the elution of successive peaks of higher concentration from the solid substrate and is clearly unsuitable for the study of PAHs on fly ash since many PAHs are irreversibly adsorbed. Frontal analysis entails the adsorption of solute on a solid substrate with incremental increases of the solute concentration in the mobile solvent at the column inlet. This method is preferred<sup>19,20</sup> because it provides accurate results and involves only the measurement of the retention time of a self-sharpening front. The design of the apparatus used in this study is based on this principle.

## EXPERIMENTAL

### *Chemicals and reagents*

Fluorene, anthracene, phenanthrene, pyrene and chrysene (Sigma, St. Louis,

MO, U.S.A.) and perylene (Analabs, North Haven, CT, U.S.A.) were used without further purification, and stock solutions ( $1.0 \text{ mg ml}^{-1}$ ) were made up in methylene chloride. Activated charcoal (14–60 mesh from Sigma) was mechanically ground to 200 mesh and oven-dried at  $105^\circ\text{C}$  overnight prior to use.

Analytical grade methylene chloride, *n*-hexane and toluene (Ajax, Sydney, Australia) were doubly-distilled from an all-glass apparatus. The distilled solvents were stored over molecular sieves (Union Carbide, Type 3A) for at least 24 h prior to use.

Fly ash samples from the combustion of Australian bituminous coals were obtained from the CSIRO pilot-scale combustion and precipitation facility (CSIRO, Division of Fossil Fuels, North Ryde, Australia)<sup>21</sup>. The fly ash from this unit is comparable with that from a full-scale coal-fired power station. To eliminate any possible interference in the adsorption study by organic compounds adsorbed on the ash, the samples were Soxhlet-extracted with 200 ml of toluene for 24 h ( $30\text{--}35 \text{ cycles h}^{-1}$ ), followed by ultrasonic washing with 100 ml of methylene chloride for 30 min. The resultant samples were chemically and physically characterised (Tables I and II). Ash samples with different residual carbon contents were prepared by combusting the washed samples in a furnace at  $650\text{--}750^\circ\text{C}$ , in an oxygen-enriched environment, for 6 h. Temperatures above  $800^\circ\text{C}$  were avoided to preserve the physical integrity of the samples<sup>22,23</sup>.

#### *Apparatus for isotherm measurement*

Fig. 1 schematically depicts the apparatus used for isotherm measurement. A Model 6000 solvent-delivery system (Millipore-Waters, MA, U.S.A.) was coupled to two two-way switching valves. Valve 1 could be switched to either valve 2 or a Model U6K Universal Liquid Chromatographic Injector (Millipore-Waters). Similarly, the effluent from valve 1 could be directed by valve 2 to either the fly ash column or a dummy column ( $4 \text{ cm} \times 0.63 \text{ mm O.D. and } 0.1 \text{ mm I.D.}$ , stainless-steel tubing). The effluent from these columns was fed to a Model 450 variable-wavelength UV detector (Millipore-Waters). The detector signal was recorded on a Sekonic Model SS250F dual-pen strip-chart recorder. The ash column was thermostatted to  $23 \pm 2^\circ\text{C}$ .

The fly ash samples were packed into  $3 \text{ cm} \times 4 \text{ mm I.D.}$  Uptight short HPLC columns (Activon Scientifics, Sydney, Australia) with methylene chloride as the slurry medium in a Micromeritics column packer (Micromeritics Instrument Corporation, GA, U.S.A.). Generally only 250–350 mg of ash were required. For adsorption of PAHs on fly ashes, the effluent from the detector was directed to waste, and this configuration is referred to henceforth as an open system. A closed system is one in which the effluent from the detector is fed directly back to the solvent reservoir, with the volume of the solvent in the reservoir being kept constant. Such a configuration was used for equilibration of the system when incremental changes of mobile solvent concentration were required.

The calibrated solvent reservoir was tightly capped with drying tubes (calcium chloride–silica gel) to keep the mobile solvent from ambient moisture, and dry helium was bubbled through the solvent intermittently to displace any dissolved air.

#### *Isotherm measurement*

The column system was initially set in the closed configuration (Fig. 1), valve

TABLE I  
CHEMICAL COMPOSITION AND CLASSIFICATION OF FLY ASHES

Fly ash	Major and minor constituents (% weight)											pH	Classification**	
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	C* (Total)	N			H
1	24.5	62.6	0.6	0.31	0.23	0.20	2.31	1.20	0.36	8.77	0.33	0.15	3.6	Acid modic
2	27.2	61.9	1.05	0.24	0.10	0.04	0.57	2.70	0.10	3.5	0.17	0.09	4.3	Acid sialic

\* Inorganic carbon <0.01%.

\*\* See ref. 24.

TABLE II  
PHYSICAL CHARACTERISTICS OF FLY ASHES

Fly ash	Particle size ( $\mu\text{m}$ , % weight)			Specific surface area ( $\text{cm}^2 \text{g}^{-1}$ )	Apparent density ( $\text{g cm}^{-3}$ )	Total pore area ( $\text{m}^2 \text{g}^{-1}$ )	Median pore diameter ( $\mu\text{m}$ )
	118.4-54.9	54.9-10.5	10.5-3.9				
1	10.9	53.4	26.5	4540	0.727	30.75	2.74
2	3.8	70.9	24.7	3510	0.500	47.95	5.00

\* Definitions of specific surface area, apparent density, total pore area and median pore diameter are given in ref. 25.

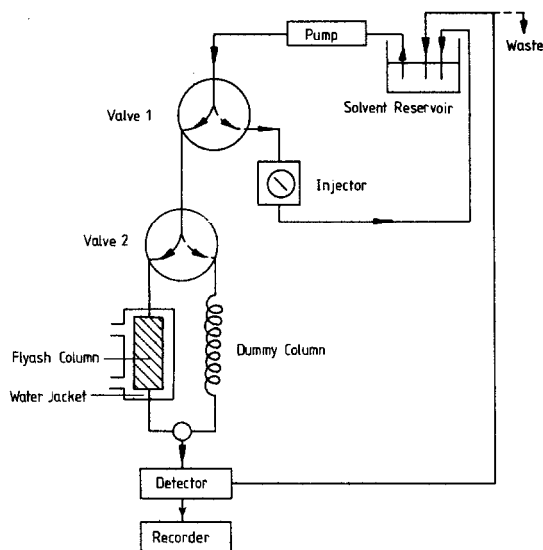


Fig. 1. Diagram of the apparatus used for isotherm measurement. Broken lines indicate alternative flow path.

1 switched to valve 2, and valve 2 directed to the dummy column (V1→V2→DC). The UV detector was set at the appropriate wavelength and attenuation (usually 10–20% full scale recorder deflection at a particular attenuation for 1  $\mu$ mole of a PAH compound). Solvent was circulated at a flow-rate of 2 ml min<sup>-1</sup> until an equilibrated baseline was obtained. Valve 2 was then switched momentarily to the ash column (V1→V2→AC) until a steady baseline was obtained, then switched back to the dummy column (V1→V2→DC). Valve 1 was then directed to the injector (V1→Inj) and the calibrated volume of the solvent reservoir was noted after 3 min. This part of the procedure ensures that the system is primed with the initial mobile solvent, and that the ash column is properly wetted.

An exact volume of a PAH compound was injected through the U6K injector and the flow-rate was increased to 9.9 ml min<sup>-1</sup> for 3 min to ensure complete mixing in the solvent reservoir before returning to the normal flow-rate of 2 ml min<sup>-1</sup>. Thereafter, valve 1 was rotated to valve 2 (V1→V2→DC) and when a steady plateau was reached (this is equivalent to the calibration of the detector by directly injecting a solution of known concentration), valve 2 was directed to the fly ash column (V1→V2→AC) and the effluent from the detector vented to waste (open configuration). An equilibrium adsorption state was reached when the response obtained here was equal to that obtained when valve 2 was directed to the dummy column (V1→V2→DC). This procedure was repeated a number of times with stepwise increases in the concentration of solute. The stepwise plateau profiles obtained were used to calculate the isothermal data points, as discussed below.

The procedure described above allows a new mobile solvent to be brought as near as possible to the inlet of the fly ash column prior to the beginning of adsorption, therefore minimising the contributions to the overall adsorption profile from diffusion (extra-column) and improper solute-solvent mixing in the system. In addition,

instantaneous calibration of the detector is permitted with each change of mobile solvent concentration. Most importantly, the system allows the operator to ascertain quickly whether or not a true plateau region has been reached, especially for slowly adsorbing compounds. This is done by momentarily switching valve 2 to the dummy column and comparing its response with that obtained with the ash column.

#### *Measurement of system dead volume*

The system dead volume comprises the volume from the exit of valve 2 to the detector, plus the column hold-up volume. All other extra-column effects need not be considered since each new mobile solvent is brought to this exit point. The volume was measured as follows.

With the detector set at 230 nm, the system was primed with methylene chloride and steady baselines were obtained for both dummy and ash columns. With valve 2 switched to the dummy column, an equal volume of *n*-hexane was added to the methylene chloride in the solvent reservoir, and, when a steady baseline was obtained, valve 2 was directed to the ash column. The volume from the leading edge of a rising signal to the starting point of the steady baseline represents the system dead volume.

#### *Calculation of isotherm points by frontal analysis*

Frontal analysis relates the rate of formation of the concentration front by a step increase in concentration of a solute in the mobile solvent, to the value of the solute's adsorption at elevated concentration. To calculate the amount of the solute adsorbed by the ash column when the solute concentration of the mobile solvent is changed from  $C_a$  to  $C_b$ , the following equation is used:

$$Q(C_b) = Q(C_a) + \frac{(t_R - t_0)(C_b - C_a)F}{W}$$

where  $t_R$  is the retention time of front, taken here as the time required to reach the point of inflection of the step profile;  $t_0$  is the retention time for an unadsorbed sample ( $t_0 F$  is the system dead volume);  $F$  is the flow of the mobile phase in the column, and  $W$  is the mass of adsorbent in the column. A single change of solvent concentration produces one discrete point on the adsorption isotherm. This operation can be repeated with successive additions of solute to yield additional points on the isotherm. The data points were fitted to five standard adsorption isotherms, as summarised in Table III.

Curve-fitting of the Henry, Langmuir and Freundlich equations was performed by computer, using least-squares linear regression analysis of manipulated data and the linearised equation in Table III. The Weber-Matthew isotherm cannot be transformed into a linear form, and the data were curve-fitted using the parametric least-squares fitting procedure, an iterative process using as initial values the  $q_0$ ,  $b$ , (and  $m = 1$ ) from the Langmuir equation. The program also calculated the coefficients of determination ( $r^2$ ) and plotted the data curve and the least-squares regression isotherms.

TABLE III  
ADSORPTION ISOTHERM EQUATIONS

Name	Equation*	Linearised equation	Capacity term	Comments
Henry	$Q = K_1 C$	$Q = K_1 C$	$K_1$	Limited to low C and/or low surface coverage
Langmuir	$Q = \frac{bq_0 C}{(1 + bC)}$	$\frac{C}{Q} = \left(\frac{1}{q_0}\right)C + \frac{1}{(bq_0)}$	$q_0$ (High C)	Describes maximum monolayer capacity
	$Q = \frac{bq_0}{(1 + bC)}$	$\frac{1}{Q} = \left(\frac{1}{bq_0}\right)\frac{1}{C} + \frac{1}{q_0}$	$bq_0$ (low C)	Reduces to Henry's Law
Freundlich	$Q = K_2 C^{1/n}$	$\log Q = \log K_2 + \frac{1}{n} \log C$	$K_2$	Empirical
Matthew-Weber	$Q = \frac{iC}{1 + jC^m}$	Non-linear	$i^{**}$	Empirical, reduces to Henry, Langmuir or Freundlich equation under appropriate conditions

\*  $Q$  is the equilibrium capacity in  $\mu\text{mole g}^{-1}$  and  $C$  is the equilibrium concentration in  $\mu\text{mole}$ .

\*\* Computer iterative process gives exact fitting to cover a wide concentration range.

RESULTS AND DISCUSSION

Choice of solvent

The adsorption of organic compounds from a solution on solid surfaces is a competitive process between solution components. Both Snyder and Poppe<sup>26</sup> and Scott<sup>27</sup> have explored these processes and have delineated different adsorption mechanisms for both the polar inorganic class of adsorbents (silica and alumina) and the non-polar inorganic group (graphite and charcoal). Generally the elution strength of the solvent used for the latter group is different from that for silica and alumina<sup>28</sup>. The weakest solvents are low-molecular-weight polar molecules such as water, methanol and acetonitrile, and the strongest solvents are larger and/or aromatic molecules, such as chloroform and xylenes. Extending Polanyi's adsorption theory<sup>29</sup> to solution, Dondi *et al.*<sup>30</sup> reported that the adsorption energy of an organic compound on active carbon decreases with increasing solvent polarity. To reduce analysis times therefore, a polar solvent is preferred. As indicated in Table I, the fly ash samples consisted primarily of alumina and silica, and a small percentage of carbon. For a particular solvent, a different adsorptive mechanism may be operating simultaneously. Soltys<sup>31</sup> demonstrated that there is a weak interaction between PAH compounds and the mineral portion of the fly ash. Selective adsorption of PAHs on carbon black was reported by Colin *et al.*<sup>28</sup>. Methylene chloride was chosen in this study to minimise the interaction of the PAH compounds with silica and alumina, while not diminishing the carbon-PAH adsorption effect.

Comparison of experimental and theoretical adsorption isotherms

Adsorption data obtained for six PAHs, fluorene, phenanthrene, anthracene, pyrene, chrysene and perylene, on fly ash 1 are shown in Fig. 2. The amount adsorbed increased with the number of fused aromatic rings in the PAH molecule. These data

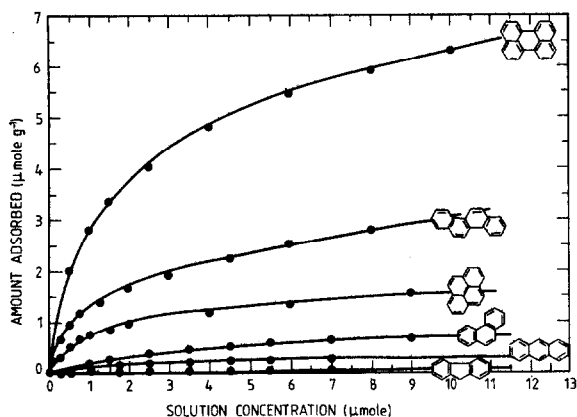


Fig. 2. Adsorption profiles for different PAH compounds on fly ash 1.

were used to obtain best-fit estimates of the parameter in the five isotherm equations shown in Table III.

These equations are based on different adsorption models. For example, Henry's equation<sup>15</sup> is a linear relationship best suited for dilute solutions. The Langmuir isotherm<sup>16</sup> is restrictive in that it assumes surface homogeneity and monolayer adsorption coverage. The empirical Freundlich model is more appropriate to heterogeneous surfaces<sup>32</sup>. In this equation the magnitude of the exponent parameter is related to the surface adsorption capacity of the solid phase. The Weber–Matthew equation is a general isotherm incorporating features of both the Langmuir and the Freundlich models. It is an “intermediate” isotherm and is a more realistic representation of a system covering a wide range of solute concentrations<sup>33</sup>. It is important, however, to emphasise here that no serious consideration was given to the relative merits of the theoretical bases of each of the adsorption models. The parameters of each equation were examined only to assess their suitability as convenient probes for the quantitative comparison of the adsorption processes for PAHs on different fly ash samples.

Fig. 3 shows typical plots of the experimental and theoretical isotherms for anthracene adsorbed on fly ash 1. Two linearised forms of the Langmuir equation (Table III) were employed to determine the adsorption parameters, since the Langmuir equation was not capable of describing the adsorption isotherm data over the entire mobile solvent concentration range. This fact is well illustrated by Fig. 3B and C. Anthracene, at concentrations greater than  $30 \mu\text{M}$ , gave data points that could be accurately fitted to the linearised Langmuir equation (for high  $C$ ) of the first form, whereas below this concentration the second form (for low  $C$ ) was most suitable.

The best-fit estimates of the parameters in the five isotherm equations, with coefficients of determination ( $r^2$ ), are summarised in Table IV. The fit to Henry's law was poor, as shown by the low values ( $< 0.90$ ) for  $r^2$ . Of the two linearised forms of the Langmuir equation, the second form gave the better  $r^2$  values. The Freundlich and the Weber–Matthew models consistently gave  $r^2$  values close to unity. For high and/or moderately low adsorption, the exponent term  $m$  in the Weber–Matthew generalised model remained consistently at the value of  $0.92 \pm 0.05$ . For extremely



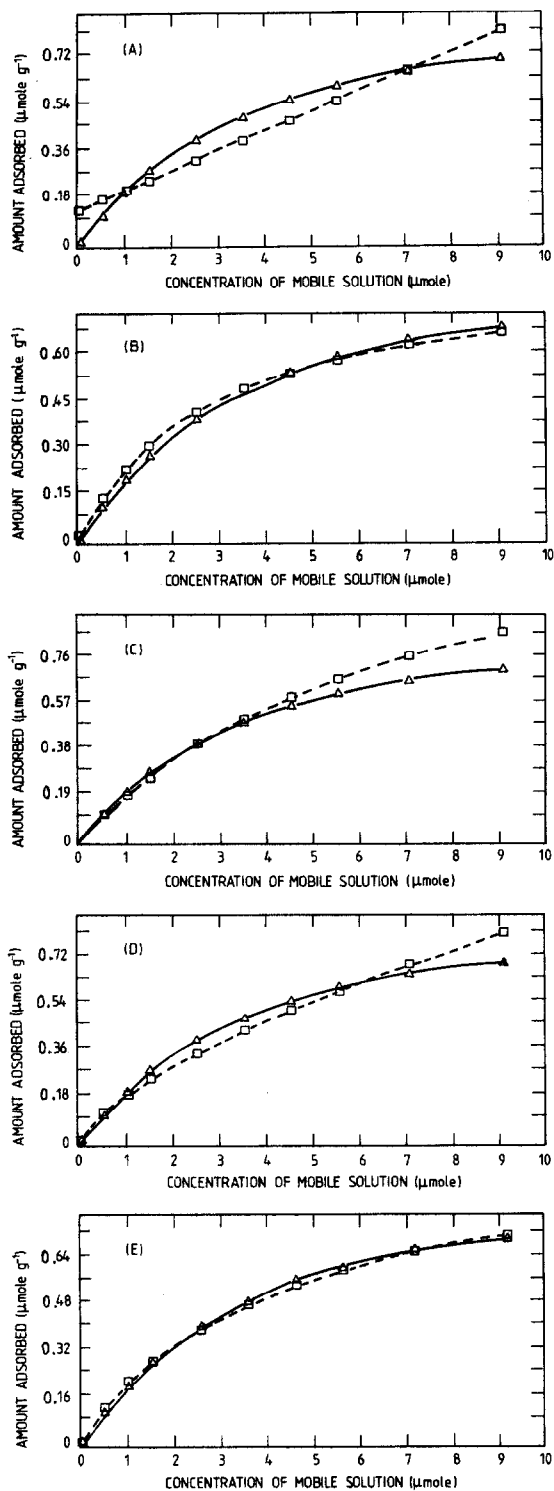


Fig. 3. Experimental curve for (A) Henry, (B) Langmuir (high concentration), (C) Langmuir (low concentration), (D) Freundlich, and (E) Weber-Matthew isotherms for adsorption of anthracene on fly ash 1.  $\Delta$  = Experimental points;  $\square$  = theoretical point.

TABLE IV  
SUMMARY OF ISOTHERM EQUATION PARAMETERS

Compound ( $\chi$ , $F$ )	Henry		Langmuir					
	$K_1$	$r^2$	High $C$			Low $C$		
			$q_0b$	$b$	$r^2$	$q_0b$	$b$	$r^2$
Fluorene (4.61, 6.5)*	0.005	0.86	0.028	0.592	0.93	0.019	0.281	0.99
Phenanthrene (4.82, 7.0)*	0.034	0.86	0.279	0.956	0.97	0.259	0.82	0.94
Anthracene (4.81, 7.0)*	0.076	0.90	0.308	0.346	0.87	0.203	0.127	0.99
Pyrene (5.56, 8.0)*	0.144	0.79	1.560	0.94	0.98	1.395	0.734	0.95
Chrysene (6.23, 9.0)*	0.295	0.85	2.789	0.94	0.96	3.133	1.072	0.89
Perylene (6.98, 10)*	0.448	0.81	4.930	0.636	0.86	5.206	0.734	0.98
Pyrene**	0.004	1.00	0.007	0.174	0.37	0.041	0.001	1.0
Chrysene**	0.036	0.67	0.514	2.415	0.99	0.411	1.587	0.97
Perylene**	0.049	0.89	0.363	1.211	0.96	0.370	1.254	0.96

\* Fly ash 1.

\*\* Fly ash 2.

low adsorption,  $m$  becomes small, and the Weber–Matthew model reduces to Henry's equation. The same is true for the Freundlich equation as  $n$  approaches unity for low adsorption. Strong adsorption is characterised by  $n \gg 1$  in the Freundlich equation. The adsorption capacity terms ( $k_1$ ,  $q_0b$ ,  $k_2$  and  $i$ ) of all five isotherm equations increase with increasing adsorption, thus giving a relative measure of the affinity for PAH adsorption.

#### PAH molecular structure–adsorption capacity relationship

The solvophobic theory<sup>34</sup> predicts an increase in the retention of organic compounds on a reversed-phase  $C_{18}$  column with the non-polar surface area of the solute molecule. Simple linear relationships have been found between the logarithm of capacity factors of PAHs and various physicochemical parameters describing their molecular structures<sup>35–37</sup>, such as the molecular connectivity index ( $\chi$ ) and the correlation factor ( $F$ ). The former is related to the topological size of the molecule and its degree of branching<sup>37</sup>, while  $F$  relates compound structures to their capacity factors on  $C_{18}$  columns [ $F = (\text{number of double bonds}) + (\text{number of primary and secondary carbon atoms}) - 0.5$  for a non-aromatic ring]. Both  $\chi$  and  $F$  values for PAHs used in this study are shown in Table IV.

The retention and adsorption capacities are linearly related<sup>20</sup>. The logarithm of the adsorption capacity term from the isotherm equations may therefore be plotted against the values of  $F$  or  $\chi$ . The relationship between  $\chi$  and the logarithm of the adsorption capacities obtained from Freundlich and Weber–Matthew isotherms for six PAHs on fly ash 1 are shown in Fig. 4. A steep increase in adsorption capacity

<i>Freundlich</i>			<i>Weber-Matthew</i>			
$K_2$	$1/n$	$r^2$	$i$	$j$	$m$	$r^2$
0.013	0.645	0.97	0.025	0.576	0.936	1.0
0.117	0.463	0.99	0.239	0.937	0.895	1.0
0.182	0.683	0.97	0.270	0.328	0.914	1.0
0.678	0.424	0.95	1.527	0.968	0.937	0.99
1.240	0.402	0.99	2.437	0.940	0.913	1.0
2.769	0.369	0.99	4.639	0.763	0.924	1.0
0.004	1.006	1.00	0.005	0.164	0.028	1.0
0.129	0.425	0.92	0.484	2.33	0.967	1.0
0.131	0.503	0.99	0.364	1.214	0.874	1.0

occurred with increasing PAH ring size, up to three rings (anthracene). Beyond this size the rate of increase was considerably lower. Whereas on a  $C_{18}$  substrate adsorption occurs in freely accessible surface sites, yielding a linear relationship between adsorption capacity and the structural factors, this will not be the case with fly ash, where the accessibility of adsorption sites will be a function of sample porosity. The initial increase in adsorption capacity with ring size therefore reflects the increased

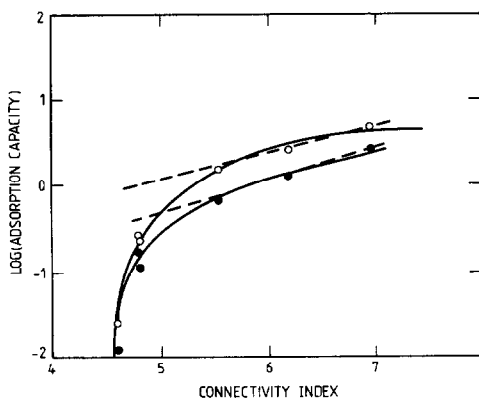


Fig. 4. Logarithm of adsorption capacity versus connectivity index. ○ = Adsorption capacity from Weber-Matthew isotherm; ● = adsorption capacity from Freundlich isotherm. Broken lines indicate regions of linearity.

$\pi$ -bonding ability of the larger PAHs as already observed (Fig. 2). For greater than three-ring PAHs the reduced slope in Fig. 4 arises because these molecules are unable to penetrate the pore network, the adsorption now occurring on the considerably lower number of exposed adsorption sites. There is still an increase in adsorption capacity with the increased  $\pi$ -bonding ability of the larger molecules.

#### *Dependence of PAH adsorption on fly ash characteristics*

The adsorption of three PAHs, pyrene, chrysene and perylene, representative of weak, medium and strong adsorbers respectively, was also examined for a second sample, fly ash 2 (Table IV). The adsorption isotherms (Fig. 5) show clearly that the amounts of these compounds adsorbed are significantly lower than for fly ash 1. In addition, there is an overlapping region of adsorption ( $< 2 \mu M$ ) for chrysene and perylene on fly ash 2, whereas the isotherms for these compounds on fly ash 1 were clearly separated.

The reasons for this behaviour are not immediately obvious. Physically the fly ashes differ to the extent that the density and specific surface area of fly ash 1 are higher, but fly ash 2 has greater porosity (Table II). The main difference in chemical composition is the much greater carbon content of fly ash 1 (Table I).

To ascertain the role of fly ash carbon content in PAH adsorption, samples of fly ash 1 were partially combusted in an oxygen-enriched environment to obtain a series of fly ash samples having the same inorganic matrix but different carbon contents. Changes in anthracene adsorption on these samples are shown in Fig. 6. A linear relationship between adsorption capacity for anthracene and the carbon content of the fly ash sample is shown in Fig. 7. The adsorption of anthracene was also examined on mixtures of fully combusted fly ash 1 (0% carbon) with various percentages of activated charcoal (Fig. 7). These mixtures were shown to have a higher affinity for anthracene adsorption than partially combusted samples containing identical amounts of carbon. One plausible explanation for this behaviour is that the carbon in the latter sample is physically different from the active charcoal used in the synthetic mixtures. Snoeyink *et al.*<sup>38</sup> reported that adsorption properties of different carbons can vary extensively owing to the nature and distribution of adsorp-

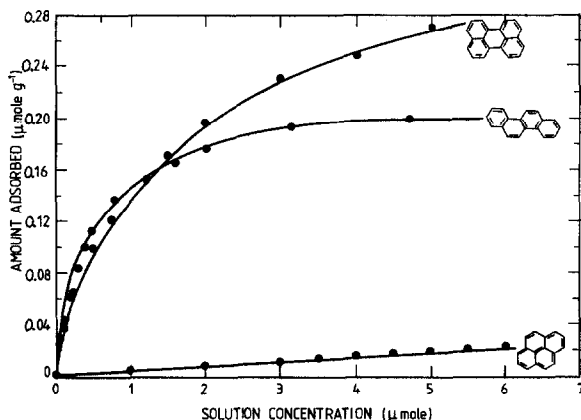


Fig. 5. Adsorption profiles for different PAH compounds on fly ash 2.

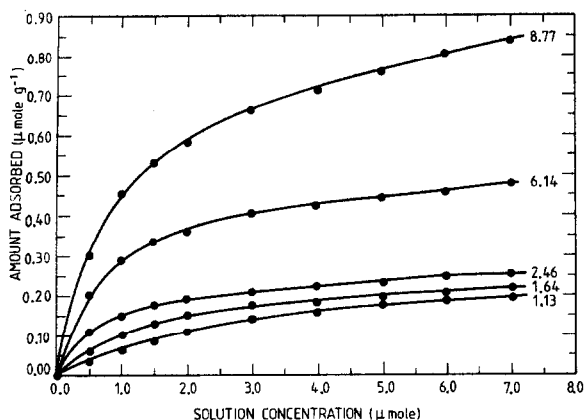


Fig. 6. Adsorption isotherm for anthracene on a partially combusted sample of fly ash 1. Carbon content (% w/w) is labelled beside each sample.

tion sites on their surfaces. The accessibility of these active carbon sites could also contribute to the overall difference in the observed adsorption processes. Physical and/or chemical agglomeration of carbon with other particles in the fly ash matrix reduces the number of sites available for adsorption. This may happen to a lesser extent when activated charcoal is mixed with fly ash.

It can be seen also from Fig. 7 that the extrapolation of the linear relationship of the carbon content in the fly ash samples to the adsorption capacity of anthracene gave approximately zero intercept on the ordinate, implying no interaction between

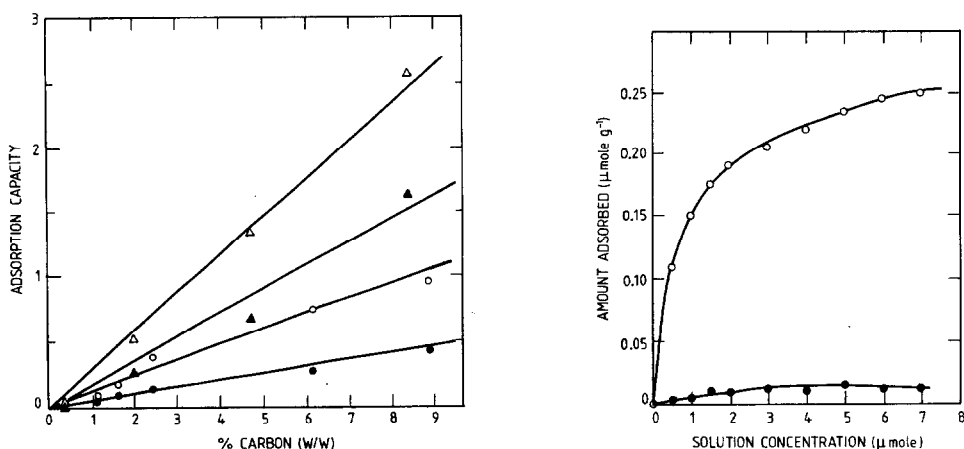


Fig. 7. Relationship between the percentage of carbon (w/w) in the fly ash and adsorption capacity of anthracene. The  $\Delta$  and  $\blacktriangle$  symbols denote the values of the adsorption capacity obtained from the Weber-Matthew model for adsorption of anthracene on synthetically mixed fly ash 1 and combusted fly ash 1, respectively. The  $\circ$  and  $\bullet$  symbols denote values of the adsorption capacity from the Freundlich equation.

Fig. 8. Adsorption isotherms for anthracene on combusted fly ash 1 containing 2.5% (w/w) carbon ( $\circ$ ), and fly ash 2 containing 3.5% (w/w) carbon ( $\bullet$ ).

PAHs and the silica-alumina matrix with methylene chloride as solvent instead of a less polar solvent such as hexane.

The importance of accessible carbon can be further illustrated by comparing the adsorption isotherms for anthracene on partially combusted samples of each fly ash with similar total carbon content (Fig. 8). Fly ash 1 again adsorbed more than fly ash 2, despite now having the lower carbon content. Clearly physical differences must also play an important role here; however it is difficult to interpret the observed results on the basis of the measured differences in porosity and surface area. Further measurements are being undertaken with these and other fly ashes to resolve this question.

## CONCLUSION

Adsorption isotherms measured by liquid chromatography have been shown to be a useful indicator of the extent of PAH adsorption on fly ashes. It was shown that adsorption is regulated predominantly by the number of accessible carbon sites, rather than the total content of carbon in the fly ash matrix. The role of pore dimensions is uncertain. Agglomeration or location of minute carbon particles within the large pores of particles may assist in obstructing adsorption sites. Further work in this area is in progress.

While incomplete coal combustion is known to result in the formation of PAHs<sup>39</sup>, it is apparent that carbon formed from incomplete combustion also plays an important role in stabilising these compounds through adsorption and prolonging their threat to the environment.

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