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Use of field-flow fractionation to study pollutant–colloid interactions

RONALD BECKETT*, DEIRDRE M. HOTCHIN and BARRY T. HART

Water Studies Centre, Monash University, Caulfield East, Victoria (Australia)

ABSTRACT

A new approach has been developed utilizing field-flow fractionation (FFF) methods to determine adsorption density distributions across the size spectrum of a particulate sample. The approach has been tested using sedimentation FFF to separate colloidal matter, concentrated from river water, to which radiolabelled pollutants (orthophosphate, glyphosate, atrazine) have been adsorbed. It is expected that the methodology will be expanded to cover the broad size range from 1 nm to 100 μm by using a number of FFF subtechniques (including sedimentation FFF): the use of various sensitive analytical methods will extend the range of adsorbates that can be studied. This provides a powerful new method for studying the pollutant–particle interactions occurring in environmental samples, as well as other similar systems.

INTRODUCTION

The association of pollutants and other trace elements and compounds with particle surfaces plays a dominant role in determining their transport, fate, biogeochemistry, bioavailability and toxicity in natural waters, sediments and soils^{1,2}. An example that has received much attention over a number of years is the adsorption of various pollutants (*e.g.* trace metals, nutrients and toxic organics) to suspended particulate matter in river water³; such interactions affect the transportation and eventual deposition of these pollutants in bottom sediments. The pollutants may then concentrate at certain locations, such as in reservoirs and estuaries, with important ecological and even human health implications. Another example, is the role of soil and rock in adsorbing materials such as fertilizers, pesticides and radionuclides, which influences their bioavailability to plants and pests and their transport through soils and groundwater aquifers⁴.

Despite the general awareness of the importance of both particulate⁵ and colloidal⁶ matter in pollutant transport, most work has been confined to the study of particulate matter–pollutant interactions. Even this work is dominated by the study of model surfaces such as clays and iron, aluminium and manganese oxides rather than the more complex natural samples. This lack of study of the interactions between

pollutants with natural colloidal matter is understandable given the difficulties in separating colloidal matter from the aqueous solution. Here we use a fairly general, but somewhat arbitrary, definition for particulate matter as material greater than $1\ \mu\text{m}$ in size and colloidal matter as material in the range $0.001\text{--}1\ \mu\text{m}$. The colloidal fraction will therefore include very small particles and macromolecules, and in most studies will be included as part of the "filterable" or "dissolved" fraction⁷.

Thus, in the many studies undertaken to measure the uptake of a pollutant by natural waters where the solid phase is separated from the liquid phase by either filtration or centrifugation, the interactions between colloidal matter and the pollutant will not have been measured accurately. In particular, those cases where significant colloidal matter-pollutant interaction occurs, the proportion of the pollutant associated with surfaces will be seriously underestimated. This may have significant implications regarding predictions of the toxicity, since surface-bound pollutants are generally found to be less toxic than uncomplexed pollutants.

It is well known that particle size has a major influence on the properties of sedimentary material and their associated pollutants⁸. It directly affects the specific surface area, settling rates, resuspension and the mechanism and extent of aggregation in natural water, as well as the ability of colloidal matter to permeate through soils and rock.

The adsorption of pollutants to sediments depends on the specific surface area and the nature of the particle surface. Although the sediment mineralogy is of some importance, particularly in the case of clay minerals and Fe and Mn oxides, we contend that the ubiquitous coatings of these oxides and organic matter, which is invariably present on the surface of natural particles⁹, may well be the dominant factor in determining the surface adsorption density (*i.e.* amount adsorbed per unit area). Evidence exists suggesting that in a given sediment sample different mineral and organic phases may be concentrated in different size ranges¹⁰.

Although there are many useful techniques available for particle size determination and fractionation all suffer from quite serious limitations making this a difficult area of scientific endeavour. The limitations include; the limited size range covered, inaccuracies in the theory, lack of resolution, and inability to fractionate as well as size the sample. These deficiencies in the commonly used separation methods have hindered attempts to gather information on the distribution of mineral phases and pollutant species within a sediment sample.

The development of a range of field-flow fractionation (FFF) techniques¹¹ over recent years now provides new experimental methods for separating particulate, colloidal and macromolecular (*e.g.* humic matter) materials from natural waters. These techniques show much promise in eliminating or at least reducing most of the shortcomings noted above¹². Sedimentation FFF has been successfully applied to the separation and characterisation of colloidal matter from natural waters¹³. Additionally, flow FFF has been utilised for the characterisation of macromolecules¹⁴, humic matter^{15,16} and smaller colloidal particles¹⁷.

With the advent of these new FFF techniques, there now exists the possibility that uptake studies can be undertaken using real water samples, with the final mixture separated using the appropriate FFF technique. One problem that still exists is that, with a few exceptions, the FFF techniques available can only process very small quantities of sample. Thus extremely sensitive analytical methods are required to

detect the often small amounts of pollutant associated with the colloidal or macromolecular matter. One such technique involves the use of radiolabelled pollutants.

In this paper we report some preliminary results of work undertaken to study the interaction of the nutrient orthophosphate (^{32}P labelled) and the herbicides glyphosate and atrazine (both ^{14}C labelled) with natural colloidal matter, in which sedimentation FFF was used as the separation technique. This work illustrates a very promising approach that will make it possible to obtain detailed information on the distribution of pollutants in natural sediment and soil samples.

THEORY

Sedimentation FFF

The mechanism and theory of FFF has been detailed fully elsewhere^{11,18-20}. The general retention equation relates the conventional retention ratio R , defined by

$$R = \frac{V^0}{V_r} = \frac{t^0}{t_r} \quad (1)$$

to a retention parameter λ as follows²¹

$$R = 6\lambda \left(\coth \frac{1}{2\lambda} - 2\lambda \right) \quad (2)$$

where V^0 and V_r are the carrier volumes required to elute unretained or retained samples respectively through the FFF channel; t^0 and t_r are the corresponding void time and retained sample elution time, assuming the carrier flow-rate is constant.

In this work a simplified approximate expression was usually used for the retention ratio²²

$$R = 6\lambda(1 - 2\lambda) \quad (3)$$

In the case of sedimentation FFF the retention parameter for sample particles of equivalent spherical diameter d and density ρ is given by²³

$$\lambda = \frac{6kT}{\pi\omega^2rw(\rho - \rho_s)d^3} \quad (4)$$

where k = Boltzmann's constant

T = absolute temperature

ω = centrifuge angular velocity

r = centrifuge radius

w = channel thickness

ρ_s = carrier density

Thus for constant field sedimentation FFF experiments, the diameter of particles eluting at a given V_r can be calculated by combining eqn. 2 or 3 with eqn. 4.

For samples with a broad size distribution such as the suspended particulate matter used in this study it is almost mandatory to use some form of field decay during the run²⁴. Since in programmed field runs a given sample component will experience a decreasing field strength during its elution, the value of λ will also decrease. This is accounted for by applying the general expression in eqn. 5 (assuming the carrier flow-rate is constant)²⁵ to obtain specific equations for a given program form.

$$t^0 = \int_0^{t_r} R dt \quad (5)$$

In previous work on river-borne colloids we used a time delayed exponential decay field program¹³. However, in the work presented here a time delayed power program²⁶ was used, where the centrifugal field [$G_{(t)} = \omega^2 r$] takes the form

$$G_{(t)} = G_0 \left(\frac{t_1 - t_a}{t - t_a} \right)^8 \quad (6)$$

where G_0 = the initial field, t_1 = the constant field period before decay begins, t_a = a constant with the restriction that $t \geq t_1 > t_a$.

The advantage of this field program is that by choosing suitable parameters for G_0 , t_1 , and t_a , it can be made to yield a fairly constant resolving power or fractionating power²⁷ over the size range of interest²⁶.

The elution time (or volume) for a particular component can be used to calculate the particle diameter as follows: (1) for $t \leq t_1$: the eqns. 1, 3 and 4, which are applicable for constant field conditions, were used; (2) for $t_r > t_1$: in all runs t_a was set to $-8t_1$, hence the simplified equation

$$\lambda_r = \frac{3t^0}{2(t_r - t_a)} \quad (7)$$

can be used to calculate the retention parameter of the particles, λ_r , at their time of elution (see eqn. 41 of ref. 26). Application of eqn. 6 above to evaluate the field strength at elution and then eqn. 4 yields the value of d .

Fractograms

The fractogram is a plot of the particular detector response *versus* volume or time. The ordinate should be a measure of the amount of sample (or sample component) per unit volume, *i.e.* dm/dV . The most common method for monitoring the concentration of particles eluting from a sedimentation FFF channel is a conventional liquid chromatography UV light detector most often operated at a wavelength of 254 nm. This measures the attenuation of light in a small cell volume which, for particle sizes the same order of magnitude as the wavelength of the light, will be primarily caused by a scattering mechanism rather than absorption. As dictated by the quite complex Mie theory³⁷ of light scattering, the relationship between solution turbidity and particle mass concentration will be size dependent, with a sample of

larger particles expected to yield a higher absorbance than the same mass concentration of smaller particles. We have not attempted to correct for this complication in the work reported here, but have simply assumed that absorbance is proportional to the mass concentration. Some evidence that this assumption may not cause excessive errors was obtained in previous work¹³ in which a fractogram of a river water sample obtained using an evaporative light scattering mass detector was quite similar to that obtained with a UV detector at 254 nm.

The other approach used was to collect fractions of the eluent and chemically analyse for specific elements or compounds in the separated fractions. Very sensitive analytical techniques are required as the particle concentration in the eluent is very low. As we were interested in looking at pollutant adsorption characteristics of natural aquatic colloids, the most convenient method was to utilize radioisotope labelled compounds in the uptake experiments. Since unadsorbed material will elute with the void peak, any measured radioactivity in the post void volume carrier will represent material associated with particles. Thus the fractogram for monitoring the adsorbed component is simply a plot of the measured counts per minute (cpm) in a ml of eluent solution plotted against the elution volume.

Particle size distributions

The particle size distribution should represent the amount of material in different size ranges and is usually in the form of a plot of dm/dd against d , where m is the mass of particles and d is the particle diameter. It is a relatively easy matter to convert the fractogram abscissa into a particle diameter scale using the equations above.

In order to obtain the correct ordinate for the size distribution $dm_{(i)}/dd_{(i)}$, we divide the volume-axis of the fractogram into a large number of increments of width $\delta V_{(i)}$ and use the expression

$$\frac{dm_{(i)}}{dd_{(i)}} \approx \frac{dm_{(i)}}{dV_{(i)}} \cdot \frac{\delta V_{(i)}}{\delta d_{(i)}} \quad (8)$$

where $dm_{(i)}/dV_{(i)}$ is the value of the fractogram ordinate at the midpoint of a given volume increment and $\delta d_{(i)}$ is the diameter increment corresponding to that same increment in V . In this way the corresponding fractogram can be converted into either a particle mass [$dm_{(i)}/dd_{(i)}$] or adsorbate amount [$dm_{\text{ads}(i)}/dd_{(i)}$] based particle size distribution. Here $m_{(i)}$ is used to indicate the mass of sample particles eluted up to fraction i and $m_{\text{ads}(i)}$ represents the mass of adsorbed material.

Adsorption density distribution

In the adsorbate based particle size distributions generated by the above method, the area under the curve between given values of d will represent the amount of pollutant adsorbed in that particular size range. This will depend on the surface area of particles in the size range as well as the relative adsorption intensity of the solid.

Since the mass of sample is represented by the UV detector response ordinate [$dm_{(i)}/dd_{(i)}$] of the particle size distribution, dividing this into the adsorbate activity ordinate [$dm_{\text{ads}(i)}/dd_{(i)}$] yields a relative measure of the amount of adsorbate per mass of solid adsorbent. The same quantity is more directly obtained using the two fractogram ordinates; *i.e.*

$$\frac{dm_{\text{ads}(i)}}{dm_{(i)}} = \frac{dm_{\text{ads}(i)}/dV_{(i)}}{dm_{(i)}/dV_{(i)}} \quad (9)$$

Furthermore, if spherical particles are assumed the particle area $A_{(i)}$ is given by $6\delta m_{(i)}/d_{(i)}\rho$. Thus, by affecting a change of variable to eqn. 9 and assuming a sample with constant density, we can compute the adsorption density [amount adsorbed per unit particle surface area (A)] for each increment by

$$\frac{dm_{\text{ads}(i)}}{dA_{(i)}} = \frac{dm_{\text{ads}(i)}/dV_{(i)}}{dm_{(i)}/dV_{(i)}} \cdot d_{(i)} \quad (10)$$

Note that $dm_{\text{ads}(i)}/dA_{(i)}$ is expressed in arbitrary units as the absolute value of $dm_{(i)}/dV_{(i)}$ is not known with the UV detector response being used as a measure of this quantity and the term $\rho/6$ is assumed to be constant across the size distribution and is thus omitted from eqn. 10. The adsorption density distribution is a plot of $dm_{\text{ads}(i)}/dA_{(i)}$ versus $d_{(i)}$.

EXPERIMENTAL

Sample collection

Suspended particulate matter from two Australian rivers was studied. Water from the Darling River was sampled near its confluence with the Murray River in NSW, and the Yarra River was sampled at Dights Falls in Melbourne. These river systems were chosen because of their high suspended solids load (Darling River: 254 mg/l; Yarra River: *ca.* 70 mg/l) at the time of sampling²⁸.

Darling River water was fractionated and concentrated about one hundred-fold using a continuous flow centrifuge and tangential flow filtration. A nominal particle size cutoff of approximately 1 μm is expected for the continuous flow centrifuge⁵ (centrifuge speed: 8200 rpm giving 5260 g; assumed particle density: 2.5 g/ml). With the tangential flow filtration apparatus, a nominal particle size cutoff of 0.2 μm was obtained using Millipore polysulphone membrane filters^{28,29}.

The water from the Yarra River was concentrated about one hundred-fold by a coagulation and settling procedure¹³. The raw sample was initially passed through a Whatman GF/C glass fibre filter to remove particles of size greater than about 1 μm . CaCl_2 solution was added to the water sample in sufficient quantity to give a final concentration of 0.03 *M*. The mixture was stirred for 1 h and allowed to settle for 24 h. The supernatant was removed and the aggregate added to a small amount of deionized water. This mixture was agitated and allowed to settle. The clarified water was drawn off, and once again deionized water introduced. This washing procedure was repeated three times to remove excess CaCl_2 .

River water concentrates were stored at 4°C and prior to use were subject to ultrasound to break up any aggregates present.

Adsorption procedure

³²P in its orthophosphate form was obtained from Australian Nuclear Science and Technology Organization (ANSTO). An aliquot of 0.3 ml of stock solution

containing 0.02 mg/ml H_3PO_4 was added to 1 ml of Darling or Yarra River colloid concentrate. The resultant activity was approximately 0.06 MBq.

^{14}C labelled glyphosate and atrazine were obtained from Amersham Australia. A small volume (0.01 ml) of the radiolabelled glyphosate solution (7.4 MBq/ml or 0.661 mg/ml) was added to 1 ml of Darling River colloid concentrate. Similarly, 0.02 ml of atrazine solution (3.7 MBq/ml or 0.862 mg/ml) was added to another 1 ml of Darling River colloid concentrate.

In each case an adsorption equilibration time of several hours was allowed before separation by sedimentation FFF was commenced.

Sedimentation FFF apparatus

The sedimentation FFF apparatus was essentially the same as described previously^{13,18}. The FFF channel was made by clamping two concentric nickel-chromium rich alloy (Hastalloy C) rings with a 0.0254-cm thick mylar spacer (which had the channel shape cut out) sandwiched between them. The channel was 93.1 cm long (inlet to outlet) and 2.1 cm in breadth. The channel void volume was 5.30 ml and detector dead volume was 0.54 ml. From these measurements, the channel thickness was calculated to be 0.0266 cm.

The channel was fitted inside a centrifuge basket so that its radius was 15.5 cm. O-ring seals at the ends of the axle allowed liquid to flow through the channel while the centrifuge rotated. The rotor was powered by a DC motor and speed controller, type DPM-6130E from the Bodine Electric Company. Rotation speed was computer controlled using hardware and software from FFFractionation, UT. The speed was measured by a photocell whose light path was interrupted as the rotor spun by a notched disc attached to the end of the centrifuge axle. This enabled the centrifuge speed to be kept constant or in the case of field programming, to be decayed during the run.

The carrier solution was pumped by a Gilson Minipuls 2 peristaltic pump and the outlet stream from the channel was passed through a Waters 441 UV detector operating at 254 nm. The detector signal was monitored on an Omniscribe chart recorder (Houston Instruments). A Gilson Microcol TDC80 fraction collector was used throughout these experiments.

FFF run parameters

An injection volume of 10 μ l was introduced onto the channel through a septum. To relax the sample, an initial field of 1000 rpm was maintained for 20 min under stop-flow conditions. The channel flow was then started and the field decay program commenced according to the power program outlined in the theory section above, using the following parameters. The initial field of 1000 rpm was held for a time lag t_1 of 10 min. A decay parameter t_a of -80 min reduced the field to a hold value of 10 rpm at 205 min. It should be noted that the time required to reach the hold rpm was far in excess of that needed for the completion of these experiments.

An aqueous solution of 0.1% sodium dodecylsulphate and 0.02% sodium azide at a flow-rate of 2 ml/min was used as the carrier. Detector sensitivity ranged between 0.02 to 0.05 a.u.f.s. The chart recorder was maintained at 10 cm/h. Fractions were collected over 4 min intervals for the phosphate experiments and over 2.5 min intervals for the herbicide experiments.

Analysis of activity

Fractions collected during these experiments were further analyzed for β radiation activity using a scintillation counter (Packard tri-carb 300 CD). An aliquot of one ml of the fractions collected during the sedimentation FFF experiment was placed in a scintillation vial. Toluene based PPO-POPOP-teric X10 scintillation fluid (5 ml) was then added (PPO = 2,5-diphenyloxazole, POPOP = phenyloxazolyphenyloxazolyphenyl, teric X10 = a non-ionic surfactant from ICI, Australia). After aggitation each sample was measured for 10 min in the scintillation counter. The data collected was uncorrected for quenching.

RESULTS AND DISCUSSION

Fig. 1 shows the raw fractograms for the adsorption experiments performed in this work. The solid lines show the UV detector response, which were used as a measure of the mass concentration of particles being eluted, and the points show the concentration of adsorbed material as measured by the radioactivity (cpm/ml) of the suspension at various elution volumes. It should be noted that the elution time is proportional to the elution volume for constant flow-rate runs. The error bars on the points indicate the calculated counting statistic errors. Fig. 2 depicts the corresponding

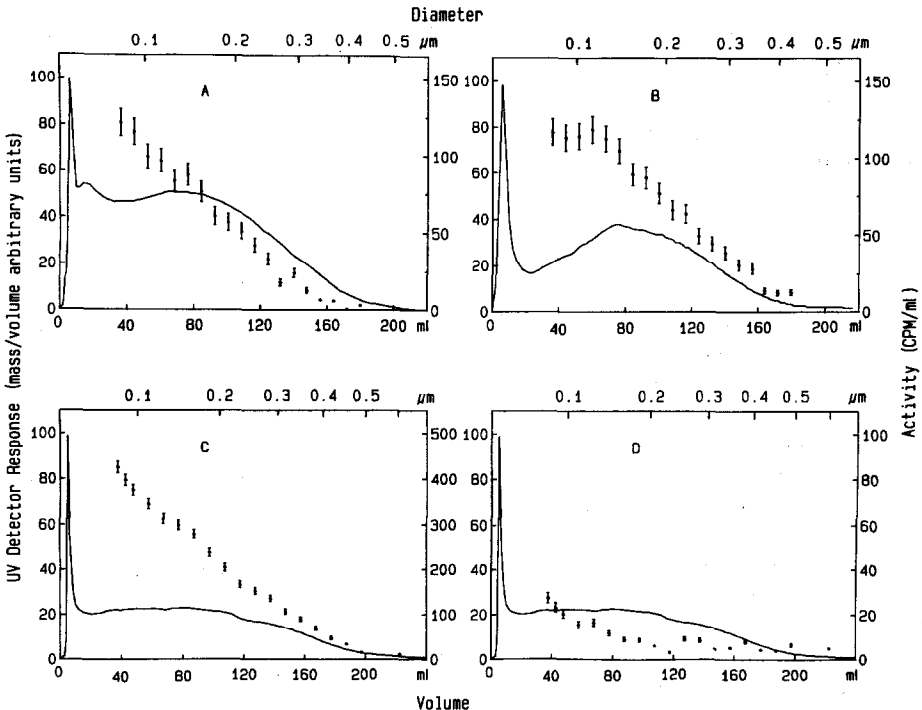


Fig. 1. Fractograms showing the sedimentation FFF separation of natural colloid samples with adsorbed radiolabelled pollutant: (A) orthophosphate onto Darling River colloid concentrate; (B) orthophosphate onto Yarra River colloid concentrate; (C) glyphosate onto Darling River colloid concentrate; (D) atrazine onto Darling River colloid concentrate. Solid lines give the UV detection response and points give the radioactivity (cpm/ml) in the effluent.

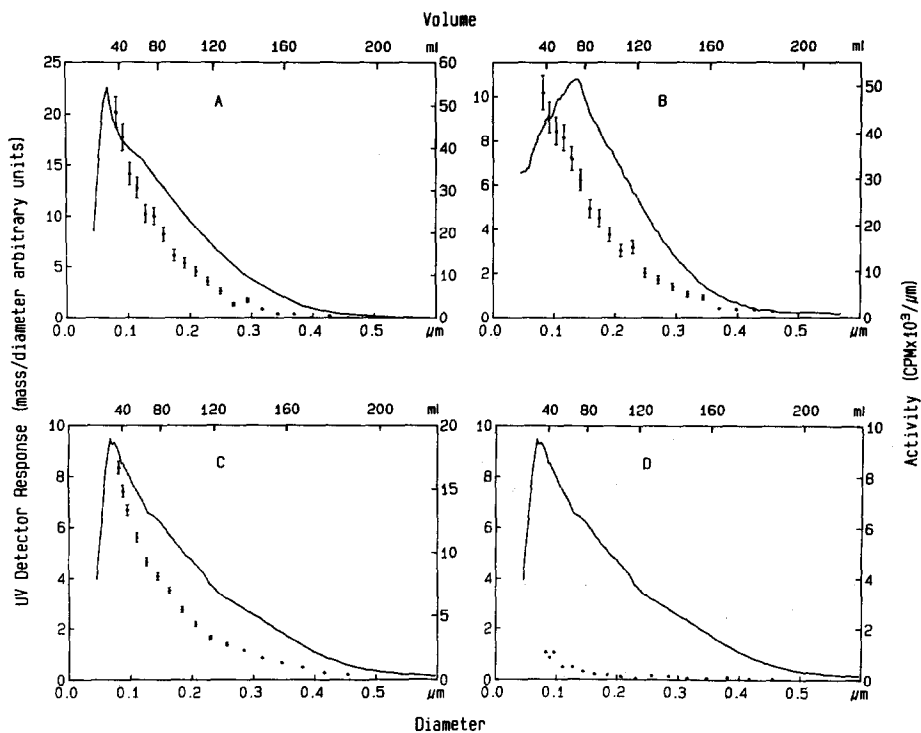


Fig. 2. Particle mass based and adsorbate based size distributions for the corresponding colloid samples and adsorbed radiolabelled pollutants given in Fig. 1A-D. Solid lines give the particle size distributions and points give the amount of pollutant adsorbed per unit mass of adsorbent (arbitrary units).

mass based (solid lines) and adsorbate based (points) particle size distributions calculated from the fractograms in Fig. 1 as outlined in the theory section. The mass based particle size distribution for the two samples (Darling and Yarra Rivers) show a broad size distribution between 0.05 and $0.5 \mu\text{m}$. The upper limit is controlled by the continuous flow centrifuge conditions used to concentrate the samples from river water. The fact that particles less than the $0.2\text{-}\mu\text{m}$ filter cutoff are present is most likely due to partial blockage of the pores during filtration or perhaps variations in the particle density, from the value of 2.5 g/ml assumed, which would affect the calculated particle size. The data show that the Darling River sample contains a higher proportion of smaller particles than the Yarra River sample as evidenced by the maxima in the particle size distributions of approximately $0.08 \mu\text{m}$ and $0.14 \mu\text{m}$, respectively. The Darling River samples are from the same stock except that the sample used in Fig. 1C and D are more dilute than for Fig. 1A.

Both the fractograms and adsorption distributions (points in Figs. 1 and 2) show that significant amounts of phosphate and glyphosate adsorb to the particles, but very little of the less polar herbicide atrazine is adsorbed. This is consistent with the results from conventional adsorption isotherm experiments that have recently been conducted in our laboratory³⁰.

The adsorption distributions given in Fig. 2 show clearly the general trend often

observed for sediment samples, with the smaller particles containing the highest pollutant content. This is an important point for pollutant transport in aquatic systems, since these particles will usually remain in suspension until an aggregation process occurs to induce settling and deposition. The two reasons often advanced to explain this trend in pollutant sorption are the increase in specific surface area as particle size decreases and changes in the geochemistry of the particles with size. Organic matter and reactive hydrous iron and manganese oxides would be the most significant phases influencing pollutant sorption, since both are known to be strong scavengers of many pollutants.

The surface adsorption density distributions calculated for these experiments are given in Fig. 3. These plots show the amount of adsorbate per unit area of particle surface (arbitrary units) as a function of particle size, calculated as outlined in the theory section.

A model that explains many of the properties of natural particles is one in which all particles irrespective of their core mineralogy are assumed to be coated with a common layer of organic matter and perhaps iron and manganese hydrous oxides⁸. For example, this model explains the observation that (with few exceptions) all natural aquatic particles are negatively charged, and that within a given sample they have a very narrow range of electrophoretic mobilities⁹. Of relevance to the studies reported here, this model would predict that the adsorption density for a given pollutant-colloid system would be constant across the size range investigated. This was found to be the case for the adsorption of orthophosphate onto Darling River suspended particulate matter (Fig. 3A).

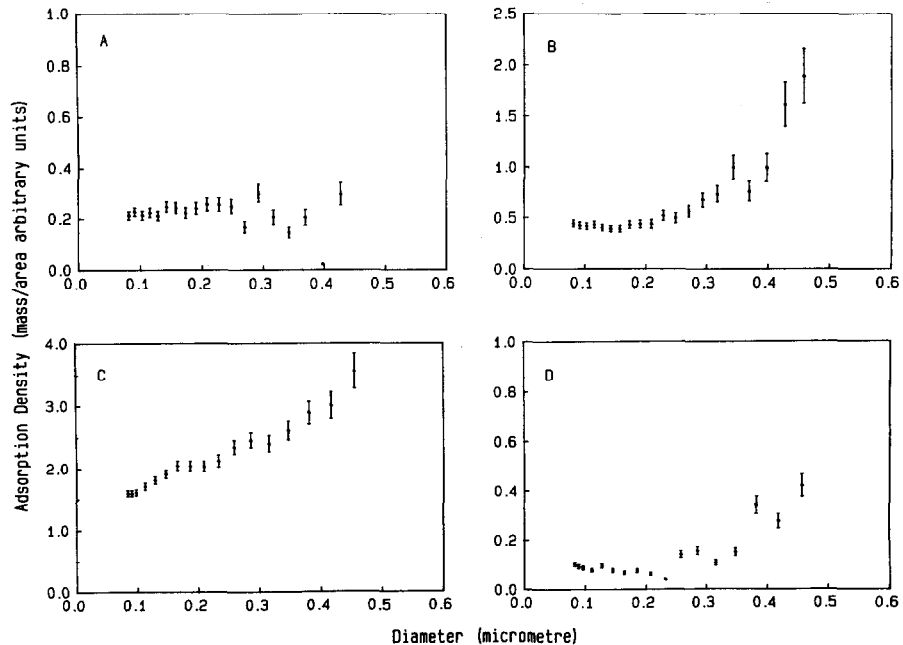


Fig. 3. Adsorption density distributions (amount adsorbed per unit area *versus* particle diameter) calculated using the data shown in Fig. 1.

However, in contrast to the orthophosphate Darling River experiment, the adsorption density distributions for the other systems showed a distinct increase towards the larger diameter end of the range (Fig. 3B-D). This is not an anomaly introduced by the use of the UV detector to monitor particle mass, since light scattering effects would in fact tend to down weight the large diameter end of the distribution. However, it is feasible that changes in shape factor could cause the specific surface area to be greater than expected for the larger particles as the calculations here are based on a constant spherical shape. Scanning electron micrographs of a limited number of Yarra River suspended particulate matter samples separated by sedimentation FFF did show higher proportions of clay-like plates in the 0.3–0.4 μm fraction³¹. However, the samples used in this series of experiments have not been examined by electron microscopy.

Perhaps the most likely explanation for the upwards trend in the adsorption density distributions is a change in mineralogy or coating density across the size range. We do not have information on this at present although two current collaborative projects, one with Dr. H. Taylor (US Geological Survey, Denver) using inductively coupled plasma-mass spectroscopy (ICP-MS) and the other with Dr. D. Chittleborough (Waite Agricultural Research Institute, University of Adelaide) using transmission electron microscopy and diffraction techniques, should provide some insights into this question.

One further point that should be noted is that the experiments performed in this study will only monitor adsorbate species which are strongly bound to the adsorbent surface. During the FFF separation processes, the colloid sample is continually washed with fresh carrier giving ample opportunity for desorption to occur. However, it is possible that equilibrium experiments could be performed by including a fixed concentration of the adsorbate in the carrier liquid. This approach would be feasible provided the experimental conditions are such that significant adsorption to the particles occurs causing the adsorbate concentration in the eluent to be elevated above the background carrier solution level, so that the changes can be detected.

The size range that can be conveniently covered using the sedimentation FFF instrument we are using (FFFractionation) is approximately 0.05–1 μm in diameter. Higher speed centrifuges (*e.g.* Dupont SF³) may reduce the lower size limit to perhaps 0.01 μm . The methodology developed here could equally be applied to data produced from other high resolution separation techniques. For example, we have used flow FFF to determine molecular weight distributions of humic substances^{15,16}. Considering the recent interest in the association of trace metals and toxic organic compounds with humic substances in natural waters^{32,33} this should be a valuable tool for investigating the molecular size dependence of such association.

Although sedimentation FFF is capable of separating particles of diameter greater than 1 μm using the steric mode³⁴, this has lower resolution and theoretical exactness than the normal mode generally used for particles less than 1 μm in size. However, recent work reported from Giddings' laboratory in Utah^{35,36} has shown excellent resolution and reproducibility for the larger particles (1–100 μm) using a new hyperlayer mode of FFF.

Thus, it is conceivable that a combination of these FFF techniques [hyperlayer FFF (1–100 μm); sedimentation FFF (0.05–1 μm); Flow FFF (0.001–0.05 μm)] could allow particles in the ranges between 1 μm to 100 μm to be separated, permitting the

complex relationship between size, geochemistry and pollutant binding in natural aquatic systems to be unravelled.

CONCLUSIONS

Previous work^{1,3} has demonstrated that aquatic colloids can be separated with high resolution and sized using sedimentation FFF. In this study we have shown how adsorption experiments using radiolabelled compounds can be used to compute surface adsorption density distributions to yield hitherto unobtainable information about the adsorption of various pollutants to natural particles. The use of other sensitive analytical techniques such as ICP-mass spectrometry or electrochemical detectors should extend the range of adsorbates that can be studied. In this preliminary study we have demonstrated the general methodology using sedimentation FFF, however, the size range that can be covered should be able to be extended by the use of different FFF subtechniques or other high resolution separation methods.

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