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Binding of Waterborne Steroid Estrogens to Solid Phases in River and Estuarine Systems

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Natural and synthetic steroid estrogens have been detected in sewage treatment work effluents discharged into rivers. An understanding of the partitioning of these estrogens between water and sediment is critical for the prediction of their fates in river systems. Hence, a series of experiments was conducted to ascertain the effects of differing environmental conditions on estrogen partitioning to sediment. Fugacity level 1 (sediment phase) output data demonstrated a good correlation with removal of estrogens from the water phase. Synthetic estrogens, with their higher K_{ow} values, were removed more readily from the water phase than the natural estrogens. Maximum sorption to the sediment phase was attained after 1 h of shaking. At higher estrogen concentrations, there was a decrease in estrogen removal, while higher levels of sediment induced greater removal. The sorption of estrogen to sediments correlated with total organic carbon content. However, the presence of organic carbon was not a prerequisite for sorption. Iron oxide alone was demonstrated to have a sorption capacity of 40% of that of a sediment containing 1.1% total organic carbon. Laboratory saline water was found to increase estrogen removal from the water phase which was found to be consistent with partitioning experiments using actual field water samples. The addition of estradiol valerate, a synthetic estrogen with a particularly high K_{ow}, suppressed sorption of other estrogens suggesting that it competed with the other compounds for binding sites.

Introduction

Feminization of male fish, indicated by vitellogenin production or imposex condition, has been identified in rivers worldwide (*1, 2*). Bioassay fractionation techniques have been used to determine that the most probable cause of such effects is the presence of steroid estrogens, particularly 17β-estradiol (estradiol), estrone, and 17α-ethinyl estradiol (EE2) in effluents from sewage treatment works (STW) (*3, 4*).

The principal endogenous phenolic steroid estrogen, in terms of binding to the human estrogen receptor, is estradiol, which is oxidized in metabolic processes to estrone and through further transformation to estriol (*5*). Estradiol is also the backbone structure used to engineer the synthetic estrogens EE2, mestranol, and estradiol valerate which are utilized in human hormone treatments, e.g. the contraceptive pill (*5*). Prior to excretion from the body, estrogens are metabolized to biologically inactive, water-soluble conjugates of sulfate-esters or glucuronides (*5, 6*). It is known that gut bacteria can deconjugate estrogens (*7*) and biodegrade them, with the synthetic estrogens exhibiting greater recalcitrance in the activated sludge process of biological wastewater treatment (*5, 8, 9*). However, estrogens present in discharged domestic effluents represent the most significant estrogenic input to the aquatic environment (*7*− *9*); total extractable estrogens and conjugates have been detected at up to 1 μg/L in effluents from sewage treatment works (*6, 10*).

On discharge to surface waters, dilution, degradation, and sorption will decrease the aqueous concentrations of estrogens (*6*). Since estrogens are hydrophobic organic compounds of low volatility, it is likely that sorption will be a significant factor in reducing aqueous phase concentrations (*6*). The fate of estrogens once bound to sediments is an important consideration in terms of transportation, degradation, and potential exposure to organisms (*11*). The octanol−water (K_{ow}) and organic carbon (K_{oc}) partition coefficients are frequently used indicators of the tendency of compounds to partition to organic matter (*12*). The greater these coefficient values are for a given compound, the greater its tendency to partition to organic matter, e.g. organic carbon rich sediments. The hypothesis that estrogens will partition to sediments is supported by modeling data (estradiol, estrone and EE2), backed by results from laboratory experiments using estradiol (*6*). However, the behavior of other natural and synthetic estrogens (e.g. estriol, mestranol, and estradiol valerate) has not been modeled nor tested experimentally.

Present knowledge on the partitioning of estrogens is also limited by the lack of information regarding the influence of environmental variables on estrogen sorption. The present study was undertaken to determine experimentally the partitioning of estradiol, estrone, estriol, EE2, mestranol, and estradiol valerate from water to sediments. The kinetics of sorption, importance of binding sites, influence of TOC, and salinity were investigated, and the results were compared to the output from a basic fugacity model.

Materials and Methods

Chemicals. A series of experiments was devised to measure the partitioning of natural and synthetic estrogens from water to sediments under a range of environmental conditions. The estrogens used in all experiments were estradiol, estrone, estriol, EE2, and mestranol. Additionally, estradiol valerate, a superhydrophobic compound (*13, 14*) was used in an evaluation of competition for sorbent binding sites.

Preparation of Materials. One thousand μg/mL individual stock solutions of the six estrogens (Sigma, Poole, U.K.) were prepared in HPLC grade acetone (Rathburn, Walkerburn, U.K.). A 100 μg/mL working stock mixture of the estrogens (except estradiol valerate) was prepared for use in the experiments. Surficial bed sediments and water samples were collected from the Blackwater estuary (A, B, and C) and River Thames, U.K. (D and E) (Table 1). The sediments were prepared by passing through a 2 mm sieve and characterized by measuring moisture content, total organic carbon TOC, and particle size distribution (Table 1). Water samples were filtered through a 0.45 μm membrane filter and characterized by TOC and salinity (as percent NaCl) measurements (Table 1). The estrogen stock solutions, sediments, and water samples were kept in refrigerated conditions (<4 °C) when not in use. All experimental work was undertaken within 1 month of collection of each sediment/water sample to minimize the impact of aging on materials. Since the reported

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TABLE 1. Physicochemical Parameters of the Sediments and Water Samples

	location						
	Blackwater estuary				Thames river		
materials	sediment A	sediment B	sediment C	water sample	sediment D	sediment E	water sample
TOC (%)	1.1	0.3	2.0	0.0003[a]	1.6	3.3	0.0006[a]
PSD (%):							
sand	1.6	0	0	NA[b]	0	0	NA[b]
silt	74	70	61		93	82	
clay	25	30	39		7	18	
moisture content (%)	40	24	68	NA[b]	30	50	NA[b]
salinity (% NaCl)	NA[b]	NA[b]	NA[b]	3.5	NA[b]	NA[b]	0.04

[a] After filtration. [b] NA, not applicable.

TABLE 2. Gas Chromatograpy and Mass Spectrometry Parameters

GC column	BPX5 capillary column 30 m (SGE, Milton Keynes, U.K.); film thickness 0.25 μm; o.d. 0.33 mm; i.d. 0.22 mm
GC injection parameters	2 μL splitless programmed from injection temp: 50 ^{o}C; heated at 100 ^{o}C/min to 300 ^{o}C
carrier gas	helium, flow programmed at 1 mL/min
GC temp	50 ^{o}C isothermal 3.5 min; 20 ^{o}C/min to 240 ^{o}C; 2 ^{o}C/min to 290 ^{o}C for 10 min
MS parameters	280 ^{o}C (transfer line); 180 ^{o}C (source) EI mode
MS electron energy	70 eV

TABLE 3. Retention Times and Selected Masses for Derivatized Estrogens

estrogen	retention time	selected masses
estradiol	24.81	285, 416
estrone	24.69	257, 342
estriol	28.91	147, 311
EE2	27.27	285, 425
mestranol	26.38	227, 367
estradiol valerate	34.65	244, 428

half-lives in river water for estradiol and EE2 are 4 and 46 days, respectively (*6*), biodegradation was expected to be insignificant over the time scales involved in the work.

Estrogen Determination. The estrogens were extracted from the aqueous phase by liquid−liquid extraction. Dichloromethane (DCM), 1 mL, was shaken vigorously with a 1 mL water sample for 30 s. An aliquot, 0.4 mL, of the organic layer was transferred to a reaction vial where it was evaporated to dryness with nitrogen. The derivatization mixture (*N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide:trimethylsilylimidazole: dithioerythritol; 1000:2:2; v/v/w) (Sigma, Poole, U.K.), 50 μL, was added (*7*, *8*), and the reaction vial was sealed and placed in a heating block at 60 °C for 30 min. The solution was again evaporated to dryness, and 0.4 mL of 2 μg/mL mirex (internal standard) in hexane was then added prior to gas chromatography−mass spectrometry (GC-MS) analysis. The GC-MS conditions were set as shown in Table 2, using a Turbomass GC-MS system (Perkin-Elmer, Beaconsfield, U.K.). Calibration was conducted using 0.00, 0.05, 0.10, 0.25, 0.50, and 2.50 μg/mL of estrogen mixtures. Identification and quantification of compounds were by selected ion monitoring, with confirmation of peak identity with a secondary ion (Table 3).

Quality Control. Prior to partitioning work commencing, controls were conducted to ensure that the estrogens did not sorb to the laboratory equipment and that estrogens were not released to the water from the sediment used in the work. The efficiency of the liquid−liquid extraction using DCM was evaluated, and percentage recoveries and standard deviations for the method at 0.1 μg/mL in water were estrone (82.5 $\pm$ 0.6); estradiol (81.8 $\pm$ 1.2); mestranol (94.3 $\pm$ 0.4); EE2 (84.8 $\pm$ 0.8); estriol (80.5 $\pm$ 1.5); and estradiol valerate (80.9 $\pm$ 1.3). The GC-MS detection limit was 5 ng/mL in final extracts. To allow for the effect of salinity on extraction efficiency, initial concentrations of estrogens were determined from NaCl adjusted mixtures, which demonstrated no statistical difference in results from samples without NaCl.

Partitioning Experiments. All batch partitioning experiments were duplicated and utilized 250 mL Teflon bottles containing 200 mL of reverse-osmosis (RO) water spiked to a concentration of 0.1 μg/mL with the mixed estrogen standard and 5 g wet weight (3 g dry weight) of sediment A. The effect of the acetone present in standard solutions on the sorption of estrogens to the sediments was evaluated by evaporating the acetone before adding RO water. No difference was observed in replicate experiments using sediment A, and the effect of the acetone in solution was deemed to be insignificant. Initial duplicate 1 mL water samples were taken from the flask prior to sediment addition to confirm spiked initial estrogen concentrations. The bottle was then capped and placed in a rotary shaker (approximately 50 rpm) for 1 h. The bottle was then centrifuged for 10 min at 750 gravitational acceleration, and duplicate 1 mL samples of the supernatant were removed. The estrogens present in the 1 mL aliquots were then extracted, derivatized, and quantified by GC-MS.

Sorption Kinetics. Bottles were shaken for a total time of 5 h, with duplicate 1 mL water samples taken at times of 0.5, 1, and 5 h. At each sampling time interval, bottles were centrifuged prior to removing samples, the sediment was resuspended by shaking vigorously, and bottles were returned to the rotary shaker.

Estrogen Concentration and Sediment Load. Competition for and availability of binding sites were investigated by varying both the concentration of estrogens in solution and by the amount of sediment added to reflect different inputs and sediment loads. Estrogen concentrations investigated were 0.01, 0.1, and 1 μg/mL. The amount of sediment added was either 0.6, 3, or 15 g (dry weight).

Evaluating the Effect of Estradiol Valerate. The superhydrophobic compound estradiol valerate was added to the spiked estrogen solution at a concentration of 0.1 μg/mL, and the basic partitioning experiment was repeated. The results were compared to the basic partitioning experiment without estradiol valerate.

Influence of TOC and Particle Size Distribution. Partitioning experiments were conducted with sediments A−E (equivalent to 3 g dry weight) and 3 g of hydrous iron oxide (haematite, $Fe_2O_3 \cdot 2H_2O$) as a model sediment with zero TOC (Merck, Dorset, U.K.).

TABLE 4. Chemical Properties of Estrogens Used in the Study[a]

estrogen	molecular weight	vapor pressure (Pa)	water solubility (mg/L)	log K_{ow} [ESC]	log K_{ow} from lit.
estradiol	272.39	3E-08	13	3.94	4.01, 3.10
estrone	270.37	3E-08	13	3.43	3.13
estriol	288.39	9E-13	13	2.81	2.60[b]
EE2	296.40	6E-09	4.8	4.15	3.67
mestranol	310.42	1E-07	0.3	4.67	4.10[b]

[a] References *6, 10, 18−22.* [b] Modeled data.

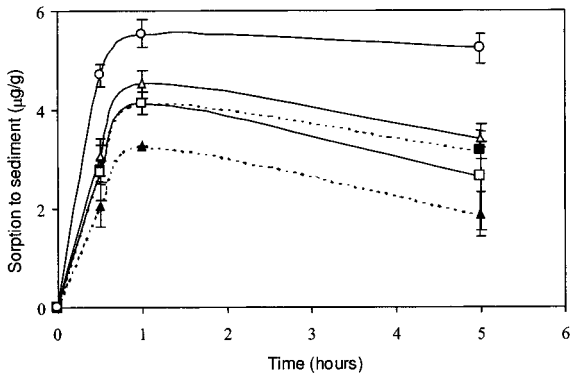

FIGURE 1. Sorption of estrogens to sediment with time: □ estrone; ■ estradiol; △ EE2; ▲ estriol; and ○ mestranol. Experimental conditions were as follows: 3 g (d.w. basis) of sediment/200 mL of 0.1 μg/mL (aqueous) estrogens shaken for 0.5, 1, and 5 h.

Effect of Salinity. The effect of changing salinity was investigated using sediment A and RO water with and without sodium chloride (2.6%). In addition, native water (Table 1) was used with sediments B−E.

Determination of Freundlich (Sorption) Isotherm. The Freundlich (sorption) isotherm was calculated by plotting the log equilibrium estrogen concentration in sediment (log C_s) against the log equilibrium estrogen concentration in the water phase (log C_w) (*15, 16*)

$$\log C_s = \log K_f + 1/n \log C_w$$

where K_f and $1/n$ are the sorption coefficient and constant, respectively. The equation of the trendline was noted, and the gradient ($1/n$) was stated. The gradient value signifies whether sorption of the compound is limited (nonlinear) ($1/n < 1$) or limitless (linear) ($1/n > 1$) (*15, 16*).

Fugacity Modeling. A Mackay-based level 1 fugacity model (*17*) was executed for the individual estrogens based on their physical properties (Table 4). All K_{ow} values used in modeling were calculated using the ESC program (*18, 19*) for consistency. Values available from the literature are also given in Table 4 for comparison.

Results and Discussion

Sorption Kinetics. An initial rapid sorption (4.0−9.4 μg/g/h) between 0 and 0.5 h, followed by a period up to 1 h of slower sorption (1.5−2.9 μg/g/h) prior to a steady decrease in sorption (0.07−0.37 μg/g/h), except for mestranol between 1 and 5 h was shown in Figure 1. In the literature, for comparable conditions, three stages of sorption have been identified (*15, 16*). This may also have occurred with the sorption of estrogens in this work; however, the temporal resolution of the data is not fine enough to clearly demonstrate this effect. However, it is likely that the decrease in sorption rate between 0.5 and 1 h may reflect both the progressive saturation of sorbent binding sites and reduction in available sorbate (estrogens) for binding (*15, 16*). The decrease in the amount of sorption by 5 h is suggested to represent estrogen desorption back into the aqueous phase, as has been observed elsewhere for estradiol (*6*) and other hydrophobic organics, which may be due to the increase in dissolved organic matter in water phase (*15, 16*). Other workers also attribute this effect to the development of a "third phase" consisting of organic macromolecules into which the estrogens may partition (*22*). Since maximum estrogen removal was observed at 1 h, the results of subsequent experiments (conducted for 1 h) are assumed to reflect maximum estrogen sorption.

TABLE 5. Freundlich Isotherm Data

estrogen	sorption constant ($1/n$)	sorption coefficient (log K_f)	R^2
estradiol	0.67	1.56	1.00
estrone	0.73	1.73	1.00
estriol	0.57	1.33	0.99
EE2	0.83	1.72	0.98
mestranol	0.78	2.26	0.98

The synthetic estrogens (mestranol, EE2) were shown to partition to the sediment to a greater extent (4.5−5.5 μg/g) than the natural estrogens (estrone, estriol) (3.2−4.1 μg/g); however, experimental error does not clearly differentiate estradiol and EE2. The amount sorbed correlated (R^2 0.97, equation of line $y = 0.392x + 44.45$) with that predicted by the level-1 fugacity model, the least overall removal was observed for estriol (log K_{ow} 2.8), and the greatest was observed for mestranol (log K_{ow} 4.6). The strong correlation between predicted and actual sorption of the estrogens implies that the fugacity model is a useful tool for predicting the partitioning of estrogens between aqueous and sediment phases.

Binding Site Availability and Competition. The effect of varying the ratio of dissolved estrogens to sediment was investigated by altering both the concentration of estrogens and the sediment load. Data for the Freundlich isotherm for each estrogen, the sorption constant ($1/n$), and sorption coefficient (log K_f) are shown in Table 5. The data indicate that the sorption constant of the isotherm is <1; this implies that sorption has approached a limit, which may indicate the complexity of the sediment components that sorb and react with the estrogens (*23*). Moreover, the inter/intraspecies competition to the binding sites may also lead to nonlinear sorption (*23*). Because of the observed nonlinear sorption, the experimental log K_{oc} was undefined. However, the relationship between log K_{oc} and water solubility (S) and log K_{ow} has been reported in the literature (*24*) as

$$\log K_{oc} = -0.686 \log S + 4.273$$

$$\log K_{oc} = \log K_{ow} - 0.317$$

According to these equations, log K_{oc} calculated from water solubility data is 3.5 for estradiol, estrone, and estriol, 3.8 for EE2, and 4.6 for mestranol, which compares to 3.6 for estradiol, 3.1 for estrone, 2.5 for estriol, 3.8 for EE2, and 4.4 for mestranol extrapolated from log K_{ow} values obtained from the ESC program (*18, 19*).

By varying the amount of sediment added (sediment load), it was established that the loss of estrogens from the aqueous phase increased with the amount of sediment present, which may reflect the greater number of available binding sites. However, the mass of estrogens sorbed per gram of sediment actually decreased with an increased sediment amount which was expected and related to the supply of estrogen sorbate approaching exhaustion (*23*).

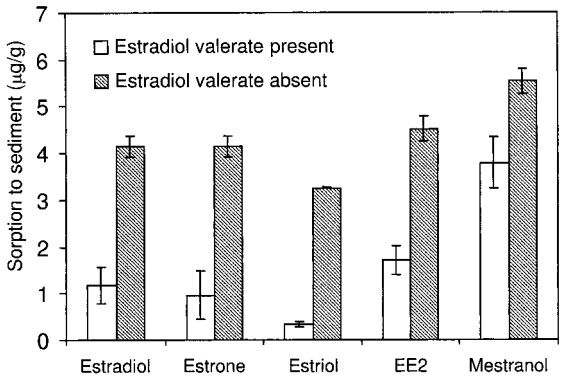

FIGURE 2. Effect of the presence of estradiol valerate on the sorption of other estrogens to sediment. Experimental conditions were as follows: 3 g (d.w. basis) of sediment/200 mL of 0.1 μg/mL (aqueous) estrogens, with or without estradiol valerate, shaken for 1 h.

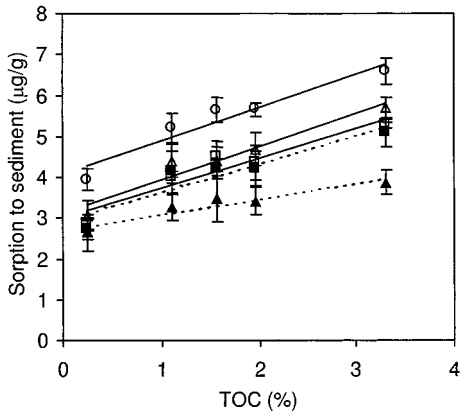

FIGURE 3. Relationship between TOC content and estrogen sorption to sediments: □ estrone; ■ estradiol; △ EE2; ▲ estriol; and ○ mestranol. Experimental conditions were as follows: 3 g (d.w. basis) of sediment with varying TOC/200 mL of 0.1 μg/mL (aqueous) estrogens shaken for 1 h.

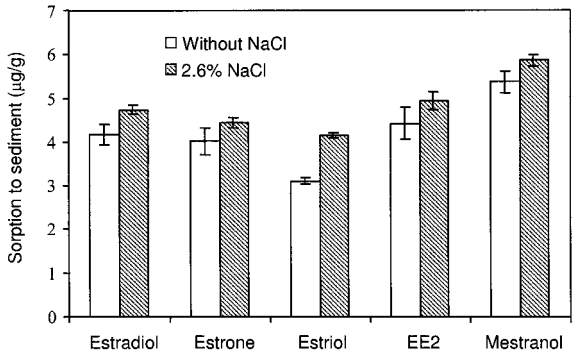

FIGURE 4. Impact of salinity on sorption of estrogens to sediment. Experimental conditions were as follows: 3 g (d.w. basis) of sediment/200 mL of 0.1 μg/mL (aqueous) estrogens, with 0 and 2.6% salinity, shaken for 1 h.

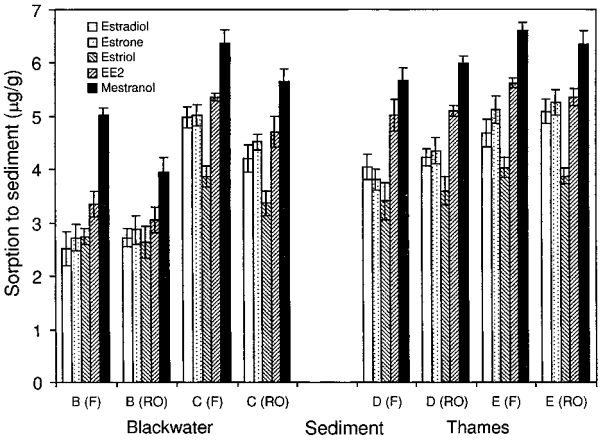

FIGURE 5. Comparison between estrogen sorption with field water (F) and reverse osmosis water (RO). Experimental conditions were as follows: 3 g (d.w. basis) of sediment/200 mL of 0.1 μg/mL (aqueous) estrogens (in field or RO water) shaken for 1 h. Sediment TOC: B = 0.3%; C = 2.0%; D = 1.6%; and E = 3.3% (Table 1).

Competition for binding sites was demonstrated by the suppressive effect of the superhydrophobic compound estradiol valerate (log K_{ow}, calculated with the ESC model, is 6.41) on the sorption of the other estrogens (Figure 2). The magnitude of this effect increased with decreasing compound hydrophobicity, hence estriol sorption was suppressed most (89%) and mestranol least (31%). This suggests that estradiol valerate is a highly efficient competitor for binding sites and has a greater affinity for these sites than less hydrophobic compounds. Similar effects have been observed for the pesticides bifenox and atrazine (*15, 16*). Competition for partitioning in tests in this work which involved a mixture of estrogens may also have occurred; however, due to the similarity of most log K_{ow}, values, it was reasoned that affinities for the sediments would be similar for these estrogens (*24*).

Importance of TOC and Particle Size Distribution for Estrogen Sorption. The sorption of estrogens to the sediments exhibited correlation with TOC contents (Figure 3). Correlation coefficients ranged from 0.86 to 0.94, and this experimental data supports the concept of fugacity modeling which predicts that sorption of estrogens will increase with increasing TOC content of sediment. However, the presence of organic carbon is not a prerequisite for sorption, as iron oxide, used as a model sediment with no organic carbon content, exhibited 40% of the estrogen sorption (estradiol 2.64 ± 0.05 ug/g; estrone 2.45 ± 0.16 ug/g; estriol 3.04 ± 0.27 ug/g; EE2 3.37 ± 0.16 ug/g; and mestranol 3.98 ± 0.33 ug/g) observed for sediment A (1.1% TOC). The adsorption mechanism of iron oxide is governed by ion exchange between the surface hydroxyl group on the oxide and charged or polar solute (*25*). It is likely that the polar phenolic steroid estrogens exhibit similar binding mechanism to iron oxide. However, further experiments are needed to investigate the binding mechanism of estrogens in the natural environment.

The sorption of estrogens by sediments in this study exhibited only a weak correlation with the particle size distribution ($R^2 < 0.2$).

Effect of Salinity on Sorption. The sorption of the estrogens to sediment was observed to increase with addition of NaCl to RO water (Figure 4). This result is consistent with the results of sorption experiments using field water with varying salinity levels. The difference in estrogen sorption between field water and RO water was more evident for samples from the Blackwater (3.5% salinity) than that of Thames river water samples, which were of very low (0.04%) salinity (Figure 5). In turn, only sediment C which had a higher TOC content than sediment B (2.0% compared to 0.3%) clearly demonstrated any significant difference in sorption with saline water. It is likely that increased removal of estrogens is due to aggregation and flocculation in the higher ionic strength medium (greater NaCl concentration), which is a typical occurrence in estuaries, resulting in high rates of sedimentation (*26*). The experimental data implies that estrogens sorbed to suspended or dissolved organic material are more likely to be deposited with sediments in estuarine areas.

Implications of Experimental Results. The data on sorption kinetics indicated that rapid estrogen sorption occurred within the first 30 min of contact between sorbate and sorbent. This suggests that dissolved estrogens discharged to the aquatic environment may rapidly become sorbed, on contact, to suspended solids. The amount of estrogens sorbed is influenced by sorbent binding site availability and competition for binding sites. In addition, the estrogens will compete for sorption sites, both between estrogens and with other hydrophobic chemicals (e.g. DDT, PCB, alkylphenols). The implications of this are that in natural systems a greater proportion of estrogens, particularly natural estrogens (lower hydrophobicities), will remain in the aqueous phase than observed in this experimental work. Dissolved natural estrogens are known to be degraded relatively rapidly in a river environment, with estradiol having a half-life of just 4 days (*6*).

The total organic content of the suspended matter will affect the amount and rate of sorption. Increasing TOC is known to increase sorption (*15*, *16*, *22*). Many studies have demonstrated that particle size distribution relates to the sorption process (*15*, *16*, *22*); however, care must be taken to evaluate if this is due to TOC rather than the particle size itself. Nevertheless, it is generally agreed that suspended particles, which have a smaller particle size and higher organic carbon content, will have a greater adsorption efficiency than that of bed sediments (*6*, *22*).

Estrogens in saline waters, e.g. the estuarine or marine environment, are expected to exhibit greater removal from the aqueous phase than in freshwaters. However, the sediment load and composition will be important factors, and salinity may also influence degradation of organic carbon (*27*).

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