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THE POTENTIAL FOR ESTRADIOL AND ETHINYLESTRADIOL TO SORB TO SUSPENDED AND BED SEDIMENTS IN SOME ENGLISH RIVERS

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Abstract—The endocrine-disrupting impact of steroid estrogens on fish will be strongly influenced by their distribution between sediment and water. Laboratory studies were performed to investigate the potential for sorption of 17β-estradiol (E_2) and 17α-ethinylestradiol (EE_2) to bed and suspended sediments taken from five British rivers. Sediment material was collected from the Rivers Aire and Calder (located in urban and industrialized areas in Yorkshire, UK), the River Thames (at a relatively rural site in Oxfordshire, UK), and from the estuaries of the Rivers Tees and Tyne. Using anaerobic conditions to inhibit biodegradation, it was found that 80 to 90% of binding to bed sediments was complete within 1 d, but that an equilibrium had not been reached after 2 d. Bed sediments gave distribution coefficients (K_d) ranging from 4 to 74 L/kg for E_2 and from 8 to 121 L/kg for EE_2 for samples taken over a range of seasons and locations. Sorption to suspended sediment gave K_d values ranging from 21 to 122 L/kg for E_2 and 19 to 260 L/kg for EE_2. However, these K_d values suggest less than 1% removal of the steroid estrogens from the aqueous phase given the ambient suspended sediment concentration. In the bed sediments, higher K_d values were associated with smaller particle size and higher organic carbon content. In most cases, the K_d values obtained for EE_2 were higher than those for E_2 by a factor of up to three.

Keywords—Sorption Estrogens Estradiol Ethinylestradiol Sediments

INTRODUCTION

International concern exists regarding estrogenic substances entering the freshwater environment and, possibly, having disruptive effects on the indigenous fauna. Steroid estrogens have been found in many sewage treatment works (STW) effluents in the United Kingdom [1–7], Germany [8–10], Italy [11], The Netherlands [12,13], Sweden [14], the United States [15,16], Canada [10,17], and Israel [18]. The compounds found to be responsible for the majority of the in vitro estrogenicity of domestic STWs have been the natural estrogens estrone (E_1) and 17β-estradiol (E_2) and the synthetic E_2 derivate 17α-ethinylestradiol (EE_2) (Fig. 1) [4]. Reported concentrations are usually in the low ng/L range [2,4,5,8–10,12], but even at such low concentrations, these compounds can be extremely potent. For example, less than 1 ng/L of EE_2 can stimulate male rainbow trout to produce vitellogenin, an egg yolk protein that normally is associated only with sexually mature females [7]. In addition, Metcalfe et al. [19] observed the formation of ova in the testis of Japanese medaka down to 4 ng/L for E_2 and 0.1 ng/L for EE_2.

The release of estrogenic chemicals into the environment does not necessarily mean that these substances will remain available to aquatic organisms. In some rivers, the estrogenic activity can disappear within a few meters of the discharge, whereas in others, it can still be detected several kilometers downstream [1,3]. The reduction of estrogen concentrations downstream of a STW discharge depends principally on dilution, degradation, and sorption to bed sediments and suspended sediments. The partitioning of E_2 or EE_2 between the water and sediments will influence the estrogenic impact of the molecule. Thus, depending on the bioavailability, benthic organisms may be exposed to higher concentrations than free-swimming fauna if the compounds are preserved, perhaps in anaerobic zones. Despite their importance, very little is known about the fate and behavior of steroid estrogens in rivers.

To our knowledge, only one study has examined the potential of steroid estrogens to bind to bed sediments [20], and no study has examined this regarding natural suspended particles. To address this shortfall, new data are provided on the potential for steroid estrogens to bind to a wide range of both bed and suspended sediments collected from UK rivers. The compounds selected for study were E_2 as an example of a natural steroid estrogen and EE_2 as a common synthetic estrogen (used mainly in oral contraceptives and hormone-replacement therapy). The results presented relate to samples collected from two types of UK riverine systems: Urban/industrial and rural. The Yorkshire Rivers Aire and Calder run through urban and industrial landscapes that have been studied under the Land Ocean Interaction Study [21]. The Tyne and Tees estuaries are also connected to important urban/industrial areas. In contrast, the River Thames at Wallingford is a relatively rural stretch of the river.

MATERIALS AND METHODS

Collection of materials

Bed sediment samples were collected in 1996 and 1997 from midstream river sites with a mechanical grab (Rivers Thames, Tees, and Tyne) or from near river banks by skimming off the top 2 to 5 cm of bed material (all other sites). Descriptions of the sites can be found in Table 1. At the Thames site, a series of bed sediment samples was taken within 15 to 20 m of each other, from inside a boathouse, midchannel, and

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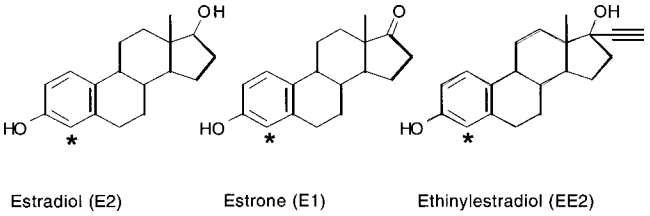

Fig. 1. Steroid estrogens. The asterisk marks the position of the radiolabel ^{14}C.

at a nearby slipway. All the bed sediments were sieved (mesh size, 2 mm), air-dried, mixed, and stored at room temperature. Suspended matter from the Rivers Aire, Calder, and Thames was collected on site using a continuous-flow centrifuge (SediSamp System II, model WSB/103-ENV; Alfa Laval, Tumba, Sweden) to concentrate the suspended sediments. The December 1999 samples of the Yorkshire rivers and the April 2001 sample of the River Thames were taken during high flow (these flow rates are exceeded 10% of the time in the Thames and 2–5% of the time for the Yorkshire rivers), whereas the other samples were taken during medium flow (20–70% exceedance) (National River Flow Archive, http://www.nwl.ac.uk/ih/nrfa/index.htm). The concentrated suspended sediments were stored for up to 4 d at 4°C. Instantaneous bulk samples of river water were collected in 1-L bottles at the same points where bed or suspended sediments were taken and were used within a month (refrigerated storage). The bed sediment sorption experiments (see below) were carried out with sediments and water collected from the same river (though generally not collected at the same time).

Assessment of water and sediment characteristics

Dissolved organic carbon (DOC), pH, and suspended sediment load were measured in the laboratory immediately after collection of water samples. Suspended sediment loads of the water or the concentrated suspended sediment slurry were determined as dry weight after 0.45-μm filtration (cellulose nitrate filter; Whatman, Maidstone, Kent, UK). The DOC in river water was measured in the filtered samples using a TOCsin II Aqueous Carbon Analyzer (Phase Separations; Watford, Herts, UK). The surface area of suspended sediments was analyzed using a Beckman Coulter SA 3100 instrument (Beckman Coulter; High Wycombe, Buckinghamshire, UK) as described by Gregg and Sing [22] after oven-drying (16 h, 40°C), gently breaking up with a pestle and mortar, and outgassing at 60°C with a nitrogen gas flow to remove any water that evolved.

The total organic carbon (TOC) content of bed and suspended sediments was determined by wet oxidation and titration [23]. The air-dried samples were disaggregated with an agate pestle and mortar, and the fraction greater than 2 mm was sieved off and discarded before grinding the samples to pass through a 80-mesh (0.18-mm) sieve. A 0.2- to 0.5-g subsample was weighed into a 250-ml conical flask and mixed with 10 ml of a 1 N $K_2Cr_2O_7$ solution and 20 ml of 98% (w/w) sulfuric acid and left for 1 h to oxidize. The samples were then diluted to 100 ml with deionized water, and 5 ml of NaF solution (40 g/L), 10 ml of 85% (w/w) orthophosphoric acid, and the indicator diphenylanaline were added. Blanks and samples were titrated with 0.5 N ferrous ammonium sulfate solution, which consisted of 196.1 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 20 ml of 98% (w/w) sulfuric acid made up to 1 L with distilled water. For each sediment, three replicate samples were measured.

The chlorophyll *a* concentration in water and the concentrated suspended sediment slurry was determined photometrically after glass-fiber filtration (GF/C; Whatman) and extraction of the filters with ethanol overnight at 4°C.

For the March 2000 samples, the particulate nitrogen content of the suspended sediments was determined to calculate the carbon-to-nitrogen (C:N) ratio. The suspended sediment slurry was further concentrated by centrifugation (30 min,

Table 1. Sampling locations in United Kingdom for bed or suspended sediments

Location	ID[a]	NGR[b]	Area	Type	Samples taken
River Aire					
Riddlesden	AiR	SE 080 418	24 km upstream of Leeds	Minor urban & wool cleaning ind.	Suspended sediments
Fleet Weir	AiF	SE 379 288	12 km downstream of Leeds	Major industrial/urban area	Bed sediments
Beal	AiB	SE 532 256	33 km downstream of Leeds	Major industrial/urban area	Suspended sediments
River Calder					
Brighouse	CaB	SE 155 222	20 km upstream of Wakefield	Industrial/urban area	Suspended sediments
Methley Bridge	CaM	SE 408 257	16 km downstream of Wakefield	Industrial/urban area	Bed and suspended sediments
Stanley Ferry	CaS	SE 355 231	Outskirts of Wakefield	Industrial/urban area	Suspended sediments
River Thames, Wallingford[c]					
Near boathouse	ThW	SU 614 903	54 km downstream of Oxford	Rural area	Bed and suspended sediments
Mid channel	ThM	SU 614 903	54 km downstream of Oxford	Rural area	Bed sediments
In boathouse	ThB	SU 614 903	54 km downstream of Oxford	Rural area	Bed sediments
Slipway	ThS	SU 614 903	54 km downstream of Oxford	Rural area	Bed sediments
River Tees					
Seal Sands	TeS	NZ 535 265	Tees estuary	Industrial/urban area	Bed sediments
Bran Sands	TeB	NZ 555 265	Tees estuary	Industrial/urban area	Bed sediments
River Tyne					
Hebburn	TyH	NA 325 658	Tyne tidal zone	Major industrial/urban area	Bed sediments

[a] Abbreviations for sites used in Tables 2–5.
[b] National Grid reference, a code of letters and numbers used on British maps to describe locations accurately. The letters may be omitted if the approximate region is known.
[c] The River Thames samples were taken within a few meters of each other.

4,750 *g*), and the overlying water was discarded. The samples were dried at 60°C overnight and homogenized in an agate mortar mill. Subsamples of 10 to 15 mg were weighed accurately (±0.01 mg) into silver cups (9 × 5 mm). The subsamples were then acidified with 20 μl of 5 M HCl and kept at 50 to 60°C for 30 min to remove inorganic carbon. Acid treatment was repeated until effervescence was no longer observed (generally three times). Water blanks were obtained using silver cups processed the same way but without sample addition. Particulate nitrogen was determined on duplicate samples by high-temperature oxidation using a Carlo Erba NA 1500 series 2 C/H/N/O/S analyzer (Milan, Italy). Sulfanilamide was used to construct the calibration curve. Nitrogen content was expressed as the percentage of total solid. Average blank levels were less than 0.5 μg of N; the detection limit (calculated according to the sensitivity of the instrument for nitrogen) was 0.5 μg, corresponding to 0.005% N for a 10-mg sample. Analytical precision was ±1.6% of the measured values.

For particle size analysis of the bed sediments, the sediments were dispersed and then further disintegrated using a rubber pestle before transfer into a Coulter LS130 laser granulometer (Beckman Coulter). A light beam of 750 nm was passed through the cell, and particle size was determined from the diffraction. The particle analysis results were given by volume (not mass) as 0- to 2-, 2- to 63-, and 63- to 900-μm fractions. When particles larger than 900 μm were present, the 900- to 2,000-μm fraction was determined by weight. The mineralogy of the clay fraction of the bed sediments was determined with an x-ray diffraction system (designed by Harwell Instruments, Harwell, Oxfordshire, UK). From the diffraction of the x-rays, the distance between the crystal planes can be calculated. These distances are characteristic for the different mineral groups. The system incorporated a B-pex goniometer, x-ray generator, and high-intensity curved graphite crystal monochromator. The results given are semiquantitative and refer to the groups, not to the individual minerals.

Determination of the octanol/water partition coefficient

The octanol/water partition coefficient (K_{ow}) of E_2 was determined using ^{14}C-labeled E_2 ([4-^{14}C]estradiol, Du Pont NEC-127, 7.4 MBq/mg, 100 mg/L in ethanol, radiochemical purity of 99%; NEN Life Science, Boston, MA, USA). Ten milliliters of 10 μg/L of [^{14}C]E_2 in purified water and 0, 50, and 200 μl of octanol (duplicates) were placed in small polypropylene containers and shaken on an orbital shaker (190 rpm) for 1 h. The samples were centrifuged for 10 min at 675 *g* before the aqueous phase was sampled, in triplicate, by transferring 1 ml into scintillation vials and mixing with 5 ml of scintillant (Ultima Gold; Packard Biosciences, Groningen, The Netherlands). The vials were then placed in a liquid scintillation counter (Beckman LS 6500; Beckman Instruments, Fullerton, CA, USA) and counted for 10 min. The counts were compared with those of the water-only solution to estimate the loss through sorption to equipment. The concentration of E_2 in octanol was then calculated by the difference between the original concentration and the remaining concentration in the water.

For EE_2, the procedure was improved in that 50 ml of purified water with a concentration 10 μg/L of [^{14}C]EE_2 ([4-^{14}C]ethinylestradiol, 7.4 MBq/mg, 818 mg/L in ethanol, radiochemical purity of 98.2% NEN Life Science) were mixed with 0, 10, 200, and 1,000 μl of octanol. The equilibration took place in 250-m glass separation funnels, which were shaken (1 h, 190 rpm) and left to separate for 1 h. To aid the phase separation, the samples were then transferred to polytetraflouroethylene (PTFE) centrifuge tubes and centrifuged for 30 min at 4,750 *g*. The aqueous phase was sampled (five replicates each) and analyzed as described above. In addition, four 20-μl aliquots of the octanol phase were taken from the 200- and 1,000-μl octanol samples and analyzed in the same way.

Sorption of E_2 to laboratory equipment

Ten milliliters of purified water with 5 μg/L of [^{14}C]E_2 were added to containers of glass, PTFE, polycarbonate, and polypropylene (three replicates each). After 48 h at room temperature (20 ± 2°C), the containers were emptied and rinsed three times with cold water. Adsorbed [^{14}C]E_2 was determined by shaking them overnight on an orbital shaker (100 rpm) with 5 ml of methanol and then counted in a scintillation counter as described above.

Sorption kinetics of E_2 to bed sediments

Air-dried sediment (1.0 g) and 15 ml of filtered river water (0.2 μm, Supor 200; Gelman Sciences, Northampton, Northamptonshire, UK) from the River Aire (Fleet Weir) and River Thames (Wallingford) were placed in PTFE centrifuge tubes and spiked with [^{14}C]E_2 to give a final concentration of 5 μg/L. The same quantity of E_2 was added to tubes containing 15 ml of pure water to provide a standard. The samples were placed in a 2.5-L anaerobic jar with an AnaeroGen gas pack (Oxoid, Basingstoke, Hampshire, UK; this product removes all O_2 from the atmosphere inside the jar within 1 h) and test strip (Anaerotest; Merck, Darmstadt, Germany; this product tests for oxygen in the atmosphere) and then incubated on an orbital shaker (90 rpm) at room temperature. Oxygen deficiency considerably slows biodegradation of E_2 by at least a factor of three [24–26] and, therefore, reduces the error due to loss of chemical through degradation. Using a sacrificial sampling technique, three replicate tubes were removed after each of 1, 2, and 6 d. Following 15-min centrifugation at 4,750 *g*, each tube was sampled three times with a syringe by removing 700 μl of the supernatant into 700 μl of methanol. This was then filtered (0.45-μm PTFE filter; Gelman Sciences) into a scintillation vial to remove remaining solids. The samples were counted as described above. The amount of radioactivity still present in the aqueous phase was compared with the standards, and the amount sorbed was calculated by difference. In the present study, the distribution between solid and aqueous phase was expressed by the distribution coefficient K_d whether or not an equilibrium was reached.

To check whether removing oxygen, as in the kinetic experiment described above, influences sorption to sediment, samples were used from the River Thames (Wallingford slipway, June 27, 1997) and the River Aire (Fleet Weir, December 18, 1996). Subsamples of 3 g of the air-dried and sieved samples were mixed with 15 ml of filtered (0.45 μm) river water in PTFE centrifuge tubes. Samples destined for anaerobic incubation were placed with loose caps in a 2.5-L anaerobic jar with an AnaeroGen gas pack for 24 h before the addition of E_2. Similarly, those for aerobic incubation were left to equilibrate for 24 h before the addition of E_2. Following this period, the tubes were opened and [^{14}C]E_2 added to give final concentrations of 2.5, 5, and 10 μg/L. A fresh AnaeroGen pack was added to the samples for anaerobic incubation, and all the samples were allowed to equilibrate for 20 h on the orbital shaker

(90 rpm). The tubes were centrifuged (15 min, 4,750 *g*), and the aqueous concentration measured by transferring 1 ml of the supernatant into a scintillation vial, mixing it with 5 ml of scintillant, and counting for 5 min in the liquid scintillation counter. The counts were compared with the standards of E_2 in purified water, and the amount sorbed was calculated by difference. The slope of a best-fit line through the data for solid-phase versus aqueous-phase concentration yielded the distribution coefficient (K_d).

Establishing sorption K_d for E_2 and EE_2 and bed sediments

Sorption distribution coefficients for E_2 with bed sediments were determined in 1997, and this was repeated in 1999 and 2000 after three to four years of dry storage. Sorption distribution coefficients for EE_2 were only established in 1999 and 2000. For the comparison of different bed sediments, 1 to 5 g (depending on the expected sorption) of the air-dried sediment and 15 ml of 0.2 μm–filtered river water from the respective sites were used. Either E_2 or EE_2 was added as three replicates at three concentrations (2.5, 5, and 10 μg/L) or two replicates at seven concentrations (0.5–10 μg/L) to establish an isotherm. After 20-h equilibration on an orbital shaker (90 rpm), the tubes were centrifuged (15 min, 4,750 *g*) and the sorption K_d(K_d1) determined as described in the previous section. For some of the samples, a second distribution coefficient for desorption (K_d2) was measured by replacing the original water with the same amount of fresh (estrogen-free), 0.45 μm–filtered river water and incubating for a further 20 h before centrifuging and sampling as above, thus allowing the tested chemical to redistribute from the sediment into the aqueous phase.

Influence of storage conditions on sorption potential of E_2 to bed sediments

The influence of air-drying and wet storage on E_2 sorption potential was compared using River Thames bed sediment (June 27, 1997). A subsample was air-dried and prepared as before, and the remaining sediment was stored wet and cool (18 d at 4°C). One gram of dry sediment or the equivalent amount of wet sediment (1.55 g) was added to water from the same site (total amount of water, 15 ml) and spiked with [^{14}C]E_2 to give a final concentration of 5 μg/L. The samples were incubated by shaking for 24 h at room temperature before centrifugation and measurement of the aqueous phase concentrations as described above.

Sorption of E_2 and EE_2 to suspended sediments

As described in *Collection of materials,* fresh suspended sediment was collected from a constant-flow centrifuge, stored at 4°C, and used within 1 to 4 d. A 5-ml volume of concentrated suspended sediments (ranging from 0.9–54 g/L, which represents a concentration factor of 60–1,550) was added to PTFE centrifuge tubes and spiked with [^{14}C]E_2 or [^{14}C]EE_2 at five concentrations (1.5–10 μg/L, two replicates each). The samples were then processed and analyzed as described for the bed sediments, except that equilibration was only for 1 h.

Assuming that the partitioning of E_2 or EE_2 between water and suspended sediments with the ambient suspended sediment loads would yield the same K_d as determined from the concentrated suspended sediments (see below), the fraction E_2 or EE_2 that would sorb to suspended sediments at their natural concentration was calculated.

Influence of suspended sediment concentration on sorption K_d of EE_2

To study how concentrating the suspended sediments influences their sorptive behavior, concentrated suspended sediment samples taken from the Rivers Calder and Thames (River Calder, Stanley Ferry, May 14, 2001, at low flow and May 15, 2001, after heavy rainfall, and River Thames, Wallingford, April 25, 2001) were rediluted to different suspended sediment concentrations with filtered water (0.45-μm cellulose nitrate; Whatman) from the same sites and days. The concentration of suspended sediments in the rediluted samples were 0.02 to 9.5 g/L for the low-flow Calder sample (ambient suspended sediments, 14 mg/L; concentration factors, 1.5–680), 0.2 to 54 g/L for the high-flow Calder sample (ambient, 40 mg/L; concentration factors, 5–1,350), and 0.1 to 31 g/L for the Thames sample (ambient, 19 mg/L; concentration factors, 5–1,630). Suspended sediment concentrations were determined by filtering a known volume (0.45-μm cellulose nitrate filter; Whatman) and determining the increase in weight following air-drying. Triplicates of these different concentrations of suspended sediments were spiked with 5 μg/L of [^{14}C]EE_2 and allowed to equilibrate for 1 h, as described previously for the suspended sediments, before being centrifuged and analyzed as described above. The concentration on the solid phase was deduced from the measured concentration in the aqueous phase.

RESULTS AND DISCUSSION

K_{ow} *and sorption of E_2 to laboratory equipment*

The K_{ow} is an index of a molecule's hydrophobicity and can be used to estimate the potential of a substance to sorb to organic matrices [27,28]. The methods used gave a log K_{ow} of 3.1 ± 0.2 for E_2 and 3.9 ± 0.2 for EE_2. However, these values must be treated with some caution, because they were not determined by exactly the same method. Lai et al. [20] used a modeling approach to indirectly calculate K_{ow} that gave values of 3.9 for E_2 and 4.1 for EE_2. This technique agrees with our experimental data on the ranking of hydrophobicity of the two molecules, but it does not agree on the ratio between them or the absolute values. It is not entirely clear from theoretical considerations what effect the extra ethinyl group of EE_2 has on log K_{ow}. This is reflected by the fact that of five different programs for log K_{ow} estimation (from www.logP.com, including KowWin, which Lai et al. [20] used), two ranked the hydrophobicity of EE_2 higher than E_2, two came to the opposite conclusion, and one ranked them almost the same. The measured log K_{ow} of EE_2 is similar to the values of the xenobiotic estrogens nonylphenol and octylphenol, which have a reported log K_{ow} of 4.5 and 4.1, respectively [29]. Therefore, E_2 would be predicted to have a lower potential to sorb to sediments in rivers than the estrogenic alkylphenols, whereas the sorption potential of EE_2 should be similar to that of octylphenol, which has previously been tested with the same sediments [30].

Over a 2-d incubation period, 1 to 4% of E_2 in water sorbed to polycarbonate and polypropylene containers, and sorption to glass and PTFE was less than 1% (data not shown). Therefore, PTFE containers were used for the sorption studies with both EE_2 and E_2.

Sorption of E_2 and EE_2 to bed sediments

Most of the bed sediments collected for this study were obtained from near the river banks, where fine particles often

Table 2. Sample characteristics of bed sediments

ID[a]	Sampling date	Particle size distribution: Clay (<2 μm)	Silt (2–63 μm)	Sand (63–2000 μm)	Mineralogy of the clay fraction[b]: Kaolinite	Illite	Smectite	TOC[c]
AiF	09/06/96	9%	73%	18%	50%	30%	20%	2.4%
	12/18/96	7%	63%	30%	20%	65%	15%	7.0%
	07/18/97	7%	66%	27%	40%	50%	10%	10%
CaM	09/06/96	3%	19%	77%	50%	40%	10%	0.1%
	01/16/97	7%	55%	38%	25%	65%	10%	5.7%
	07/18/97	7%	50%	43%	60%	30%	10%	3.3%
ThW	09/23/96	3%	12%	85%	10%	10%	80%	0.1%
ThM	12/05/96	6%	38%	56%	10%	10%	80%	1.8%
ThB	04/15/97	5%	43%	52%	10%	10%	80%	2.9%
ThS	06/27/97	6%	41%	53%	40%	15%	45%	1.1%
TeS	07/31/97	8%	52%	40%	55%	40%	5%	2.0%
TeB	07/31/97	6%	43%	51%	60%	35%	5%	0.9%
TyH	08/01/97	9%	77%	14%	55%	40%	5%	3.7%

[a] Identification code. For description of the sites, see Table 1.
[b] Semiquantitative, referring to the groups and not the individual minerals.
[c] TOC = Total organic carbon.

predominate. Therefore, they may not represent all the types of sediment in each river; thus, the K_d values obtained are likely to be at the upper end of what might be expected from a river cross section. The properties of the bed sediments are given in Table 2.

The basic assumption of the sorption experiments is that [^{14}C]E_2 or [^{14}C]EE_2 not detected in the aqueous phase must be associated with the solid phase, assuming negligible loss of E_2 or EE_2 through degradation. However, degradation experiments carried out with river water showed that, especially in the River Aire and River Calder, most of the E_2 may be transformed to E_1 within a few days [25] even under anaerobic conditions, although in that case more slowly than when oxygen is present [24–26]. When E_2 is converted to E_1, a hydrogen molecule is removed from the E_2 molecule, leaving the steroid ring system unaffected, so no loss of the radiolabel (see Fig. 1) would occur. Because the solubility of E_2 and E_1 in water is very similar [15], the transformation of a proportion of E_2 to E_1 would probably not significantly affect the interpretation of the sorption results, but it is worth remembering that the distribution coefficients attributed to E_2 actually refer to a mixture of E_2 and its degradation products (mainly E_1). It has previously been observed that the sorption of E_2 and E_1 to bed sediments is similar, with K_d values for E_1 only approximately 10% higher than those of E_2 (values derived from published graph) [20]. For EE_2, the question of degradation distorting the sorption results is less of an issue, because this molecule is much more persistent than E_2 [25].

As a preliminary study, an assessment of the impact of drying and ambient conditions on E_2 sorption to bed sediments was made. The storage conditions did not have a major impact on the sample behavior, with wet-stored and dry-stored sediment giving K_d values for E_2 of 25.4 (standard deviation [SD], 2.7) and 19.9 L/kg (SD, 2.9), respectively. Comparing sorption to bed sediments under aerobic with anaerobic conditions gave K_d values of 18 and 24 L/kg, respectively, for the River Thames samples and of 40 and 47 L/kg, respectively, for the River Aire samples. When the data points of the respective curves were compared using a *t* test for the slope, the differences between aerobic and anaerobic treatment were not found to be significant at the 10% level. Microbial degradation of E_2 is faster under aerobic than under anaerobic conditions [25,26], but as discussed above, the first step in the breakdown of the molecule is transformation to E_1, which probably did not influence the results of the sorption experiments significantly.

Kinetic experiments with bed sediments from the River Thames and River Aire showed that 80 to 90% of the sorption occurred in the first 24 h, but an equilibrium was not reached within 2 d (Fig. 2). It must be recognized that, when studying a labile compound in an active biological medium (e.g., sediments), a true equilibrium cannot be reached and is, in fact, irrelevant. Notwithstanding this practical difficulty, an impression of the possible initial distribution of steroids onto sediments would be useful. Thus, an equilibration period of no more than 1 d was regarded as a useful compromise between incomplete sorption and beginning degradation, and 20 h, rather than the more usual 24 h, was chosen for practical reasons. The values therefore constitute a snapshot of the sorption for these conditions. It is acknowledged that the comparative K_d values generated from this approach may not represent the maxima, because hydrophobic reaction kinetics can be slow. However, the timescale selected may be considered relevant for a river.

The Freundlich isotherm $C_s = K_f \cdot C_w^{1/n}$, where C_s and C_w are

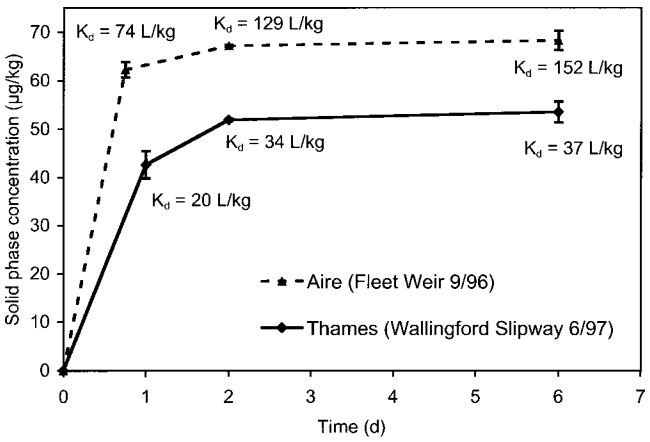

Fig. 2. Sorption distribution coefficient (K_d) of estradiol to air-dried River Thames (Oxfordshire, UK) and River Aire (Yorkshire, UK) bed sediment under an anaerobic atmosphere over 6 d (mean of three replicates plus standard deviation).

Table 3. Sorption and desorption distribution coefficients K_d1 and K_d2, L/Kg) for bed sediments with estradiol

		1997				1999/2000 (after 3–4 years of dry storage)			
		Sorption		Desorption		Sorption		Desorption	
ID[a]	Sampling date	K_d1 (SE)[b]	K_{oc}[c]	K_d2 (SE)	K_2/K_d1	K_d1 (SE)	K_{oc}	K_d2 (SE)	K_2/K_d1
AiF	09/06/96	72 (3.2)	2,975	143 (3.3)	2.0	54 (1.3)	2,231	119 (2.6)	2.2
	12/18/96	45 (1.6)	641	ND[d]	ND	57 (1.1)	812	90 (2.3)	1.6
	07/18/97	74 (1.9)	740	131 (2.7)	1.8	ND	ND	ND	ND
CaM	09/06/96	ND	ND	ND	ND	6.8 (0.2)	5,667	ND	ND
	01/16/97	57 (1.6)	998	ND	ND	41 (0.8)	718	96 (2.1)	2.3
	07/18/97	36 (1.4)	1,081	80 (1.9)	2.2	35 (0.6)	1,051	ND	ND
ThW	09/23/96	ND	ND	ND	ND	4.3 (0.1)	5,375	11 (0.5)	2.6
ThM	12/05/96	16 (1.2)	909	ND	ND	16 (0.4)	909	38 (1.3)	2.4
ThB	04/15/97	51 (1.2)	1,771	ND	ND	27 (1.2)	938	87 (1.6)	3.2
ThS	06/27/97	20 (1.0)	1,852	53 (0.8)	2.7	14 (0.3)	1,296	48 (0.7)	3.4
TeS	07/31/97	34 (0.7)	1,700	86 (0.8)	2.5	ND	ND	ND	ND
TeB	07/31/97	20 (0.5)	2,174	40 (0.6)	2.0	ND	ND	ND	ND
TyH	08/01/97	50 (2.8)	1,337	132 (1.9)	2.6	ND	ND	ND	ND

[a] Identification code. For description of the sites and sediment properties, see Tables 1 and 2.
[b] Standard error of the slope (i.e., of K_d).
[c] Organic carbon normalized distribution coefficient.
[d] ND = not determined.

the concentrations in the sediment and water, respectively, K_f is the Freundlich sorption coefficient, and $1/n$ is the sorption constant, was calculated for the 1999 and 2000 bed sediment sorption results (for those with sufficient observations to fit the isotherm). No significant difference (paired *t* test, 10% level) of the sorption constants ($1/n$) was found between sorption and desorption or between E_2 and EE_2, and the average $1/n$ value was 0.97 (range, 0.82–1.43, with 90% of the values between 0.85 and 1.12). Because the calculated sorption constants are so close to 1.0, the Freundlich isotherm can be simplified to a linear isotherm (linear range of the Langmuir isotherm): $C_s = K_d \cdot C_w$, where K_d is the linear distribution coefficient. The K_d value was determined as the slope of a best-fit line of solid versus aqueous concentration for all suspended and bed sediments. The r^2 values were normally in excess of 0.9 for the selected concentration range of 0.5 to 10 μg/L, which is well below the aqueous solubility of E_2 (13 mg/L) and EE_2 (4.8 mg/L) [15].

In contrast to the essentially linear sorption isotherms found in the present study, Lai et al. [20] published Freundlich isotherm data for different steroid estrogens and 1-h sorption to bed sediment, which represent limited sorption ($1/n$ = 0.67, 0.73, and 0.83 and K_f = 36, 54, and 52 for E_2, E_1, and EE_2, respectively). However, their experiments were carried out with a mixture of five estrogens at higher concentrations of 10 to 1,000 μg/L each, whereas the solids-to-water ratio was the same or lower than that used in the present study. The loading of the sediment with the tested chemicals therefore may have exceeded the linear range of the Langmuir isotherm. Environmental estrogen concentrations are in the low ng/L range, so even the lower concentrations used in the present study are an order of magnitude higher than the environmental concentrations of interest.

Despite the three- to four-year storage, the results obtained in 1999 and 2000 for the sorption and desorption distribution coefficients for E_2 and the bed sediments were comparable to the results of 1996 and 1997 for the same material (Table 3). The EE_2 showed a greater affinity for the bed sediments in all cases, with sorption K_d values 1.6- to 3.1-fold higher than those determined for E_2 (Table 4). A higher sorption capacity for EE_2 was expected because of its higher K_{ow} value.

To compare our K_d values quantitatively with the findings

Table 4. Sorption and desorption distribution coefficients (K_d1 and K_d2, L/kg, determined 1999/2000 after 3–4 years storage) for bed sediments with ethinylestradiol (EE_2) and comparison with K_d1 of estradiol (E_2)

		Sorption			Desorption			
ID[a]	Sampling date	K_d1	(SE)[b]	K_{oc}[c]	K_d2	(SE)	K_d2/K_d1	$K_d1(EE_2)/K_d1(E_2)$[d]
AiF	09/06/96	121	(4.7)	5,000	227	(3.6)	1.9	2.2
	12/18/96	102	(3.8)	1,453	165	(6.0)	1.6	1.8
CaM	09/06/96	12	(0.4)	10,000	ND[e]		ND	1.8
	01/16/97	110	(5.0)	1,926	166	(3.9)	1.5	2.7
	07/18/97	108	(3.3)	3,243	ND		ND	3.1
ThW	09/23/96	8.0	(0.2)	10,000	29	(1.6)	3.6	1.9
ThM	12/05/96	41	(1.7)	2,330	69	(1.3)	1.7	2.6
ThB	04/15/97	67	(1.7)	2,326	104	(2.0)	1.6	2.5
ThS	06/27/97	22	(0.8)	2,037	32	(0.4)	1.5	1.6

[a] Identification code. For description of the sites and sediment properties, see Tables 1 and 2.
[b] Standard error of the slope (i.e., of K_d).
[c] Organic carbon normalized distribution coefficient.
[d] Calculated with the 1999/2000 E_2 sorption distribution coefficients from Table 2.
[e] ND = not determined.

by Lai et al. [20], we estimated K_d values from their published data for sorption of a single concentration of E_2 and EE_2 to five bed sediments by dividing the solid-phase concentration by the aqueous concentration. This approach, which must be handled with some caution because they observed nonlinear isotherms, gives estimated K_d values of approximately 40 to 210 L/kg for E_2 and 55 to 350 L/kg for EE_2, with an EE_2-to-E_2 K_d ratio of 1.1 to 2.2. This compares to a range of 4 to 72 L/kg for E_2 and 8 to 121 L/kg for EE_2, with a EE_2-to-E_2 K_d ratio of 1.6 to 3.1 reported in the present study. The sorption capacity of the bed sediments used by Lai et al. [20] was generally higher, whereas the ratio of K_d for EE_2 versus E_2 was generally lower, than the values reported in the present study. However, for all parameters, an overlap is observed between the values measured by Lai et al. [20] and those reported here. The very high proportion of fine particles in the sediments used by Lai et al. (sand content, 0–1.6%) may explain the generally higher sorption they observed [20], but because the two groups used different methods, any comparison must be treated with caution.

When a second distribution coefficient (desorption, K_d2) was determined, it was always greater (1.5–3.2-fold) than the original sorption distribution coefficient (Tables 3 and 4). Hysteresis effects have been noted before with hydrophobic organic chemicals and bed sediments [31], which implies that sorbed E_2 or EE_2 that is not degraded would, over time, become increasingly difficult to desorb from the bed sediments. However, because of the experimental design, it is not possible to distinguish between hysteresis effects and differing K_d values due to insufficient time to establish a true equilibrium.

Higher K_d values were generally associated with smaller particle sizes, which could be seen by a positive correlation between K_d and silt content and a negative correlation between K_d sand content ($r^2 = 0.7$ for E_2 and silt or sand content and 0.8 for EE_2 and silt or sand content). Weaker positive correlations were found for clay content ($r^2 = 0.5$ for E_2 and 0.7 for EE_2) and organic carbon content ($r^2 = 0.6$ for both E_2 and EE_2).

When the clay mineralogy was taken into account, some indication was found that the clay fraction of the illite group was a more attractive sorbent ($r^2 = 0.49$ for E_2 and 0.56 for EE_2) than kaolinite ($r^2 = 0.2$ for E_2 and 0.3 for EE3) and smectite (negative correlation, $r^2 = 0.1$ for both E_2 and EE_2).

Therefore, E_2 and EE_2 were more significantly attracted to particularly fine bed sediments than to those with a high organic carbon content. This contrasts with the findings of Lai et al. [20], who reported correlations that were good with TOC but less so with particle size, when looking at the sorption of five steroid estrogens to five different bed sediments, which all consisted predominantly of fine material (maximal sand content, 1.6%). Those authors also showed, however, that organic carbon is not a prerequisite for estrogen sorption by demonstrating sorption of estrogens to pure iron oxide. It is, of course, difficult to clearly distinguish between TOC and particle size, because the two are intimately related in natural systems.

Organic carbon normalized distribution coefficient (K_{OC}) values were calculated from the K_d values (Tables 3 and 4), but given the relatively poor r^2 correlation with TOC, these values must be treated with caution.

Sorption of E_2 and EE_2 to suspended sediments

Great practical difficulties are involved with assessing the ability of relatively weak sorbates, such as the steroid estrogens, to sorb to suspended sediments. Sediment collection through the centrifugation process may cause a reduction in the surface area-to-volume ratio of the particles despite vigorous resuspension. Also, DOC may be released from the suspended sediments, thus reducing the organic carbon of the sediments and causing a third phase, which might increase the sorbate solubility [32,33]. Incomplete separation of the solid and the aqueous phase may also add to an underestimation of K_d, particularly at higher concentrations of solids [33]. However, to make any sort of measurement, some concentration is essential. With three separate suspended sediment samples having a concentration of approximately 1 to 54 g/L (a concentration factor between 25 and 1,600), consistent K_d values were obtained (Fig. 3). Concentrations less then 1 g/L dry weight cannot give a repeatable or consistent K_d value due to the difficulty of measuring very small changes in aqueous concentration. Therefore, providing that the sediments are concentrated by approximately 50- to 100-fold, repeatable measurements can be made. With the possible artifacts introduced by this experimental approach, the suspended sediment K_d values must be seen as a guide only. What is not in doubt is that, given the necessity of concentration to enable a measurement to be made, the impact of these suspended sediments on the water-column steroid estrogen concentration will be low.

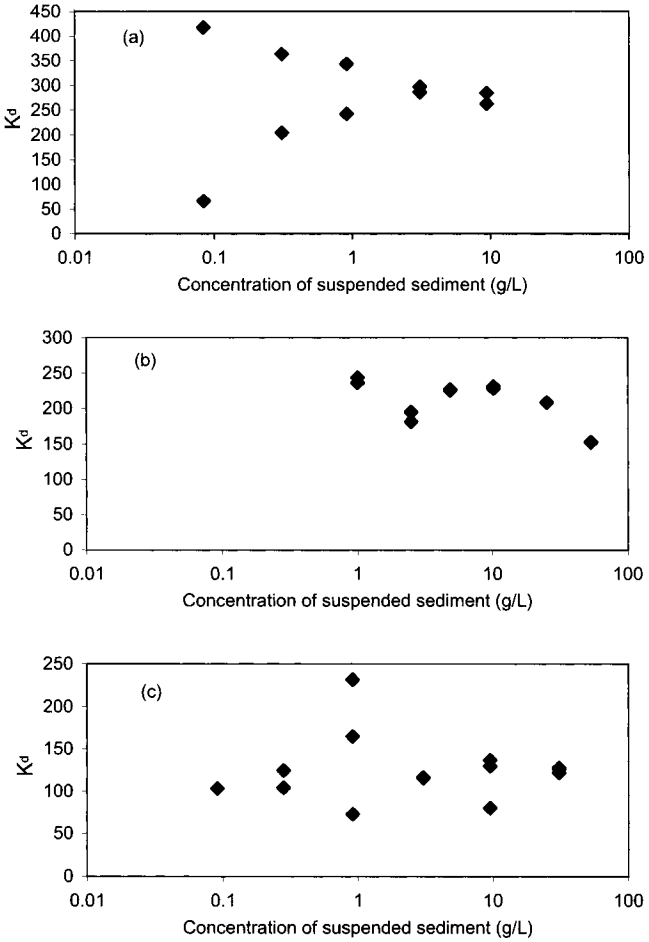

Fig. 3. Sorption distribution coefficient (K_d) of different dilutions of concentrated suspended sediment collected from the River Calder (Stanley Ferry, Yorkshire, UK) on May 14, 2001, during normal flow (**a**) and on May 15, 2001, during a high flow event (**b**) and from the River Thames (Wallingford, Oxfordshire, UK) on April 25, 2001 (**c**).

The characteristics of the water and suspended sediment

Table 5. Sample characteristics and sorption distribution coefficients (K_d) for estradiol (E_2) and ethinylestradiol (EE_2) with suspended sediments

		Water characteristics			Suspended sediment characteristics					E_2 sorption				EE_2 sorption			
ID[a]	Sampling date	Flow (m^3/s)[b]	pH	DOC[c] (mg/L)	Load (mg/L)[d]	Surface area (m^2/g)	Chloro-phyll-*a* (μg/L)	POC[e]	C:N ratio	K_d (L/kg)	(SE)[f]	K_{oc}[g] (L/kg)	Estimated removal by suspended sediment[h]	K_d (L/kg)	(SE)	K_{oc} (L/kg)	Estimated removal by suspended sediment[h]
AiR	Dec 99	67	7.5	5.3	15	12.6	0.7	7.6%	ND[i]	50	(1.3)	658	0.07%	80	(1.3)	1,053	0.12%
	Mar 00	9.0	8.2	3.1	8.0	8.6	3.2	9.9%	5.4	21	(1.4)	212	0.02%	19	(1.1)	192	0.02%
AiB	Dec 99	137	7.3	5.8	52	8.6	2	7.6%	ND	122	(2.7)	1,605	0.6%	165	(5.8)	2,171	0.9%
	Mar 00	15	7.6	6.5	12	6.5	7.9	10.7%	5.7	75	(2.7)	701	0.09%	177	(2.5)	1,654	0.21%
CaB	Dec 99	28	7.1	4.5	25	8.2	0.6	6.9%	ND	64	(3.9)	928	0.16%	80	(3.4)	1,159	0.20%
	Mar 00	4.0	7.8	3.2	7.6	6.4	2.5	10.5%	5.8	159	(7.2)	1,514	0.12%	164	(8.5)	1,562	0.12%
CaM	Dec 99	65	7.4	5.8	36	9.7	1.3	10.2%	ND	44	(1.6)	431	0.16%	107	(5.4)	1,049	0.4%
	Mar 00	12	7.6	6.0	10	5.8	6.5	8.8%	7.5	113	(4.0)	1,284	0.11%	260	(3.7)	2,955	0.3%
CaS	05/14/01	17	7.9	9.2	14	5.5	ND	14.3%	ND	ND	ND	ND	ND	262	(3.9)	1,832	0.4%
	05/15/01	22	7.5	8.6	40	5.4	ND	14.2%	ND	ND	ND	ND	ND	155	(3.6)	1,083	0.6%
ThW	Dec 99	38	8.1	4.3	22	14.9	1.9	6.7%	ND	38	(1.9)	567	0.08%	65	(1.1)	970	0.14%
	Mar 00	30	8.1	2.9	8.0	10.1	27.6	7.0%	8.0	113	(2.3)	1,614	0.09%	87	(3.8)	1,243	0.07%
	Apr 01	90	ND	ND	19	10.9	ND	8.2%	ND	ND	ND	ND	ND	117	(2.6)		0.2%

[a] Identification code. For description of the sites, see Table 1.
[b] Average daily flow registered by gauging station nearest to river reach. At Aire Beal and Calder Methley Bridge a gauging station is close by. For Aire Riddlesden, the values are for Lemonroyd Weir gauging station (~40 km upstream of Riddlesden, NGR SE 382 282), for Calder Brighouse—Elland gauging station (c.a. 5 km upstream of Brighouse, NGR SE 106 213) and for Thames Wallingford—Reading gauging station (c.a. 30 km downstream of Wallingford, NGR SU 718 741).
[c] DOC = dissolved organic carbon.
[d] Ambient suspended sediment loads. The K_d values were determined at higher suspended sediment loads (0.9–23 g/L).
[e] POC = Particulate organic carbon.
[f] Standard error of the slope (i.e., of K_d).
[g] Organic carbon normalized distribution coefficient.
[h] Calculated amount for ambient concentrations of suspended sediments.
[i] ND = not determined.

samples are shown in Table 5. The River Thames showed higher surface area and chlorophyll than the other rivers in spring that may be related to a higher algal population. The relatively poor algal production in the urban/industrial reaches of the Yorkshire rivers has been noted previously [34].

Many factors could influence the suspended sediment quality, such as intensity of rainfall, change in land use, and inputs from STWs and industrial sources [35]. The hydrophobicity of the organic matter [36], as measured by the C:N ratio has been suggested to be particularly important in this respect. A higher C:N ratio is associated with greater hydrophobicity of the organic carbon in the sediment and, therefore, with a larger capacity to bind hydrophobic molecules, but it is not possible to confirm that based on our spring 2000 samples only. No clear correlations could be found between the K_d values of the suspended sediments and the river and sample parameters measured (Table 5). As noted previously with the bed sediments, generally higher K_d values were obtained with EE_2 than with E_2; however, this was less clear for suspended sediments, with some samples showing even lower K_d values for EE_2 than for E_2. Overall, suspended sediments would, in most cases, remove less than 1% from the water column (Table 5).

CONCLUSIONS

This study has demonstrated the potential for E_2 and EE_2 to sorb to sediments in a range of English rivers. Sorption of E_1 has not been measured in the present study, but given its similar characteristics, E_1 is expected to bind to sediments to a similar extent as E_2. Regression analysis indicated that sorption to bed sediments was most closely associated with particle size. Although the K_d values for suspended sediments tended to be higher than those for bed sediments, they are not likely, given the ambient concentrations of suspended sediments, to be important in reducing the water concentration. From the environmental point of view, the removal of a proportion of the steroid estrogens from the water phase and onto sediments, where they are consumed by the resident microorganisms, could be considered a benefit. We know that E_2 and E_1 have a short half-life under aerobic conditions in river water [25]. It has been found that E_2 is particularly susceptible to biodegradation under both aerobic and anaerobic conditions in bed sediment and, so, would be unlikely to accumulate. A short-duration microcosm experiment suggested that E_1 might persist in anaerobic sediments [25]. Whether EE_2, which is more resistant to biodegradation, may be preserved, at least to a limited extent, and remain bioavailable has still to be established. The potential for E_1 and EE_2 to bind and persist in natural bed sediments should receive further attention.

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