The fate of steroid estrogens: partitioning during wastewater treatment and onto river sediments

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Abstract

The partitioning of steroid estrogens in wastewater treatment and receiving waters is likely to influence their discharge to, and persistence in, the environment. This study investigated the partitioning behaviour of steroid estrogens in both laboratory and field studies. Partitioning onto activated sludge from laboratory-scale Husmann units was rapid with equilibrium achieved after 1 hour. Sorption isotherms and Kd values decreased in the order 17α-ethinyl estradiol (EE2) > 17α-estradiol (E2) > estrone (E1) > estriol (E3) without a sorption limit being achieved ($1/n>1$). Samples from a wastewater treatment works indicated no accumulation of steroid estrogens in solids from primary or secondary biological treatment, however, a range of steroid estrogens were identified in sediment samples from the River Thames. This would indicate that partitioning in the environment may play a role in the long term fate of estrogens, with an indication that they will be recalcitrant in anaerobic conditions.

Keywords: Steroid; Sewage; Sediment; Activated sludge; Partitioning

Introduction

A wide range of organic micropollutants enter sewage treatment works (STWs) (Bedding et al. 1982) and some of these posses endocrine disrupting properties, in particular the steroid estrogens (Koh et al. 2008) and the alkylphenol polyethoxylates (Chiu et al. 2009) and their breakdown products particularly nonylphenol (Soares et al. 2008). Investigations into the fate and behaviour of steroid estrogens in wastewater treatment processes are difficult due to the low concentrations at which they are present and the problems associated with analysis in such complex matrices containing co-extractives (Buisson et al. 1984; Robertson and Lester 1994; Schafer et al. 2003; Koh et al. 2008). The steroid estrogens are the most potent of these compounds (Jobling et al. 1998) and also the most abundant (Koh et al. 2009). They can cause adverse effects on the sexual and reproductive systems in wildlife, fish and humans (Purdom et al. 1994; Jobling et al 2008, Martin et al. 2008). As a consequence of these effects considerable effort has been expended to develop reliable analytical methodologies for the synthetic and natural steroid estrogens in wastewater matrices (Gomes et al. 2004a; Gomes 2005; Koh et al. 2007).

Inter-site variation in operational parameters, influent characteristics and geographical location coupled with different analytical methodologies, can result in varying removal rates for steroids estrogens. In a study of 20 sewage treatment works (STWs) in Sweden, removal efficiencies of estrogenic activity using a yeast based assay ranged from nearly 0% to >99% (Svenson et al. 2003). In the UK, results from five STWs using the same assay observed removal rates of 70% and above (Kirk et al. 2002). Whilst another study in the UK at two works one of which was examined in winter and summer gave removals of > 90% (Koh et al. 2009).

Estrogens are discharged to sewer from human sources in the conjugated form as either gluconorides or sulphates (Koh et al. 2008). The gluconorides are usually totally deconjugated in the sewerage system, however, the sulphate conjugates are more persistent and often only deconjugate in the STWs, an essential precursor to biodegradation (Gomes et al. 2009). Whilst significant reductions in their concentrations occur during wastewater treatment secondary biological treatment as presently configured, cannot afford adequate protection of the aquatic environment (Langford and Lester 2002; Jones et al. 2007a; Koh et al. 2008). Consequently sewage effluent discharges are major sources of steroid estrogens to the aquatic environment. Tertiary treatment technologies have been proposed as a future solution to these problems (Environment Agency 2002) and Granular Activated Carbon (GAC) has been demonstrated as a potentially effective treatment technology (Ifelebuegu et al. 2006; UKWIR 2009). However, if modifications to existing biological treatment plants could achieve lower residual estrogen concentrations this would

be a much more environmentally sustainable solution and therefore preferable as they would minimise both capital and operating costs (Jones et al. 2007a) and energy demand (Koh et al. 2009).

Physical factors such as pH, temperature, loading and dissolved oxygen (DO) may all influence biodegradation by affecting bacterial growth. Most activated sludge plants (ASPs) operate at a neutral pH, however, pH can influence the bioavailability of contaminants by changing solubility and sorption potential, as well as microbial growth (Gray 2004). Adsorption is important, as it is a precursor to biodegradation, which can occur by intra- or extra-cellular enzymes. Temperature influences the activity of the microbial community and metabolic pathways, a reduction in temperature can reduce the effluent quality as the metabolic rate of the organisms slows. During winter months in the UK, operating temperatures in biological wastewater treatment may be as low as $7.5^{o}C$ (Stephenson et al. 1983; Hunter et al. 1985), this is likely to have detrimental effects on micropollutant compound removal and nitrification can be inhibited, although solids and BOD removal are only slightly affected. At varying temperatures no differences in the first order rate constant for removal of 17α-ethinyl estradiol (EE2) was observed, however, that for 17α-estradiol (E2) demonstrated significant differences, although it was rapidly removed by biosolids even at lower temperatures (Layton et al. 2000). In addition the deconjugation of estrone-3-sulphate (E1-3S) under winter conditions can be adversely impacted by lower temperatures (Koh et al. 2009). The loading of the steroid estrogen compounds maybe critical in determining the degree of biodegradation. The absolute value (Stoveland et al. 1979a) whether constant or variable (Stoveland et al. 1979b) and the concentration of compound per kg of biomass per day (Koh et al. 2009, McAdam et al. submitted) are all important in determining the ultimate final effluent value.

As steroid estrogens are present at low ng l^{-1} concentrations in wastewaters, biological degradation is likely to be due to either a minority of bacteria which do not utilize compounds at higher concentrations as they are out competed or more probably co-metabolism (Ternes et al. 2004). However, organisms sometimes referred to as 'K strategists' with high substrate affinity (i.e. low Monod half saturation coefficient) and low growth rate (i.e. low μ_{max}) can very efficiently utilise low levels of resource and may therefore play an important role in the removal of micropollutants at low ng l^{-1} concentrations (Graham and Curtis 2003). The presence of hypothetical scavenging K strategists is also consistent with other observations that high loading rates can inhibit the degradation of endocrine disrupters (Joss et al. 2004; Koh et al. 2008), as in the presence of other more readily degradable substrates the organisms might switch to these. Activated sludge contains microbial species capable of degrading natural and synthetic compounds (Arcand-Hoy et al. 1998). Anthropogenic compounds such as EE2 are more resistant, as the majority of organisms lack the

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enzymes necessary to transform such compounds. A study of mass balances of steroids at a German STWs demonstrated that most of the estrogenic activity in the wastewater was biodegraded during treatment rather than adsorbed onto suspended solids. There was a 90% reduction in estrogenic load and less than 3% of the initial estrogenic activity was found in the sludge (Körner et al. 2000). Mineralisation of steroids present in biosolids has been observed, although removal for 14C-EE2 was less than 14C-E2 (20% and 75%, respectively) confirming that the ethinyl group plays a role in inhibiting degradation (Layton et al. 2000).

With the exception of the hydrophilic estriol (E3) and conjugated estrogens, partitioning to the solid phase is though to be important in determining the fate of steroids (Williams et al. 1999; Lai et al. 2000). Suspended solids have been shown to be an important factor in steroid removal, higher concentrations of suspended solids resulting in an increased removal of the more hydrophobic free steroids (Koh et al. 2008). The presence of other hydrophobic organic contaminants in the STWs is likely to influence the amount of steroids sorbed to the solids as a result of competition for binding sites (Lai et al. 2000). It has been suggested that up to 20% of compounds in sewage effluent may be bound to particulates (Johnson et al. 2000).

Studies in the UK, USA, Germany, Sweden and Spain have all observed varying concentrations of estrone (E1), E2 and EE2 in effluent from STWs (Koh et al. 2008). In the aquatic environment these compounds are amenable to biotransformation (Lai et al. 2002a), although they also demonstrate bioaccumulation (Gomes et al. 2004b) and as a consequence of this behaviour, complex issues for environmental health arise (Lai et al. 2002c; b). Sediments may become both a sink and a source for contaminants and thus an understanding of the potential for steroid estrogens to become deposited in sediments is important in understanding their environmental impact (Dowson et al. 1993; Scrimshaw and Lester 1997; Braga et al. 2000; Scrimshaw et al. 2005; Jones et al. 2006).

The objective of this study was to evaluate the significance of sorption in the removal of steroid estrogens, E1, E2, EE2 and E3, and to subsequently determine how the fate of steroid estrogens discharged to receiving waters is influenced by sorption to solids.

Experimental

Husmann laboratory scale activated sludge simulations were operated at a temperature of $17\pm1^{o}C$ and a sludge age of 5.0 days with a DO content of 3.5 mg l^{-1} and pH of 7.1. Other parameters were varied as follows; steroid concentrations added (650, 1150, 1850, 2300, 4000 ng l^{-1}) and mixed liquor suspended solids (MLSS) concentrations were varied (2900; 4000; 5000; 8300; 11900; 14300

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mg l^{-1}). To obtain these experimental concentrations, MLSS (4000 mg l^{-1}) was centrifuged at 3 000 g for 10 minutes and aliquots of the solids obtained were mixed with effluent from the Husmann plant to obtain the higher MLSS concentrations. For the lower MLSS concentrations, effluent was added to dilute the solids in the MLSS liquor. Thus the influence of MLSS solids on steroid behaviour was assessed with all samples containing the same microbial consortium, which would not have been the case had the range of MLSS concentrations been obtained by varying sludge age. The construction and operation of the Husmann units was as described in (Stoveland and Lester 1979a; 1980), the composition of the synthetic settled sewage has been reported previously (Langford et al. 2007).

Sediments and sludges were prepared by sieving (2 mm mesh), then dried at room temperature and ground to a powder. Extraction of 5 g dried sediment or 0.5 g dried sludge was undertaken with 10 ml of hexane/acetone (1:1) in 25 ml Teflon tubes, on a rotary shaker (IKA-Vibramax-VXR, VWR Lutterworth, UK) for 1 hour. This was followed by a clean up using gel permeation chromatography and quantification by LC/MS (Gomes et al. 2004a).

Partitioning Studies
All partitioning experiments were carried out in 250 ml Teflon bottles containing 200 ml of activated sludge (AS) obtained from the aeration chamber of the Husmann unit. Autoclaving at 121°C for 20 minutes was used to achieve abiotic conditions and allow investigation into partitioning processes without interference from biodegradation. Samples were spiked with concentrations of steroids while blanks were inoculated with the respective solvents. Duplicate samples were then taken at intervals. The sorption or distribution coefficient (Kd) denotes the ratio of the substrate's total equilibrium concentrations in the solids (C_S) to that in the aqueous matrix (C_W), irrespective of the organic matter content of the sorbent (Eq. 1). The higher the sorption coefficient, the more likely the chemical is to bind to the solid phase rather than remain in the aqueous environment.

$$Kd = \frac{C_S}{C_W}$$
Eq. 1

When estimating Kd values from experimental data, depending on the concentration range, choices must be made with respect to the selection of data points as well as with respect to the type of isotherm used to fit the data (Schwarzenbach et al. 2003). Using experimentally determined

sorption data allows for derivation of an empirical relationship, the Freundlich isotherm, where (K_f) and ($1/n$) are the sorption coefficient and sorption constant, respectively (Eq. 2).

$$\log C_S = \log K_f + \frac{1}{n}\log C_W$$

Eq. 2

The treatment works studied was located in the South East of the UK consisting of an ASP operating with nitrifying and denitrifying zones, a hydraulic retention time of 13.6 hours and solid retention time (sludge age) of 13 days. Sampling points for the study are identified in Fig. 1 focusing on the crude sewage and then across the ASP; settled sewage, final effluent and waste activated sludge. The ASP treats approximately 30% of the total flow entering the works, with the remaining portion passing through trickling filters. The sampling was undertaken during June 2004 with an average ambient temperature of 20.6°C (range during 96 hour study 17.5-23.2 °C). No rainfall occurred prior to or during the sampling period. The operation of the plant and the sampling protocol has been described previously (Koh et al. 2005; Jones et al. 2007b).
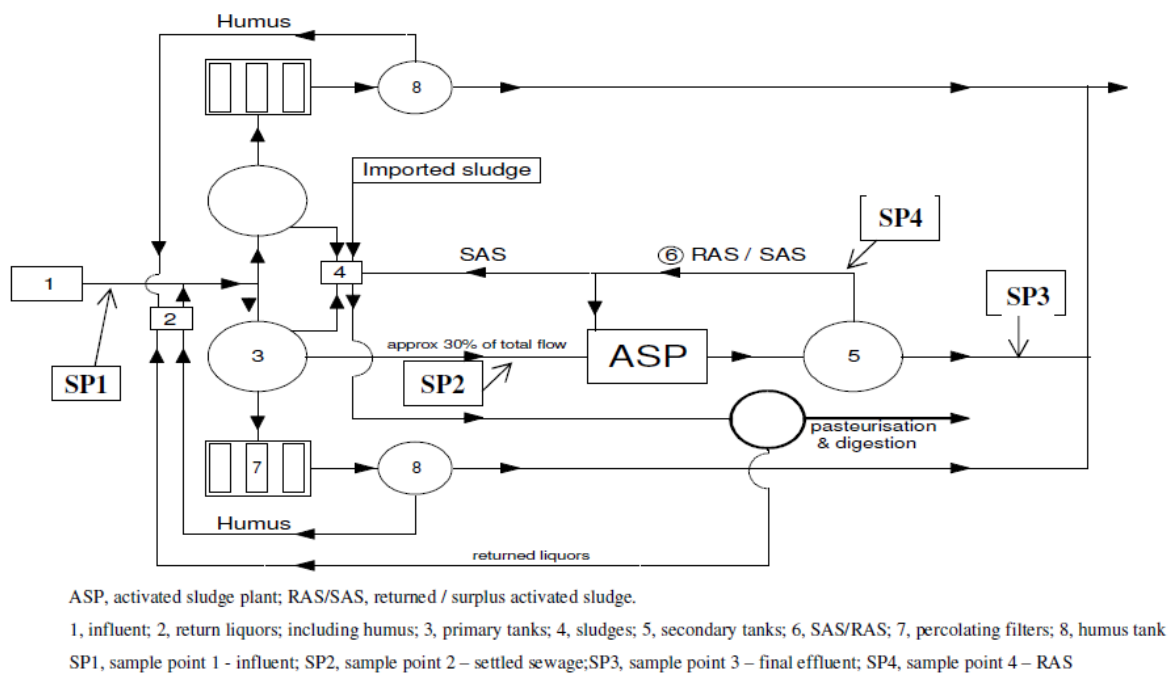

ASP, activated sludge plant; RAS/SAS, returned / surplus activated sludge.

1, influent; 2, return liquors; including humus; 3, primary tanks; 4, sludges; 5, secondary tanks; 6, SAS/RAS; 7, percolating filters; 8, humus tank
SP1, sample point 1 - influent; SP2, sample point 2 – settled sewage; SP3, sample point 3 – final effluent; SP4, sample point 4 – RAS

Fig. 1 Schematic of the sewage treatment works

Concentrations in sediments

In 1994, samples of bed sediments were cored from the Tidal Basin at Tilbury Docks, London, UK. These docks were built in the 1880s, 42 km downstream of London Bridge, on the Gravesend Reach of the River Thames. The sediment had accumulated undisturbed from 1962 during the

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period when significant improvements were made to the nearby Becton and Crossness STWs between 1963 and 1974 and records of dredging, accumulation patterns and soundings charts allow for the sediment core to be dated. The core has been extensively characterized for a range of environmental contaminants and sampling, storage and chemical characteristics have been described previously (Taylor and Lester 1995; O'Reilly-Wiese et al. 1997a; O'Reilly-Wiese et al. 1997b; Scrimshaw and Lester 1997; Scrimshaw et al. 2005). Frozen sediment samples ($-18^{o}C$) were defrosted in the fridge at $4^{o}C$ and then tipped into boats to allow the sample to air dry. The dried solids were homogenised and ground down to fine particles and 5 g were processed and analysed by LC/MS (Gomes et al. 2004a).

Results

Establishing sorption equilibrium

Samples of Husmann activated sludge (200 ml at SRT 5 days with MLSS content of 4000 mg l^{-1}) were autoclaved to achieve abiotic conditions and then allowed to cool. These were then individually inoculated with approximately 2000 ng l^{-1} of each of the four free steroids and left for 4 hours to establish the time necessary to achieve equilibrium (Fig. 2). Apparent equilibrium was reached after 1 hour with concentrations remaining unchanged for the following 3 hours (0.38-0.65% variation). Since removal did not increase after 1 hour, the results of subsequent experiments conducted for 2 hours are assumed to reflect maximum steroid sorption. Steroid sorption to the AS after 2 hours was $27.3 \pm 2.0\%$, $43.9 \pm 1.8\%$, $40.7 \pm 1.4\%$ and $50.0 \pm 2.3\%$ for E3, E2, E1 and EE2. As partitioning to AS solids at 2 hours favoured EE2 > E2 > E1 > E3, this was compared to the log K_{ow} of each steroid resulting in a strong correlation of $r^2 = 0.949$ inferring that log K_{ow} is an accurate predictor of sorption capability.

3.2 The influence of mixed liquor suspended solids concentration on partitioning

Various MLSS concentrations were utilised to investigate the relationship between partitioning and the solid content of the AS after 2 hours. To ensure the bacterial consortium did not influence any outcome, MLSS concentrations were all prepared from MLSS of SRT = 5 days (4000 mg l^{-1}). As the MLSS concentration increased there was an increase in steroid removal from the aqueous phase with a correlation of $r^2 >0.972$. At the highest MLSS concentration, sorption to the solid phase was 50.6%, 78.7%, 83.3% and 85.1% for E3, E1, E2 and EE2, respectively. Being more hydrophobic, EE2, E2 and E1 accumulated onto the solids more rapidly and in a similar manner than E3.
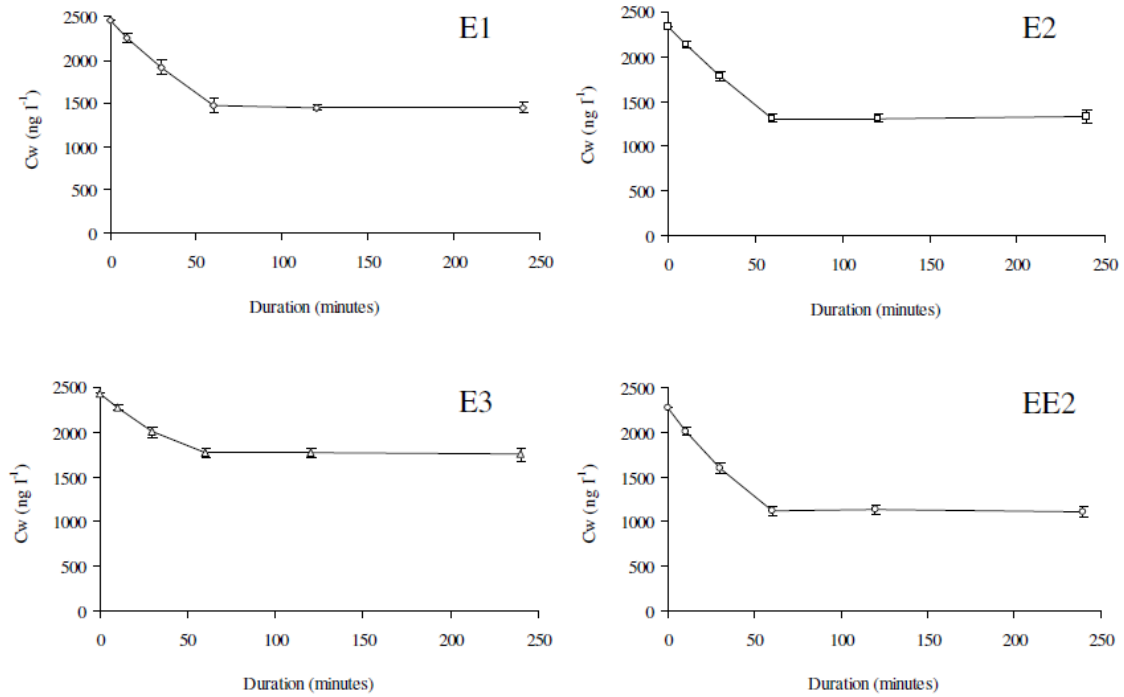
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Fig. 2   Duration to achieve sorption equilibrium for the free steroids in activated sludge

Assessment of sorption isotherms

The adsorption behaviour was assessed by both the sorption or distribution coefficient (Kd) using Eq. 1 and the Freundlich isotherm calculated from Eq. 2. In the case of a linear isotherm when the sorption constant $1/n$ corresponds to 1, the sorption coefficient from the Freundlich adsorption isotherm (K_f) equates to the Kd value. The graphical representation of the Freundlich isotherm for estrone is given in Fig. 3.
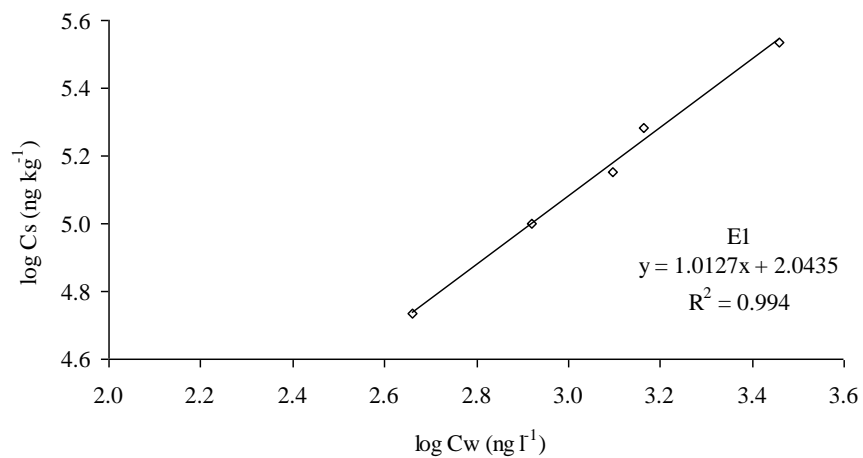

Fig. 3   Freundlich isotherm for estrone

The adsorption constant ($1/n$) was greater than 1 for each steroid and the concentration range utilised ($650 - 4000$ ng l^{-1}) resulted in a linear isotherm as only a limited amount of the sorption capacity was utilised. A summary of the sorption coefficients Kd and Kf is given in Table 1 and all correlations were >0.96. The relationship between log Kd and log K$_{ow}$ demonstrated a weaker correlation ($r^2 = 0.8385$) whilst for the neutral steroids only (E1, E2 and EE2), the correlation increased ($r^2 = 0.923$). When the sorbed fractions of the steroids are assessed against log K$_{ow}$ the correlation between the two is improved.

Fate and behaviour during wastewater treatment

The treatment works received predominately municipal wastewater and the estrogens were identified in the crude sewage samples with E3 proving the most abundant at 67.3 ± 3.3 ng l^{-1}. Estrone and E2 were also observed at 21.1 ± 0.2 ng l^{-1} and 42.6 ± 18.4 ng l^{-1} respectively. The conjugate, E1-3S was detected at 12.7 ± 2.3 ng l^{-1} and its presence was most probably due to the recalcitrant nature of the sulphate moiety. Upon complete deconjugation, this would release 9.8 ng l^{-1} of E1 into the waste stream. Transit in the sewerage system prior to entering to the STW is typically 10-13 hours but at low summer flows, the retention in the sewers can reach over 14 hours which would provide additional exposure and hence opportunity for deconjugation. No EE2, either in the free or conjugated forms were detected in any samples.

Table 1   Sorption coefficients for the free steroids in Husmann activated sludge

Steroid	Distribution Coefficient			Freundlich Isotherm		
	Log Kd	Kd (l kg^{-1})	r^2	Kf	n	r^2
E3	2.02 ± 0.05	106.4 ± 12.6	0.9682	95.5	0.99	0.9698
E2	2.26 ± 0.03	182.7 ± 11.9	0.9934	141.3	0.96	0.9932
E1	2.08 ± 0.02	121.1 ± 6.7	0.9928	109.7	0.99	0.9940
EE2	2.45 ± 0.03	280.6 ± 21.7	0.9805	234.5	0.97	0.9887

In the settled sewage entering the ASP, only E1 was identified, in two instances at 3.0 ng l^{-1} and 2.1 ng l^{-1}. No other steroids were detected following primary or biological treatment (in the final effluent), probably as they were present at below limits of detection which ranged from 1.3-5 ng l^{-1}. As no steroids were detected in solids from primary or biological settling this would, however, indicate that the estrogens are not removed by sorption processes.

Concentrations in sediments

Sediment samples used for the analysis were part of a sediment core which was collected from Tilbury Basin in 1994 and subsequently frozen for storage. The location of the coring site was fixed in such a way that there was a correlation of sediment depth with dates from historical sounding (depth) charts (Scrimshaw and Lester 1997). Table 2 shows the distribution of steroid estrogens in the core sediments. Results illustrate that E1 was the most frequently detected estrogen (50% of the samples), possibly a result of transformation of E2 during sample drying. In comparison, E2, E3 and EE2 were detected infrequently. There is an indication of higher concentrations of E1 and E3 in samples deemed to be deposited before the mid-1960's, prior to the introduction of biological treatment at STWs discharging to the estuary (O'Reilly-Wiese et al. 1997a; O'Reilly-Wiese et al. 1997b; Scrimshaw and Lester 1997). No EE2 was detected in the lower parts of the core which would date from before the contraceptive pill was introduced, although it is detected in the upper samples, which date from post the mid 1960's.

Discussion

Partitioning equilibrium for the free steroids was achieved in the first hour, and these values remained stable for the following 3 hours. This correlates to adsorption processes as opposed to absorption which requires increased contact to allow partitioning into the cell. Equilibration has also been demonstrated to be a rapid process in other studies that have evaluated steroid adsorption in sediments and sludge solids (Lai et al. 2000; Ying et al. 2003; Joss et al. 2004). Though desorption was not observed within these batch studies this may be attributed to the timeframe being limited to four hours as periods in excess of five hours have demonstrated desorption of the steroid from the solid phase (Jurgens et al. 1999; Lai et al. 2000).

When the impact of MLSS concentration on partitioning was assessed, a positive correlation between MLSS concentrations and removal from the aqueous phase of the AS was observed. Preference to the solid phase was greatest for EE2 > E2 > E1 > E3 and the percentage of steroid sorbed to the MLSS correlated to the log K_{ow}. Freundlich isotherm data demonstrates that sorption did not approach a limit ($1/n > 1$) after two hours. When $n = 0.6 - 1$, this indicates that there is an

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Table 2   Concentrations (ng g^{-1}) of estrogens in the sediment core

Depth below OD (cm)	E1	E2	E3	EE2	Timeline
73-82	7.3	7.2			Constantly reworked through
102-112				17.8	tidal and storm activity
112-122	7.6				
141-151					Post 1980
337-347					
376-386			2.2		
416-425	3.2				
455-465		1.0			
494-504	4.7		1.5		
533-543					
572-582	5.7			1.8	Post January 1966
621-631	206.4		30.8	10.1	Pre January 1966
651-661	12.4				
690-700					
739-749	8.9				
778-788	15.2				
817-827					
857-866					
896-906	19.7				
935-945			60.9		Clay below 955

A blank space indicates < 0.1 ng g^{-1}

increase in the partitioning coefficient as concentration decrease, thus the Freundlich equation may be considered a more realistic description of sorption behaviour than the distribution coefficient (Wauchope and Russell 2002). The evaluation of partitioning behaviour in autoclaved AS ensured that only physical (rather than biologically mediated uptake) adsorption processes were assessed, although other data indicated no differences between inactivated and activated sludge (Clara et al. 2004).

The distribution coefficients (Kd) were between 106 - 280 for the four steroids. The Kd values obtained in this study are in the same range as others reported in the literature (Williams et al. 2001; Bowman et al. 2002; Holthaus et al. 2002). Correlation of log K_{ow} with log Kd, indicated that the

hydrophobic nature of the steroids is not a good predictor of sorptive behaviour. The correlation improved when E3 was ignored illustrating that the log K_{ow} is not a useful tool in assessing the distribution coefficient between the solid and aqueous phases of Husmann activated sludge for E3. This is due to the polar nature of E3 decreasing the ability of log K_{ow} to predict log Kd, and this has been observed for other polar compounds (Goss and Schwarzenbach 2001). Sorption in STWs can be predicted by the use of the distribution coefficient (Schwarzenbach et al. 2003) and for substances with log Kd values > 4, sorption to the sludge is a major removal process (Clara et al. 2004). This is not the case for E1, E2, E3 and EE2 with log Kd values of 2.10, 2.27, 2.03 and 2.45, respectively.

Partitioning to the solid phase of the Husmann AS was evaluated on an individual basis excluding degradation processes and the presence of other organic compounds. Steroids compete for sorption sites, both between themselves and with the other hydrophobic compounds present in the matrix (Lai et al. 2000), therefore a greater proportion of steroids will remain in the aqueous phase and the degree of sorption exhibited in the batch studies may be an overestimation of what may occur *in situ*.

In the field study no steroids were detected in any of the solids (settled or suspended) which may be a consequence of the detection limits determined for this study, as E1, E2 and EE2 have been identified at low ng g^{-1} in sewage sludges (Ternes et al. 2002; Joss et al. 2004). A low sorption potential was deduced from the batch studies and competition from compounds with preferential binding to the solid phase will also occur (Lai et al. 2000), however, the relationship between K_{oc} and predicted binding has also been investigated in environmental matrices, where it is also apparent that factors other than organic carbon play a role in the sorption process (Bowman et al. 2002).

In the sediment core taken from the Tilbury Basin a reduction in steroid deposition to the sediment phase was observed which may be linked to the introduction of biological treatment in nearby STWs (Becton and Crossness) during the 1960's. This provides indirect evidence that historical improvements to wastewater treatment have resulted in a decrease in the concentrations of steroids in the effluent, as observed for PCBs and DDT from the same core (Scrimshaw and Lester 1997). The detection of EE2 in samples from the upper part of the core adds evidence to support the dating technique used. The predominant steroid detected was E1, most probably as a result of conversion from E2, and it is known that in the analytical method used, air drying did result in some conversion of E2 to E1 (Gomes et al. 2004a), it is not possible to determine if transformation had already

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occurred *in situ* or was solely a result of sample handling. E3 was also identified at concentrations up to 60 ng g^{-1}. A reduction in steroid deposition to the sediment phase was observed during the 1960s which correlated to the introduction of biological treatment to nearby STWs and is indicative of the effectiveness of biological treatment in reducing concentrations of steroid estrogens.

Estrogens, both E1 and E2, have been observed in sediments at concentrations of up to $20 - 30$ ng g^{-1}, and at depths relating to over 100 years of sedimentation, although migration was attributed to their presence at depth at this location (Labadie et al. 2007). In the core from Tilbury, accumulation was relatively rapid, and the presence of contaminants is deemed to reflect historic inputs. It is possible, using the Freundlich isotherm (Eq. 2) and values for log Kd (1.72) and 1/n (0.83) from (Lai et al. 2000), to make a first estimate of the aqueous concentration of EE2 that would have been present to result in sediment concentrations of 17.8 ng g^{-1}, at $102 - 112$ cm. This results in a calculated aqueous concentration, corrected for 90 mg l^{-1} suspended sediment load typical of the Tilbury area (Trimmer et al. 2000) of 0.024 ng l^{-1} EE2 in the estuary. Recent, reported values from accredited analysis, of concentrations of steroid estrogens in effluents from UK treatment works indicate that EE2 is likely to be present at concentrations of around 1 ng l^{-1}, (Huo and Hickey 2007; Kanda and Churchley 2008) and aqueous concentrations in a receiving water of the order calculated would, therefore, seem realistic, supporting the validity of the occurrence of EE2 in the sediments at 17.8 ng g^{-1}.

The presence of estrogens in sediments after a period of three decades indicates that the sediments could become a potential source of these compounds to the overlying surface waters. Whilst secondary biological treatment of wastewater significantly reduces the concentration of some of these compounds, as presently configured and operated, these processes cannot afford adequate protection of the aquatic environment (Langford and Lester 2002; Chiu et al. 2008; Koh et al. 2008).

5. Conclusions

Sorption to sewage sludge was a rapid process, with apparent equilibrium reached within one hour. The role of sorption processes in the removal of the steroid estrogens during wastewater treatment are, however, likely to be less significant than for more hydrophobic compounds, although in receiving waters, it is likely that partitioning to suspended solids will result in deposition to bed sediments. There is evidence that once steroid estrogens are deposited into bed sediments, residues are likely to persist under anaerobic conditions.

Acknowledgements

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