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Sorption, Mobility, and Transformation of Estrogenic Hormones in Natural Soil

Francis X. M. Casey,* Jiří Šimůnek, Jaehoon Lee, Gerald L. Larsen, and Heldur Hakk

ABSTRACT

Potent estrogenic hormones are consistently detected in the environment at low concentration, yet these chemicals are strongly sorbed to soil and are labile. The objective of this research was to improve the understanding of the processes of sorption, mobility, and transformation for estrogens in natural soils, and their interaction. Equilibrium and kinetic batch sorption experiments, and a long-term column study were used to study the fate and transport of 17β-estradiol and its primary metabolite, estrone, in natural soil. Kinetic and equilibrium batch experiments were done using radiolabeled 17β-estradiol and estrone. At the concentrations used, it appeared that equilibrium sorption for both estrogens was achieved between 5 and 24 h, and that the equilibrium sorption isotherms were linear. The log K_{oc} values for 17β-estradiol (2.94) and estrone (2.99) were consistent with previously reported values. Additionally, it was found that there was rate-limited sorption for both 17β-estradiol (0.178 h^{-1}) and estrone (0.210 h^{-1}). An approximately 42 h long, steady-flow, saturated column experiment was used to study the transport of radiolabeled 17β-estradiol, which was applied in a 5.00 mg L^{-1} solution pulse for 44 pore volumes. 17β-estradiol and estrone were the predominant compounds detected in the effluent. The effluent breakthrough curves were asymmetric and the transport modeling indicated that sorption was rate-limited. Sorption rates and distributions of the estrogens were in agreement between column and batch experiments. This research can provide a better link between the laboratory results and observations in the natural environment.

Animal manures are typically managed for their nutrient content and applied to field soil accordingly. Manures can contain hormones, which have the potential to contaminate soils as well as surface and subsurface waters. With their extensive reconnaissance of U.S. surface freshwaters, Kolpin et al. (2002) showed a potential connection between animal feedlot operations and the presence of pharmaceuticals and hormones in surface waters. Soto et al. (2004) have shown that runoff from concentrated feedlot operations can enter surface waters and result in hormone concentrations that could adversely affect aquatic health. The potency and potential for widespread contamination are the major concerns regarding hormones in the environment. Some studies have shown that 17β-estradiol concentrations of <1 to 7 ng L^{-1} can significantly increase vitellogenin production in female painted turtles (*Chrysemys picta*) when exposed for durations of 28 d (Irwin et al., 2001). Also, vitellogen production, which is only normal for females, has been induced in male fathead minnows (*Pimephales promelas*) exposed to 17β-estradiol for 21 d at concentrations as low as 30 ng L^{-1} (Panter et al., 2000).

Recent batch (Lee et al., 2003) and column studies (Das et al., 2004; Casey et al., 2003, 2004) have found that hormones have short half-lives and a high affinity for sorption in natural soils. However, definitive mechanisms of hormone sorption and transformation in soil are still not fully understood. A better understanding of these mechanisms and their interaction is necessary for explaining why these hormones are consistently detected in natural aquatic systems (e.g., Kolpin et al., 2002; Gentili et al., 2002; Kuch and Ballschmitter, 2001), albeit in small concentrations. The objective of this research was to improve the understanding of the processes of sorption, mobility, and transformation for estrogens in natural soils, and their interaction, using improved batch and continuous flow column experiments.

MATERIALS AND METHODS

Experimental procedures were similar to those described by Casey et al. (2003, 2004). Radiolabeled (^{14}C) 17β-estradiol (American Radiolabeled Chemicals, St. Louis, MO) was used as an input for both the batch and column experiments, while radiolabeled estrone was only used as an input for the batch experiments. Any ^{14}C estrone detected in the column experiment was a result of ^{14}C 17β-estradiol transformation. The radiolabeled C located at the C-4 position of the A-ring is maintained in the steroidal structure when the 17β-estradiol is transformed to estrone. The soil that was used in both column and batch experiments was a LaDelle silt loam (fine-silty, mixed, superactive, frigid Cumulic Hapludolls), which was sampled from a cultivated area near Northwood, ND, by Ag-Vise Company (Northwood, ND). The LaDelle has an organic matter content of 9.2% (Nelson and Sommers, 1982), a pH of 7.9, a specific surface area of 1.51×10^5 m^2 kg^{-1} (Cihacek and Bremner, 1979), and a particle size distribution of 10% sand, 64% silt, and 26% clay (Gee and Bauder, 1986). All the physical soil properties, except specific surface, were determined at the Soil and Water Environmental Laboratory at North Dakota State University. The soil was prepared for the column and batch experiments by air drying and sieving with a 2-mm sieve.

Chemical Preparation and Analysis

Ethanol was used to initially dissolve the stock ^{14}C labeled 17β-estradiol and the estrone in a 0.001*M* $CaCl_2$ solution. The percentages of the ethanol in each batch solutions were 0.163 and 0.125% for 17β-estradiol and estrone, respectively. The percentage of ethanol in the initial concentration of the column experiment was 0.17%. All these ethanol concentrations were <0.5%, which has been shown not to affect the sorption

F.X.M. Casey, Dep. of Soil Science, North Dakota State Univ., Fargo, ND 58105; J. Šimůnek, Dep. of Environ. Sciences, Univ. of California, Riverside, CA 92521; J. Lee, Dep. of Biosystems Eng. and Environ. Sciences, Univ. of Tennessee, Knoxville, TN 37996–4531; and G.L. Larsen and H. Hakk, Animal Metabolism: Agricultural Chemicals Research, Biosciences Research Lab., USDA-ARS, Fargo, ND 58105-5674. Received 26 July 2004. *Corresponding author (francis.casey@ndsu.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: ASE, accelerated solvent extractor; CI, confidence interval; LCMS, liquid chromatography/mass spectrometer; SSQ, sum-of-squares error; TLC, thin-layer chromatography.

of an organic pollutant to soil (Wauchope and Koskinen, 1983). The initial radioactivity of the ^{14}C 17β-estradiol (specific activity = 4.21×10^{14} dpm kg^{-1}) in the batch experiments ranged from 14 230 dpm to 761 869 dpm, and the minimal radioactivity detected was 560 dpm, which was equivalent to 1.7×10^{-4} mg L^{-1}. The initial radioactivity for the ^{14}C estrone (specific activity = 4.18×10^{14} dpm kg^{-1}) in batch experiments ranged between 5536 dpm to 509 407 dpm, and the minimal radioactivity detected was 213 dpm, which was equivalent to 6.4×10^{-5} mg L^{-1}. For the column experiment, 124.3 μg ^{14}C 17β-estradiol was mixed with 8518 μg of ^{12}C 17β-estradiol in 1.73 L to create the application concentration of 5.0 mg L^{-1}. The total ^{14}C labeled 17β-estradiol (specific activity = 5.96×10^{12} dpm kg^{-1}) applied in the column experiment was 5.2×10^{7} dpm and the minimal dpm detected in the effluent was 42 dpm, which was equivalent to 4.1×10^{-6} mg L^{-1}.

Several analytical procedures were used to determine the concentrations of 17β-estradiol and its metabolites in the experiments. Liquid scintillation counting was used to analyze for total ^{14}C, and thin-layer chromatography (TLC) was used to analyze for metabolites of ^{14}C 17β-estradiol. Liquid chromatography/mass spectrometer (LCMS) was also used to analyze selected samples from the column transport experiments. Liquid scintillation counting was done using a 1900 CA Scintillation Counter (Packard, Downers Grove, IL), and TLC analysis was done using a System 2000 Imaging Scanner (Bioscan, Washington, DC). Thin-layer chromatography was conducted using silica gel plates (250 mm; Whatman Lab. Div., Clinton, NJ) and a 25:25:50 tetrahydrofuran/ethyl acetate/hexane mobile phase. A combustion analysis assay (Packard Model 307 Oxidizer; Downers Grove, IL) was also used to determine total ^{14}C sorbed to the soil.

The liquid chromatograph system of the LCMS was an Alliance 2695 Separation Model (Waters, Beverly, MA) equipped with a Symmetry C18 column (3.5 μm, 2.1 by 100 mm), a C18 guard column (2.1 by 10 mm), and a quadrupole-time of flight mass spectrometer (Waters Q-TOF Ultima API-US; Waters, Beverly, MA). A linear binary gradient pump was used, which consisted of 95/5 aqueous 7.4 m*M* NH_4OH/acetonitrile (A) and 100% acetonitrile containing 7.4 m*M* NH_4OH (B). The linear gradient that was used began with 40% B at time 0 min and increased to 100% B at 10 min. The flow rate of the mobile phase was 0.2 mL min^{-1}. The mass spectrometer analysis was performed in negative ion mode (ES−) with capillary and cone voltages of 2.33 and 55, respectively; source and desolvation temperatures of 120 and 400°C, respectively; and desolvation gas flows of 0 and 500 L h^{-1}, respectively. The LCMS sample injection volumes were always 10 μL, and 25 pg mass on column could be reliably detected using selected ion monitoring.

Batch Experiments

In 10-mL vials, 1.6 g of soil and 8 mL of 0.0l *M* $CaCl_2$ were added. The ^{14}C solution was then added to the vials to create solution concentrations of 0.0015, 0.015, 0.0825, and 0.150 mg L^{-1} for 17β-estradiol and 0.0014, 0.014, 0.076, and 0.138 mg L^{-1} for estrone. These concentrations were chosen because they span the range of concentrations reported for manures that are applied to fields (Shore et al., 1993, 1995; Finlay-Moore et al., 2000). Each batch experiment was replicated three times. The soil–water slurries were agitated by rotation of the vials top to bottom (360°/5 s). After 0.5, 1, 5, 24, and 48 h, the bottles were centrifuged at $1000 \times g$ (1700 rpm), 100 μL aliquots were removed, and the solution was analyzed using the liquid scintillation and TLC methods described earlier.

Batch Sorption Model

The aqueous concentrations (C; mg L^{-1}) of steroidal estrogens will decrease at the same time the sorbed phase concentrations (S; mg kg^{-1}) increase. The mass balance of the solute partitioning through time can be expressed with the following ordinary differential equation when sorbed phase degradation (μ_s; h^{-1}) is considered as follows:

$$V\frac{dC}{dt} = -M\left(\frac{dS}{dt} + \mu_s S\right) \quad [1]$$

In Eq. [1] there are two dependent variables, C and S, and one independent variable, t.

The following first-order expression was used as the driving force of sorption through time, as follows:

$$\frac{dS}{dt} = \alpha(K_d C - S) - \mu_s S \quad [2]$$

where α is the sorption rate coefficient (h^{-1}) and K_d (L mg^{-1}) is the linear distribution coefficient between the sorbed and aqueous phases. At equilibrium $S = K_d \times C$.

Equation [1] was solved in a spreadsheet using an Euler numeric method with a time step of 0.001 h. This solution was done by coupling Eq. [2] with the following ordinary differential equation as follows:

$$\frac{dC}{dt} = -\frac{M}{V}\alpha(K_d C - S) \quad [3]$$

A nonlinear, least-square fitting algorithm was used to fit the solution of Eq. [1] to the measured batch data. The K_dC term of Eq. [2] and [3] was fit to the 24-h equilibrium sorption data, while the time series data was simultaneously fit with the numerically calculated C values. The time series batch data were a set of measured $C(t_i)$ values at specific time increments, t_i ($i = 1,2,\ldots N$). These $C(t_i)$ values are the input data for the numerical inversion problem. The numerically calculated aqueous concentrations are represented by $\overline{C}$ (t_i, $\mathbf{b}$), which corresponds to a trial vector of parameter values $\boldsymbol{b}$, where $\boldsymbol{b}$ is the vector of optimized parameters α, K_d, and μ_s. An optimum combination of parameters $\boldsymbol{b}^o$ is then sought to minimize the following objective function:

$$E(\boldsymbol{b}) = \sum_{i=1}^{N}\{w_i[C(t_i) - \overline{C}(t_i,\boldsymbol{b})]\}^2 \quad [4]$$

where w_i is a weighting function. The Solver tool in Microsoft Excel that uses a Newton method of minimization was used to determine $\boldsymbol{b}^o$.

For all our calculations, S was determined by mass-balance difference (i.e., whatever mass of ^{14}C not present in solution was considered to be sorbed). No metabolites were detected in the aqueous phases so it was assumed that transformations took place in the sorbed phase. It was also possible that transformations took place in the aqueous phase and then quickly reabsorbed to the solid, but this was assumed not to happen. The μ_s value that we obtained from the column experiment was considered in the numerical solution of Eq. [1] to determine the affect of sorbed phase transformation on the batch K_d estimates.

Column Transport Experiments

A glass column with diameter of 0.03 m was packed with 0.047 kg of dry soil to a length of ≈0.074 m. The column was saturated from the bottom up over 24 h using a solution of 0.01 *M* $CaCl_2$. After the column was saturated, steady state flow was established through the column using the same 0.01 *M*

$CaCl_2$ solution. The steady state pore-water velocity was 0.145 m h^{-1}. Once steady state velocity was achieved a $CaCl_2$ breakthrough curve was run to characterize the transport of a nonreactive solute (i.e., Cl^-) through the column. This was done by applying a 5.16 pore volume pulse of 0.05 *M* $CaCl_2$ solution to the column, followed by the application of the 0.01 *M* $CaCl_2$ solution. The column effluent was collected in approximately 0.13 pore volume increments and analyzed using an ion-specific electrode. The 0.01 *M* $CaCl_2$ solution was applied for several pore volumes, after which a 1.721-L (44 pore volume) pulse of 5.00 mg L^{-1} 17β-estradiol in 0.01 *M* $CaCl_2$ was applied to the column, followed by 0.01 *M* $CaCl_2$ without 17β-estradiol for approximately 66 pore volumes. The effluent was collected in 0.1 pore volume increments and analyzed for total ^{14}C and metabolites using scintillation counting and TLC, respectively, with LCMS analysis on selected samples. The total duration for the 17β-estradiol breakthrough curve experiment was approximately 42 h and the total mass of ^{14}C 17β-estradiol applied to the column during this time was 8.605 mg.

When the column experiment was complete, the soil was extruded from the glass column in approximately 1-cm increments. This was done to identify the redistribution of the ^{14}C with soil depth. The soil was then analyzed for total ^{14}C using combustion analysis. Sequential solution extraction was done by eluting with toluene, ethyl acetate, and finally methanol in the cell of an accelerated solvent extractor (ASE, model 200; Dionex, Sunnyvale, CA). Liquid scintillation was done on all ASE extractions to quantify total ^{14}C. Also, TLC was used to detect any metabolites in these extractions.

Column Transport Model

The $CaCl_2$ and 17β-estradiol miscible-displacement experiments were inversely modeled using the program HYDRUS-1D version 2.0 (Šimůnek et al., 1998). This inverse model routine uses a least-squares method that minimizes an objective function, which provides a best-fit model solution to the measured transport data. The best-fit model solution to the transport data is obtained by finding the optimum combination of reaction and transport parameters. The code of HYDRUS-1D was modified to inversely model two solutes involved in a transformation chain reaction.

Two model variations, one with instantaneous sorption and the other with time dependent sorption, were used to describe the transport data. In both model variations it was assumed that the solute was transported in the aqueous phase by convection and dispersion, and that there was a first-order transformation reaction of 17β-estradiol into estrone. The following differential equations represent the convective–dispersive transport of a solute undergoing transformation (van Genuchten, 1985), and instantaneous or time-dependent sorption (Selim et al., 1977; van Genuchten and Wagenet, 1989) as follows:

$$\theta\frac{\partial C_1}{\partial t} + \rho_b\frac{\partial S_1}{\partial t} = \theta v\lambda\frac{\partial^2 C_1}{\partial x^2} - \theta v\frac{\partial C_1}{\partial x} - \mu'_{s,1}\rho_b S_1 \quad [5]$$

$$\theta\frac{\partial C_2}{\partial t} + \rho_b\frac{\partial S_2}{\partial t} = \theta v\lambda\frac{\partial^2 C_2}{\partial x^2} - \theta v\frac{\partial C_2}{\partial x} + \mu'_{s,1}\rho_b S_1 - \mu'_{s,2}\rho_b S_2 \quad [6]$$

where the subscripts 1 and 2 represent the parent solute, 17β-estradiol, and the daughter product, estrone, respectively; ρ_b is soil bulk density (kg m^{-3}), θ is the volumetric water content (m^3 m^{-3}), λ (m) is the dispersivity, v is steady state pore velocity (m h^{-1}), x is depth (m), and μ_s' is a first-order transformation rate constant in the solid phase (h^{-1}) that provides connection between parent and daughter compounds. In Eq. [5] and [6], when sorption is considered to be only instantaneous then

$$S = K_d C \quad [7]$$

When sorption is partially dependent on time, then the concept of two-site sorption is implemented, where sorption can occur instantaneously on equilibrium exchange sites (S^e) or kinetically on the remaining exchange sites (S^k) (Selim et al., 1977; van Genuchten and Wagenet, 1989). The following provides the mass balance for this two-site sorption concept:

$$S = S^e + S^k \quad [8]$$

$$S^e = fK_d C \quad [9]$$

$$\frac{\partial S^k}{\partial t} = \alpha[(1-f)K_d C - S^k] - \mu'_s S^k \quad [10]$$

where f is the fraction of sorption sites that are considered equilibrium, and α is a first-order sorption rate coefficient (h^{-1}). To model the $CaCl_2$ breakthrough, Eq. [5] was used with no transformations or sorption (i.e., $\mu'_{s1} = S_1 = 0$), and λ was estimated.

RESULTS AND DISCUSSION

Batch Results

The sorbed concentrations of 17β-estradiol and estrone were determined by mass-balance difference for the batch experiments and were not measured directly. Other studies have indicated that degradation of estrogens occurs rapidly. Colucci et al. (2001) reported high degradation values for 17β-estradiol (0.060–0.134 h^{-1}) in soil; therefore, it is possible that transformation occurs even over a short period of time. Our TLC analysis, however, indicated that no metabolites were present (or were below our detection limits) in the aqueous phase for either the 17β-estradiol or estrone batch experiments. This could have indicated that transformation occurred in the aqueous phase and the metabolite quickly reabsorbed, or that degradation occurred in the solid phase, or that there was no degradation. In a similar study, Holthaus et al. (2002) used anaerobic conditions to decrease biodegradation of ^{14}C 17β-estradiol; however, transformation of 17β-estradiol into estrone still occurred. They reported that their 17β-estradiol distribution coefficients probably reflected a combination of both estrogen species. Holthaus et al. (2002) also noted that both 17β-estradiol and estrone had very similar solubilites, which would make their sorption parameters very similar. When ^{14}C 17β-estradiol is converted into estrone the steroid ring system remains intact and the radiolabel is not lost. Thus, the 17β-estradiol K_d values of this study may reflect a mixture of 17β-estradiol and its metabolite estrone. Estrone, on the other hand, is more resistant to degradation (Colucci et al., 2001) and its K_d values likely represent the parent molecule.

Sorption Kinetics and Degradation

The slopes of the sorption isotherms of 17β-estradiol and estrone (Fig. 1a and 1b) increased through time, and aqueous concentration decreased through time (Fig. 2a and 2b). These results indicated that there was a kinetic process occurring, which may be explained by sorption

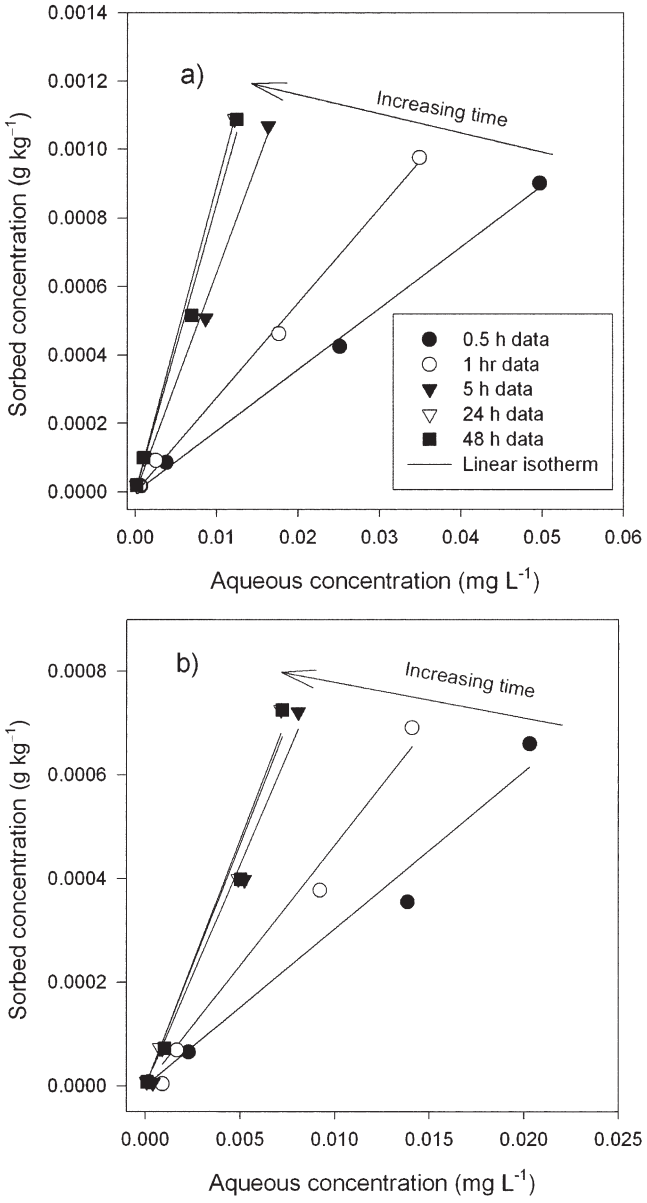

Fig. 1. Batch sorption data of sorbed vs. aqueous concentrations for (a) 17β-estradiol and (b) estrone. Five different batch sample times are presented with their corresponding linear sorption isotherms.

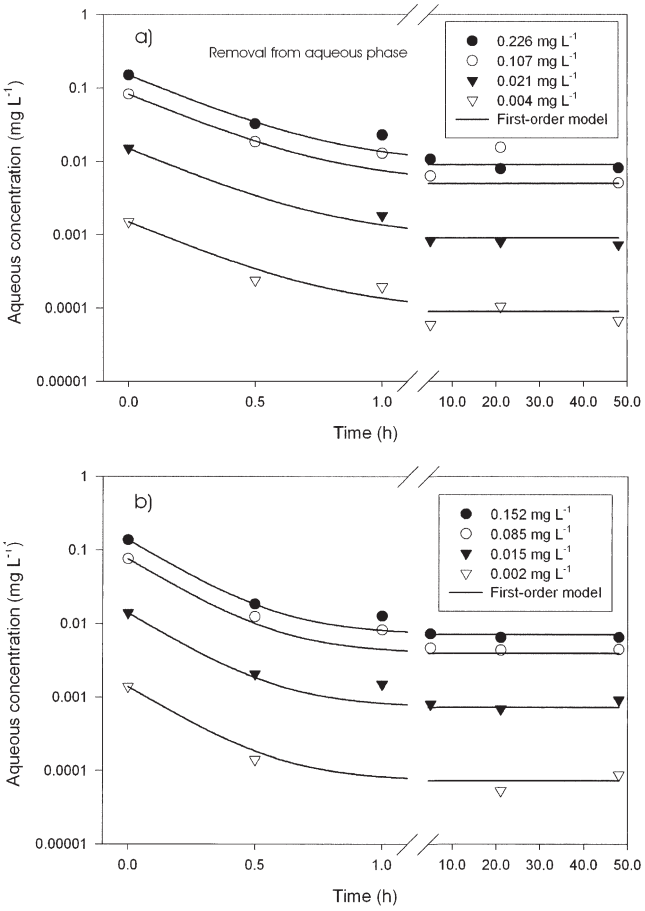

Fig. 2. Kinetic sorption batch data showing the aqueous concentration of (a) 17β-estradiol and (b) estrone vs. time. The batch data shown are from the different initial aqueous concentrations, which are fit with a first-order kinetic sorption model, Eq. [1].

kinetics, degradation, or a combination of these processes. In this section we look at the effect of sorbed phase degradation and sorption kinetics on the interpretation of the 17β-estradiol batch experiments. We assumed that if degradation occurred, then it was in the sorbed phase, because no metabolites were detected in the aqueous phase. Equation [1] was fit to the time series of C values (e.g., Fig. 2a) using a fixed μ_s' value obtained from the column experiment ($\mu_s = 0.09$ h^{-1}, presented later) and optimizing α and K_d. The optimized α and K_d values were 0.44 h^{-1} and 41.00 L kg^{-1}, respectively, and the model fit was excellent for the measured points ≤5 h ($r^2 = 0.99$). However, at times ≥24 h, the μ_s of 0.09 h^{-1} provided an over-prediction of 17β-estradiol dissipation. This model solution predicted a continual decrease in concentrations instead of approaching a more steady value, as our data indicated (Fig. 2a and 2b). This result suggests that within the first 24 to 48 h sorption kinetics was more significant than degradation, because the aqueous concentrations converged to an apparent constant rather than continually decreasing as a result of degradation (Fig. 2).

Sorbed-Phase Distributions

For the range of concentrations used in this study, it was found that both 17β-estradiol and estrone sorption isotherms were linear for each time step of 0.5, 1, 5, 24, and 48 h (Fig. 1a and 1b), and that sorption equilibrium was achieved between 5 and 24 h. This equilibration period (~5–24 h) for hormone sorption has been observed in other studies (Lai et al., 2000; Holthaus et al., 2002; Yu et al., 2004). Our 24 to 48 h log K_{oc} (log K_{oc} = $\log_{10}[K_d/(OC/100)]$ values for 17β-estradiol (≈3.2) and estrone (≈3.3) were comparable to values reported by other studies for soil. Yu et al. (2004) reports log K_{oc} values for 17β-estradiol that range from 3.14 to 5.38 and estrone values that range from 3.3 to 5.25. Lee et al. (2003) also report values for 17β-estradiol that range from 3.21 to 3.46 and estrone values that range from 3.19 to 3.22.

Lee et al. (2003) indicate that the primary sorption

Table 1. The linear partitioning coefficient (K_d), the $\log_{10}$ of the organic C normalized partitioning coefficients (log K_{oc}), the $\log_{10}$ octanol–water portioning coefficient (log K_{ow}), and the coefficient of determination (r^2) of the linear isotherm fit of the batch sorption data for 17β-estradiol and estrone through time.

Time	K_d	Log K_{oc}	r^2
h	L kg^{-1}		
	17β-estradiol		
0.5	17.98	2.27	0.98
1	27.74	2.46	1.00
5	64.27	2.83	1.00
24	89.47	2.97	1.00
48	84.41	2.94	0.99
	Estrone		
0.5	30.36	2.50	0.98
1	46.53	2.69	0.98
5	84.91	2.95	0.98
24	95.19	3.00	0.98
48	93.37	2.99	0.98

domain for the estrogen hormones is organic C, and that partitioning is consistent with hydrophobic partitioning process; that is, there is a direct linear correlation between the $\log_{10}$ octanol–water portioning coefficient (log K_{ow}) and log K_{oc}. Our 24-h log K_{oc} values (Table 1) were used to calculate the log K_{ow} values using the Means et al. (1980) linear relation, where log K_{oc} = log K_{ow} − 0.317. The calculated log K_{ow} values for 17β-estradiol and estrone were 3.25 and 3.28, respectively, and fell within the range of values reported in the literature, which was 3.10 (Hansch et al., 1995) to 4.01 (Suzuki et al., 2001) for 17β-estradiol, and 2.45 (Suzuki et al., 2001) to 3.43 (cited by Lai et al., 2000) for estrone. This result suggests that the log K_{oc} information is useful in predicting partitioning of these estrogens.

Rate-Limited Sorption

An explanation for the time-dependent sorption is rate-limited sorption caused by soil organic matter. Figures 2a and 2b show the first-order kinetic sorption model (Eq. [1]) fit with the measured aqueous concentrations through time. The same α and K_d values were used to model the data for each initial concentration of both 17β-estradiol (α = 0.178 h^{-1}, K_d = 86.00 L kg^{-1}) and estrone (α = 0.210 h^{-1}, K_d = 94.00 L kg^{-1}). This model provided excellent descriptions of the sorption data for 17β-estradiol (r^2 ranged from 0.94 to 0.98 with mean of 0.98) and estrone (r^2 ranged from 0.94 to 1.00 with mean 0.98). This sorption data obeyed Fick's law, where sorption was found to be linear and proportional to the square root of time, and α was the same for each C_0 (Rogers, 1965). Pignatello and Xing (1996) indicate that this type of Fickian behavior is consistent with sorption of dilute contaminants (penetrant concentrations in this study ≈1 × 10^{-7} to 1 × 10^{-5} kg kg^{-1}) into soft organic C or the amorphous organic matter domain. Others (e.g., Brusseau et al., 1991; Luthy et al., 1997; Xing et al., 1996) have also observed this type of rate-limited diffusion process.

The 17β-estradiol batch data from the Casey et al. (2003) study were revisited to see whether the data were consistent with our current study. The sorption model (Eq. [1]) described the Casey et al. (2003) batch data well for the various soils (see r^2 values presented in Table 2). The resulting log K_{oc} values (Table 2) were consistent with the values of the current study (Table 1). These log K_{oc} values increased with time, which was also similar to the current study. There was a negative correlation between log K_{oc} values and OC (correlation coefficient = −0.872), which indicated that other nonhydrophobic processes contributed to sorption. The predominant sorption process remains hydrophobic as Lee et al. (2003) demonstrates; however, the contribution of other nonhydrophobic processes increases as OC decreases, and the apparent K_{oc} values increase. One explanation for nonhydrophobic sorption is provided by Yu et al. (2004), who suggests that the phenolic group of 17β-estradiol and estrone can interact with humic acids or mineral surfaces via hydrogen and covalent bonding. They propose that the polar groups at the C-17 position of both molecules can react with humic acids and mineral surfaces causing sorption to follow some specific interactions in addition to hydrophobic interactions.

Column Results

The total mass of ^{14}C 17β-estradiol applied to the cross-sectional area of the soil column was 8.605 mg over an approximate time of 19 h. This amount of 17β-estradiol appears to be large. However, pregnant dairy cattle (*Bos taurus*) and sows (*Sus scrofa*) have been shown to eliminate quantities of 163 000 ± 20 000 μg d^{-1} and 108 000 ± 103 000 μg d^{-1}, respectively, based on 1000 kg of live animal mass (Raeside, 1963). A number of pregnant stock animals in a confined area can eliminate large amounts of hormones possibly posing a risk to surface and subsurface water quality. In the soil column effluent, 26% of the total ^{14}C 17β-estradiol applied was recovered as parent compound, and 36.7% was recovered as estrone.

Table 2. The organic carbon (OC) content of the soils from the Casey et al. (2003) study. Also, the calculated $\log_{10}$ of the organic C normalized partitioning coefficients (log K_{oc}) and first-order kinetic sorption coefficients (α) from the Casey et al. (2003) batch experiments.

Soil series/texture	OC	Log K_{OC} 0.5 h†	1 h	5 h	24 h	48 h	α	r^2
	%						h^{-1}	
Bearden silty clay loam	7.5	2.65	2.76	3.02	3.17	3.20	0.200	0.99
Gardena clay loam	5.3	2.46	2.64	3.06	3.17	3.18	0.178	0.99
Glyndon sandy clay loam	3.3	3.94	4.03	4.18	4.13	4.14	instantaneous	1.00
LaDelle silt loam	9.2	2.29	2.48	2.84	2.99	2.96	0.184	0.99
Sioux loam	7.5	2.58	2.75	2.94	2.75	2.73	0.543	0.99

† The log K_{oc} values are segregated by the time at which the isotherms were determined.

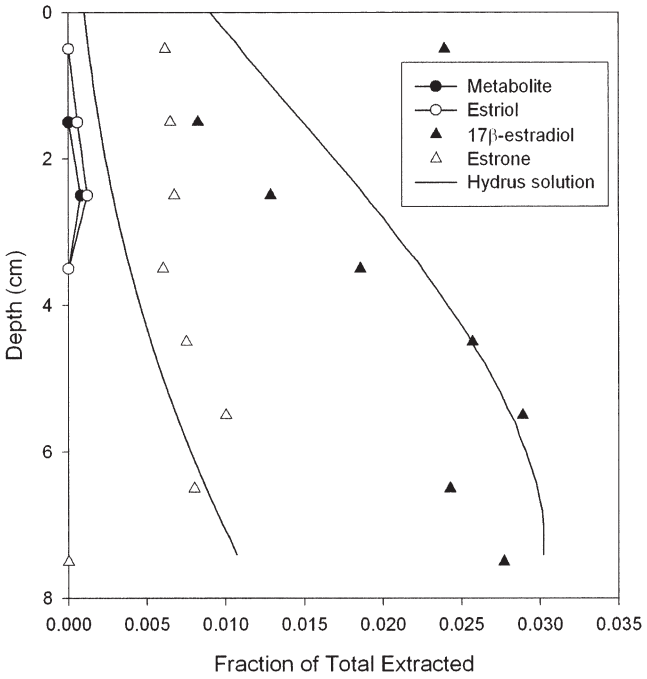

Fig. 3. Concentrations of 17β-estradiol and its transformation products through the depth of the soil column. Also included is the prediction using the "two-site/2" parameter estimates obtained from the effluent breakthrough curves in Table 3.

An additional 22.4% was recovered from the soil inside the column through combustion analysis. Thus, the total ^{14}C recovery was approximately 84%. Analysis of the soil extractions indicated that 16.9% 17β-estradiol, 5.08% estrone, 0.18% estriol, and 0.08% of an unidentified metabolite of higher polarity were recovered based on the total ^{14}C applied. The estriol and the unidentified metabolite were not eluted until the final solvent extraction, and 17β-estradiol and estrone were eluted from the three solvent extractions in approximately equal amounts. Figure 3 shows the distribution of each of the ^{14}C compounds recovered from the soil extractions relative to the total amount applied. In general, 17β-estradiol increased with depth and estrone was distributed equally with depth, except in the bottom layer where it was not detected. The other metabolites (estriol and unidentified) were only found in the upper 3 cm of soil. The incomplete ^{14}C mass balance (84%) may be a result of incomplete combustion, or could have also resulted from mineralization of the ^{14}C 17β-estradiol to form $^{14}CO_2$.

Modeling Approach

The $CaCl_2$ breakthrough curve was symmetric and was fit with an advective–dispersive model using a retardation coefficient of 1 (data not shown) and an optimized λ value of 0.024 m. The model fit to the Cl^- breakthrough curve was good ($r^2 = 0.98$) and indicated that transport was a physical equilibrium process. The breakthrough curves of 17β-estradiol, estrone, and total ^{14}C were all asymmetric (Fig. 4). The asymmetric breakthrough curves indicated chemical nonequilibrium transport of the estrogens and not physical nonequilibrium,

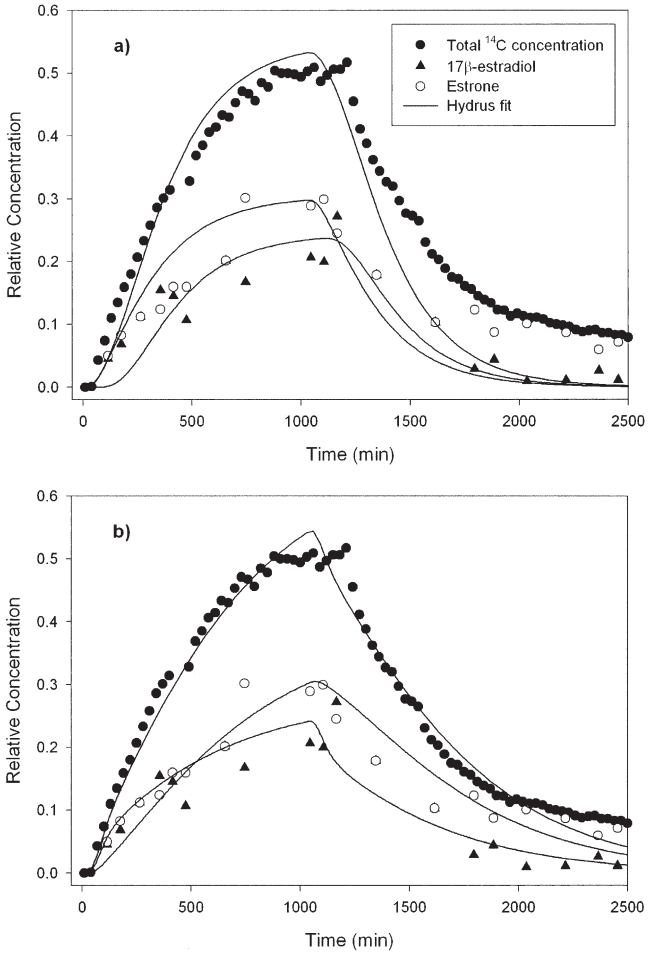

Fig. 4. The soil column, relative, effluent concentrations of total ^{14}C, 17β-estradiol, and estrone through time. The 17β-estradiol and estrone data were fit with (a) an instantaneous sorption model option (Table 3, Instantaneous) and (b) a two-site sorption model option (Table 3, Two-site/2).

because the $CaCl_2$ was transported as a physical equilibrium process. Instantaneous and two-site sorption scenarios were considered in modeling the estrogen breakthrough curves. For two-site sorption, sorption takes place on both instantaneous and kinetic sites, and there is a fixed ratio (f) between these two sorption sites (van Genuchten and Wagenet, 1989). The batch sorption parameters (Tables 1) and the λ value from the $CaCl_2$ column experiment were fixed in our initial model runs, whereas μ_s' and f values were estimated. Then, various model parameters were optimized to obtain a better model description of the data. Also, the 17β-estradiol and estrone breakthrough curves were optimized simultaneously, which improves the uniqueness of parameter estimates (Casey and Šimůnek, 2001).

Fitting Results

Table 3 summarizes the inverse modeling results, where estimated parameters are presented with their 95% confidence intervals (CI). Also, Fig. 4a and 4b show the model fits to the estrogen breakthrough curves using instantaneous and kinetic sorption models, respec-

Table 3. The model parameter estimates of the instantaneous and two-site sorption miscible-displacement models. The goodness of the model fit was indicated by the sum-of-squares error (SSQ) between the measured and calculated effluent concentrations. The model parameters were linear partitioning coefficient (K_d), sorbed phase transformation (μ_s'), first-order kinetic sorption (α), and fraction of equilibrium sorption sites (f). Subscripts 1 and 2 indicate 17β-estradiol and estrone, respectively.

Sorption type/run	SSQ	K_{d1}	μ_{s1}'	α_1	K_{d2}	μ_{s2}'	α_2	f
		L kg^{-1}	h^{-1}		L kg^{-1}	h^{-1}		
Instantaneous	0.165	27.74	0.15	NA†	2.65 (−0.87–6.18)‡	1.02 (−0.30–2.34)	NA	NA
Two-site/1	0.629	86.00	0.14 (−0.02–0.30)	0.18	94.00	0.019 (−0.00–0.04)	0.21	0.0004 (−0.006–0.006)
Two-site/2	0.028	55.87 (49.20–62.53)	0.09 (0.07–0.11)	0.18	30.36 (19.00–41.73)	0.14 (0.05–0.23)	0.21	0.145 (0.092–0.177)

† NA indicates that this parameter is not applicable to this particular model.
‡ The values inside parentheses represent the 95% confidence interval, and indicate that this parameter was estimated.

tively. The instantaneous sorption model option (Fig. 4a) could only provide a realistic description of the solute breakthrough curves when the 1-h batch K_d value for 17β-estradiol was fixed, and when estrone K_d and μ_s' were fitted. The 17β-estradiol K_d value made sense, because the contact time within the soil column was approximately 0.5 h and corresponded to the batch K_d value determined at approximately the same time. The optimized values for estrone had large 95% CIs, which indicates more uncertainty in these parameter estimates. The K_d value for estrone was lower than expected (log K_{oc} = 1.44), which may be attributed to the shorter contact times in the soil column. The 17β-estradiol μ_s' (0.15 h^{-1}) was similar to values reported by Colucci et al. (2001), which ranged from 0.13 to 0.06 h^{-1}. The estrone μ_s' (1.02 h^{-1}) estimate was large and fell out of the range of values reported in the literature for soil, 0.006 (Das et al., 2004) to 0.05 h^{-1} (Colucci et al., 2001). Although the instantaneous sorption model provided a reasonable fit of the observed breakthrough curves (Fig. 4a), the estrone parameter estimates were not satisfactory and the tail of the breakthrough curves were poorly described (Fig. 4a).

Das et al. (2004) used a two-site sorption model (van Genuchten and Wagenet, 1989) to describe estrogen breakthrough curves from a 1.0-cm long soil column. The two-site sorption concept was also appropriate for describing our breakthrough curves, because there appeared to be a rate-limiting sorption process, which caused the breakthrough curve tail and was observed in our batch experiments. In the first two-site sorption model simulation (Table 3, two-site/1), K_d and α were fixed to values obtained from the batch study (K_{d1} = 86.00 L kg^{-1}, K_d = 94.00 L kg^{-1}, α_1 = 0.18 h^{-1}, α_2 = 0.21 h^{-1}) and μ_{s1}', μ_{s2}', and f were optimized. The SSQ value for this simulation was reasonable. However, the peak concentrations of 17β-estradiol were underestimated, and the tail of the estrone was over-predicted (fit not shown). Still, the two-site sorption model option was able to capture the shape of the breakthrough curve better than the instantaneous sorption option using the batch determined parameters.

The two-site sorption model was fit to the breakthrough data again using fixed values of λ, α_1, and α_2, while optimizing for μ_{s1}', μ_{s2}', K_{d1}, K_{d2}, and f (Table 3; two-site/2). The K_d values were estimated because it was not clear from the batch experiments how degradation/transformation affected this parameter. The number of parameters that were estimated was five, which appears to be large. However, there were two breakthrough curves or 2.5 parameters estimated per curve, which is not unreasonable. The model fit was excellent (Fig. 4b; SSQ = 0.028) and the confidence intervals of the parameter estimates were narrow (Table 3), which indicates a more unique solution. The K_d estimates for 17β-estradiol and estrone fell within the range of values calculated from the batch studies. Also, the 17β-estradiol μ_s' estimate was similar to values reported by Colucci et al. (2001), but the estrone μ_s' value was higher than the 17β-estradiol value. Das et al. (2004) found that estrone degraded faster than 17β-estradiol for their flow-interruption soil column experiment. The α values from the batch experiments provided a good prediction of the breakthrough curve tail. Also, the f value indicated that about one-sixth of the sorption sites were instantaneous or readily available to sorption.

To further evaluate the confidence in these column parameter estimates, the 17β-estradiol K_{d1}, α_1, and μ_{s1}' values (Table 3, two-site/2) were used to solve the kinetic sorption model, Eq. [2]. This solution was then compared with the 17β-estradiol batch aqueous concentrations through time. This model provided a good description of the batch data through 5 h (r^2 = 0.95, SSQ = 0.001), but at times ≥24 h this solution over-predicted the dissipation of 17β-estradiol. This result may suggest that degradation slows as aqueous concentrations decrease, and may not, as Das et al. (2004) suggests, follow a first-order process. This may also explain why the aqueous 17β-estradiol concentrations in the batch experiments did not go to zero but approached an apparent constant. Lastly, the two-site sorption option and parameter estimates (Table 3, two-site/2) were used to predict profile distribution of 17β-estradiol and estrone, and compared well to the measured distribution of these hormones (Fig. 3). This further confirmed the confidence in this model and these parameter estimates.

CONCLUSIONS

This research can provide a better link between laboratory results and observations in the natural environment. The batch and column experiments of this study resulted in close agreement. A first-order, rate-limited sorption process was evident in both the batch and column experiments and was found to be rapid. The column experiments indicated that degradation was rapid and was adequately modeled with a first-order process. There was also evidence that degradation rates decreased through time or with lower concentrations. Although the estrogen hormone escaped the 7-cm organic rich topsoil, these ex-

perimental conditions (i.e., continuous application of hormone, and flowing, saturated conditions) are likely not to be found under natural conditions. Under natural conditions, the sorption and degradation rates of these estrogens would likely result in little mobility and little persistence. Nonetheless, hormones are consistently detected in the environment at low concentrations. There is a need to better understand the degradation process of these hormones under natural conditions and their natural background levels and sources.

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