Modeling coupled degradation, sorption, and transport of 17β-estradiol in undisturbed soil

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The presence of 17β-estradiol in the environment, even at parts-per-trillion concentrations, raises significant concern regarding the health of aquatic organisms. Once 17β-estradiol is released into the environment from human and animal sources, its fate and transport is controlled by factors such as sorption and transformation, which need to be understood to fully assess potential exposures. The objective of this study was first to discern, through controlled batch experiments, the simultaneous transformation (i.e., chemical and biological) of natural estrogentic compounds and their mass exchange between the aqueous and solid phase (i.e., reversible and irreversible sorption sites). In addition, a model was developed that used a series of first-order expressions to describe the various fate and transport processes of parent and metabolite estrogens in the nonequilibrium batch experiments. A global optimization method was used to estimate the parameters of this nonequilibrium batch model. The model provided a good description of the data, and the parameter estimates were reliable. The batch studies parameter estimates were then incorporated into a convective-dispersive model to describe two undisturbed column experiments. The consistency of parameter estimates between the batch and column experiments indicated a high capability and reliability of this model and the parameter values.


1. Introduction

[2] Literature suggests that there are links between sources of estrogenic hormones (e.g., animal feeding operations, wastewater treatment plants) and their occurrences in surface water [Baronti et al., 2000; Kolpin et al., 2002; Tabata et al., 2001], groundwater [Peterson et al., 2000], and soil [Finlay-Moore et al., 2000; Herman and Mills, 2003]. The main concern regarding estrogen hormones is their potency, especially 17β-estradiol, which can alter endocrine function of aquatic organisms at concentrations as low as 10 ng L⁻¹ [Routledge et al., 1998]. It is necessary to obtain an accurate, integrated, and quantified understanding of estrogenic hormone fate and transport in order to assess their effects on the environment.

[3] Some studies [Casey et al., 2003, 2005; Das et al., 2004; Lee et al., 2003] have explored the sorption, biodegradation, and transport processes of 17β-estradiol that occur simultaneously in soil-water systems using batch and miscible-displacement experiments. However, the reactive nature of hormones in soils still presents a major challenge in accurately discerning and modeling fate and transport processes. For example, Colucci et al. [2001] reported that approximately 56-91% of applied 17β-estradiol became nonextractable after 3-day incubation. Also, Fan et al. [2007a] reported that 70-73% of applied radiolabeled 17β-estradiol was nonextractable after 5-day incubation. However, previous studies miss this irreversible sorption process [Casey et al., 2003, 2005; Das et al., 2004], which may overestimate the risk of 17β-estradiol mobility in the soil. Another difficulty is hormone transformations. Jacobsen et al. [2005] found that ~24% of 17β-estradiol is immediately transformed into estrone only minutes after the start of an incubation experiment. Colucci et al. [2001] reported that 50% of 17β-estradiol was degraded after 12-h incubation. Also, Fan et al. [2007a] found 17β-estradiol was transformed into metabolites after 5d (consisting 28% estrone and 61% polar metabolite). The continuous transformation of 17β-estradiol would result in a constant state of nonequilibrium. Several studies have used equilibrium approaches to identify hormone distributions and sorption parameters, but this would not be accurate.

[4] Using soil incubation experiments, Fan et al. [2007a] investigated the transformations (e.g., degradation, mineralization) of 17β-estradiol and testosterone under aerobic and anaerobic conditions, in sterile and natural soils, and the distributions of these hormones and their metabolites in aqueous solution and in various reversible and irreversible sorption locations. The fate processes for androgenic hor-
mones were exclusively biological, while both biological and chemical processes controlled estrogenic hormone fate. Using some conclusions from the Fan et al. [2007a] study, Fan et al. [2007b] conducted batch sorption and column transport studies and successfully developed a model to describe the nonequilibrium fate and transport of testosterone in undisturbed soils. The goals of this current study were similar, which were to obtain a comprehensive understanding of the numerous concurrent fate and transport processes of 17β-estradiol in undisturbed soil column experiments. To achieve this objective, the knowledge gained by the Fan et al. [2007a, 2007b] investigations and several controlled experiments were used to discern individual processes. Furthermore, a model was developed and coupled with a genetic algorithm parameter estimation method to describe and quantify these fate and transport processes.

2. Materials and Methods

2.1. Chemicals

[6] 17β-estradiol has a molecular weight of 272.4 g mol⁻¹, a water solubility of 13.0 mg L⁻¹ at 25°C, and an octanol-water partition coefficient (log Kow) of 4.01 [Lintelmann et al., 2003]. Estrone, one of the main metabolites of 17β-estradiol, has a molecular weight of 270.37 g mol⁻¹, a water solubility of 13.0 mg L⁻¹ at 25°C, and log Kow of 3.43 [Lai et al., 2000a]. Laboratory experiments used [4-14C]-radiolabeled 17β-estradiol (purity >99%) (American Radiolabeled Chemicals, St. Louis, MO, USA). The radiolabel analytical approaches, along with global optimization parameter estimation method (explained later), made it possible to discern individual fate processes, where it would have been difficult or impossible using other analytical methods. Radiolabel methods made it possible to distinguish experimentally introduced 17β-estradiol from any antecedent 17β-estradiol, allowed mineralization to be quantified by collecting 14CO2, provided a simple method to quantify mass balance, and very low detection limits could be achieved.

2.2. Batch Sorption Experiments

[7] A series of batch experiments were conducted in the laboratory to determine the sorption of 17β-estradiol in natural soils, and the methods were similar to those used by Fan et al. [2007b]. Briefly though, batch experiments were triplicated and conducted at room temperature (21 ± 1°C). A ratio of 1.6 g of sieved (2 mm) Hamar soil to 8 mL 0.01 M CaCl2 (Sigma-Aldrich, St. Louis, MO, USA) were added to 10-mL clear vials and sealed. [4-14C]-Radiolabeled 17β-estradiol was then added resulting in final concentrations of 0.138, 0.069, and 0.015 mg L⁻¹, which span detections found in animal manure [Lorenzen et al., 2004; Shore and Shemesh, 2003]. The test vials were placed on a rotating shaker, and triplicate 100-μL aliquots were taken at 0.5, 1, 5, 24, 48, and 168 h. These aliquot samples were assayed for radioactivity by liquid scintillation counting using a 1900 CA scintillation counter (Packard, Downers Grove, IL, USA). Also, to examine the possibility of photodegradation of 17β-estradiol in the natural soils during the batch experiments, another two sets of controlled batch experiments were conducted in clear and amber vials with autoclaved sterile soil [Fan et al., 2007b]. The initial concentrations of 17β-estradiol in these sterile soil batch experiments were the same as natural soil batch experiments.

2.3. Miscible-Displacement Experiments

[8] The soil column experimental methods were also similar to those presented by Fan et al. [2007b], where two experiments were conducted (referred to as Experiments 1 and 2). For both experiments the soil columns were turned upside down to saturate the column and to easily control flow rates using a high-pressure solvent pump to apply a weak salt solution (0.01 M CaCl2). After saturation was achieved, a steady pore water velocity of approximately 0.09 cm min⁻¹ was established. A pulse (about 2 pore volumes) of higher-concentration CaCl2 solution (0.05 M CaCl2) was then passed through the column and eluted with the 0.01 M CaCl2 solution. Column effluent fractions were collected every 3.5 min, and analyzed for Cl⁻ concentration. This CaCl2 breakthrough experiment provided information about the transport of a conservative, nonsorbing solute (Cl⁻) in this undisturbed Hamar soil.

2.3.1. Experiment 1

[9] Following this chloride breakthrough curve experiment, a pulse of [4-14C]-17β-estradiol (approximately 3 μCi, 6,000,000 dpm) was applied to the column in 300 mL (≈0.13 pore volume) of 0.01 M CaCl2-estradiol solution and eluted with at least 17 L (~7.5 pore volumes) of 0.01 M CaCl2. Fractions of column effluent were collected every 3.5 min, and each fraction was analyzed for 14C using liquid scintillation counting. Thin-layer chromatography (TLC) [System 2000 Imaging Scanner (Bioscan, Inc., Washington D.C., USA)] with a silica gel TLC plate (5 × 20 cm, Uniplate™, Analtech, Newark, DE, USA) and 1:1:2 tetrahydrofuran:ethyl acetate:hexane mobile phase was used to determine the presence of any 17β-estradiol metabolites in the column effluent by comparing the samples with standards.

2.3.2. Experiment 2

[10] A second column experiment was commenced as a result of a low total 14C mass recovery (79.0%) from Experiment 1. Initially, the mass balance errors were thought to have resulted from 17β-estradiol mineralization during and at the completion the experiment. This second column experiment was the same as Experiment 1, but had two modifications to try to minimize 14C mass loss by (1) accounting for volatile metabolites, and (2) halting biotransformations at the end of the experiment. A schematic of these experimental modifications and chemical analyses are provided by Fan et al. [2007b], and briefly
The column transport model described these same processes of 17β-estradiol and its metabolites. A batch model described the kinetics of degradation/transport from a column, as evidenced by high mass recovery of 14CO2 while extruding the outlet gas was then first passed through a 3 M NaOH solution that trapped 14CO2. The second experimental modification, to stop biological activity, was achieved by introducing 1 pore volume of 1.8 mg mL−1 (approximately 500 mg per 1 kg of dry soil) of HgCl2 [Trevors, 1996] at the end of the experiment. For testosterone, Fan et al. [2007b] showed that HgCl2 inhibits biological activity and minimized mineralization losses of 14CO2 while extruding the from a column, as evidenced by high mass recovery of 14CO2.

2.3.3. Resident Concentrations

The redistributions of 14C inside the soil columns for Experiments 1 and 2 were also measured. This was done by (1) extruding the soil from the column in 5-cm increments, (2) eluting the extruded soil with toluene, ethyl acetate, and methanol in the cell of an accelerated solvent extractor (ASE, model 200; Dionex, Sunnyvale, CA, USA), (3) drying the extruded soil, and (4) assaying it for 14C with combustion analysis using a Packard Model 307 Oxidizer (Meridian, CT, USA). Separation and analysis for 14C-metabolites in the soil extracts were performed with TLC.

2.4. Model Solutions

The fate and transport processes discerned from the batch and column experimental results were used to develop conceptual models. These models were expressed as differential equations that were solved using a finite difference method, CVODE [Cohen and Hindmarsh, 1994] using a spatial increment of 1 cm and time step of 6.0 sec. The batch model described the kinetics of degradation/transport and sorption of 17β-estradiol and its metabolites. The column transport model described these same processes under advection-dispersive transport. The batch and column models were then applied inversely to match the model solutions to the experimental data by optimizing the model process parameters. However, owing to the large number of model parameters, the objective function (a measure of the error between the observed and predicted) will have many local optima. Traditional inverse local optimization methods are not suitable to find global optimum parameter sets for these types of problems, and so the stochastic ranking evolutionary strategy (SRES) [Runarsson and Yao, 2000], a global optimization method, was used to solve this identification problem. Fan and Casey [2008] demonstrated the use of the SRES to uniquely estimate parameter sets, as large as thirteen, for chemicals that undergo complex fate and transport processes such as hormones. This SRES method was used here to estimate the process parameters. Additionally, constraints were placed on the parameters based on experimental results, which further improved the uniqueness of the parameter estimates. The 95% confidence intervals of the parameter estimates were determined with a nonparametric bootstrap resampling method [Efron and Tibshirani, 1993; Fan and Casey, 2008].

3. Results and Discussions

3.1. Batch Experiments

For all three of the initial concentrations of 17β-estradiol in the batch experiments, the aqueous concentration of 14C decreased through time (Figure 1). Previous 17β-estradiol sorption studies attributed this aqueous phase attenuation to transformation and sorption processes [Lee et al., 2003; Mansell and Drewes, 2004; Mansell et al., 2004]. To identify the potential effect of photodegradation in the batch experiments, time series concentrations relative to their initial concentration for the natural and sterile soil, in amber and clear vials, were compared using a standard least squares regression statistical model (model root mean square error = 0.021; F-ratio = 29.37; probability (p) <0.0001) [Soll et al., 2004]. The factors of sterility (p = 0.008) and time (p < 0.0001) were highly significant in explaining the variations in relative concentrations, but vial color was not (p = 0.9937). This result indicated that photodegradation in the clear vials was not significant compared to other processes, which agrees with earlier studies that found photodegradation to be minimal in soil [Casey et al., 2003; Fan et al., 2007a; Lai et al., 2000a; Gray and Sedlak, 2005; Jürgens et al., 2002]. Thus it was reasonable to exclude photodegradation as a process in developing the fate and transport model. Additionally, the significance of the sterility effect (p = 0.008) reiterated the importance of biological processes for 17β-estradiol fate.

3.2. Miscible-Displacement Experiments

3.2.1. Effluent Concentrations

The 14C breakthrough curves from Experiments 1 and 2 were very similar and highly asymmetric, showing a long elution tail (Figure 2). Two mechanisms that may explain this elution tail are physical (e.g., preferential flow) and/or chemical nonequilibrium (kinetic sorption). Mathematically expressed, physical and chemical nonequilibrium concepts are identical; however, the conservative, nonsorbing chloride breakthrough curves were symmetric (Figure 2), indicating physical equilibrium transport.
caused preferential flow. The effluent breakthrough curves for (a) Experiment 1, and (b) Experiment 2. 

Even though undisturbed columns were used, the soils were sandy texture and there was little structure that may have caused preferential flow. The effluent breakthrough curves also showed apparent early peaks of 17β-estradiol metabolites (Figure 2), which can result from a combination of large dispersivities and sorption kinetics and has been observed by Das et al. [2004] for steroidal hormones.

[15] About 6% of 14C was recovered from the column effluents (Figure 2) for both miscible-displacement experiments (Table 1). The TLC analyses of the column effluent from Experiments 1 and 2 revealed that two metabolites, estrone (~25%) and a higher polarity unidentified metabolite (~70%), accounted for nearly all of the effluent 14C. The TLC analysis also indicated that there was no 17β-estradiol present in the effluent of either column. Possible candidates for the polar metabolite are estriol, quinine, or semiquione [Casey et al., 2003; Lai et al., 2000b]. The higher polarity of this metabolite would also result in a higher water solubility compared to estrone or 17β-estradiol, which would explain its greater proportion in the column effluent.

[16] The total 14CO2 trapped in the 3 M NaOH in Experiment 2 was about 0.01%, which indicated that 17β-estradiol was resistant to mineralization under these experimental conditions. This 14CO2 recovery was significantly smaller compared 14C-testosterone in the same soil, where 23.4% 14C-testosterone was mineralized into 14CO2 [Fan et al., 2007b]. Nonetheless, this greater mineralization of testosterone compared to 17β-estradiol was consistent with other studies [Casey et al., 2004; Layton et al., 2000]. Also, no volatile compounds were trapped in the Porapak column of Experiment 2. The above results were all consistent with the Fan et al. [2007a] study, where 0.9% 17β-estradiol and 46% testosterone were mineralized to 14CO2 and little or no 14CH4 was detected under low-oxygen experimental conditions for either compound. The incomplete 14C mass recovery (78%) in Experiment 2 may have resulted from incomplete soil matrix combustion, where some noncom-

Figure 2. Measured and fitted breakthrough curves of 14C labeled 17β-estradiol and its metabolites for miscible-displacement experiments for (a) Experiment 1, and (b) Experiment 2.

Table 1. Model Parameter Estimates for Batch and Miscible-Displacement Experiments

<table>
<thead>
<tr>
<th>Model Parametera</th>
<th>Batch Experiment</th>
<th>Miscible-Displacement Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experiment 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17β-Estradiol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl-</td>
</tr>
<tr>
<td>v0 (cm h⁻¹)</td>
<td>NAa</td>
<td>0.10</td>
</tr>
<tr>
<td>λ (cm)</td>
<td>NAa</td>
<td>1.4 (1.3, 1.8)b</td>
</tr>
<tr>
<td>Kd,1 (L g⁻¹) (× 10⁻²)</td>
<td>9.1 (8.9, 9.4)</td>
<td>NA</td>
</tr>
<tr>
<td>Kd,2 (L g⁻¹) (× 10⁻³)</td>
<td>2.8 (2.6, 3.3)</td>
<td>NA</td>
</tr>
<tr>
<td>Kd,3 (L g⁻¹) (× 10⁻⁴)</td>
<td>2.8 (1.8, 3.2)</td>
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</tr>
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<td>ων,1 (h⁻¹) (× 10⁻⁵)</td>
<td>16.5 (16.4, 17.2)</td>
<td>NA</td>
</tr>
<tr>
<td>ων,1 (h⁻¹) (× 10⁻⁵)</td>
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</tr>
<tr>
<td>ων,1 (h⁻¹) (× 10⁻⁵)</td>
<td>3.3 (3.0, 3.4)</td>
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</tr>
<tr>
<td>ων,1 (h⁻¹) (× 10⁻⁵)</td>
<td>7.9 (7.2, 8.1)</td>
<td>NA</td>
</tr>
<tr>
<td>ων,2 (h⁻¹) (× 10⁻⁴)</td>
<td>3.5 (3.1, 3.6)</td>
<td>NA</td>
</tr>
<tr>
<td>ων,2 (h⁻¹) (× 10⁻⁴)</td>
<td>7.9 (7.2, 8.1)</td>
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</tr>
<tr>
<td>α1 (h⁻¹) (× 10⁻⁵)</td>
<td>39.7 (34.4, 41.5)</td>
<td>0.6 (0.4, 0.7)</td>
</tr>
<tr>
<td>α2 (h⁻¹) (× 10⁻⁴)</td>
<td>12.0 (11.8, 12.9)</td>
<td>47.8 (37.2,53.1)</td>
</tr>
<tr>
<td>α3 (h⁻¹) (× 10⁻⁵)</td>
<td>10.4 (9.8, 13.7)</td>
<td>2.1 (1.8,2.3)</td>
</tr>
<tr>
<td>Effluent (%)</td>
<td>NA</td>
<td>99</td>
</tr>
<tr>
<td>Reversible (%)</td>
<td>NA</td>
<td>5.9</td>
</tr>
<tr>
<td>Irreversible (%)</td>
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<td>21.9</td>
</tr>
<tr>
<td>Total (%)</td>
<td>NA</td>
<td>51.2</td>
</tr>
</tbody>
</table>

aThe subscripts 1, 2, and 3 represent the parent compound 17β-estradiol, the unknown polar metabolite, and estrone, respectively.
bAverage pore water velocity.
cNA. parameter is not applicable to this particular model.
dThe values inside parentheses represent the 95% confidence interval and indicate that this parameter was estimated.
eReversible and irreversible sorption represents the sorbed 14C that is extractable and nonextractable with organic solvent (i.e., toluene, ethyl acetate, or methanol), respectively.
Experiment 1

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>M 0%</th>
<th>P 0%</th>
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</tr>
<tr>
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<tr>
<td>2</td>
<td>2.0%</td>
<td>1.2%</td>
</tr>
<tr>
<td>3</td>
<td>3.5%</td>
<td>2.2%</td>
</tr>
<tr>
<td>4</td>
<td>5.5%</td>
<td>3.5%</td>
</tr>
<tr>
<td>5</td>
<td>18.4%</td>
<td>11.2%</td>
</tr>
<tr>
<td>6</td>
<td>20.9%</td>
<td>13.8%</td>
</tr>
<tr>
<td>7</td>
<td>24.3%</td>
<td>16.2%</td>
</tr>
<tr>
<td>8</td>
<td>31.0%</td>
<td>19.4%</td>
</tr>
<tr>
<td>9</td>
<td>37.8%</td>
<td>22.5%</td>
</tr>
<tr>
<td>10</td>
<td>40.5%</td>
<td>24.6%</td>
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Experiment 2

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<tr>
<td>2</td>
<td>0.2%</td>
<td>0.1%</td>
</tr>
<tr>
<td>3</td>
<td>0.5%</td>
<td>0.3%</td>
</tr>
<tr>
<td>4</td>
<td>1.2%</td>
<td>0.4%</td>
</tr>
<tr>
<td>5</td>
<td>1.8%</td>
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<td>6</td>
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<td>7</td>
<td>3.8%</td>
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<td>8</td>
<td>4.5%</td>
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<tr>
<td>9</td>
<td>5.3%</td>
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</tr>
<tr>
<td>10</td>
<td>5.9%</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

Figure 3. Measured and predicted vertical distribution of $^{14}$C associated with the reversibly and irreversibly sorbed phase in the soil column for Experiments 1 and 2. Included are the measured (M) and predicted (P) mass recoveries for each 5-cm increment. Note that the top 1–5 cm of soil columns were filled with sand.

Busted $^{14}$C material remained in the soil and was not released as a gas when the soil was combusted (i.e., combustion gas was trapped and analyzed for $^{14}$C). Another possibility was that the HgCl$_2$ solution was not evenly distributed in the column owing to HgCl$_2$ sorption [Yin et al., 1996], which would result in biological activities that caused unaccounted 17β-estradiol mineralization.

### 3.2.2. Resident Concentrations

[17] The sequential solution extraction and combustion analyses of both column experiments indicated that resident $^{14}$C was 47–51% irreversibly and 22–25% reversibly sorbed (Table 1 and Figure 3). This result was consistent with earlier incubation experiments [Fan et al., 2007a], where 51% and 20% of $^{14}$C was recovered from irreversible and reversible sorption sites after a 5-day incubation under low-oxygen conditions, respectively. The TLC analysis of the resident soil extracts from the reversible sorption sites indicated that 55%, 20%, and 22% of $^{14}$C was recovered as the polar metabolite, estrone, and 17β-estradiol, respectively. Both irreversible and reversible resident $^{14}$C were expressed as the percentage of the total radioactivity applied to the column in Figure 3. Most of $^{14}$C was retained in the 5–10 cm depth of this Flamar soil column. It should be noted that the top 0–5 cm of the column contained little $^{14}$C because it was filled with clean sand, which should not sorb hormones nor effect hormone transport [Das et al., 2004; Larsen et al., 2001]. For Experiment 1, 0.92% of $^{14}$C was recovered from the sand layer, while 8.54% of $^{14}$C was recovered from the sand in Experiment 2. The radioactivity recovered in the sand layers likely resulted from soil being scraped from the column surface and mixed with the sand layer as it was extruded from the column.

### 3.3. Model Development

#### 3.3.1. Batch Experiments

[18] A one-site sorption model was conceived (Figure 4) from the experimental results and previous incubation studies [Fan et al., 2007a]. This model considers the simultaneous transformation and sorption process of 17β-estradiol and its metabolites, and their distributions among the aqueous and reversible and irreversible sorbed phases.

The following system of differential equations represents the linear sorption of 17β-estradiol with degradation:

$$
\begin{align*}
\frac{\partial S_{r,1}}{\partial t} &= \alpha_1 (K_d,1 C_1 - S_{r,1}) - \omega_{irr,1} S_{r,1} - \omega_{r,1} S_{r,1} \\
\frac{\partial C_1}{\partial t} &= -\frac{M}{T} \alpha_1 (K_d,1 C_1 - S_{r,1}) - \omega_{r,1} C_1 - \omega_{irr,1} C_1 \\
\frac{\partial S_{irr,1}}{\partial t} &= \omega_{irr,1} S_{r,1}
\end{align*}
$$

(1)
unknown parameters:

Equations (1), (2), and (3) contain twelve (h); and between the reversibly sorbed phase and the aqueous phase transfer rate constant from the reversibly to the irreversibly phases (h), respectively; transformation rate constants in the aqueous and sorbed phases; ce, and are the reversibly and irreversibly sorbed phase respectively; estradiol, an unidentified polar metabolite, and estrone, The subscripts 1, 2, and 3 represent the parent 173-

The mass balance of the batch experiment was expressed as

\[
\begin{align*}
\frac{dS_{r,2}}{dt} &= \alpha_2 (K_{d,2} C_2 - S_{r,2}) - \omega_{pr,2} S_{r,2} + \omega_{w,1} S_{r,1} \\
\frac{dC_2}{dt} &= -\frac{M}{V} \alpha_2 (K_{d,2} C_2 - S_{r,2}) + \omega_{w,1} C_1 \\
\frac{dS_{pr,2}}{dt} &= \omega_{pr,2} S_{r,2} \\
\frac{dS_{r,3}}{dt} &= \alpha_3 (K_{d,3} C_3 - S_{r,3}) - \omega_{pr,3} S_{r,3} \\
\frac{dC_3}{dt} &= -\frac{M}{V} \alpha_3 (K_{d,3} C_3 - S_{r,3}) + \omega_{w,3} C_1 \\
\frac{dS_{pr,3}}{dt} &= \omega_{pr,3} S_{r,3} \\
\frac{d[C^{14}C]}{dt} &= \frac{\partial C_1}{\partial t} + \frac{\partial C_2}{\partial t} + \frac{\partial C_3}{\partial t}
\end{align*}
\]

The transformation of the 17β-estradiol into estrone is predominantly a biological process under both aerobic and anaerobic conditions [Fan et al., 2007; Jacobsen et al., 2005]. Thus, equations (1)–(3) consider this transformation as an aqueous phase process, where only dissolved chemical is available to biological degradation. In a review of numerous studies, Harms and Bosma [1997] concluded that organic contaminants need to be dissolved in the aqueous phase in order to be available for microbial consumption. Additionally, Fan et al. [2007] reported that some 17β-estradiol can be degraded to an unidentified polar metabolite in sterilized soil under anaerobic conditions, which indicated an abiotic degradation processes. It was not clear whether this abiotic process occurred in the sorbed or aqueous phase. Therefore, the transformation of 17β-estradiol into the unidentified polar metabolite was assumed to occur in both aqueous and sorbed phases. Although some studies [Colucci et al., 2001; Jacobsen et al., 2005] have shown that 5–14% of 17β-estradiol is mineralized to CO2 in soil in an aerobic environment, Fan et al. [2007] showed that less than 1% of 17β-estradiol is mineralized under reduced oxygen conditions in the same Hamar soil used in this study. The results from the soil column experiments of this study (presented later) also indicated that only 0.01% of 17β-estradiol was mineralized to CO2. To make the model simple, it was safe to assume in equations (1)–(3) that 17β-estradiol, estrone, and the unidentified polar metabolite would not undergo further mineralization. It should also be noted that the values in equations (1)–(4) have different meanings from those used in the equilibrium models of other studies [e.g., Casey et al., 2003; Mansell et al., 2004]. In the other studies, the values were associated with both reversible and irreversible sorbed phase, while the values of this study were only associated with the reversible sorption sites. Irreversible sorption of organic contaminants have been attributed to diffusion into soil micropores [Pignatello and Xing, 1996], or physical entrapment in soil organic matter [Huang and Weber, 1997]. Since 17β-estradiol and estrone have similar chemical structure, molecular size, and diffusion coefficients, it was reasonable to assume that the irreversible sorption rate constants (ω_{pr,1} and ω_{pr,2}) for 17β-estradiol and estrone were the same.

\[
\begin{align*}
\frac{-M S}{V} &= \frac{\partial [C^{14}C]}{\partial t} \\
S &= S_{r,1} + S_{r,2} + S_{r,3} + S_{pr,1} + S_{pr,2} + S_{pr,3}
\end{align*}
\]
The inverse problem for the batch experiments was sought to minimize the objective function $J$ that was defined as

$$J = \sum_{i=1}^{n} \sum_{j=1}^{n} w_{ij} \left( [C(14C)] - \bar{C}(14C) \right)^2$$

(6)

To estimate parameters of equations (1)–(4), appropriate constraints were needed for the aqueous and sorbed phases. Thin layer chromatography could not be used to obtain relative amounts of various estrogenic compounds owing to insufficient radioactivity in the aqueous phase of the batch studies. However, the appropriate constraints for the aqueous and sorbed phases could be independently obtained from the column experiments. The results of column experiments indicated that an unidentified polar metabolite and estrone contributed 70% and 25% of the aqueous $^{14}$C after a 2-day duration, respectively. Therefore, 70% and 25% of $^{14}$C in the aqueous phase was assumed to be the unidentified polar metabolite and estrone, respectively, at the time point of 48 h. Initial bounds for other parameters were determined based on previous studies [Casey et al., 2003, 2005; Das et al., 2004; Lee et al., 2003] and physical meanings. Taken together, equation (6) was subjected to the following constraints:

- $C(14C)_1 \rightarrow 0$ for $t = 48$h
- $C(14C)_2 = 7$ for $t = 48$h
- $C(14C)_3 = 3$ for $t = 48$h
- $M(14C)_{ir} = 35\% \times M(14C)_0$ for $t = 48$h
- $60.0(\text{h}^{-1}) \geq \omega_{h,1} \geq 10^{-7}(\text{h}^{-1})$, $60.0(\text{h}^{-1}) \geq \omega_{h,2} \geq 10^{-7}(\text{h}^{-1})$, $60.0(\text{h}^{-1}) \geq \omega_{l,1} \geq 10^{-7}(\text{h}^{-1})$, $60.0(\text{h}^{-1}) \geq \omega_{l,2} \geq 10^{-7}(\text{h}^{-1})$, $60.0(\text{h}^{-1}) \geq \alpha_1 \geq 10^{-7}(\text{h}^{-1})$, $60.0(\text{h}^{-1}) \geq \alpha_2 \geq 10^{-7}(\text{h}^{-1})$, $60.0(\text{h}^{-1}) \geq \omega_{l,3} \geq 10^{-7}(\text{h}^{-1})$, $60.0(\text{h}^{-1}) \geq \omega_{l,4} \geq 10^{-7}(\text{h}^{-1})$.

In equations (6) and (7), $n$ is the number of experiments; $l$ is the number of data for each experiment; $C(14C)_i$ is the experimental concentration of $^{14}$C; $\bar{C}(14C)_i$ is the predicted concentration of $^{14}$C; $C(14C)_1$, $C(14C)_2$, and $C(14C)_3$ are concentrations of $17/3$-estradiol, the unidentified polar metabolite, and estrone in the aqueous phase, respectively; $M(14C)_{ir}$ is the mass of $^{14}$C that is irreversibly sorbed; $M(14C)_0$ is the total applied mass of $^{14}$C; $t$ is the time (h); and $w_{ij}$ is a weighting function. For the batch experiments, $n$ was set to 3 representing the three initial concentrations of $^{14}$C (0.138, 0.069, and 0.015 mg L$^{-1}$); $l$ was set to 6 representing the six time points (0.5, 1, 5, 24, 48, and 168 h), and $w_{ij}$ was set to 1 meaning all the experimental data were treated equally.

### 3.3.2. Miscible-Displacement Experiments

A chemical nonequilibrium transport model with steady state flow, reversible and irreversible sorption, and degradation was used to describe the transport of $17/3$-estradiol and its metabolites in the columns [van Genuchten, 1985]. The following partial differential equations describe the transport model (Figure 4):

$$\theta \frac{\partial C_1}{\partial t} + \rho_b \frac{\partial \bar{S}_{r,1}}{\partial t} = \omega_{l,1} \frac{\partial^2 C_1}{\partial x^2} - \theta \frac{\partial C_1}{\partial x} - \omega_{l,1} \rho_b \bar{S}_{r,1} - \omega_{l,1 \alpha} \bar{S}_{r,1}$$

$$\theta \frac{\partial C_2}{\partial t} + \rho_b \frac{\partial \bar{S}_{r,2}}{\partial t} = \omega_{l,2} \frac{\partial^2 C_2}{\partial x^2} - \theta \frac{\partial C_2}{\partial x} + \omega_{l,2} \rho_b \bar{S}_{r,2} + \omega_{l,2 \alpha} \bar{S}_{r,2}$$

$$\theta \frac{\partial C_3}{\partial t} + \rho_b \frac{\partial \bar{S}_{r,3}}{\partial t} = \omega_{l,3} \frac{\partial^2 C_3}{\partial x^2} - \theta \frac{\partial C_3}{\partial x} + \omega_{l,3} \rho_b \bar{S}_{r,3}$$

(8)

where subscripts 1, 2, and 3 represent the parent compound $17/3$-estradiol, the unknown polar metabolite, and estrone, respectively; $\rho_b$ is soil bulk density (kg m$^{-3}$); $\theta$ is the volumetric water content (cm$^3$ cm$^{-3}$); $t$ is time (min); $x$ is distance (cm); $\lambda$ is dispersivity (cm); $v$ is the average pore water velocity (cm min$^{-1}$); and $\omega_{l,1}$, $\omega_{l,2}$, $\omega_{l,3}$, $\omega_{l,1 \alpha}$, $\omega_{l,2 \alpha}$, $\omega_{l,3 \alpha}$, $C$, $S_r$, and $S_{ir}$ are defined in equations (1), (2), and (3). Equations (1–3) are substituted into equation (8) to obtain column $\alpha$ values.

The inverse problem for the miscible-displacement experiments was sought to minimize the objective function $J$, which was defined as

$$J = \sum_{i=1}^{l} \left[ C(14C)_i - \bar{C}(14C)_i - \bar{C}(14C)_2 - \bar{C}(14C)_3 \right]^2$$

(9)

and subjected to the following constraints

$$10^{-7}(\text{h}^{-1}) \leq \alpha_1 \leq 60.0(\text{h}^{-1})$$

$$10^{-7}(\text{h}^{-1}) \leq \alpha_2 \leq 60.0(\text{h}^{-1})$$

$$10^{-7}(\text{h}^{-1}) \leq \alpha_3 \leq 60.0(\text{h}^{-1})$$

(10)

In equations (9) and (10), $l$ is the number of data for column experiments; $C(14C)_i$ is the detected outflow concentration of $^{14}$C; $\bar{C}(C_1)_i$, $\bar{C}(C_2)_i$, and $\bar{C}(C_3)_i$ are the predicted concentrations of $17/3$-estradiol, the unidentified polar metabolite, and estrone, respectively.

### 3.4. Modeling Results

#### 3.4.1. Batch Experiments

For batch experiments, the fitted results were good (Figure 1 and Table 1) and the parameter estimates had...
narrow 95% confidence intervals (Table 1), indicating high confidence in these parameters ($K_{d,1}$, $K_{d,2}$, $K_{d,3}$, $\omega_{w,1}$, $\omega_{w,2}$, $\omega_{w,3}$, $\omega_{w,p,1}$, $\omega_{w,p,2}$, $\omega_{w,p,3}$, $\alpha_1$, $\alpha_2$, and $\alpha_3$) and high confidence in the model accuracy. The estimated mass transfer coefficients for estrone and estradiol were similar to those estimated in the similar batch experiments for testosterone [Fan et al., 2007b], which has a similar chemical structure.

[23] The batch simulation results indicated that $17\beta$-estradiol was quickly degraded to estrone and the polar metabolite in the aqueous phase (the calculated half-life of $17\beta$-estradiol was less than 5 h), and then $17\beta$-estradiol's concentration continually decreased to nearly zero (Figure 1). Fast degradation rates of $17\beta$-estradiol are also reported by Casey et al. [2003, 2005] and Colucci et al. [2001]. However, Lim et al. [2007] reported longer timescales for degradation in a recharge aquifer system, with half-lives of 5.6 and 17.8 days under aerobic and anaerobic conditions, respectively. These differences might be caused by different moisture contents, temperatures, and/or nutrient conditions [Colucci et al., 2001]. These results also indicated that 100% of polar metabolite on the sorbed phase was associated with the reversible sorption sites, while 100% and 94% of $17\beta$-estradiol and estrone on the sorbed phase were associated with the irreversible sorption sites, respectively. This result would be reasonable because the unidentified polar metabolite was likely to be more soluble, and thus less attracted to the soil particles.

[26] The results also indicated that the mass transfer coefficient ($\alpha$) of $17\beta$-estradiol was approximately four times greater than that of estrone, despite their similar chemical structures (Table 1). This might be caused by $17\beta$-estradiol competing strongly with estrone for limited sorption sites. As $17\beta$-estradiol was transported with the soil-water, it would transform into estrone and a polar metabolite. Many of the potential estrone sorption sites had already been occupied by $17\beta$-estradiol, thus resulting in a lower $\alpha$ for estrone compared to $17\beta$-estradiol.

### 3.4.2. Miscible-Displacement Experiments

[27] Both chloride breakthrough curves for the two columns were successfully fitted with equation (8) by setting $\omega_{w,1}$, $\omega_{w,2}$, $\omega_{w,p,1}$, $\omega_{w,p,2}$, $\omega_{w,p,3}$, $K_{d,1}$, $K_{d,2}$, $K_{d,3}$, $\alpha_1$, $\alpha_2$, and $\alpha_3$ equal to 0, and optimizing dispersivity, $\lambda$. Reasonable $\lambda$ values were obtained (Table 1), which further indicated the lack of physical nonequilibrium transport. These $\lambda$ values were then used to model $17\beta$-estradiol and its metabolites. Furthermore, the sorption and degradation parameters ($\omega_{w,1}$, $\omega_{w,2}$, $\omega_{w,p,1}$, $\omega_{w,p,2}$, $\omega_{w,p,3}$, $K_{d,1}$, $K_{d,2}$, and $K_{d,3}$) used to model $17\beta$-estradiol and its metabolites were set equal to values estimated from the batch studies and held constant. Therefore, only three parameters (i.e., $\alpha_1$, $\alpha_2$, and $\alpha_3$) were estimated, which greatly reduced any uncertainty of these parameter estimates. Additionally, the SRES global optimization technique ensured the most reliable parameter estimates [Fan and Casey, 2008]. The resulting parameter estimates (Table 1) all had low 95% confidence intervals, which further indicated the high confidence and uniqueness of these parameter values.

[28] The estimated mass transfer rates ($\alpha_1$, $\alpha_2$, and $\alpha_3$) from the columns were lower for $17\beta$-estradiol and estrone compared to the batch values. Also, the unidentified polar metabolite $\alpha$ values were higher for the column compared to the batch values. The lower $\alpha$ values may have indicated a slower exchange between the reversibly sorbed phase and the aqueous phase [Zheng and Bennett, 2002], and/or a higher solid-to-solution ratio [Environmental Protection Agency (EPA), 1999]. There are two possible effects of a high solid-to-solution ratio. First, complexing agents such as soil organic matter would desorb from the soil matrix into solution [EPA, 1999] and facilitate the transport of organic compounds with high sorption affinity (e.g., $17\beta$-estradiol and estrone) [McGeochan and Lewis, 2002]. Such effect will increase with the increase in solid-to-solution ratio (e.g., column studies) and hydrophobicity. Second, individual soil particles tend to flocculate to form closed pores and irregularly shaped pores, which would reduce the desorption of $17\beta$-estradiol and estrone owing to steric hindrance [Pignatello and Xing, 1996]. The solid-to-solution ratio would have a stronger effect on the sorption of $17\beta$-estradiol than its metabolites, because $17\beta$-estradiol and estrone were bound more strongly and quickly to soil particles compared to the polar metabolite [Casey et al., 2003]. Additionally, the polar metabolite may tend to be more readily transported and eluted from the soil column because of its higher water solubility. As a result, the polar metabolite, sorbed to the reversible sorption sites, would desorb back into the aqueous phase to maintain equilibrium between the aqueous and reversibly sorbed phases. Therefore, the mass exchange between the aqueous and reversibly sorbed phase would be more rapid for the polar metabolite in the column compared to the batch studies, resulting in a higher $\alpha$ value for the polar metabolite.

[29] The column estimate of $\alpha$ for $17\beta$-estradiol was approximately three times lower than the estrone value (Table 1). These were also lower than the batch estimates of $\alpha$, which indicated that the $17\beta$-estradiol $\alpha$ was four times greater than estrone value (Table 1). The lower $\alpha$ values in the column compared to the batch can be caused by mass transfer limitations, where the flowing water in the soil column would limit the diffusive exchange with the soil surface. Additionally, the difference between the $17\beta$-estradiol and estrone $\alpha$ values in the column could have resulted from the assumption that the soil was uniform and that the estimated $\alpha$ values were the same throughout the soil column. In reality, the columns were undisturbed and the organic matter was not evenly distributed with depth, while the batch soil was homogenized. Since $17\beta$-estradiol was quickly degraded to estrone, both compounds would compete for the sorption sites at the top part of soil column (especially top 5 cm). At the lower part of the column, estrone and the polar metabolite would only be present (recall $17\beta$-estradiol was not present in effluent), resulting in a higher $\alpha$ value for estrone because there was limited competitive sorption.

### 3.4.3. Model Evaluation

[30] A final test of the model and the parameter estimates was to use them in a forward fashion to predict the relative concentrations of the reversible and irreversible sorbed $^{14}$C concentrations (Figure 3). The overall prediction was good and the prediction was better for Experiment 2 compared to Experiment 1. The better prediction of Experiment 2 was likely caused by the addition of HgCl$_2$ at the end of the experiment to eliminate hormone loss from biodegradation. Discrepancies between the observed and predicted results from both experiments could have been caused by a failure...
to fully extract all the $^{14}$C bound to the soil. Nonetheless, this good forward prediction of $^{14}$C redistribution in the column exemplifies the appropriateness of the modeled processes and the parameter estimates.

4. Conclusions

[31] The model proposed in this study was successful in identifying and quantifying the fate and transport 17$\beta$-estradiol in the controlled laboratory batch and column experiments. However, the laboratory determined processes and rates are based on chemical, biological, and physical properties of soil, which are inherently variable across space and time in the environment. A major challenge in applying these process models to field situations is the identification of meaningful process rates, and scaling (up or down) these rates through space and time. For example, Alexander [1985] suggested that biodegradation rates of organic contaminants positively related to the initial concentrations of these contaminants, and the rates obtained at high concentrations in the lab could be used to predict the rates in the field where concentrations may be low (if such relationship was known). Alexander [1985] also suggested that the mineralization could be inhibited when the concentration of organic compounds in soils, water, or sediments was below a certain threshold value. Therefore, to identify the threshold values and the relationship between the concentration and biodegradation rate would be helpful for implementing management strategies and evaluating risk. This type of strategy can be used for other processes, such as sorption, that can control the fate and transport of 17$\beta$-estradiol.

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