Modeling coupled sorption and transformation of 17β-estradiol–17-sulfate in soil–water systems

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A R T I C L E   I N F O

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A B S T R A C T

Animal manure is the primary source of exogenous free estrogens in the environment, which are known endocrine-disrupting chemicals to disorder the reproduction system of organisms. Conjugated estrogens can act as precursors to free estrogens, which may increase the total estrogenicity in the environment. In this study, a comprehensive model was used to simultaneously simulate the coupled sorption and transformation of a sulfate estrogen conjugate, 17β-estradiol–17-sulfate (E2–17S), in various soil–water systems (non-sterile/sterile; topsoil/subsoil). The simulated processes included multiple transformation pathways (i.e., hydroxylation, hydrolysis, and oxidation) and mass transfer between the aqueous, reversibly sorbed, and irreversibly sorbed phases of all soils for E2–17S and its metabolites. The conceptual model was conceived based on a series of linear sorption and first-order transformation expressions. The model was inversely solved using finite difference to estimate process parameters. A global optimization method was applied for the inverse analysis along with variable model restrictions to estimate 36 parameters. The model provided a satisfactory simultaneous fit ($R^2_{adj} = 0.93$ and $d = 0.87$) of all the experimental data and reliable parameter estimates. This modeling study improved the understanding on fate and transport of estrogen conjugates under various soil–water conditions.

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1. Introduction

Estrogenic hormones are excreted from humans and animals as intact molecules, which are mostly in conjugated forms of glucuronide and/or sulfate (Johnson and Williams, 2004). Unconjugated or free estrogenic hormones are known as potent endocrine-disrupting chemicals, because they can cause adverse effects to reproduction system of aquatic life at part-per-trillion levels (Irwin et al., 2001; Jobling et al., 1998; Panter et al., 1998). Estrogen conjugates can act as precursors to free estrogens and increase the total estrogen load in the environment via deconjugation. 17β-Estradiol (E2) is the most potent natural estrogen that is frequently detected in the environment, and sulfate (Bai et al., 2013; Scherr et al., 2009) and glucuronide (Shrestha et al., 2012) conjugates of E2 have drawn increasing attention as potential precursors to free E2. Compared to other estrogen conjugates, the sulfate conjugate, 17β-estradiol–17-sulfate (E2–17S), is of particular importance because it was detected at relatively high concentrations in animal manure lagoons (87 ng L$^{-1}$) (Hutchins et al., 2007) and in surface runoff after manure application (107 ng L$^{-1}$) (Dutta et al., 2012). Bai et al. (2013) studied the fate of E2–17S in agricultural soils and found that E2–17S underwent coupled sorption and transformation pathways, forming multiple metabolites including free estrogens. However, advanced mathematical models are necessary to fully understand the processes governing the fate and transport of E2–17S and its potential to be a precursor to free estrogens in the environment.

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Mathematical models have been used to predict the behavior of reactive steroid hormones in soil batch and column studies. Das et al. (2004) applied a forward modeling approach (predictive mode) to predict sorption and degradation of several steroid hormones in soil columns. This two-region modeling approach consisted of advective-dispersive transport with non-equilibrium, two-site sorption, and first-order transformation mechanisms. Their results suggested that the first-order kinetic process was sufficient for modeling hormone degradation, but not accurate. Casey et al. (2003) used two convective-dispersive transport models, with and without transformation, and two-site kinetic Freundlich sorption to fit breakthrough curves of E2 from miscible-displacement experiments. The modeling results provided good descriptions of the experimental data, but solutions were non-unique, and parameter estimates had low confidence. Another study by Casey et al. (2004) applied a one-site fully kinetic convective-dispersive model with sorbed phase transformation and Freundlich sorption to simulate the fate of testosterone in soils, which resulted in satisfactory fits and reasonable parameter estimates.

These previous studies considered a two-phase system (aqueous and reversibly sorbed phases) for sorption and degradation of hormones; however, later studies reported that a significant fraction of the applied steroid hormones became irreversibly bound to soil (Colucci et al., 2001; Fan et al., 2007b). Without considering irreversible sorption, the models may give rise to inaccurate descriptions. Additionally, the previous models provided parameter estimates of relatively low confidence. To improve the modeling techniques for labile steroid hormones, Fan et al. (2008) developed a one-site kinetic sorption and first-order transformation model to simulate the distribution of E2 in the aqueous, reversibly sorbed, and irreversibly sorbed phases of soils simultaneously. The model was inversely solved using the stochastic ranking evolutionary strategy (SRES) (Runarsson and Yao, 2000), a global optimization method. The one-site model provided satisfactory fits to the data with unique solutions, which advanced the understanding of fate and transport processes of E2 (Fan et al., 2008).

As a result of their labile nature and coupled governing processes, a complete understanding of the fate and transport of conjugated hormones is difficult to achieve with experimental observations alone. Advanced modeling approaches can be used to better understand the behavior of estrogen conjugates and identify key processes forming free estrogens. Herein, the objective of this study was to develop and apply an integrated modeling approach (Fan et al., 2008) to discern and quantify the coupled sorption and transformation mechanisms of E2–17S and its multiple metabolites based on soil batch experiments.

2. Soil batch experiments

2.1. Methods

The soils were collected from southeastern North Dakota, and were similar to those used in previous laboratory (Fan et al., 2007a,b, 2008; Shrestha et al., 2012) and field (Schuh et al., 2011a,b; Thompson et al., 2009) studies on the fate and transport of hormones. The soils were mapped as a Hecla–Hamar Series (sandy, mixed, frigid Oxyaquic Hapludolls) and were collected from two depths, denoted as topsoil (0–15 cm) and subsoil (46–61 cm). Most properties of the topsoil and subsoil were similar except for soil organic carbon (OC) content (Table 1).

To conduct the soil batch studies using both non-sterile and sterile soils, 1.6 g soil was mixed with 8 mL of 0.1 M CaCl2 solution; and irradiation for 14 h using a 7.6 kGy gamma source (M38-4 Gammaray, Radiation Machinery Corp., Parsippany, NJ) was the means to sterilize the soil–water slurries. Synthesized radiolabeled [14C]E2–17S (Shrestha et al., 2011) was injected to the soil–water slurries to reach an initial concentration of 0.5 mg L−1. At times of 4, 8, 24, 48, 72, 168, and 336 h, samples were collected from the aqueous and reversibly sorbed (extractable fraction) phase of the batch vials and analyzed for the parent and metabolite compound concentrations using a combined high performance liquid chromatography (HPLC; Beckman Coulter Inc., Fullerton, CA) and liquid scintillation counting (LSC; 1900 CA, Packard, Downers Grove, IL) method (Shrestha et al., 2013). The detected metabolites were characterized by liquid chromatography with tandem mass spectroscopy (LC-MS/MS; Waters, Beverly, MA). For the irreversibly sorbed (non-extractable fraction) phase, radioactive residue was measured by soil combustion using a Packard Model 307 Oxidizer (Downers Grove, IL). All experimental procedures and analytical methods are thoroughly described in other studies (Bai et al., 2013, in press; Shrestha et al., 2013).

2.2. Experimental results

The batch experimental results showed the parent compound, E2–17S, dissipating more quickly from the aqueous phase of the topsoil (Fig. 1a and b) compared to the subsoil (Fig. 1c and d) regardless of soil sterility, which demonstrated the significant role that soil OC played. The primary transformation pathway for E2–17S was found to be hydroxylation, forming mono-hydroxy–E2–17S (OH–E2–17S) and di-hydroxy–E2–17S (diOH–E2–17S) as major metabolites. The aqueous concentrations of the hydroxylated metabolites were slightly higher in the topsoil (Fig. 1a and b) compared to the subsoil (Fig. 1c and d) under both non-sterile and sterile conditions. The reversibly sorbed radioactive residue (Fig. 1e–h) remained at relatively low levels (<15% of applied dose). Free estrogens, E2 and estrone (E1), were observed from the reversibly sorbed phase in addition to the hydroxylated metabolites (Fig. 1e–h), demonstrating that deconjugation of E2–17S had occurred. The irreversibly sorbed radioactive residue was found greater for the topsoil (Fig. 1e and f) than the subsoil (Fig. 1g and h), and irreversible sorption appeared to be the predominant sorption process under all conditions. The overall radioactive recoveries were more than 90% for all soils, which were acceptable for the following model simulation.

<table>
<thead>
<tr>
<th>Table 1 Selected properties of soil samples.</th>
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<td>Depth (cm)</td>
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<td>Organic matter (OM) (%)</td>
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<td>Organic carbon (OC) (%)</td>
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<td>Inorganic carbon (IC) (%)</td>
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<td>pH</td>
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<td>Cation exchange capacity (CEC) (cmol, kg⁻¹)</td>
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<td>Sand:silt:clay (%)</td>
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<td>MnO₂ (μg g⁻¹)</td>
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</table>
3. Modeling approach

3.1. Conceptual model development

In order to simultaneously describe the distribution of all observed compounds in the aqueous, reversibly sorbed, and irreversibly sorbed phases of all soils (non-sterile/sterile, topsoil/subsoil), a one-site model with linear kinetic sorption and first-order transformation was developed. Linear sorption isotherms have been applied to efficiently describe hormone sorption in soils (Das et al., 2004; Fan et al., 2007a); and first-order kinetic transformation was sufficient to modeling...
hormone transport (Das et al., 2004; Fan et al., 2008). Given the complexity of the present observations, the one-site kinetic model was chosen to reduce the total numbers of parameters.

The schematic conceptual model is shown in Fig. 2, where several assumptions were applied to conceive the model:

The first assumption was that the formation of OH–E2–17S and diOH–E2–17S occurred simultaneously following parallel reactions. The hydroxyl positions could not be characterized for OH–E2–17S and diOH–E2–17S, and the hydroxylation mechanisms were not known. One possible mechanism for E2–17S hydroxylation is enzymatic catalysis. Mono- and di-oxygenases (e.g. cytochromes P450) in soils can add one and two hydroxyl groups to steroids, respectively (Ullrich and Hofrichter, 2007). Also, oxidation catalyzed by metal-oxides (e.g. MnO₂) is likely to be another hydroxylation mechanism (Bai et al., in press). However, the interactions between enzyme and metal-oxides mediated hydroxylation are not understood. To further verify the hypothesis with the parallel reactions, two conceptual models were developed using either a parallel or stepwise hydroxylation pattern, and the model fit was more satisfactory with the parallel rather than the stepwise pattern, meaning a more reasonable assumption.

The second assumption was that deconjugation/hydrolysis of E2–17S occurred on the soil surface. Free estrogens, E2 and E1, were not detected in the aqueous phase during the entire batch experiments; however, they were only observed on the reversibly sorbed phase for all soils, indicating a solid phase process. After E2–17S hydrolysis, the released E2 can be subsequently oxidized to yield E1, which is demonstrated to be a surface process (Sheng et al., 2009). Several studies have also provided evidence for sorbed phase transformation of E2 (Casey et al., 2003; Layton et al., 2000). Therefore, it was appropriate to assume that hydrolysis of E2–17S and oxidation of E2 both occurred on the solid phase.

The third assumption was that only hydrophobic free estrogens (E2 and E1) were present on the irreversibly sorbed phase. According to Fan et al. (2008), most of the hydrophobic compounds would be associated with irreversible sorption sites, but polar metabolites would bind to reversible sites only. In the current conceptual model the less hydrophobic compounds, E2–17S, OH–E2–17S, and diOH–E2–17S, were assumed to be present in the reversibly sorbed phase only. For the irreversibly sorbed phase, only total radioactive residue could be measured using combustion analysis; therefore, the more hydrophobic metabolites, E2 and E1, were considered bound both reversibly and irreversibly to the soil surface.

Additionally, in previous studies with similar soil–water systems, mineralization of E2 (Fan et al., 2007b) and E2 glucuronide conjugate (Shrestha et al., 2012) did not occur, and thus gas phase distribution was not considered in the present model. Incorporating the three assumptions above, the one-site kinetic sorption and first-order transformation model

![Diagram](image)

Parameters include linear sorption coefficient $K_d$ (L g⁻¹); first-order transformation rate coefficients in the aqueous and reversibly sorbed phase $\omega_w$ and $\omega_r$ (h⁻¹); mass transfer rate constant between the aqueous and reversibly sorbed phase $\alpha$ (h⁻¹); and mass transfer rate constant between the reversibly and irreversibly sorbed phase $\beta$ (h⁻¹).

**Fig. 2.** Schematic conceptual model for sorption and transformation processes of [¹⁴C]17β-estradiol–17-sulfate and its multiple metabolites in the aqueous, reversibly sorbed, and irreversibly sorbed phases in the soil–water systems.
A model was developed to describe the fate of E2–17S and its metabolites as a series of differential equations (Eqs. (1)–(3)):

\[
\begin{align*}
\frac{dC_{E2S}}{dt} &= -\omega_{w,1}C_{E2S} - \omega_{w,2}C_{E2S} - \frac{M}{V} \alpha_1 \left( K_{d,1}C_{E2S} - S_{E2S} \right) \\
\frac{dS_{OHE2S}}{dt} &= \omega_{w,1}C_{E2S} - \frac{M}{V} \alpha_2 \left( K_{d,2}C_{OHE2S} - S_{OHE2S} \right) \\
\frac{dS_{OHE2S}}{dt} &= \omega_{w,2}C_{E2S} - \frac{M}{V} \alpha_3 \left( K_{d,2}C_{OHE2S} - S_{OHE2S} \right) \\
\end{align*}
\]

The differential equations (Eqs. (1)–(3)) were inversely solved using a finite difference method, CVODE (Cohen and Hindmarsh, 1994) that was written in C using libSRES (Ji and Xu, 2006), and a time step of 6 s was applied for computation. In the present study, local optimization was not suitable due to the nonlinearity of the mathematical model and the large numbers of parameters (Fan and Casey, 2008). The parameters were thus optimized with a global optimization method, SRES, which has been successfully used for parameter estimation in previous studies (Fan and Casey, 2008; Fan et al., 2007a, 2008). Using the global optimization method, the following objective function (Eq. (5)) was minimized:

\[
J = \sum_{i=1}^{l} \sum_{j=1}^{m} \sum_{k=1}^{n} \left( O - P \right)^2.
\]

In the objective function, \( O \) is the observed value, \( P \) is the predicted value, \( l = 4 \) indicating four soils, \( m = 7 \) indicating seven sampling time points (i.e. 4, 8, 24, 48, 72, 168, and 336 h), and \( n = 13 \) representing all compounds in the three phases of each soil, which was equal to the number of differential equations for each soil. All data were treated equally with weight of unity.

### 3.3. Constraints on model processes and parameters

The model simulated all governing processes in the aqueous, reversibly sorbed, and irreversibly sorbed phases of all soils simultaneously, which reduces confidence intervals of optimized parameters and provides more reliable determination (Casey and Simunek, 2001). Simultaneous fit for all soil conditions also allows additional constraints that improve uniqueness of parameter estimates (Casey and Simunek, 2001). The objective function (Eq. (5)) was thus subjected to the following constraints (Eqs. (6)–(8)) to best ensure that the appropriate processes were modeled and that unique sets of parameters were optimized.

\[
\begin{align*}
K_{d,topsoil} &< K_{d,subsoil} \\
K_{d,E2S} &< K_{d,OHE2S} = K_{d,OHE2S} \\
\omega_{w,soil} &< \omega_{w,subsoil}
\end{align*}
\]

The observed faster aqueous dissipation of E2–17S in the topsoil compared to the subsoil was attributed to the greater sorption and transformation rates (Bai et al., 2013, in press). Soil OC is the primary sorption domain for estrogenic compounds (Sarmah et al., 2008); therefore, the \( K_d \) values for E2–17S and its metabolites were constrained to be greater in the topsoil of higher OC (Eq. (6)). Furthermore, sorption of steroid hormones to soil is governed by hydrophobic interactions (Das et al., 2004; Yu et al., 2004), where the \( K_d \) values for E2–17S are inversely correlated to compound polarities. Compound polarity was inferred by the reverse-phase HPLC elution times, which was the following (in order of highest to lowest polarity): diOH–E2–17S, OH–E2–17S, and E2–17S. A constraint was added to include the inverse relation between compound polarity and \( K_d \), where the \( K_d \) values for E2–17S were set greater than the hydroxylated metabolites (Eq. (7)). Furthermore, the \( K_d \) values of the two hydroxylated metabolites were set equal.
(Eq. (7)) because they have similar molecular structures, and their HPLC elution times were close (approximate 4 and 6 min for diOH–E2–17S and OH–E2–17S, respectively). Setting $K_d$ values equal for the two hydroxylated metabolites further reduced the total numbers of parameters and increased parameter confidence.

Restrictions were also given to the transformation rate constants, $\omega_w$ and $\omega_s$ in the aqueous and reversibly sorbed phase, respectively. Compared to subsoil, topsoil had higher OC and thus higher microbial and enzymatic activities (Watts et al., 2010), which would cause greater transformation. Also, the measured MnO$_2$ was higher for topsoil than subsoil (Table 1), causing more rapid metal oxides–promoted reactions. Moreover, the detected metabolite concentrations were consistently higher for the topsoil than the subsoil; therefore, both $\omega_w$ and $\omega_s$ values were set greater for the topsoil (Eq. (8)). In addition to these major constraints, the $K_d$, $\omega_s$, $\alpha$, and $\beta$ values were set to be equal for non-sterile and sterile conditions because gamma irradiation would not alter the total soil OC content or soil minerals (Shrestha, 2011).

### 3.4. Parameter optimization and goodness-of-fit

To optimize the computational time, the program was initially run with a lower bound of $1.00 \times 10^{-8}$ and an upper bound of 1.00 until parameter values stabilized. The parameters were then refined by new upper and lower bounds as 3 and 0.3 times the old values until there were no more changes in the parameter estimates (Shrestha, 2011). The final simulation was run 30 times to compute the 95% confidence intervals, which was twice the standard deviation of the 30 optimized values. For model evaluation, two statistical indices were used to determine the goodness-of-fit, the adjusted coefficient of determination ($R^2_{adj}$) and the modified index of agreement $d$ (Willmott et al., 1985). The $d$ value was calculated as follows (Eq. (9)):

$$d = 1 - \frac{\sum |O_i - P_i|}{\sum (|P_i - \bar{O}| + |O_i - \bar{O}|)}$$

where $O_i$ is the observed value; $P_i$ is the predicted value; and $\bar{O}$ is the mean of all observed values. The $d$ value ranges from 0 to 1, and 1 indicates a perfect fit (Helmk et al., 2004; Legates and McCabe, 1999; Shrestha, 2011).

### 4. Results and discussion

#### 4.1. Model fit

In general, the model provided an excellent fit for the measured data under all soil conditions. The goodness-of-fit was shown by the $R^2_{adj}$ value (0.93) and the $d$ value (0.87) calculated from the simultaneous fit of all measured data. The satisfactory fit demonstrated that the assumptions made in the conceptual model were suitable to describe the governing processes of all compounds. The model successfully captured the overall trends of E2–17S in the aqueous phase for all soils (Fig. 1a–d); but underestimated the aqueous levels of E2–17S at the end time point (336 h) for the two subsoils (Fig. 1c and d). It suggested that sorption kinetics were more significant than transformation, because the aqueous concentrations of E2–17S converged to reach steady-state rather than rapidly decreasing as the model results showed. Additionally, the model provided good approximations of the aqueous hydroxylated E2–17S concentrations (Fig. 1a–d), except for the late stages (after 168 h) of the non-sterile topsoil (Fig. 1a) and sterile topsoil (Fig. 1b), where diOH–E2–17S concentrations were overestimated, and OH–E2–17S concentrations were slightly underestimated. These deviations may be caused by the assumption that the unidentified scatters ($X$) were produced from OH–E2–17S rather than from diOH–E2–17S (Fig. 2), and as a result, the simulated concentrations of OH–E2–17S were lower than the observed data.

For the sorbed phase (Fig. 1e–h), the model could describe the total radioactive residue distribution under all soil conditions. Deviations were found for the irreversibly sorbed phase, where the model appeared to overestimate the irreversibly sorbed radioactivity at the late stages (72 to 336 h) for all soils. These deviations may be due to the incomplete soil combustion causing the mass balance to be ~90%, whereas the model considered the recovery to be 100% and resulted in overestimated distribution on the irreversible sorption sites. Additionally, the one-site fully kinetic sorption would not take into consideration other complex sorption processes (e.g. instantaneous sorption), which may have contributed to the observed disagreements between the modeled and measured sorbed concentrations at the initial stages (4–8 h; Fig. 1f–h) of the batch experiments. Nonetheless, considering the multiple restrictions and forced simultaneous fit, the model succeeded in capturing the overall time-series disposition of the multiple compounds in the aqueous and sorbed phases of all soils.

#### 4.2. Parameter estimates

All estimated parameters are listed in Table 2 with their 95% confidence intervals. Generally, compared to the previous study to estimate 12 parameters (Fan et al., 2008), the one-site kinetic model was demonstrated to be able to simulate more complex scenarios with larger numbers (36) of parameters. The 95% confidence intervals for $K_d$, $\omega_w$, $\omega_s$, and $\alpha$ were narrow, indicating high confidence. The estimated $K_d$ values for E2–17S and its hydroxylated metabolites were similar, which was reasonable because the polarities for the parent and metabolite compounds were similar, as inferred by the HPLC elution times. According to the estimated hydroxylation rate constants ($\omega_w$), the corresponding half-lives of E2–17S were 7.53, 99.0, 231, and 693 h for the non-sterile topsoil, sterile topsoil, non-sterile subsoil, and sterile subsoil, respectively; which were greater than the half-life (i.e. 5 h) for free E2 reported by Fan et al. (2008) using non-sterile topsoil. The longer half-life for E2–17S demonstrated greater persistence in the soil–water systems than its free counterpart E2. Moreover, the hydroxylation rates were estimated to be 1 to 2 orders of magnitude greater in the topsoils than the subsoils. Compared to hydroxylation, deconjugation/hydrolysis of E2–17S was estimated to be 1 to 2 orders of magnitude lower for all soils, indicated by the $\omega_s$ values for E2–17S. Previous studies have reported that hydrolysis is not a primary transformation pathway for the sulfate conjugates, E2–17S (Bai et al., 2013) and E2–35 (Scherr et al., 2009) in agricultural soils. The present modeling results gave further evidence that E2–17S was resistant to hydrolysis in the soil–
Table 2

Parameter estimates for [14C]17\textsuperscript{-}estradiol–17-sulfate and its metabolites in various soil–water systems. The values inside the parentheses represent the 95% confidence interval of the estimated parameter.

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<td><strong>Non-sterile topsoil</strong></td>
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<tr>
<td>(K_a) (L g(^{-1}))</td>
<td>2.8 (2.7, 2.9) ((\times 10^{-1}))</td>
<td>2.8 (2.7, 2.9) ((\times 10^{-1}))</td>
<td>2.8 (2.7, 2.9) ((\times 10^{-1}))</td>
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<tr>
<td>(\omega_{a,1}) (h(^{-1}))</td>
<td>7.1 (6.8, 7.4) ((\times 10^{-2}))</td>
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<tr>
<td>(\omega_{a,2}) (h(^{-1}))</td>
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<tr>
<td>(\alpha) (h(^{-1}))</td>
<td>0.92 (0.27, 1.57)</td>
<td>0.87 (−0.04, 1.78)</td>
<td>0.87 (−0.04, 1.78)</td>
<td>0.16 (−0.01, 0.33)</td>
<td>0.62 (−0.03, 1.27)</td>
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<td>(\beta) (h(^{-1}))</td>
<td>4.4 (2.0, 6.7)</td>
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<td>2.8 (2.7, 2.9) ((\times 10^{-1}))</td>
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<td>(\beta) (h(^{-1}))</td>
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<td>0.16 (−0.01, 0.33)</td>
<td>0.62 (−0.03, 1.27)</td>
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<td>(\omega_{a,2}) (h(^{-1}))</td>
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<td>0.71 (0.13, 1.3)</td>
<td>0.89 (0.42, 1.4)</td>
<td>1.7 (0.7, 2.8)</td>
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<tr>
<td>(K_a) (L g(^{-1}))</td>
<td>1.4 (1.3, 1.4) ((\times 10^{-1}))</td>
<td>1.3 (1.3, 1.4) ((\times 10^{-1}))</td>
<td>1.3 (1.3, 1.4) ((\times 10^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\omega_{a,1}) (h(^{-1}))</td>
<td>4.3 (3.6, 5.1) ((\times 10^{-4}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\omega_{a,2}) (h(^{-1}))</td>
<td>6.5 (5.8, 7.3) ((\times 10^{-4}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha) (h(^{-1}))</td>
<td>1.7 (1.6, 1.7) ((\times 10^{-4}))</td>
<td>1.8 (0.7, 2.9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\beta) (h(^{-1}))</td>
<td>1.2 (0.5, 1.9)</td>
<td>0.71 (0.13, 1.3)</td>
<td>0.71 (0.13, 1.3)</td>
<td>0.89 (0.42, 1.4)</td>
<td>1.7 (0.7, 2.8)</td>
</tr>
</tbody>
</table>

\(K_a\) is the linear sorption coefficient. \(\omega_{a,1}\) and \(\omega_{a,2}\) are the first-order transformation rate coefficients in the aqueous and reversibly sorbed phase respectively. \(\alpha\) and \(\beta\) are the mass transfer rate constants between the aqueous and reversibly sorbed phase, and the reversibly and irreversibly sorbed phase, respectively.

5. Conclusions

A comprehensive model was developed to simultaneously simulate the coupled sorption and transformation of E2–17S and its metabolites in the aqueous, reversibly sorbed, and irreversibly sorbed phases in various soil–water systems. This model successfully identified and quantified the multiple governing processes, which could not be determined from experimental data alone. Given that all of the parameters were estimated simultaneously, the parameters were of acceptable confidence and uniqueness. Although the assumptions may provide challenges in applying the model to conditions such as column studies and field scale studies, the model has given significant insights in understanding the fate and transport processes of manure-borne estrogen conjugates. These insights can lead to a better understanding of how conjugated hormones can serve as precursors to potent free hormones in the environment, perhaps leading to better manure management practices.

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References


