



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



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ABSTRACT

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, 17 β -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 ($R^2_{\text{adj}} = 0.93$ 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 wildlife 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. 17 β -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, 17 β -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 Gammator, 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 1
Selected properties of soil samples.

	Topsoil	Subsoil
Depth (cm)	0–15	46–61
Organic matter (OM) (%)	1.70	0.50
Organic carbon (OC) (%)	1.29	0.26
Inorganic carbon (IC) (%)	0.00	0.00
pH	7.0	7.4
Cation exchange capacity (CEC) (cmol _c kg ⁻¹)	9.3	9.8
Sand:silt:clay (%)	83:10:7	90:4:6
MnO ₂ (μg g ⁻¹)	292	223

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