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Testosterone sorption and desorption: Effects of soil particle size

Yong Qi[a,*], Tian C. Zhang[a], Yongzheng Ren[b]

[a] Civil Engineering Dept., University of Nebraska-Lincoln at Omaha Campus, Omaha, NE 68182, USA
[b] School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

HIGHLIGHTS

- Smaller soil particles have higher sorption and lower desorption rates.
- The sorption capacity ranks as clay > silt > sand.
- Small particles like clays have less potential for desorption.
- Colloids (clays) have high potential to facilitate the transport of hormones in soil–water environments.

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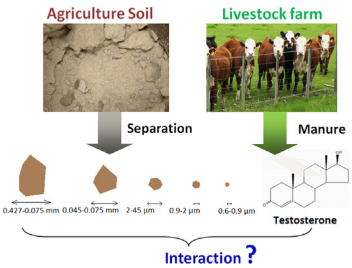
GRAPHICAL ABSTRACT



ABSTRACT

Soils contain a wide range of particles of different diameters with different mobility during rainfall events. Effects of soil particles on sorption and desorption behaviors of steroid hormones have not been investigated. In this study, wet sieve washing and repeated sedimentation methods were used to fractionate the soils into five ranges. The sorption and desorption properties and related mechanisms of testosterone in batch reactors filled with fractionated soil particles were evaluated. Results of sorption and desorption kinetics indicate that small soil particles have higher sorption and lower desorption rates than that of big ones. Thermodynamic results show the sorption processes are spontaneous and exothermal. The sorption capacity ranks as clay > silt > sand, depending mainly on specific surface area and surface functional groups. The urea control test shows that hydrogen bonding contributes to testosterone sorption onto clay and silt but not on sand. Desorption tests indicate sorption is 36–65% irreversible from clay to sand. Clays have highest desorption hysteresis among these five soil fractions, indicating small particles like clays have less potential for desorption. The results provide indirect evidence on the colloid (clay)-facilitated transport of hormones (micro-pollutants) in soil environments.

1. Introduction

Recently, there has been an increasing concern about steroid hormones in the environment. Koplin et al. [1] reported that reproductive hormones were found in approximately 40% of the 139 streams sampled across 30 states in the United States. Synthetic steroid hormones and their metabolites have been detected in cattle waste [2]. Testosterone has been detected in sediments 45 m below a dairy-farm wastewater lagoon [3]. The primary steroid hormones are estrogen, estradiol, progesterone, testosterone and cortisol [4]. Excess amounts of hormones in the environment are hazardous due to their potential to cause adverse health effects in humans and wildlife [5]. Soil has been identified as a medium to retain steroid hormones [6]. Being lipophilic in nature with most of their $\log K_{ow}$ being 2.6–4.0 [7–9], most steroid hormones are expected to be sorbed on soils and/or organic matter and are unlikely to be very mobile. However, this conclusion cannot explain the frequent detections of hormones in ground and surface water, which is difficult to be explained with our knowledge obtained from traditional tests on sorption–desorption behaviors of hormones

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* Corresponding author. Tel.: +1 4022051688.
E-mail addresses: yqi01@unomaha.edu, wqzxqiyong@126.com (Y. Qi).

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[10,11]. This is because although soils contain a wide range of particles of different diameters with different mobility during rainfall events, most of the traditional tests were conducted with soil mixtures that lumped all soil particles in the same samples. Therefore, these tests may not provide comprehensive information on what kind of soil particles contribute more to hormone transport in runoff or leachate, and what are the mechanisms associated with these different contributions.

On the other hand, when studying the sorption capacity and mobility of soil particles for other contaminants, some researchers proposed to separate bulk soils into different size fractions to make better predictions of transport of sorbed contaminants in groundwater [12]. The colloidal particles in runoff after storm was reported to facilitate the transport of phosphorus and other contaminants [13]. It was reported that some strongly adsorbed contaminants (e.g., pesticide, polystyrene, cesium) moved deeper to groundwater than expected due to the colloid facilitated transport [14–16]. Furthermore, Zhou et al. [17] reported that about 10–29% of endocrine disrupting chemicals (EDCs) were associated with aquatic colloids, and they would play a significant role in the environmental fate and behavior of EDCs. Currently, there is still a knowledge gap concerning the roles of soil particles of different size fractions play on the fate and transport of hormones in the environment. The sorption and desorption properties of separated soil fractions on hormones have not been studied yet.

In this study, wet sieve washing and repeated sedimentation methods were used to separate the soils into five diameter size ranges. Sorption–desorption behaviors of these particles were evaluated by conducting kinetics and isotherm tests. The objectives of this study were to (1) determine the sorption and desorption properties of testosterone and (2) elucidate the related sorption–desorption mechanisms under the influence of the five soil particle size fractions. Testosterone was selected because it is a prototype for other synthetic androgenic hormones and little is known about the fate and transport of androgenic hormones [18].

2. Materials and methods

2.1. Soil particles collection and characterization

Soil particles of five different size fractions were obtained from top 0–5 cm (0–2 in.) HAL (Haskell Agriculture Laboratory, Concord, NE, USA) soils, which is a Nora silty clay loam (fine-silty, mixed, mesic Udic Haplustoll). No residual testosterone was detected in the soil sample. The wet sieve washing method was adopted to separate fine sand (0.425–0.075 mm), medium silt (0.075–0.045 mm), fine silt (0.045–0.002 mm). The repeated sedimentation method was used to separate and collect clay 1 (0.9–2 μm) and clay 2 (0.6–0.9 μm). The American Society for Testing and Materials (ASTM) standard method (ASTM D422) was conducted to check the aggregation percentage of the soil particles of different fractions using 40 g/L sodium hexametaphosphate solution $(NaPO_3)_6$ [19]. Detailed separation and characterization procedures are described in Supplementary Materials.

2.2. Hormone test solution

^{14}C-labeled testosterone came from the American Radio Chemicals Society (St. Louis, MO, USA). Unlabeled testosterone at purity > 98% was obtained from Sigma-Aldrich (St. Louis, MO, USA). Low activity stock solution (directly used in the experiment) was made by adding 20 μL of high activity (=50 μCi) stock solution of ^{14}C-labeled testosterone to 10 mL deionized (DI) water (electrical conductivity = 18 MΩ cm). The Millipore Simplicity System (Thermo Fisher Scientific Inc. U.S.) was used to produce the DI water. Unlabeled testosterone stock solution (=10 μg/mL) was made by dissolving 0.0010 g testosterone into 100 mL methanol, and conserved at 4 °C in a brown glass container under the dark condition. The concentration of methanol was less than 1% by volume in batch reactors. At this concentration, no effect of methanol on sorption was observed by other researchers [20,21].

2.3. Sorption kinetics

Soil particles (0.2 g) of each of five fractions were placed into each of two 15 mL glass centrifuge tubes (Corning Screw Thread Finish, Fisher Scientific) for testing sorption kinetics and isotherms. Then, 9.8 mL of DI water containing 0.01 M (1.1 g/L) $CaCl_2$ (for control of ion strength) and 200 mg/L NaN_3 (for eliminating the microbial influence) was added to each tube. 100 μL ^{14}C-labeled of low activity stock solution and 8 μL unlabeled testosterone stock solution were added to reach the hormone concentration of 10 ng/mL. For sand, medium and fine silt, 100 μL ^{14}C-labeled of low activity stock solution and 100 μL unlabeled testosterone stock solution were added to reach the concentration of 100 ng/mL. While for clays 1 and 2, 100 μL ^{14}C-labeled low activity stock solution and 20 μL unlabeled testosterone stock solution were added to reach the concentration of 24 ng/mL. The test tubes were sealed with Teflon-lined caps and rotated (top to bottom, 360°/5 s) for 5, 15, 30, 60, 90, 150, 300, 600, or 1440 min. At the end of each time, two tubes were taken randomly for centrifugation (Kendro Inc. Asheville, NC, USA) at 2000 rpm (1350 g) for 15 min and sacrificed. Then, 200 μL top liquid from the centrifuge tubes was pipetted into a 20 mL counting vial (Wheaton Millville, New Jersey, USA) with 5 mL cocktail (PerkinElmer, Waltham, MA, USA).The radioactivity of the vial was measured with 2500 TR Liquid Scintillation Counter (Packard, Downers Grove, IL, USA). The distribution of the testosterone in the liquid (ng/mL) and soil particles (μg/g) were calculated based on mass balance. The sorption process can be treated as a first-order reaction for the first 2.5 h [18]:

$$\ln(C) = \ln(C_0) - kt \tag{1}$$

where C is the aqueous testosterone concentration (ng/mL); C_0 is the original concentration in aqueous phase (ng/mL); t is time (hour), and k is the sorption coefficient (1/h).

2.4. Sorption isotherm

For sorption isotherm, all the test procedures were the same as sorption kinetics except that different initial hormone concentrations and 24 h reaction time were used at 4, 23, 35 °C. The rotator (Model C415110, Thermo Scientific Inc.) with centrifuge tubes was put in low temperature incubator (Model no. 307, Fisher Scientific Inc.) to keep 4 °C and Isotemp Oven (Model 516G, Fisher Scientific Inc.) to keep 23 and 35 °C. Seven different initial concentrations (0.04–200 ng/mL) were chosen for sand and silts, and 0.04 – 50 ng/mL for clays. These concentrations were selected as per reported field concentrations of testosterone (0.012–0.125 ng/mL) [3,22]. The 24-h equilibrium time was selected as per our sorption kinetics results and previous literature reports [18]. The linear, Freundlich and Langmuir models were tried to fit sorption data:

$$\text{Linear}\ S = K_d C \tag{2}$$

$$\text{Freundlich}\ S = K_f C^n \tag{3}$$

$$\text{Langmuir}\ S = \frac{q_m C}{1/b + C} \tag{4}$$

where S is the concentration of testosterone adsorbed on the solid phase (μg/g); C is the aqueous phase concentration after sorption reaching equilibrium (ng/mL); K_d and K_f are the linear (L/kg)