Influence of Soil Properties and Test Conditions on Sorption and Desorption of Testosterone

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Abstract: In this study, batch sorption and desorption experiments were conducted for testosterone using four agricultural soils and five clay minerals. Significant differences in sorption behavior were observed between abiotic and biotic systems. The Freundlich sorption coefficient \( K_f (\mu g/g)/(\mu g/mL)^n \) ranged from 8.53 to 74.46 for soils and from 35.28 to 1,243 for clays. The maximum sorption capacity (\( \mu g/g \)) of soils ranged from 25.25 to 440.61 for soils and from 168.46 to 499.84 for clays. Correlation of the sorption model parameters with the soil properties indicated that both clay content and soil organic matter are important variables in predicting testosterone sorption behavior. Observed testosterone desorption from agricultural soils ranged from approximately 14 to 100% after three desorption cycles, and the desorption percentage decreased as the initial testosterone concentration decreased. It was determined that the temperature, ionic strength, water/solid ratio, and soil depth influenced the sorption and desorption of testosterone. Desorption significantly increased with the soil depth (\( p < 0.05 \)) and with the increase in the water/solid ratio. Temperature had an inverse effect on the sorption capacity of the soils tested. Thermodynamic calculations showed that the enthalpy change (\( \Delta H^\circ \)) of the soils tested ranged from 12.9 to 20.7 kJ/mol, indicating a weak interaction between the testosterone and soil. The authors’ results suggest that additional studies on how soil particles with different size fractions affect hormones’ fate and transport are needed to determine the potential risk of testosterone leaching or runoff. DOI: 10.1061/(ASCE)EE.1943-7870.0000937, © 2015 American Society of Civil Engineers.

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Introduction

As one of the reproductive androgenic hormones, testosterone is produced by different animals in livestock production and thus can be potentially widespread in the environment. As it is a precursor to major estrogens such as estrone and estradiol (Kim et al. 2007), when it is released into the environment, testosterone can metabolize to produce other potent metabolites to cause adverse health impacts to aquatic organisms (Kirk et al. 2002; Lange et al. 2002; Casey et al. 2004). Testosterone is moderately hydrophobic, with a logarithmic octanol-water partition coefficient (LogKow) of approximately 3.32 and a solubility (18–25 mg/L) that is greater than most steroid estrogens (Hanselman et al. 2003). Testosterone has been detected in groundwater (Wicks et al. 2004; Swartz et al. 2006; Arnon et al. 2008), surface waters (Koplin et al. 2002), soils (Finlay-Moore et al. 2000), and sediments (Campbell et al. 2006). Although sorption and degradation of testosterone in the environment have been extensively studied (Lee et al. 2003; Casey et al. 2004; Sangsupan et al. 2006; Arnon et al. 2008; Ma 2009), the current knowledge cannot fully explain the occurrence and persistence of testosterone in the environment (Bartlet-Hunt et al. 2012; Biswas et al. 2013a).

Sorption of testosterone in soils and sediments has been reported to be rapid and linear or slightly nonlinear, with reported linear sorption coefficient \( K_L \) (liquid and solid phase partition coefficient) values ranging from 0.5 to 1,200 L/kg and Freundlich sorption coefficient (\( K_f \)) values ranging from 14 to 59.1 (\( \mu g/g \))/(\( \mu g/mL \))^n (Lee et al. 2003; Casey et al. 2004; Sangsupan et al. 2006), where both \( K_L \) and \( K_f \) reflect the sorption capacity of testosterone onto soils. Although sorption sometimes reduces the bioavailability of chemicals (Chung et al. 1998), Lee et al. (2003)
found that, among the soils being tested, most degradation of testosterone occurred in the soil that had the greatest organic carbon and greatest sorption. However, a study of testosterone sorption in five soils did not identify strong correlations between sorption and soil properties, such as soil texture, surface area, organic matter, and particle size (Casey et al. 2004). It is known that soil microorganisms can degrade testosterone rapidly and effectively, as the half-lives of testosterone range from 0.3 to 7.3 days (Hakk et al. 2005; Lorenzen et al. 2005; Fan et al. 2007). However, limited information is available on the effects of abiotic versus biotic conditions under similar test conditions (e.g., using sterile or nonsterile soils). Furthermore, once testosterone is desorbed from soil and enters the aqueous phase, its natural attenuation should be very slow because its degradation rate is 0.001 (1/d) (Wicks et al. 2004). These studies imply that both sorption and desorption play important roles in the persistence of testosterone in the environment. To date, however, studies on desorption immediately after sorption of testosterone have been limited. Filling this knowledge gap would allow the authors to estimate the fate and transport in the soil environment.

The objective of this study was to determine the sorption and desorption of testosterone under several conditions (e.g., different soils/testing materials, soil from different depths, temperature, ionic strength, and water/soil ratio). It is anticipated that the results of this study will be used to predict the fate and behavior of testosterone in the soil-water environment.

Methods and Materials

In this study, the authors used four agricultural soils and five clay materials (three were purchased and two were created from one of the agricultural soils) to conduct the following tests: (1) kinetic tests to identify the equilibrium time that was needed for the sorption and desorption tests, (2) sorption tests for isotherms, and (3) desorption tests. Sorption tests were conducted under different conditions, including (1) at three different temperatures (6, 24, and 35°C), (2) with or without adding the biocide (sodium azide, NaN₃), and (3) at different ion strengths. Desorption tests were conducted at 24°C with different ion strengths and water/soil ratios. Details for the kinetic tests are described in Ma (2009), and details of the sorption and desorption tests are described in the following sections.

Chemicals and Sorbents

Testosterone, sodium azide, calcium chloride, ethyl ether, and acetone/titrile were obtained from Sigma-Aldrich (St. Louis, Missouri). All chemicals had a purity >98%. ¹⁴C-labeled testosterone was obtained from American Radiolabeled Chemicals (St. Louis, Missouri). Unlabeled testosterone stock solutions (100 mg/L) were prepared with high performance liquid chromatography (HPLC)-grade methanol and stored in a −20°C freezer before use; ¹⁴C-labeled testosterone series of stock solutions with different activity levels of 0.1–50 μCi were prepared in solutions of methanol and ultrapure water (resistance of 18 Ωm) and were stored in a −4°C freezer (Ma 2009).

Soils obtained from North Platte, Nebraska (NP soil) and Haskell Agricultural Lab near Concord, Nebraska (HAL soil) were sampled at three depths (0–15, 15–31, and 31–61 cm) using a Giddings soil probe (Giddings Machine Company, Windsor, Colorado). The NP soil was a Cozad silt-loam soil (coarse-silty, mixed, mesic Fluvic Haplustoll), and the HAL soil was a Nora silty clay loam (fine-silty, mixed, mesic Udic Haplustoll). These soils were used because this study was part of a large project at these two sites (Bartlet-Hunt et al. 2012; Biswas et al. 2013b; Van Donk et al. 2013). The other two agricultural soils (Iowa Light and Iowa Dark) were obtained from the surface of agricultural fields in Iowa. Iowa Light was a Rinda silty clay loam soil (fine, smectitic, mesic Vertic Epiaqualfs). Iowa Dark was a Dickinson sandy loam soil (coarse-loamy, mixed, superaqueous, mesic Typic Hapludolls). These soils were chosen because the authors have used them in several other studies and are very familiar with their other properties. These four soils were air-dried and passed a 2-mm sieve before use.

Reference clays (SWy-2 montmorillonite and KGa-1 kaolinite) were purchased from the Source Clay Projects at Purdue University (West Lafayette, Indiana). Wyoming bentonite CG-50 was purchased from American Colloid Company, Chicago, Illinois. All clays were used as received.

To extract HAL Clays 1 and 2 from the HAL topsoil (0–15 cm), soil was collected that passed a 2-mm sieve and then was washed three times (with a water/soil ratio of 100 g of soil to 1 L of water) to remove dissolved organic matter (DOM). For each washing, the soil slurry was allowed to settle for 24 h, and then the supernatant was decanted. After the third wash, the sediment was mixed with 1 L of tap water for resuspension and then allowed to settle. The supernatant of this slurry was siphoned and collected as Clay 1 after 4 h of settling or as Clay 2 after 12 h of settling. The supernatant containing Clay 1 or 2 was then air-dried at 23–1°C. The particle size distribution was 0.9–2 μm for Clay 1 and 0.6–0.9 μm for Clay 2, as per the measurements with a Zetasizer (Nano ZS90, Malvern, U.K.). Table 1 provides the selected properties of the soil and clays.

Sorption and Desorption Tests

Sorption experiments were conducted at 6, 24, and 35°C on all the soils and clays. Sorption isotherms were conducted in 10-mL glass reactors. Each reactor was loaded with 1 g of dry soil or 0.05 g of clay and 10 mL of ultrapure water containing 0.01 M CaCl₂. Treatments were created by combining unlabeled and ¹⁴C-labeled testosterone to form a desired initial testosterone concentration (100 ng/L–2 mg/L). Sorption experiments were conducted at...
the ionic strengths of 0.06–1 M (adjusted with NaCl). In the abiotic experiments, 200 mg/L NaNO₃ was added to the reactors. The batch reactors were sealed with Teflon-lined caps and rotated top to bottom (360°/5 s) for certain time intervals (e.g., 24 or 48 h). At the end of the time interval, triplicate reactors were removed and centrifuged. A 500-μL aliquot was removed from each reactor and placed in a 20-mL scintillation vial with a 5-mL Ultima Gold (PerkinElmer, Waltham, Massachusetts) scintillation cocktail to test for radioactivity. Radioactivity levels were determined by scintillation counting using a 2,500-TR liquid scintillation counter (Packard, Downers Grove, Illinois). The difference between the initial and final radioactivity in the liquid phase was attributed to sorption. The experimental data were fit to linear, Freundlich, and Langmuir isotherm models.

Table 2 provides the results.

Prior to batch studies, kinetic sorption experiments were performed to determine the required equilibration period. An equilibration period of 24 h was used for experiments with NP and HAL soils and 48 h for experiments with clays. After sorption, the sorbent phase was extracted using the method described in Lorenzen et al. (2005). The extracts and the liquid phase were analyzed using a high-performance liquid chromatograph (Waters Alliance 2695 HPLC, Waters Corporation, Milford, Massachusetts) and a mass spectrometer (Finnegan LCQ Ion Trap MS, Thermo Scientific, San Jose, California). Further details of the analytical methods are provided in Ma (2009).

Desorption tests were conducted at 24°C by first decanting the liquid phase in the batch reactor that had reached equilibrium in the sorption tests and then adding 10 mL of a solution containing 0.01 M of CaCl₂ and 200 mg/L of NaNO₃. Seven different initial concentrations (100 ng/L–2 mg/L) were used to investigate the effect of the initial testosterone concentration on the sorption percentage. The reactors were equilibrated for 24 h—the time for reaching one-cycle desorption equilibrium as tested in the kinetic study described by Ma (2009). This will be referred to as the Cycle 1 desorption test. After the Cycle 1 test, the liquid phase in the reactor was replaced with 10 mL of a solution containing 0.01 M of CaCl₂ and 200 mg/L of NaNO₃ for the Cycle 2 test. In this study, three cycles of desorption tests were conducted for each reactor. After each cycle, the reactors were centrifuged (2,000 g for 40 min), and an aliquot of 500 μL was taken to test for radioactivity.

At the end of the desorption experiments, the solid phase remaining in the reactor was extracted and analyzed by high performance liquid chromatography/mass spectrometry (HPLC/MS) to confirm the testosterone mass balance. The effects of ionic strength (0.06–1.0 M, adjusted with NaCl) and the water/soil ratio (0.1–1 g/mL) on ¹⁴C-labeled testosterone desorption were also investigated to allow the development of a family of desorption curves.

### Data Analysis

The data obtained from the sorption and desorption tests were fit to linear, Freundlich, and Langmuir models

\[
S = K_d C 
\]

(1)

\[
S = q_m C / (1 + b C) 
\]

(2)

\[
S = K_f C^n 
\]

(3)

where \( S \) = concentration of the hormone adsorbed on the soil (mg/g); \( K_d \) = sorption coefficient (L/g); \( C \) = hormone aqueous concentration (mg/L); \( q_m \) = maximum sorption capacity (μg/g); \( b \) = sorption equilibrium constant (L/mg); \( K_f \) = Freundlich sorption coefficient \([(μg/g)/(μg/mL)^n]]; and \( n \) = Freundlich intensity parameter (unitless). The temperature

![](https://www.asce.org/content/dam/asc/pdfs/async/www/1500231.pdf)
influence on the \( \Delta G^0 \), \( \Delta H^0 \), and \( \Delta S^0 \) values is calculated as follows (Ma 2009):

\[
\Delta G^0 = -RT \ln K_d
\]

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

where \( \Delta G^0 \) (kJ/mol), \( \Delta H^0 \) (kJ/mol), and \( \Delta S^0 \) (kJ/mol) = Gibbs free energy change, enthalpy change, and entropy change, respectively, in the sorption process; \( T \) = temperature (K); and \( R \) = ideal gas constant [J/(K mol)]. The data were tested for significant differences using a Student’s t-test for two sample means with unequal variances. Two-tail \( p \) values of less than 0.05 were considered significant (Ma 2009).

Results and Discussion

Sorption Isotherms

The best-fit lines for testosterone sorption to NP and HAL soils and clays were determined to be slightly nonlinear (Fig. 1 and Table 2). The Freundlich sorption coefficient \( K_f \) ranged from 8.53 to 74.46 (\( \mu g/g \))/(\( \mu g/mL \)) for soils and from 35.28 to 1,243 (\( \mu g/g \))/(\( \mu g/mL \)) for clays (Table 2). These results are consistent with the Freundlich coefficients of 10.3 to 42 (\( \mu g/g \))/(\( \mu g/mL \)) for testosterone sorption on a silt-loam soil reported by Gineys et al. (2012) and 59.1 (\( \mu g/g \))/(\( \mu g/mL \)) reported by Das et al. (2004). The maximum sorption capacity of soils calculated from the Langmuir model ranged from 25.25 to 440.61 \( \mu g/g \) for soils and from 168.46 to 499.84 \( \mu g/g \) for clays (Table 2). Lee et al. (2003) reported that the Drummer soil (silt loam) had the highest sorption capacity among the investigated soils because of its fine texture, resulting in a high surface area, which is consistent with the authors’ findings that clay and silt loam have a relatively higher sorption capacity on testosterone compared with sandy loam. Also, the clays were observed to have a larger testosterone sorption capacity when compared to the whole soils, which is likely attributable to the larger surface area of clays compared to other soil fractions. Clay 2 and montmorillonite exhibited very high testosterone sorption capacity (high \( K_f \)), which is possibly due to testosterone diffusing into the interlamellar spaces of the clay (Shareef et al. 2006).

Because testosterone is neutral in aqueous solutions at neutral pH ranges, the cation exchange capacity (CEC) is not believed to affect sorption. This is verified by the low correlation coefficient (\( R^2 = 0.1465 \)) for a linear regression between CEC and \( K_f \) (data not shown). The authors also observed variable \( \log K_{oc} \) values as a function of soil type, indicating that other soil properties, such as clay or sand content and organic matter (OM), might be important in predicting testosterone sorption. Regression analysis indicated that sorption (\( K_f \)) is related to sand (\( R^2 = 0.8472 \); inverse correlation), clay (\( R^2 = 0.7999 \)), and OM (\( R^2 = 0.5200 \)). The positive correlation between clay content and testosterone sorption is presumably due to the partitioning of testosterone onto clay mineral surfaces through hydrophobic interactions with siloxane (\( \langle \mathrm{Si-O-Si} \rangle \) groups (van Emmerik et al. 2003). Interestingly, the \( K_f \) values of Clays 1 and 2 are much greater than those of the HAL 0–15 soil, which indicates the potential of colloid-facilitated transport of testosterone if the clay particles are released into runoff or leachate during a storm event.

Table 3 summarizes the recovery of testosterone and the formation of a testosterone metabolite 4-androstene-3,17-dione in sorption experiments conducted with and without a biocide (NaNO\(_3\)). The amount of the testosterone metabolite detected in the abiotic reactors was less than that in the biotic reactors. Microbial transformation of testosterone via dehydrogenation and potentially by actinobacteria has been previously reported in soils and livestock manure (Das et al. 2004; Yang et al. 2009). Additionally, the mass recovery of testosterone and metabolites is greater in the abiotic reactors (95–97% recovery) and is indicative of good quality control.

Desorption

After Cycle 3, the accumulated desorption percentages ranged from 16.3 to 44.3% for the HAL soils, from 34.3 to 102.4% for the NP soils, from 26.2 to 72.2% for the Iowa Dark soil, and from 14.1 to 18.2% for the Iowa Light soil (Fig. 2). Generally, desorption percentages with the same initial concentration are in a decreasing order as NP soils > Iowa Dark soil > HAL soils > Iowa Light soil, which is consistent with the reverse order of the sorption strength. For all soils, the testosterone desorption percentages decreased significantly with a decrease in the initial liquid testosterone concentration (Fig. 2), which indicates the necessity of using a wide range of testosterone concentration to conduct sorption and desorption tests, particularly at low concentrations. Reported testosterone concentrations in the environment are in the range of 5–2,520 ng/L (Kolpin et al. 2002; Das et al. 2004; Bhandari et al. 2009).
Table 4. Freundlich Parameters for Sorption and Desorption of Soils at 24°C and Desorption Hysteresis

<table>
<thead>
<tr>
<th>Soil</th>
<th>LogK_{fc}</th>
<th>K_{fs}</th>
<th>n_s</th>
<th>K_{fd}</th>
<th>n_d</th>
<th>H^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAL 0–15</td>
<td>3.60</td>
<td>38.82</td>
<td>0.7996</td>
<td>44.53</td>
<td>0.8068</td>
<td>1.0090</td>
</tr>
<tr>
<td>HAL 15–31</td>
<td>3.59</td>
<td>33.67</td>
<td>0.7582</td>
<td>42.87</td>
<td>0.8185</td>
<td>1.0795</td>
</tr>
<tr>
<td>HAL 31–61</td>
<td>3.70</td>
<td>32.22</td>
<td>0.8573</td>
<td>41.50</td>
<td>0.9349</td>
<td>1.0905</td>
</tr>
<tr>
<td>NP 0–15</td>
<td>3.25</td>
<td>16.47</td>
<td>0.8025</td>
<td>20.97</td>
<td>0.8293</td>
<td>1.0334</td>
</tr>
<tr>
<td>NP 15–31</td>
<td>3.23</td>
<td>11.89</td>
<td>0.7927</td>
<td>14.62</td>
<td>0.8181</td>
<td>1.0241</td>
</tr>
<tr>
<td>NP 31–61</td>
<td>3.42</td>
<td>9.98</td>
<td>0.7602</td>
<td>9.77</td>
<td>0.7969</td>
<td>1.0483</td>
</tr>
<tr>
<td>Iowa Dark</td>
<td>3.24</td>
<td>10.60</td>
<td>0.7974</td>
<td>17.98</td>
<td>0.8762</td>
<td>1.0988</td>
</tr>
<tr>
<td>Iowa Light</td>
<td>4.05</td>
<td>74.46</td>
<td>0.9683</td>
<td>212.45</td>
<td>0.7271</td>
<td>0.7509</td>
</tr>
</tbody>
</table>

*Desorption hysteresis H = n_d/n_s.

Fig. 2. Desorption percentages of testosterone from soils after desorption Cycles 1, 2, and 3 at 24°C as a function of varied initial testosterone concentrations that are used in previous sorption tests; percentages were calculated based on the amount of testosterone presorbed in the sorption step; error bars stand for ±1 standard deviation (n = 3).

Therefore, the results of the authors’ desorption tests indicate that testosterone desorption in the environment will be relatively low, particularly if the testosterone is sorbed in the top soil or by soils with a high clay content. For example, the Iowa Light soil had relatively low desorption percentages (Fig. 2) because it had the lowest sand content and the greatest clay content among the soils in the experiment. The Iowa Dark soil had lower desorption than the NP 31–61 soil (Fig. 2), which may be due to the greater OM content of the Iowa Dark soil. A greater OM content is believed to cause stronger binding of testosterone (Carroll et al. 1994), leading to less desorption.

Desorption from the NP soils was greater than from the HAL soils at each initial concentration. This was the result of the NP soils having more sand content than the HAL soils (Table 1), and sorption on the sandy soil tends to be more reversible. Additionally, the desorption percentages significantly increased with the soil depth (p < 0.05). This may be because the OM content decreases with increasing depth. One exception is that there are no significant differences in the desorption percentages (p ranged from 0.052 to 0.134) between the NP 0–15 and 15–31 soil (Fig. 2). While the NP 0–15 soil had a greater OM content than the NP 15–31 soil, the NP 15–31 soil had less sand content (Table 1).

The desorption hysteresis coefficient (H) is calculated based on the ratio of the desorption and sorption isotherm parameters (H = n_d/n_s) (Yuan and Xing 2001), where n_d and n_s are the Freundlich intensity parameter n for desorption and sorption, respectively. In general, if H ≈ 1, there is no (or very limited) desorption hysteresis in the sorption/desorption processes, and a larger H value (toward 1) corresponds to a lower degree of hysteresis. According to the literature, desorption hysteresis is usually due to (1) irreversible binding of chemicals to the OM or clay mineral of soil aggregates (Bhandari et al. 1996), and (2) entrapment of sorbed molecules in mesoporous and microporous structures within mineral structures and the OC matrix of soil aggregates (Carroll et al. 1994; Farrell et al. 1994; Weber et al. 1998). A desorption process with an H value much lower than 1 must be associated with irreversible thermodynamic change, which is often dictated by the location difference of the OM and mineral (Yuan and Xing 2001; Li et al. 2013). In this study, no desorption hysteresis was found (Table 4) for all the soils (H ≈ 1), except Iowa Light, which had an H value of approximately 0.7509 and thus had desorption hysteresis. To the authors’ knowledge, no H values of testosterone have been reported previously, but Li et al. (2013) reported that the desorption hysteresis of 17α-ethinyl estradiol (EE2) was observed in all sorbents with H values of 0.173–0.673. While most of the authors’ H values are close to 1, the authors did observe that sorption is partially reversible (14–100% after three desorption cycles) (Fig. 2), indicating that it is possible for the authors’ soils (except Iowa Light) to achieve 100% desorption with more desorption cycles. The environmental implication of this result is that, for these soils, testosterone transport is more likely to occur under the condition of frequent storm events.

**Impact of Environmental Factors**

Temperature has an inverse effect on the sorption capacity of the soils tested (Fig. 3), even though Langmuir’s maximum sorption


capacity, \( q_m \), increases with temperature (Table 2). The linear sorption coefficient \( K_d \) and Freundlich sorption coefficient \( K_f \) decreased significantly (\( p \) ranged from 0.0021 to 0.0412 for \( K_f \)) with an increasing temperature of between 6 and 35°C (Table 2), with the exception of the NP 31–61 soil at 24 and 35°C (\( p = 0.061 \)). Table 5 indicates that all \( \Delta H^0 \) values are negative, indicating that sorption of testosterone to soil is exothermic. Physisorption is typically associated with \( \Delta H^0 \) in the range of 5–20 kJ/mol and is believed to be an overall weak interaction. Chemisorption is typically associated with much higher enthalpy values in the range of 100–400 kJ/mol and is regarded as a strong binding (Xu et al. 2008). The enthalpy change data of the NP soil and HAL 31–61 soil were in the range of 12.9–20.7 kJ/mol (Table 5), which suggests that a physical sorption of testosterone dominates in the sandy NP soil. Calculated enthalpy changes for the HAL 0–15 and HAL 15–31 soils were approximately 30 kJ/mol (Table 5), which suggests that both physical and chemical sorption processes were present, but physical sorption appeared to be dominant.

Soil depth has an inverse effect on the sorption of testosterone for both the HAL and NP soils (Fig. 1 and Table 2), resulting in a decrease in \( K_f \) with an increase in soil depth [Fig. 4(a)].

### Table 5. Calculation of Thermodynamic Parameters

<table>
<thead>
<tr>
<th>Soil</th>
<th>( T ) (°C)</th>
<th>( T ) (K)</th>
<th>( q_m ) (L/kg)</th>
<th>( q_m ) (L/mol)</th>
<th>( \Delta G^0 ) (kJ/mol)</th>
<th>( \Delta H^0 ) (kJ/mol)</th>
<th>( \Delta S^0 ) (kJ/(mol · K))</th>
<th>( R^2 )</th>
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<td>HAL 0–15</td>
<td>6</td>
<td>279</td>
<td>97.12</td>
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<td>-7,730.65</td>
<td>-7.73</td>
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<td>—</td>
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<td></td>
<td>24</td>
<td>297</td>
<td>50.54</td>
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<td></td>
<td>35</td>
<td>308</td>
<td>30.74</td>
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<td>-5.48</td>
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<td>—</td>
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Note: \( R^2 \) = linear fitting parameters of equation.
15 cm of soil had the greatest sorption capacity. All depths were significantly different from each other \((p < 0.05)\) regarding sorption. In contrast, Fig. 2 shows that the desorption percentages significantly increased with the soil depth \((p < 0.05)\). Fig. 4(b) shows that, for the HAL soil, the accumulated desorption percentage (ADP) after three desorption test cycles increased with soil depth. One exception was noted between the NP 0–15 and NP 15–31 soils, as the NP 15–31 soil had less sand content than the NP 0–15 soil (Table 1). Therefore, both OM and soil components affect the sorption and desorption of testosterone. Fig. 4(c) shows that the water/soil ratio was another important factor; when it increased, desorption increased almost linearly, indicating a potential risk of testosterone leaching or surface runoff. Sorption increased with an increase in ion strength, while the opposite occurred for desorption [Fig. 4(d)]. This may be due to the salting-out effect—that is, when the ion strength increases, the solubility of testosterone in the solution decreases, resulting in an increase in sorption.

**Environmental Implications**

To the authors’ knowledge, no previous studies have evaluated both the sorption and desorption of testosterone in soils. Nevertheless, this study may be viewed as a preliminary study, as the results of this study still cannot be utilized to explicitly define the fate and transport of testosterone in different environmental settings. For example, it is unclear how soil particles (e.g., clay) with high sorption capacities of hormones affect the hormones’ fate and transport. Factors such as soils or clay minerals from different sources, soil depth, temperature, and the water/soil ratio are very important in determining the fate and transport of testosterone in the environment. The authors’ results indicate that the topsoil had a greater sorption capacity than the subsurface soil because of the higher OM content in the topsoil; deeper soils have less sorption and tend to desorb more testosterone. Therefore, if testosterone penetrates through the topsoil (e.g., 0–15 cm), it might have greater potential to pass through the deeper soil and hence leach to the groundwater. Temperature increases may decrease the soil sorption of testosterone and therefore increase the potential of testosterone leaching. Under field conditions, the ionic strength in the soil/water system may be lower than that used in the lab (0.061 M), especially during a storm event, which decreases sorption and increases desorption of testosterone. The water/soil ratio in the laboratory studies tended to be greater than that in field conditions. However, in a storm event, the water/soil ratio will increase, which may increase the concentration of testosterone in surface runoff or leachate.

**Conclusions**

This study provides information on the sorption and desorption of testosterone onto and from soils and clay minerals under the influence of several factors. The Freundlich sorption coefficient \(K_f\) \(\left[\frac{(\mu g/g) / (\mu g/mL)^n}{\text{g}}\right]\) ranged from 8.53 to 74.46 for soils and from
35.28 to 1.243 for clays. The maximum sorption capacity (μg/g) of soils ranged from 25.25 to 440.61 for soils and from 168.46 to 499.84 for clays. The sorption mechanism is believed to be dominated by a combination of hydrophobic partitioning into OM domains and sorption onto soil mineral surfaces. In general, temperature has an inverse effect on the sorption capacity of the soils tested. On the basis of the interpretation of the thermodynamic data, the interaction between soil and testosterone may be a weak physiosorption supplemented by a strong chemisorption. Soil depth has an inverse effect on the sorption of testosterone for both the HAL and NP soils. The top 15 cm of soil had the greatest sorption capacity, and \( K_f \) decreased with the soil depth. A large portion of testosterone sorption was found to be reversible based on three cycles of desorption—14 to 100% of the adsorbed testosterone desorbed from the tested soils. Sandy soils had greater potential for testosterone desorption. In addition, more sorbed testosterone in the solid phase will lead to a greater desorption percentage. The desorption percentage decreased as the initial testosterone concentration decreased. Desorption significantly increased with the soil depth (\( p < 0.05 \)) and with the increase in the water/soil ratio. The authors’ results indicate that the topsoil had a greater sorption capacity than the subsurface soil because of the higher OM content in the topsoil; deeper soils have less sorption and tend to desorb more testosterone. However, additional studies are needed to determine the potential risk of testosterone leaching or runoff.

Acknowledgments

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