Adsorption–desorption behavior of the endocrine-disrupting chemical quinestrol in soils

Mingcheng Guo1, Qin Lin2, Zhenlan Xu2, Chunrong Zhang2, Xueping Zhao2 & Tao Tang2*

Quinestrol (QUN), a synthetic estrogen used as an oral contraceptive or emergency contraceptive component, has been shown to be an endocrine-disrupting chemical. To assess the environmental risk of QUN, batch equilibration experiments were conducted to investigate the adsorption–desorption of QUN in five contrasting soils from different areas of China. The leaching properties were also calculated based on the adsorption and degradation data from our previous study with the same soils. The Freundlich and Langmuir models were applied to the sorption–desorption data to examine the affinity towards QUN of the soils, which had varying physical and chemical properties. The \(K_f\) and \(K_{f,\text{des}}\) values of QUN in the tested soils ranged from 3.72 to 20.47 mg\(^{-1}\) L\(^n\) kg\(^{-1}\) and from 1.26 to 7.8 mg\(^{-1}\) L\(^n\) kg\(^{-1}\), respectively, and \(Q_m\) ranged from 28.25 to 126.58 mg/kg. The desorption data showed that hysteresis occurred. The \(K_f\) and \(K_{f,\text{des}}\) values of QUN were positively correlated with the soil total organic carbon (TOC) and cation exchange capacity (CEC), and it may be due to the content of TOC and CEC exhibited a positive correlation. A low mobility potential of QUN in soils was predicted and verified the adsorption results by the groundwater ubiquity score (GUS) and retardation factor (Rf).

Steroid hormones are an emerging endocrine disrupting chemicals (EDCs) that can interfere with the endocrine function in organisms at low concentrations. Synthetic steroid hormones have frequently been reported to demonstrate the higher affinities for binding to hormone receptors than natural steroid hormones and thus great disruption potencies. Quinestrol (QUN) is a synthetic progestogen that has been used as an oral contraceptive and hormone replacement for women since the 1960s. In recent years, some studies have reported on the adverse effects of QUN on male rat, crucian carp and duckweed after they enter the environment. Moreover, previous reports demonstrated that the half-life periods of QUN in nature waters were in the range of 60–90 days, and the degradation rate for fifty percent (DT\(_{50}\)) and 90% (DT\(_{90}\)) in soils were approximately 15 days and 50 days, respectively. The longer residual period of QUN in the environment indicated that QUN may exert toxic effects on organisms for a long time in its great disruption potencies. Thus, it is very necessary to understand the environmental fate of QUN and whether it is safe for organisms. QUN is not efficiently eliminated by municipal treatment plants like other endocrine-disrupting chemicals. The municipal treatment plant effluents and wastewater discharges are considered to be the major source of QUN that are directly released into the environment. QUN is generally generated by natural and anthropogenic processes and can be introduced into the soil through various routes, including human and animal excretion, farmland irrigation with municipal wastewater effluent and improvement in farmland fertility with sludge. QUN is the 3-cyclopentyl ether of ethinyl estradiol (EE2). After oral administration, it is stored in adipose tissue where it is gradually released and metabolized principally to EE2. The potent effect of QUN is approximately several times higher than EE2 with a very long biological half-life of more than 5 days. The sulfate and glucuronate conjugates of QUN and EE2 are formed in the kidney and excreted by human and livestock in the urine, and they can be desulfated and deglucuronidated by corresponding enzymes in the environment and converted back into its precursors.

1Institute for the Control of Agrochemicals, Ministry of Agriculture and Rural Affairs, Beijing 100125, People’s Republic of China. 2State Key Laboratory for Quality and Safety of Agro-Products, Key Laboratory for Pesticide Residue Detection of Ministry of Agriculture and Rural Affairs, Institute of Quality and Standard for Agro-Products, Zhejiang Academy of Agricultural Sciences, NO. 298 Desheng Road, Hangzhou 310021, People’s Republic of China. *email: tangtao80@126.com

10.1038/s41598-020-70300-x
After entering soil, the endocrine-disrupting chemical QUN mainly undergo adsorption/desorption, leaching, biodegradation and biotransformation. In recent decades, most studies concerning the degradation, migration, transformation, and photodegradation of natural estrogens, such as estrone (E1), 17α-estradiol (αE2), 17β-estradiol (βE2), and estriol (E3), and the synthetic estrogen EE2 in soil have been investigated extensively. Although the adverse effects caused by synthetic steroid hormones, such as QUN, have received increasing attention, only a few studies about the photodegradation, degradation, and accumulation in organisms of QUN in the environment were available when this work began. In view of the low-dose effect of QUN as endocrine disruptors, knowledge of adsorption and desorption of QUN is urgently required because information on the soil transport is significant for accurate evaluation of its environmental risks.

To obtain this information, the batch equilibration method recommended by the United States Environmental Protection Agency was used to study the adsorption–desorption behavior of QUN in five contrasting soils from different areas of China. The Freundlich and Langmuir models were applied to fit the observed sorption–desorption data to derive kinetics and isotherms of QUN in the tested soils. Additionally, the groundwater ubiquity score (GUS) and retardation factor (Rf) was used to calculate and verify the mobility potential of QUN in soils. This work would provide a supplement for the adsorption–desorption behavior and improve our understanding of potential environment risk concerning the endocrine-disrupting chemical QUN.

### Materials and methods

#### Chemicals and reagents

QUN (purity > 99%) was obtained from Sigma-Aldrich (Dorset, U.K.). Ammonium acetate, anhydrous calcium chloride, and acetic acid were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Methanol and acetonitrile were high-performance liquid chromatography (HPLC)-grade chemicals obtained from Fisher Scientific (Fair Lawn, NJ). Ultrapure water used for the preparation of samples and mobile phases was obtained in the laboratory using a Milli-Q water purification system (Millipore, Billerica, MA) and had a resistivity greater than 18.2 MΩ cm.

#### Soil samples

The tested soil samples included 4 farmland soils and 1 natural grassland soil. The farmland soils were taken from Heilongjiang Province (HLJ), Beijing (BJ), Yunnan Province (YN), and Guangxi Province (GX), China, and the grassland soil was taken from Inner Mongolia (NMG), China. Each soil sample was taken from the surface layer (0–20 cm). After the soil samples were collected, they were dried evenly in a clean laboratory. Next, the plant residues, stones and other debris were removed, and the samples were air-dried and passed through a 2 mm sieve. The content of total organic carbon (TOC) and nitrogen (N) in soil samples were determined by dry combustion with a CN analyzer Variomax (Elementar Analysensysteme GmbH, Hanau, Germany). The cation-exchange capacity (CEC) was determined using a 1.0 mol/L ammonium acetate solution (pH 7.04). The particle size was determined by the hydrometer method. Soil pH values in 0.01 M CaCl$_2$ with a soil/solution ratio of 1:1 was determined with a pH meter. The treated soil samples were placed in plastic bags and stored in a refrigerator at 4 °C for future use. Soil sterilization was accomplished by autoclaving the soils at 120 °C under 300 kPa 3 times for 45 min in consecutive days with 24 h intervals. The properties of these soils have been determined in a previous study of ours, and these soils parameters are shown in Table 1.

### Table 1. Properties of tested soils. TOC$^a$ = total organic carbon content. CEC$^b$ = cation-exchange capacity.

| Soil site | Soil type   | pH  | N (%) | TOC$^a$ (%) | CEC$^b$ (cmol/kg) | Particle size (%) |
|-----------|-------------|-----|-------|-------------|-------------------|------------------|
| BJ        | Loam       | 7.1 | 0.13  | 1.95        | 25.6              | 46.7             |
| NMG       | Sandy loam | 7.5 | 0.08  | 1.14        | 8.7               | 85.0             |
| YN        | Clay loam  | 6.8 | 0.19  | 1.30        | 12.9              | 6.4              |
| HLJ       | Silty loam | 7.0 | 0.21  | 2.45        | 43.6              | 15.3             |
| GX        | Silty loam | 6.7 | 0.12  | 1.97        | 22.4              | 38.2             |

Adsorption–desorption kinetics. A batch equilibration method with parallel sampling was used, as recommended by the Test Guideline OPPTS 835.1230. In the adsorption test, a 2.0 g soil sample was accurately weighed in a 100 mL glass conical flask with a grinding stopper, and 50 mL of 0.01 M CaCl$_2$ solution containing 1 mg/L QUN was added, resulting in a ratio of soil to water of 1:25 (W/V). The conical flasks were placed on a vibrator and continuously vibrated in the dark. After adsorption equilibrium, centrifugation at 4,500 rpm for 5 min was applied to separate the aqueous phase and solid phase with a plastic (polytetrafluoroethylene) centrifugal cup. The supernatant (10 mL) was transferred into a tube and stored in a refrigerator at −21 °C for further extraction and analysis.

The desorption test was performed as follows. After the QUN reached adsorption equilibrium in the soil, the remaining samples in the conical flasks were transferred into 100 mL centrifuge tubes and centrifuged for 5 min at 4,500 rpm (3,560 g), and the supernatant was discarded. Then, an equal volume of 0.01 M CaCl$_2$ solution was added again. After full rotational mixing, the samples were placed on an oscillator. As was the case in the desorption test, at certain intervals, the flasks were removed to collect 10 mL samples of supernatant, and the supernatants were stored in the refrigerator at −21 °C before analysis. Two blank tests were conducted without QUN and soil. Three replications were set in each treatment.
**Adsorption–desorption isotherms.** The adsorption isotherms were tested by weighing 2.0 g tested soil in a 100 mL glass conical flask with a grinding stopper and mixing in 50 mL CaCl₂ solution with QUN concentrations ranging from 0.2 to 2 mg/L. The conical flasks were shaken for 24 h in the darkness, and then supernatant (10 mL) was transferred into a tube and stored in a refrigerator at −21 °C for further extraction and analysis. When the different concentrations of QUN reached adsorption equilibrium in the soil, the desorption isotherms were determined. The suspensions were transferred to 100 mL centrifuge tubes, and all tubes were centrifuged at 4,000 rpm for 5 min. The supernatant was discarded, and the pellet was mixed with an equal volume of CaCl₂ solution. After testing the samples throughout mixing, they were shaken again for 48 h. Then, supernatant (10 mL) was transferred into a tube and stored in a refrigerator at −21 °C for further extraction and analysis.

**Sample extraction and HPLC analysis.** For the adsorption step, a spiked control experiment indicated that no QUN sorption on the test vessel surfaces occurred, and a mass balance experiment (At the end of adsorption and desorption test, the concentrations of QUN were analyzed in aqueous phase and soil respectively to verify whether the biodegradation of QUN occurred all along the adsorption–desorption experiment) demonstrated that no abiotic degradation occurred. Therefore, only the aqueous phase was analyzed, as recommended in the U.S. EPA Test Guideline. The aqueous sample was transferred to a 60 mL separatory funnel with 10 mL of ethyl acetate and shaken for 5 min on a mechanical shaker. Then, the solvent was collected, and the aqueous sample was extracted again. Finally, the solvent extracts were combined and evaporated to dryness on a vacuum rotary evaporator at 45 °C. The residue was reconstituted with 1 mL of HPLC-grade methanol and used for analysis by HPLC.

The analysis of QUN was performed using the HPLC method coupled with an ultraviolet–visible detector according to our previous report. Preliminary experiments showed that the limit of quantification (LOQ) was 10 μg/L for aqueous samples. External calibration curves were generated to estimate the sample concentrations from peak areas. The percent recovery of QUN was higher than 95% with relative standard deviations of 2.8–4.6% for the adsorption experiment.

**Data analysis.** The adsorbed concentration of QUN in the soil was calculated by the following equation:

\[ C_s = 50 \left( C_0 - C_{aq} \right) / 2 \]

where \( C_{aq} \) (mg/L) is the concentration of QUN in the water after adsorption by the soil and \( C_s \) (mg/kg) is the residual QUN in the soil.

The formula for calculating the residual after the QUN in the soil reached desorption equilibrium was as follows:

\[ C_s^{des} = \left( 2C_s - 50C_{aq}^{des} \right) / 2 \]

where \( C_{aq}^{des} \) (mg/L) and \( C_s^{des} \) (mg/kg) are the concentrations of QUN after desorption in the water and soil, respectively.

The expression of the Freundlich equation is as follows:

\[ C_s = K_f C_s^{des} \]

\[ C_s^{des} = K_f C_{aq}^{des} N_{des} \]

where \( K_f \) (mg\(^{-1/2}\) L\(^{1/2}\) kg\(^{-1}\)) and \( K_s^{des} \) are the adsorption and desorption constants, respectively, and \( N \) and \( N_{des} \) are constants that are related to the nonuniformity of the soil surface.

The Langmuir equation is provided by the following:

\[ 1 / C_s = 1 / Q_m + 1 / K_l Q_m C_{aq} \]

\( Q_m \) (mg/kg) was the maximum adsorption concentration of QUN in the soil. \( K_l \) (L/mg) is the constant of the Langmuir equation, which is related to the adsorption bond energy.

The sorption and desorption data were fit by Freundlich and Langmuir models that were calculated using Sigma Plot, version 13.0. The analysis of variation (ANOVA) and regression analysis were calculated using SPSS, version 17.0.

**Results and discussion**

**Adsorption–desorption kinetics of QUN in soils.** The adsorption–desorption kinetic experiment was designed to evaluate the minimum time of equilibrium for the tested soils. Figure 1 shows the results of QUN adsorption and desorption as a function of time for 5 selected soils. The adsorption kinetics of QUN in soils consisted of two steps: a fast phase and a slow phase. In the early stage, QUN adsorption occurred as a rapid reaction, showing a sharp decrease in solution concentration, around 12 h, the concentration of QUN decreased slightly into balance. The adsorption equilibrium time of QUN in the soil sample from NMG was the shortest, only 4 h, followed by 6 h in Yunnan soil, 8 h in Beijing soil and Guangxi soil, and 12 h in Heilongjiang soil. This phenomenon was likely due to the fact that the vacant sites in NMG soil (sand) with less contents of TOC (1.14%) were fully exposed and easily filled up, and the vacant sites of other soils were slowly occupied because of the competition between solute molecules and soil cations. This trend is similar to the kinetics of adsorption
of estrogen\textsuperscript{22,23}. To ensure the adequacy of adsorption equilibrium and the accuracy of the results, the adsorption equilibrium time of QUN in all soil samples was set to 24 h.

The time to reach desorption equilibrium of QUN was slower than the time to reach adsorption equilibrium. The results showed that no concentration of QUN in aqueous phase was detected within 2 h of the initial stage. Until 4 h of the desorption test, the concentration of QUN in aqueous phase was just detected. The desorption equilibrium time of QUN in the five tested soils varied widely: 6 h in NMG soil, 12 h in Yunnan and Guangxi soils, 24 h in Beijing soil, and 48 h in Heilongjiang soil with the highest TOC contents (2.45%). The phenomenon indicated that TOC content maybe the main factor controlling desorption of QUN in soils. In fact, the desorption of QUN in our study was ordered according to the TOC content of the soils. This hypothesis is supported by the previous reports, which have shown that TOC is the most important factor in the adsorption and desorption of EE2\textsuperscript{24}. Then, the test time was set for 48 h to ensure the establishment of a desorption equilibrium.

### Adsorption–desorption isotherms of QUN in soils

Table 2 summarizes the adsorption isotherm constants and characteristics derived from Freundlich and Langmuir equations for QUN in the five types of soil. $K_{oc} = 100 \frac{K_f}{TOC} (\%)$. \( \Delta G^{\circ} = -1.724RT\ln K_{oc} \).

| Soil site | Freundlich model | Langmuir model |
|-----------|-----------------|---------------|
|           | \( K_r \) (mg$^{1-n}$*L$^{-1}$) | \( N \) | \( R^2 \) | \( K_w^{\circ} \) (L/kg) | \( \Delta G^{\circ} \) (KJ/mol) | \( K_f \) (mg$^{1-n}$*L$^{-1}$) | \( N \) | \( R^2 \) | \( K_L \) (mg/kg) | \( Q_m \) (mg/kg) | \( R^2 \) |
| BJ        | 12.64           | 1.268         | 0.952 | 648.21       | -27.67       | 0.070 | 126.58 | 0.070 | 0.918 |
| NMG       | 3.72            | 0.959         | 0.926 | 326.32       | -24.73       | 0.114 | 34.97  | 0.114 | 0.958 |
| YN        | 6.95            | 1.148         | 0.970 | 534.62       | -26.84       | 0.174 | 30.86  | 0.174 | 0.980 |
| HLJ       | 20.47           | 1.098         | 0.982 | 835.51       | -28.75       | 0.159 | 105.26 | 0.159 | 0.987 |
| GX        | 11.33           | 1.171         | 0.905 | 575.13       | -27.16       | 0.370 | 28.25  | 0.370 | 0.913 |

Figure 1. Adsorption–desorption kinetics of QUN in soils.

Table 2. Adsorption isotherm constants and characteristics derived from Freundlich and Langmuir equations for QUN in the five types of soil.
in four different soils of 28–121 ng L⁻¹ g⁻¹ mL⁻¹ and 1,127–3,941 mL/g, respectively, and soils containing more soil OC content and clay content sorbed more EE₂, but the effect on the process of desorption was minimal²⁶.

The free energy change for adsorption can be used as a preliminary indicator of the soil adsorption mechanism. According to the change in the free energy of adsorption, the process of the adsorption reaction can be inferred. When the absolute value of G is less than 40 kJ/mol, the process belongs to physical adsorption, the adsorption equilibrium of compounds in the soil is fast, and the process is reversible. When the absolute value of G is greater than 40 kJ/mol, the process belongs to chemical adsorption, the adsorption equilibrium is slow, and the adsorption process is irreversible²⁷. Based on the Koc value, the free energy of QUN adsorption was calculated by the following formula:

\[ \Delta G = -1.724RT\ln K_{oc} \]

The ΔG of QUN in the soils was between −28.75 and −24.73 kJ/mol, and the absolute values were less than 40 kJ/mol, which demonstrated that the absorption of QUN in soils corresponded to physical adsorption.

The related Freundlich isotherm parameters for the desorption of QUN are presented in Table 3. The values of \( K_{des} \) ranged from 1.26 to 7.80 mg L⁻¹ g⁻¹ L_n kg⁻¹ with R² in the range 0.935–0.999, and the hysteresis coefficient (H) values between 0.75 and 1.24. Hysteresis phenomena occur when desorption isotherms do not coincide with adsorption isotherms, which is commonly observed in chemical pollutants in soils. Theoretically, there is no hysteresis when H = 1, but in practice no hysteresis is considered when H lies between 0.7 and 1²⁸. The hysteresis coefficient (H) values in soils from BJ, HLJ and GX were slightly greater than 1, indicating that the desorption

---

**Figure 2.** Adsorption–desorption isotherms derived from Freundlich equations for QUN in soils.
of QUN in these soils was slightly hysteretic. In general, when chemical compounds are transferred to soil, their molecules can form stable bonds with soil colloids, especially organic matter and clay minerals. Durán–Álvarez et al. proposed that the hysteresis of estrone and 17β-estradiol was primarily caused by the quantity of organic matter in the soil. The higher the content of organic matter in the soil is, the lower the desorption effect. In addition to binding hysteresis, hysteresis is associated with fractions of soil that undergo structural hysteresis. Hence, an obvious desorption hysteresis phenomenon can easily form. The results of this study were consistent with this conclusion.

**Correlation between $K_f/K_{f_{\text{des}}}$ and soil physical and chemical properties.** In addition to the properties of the compound of interest, the adsorption capacity of a compound in soil is mainly related to the physical and chemical properties of the soil, such as the soil pH, OC content, nitrogen content, CEC and clay content. Based on the data, we found that the numerical values of the adsorption coefficient $K_f$ and desorption coefficient $K_{f_{\text{des}}}$ varied greatly, which indicated that the adsorption and desorption capacities of QUN were obviously different and were possibly influenced by the differences in physical and chemical properties in the soils. Figure 3 shows the relationship between $K_f/K_{f_{\text{des}}}$ and the soil physical and chemical properties. The equation relating $K_f$
and soil TOC content was $K_f = -9.30 + 11.53\ TOC$, with an $R^2$ of 0.929 ($p < 0.05$). The CEC was related to $K_f$ by

$$K_f = 0.45 + 0.47\ CEC,$$

with an $R^2$ of 0.990 ($p < 0.01$). An $R^2$ of 0.922 was obtained between $K_f$ and the soil total nitrogen content, but $K_f$ was not associated with clay content, which means that the adsorption capacity of QUN has a positive relationship with OC and CEC. The $R^2$ between $K_f$ and soil OC was 0.422, and the $R^2$ between $K_f$ and CEC was 0.489, with a correlation equation of $K_f^{des} = 1.92 + 0.14\ CEC$, which indicated that the QUN desorption capacity had a positive relationship with CEC. In addition, the $R^2$ for the relationship between $K_f^{des}$ and the soil total nitrogen content was 0.347, but $K_f^{des}$ was not related to the clay content. The results showed that the adsorption and desorption characteristics of QUN in soil were mainly controlled by the soil OC content and CEC, but were poorly correlated with other soil properties. For the synthetic estrogen EE$_2$, $K_f$ increased with increased carbon concentration with the relationship $K_f = -1.222 + 0.381\ OC$ and $R^2 = 0.922$, but the trend of $K_f^{des}$ was opposite to that of $K_f$, where $K_f^{des} = 46.382 - 4.371\ OC$, with $R^2 = 0.999^{16}$. Durán-Álvarez et al. found that irrigating soil with wastewater containing organic matter influenced the absorption of hormones in the soil.$^{30}$

### Leaching characteristics of QUN in soil.

Based on the values of $K_f$ and the degradation half-life of QUN in soil from our previous report$^{12}$, the leaching characteristics were estimated by the groundwater ubiquity score (GUS)$^{33}$ and retardation factor ($R_f$)$^{34}$, which are listed in Table 4.

The $R_f$ of QUN in the tested soils was between 17.15 and 69.85, where the $R_f$ of HLJ soil was the minimum; these results are in good agreement with the soil OC content and the adsorption capacity of QUN in these two types of soils. GUS has been widely used in the field of pollutants and is a useful index to describe the leachability of compounds in soil. When GUS < 1.8 in soil, compounds are considered to undergo little leaching and migration; when 1.8 < GUS < 2.8, it indicates the possibility of leaching under certain conditions; and when GUS > 2.8, it means that compounds have high leaching mobility$^{35}$. In this study, the GUS of QUN in soil was less than 1.8, suggesting that QUN is a low-leaching substance in soil. However, the leaching characteristics of compounds in the field are complex. In addition to the properties of the compounds themselves, the leaching characteristics are related to the permeability, water content, uniformity, texture and mineral content of the soil. Therefore, the assessment of the leachability of QUN in the environment needs to take all factors into account.

### Conclusions

In this research, five contrasting soils from different areas of China were used to test the adsorption and desorption behavior of QUN, and the GUS and $R_f$ were calculated and verified the leaching characteristics of QUN. The results showed that the Freundlich and Langmuir models fitted well the observed sorption–desorption data to derive kinetics and isotherms of QUN in the tested soils, and QUN could be adsorbed strongly in agricultural and grassland soils. The desorption equilibrium time of QUN was slower than the adsorption equilibrium time, and there was hysteresis in the desorption process. Binding to soil TOC appears to be the dominant sorption and desorption mechanism. The predicted GUS and $R_f$ values were also verified the low mobility of QUN in tested soils. In view of the low-dose effects of QUN and its great disruption potencies, further study ought to be conducted on its distribution, transfer and dissipation in water–sediment systems.

Received: 4 February 2020; Accepted: 24 July 2020
Published online: 06 August 2020

### References

1. Wu, Q., Lam, J. C. W., Kwok, K. Y., Tsui, M. M. P. & Lam, P. K. S. Occurrence and fate of endogenous steroid hormones, alkylphenol ethoxylates, bisphenol A and phthalates in municipal sewage treatment systems. J. Environ. Sci. 61, 49–58 (2017).
2. Raman, D. R. et al. Estrogen content of dairy and swine wastes. Environ. Sci. Technol. 38, 5367–5373 (2004).
3. Fang, H. et al. Study of 202 natural, synthetic, and environmental chemicals for binding to the androgen receptor. Chem. Res. Toxicol. 16, 1338–1358 (2003).
4. Greenblatt, R. B. One-pill-a-month contraceptive. Fertil. Steril. 18, 209–211 (1967).
5. Larrañaga, A. & Berman, E. Clinical study of a once-a-month oral contraceptive: quinestrol–quinogestanol. Contraception 1, 137–148 (1970).
6. Baumgardner, S. B. et al. Replacement estrogen therapy for menopausal vasomotor flushes: comparison of quinestrol and conjugated estrogens. Obstet. Gynecol. 51, 445–452 (1978).
7. Li, J. et al. Abnormal secretion of reproductive hormones and antioxidant status involved in quinestrol induced reproductive toxicity in adult male rat. Tissue Cell 46, 27–32 (2014).

| Soil site | Bulk density, $p_b$ | Porosity, $\theta$ | Retardation factor ($R_f$) | GUS | $\log(DT_{50}) \times [4 - \log (K_{OC})]$ |
|-----------|-------------------|-------------------|-----------------------------|-----|------------------------------------------|
| BJ        | 1.36              | 0.49              | 36.08                       | 9.44| 1.16                                      |
| NMG       | 1.65              | 0.38              | 17.15                       | 14.72| 1.74                                      |
| YN        | 1.29              | 0.51              | 18.58                       | 13.12| 1.42                                      |
| HLJ       | 1.48              | 0.44              | 69.85                       | 9.92| 1.07                                      |
| GX        | 1.33              | 0.50              | 31.13                       | 9.83| 1.23                                      |

Table 4. Retardation factors and groundwater ubiquity score of QUN in soils. *Soil porosity = 1 – (soil bulk density/2.65). $^{b}$DT$_{50}$ values from our previous report$^{16}$. 
8. Geng, Q. Q. et al. The bioaccumulation and biotransformation of synthetic estrogen quinestrol in crucian carp. *Aquat. Toxicol.* **155**, 84–90 (2014).
9. Geng, Q. Q. et al. The accumulation, transformation, and effects of quinestrol in duckweed (*Spirodela polyrhiza* L.). *Sci. Total Environ.* **634**, 1034–1041 (2018).
10. Tang, T. et al. Photodegradation of quinestrol in waters and the transformation products by UV irradiation. *Chemosphere* **89**, 1419–1425 (2012).
11. Zhang, Q. et al. Degradation of the potential rodent contraceptive quinestrol and elimination of its estrogenic activity in soil and water. *Environ. Sci. Pollut. Res.* **21**, 652–659 (2014).
12. Tang, T. et al. Degradation kinetics and transformation products of levonorgestrel and quinestrol in soils. *J. Agric. Food. Chem.* **67**, 4160–4169 (2019).
13. Liu, Z. H., Kanjo, Y. & Mizutani, S. Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment physical means, biodegradation, and chemical advanced oxidation: a review. *Sci. Total Environ.* **407**, 731–748 (2009).
14. Odell, W. D. & Moulitch, M. E. The pharmacology of contraceptive agents. *Annu. Rev. Pharmacol. Toxicol.* **14**, 413–434 (1974).
15. Giannina, T. & Meli, A. Prolonged oestrogenic activity in rats after single oral administration of ethinyloestradiol-3-cyclopentyl ether. *J. Pharm. Pharmacol.* **21**, 271–283 (1969).
16. Scherr, F. F., Sarmah, A. K., Di, H. J. & Cameron, K. C. Degradation and metabolite formation of 17β-estradiol-3-sulphate in New Zealand pasture soils. *Environ. Int.* **35**, 291–297 (2009).
17. Stumpe, R. & Marschner, B. Factors controlling the biodegradation of 17β-estradiol, estrone and 17α-ethinylestradiol in different natural soils. *Chemosphere* **74**, 556–562 (2009).
18. Goepfert, N., Dror, I. & Berkowitz, B. Detection, fate and transport of estrogen family hormones in soil. *Chemosphere* **95**, 336–345 (2014).
19. Ma, L. & Yates, S. R. Degradation and metabolite formation of estrogen conjugates in an agricultural soil. *J. Pharm. Biomed. Anal.* **145**, 634–640 (2017).
20. Wang, S. et al. Photodegradation of 17β-estradiol on silica gel and natural soil by UV treatment. *Environ. Pollut.* **242**, 1236–1244 (2018).
21. United States Environmental Protection Agency (U.S. EPA). Fate, transport and transformation test guidelines. OPPTS 835.1230. Adsorption/desorption (batch equilibrium) for pesticides and toxic substances. EPA 712-C-08–009 (2008).
22. Lai, K. M., Johnson, K. L., Scrimshaw, M. D. & Lester, J. N. Binding of waterborne steroid estrogens to solid phases in river and estuarine systems. *Environ. Sci. Technol.* **34**, 3890–3894 (2000).
23. Gineys, N., Giroud, B., Gineys, M. & Vulliet, E. Retention of selected steroids on a silt-loam soil. *Environ. Lett.* **47**, 2133–2140 (2012).
24. Li, J., Fu, J., Xiang, X., Wu, M. M. & Liu, X. Kinetics, equilibrium, and mechanisms of sorption and desorption of 17α-ethinyl estradiol in two natural soils and their organic fractions. *Sci. Total Environ.* **452–453**, 404–410 (2013).
25. Giles, C. H., Smith, D. & Huitson, A. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *J. Colloid Interface Sci.* **47**, 755–765 (1974).
26. Hildebrand, C., Londry, K. L. & Farenhorst, A. Sorption and desorption of three endocrine disrupters in soils. *J. Environ. Sci. Heal. B*. **41**, 907–921 (2006).
27. Rama Krishna, K. & Philip, L. Adsorption and desorption characteristics of lindane, carbofuran and methyl parathion on various Indian soils. *J. Hazard. Mater.* **160**, 559–567 (2008).
28. Kleineidam, S., Rugner, H. & Grathwohl, P. Desorption kinetics of phenthanrene in aquifer material lacks hysteresis. *Environ. Sci. Technol.* **38**, 4169–4175 (2004).
29. Carrasquillo, A. J., Bruland, G. L., MacKay, A. A. & Vasudevan, D. Sorption of ciprofloxacin and oxytetracycline zwitterions to soils and soil minerals: influence of compound structure. *Environ. Sci. Technol.* **42**, 7634–7642 (2008).
30. Durán-Álvarez, J. C., Prado, B., Ferroud, A., Juayerk, N. & Jiménez-Cisneros, B. Sorption, desorption and displacement of ibuprofen, estrone, and 17β-estradiol in wastewater irrigated and rainfed agricultural soils. *Sci. Total Environ.* **473–474**, 189–198 (2014).
31. Zhang, Z. H., Feng, Y. J., Gao, P., Liu, J. F. & Ren, N. Q. Comparing the adsorption and desorption characteristics of 17α-ethinylestradiol on sludge derived from different treatment units. *Int. J. Environ. Sci. Technol.* **9**, 247–256 (2012).
32. Lima, D., Schneider, R. J. & Esteves, V. I. Sorption behavior of EE2 on soils subjected to different long-term organic amendments. *Sci. Total Environ.* **423**, 120–124 (2012).
33. Gustafson, D. I. Groundwater ubiquity score-A simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* **8**, 339–357 (1989).
34. Turin, H. J. & Bowman, R. S. Sorption behavior and competition of bromacil, napropamide, and prometryn. *J. Environ. Qual.* **26**, 1282–1287 (1997).
35. Webb, R. M. T. et al. Variations in pesticide leaching related to land use, pesticide properties, and unsaturated zone thickness. *J. Environ. Qual.* **37**, 1145–1157 (2008).

Acknowledgements
This work was supported by the national key research and development program of China (Grant No. 2017YFD0201600, 2016YFD0200204) and the National Natural Science Foundation of China (Grant No. 31501668).

Author contributions
T.T. and X.Z. conceived and designed the ideal of the study. M.G. and Q.L. performed the experiments and wrote the manuscript. Z.X. and C.Z. revised the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to T.T.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher’s note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
