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Study of Steroid Estrogen Loss in Soil after the Application of Composted Manure as a Fertilizer

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Abstract: Steroid estrogens (SEs) play a significant role as endocrine-disrupting substances, and one of their major sources is animal manure. However, there is limited information available regarding the loss of SEs in farmland soil after the application of commercial composted animal manure or fertilizers. To address this gap, our study aimed to simulate rainfall and flood irrigation scenarios and investigate the loss characteristics of SEs, as well as Chemical Oxygen Demand (COD), Total Nitrogen (TN), and Total Phosphorus (TP) in runoff from soil–manure mixtures. The results demonstrated that the loss concentrations of SEs (73.1 ng/L of the mean E2β active equivalent factor) presented a potential environmental risk. Additionally, substituting composted manure with commercial organic fertilizers lead to a significant reduction in TP (maximum 56%) and TN (maximum 24%) loss. Consequently, the application of commercial organic fertilizers offers considerable advantages in maintaining nitrogen and phosphorus fertilization efficiency while controlling SEs loss. Furthermore, our study explored the synergistic pollution mechanism among these pollutants and observed significant correlations between SEs and TN, TP, and COD loss concentrations, indicating the simultaneous occurrence and migration of these pollutants in agricultural non-point source pollution. These results provide valuable insights into the environmental risk associated with SEs from agricultural non-point sources.

Keywords: steroid estrogen; precipitation; flood irrigation; composted manure; commercial organic fertilizer

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1. Introduction

Steroid estrogens (SEs) modulate physiology, development, and reproduction of animals [1]. Estrone (E1), 17β-estradiol (E2β), 17α-estradiol (E2α), estriol (E3), and 17α-ethinylestradiol (EE2) are currently recognized as important female hormones, known for their potent endocrine-disrupting activity [2,3]. These steroid estrogens (SEs) are primarily excreted into the environment by humans, livestock, and poultry [4]. Long-term exposure to estrogen-contaminated water at nanomolar levels can disrupt the endocrine system and sexual development in animals [5–7]. Numerous researchers have been monitoring the fate of estrogens in Waste Water Treatment Plants (WWTPs) and assessing the efficiency of different treatment processes in removing SEs [8,9]. The degradation, sorption, and mobility of SEs have been areas of concern, with their potential risks to surrounding surface water and groundwater being widely acknowledged [10–12]. For animal manure, composting is the most commonly adopted method of bioresource utilization. Manure supplies nutrients for plant growth, improves soil properties, and is more environmentally friendly than chemical fertilizers [13,14]. When composted animal manure is used on farmland, the nitrogen and phosphorus needed by crops are partly lost with rainfall or irrigation, which may affect fertilizer efficiency. This problem has attracted the attention of researchers [15–21]. However, there is limited information available in the literature on the loss of SEs from farmland soil after application of composted animal manure.

The government encourages farmers to replace chemical fertilizers with organic fertilizers from the view of the quality of agricultural products and the sustainable use of soil [22], and many farmers do so, but farmers are also torn as to whether they should use animal manure for in situ composting or buy commercial organic fertilizers, a question to which policy makers are unable to give an answer. In addition, after a large amount of domestic wastewater in the watershed has been controlled, the impact of agricultural non-point pollution on surface water quality is becoming more and more prominent. Previous scholars have focused on the occurrence and transport of nitrogen, phosphorus, or organic matter from agricultural surface pollution [18,23–25], but have not paid much attention to estrogen accompanied by manure runoff from farmland, which is often homologous to conventional indicators of water quality pollution. The most effective control measures for agricultural non-point source pollution are source reduction and loss process control [22]. Therefore, we would like to explore the characteristics of manure field utilization and runoff to subsequently achieve the goal of control of SEs.

In this study, we designed an experimental setup simulating rainfall and flood irrigation, and five selected SEs (E1, E2α, E2β, EE2, E3) and COD, Total Nitrogen (TN), and Total Phosphorus (TP) runoff characteristics were studied together. Then, the mechanism of synergistic pollution among them was explored. The results of this study can provide reference for the environmental risk of SEs when agriculture and environmental protection departments of government formulate measures to control nitrogen and phosphorus pollution from an agricultural non-point source.

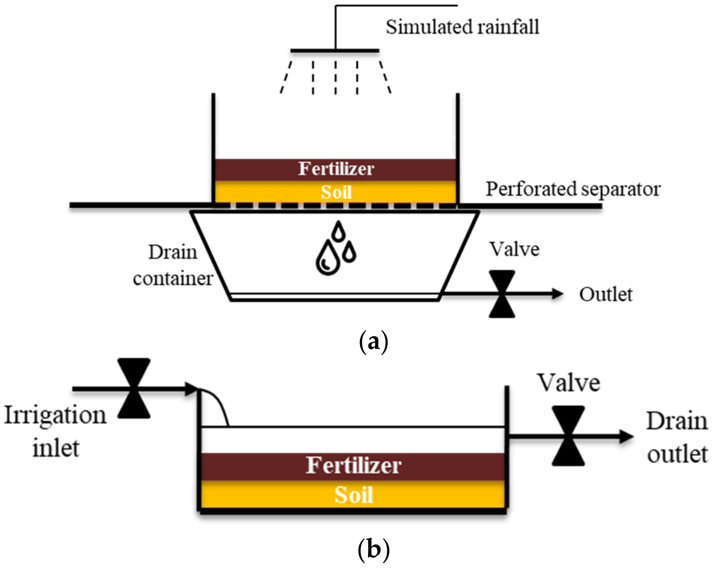
2. Materials and Methods

2.1. Experimental Procedures

The dairy manure utilized in this experiment was sourced from dairy farmers located in Fengyi Town (25.547213° N, 100.332926° E), Dali, China. Commercial organic fertilizers used in the experiment were taken from Yunnan Shunfeng Organic Fertilizer Factory, where it was made from composting local dairy manure in Fengyi Town. According to "Technical specification for animal manure composting" [26], the dairy manure was composted and then were determined by the raw SEs; moisture content; and solid physical and chemical properties. These indicators were also applied to the initial analysis of commercial organic fertilizers, red soils, and paddy soils used in this study, and the analysis results mentioned above will be provided in Section 3.1. The composted manure was put into experimental devices and mixed with the soils. The amount of dairy manure used referred to the "Technology code for land application rates of livestock and poultry manure" [27]. In this experiment, the composed manure application to the land was 20 t/hm^2, that is, 375 g of dairy manure was put into the soil with the thickness of 15 cm in each device.

Simulated rainfall experiment. The experimental setup is shown in Figure 1a, and the carrier for the soil and manure/fertilizer mixture was a Plexiglas cylinder with a diameter of 0.49 m and a height of 0.5 m. There were 8 experimental groups. In a total of 4 experimental groups composted manure was added, and in 4 other groups, commercial organic fertilizers were added. The experimental groups considered different rain events (5 mm/d and 10 mm/d) and soil types (red soil and paddy soil), respectively. The experiment spanned a duration of 30 days and involved 10 rounds (R1–R10), including a designated 3-day rainfall round. During each simulated rainfall cycle, the drainage liquid from the container was collected, and concentrations of SEs, COD, TN, and TP were measured.

Simulated flood irrigation experiment. The experimental setup is shown in Figure 1b, and the carrier for the soil and manure/fertilizer mixture was a Plexiglas cylinder with a diameter of 0.49 m and a height of 0.5 m. There were 8 experimental groups. In a total of 4 experimental groups composted manure was added, and in 4 other groups, commercial organic fertilizers were added. The experimental groups considered different irrigation flooding depths (5 cm and 20 cm) and soil types (red soil and paddy soil), respectively. The experiment lasted for 30 days and experienced 10 rounds (R1–R10), of which 3 days were designed as a flood irrigation round. The drain liquid in the container was collected and the concentrations of SEs, COD, TN and TP were determined after each simulated rainfall cycle.



(**a**)

(**b**)

Figure 1. Experimental setup ((**a**). Simulated rainfall; (**b**). Simulated flood irrigation).

TN was determined by alkaline potassium persulfate digestion-UV spectrophotometric method [28], and TP was measured by using ammonium molybdate spectrophotometric method [29], and the analysis of COD was carried out in accordance with standard method [30].

2.2. Sample Pre-Treatment

Water sample. Prior to extracting the sample, the solid-phase extraction cartridge underwent a rinsing process with a suitable solvent. This step ensured that the analyte came into close contact with the solid-phase surface, thereby enhancing the recovery rate and reproducibility of the extraction. For activation of the column, a sequence of 2 × 3 mL of n-hexane, 2 × 3 mL of ethyl acetate, 2 × 3 mL of methanol, and 2 × 5 mL of ultrapure water was employed. The liquid was dripped at a rate of approximately 1 mL/min for 5 min to ensure thorough saturation of the filler with the activating reagent. Following activation, the pre-treated water sample ranging from 0.5 L to 1.0 L was passed through the activated solid-phase extraction cartridges under a controlled vacuum pressure, with a flow rate regulated at about 4 mL/min. This step facilitated the adsorption and retention of the target substances (SEs) as well as certain impurities onto the solid-phase extraction cartridges. Subsequently, the cartridges were washed with 10 mL of a 10% methanol–water solution at a flow rate of roughly 5 mL/min. For elution, 10 mL of ethyl acetate was used, with the drip rate controlled at approximately 1 mL/min, and the resulting eluate was collected. The eluent containing the dried SEs was subjected to mild high-purity nitrogen at 30 °C. To enable derivatization, 25 µL of N,O-Bis(trimethylsilyl)trifluoroacetamide reagent (containing 1% TMCS by mass) and 50 µL of pyridine solution were added to the SEs eluent. The mixture underwent derivatization utilizing a microwave at 300 W for 4 min. After nitrogen blowing, 400 µL of a 1 mg/L internal standard (Mirex) was added to dissolve the SEs. The resulting solution was then transferred to a 2 mL sample bottle for subsequent detection.

Manure/soil sample. The manure samples were subjected to centrifugation at 3000 rpm for 10 min. The resulting supernatant was discarded, and the remaining material was freeze-dried for 24 h. Then, 5 g of freeze-dried sample was mixed with 10 mL of a methanol and ethyl acetate mixture (in a volume ratio of 1:1). The mixture was subjected to ultrasonic extraction for 20 min at a power of 250 W and frequency of 40 kHz. After extraction, the mixture was centrifuged at 5000 rpm for 15 min, and the supernatant was carefully collected. This extraction process was repeated three times, and the collected supernatants from the three extractions were combined. The combined supernatants were then dried under high-purity nitrogen. The resulting dried material containing the target substance was dissolved in 2 mL of n-hexane. The subsequent pre-treatment steps for the manure samples were the same as those used for the water samples.

2.3. GC/MS Analysis and Quality Control

The chemical analysis standards for SEs (purity $\geq$ 97.0%) were obtained from Aladdin Reagent (Shanghai, China) Co., Ltd., while the standard substitute E2β-d2 was purchased from C/D/N ISOTopes in Canada. The analysis was conducted using a Thermo Fisher (Waltham, MA, USA) TRACE 1300-ISQ Series Quadrupole instrument. For gas chromatography (GC), a TR-5 MS quartz capillary column with dimensions of 30 m × 0.25 mm × 0.25 μm was employed. High-purity helium (99.999%) was used as the carrier gas, with a constant flow rate of 1.2 mL/min. Splitless injection was utilized, with each sampling volume set at 1.0 μL. The author has previously optimized the analytical method [31,32]. The inlet temperature was maintained at 280 °C, and septum purges were set at 5.0 mL/min. The column heating program consisted of an initial temperature of 50 °C, held for 2 min, followed by an increase to 260 °C at a rate of 20 °C/min and held for 5 min. Subsequently, the temperature was raised to 280 °C at a rate of 10 °C/min and held for 5 min. For mass spectrometry (MS), an electron bombardment ion source (EI) was used with an ionization voltage of 70 eV. The ion source temperature was set at 250 °C, while the transmission line temperature was maintained at 280 °C. A solvent delay time of 10 min was implemented. The analysis employed the full scan mode (SCAN) for qualitative analysis and the selective ion scan mode (SIM) for quantification. The Xcalibur software (Version 4.3) was utilized for analyzing the SEs and internal standards.

To assess the accuracy and precision of the method, a standard solution containing 50 ng and 500 ng of the target component was used as a sample, and the measurement was conducted 7 times within a single day. The limits of detection (LOQ), which were defined as 10 times the signal-to-noise ratio, were determined to be 1.48 μg/L, 1.13 μg/L, 1.65 μg/L, 2.03 μg/L, and 0.97 μg/L for E1, E2α, E2β, EE2, and E3, respectively. The average spike recovery of SEs was found to be 98.0%, indicating a high level of accuracy. The relative standard deviation (RSD) ranged from 0.4% to 6.8%, demonstrating good precision within the tested samples.

2.4. Estrogen Equivalent (EEQ) Calculation

In this study, the EEF (E2β active equivalent factor) data reported in the literature were utilized to calculate the EEQ (estrogen equivalent concentration, measured in ng/L). The following EEF values were utilized: E1 = 1/3 [33,34], E2β = 1, E2α = 1/8 [35], E3 = 1/12 [36], and EE2 = 2.2 [34]. To simplify the assessment and ease comparison with the literature, the standardization of estrogen evaluations as EEQ-E2β was calculated using the following equation:

$$\mathrm{EEQ} = \sum\nolimits_{\mathrm{i}}^{\mathrm{n}} \mathrm{EEF_i} \times \mathrm{C_i} \tag{1}$$

where EEQ represents the estrogen equivalent concentration (in ng/L or ng) of E2β; $\mathrm{EEF_i}$ denotes the E2β equivalent of the estrogen species i; $\mathrm{C_i}$ (ng/L or ng) denotes the measured ambient concentration of estrogen i (in ng/L or ng); n = 5 (i.e., E1, E2β, E2α, E3, and EE2).

2.5. Statistical Analysis

Spearman correlation analysis was used to observe the association between various pollutants in the leachate. The figures were plotted using Origin Pro 2021 software (Version 9.8.0.200, Origin Lab Corporation, Northampton, MA, USA).

3. Results and Discussion

3.1. SEs Background Content in Soil and Fertilizer

The basic properties of the two selected soils, composted dairy manure, and commercial organic fertilizers are shown in Table 1, and the original content of the five SEs is shown in Figure 2. Due to year-round cultivation, the OM content of paddy soil is much higher than that of red soil, and N and P are also slightly higher than that of red soil. There is not much difference in the composition of particle size (Figure S1), EEQ and various SEs. The nitrogen, OM, SEs, and moisture in naturally composted feces are significantly higher than those in commercial organic fertilizers, except for P. After investigation, the processing steps of commercial organic fertilizer is as follows: manure is transported to the yard, weighed, mixed, and stirred, and the moisture and C/N ratio of the fertilizer are roughly adjusted according to the raw material composition. Generally, sugarcane bagasse (auxiliary material) and biogas bagasse are mixed, and fermentation bacteria are added for the first fermentation. The fermentation temperature is controlled at 50–65 °C, and after 30 days of fermentation, it is stacked again for the second fermentation (about 20 days). Then, it is crushed, and mixed and stirred, humic acid and trace elements are added to the mixing and stirring system to form organic fertilizer products after crushing, screening, and granulation.

Table 1. Properties of selected soil and fertilizer for experiment.

Soil/Fertilizer Type	TN g/kgDW	TP g/kgDW	OM g/kgDW	EEQ µg/kgDW	Moisture %
Paddy soil	2.5 ± 0.2	1.4 ± 0.0	54.0 ± 2.3	40.4	5.91
Red soil	1.1 ± 0.1	1.2 ± 0.1	5.2 ± 0.5	34.9	4.99
Commercial organic fertilizer	9.8 ± 1.3	8.5 ± 0.4	328.0 ± 12.0	282.8	37.51
Composted manure	24.1 ± 2.5	6.6 ± 1.2	646.4 ± 17.4	506.1	80.25

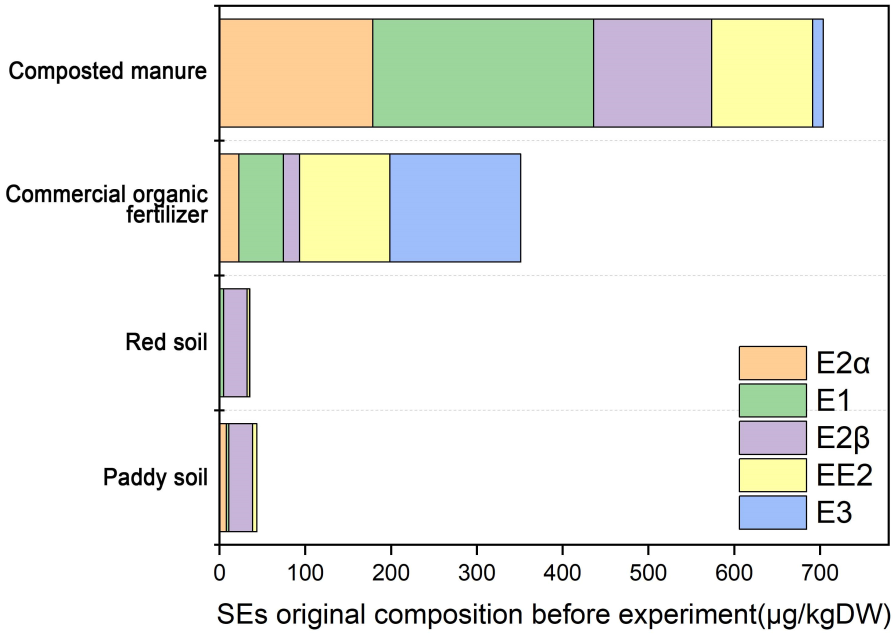


Figure 2. SEs composition in experimental fertilizer before experiment.

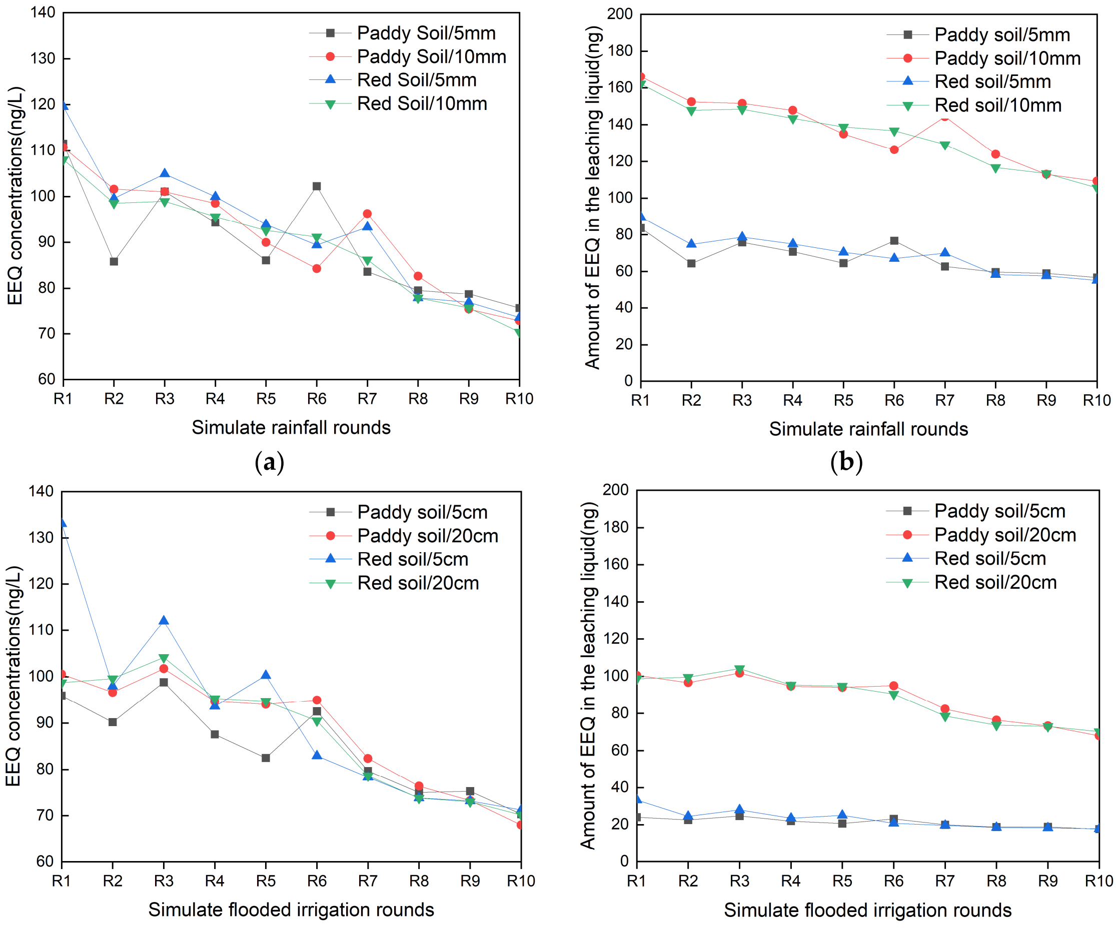
The results shown in Figure 2 indicate that the SEs fractions and EEQs of commercial organic fertilizer products were significantly lower than those of naturally composted manure, indicating that the degradation of SEs during organic fertilizer processing was significantly better than that of the natural composting and fermentation process. The amount of SEs was consistent with the results of Odinga [37], who also proposed that different animals contribute differently, and in this study, most of the manure was dairy manure, with a lower production of SEs compared to pig manure. The fertilizers used in this research basically meet the standards for organic fertilizers [38], except for the high moisture of composted manure. The difference in degradation effect was mainly due to the fact that the organic fertilizer-processing process ensured sufficient oxygen through regular mechanized turning of the pile, and was more conducive to the growth of microorganisms through batching and C/N ratio regulation. Ji's research found that optimized aeration did not affect GI (germination index), final C/N and (Final C/N)/(Initial C/N) [39]. The difference of C, N, P and moisture between commercial organic fertilizer and composted manure mainly lay in C/N ratio regulation (sawdust, straw, and by-product) and chemical additives (phosphoric acid, Ca-superphosphate, phosphogypsum, and Mg-P salts).

3.2. Characteristics of SEs-EEQ Loss from Soil–Manure Mixture

When composted manure is utilized on farmland for a period of time, two scenarios may be encountered that significantly impact the loss of SEs, one being natural rainfall and the other being flooded irrigation.

In Figures 3a and S2, it can be found that the rapid loss of TN, TP, COD and SEs occurred at the arrival of the first rainfall round after application of manure in the field, in which the initial loss concentration of TN, TP and COD was much higher than that of the subsequent rounds of rainfall, and the proportion of the initial loss of EDCs was relatively low, which was obviously different from that of the rate of loss of livestock manure in the state of natural stockpile [32], and reflected that the soil after the return to the field had an important effect on the adsorption and retention of SEs, TN, TP and COD were mainly lost in the granular state. Starting from the 2nd round of rainfall, the loss rates of TN, TP and COD decreased significantly and were maintained at a low level. Soil type had a significant effect on TN, TP and COD loss concentrations, and the loss concentration of rice soil was higher than that of red soil, which might be mainly due to the difference in soil background values. Rainfall intensity was not associated with TN, TP, and COD loss concentrations. Starting from the 1st round of rainfall, the loss concentration of EDCs showed a slowly decreasing trend, which was not significantly associated with soil type and rainfall intensity, but until the end of the experiment, the loss EEQ concentration could still reach the average value of 73.1 ng/L, which is a certain environmental risk. The amount of TN, TP, COD and SEs lost per rainfall round is shown in Figures 3b and S3, and they imply that (1) total TN, TP and COD loss, paddy soil > red soil; (2) TP, COD and SEs loss, 10 mm rainfall > 5 mm rainfall; and (3) SEs are more affected by rainfall, suggesting that the loss of SEs is directly correlated with the loss of dissolved organic matter (DOM).

Ordinary water-saving irrigation practices may have impacts similar to those of natural rainfall; therefore, we experimentally simulated flooded irrigation, i.e., irrigation resulting in soil inundation. The experimental results are shown in Figures 3c,d, S4 and S5. The results showed that, compared to rainfall conditions, (1) the average concentrations of TN, TP and COD lost from soakaway water were significantly lower than those lost under rainfall conditions; (2) there was no significant loss of particulate state from the first roaming round of roaming water, and therefore rapid loss of TN, TP and COD did not occur; and (3) the concentrations of SEs lost from high water roaming conditions were comparable to those lost under rainfall conditions. The above suggests that under high water flooding conditions, a large loss of TN, TP and COD from particulate pollutants was avoided, but the leaching process of SEs with dissolved organic matter was not altered. The loss results (Figures 3d and S5) showed that (1) TP and COD losses were affected by both soil type and diffuse irrigation water, and the greater the diffuse irrigation water, the greater the TP and COD losses under rice soil type, and the effect of diffuse irrigation water was greater than the effect of soil type; and (2) the trend of changes in the loss of TN and EDCs was similar, and they were both directly correlated with the diffuse irrigation water, and there was no obvious correlation with soil type.



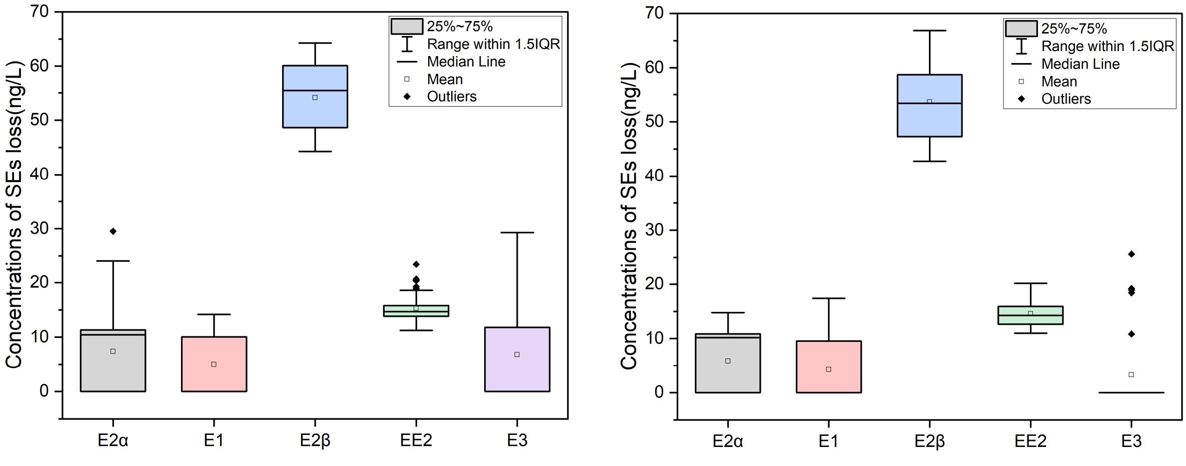
(**a**) (**b**)

(**c**) (**d**)

Figure 3. SEs-EEQ loss from soil–manure mixture ((**a**). SEs runoff concentration under simulated rainfall; (**b**). SEs runoff amount under simulated rainfall; (**c**). SEs runoff concentration under simulated irrigation; (**d**). SEs runoff amount under simulated irrigation).

3.3. Differences in Concentrations of Various SEs

The concentrations of various SEs in the composted manure before the start of the experiment were 178.9 µg/(kgDW) E2α, 257.4 µg/(kgDW) E1, 137.4 (kgDW) E2β, 118.0 (kgDW) EE2 and 12.3 (kgDW) E3. However, the comparison of SEs loss concentrations (Figures 2 and 4) revealed a significant change from the original ratio in both simulated rainfall conditions and high water flooding conditions. E2β had the largest average loss concentration, followed by EE2. E3 had the largest range of variation in loss concentration and EE2 had the smallest range of variation in concentration. The reasons for this phenomenon could be the degradation of free-state SEs, interconversion, and conversion of conjugated-state SEs to the free-state by microbial action in agricultural soils. According to our current understanding [40], it has been reported that E1 and E3 are degradation intermediates of E2α and E2β. Additionally, under aerobic conditions, E1 has the ability to degrade into E3. During the leaching process with water, significant degradation of SEs was observed, particularly noticeable for E2α, E2β, and E1, which were converted to E3 in considerable amounts. It is important to note that E1, E2α, and E3 are highly active compounds that exhibit dynamic synergistic reduction throughout the process. As a result, their concentrations appear relatively low in the samples due to the significant losses associated with this active degradation process. The highest concentrations of E2β are due to the conversion of undetected conjugate-state SEs in the original composted manure, including estrogen sulphates and glucuronides [41–43], specifically again E2-3S, E2-17S, E2-3G, and E2-17G [44,45]. In addition, for both the simulated rainfall and heavy water irrigation scenarios, there were no particularly significant differences in the concentrations of the various SEs lost, probably due to the fact that the rainfall and irrigation were not continuous, but rather intermittent, and sufficient aerobic conditions were ensured between rounds for further degradation of the SEs.



(**a**) (**b**)

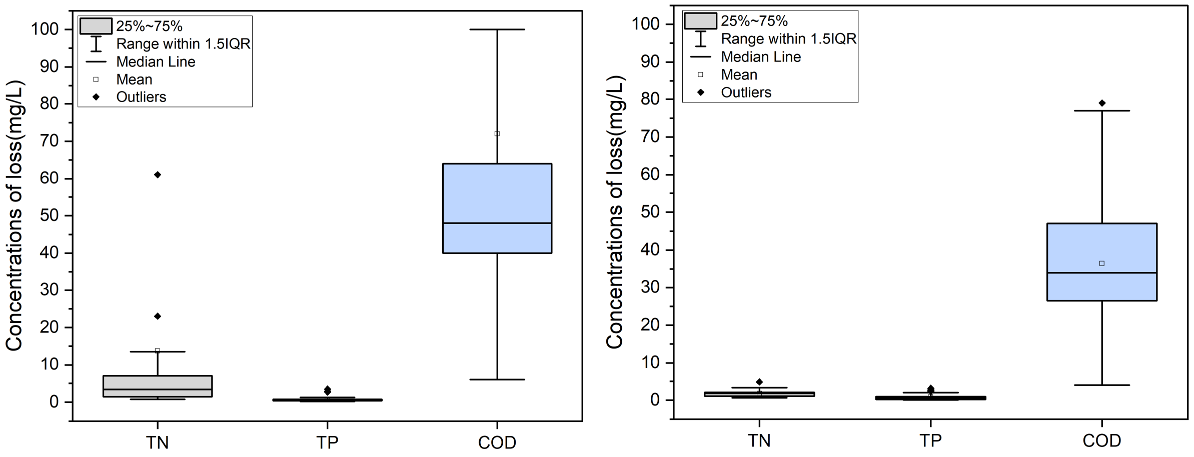
Figure 4. Five SEs concentrations of the leaching liquid under simulated rainfall and irrigation ((**a**). under simulated rainfall; (**b**). under simulated irrigation).

3.4. Correlation between TN, TP, COD and SEs Loss

Many previous scholars of agricultural non-point pollution have focused on the characterization of TN, TP or COD loss from the field [18,23–25], whereas this study focused on the characterization of SEs loss; however, in most scenarios, TN, TP and COD occur concurrently with the loss of SEs—how do they relate to each other? Figure 5 shows that COD, TN, and TP loss concentrations were higher under rainfall conditions than under diffuse irrigation conditions, specifically from Figure S2, where it was found that the first round of rainfall contributed significantly. In the first round of rainfall, COD, TN, and TP loss concentrations could reach 76–526 mg/L, 23–206 mg/L and 0.68–3.48 mg/L, respectively. In contrast, in the first round of flooded irrigation (Figure S4), only 40–71 mg/L, 2.08–4.84 mg/L, and 2.42–3.14 mg/L of COD, TN, and TP were lost, respectively. The biggest difference between the two scenarios is the dramatic loss of particulate matter from rainfall, which is mechanistically the same as the first flush effect of agricultural non-point source pollution [46].

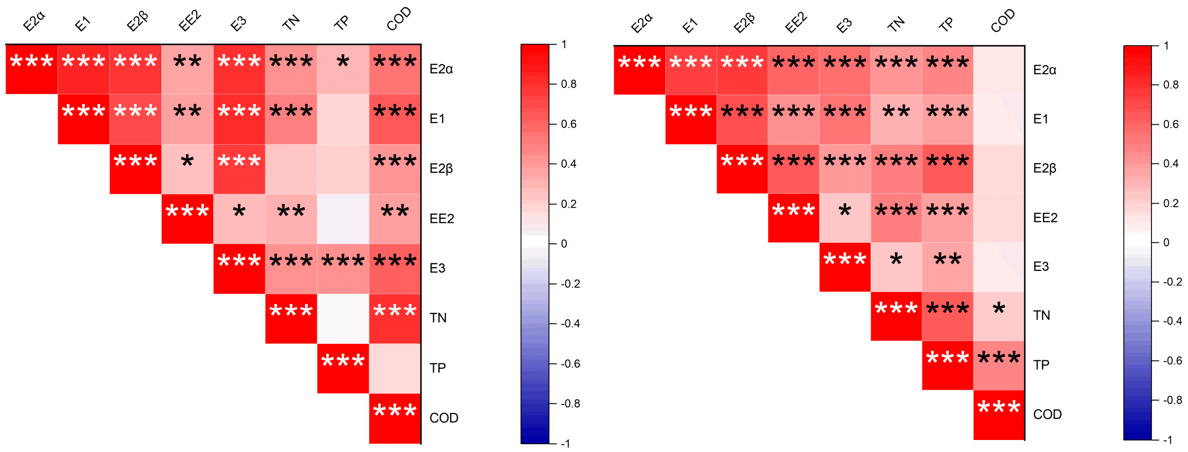
We correlated the raw data from each round of experiments and the results (Figure 6) showed that under rainfall conditions, the various SEs were significantly correlated with each other at $p \leq 0.001$ level, except for EE2, which was almost always significantly correlated with COD and TN at $p \leq 0.01$ level, whereas under flooded irrigation conditions, all kinds of SEs were almost significantly correlated at $p \leq 0.001$ level and SEs were almost always significantly correlated with TN and TP at $p \leq 0.01$ level. In our preliminary leaching experiments, it was found that the hydrophobicity of SEs had a significant effect on the release. Most of the SEs were adsorbed on the granular OM, and a few were adsorbed on DOM. The granular OM was lost in large quantities with rainfall, which led to the loss of SEs being carried in large quantities as well, and this was the reason for the largest correlation between the SEs and the COD under rainfall conditions. Under diffuse irrigation conditions, a large amount of settling of particulate matter occurred due to the high water level in the field, and the lost SEs were lost with the small particulate OM and DOM, which was closer to the characteristics of TP, especially SRP adsorption, which was the reason for the largest association of SEs with TP under the condition of high water diffuse irrigation. It can be further associated that in the future, more convenient and cost-effective COD and

TP indicators can be considered as a reference for the regulation of the risk of loss of SEs from agricultural land receiving composted manure.



(**a**) (**b**)

Figure 5. Concentrations of TN, TP, and COD in the leaching liquid under simulated rainfall and irrigation ((**a**). under simulated rainfall; (**b**). under simulated irrigation).

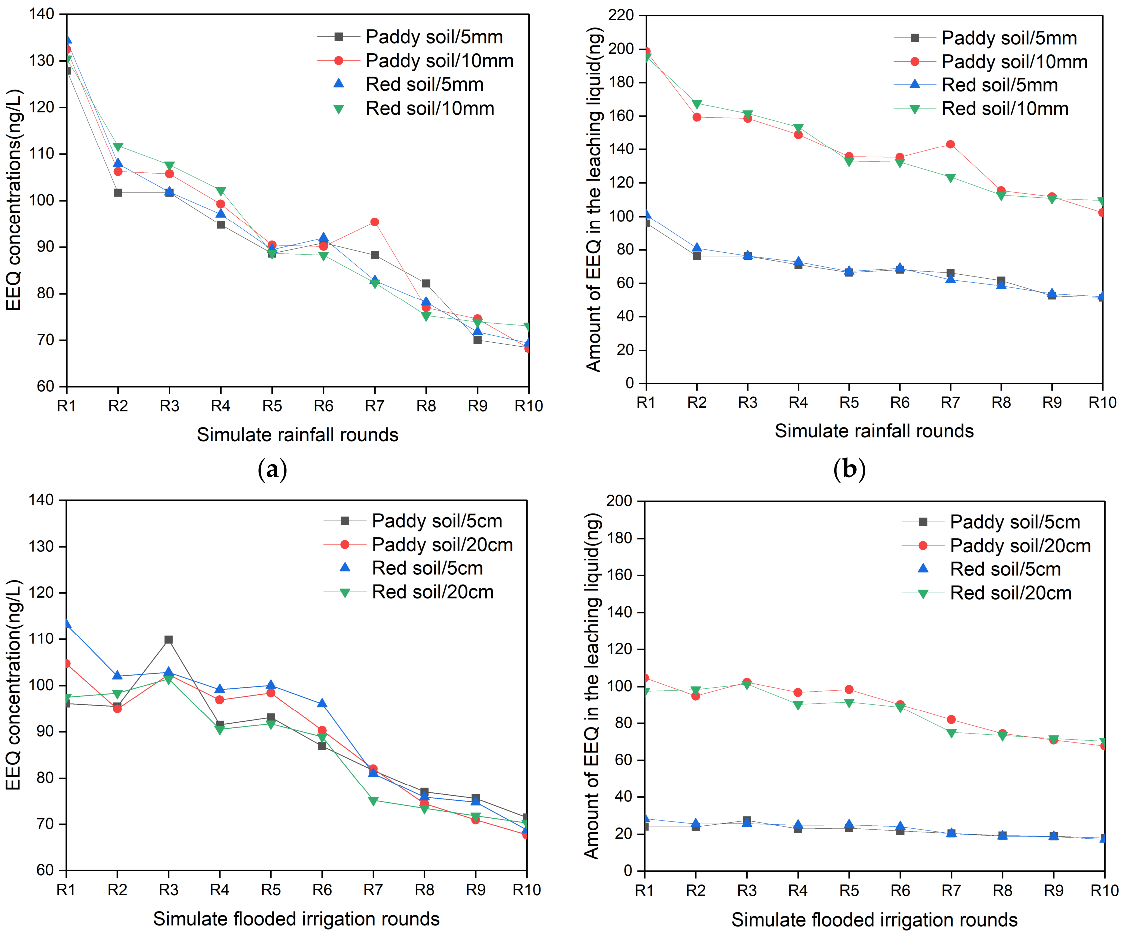


(**a**) (**b**)

Figure 6. Spearman correlation analysis of TN, TP, COD and five SEs concentrations in the leachate ((**a**). under simulated rainfall; (**b**). under simulated irrigation; *, **, *** represent $p < 0.05$, $p < 0.01$, $p < 0.001$, respectively).

3.5. Replacing Composted Manure with Commercial Organic Fertilizers

As farmers compost on their own in a sloppy manner, the fertilizer efficiency and hygiene of the compost is not always guaranteed; therefore, buying commercial organic fertilizer is another option. We chose the commercial organic fertilizer from the organic fertilizer factory to replace the composted manure to repeat the above experiment. Characteristics of SEs-EEQ loss from soil–fertilizer mixture are shown in Figure 7. As expected, due to the close proximity of the cow dung feedstock (originating from the same village and town), the SEs loss curves were very close to each other, both for simulated rainfall and flooded irrigation conditions. Commercial organic fertilizers did not demonstrate better control of SEs loss in terms of loss concentration and loss volume.



(**a**) (**b**)

(**c**) (**d**)

Figure 7. SEs-EEQ loss from soil–fertilizer mixture ((**a**). SEs runoff concentration under simulated rainfall; (**b**). SEs runoff amount under simulated rainfall; (**c**). SEs runoff concentration under simulated irrigation; (**d**). SEs runoff amount under simulated irrigation).

Under simulated rainfall conditions, we found that farmland applied with commercial organic fertilizer could be compared with composted manure returned to the field in the following ways: TN concentration was significantly lower, especially in the rapid loss of the 1st round of rainfall, the highest TN loss concentration decreased from 206 mg/L to 132 mg/L; TP loss concentration was also greatly reduced, and in the 1st round of rainfall, the highest TP loss concentration decreased from 3.48 mg/L to 1.10 mg/L; however, COD loss concentration increased significantly; along with the dissolution and loss of organic matter, the initial loss concentration of SEs was also higher than that of composted manure, but in the later rainfall rounds, the loss concentration of SEs decreased at a faster rate. According to Figure 8, TN and TP losses were significantly reduced, COD losses increased, and SEs losses increased slightly. Composted manure under rainfall conditions brought significant TN and TP losses, meaning that manure nitrogen and phosphorus fertilizer efficiency was greatly reduced (2% decrease in TN and 54% decrease in TP). Although commercial organic manure application brought about a 2% increase in SEs loss, it was considered to be a decrease in SEs loss under equal nitrogen and phosphorus fertilizer efficacy in the rainfall loss condition. Therefore, we concluded that the farmland applied with commercial organic fertilizer has some advantages in the maintenance of nitrogen and phosphorus fertilizer efficacy and the control of SEs loss under intermittent rainfall conditions.

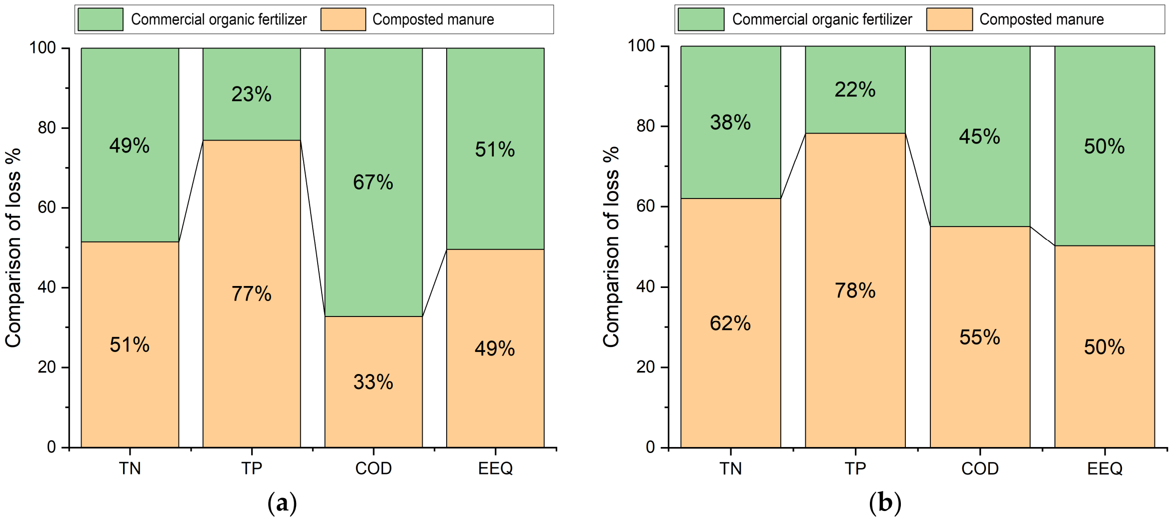


Figure 8. Comparison of pollutant loss of TN, TP, COD and SEs per mass unit of fertilizer between commercial organic fertilizer and composted manure fertilizer after application ((**a**). under simulated rainfall; (**b**). under simulated irrigation).

In the case of flood irrigation, after the use of commercial organic fertilizer the average concentration of TN loss was reduced from 1.76 mg/L to 1.14 mg/L; the average concentration of TP loss was reduced from 0.82 mg/L to 0.26 mg/L; the average concentration of COD loss was reduced from 36.45 mg/L to 28.52 mg/L; and the average concentration of SEs loss was basically the same. Total TN loss was reduced by 24%, total TP loss by 56% and total COD loss by 10%. Therefore, application of commercial organic fertilizers has great advantages in the maintenance of OM and nitrogen and phosphorus fertilization efficiency, and the control of SEs loss under the flooded irrigation conditions.

4. Conclusions

This study investigated SEs loss from farmland soil after the application of composted manure and commercial organic fertilizer under simulated rainfall and flood irrigation conditions. This study found that the initial loss of SEs, TN, TP and COD was higher after the first round of rainfall, indicating the importance of soil adsorption and retention of these substances. The loss rates of TN, TP, and COD decreased significantly in subsequent rounds of rainfall, while the loss concentrations of SEs remained relatively constant, posing a potential environmental risk. Under flood irrigation conditions, the loss concentrations of TN, TP and COD were significantly lower compared to rainfall conditions, suggesting that flood irrigation can prevent the loss of particulate matter but does not alter the leaching process of SEs with DOM.

This study also found that the standardized composting and fermentation process of organic fertilizer significantly degraded SEs, leading to lower SEs fractions and EEQ compared to naturally composted manure. The replacement of composted manure with commercial organic fertilizer resulted in significantly lower TP and TN loss concentrations under both rainfall and flood irrigation conditions. TN and TP losses were reduced, while COD losses increased slightly, and SEs losses increased slightly or remained the same. Therefore, the use of commercial organic fertilizers has advantages in maintaining nitrogen and phosphorus fertilizer efficacy and controlling SEs loss.

Furthermore, the study found significant correlations between SEs and TN, TP, COD loss concentrations, indicating the simultaneous occurrence of these pollutants in agricultural non-point source pollution. The hydrophobicity of SEs and their adsorption on different OM fractions influenced their release during leaching. This study suggests that TN, TP and COD can be considered as reference indicators for regulating the risk of SEs loss from agricultural land receiving composted manure.

Overall, this study provides important insights into the fate and transport of SEs and other pollutants from farmland soil after the application of composted animal manure. The findings highlight the need for better management practices to minimize the environmental risks associated with SEs and nutrient losses from agricultural non-point sources.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16101374/s1, Figure S1: Grain size distribution of paddy soil and red soil; Figure S2: Concentrations of TN, TP and COD lost under simulated rainfall; Figure S3: Amount of TN, TP and COD lost under simulated rainfall; Figure S4: TN, TP, and COD loss concentrations under flooded irrigation; Figure S5: TN, TP, and COD loss amount under flooded irrigation; Figure S6: Concentrations of COD, TN, and TP in the leaching liquid after application of commercial organic fertilizer under simulated rainfall conditions; Figure S7: Amount of COD, TN, and TP in the leaching liquid after application of commercial organic fertilizer under simulated rainfall conditions; Figure S8: Concentrations of COD, TN, and TP after commercial organic fertilizer application under flood conditions; Figure S9: Losses of COD, TN, and TP after commercial organic fertilizer application under flood conditions. Table S1. Rainfall. Table S2. Irrigation.

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