



## Estrogen degradation and sorption onto colloids in a constructed wetland with different hydraulic retention times



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### HIGHLIGHTS

- The degradation rates were 0–46% and 40–84% for HRT 45.9 and 137.5 h, respectively.
- The higher rate of E1 degradation than E2 and E3.
- Log  $K_{DOM}$  values for estrogens ranged from 3.37 to 4.89.
- Average log  $K_{DOM}$  were 4.08, 4.04 and 4.11 L/kg-C for E1, E2, and E3, respectively.

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### ABSTRACT

Endocrine disrupting compounds are a global concern, owing to their interference with the endocrine system of wildlife. In particular, natural estrogens at concentrations as low as ng/L level can interrupt the endocrine system of many organisms. A constructed wetland is an effective means of removing the residual levels of estrogen. This study investigates the estrogen degradation and sorption on colloids in a constructed wetland at hydraulic retention times (HRTs) of 27.5, 45.9, and 137.5 h. Three natural estrogens (i.e. estrone (E1), 17 $\beta$ -estradiol (E2), and estriol (E3)) are analyzed with liquid chromatography/tandem mass spectrometry. At HRT = 27.5 h, no degradation occurs; at HRT = 45.9 h, the degradation rates are 0–46.2%; and at HRT = 137.5 h, the degradation rates are 40–84.3%. Additionally, estrogen sorption coefficients (log  $K_{COC}$  values) range from 3.37 to 4.89. Average log  $K_{COC}$  values are  $4.08 \pm 0.33$ ,  $4.04 \pm 0.34$ , and  $4.11 \pm 0.28$  for E1, E2, and E3, respectively. At different HRTs, values of log  $K_{COC}$  increase with an increasing HRT. Analytical results indicate that constructed wetlands can remove residual natural estrogens. With an increasing HRT, the estrogen degradation rate increases as well as the estrogen sorption on colloids.

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### 1. Introduction

Many endocrine disrupting compounds (EDCs) have been found in aquatic environments. EDCs can interfere with the estrogenic function of an organism at rather low concentrations (levels of ng/L) [1–8]. Adverse health impacts include reproductive abnormalities [1], abnormal sex ratios [3], as well as feminization and plasma

vitellogenin induction in male fish [7]. The natural steroid hormones 17 $\beta$ -estradiol (E2), estrone (E1), and estriol (E3) are of most concern [4,5]. Chen et al. discovered high estrogen concentrations in river waters receiving large amounts of livestock wastewater. The E1 concentration exceeded 1000 ng/L [9].

As moderately hydrophobic compounds, estrogens are biodegradable in the environment. Biological wastewater treatment processes and animal waste storage facilities can remove estrogens [10–16]. Under different conditions, the estrogen concentrations in an effluent are a few to hundreds of ng/L. Many factors including long hydraulic retention times (HRT) and aerobic conditions, affect estrogen degradation rates. Unfortunately, in densely populated areas, limited land resources are available for

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biological wastewater treatments, necessitating an alternative method in terms of lower construction and operating costs to remove residual estrogens in river water.

Characterized by its low construction and operating costs as well as its environmental friendliness, a constructed wetland is a feasible means of removing residual estrogen [14,17,18]. A constructed wetland can also remove residual estrogen and traditional pollutants from wastewater treatment plant effluent [17,19]. In three vertical flow constructed wetlands, the wastewater contained E1 and E2 and the removal rate reached 67.8% and 84.0% [17]. A free-surface flow constructed wetland only removed 36% and 41% of E2 and EE2, respectively [20]. Constructed wetland can also reduce dairy wastewater estrogenic activity, with an average removal rate of 95.2% [21].

Additionally, animal wastewater often contains high concentrations of dissolved organic matter (DOM). Aquatic DOM is a heterogeneous mixture containing molecules with different sizes, structures, functions, and properties, which cannot be removed by settling [22,23]. Usually, the dissolved organic compound in a water sample is defined as that in the liquid passing through a filter (i.e. commonly 0.45  $\mu\text{m}$ ). However, the organic compound in the filtrate presents as the truly dissolved phase (<1 kDa) and sorption onto colloidal (1 kDa–0.45  $\mu\text{m}$ ) phase [24]. Moreover, humic colloids have a large range of molecular weights that affects various environmental behaviors of organic and inorganic contaminants, including solubility, bioavailability, transport, and fate [25–27]. In an aquatic environment, the interaction of estrogens with colloids affects the estrogenic activity, and the effect is markedly affected by the colloidal composition [25,27,28]. An increased colloid concentration usually results in a decreased bioavailability, bioaccumulation, and toxicity of the compounds [25,27].

Related studies in recent years have investigated estrogen sorption on colloids, including E1, E2, E3 and EE2 sorption on colloid from commercial humic acid, fulvic acid, isolated from wastewater biological treatment processes, river water, sewage effluent, and seawater [26,27,29–31]. These findings generally demonstrate that the partition coefficient normalized colloidal organic carbon  $K_{\text{COC}}$  values were greater than  $K_{\text{OW}}$  ( $2.69 \times 10^3$  [E1]– $14.1 \times 10^3$  [EE2] L/kg-C), and the values varied greatly from different sources. The different levels of colloidal humification accounted for this discrepancy [27,30]. Therefore, while the colloid properties may change when wastewater flows through a constructed wetland, the estrogen sorption capability on colloids remains unclear. Related studies have shown that one of the most important factors that affect estrogen removal in constructed wetlands is HRT. This study investigated degradation of estrogen in water with different HRTs in a constructed wetland, as well as the characteristics of estrogen sorption on colloid.

## 2. Materials and methods

### 2.1. Study site

The constructed wetland study area is located outside of a dike along Donggang River flowing through Wandan Township of Pingtung County in southern Taiwan. Domestic sewage and livestock wastewater are the major pollutant sources of Donggang River. The constructed wetland is built with concrete, which is the common material of storage pit for animal manure with a low sorption ability to estrogen [32]. The wetland dimensions are 135 m in length, 5 m in width, and 1 m in depth. Also, the effective water depth in wetland ranges from 0.65 to 0.8 m. The treatment processes include a buffer pond, a sand settle pond, two air pre-aeration ponds, two contact aeration tanks, two set surface-flow wetlands, and a filtration pond. Moreover, this study investigates estrogen degradation

in water and estrogen sorption onto colloids at HRTs of 27.5, 45.9 and 137.5 h. Air diffusers with sufficient power are arranged in the bottoms of each pre-aeration pond, contact aeration tank and surface-flow wetland (15 diffusers with a total of 1 HP, 14 diffusers with a total of 1.5 HP, and 15 diffusers with a total of 0.5 HP, respectively). With a good mixing by the diffused air, we expect little solid precipitation except in the sand settle pond. Therefore, the sorption of estrogens on the sediments is insignificant.

### 2.2. Sampling

The sampling and analysis lasted from December 2012 to February 2013. Water samples were taken from the outlets of sand settling pond (influent), the aeration tank (middle) and the filtration pond (effluent). Sampling was performed twice weekly with six samples per HRT. When the HRT was changed, the water flow was kept steady for one week and no sampling was conducted. Additionally, two L of water was taken per sample; 1 L was analyzed for estrogen concentration and the other for water quality. In total, 54 samples were analyzed.

Estrogen evaluation includes two parts: estrogen degradation in the wetland at the three HRTs, and the estrogen concentration in the truly dissolved and colloidal phases. Ten L of water was taken at each point. Four samples for HRT = 27.5 and 45.9 h and five for HRT = 137.5 h. After the water samples were transported back to the laboratory, the water samples were filtered (0.45  $\mu\text{m}$ ), and the filtrate was separated to colloid (1 kDa–0.45  $\mu\text{m}$ ) and truly dissolved phase (<1 kDa) by a tangential flow filtration system equipped with a 1 kDa membrane cartridge. In total, 26 water samples were analyzed. The separated solutions were analyzed for estrogen and DOC concentrations. The cleaning procedure of the membrane followed the manufacturer's protocol. Vitamin B12 (1.3 kDa, Sigma–Aldrich, USA) and Rhodamine 6G (R6G, 0.48 kDa, Sigma–Aldrich, USA) were used to test the separation efficiency of the membrane. The mass recovery of vitamin B12 in the retention solution (>1 kDa) and R6G in the permeate solution (<1 kDa) was 93% and 89%, respectively.

### 2.3. Chemicals

All natural estrogen standards were obtained from the Cambridge Isotope Laboratories (Andover, Massachusetts, USA). Individual 100 mg/L chemical stock solutions were prepared in HPLC-grade acetonitrile (ACN) and stored at  $-20^\circ\text{C}$ . Standard solutions containing all chemicals were mixed and diluted with methanol, and working solutions of all chemicals. Additionally, calibration concentrations were prepared by appropriately diluting the stock solutions in the study waters. HPLC-grade water was purchased from Honeywell (Morristown, NJ, USA). ACN, methanol, and formic acid were purchased from Echo (Miaoli, Taiwan).

### 2.4. Analytical procedures

#### 2.4.1. Pretreatment of water samples

All filtered water samples were acidified to pH 3.0 using sulfuric acid (18N), and, then, stored at  $4^\circ\text{C}$  until analysis. Oasis HLB cartridges (200 mg/6 ml, Waters, USA) used for solid phase extraction were preconditioned with 10 ml of 5% methanol and 10 ml of deionized (DI) water. Aliquots of 1000 ml water samples were then loaded to the cartridges with a flow rate of 3–5 ml/min. After sample passage, cartridges were rinsed with 50 ml DI water and vacuum-dried for 60 min. Following drying, analytes were eluted with 8 ml of methanol. The eluted analytes were collected, evaporated to dryness with a nitrogen stream, and reconstituted to 2 ml with ACN/DI water at 1/9 = v/v. Final solutions were filtered through a 0.22  $\mu\text{m}$  PTFE membrane filter before HPLC–MS/MS analysis.

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