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# Quantifying estrogen compound and nutrient reduction in a coupled wetland and ground water flow-through system

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Eric W. Peterson, Ph.D.

Department of Geography-Geology, Illinois State University

Normal, IL

The objective of this project was to investigate the reduction of 17β-estradiol (E2) and Estrone (E1) in treated wastewaters that were subjected to a tertiary treatment composed of a coupled wetland and ground water flow through system. The goal was to generate preliminary data to support a future proposal examining the long term efficiency of wastewater treatment to remove hormones from the system. Specifically, the goals of the project were to A) quantify the presence of E2 and E1 in treated wastewater and along ground water pathways from a wetland, B) determine the potential reduction of E2 and transformation of E2 to E1 along the ground water pathways, C) expand upon the results by Peterson and Lanning (2009) showing the effectiveness of wetlands as a treatment for E2 removal, and D) use the pilot data gathered to develop a more thorough assessment of the wastewater treatment process.

## Study Area

The study site is located within property owned by the Bloomington-Normal Wastewater Reclamation District (BNWRD) facility located south of Bloomington, Illinois. The facility houses a wastewater treatment facility, two constructed wetlands, and Little Kickapoo Creek (LKC) (Figure 1). The BNWRD facility has constructed two wetlands to help reduce nutrients in the wastewater and provide wetland habitat. Both wetlands sit upland from the creek. Some of the effluent seeps into the subsurface and will eventually end up in the creek along with regular ground water flow. Geochemical conditions along the flow path can potentially remove E2 and E1 from the water.

This project focused on the southern, and larger, wetland, which is located between the treatment facility and LKC. The wetland receives a fraction of the treated wastewater effluent, while the majority of the treated wastewater flows into a channel discharging directly into LKC. The wetland sits above the water table on alluvium deposits, below which is glacial outwash deposited during the Wisconsinan Episode. The wetland was constructed by excavating the upper part of the alluvium, grading the area, and then using the alluvium to form the berm around the wetland. The geologic units underlying the site are the Cahokia Alluvium, the Henry Formation and the Wedron Formation. The Cahokia Alluvium was deposited on top of the outwash during the Holocene. The Henry Formation is an outwash unit that serves as the shallow water table aquifer. The top of the Henry Formation serves as the streambed for LKC and is the main pathway for shallow water movement in the area. The Wedron Formation is a till unit that underlies the Henry Formation and serves as a lower confining unit for the Henry Formation.

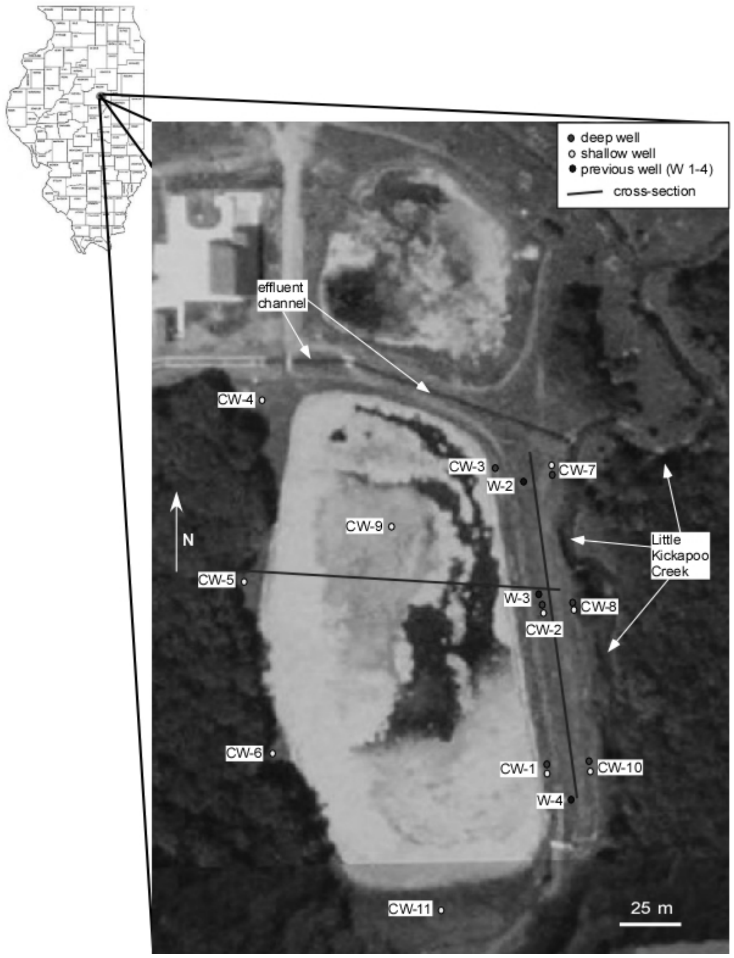


**Figure 1:** BNWRD study site highlighting the constructed wetlands. Well locations and the position of Little Kickapoo Creek are identified. Note three wells, CW-9, CW-6, and CW-11, were not used in this study and Wells W1, W2, W3, and W4 are no longer present.

Samples were collected from fourteen wells, the wetland surface waters, and the treated effluent channel waters. Two of the wells are located upgradient of the wetland on the west side and the other 12 wells are located on the east and south side of the wetland. CW-1, 2, 7, 8, and 10 are nested with one deep well (within the Henry Formation) and one shallow well (within the Cahokia Alluvium). CW-3, 4, 5, and 9 are all shallow wells (4 and 5 are the upland wells). Figure 2 illustrates a north-south and an east-west geological cross-section of the area.

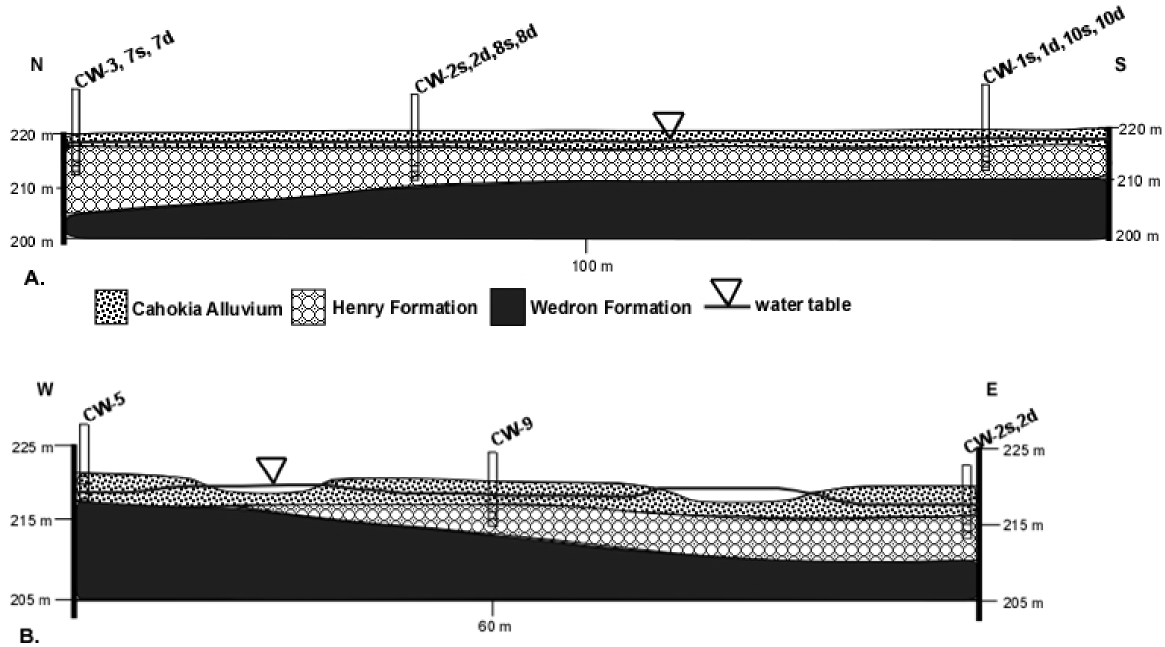


**Figure 2:** A a) north-south and b) east-west geological cross-section showing well locations, ground surface elevation, water table elevation, alluvium-outwash boundary and outwash-till boundary.

## Hydrogeology

The general ground water flow in the study area is from the wetland, vertically through the alluvium and then horizontally through the outwash (both shallow and deeper flow paths) towards LKC where the stream gains the ground water – this can be seen in a water table contour map (Figure 3). There is also a ground water flow path starting west of the wetland and moving under the wetland towards LKC. Vertical gradients between nested wells CW-2, 7, 8, and 10 range from 0.0 – 0.02 over the course of a year. All of the vertical gradients are in the upwards direction, except for CW-2 measurements taken in June 2010. The vertical gradient is the result of ground water discharging into LKC. Horizontal gradient in the area ranges from 0.02 – 0.04 between wells screened in the outwash on the east side of the wetland. The direction of the horizontal gradient is west to east or from the wetlands towards the creek.

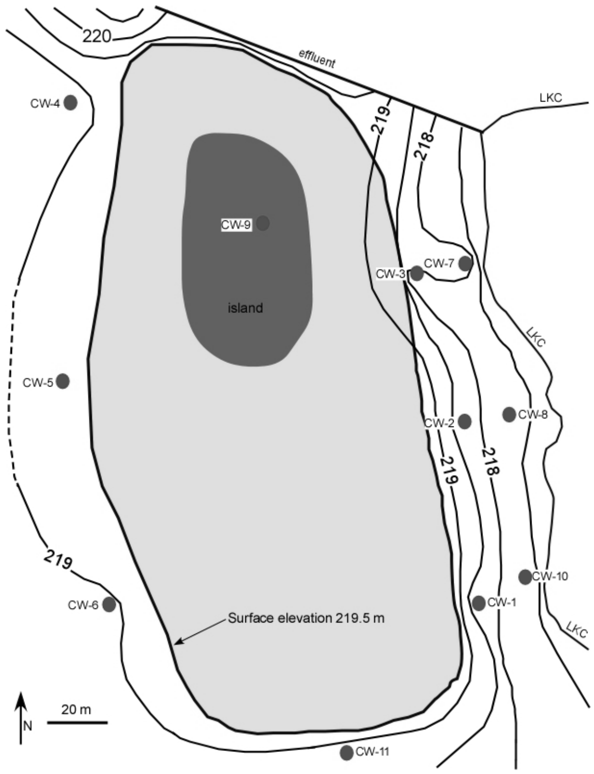


**Figure 3:** Water table contour map of BNWRD study site – constructed using hydraulic head measurements from October 2010.

## Methods

Sampling was conducted between July 18 and September 29, 2011. A total of eight rounds of samples were collected from the wells, wetland, and effluent channel. Wells were first purged until a stable conductivity was reached. Samples were collected in a sealed plastic container using a peristaltic pump and then immediately preserved in a cooler with an ice pack. Estrogen concentrations were analyzed using ELISA kits (Ecologienia ®, Japan EnviroChemicals, Ltd.) with detection limits of 25 ng/L for E2 and 15 ng/L for E1.

## Results

1. Quantification of Estradiol (E2) and Estrone (E1) in the studied system (Goal A)

Both 17β-estradiol (E2) and Estrone (E1) were measured in the treated effluent entering the wetland, the wetland waters, and in the ground water downgradient of the wetlands. Neither E2 nor E1 were measured in the ground water upgradient of the wetland (CW 4 and CW 5). Concentrations of E2 ranged from below detectable level (BDL) to 178 ng/L of E1 and 762 ng/L of E2 (Table 1).

While E2 and E1 were identified in the treated effluent and wetlands during each sampling event, ground water from CW 2D was the only one that either E2 or E1 was measured above the detection limit at more than one sampling. Only one shallow well, CW 1S, recorded an E2 concentration above the detection limit. All of the deep wells witnessed at least one sampling when E2 was above the detection limit. The data suggest the dominant pathway is through the Henry Formation, with little ground water flow through the alluvium, a finding consistent with Ackerman (2011).

**Table 1**: 17B-estradiol and Estrone concentrations within the wetland-ground water system.

| **Location** | **17 β-Estradiol (E2) ng/L** | | | **Estrone (E1) ng/L** | | |
|---|---|---|---|---|---|---|
| | **Minimum** | **Maximum** | **Average** | **Minimum** | **Maximum** | **Average** |
| **Treated Effluent** | B.D.L.# | 60 | 20 | B.D.L.# | 178 | 76 |
| **Wetland** | B.D.L.# | 20 | 17 | B.D.L.# | 100 | 55 |
| **CW 1S** | B.D.L.# | 18 | 18 | B.D.L.# | B.D.L.# | — |
| **CW 1D** | B.D.L.# | 18 | 18 | B.D.L.# | B.D.L.# | — |
| **CW 2S** | B.D.L.# | B.D.L.# | — | B.D.L.# | B.D.L.# | — |
| **CW 2D** | B.D.L.# | 762 | 258 | B.D.L.# | 58 | 58 |
| **CW 3** | B.D.L.# | B.D.L.# | — | B.D.L.# | B.D.L.# | — |
| **CW 4** | B.D.L.# | B.D.L.# | — | B.D.L.# | B.D.L.# | — |
| **CW 5** | B.D.L.# | B.D.L.# | — | B.D.L.# | B.D.L.# | — |
| **CW 7S** | B.D.L.# | B.D.L.# | — | B.D.L.# | B.D.L.# | — |
| **CW 7D** | B.D.L.# | 16 | 16 | B.D.L.# | B.D.L.# | — |
| **CW 8S** | B.D.L.# | B.D.L.# | — | B.D.L.# | B.D.L.# | — |
| **CW 8D** | B.D.L.# | 16 | 16 | B.D.L.# | B.D.L.# | — |
| **CW 10S** | B.D.L.# | B.D.L.# | — | B.D.L.# | B.D.L.# | — |
| **CW 10D** | B.D.L.# | 17 | 17 | B.D.L.# | 139 | 139 |

**#B.D.L. – Below Detection Limit**

*** For Average values equal to the maximum value, only one sample was above the diction limit.**

2. <u>Potential reduction of E2 and transformation of E2 to E1 along the ground water pathways (Goals and C)</u>

The higher concentrations of both E2 and E1 in the treated effluent than in the wetlands indicate that the wetlands are serving as a sink for E2 and E1. The design conditions of the wetland are different than those examined by Peterson and Lanning (2009), but the results are consistent among the studies. However, a conclusion about the fate, sorption or transformation to E1 cannot be discerned with the data.

The absences of E2 and E1 within the ground water indicate that both are being effectively removed within the ground water system. However, the high number of BDL samples suggests that a method with a lower detection limit may be needed to better discern the effectiveness. This concern is addressed in the next section.

3. <u>Future direction and Outcomes</u>

The data provide a starting point for future research into the fate and transport of E2 and E1 in a wetland-ground water system. The data will be used in a M.S. thesis to be completed by Laura Hanna. She is currently working on continued data collection and refinement of an analytical method to improve the resolution of the sampling. The method uses Gas chromatography with tandem mass spectrometry (GC-MS/MS) and expands upon the method presented by Fine et al. (2003). The protocol requires a solid phase extraction (SPE) for the enrichment of estrogens in the samples and reduces the interference from other chemicals during analysis. The improved resolution should allow for better detection of E2 and E1 in the ground waters.

In development of the improved analytical method, collaboration between my research group and that of Dr. Michael Byrns, a professor in the Department of Health Sciences (ISU) has begun. Dr. Byrns, who recently began his tenure at ISU, examines the emerging contaminate exposure, specifically estrogen hormones, in humans. He is interested in our work and in generating a larger proposal towards better understanding estrogens in water systems. The preliminary data generated from this work will be used in the generation of the collaborative grant.

**Cited References:**

Ackerman, J. R., 2011, Quantifying nutrient removal from ground water seepage out of a constructed wetlands receving wastewater effluent.: Normal, IL, Illinois State University, 75 p.

Fine, D. D. D. D., Breidenbach, G. P. G. P., Price, T. L. T. L., and Hutchins, S. R. S. R., 2003, Quantitation of estrogens in ground water and swine lagoon samples using solid-phase extraction, pentafluorobenzyl/trimethylsilyl derivatizations and gas chromatography-negative ion chemical ionization tandem mass spectrometry: Journal of chromatography. A, v. 1017, no. 1-2, p. 167-185.

Peterson, E. W., and Lanning, A., 2009, Effectiveness of pilot-scale wetland designs in removing estrogenic compounds from municipal wastewater plant effluent: Environmental Geosciences, v. 16, no. 2, p. 61-69.