Wastewater Irrigation: The Potential to Increase Biofuel Production While Removing Endocrine Disrupting Hormones.

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Abstract:

Irrigation is not a common practice in Pennsylvania, although previous studies have shown that there is a precipitation deficit for crop production. Water availability and industrial competition are several reasons for the lack of irrigation. However, wastewater irrigation can provide adequate moisture for growing crops such as corn for biofuels. In addition, the soils may also provide treatment of endocrine disrupting hormones such as estrone, a form of estrogen. The objective of our research was to determine transport parameters of estrone in agricultural soils that receive wastewater irrigation. Adsorption experiments were carried out in triplicate using 0.2-g samples of Hagerstown soil. The distribution coefficient (K_f = 66.9413) indicated strong sorption showing a high degree linearity (N = 0.9316). Unsaturated column experiments have also been conducted with pure sand and a 1:18 mixture of soil (Hagerstown silt loam with a carbon content of 1.1%) to sand under the same conditions with the addition of the Hagerstown soil causing the breakthrough curve to shift to the right and decrease in amplitude. Our preliminary results suggest that the soil can act as a natural treatment alternative in place of energy intensive practices such as micro-filtration or reverse osmosis.

Introduction:

In 2006, the United States used fossil fuels to provide approximately 85% of its total energy, which includes importing over 60% of its oil (Committee on Water Implications of Biofuels Production in the United States, 2008). The United State’s dependence on energy imports, particularly oil, puts it at a serious economical and energy security risk. Therefore, much attention has focused on the development of renewable, “green” energy resources such as biofuels. According to the United States Department of Energy, the U.S. produced 6.5 billion gallons of ethanol in 2007. As of March 2008, ethanol production capacity was at 7.2 billion gallons with an additional 6.2 billion gallons under construction (USDOE, 2008). An increase in biofuel production will also cause an increase in water consumption, which is likely to affect areas that are already experiencing water deficits (Committee on Water Implications of Biofuels Production in the United States, 2008). Although not very typical in Pennsylvania, irrigation could be economical for increasing crop production (Kibler et al., 1977)

In the year 2000, irrigation accounted for the largest use of freshwater (137Bgal/day) in the United States (Hutson et al., 2005). In addition, consumptive use of groundwater for irrigation has almost doubled over the last 50 years. The need for fresh water supplies for crop production will continue to grow in the future, part of which is a result of an exponentially growing population that will require record amounts of food and energy. These factors are compounded by the reduction of water quality burdening our finite fresh water supply.

From pesticides to personal care products, organic chemicals have been entering and persisting in our environment for many years (Kolpin et al., 2002). Recent advances in analytical technology have provided the necessary tools to detect trace amounts of organic chemicals such as hormones in our water (Chen et al., 2007; Shappell, 2006; Snyder et al., 1999; Yamamoto et al., 2006). The main sources for the hormones in the water are two-fold, animal manure and wastewater treatment plants (Hanselman et al., 2003; Kolpin et al., 2002). Conventional wastewater treatment plants typically have not been able to totally remove endocrine disrupting chemicals (Wintgens et al., 2002). In turn, the presence of these chemicals in wastewater may be causing feminization of male fish (Sumpter, 1995).

An alternative to discharging secondary treated wastewater into surface waters is land application, where the soil acts as a tertiary filter. Previous studies have demonstrated that wastewater irrigation can be beneficial in a number of different ways - provide water to plants, remove nutrients, enhance groundwater recharge and reduce impacts on surface water quality (Parizek, 1967; Toze, 2006). In addition to removing nutrients, soils have also shown a strong affinity to bind endocrine disrupting hormones such as estrone, resulting in little to no mobility (Casey et al., 2005). Therefore, we are currently investigating a potential synergistic relationship between wastewater irrigation, biofuel production, and endocrine disrupting hormone remediation. Our objectives were to monitor yields of corn and wheat in the irrigated area and compare those with non-irrigated crops in the same area; determine the estrone sorption characteristics for the soil at the wastewater irrigation facility, model the unsaturated flow of estrone using mixtures of soil and sand columns, and perform extractions from the soil to determine if there is any buildup of estrogen in the soil profile.

Materials and Methods:

Study Site

The Pennsylvania State University has used a wastewater spray irrigation system for over 40 years. Originally designed as a research system in the early 1960's, the system went to a full-scale operation in 1982. Since 1982, the university has ceased the discharge of its wastewater effluent into Spring Creek, a class one trout stream. Instead, the water is irrigated onto three different types of land uses - cropped, grass covered, and forested. The facility is permitted to apply two inches of irrigation per week per acre in addition to the normal precipitation of 30 to 40 inches. Irrigation is applied regardless of weather conditions. The soils are very deep and well drained from the Hagerstown Soil Series (*Typic Hapludalf*). The cropped areas are in a corn (Zea mays L.) and wheat (Triticum aestivum L.) rotation planted with no-till cropping methods (Walker and Lin, 2008). Nutrient management is a main focus of the facility, therefore nutrient budgets are strictly monitored and fertilizers are sometimes under applied to maintain a zero net nitrogen balance. The need for nitrogen application is a result of denitrification taking place at the wastewater treatment plant, however, the wastewater supplies sufficient phosphorus for crop growth.

Soil adsorption studies

Adsorption experiments were carried out using ^{3}H-labeled estrone and a Hagerstown soil. The use of tritiated estrone afforded a detection limit about 2 orders of magnitude lower than ^{14}C labeled materials(Colluci and Topp, 2002). Colucci and Topp (2002) determined that the tritiated estrone did not exchange radioactivity with bulk water. The major characteristics of the soil were as follows: sand 24%, silt 64%, clay 12%, CEC 11.5 meq/100g, C 1.1%, N 0.1%, pH 7.0, kaolinite 7%, illite 7%, vermiculite 34%, montmorillonite 0%, chlorite 17%). In previous studies (Das et al., 2004; Lai et al., 2000; Lee et al., 2003), adsorption isotherm experiments involving hormones were usually terminated within 24 h, which prevented the evaluation of the possible long-term sequestration processes. In contrast, in this project, the contact time (or equilibration period) ranged from 5 minutes (0.1 h) to 8 days (192 h). The experiments were performed in triplicate, using 0.2-g soil samples, which were mixed (at 1:50 w/v ratio) with 10 mL of aqueous ^{3}H-labeled estrone solutions, containing 0.005 M $CaCl_2$ to mimic soil solution ionic strength, and 0.001 M $HgCl_2$ to eliminate biodegradation (Xing and Pignatello, 1997). In the initial 24-h experiment, ^{3}H-labeled estrone concentrations ranged from 1 ng L^{-1} to 2, 4, 16, 32, 64, 100, 128, 200, 400, 800, 1600, 3200, 6400, 10000, 12800, 20000, 40000, 80000, 160000, 320000, 640000, and 1280000 ng L^{-1}, which spanned all observed hormone concentration levels. In the follow up experiments, aimed at determining the adsorption kinetics, ^{3}H-labeled estrone concentrations ranged from 1 ng L^{-1} to 10, 100, 1000, 10000, 100000, and 1000000 ng L^{-1}. Controls consisting of ^{3}H-labeled estrone in the absence of soil served as controls. The experiments were carried out in darkness (aluminum foil cover) with shaking at 25ºC. At specific times (0.1, 0.3, 1, 6, 24, 48, 96 and 192 h), the aqueous phase was separated by centrifugation and analyzed by liquid scintillation counting for the remaining (not adsorbed) hormones.

The concentration of adsorbed hormones, S (ng g^{-1}), was quantified, based on a mass balance of the solute between the two phases, with the following equation: [$S = V (C_0 – C_e)/W$], where W is the mass of soil (g), V is the volume of aqueous solution (L), C_0 is the initial hormone concentration (ng L^{-1}), and C_e is the final hormone concentration (ng L^{-1}). The Freundlich nonlinear equilibrium model was used to evaluate estrone adsorption in soil:

$$S = K_f C_e^{N} \qquad (1)$$

where K_f is the distribution coefficient ($ng^{1-N}\ g^{-1}\ mL^{N}$), and N is the soil-hormone interaction order, a dimensionless parameter, usually less than unity. K_f and N were obtained from the logarithmic (straight-line) form of the Freundlich equation: [$\log S = \log K_f + N \log C_e$] where $\log K_f$ is the intercept and N is the slope.

Column Transport Experiments

Estrone transport experiments were carried out using an unsaturated column setup similar to Hutchinson (2003). The initial media selected for the study was medium sand. Columns were packed to a density of 1.6 gm/cm^3. The columns were saturated with a 0.01 M solution of $CaCl_2$ at a steady rate of 0.25 mg/L. The column was maintained at a -10 cm water potential using a vacuum chamber (Jin et al., 2000). A pulse of 0.87 mg/L estrone and 0.03 M KCl (as a non-conservative tracer) was then applied for a designated period of time. The pulse was followed by a 0.01 M solution $CaCl_2$. The concentration of estrone followed the solubility described in Shareef et al., (2006). Samples were collected with a fraction collector every half-hour following application of estrone. The non-conservative tracer was monitored using an electrical conductivity detector built into the column (Walker et al., 2008)

Estrone analysis for Column Transport Experiments

Column effluent samples were analyzed with a Waters 2695 separations module equipped with a photodiode array detector. The HPLC was outfitted with a C-18 reverse phase column using a 60/40 methanol to water mobile phase. Prior to analysis, samples were filtered with a 0.3 micron glass fiber filter. A preliminary study investigated estrone sorption onto filter membranes. Nylon and Teflon membranes were determined to adsorb estrone from the sample solution, whereas glass fiber filters did not appear to capture the estrone (data not shown). One hundred microliters of sample were loaded into the separations module by an auto-sampler. Each run lasted 9 minutes.

Soil Extractions for Estrogens

Bulk soil samples were collected from the Pennsylvania State University's Wastewater Irrigation Site. The soils have received wastewater irrigation for approximately 40 years and are located in a depression. Samples were collected based on depth of soil, 0 to 5, 5 to 10 and 10 to 15 cm samples were collected. The soils were dried and sieved to a particle size of less than 2 mm. One hundred fifty mL of ethyl acetate was added to 75 grams of soil in a 200 mL glass centrifuge bottle and shaken for 2 hours. The sample was then centrifuged at 1500 rpm for 45 minutes and 100 mL of the ethyl acetate supernatant was removed and evaporated to dryness under a gentle stream of nitrogen. The residue was redisolved in 1 mL of a 50:50 water to acetonitrile mixture and analyzed on the HPLC. The HPLC was outfitted with a C-18 reverse phase column and used a mobile phase of 55:45 water to acetonitrile. The compounds were initially indentified based on peak time, with PDA spectra and method of addition providing confirmatory evidence.

Results and Discussion:

Crop Yield

Figure 1 shows winter wheat yields from: the irrigated area, adjacent Penn State farms and the Pennsylvania average for the year 2007. With a yield of 85 bushels per acre, the irrigated area yielded more than adjacent fields and the state averages. Although not a widely used biofuel, irrigated corn silage produced higher yields than non-irrigated corn silage (Figure 1). Corn silage can serve as an indicator for corn grain potential (Lauer, 2006). These data suggest that the synergies between wastewater irrigation and farming include: higher yields, consistent yields and lower fertilizer applications.

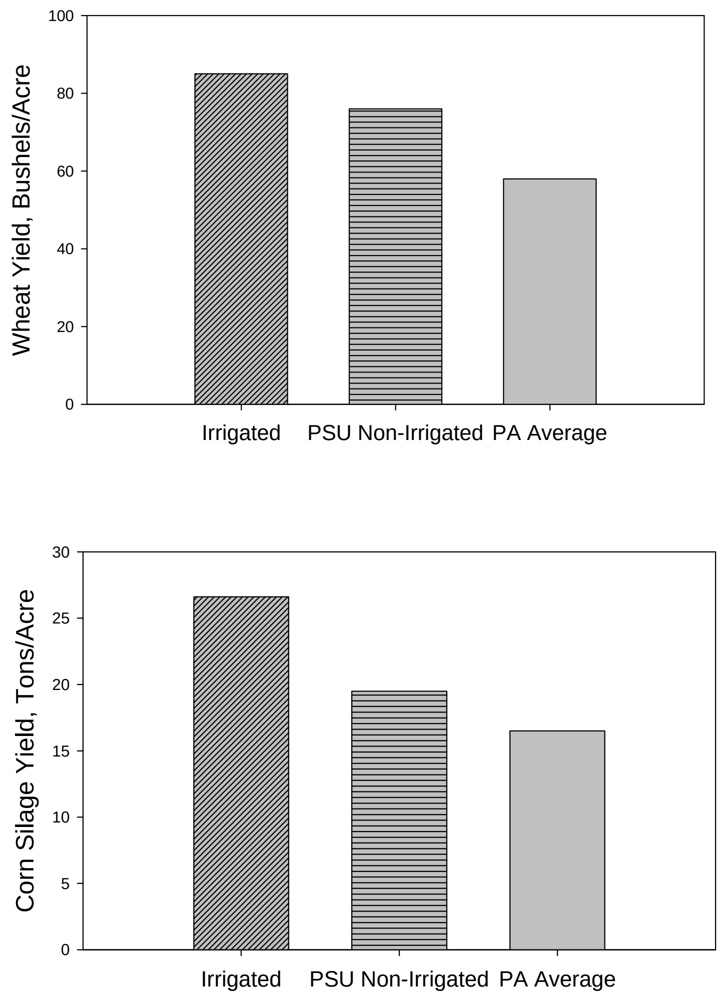


Figure 1. Yields from irrigated and non-irrigated cropland (2007). Pennsylvania averages were acquired from Tosiano (2008).

Estrone Adsorption Studies

As shown in Figure 2, the adsorption isotherm for estrone on Hagerstown soil was well-described by the Freundlich model (R^2 = 0.9985). The distribution coefficient following the 24-h contact time (K_f = 66.9413) indicated strong sorption, showing a high degree of linearity (N = 0.9316).

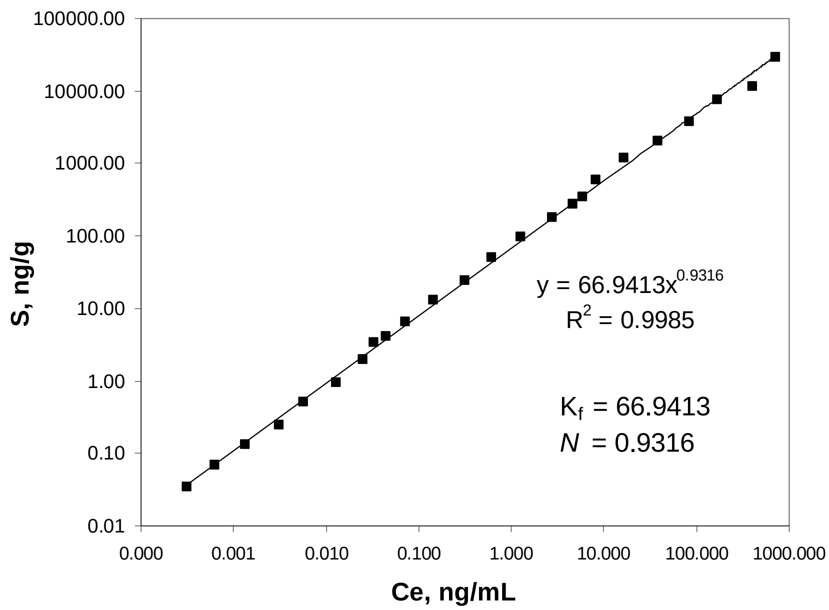


Figure 2. Adsorption isotherm of estrone on Hagerstown soil for initial solute concentrations ranging from 1 to 1280000 ng L^{-1}

However, it needs to be kept in mind that N and K_f values may be constant only at equilibrium. At any time prior to reaching equilibrium, N and K_f are subject to changes (N usually toward lower values, and K_f toward higher values) as adsorption progresses (Weber and Huang, 1996). According to the accumulated evidence (Dec and Bollag, 1997), organic chemicals are first expected to reach a semi-equilibrium, signifying a completion of strictly adsorptive behavior, and a commencement of sequestration processes, when N and K_f values should probably continue to change with time at ever decreasing rate until an actual equilibrium is achieved after weeks, months, or even years. Therefore, in order to address this possibility, a series of experiments was carried out to monitor the kinetics of estrone adsorption for at least one week, using seven initial solute concentrations, ranging from 1 to 1000000 ng L^{-1}.

As shown in Figure 3, estrone kinetics courses for different initial concentrations differed considerably, which was a strong indication that contact time should be considered an essential factor in the assessment of adsorption behavior of estrogen hormones.

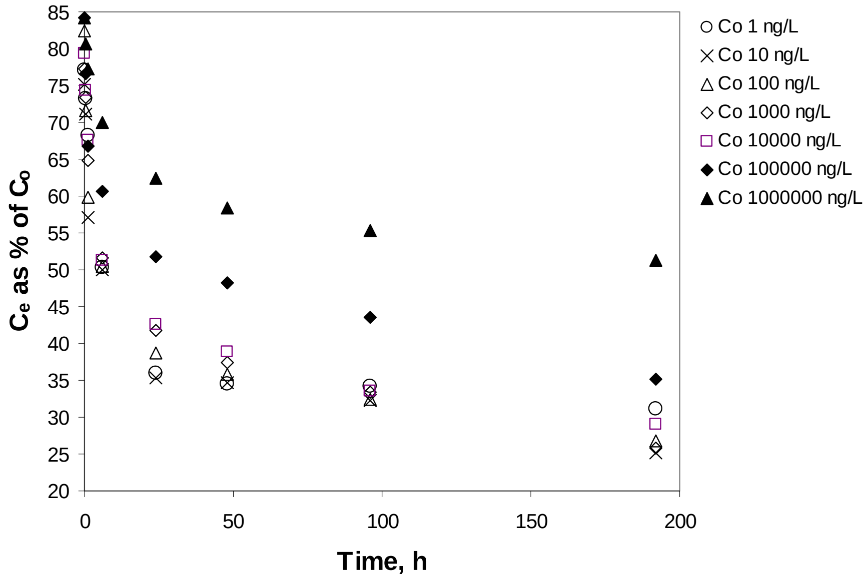


Figure 3. Adsorption kinetics for seven different estrone concentrations.

In view of these data, it is clear that any predictions in terms of hormone transport based on adsorption isotherm data for a single, arbitrarily selected contact time may be highly misleading. The need for temporal considerations in the assessment of sorption behavior is even more evident when one looks at adsorption isotherms at different contact times (Figure 4). It is clear from this chart that estrogen adsorption isotherms may shift considerably as the contact time increases.

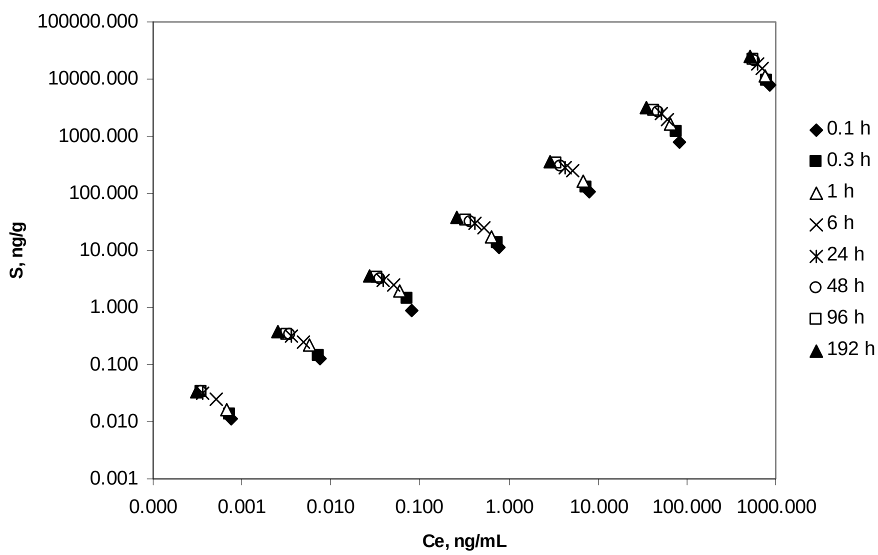
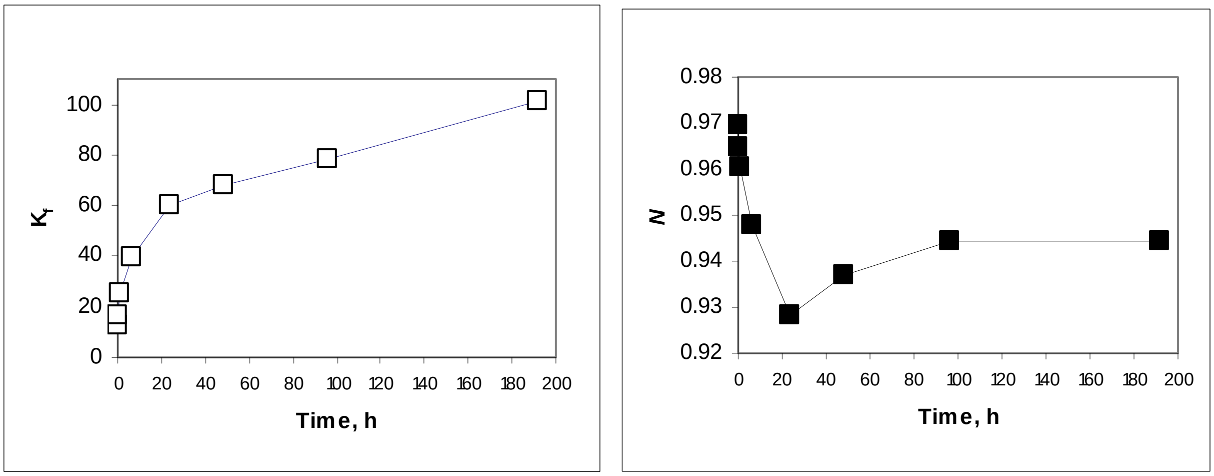


Figure 4. Adsorption isotherms of estrone for different contact times.

Consequently, there were considerable changes in K_f and *N* values (Figures 5a and 5b) as the system was approaching an equilibrium. The K_f value, which for a contact time of 0.1 h was 12.2744, increased to 101.2745 by 192 h. On the other hand, N values decreased from 0.9646 at 0.1 h to 0.9284 at 24 h. Thereafter, an increase was observed to 0.9442 at 96 h, at which level N values seemed to start stabilizing.



Figures 5a and 5b. Changes in adsorption coefficients for estrone isotherm adsorptions at different contact times.

The observed increase of the N value after the initial fast decrease may indicate an anticipated, but until now not well documented, change in estrone adsorption mechanism (Figure 5b). Clearly, it appears the K_f value had not reached its maximum even after 192 hours (Figure 5a).

Column Transport Experiments

To ensure a breakthrough of estrone in the column, the first unsaturated column utilized 100% sand as the media (graph below, on left). The application time for estrone was for 8 hours at a rate of 0.25 mL/min. The sand column had a bulk density of 1.6 gm/cm3 and an average volumetric water content of 38.1%. To normalize the results, estrone is expressed as a ratio of effluent to influent concentrations (C/Co). The influent concentration of estrone was 0.8 mg L^{-1}. The concentration of estrone peaked 9 h after application, whereas the conductivity of the effluent (representing a conservative tracer) peaked 6 h after application (Figure 6). We are able to use a nonlinear least squares fitting method (CXTFIT; (Toride et al., 1995)) to fit the effluent concentration curve. Selecting the convective velocity (0.0325 cm/min) based on soil bulk density and water application rates, CXTFIT calculated the following parameters, D = 0.013 cm^2/min (dispersion coefficient); R = 1.47 (retardation factor), μ = 0.0016 min^{-1} indicating a match between conservative tracer and estrone dispersion, a low sorption coefficient, and slight degradation (sorption coefficient not calculated here, but easily calculable based on soil bulk density and volumetric water content).

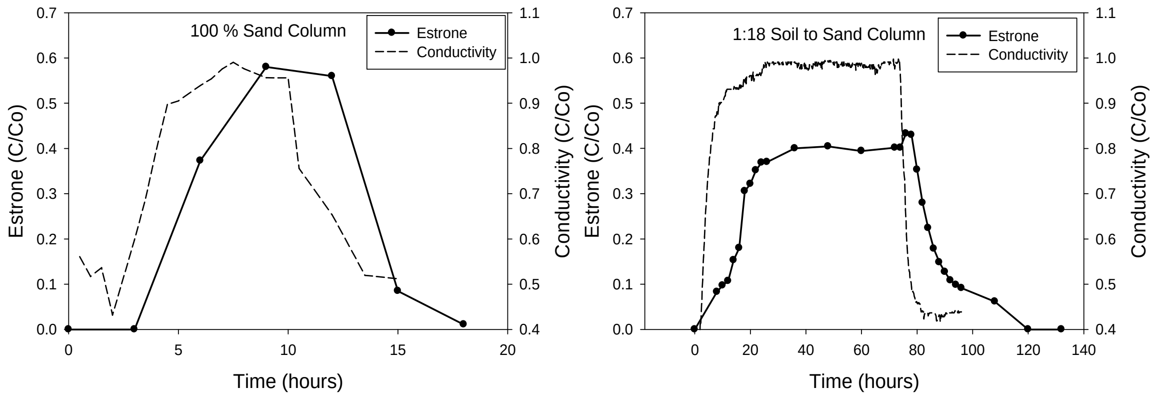


Figure 6. Results from the unsaturated column experiments.

The second set of column experiments used a 1:18 mixture of soil (Hagerstown silt loam with an organic carbon content of 1.1%) to sand under the same conditions, except that the application time of estrone increased from 8 hours to 72 hours at the same rate of 0.25 mL/min (graph above on right). The organic carbon content of the mixture was estimated to be 0.06%. As shown in the graphs above, the addition of soil caused the peak of estrone to shift to the right and decrease in amplitude. The corresponding R value was 6.73, which also indicates a greater retention in the mixture of soil and sand compared to sand alone.

Soil Extractions

Wastewater effluent typically contains 17-beta estradiol which then degrades into estrone (Schlusener and Bester, 2005). Soil extractions are currently underway to determine if there has been an accumulation of estrogenic compounds in the soil. Preliminary results from the extractions have indicated a possible accumulation of estrone (a degradation product of 17- alpha and beta) and an estrone derivative, methoxyestrone. The occurrence of these hormones were the most frequent in the 5 to 10 cm depth of soil. It is unknown at this point if there is photodegradation going on in the surface sample (0 to 5 cm) or if the large amount of organic matter is masking the presence of the hormones. However, if there is indeed an accumulation of methoxyestrone, this particular compound has a very low estrogenic activity, suggesting the soils are degrading the more powerful estrogens, such as 17-B estradiol and estrone, into an estrogen with less estrogenic activity (Kraychy and Gallagher, 1957). These results are still awaiting confirmation from a Mass Spectrometer.

Conclusions and Considerations

Overall, it appears that there is a potential synergistic relationship between wastewater irrigation and biofuel production. The yield data suggests that in a Pennsylvania climate, the crops can perform better with the application of irrigation. It is important to note that due to year round irrigation of the wastewater, the nitrogen budget is very important in this system. The practice at the Spray Irrigation site has been that most crops are either fertilized at the target level of non-irrigated production or under fertilized; therefore the yields become nitrogen limited due to N removal through the denitrification process at the wastewater treatment plant. In addition to increasing yields, the wastewater resides in the watershed from which it was withdrawn helping maintain ground water levels, while the soil and plant system acts as a tertiary filter protecting the ground water from sorbed chemicals of interest.

From our early experiments, the soil system appears to be a suitable filter for removing estrone from the soil solution. Our batch sorption studies and unsaturated column studies suggest that the soil has a high affinity for estrone, thus removing it from the wastewater as it moves downward through the soil profile. In traditional wastewater systems, this level of treatment would require additional energy intensive steps be incorporated into the treatment process, so that the use of the wastewater for irrigation of cropland decreases the energy consumption otherwise needed for treatment. The apparent presence of methoxyestrone in the soil also suggests that not only is the soil acting to adsorb estrogen, it is also allowing it to be degraded into a less active estrogenic form.

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