Fate and transport of manure estrogenic compounds during integrated treatment for water quality and bioenergy production

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INTRODUCTION - Now what?

What can be done to reduce emerging contaminant (ECs) discharges to the environment?

- Eliminate use of ECs at the source
  - Some ECs produced naturally (hormones)
  - Benefits of synthetic ECs could be lost (pharmaceuticals)
  - EC alternatives can have unknown effects (GenX fluoropolymers)

- Treat wastewaters to remove ECs
  - Existing wastewater management systems not designed to remove ECs
  - Additional treatment steps can be costly and may only concentrate/transfer ECs
    - Adsorption on ion-exchange resins or activated carbon
  - Can we derive any new economic value from wastewater treatment?

- New approach → Novel wastewater systems aimed at transforming ECs to biofuels
  - Concentrate ECs into microbial biomass (bacteria and/or algae)
  - Thermochemically convert biomass & ECs into bio-oil or bio-gas
Livestock animals produce hormones

Feeding with antibiotics

Storage of livestock manure (Pit or Lagoon)

Land application of livestock manure

Runoff/Drainage/flooding from soil to surface water

River or Lake water

Fish feminization

Antibiotic resistant infection

Animals excrete Antibiotics, Antibiotic resistant bacteria & hormones

Study Context: USDA study on EC removal from Liquid Portion of Animal Manure (LPAM)

Hormones: Estrone (E1), 17β-estradiol (E2), Estriol (E3), & ethinyl-estradiol (EE2)

Antibiotics (Florfenicol) and antibiotic resistant genes in poster session (#12)

INTERRUPTING TRANSPORT OF ECs TO THE ENVIRONMENT

Integrated manure management system to remove emerging contaminants
Process Flow Diagram for Novel Manure Management System

RAW MANURE (~ 90% H₂O) → SEDIMENTATION → SCREENING → FILTRATION → ECs → ALGAL-BACTERIAL BIOREACTOR (+/- Activated Carbon) → BIOMASS SEPARATION → TREATED WASTEWATER

Light (sun) O₂/CO₂ (air)

CO₂/HTL-WW/CHG-WW → HYDROTHERMAL CONVERSION (HTL/CHG) → BIO-CRude OIL/GAS

Fate and transport of estrogenic compounds in an integrated swine manure treatment systems combining algal-bacterial bioreactor and hydrothermal processes for improved water quality

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**BIOREACTOR OPERATING CONDITIONS**

<table>
<thead>
<tr>
<th></th>
<th>Mixed Algal-Bacterial Bioreactor (MABB)</th>
<th>Conventional Activated Sludge Reactor (CAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor type</td>
<td>Sequencing Batch Reactor</td>
<td>Sequencing Batch Reactor</td>
</tr>
<tr>
<td>Total Volume (L)</td>
<td>189.3</td>
<td>189.3</td>
</tr>
<tr>
<td>Light intensity (µ-photons/m²/s)</td>
<td>350</td>
<td>-</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>Aeration rate (L/min)</td>
<td>6 (0.03 vvm)</td>
<td>11 (0.058 vvm)</td>
</tr>
<tr>
<td>Organic Loading Rate (mg/L/d)</td>
<td>48.6 - 152</td>
<td>48.6 - 152</td>
</tr>
<tr>
<td>HRT (day)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>SRT (day)</td>
<td>25 - 30</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Feed volume ratio (V_{Feed}/V_{Total} %)</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

![Diagram of the bioreactor system](image)
Proposed biotransformation of estrogens in aerobic mixed algal bioreactor

(a) E2 & EE2 transformed to E1, then goes to E3
Solid & dotted line found 90% & 10% in total samples

(b) Light deformation of hormones in an algal bioreactor

Proposed transformation pathway of E1, E2, and EE2 in aerobic water-soil system (J. Li et al., 2013)

Proposed transformation pathway of E1, E2, and EE2 by Chlorella vulgaris (Lai et al., 2002)
Sorption onto biomass is dominant mechanism & desorption is insignificant \((\text{Andaluri et al., 2012})\)

MABB removed 2-5% more hormones than CAS \((P=0.02)\)

Why? Algal biomass, slightly higher temperatures photochemical degradation \((\text{He et al., 2012; Lin & Reinhard, 2005; Puma et al., 2010; Whidbey et al., 2012})\).

GAC improved the remove of total hormones by 4-7%
COMPARISON OF BIOREACTOR EFFECTS ON ESTROGENICITY

- Xenoscreen YES assay used for Estrogenicity (Yeast)
- EEQ (estrogen equivalents): E2 concentration that gives the same activity of the sample

- **MABB** had ~50% lower estrogenicity than **CAS**
- **GAC** reduced the level of estrogenicity by >70%
- EEQ >> Measured E2 concentration
What is Hydrothermal Liquefaction (HTL)?
*Thermochemical conversion of whole biomass into crude oil*

**Demonstrated HTL Feedstocks**
- Municipal sludge
- Manure
- Algae
- Crop residues
- Woody materials

**Reactor**
- High T: 200 – 350 °C
- High Pressure: 80 – 120 atm
- Retention Time 5-60 minutes

**Products**
- **Gas Product** (CO₂ rich)
- **Aqueous Product** (N, P, & sCOD rich)
- **Solid Residue** (Mineral rich ash)
- **Oil Product** (Energy Rich, CₓHᵧ)

**HTL has a positive net energy balance**
Eout : Ein > 3:1 at lab-scale (% solids =20%)
Eout : Ein > 10:1 w/ heat exchangers

Oil characterization: *Vardon et al. 2011, Bioresource Tech.*
HTL: EFFECTS OF TEMPERATURE ON EC REMOVAL

- 300°C/60min had the highest total hormone removal and the highest oil yield

Oil yield (dry basis) 16.7% 40% 27.6%

![Graph showing hormone removal and oil yield at different temperatures.](image-url)
CATALYTIC HYDROThERMAL GASSIFICATION (CHG): TEMP EFFECTS ON EC REMOVAL

- Removal of total hormones plateaued at 99.9% when T > 450°C
- EE2 removal plateaued at 97% (limit of detection, LOD) with increasing temperature
- 500°C was optimal for energy recovery

![Graph showing removal of total hormones and EE2 at different temperatures]

**EE2 had a Lower LOD**
ESTROGENIC ACTIVITY IN HYDROTHERMAL AQ. PRODUCTS

- **EEQ**: Concentration of E2 which would give the same activity as the sample
- **HTL**: EEQ decreased with increasing temperature ($r=-0.9$, $P=0.06$)
  - $>350^\circ C$ in HTL was effective for EEQ removal
- **CHG**: EEQ was sharply decreased with higher than $450^\circ C$ ($r=-0.6$, $P=0.18$)
  - $>450^\circ C$ in CHG was better for removal of estrogenic activity
CONCLUSIONS

BIOREACTOR REMOVAL OF ECs

- **MABB** had slightly higher removal of hormones & estrogencity from manure liquids than CAS
  - Biomass adsorption is the most important removal mechanism
- Adding **GAC** further increased removal of hormones and estrogenicity in MABB and CAS
  - GAC is biologically regenerated in-situ and thus can have a long service life

HYDROTHERMAL CONVERSION OF ECs

- Hydrothermal conversion effectively removed hormones and estrogenicity in biomass harvested from MABB and CAS reactors
  - **HTL** Temp.>300 °C were sufficient for hormone removal and good bio-oil yield, but estrogenicity removal was significantly improved at >350°C
  - **CHG** Temp.>500 °C provided good bio-gas yield and removal of hormones/estrogenicity
- Cost of hydrothermal biofuels ranges from $1.20 - $3.60 /gal depending on scale & context
- *Ongoing work… HTL & CHG also look promising for destruction of PFAS*
THANK YOU

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