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

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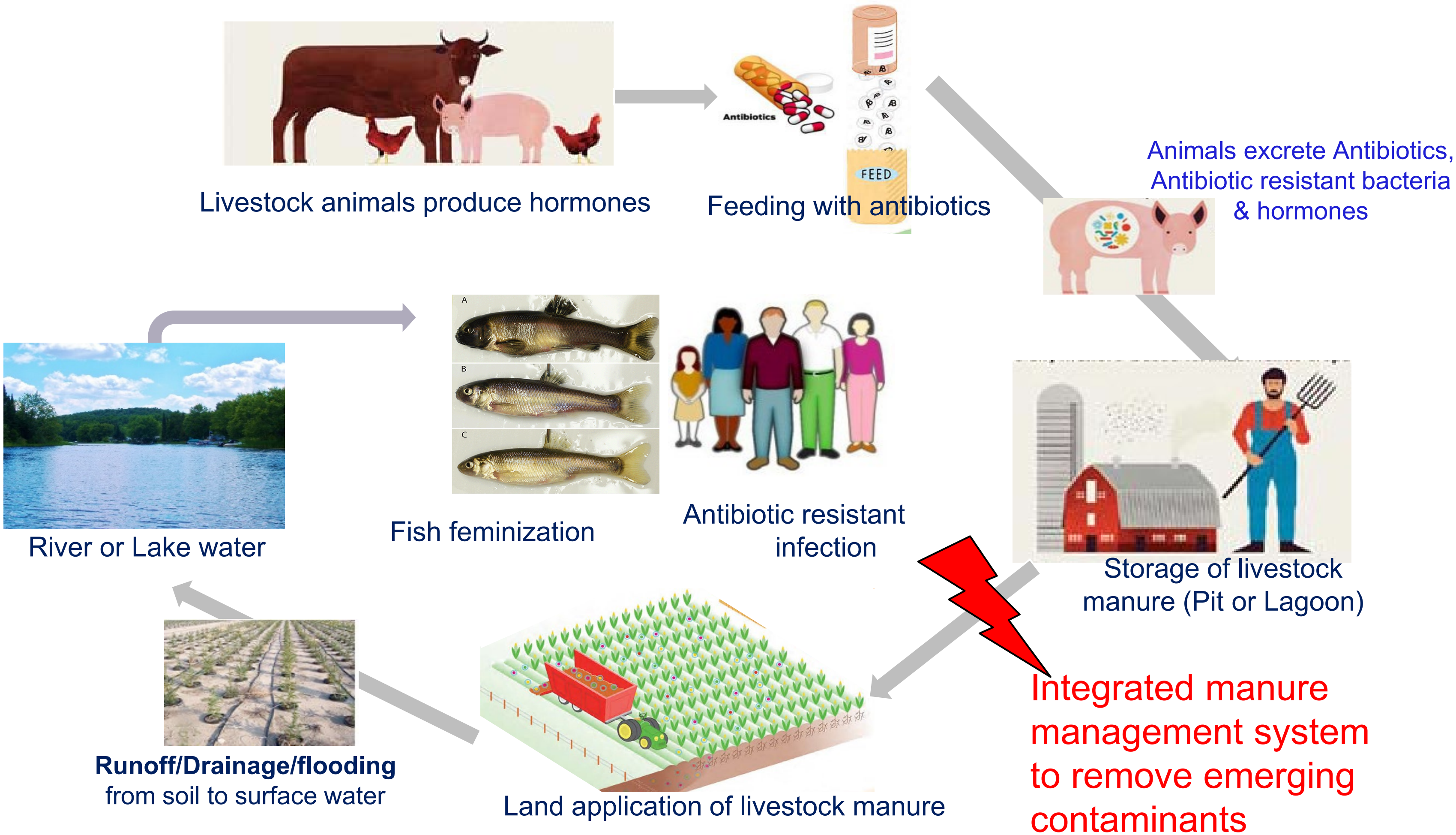
INTRODUCTION- Now what?

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

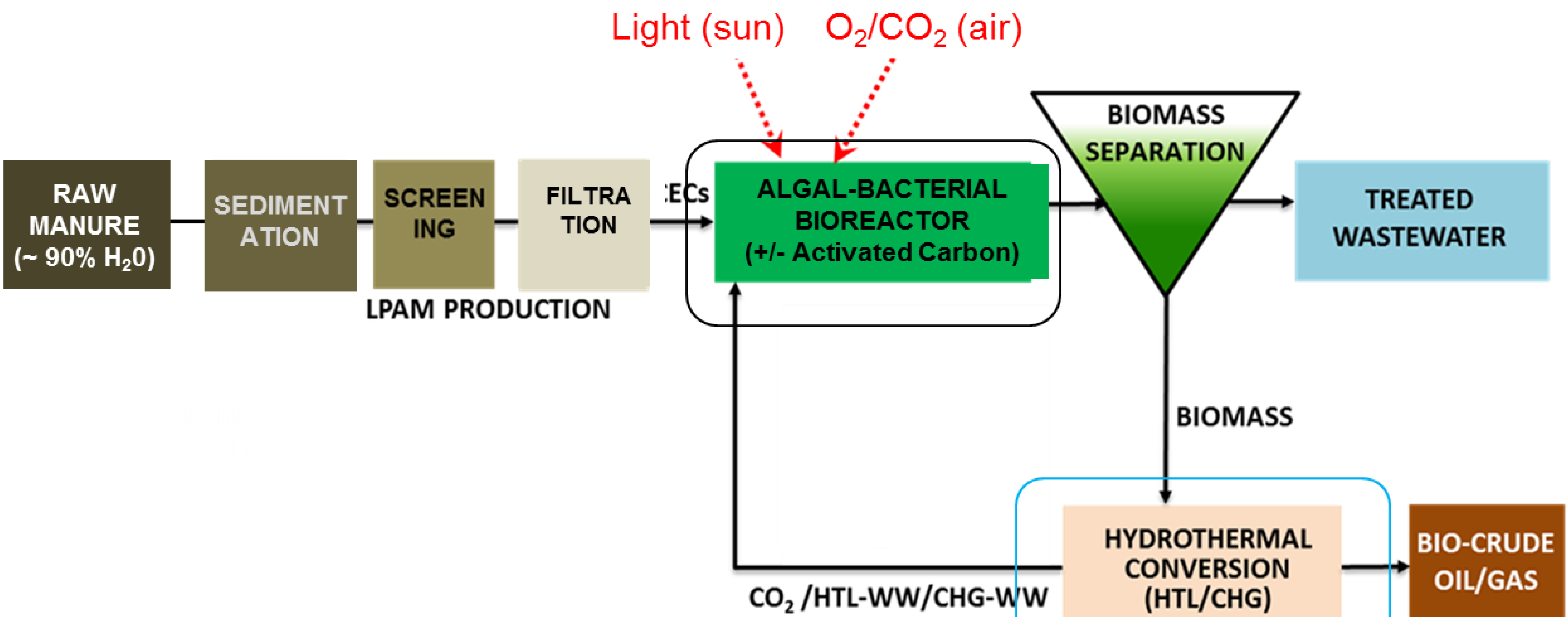
- Eliminate use of ECs at the source
  - Some ECs produced naturally (hormones)
  - Benefits of synthetic ECs could be lost (pharmaceuticals)
  - EC alternatives can have unknown effects (GenX fluoropolymers)
- Treat wastewaters to remove ECs
  - Existing wastewater management systems not designed to 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

INTERRUPTING TRANSPORT OF ECs TO THE ENVIRONMENT

- Study Context: USDA study on EC removal from **L**iquid **P**ortion of **A**nimal **M**anure (LPAM)
- Hormones: Estrone (E1),17β-estradiol (E2), Estriol (E3), & ethinyl-estradiol (EE2)
- Antibiotics (Florfenicol) and antibiotic resistant genes in poster session (#12)



Process Flow Diagram for Novel Manure Management System



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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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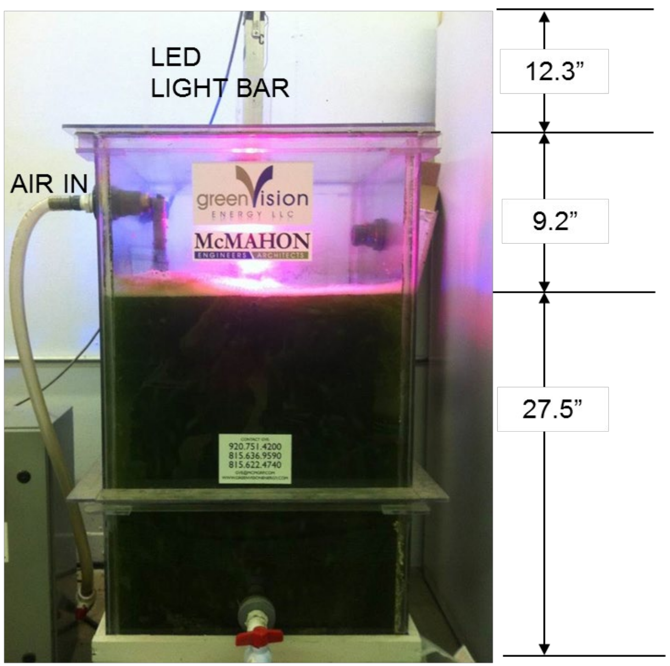
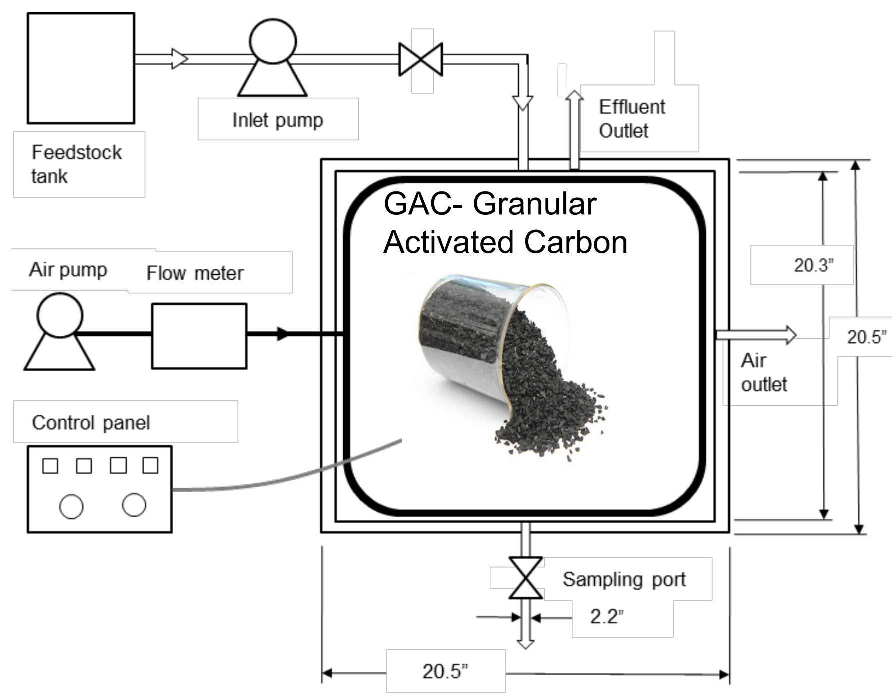
BIOREACTOR OPERATING CONDITIONS

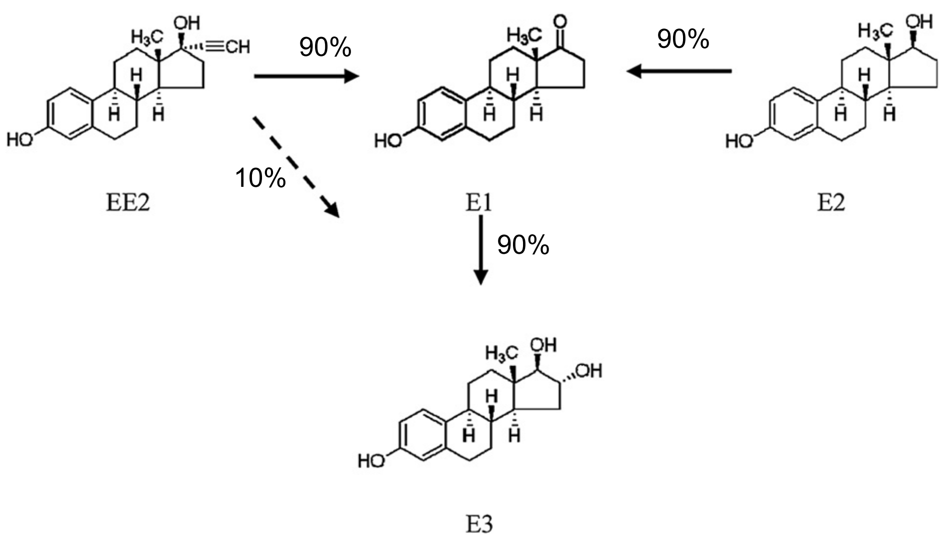
	Mixed Algal-Bacterial Bioreactor (MABB)	Conventional Activated Sludge Reactor (CAS)
Reactor type	Sequencing Batch Reactor	Sequencing Batch Reactor
Total Volume (L)	189.3	189.3
Light intensity (μ-photons/m^2/s)	**350**	-
Temperature (˚C)	18	16
Aeration rate (L/min)	**6 (0.03 vvm)**	11 (0.058 vvm)
Organic Loading Rate (mg/L/d)	48.6 - 152	48.6 - 152
HRT (day)	4	4
SRT (day)	25 - 30	25 - 30
Feed volume ratio (V_{Feed}/V_{Total}, %)	50	50



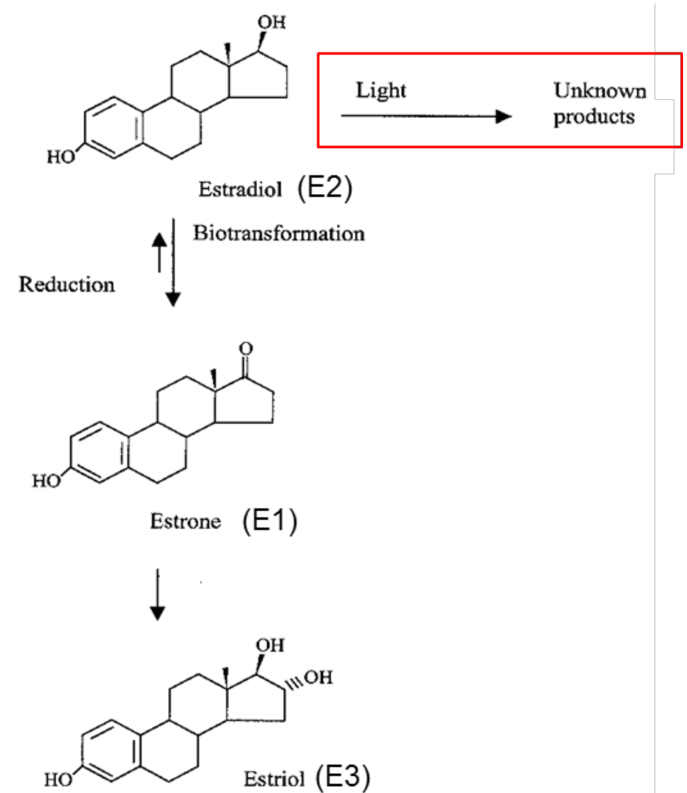


AEROBIC TRANSFORMATION PATHWAYS OF HORMONES

- 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



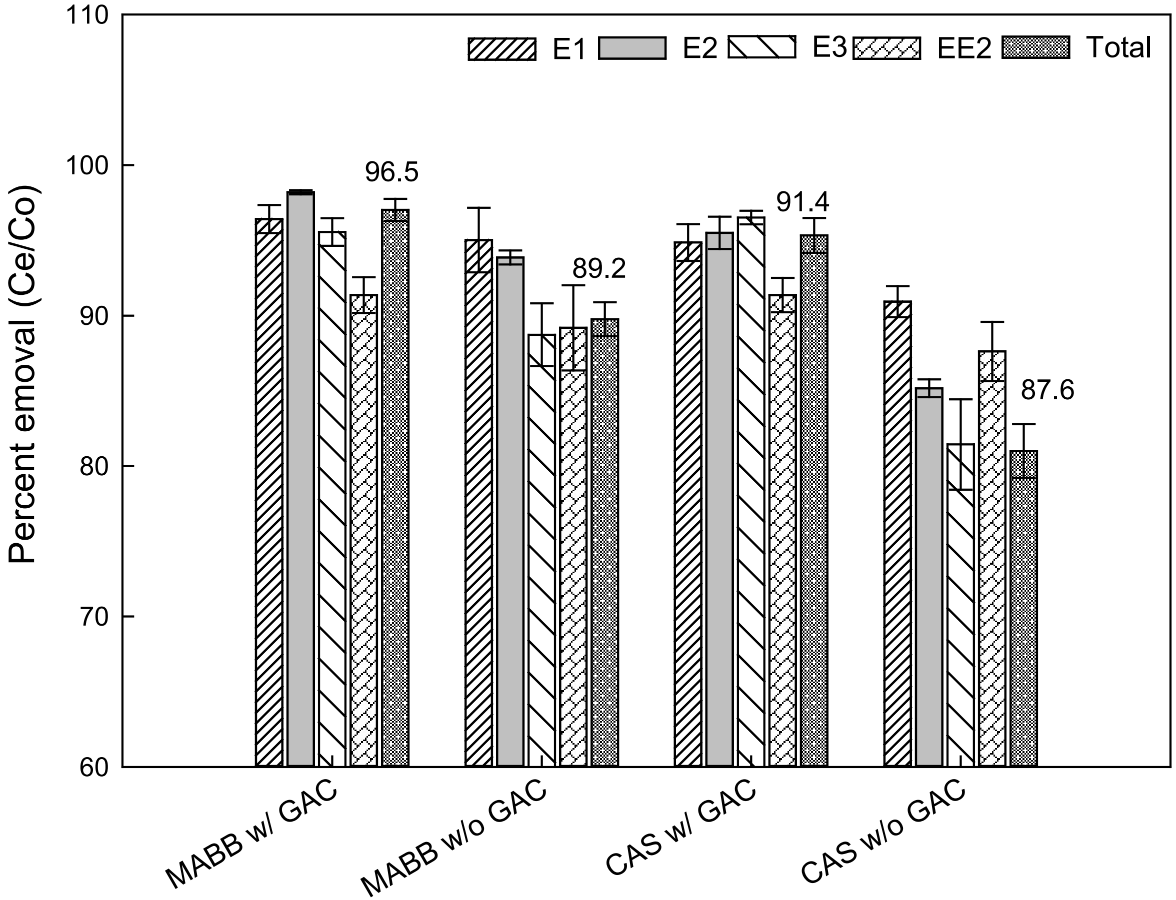
Proposed transformation pathway of E1, E2, and EE2 in aerobic water-soil system (J. Li et al., 2013)



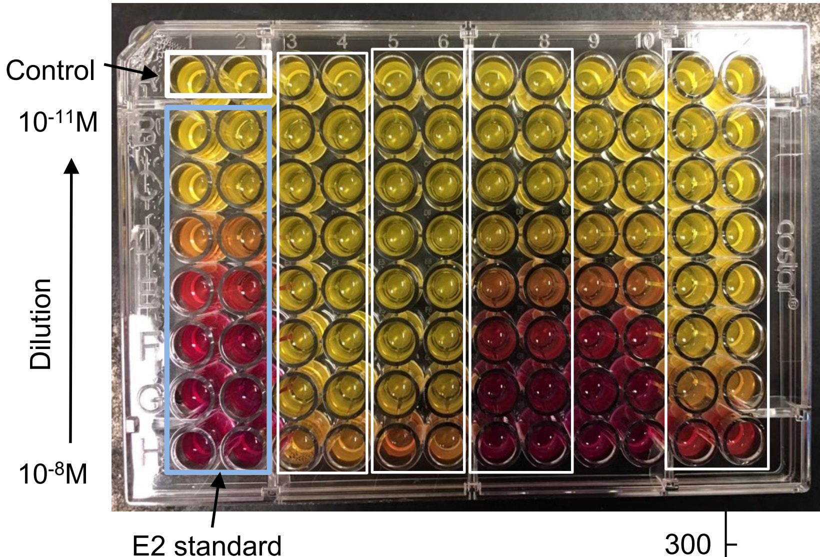
Proposed transformation pathway of E1, E2, and EE2 by *Chlorella vulgaris* (Lai et al., 2002)

COMPARISON OF HORMONE REMOVAL IN BIOREACTORS

- **Sorption** onto biomass is dominant mechanism & desorption is insignificant *(Andaluri et al., 2012)*
- **MABB** removed 2-5% more hormones than **CAS** (P=0.02)
  - Why? Algal biomass, slightly higher temperatures photochemical degradation *(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%

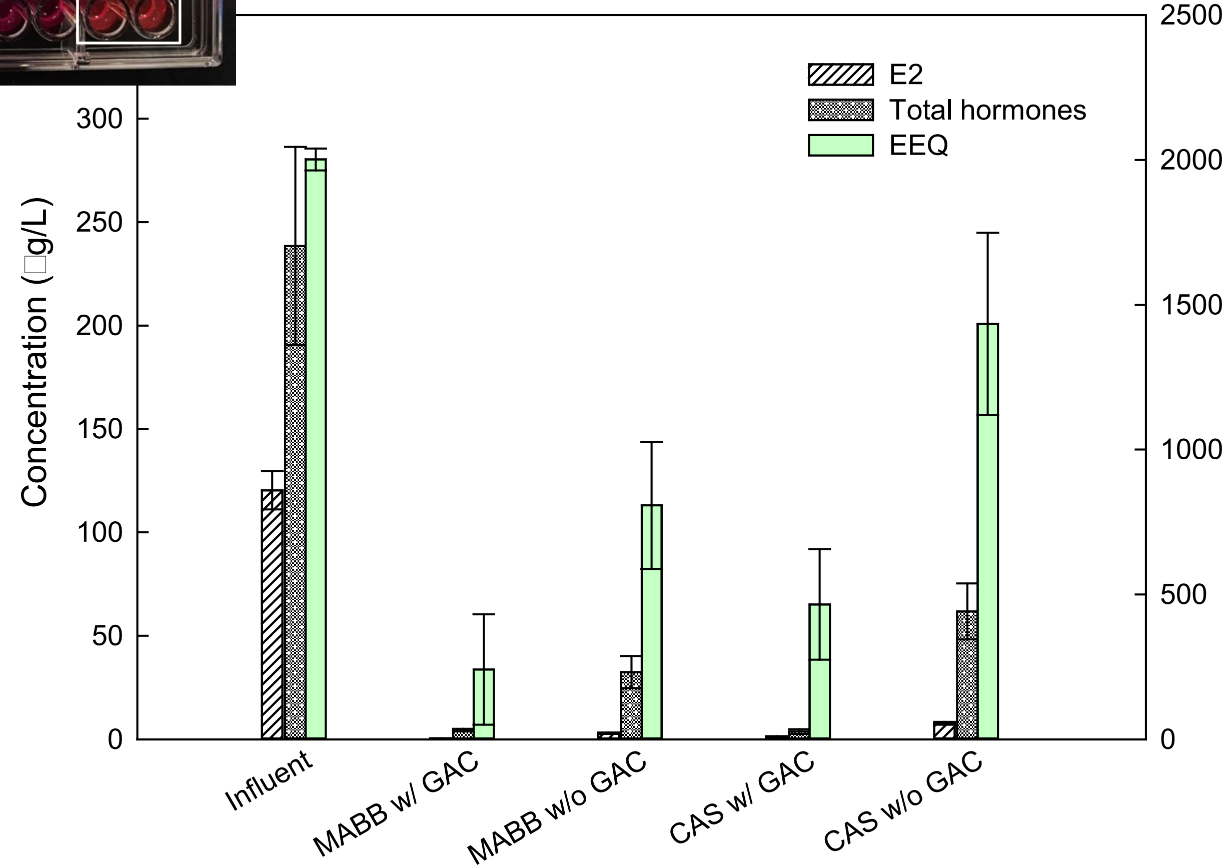


COMPARISON OF BIOREACTOR EFFECTS ON ESTROGENICITY



- 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

Gas Product (CO_2 rich)

Aqueous Product (N, P, & sCOD rich)

Solid Residue (Mineral rich ash)

Oil Product (Energy Rich, C_xH_y)

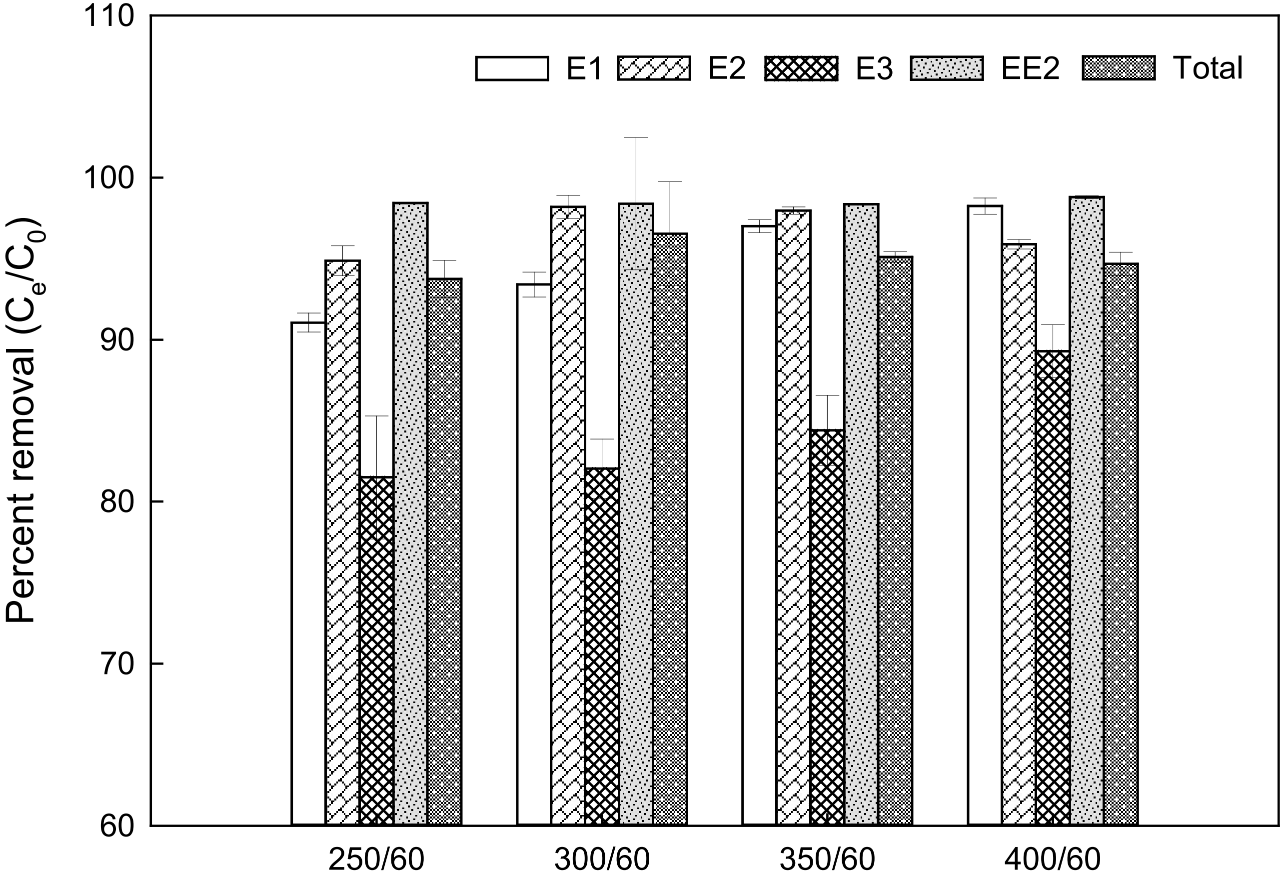
HTL has a positive net energy balance

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

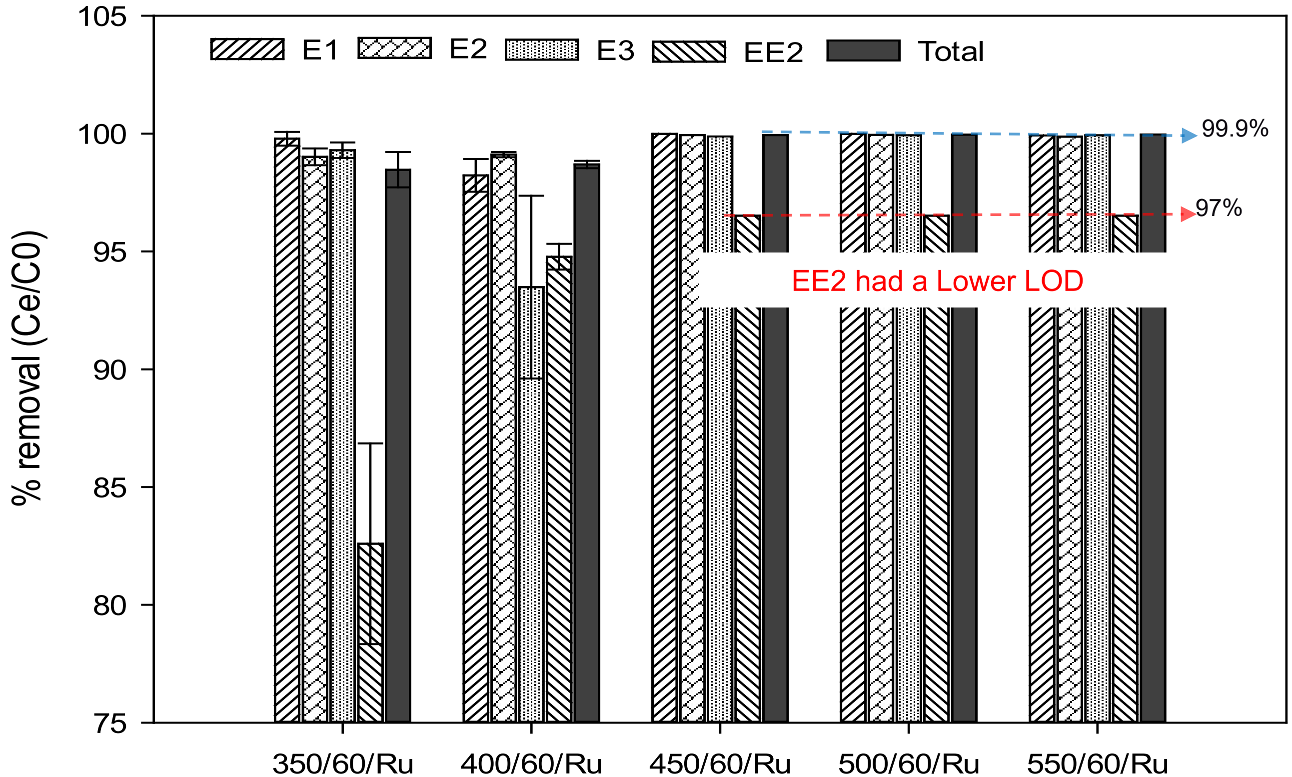
- **300˚C/60min had the highest total hormone removal and the highest oil yield**

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



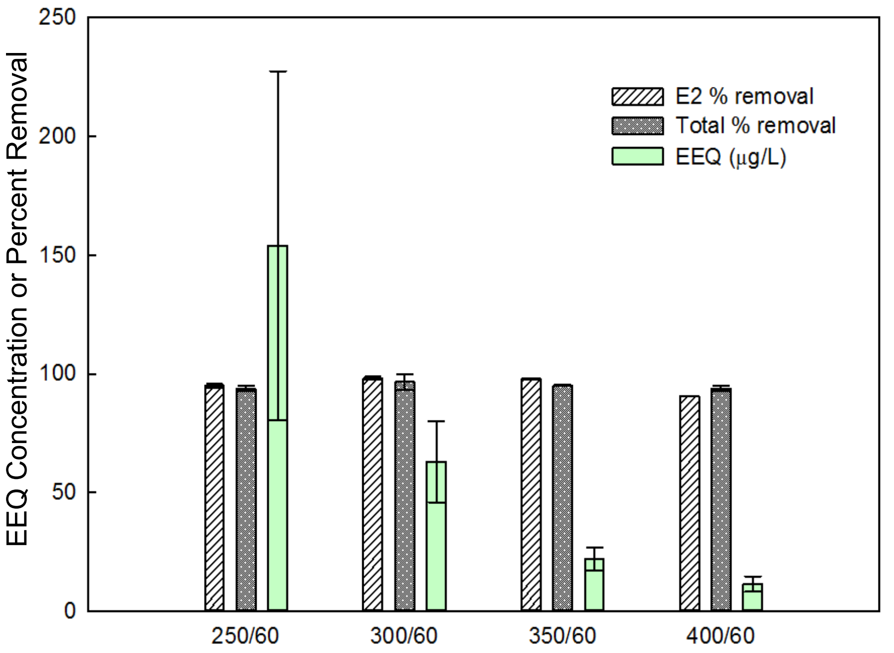
CATALYTIC HYDROTHERMAL GASSIFICATION (CHG): TEMP EFFECTS ON EC REMOVAL

- 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**



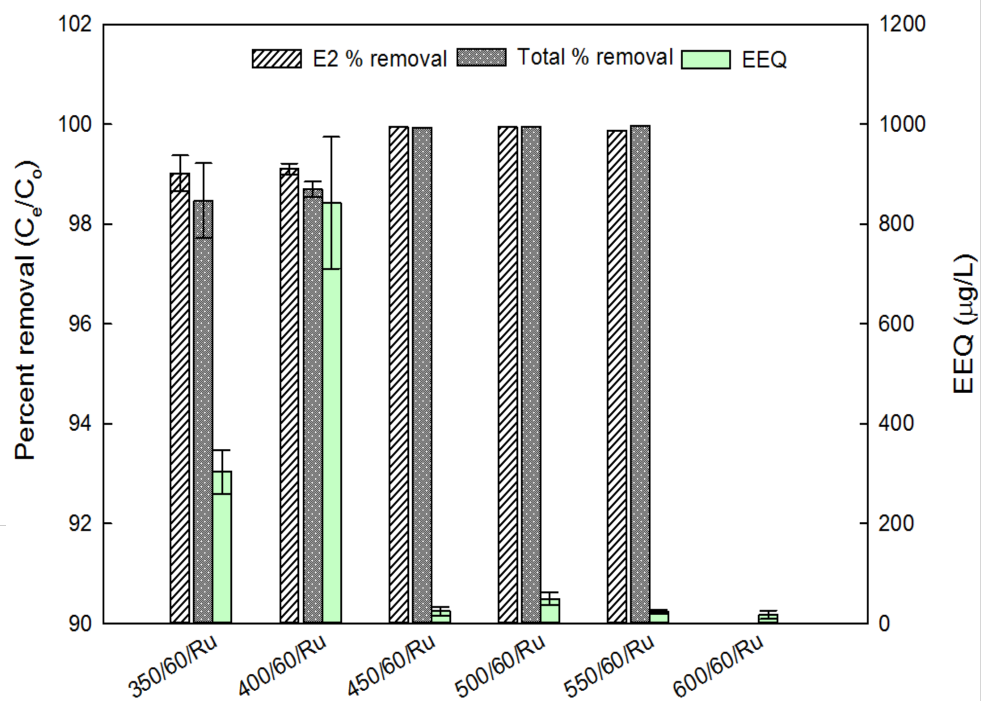
ESTROGENIC ACTIVITY IN HYDROTHERMAL AQ. PRODUCTS

- **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˚C in HTL w effective for EEQ removal**
- **CHG:** EEQ was sharply decreased with higher than 450˚C (r=-0.6, P=0.18)
  - **>450˚C in CHG was better for removal of estrogenic activity**



HTL

CHG



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 ^{o}C** were sufficient for hormone removal and good bio-oil yield, but estrogenicity removal was significantly improved at >350^{o}C
  - **CHG Temp.>500 ^{o}C** provided good bio-gas yield and removal of hormones/estrogencity
- 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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