Removal of endocrine disrupting chemicals by a constructed wetland for on-site domestic wastewater treatment

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Science Questions

- What are monitoring and measurement tools to improve the characterization of endocrine disrupting chemicals ?
- What are the major sources and environmental fates of EDCs?
- How can unreasonable risks be managed?
- How and to what degree are human and wildlife populations exposed to EDCs?

Experimental Objectives

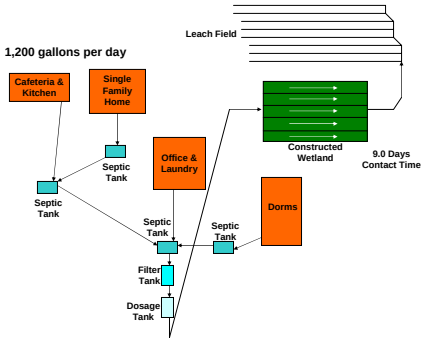
- **Develop and implement an experimental system for treatment technology testing at the full-scale.**
- **Track longer-term performance with respect to traditional regulatory variables.**
  - **Nitrogen and Phosphorus speciation and dynamics**
  - **Pathogenic indicators**
- **Track longer-term performance for select EDCs …**
  - **Steroid hormones**
  - **Alkylphenol compounds**
- **…with respect to traditional regulatory variables.**
  - **Nitrogen and Phosphorus speciation and dynamics**
  - **Pathogenic indicators**
- **Relate treatment efficacy to wetland performance characteristics.**

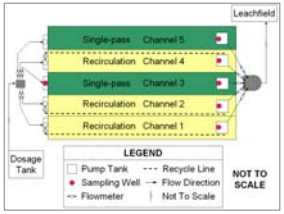
Study Location

Grailville, Loveland, Ohio

- Nonprofit Organization
- 300-acre Farm Cooperative
- Women's Center
- Environmental & Educational Retreat

Grailville CW Treatment System



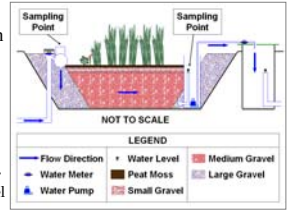


Wetland Research Setup (A)

- 5 wetland channels
- Recirculating channels
- Monitor flows
- Sample Nutrients

Wetland Research Setup (B)

- Similar channel dimensions
- Even hydraulic loading
- 1615 gallons water volume per channel



Materials and Methods

EDC Analytical Methods

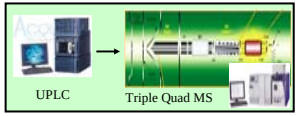
Analyte	Method
Steroid hormones	NRMRL SOP
APs, AP1EOs, AP2EOs, BPA	EPA Reg 5
APEOs 3-18	EPA Reg 5
NPECs	EPA Reg 5

Steroid Hormones – evaluation of two approaches

- Derivatized followed by GC-MSD analysis
  - Through put = many days
  - Susceptible to interferences
- Derivatized followed by LC-MS/MS analysis
  - Throughput = hours
  - More specificity, less interferences

Alkylphenol ethoxylates

- APs – GC-MS (ASTM)
- APEOs – LC-MS/MS
- APECs – LC-MS/MS



Nutrient Sampling

Wastewater samples collected quarterly at same time as EDCs

Analyzed for species of N and P including TN and TP by FIA using standard methods

Pathogenic Indicators

Wastewater samples collected quarterly along with EDCs

Fecal coliforms	E. Coli	Enterococcus
• MFC • 44.5°C for 24 hours • Blue colonies	• MUG • 35.0°C for 4 hours • Fluoresces under UV (366nm)	• ME agar • 41.0°C for 48 hours • Pink/red colonies

Additional Study Variables

Analyte	Method	Analyte	Method
Total Phosphorus	Acid Persulfate-Ascorbic Acid-Molybdate	Enterococcus	Membrane Filtration
Total Dissolved Phosphorus	Acid Persulfate-Ascorbic Acid-Molybdate	E. Coli	Membrane Filtration
Total Reactive Phosphorus	Ascorbic Acid-Molybdate	Rhodamine (as tracer)	YSI-Optical Sensor
Dissolved Reactive Phosphorus	Ascorbic Acid-Molybdate	Dissolved Oxygen	YSI-sensor
Acid Hydrolyzable Phosphorus	Hydrolysis-Ascorbic Acid-Molybdate	pH	YSI-probe
Particulate and Dissolved Organic Phosphorus	By Difference	Oxidation Reduction Potential	YSI-probe
Particle Associated Reactive Phosphorus	By Difference	Water Temp.	YSI-probe
Total Nitrogen	Alkaline Persulfate	Conductivity	YSI-probe
Total Dissolved Nitrogen	Alkaline Persulfate	Turbidity	YSI-Optical Sensor
Ammonium (NH4)	Straight Phenolate	Level	YSI-Pressure Transducer
Ammonium (NH4)	Distillation then Phenolate	Precipitation	Meteorological Station
Ammonium (NH4)	Ion Chromatography	Barometric Pressure	Meteorological Station
Nitrite-Nitrate	Cadmium Reduction	Irradiance	Meteorological Station
Biological Oxygen Demand	5-day	Azm Temp	Meteorological Station
Particulate and Dissolved Organic Nitrogen	By Difference	Dew Point	Meteorological Station
Lithium	Ion Chromatography	Relative Humidity	Meteorological Station
Sodium	Ion Chromatography	Wind speed	Meteorological Station
Potassium	Ion Chromatography	Gust Speed	Meteorological Station
Magnesium	Ion Chromatography	Wind Dir.	Meteorological Station
Calcium	Ion Chromatography	Flow rate	P-D in line totalizer
Fecal coliform	Membrane Filtration	Aboveground Biomass	Random Harvest and Allometry

Study Results

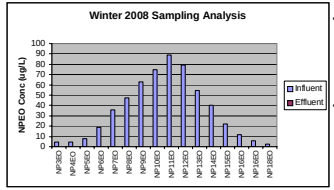
Steroid Hormones

- Results for wetland removal only shown here (in/out of CW)
- Removal varies seasonally… But generally in the 60-80+%
- Apparent "production of hormones" likely an artifact of episodic flows and conjugated hormones in influent… more work to be done here

Steroid	February 2007			April 2007			July 2007			October, 2007			February 2008			April 2008		
	Mean Influent	Mean Effluent	Mean % Removal	Mean Influent	Mean Effluent	Mean % Removal	Mean Influent	Mean Effluent	Mean % Removal	Mean Influent	Mean Effluent	Mean % Removal	Mean Influent	Mean Effluent	Mean % Removal	Mean Influent	Mean Effluent	Mean % Removal
Dihydrotestosterone	249.1	38.9	**84.4**	32.8	34.5	**-5.2**	75.6	81.3	**-7.6**	407.2	92.9	**81.3**	376.5	68.6	**81.8**	306.6	59.3	**80.7**
17-β-estradiol (E2)	6.9	2.9	**57.5**	2.2	6.3	**-185.4**	2.7	3.8	**-41.1**	9.9	1.3	**84.8**	3.6	3.8	**-8.2**	NPD	5.5	-
Estrone (E1)	44.6	19.2	**56.9**	9.3	17.1	**-84.0**	14.8	23.7	**-59.8**	234.1	35.6	**84.8**	53.1	19.4	**63.4**	34.0	15.7	**53.7**
Testosterone (TEST)	27.4	4.4	**84.0**	4.7	2.7	**42.7**	8.0	5.1	**36.7**	32.0	5.6	**82.6**	10.8	2.4	**77.7**	8.7	5.3	**38.9**
Androstenedione (AND)	110.3	7.9	**92.8**	18.6	5.8	**69.0**	36.8	19.4	**47.3**	264.3	39.8	**84.9**	102.2	17.1	**83.2**	142.7	21.5	**84.9**
17-α-ethynylestradiol (EE2)	NPD	NPD	-	NPD	NPD	-	NPD	NPD	-	2.0	NPD	**>30**	NPD	NPD	-	NPD	NPD	-
Estriol (E3)	211.3	76.5	**63.8**	4.3	26.4	**-520.3**	4.4	16.7	**-283.0**	612.0	137.5	**77.5**	161.1	102.3	**36.5**	23.0	115.8	**-404.4**
Progesterone	15.3	NPD	-	12.3	NPD	-	4.4	NPD	-	57.9	NPD	**>98**	11.3	NPD	**>87.7**	NPD	NPD	-

NPD: No Peaks Detected above noise
- : removal rate determination not possible
% removal determined by % removal = [1 - (Cout/Cin)]*100

APEOs comparing sources

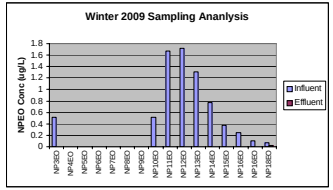


- APs in influent dominated by higher ethoxylated APEOs.
- Effluent shows almost complete removal of the EO forms and "production" of NP (NP not shown).

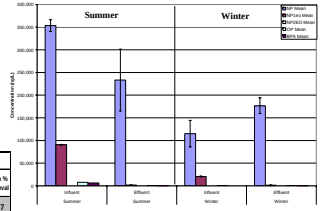
- APs in influent dominated by higher ethoxylated APEOs but…

… appears to be a different source of APEOs to the system.

- Effluent shows almost complete removal of the EO forms and "production" of NP (NP not shown).



APs – seasonal comparisons



Discussion

- Nutrient removal
  - TN removed limited by nitrification
    - Requires oxygen source
    - Recirculation did not provide significant oxygen
  - TP removed limited by adsorption or precipitation
    - Requires contact time in channel
    - Recirculation did not affect average contact time as compared with single-pass
- EDC removal
  - Highly variable episodic flows make data interpretation difficult.
  - Degradation of selected EDCs is variable by season and with changing flow conditions
- Future work with the CW owner to:
  - Conduct controlled studies with fixed volume pulsed flows to allow for more controlled studies
  - Evaluate a product replacement option for their detergents
  - Moving to the leachfield to evaluate the entire system and the potential for release in the environment

Responsiveness and Collaborations

Findings from this research to be used directly by :

- EPA's Office of Water
- The Great Lakes National Program Office
- EPA Regional offices and State/local regulators