Estrogens in Wastewater

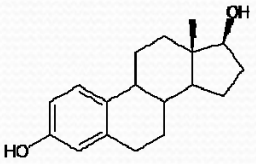
LeeAnn Racz, PE
Dr. Ramesh Goel
University of Utah
November 2008

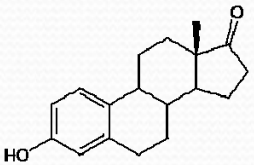
Overview

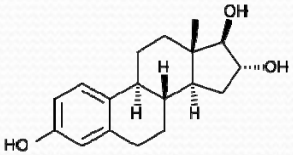
- What are estrogens?
- Why do we care about estrogens in wastewater?
- Analytical methods
- Ongoing research
- How do we reduce the amount released to the environment?

What are estrogens?

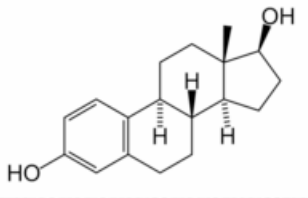
- Natural hormones
  - 17β-Estradiol (E2)
  - Estrone (E1)
  - Estriol (E3)







- Synthetic hormones
  - 17α-Ethinyl estradiol (EE2)



What are estrogens?

- Class of endocrine disrupting compounds (EDC)
  - Mimic or block natural estrogen
  - Estrogens have three orders of magnitude greater estrogenic potencies than other EDCs identified in wastewater
  - E2 and EE2 most potent
- Humans excrete in urine and feces as inactive polar conjugates
  - Women typically excrete 0.5 to 5 µg/day of E2 (up to approximately 400 µg/day for pregnant women)
  - Excretion rates for the other estrogens are 3 to 20 µg/day of E1 and up to about 64 µg/day of E3

Why do we care about estrogens in wastewater?

- Bacterial enzymes in raw wastewater and in activated sludge convert the excreted conjugates back to the active unconjugated forms
  - Possible to have effluent concentrations exceed influent concentrations
  - Estrogens that are not degraded during the wastewater treatment process are released to the environment with the effluent
  - **Treated municipal wastewater is one of the most likely sources of estrogenic compounds in the environment**

Why do we care about estrogens in wastewater?

- Estrogen concentrations in municipal wastewater and surface water receiving effluent in ng/L liter level
  - Concentrations of 40-100 ng/L found in municipal wastewater
  - Concentrations of 10-100 ng/L commonly found in wastewater effluents

Why do we care about estrogens in wastewater?

- Predicted-no-effect-concentration (PNEC) of **1 ng/L for E2** and **3-5 ng/L for E1**,
- Lowest-observable-effect-level (LOEL) affecting production of vitellogenin (egg yolk protein normally associated with sexually mature females) in juvenile female rainbow trout is **3.3 ng/L for E1** and **14 ng/L for E2**

- Less than **1 ng/L of EE2** can stimulate male rainbow trout to produce vitellogenin
- Concentration of **4 ng/L EE2** can cause failure in the male fathead minnow to develop normal secondary sexual characteristics

Why do we care about estrogens in wastewater?

- Exposure to estrogen levels as low as **1 ng/L** can cause the development of intersex roaches in rivers
- Measurable changes in fish reproduction can result at **E2 and EE2** concentrations as low as **2 ng/L**
- Although controversial, suggested associations between EDCs in the environment and human sperm quality as well as breast, testicular and prostrate cancers

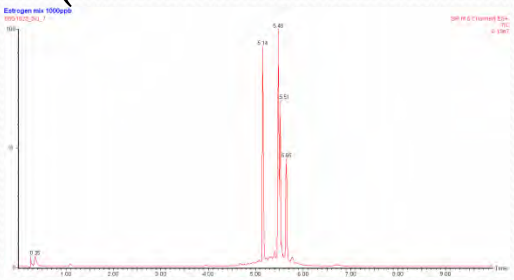
Analytical Methods

- Current EDC laws regulate only industries producing or using raw chemicals
- No federal regulations for estrogens in drinking or natural waters
- State of CA monitoring EDCs and PPCPs , especially when municipal wastewater effluent used for indirect potable reuse

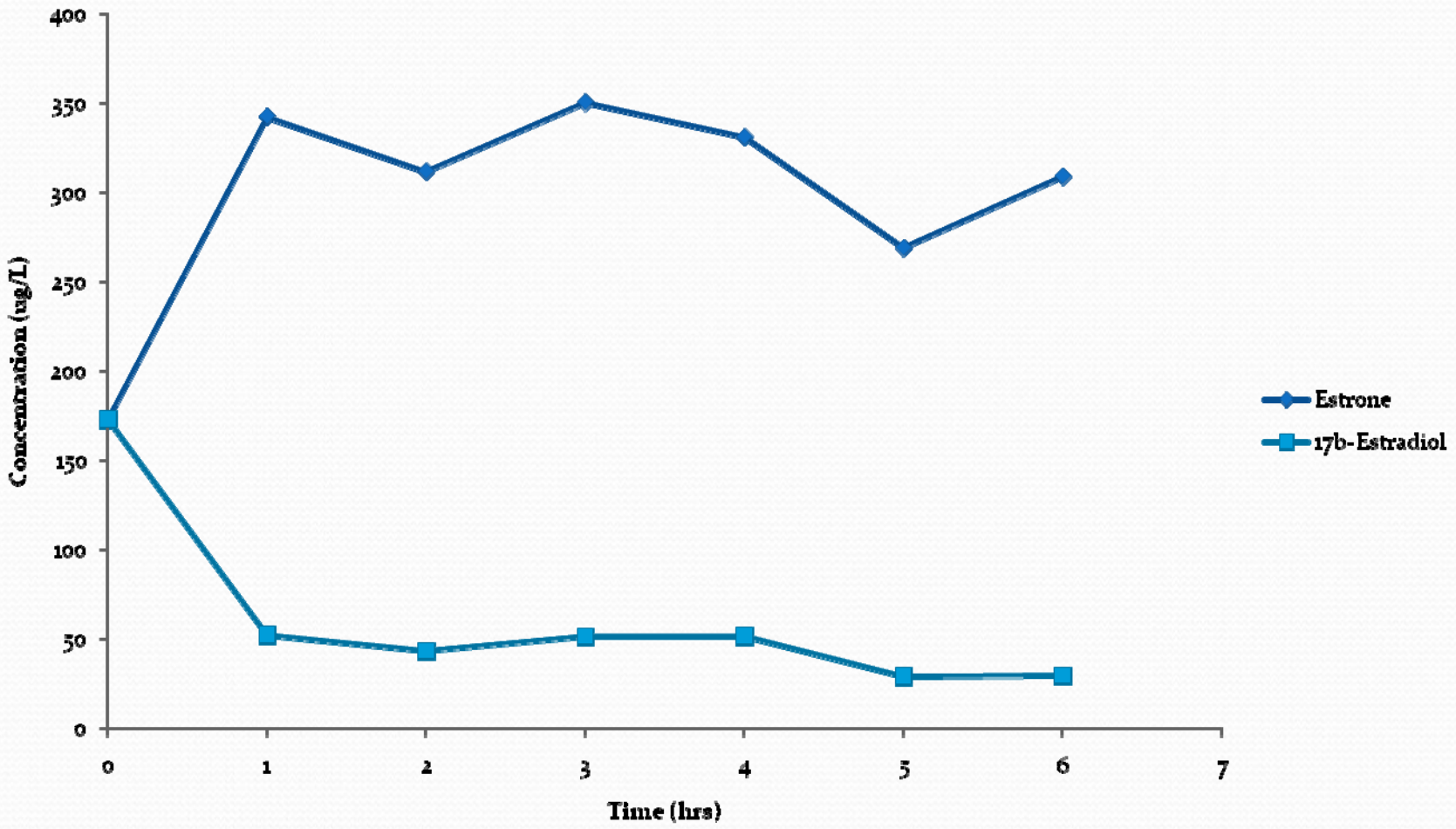
Analytical Methods

- No standard methods for estrogens
- A few commercial laboratories can analyze
- Desire to quantitate at ultratrace concentrations (sub-ng/L)

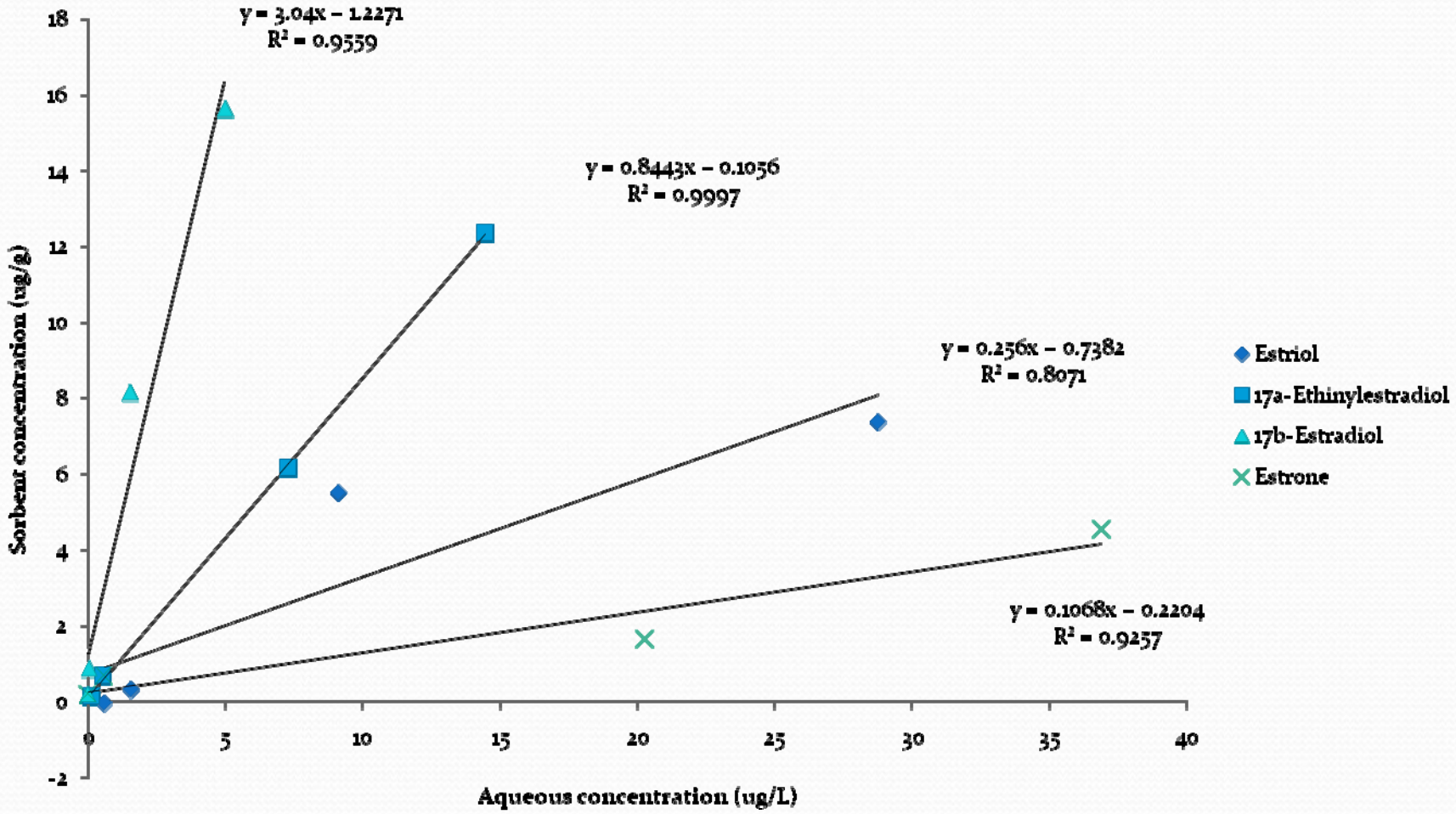
- Most methods involve an extraction procedure followed by instrumental and/or immunoassay analysis
  - Solid phase extraction (to extract and concentrate)
  - GC/MS or LC/MS



Estrogen Degradation in Activated Sludge



Estrogen Sorption Isotherms for Activated Sludge



Full-scale Plant Study

Sample Location	Estrone (E1)	Estradiol (E2)	Estriol (E3)	17α-Ethyinyl-estradiol (EE2)
Plant A Influent	N/D	N/D	N/D	N/D
Plant A Effluent	0.0417*	0.0934*	N/D	N/D
Plant BInfluent	N/D	N/D	N/D	N/D
Plant B Effluent	N/D	N/D	N/D	0.0781*
Plant C Influent	N/D	N/D	N/D	N/D
Plant C Influent (Duplicate)	N/D	N/D	N/D	N/D
Plant C Effluent	N/D	N/D	N/D	N/D
Plant C Effluent (Duplicate)	N/D	0.368	0.410	0.248
Plant D Influent	N/D	N/D	0.021*	N/D
Plant D Effluent	N/D	0.153	N/D	0.051*
Plant E Influent	N/D	N/D	0.214	N/D
Plant E Influent (Duplicate)	N/D	N/D	0.005*	N/D
Plant E Effluent	0.024*	N/D	0.141	N/D
Plant E Effluent (Duplicate)	0.053*	0.102*	N/D	0.039*

* Below the limit of quantitation

Ongoing Research

- Full-scale studies
  - ND to 0.410 µg/L in effluent
  - ND to 0.214 µg/L in influent
- Nitrifying activated sludge
  - Solvent application
  - Nitrifying community changes with non-nitrifying community changes

How do we reduce the amount released to the environment?

- Primary settling – Poor
- Trickling filters – Less effective than activated sludge
- Nitrifying activated sludge – Good
  - Synthetic EE2 removed more effectively than in non-nitrifying activated sludge

- Denitrification process – Good
- Sludge retention time is likely an important factor

How do we reduce the amount released to the environment?

- Chemical precipitation – Maybe OK
  - Could be associated with organic phases of particulates
- Activated carbon – Good
  - PAC can remove 60-80% of E2 and EE2

- Chlorination – Conflicting results
  - Free Cl reacts with phenolic compounds
  - Other studies found Cl ineffective in degrading estrogens

How do we reduce the amount released to the environment?

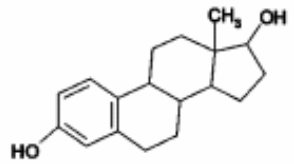
- Ozonation – Some removal
- Ultraviolet Irradiation – Not effective
  - Typical UV doses for disinfection several orders of magnitude less than those needed to treat estrogens
- Reverse Osmosis – Good
  - >90% removal of steroid hormones
  - Microfiltration (0.1 – 0.4 µm) do not remove compounds

Summary

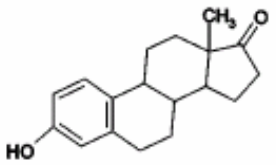
- Estrogens are powerful EDCs
- No current legislation
- Problematic to measure
- Can be removed by
  - Biotransformation, especially nitrifying activated sludge
  - Denitrification
  - Activated carbon
  - Reverse osmosis

Questions?

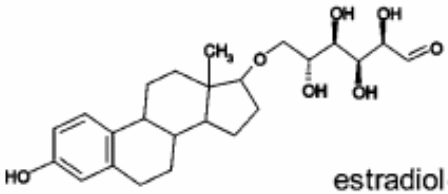
Conjugated vs. Unconjugated



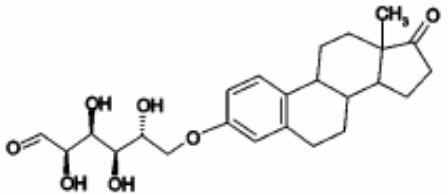
17β-estradiol



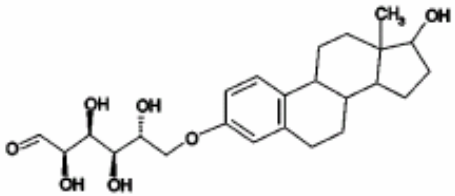
estrone



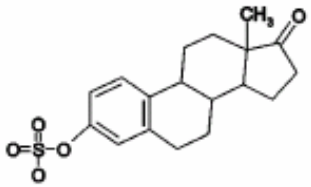
estradiol-17-glucuronide



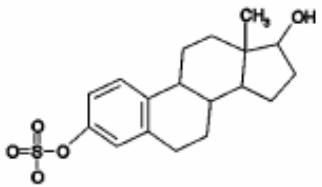
estrone-3-glucuronide



17β-estradiol-3-glucuronide



estrone-3-sulphate



17β-estradiol-3-sulphate