Fate of Endocrine Disrupting Contaminants in WWTPs and Their Impact on Receiving Streams

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Water Reclamation Reuse

Intended Reuse
- Direct
- Indirect

Unintended
Consumer Products

Cleaning

Pharmaceutical

Agricultural
Aerobic Degradation of Surfactants

Anionic
Linearalkylbenzenesulfonate (LAS)

Nonionic
Alkylphenolethoxylates (APEO)

Hydrophobe

Hydrophile

Decreasing Toxicity

Complete Mineralization

1991 LAS use = 390 million kg (Modler and others, 1993)

1988 APEO use = 200 million kg (Talmidge, 1994)
Endocrine Effects of Alkylphenols

![Graph showing absorbance at 540nm against concentration (g/L) for different alkylphenols.](image-url)
The Human Endocrine System

System of glands that produce hormones and corresponding receptors

- Sexual Development
- Reproduction
- Growth
- Metabolism
- Neurological Development
- Cancers

After Colborn and others, 1996
What are hormones?

*Chemical regulators, secreted by glands to the blood that effect a change at a target site.*

### Types of chemical regulators

- **Amino acids, amines, peptides, proteins**
- **Steroids**
  - Cholesterol
  - Glucocorticoids (Cortisol, Corticosterone)
  - Mineralocorticoids (Aldosterone)
- **Thyroid Hormones**
  - 1,25-Dihydroxycholecalciferol (Vitamin D)
- **Other Molecules**
  - Steroids
  - CORTICOSTEROIDS
    - Glucocorticoids
      - Cortisol
      - Corticosterone
    - Mineralocorticoids
      - Aldosterone
  - ESTROGENS
    - 17b-Estradiol
    - Estrone
    - Estriol
    - Progestogens
      - Progesterone
      - Pregnenolone
    - Androgens
      - Testosterone
      - Androstenedione
      - 11-Ketotestosterone
      - Androsterone
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### Hormone Functions

- **CORTICOSTEROIDS**
  - Stress: carbohydrate metabolism and ionic regulation
  - Maintains pregnancy or endometrium, inhibits gonadotropin release
- **ESTROGENS**
  - Supports and stimulates female reproduction
  - Stimulates endometrial proliferation, positive and negative feedback on estrous cycle
  - Converted from androgens, stimulates hypothalamus and sexual behavior
- **PROGESTOGENS**
  - Maintains pregnancy or endometrium, inhibits gonadotropin release
  - Supports and stimulates female reproduction
- **ANDROGENS**
  - Stimulates development of male characteristics
  - Stimulates spermatogenesis, sex glands, and secondary sex characteristics
- **1,25-DIHYDROXYCHOLECALCIFEROL (Vitamin D)**
  - Regulates calcium absorption by intestine
Biogenic and Synthetic Steroidal Hormones

**Natural**

*17β-Estradiol*

*17α-Estradiol*

**Pharmaceutical**

*17α-Ethynylestradiol*

**Contraception**
- 10 million use oral contraceptives
- 88 kg/yr, PEC =

**Hormone Replacement Therapy**
- 13 million use hormone replacement
- 1688 kg/yr, PEC =

**Biogenic**
- 98 million excrete ~0.1 mg/day/person
- 3577 kg/yr, PEC =

Premarin - 45 million prescriptions in 2001 = $2,000,000,000 (C&E News)

Arcand-Hoy and others, 1998
Effects of Endocrine Disrupting Chemicals

Ecosystem

Population

Individual reproduction

Secondary behavior and morphology

Primary molecular and biochemical responses

Exposure to potential environmental agents

Campbell and Hutchinson, 1998
Emerging Contaminant Reconnaissance


- 139 Streams in 30 States
- 62 Intense AFO Activities
- 52 Intense Urbanization
- 17 Mixed Land Use
- 8 Minimally Developed
- 22 Antibiotics
- 14 Prescription Drugs
- 5 Nonprescription Drugs
- 15 Hormones and Steroids
- 39 Household and Industrial
Study Sites

Akron
Chicago
Detroit
Duluth
Indianapolis
Minneapolis
Calumet River
Chicago Ship and Sanitary Canal
Cuyahoga River
Mississippi River
Effluent Contribution to Des Plaines River

- 7 day precipitation total
- Combined effluent flows
- River flow (Romeoville)

Graph showing trends in effluent and precipitation from 1/7/02 to 12/7/02.
OWCs in WWTP Effluents
Fate of OWCs in Calumet WRP
OWCs in Chicago Waterways
Hormones in CWRP Aqueous Streams

Influent → Aerated Grit → 1º Settling → Aeration Tank → 2º Settling

Graphs showing hormone levels (E2, aE2, E3, E1, AND, COP) before and after each treatment step.
Hormone Occurrence in Cal Sag

17beta-estradiol

-1 km, Eff, 1 km, 5 km, 11 km, 18 km
Comprehensive Chemical Analysis

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| 92 | Pa | Protactinium| 231.0|
| 93 | U | Uranium | 238.0|
| 94 | Np | Neptunium| 237.0|
| 95 | Pu | Plutonium| 242.0|
| 96 | Am | Americium| 243.0|
| 97 | Cm | Curium   | 247.0|
| 98 | Bk | Bismuth | 247.0|
| 99 | Cf | Californium| 251.0|
| 100 | Fm | Flerovium| 253.0|
| 101 | Md | Mendelevium| 256.0|
| 102 | No | Nihonium | 259.0|

**Types of Elements Key**
- Alkaline earth metals
- Alkaline metals
- Transition metals
- Lanthides
- Actinides
- Poor metals
- Post-transition metals
- Non-metals
- Noble gases

**USGS**
Rare Earth Element Distributions

The Gadolinium Anomaly

Gadolinium complex of diethylenetriamine pentaacetic acid

The Link to Biology?

All life depends on water

Molecular, Cellular, and Developmental

in vitro

in vivo

Environmental, Population, and Organismic
Since the Early 1980s Endocrine Disruption in Wild Fish Has Been Shown to be an Issue of Global Concern
Barber and others, 2006, Chemical loading into surface water along a hydrological, biogeochemical, and land use gradient - A holistic watershed approach: Environ. Sci. Technol., v. 40,
Evidence of Reproductive Disruption in Boulder Creek

White Sucker (*Catostomus commersoni*)
Estradiol in Boulder Creek

- <0.8 ng/L E2
- 2.1 ng/L E2
- 1.4 ng/L E2
- 2.9 ng/L E2
- 1.2 ng/L E2
Shift in Sex Ratio

Intersex in Downstream Fish

Vajda and others, 2006
Exposure Conditions
- 5 adult males per tank
- equal length and weight
- temperature = 21°C ±1
- photoperiod 16:8 L:D
- fed frozen brine shrimp
- Flow = 200 mL/min
- Aeration
Effluent Inhibits Spermatogenesis

% of Male Fish per Stage

Reference 50/50 Mixture Effluent

Exposure Duration (Days)

++++
+++
++
+

R4 R7 R14 R28 M4 M7 M14 M28 E4 E7 E14 E28
Pay attention to unusual biological observations. What is normal? One animal’s poison may not be another’s. Potency is a key factor. Degradation products may bite! Beware of continual exposure to low concentrations and mixtures. Beware of nontraditional pollutants from unexpected sources. Acute toxicity tests may not be very helpful. Central role played by sewage treatment. Hydrology will tell you where to look!