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ECs in the United States: Understanding Their Occurrence, Fate and Effects

James Gray
National Water Quality Laboratory and Toxic Substances Hydrology Program

Emerging Contaminants

- Several Names Pharmaceutical and Personal Care Products (PPCPs), Organic Wastewater Contaminants (OWCs), Emerging Pollutants of Concern (EPOCs)
- New chemicals produced to offer improvements in industry, agriculture, medicine, and common conveniences.

- New reasons for concern for existing contaminants.
- New capabilities enabling improved examination of contaminants.

EC Project "Source-to-Receptor" Research

http://toxics.usgs.gov/regional/emc/

Sources & Pathways

Methods Development

Environmental Occurrence

Transport and Fate

Modeling

Receptors (Eco exposure and effects)

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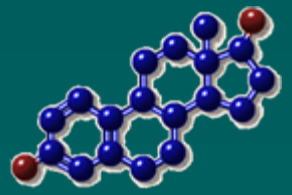
>130 pubs since '98

Methods Development



Special emphasis:
- PhAC
- HAC

What chemicals we find in the environment, <u>and what we can understand about them</u>, often depends on what we look for and how hard we look.

<u>158 Compounds in Water</u>

- 45 Antibiotics
- 12 Prescription Drugs
- 8 Nonprescription Drugs
- 14 Hormones and Steroids
- 79 Household and Industrial Compounds

<u>83 Compounds in Sediment</u>

- 3 Antibiotics
- 12 Prescription Drugs
- 7 Nonprescription Drugs
- 61 Household and Industrial Compounds

These methods are designed to detect ECs at expected ambient concentrations (ppb to ppt to ppq)

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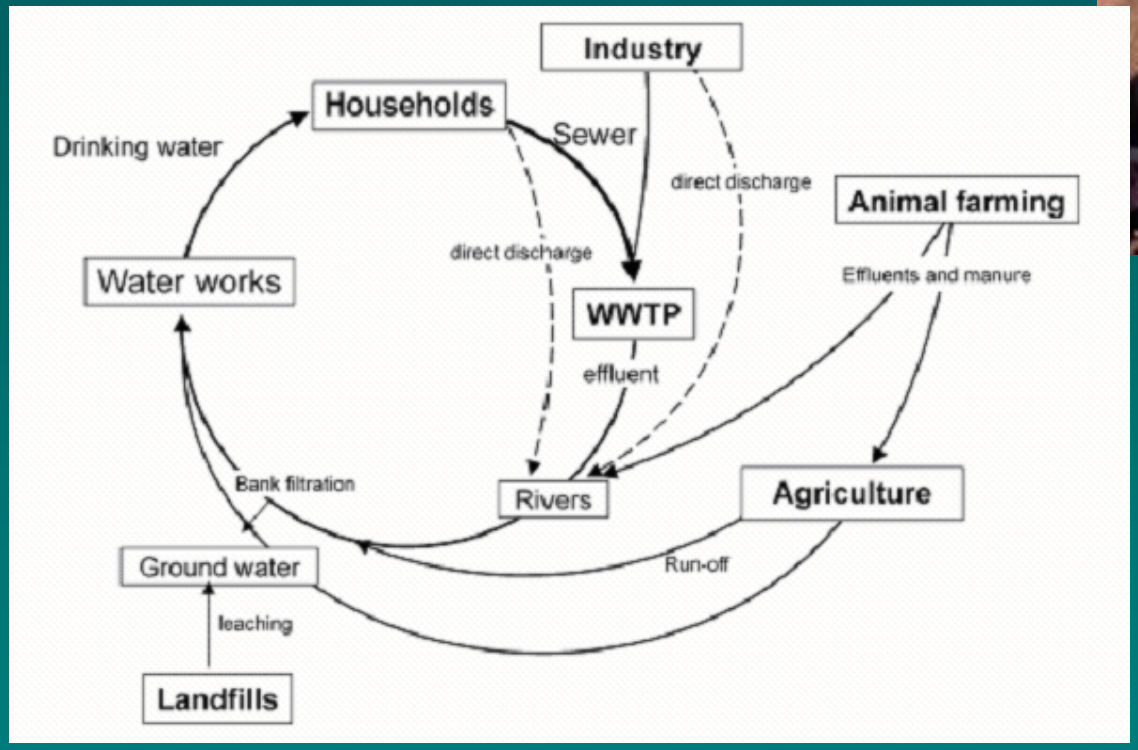
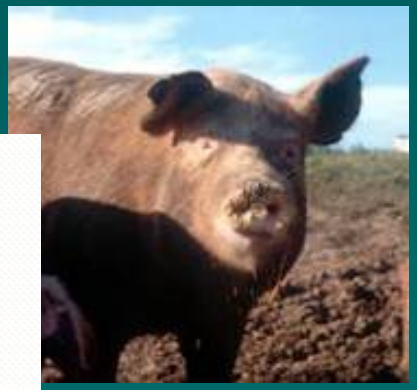
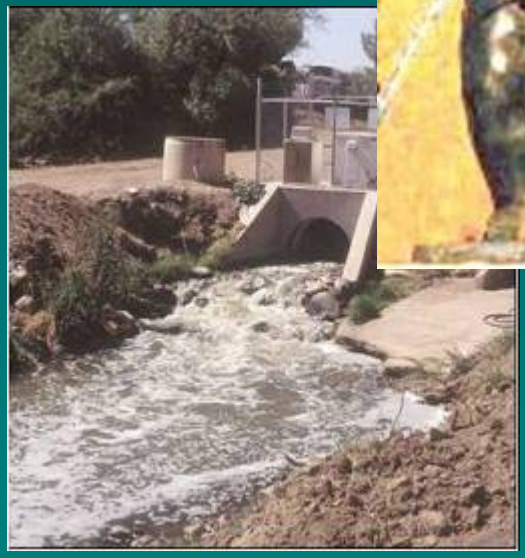
Sources and Source Pathways







To effectively minimize environmental contamination, it is necessary to understand potential contaminant origins and pathways to the environment.

Human and Animal Sources

Human

- Wastewater treatment plants
- Combined sewer overflows
- Onsite septic systems
- Industrial Discharge
- Landfills
- Water Reuse

Animal

- Waste lagoons, etc.
- Land application
- Processing plants
- Aquaculture

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Occurrence

The first step in the road to understanding the fate of a contaminant is determining if contamination is actually taking place.

- Which compounds enter the environment?
- How frequently do they occur?
- At what concentrations do they occur?
- In what mixtures?

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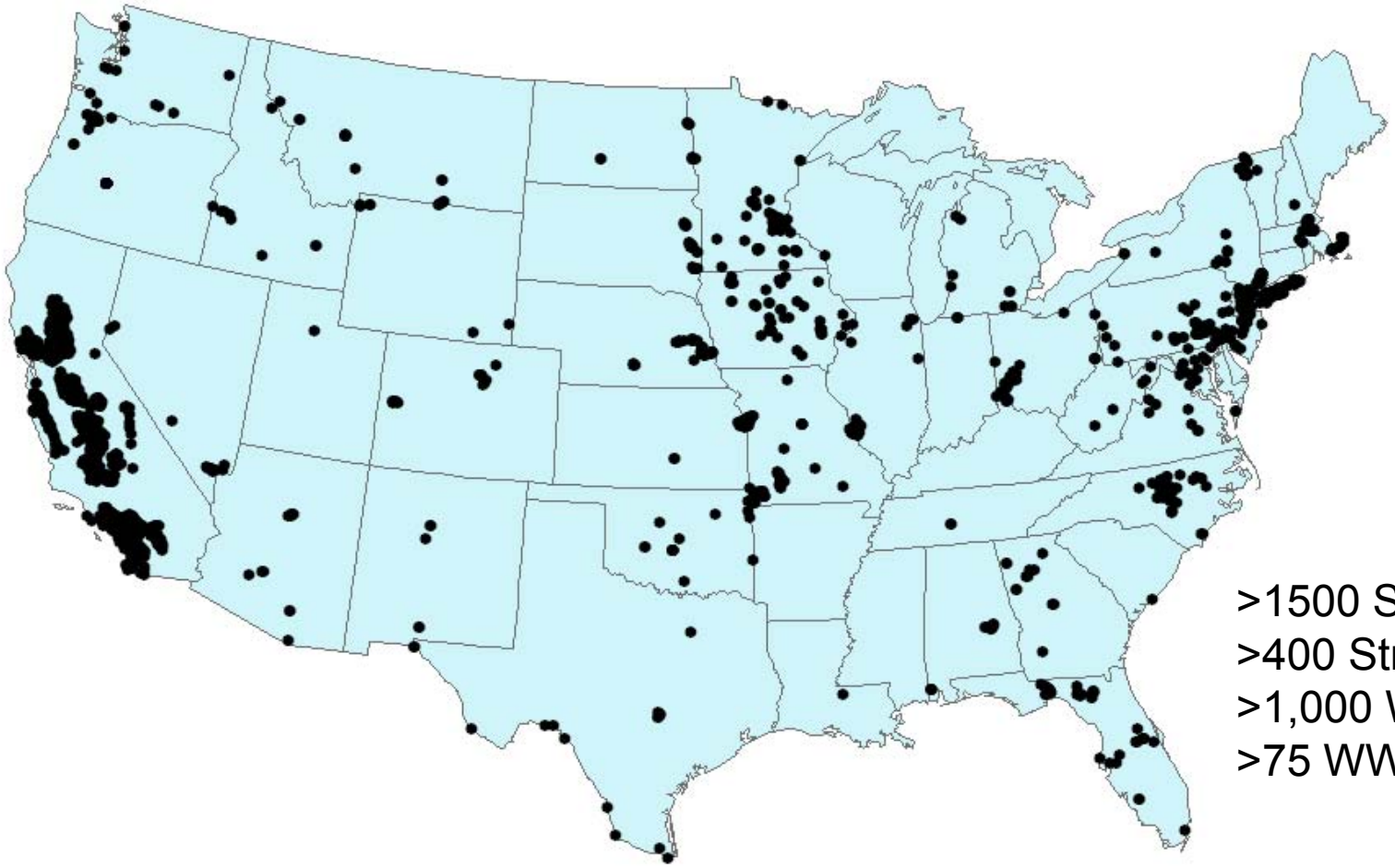
Chemicals of Emerging Environmental Concern

Sample Locations



>1500 Sites
>400 Streams
>1,000 Wells
>75 WWTPs

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Preliminary, in preparation

0 145 290 580 Miles

WWTP Study - 2002

10 WWTP Settings

- upstream
- effluent
- 1st downstream
- 2nd downstream

2 Background settings

ES&T, 2005, v. 39, n. 14, p. 5157-5169

Most Frequently Detected Compounds

78 of 110 ECs detected

- Cotinine (92.5%)
- Cholesterol (90.0)
- Carbamazepine (82.5)
- Tonalide (80.0)
- Tri(dcp)phosphate (77.5)
- Tri(2-ce)phosphate (75.0)
- 3,4-dcp isocyanate (72.5)
- b-sitosterol (72.5)
- Codeine (72.5)
- Ethyl citrate (72.5)
- Sulfamethoxazole (72.5)
- Caffeine (70.0%)
- DEET (70.0)
- Tributylphosate (70.0)
- Ethanol,2-b,p (70.0)
- Benzophenone (67.5)
- Diltiazem (67.5)
- NPEO2 (62.5)
- NPEO1 (62.5)
- Triclosan (62.5)
- 3b-coprostanol (60.0)
- Trimethoprim (60.0)

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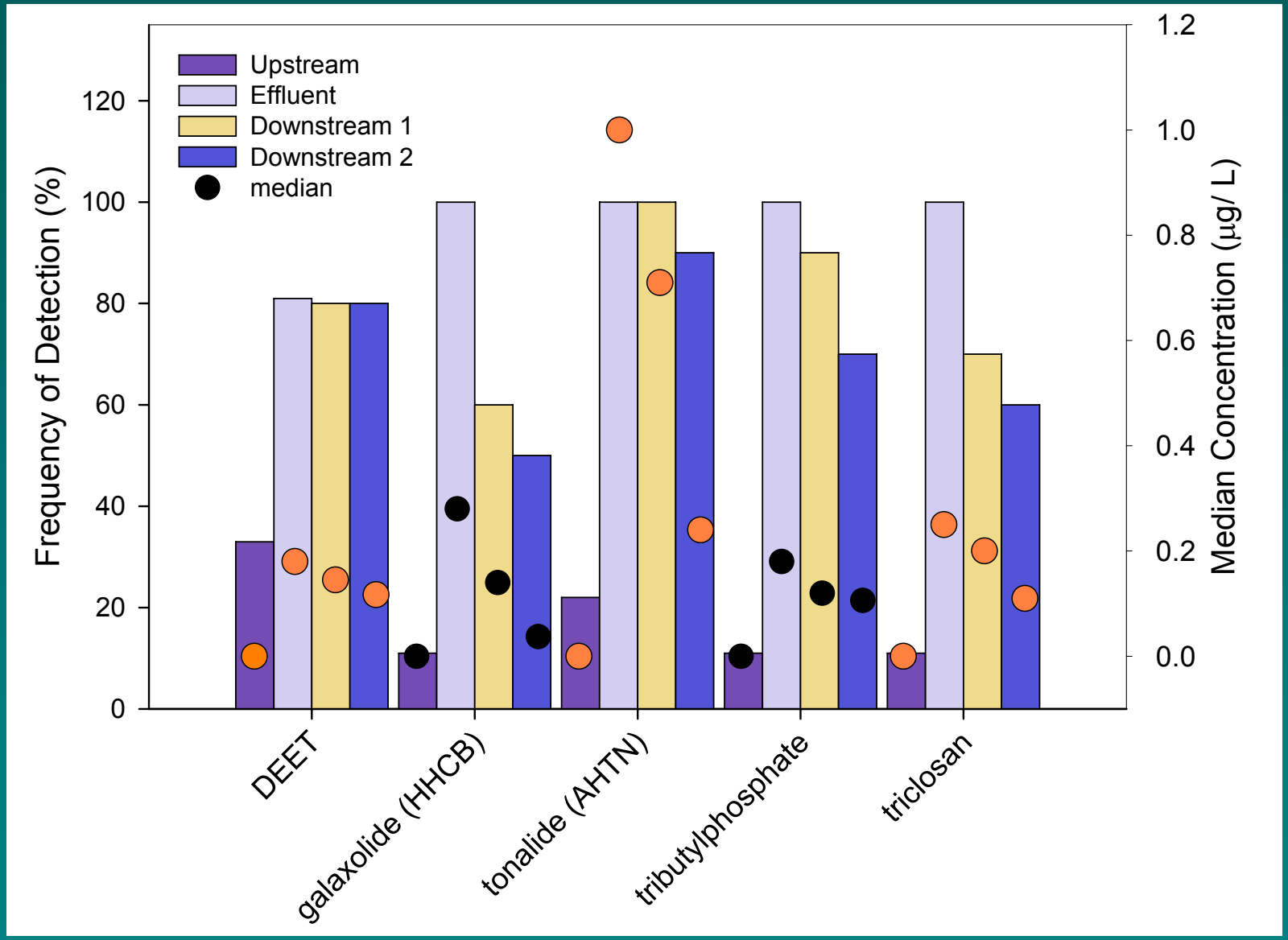
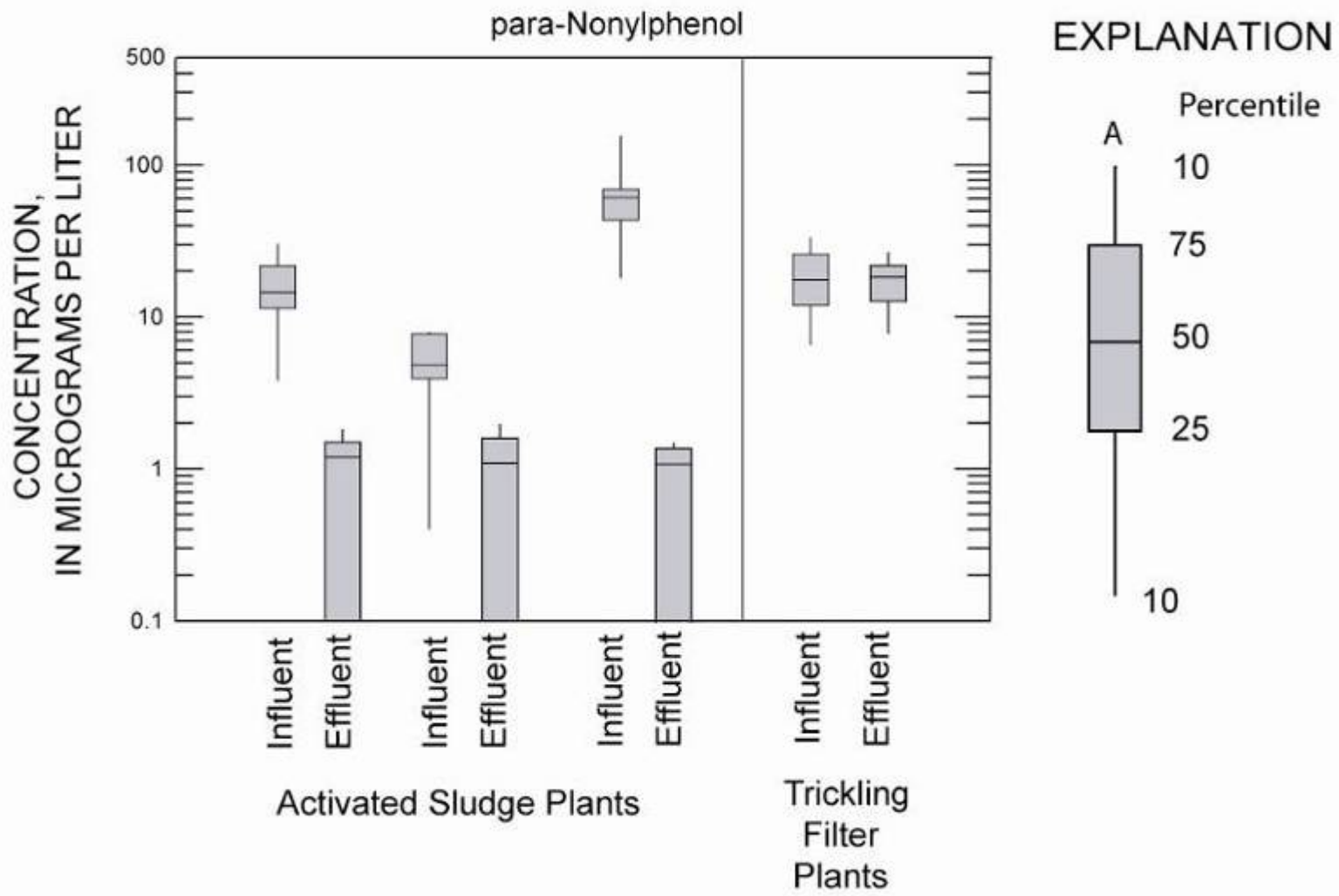
WWTP Study—Summary Results



Plants Vary In Ability To Reduce ECs



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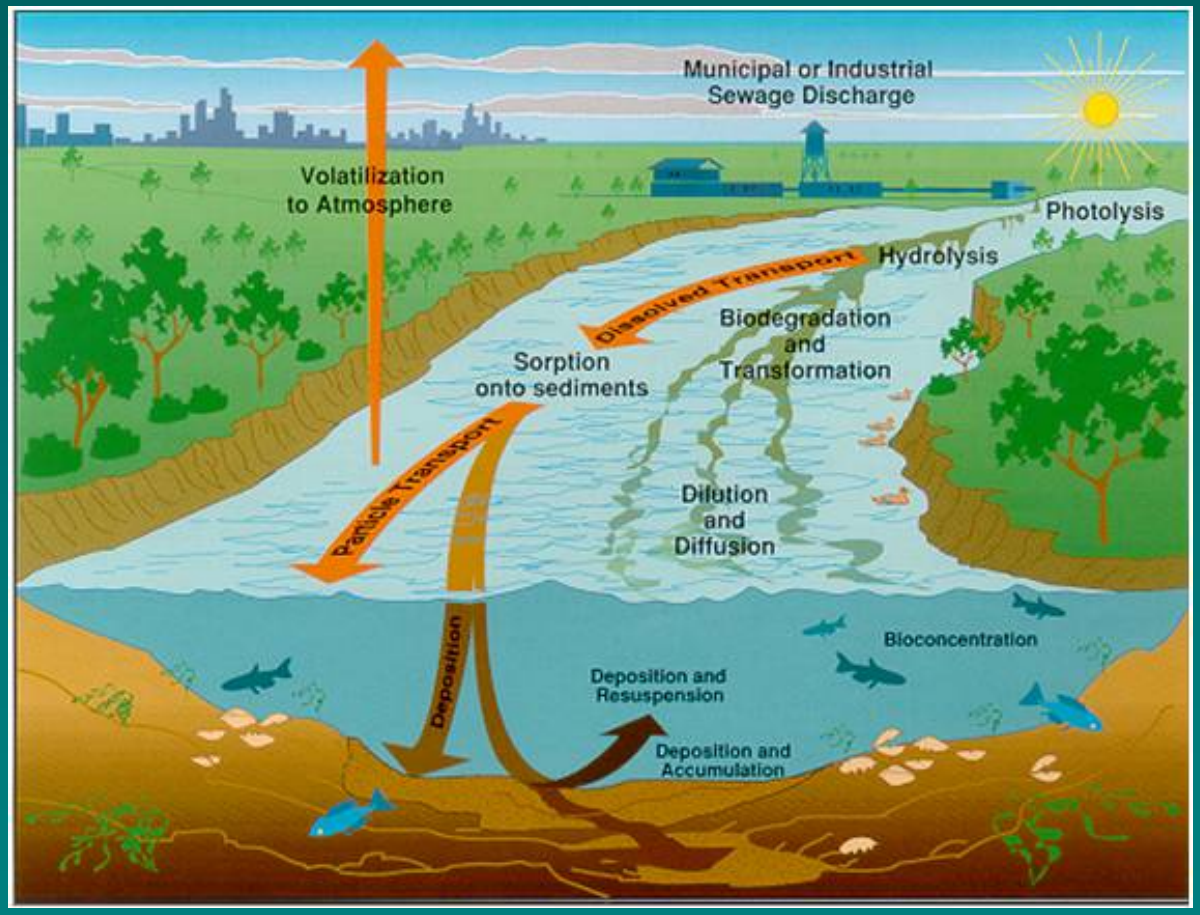
Transport and Fate



In order to minimize ecologic effects, it is essential to understand how a contaminant moves and is altered in the environment.

(Barber and others, 1995)

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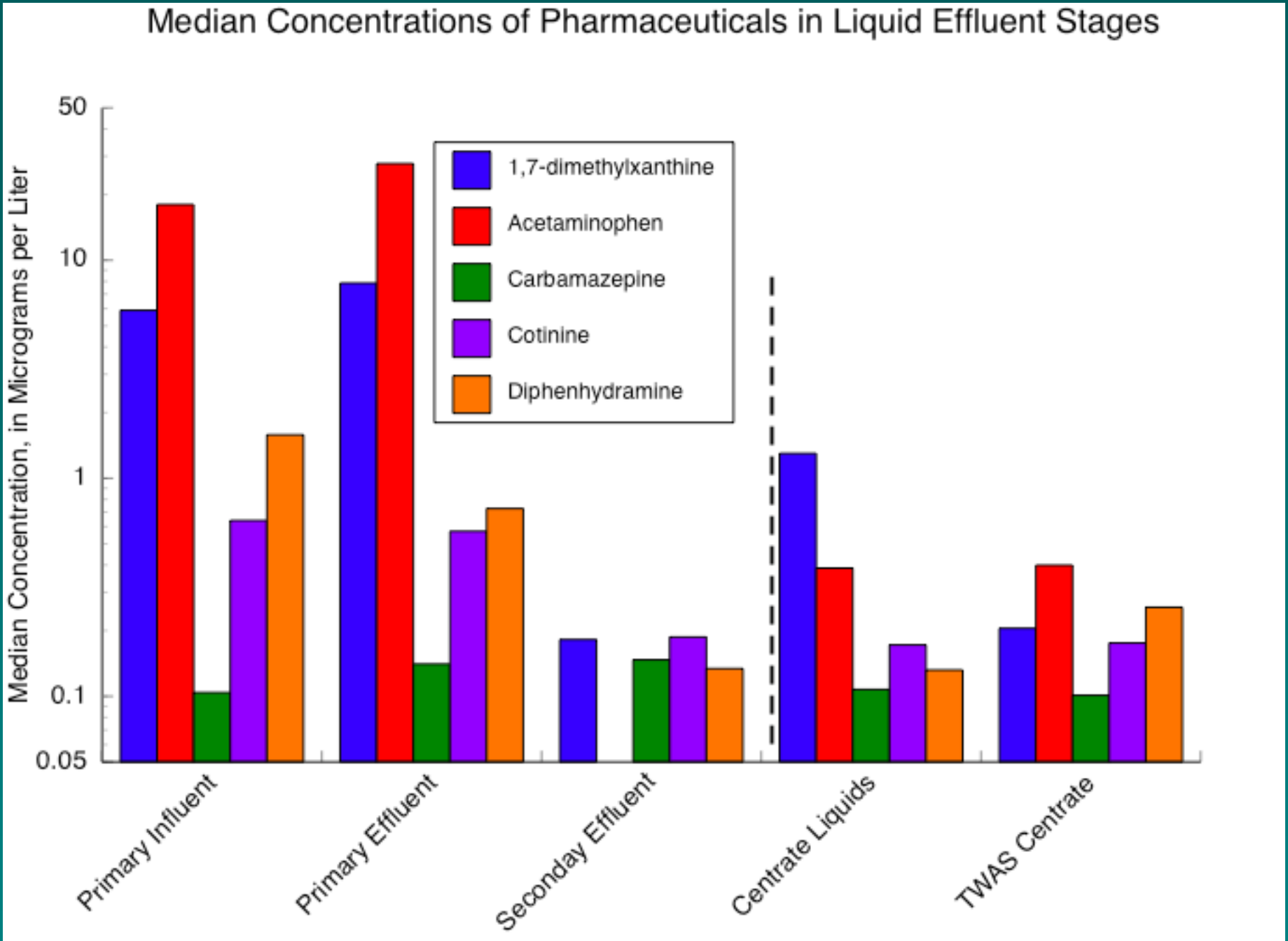
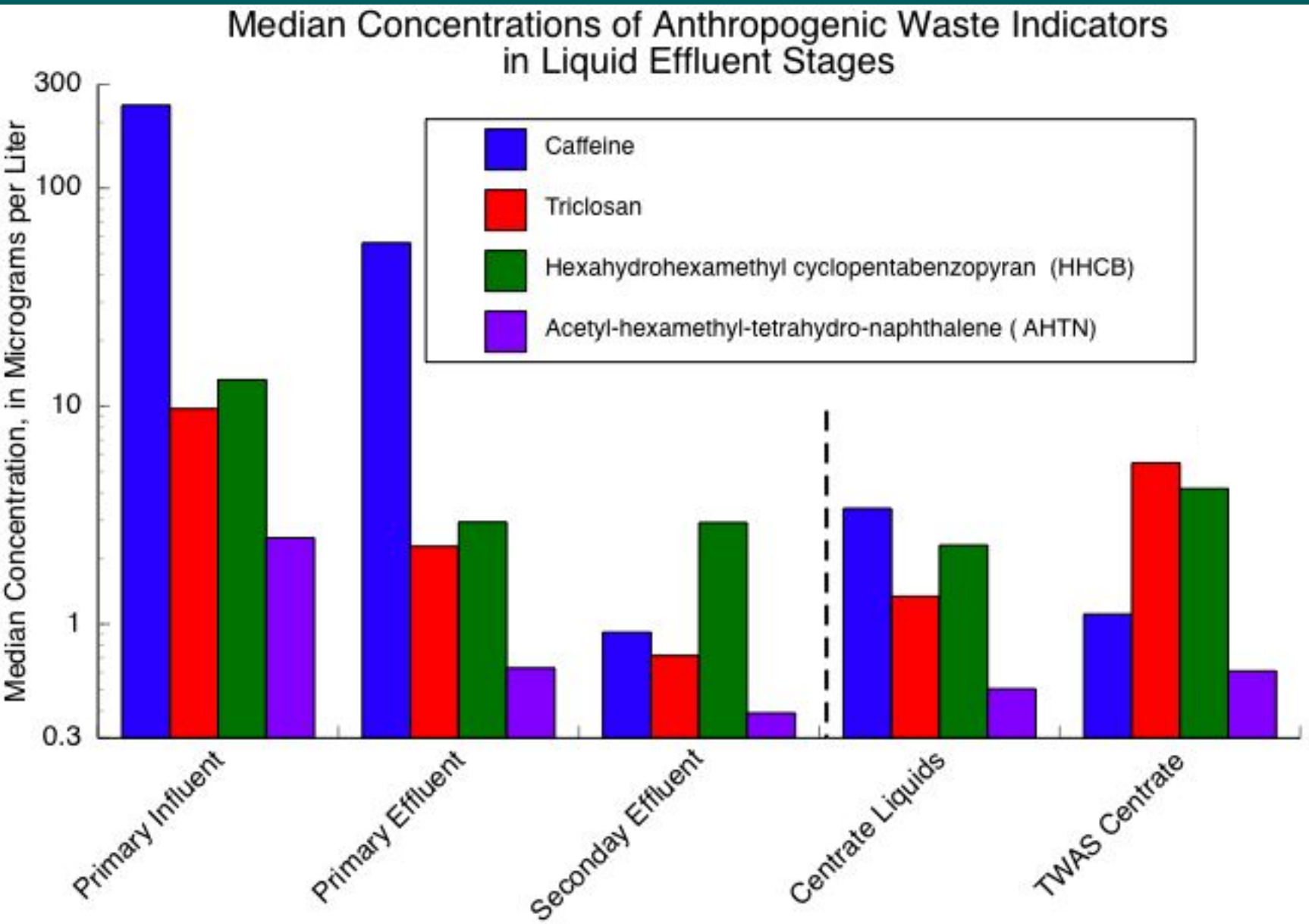
WERF Project Overview

- Evaluate the fate of known estrogenic compounds and total estrogenic activity in solids derived from wastewater treatment and through commonly used sludge and solids treatment processes.

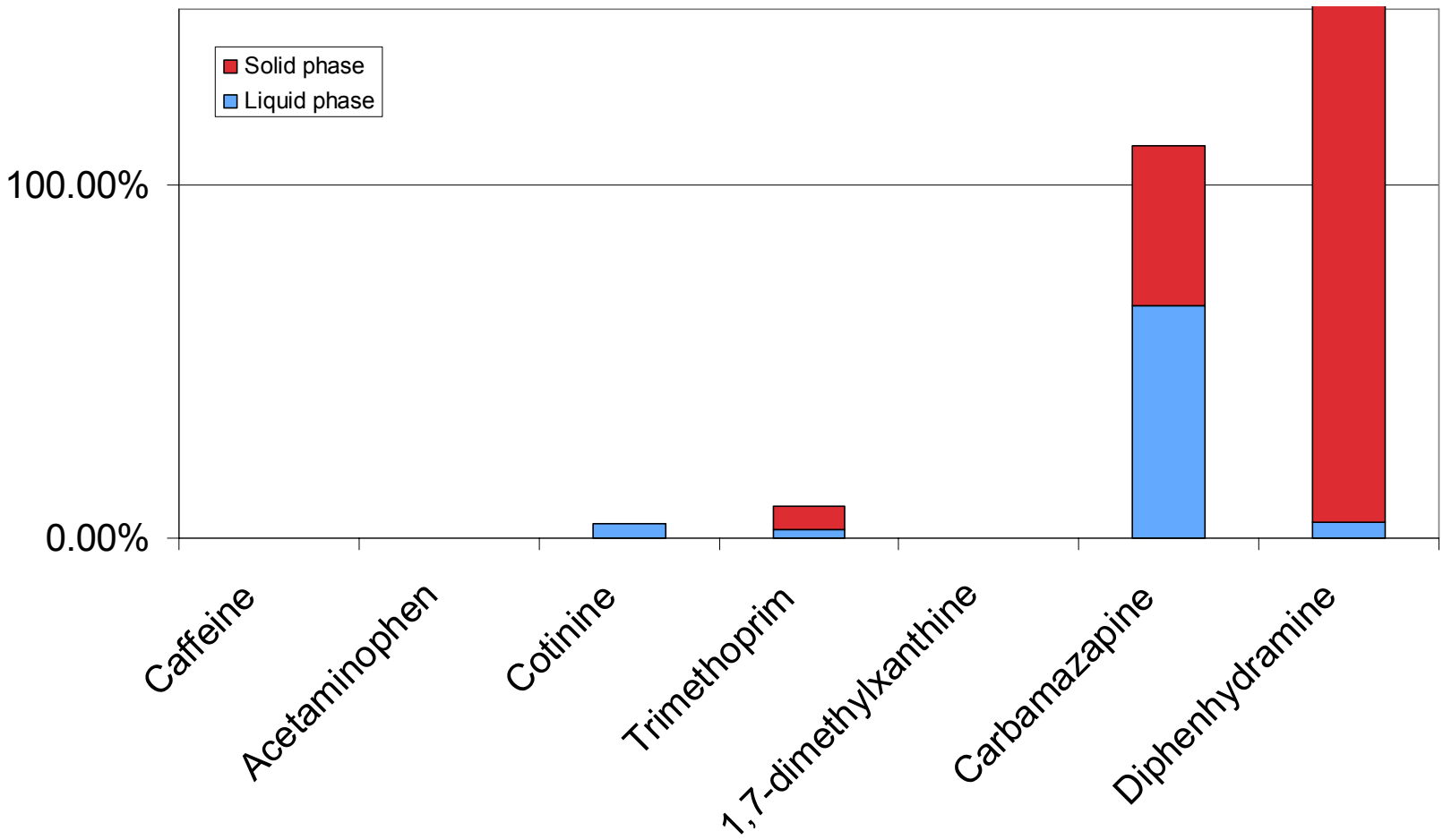
- 2 Phases:
  - Phase I: Full Scale Plants
  - Phase II: Bench & Pilot Scale Studies

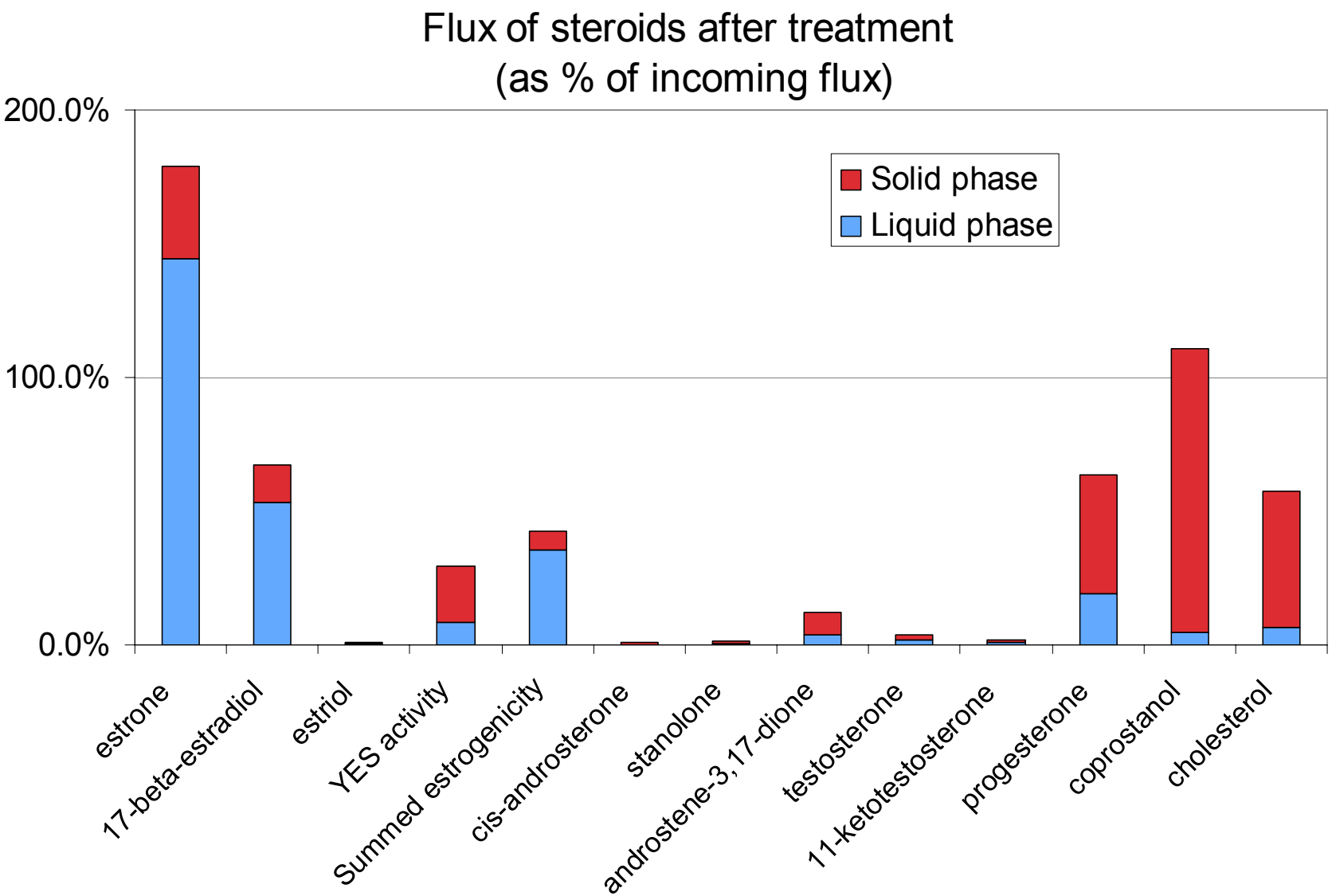
- Chemical & Bioassay Measurements


Median Concentrations of Pharmaceuticals in Liquid Effluent Stages
Median Concentration, in Micrograms per Liter
50
10
1
0.1
0.05
1,7-dimethylxanthine
Acetaminophen
Carbamazepine
Cotinine
Diphenhydramine
Primary Influent
Primary Effluent
Seconday Effluent
Centrate Liquids
TWAS Centrate


Median Concentrations of Anthropogenic Waste Indicators
in Liquid Effluent Stages
Median Concentration, in Micrograms per Liter
300
100
10
1
0.3
Caffeine
Triclosan
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)
Primary Influent
Primary Effluent
Seconday Effluent
Centrate Liquids
TWAS Centrate

Pharmaceutical flux after treatment (as % of incoming flux)



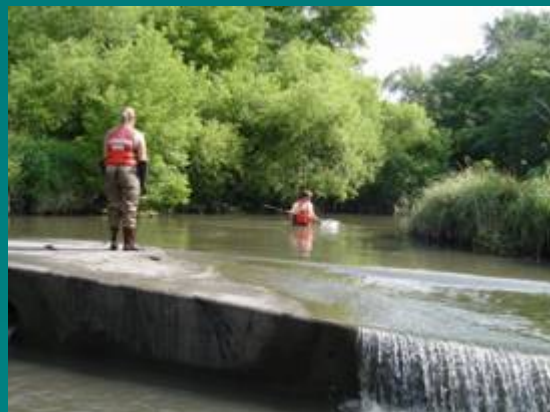

Flux of steroids after treatment
(as % of incoming flux)
200.0%
100.0%
0.0%
Solid phase
Liquid phase
estrone
17-beta-estradiol
estriol
YES activity
Summed estrogenicity
cis-androsterone
stanolone
androstene-3,17-dione
testosterone
11-ketotestosterone
progesterone
coprostanol
cholesterol

In-stream Study of ECs

Fourmile Creek (IA)

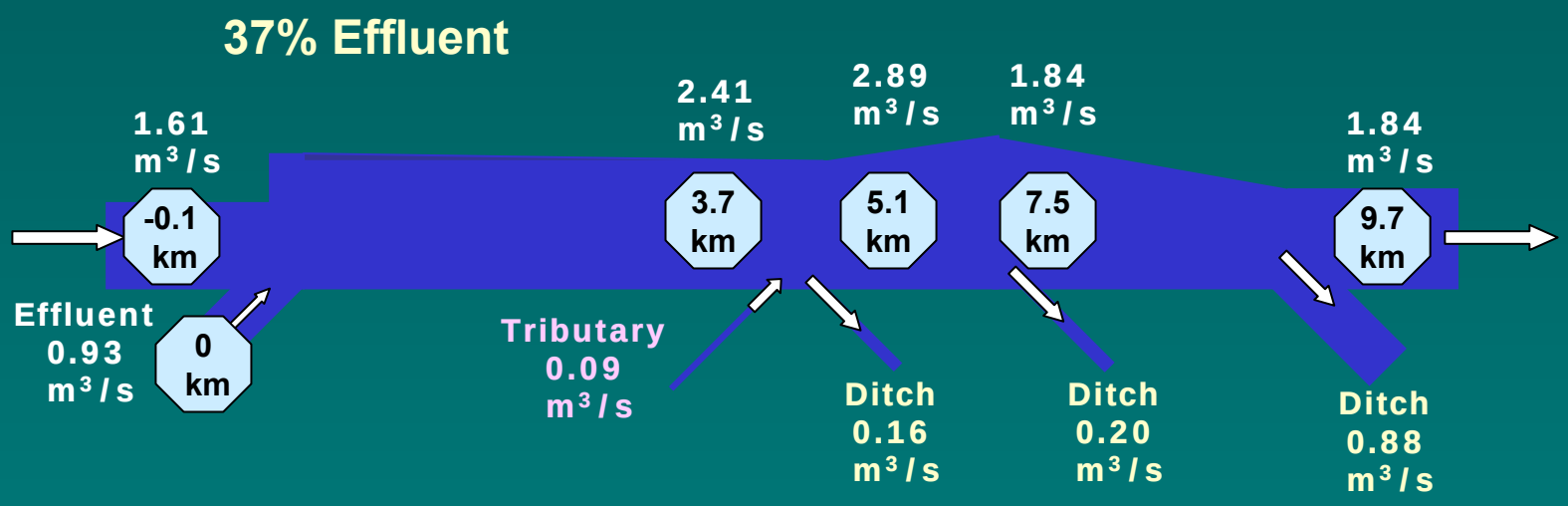
Boulder Creek (CO)

- Effluent dominated systems (WWTP discharge)
- Background data denote multiple ECs present
- Relatively small basin sizes
- Basic understanding of the flow system
- Controls present above WWTPs

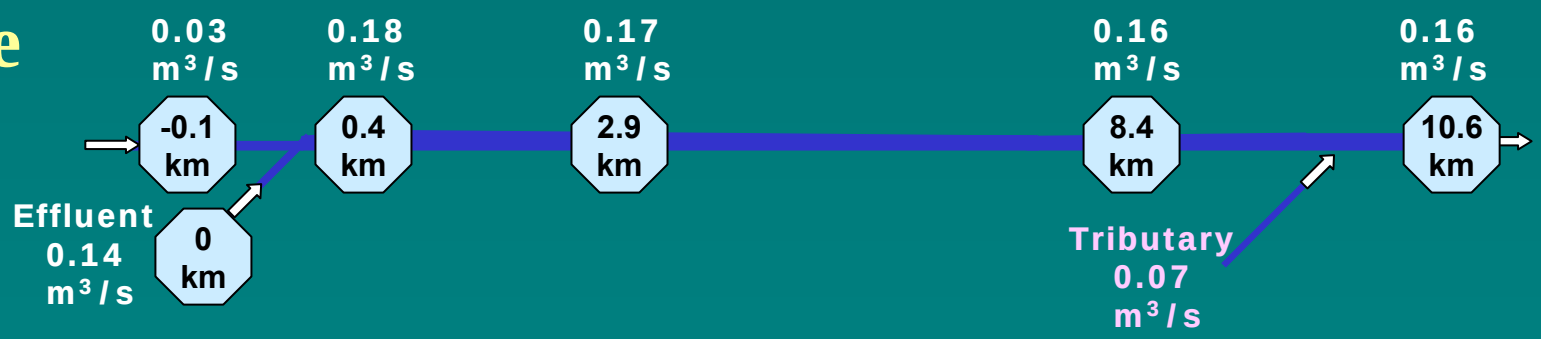


Hydrologic Mixing

Boulder Creek (9/3/03)



Fourmile Creek (8/5/03)



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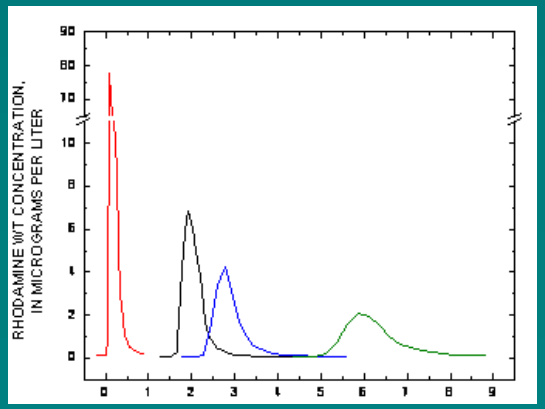
Time of Travel

Dye Injection

Leading Edge

Peak

Trailing Edge



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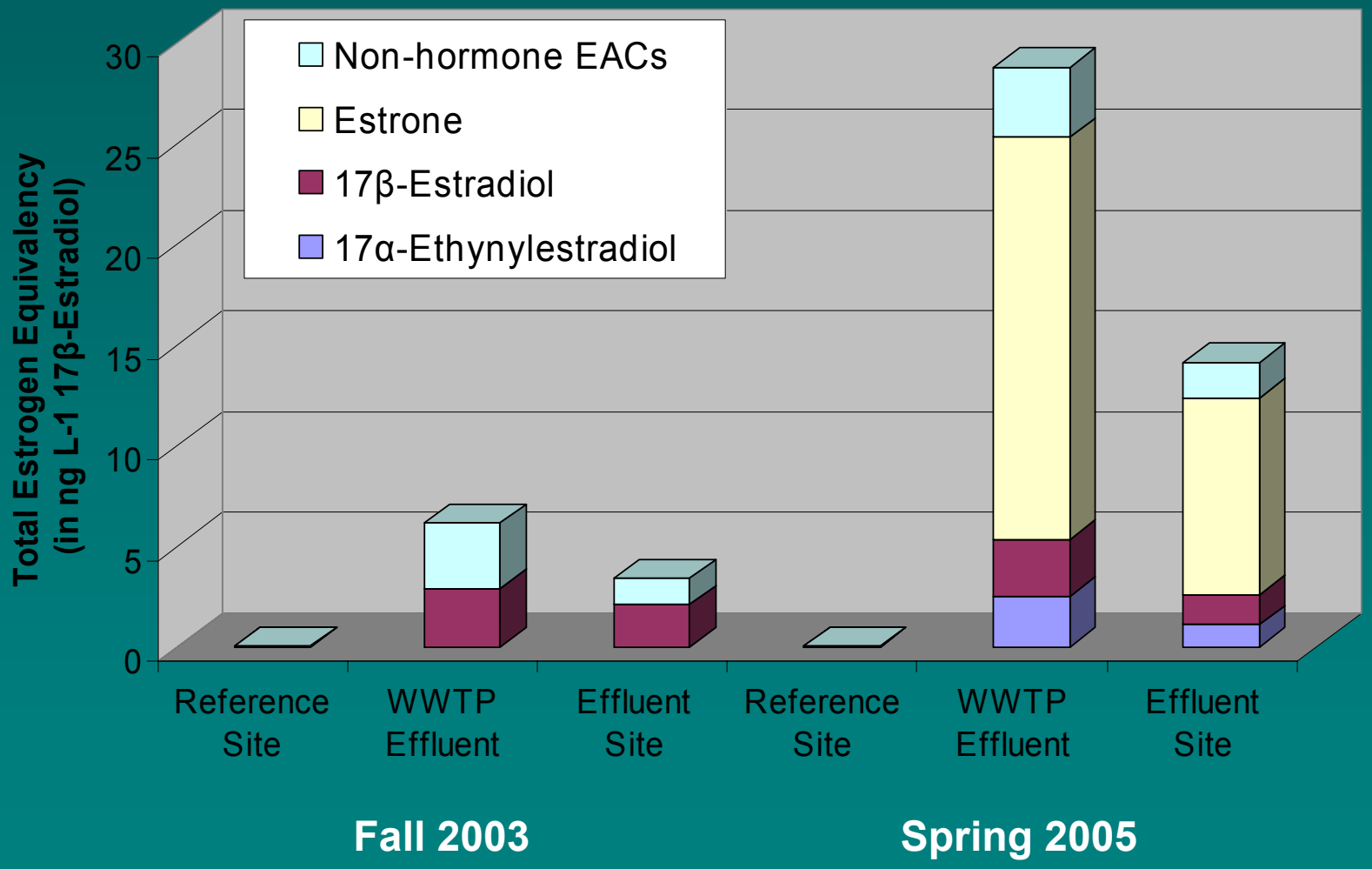
Estrogenicity of Boulder Effluent and Boulder Creek



Receptor Effects

- Contaminant uptake
- Endocrine Disruption
- Antibiotic Resistance
- Pathogens

Our ability to measure contaminants currently exceeds our understanding of their environmental effects.

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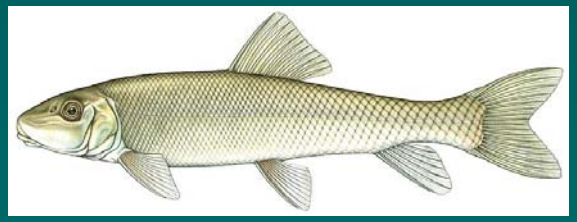
Evidence of Reproductive Disruption in Boulder Creek white suckers

1. Sex Ratio: Skewed toward females at downstream sites ~ 1:4 M:F



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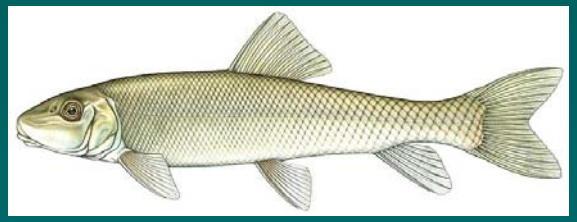
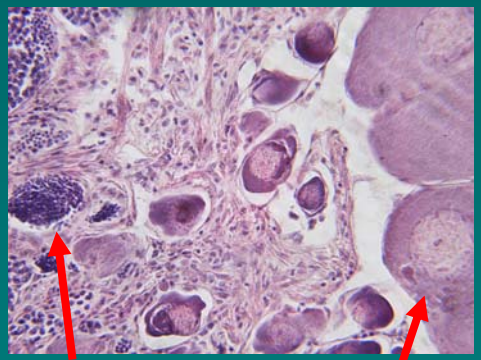


2. Intersex: only at downstream sites. (1 in 10)



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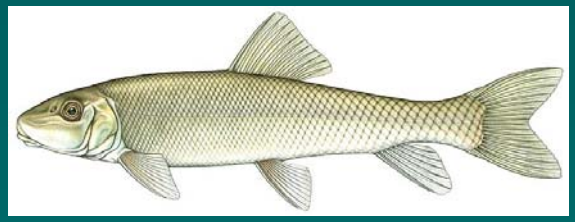

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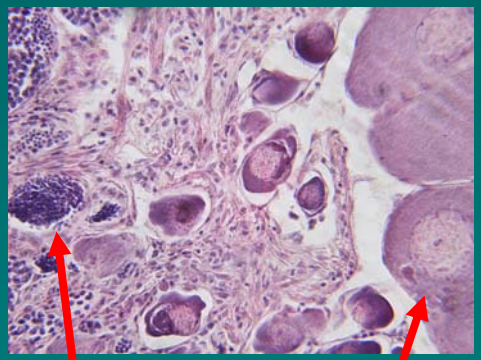


3. Vitellogenin:
An estrogen-dependent female yolk protein is elevated in downstream males.

(Woodling et al., submitted 2005; Vajda et al., in prep)

Mobile Exposure Laboratory (MEL)

- in situ (captures true variability in water chemistry)
- Photo-period and temperature controlled

Linking Chemistry and Biology

What do we know for sure?

Downstream of Boulder WWTP:

-Hormones/NPs elevated
-Levels cause ED elsewhere
-Relatively persistent downstream
-White suckers show signs of ED
-No direct causative link

Linking Chemistry and Biology

HYPOTHESIS: The differences in sexual development of white suckers observed above and below the Boulder WWTP are the result of exposure to chemical constituents of the effluent.

Treatments with fathead minnows (*Pimephales promelas*)

Similar protocols
Easy to obtain
Comparability to other literature

Boulder WW

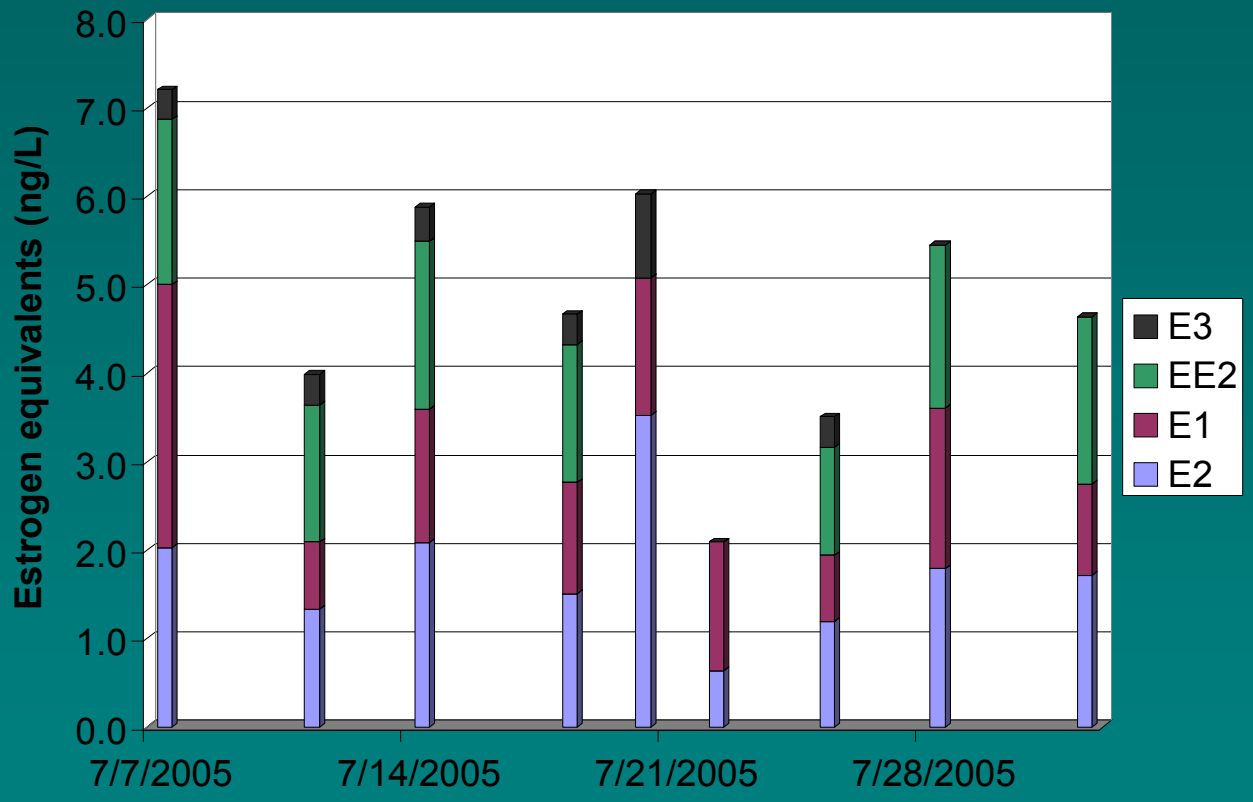
BC Upstream

WW/BC Mixes

+ Controls (E2)

Complex mixtures

Total EEQ during exposure (July 2005)



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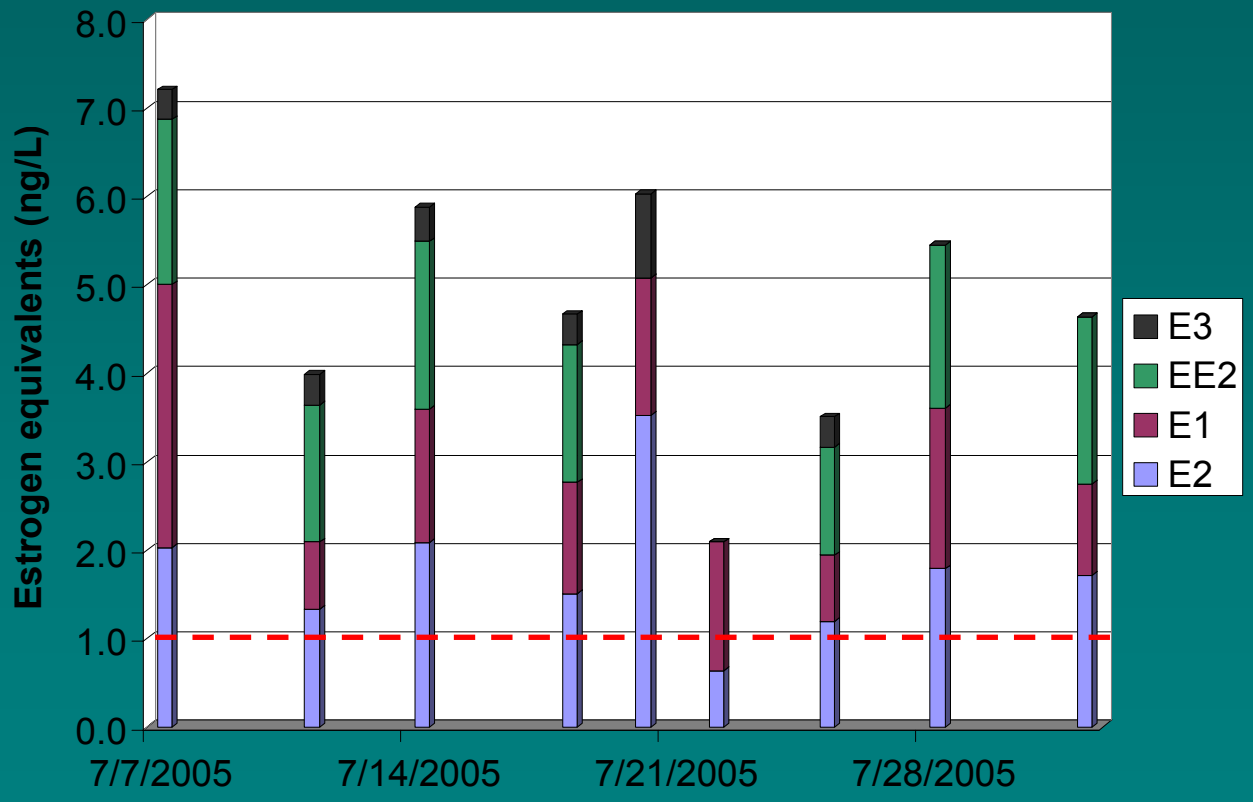
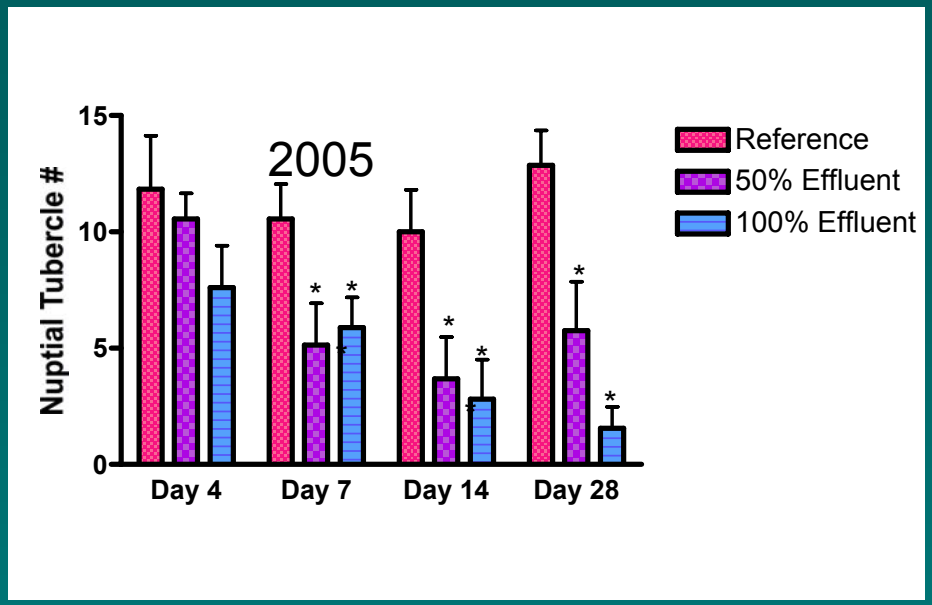
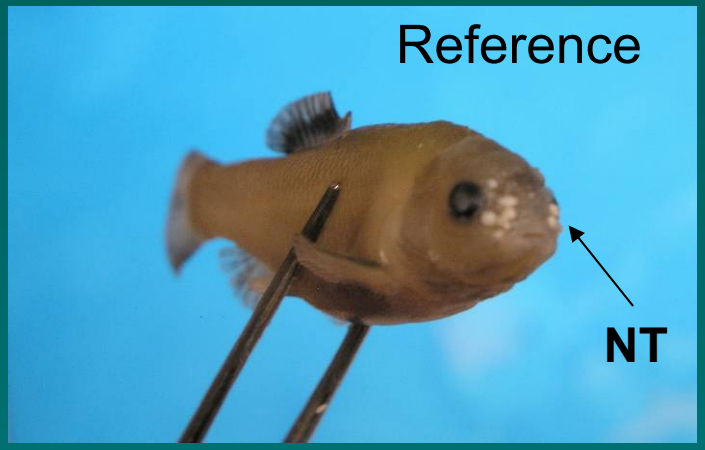
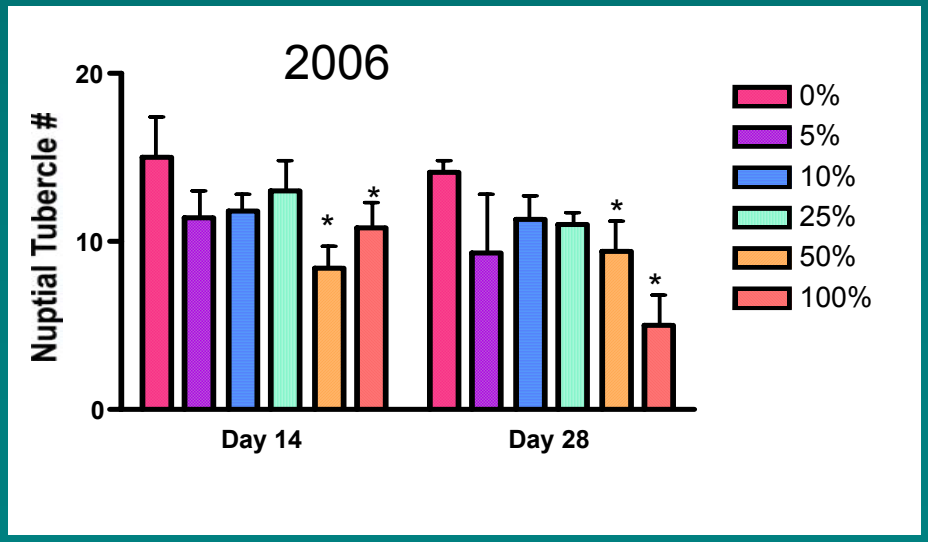


Effluent Reduces Nuptial Tubercle Expression

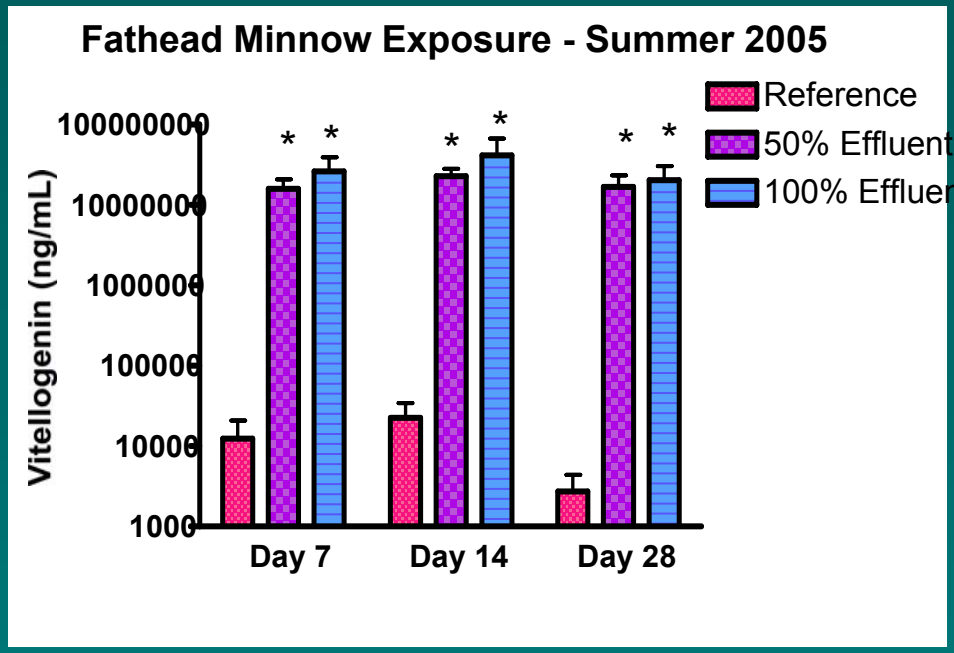


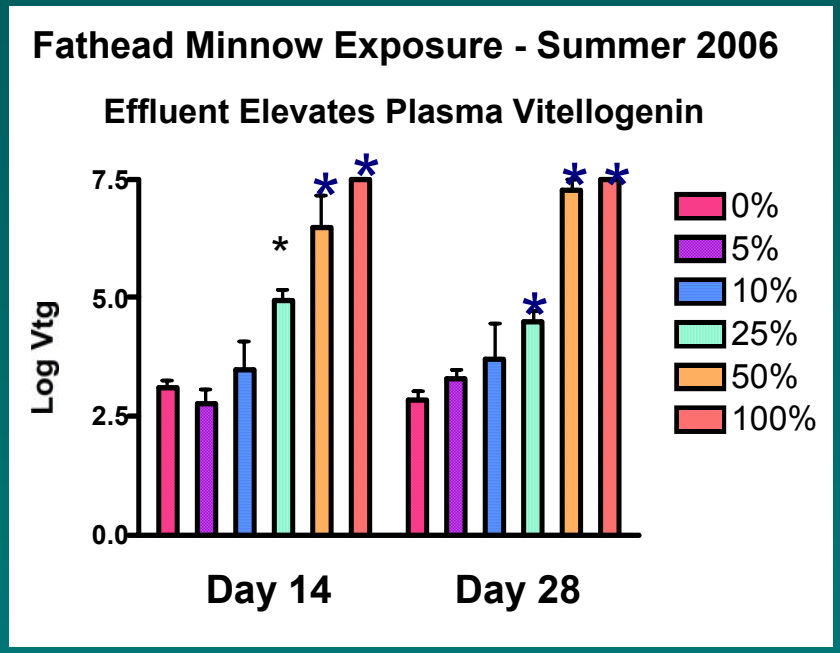




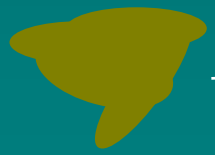
Significant effect of exposure ($P<0.0001$)

Effluent Elevates Plasma Vitellogenin





Liver

Estrogens →  → Vitellogenin

Significant main effect of exposure ($P<0.0001$)

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Acknowledgements

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dwkolpin@usgs.gov
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