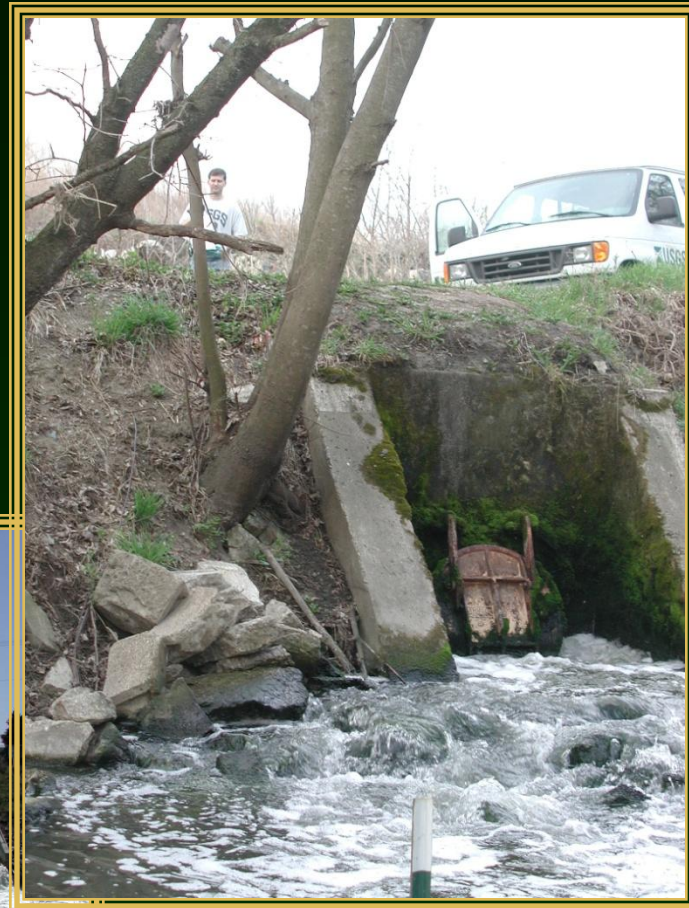


# Biodegradation of EDCs in Streams



# USGS TOXICS- CEC Research Progression

- I. Methods Development.
- II. Occurrence.
- III. Sources and Pathways.
- IV. Ecological Impacts.
- V. Fate and Transport.**



# V. Fate and Transport:

## Potential for Biodegradation of Endocrine Disruptors?

# THE SUNDAY DENVER POST

DENVERPOST.COM | THE DENVER POST | Rocky Mountain News | \$1.00 MAY VARY OUTSIDE METRO DENVER

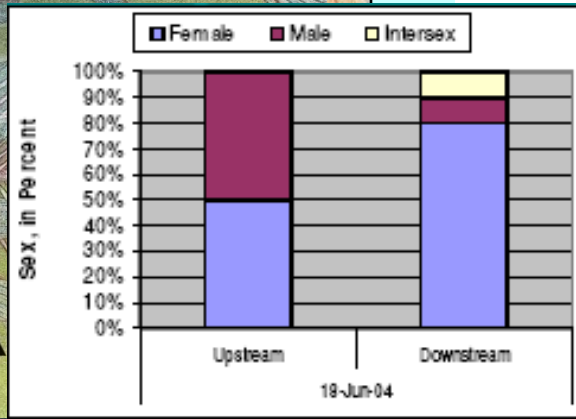
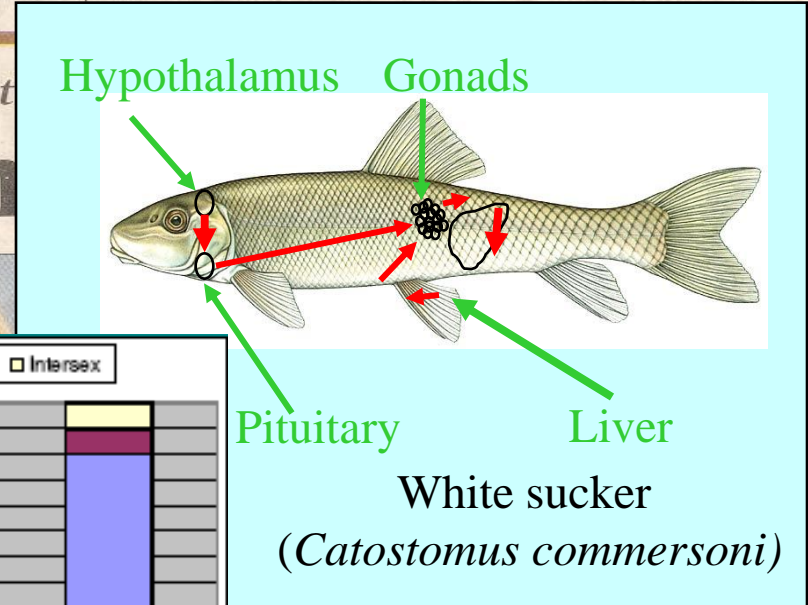
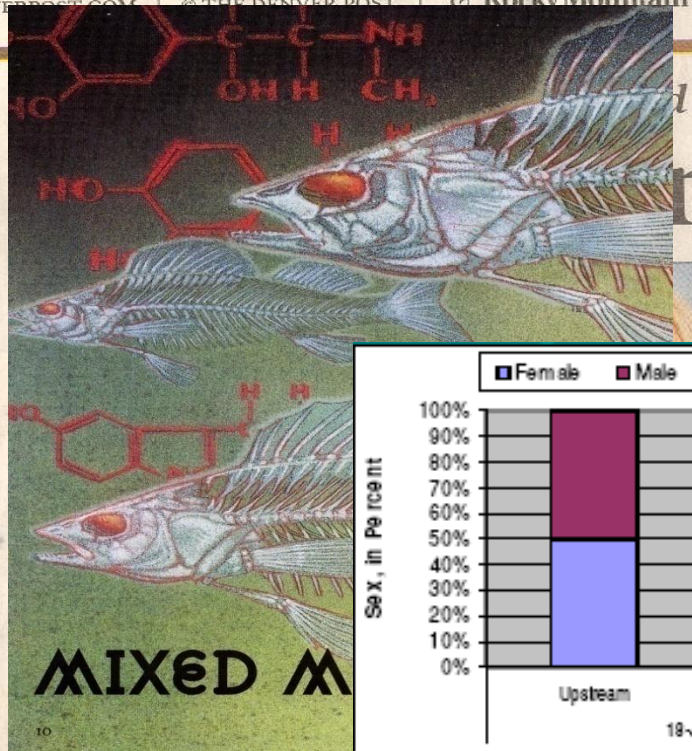
## Mutant fish prompt concern

Study focuses on sewage plants

CU researchers are trying to determine if chemicals in area wastewater are causing deformities.

By Theo Stein and Miles Moffett  
Denver Post Staff Writers

When Colorado biologist John Woodling and a team of researchers pulled fish from the South Platte River and Boulder Creek two years ago, they found deformities they'd never

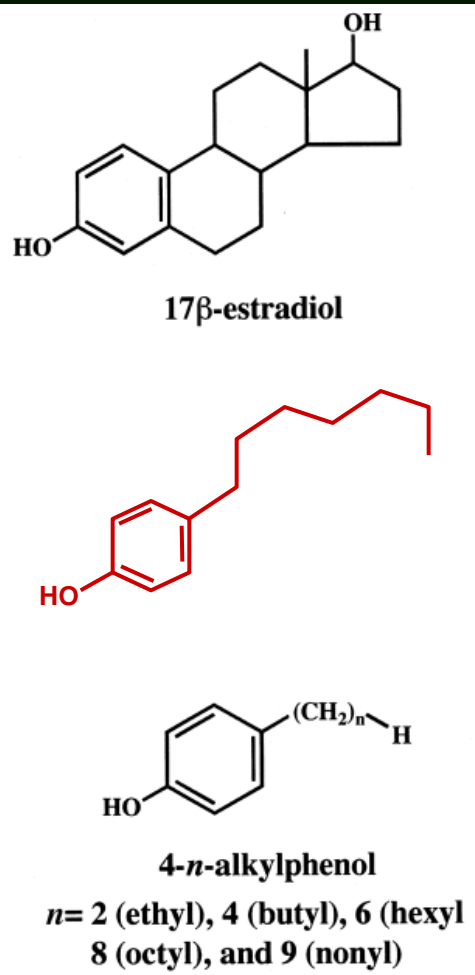


and inviting friends and family to a wedding celebration.  
But Boyyer, 27, has been ordered back to Iraq for a second tour. And the foundation they had hoped to build is now uncertain.  
"I don't want to go, but I will

(Woodling et al. 2006)

# V. Fate and Transport:

## Potential for Biodegradation of Endocrine Disrupters?



- Endocrine Hormones:
  - 17-β-Estradiol (E2) (natural)
  - Estrone (E1) (natural)
  - Testosterone (T) (natural)
  - 17-α-Ethinylestradiol (EE2)(synthetic)
  - ...

- **Endocrine Disrupting Compounds:**
  - **Structural Mimics:**
    - Phenol Group
    - Extended Carbon Backbone
  - **APE Metabolites**
  - ...

# V. Fate and Transport:

## Alkyphenolpolyethoxylate Metabolite EDCs

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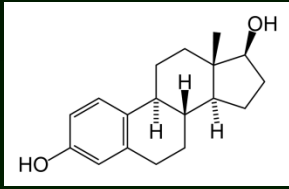
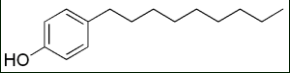
- APE:
  - Nonionic surfactants
  - Detergents, wetting agents, dispersants, emulsifiers, solubilizers and foaming agents
  - Isomeric mixtures produced by ethoxylation (ethylene oxide reaction) of alkylphenol technical mixtures.
  - Applications:
    - Industrial applications(55%)
    - Industrial detergents (30%)
    - Domestic detergents(15%)
    - Miscellaneous (<1%)
- **NPE - about 80% of commercial APE worldwide.**

# V. Fate and Transport:

## Nonylphenolpolyethoxylate Metabolite EDCs

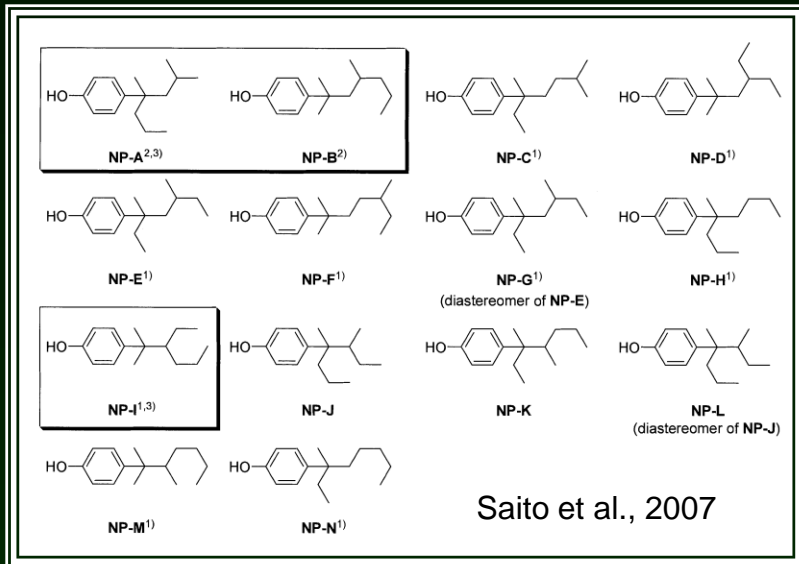
- NP:
  - NP polyethoxylates (NPE) efficiently removed (up to 99%) in WWTP waste stream.
  - NPE metabolites in WWTP effluent:
    - NP2EO (NP diethoxylates)
    - NP1EO (NP monoethoxylates)
    - **NP**
  - NP1EO and NP2EO degrade to **NP** in anoxic surface water sediments.
  - 4-NP Toxicity (EPA):
    - Acute = 55.7  $\mu\text{g/L}$
    - Chronic = 7.4  $\mu\text{g/L}$
  - Efficient sorption to sediment matrix

# Potential for EDC Biodegradation: Environmental Endocrine Disruption?

Parameter	17 $\beta$ -Estradiol 	4-NP 
Relative Estrogenicity*	1000	1
Concentration <sub>effluent</sub>	10 ng/L	to 343 $\mu$ g/L
Concentration <sub>receptor</sub>	10 ng/L	to 644 $\mu$ g/L
Concentration <sub>sediment</sub>	10 $\mu$ g/kg	to 14 mg/kg
Detection <sub>WWTP-Streams</sub>	<20 %	majority

\*Depends on study and NP isomer

# Potential for 4-NP Biodegradation: Assessment?

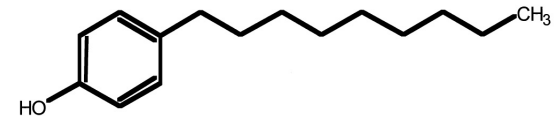


## 4-NP Environmental Mixture:

- Theoretical - 4-NP:
  - > 200 isomeric forms.
  - Branching of nonyl group.
  - Chemical and Optical.
- Commercial 4-NP Technical Mix:
  - > 22 isomers (Wheeler et al. *JCS*. 1997).
  - > 102 isomers (Ieda et al. *ES&T*. 2005).

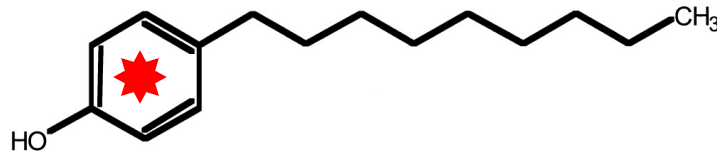
- **Most biodegradable.**
- **Estimate upper bound for 4-NP biodegradation in SW systems.**

## 4-*n*-Nonylphenol



# Potential for 4-NP Biodegradation: <sup>14</sup>C-Radiotracer Experiment

4-*n*-Nonylphenol



## [U-ring-<sup>14</sup>C]-4-*n*-nonylphenol

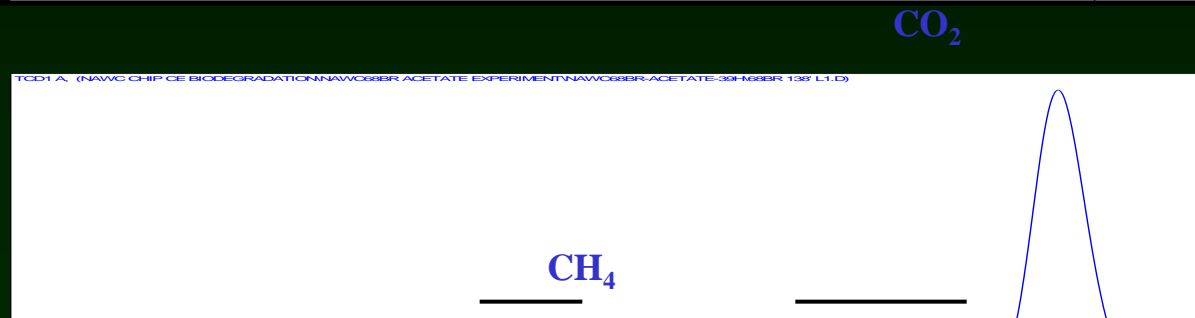
- Uniformly ring labeled.
- <sup>14</sup>C-mineralization indicates ring destruction.
- <sup>14</sup>C-mineralization indicates loss of estrogenicity.

# Potential for 4-NP Biodegradation: $^{14}\text{C}$ -Radiotracer Experiment

Radiometric



TCD



Retention Time  $\longrightarrow$



## Radiotracer approach:

- $^{14}\text{C}$  Substrate.
- GC with TCD and Radiometric Detection.
- $^{14}\text{CO}_2$ ,  $^{14}\text{CH}_4$ .
- Sediment microcosms.
- Static conditions to emphasize oxygen effects.

# Triple Watershed Study

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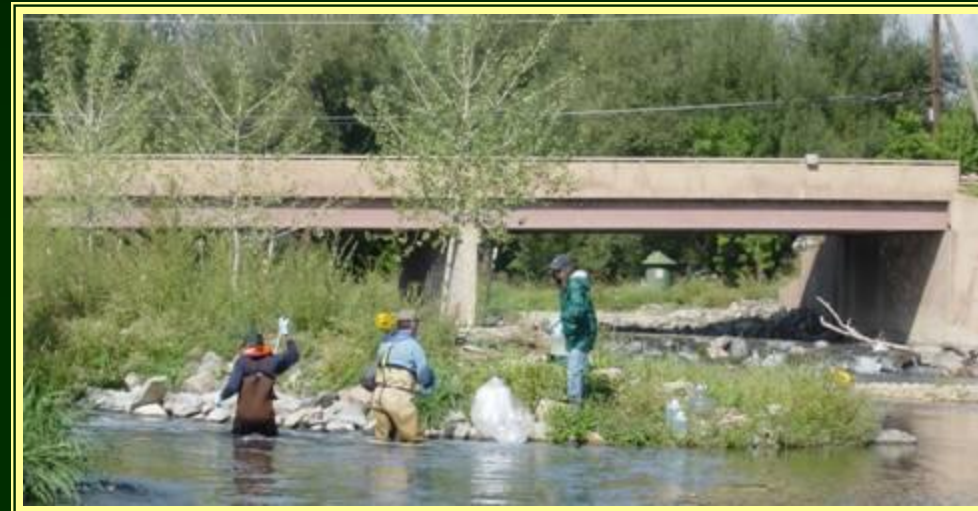
## Fourmile Creek (IA)

- Drainage Area = 410 km<sup>2</sup>
- Gradient = 1 m/km
- Population ~ 27,000
- Fine Grain Sand
- WWTP Discharge = 15-80 % DSF



## Boulder Creek (CO)

- Drainage Area = 1160 km<sup>2</sup>
- Gradient = 4 m/km
- Population ~ 174,000
- Coarse Sand & Gravel
- WWTP Discharge = 20-50 % DSF

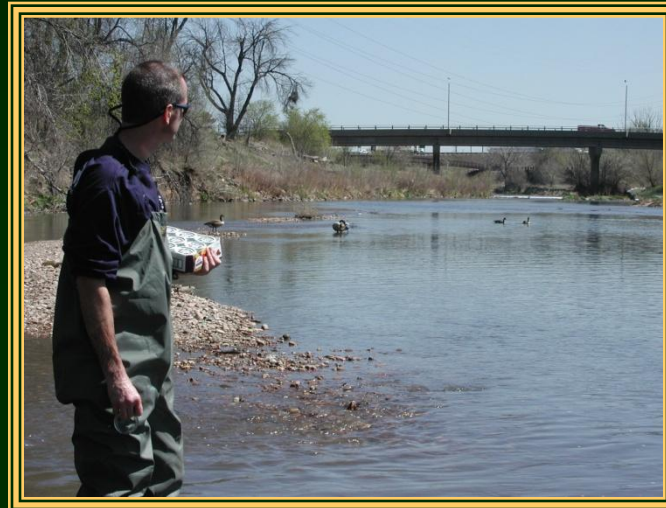


# Triple Watershed Study

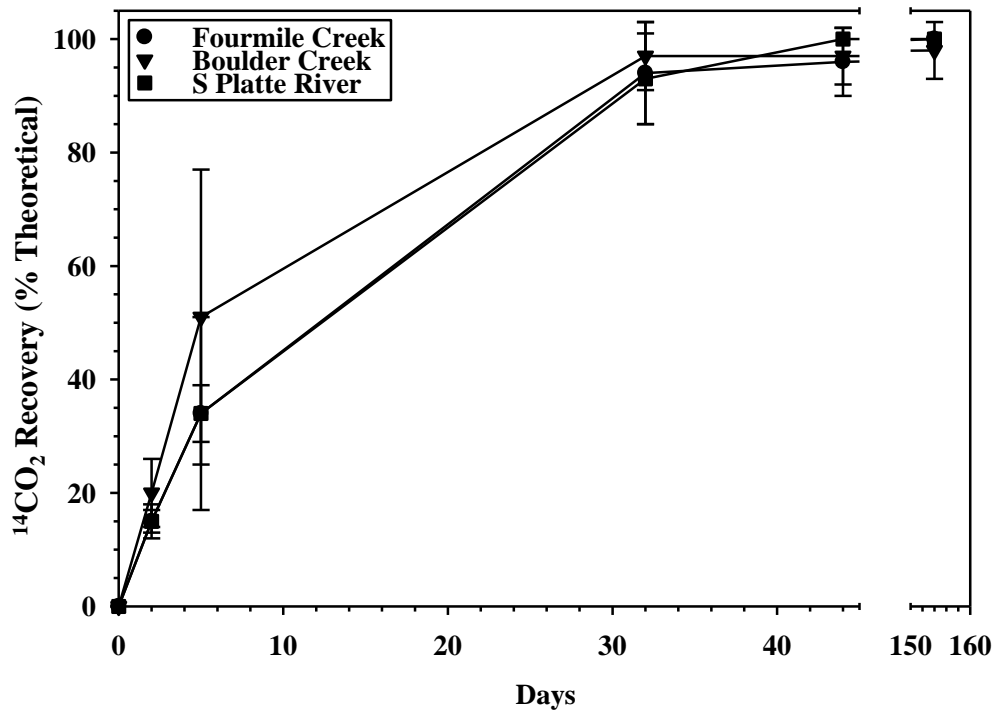
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## South Platte River (CO)

- Drainage Area = 10000 km<sup>2</sup>
- Gradient = 2 m/km
- Population ~ 1,700,000
- Coarse Sand and Gravel
- WWTP Discharge > 90 % DSF



# Potential for 4-NP Biodegradation: Oxic Sediment?



- Sediment upstream of WWTP outfall.
- **Efficient mineralization under oxic conditions.**
  - 15-20% in 48 h.
  - Complete in 32 d.

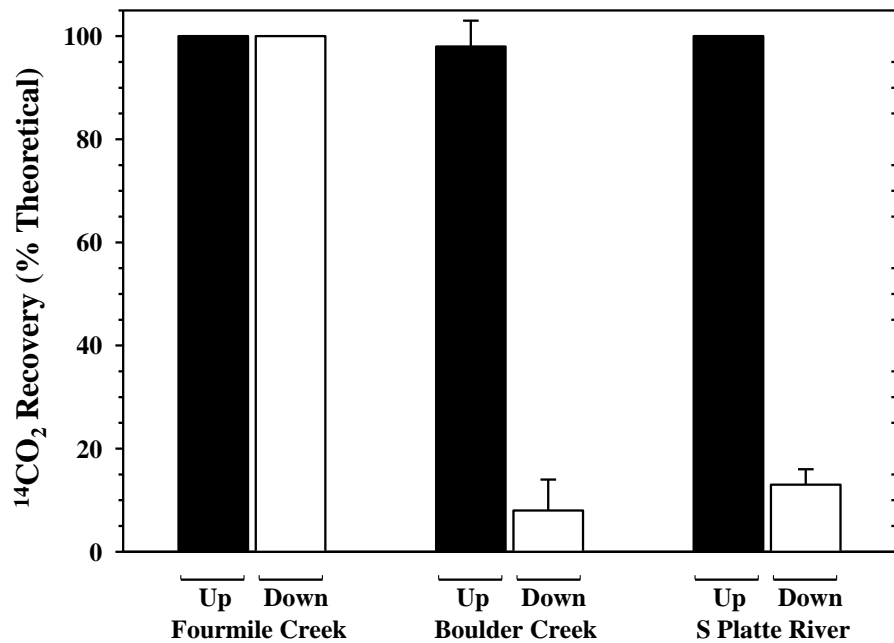
# Potential for 4-NP Biodegradation: Anoxic Sediment?

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- **No evidence of 4-*n*-NP mineralization under anoxic conditions!**
- Methanogenic conditions.

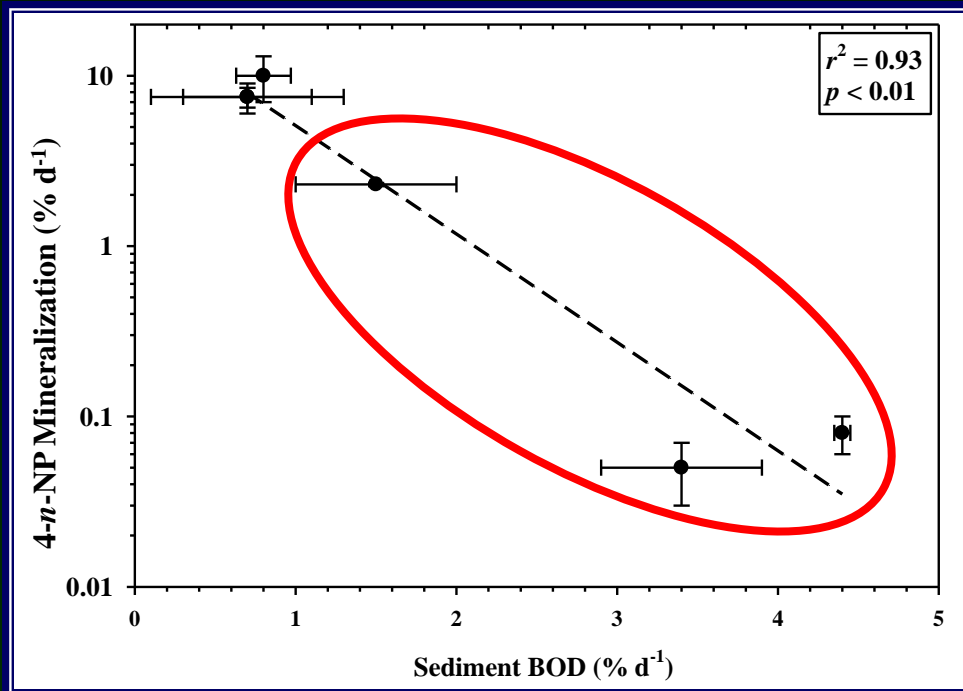
**Suggests that balance between oxygen supply and oxygen demand is an important determinant of NP biodegradation in WWTP-impacted stream systems.**

# Potential for 4-NP Biodegradation: Upstream vs Downstream of WWTP Outfall



- Oxidic microcosm headspace.
- Static conditions emphasize oxygen limitations.
- 154 d incubation.
- Upstream sediments degrade 4-*n*-NP under oxidic conditions.
  - 100 % in 154 d.
- Degradation inhibited in downstream SPR and BC sediments.
  - Higher BOD in SPR and BC.
  - **Onset of anoxic (methanogenic) sediment conditions.**

# Potential for 4-NP Biodegradation: 4-*n*-NP Mineralization vs BOD



- Oxygen supply limited to diffusion.
- BOD (oxygen sink) significant impact on 4-*n*-NP mineralization.

Effluent-associated increases in BOD have potential to substantially limit 4-NP biodegradation and may contribute to persistence of 4-NP in WWTP-impacted stream systems.

# Potential for 4-NP Biodegradation: *In Situ* Oxygen?



## Microcosm:

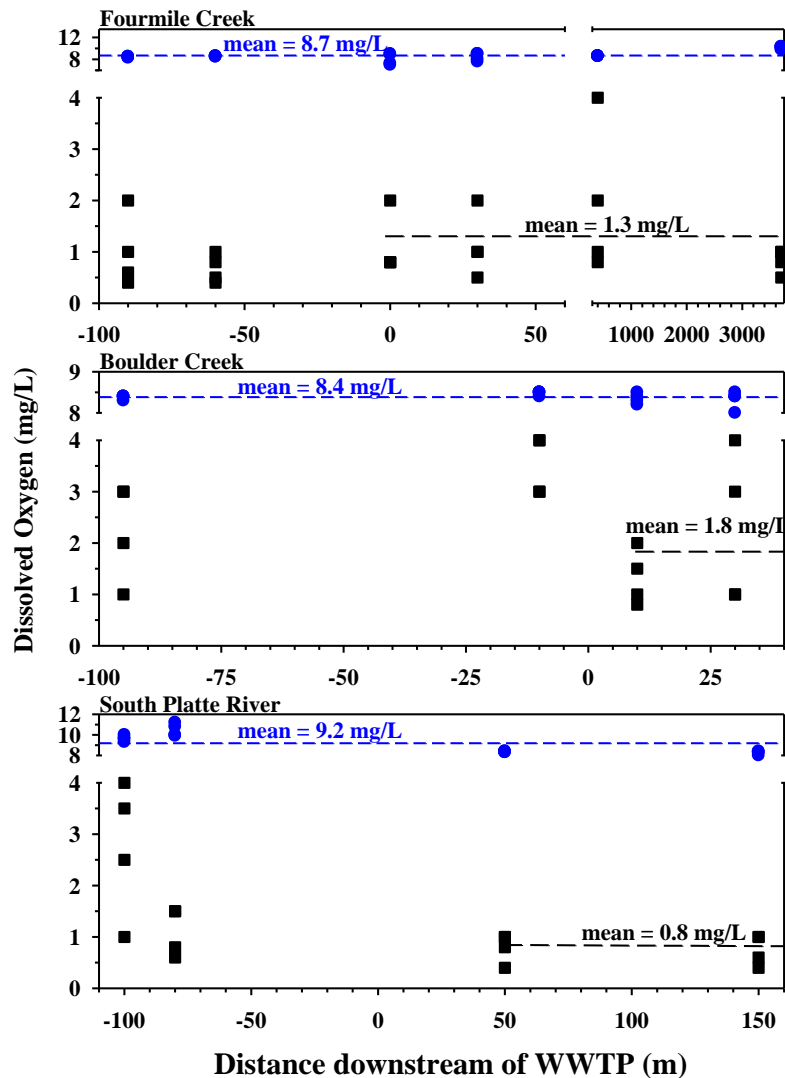
- Oxygen supply limited to diffusion.
- BOD (oxygen sink) significant impact on 4-n-NP mineralization.



## WWTP-Impacted Streams:

- Engineered effluent oxygenation.
- Artificial hydraulic head increase promotes infiltration of surface water.
- **Advective oxygen supply sufficient to offset WWTP effects on sediment BOD?**

# Potential for 4-NP Biodegradation: Upstream vs Downstream of WWTP Outfall



## Water-Column Dissolved Oxygen:

- YSI 556 multiparameter meter.
- Four points, mid-depth.
- Saturated.
- No change upstream to downstream.

## Sediment Dissolved Oxygen:

- Four points, 10 cm depth.
- 0.5-4.0 mg/L.
- No significant change upstream to downstream.

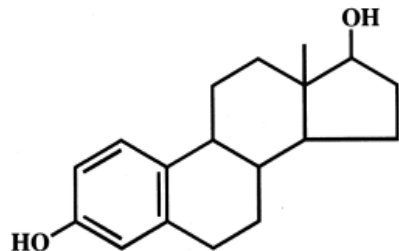
# 4-Nonylphenol Biodegradation: Conclusions

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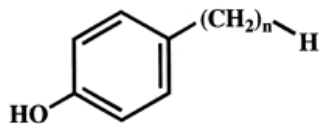
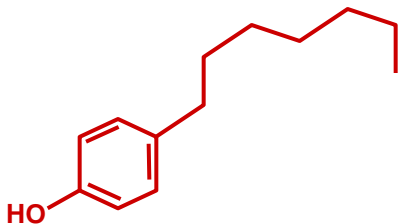
- Potential for 4-NP biodegradation can be significant in surface water sediments under oxic conditions.
- Stability of 4-NP in stream sediment, and consequently its potential impact on the stream ecosystem, is strongly affected by the sediment dissolved oxygen supply.

# V. Fate and Transport:

## Potential for Biodegradation of Endocrine Hormones?



17β-estradiol



4-*n*-alkylphenol

*n* = 2 (ethyl), 4 (butyl), 6 (hexyl)  
8 (octyl), and 9 (nonyl)

### • Endocrine Hormones:

- **17-β-Estradiol (E2)** (natural)
- **Estrone (E1)** (natural)
- **Testosterone** (natural)
- **17-α-Ethinylestradiol (EE2)** (synthetic)
- ...

### • Endocrine Disrupting Compounds:

#### • Structural Mimics:

- Phenol Group
- Extended Carbon Backbone
- **APE Metabolites**
- ...

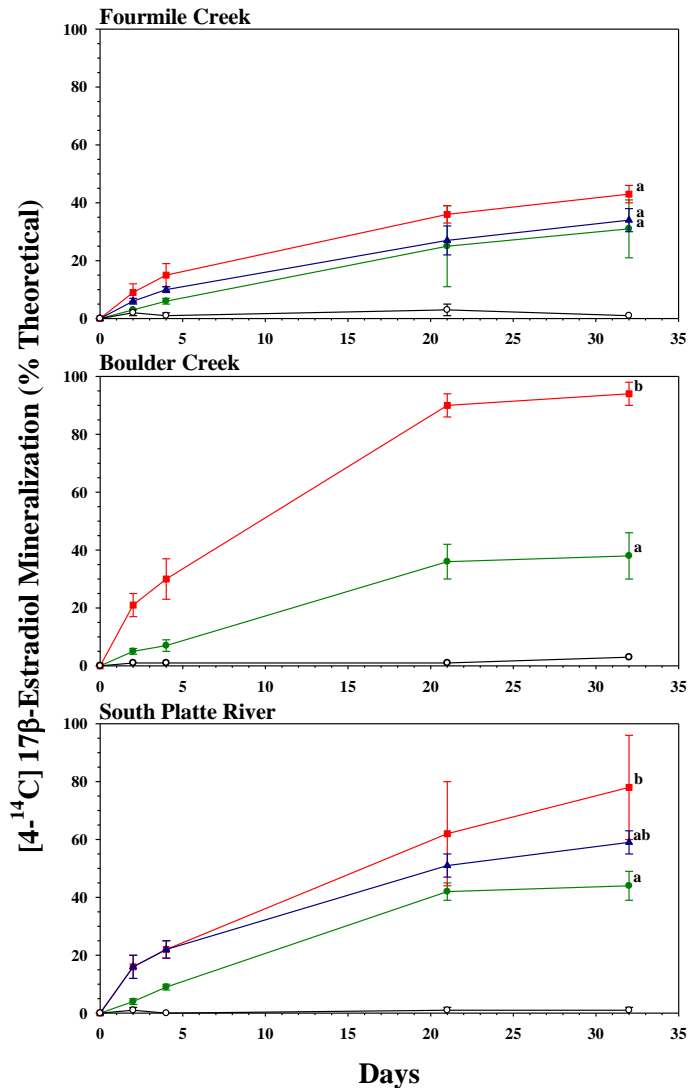
# Potential for Hormone Biodegradation: Previous Research Experience

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## Endocrine Hormone Biodegradation:

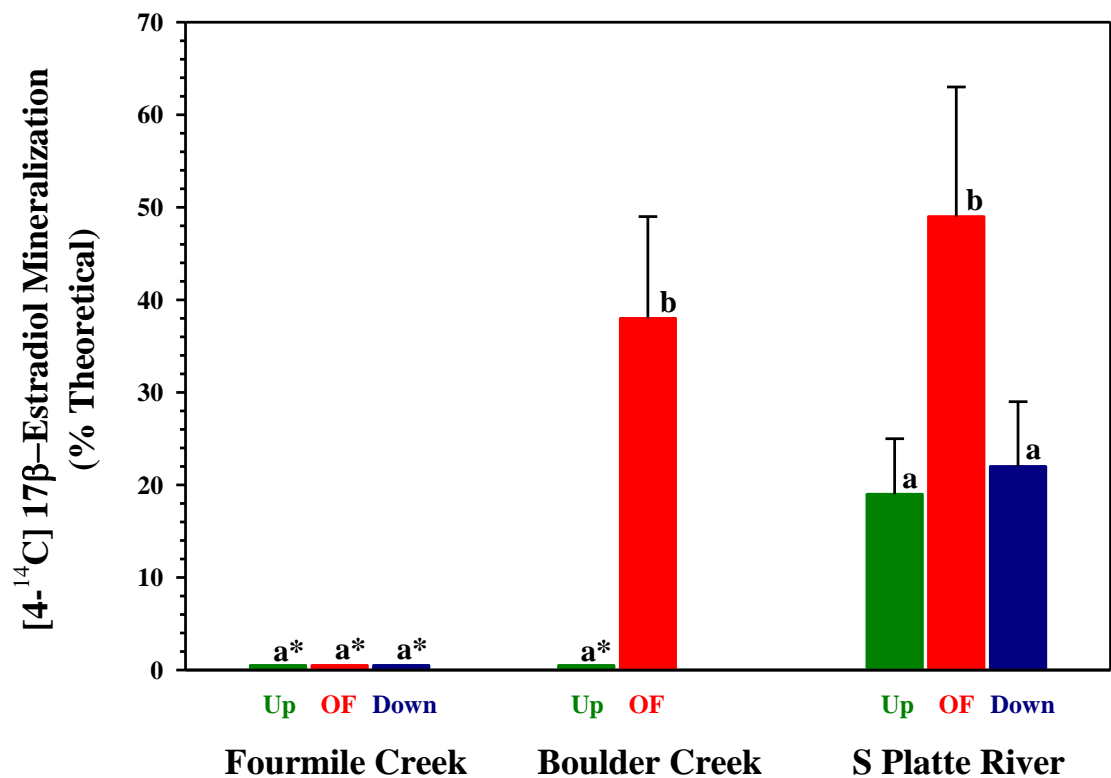
- Significant oxic biodegradation:
  - WWTP.
  - Sewage sludge cultures.
- Efficient removal in WWTP.
- Low concentrations in WWTP effluent.
- Sorbs to sediment.
- Sediment concentrations up to 40  $\mu\text{g}/\text{kg}$ .

# Potential for $17\beta$ -Estradiol Biodegradation: Oxic Sediment?



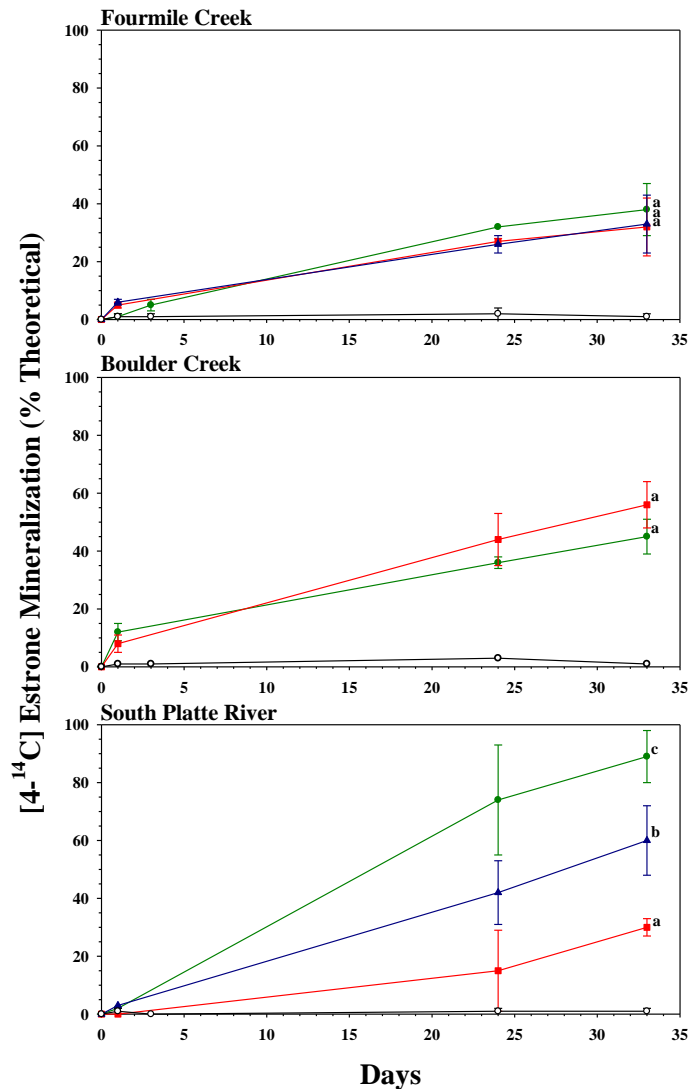
- **Upstream sediment:**
  - 30-40% in 32 d.
- **Outfall sediment:**
  - 40-90% in 32 d.
- **Potential for  $17\beta$ -Estradiol biodegradation in oxic sediments.**
- **$17\beta$ -Estradiol biodegradation efficiency stimulated by effluent:**
  - Adapted microbial population?
  - ...

# Potential for $17\beta$ -Estradiol Biodegradation: Oxic Water?



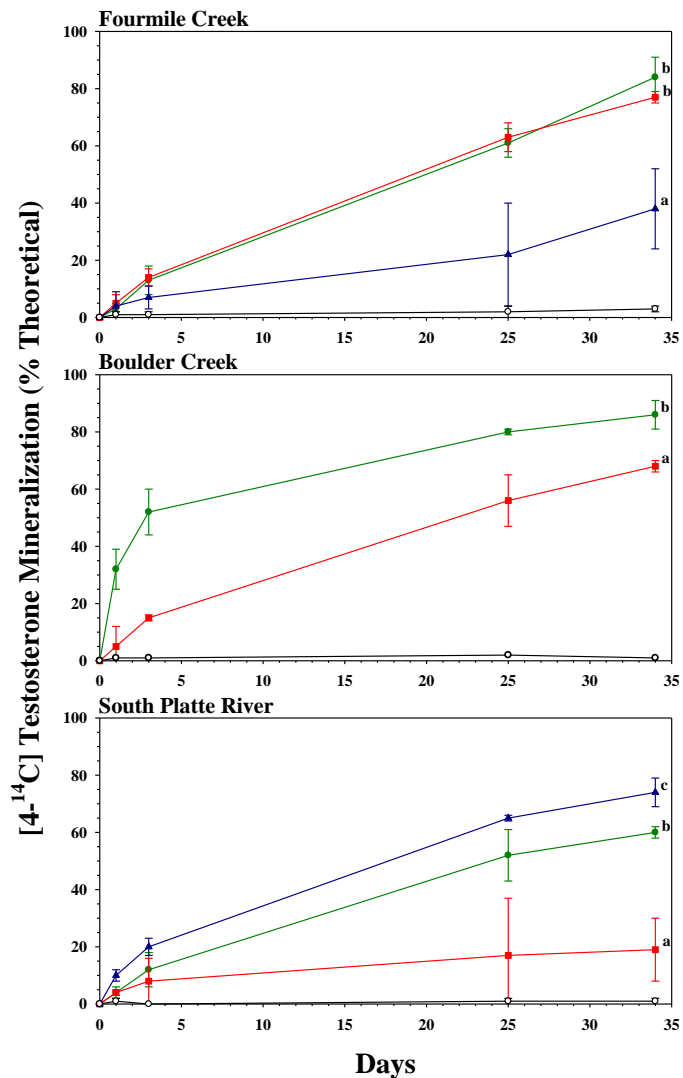
- 154 days.
- FC - no biodegradation.
- Biodegradation at outfall in BC & SPR.
- Biodegradation efficiency stimulated by effluent:
  - Adapted microbial population?
  - ...

# Potential for Estrone Biodegradation: Oxic Sediment?



- **Upstream sediment:**
  - 40-90% in 32 d.
- **Outfall sediment:**
  - Same at FC & BC.
  - 70% inhibition at SPR.
- **Downstream sediment:**
  - Same at FC.
  - 40% inhibition at SPR.
- **Potential for Estrone biodegradation in oxic sediments.**

# Potential for Testosterone Biodegradation: Oxic Sediment?



- **Upstream sediment:**
  - 60-90% in 32 d.
- **Outfall sediment:**
  - Same at FC.
  - 20-50% inhibition at BC & SPR.
- **Downstream sediment:**
  - 50% inhibition at FC.
  - Similar at SPR.
- **Potential for Testosterone biodegradation in oxic sediments.**

# V. Fate and Transport:

## Potential for Biodegradation of Endocrine Hormones?

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- **Hormones:**
  - **17 $\beta$ -Estradiol**
  - **Estrone**
  - **Testosterone**
- **Preliminary evidence indicates:**
  - **Significant biodegradation potential in oxic sediments.**
  - **Some potential for biodegradation in oxic water particularly downstream of WWTP.**

# V. Fate and Transport:

## Biodegradation of Endocrine Disrupting Compounds

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- **EDCs:**
  - **Endocrine Hormones.**
  - **Endocrine Mimics.**
- **Evidence indicates potential for EDC biodegradation exists in stream sediments.**

**“Assimilative Capacity” approach may be feasible for EDCs in WWTP affected streams.**

# USGS Researchers

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**The Toxics Program:**

*[toxics.usgs.gov](http://toxics.usgs.gov)*

**Emerging Water Quality Issues:**

*[toxics.usgs.gov/regional/emc.html](http://toxics.usgs.gov/regional/emc.html)*

**Paul Bradley, Columbia SC**

**Frank Chapelle, Columbia SC**

**Dana Kolpin, Iowa City IA**

**Larry Barber, Boulder CO**

**Pete McMahon, Denver CO**

**James Gray, Denver CO**