

# Pharmaceutical Compounds, Antibiotics, Hormones, and Wastewater Compounds in Pennsylvania Waters

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*U.S. Geological Survey  
Pennsylvania Water Science Center*

**PaDEP Emerging Contaminant Forum  
Rachael Carson State Office Building  
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# Occurrence of Emerging Contaminants in Pennsylvania Waters



**Collaborative Partnership**

# **Project Team**

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**Justin Knudsen**

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**Arianne Proctor**

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**Paul Curry**

**Phil Consonary**

**Pat Bowling**

# Objectives

Determine sources of emerging contaminants.

Evaluate the potential for impacts on fish.

Define the occurrence of emerging contaminants in source waters.

# Laboratory Methods Development



New lab capabilities for ECs:

- Pharmaceuticals
- Antibiotics
- Hormones
- Wastewater compounds



*Detection levels at expected ambient concentrations  
(ppb, ppt, ppq)*

# Target Pharmaceuticals

**Acetaminophen**

**Caffeine**

**Carbamazepine**

**Codeine**

**Cotinine**

**Dehydronifedipine**

**Diltiazem**

**Diphenhydramine**

**Fluoxetine**

**p-Xanthine**

**Rantidine**

**Salbutamol**

**Sulfamethoxazole**

**Thiabendazole**

**Warfarin**



15 compounds

# Target Antibiotics

## Macrolides

Azithromycin  
Erythromycin  
Anhydro-erythromycin  
Roxithromycin  
Tylosin  
Virginiamycin

## Quinolones

Ciprofloxacin  
Lomefloxacin  
Norfloxacin  
Ofloxacin  
Sarafloxacin  
Enrofloxacin

## Sulfonamides

Sulfachloropyridazine  
Sulfadiazine  
Sulfadimethoxine  
Sulfamethazine  
Sulfamethoxazole  
Sulfathiazole

## Tetracyclines

Chlorotetracycline  
Epi-chlorotetracycline  
Iso-chlorotetracycline  
Epi-iso-chlorotetracycline  
Doxycycline  
Oxytetracycline  
Epi-oxytetracycline  
Tetracycline  
Epi-tetracycline

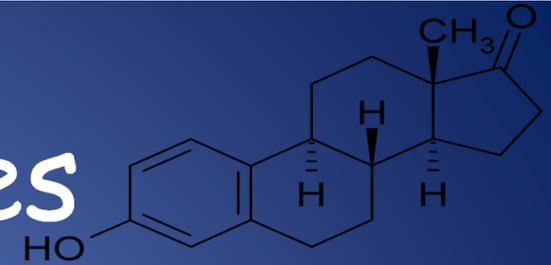
## Other Antibiotics

Lincomycin  
Trimethoprim  
Chloramphenicol  
Ormetoprim



31 compounds

# Target Hormones



11-ketotestosterone

17-alpha-ethynylestradiol

17-beta-estradiol

Norethindrone

3-beta-coprostanol

4-androstene-3,17-dione

Cholesterol

Cis-androsterone

Trans-diethylstilbestrol

Epitestosterone

Equilenin

Estriol

Mestranol

Progesterone

Dihydrotestosterone

Testosterone

Bisphenol A

17 compounds

# Target Wastewater Compounds

Nonylphenol

Octylphenol

Cotinine

Caffeine

3-beta-coprostanol

Cholesterol

Bisphenol-A

N,N-diethyl-*meta*-toluamide

others

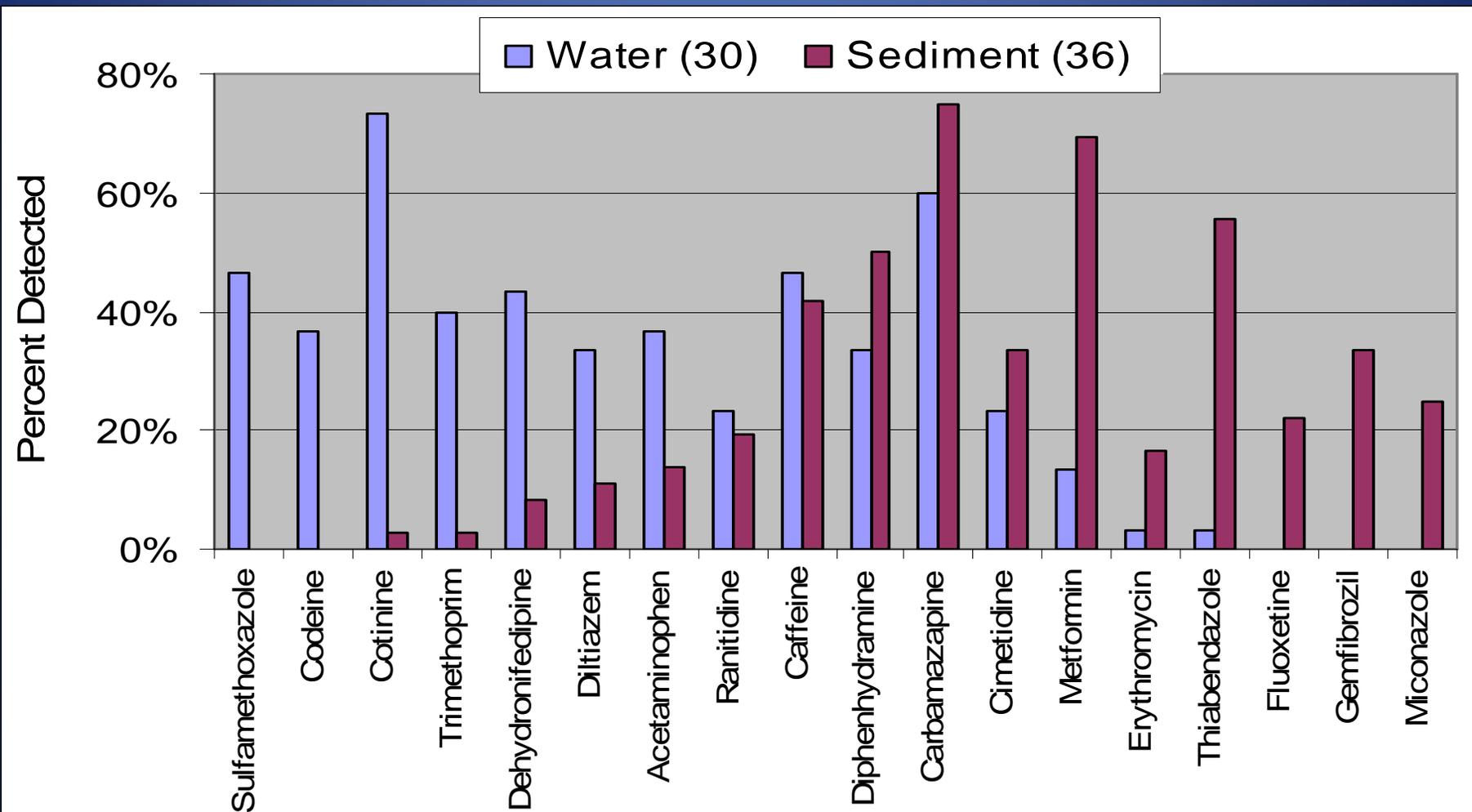
62 compounds

# Endocrine Disruptors



- Interfere with or mimic natural hormones.
- Can cause changes in reproduction, development, and/or behavior of an organism.
- Hormones – estrogen, testosterone.
- Some wastewater compounds – nonylphenol, octylphenol
- Fish health issues – intersex fish.
- Potential human health issues.

# Water and/or Sediment



# Study Components

1. Wells used to supply livestock
2. Streams upstream and downstream from animal-feeding operations
3. Streams upstream and downstream from WWTP effluents
4. Streams targeted for fish health evaluations
5. Streams near drinking-water intakes

# Wells used to supply livestock:

- Six wells
- South central Pennsylvania
- Limestone geology
- Analysis for pharmaceuticals and antibiotics

# Wells used to supply livestock:

- Only 2 pharmaceutical compounds detected
- Only 2 antibiotics detected
- All less than laboratory reporting level except for tylosin



# Streams upstream and downstream from animal-feeding operations

- Six streams
- South central Pennsylvania
- Poultry, swine, cattle
- Analysis for pharmaceuticals and antibiotics

# Stream affected by agricultural land use: Muddy Run

## Dairy farm on Muddy Run, Chester County, Pennsylvania



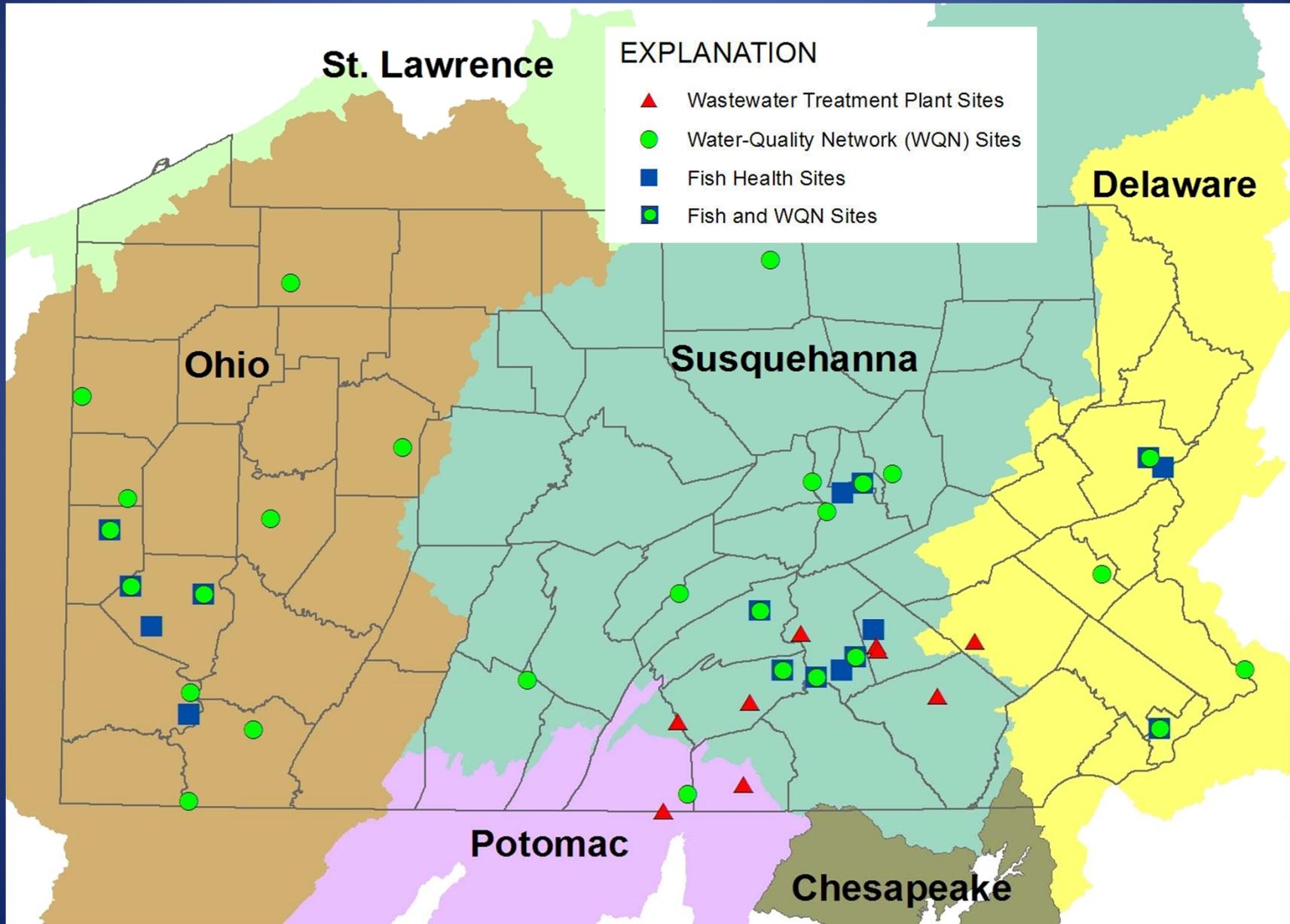
# Streams upstream and downstream from animal-feeding operations

- Six pharmaceuticals detected
- Four antibiotics detected
- All concentrations less than the laboratory reporting level except for caffeine

# Streams upstream and downstream from wastewater treatment plants

- Eight streams + one reference stream
- Small streams
- South central Pennsylvania
- Analysis for pharmaceuticals, antibiotics, hormones, and wastewater compounds

# Sampling Locations

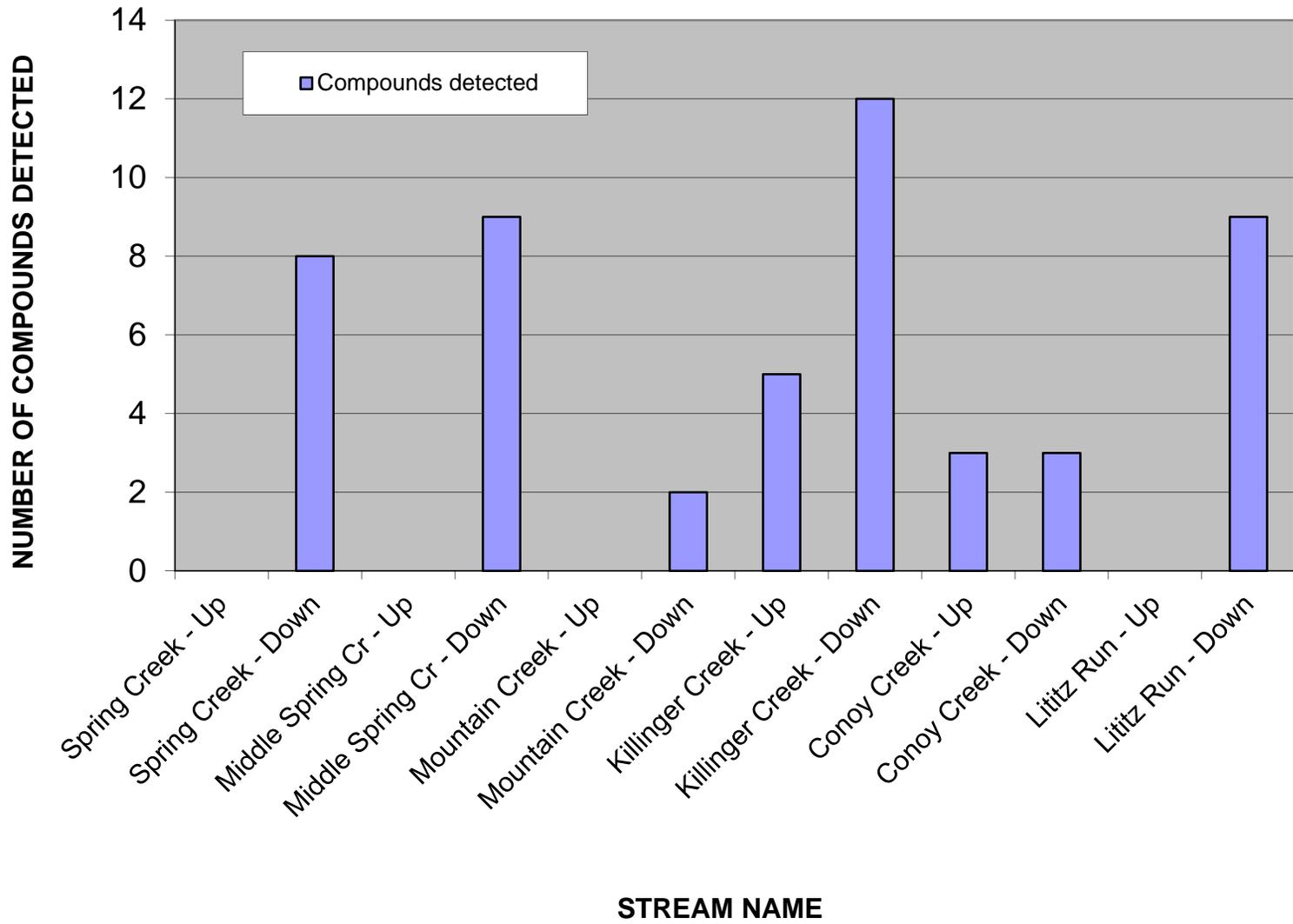


# Streams upstream and downstream from wastewater treatment plants

## Results:

- Very few detections upstream from WWTPs.
- Lots of detections downstream from WWTPs.
- All concentrations are low (sub microgram/liter levels)

### Wastewater Streams - Pharmaceuticals in Water 2006

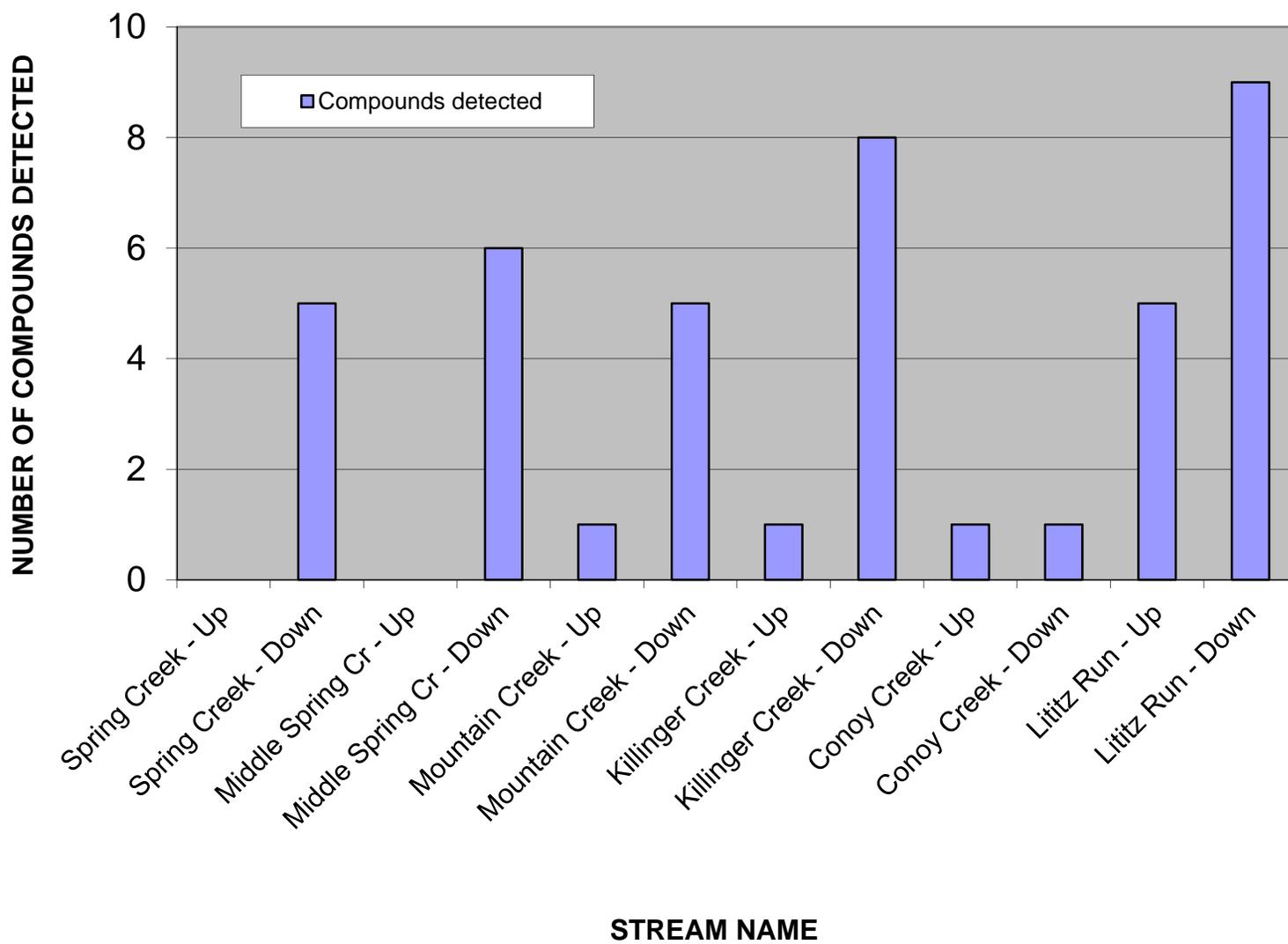


# Killinger Creek, Lebanon County

**Sinkhole**



### Wastewater Streams - Antibiotics in Water 2006



# Lititz Run, Lancaster County



# Streams upstream and downstream from wastewater treatment plants

- Low concentrations of 12 antibiotics:
  - Several streams
  - Erythromycin
  - Sulfamethoxazole
- Low concentrations of 14 pharmaceuticals
  - Diphenhydramine (antihistamine – Benadryl)
  - Cotinine (metabolite of nicotine)
  - Carbamazepine
    - Mood-stabilizing drug
    - Bipolar disorder

# Streams upstream and downstream from wastewater treatment plants

- Low concentrations of 9 hormones:
  - Highest concentration – Estrone (25 ug/L)
  - Killinger Creek
- Low concentrations of 45 wastewater compounds
  - Killinger Creek – 34 compounds
  - Middle Spring Creek – 29 compounds
  - Clark Creek (reference stream) – 5 compounds

# In-stream Study of ECs

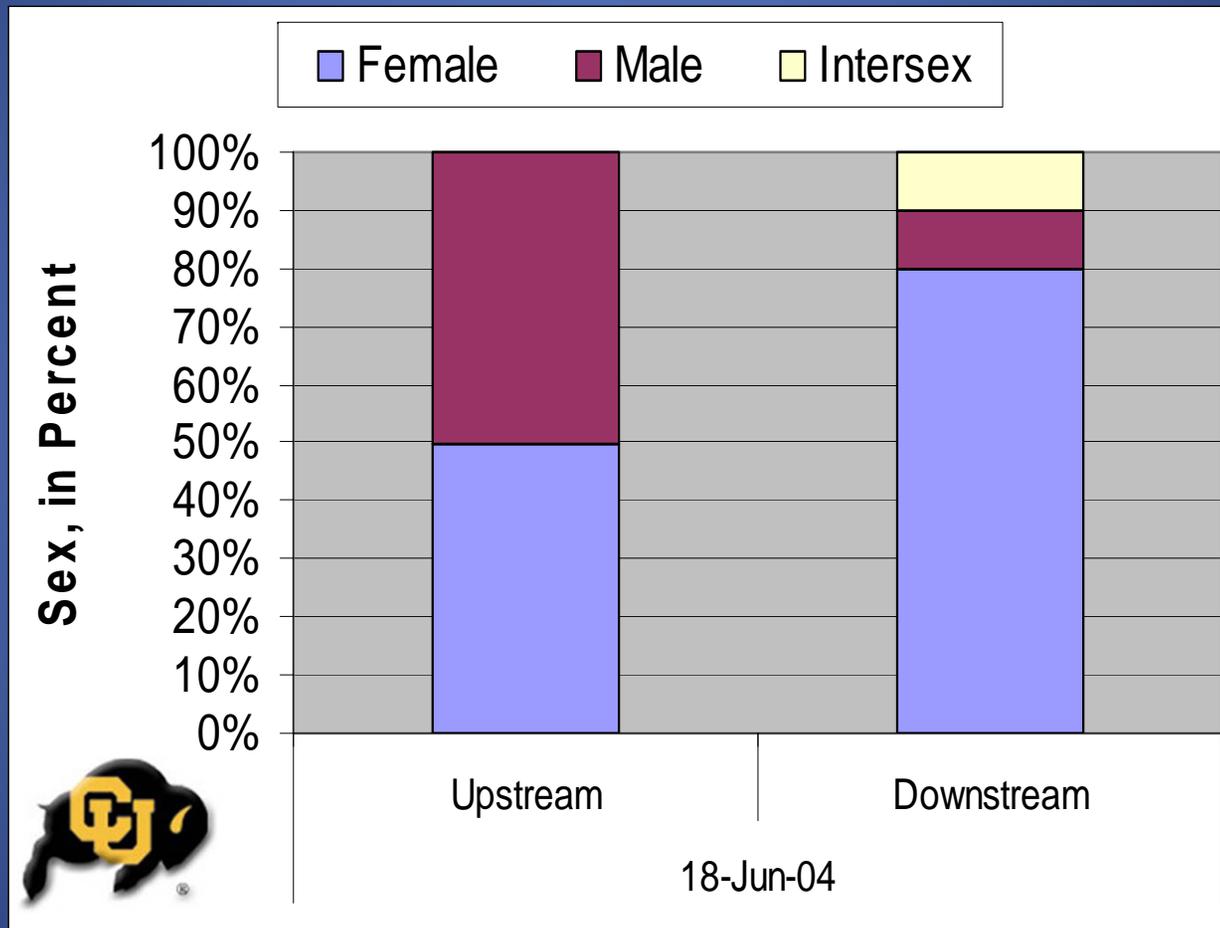
## Boulder Creek (CO)



- Effluent-dominated systems (WWTP discharge)
- Multiple ECs present
- Relatively small basin size



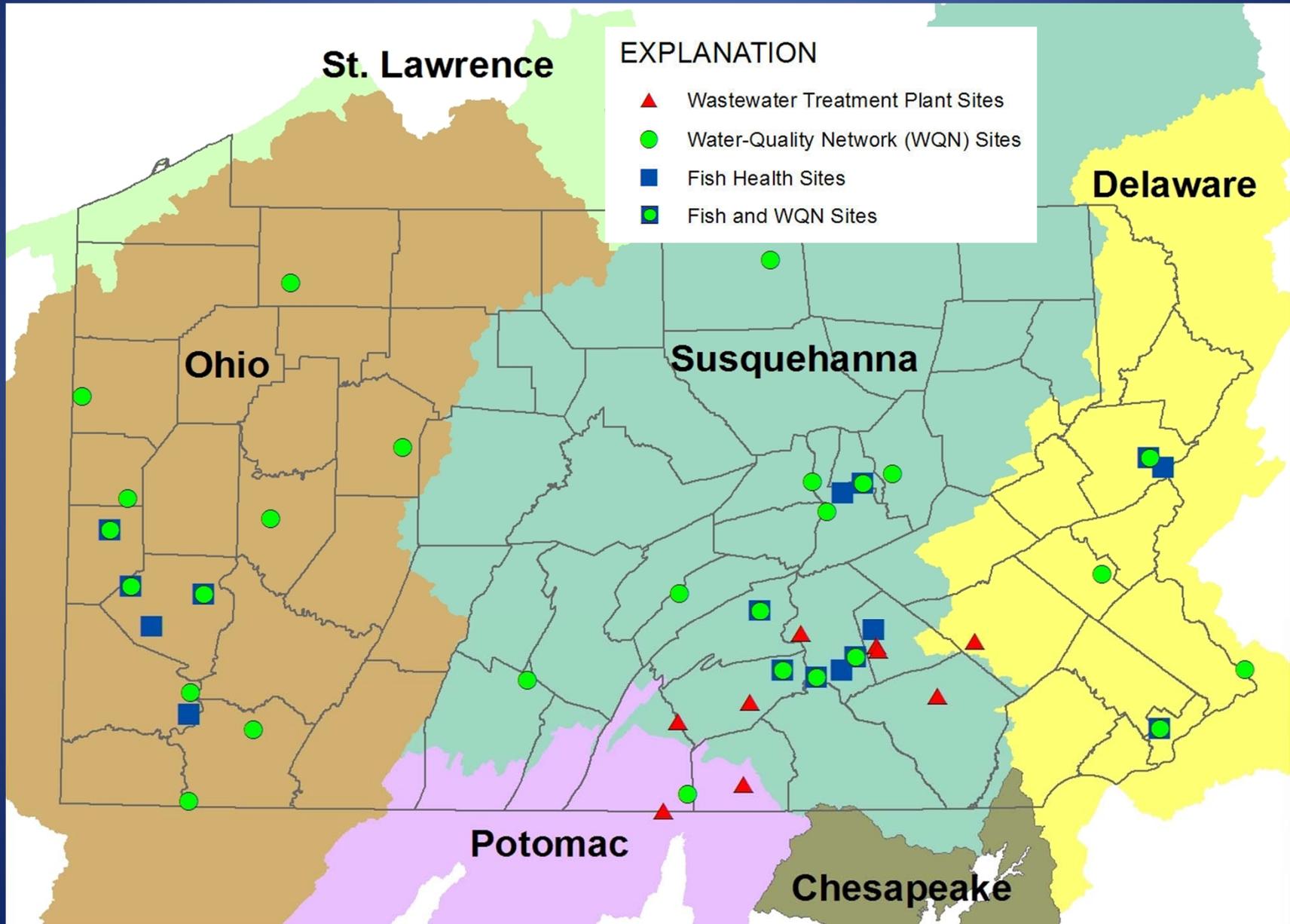
# Effects Research -- Boulder Creek, CO



# Streams targeted for fish health evaluations

- Sixteen sampling locations
- Throughout Pennsylvania
- Some sites paired (up/down)
- Analysis for pharmaceuticals, antibiotics, hormones, and wastewater compounds

# Sampling Locations



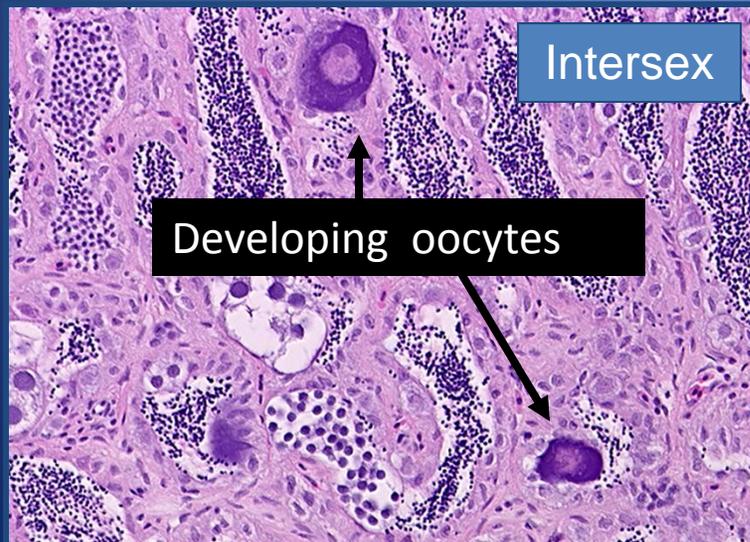
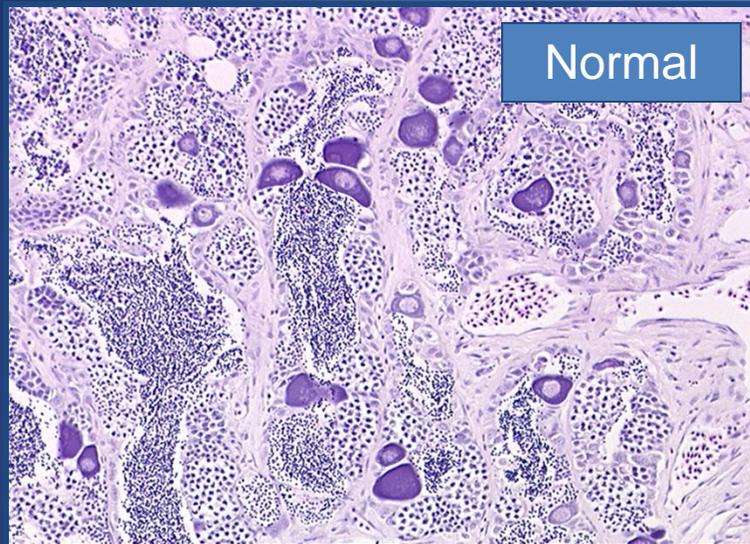
# Streams targeted for fish health evaluations

- **Six pharmaceuticals detected**
- **Five antibiotics detected**
- **Six hormones detected**
- **Thirty-five wastewater compounds detected**

# Pennsylvania Results

Intersex condition  
found in some Pennsylvania fish

# Intersex in Bass



🐟 Most often observed microscopically as immature oocytes within testes

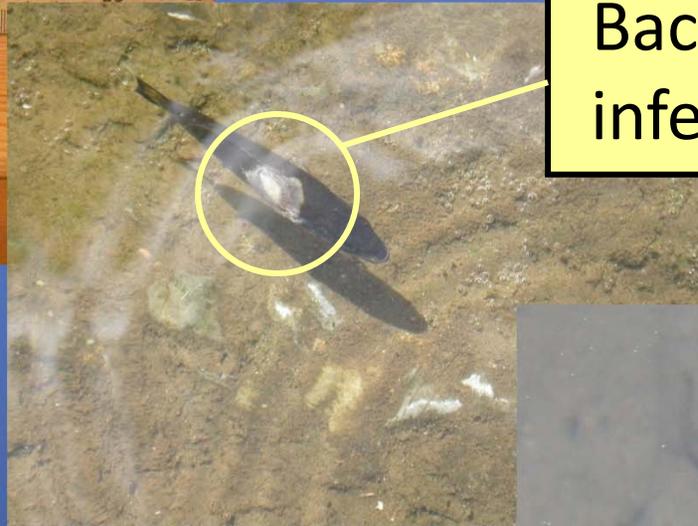
🐟 Suggested as a marker of endocrine disruption

🐟 Used as an indicator of exposure to estrogenic compounds

# What is the Impact of Intersex?

- Not sure.
- Fish still spawn.
- Sperm are less motile.
- Fewer fertilized eggs?
- Fewer baby fish?
- Smaller population?
- Immune system compromised?

# PFBC Surveys of Young-of-the-Year Smallmouth Bass

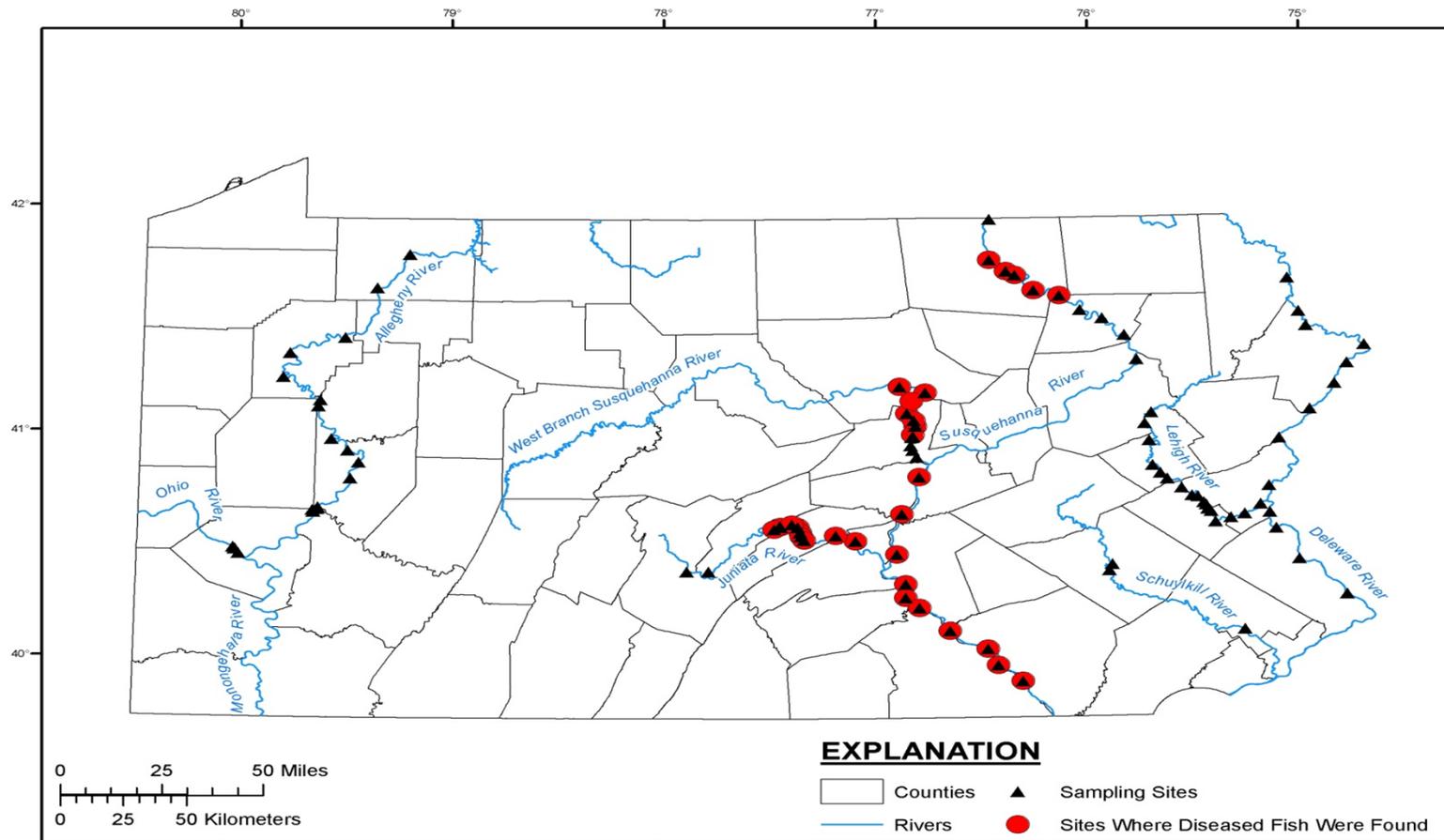


Bacterial  
infection



“Columnaris bacteria (*Flavobacterium columnare*) appears to be the primary pathogen” (Ken Stark PFBC, 2008)

# Diseased or Dead YOY SMB -- July 2007





**Dr. Karen Kidd**  
**Professor, University of New Brunswick**

**Kidd, K.A., P.J. Blanchfield, K.H. Mills, V.P. Palace, R.E. Evans, J.M. Lazorchak and R. Flick. 2007. Collapse of a fish population following exposure to a synthetic estrogen. Proceedings of the National Academy of Sciences 104(21):8897-8901.**

# Experimental Lakes Area





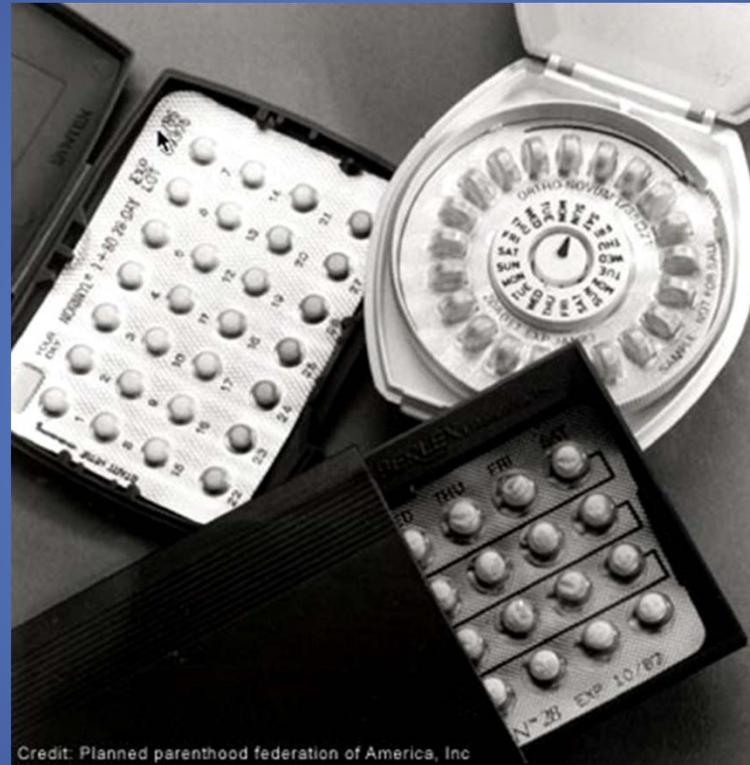
# Fathead minnows

Photo courtesy of Cornell University.



Photo courtesy of Aquatic Environmental Services, Inc.

# Birth Control Pills



Credit: Planned parenthood federation of America, Inc

Birth control pills = 17 $\alpha$ -ethynylestradiol

# Canadian Study

- Seven-year study
- Two similar lakes
- Fathead minnows
- Add estrogen to one lake



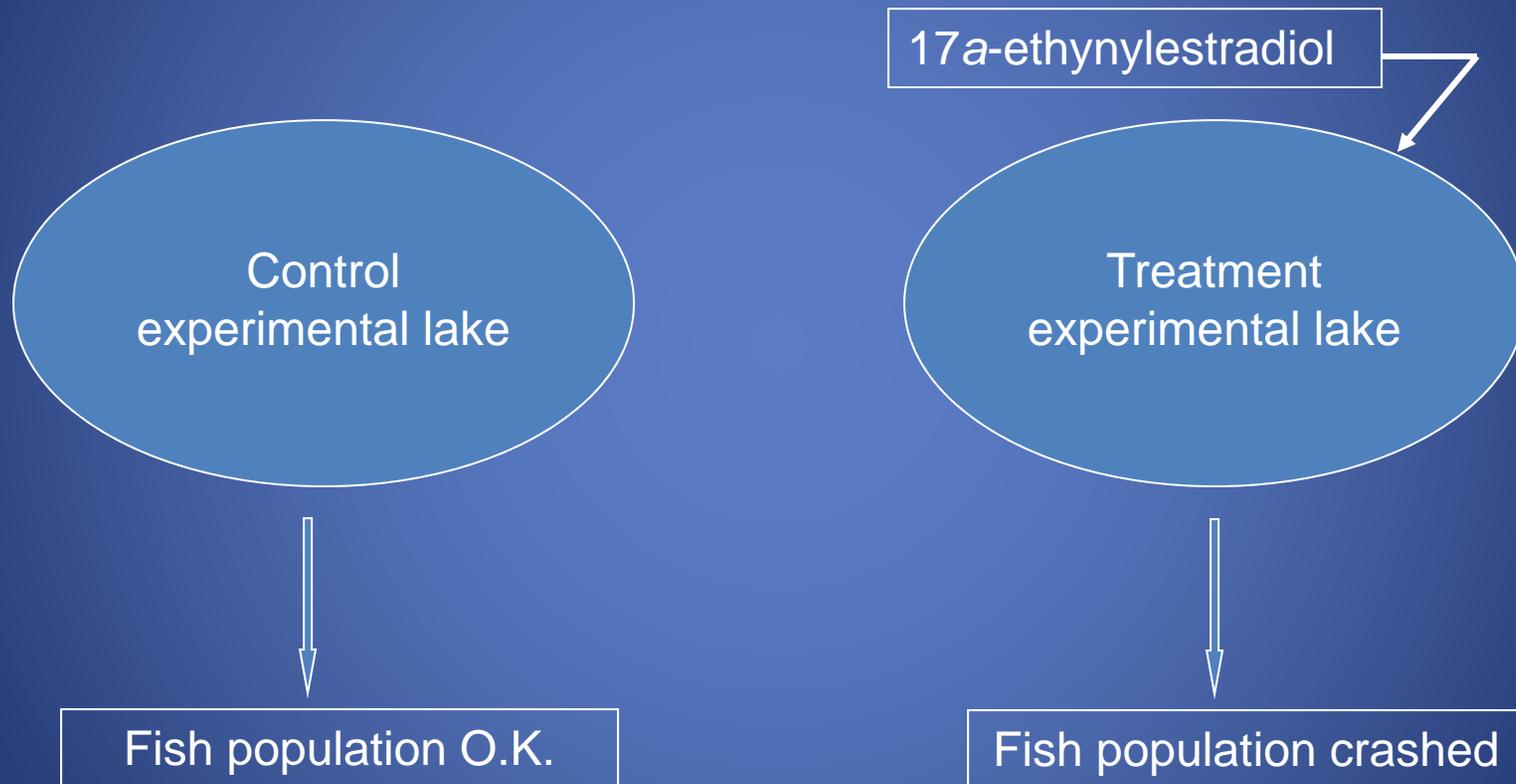
Control  
experimental lake

17 $\alpha$ -ethynylestradiol



Treatment  
experimental lake

# Canadian Study



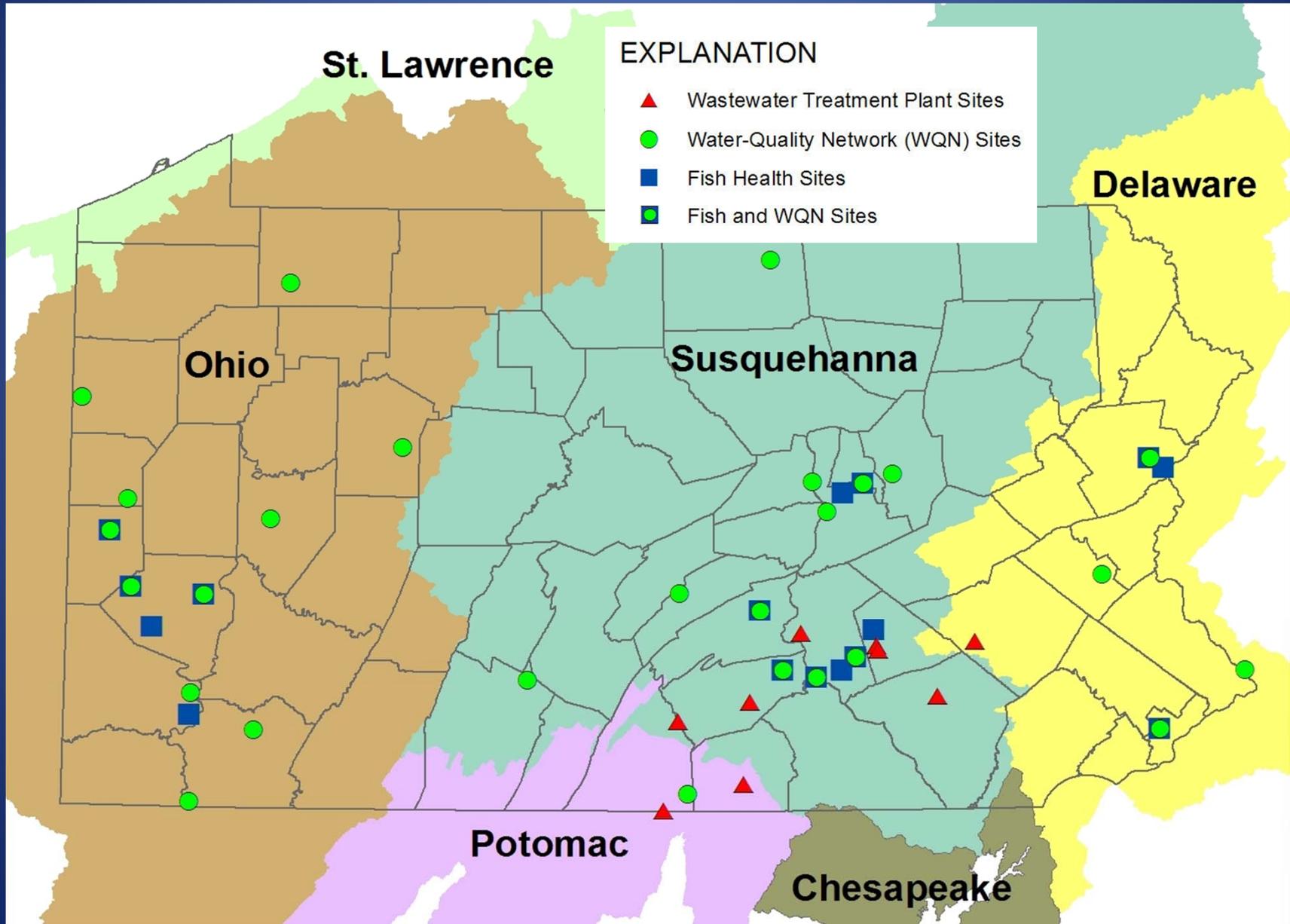
Kidd and others, 2007

# Streams near drinking-water intakes

- Cooperative project with PaDEP, U.S. EPA.
- DEP Water Quality Network sites
- Started in March 2007.
- Three years of sampling
- 27 sites across the state.
- Sites selected near drinking water intakes.
- Sampling quarterly
- Pharmaceuticals, antibiotics, and hormones.



# Sampling Locations



# Sampling

- All Teflon equipment
- Critically cleaned – methanol rinsed
- Two person field crew
- Composite sample from 3-15 locations in the stream
- All samples analyzed at USGS labs.



# Source-Water Results

- All 27 sites had at least 1 compound detected.
- 12 of the 15 (80 %) pharmaceutical compounds analyzed were detected at least once.
- 16 of 31 (52 %) antibiotic compounds detected at least once.
- 9 of 17 (53 %) hormone compounds detected at least once.

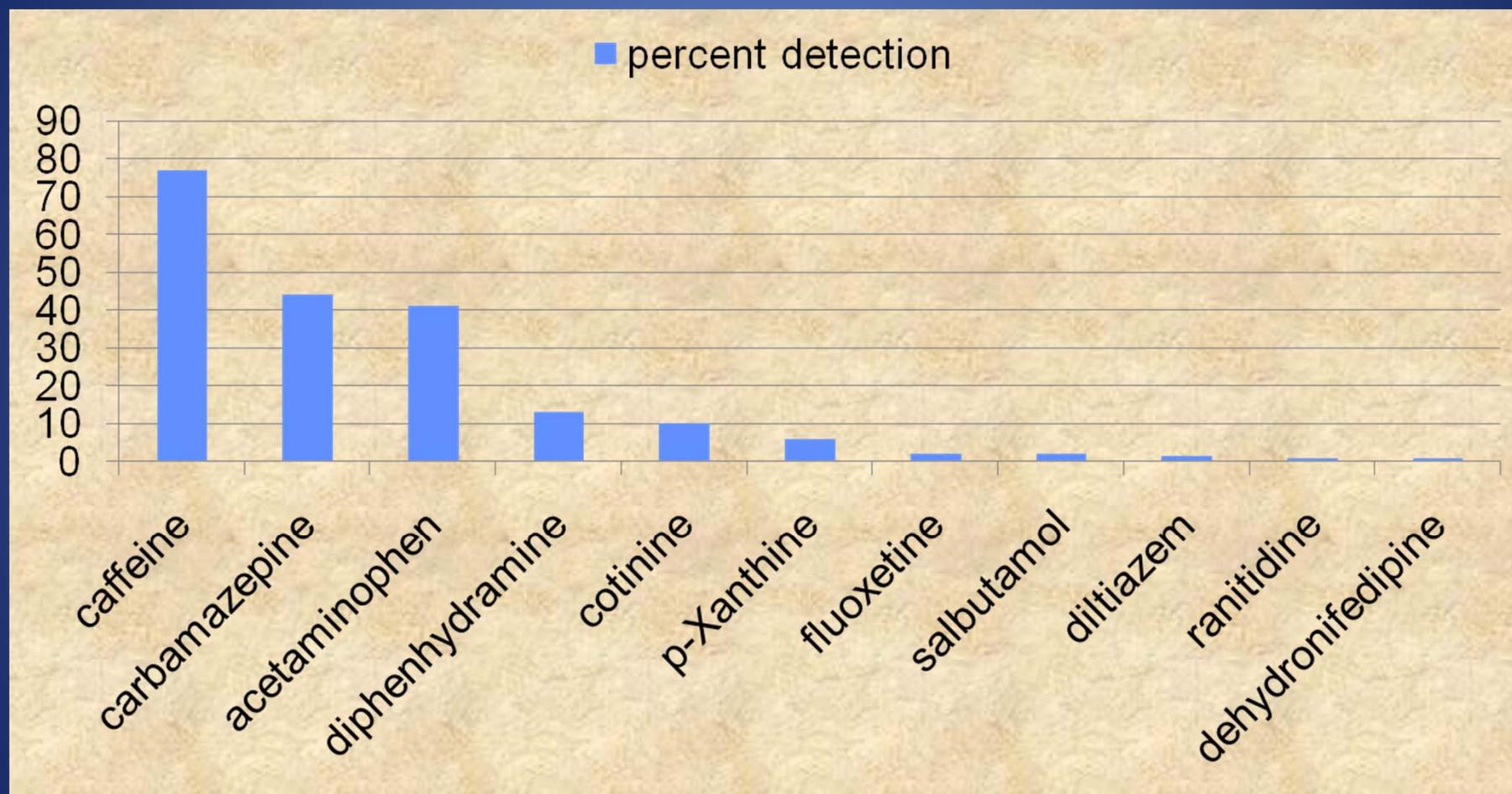


# Commonly Detected Pharmaceuticals

- Caffeine - Stimulant
- Carbamazepine - Mood stabilizing (epileptic)
- Acetaminophen- Analgesic (Tylenol)
- Diphenhydramine - Antihistamine (Benadryl)
- Cotinine - Metabolite of nicotine



# Pharmaceuticals detected



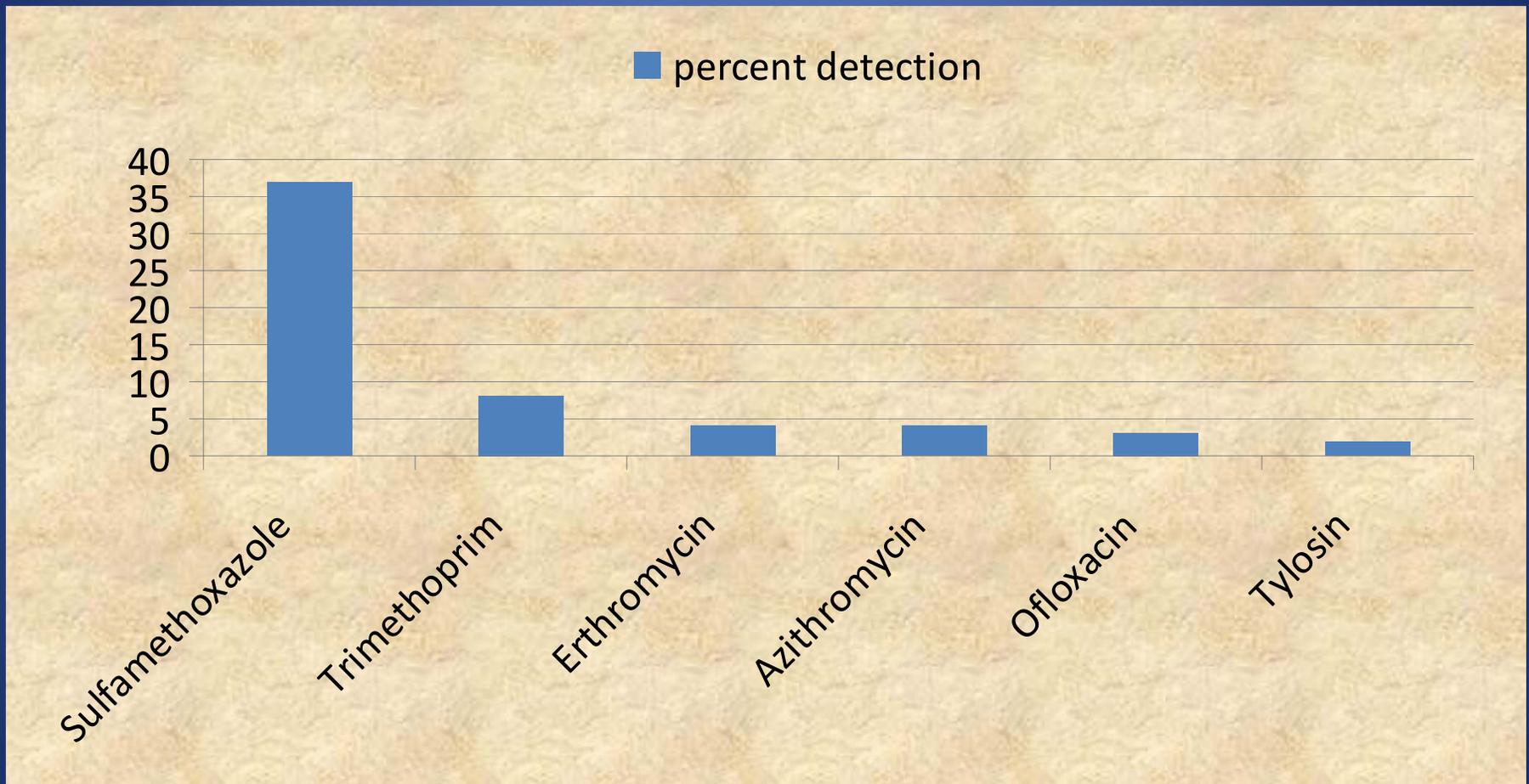
Provisional data

# Commonly Detected Antibiotics

- Sulfamethoxazole - Human use
- Trimethoprim - Human use
- Azithromycin - Human use
- Ofloxacin - Human use



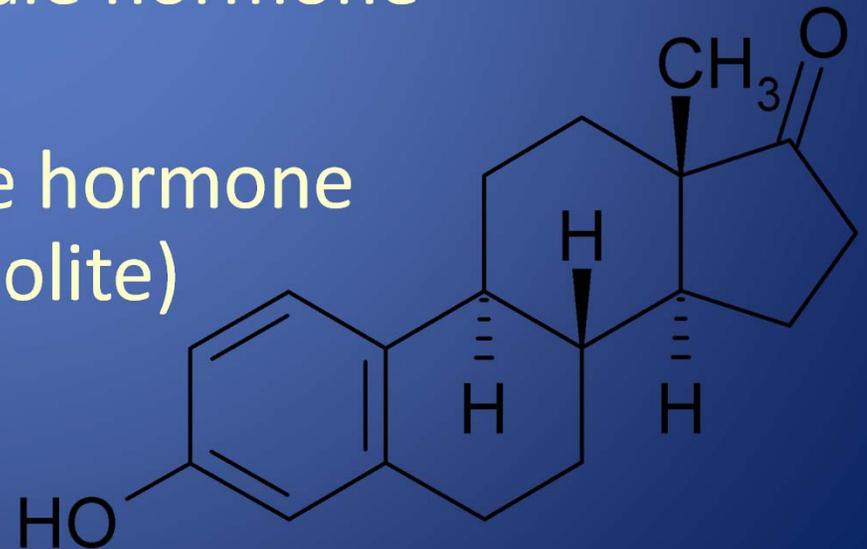
# Antibiotics detected



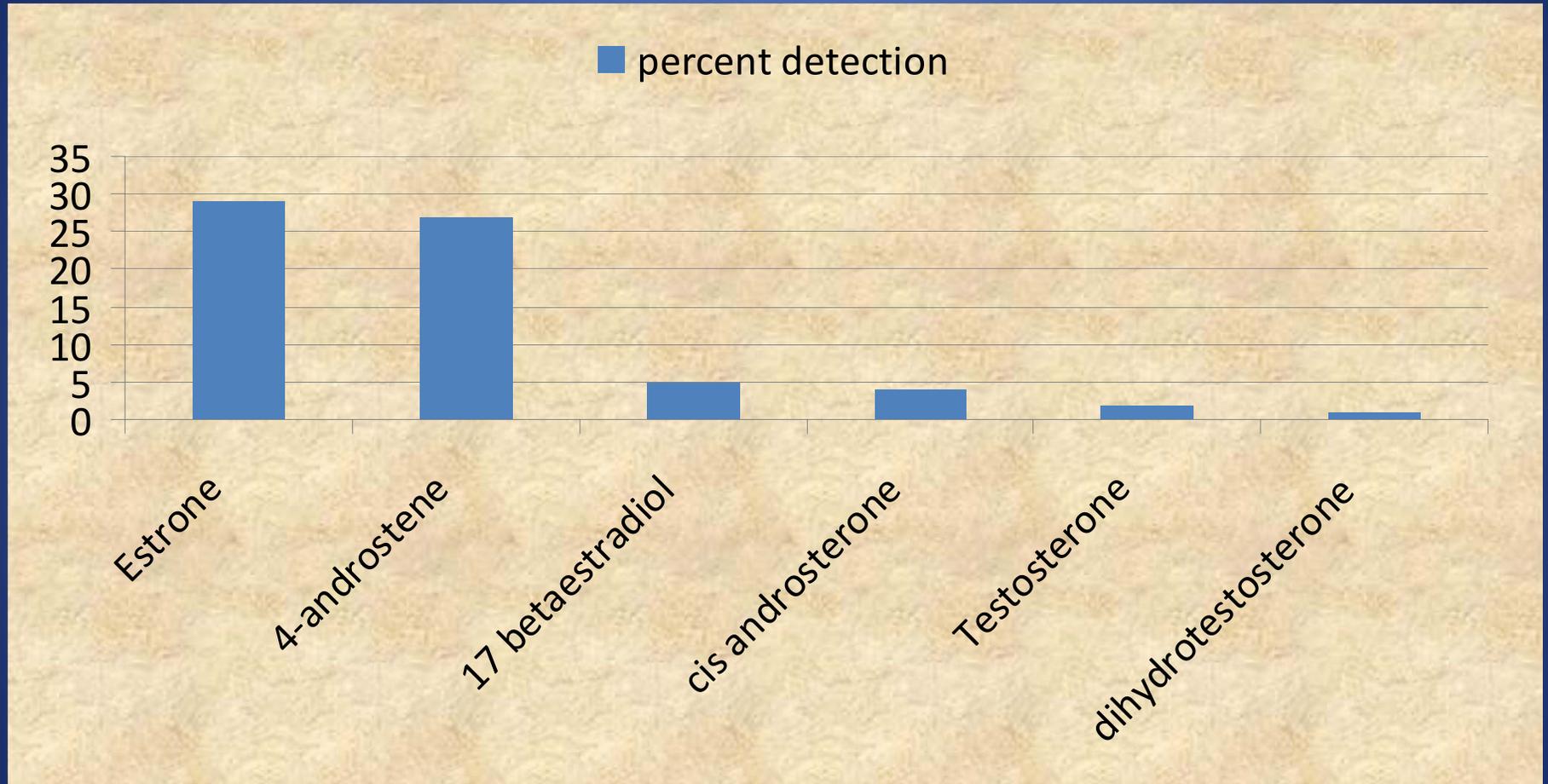
Provisional data

# Commonly Detected Hormones

- Estrone -- Female hormone
- 4-androstene - 3,17 dione -- Male hormone (testosterone precursor)
- 17 beta estradiol -- Female hormone
- Cis-androsterone -- Male hormone (testosterone metabolite)



# Hormones detected



Provisional data

# Low-Low-Low Concentrations

- Measured in nanograms (parts per trillion).
  - No regulatory limits.
  - Concentrations in surface waters are miniscule when compared to pharmaceutical doses.
- 
- Acetaminophen in Tylenol  
325 mg
  - Acetaminophen in water  
0.00000005 mg/L



# Mediterranean Sea

You would have to drink  
**6.5 billion liters of water**  
to get one dose of regular strength Tylenol



Human health risks  
???

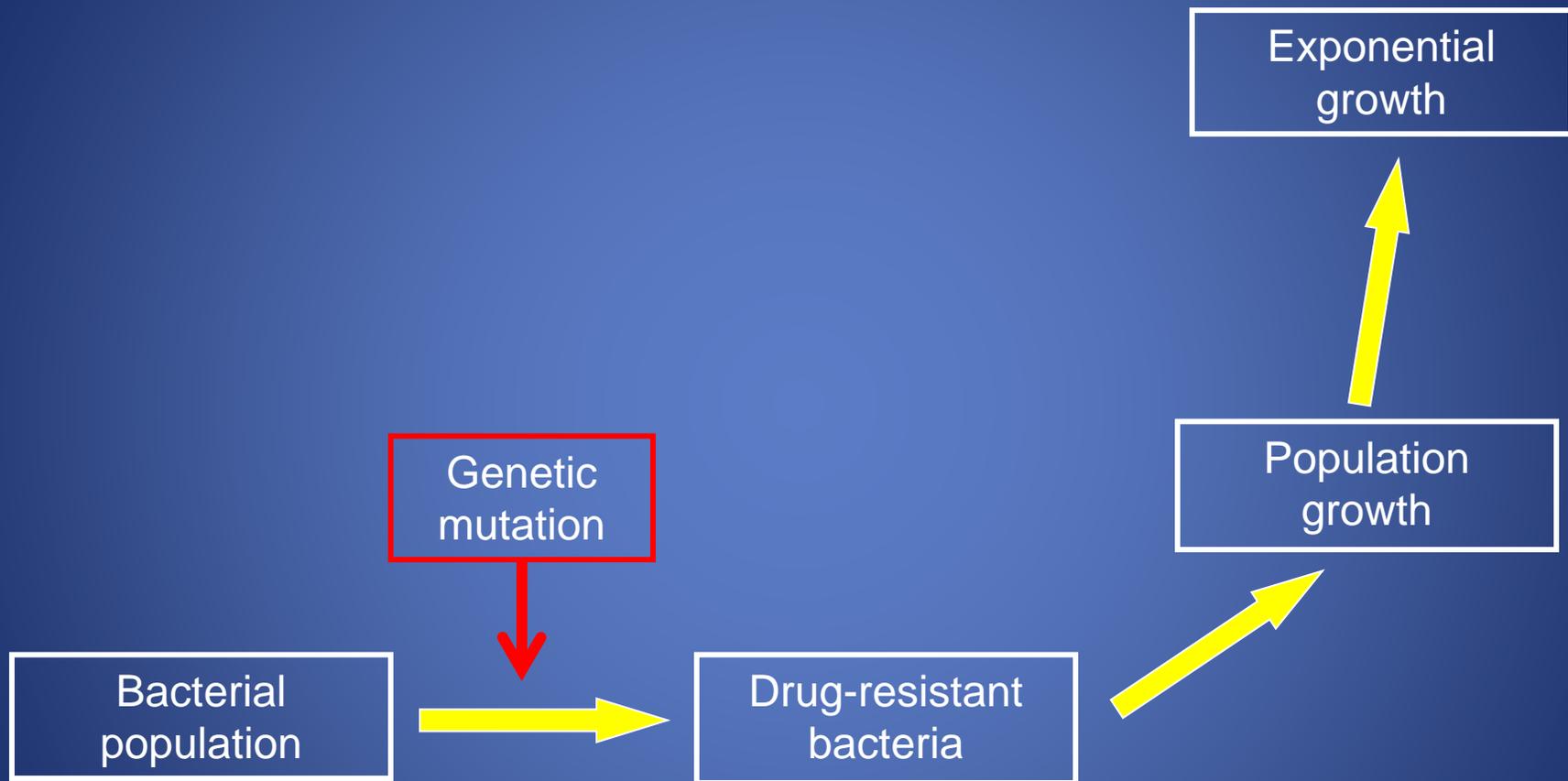
# Human Health Risks

Antibiotic resistant bacteria

Endocrine disruption

Neurological interference

# Antibiotic Resistance



MRSA – Methicillin-resistant *Saphylococcus aureus*

# Antibiotic Resistance

*“Only one bacterium out of a population has to survive in order to replenish ... a complete new population of resistant organisms.”*

Dr. Stuart Levy, Tufts University

# What does it all mean ?

- No water-quality standards.
- No evaluation of mixtures, synergistic effects.
- Few studies on human health effects.

Don't Panic!

but...

Be Concerned



# Questions???

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