Contaminants of Emerging Concern in Pennsylvania Waters 2006-2009

Data collection and analysis from surface-water, ground-water, stream sediment and fish.

U.S. Department of the Interior
U.S. Geological Survey

What are contaminants of emerging concern ?

- Compounds that we are now beginning to track in the environment.
- Not only new compounds but existing compounds.
- Also called personal care products or chemicals of emerging concern.

USGS

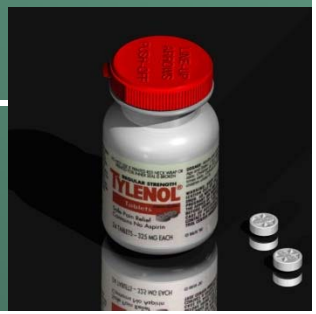
Contaminants of Emerging Concern

- Human Drugs
- Vet. Drugs
- Antibiotics
- Hormones
- Steroids
- Detergents
- Plastics
- Pathogens
- Antioxidants
- Fire retardants
- Disinfectants
- Fumigants
- Fragrances
- Insecticides/ Repellants
- Nanomaterials

USGS

Low-Low-Low Concentrations

- Concentrations that are being found are measured in nanograms (Parts Per Trillion).
- No regulatory limits set because there is little know about long term exposure in aquatic systems.
- Concentrations found in surface waters are miniscule when compared to pharmaceutical doses.
  - Acetaminophen pharmaceutical = 200 mg
  - Acetaminophen in water = 0.00000005 mg/L



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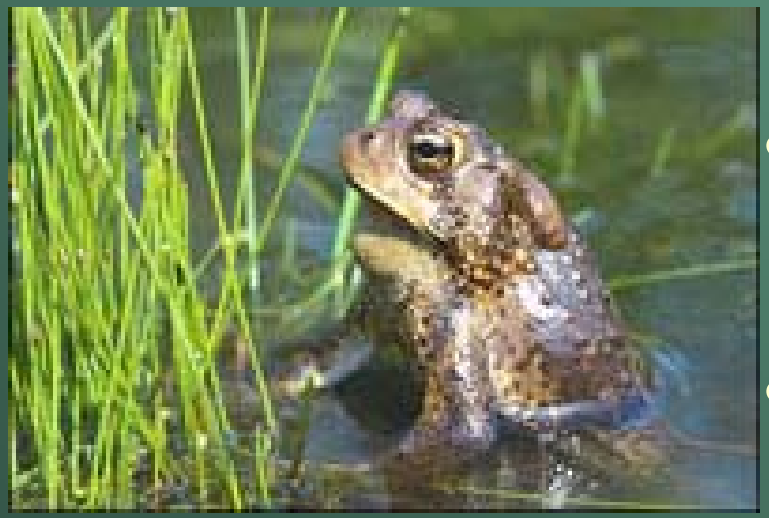
Endocrine Disruptors



- External compounds that interferes with or mimics natural hormones.
- Can cause reproduction, development, and or behavior of an organism.
- Hormones – estrogen, testosterone.
- Fish health issues – intersex fish.
- Potential human health issues.

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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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A single source can have multiple environmental pathways

WWTP

Aquatic

- low levels (ppb)
- continual release

Terrestrial

- higher levels (ppm)
- episodic release

USGS

Initial USGS Studies

- 1994 - NAWQA reconnaissance looking at fish health.
  - Nationwide sampling effort.
  - Potential for endocrine disruption was widespread and related to pesticide and PCB concentrations.
  - High levels of vitellogenin (egg protein found in females) found in male carp near STP's.
  - Further studies were needed.

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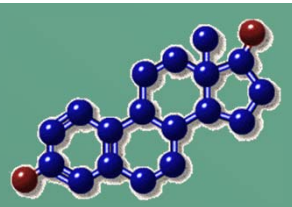
Methods Development



New lab capabilities for ECs:

- Pharmaceuticals
- Antibiotics
- Hormones
- Wastewater compounds

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

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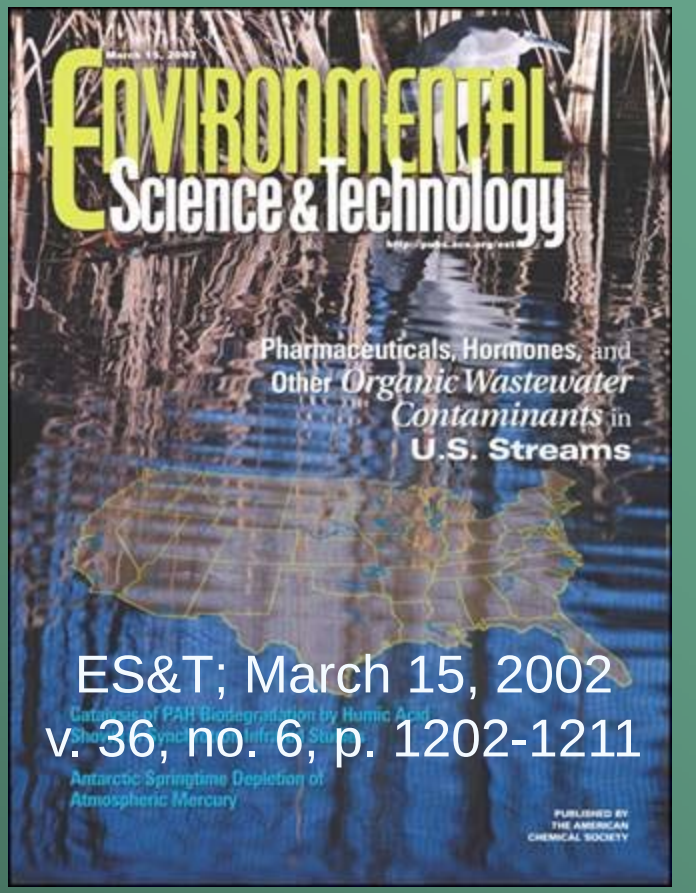
Occurrence - National Recon Studies

- Streams (1999-2000)
- Ground Water (2000)
- Sources of Drinking Water (2001)
- Streambed Sediment (2002)



ES&T; March 15, 2002
v. 36, no. 6, p. 1202-1211

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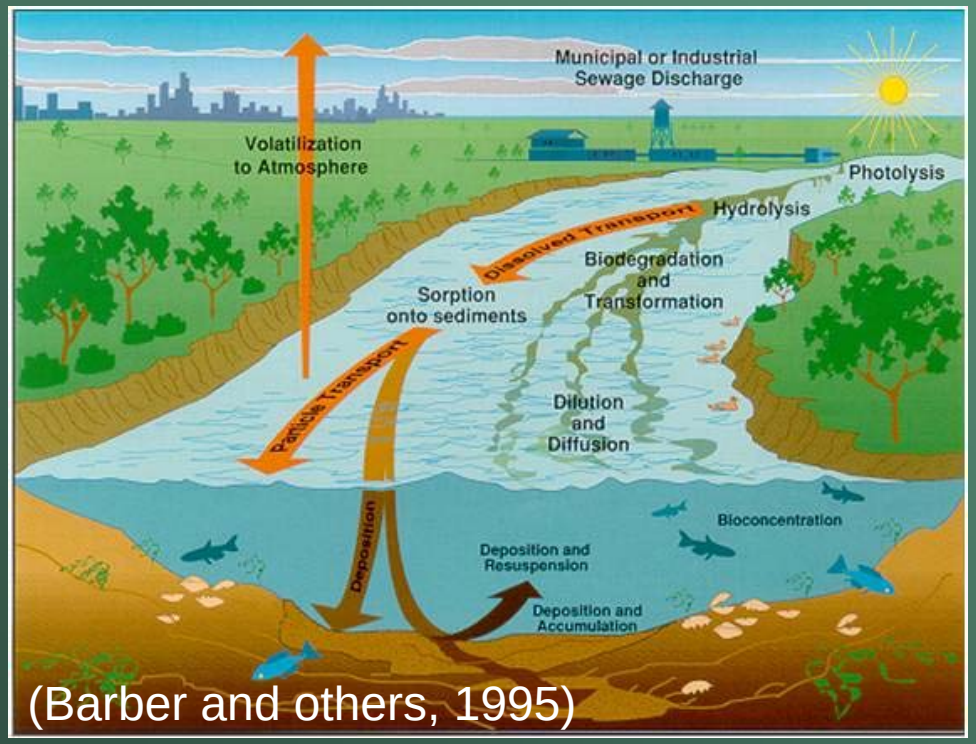
Transport and Fate



(Barber and others, 1995)

Research underway:

- Fate through WWTPs
  (WERF, Metcalf & Eddy, U of AZ)
- Fate through DWTPs
  (USGS, USEPA)
- Surface transport
  2 research basins
  (Boulder Creek, CO
  Fourmile Creek, IA)
- Subsurface transport
  Cape Cod Research Site

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

Sampling

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

A water-quality sampler. USGS

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Target Pharmaceuticals

Acetaminophen
Caffeine
Carbamazepine
Codeine
Cotinine
Dehydronifedipine
Diltiazem
Diphyenydramine

Fluoxetine
p-Xanthine
Rantidine
Salbutamol
Sulfamethoxazole
Thiabendazole
Trimethoprim
Warfarin

16 compounds

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Target Antibiotics

Macrolides
- Azithromycin
- Erythromycin
- Anhydro-erythromycin
- Roxithromycin
- Tylosin
- Virginiamycin

Quinolines
- 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

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Target Hormones

Natural androgens
4-Androstene-3,17-dione
cis-Androsterone
Epitestosterone
11-Ketotestosterone
Dihydrotestosterone
Testosterone

Natural Progestin
Progesterone

Synthetic progestin
Norethindrone

Natural estrogens
Equilenin
Equilin
17-alpha-Estradiol
17-beta-Estradiol
Estriol
Estrone

Synthetic estrogens
Diethylstilbestrol
17-alpha-Ethynylestradiol
Mestranol

17 compounds

USGS

Target Organic Wastewater Compounds

Detergent Matabolites
OPEO2
NPEO2

Fragrances and flavors
Camphor
Indole
Menthol

Disinfectants
Bromoform
Phenol
Triclosan

Industrial Compounds
Benzophenone
Para-Cresol
Tetrachloroethylene

Pesticides
Atrazine
Bromacil
Carbazole
Diazinon
DEET
Metolaclor

Polycyclic aromatic hydrocarbons
Benzo[a]Pyrene
Naphthalene
Pyrene

Flame retardants and plasticizers
Tributyl phosphate
Triphenyl phosphate
Diethyl phthalate

60 compounds

USGS

Occurrence of Emerging Contaminants in Pennsylvania Waters

Collaborative Partnership

USGS Contaminants of Emerging Concern Sampling in Pennsylvania.

- 2 major projects were conducted in Pa.
- Both funded by PaDEP and USEPA
  - Occurrence of Pharmaceuticals and Antibiotic Compounds in Pennsylvania Waters:
  - Contaminant of Emerging Concern sampling near drinking water intakes at PaDEP Water Quality Network sites.

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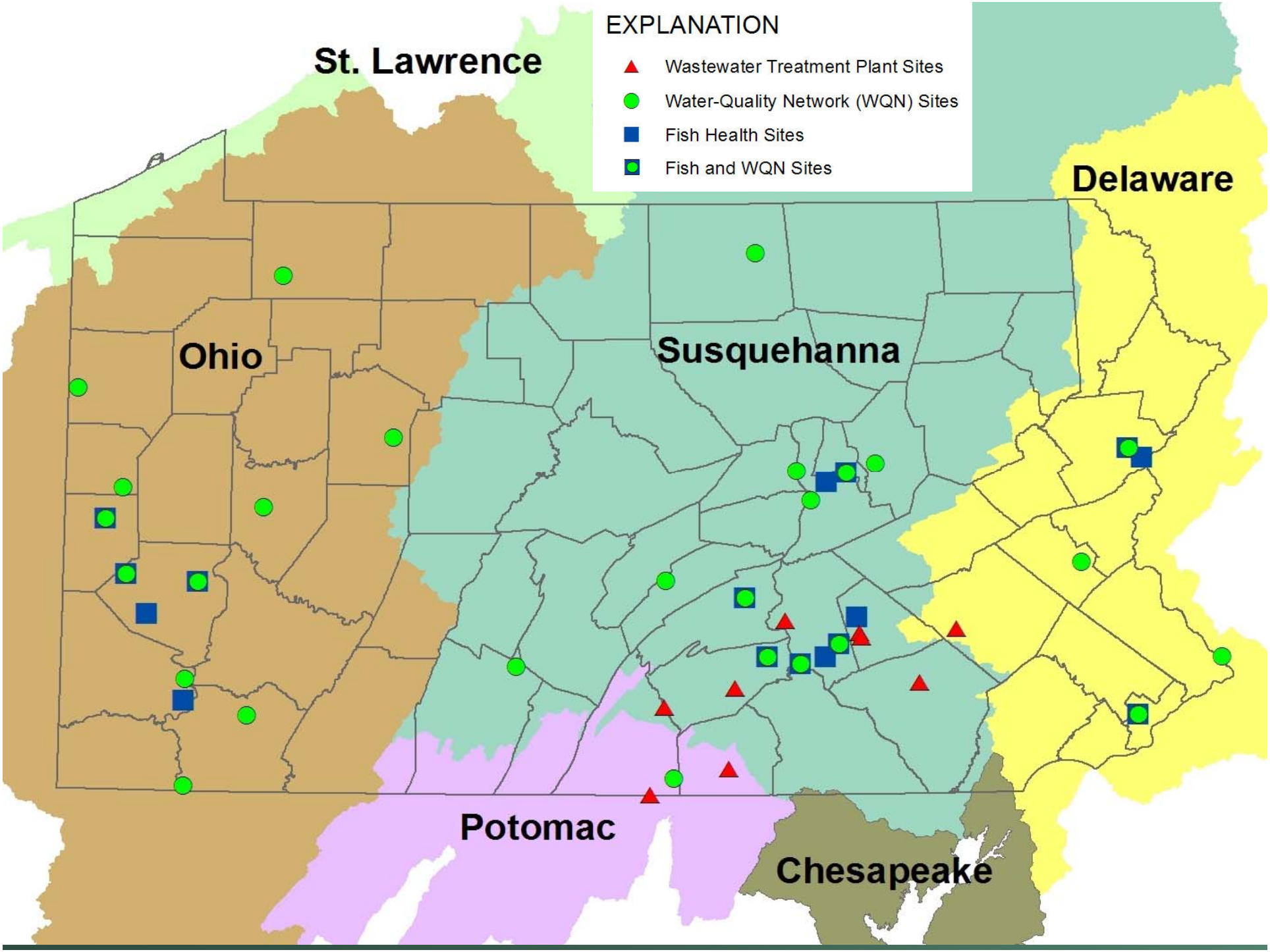
EXPLANATION
Wastewater Treatment Plant Sites
Water-Quality Network (WQN) Sites
Fish Health Sites
Fish and WQN Sites
St. Lawrence
Delaware
Ohio
Susquehanna
Potomac
Chesapeake

Phase I - 2006 sampling

- Surface-water sites
  - Ag affected
    upstream
    downstream
- Surface-water sites
  - WWT affected
    upstream
    downstream
- Ground-water wells in agricultural areas
- Sites located in south-central Pa.
- Sampled for pharmaceuticals and antibiotics in water.
- No hormones or OWC
- No sediment sampling

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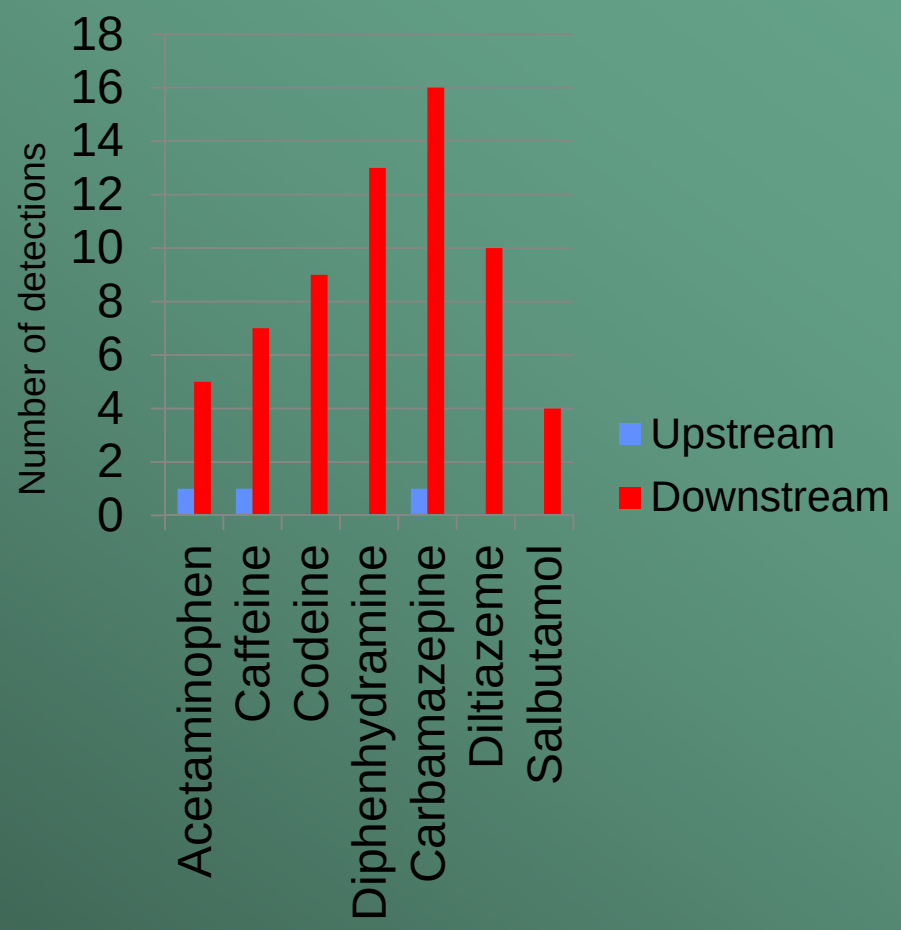
Results – Phase I (Occurrence Survey):

- Very few detections upstream from WWTPs.
- More detections downstream from WWTPs.
- All concentrations are low (sub microgram/liter levels)
- Few detections in agricultural streams
- Almost no detections in stock wells

USGS

Results from Phase I

- Most compounds were rarely detected.
- Low concentrations of some compounds detected below WWTPs:
  - Occurance dependant on:
    - Flow
    - % of flow from WWTP



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Results from Phase I

- **Streams with a large % of flow from a WWTP had more compounds detected at higher.**

Site	Number of detections		% flow from WWTP	
Spring Creek	19		7	
Middle Spring Creek	36		22	
Mountain Creek	7		5	
Killinger Creek	52		49	
Lititz Run	34		40	

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Commonly Detected Compounds

- Caffeine - Stimulant
- Carbamazepine - Mood stabilizing (epileptic)
- Acetaminophen- Analgesic
- Diphenhydramine - Antihistamine (Benadryl)
- Cotinine - Metabolite of nicotine
- Sulfamethoxazole - Human use
- Trimethoprim - Human use
- Azithromycin - Human use
- Ofloxacin - Human use
- Tylosin - Used for cattle, swine, and poultry.

USGS

Emerging Contaminants Project – Phase II 2007-2009

- **Focus on downstream of WWTPs.**
- **Added Hormone analysis.**
- **Added Organic Wastewater Compound analysis**
- **Added sediment sampling**
- **Fish Health sites added**

USGS

Results – Phase II:

- Some detections upstream from WWTPs.
- More detections downstream from WWTPs.
- All concentrations are low (PPT levels)
- OWC detected included compounds that are known or suspected endocrine disruptors.
- Concentrations and detected compounds in sediment varied.

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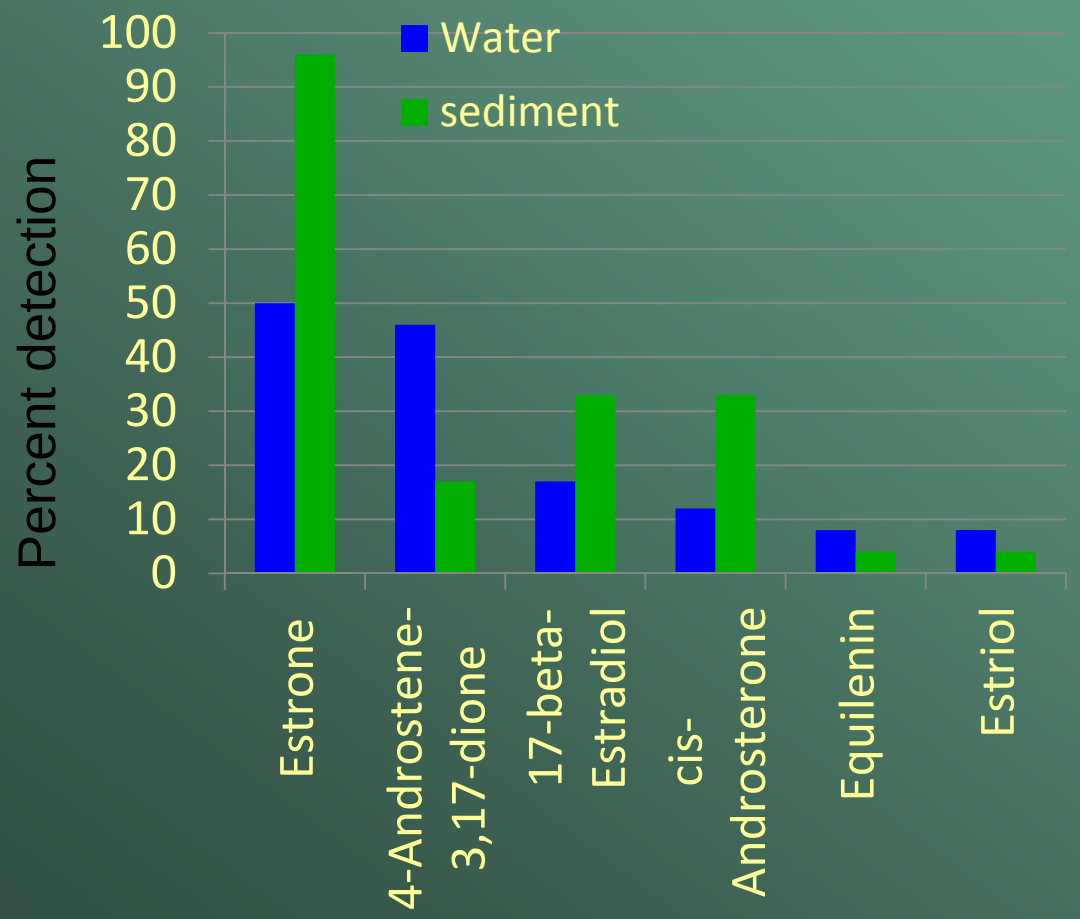
Hormone detections



- Most hormones were rarely detected.
- Commonly detected hormones included: 4-Androstene and estrone.
- Very low concentrations.

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OWC detections

- Similar pattern to other compounds – most compounds were rarely detected – a few compounds were commonly detected.
- Some OWC were found exclusively in water and others only in sediment.
- Polycyclic aromatic compounds were found concentrated in sediment samples.
- Flame retardants and plasticizers were detected primarily in water samples.

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Drinking water intake sites

- Started in March 2007.
- Three years of sampling (Completed in August 2009).
- 27 sites across the state.
- Sampling is focused near drinking water intakes.
- Sampling quarterly for pharmaceuticals, antibiotics and hormones.

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Drinking water intake sites

- Samples collected at various flows. (Low flows are not targeted)
- Regular WQN QW sample collected at all sites along with EC sample.
- E-coli, Enterococci, Giardia, Cryptosporidium samples collected quarterly.
- Various size streams including 5 reference sites.

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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 32 (50%) antibiotic compounds were detected at least once.
- 9 of 19 (47%) hormone compounds were detected at least once.

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Commonly Detected Pharmaceuticals

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

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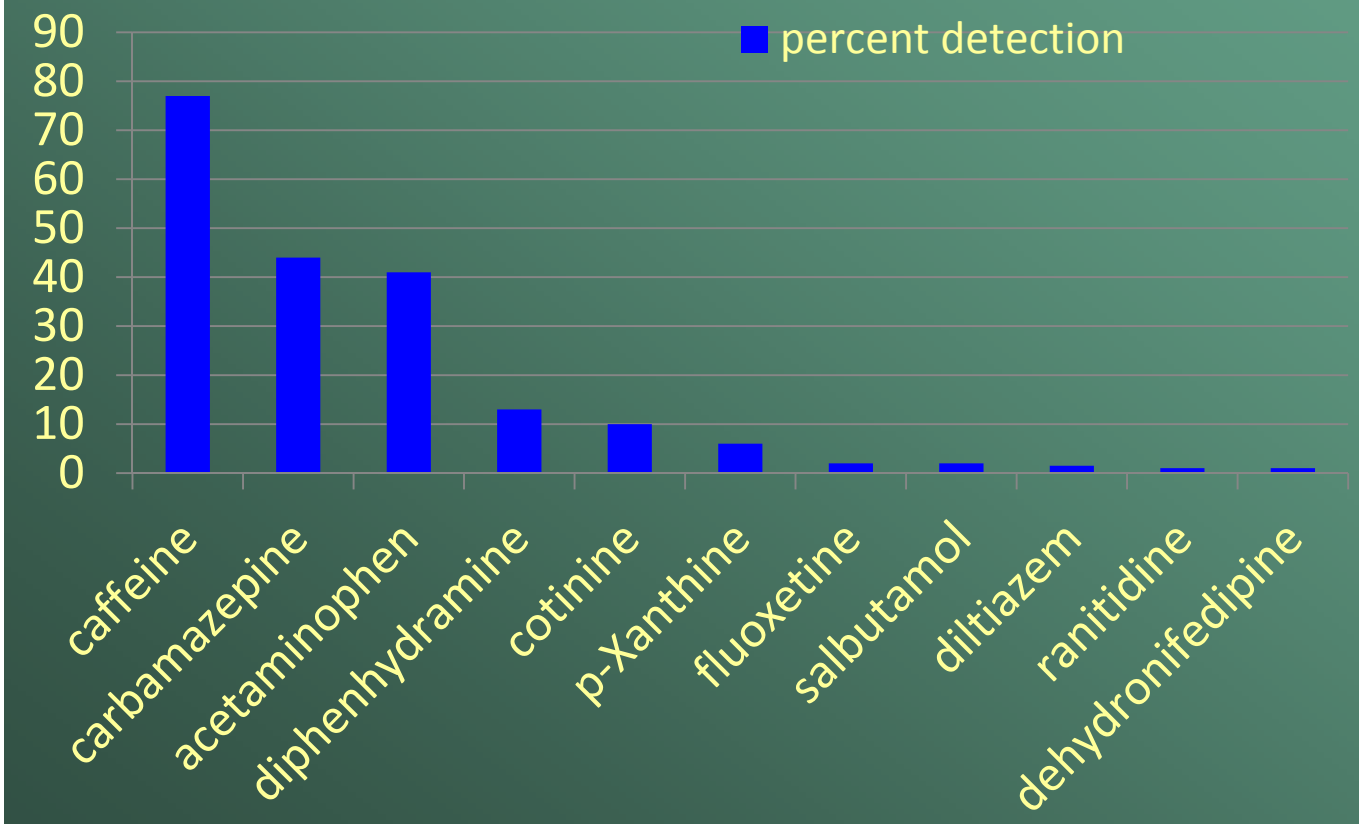
Pharmaceuticals detected



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Commonly Detected Antibiotics

- Sulfamethoxazole - Human use
- Trimethoprim - Human use
- Azithromycin - Human use
- Ofloxacin - Human use
- Tylosin - Used for cattle, swine, and poultry.

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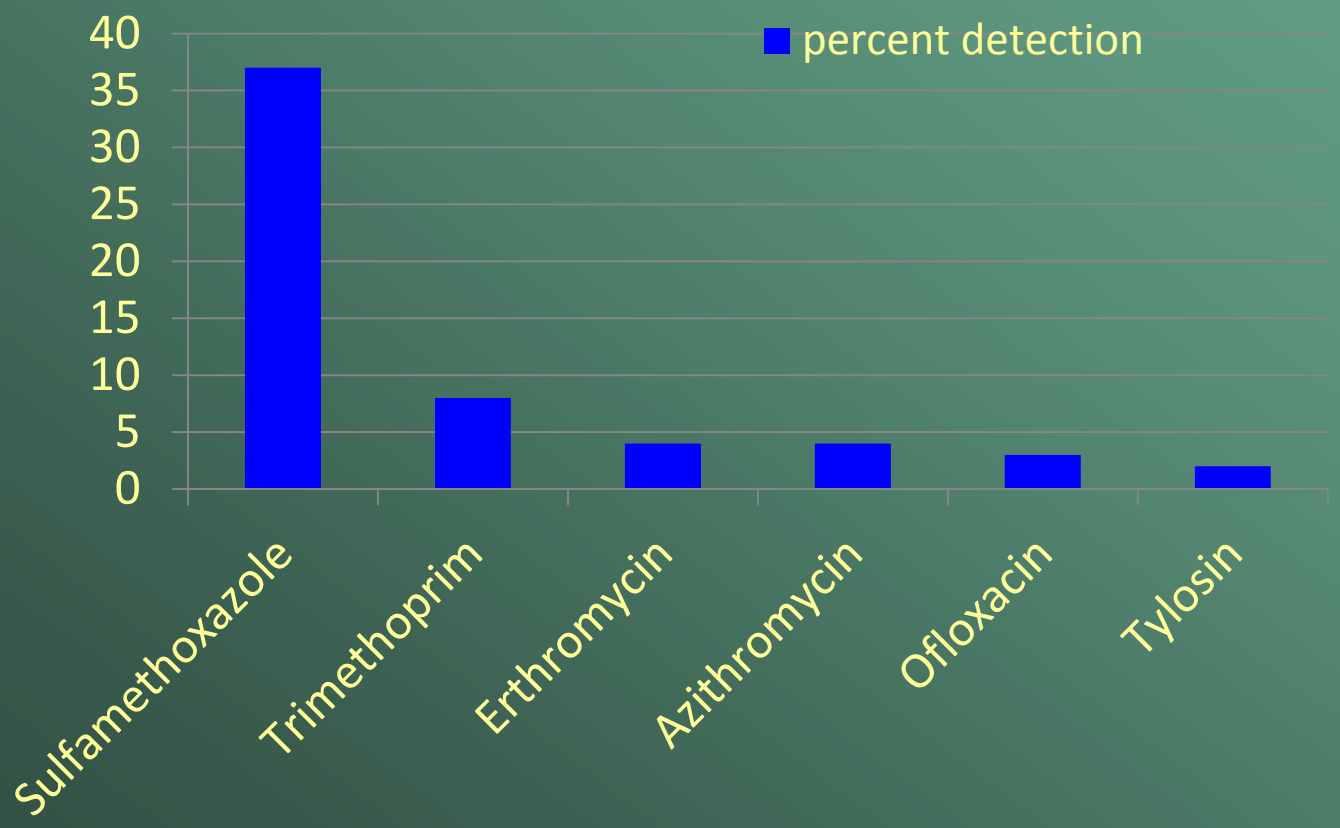
Antibiotics detected



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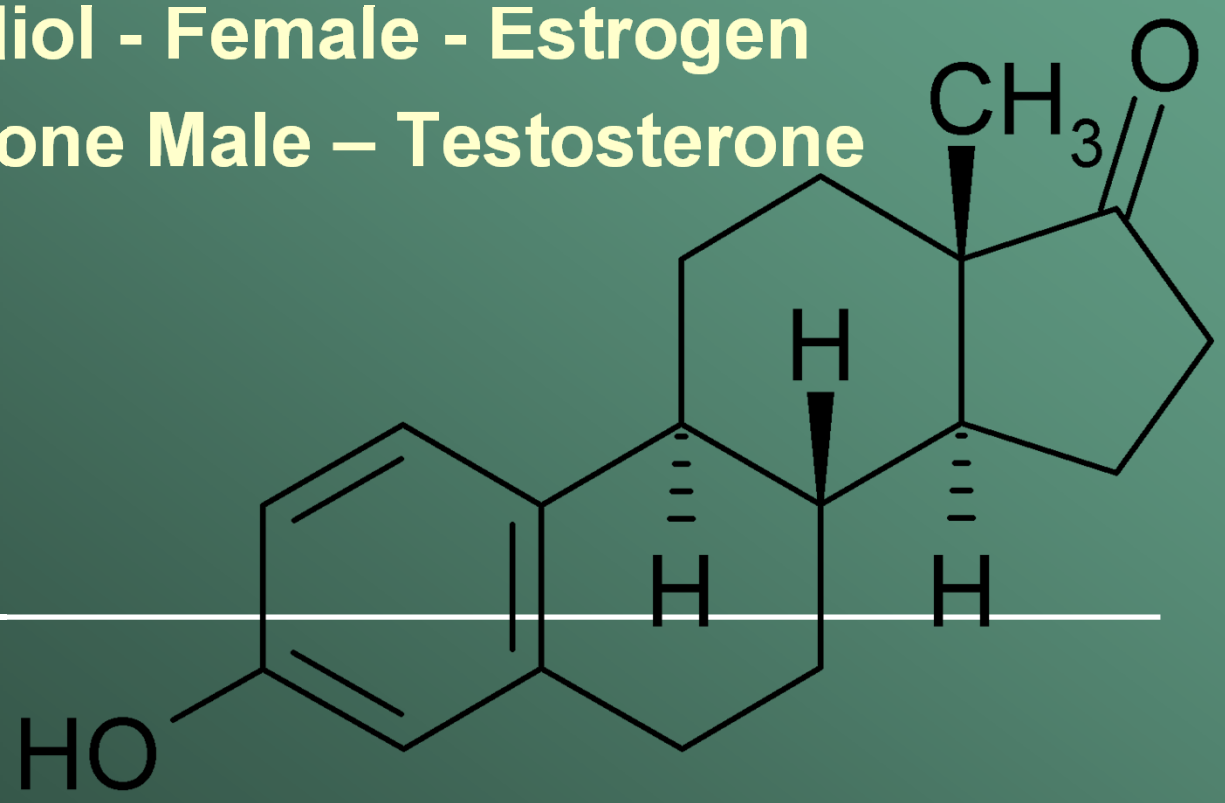
Commonly Detected Hormones

- Estrone - Female - Estrogen
- 4-androstene 3,17 dione Male – testosterone precursor)
- 17 beta estradiol - Female - Estrogen
- Cis-androsterone Male – Testosterone metabolite



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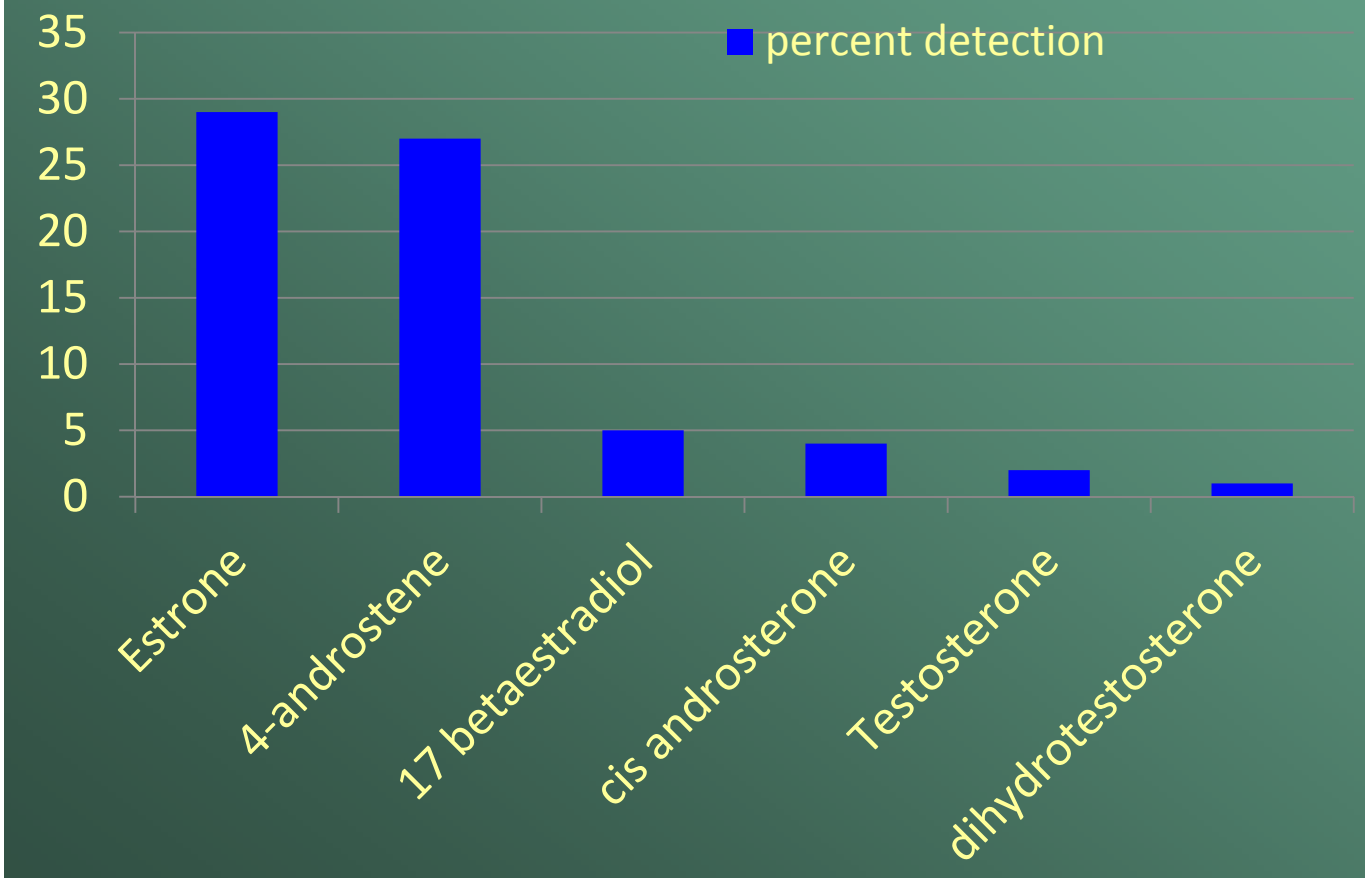
Hormones detected



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Reference Sites

- Sites were established on small watersheds used for drinking water that had limited disturbance in the basin.
- Used to validate the results and to look for contamination in non-point source areas.

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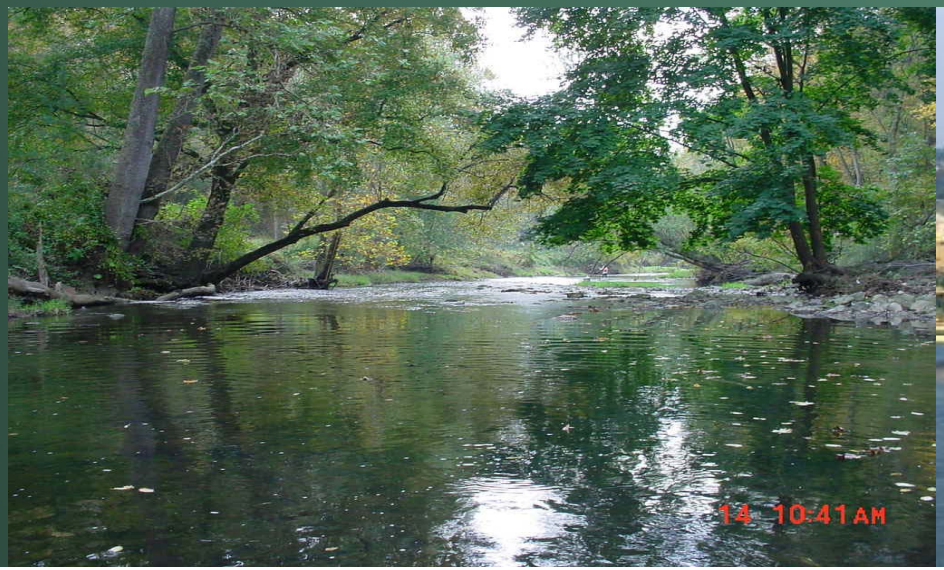
Reference Sites

- 5 Reference sites
  - Average # detections per sample = 1 Max = 4
  - Number of compounds detected = 5
  - Max concentration (acetaminophen) = .03 μg/l
- 21 other sites
  - Average # detections per sample = 4 Max = 10
  - Number of compounds detected = 12
  - Max concentration (acetaminophen) = .21 μg/l



Findings

- Only a few compounds are commonly detected and concentrations are in the PPT range.
- Concentrations lower than at sites downstream of WWTPs.
- Detections and concentrations are flow related. Compounds were concentrated at low flow.

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Findings

- Detections related to number of discharges upstream – basin size.
- Land use related to detection pattern – forested basins had low detection frequencies.

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Fish Health

- 11 sites sampled in 2007 (Susquehanna and Delaware Basins)
- 5 Sites sampled in 2008 (Ohio Basin)
- Chemical sampling along with fish histopathological and molecular-biological examinations
- One time sampling
- Not the primary focus of sampling design.
- Fish work done by Vicki Blazer –USGS Leetown WV.
- Only Chemistry data was looked at in the USGS-Pa study

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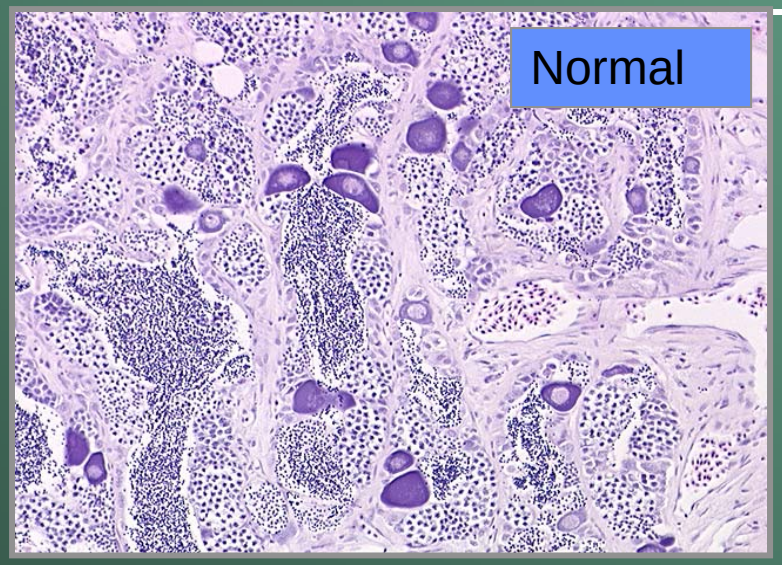
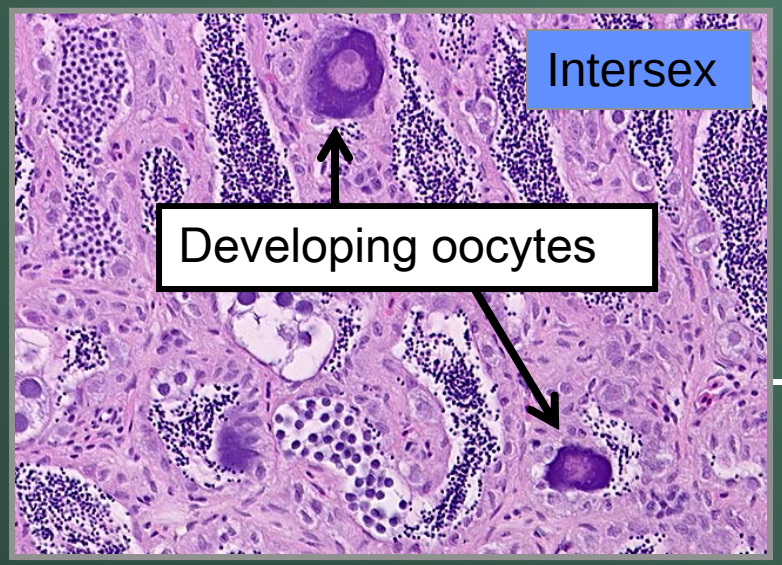
Intersex in Bass





- 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 young fish?
- Smaller population?
- Immune system compromised?

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Fish Health Chemical Results

Detection frequencies of selected compounds in samples collected from sites downstream from wastewater-effluent-discharge sites, 2007-09, sites near drinking-water intakes, 2007-09, and fish-health sites, 2007 and 2008, in Pennsylvania. [ng/L, nanograms per liter]

Compound	Number of analyses	Number of detections at concentrations greater than reporting level	Number of detections at concentrations less than reporting level	Percent detections at any concentration	Concentration range (ng/L)
Sites located downstream from wastewater-effluent-discharge sites (2007-2009)					
Carbamazepine	24	21	0	87	15 - 212
Diphenhydramine	24	11	3	58	3 - 85
Sulfamethoxazole	24	24	0	100	5 - 1,150
Trimethoprim	24	18	0	75	6 - 704
Estrone	24	12	0	50	0.6 - 25
Sites located near drinking-water intake (2007-2009)					
Carbamazepine	297	61	36	33	1 - 95
Diphenhydramine	297	0	20	7	1 - 6
Sulfamethoxazole	294	119	0	40	5 - 146
Trimethoprim	294	23	0	8	5 - 18
Estrone	270	48	3	19	0.3 - 3.1
Fish-health sites (2007 and 2008)					
Carbamazepine	16	10	3	81	3 - 64
Diphenhydramine	16	0	0	0	0
Sulfamethoxazole	16	10	0	62	7 - 101
Trimethoprim	16	1	0	6	12
Estrone	16	9	1	62	0.3 - 2.72

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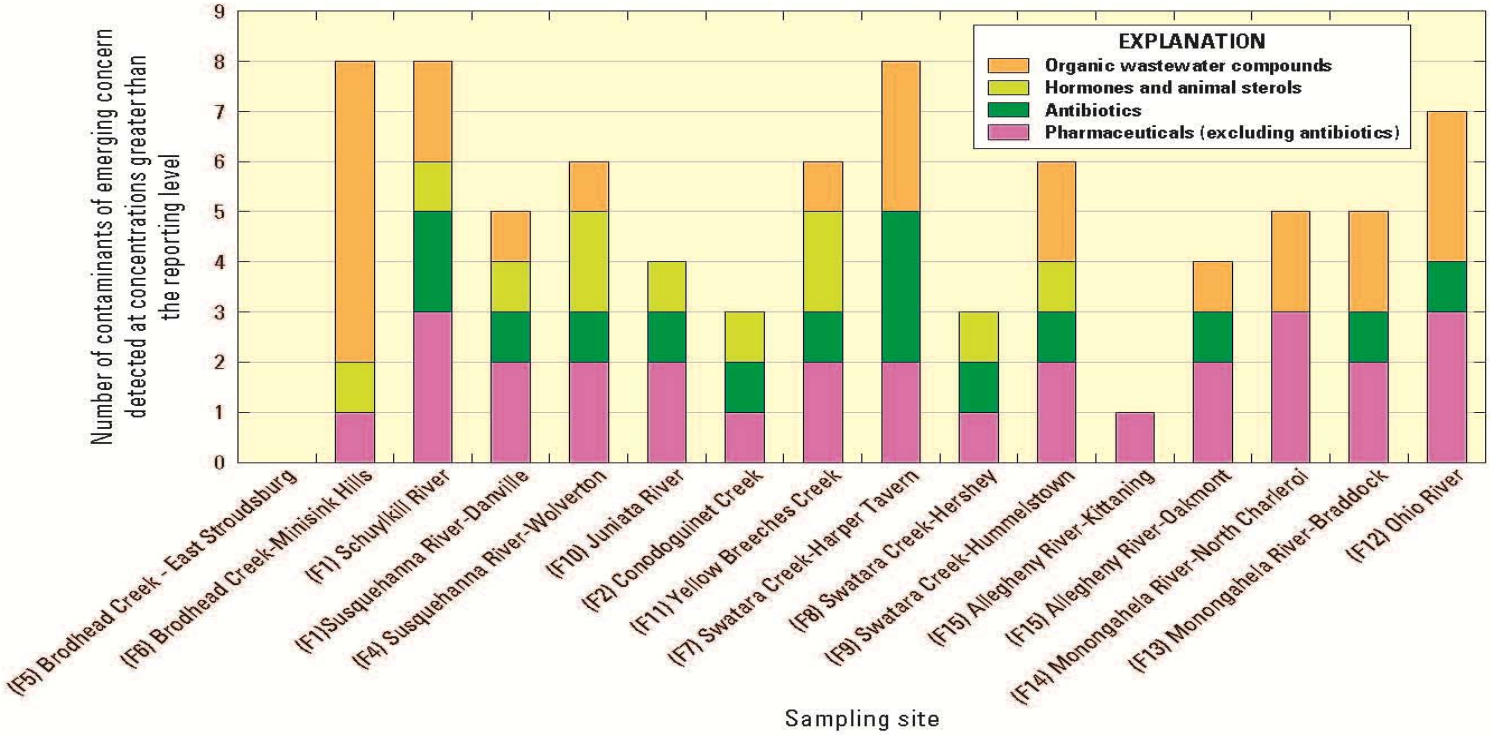

Figure 27. Number of contaminants of emerging concern detected at concentrations greater than the reporting level in streamwater samples collected at 16 fish-health sites sampled in Pennsylvania, 2007 or 2008. (F5, identifier in figure 2)

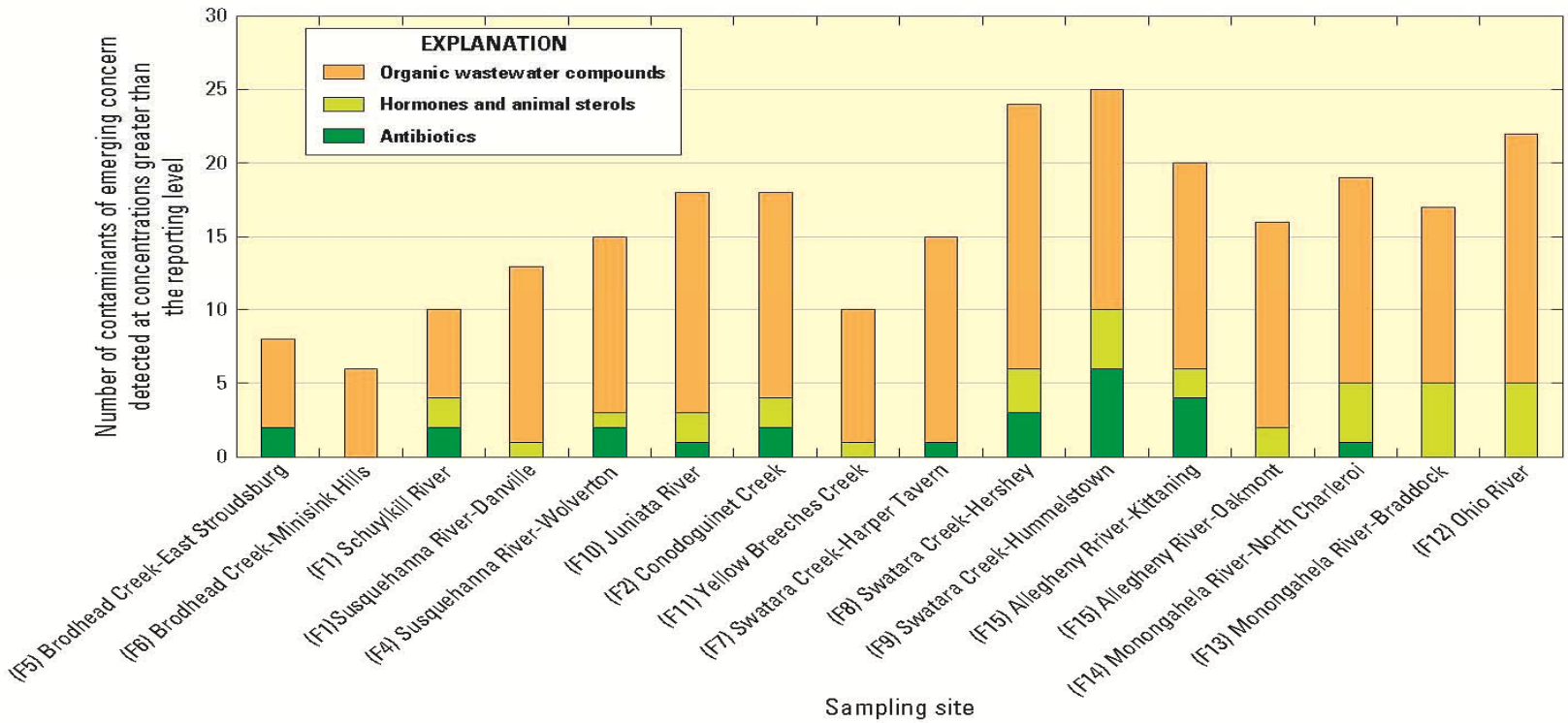

Figure 28. Number of contaminants of emerging concern detected at concentrations greater than the reporting level in streambed-sediment samples from 16 fish-health sites sampled in Pennsylvania, 2007 or 2008. (F5, identifier in figure 2)

Fish Health Chemical Results

- Fish Health Sites in the Susquehanna did not have a significantly high detection frequency or maximum concentration of compounds compared to the Ohio or Delaware basin.
- Hormone concentrations detected were below what has been associated with fish health issues in research studies.

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Fish Health Chemical Results

- Histopathological and molecular-biological examination results will give more info but from the limited chemical data collected there was no conclusive connection between the chemical data and fish issues.

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Ecological Effects

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

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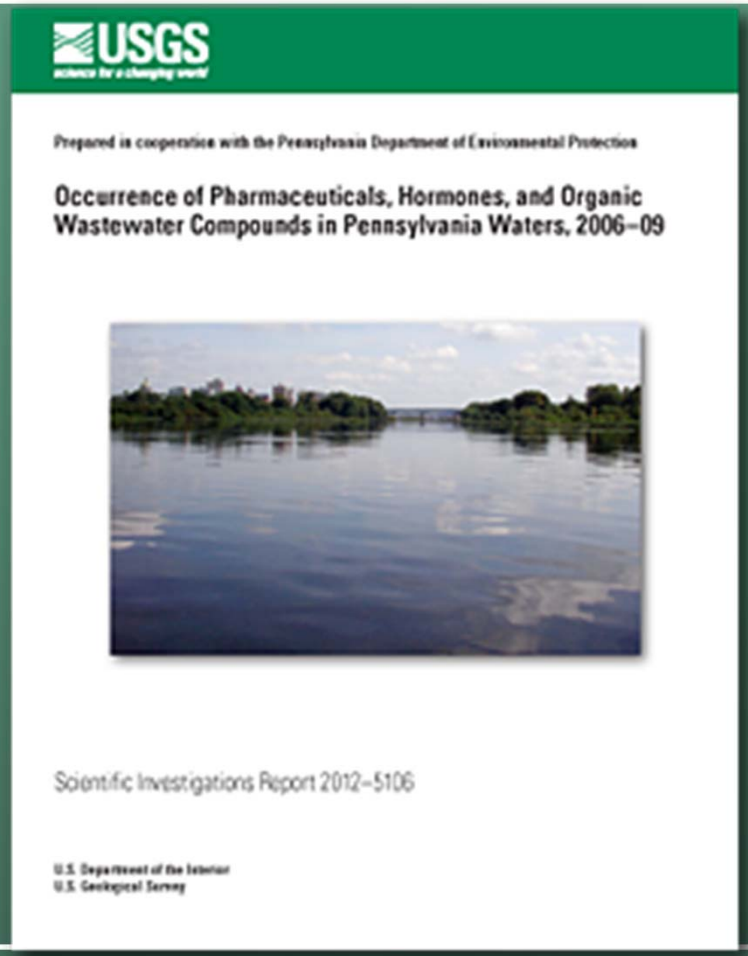
Report

- Available at the USGS PaWSC web site (pa.water.usgs.gov) under highlighted publications.
- Also available from the USGS Pubs warehouse (pubs.er.usgs.gov/publication/sir20125106



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Questions/Thank You

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