Emerging Contaminates in Pennsylvania Waters 2006-2008

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

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

Emerging Contaminates

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

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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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USGS Emerging Contaminate Sampling in Pennsylvania.

- 2 Major projects are being conducted in Pa.
- Both are funded by PaDEP and USEPA
  - Occurrence of Pharmaceuticals and Antibiotic Compounds in Pennsylvania Waters: Phase I – III.
  - Emerging contaminate sampling near drinking water intakes at PaDEP Water Quality Network sites.

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Sample Collection

- Surface-water samples were collected by USGS PaWSC personnel.
- Fish samples were collected by USGS, PaDEP, Pa Fish and Boat, and other State agencies.

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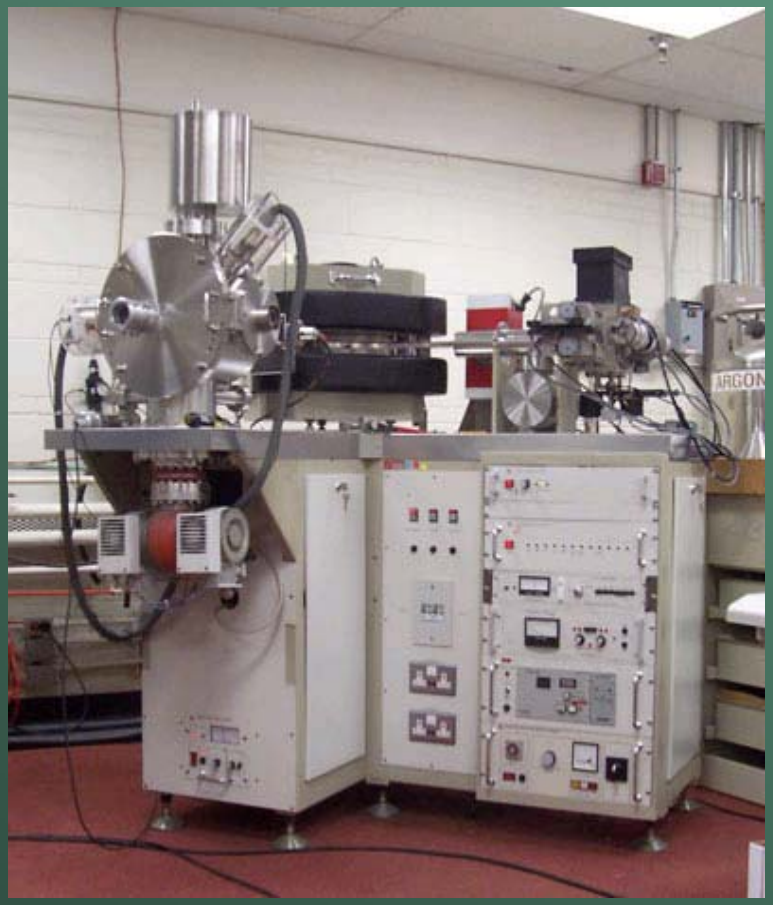
USGS Labs – Water and Sediment



Denver NWQL

- OWC – full production
- Pharmaceutical analysis – full production
- Hormone – custom analysis – research lab

Kansas OGRL

- Antibiotic – custom analysis - research lab

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Fish Health Samples

- USGS BRD West Virginia are doing the fish health analysis including fish necropsy and blood analysis.

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Occurrence of Pharmaceuticals and Antibiotic Compounds in Pennsylvania Waters:

Phase I

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Emerging Contaminates Project – Phase I

The study:

- Occurrence and distribution with temporal component.
- Pharmaceutical compounds
- Antibiotic compounds
- Sample each site four times over a one-year period (Accomplished in 2006)

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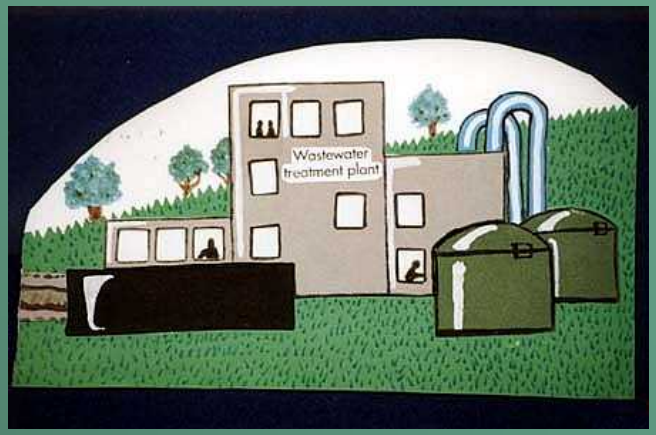
Phase I Scope

- 6 surface-water sites
  - Ag affected
    upstream
    downstream
- 6 surface-water sites
  - WWT affected
    upstream
    downstream
- 6 ground-water wells –
  in agricultural areas



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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

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

Sulfonamides
Sulfachloropyridazine
Sulfadiazine
Sulfadimethoxine
Sulfamethazine
Sulfamethoxazole
Sulfathiazole

Other Antibiotics
Lincomycin
Trimethoprim
Chloramphenicol
Ormetoprim

31 compounds

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Emerging Contaminates Phase I – Results -Livestock Wells

Results:

- Few detections in livestock wells. 5 detections in 24 samples.
  - Four compounds were detected – two pharmaceuticals (cotinine and diphenhydramine) and two antibiotics (tylosin (2) and sulfamethoxazole).
  - Tylosin is the only compound detected that is usually used in agriculture. Others are related to human uses.

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Emerging Contaminates Phase I – Results – Stream sampling

- 12 of 16 (81%) pharmaceuticals were detected at least once.
- 12 of 32 (38%) antibiotic were detected at least once.
- 78% of all detections were downstream from wastewater discharges.
- There were few detections above discharges and the concentrations were lower than the downstream samples.

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Emerging Contaminates Phase I – Results – Stream sampling

- The average number of compounds detected downstream of:
  - Animal feeding operation = 3
  - Municipal-wastewater discharges = 13
- Carbamazepine (Mood stabilizing (epileptic) drug) was the most frequently detected compound below both AFO and WWT discharges.
- All concentrations are low – PPT

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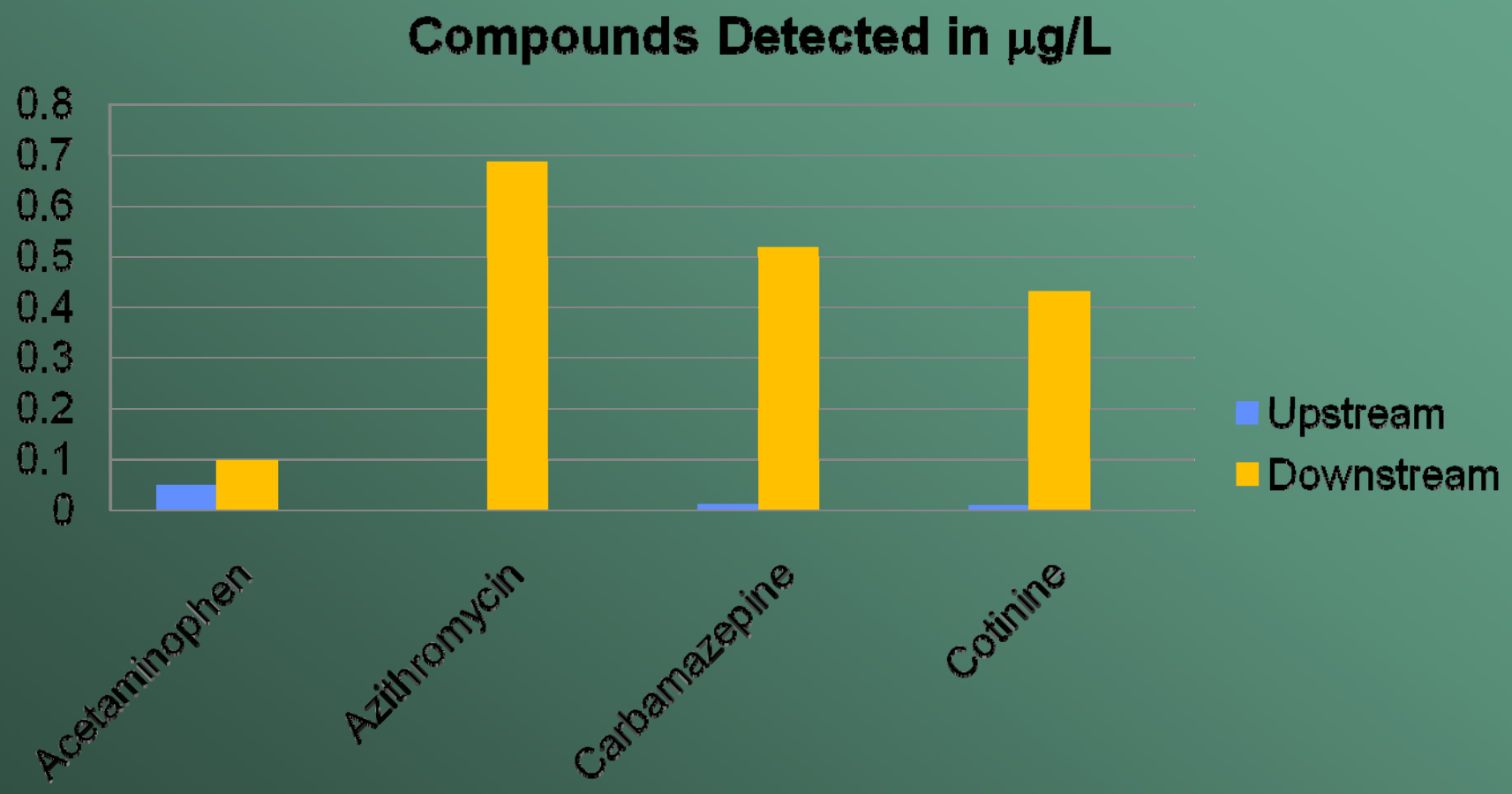
Killinger Creek Upstream vs Downstream



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Compounds with highest concentrations

Below WWT

- Caffeine - stimulant
- P-xanthine – caffeine by-product.
- Carbamazepine - Mood stabilizing (epileptic) drug
- Ibuprofen - analgesic
- Azithromycin - Antibiotic human use
- Sulfamethoxazole - Antibiotic human use
- Ofloxacin Antibiotic human use
- Trimethoprim - Human use usually used with sulfamethoxazole.

Below AFO

- Caffeine - stimulant
- Cotinine – nicotine byproduct
- Diphenhydramine - antihistamine
- Carbamazepine - Mood stabilizing (epileptic) drug
- Oxytetracycline - Antibiotic human use
- Sulfadimethoxine - Antibiotic animal use
- Sulfamethoxazole - Antibiotic human use
- Tylosin – Antibiotic livestock use

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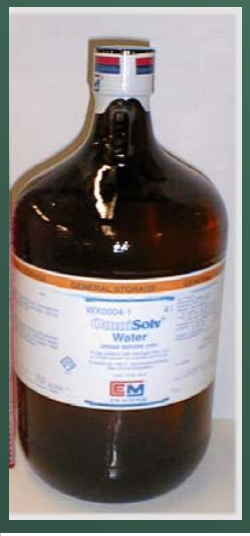
QA samples

Blanks

- 1 detection in 8 blanks submitted to the lab.
  - Tylosin (0.006 μg/L)



Duplicates

- 4 stream sample duplicates and 4 well duplicates.
- Detections in the stream samples were less than 30% relative percent difference.
- There were no detections in well duplicates

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Emerging Contaminates Project – What's Next?

Phase II: 2007-2008

- Continued sampling upstream and downstream of STP and animal Ag areas.
- Groundwater near Ag areas.
- Sediment sampling
- Hormone sampling
- Organic Wastewater Compounds
- Fish sampling (blood and tissue).
  - Inter-sex fish issue

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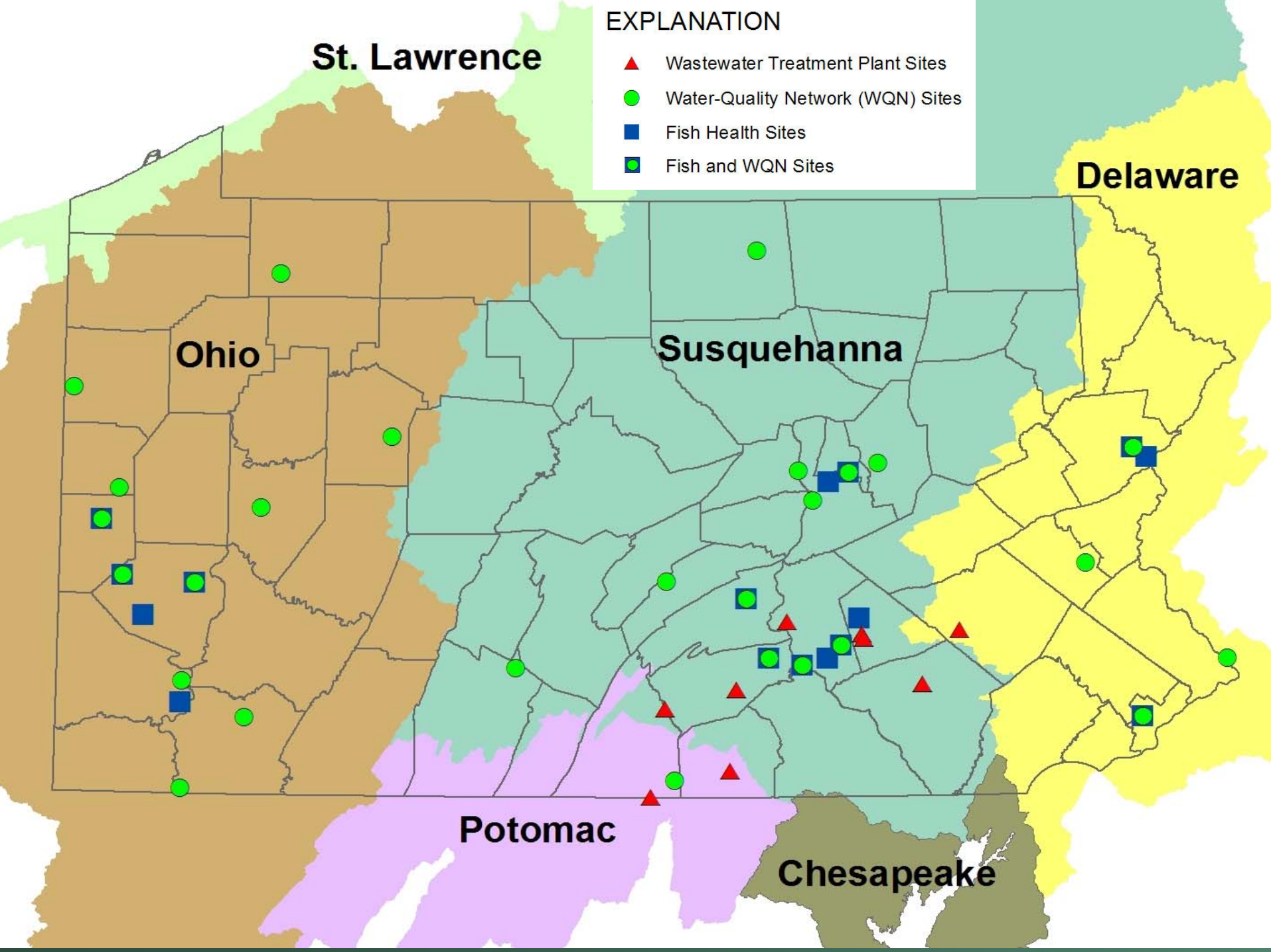
EXPLANATION
Wastewater Treatment Plant Sites
Water-Quality Network (WQN) Sites
Fish Health Sites
Fish and WQN Sites
St. Lawrence
Delaware
Ohio
Susquehanna
Potomac
Chesapeake

Data Report Phase I

Concentrations of Selected Pharmaceuticals and Antibiotics in South-Central Pennsylvania Waters, March through September 2006

By Connie A. Loper, J. Kent Crawford, Kim L. Otto, Rhonda L. Manning1, Michael T. Meyer, and Edward T. Furlong

Data Series 300

http://pa.water.usgs.gov/pa_pubs.html

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Emerging Contaminates near Drinking-Water Intakes

Data collection for pharmaceuticals, antibiotics and hormones in surface-water.

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

USGS PaWSC – PaDEP WQN Sampling

- Coop project with PaDEP – USEPA.
- Started in March 2007.
- Projected 5 years of sampling.
- 27 sites across the state.
- Sampling is focused near drinking water intakes.
- Sampling quarterly for pharmaceuticals, antibiotics and hormones.

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USGS PaWSC – PaDEP Sampling

- 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.

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USGS – City of Wilmington Sampling

- 3 sites in the Brandywine Basin (City of Wilmington Drinking Water Supply)
- Sampled quarterly for pharmaceuticals, antibiotics, hormones, and wastewater compounds.
- Sampling locations are below major wastewater discharges and near the Pa/De border.

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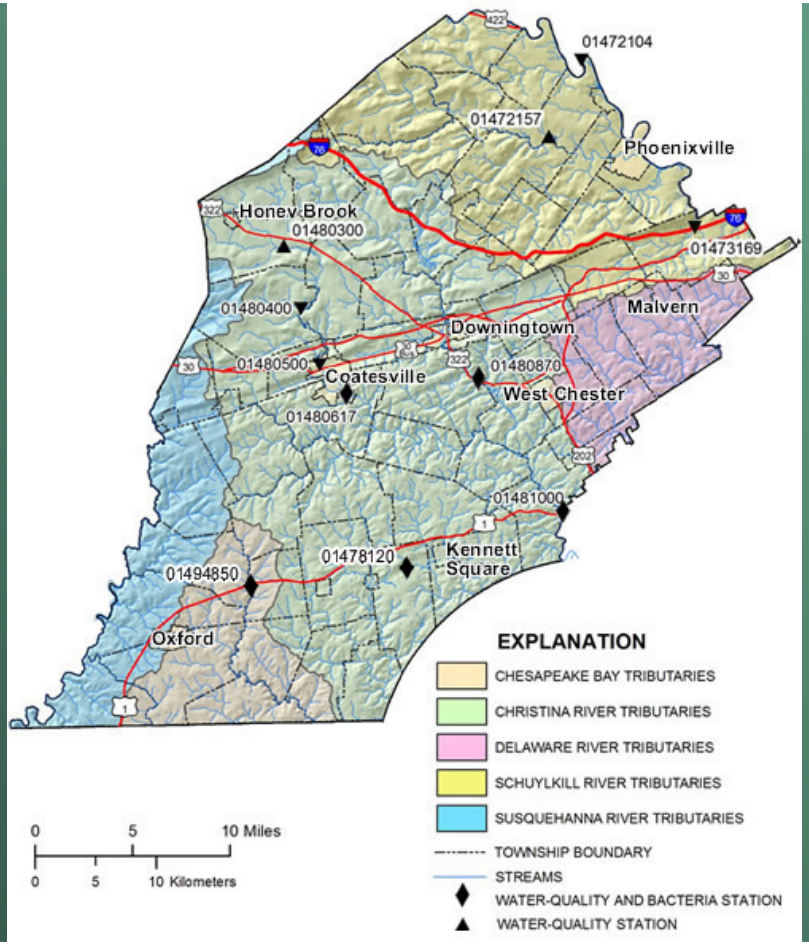
Brandywine Monitoring Sites



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Results

- Chemical results take 2 – 10 months to complete.
- Only partial results have been received.
- Many of the results have “estimated values”
- 147 samples collected
  - pharmaceutical compound (141 analyzed)
  - antibiotic compounds (112 analyzed).
- 120 samples collected for hormones
  - (0 analyzed).

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Results

- All 30 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.

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Results (Pharmaceutical)

- **caffeine** (77% of samples 93% of sites)
  - max = 0.332 μg/L - Stimulant
- **carbamazepine** (43% of samples 80% of sites)
  - max = 0.064 μg/L - Mood stabilizing (epileptic) drug
- **acetaminophen** (41% of samples 80% of sites)
  - max = 0.174 μg/L - Analgesic
- **diphenhydramine** (13% samples 40% sites)
  - max = 0.009 μg/L - Antihistamine (Benadryl)

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Results (Pharmaceutical)

- cotinine (9% samples 37% sites)
  - max = 0.035 μg/L - Metabolite of nicotine
- p-Xanthine (6% samples 23% sites)
  - max = 0.091 μg/L - Caffeine metabolite
  - Diltiazem (3% samples 7% sites)
  - Max = 0.008 μg/L – High blood pressure / heart drug

USGS

Results (Pharmaceutical)

- All other pharmaceutical compounds detected were in less than 2% of the samples analyzed.
  - Dehydronifedipine - high blood pressure
  - Ranitidine – Heartburn (Zantac)
  - Salbutamol - Asthma medication
  - Fluoxetine - Antidepressant (Prozac)

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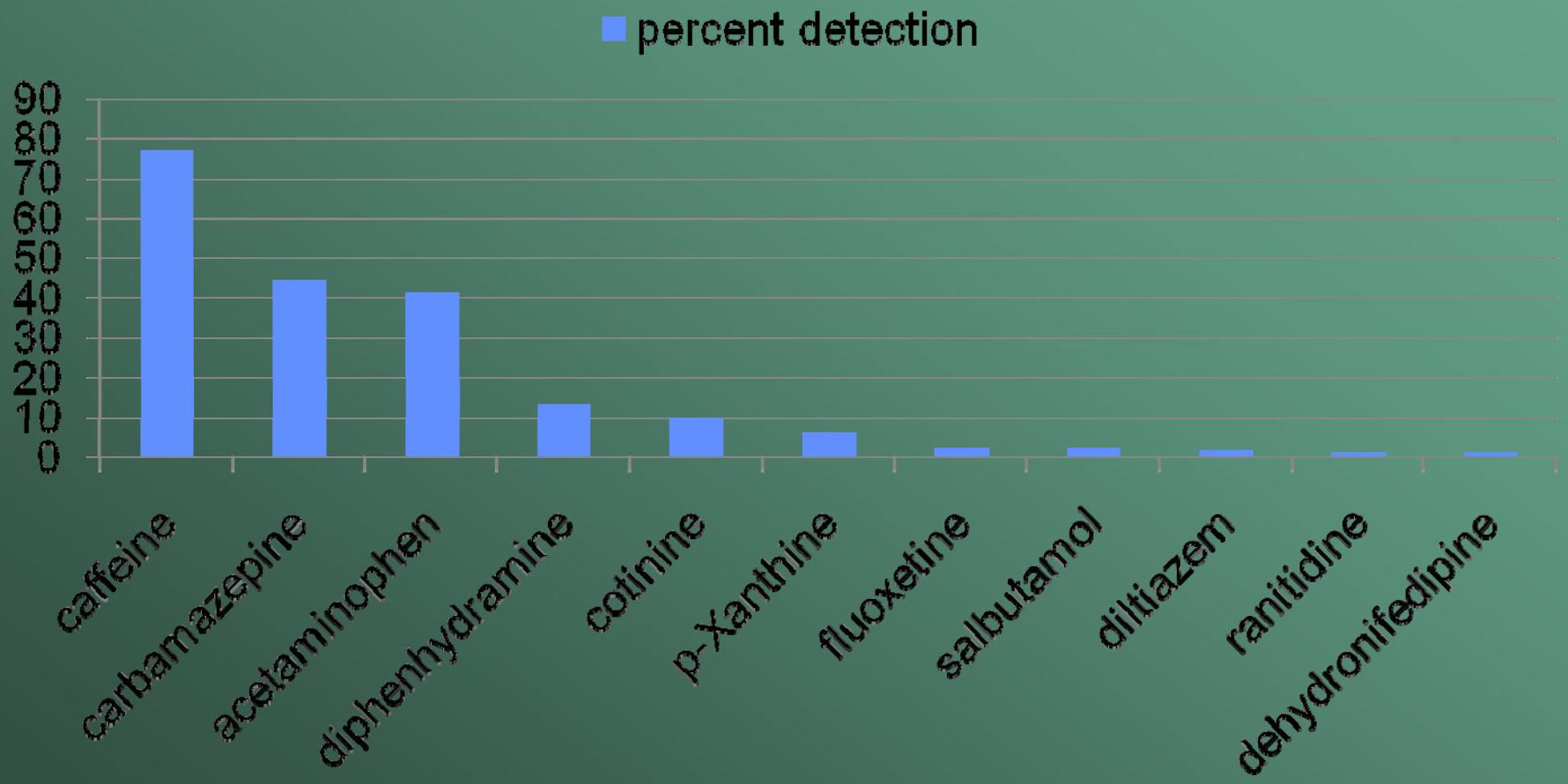
Pharmaceuticals detected



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Results (Antibiotic)

- **sulfamethoxazole (30% samples-57% sites**
  - **max = 0.142 μg/L - Human use**
- **trimethoprim (12% samples-23% sites)**
  - **max = 0.018 μg/L - Human use**
- **azithromycin (7% samples-27% sites)**
  - **max = 0.076 μg/L - Human use**
- **tylosin (3% samples-10% sites)**
  - **max = 0.542 μg/L - Used for cattle, swine, and poultry.**

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Results (Antibiotic)

- ofloxacin (3%) max = 0.033 μg/L
  - Human use
- roxithromycin (2%) max = 0.073 μg/L
  - Human use.
- sulfachloropyridazine (2%) max = 0.015 μg/L
  - Used for cattle, swine, and poultry

- 9 other antibiotic compounds were found once in the 112 samples.

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Results (Antibiotic)

- virginiamycin (conc = 0.043 μg/L)
  - Ethanol fuel production
- ciprofloxacin (conc = 0.029 μg/L)
  - Human use
- iso-chlorotetracycline (conc = 0.261 μg/L)
  - Agricultural use
- epi-iso-chlorotetracycline (conc = 0.149 μg/L)
  - Agricultural use
- tetracycline (conc = 0.019 μg/L)
  - Human use - acne
- lincomycin (conc = 0.007 μg/L)
  - Human use – resistant bacteria

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QA Samples

- 9 blank samples collected
  - 6 samples had no detects
  - 3 samples had 1 detect
    - 0.002 μg/L of acetaminophen - Analgesic
    - 0.011 μg/L of salbutamol - Asthma medication
    - 0.008 μg/L of erythromycin-H_2O – Antibiotic
- Replicate samples were generally within 30 %

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Summary of Pa Results

- Very preliminary - no hormone data.
- Similar very common. Detection pattern in both studies
  - (80-81%) pharmaceutical compounds analyzed were detected at least once.
  - (50-35%) pharmaceutical compounds analyzed were detected at least once.

Higher concentratons near wastewater treatment discharges.

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Summary of Pa Results

- Several compounds are commonly detected.
  - acetaminophen, caffeine, carbamazepine
- Found at large and small sites in various settings.
- We will be looking at the data for patterns in seasonality – land use – flow conditions.
- Need several years of data.

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Questions/Thank You

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