Emerging Contaminants

Assessing Pennsylvania's Watersheds and Drinking Water Supplies

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The Name Game

- *Emerging Contaminants*
- *PiE – Pharmaceuticals in the Environment*
- *PPCP – Pharmaceuticals and Personal Care Products*
- *Microconstituents*
- *Contaminants of Concern*
- *EDCs - Endocrine Disrupting Compounds*

Every Day Products

- OTC drugs
- Prescription pharmaceuticals
- Veterinary drugs
- Nutriceuticals
- Antibacterial soaps
- Fragrances
- Lotions
- Flame retardants
- Plasticizers
- Pesticides
- PCBs
- Detergents
- Shampoos
- Sunscreens
- Cosmetics

Emerging Contaminants

- Comprised of thousands of distinct chemical entities.
- Numerous therapeutic classes and end uses.
- Enter the environment at the rate of thousands of tons per year
- Little is known regarding the potential for effects.
- In general, they are not regulated water pollutants.

Emerging Contaminants

- Not a new phenomenon
- Recent advancements in laboratory chemical analysis methodologies have lowered the limits of detection
- **Have existed in the environment for as long as they have been used commercially**

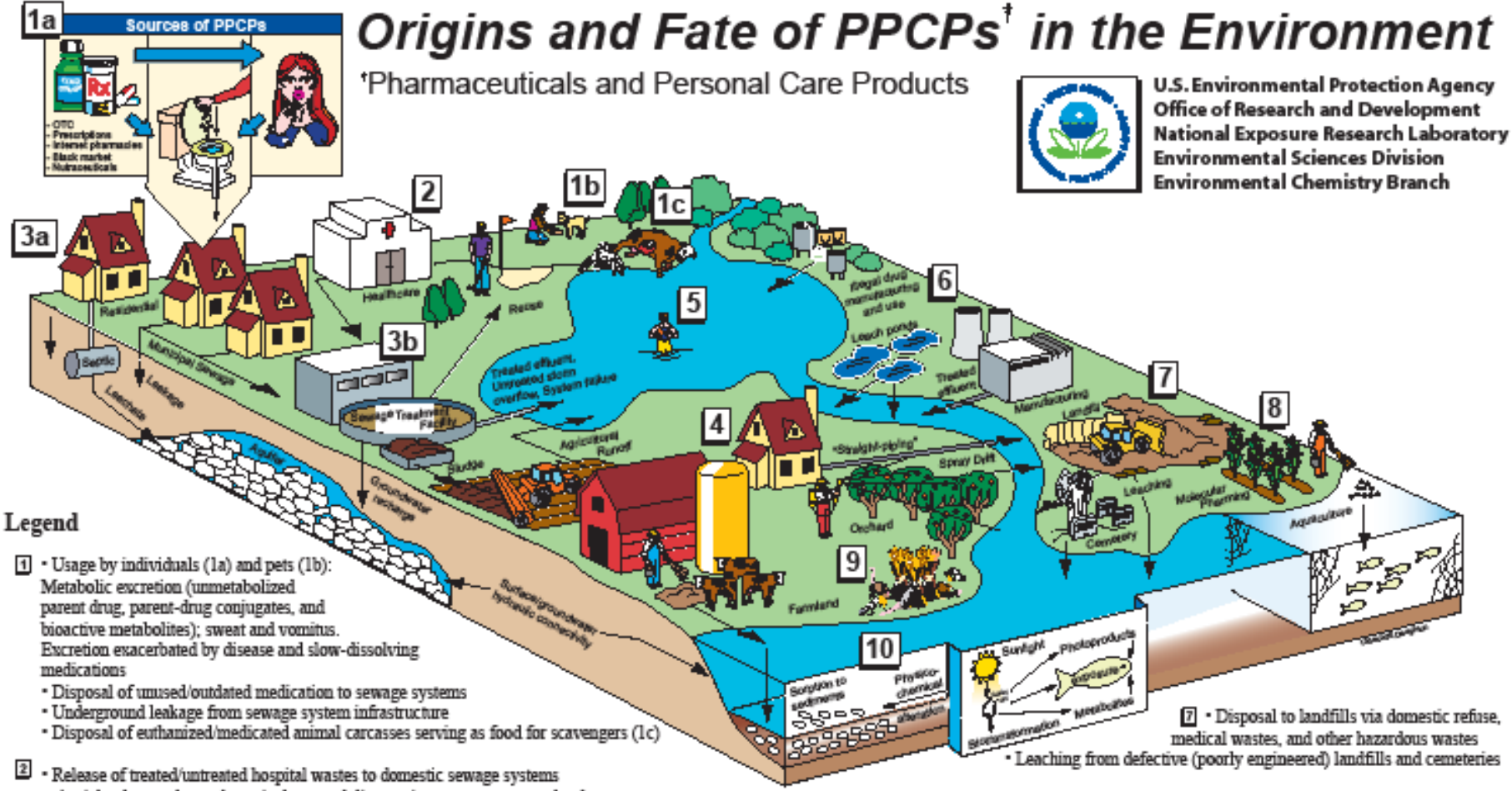
Emerging Contaminants

- Far from “Emerging”
- High public visibility – media interest
- Multi-disciplinary

Origins and Fate of PPCPs† in the Environment

†Pharmaceuticals and Personal Care Products

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Environmental Chemistry Branch



Legend

1 • Usage by individuals (1a) and pets (1b): Metabolic excretion (unmetabolized parent drug, parent-drug conjugates, and bioactive metabolites); sweat and vomitus. Excretion exacerbated by disease and slow-dissolving medications
- Disposal of unused/outdated medication to sewage systems
- Underground leakage from sewage system infrastructure
- Disposal of euthanized/medicated animal carcasses serving as food for scavengers (1c)

2 • Release of treated/untreated hospital wastes to domestic sewage systems (weighted toward acutely toxic drugs and diagnostic agents, as opposed to long-term medications); also disposal by pharmacies, physicians, humanitarian drug surplus

3 • Release to private septic/leach fields (3a)
- Treated effluent from domestic sewage treatment plants discharged to surface waters, re-injected into aquifers (recharge), recycled/reused (irrigation or domestic uses) (3b)
- Overflow of untreated sewage from storm events and system failures directly to surface waters (3b)

4 • Transfer of sewage solids ("biosolids") to land (e.g., soil amendment/fertilization)
- "Straight-piping" from homes (untreated sewage discharged directly to surface waters)
- Release from agriculture: spray drift from tree crops (e.g., antibiotics)
- Dung from medicated domestic animals (e.g., feed) - CAFOs (confined animal feeding operations)

5 • Direct release to open waters via washing/bathing/swimming

6 • Discharge of regulated/controlled industrial manufacturing waste streams
- Disposal/release from clandestine drug labs and illicit drug usage

7 • Disposal to landfills via domestic refuse, medical wastes, and other hazardous wastes
- Leaching from defective (poorly engineered) landfills and cemeteries

8 • Release to open waters from aquaculture (medicated feed and resulting excreta)
- Future potential for release from molecular pharming (production of therapeutics in crops)

9 • Release of drugs that serve double duty as pest control agents: examples: 4-aminopyridine, experimental multiple sclerosis drug → used as avicide; warfarin, anticoagulant → rat poison; azacholesterol, antilipidemics → avian/rodent reproductive inhibitors; certain antibiotics → used for orchard pathogens; acetaminophen, analgesic → brown tree snake control; caffeine, stimulant → *coqui* frog control

10 Ultimate environmental transport/fate:
- most PPCPs eventually transported from terrestrial domain to aqueous domain
- phototransformation (both direct and indirect reactions via UV light)
- physicochemical alteration, degradation, and ultimate mineralization
- volatilization (mainly certain anesthetics, fragrances)
- some uptake by plants
- respirable particulates containing sorbed drugs (e.g., medicated-feed dusts)

Christian G. Daughton, U.S. EPA-Las Vegas

March 2006
(original February 2001)

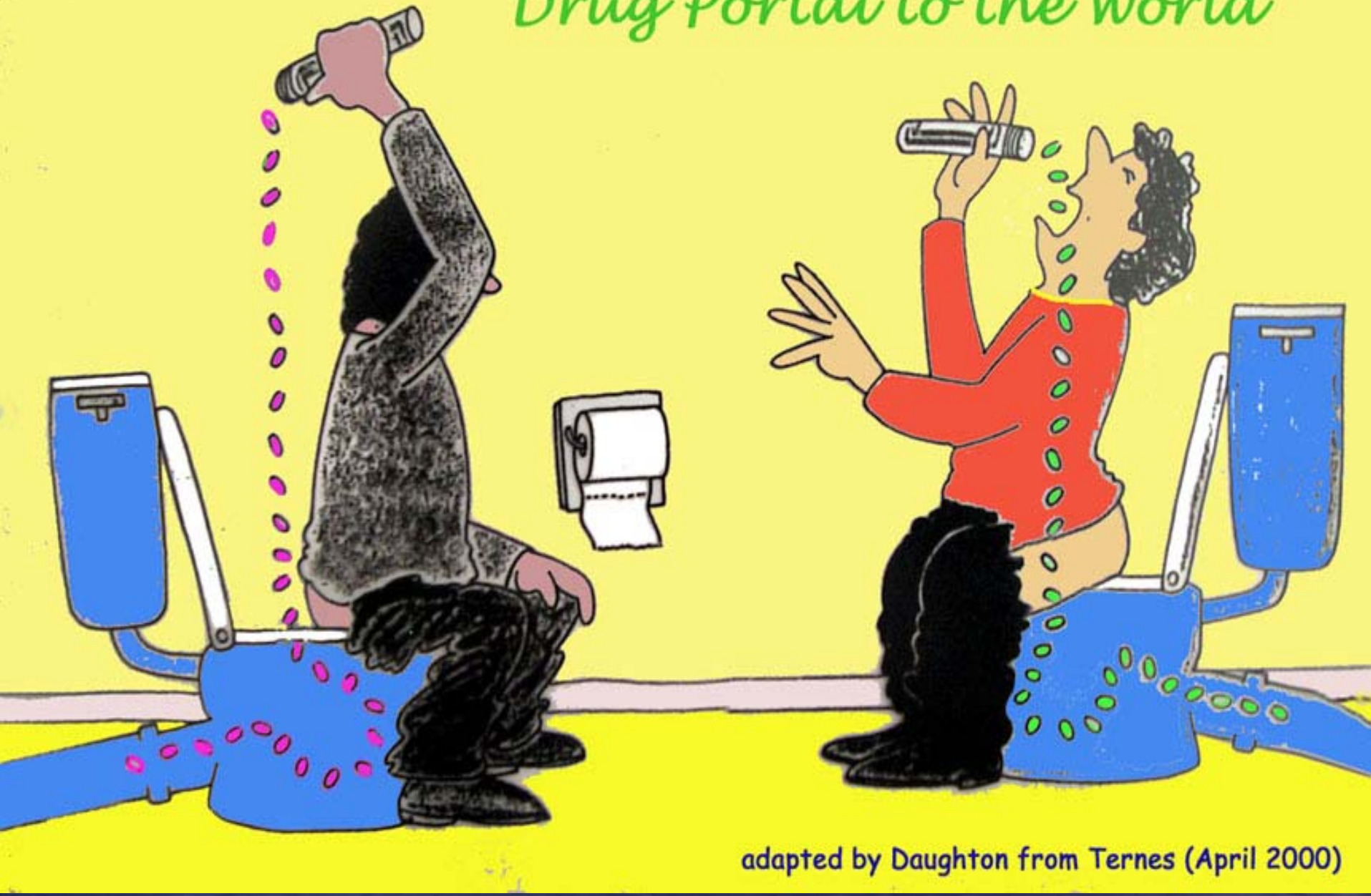
http://epa.gov/esd/esd1/chemistry/pharms/images/drawing.pdf
from: http://epa.gov/esd/esd1/chemistry/pharms/

http://www.epa.gov/ppcp/basic2.html

Origins of Emerging Contaminants

- Human excretion
- Veterinary use of medications
- Livestock operations
- Hospital pharmaceutical waste
- Common practice of flushing unused or expired meds

Drug Portal to the World



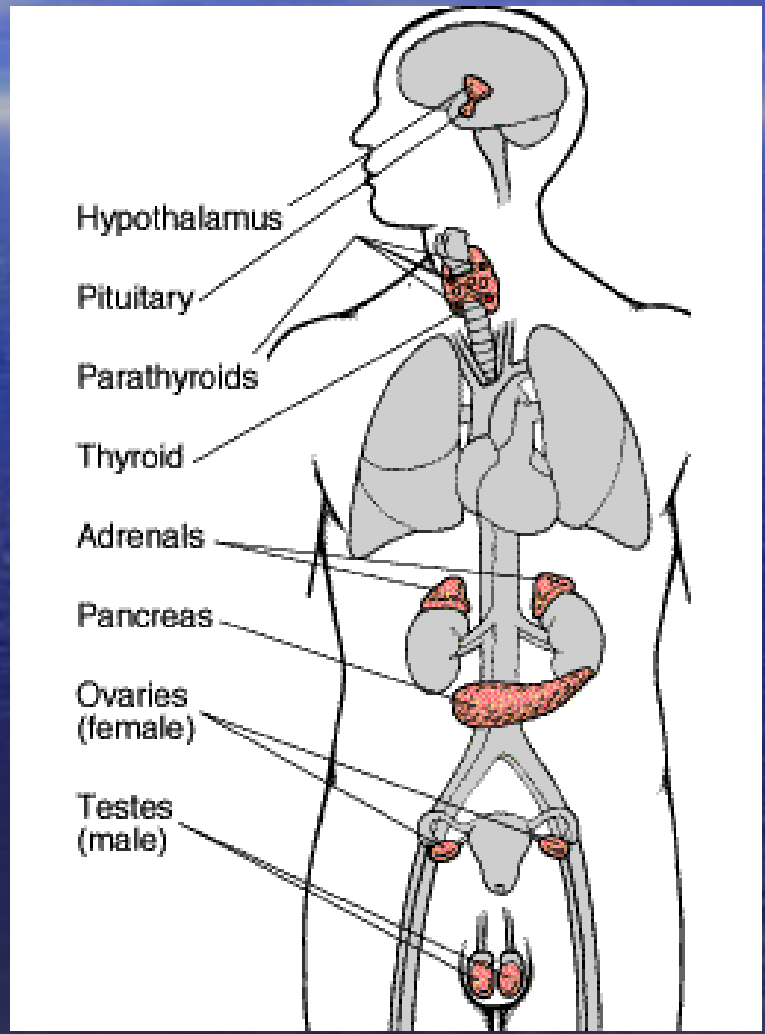
adapted by Daughton from Ternes (April 2000)

Concerns

- May degrade quickly, but constant input to water
- Possible subtle effects, even at ppb
- Chlorine in DW or WW makes some by-products more toxic
- Potential for cumulative and synergistic effects from multiple exposures
- Antibiotic resistant bacteria
- More questions than answers about effects of pharms on aquatic species & human health

Endocrine Disruptors

- Synthetic chemicals that when absorbed into the body can either mimic or block hormones in turn disrupting the body's normal functions.



http://ec.europa.eu/research/endocrine/images/major-endo.gif

Concerns

- Effects on aquatic life are a major concern.
- Exposure risks for aquatic organisms are much larger than those for humans.
- Aquatic organisms have:
  - continual exposures
  - multi-generational exposures
  - exposure to higher concentrations of PPCPs in untreated water
  - possible low dose effects

Why Can't We Take the Compounds out of the Water?

- POTWs are not designed to remove emerging contaminants
- Promising technologies include:
  - Oxidation
  - Ozonation
  - Ultrasound
  - Activated carbon
  - Reverse osmosis
- Longer retention times (POTWs with nutrient removal) look promising
- Focus on controlling disposal at source

Motivation

- **USGS "Reconnaissance" study in 1999-2000 was 1st nationwide investigation of pharms, hormones, & other organic contaminants in 139 streams in 30 states:**
  - 82 of 95 antibiotics, prescription & non-prescrip drugs, steroids, & hormones were found in at least 1 sample
  - 80% streams had 1 or more contaminant
  - 75% streams contained 2 or more
  - 54% had more than 5
  - 34% had more than 10
  - 13% tested positive for more than 20 targeted contaminants

Kolpin, D.W. et al. 2002. "Pharmaceuticals, hormones, & other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance." Environmental Science & Technology. 36(6):1202-1211.

Recent Issues Attracted Public Attention

- **Fish Kills of Smallmouth Bass and Sunfish**
  - South Branch Potomac, WV - 2002
  - North Fork, Shenandoah, VA – 2004, 2006
  - South Fork, Shenandoah – 2005
  - Juniata River, Susquehanna, PA - 2005

- **Intersex in Smallmouth Bass**
  - Condtion in which immature eggs are found in the testes
  - Intersex (ovotestis; testisova) is a general term for gonadal abnormalities most often noted microscopically, occasionally macroscopically, in which both male and female characteristics are present
  - Indicator of exposure to estrogenic compounds

Vitellogenin in Male Fishes

- Egg yolk precursor protein
- Males have the gene to produce vitellogenin - usually not turned on
- Exposure to natural and synthetic estrogens may stimulate vitellogenin production by males

Journal of Aquatic Animal Health

- ***Intersex (Testicular Oocytes) in Smallmouth Bass from the Potomac River and Selected Nearby Drainages***
  - V. S. Blazer, L. R. Iwanowicz, D. D. Iwanowicz, D. R. Smith, J. A. Young, J. D. Hedrick, S. W. Foster, and S. J. Reeser

- *Journal of Aquatic Animal Health* 2007;19:242–253

- The prevalence of testicular oocytes is discussed in terms of human population and agricultural intensity.

DEP Project Overview Phase I

- **Purpose:**
  - To document the occurrence and distribution of selected emerging contaminants in streams and well water in South Central PA

DEP Project Overview Phase I

- Screen for pharmaceutical and antibiotic compounds in southcentral PA
  - 5 streams—effluent dominated
  - 6 streams—agricultural areas
    - Samples were collected at locations upstream and downstream of the municipal effluents or animal feeding operations
  - 6 wells
- Analyze the data
  - compounds detected?
  - at what concentrations?
- Future activities
  - Part 2 study/follow-up
  - collaboration and coordination

Streams Receiving Wastewater Effluent

- Spring Creek, Berks County
- Lititz Run, Lancaster County
- Killinger Creek, Lebanon County
- Middle Spring Creek, Franklin County
- Mountain Creek, Cumberland County
- *Conoy Creek, Lancaster County

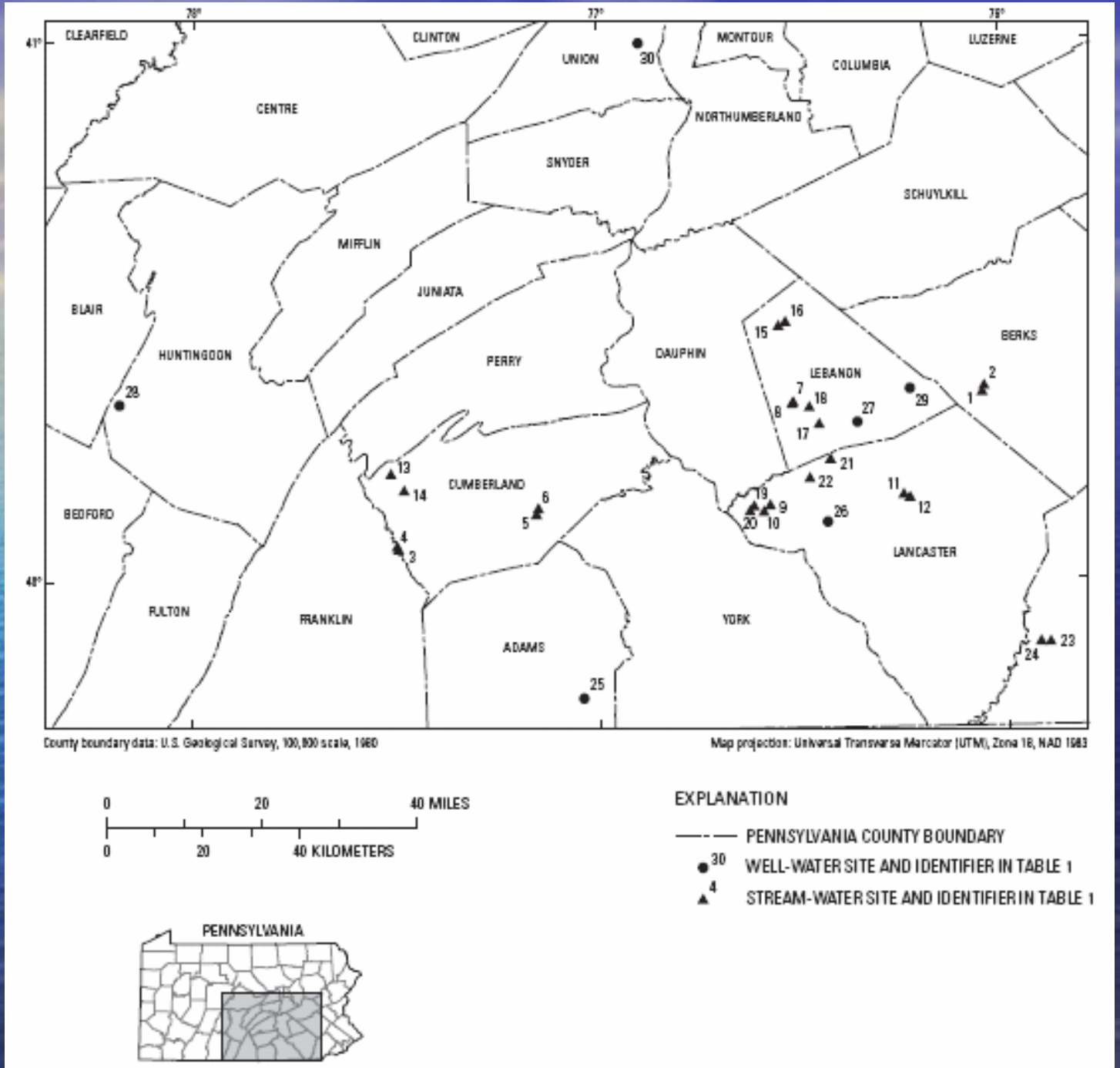
*disqualified

Streams in Agricultural Areas Dominated by AFOs

- Muddy Run, Chester County
- Bachman Run, Lebanon County
- Snitz Creek, Lancaster County
- Trout Run, Lebanon County
- Little Chickies Creek, Lancaster County
- Three Square Hollow Run, Cumberland County

Wells

- 6 locations in Adams, Huntington, Lancaster and Union Counties
- Primarily represent agricultural areas
- Not used for drinking water


78°
77°
76°
41°
40°
CLEARFIELD
CLINTON
UNION
MONTOUR
LUZERNE
COLUMBIA
CENTRE
NORTHUMBERLAND
SNYDER
SCHUYLKILL
MIFFLIN
JUNIATA
BLAIR
HUNTINGDON
PERRY
DAUPHIN
BERKS
LEBANON
CUMBERLAND
BEDFORD
LANCASTER
FULTON
FRANKLIN
ADAMS
YORK
County boundary data: U.S. Geological Survey, 100,000 scale, 1980
Map projection: Universal Transverse Mercator (UTM), Zone 18, NAD 1983
0 20 40 MILES
0 20 40 KILOMETERS
PENNSYLVANIA
EXPLANATION
PENNSYLVANIA COUNTY BOUNDARY
30 WELL-WATER SITE AND IDENTIFIER IN TABLE 1
4 STREAM-WATER SITE AND IDENTIFIER IN TABLE 1

Data Analysis

- Samples collected in March/April, May, July and September 2006
- Analyses were completed on 120 environmental samples and 21 quality-control samples
- Of the 120 environmental samples:
  - 24 samples were collected from wells in ag. areas used to supply water to livestock
  - 48 from stream water locations adjacent to municipal wastewater effluents
  - 48 from stream water locations adjacent to animal feeding operations

Data Analysis

- Pharmaceuticals
  - Suite of 15 compounds
  - USGS National Water Quality Laboratory (NWQL) in Denver, CO
- Antibiotics
  - Suite of 31 compounds
  - USGS Organic Geochemistry Research Laboratory (OGRL) in Lawrence, KS

Results

- In stream samples, 13 pharmaceuticals and 11 antibiotics were detected at least once
- 78% of all detections were analyzed in samples collected downstream of municipal wastewater effluents
- A total of 5 detections in well samples

Results

- **Streams Receiving Wastewater Effluent**
  - Pharmaceuticals:
    - Caffine (4.75 µg/L) (micrograms per liter)
    - Para-xanthine (0.853 µg/L)
    - Carbamazepine (0.516 µg/L)
    - Ibuprofen (0.227 µg/L)
  - Antibiotics:
    - Azithromycin (1.65 µg/L)
    - Sulfamethoxazole (1.34 µg/L)
    - Ofloxacin (0.329 µg/L)
    - Trimethoprim (0.256 µg/L)

Results

- **Streams receiving runoff from animal feeding operations**
  - Pharmaceuticals: (max. conc. of 0.053 µg/L)
    - Acetaminophen
    - Caffine
    - Cotinine
    - Diphenhydramine
    - Carbamazepine
  - Antibiotics: (max. conc. of 0.157 µg/L)
    - Oxoxytetracycline
    - Sulfadimethoxine
    - Sulfamethoxazole
    - Tylosin

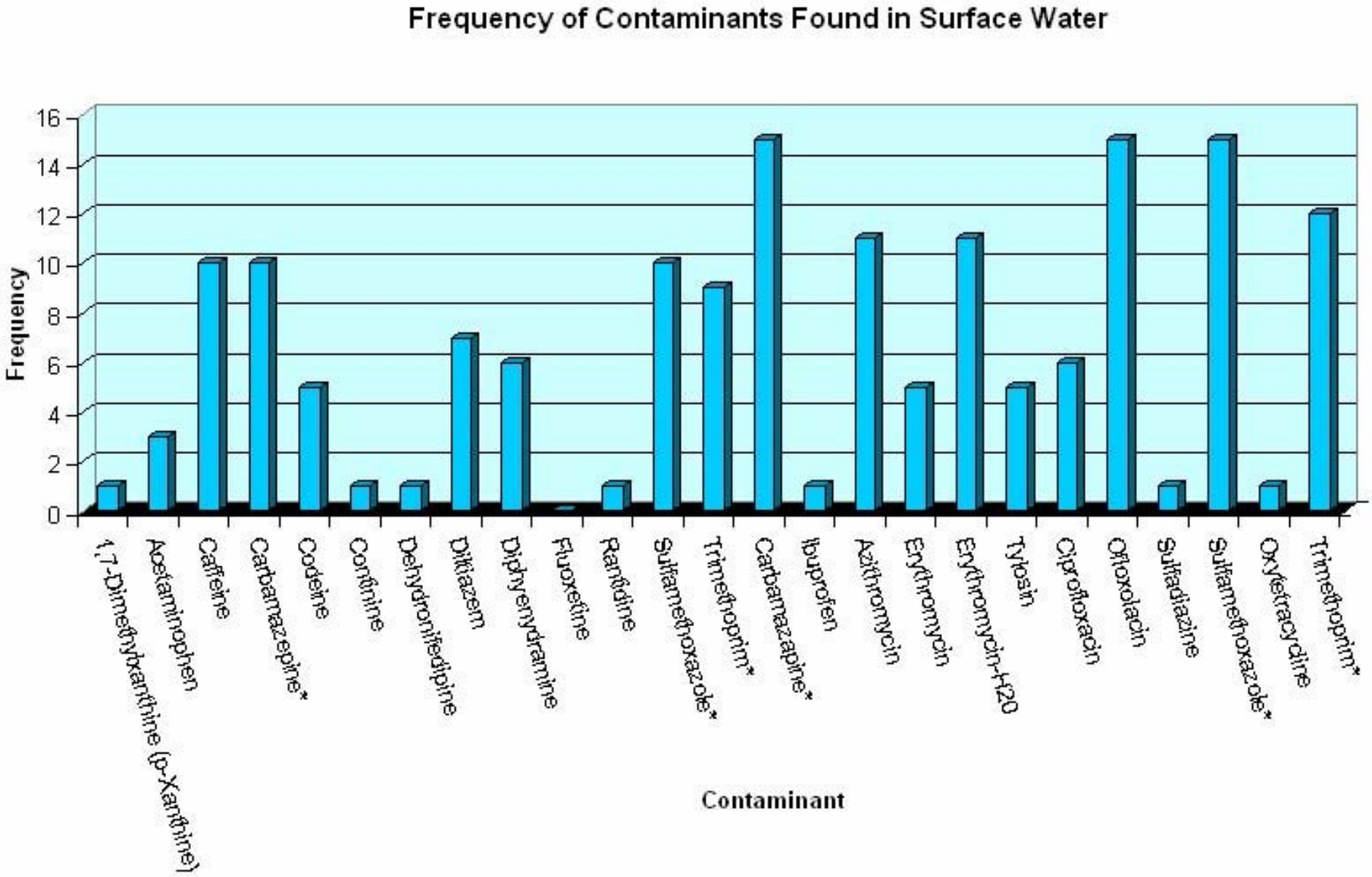
Results

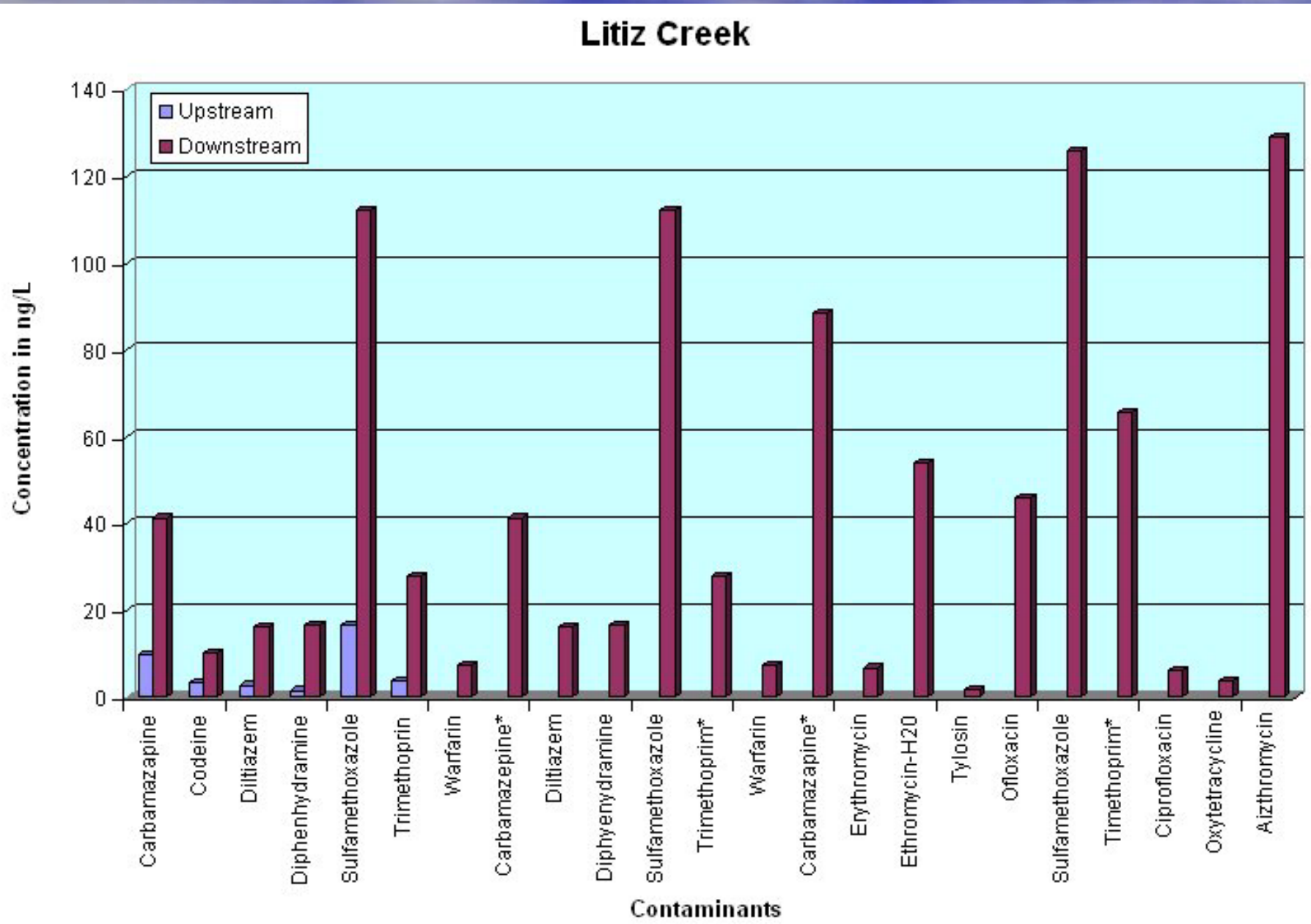
- The average number of compounds detected downstream from municipal-wastewater effluents was 13.

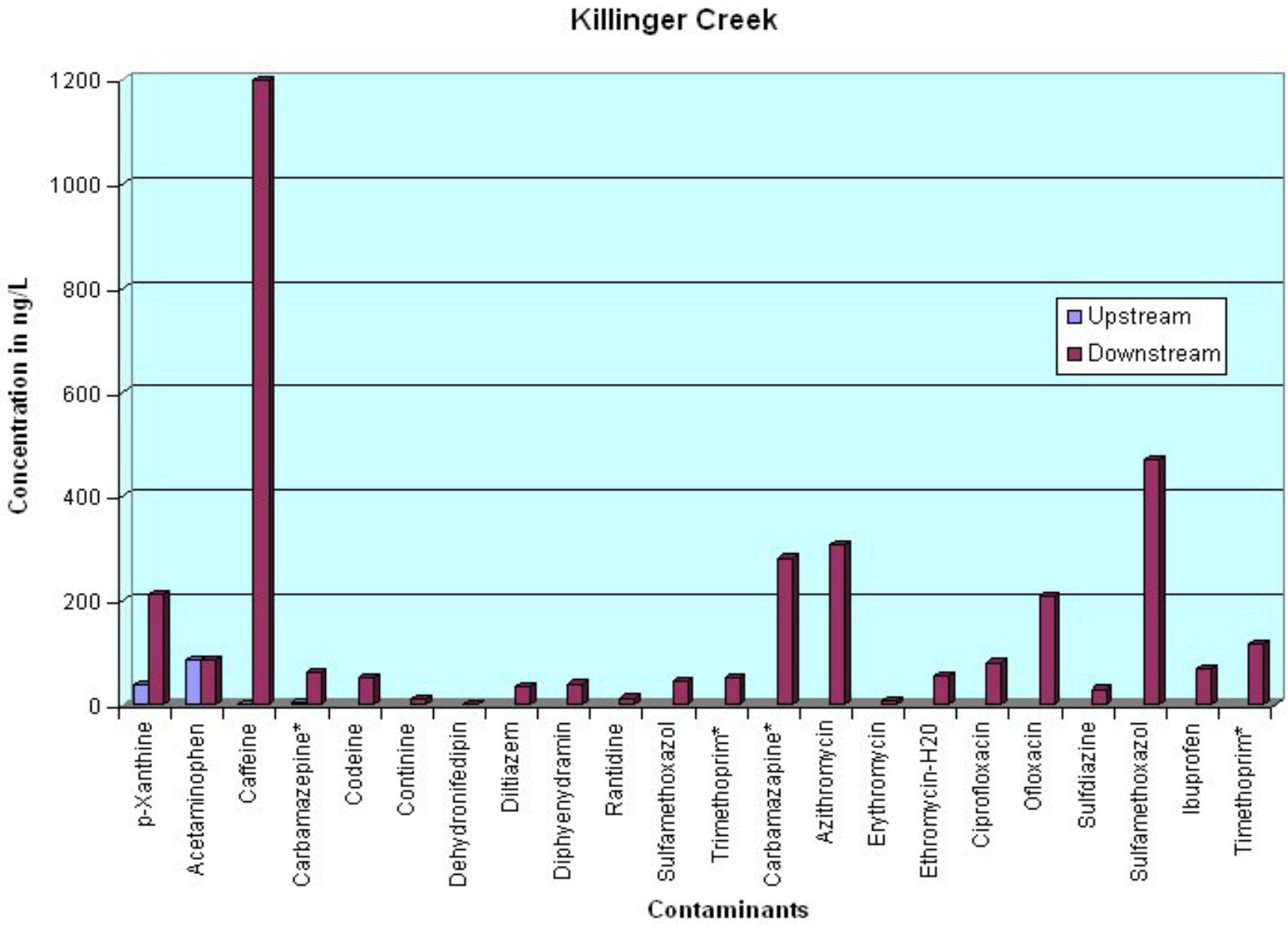
- The average number of compounds (pharmaceuticals and antibiotics) detected in sites downstream from animal-feeding operations was 3.

Results

- Well-water samples
  - 5 detections total
    - Tylosin was detected 2 times
    - Cotinine
    - Sulfamethoxazole
    - Diphenhydramine


Frequency of Contaminants Found in Surface Water
Frequency
0
2
4
6
8
10
12
14
16
1,7-Dimethylxanthine (p-Xanthine)
Acetaminophen
Caffeine
Carbamazepine*
Codeine
Cotinine
Dehydronifedipine
Diltiazem
Diphenydramine
Fluoxetine
Ranitidine
Sulfamethoxazole*
Trimethoprim*
Carbamazapine*
Ibuprofen
Azithromycin
Erythromycin
Erythromycin-H20
Tylosin
Ciprofloxacin
Ofloxolacin
Sulfadiazine
Sulfamethoxazole*
Oxytetracycline
Trimethoprim*
Contaminant


Litiz Creek
Upstream
Downstream
Concentration in ng/L
0
20
40
60
80
100
120
140
Carbamazapine
Codeine
Diltiazem
Diphenhydramine
Sulfamethoxazole
Trimethoprin
Warfarin
Carbamazepine*
Diltiazem
Diphyenydramine
Sulfamethoxazole
Trimethoprim*
Warfarin
Carbamazapine*
Erythromycin
Ethromycin-H20
Tylosin
Ofloxacin
Sulfamethoxazole
Timethoprim*
Ciprofloxacin
Oxytetracycline
Aizthromycin
Contaminants


Killinger Creek
Concentration in ng/L
1200
1000
800
600
400
200
0
Upstream
Downstream
p-Xanthine
Acetaminophen
Caffeine
Carbamazepine*
Codeine
Continine
Dehydronifedipin
Diltiazem
Diphyenydramin
Rantidine
Sulfamethoxazol
Trimethoprim*
Carbamazapine*
Azithromycin
Erythromycin
Ethromycin-H20
Ciprofloxacin
Ofloxacin
Sulfdiazine
Sulfamethoxazol
Ibuprofen
Timethoprim*
Contaminants

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

http://pubs.usgs.gov/ds/300/

U.S. Geological Survey Data Series 300

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

Phase II

- **PART 1: Continuation of Phase I**
  - **Continue to characterize surface water downstream of wastewater treatment plants**
    - 5 locations from Phase I plus 3 new sites and 1 reference stream
    - There are 6 sampling sites are in the Susquehanna watershed, 2 sites in the Potomac watershed, and one sampling site in the Delaware watershed
  - **Analysis will include additional suites for hormone analytes and wastewater compounds in water and streambed sediment**
  - **Sampling will occur one time per year for 3 years beginning May 2007**

Phase II

- **PART 2: Analysis at WQN Stations**
  - Chemical analysis of surface water at 27 Water Quality Network (WQN) Stations
  - Stations were chosen based on their proximity to Public Water Supply surface water intakes (within 3 miles)
  - Samples will be analyzed quarterly for pharmaceuticals, antibiotics, and hormones as well as pathogens and bacteria
  - There are 11 sampling locations in the Susquehanna watershed, 11 in the Ohio watershed, 4 in the Delaware watershed and 1 in the Potomac watershed.

Phase II

- **PART 3: Comprehensive Fish Health Assessment**
  - **16 sites statewide**
  - **Target species include white suckers and smallmouth bass**
  - **Water and bed sediment will also be analyzed for pharmaceuticals, antibiotics, hormones, and waste water compounds**
  - **A final report is anticipated in 2009.**

Phase II

- **Part 4: Identification of Pathogenic Bacteria**
  - **USGS Michigan Water Science Center has developed assays for actual bacterial pathogens such as *E. coli* O157, a broad class of pathogenic *E. coli* called Shiga-toxin producing *E. coli* (STEC) and Enterococci that carry the *esp* gene**
  - **These DNA-based methods may be used to identify the source of fecal pollution**
  - **The USGS MI WCS and the DEP BOL will analyze for pathogenic and fecal source markers from *E. coli* and enterococci in a side by side PCR method comparison**

Acknowledgements

US EPA

USGS Water Science Center

Resources

- http://www.epa.gov/ppcp/
- http://toxics.usgs.gov/
- http://lists.dep.state.fl.us/cgi-bin/mailman/listinfo/pharmwaste

Questions??

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Program Analysis and Support

Bureau of Water Standards and Facility Regulation

PA Department of Environmental Protection