



# Pharmaceuticals and Personal Care Products in Waters of Ohio and the United States

Ralph Haefner

U.S. Geological Survey  
Ohio Water Science Center  
Columbus, Ohio

OWEA Plant Operations & Laboratory Analysis Specialty Workshop  
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# Outline

- Background
- Results of USGS National Surveys
- Ecological and Human Health Significance
- Analytical Methods
- Regulatory Implications
- National Studies of Drinking Water
- Studies of Drinking Water in Ohio
- What Have We Learned

# Acknowledgements

- Toxics Substances Hydrology
- USGS Ohio Water Science Center Team
  - Donna Francy
  - Greg Koltun
  - John Tertuliani
  - Dennis Finnegan
  - Stephanie Janosy

# Why the recent interest?

## **AP Probe Finds Drugs in Drinking Water**

By JEFF DONN, MARTHA MENDOZA and JUSTIN PRITCHARD – Mar 9, 2008

A vast array of pharmaceuticals — including antibiotics, anti-convulsants, mood stabilizers and sex hormones — have been found in the drinking water supplies of at least 41 million Americans, an Associated Press investigation shows.

To be sure, the concentrations of these pharmaceuticals are tiny, measured in quantities of parts per billion or trillion, far below the levels of a medical dose. Also, utilities insist their water is safe.

But the presence of so many prescription drugs — and over-the-counter medicines like acetaminophen and ibuprofen — in so much of our drinking water is heightening worries among scientists of long-term consequences to human health.

In the course of a five-month inquiry, the AP discovered that drugs have been detected in the drinking water supplies of 24 major metropolitan areas — from Southern California to Northern New Jersey, from Detroit to Louisville, Ky.

Water providers rarely disclose results of pharmaceutical screenings, unless pressed, the AP found. For example, the head of a group representing major California suppliers said the public "doesn't know how to interpret the information" and might be unduly alarmed.

How do the drugs get into the water?

# Drugs are not the only concern!

Debate rages over safety of BPA in everyday plastics

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## Bisphenol A

What's New

**Bisphenol A Safety Confirmed In Final National Toxicology Program Report**

September 17, 2008

Summary

The US National Toxicology Program (NTP) has announced that its study of the effects of exposure to bisphenol A (BPA) has found no direct evidence for health effects from exposure to BPA.

NTP's overall conclusion is that there are no concerns for any age group for adult men and women from laboratory animal studies on the mammary and 'some concern' regarding...

Join the Bisphenol-A mailing list.

email address

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- About Bisphenol A
- Human Health & Safety
- Environmental Safety
- Scientific Publications
- Press Room

Monday, May 18, 2008

5 and HOLLY YAN / The NEWS

The debate about one of the most commonly used chemicals has moved quickly from biotech experts and scientists to moms and dads shopping in their grocery stores.

Unlabeled BPA, can be found in products such as those in baby bottles, in the...

CLICK IMAGE TO ENLARGE

Government of Canada / Gouvernement du Canada

Canada

Chemical Substances  
an ecoACTION Initiative

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Home > The Challenge

Thursday, Nov 20 2008

### Government of Canada Protects Families With Bisphenol A Regulations

**Chemical Substances in Canada**

Canada's approach on chemical substances

The Canadian Environmental Protection Act, 1999

**Categorization**

What is categorization?  
How were substances categorized?

On October 17, the Government of Canada announced it will immediately proceed with drafting regulations to prohibit the importation, sale and advertising of polycarbonate baby bottles that contain bisphenol A (BPA). The Government will also take action to limit the amount of bisphenol A that is being released into the environment.

See below for more information on the Government's approach to bisphenol A:

Government of Canada Protects Families With Bisphenol A Regulations



# Drugs are not the only concern!

## Fate Of Personal Care Products Linked To Environmental Human Health Concerns

*ScienceDaily* (May 19, 2008) — Parental concerns in maintaining germ-free homes for their children have led to an ever-increasing demand and the rapid adoption of anti-bacterial soaps and cleaning agents. But the active ingredients of those antiseptic soaps now have come under scrutiny by the EPA and FDA, due to both environmental and human health concerns.

See also:

### Health & Medicine

- Workplace Health
- Health Policy

### Plants & Animals

- Nature
- Fish

### Earth & Climate

- Environmental Issues
- Sustainability

### Reference

- Estuary

Two closely related antimicrobials, triclosan and triclocarban, are at the center of the debacle. Whereas triclosan (TCS) has long captured the attention of toxicologists due to its structural resemblance to dioxin (the Times Beach and Love Canal poison), triclocarban (TCC) has ski-rocketed in 2004 from an unknown and presumably harmless consumer product additive to one of today's top ten pharmaceuticals and personal care products most frequently found in the environment and in U.S. drinking water resources.



Researchers have traced

INTERNATIONAL  
**Herald Tribune** | AMERICAS

SEARCH

HOME BUSINESS TECH TRAVEL STYLE CULTURE HEALTH/SCI SPORTS REGIONS

## Sierra Club asks U.S. government to ban detergent chemical compound linked to intersex fish

The Associated Press Published: June 5, 2007

**HAGERSTOWN, Maryland:** An environmental group asked the federal government Tuesday to ban the use of certain toxic chemical compounds in industrial and household detergents because the ingredients are believed to cause male fish to develop female characteristics.

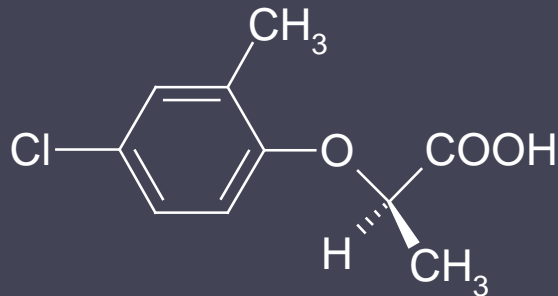
The Sierra Club also asked the Environmental Protection Agency to bar the use of these products in areas where wastewater treatment plants are not equipped to remove nonylphenol ethoxylates, or NPEs.

The compounds, which are derived from petroleum, are used mainly in detergents but also in paper manufacturing and flame retardants. The Sierra Club, along with the Pacific Coast Federation of Fisherman's Associations and the textile-and-hotel-workers union UNITE HERE, also seeks to require labeling on all products containing NPEs.

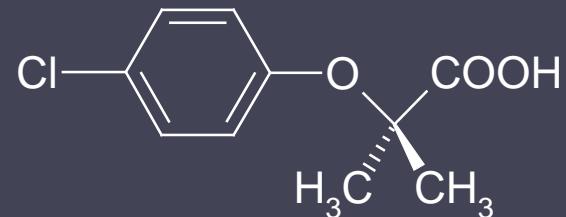
- E-Mail Article
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# USGS interest in pharmaceuticals began over 10 years ago...

Researchers looking for a pesticide in Swiss lakes and the North Sea and found clofibric acid...



Mecoprop  
(Herbicide)



Clofibric Acid  
(Cholesterol Drug)

# Organic Wastewater Compounds (OWCs)

EDC's

- Human Drugs
- Vet. Drugs
- Antibiotics
- Hormones
- Steroids
- Detergents
- Plastics

HAA's

OWC's

CEC's

MP's

MC's

PPCP's

PhAC's

ES's

- Antioxidants
- Fire retardants
- Disinfectants
- Fumigants
- Fragrances
- Insecticides/  
Repellants

# Human Waste Pathways

- WWTPs
- CSOs
- Septic Systems
- Industry
- Landfills
- Water Reuse



# Animal Waste Pathways

- Waste Lagoons
- Land Application
- Processing
- Aquaculture



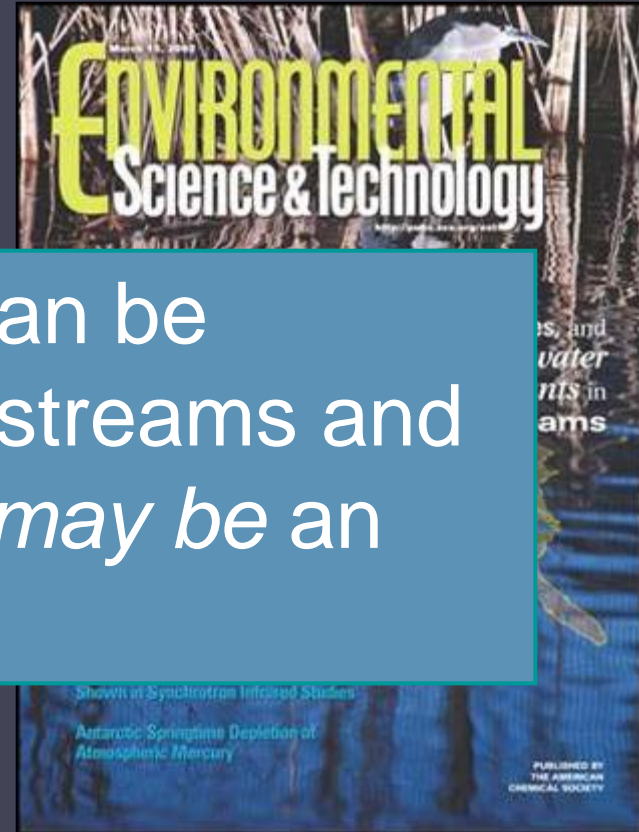
# USGS National Stream Survey

Are OWCs present in rivers?

Chemicals we use every day can be concentrated in various waste streams and enter our waters at levels that *may be* an environmental health concern.

139 streams in 30 states

Stream Reconnaissance 1999-2000



# USGS National Stream Survey

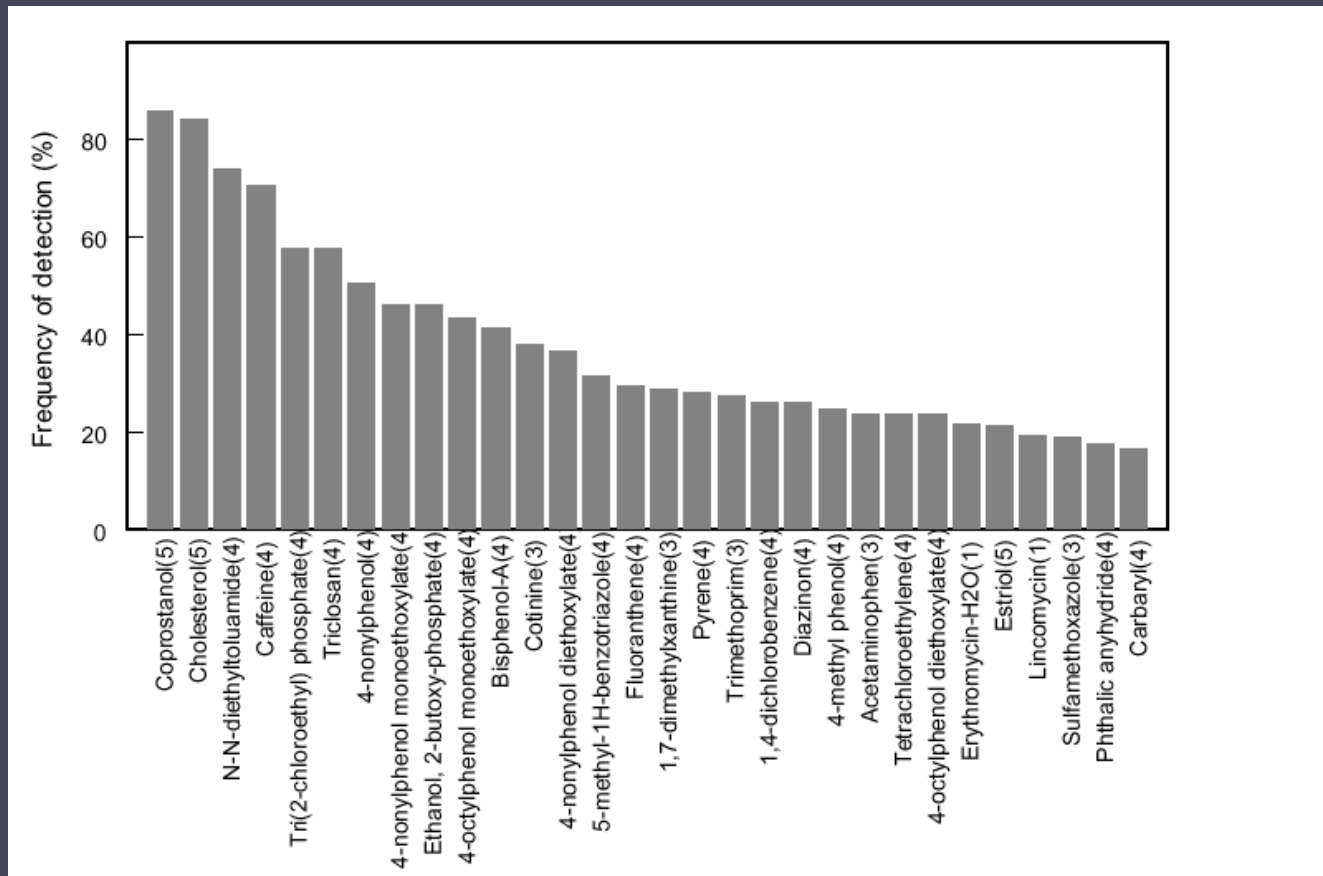
- One or more chemicals were detected in 80% of

How much exactly is one part per billion?

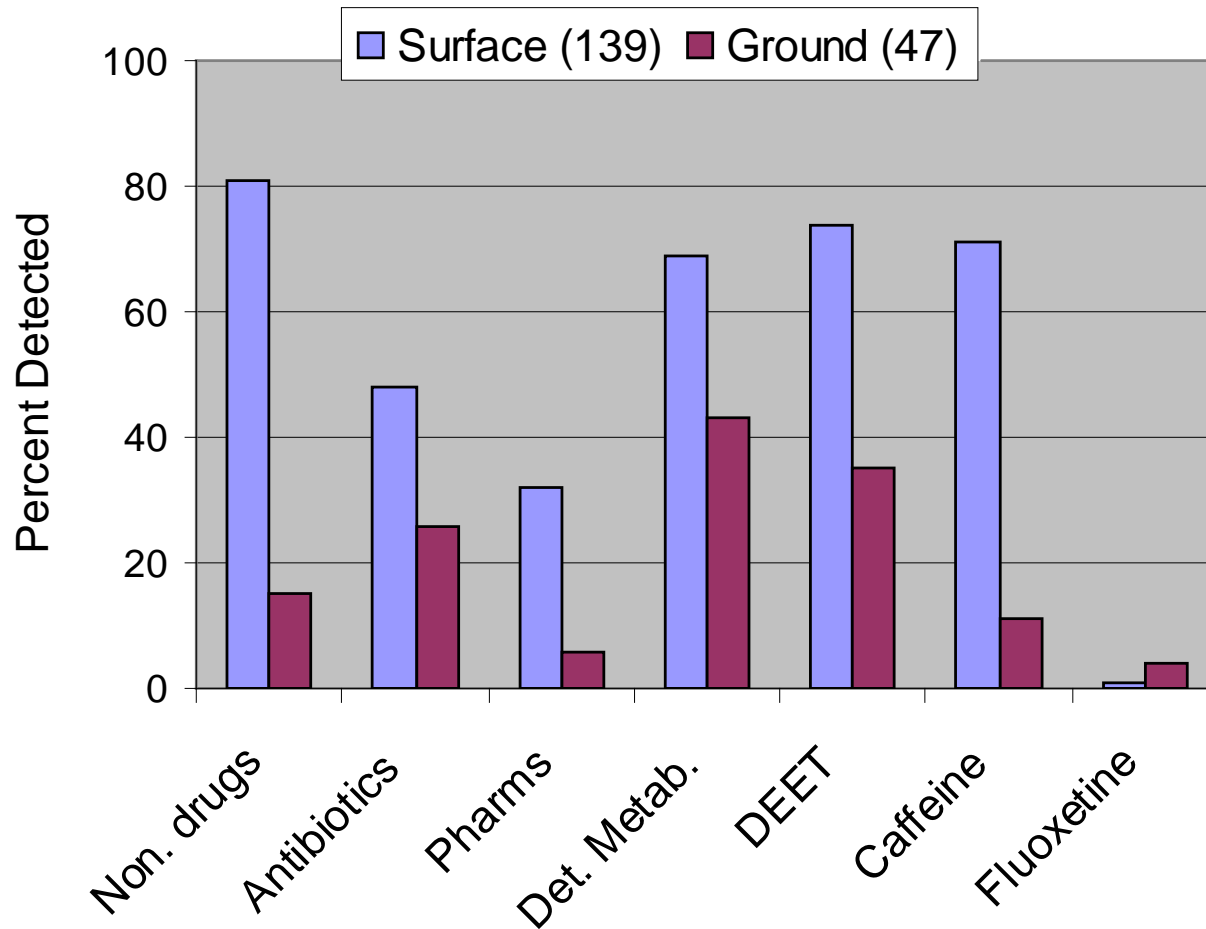
- one drop in a railroad tanker car
- one second over 32 years
- one hamburger in a chain of hamburgers circling the earth at the equator 2.5 times

- 75% of the streams had more than one
- 50% had 7 or more
- 34% had 10 or more

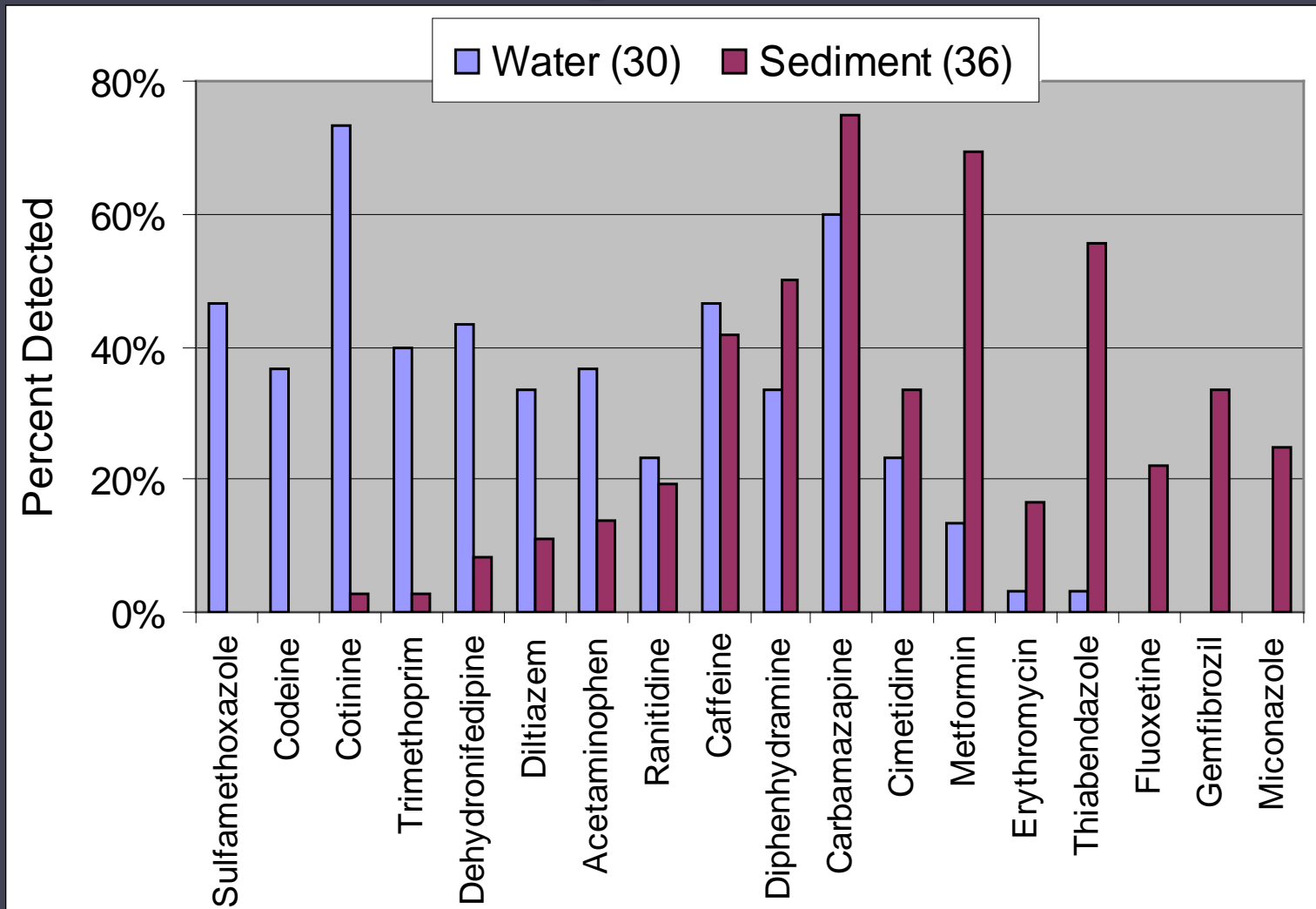
# Frequently Detected Compounds



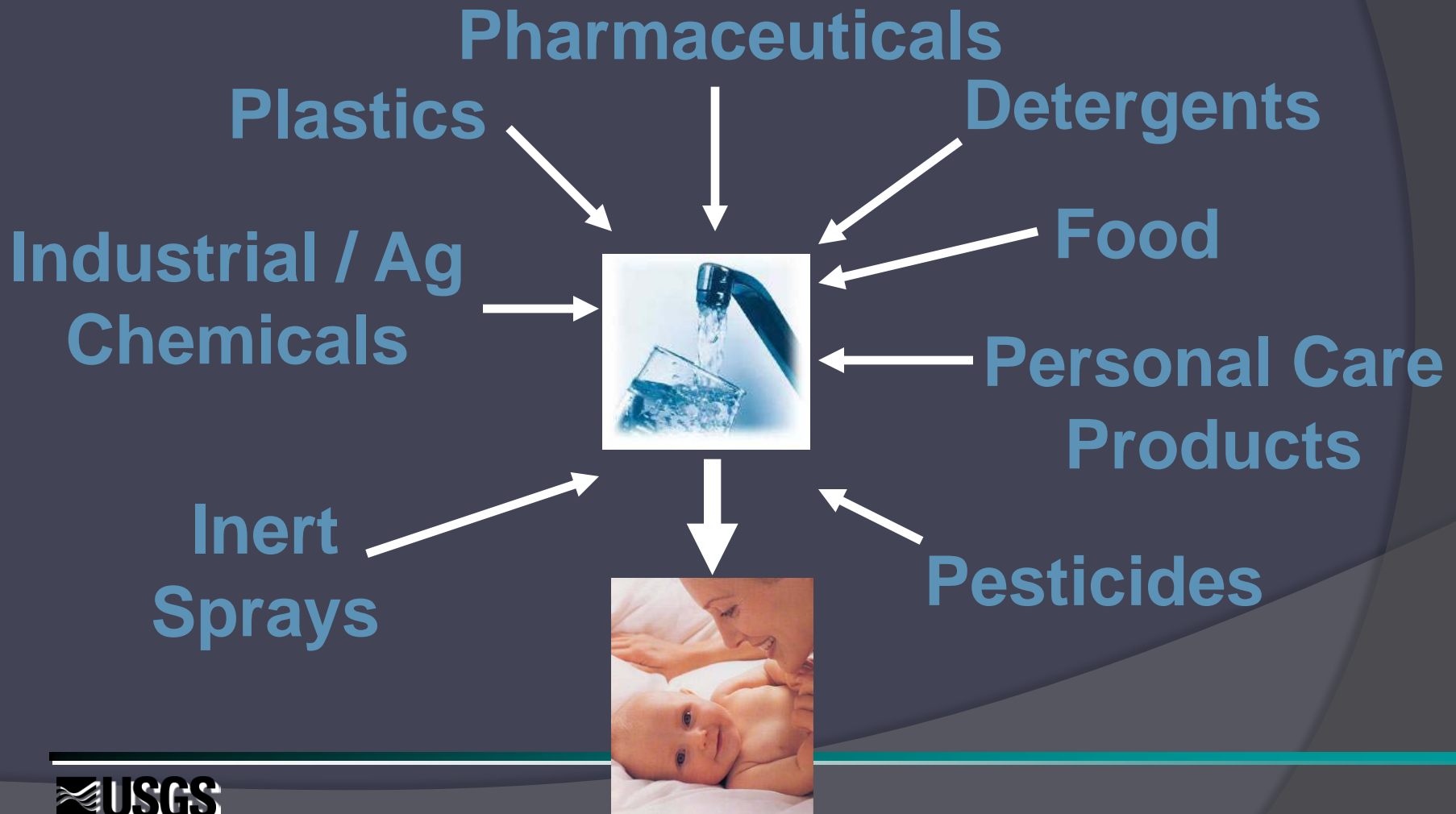
# SW versus GW



# Don't look just in the water!



# If OWC concentrations are so low, why all the fuss?



# Ecological Concerns

- Toxicity
- Uptake by organisms
- Antibiotic resistance of pathogens
- Endocrine disruption



# Antibiotic Resistance

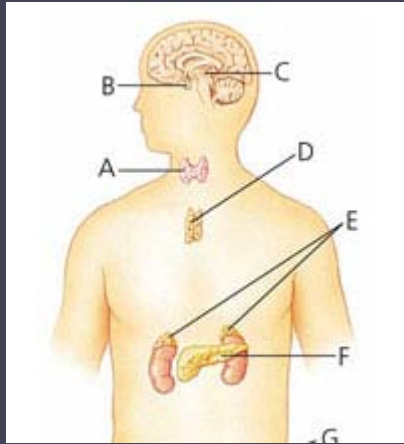
- More than 50 million pounds of antibiotics are produced annually in the U.S.
- 25 to 75 percent of an antibiotic taken can be excreted unaltered
- Many antibiotics are not completely removed during secondary wastewater treatment
- Bacteria exposed to non-lethal concentrations of antibiotics can develop resistance

# Antibiotic Resistance

Most frequently detected antibiotics in water

	(% of samples)
• Trimethoprim	27.4
• Erythromycin	21.5
• Lincomycin	19.2
• Sulfamethoxazole	19.0
• Tylosin (cattle and swine)	13.5

# Endocrine Disruption



- Natural and synthetic compounds mimic or block the action of natural hormones that may cause health effects at the parts per trillion range

- Potential health effects include
  - reproductive abnormalities
  - behavioral problems
  - impaired immune functions
  - various cancers

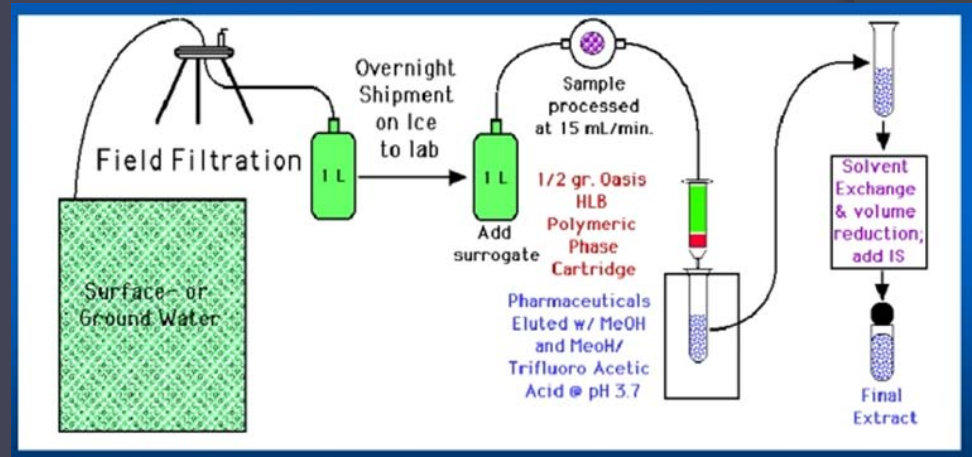


# Analytical Methods

## Field sample collection



## Solid-phase extraction and isolation



- High Performance Liquid Chromatography / Mass Spectrometry
- Gas chromatography / Mass Spectrometry

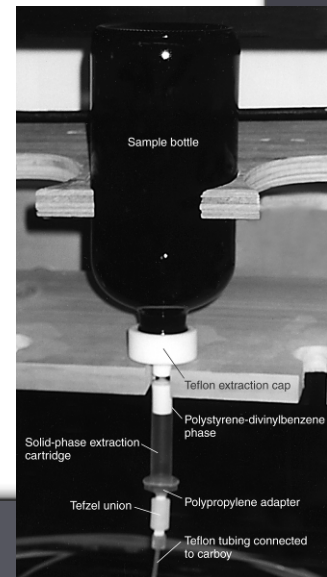
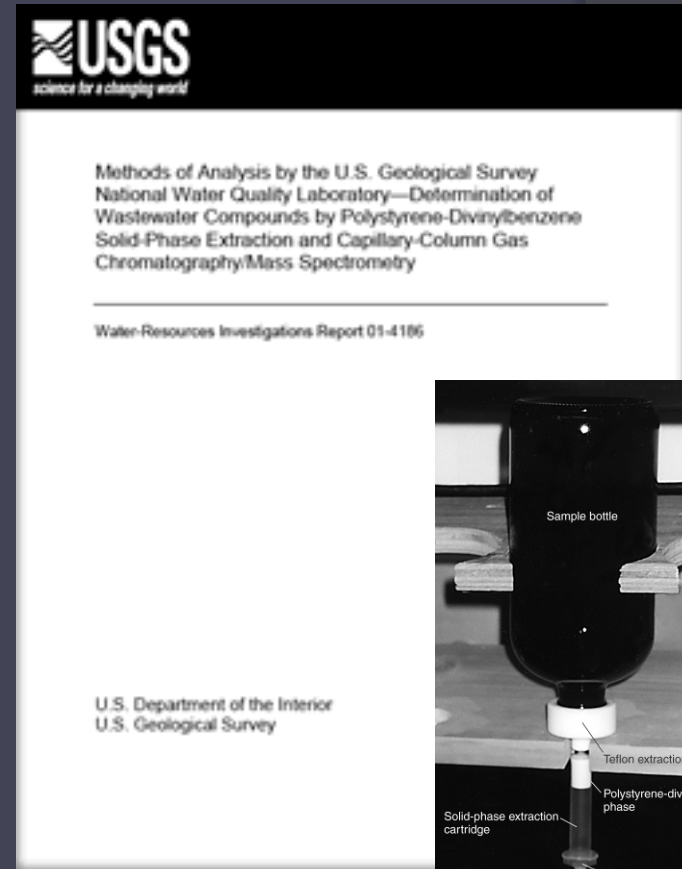
# Analytical Methods

## 67 Wastewater Indicators

Fragrances, detergents, dyes, fuels, disinfectants, flame retardants, pesticides, herbicides, and 3 pharmaceuticals (menthol, cotinine, and caffeine)

USGS PUBLISHED METHOD  
Solid-phase extraction, gas chromatography / mass spectrometry

RL range of 0.08 to 5  $\mu\text{g/L}$



# Analytical Methods

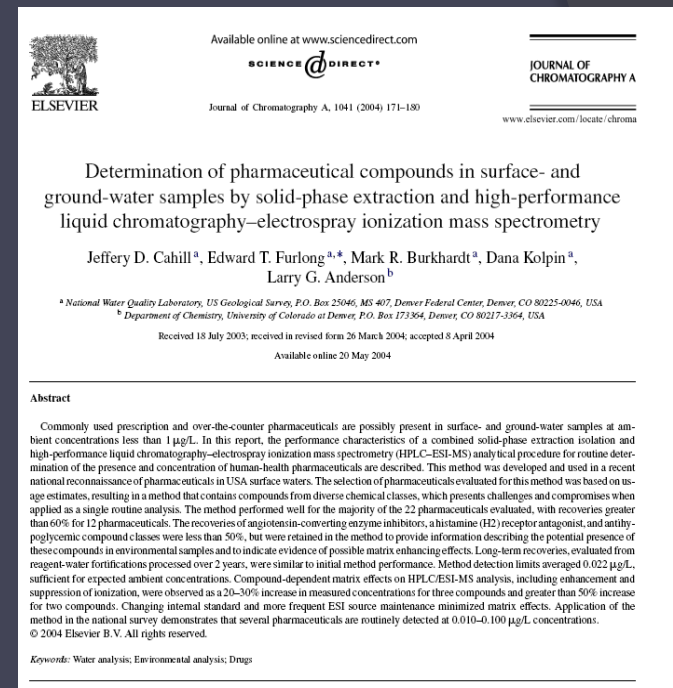
## 18 Human Pharmaceuticals

Acetaminophen, albuterol (asthma), caffeine, codeine, cotinine, 2 antibiotics, other drugs

USGS PUBLISHED METHOD

Solid-phase extraction, high performance liquid chromatography / mass spectrometry

RL range of 0.026 to 0.1 µg/L



# Analytical Methods

## 33 Human and Veterinary Antibiotics

Fluroquinolones, macrolides (erythromycin), sulfonamides, tetracyclines, 2 pharmaceuticals (carbamazepine and ibuprofen), degradates, and other antibiotics

USGS PUBLISHED METHOD  
Liquid chromatography / mass spectrometry

RL range of 0.005 to 0.1 mg/L

# Analytical Methods

## 19 Natural and Synthetic Hormones

Estradiol, cholesterol, progesterone, testosterone, androsterone (anabolic steroid), mestranol (oral contraceptives), equilin (equine estrogen and hormone replacement)

USGS RESEARCH (CUSTOM) METHOD

Gas chromatography / tandem mass spectrometry

RL range is 0.8 to 4 ng/L

# Are these compounds regulated?

Out of the 137 compounds included in the previous analytical schedules, only three are regulated

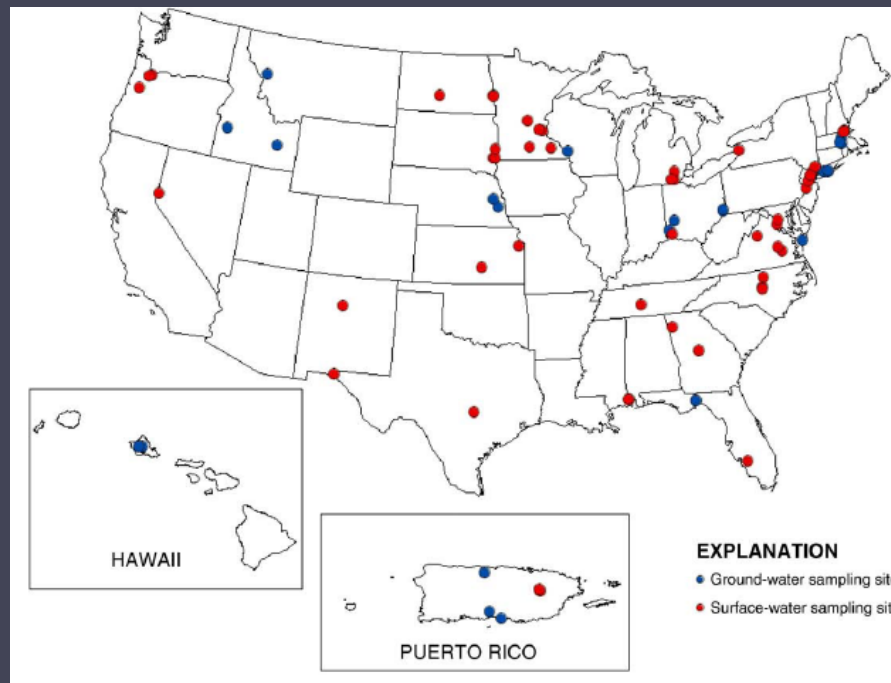
## USEPA Maximum Contaminant Levels

- 1, 4-Dichlorobenzene (fumigant) @ 75 µg/L
- Benzo(a)pyrene (PAH from incomplete combustion) @ 0.2 µg/L
- Tetrachloroethylene (dry cleaning/solvent) @ 5 µg/L

## USGS Health Based Screening Levels (HBSL)

- Bisphenol A (plastics) @ 400 µg/L

# USGS National Recon II: Untreated Drinking Water Sources



# USGS National Recon II

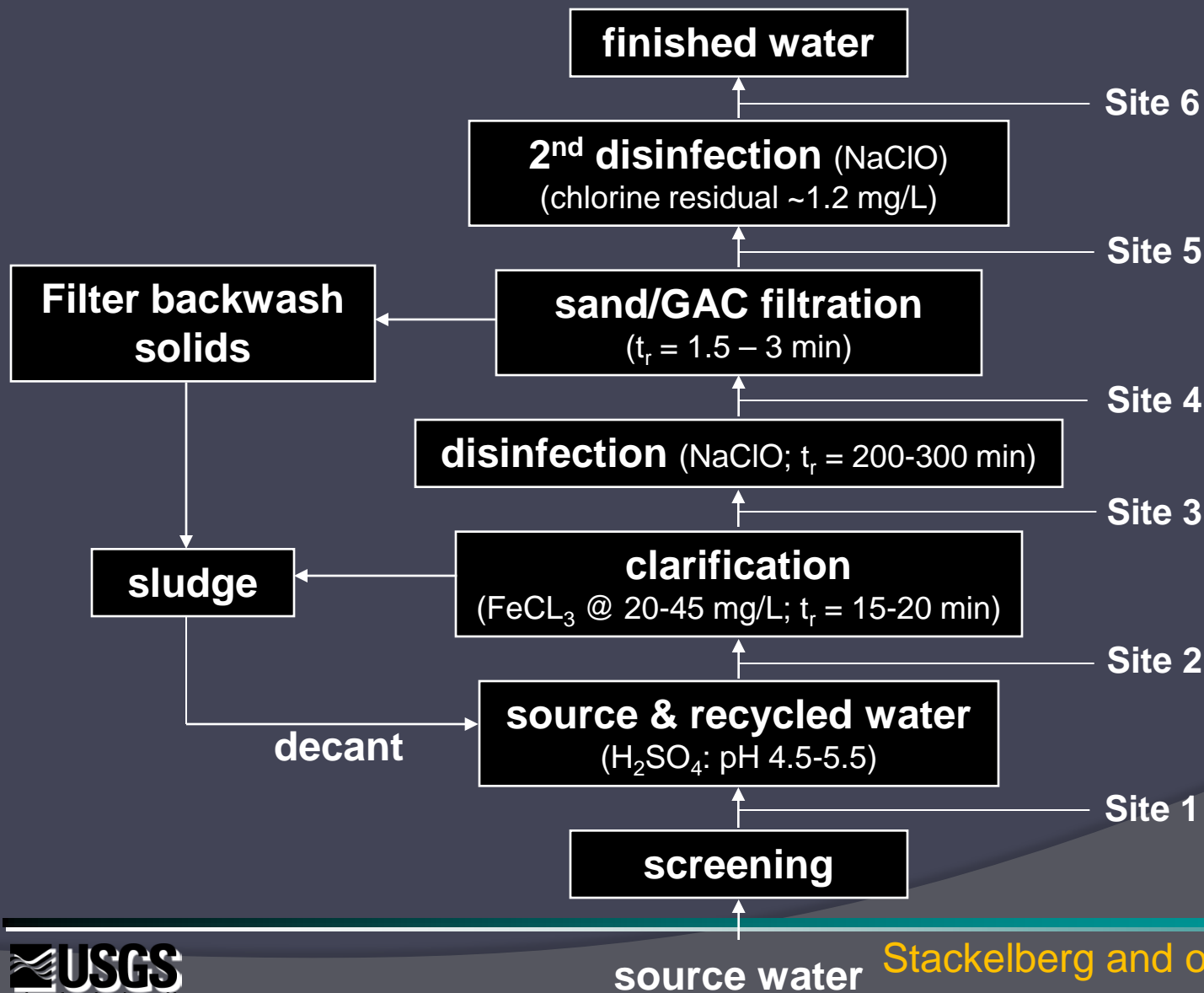
- 100 wastewater, pharmaceuticals, and antibiotic compounds analyzed
- 63 detected at least once; however, 36 pharmaceuticals/antibiotics were not detected in any water sample
- Median of 4 compounds were detected at every site
- Concentrations were typically in the sub- $\mu\text{g}/\text{L}$  range

# NJ Study of Drinking Water

Objective: Identify the treatment steps that are most effective at reducing concentrations of OWCs

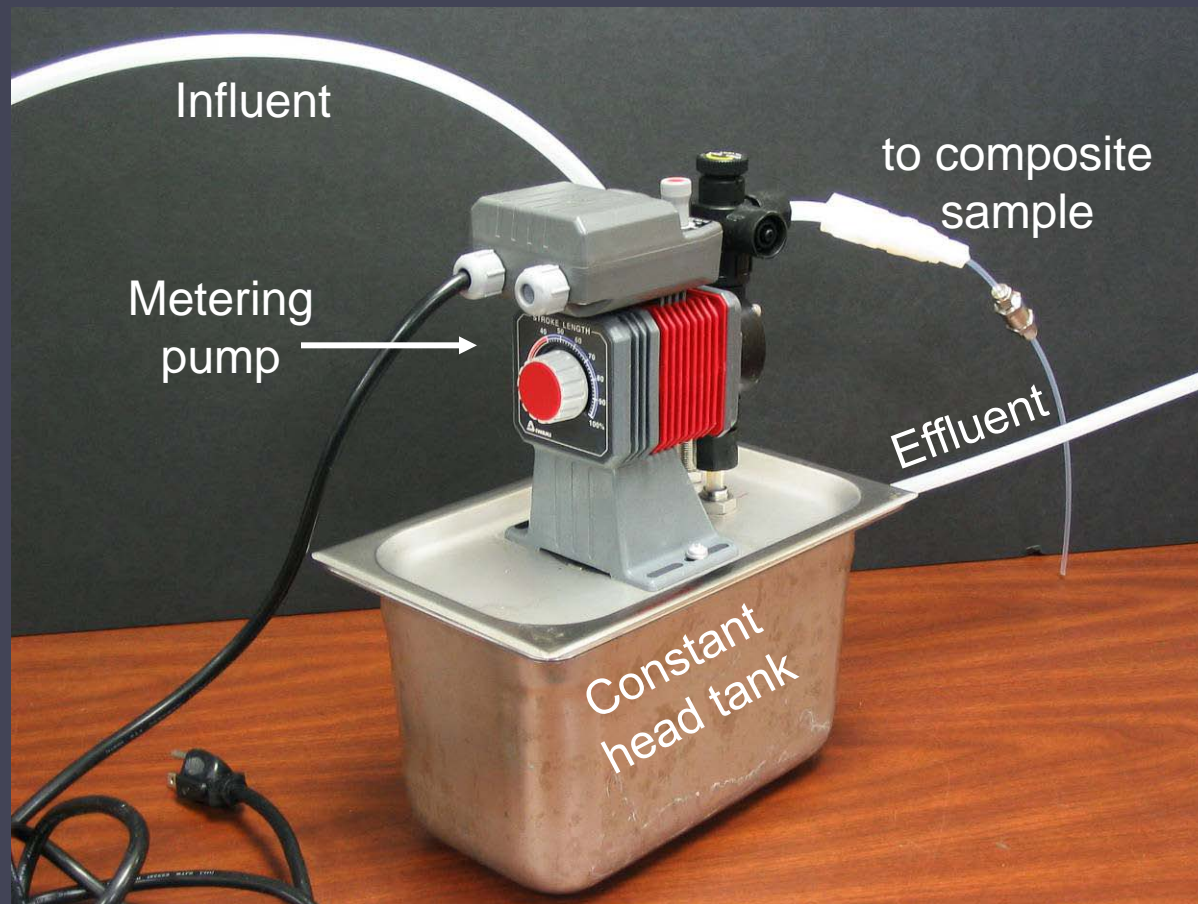
Approach: Obtain 12 samples at each of 6 sites in a drinking-water plant in a heavily developed drainage basin

# NJ Drinking Water Plant



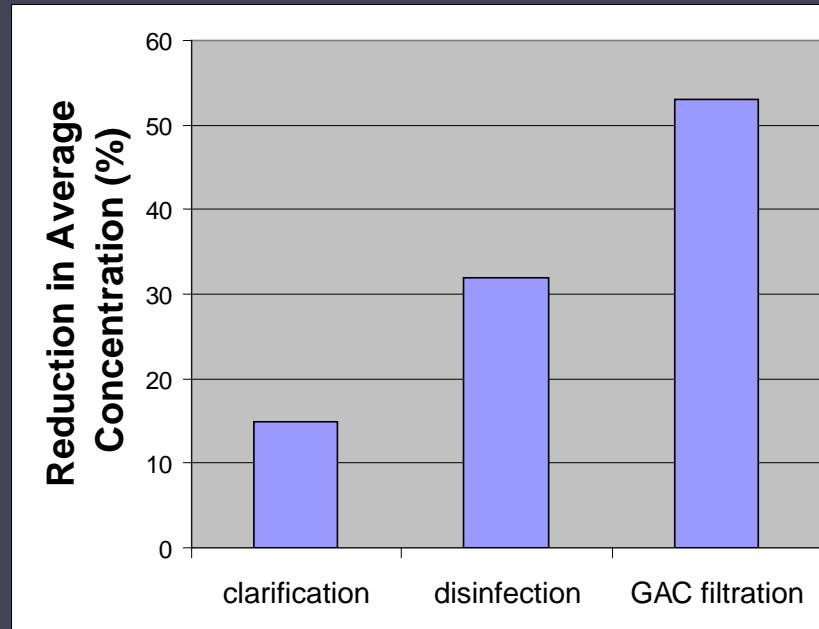
Stackelberg and others (2007)

# NJ Drinking Water Plant



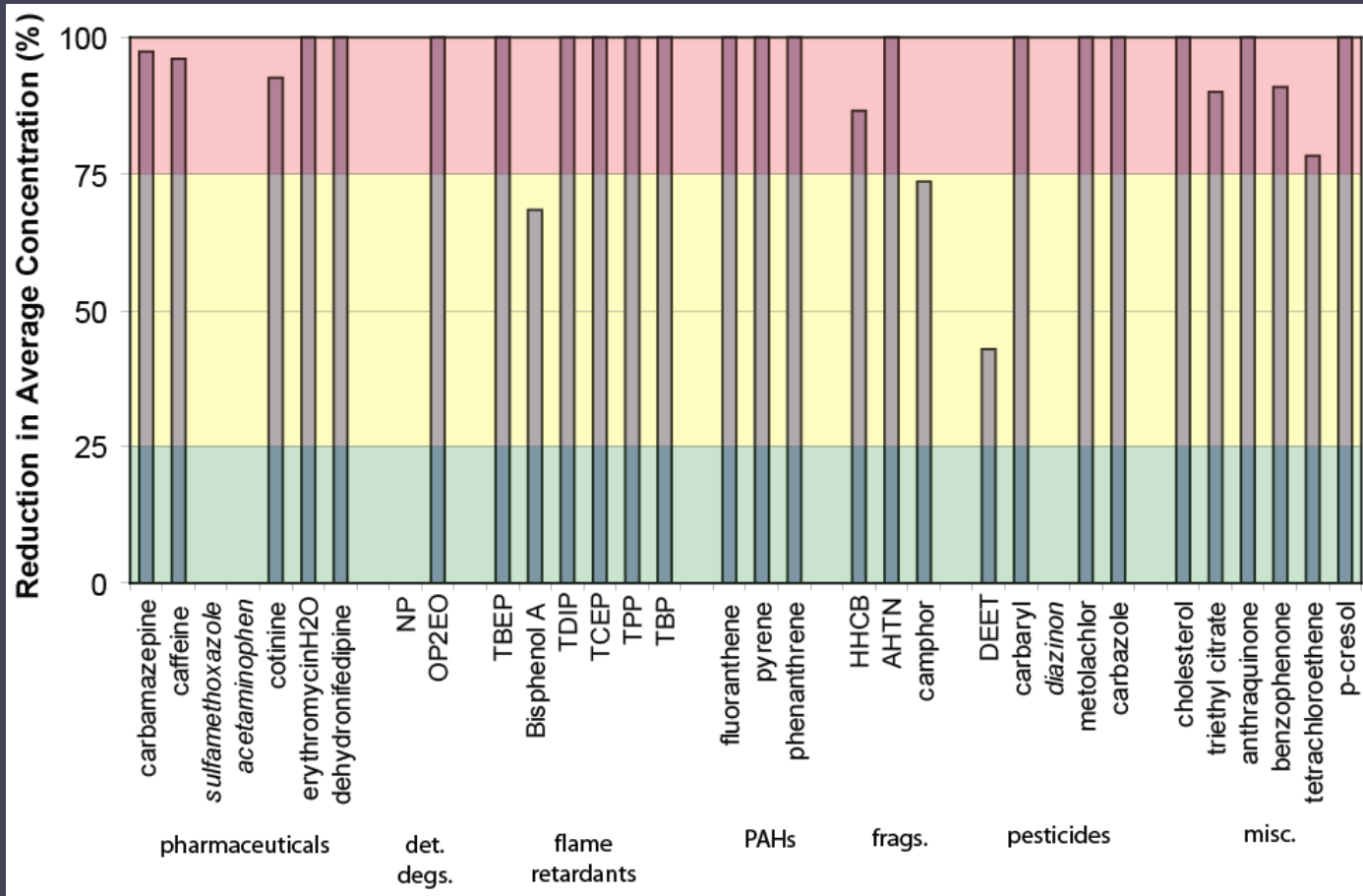
24-hour  
composite  
water  
samples

# NJ Drinking Water Plant



Cumulative reduction in average concentration through treatment processes

# NJ Drinking Water Plant

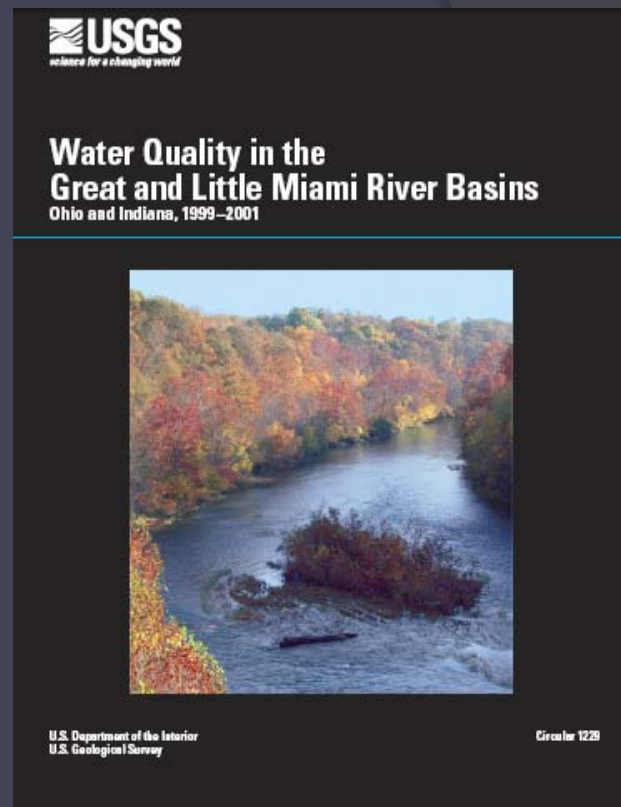


GAC  
filtration

# Ohio Studies

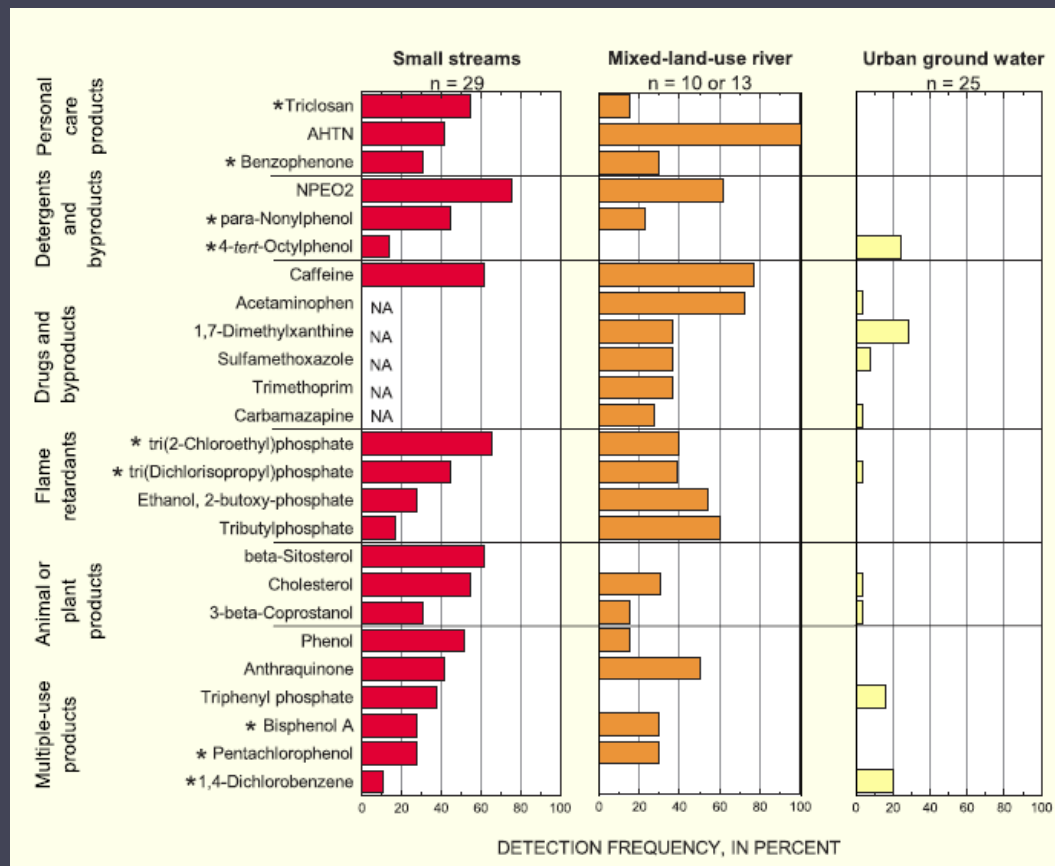
## Great and Little Miami Rivers (NAWQA)

- Sampled 29 small streams with varied land use, a mixed-land-use river (GMR at Hamilton), and 25 urban wells
- Analyzed for wastewater & pharmaceutical compounds



# Ohio Studies

## Great and Little Miami Rivers (NAWQA)



# Ohio Studies



## Great Miami River Basin

### ● 14 surface-water sites

Greenville Ck Wildcat

Stillwater Boyer

GMR Indian Lake

Bockengahelas Creek

Stillwater Covington

Greenville Cr Croft Mill

Stillwater Horseshoe Bend

Honey Ck at MCPD

Lost Creek

Stillwater Siebenthaler

Upper Great Miami R Huber Hts

Tawawa Creek

Loramie Ck Fort Loramie

Loramie Ck at Lockington Dam

### ● 1 groundwater site

Troy MI44

# Ohio Studies



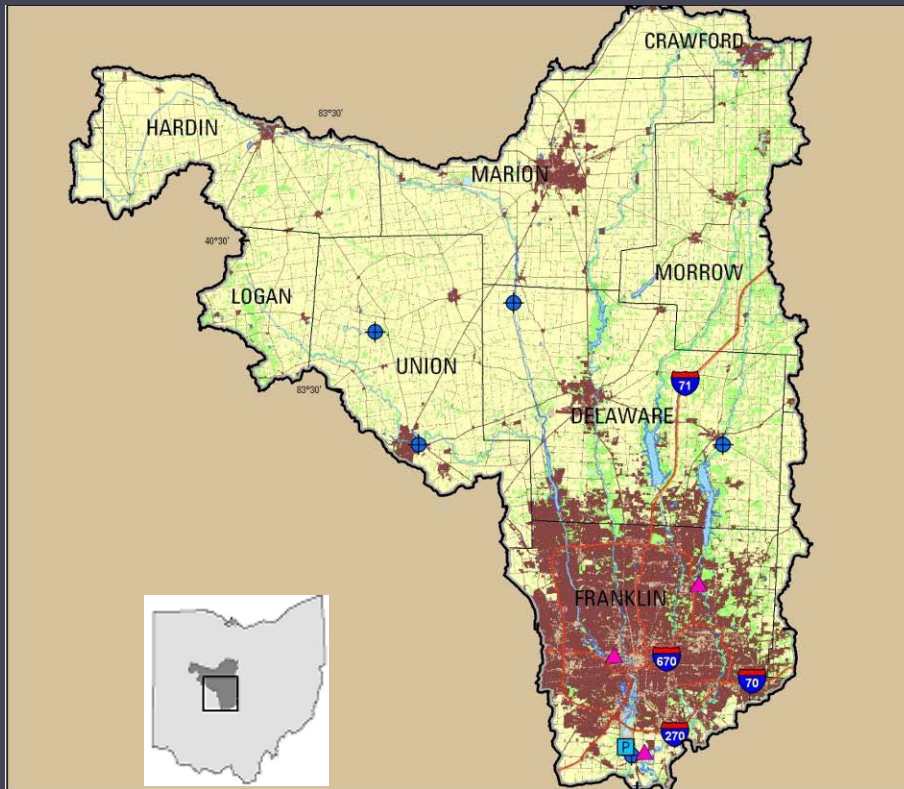
## Great Miami River Basin

### Detections of

- Acetaminophen
- Caffeine
- Carbamazepine
- DEET
- Esterone
- Estradiol
- Fluoxetine (Prozac)
- Gemfibrozil
- Ibuprofen
- Progesterone
- Sulfamethoxazole
- Testosterone
- Triclosan
- Trimethoprim
- Triphenylphosphate
- Tris (1,3-Dichloropropyl-2) Phosphate (TDCPP)

# Ohio Studies

## City of Columbus and the Upper Scioto River Basin



Objective: determine occurrence and concentrations of OWCs in source and finished drinking waters of Columbus-area plants

# Ohio Studies

## City of Columbus and the Upper Scioto River Basin

### Surface Water

depth and width-integrated  
collection

5 stream sites  
sampled 3-4 times



### Drinking Water (source and finished)

grab sample

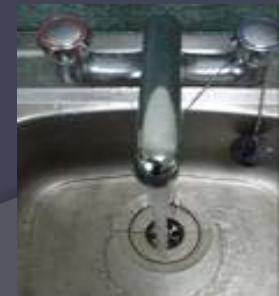
3 water treatment plants  
sampled 3-4 times



### Ground Water

grab sample

1 production well  
sampled 2 times



# Ohio Studies

City of Columbus and the Upper Scioto River

Detections of wastewater compounds and antibiotics in both source and finished waters

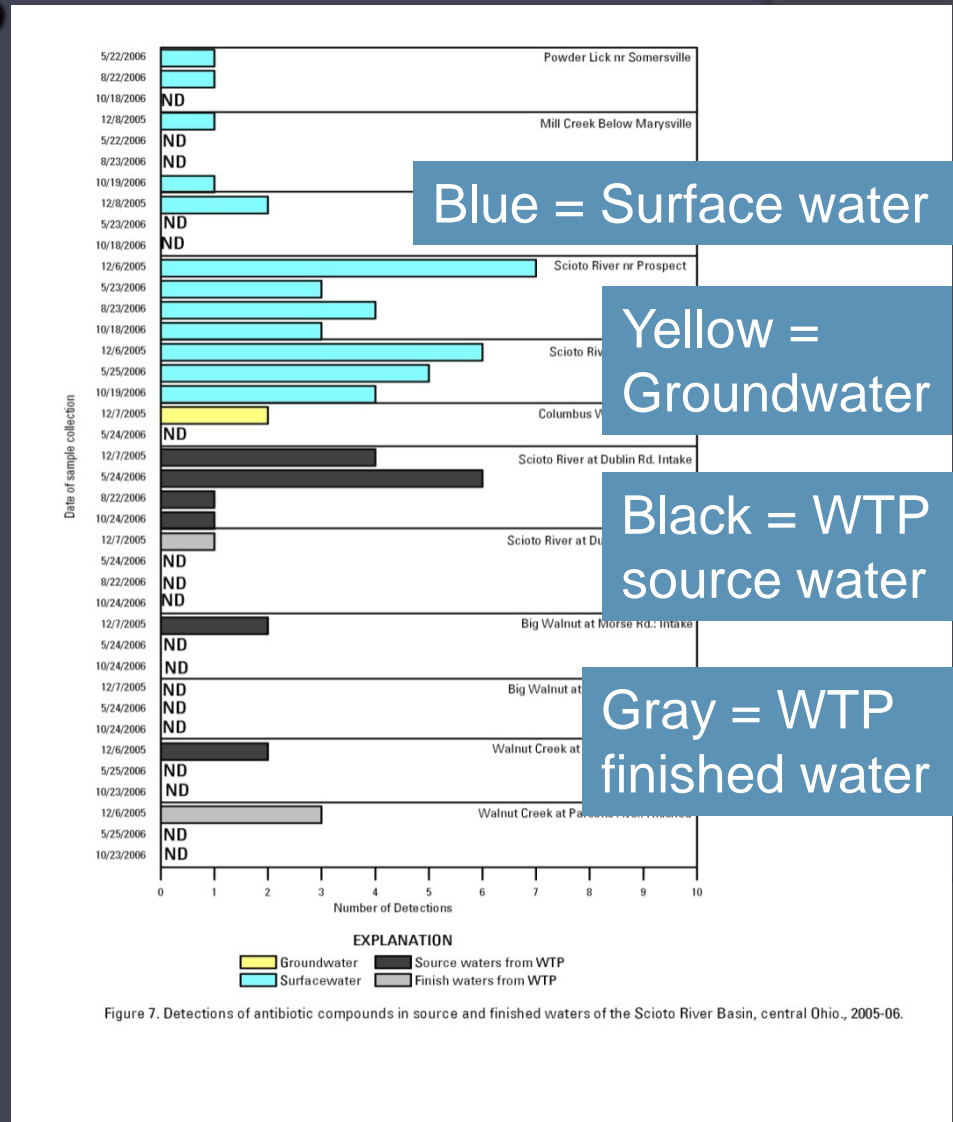
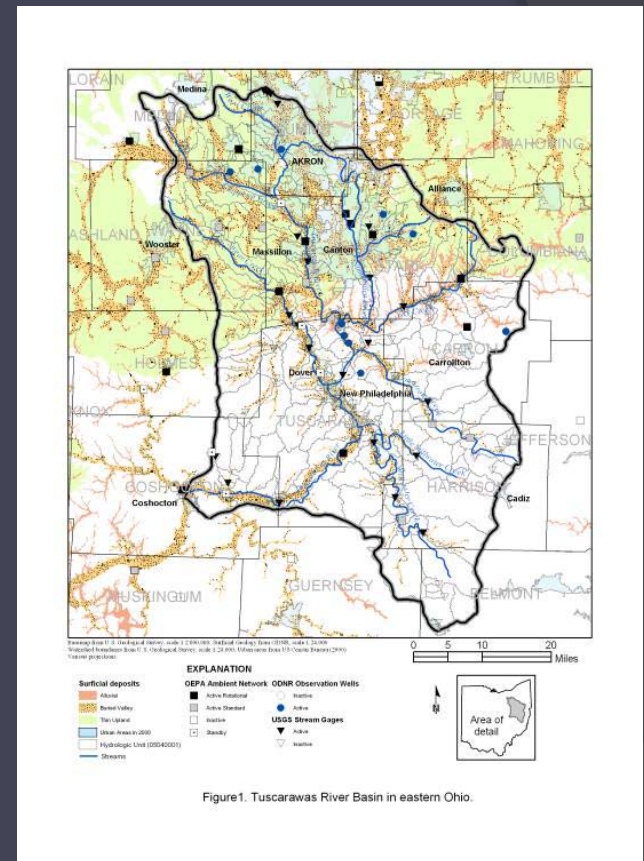


Figure 7. Detections of antibiotic compounds in source and finished waters of the Scioto River Basin, central Ohio., 2005-06.

# Ohio Studies

## Tuscarawas River Basin

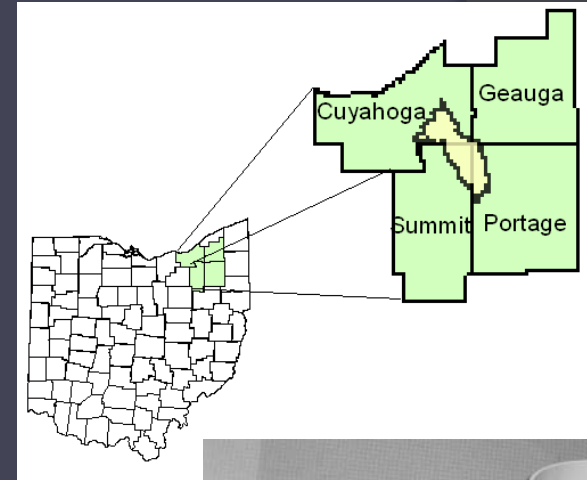
- Sampled 2 stream sites and 7 wells for wastewater compounds
- Surface water contained detectable concentrations of N,N-diethyl-meta-toluamide (DEET) but did not contain detectable concentrations of any other wastewater compounds



# Ohio Studies

## Tinkers Creek, northeast Ohio

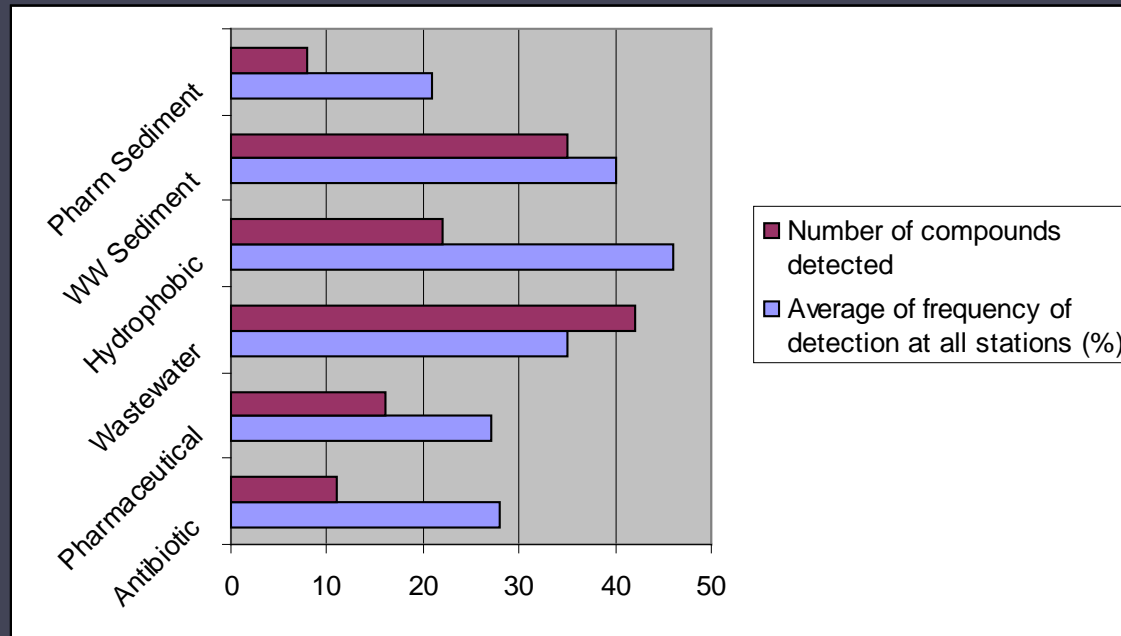
- Objective: assess the occurrence & distribution of OWCs at locations upstream and downstream from 7 WWTPs and 2 reference sites outside the watershed
- Used Polar Organic Chemical Integrative Sampler (passive samplers)



POCIS Sampler

# Ohio Studies


## Tinkers Creek, Northeast Ohio



**USGS**  
science for a changing world

In cooperation with the Ohio Water Development Authority, National Park Service; Cities of Aurora, Bedford, Bedford Heights, Solon, and Twinsburg; Parke and Summit Counties; and in collaboration with the Ohio Environmental Protection Agency

**Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed and Two Other Tributaries to the Cuyahoga River, Northeast Ohio**



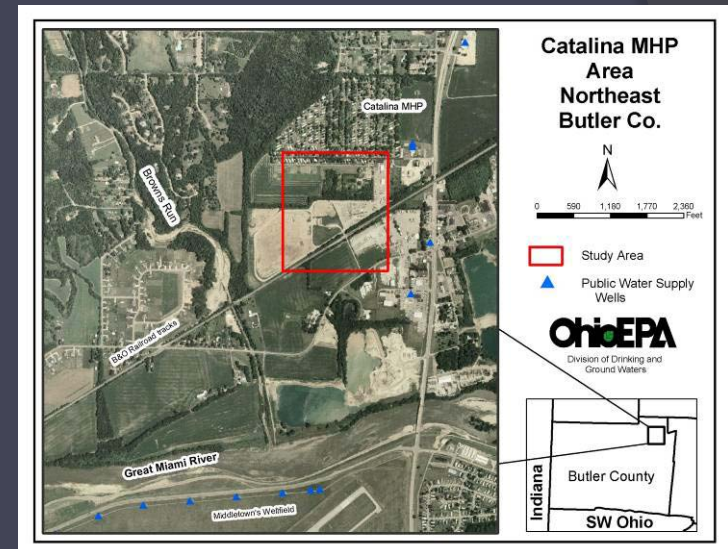
Scientific Investigations Report 2008-5173

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

# Ohio Studies

## Catalina Mobile Home Park, Butler County

- Partially treated wastewater discharged to unlined lagoons since late 1960's
- Objective: Determine if infiltration to groundwater poses a public health threat



# Ohio Studies

## Catalina Mobile Home Park, Butler County

- GW samples detected sulfamethoxazole and carbamazepine in boring and monitoring wells
- Distribution of detections consistent with chloride and TDS plume geometry
- Within single boring, concentration of pharmaceuticals decrease with depth



# What have we learned about OWCs?

- Present at sub-ppb concentrations in both streams and ground water
- Present as complex mixtures
- Reflect a wide range of human activities
- Some compounds mobile and persistent
- Present in various environmental media (water, sediment, tissue)

# What have we learned about OWCs?

- Effects of endocrine disruptors on aquatic organisms have been documented
- Little is known about human-health effects associated with chronic exposure to trace levels of OWCs
- Little is known about synergistic human-health effects of combinations of compounds

# For more information...

- USGS Toxics Substances Hydrology Program  
<http://toxics.usgs.gov>
- Health Based Screening Levels  
<http://water.usgs.gov/nawqa/HBSL/>
- Ohio Water Science Center  
<http://oh.water.usgs.gov>

# Contact Information

**Ralph Haefner**  
(Groundwater)  
614.430.7709  
rhaefner@usgs.gov

## **Water Quality**

Donna Francy  
614.430.7769  
dsfrancy@usgs.gov

## **Surface Water**

Greg Koltun  
614.430.7708  
gfkoltun@usgs.gov

## **Columbus Project**

Dennis Finnegan  
614.430.7731  
dpfinneg@usgs.gov

## **Tinkers Creek / POCIS Project**

John Tertuliani  
614.430.7778  
tertulia@usgs.gov