



# Expanding the Knowledge of CECs in the Environment: Recent Research by the USGS

## NORMAN Workshop, Amsterdam

Dana W. Kolpin

Emerging Contaminants in the Environment Project

Toxic Substances Hydrology Program

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U.S. Department of the Interior

U.S. Geological Survey



# CECs

*“umbrella term”*

- Pharmaceuticals
- Fungicides
- Mycotoxins
- Fragrances
- Detergents
- Plastics
- PFCs
- Pathogens
- Hormones
- Fire retardants
- Disinfectants
- Fumigants
- Plant/animal sterols
- Phytoestrogens
- Algal toxins
- Nanomaterials



# Fundamental Research Questions

- *Are CECs entering our environment?*
- *What are the sources (signatures)?*
- *What happens to them in the environment?*
- *Do they have adverse ecological health effects?*
- *Do unintended exposures pose a human health risk?*
- *How can we minimize their entry to the environment or remove them?*

# USGS Team

## (multidisciplinary approach)

### Hydrologists

Dana Kolpin (IA WSC)  
Mike Focazio (Reston)  
Frank Chapelle (SC WSC)  
Ron Harvey (NRP)  
Pat Phillips (NY WSC)  
Jason Masoner (OK WSC)  
Kathy Lee (MN WSC)  
Kymm Barnes (IA WSC)  
Laura Hubbard (IA WSC)  
Denis LeBlanc (MA WSC)

### Chemists

Ed Furlong (MRDP)  
Bill Foreman (MRDP)  
Steve Zaugg (MRDP)  
James Gray (MRDP)  
Mark Sandstrom (MRDP)  
Dave Alvarez (CERC)  
Keith Loftin (OGRL)  
Michelle Hladik (CA WSC)

### Microbial Ecologists

Sheridan Haack (MI WSC)  
Paul Bradley (SC WSC)  
Joe Duris (MI WSC)

### Biologists

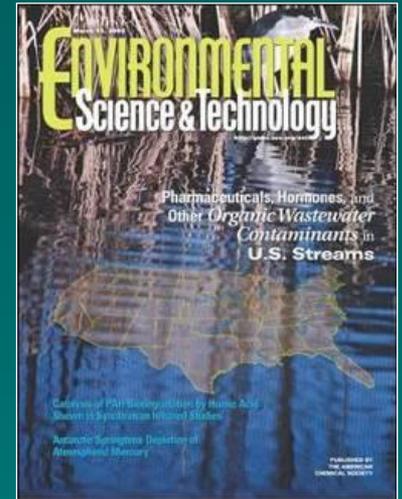
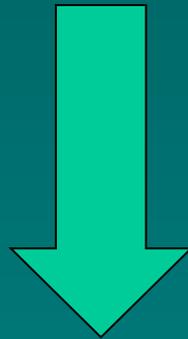
Vicki Blazer (LSC)  
Luke Iwanowicz (LSC)  
Marie-Noele Croteau (NRP)

### Geochemists

Larry Barber (NRP)  
Mike Meyer (OGRL)  
Phil Verplanck (GD)

# Evolution of occurrence question

Are CECs entering  
our environment?



2455 citations

What CECs are entering  
our environment?

# Recent USGS Analytical Efforts

## New Methods

- Hormones in water (19): GC/MS/MS
- Pharmaceuticals in water (112): DAI LC/MS/MS
- Halogenated OCs in solids and tissue (63): GC/MS

## Ongoing methods development activities

- Phytoestrogens
- Hormone conjugates
- Veterinary growth promoters
- Mycotoxins
- Halogenated OCs in bird eggs
- Surfactants
- Next generation waste-indicator method

## Recently purchased LC TOFs (2)

- Provide enhanced forensics capabilities

# What are the potential sources?

## Toxicant Source Pathways to the Environment

Cropland with applied pesticides, manure, biosolids and fertilizer



WIND

Stack emissions

Industrial discharges and urban runoff

Waste water treatment plant discharge

WIND

RUNOFF

RUNOFF

Mine and mineralized rock drainage

Animal feeding operations

Residential leach and septic

RUNOFF

SEEPAGE

SEEPAGE

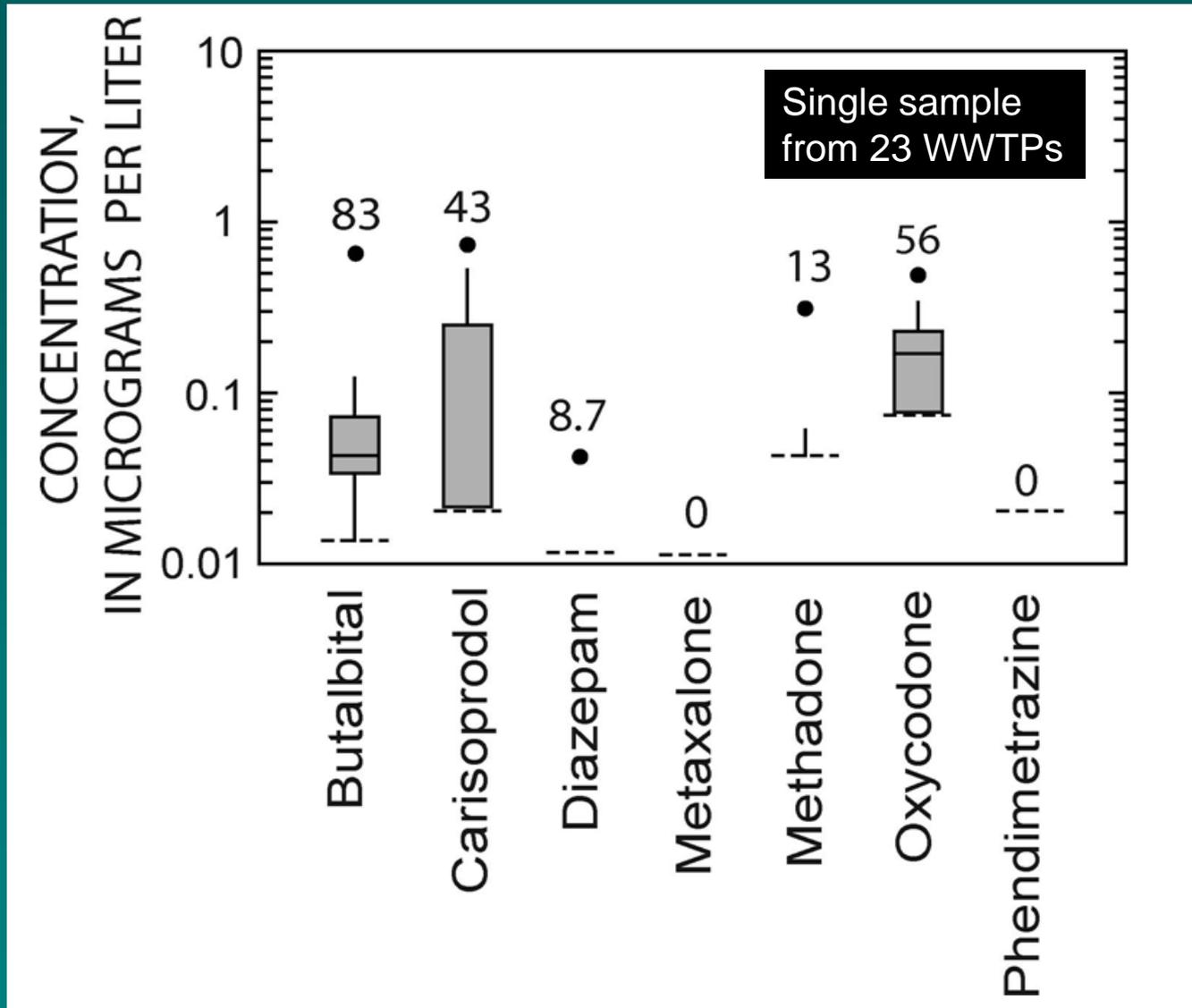
SEEPAGE

WATER TABLE

WATER TABLE

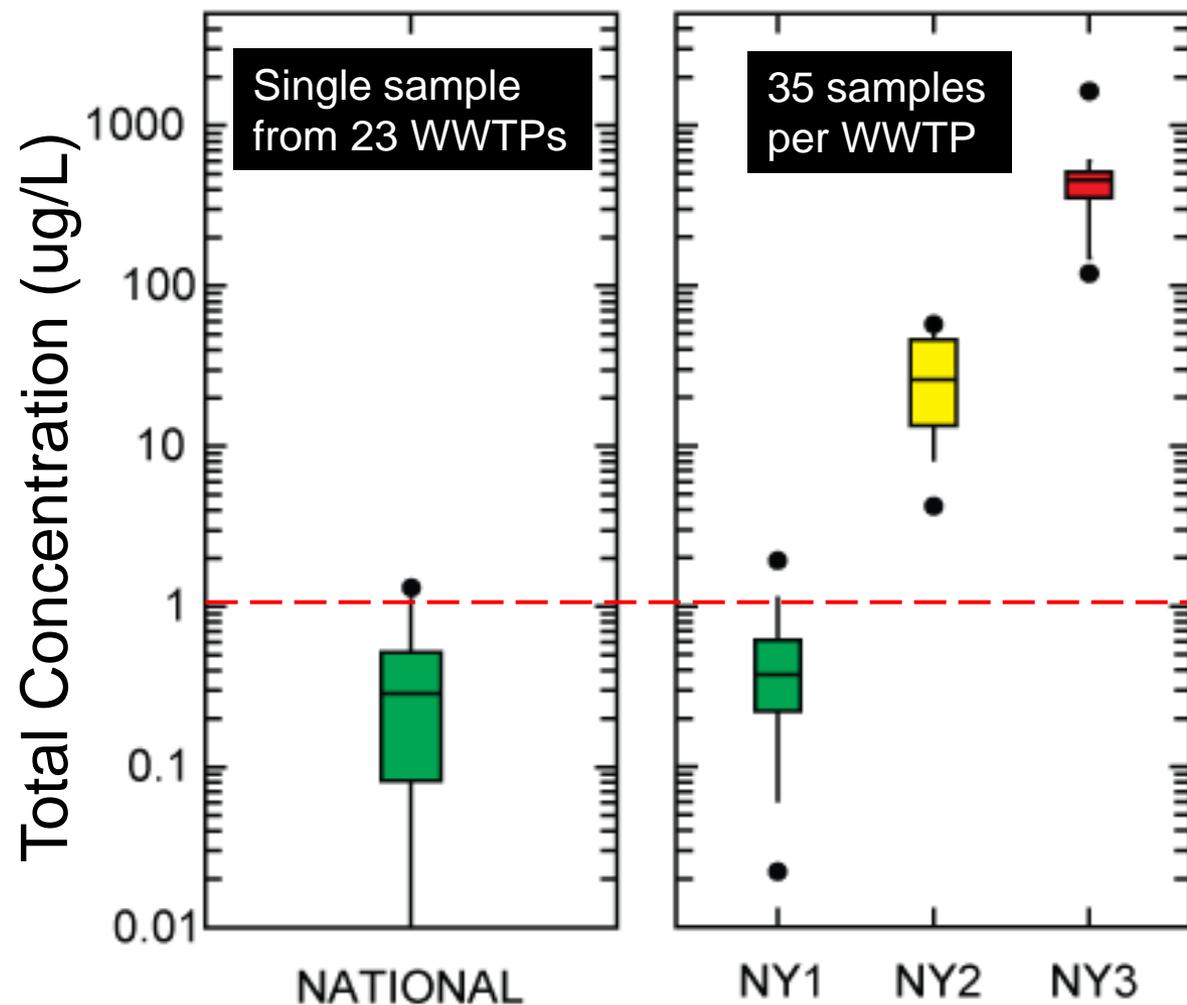
Illustration by Eric A. Morrissey

# National WWTP Network



# PMFs – Environmental Sources of CECs

Phillips et al., 2010



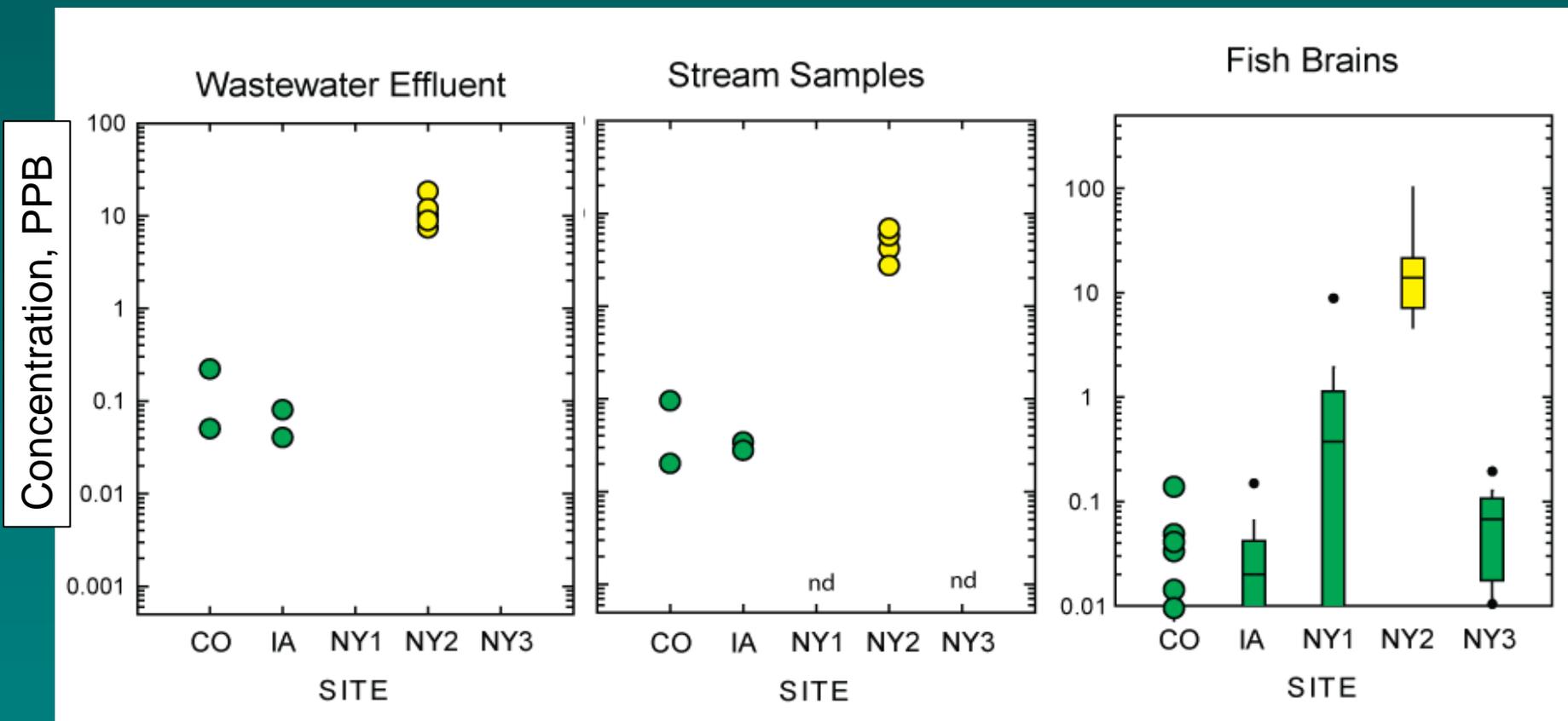
Max Conc. (ug/L)  
3800 metaxalone  
1700 oxycodone  
>400 methadone  
160 butalbital  
>40 phendimet.  
>40 carisoprodol  
4 diazepam

# PMFs – Additional Research

Comprehensive analysis of effluent (DAI method)

- 6 additional pharms at elevated levels ( $>10 \mu\text{g/L}$ )
  - bupropion (antidepressant)
  - chlorpheniramine (antihistamine)
  - fexofenadine (antihistamine)
  - hydrocodone (narcotic analgesic)
  - metformin (anti-diabetic)
  - temazepam (psychoactive)

# Bupropion Env'l Exposure @ PMF



# Laboratory Exposure Experiment 2012:

- Antidepressants (4)
  - Opioids (4)
  - Muscle Relaxant (methocarbamol)
  - Sleep Aid (temazepam)
  - Opiate Agonist (tramadol)
  - Complete Mixture
  - Carrier Control
- 
- Water Chemistry (USGS - NWQL)
  - Fecundity, fertility, hatching (SCSU)
  - Liver, gonad histopathology (SCSU)
  - Vitellogenin concentrations (SCSU)
  - Gene expression (U. of St. Thomas)
  - Immunological response (SCSU)
  - Bioaccumulation (Wooster College)

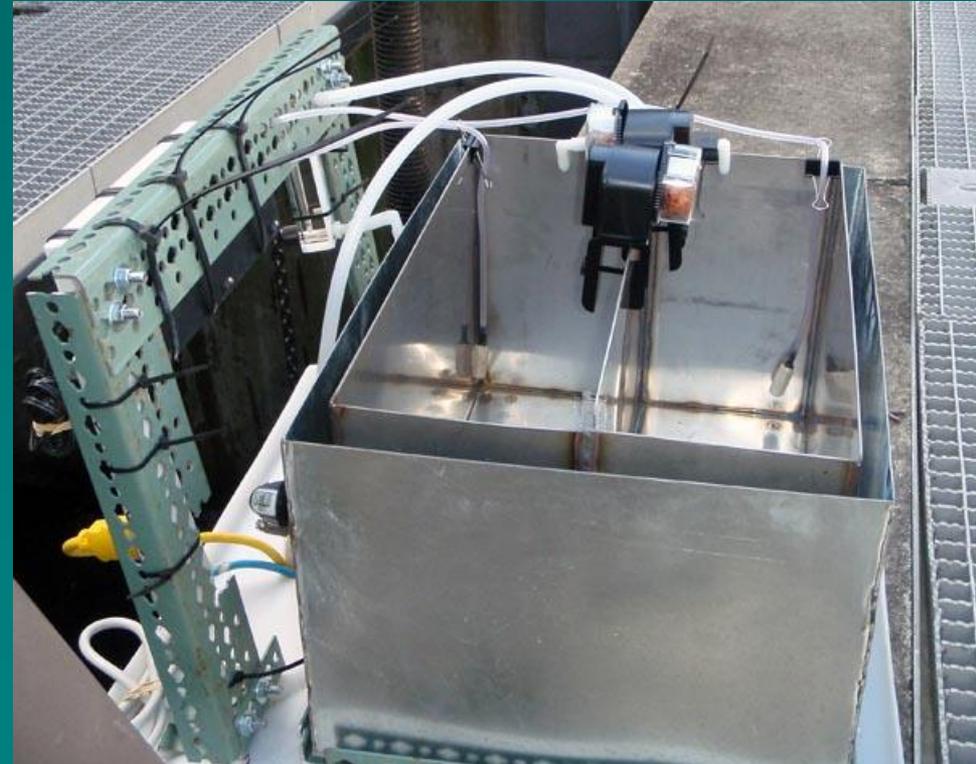
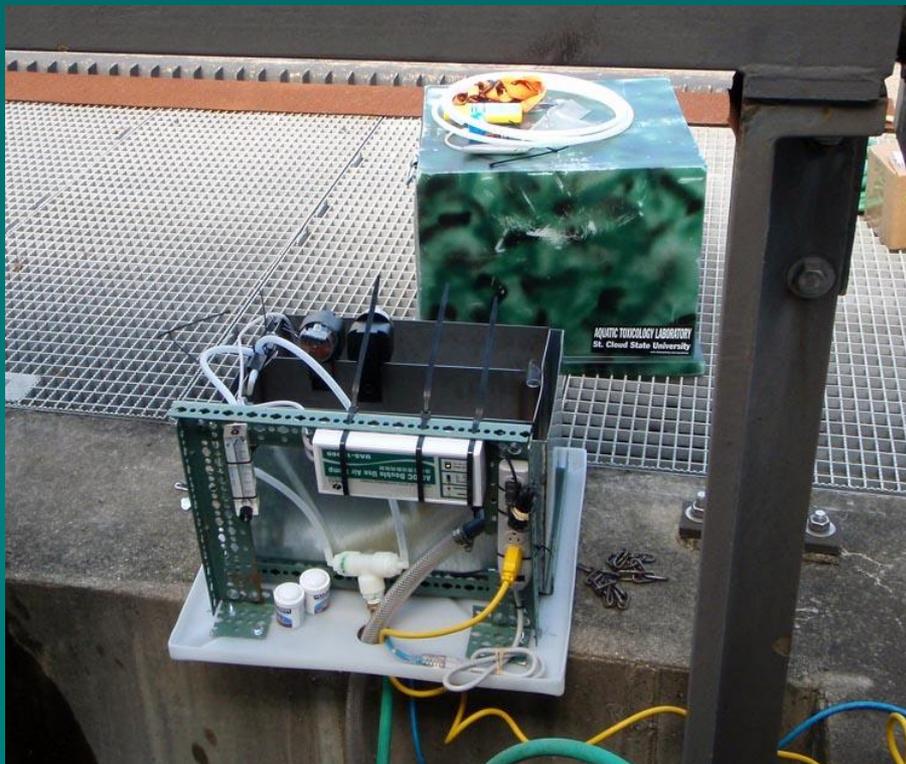
21-day flow-through mature fathead minnow exposure (two week pre-exposure baseline). Ten spawning scenarios (1 male, 2 females) per treatment.



# Field Exposure Experiment 2012:

*Assessing the effects of pharmaceuticals in whole effluent.*

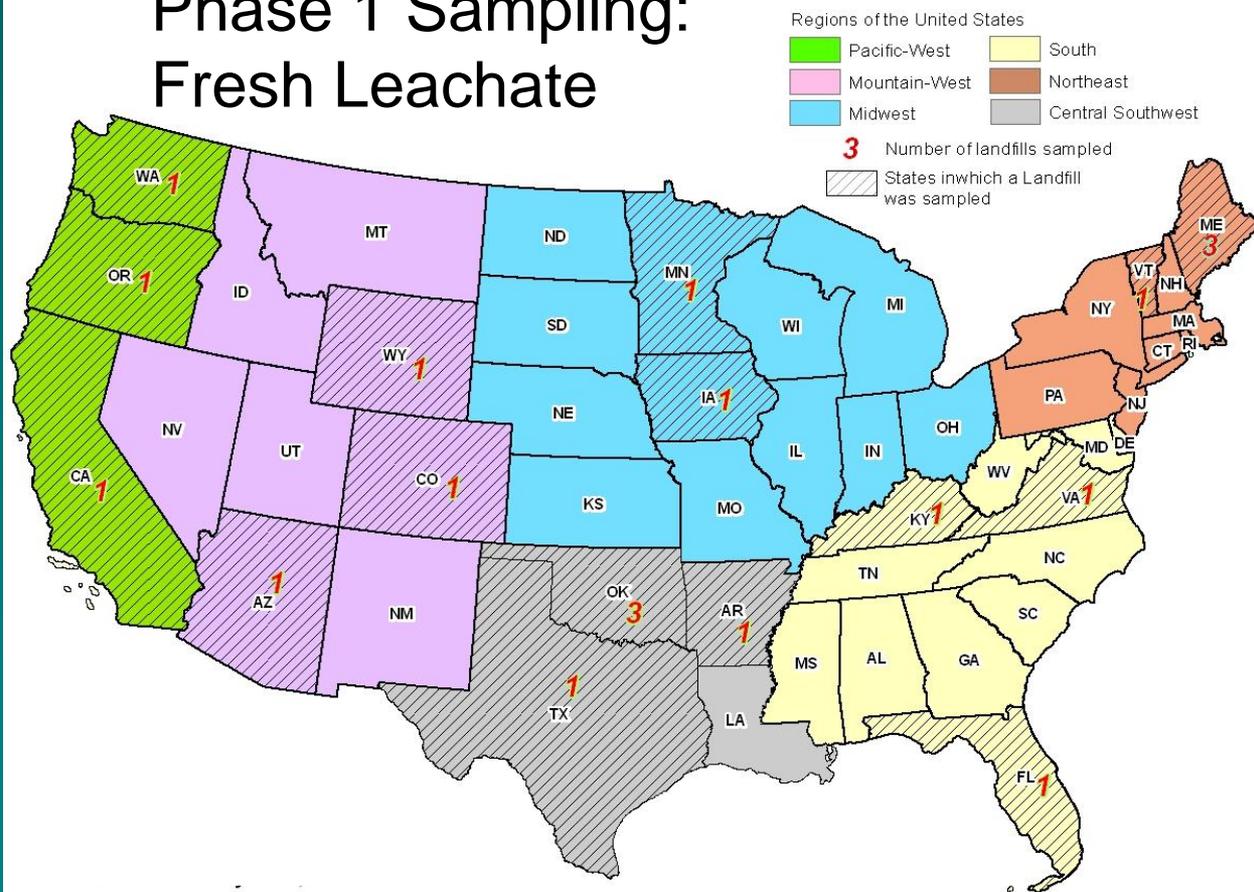
21-day *in-situ* flow-through mature fathead minnow exposure. 20 males, 20 females in on-site mini-mobile exposure unit (MMU). March 2012.



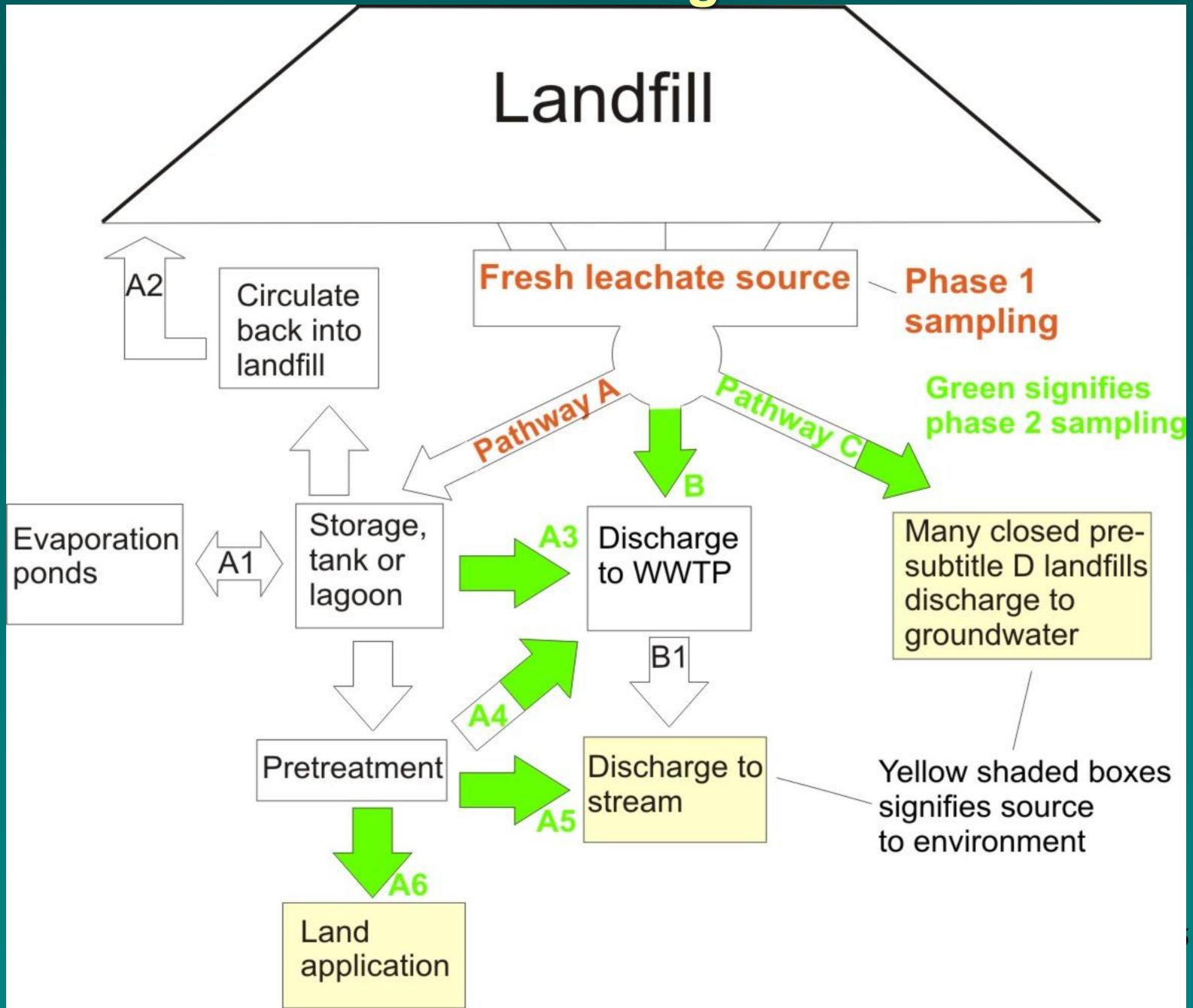
# National Landfill Leachate Study



## Phase 1 Sampling: Fresh Leachate

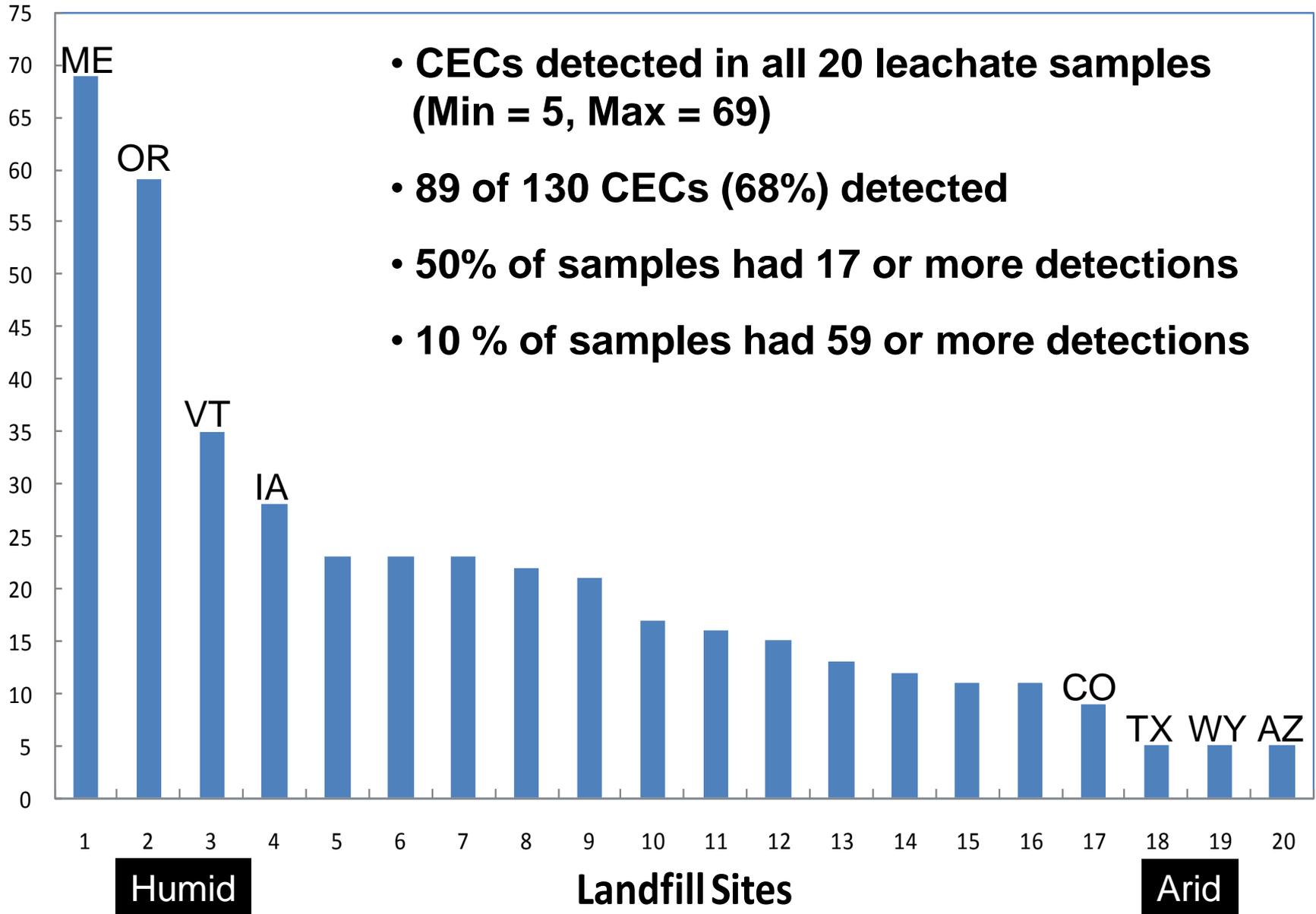


# Common Leachate Management Practices

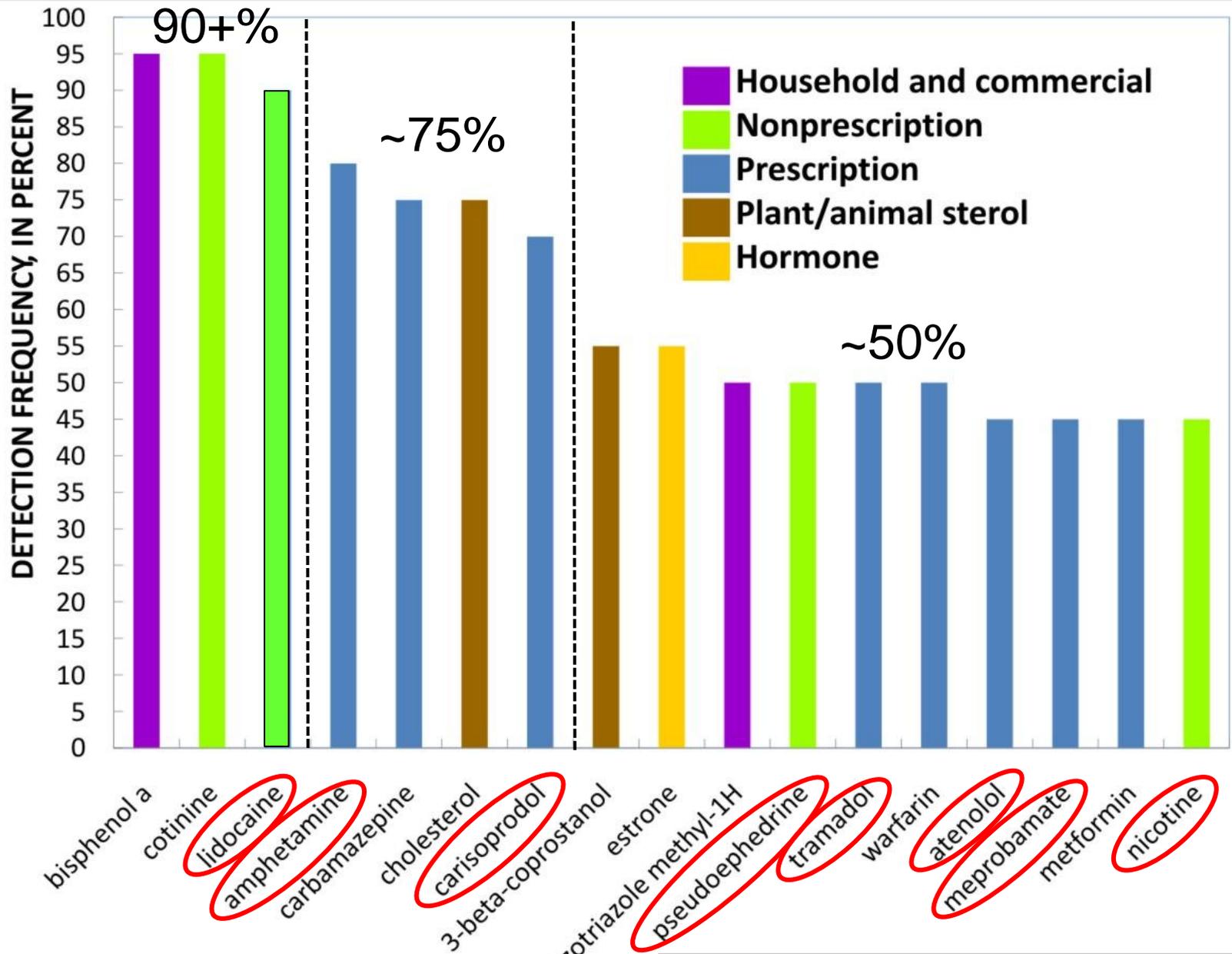


# CECs Detected by Landfill Site

NUMBER OF DETECTED EMERGING  
CONTAMINANTS

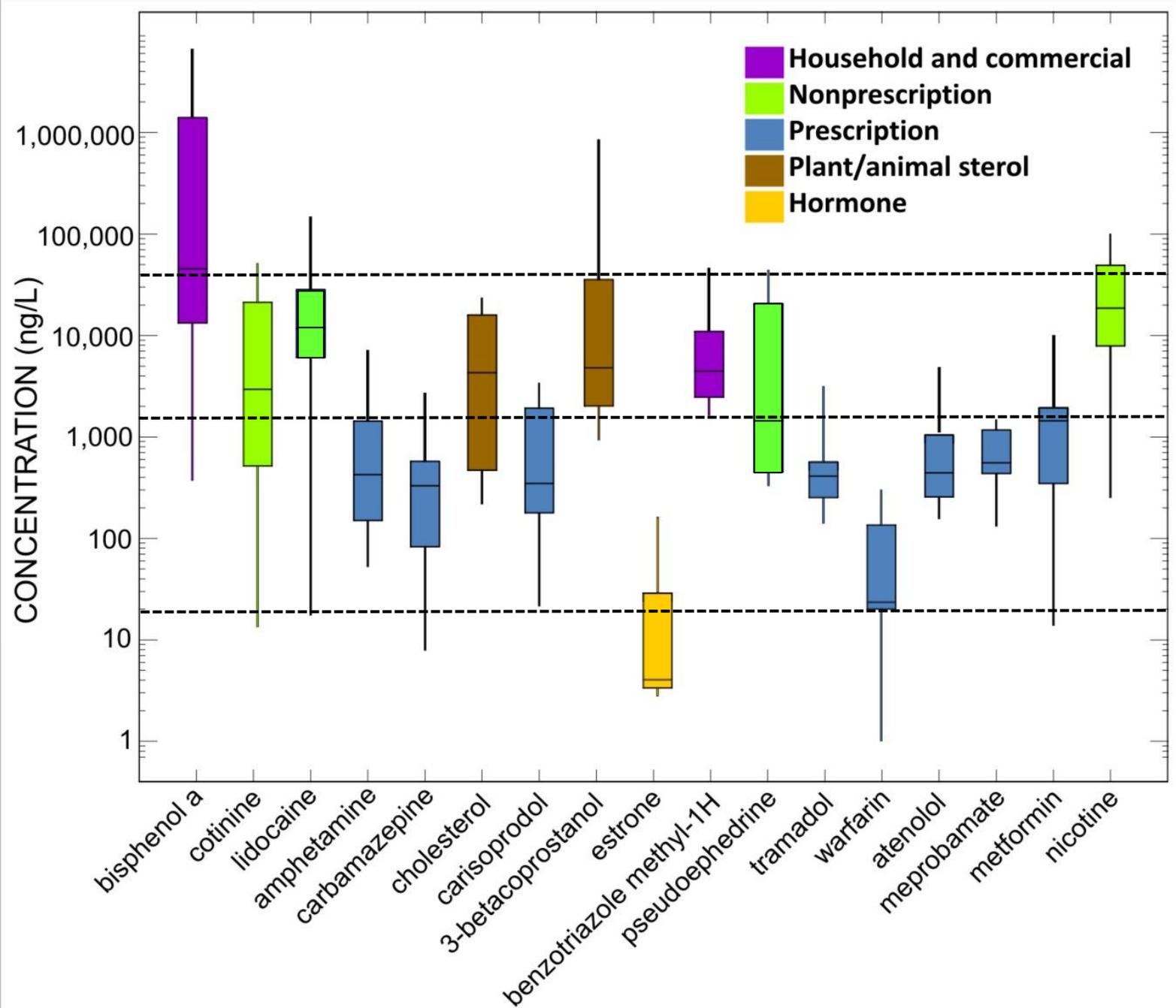


# CECs Detected in 45% or More in Leachate Samples



**89 of 130 CECs detected**

# Concentration Ranges, ECs Detected in 45% or More in Leachate Samples



# Fourmile and Boulder Creeks: Field labs to conduct hypothesis-driven research



Fourmile Creek (IA)



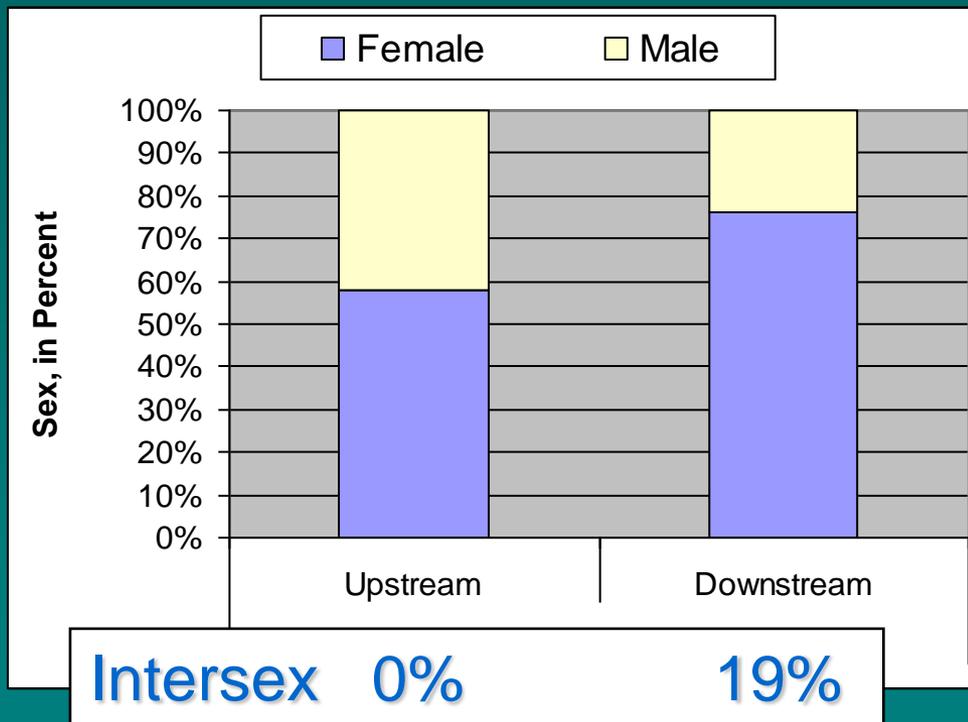
Boulder Creek (CO)

- Relatively small, headwater basins
- Effluent impacted systems (single WWTP discharge)
  - clear perturbations to the system
- WWTPs undergoing major changes
  - allows unique process-oriented research
- Controls present above WWTPs

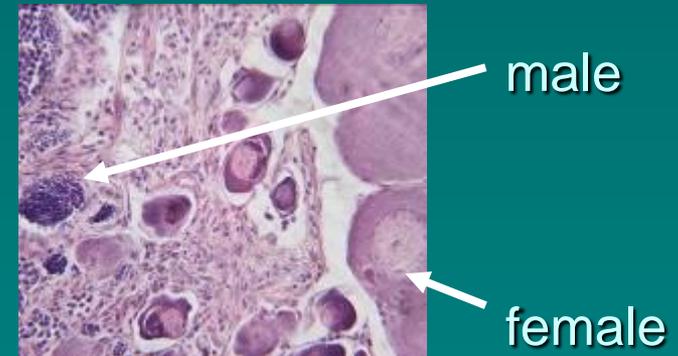


# Evidence of Endocrine Effects in WWTP Impacted Stream (Boulder Creek)

## White sucker

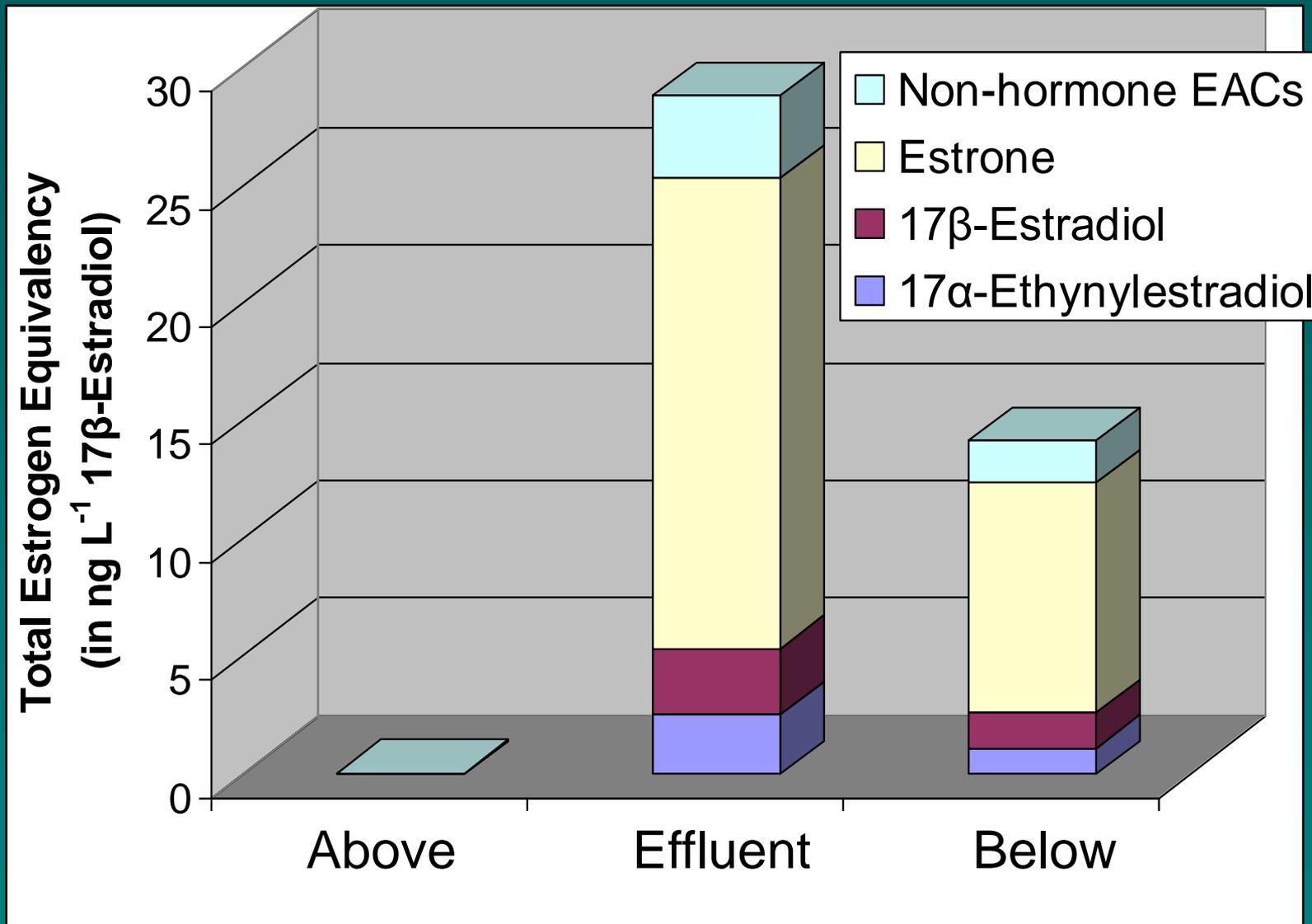


Intersex  
Blood Vitellogenin  
Cellular Abnormalities



*Vajda et al., 2008*

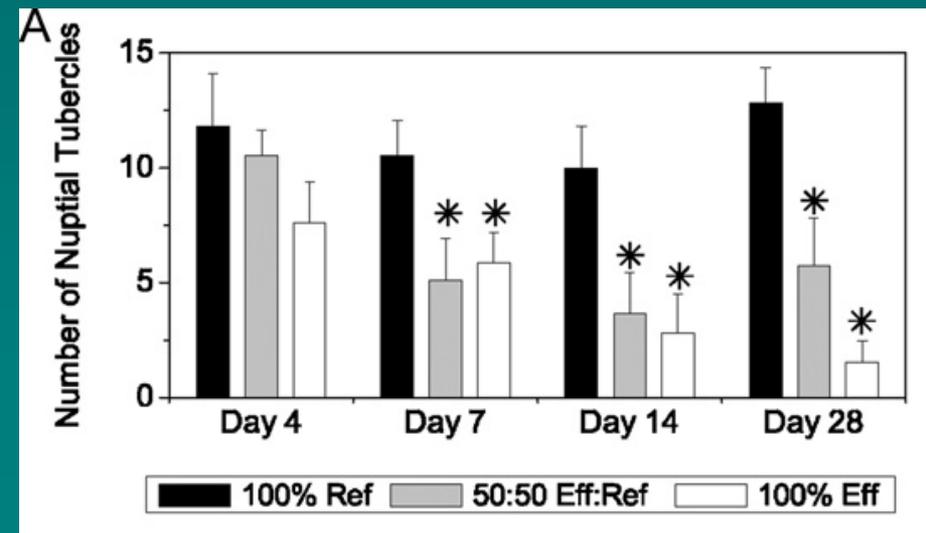
# WWTP: dominant source for CECs



# Boulder WWTP Effluent Estrogenic (trickling filter treatment process)



Onsite stream waters with controlled photo-period and water temp.



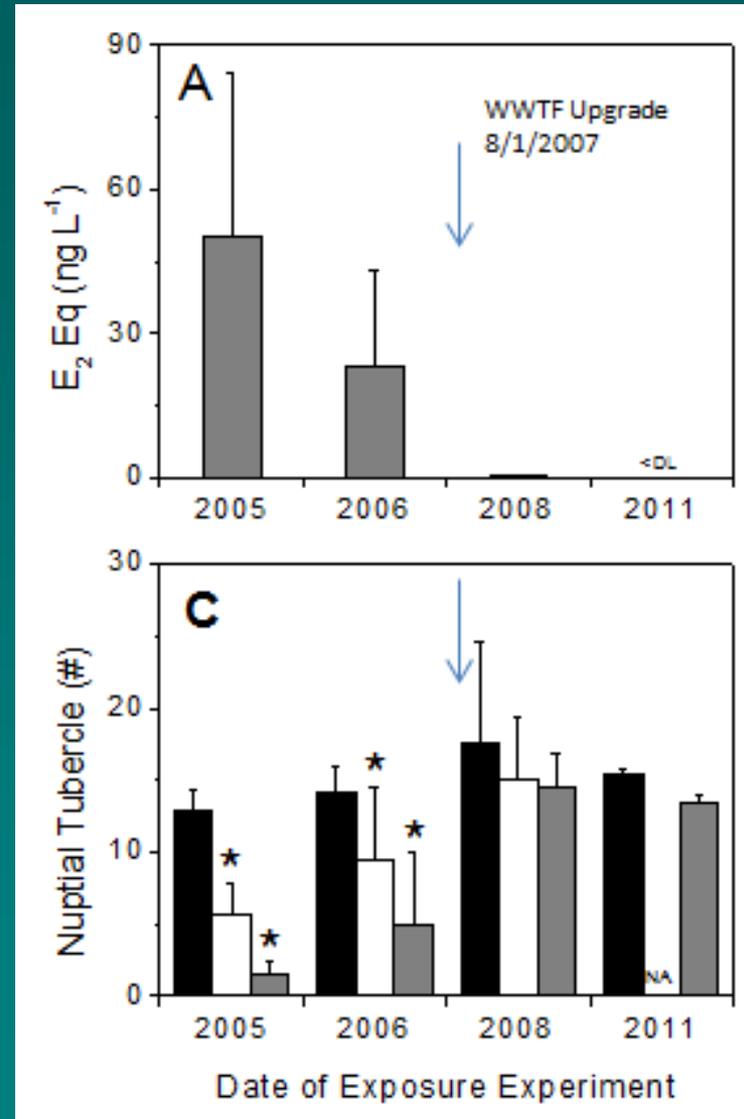
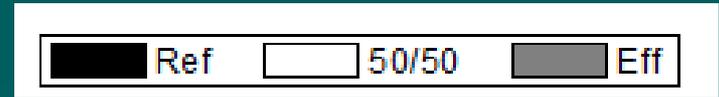
Vajda et al., 2011

# Boulder WWTP Post-Upgrade Results

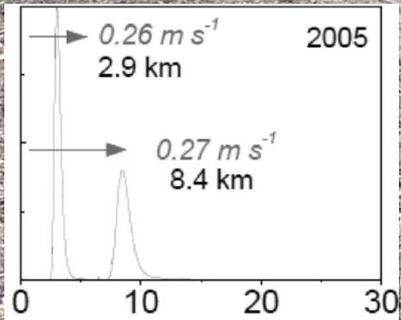
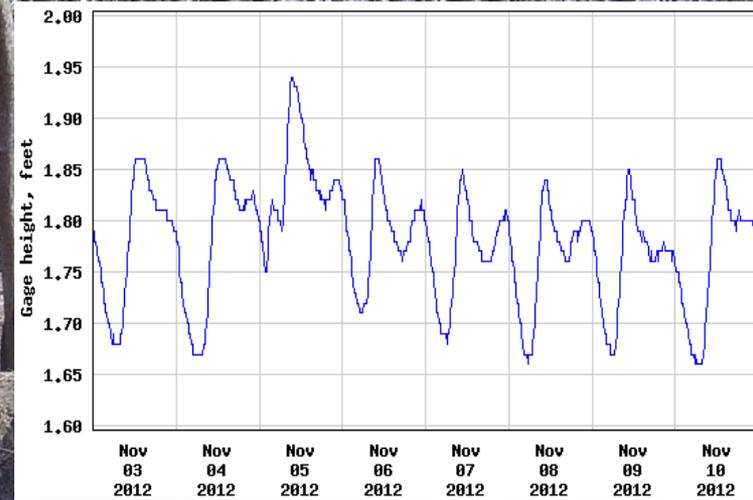
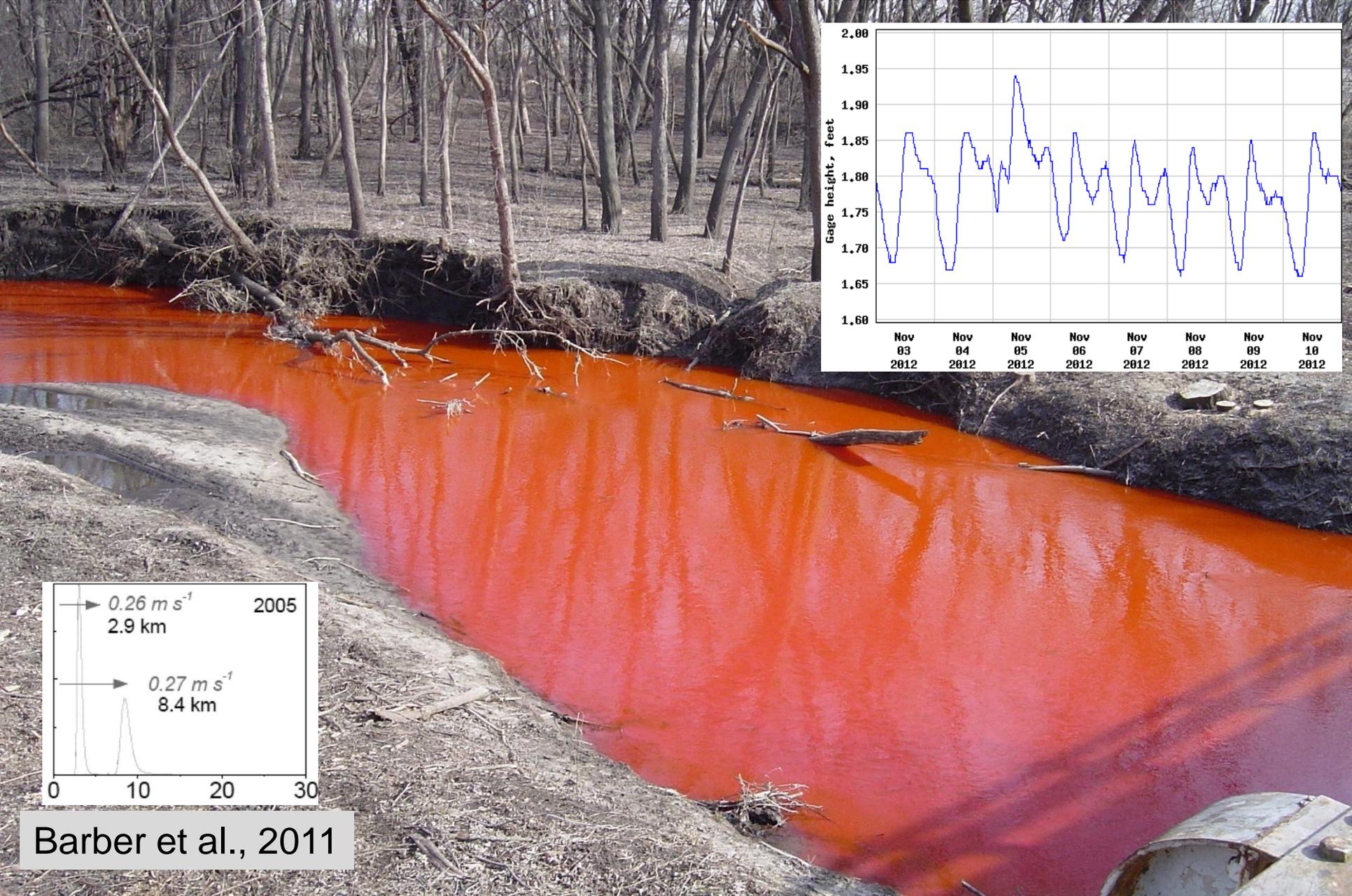
Switch from trickling filter to an activated sludge process:

- Improved the removal efficiencies of many CECs
- Decreased the estrogenicity of discharged effluent
- Reduced endocrine disruption relative to pre-upgrade conditions

Field survey of fish populations and endocrine disruption in white suckers (Oct. 2011)



# Fourmile Creek: Understanding the Hydrology

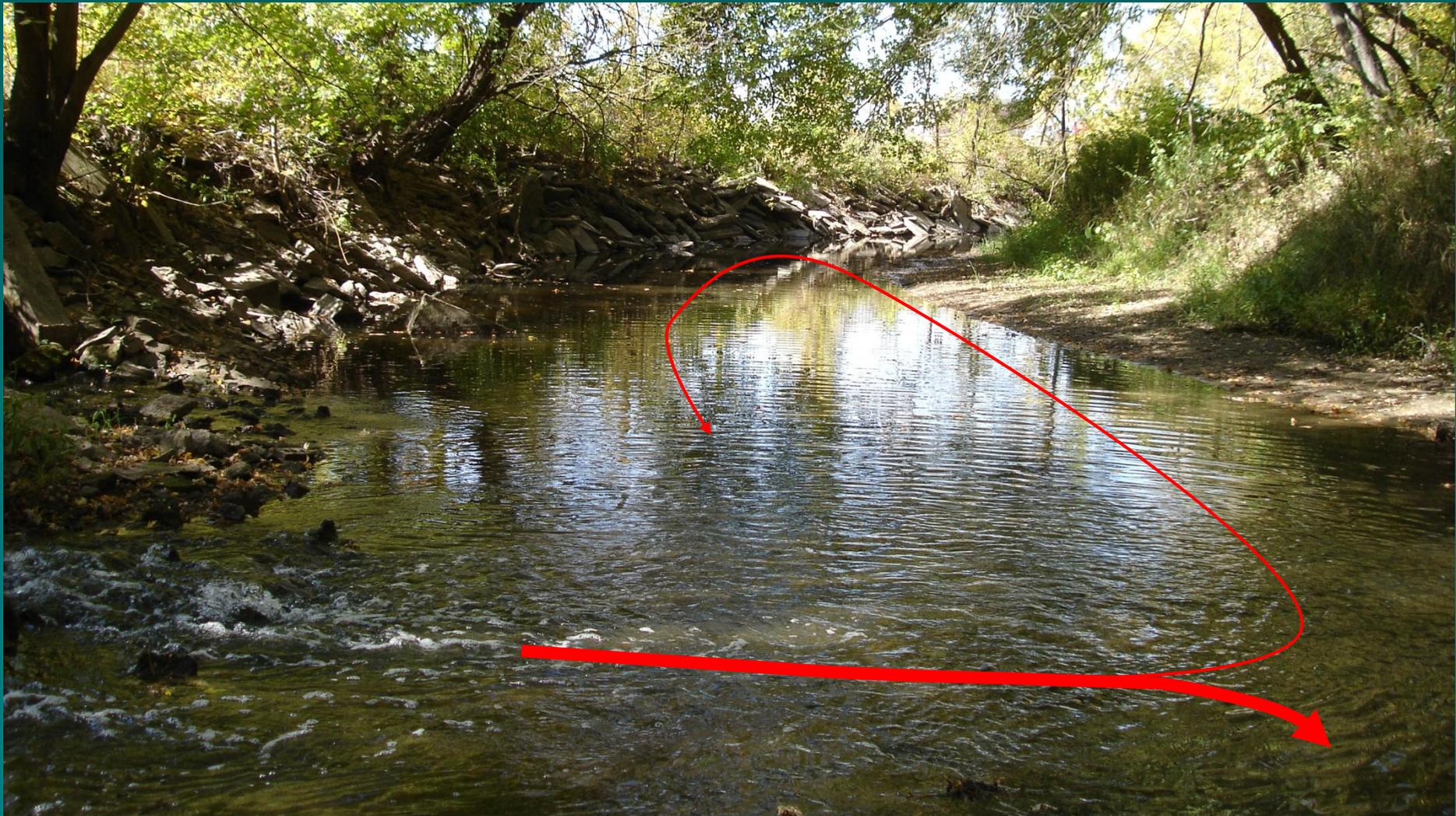


Barber et al., 2011

# Unexpected Phenomena (eddy effect above outfall)

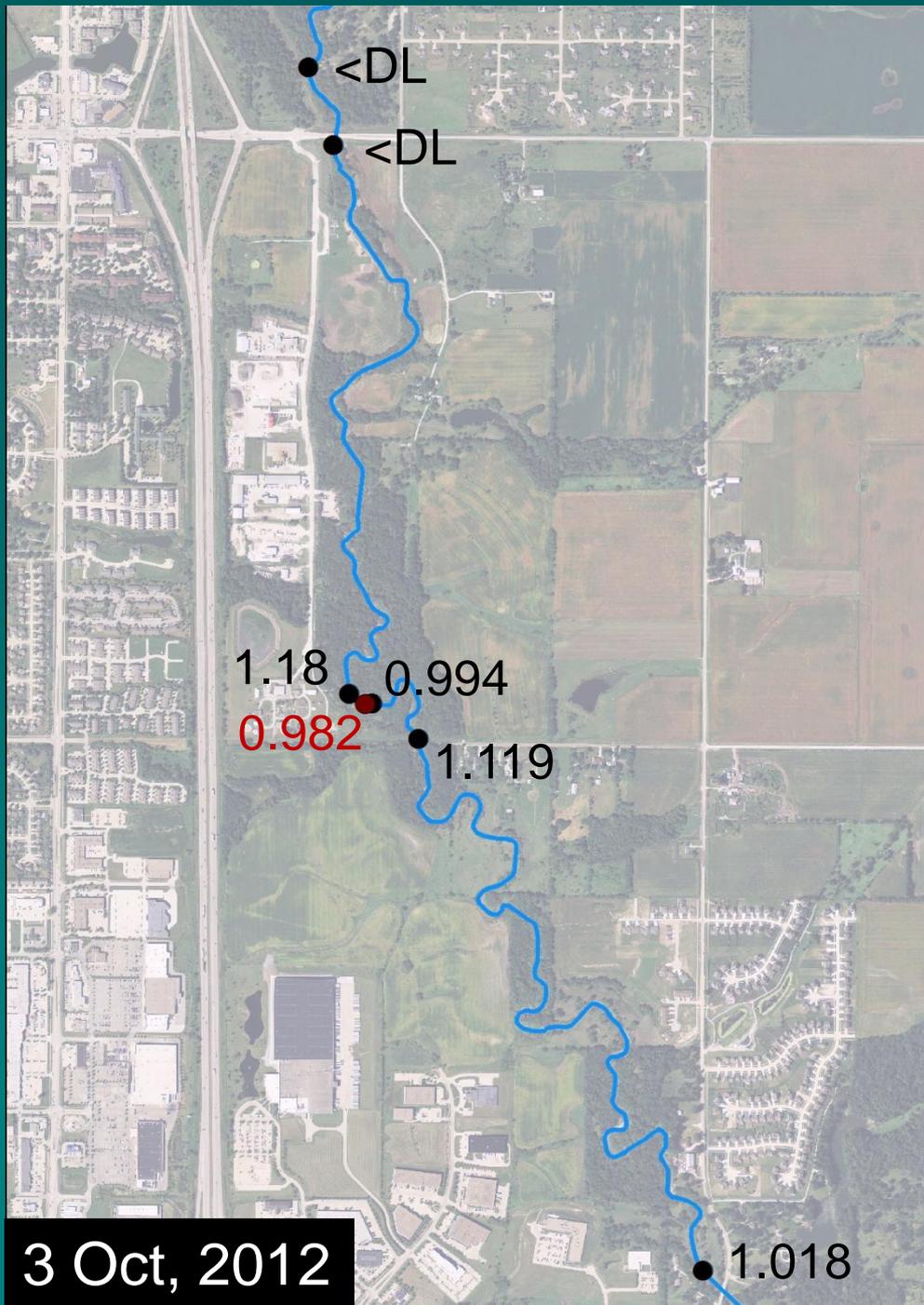


# Unexpected Phenomena (eddy effect above outfall)



# Carbamazepine by ELISA ( $\mu\text{g}/\text{L}$ )

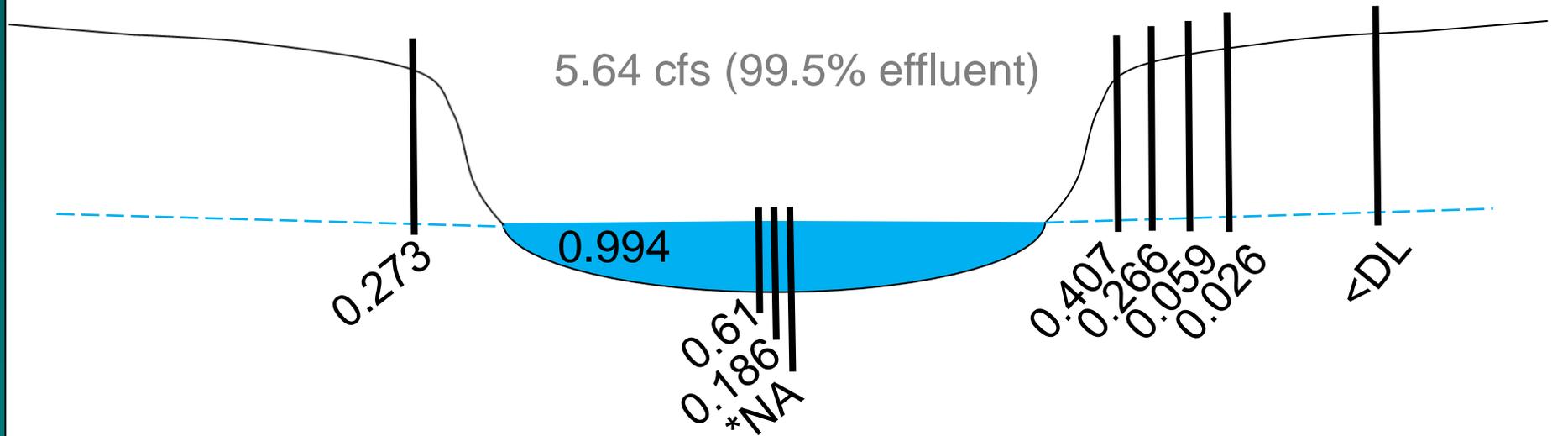
- No detections at upstream most sites
- Eddy effect causing detection proximal above outfall
- Conservative transport



# Fourmile Creek below WWTP outfall

3 October, 2012

ELISA Carbamazepine ( $\mu\text{g/L}$ )



Bed = sand + gravel, some biofilm

# Swine Hepatitis E in Streams

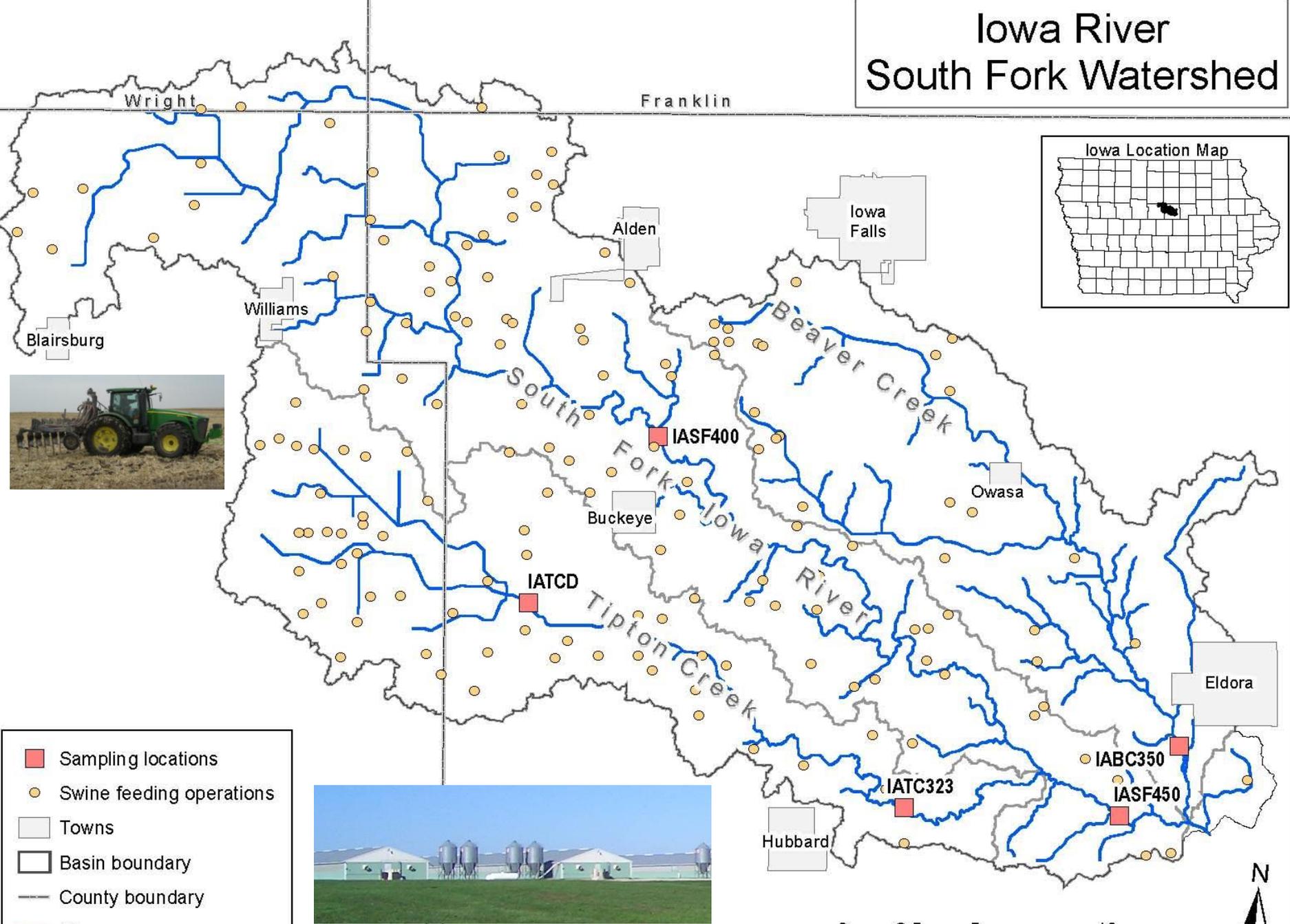
- HEV important pathogen
- High prevalence of sHEV in swine herds worldwide
- Cross species infection of HEV demonstrated



# Iowa River South Fork Watershed



- Sampling locations
- Swine feeding operations
- Towns
- Basin boundary
- County boundary
- Streams



Source: USDA ARS, Iowa DNR

# Swine Hepatitis E

- Large sHEV in manure from 2 hog facilities
- sHEV related to manure applications
  - Aug → (fall manure) → Oct
  - March → (spring manure) → April  
20% 70%
- Results confirmed by sequencing
- No sHEV in out-of-basin reference



# Mycotoxins

Naturally occurring toxic secondary metabolites of fungal species (e.g. *Fusarium spp.*)

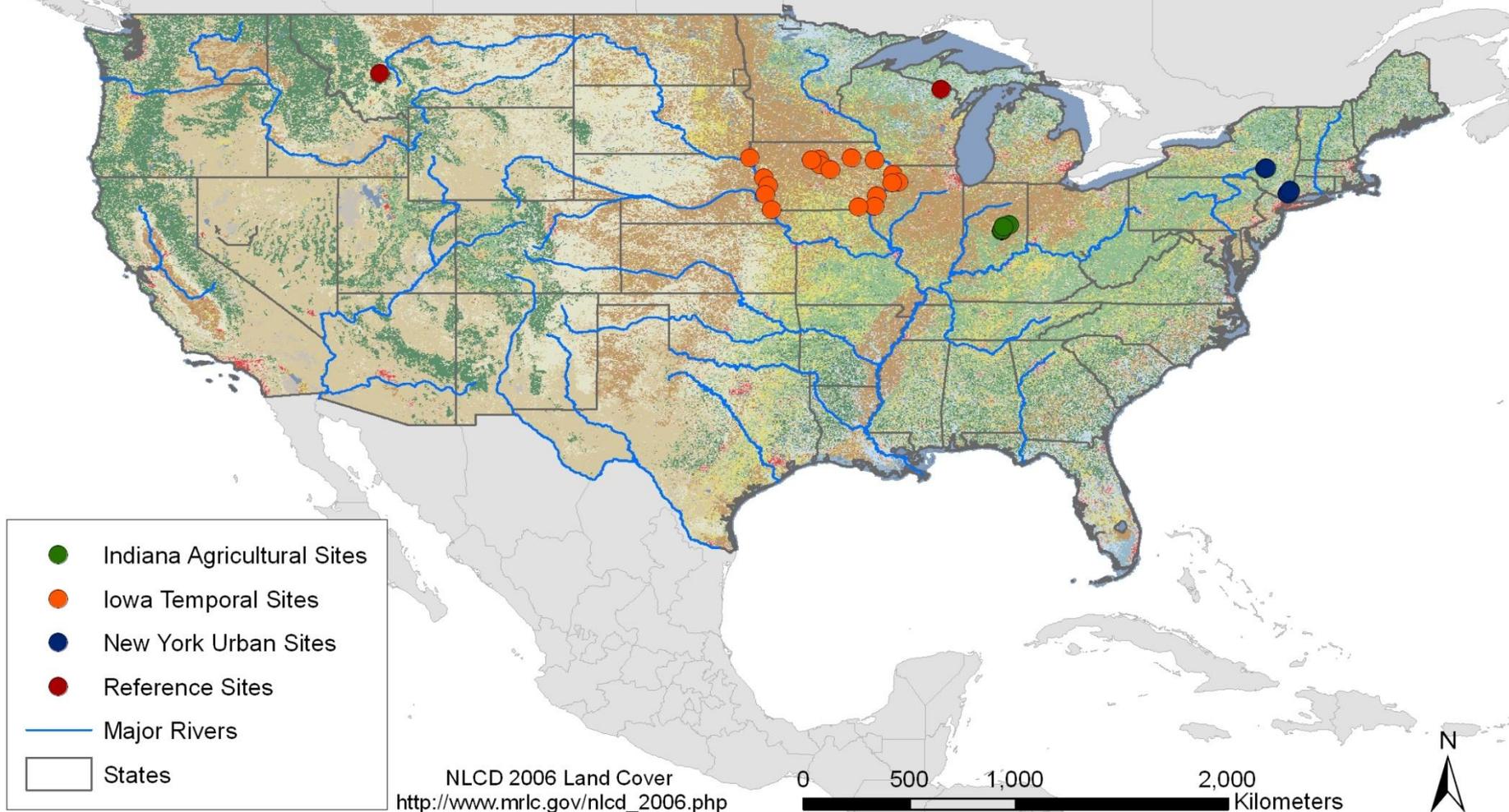


## Principal sources

- infected crops
- livestock manure
- WWTP effluent

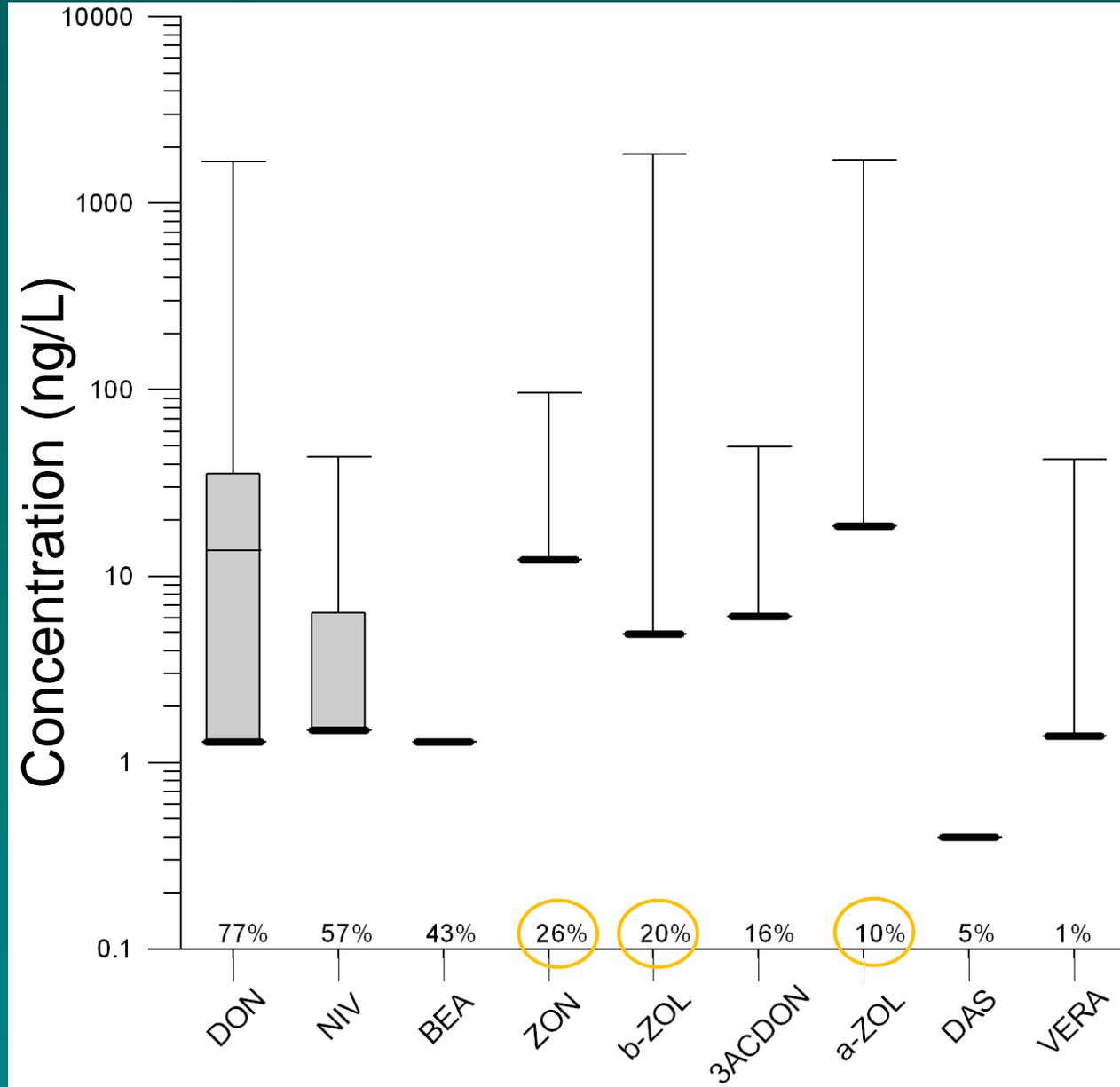


# Sampling Network (116 samples from 35 sites)



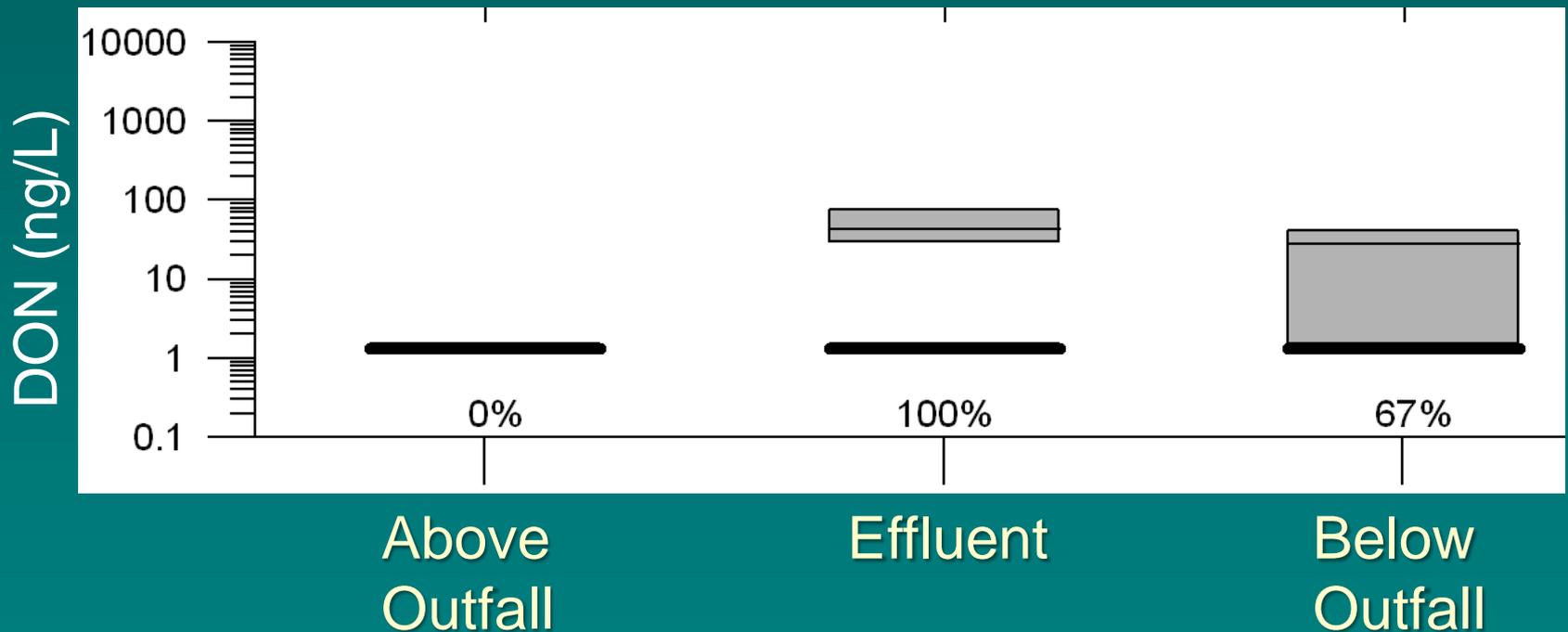
# Overall Summary

- At least one mycotoxin detection in 94% of 116 samples
- 9 compounds detected
- 80% of samples >1 mycotoxins
- 42% had >1 estrogenic myco
- 3 concentrations exceeded 1000 ng/L



# WWTP Effluent a Source of Mycotoxins to streams

- 3ACDON, DON,  $\alpha$ -ZOL,  $\beta$ -ZOL



Max effluent concentrations exceeded 1000 ng/L for  $\alpha$ -ZOL,  $\beta$ -ZOL

# Questions?

