

# PPCPs, Bacteria, and Other Contaminants in Karst Springs and Caves in Southwestern Illinois

(c) Michael Bradford 2014

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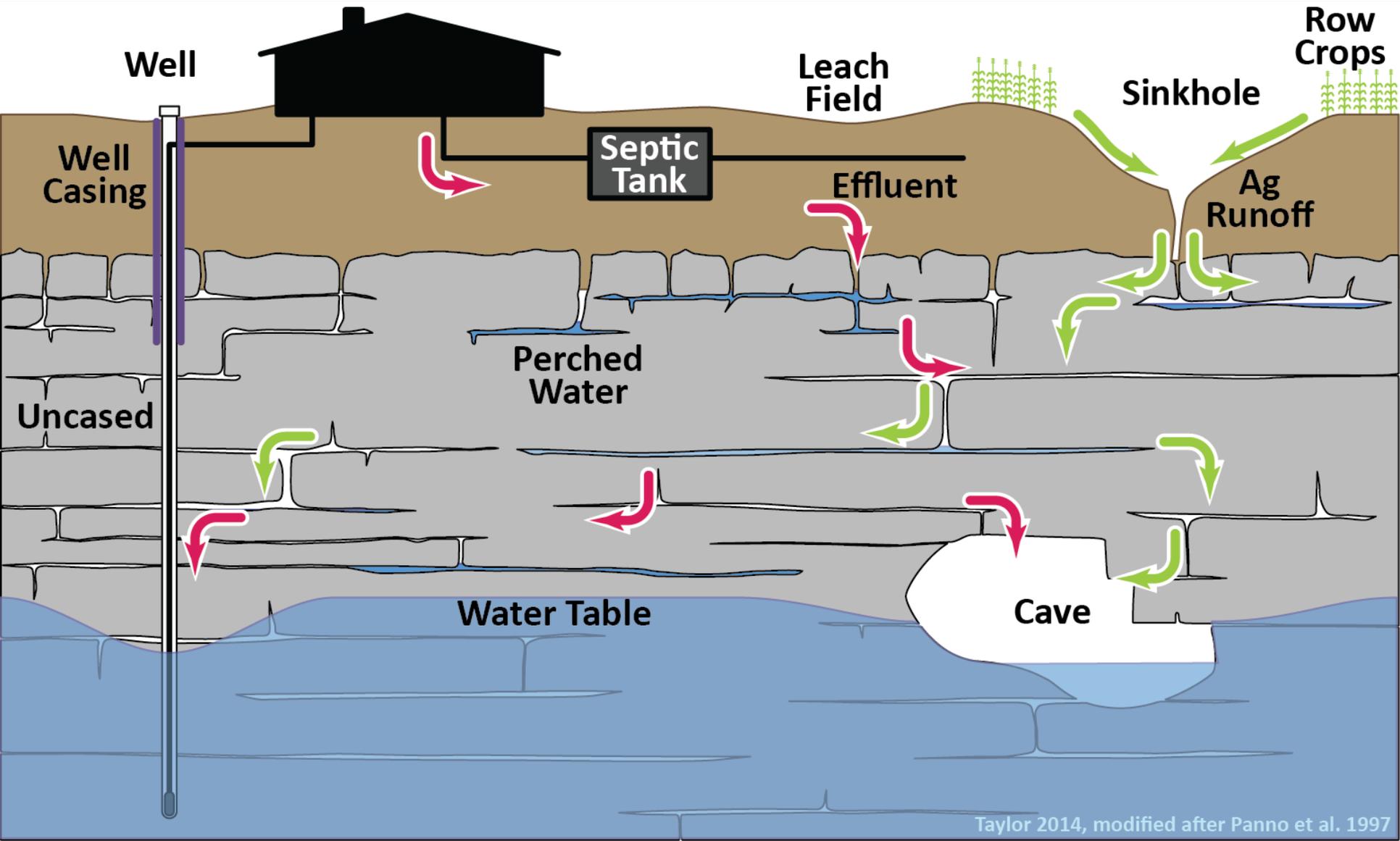


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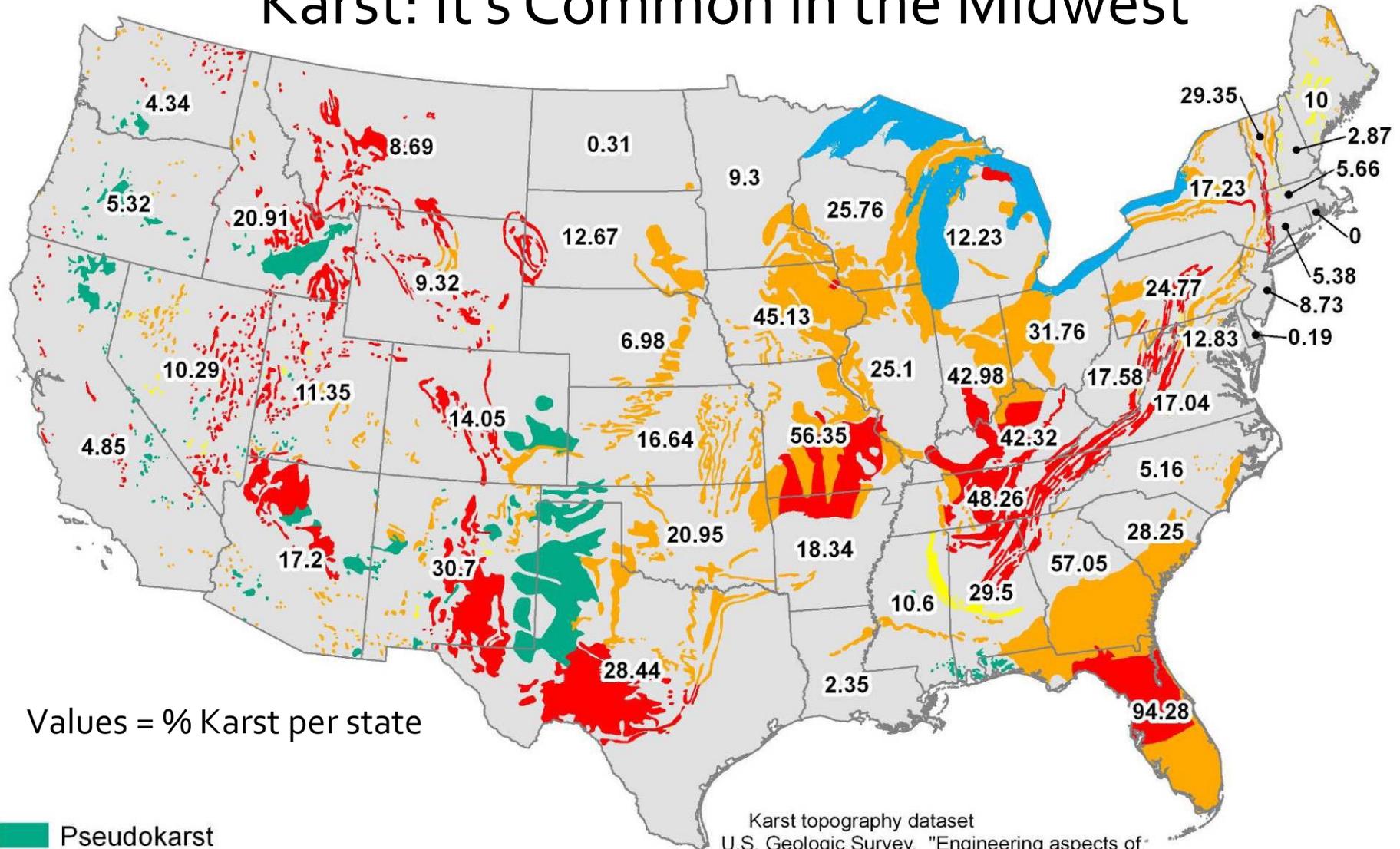
# The Urban Footprint



# Karst: Vulnerable to Contamination



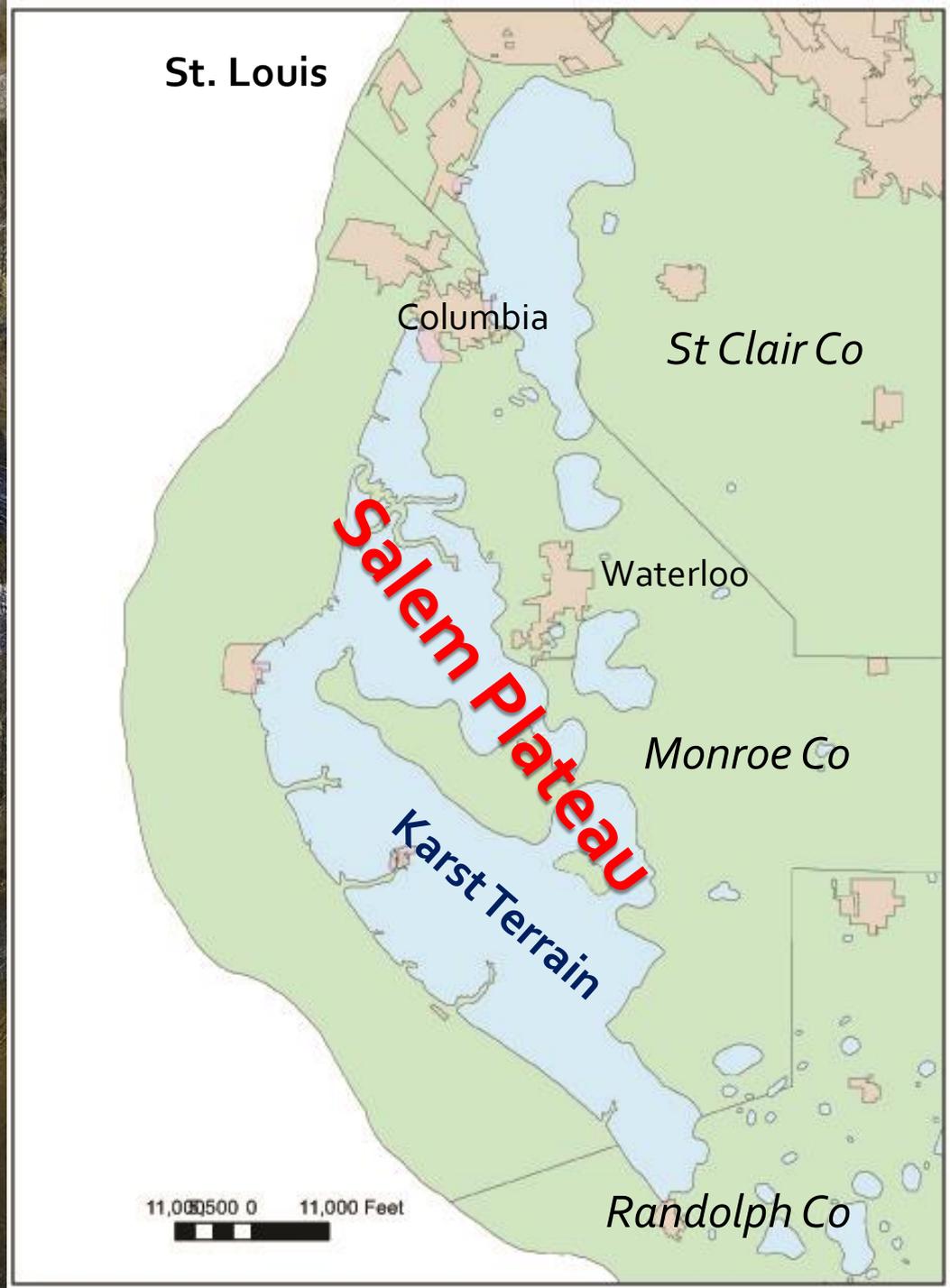
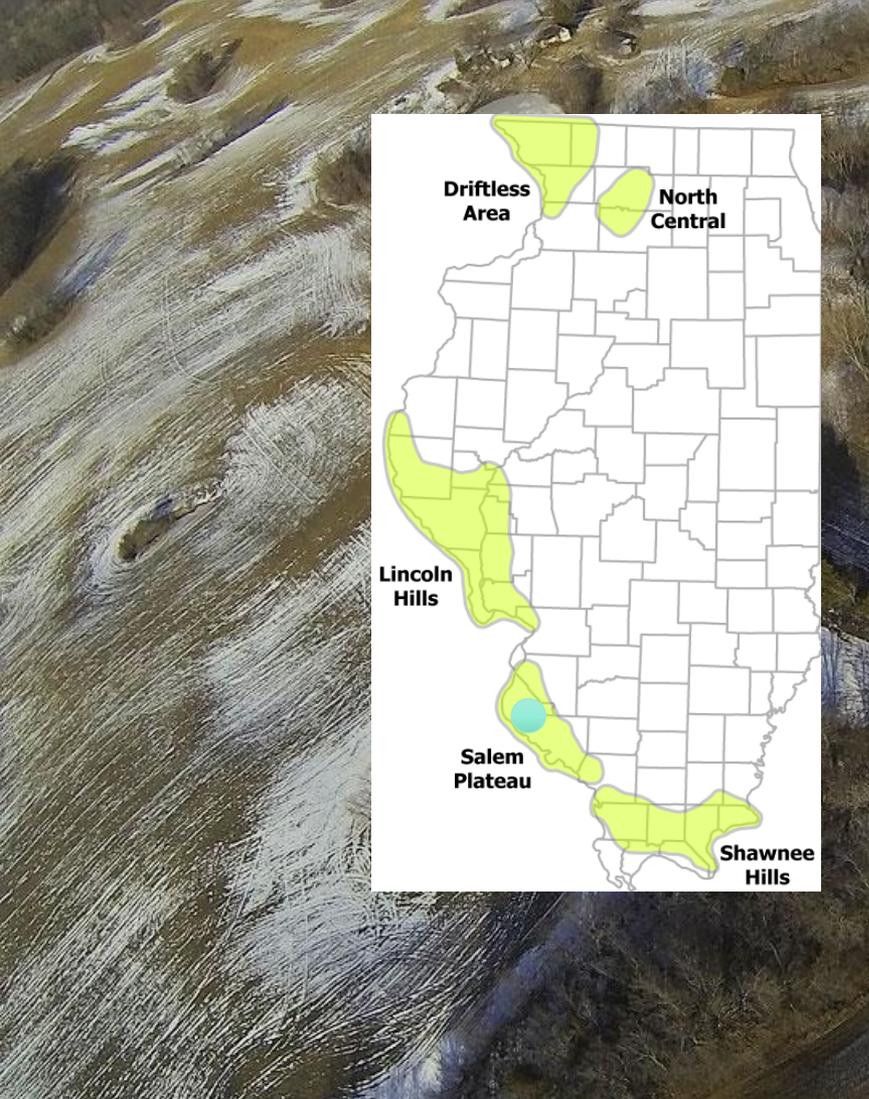
# Karst: It's Common in the Midwest



Values = % Karst per state

- Pseudokarst
- Fissures and caves over 1,000 ft long
- Fissures and caves generally less than 1,000 ft long
- Fissures and caves generally absent
- USA Contiguous

Karst topography dataset  
 U.S. Geologic Survey. "Engineering aspects of karst." [ESRI shapefile]. Created by Davies, W.E., Simpson, J.H., Ohlmacher, G.C., Kirk, W.E., and Newton, E.G.  
 Analysis & Cartography  
 Chuck Sutherland  
 Projection  
 US National Atlas Equal Area



Salem Plateau  
(Sinkhole Plain)

Waterloo, IL

Land Use Changes in Salem Plateau:  
Becoming a bedroom community for St. Louis

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Google earth

Imagery Date: 10/21/2014 38°19'53.10" N 90°09'33.13" W elev 644 ft eye alt 7483 ft

1993

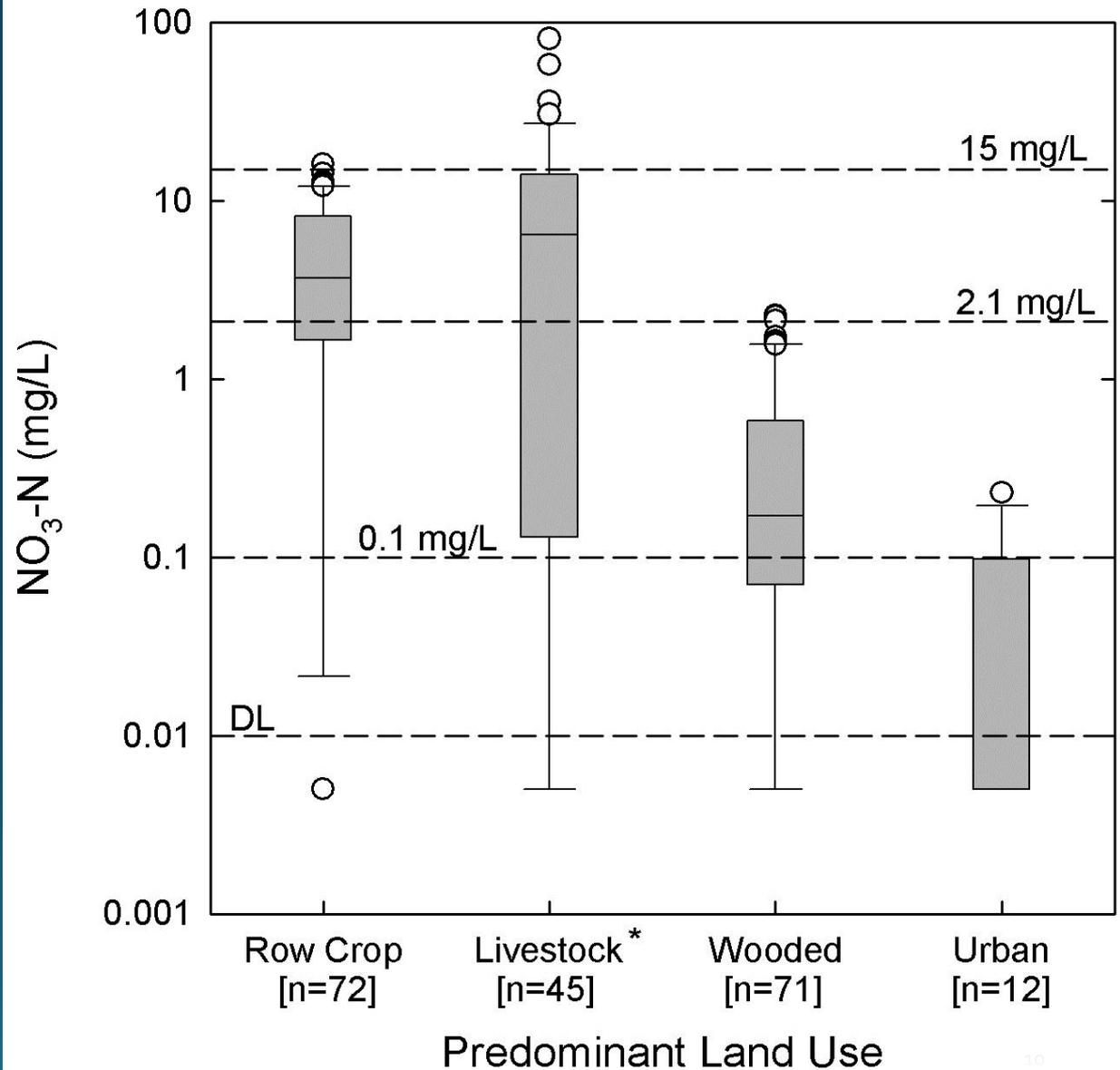






# We Know Land Use Activities Affect Water Quality in Karst Regions

Well water data from Sinkhole Plain



# Seasonal Sampling of Karst Springs and Cave Streams in Salem Plateau

- Effects of increased residential areas
- Compare to samples collected 15 years earlier

# Springs vs. Wells in Karst Areas

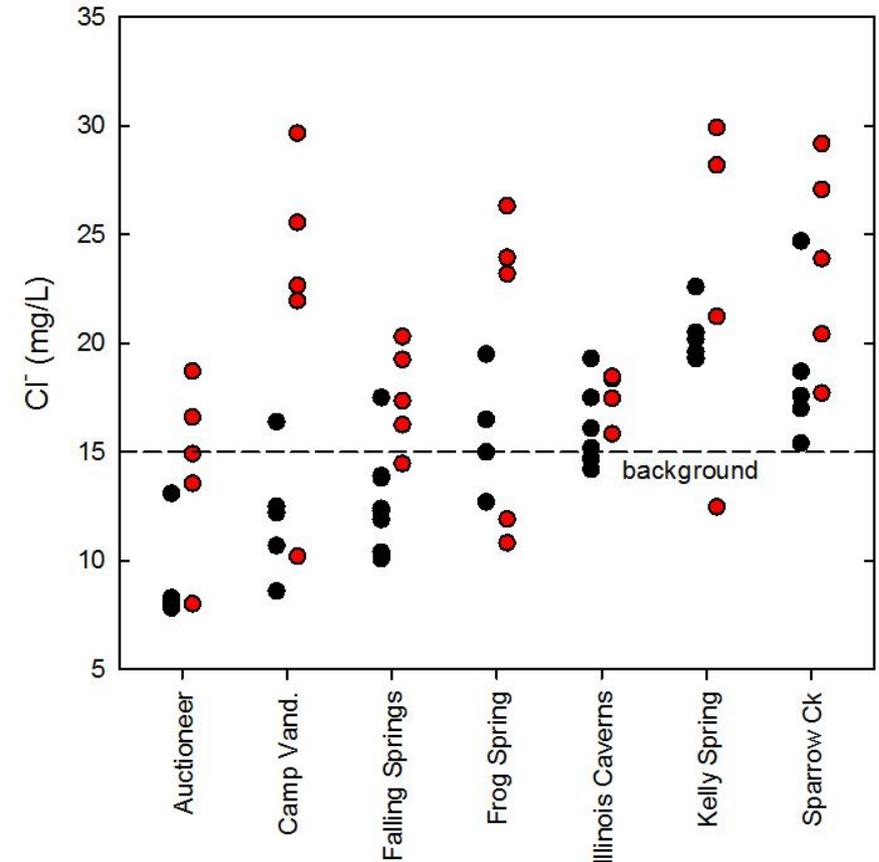
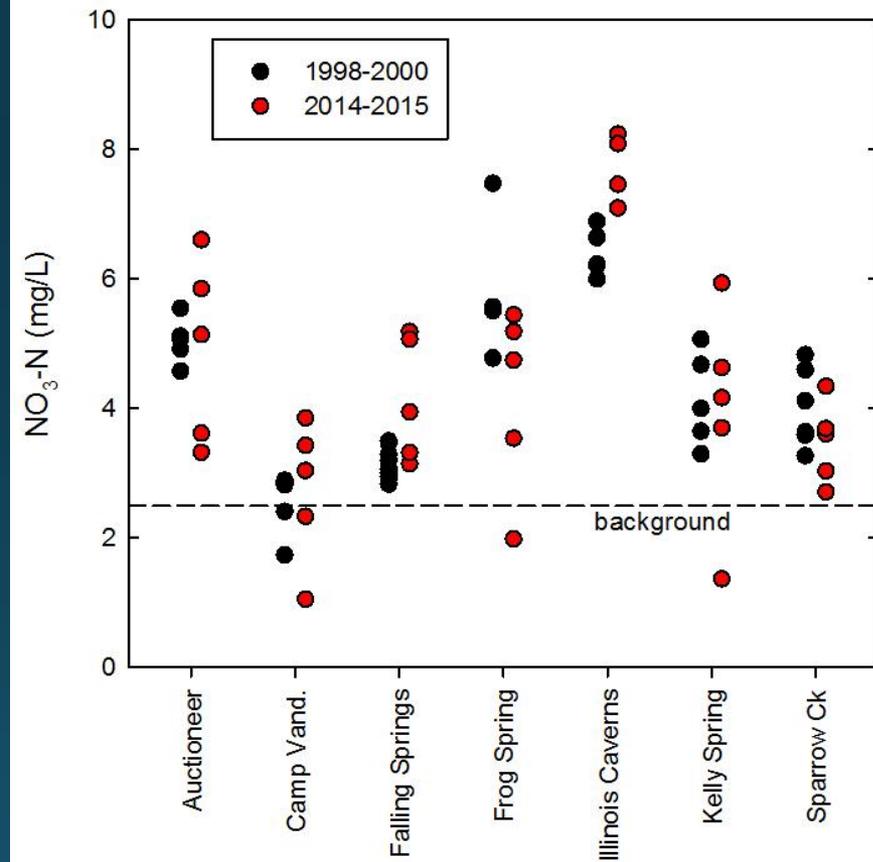


- Relatively large contributing area
- More mixing
- Chemical contamination diluted



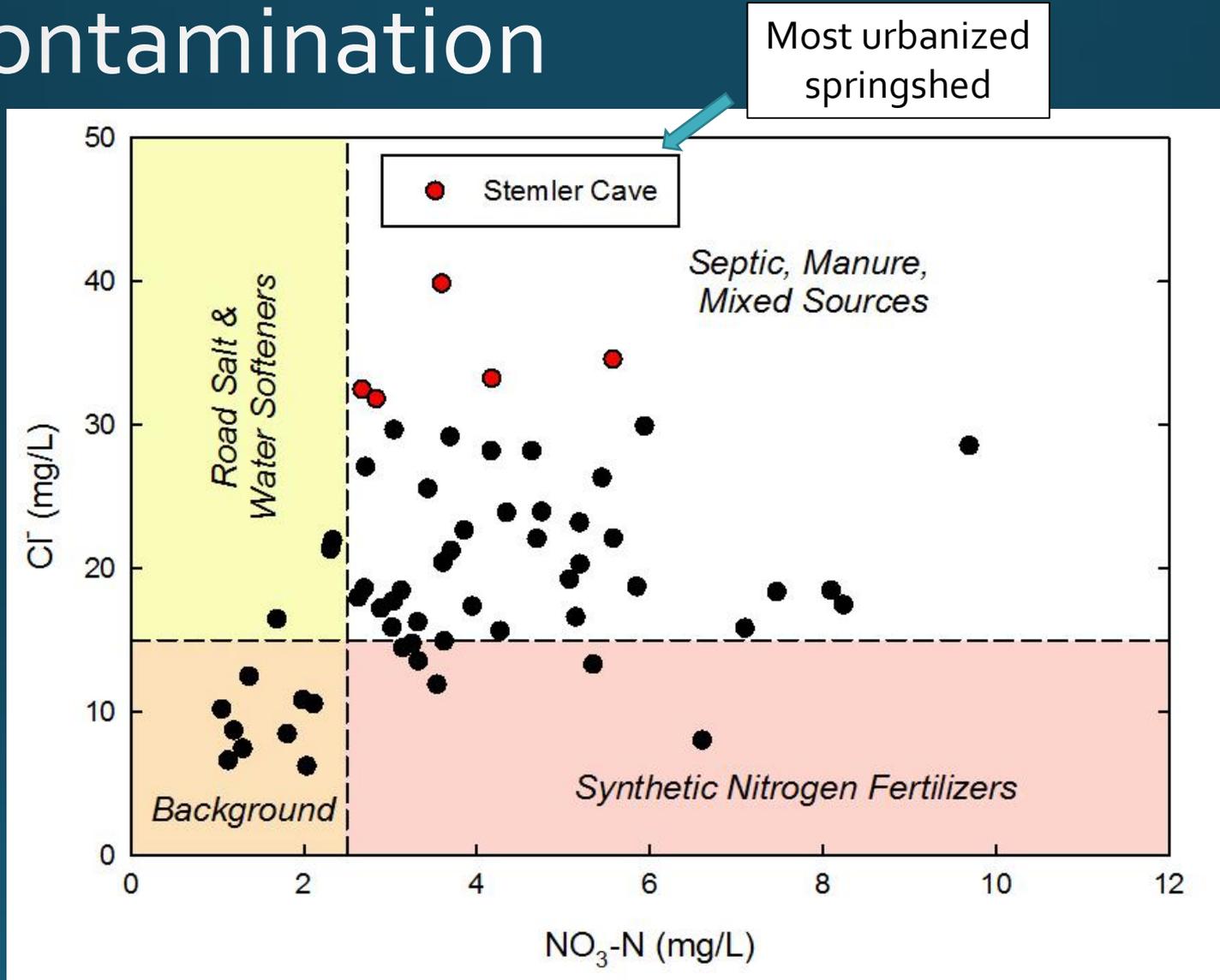
- Relatively small contributing area
- Less mixing
- More highs, more lows

# Comparison of Spring Water Quality 1998-2000 to 2014-15

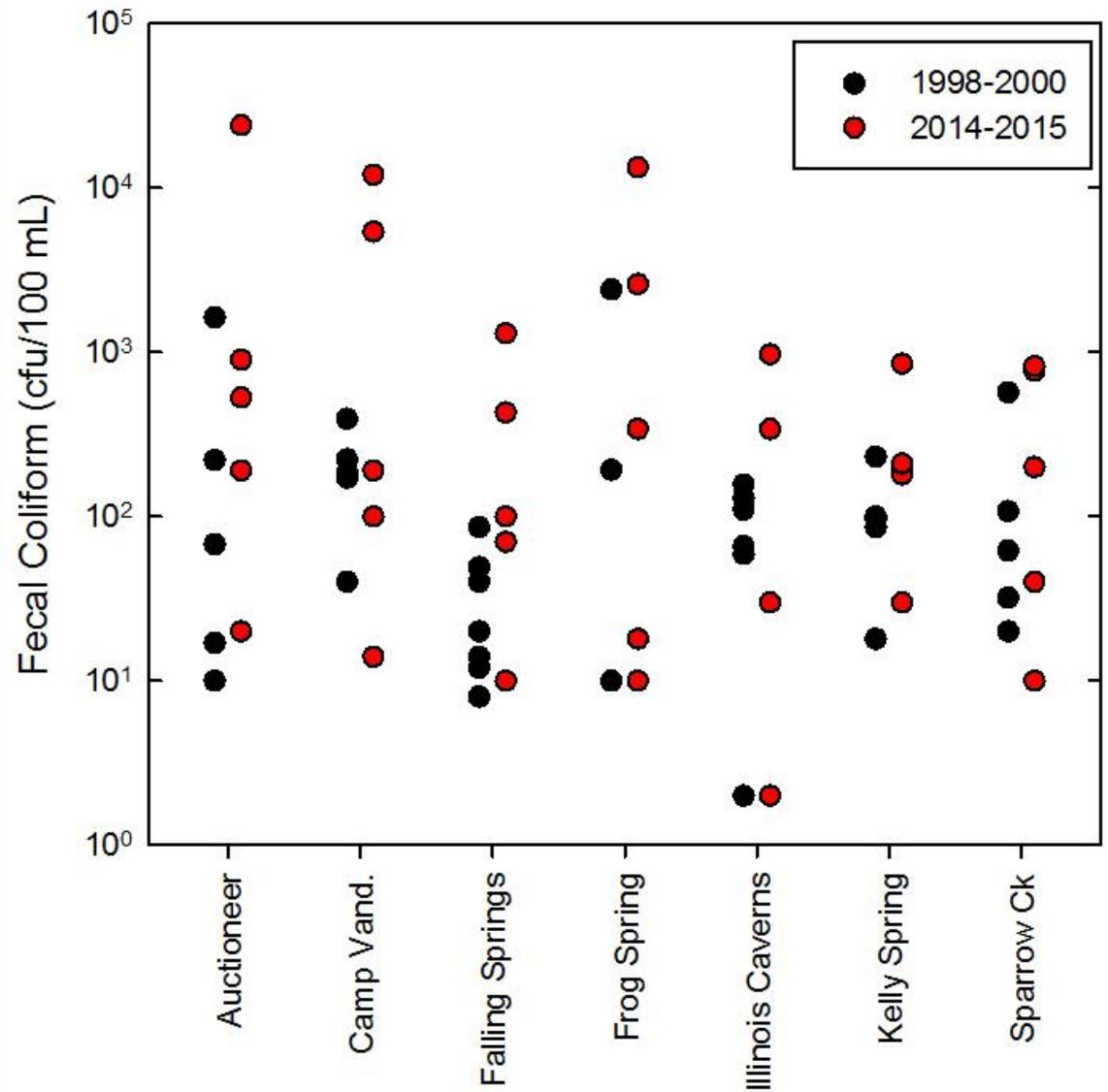


# Potential Sources of Spring Contamination

2014-15  
Data



# All Springs Contaminated by Fecal Bacteria



# Identification of Bacterial Taxa

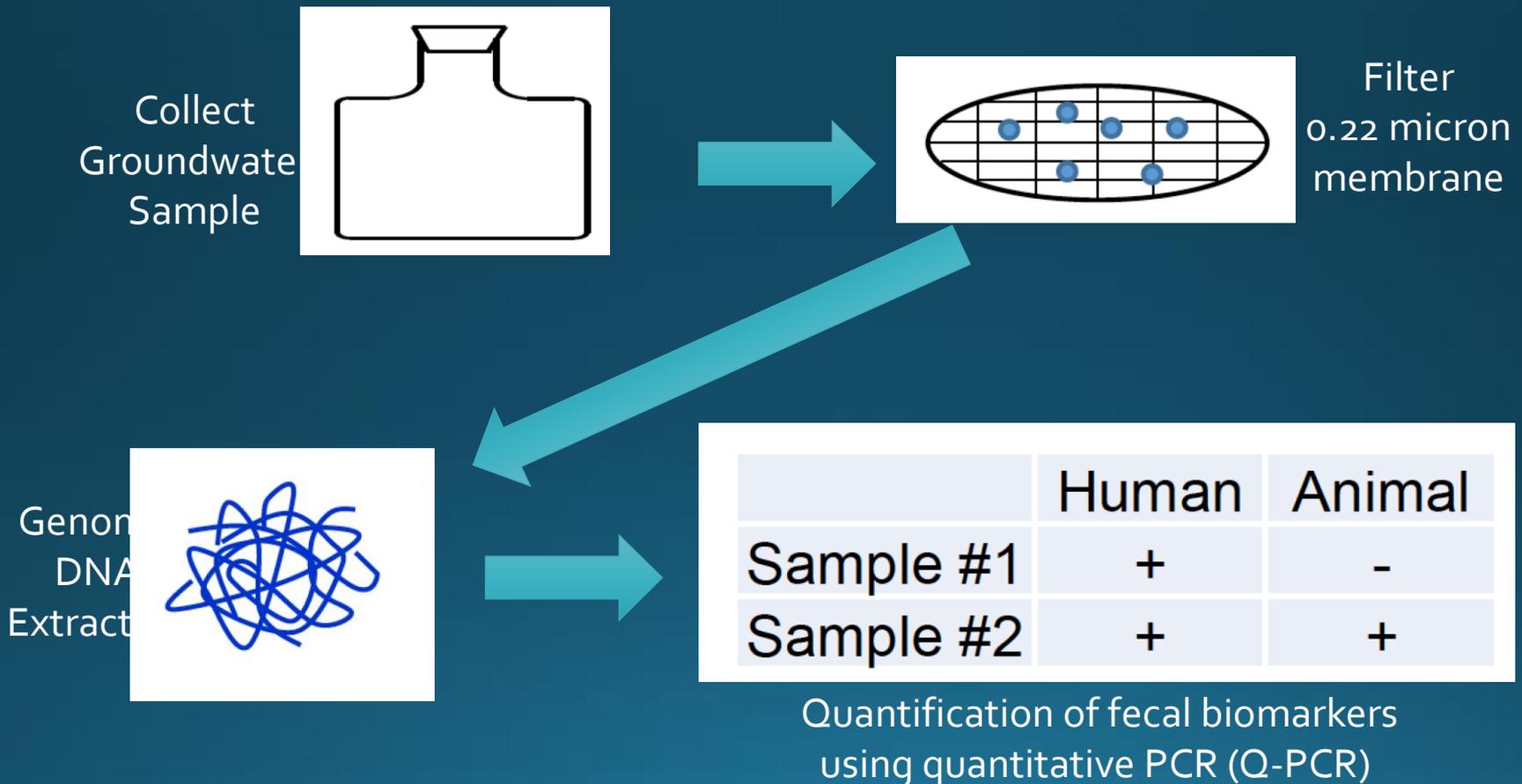
1998-2000 Data

<u>Taxon</u>	<u>% of Sites</u>
<i>Bacillus</i> sp.	92.2
<i>Enterobacter aerogenes</i>	85.3
<i>Esherichia coli</i>	85.3
<i>Enterococcus faecium</i>	82.8
<i>Enterococcus faecalis</i>	77.6
<i>Pseudomonas</i> sp.	72.4
<i>Klebsiella pneumoniae</i>	62.1
<i>Serratia</i> sp.	50.9
<i>Staphylococcus aureus</i>	43.1
<i>Citrobacter freundii</i>	37.9
<i>Pseudomonas aeruginosa</i>	29.3



# Groundwater Contamination Determined by Microbial Source Tracking

*U. Illinois Dept. Civil & Environ. Engr.*



# Fecal Biomarkers (*Bacteroidales*) from Q-PCR

Units: copies/ng gDNA						
Human				Animal		
	<i>B. fragilis</i>	<i>B. caccae</i>	<i>B. uniform</i>	<i>B. vulgatus</i>	Swine	Bovine
Fogelpole Cave 1	54	0	11.72	10.96	3.98	422
Fogelpole Cave 2	37.2	0	4.26	2.16	4.28	132.4
Fogelpole Cave 3	14.4	0	4.68	6.52	2.7	184.6
Auctioneer Cave	12.2	0	11.44	7.4	0	62
Frog Spring	6.36	0	3.92	4.1	0	1202
Camp Vandeventer Spring	13.3	0	15.52	14.22	1.834	105.2
Stemler Cave	3.02	0.734	13.54	10.1	3.68	264
Sparrow Spring	7.42	0.542	37.8	51.2	0.238	2240
Collier Spring	5.2	0	5.54	14.04	3.68	159
Indian Hole Spring	2.26	0	0.878	0.442	0	65.8
Kelly Spring	31.4	0.404	9.8	10.38	0	189.6
Illinois Caverns	167.4	0	3.38	6.88	0	1004

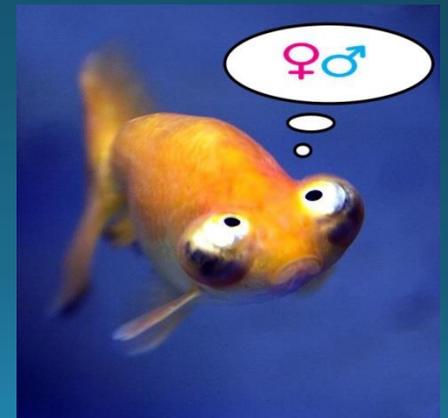
# Pharmaceuticals and Personal Care Products (PPCPs)

- Products used for personal health or cosmetic reasons or by agribusiness to enhance growth or health of livestock
- Comprise a diverse collection of thousands of chemical substances, including
  - Prescription and over-the-counter therapeutic drugs
  - Veterinary drugs
  - Fragrances
  - Cosmetics



# Steroid Hormones

- Can be natural or synthetic compounds
- Synthetic hormones used for reproductive control, to treat symptoms of menopause, and prevent osteoporosis (bone loss)
- Most steroid hormones are highly potent endocrine-disrupting chemicals (EDCs)
  - Can interfere with the normal function of the endocrine system of humans and animals
  - Even at very low concentration (nanograms-per-liter, or parts per quadrillion) can adversely affect the reproduction of freshwater species
  - e.g., feminization of male fish



# PPCPs Analyzed

Caffeine: 

**Carbamazepine:** anticonvulsant and mood-stabilizing drug

**Naproxen:** nonsteroidal anti-inflammatory drug (Aleve)

**Ibuprofen:** nonsteroidal anti-inflammatory drug (Advil)

**Gemfibrozil:** fibrate class, lowers lipid levels (Lopid)

**Triclosan:** antibacterial and antifungal agent found in soaps, detergents, etc.

**Sulfamethoxazole:** sulfonamide bacteriostatic antibiotic (Bactrim)

**Trimethoprim:** bacteriostatic antibiotic used mainly in the prevention and treatment of urinary tract infections

**Sulfamethazine:** sulfonamide antibacterial

**Acetaminophen:** analgesic and antipyretic (fever reducer) (Tylenol)

**Diphenhydramine:** antihistamine mainly used to treat allergies (Benadryl)

**Erythromycin:** antibiotic of the macrolide class

**Fluoxetine:** antidepressant (Prozac)

**Triclocarban:** antibacterial agent common in soaps and lotions

**Ciprofloxacin:** antibiotic in fluoroquinolone group

# Hormones Analyzed

- Estrone:** One of several natural estrogenic hormones secreted by the ovary and adipose tissue. Known carcinogen for human females.
- 17 $\beta$ -Estradiol:** Primary female sex hormone, commonly detected at poultry and swine farms
- 17 $\alpha$ -Estradiol:** Used topically for the treatment of hair loss, commonly detected in dairy farms.
- Ethinyl estradiol:** Orally bioactive estrogen used in many formulations of combined oral contraceptive pills.
- Estriol:** One of three main estrogens produced by the human body; only produced in significant amounts during pregnancy. One of main metabolites of estrone.
- Estrone-3-Sulfate:** Conjugated estrogen in animal and human bodies, used in medication to treat symptoms of menopause (*Premarin*).
- 17 $\beta$ -Estradiol-3-Sulfate and 17 $\alpha$ -Estradiol-3-Sulfate:** Conjugated estradiol formulation. Present in the maternal circulation of pregnant mammals including cattle and other livestock, excreted in urine.

# PPCPs Detected in Springs/Cave Streams

<u>Compound</u>	Dec/13-Apr/14 (n=13)	June/14 (n=10)	Sept/14 (n=10)	Jan/15 (n=9)
Caffeine	<b>2</b>	0	<b>6</b>	0
Carbamazepine	<b>9</b>	<b>2</b>	<b>3</b>	0
Naproxen	<b>4</b>	<b>2</b>	<b>1</b>	<b>2</b>
Ibuprofen	<b>1</b>	0	0	0
Gemfibrozil	<b>10</b>	<b>5</b>	<b>1</b>	<b>1</b>
Triclosan	<b>1</b>	0	0	0
Sulfamethoxazole	<b>5</b>	0	<b>1</b>	0
Trimethoprim	<b>12</b>	0	0	<b>4</b>
Sulfamethazine	<b>2</b>	0	0	0
Acetaminophen	0	0	0	0
Diphenhydramine	0	0	0	<b>2</b>
Erythromycin	0	0	0	0
Fluoxetine	0	0	0	<b>6</b>
Triclocarban	<b>13</b>	<b>6</b>	<b>7</b>	<b>8</b>
Ciprofloxacin	0	0	0	0

# Hormones Detected in Springs/Cave Streams

Compound	June/14 (n=10)	Sept/14 (n=10)	Jan/15 (n=9)
Estrone	0	3	0
17 $\beta$ -Estradiol	1	0	0
17 $\alpha$ -Estradiol	0	0	0
Ethinylestradiol	1	0	0
Estriol	0	0	0
Estrone-3-Sulfate	0	0	0
17 $\beta$ -Estradiol-3-Sulfate	0	0	0
17 $\alpha$ -Estradiol-3-Sulfate	0	0	0

# Summary

- Increased urbanization (septic density) increases  $\text{Cl}^-$  concentrations in springs, but not necessarily  $\text{NO}_3^-$ -N concentrations
- Fecal bacteria ubiquitous in springs, mixed sources
- PPCPs detected in most spring samples, indicating human sources
- Triclocarban most common PPCP
  - Carbamazepine, Gemfibrozil, Trimethoprim also commonly detected
  - Concentrations generally  $< 10$  ng/L
  - Highest concentrations 171 ng/L (Gemfibrozil in Sparrow Ck, 02/2014) and 71.7 ng/L (Triclosan in Fogelpole Cave, 04/2014)
- Hormones rarely detected
- PPCP and bacteria results show considerable variability