

A photograph of a river with a rocky shoreline. In the background, there is a construction site with a yellow excavator and a red container. The text "Urban Water Monitoring for Organic Contaminants" is overlaid in orange.

Urban Water Monitoring for Organic Contaminants

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Prior to 2011

- Two extractions:
- Liq-liq and SPE
- Requires 1 L sample, organic solvents
- Three analytical methods:
- GC/ECD, GC/NPD, GC/MS
- No PPCPs on lists

New Method in 2011

- Stir Bar Sorptive Extraction
- Less than 20 mL solvent (methanol) used
- 5 mL or 100 mL sample
- Non-labor intensive
- GC/MS

Analysis of Water for Organics



Gerstel Twister® SBSE

- 1.5 cm magnetic stir bar coated with 0.5 mm polydimethylsiloxane (PDMS)
- Dropped in water sample and sample is stirred on stir plate for 1.5 to 21 hours, depending on sample volume
- Extraction efficiency depends on compound's affinity for water vs. PDMS



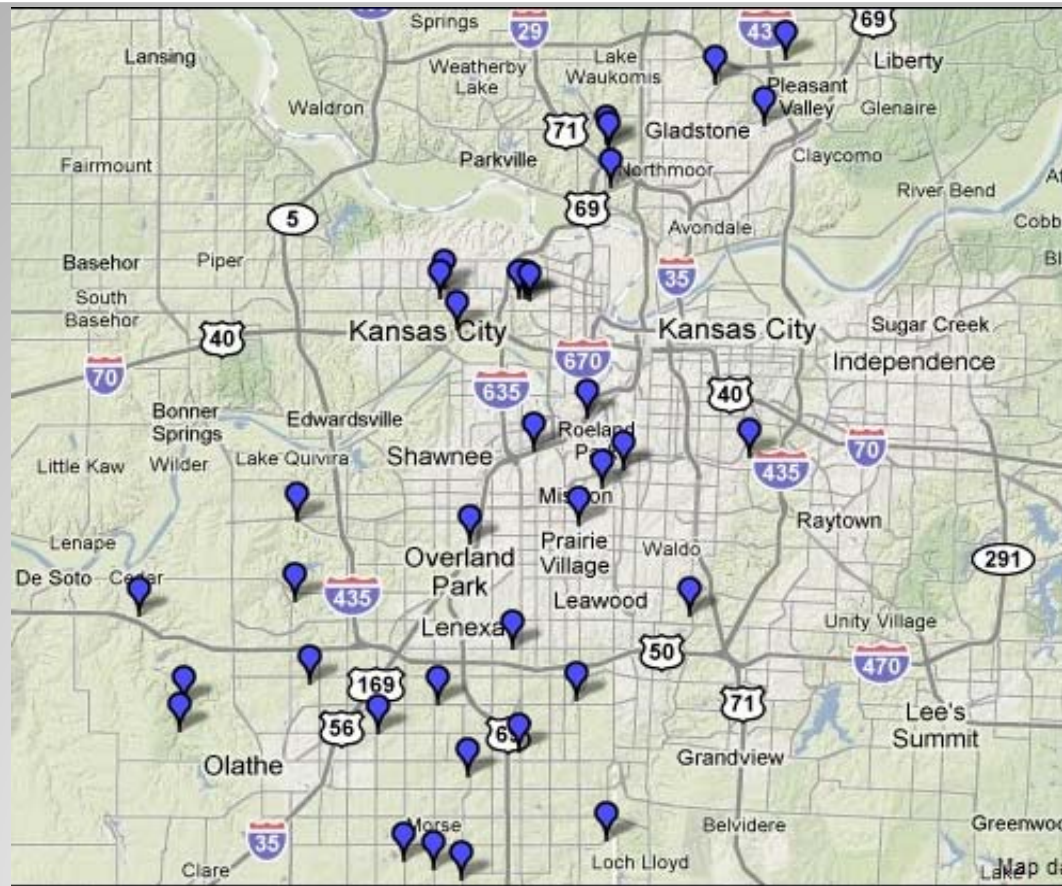
Analysis

- Thermally desorb twister in GC/MS inlet
- Entire sample is introduced into instrument
- Two analytical runs, less than 40 minute each
- Full Scan for most compounds
- SIM for 9 compounds



- Smaller sample size requirements
- No toxic organic solvents
- Easy, unattended extraction
- No time consuming concentration steps
- Entire extract is consumed (no disposal issue)
- Lower reporting limits on many compounds
- New PPCP compounds

Advantages



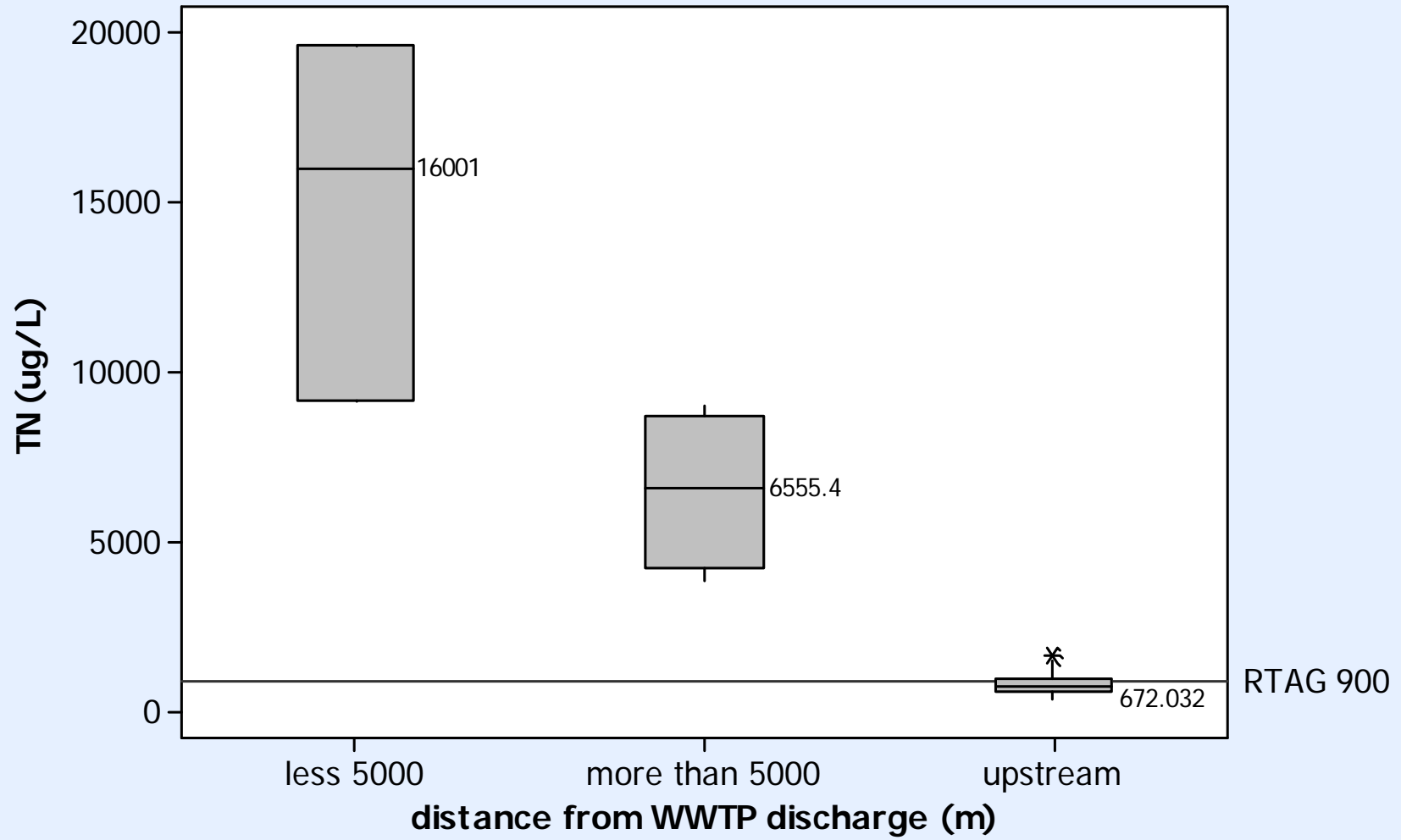
Results



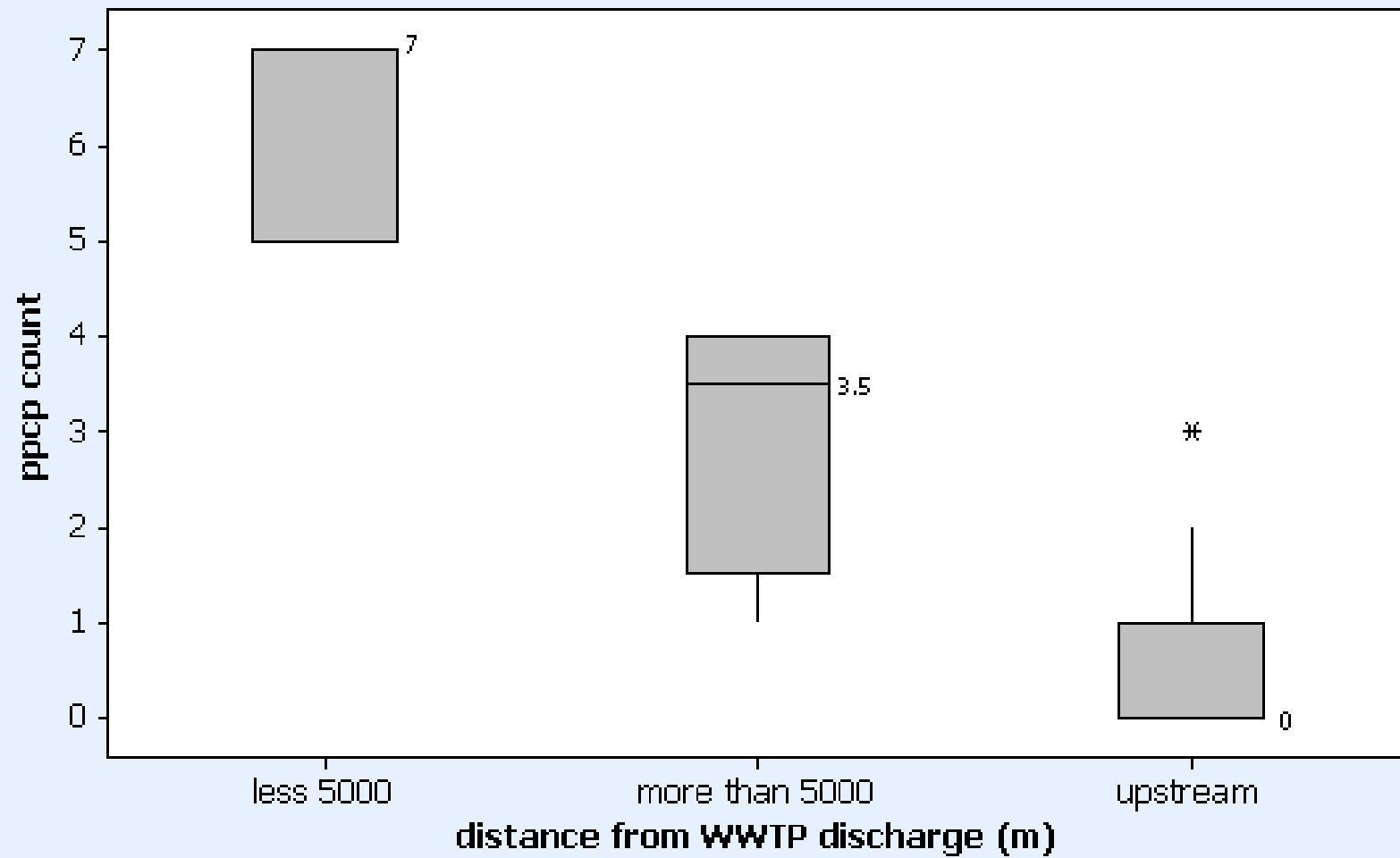
2011 Urban Stream Sampling

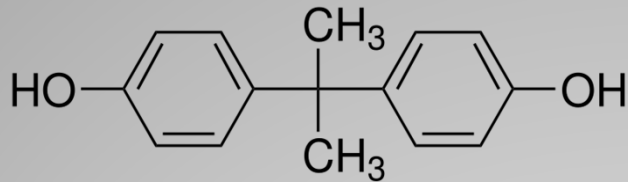
PPCP - new in 2011	2011 RL (µg/L)	2011 detections
Bisphenol A	0.2	9 (5)
Coprostanol	0.2	2 (2)
17B-Estradiol	0.1	0 (1)
Estrone	0.1	1 (1)
17A-Ethynyl Estradiol	0.1	0 (1)
4-n-Nonylphenol	0.02	0 (2)
4-n-Nonylphenol Diethoxylate	0.05	0 (1)
4-tert-Octylphenol Diethoxylate	0.02	2
4-tert-Octylphenol Monoethoxylate	0.02	3 (20)
Triclosan	0.02	5 (1)
Tris(2-chloroethyl) phosphate (TCEP)	0.04	11 (10)

WWTP influence on TN

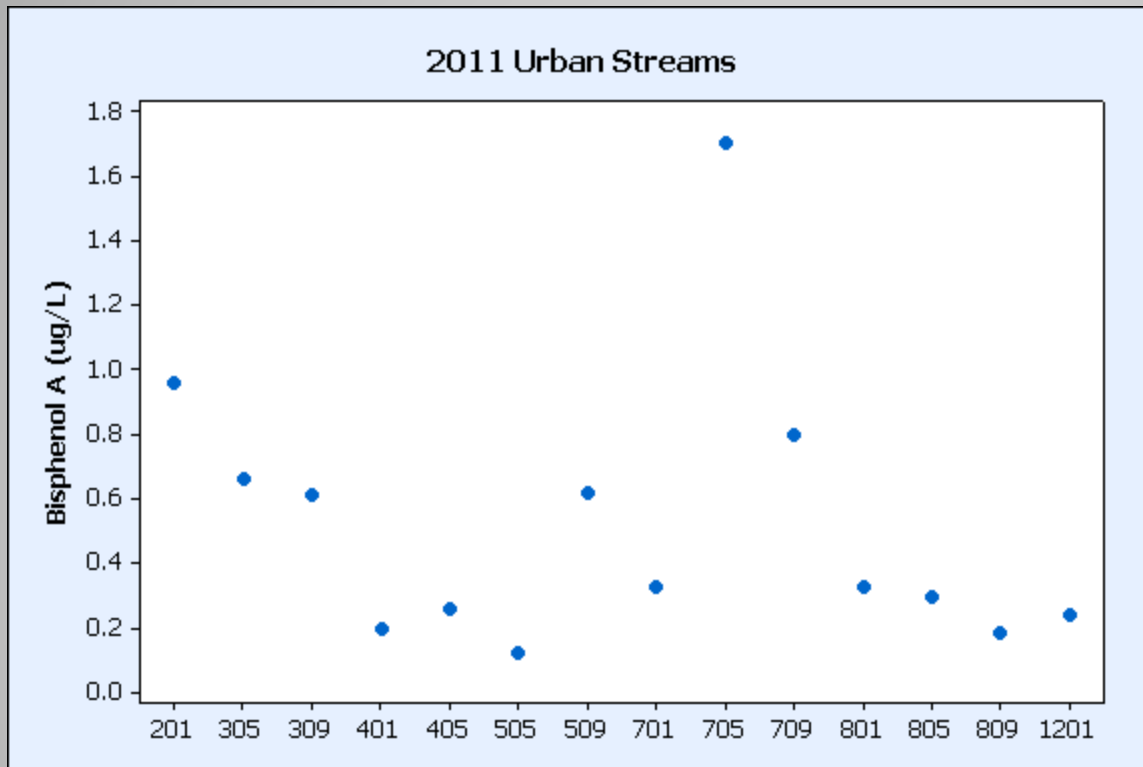


WWTP influence on Personal Care Products

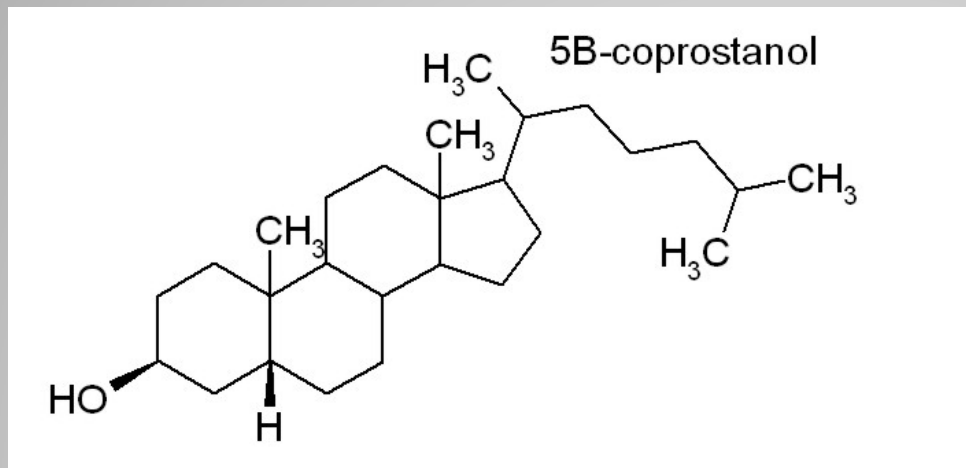




Bisphenol A

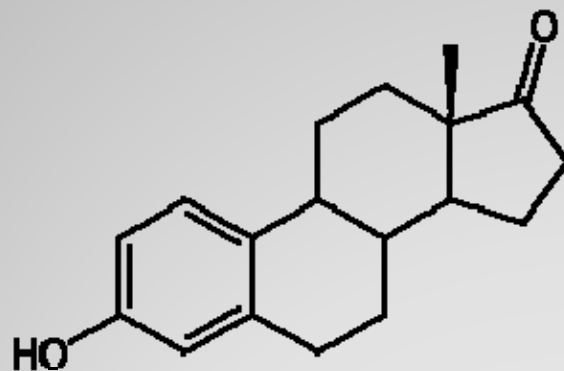


- RL = 0.2 μ g/L
- Range 0.20 to 1.7 μ g/L
- 9 detections above RL, 5 more between MDL and RL
- 6 of 14 associated with WWTP discharge: 201, 401, 405, 505, 509, 1201
- 300's from urbanized area, possible CSOs
- 700's, 800's rural



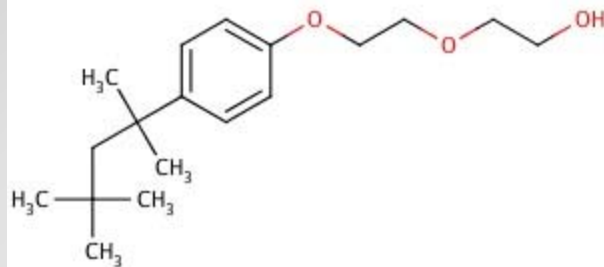
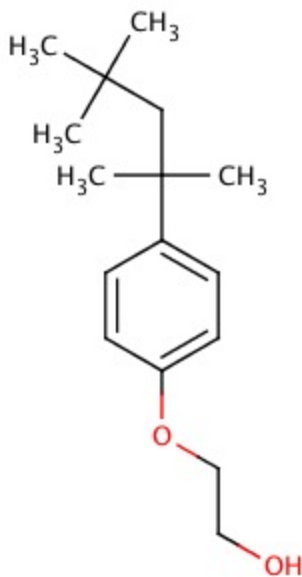
Coprostanol

- Formed by the degradation of cholesterol in higher animals and birds (carnivores)
- Used as a biomarker for human feces
- RL = 0.2 µg/L
- Range 0.03 to 0.84
- Found at 2 sites above the RL, the two most influenced by WWTP discharge
- Also found at two highly urbanized sites between RL and MDL



Estrogens

- Three estrogen compounds evaluated
- Only Estrone was detected above RL = 0.1 $\mu\text{g/L}$
- Site heavily influenced by WWTP
- Two compounds found between MDL and RL at highly urbanized site
- Currently evaluating ELISA to measure to 0.05 $\mu\text{g/L}$
- Developing LCMS method

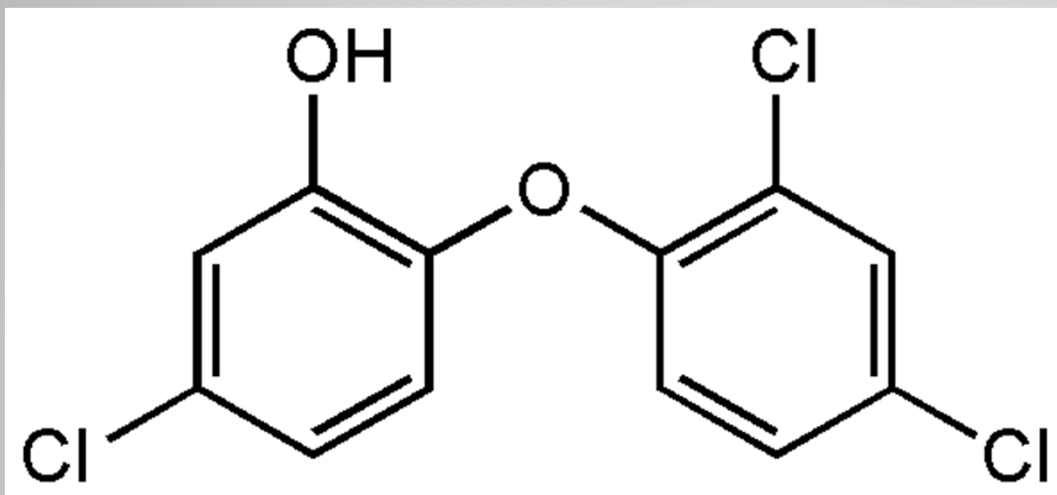


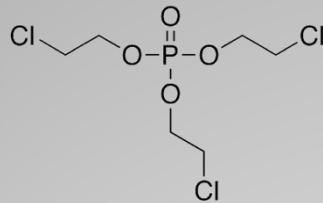
Nonyl phenol and derivatives

- 4 compounds analyzed
- RL = 0.02 – 0.05 µg/L
- 4-tert-Octylphenol Diethoxylate and 4-tert-Octylphenol Monoethoxylate detected
- All detections at WWTP influenced sites
- 0.02 to 0.33 range
- OPEO1 found at 20 additional sites between MDL and RL

Triclosan

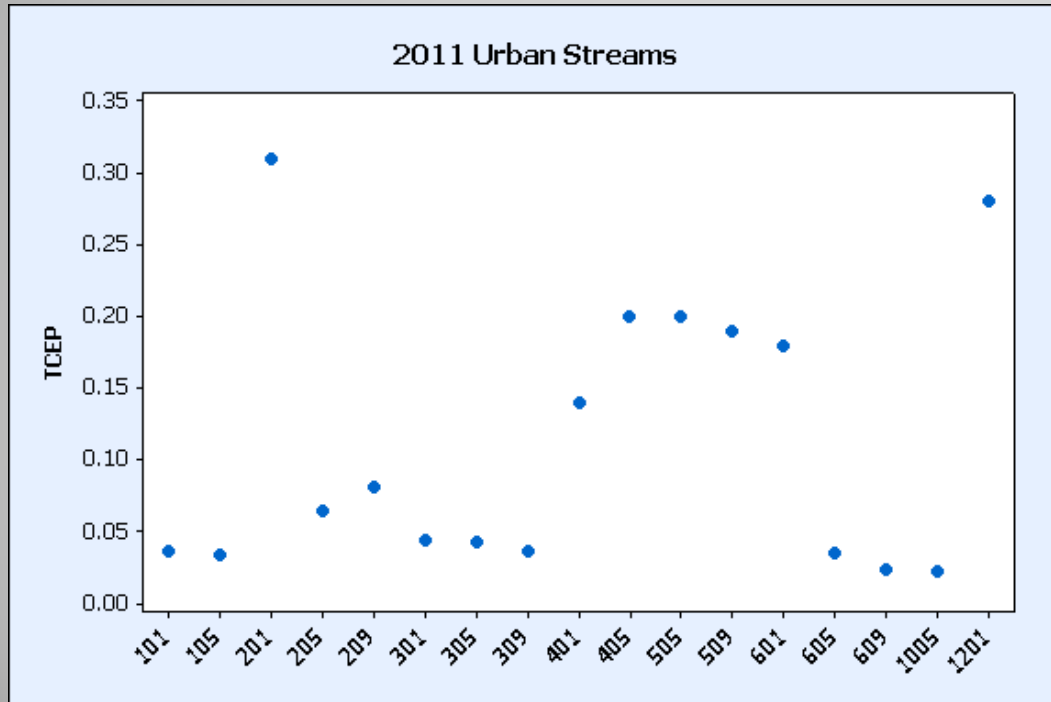
- RL = 0.02
- Range 0.02 – 0.36
- Detected 5 times, all WWTP influenced sites





Tris(2-chloroethyl) phosphate (TCEP)

- RL = 0.04
- Detected 17 times
- Range = 0.04 – 0.31
- Higher levels associated with WWTP, but lower levels (101, 105, 205, 209, 301, 305, 309, 605, 609, 1005, 1201) are not
- Tentatively identified several other flame retardants in samples not associated with WWTP

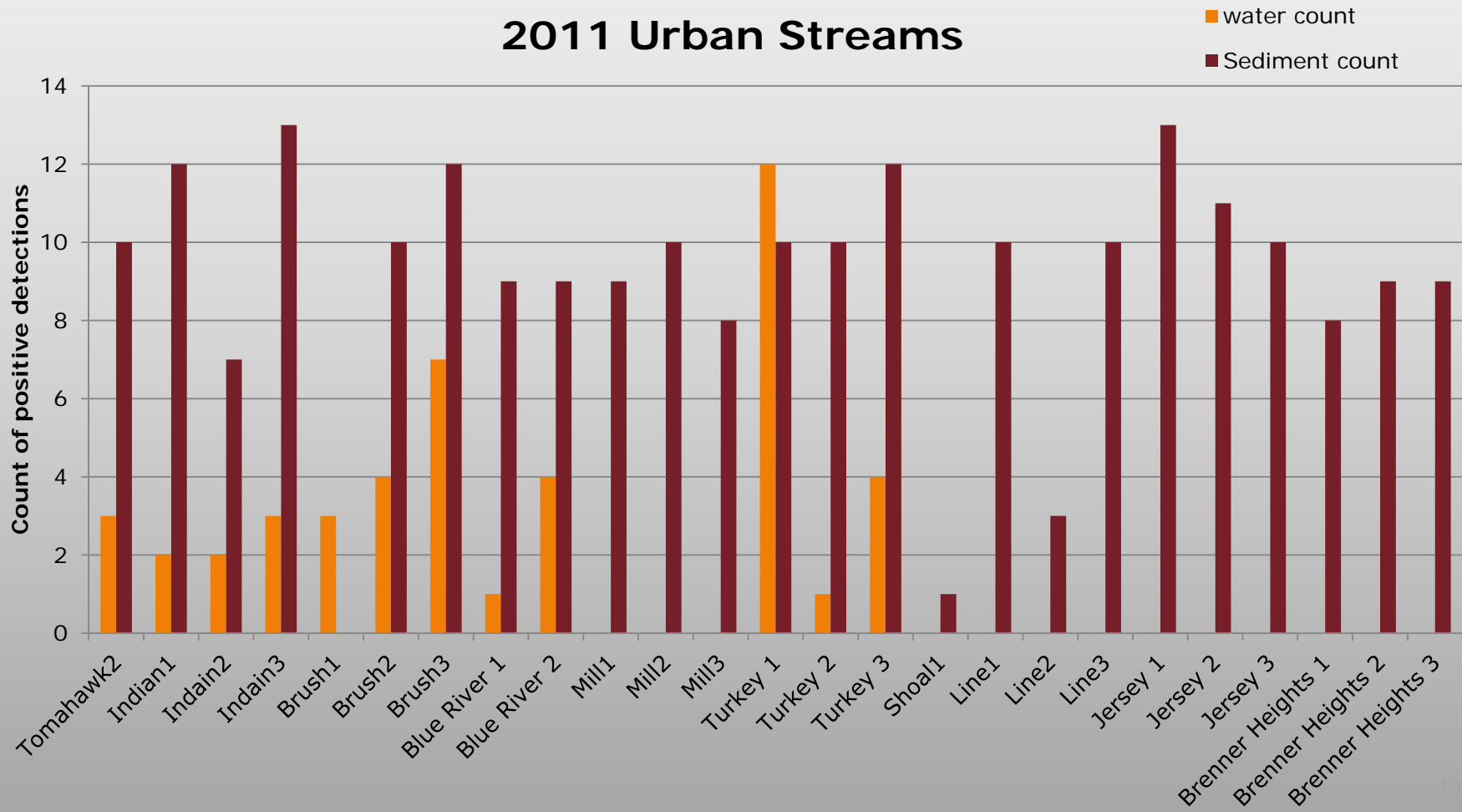


PAH	2011 RL (µg/L)	2010 RL (µg/L)	2011 detections	2010 detections
Acenaphthene	0.02	2	2	0
Acenaphthylene	0.02	2	0	0
Anthracene	0.02	2	1	0
Benzo(a)anthracene	0.02	2	1	0
Benzo(a)pyrene	0.02	2	1	0
Benzo(b)fluoranthene	0.02	2	3	0
Benzo(g,h,i)perylene	0.04	2	0	0
Benzo(k)fluoranthene	0.02	2	2	0
Chrysene	0.02	2	7	0
Dibenz(a,h)anthracene	0.04	2	0	0
Fluoranthene	0.02	2	13	0
Fluorene	0.02	2	2	0
Indeno(1,2,3-cd)pyrene	0.04	2	0	0
2-Methylnaphthalene	0.02	2	0	0
Naphthalene	0.02	2	1	0
Phenanthrene	0.02	2	4	0
Pyrene	0.02	2	12	0

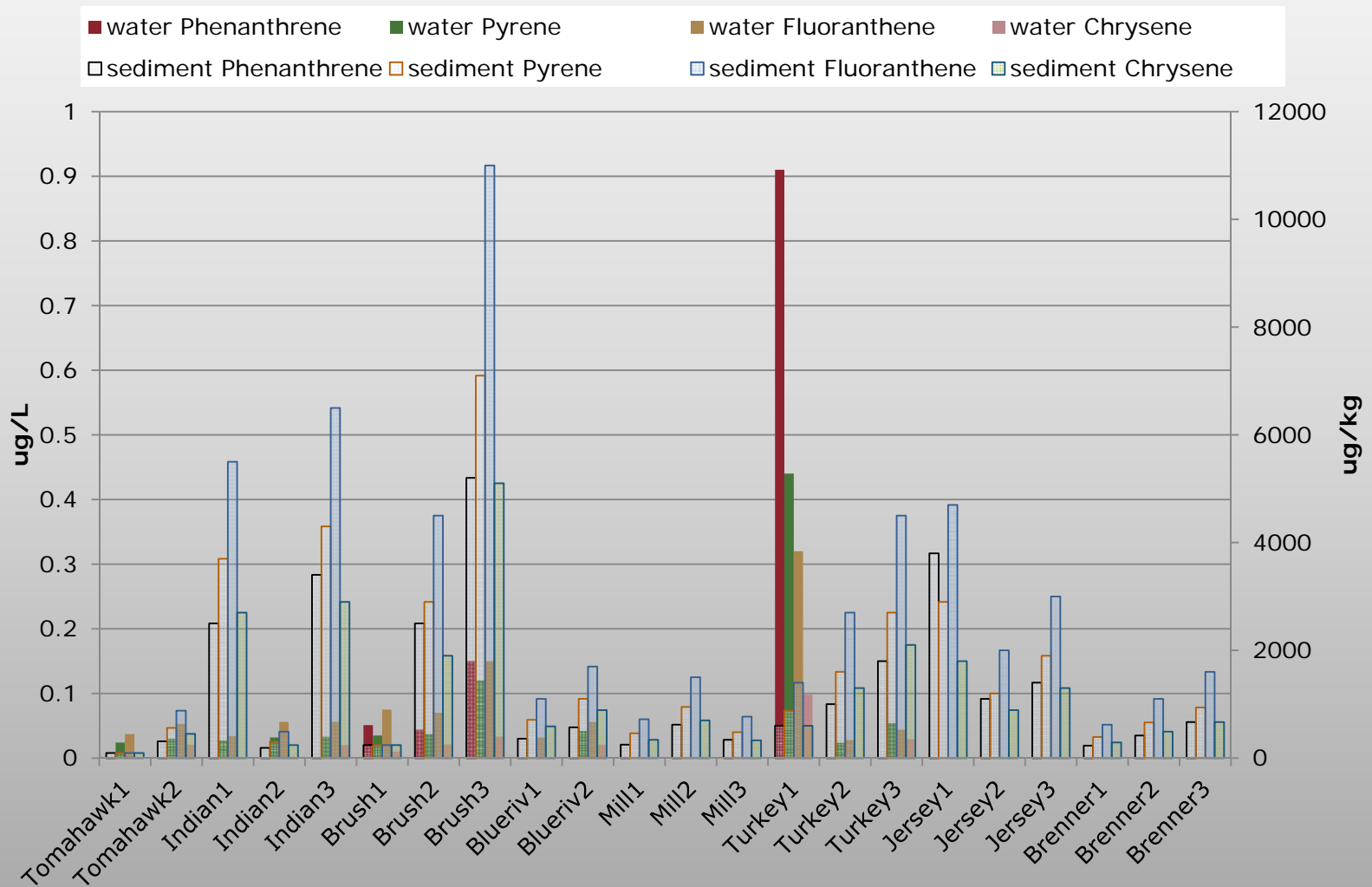
PAHs

- Little to no correlation between sediment PAH detections and water PAH detections

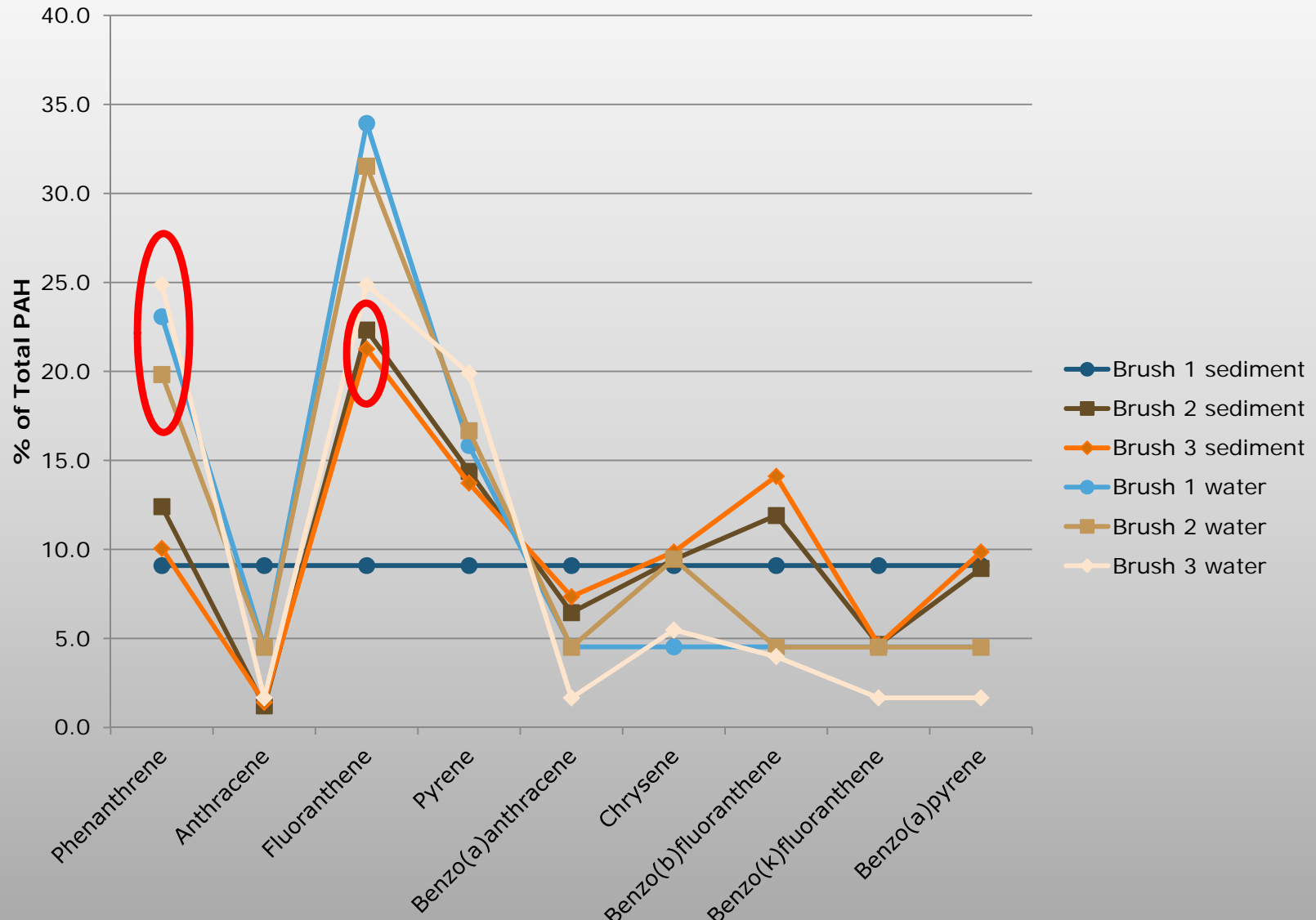
2011 Urban Streams



2011 Water and Sediment PAHs



2011 Brush Creek PAHs

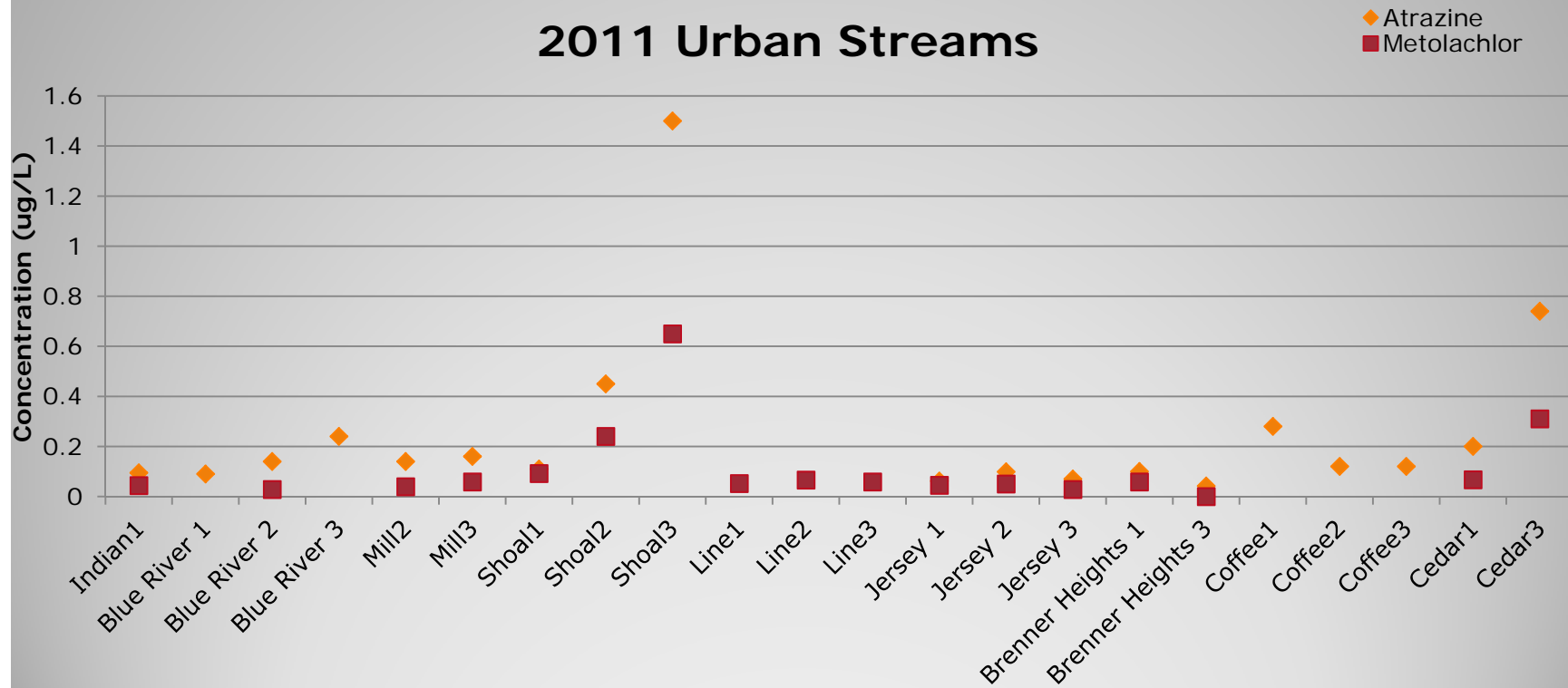


Pesticides	2011 RL (µg/L)	2010 RL (µg/L)	2011 detections	2010 detections
Alachlor	0.04	0.1	0	0
Atrazine	0.1	1	13	1
Bifenthrin	0.04	0.099	0	0
Bromacil	0.2	4	2	0
Chlordane, technical	0.2	0.19	0	0
Chlorothalonil	1	0.049	0	0
Chlorpyrifos	0.02	0.025	0	0
Diazinon	0.02	0.2	0	0
Dieldrin	0.02	0.02	1	5
Diethyltoluamide (DEET)	0.1	1.5	17	3
Malathion	0.05	0.02	0	0
Metolachlor	0.04	0.5	13	0
Permethrin	0.4	0.5	0	0
Pyrethrins	0.2	1.5	0	0
Simazine	0.04	1	0	5
Tebuthiuron	0.5	2	0	0
Trifluralin	0.02	0.015	0	1

Atrazine & Metolachlor

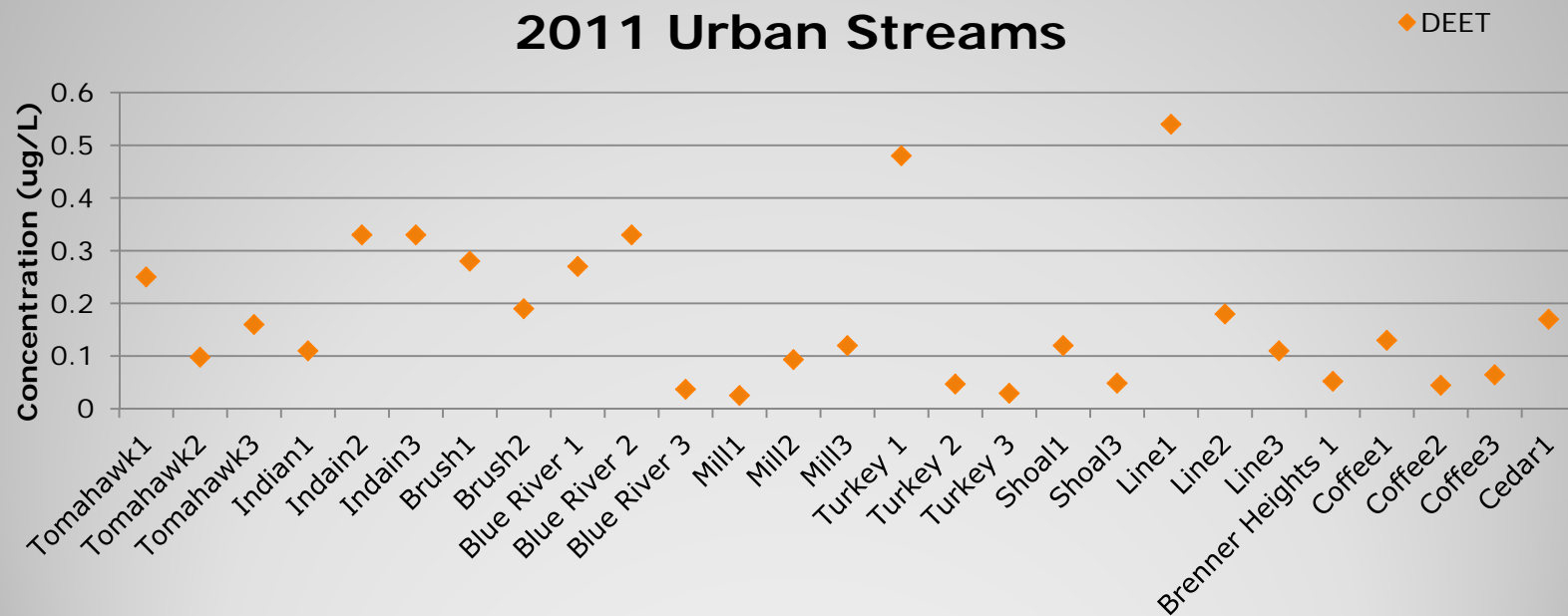
- Both herbicides used for broadleaf and grass control in crops.
- Strong positive correlation between the two herbicides.

2011 Urban Streams



N,N-Diethyl-*meta*-toluamide (DEET)

- Not correlated with Atrazine and Metolachlor
- More of a personal care product, used in topical pesticide repellent
- Found an additional 10 times between the MDL and RL



- New method in 2011 made sampling easier (less containers, less water volume collected)
- Easier analysis
- Greener analysis
- Lower detection limits on most organic compounds, resulting in more detections
- Expanded list of compounds, including emerging contaminants

Conclusions