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In Cooperation with the Minnesota Pollution Control agency:

# Assessing BMP removal of chemicals of emerging concern in urban stormwater

## 2019 Chesapeake Bay STAC Workshop
## May 23, 2019


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# Chemicals of Emerging Concern (CECs):

## Broad analytical group of chemicals including pharmaceuticals, personal care products and other wastewater compounds

- Drugs
- Antibiotics
- Hormones
- Steroids
- Detergents / surfactants
- Plastics
- Antioxidants
- Fire retardants
- Disinfectants
- Fumigants
- Fragrances
- Insecticides / repellants

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# Why study BMP treatment of CECs?

- CECs have been identified in urban stormwater
  - Limited studies have documented BMP removal of pesticides, alkylphenols, PAHs, and phthalates
- Possible treatment technologies
  - bio-enhanced sand filtration - 44-85% removal of atrazine; 57-93% removal of metolachlor (Popov et al. 2006)
  - iron-oxide treatment of 2,4-D in groundwater
- Iron-enhanced sand filters (IESF) suggested as treatment option (Pitt et al. 2013; Ellis et al. 2013; Scholes et al. 2008)

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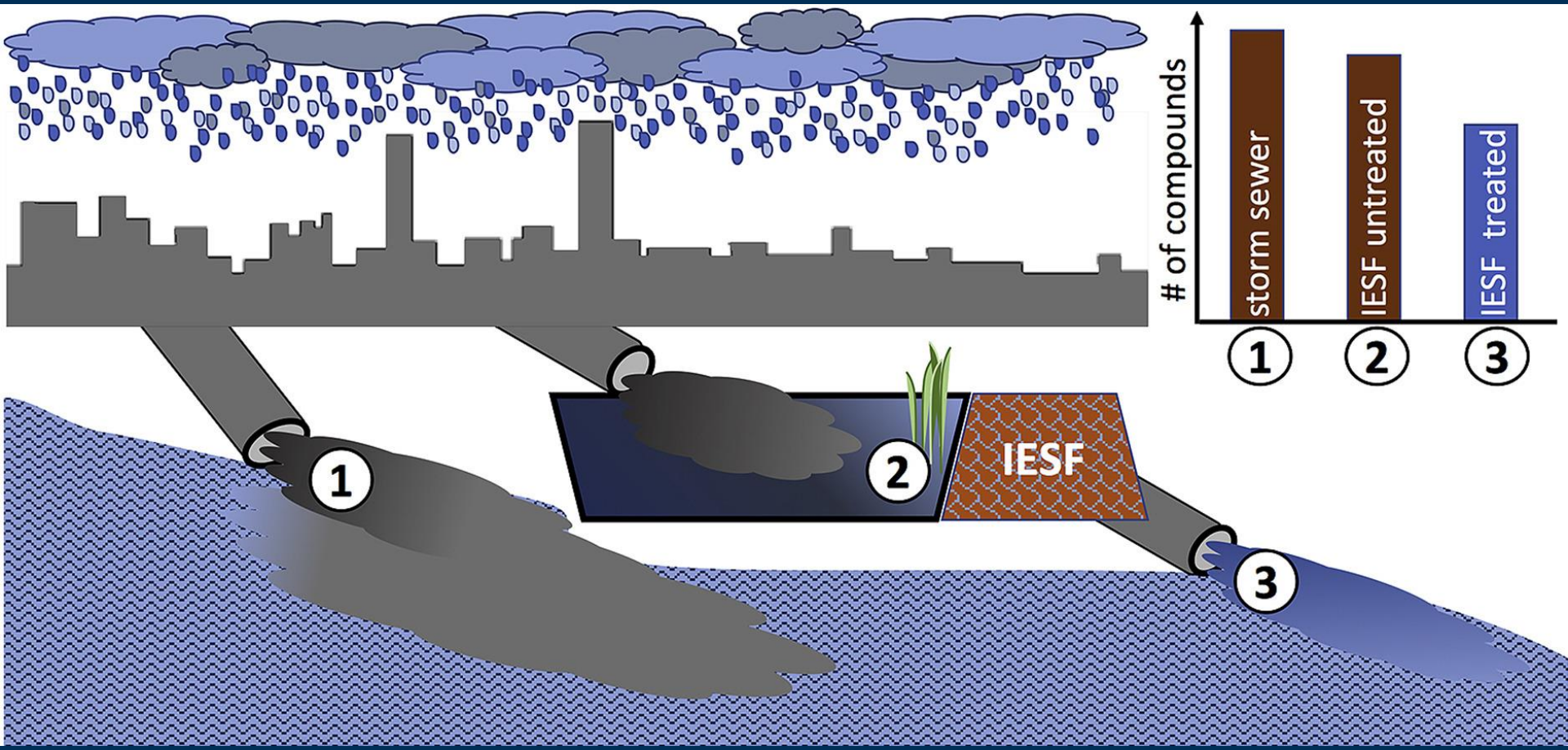
# Why study BMP treatment of CECs?

D. Fairbairn et al. 2018. Water Research 145: 332-345 https://doi.org/10.1016/j.watres.2018.08.020

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# MPCA Overall Study Approach

- Monitor contaminants of emerging concern in stormwater inflows and outflows at three IESF stormwater treatment ponds
- Sample stormwater during snowmelt runoff, in late spring, early summer and early fall
- Measure potential for biological activity of all collected stormwater samples using multiple biomarkers (SCSU, UST)

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# LOGISTICS – sampling design

- Nine total sites
  - Three IESF Ponds each with an inlet and an outlet (6 total sties)
  - Three urban integrator stormwater outfalls – one light industrial
- Four seasonal sampling events (February, April, late May, September)
- 408 chemicals analyzed (384 unique)
  - 229 pesticides (Pest)
  - 110 pharmaceuticals (Pharm)
  - 69 wastewater indicators (WWI)

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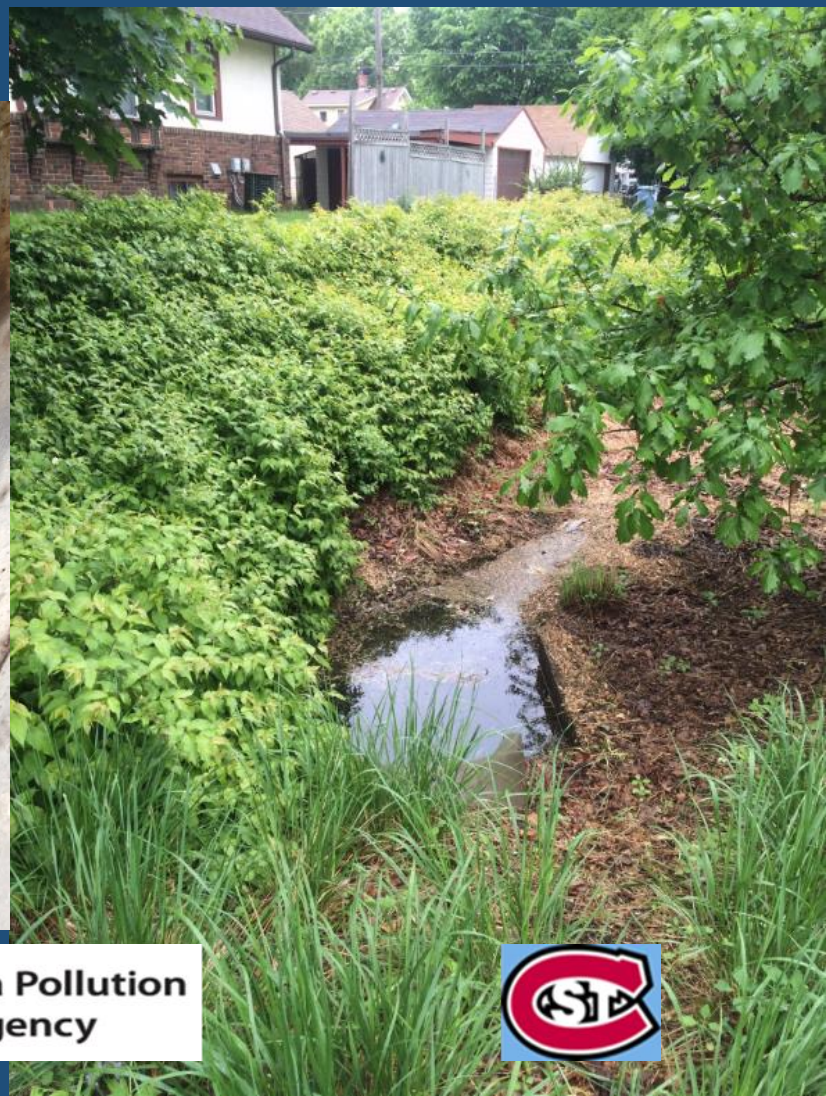
# LOGISTICS – sampling sites

- 37th Ave. site: overflow diversion to raingarden with IESF benches



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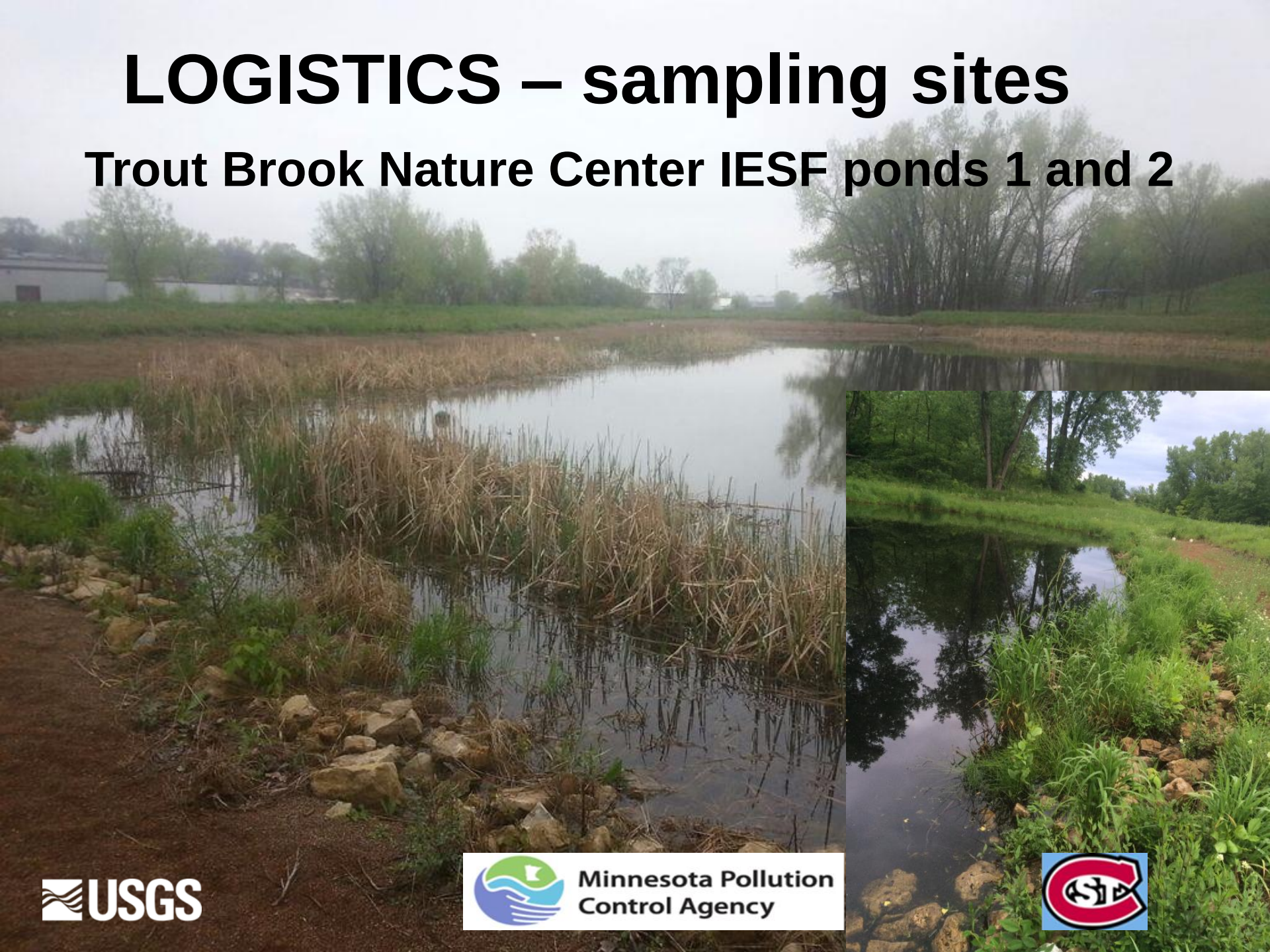
# LOGISTICS – sampling sites

## Trout Brook Nature Center IESF ponds 1 and 2



# Summary of Detections in Stormwater Sampling

- 123 of the 384 chemicals detected in at least one sample (32%)
- Between 18 and 54 chemicals were detected in each sample
- Total CEC concentrations ranged from 0.63 to 11.65 ug/L
- 229 pesticides (Pest) – 25% detected
- 110 pharmaceuticals (Pharm) – 71% detected
- 69 wastewater indicators (WWI) – 25% detected

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# Pesticide Detection Frequency: all samples

| Chemical | Use | Detection frequency (%) | Concentration range, ng/L |
|---|---|---|---|
| 2,4-D | Herbicide | 100 | 24 – 11,600 |
| Hydroxyatrazine (OIET) | Herbicide | 83 | 5.1 – 25 |
| Metolachlor | Herbicide | 80 | 1.2 – 238 |
| Deethylatrazine (CIAT) | Herbicide | 69 | 6.8 – 499 |
| Prometon | Herbicide | 60 | 1.4 – 24 |
| Deisopropylatrazine (CEAT) | Herbicide | 57 | 15 – 298 |
| Deethylhydroxyatrazine (OIAT) | Herbicide | 54 | 2.8 – 53 |
| Didealkylatrazine (CAAT) | Herbicide | 54 | 18 – 546 |
| Carbendazim | Fungicide | 51 | 2.4 – 33 |

**Analyzed by more than one analytical method**

# Pharm Detection Frequency: all samples

| Chemical | Pharm Type | Detection frequency (%) | Concentration range, ng/L |
|---|---|---|---|
| 5-Methyl-1H-benzotriazole | Drug precursor | 100 | 83 – 5,550 |
| Cotinine | Nicotine metabolite | 100 | 8 – 540 |
| Atrazine | Herbicide | 100 | 3.2 – 640 |
| Nicotine | Stimulant | 94 | 22 – 3,890 |
| Caffeine | Stimulant | 94 | 20 – 1,710 |
| Lidocaine | Anesthetic/antiarrhythmic | 91 | 1.2 – 18.2 |
| Acetaminophen | Pain reliever | 69 | 2.4 – 2,110 |
| Metformin | Anti-diabetic | 63 | 11 - 247 |

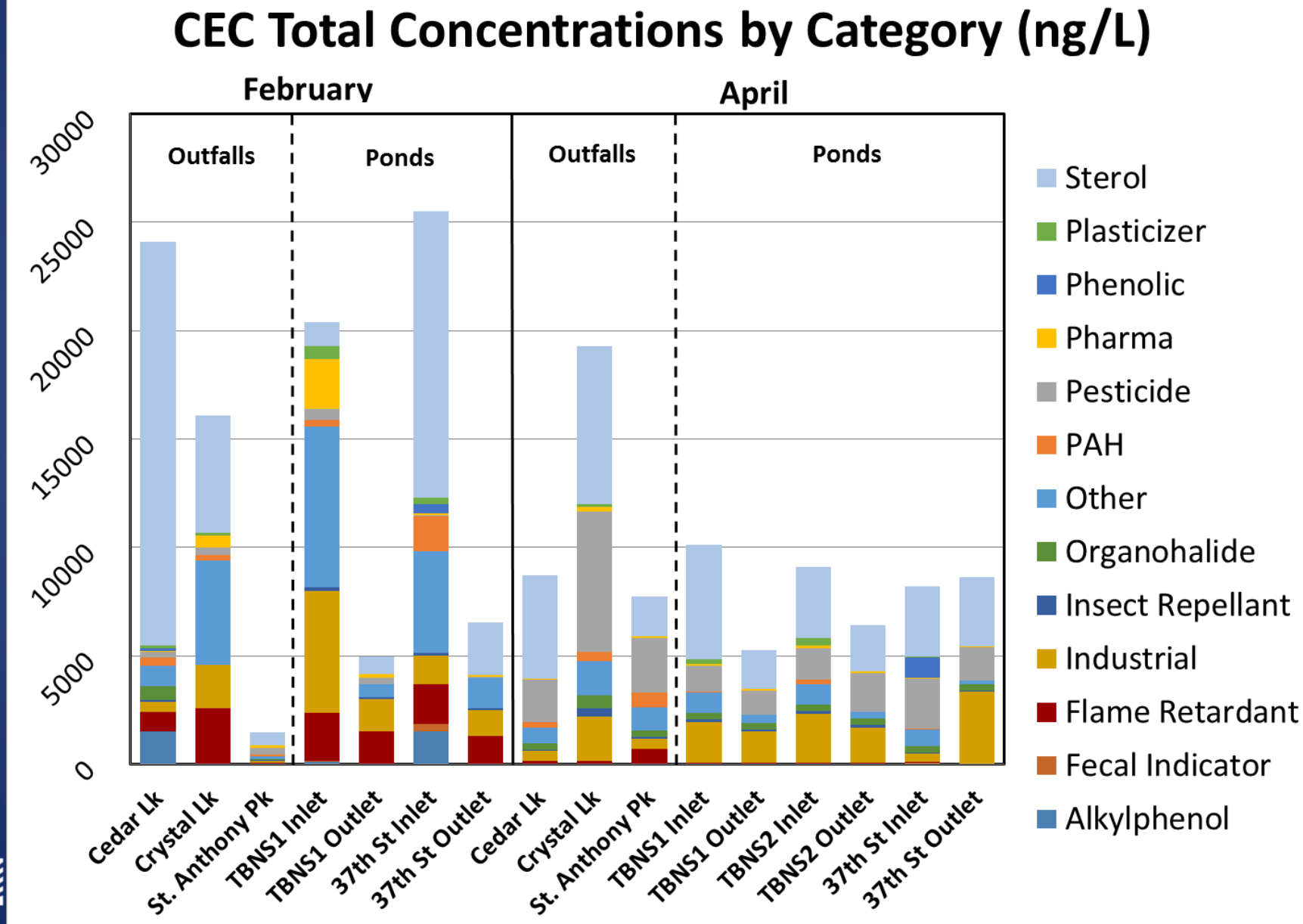
**Analyzed by more than one analytical method**

# WWI Detection Frequency: all samples

| Chemical | Chemical class | Detection frequency | Concentration range, ng/L |
|---|---|---|---|
| DEET | Insecticide | 97 | 30 – 490 |
| Tributyl phosphate | Flame retardant/plasticizer | 94 | 7 – 299 |
| Isophorone | Solvent | 78 | 9 – 91 |
| Caffeine | Stimulant | 72 | 70 – 1920 |
| Menthol | Fragrance | 69 | 40 – 1340 |
| beta-Sitosterol | Plant sterol | 61 | 600 – 16300 |
| Atrazine | Herbicide | 56 | 10 – 540 |
| 5-Methyl-1H-benzotriazole | Corrosion inhibitor | 56 | 40 – 1340 |
| 9,10-Anthraquinone | Dye base | 56 | 10 – 280 |
| Pentachlorophenol | Pesticide | 53 | 100 – 600 |
| Cholesterol | Sterol | 53 | 300 – 3600 |
| Indole | Fecal indicator | 53 | 10 – 380 |
| Metolachlor | Herbicide | 50 | 40 – 400 |
| Pyrene | PAH | 50 | 10 – 460 |
| Tris(2-butoxyethyl) phosphate | Flame retardant/plasticizer | 50 | 110 – 5930 |

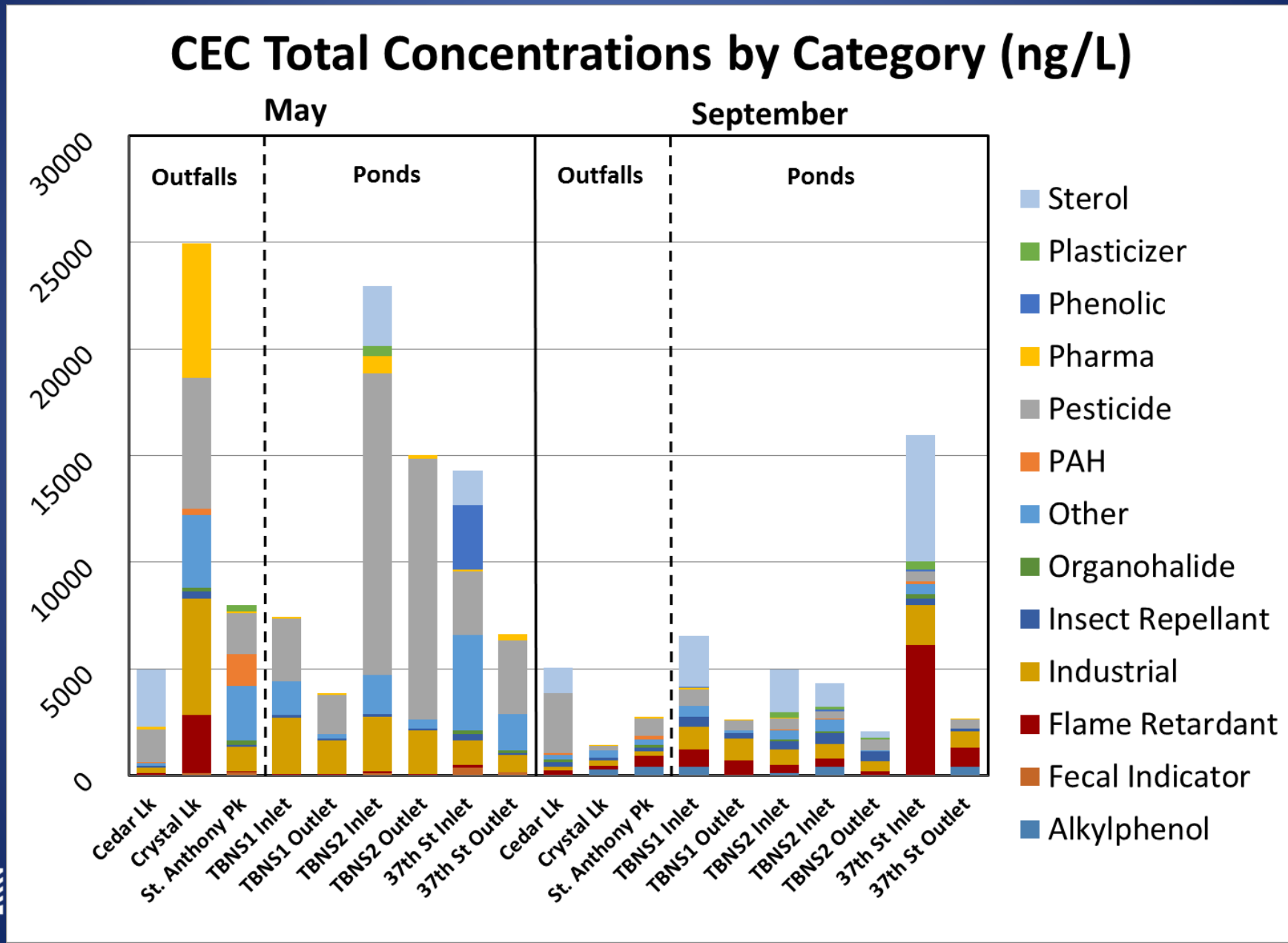
# Detailed Comparisons between Sites:

## Inflows and Outflows



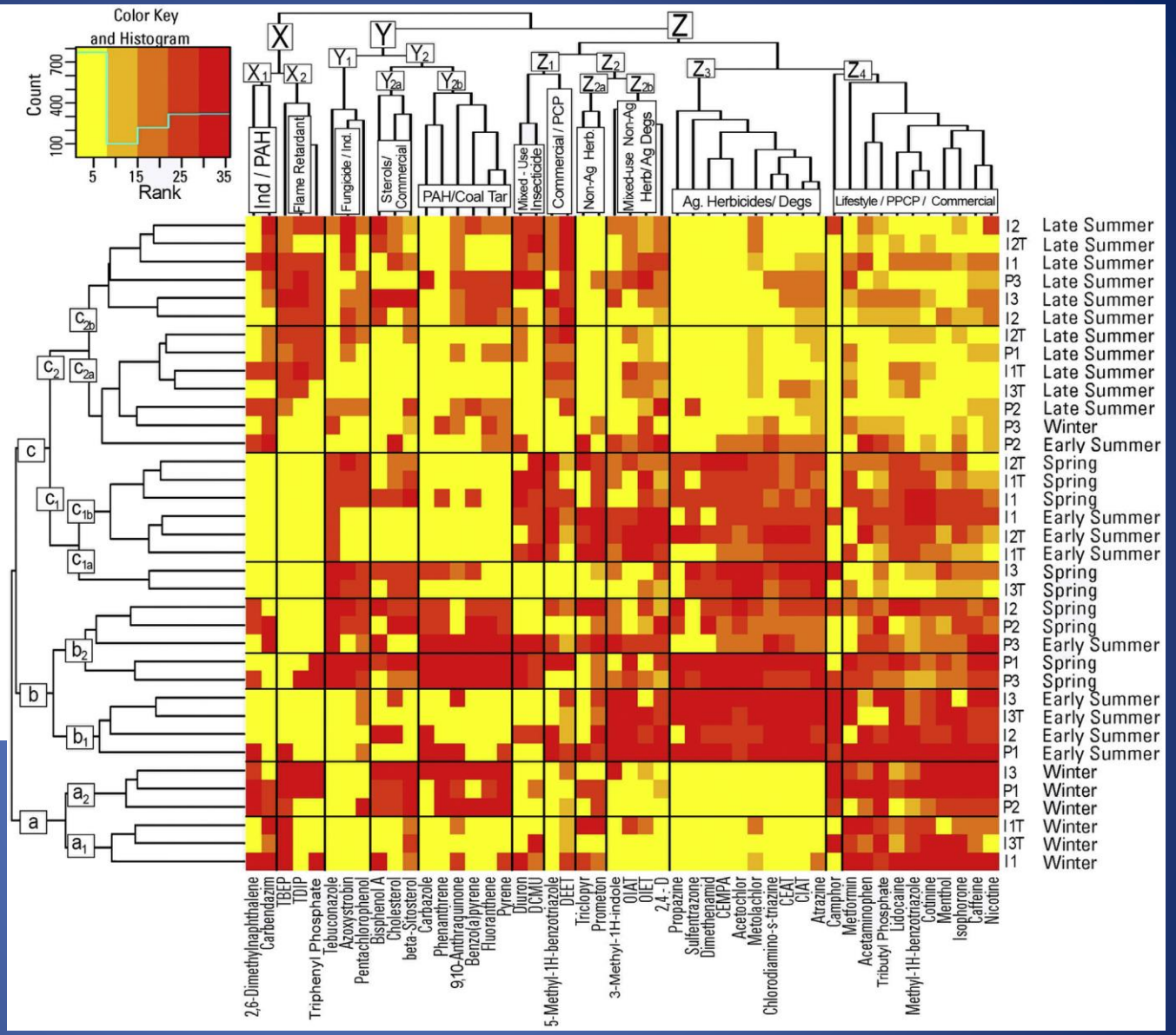
# Detailed Comparisons between Sites:

## Inflows and Outflows



# CECs groups varied by season

- Cluster analysis and heatmap of samples
  - Compound
    - (x-axis)
  - sample event
    - (y-axis).
- X axis annotated with groups for reference
- Clusters reflect use

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# Summary of Concentration Reductions from IESF

- IESF ponds reduced CEC concentrations
  - total concentrations were significantly reduced
  - concentrations of 14 of the 48 compounds with > 25% detection were significantly reduced
- Reductions were observed in 83% of the paired IESF inflow/outflow samples
  - reduced numbers of pesticides and WWI contaminants in IESF outflow samples
  - reductions were highest in February (38%) and September (36%), and lowest in May (< 2%)

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# CEC Compounds Showing IESF Reduction

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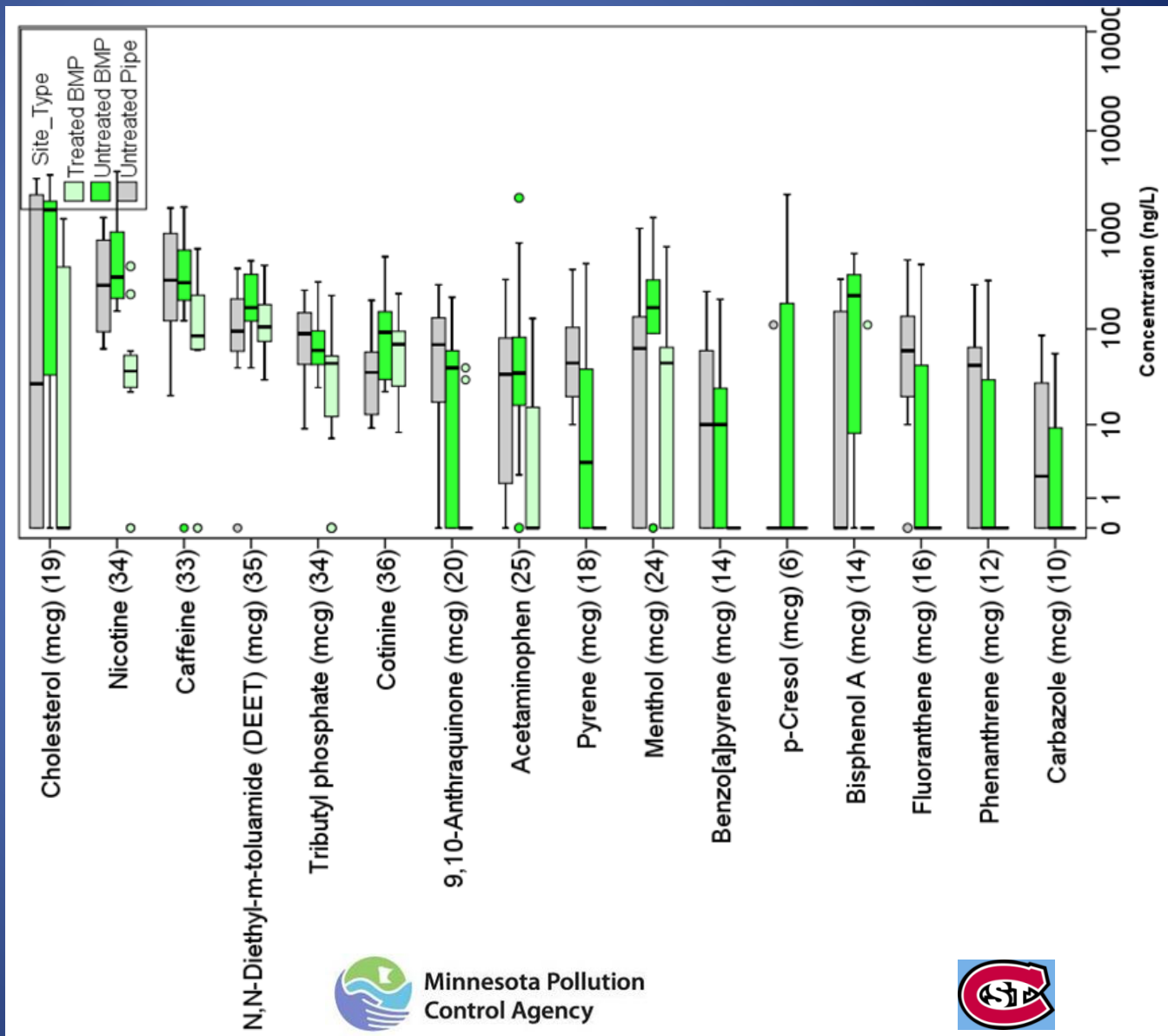
**Compounds Removed Hydrophobic:**

Cholesterol
PAHs
BPA

**Other Compounds:**

Plant sterols
Nicotine
Acetaminophen
Menthol
Caffeine
DEET
Tributyl-phosphate

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# Lessons Learned from IESF Stormwater Sampling

- Urban stormwater is a significant source of CEC discharge to surface water
- Overall, median concentrations were >10 ng/L for 25 CECs and > 100 ng/L for 9 CECs
- Iron-enhanced sand filtration detention ponds reduce some CEC concentrations depending upon season
  - Reductions were observed in 83% of the paired BMP inflow/outflow samples
    - Median removal efficiencies were 26% to 100% for significantly reduced compounds
    - Removal observed for both hydrophobic and polar-hydrophilic compounds
  - Some season by site-type effects on removal

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# More information on IESF treatment of urban stormwater

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## Contaminants of emerging concern in urban stormwater: Spatiotemporal patterns and removal by iron-enhanced sand filters (IESFs)

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ABSTRACT

Numerous contaminants of emerging concern (CECs) typically occur in urban rivers. Wastewater effluents are a major source of many CECs. Urban runoff (stormwater) is a major urban water budget component and may constitute another major CEC pathway. Yet, stormwater-based CEC field studies are rare. This research investigated 384 CECs in 36 stormwater samples in Minneapolis-St. Paul, Minnesota, USA. Nine sampling sites included three large stormwater conveyances (pipes) and three paired iron-enhanced sand filters (IESFs; untreated inlets and treated outlets). The 123 detected compounds included commercial-consumer compounds, veterinary and human pharmaceuticals, lifestyle and personal care compounds, pesticides, and others. Thirty-one CECs were detected in ≥50% of samples. Individual samples contained a median of 35 targeted CECs (range: 18–54). Overall, median concentrations were ≥10 ng/L for 25 CECs and ≥100 ng/L for 9 CECs. Ranked, hierarchical linear modeling indicated significant seasonal- and site type-based concentration variability for 53 and 30 CECs, respectively, with observed patterns corresponding to CEC type, source, usage, and seasonal hydrology. A primarily warm-weather, diffuse, runoff-based profile included many herbicides. A second profile encompassed winter and/or late summer samples enriched with some recalcitrant, hydrophobic compounds (e.g., PAHs), especially at pipes, suggesting conservative, less runoff-dependent sources (e.g., sediments). A third profile, indicative of mixed conservative/non-runoff, runoff, and/or atmospheric sources and transport that collectively affect a variety of conditions, included various fungicides, lifestyle, non-prescription, and commercial-consumer CECs. Generally, pipe sites had large, diverse land-use catchments, and showed more frequent detections of diverse CECs, but often at lower concentrations; while untreated sites (with smaller, more residential-catchments) demonstrated greater detections of "pseudo-persistent" and other ubiquitous or residentially-associated CECs. Although untreated stormwater transports an array of CECs to receiving waters, IESF treatment significantly removed concentrations of 14 (29%) of the 48 most detected CECs; for these, median removal efficiencies were 26%–100%. Efficient removal of some hydrophobic (e.g., PAHs, bisphenol A) and polar-hydrophilic (e.g., caffeine, nicotine) compounds indicated particulate-bound contaminant filtration and for certain dissolved contaminants, sorption.



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# Next Steps – Current Studies

- **Monitor contaminants of emerging concern in stormwater inflows and outflows for two emerging stormwater BMP technologies – IESF BMP ponds and underground infiltration basins**
- **Measure contaminants of emerging concern in stormwater during snowmelt runoff and in late spring in four Minnesota cities**
- **Measure the biological activity of all collected stormwater samples across a range of seven species commonly found in receiving waters using a common cell-based assay**
- **Measure fate of CECs in shallow ground water following infiltration**

# Questions –


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