Development of Indicators for Emerging Trace Organic Compounds

National Water Quality Monitoring Conference

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Outline

- WERF's Trace Organic Compounds (TOrCs) Knowledge Area
  - Research Interests
  - Our Project Objectives
- Development of a List of TOrC Indicators
- Analytical Methodology

WERF's Research on TOrCs

- Research Areas
  - Treatability
  - Aquatic Ecological Effects
  - Risk Communications
- Project Summary
  - 50 TOrC-related funded projects
- Objective
  - Help facility and industry managers make decisions

https://www.werf.org/c/KnowledgeAreas/TraceOrganics/Trace_Organics_Research_at_a_Glance.aspx

WERF Subscriber Questions

1. "Are measured TOrC concentrations in an effluent discharge (or in the receiving water) likely to cause adverse effects to aquatic populations or communities?"
2. "Is my receiving water "especially sensitive" to the presence of TOrCs?"
3. "Are observed impacts on aquatic populations and communities in my receiving water likely caused by TOrCs or other stressors?"
4. "What is the contribution of TOrCs relative to other (e.g., physical, chemical) causes of ecological impairment?"

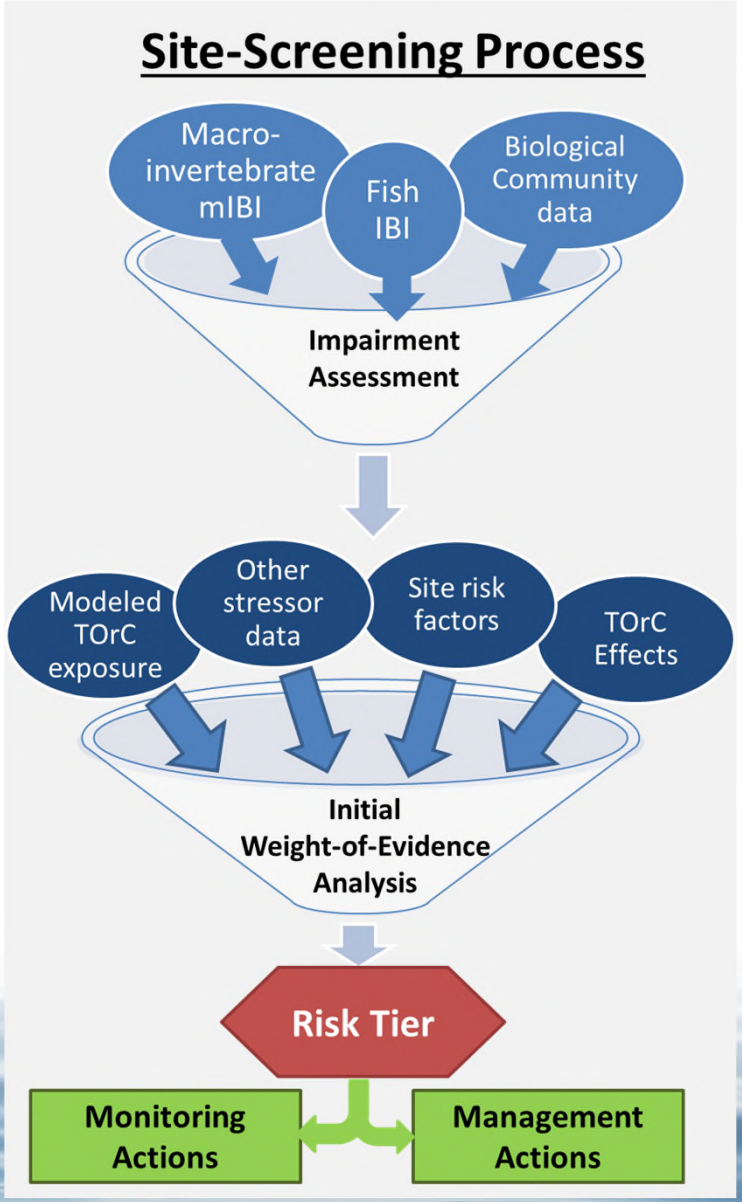
WERF Project CEC6R12: Testing and Refining Site Screening Tools (Phase 2)

Vision for Screening Tools

- Must be useful and usable by utilities
  - Good fit for existing utility data
  - Easy to interpret results
- Support sound decisions by utilities
  - Targeted data gathering
  - Effective source control and treatment
- Promote clearer understanding of complex issues
  - Assist communication with stakeholders & regulators

Elements of Phase 2 Approach

- Enhancing the site screening process
  - Prominence of regulatory drivers
  - Making it both risk- and action based
  - Recognizing potential roles of habitat and other stressors
  - Flexible enough to work with available data
  - Iterative to support smart data gathering
- Developing a more complete Weight of Evidence analysis, with field studies
- Streamlining list of indicator compounds
  - With a proposed method of analysis



Importance of Indicator TOrCs

- Objective is to screen for TOrC risk
  - Should reliably indicate presence/absence of High Priority TOrCs
  - Should help understand extent of removals
  - Should be manageable for WW utility staff
  - Should be efficient in terms of analytical cost
- Each should be a reliable indicator for a class of TOrCs
  - Analysis for additional compounds may then be triggered and a need for weight of evidence based on initial site screening
- Phase 1 study developed 3 High Priority lists, with some overlap, based on:
  - Risk (41 compounds)
  - Risk and fate (60 compounds)
  - Toxicity and fate (108 compounds)

Objectives of Indicator TOrC List

- Add clarity to prioritization process
- Facilitate use of site screening framework and subsequent monitoring by target audience
- Potentially reduce analytical costs

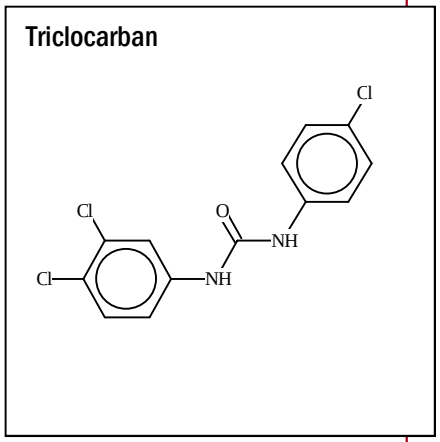
Methods

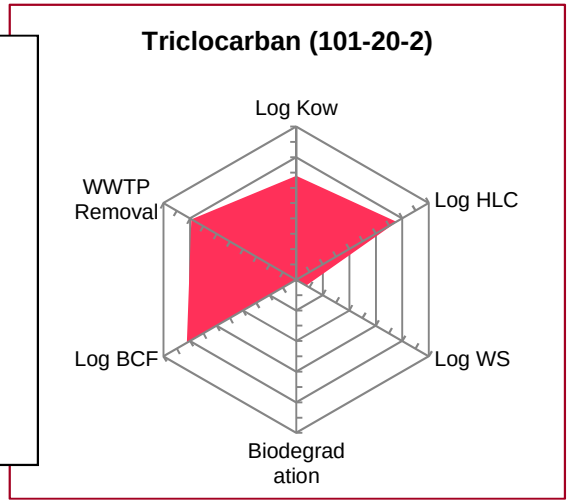
- High Priority: Based on WERF Phase 1 high risk compound list
- Ubiquitous: More frequently detected TOrCs
  - Dickenson: meta-analysis of WWTP effluent
  - Criteria:
    - Detected in at least 75% of conventionally treated effluents
    - Detected at level at least 5x> LOQ
- Reliability: If a single compound is detected, how well does that predict whether compounds in its class would also have been detected?

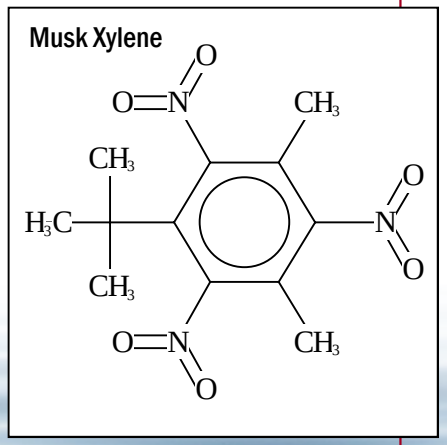
Reliability as an indicator for:	At locations where this indicator was:	Other TOrCs in its chemical class met this criterion:
Absence of similar TOrCs	Not detected	100% were also not detected
Presence of similar TOrCs	Detected	At least 25% were detected, on average

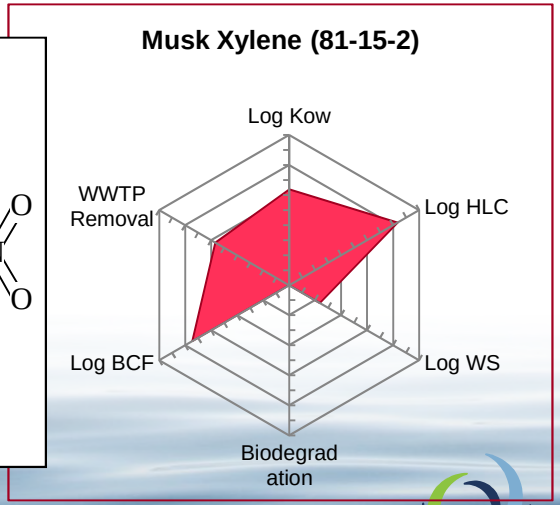
Chemical Structure & Properties

- We independently considered fate and persistence of candidate TOrCs based on structure and reactivity relationships
  - Grouped compounds by structural features
  - Also used EpiSuite to predict partitioning and degradation parameters and looked for similarity
- We also considered toxicity
  - Used ECOSAR to predict acute and chronic toxicity
  - Used as tie-breaker for otherwise similar TOrCs

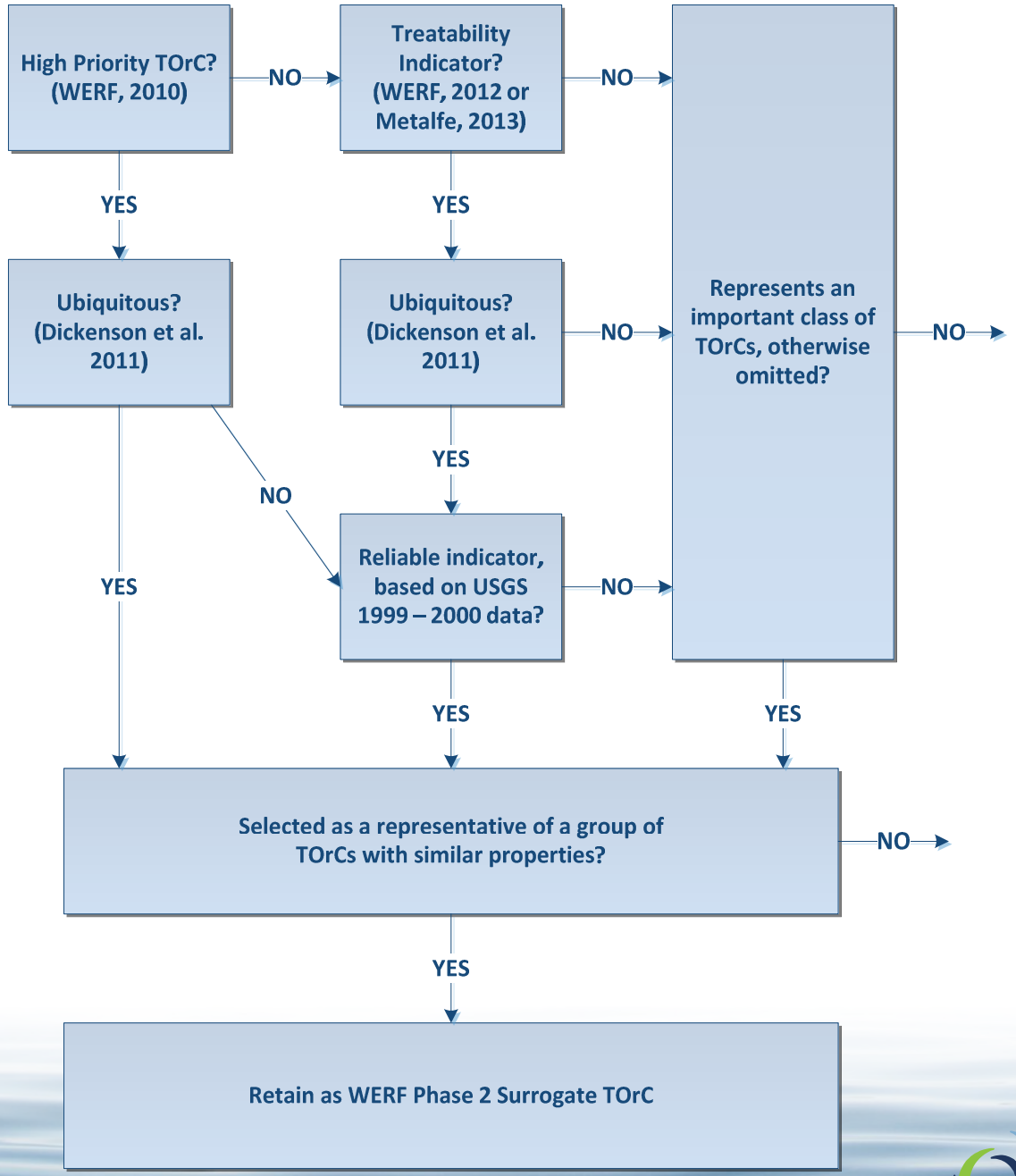








Process for Selecting Indicator TOrCs



23 Indicator TOrCs Identified

Basis for Inclusion

- Priority based on risk, fate, toxicity
- Presence in effluents
- Predictive reliability based on co-occurrence
- Chemical structure
- Other (non-POTW) wastewater sources
- Published analytical methods
- Modes of action

Distribution by TOrC Type

- 6 Personal Care Products
- 8 Pharmaceuticals
- 3 Hormones
- 2 Plasticizers
- 1 Flame Retardant
- Local/Regional Pesticide(s) and PAHs

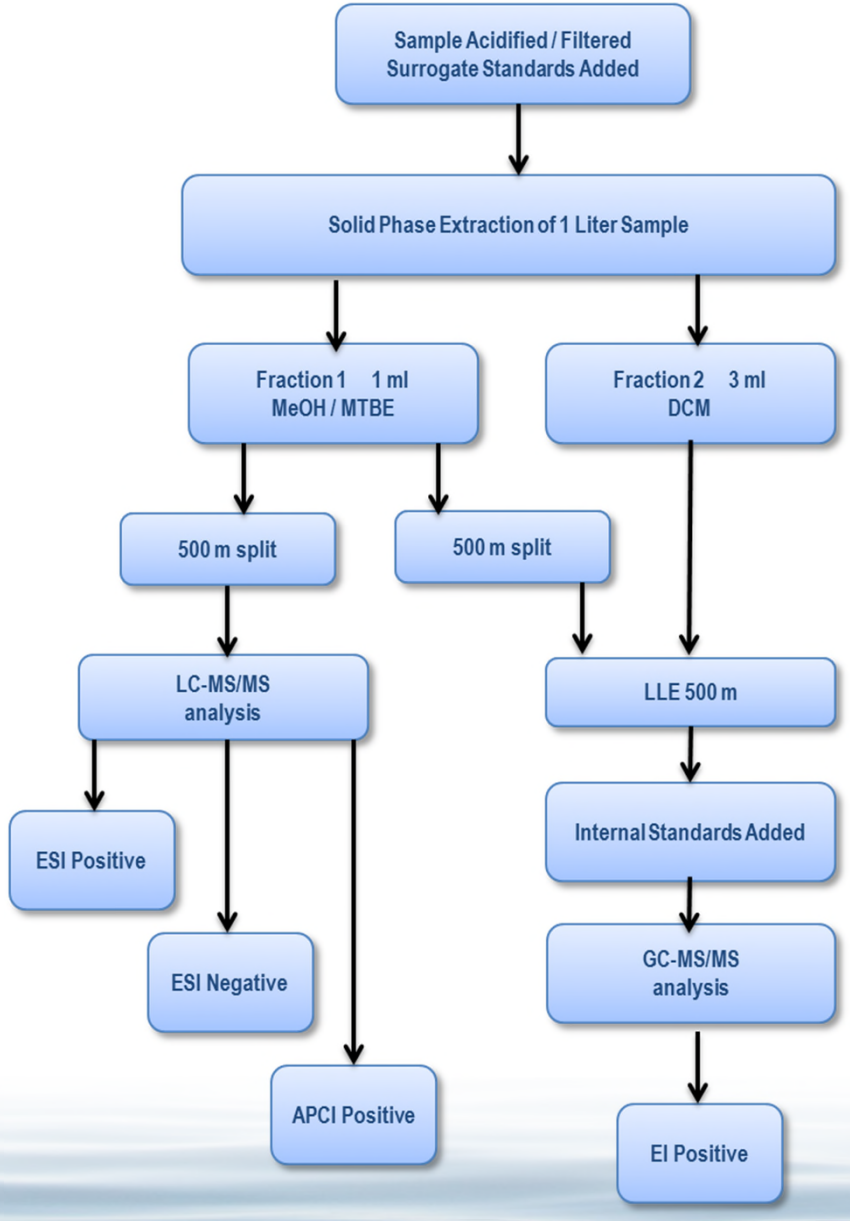
Indicator Compounds Selected

Compound	CAS #	TOrC Type	TOrC Category	Ecological Risk	Ubiquitious	Treatability	Reliability		Mode of Action	Approved Method	Removal
				High Priority TOrC?	Ubiquitious ?	Treatability Indicator?	Presence Indicator?	Absence Indicator?	Mode of Action identified	EPA Analytical Method	High WWTP Removal?
N,N-diethyltoluamide (DEET)	134-62-3	Personal Care Product	Insecticide		89	Y	Y	N			
Nonylphenol	25154-52-3	Personal Care Product	Surfactant	1,2,3	100		Y	Y	Estrogen EDC		Y
Tonalide (AHTN)	21145-77-7	Personal Care Product	Fragrance	1,2,3	100	Y					Y
Triclocarban	101-20-2	Personal Care Product	Antimicrobial		100	Y	Y	Y		1694	
Triclosan	3380-34-5	Personal Care Product	Antimicrobial	1,2	98	Y	Y	Y		1694	
Miconazole	22916-47-8	Personal Care Product	Antifungal	2,3		N		Y	Steroidogenesis disruptor	1694	Y
Carbamazepine	298-46-4	Pharmaceutical	Anticonvulsant		88	Y	N	Y		1694	
Trimethoprim	738-70-5	Pharmaceutical	Antibiotic		86	Y	Y	Y		1694	
Fluoxetine	54910-89-3	Pharmaceutical	Antidepressant		94	Y		Y		1694	
Gemfibrozil	25812-30-0	Pharmaceutical	Lipid regulator		92	Y	Y	Y		1694	
Ibuprofen	15687-27-1	Pharmaceutical	Analgesic		78	Y	Y	Y		1694	
Meprobamate	57-53-4	Pharmaceutical	Anxiolytic		83	Y	N	Y			
Sulfamethoxazole	723-46-6	Pharmaceutical	Antibiotic		94	Y		Y		1694	
Caffeine	58-08-2	Pharmaceutical	Stimulant		81	Y	Y	Y		1694	
Estrone	53-16-7	Hormone	Estrogen	1	<75	Y	Y	Y	Estrogen EDC	1698	
17a-Ethynylestradiol (EE2)	57-63-6	Hormone	Estrogen	1,2,3	<75		Y	Y	Estrogen EDC	1698	
Testosterone	58-22-0	Hormone	Androgen	1	<75		Y	Y	Androgen EDC	1698	
Bis(2-ethylhexyl) phthalate (BEHP)	117-81-7	Plasticizer	Plasticizer	1,2,3	<75		Y	Y	Androgen EDC	8270, 525.2	Y
Bisphenol A	80-05-7	Plasticizer	Plasticizer	1	100	Y	Y	Y	Estrogen EDC	525.2	
Tri(2-chloro-ethyl)phosphate (TCEP)	115-96-8	Flame Retardant	Flame retardant		94	Y	Y	Y			
Fluoranthene	206-44-0	PAH	PAH	2,3	na		Y	Y	Carcinogen, Gene mutagen	8270, 525.2	
Pentachlorophenol	87-86-5	Pesticide	Industrial Pesticide	1,2,3	na				EDC	8270, 525.2	
Trifluralin	1582-09-8	Pesticide	Urban Pesticide	1,2,3	<75%				Reproductive EDC	525.2	Y
Atrazine	1912-24-9	Pesticide	Agricultural Pesticide		na					1699	
Chlorpyrifos	2921-88-2	Pesticide	Insecticide	3			Y		Neurotoxin	1699	
Bifenthrin	82657-04-3	Pesticide	Pyrethroid pesticide								Y
Permethrin	52645-53-1	Pesticide	Pyrethroid Pesticide	3	na				Neurotoxin	1699	Y
Vinclozolin	50471-44-8	Pesticide	Fungicide						Hormone antagonist	na	

Analytical Method for Indicator TOrCs

- Objective: Minimize # of analytical procedures
- Method of Trenholm (2006)
  - Extract with hydrophilic-lipophilic solid phase extraction cartridge
  - Precondition SPE cartridges with DCM and MTBE
  - Separate LC-MS/MS and GC-MS/MS analyses
- Caveats:
  - Weak bases will require skillful analyst
  - Several of these indicators can occur as lab background, requiring ultraclean procedures

Analytical Method for Indicator TOrCs



Caveats

- List of indicators can and should be modified to reflect regional differences in prevalence
- Indicators represent members of their group but their presence alone in unlikely to reflect the additive ecological effects that may occur from mixtures of multiple TOrCs at a site.

Questions

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WERF Project CEC6R12: Testing and Refining Site Screening Tools

- "Demonstrate and refine the application of site screening tools previously developed by WERF"
- "Guidance on how to use the site screening tools supported by detailed demonstrations"
- "Purpose is to assist water quality managers who are considering
  - chemical and biological monitoring programs, upgrades to treatment facilities, source control initiatives
  - future regulatory requirements, and possible concerns expressed by utility boards, environmental groups and the public."

WERF's Phase 1 Approach (CEC5R08)

- Provided a valuable compendium of TOrCs, with risk evaluations
  - Three large sets of High Priority TOrCs were presented, using different approaches to risk
- Proposed a useful screening-level risk characterization, based on critical factors related to TOrC exposures
  - Those proposed screening methods may be difficult for utility staff to apply and interpret
- We also see other stressors as deserving additional attention, where they co-occur with TOrCs

Phase 2 Goals and Scope

- Build on screening framework developed in WERF Phase 1 project
  - Characterize TOrC risk within context of site features, community, and stressors
- Refine and verify a practical and usable screening protocol for WERF member utilities
- Screening procedure should support management decisions
- Recognize challenges in establishing cause/effect

Indicator TOrCs

Personal Care Products

- DEET
- Nonylphenol
- Tonalide
- Triclocarban
- Triclosan
- Miconazole

Pharmaceuticals

- Carbamazepine
- Trimethroprim
- Fluoxetine
- Gemfibrozil
- Ibuprofen
- Meprobamate
- Sulfamethoxazole
- Caffeine

Indicator TOrCs

Hormones

- Estrone
- EE2
- Testosterone

Others

- Plasticizers
  - Bis(2-ethylhexyl) phthalate
  - Bis-Phenol A
- Flame retardants
  - TCEP

Indicator TOrCs

Pesticides

- Trifluralin
- Bifenthrin (or Permethrin)
- Pentachlorophenol
- Atrazine
- Chlorpyrifos
- Vinclozolin

PAH

- Fluoranthene