CALIFORNIA Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Constituents of Emerging Concern Science Advisory Panel for Recycled Water

Jörg E. Drewes
Technical University of Munich
Panel Chair

Costa Mesa, CA
July 19-21, 2017

Outline

- Approach, assumptions and recommendations of the 2009/2010 Science Advisory Panel
- Advances regarding recycled water CEC monitoring since 2009/2010
- Considerations and tasks for the 2017 Panel

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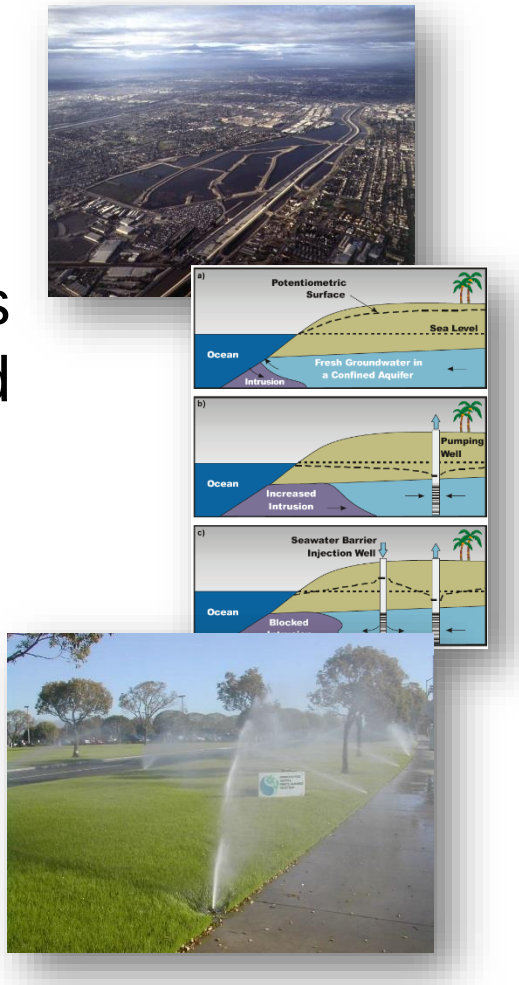
Motivation

- What are appropriate chemicals of emerging concern (CECs) to be monitored, including analytical methods and MDLs?
- What is the known toxicological information for these constituents?
- Would the above lists change based on level of treatment and use? If so, how?
- What are possible indicators that represent a suite of CECs?
- What levels of CECs should trigger enhanced monitoring?

California Water Recycling Policy

- Develop uniform recommendations for CEC monitoring statewide

- Focus on three reuse practices in which CECs may represent a potential threat to human and aquatic health
  1. Indirect potable reuse via **surface spreading** of recycled water
  2. Indirect potable reuse via **subsurface injection** of recycled water into a potable aquifer
  3. **Urban landscape irrigation** with recycled water



2009 Science Advisory Panel Members

- **Dr. Paul Anderson**
  - Human Health Toxicologist
  - AMEC
- **Dr. Adam Olivieri**
  - Risk Assessor
  - EOA, Inc.
- **Dr. Nancy Denslow**
  - Biochemist
  - University of Florida
- **Dr. Daniel Schlenk**
  - Environmental Toxicologist
  - University of California-Riverside
- **Dr. Jörg Drewes**
  - Civil Engineer
  - Colorado School of Mines
- **Dr. Shane Snyder**
  - Analytical Chemist
  - Total Environmental Solutions, Inc.

2017 Science Advisory Panel Members

- **Dr. Paul Anderson**
  - Human Health Toxicologist
  - AMEC
- **Dr. Nancy Denslow**
  - Biochemist
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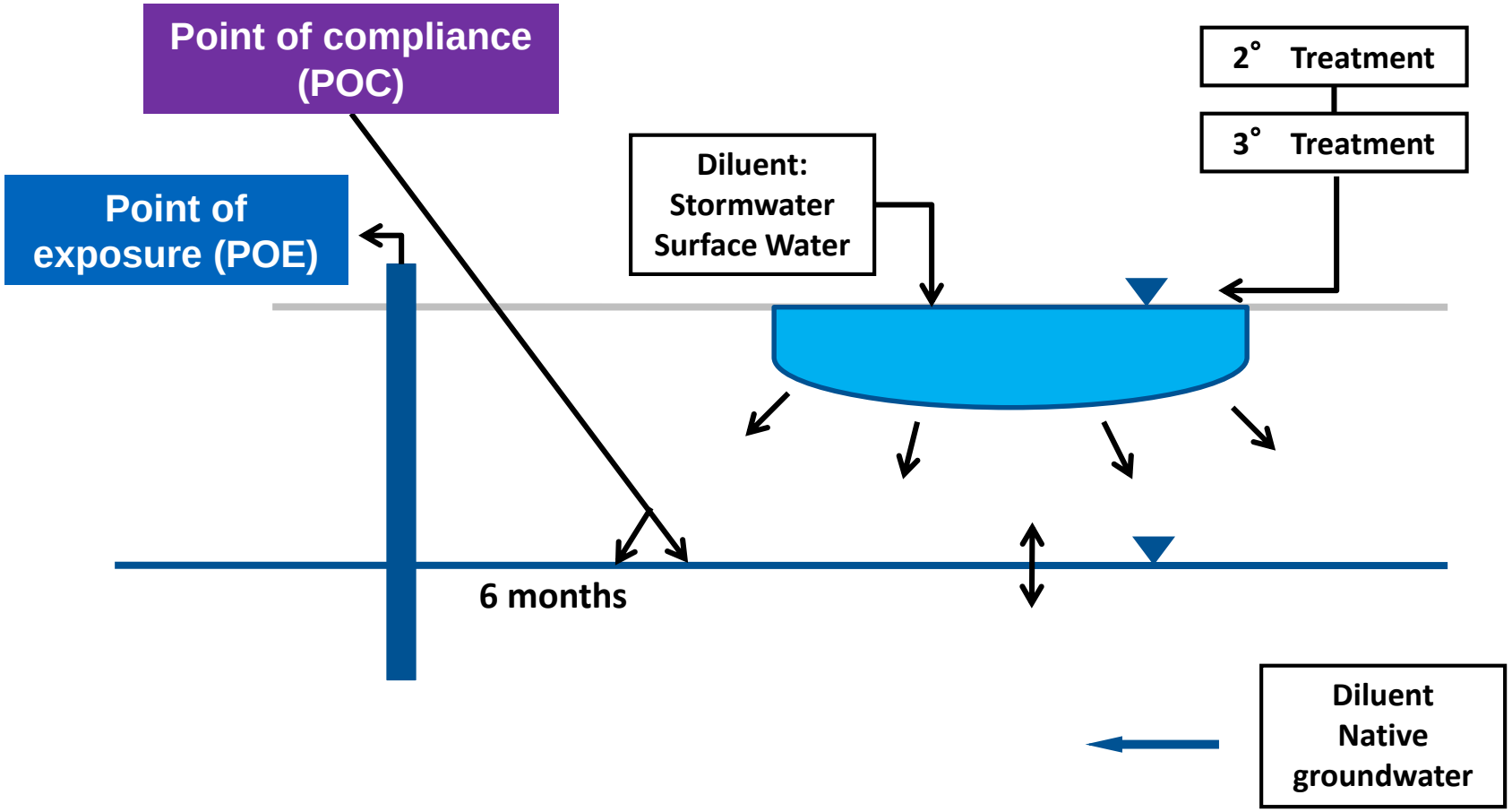
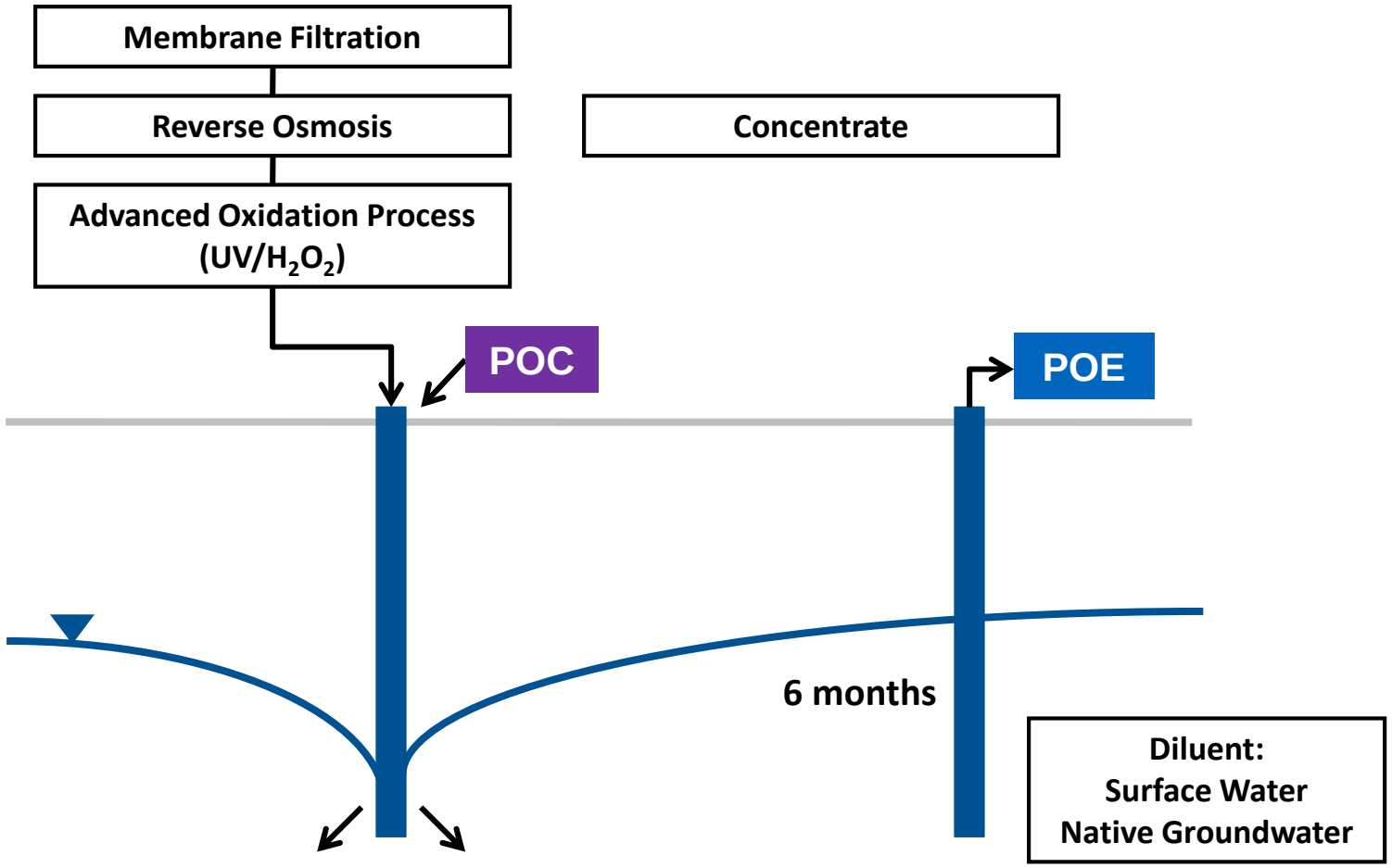
- **Dr. Shane Snyder**
  - Analytical Chemist
  - National University of Singapore
- **Dr. Walter Jakubowski**
  - Human Health Microbiologist
  - WaltJay Consulting

Surface Spreading Operation - Conceptual Model



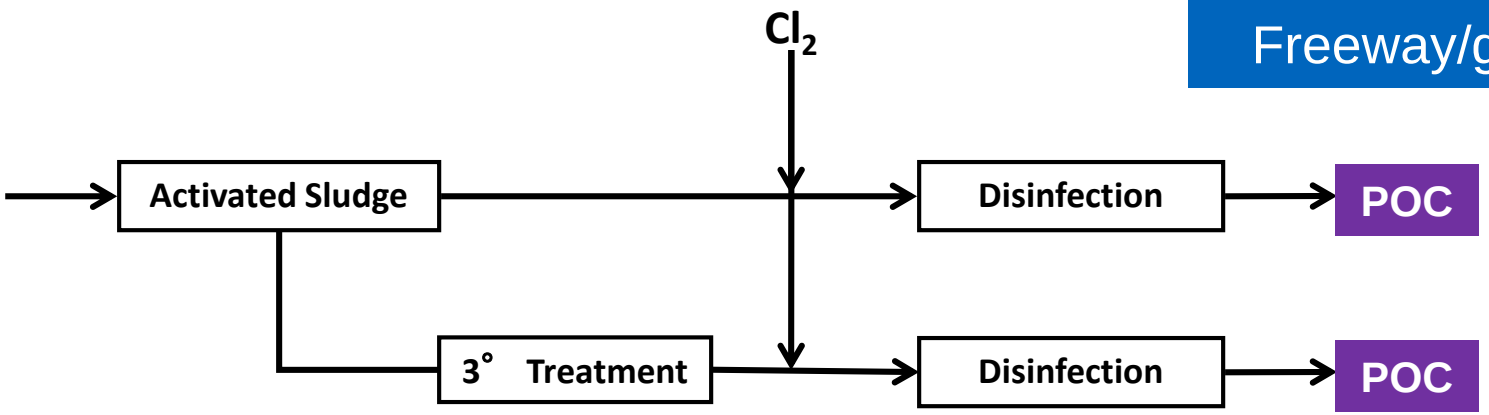
Subsurface Injection - Conceptual Model



Non-potable Reuse: Urban Landscape Irrigation (Title 22)

POE Restricted access:

- Landscape
- Freeway/golf course



POE terrestrial

POE Unrestricted access:

1. Residential
2. Golf course
3. Urban landscape

CEC Definition (2009)

- Personal care products
- Pharmaceuticals
- Industrial
- Agricultural
- Natural hormones
- Inorganic constituents (boron, chlorate)
- Food additives and constituents (phytoestrogens, caffeine, sweeteners)
- Transformation products
- Nanomaterials

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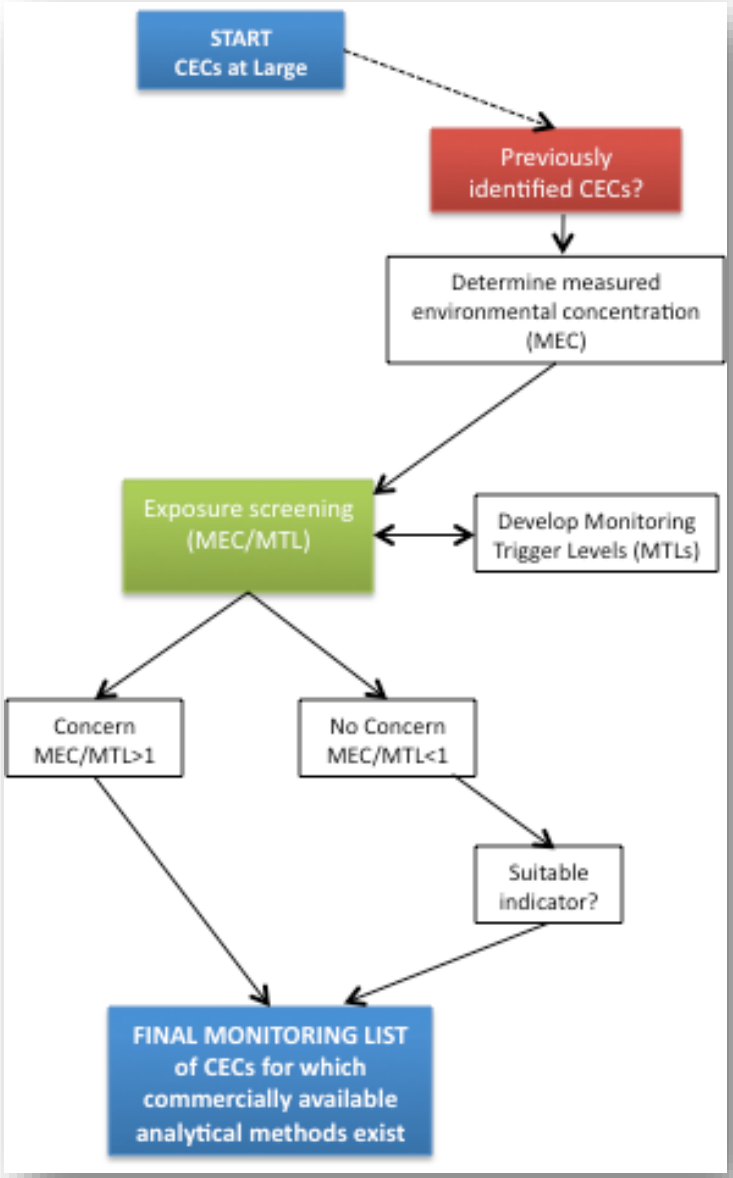
- Microplastics
- Antibiotic resistance

Outcomes of the 2009 Panel

- #1: Develop decision making framework
  - A tool to prioritize CECs now and into the future
- #2: Application of framework to recycled water projects in California
  - Preliminary CEC monitoring list ("what" to monitor)
- #3: Monitoring recommendations and interpretation
  - How, where and when to monitor; and how to respond to results
- #4: Future recommended activities
  - Research, support tools and audits to improve & refine the process

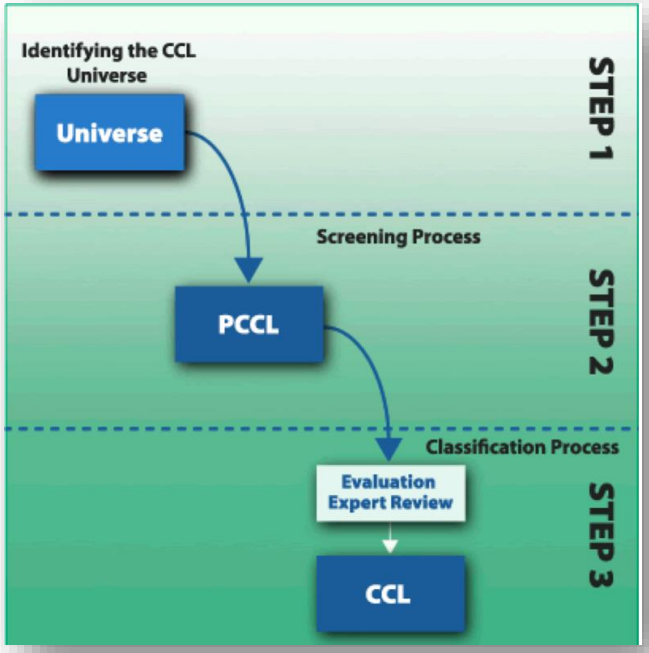
#1: Decision Making Framework (2009)

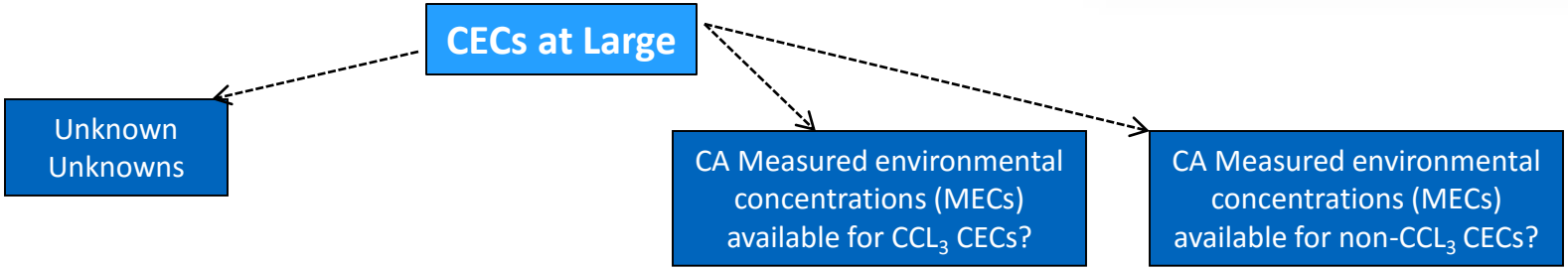
- **Step 1:** Measure CEC concentration in recycled water
- **Step 2:** Determine allowable concentration that is protective of human health ("Monitoring Trigger Level")
- **Step 3:** Combine Steps 1 and 2 (measured / allowable)
  - If ratio is < 1, no concern
  - If ratio is ≥ 1, add to candidate list
- **Step 4:** Screen candidate CECs for availability of reliable methods



How to prioritize CECs?

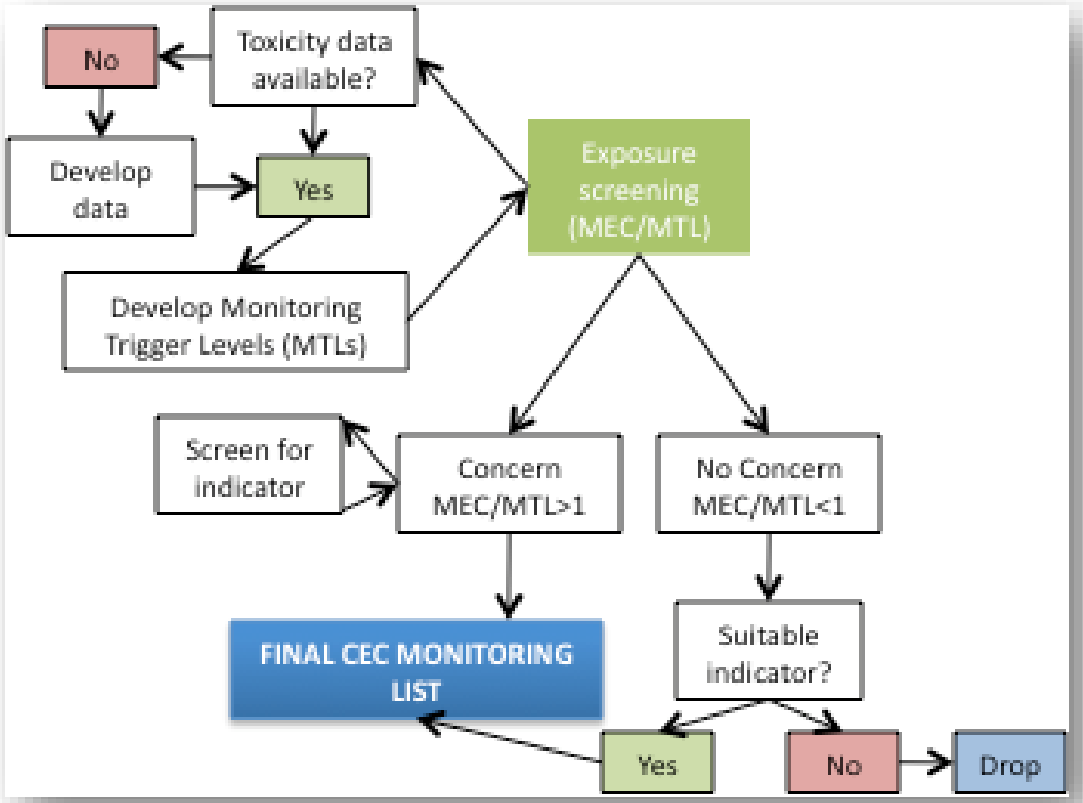
- CECs at Large: EPA's Candidate Contaminant List (CCL3) "Universe of Chemicals"
  - 40 databases: 26,000 compounds
  - Reduced to 7,720 compounds
- Excluded compounds that are already regulated in California





Determining Toxicological Relevance

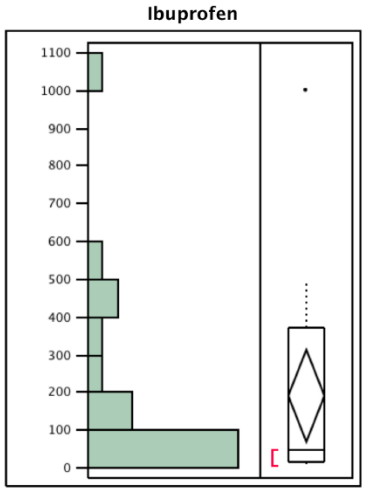
- Exposure assessment at point of compliance (POC) (=conservative)
- Central: monitoring trigger levels (MTLs)



$$Monitoring\_Trigger\_Level = \frac{Screening\_level\_ADIx60kgxRSC}{2L/day}$$

Measured environmental concentrations (MECs)

- Based on California monitoring data for secondary/tertiary treated effluents
- Distribution plots; 90th percentile as MEC
- CCL3 CECs: 7
- Non-CCL3 CECs: 44



Quantiles

100.0%	maximum	1000
99.5%		1000
97.5%		1000
90.0%		500
75.0%	quartile	370
50.0%	median	50
25.0%	quartile	16
10.0%		10
2.5%		5.5
0.5%		5.5
0.0%	minimum	5.5

Moments

Mean	191.21053
Std Dev	253.12773
Std Err Mean	58.071484
Upper 95% Mean	313.21419
Lower 95% Mean	69.206866
N	19

#2: Application of Framework
- Suggested short-list of CECs with health relevance

	Secondary/Tertiary Treated MEC 90th (ng/L)	Initial MTLs		MEC/MTLs	
		Potable Reuse	Irrigation	Potable Reuse	Irrigation
CCL3 CECs					
17β-estradiol	8.4	9.0E-01	9.0E+00	9.33	0.93
NDMA	68	1.0E+01	1.0E+02	6.8	0.68
Non-CCL3 CECs					
Caffeine	900	350	3500	2.57	0.26
Triclosan	485	350	3500	1.39	0.14

Initial MTL of **E2** was based on the California Office of Environmental Health Hazard Assessment (OEHHA) cancer slope factor, as opposed to the ADI developed by the World Health Organization (WHO)

The initial MTL for **caffeine** of 0.35 µg/l is the drinking water guideline established by Australia because chemicals for which structural features or likely metabolic pathways either permit no strong presumption of safety, or actually suggest significant toxicity

#2: Application of Framework – CEC List for Landscape Irrigation (Title 22)

- No CECs identified based on health risk
- Human consumption (incidental) of recycled water in this scenario is very low
- Surrogate measurements are best way to assess Title 22 recycled water quality

What is a proper number of chemicals?

- How to assess whether a process can remove CECs to safe levels?
  - Select chemicals that are toxicologically relevant at low concentrations and monitor removal

    => **“health-based indicator” chemical**

  - Select chemicals with different physicochemical properties and structures and demonstrate that they can be removed by a particular water treatment process

    => **“performance-based indicator” chemical**

    => Certain “performance-based indicators” correlate with bulk parameters (**“surrogates”**), which are much easier to measure

  - For both groups, selected indicator chemicals should represent multiple CEC source classes (e.g., pharmaceuticals, personal care products, food additives, hormones)

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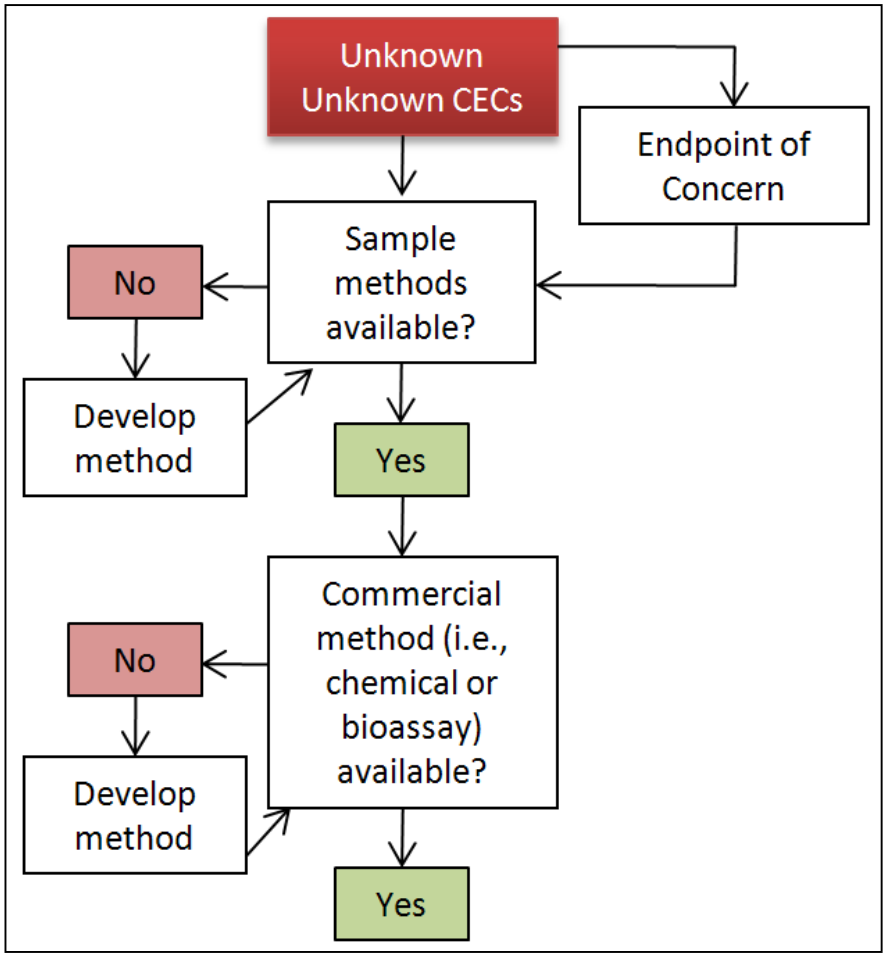
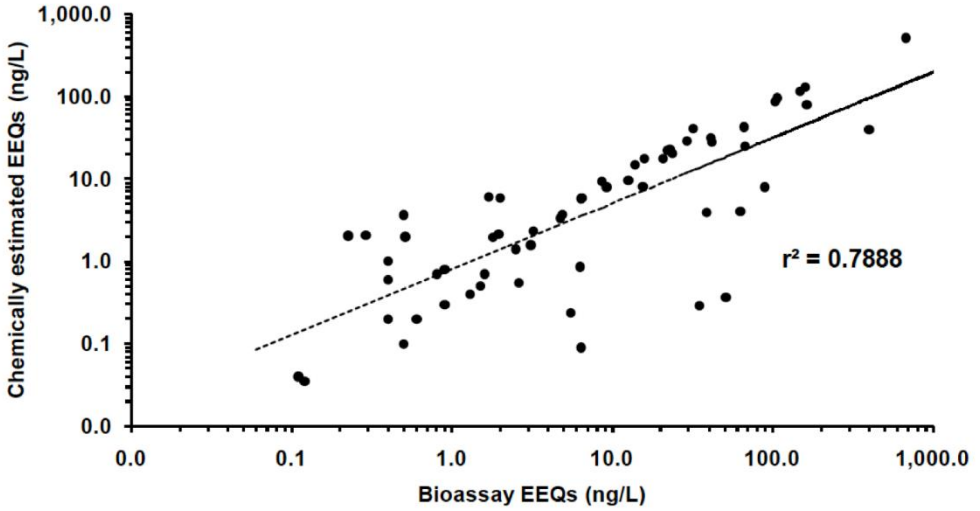
#2: Application of Framework - Suggested final list of CECs

Reuse Practice	Health-based Indicator	MRL (ng/L)	Performance-based Indicator	Expected Removal[8]	MRL (ng/L)	Surrogate	Method	Expected Removal[8]
Groundwater Recharge	17β-estradiol[1]	1	Δgemfibrozil[5]	>90%	10	Δammonia	SM	>90%
SAT	Triclosan[2]	50	ΔDEET[6]	>90%	10	Δnitrate	SM	>30%
	Caffeine[3]	50	ΔCaffeine[3]	>90%	50	ΔDOC	SM	>30%
	NDMA[4]	2	Δiopromide[5]	>90%	50	ΔUVA	SM	>30%
			ΔSucralose[7]	<25%	100			
Direct Injection	17β-estradiol[1]	1	ΔDEET	>90%	10	Δconductivity	SM	>90%
	Triclosan[2]	50	ΔSucralose	>90%	100	ΔDOC	SM	>90%
	Caffeine[3]	50	ΔNDMA	25-50%	2			
	NDMA[4]	2	ΔCaffeine	>90%	50			
Landscape Irrigation	None		None			Turbidity	SM	
						Cl2 Residual	SM	
						Total Coliform	SM	

"Unknown unknowns" (Status 2009)

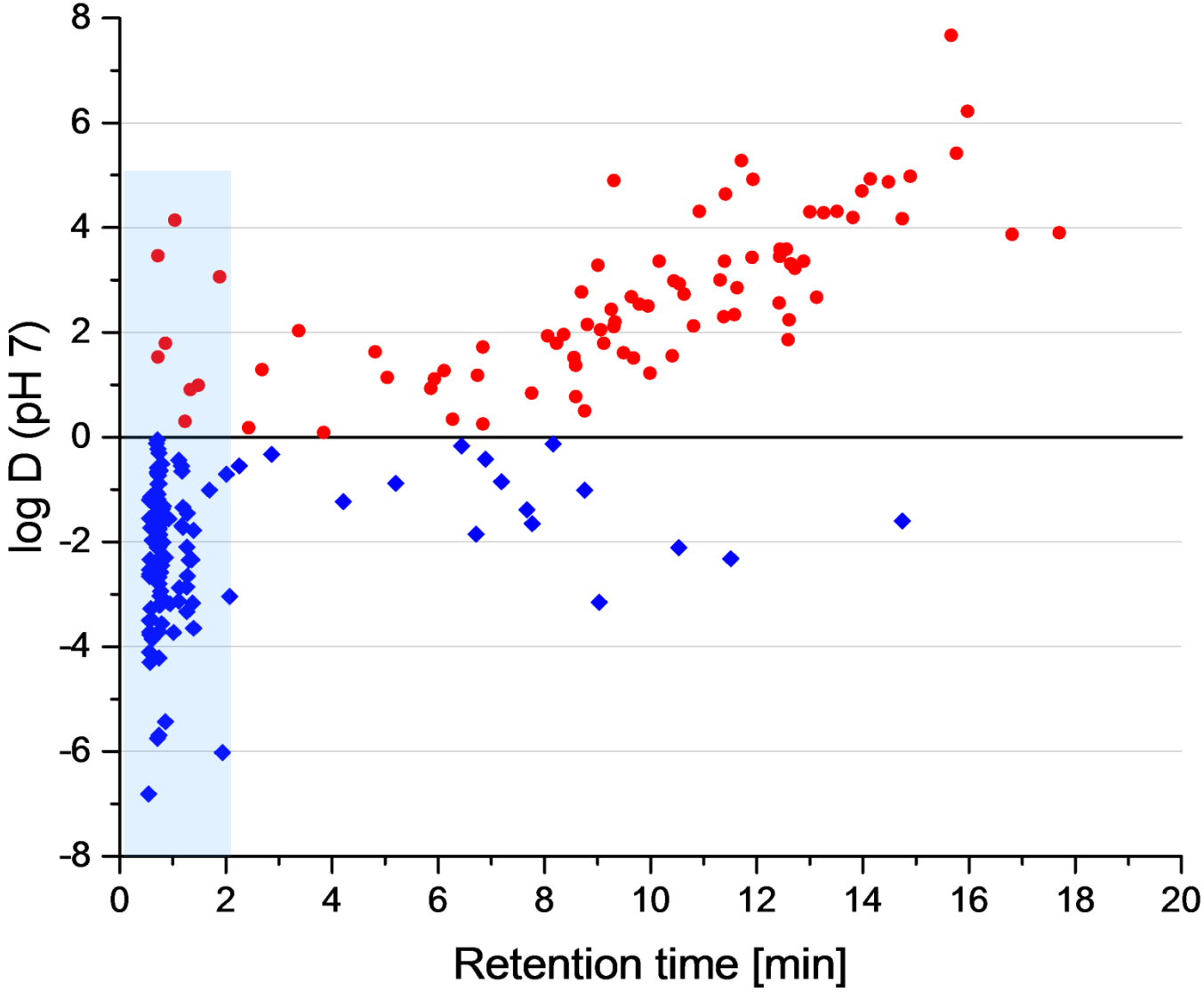


- Bioanalytical screening tools



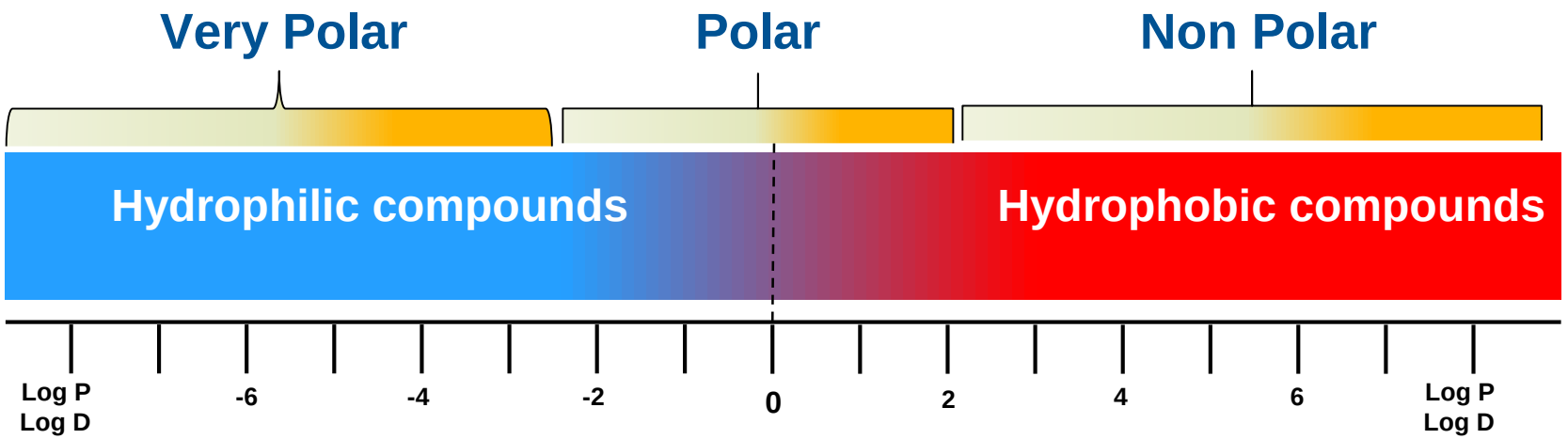
- The Panel recommended the use of bioanalytical screening tools to overcome limitations associated with measuring individual chemicals
- However, the Panel also acknowledged that additional research was needed to develop these methods

C18 RP-Liquid Chromatography



Bieber et al. (2017). *Analytical Chemistry*

Definition ‘Polarity’ via LC Columns



RPLC (e.g. C18)

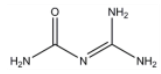
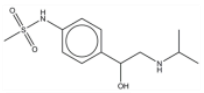
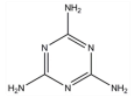
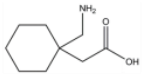
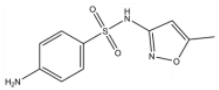
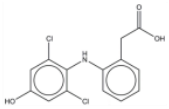
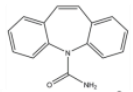
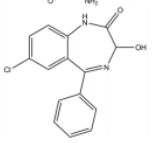
Polar mod. RPLC (e.g. polar-embedded C18)

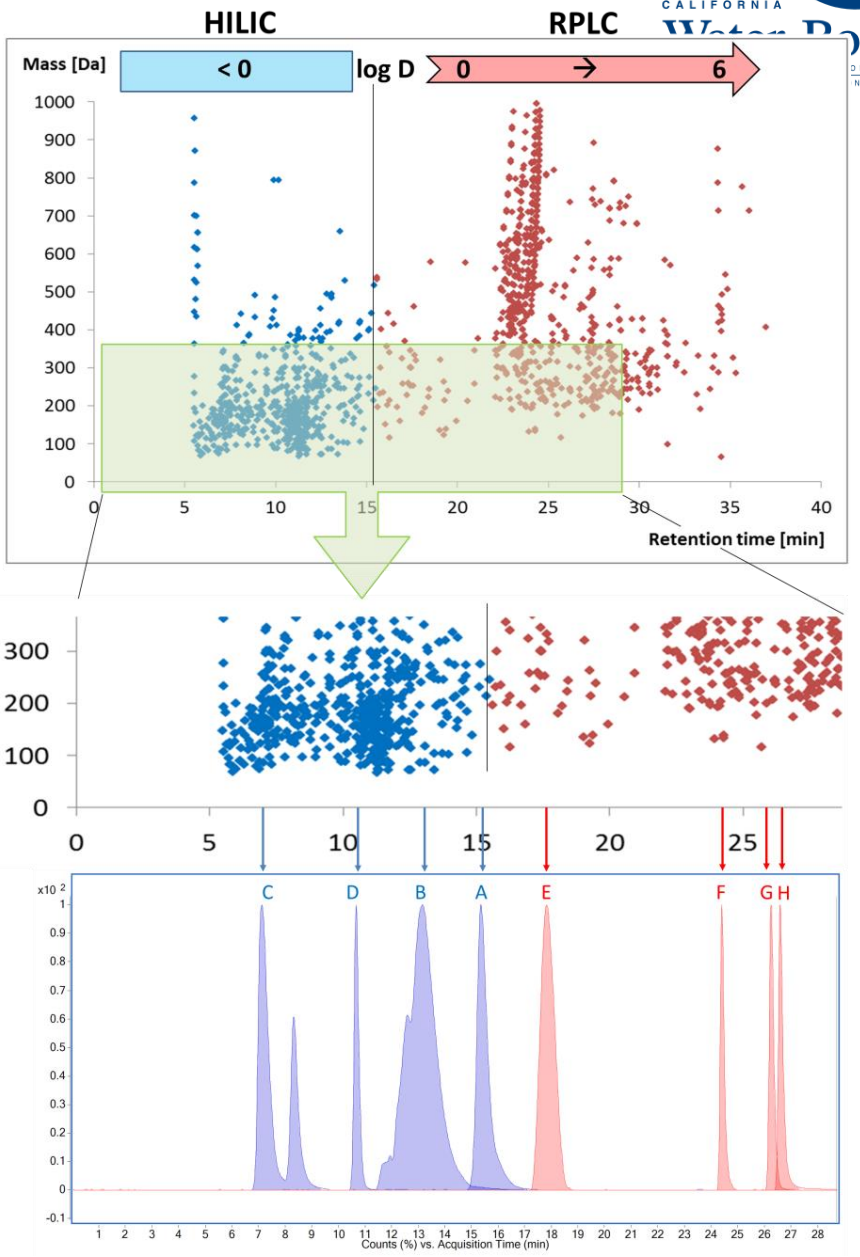
Hydrophilic Interaction Liquid Chr.

Supercritical Fluid Chromatography

Bieber et al. (2017). *Analytical Chemistry*

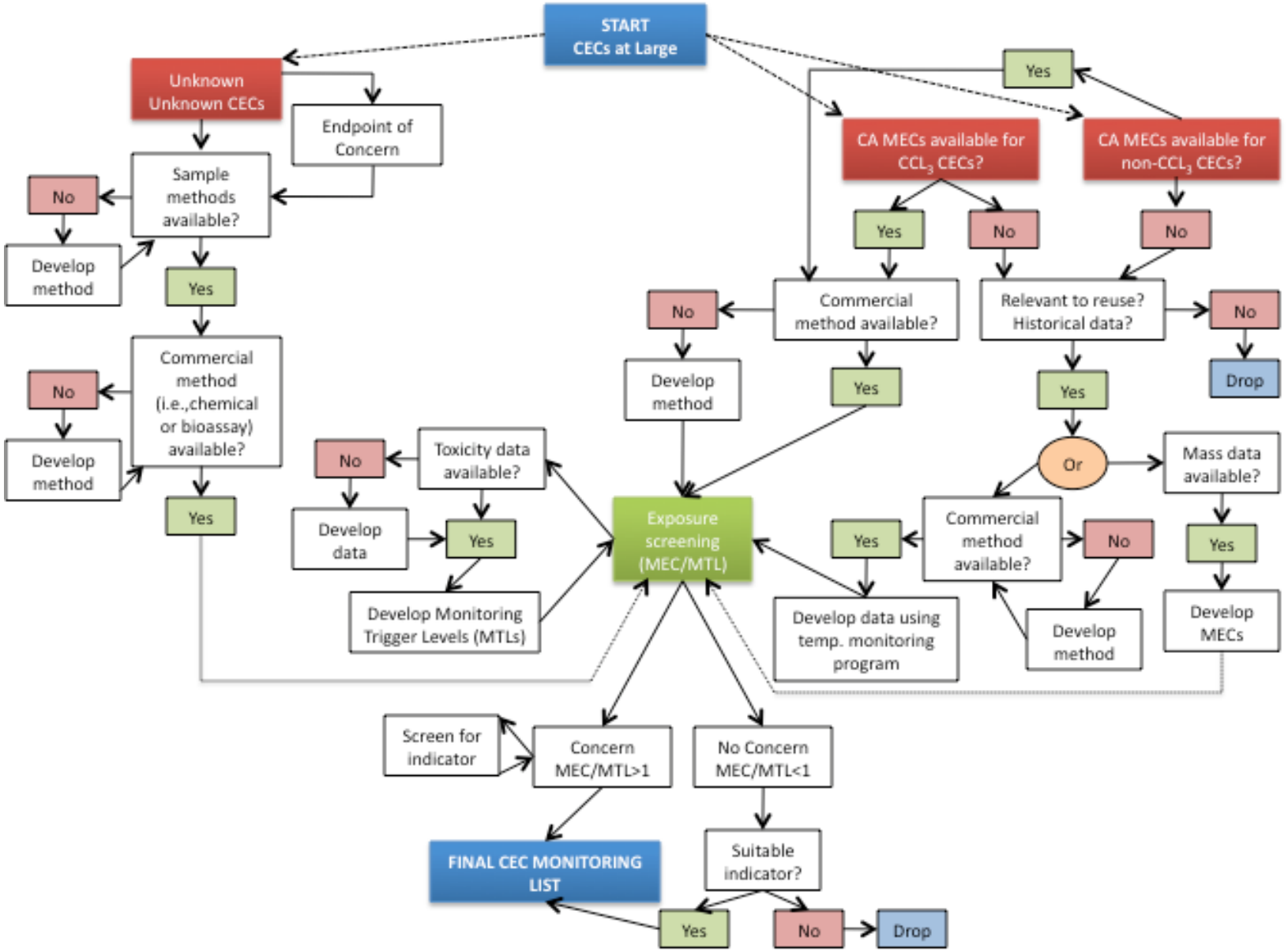
RPLC-HILIC/TOF-MS

Identifier	Substanz	log D pH 7	Strukturformel
A	Guanylurea	-2,64	
B	Sotalol	-2,47	
C	Melamin	-1,97	
D	Gabapentin	-1,27	
E	Sulfamethoxazol	0,18	
F	4-OH Diclofenac	0,89	
G	Carbamazepine	2,77	
H	Oxazepam	2,92	



Bieber et al. (2017). *Analytical Chemistry*

CEC Science Advisory Panel



#3: Monitoring Recommendations - Data Collection

- **Panel recommended that all permitted recycled water facilities should perform monitoring**
  - Distinguish between plant start-up & mature operations
  - Sample recycled water before it is consumed ("point of compliance")
- **Sampling & instrumental methods that can do the job**
  - GC-MS; LC-MS/MS
  - Incorporation of isotope labeled standards
- **And the need for rigorous QA/QC**
  - Adequate detection or reporting limits
  - Precision and accuracy
  - Participation in round-robin exercises

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Conclusions (2010)

- Transparent framework that can assist in identifying suitable CECs for monitoring programs of drinking water and recycled water projects
- Proposed approach is conservative
- Considers toxicological relevance and allows assessment of proper performance of unit processes
- Provides guidance on analytical methods and interpretation of monitoring results
- Recommendations were adopted in California Recycled Water Policy, Amendment A (2013)

Considerations regarding Antimicrobials and Antibiotic Resistance (2009)

- Antimicrobials *were* considered by the Panel
- Since occurrence of antimicrobials in recycled water is expected to be very low, they would have an insignificant impact on any risk associated with reuse practices of interest
- Antibiotic resistant bacteria were NOT considered by the Panel since microorganisms were outside the Panel's charge
- However, the Panel acknowledged that antibiotic resistant genes have been reported in groundwater, drinking water and wastewater and therefore represent a national problem that requires further study. It is the view of the Panel that the specific reuse practices of interest here do not cause the problem nor add to it at the present time

Antibiotic Resistance (2017)

- Risk of antibiotic resistance transfer through water reuse practices (like agricultural irrigation) has been documented
- Risk levels associated with ARBs/ARGs in water have not been determined yet
- What are suitable indicator for human sources of antibiotic resistance (e.g., cefotaxime resistant *E. coli)*?
- Need for standardized methods for their quantification

Recommended Future Activities (2010)

- Improving the database for CEC monitoring information
  - Conduct comprehensive review of peer-reviewed literature and occurrence studies *outside California* to populate a recycled water database for CECs
  - Use that database as a basis to execute the selection framework
- Development of bioanalytical screening techniques
  - Develop techniques that can address “unknown” chemicals potentially present in recycled water
- Programmatic support to manage the process
  - Develop a process to manage data & apply framework
  - Perform independent audit of Panel’s initial recommendations
  - Revisit monitoring recommendations every 3-5 years

Conclusions (2017)

- Suitability and practicability of framework to identify suitable CECs for monitoring programs for recycled water will be critically reviewed
- Lessons learned from monitoring data collected by utilities
- Consider advances in environmental analytical chemistry and bioanalytical methods
- Consider advances in screening methods to assess toxicological relevance
- Recommendations of CEC monitoring for a broader list of reuse practices (approved under Title 22)