Direct Potable Reuse (DPR) Criteria Expert Panel (AB 574)

DPR-4:Treatment for Averaging Potential Chemical Peaks

August 25, 2021

Jean Debroux, PhD, Kennedy Jenks Consultants

Shane Trussell, PhD, PE, BCEE, Trussell Technologies

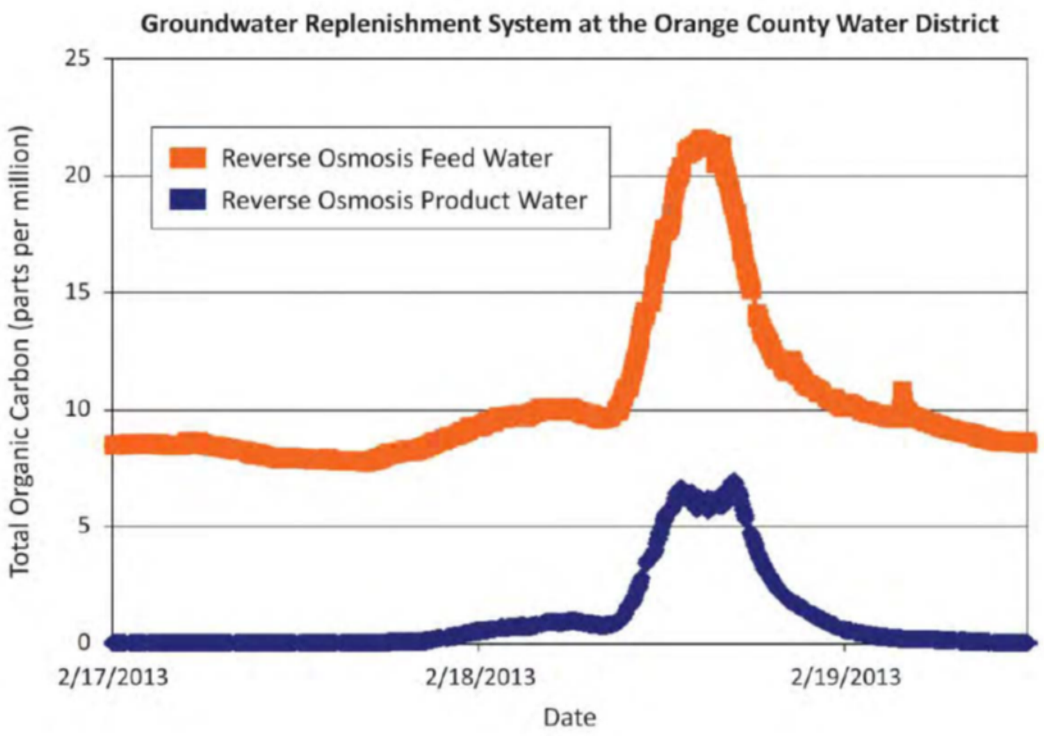
Megan H. Plumlee, PhD, PE, Orange County Water District

California Water Boards

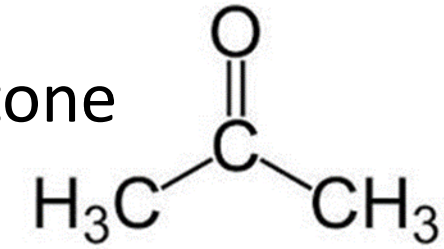
NATIONAL WATER RESEARCH INSTITUTE

DPR-4: Treatment for Averaging Potential Chemical Peaks

- Full advanced treatment (MF/RO/UV-AOP) is a highly effective treatment train employed today for groundwater recharge
- Water quality excursions have been observed

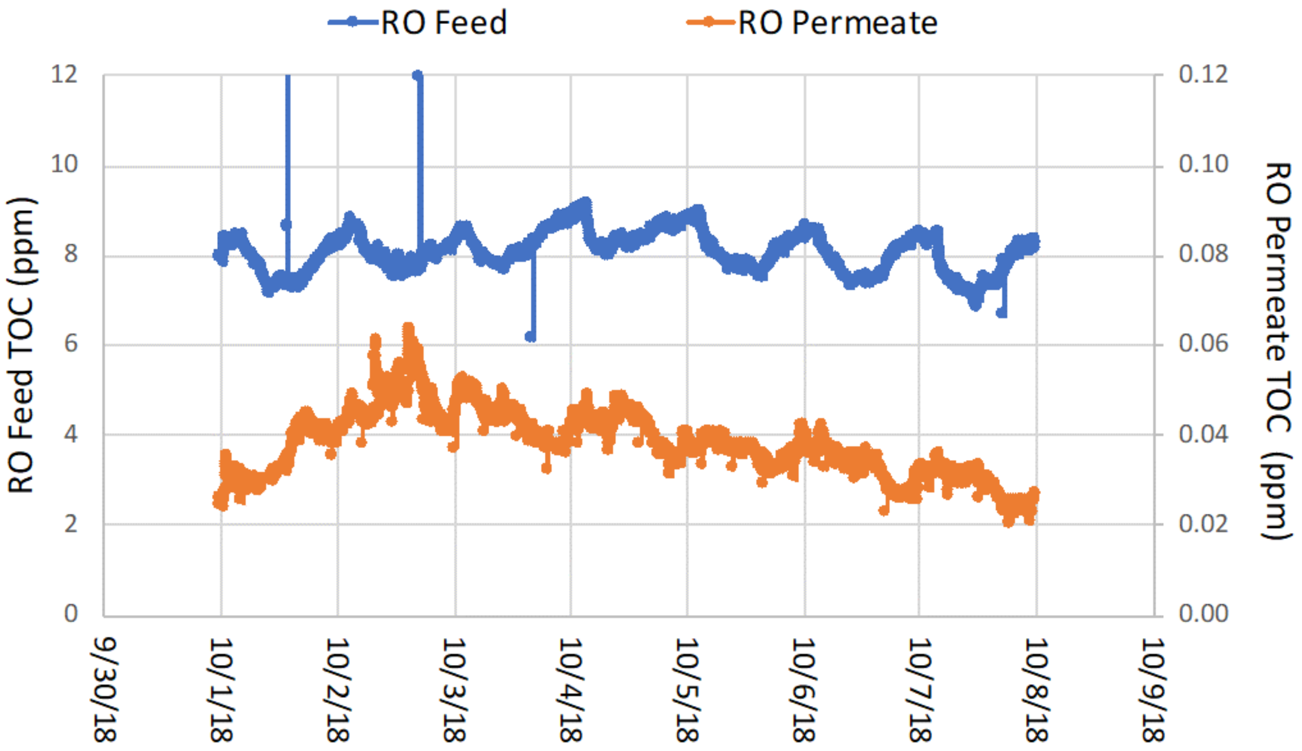


Acetone



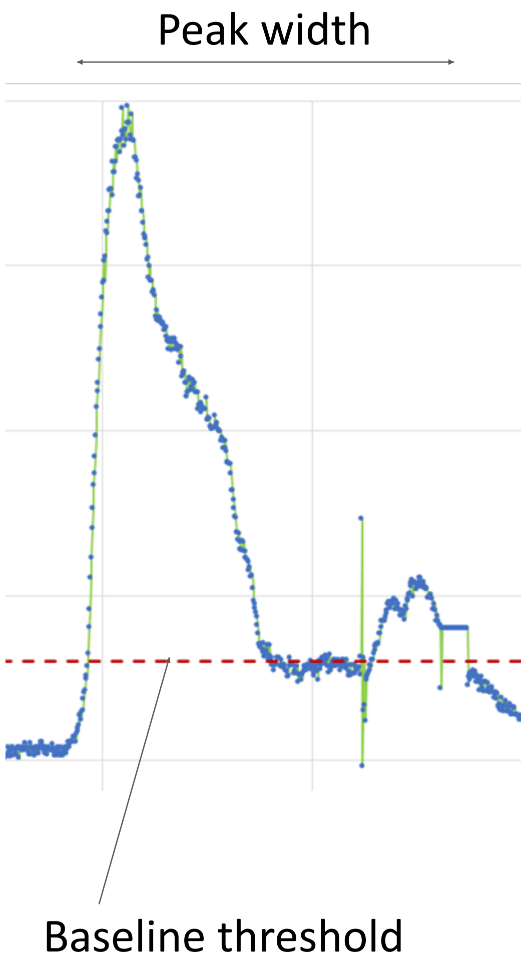
What is a chemical peak?

- Diurnal and process-related TOC baseline variations
- Outliers



Defining a chemical peak

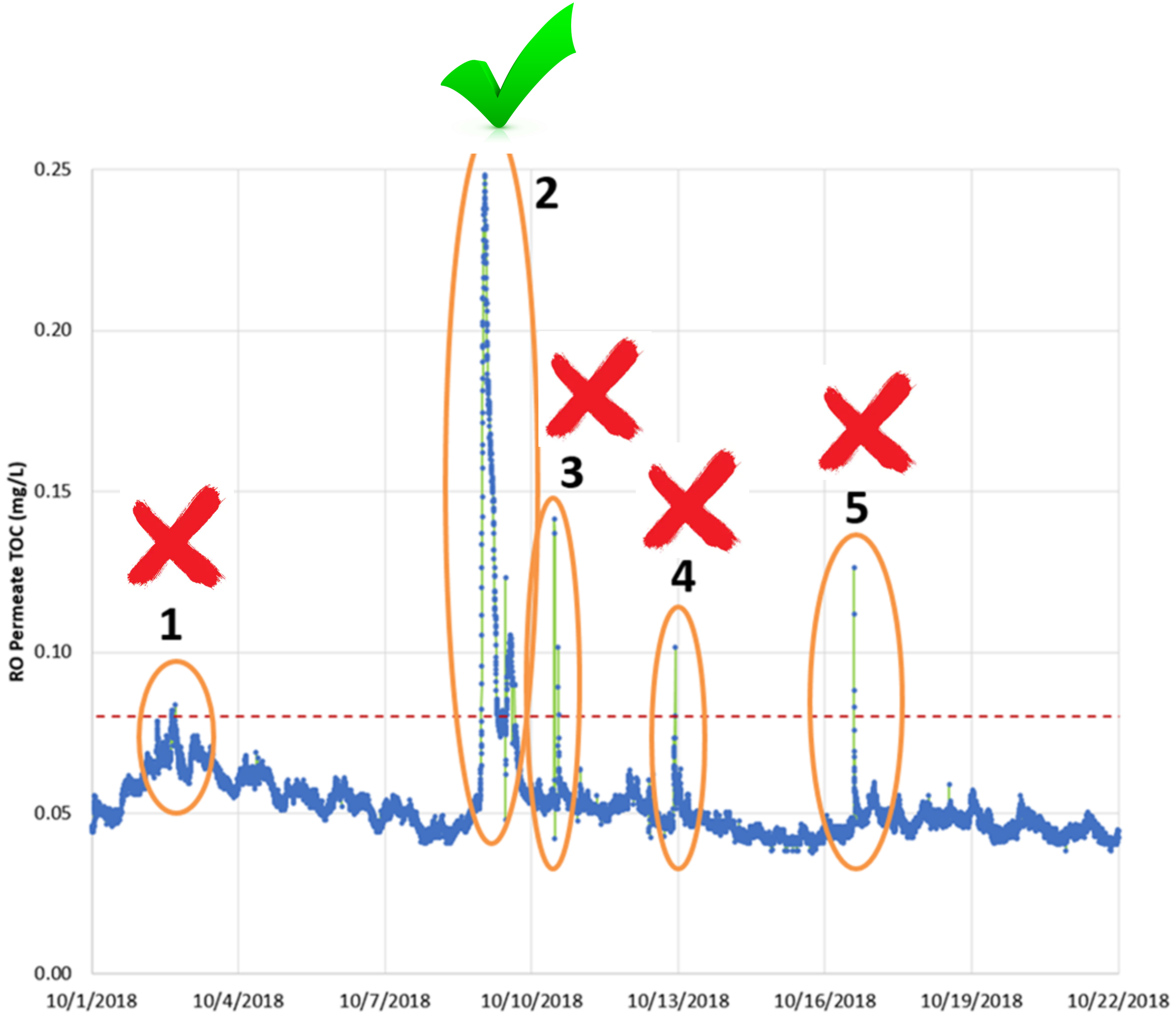
- Peak height – must exceed baseline threshold
  - Due to outliers, non-normal distribution
  - All data used
  - Baseline Threshold = Q3 + 1.5 * IQR, where IQR = Q3- Q1
- Peak width – Due to non-plug flow processes and recycle flows in WWTP, an instantaneous illicit discharge results in a peak width of hours to days
  - On-line data every 15 minutes



CALIFORNIA Water Boards

NWRI
NATIONAL WATER RESEARCH INSTITUTE

Example excursions from baseline



What chemicals can pass through FAT?

Summary of RO rejection of organic compounds and chemical families

Chemical Family	Sub-group	Good (>90%)	Intermediate (50-90%)	Poor (<50%)
VOCs	Solvents and Industrial Compounds	Ethers	Halobenzenes; 1,1,2-TCE	Nitriles; Haloalkenes
	Haloalkanes	CCl_4; Ethanes with 3-4 Cl atoms; Most C_{4+} haloalkanes	Some C_1-C_3 haloalkanes	C_1-C_2 haloalkanes with 1-2 halogen atoms
	Alkylbenzenes	C_{10+}	C_6-C_9	
	Pesticides/ Herbicides	1,2,3-TCP		MITC
LMW Oxygenated Compounds	Alcohols	Branched C_{4+} alcohols	Isopropyl alcohol; Most unbranched alcohols	Methanol; Ethanol;
	Aldehydes, Ketones	Methyl isobutyl ketone (MIBK)	Acetone; Most Ketones	Formaldehyde; Most Aldehydes
PPCPs	Flame Retardants	Chlorophosphates; PFAS		
	Pharmaceuticals	Steroids; β-blockers; NSAIDs; X-ray Contrast Media		
DBPs	Nitrosamines	C_{4+} nitrosamines; NMOR	NDMA; NDEA	
	Halogenated DBPs	HAAs	HANs	THMs

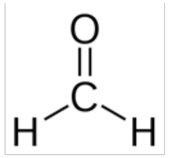
References: Howe 2019, Zeng 2016, Rodriguez 2011, Snyder 2007, Kiso 2011, Tackaert 2019, Fujioka 2012; Doederer 2014

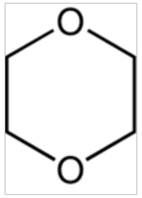
Predicted removal of organic compounds via AOP

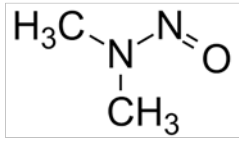
Family	Greater than 1,4-dioxane	Less than 1,4-dioxane
VOCs	Haloalkenes Halobenzenes Alkylbenzenes C_4+ Alcohols C_4+ Aldehydes C_6+ Ketones Acrylonitrile	C_1-C_3 Haloalkanes C_1-C_3 Alcohols C_1-C_3 Aldehydes C_3-C_5 Ketones Acetonitrile MITC
PPCPs	Most pharmaceuticals	Flame Retardants
DBPs	Nitrosamines[1]	THMs

Notes: 1. High removal in UV/AOP systems

References: Drewes 2008, Howe 2019, Ahmed 2017, Drewes 2006, Buxton 1988, Swancutt 2010

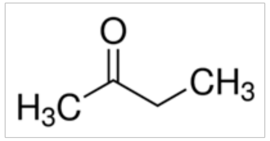


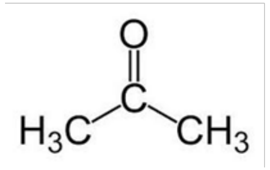




Organic compounds poorly removed by FAT

Family	Compounds poorly removed by FAT
VOCs	LMW haloalkanes LMW alcohols, aldehydes, ketones Acetonitrile MITC
DBPs	THMs



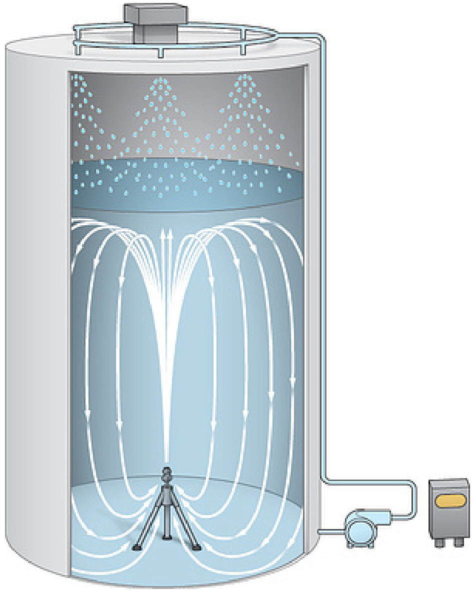


Potential Treatment/Blending Technologies

Ozone/BAC Pre-treatment

Blending

Air Stripping



Additional RO/AOP Treatment

Activated Carbon

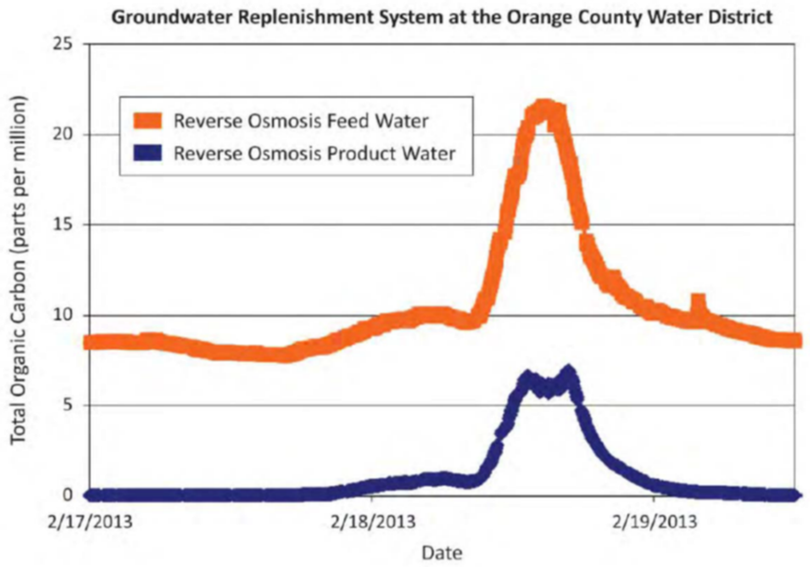
CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

Case Studies

- Compare elements of source control measures, experiences, monitoring and detection of chemical peaks
  - Orange County Water District Ground Water Replenishment System
  - Singapore Public Utilities Board
  - City of San Diego North City Pure Water Demonstration Facility
- Compare strategies for averaging Chemical Peaks

TOC and Acetone grab sample results during 2013 GWRS Acetone event



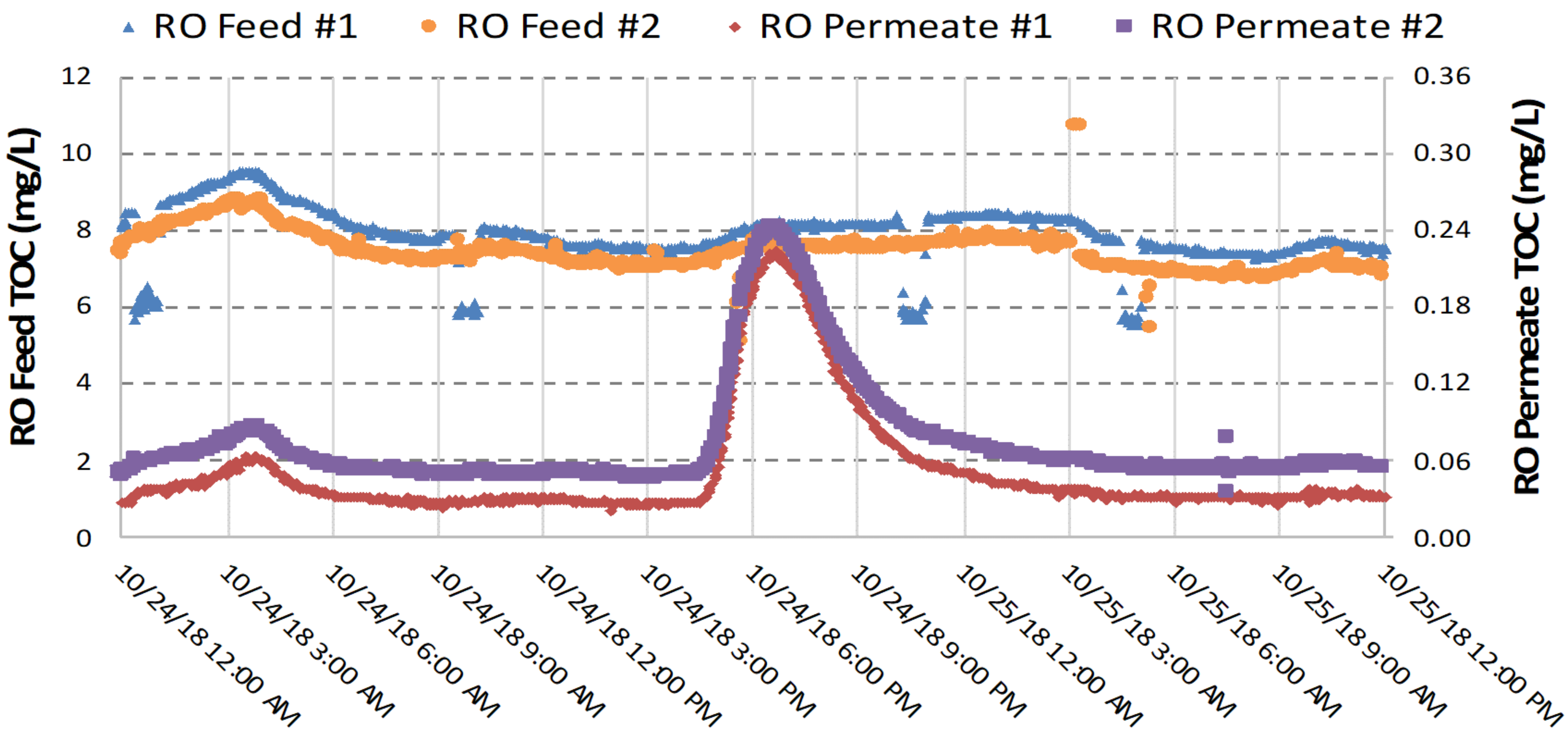
Sample Date	Sample Location	EPA 524.2 Acetone	Theoretical TOC from Acetone[1]	EPA 415.3 TOC	Baseline TOC[2]	Acetone Contribution to Elevated TOC[3]
2/18/2013 6:00AM	RO Feed	1,940 µg/L	1.2 mg/L	9.39 mg/L	~ 8.0 mg/L	~ 86%
	RO Permeate	1,410 µg/L	0.9 mg/L	1.18 mg/L	~ 0.025 mg/L	~ 78%

1 – acetone carbon contribution is approximately 62%
2 – from online TOC data preceding the acetone event
3 – Baseline TOC subtracted from EPA 415.3 TOC used to calculate % acetone that contributed to elevated TOC (e.g., for RO feed → 1.2 mg/L / (9.39 mg/L – 8.0 mg/L) = 86%

CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

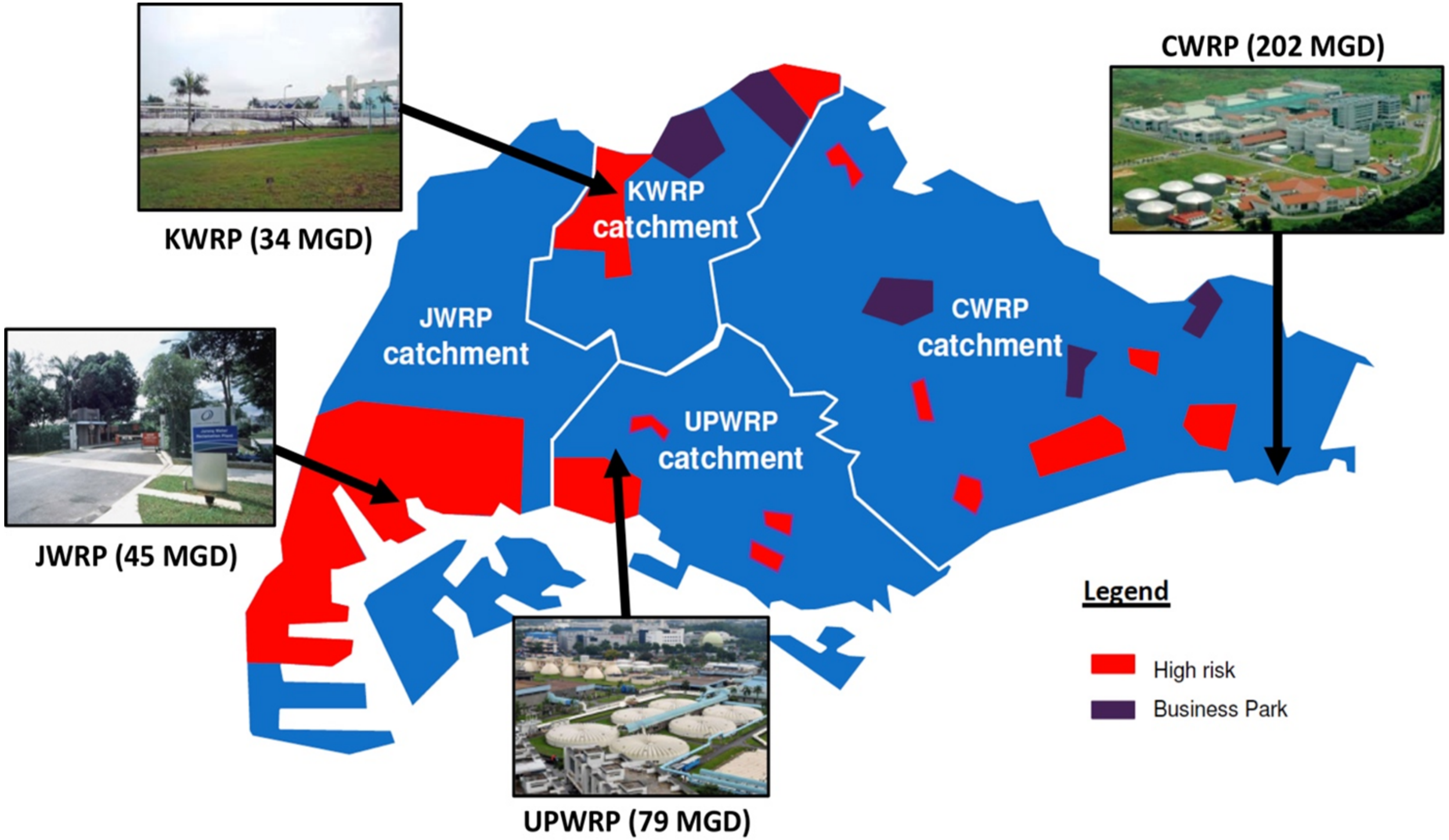
OCWD TOC monitoring October 24, 2018 acetone event



CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

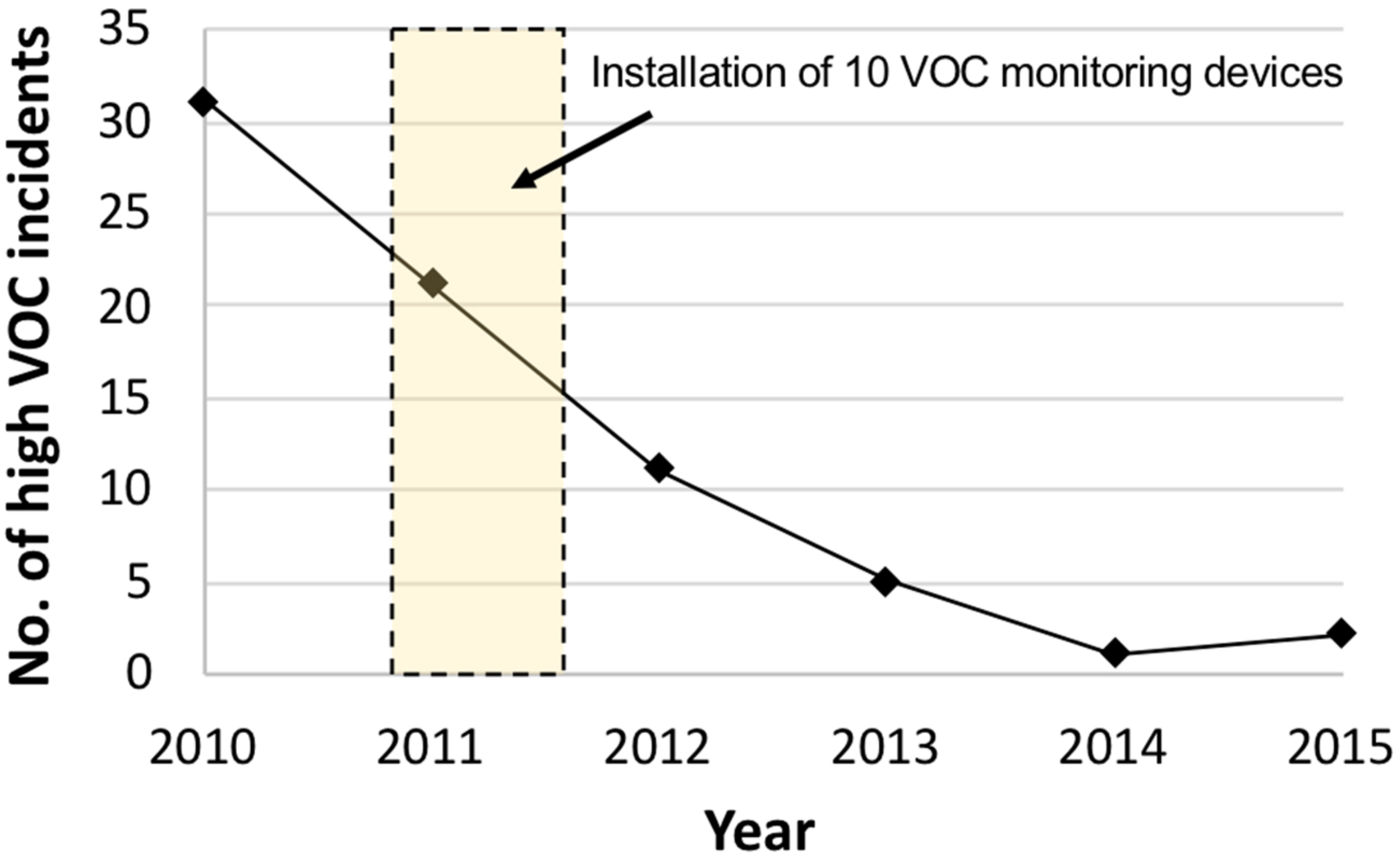
Singapore PUB



Singapore PUB

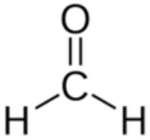
List of Prohibited Organic Compounds (PUB)		
1,2,4-Trimethylbenzene	Furan	Octane
1,1,1-Trichloroethane	Heptane	Polybrominated diphenyl ether
1,1,2-Trichloroethane	Hexane	Styrene
Benzene	Isobutanol	Tetra-chloromethane
Decane	Isopropyl ether	Tetra-chloroethylene
Diethyl ether	Methyl ethyl ketone	THF (Tetrahydrofuran)
Dimethyl sulphide	Methyl isobutyl ketone	Toluene
Dimethyl sulphoxide	Methyl tert-butyl-ether	Trichloroethylene
DMF (N,N-Dimethylformamide)	Methylene chloride	Turpentine
Ethylbenzene	Nonane	Xylene (o,m,p)

Singapore PUB VOC Monitoring in the Sewershed

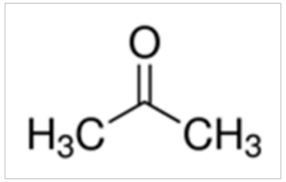


San Diego Pure Water Demonstration Facility Chemical Challenge Testing

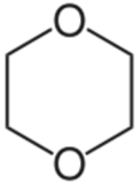
- Spike of Acetone, NDMA, Formaldehyde, and 1,4-dioxane into Feed Water
- Evaluate O_3 & BAC as additional barrier
- Test removal of O_3-BAC-MF-RO-UV/AOP vs. MF-RO-UV/AOP



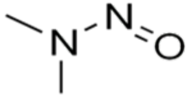
Formaldehyde
~300 µg/L



Acetone
~2,600 µg/L



1,4-dioxane
~900 µg/L

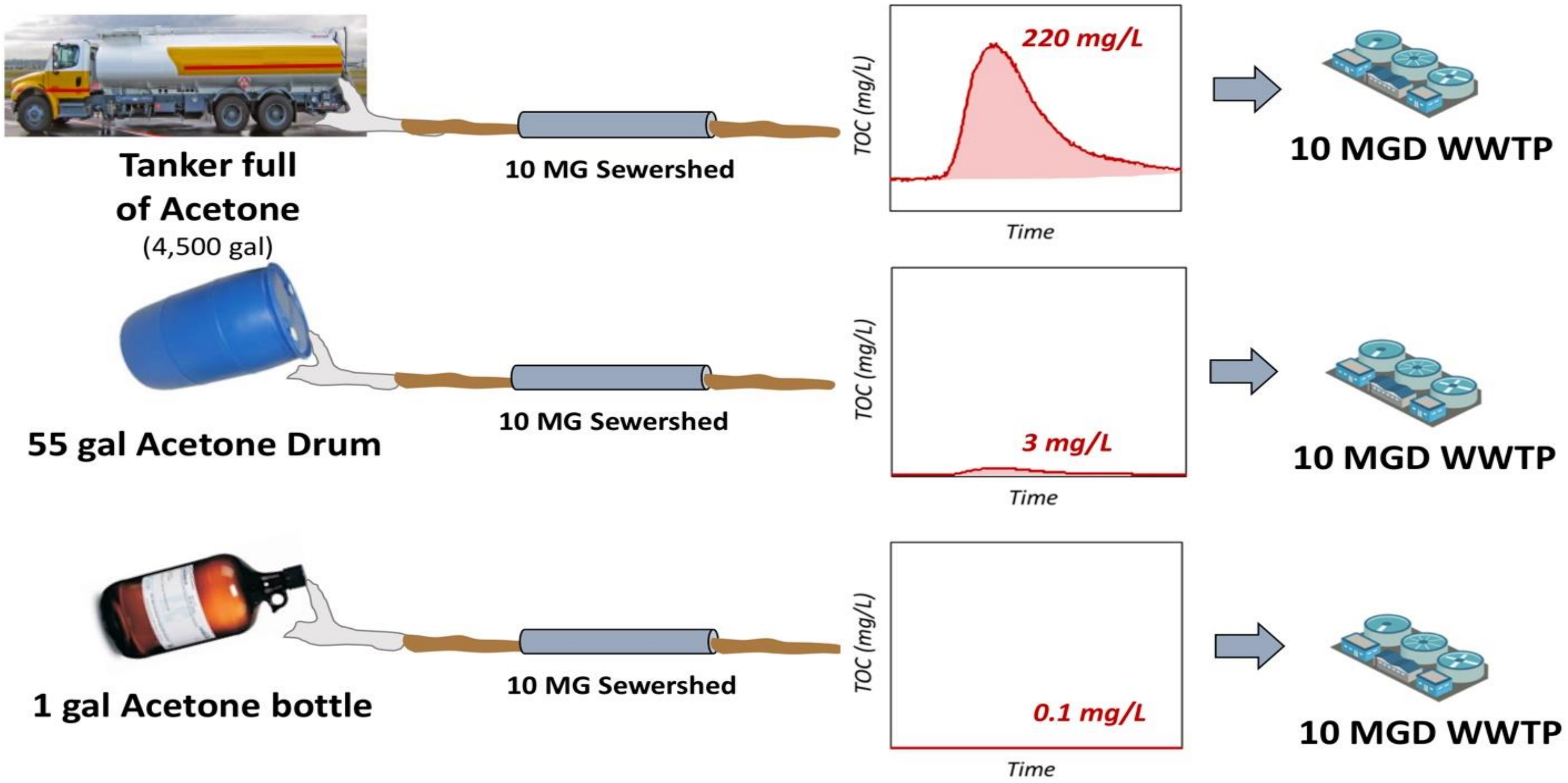


NDMA
~500 ng/L

CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

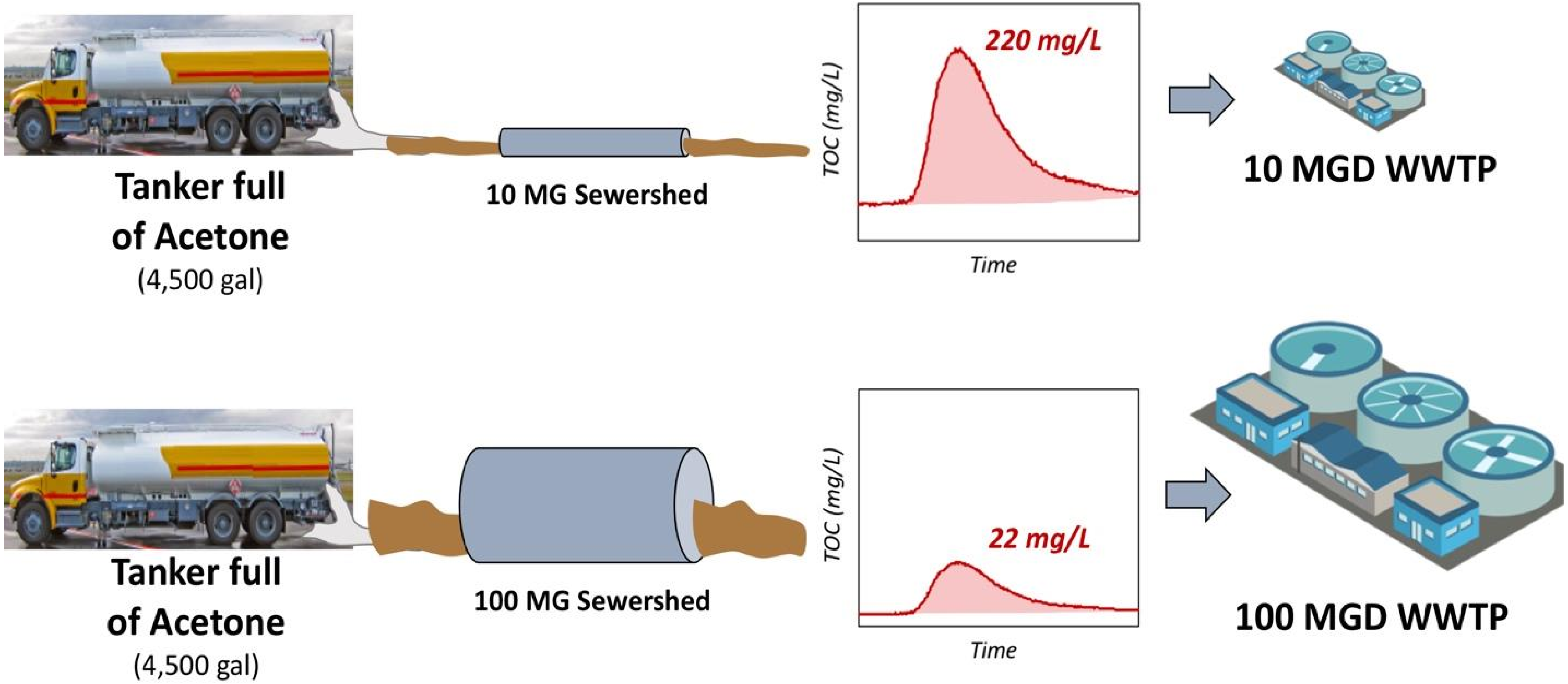
Discharge Volume



California Water Boards

NWRI National Water Research Institute

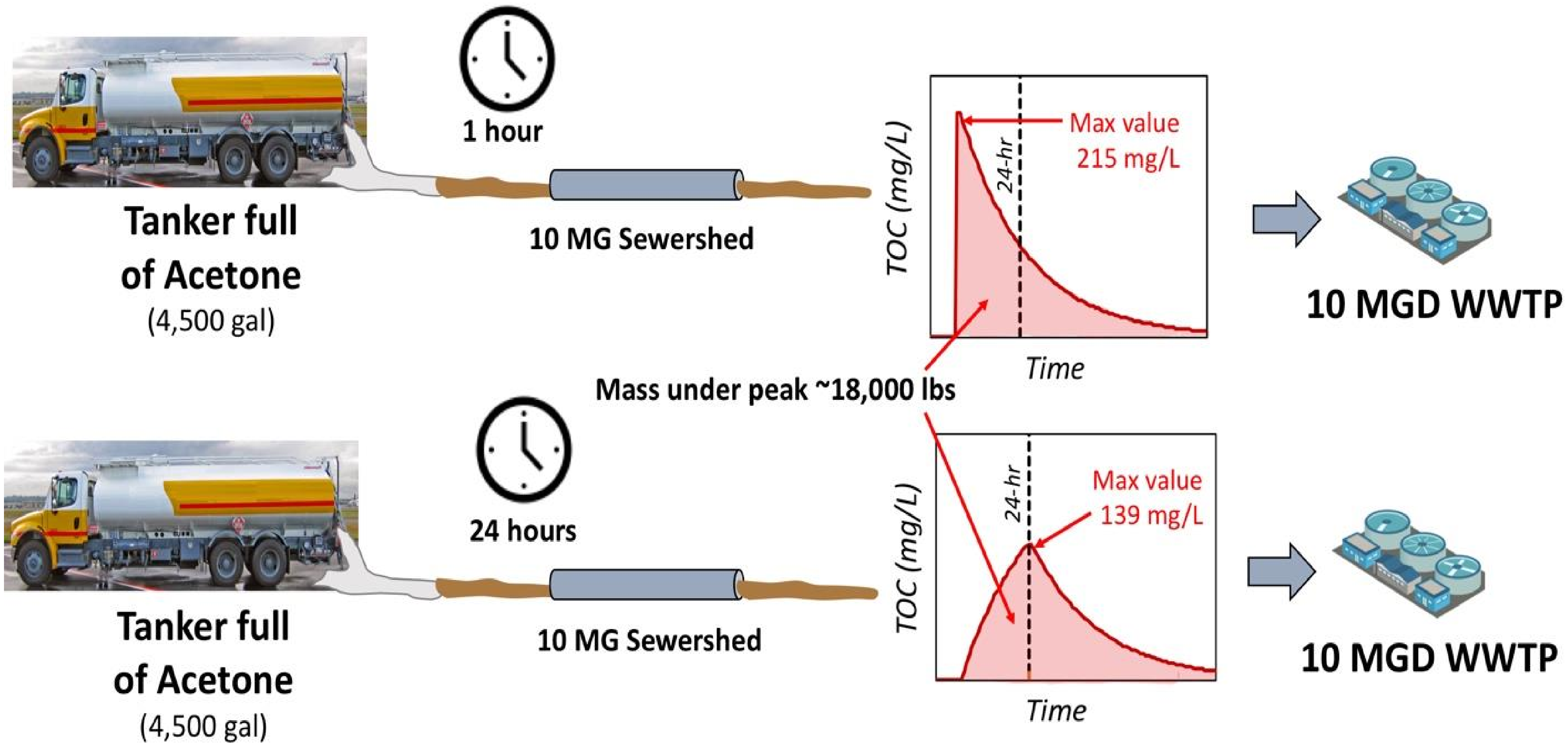
Impact of Sewershed Size



CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

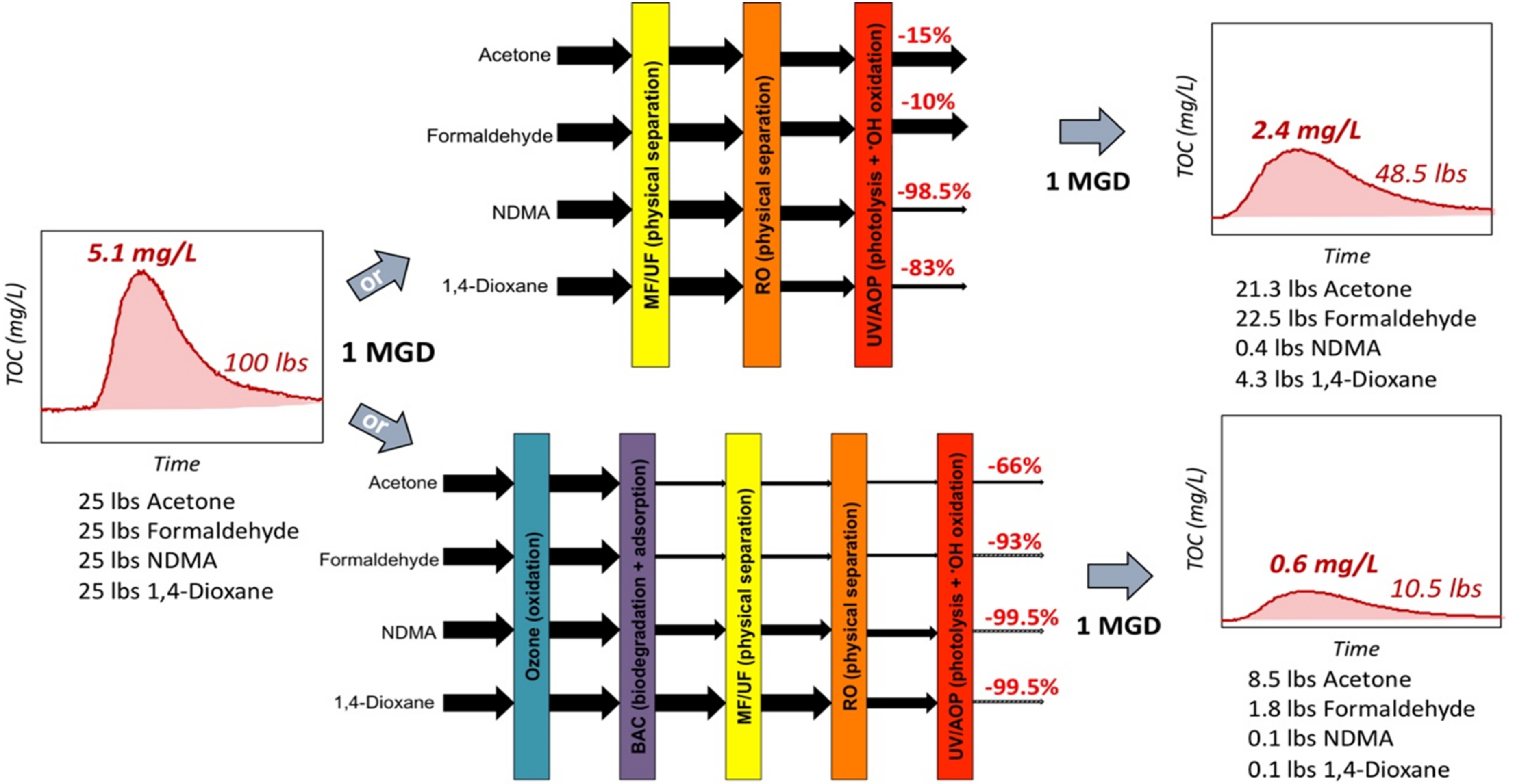
Chemical Discharge Duration



CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

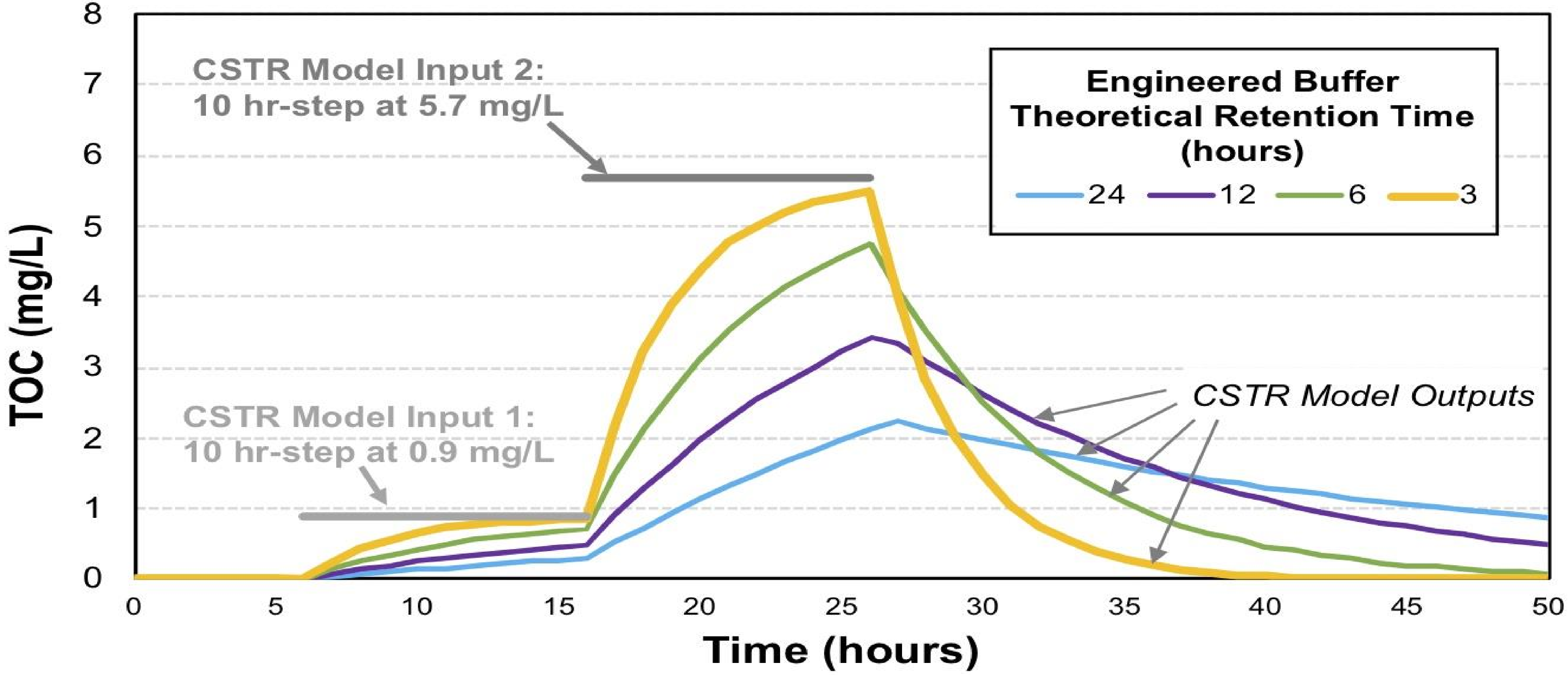
Treatment Robustness for Averaging Chemical Peaks



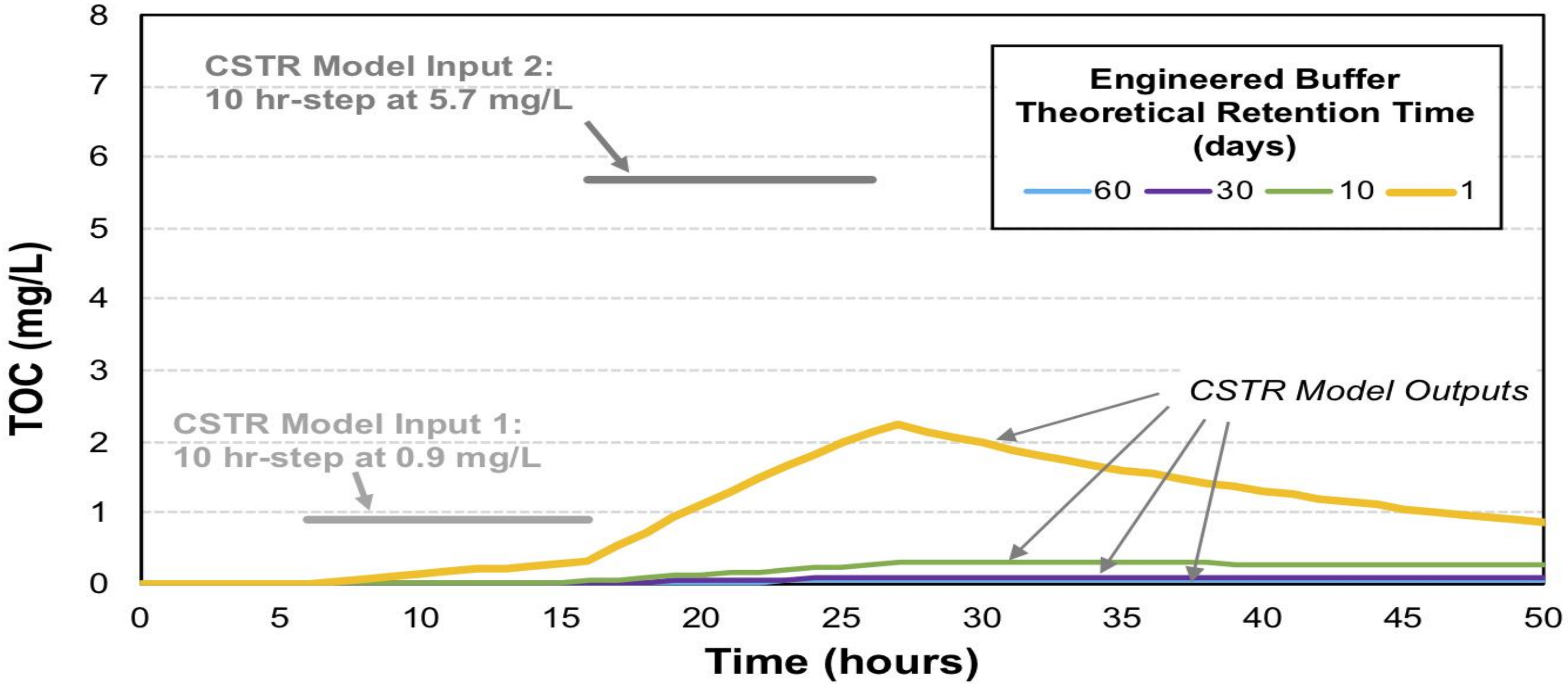
CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

Engineered Buffer with Residence up to 24 Hours



Engineered Buffer with Residence up to 60 Days



How will online TOC analyzers be used?

- Advanced oxidation reactions to mineralize organic carbon in sample (UV/persulfate and O_3/hydroxide)
- Expert panel expressed concern that highly volatile organics might not be captured with online TOC

Experimentation to Evaluate TOC Analyzers

Southern Nevada
Water Authority

Principal Investigator:
Eric Dickenson, PhD, PE

Compounds Considered and Tested:

- Carbon tetrachloride
- Vinyl Chloride
- Toluene
- Carbon Disulfide
- 1,2-dichloropropane
- Methylene Chloride (Dichloromethane)
- Acetone
- Methyl isobutyl ketone

CALIFORNIA
Water Boards

NWRI
NATIONAL WATER RESEARCH INSTITUTE

Compounds tested

*OH rate constant (k_{*OH}, L/Mol*s)	Henry's Law Constant (Hyc)		
	HYC > 1.0	0.1 < HYC < 1.0	0.01 < HYC < 0.1
$k_{*OH} > 1 \times 10^9$	Vinyl chloride	Toluene	MIBK
$1 \times 10^8 < k_{*OH} < 1 \times 10^9$			Acetone
$1 \times 10^7 < k_{*OH} < 1 \times 10^8$		Methylene chloride	

CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

Experimentation to Evaluate TOC Analyzers

Round 1 Participants	Model	Instrument Type		Measured Parameters
		Bench Top	Online	
OCWD	M9 portable		√	TOC/TC/TIC
City of San Diego	M5310C		√	TOC/TC/TIC (w/ and w/o ICR)
	Shimadzu TOC-L (Low Level)	√		TOC (w/ ICR)
Suez	M9 portable		√	TOC (w/ ICR)
	M5310C	√		TOC/TC/TIC (w/ and w/o ICR)
Shimadzu	Shimadzu TOC-L	√		TOC/TC/TIC (w/ and w/o ICR)
Valley Water	M5310C		√	TOC/TC/TIC
Hach	Biotector 3500		√	TOC/TC/TIC
SNWA	Shimadzu TOC-L	√		TOC (w/ and w/o ICR)

TOC analyzers demonstrated acceptable performance of measurement of volatile organic compounds (Hyc ≤ 0.133) with at least 50% recovery

CALIFORNIA Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

Chemical Control Strategies

Enhanced Source Control	Sewershed Monitoring	NDN + Filters	O_3/BAC	Response Time	Diversions	Blending	Dilution

California Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

Chemical Control – Public Health Protection

Enhanced Source Control	Sewershed Monitoring	NDN + Filters	O_3/BAC	Response Time	Diversions	Blending	Dilution

This box represents what is required for public health protection…

California Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

Chemical Control – Public Health Protection

Enhanced Source Control	Sewershed Monitoring	NDN + Filters	O_3/BAC	Response Time	Diversions	Blending	Dilution

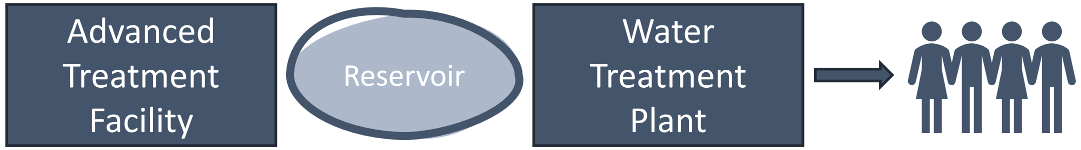
This box represents what is required for public health protection…

…and there may be many ways to fill this box.

Chemical Control – Balance is Key

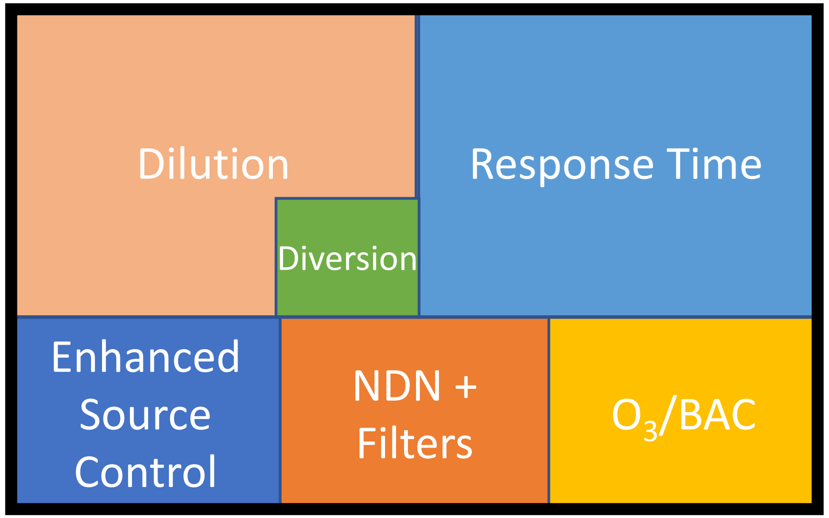
Enhanced Source Control | Sewershed Monitoring | NDN + Filters | O_3/BAC | Response Time | Diversions | Blending | Dilution

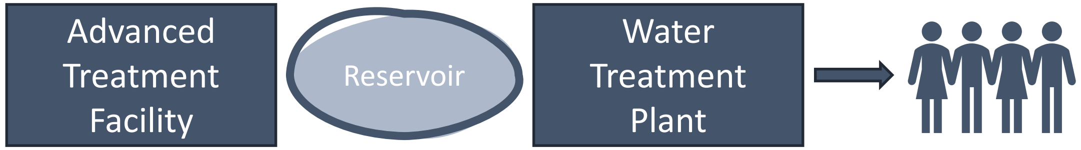
Dilution



Chemical Control – Balance is Key

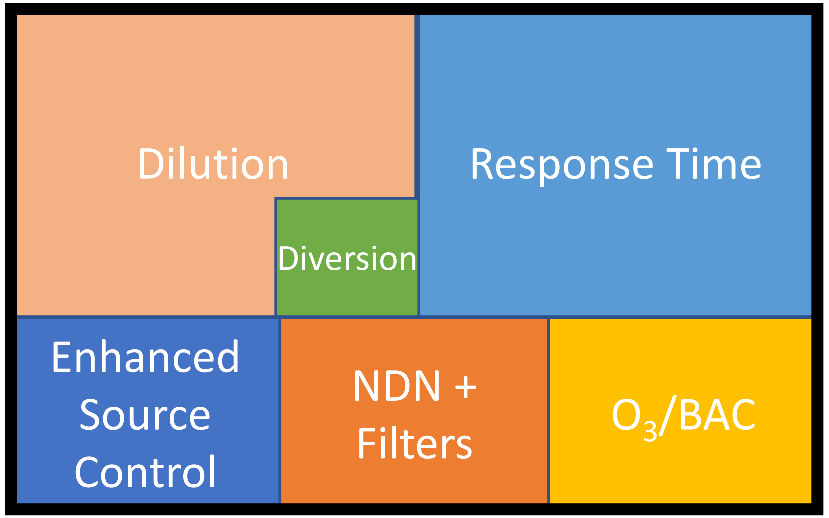
	Sewershed Monitoring	NDN + Filters	O_3/BAC	Response Time	Diversions	Blending	Dilution

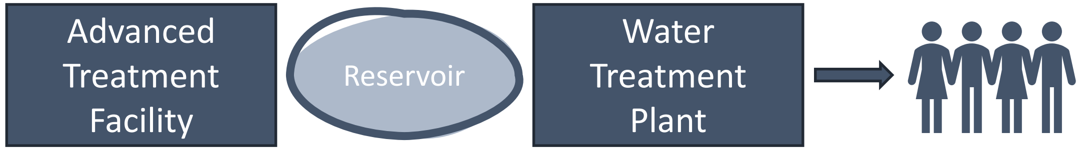


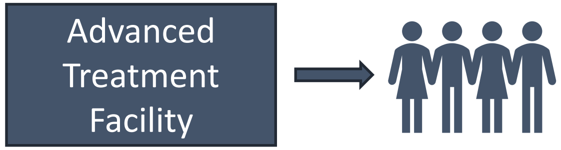


Chemical Control – Balance is Key

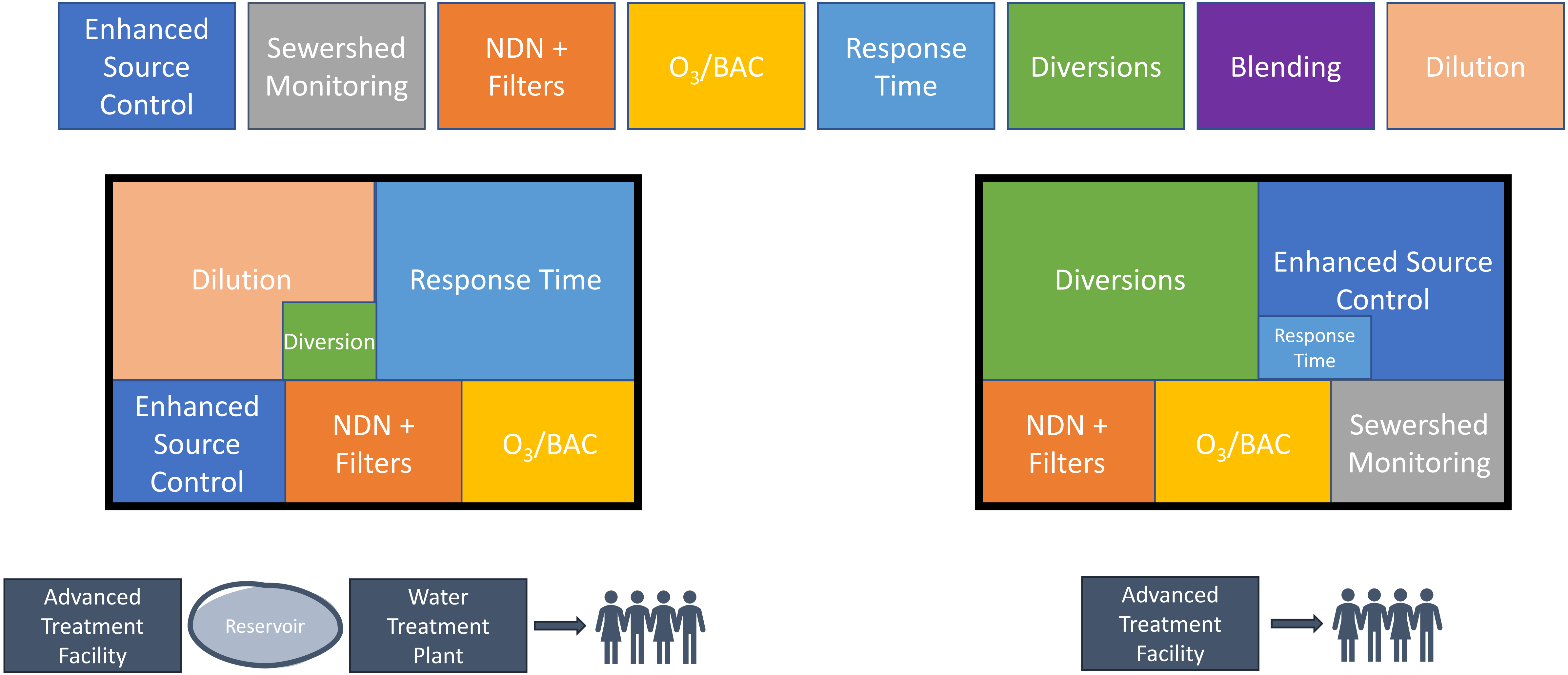
Enhanced Source Control | Sewershed Monitoring | NDN + Filters | O_3/BAC | Response Time | Diversions | Blending | Dilution



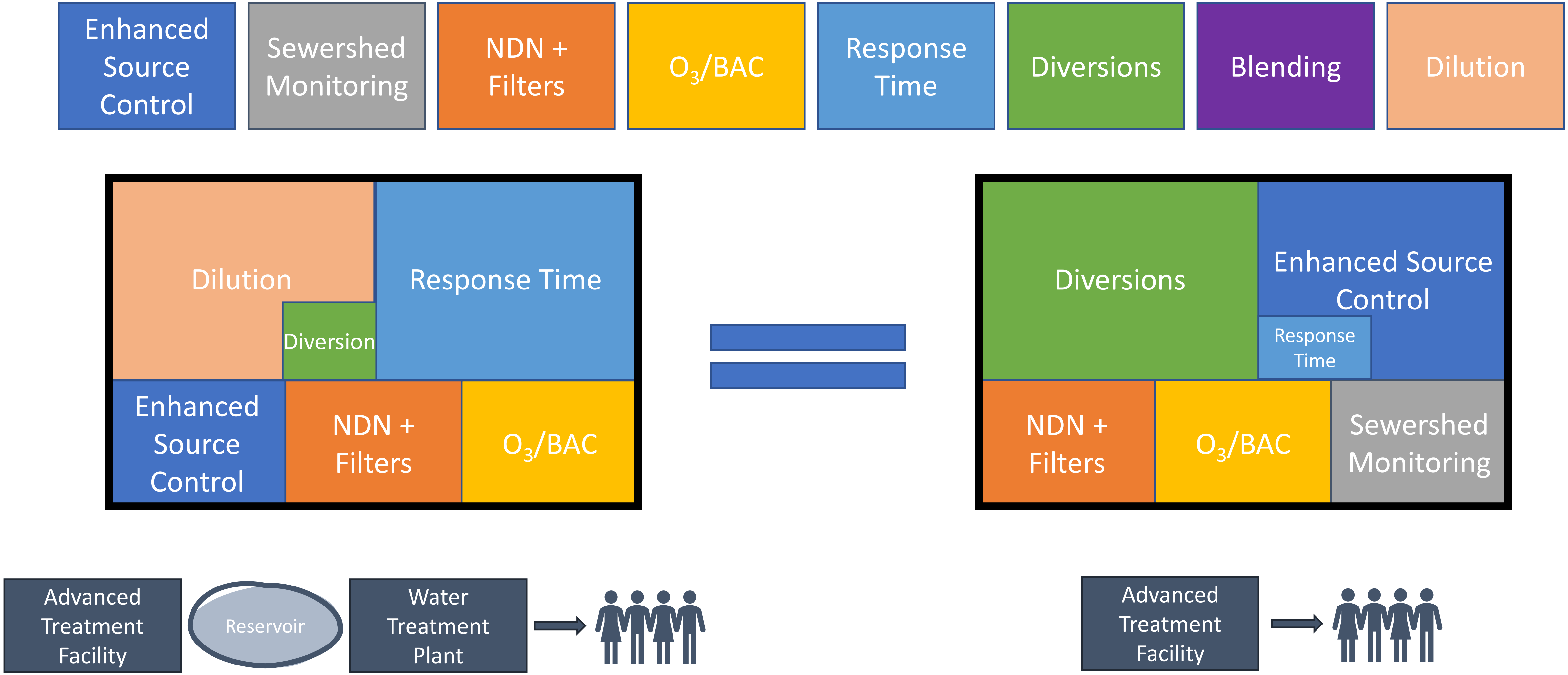




Chemical Control – Balance is Key



Chemical Control – Equivalence



DPR-4 Recommendations

1. A definition of a chemical peak (Chapter 3) is recommended to differentiate normal facility variation in water quality from true chemical peaks. In this study, chemical peaks are defined as resulting from intentional or unintentional illicit discharges of chemicals to the sewershed.
2. Online monitoring of TOC (Chapters 4 and 6) is recommended as a feasible option for capturing chemical peaks. TOC is already used as a critical control point (CCP) monitoring device for RO systems related to compliance.
3. Experimental results suggest that commercially available TOC analyzers have the ability to detect chemical peaks originating from volatile organic compounds (Chapter 6 and Appendix). Amongst the TOC meters that were tested, at least two models demonstrated acceptable performance and are recommended for DPR projects.
4. Given that chemical peaks are expected to last on the order of hours to days, no more frequent than a fifteen minute minimum sampling interval is recommended for the online TOC analyzers (Chapter 3).

California Water Boards

NWRI NATIONAL WATER RESEARCH INSTITUTE

DPR-4 Recommendations

5. Due to the very limited expected frequency of chemical peaks (< 0.5% of case study data evaluated), periodic grab sampling (e.g. weekly, monthly, quarterly) for compounds known to potentially escape FAT is not recommended for DPR for the explicit purpose of discovering an illicit discharge (Chapters 3 and 4).
6. Utilities should prepare a formal TOC response protocol in the event of a TOC peak (Chapter 4)… As part of a response protocol, grab sampling is recommended when a peak has been observed and confirmed by the TOC analyzers in an effort to identify the responsible chemical(s) and inform the source control program.
7. An enhanced source control program is recommended for DPR that proactively deters and diminishes the occurrence of chemical discharges (Chapter 4). A tailored source control monitoring program… can help identify the source of an illicit discharge.
8. Additional treatment barriers in conjunction with FAT should be considered to increase robustness and further reduce the concentration of chemical constituents (Chapter 3). Examples of such barriers include ozone/BAC, air stripping, activated carbon, and additional RO and/or AOP.

CALIFORNIA Water Boards

NATIONAL WATER RESEARCH INSTITUTE

DPR-4 Recommendations

9. DPR applications that have the option to use “small reservoirs” should consider doing so given the benefits of small reservoirs for chemical peak “averaging” (Chapter 5) due to blending.
10. Utilities considering DPR should pursue a balanced approach to control chemical peaks that includes an appropriate combination of two or more of the following: source control, enhanced monitoring, additional treatment barriers, and/or blending (Chapter 5).

DPR-4:Treatment for Averaging Potential Chemical Peaks

Thank you to:

Research Team: Stephen Timko, PhD, Rodrigo Tackaert, PhD, Aleks Pisarenko, PhD

TWG: Jim Crook, PhD and Adam Olivieri, Dr. PH

PAC: Mehul Patel, PE

Guidance: SWRCB, Water Research Foundation, California DDW