Hormones, Pharmaceuticals, Personal Care Products (CECs) in **Potable Water Reuse Applications**

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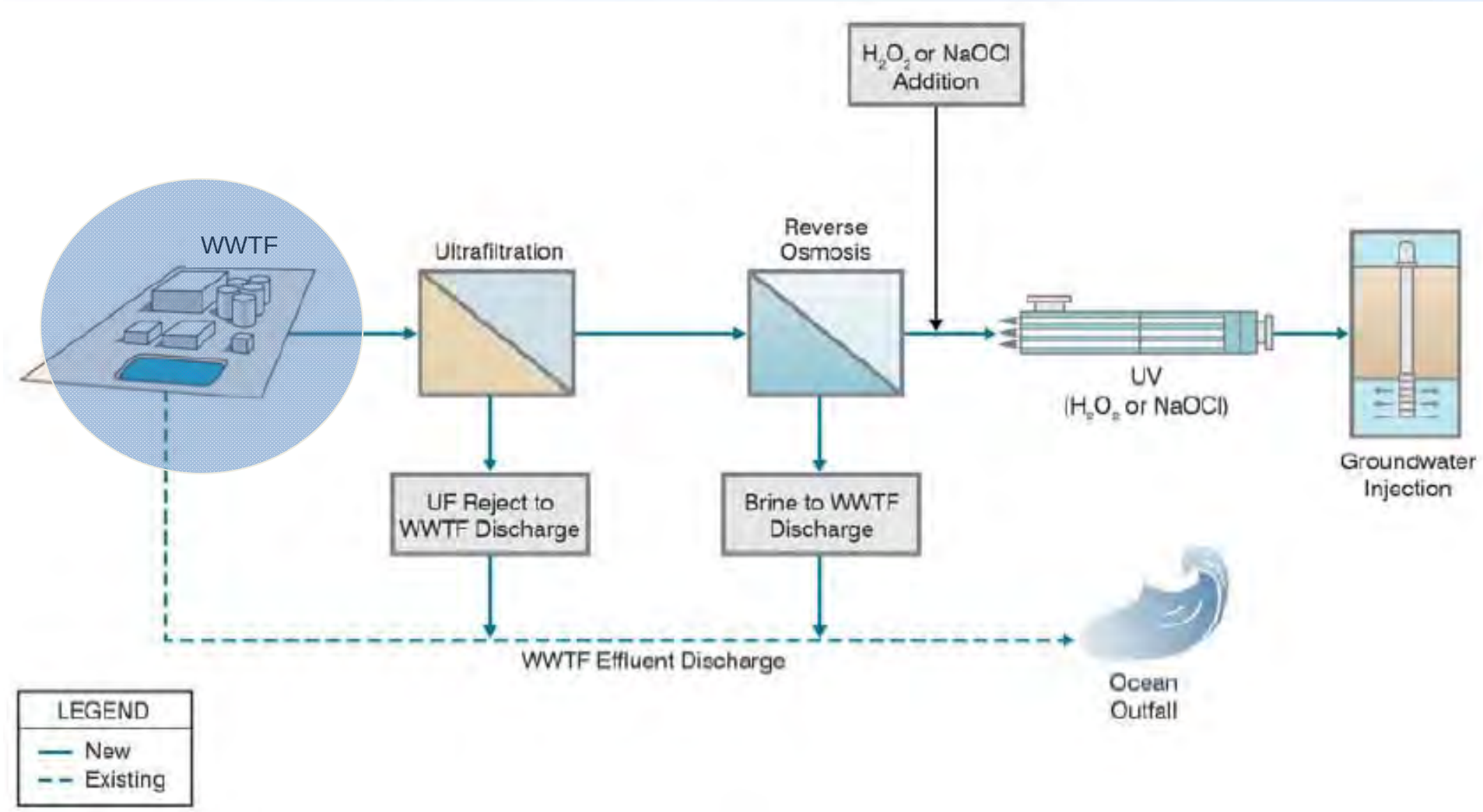
Engineers...Working Wonders With Water®

Acknowledgements

1. **Primary Funding Partners:** Texas Water Development Board, Santa Clara Valley Water District, WateReuse Research Foundation, Water Research Foundation, Water Environment Research Foundation, Ventura Water, Los Angeles (LABOS, LADWP)
2. **Primary Research Partners:** National Water Research Institute, Southern Nevada Water Authority, Trussell Technologies

Presentation Goals

1. **Review several mechanisms for CEC removal by water purification systems**
   a) **Topics considered today: Biological treatment, RO, UV AOP**
   b) **Other technologies: ozone, ballasted flocculation/PAC, UF with chemical addition, GAC…**
2. **Document successful CCP approaches for CEC reduction**
3. **Demonstrate knowledge gaps for CCP control for CECs**


H_2O_2 or NaOCl Addition
WWTF
Ultrafiltration
Reverse Osmosis
UV (H_2O_2 or NaOCl)
Groundwater Injection
UF Reject to WWTF Discharge
Brine to WWTF Discharge
WWTF Effluent Discharge
Ocean Outfall
LEGEND
New
Existing

CEC Removal Begins in the Wastewater Treatment Process (WERF CEC4R08)

Sampling Event	Date of Sampling	Sec. Inf. Flow, mgd	Total / Aerobic) SRT, days[1)]	MLSS, mg/L	HRTin ABs, hrs.[2)]	Redox Condition in ABs	WW Temp., °C
A (winter)	3/28-31/2011	14.9	10/8.2	1,590	11/3.7	Anx./Aer.	13.8
A (summer)	7/11-14/2011	19.9	12.5/8.7	1,740	6.7/2.1	Anx./Aer.	20
B (winter)	2/7-10/2011	39.8	16-20/11-14	4,480	8.8/5.5	Anx./Aer.	14
B (summer)	8/16-19/2010	36.4	18.2/18.2	3,620	9.6/5.7	Aer.	25.8
C (winter)	3/15-18/2010	66.9	2/2	2,560	2.4/0.9	Aer.	15
C (Summer)	9/20-23/2010	54.7	1.4/1.4	2,230	2.3/1.0	Aer.	22
D (summer)	9/20-23/2010	83.2	6.7/4.6	2,590	5.3/1.6	Anx./Aer.	22
E (winter)	4/12-15/2010	0.11	>50	7,860	4.1/0.5	Anx./Aer.	17
E (summer)	8/23-26/2010	0.1	40-80	8,050	4.2/0.3	Anx./Aer.	24
F (summer)	4/26-29/2010	91	6.5/4.9	3,700	3.7/2.6	Anx./Aer.	25
G (high SRT)	1/14-17/2011	5	42/34	5,070	11.1/6	An./Anx./Aer.	22.6
G (medium SRT)	1/14-17/2011	6.5	20/16	5,650	8.5/5.7	An./Anx./Aer.	22.6
G (low SRT)	1/14-17/2011	9.7	6/4.8	2,260	5.8/4	An./Anx./Aer.	22.6

Overall TOrC Removal During Secondary Treatment

	A - Winter	A - Summer	B - Winter	B - Summer	C - Winter	C - Summer	D - Summer	E - Summer	E - Winter	F – Winter	G -High SRT	G - Medium SRT	G - Low SRT	Average	Minimum	Maximum
Rapid Removal																
Caffeine	n.q	100%	100%	100%	100%	n.q.	100%	100.0%	n.q.	99.9%	100.0%	100.0%	100.0%	100%	100%	100%
Acetaminophen	100%	99%	100%	99%	99%	100%	n.q.	100.0%	n.q.	n.q.	n.q.	100.0%	100.0%	100%	99%	100%
Ibuprofen	100%	100%	100%	100%	88%	94%	99%	99.9%	100.0%	100.0%	99.9%	100.0%	99.8%	98%	88%	100%
Naproxen	95%	99%	100%	100%	71%	89%	88%	99.8%	100.0%	98.8%	100.0%	100.0%	98.4%	95%	71%	100%
Iopromide	n.q	n.q	99%	99%	n.q.	n.q.	n.q.	91.1%	79.8%	64.2%	n.q.	99.6%	98.5%	90%	64%	100%
Bisphenol A	n.q	n.q	99%	98%	n.q.	n.q.	n.q.	99.0%	n.q.	n.q.	n.q.	n.q.	n.q.	99%	98%	99%
Moderate / Site Specific Removal																
Triclosan	94%	96%	99%	99%	56%	83%	93%	98.8%	99.2%	86.5%	97.2%	92.3%	85.7%	91%	56%	99%
Gemfibrozil	75%	89%	94%	100%	-1%	6%	49%	99.8%	99.1%	82.8%	99.5%	98.1%	83.5%	75%	-1%	100%
DEET	61%	96%	81%	100%	2%	66%	91%	99.9%	97.3%	30.3%	78.9%	62.6%	5.3%	67%	2%	100%
BHA	26%	73%	95%	100%	18%	46%	1%	90.2%	95.0%	-	99.6%	99.3%	50.0%	66%	1%	100%
Diphenhydramine	61%	70%	82%	90%	-5%	18%	62%	n.q.	96.1%	39.5%	96.3%	96.5%	41.1%	62%	-5%	96%
Atenolol	34%	42%	82%	84%	-10%	24%	31%	94.0%	93.2%	34.8%	n.q.	100.0%	52.0%	55%	-10%	100%
Trimethoprim	15%	n.q	29%	98%	9%	n.q.	5%	94.2%	95.6%	10.8%	98.2%	97.0%	22.5%	52%	5%	98%
Benzophenone	n.q	n.q	22%	57%	85%	n.q.	n.q.	99.5%	91.2%	n.q.	n.q.	99.3%	n.q.	76%	22%	100%
TCPP	n.q	n.q	-10%	-19%	n.q.	n.q.	n.q.	48.7%	63.1%	n.q.	n.q.	n.q.	n.q.	21%	-19%	63%
Mass Balance Inconsistencies																
Sulfamethoxazole	-4%	12%	25%	45%	23%	36%	21%	61.2%	42.9%	-85.9%	-41.7%	-91.7%	-108.4%	-5%	-108%	61%
Fluoxetine	15%	33%	10%	-22%	55%	n.q.	2%	42.7%	6.5%	-117.8%	38.1%	32.9%	29.0%	10%	-118%	55%
Meprobamate	-8%	2%	-17%	-36%	2%	3%	-3%	61.2%	83.6%	-26.7%	90.4%	89.6%	11.1%	19%	-36%	90%
Cimetidine	31%	99%	57%	99%	-34%	-12%	-2%	61.8%	74.6%	38.3%	12.8%	25.5%	-16.5%	34%	-34%	99%
Triclocarban	45%	63%	96%	91%	-31%	87%	82%	79.4%	63.0%	-81.6%	74.6%	68.0%	50.5%	53%	-82%	96%
Slow / Refractory																
TCEP	n.q	n.q	4%	-15%	-1%	n.q.	n.q.	-3.0%	6.4%	0.4%	15.1%	12.1%	12.0%	3%	-15%	15%
Sucralose	n.q	n.q	21%	-12%	n.q.	n.q.	n.q.	28.7%	n.q.	n.q.	1.7%	n.q.	-22.0%	4%	-22%	29%
Carbamazepine	13%	27%	-19%	2%	7%	-13%	3%	34.2%	-4.4%	-3.6%	-17.2%	-17.2%	-8.9%	0%	-19%	34%
Primidone	9%	23%	-12%	14%	14%	-6%	8%	n.q.	n.q.	8.1%	-4.0%	-4.0%	-4.0%	4%	-12%	23%

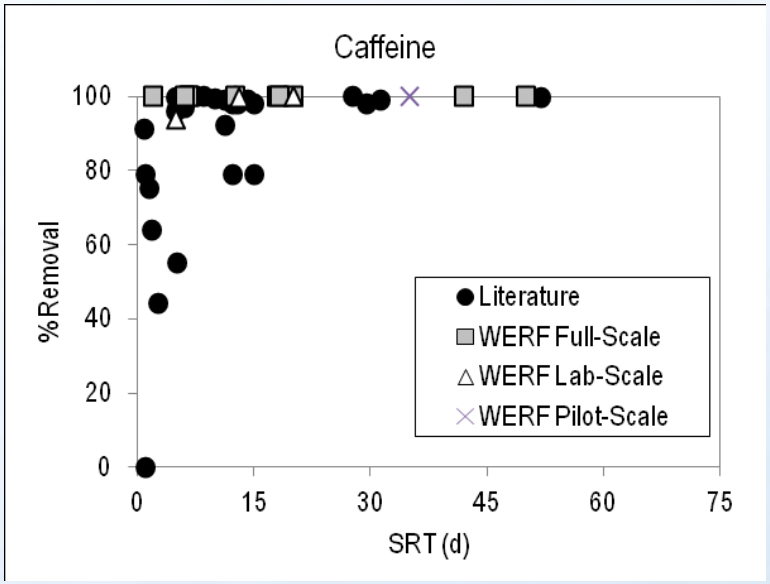
Removal by Sorption

		% TOrC Removal by Sorption		
Indicator	n	Average	Minimum	Maximum
High Sorption				
TCPP	3	17.4%	2%	46%
Triclocarban	3	72.7%	46%	88%
Triclosan	13	12.7%	2%	33%
Bisphenol A	2	18.9%	11%	27%
Fluoxetine	10	16.4%	0%	38%
Benzophenone	6	8.1%	2%	37%
Site-Specific Efficiency / Moderate Sorption				
TCEP	9	4.0%	0%	20%
Iopromide	7	8.3%	0%	16%
Sulfamethoxazole	13	2.8%	0%	15%
Cimetidine	12	4.3%	0%	14%
BHA	13	2.2%	0%	13%
Trimethoprim	11	2.2%	0%	10%
Carbamazepine	13	1.6%	0%	9%
No / Low Sorption				
Caffeine	12	0.1%	0%	0%
Primidone	13	0.3%	0%	1%
Sucralose	5	1.2%	0%	5%
Diphenhydramine	12	1.6%	0%	3%
Meprobamate	13	0.3%	0%	2%
Atenolol	13	0.1%	0%	0%
DEET	4	0.0%	0%	0%
Gemfibrozil	13	0.3%	0%	0%
Naproxen	13	0.0%	0%	0%
Ibuprofen	13	0.0%	0%	0%
Acetaminophen	12	0.0%	0%	0%

Removal by Biotransformation

	% TOrC Removal by Biotransformation			
Indicator	n	Average	Minimum	Maximum
Rapid Biotransformation				
Acetaminophen	7	100%	100%	100%
Caffeine	8	100%	100%	100%
Ibuprofen	13	98%	88%	100%
Moderate Biotransformation / Site specific Efficiency				
Naproxen	13	95%	71%	100%
DEET	9	80%	30%	100%
Triclosan	13	80%	25%	98%
Gemfibrozil	12	80%	2%	100%
Diphenhydramine	12	66%	13%	96%
Atenolol	10	57%	20%	100%
BHA	12	63%	0%	99%
Trimethoprim	11	49%	2%	98%
Meprobamate	6	55%	0%	90%
Cimetidine	7	55%	14%	98%
Fluoxetine	6	23%	0%	36%
Sulfamethoxazole	8	27%	9%	45%
Benzophenone	2	76%	63%	90%
Iopromide	3	69%	55%	88%
Recalcitrant / Slow Biotransformation				
Carbamazepine	6	10%	0%	24%
Sucralose	3	12%	1%	18%
Primidone	8	11%	5%	22%
Mass Balance Uncertainties / Limited Data				
TCPP	-	NA	NA	NA
Triclocarban	-	NA	NA	NA
Bisphenol A	1	89%	89%	89%
TCEP	2	10%	9%	13%

Removal Versus Solid Residence Time



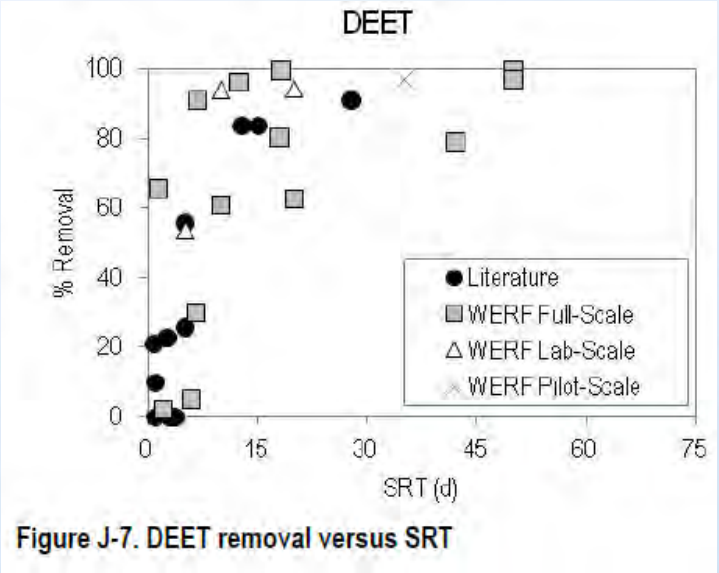


Figure J-7. DEET removal versus SRT

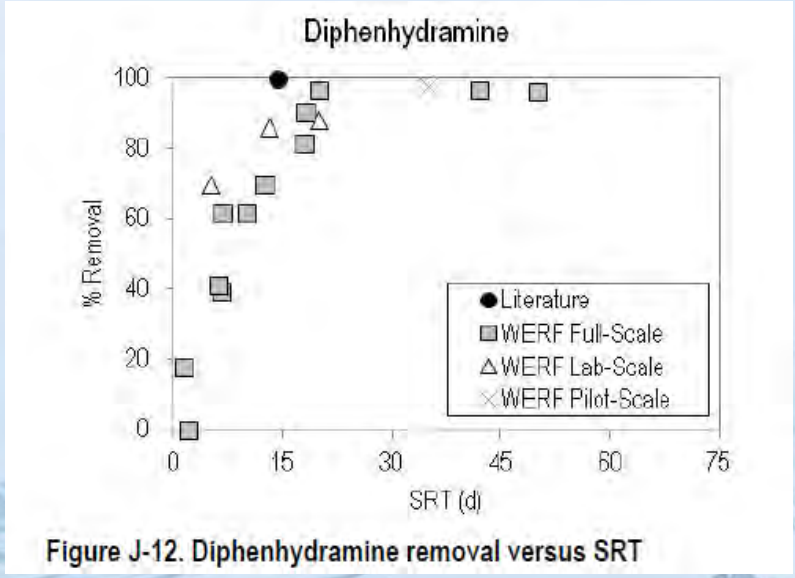
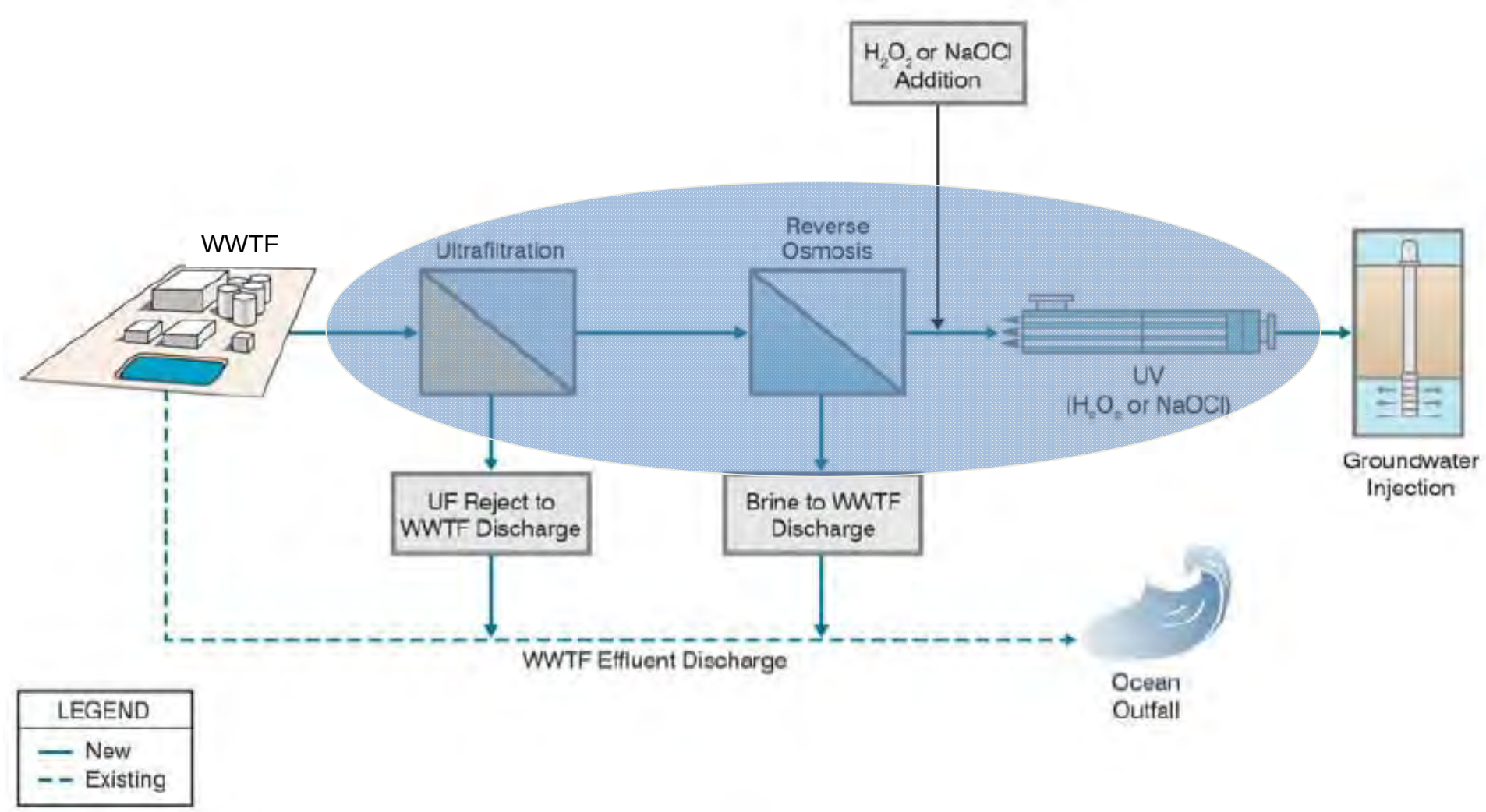


Figure J-12. Diphenhydramine removal versus SRT

Threshold $SRT_{80\%}$ Can be a CCP for CECs

	SRT, days
Acetaminophen	2
Caffeine	2
Ibuprofen	5
Naproxen	5
Bisphenol A	10
Triclosan	10
DEET	15
Gemfibrozil	15
Atenolol	15
BHA	15
Iopromide	15
Cimetidine	15
Diphenhydramine	20
Benzophenone	20
Trimehoprim	30

Threshold SRT values could not be determined for fluoxetine, TCPP, TCEP, primidone, sulfamethoxazole, carbamazepine, triclocarban, or sucralose because compounds are recalcitrant or removal was too variable.


H_2O_2 or NaOCl Addition
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LEGEND
New
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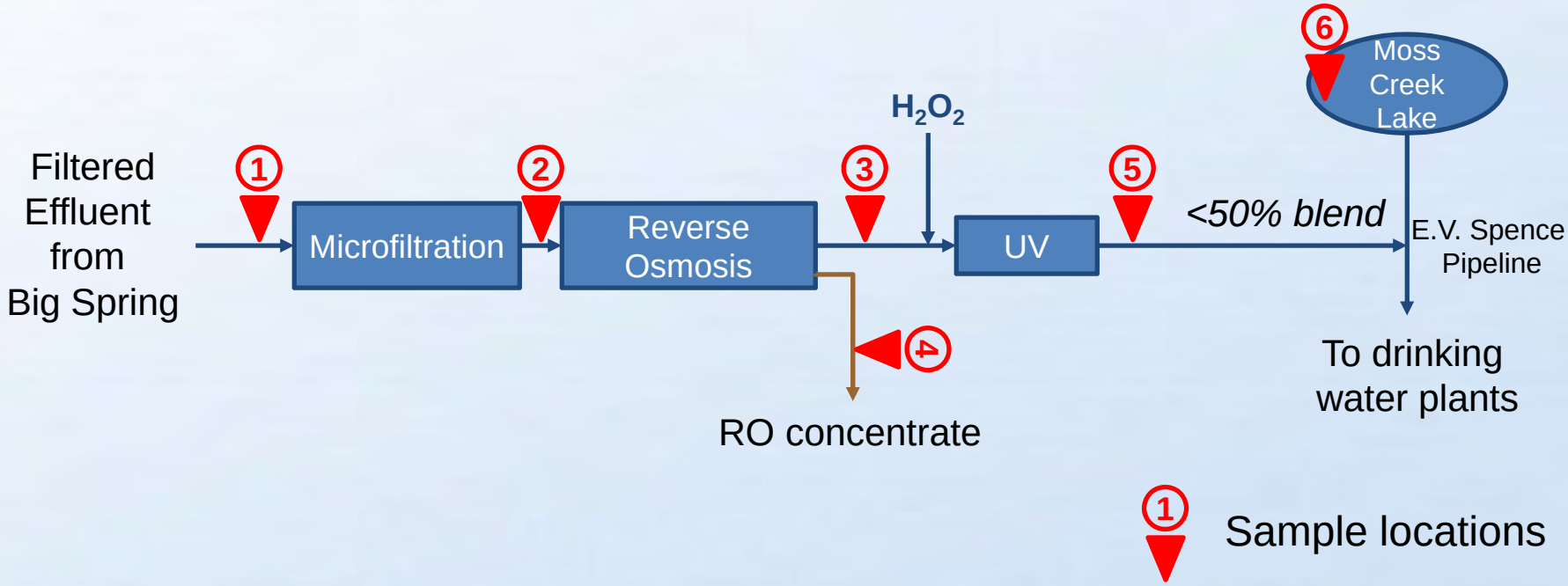
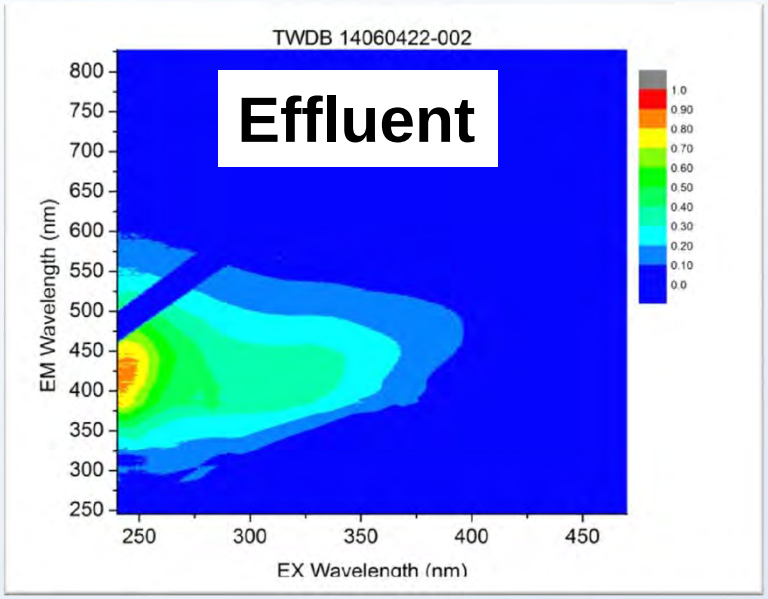
TWDB Research Demonstrates High Quality Water for DPR in Texas

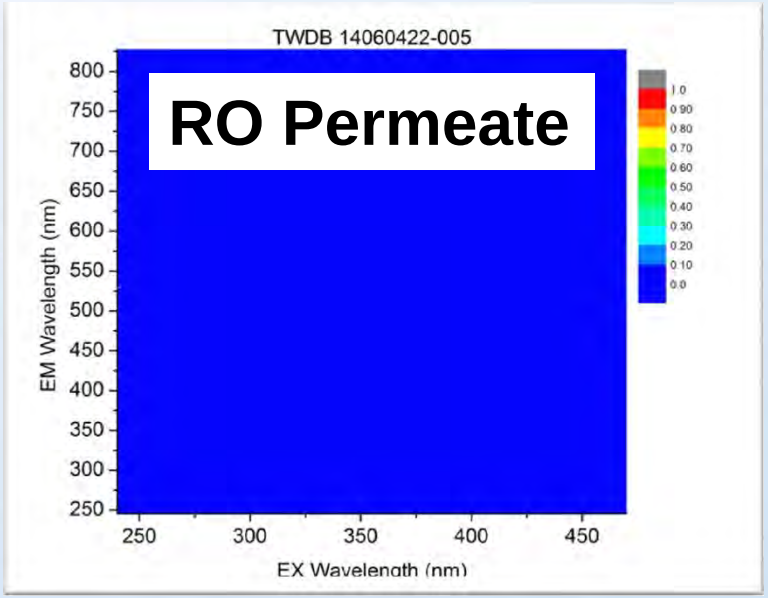


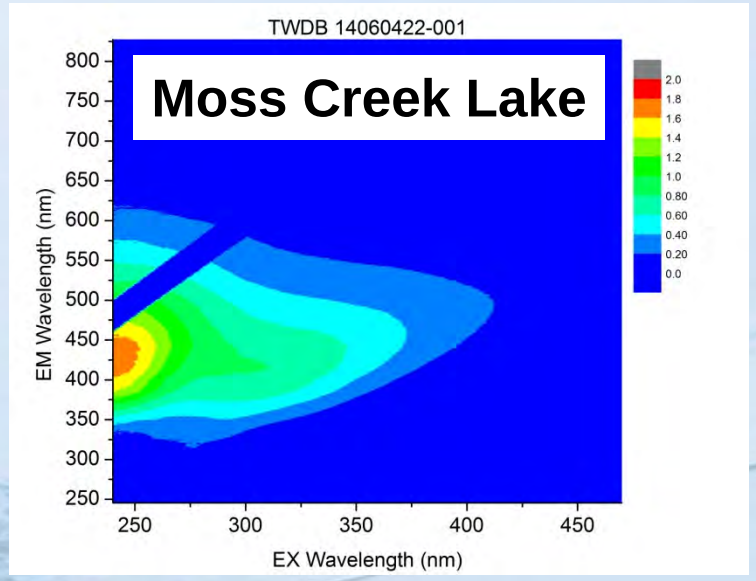
Testing Summary List

Lab	Analysis
SNWA	PPCPs
	Hormones
	PFCs
	Nitrosamines
	TTHMs
	HAA5
	NDMA Formation Potential (with chloramines)
	THM/HAA Formation Potential (with chlorine)
	YES Assay
	TONO Assay
	Fluorescence EEMs
BioVir	Norovirus/Enterovirus (EPA 1615) – ultra-low level
	Giardia / Cryptosporidium (EPA 1623) – LT2 standard level
	MS-2 Bacteriophage, Low-Level (Adams, 1959)
Odessa	E. Coli and Total Coliform (SM9223)
Nalco	TRASAR(R) RO integrity monitoring
Carollo	Particle Size Distribution Testing (pre/post MF)
	Chloramines testing (pre/post UV)
	ATP tests
Trussell	Collimated Beam Testing on RO permeate

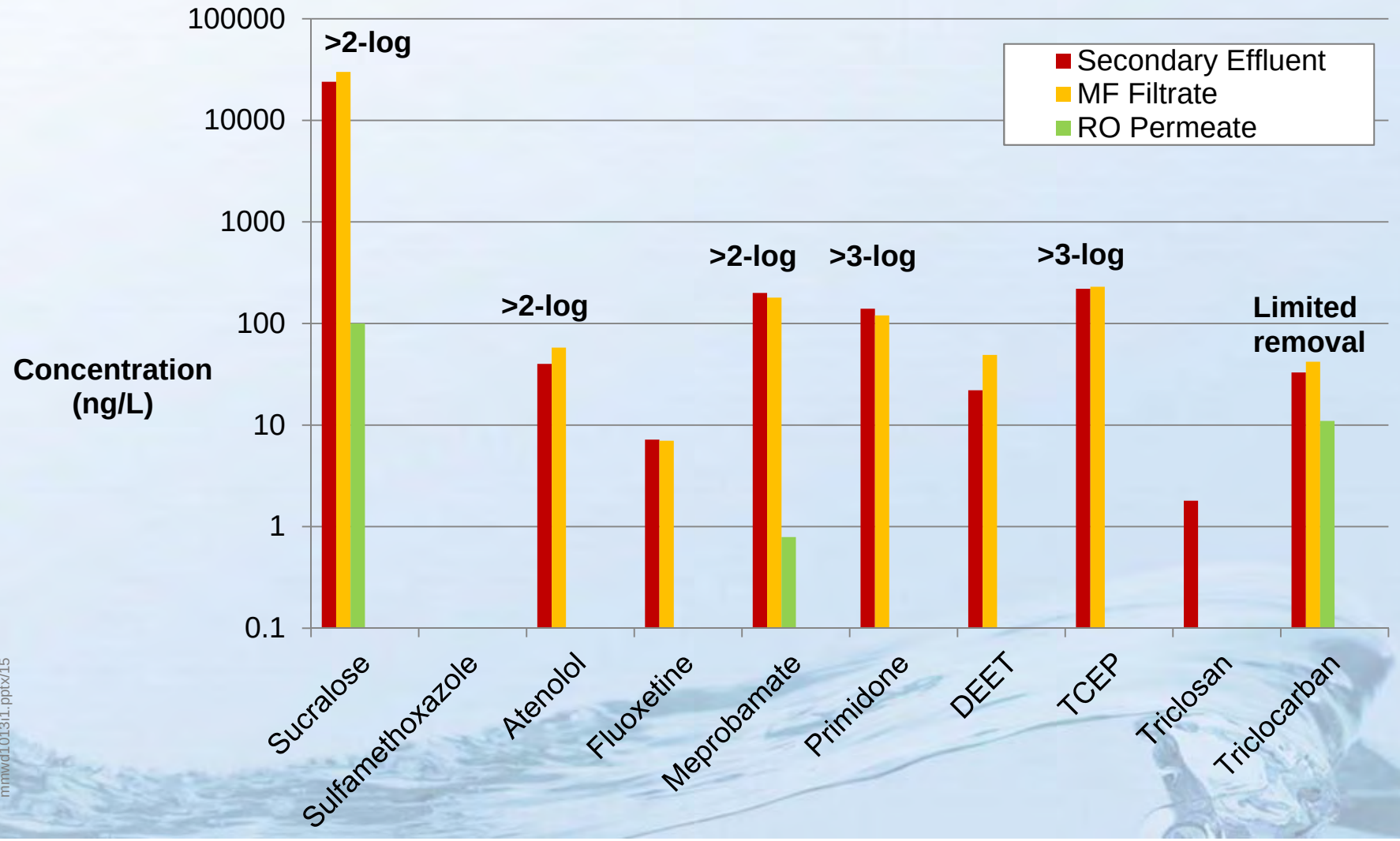
Fluorescence Images Tell a Good Story



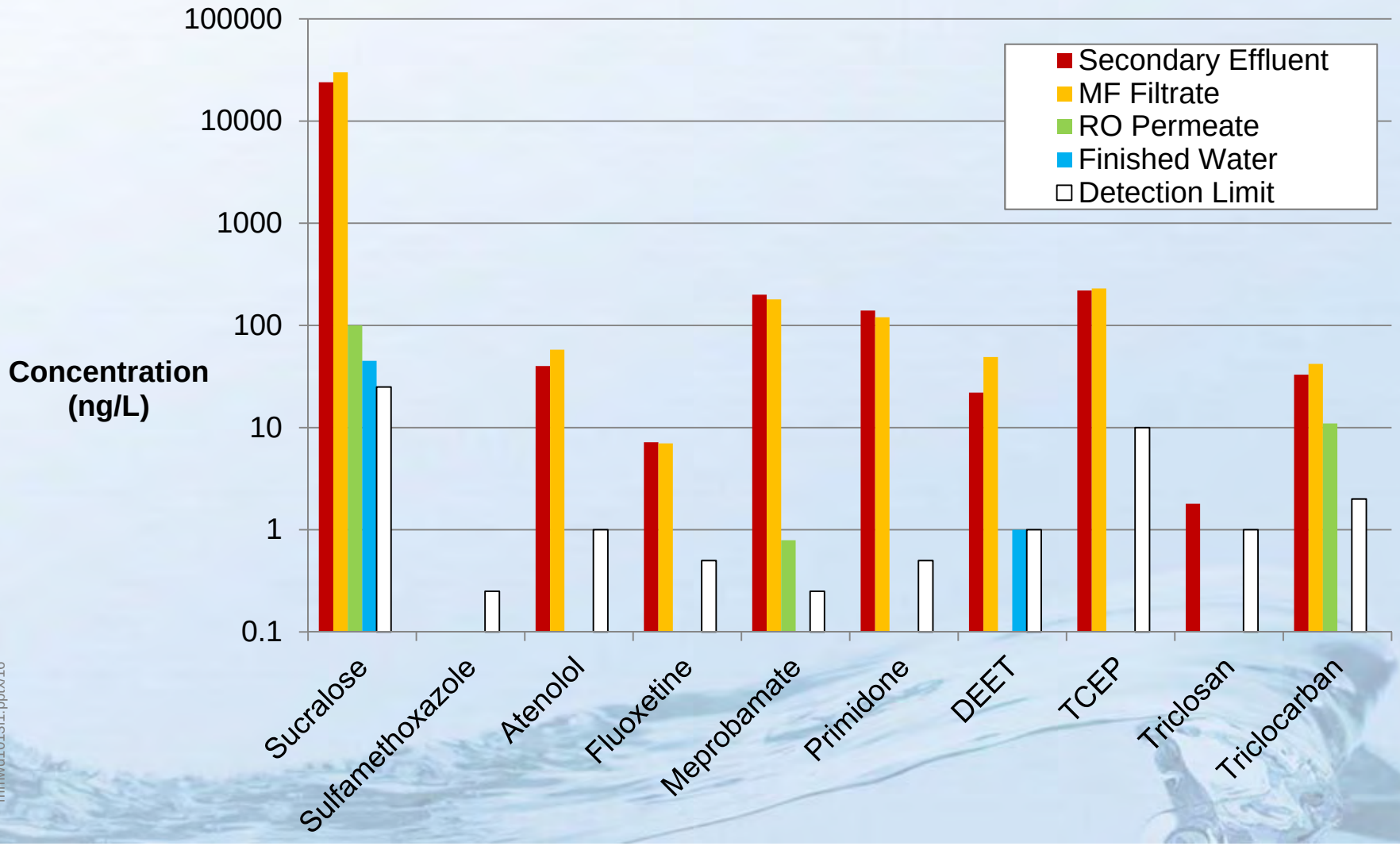




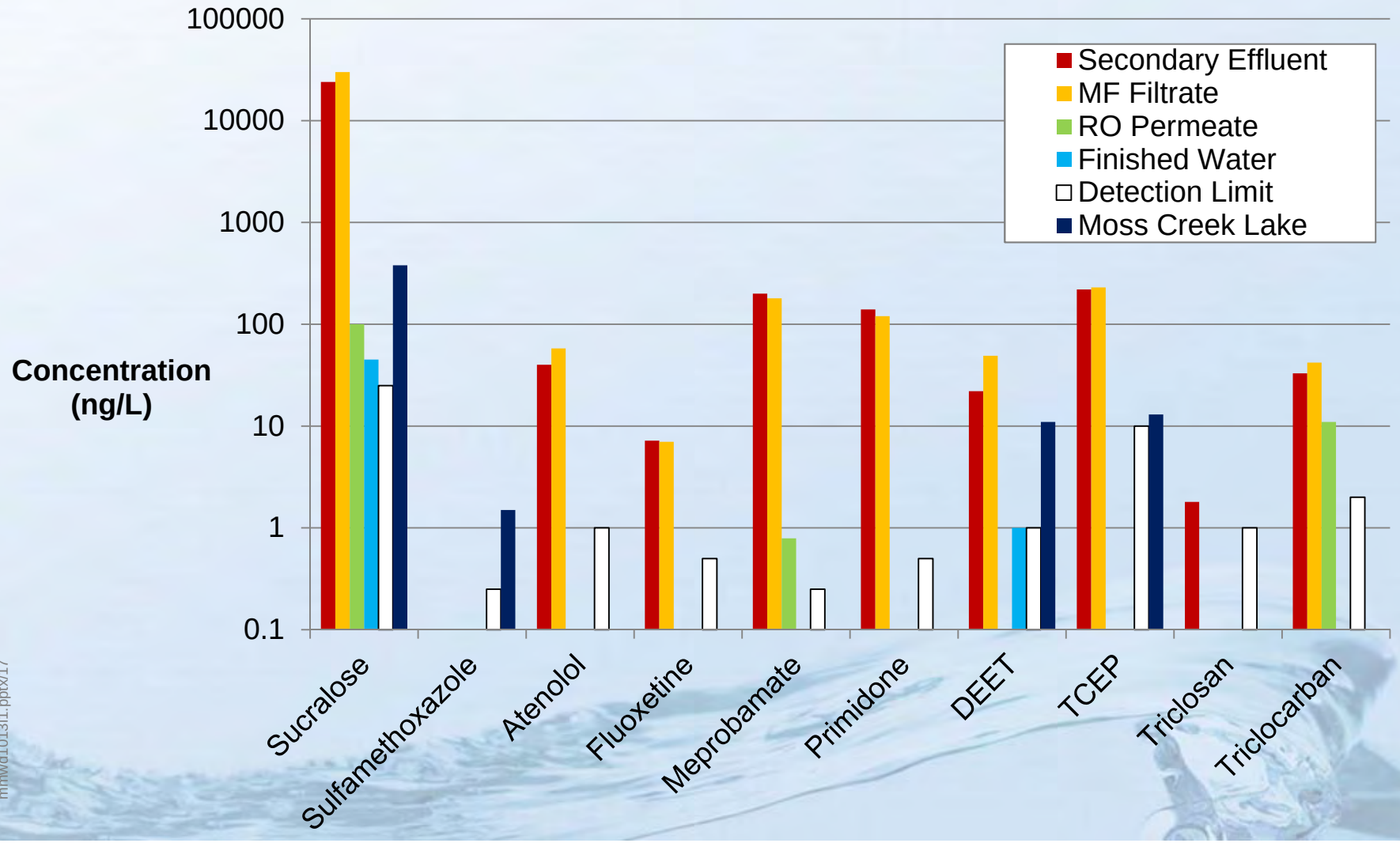
RO Achieves Robust Removal of Trace Organics (Pharmaceuticals etc.)



AOP Finishes the Job



DPR Finished Water Improves Blended Water Quality wrt Trace Organics



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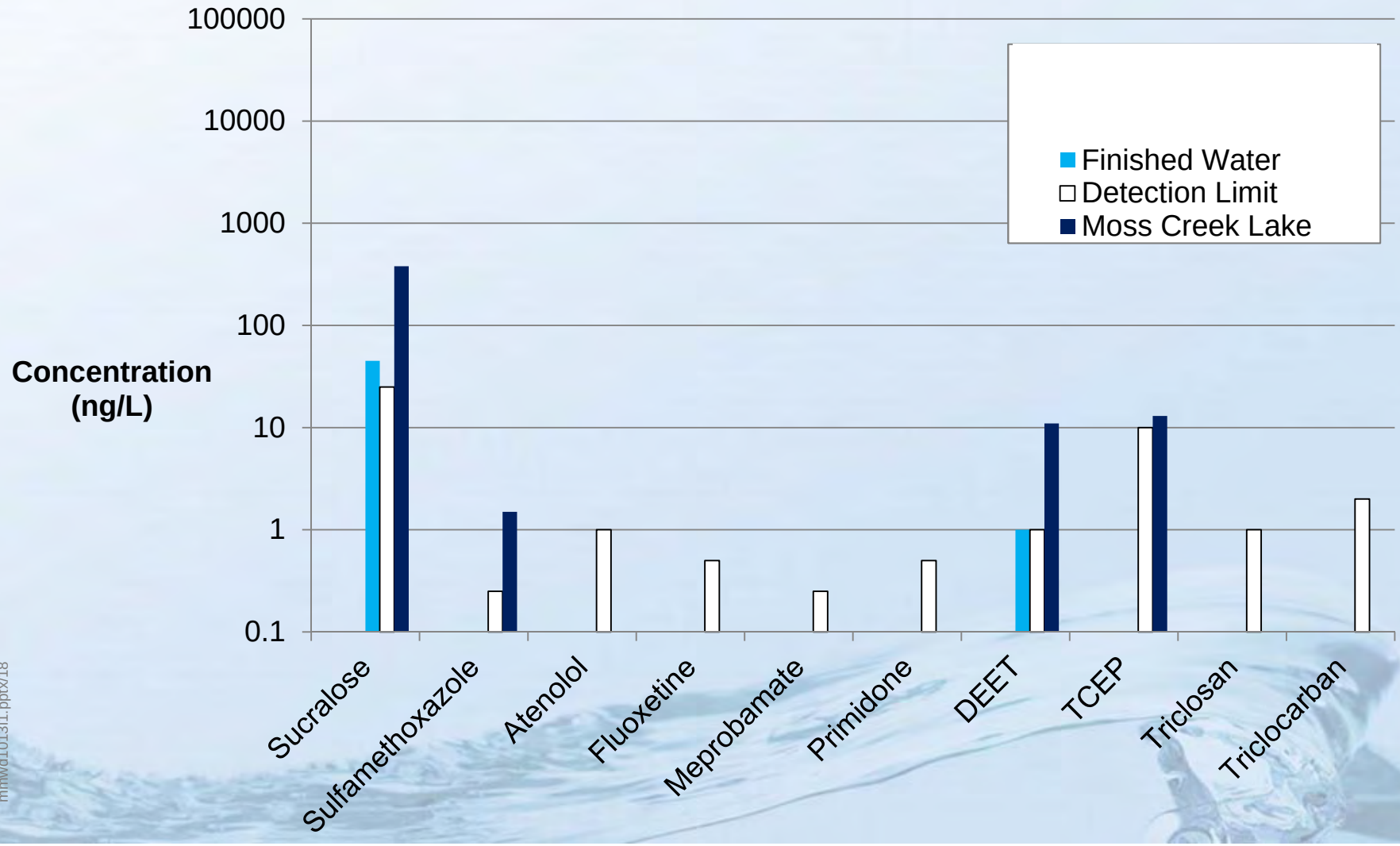
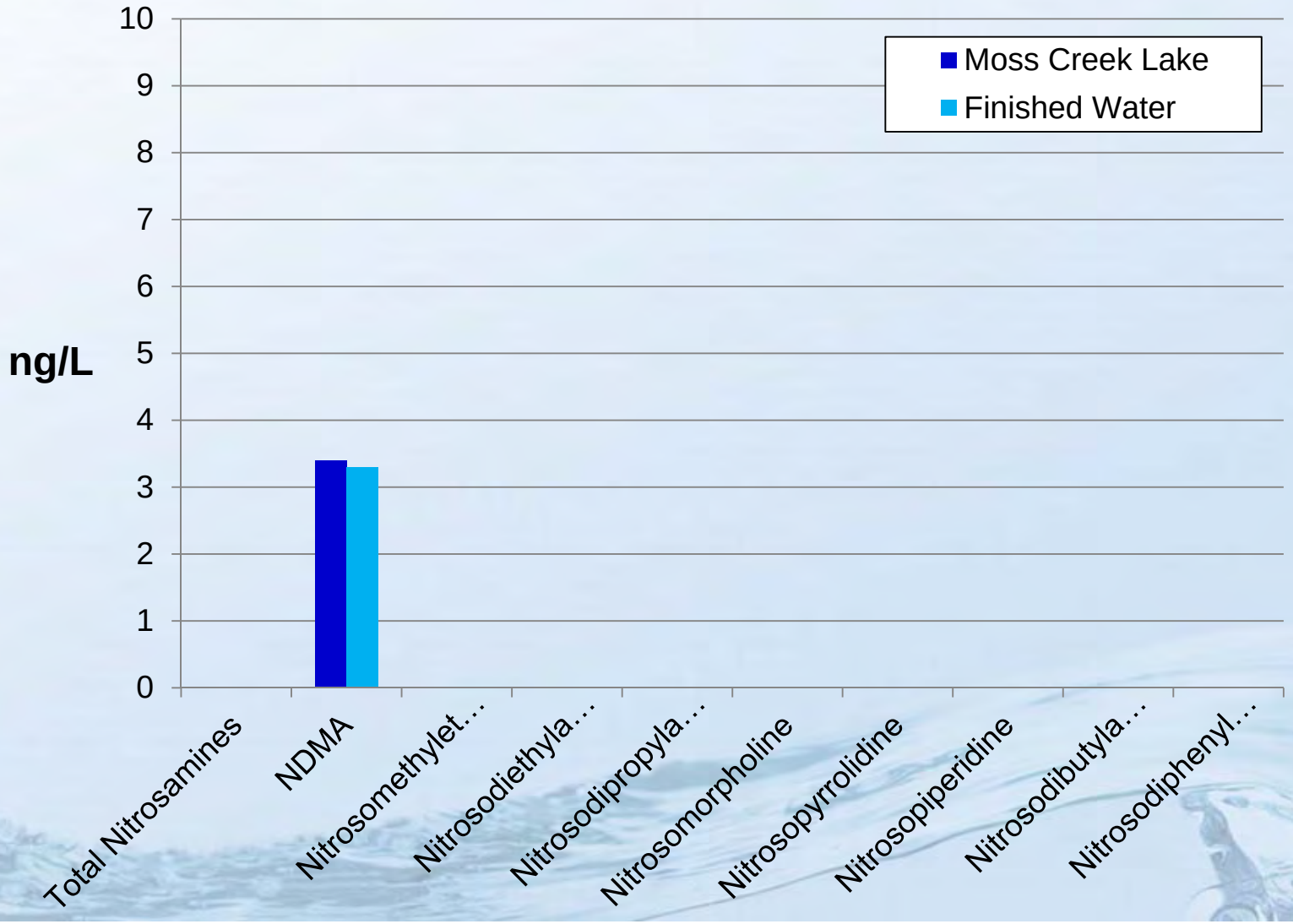
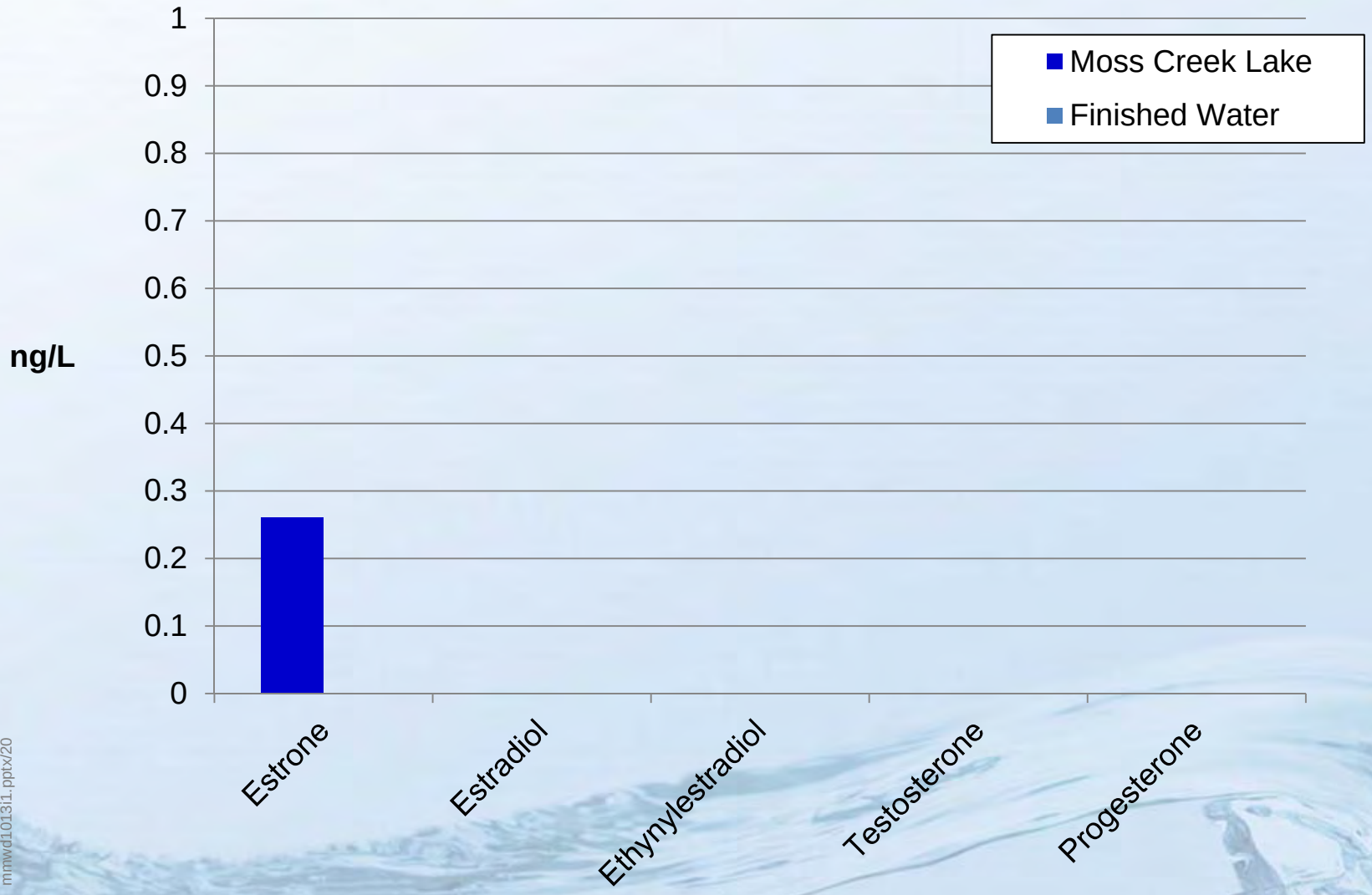


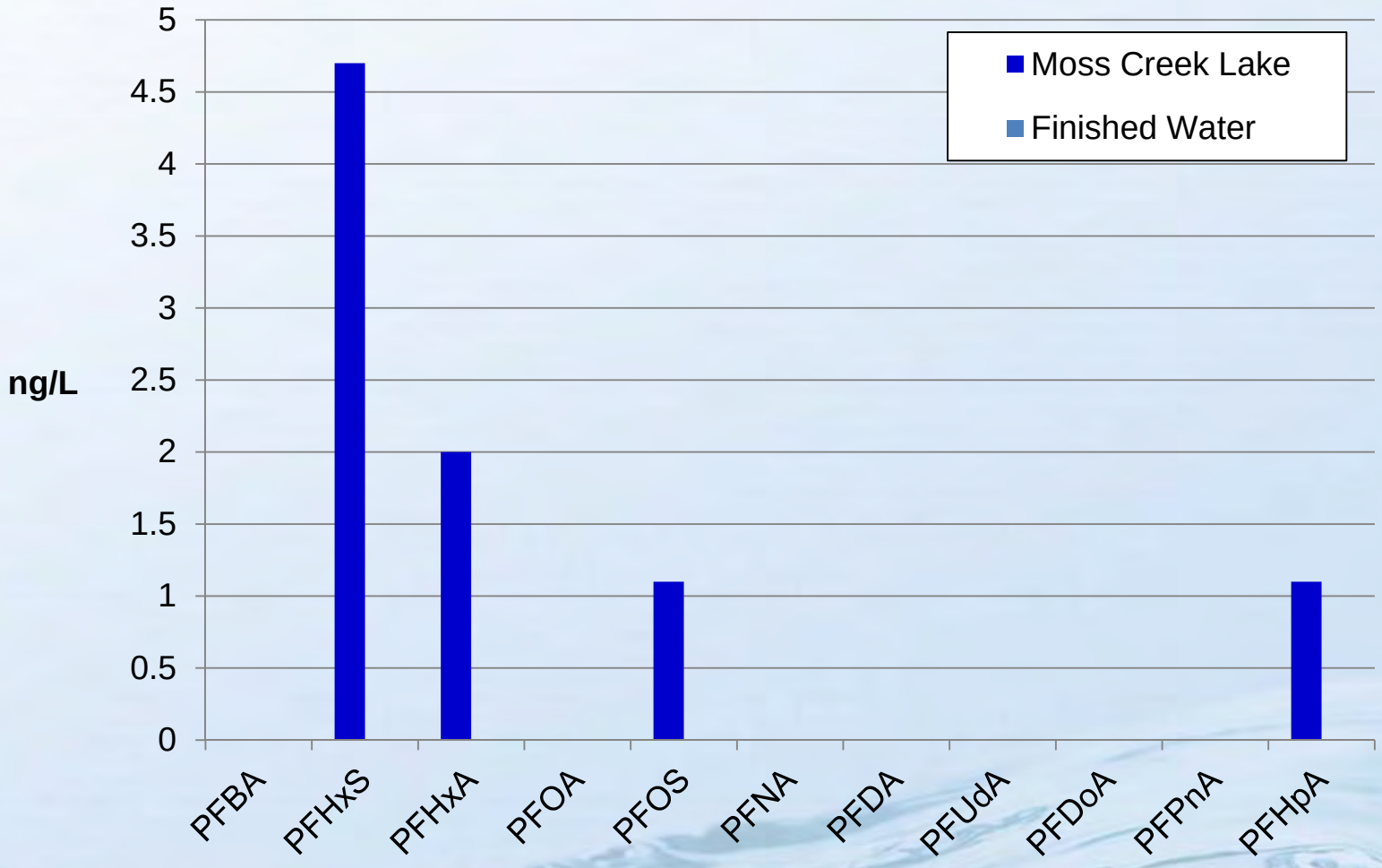
The Story is similar for Nitrosamines…



… and Estrogens…



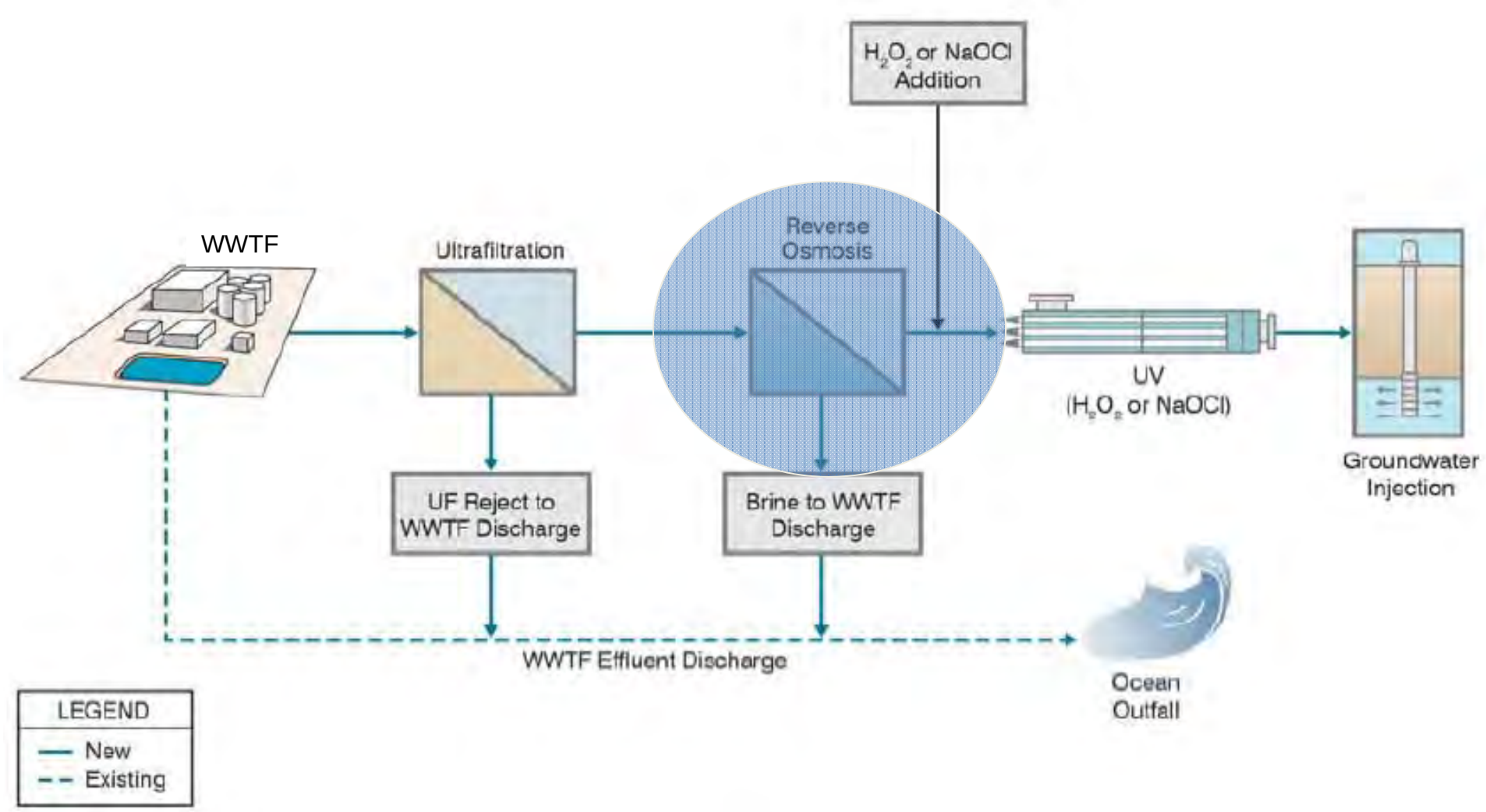
… and Perfluorinated Chemicals…



How Do We Gain Confidence in Water Quality Pertaining to CEC Removal?

1. CCPs for RO

2. CCPs for UV AOP


H_2O_2 or NaOCl Addition
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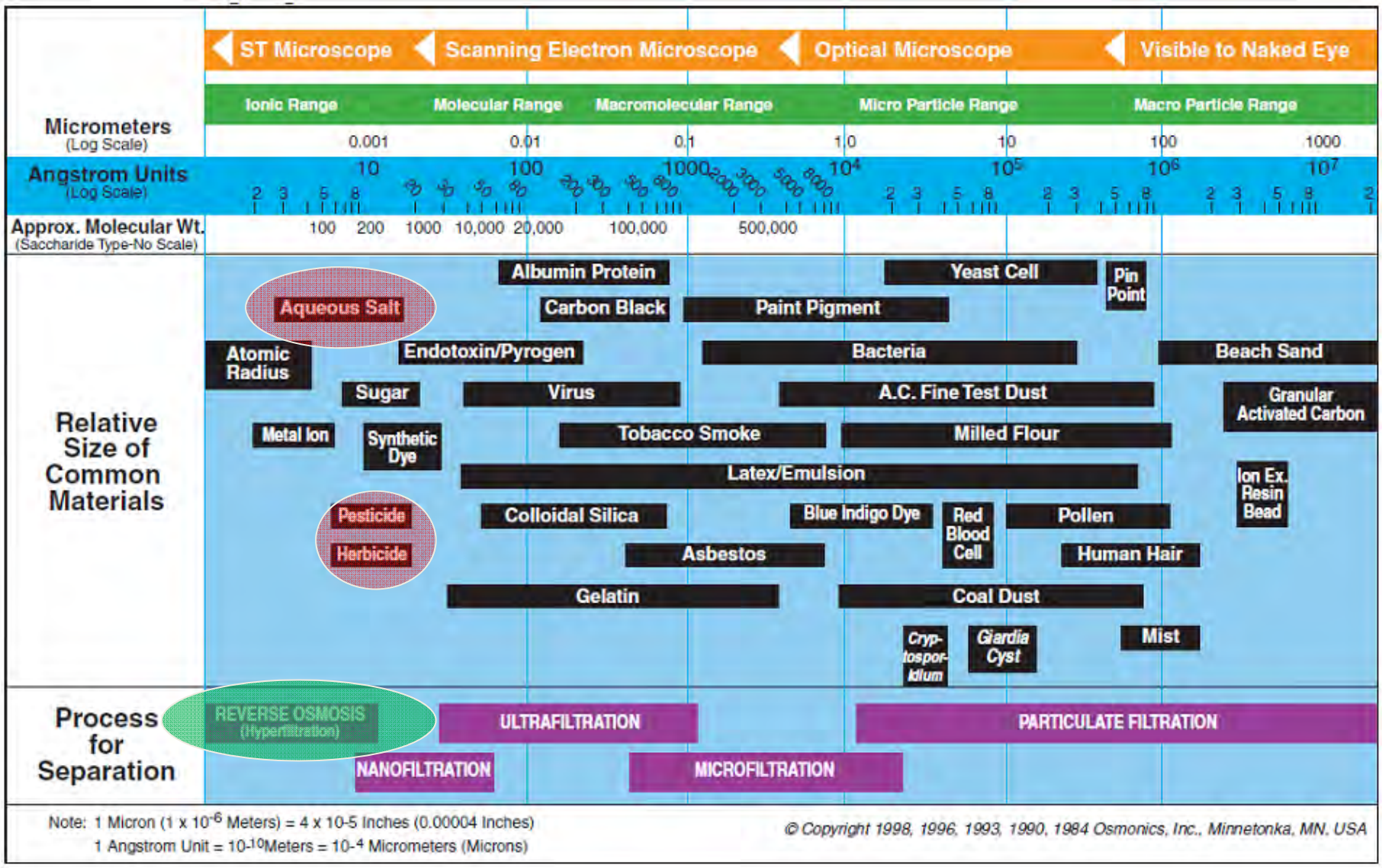
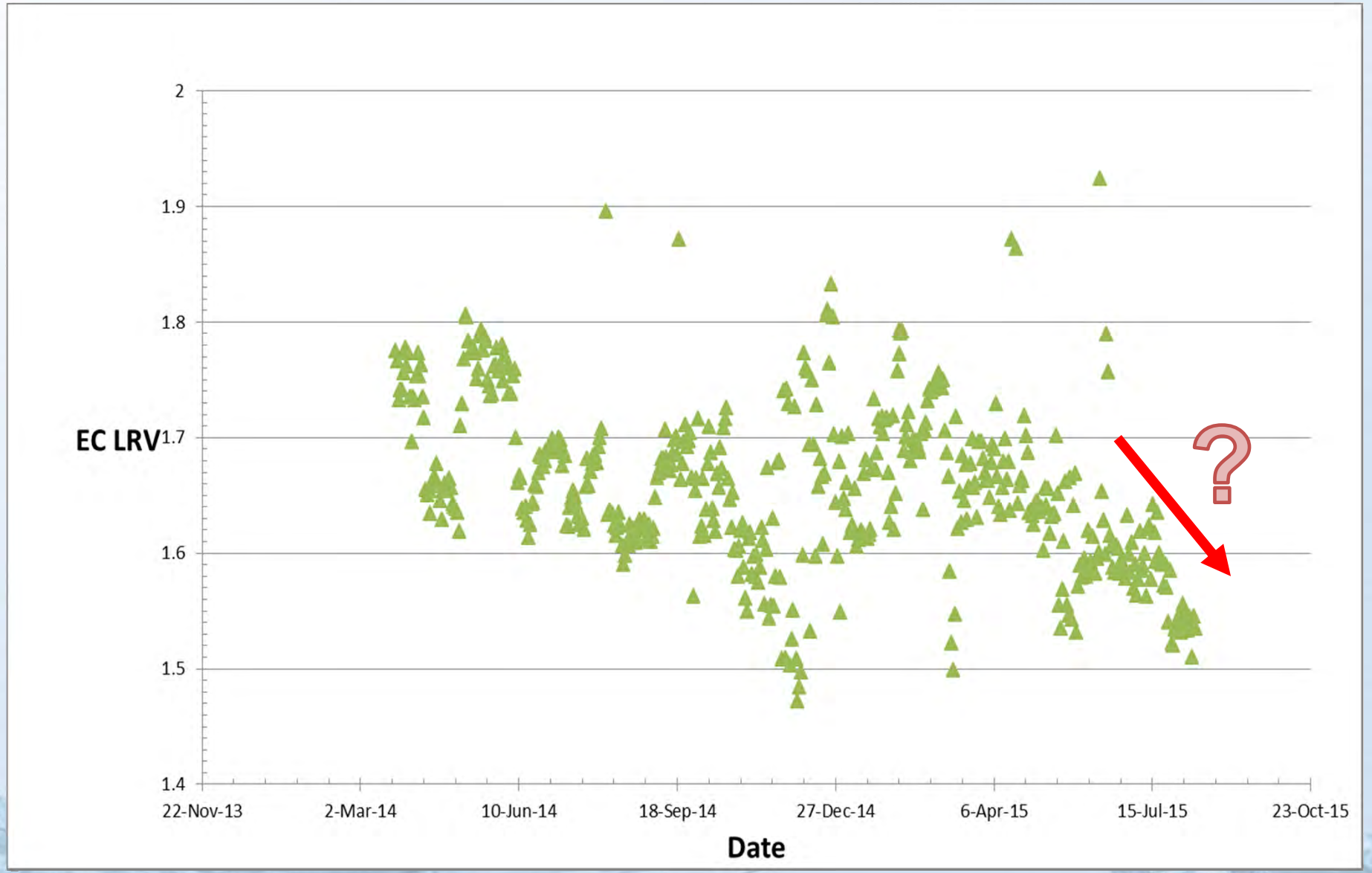
Ocean Outfall
LEGEND
New
Existing

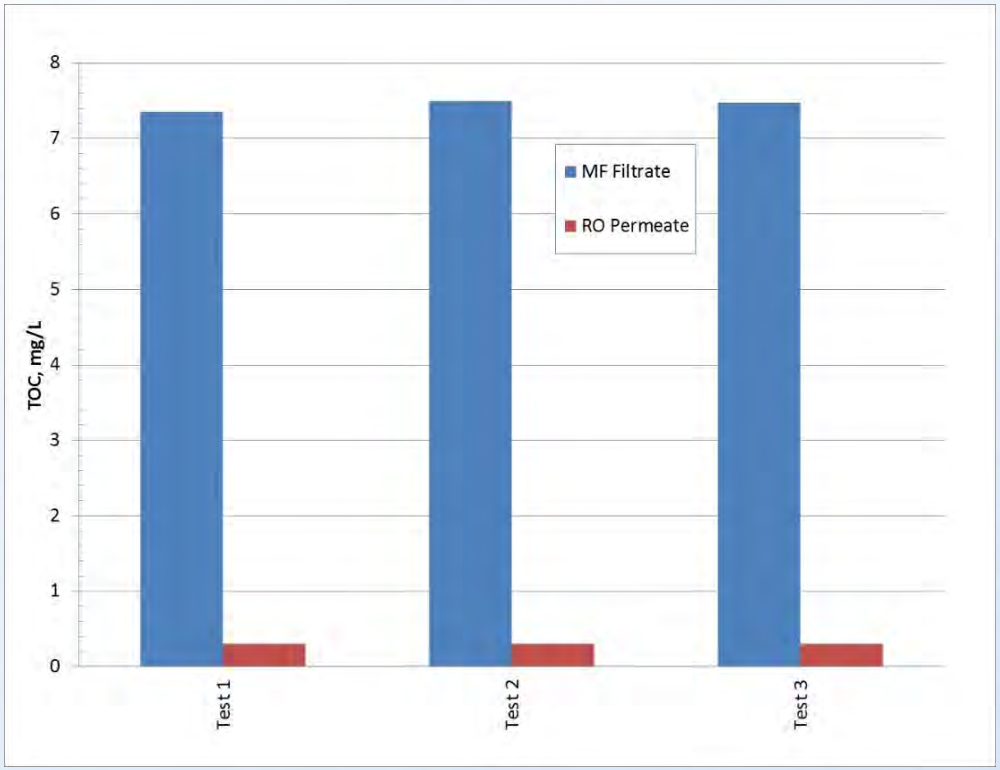
Is EC Sufficiently Sensitive as a Surrogate for CEC Reduction?



Do Trends in EC LRV Correlate to Changes in CEC Reduction?

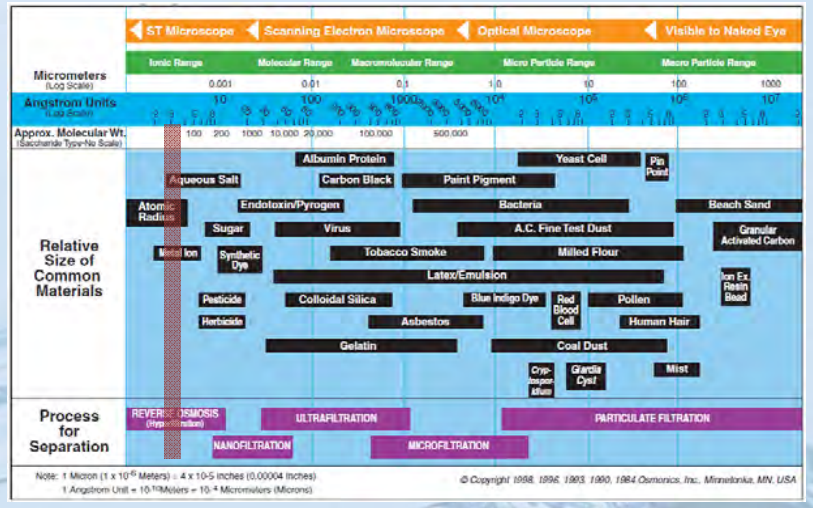


Can TOC Reduction Correlate with CEC Reduction?

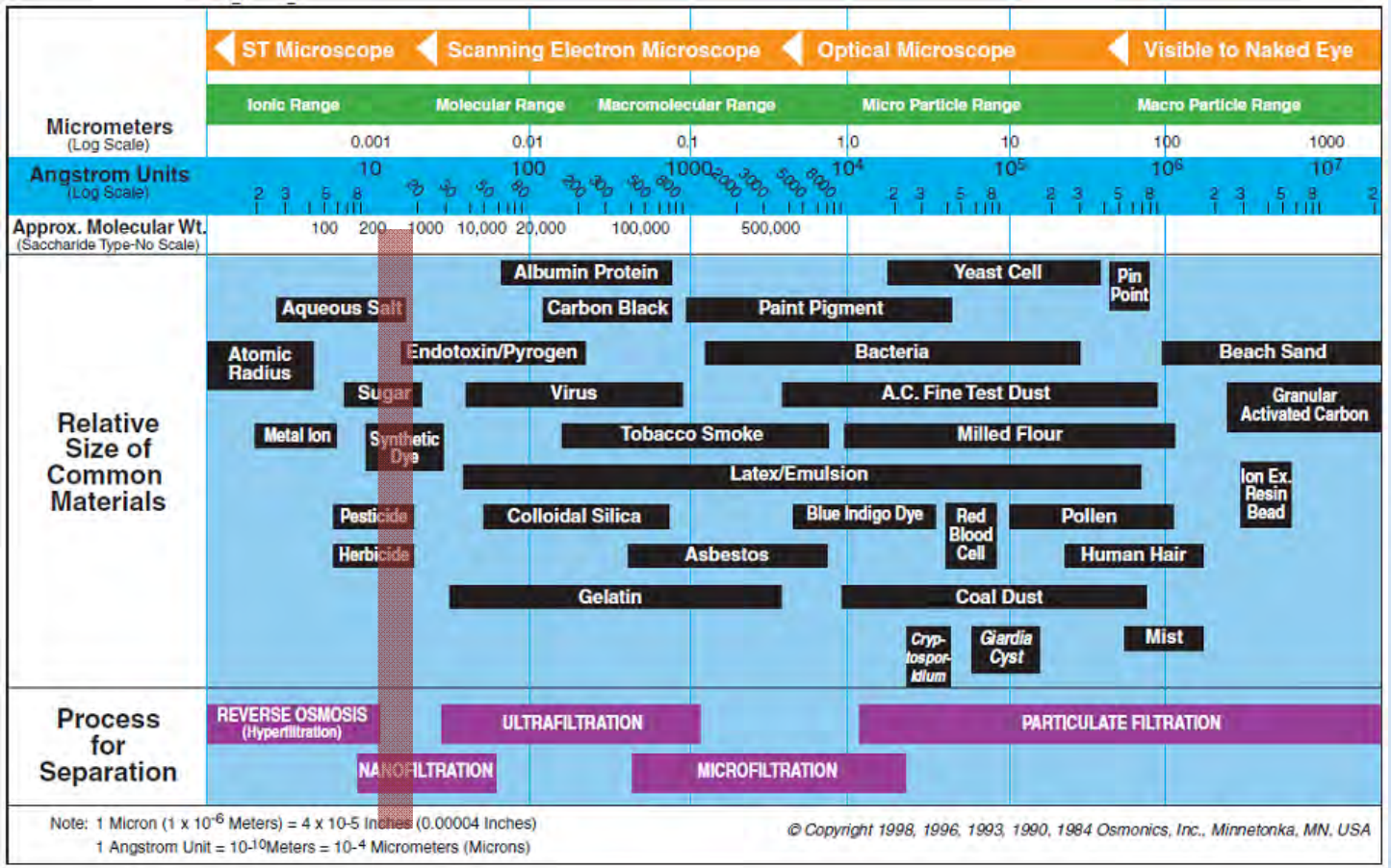


91 percent of EfOM was under 100 kDa and 62 percent of the EfOM was <1 kDa (<0.0005 *u*m).

Kim and Dempsey (2008)

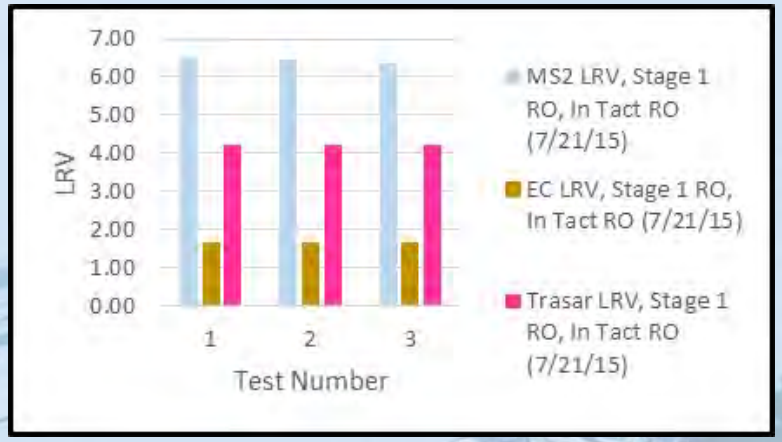


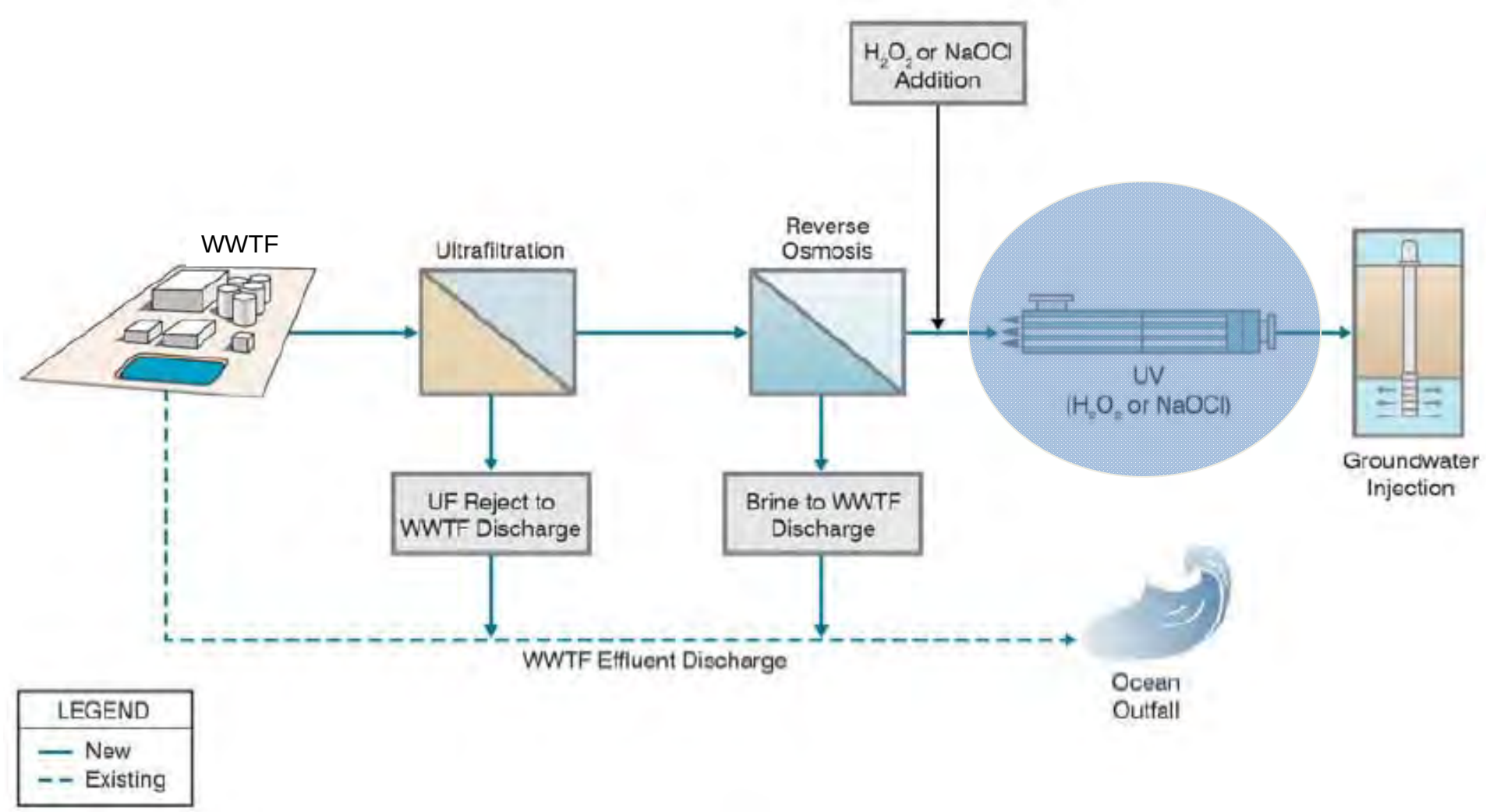
Can a Fluorescent Dye Correlate with CEC Reduction?



At 600 g/mole, the Trasar fluorescent dye is larger than the openings in the RO membrane

Can a Fluorescent Dye Correlate with CEC Reduction?

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Brine to WWTF Discharge
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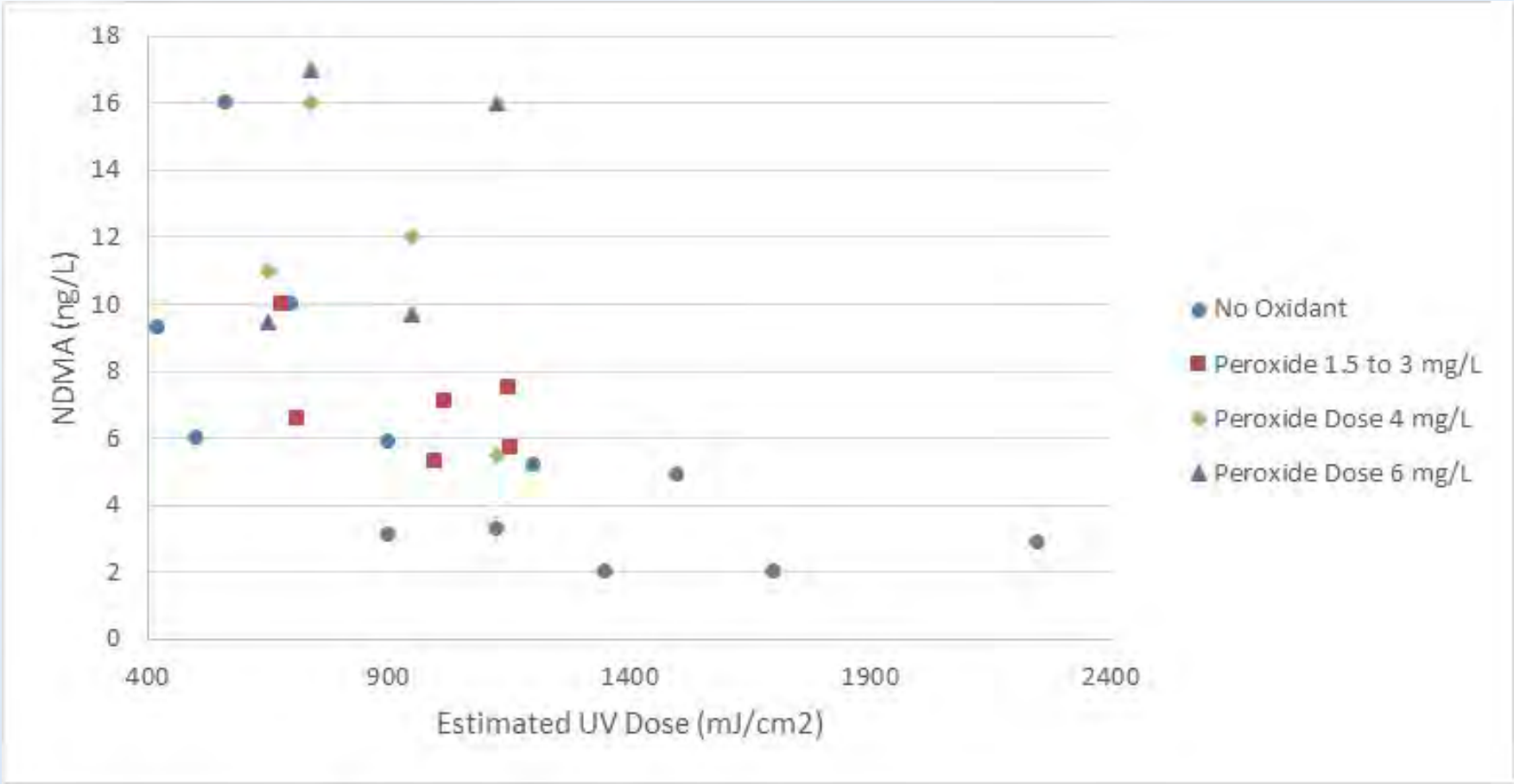
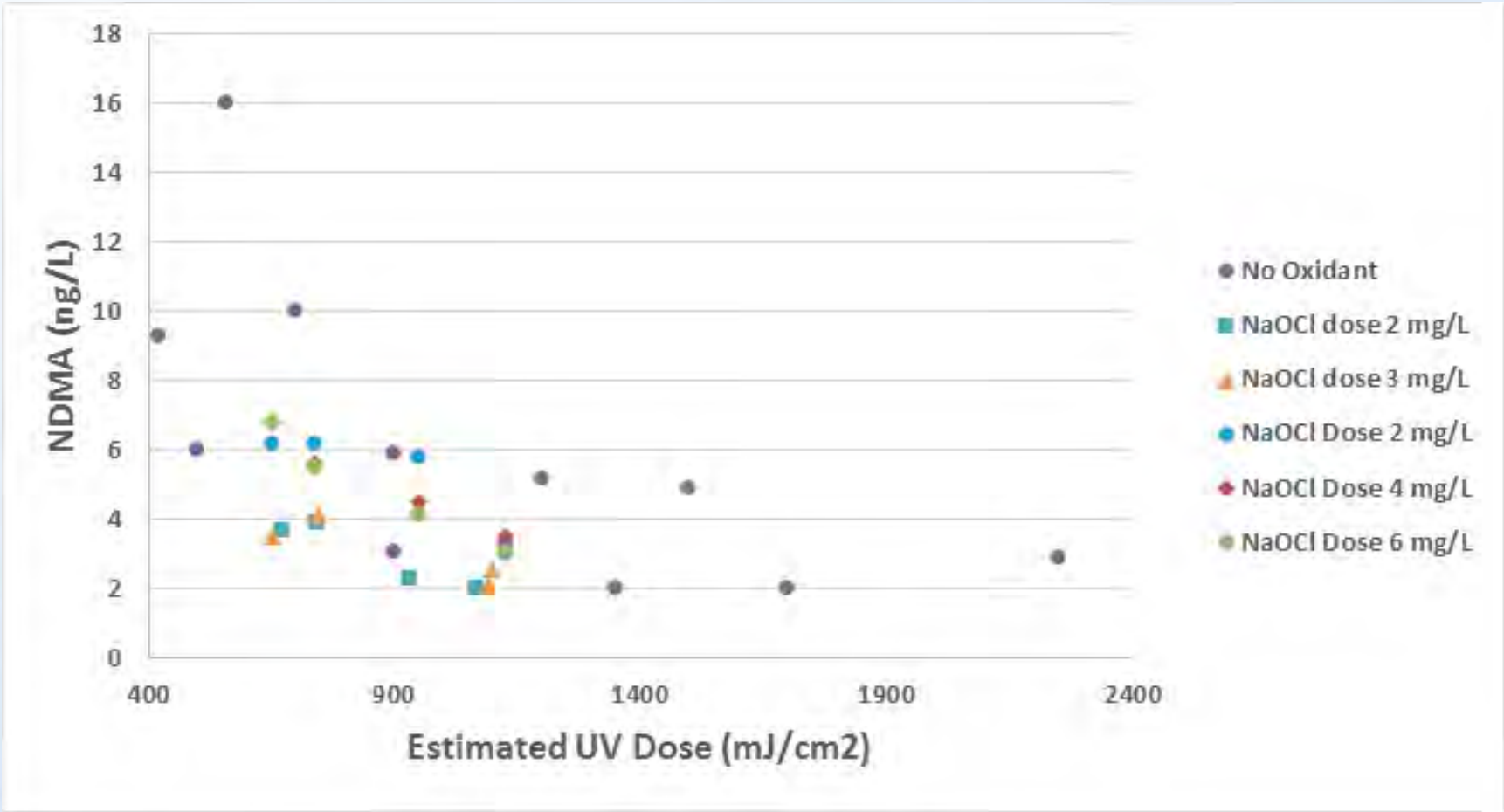
Ocean Outfall
LEGEND
New
Existing

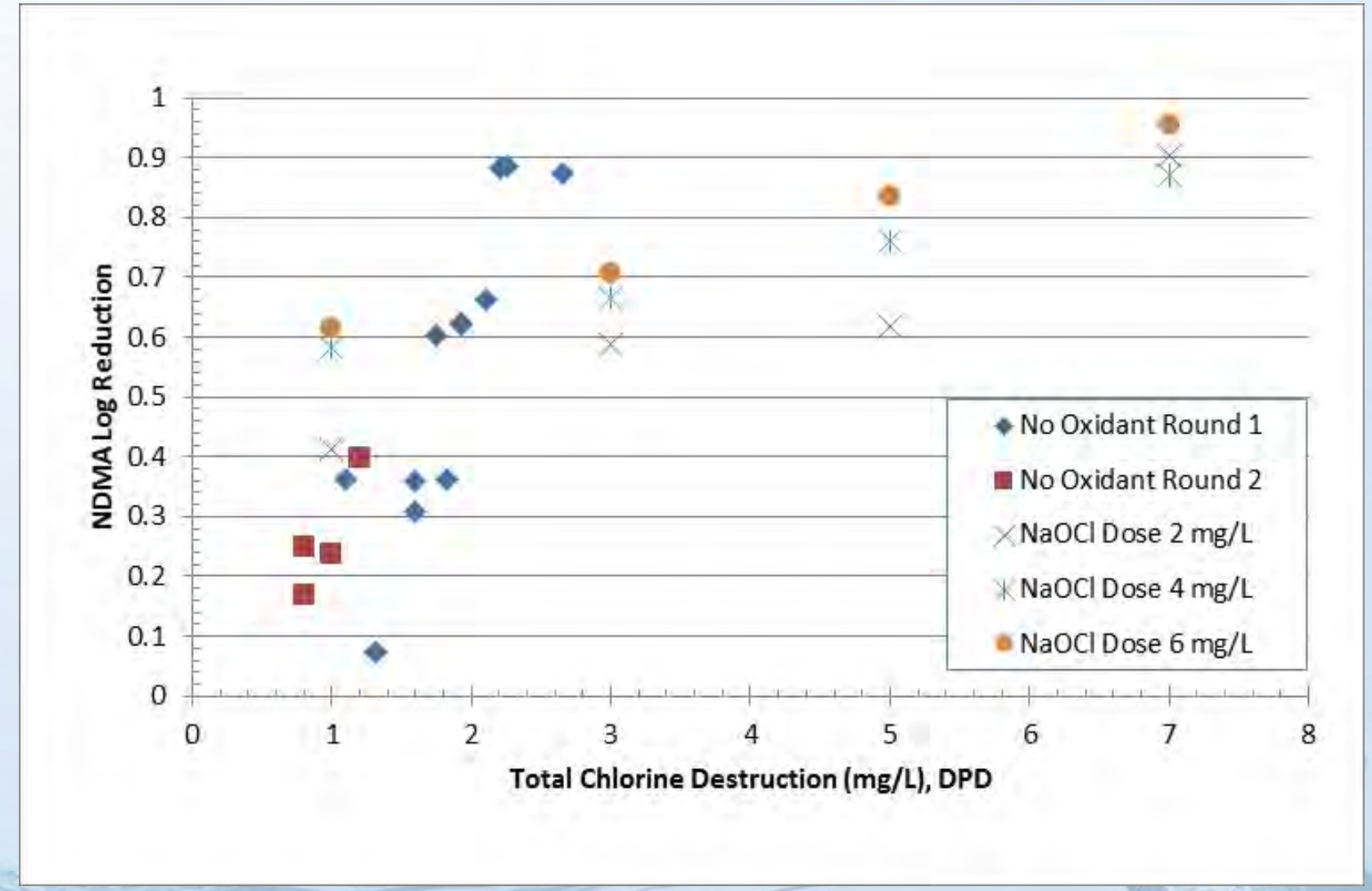
NDMA Destroyed by UV Photolysis, ~1-log at a dose of 900 mJ/cm^2



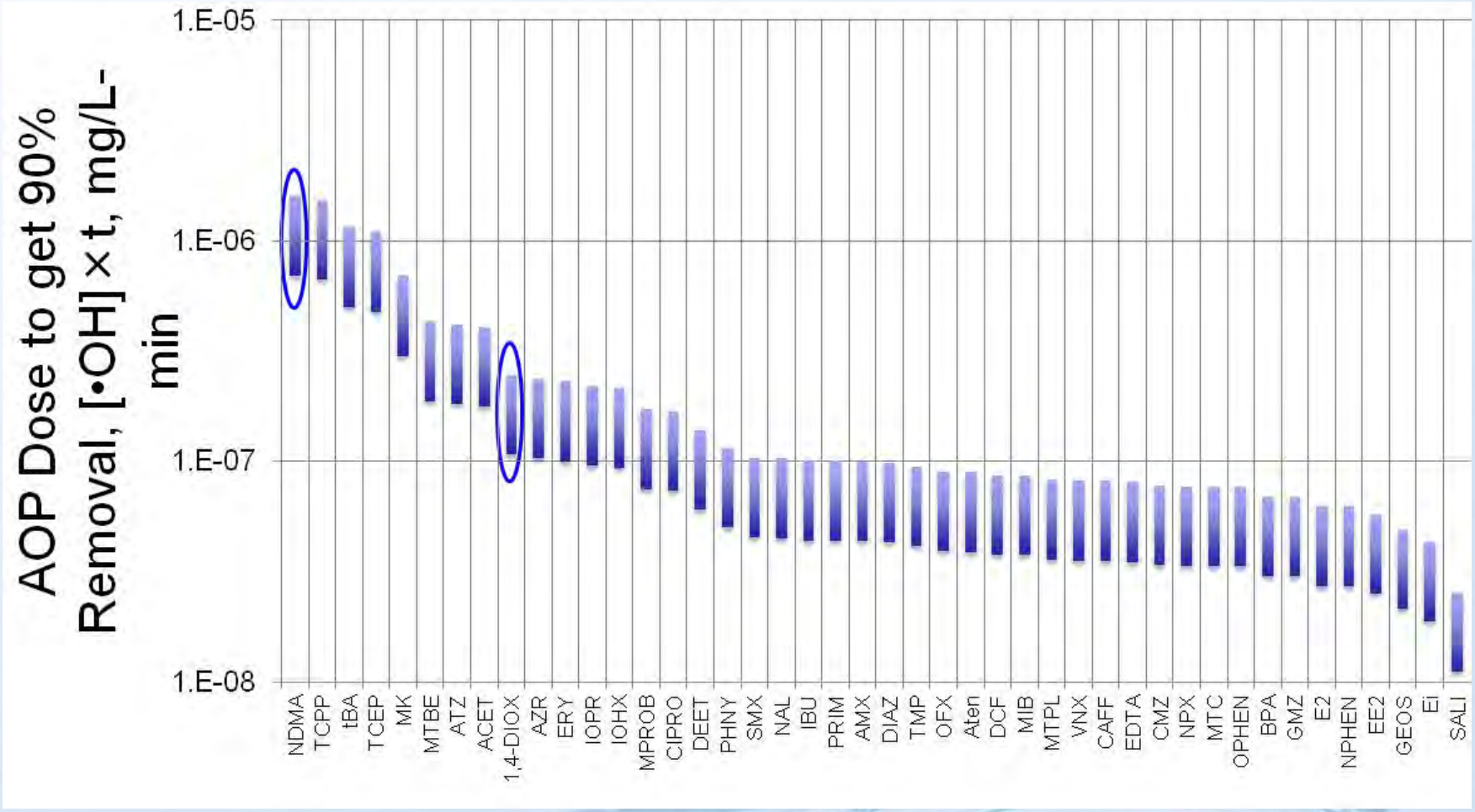
NDMA Destroyed by UV Photolysis, ~1-log at a dose of 900 mJ/cm^2



Total Chlorine Destruction Can Be a CCP for NDMA Destruction

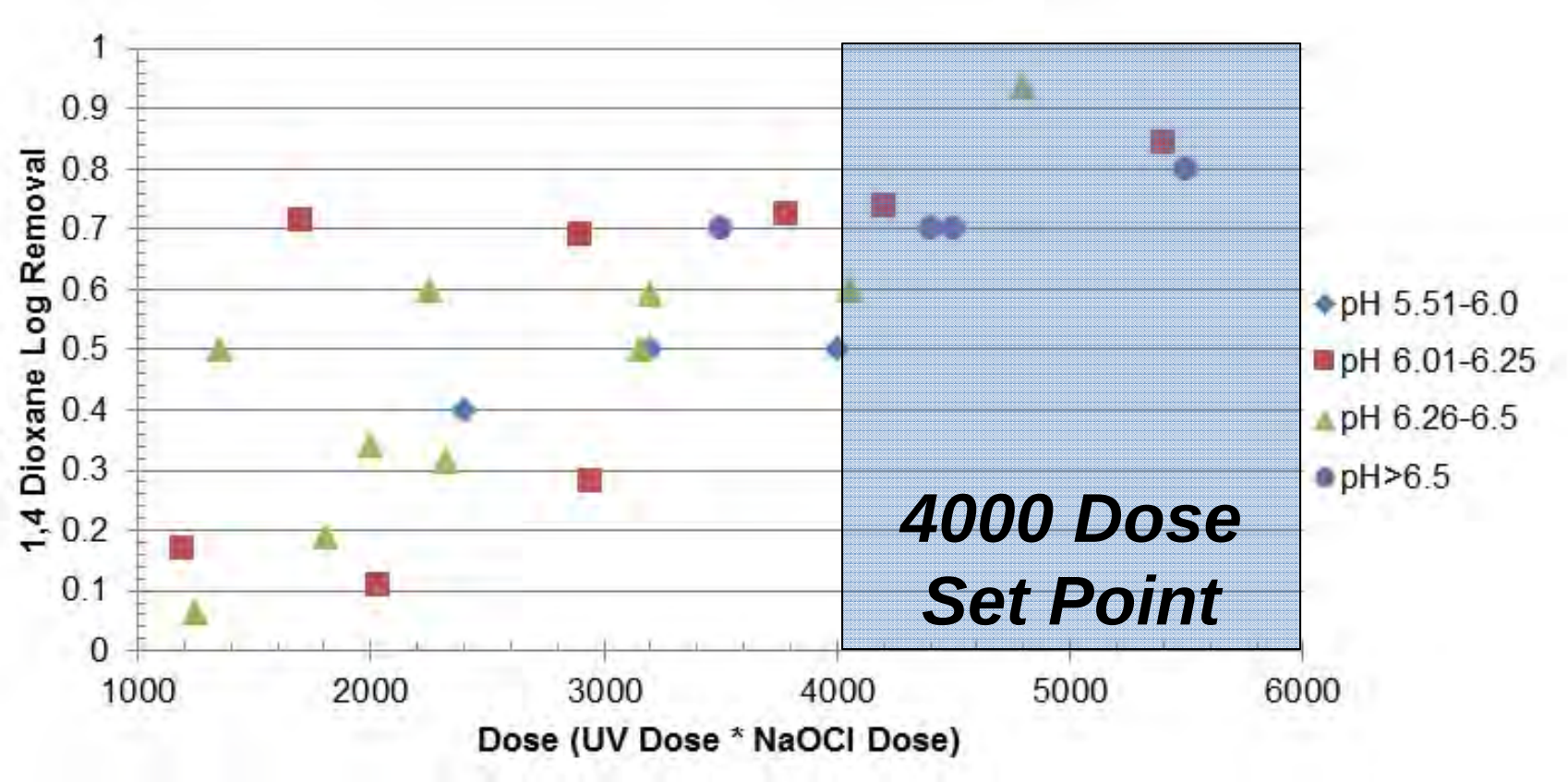


1,4-Dioxane Destruction is a Conservative Surrogate for a Wide Range of CECs

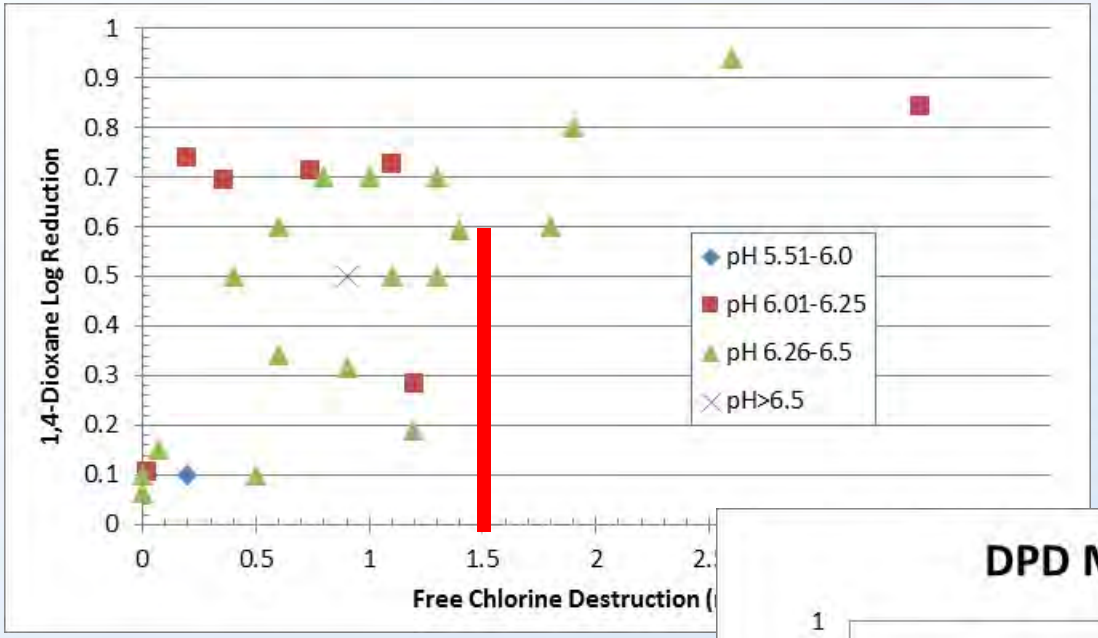


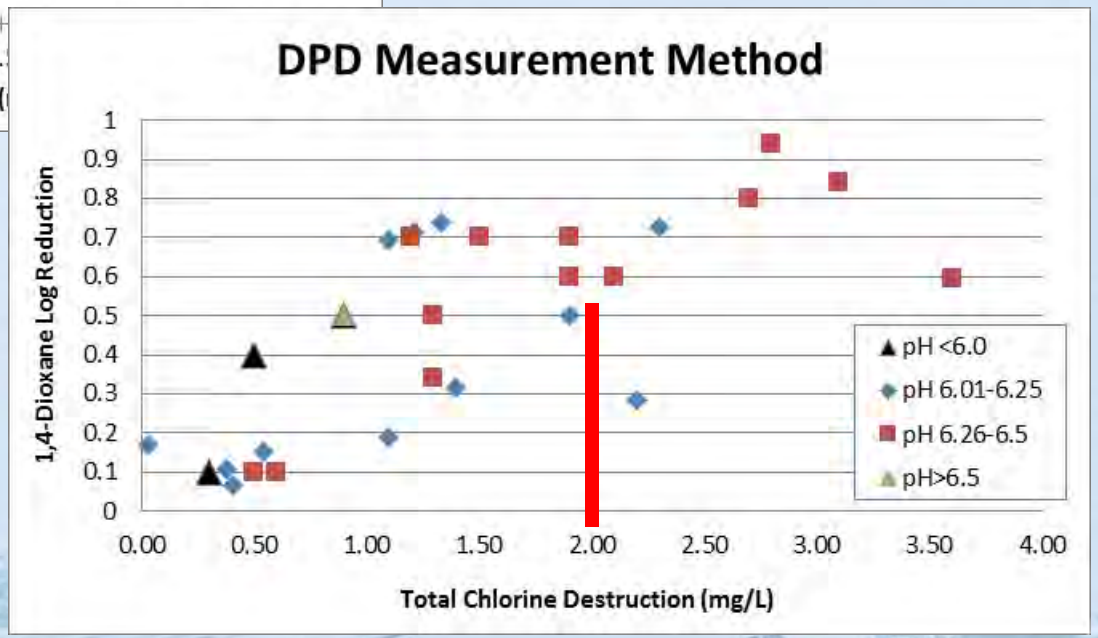
Hokanson et al., 2011

For UV/NaOCl, Free Chlorine Weighted Dose Can be a CCP for 1,4-dioxane Destruction

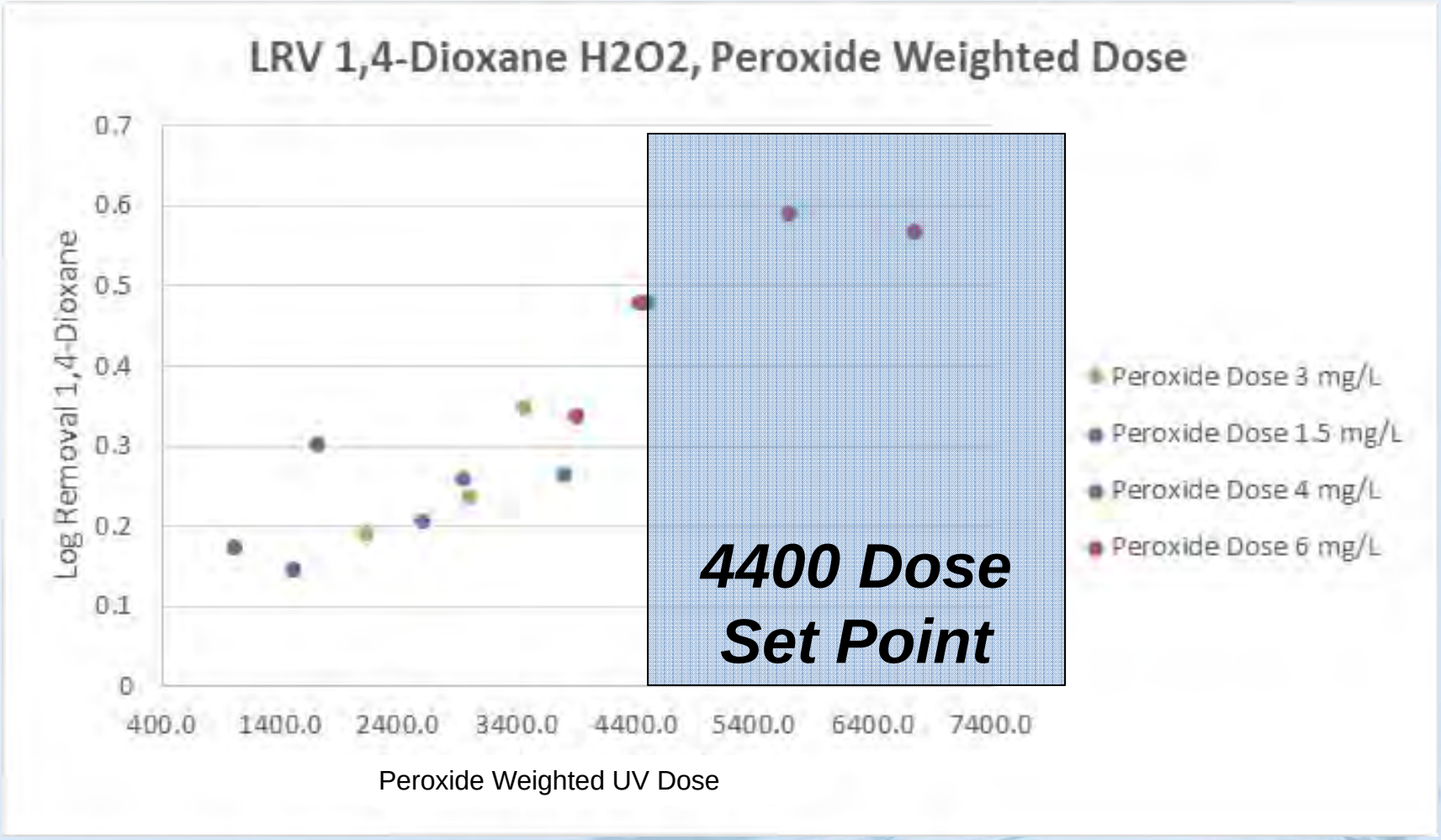


For UV/NaOCl, Total and Free Chlorine Destruction Can be a CCP for 1,4-dioxane Destruction





For UV/H2O2, Peroxide Weighted Dose Can be a CCP for 1,4-dioxane Destruction



Where Are We Going and How Do We Get There?

$$C/C_o = Photolysis + AOP = \exp\left(-k'_d \times D - k'_{OH} \times D\right)$$

$$C/C_o = \exp\left(\begin{array}{l} -k'_d\, D_{Cont} \\ \\ -\dfrac{\dfrac{2.3025 k_{Cont}[H_2O_2]}{hcN_A}\varepsilon_{H_2O_2}(254)\lambda_{254nm}\Phi(254)D_{H_2O_2}}{k_{TOC}[TOC] + k_{HCO_3^-}[HCO_3^-] + k_{CO_3^{-2}}[CO_3^{-2}] + k_{H2O2}[H_2O_2] + k_{HO_2}[HO_2^\bullet]} \end{array} \right)$$

C	=	Contaminant concentration
C_0	=	Initial contaminant concentration
D_{Cont}	=	Contaminant weighted UV Dose (mJ/cm^2)
D_{H2O2}	=	Peroxide weighted UV Dose (mJ/cm^2)
k'_d	=	Pseudo 1st Order Kinetic constant for photolysis (cm^2/ mJ)
k'_{OH}	=	Pseudo 1st Order Kinetic constant for advanced oxidation (cm^2/ mJ)
λ	=	Wavelength (nm)
k_x	=	Second order rate constant for reactor of water quality parameter “x” with the hydroxyl radical (L/mol-s)
h	=	Planck’s constant (m^2-kg/s)
C	=	Speed of light (m/s)
N_A	=	Avogadro’s number
Φ	=	Quantum efficiency of hydroxyl radical formation
ε	=	Molar extinction coefficient of hydrogen peroxide (L/mol-cm)

Conclusions and Research Needs

- CEC removal through WWTPs is reasonably predictable based upon chemical characteristics and operational configuration of the secondary process.
- More work is needed to correlate online surrogates for CEC removal with RO. This can be done through extensive monitoring and challenge studies, including failure analysis.
- New trends suggest good online surrogates for CEC removal by UV AOP. Further work on defining the impact of water quality variables, *even in RO permeate*, is needed.

A Toast to Your Health!