TREATMENT FOR REUSE: THE OCCURRENCE AND REMOVAL OF ACRONYMS (PPCPs, EDCs, THMs and NDMA)

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Pasadena, CA

MWH

BUILDING A BETTER WORLD

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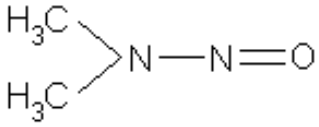
Outline of Discussion

- **Microconstituents**
- Conventional Treatment for Reuse
- Membrane Treatment
- Disinfection

Microconstituents of Interest

- EDCs: Endocrine disrupting compounds
- PPCPs: Pharmaceuticals & personal care products
- NDMA: N-Nitrosodimethylamine
- THMs = Trihalomethanes
- Others we don’t know about, yet.

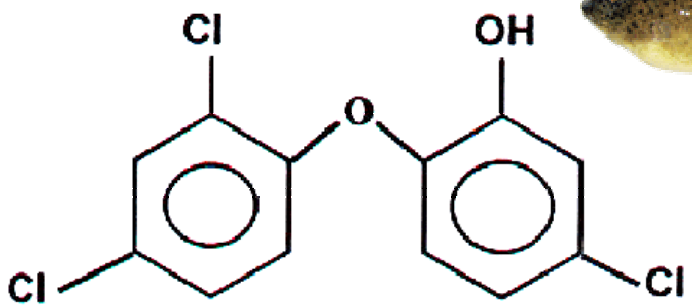


EDC/ PPCP Sources

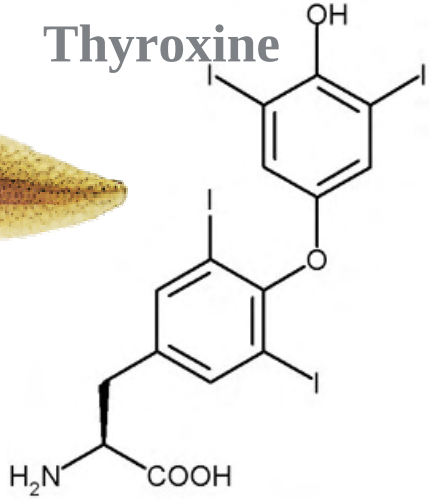
- Municipal wastewater
  - Unused drugs flushed (once recommended)
  - Cleaning products
  - Waste food products and excretion
- Synthetic chemical manufacture, use, delivery, storage, and disposal
- Urban, industrial, and agricultural runoff

Recent Findings Illustrate that some PPCPs might be EDCs

Triclosan



Thyroxine



"Triclosan is of particular concern to toxicologists because it is structurally similar to thyroid hormone, which plays a crucial role in early human development"

University of Victoria Oct 2006 media release about Dr. Caren Helbing's findings Published in Aquatic Toxicology

EDC/PPCP Occurrence in Surface Waters

Category	Compounds	Frequency Detected
Steroids (fecal indicators)	Coprostanol Cholesterol	86% 85%
Insect Repellent	DEET	75%
Nonprescription Stimulant Nonprescription Nicotine Metabolite Nonprescription Stimulant Metabolite	Caffeine Cotinine 1,7-dimethylxanthine	60% 38% 30%
Fire Retardant	Tri(2-chloroethyl)phosphate	58%
Antimicrobial Household Disinfectant	Triclosan	58%
Detergents	4-Nonylphenol 4-Nonylphenol monoethoxylate 4-Octylphenol monoethoxylate 4-Nonylphenol diethoxylate	52% 46% 44% 38%
Plasticizers	Ethanol-2-butoxy-phosphate	46%
Polymer Ingredient	Bisphenol-A	42%
Antioxidants (food preservatives)	5-methyl-1H-benzotriazole	33%
Polyaromatic Hydrocarbons	Fluoranthene* Pyrene*	31% 29%
Antibiotics	Trimethoprim	27%

*Priority Pollutant compound

Source: Kolpin et. al., 2001

N-Nitrosodimethylamine

- Known animal/ potential human carcinogen
- California list of cancer-causing chemicals
- California Notification Level = 10 ppt (trillion)
- No federal or state MCL
- USEPA ambient water criterion = 1.4 ppt

Sources of NDMA and Precursors

- Industrial manufacturing by-product, rocket fuel decomposition product
- Root control & metals treatment chemicals
- Unidentified nitrogen species
- Median ~80 ppt (trillion) in primary effluent, removal by conventional treatment not consistent
- Byproduct of chlorination (specifically chloramination)
- Polymers for coagulation

Trihalomethanes

- Chlorinated organic compounds
- Potential carcinogens
- Produced during free chlorination
- Regulated in drinking water

Four THMs of Concern in Florida

	Discharge Limit (ug/L or ppb)
• Chloroform	<80
• Bromoform	-
• Dichlorobromomethane	<22
• Dibromochloromethane	<34

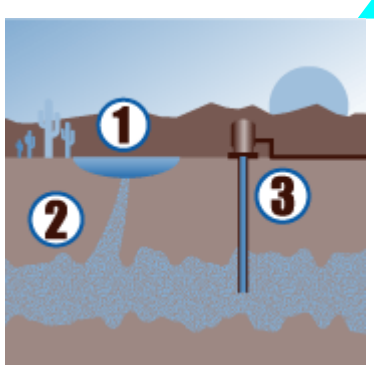
Pathway for Microconstituents passes through WWTPs

Treated
Effluent Discharge

Microconstituents

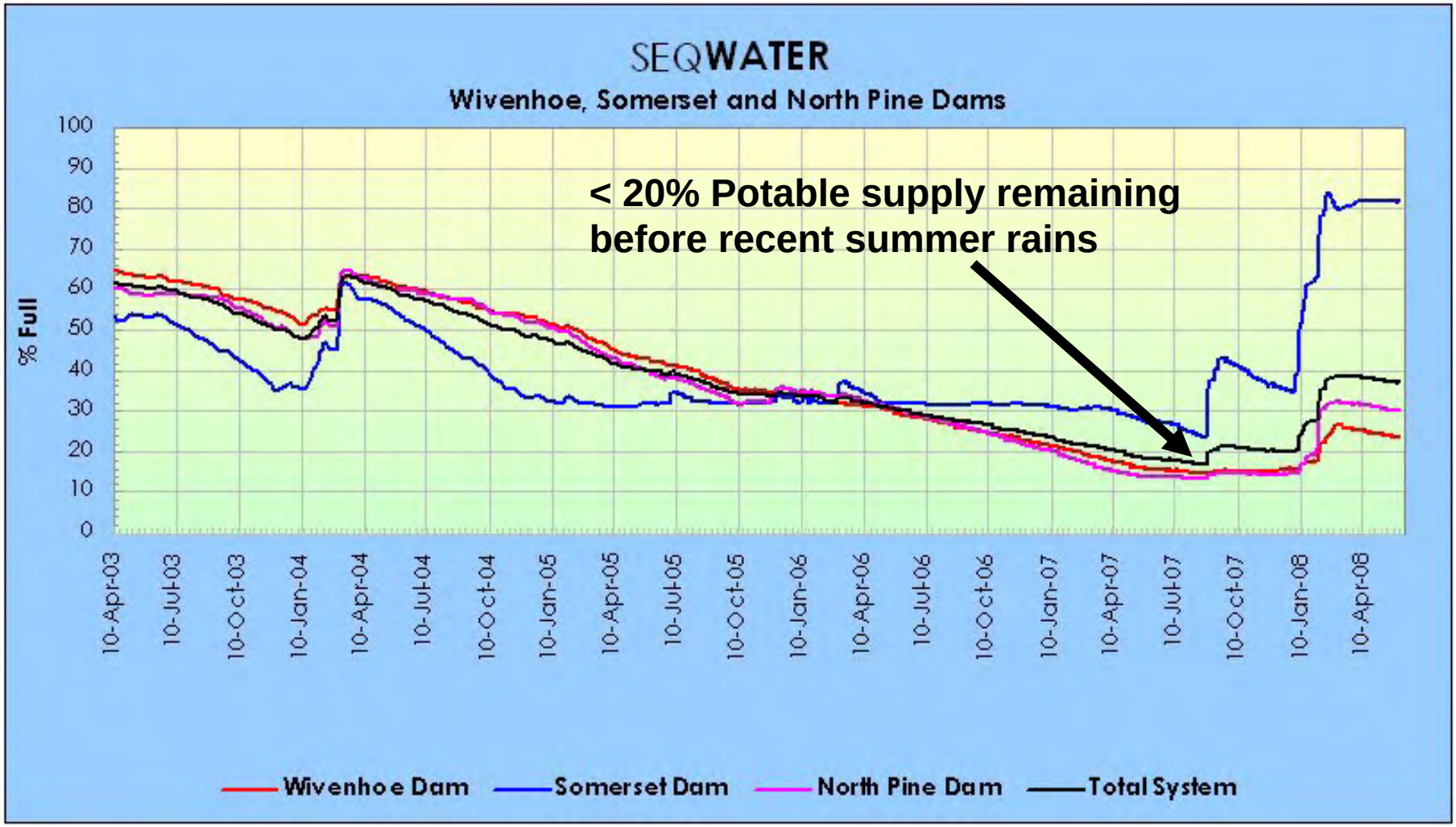
POTW
(Point
Source)

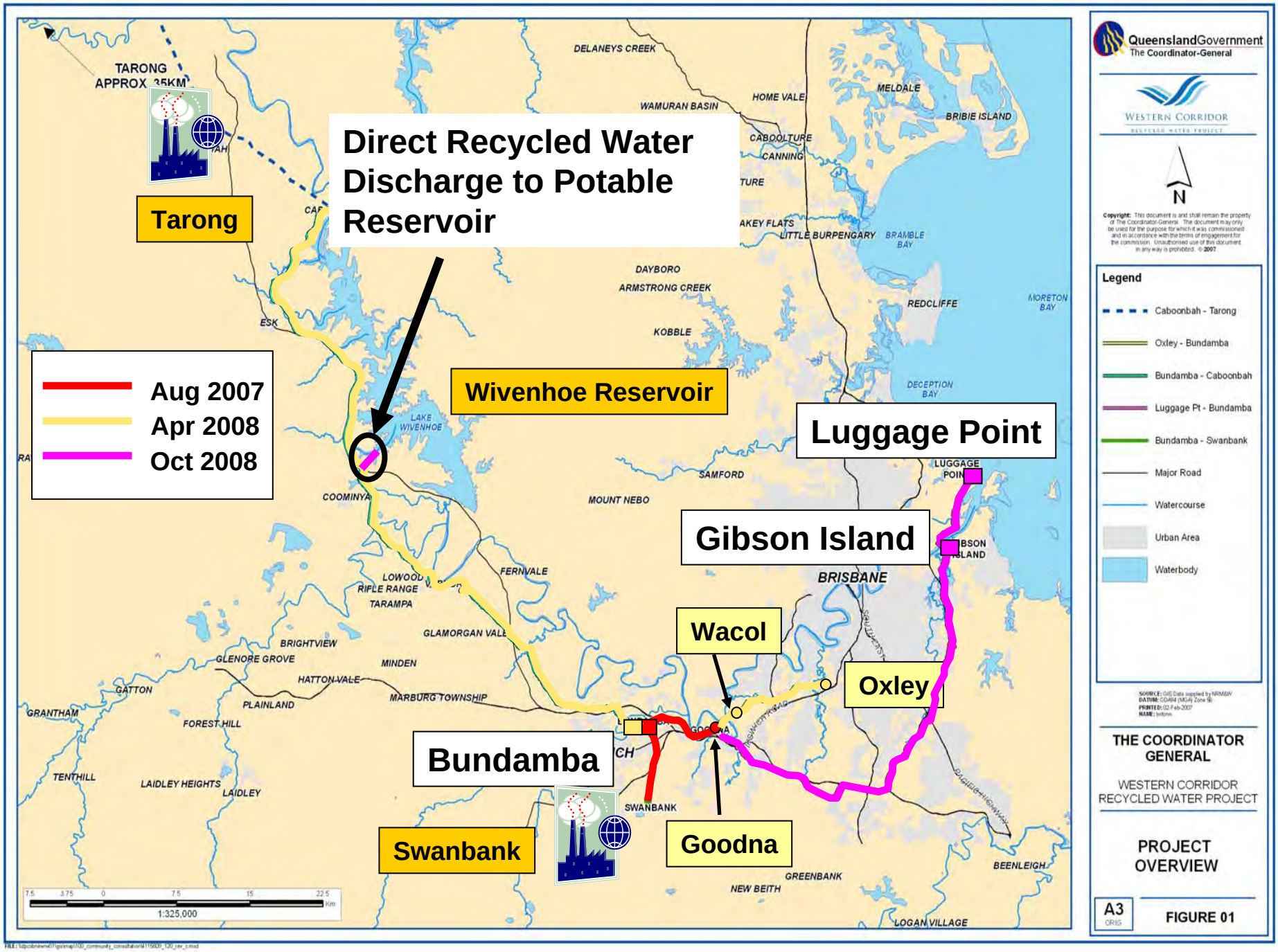
Groundwater
Recharge



Irrigation/
Biosolids
reuse

Recent Draught Conditions in Australia





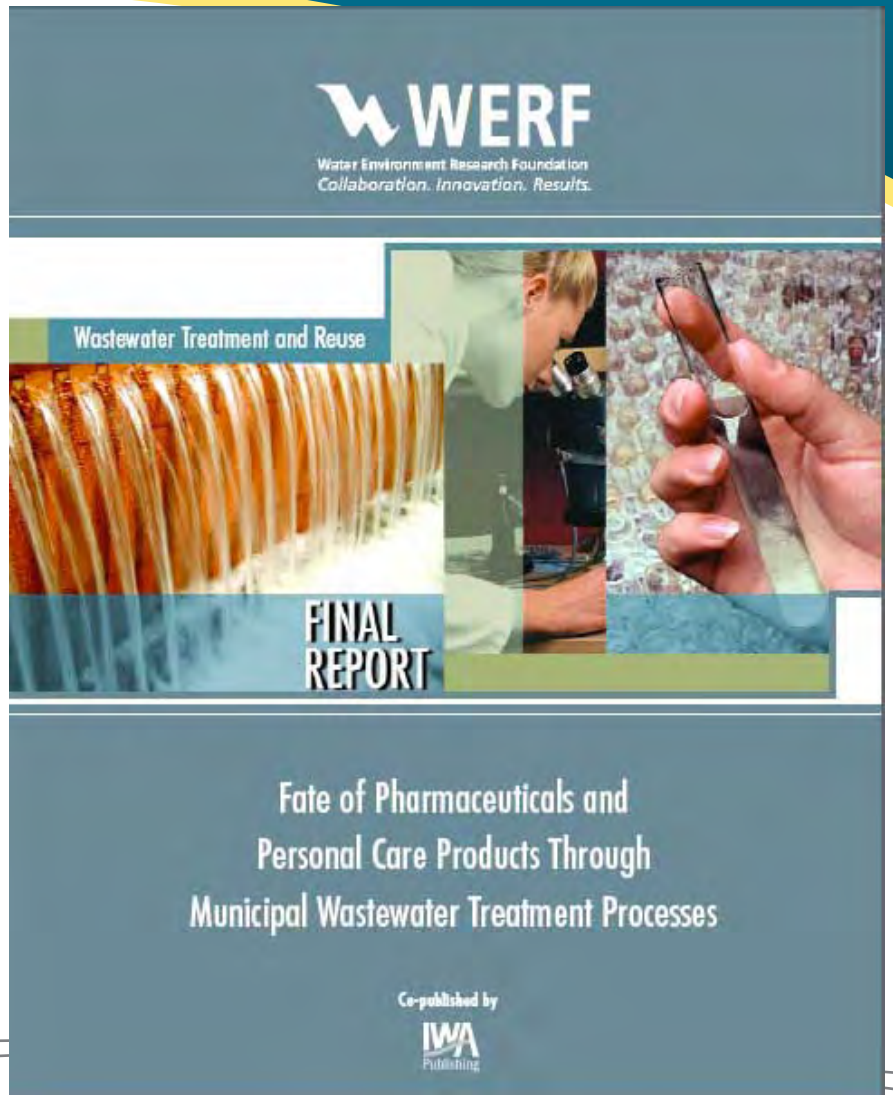
Direct Recycled Water Discharge to Potable Reservoir
Tarong
Wivenhoe Reservoir
Luggage Point
Gibson Island
Wacol
Oxley
Bundamba
Goodna
Swanbank
Aug 2007
Apr 2008
Oct 2008
TARONG APPROX 35KM
DELANEYS CREEK
WAMURAN BASIN
HOME VALE
MELDALE
BRIBIE ISLAND
CABOOLTURE
CANNING
LITTLE BURPENGARY
BRAMBLE BAY
DAYBORO
ARMSTRONG CREEK
KOBBLE
REDCLIFFE
MORETON BAY
DECEPTION BAY
ESK
LAKE WIVENHOE
COOMINYA
SAMFORD
MOUNT NEBO
LUGGAGE POINT
BRISBANE
FERNVALE
LOWOOD
RIFLE RANGE
TARAMPA
GLAMORGAN VALE
BRIGHTVIEW
GLENORE GROVE
MINDEN
HATTON VALE
MARBURG TOWNSHIP
GATTON
PLAINLAND
GRANTHAM
FOREST HILL
TENTHILL
LAIDLEY HEIGHTS
LAIDLEY
SWANBANK
GREENBANK
NEW BEITH
BEENLEIGH
LOGAN VILLAGE
1:325,000
QueenslandGovernment
The Coordinator-General
WESTERN CORRIDOR
RECYCLED WATER PROJECT
N
Legend
Caboonbah - Tarong
Oxley - Bundamba
Bundamba - Caboonbah
Luggage Pt - Bundamba
Bundamba - Swanbank
Major Road
Watercourse
Urban Area
Waterbody
THE COORDINATOR GENERAL
WESTERN CORRIDOR RECYCLED WATER PROJECT
PROJECT OVERVIEW
A3
FIGURE 01

Outline of Discussion

- Microconstituents
- **Conventional Treatment for Reuse**
- Membrane Treatment
- Disinfection

Fate of Pharmaceuticals and Personal Care Products Through Municipal WWTPs

- WERF Report 03-CTS-22UR
- Published 2007 and available through www.WERF.org

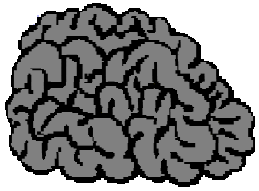


Acknowledgements

- Joan Oppenheimer, MWH, Co-PI
- WERF ($125K funding to support $65K in-kind)

- Participating Facilities
  - 6 full-scale plants in CA and NM
  - 2 pilot-scale MBR systems

- Analytical Support
  - Dr. Greg Loraine of Dynaflow (MD)



- Technical Advisors
  - Shane Snyder, David Sedlak, Rolf Halden, John Novak, Rhodes Trussell, Neil Park, Bernard Sawyer, Kenneth Banks

Key Aspects of the Work

- Evaluate passage of target PPCPs through a variety of activated sludge processes
- Three discrete sampling events at each facility
- Limited to aqueous phase treatment
- Focus on impact of treatment process SRT

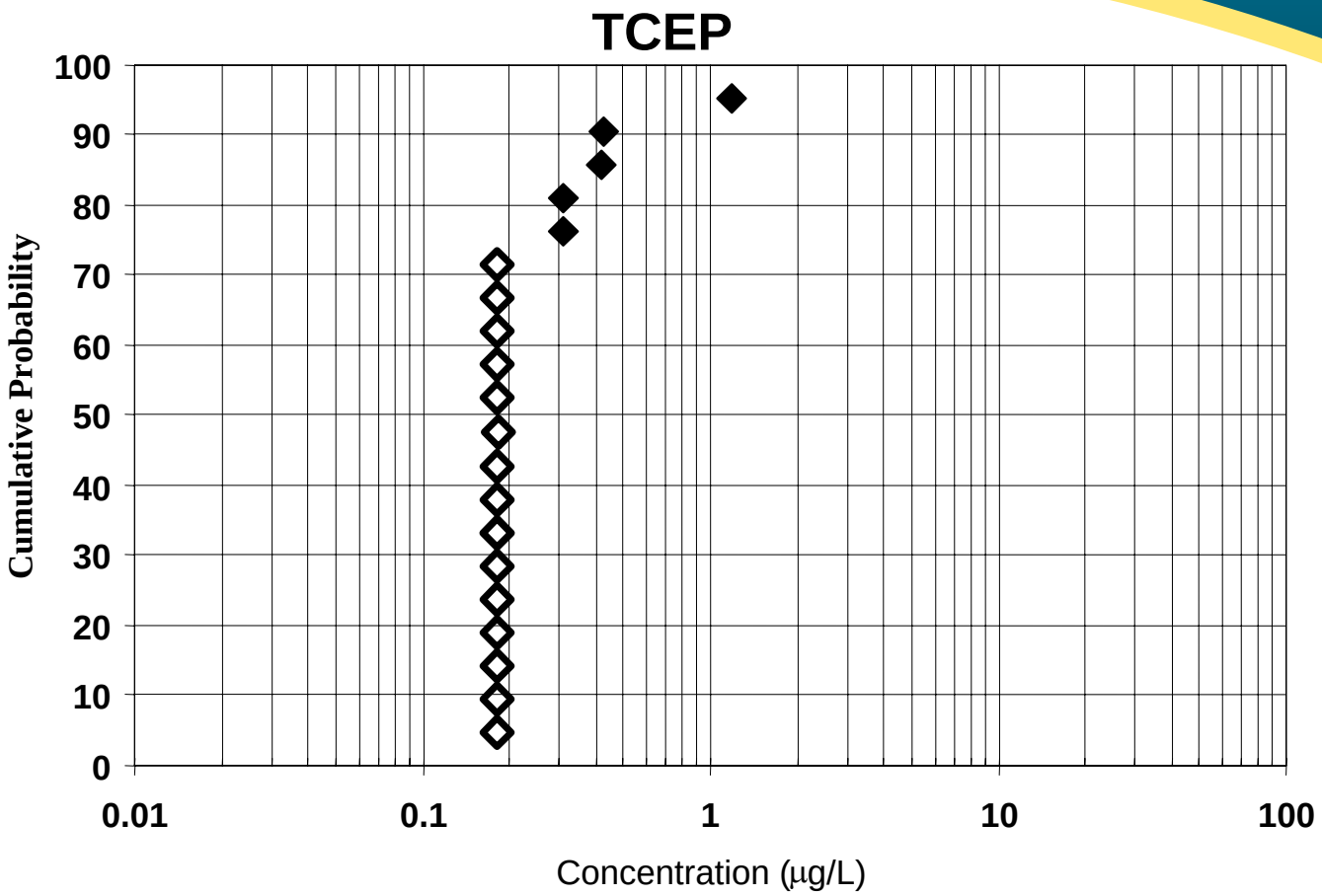
Participating Treatment Facilities

Facility	Primary Treatment	Secondary Treatment	Secondary Aeration	MLSS (mg/L)	SRT (days)	Filters	Disinfection
A	Polymer Ferric	Activated Sludge	Pure Oxygen	1,300 to 2,600	0.5 - 1.5	None	None
B	No Chemicals	MLE Nit/Denit	Diffused Air	1,800 to 2,000	3 - 5	Granular Deep Bed	Chlorine
C	No Chemicals	Activated Sludge	Diffused Air	2,000 to 3,000	4 - 6	Granular Deep Bed	UV
D	No Chemicals	MLE Nit/Denit	Diffused Air	2,500 – 3,000	7 - 20	Granular Deep Bed + MF/RO	Chlorine
E	No Chemicals	Nit/Denit and Pilot MBR	Diffused Air	2,100	11 - 16	None	UV
F	None	Extended Aeration Nit/Denit	Surface Air	4,000	20 - 30	Granular Deep Bed	UV

Target List of PPCPs

Fragrance	Galaxolide, Musk ketone, 3-phenylpropionate, Ethyl 3-phenylpropionate, Methyl 3-phenylpropionate
Sunscreen	Benzophenone, Octyl methoxycinnamate, Oxybenzone, Benzyl salicylate
Pharmaceutical	Ibuprofen, Caffeine
Germicide	Triclosan, Chloroxylenol
Fire Retardant	Trichloroethylphosphate, Triphenylphosphate
Anti-Oxidant	Methylparaben, Butylated hydroxyanisol
Plasticizer	Butylbenzylphthalate
Insect Repellent	DEET
Surfactant	Octylphenol

Example Combined Influent Data Set (All Plants)



(◇--- Below MDL; ♦ --- Above MDL)

Influent Data Grouped into Occurrence Bins

Bin Number	Description	Bin Assignment Criteria
O1	Infrequent Occurrence	Detected < 25%
O2	Intermediate Occurrence	25% ≤ Detected ≤ 75%
O3	Frequent Occurrence	Detected > 75%

Target PPCPs Grouped by Occurrence Bin

BIN	COMPOUNDS	Concentration (μg/L) 50th percentile
O1	(1) Triphenylphosphate	ND
	(2) Octylphenol	ND
	(3) Methyl-3-phenylpropionate	ND
	(4) TCEP	ND
O2	(1) Musk Ketone	ND
	(2) Ethyl-3-phenylpropionate	0.12
	(3) BHA	0.070
	(4) DEET	0.026
O3	(1) Methylparaben	3.0
	(2) Benzyl salicylate	0.45
	(3) Chloroxylenol	0.52
	(4) Triclosan	5.2
	(5) Octylmethoxycinnamate	1.4
	(6) Butylbenzyl phthalate	2.0
	(7) Benzophenone	0.94
	(8) Galaxolide	1.9
	(9) Ibuprofen	6.3
	(10) Oxybenzone	1.9
	(11) Caffeine	1.9
	(12) 3-phenylpropionate	205

Treatment Bins Summarize Removals

Bin Number	Description	Bin Assignment Criteria
T1	Good Removal	Median Removal > 80%
T2	Moderate Removal	50% ≤ Median Removal ≤ 80%
T3	Poor Removal	Median Removal < 50%

PPCP Occurrence and Treatment Summary

Treatment / Occurrence	Bin TI Good Removal	Bin T2 Moderate Removal	Bin T3 Poor Removal
Bin O1 Infrequent	Methyl-3-phenyl-propionate	Octylphenol	TCEP Triphenyl-phosphate
Bin O2 Intermediate		Ethyl-3-phenyl-propionate	BHA DEET Musk Ketone
Bin O3 Frequent	9 compounds	Triclosan Benzophenone	Galaxolide

PPCP Occurrence and Treatment Summary

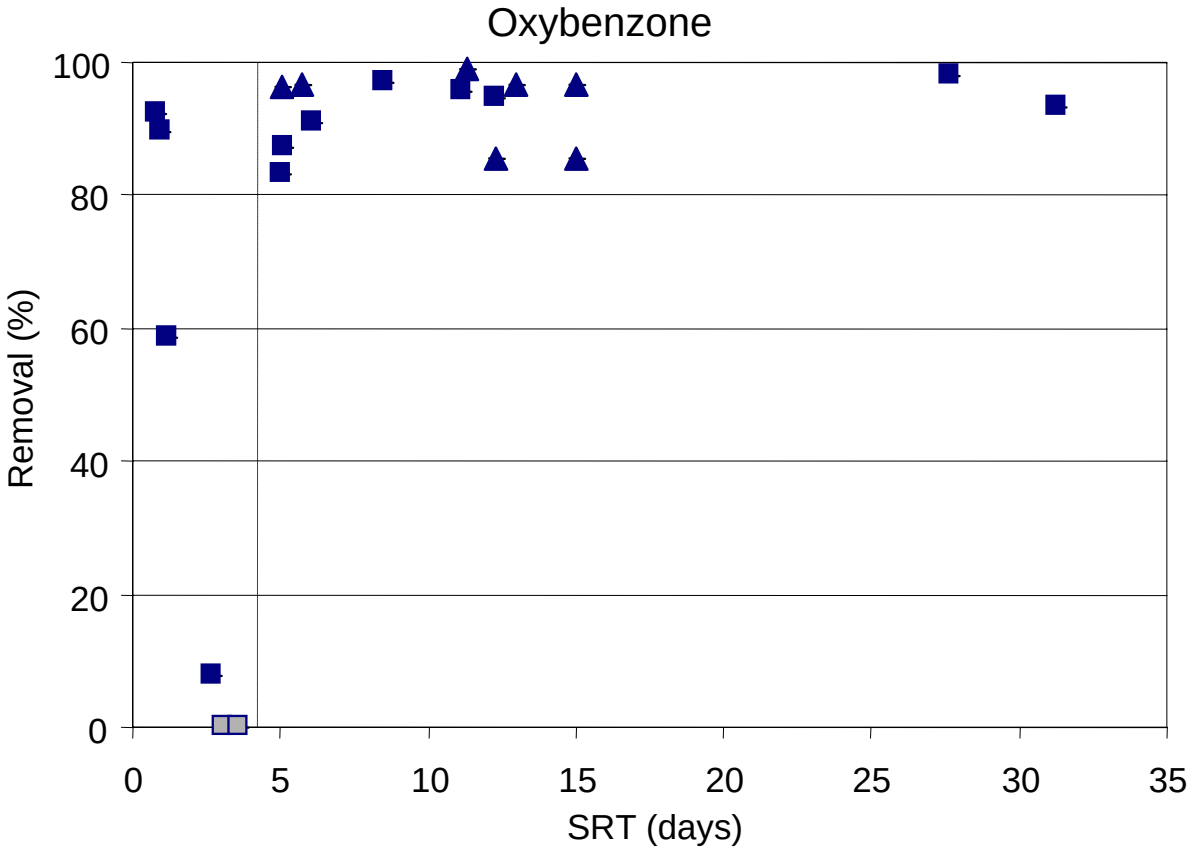
Treatment / Occurrence	Bin TI Good Removal	Bin T2 Moderate Removal	Bin T3 Poor Removal
Bin O1 Infrequent	Me phen		
Bin O2 Intermediate			
Bin O3 Frequent	9 con		

- Caffeine
- Ibuprofen
- Oxybenzone
- Chloroxylenol
- Methylparaben
- Benzyl salicylate
- 3-phenylpropionate
- Butylbenzylphthalate
- Octylmethoxycinnamate

Occurrence and Treatment Summary

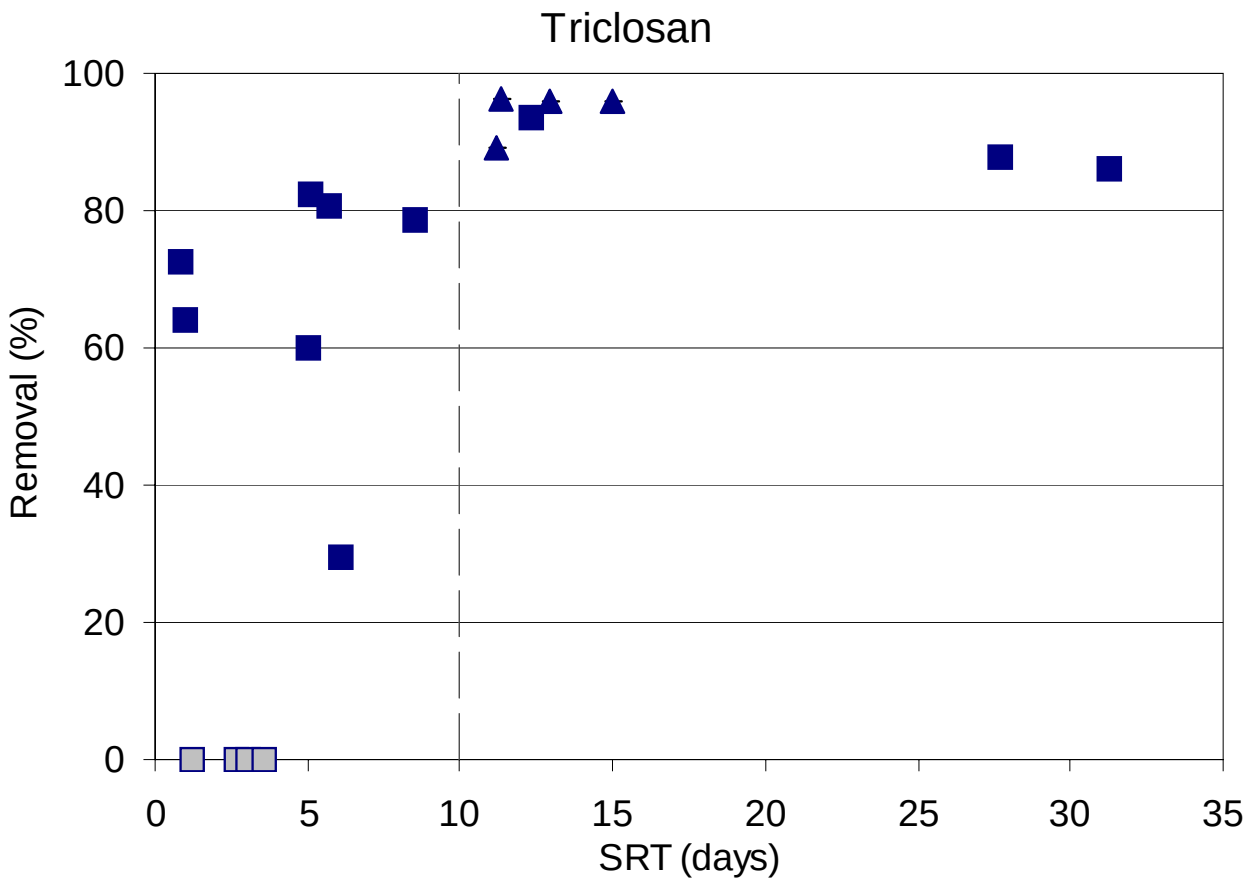
Treatment / Occurrence	Bin TI Good Removal	Bin T2 Moderate Removal	Bin T3 Poor Removal
Bin O1 Infrequent	Methyl-3-phenyl-propionate	Octylphenol	TCEP Triphenyl-phosphate
Bin O2 Intermediate		Ethyl-3-phenyl-propionate	BHA DEET Musk Ketone
Bin O3 Frequent	9 compounds	Triclosan Benzophenone	Galaxolide

SRT at 80% Removal for Oxybenzone (Bin T1)



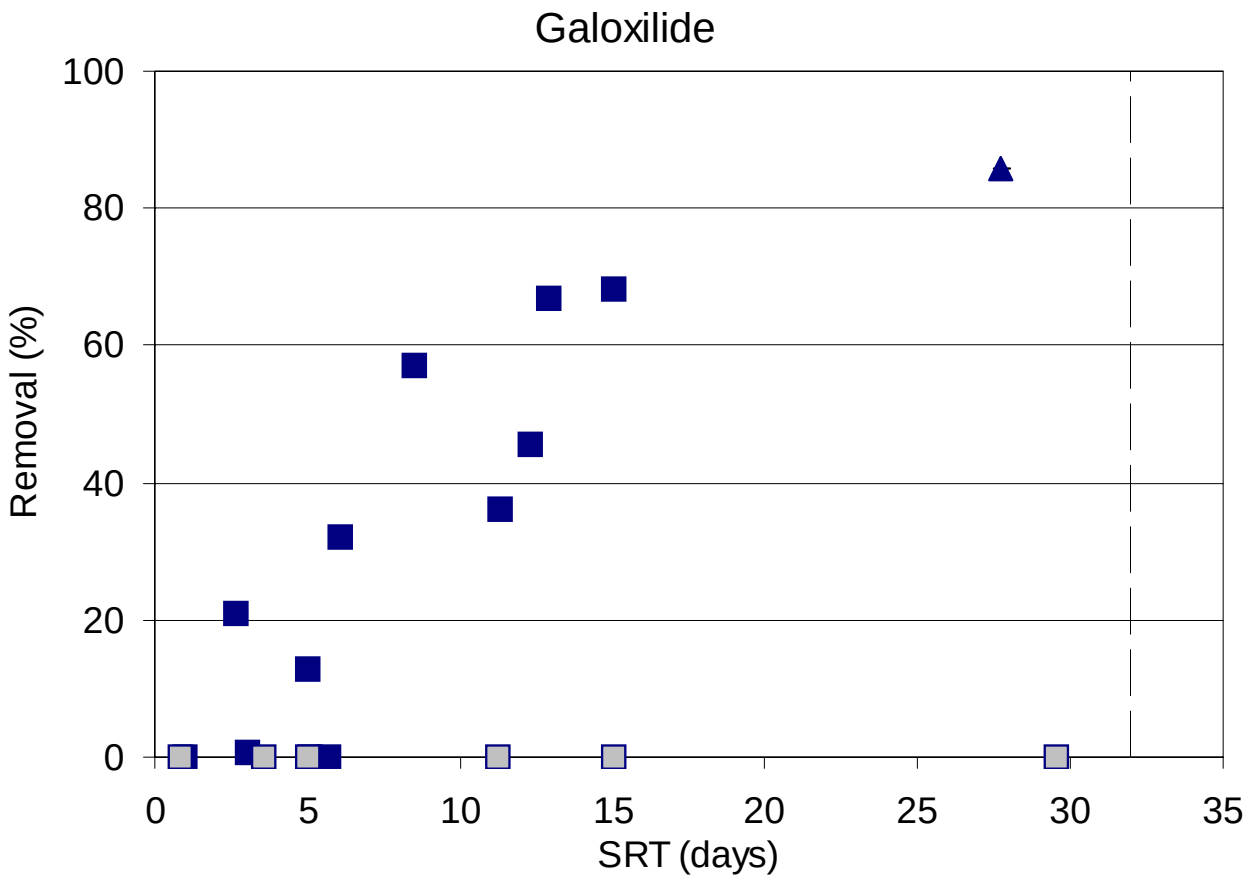
■ = Actual Removal ▲ = Removal greater than percentage value ▢ = Effluent > Influent

SRT at 80% removal for Triclosan (Bin T2)



■ = Actual Removal ▲ = Removal greater than percentage value ▢ = Effluent > Influent

SRT for 80% removal for Galaxolide (Bin T3)



■ = Actual Removal ▲ = Removal greater than percentage value ▢ = Effluent > Influent

Conclusion: Removal Dependent on SRT

- $SRT_{80} \leq 5$ days for Bin T1 compounds (10)
- $5 \leq SRT_{80} \leq 15$ days for Bin T2 compounds (2)
- $SRT_{80} \geq 15$ days for Bin T3 compounds (6)
- Notes
  - Insufficient data for octylphenol and triphenylphosphate
  - SRT (a measure of total biomass) and HRT (measure of reaction time) are not mutually exclusive

Outline of Discussion

- Microconstituents
- Conventional Treatment for Reuse
- **Membrane Treatment**
- Disinfection

Tertiary Treatment Results from WERF Study Plant F - GMF, Plant D – GMF with MF/RO

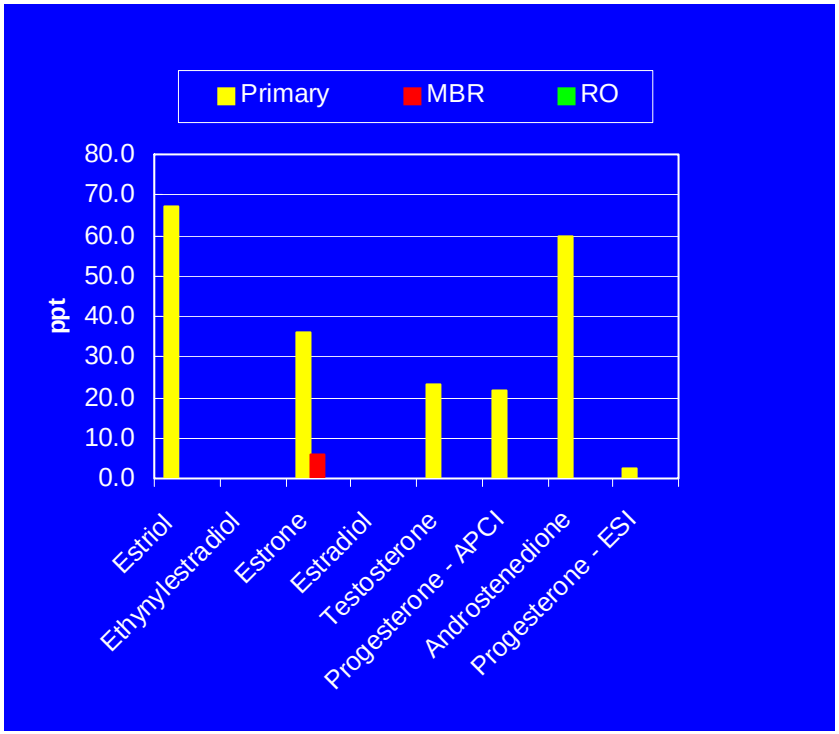
	Plant F	Plant D
Chloroxylenol	-27%	ND
Methylparaben	>97%	ND
DEET	26%	0.050
Benzophenone	-88%	ND
TCEP	-17%	ND
Galaxolide	-18%	ND
Musk Ketone	12%	ND
Oxybenzone	0%	ND
Triclosan	15%	ND

Pilot Test Results for Integrated Membrane Systems

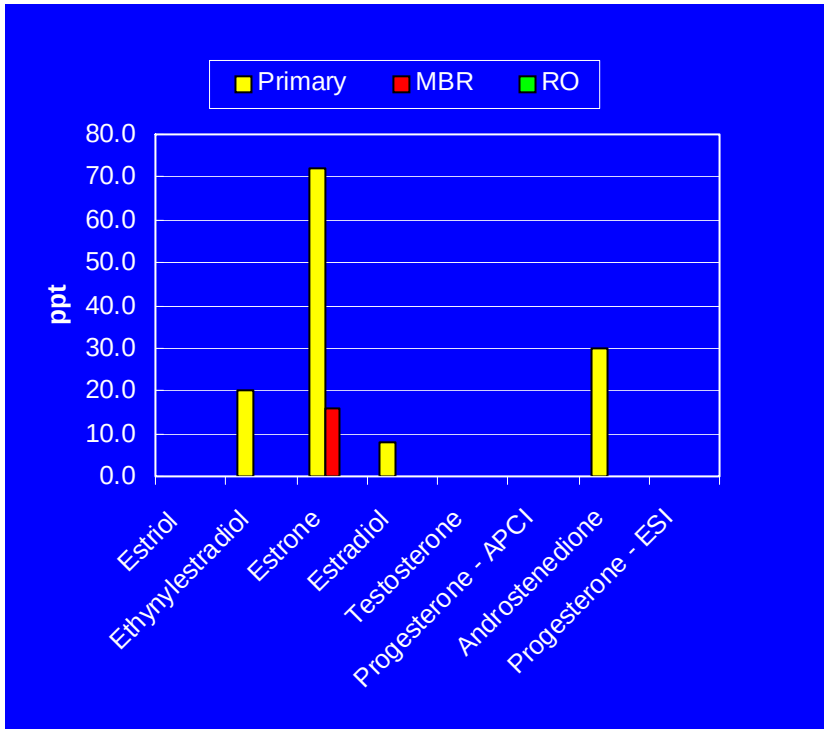
- Four locations
- Raw and advanced primary followed by membrane bioreactor (MBR) and RO
- Secondary effluent followed by Microfiltration (MF) and RO

MBR/RO Integrated Membrane System (IMS) Pilot Results (Detected Steroids)

California

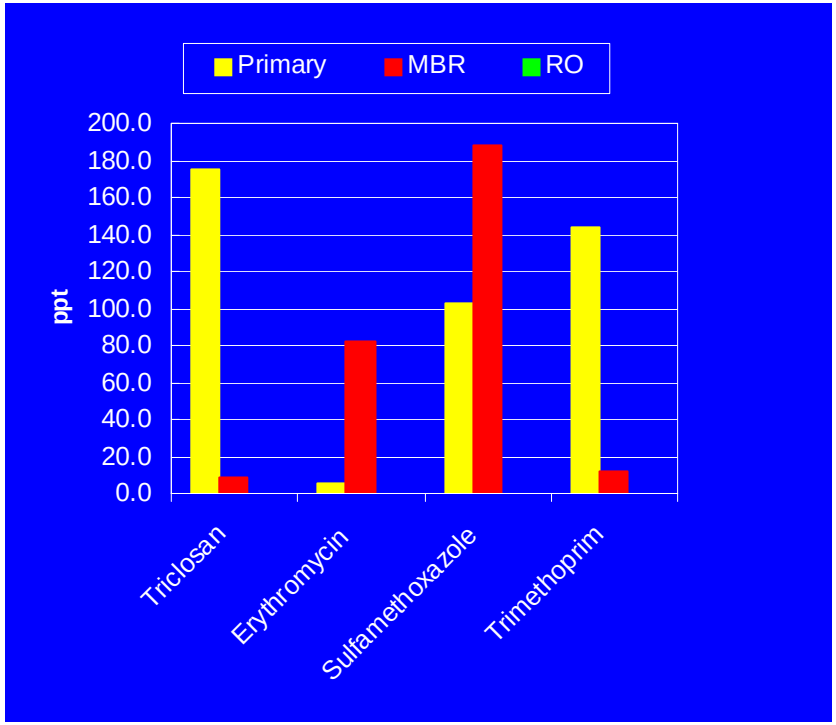


New Mexico

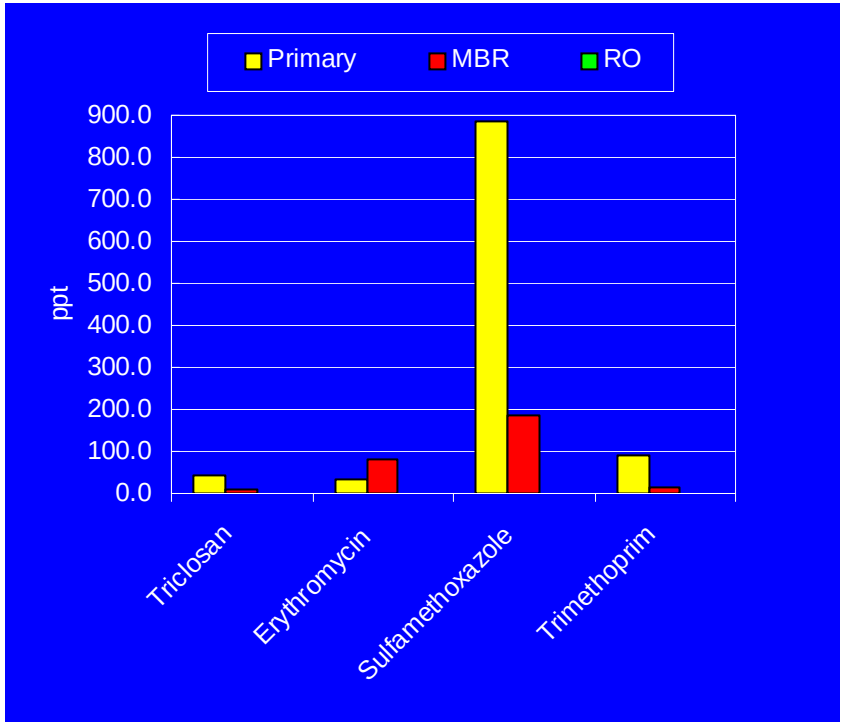


IMS Pilot Results (Detected Anti-Microbials)

California

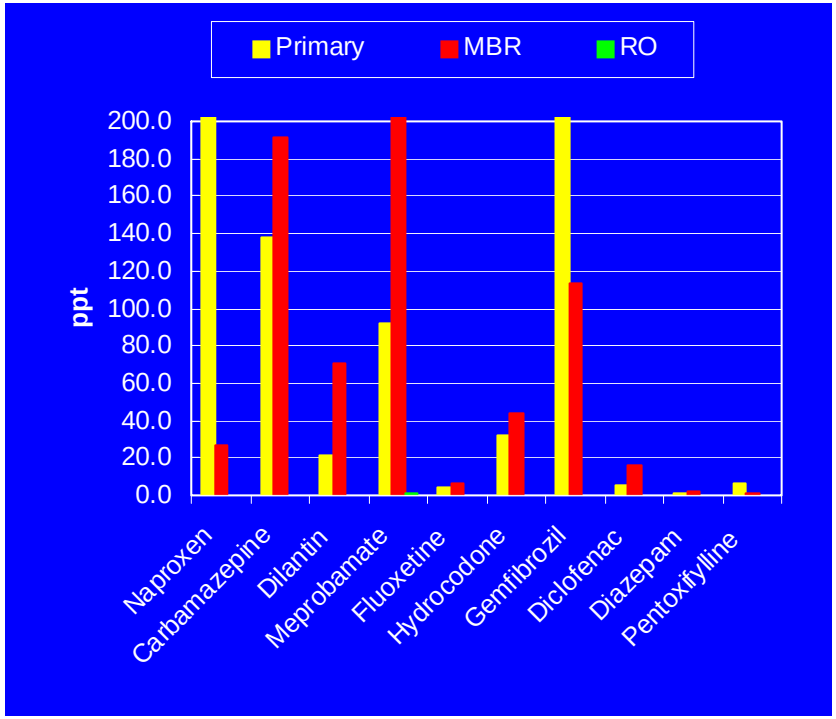


New Mexico

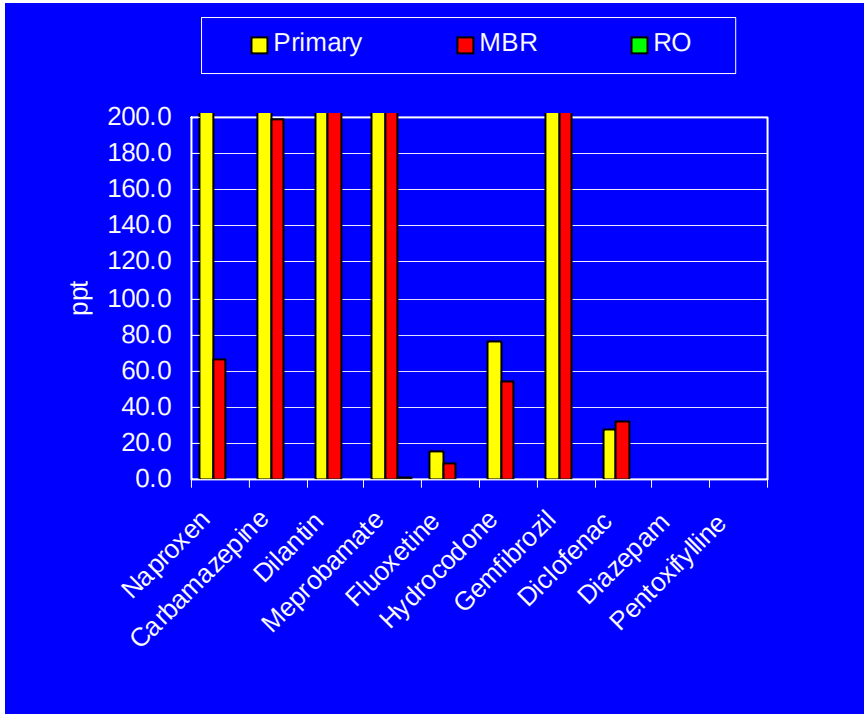


IMS Pilot Results (Detected Pharmaceuticals)

California

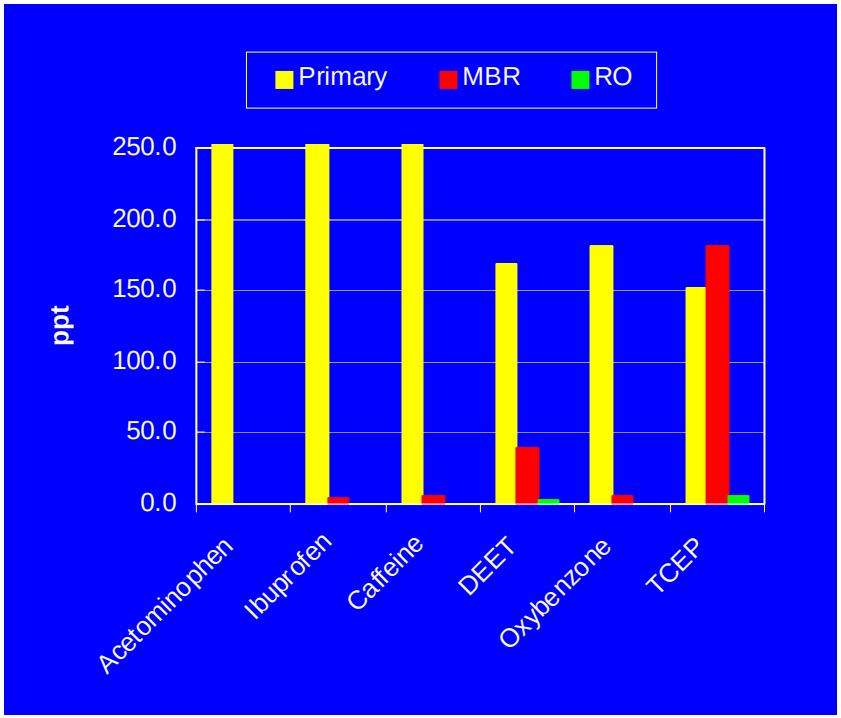


New Mexico

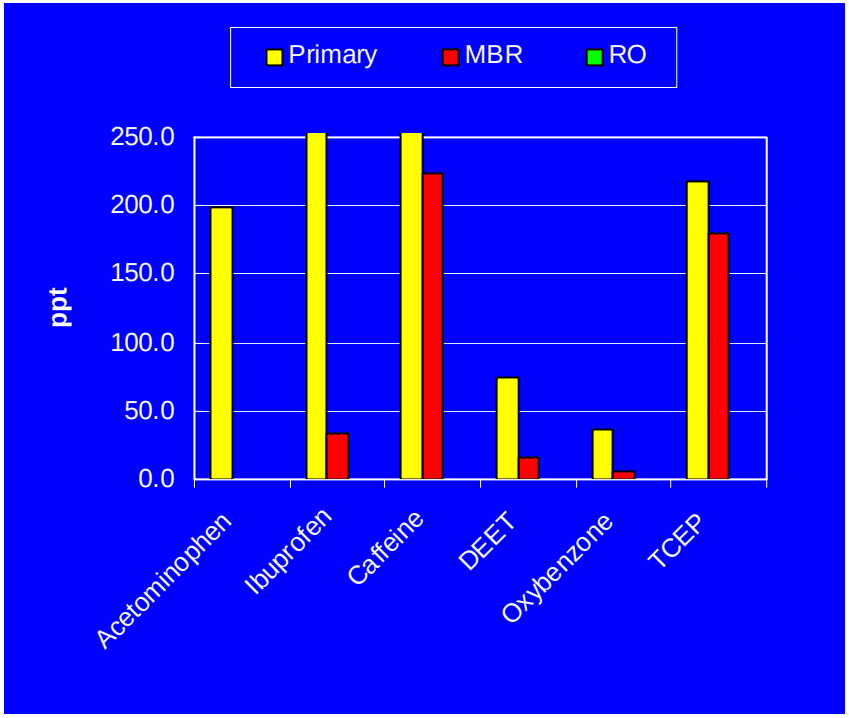


IMS Pilot Results
(Detected Personal Care Products)

California



New Mexico



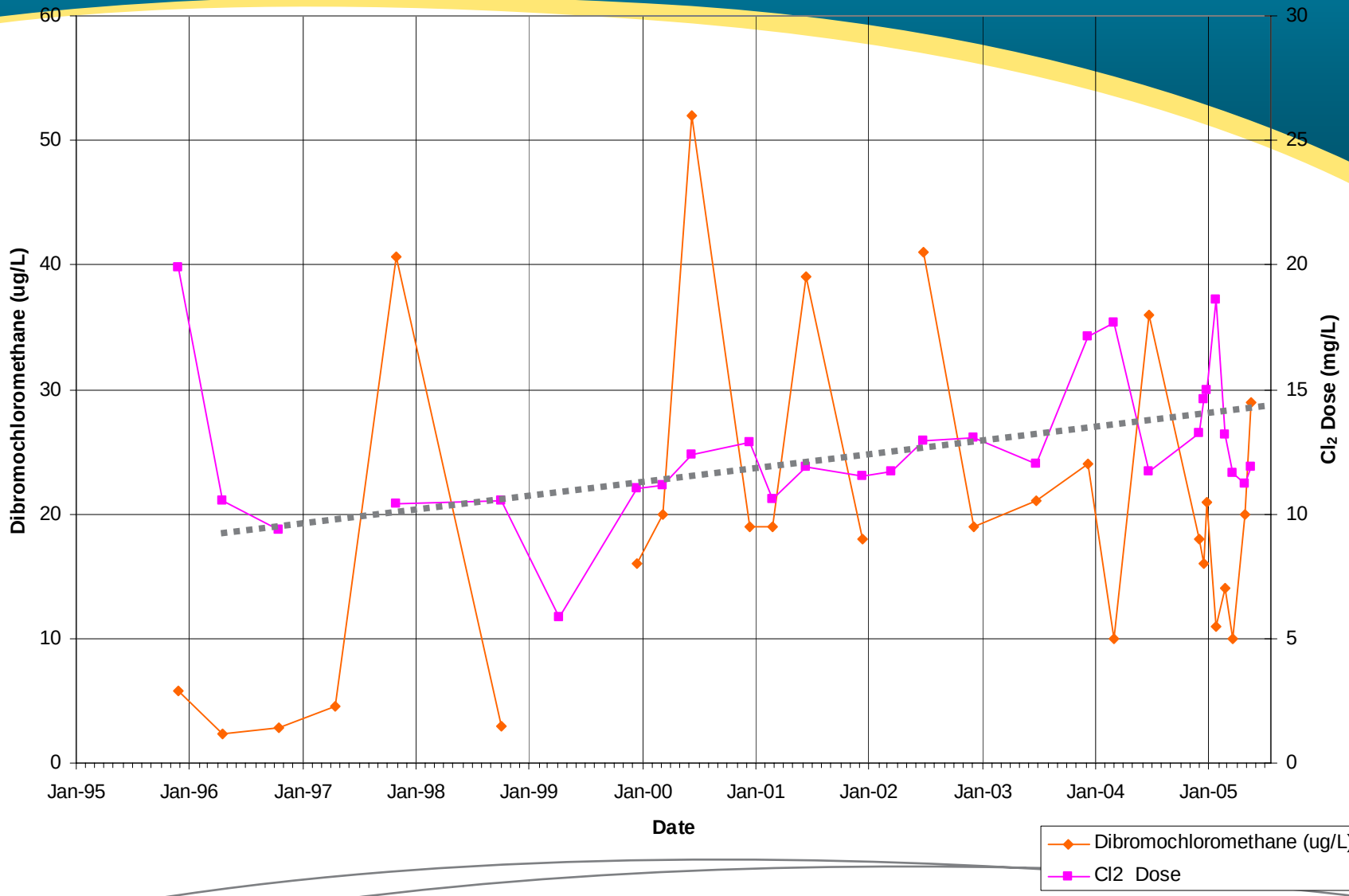
Conclusions for Membrane Systems

- Membrane bioreactors and microfiltration systems do not improve removals of microconstituents above what the activated sludge microorganisms can achieve
- Reverse osmosis is an effective barrier

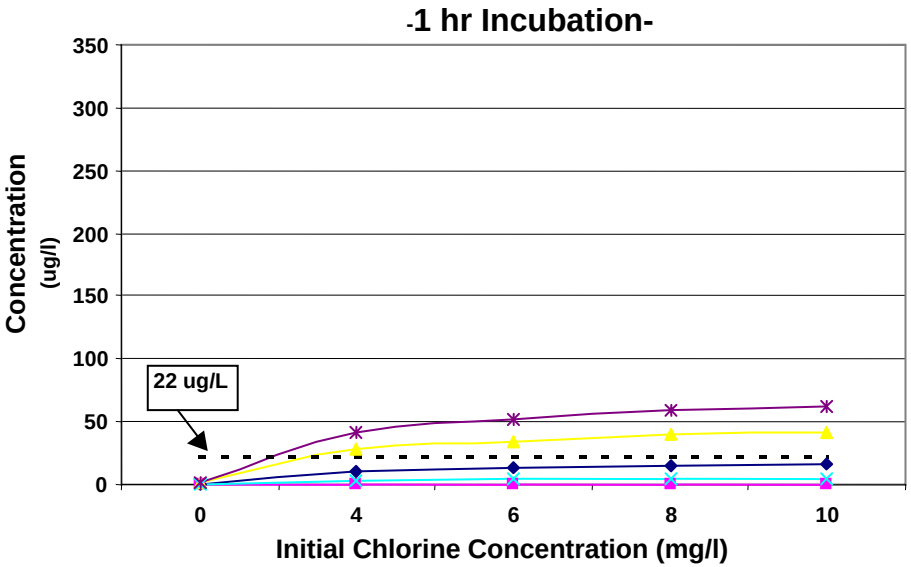
Outline of Discussion

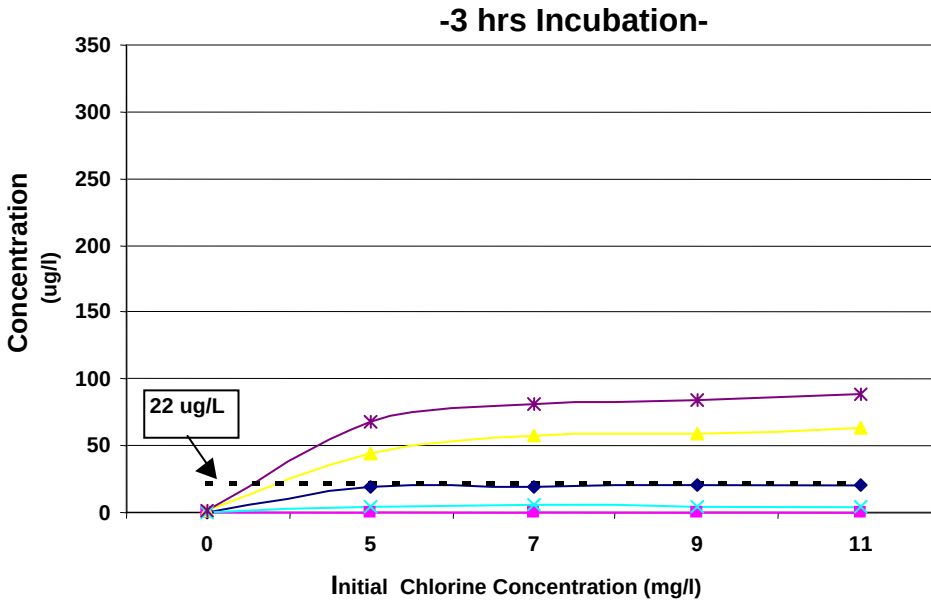
- Microconstituents
- Conventional Treatment for Reuse
- Membrane Treatment
- **Disinfection**

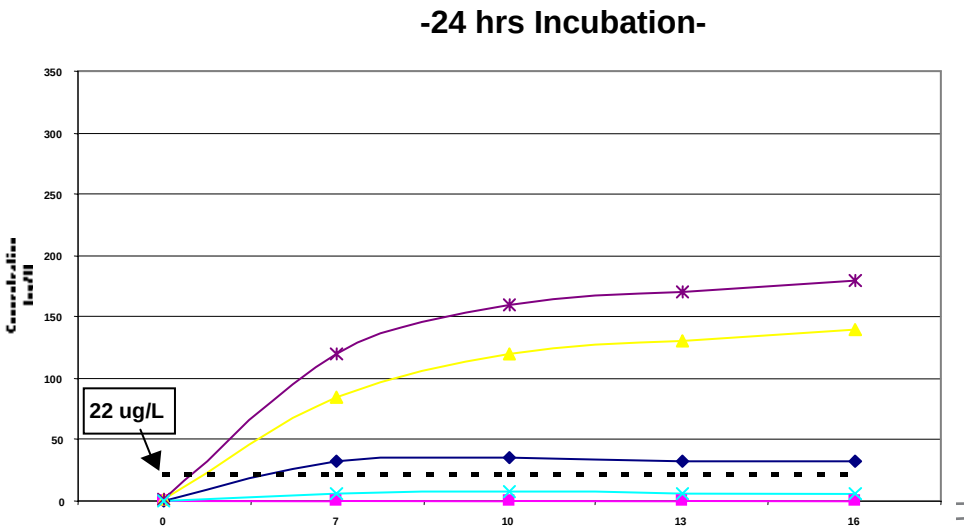
THMs Increase with Cl_2 Dose

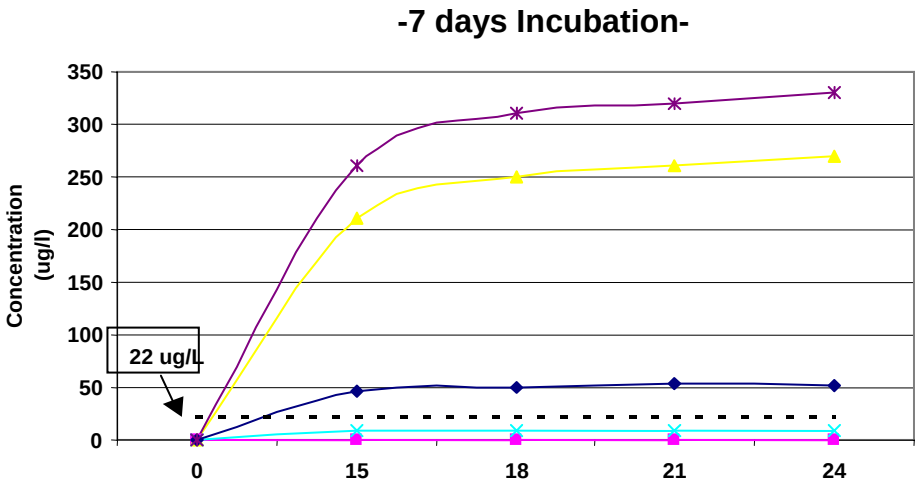


THM Formation at Various Detention Times







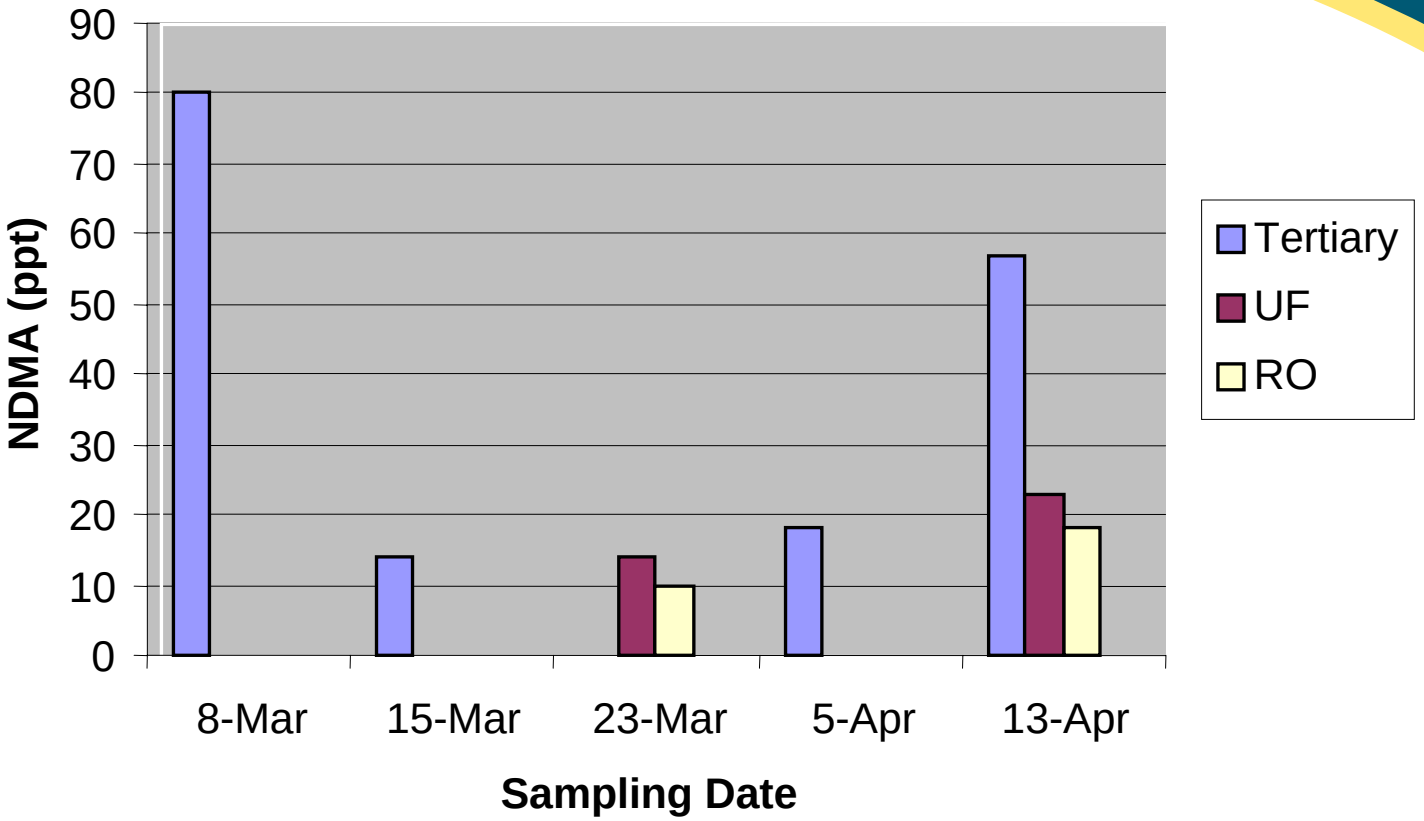


Bromodichloromethane | Dibromochloromethan | Bromoform | Chloroform | TTHM's

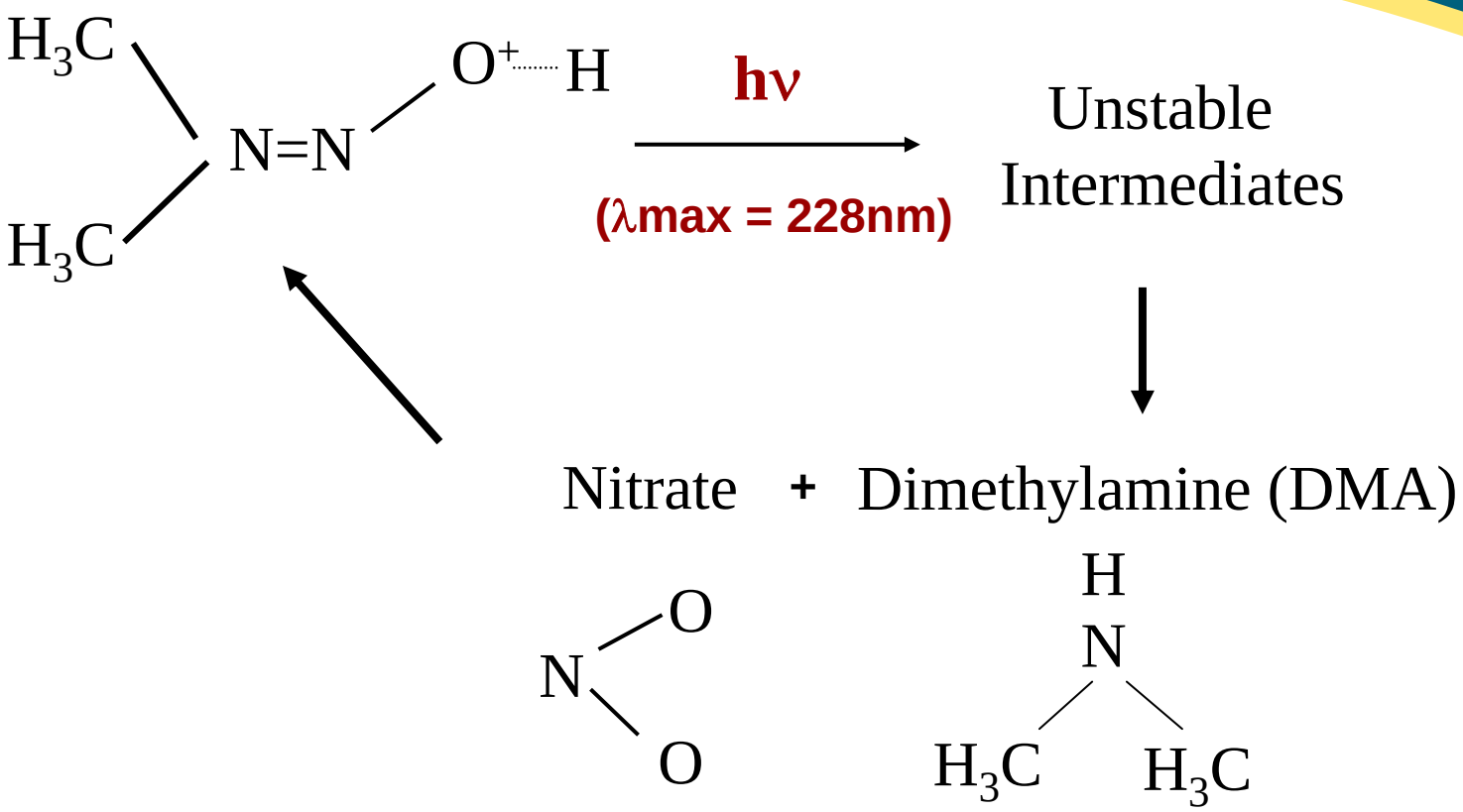
Potential THM Formation Control Methods

- Minimize Cl_2 dose and detention time
  - Disinfection process
  - Distribution system residual
  - Maintenance (algae control)
- Chloramination (Cl_2w/ ammonia)
- Reduce total organic carbon (not practical)
- Air stripping
- Mixing zone considerations, pH control
- Alternative disinfection (UV, Ozone)

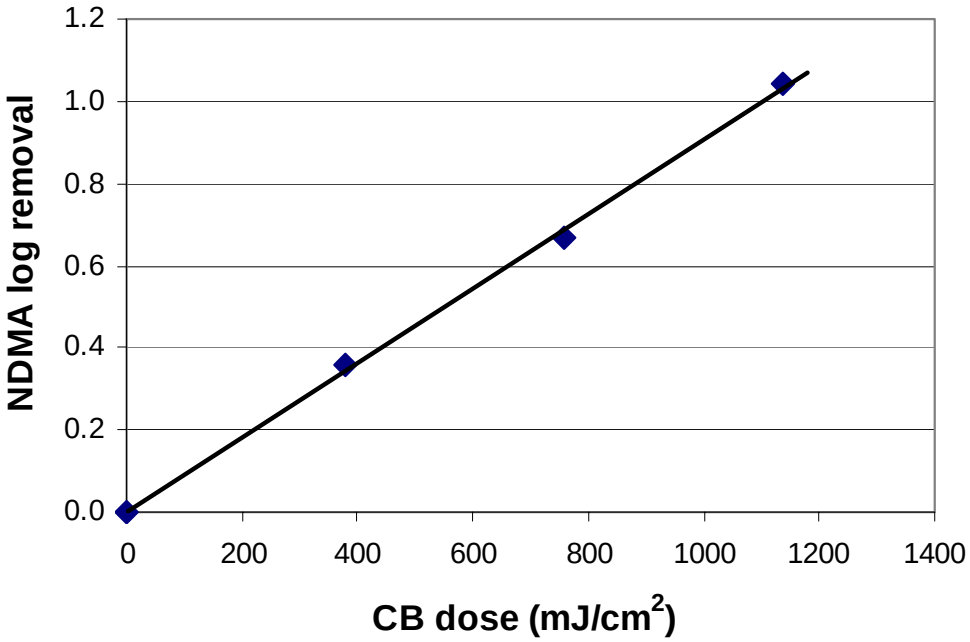
NDMA Removal with Advanced Treatment (Pilot on Filtered Effluent)

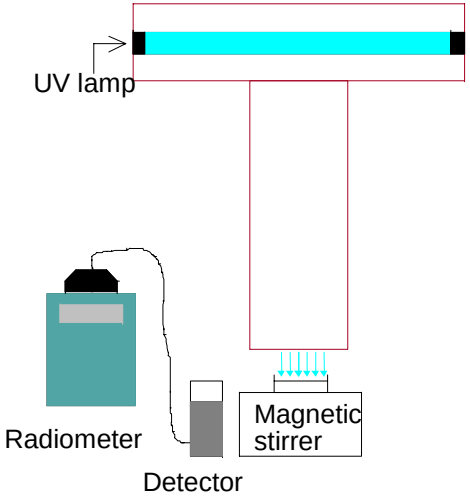


NDMA Treatment by UV for Drinking Water



Collimated Beam Tests Indicate High Dose





Approaches to NDMA Control

- UV dose per log removal = ~1000 mJ/cm^2 is not practical
- Advanced oxidation with UV/Peroxide has no impact on NDMA reduction
- RO results inconclusive
- Source control both external and at the WWTP may be necessary

In Summary

- Microconstituents of interest will be present
- Many microconstituents are removed by conventional activated sludge processes
- Higher SRT systems perform better
- RO is the only effective membrane process
- Disinfection related microconstituents, notably NDMA, present a challenge

Your Questions