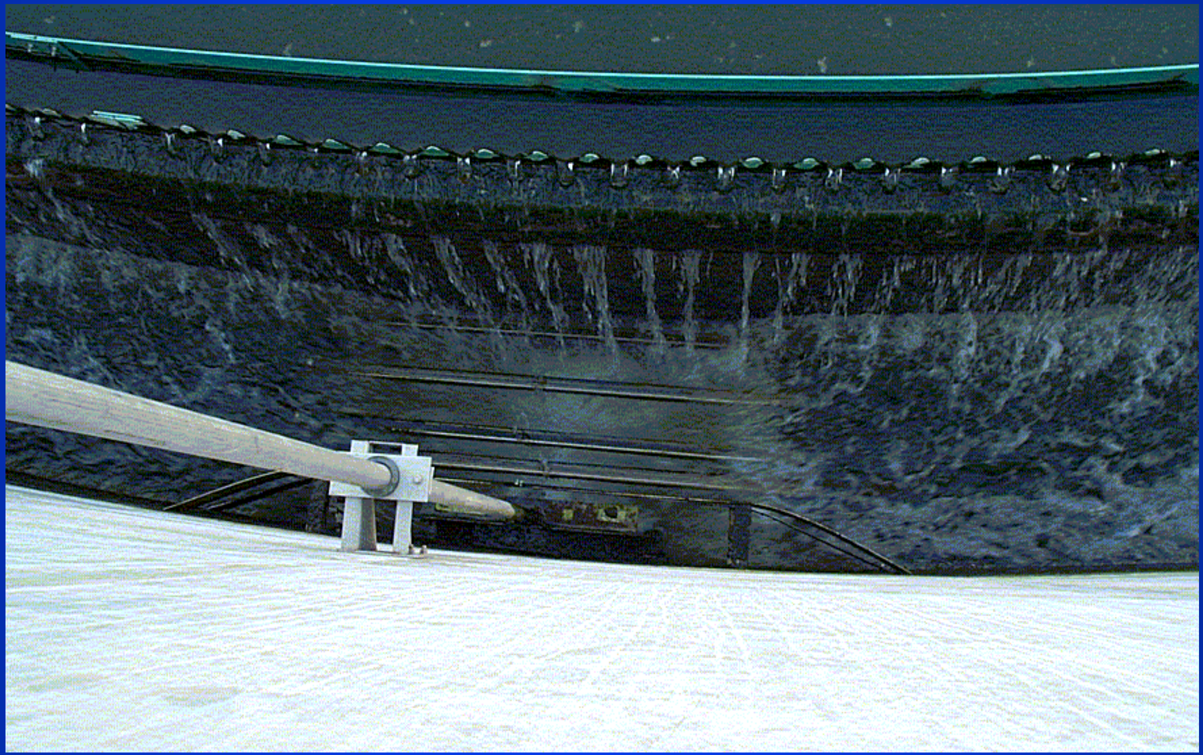
Occurrence and Fate of PPCPs in Wastewater Treatment Processes

Joan Oppenheimer, M.S.P.H., B.C.E.S. (Stantec)



ACKNOWLEDGMENTS

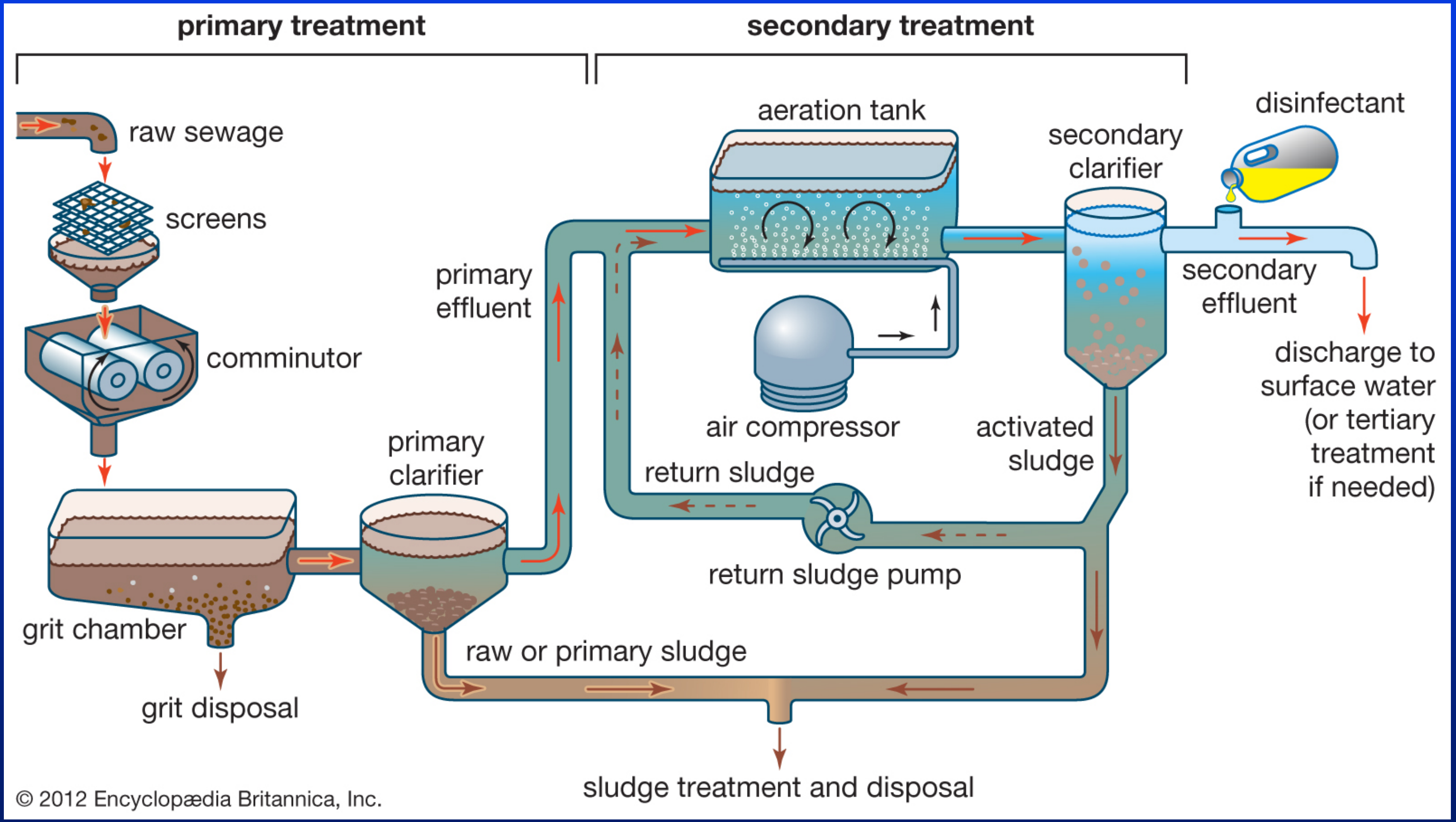
- Water Environment Research Foundation (WERF 03-CTS-22UR)
  "Fate of PPCPs through Municipal Wastewater Treatment Processes"
  (Co-PI : Dr. Roger Stephenson, Stantec)

- WateReuse Foundation (WRF-06-007)
  "Investigation of Membrane Bioreactor Effluent Water Quality and Technology"
  (Co-Sponsors – U.S. Bureau of Reclamation & Global Water Research Coalition)
  (Co-PI : Dr. Bruce Rittmann, Arizona State University

WERF Study
Goals and Objectives

- Survey occurrence/passage of PPCPs through soluble phase of WWTP facilities
  - 3 discrete sampling events @ 6 facilities
- Compare PPCP passage through activated sludge plant and MBR pilot process

Aqueous Wastewater Treatment



Process Descriptions of Participating Treatment Facilities

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

PPCP Occurrence & Treatment Bins: Activated Sludge Process

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**	**Galoxolide**

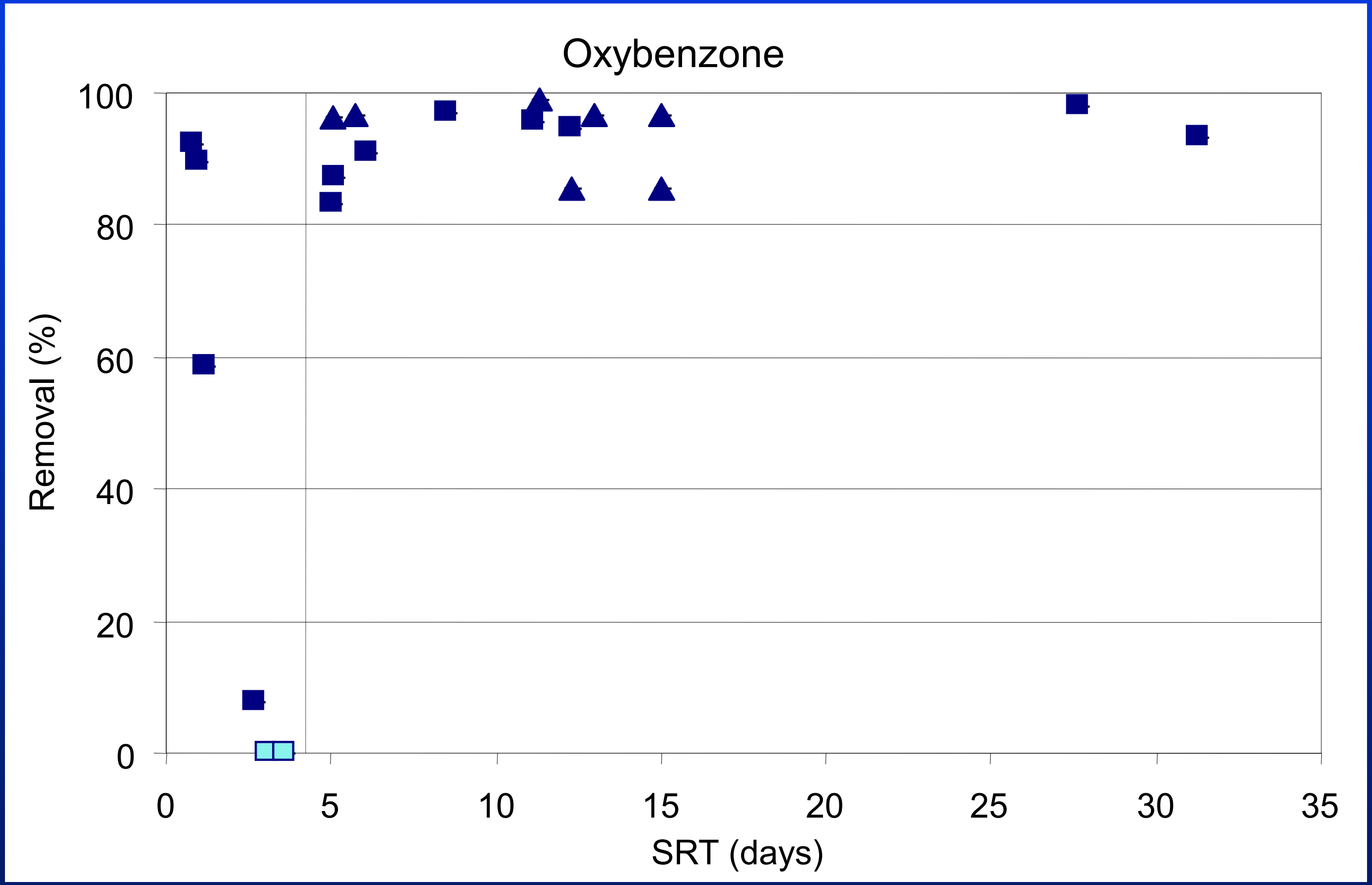
PPCP Occurrence & Treatment Bins – Activated Sludge Process

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

$SRT_{80} \leq 5$ Days

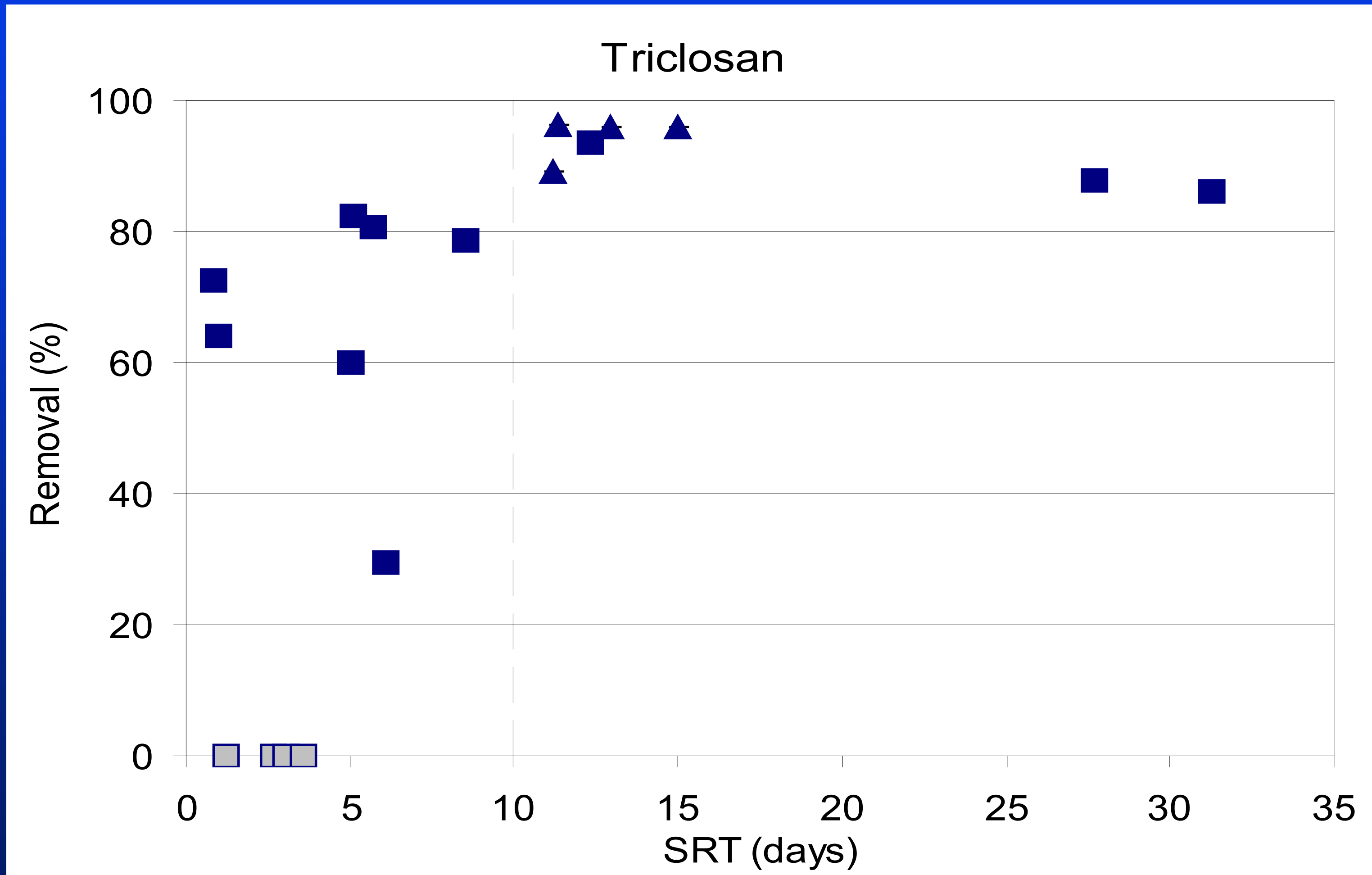
- Caffeine
- Ibuprofen
- Oxybenzone
- Chloroxylenol
- Methylparaben
- Benzyl salicylate
- 3-phenylpropionate
- Butylbenzylphthalate
- Octylmethoxycinnamate

SRT for Oxybenzone (Bin T1)



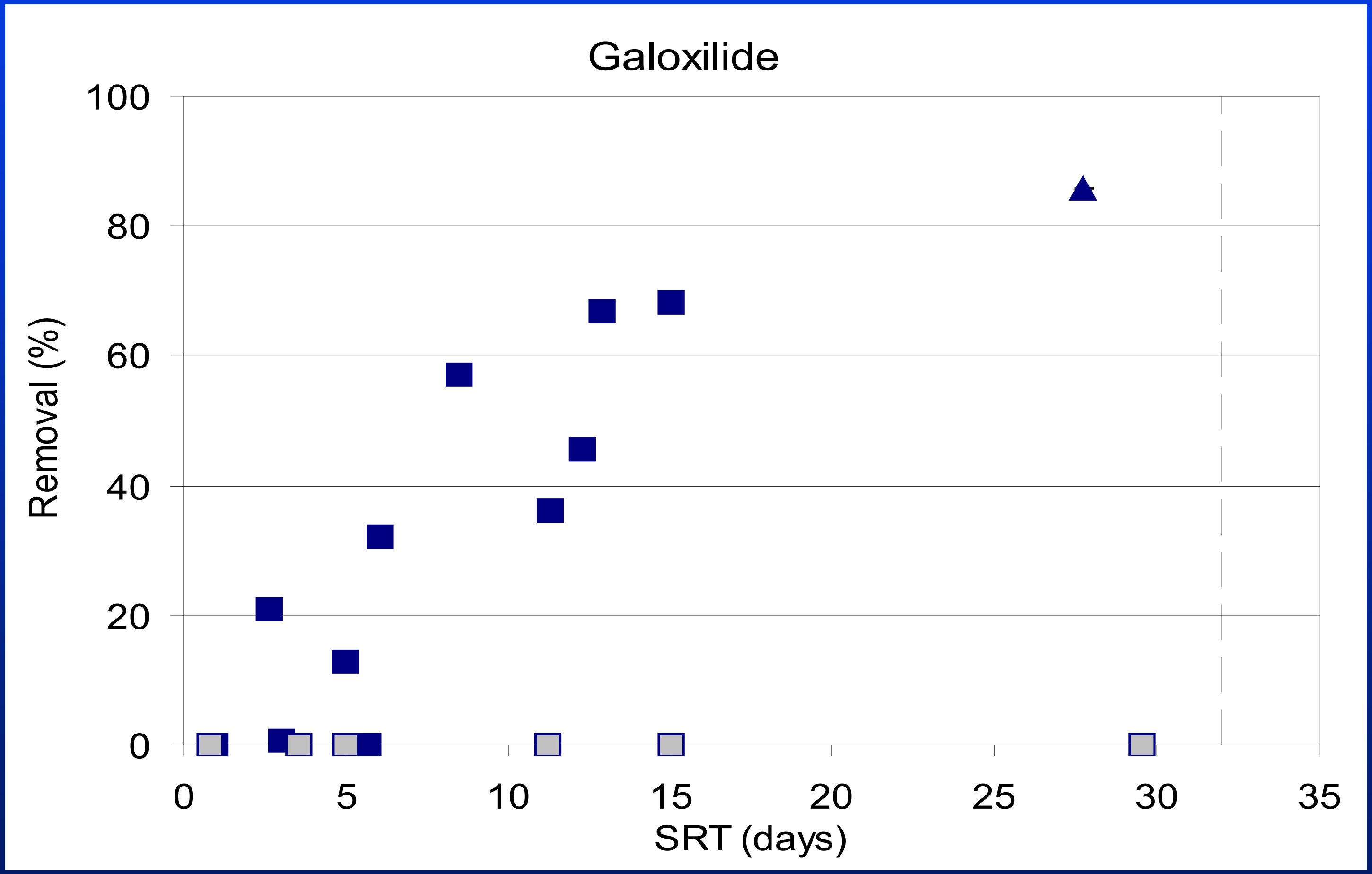
■ = Actual Removal ▲ = Removal greater than percentage value □ = Effluent > Influent

SRT for Triclosan (Bin T2)



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

SRT for Galoxolide (Bin T3)



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

Longer SRT_{80} Compounds

- SRT >8 Days: BHA
- SRT 10 Days: Triclosan
- SRT 13 Days: Benzophenone
- SRT >13 Days: DEET
- SRT > 15 Days: Galaxolide, Musk Ketone, TCEP

Media Filtration / RO

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

WERF Project Conclusions

- SRT dependence demonstrated for PPCPs

  $SRT_{80} \leq 5$ 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)

- Media filtration shows little evidence of removal while RO is very effective

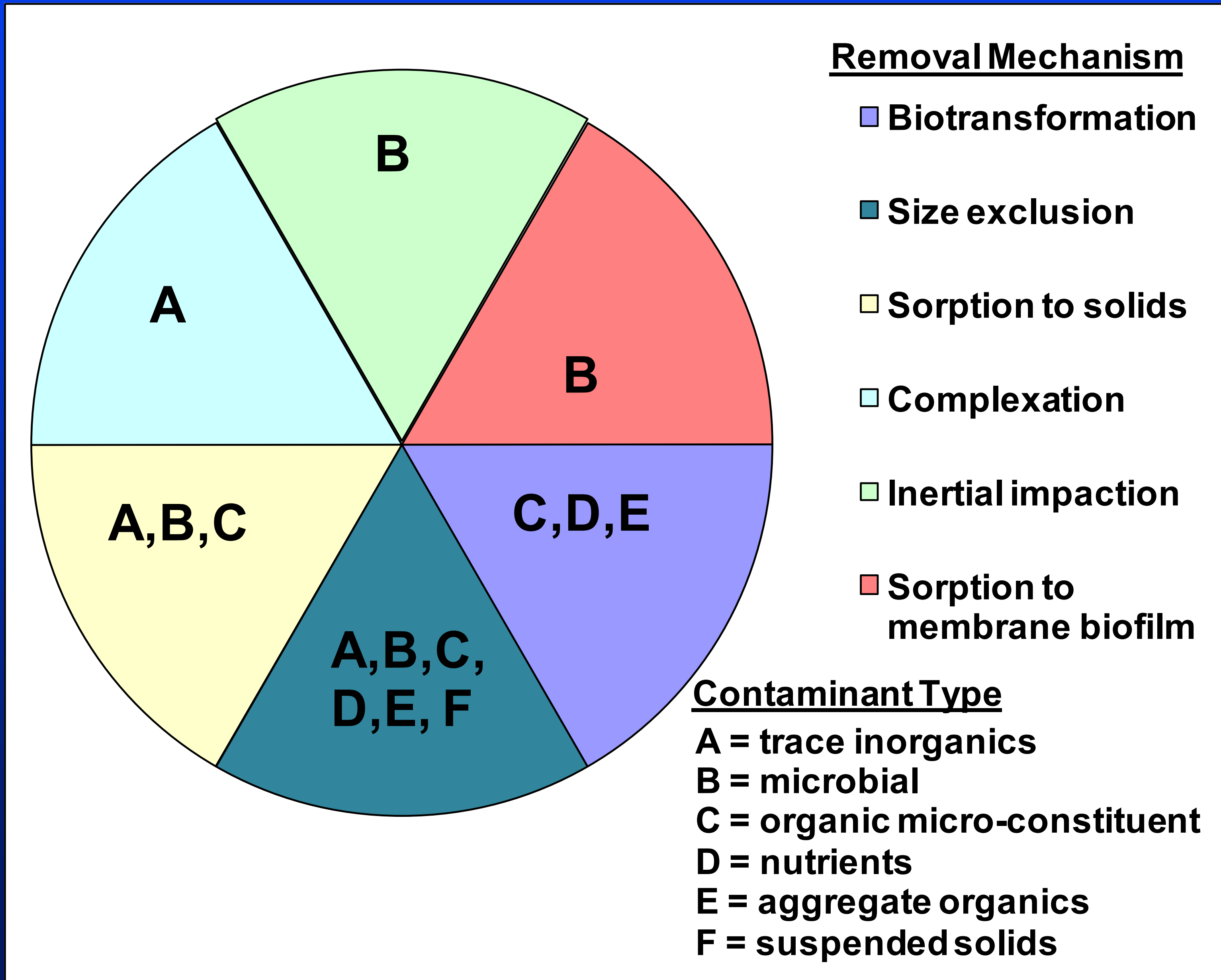
- MBR performance equivalent to activated sludge operated above 10 days

WateReuse Foundation

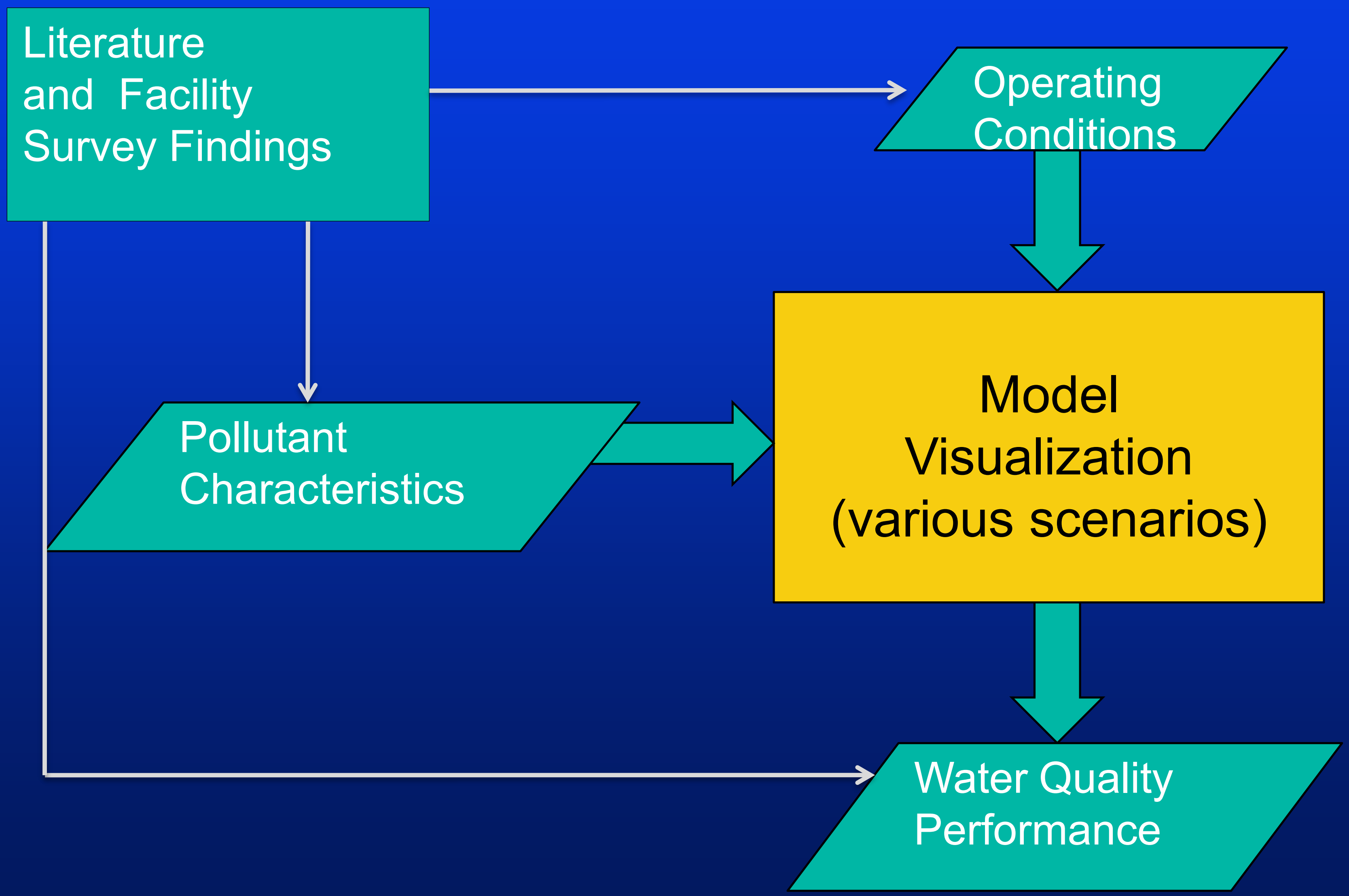
MBR Study Project Objectives

- Consolidate Global Water Quality Performance Data
- Understand Water Quality Performance Boundaries
- Understand Operational Impacts on Water Quality Performance
- Optimize Water Quality and Energy Performance

MBR REMOVAL MECHANISMS



PROJECT APPROACH



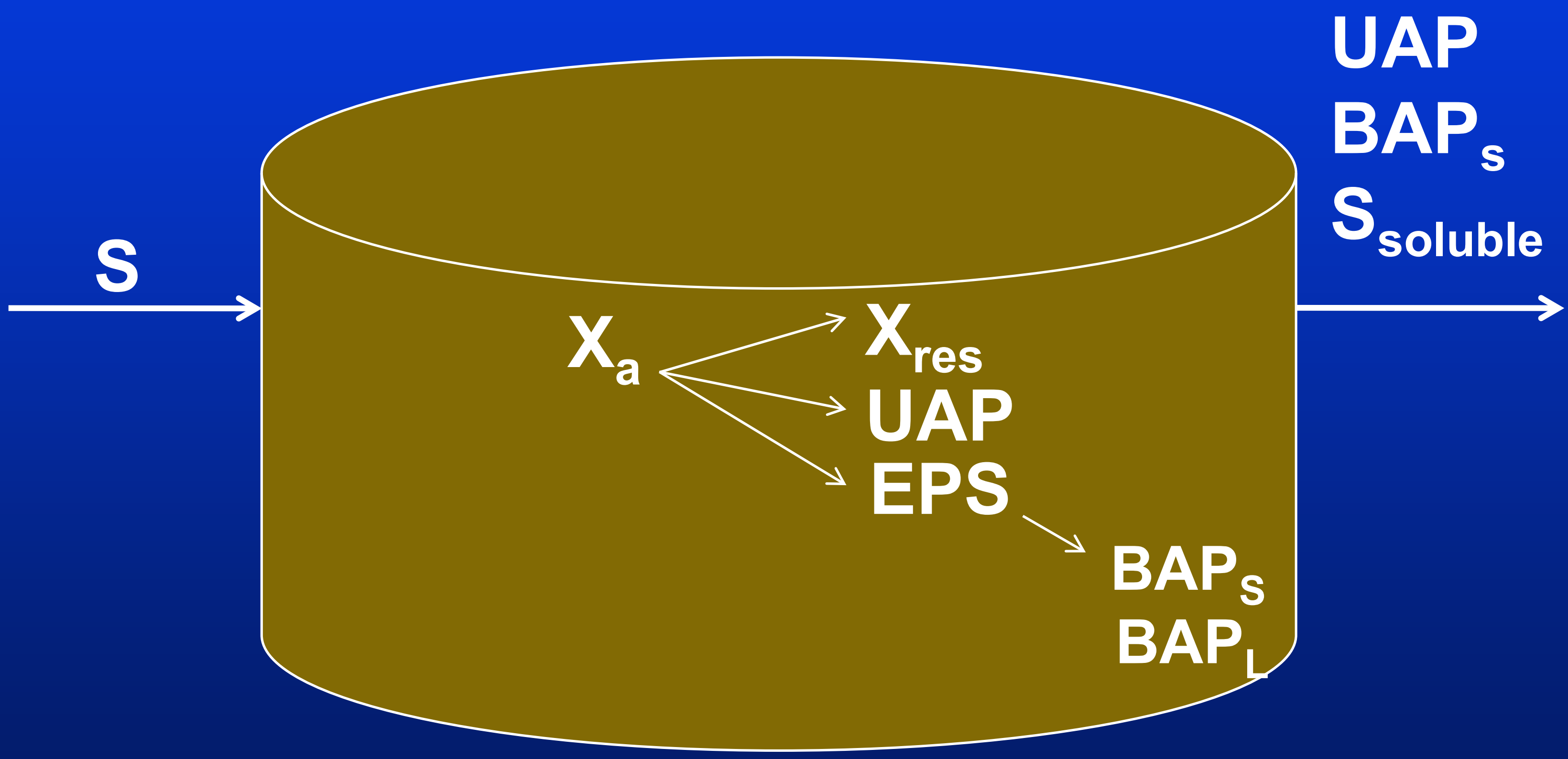
Modeling Approach

- Mechanistic Principles - Merging of 2 Models:
  - Rittmann & McCarty 2001 Activated Sludge Model
  - Laspidou & Rittmann's 2002 Unified Model for active biomass, inert biomass, EPS, and SMP
- Incorporation of Organic Micropollutant Fate Model
  - Lee, Rittmann, Shi, and McAvoy (1998) Fate Model
- Inclusion of Autotrophs for Cyclic Nitrification and Facultative Heterotrophs for Denitrification *(not yet)*

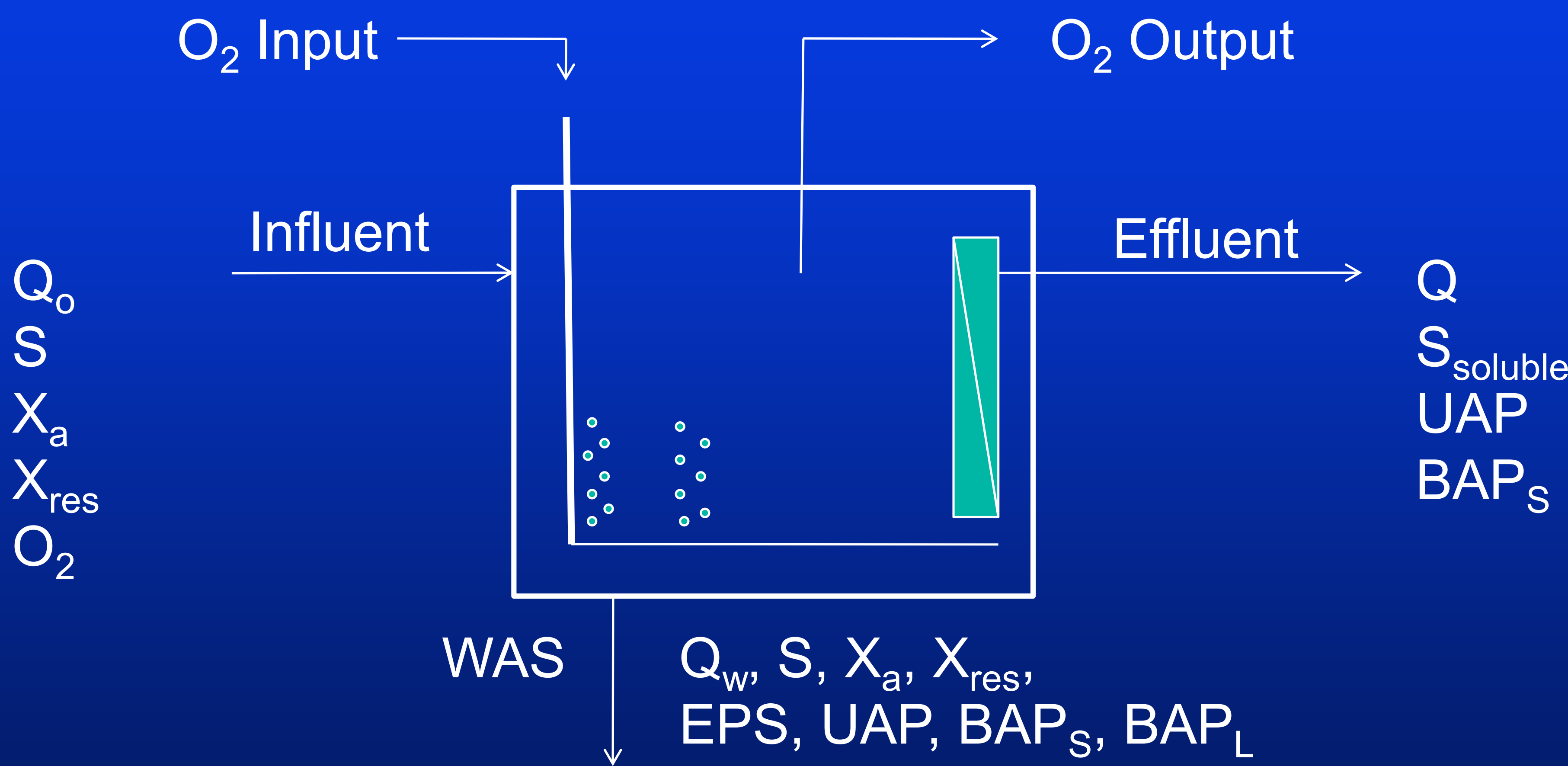
NOMENCLATURE OF COMPONENTS

- S = substrate (COD)
- X_a = active biomass
- X_{res} = residual inert biomass
- **BAP_S = small biomass-associated products**
- BAP_L = large biomass-associated products
- **EPS = extracellular polymeric substances**
- **UAP = utilization-associated products**

ACTIVATED SLUDGE BIOMASS FRACTIONS

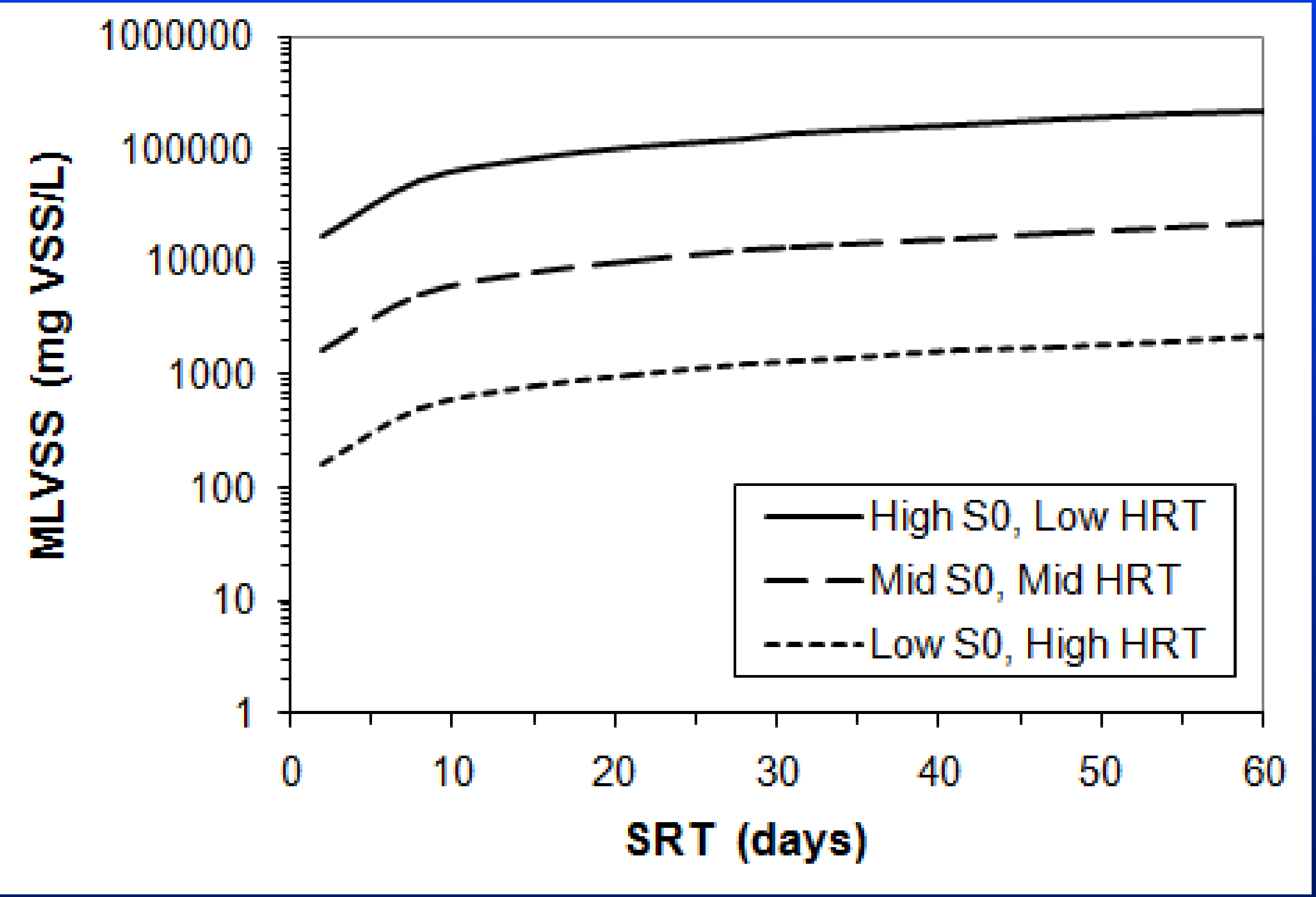


MBR MODEL INPUTS and OUTPUTS



V, SRT, Q_w = Key Operating Parameters

Impact of SRT on MLVSS



MICROPOLLUTANT FATE EQUATIONS

- Steady-state mass balance

Advection In = Advection Out-Volatilization-Sorption-Biodegradation

- Volatilization at the water surface and bubble aeration
- Sorption assumes equilibrium conditions
- Biodegradation assumes first-order in C and Xa

MODEL SCENARIO INPUTS

- Biodegradation Rate
- Sorption Coefficient
- Henry's Constant

→ Micro-constituent Properties

- BAP Fraction
- DO
- Influent Flow rate
- SRT, MLSS, Volume, HRT

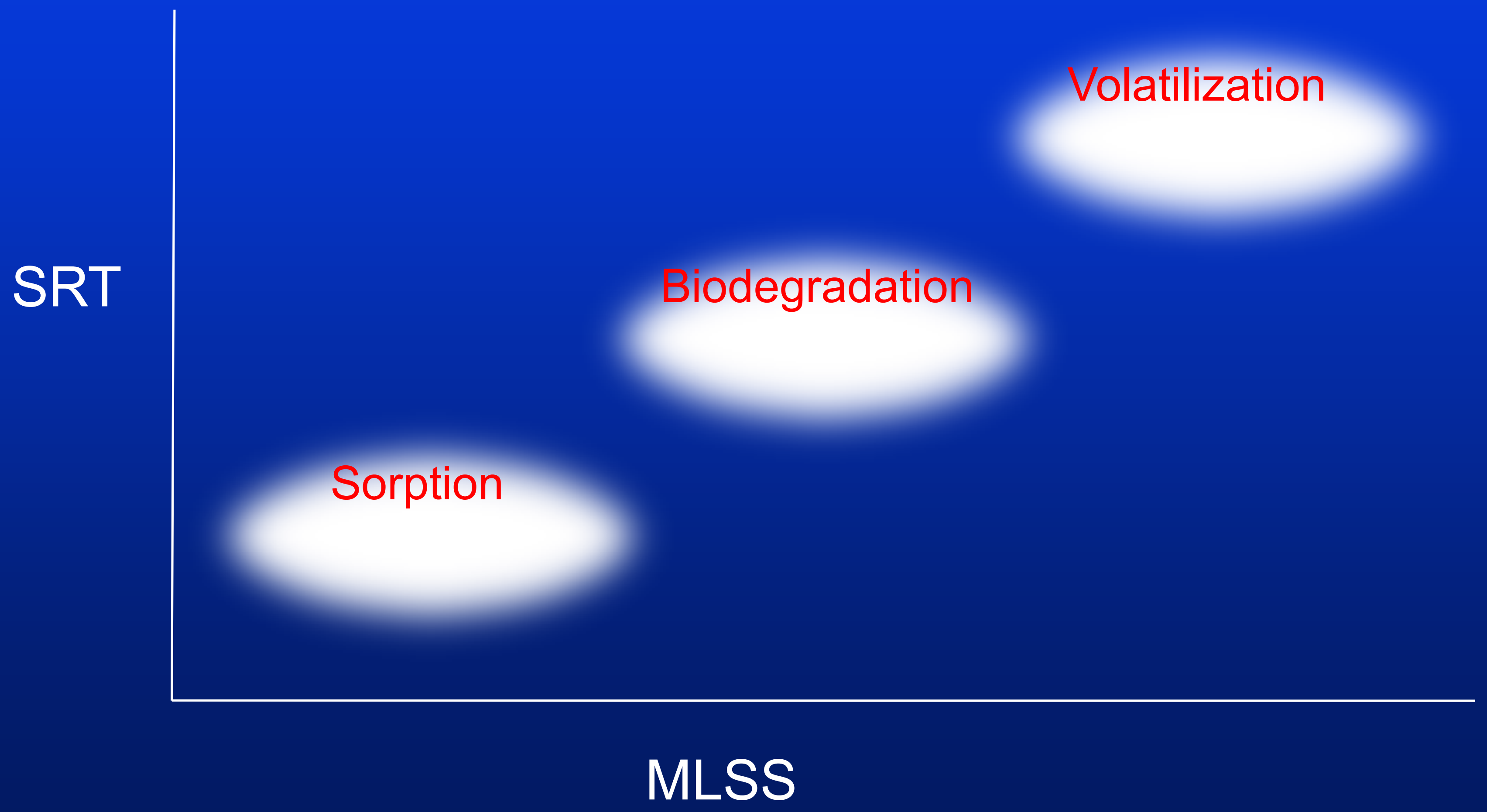
→ MBR Design Parameters

Influent Substrate COD

- Influent Micro-constituent

→ Influent Water Quality

Biodegradation Controlling Variable for Many Organic Micropollutants

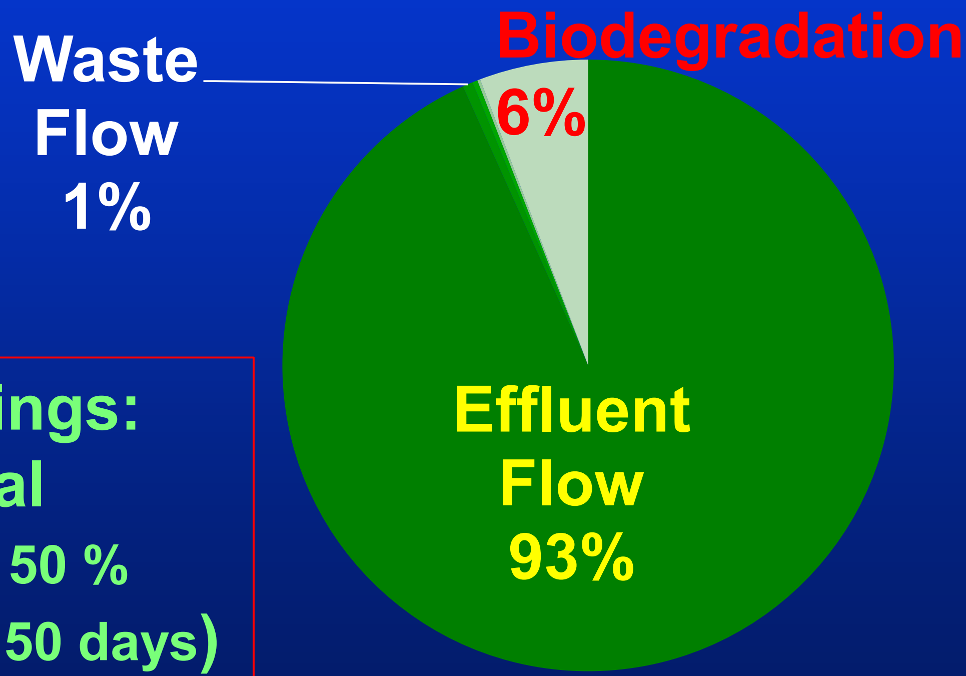


MODELING FOUR PHARMACEUTICALS

	K_b (L/gSS-d)	K_D (L/kgSS)
• Diclofenac (NSAID)	0.1	16
• Clofibric Acid (hyperlipidemia)	0.165	5
• Naproxen ((NSAID)	0.6	13
• Ibuprofen (NSAID)	15.5	7

LOW K_b and LOW K_D

Diclofenac
15-day SRT
20,000 mg/L MLSS

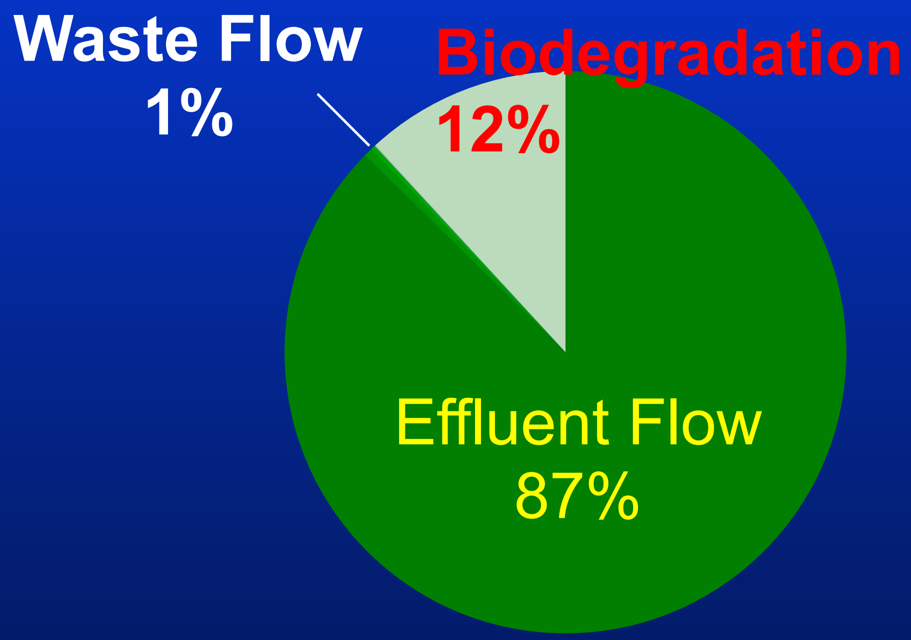


Literature Findings:
0 -35 % Removal
(Two papers cited 50 % removal at SRT > 50 days)

SLIGHTLY HIGHER K_b

Literature Findings:
54 - 88 % Removal

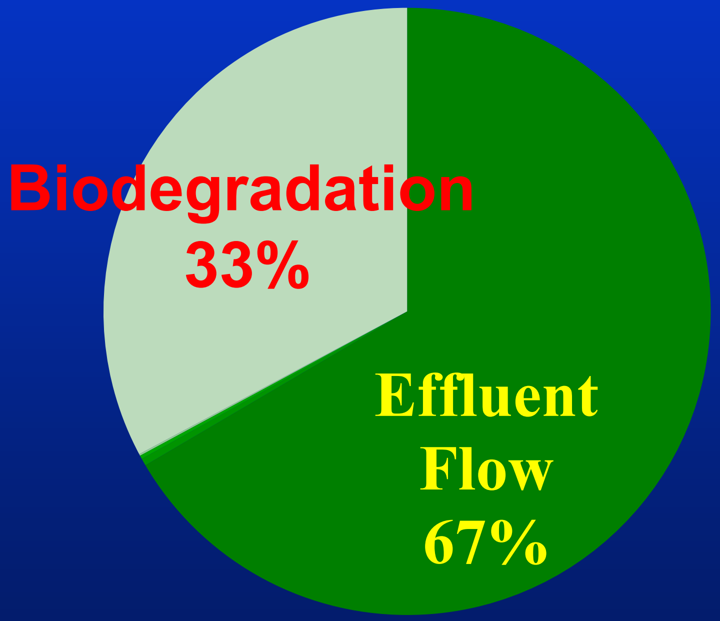
Clofibric Acid
15-day SRT
20,000 mg/L MLSS



STILL HIGHER K_b

Literature Findings:
69 - 99 % Removal

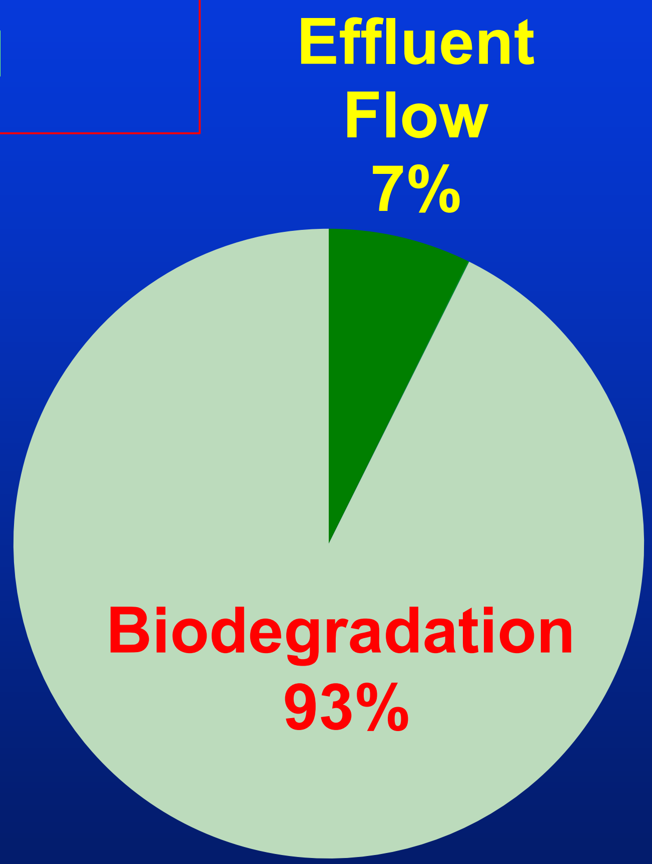
Naproxen
15-day SRT
20,000 mg/L MLSS



SIGNIFICANT K_b

Literature Findings:
88 - 100 % Removal

Ibuprofen
15-day SRT
20,000 mg/L MLSS



BIN CATEGORIZATION of MICROPOLLUTANTS from LITERATURE

Low Removal (<20%)	Moderate Removal	High Removal (> 80%)
Atrazine	Atenolol	Androstenedione
EDTA	Iopromide	Caffeine
TCEP	Clofibric Acid	Estradiol
TCPP	Gemfibrozil	Estriol
Carbamezapine	Sulfamethoxazole	Acetominophen
Diclofenac	DEET	Nonylphenol
	Ethinylestradiol	Benzfibrate
	Naproxen	Ibuprofen

BIN CATEGORIZATION of MICROPOLLUTANTS from MODELING

Low Removal	Moderate Removal	High Removal
K_b < 0.5 L/g_{SS}-day OR K_D < 4 L/g_{SS}	K_b ~ 1 L/g_{SS}-day	K_b> 2.5 L/gSS-day OR K_D > 40 L/g_{SS}

RELEVANT CONCLUSIONS

- MBR micropollutant removal mainly biological rather than membrane barrier
- Heterotroph model predicts approximately 50% reduction for K_b value of $1\ L \cdot g_{SS}^{-1}\ d^{-1}$
- Literature values may be higher than model predictions because of presence of autotrophs
- Biodegradation enhanced at higher MLVSS, but only up to SRT of ~ 20 days when Xa predominates

THANK YOU

joan.oppenheimer@stantec.com