Organic Micro-Pollutants in Direct and Indirect Potable Wastewater Reuse: Robust, Reliable, and Resilient Process Barriers

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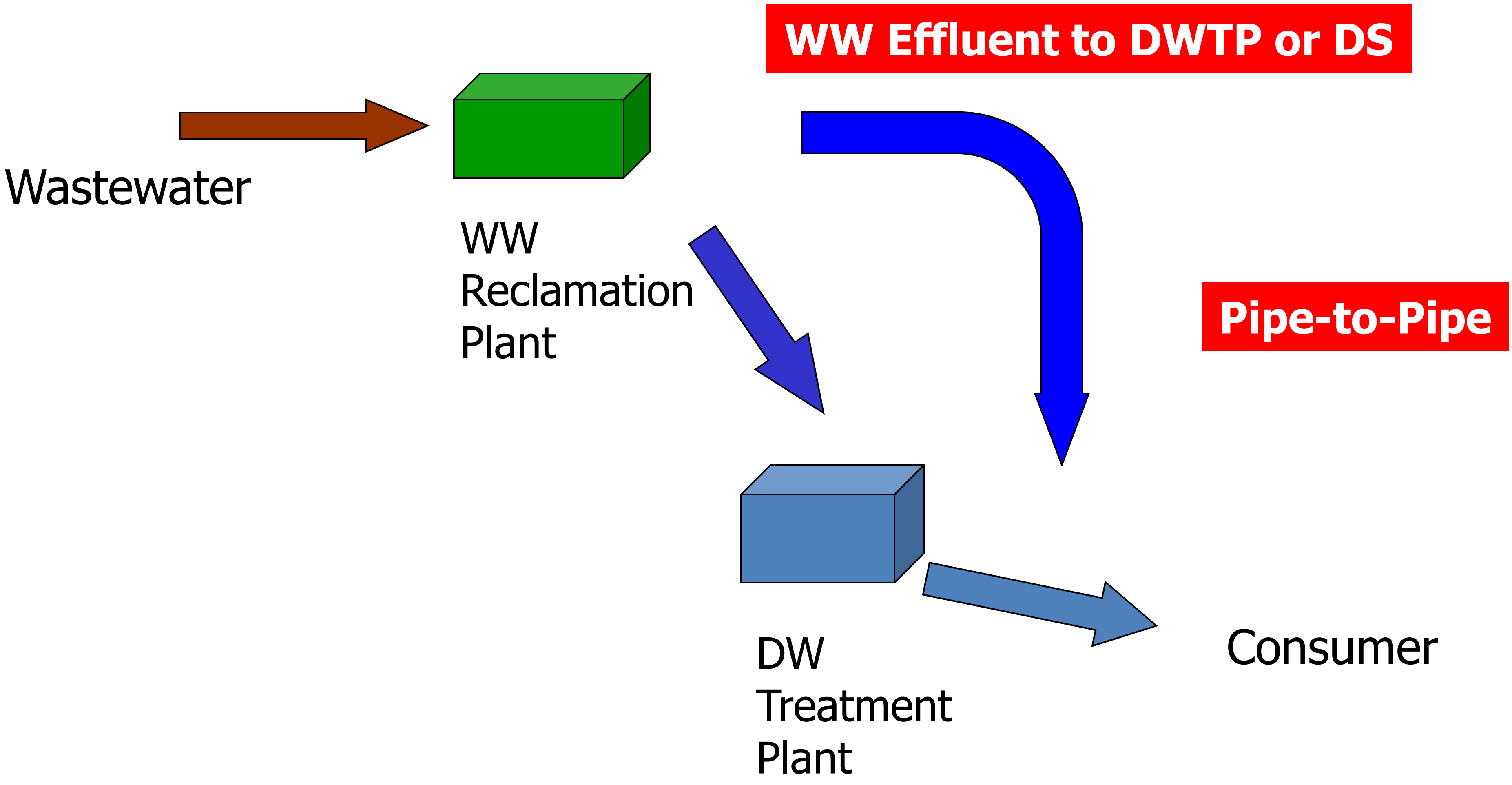
Acknowledgements (Co-Authors)

- Joerg Drewes, Technical University of Munich
- Thomas Missinger, Florida Gulf Coast University
- Sairam Sudhakaran, Nalco
- Andrew Maeng, Sejong University
- Victor Yangalli, Grunfos
- David de Ridder, TU-Delft

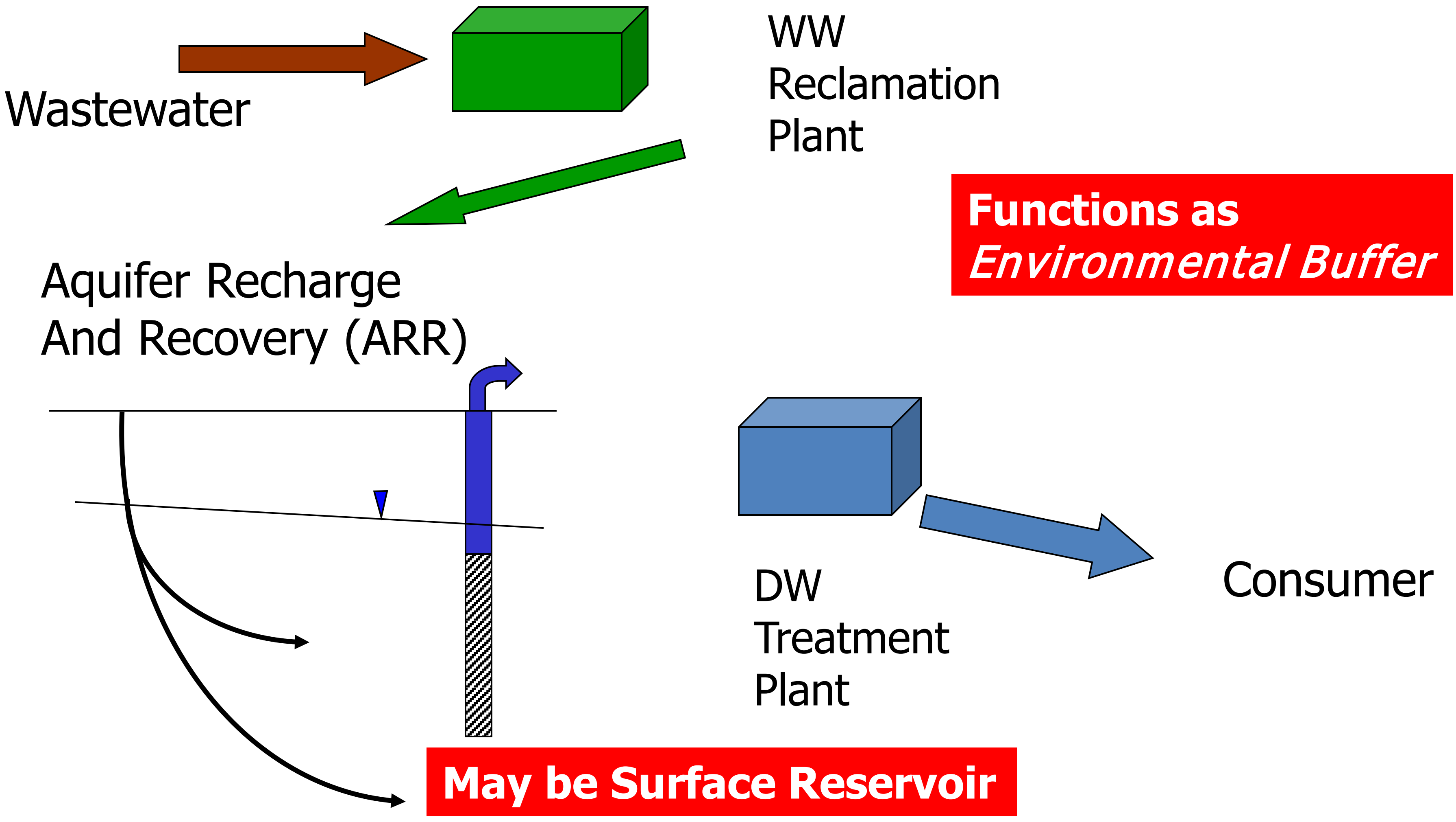
(Wastewater-Derived) Organic Micropollutants (OMPs)

- Endocrine disrupting compounds (EDCs)
  - Steroidal hormones (e.g., estrone, testosterone)
  - Industrial chemicals (e.g., nonylphenol, bisphenol A)
- Pharmaceutical active compounds (PhACs)
  and personal care products (PCPs)
  - analgesics, antiepileptics, lipid regulators, antibiotics
  - flame retardants
- Emerging disinfection by-products (e.g., NDMA)

Direct Potable Reuse (DPR)



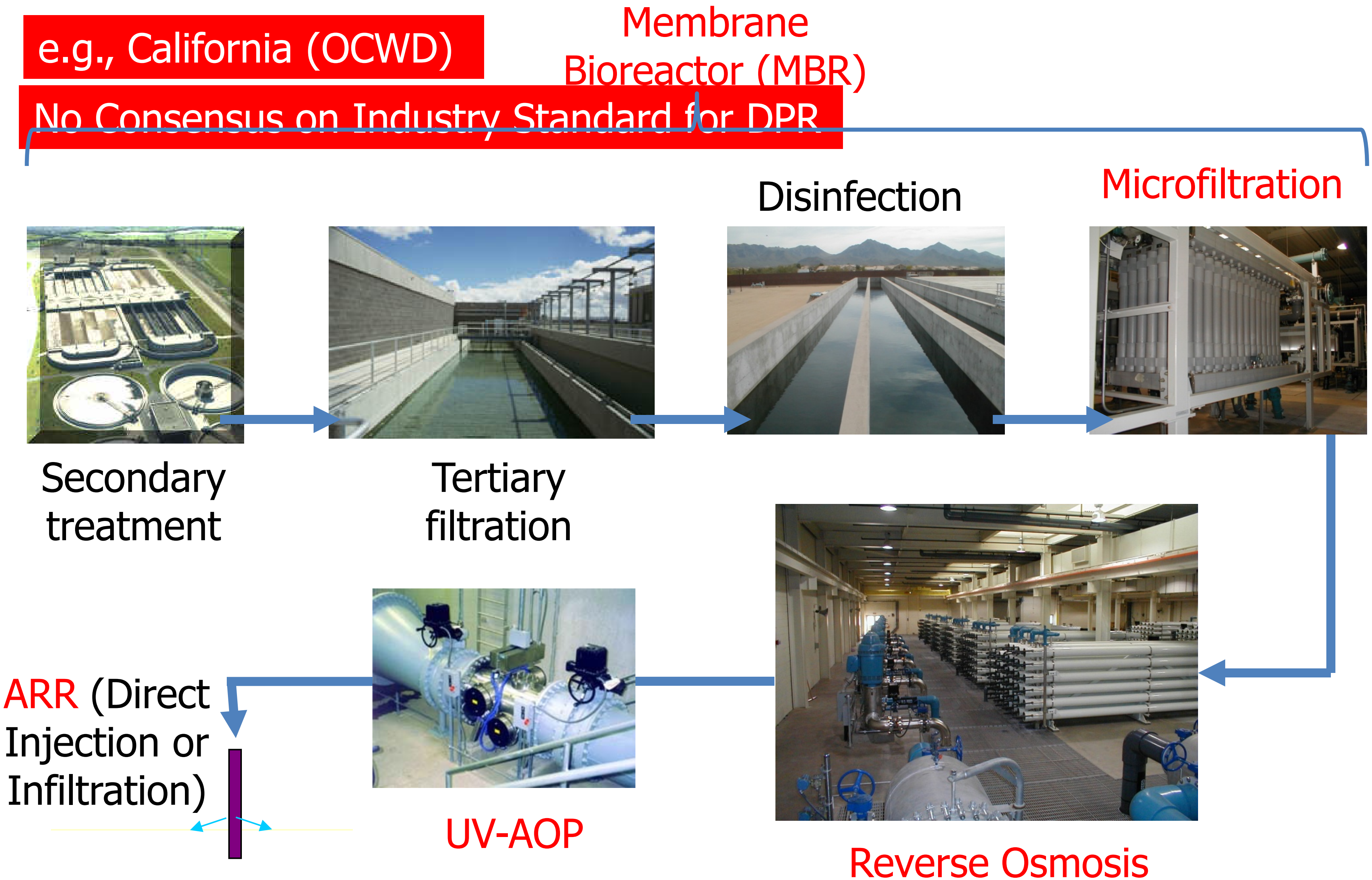
Indirect Potable Reuse (IPR)



Advanced Treatment Processes for Chemical Risk Reduction

- Oxidation (Ozonation, Advanced Oxidation (AOP)
  - *Destruction/Transformation of OMPs*
  - *Constraint: Metabolites (by-products)*
- Granular Activated Carbon (GAC) Adsorption
  - *(Physical) Removal of OMPs*
  - *Constraint: Polar OMPs*
  - *If Preceded by Oxidant: Biological AC (BAC)*
- High-Pressure Membrane Rejection (RO and NF)
  - (Physical) Removal of OMPs
  - *Constraint: Removal of Small MW OMPs*
- Aquifer Recharge and Recovery (ARR)
  - Removal of Most OMPs by *Biodegradation*
  - *An Advanced Process!*

Water Industry Standard for IPR



Multi-Barrier System Approach for Effective Chemical Risk Management

- Barriers (Processes) and Process Hybrids for OMPs
- Barrier (Process) Robustness, Reliability, Resilience
- Process Hybrid Synergies
- Redundancy

Process Hybridization

- Process Synergies (sequence of processes)
- Redundancy (multi-barriers)
- Engineered and/or Natural Processes (ARR)

Important OMP Properties Affecting Removal

- Molecular Weight/Size
  - Membrane Rejection (steric)
- Neutral or Charged (pK_a or pK_b)
  - Membrane Rejection (electrostatics)
  - Adsorption (ion exchange)
- Hydrophobicity/Polarity ($\log K_{OW}$)
  - Adsorption (physical)
- Aromatic Structure
  - Oxidation
- Halogen Content
  - Oxidation
  - ARR

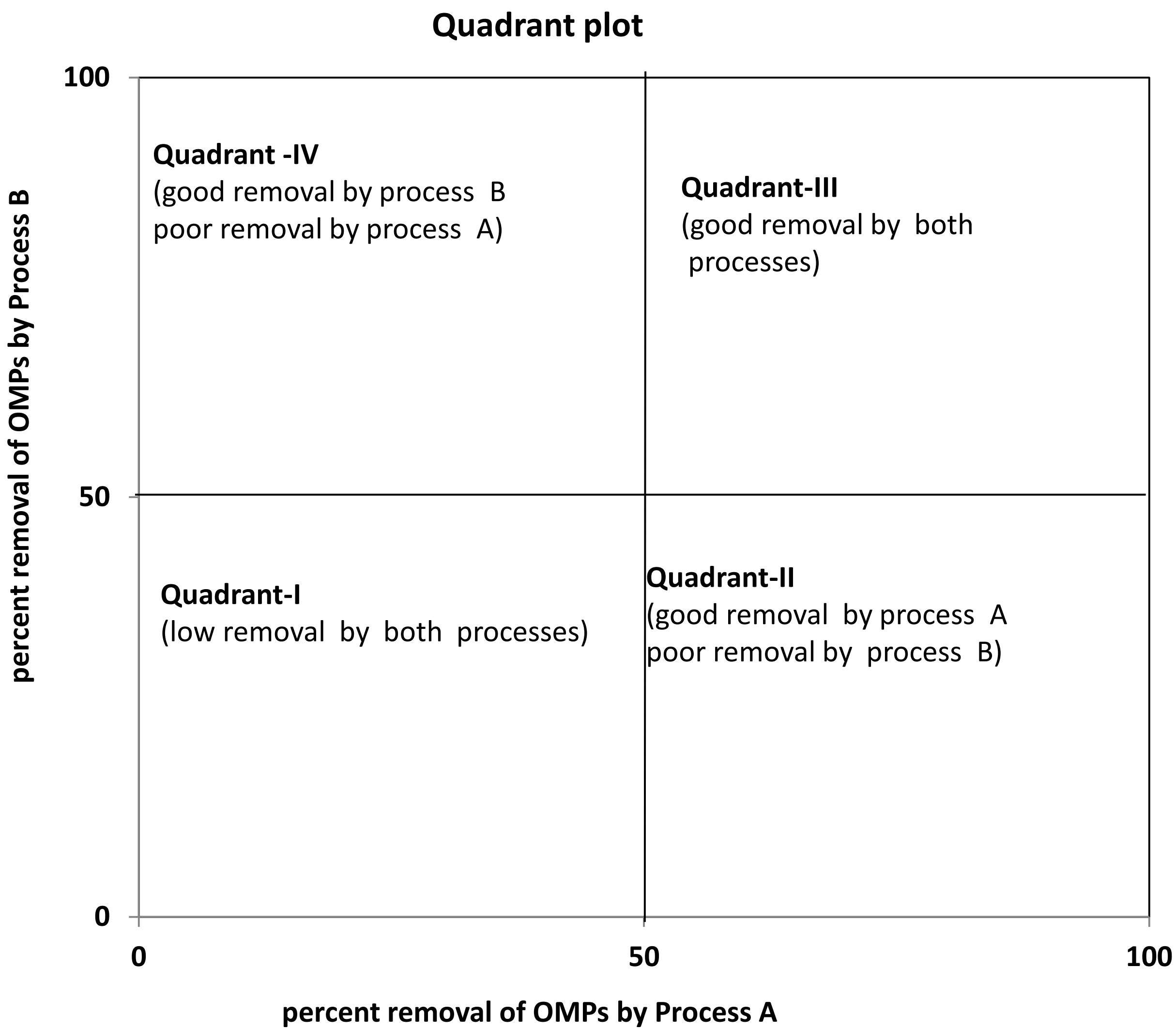
Performance of Individual Processes for Removal of PhACs and EDCs

(Janex-Habibi, 2007)

Process	Acidic compounds	Neutral compounds	X-ray contrast media	Antibiotics	Estrogens, EE2	Detergents, NPEO, NP, OPEO, OP
Ozonation	**10 - >90 %**	**10 - >90 %**	**10 – 50 %**	**>90 %**	**>90 %**	**50 – 90 %**
GAC/PAC	**>90 %**	**>90 %**	**50 – 90 %**	**50 - >90 %**	**>90 %**	**>90 %**
PAC/UF	**>90 %**	**>90 %**	**50 – 90 %**	**50 - >90 %**	**>90 %**	**>90 %**
NF	**>90%**	**>90%**	**>90%**	**>90%**	**>90%**	**>90%**
UV	**<10%**	**10 - 50%**	**10 - 50%**	**10 - 50%**	**<10%**	**40 - 90%**
RBF/ARR	**50 - >90 %**	**<10%**	**50 – 90**	**50 - 90%**	**>90%**	

- *Every Process: Effective Barrier for Some Similar Groups of OMPs*
- (Ozone) Ozonation: Poor Removal of X-Ray Contrast Media (Iodinated)
- AOP: Slow Oxidation of Chlorinated Compounds
- GAC: Poor Adsorption of Polar Compounds (e.g., 1,4 Dioxane)
- NF/RO: Poor Retention of Low MW Compounds (e.g., NDMA)
- ARR: Poor Biodegradation of Aromatic Compounds (e.g., Primidone)

Quadrant Plots for Process Performance Assessment: Compare Processes and/or Identify Process Synergies



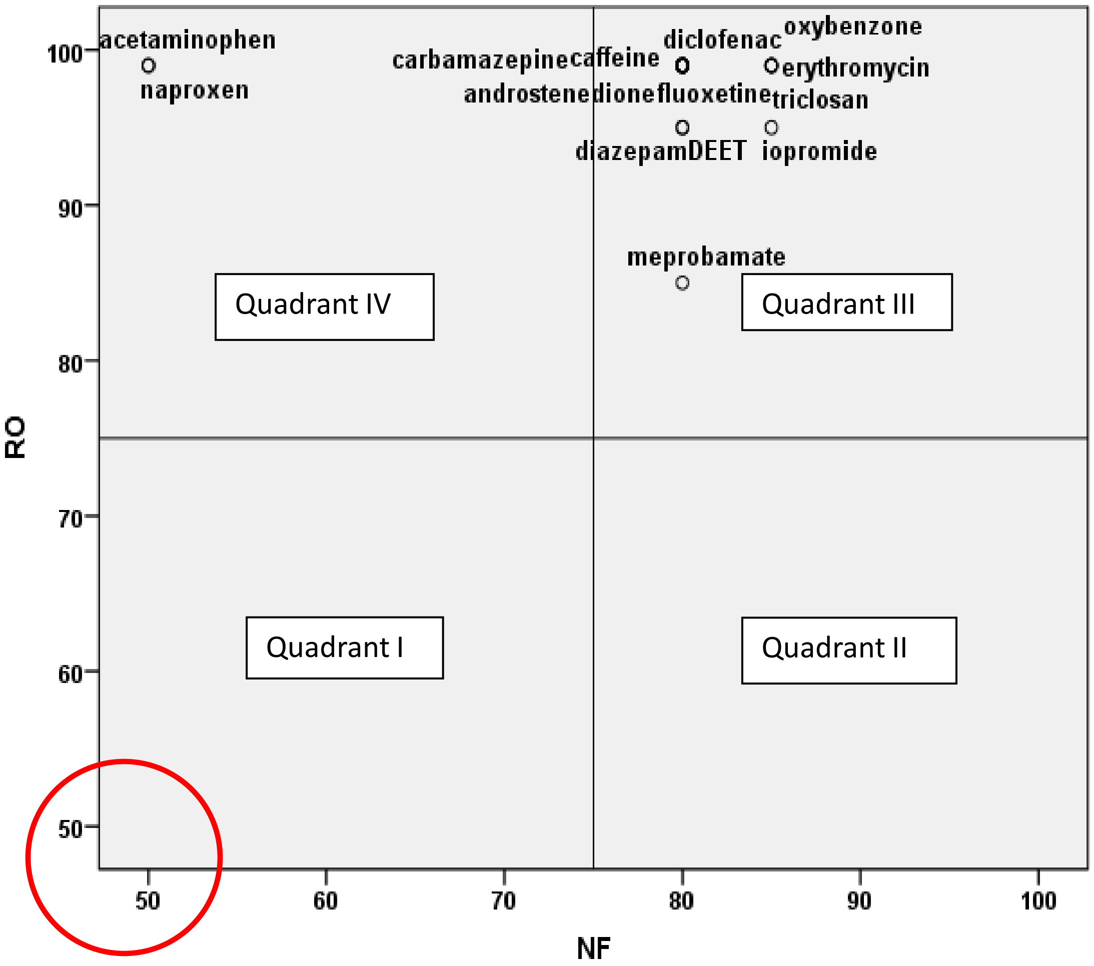
OMPs Data Base: Percent (%) Removal of OMPs (*Pilot scale study by Snyder et al.*)

Compound	Abbreviation	ARR	GAC	NF	RO	O_3	AOP	UV-AOP
acetaminophen	ACT	99	85	50	99	99	99	97
androstenedione	AND	99	95	80	99	99	99	96
caffeine	CAF	98	85	80	99	97	97	89
carbamazepine	CARB	13	85	80	99	99	99	88
DEET (N,N-diethyl-3-methylbenzamide)	DEET	91	85	80	95	76	82	89
diazepam	DIAZ	65	80	80	95	82	85	93
diclofenac	DICLO	99	50	80	99	99	99	98
dilantin	DIL	22	50	80	99	86	88	97
erythromycin	ERY	98	85	85	99	92	92	64
estradiol	ESTR2	99	95	80	99	99	99	98
estriol	EST	99	85	80	99	99	99	99
estrone	ESTRO	99	95	80	99	99	99	99
ethinyl estradiol	ET-ESTR2	99	95	80	99	99	99	99
fluoxetine	FLX	99	85	85	99	99	99	99
gemfibrozil	GEM	99	50	80	99	99	99	95
hydrocodone	HYDRO	99	85	80	99	99	99	99
ibuprofen	IBU	99	50	80	99	87	88	94
iopromide	IOPRO	95	50	85	95	61	58	91
meprobamate	MEP	74	50	80	85	59	60	75
naproxen	NAPRO	98	50	50	99	99	99	99
oxybenzone	OXYB	97	95	85	99	99	99	66
pentoxifylline	PENT	99	85	80	99	99	99	90
TCEP (tris-2-chloroethylphosphate)	TCEP	32	40	80	99	8	9	16
triclosan	TRICLO	98	95	85	99	99	98	97
trimethoprim	TRIMET	99	85	80	99	99	99	94

Reverse Osmosis (RO) versus Nanofiltration (NF)

Is NF sufficient for OMP removal?

- NF: lower operating pressure and high flux vs RO



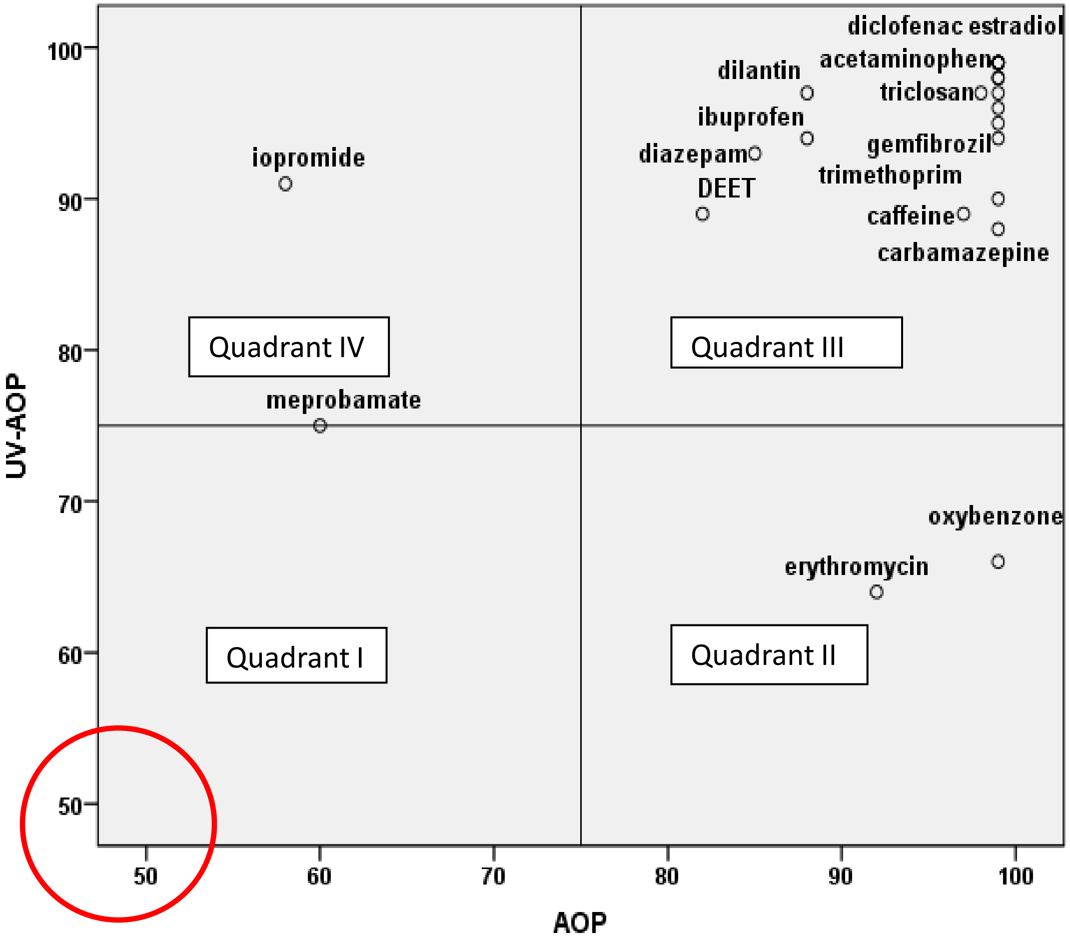
Quadrant IV - Only two (acetaminophen, naproxen) - Poor removal by NF; good removal by RO	**Quadrant III** --Most OMPs - Good removal by both NF and RO
Quadrant I -None	**Quadrant II** -None

- Acetaminophen: MW = 151 vs. MWCO of NF = 200
- RO > NF But …
- For Higher MW OMPS, NF can be Effective Barrier

UV-Advanced Oxidation Process (UV-AOP) versus Peroxide-Ozone AOP

UV-AOP versus AOP (H_2O_2-O_3)

- No bromate formation
- Disinfection also provided by UV
- Possible photolysis



Quadrant IV -Two (iopromide, meprobamate) Poorly removed by AOP and well removed by UV-AOP	**Quadrant III** -Most OMPs Well removed by AOP and UV-AOP
Quadrant I -None	**Quadrant II** -Two Compounds (erythromycin, oxybenzone) -AOP better removal than UV-AOP

- UV-AOP > AOP for some halogens or amides
- AOP > UV-AOP for some non-aromatics
- UV-AOP is an effective barrier

Nano Filtration (NF) versus Granular Activated Carbon (GAC)

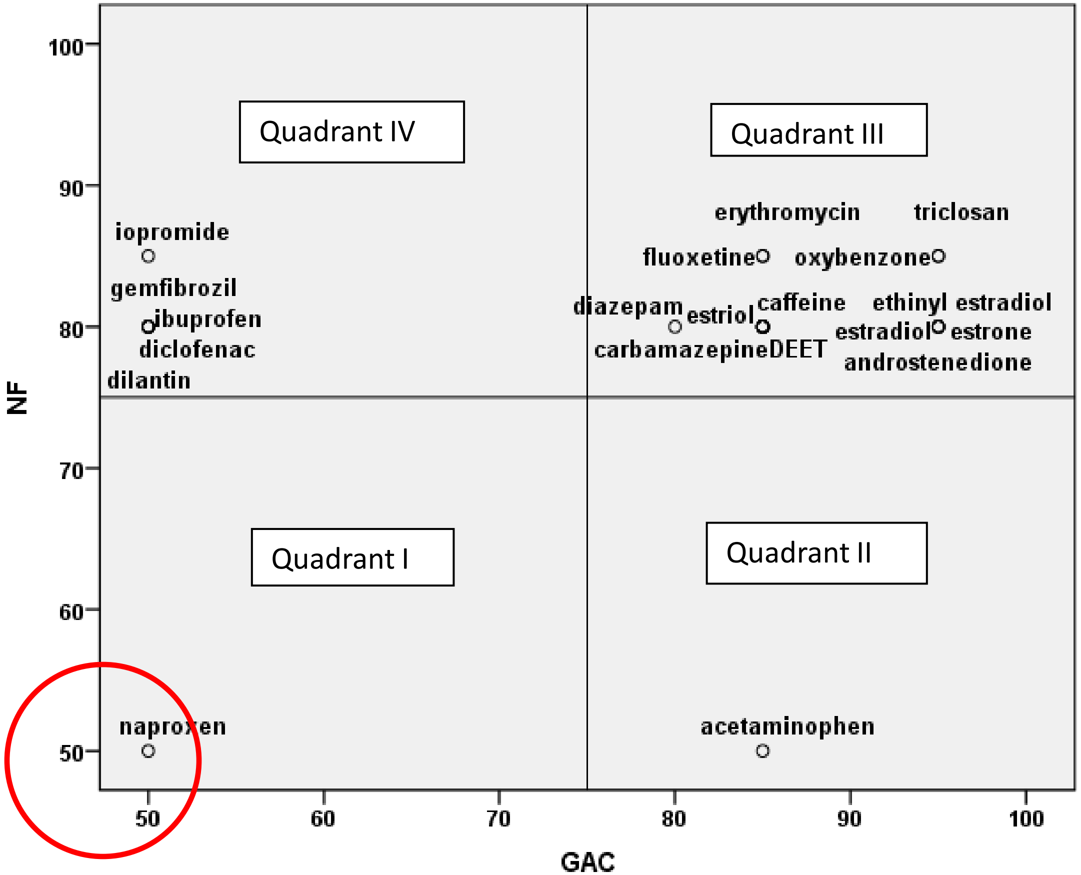
NF: OMP MW (Size) vs. GAC: OMP Polarity (K_{OW})

NF as pretreatment to GAC

- Lower natural organic matter (NOM) loading on GAC

GAC as pretreatment to NF

- Lowers NF fouling reduction



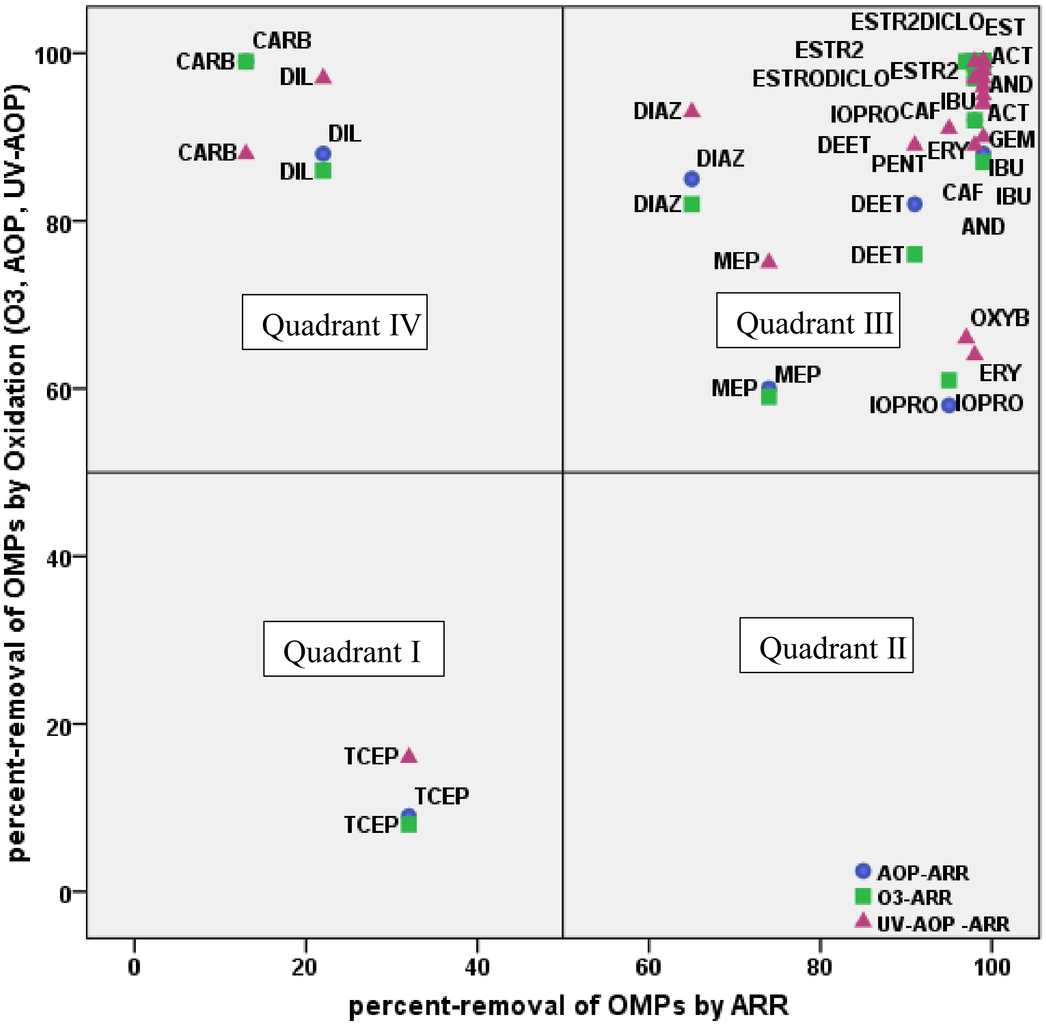
Quadrant IV	Quadrant III
- Five (iopromide, gemfibrozil, ibuprofen, diclofenac, dilantin) - Poor removal by GAC and good removal by NF	- Most OMPs - Good removal by both NF and GAC
Quadrant I	**Quadrant II**
- One (naproxen) - Poor removal by GAC and NF	- One (acetamiophen) - Poor removal by NF and good removal by GAC

- NF: Acetaminophen: MW = 151
- GAC: Naproxen: pKa = 4.2
- Both: Effective Barriers (Can Provide Redundancy)

Oxidation (O_3, AOP (H_2O_2-O_3, UV-AOP) versus ARR Hybrid

O_3 or AOP as pre-treatment to ARR
- couples oxidation with biodegradation
- ARR-removes oxidation by-products
- O_3 or UV as disinfectant, pathogen barrier

ARR as pre-treatment to O_3 or AOP
- Lower oxidant demand due to NOM removal

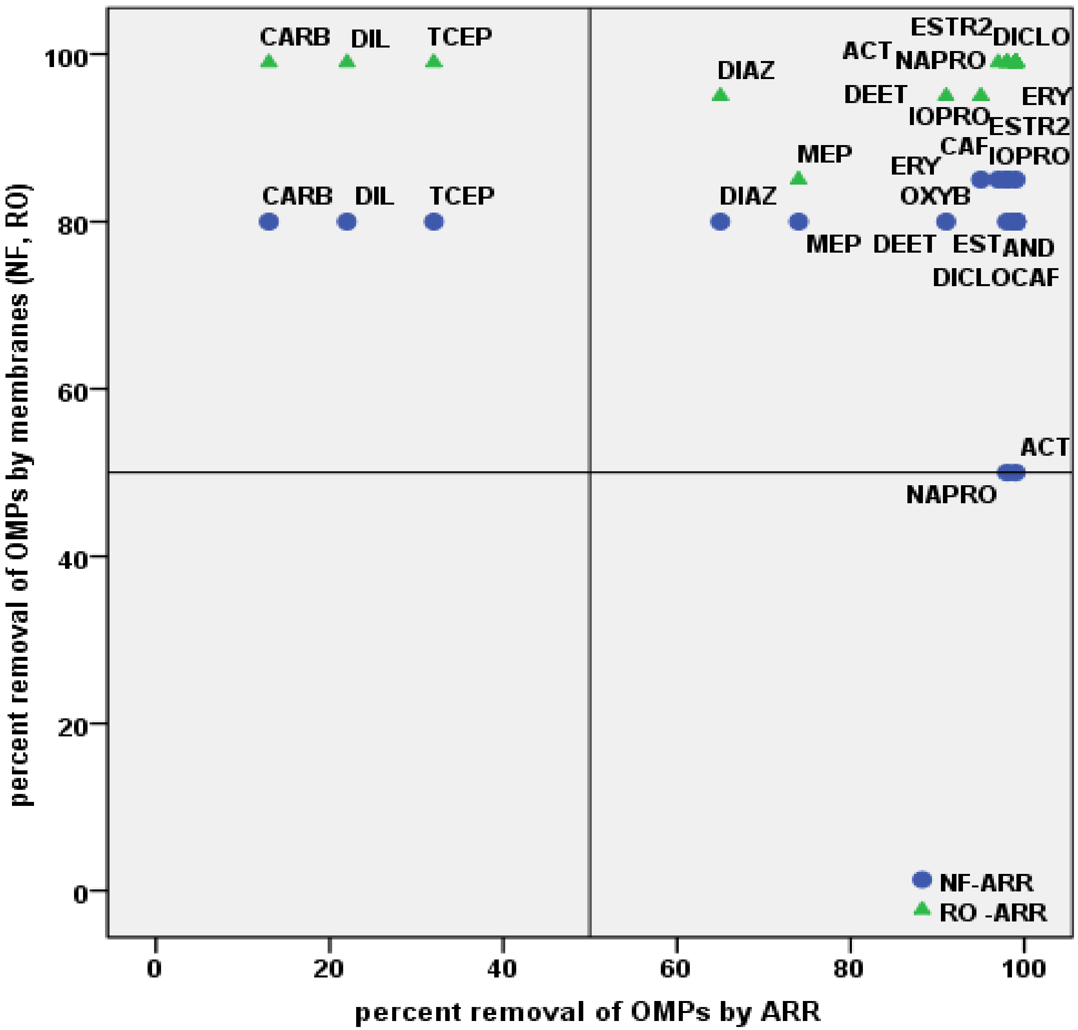


Quadrant IV Poor removal by ARR for Carbamazepine, dilantin	**Quadrant III** -Most OMPs Well removed by Oxidation and ARR
Quadrant I -TCEP, poor removal by both	**Quadrant II** -None

- Both: Effective Barriers (Redundancy)
- Attractive Hybrid Synergies

Membranes (RO and NF) versus ARR hybrid

- ARR as pre-treatment to Membranes
  - reduces membrane fouling
  - couples biodegradation with membrane rejection

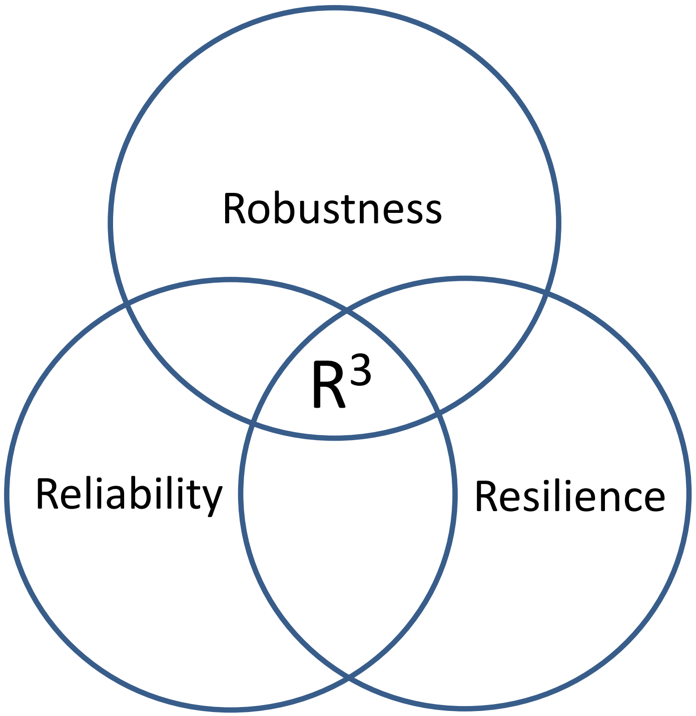


Quadrant IV Poor removal by ARR for Carbamazepine, dilantin, TCEP	**Quadrant III** -Most OMPs Well removed by RO/NF and ARR
Quadrant I -No OMPs	**Quadrant II** -No OMPs

- IPR Industry Standard: RO + ARR vs. ARR + RO?

Robust, Reliable, Resilience (R^3) Processes

- Robust: *Strong* Performance (effective)
- Reliable: *Consistently* Good Performance (over time)
- Resilience: Capacity to *Recover* Performance (from perturbation)
- *Redundancy (fail safe)*



R^3 Improved through Hybridization

Conclusions

- Problematical Compounds
  - Oxidation: Oxidant-Resistant Structures (e.g., halogens); NF/RO; Low MW; GAC: Polarity; ARR: Biorefractory
  - However, Virtually All OMPs Studied Effectively Removed by at least One, and in Most Cases, Two Barriers (Hybridization and Redundancy)
- Effective Multi Barrier Approaches for OMPs
  - Industry Standard for IPR: (MF +) RO + UV-AOP + ARR (move RO after ARR?)
  - Potential DPR Industry Standard: (MF +) UV-AOP + GAC/BAC + RO/NF
- Hybridization Synergies
  - IPR: Ozone + ARR or ARR + NF
  - DPR: GAC + RO/NF or UV-AOP + GAC/BAC
- What About Microbial Risk (Pathogens) in IPR or DPR?
  - O_3 or UV-AOP, and ARR: Effective Barriers
  - MF or UF instead of RO and NF: Effective Barriers (IPR Ind. Std.: MF)
- Potentially Important Role of ARR in Hybridization (an attribute of IPR)

General Conditions for Different Processes in Pilot Studies…

	Residence time	Dosage	Membranes	GAC
ARR	36 days	not applicable	not applicable	not applicable
Ozone (O_3)	24 min	2.5 mgL^{-1}	not applicable	not applicable
AOP (O_3/H_2O_2)	24 min	2.5 : 0.065 mgL^{-1}	not applicable	not applicable
UV-AOP	not applicable	H_2O_2: 5-7mgL UV: 4 lamps@ 60% power	not applicable	not applicable
GAC	Empty bed contact time: 7.6 min	not applicable	not applicable	Norit Americas, Hydrodarco 4000
NF	not applicable	not applicable	ESNA, Hydranautics	not applicable
RO	not applicable	not applicable	Koch, Saehan, Osmonics	not applicable

- **Typical Operating Conditions**