


DPR Decision Tool: Nanofiltration Rejection Model for Recalcitrant CECs

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Acknowledgements

Agenda

- IPR vs DPR
- Contaminants of Emerging Concern
- DPR Regulations
- Advanced Barrier Technology for DPR: RO vs NF
- Scope of this Research
- Methods & Results
- NF Rejection Modeling
- Conclusions

What is Potable Reuse?

- The reuse of municipal water resource recovery facility (WRRF) effluent for augmentation of fresh water supply of public water systems (PWS). (Water Environment Federation)

- PWS alternatives when additional fresh water (TDS < 500 mg/L) is not an option:
  - Nothing = rationing, conservation, no growth
  - WRRF reuse (TDS 500 to 1,000 mg/L): readily available
  - Brackish water (TDS > 1,000 mg/L): may be available
  - Seawater (TDS > 35,000 mg/L): coastal option

Indirect vs Direct Potable Reuse in US

- Indirect Potable Reuse (IPR)
  - Environmental buffer separates WRRF from WTP
  - Practiced for years: planned or unplanned planned
  - Examples: El Paso, TX and Fayetteville, AR

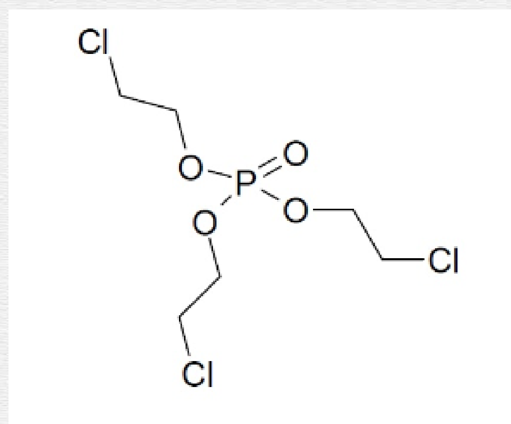
- Direct Potable Reuse (DPR)
  - Advanced treatment technology separates WRRF from WTP
  - Operating in US:
    - Big Spring, TX (2013) – year-round operation (2.5 MGD)
    - Wichita Falls, TX (2014) – seasonal peak-demand operation (5.0 MGD)

Contaminants of Emerging Concern

Defined:
Chemical solutes potentially found in surface waters at trace levels, ng/L, that may have an impact on aquatic and animal life (US EPA 2015)

- **Over 84,000 chemicals in use today** as inventoried by US EPA under the Toxic Substances Control Act (TSCA)
- **Approximately 700 new chemicals added each year** to the US EPA inventory
- Since the 1976 TSCA, **only five chemicals have been banned** from manufacturing: PCBs, chlorofluorocarbons, dioxin, hexavalent chromium, and asbestos

Are CECs in Municipal Wastewater Effluent?



CEC Classifications

- Endocrine Disruptor Compounds (EDCs)
- Pharmaceuticals
- Stimulants
- Preservatives
- Artificial Sweeteners
- Pesticides / Herbicides
- Flame Retardants

Refs: CDPH 2011, NRC 2012, MDH 2015

CECs in WRRF Secondary Effluent

If we consider WRRF primary and secondary treatment as the first barriers for reuse, we must ask

What is the recalcitrant (i.e. non-biodegraded) CEC fraction?

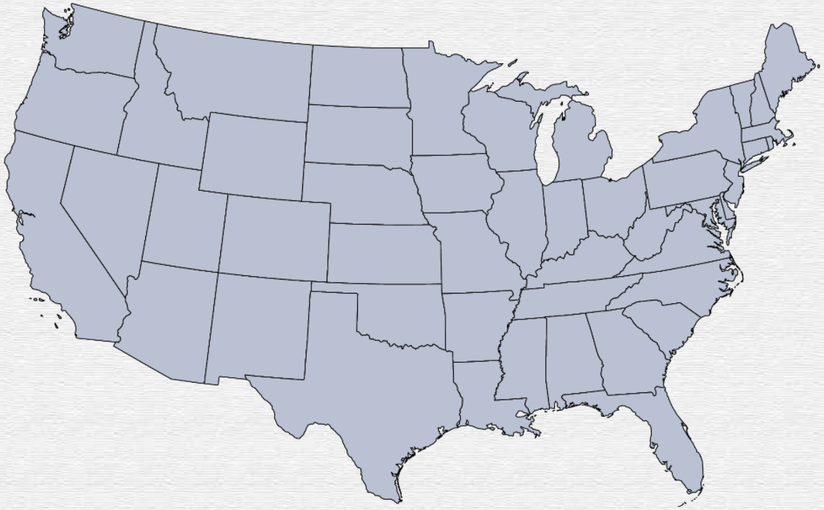
SE Surveys (Drewes, 2006; Behera, 2011; Luo, 2014) have found:

- EDCs, Pharmaceuticals, Pesticides in ng/L
- Sweeteners & Flame retardants in ug/L (<u>most recalcitrant</u>)

Federal CEC and DPR Regulations

US EPA SDWA, as amended in 1996, established:

- UCMR program and NCOD
- CCL update every 5 years
- CCL4 (2015 draft): 100 chemical and 12 microbial contaminants
- To date, NPDWR MCLs for only 3 CEC herbicides:
  - Atrazine MCL = 3,000 ng/L
  - 2,4 D MCL = 70,000 ng/L
  - Simazine MCL = 4,000 ng/L



No federal DPR regulations, EPA leaving it to the states …

States & PWS Managers Need Guidance; 5 SDWA Primacy States are developing DPR programs:

California:
"If DPR can be demonstrated to be safe and feasible, the State Water Plan goal of reusing 1.8 BGD by 2025 will be achieved." (CDH Title 22)
Demonstration piloting recommended with monitoring for 15 CECs (CSWRCB)

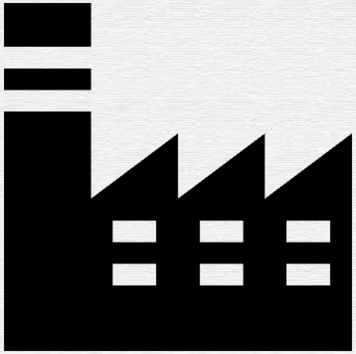
Texas:
- 2012 State Water Plan: 1.5 million ac-ft/yr by 2060
- Leading nation with first DPR systems (4 approved by TCEQ)
- 51 CECs recommended for source water monitoring (TWDB)

Oklahoma: in advisory committee

Arizona: in advisory committee

New Mexico: Cloudcroft in construction

Technology Default: Reverse Osmosis



Feds:

US EPA 2012 “Guidelines for Water Reuse”: BAT = RO

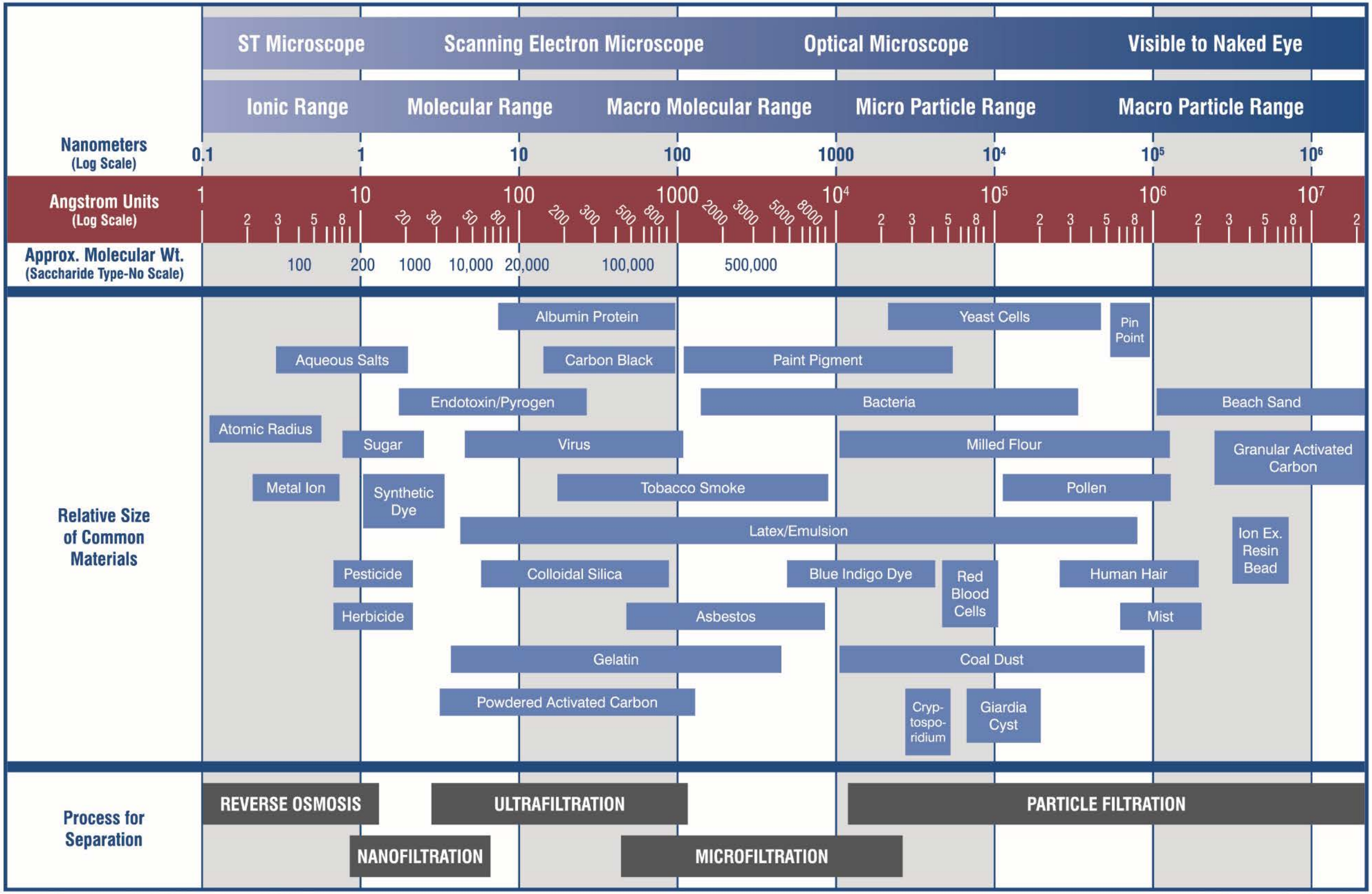
States:

- 2012 CDPH Title 22: FAT = RO
- 2015 TWDB “DPR Resource Document”: 6 ABT (5 RO, 1 BAC)
- CA, FL, WA regs for IPR with ASR require RO
- 2016 ODEQ named RO as the “default advanced barrier” for new IPR regulations

Industry:

2015 “Framework for DPR”: AWT = RO/AOP (WRA, AWWA, WEF, NWRI)

The Filtration Spectrum



Note: 1 Nanometer (1×10^{-9} Meters) = 4×10^{-8} Inches
1 Angstrom Unit = 10^{-10} Meters = 0.1 Nanometers

Reference: GE Osmonics

NF has significant advantages over RO

- Less operating pressure (<100 psi vs >150 psi)
  - Less power cost: 10 MGD = $137,500/yr savings
  - Less capital cost: standard line class vs high pressure class

- Less waste generated:
  - NF provides equivalent rejection (to RO) of divalent and trivalent ions (Ca, Mg, PO_4, SO_4) – major contributors to TDS
  - NF will pass smaller, monovalent ions (Na, Cl)
  - Less salinity in the reject stream
  - Less stabilization required for permeate

NF Rejection of CECs: Research to Date

2014 US EPA 5-year extensive CEC Literature Review:

Found over 400 publications regarding CECs

Less than 100 publications involved membrane treatment

13 bench-scale NF CEC-rejection studies

- All synthetic lab prepared CEC samples
- None with recalcitrant CEC in WRRF effluent matrix

No pilot-scale NF CEC-rejection research

No full scale NF CEC-rejection research

NF Rejection of CECs: Research to Date

"… the overwhelming majority of predictive rejection models to date are inadequate because they have been developed with idealized solutions typically containing only 2, 3, or sometimes 4 solutes. If accurate modeling of concentrated multi-solute solutions realistic of reuse processing is to become common place then more effort needs to be placed into modeling systems of real industrial relevance."

Mohammed, et al. 2015: review of recent advancements in commercial TFC NF membranes for reuse applications

Scope of our Research

Select and characterize a CEC study set of anthropogenic, recalcitrant organic solutes suspected to occur in SE and with broad physical-chemical variability

Collect samples and conduct certified CEC MRL analyses of effluents from 3 typical WRRFs where PWS managers are considering DPR – profile full-scale secondary treatment

Determine SE recalcitrant fraction of CEC study set

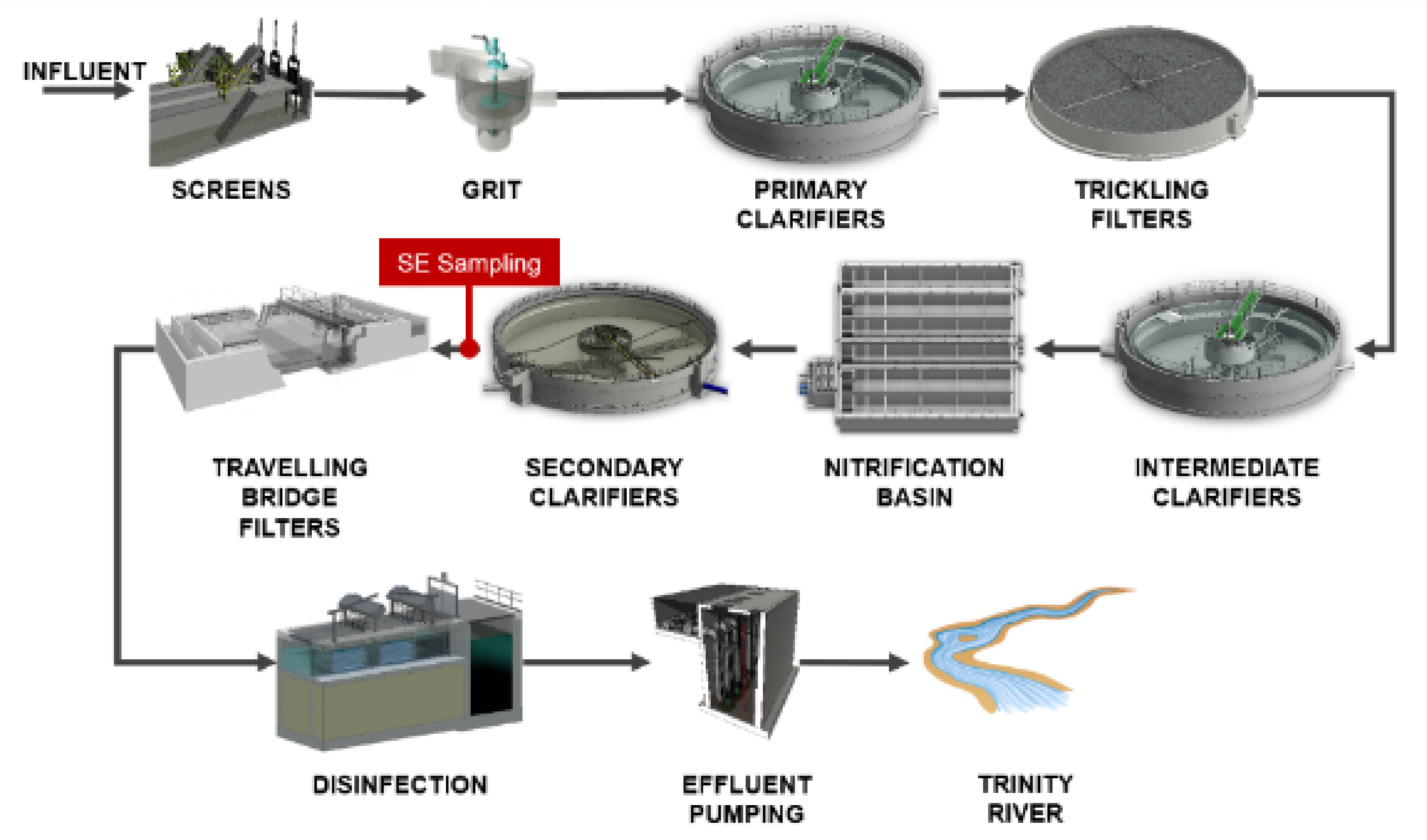
Determine rejection efficacy of the recalcitrant CECs by TFC RO and NF (MWCO ≤ 200 Da) membranes

Develop and validate a QSAR-based NF rejection model

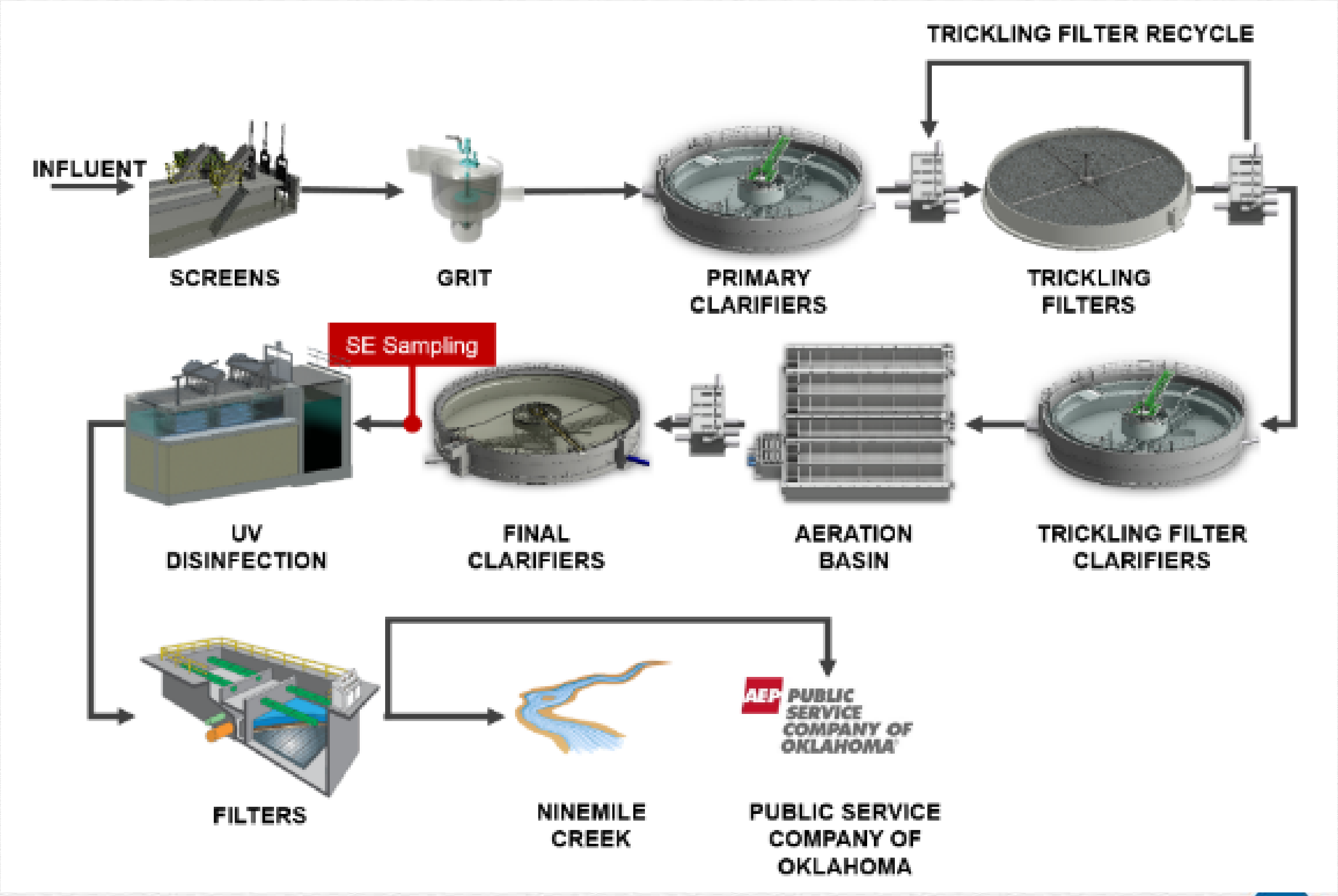
Survey of 96 CECs in OK/TX WRRF Effluents

- Samples taken over multiple weeks in August and September (2014)

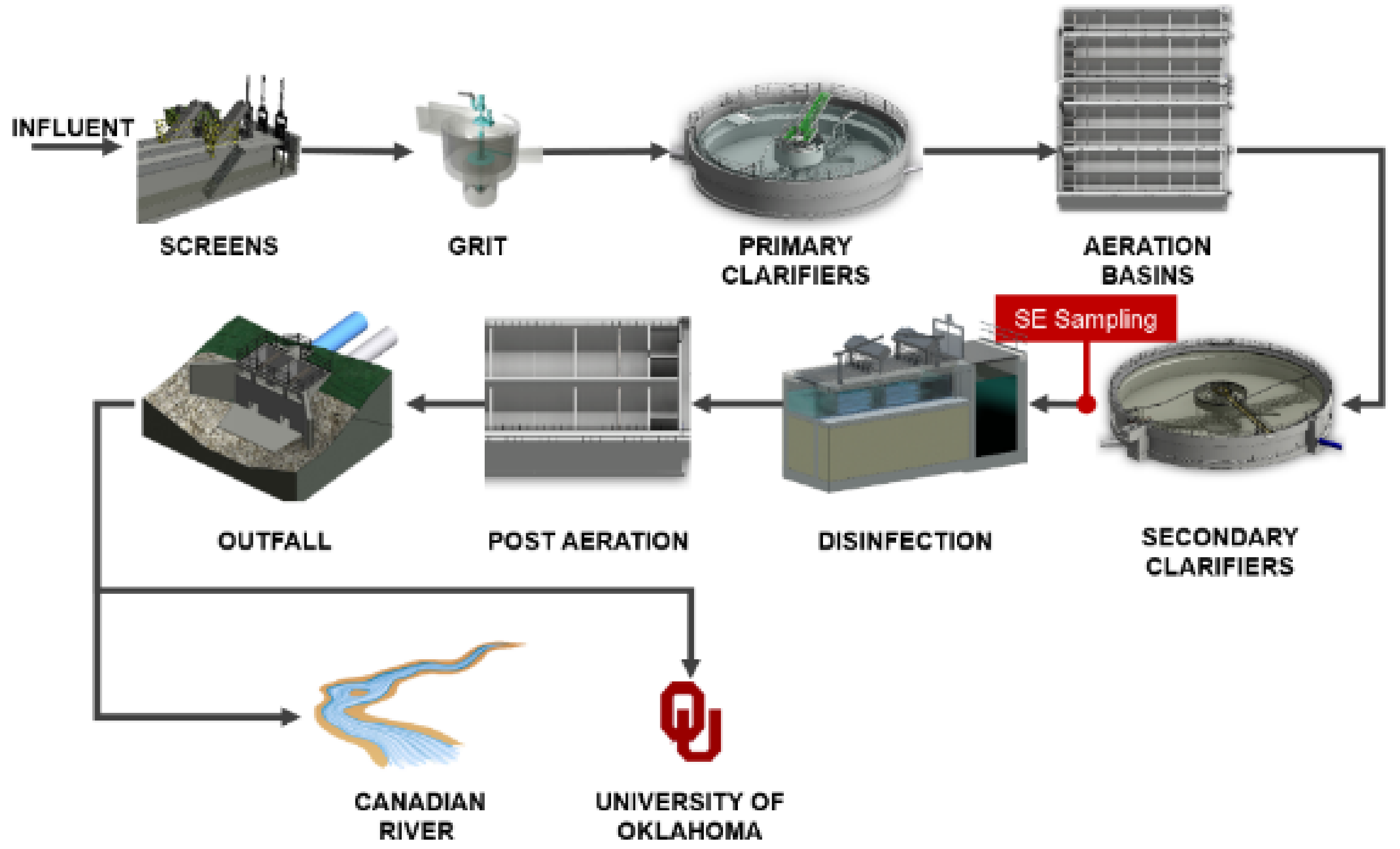
WRRF Effluent Sample Sites – Garland



WRRF Effluent Sample Sites - Lawton



WRRF Effluent Sample Sites - Norman



96 CEC Survey

- 10 EDCs
  - MW = 206 to 298 g/mol
- 49 Pharmaceuticals
  - MW = 151 to 821 g/mol
- 4 Stimulants
  - MW = 176 to 194 g/mol
- 8 Preservatives
  - MW = 129 to 316 g/mol
- 2 Artificial Sweeteners
  - MW = 201 to 398 g/mol
- 18 Pesticides
  - MW = 146 to 284 g/mol
- 3 Flame Retardants
  - MW = 285 to 431 g/mol

Analytical Methods

- WRF Project 4167 (2012) identified LC/MS/MS-ESI analytical method as most reliable for trace CEC detection in water
- Eurofins Eaton Analytical, EEA (Monrovia, CA) was the test lab for WRF Project 4167, and a developer of the LC/MS/MS-ESI approach (based on EPA Method 539)
- EEA is a certified laboratory by US EPA and 46 states for Method 539 and the UCMR program
- All 3,456 discrete analytical events from the reported work were processed by EEA

Compound	MRL (ng/L)	Analytical Mode	Compound Class
Gemfibrozil	5	ESI -	Lipid Regulator
Ib[illegible]	10	ESI -	Analgesic-NSAID
Iohexol ([illegible]hexal)	10	ESI -	X-ray Contrast Agent
Iopromide	5	ESI -	X-ray Contrast Agent
[illegible]butylparaben	5	ESI -	Preservative
Isoproturon	100	ESI +	Herbicide
Ketoprofen	5	ESI +	Anti Inflammatory
Ketorolac	5	ESI +	Anti Inflammatory
Lidocaine	5	ESI +	Analgesic
Lincomycin	10	ESI +	Antibiotic
Linuron	5	ESI +	Herbicide
Lopressor (Metoprolol)	20	ESI +	Beta Blocker

TFC Membranes Tested

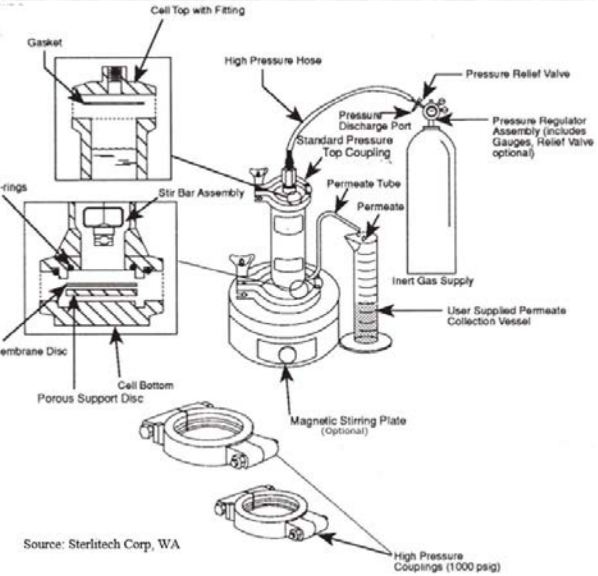
- 1st layer: polyester backing
- 2nd layer: polysulfone UF membrane
- 3rd layer: proprietary to establish surface charge (zeta)
- 4th layer: polyamide NF/RO membrane

Test Membrane	MWCO (Da)	Zeta Potential[a] (mV)	Contact Angle (degrees)
AG Series RO	100	-20	23
DK Series NF	200	-12	20

Sources: GE Osmonics, NSF MAST Research Center at University of Arkansas

[a] Zeta Potential at neutral pH

NF/RO Rejection Methods - Apparatus



Source: Sterlitech Corp, WA

Parameter	Specification
Membrane Coupon Diameter[a]	49 mm (1.93 in)
Active Membrane Area[a]	14.6 cm^2 (2.26 in^2)
Batch Process Volume[a]	300 mL
Constant TMP (Pressure Head)[a]	DK: 65 psi; AG: 145 psi
Specific Flux Range[a]	10 -12 GFD
Sample Temperature[a]	$20^\circ C \pm 0.5$
Sample pH[a]	7.0 – 7.5 (no sample adjustment)
Pressure Inlet	1/4 inch FNPT
Permeate Outlet	1/8 inch 316SST tubing
Wetted Materials of Construction:	
Cell Body	316 SST
O-Rings and Gaskets	Buna-N
Stir Bar	PTFE-coated magnet
Cell Dimensions:	
Body Diameter	5.1 cm (2.0 in)
Top Width (w/ clamp)	10.2 cm (4.0 in)
Bottom Width (w/ clamp)	13.3 cm (5.25 in)
Height	22.1 cm (9.5 in)

Sources: GE Osmonics; Sterlitech

[a] *As tested & verified*

CECs Detected in WRRF Effluents

- 82 CECs were detected above MRL in the PE samples
  - 14 CECs either did not exist at measurable level or were effectively removed by primary treatment
- 18 CECs were 100% removed by the WRRF biological processes (i.e. secondary treatment)
- 64 CECs were found to be recalcitrant above MRL in the SE
  - This group of CECs was the “focus set” of the membrane rejection research

Recalcitrant CECs

- 3/10 EDCs (2 artificial and 1 natural)
- 36/49 Pharmaceuticals:
  - 19 neutral
  - 17 ionic
- 4/4 Stimulants (all HL-N)
- 3/8 Preservatives
- 2/2 Artificial sweeteners (all HL-N)
- 3/3 Flame retardants (all HB-N)
- 13/18 Pesticides

NF Rejection Model Approach

Determine CEC-specific molecular properties that are relevant to known NF rejection mechanisms

- Quantitative Structural Activity Relationship (QSAR) properties

Differentiate NF Rejection Mechanisms (as cited in literature)

- Steric (Size) Exclusion
- Electro-Static (Ionic) Exclusion
- Dipole-Dipole (Hydrophobic) Sorption

- How useful are QSAR properties in modeling the rejection of recalcitrant CECs in simulated NF rejection for water reuse?

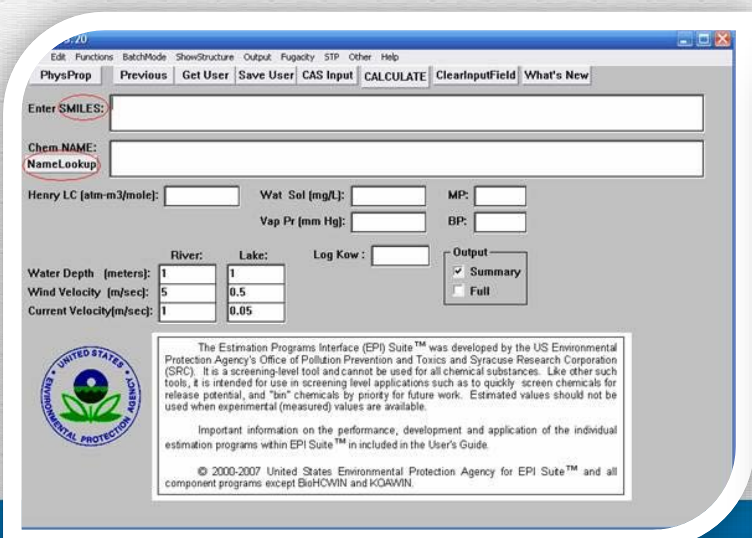
Central Question

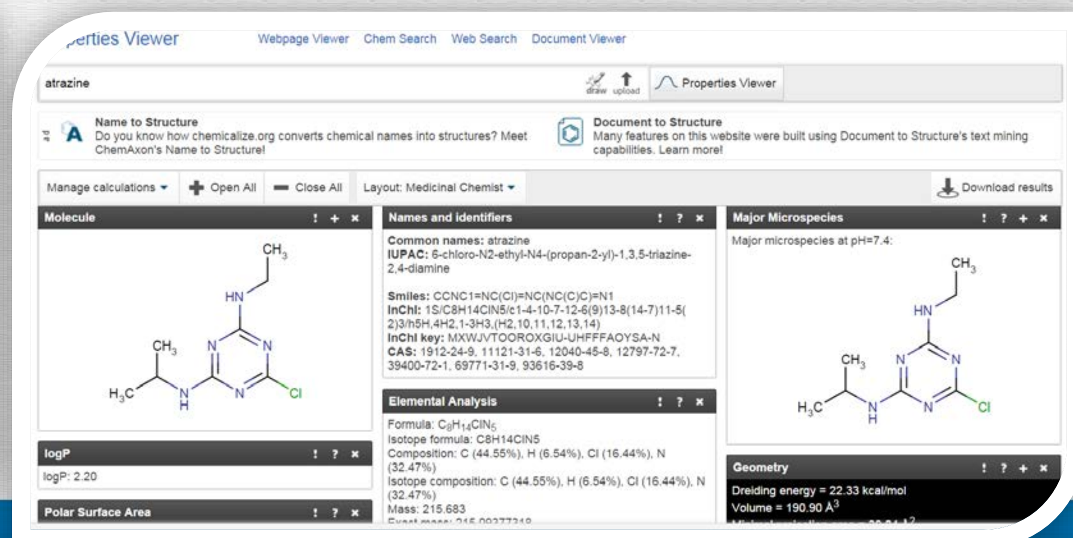
Predictive Parameters Tested

	Parameters	Relevant Rejection Mechanisms
Phase Partitioning	K_{ow}	Dipole-Dipole Sorption (Hydrophobicity)
	K_{aw}	
	K_{oa}	
Water Solubility	Solubility (S)	Dipole-Dipole Sorption (Hydrophobicity)
Surface Charge	Molecular Charge at Neutral pH (+/-)	Electro-Static Exclusion
Molecular Size	Molecular Weight (MW)	Steric (Size) Exclusion
	Polar Surface Area (PSA)	Steric (Size) Exclusion Dipole-Dipole Sorption
	Polarizability (α)	

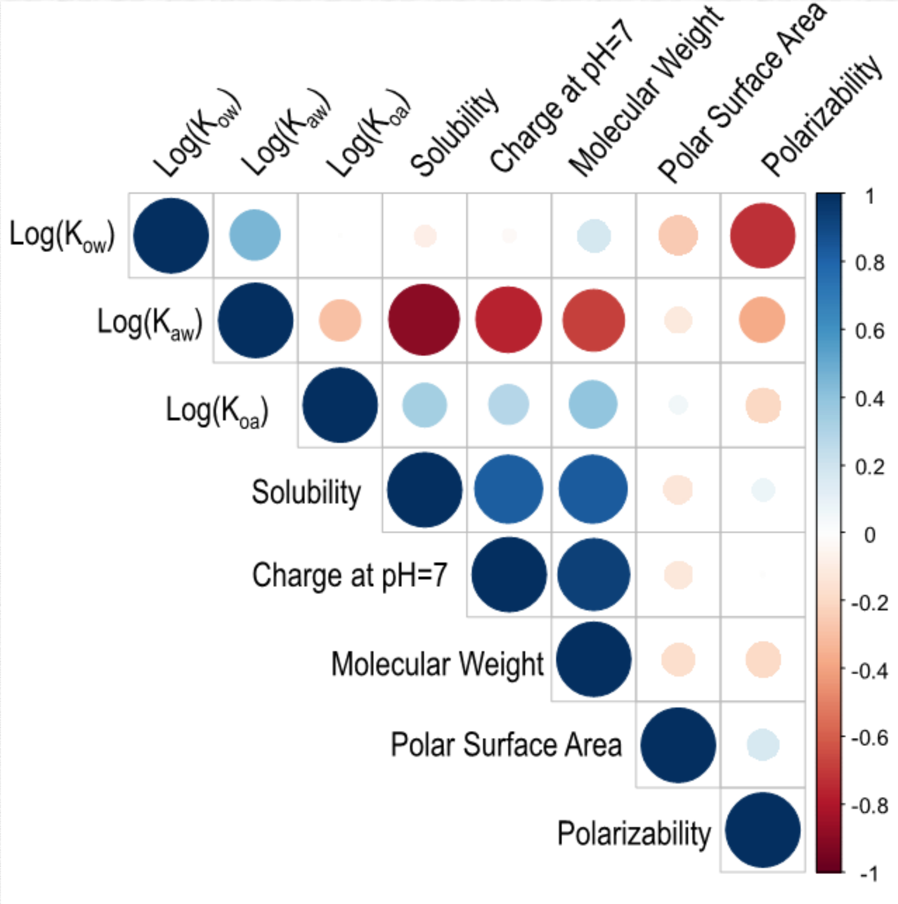
Libraries of Chemical Data (all 96 CECs)

Parameter	Source
K_{ow}, K_{oa}, K_{aw}	EPA EPI Suite v.4.11
Solubility (S)	EPA EPI Suite v.4.11
Molecular Weight (MW)	chemicalize.org
Polar Surface Area (PSA)	chemicalize.org
Polarizability (α)	chemicalize.org
Molecular Charge at Neutral pH (+/-)	chemicalize.org





Predictor Collinearity (Pearson Correlation)

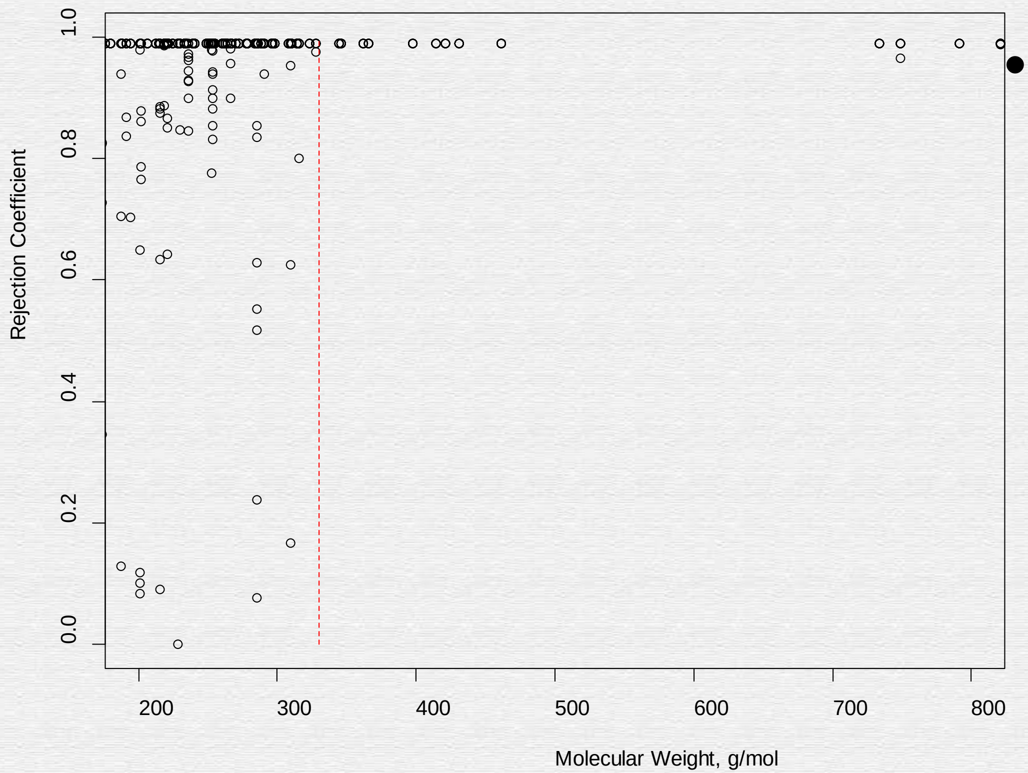


Predictor Variables <u>without</u> Collinearity
Log(K_{oa}) vs Polar Surface Area
Log(K_{ow}) vs Log(K_{oa})
Log(K_{ow}) vs Charge at pH = 7
Log(K_{oa}) vs Polar Surface Area
Charge at pH = 7 vs Polarizability

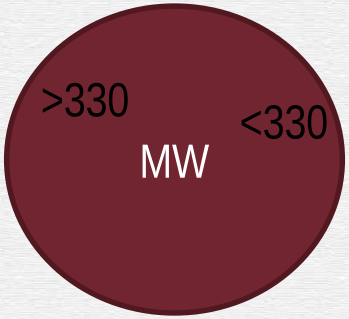
All Potential Predictor Variables for a Multivariate Model

Collinearity is a phenomenon in which two predictor variables in a regression model are highly correlated, meaning that one can be linearly predicted relative to the other with a high degree of accuracy (Weisberg, S. 2005)

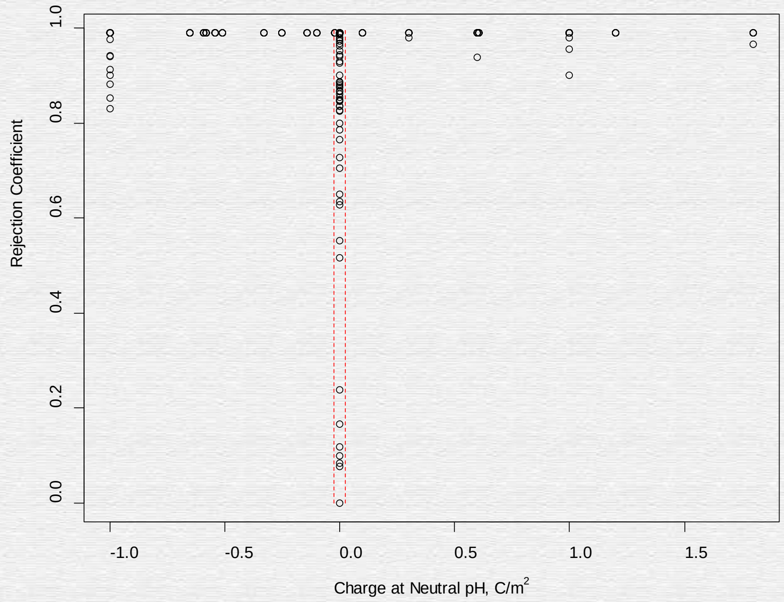
Steric Exclusion: Molecular Weight



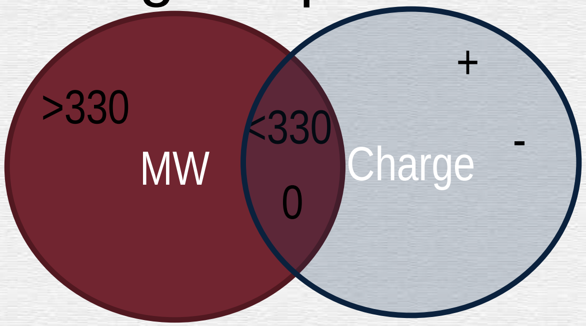
- Clear *molecular weight cut-off* at 330 g/mol:
  - CECs with MW > 330 g/mol → 100% rejection by NF
  - CECs with MW < 330 g/mol → significant variability in observed NF rejection



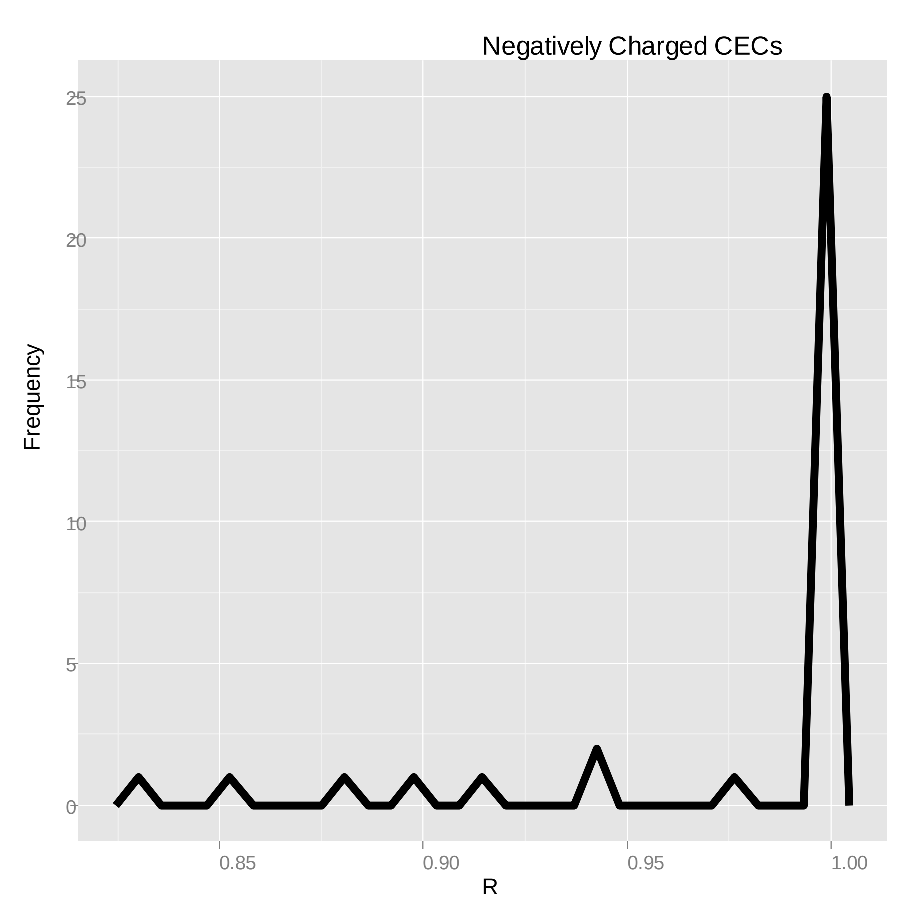
Ionic Exclusion:
Molecular Charge at Neutral pH



- Both positively and negatively charged CECs at pH 7 are highly rejected
- Significant variability in rejection of CECs with no surface charge at pH 7

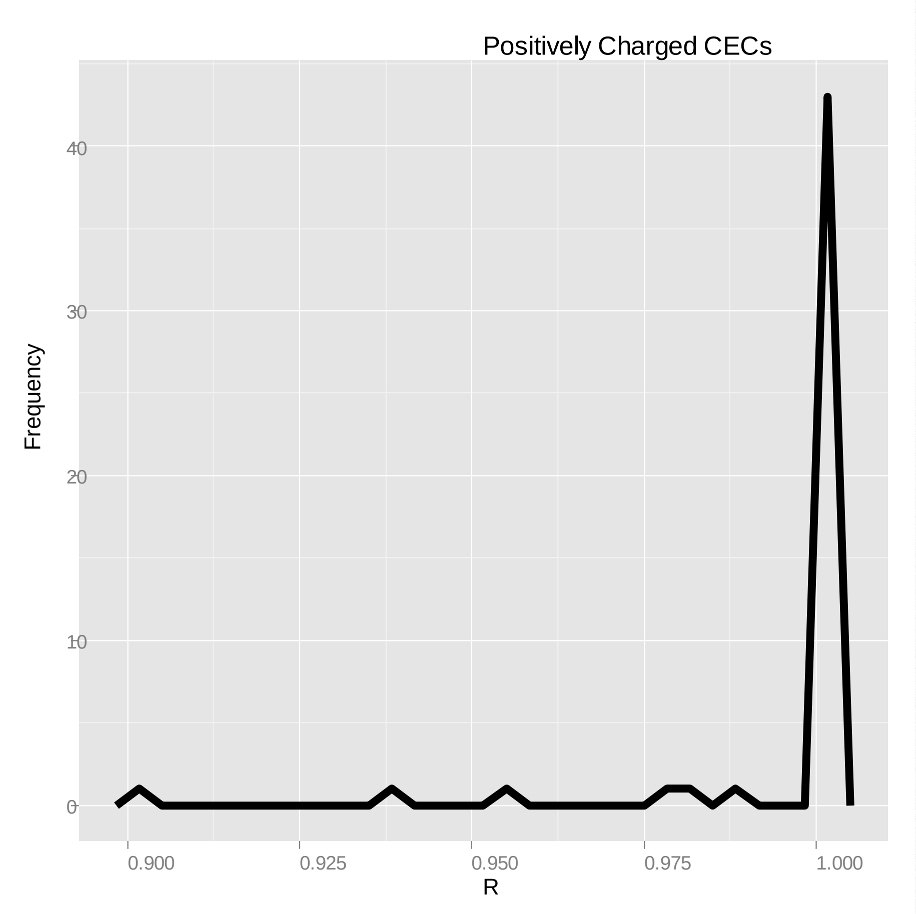


100% Rejection Observed for Negatively Charged CECs



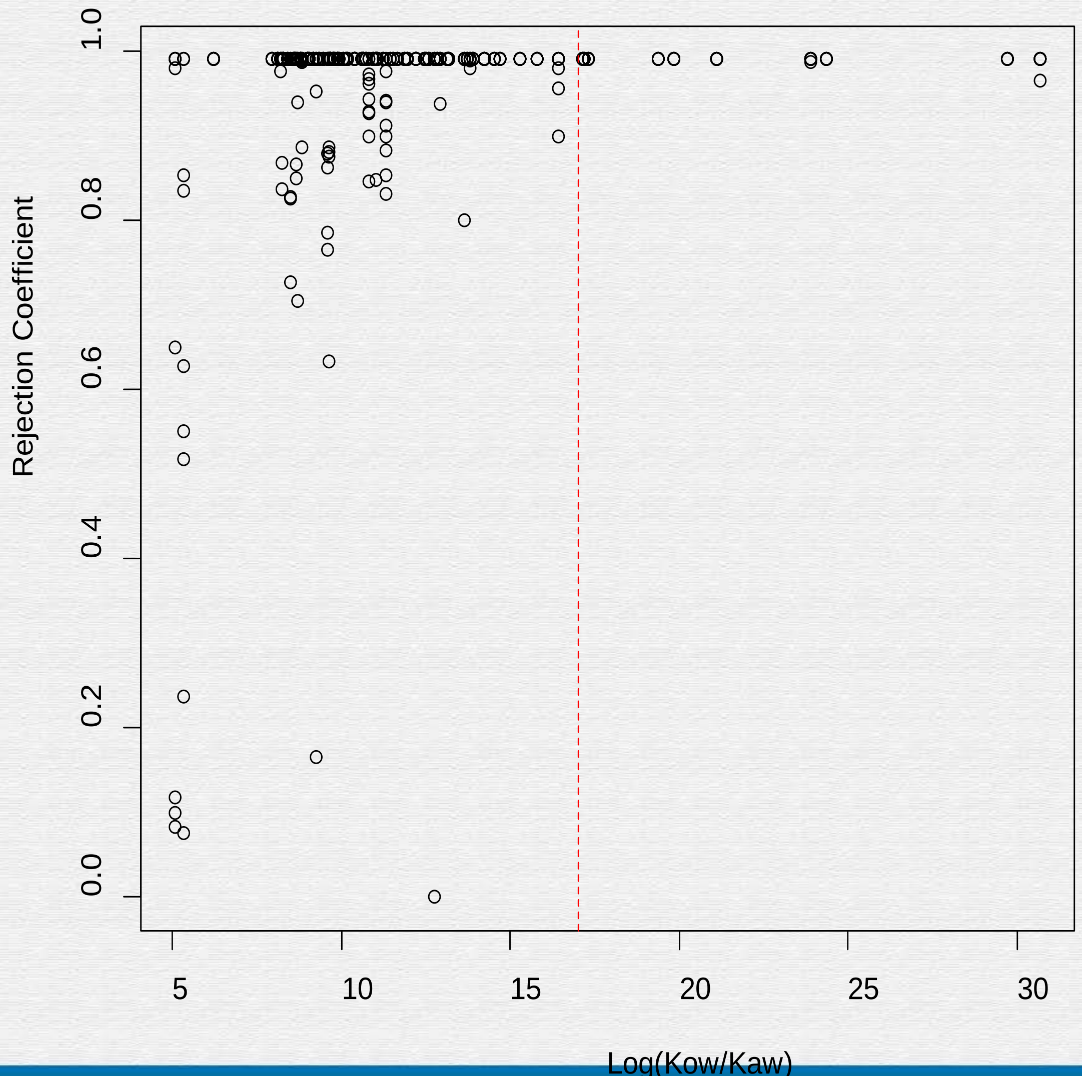
	R
1st Quartile	1.0
Median	1.0
3rd Quartile	1.0

100% Rejection Also Observed for Positively Charged CECs

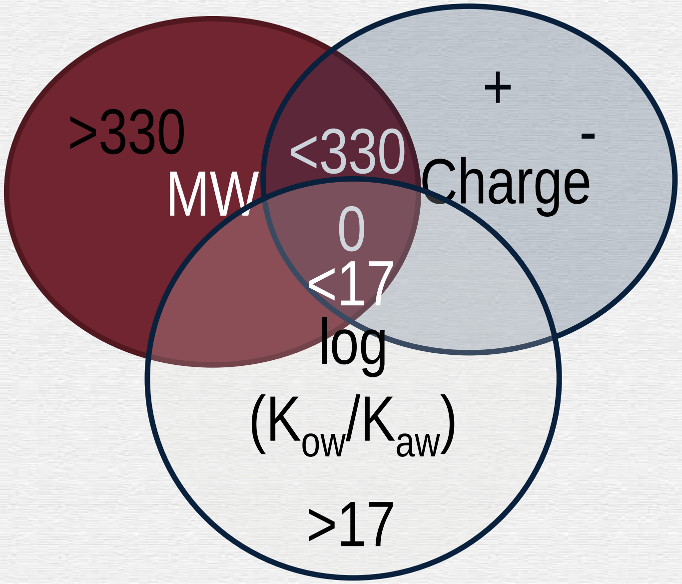


	R
1st Quartile	1.0
Median	1.0
3rd Quartile	1.0

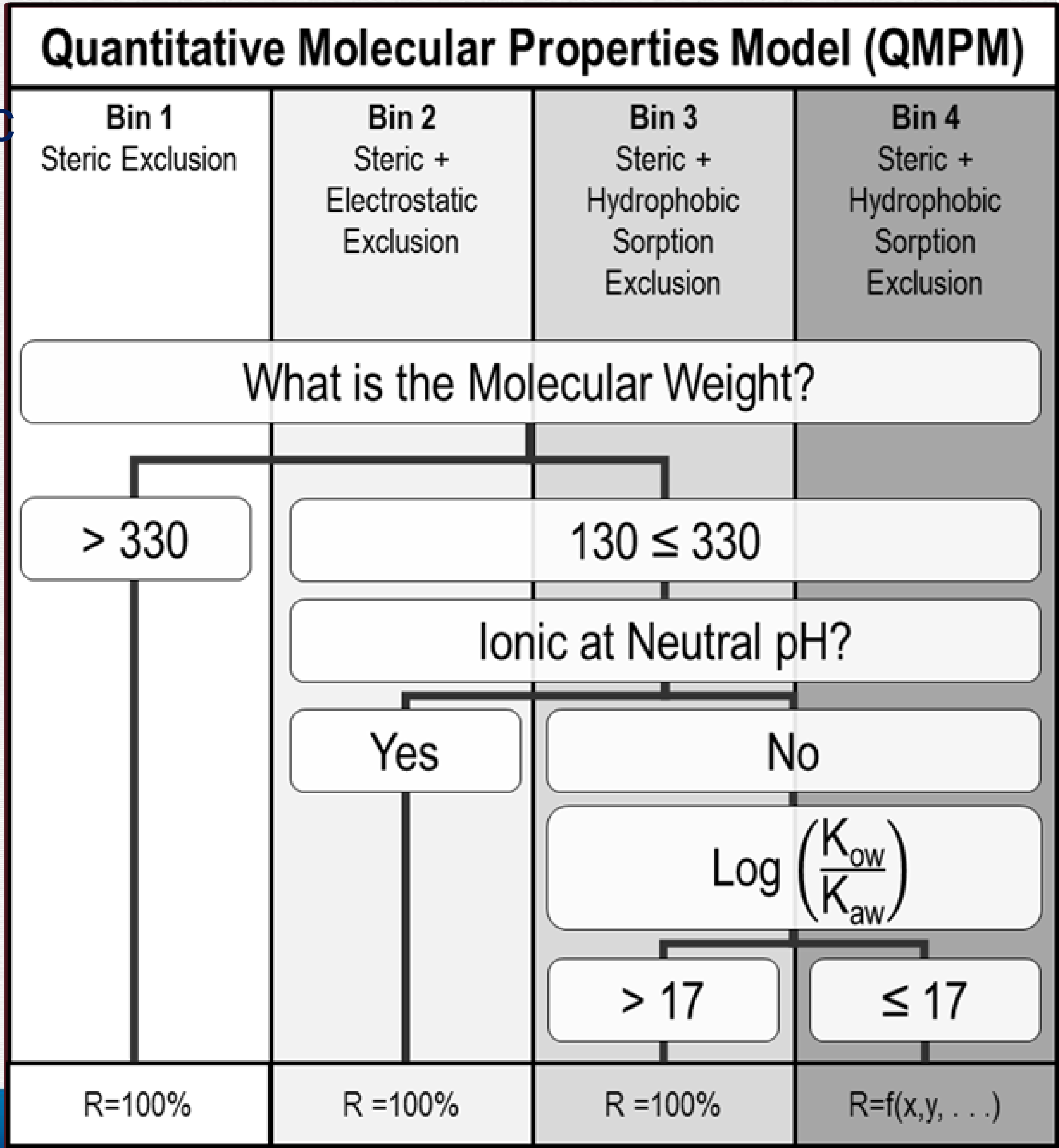
Hydrophobic Sorption: log (Kow/Kaw)



- CECs with log (K_{ow}/K_{aw}) > 17
  - *100% rejection*
- Significant variability in rejection of CECs with log (K_{ow}/K_{aw}) < 17



Can a deterministic multivariate model explain the remaining rejection coefficient variation?



If we separate the observed 100% CEC rejection events from Bin 4. . .

. . . There are two predictor variables that can explain a significant amount of the remaining variation in observed CEC rejection:

- $\log(K_{ow}/K_{aw})$
- Polar Surface Area (PSA)

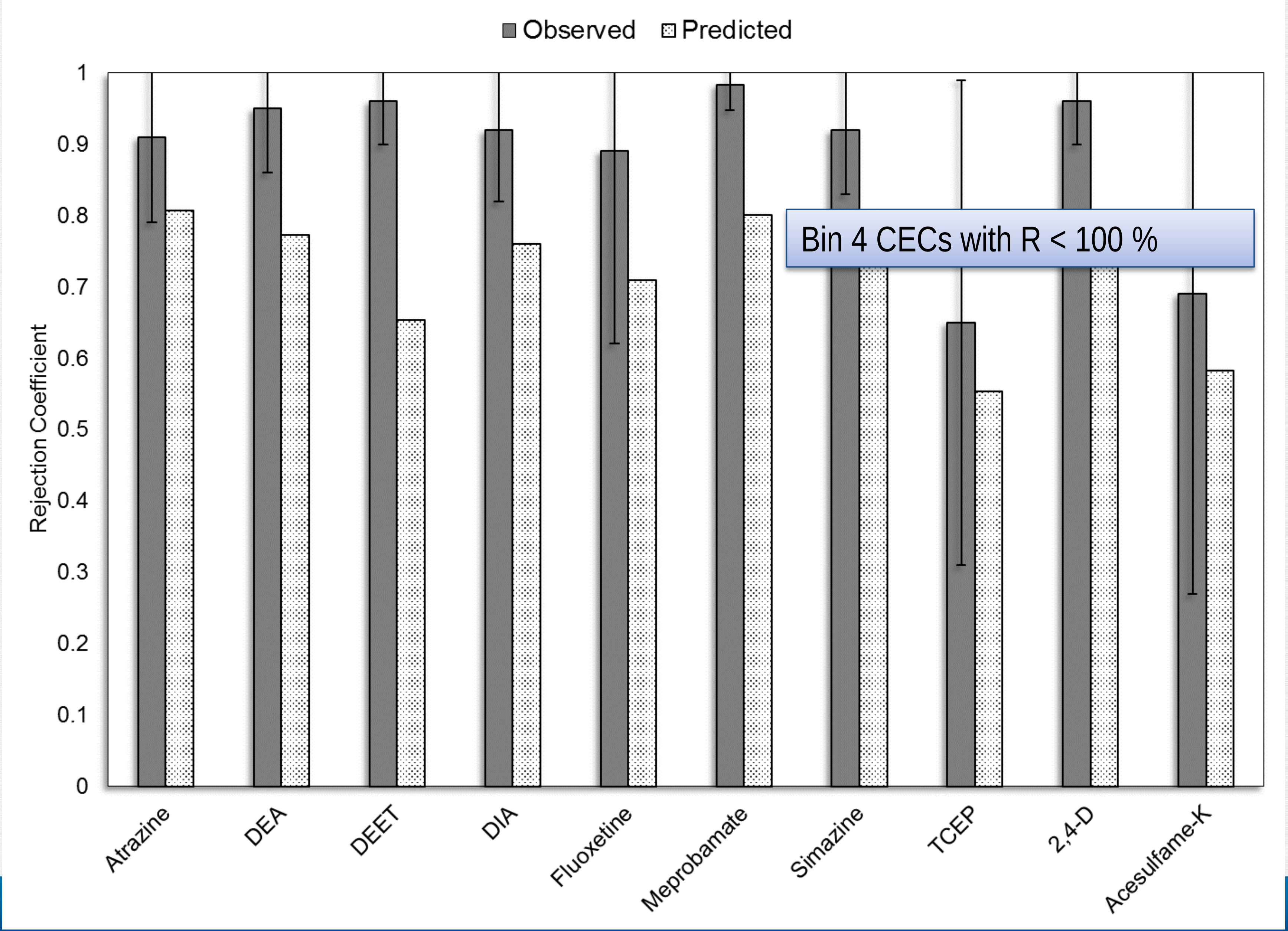
Coefficient	Mean **Value**	StdDev (+/-)	Confidence p-value
β_1	0.05301	0.01520	0.0011
β_2	0.16502	0.07720	0.0380

$$R = \begin{cases} \beta_1 \log(\frac{K_{ow}}{K_{aw}}) + \beta_2 \log(PSA), & log\left(\frac{K_{ow}}{K_{aw}}\right) \leq 17 \\ \geq 99\%, & log\left(\frac{K_{ow}}{K_{aw}}\right) > 17 \end{cases}$$

Rejection

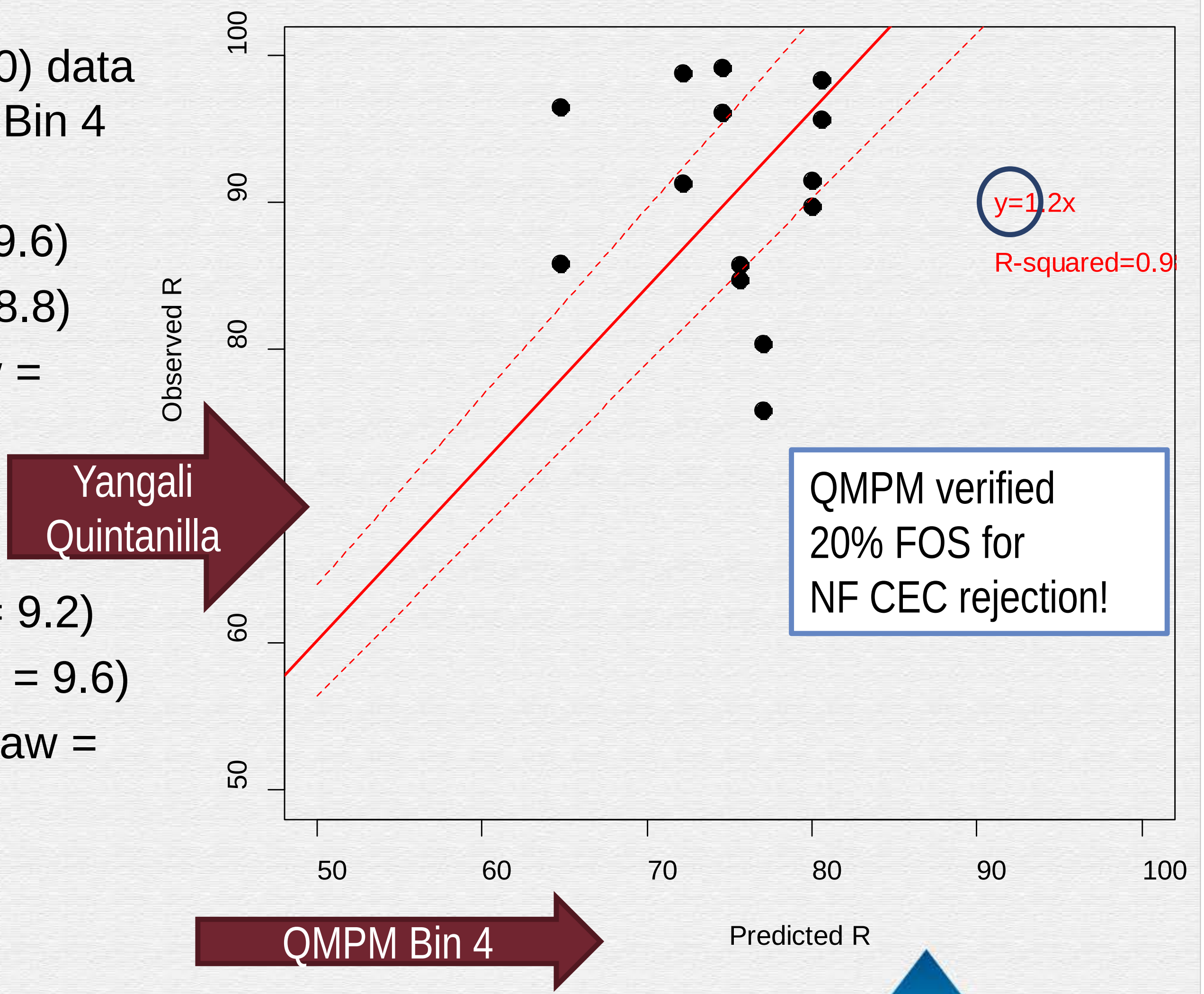
Bin 4

Validation with Observed Bin 4 Data



Model Bin 4 Eqn Verification: Independent NF Rejection Dataset

- Yangali Quintanilla's (2010) data set included the following Bin 4 CECs:
- Atrazine (log Kow/Kaw = 9.6)
- Caffeine (log Kow/Kaw = 8.8)
- Phenazone (log Kow/Kaw = 7.95)
- 4-Nonylphenol (log Kow/Kaw = 9.4)
- Ibuprofen (log Kow/Kaw = 9.2)
- Phenacetin (log Kow/Kaw = 9.6)
- Metronidazole (log Kow/Kaw = 9.14)



Bin Classification of 96 CEC Studyset

Bin 1

Bin 2

Bin 3

Bin 4

A
Benc
Deh
E

Al
A
Ca
Chlora
Cir
Dic
Flu
Lic
Lo
Meclofe
Oxo
Sulfachl
Sulf

1,7-Dimethylxanthine	Chloridazon	Fluoxetine	Primidone
2,4-D	Chlorotoluron	Gemfibrozil	Progesterone
4-nonylphenol	Clofibric Acid	Ibuprofen	Propazine
4-tert-Octylphenol	Cotinine	Isobutylparaben	Propylparaben
Acesulfame-K	Cyanazine	Isoproturon	Quinoline
Acetaminophen	DACT	Ketoprofen	Simazine
Andorostenedione	DEA	Ketorolac	TCEP
Atrazine	DEET	Linuron	TCPP
BPA	DIA	Meprobamate	Testosterone
Bromacil	Diazepam	Metazachlor	Theobromine
Butalbital	Dilantin	Methylparaben	Triclocarban
Butylparaben	Diuron	Metolachlor	Warfarin
Caffeine	Estradiol	Naproxen	
Carbamazepine	Estrone	Norethisterone	
Carisoprodol	Ethinyl Estradiol	Pentoxifylline	
	Ethylparaben	Phenazone	

Research Conclusions

- CEC control for DPR applications:
  - WRRF secondary treatment proved a significant barrier for CEC control in reuse applications
  - NF proved a suitable FAT alternative barrier to RO for CEC control
  - RO proved an absolute barrier for CEC control
- NF rejection & QSAR modeling:
  - For MW > 330 g/mol, R = 100%
  - For MW = 130 to 330 g/mol:
    - Ionic charged (I), R = 100%
    - HB-N, R = 100%
    - HL-N, R = 0.05301 log(Kow/Kaw) + 0.16502(PSA)
  - QMPM was validated and proved portable as a decision tool for the selection of NF as an effective barrier technology for DPR

Conclusions: Barrier FOS for the SDWA Regulated CECs

CEC	Max WRRF SE	Max NF Permeate	NPDWR MCL	FOS WRRF / NF
2,4-D	280 ng/L	34 ng/L	70,000 ng/L	250 / 2,058
Atrazine	610 ng/L	27 ng/L	3,000 ng/L	4.9 / 111
Simazine	210 ng/L	31 ng/L	4,000 ng/L	6.7 / 129

How does the NF permeate compare to suggested NWRI risk-based protection levels?

CEC	Min. (ng/L)	Mean (ng/L)	Max (ng/L)	NWRI Criterion (ng/L)	**NF FOS**
Ethinyl Estradiol	*Not Detected in PE*			5	**--**
17–β-estradiol	*Not Detected in SE*			5	**--**
Cotinine	ND	ND	ND	1,000	**100**
Primidone	ND	ND	ND	10,000	**2,000**
Dilantin	ND	ND	ND	2,000	**100**
Meprobamate	ND	<5	9	200,000	**22,222**
Atenolol	ND	<5	27	4,000	**148**
Carbamazepine	5	12	19	10,000	**526**
Estrone	ND	ND	ND	320	**64**
Sucralose	ND	<100	160	150,000,000	**937,500**
TCEP	ND	92	160	5,000	**31**
DEET	ND	<5	21	200,000	**9,524**
Triclosan	ND	9	35	50,000	**1,429**

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