New Techniques for Real-Time Monitoring of Reverse Osmosis (RO) Membrane Integrity

April 10, 2014

WateReuse Research Foundation Webcast Series

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WATEREUSE RESEARCH

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New Techniques for Real-Time Monitoring of Membrane Integrity for Virus Removal

WRF-09-06b

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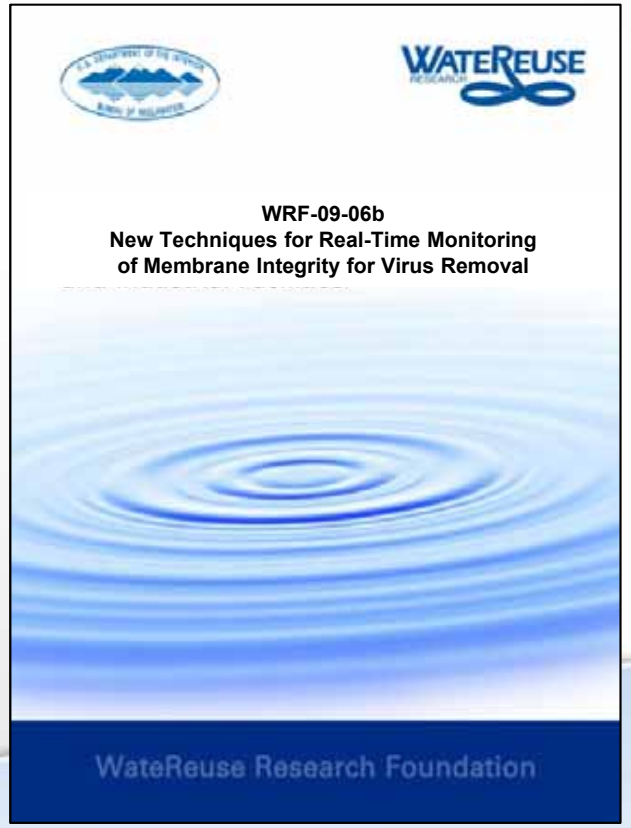
WateReuse 09-06b report published in 2014



Overview

- Introductions
- Current Status of MIT for RO/NF
- Objectives and Research Methods
- Theoretical Concept of newly Proposed PM-MIMo
- Practical Testing of Newly Proposed PM-MIMo
- Summary of Research Result

Introductions

Principal Investigator

Val S. Frenkel, Ph.D., P.E., D.WRE., *EKI*

Co-Principal Investigator

Prof. Yoram Cohen, Ph.D., UCLA

Research Project Team

- Anditya Rahardianto, Ph.D., *UCLA*
- Sirikarn Surawanvijit, *UCLA*
- John Thompson, *UCLA*
- Gregg Cummings, P.E., *PARSONS*

Introductions

Project Advisory Committee

- Michelle Chapman, *U.S. Bureau of Reclamation (USBR)*
- Bob Hultquist, *California Department of Public Health (CDPH)*
- Kevin Alexander, *Hazen & Sawyer*
- Zia Bukhari, *American Water*

Introductions

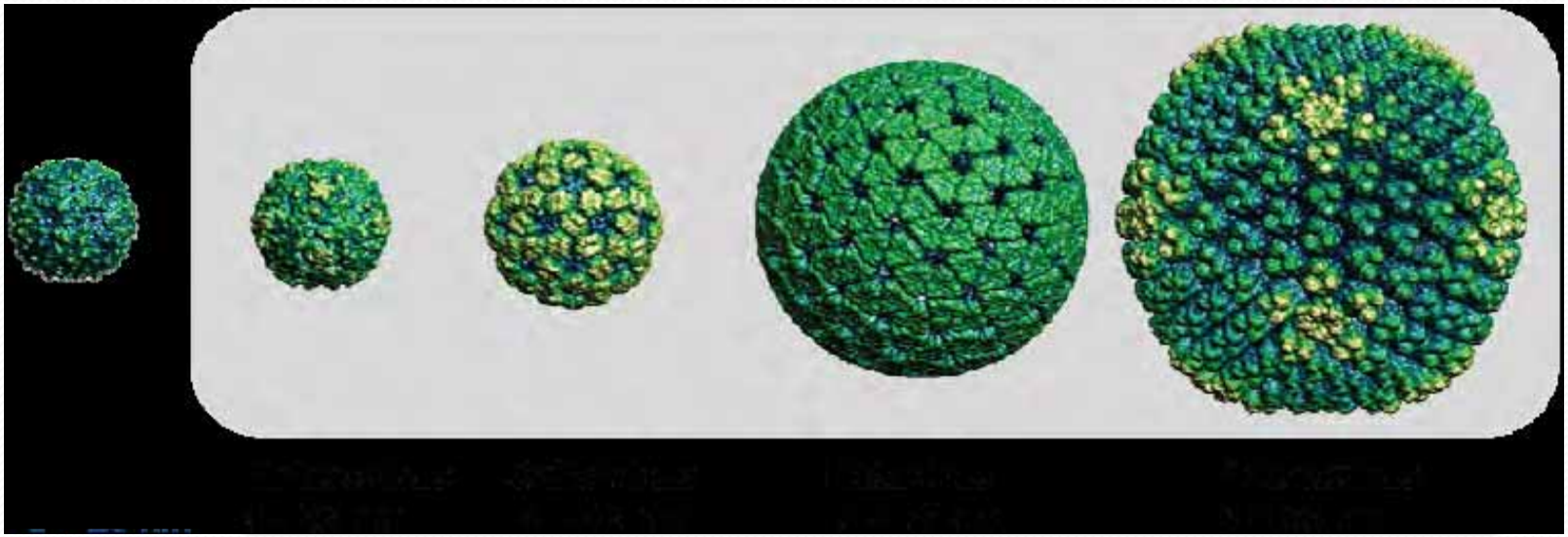
Participating Organizations

- Kennedy/Jenks Consultants (California)
- UCLA Water Technology Research (WaTeR) Center (California)
- El Paso Water Utilities (Texas)
- East Bay Municipal Utilities District (California)
- Tampa Bay Water (Florida)

Abbreviations

- RO Reverse Osmosis
- NF Nanofiltration
- Q Flow
- PM-MIMo Pulsed-marker membrane integrity monitoring
- MIM Membrane Integrity Monitoring
- MIT Membrane Integrity Testing
- PFRO Plate-and-Frame Reverse Osmosis
- SPRO Spiral-Wound Reverse Osmosis

Viruses



MS2 d= 28nm | **Enterovirus** d= 32 nm | **Calicivirus** d = 42 nm | **Rotavirus** d = 77 nm | **Adenovirus** d = 95 nm

Depiction of surfaces of common waterborne enteric virus capsids (grey background) and their typical surrogate (MS2) bacteriophage

Regulations

According to the U.S. Environmental Protection Agency (EPA) Surface Water Treatment Rule (SWTR), inadequately treated water may contain disease-causing microorganisms, which include bacteria, viruses, and parasites (California Department of Public Health, 2009a). In 1986, SWTR established requirements for removal and inactivation of these pathogens from the surface water systems. These regulations are on the basis of a minimum log removal value (LRV):

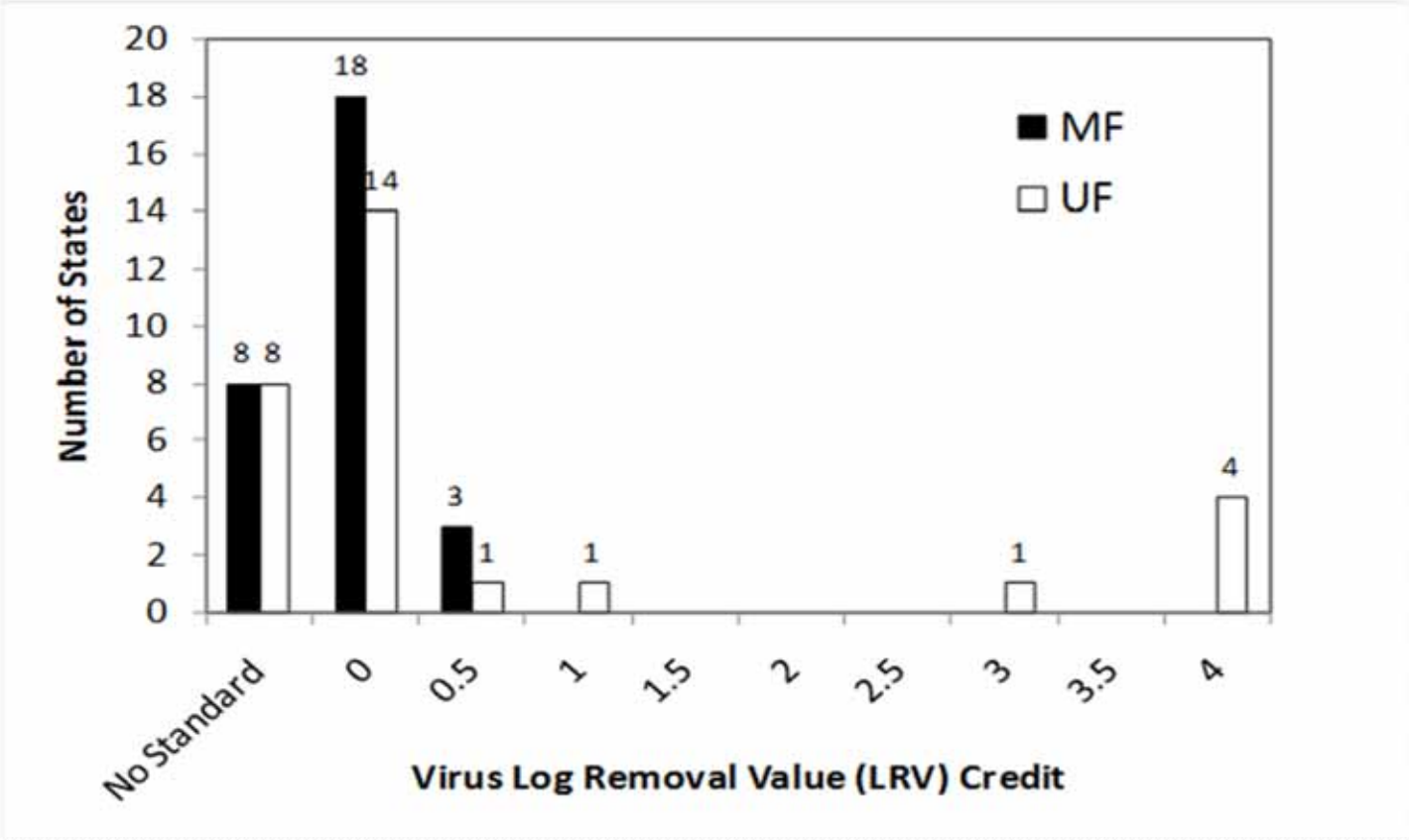
$$LRV = \log_{10}\left(\frac{C_f}{C_p}\right)$$

where C_f and C_p are the concentrations of the pathogen or microorganism in the feed and permeate streams, respectively. Under SWTR, LRVs in water treatment processes are regulated as follows (U.S.EPA, 2001):

- 99 % (2-log) removal and/or inactivation of Cryptosporidium
- 99.9% (3-log) removal and/or inactivation of Giardia
- 99.99% (4-log) removal and/or inactivation of viruses

In California, 4-log removal and/or inactivation of Cryptosporidium and 99.999% (5-log) removal and/or inactivation of viruses are required for disinfected recycled water (California Department of Public Health, 2009b).

Regulations

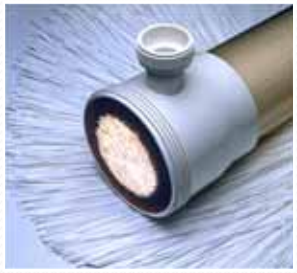


Summary of state virus removal credit for MF and UF

CDPH Pathogen Removal Credits

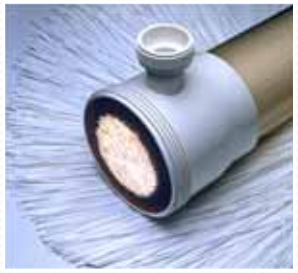
	Conventional Clarification – Filtration	CDPH MF Membrane Filtration	CDPH UF Membrane Filtration
Giardia Removal Credit	2.5-log	4-log	4-log
Required Giardia Inactivation	0.5-log	0.5-log for multi-barrier	0.5-log for multi-barrier
Virus Removal Credit	2-log	0.5 to 2.5-log	3.5 to 4 log
Required Virus Inactivation	2-log	2 to 3.5-log for multi-barrier	2-log for multi-barrier

Membrane Technologies



- *Microfiltration (MF)* - separates particles from 0.1 to 0.5 microns
- *Ultrafiltration (UF)* - rejects materials from 0.005 to 0.05 microns (1,000 – 500,000 Daltons MWCO)
- *Nanofiltration (NF)* - rejects materials from 0.0005 to 0.001 microns (200 – 1,000 Daltons MWCO)
- *Reverse Osmosis (RO)* – rejects species ranging in molecular size down to 10 Daltons MWCO

Membrane Technologies



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- *Reverse Osmosis (RO)* – rejects species ranging in molecular size down to 10 Daltons MWCO

YES – Direct MIT

NO – Direct MIT

MIT Methods: Indirect, Direct

Indirect MIT:

- ***Turbidity***
- ***Conductivity***
- ***Particle Counting (Particle Size Distribution – PSD)***
- ***Sulfate Concentration (sensitivity up to 3 LRV)***
- ***TOC Concentration (sensitivity up to 4 LRV)***

MIT Methods: Indirect, Direct

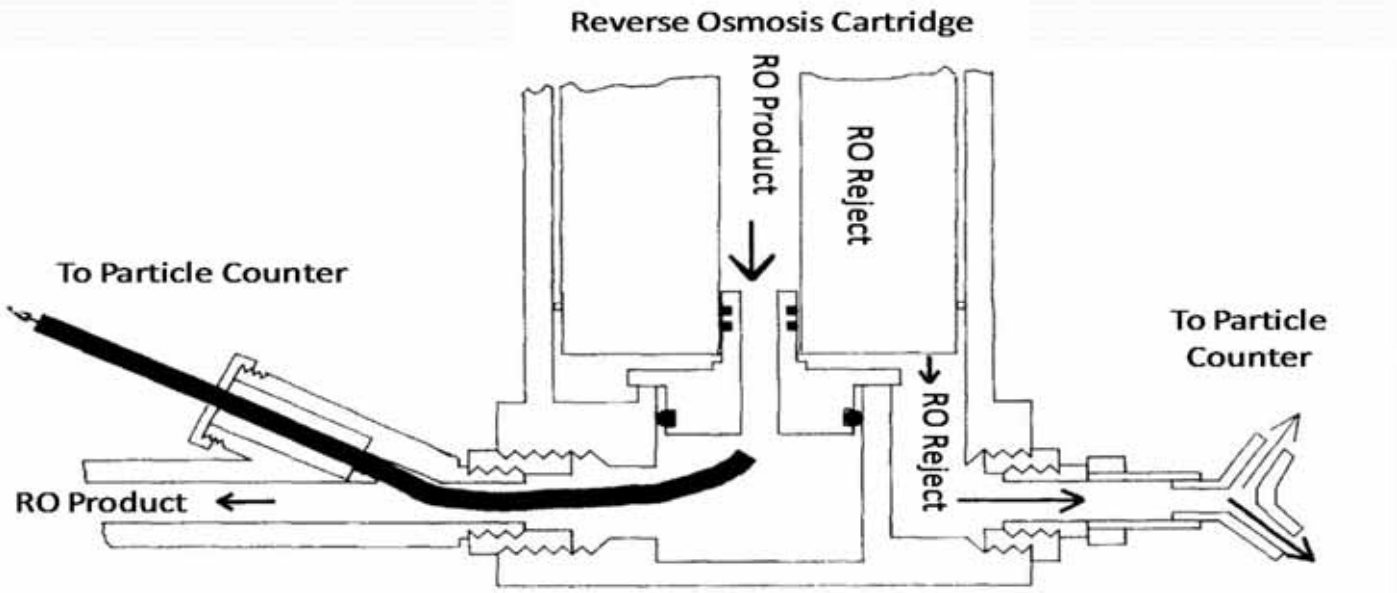
Indirect MIT:

- ***Turbidity***
- ***Conductivity***
- ***Particle Counting (Particle Size D… …D)***
- ***Sulfate Con… …ivity up to 3 LRV)***
- ***TO… …centration (sensitivity up to 4 LRV)***

Indirect MIT methods are inaccurate: dependent on RO/NF feed water quality and on membrane system operating conditions

Indirect MIT

An experimental setup for testing membrane integrity of an RO membrane cartridge via particle counting

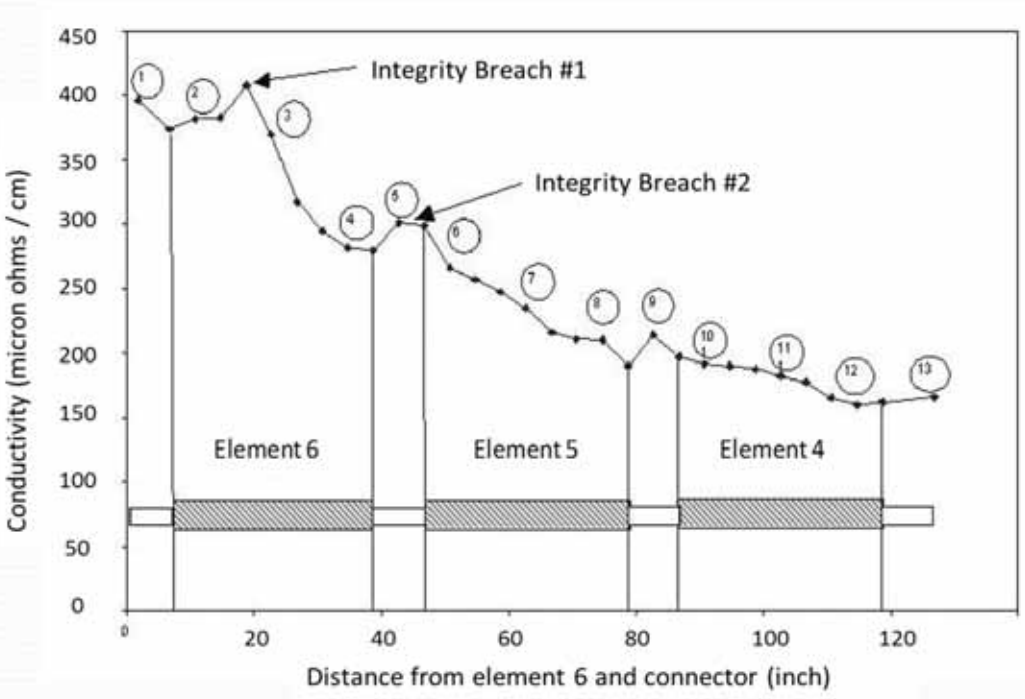


Membrane	LRV	Median Particle Load (particles/mL)	
		RO Reject	RO Product
CA1	1.61−1.90	3.1×10^3	60
CA1	1.53−1.87	5.6×10^3	155
CA2	3.70−3.97	3.2×10^3	0.48
PS	4.47−4.76	5.0×10^3	0.13
PA	3.67−3.93	3.2×10^3	0.44
CA2	4.61−4.83	5.2×10^3	0.09

Log Removal of Particles by Different Types of RO Membranes[(a)] as Determined via Laser Diffraction Particle Counter

MIT Methods: Indirect, Direct

Indirect MIT: Axial Probing



Conductivity probing data in Stage 2 of a 2-stage RO system, indicating multiple suspected integrity breaches

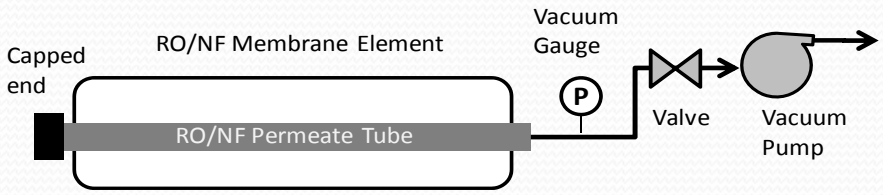
MIT Methods: Indirect, Direct

Direct MIT:

Pressure Methods (off-line pressure decay test)

Vacuum Methods

Marker Based Methods (biological, non-biological markers, fluorescent-tagged bacteriophages, nanoparticles molecular dyes and macromolecules)



Schematic of vacuum-hold test for an RO membrane element

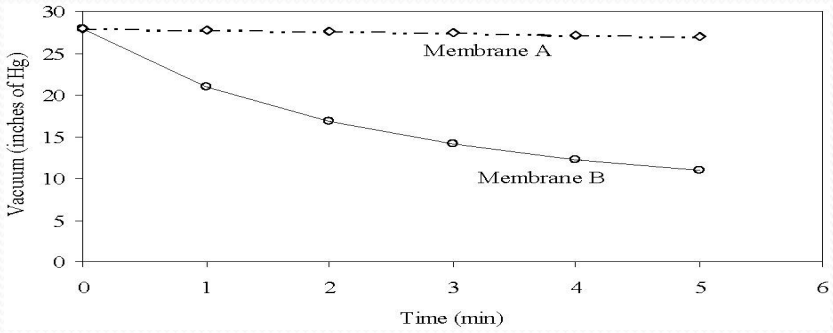


Illustration of vacuum decay test profile for an intact (membrane A) versus a compromised (membrane B) membrane

MIT Marker Based Methods:

Phages:

- MS2 bacteriophages,
- PRD1 bacteriophages,
- QB coliphages
- T4 coliphages

MIT Marker Based Methods:

Phages:

- MS2 bacteriophages,
- PRD1 bacteriophages,
- QB coliphages
- T4 coliphages

Phages as surrogates for testing are biological in nature, and can undergo biological inactivation and grow in water systems

MIT Marker Based Methods:

Fluorescent-tagged Nanoparticles (1 – 100 nm):

- Gold (Au)
- Silver (Ag)
- Copper (Cu)
- Silica (Si)
- Polystyrene (PS) microspheres

MIT Marker Based Methods:

Fluorescent-tagged Markers Selection Based on:

- *Toxicological effects*
- *pH dependency*
- *Salinity dependency*
- *Temperature dependency*
- *Photochemical decay*

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High cost, for gold $45–$120/mL

MIT Marker Based Methods:

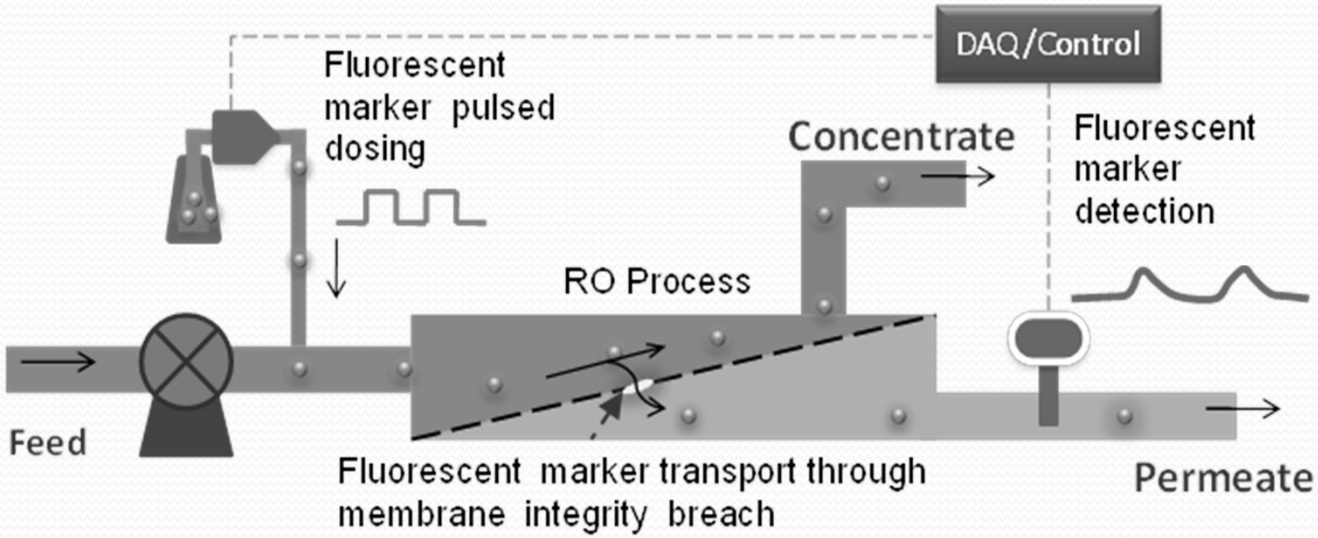
Fluorescent Molecular Dyes

Fluorescent Dyes	Ex/Em[(a)] (nm)	Chemical Formula	Mol Wt	Solubility in Water (mg/mL)
Rhodamine WT	554/580	$C_{29}H_{29}N_2NaO_5$	480.55	Very soluble
Rhodamine B	554/576	$C_{28}H_{31}ClN_2O_3$	479.02	50
Rhodamine 6G	526/552	$C_{28}H_{31}ClN_2O_3$	497.02	20
Sulforhodamine B	554/576	$C_{27}H_{29}N_2NaO_7S_2$	580.65	10
Amidorhodamine G	530/551	$C_{25}H_{25}N_2NaO_7S_2$	552.59	Very soluble
Fluorescein	490/520	$C_2oH_{12}O_5$	332.31	0.3
Uranine	491/512	$C_{20}H_{10}Na_2O_5$	376.28	40
Eosin B	516/538	$C_{20}H_6Br_4Na_2O_5$	691.88	40
Pyranine	455/512	$C_{16}H_7Na_3O_{10}S_3$	524.39	178
Tinopal CBS-X	346/435	$C_{28}H_{20}Na_2O_6S_2$	562.57	25
Erythrosine	525/547	$C_{20}H_6I_4Na_2O_5$	879.87	20
Sodium naphthionate	320/430	$C_{10}H_8NNaO_3S$	245.23	240
Lanaperl fast yellow	469/508	$C_{25}H_2ON_5NaO_6S_2$	549.55	Very soluble
Lissamine FF	432/508	$C_{19}H_{13}N_2NaO_5S$	404.38	40
Bengal rose	518/535	$C_{20}H_2Cl_4I_4Na_2O_5$	1017.67	100
Fluorescent brightener 28	349/430	$C_4oH_{42}N_{12}Na_2O_{10}S_2$	960.96	Very soluble

Commonly Used Fluorescent Molecular Dyes for Tracers in Water Systems

Ex/Em = Wavenumbers for fluorescence excitation (Ex) and emission (Em) peaks

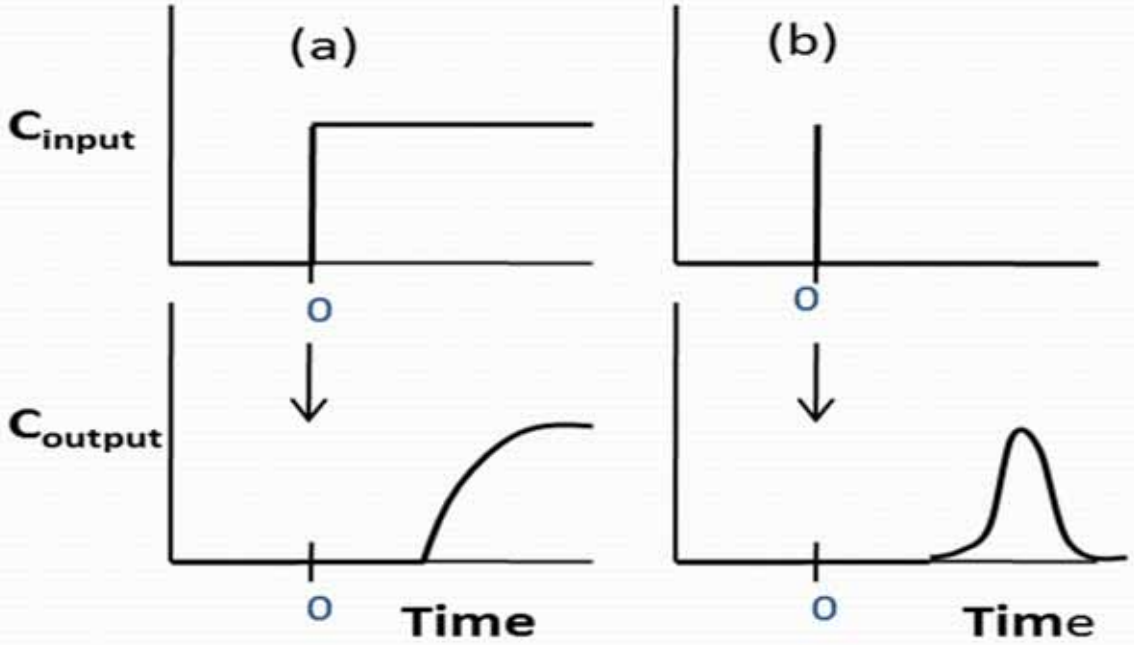
Membrane Technologies



Pulsed-marker membrane integrity monitoring (PM-MIMo) scheme

PM- MIMo™ , UCLA Patent pending technology

Membrane Technologies



Schematic Illustration of dynamic response curves of marker step (left) and impulse (right) inputs in a laminar flow channel

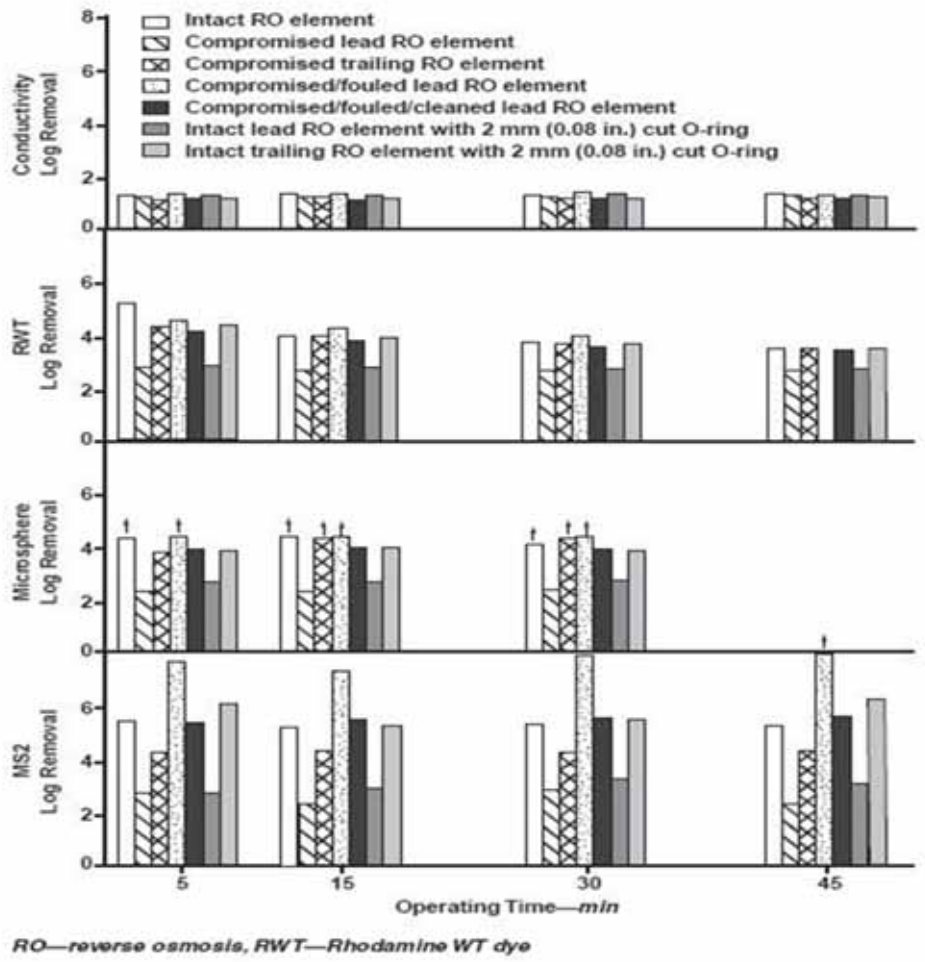
C_{input} and C_{output} refer to the marker concentrations in the RO feed and permeate streams, respectively

MIT Marker Based Methods:

Fluorescent-tagged Markers Selection Based on:

- *Toxicological effects*
- *pH dependency*
- *Salinity dependency*
- *Temperature dependency*
- *Photochemical decay*

MIT Marker Based Methods:



Performance of RO MIT for intact and compromised membranes on basis of 4 different testing methods

NOTE: MVTU = multi-vessel testing unit

MIM Marker Based Methods:

Fluorescent-tagged Markers Selection Criteria:

- Sensitive for detecting nano-sized (1 nm – 100 nm) contaminants at low concentration levels
- Capable of detecting membrane breach in (near) real_time to enable timely corrective actions
- Informative regarding breach characteristics
- Cost effective for municipal applications

MIT Marker Based Methods:

Constant Marker Concentration Approach (Current):

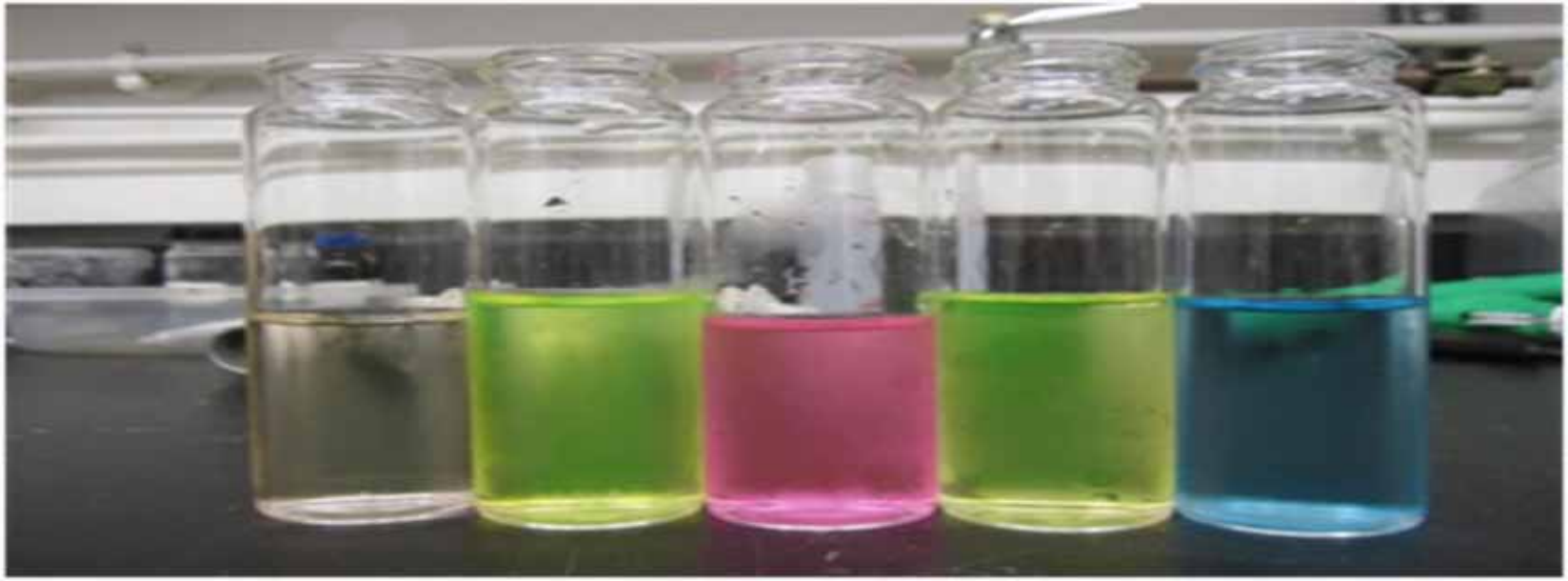
- High cost of markers
- Temporal variations in water quality
- LRV of the marker for a constant feed marker concentration (between intact and compromised membranes) may be insufficient for assessing the extent and characteristics of membrane breaches

MIT Marker Based Methods:

Fluorescent-tagged Markers Selection Criteria:

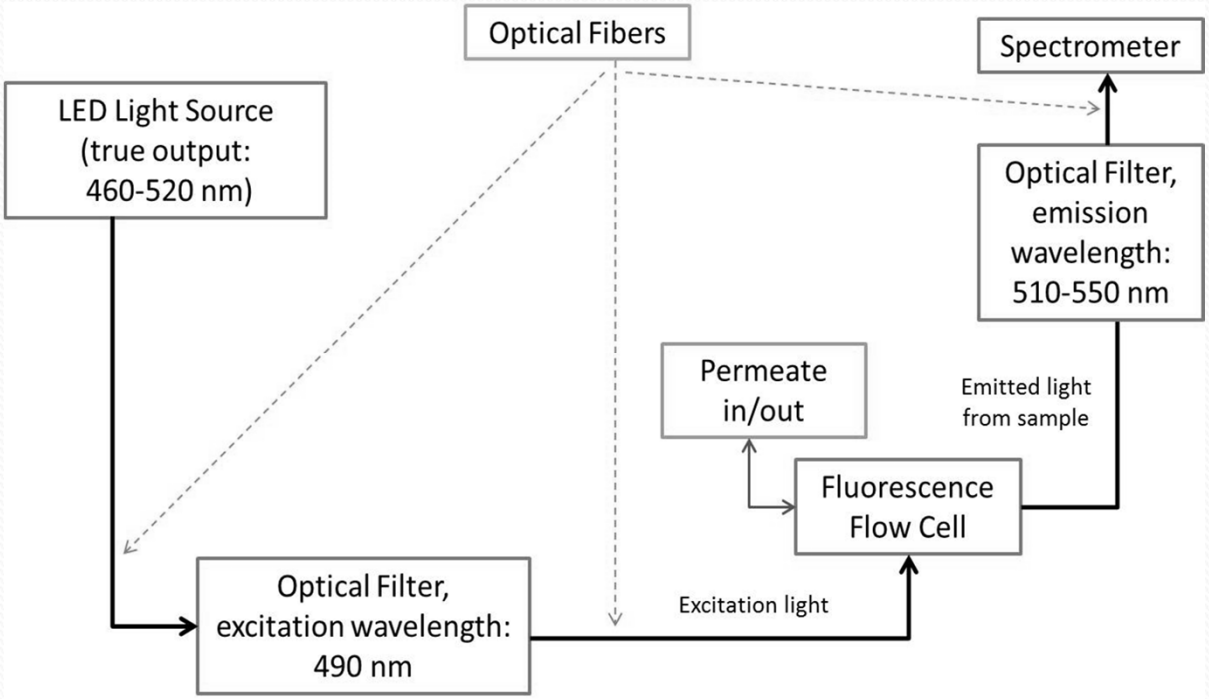
Characteristics	Description
Sensitive	· Detect low concentrations of target species in permeate from a single or multiple element breaches within a full-scale membrane train · Quantify the range of target species LRV
Real-time	· System shutdown is not required · Normal filtration continues during integrity monitoring
Comprehensive	· Characterize the extent of breach · Provide useful information to identify membrane breach location for corrective actions
Cost-Effective	· Do~~es~~ not require significant additional equipment or overhauls for existing plants · Expensive or rare/specialty chemicals are not required

PM-MIM Marker Based Methods



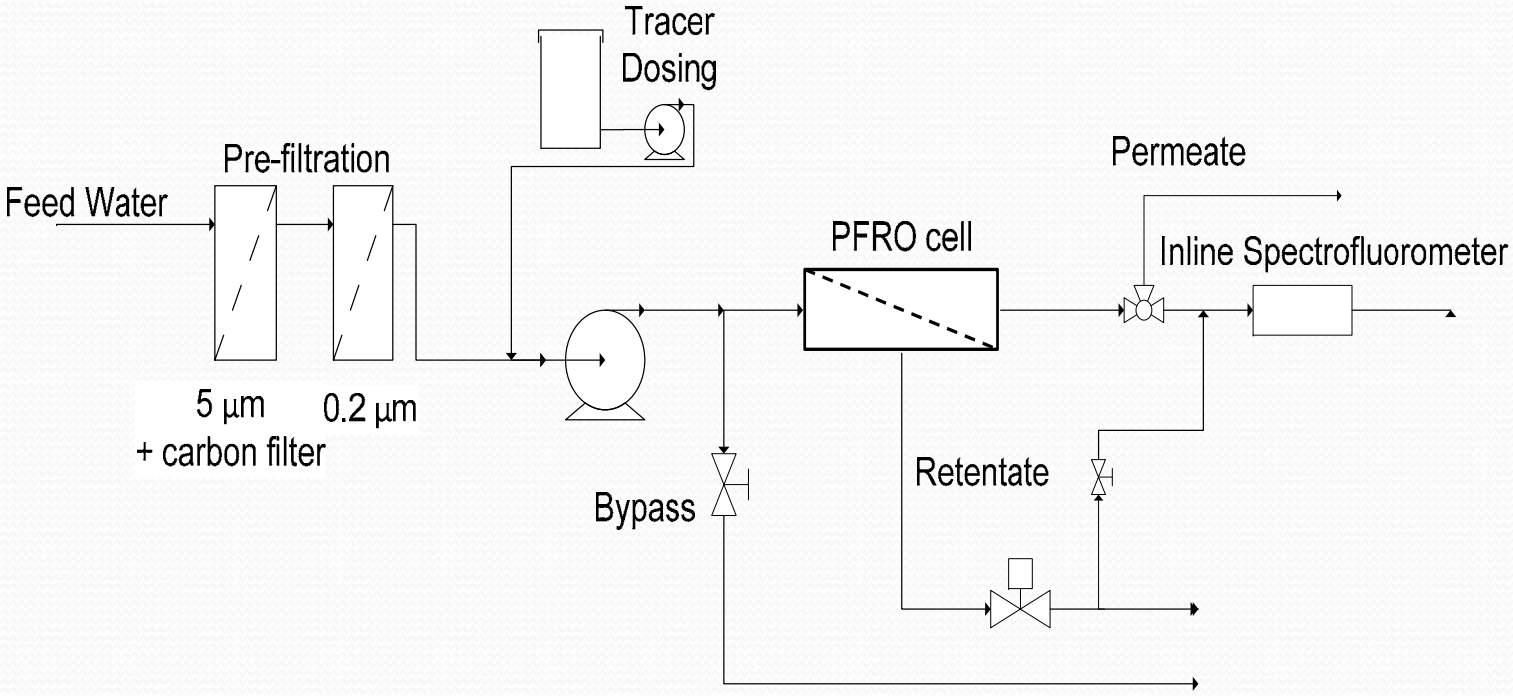
2.5 - ppm fluorescent marker solution from left to right:
eosin B, uranine, rhodamine WT, fluorescein, and lissamine green B

PM-MIMo Spectrofluorometer



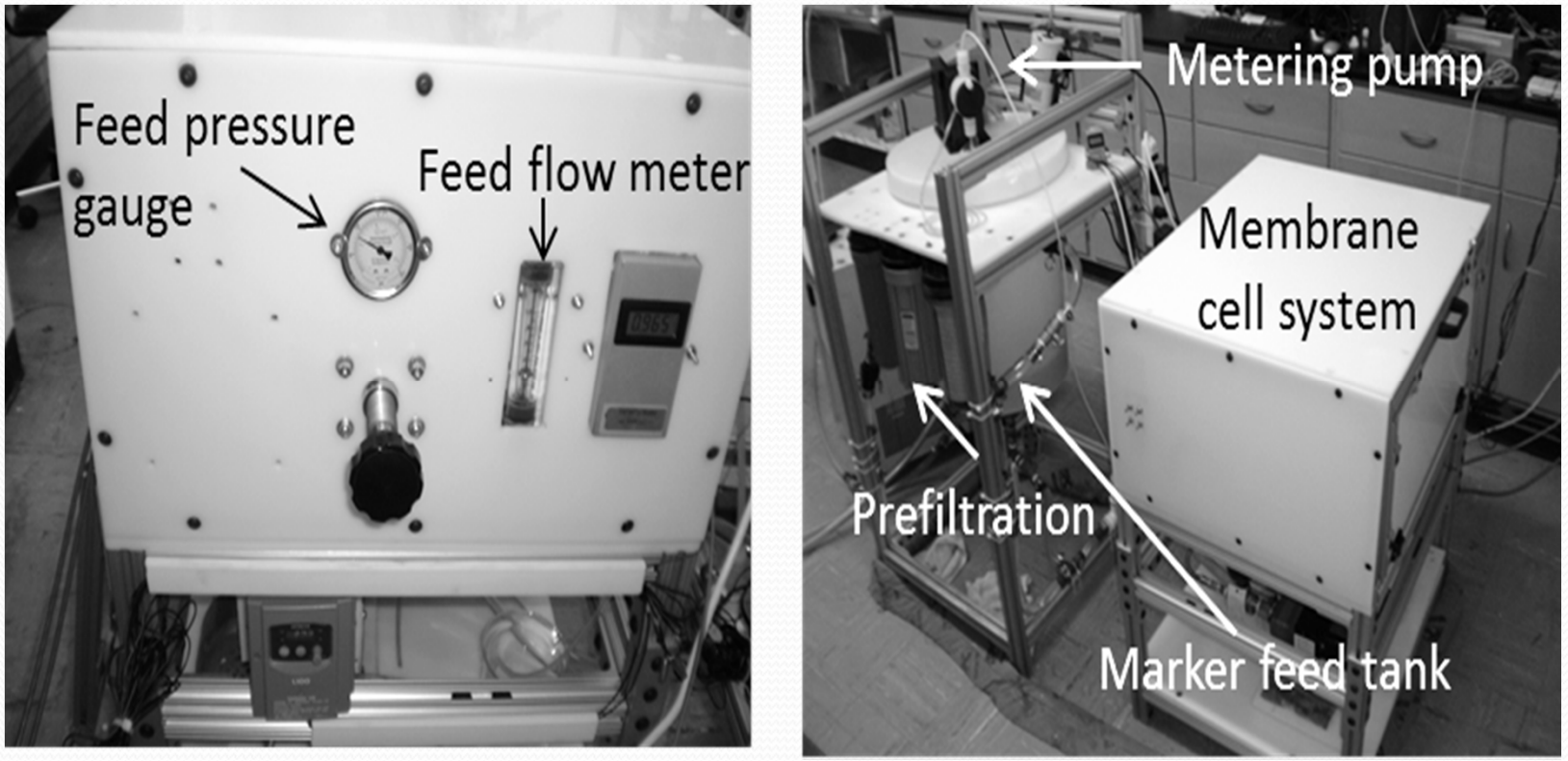
Schematic representation of PM-MIMo spectrofluorometer system

PM-MIMo Experimental System



Schematics of the experimental PFRO−ISPF system

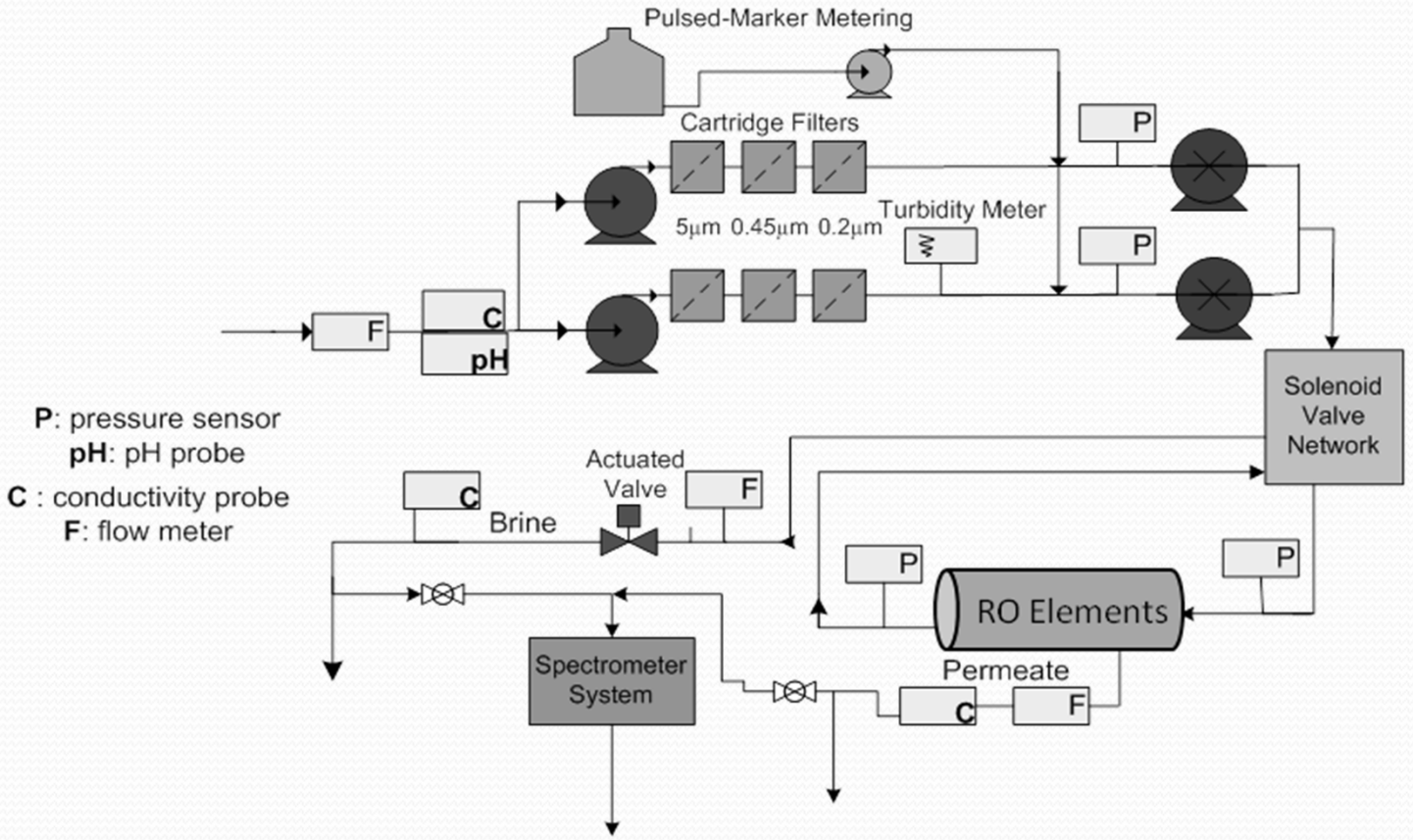
PM-MIMo Experimental System



Photographs of the PFRO membrane system.

PM- MIMo™, UCLA Patent pending technology

PM-MIMo Experimental System



Schematic of the UCLA M3 system integrated with the PM-MIMo system

MIM Marker Based Methods:

5 Markers Screened for:

- Determine the fluorescence spectra of the markers
- Quantify the minimum detection limit
- Develop concentration calibration curves
- Evaluate the impact of pH and chlorine concentration on the fluorescence signal stability

Fluorescent Markers Commonly Used

Fluorescent Marker	Chemical Formula	Mol Wt	Prescreening Criteria		
			Non--toxic	Commercially Available	Insensitive to UV Light
Rhodamine WT	$C_{29}H_{29}N_2NaO_5$	480.55	Y	Y	Y
Rhodamine B	$C_{28}H_{31}ClN_2O_3$	479.02		Y	Y
Rhodamine 6G	$C_{28}H_{31}ClN_2O_3$	497.02		Y	Y
Sulforhodamine B	$C_{27}H_{29}N_2NaO_7S_2$	580.65		Y	Y
Sulforhodamine 101	$C_{31}H_{30}N_2O_7S_2$	606.71		Y	Y
Amidorhodamine G	$C_{25}H_{25}N_2NaO_7S_2$	552.59	Y		
Fluorescein	$C_20H_{12}O_5$	332.31	Y	Y	Y
Uranine	$C_{20}H_{10}Na_2O_5$	376.28	Y	Y	Y
Eosin B	$C_{20}H_6Br_4Na_2O_5$	691.88	Y	Y	Y
Pyranine	$C_{16}H_7Na_3O_{10}S_3$	524.39	Y	Y	
Tinopal CBS-X	$C_{28}H_{20}Na_2O_6S_2$	562.57	Y		N/A
Erythrosine	$C_{20}H_6I_4Na_2O_5$	879.87	Y		N/A
Sodium naphthionate	$C_{10}H_8NNaO_3S$	245.23	Y	Y	N/A
Lanaperl fast yellow	$C_{25}H_2ON_5NaO_6S_2$	549.55	N/A	Y	N/A
Bengal rose	$C_{20}H_2Cl_4I_4Na_2O_5$	1017.67	Y	Y	N/A
Brightener 28	$C_4 0H_{42}N_{12}Na_2O_{10}S_2$	960.96	N/A	Y	Y
Amino G acid	$C_{10}H_9NO_6S_2$	303.32	Y	Y	N/A
Amidoflavine	$C_{24}H_7NO_2$	341.28	N/A		Y
Leucophor PBS	$C_{29}H_2N_2O_2$	428.48	N/A	X	Y

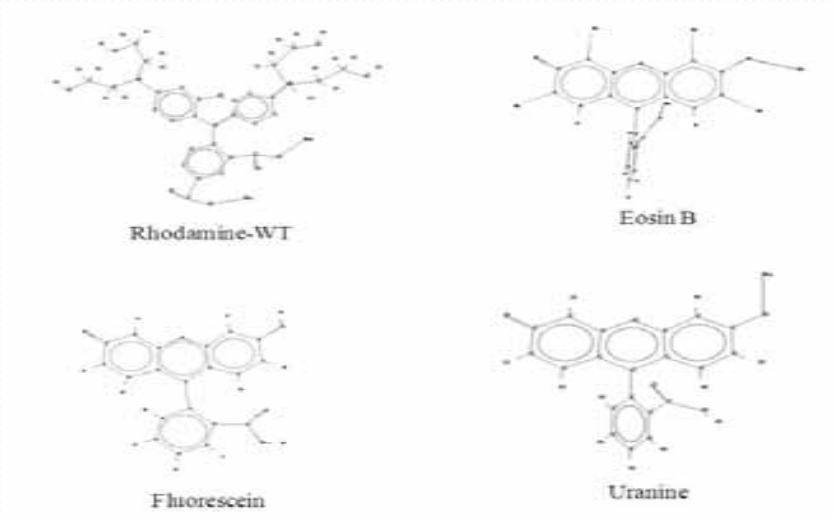
Commonly Used Fluorescent Molecular Markers in Water Tracing Applications

Y - marker meets the specific screening criterion; N/A, A - information lacking to evaluate the criterion.

Fluorescent Markers Shortlisted

Marker	Diameter (nm)	MW (g/mol)	Density (g/cm^3)	Molar~~ar~~ Vol (cm^3/mol)	Estimated Diffusivity (10^{-6} cm^2/s) of Marker from:		
					Scheibel	Wilke and Chang	Ha~~e~~yduk and Laudie
Fluorescein	1.16	332	1.04	319	4.67	4.43	4.45
Eosin	1.22	692	0.90	769	3.12	2.61	2.65
Uranine	1.15	376	1.51	249	5.28	5.13	5.14
R-WT	2.01	566	1.19	476	3.86	3.48	3.51

Molecular Properties and Aqueous-Phase Diffusivity of the Candidate Markers



Molecular structures of candidate molecular markers

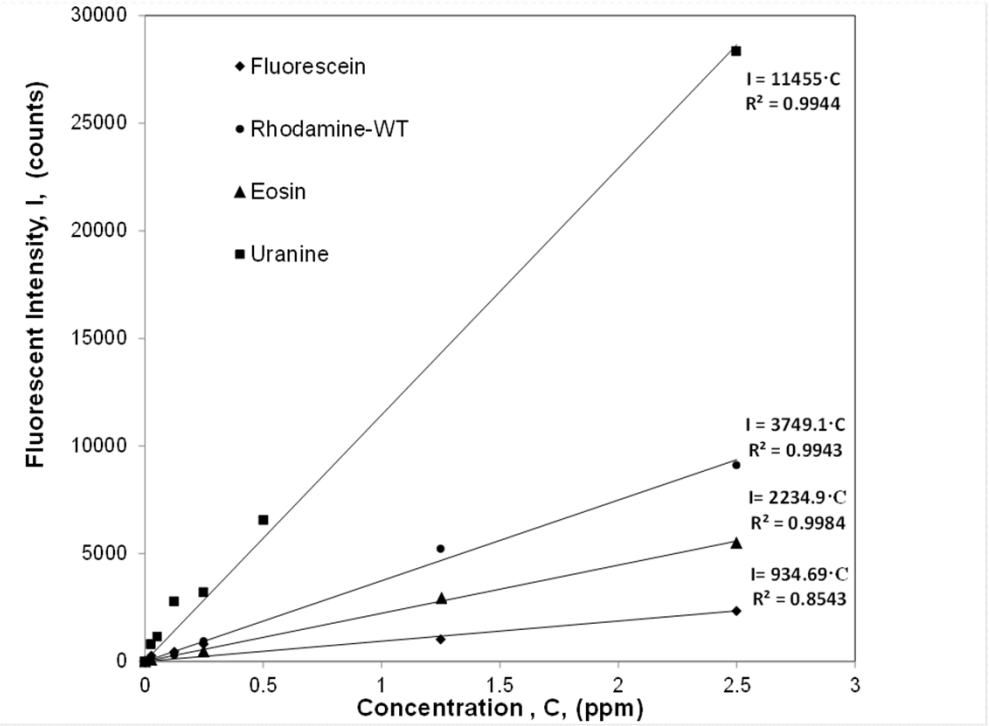
Fluorescent Markers Shortlisted

Marker	Optimum Excitation–Emission Wavelength (nm)
Rhodamine WT	530/580
Uranine	485/520
Fluorescein	485/510
Eosin	485/534

Optimal Fluorescence Excitation and Emission Wavelengths for the Candidate Markers

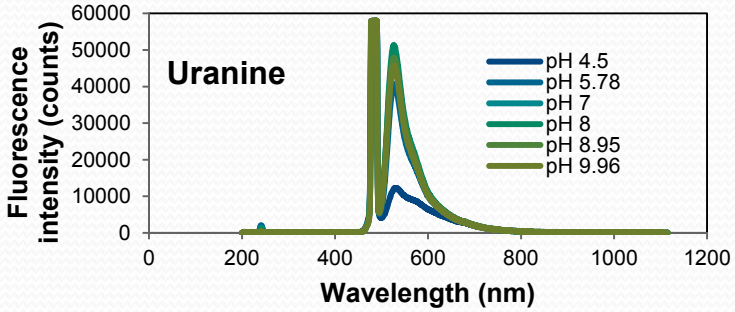
Marker	Detection Limit (ppm)
Rhodamine WT	0.25
Uranine	0.01
Fluorescein	0.125
Eosin	0.25

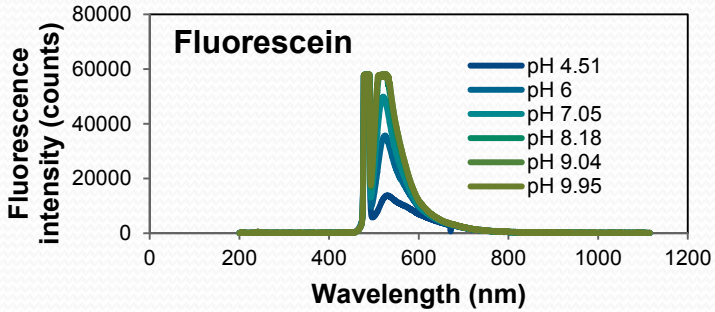
Detection Limit of Candidate Markers

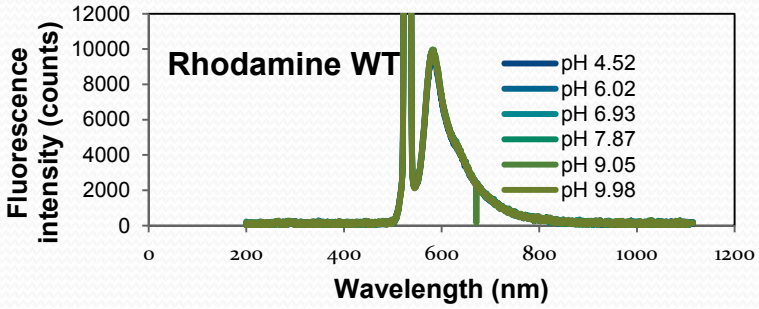


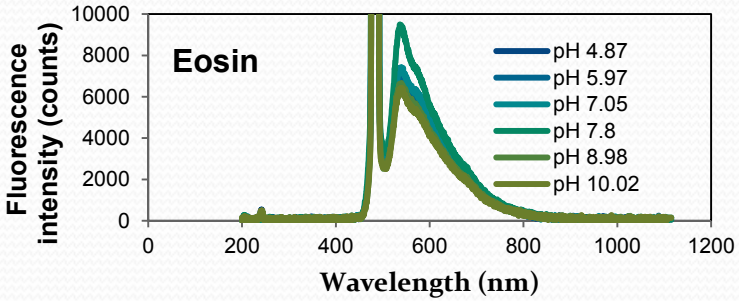
Fluorescent- concentration calibration curves of the candidate molecular markers

Fluorescent Markers Shortlisted



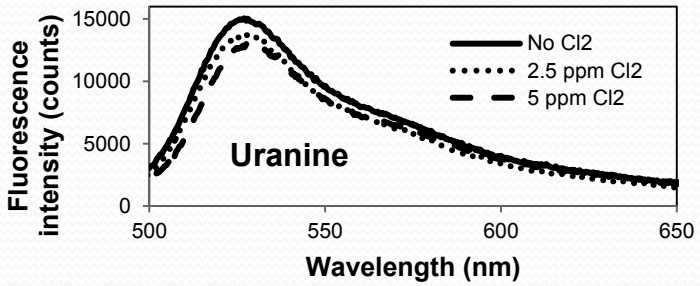


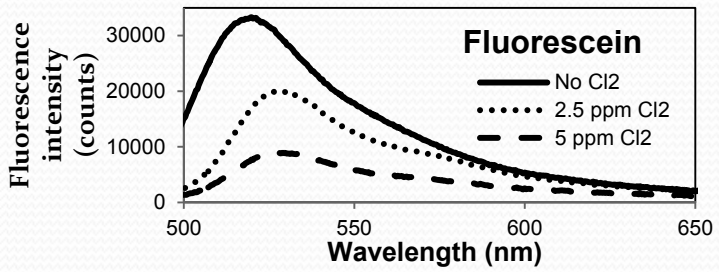


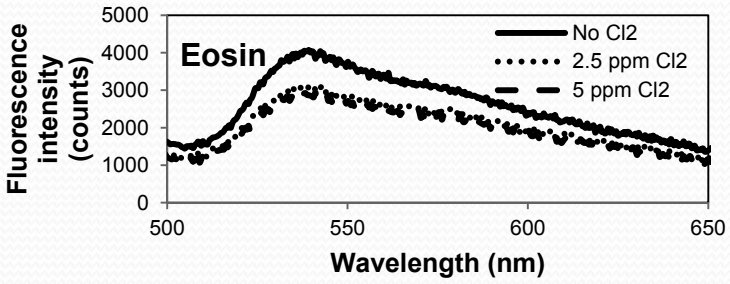


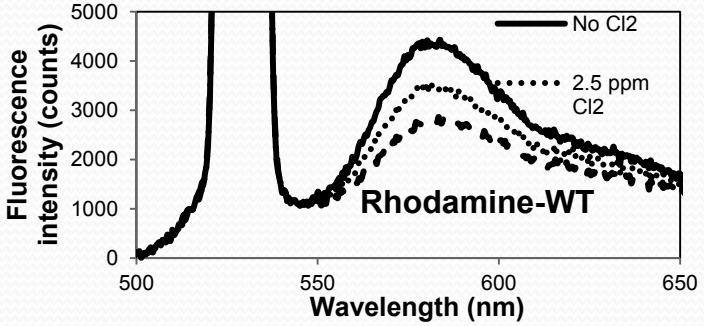
pH effect on fluorescence intensity of candidate markers at concentration of 2.5 ppm in water

Fluorescent Markers Shortlisted



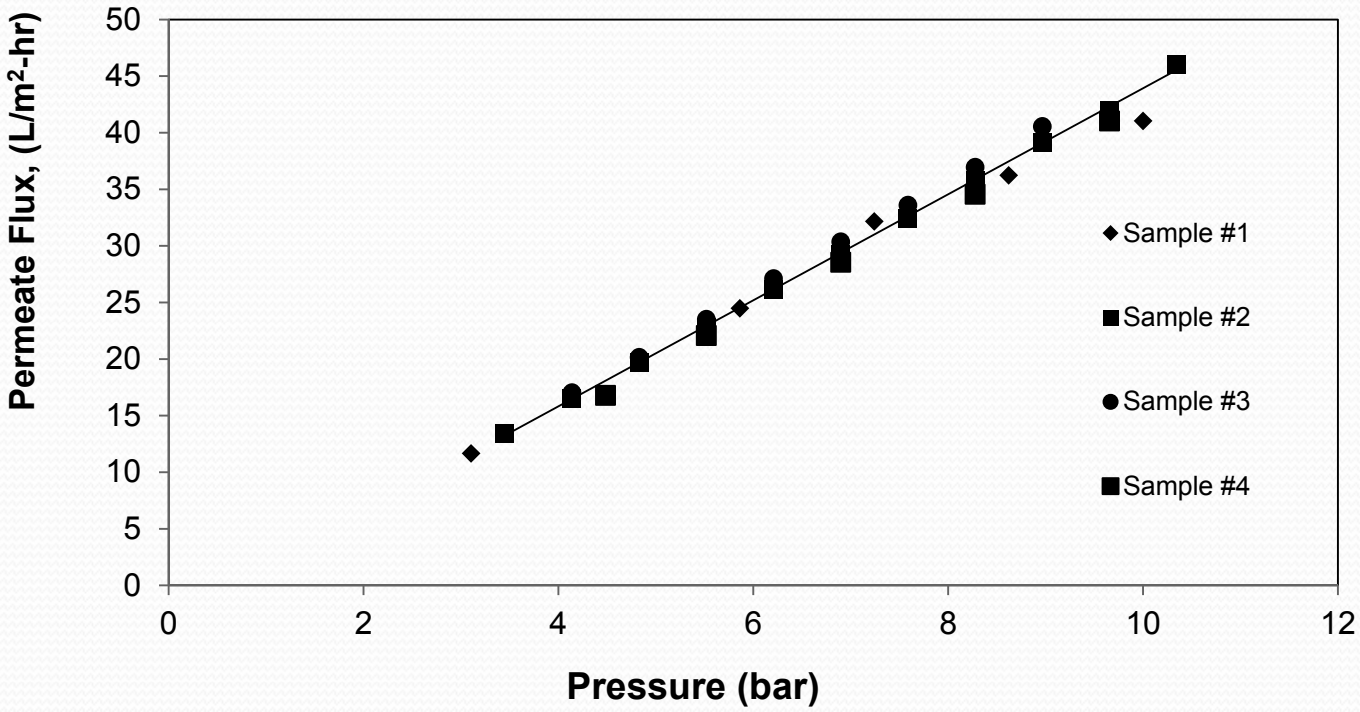






Impact of chlorine concentration on fluorescence intensity of the candidate markers

Membrane Permeability: PFRO – ESPA2



Flux versus transmembrane pressure for determination of water permeability of different ESPA2 membrane coupons

Membrane Permeability

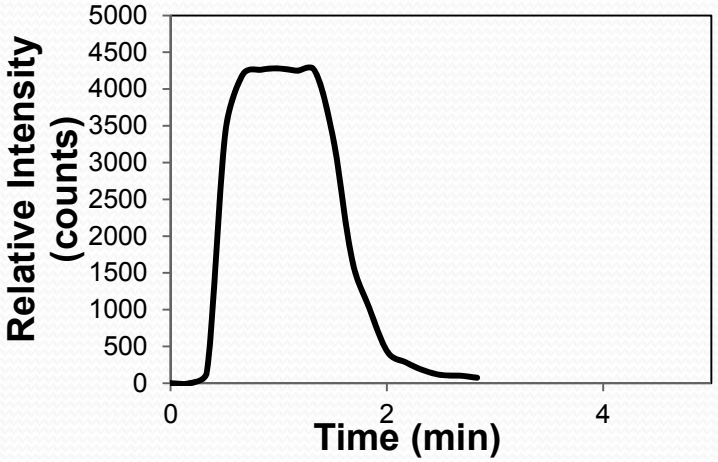
Membrane or Value	Membrane Water Permeability (LMH/bar)
Sample No. 1	4.33
Sample No. 2	4.68
Sample No. 3	4.87
Sample No. 4	4.65
Avg. Permeability	4.63
SD	0.22

Permeability of Intact ESPA2 RO Membrane Coupons

Membrane Source or Value	Observed NaCL Rejection for 500 ppm solution
Sample No. 1	97.65%
Sample No. 2	98.50%
Sample No. 3	97.69%
Sample No. 4	96.80%
Mean	97.66%
Standard Deviation - SD	0.69%

Observed Salt Rejection of Intact ESPA2 RO Membranes

Fluorescent Marker Selected - URANINE



Marker input resulting from injection of uranine to achieve uranine concentration of 40 ppm in the RO feed stream for 60 s

ΔP (psi) or ppb Value	J_v (m^3/m^2 s)	R_{obs} (%)	LRV
90	8.33×10^{-6}	99.984	3.80
100	9.73×10^{-6}	99.989	3.96
110	1.06×10^{-5}	99.993	4.15
120	1.18×10^{-5}	99.994	4.22
At minimum detection limit (2.45 ppb)		99.996	4.40

Uranine Rejection by Intact RO Membrane[a] Following a 60-s Pulse of 40-ppm Uranine Concentration in the RO Feed Stream[b]

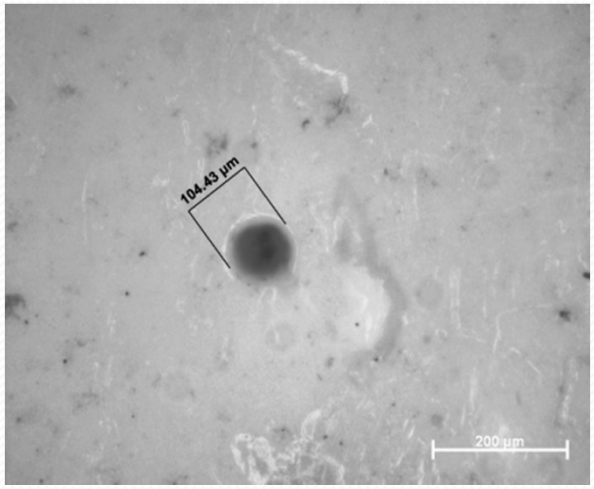
[a]ESPA2 (Hydranautics).

[b]RO feed flow rates of 1 L/min and 600-ppm uranine solution injection feed flow rate of 186 mL/min. Experimental conditions: C_f = 40 ppm, feed cross-flow velocity = 18.4 cm/s.

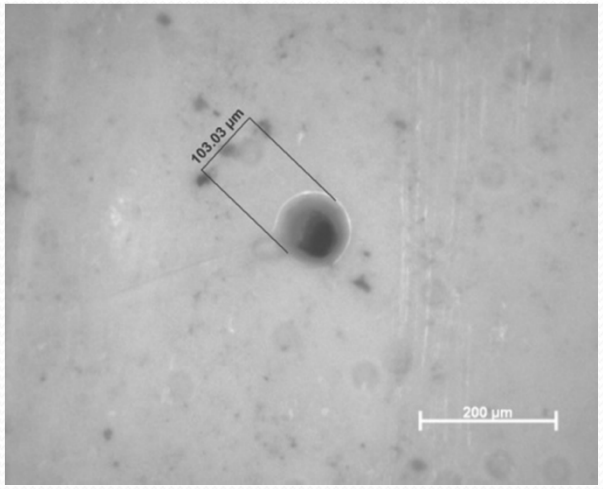
Membrane Breach - Pinholes

Characteristics of Membrane Breaches

Extent of Membrane Breach	Approx. Breached Surface Area (mm^2)
Single small pinhole (70 µm)	3.85×10^{-3}
Single large pinhole (104 µm)	8.49×10^{-3}
Double large pinhole (104 and 103 µm)	16.8×10^{-3}



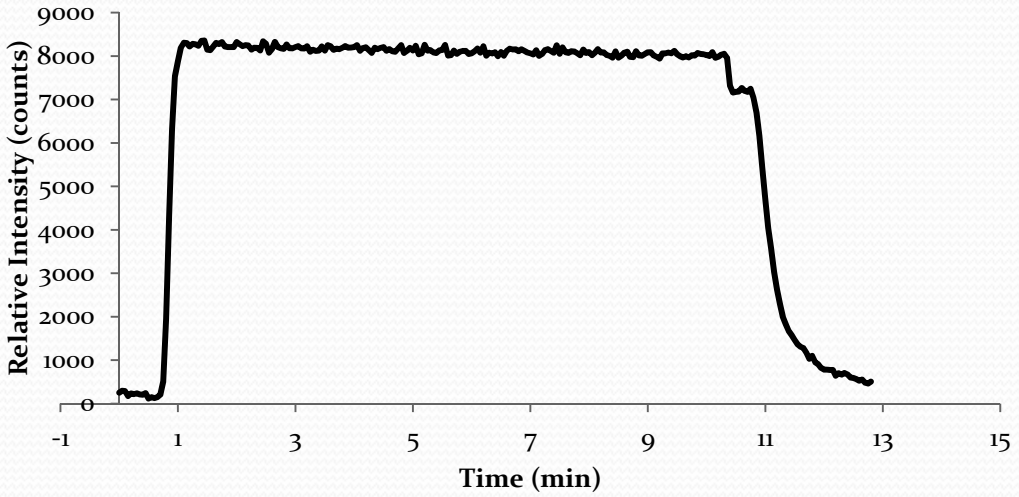
Large pinhole No. 1:
104 µm diameter



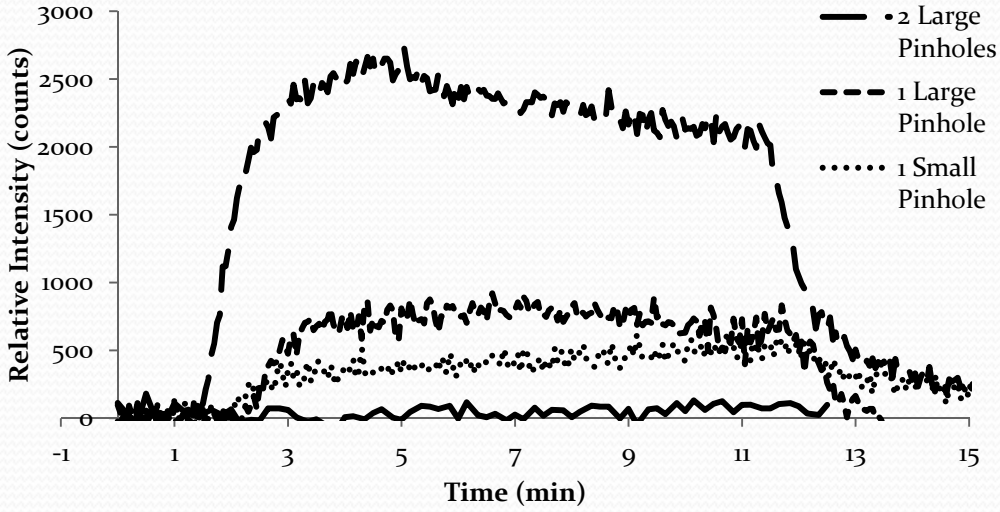
Large pinhole No. 2:
103 µm diameter

PM-MIMo Experiment: Intact vs. Impacted Membrane

Feed Marker Input
Uranine – 10 mg/l



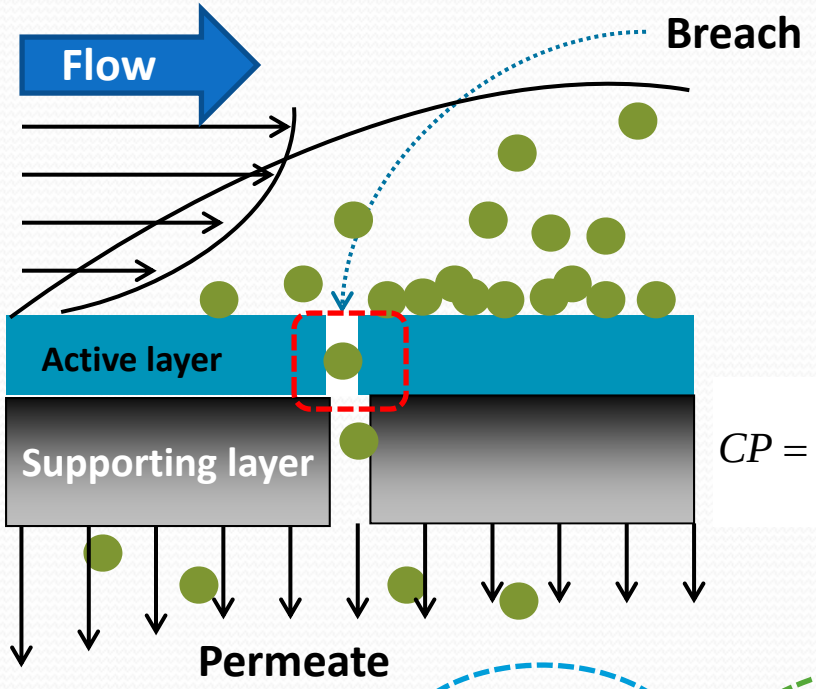
Permeate Marker Response

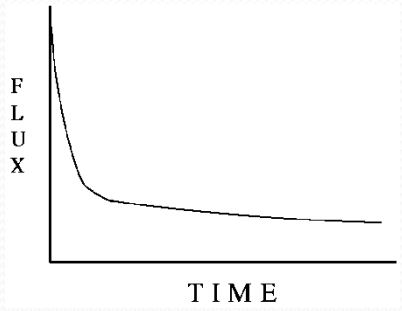


Step input and response data obtained from a continuous dosing of uranine to achieve 10 ppm marker concentration in the RO feed stream

PFRO was operated at 100 psi and cross-flow velocity of 18.4 cm/s

Marker Transport





$$CP = \frac{(C_m - C_p)}{(C_b - C_p)} = exp\left(\frac{J_v}{k_f}\right)$$

Concentration Polarization

k_f: average feed-side mass transfer coefficient; determines level of solute transport across the membrane/ fluid concentration boundary layer

$$J_s = B(C_m - C_p) + (1-\sigma)\frac{1}{2}J_v(C_m + C_p)$$

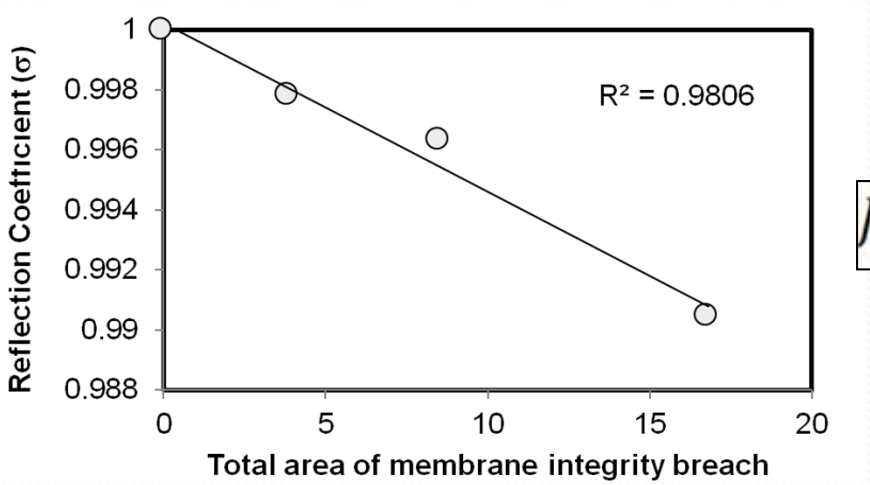
Solution diffusion

B: solute transport parameter; determines solute potential for passing through RO membranes via solution-diffusion mechanism

Convective transport

σ: reflection coefficient; If σ decreases (<1) relative to intact membrane, this would suggest possible membrane integrity breach and thus degradation of permeate quality

PM-MIMo Experiment: Reflection Coefficient vs. Size of Breach

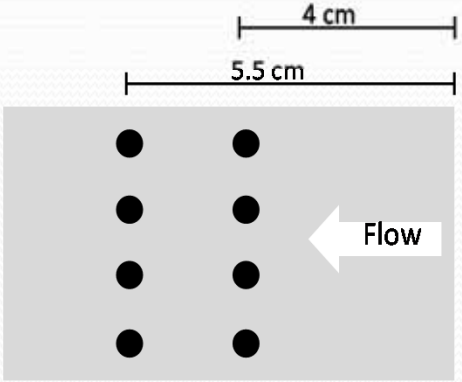


$$J_v = L_p(\Delta P - \sigma\Delta\pi)$$

Relationship between reflection coefficient of uranine transport through ESPA2 membrane with the total area of membrane integrity breach (pinholes)

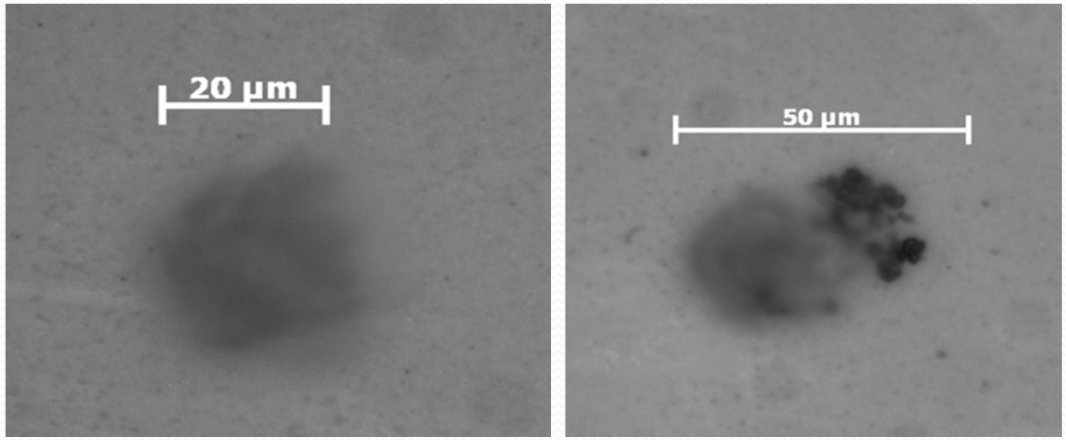
Note: PFRO was operated at 100 psi and cross-flow velocity of 18.4 cm/s; uranine was continuously dosed to achieve a 10-ppm concentration in the RO feed.

PM-MIMo Experiment: Size and Location of Breach



Depiction of pinhole locations on the membrane coupon

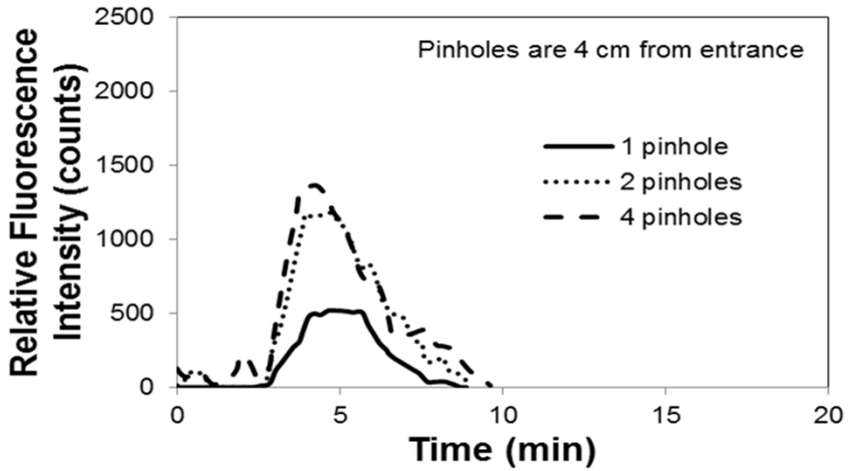
Micrographs of pinholes located 4 cm (left) and 5.5 cm (right) away from the PFRO channel inlet

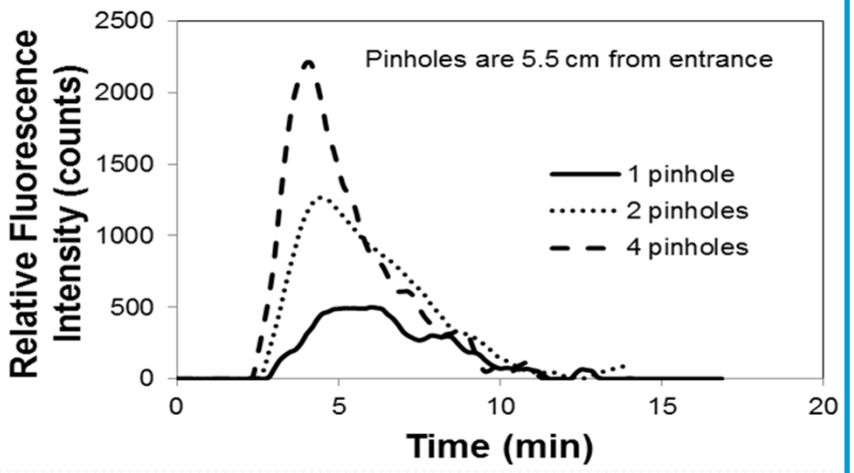


Pinhole Location	No. of Pinholes	Approx. Breached Area (mm^2)
4 cm from entrance	1	1.96×10^{-3}
	2	3.92×10^{-3}
	4	7.85×10^{-3}
5.5 cm from entrance	1	3.14×10^{-3}
	2	6.28×10^{-3}
	4	1.26×10^{-3}

Size of Membrane Integrity Breaches

PM-MIMo Experiment: Size and Location of Breaches





Size of Membrane Integrity Breaches

Pinhole Location	No. of Pinholes	Approx. Breached Area (mm^2)
4 cm from entrance	1	1.96×10^{-3}
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	4	7.85×10^{-3}
5.5 cm from entrance	1	3.14×10^{-3}
	2	6.28×10^{-3}
	4	1.26×10^{-3}

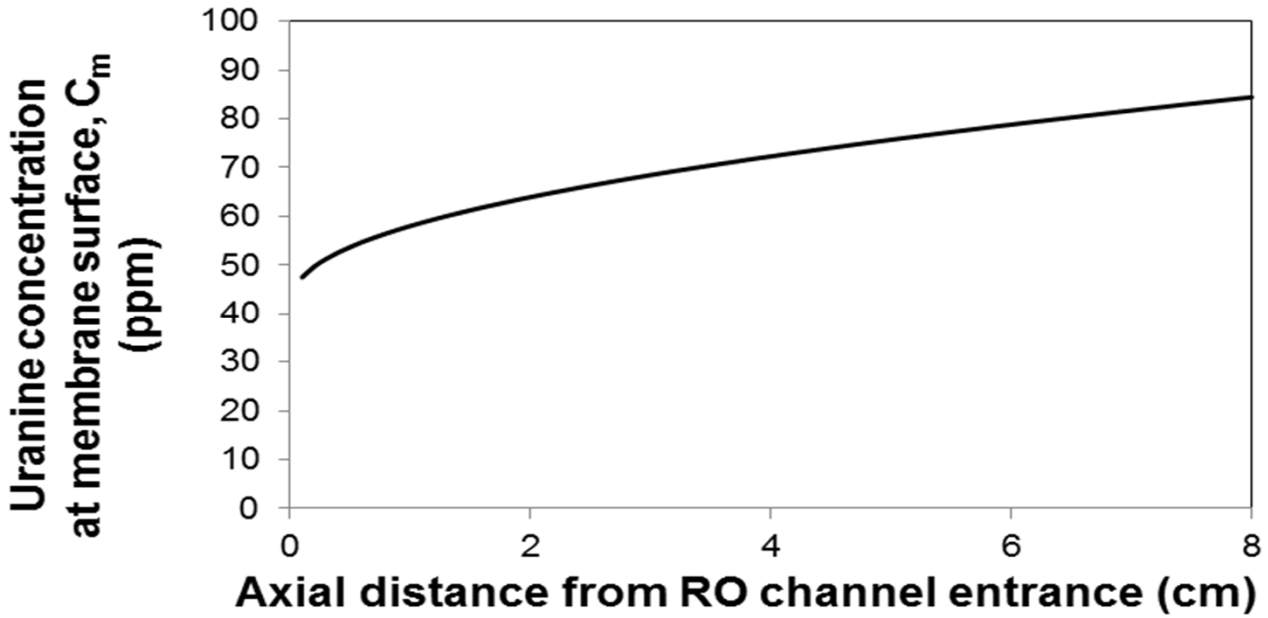
Marker fluorescence intensity−time profiles for the RO permeate,

for membranes with pinholes, in response to marker injection to the RO feed

Notes: PFRO was operated at 100 psi at a cross-flow velocity of 18.4 cm/s; uranine dosing was set to attain a concentration of 40 ppm in the RO feed for a duration of 60 s.

Fluorescence intensity for the marker in the permeate stream, for the intact membrane, was below relative intensity of 180 counts.

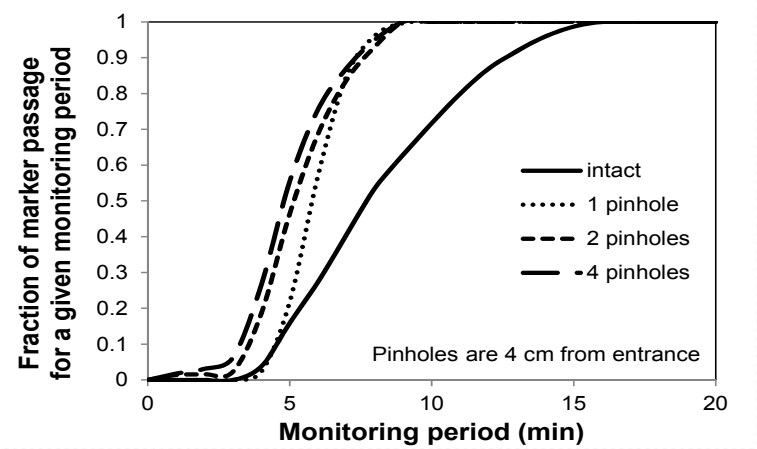
Illustration of the Effect of Concentration Polarization on Marker Concentration at the Membrane Surface

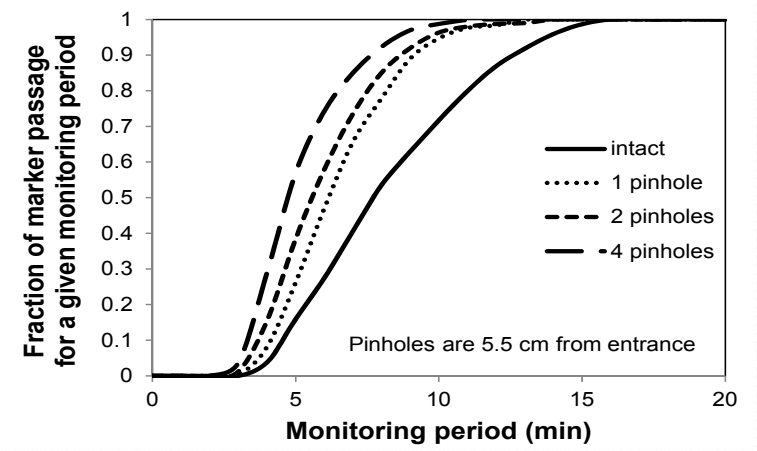


Estimated marker concentration at the membrane surface (C_m) corresponding to a 40 ppm uranine marker concentration in the RO feed.

Notes: Permeate flux of 9.8×10^{-6} m^3/m^2 s at transmembrane pressure of 100 psi and cross-flow velocity of 18.4 cm/s.

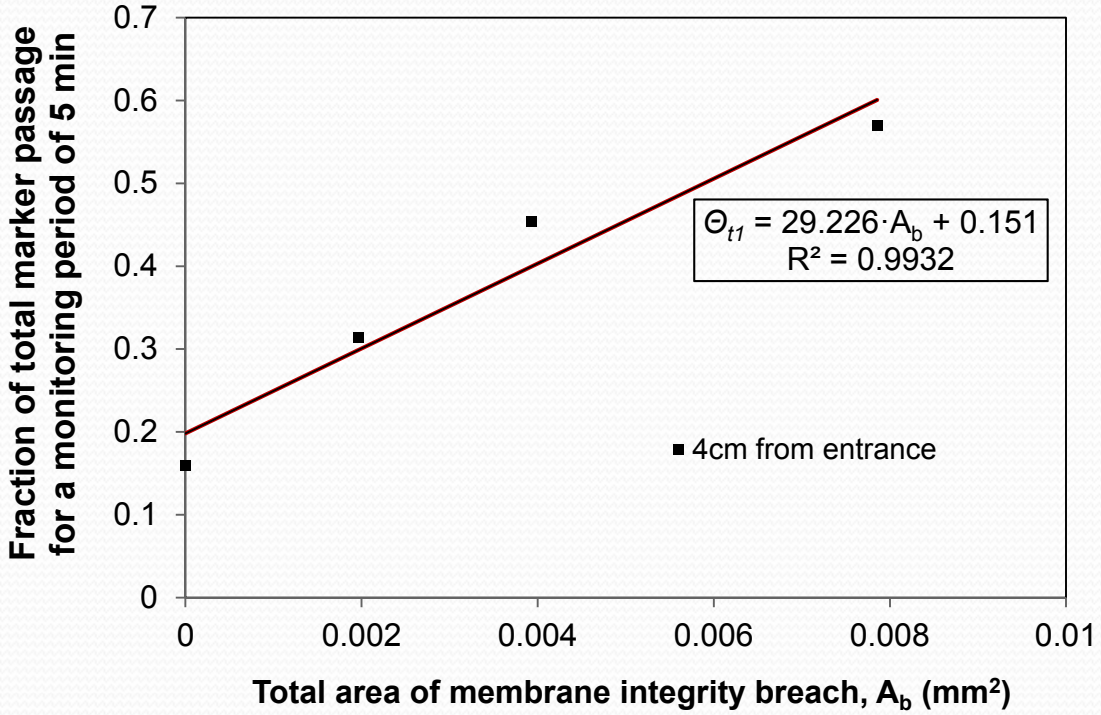
PM-MIMo Experiment: Size and Location of Breach





Fraction of marker passage through the RO membranes after a given monitoring period at distances of (a) 4 cm and (b) 5.5 cm from the channel entrance for different membrane breached areas

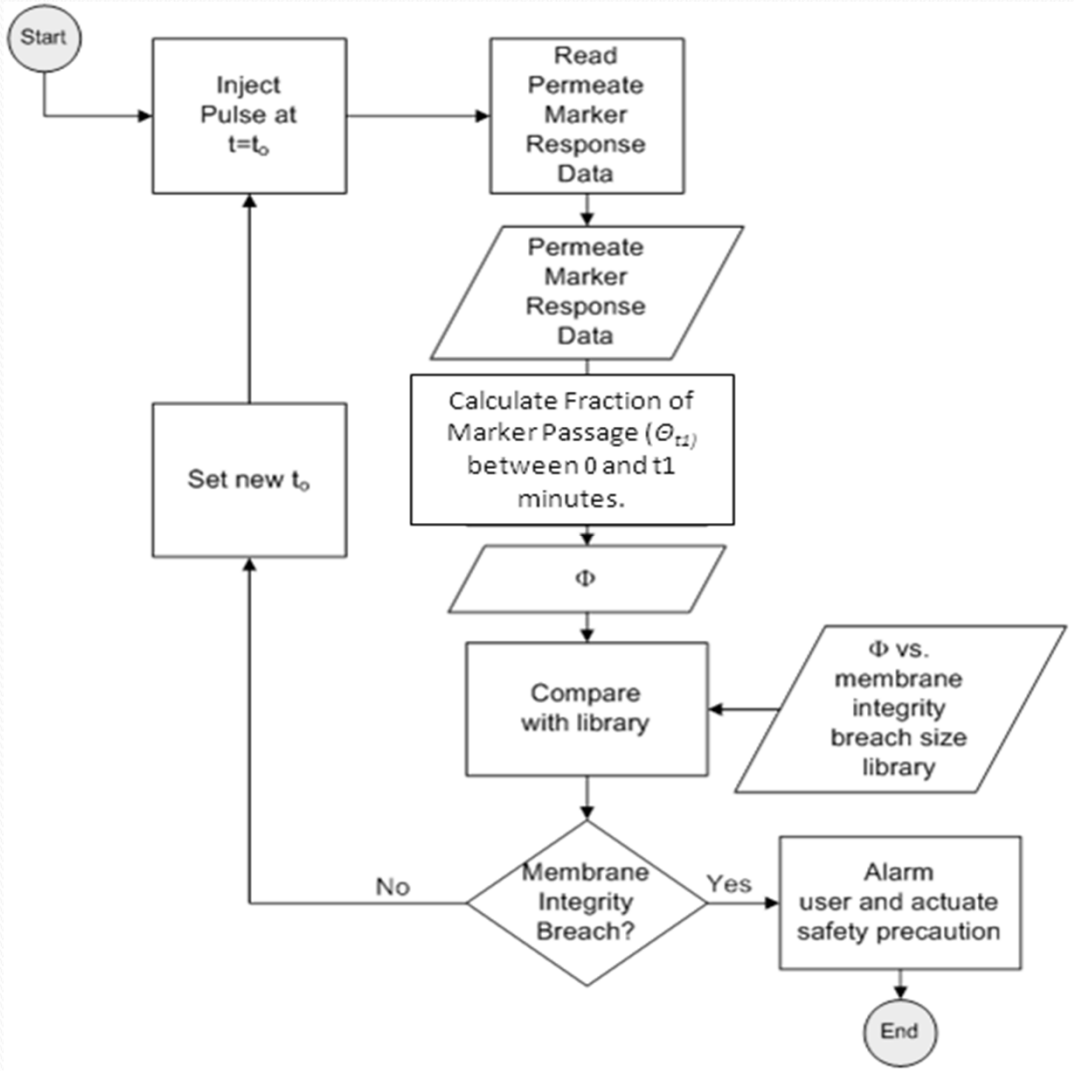
Correlation of Total Marker Passage trough the membrane with Area of Integrity Breach



Relationship between the FTMP through the membrane and the total area of membrane integrity breach.

Note: Monitoring period of 5 min from the commencement of marker feed injection; 60 s of marker injection to achieve 40-ppm marker RO feed concentration.

Schematic of Proposed PM-MIMo Protocol



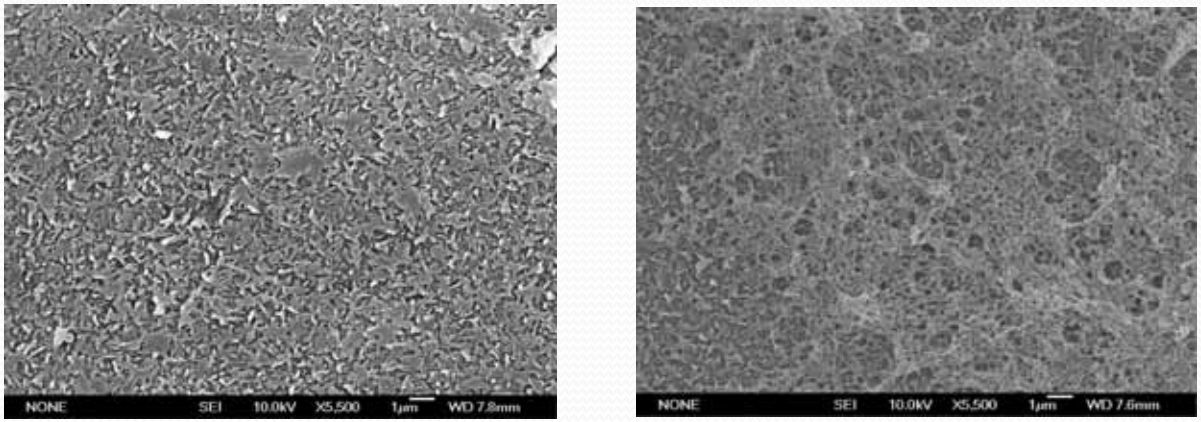
PM- MIMo™, UCLA Patent pending technology

Membrane Breach – Oxidation by NaOCl

Test	Membrane Exposure Conditions			Normalized Membrane Permeability[a]	Normalized Salt Rejection	Contact Angles (º)
	NaOCl Conc (ppm)	Exposure Time (h)	NaOCl Dose (ppm-h)			
1	0	0	0	1	1	69.00
2	20	8	160	1.043	1.003	66.78
3	40	4	160	1.245	1.006	64.10
4	80	2	160	1.326	0.998	60.75

Effect of Membrane Exposure to NaOCl Solutions on Membrane Permeability and Salt Rejection

[a]The normalized permeability and salt rejection are the ratios of these values relative to those for the intact membrane.



SEM images of the surface of commercial ESPA2 polyamide RO membranes before and after exposure to 80 ppm NaOCl solution for 2 h.

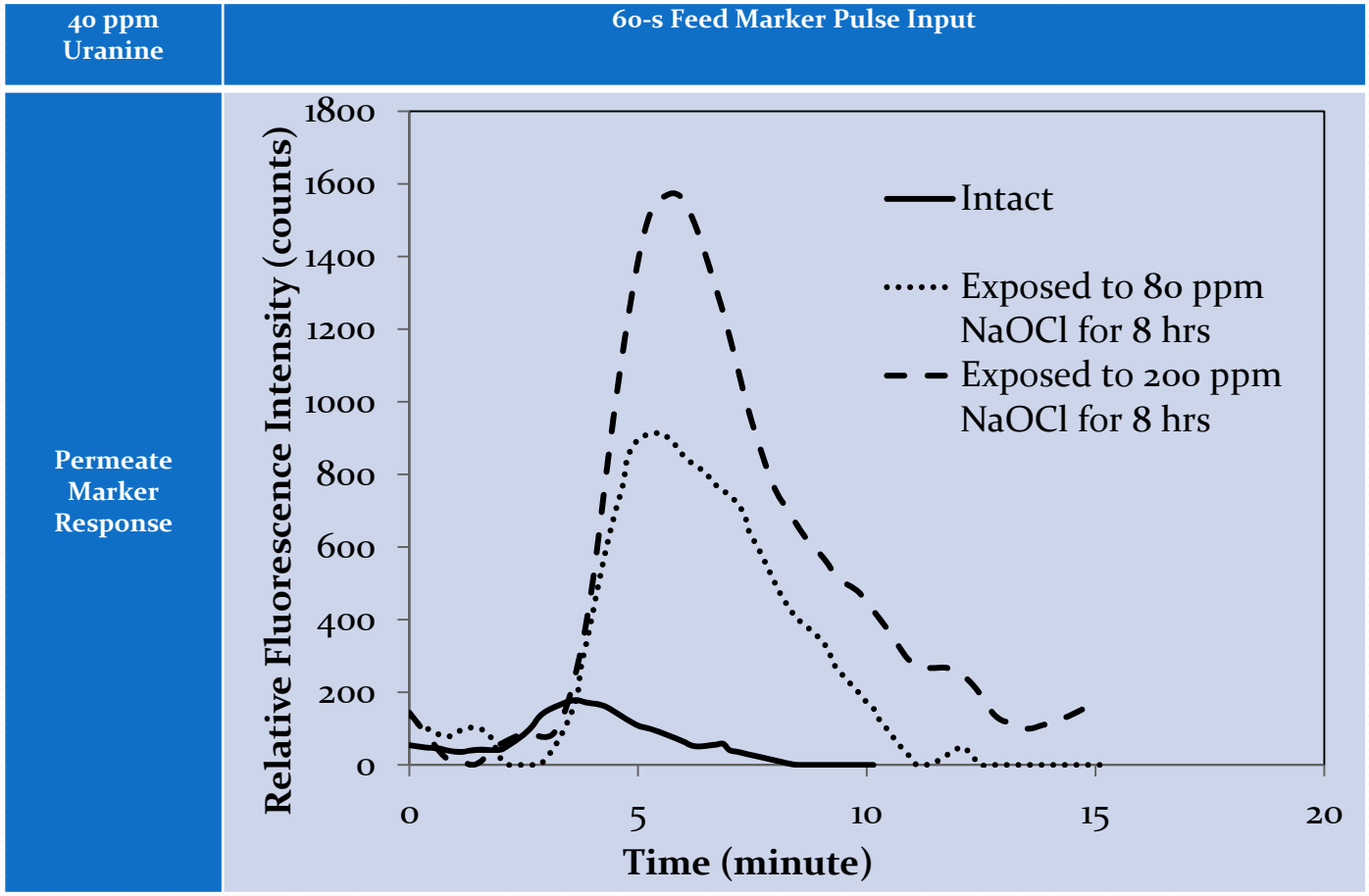
Membrane Breach – Oxidation by NaOCl

J_v (m^3/m^2 s)	R_{obs} (%)			Marker LRV		
	Intact Membrane	80-ppm NaOCl for 8 h	200-ppm NaOCl for 8 h	Intact Membrane	80-ppm NaOCl for 8 h	200-ppm NaOCl for 8 h
8.33×10^{-6}	99.984	99.946	99.912	3.80	3.26	3.06
9.73×10^{-6}	99.989	99.952	99.933	3.96	3.32	3.17
1.06×10^{-5}	99.993	99.980	99.945	4.15	3.70	3.26
1.18×10^{-5}	99.994	99.985	99.949	4.22	3.82	3.29

Effect of Permeate Flux on Marker Rejection and LRV for Intact and Compromised RO Membranes

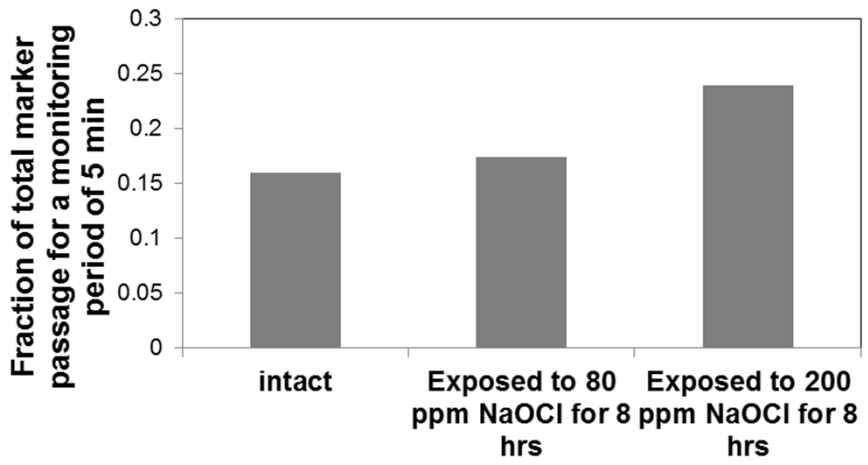
Notes: Marker was injected at a flow rate of 185.7 mL/min (marker concentration of 600 ppm) into the RO feed stream with a flow rate of 2.6 L/min in order to achieve a marker concentration of 40 ppm in the RO feed stream. The cross-flow velocity in the PFRO channel was 18.4 cm/s.

Membrane Breach – Oxidation by NaOCl



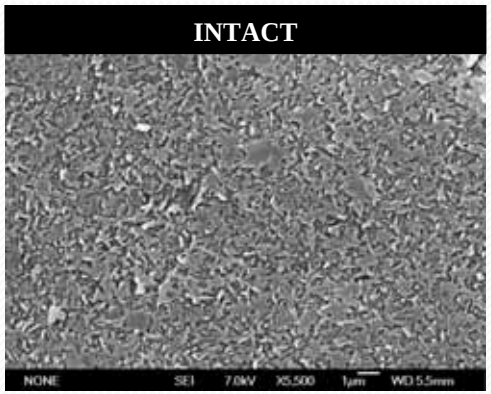
Marker fluorescence intensity−time profiles for the RO permeate, for membranes exposed to 80 and 200 ppm NaOCl for 8 h, in response to marker injection to the RO feed to attain 40 ppm feed concentration to the PFRO cell for a pulse period of 60 s.
Note: PFRO was operated at 100 psi and cross-flow velocity of 18.4 cm/s.

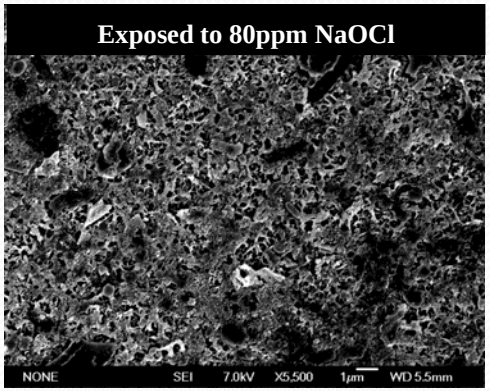
Membrane Breach – Oxidation by NaOCl



FTMP detected in the permeate for intact ESPA2 membranes and membranes exposed to 80 and 200 ppm NaOCl for 8 h.

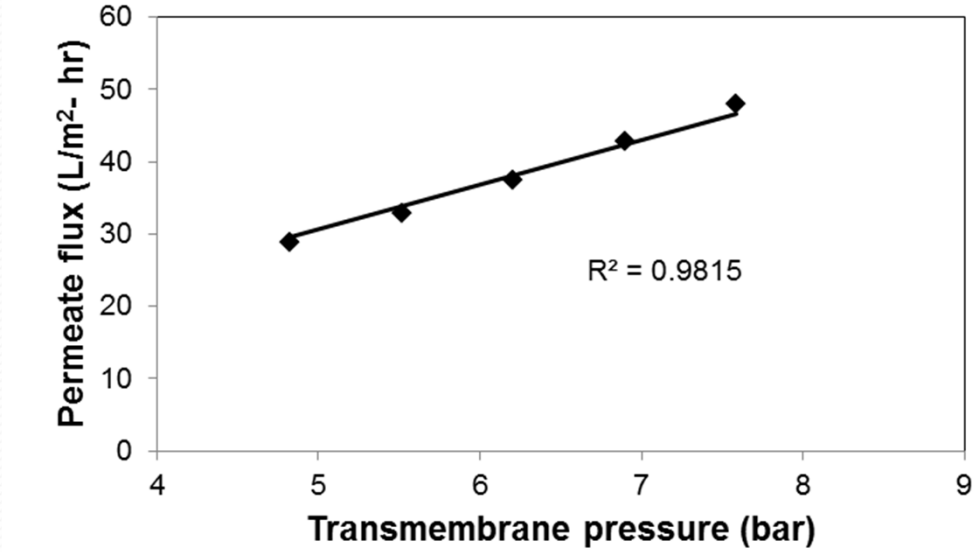
Notes: Monitoring period of 5 min; uranine dosing to achieve 40 ppm marker concentration in the RO feed for a 60 s pulse. PFRO was operated at transmembrane pressure of 100 psi and channel cross-flow velocity of 18.4 cm/s.





SEM images of the commercial ESPA2 polyamide RO membranes before and after 8 - hr exposure to 80 - and 200 - ppm NaOCl solutions

Membrane Permeability: SPRO – XLE-2540



Flux versus transmembrane pressure for determination of water permeability of the XLE-2540 membrane
(*Note*: Cross-flow velocity = 20.95 cm/s in the PFRO system)

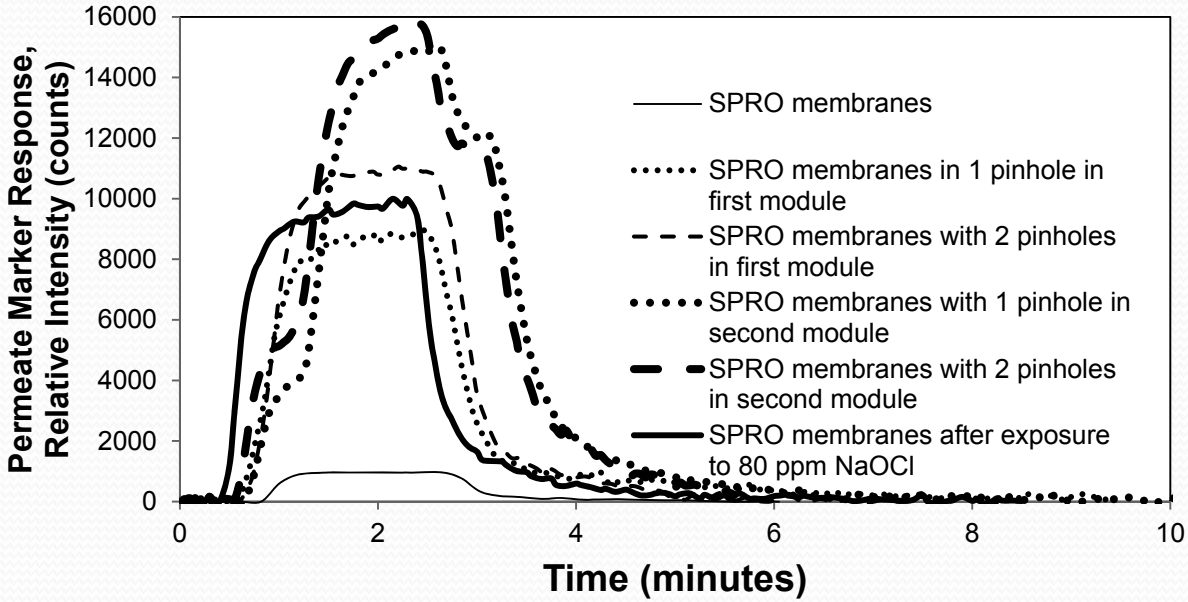
Transmembrane Pressure, psi	Permeate Flux, L/m²·h	Observed Salt Rejection, %
160	45.7	96.0
157	38.3	96.2
152	36.9	96.3
149	35.4	96.1
146	34.0	95.8
Mean		96.1
SD		0.2

Observed Salt Rejection for the XLE-2540 Membrane as Determined in the SPRO Membrane System at Various Transmembrane Pressures
(*Note:* Cross-flow velocity = 12.12 cm/s)

Marker Response Intensity in SPRO

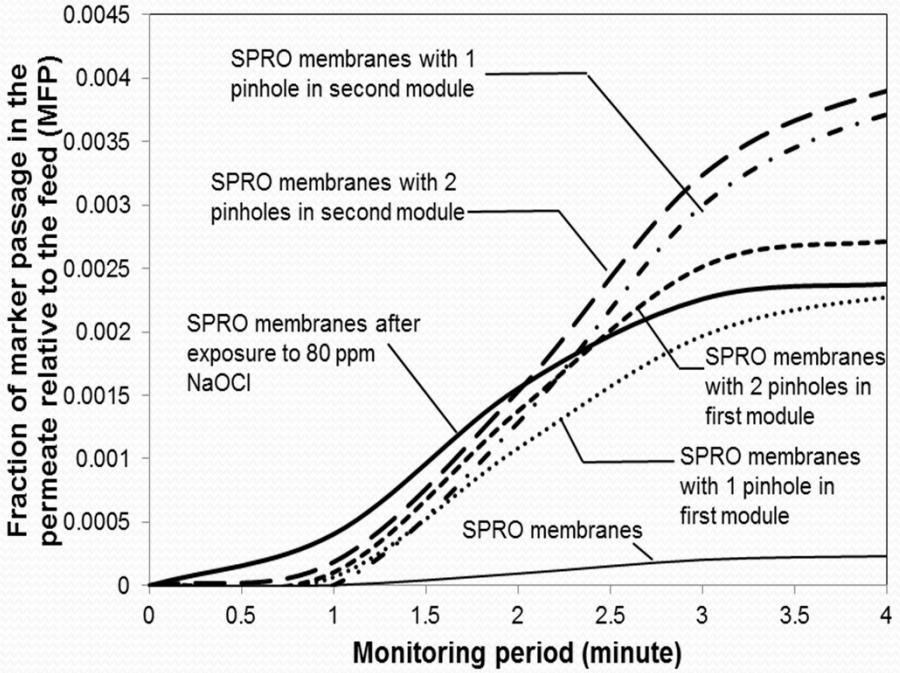
Permeate Flux (m/s)	C_m (ppm)	C_p (ppb)	Observed Rejection (R_{obs})
2.27×10^{-5}	31.1	9.85	99.951
2.09×10^{-5}	30.1	10.30	99.948
1.91×10^{-5}	29.1	10.87	99.946

Observed Uranine Rejection for Different Permeate Fluxes for the Flat-Sheet XLE-2540 Membrane *(Note:* Uranine concentration in the RO feed stream is 20 mg/L)

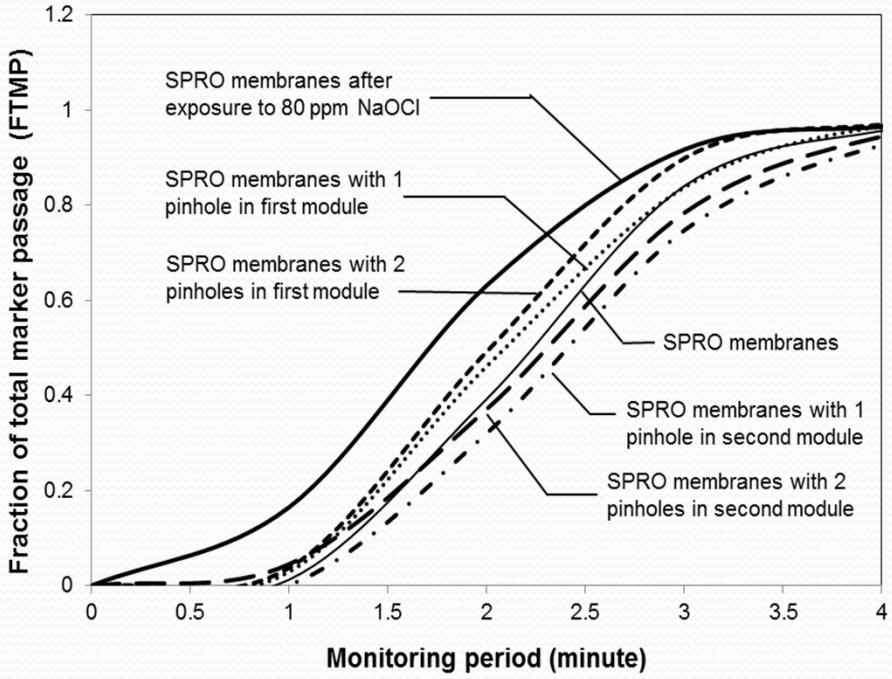


RO permeate marker fluorescence intensity−time profiles in response to marker injection into the SPRO feed.
Note: The SPRO system was operated at 160 psi at a cross-flow velocity of 12.12 cm/s; uranine dosing was set to attain SPRO marker feed concentration of 20 ppm for 2 min.

Marker Passage in SPRO



Marker feed passage (MFP) at various monitoring times (Equation 15c). (*Notes:* SPRO system was operated at 160 psi at a cross-flow velocity of 12.12 cm/s. Uranine dosing was set to attain a 20-ppm concentration in the SPRO feed for a pulse duration of 2 min. MFP is the passage fraction of the total injected marker feed over the designated monitoring period)



FTMP to the permeate stream at various monitoring (*Notes*: SPRO system was operated at 160 psi at a cross-flow velocity of 12.12 cm/s. Uranine dosing was set to attain a concentration of 20 ppm in the SPRO feed for a pulse duration of 2 min)

PM-MIMo Experiment: Impact Caused by Convection

Uranine Rejection by Intact XLE-2540 RO Membranes in a PFRO Cell Following a Steady-State 10-min 20-ppm Pulse of Uranine in the RO Feed

ΔP (psi)	J_v (m^3/m^2 s)	Marker LRV_{total}	Marker LRV_{diff}	Marker LRV_{conv}
90	1.91×10^{-6}	3.26	3.27	5.11
100	2.09×10^{-6}	3.29	3.29	5.11
110	2.27×10^{-6}	3.31	3.31	5.08

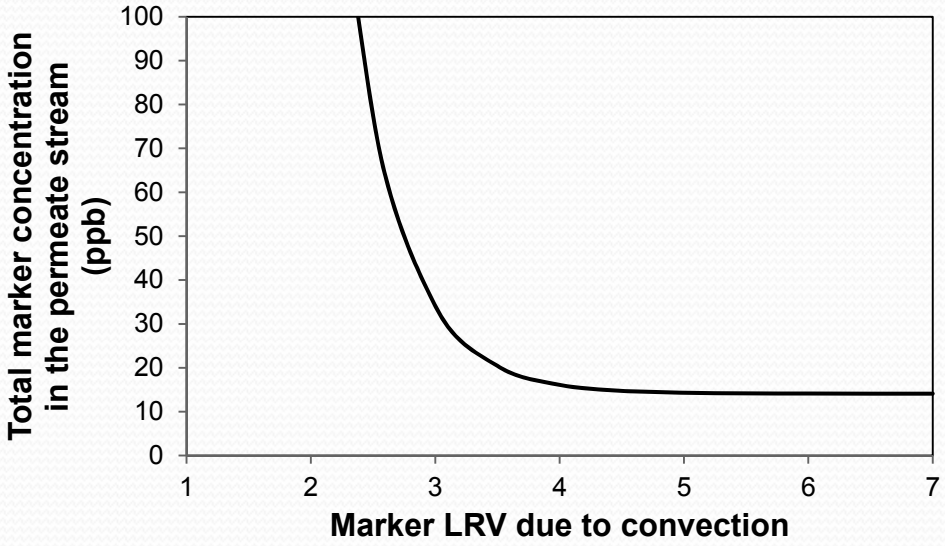
Membrane Condition	Reflection Coefficient (σ)	Marker LRV_{total}	Marker $LRV_{diffusion}$	Marker $LRV_{convection}$
Intact flat-sheet XLE membrane[b]	0.999989	3.15	3.15	5.19
SPRO system	0.9997	3.05	3.15	3.74
SPRO system with 1 pinhole in the 1st membrane module	0.9882	2.10	3.15	2.14
SPRO system with 2 pinholes in the 1st membrane module	0.9848	2.00	3.15	2.03
SPRO system with 1 pinhole in the 2nd membrane module	0.9797	1.88	3.15	1.90
SPRO system with 2 pinholes in the 2nd membrane module	0.9780	1.84	3.15	1.86
SPRO system after exposure to 80-ppm NaOCl solution for 8 h	0.9867	2.05	3.15	2.08

Impact of Membrane Breaches on Reflection Coefficient and Marker LRV Determined on the Basis of a 2-min Pulse Dosing of Uranine to Achieve 20 ppm Uranine Concentration in the SPRO Feed

Note: The SPRO system was operated at 160 psi and feed flow rate of 6.8 L/min (average cross-flow velocity of 12.12 cm/s); The marker LRV_{diff} and LRV_{conv} were estimated under the SPRO operating conditions using B and σ values determined from the PFRO experiment (Table 9.2). Experimental conditions: C_f = 20 ppm, feed cross-flow velocity = 12.12 cm/s.

[a]Section 9.3.

PM-MIMo Experiment: Impact Caused by Convection



Total marker concentration in the permeate stream in response to marker LRV due to convection of the SPRO membrane system.

Note: The example is for SPRO system operation at 160-psi feed pressure and cross-flow velocity of 12.12 cm/s with uranine RO feed concentration of 20 ppm in the SPRO feed for a pulse period of 2 min. Total permeate concentration for a given LRV due to convective transport was calculated

Summary

- With more reliance on high pressure membranes when providing water for drinking purposes, IPR and DPR the MIT/MIM of RO and NF membranes need to be well established and adopted by the industry
- Current direct MIT and MIM methods and technologies are not in the stage to meet the industry needs and not well adapted by the industry
- The newly developed PM-MIMo approach is very promising to fill the industry gap to monitor RO/NF membranes integrity and PM-MIMo approach can be utilized to detect and provide information on the characteristics of various types of membrane integrity breaches in the SPRO membrane system via real-time monitoring
- The PM-MIMo approach is sensitive to minor breaches and should be able to demonstrate greater than 4 LRVs of the marker through the intact membranes of the SPRO system
- The PM-MIMo approach clearly has potential for use as a real-time integrity monitoring technique for full-scale applications
- Field studies by UCLA are now underway demonstrate the accuracy, versatility, and robustness of this (patent pending) PM-MIMo technology

Questions?

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