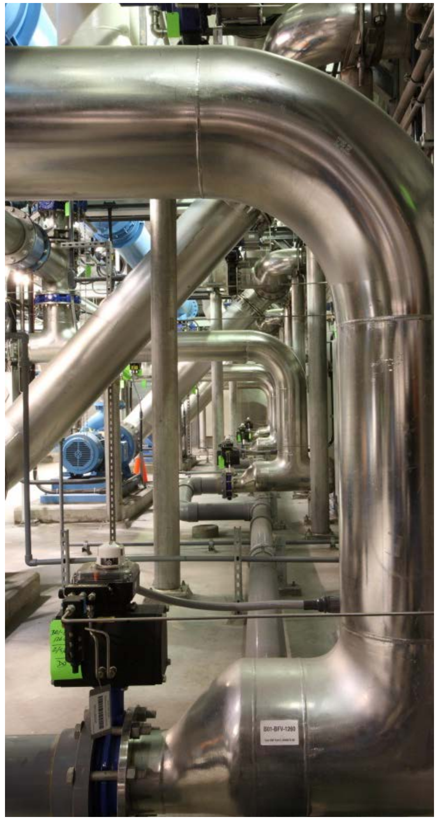
Assessment of Selected Methodologies for Monitoring the Integrity of Reverse Osmosis Membranes for Water Recycling

Joseph G. Jacangelo, MWH
Stephen Gray, Victoria University



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WateReuse Webcast Series

The WateReuse Research Foundation

The WateReuse Research Foundation conducts and promotes applied research on the reclamation, recycling, reuse, and desalination of water.

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A Few Notes Before We Get Started…

- Today's webcast will be 60 minutes.
- There is 1 (one) Professional Development Hour available.
- A PDF of today's presentation can be downloaded when you complete the survey at the conclusion of this webcast.
- Links to view the recording and to download the presentation will also be emailed later.
- If you have questions for the presenters, please send a message by typing it into the chat box located on the panel on the left side of your screen.
- If you would like to enlarge your view of the slides, please click the Full Screen button in the upper right corner of the window. To use the chat box, you must exit full screen.

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Today’s Presenters

Joseph G. Jacangelo
MWH

Stephen Gray
Victoria University

Marlene Cran
Victoria University

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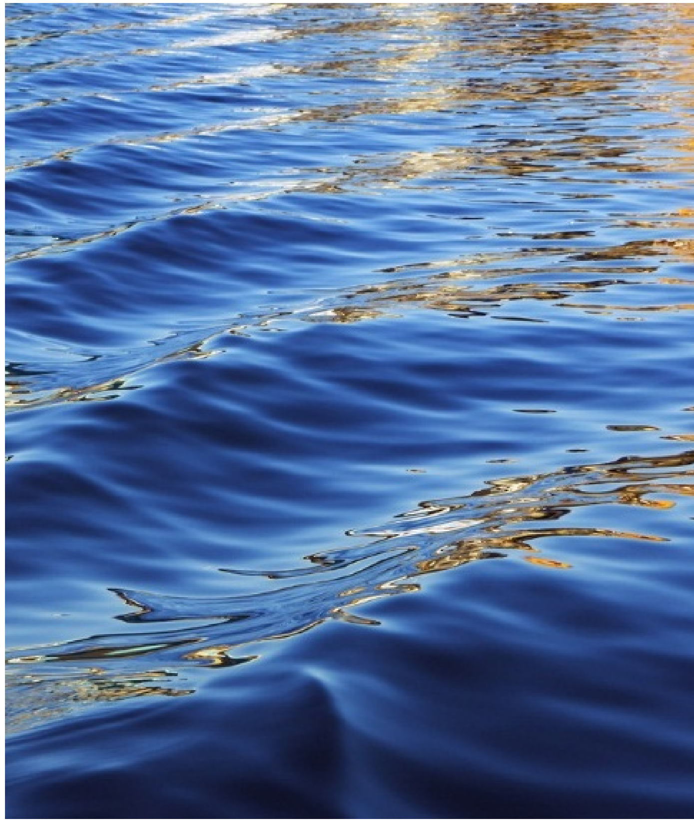
Introduction and Project Objectives



Project Team

- MWH: Geno Lehman, Eric Bruce
- Victoria University: Marlene Cran
- Johns Hopkins University: Kellogg Schwab, Jason Bishai, Nate Dunkin
- Chesapeake Energy: Arun Subramani

Acknowledgements

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- WRRF Project Advisory Committee
- ZAPS Technologies, Inc.
- Nalco
- Membrane Manufacturers: DowFilmtec, CSM Woongjin.
- Water Utilities: OCWD (Tom Knoell), West Basin, City of San Diego, El Paso, Tampa Bay, Coliban Water (Australia), TasWater (Australia), Australian Antarctic Division (Australia), PUB Singapore, Veolia Water, United Water
- University of Nevada, Las Vegas (Daniel Gerrity)

Introduction

- Reverse osmosis (RO) systems are widely used in wastewater recycling and will continue to play an important role in potable reuse.
- RO provides a barrier to salts, dissolved chemicals, particles, and microorganisms.
- There are no integrity monitoring methods for RO systems at full-scale that directly demonstrate microbial removal.
- The true barrier potential not often recognized by regulatory agencies (≤ 2 log removal credits).

Introduction (continued)

- The microbial removal capabilities for RO, particularly viruses, have been documented in the gray and peer-reviewed literature. However, there is a paucity of information on monitoring for membrane integrity (particularly on-line techniques) that will demonstrate greater than 2-log removal of an indicator (4 log removal is goal).
- Establishing more efficacious RO membrane integrity monitoring techniques will potentially allow greater credit for virus removal for IPR/DPR applications.

Viruses	Bacteria	Protozoa	References
6.7		4.2	Madireddi et al. 1997
2->5.9		<4.8	Gagliardo et al. 1997a; Gagliardo et al. 1997b
3.4	2.7->6.5	4.5->5.7	Adham et al. 1998a
2.7->6.5			Adham et al. 1998b
3-4.8			Kruithof et al. 2001
4			Lozier et al. 2004
5.4			Mi et al. 2004
7			Casani et al. 2005
1.4->7.4	2.9->5.3	>4.7->5.4	Kumar et al. 2007

avg. 4.8

Presentation Objectives

- Update on current and emerging RO integrity monitoring techniques
- Outcomes of workshop on monitoring
- Bench testing findings
- Pilot testing findings
- Feasibility of monitoring techniques evaluated and identify future direction

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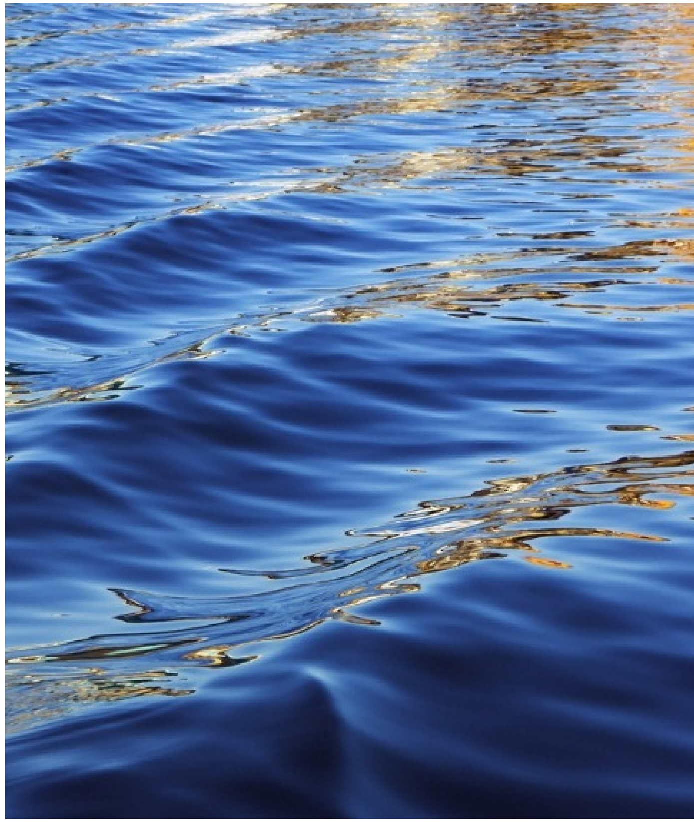
Questionnaire and Workshop Outcomes



Questionnaire Sent to Utilities on RO Monitoring Techniques

Standard Methods for Integrity Monitoring and On-line Monitoring of NF and RO Membranes (WateReuse-12-07)

MWH | VICTORIA UNIVERSITY MELBOURNE AUSTRALIA | WATEREUSE FOUNDATION

PROJECT BACKGROUND AND SURVEY REQUEST

The goal of this project is to develop a scientifically proven method for integrity monitoring of NF and RO membranes. The objective of the survey is to gather information on NF/RO integrity monitoring technologies, their performance and water quality evaluation, CAPEX and OPEX, and case studies. The outcome of the project will answer several key questions, such as:

- What methods are currently being utilized in full-scale installations for monitoring integrity?
- What parameters can be monitored in the feed and permeate stream to confidently assess microbial removal capability by more than 4 logs?
- What are the existing and proposed regulatory requirements to obtain microbial removal credits?
- What procedures are required for evaluating on-line integrity monitoring methods?
- What are the CAPEX and OPEX costs for implementing such monitoring methods?
- What are the implementation & operational benefits and challenges?
- What are the factors that the utilities need to know in order to integrate these technologies into their existing plant?

The technology providers and water utilities participating in this survey will be acknowledged in any reports, peer-reviewed papers, conference papers/presentations, webcasts generated from this project. Furthermore, a final copy of the report will be provided to the participating technology providers.

Should you have any questions regarding this project, please feel free to cont

2. MEMBRANE INTEGRITY

1. What methods are used to determine NF/RO membrane element integrity after manufacturing?
   - ☐ Vacuum decay test: What is the test pressure? ____ psi; What is the acceptable limit to pass the test? ____ psi/min
   - ☐ Pressure decay test: What is the test pressure? ____ psi; What is the acceptable limit to pass the test? ____ psi/min
   - ☐ Other (please provide details):
2. If NF/RO membrane element manufacturing is not fully automated, please specify the stages of manufacturing that are not automated (for example, glue line addition, etc.).
3. If the NF/RO membrane elements have permeate tube interlocking capability, does this prevent integrity breaches? Please explain briefly.
4. In the past, what have been the major causes of integrity breaches in NF/RO membrane elements? Tick all that apply.
   - ☐ Oxidant damage
   - ☐ Glue line leaks
   - ☐ Damaged O-rings
   - ☐ Preservative damage
   - ☐ Damage due to particulates/foulants
   - ☐ Exceeding manufacturer recommended operating conditions (e.g. flux, recovery, feed pressure, etc.)
   - ☐ System/piping leaks
   - ☐ Other (please specify):

4. LESSONS LEARNED

1. Please describe any large-scale manufacturing issues associated with membrane element integrity. How can this be overcome?
2. Please describe any lessons learned during pilot testing stage that was related to NF/RO integrity.
3. Please describe any operational issues encountered while testing NF/RO membrane element integrity. How were they rectified?
4. Please describe any other issues associated with NF/RO membrane integrity.

Causes of Integrity Breaches as Reported by Manufacturers

Cause of Integrity Breach	Manufacturer		
	A	B	C
Damaged O-rings	X	X	X
Glue line leaks	X	X	X
Oxidant Damage	X		X
Permeate Back Pressure			X
System/piping leaks	X	X	
Exceeding operating conditions	X		
Damage due to particulates/foulants	X	X	X
Preservative damage			

- Major breaches caused by damaged O-rings, glue line leaks and particulate damage.

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RO Permeate Monitoring Techniques as Reported by Utilities

Permeate Monitoring Technique	Water Utility				
	A	B	C	D	E
Turbidity	X			X	
Total Organic Carbon (TOC)			X	X	
Conductivity	X	X	X	X	X
Sulfate					
Particle Counting					
UV254			X	X	

- Several monitoring tests employed.
- Conductivity the most common.
- Overview of plant performance, not necessarily for membrane integrity.

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RO Challenge Testing as Reported by Utilities

Challenge Test at Full-scale	Water Utility				
	A	B	C	D	E
Conductivity probing		X			
Rhodamine WT					
MS2 virus				X	
None	X		X		X

- Most utilities do not perform membrane integrity challenge tests at full-scale.
- Test not undertaken as no microbial credits claimed.

Lessons Learned As Reported by Utilities

- Some water utilities reported no integrity breaches.
- Damaged, degraded and rolled O-rings were the major cause of integrity breach.
- Some water utilities reported MS2-phage virus testing. Others report no challenge testing is performed.
- Cost for installing (CAPEX) reported was $8,000 - $100,000 and operating cost (OPEX) reported was $1,500 - $25,000.
- Online monitoring of combined permeate can be misleading.
- Conductivity should be performed on individual stages periodically.
- Fouling/scaling can also present higher conductivity which resolves after chemical cleaning.
- Online TOC has lower sensitivity than lab-scale instruments and not as reliable as conductivity, UVT.
- Issues can arise from online TOC due to maintenance, calibration and consumables/reagent packs.

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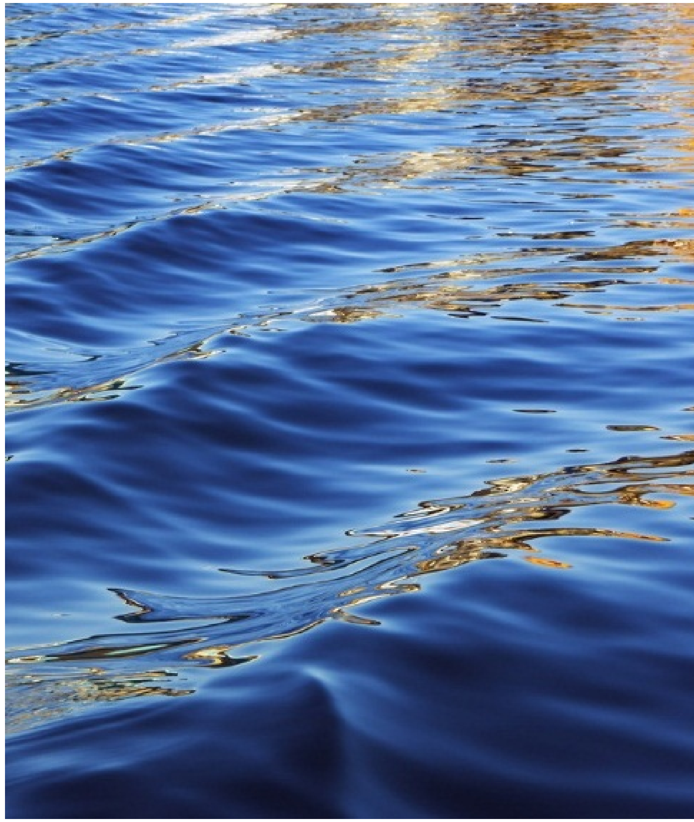
Monitoring Techniques



Criteria for Ideal Integrity Monitoring Systems

Category	Criteria	Requirement(s)
Capital & Equipment	Capital cost	Reasonable capital investment.
	Installation/integration	The ability to be fully integrated into existing systems as well as new systems.
	Operation	Should require minimal training for operators.
	Operation costs	Reasonable operation costs.
Technique	Test type	Test should be real-time and online.
	Sensitivity	High sensitivity at low challenge species concentration.
	Selectivity	Challenge species should be representative of pathogens of concern.
	Output	Test should deliver minimum LRV of 4+.

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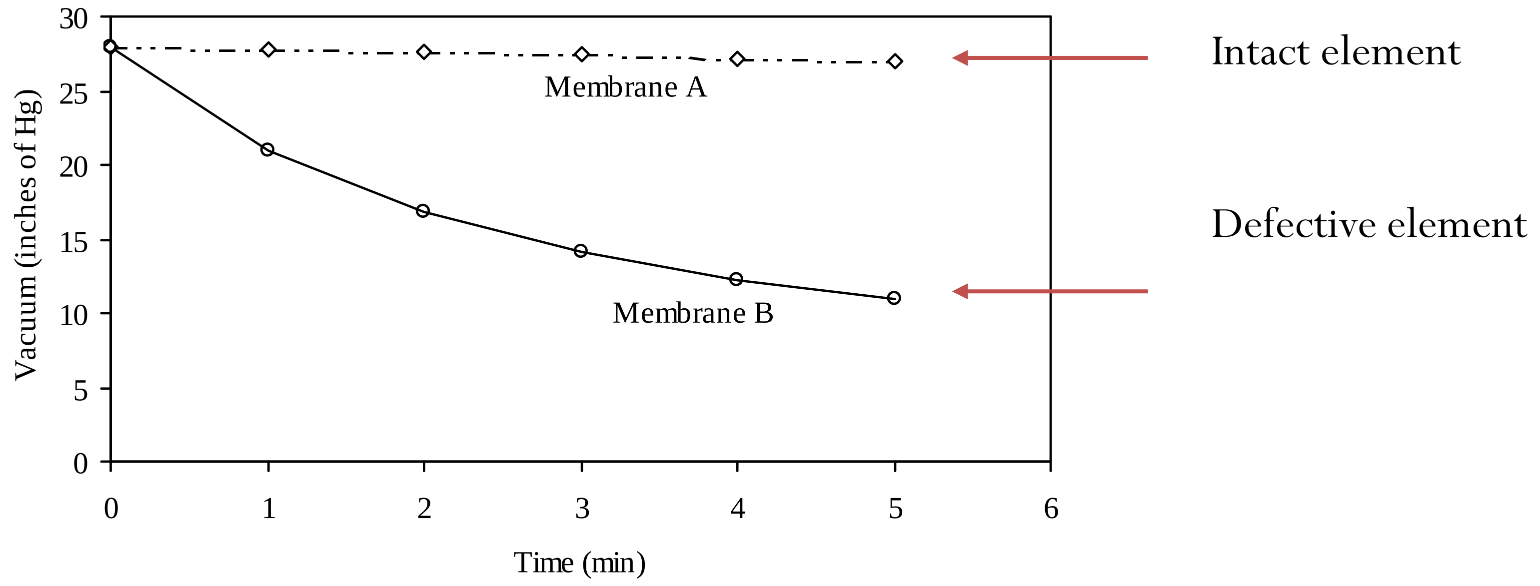
Direct Integrity Monitoring Techniques

- Pressure-based tests: vacuum, pressure decay
- Primarily a screening test



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RO Indirect Integrity Monitoring Techniques

- Particle monitoring – limited to relatively large particles (0.5 micron).
- Turbidity monitoring – low sensitivity.
- Sulfate monitoring – online systems expensive.
- Conductivity monitoring – low resolution, probing more effective.
- TOC monitoring – similar capability as conductivity.
- Periodic testing – combination of other tests, higher sensitivity
- Multi-parameter monitoring – measures multioptical parameters at one time.

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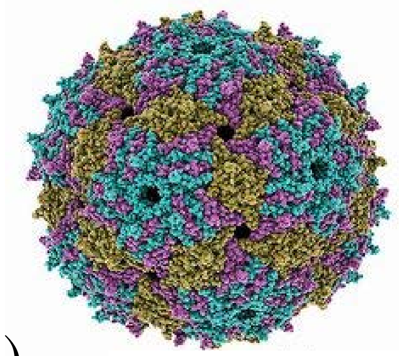
Challenge Testing to Assess RO Integrity

- Dye Testing – RWT (566 MW), Uranine (376 MW), Traser (610 MW); <1 nm
- Biological Surrogates - MS2 bacteriophage (3.6-3.87 x 10^6 MW; 15 nm)
- Fluorescent Microspheres – low sensitivity
- Pulse Integrity Testing – used for factory integrity testing
- Nanoparticles – food grade, novel detection, IP protection (WaterRA)



Sciencephoto.com

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On-line Pathogen Detection Techniques

Quantum Dots (QDs)
- Nanocrystals of semiconducting material that have "tunable" properties, biocompatible, highly flurorescent, easy to synthesize and can be formed in a range of sizes (20 – 30 nm).

Fiber Optic Biosensors
- Laser derived evanescent wave is excited over sample and fluorescence measured.

Electrochemical Biosensors
- Immobilization of antibodies onto biofunctionalized electrodes (gold).

Resonance Biosensor
- Visible or near IR radiation via a hemispherical prism. Electromagnetic waves generated and detected.

Whispering Gallery Microlasers
- Label-free detection of single viral pathogens using evanescent wave (acoustic) sensor.

Fluorescence and scattering from same particles using UV laser light source – Rion Co. Japan

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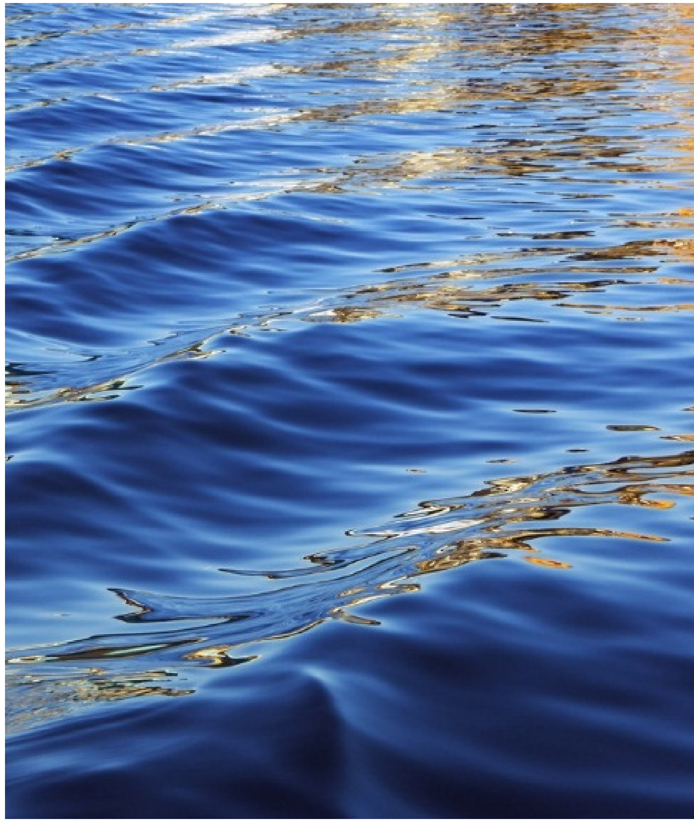
Bench-Scale Work



LRV Using Water Quality Parameters

Plant/location	Details
1 / Regional Victoria	Wastewater treatment plant, primarily industrial water
2 / Metropolitan Melbourne	Wastewater treatment plant, domestic
3 / Metropolitan Melbourne	Wastewater treatment plant, small volume, domestic
4 / Metropolitan Melbourne	Wastewater treatment plant, high volume, domestic
5 / Regional Victoria	Seawater, pretreated for aquaculture
6 / Metropolitan Melbourne	Wastewater treatment plant, domestic

LRV following UF and RO treatment
(RO at lab scale for some plants)

Parameter	LRV
EC (µs)	1.39 - 1.98 (3.12)
TDS (ppm)	1.22 - 1.45 (3.12)
TOC (mg/L)	1.06 -1.88
TN (mg/L)	0.40- 1.09
Turbidity (NTU)	0.30 – 1.38
UV254 (Abs)	1.26 - 2.33
fDOM (AU, 330/425, 310/350, 360/382)	0.35 – 2.08

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Variables Evaluated for Dye Testing at Bench-Scale

Screening variable	Conditions
Temperature	10-30°C
pH	5-8 (adjusted with HCl and NaOH)
Salts	NaCl - up to 16000 ppm
	$CaCl_2$ - up to 8000 ppm
Disinfectants	Hypochlorite – up to 1 ppm Chloramine – up to 3 ppm
UV light	UVA (dose to be confirmed), 0-9 h
RO feedwater	Spiked sample of dye in colored water

Impact of Selected Variables on Three Dyes

	Relative effect		
Screening variable	**RWT**	**UR**	**TR**
Sensitivity	Green	Yellow	Blue
Temperature	Yellow	Green	Green
pH	Green	Yellow	Green
NaCl	Blue	Green	Blue
$CaCl_2$	Blue	Blue	Blue
Hypochlorite	Red	Green	Yellow
Chloramine	Blue	Red	Blue
UV light	Green	Green	Yellow
RO feedwater	Green	Red	Green

Key:	
Excellent/no effect	Blue
Good/minimal effect	Green
Average/moderate effect	Yellow
Poor/significant effect	Red

Summary:

- TR and RWT the most stable under test conditions.
- In some cases, application of specific calibrations can be used.
- An insertion scratch in the permeate channel was implemented.

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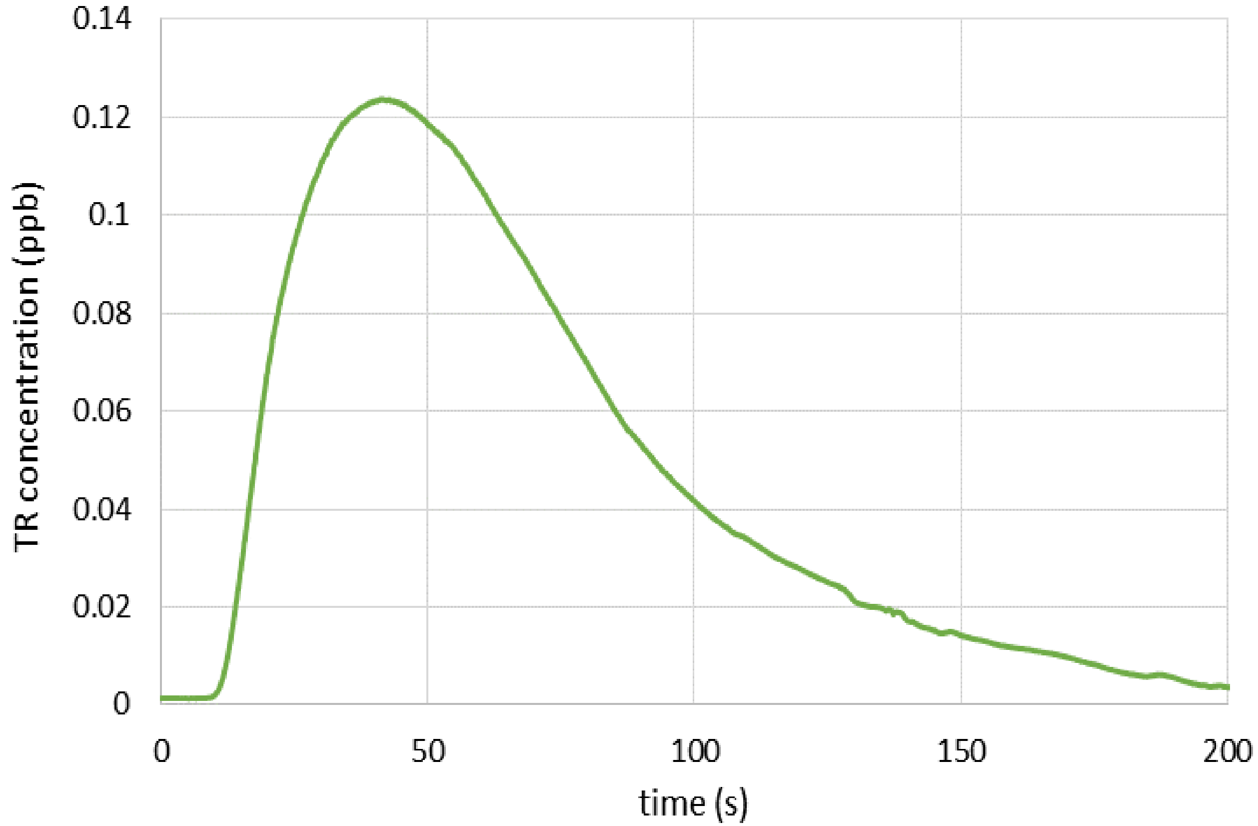
Continuous versus pulse dosing

Continuous	Pulse
Cost of dye	Intermittent addition of dye, lower cost
Provides continuous online monitoring	Intermittent testing, higher doses possible
Potential for dye adsorption, fouling	Lower risk, adsorbed dyes flushed between tests
Result one-dimensional, not time specific	Can be calibrated with time, detect known defects
No need for extensive data/peak evaluations	Need ability to probe pressure vessels to account for dilution effects

Continuous versus pulse dosing



- C/t plot of pulsed dose of TR at 10 mg/L for 60 s on intact membrane.
- Peak value of 0.12 ppb corresponds to an LRV of 4.91.
- Slightly higher than LRV of 4.59 obtained via continuous dosing at 1 mg/L.
- Can correlate peak shape to known defects.

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Average LRV of Dyes Based on Different Dosing Experiments

Dye	Continuous dose	Pulse dose
RWT	4.19 ± 0.13	4.77
UR	3.96 ± 0.10	4.04
TR	4.59 ± 0.18	4.91

Continuous dosing at 1 mg/L and pulse dosing at 5 mg/L

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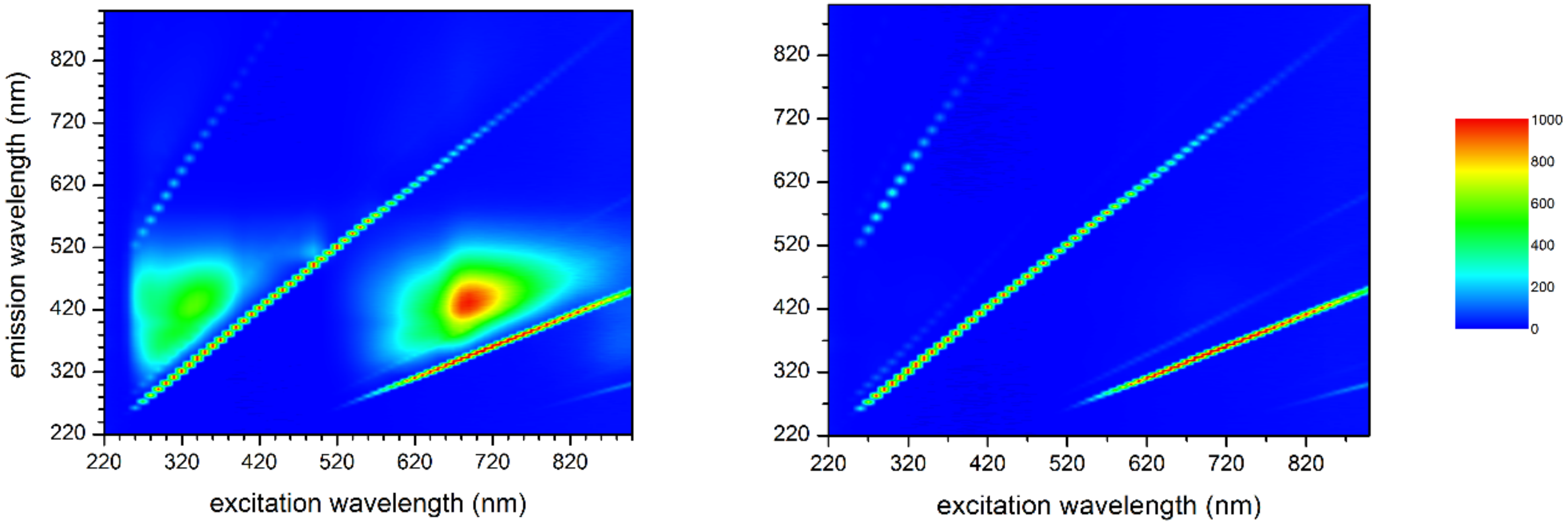
Emission Excitation Matrices (EEMs)



Water Recycling Plant, Victoria

- EEM is used for organic matter finger printing.
- EEM combined with size exclusion chromatography (SEM) can be used for NF/RO integrity (Pype et al., J. Membr. Sci., 2012).
- EEM more sensitive than conductivity measurements with quantification of DOM rejection > 99.9% (Pype et al., J. Membr. Sci., 2012).

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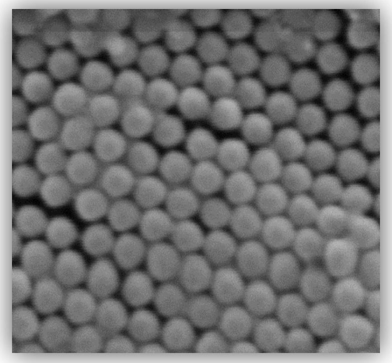
Nanoparticle challenge tests

- Synthesis of non-labelled nanoparticles of similar size as smallest virus.
- Unique optical/light scattering properties.
- New technique under development based on light scattering.
- Has shown LRV > 7 with relatively low feed concentration in bench scale trials, consistently ~5 LRV at pilot scale.
- Exploring IP protection.



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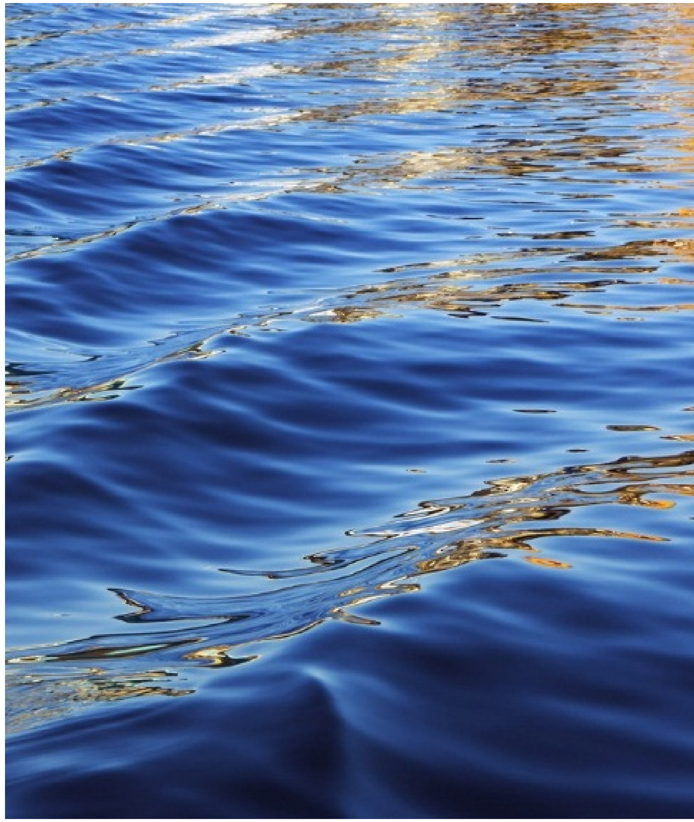
Pilot Work

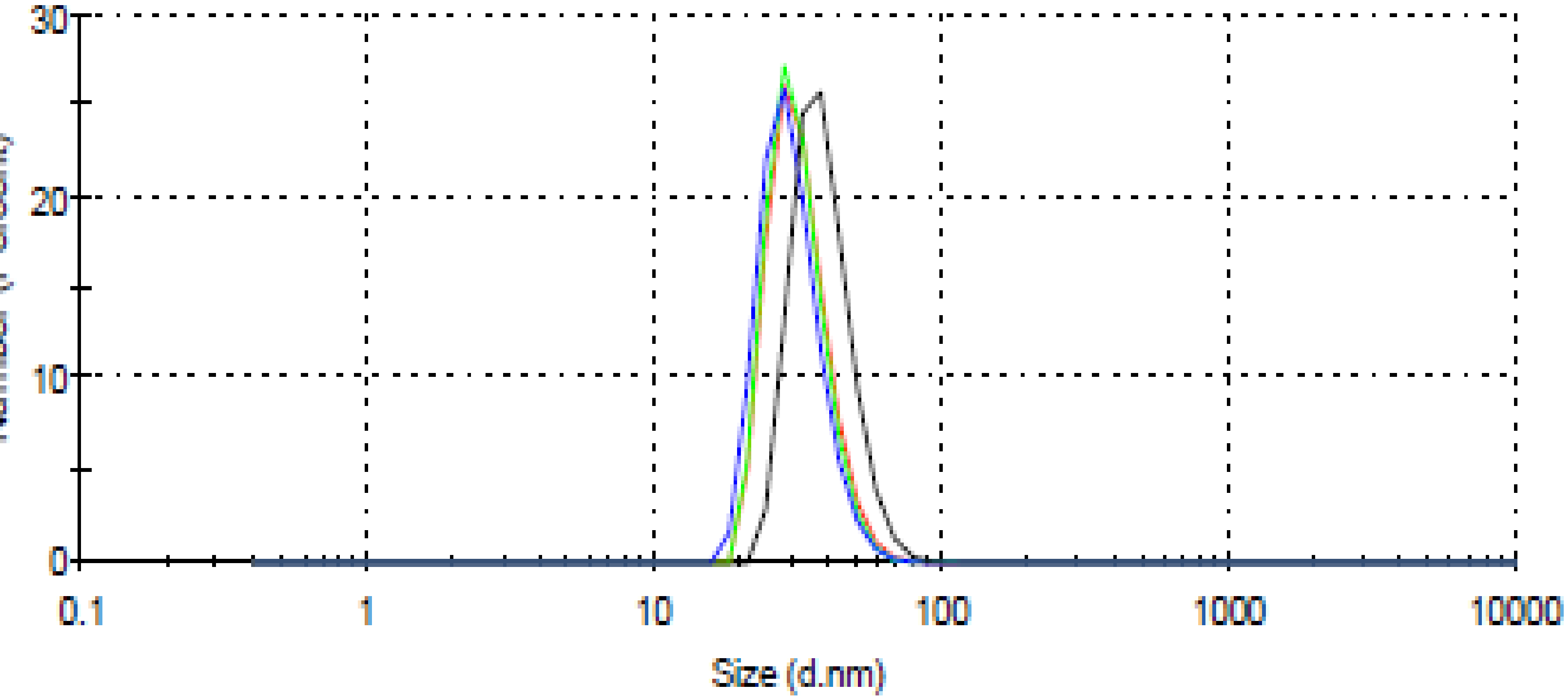
Orange County Water District, California
Hobart, Australia



Piloting – Orange County Water District

- 2:1 Array
- 4 inch pressure vessels
- DowFilmtec BWRO
- 14 gfd
- FWR 20-30%

Size Distribution of MS2 Bacteriophage Stock Solution by Dynamic Light Scattering after 0.1 um Filtration



Courtesy of N. Dunkin and K. Schwab, JHU, 2015

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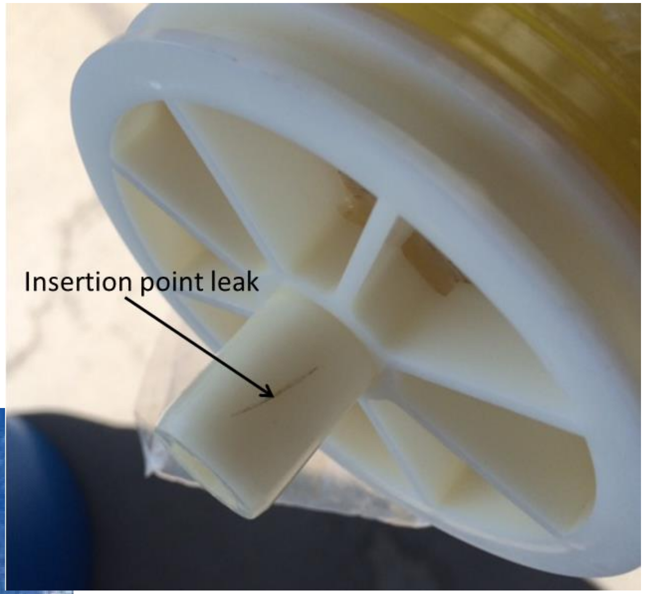
Types on Membrane Impairment

- Surface scratches created by rubbing pin across the membrane leaf.
- Point source leak created near glue line with a pin.
- Insertion point leak created with pin at the intersection of the scroll face and end cap.
- Element exposed to chlorine (5,000 ppm, 24 hrs, pH 11).
- Cut o-ring (manual cut).



Impairments confirmed by vacuum pressure decay tests.

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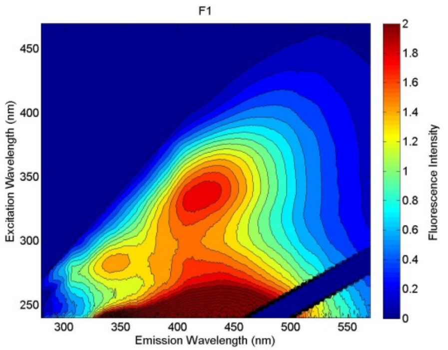
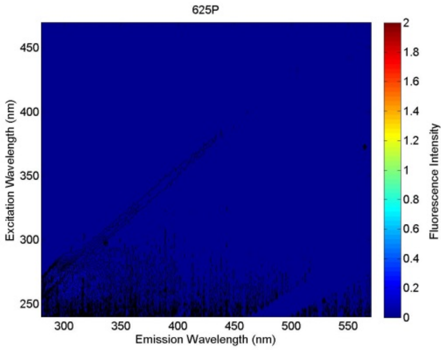
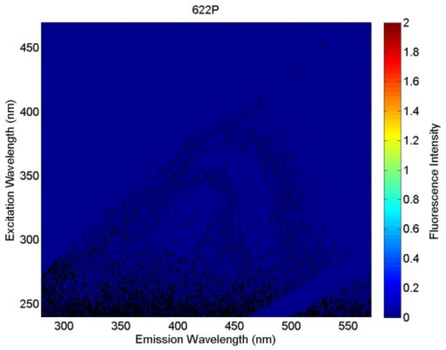
Emission Excitation Matrices (EEMs)



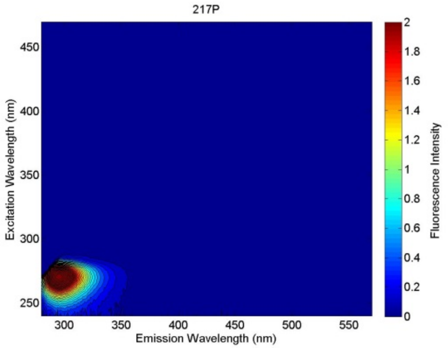
Feed



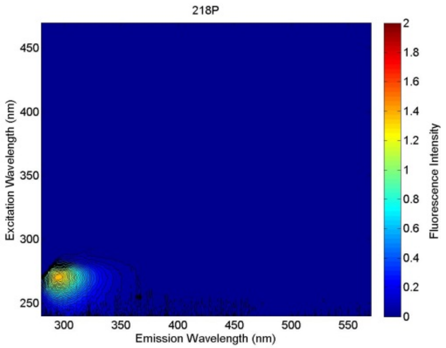
Intact element



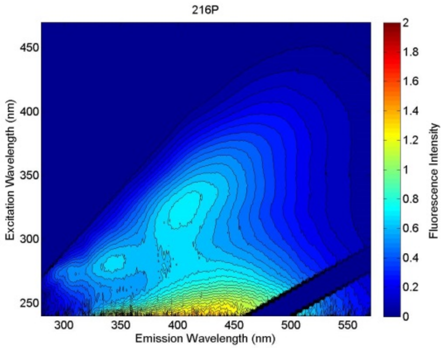
Glue line leak



Surface scratch



Insertion point leak



Chlorine damage

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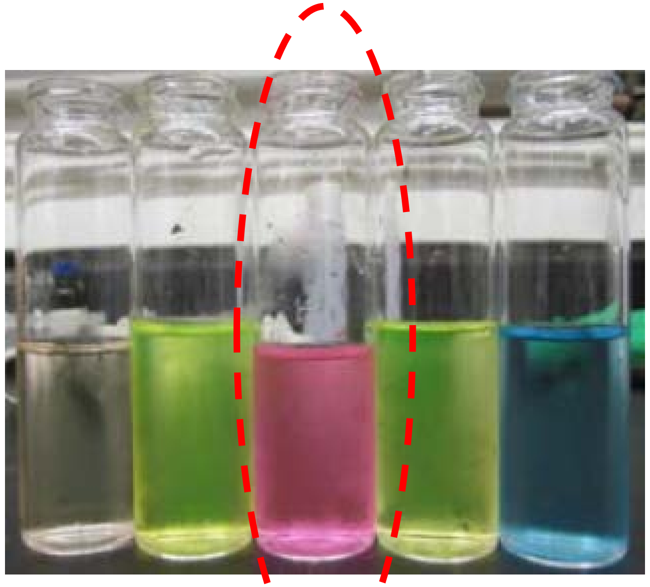
Rhodamine WT (RWT)

- RWT – $C_{29}H_{29}N_2NaO_5$; 480.55 Da; 2.01 nm hydrodynamic diameter
- Non toxic
- Commercially available
- Insensitive to UV light

Feed Concentration (type*)	LRV	Reference(s)
0.1-1 mg/L (C)	3.5-5.3	(Kitis et al. 2003a)
1-2 mg/L (C)	3.9	(Kitis et al. 2003b)
1 mg/L (C)	2.7-3	(Lozier et al. 2003)
0.1-1 mg/L (C)	2-5	(Lozier et al. 2013)
0.1 mg/L (C)	2.6	(Lozier et al. 2011)
5-10 mg/L (P)	>4	(Ostarcevic et al. 2013)

*type: C = continuous, P = pulse



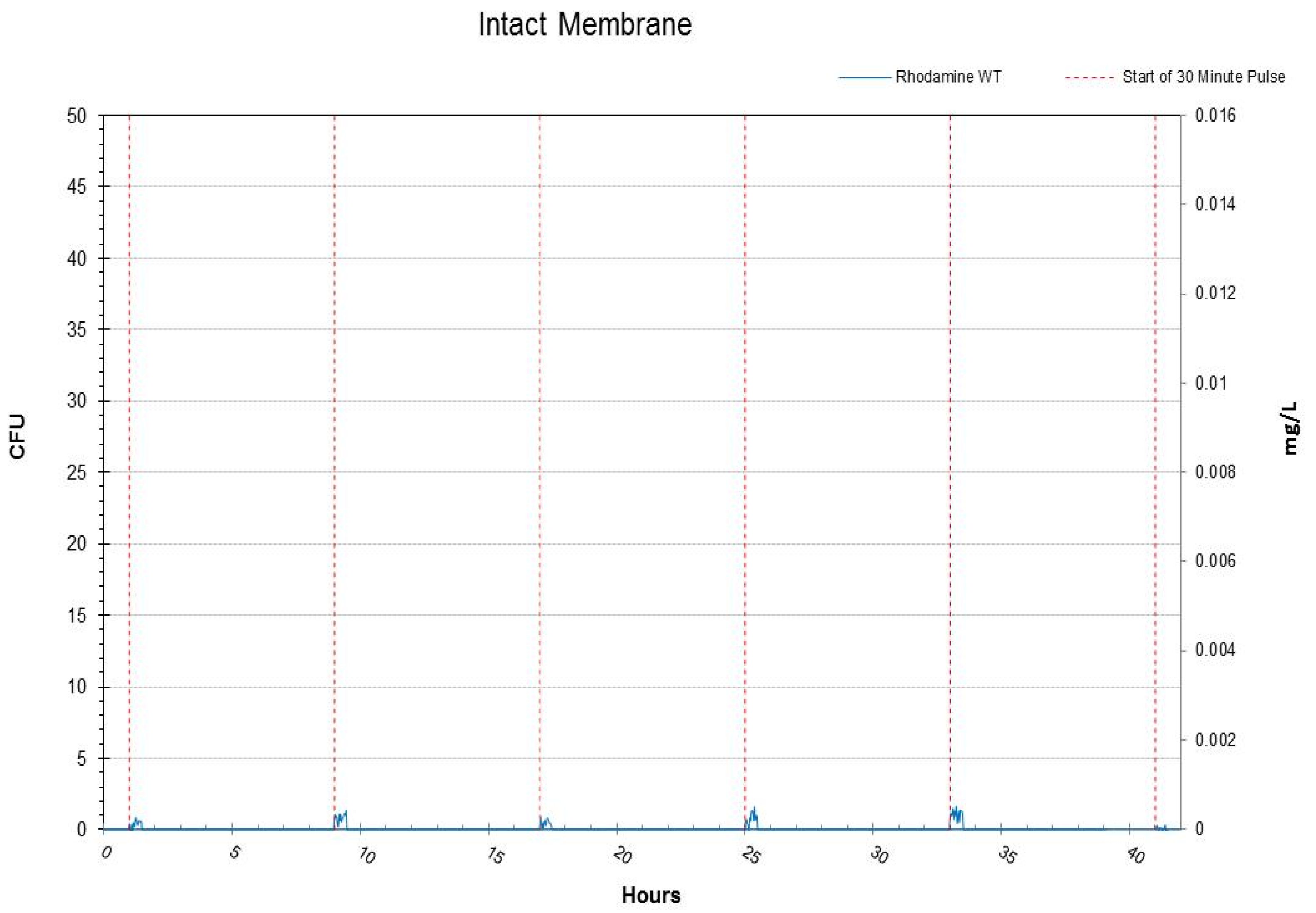
RWT

Source: UCLA, WRRF-09-06b

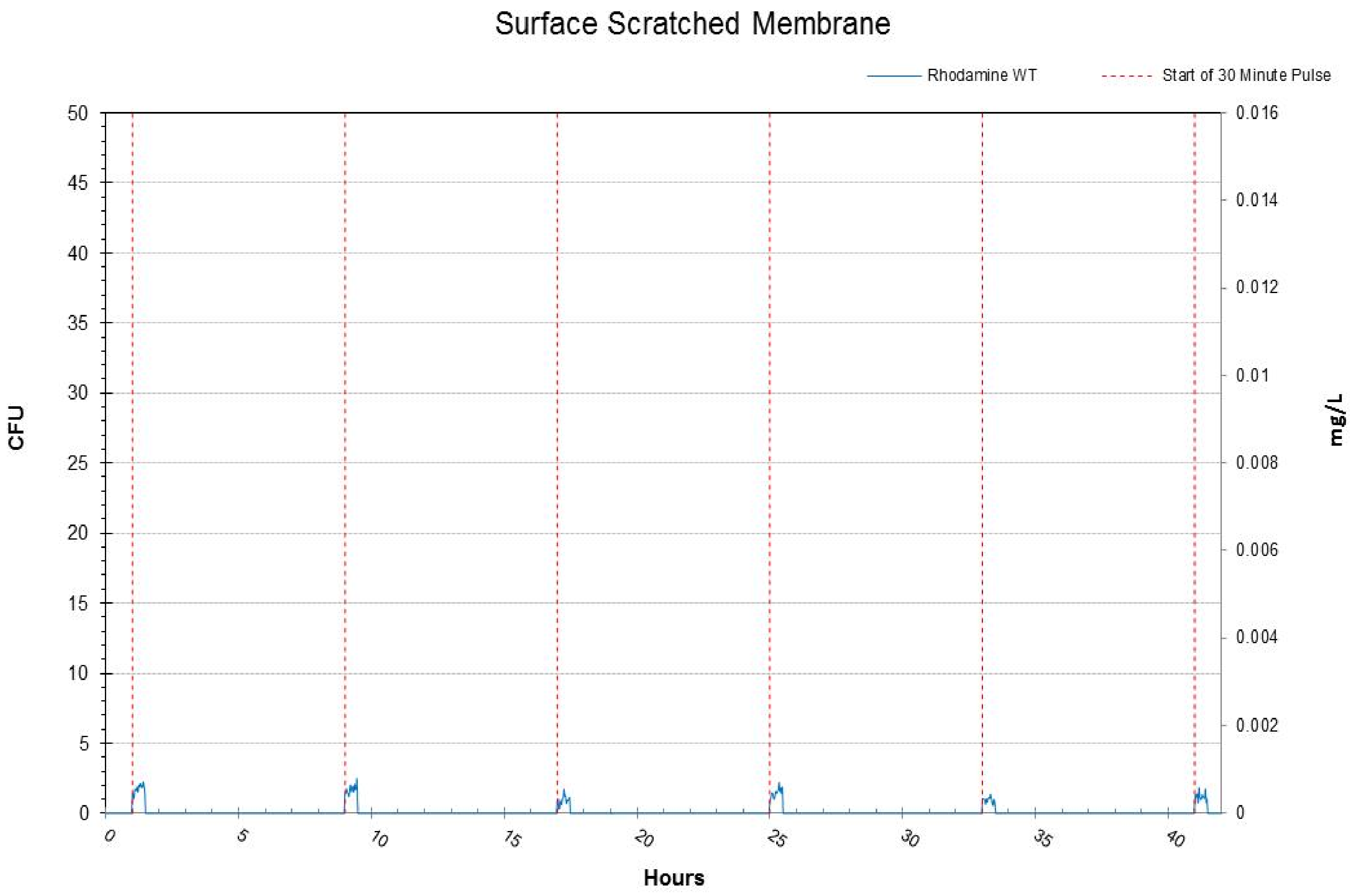
This study

- Pulsed feed (10 mg/L)
- Continuous feed (10 mg/L) for microbial seeding studies

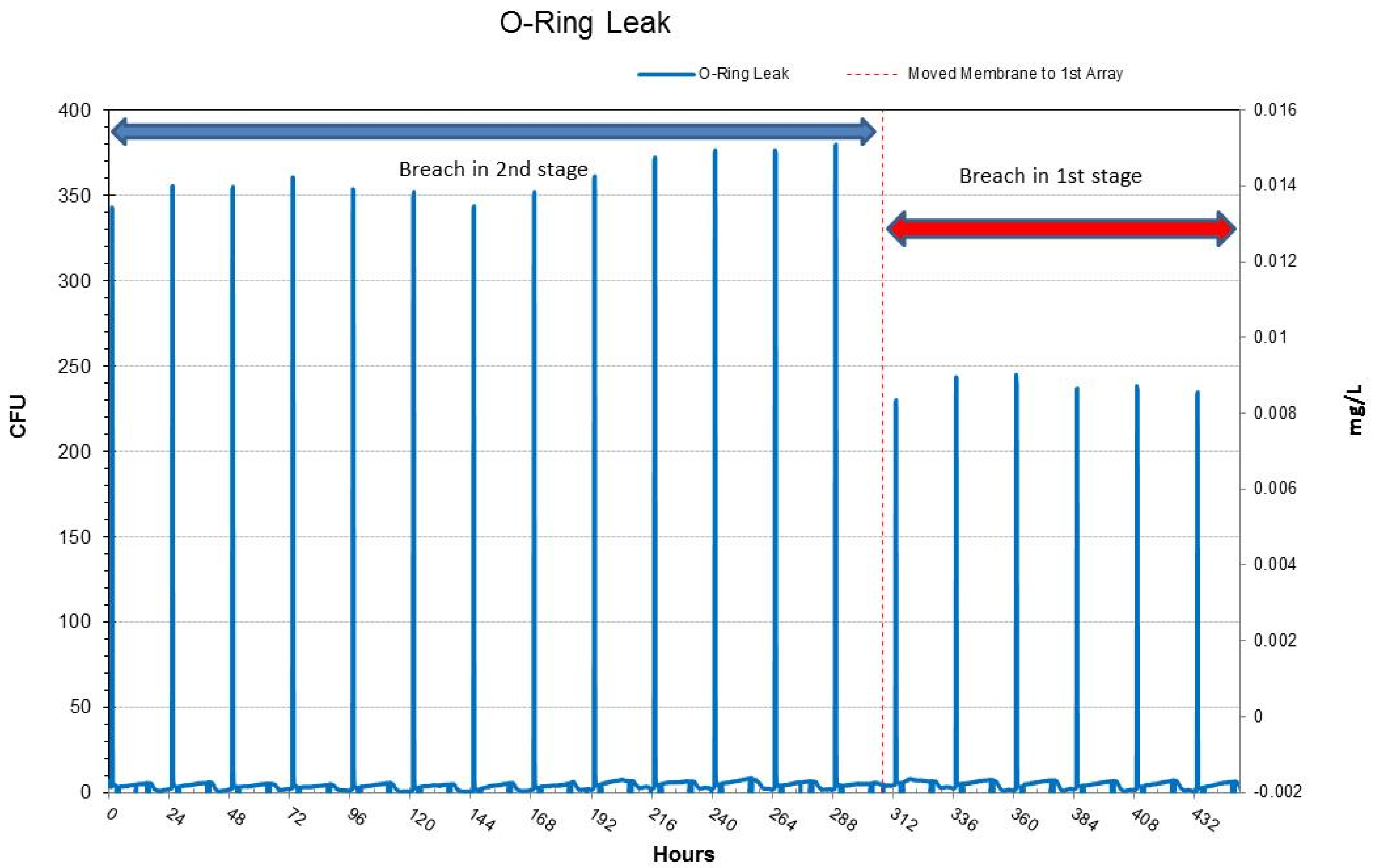
Measurement of RWT in RO Permeate Using an Intact Membrane



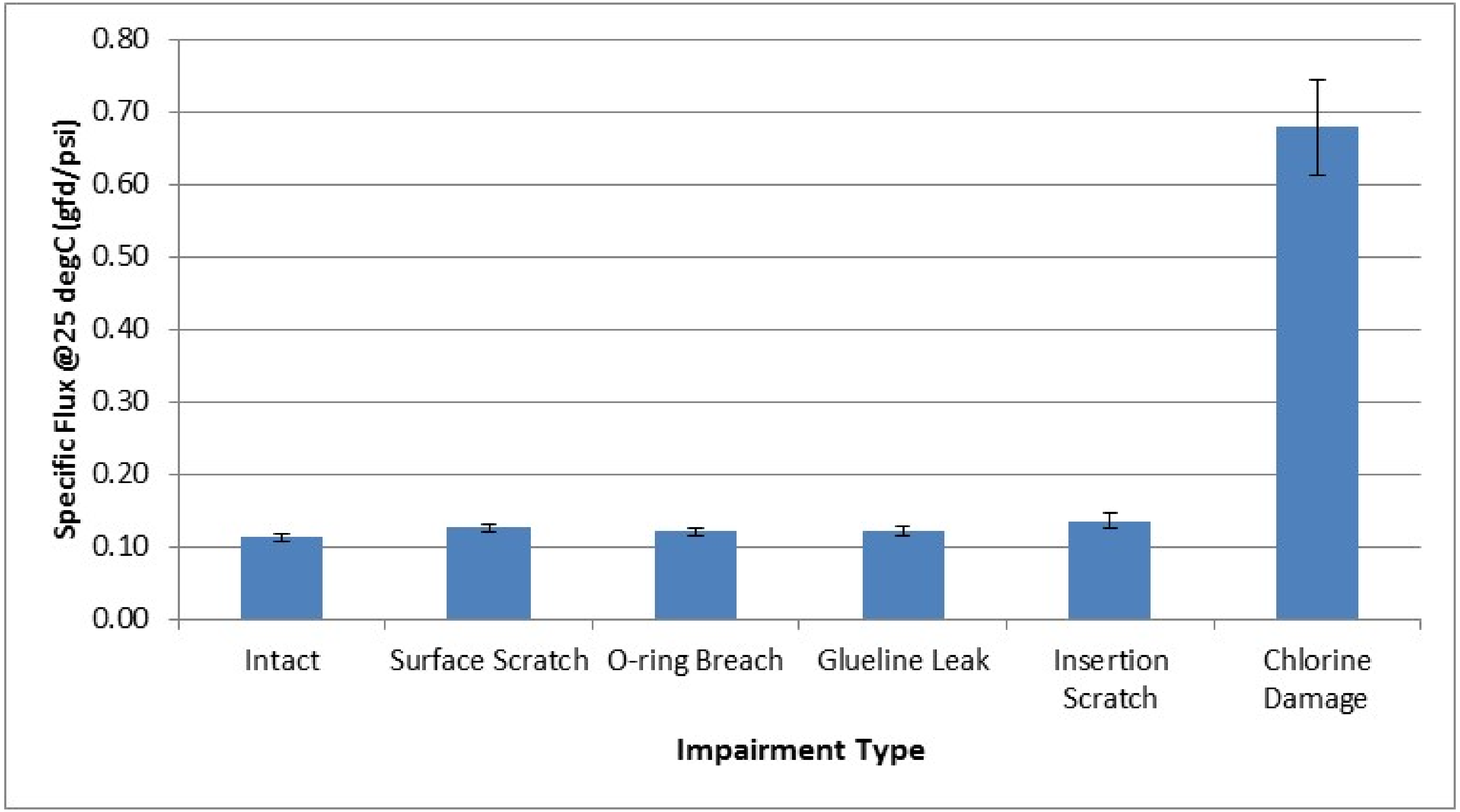
Measurement of RWT in RO Permeate with Surface Scratch Impairment



Measurement of RWT in RO Permeate with O-Ring Impairment



Impact of Impairment Type on Membrane Specific Flux



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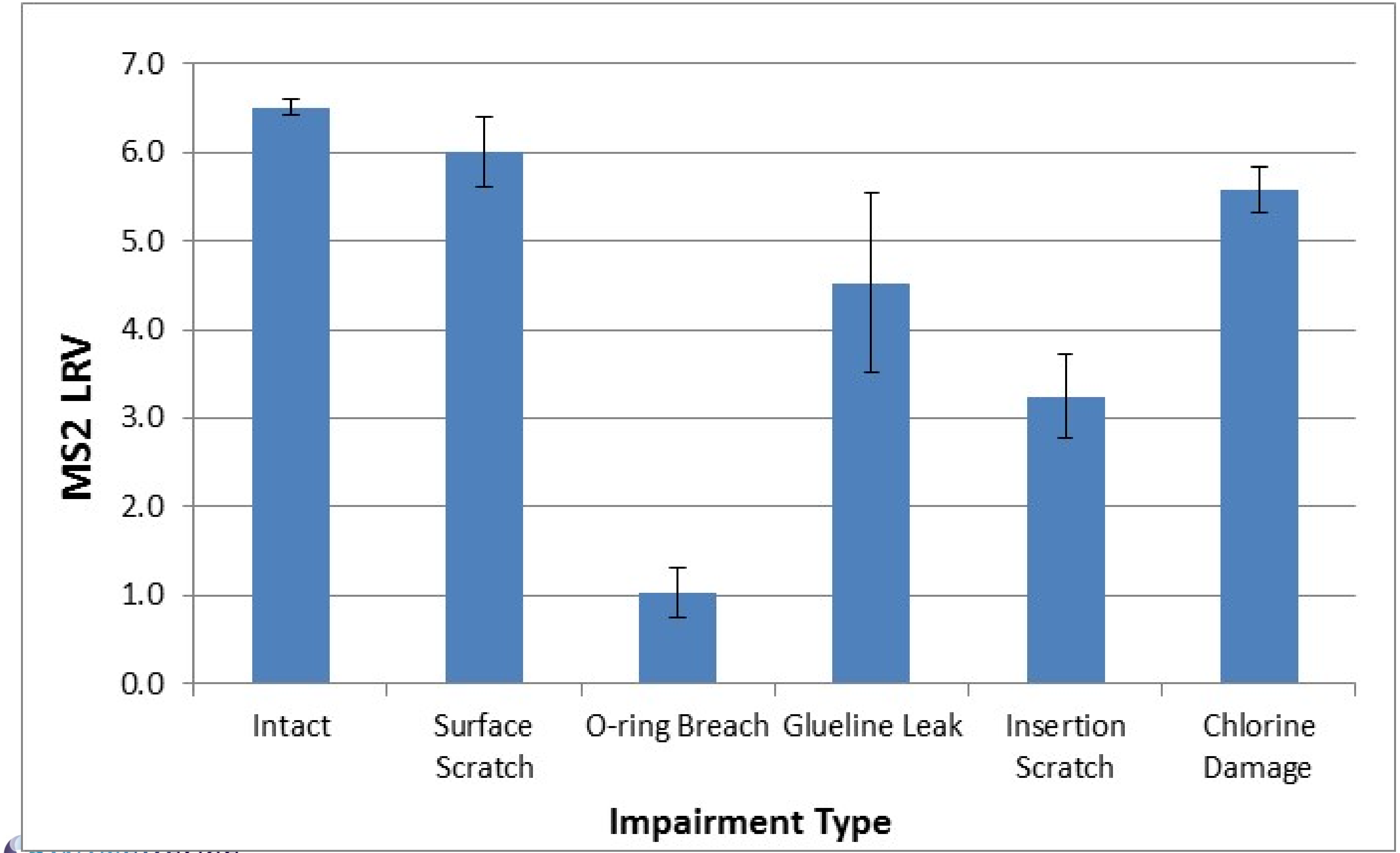
Impact of Membrane Impairment Type on Removal of MS2 Bacteriophage



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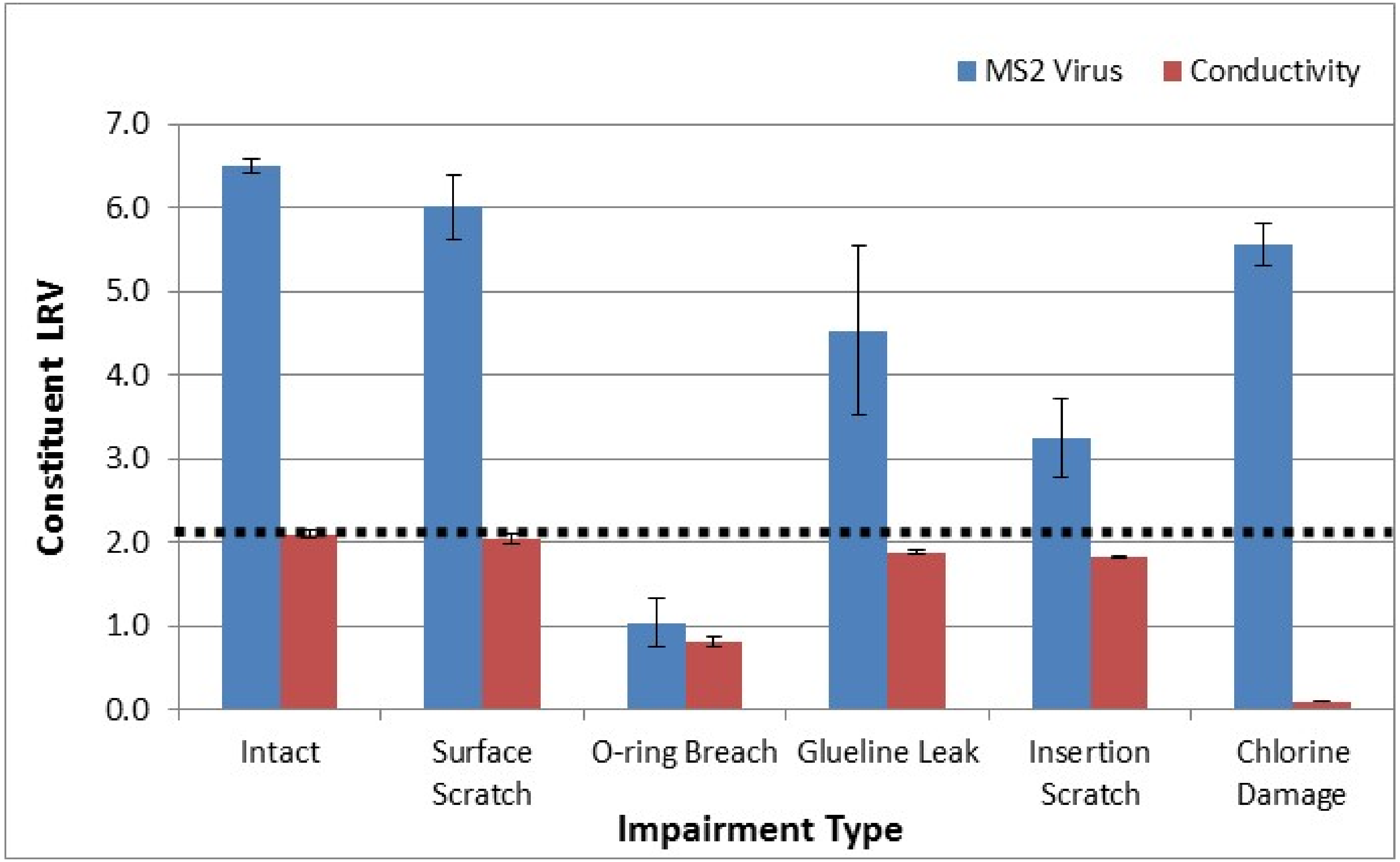
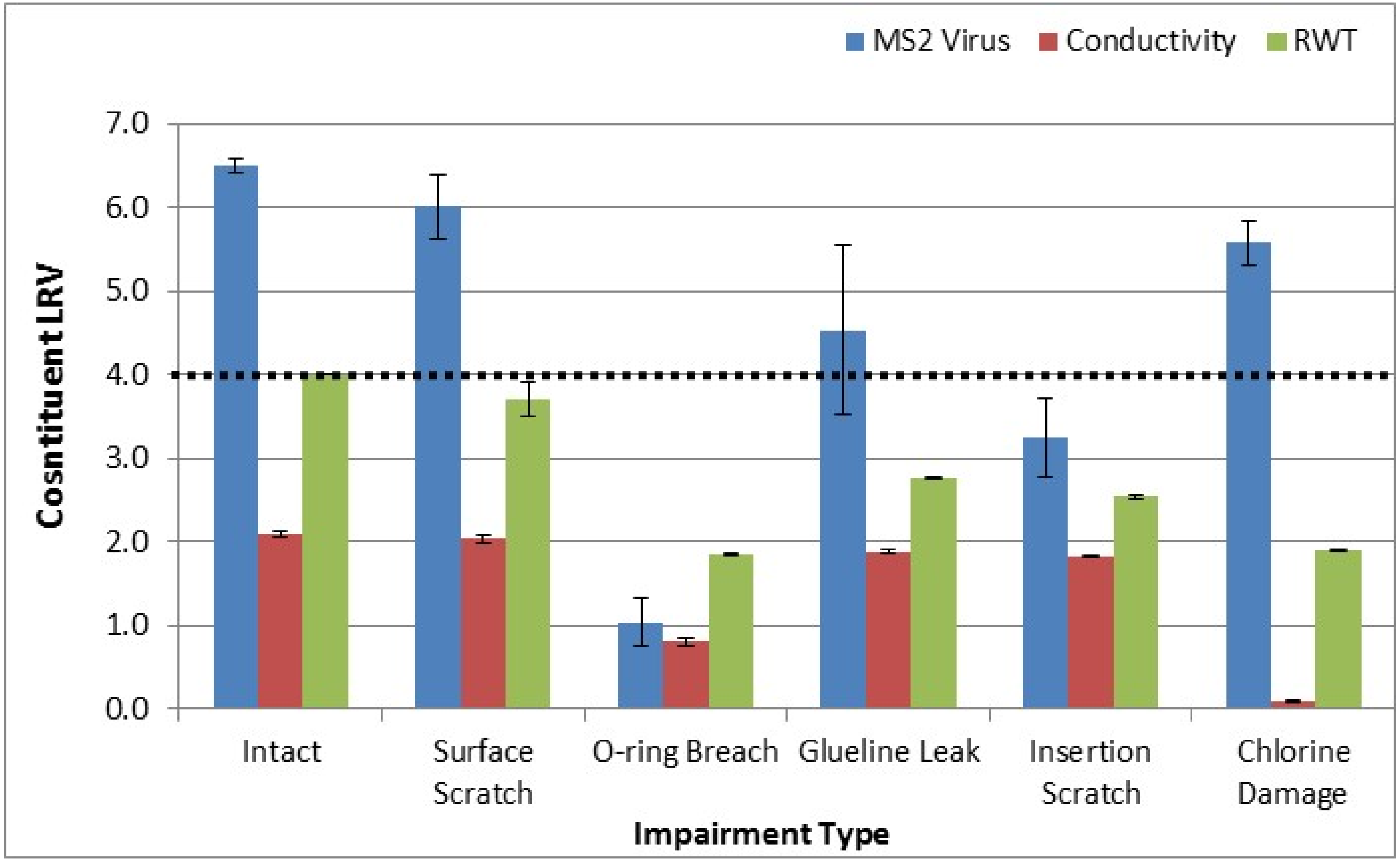
Impact of Impairment Type on Removal of MS2 Virus and Conductivity



Impact of Membrane Impairment Type on Removal of MS2 Bacteriophage, Conductivity and RWT



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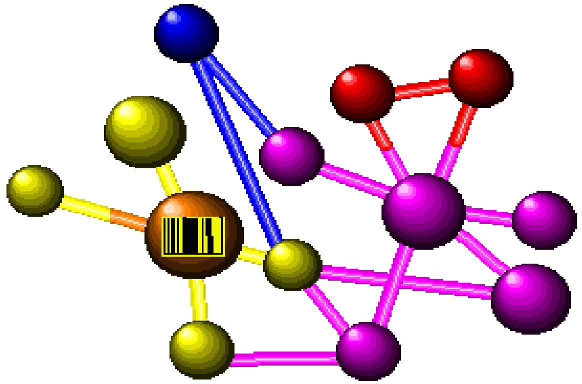
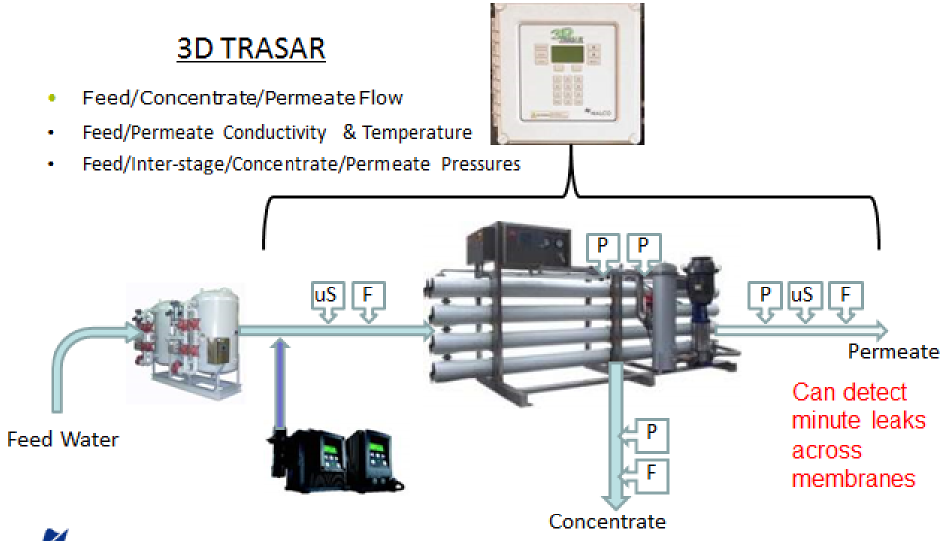
TRASAR®

- Fluorescent compound coupled with an anti-scalant (PC-191T)
- Currently approved by NSF up to 15 mg/L feed concentration.
- Capability to feed and monitor online continuously.
- Proprietary detector to measure ultra-low concentrations.





This study

- Continuous feed over course of virus seeding runs.
- Concentrations evaluated: 4 to 100 mg/L.

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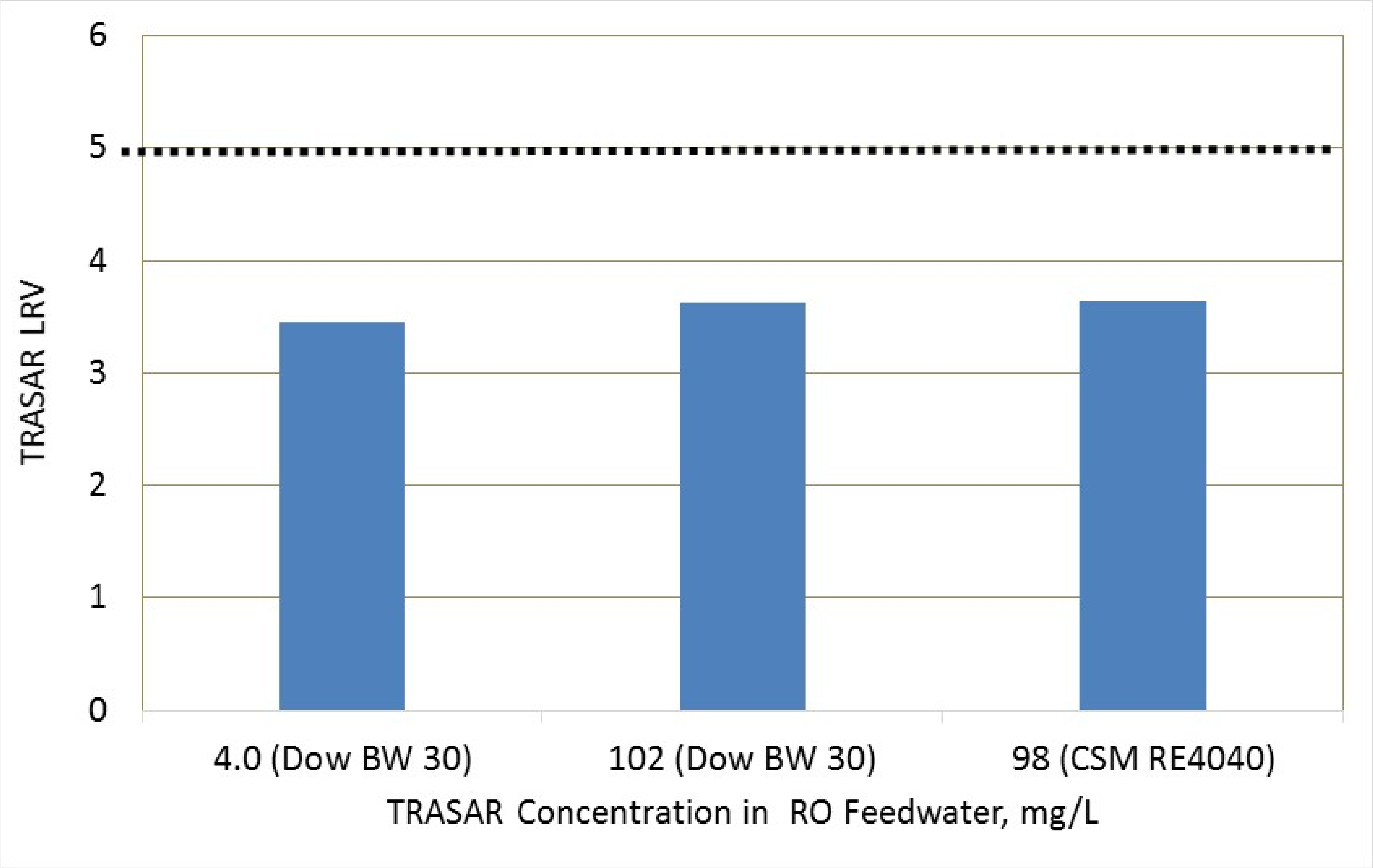
Impact of Membrane Type and Concentration on Removal of TRASAR



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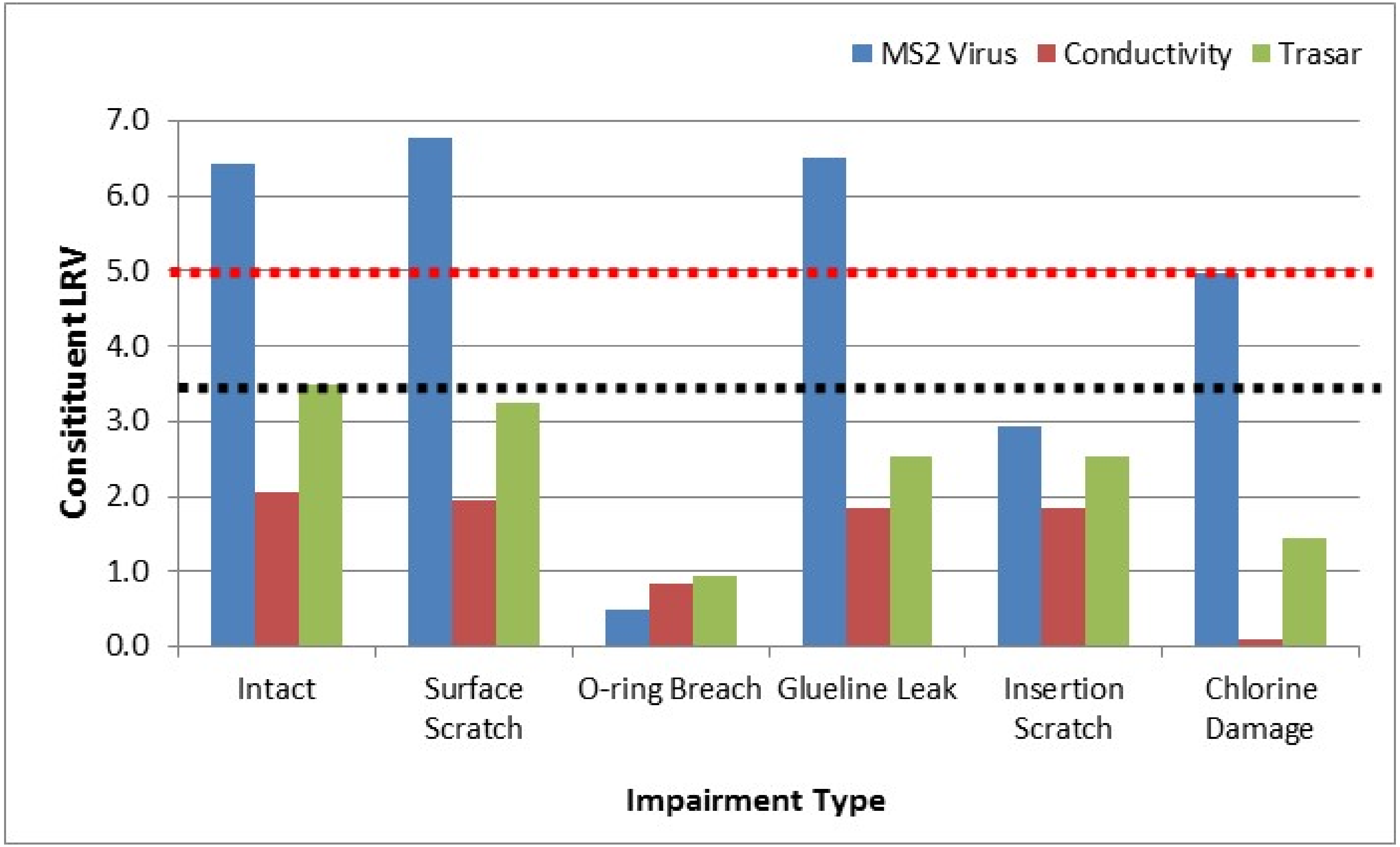
Impact of Membrane Impairment Type on Removal of MS2 Bacteriophage, Conductivity and TRASAR



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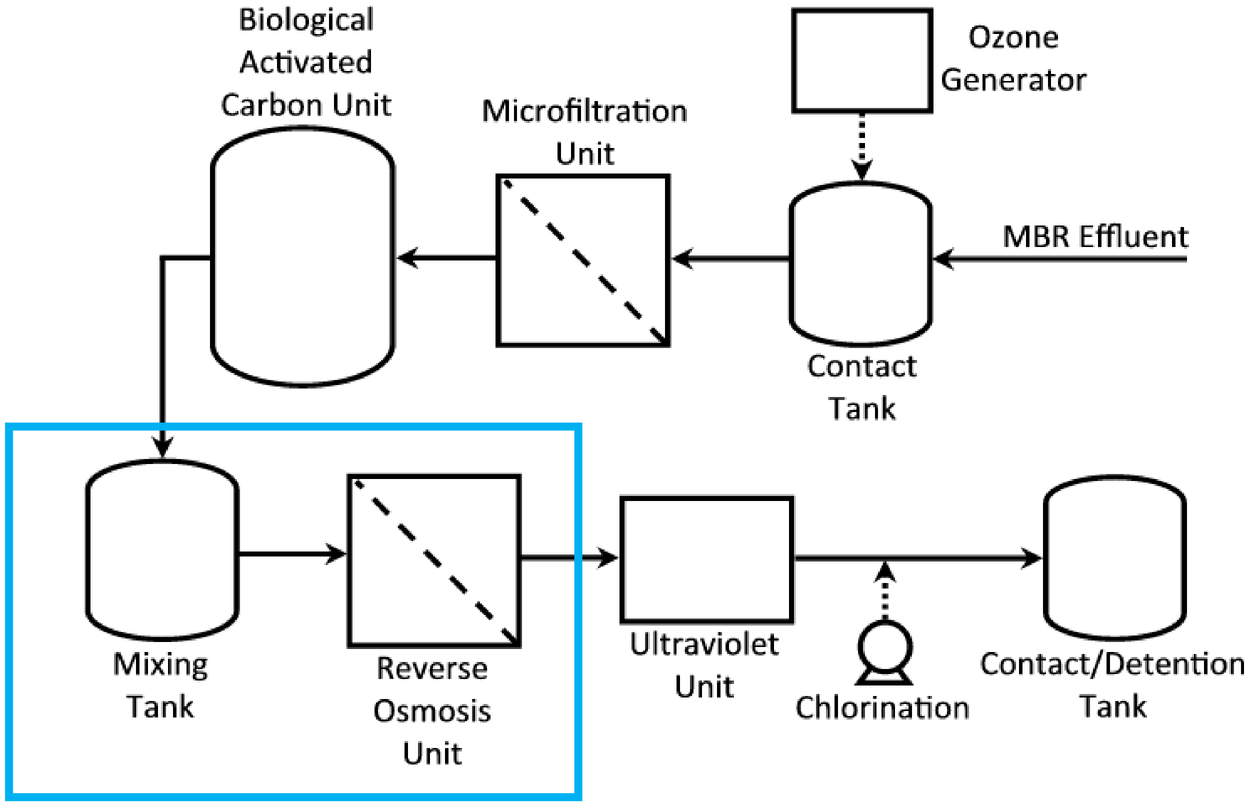
Piloting - Australia



<u>Australian Antarctic Division pilot plant</u>

3 challenge tests performed:

- Nanoparticle test (~ 2 mg/L)
- Mixed dye test (1 mg/L each dye)
- MS2 test (~3 $\times 10^6$ PFU/mL)

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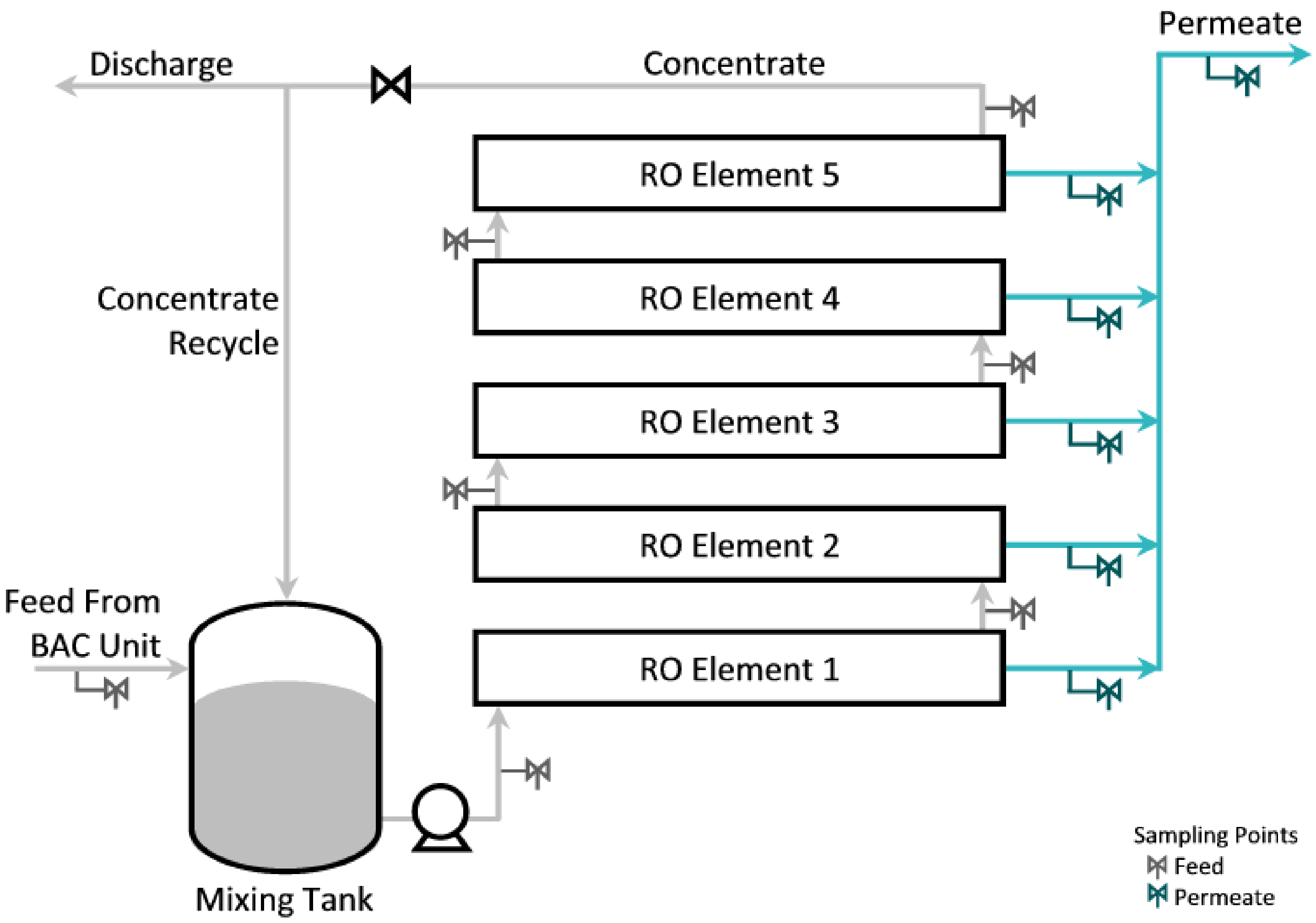
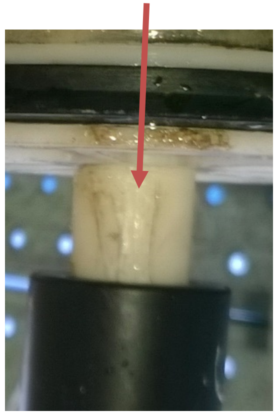
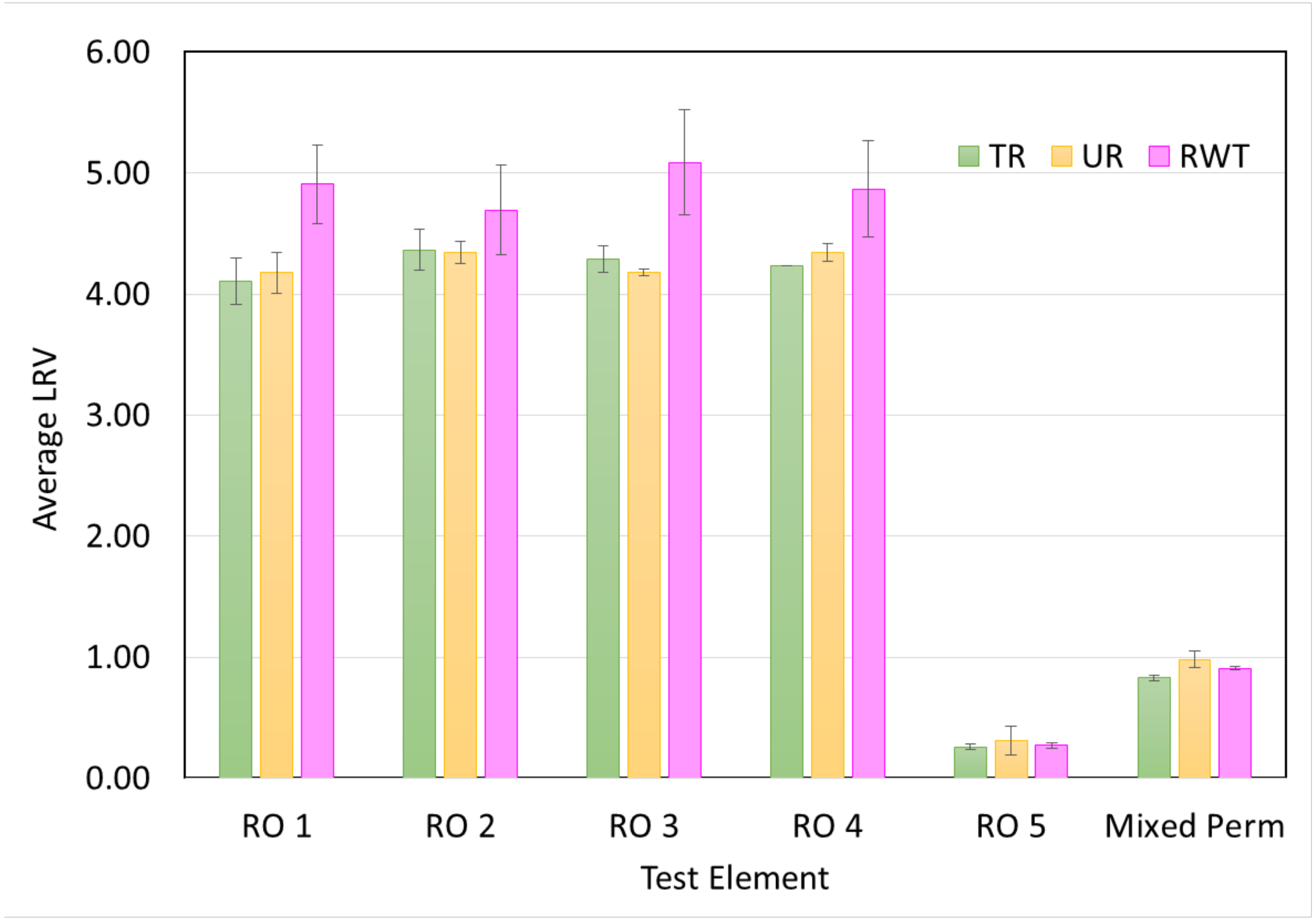
Pilot Plant Experimental Set-Up



- System operated at 70% recovery.
- Feed/permeate sampling points and conductivity monitoring for each element.
- Concentrate from element n = feed for element n+1.
- Element 5 was compromised.
- Initial attempts to damage the O-ring were unsuccessful.
- An insertion scratch in the permeate channel was implemented.



Removal of Mixed Dyes by RO Elements



- At ~1 mg/L, all intact elements achieved >4 LRV for each dye.
- RWT most sensitive dye.
- All dyes passed through defect with significant reduction in LRV.

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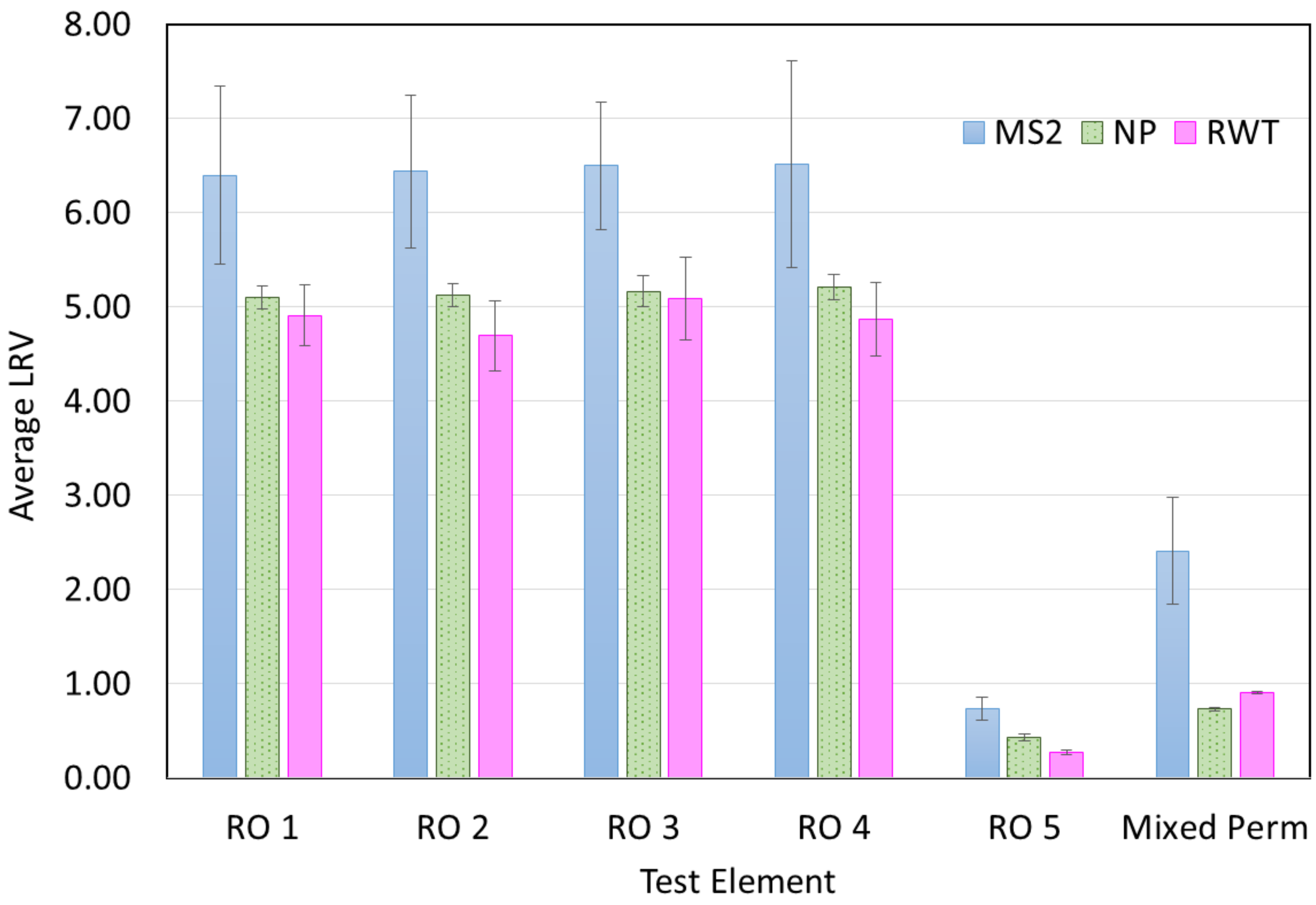
Removal of MS2, Nanoparticles, RWT by RO Elements



- All intact elements achieved :
- >6 LRV for MS2
- >5 LRV for NP
- >4 LRV for RWT
- Relatively high error for MS2.
- Lowest error for nanoparticle detection.

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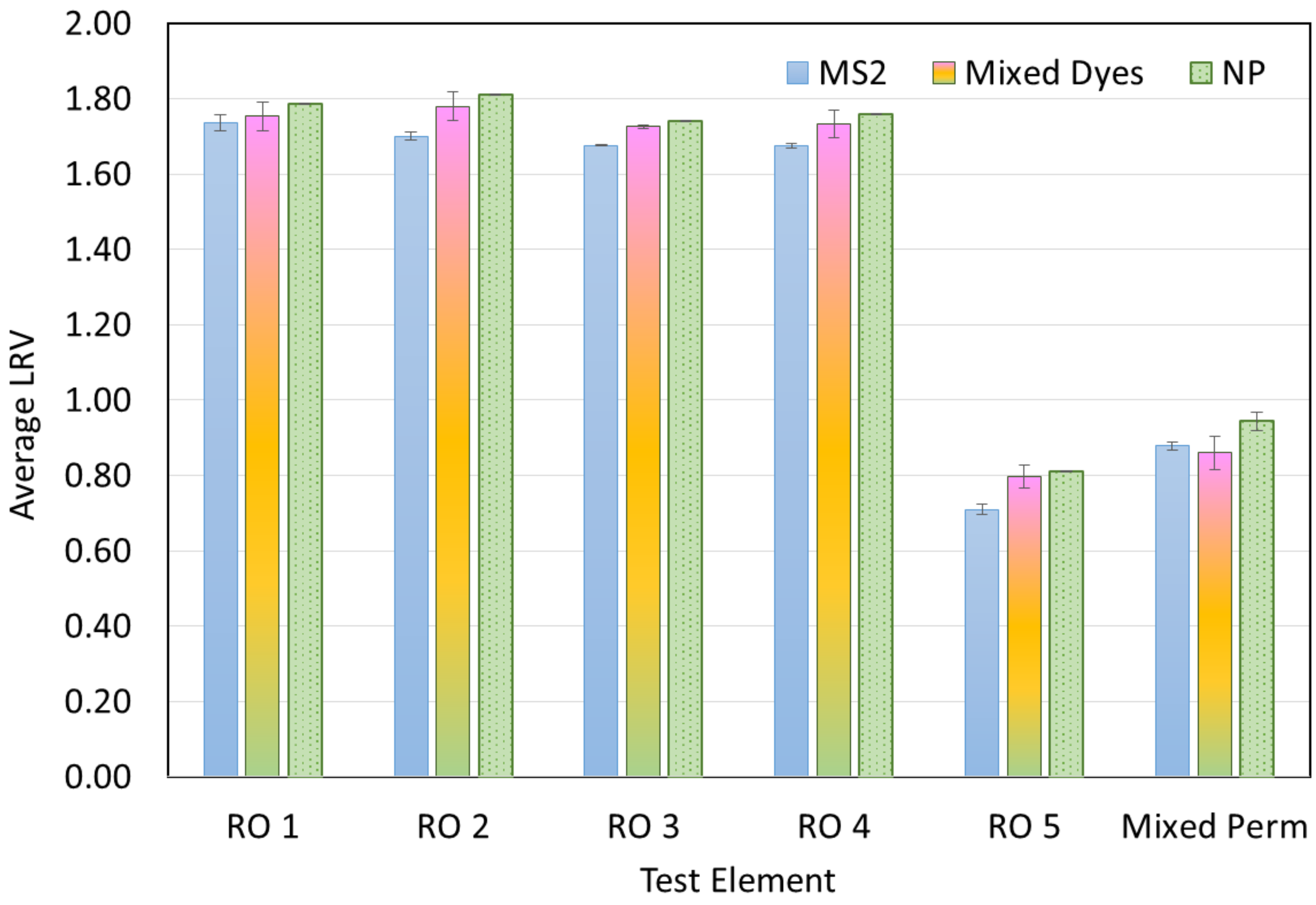
Removal of Conductivity by RO Elements



Notes:

- Online conductivities measured concurrently with each challenge test.
- <1.8 LRV for all tests.
- Addition of challenge species had minimal effect on conductivity.
- Most conservative test, least sensitive.

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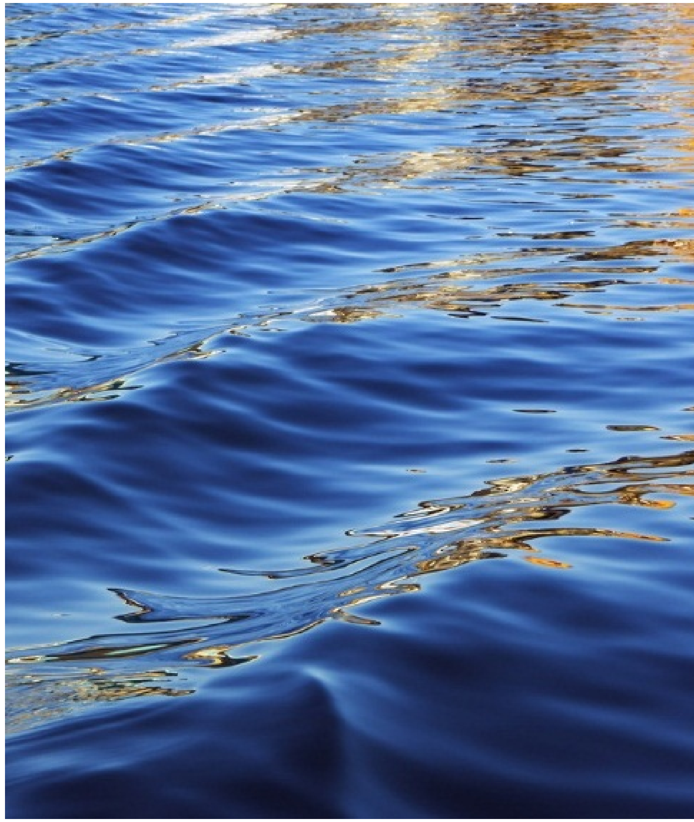
Summary and Concluding Work



Summary and Future Direction

- There are several new and emerging technologies that have the potential to be employed for RO membrane integrity monitoring in the future but are not yet developed to the point for full-scale application.
- Several on-line techniques can be effective at full-scale to evaluate process performance (traditional monitoring, zero-angle photospectroscopy). Other techniques, while not on-line, can also be applied to provide insights into process integrity (EEMs).
- Pulse testing of selected constituents (nanoparticles, RWT) provide the potential to achieve $\geq$ 4 log sensitivity for RO membrane integrity monitoring. However, they need to be conducted off-line on a periodic basis.
- TRASAR has the capability to monitor for membrane integrity on a real-time, continuous basis.
- <u>FINAL REPORT:</u> To include full-scale application protocol and costs.
- <u>FUTURE WORK:</u> Full-scale, long-term trials of pulse and continuous monitoring techniques.

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